

AQ-SPEC

Air Quality Sensor Performance Evaluation Center

Laboratory Evaluation of VOC Sensors

Laboratory Setup and Testing Protocol

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Executive Summary

The Air Quality Sensor Performance Evaluation Center (AQ-SPEC) program was established by the South Coast Air Quality Management District (South Coast AQMD) in 2014 to evaluate the performance of commercially-available air quality sensors. The initial focus of the program was on the evaluation of air quality sensors measuring criteria pollutants, and currently AQ-SPEC has evaluated many commercial sensors for those pollutants. From ongoing community engagement and especially under the AB 617 program, South Coast AQMD staff have worked with communities expressing their environmental justice and exposure concerns to volatile organic compounds (VOC) and air toxics. These concerns have increased interest in using VOC sensors for air quality and fence-line VOC monitoring due to their potential to provide high time and spatial resolution at lower cost. While VOC sensors may provide valuable information on air quality, no standards exist for VOC sensor performance, and the variety of operational principles of VOC sensors further obscures VOC sensor data quality. Recognizing the urgent need for protocols to systematically evaluate VOC sensors to better understand their operation/function, sensitivity, and selectivity, AQ-SPEC has developed a testing protocol to evaluate VOC sensors. This new test protocol builds upon and expands previous limited VOC sensor laboratory evaluation efforts by the U.S. EPA.

The performance of VOC sensors is quantified using metrics such as data recovery, intra-sensor variability, accuracy, and correlation to reference instruments. Statistical tests are also performed to determine important explanatory variables that drive sensor response. All data collected, results, and evaluation reports developed from this protocol are organized and posted online as part of the AQ-SPEC website (www.aqmd.gov/aq-spec), and made available for free to inform and educate the public on the capabilities of the commercially-available VOC sensors and their potential applications.

A selection of VOC sensors was first evaluated according to this VOC testing protocol for method development and validation. Preliminary results suggest that while currently available VOC sensors may provide qualitative indications of VOC levels observed, they may not provide accurate VOC concentration values. Depending on the operating principles of a given sensor, it may show cross sensitivities to temperatures and/or relative humidity, or may be susceptible to gaseous interferences. Uncertainty of data quality from VOC sensors suggests that there is room for currently available VOC sensor technology to improve for them to be used for ambient monitoring

purposes. Furthermore, the currently available VOC sensors have detection limits that are higher than ambient VOC levels, and therefore they are likely not suitable for ambient background air applications at this time. The protocol developed is based on the current state of knowledge and technology, and it will be used going forward for AQ-SPEC VOC sensor laboratory evaluations. Additional testing aspects and approaches may be considered for inclusion in the future as needed in response to VOC sensor technology changes, improvements in AQ-SPEC testing infrastructure, or public concern over specific VOC species.

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1 Background

1.1 Air Quality Sensor Performance Evaluation Center (AQ-SPEC)

In 2014, the South Coast Air Quality Management District (South Coast AQMD) established the Air Quality Sensor Performance Evaluation Center (AQ-SPEC) to characterize the performance of commercially available air quality sensors that measure criteria pollutants (i.e., PM_{2.5}, PM₁₀, O₃, NO, NO₂, CO) when deployed in the field (under real-world conditions) and laboratory (under expanded ranges of pollutant concentrations and climates). The AQ-SPEC field and laboratory testing protocols for criteria pollutant sensors specify how sensors qualify for testing, the experimental setup, testing procedures, and calculation of performance metrics.

As of the start of 2023, AQ-SPEC has cooperated with 100+ sensor manufacturers and evaluated the performance of 230+ sensors that measure criteria pollutants. Sensor evaluation reports from field and laboratory testing, as well as the respective test protocols, are publicly available on the AQ-SPEC website (<http://www.aqmd.gov/aq-spec>), while additional discussions of AQ-SPEC field and laboratory testing can be found in Feenstra et al. (2019) and Papapostolou et al. (2017), respectively. The performance of sensors measuring criteria pollutants is first performed in the field, in which they are operated side-by-side with reference instruments measuring the same pollutants for 8 weeks at a fixed air monitoring station. If a sensor shows adequate performance in the field (i.e. $R^2 > 0.5$ compared to the corresponding reference monitor), it will advance to laboratory testing. In the laboratory, a 1.3 m³ test chamber (hereafter “Chamber 1”) was originally used to challenge the sensors with known pollutant concentrations under controlled environmental conditions, as well as in the presence of potential interferents. Due to the need for a chamber with the ability to simultaneously evaluate a larger number of sensor units, as well as accommodate needs for more complex projects (e.g. sensor library calibration and ASTM sensor testing), AQ-SPEC has developed a second, larger 1.6 m³ test chamber (hereafter “Chamber 2”) with additional specialized testing capabilities (i.e. wind speed, vibration, and altitude testing). Since Chamber 2 is now used for testing criteria pollutant-measuring sensors, Chamber 1’s setup has now been modified for performance evaluation of sensors that measure volatile organic compounds (VOC).

The traditional AQ-SPEC field and laboratory testing protocols have served as useful foundational frameworks for newer protocols. The United States Environmental Protection

Agency (U.S. EPA) published sensor testing protocols for PM_{2.5} and O₃ sensors in 2021 (U.S. EPA 2021a and U.S. EPA 2021b); these protocols include elements of field and laboratory testing inspired by AQ-SPEC testing protocols. AQ-SPEC recently published a protocol to evaluate the performance of sensors measuring criteria pollutants when deployed on mobile platforms (<http://www.aqmd.gov/aq-spec/special-projects/mobile-sensors>), and the results of pilot-testing using this novel evaluation protocol were published in Mui et al. 2021. Furthermore, AQ-SPEC played a significant role in developing an ASTM International standard test method for the performance evaluation of PM_{2.5} sensors used in indoor applications, which was also published in 2021 as [ASTM D8405-21](#).

While protocols for testing criteria pollutant-measuring sensors are maturing, there is a lack of systematic evaluation procedures for VOC sensors. Due to increasing concerns from the public about adverse health impacts from air toxics and recent emphasis on community monitoring, especially in communities where air toxics are of major concern, AQ-SPEC is now expanding its efforts to test sensors that measure VOCS, which includes gaseous air toxics. Ambient VOC concentrations have been routinely quantified using methods such as TO-14a (U.S. EPA 1999a) and TO-15 (U.S. EPA 1999b), both of which are used to measure subsets of the 97 VOC that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. Method TO-15 is used to analyze VOC samples collected in canisters and only using a gas chromatograph coupled to a mass spectrometer; Method TO-14a on the other hand measures fewer VOC species (e.g., it cannot be used for polar VOCs), but it allows for the use of detectors other than a mass spectrometer, such as a flame ionization detector (FID). These methods are time consuming and thus inherently cannot provide high time resolution data, while VOC sensors can provide real-time measurements of VOC concentrations. Furthermore, VOC sensors can be an important tool to gauge exposure to VOC in ambient air, occupational, and indoor spaces, as well as support existing programs that monitor ambient air toxics, such as the U.S. EPA's [National Air Toxics Trends Station \(NATTS\)](#) Network, the [Multiple Air Toxics Exposure Study \(MATES\)](#) conducted by South Coast AQMD, and [Rule 1180](#) that was adopted by South Coast AQMD in 2017. The NATTS Network's presence in the South Coast Air Basin is limited to monitoring at the downtown Los Angeles and Riverside-Rubidoux sites, with sampling performed once every six days, and public reports published annually. Meanwhile air toxics sampling is conducted at approximately 10 sites, once every six days, for approximately one year,

for the South Coast AQMD MATES reports, which are published every 6-10 years. VOC monitoring data under some existing programs is infrequent and spatially sparse, while VOC exposure can vary greatly in time and space. While there exist numerous real-time VOC monitoring techniques, such as Fourier Transform Infrared (FTIR) spectroscopy, Differential Optical Absorption Spectroscopy (DOAS), Cavity Ring-Down Spectroscopy (CRDS), and total nonmethane organic compound monitors (e.g., auto gas chromatograph), these monitoring techniques are expensive and require strong technical expertise, additional calibration gases/systems and data manipulation/interpretation. VOC sensors on the other hand are comparatively more cost effective and easy to deploy, and therefore could play an important role in filling in the spatiotemporal gaps in understanding VOC exposure in communities. In recent years, community concerns over VOC emitted from petroleum refineries have increased and in response, South Coast AQMD Rule 1180 was established that requires petroleum refineries to install and operate fence-line air monitoring systems to measure select criteria and VOC pollutants. VOC sensors could support the implementation and enforcement of Rule 1180 if adequate data quality from the sensors can be demonstrated, such as through AQ-SPEC sensor testing.

This document describes the laboratory testing procedures developed by South Coast AQMD staff, which is built upon and expands on previous VOC sensor testing efforts by the U.S. EPA to systematically evaluate the performance of commercially-available VOC sensors under known laboratory chamber conditions of relative humidity (RH), temperature (T), and target VOC and interfering species concentrations. A field testing protocol for the performance of VOC sensors is under development and commencement of field testing is estimated to start in late Spring 2023. All data collected, documentation developed, and testing results obtained from laboratory testing of VOC sensors project are organized and posted online as part of the AQ-SPEC website (www.aqmd.gov/aq-spec) and made available for free to inform and educate the public on the capabilities of commercially-available VOC sensors and their potential applications. Sensor-related events and workshop information are also posted on this website.

1.2 VOC Sensors

VOC include a wide variety of chemical families including aliphatic hydrocarbons (alkanes), carbonyls (e.g., formaldehyde, acetaldehyde), aromatic hydrocarbons (e.g., benzene, toluene, xylene), and halogenated hydrocarbons (e.g., tetrachloroethylene). Major sources of VOC

in urban areas originate from vehicular emissions, gasoline evaporation, oil refineries, industrial emission, and biogenic emissions.

Conventional VOC monitoring relies on methods that are time consuming, labor intensive and expensive to operate, including calibration, sampling, sample storage, separation, and quantification of the VOC. With recent advancements in sensor technology, the emergence of “low-cost” VOC sensors can provide a better time and spatial resolution for air quality monitoring. In addition, these sensors can be deployed in near-source locations, fence-line monitoring and in indoor environments to gain a more comprehensive understanding of the levels of VOC emitted locally and provide real-time feedbacks to the public.

The performance of air quality sensors measuring criteria pollutants (i.e., PM_{2.5}, PM₁₀, O₃, CO, and NO_x), has been extensively evaluated by AQ-SPEC and others (Northcross et al. 2013, Spinelle et al. 2014, Williams et al. 2014, Wang et al. 2015, Sousan et al. 2016). However, systematic and comprehensive evaluation of VOC sensor performance is scarce. Maughan et al. (2005) evaluated three total hydrocarbons sensors (ppbRAE, AreaRAE and EZ-580) in stepped tests (subjecting sensors to stepwise steady state concentrations of a blend of six hydrocarbons) and transient tests (tests for sensor response to rapid concentration change) at the Pacific Northwest National Laboratory using a collapsible chamber and dynamic dilution system to test for accuracy, precision, detection limits, response, and interferences from other compounds. The results showed that all RAE VOC sensors tested have high precisions (>94%) but varying accuracy when compared to the test gas (47–92%) depending on the test concentrations (about 2-100 ppm) during the transient tests. The response time to reach 90% of the test value was about a minute for both ppbRAE and AreaRAE sensors. The EZ-580 sensors tended to show lower accuracy and precision compared to both RAE sensors.

A more recent evaluation (both laboratory and field) on next generation VOC sensors was conducted by the U.S. EPA’s Office of Research and Development (ORD) (Williams et al. 2015). In their laboratory evaluations, five VOC sensors (i.e., UniTec SENS-IT, AirBase CanarIT, CairPol CairClip, APPCD PID, and ToxiRAE Pro) were selected and evaluated for responsiveness, linearity of response, and precision. The effects of RH, T, and interfering compounds were also investigated. The sensors were challenged with either benzene alone or a mixture of benzene, 1,3-butadiene, and tetrachloroethylene to concentrations up to 25 ppb in a concentration ramping manner. The laboratory evaluation results showed that three of the five devices (i.e., AirBase,

ToxiRAE Pro, and CanarIT) tested either did not show a response to the VOC challenge concentrations or were unsuccessful in establishing detection limits under the challenge conditions. On the other hand, the APPCD PID showed high sensitivity. The UniTEC SENS-IT was able to detect VOC levels between 5 and 25 ppb, though its cyclic behavior below 10 ppb rendered it impossible to determine its detection limit and precision. Sensor performance against the gas chromatography flame ionization detector (GC-FID) was inconclusive due to nonviable GC-FID data acquired.

In the KEY-VOC EURAMET joint research project, Spinelle et al. (2017a) evaluated commercially available as well as research grade sensors to measure benzene, covering a wide range of sensor types including photoionization detector (PID), metal oxide semiconductor (MOS), electrochemical cell (EC), and miniaturized gas chromatography (miniGC). The results showed that the PID sensors exhibited great linearity but showed high cross-sensitivities with the interfering compounds such as toluene, xylene, ethane, propane, butane, and pentane. In addition, PID and EC sensors suffered from large hysteresis effects. RH was shown to have great impacts on EC and MOS sensors; these sensors tended to lack sensitivity. The miniGC and MOS sensors that incorporated temperature cycling compensation features, on the other hand, did not seem to have cross sensitivities with the interfering compounds.

1.2.1 General Review of Technology Status

Commercially available sensors to detect VOC utilize four main principles of operation, including PID, MOS, EC, and nondispersive infrared sensors (NDIR).

1.2.1.1 Photoionization Detection (PID) Sensors

Operating Principle

PID sensors utilize an energetic light source (ultraviolet radiation between 10-200 nm) to ionize compounds with ionization energy less than or equal to the output of the lamp. The photon emission from the lamp depends on the type of fill gas (e.g., krypton, argon, hydrogen gas, or xenon), which is typically less than 12 eV. The 10.6 eV lamp is the most used due to its broad sensitivity to many compounds and long lamp lifetime. The electric current produced by the resulting ions is proportional to the concentration of the molecules. The larger molecules or compounds containing double or triple bonds will have lower ionization energy and will be more likely to be detected.

Generally, these instruments can perform accurately when calibrated with a standard of known concentrations. Due to the large number of compounds of interest, it is not plausible to employ standards for all compounds. Thus, response factors are determined to allow for quantification of a wide range of compounds with one single compound as the calibration standard. Isobutylene is often used as a calibration standard for PID sensors because of its intermediate sensitivity (its ionization point is near the midpoint of most VOC), low toxicity and flammability at concentrations used in the calibration processes (Haag and Wrenn 2006).

Measurement Range and Application

There are currently numerous commercially available VOC sensors for a wide range of applications, as summarized in Szulczyński and Gębicki (2017) and Spinelle et al. (2017b). Some of these sensors are shown in Table A1 and Table A2. Depending on the sensing technique and the design, a sensor may cover a wide range of VOC concentrations present in different environments. The measurement range of PID sensors can vary between sub-ppb and thousands of ppm levels depending on the photon output of the light source. This wide measurement range makes PID sensors suitable for industrial hygiene applications, low concentration gas leak detection, and hazardous material identification.

Selectivity and Interference

PID sensors are subject to interferences from RH, T, sensor supply voltage, as well as VOC concentration. Lewis et al. (2016) showed that careful signal handling can improve the limit of detection by an order of magnitude. Because PID sensors can ionize all compounds with an ionization energy less than or equal to the lamp output, this technique is not selective, and not able to speciate different compounds in the gas mixtures. The major components in air (i.e., nitrogen, oxygen, argon) cannot be ionized by the energy output of the lamp and will not interfere with the measurements. Most VOC species have an ionization energy below 12 eV and thus can be detected using the PID technique. The classes of compounds that can be measured using PID include, in decreasing order of sensitivity: aromatics, alkenes, sulfides, organic amines, ketones, ethers, aldehydes, alcohols and alkanes.

1.2.1.2 Metal Oxide Semiconductor (MOS) Sensors

Operating Principle

MOS sensors generally consist of a metal oxide layer maintained at some temperature using a heater and electrodes that measure changes in resistance. There are mainly two types of metal

oxides: 1) the n-type, i.e., tin oxide (SnO₂) and zinc oxide (ZnO), which respond to reducing gas molecules; and 2) the p-type, including nickel oxide (NiO) and cobalt oxide (CoO), which respond to oxidizing gas molecules (Szulczyński and Gębicki 2017). For the n-type metal oxide, oxygen in air can be chemisorbed on the metal oxide layer to trap electrons from the conduction band of the metal oxide, which prevents any electric current flow and thus lowers conductivity. The presence of reducing gas compounds will react with the bound oxygen, releasing electrons to the metal oxide layer, resulting in change of resistance and increase in conductivity. The reverse operating principle applies to p-type metal oxides, where oxidizing gas compounds will remove electrons from the metal oxide layer. These reactions induce changes in the sensor resistance, which will be recorded as a signal, and it is proportional to the concentration of the target gas(es).

Measurement Range and Application

Most MOS sensors have a limit of detection of 1 ppm and can measure up to 6000 ppm of VOC. MOS sensors are widely used to monitor indoor air quality, fire detection, and ventilation control/air purifiers.

Selectivity and Interference

The determining factors for the performance of MOS sensors are morphology and structure of the sensing material (Sun et al. 2012). MOS sensors are generally not selective, as they also respond to inorganic gases such as NO_x and CO, potentially making MOS sensors not suitable for the measurement of VOC at concentrations considerably lower than those of inorganic gases when present. Such responsiveness should be thoroughly checked for each sensor to ensure usability for VOC detection.

High RH could potentially reduce the sensitivity of the MOS sensors because adsorption of water molecules on the metal oxide layer would reduce chemisorption of oxygen and the reaction between water molecules and adsorbed oxygen molecules could lead to a decrease in baseline resistance of the sensor (Wang et al. 2010). Hexamethyldisiloxane has been shown to contaminate metal oxide sensors by acting as an inhibitor to reduce the number of active sites, thus reducing the sensitivity and selectivity of the sensors (Schüler et al. 2015).

1.2.1.3 Electrochemical (EC) Sensors

Operating Principle

EC sensors can be potentiometric (voltage), amperometric (current) and conductometric (conductance), in which the gases of interest react with the sensing electrode to produce a signal

that is proportional to the concentration of the gases. EC sensors typically consist of three electrodes: a working electrode, a reference electrode, and a counter electrode, each separated by an electrolyte. The gases of interest are introduced to the system via diffusion through a porous membrane to the working electrode, where electrochemical (oxidation or reduction) reactions take place. An equal and opposite reaction happens on the counter electrode to provide electron balance.

Measurement Range and Application

EC sensors have a relatively narrow measurement range (between 0 – 100 ppm) with a limit of detection of around 0.1 ppm. EC sensors can be used in environmental monitoring, odorant monitoring and breath analyzers.

Selectivity and Interference

EC sensors are not able to identify individual compounds in a gas mixture. They are primarily sensitive to gases that are electrochemically active, which could include inorganic gas species that may serve as interferents. However, the working electrode can be modified in a way to specifically target VOC such as benzene, toluene, ethanol, o- and p-xylene (Mori and Sadaoka 2010).

1.2.1.4 Nondispersive Infrared (NDIR) Sensors

Operating Principle

NDIR sensors utilize the absorption characteristics of gas molecules in the infrared (IR) region of the electromagnetic spectrum. These sensors typically are equipped with an IR light source, optical filter, and a detector. The gas molecules will absorb IR radiation at a particular wavelength as they pass through the gas chamber, and the amount of light absorbed is proportional to the concentration of the gas molecules that is quantified using Beer-Lambert's law.

Measurement Range and Application

Compared to other VOC sensors, NDIR sensors have a very high limit of detection, typically greater than a few hundreds of ppm. Thus, NDIR sensors may be better suited to measure high VOC concentrations in indoor air quality applications and combustion processes.

Selectivity and Interference

The use of an optical filter provides a certain level of selectivity. However, NDIR sensors suffer from a high limit of detection and are subject to interferences from other gases absorbing at similar wavelengths.

2 Laboratory Setup

2.1 Laboratory Chamber System

AQ-SPEC has developed two chamber systems: Chamber 1, the original chamber that was developed in 2015 and was primarily used to evaluate sensors measuring criteria pollutants, is now used exclusively for the performance evaluation of VOC sensors; and Chamber 2, which was developed in 2020, has greater sensor testing capacity, can perform specialty tests such as wind speed, altitude, and vibration, and is now being used for the evaluation of sensor measuring criteria pollutants. Chamber 1 has been modified for VOC sensor testing by enhancing airtightness and operation under slight negative pressure, while other aspects remain the same. Details of Chamber 1 are described in the [AQ-SPEC laboratory testing protocol](#) and Papapostolou et al. (2017). Briefly, the chamber system used for VOC sensor testing consists of a 1.3 m³ stainless steel test chamber, capable of controlling T/RH to produce targeted climate conditions using air produced from the zero-air generation system, that envelops a smaller 0.11 m³ stainless steel enclosure in which sensors are installed. Details of the chamber system components are presented below:

- A professional grade environmental test chamber (G-Series Elite, model GD-32-3-AC, Russells, Holland, MI) capable of creating a wide range of temperature and RH. This includes a stainless steel rectangular-shaped enclosure (1.3 m³, hereafter referred to as “outer chamber”), a heating/cooling system for controlling the test T, and a humidifier/de-humidifier for varying the RH;
- A custom-made stainless steel cylindrical-shaped enclosure (0.11 m³, hereafter referred to as “inner chamber”), installed inside the outer chamber;
- A dry, gas- and particle-free zero-air generation system equipped with a series of scrubbers;
- A Teledyne T700U dynamic dilution calibrator (Teledyne API, San Diego, CA; hereafter referred to as “dilution calibrator”);
- An Entech 7100A Preconcentrator (Entech Instruments, Simi Valley, CA; hereinafter referred to as “preconcentrator”);
- An Agilent 6890N Network Gas Chromatograph with Flame Ionization Detection (Agilent Technologies Inc., Santa Clara, CA; hereafter referred to as “GC-FID”);
- A Thermo Fisher 55i Direct Methane and Non-Methane Hydrocarbon analyzer (Thermo Fisher Scientific, Franklin, MA; hereafter referred to as “Thermo 55i monitor”);
- A Thermo Fisher 48iQ Carbon Monoxide analyzer (Thermo Fisher Scientific, Franklin, MA; hereafter referred to as “CO monitor”);
- An Ecotech Serinus 10 O₃ Analyzer (American Ecotech, Warren, RI; hereafter referred to as “O₃ monitor”); and
- A Thermo Fisher 410iQ Carbon Dioxide analyzer (Thermo Fisher Scientific, Franklin, MA; hereafter referred to as “CO₂ monitor”).



Figure 1. AQ-SPEC's laboratory environmental Chamber 1 used for VOC sensor testing

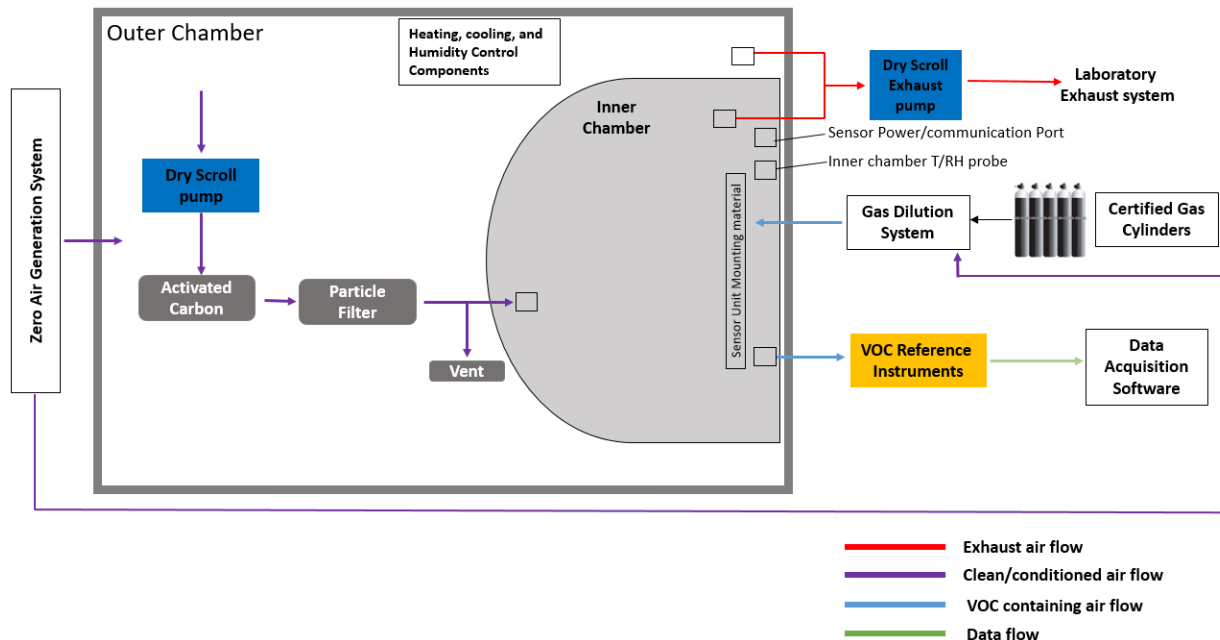


Figure 2. Schematic of AQ-SPEC's Chamber 1 VOC sensor testing system

2.1.1 Zero-air generating system

This system is comprised of a series of scrubbers used to remove gaseous and particulate impurities from the laboratory-supplied compressed dried air. As shown in Figure 3, from right to left (direction of house air flow), the scrubbers in this system are:

- i. one heated catalyst scrubber for the removal of carbon monoxide (CO);
- ii. two scrubbers of activated carbon to remove VOC and NO₂;
- iii. two scrubbers of sodium permanganate (NaMnO₄) impregnated on porous alumina to remove H₂S, SO₂, NO₂, NO, and HCHO;
- iv. one cylinder of manganese dioxide/copper oxide (MnO₂/CuO) catalyst to remove ozone;
- v. one cylinder of 13X molecular sieve to remove moisture;
- vi. two cylinders of calcium sulfate (CaSO₄) in series to further dry the house air; and
- vii. one in-line HEPA filter to remove particulate impurities.

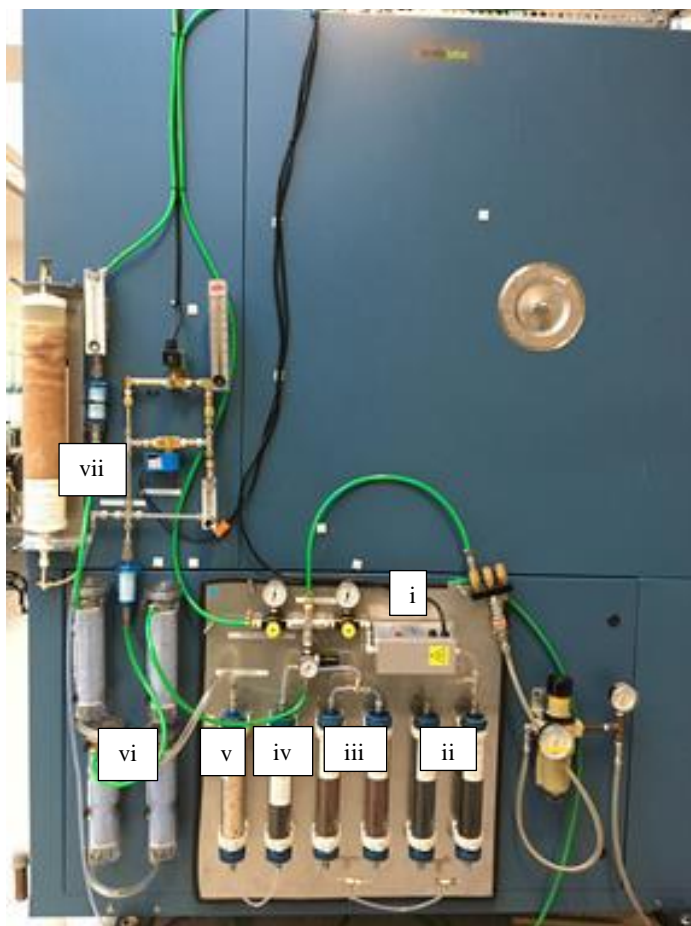


Figure 3. Chamber 1 zero-air generation system

The zero-air generation system outputs dry, gas- and particle-free air that is supplied to the dilution calibrator for the dilution of gases supplied by the certified compressed gas cylinders to achieve target gas concentrations. The zero-air is also used to flush the inner and outer chambers and to condition them under controlled temperature and relative humidity.

2.1.2 Outer chamber

The rectangular-shaped outer chamber [1 m (width) x 1 m (height) x 1.3 m (depth) with a volume of 1.3 m³] is made of stainless steel where zero air is conditioned to the target T and RH values, and is directly delivered to the inner chamber using a hermetic pump connected to an activated carbon scrubber and a particle filter on the output (Figure 2; indicated by purple arrows). The bottom of the outer chamber is sloped to allow drainage of condensate out of the chamber. A fan in the rear wall of the outer chamber, behind the upper wall perforations, generates a recirculating airflow in the chamber, with air flowing in from the bottom first through the cooling and dehumidifier fins and then passing through the heating elements. This air movement

mechanism provides for uniform mixing throughout the outer chamber. All parts are stainless steel or other inert material to prevent unwanted chemical reactions of the gases.

2.1.3 Inner chamber system

2.1.3.1 Inner chamber

The sensor triplicate is installed inside the stainless-steel cylindrical-shaped inner chamber (0.3 m (radius) x 0.4 m (height), volume of 0.11 m³) used to conduct the laboratory evaluation of VOC sensors. The total flow rate passing through the inner chamber is 8 L/min. For a 0.11 m³ volume of the inner chamber, the gas molecule residence time t in the chamber is calculated by

$$t = \frac{V}{Q} = \frac{110 \text{ L}}{8 \frac{\text{L}}{\text{min}}} = 13.8 \text{ min}$$

where,

V is the volume of the inner chamber

Q is the total zero-air diluted gas flow through the chamber

To reach a steady-state condition inside the inner chamber, 2-3 residence times are needed for a total of about 28 to 41 minutes.

2.1.3.2 Gas Dilution

Target gas from a certified compressed gas cylinder with known stock concentration is delivered, undiluted, through the dilution calibrator at a controlled flow rate to the inner chamber; the target gas is then diluted inside the inner chamber with zero-air, which has been conditioned to the outer chamber's temperature and humidity and transported into the inner chamber by a dry scroll pump (Agilent IDP-3, Santa Clara, CA). The flow rates of undiluted cylinder gas are set based on historical recipes of stock gas flow rate and inner chamber total flow rate to achieve target VOC concentrations in the inner chamber. The VOC gas dilution technique is similar to the "Mode B" technique described in the [AQ-SPEC laboratory testing protocol](#), with the exception that the flow rate of outer chamber conditioned air is controlled, rather than the inner chamber's vacuum flow rate, in order to maintain slight negative pressure in the inner chamber.

2.2 Chamber Software System

A suite of custom software programs (Envidas Ultimate, DR DAS Ltd, Granville, OH) is used to perform data acquisition, data storage, visualization, and control for the AQ-SPEC laboratory environmental chamber and various reference instruments. It can send control commands via serial or ethernet communication for chamber control and generation of reference

gas concentrations. The experimental sequences can be pre-programmed and operated/controlled remotely. The sequences can be logged, saved, and modified as needed. Data is stored in a database and can be explored as .csv files.

2.3 Certified Gas Cylinders

Compressed gas cylinders are usually purchased from Airgas (Riverside, CA). Specifications of the VOC cylinders are presented in Table 1.

2.3.1 Calibration Certified Gas Cylinders

A cylinder containing 10 ppm of 1,3-butadiene, benzene, ethane, and tetrachloroethylene each in ultra-pure nitrogen is used for canister standard preparation for calibration of the GC-FID. These concentrations allow for the MFCs inside the Entech 4600A precision dynamic diluter (Entech Instruments Inc., Simi Valley, CA; hereinafter referred to as “precision dynamic diluter”) used for canister preparation to generally remain within recommended flow rate ranges for maximum accuracy. These compounds were chosen to be consistent with precedent work by U.S EPA (Williams et al. 2015) that used these compounds (1,3-butadiene, benzene, and tetrachloroethylene) for VOC sensor testing, along with the addition of ethane to this testing protocol to include a light alkane species. These compounds represent different classes of compounds such as aromatics, alkanes, alkenes, and halogenated alkenes, which are relevant to exposure and health concerns as well as oil and gas emissions. Of the four compounds, only benzene and tetrachloroethylene are targeted under Method TO-14a, while Method TO-15 also targets 1,3-butadiene.

A cylinder containing 2 ppm of methane and 2.5 ppm of 1,3-butadiene, benzene, ethane, and tetrachloroethylene each in ultra-pure nitrogen (for a total VOC [tVOC] concentration of 10 ppm), is used for calibration of the Thermo 55i monitor. The maximum nominal tVOC concentration that the Thermo 55i monitor would be subjected to in any given experiment is 8 ppm, which is 80% of the tVOC concentration against which the Thermo 55i monitor is calibrated.

For benzene-only experiments, a cylinder containing 2 ppm of methane and 2.5 ppm of benzene in nitrogen is used for calibration of the Thermo 55i monitor. The maximum nominal benzene concentration that the Thermo 55i monitor would be subjected to in any given benzene-only experiment is 2 ppm, which is 80% of the benzene concentration against which the Thermo 55i monitor is calibrated.

2.3.2 Test Certified Gas Cylinders

A VOC mixture containing nominally 80 ppm of 1,3-butadiene, benzene, ethane, and tetrachloroethylene each in ultra-pure nitrogen is used for the chamber experiments, while an 80ppm benzene in nitrogen cylinder is used for benzene-only experiments. These concentrations allow for the MFCs inside the dilution calibrator to generally remain within recommended flow rate ranges for maximum accuracy.

Table 1. Content and concentrations of the VOC cylinders

Calibration Cylinders			
<i>10 ppm VOC Mixture for Canister Standard Preparation and GC-FID Calibration</i>			
Component	Nominal Concentration (v/v, ppm)	Maximum Tolerance	
1,3-butadiene	10	± 10 %	
benzene	10	± 10 %	
ethane	10	± 10 %	
tetrachloroethylene	10	± 10 %	
<i>2.5 ppm VOC Mixture for Thermo 55i Analyzer Calibration</i>			
Component	Nominal Concentration (v/v, ppm)	Maximum Tolerance	
methane	2	± 10 %	
1,3-butadiene	2.5	± 10 %	
benzene	2.5	± 10 %	
ethane	2.5	± 10 %	
tetrachloroethylene	2.5	± 10 %	
<i>2.5 ppm Benzene for Thermo 55i Analyzer Calibration</i>			
Component	Nominal Concentration (v/v, ppm)	Maximum Tolerance	
methane	2	± 10 %	
benzene	2.5	± 10 %	
Test Cylinders			
<i>80 ppm VOC Mixture for Experiments</i>			
Component	Nominal Concentration (v/v, ppm)	Maximum Tolerance	Target Gas Concentrations (ppm)
1,3-butadiene	80	± 10 %	0.015 to 2
benzene	80	± 10 %	0.015 to 2
ethane	80	± 10 %	0.015 to 2
tetrachloroethylene	80	± 10 %	0.015 to 2
<i>80 ppm Benzene for Experiments</i>			
Component	Nominal Concentration (v/v, ppm)	Maximum Tolerance	Target Gas Concentrations (ppm)
benzene	80	± 10 %	0.015 to 2

2.4 Reference Analyzers

There are two reference analyzers used to measure VOC concentrations in low (0.06 to 1.6 ppm) and high concentration (2 to 8 ppm) ranges. A Thermo 55i monitor is used for both low and high concentration testing, while an Agilent 6890N GC-FID is used for the low concentration testing only due to its maximum measurement limit being 0.4 ppm per species (or 1.6 ppm tVOC for four species). Rationale of the chosen concentration ranges is detailed in Section 4.5.2.

2.4.1 High VOC Concentration Analyzer (Thermo 55i Monitor)

A Thermo 55i monitor is used to measure VOC concentrations for all experiments stated in this protocol. It is a back-flush gas chromatography system that provides accurate and precise measurements of low NMHC concentrations. The Thermo 55i monitor has several selectable measurement ranges; for the purposes of VOC sensor testing, it is set at 0 – 50 ppm. It has an instrument detection limit of 50 ppb and analysis cycle time of 70 seconds.

2.4.1.1 Calibration

The sensors are tested in 6 phases (Section 4.5) with the VOC mixture used in all phases and benzene-only used in Phases 2 and 6. Therefore, the Thermo 55i monitor is calibrated with either 1) a VOC mixture cylinder containing equal concentrations of each individual VOC species plus 2 ppm of methane or 2) a benzene-only cylinder plus 2 ppm of methane, depending on which VOC species are desired for a given chamber experiment. Calibration of the Thermo 55i monitor is performed prior to testing of the VOC sensors or whenever the test gas is changed between the VOC mixture or benzene-only cylinder. The Thermo 55i monitor has an *instrument* detection limit (IDL; this is the detection limit of the instrument only that is reported by the manufacturer and does not account for effects of detection limit imposed by the *method*) of 50 ppb.

2.4.1.2 Method Detection Limit

Method Detection Limit (MDL) is defined as “the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results” (Definition and Procedure for the Determination of the Method Detection Limit, 2016). Prior to determining the MDL of the Thermo 55i monitor, all surfaces and elements in the inner chamber including power and communication ports, all probes, gas ports, sensor mounting platform, and sensors to be tested are cleaned thoroughly with isopropyl alcohol. Then, the inner chamber is flushed with zero-air until the background VOC concentration in the chamber is below the IDL of the Thermo 55i monitor. The determination of the MDL of the

VOC reference instruments follows the DQ FAC procedure (DQ FAC Single Laboratory Procedure v 2.4; (EPA 2016)). This procedure requires at least 50% of the method blank data to be numerical (zero, positive, or negative concentration). At least seven blanks meeting these criteria are required to determine MDL. For the MDL determination of the Thermo 55i monitor, 20 method blanks are used.

MDL is calculated as follows, according to the DQ FAC procedure:

$$MDL = \bar{x}_{mb} + S * K$$

Where:

\bar{x}_{mb} is the average of the method blanks; if \bar{x}_{mb} is a negative value, substitute it with zero;

S is the standard deviation of the method blanks;

K is a multiplier for a tolerance limit based on the 99th percentile for n-1 degrees of freedom. Values can be found in Table A3 in the Appendix

If 5% or more of the blank results are greater than the calculated MDL, then raise the MDL as follows, according to the DQ FAC procedure:

- To the highest method blank result if less than 30 method blank results are available.
- To the next highest method blank result if 30 to 100 method blank results are available.
- To the 99th percentile, or the level exceeded by 1% of all method blank results, if there are more than 100 method blanks are available.

Using the MDL procedure described above and results from investigative datasets, the MDL of the Thermo 55i monitor is calculated to be ~50 ppb, the same as the IDL.

2.4.2 Low VOC Concentration Analyzer (GC-FID)

The low VOC concentration testing measurement system is comprised of a preconcentrator and a GC-FID. Due to the measurement range of the GC-FID, it is only used for the low VOC concentration testing. Description and methods of the preconcentrator and GC system components are explained in more details in the following sections.

2.4.2.1 Preconcentrator

A preconcentrator is used for sample preparation prior to injection to the GC-FID system. This allows for the concentration of samples and increased efficiency of sample trapping by removing excess air and water vapor from the samples. A detailed preconcentrator method is described in Section 2.4.2.3.1.

2.4.2.2 GC-FID

The GC-FID is used for the quantification of speciated VOC concentrations. The use of electronic pneumatic control modules and precise temperature control provides high retention time repeatability and peak symmetry. The VOC mixture is separated on a 29 m x 0.32 mm x 1.5 μ m capillary column (RTX-1, Restek), with retention times of approximately 2.01, 2.54, 4.92 and 6.55 minutes for ethane, 1,3-butadiene, benzene, and tetrachloroethylene, respectively. A detailed GC-FID method is described in Section 2.4.2.3.2.

2.4.2.3 Analysis methods

2.4.2.3.1 Preconcentrator method

The preconcentrator includes three modules. In Module 1, VOC are cryogenically trapped on the glass beads and then desorbed in room temperature to leave water behind. In Module 2, VOC are trapped on the Tenax beads that are cooled to -40°C while letting CO₂ pass through. VOC are backflushed at 195°C from Module 2 and focused at -160°C in the Module 3 cryofocusing trap. The cryofocusing trap is heated which prompts the injection to the GC-FID system. The preconcentrator conditions are presented in Table 2 and a screenshot of the preconcentrator control software is shown in Figure 4.

Table 2. Preconcentrator method setup

Module 1	Module 2	Module 3
Set point : -140 °C	Set point : 40 °C	Set point : off
Trap : -140 °C	Trap : -40 °C	Focus : -160 °C
Preheat : -10 °C	Preheat : 100	Inject : 2.5 min
Desorb Temp : 20 °C	Desorb Temp : 195 °C	Bake : 2 min
Bake : 200 °C	Bake : 200 °C	Event : 3
Time : 3 min	Time : 2.6 min	Wait : 3 min

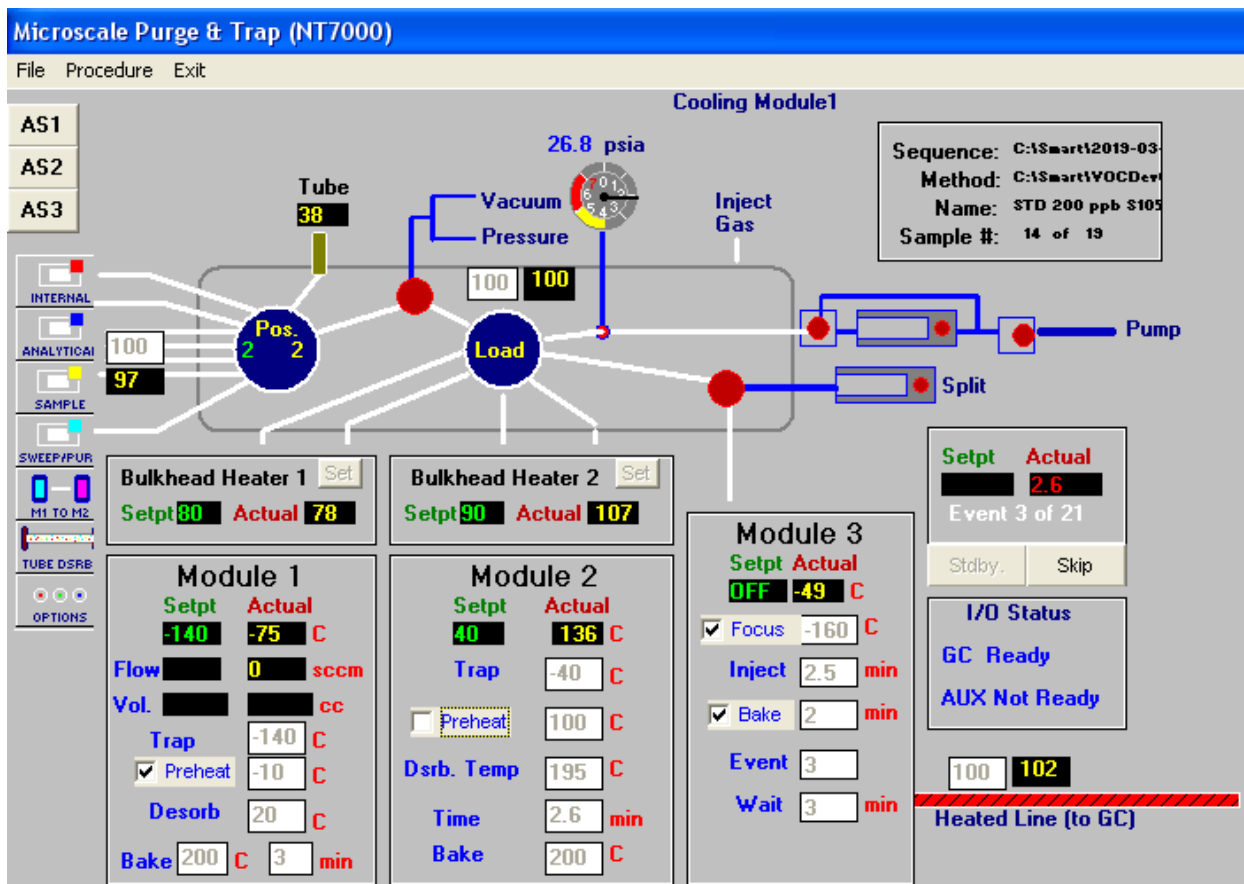


Figure 4. Preconcentrator method

2.4.2.3.2 GC-FID method

The oven temperature is initially set at 40 °C and held for 2 minutes; this is followed by two ramping steps. First the oven temperature is ramped to 160 °C at 20 °C per minute then ramped to 220 °C at 50 °C per minute and held for 6.8 minutes. The oven temperature of the GC-FID is set to 300 °C, with H₂, air, and make up air flow rates of 30, 300 and 30 mL/min, respectively (Figure 5).

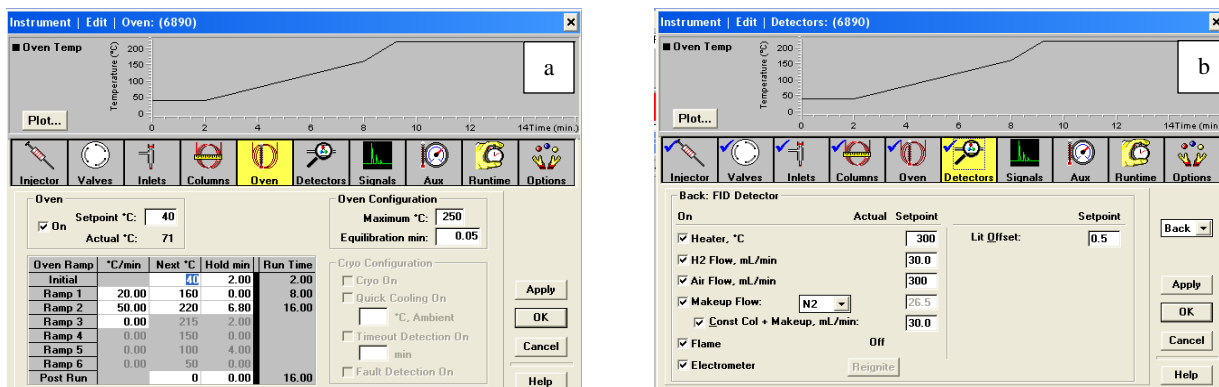


Figure 5. Oven (a) and detector (b) method used for all GC-FID analysis.

2.4.2.4 GC-FID and Preconcentrator Sequence Setup

A sequence of all samples to be run is programmed to allow the samples to be analyzed in a particular order. An example of such sequence for a calibration is shown in Figure 6. Typically, the first sample in the sequence is the system blank to ensure stability of all GC-FID components, followed by a nitrogen blank. During calibration, standards are analyzed sequentially and finished with another nitrogen blank to check for carry-over effect. During sensor evaluation experiments, samples drawn from the inner chamber are analyzed in an uninterrupted, continuous sequence but without the nitrogen blanks.

The screenshot displays the 'NT7000Sequence Table' software interface. At the top, there is a toolbar with various icons for file operations (OPEN, SAVE, NEW, ADD, CUT, PASTE, REPLC, FILL, METH, PRINT, EXIT, QAQC, SQTBL, LEAK, MANL, FLUSH, CNFG, START, STOP, VIEW, BAKE, REAL, DATA, TOOL) and control functions (INLET 1-4, ASP 1-16, MODE STRD, REAL, and ABOUT). Below the toolbar, the 'Sequence Table' is titled 'C:\Smart\2022-07-21-Cal.SEQ'. It includes input fields for 'Internal Std. Vol.' (set to 0) and 'QAQC Report' (set to R_220721). The main table lists the sequence of samples to be analyzed, including system blanks, nitrogen blanks, and various standards.

Sample Name	Samp Inlet#	Auto Pos#	Samp Vol.	Cal.Std. Vol.	Method:
system blank	3	1	0	0	C:\Smart\VOCDev02.MPT
system blank	3	1	0	0	C:\Smart\VOCDev02.MPT
N2 Blank 1917	3	1	320	0	C:\Smart\VOCDev02.MPT
N2 Blank 1917	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 2 ppb 1054	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 2 ppb 1054	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 10 ppb 1916	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 10 ppb 1916	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 50 ppb 1915	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 50 ppb 1915	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 100 ppb 3759	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 100 ppb 3759	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 400 ppb 1930	3	1	320	0	C:\Smart\VOCDev02.MPT
STD 400 ppb 1930	3	1	320	0	C:\Smart\VOCDev02.MPT
N2 blank 1917	3	1	320	0	C:\Smart\VOCDev02.MPT
N2 blank 1917	3	1	320	0	C:\Smart\VOCDev02.MPT
END	1	1	0	0	C:\Smart\END.MPT

Figure 6. Example of a sample VOC calibration sequence programmed for the preconcentrator.

2.4.2.5 GC-FID system calibration (2-400 ppb benzene / VOC mixture)

2.4.2.5.1 Canisters

All calibration standards are prepared in 6-L stainless steel air sampling canisters (model SilcoCan, Restek, Bellefonte, PA) with maximum operating pressure of 40 psig. The canisters are surface treated with Siltek to provide exceptional inertness and analyte stability even at parts per billion concentrations. The canisters are equipped with Restek Air Valve Excellence (RAVE™) valves, a metal-to-metal seal diaphragm valve that prevents sample adsorption on the valve and provides durability and leak-free performance to offer more accurate measurement.

Prior to preparing the VOC standards, the canisters are cleaned rigorously and evacuated. The background level of VOC is checked with the GC-FID. Once the canisters satisfy the blank canister criteria (in which no detectable compound of interests are observed such that the integrated peak for the 4 species of interest are less than 0.2 ppb [10% of the lowest canister standard concentration of 2 ppb]) based on the most recent GC-FID calibration curve, it is humidified by injecting 80 µL of deionized water to reach an internal RH of 40% and equilibrated for 24 hours before preparing the VOC standards.

2.4.2.5.2 Calibration Standards

The calibration standards are prepared using the precision dynamic diluter that allows for the preparation of standards as low as parts per trillion levels. The precision dynamic diluter prepares standards from a stock cylinder with a diluent gas using MFCs. To ensure the homogeneity of the standards, the controlled flows are first combined in a blending region before injection into the canisters. The concentrations of the standards are obtained using the precision dynamic diluter software. Five canister standards of 2, 10, 50, 100 and 400 ppb per species are prepared from the 10 ppm per species stock VOC mixture cylinder up to a maximum pressure of 30 psig. The valves of the canisters are closed and the pressure gauges on the canisters are periodically monitored to confirm no leakage.

The standards are analyzed in serial duplicate samples as programmed in the sequence table (Figure 6). The peak areas from the second sample of the duplicate are integrated to obtain a calibration curve for each species in the mixture. An example of the VOC mixture calibration is shown in Table 3 and Figure 7.

Table 3. Example of VOC calibration results

Nominal VOC (ppb, per species)	Injection Volume (cm ³)	Peak Area (pA·s)			
		ethane	1,3-butadiene	benzene	tetrachloroethylene
2	320	18.4	30.4	34.3	14.1
10	320	85.1	149.3	172.2	68.8
50	320	425.4	724.7	882	356.5
100	320	838.4	1405.8	1754.3	704
400	320	3204.8	5665.4	7161.2	2749.7

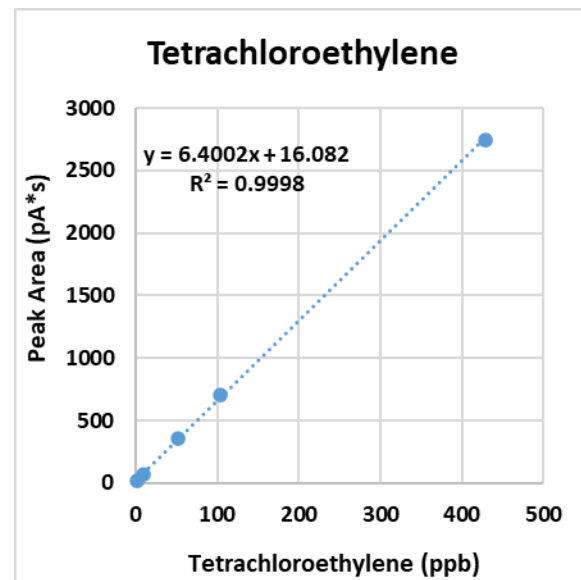
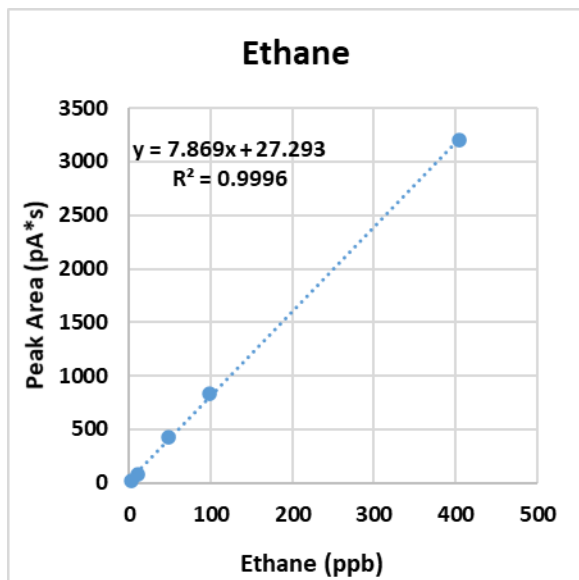
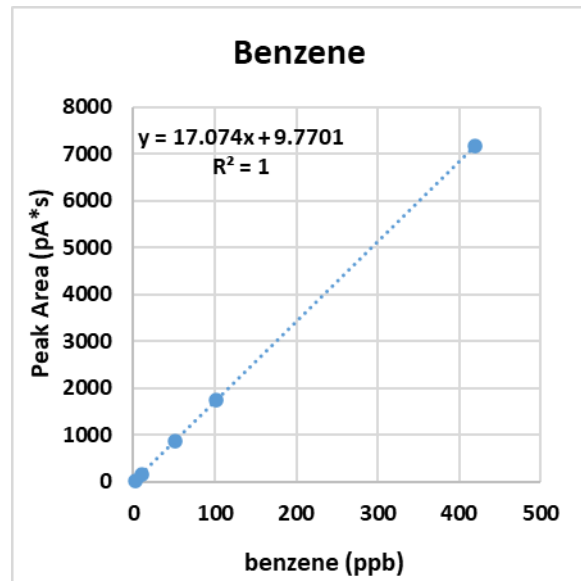
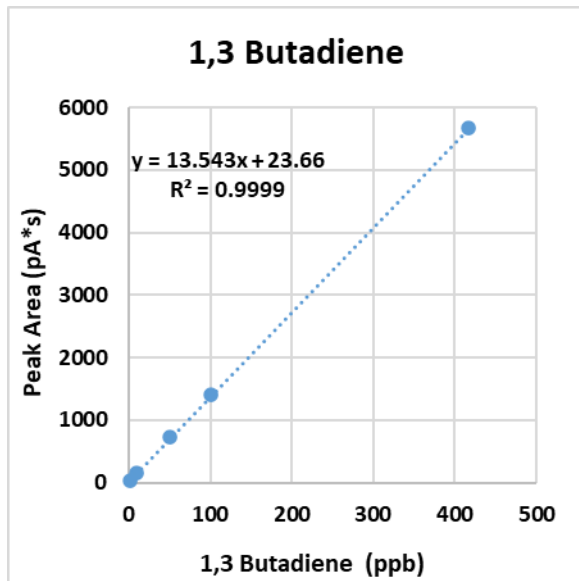


Figure 7. Example of VOC standard calibration results ranging from 2 to 400 ppb.

2.4.2.6 GC-FID IDL and MDL

According to the U.S. EPA's *Guidance for Data Usability in Risk Management (DURA)* (EPA 1992), IDL is defined as the three times the standard deviation from seven measurements of the lowest concentration of a standard that is statistically different from a blank. Thus, the IDL of the GC-FID is determined using seven measurements from the 2 ppb canister (lowest canister standard concentration used in the calibration, Table 3) and the IDL for 1,3-butadiene, benzene, ethane, and tetrachloroethylene was calculated from preliminary investigative datasets to be 0.046 ppb, 0.073 ppb, 0.048 ppb and 0.060 ppb, respectively.

The MDL of the GC-FID is determined using the method described in Section 2.4.1.2. The MDL for the VOC blend (i.e., 1,3-butadiene, benzene, ethane, and tetrachloroethylene) was calculated from preliminary investigative datasets to be 0.12 ppb, 0.12 ppb, 7.40 ppb and 0.60 ppb, respectively. It should be noted that the IDL measurements are made with a canister standard, while the MDL measurements are made with "blank" samples from the inner chamber (since it is the *method* detection limit, so it must consider the totality of the entire experimental setup and not only the instrument alone). Since ethane is ubiquitous in ambient air, which is the source of the air supplied to the zero-air generating system, and difficult to scrub out, the MDL "blank" samples contain ambient ethane concentrations, which is why the MDL for ethane is relatively high at around 8 ppb compared to the MDL for the other VOC species.

2.5 Safety Measures

2.5.1 Safety Cabinets

The VOC cylinders are stored in a safety cabinet (Model 7200, Safety Equipment Corporation, Belmont, CA), which is connected to the laboratory exhaust system. There are two flexible stainless-steel tubes connecting the cylinders and the dilution calibrator. The stainless-steel tubes are leak checked separately with a compressed cylinder containing a relatively safer gas, such as CO or CO₂. The compressed cylinder is first pressurized to about 30 psig, and the tubes are then flushed with the relatively safer gas. The tubes are then capped, resulting in a pressure increase to about 33-34 psig in the first two days. The tubes are monitored for one week. The results show that pressure drop was negligible over a period of one week (around 2×10^{-4} psig/min, Figure 8).

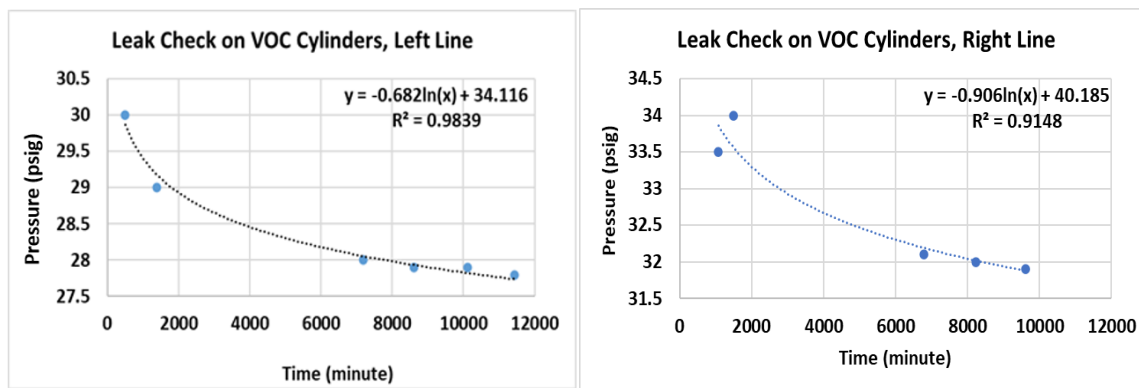


Figure 8. Leak check on the VOC cylinders

2.5.2 Ventilation and Safety Practice

The Chamber 1 exhaust is integrated with the South Coast AQMD laboratory exhaust system. A pump is used to continuously transport flow from both the inner and outer chambers to the laboratory exhaust system. The total exhaust flow from the chamber is around 50 L/min due to the chamber rooftop hermetic scroll pump (Agilent IDP-3, Santa Clara, CA) that creates slight negative pressure in both the inner and outer chambers for lab safety. The pump vents to the laboratory building HVAC exhaust ducting, which pulls sufficient flow rate to capture all the exhaust pumped from the chamber and all active gas analyzers. The face velocity of the HVAC exhaust duct is checked and verified annually using a velocity probe (Series 641RM, Dwyer, Michigan City, Indiana), which measures velocities ranging from 0.01 to 1.40 m/s. The velocity probe is located 8 cm downstream of the 4" HVAC exhaust duct inlet. The measured air velocity in the 4" HVAC exhaust duct is 1.33 ± 0.03 m/s, corresponding to around 600 L/min. This volume flow rate greatly exceeds the required air flow to capture 50 L/min chamber exhaust. An HVAC exhaust low flow alarm is paired with a measurement and control data logger (CR 1100, Campbell Scientific, Logan, UT) that receives an analog signal from the velocity probe. When the signal from the probe drops below 0.2 m/s (around 100 L/min), an audible alarm is triggered and experimental activities are suspended until the low HVAC exhaust flow is resolved.

2.5.3 Dry Scroll Pump

To ensure safe operations and prevent any potential leakage, the inner and outer chamber are operated under negative pressure by utilizing an air-tight hermetic dry scroll pump to exhaust air from both the outer and inner chambers to the laboratory HVAC exhaust system (Figure 2). The hermetic design of this pump and completely isolated motor and bearings decrease the likelihood of chamber air inadvertently entering the laboratory.

3 Sensor Evaluation Parameters

The performance of the sensors is evaluated by comparing the sensors side-by-side with the reference analyzers (i.e., Thermo 55i, and GC-FID). A series of parameters that are representative of the sensor performance in the field are tested with carefully designed laboratory chamber experiments. These parameters include ability to detect transient events, sensor response time delay, sensor detection limit (SDL), data recovery, intra-model variability, accuracy, precision, coefficient of determination, mean absolute error (MAE), mean bias error (MBE), root mean square error (RMSE), normalized RMSE, interferences, climate susceptibility, and short-term changes in sensor response. Each parameter is explained in detail in the following sections and sensor testing procedure is detailed in Section 4.

3.1 Data Recovery

Data recovery is calculated using a percentage ratio of the number of valid sensor data points over the total number of data points ideally collected during the testing period (e.g., 10 hours of testing at 1-min time resolution should result in a total of 600 data points). Completeness is an important factor for producing reliable and representative data, as indicated in the EPA guidelines for regulatory data collection.

$$\text{Data recovery (\%)} = \frac{N_{\text{valid data}}}{N_{\text{test period}}} * 100 \quad (1)$$

where,

$N_{\text{valid data}}$ is the number of valid sensor data points during the testing period

$N_{\text{test period}}$ is the ideal total number of data points for the testing period (from start to end)

3.2 Sensor Detection Limit

The sensor detection limit (SDL) is the lowest VOC concentration that can be reported with confidence. There are several ways to estimate SDL. One of the more common procedures involves the collection of several blank samples; however, this approach fails for VOC sensors with high detection limits that will likely report zero values for blank samples, leading to a false calculation of an SDL of 0 ppb VOC. Another approach involves exposure of the VOC sensors to serially decreasing concentrations of VOC to until the lowest-possible concentration is reached that elicits a response that is statistically different than zero or the signal noise; however, this approach is extremely resource- and time-intensive. Thus, a procedure that leverages the existing sensor vs.

GC-FID correlation determined from the Phase 2 initial and Phase 6 final low concentration ramps is chosen to provide sensor users with an *estimate* of the SDL. The GC-FID instrument is chosen over the Thermo 55i monitor as the reference monitor for SDL calculations, since it has the lower IDL/MDL among the two reference instruments.

The SDL can be estimated as long as the sensors satisfy the following requirements: 1) the coefficient of determination (R^2) for the correlation between the sensors and the reference instrument is ≥ 0.8 ; and 2) the slope of the sensor vs. GC-FID regression line is positive. The SDL is estimated as follows, according to the ICH guideline “*Validation of Analytical Procedures: Text and Methodology Q2(R1)*” (International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use, 2005):

$$\text{Detection Limit} = \frac{3.3 \sigma}{S} \quad (2)$$

where,

σ is the residual standard deviation of a regression line, or the standard deviation of the y-intercept of the regression line; and

S is the slope of the calibration curve

SDL is estimated for each individual VOC sensor unit using all paired nonzero sensor vs. GC-FID measurements from the low concentration ramping measurements in Phase 2 and Phase 6 (see Section 4.5.2 and Section 4.5.6), with sensor measurements on the y-axis and GC-FID measurements on the x-axis. Both the residual standard deviation of a regression line and the standard deviation of y-intercepts of regression lines are used as σ to report a possible range of SDL. The SDL of indexing sensors, namely those that report VOC levels as a relative, unitless quantity (often through an index value) cannot be determined.

3.3 Intra-model variability

Intra-model variability is related to how close the measurements from three units of the same sensor are to each other. It is evaluated through a set of descriptive statistical parameters, such as mean, median, and standard deviation (each calculated at the different steady-state VOC concentrations). The average of 20 sensor measurements from each steady-state VOC concentration period in the chamber is considered for this analysis. For a set of three sensors the intra-model variability is reported as a percentage and calculated as follows:

$$\text{Intra-model variability (\%)} = \frac{\text{Mean}_{\text{highest}} - \text{Mean}_{\text{lowest}}}{\text{Mean}_{\text{average}}} * 100 \quad (3)$$

where,

Mean_{highest} is the highest of the three sensors' average concentrations

Mean_{lowest} is the lowest of the three sensors' average concentrations

Mean_{average} is the average of the three sensors' average concentrations

3.4 Accuracy

Accuracy is the degree of closeness between the sensors' measured values and the reference value. For these chamber tests, accuracy is derived from a concentration ramping experiment at 20 °C and 40% RH. At each pollutant concentration, the difference between the average of the three sensors and the reference instrument is calculated. In this context, accuracy is defined as follows:

$$A (\%) = 100 - \frac{|\bar{X} - \bar{R}|}{\bar{R}} * 100 \quad (4)$$

where,

\bar{X} is the average concentration measured by the three sensors throughout the steady-state period considered

\bar{R} is the reference instrument average concentration during the same steady-state period

It is worth mentioning that accuracy may vary across the same type of sensors at different pollutant concentrations. For simplicity, accuracy is summarized in a table with information acquired at each steady-state condition during a concentration ramping experiment. The higher the positive value (percentage), the higher the sensor's accuracy. For example, a value of 100% implies that sensors measure exactly what the reference instrument measures. In cases where sensors overestimate the reference instruments by more than 100%, sensor accuracy is reported as a negative value, using Equation 4. The accuracy of indexing sensors cannot be determined.

3.5 Precision

Precision represents the variation around the mean of repeated measurements of the same pollutant concentration under identical or similar experimental conditions. For the purposes of this analysis, the sensor's precision is expressed as follows:

$$P (\%) = 100 - \frac{SE_{\text{sensor}}}{\bar{X}} * 100 \quad (5)$$

where,

$\overline{SE}_{\text{sensor}}$ is the averaged standard error of the three sensors during the steady-state period considered

\bar{X} is the average concentration (or index) measured by the three sensors throughout the same steady-state period

Standard error of an individual sensor is calculated as:

$$SE_{\text{sensor}} = \frac{\sqrt{\sum (X - \bar{X}_i)^2}}{n} \quad (6)$$

where,

X is the value of a sensor's concentration (or index) at different times during the steady-state period considered

\bar{X}_i is the average concentration (or index) measured by the sensor in question throughout the same steady-state period

n is the number of measurements taken

During a VOC sensor testing experiment, a minimum of 20 steady-state measurement data points are used for this analysis. Precision may be affected by the environmental conditions chosen. Therefore, this parameter is calculated for each combination of pollutant concentration, T, and RH in climate susceptibility experiments, and presented in a summary table. The higher the percentage value, the higher the sensor's precision. An example of precision calculated for different T/RH conditions is presented in Table A4.

3.6 Coefficient of Determination (R^2)

This parameter expresses the strength of the linear relationship between the averaged measurements from the three sensors tested and the corresponding reference instrument values. The paired data set acquired from the concentration ramping experiment at 20 °C and 40% RH is entered in an Excel spreadsheet and a best-fitting regression curve is calculated along with the corresponding correlation coefficient (R^2), slope, and intercept values. An R^2 approaching the value of 1 reflects a near perfect agreement between the sensors and the reference instrument readings, whereas a value of 0 indicates a complete lack of correlation.

3.7 Mean Absolute Error (MAE)

MAE is the absolute difference between the sensors and the reference instrument measurements. 20 paired data sets acquired from the concentration ramping experiments at 20 °C

and 40% RH at steady-state for each concentration step is used for calculating MAE. The larger the MAE values, the higher measurement errors as compared to the reference instrument.

MAE is calculated as:

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^n |(\bar{X} - \bar{R})| \quad (7)$$

where,

n is the number of valid data points during steady state;

\bar{X} is the average concentration measured by the three sensors throughout the steady-state period considered; and

\bar{R} is the reference instrument average concentration during the same steady-state period

The MAE of indexing sensors cannot be determined.

3.8 Mean Bias Error (MBE)

MBE is the difference between the sensors and the reference instrument measurements. A minimum of 20 paired data set acquired from the concentration ramping experiments at 20 °C and 40% RH at steady state for each concentration step is used for calculating MBE. MBE indicates the tendency of the sensors to underestimate (negative MBE values) or overestimate (positive MBE values) the reference instrument measurements.

MBE is calculated as:

$$\text{MBE} = \frac{1}{n} \sum_{i=1}^n (\bar{X} - \bar{R}) \quad (8)$$

where,

n is the number of valid data points during steady state;

\bar{X} is the average concentration measured by the three sensors throughout the steady-state period considered; and

\bar{R} is the reference instrument average concentration during the same steady-state period

The MBE of indexing sensors cannot be determined.

3.9 Root Mean Square Error (RMSE) and Normalized Root Mean Square Error (NRMSE)

RMSE, defined as the error between the sensor and the reference instruments, is another metric used to help understand the errors associated with the sensor VOC measurements. A minimum of 20 paired data sets acquired from the concentration ramping experiments at 20 °C and 40% RH at steady state for each concentration step is used for calculating RMSE. The

normalized RMSE is another form of an error metric that accounts for testing conditions. RMSE and NRMSE are calculated as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (\bar{X} - \bar{R})^2}{n}} \quad (9)$$

$$NRMSE (\%) = \frac{RMSE}{\bar{R}} * 100 \quad (10)$$

where,

n is the number of valid data points during steady state;

\bar{X} is the average concentration measured by the three sensors throughout the steady-state period considered; and

\bar{R} is the reference instrument average concentration during the same steady-state period

The RMSE/NRMSE of indexing sensors cannot be determined.

3.10 Interferents

The accuracy of the sensors is affected by the presence of interferents that may include T and RH, dust, and the other gaseous species. VOC sensors can suffer from cross-sensitivity of other gas pollutants. Depending on the measurement technology employed by the VOC sensors, the effect of interferents on the sensors may differ (Section 1.2.1). In the laboratory, the effect of interferents on the VOC sensors are evaluated by exposing the sensors to gaseous interferents at varying concentrations.

3.11 Detection of Transient Events

The sensors are determined to be able to detect VOC peaks when the sensors report a peak with an amplitude at least 3 times the standard deviation of the 20 pre-peak measurements. The percent of events detected by the sensor is calculated as:

$$Event\ Detection\ (\%) = \frac{N_S}{N_R} * 100 \quad (11)$$

where,

N_S is the number of peaks (having an amplitude at least 3 times the standard deviation of 20 pre-peak measurements) observed by the sensors; and

N_R is the number of peaks observed by the reference instrument

Sensor response time delay is calculated as the difference between the time it takes the sensors to reach a peak in VOC signal compared to that of the reference monitor:

$$Sensor\ response\ time\ delay = T_S - T_R \quad (12)$$

where,

T_S is the time it takes for the sensors to detect a VOC peak following a VOC injection event and T_R is the time it takes for the reference monitor to detect a VOC peak following a VOC injection event.

3.12 Climate Susceptibility

Climate susceptibility is an exploration of a sensor's response to variations in environmental conditions, including changes in T and RH. A sensor is most useful if it can operate reliably in many different environments. In the laboratory, VOC sensors are tested under a wide range of T and RH conditions. For each T and RH combination considered, the sensors' precision is calculated as a one type of indicative parameter of climate susceptibility.

3.13 Short-Term Sensor Response Change

Short-term change in sensor response is determined in the last phase of testing to investigate the gradual change in sensor response after they have been subjected to various climate conditions and interferents. Short-term sensor response change is described by comparing the regression results (e.g. slope and intercept) between the sensors and reference instruments with all concentration levels from the initial and final concentration ramping experiments.

3.14 Analysis of Variance (ANOVA)

ANOVA (type II) is used to determine the importance of the explanatory variables in explaining sensor VOC response. The explanatory variables include VOC concentrations from the Thermo 55i monitor, inner chamber temperature (T), inner chamber absolute humidity (AH), and ozone concentrations from the O₃ monitor. AH is used to avoid the issue of multicollinearity between RH and temperature. AH is calculated using the *Humidity* package from R using T and RH values from the inner chamber meteorological probe. ANOVA is performed for each sensor using four sets of statistical tests:

Statistical Test 1: NMHC only

Statistical Test 2: T + AH

Statistical Test 3: NMHC + T + AH

Statistical Test 4: NMHC + T + AH + Ozone

A type II ANOVA statistical test is used to avoid the effect of the order of explanatory variables entered into ANOVA. The higher the percentage explained by a particular variable, the more the sensor responds to that variable.

4 Sensor Evaluation Procedures

VOC sensor evaluation in the AQ-SPEC program follows a different path than that used for criteria pollutant-measuring sensors. Due to the potential for aging effects to severely impact VOC sensor performance, ideally two triplicate sets of VOC sensors from the same production and quality control (QC) batch would be provided to AQ-SPEC, so that new sensors can be simultaneously tested in the field and in the laboratory. However, if only one triplicate set of sensors can be provided/obtained, then the VOC sensors will undergo laboratory testing before field testing, since ambient VOC concentrations are often below detection limits of sensors, and thus laboratory testing can more rapidly provide insight on VOC sensor performance. Figure 9 summarizes the pre-testing activities that must occur before the sensors are evaluated, with details in later sections.

VOC sensors in the laboratory can be subjected to various climatic conditions such as cold/dry and hot/humid, a wide range of temperate and humidity combinations, and various concentrations of potentially interfering gas compounds such as NO_x, CO, and CO₂ to study their effects on the performance of the VOC sensors. Performance of VOC sensors later tested in the field is not expected to be impacted by preceding laboratory testing since the sensors are not exposed to known contaminating species during laboratory testing.

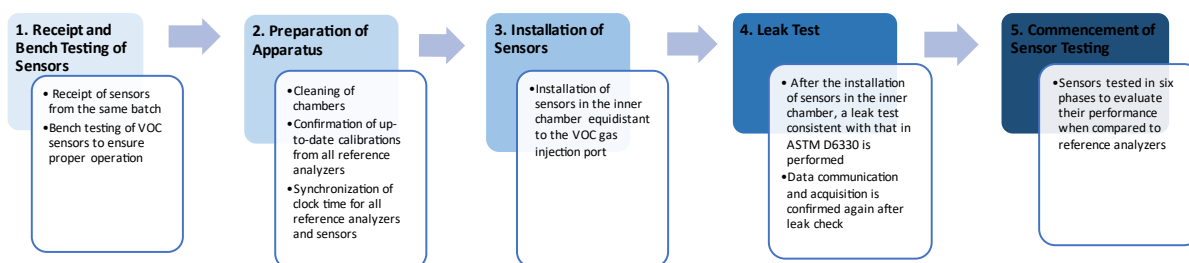


Figure 9. Sensor Evaluation Procedures

4.1 Receipt and Bench Testing of VOC Sensors

Prior to any laboratory testing, the VOC sensors are first bench tested for normal operations, including but not limited to power options, data communication and logging options, and data output format. All routine maintenance and installation procedures are performed as specified in the manufacturer's user manual. This includes but not limited to flow rate checks, zeroing, acclimation to the test environment, date/time synchronization, and battery replacement. The VOC sensors are tested as they are received and no further sensor calibration is performed, since VOC sensor response depends on the calibration gas, and the intent of this testing is to investigate sensor

performance as if a layperson were to receive the product and immediately use it without additional calibration.

4.2 Preparation of Apparatus

Prior to VOC sensor testing, all surfaces of the outer chamber and inner chamber are cleaned with non-abrasive wipes dampened with isopropyl alcohol or equivalent. All scrubber material used to generate zero-air are replaced according to the manufacturer's recommended schedule. All certified cylinders should be used before their certification expiration date. All reference instruments are calibrated prior to sensor testing at a frequency recommended by the manufacturer or experimental requirements. The clock times on the various computers that collect data from the GC-FID, Thermo 55i monitor, and the sensors are synchronized prior to each sensor testing experiment to make it possible to time-align the VOC reference instruments and sensors.

4.3 Sensor Installation

After confirming normal operations, the VOC sensors are installed on the stainless-steel mounting apparatuses in the inner chamber. The sensors are placed at equal distance from the VOC gas injection port, and thus all sensors and the reference instruments are exposed to equivalent VOC concentration and air movement simultaneously, as shown in Figure 10.

Appropriate connections are provided for sensors of different power (120 VAC or 5 VDC USB) and data communication needs (e.g., Ethernet, Wi-Fi, SD card, USB, serial). If the VOC sensor data is logged using a terminal program, a computer cable that connects the sensors inside the inner chamber with a computer placed outside of the chamber is provided. Only one sensor model is tested at a time to avoid off-gassing from one sensor model affecting the performance results of a different sensor model.

Once the sensors are installed in the chamber, the leak test procedure is performed to ensure the air-tightness of the inner chamber (Section 4.4). After the inner chamber passes the leak test, the sensors are powered on and checked for connectivity and proper data acquisition. Subsequently the outer chamber system is sealed (e.g., outer chamber door is closed) and powered on. Then the chamber is purged with zero-air until the background VOC level reaches a stable concentration below the Thermo 55i monitor's MDL. The VOC background concentration in the chamber is monitored by the Thermo 55i monitor and data is recorded by the Envidas Ultimate software. The stable background VOC concentration as well as target T and RH conditions are maintained for at least 20 minutes prior to starting sensor testing.

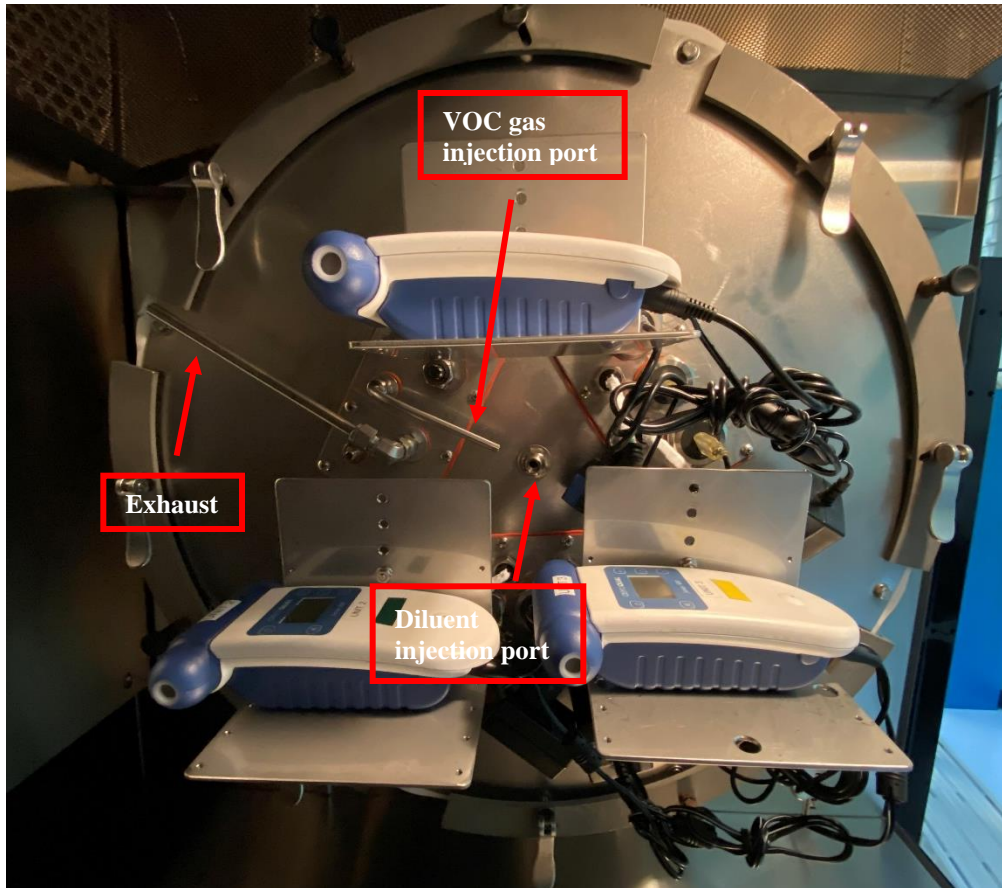


Figure 10. An example of sensor placement in the chamber

4.4 Inner chamber leak check

After installing the VOC sensor triplicate in the inner chamber, the airtightness of the inner chamber is measured by sealing all outlets of the inner chamber and adjusting the input air flow rate such that the pressure difference between inside and outside of the chamber is 10 ± 1 Pa and confirming that the air leakage rate is less than 1% of the air change rate under normal operation during sensor testing, to be consistent with leak testing procedures in ASTM D6330. A differential pressure gauge (PCE-PDA 1L, PCE Instruments, Jupiter, FL) is used to measure the pressure difference between inside and outside of the chamber.

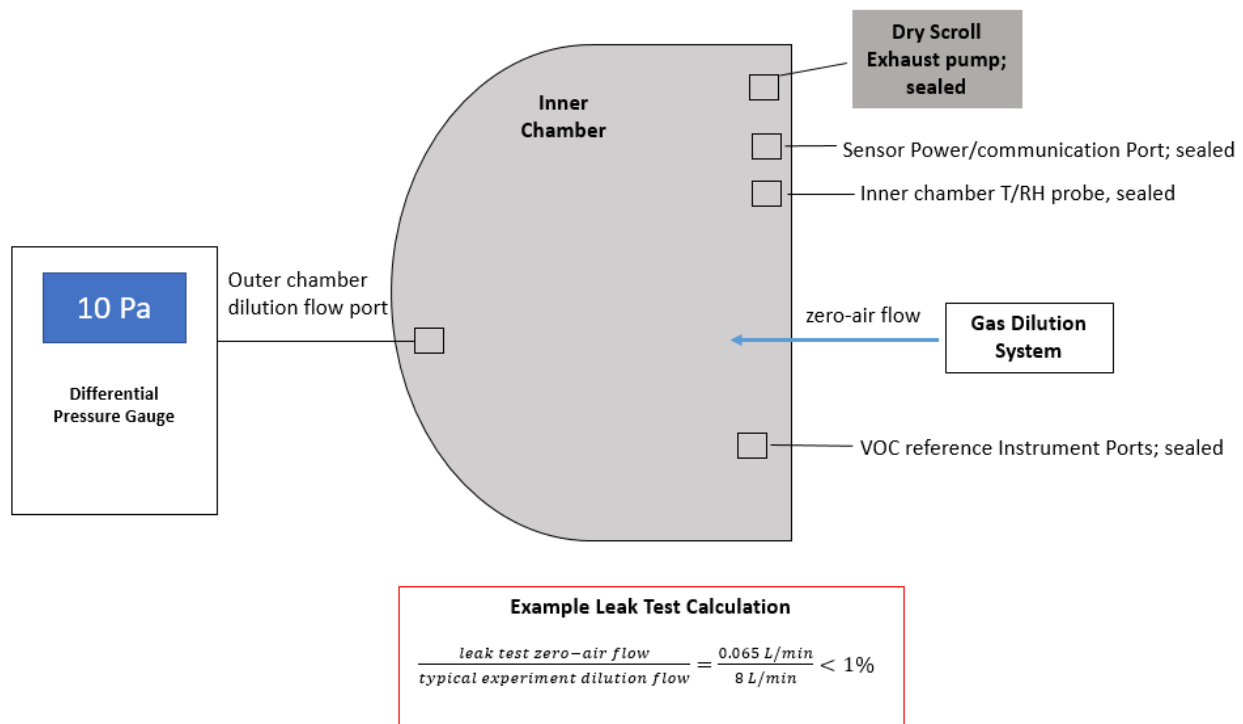


Figure 11. Schematic of the leak check setup. All outlets of the inner chamber including the dry scroll exhaust pump, power and communication ports, T/RH probe, and VOC reference instrument ports are sealed. The example leak test calculation shows a satisfactory leak tight condition, in which the zero-air flow (0.065 L/min) needed to pressurize the inner chamber to 10 Pa is less than 1 % of the dilution flow used in a typical experiment (8 L/min).

4.5 Sensor Testing Procedure

The testing of VOC sensors includes six phases, as follows:

- Phase 1 - Transient plume detection to study sensors' responsiveness to VOC plumes of various peak concentrations
- Phase 2 - Initial concentration ramping to study the sensors' response to a wide range of VOC concentrations
- Phase 3 - Effect of temperature and relative humidity
- Phase 4 - Effect of gaseous interferents
- Phase 5 - Sensor performance in simulated outdoor conditions
- Phase 6 - Final concentration ramping to study sensor drift

Note that Phases 1, 3, 4, and 5 are done with the VOC mixture only, while Phases 2 and 6 are conducted first with the VOC mixture and then the benzene-only gas.



Figure 12. Sensor testing procedures

4.5.1 Phase 1: Transient VOC Plume Detection

The ability of the sensors to detect VOC plumes is determined by injecting high concentrations of VOC directly into the chamber at injection durations of 2, 5, 8, 10 and 15 seconds in a randomized order, from a certified VOC cylinder containing 80 ppm each of 1,3-butadiene, ethane, benzene, and tetrachloroethylene. The exhaust flow rate of the inner chamber is set to 20 L/min and the incoming zero-air flow rate is set to 19 L/min in order to maintain slight negative pressure in the inner chamber and achieve quick dissipation of the VOC plume event; the outer chamber dilution flow rate from the zero-air generator is set to 40 L/min in order to maintain VOC-free air in the outer chamber that becomes the source for the 19 l/min air that is pumped into the inner chamber. At least 30 minutes are allowed to elapse between VOC injections, to allow for the Thermo 55i monitor to return to baseline concentration. The Thermo 55i monitor may not report the same VOC concentration for injections of the same duration due to variations in timing between when actual maximum concentration is achieved in the inner chamber and when the Thermo 55i monitor draws a sample from the inner chamber. An example of the sequence is shown in Figure 13. This test phase is used as a screening tool to see if sensors even respond to VOC at all; if the sensors do not appear to respond to the transient VOC events, further testing phases are unnecessary.

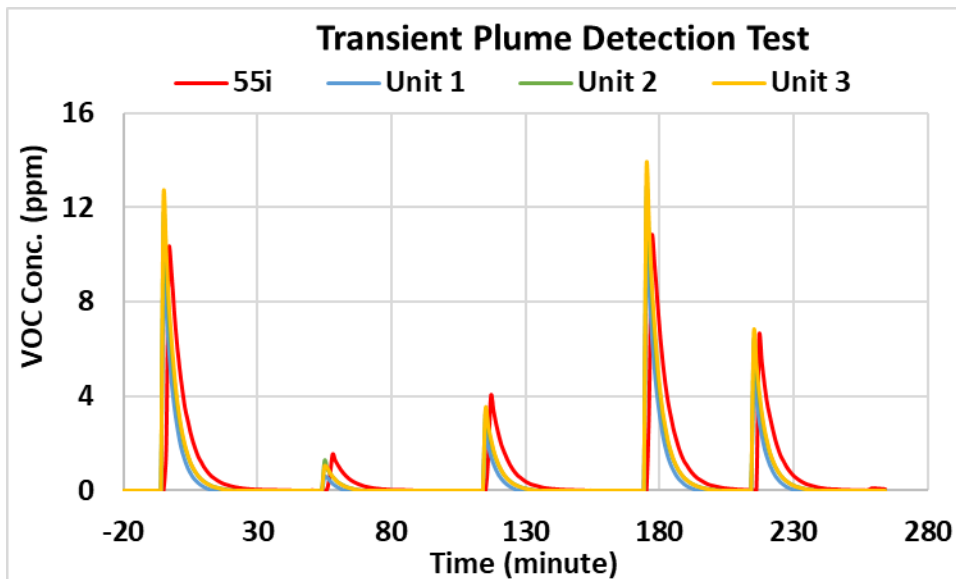


Figure 13. Example of a transient plume detection test. In this instance, the sensors appear to report the transient event earlier than the reference monitor due to the Thermo 55i monitor's (55i) 70-second reporting interval. This result would be interpreted to mean that the sensors do not experience any additional delay in reporting a transient event longer than the delay from the Thermo 55i monitor.

4.5.2 Phase 2: Initial Concentration Ramping

Due to the maximum range of the GC-FID with the column used in this testing (400 ppb of each VOC compound, 1.6 ppm tVOC), the initial concentration ramping experiment is carried out in two different tests: low concentration ramping with tVOC blend concentrations ranging from 60 ppb to 1.6 ppm using both the GC-FID and Thermo 55i monitor, and a higher concentration ramping with tVOC blend concentrations ranging from 2 ppm to 8 ppm using the Thermo 55i monitor only (Table 4). Note that all concentration values listed here are for the VOC blend (expressed as the sum of the four VOC species). The lowest target concentration of 60 ppb (15 ppb of each species) in the low concentration ramp is chosen because the concentration of each species is about twice the GC-FID MDL of the most prominent species, ethane (8 ppb), and the tVOC concentration is above the MDL of the Thermo 55i monitor (50 ppb). The highest concentration of 1.6 ppm (400 ppb of each species) in the low concentration ramp is chosen because it is the maximum concentration limit for the GC-FID and the GC column that is installed. The lowest concentration of 2 ppm (0.5 ppm per species) in the high concentration ramp is chosen because it is near the highest concentration of 1.6 ppm for the low concentration ramp. The highest concentration of 8 ppm (2 ppm per species) in the high concentration ramp is the maximum concentration that can be generated using the dilution calibrator and the VOC cylinder standard.

The exhaust flow rate of the inner chamber is set to 8 L/min and the incoming zero air flow rate is set to 6 L/min to keep a slight negative pressure on the inner chamber; the outer chamber dilution flow rate from the zero-air generator is set to 30 L/min to maintain VOC-free air in the outer chamber that becomes the source for the 6 L/min air that is pumped into the inner chamber. All VOC concentration ramping experiments are carried out at 20°C and 40% RH. For each concentration, the VOC concentration is maintained at steady state long enough to record a minimum of 20 measurements from the VOC sensors or VOC reference instrument, whichever has the longer measurement interval. This initial concentration ramping test is repeated using benzene-only as the source of VOC and the concentrations used are shown in Table 4.

Table 4. *t*VOC concentration levels for low and high concentration ramping experiments

	VOC Level	Low Concentration Ramping	High Concentration Ramping
VOC Mixture	Very low	60 ppb	2 ppm
	Low	200 ppb	4 ppm
	Medium	400 ppb	6 ppm
	High	1600 ppb	8 ppm
Benzene-Only	Very low	15 ppb	0.5 ppm
	Low	50 ppb	1 ppm
	Medium	100 ppb	1.5 ppm
	High	400 ppb	2 ppm

4.5.2.1 Low Concentration Ramping

Target VOC concentrations are achieved using the dilution calibrator. VOC gas from a certified compressed cylinder is introduced into the inner chamber where it is then diluted with conditioned zero-air from the outer chamber. Due to the sampling and analysis time of the GC-FID (23 minutes per sample), each concentration step is about 2 hours; it usually takes about one hour for the VOC concentration to reach steady-state. The exact GC-FID sample timestamp is determined using an *R* script and the GC-FID data is time-aligned with that of the Thermo 55i monitor. The VOC concentrations measured by the GC-FID and the Thermo 55i monitor are in good agreement with each other (Figure 14), with differences of 40% at the lowest level (0.06 ppm) to 3% at the highest level (1.6 ppm). The GC-FID vs. Thermo 55i monitor regression must satisfy an $R^2 > 0.9$ condition in order for results to be considered valid.

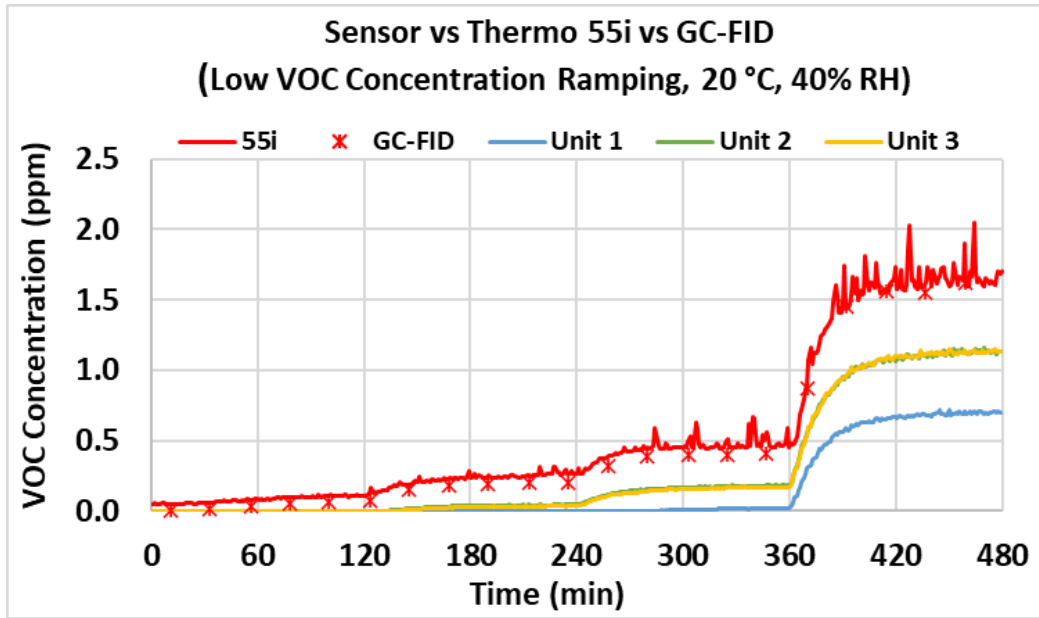


Figure 14. An example of a low VOC concentration ramping showing total VOC concentrations measured by Thermo 55i monitor (55i), GC-FID, and the sensors.

4.5.2.2 High Concentration Ramping

Due to the maximum concentration range allowable with the column used in this testing, the GC-FID is not used in the high VOC concentration ramping experiment, and only the Thermo 55i monitor is used to monitor the VOC concentrations. Each concentration step as indicated in Table 4 is 1.5 hours; an example of the high VOC concentration ramp is shown in Figure 15.

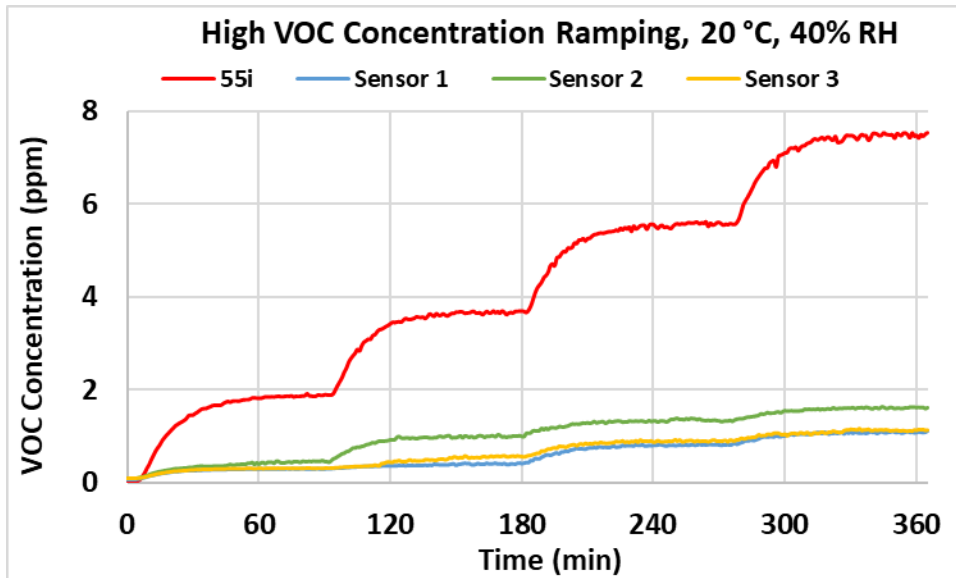


Figure 15. An example of a high VOC concentration ramping experiment

4.5.3 Phase 3: Effect of Temperature and Relative Humidity

For Phase 3, only the Thermo 55i monitor is used because the VOC concentration is 4 ppm (1 ppm per species) and this exceeds the measurement range of the GC-FID. The exhaust flow rate of the inner chamber is set to 8 L/min and the incoming zero air flow rate is set to 6 L/min to keep a slight negative pressure on the inner chamber; the outer chamber dilution flow rate from the zero-air generator is set to 30 L/min in order to maintain VOC-free air in the outer chamber that becomes the source for the 6 L/min air that is pumped into the inner chamber.

4.5.3.1 Normal and Extreme conditions

The first part of Phase 3 tests the sensors under normal conditions (20°C and 40% RH) and extreme conditions, such as cold and dry conditions (5°C and 20% RH) and hot and humid (35°C and 80% RH). The sensors are first tested at 5°C and 20% RH, then 20°C and 40% RH, and finally 35°C and 80% RH, while holding the VOC concentration constant at 4 ppm (Figure 16).

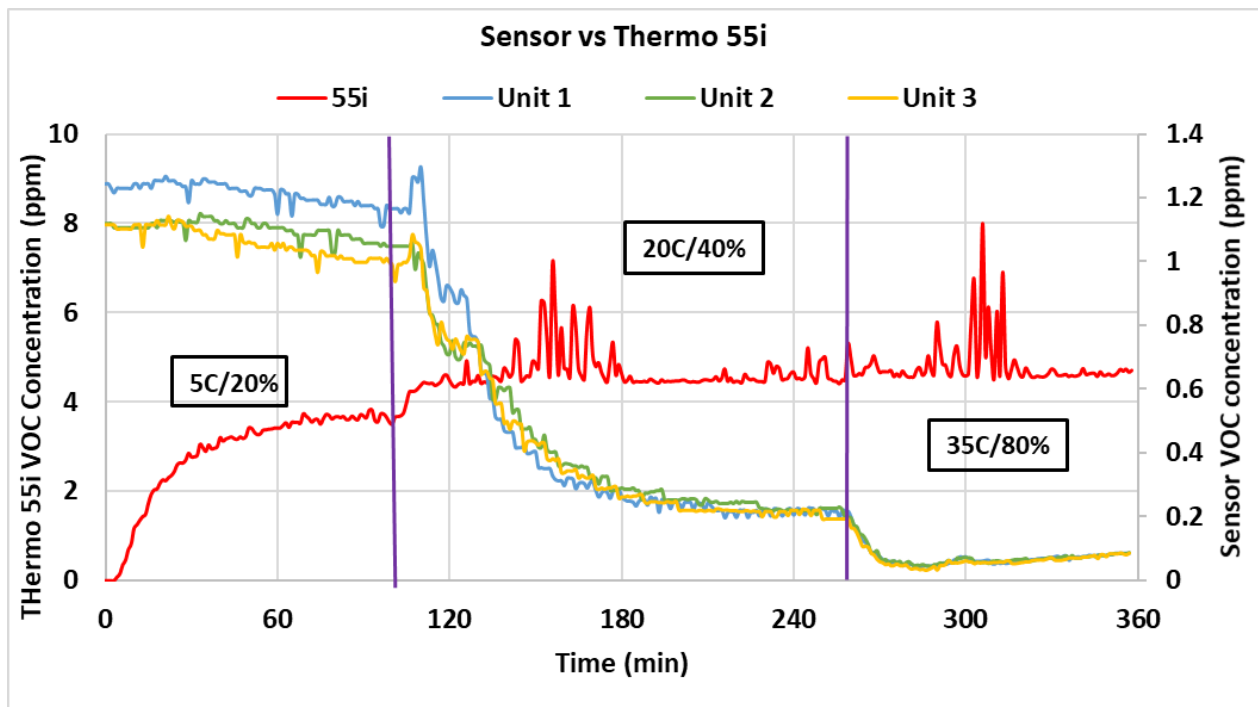


Figure 16. An example of testing sensors under normal and extreme conditions.

4.5.3.2 Effect of Relative Humidity

The effect of relative humidity (RH) is determined by increasing the RH values from 25% to 80% in four steps (25%, 40%, 65% and 80%), while holding temperature constant at 20°C and VOC concentration constant at 4 ppm. Each RH setpoint is maintained until an RH steady state

period is reached and contains a minimum of 20 measurements from the VOC sensors or VOC reference instrument, whichever has the longer measurement interval. The preliminary results show that RH does not have an impact on the Thermo 55i monitor measurements as shown in Figure 17.

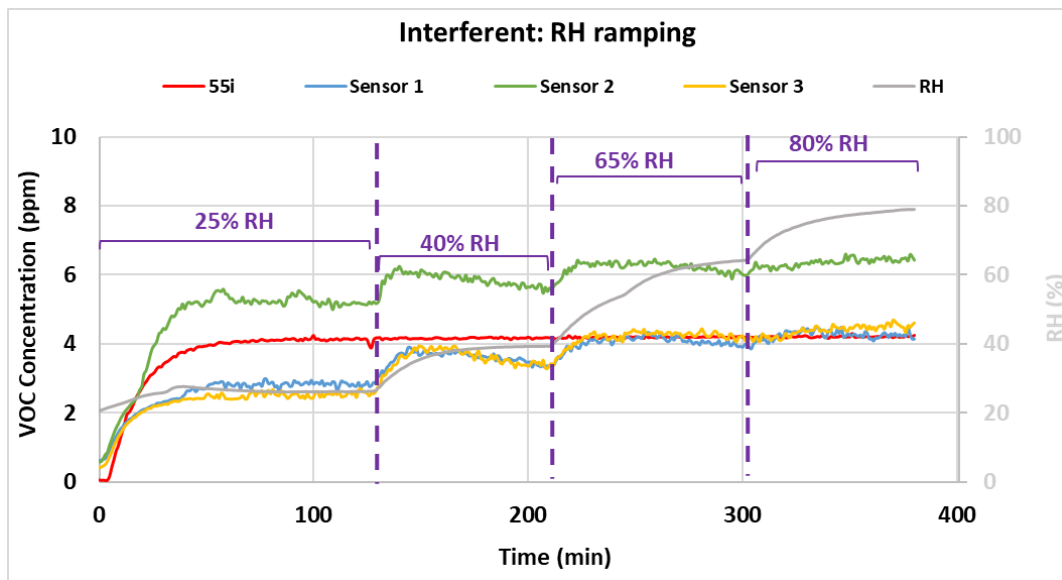


Figure 17. An example of a RH interference experiment (temperature is held constant at 20 °C).

4.5.3.3 Effect of Temperature

The effect of T is determined by cycling the T from 20°C to 10°C to 30°C, and finally back to 20°C, while holding RH constant at 40% and VOC concentration constant at 4 ppm. Each T setpoint is maintained until an T steady state period is reached and contains a minimum of 20 measurements from the VOC sensors or VOC reference instrument, whichever has the longer measurement interval. The preliminary results show that temperature does not have an impact on the Thermo 55i monitor measurements as seen in Figure 18.

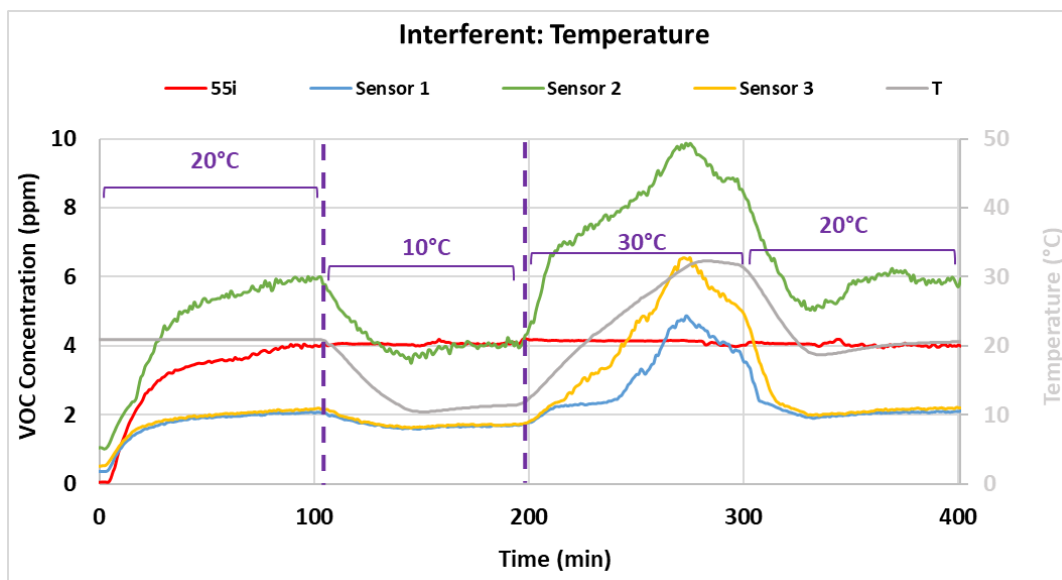


Figure 18. An example of a temperature as an interferent experiment (RH is held constant at 40%).

4.5.3.4 Effect of Temperature at constant Absolute Humidity

The effect of T is further determined by cycling the T values from 20°C to 10°C to 30°C, and finally back to 20°C, at constant *absolute humidity* (AH) of 0.007 kg/m³ (the moisture content corresponding to 20°C/40% RH) and VOC concentration constant at 4 ppm. Each T setpoint is maintained until an T steady state period is reached and contains a minimum of 20 measurements from the VOC sensors or VOC reference instrument, whichever has the longer measurement interval.

4.5.4 Phase 4: Effect of Gaseous Interferents

To study the cross interference from other gases, the VOC sensors are exposed to varying concentrations of interferent gases. The effect of the interferent gas can be dependent on the detection technology of the VOC sensors. For MOS sensors, O₃ and CO can be interferent gases since MOS sensors can be sensitive to oxidizing and reducing species. For NDIR sensors, CO₂ may be an important interferent. The exhaust flow rate of the inner chamber is set to 8 L/min and the incoming zero air flow rate is set to 6 L/min to keep a slight negative pressure on the inner chamber; the outer chamber dilution flow rate from the zero-air generator is set to 30 L/min in order to maintain VOC-free air in the outer chamber that becomes the source for the 6 L/min air that is pumped into the inner chamber. Because the internal data processing algorithm of VOC sensors could be proprietary information, all gaseous interferent species (O₃, CO, and CO₂) testing is applied to all VOC sensors, regardless of detection technology utilized.

4.5.4.1 Effect of Ozone

The effect of ozone on VOC sensors is investigated using concentrations ranging from 1 to 500 ppb O₃ at 20°C and 40% RH (Table 5 and Figure 19). The O₃ concentrations are chosen to ensure the ranges are within the ozone generation capacity of the dilution calibrator and a VOC concentration of 200 ppb was chosen to ensure the experiment is conducted considerably above the Thermo 55i monitor's MDL of 50 ppb, but also to allow for wide range in the O₃:VOC ratio. To study the effect of ozone, the target VOC concentration is reached and held at steady state at 20°C and 40% RH without ozone generation and then a range of ozone concentrations (Table 5) is introduced through the dilution calibrator; the concentration of VOC remains constant. Each step lasts for an hour.

The ozone monitor used (model Serinus 10, American Ecotech, Warren, RI) uses a non-dispersive ultraviolet photometer which alternately switches a selective O₃ scrubber in and out of the measuring stream and computes the ratio of transmitted light giving a measure of O₃ concentration. A mercury vapor lamp is used as the light source. The Serinus 10 is designated as a federal equivalent method EQOA-0809-187 by the U.S. EPA (40 CFR Part 53). A stainless-steel tee is added into the Thermo 55i monitor sample line from the chamber, so that one branch connects to the O₃ monitor and the other branch connects to the Thermo 55i monitor.

Table 5. Experimental conditions for Ozone as an interferent

Step	Ozone, ppb	VOC, ppb	O₃:VOC Ratio	T, °C	RH, %
1	1	200	0.005	20	40
2	50	200	0.25	20	40
3	100	200	0.5	20	40
4	200	200	1	20	40
5	400	200	2	20	40

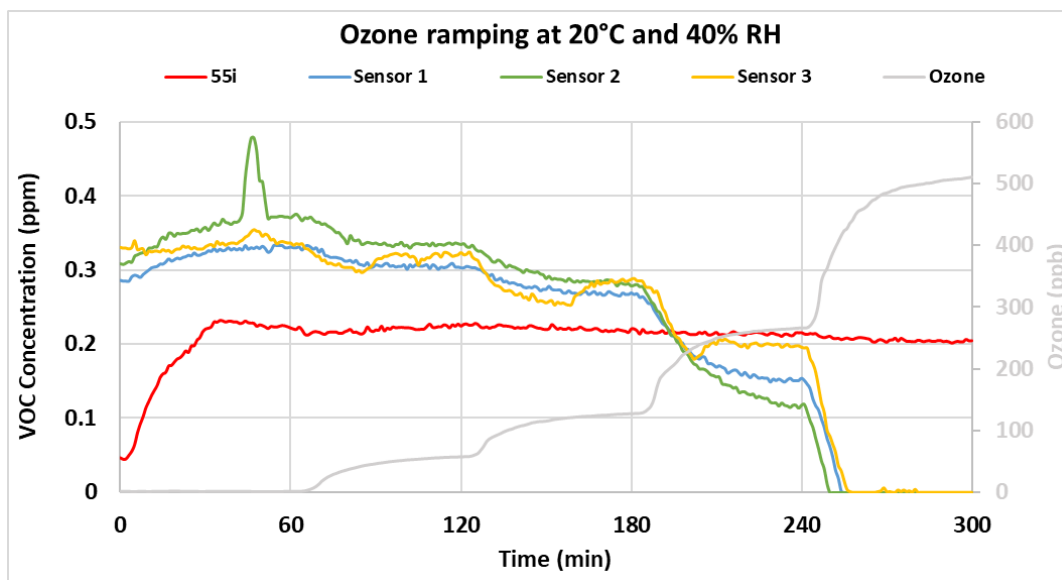


Figure 19. An example of an ozone as an interferent experiment

4.5.4.2 Effect of Carbon Monoxide

The effect of carbon monoxide (CO) on VOC sensors is investigated by increasing the CO concentrations from background concentration to 8 ppm while holding VOC concentrations at 4 ppm at 20°C and 40% RH (Table 6 and Figure 20). Each step lasts for an hour. The CO reference instrument used (model 48iQ, Thermo Fisher Scientific, Waltham, MA) is a non-dispersive infrared CO detector. The Thermo 48iQ is designated as a federal reference method RFCA-0981-054 by the U.S. EPA (40 CFR Part 53). A stainless-steel tee is added into the Thermo 55i monitor sample line from the chamber, so that one branch connects to the CO monitor and the other branch connects to the Thermo 55i monitor.

Table 6. Experimental conditions for CO as an interferent

Step	CO, ppm	VOC, ppm	T, °C	RH, %
1	Background (~0.2 to 1 ppm)	4	20	40
2	2	4	20	40
3	4	4	20	40
4	8	4	20	40

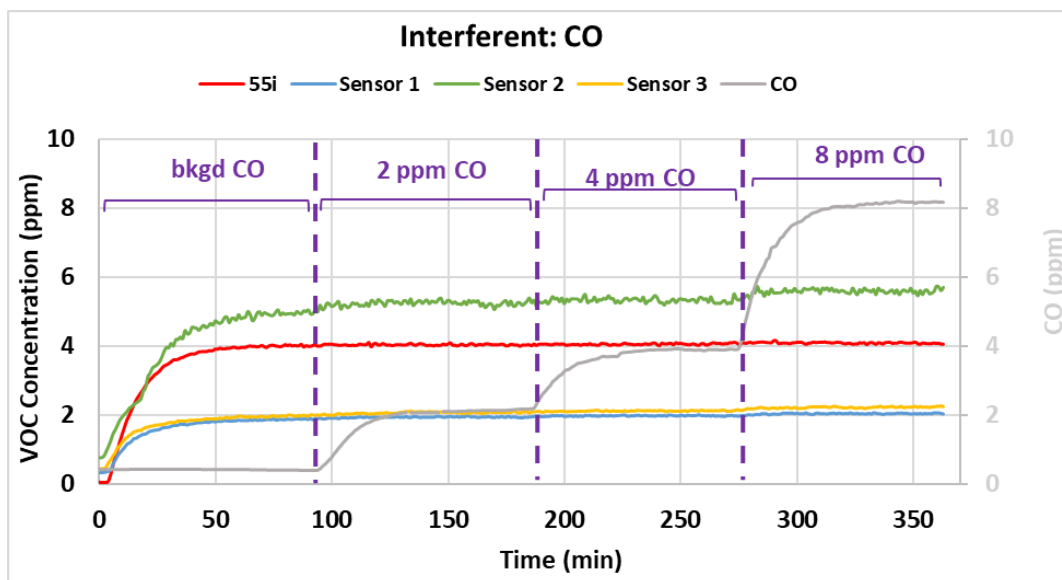


Figure 20. An example of a CO as an interferent experiment

4.5.4.3 Effect of Carbon Dioxide

The effect of carbon dioxide (CO₂) on VOC sensors is investigated by increasing the CO₂ concentrations from background concentration to 8000 ppm while holding VOC concentrations at 4 ppm at 20°C and 40% RH (Table 7 and Figure 21). Each step lasts for an hour. The CO₂ reference instrument used (model 410iQ, Thermo Fisher Scientific, Waltham, MA) is a non-dispersive infrared CO₂ detector. A stainless-steel tee is added into the Thermo 55i monitor sample line from the chamber, so that one branch connects to the CO₂ monitor and the other branch connects to the Thermo 55i monitor.

Table 7: Experimental conditions for CO₂ as an interferent

Step	CO Setpoint, ppm	VOC, ppm	T, °C	RH, %
1	Background (~400 ppm)	4	20	40
2	1000	4	20	40
3	5000	4	20	40
4	8000	4	20	40

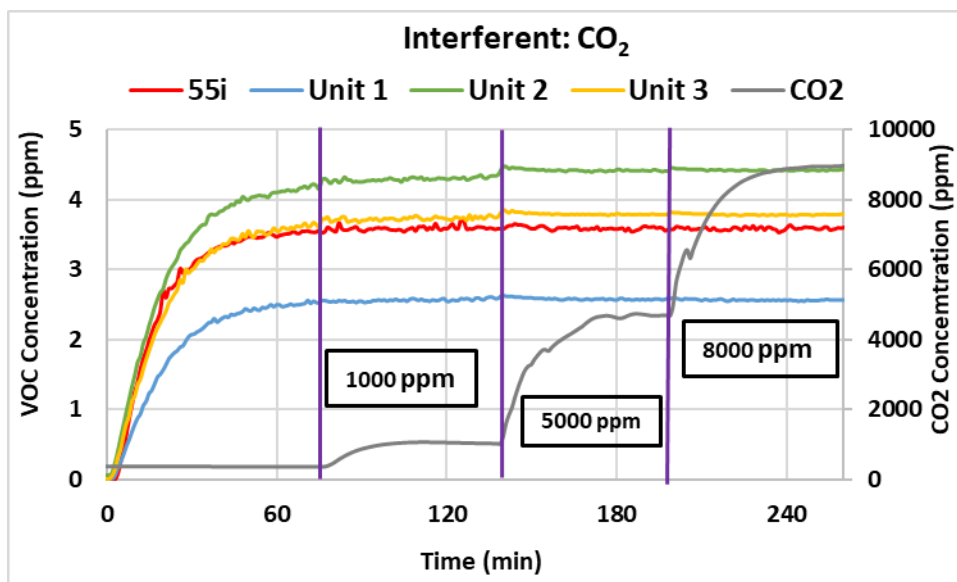


Figure 21. An example of a CO₂ as an interferent experiment

4.5.5 Phase 5: Outdoor Simulation

The outdoor simulation experiment aims to subject sensors to typical diurnal T/RH conditions found in the South Coast Air Basin, along with atmospherically relevant VOC and O₃ concentrations. The experiment is designed to avoid the issue of confounding the effect of coinciding T and O₃ increases as a day progresses by not changing T and O₃ at the same time (Table 8 and Figure 22). Each step lasts for an hour. The exhaust flow rate of the inner chamber is set to 8 L/min and the incoming zero air flow rate is set to 6 L/min to keep a slight negative pressure on the inner chamber; the outer chamber dilution flow rate from the zero-air generator is set to 30 L/min in order to maintain VOC-free air in the outer chamber that becomes the source for the 6 L/min air that is transported into the inner chamber.

Table 8. Outdoor Simulation Experiment

Step	Ozone, ppb	VOC, ppb	T, °C	RH, %
1	0	200	10	80
2	0	400	10	80
3	0	200	20	50
4	0	400	20	50
5	50	200	20	50
6	50	400	20	50
7	50	200	30	10

8	50	400	30	10
9	100	200	30	10
10	100	400	30	10

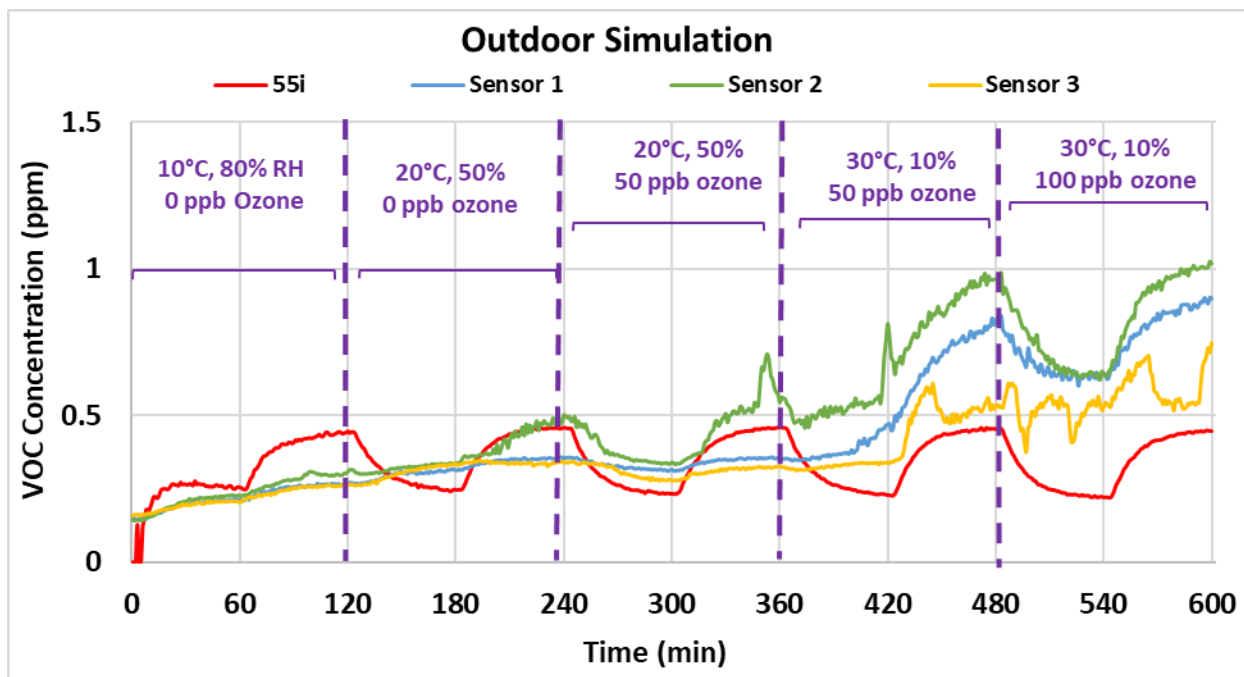


Figure 22. An example of an outdoor simulation experiment.

4.5.6 Phase 6: Final Concentration Ramping

The final concentration ramping is performed in the exact same way as the Phase 2 Initial Concentration Ramping experiment and the short-term change in response of sensors is determined. The minimum amount of time that passes between the end of Phase 2 and the start of Phase 6 needs to be at least 14 days.

5 Data analysis

After the completion of a phase of testing, the sensors' and reference instruments' data are retrieved and analyzed in the same manner. First, the sensors and reference instruments data are validated following basic QA/QC rules (e.g., obvious outliers, negative values, non-numeric values, and invalid data points are eliminated from the data-set). The valid reference instrument-sensor matched data are used as 1-min or 5-min averages depending on the sensor reporting interval. The statistical analysis is conducted for each parameter in each phase of testing listed in Section 3 and Table 9.

Table 9. Parameter calculation by test phase

Parameter	Phase 1 Transient VOC Plume Detection	Phase 2 Initial Concentration Ramping	Phase 3 Effect of Temperature and RH	Phase 4 Effect of Gaseous Interferents	Phase 5 Outdoor Simulation	Phase 6 Final Concentration Ramping
Accuracy		✓	✓	✓	✓	✓
Precision		✓	✓	✓	✓	✓
IMV		✓	✓	✓	✓	✓
R^2		✓				✓
Detection Limit		✓				✓
Detection of Transient Events	✓					
Climate Susceptibility			✓			
Response to Interferents				✓		
ANOVA					✓	
Short-Term Change in Response						✓
Data Recovery		✓	✓	✓	✓	✓

6 Limitations

The AQ-SPEC Chamber 1 system can generate a stable and reproducible range of VOC concentrations under normal and extreme environmental conditions, offering high time resolution and automated VOC measurements. However, several limitations need to be recognized.

Evaluation parameters, such as SDL, can be determined only when several conditions are met: 1) sensors must provide absolute concentration values; 2) sensors must show adequate R^2 values and 3) the slope of the regression line must be positive. SDL cannot be determined for sensors that do not meet those requirements. There are also additional parameters that cannot be calculated for indexing sensors.

In the climate susceptibility testing phase, only a few T/RH combinations are tested due to unreasonable labor and time requirements, and also some of the extreme temperature (e.g., 0°C) and extreme RH (> 95%) conditions are outside of the sensor manufacturer's recommended

operation conditions or are not practically achievable in the chamber. Therefore, these conditions are not part of this testing protocol.

Although the GC-FID instrument can identify individual VOC species, due to its maximum concentration range using the GC column in this testing, it is only used for the low concentration experiments; VOC speciation at higher VOC concentrations cannot be achieved with the current GC-FID system. Meanwhile, the Thermo 55i monitor does not report a response to specific VOC species but rather total VOC concentration present in the gas samples. In the case where sensors report specific response to specific VOC species, quantitative conclusion may not be accurately drawn where other non-target VOC species are present due to the non-selective nature of the Thermo 55i monitor.

The VOC sources employed in this testing protocol are 1) a VOC blend containing 1,3-butadiene, benzene, ethane, and tetrachloroethylene and 2) benzene-only. The 4-VOC blend represents a wide class of VOC species, but this simple mixture is not necessarily representative of VOC species present in the ambient air. Future adaptations or updated versions of this testing protocol may include different VOC mixtures, for example natural gas/light alkanes and/or BTEX to represent oil/natural gas activity emissions.

Finally, the lowest VOC species concentration levels that commercially available sensors are tested at, using this testing methodology, are still way above typical levels of these pollutants seen in ambient air. Such sensor devices may be used with source/near-source monitoring applications where elevated VOC species concentrations are expected/observed and not with ambient monitoring applications. Eventually, as sensor technology evolves, lower detection levels of VOC species concentrations may be achieved.

7 Conclusions

This VOC laboratory testing protocol is the first comprehensive method to systematically evaluate the performance of commercially-available VOC sensors. This protocol is based on the current knowledge and technology of both VOC reference instruments and sensors and will be used going forward for AQ-SPEC VOC laboratory sensor evaluations.

The protocol provides detailed information on reference instruments, standard test gas cylinders, testing procedures and evaluation parameters employed. This protocol was validated by testing a limited set of triplicates of VOC sensors according to the procedures in this document. Results are organized and published as part of the AQ-SPEC website. Preliminary results from testing a

selection of VOC sensors according to this protocol suggests that the currently available VOC sensor may provide qualitative information on the VOC levels observed; however, these sensors may not be suitable for ambient VOC monitoring at this time due to their high detection limit and uncertainty in data quality. Future advances in VOC sensor technology and AQ-SPEC testing infrastructure, as well as different VOC species of concern can be considered for future improvements to this testing protocol.

Appendix

Below is a list of commercially available VOC sensor systems that have power options to last the duration of each phase of testing, have means of communication, data logging/retrieval and commercially available VOC OEMs (as of June 2023).

Table A1. Collected information for commercially available VOC sensor systems

Manufacturer (Model)	Sensor Type	Range (ppm)	LOD (ppm)	Accuracy	Reference Gas	Response Time (s)	Lifetime (years)	Operating Conditions
Aeroqual (S500)	PID	0-30	0.01	< ± 0.02 ppm + 10%	isobutylene	30		0-40 °C 0-95% RH
Baseline (VOC-Traq II)	PID	0-2 (blue) 0-20 (yellow)	0.0005 (blue) 0.0015 (yellow)			< 4s to 90% response		
Dräger (Multi-PID 2)	PID	0-2000	0.1 ppm isobutylene	± 10% or ± 2 ppm	100 ppm isobutylene	≤3		0-40 °C 0-95% RH
Graywolf (AdvancedSense DirectSense IAQ)	PID	0.005-20	0.0025			<60		
Igienair (Zaack)	PID	0-50	0.001		isobutylene			-40-60 °C 0-95% RH
Ion Science (Tiger Select Benzene)	PID	0-200 (benzene)	0.01	± 10% ± 1 digit benzene		130		-20-40 °C 0-99% RH, non-condensing
Lunar Outpost (Canary-S)	PID	0-50	0.001					
PID Analyzers (Model 102)	PID	0.1-3000 or to 30,000		± 5%	isobutylene	< 1s to 90% response		5-40 °C 0-95% RH, non-condensing

		with dilution probe						
RKI Instruments (GX-6000, 10.0 eV lamp)	PID	0.1-50 for benzene 0-100 for 300 VOC	0.001	± 10% ± 1 digit				-20-50 °C 0-95% RH
RAE System (PPB)	PID	0-200		0.01		15		-20-60 °C 0-90% RH
SENSIT (SPOD)	PID	0.01-2		± 20 ppb min or 10%		5-10	1	
Aeroqual (S500)	MOS	0-25	0.1	< ±0.1ppm + 10%		60		0-40 °C 10-90% RH
	MOS	0-500	1	< ± 5ppm + 10%		30		0-40 °C 10-90% RH
Atmotube (Pro)	MOS	0.3-30 specified range		15%				
FabLab (Smart Citizen Kit)	MOS	0-30					>5	
Magnasci (uRADMonitor A3)	MOS	0-10 mg/m ³ (oxidizers) 0-100 mg/m ³ (reducers)				< 1s to 33-63% response		
Sensirion (SGP40)	MOS	0-500 (as VOC index)	< 0.05 ppm ethanol or < 10% of concentration setpoint		ethanol (index value can also be expressed in terms of isobutylene)	<10		-10 – 50 °C 0-90% RH
Airthinx (IAQ)	Not Disclosed	0-10 ppm						

Elitech (Temptop LKC- 1000S+)	Not Disclosed	0-5 mg/m ³						0-50 °C 0-90% RH
Qingping (Air Monitor)	Not Disclosed	0.005-9.999 mg/m ³						-10 – 50 °C 0-90% RH

Table A2. Collected information for commercially available VOC sensor OEM

Manufacturer (Model)	Sensor Type	Range (ppm)	LOD (ppm)	Accuracy	Sensitivity	Response Time (s)	Lifetime (years)	Operating Conditions
Ion Science (ppb MiniPID2)	PID	0-40	0.001		50mV/ppm	< 3	5	-40-55°C 0-99% RH
Mocon Baseline (piD-TECH eVX)	PID	0-2	0.05		>0.3 mV/ppm	< 3		-40-55°C 0-99% RH
Alphasense (PID AH2)	PID	0-50	0.001		>20 mV/ppm	< 3		-40-55°C 0-99% RH
Alphasense (PID A12)	PID	0-300 (linear range) (as isobutylene)	0.05		>0.3 mV/ppm	< 3		-40-55°C 0-99% RH
Alphasense (p-type)	MOS	1-100 (as isobutylene)						-20-120 °C
Figaro (TGS2602)	MOS	1-30 (as ethanol)	1					

Table A3. *K* values for *n* replicates

n	K	n	K	n	K	n	K
7	6.101	30	3.317	53	2.993	76	2.855
8	5.529	31	3.295	54	2.977	77	2.851
9	5.127	32	3.273	55	2.970	78	2.847
10	4.829	33	3.253	56	2.963	79	2.843
11	4.599	34	3.234	57	2.956	80	2.839
12	4.415	35	3.216	58	2.949	81	2.836
13	4.264	36	3.199	59	2.943	82	2.832
14	4.138	37	3.182	60	2.936	83	2.828
15	4.031	38	3.167	61	2.930	84	2.825
16	3.939	39	3.152	62	2.924	85	2.821
17	3.859	40	3.138	63	2.919	86	2.818
18	3.789	41	3.125	64	2.913	87	2.815
19	3.726	42	3.112	65	2.907	88	2.811
20	3.670	43	3.100	66	2.902	89	2.808
21	3.619	44	3.088	67	2.897	90	2.805
22	3.573	45	3.066	68	2.892	91	2.802
23	3.532	46	3.055	69	2.887	92	2.799
24	3.494	47	3.045	70	2.882	93	2.796
25	3.458	48	3.036	71	2.877	94	2.793
26	3.426	49	3.027	72	2.873	95	2.790
27	3.396	50	3.018	73	2.868	96	2.787
28	3.368	51	3.009	74	2.864	97	2.784
29	3.342	52	3.001	75	2.860	98	2.782

Table A4. Example of average sensor precision calculated from T and RH interference experiments.

RH (%)	T (°C)				
	5	10	20	30	40
20	99.8		99.7		
40		99.9	99.8	99.7	
65			99.8		
80			99.6		99.3

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