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Efficacy of Paired Electrochemical Sensors for Measuring Ozone Concentrations

Christopher Zuidema^a , Nima Afshar-Mohajer^a , Marcus Tatum^b, Geb Thomas^b ,
Thomas Peters^c , and Kirsten Koehler^a 

^aDepartment of Environmental Health and Engineering, Johns Hopkins Bloomberg School of Public Health, Baltimore, Maryland;

^bDepartment of Mechanical and Industrial Engineering, University of Iowa, Iowa City, Iowa; ^cDepartment of Occupational and Environmental Health, University of Iowa, Iowa City, Iowa



ABSTRACT

Typical low-cost electrochemical sensors for ozone (O₃) are also highly responsive to nitrogen dioxide (NO₂). Consequently, a single sensor's response to O₃ is indistinguishable from its response to NO₂. Recently, a method for quantifying O₃ concentrations became commercially available (Alphasense Ltd., Essex, UK): collocating a pair of sensors, a typical oxidative gas sensor that responds to both O₃ and NO₂ (model OX-B431) and a second similar sensor that filters O₃ and responds only to NO₂ (model NO2-B43F). By pairing the two sensors, O₃ concentrations can be calculated. We calibrated samples of three NO2-B43F sensors and three OX-B431 sensors with NO₂ and O₃ exclusively and conducted mixture experiments over a range of 0–1.0 ppm NO₂ and 0–125 ppb O₃ to evaluate the ability of the paired sensors to quantify NO₂ and O₃ concentrations in mixture. Although the slopes of the response among our samples of three sensors of each type varied by as much as 37%, the individual response of the NO2-B43F sensors to NO₂ and OX-B431 sensors to NO₂ and O₃ were highly linear over the concentrations studied ($R^2 \geq 0.99$). The NO2-B43F sensors responded minimally to O₃ gas with statistically non-significant slopes of response. In mixtures of NO₂ and O₃, quantification of NO₂ was generally accurate with overestimates up to 29%, compared to O₃, which was generally underestimated by as much as 187%. We observed changes in sensor baseline over 4 days of experiments equivalent to 34 ppb O₃, prompting an alternate method of calculating concentrations by baseline-correcting sensor signal. The baseline-correction method resulted in underestimates of NO₂ up to 44% and decreases in the underestimation of O₃ up to 107% for O₃. Both methods for calculating gas concentrations progressively underestimated O₃ concentrations as the ratio of NO₂ signal to O₃ signal increased. Our results suggest that paired NO2-B43F and OX-B431 sensors permit quantification of NO₂ and O₃ in mixture, but that O₃ concentration estimates are less accurate and precise than those for NO₂.

Introduction

Low-cost sensor networks are playing a profound role in the lower-accuracy/larger sample measurement paradigm emerging in environmental health.^[1–5] Each node within such networks is commonly equipped with sensors that produce an electrical signal proportional to the concentration of a target gas.^[6,7] Reference instruments for gas pollutants commonly utilize technologies such as optical (UV) spectroscopy (e.g., fluorescence, chemiluminescence, and absorption), but these technologies have a number of disadvantages for producing

highly resolved temporospatial measurements in the environment, including high initial costs, the need for skilled operators, and designs geared towards benchtop, laboratory or regulatory applications.^[2,4–6] The low cost, small size, portability, and low power consumption, of gas sensors present an opportunity to overcome some of the disadvantages of reference instruments.^[3,4,8,9] However, compared to reference instruments, gas sensors require thorough laboratory/field calibration by end users, have lower sensitivity/specificity, exhibit greater cross-sensitivity with non-target species, are subject to

CONTACT Kirsten Koehler  kirsten.koehler@jhu.edu  Department of Environmental Health and Engineering, Johns Hopkins Bloomberg School of Public Health, 615 N. Wolfe St. Room E6632, Baltimore, MD 21205

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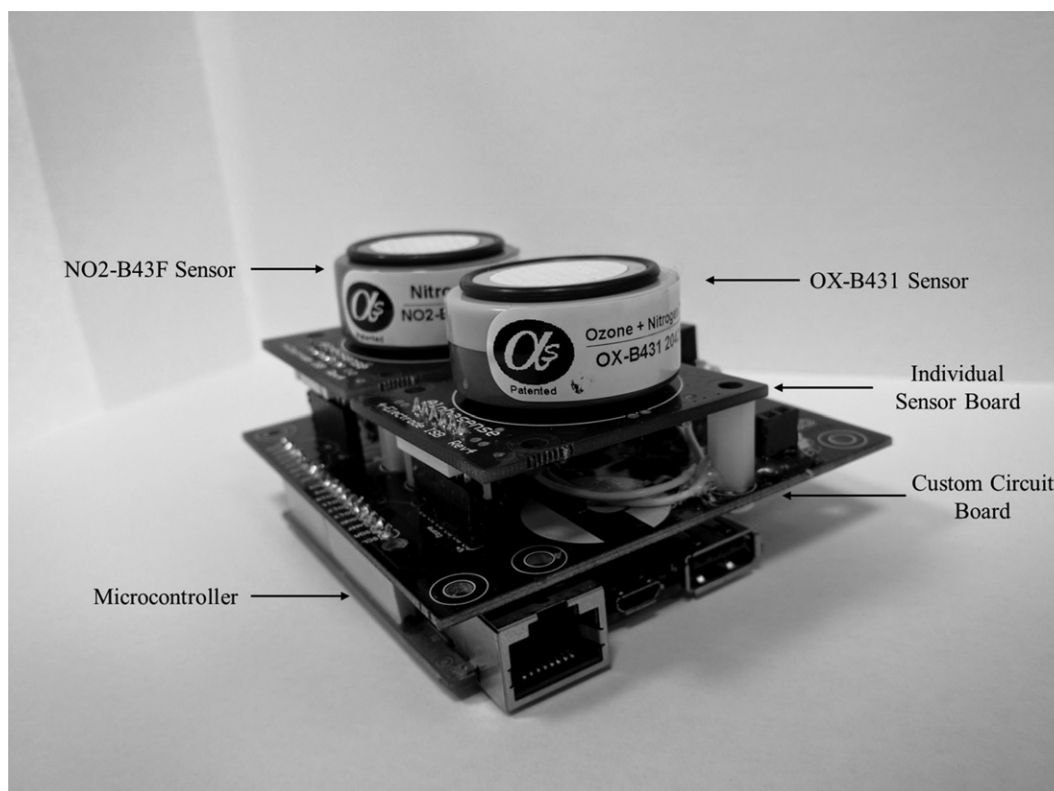


Figure 1. Sensor setup. Oxidative gas and NO₂ sensors were mounted onto Individual Sensor Boards. A custom circuit board connected the sensor-ISB assembly to a microcontroller.

larger amounts of signal baseline drift over time, and produce data of lower quality.^[2–5,10]

Electrochemical gas sensors are capable of quantifying a range of target gases including carbon monoxide, ozone, oxides of nitrogen, hydrogen sulfide, chlorine, and sulfur dioxide at part-per-million and -billion concentrations.^[7,11] The principle of operation of electrochemical sensors relies on a chemical reaction, typically an oxidation or reduction reaction, taking place between an electrode and the target gas that produces an electrical signal proportional to the gas concentration. The electrode composition depends on the gas of interest and the chemical reaction that must take place to detect the target gas.^[7,12–14] The reaction creates a difference in electric potential between the sensor's working and counter electrodes, which generates an electric current that constitutes the sensor's output signal.^[7,12–15] Electrochemical sensors are typically paired with a potentiostatic circuit, which processes the sensor signal from a current to a voltage.^[16] Despite lower performance compared to reference instruments, electrochemical sensors may demonstrate sufficient selectivity, accuracy, linearity, and repeatability for many applications, and in conjunction with their low power consumption, they are widely used in many settings.^[3] The disadvantages of

electrochemical sensors include electrolyte loss, a life-span limited to 2 years or less (especially in low relative humidity or high concentration environments), sensitivity to electromagnetic frequencies, and cross-sensitivity with interfering gases.^[7,9]

Although electrochemical sensors can be customized for particular applications and configurations, the need for laboratory set up, calibration and a characterization of cross-sensitivities is well recognized and inhibits their ease of use.^[3,5,13] For example, many existing commercial electrochemical sensors for O₃ and NO₂ respond to both gases simultaneously, without discrimination, due to the fact that NO₂ and O₃ are both reducible at similar potentials on carbon and gold electrodes.^[17] These are in effect “oxidative gas” sensors, and their response is proportional to the combined concentration of O₃ and NO₂. This non-selectivity is particularly challenging when NO₂ and O₃ are both present, for example, in manufacturing facilities where these gases are produced by welding and other combustion processes, or in the ambient environment where both gases are associated with traffic-related air pollution. Previous studies have characterized the response of oxidative gas sensors to their target and interfering gases,^[5,14] while others have attempted to differentiate sensor response

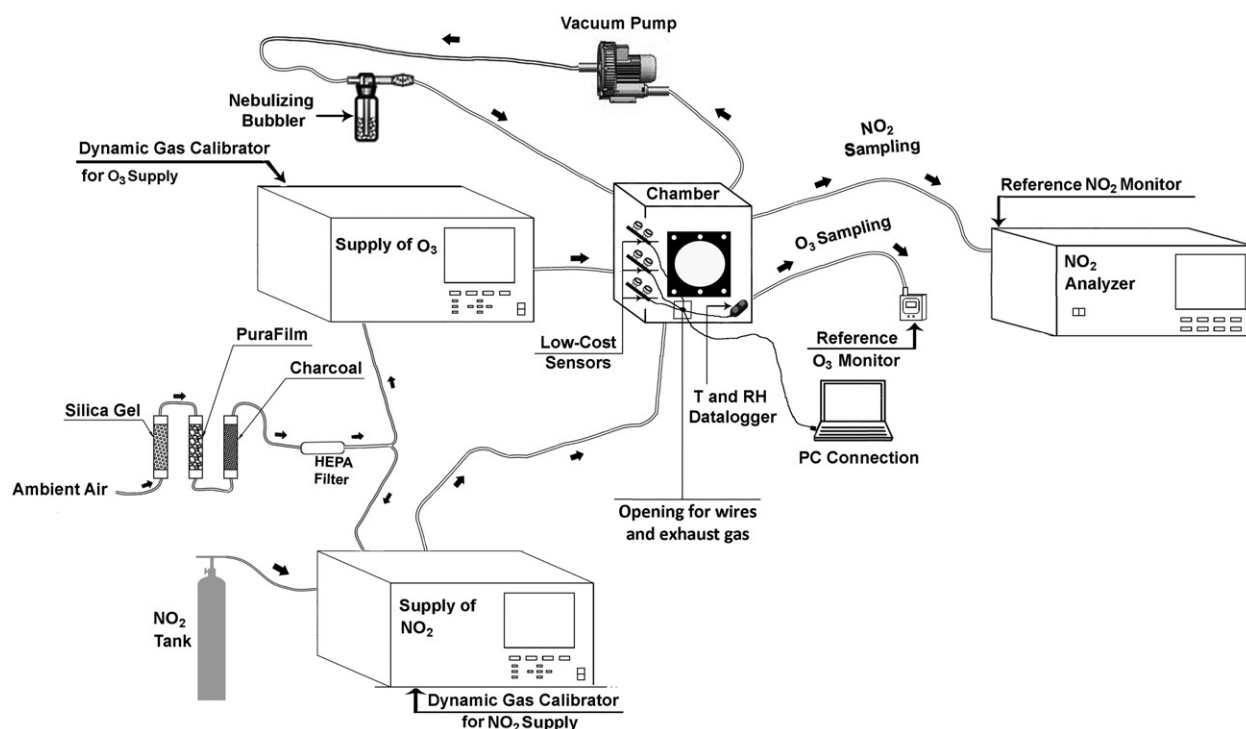


Figure 2. Setup used for the calibration of NO₂-B43F and OX-B431 sensors and experiments exposing paired electrochemical sensors to mixtures of O₃ and NO₂.

between target and interfering gas using statistical modelling techniques such as linear regression and artificial neural networks.^[15]

To address the simultaneous quantification of O₃ and NO₂ concentrations, Alphasense Ltd. (Essex, UK) has proposed utilizing a pair of collocated electrochemical sensors: one that responds to NO₂ and O₃ (model OX-B431; a typical “oxidative gas” sensor) and one sensor that only responds to NO₂ (model NO₂-B43F). The NO₂-B43F sensor is equipped with a manganese dioxide (MnO₂) filter which catalyzes O₃ into oxygen (O₂), thereby preventing sensor response to O₃ in the environment. The response of the oxidative gas sensor to O₃ is calculated by subtracting the response to NO₂. This paired sensor method of quantifying O₃ was previously introduced and the differential response (in nA) of one pair of sensors was demonstrated for concentrations of 1 ppm O₃, 1 ppm NO₂ and a mixture of 1 ppm O₃ and 1 ppm NO₂; however, the authors did not evaluate how well the paired sensor method quantified NO₂ and O₃ concentrations.^[17] We have previously reported on an earlier generation of the OX-B431 sensor (model OX-B421) only, and its response to NO₂ and O₃ exclusively.^[18] This study examines the ability of the paired sensors to distinguish NO₂ and O₃ concentrations simultaneously. We also assessed the bias and precision of the paired sensor method for quantifying NO₂ and O₃

concentrations at atmospherically relevant concentrations. The response of the sensors to NO₂ and O₃ gas individually was used to create calibration curves and those calibration curves were used to calculate the concentration of each gas in mixtures over a range of NO₂ and O₃ concentrations. We outline the practical aspects of setting up, calibrating and using the paired sensor method for quantifying NO₂ and O₃. We also present two separate methods to calculate gas concentrations from sensor signal and have described the utility of each method, depending on the end user’s application.

Methods

Sensor configuration

We mounted three pairs of new NO₂ (model NO₂-B43F, Alphasense Ltd., Essex, UK) and oxidative gas (model OX-B431, Alphasense Ltd., Essex, UK) sensors onto Individual Sensor Boards (000-0ISB-02) produced by the same manufacturer (Figure 1). These assemblies were connected to a microcontroller (model Seedeuino Cloud, Seeed Technology Inc., Shenzhen, China) through a customized circuit board, two sensors to each board. The working electrode and reference electrode signals were each amplified by a factor of 2 with signal amplifiers (model MCP6002, Microchip Technology Inc., Chandler, AZ) and fed

into a 10-bit analog-to-digital convertor on the micro-controller. The 5-volt power for the device was smoothed with a 5-volt LM7805 linear regulator to reduce signal noise. Voltage outputs from each sensor were calculated by taking the difference between the working and reference electrode values and were transmitted over a serial channel approximately every 2 sec to a computer.

Experimental setup

The sensors were opened and installed on their assemblies for 50 days prior to the start of experiments and data collection, during which time we ran sensors in ambient laboratory air, conducted preliminary test, and made hardware and software adjustments on the sensor boards. Over the course of 4 days, we carried out a series of experiments on three pairs of OX-B431 and NO2-B43F sensors under different O₃ and NO₂ concentrations and mixtures of the two gases. The concentrations of O₃ studied were approximately 0, 30, 65, 95, and 125 ppb, and the concentrations of NO₂ studied were 0, 0.1, 0.25, 0.5, and 1.0 ppm. These concentrations were chosen to reflect current occupational and environmental standards (NO₂: OSHA Permissible Exposure Limit (PEL) = 5 ppm; ACGIH® Threshold Limit Value (TLV®) = 0.2 ppm; and EPA National Ambient Air Quality Standards (NAAQS) = 100 ppb and O₃: OSHA PEL = 0.1 ppm; ACGIH TLV = 0.05–0.20 ppm; and EPA NAAQS = 0.070 ppm).

We exposed sensors to NO₂ and O₃ in a 22 cm x 15 cm x 24 cm (7.92 L) acrylic chamber (Figure 2). A small vent in the chamber allowed gas to escape and the chamber to operate at a slightly positive pressure with respect to the room. A digital thermometer/hygrometer (model Hygrochron iButton, Maxim Integrated Inc., San Jose, CA) monitored the chamber's temperature and relative humidity. Both NO₂ and O₃ concentrations in the chamber were measured with highly specific reference instruments (NO₂: model 42c, Thermo Environmental Instruments Inc., Franklin, MA; O₃: model Personal Ozone Monitor, "POM," 2B Technologies Inc., Boulder, CO). The Thermo 42c chemiluminescent analyzer is a designated federal reference method (FRM) for NO₂ (with a precision of ± 0.4 ppb) and the POM UV absorption instrument is a designated federal equivalent method (FEM) for O₃ (with a precision of ± 2 ppb). Both instruments were calibrated before use, and experimental conditions were within the instruments' operating ranges. Nitrogen dioxide was supplied to the chamber with a dynamic gas

calibrator (model 146i, Thermo Environmental Instruments Inc., Franklin, MA) by diluting high-concentration (500 ppm) NO₂ from a tank with zero-air. Ozone was supplied to the chamber by an O₃ generator (model 146c, Thermo Environmental Instruments Inc., Franklin, MA). Airflow from both the dynamic gas calibrator and ozone generator were supplied to the chamber at 5.0 L/min during all experiments (including at gas concentrations equal to zero), and concentrations of NO₂ and O₃ were adjusted to achieve the target gas concentrations in the chamber. We maintained temperature between 24.6–27.8 °C and relative humidity (RH) between 36.3–51.8% by circulating chamber air through a bubbler filled with water at a flowrate of 25 L/min with a vacuum pump (MEDO VP0435A, Roselle, IL).

Although the manufacturer provides calibration slopes and intercepts for each sensor, we first conducted experiments to develop sensor-specific calibration curves for O₃ and NO₂ exclusively with the sensor setup and configuration used in this study. We also performed experiments to assess how well the sensor pairs quantified concentrations of NO₂ and O₃ in mixtures with one another. For each target concentration of 0.1, 0.25, 0.5, and 1.0 ppm NO₂, the chamber was first flushed with zero air for 10 min during which the sensor baseline response was recorded. Then, the steady-state NO₂ concentration for each experiment was established, for 10 min before the introduction of O₃. Then O₃ was introduced at varying levels to maintain concentrations of approximately 65, 125, 30, 95, and 0 ppb for 10 min each without altering the NO₂ concentration. This procedure is exemplified by the time series of the reference instrument measurements, shown in Figure SA1 of the Supplemental Materials during the 0.1 ppm NO₂ experiment (panel a) and the 0.25 ppm NO₂ experiment (panel b). Similarly, time series for one of the sensor pairs' (sensor pair 1) responses for the same experiments are shown in Figure SA2 of the Supplemental Materials during the 0.1 ppm NO₂ experiment (panel a) and the 0.25 ppm NO₂ experiment (panel b). A 10-min average of the sensors' 2-sec voltage output from each experimental condition was used to establish the response of the sensor to the target concentration(s).

Calculating nitrogen dioxide and ozone concentrations with low-cost sensors

The OX-B431 sensors respond to both NO₂ and O₃, and the NO2-B43F sensors respond only to NO₂, although the sensitivities of both types of sensors to

each of the gases differs. Consequently, separate calibration curves for the OX-B431 sensors to NO₂, OX-B431 sensors to O₃ and NO2-B43F sensors to NO₂ were first determined. Here, calibration curves for each sensor were developed by applying least-squares linear regression to sensor signal in response to NO₂ and O₃ exclusively. To measure O₃ in mixture with NO₂, the NO2-B43F and OX-B431 sensors must be collocated and the NO₂ contribution to the OX-B431 sensor response is subtracted by first calculating the NO₂ concentration with the NO2-B43F sensor. To test this procedure, we conducted experiments mixing NO₂ and O₃, and measuring both gases with electrochemical sensor pairs. We then calculated NO₂ and O₃ concentrations for experimental conditions using two different methods in response to an observed change in sensor baseline values over the course of experiments.

Additionally, we estimated the limit of detection for each sensor from data collected during the first 10 min of each experiment when the sensors were exposed to zero air according to (Equation (1)):

$$LOD_g = \frac{3\sigma_{mV}}{m_g}, \quad (1)$$

where LOD_g is a sensor's limit of detection for NO₂ or O₃ gas, σ_{mV} is the standard deviation of each sensor's baseline response calculated from 1-min averages of sensor baseline in millivolts (mV), and m_g is the calibration slope or sensitivity of the sensor for either NO₂ or O₃.

Method 1: Applying calibration slope and intercept

In the first method to calculate gas concentration, subsequently referred to as "Method 1," the slopes and intercepts of each of the sensors determined by our calibration experiments with a single gas were applied to the sensor response. Method 1 would reasonably be employed by typical end users for a low-cost sensor network deployment, where frequent recalibration or baseline correction is not practical. The calibration curve derived for the NO2-B43F (Equation (2)) was rearranged to solve for the NO₂ concentration (Equation (3)):

$$mV_{NO2-B43F} = [NO_2]m_{NO2-B43F} + b_{NO2-B43F} \quad (2)$$

$$[NO_2] = \frac{mV_{NO2-B43F} - b_{NO2-B43F}}{m_{NO2-B43F}}, \quad (3)$$

where $mV_{NO2-B43F}$ is the response of the NO2-B43F sensor in mV, $[NO_2]$ is the concentration of NO₂, $m_{NO2-B43F}$ is the slope of the calibration curve of the NO2-B43F sensor, and $b_{NO2-B43F}$ is the intercept of the calibration curve for the NO2-B43F sensor. In

Method 1, we approached the signal from the OX-B431 sensor in a similar fashion as the NO2-B43F sensor, including terms for the OX-B431 sensor calibration slope to NO₂ and O₃ and the calibration intercept for O₃ (Equation (4)):

$$mV_{OX-B431} = [NO_2]m_{OX-B431,NO_2} + [O_3]m_{OX-B431,O_3} + b_{OX-B431}, \quad (4)$$

where $mV_{OX-B431}$ is the response of the OX-B431 sensor in mV, $m_{OX-B431,NO_2}$ is the slope of the calibration curve of the OX-B431 sensor to NO₂, $[O_3]$ is the concentration of O₃, $m_{OX-B431,O_3}$ is the slope of the OX-B431 sensor to O₃ and $b_{OX-B431}$ is the intercept of the OX-B431 sensor determined in the OX-B431 sensor O₃ calibration. In this approach the calibration intercepts for both gases are conceptually the same (e.g., sensor response to air containing neither NO₂ or O₃), but in practice are not equal (Table SA3 of the Supplemental Materials), therefore including intercept terms for both gases would be duplicative. We observed variability in sensor intercepts in NO₂ and O₃ calibration experiments and chose to use the O₃ calibration intercept because O₃ was the gas of interest. The contribution of NO₂ gas to the OX-B431 sensor response can be inferred with the OX-B431 sensor NO₂ gas slope, $m_{OX-B431,NO_2}$, and the concentration of NO₂ estimated from the NO2-B43F sensor. To solve for the concentration of O₃, both the intercept of the OX-B431 sensor and the contribution of NO₂ gas to the OX-B431 sensor response was subtracted from the total OX-B431 sensor response and divided by the slope of the OX-B431 O₃ gas calibration curve (Equation (5)):

$$[O_3] = \frac{mV_{OX-B431} - b_{OX-B431} - [NO_2]m_{OX-B431,NO_2}}{m_{OX-B431,O_3}}. \quad (5)$$

Method 2: Baseline-correcting sensor response and applying calibration slope

In an alternate analysis, prompted by an observed change in sensor baseline values and subsequently referred to as "Method 2," we applied only the slopes determined in the calibration experiments to the baseline-corrected sensor response. This approach, while not necessarily practical in the context of a sensor network deployment, may be useful for other applications where sensor baseline can be more frequently corrected for, and offers insight into the sources of error for these paired electrochemical sensors. The baseline response for each sensor was recorded at a concentration of 0 ppm NO₂ and 0 ppb O₃ at the beginning of each of the NO₂ and O₃ mixture experiments and

Table 1. Summary of least-squares linear regression.

| Sensor Pair | NO ₂ Calibration | | | O ₃ Calibration | | |
|----------------------------------|-----------------------------|----------------------------|----------------|----------------------------|----------------------------|----------------|
| | Slope (Est ± SE) mV/ppm | Intercept (Est ± SE) mV | R ² | Slope (Est ± SE) mV/ppm | Intercept (Est ± SE) mV | R ² |
| a) NO ₂ -B43F Sensors | | | | | | |
| 1 | 282.0 ^B ± 1.3 | 7.4 ± 0.7 | 1.00 | 7.8 ± 14.8 | 14.5 ± 1.2 | 0.09 |
| 2 | 256.4 ^B ± 1.6 | −2.4 ± 0.9 | 1.00 | 10.0 ± 15.6 | 3.9 ± 1.2 | 0.12 |
| 3 | 309.5 ^B ± 4.8 | 2.0 ± 2.6 | 1.00 | 22.2 ± 12.2 | 11.8 ± 1.0 | 0.53 |
| Mean (SD) | 282.7 (26.6) | 2.3 (4.9) | – | 13.4 (7.8) | 10.1 (5.5) | – |
| b) OX-B431 Sensors | | | | | | |
| 1 | 376.6 ^B ± 3.2 | 5.5 ± 1.7 | 1.00 | 424.3 ^A ± 25.5 | 13.2 ± 2.0 | 0.99 |
| 2 | 328.1 ^B ± 2.7 | −5.7 ± 1.5 | 1.00 | 354.5 ^A ± 21.2 | 2.3 ± 1.7 | 0.99 |
| 3 | 440.0 ^B ± 3.5 | 8.7 ± 1.9 | 1.00 | 515.3 ^A ± 27.4 | 17.4 ± 2.2 | 0.99 |
| Mean (SD) | 381.5 (56.1) | 2.8 (7.6) | – | 431.4 (80.6) | 11.0 (7.8) | – |

Notes: SE: standard error of the regression

^Aleast-squares regression coefficient of sensor slope with p -value < 0.0005

^Bleast-squares regression coefficient of sensor slope with p -value < 0.00001

subtracted from all the sensor's readings in the experiment, thus eliminating the need for a sensor intercept. The comparison of sensor calibration intercepts and baseline responses are shown in Table SA3 of the Supplemental Materials. The relationship between sensors' response and gas concentrations were therefore:

$$mV_{NO_2-B43F, baseline-corrected} = [NO_2]m_{NO_2-B43F, NO_2} \quad (6)$$

and

$$mV_{OX-B431, baseline-corrected} = [NO_2]m_{OX-B431, NO_2} + [O_3]m_{OX-B431, O_3}, \quad (7)$$

where $mV_{NO_2-B43F, baseline-corrected}$ and $mV_{OX-B431, baseline-corrected}$ are baseline-corrected signals from the NO₂-B43F and OX-B431 sensors, respectively, and all other terms remain the same. Method 2 provides a strategy to manage transient changes in sensor baseline, which is comparable to the calibration intercept, but assumes that sensor calibration slope is constant for the dataset.

Bias and precision of NO₂ and O₃ concentrations estimated by electrochemical sensors

To quantify the accuracy of sensor concentration estimates, measurement error was taken as the percent bias of each NO₂ and O₃ concentration estimate for each sensor pair and the average of the three sensor pairs compared to the reference instruments. Bias was calculated according to:

$$\%Bias = \frac{Sensor - Reference}{Reference} \times 100\%, \quad (8)$$

where *Sensor* is the concentration estimated from the electrochemical sensors and *Reference* is the concentration according to the reference instruments. We estimated the concentration of NO₂ and O₃ using

each sensor pair and then took the mean concentration of the three sensor pairs. This mean concentration estimate was evaluated against the reference instruments to calculate the mean bias of NO₂ and O₃ concentration estimates for each experimental condition. Bias was compared to guidance values from NIOSH and the EPA for direct reading monitors and air sensors. NIOSH specifies that percent bias should be within ±10%,^[19] whereas the EPA recommends that bias be within 20–50%, depending on the application area, including Education and Information (<50%), Hotspot Identification and Characterization (<30%) Supplemental Monitoring (<20%), and Personal exposure (<30%).^[20] Similarly, the mean absolute percent error (MAPE) was calculated to summarize the measurement error of NO₂ and O₃ concentration estimates of mixture experiments for each sensor pair and the average of three sensor pairs, according to:

$$MAPE = \frac{100\%}{n} \times \sum_{i=1}^n \left| \frac{Sensor - Reference}{Reference} \right|, \quad (9)$$

where n is the number of NO₂ or O₃ experimental concentrations studied, *Sensor* is the NO₂ or O₃ concentration measured by the electrochemical sensors, and *Reference* is the O₃ or NO₂ concentration measured by the reference instrument. Percent bias and MAPE were not calculated for the lowest concentrations of NO₂ and O₃ where the target concentration was zero. Here, bias provides a measure of error at each experimental condition within mixture experiments, and MAPE summarizes the bias observed across the range of conditions for each mixture experiment.

To characterize the precision of gas concentration estimates, we calculated the coefficient of variation (CV) by dividing the standard deviation of the three sensor concentration estimates, σ_{conc} , by the absolute

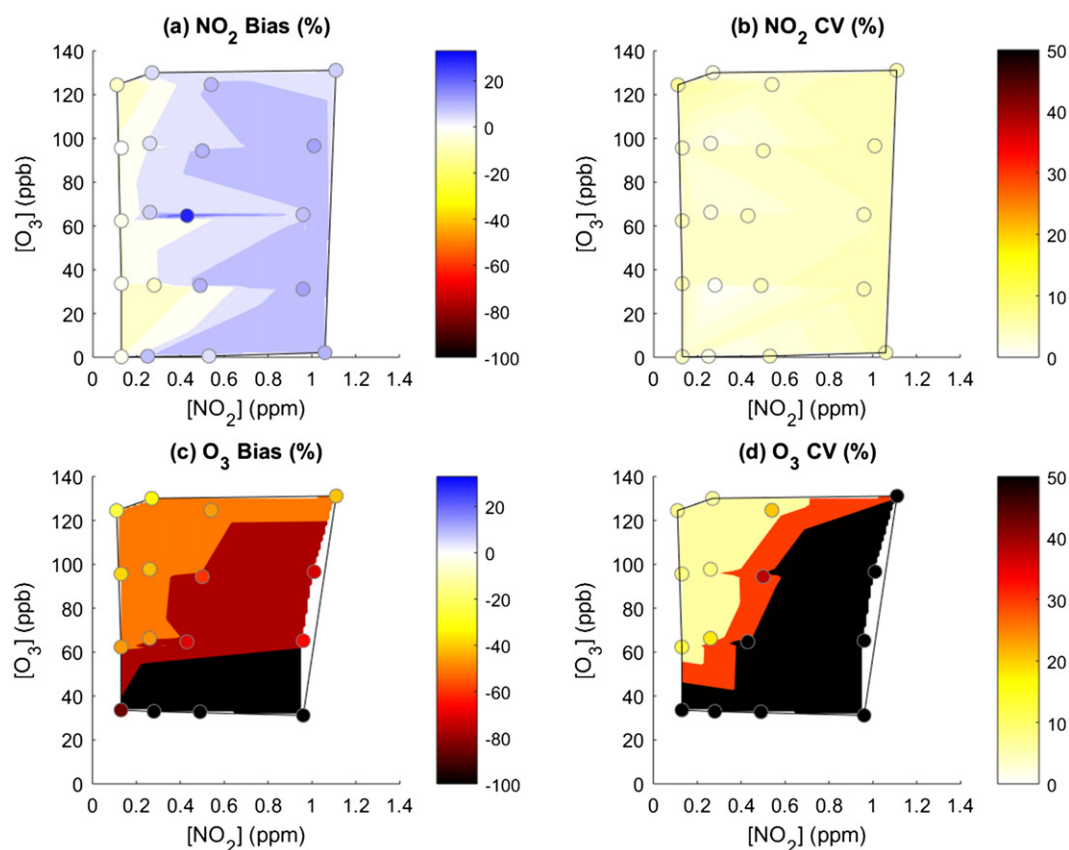


Figure 3. Bias and CV maps of NO₂ and O₃ concentration estimates for Method 1. CV was calculated as the standard deviation of the concentration estimates of three sensor pairs divided by the absolute value of the mean estimate.

value of the mean concentration estimate of the sensors, μ , and expressed it as a percent:

$$CV = \frac{\sigma_{conc.}}{|\mu|} \times 100\% \quad (10)$$

Taking the absolute value of the mean of sensor concentration estimates allowed for the calculation of precision when sensor signals produced concentration estimates that were negative. Negative estimates of gas concentration are an artifact of processing sensor signal to gas concentration, particularly at low concentrations. A higher CV indicates more variability and more imprecision in concentration estimates. As with bias, we compared calculated CVs to guidance values from the EPA which recommends precision between 20 and 50% depending on the application.^[20] NIOSH does not provide a recommended value for precision. All data were analyzed with MATLAB R2017a (Natick, MA).

Results

Sensor response to NO₂ or O₃ exclusively

The results of the linear regression on voltage output from each sensor with respect to NO₂ and O₃ exclusively are shown in Table 1. Among the three NO₂-

B43F sensors, the mean of the slopes of the response observed to NO₂ was 283 mV/ppm with a standard deviation of 27 mV/ppm (9% of the mean). Individual sensors' response to NO₂ was highly statistically significant ($p < 0.00001$) and linear ($R^2 = 1.00$). In contrast, the slopes of the response of the NO₂-B43F sensors to O₃ were low (mean slope = 13 mV/ppm), not statistically significant ($p \geq 0.165$), and nonlinear ($R^2 \leq 0.53$), consistent with the expectation that these sensors do not respond to O₃.

The mean slope of the response of the OX-B431 sensors to NO₂ was 382 mV/ppm and to O₃ was 431 mV/ppm. The standard deviations of the mean slopes were 56 mV/ppm NO₂ (15% of the mean) and 81 mV/ppm for O₃ (19% of the mean). Individual OX-B431 sensor response to NO₂ was highly statistically significant ($p < 0.00001$) and linear ($R^2 = 1.00$). Similarly, the individual OX-B431 sensor response to O₃ was highly statistically significant ($p < 0.0005$) and linear ($R^2 = 0.99$). Of note, the mean OX-B431 sensor response to NO₂ gas was 1.35 times greater than the NO₂-B43F sensors (382 vs. 283 mV/ppm) and the mean OX-B431 sensor response to O₃ gas was 1.13 times greater than to NO₂ gas on a concentration basis (431 mV/ppm vs. 382 mV/ppm). The mean LOD

Table 2. Sensor response (mV) to zero air and temperature and relative humidity of zero air during baseline.

| | Temp \pm SD ($^{\circ}$ C) | RH \pm SD (%) | NO2-B43F Sensor | | | OX-B431 Sensor | | |
|------------------|-------------------------------|-----------------|-----------------|---------------|----------------|----------------|---------------|----------------|
| | | | 1 | 2 | 3 | 1 | 2 | 3 |
| Day 1 AM | 23.4 \pm 0.3 | 25.9 \pm 1.7 | 23.0 | 12.8 | 22.7 | 23.8 | 14.2 | 31.8 |
| Day 1 PM | 27.7 \pm 0.0 | 44.0 \pm 0.4 | 19.4 | 9.9 | 19.1 | 14.1 | 9.4 | 24.5 |
| Day 2 AM | 23.7 \pm 0.3 | 26.9 \pm 5.9 | 18.7 | 8.2 | 19.0 | 20.3 | 10.8 | 25.6 |
| Day 2 PM | 27.7 \pm 0.0 | 42.5 \pm 2.6 | 17.0 | 6.4 | 16.6 | 17.2 | 6.1 | 23.3 |
| Day 4 AM | 23.6 \pm 0.2 | 48.1 \pm 0.6 | 13.4 | 2.9 | 10.5 | 10.5 | 0.1 | 14.6 |
| Day 4 PM | 26.2 \pm 0.2 | 46.8 \pm 0.4 | 10.1 | 1.1 | 0.8 | 10.5 | -1.1 | 14.4 |
| Average \pm SD | 25.3 \pm 2.1 | 39.0 \pm 10.0 | 18.3 \pm 4.6 | 6.9 \pm 4.4 | 14.8 \pm 7.9 | 17.2 \pm 5.4 | 8.1 \pm 6.1 | 24.0 \pm 6.8 |
| Change, mV (%) | – | – | -12.9 (-56) | -11.7 (-92) | -21.8 (-96) | -13.3 (-56) | -15.3 (-107) | -17.4 (-55) |

Note: SD: standard deviation

Table 3. MAPE for NO₂ and O₃ averaged for three sensor pairs.

| Experiment | Method 1 | | Method 2 | |
|--------------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|
| | MAPE [NO ₂] (%) | MAPE [O ₃] (%) | MAPE [NO ₂] (%) | MAPE [O ₃] (%) |
| 0.1 ppm NO ₂ | 3 | 47 | 34 | 11 |
| 0.25 ppm NO ₂ | 6 | 57 | 14 | 23 |
| 0.5 ppm NO ₂ | 12 | 87 | 5 | 36 |
| 1.0 ppm NO ₂ | 10 | 91 | 4 | 51 |
| Overall Mean | 8 | 71 | 14 | 30 |

Note: MAPE: mean absolute percent error

for NO₂ was 5 ppb for the NO2-B43F sensors and 3 ppb for the OX-B431 sensor. The LOD for O₃ was 4 ppb for the OX-B431 sensor.

Calculating NO₂ and O₃ concentrations by applying calibration slope and intercept: Method 1

The mean bias of NO₂ and O₃ concentration estimates for Method 1 are shown in Figure 3, Panels (a) and (c). The mean bias of NO₂ and O₃ concentration estimates for each experimental condition was calculated using the mean gas concentration estimate of the three sensor pairs. The mean bias points shown in Figure 3 are colored based on this value. The contour plot was created by linear interpolation of the overlying mean bias points to describe the bias between experimental conditions. Bias is an indicator of accuracy and values closer to zero represent closer agreement of the electrochemical sensors to the reference instrument. For Method 1, the mean bias for of NO₂ ranged from -8 to 29%, with bias of a larger magnitude observed at higher NO₂ concentrations (Figure 3a). The mean O₃ bias was between -187 and -24% with higher bias (greater underestimation) observed at lower O₃ concentrations (Figure 3c). For Method 1, 17 out of 20 (85%) NO₂ concentration estimates and 0 out of 16 O₃ concentration estimates met the NIOSH criterion of bias \pm 10%. The bias of individual sensor pair concentration estimates of NO₂ and O₃

for Method 1 are presented in Table SA4 of the Supplemental Materials. The MAPE is interpreted here as a summary measure of experimental biases and shown in Table 3. For NO₂ concentration estimates, the overall MAPE was equal to 8%, less than NIOSH's bias criterion of \pm 10% (Table 3). For O₃ concentration estimates, the overall MAPE was equal to 71% (Table 3) and was greater than the largest EPA criterion for bias of \pm 50%.

The mean CV in NO₂ and O₃ concentrations estimated with the three sensor pairs at each experimental condition for Method 1 is shown in Figure 3, Panels (b) and (d). We observed generally uniform CV in concentration estimates between 1 and 7% (median = 5%) for NO₂ (Figure 3b), but strongly increasing CV in ozone ranging from 6 to 146% (median = 44%) for O₃ that increased with increasing NO₂ and decreasing O₃ concentrations (Figure 3d). The NO₂ concentrations estimated via Method 1 met the most stringent EPA guidelines for precision (<20%), whereas 6 out of 16 (38%) of the O₃ concentration estimates met the same guideline.

Calculating NO₂ and O₃ concentrations by applying calibration slope to baseline-corrected sensor response: Method 2

We observed decreases in sensor response to zero air (0 ppm NO₂ and 0 ppb O₃) ranging from 12–22 mV over the 4 days of experiments that were unrelated to temperature or relative humidity differences (Table 2). These baseline voltages decreased over the 4 days by as much as 107% for the OX-B431 and 92% for the NO2-B43F sensors comparing the first day of experiments to the last day. Of particular note was the observed change in sensor baseline compared to the magnitude of the sensor response to target gas. For example, the OX-B431 sensor with the largest absolute change in sensor baseline among the OX-B431 sensors had a change of 17 mV, corresponding to

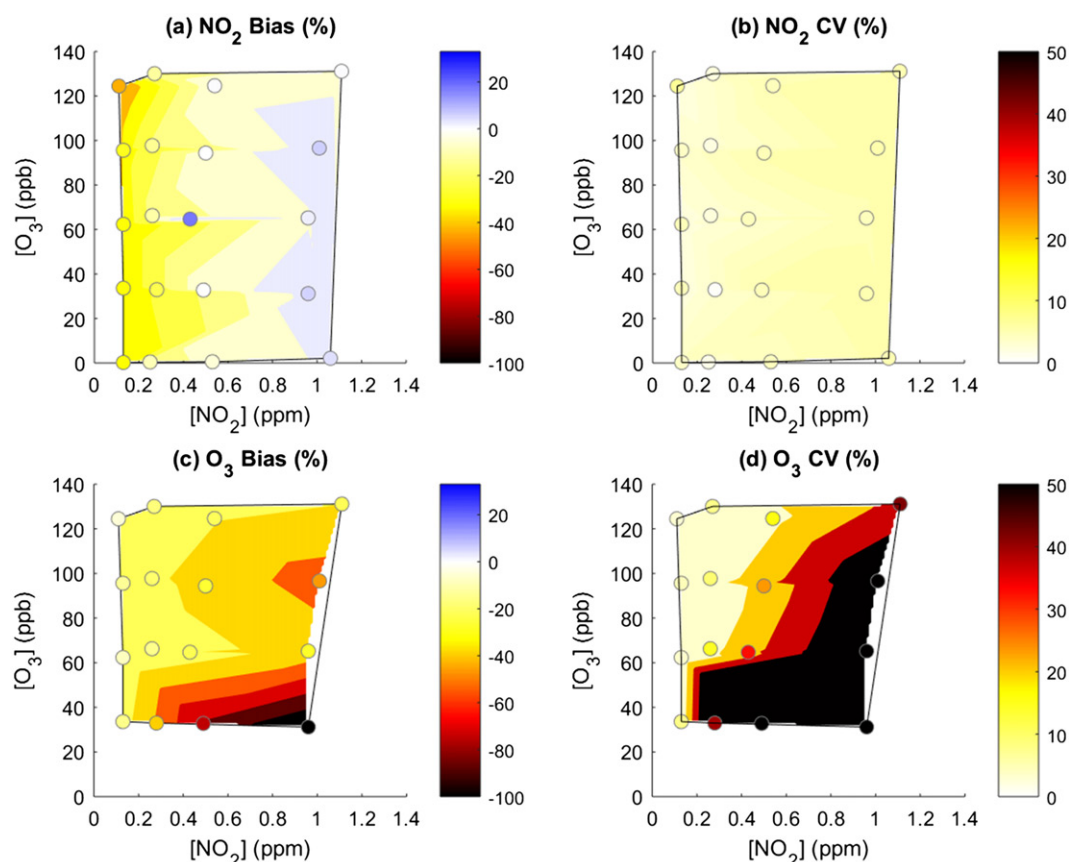


Figure 4. Bias and CV maps of NO₂ and O₃ concentration estimates for Method 2. CV was calculated as the standard deviation of the concentration estimates of three sensor pairs divided by the absolute value of the mean estimate.

approximately 0.040 ppm NO₂ or 0.034 ppm (~34 ppb) O₃. The NO₂-B43F sensor with the greatest absolute change in sensor baseline among the NO₂-B43F sensors had a change of 22 mV, corresponding to approximately 0.070 ppm NO₂. The mean baseline changes observed at the beginning and end of experiments were 4.0 ± 2.4 mV.

For Method 2, we observed higher levels of bias for NO₂ concentration estimates but lower levels of bias for O₃ concentration estimates compared to Method 1 (Figure 4). For Method 2, the mean bias for NO₂ ranged from -44 to 17%, with the magnitude of the bias higher at lower NO₂ concentrations (Figure 4a). For O₃ concentration estimates, the mean bias for Method 2 was between -107 and 5% and displayed a pattern of bias similar to Method 1 with higher bias observed at lower O₃ and higher NO₂ concentrations (Figure 4c). For Method 2, 10 out of 20 (50%) NO₂ concentration estimates and 2 out of 16 (13%) O₃ concentration estimates met the NIOSH criterion of bias $\pm 10\%$. The bias of individual sensor pair concentration estimates of NO₂ and O₃ for Method 2 are presented in Table SA5 of the Supplemental Materials. The overall MAPE of NO₂ concentration estimates

was equal to 14% and of O₃ concentration estimates was 30% (Table 3), which were greater than the NIOSH criterion of 10%, but for NO₂ within the most stringent limits suggested by the EPA for supplemental monitoring activities ($\pm 20\%$) and hotspot identification and characterization ($\pm 30\%$). CV for Method 2 was calculated the same way as in Method 1, and we observed comparable CV in concentration estimates between 2 and 6% (median = 5%) for NO₂ (Figure 4b). For O₃, CV was between 3 and 1753% (median = 20%) and increased with increasing NO₂ and decreasing O₃ concentrations (Figure 4d). NO₂ concentrations estimated via Method 2 met the most stringent EPA guidelines for precision ($<20\%$), whereas 9 out of 16 (56%) of the O₃ concentration estimates met the same guideline.

For Methods 1 and 2 overall, the bias and CV of NO₂ concentration estimates were less than for O₃ (Figures 3 and 4), indicating that concentration estimates of NO₂ were more accurate and precise compared to those for O₃. We observed a larger overall error of O₃ concentration estimates for Method 1 compared to Method 2 (MAPE = 71 vs. 30%) and a larger overall error of NO₂ concentration estimates for

Method 2 compared to Method 1 (MAPE = 14 vs. 8%) (Table 3). Method 1 produced NO₂ concentration estimates with MAPE between 3 and 12% with generally smaller error at low NO₂ concentrations, and Method 2 produced concentration estimates between 4 and 34% with smaller error at high NO₂ concentrations (Table 3). In addition, while the CV of concentration estimates with both methods was comparable for NO₂, for O₃, the CV increased as the concentration of NO₂ increased and O₃ decreased and was generally smaller for Method 2 except for one outlier. (Figures 3d and 4d).

Discussion

Our calibration experiments demonstrated that the NO2-B43F sensors had a highly linear response to NO₂, and that the OX-B431 sensors had a highly linear response to NO₂ and O₃, comparable with previous studies.^[21] The variability we observed in the calibration slope among the three sensors of each type (Table 1) is consistent with the variability in the sensor-specific calibration slopes provided by the manufacturer. In our sample of three sensors of each type, the standard deviation of the mean of the calibration slopes among the three NO2-B43F sensors to NO₂ was equal to 27 mV/ppm, and for the OX-B431 sensors to O₃ was equal to 81 mV/ppm, and to NO₂ was equal to 56 mV/ppm. These results suggest it is appropriate to use sensor-specific calibration curves rather than a common curve for each type of sensor, although our sample size was small.

In the case of NO₂ and O₃, the strategy of paired sensors works, although with decreasing accuracy and precision when the signal from NO₂ obscures the signal from O₃. On an individual sensor pair level, the accuracy of NO₂ and O₃ concentration estimates varied across the three sensor pairs studied, with one of the sensor pairs out-performing the other two according to the MAPE. This also suggests that sensor pairs should be calibrated and tested in the laboratory prior to deployment in the field to identify sensor pairs with unacceptable levels of measurement error.

We observed the specificity of the NO2-B43F sensors, and although they responded slightly to increasing concentrations of O₃ gas, on average, their response to NO₂ gas was over 20 times greater than the response to O₃. Furthermore, least-squares regression of the response among the three NO2-B43F sensors to O₃ produced p -values $0.16 \leq p \leq 0.63$, indicating that O₃ concentration was not a significant predictor of NO2-B43F sensor response. These results

provide further evidence that the MnO₂ filter on the NO2-B43F sensor is effective at excluding O₃ from the sensor and are consistent with prior studies.^[17]

Over the course of the 4 days in which we carried out experiments, we observed changes in sensor baseline that affected the quantification of NO₂ and O₃ and the measurement error associated with each sensor concentration estimate. We investigated whether temperature or relative humidity could explain this drift, but ultimately the reasons for the changes in baseline are not known. Compared to the NO2-B43F sensor, a unit of the OX-B431 sensor signal is associated with a greater concentration of gas, making concentration estimates more vulnerable to errors given a change in sensor baseline. This is an especially acute problem given that O₃ concentrations of interest are often less than 100 ppb, compared to NO₂ concentrations which are often greater than 100 ppb. Our strategy to correct for changes in sensor baseline resulted in a differential change in error associated with NO₂ and O₃ concentration estimates between the two methods. For Method 1 compared to Method 2, we observed a higher degree of accuracy in NO₂ concentration estimates (MAPE = 8 vs. 14%), but worse accuracy for O₃ concentration estimates (MAPE = 71 vs. 30%). In this laboratory study we were easily able to accommodate changes in sensor baseline with Method 2, however, a comparable methodology in the field on the day-to-day timescale may be impractical.

One reason there is more error estimating O₃ concentration in a mixture with NO₂ with paired electrochemical sensors compared to estimating NO₂ concentration with a single sensor is that the error associated with two sensors is propagated through the subtraction procedure. Additionally, if using a common sensor calibration slope for sensors of the same type, the mean response of the OX-B431 sensors to O₃ may be smaller in magnitude than the variability of the OX-B431 sensors' response to NO₂. For example, we observed the range of response across the 3 OX-B431 sensors exposed to 0.5 ppm NO₂ equal to 57 mV which is equivalent to the mean OX-B431 sensor response to 132 ppb O₃. Another challenge is that the changes in sensor baseline are large relative compared to the response of the sensor to O₃ at typical ambient and occupational concentrations. Here we observed maximum changes of 17 mV with the OX-B431 sensor associated with 34 ppb O₃ and 22 mV with the NO2-B43F associated with 0.070 ppm NO₂.

These dynamics make accurate O₃ concentration estimates in a mixture with NO₂ challenging with pairs of electrochemical sensors, especially if the end-

user chooses to use a common calibration curve for sensors of each type. For these reasons, when measuring O_3 concentrations with paired electrochemical sensors, we caution against using single calibration curves for each sensor type without previously examining individual sensor response to target gas. This conclusion may not be consistent with previous evaluations of an earlier-generation oxidative gas sensor (model: OX-B421, Alphasense Ltd., Essex, UK) where a single calibration curve for NO_2 and a single calibration curve for O_3 adequately characterized the response of a sample of three sensors.^[18]

Our evaluation of these sensors occurred over a stable and controlled range of temperature and RH for each experimental condition (mean temperature \pm SD: $27 \pm 1^\circ C$, mean RH \pm SD: $39 \pm 5\%$ RH) to reduce their influence on sensor response. Purposefully characterizing sensor response under a larger range of temperature and RH or applying temperature and RH correction factors from the manufacturer would be particularly important for deployment in environments where temperature and RH are highly variable.

A limitation of this study is that we did not examine other gases that interfere with the quantification of NO_2 and O_3 with electrochemical sensors, such as nitrogen monoxide (NO) and carbon dioxide (CO_2). In a study using previous generations of the sensors used here at ambient concentrations of CO_2 , NO, NO_2 , and O_3 , the impact observed on O_3 concentration estimates by the OX-B421 sensor was 20.6% for NO and 365.8% for CO_2 , whereas the impact on NO_2 concentration estimates by the NO2-B4 sensor was -20.6% for NO and 118.9% for CO_2 .^[5] These interfering gases co-occur with O_3 and NO_2 in ambient and occupational environments and would decrease the accuracy of concentration estimates or may completely obscure target gas signals if present in high concentrations. The present study with NO_2 and O_3 provides evidence that the strategy of filtering out cross sensitive gases and deploying collocated sensors could be successfully developed for other target gases with known interferents depending on the required accuracy of the application.

Conclusions

We evaluated a method for measuring NO_2 and O_3 in mixture using paired electrochemical sensors: one sensor that responds to O_3 and NO_2 (OX-B431) and another that responds to NO_2 only (NO2-B43F). We observed the strategy works over a range of

concentrations and mixtures of the two gases, but the precision and accuracy of O_3 concentration estimates declined as NO_2 concentration increased. We observed substantial variability in the concentration estimates of O_3 in a sample of three sensor pairs. Over the course of the 4 days of experiments, we also observed a change in sensor baseline, complicating the calculation of O_3 , and prompting an alternate method of baseline-correcting sensor signal to calculate concentration. Although the paired sensor method has potential to improve the specificity of O_3 concentration estimates compared to a single oxidative gas sensor, concentrations of NO_2 and O_3 where the ratio of NO_2 signal to O_3 signal is large may still challenge their performance, performance among sensor pairs is variable, sensor baseline voltage is subject to drift, and the cost to measure O_3 effectively doubles. Increases in target gas specificity will ameliorate a major drawback and improve the utility of electrochemical sensors and has the potential to provide higher-quality data for environmental and occupational sensor networks.

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ORCID

Christopher Zuidema  <http://orcid.org/0000-0002-2233-2706>

Nima Afshar-Mohajer  <http://orcid.org/0000-0002-6337-1824>

Geb Thomas  <http://orcid.org/0000-0001-5032-4001>

Thomas Peters  <http://orcid.org/0000-0002-1698-8856>

Kirsten Koehler  <http://orcid.org/0000-0002-0516-6945>

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