The U.S. Environmental Protection Agency (EPA), as part of its Air Climate & Energy research program on emerging technologies, developed a research initiative in collaboration with developers/manufacturers of low-cost ozone (O₃) and nitrogen dioxide (NO₂) sensors to gain a better understanding of the basic performance characteristics of these sensors. This research initiative was performed through laboratory investigations at EPA laboratories in Research Triangle Park, NC.
Upon receipt of the sensor devices from the developers/manufacturers, each was integrated into the established evaluation protocol described hereafter. For each candidate sensor device, the following parameters were investigated:

1. linearity of response (range);
2. precision of measurements;
3. lowest established concentration in which a response was detected (i.e., lower detectable limit [LDL]);
4. concentration resolution;
5. response time;
6. interference equivalents; and
7. relative humidity (RH) and temperature influences.

**Evaluation Procedures**

**Exposure Chamber**

The exposure chamber (Ace Glassware) shown in Figure 1 was designed and constructed for the evaluation testing. The length and diameter of the glass chamber are large enough to accommodate at least one or more of the test sensors. The chamber has four sampling ports spaced 3.8 cm apart. Reference analyzer sample lines and sensor signal and power supply lines pass through Teflon-lined fitting caps into the exposure chamber. Unused port positions are filled with solid Teflon plugs so that laboratory air cannot dilute the generated test atmosphere. Reference analyzer sampling lines were made of 6.4-mm outer diameter perfluoroalkoxy (PFA) Teflon. Particulate filters (5-µm pore size) were fitted to each
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reference analyzer’s inlet port. Air containing known concentrations of the test atmosphere and/or suspected interferents was connected to the chamber inlet and generated using a dynamic dilution calibration system. An exhaust line was attached to the chamber outlet and placed into the laboratory’s ceiling vent. The entire chamber was housed within an environmentally controlled shelter.

**Physical Parameters (Temperature and Relative Humidity)**

Temperature within the exposure chamber was controlled through the use of the shelter’s HVAC system and supplemented with heating pads and dry ice to obtain test conditions. Relative Humidity (RH) within the exposure chamber was controlled through the use of a de-ionized water bubbler. Temperature and RH were measured with a temperature/RH probe designed by Alion.

The temperature sensor consists of a precision thin-film platinum 1000-Ω resistive temperature device (RTD) that employs a linear resistance change with temperature converted to a 0–10 V DC output proportional to 0–100.0 °C. The sensor is calibrated (zero and span) using a NIST-traceable reference thermometer.

The RH sensor consists of a HyCal Inc. IH-3602-C monolithic integrated circuit capacitance sensor that produces a linear voltage proportional to RH (0–100% RH). The RH sensor is calibrated using saturated salt solutions that have known RH over head space. The temperature and RH signal response are shown on a liquid crystal display.

Both sensors share a common probe that was inserted into one of the ports of the sampling manifold, typically at the end of the series of ports to lessen the chance of contamination from the probe’s stainless steel composition. The RH measurements require a minimal face velocity of 10 cm s⁻¹ to be accurate. The analog output signals that correspond to the temperature and RH signals were recorded by the data acquisition system during each experiment.

Test atmospheres were established using a NIST-traceable and programmable gas delivery system (Teledyne API Model T700U) with constituents delivered to the system from either EPA reference gas standards (for sulfur dioxide [SO₂], NO₂ or independent generation device (for O₃). Dilution air that had been scrubbed of particulate matter, moisture, and hydrocarbons was delivered to the mixing system to meet test gas dilution and chamber flow through needs.

**Continuous Gas (Reference) Monitors**

Samples for the continuous reference analyzers (for nitric oxide [NO] /NO₂/nitrogen oxides [NOₓ], O₃, and SO₂) were drawn to the monitors through the previously described sample ports and PFA lines at flow rates from 500 to 1000 mL/min. Flow measurements were taken at the beginning of each test run to ensure the total sampling flow requirements of the instruments did not exceed that of the source atmosphere introduced into the sampling manifold during the test. The continuous analyzers used in this study are given in Table 1.

The operating procedure for the NO₂ analyzers is based on the NO₂ Federal Reference Method (FRM)¹,² and recommendations given in the manufacturer’s operator’s manual. Likewise, the operating procedure for the SO₂ analyzers is based on the SO₂ FRM³,⁴ and recommendations given in the manufacturer’s operator’s manual. The operating procedure for the UV O₃ analyzer (a Federal Equivalent Method [FEM]) is based on the standard EPA ambient measurements of O₃ and recommendations given in the manufacturer’s operator’s manual.⁵ Prior to the beginning...
of the sensor tests, the reference analyzers were calibrated according to the individual FRMs\textsuperscript{1,3} and operators manuals.

Data from the reference analyzers and a temperature and humidity monitor were continuously recorded by the data acquisition system. The sensors’ data were transmitted either by Blue Tooth or USB/RS-232 directly to their special application software or smart phone applications. The date, time, and results of each novel sensor test were documented.

System Characterization
Prior to the start of the sensor tests, the overall system was characterized through a series of characterization experiments. The results of these characterization runs indicated the system was capable of obtaining and maintaining (over a multiple day period) a temperature range of <5 °C–>45 °C. In addition, RH control in the range of 20% to near 100% was achieved. It was also determined that the system residence time was less than 5 minutes. The residence time being the amount of time it takes for a change in a system parameter to be recorded by the corresponding reference instrument.

Test Samples
The sensors under test were placed inside the glass exposure chamber after following start-up procedures found in either a standard operating procedure or research operating procedure provided by each participating organization. Samples were drawn to the monitor through a sample pump/fan located inside the instrument or by exposure of its internal sensor to the chamber atmosphere.

Research Protocol and Test Procedures
The following parameters were investigated for each device under each test condition:

1. linearity of response (range);
2. precision of measurements;
3. lowest established concentration in which a response was detected (lower detectable limit [LDL]);
4. concentration resolution;
5. response time;
6. interference equivalents; and
7. RH and temperature influences.

A minimum of two RH conditions (e.g., dry air ≤ 25% RH, humid air ≥ 85% RH) were incorporated into the evaluation runs, as well as a minimum of two temperature ranges (e.g., low near 0 °C and high near 50 °C).

The following performance specifications and testing procedures were adapted from 40 CFR part 53 subpart B.\textsuperscript{6} Subpart B of 40 CFR part 53, details the procedures for testing performance specifications of federal reference and equivalent methods (FRMs and FEMs, respectively), which are routinely used for monitoring attainment to National Ambient Air Quality Standards (NAAQS) for gas-phase criteria pollutants, such as O\textsubscript{3} and NO\textsubscript{2}. These established procedures give a good starting point for sensor evaluations and involve elements such as response characterization over three orders of concentration magnitude, establishment of the device’s response time to changing challenge conditions, and the impact of potentially interfering co-pollutants on sensor response. The statistical treatments are those specified in the aforementioned CFR references and do not take into account potential serial correlation that might exist when repeated measures are involved. Specifics about these procedures are reported below.

Linearity (range)—Nominal minimum and maximum concentrations that a method is capable of measuring.

Test procedure: Determine a suitable calibration curve showing the test analyzer’s measurement response over at least 95% of the required or indicated measurement range (0–500 parts per billion [ppb]).

<table>
<thead>
<tr>
<th>POLLUTANT</th>
<th>ANALYZER</th>
<th>PRINCIPLE OF OPERATION</th>
</tr>
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<tbody>
<tr>
<td>NO\textsubscript{2}</td>
<td>Thermo Model 42C NO/NO\textsubscript{2}/NO\textsubscript{x} Analyzer</td>
<td>O\textsubscript{3}-chemiluminescence</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>2B Model 205 O\textsubscript{3} Analyzer</td>
<td>UV Absorption</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>Thermo Model 43C SO\textsubscript{2} Analyzer</td>
<td>Pulsed Fluorescence</td>
</tr>
</tbody>
</table>
Precision of Measurements (three replicates)—Variation about the mean of repeated measurements of the same pollutant concentration, expressed as 1 standard deviation.

Test procedure: (1) Sample test atmosphere $A_0$ (zero air). (2) Measure test atmosphere, $A_p$, and record the stable reading (in ppb) as $P_1$. (3) Repeat the second step two more times, record values for $P_2$ and $P_3$ after each test, and calculate precision ($P$) as follows:

$$P = \frac{1}{2} \left[ \sum_{i=1}^{3} P_i^2 - \frac{1}{3} \left( \sum_{i=1}^{3} P_i \right)^2 \right]$$

Lower Detectable Limit—Minimum pollutant concentration that produces a measurement or measurement output signal of at least twice the noise level.

Test procedure: Measure zero air and record the stable measurement reading in ppb as $B_Z$. Generate and measure a pollutant test concentration equal to the value for the lower detectable limit specified in Table B–1 to Subpart B of Part 53. Record the test analyzer’s stable measurement reading (in ppb) as $B_L$. Determine the LDL test result as $LDL = B_L - B_Z$.

Resolution—Smallest amount of input signal change that the instrument can detect reliably. This term is determined by the instrument noise. Noise is the spontaneous, short-duration deviations in measurements or measurement signal output about the mean output that are not caused by input concentration changes. Measurement noise is determined as the standard deviation ($S$) of a series of measurements of a constant concentration about the mean and is expressed in concentration units.

Test procedure: (1) Measure zero air with the test analyzer. Record 10 test analyzer concentration measurements with at least two minutes separating successive measurements. Label and record the test measurements as $r_1, r_2, r_3...r_{10}$. (2) Repeat step 1 using a pollutant test atmosphere 80% of the upper range limit (URL). Calculate $S_0$ and $S_{80}$ as follows:

$$S = \sqrt{\frac{1}{n-1} \left[ \sum_{i=1}^{10} r_i^2 - \frac{1}{n} \left( \sum_{i=1}^{10} r_i \right)^2 \right]}$$

Response Time

1. Lag Time—Time interval between a step change in input concentration and the first observable corresponding change in measurement response.

Test procedure: Determine the elapsed time between the change in test concentration from zero air to 80% URL and the first observable (two times the noise level) measurement response.

2. Rise Time—Time interval between initial measurement response and 95% of final response after a step increase in input concentration.

Test procedure: Calculate 95% of the measurement reading and determine the elapsed time between the first observable (two times noise level) measurement response and a response equal to 95% of the reading.

Interference Equivalent—Positive or negative measurement response caused by a substance other than the one being measured.

Test procedure: (1) Sample and measure test atmosphere zero air. Allow for a stable measurement reading and record the reading as $R$ (in ppb). (2) Sample and measure the interferent test atmosphere and record the stable reading in ppb as $R_I$. (3) Calculate the interference equivalent ($IE$) as $IE = R_I - R$.

The test analyzers were challenged, in turn, with each potential interfering agent (interferent) along with corresponding standard deviations and interference equivalents. The following tables provide specifics.

### Table 2. Interference test atmospheres for apps/sensors.

<table>
<thead>
<tr>
<th>INTERFERENT</th>
<th>CONCENTRATION (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O₃ Sensors</strong></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>500</td>
</tr>
<tr>
<td>NO₂</td>
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<td>O₃</td>
<td>500</td>
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<tr>
<td>NO</td>
<td>500</td>
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</tbody>
</table>
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specified in Table 2 at a concentration substantially higher than that likely to be found in the ambient air.

**RH and Temperature Influences**

1. **RH.**  
   **Test procedure:** Determine response to a known test concentration under dry (RH < 25%) and high humidity (RH > 85%) conditions.

2. **Temperature.**  
   **Test procedure:** Determine response to a known test concentration under low (near 0 °C) and high (≥ 50 °C) temperature conditions.

**SUMMARY**

This article describes the systems and procedures used by EPA during its laboratory-based research initiatives to evaluate basic performance characteristics of low-cost O₃ and NO₂ sensors. Similar evaluation studies can be performed by other using similar procedures and systems. In addition, the systems, procedures and methods can be modified to accommodate individual research/evaluation needs. Although not given here, the results of the aforementioned sensor evaluation initiative can be found in the publicly available EPA report, entitled “Sensor Evaluation Report.”

**References**