This article summarizes ambient evaluations of the performance of ozone and nitrogen dioxide methods that were conducted under the umbrella of the NASA-led DISCOVER-AQ mission.
Under the U.S. Clean Air Act, the U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for six “criteria” pollutants—carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide, lead, and particulate matter—that are set forth in Title 40, Part 50 of the Code of Federal Regulations (40 CFR Part 50). EPA and the states are jointly responsible for monitoring the ambient air for these pollutants. This monitoring is carried out as part of a national network of monitoring sites, called the State and Local Air Monitoring Stations (SLAMs). The air quality data obtained from these sites are reported to EPA’s Air Quality System (AQS) database, along with other information, and are used for determining compliance with the NAAQS; assessing effectiveness of State Implementation Plans (SIPs) in addressing NAAQS nonattainment areas; characterizing local, state, and national air quality status and trends; and associating health and environmental damage with air quality levels/concentrations.

To assure the accuracy, integrity, and uniformity of the SLAMs air quality monitoring data collected, EPA has established one or more Federal Reference Methods (FRMs) for measuring each of the six criteria pollutants. These FRMs are set forth in appendices to 40 CFR Part 50 and specify a particular measurement principle to be implemented in commercially produced monitoring instrumentation. These FRMs must be shown to meet detailed performance specifications in addition to other requirements detailed in the EPA regulations at 40 CFR Part 53.

To encourage innovation and development of new air quality monitoring methods, EPA has provided for Federal Equivalent Methods (FEMs). An FEM is not constrained to the particular measurement principle specified in the corresponding FRM. However, an FEM must meet the same or similar performance requirements as specified for the corresponding FRM, and must show a high degree of comparability to colocated FRM measurements at one or more field testing sites. These FEM requirements are also detailed in 40 CFR Part 53, and a monitor that is shown to meet all applicable requirements may be designated by EPA as an FEM monitor and used for NAAQS compliance monitoring.

This article summarizes ambient evaluations of the performance of ozone and nitrogen dioxide methods that were conducted under the umbrella of the NASA led DISCOVER-AQ Earth Venture Mission. In addition to contributing to the overall goals and desired outcomes established for the DISCOVER-AQ study, EPA conducted extensive ambient testing of the various ozone and nitrogen dioxide methods to verify that the methods meet all existing and anticipated future requirements for FRM and FEM analyzers used in NAAQS compliance monitoring.

The tests also evaluated the various analyzers’ performance (comparability) relative to each other in unique operating environments such as near roadway sampling locations.

**Experimental Methods**

Ambient evaluations of the various ozone and nitrogen dioxide methods were conducted during field intensive studies as part of the NASA DISCOVER-AQ project conducted during July 2011 near Baltimore, MD; January–February 2013 in the San Juaquin Valley, CA; September 2013 in Houston, TX; and July–August 2014 near Denver, CO. During field intensive studies, instruments were calibrated according to manufacturers’ operation manuals and in accordance with FRM requirements listed in 40 CFR 50.

During the ambient evaluation campaigns, nightly automated zero and span checks were performed to monitor the validity of the calibration and control for drifts or variations in the span and/or zero response. Both the calibration gas concentrations and the nightly zero and span gas concentrations were delivered using a dynamic dilution calibration system (T700U/T701H, Teledyne API). The analyzers were housed in...
within a temperature-controlled shelter during the sampling campaigns. A glass inlet with sampling height located approximately 5 m above ground level and a subsequent sampling manifold were shared by all instruments. Data generated by all analyzers were collected and logged using a field deployable data acquisition system (Envidas Ultimate). A summary of instruments used during DISCOVER-AQ deployments is listed in Table 1. Figure 1 shows a typical DISCOVER-AQ site (Houston 2013) where EPA (and others) instrumentation was deployed.

### Table 1. Methods for ozone and nitrogen dioxide used during DISCOVER-AQ.

<table>
<thead>
<tr>
<th>Manufacturer and Model</th>
<th>Operation Principle (Abbreviation)</th>
<th>FRM/ FEM</th>
<th>DISCOVER-AQ Field Deployment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ozone Methods</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bendix Model 8002</td>
<td>Ethylene-Chemiluminescence (ET-CL)</td>
<td>FRM1</td>
<td>Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>Teledyne API Model T265</td>
<td>NO-Chemiluminescence (NO-CL)</td>
<td>FEM1, FRM1</td>
<td>Baltimore 2011; Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>2B Technologies Model 211</td>
<td>“Scrubberless” UV Photometric (SL-UV)</td>
<td>FEM</td>
<td>Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>2B Technologies Model 205</td>
<td>UV Photometric (UV-Drier)</td>
<td>FEM</td>
<td>Houston 2013</td>
</tr>
<tr>
<td>Ecotech Model EC9810</td>
<td>UV Photometric (UV-Drier)</td>
<td>FEM</td>
<td>Baltimore 2011</td>
</tr>
<tr>
<td>Thermo Scientific Model 49i</td>
<td>UV Photometric (UV)</td>
<td>FEM</td>
<td>Houston 2013</td>
</tr>
<tr>
<td><strong>NO2 Methods</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teledyne API Model T200U</td>
<td>Thermal converter-chemiluminescence (Moly-CL)</td>
<td>FRM</td>
<td>San Joaquin Valley 2013; Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>Thermo Scientific Model 42c</td>
<td>Thermal converter-chemiluminescence (Moly-CL)</td>
<td>FRM</td>
<td>Baltimore 2011</td>
</tr>
<tr>
<td>Teledyne API Model 200EUP</td>
<td>Photolytic Converter-Chemiluminescence (Photo-CL)</td>
<td>FEM</td>
<td>Baltimore 2011; San Joaquin Valley 2013; Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>Teledyne API Model T500U</td>
<td>Cavity Attenuated Phase Shift spectroscopy (CAPS)</td>
<td>FEM</td>
<td>Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>Environment SA Model AS32M</td>
<td>Cavity Attenuated Phase Shift spectroscopy (CAPS)</td>
<td>FEM</td>
<td>Houston 2013; Denver 2014</td>
</tr>
<tr>
<td>Aerodyne CAPS NO2 Analyzer</td>
<td>Cavity Attenuated Phase Shift spectroscopy (CAPS)</td>
<td>NA6</td>
<td>San Joaquin Valley 2013; Houston 2013</td>
</tr>
<tr>
<td>Los Gatos Research CRDS NO2 Analyzer</td>
<td>Cavity Ringdown Spectroscopy (CRDS)</td>
<td>NA6</td>
<td>San Joaquin Valley 2013; Houston 2013</td>
</tr>
</tbody>
</table>

**Notes:**
1. The ET-CL method was established as a FRM for Ozone in 1971.
2. The Teledyne API T265 analyzer was designated and operated as an FEM during all DISCOVER-AQ deployments. The T265 has since been re-designated as a FRM after the NO-CL method was established as a new FRM for ozone as part of the October 1, 2015 Ozone NAAQS rulemaking.
3. Both the 2B Technologies Model 205 and Ecotech EC9810 contain sample conditioning systems to remove water from the sample stream.
4. Thermo Scientific Model 49i does not contain a sample conditioning system to remove water from the sample stream.
5. Instrum ents were deployed in near roadway locations.
6. The Aerodyne CAPS and Los Gatos Research CRDS NO2 analyzers are research grade instruments that have not been designated as FEMs.

### Ozone Methods Results and Implications

On October 1, 2015, revisions to the NAAQS for Ozone were promulgated setting the level at 0.070 parts per million (ppm) or 70.0 parts per billion (ppb) in the form of the annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years. Prior to the 2015 revision, the NAAQS for ozone was 0.075 ppm (75.0 ppb) in the same form as the revised NAAQS. During the DISCOVER-AQ campaigns, field evaluations and comparisons of existing FRM and FEM analyzers for ozone show good agreement among the methods for 1-hr average ozone determinations.
To allow for evaluation of the various ozone analyzers’ performance as compared to the ET-CL FRM with respect to monitoring for the ozone NAAQS and in preparation for proposing a new FRM for ozone, maximum daily 8-hr average (MDA8) ozone concentrations were calculated. In ambient air evaluations during DISCOVER-AQ deployments in Houston, TX, and Denver, CO, MDA8 ozone results from the T265 and 2B Model 211 compared very closely with those from the Bendix 8002 FRM, as shown in Figure 2. Further results of the ozone methods evaluation and comparisons performed during DISCOVER-AQ are given in Long et. al. 2014.

Two methods for determining ozone in ambient air, the NO-chemiluminescence method (T265) and the scrubberless UV photometric method (2B 211), performed particularly well. As a direct result of the ozone methods research performed during DISCOVER-AQ deployments, a new ozone FRM based upon NO-chemiluminescence was promulgated as part of the October 1, 2015, revisions to the NAAQS for Ozone.

Nitrogen Dioxide Methods Results and Implications

In 2010, EPA promulgated a 1-hr nitrogen dioxide primary NAAQS to limit exposures to short-duration concentrations of nitrogen dioxide. Along with the new standard, EPA enacted new monitoring requirements targeted at areas of potential maximum exposure (e.g., near major roadways). The current automated Federal Reference Method (FRM) for measuring nitrogen dioxide is an indirect method based on...
on thermal conversion/gas-phase chemiluminescence where nitrogen dioxide is determined by the difference of measured oxides of nitrogen and nitric oxide. Due to potential interferences/artifacts in the FRM nitrogen dioxide determination, other methods for quantifying nitrogen dioxide have been explored, including replacement of the FRM thermal converter with a photolytic converter. Although more specific for nitrogen dioxide, the photolytic converter-chemiluminescence based option is still an indirect method and prone to similar artifacts as those associated with the FRM. Optical analyzers based on cavity ring-down spectroscopy and cavity attenuated phase shift spectroscopy provide for the direct, high-time resolution, spectroscopic determination of nitrogen dioxide concentration in ambient air.

During DISCOVER-AQ, EPA performed research on methods for the measurement of nitrogen dioxide in near-roadway environments during the field deployments in Visalia, CA (January–February 2013) and Denver, CO (July–August 2014). The Visalia and Denver near-roadway sampling sites relative to the nearby roadways are shown in Figure 3. EPA also evaluated the same nitrogen dioxide methodology at other urban and background locations during DISCOVER-AQ deployments. At the near-roadway sites, direct impact on the nitrogen dioxide concentrations was observed from the adjacent roadways with the highest nitrogen dioxide concentrations occurring when winds were blowing from the direction of the roadway, as shown in Figure 4.

The results of the nitrogen dioxide comparisons at the near-roadway locations indicate that indirect nitrogen dioxide analyzers (FRM and photolytic) may struggle in the dynamic near-roadway environment when measuring high-time resolution (1-minute average) nitrogen dioxide concentrations. Large, rapid increases and/or decreases in nitric oxide cause positive and negative artifacts in the 1-minute average indirect nitrogen dioxide determination resulting in significant scatter in the nitrogen dioxide results. However, when averaged to 1-hr concentrations, the scatter was minimized. The nitrogen dioxide comparisons at the urban and background sites show a significant improvement (decreased scatter) in the performance of the indirect methods as compared to indirect method results at near-roadway locations.

The direct spectroscopic nitrogen dioxide methods performed extremely well at both the near-roadway and urban background locations. One-hour average comparison results collected at both the near roadway and urban background studies indicate that the indirect nitrogen dioxide analyzers are adequate for determining nitrogen dioxide concentrations for comparison to the 1-hr primary NAAQS even in near-roadway locations.

**Conclusion**

During the DISCOVER-AQ study, EPA performed research on methods for the measurement of ozone and nitrogen dioxide in ambient air. Ozone and nitrogen dioxide methods evaluations and comparisons performed during DISCOVER-
As a direct result of the DISCOVER-AQ study, a new ozone FRM was promulgated as part of the October 1, 2015, revisions to the NAAQS for Ozone.

AQ deployments in Baltimore, MD, San Joaquin Valley, CA, Houston TX, and Denver, CO, have directly contributed to the establishment of a new ozone FRM based upon nitric oxide-chemiluminescence. The results of the methods research performed during DISCOVER-AQ have and will continue to serve an informative role in the NAAQS review process for both ozone and nitrogen dioxide, including the identification and designation of a new FRMs and FEMS for use in regulatory determinations.

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