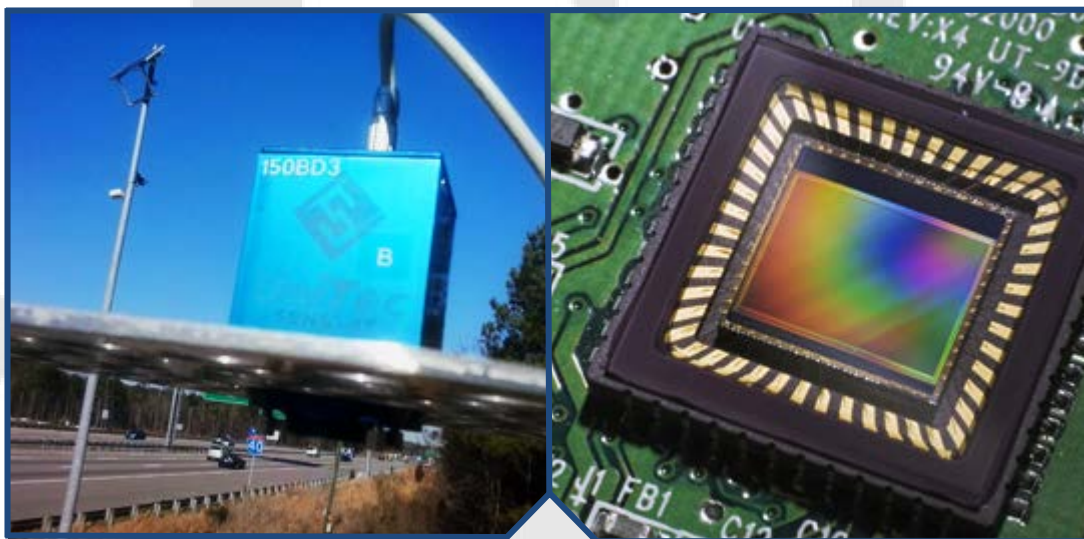


Next Generation Air Monitoring (NGAM) VOC Sensor Evaluation Report



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Ron Williams
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC, USA 27711

Amanda Kaufman
ORISE Participant
Oak Ridge Institute for Science and Education
Oak Ridge, TN, USA 37831

Sam Garvey
Alion Science and Technology
Research Triangle Park, NC 27709

Disclaimer

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Abstract

This report summarizes the results of next generation air monitor (NGAM) volatile organic compound (VOC) evaluations performed using both laboratory as well as field scale settings. These evaluations focused on challenging lower cost (<\$2500) NGAM technologies to either controlled or ambient conditions. The cost ceiling applied to the technologies selected for evaluation reflected a value believed to be the limit to what citizen scientists might seek to obtain for their use. The work conducted here and the summary of findings is not meant to be a definitive description of all such technologies. It represents a first step in understanding the capabilities of lower cost VOC technologies and their limitations.

An exhaustive search of commercially-available VOC NGAM products under the \$2500 limit yielded a very modest number of devices available for inclusion in the research. Ultimately a total of five (5) devices were incorporated into the evaluation with one of those being an EPA developed device which used a commercially-available VOC photoionization detector (PID) as the sensing element.

The laboratory evaluations involved challenging the devices to a stepwise pattern of VOC concentrations at levels believed to be environmentally relevant (< 25 ppb) using a chamber. Reference gas chromatographic (GC) detection was utilized to verify the challenge conditions being established. The devices were first evaluated for their response to a single VOC (benzene). If the device revealed some ability to detect benzene at even 25 ppb it was then challenged with an atmosphere consisting of three VOCs (benzene, 1,3-butadiene, and tetrachloroethylene). These compounds were selected because of the availability of well qualified test gases and the fact they represented a variety of VOC moieties (structural variability). The response of the devices to the various challenge conditions are reported.

NGAM devices were deployed at an outdoor near road test platform for an extended period where wide variability of VOC conditions were expected to exist. The research plan involved direct comparison of the NGAM response to GC reference data from collocated measurements obtained at the test site. Reference data were ultimately not available for the intended comparisons (instrument malfunction and insufficient resources to conduct a timely repair). Therefore, field data provided here are limited to non-reference comparisons between NGAM devices. Such comparisons, providing a non-quantitative assessment of true VOC response still have the potential of yielding useful information on the relative response characteristics of the NGAM VOC devices evaluated.

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Acronyms and Abbreviations

AC	alternating current
°C	degrees Celsius
FID	flame ionization detector
GC	gas chromatograph
GSM	Global System for Mobile Communication
h	hour
in.	inch
L	liter
μm	micrometer
m	meter
min	minute
mm	millimeter
MS	mass spectrometer
NERL	National Exposure Research Laboratory
NIST	National Institute of Standards and Technology
NRMRL	National Risk Management Research Laboratory
o.d.	outer diameter
ORD	Office of Research and Development
PID	photoionization detector
ppb	parts per billion
ppm	parts per million
QAPP	quality assurance project plan
r ²	coefficient of determination
RH	relative humidity, i.e., water vapor content of air expressed as a percentage of vapor pressure of water at a given temperature and pressure
RSD	relative standard deviation
SD	secure digital
SIM	subscriber identity module
V	voltage
VOC	volatile organic compound
WA	work assignment

Executive Summary

Background

Low cost air quality sensors are indicative of emerging technologies that have a wide appeal to both professional researchers and citizen scientists. They exist in numerous configurations (e.g., cell phone, hand-held) and are often available with a wide assortment of sensor configurations. One area of increasing interest represents NGAM devices that might have the ability to detect either total VOCs (tVOCs) or specific VOCs (e.g., benzene) in a continuous fashion and at low cost. While the commercial availability of such devices has increased in the near recent past, uncertainty about the quality of data such devices might be capable of providing has been raised.

Study Objectives

The U.S. Environmental Protection Agency (U.S. EPA) sought to discover what NGAM VOC devices existed that might be available for citizen scientists and others at a relatively low cost (<\$2500). This cost threshold being the upper ceiling that citizen scientist and others might consider acceptable for a lower cost (non-reference) continuous monitor. It should be recognized that the value cited is arbitrary but would seem to capture conversations with citizen scientists concerning such thresholds.

The study objectives involved both establishment of general findings as well as analytically-based evaluations. One such objective was the performance of a market survey to discover representative versions of the VOC sensors available under the aforementioned cost threshold. All devices considered had to have the capability of detecting and reporting either tVOCs or specific VOCs in a continuous fashion without any laboratory analyses. Analytical objectives included the determination of response characteristics of the NGAM devices under controlled laboratory evaluations. Response characteristics included the response factor, linearity of the response, and precision of the response across the range of evaluation concentrations. The relative response of the devices to both a single (benzene) as well as a multi-component test gas were performed. Lastly, collocated operation at a near road test site was performed to establish the relative performance of the devices under a widely variable real-world test scenario.

Study Approach

Direct communication with sensor manufactures was pursued to gain an understanding of the availability, cost, and potential performance features of NGAM VOC sensors. It was apparent that most of the VOC sensing technology available for purchase fell into only a few

categories based upon an extensive literature review¹. The first was the occupational exposure market. These represented mostly photoionization detector-enabled (PID) devices often costing in the range of \$2-5K per copy. The next category we discovered was high end devices (fast response gas chromatography or UV-optical) devices with retail costs often exceeding \$10K. The last category we discovered involved devices potentially having retail costs below \$2500 and which consumers (citizen scientists) might be able to acquire. This category was extremely limited in both the number and variety of devices suitable for our purposes. The vast majority of the true sensing elements in this category consisted of PIDs with one thick film sensor element (UniTec) identified. Ultimately a total of five NGAM devices were obtained that provided a general representation of those deemed available at the lower cost range of the market. These devices consisted of a UniTec SENS-IT (thick film sensor), Cairpol CairClip (NM-VOC-PID), CanAirIT-PID, Toxi-RAE Pro-PID, and an in-house developed sensor employing the latest generation miniature PID (APPCD with blue Mocon PID). Standard operating procedures were developed for each of these devices and telecommunication/data storage/recovery procedures were established to facilitate data collections in both a chamber and field environment.

Each of the devices were challenged to known concentrations of a challenge VOC gas containing laboratory established concentrations of benzene and as a follow-up a tri-mix of multiple VOCs (benzene, 1,3-butadiene, tetrachloroethylene). The follow-up chamber evaluation was performed only if the device provided satisfactory response to the original benzene challenge (linearity of response and sensor sensitivity). Data review and reduction was performed summarizing the sensor's response to the various challenge condition.

A second phase of the proposed research approach was operation of the NGAM devices for those showing the potential to provide useful (even indicative) indications of changing VOC concentrations in comparison with collocated reference grade monitors (in-line gas chromatography) under real world conditions². In our situation, this was a mobile source test platform in close proximity to a major interstate highway. The deployment of the NGAM devices was successful and data collection for approximately 30-60 days for each device was accomplished. Failure of the collocated research grade reference monitors at this test site ultimately prevented any direct comparison of the NGAM response with reference data so no summarization of that comparison could be performed. Intra-comparison of the NGAM devices and their relative responses were summarized to provide some understanding of how these sensors might relate to one another.

¹ MacDonnell, M., M. Raymond, D. Wyker, M. Finster, Y. Chang, T. Raymond, B. Temple, M. Scofield, D. Vallano, E. Snyder, AND R. Williams. Mobile Sensors and Applications for Air Pollutants. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-14/051 (NTIS PB2014 105955), 2014.

² Williams, R., Vasu Kilaru, E. Snyder, A. Kaufman, T. Dye, A. Rutter, A. Russell, AND H. Hafner. Air Sensor Guidebook. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-14/159, 2014.

Sensor Performance Results Associated with Chamber Challenge

A wide range of potential detection limits would appear to be evident with the NGAM technologies evaluated. For example, the ToxiRAE-PRO showed no response to challenge concentration at levels at or below 25 ppb (the maximum chamber concentration established). On the other hand, the in-house fabricated device employing a Mocon “blue” PID appeared to have sensitivity capabilities at concentrations below 2.5 ppb. Other devices showed outputs that did not provide a consistent response to allow determination of detection limits. For example, the CanAirIT provided a response under known challenge conditions that exhibited a widely fluctuating series of spikes that had no relationship with the true chamber condition. Likewise the CairClip NMVOC device provided no data useful for establishing detection limits under the challenge conditions employed. One of the more interesting devices, the UniTEC SENS-IT, employing a proprietary thick film sensing element, appeared to be capable of detecting VOC concentrations between 5 and 25 ppb. Even so, this device had a near sinusoidal electrical output, especially at concentrations below 10 ppb that made it difficult to truly ascertain detection limits and precision.

Ease of Use Features Evaluation

The field evaluations (collocation at the near road monitoring platform) provided the best opportunity to examine ease of use features. The devices deployed had to be provided weather shielding as they did not come factory-ready for the all-weather environment. In our situation, a rain helmet was utilized to shield the device from precipitation while ensuring the sensor element had open access to the ambient environment. It should be stated that the impact of ambient temperature on the devices deployed at this site was not established. Correlation between temperature and sensor output was determined but due to the lack of reference data no specific impact of temperature upon estimating VOC concentrations could be established. It is anticipated that such effects would exist in some degree due to the nature of the sensor element itself and the reported range of operation manufacturers specify with these devices.

Of interest to the potential users of these devices are some of the ease of use features associated with electrical requirements. We needed to establish long time period operational status so none of the units were operated using any internal battery configuration. The UniTec SENS-IT required a direct AC power supply and access to a third-party data acquisition system. Concerning the latter, this represents a significant limitation on the mobility one might have with deploying this under a variety of field conditions. The CanAirIT device was proven to be easy to deploy once the initial set-up and operation was established. It too requires AC power for extended operational times and connection to its proprietary data server. The CairClip NMVOC proved itself to be easy to operate as many of the CairPol products appear to function. A mini-USB connection provided the means to establish long-term power to the unit. The unit we tested had a malfunctioning microfan for its inlet which resulted in a shortened period of operational status. The in-house produced APPCD PID provided some of the best ease of use features we encountered. It is a rather large device (6 inches wide) in comparison to many of the other hand-size sensors we examined. Even so, it was not unwieldy and we were able to easily accommodate its size in both the chamber and field deployment activities. This sensor does require direct 115V access and therefore battery or other non-AC power supplies are not applicable. It should be

clearly stated that the most robust device examined was the ToxiRAE Pro relative to the field environment. This commercially available product represents one of many similar devices often sold to occupational safety specialists. It has numerous worthy features such as a high impact casement, highly adaptable user interface (keypad) to allow operator control of detection parameters, and built-in calibration programs. This device was tested specifically here to see if such a device might have any viability in the low concentration (environmentally relevant) conditions where citizen scientists might wish to attempt VOC measurements.

Conclusions

This early examination of the “best of the best” lower cost NGAM VOC devices clearly indicates that some of these sensors may provide indicative response to environmentally relevant concentrations of VOCs. As an example, the target VOC benzene often observed in urban environments at concentrations well below 25 ppb would suggest that only two of the devices evaluated (APPCD-PID and UniTec SENS-IT) showed detection capabilities in this general area that would be useful for non-industrial environmental monitoring. Even so, we observed issues with noisy response outputs that limited the usability of some of the named devices. It should be clearly stated that there may be circumstances where any of the devices evaluated might provide some value to the end-users, especially when all of the key features such as ease of use, simplicity of operation, and ease of data recovery have been considered. In conclusion, lower cost NGAM VOC technologies would appear to be limited in both their capability and variety of technologies being employed in this market segment. PID components would still appear to be the prominent sensing element available and as such, these come with inherent pros and cons which one must consider in trying to use such a device to estimate VOC concentrations under a variety of monitoring scenarios.

1.0 Introduction

EPA's Office of Research and Development (ORD) has been continuing a body of research associated with examining emerging technologies that might prove useful for citizen scientist as well as professionals interested in use of lower cost next generation air monitor (NGAM technology. A majority of the aforementioned research has been summarized and has been made available through a primary data portal, the Air Sensor Citizen Science Toolbox (<http://www.epa.gov/heasd/airsensortoolbox/>)³. To this end, NERL has been continually seeking out novel sensor technologies for the measurement of pollutants of interest. One area of growing interest is that involving volatile organic compounds (VOCs). ORD has received numerous inquiries from Regional offices, Program Offices, State Air Offices, industrial concerns, and community groups about the state of the science for this type of sensing technology. To meet this stakeholder need, primary research was conducted that attempted to discovery the availability of lower cost VOC monitors and provide preliminary assessments of its capabilities under known conditions (chamber evaluations). Operation under ambient conditions was also conducted to determine some of the ease of use characteristics stakeholders need to understand.

This report documents efforts to survey sensor/application technologies for the measurement of volatile organic compounds (VOCs) through direct contact with inventors and commercial and research institutions. This project aimed to provide data for identifying which technologies might prove valuable in conducting air quality measurements under a variety of conditions. Five VOC sensors were ultimately selected and secured for evaluation under laboratory and field conditions. This report details the materials and methods used to conduct the evaluations (Section 2) and results for both the laboratory (Section 3) and the field (Section 4) components. Section 5 summarizes our evaluation findings.

³ The U.S. EPA's Air Sensor Toolbox for Citizen Scientists. Website available at www.epa.gov/heasd/airsensortoolbox/. 2015

2.0 Materials and Methods

The five VOC sensors selected for evaluation are listed in Table 1-1. All sensors were first evaluated in the laboratory under controlled conditions. These same sensors, with the exception of the CairPol CairClip, were then deployed to the field for assessment of VOC response under ambient conditions. The CairClip was not evaluated in the field because it developed mechanical problems during the laboratory evaluation, and resource constraints prevented acquisition of a new unit.

Table 1-1. VOC Sensors Evaluated under WA 4-03

Laboratory	Field
UniTec SENS-IT	UniTec SENS-IT
AirBase CanarIT	AirBase CanarIT
CairPol CairClip	APPCD PID
APPCD PID	ToxiRAE Pro
ToxiRAE Pro	

The evaluation focused on the following performance characteristics of each sensor:

- Linearity of response
- Precision at each concentration range point
- Lowest established concentration in which a response was detected
- Concentration resolution
- Response time (if it could be easily established)
- Suggested range of operation to achieve best practical operation conditions

The effects of temperature, relative humidity (RH), pollutant atmospheres, and interfering species on sensor performance were also considered in the evaluation.

Unless otherwise noted in the text, the values used for statistical analysis were the last 5-min average values at each input concentration level, or set point, which is the target or desired value as opposed to the measured concentration. This ensured maximum stabilization time and generated one value per set point per test.

The coefficient of determination (r^2) is the square of the sample correlation coefficient and was used as a measure of linearity. Microsoft Excel was used to calculate r^2 by plotting all measured values against their set points, which displayed the linear regression. The same plot was used to determine response factors and offsets.

Relative standard deviation (RSD) was used to define precision at a given set point. For each sensor, measured values at each set point for all tests were examined together. For example, all measured values for the 25 ppb target concentration for the UniTec SENS-IT comprised one data set. For each data set, the standard deviation was divided by the mean to calculate the RSD.

2.1 Laboratory Evaluations

The five sensors were independently challenged in triplicate with four concentrations each of benzene only or a three-component VOC mixture containing benzene, 1,3-butadiene, and tetrachloroethylene in a temperature and RH controlled exposure chamber. The sensors were evaluated for responsiveness, linearity, and precision. Data ultimately in hand revealed that our ability to establish response time (in a very definitive degree) was not a practical statistical operation due to the pattern of response or the conditions of the evaluation parameters (chamber characteristics). Concerning this latter statistical output, the graphical data provided to the reader might still provide some information of use in practical response times but we make no attempt to formally calculate these values as specified above. This section describes the laboratory setup and the methods used for testing the sensors in the laboratory.

2.1.1 Laboratory Setup

The laboratory setup shown in Figure 2.1-1 was used for evaluating the performance of the sensors. The setup consisted of an exposure chamber, a model 111 zero air generator (Thermo Scientific, Waltham, MA), and a 146C dynamic gas calibrator (Thermo Scientific). The temperature was maintained during test runs at the ambient conditions of the climate-controlled laboratory (~20 to 25 °C). An all-glass impinger was used to humidify the zero air. The test atmospheric conditions within the exposure chamber were verified using a temperature/humidity probe based on the Honeywell HIH-4602-C. An Agilent Technologies (Santa Clara, CA) 7890A gas chromatograph with flame ionization detector (GC-FID) using an Entech Instruments (Simi Valley, CA) 7200 pre-concentrator was used to monitor the gas concentrations within the chamber.

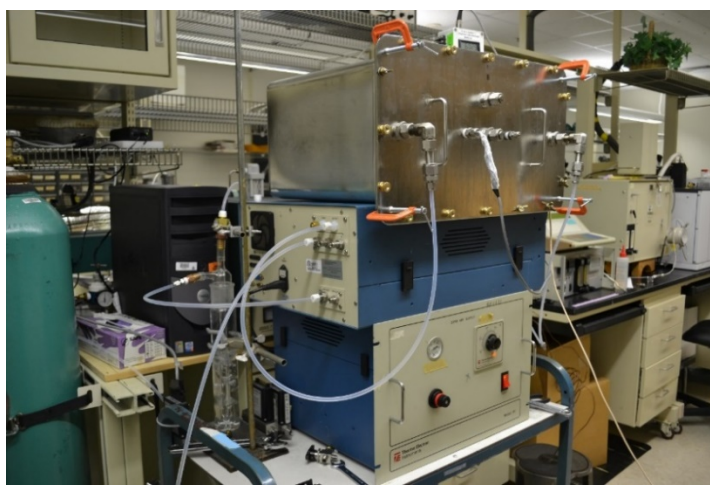


Figure 2.1-1. Laboratory VOC sensor testing setup: exposure chamber (top), Thermo Scientific 146C gas calibrator (middle), and Thermo Scientific model 111 zero air generator (bottom). The impinger is shown to the left of the setup

2.1.1.1 Exposure Chamber

The exposure chamber was a 52-L stainless steel test chamber with two ports that were used as the inlet and outlet ports for the experiments. Through each port, a long perforated steel tube extended deep inside the chamber, as shown in Figure 2.1-2. The perforated tube assisted with even diffusion of the challenge gas in the chamber.



Figure 2.1-2. Port with long perforated tube attached

Four ports were added to the lid of the chamber to allow 1/8-, 1/4-, and 3/8-in. (two ports) o.d. Teflon lines to be connected to the chamber. Any cables needed for operating the sensors were run through the two 3/8-in. sampling ports. The number and size of cables required varied significantly depending on which sensors were being tested. Adapters and fittings were added to the ports to reduce the diameter to a size that would more closely fit the cabling. In addition, parafilm was used inside compression fittings and wrapped around cables and the opening where the cables emerged from the fittings to achieve a seal. A chamber test was conducted that confirmed the parafilm did not outgas detection limit of concentration of VOCs (< 1ppb) and thus could be used for sealing ports without affecting measurements.

The chamber was pressurized and a leak test was performed. The chamber was cleaned prior to exposures. The inside of the chamber was first wiped with acetone, then with ethanol, and finally three times with deionized water. The empty test chamber atmosphere was measured via GC-FID, which showed no measurable VOCs at the 1 ppb threshold as being present in the chamber.

2.1.1.2 Zero Air Generator

Zero air was introduced into the exposure chamber by passing in-house pressurized air through a Thermo Scientific model 111 zero air generator. The zero air was then passed through an all-glass impinger filled with deionized water to humidify the air. A bypass valve attached to the impinger allowed the operator to maintain the humidity in the test chamber at approximately 50%. Exposure chamber conditions were monitored and verified via a custom-designed

temperature/humidity probe based on a Honeywell (Morristown, NJ) 4602C sensor. Temperature and humidity data were recorded using a Personal Daq/55 data acquisition system (Measurement Computing Corp., Cleveland, OH). The zero air generator temperature was set at either 350 or 425 °C as part of the determining best operational status. Both temperature set points provided equivalent baseline characteristics and the vast majority of all chamber evaluations were performed using the 350 °C scrubber temperature.

2.1.1.3 Gas Chromatograph System

Gas was introduced into the CG-FID system via a 1/8-in. o.d. Teflon line run through the smallest of the test chamber's ports. An Agilent Technologies 7890A GC-FID system with a 60 m × 0.32 mm × 1 µm Rxi-1MS capillary column and a 1.5 mL/min carrier gas flow rate was used to monitor the concentration of each test gas mixture introduced into the test exposure chamber. The initial oven temperature was set to 35 °C and was held for 5 min. The oven temperature was ramped up to 220 °C at a rate of 10 °C/min. The temperature was set to hold for 5 min to allow good resolution of the peaks of interest.

2.1.1.4 Dynamic Gas Calibrator

A Thermo Scientific 146C dynamic gas calibrator was used to dilute gas standards. The two standards used were benzene at 0.99 ppm as a single component (Linde, NIST traceable by weight) and a three-component mixture of benzene (1.03 ppm), 1,3-butadiene (0.96 ppm), and tetrachloroethylene (1.03 ppm) (Air Liquide, traceable to Scott reference standard). The three-component mixture was used to determine if the sensors were specific to benzene. Sensors that are specific to benzene should respond the same to both the benzene challenge and the three-component mixture. Sensors that are equally sensitive to all three components of the three-component mixture might be expected to respond in some fashion to approximately three times as much to the mixture as to benzene only.

Four concentrations were chosen for testing that covered two orders of magnitude while being evenly spaced on a logarithmic scale. This allowed for lower concentrations to be spaced closer together and thus more precise visualization of limits of detection. Test concentrations were ≤ 25 ppb to reduce the possibility of carryover effect when trace-level analysis resumed for other chamber projects. The VOC test concentrations for each analyte are listed in Table 2-1.

The use of the dynamic gas calibrator limited the automation of the test procedure. Limitations on the range of the mass flow controllers prevented use of a single total flow rate. The flow rates used to obtain each concentration are shown in Table 2-1.

Table 2-1. Sensor Exposure Concentrations Used in Laboratory Experiments

Benzene from Tank (ppb)	Three-Component Mixture (ppb)				Feed Rate (L/min)
	Benzene	1,3-Butadiene	Tetrachloroethylene	Total VOCs	
24.75	25.75	24.00	25.75	75.50	2
5.25	5.46	5.09	5.46	16.01	5
1.14	1.18	1.10	1.18	3.47	5
0.25	0.26	0.24	0.26	0.76	8

2.1.2 Evaluation Methods

Each sensor was exposed to the VOCs in the chamber over 15 hours while the concentration was stepped through each set point and the sensor response to the VOCs was recorded. The concentration of each gas was prepared using the Thermo 146C, which allowed automation of a single cycle of 10 steps. Each step could be held for a maximum of 99 min. The sequence to produce the test concentrations began with a period of zero air for at least 2 hours before the program started. The zero air was introduced at a flow rate of 5 L/min. The flow into the dynamic chamber equaled the flow out of the chamber, which prevented any buildup of pressure.

During the first sensor test (UniTec SENS-IT), the Thermo 146C program started at the highest set point and then stepped down to each subsequently lower set point until reaching zero air and then repeated the sequence. Each of the 10 steps was 90 min, which was only long enough to allow two GC-FID runs per step. This was insufficient to determine if equilibrium had been reached in the test chamber. In addition, data from previous internal research not reported here showed that the test chamber required 6.9 air exchanges, or a total of 359 L, to equilibrate to 99.9%.

Based on data from the initial test, changes were made to the original calibrator program. The highest concentration (25 ppb) in the calibrator program could be achieved only by reducing the total flow rate to 2 L/min. Thus, approximately 180 min was required to equilibrate to 99.9% of 25 ppb. The calibrator program was modified to allow for 180 min at each concentration set point. EPA staff who oversee the laboratory where the work was conducted suggested reversing the order of concentrations used. As such, subsequent tests reversed this order, starting at low concentrations and stepping up while repeating each concentration once. Thus, each concentration was held for two back-to-back steps of 90 min for a total of 3 h. The two calibrator programs used are shown in Figure 2.1-3.

At times, multiple sensors were tested in the chamber simultaneously. Analysis of zero air showed no sign of outgassing from any of the sensors that might affect data acquired by the other sensors.

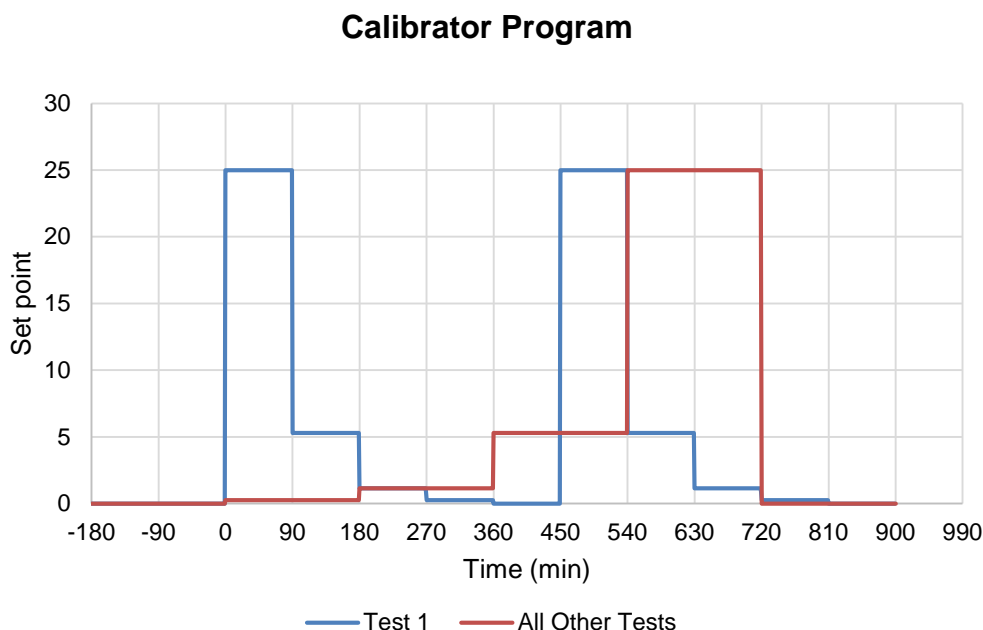


Figure 2.1-3. Calibration programs used

2.1.2.1 UniTec SENS-IT

The UniTec SENS-IT is a small VOC sensor (approximately 5 by 5 by 8 cm) that was claimed to have benzene specificity. Two UniTec SENS-IT units, designated A and B, were tested. The SENS-IT was connected directly to the Personal Daq/55 that was used for recording temperature and humidity, and the voltage (V) output of the SENS-IT was recorded at a rate of one data point per minute. All data used in this evaluation of the SENS-IT was collected with unit A in the chamber by itself, as shown in Figure 2.1-4. A single qualitative test of unit B in the chamber alongside the AirBase CanarIT and the CairPol CairClip (Figure 2.1-5) was run, which confirmed that both UniTec SENS-IT units performed similarly. Three benzene-only tests and three tests of the three-component mixture were successfully completed with the SENS-IT.

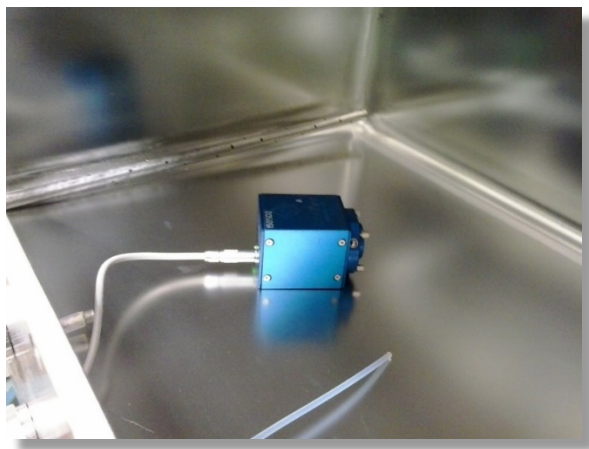


Figure 2.1-4. Orientation of UniTec SENS-IT in test chamber

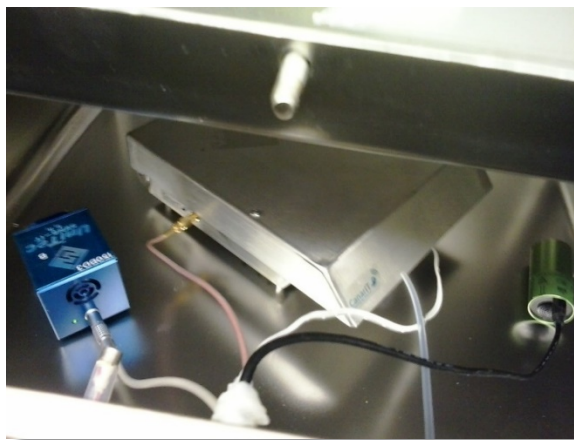


Figure 2.1-5. Orientation of UniTec SENS-IT unit B (left), AirBase CanarIT (center), and CairPol CairClip (right) inside test chamber

2.1.2.2 AirBase CanarIT

The AirBase CanarIT (approximately 25 by 25 by 10 cm) is a multi-sensor unit capable of measuring total VOCs (ppb) once every 20 seconds in addition to measuring several other analytes not covered in this report. This sensor transmits all data to a Web server where it can be accessed online using a Global System for Mobile Communication (GSM) subscriber identity module (SIM) card and data plan. The CanarIT is no longer commercially available and was reestablished under the Perkin Elmer ELM branding. Since an actual Perkin Elmer ELM product has not been evaluated, no linkages should be made between the performance of the CanarIT and the ELM should be attempted as they may contain significantly different sensing components and estimating algorithms.

The AirBase CanarIT was placed in the chamber alongside the CairClip and UniTec SENS-IT unit B to conserve time and resources (Figure 2.1-5). Early attempts to use the CanarIT involved attaching an external antenna to the unit via a cable run through one of the 3/8-in. sampling ports in the test chamber in order to establish communication with its Web service. It was thought that the steel test chamber might be causing a Faraday cage effect, i.e., the steel chamber was acting as a shield that blocked all radio or electromagnetic signals. However, even after the antenna was placed outside the chamber, a reliable connection could not be established. Many variations of antenna length and positioning were tried, but these efforts also failed to achieve a reliable connection to the GSM network from inside the EPA building. The manufacturer was contacted and disclosed that all data awaiting transmission to the server were stored on a secure digital (SD) card on the underside of the main circuit board inside the CanarIT. With this knowledge, testing resumed and all previously acquired data were accessible.

As all other sensors had undergone initial testing, further testing of the CanarIT was conducted with no other sensors sharing the chamber. The CanarIT was tested three times with the three-component mixture. Testing was terminated when it was determined that there was little if any response to test concentrations under any challenge condition.

2.1.2.3 CairPol CairClip

The CairPol CairClip is an extremely compact sensor (approximately 6.4 cm long, 3.2cm diameter) for measuring total VOC concentration (ppb). While this sensor can operate on battery power for approximately 24 hours, for this study it was operated continuously plugged into a powered mini-USB cable so that it would remain powered throughout testing. The CairClip generates data once per minute. Initial data showed no observable trends that would be expected to correlate with the test conditions. In addition, every other data point provided zero response values. Mechanical problems were suspected, but resource constraints prevented a thorough investigation of the problems or acquisition of a replacement unit. It was noted that the microfan used to bring fresh air over the sensing element sometimes did not self-activate (turn on when power was applied) and this might have been one component of the malfunctioning we observed. Therefore, testing of the CairClip was stopped to preserve study resources. This is further elaborated on in the results section.

2.1.2.4 APPCD PID

The APPCD PID sensor (approximately 11.5 cm tall and 11.5 cm in diameter), developed internally by EPA staff (ORD's National Risk Management Research Laboratory), is a photoionization detector (PID)-based sensor that measures total VOC concentration (V). The device they developed employed a Mocon (blue -pID-TECH eVx 10.6 eV). This particular Mocon PID sensor is no longer available as the manufacturer has developed new products, but at the time of its purchase it had reported detection capabilities down to 0.5 ppb (isobutylene). Raw 1-second data were recorded and then processed into 5-min averages because the large volume of 1-second data was difficult to manage. The APPCD PID was tested five times with the benzene-only tank and three times with the three-component mixture. The APPCD PID sensor was tested alongside the ToxiRAE Pro, which is also a PID-based sensor (Figure 2.1-6). The sensor head was placed in the test chamber upside down to allow sufficient ventilation to its inlets, and its data-logging module remained outside the test chamber with the cable connecting them run through one of the 3/8-in. sampling ports.

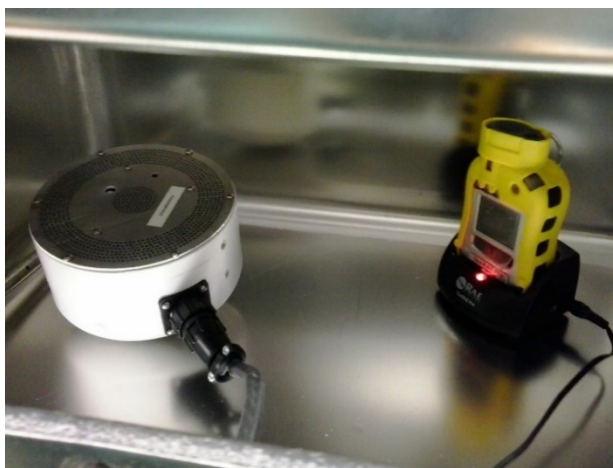


Figure 2.1-6. Orientation of APPCD PID (left) and ToxiRAE Pro (right) in test chamber

2.1.2.5 ToxiRAE Pro

The ToxiRAE Pro is a PID-based sensor (approximately 15 by 10 by 10 cm when on its charging cradle) that measures total VOC concentrations. It can operate on battery power or be plugged into a wall outlet via a proprietary charging cradle. For these tests, the unit was installed in its charging cradle connected to power. The ToxiRAE Pro can be programmed to measure concentrations of a specified compound automatically and has a real-time reading of VOC concentrations (ppm). The ToxiRAE Pro was designed for industrial hygiene use and is one of the more market-established sensors evaluated in this study. The sensor was designed with occupational safety issues in mind. Thus, its focus is on alerting the user of VOC levels (ppm) above preset thresholds rather than accurately measuring at trace levels. The ToxiRAE Pro was tested five times with the benzene-only tank and three times with the three-component mixture. It should be mentioned that the manufacturer does have devices more sensitive than the item evaluated but at substantially greater cost.

2.2 VOC Field Evaluations

The Triple Oaks near-road sampling site, located on Interstate 40 (I-40) in Raleigh, NC, and maintained by EPA's National Risk Management Research Laboratory (NRMRL), was selected for all ambient VOC testing. Three of the custom-made "bowl on pole" shelters were attached via zip tie to the railing of the Triple Oaks sampling trailer roof as shown in Figure 2.2-1. The design and utility of these sensor weather shields have been discussed in depth elsewhere⁴. A "bowl on pole" shelter consists of a pole with mounting flanges, a grating that acts as a stable floor for the samplers while allowing airflow to pass through, and a bowl-shaped rain shield connected to the grating with a hinge. In order from left to right, these contained the APPCD PID, the ToxiRAE Pro PID, and the UniTec SENS-IT. The AirBase CanarIT, was attached to a laboratory stand with wire and was C-clamped into place at the same height as the other sensors. A sampler shelter was used to house a laptop computer for data recovery and most of the electrical connections. Any connections that could not be made inside the shelter were instead encased in a zip-lock bag, which was closed with a zip tie to further protect against water.

⁴ Williams, R., Kaufman, A., Hanley, T., Rice, J., Garvey, S. Evaluation of Field-deployed Low Cost PM Sensors. EPA/600/R-14/464. December 4, 2014. Research Triangle Park, NC.



Figure 2.2-1. Triple Oaks sampling site with shelters

Because the gas chromatographic systems anticipated to provide collocated reference grade data comparisons at the Triple Oaks site during the field deployment time period was ultimately determined to be non-operational, the VOC sensor data were compared with one another and with NRMRL-supplied meteorological data. Meteorological data was available for just the first 13 days of the study due to other instrumentation problems the operator of the site encountered.

2.2.1 UniTec SENS-IT

The UniTec SENS-IT was oriented with its inlet protruding through the sample grating as shown in Figure 2.2-2. The SENS-IT experienced frequent failures of its data logger, the Personal Daq/55, throughout the study. When these failures occurred, the Personal Daq/55 would suddenly stop recording data until it was manually reset. The Personal Daq/55 was replaced with a DATAQ Instruments (Akron, OH) DI-145, but data collected with the DI-145 featured a strange sinusoidal curve that appeared to overwhelm the VOC response (see section 3.2.1). Voltage would rise to 1 V over the course of about a minute and then fall to -1 V over the course of another minute and repeat. The Personal Daq/55 unit was used for the remainder of the effort to record data at the near road site.



Figure 2.2-2. UniTec SENS-IT oriented in its sampling shelter with the lid up

2.2.2 AirBase CanarIT

The AirBase CanarIT was deployed on the opposite side of the trailer from the other sensors, but at the same height as shown in Figure 2.2-3. It was held in place on a laboratory stand with wire, and the stand was C-clamped to the railing.

The CanarIT maintained excellent uptime throughout the field study. The only time it went down was during a power outage on June 20, 2014. When the circuit breakers were turned back on a few days later, the sensor resumed operation until it was removed at the conclusion of the study.



Figure 2.2-3. AirBase CanarIT installed at the near-road site

2.2.3 APPCD PID

The APPCD PID was placed on the grating with its ventilation holes oriented downward as shown in Figure 2.2-4. The 9-pin connector was too large to fit through the holes in the grating, so the cable was cut, fed through the holes, and spliced back together.

The APPCD PID sensor maintained excellent uptime throughout the field study. The only time it went down was during a power outage on June 20, 2014. When the circuit breakers were turned back on a few days later, the sensor resumed operation until it was removed at the conclusion of the study.



Figure 2.2-4. APPCD PID oriented on its shelter with the lid up

2.2.4 ToxiRAE Pro

The ToxiRAE Pro was deployed upside down so that its inlet would be protruding through the grating (Figure 2.2-5), thus maximizing exposure to ambient air. The ToxiRAE developed a fan error prior to deployment in the field and had to be sent to the manufacturer for repairs. Upon its return, it performed without error. Because it started sampling late in the study, it was left at the field site two weeks later than the other sensors. No meteorological data were available during the period that the ToxiRAE was sampling.



Figure 2.2-5. ToxiRAE Pro oriented in its sampling shelter with the lid up

3.0 VOC Laboratory Evaluation Results and Discussion

3.1 Verification of Test Atmospheres

Data from the exposure chamber were collected using a GC-FID during 17 days of testing. The dynamic calibrator supplied four VOC concentration levels beginning with the highest concentration (25 ppb). Each input concentration level is referred to as the “set point,” which is the target or desired value as opposed to the measured concentration. In this case, the dynamic calibrator is that system. Each concentration was held for 180 minutes. For least-squares regression only, the last data point for each set point for each test was used. This was done to minimize conditioning effects on the data used for least-squares regression. The first test run with this calibrator program yielded an area count for benzene 18% lower than the average at 25 ppb. However, all other concentration levels were within 5% of average. The low area count was likely the result of conditioning effects in the lines to the GC system. The other anomalous GC result was on the first day of testing using the three-component mixture. The GC signal of all three components began to level off as normal for the 25 ppb set point but then spiked approximately 30%. The cause of this spike is currently unknown.

With the exception of two tests, GC area counts (concentration) for benzene and tetrachloroethylene were highly consistent ($RSD < 3\%$ at 25 ppb) and linear with respect to set point ($r^2 > 0.99$). Measurements for 1,3-butadiene were highly variable ($RSD = 15\%$ at the 25 ppb set point, $r^2 = 0.975$). Based on these data, the atmospheres produced in the test chamber were deemed consistent and precise throughout the study.

Figures 3.1-1 through 3.1-3 show the GC-FID area counts recorded for all tests for each analyte plotted against time overlaid with the set-point concentration plotted against time. Figures 3.1-4 and 3.1-5 show the GC-FID area counts plotted against set-point concentration for all tests of the benzene-only and three-component mixture tests, respectively. Table 3-1 tabulates the coefficient of determination, response factor, and offset for each analyte as well as the relative standard deviation (RSD) at each set point. Response factors are equal to the slope of the least-squares regression line plotted for the data in area counts per ppb. Offsets are the y-intercept of the same scatterplot in area counts. RSDs were found by taking the standard deviations of the area counts found for each set point across all tests and dividing them by the average of the same set. High RSDs are generally found only at the zero air and 25 ppb set points. At zero air, this represents the variability one would expect from an instrument attempting to measure below its detection limit. At the 25 ppb set point, this is likely due to the long equilibration time combined with the poor time resolution of the GC-FID. If some of the 25 ppb GC-FID data points were taken before equilibrium had been established, this might explain the increased variability.

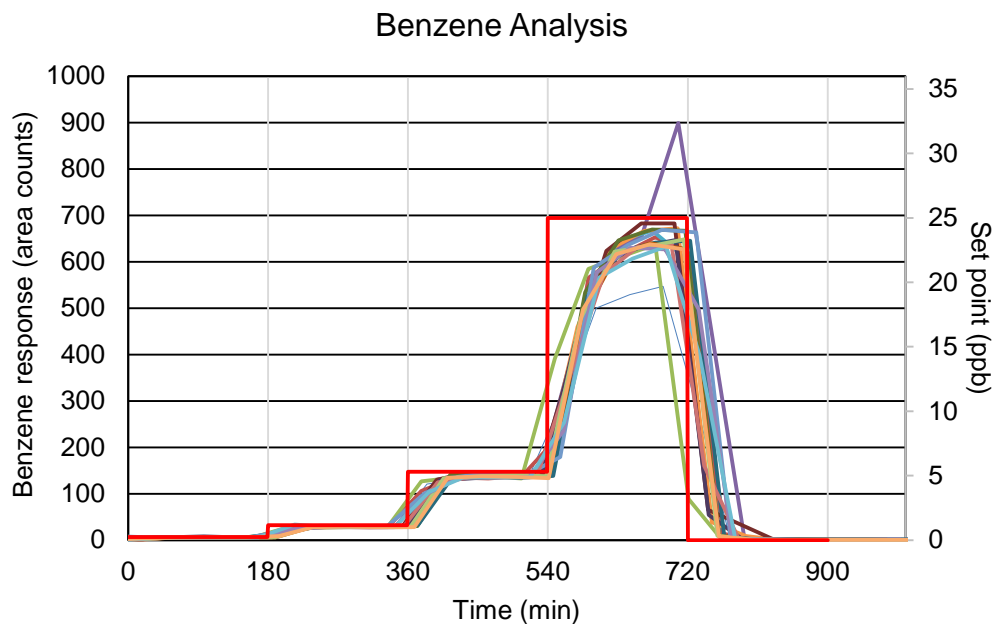


Figure 3.1-1. GC-FID benzene area counts vs. time. All 17 tests are shown together. The red stair step pattern is the set-point concentration in ppb.

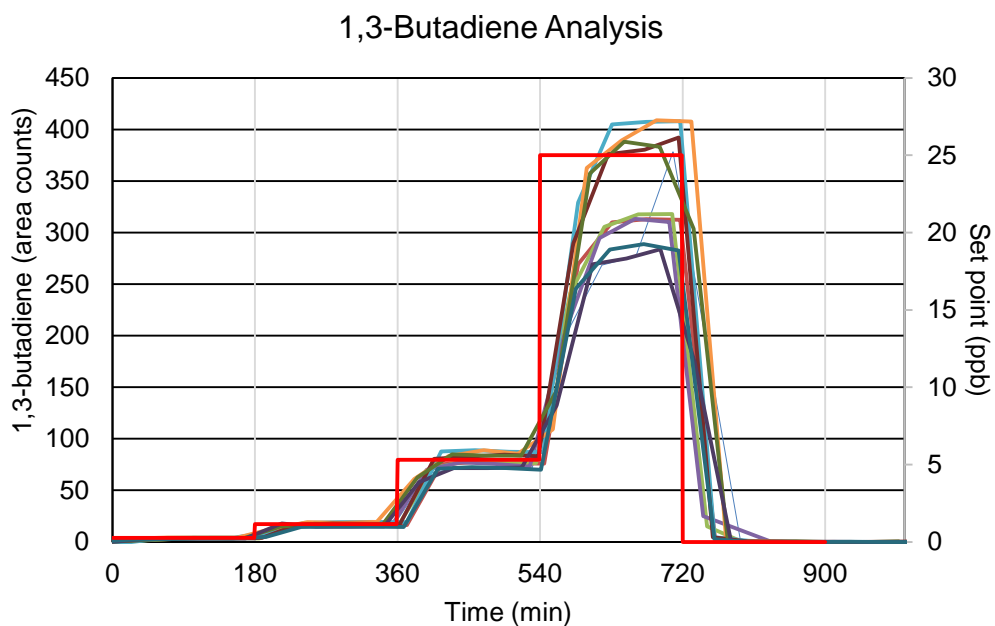


Figure 3.1-2. GC-FID 1,3-butadiene area counts vs. time. All 10 three-component mixture tests are shown together. The red stair step pattern is the set-point concentration in ppb

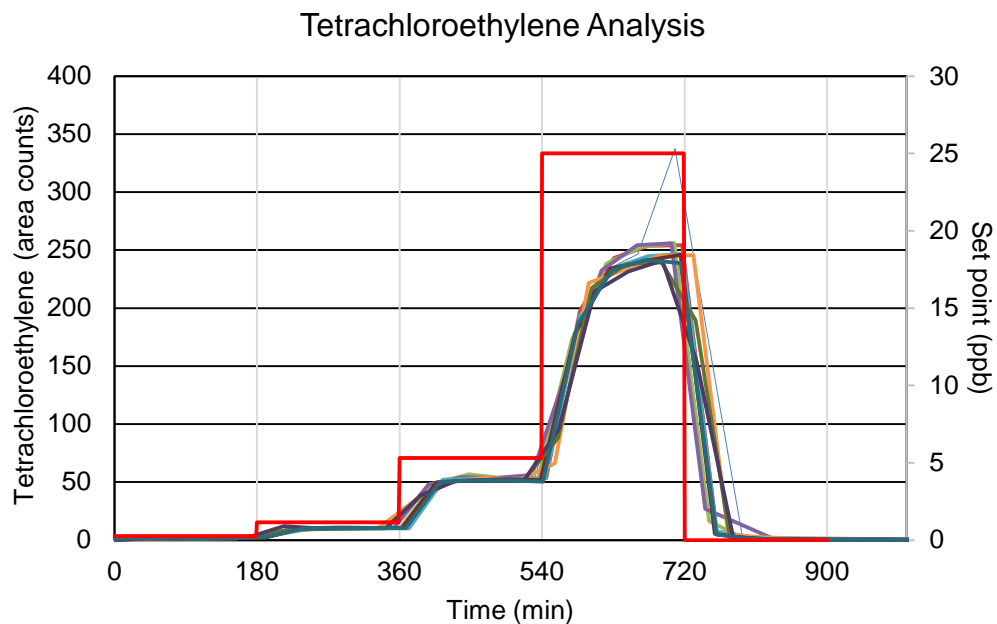


Figure 3.1-3. GC-FID tetrachloroethylene area counts vs. time. All 10 three-component mixture tests are shown together. The red stair step pattern is the set-point concentration in ppb

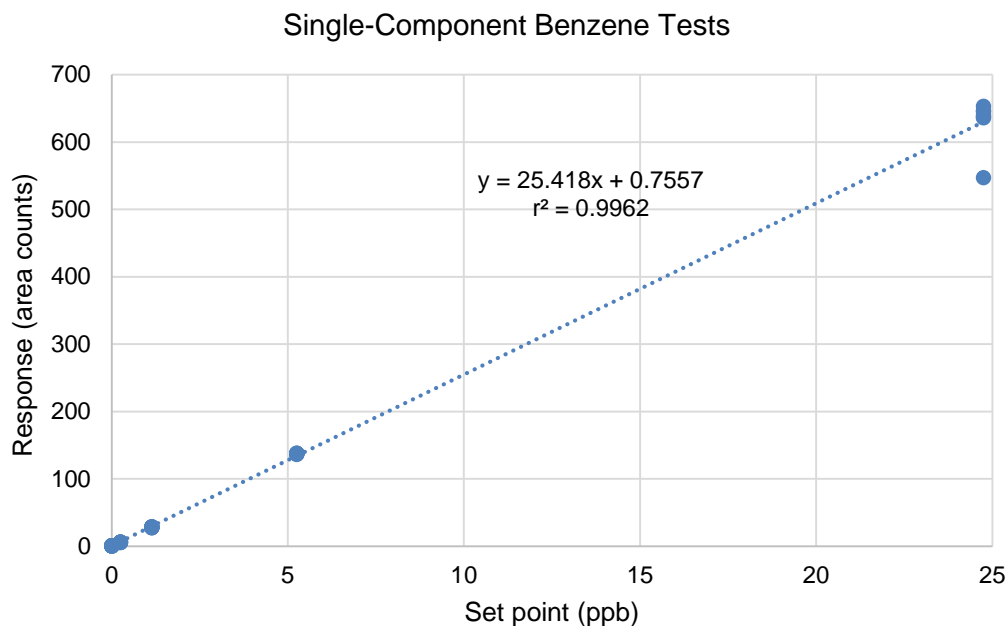


Figure 3.1-4. Final GC-FID benzene area counts vs. set point in all seven single-component benzene tests

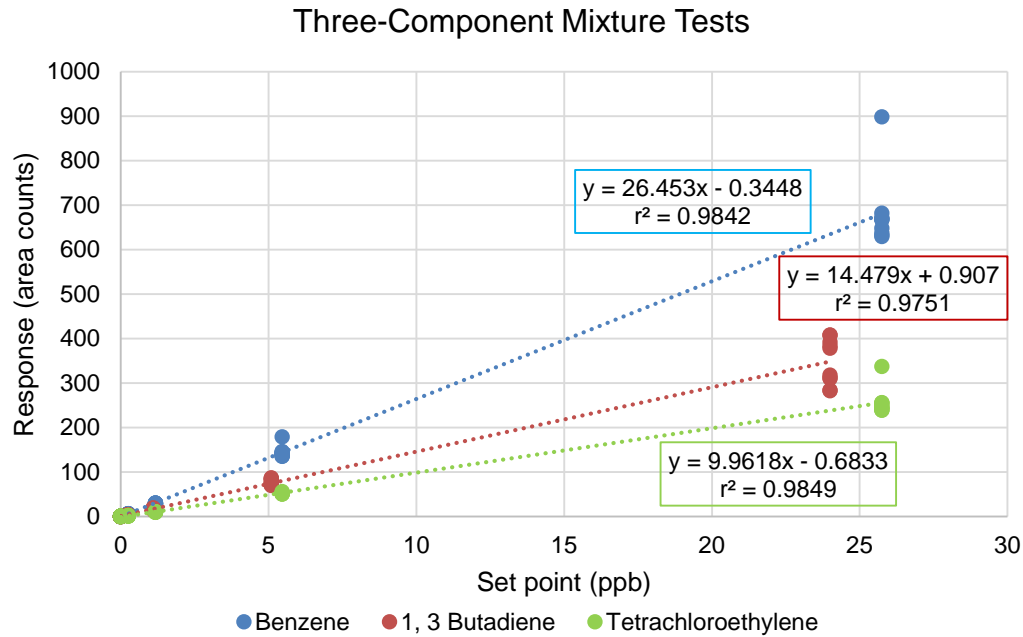


Figure 3.1-5. Final GC-FID benzene area counts vs. set point in three-component mixture tests

Table 3-1. Summary of GC-FID Data

	Single-Component Benzene	Three-Component Benzene	1,3-Butadiene	Tetrachloroethylene
r^2	0.9962	0.9842	0.9751	0.9849
Response factor (area counts / ppb)	0.0393	0.0378	0.0691	0.1004
Offset (area counts)	0.7557	-0.3448	0.907	-0.6833
RSD at 25 ppb	5.8%	11.6%	14.6%	11.4%
RSD at 5.3 ppb	0.5%	8.8%	8.1%	3.0%
RSD at 1.15 ppb	1.7%	3.7%	10.4%	3.1%
RSD at 0.25 ppb	3.0%	4.9%	12.7%	16.6%
RSD at zero air	27.2%	30.4%	200.7%	93.9%

3.2 Laboratory Evaluation Results

3.2.1 UniTec SENS-IT

Concentration data (V) for the UniTec SENS-IT were collected using the Personal Daq/55 and recorded in 1-min averages. The tests performed on April 12 and April 14, 2014, were both cut short when the Personal Daq/55 system malfunctioned. When these malfunctions occurred, the Personal Daq/55 would simply stop recording data. The cause remains unknown. The reference GC-FID failed on April 13 and could not be used to verify test conditions on that day.

The primary observation of the SENS-IT performance in the laboratory challenge was a wave-like pattern in the data that obscured the response to the challenge concentration. This cyclic pattern had a period of approximately 80 min, which can be most easily seen over a long period of sampling zero air, as shown in Figure 3.2.1-1.

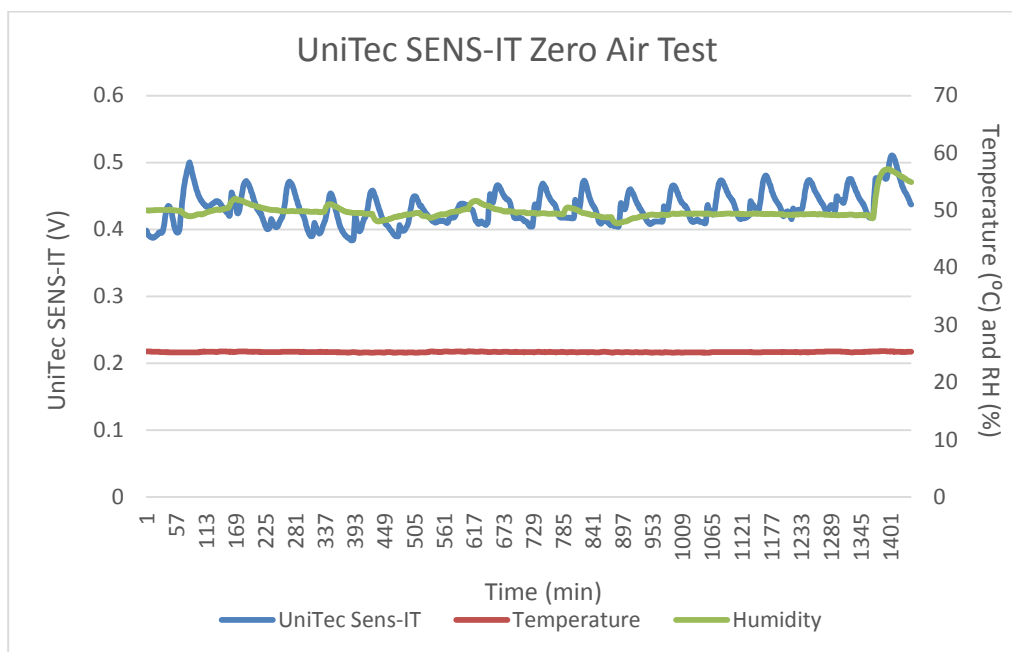


Figure 3.2.1-1. UniTec SENS-IT voltage, temperature, and humidity during an extended run of zero air

When temperature and RH are graphed alongside the voltage output of the SENS-IT, the cyclic pattern of the SENS-IT output does not correlate with either temperature or RH. Because the amplitude of the cycle is significant compared to the response to the challenge VOC, it must be accounted for. However, we believe the effect was likely not so great as to obscure the response to challenge completely. Therefore, an effort was made to mathematically compensate for this cycle, but it could not be determined conclusively if the cycle was additive to the signal or subtractive from it. Therefore, all data points were measured for a given set point at both the peaks and the troughs of the cycle. Figure 3.2.1-2 plots the UniTec SENS-IT and the GC-FID benzene response against time. GC-FID area counts were converted to ppb using the response

factor and offset from Table 3-1. Figures 3.2.1-3 and 3.2.1-4 show the SENS-IT response from initiation of the testing program for benzene and three-component mixture tests, respectively.

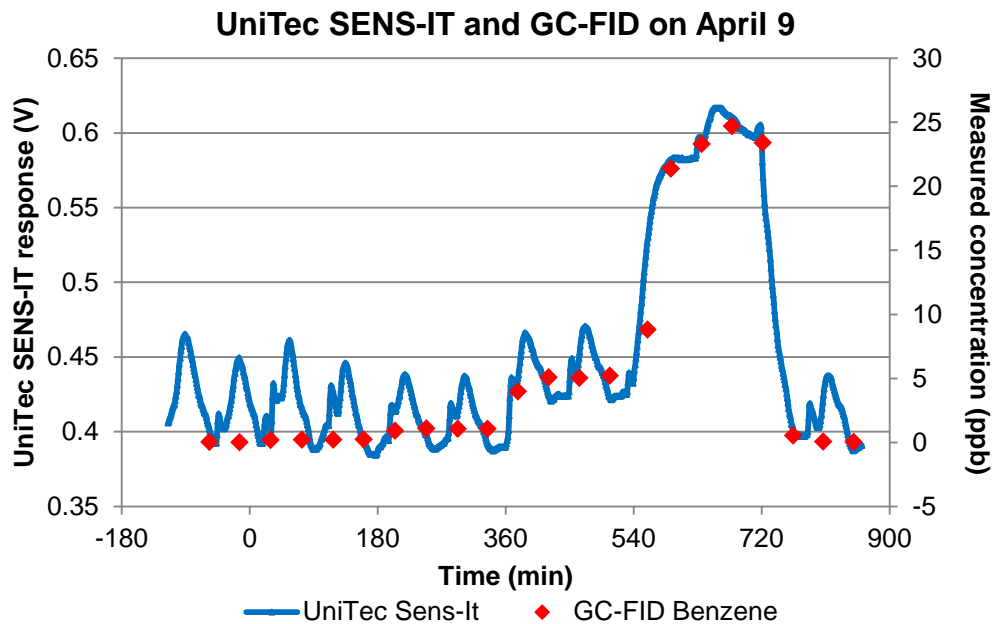


Figure 3.2.1-2. UniTec SENS-IT data and GC-FID benzene data from the single-component benzene test on April 9, 2014

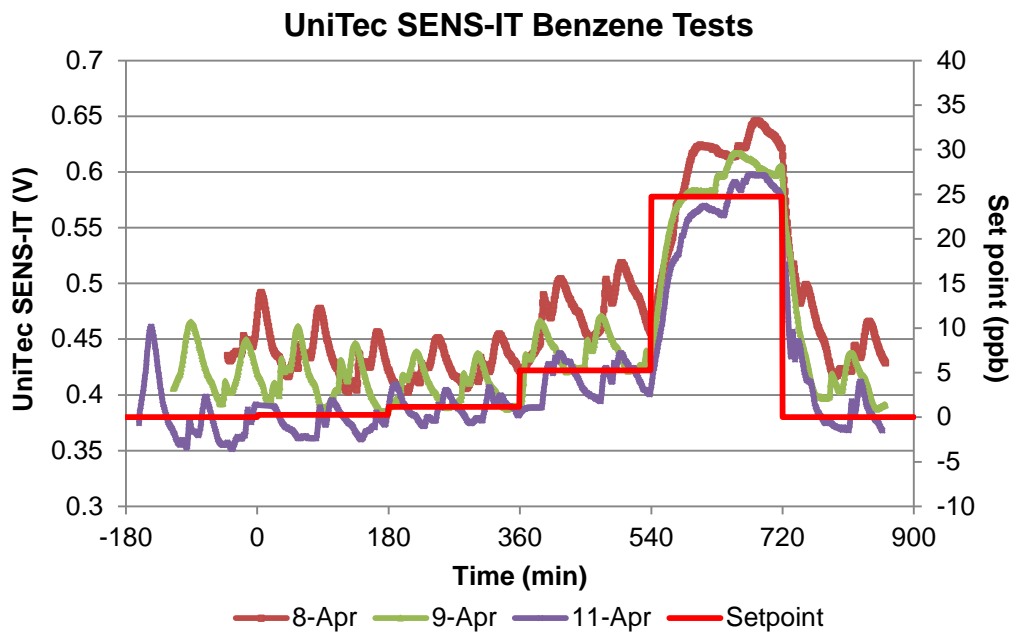


Figure 3.2.1-3. Three UniTec SENS-IT tests using benzene challenge

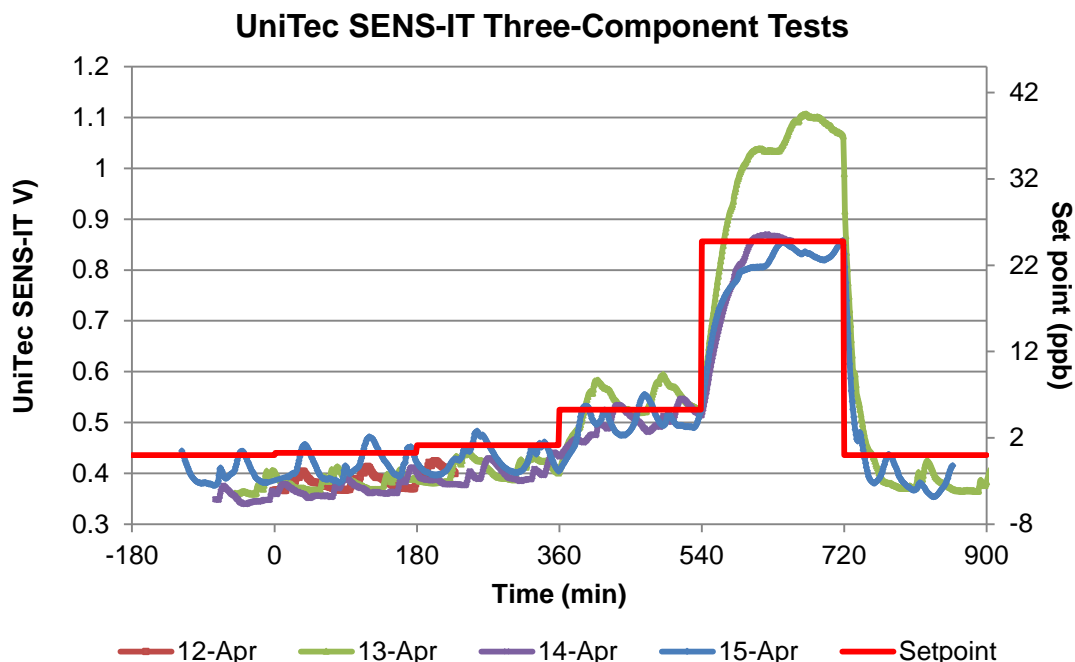


Figure 3.2.1-4. Four UniTec SENS-IT tests using the three-component mixture

In these graphs, the SENS-IT appears to be losing sensitivity as evidenced by its diminishing response to challenge conditions. Figure 3.2.1-3 shows that the response to the challenge concentration was decreasing with each subsequent day of testing. This apparent declining sensitivity might artificially inflate the measured precision of the SENS-IT. The linearity and precision of any one day of testing might be much better than that of the aggregate data.

This effect was investigated by plotting each test individually to display trends over time. An example from April 15, 2014, is shown in Figure 3.2.1-5. Figure 3.2.1-6 shows the UniTec SENS-IT response against benzene concentration as measured by the GC-FID. Area counts were converted to concentration using the benzene response factor and offset measured, as described in Section 3.1. The response factor and offset of Figure 3.2.1-6 is nearly identical to that of the trough response factor and offset in Figure 3.2.1-5 as expected.

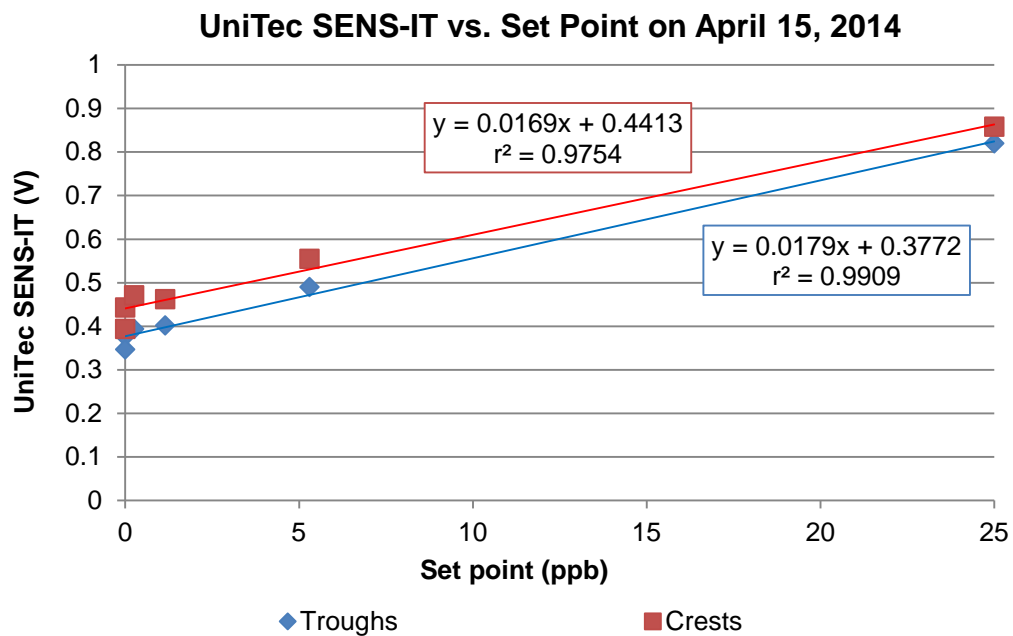


Figure 3.2.1-5. UniTec SENS-IT response in both peaks and troughs vs. set point

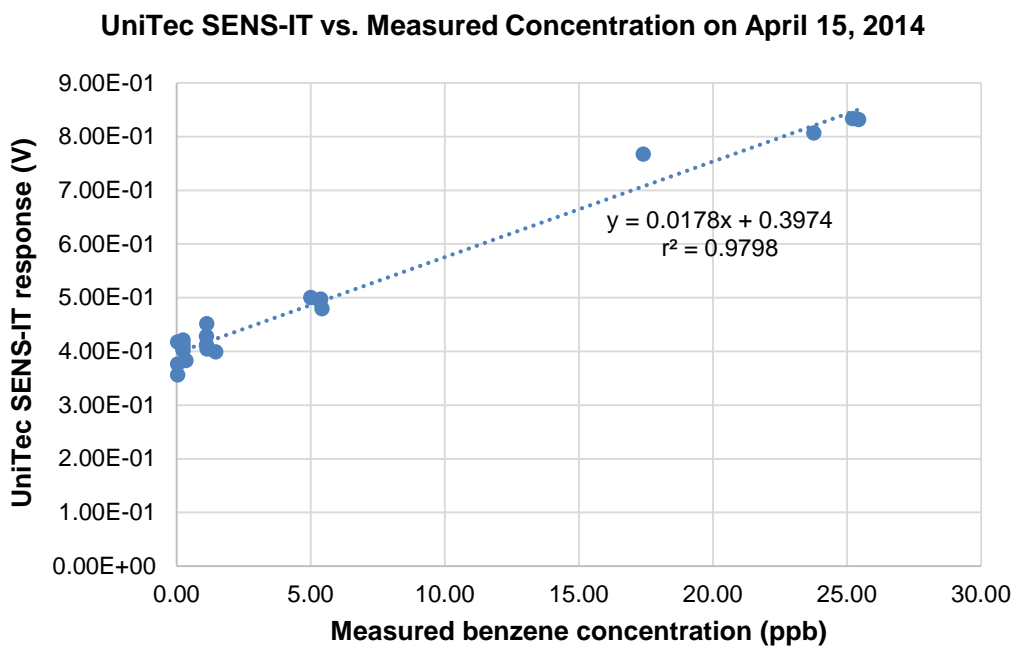


Figure 3.2.1-6. UniTec SENS-IT vs. measured benzene concentration. Benzene concentration was calculated using the response factors and offsets in Table 3-1

The response factors and offsets for all data were plotted on one graph by date (Figure 3.2.1-7). Note that the tests on the April 8, 9, and 11 used only a benzene challenge. All other test days used the three-component mix.

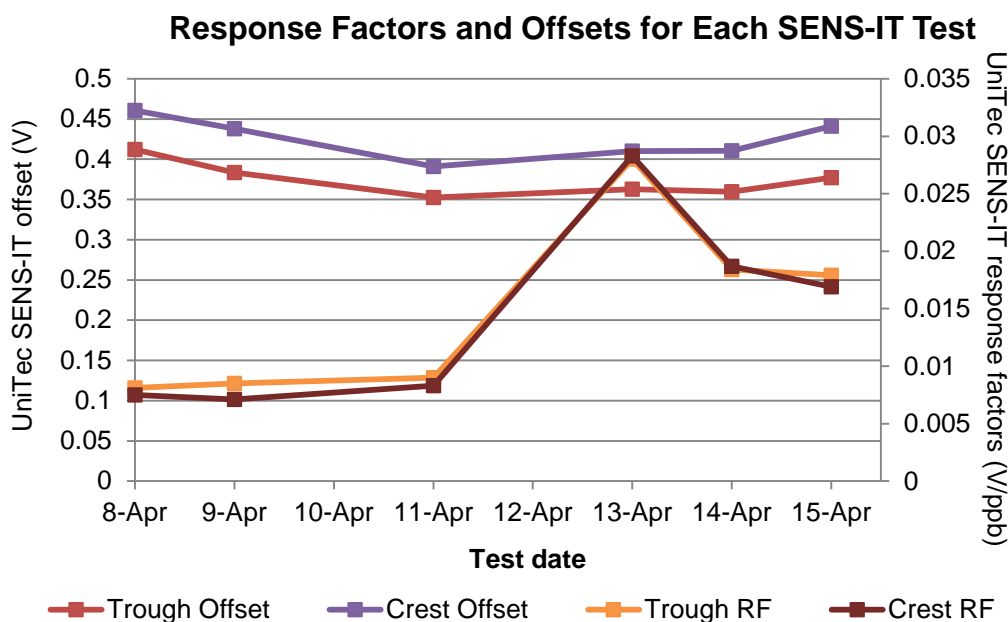


Figure 3.2.1-7. Response factors and offsets for all UniTec SENS-IT tests for both crests and troughs

The tests performed with the three-component mixture featured a response factor between two and three times the response factor of the benzene-only tests. It is difficult to quantify this ratio precisely because the test on April 13 is possibly an outlier. However, the tests on April 14 and 15 feature response factors more than two times that of the benzene-only tests. This suggests that the UniTec SENS-IT might not be specific to benzene, as suggested. It is likely sensitive to at least one of the other two components and possibly both. If the SENS-IT was sensitive to all three components equally, then one could measure the benzene signal by dividing the total signal by the ratio of the total concentration of the three-component mixture to that of the benzene tank, as shown in Figure 3.2.1-8.

Figure 3.2.1-8 shows that the offsets fall steadily over the course of the benzene tests, but rise again during the three-component tests. The response factors behave just the opposite. It should be noted that the test on April 13 did not have any corresponding GC-FID data, and therefore test conditions could not be verified. While a net downward trend for both response factor and offset can be established, the correlation with time is not as strong as was initially suspected. Therefore, all of the troughs were averaged with their corresponding crests and graphed together against set point in Figure 3.2.1-9.

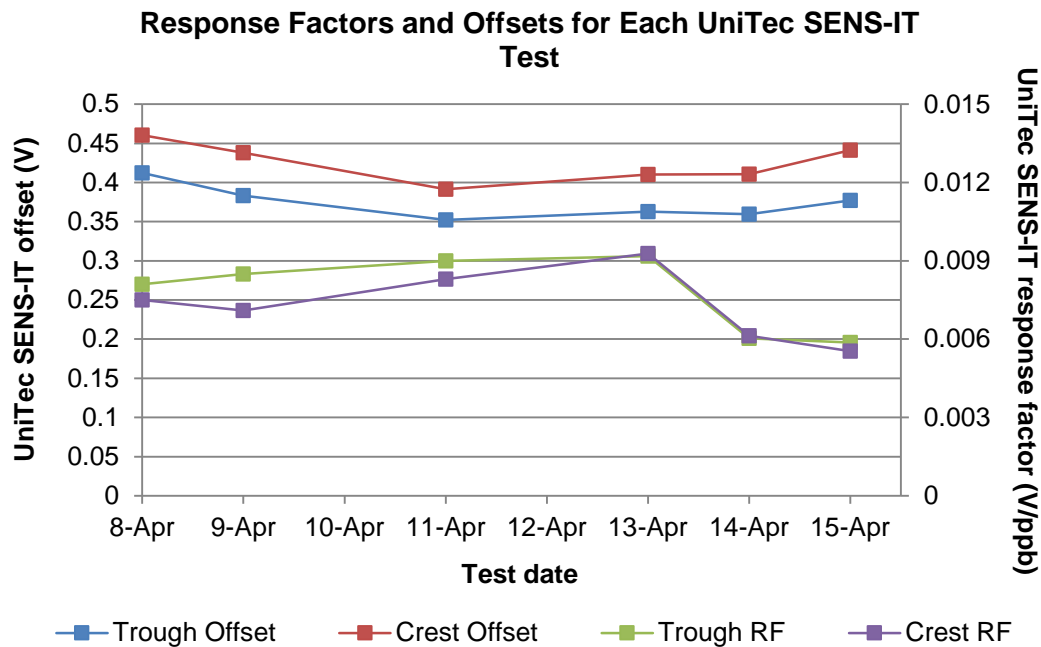


Figure 3.2.1-8. Response factors and offsets for all UniTec SENS-IT tests for both crests and troughs. Three-component mixture data have been normalized against the ratio of the total VOC concentration in the three-component tank to the concentration of benzene challenge

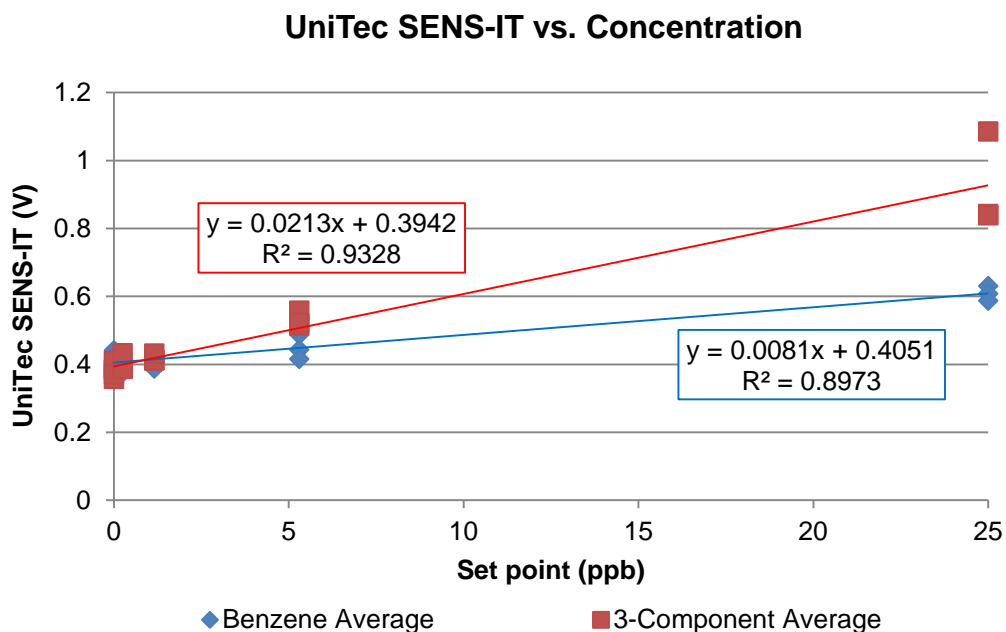


Figure 3.2.1-9. UniTec SENS-IT vs. set point for both benzene-only and three-component tests

As can be seen from Table 3-2, the response factor for the three-component mixture was 2.6 times that of the benzene-only tests, although this might be inflated by the unusually strong response to challenge during the three-component mixture test on April 13. In addition, the RSD held fairly steady at all concentration set points except at 25 ppb for the three-component mixture. This suggests there were no limit of detection issues with this experiment. The high RSD at the 25 ppb concentration in the three-component mixture was likely due to the unusually high test results on April 13, as discussed earlier.

Table 3-2. UniTec SENS-IT Summary

	Single-Component Benzene	Three-Component Benzene
r^2	0.8973	0.9328
Response factor (V/ppb)	0.0081	0.0213
Offset (V)	0.4051	0.3942
RSD at 25 ppb	3.5%	15.3%
RSD at 5.3 ppb	8.0%	4.4%
RSD at 1.15 ppb	5.3%	2.8%
RSD at 0.25 ppb	6.8%	6.6%
RSD at zero air	7.7%	5.1%

3.2.2 AirBase CanarIT

CanarIT data are transmitted via a GSM cellular signal to a Web server. However, due to poor signal strength, we had to download data from the internal SD card, with guidance from the manufacturer. The CanarIT was tested three times with the three-component mixture, all with similar results.

As seen in Figure 3.2.2-1, the CanarIT displays a similar 80-min cyclical response as seen with the UniTec SENS-IT, but to a much greater degree relative to the response to challenge. As such, no correlations can be made between the CanarIT and the challenge conditions at this time. It is interesting to note that this cyclic signal is extremely weak during the challenge at a concentration of 25 ppb. It is possible that the cyclic signal is related to flow rate, which is at the minimum of 2 L/min at the 25 ppb concentration.

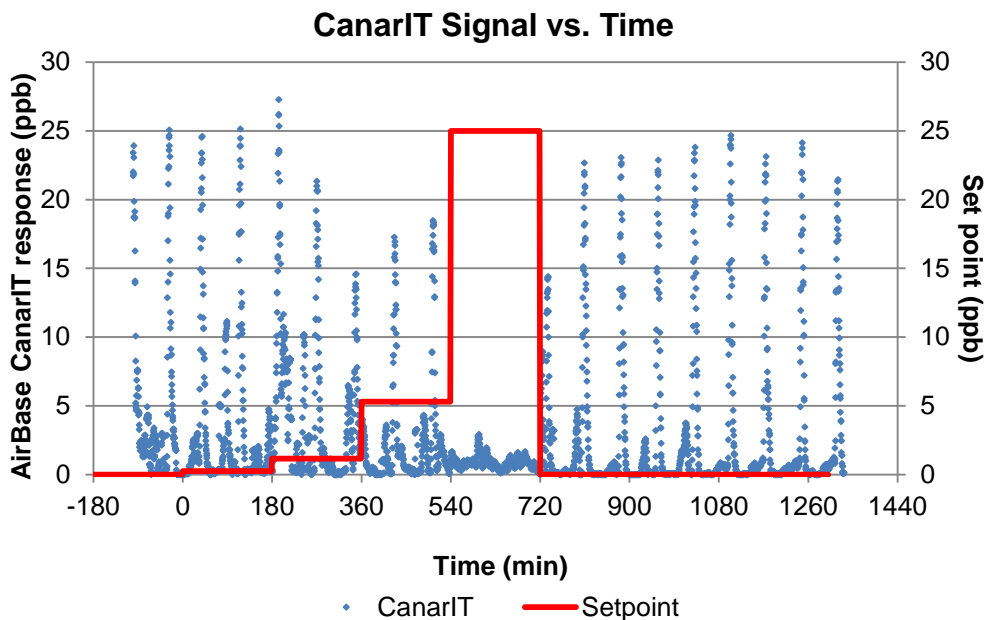


Figure 3.2.2-1. AirBase CanarIT signal over time during a three-component mixture test

3.2.3 CairPol CairClip

The CairClip was tested in the exposure chamber and produced erratic results. Every other data point was a 0, and even when the 0s were removed, no conclusions could be drawn from the remaining data, as illustrated in Figure 3.2.3-1. The CairClip was removed from testing after this exposure.

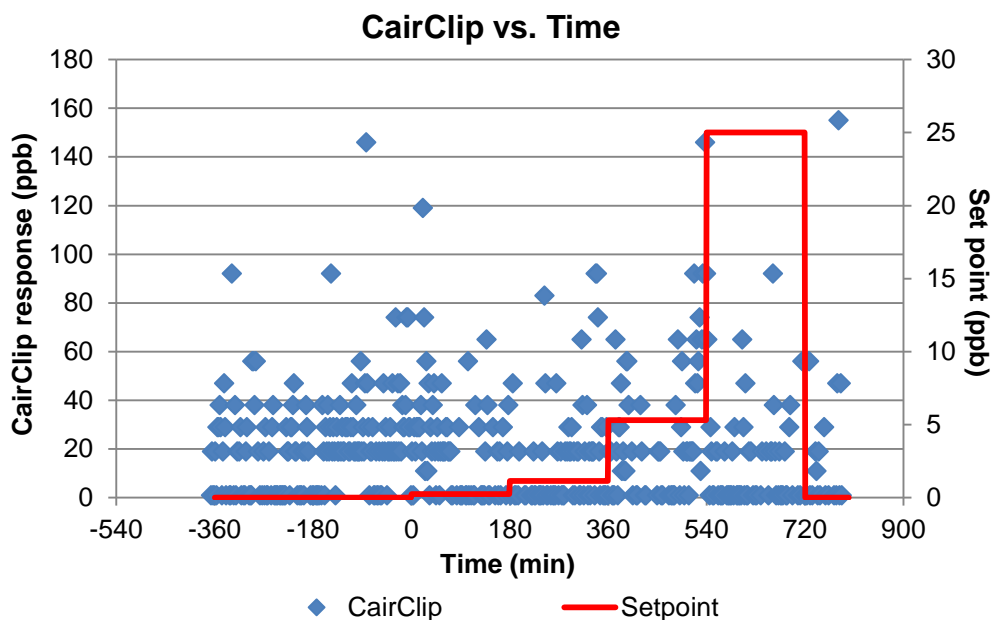


Figure 3.2.3-1. CairPol CairClip over time during a three-component mixture test

3.2.4 APPCD PID

The APPCD PID sensor is a photoionization detector (PID)–based sensor that measures total VOC concentration in volts (V). The raw 1-second data were processed into 5-min averages to ease data processing and interpretation.

The test data for the APPCD PID, such as that from April 23, 2014, shown in Figure 3.2.4-1, show several interesting phenomena. The unit sampled zero air at both the beginning and the end of the exposure. The response (V) of the zero air samples collected at the end of the test had drifted far lower than what was found at the beginning. With the exception of the 25 ppb concentration level, all responses began to decay after reaching equilibrium. The most likely reason the sensor responded to the 25 ppb set point in this manner is that at the lower flow rate the chamber was just achieving equilibrium at the end of the 180-min sampling period..

An attempt was made to compensate for the signal decay exhibited by the APPCD PID sensor. This was done by taking slopes of 30-min segments of data over time to approximate the slope of the baseline at that time. These slopes were then compiled with the beginning and end zero air set points. The end result was an approximation of a smooth curve in which the slope at any given point was approximately the slope of the decay of the signal. This smooth curve was also developed to intersect the data during the zero air set points, thus forming a baseline. These baselines were overlaid on data from April 22, 2014, and the APPCD PID data were then subtracted from these baselines, as shown in Figure 3.2.4-2.

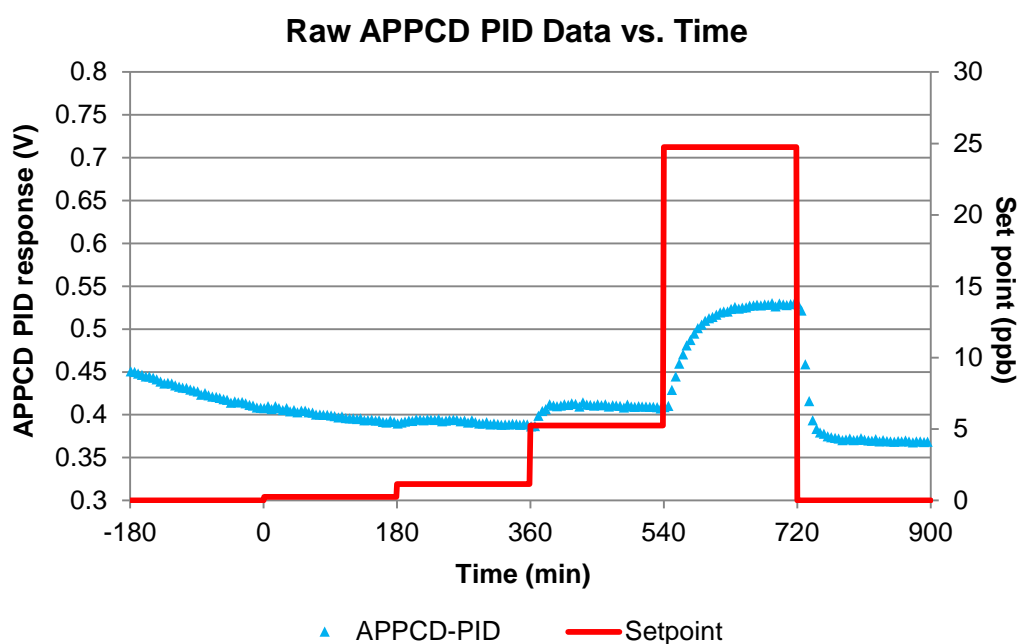


Figure 3.2.4-1. APPCD PID response over time during the benzene test on April 23, 2014

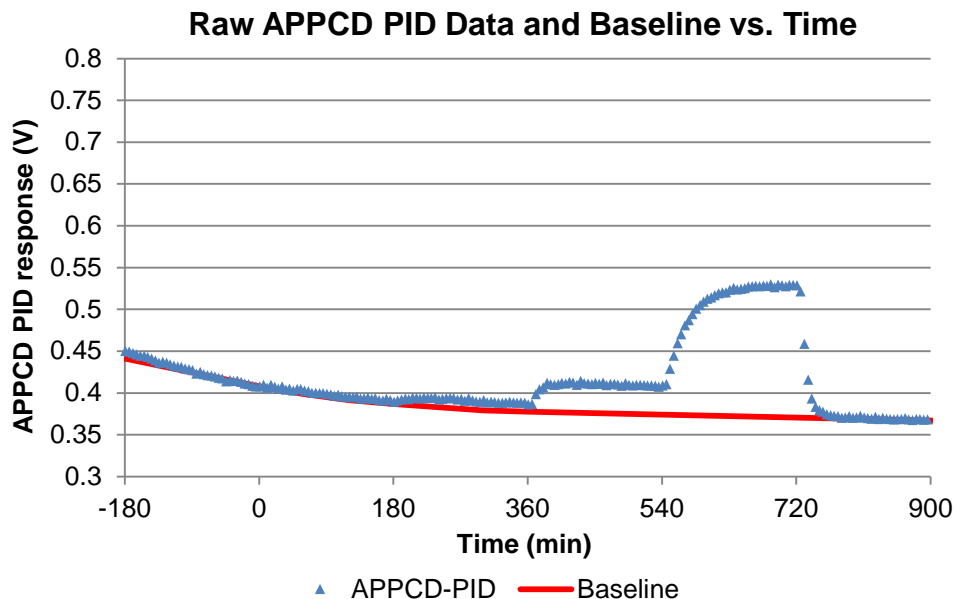


Figure 3.2.4-2. APPCD PID response over time during the three-component mixture test on April 22, 2014

Figures 3.2.4-3 and 3.2.4-4 show the results of this baseline correction. The baseline was subtracted from the APPCD PID raw data and graphed over time. Figure 3.2.4-3 compares the corrected APPCD PID response with set point. The results are nearly parallel with the set point. Figure 3.2.4-4 compares the corrected APPCD PID response with GC-FID measurements. The GC-FID response was converted from area counts to concentration using the benzene response factor and offset in Table 3-1.

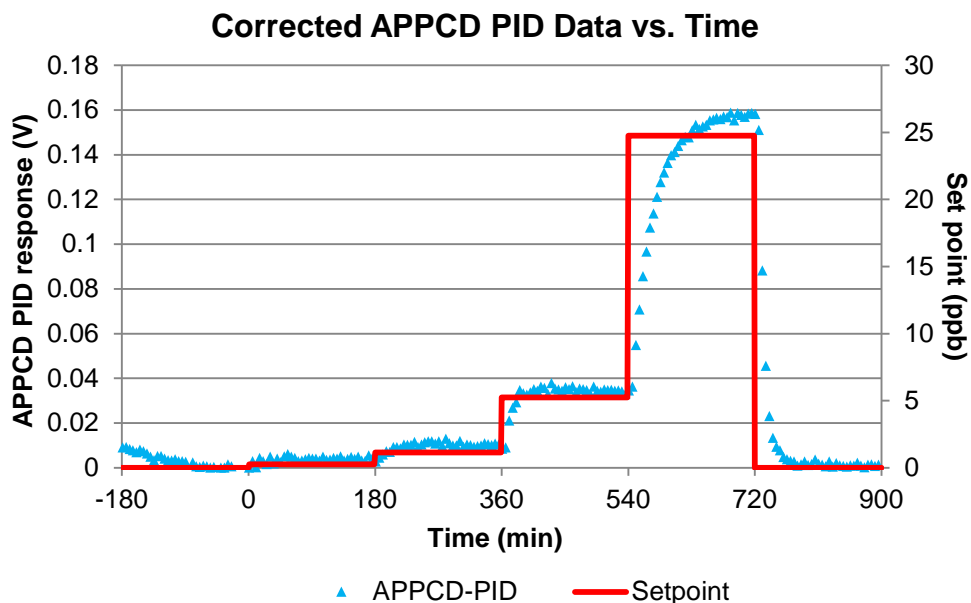


Figure 3.2.4-3. APPCD PID response over time after baseline subtraction

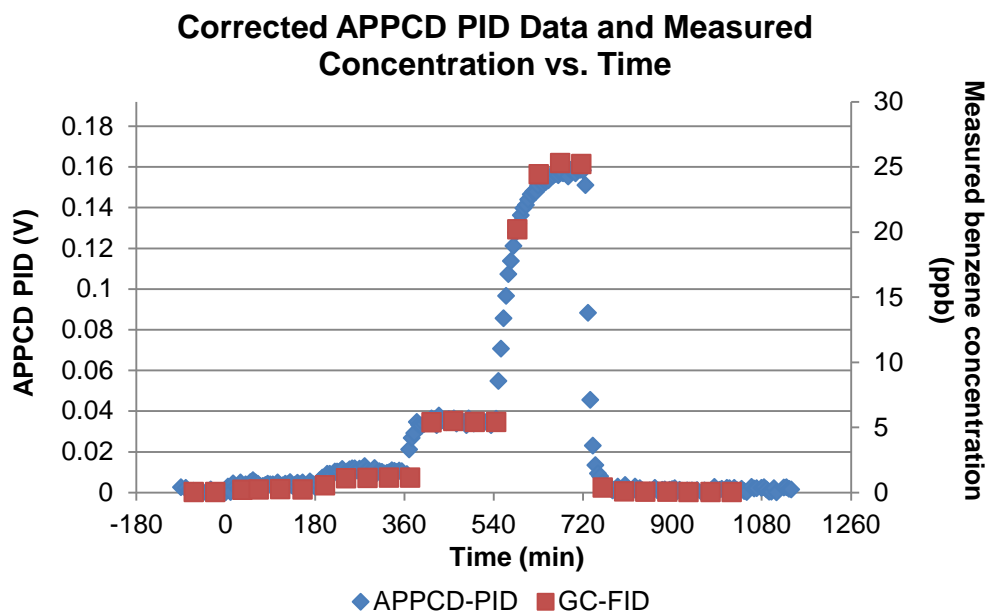


Figure 3.2.4-4. APPCD-PID response over time after baseline subtraction

The corrected APPCD PID data are shown below versus concentration set point (Figure 3.2.4-5) and GC-FID response (Figure 3.2.4-6). The GC-FID response in Figure 3.2.4-6 was converted from area counts to concentration using the benzene response factor and offset in Table 3-1. These two figures have nearly identical slopes and intercepts.

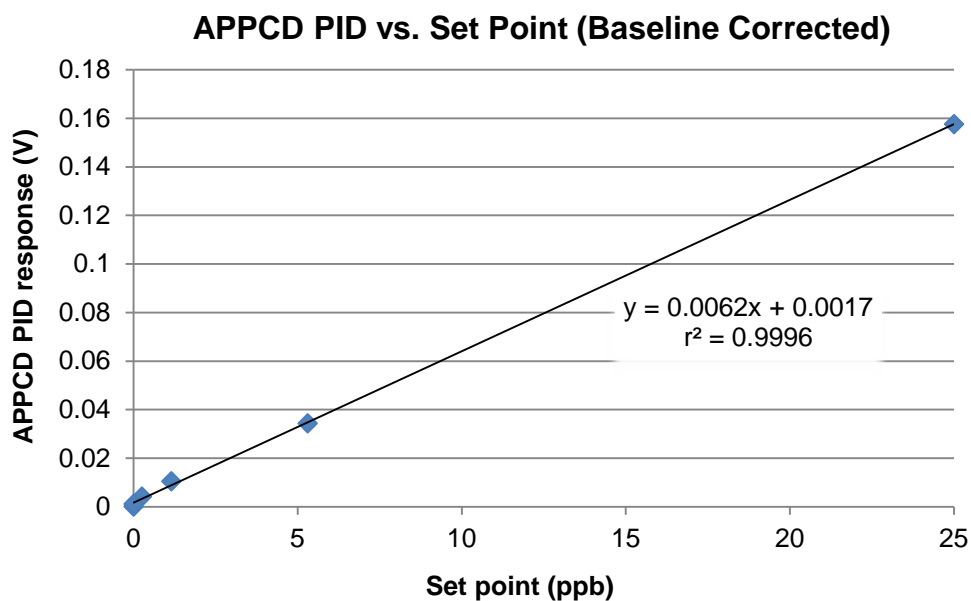


Figure 3.2.4-5. APPCD PID response vs. set point after baseline subtraction

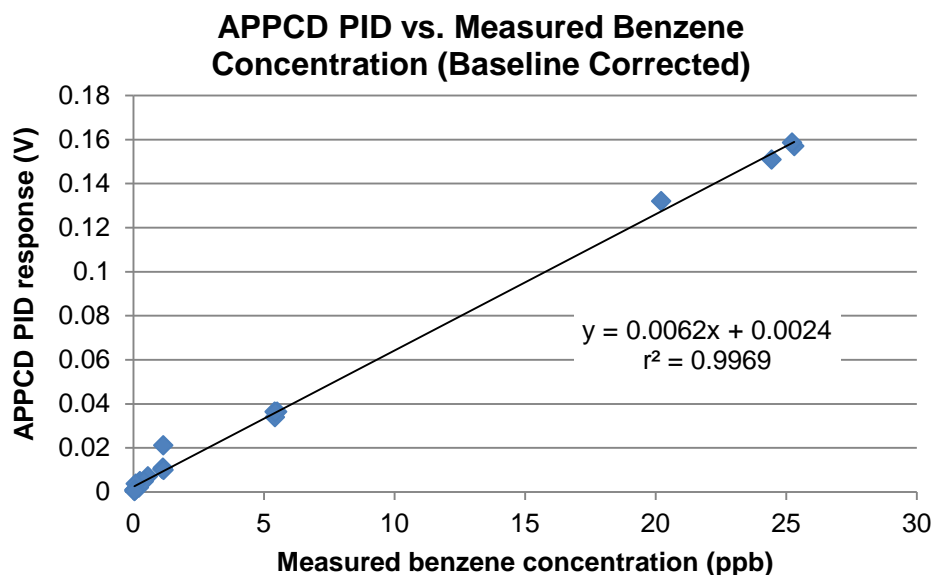


Figure 3.2.4-6. Baseline-corrected APPCD PID response vs. benzene concentration measured by the GC-FID. The response factor and offset listed in Table 3-1 were used to calculate concentration from area counts

While this process yields a very tight best-fit line, the level of effort required might not be suitable for field operators. Therefore, uncompensated data were examined. Uncompensated data consisted of the last 5-min average per set point with no further modifications, as shown in Figure 3.2.4-7 for the test on April 22, 2014. A very strong coefficient of determination ($r^2 = 0.9385$) is seen, and all variability appears to be restricted to the extreme low end of the concentrations used.

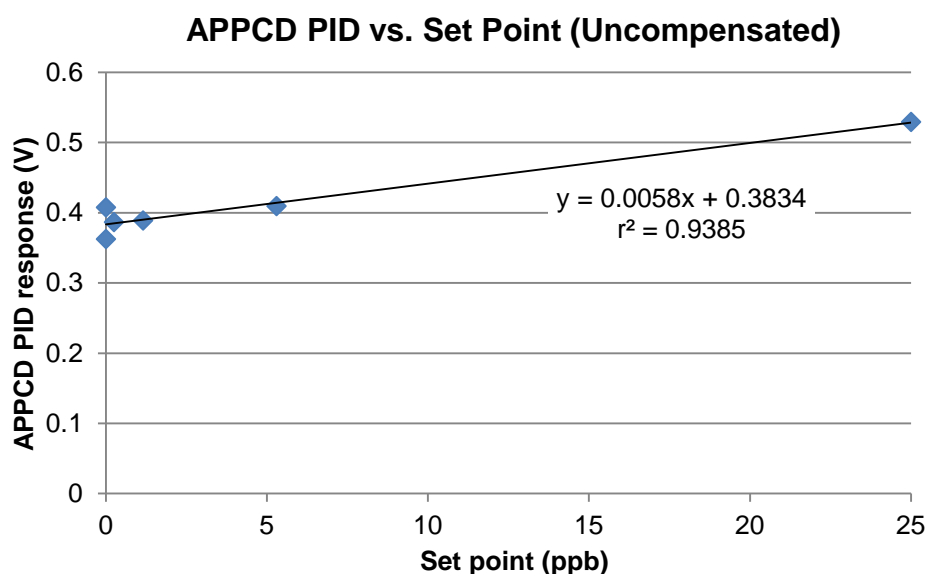


Figure 3.2.4-7. APPCD PID raw data vs. set point for three-component mixture test on April 22, 2014

Figure 3.2.4-8 shows data for all tests graphed together. The ratio of the slopes for the three-component tests and the benzene-only tests is 2.73:1. This is slightly less than the ratio of total VOC concentration in the three-component test to the benzene concentration in the benzene-only tests (3.05:1). This suggests that the APPCD PID is slightly less sensitive to 1,3-butadiene and/or tetrachloroethylene than it is to benzene.

Figures 3.2.4-9 and 3.2.4-10 show the response factors and offsets, respectively, of all tests by date so that any trends over time can be determined. It can be seen from these graphs that the offsets are falling steadily for all eight days of testing for reasons that are as of yet unknown. The slopes appear to hold steady throughout testing, however.

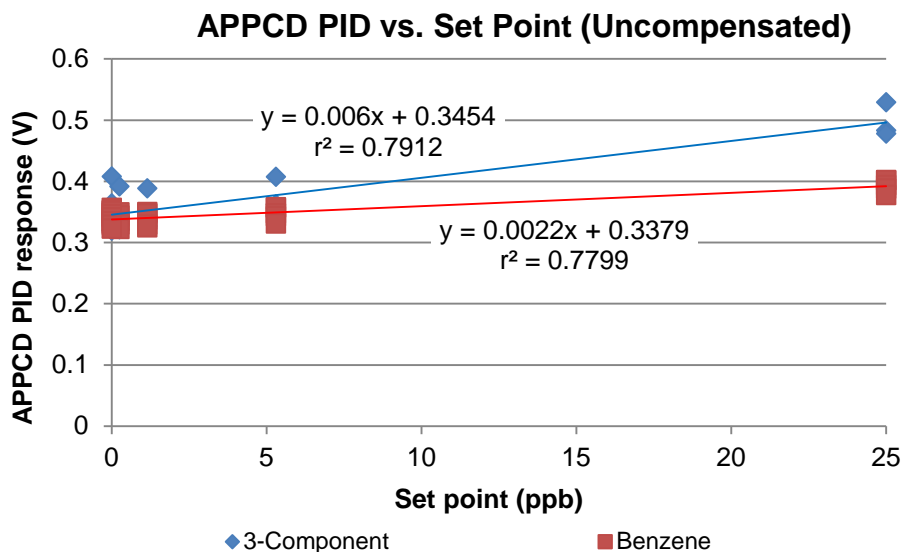


Figure 3.2.4-8. Raw APPCD PID data vs. set point for all tests

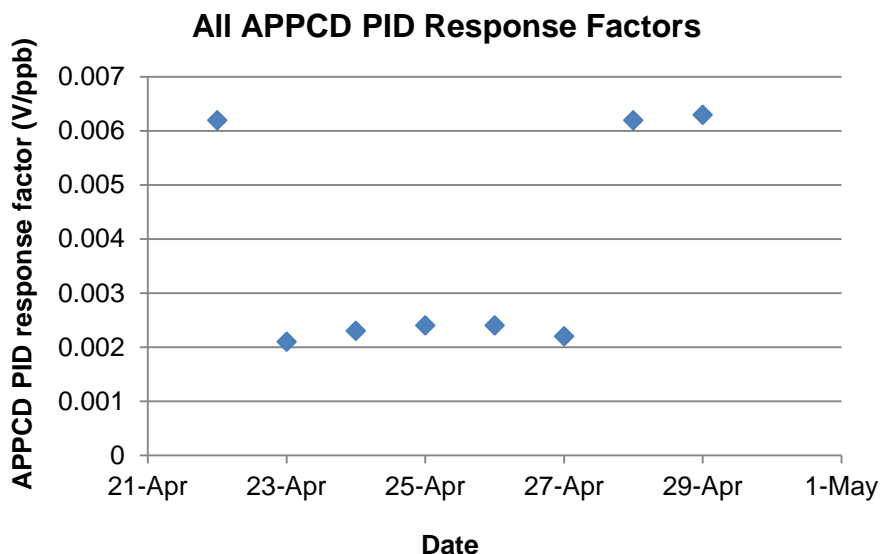


Figure 3.2.4-9. All response factors for APPCD PID tests vs. date. The higher response factors on April 22, 28, and 29 correspond to three-component mixture tests

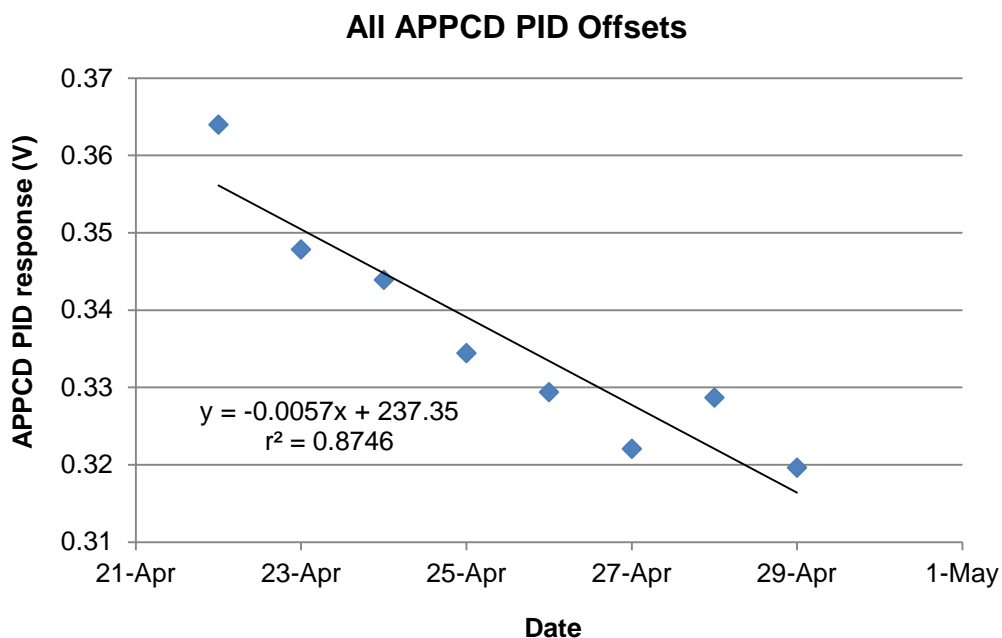


Figure 3.2.4-10. All offsets for APPCD PID tests vs. date, demonstrating a downward trend over time

Table 3-3 was populated from the following sources: Response factors, offsets, and r^2 derived from Figure 3.2.4-8. RSDs were found by taking the standard deviation of all last 5-min averages at each set point across all tests and dividing it by the average of that same set.

Table 3-3. APPCD PID Summary

	Single-Component Benzene	Three-Component Benzene
r^2	0.7799	0.7912
Response factor (V / ppb)	0.0022	0.0060
Offset (V)	0.3379	0.3454
RSD at 25 ppb	2.6%	5.7%
RSD at 5.3 ppb	3.2%	7.5%
RSD at 1.15 ppb	3.2%	9.6%
RSD at 0.25 ppb	3.2%	11.2%
RSD at zero air	3.3%	9.6%

The decay of APPCD PID offsets shown in Figure 3.2.4-10 and the comparison between baseline-corrected and uncompensated data (Figures 3.2.4-5 and 3.2.4-7) suggest that imprecision in the APPCD PID is a result of signal decay over time. Post study discussions with the APPCD research team indicates that the sensor element used in the device had revealed drift characteristics in their separate evaluations, thus confirming our data conclusions. The RSD data in Table 3-3 support this because the three-component data has much greater variability than the single-component data taken over five consecutive days. The gap between data points for the three-component tests allowed for a significant amount of decay to the offsets, which in turn resulted in greatly increased variability in the data set. The nature of this decay requires further study. It is possible that it is the result of a prolonged equilibration period of the APPCD PID while adjusting to an environment that has lower total VOCs than ambient conditions. The steady, approximately 3% RSD at all single-component concentration set points suggests that the APPCD PID had no problems with limit of detection during testing.

3.2.5 *ToxiRAE Pro*

The ToxiRAE Pro PID sensor has a lower limit of detection at 0.1 ppm total VOCs. This is not necessarily a technical limitation of the sensor itself, but rather a software-defined limit on what the ToxiRAE Pro PID can display and record. The sensor was exposed to eight challenges at the various concentrations and yielded a 0 response to each. Because test concentrations were limited to ≤ 25 ppb to reduce the possibility of carryover effect when trace-level analysis resumed for other chamber projects, it was expected that the ToxiRAE Pro would not respond to total VOC concentration even at our highest set point of 25 ppb.

4.0 VOC Field Evaluation Results and Discussion

Four of the five sensors under evaluation—UniTec SENS-IT, AirBase CanarIT, APPCD PID, and ToxiRAE Pro—were placed at the Triple Oaks sampling site for approximately two months during the summer of 2014. The CairPol CairClip, which was tested initially in the laboratory, experienced mechanical problems and was unable to be deployed in the field, and resource constraints prevented acquiring a replacement unit.

4.1 Field Evaluation Reference Data

The GC-FID operated by NRMRL at the Triple Oaks site, which was to be used as a reference instrument, failed to produce viable data. Research staff were unaware that the GC reference data provided by NRMRL was not viable until late in the data-processing stage. As such, all data had already been organized to match the 30-min averaged data acquired by the GC, even though no GC data are presented in this report. As such, all sensors are compared with each other, meteorological data (provided by NRMRL), and time of day.

Correlations with time of day were examined to determine if the sensors showed daily patterns of behavior that might correspond with local conditions. All data for a given hour across all days of the field study were averaged in order to identify any daily cyclic trends.

4.2 Field Evaluation Results

4.2.1 UniTec SENS-IT

Figure 4.2.1-1 shows the UniTec SENS-IT data over the course of the study. The x-axis major unit labels are all at midnight of the date shown. The data show variation both over the course of the day and across days. This suggests that it is measuring actual pollutants.

In Figure 4.2.1-2, the SENS-IT data were split into blocks based on the hour the data were acquired. The SENS-IT response appears to dip to its minimum value at 04:00 and peak at 10:00. It dips slightly before holding an intermediate value from 13:00 to 24:00. The cause of this pattern is currently unknown and cannot be determined without reference GC data and further investigation.

Figures 4.2.1-3 through 4.2.1-5 compare the APPCD PID with the other sensors in the study. The only correlation is a very strong one ($r^2 = 0.57$) with the ToxiRAE Pro.

Figures 4.2.1-6 and 4.2.1-7 compare the SENS-IT to temperature and RH, respectively. Only a slight correlation is observed with temperature ($r^2 = 0.1$) and none with RH.

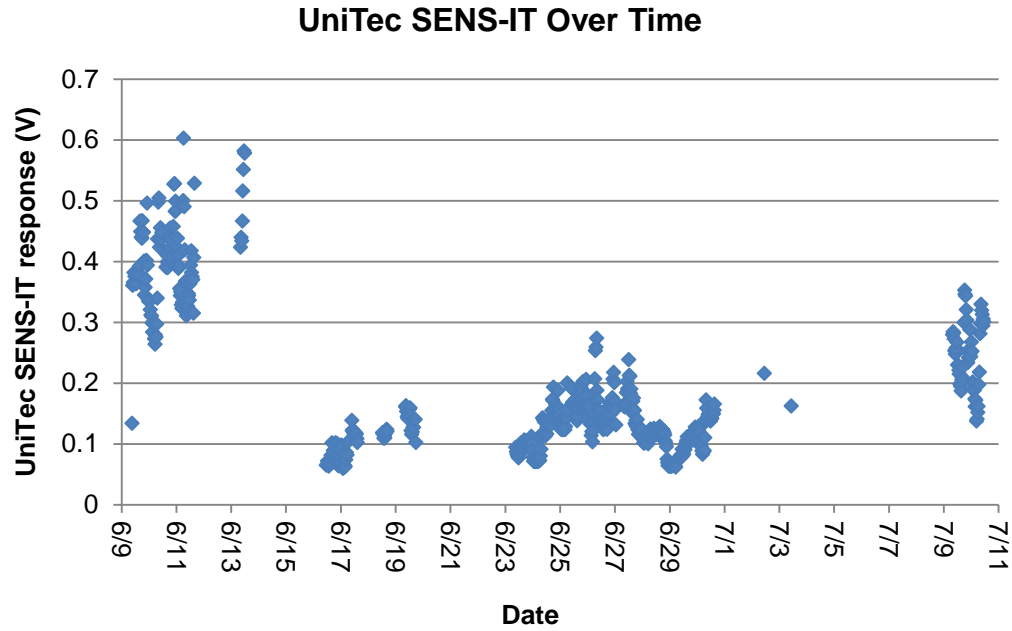


Figure 4.2.1-1. UniTec SENS-IT field data over time

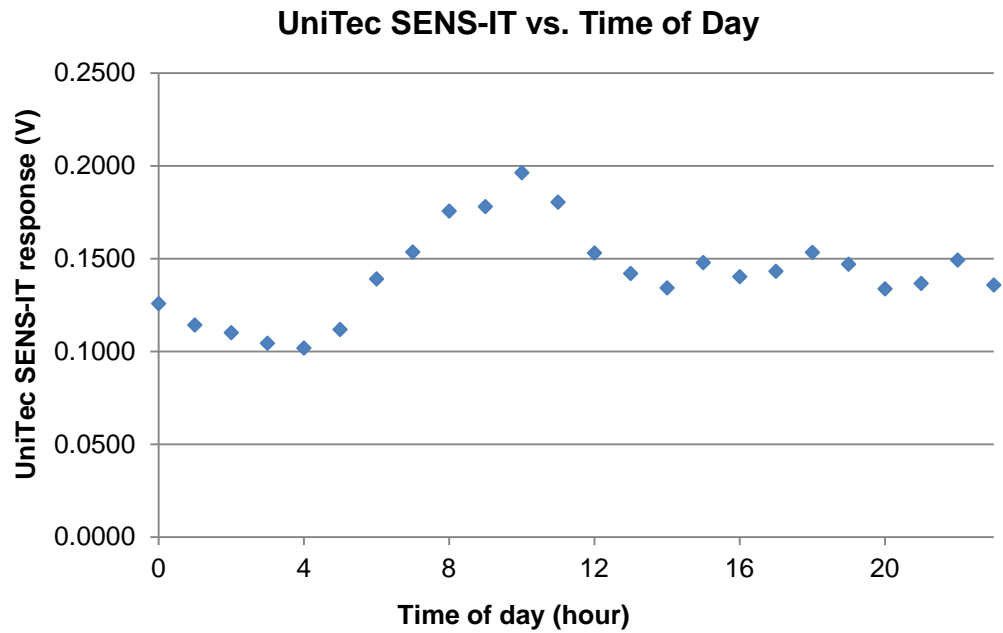


Figure 4.2.1-2. UniTec SENS-IT vs. time of day

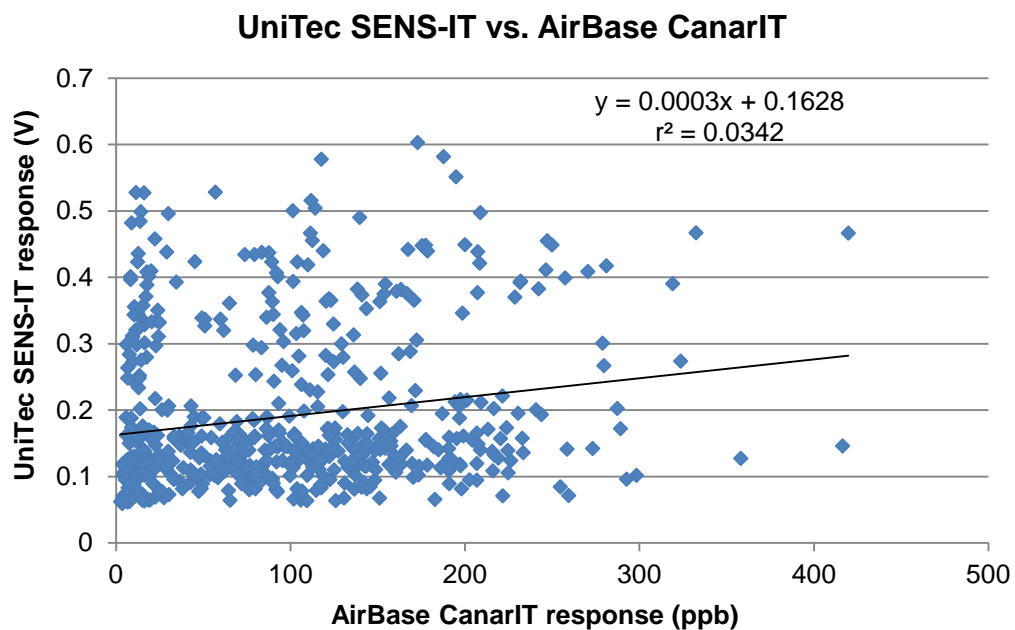


Figure 4.2.1-3. UniTec SENS-IT vs. AirBase CanarIT

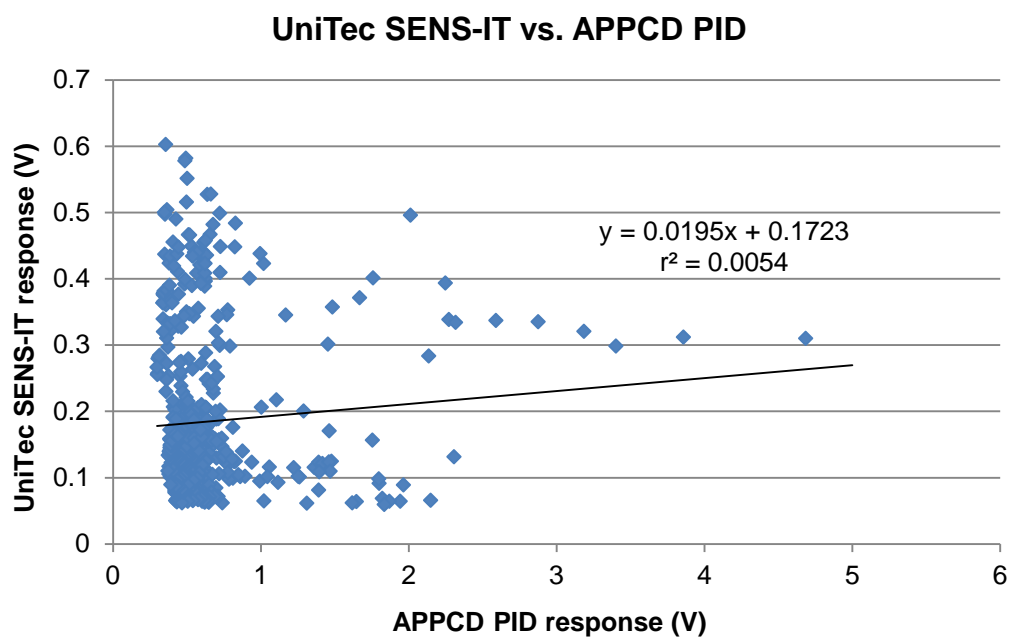


Figure 4.2.1-4. UniTec SENS-IT vs. APPCD PID

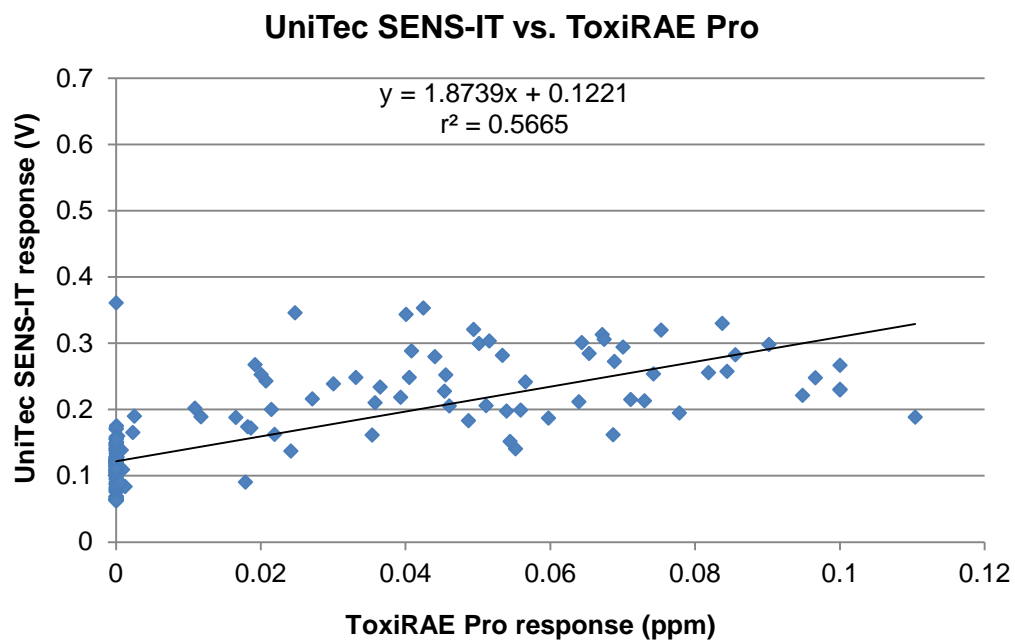


Figure 4.2.1-5. UniTec SENS-IT vs. ToxiRAE Pro

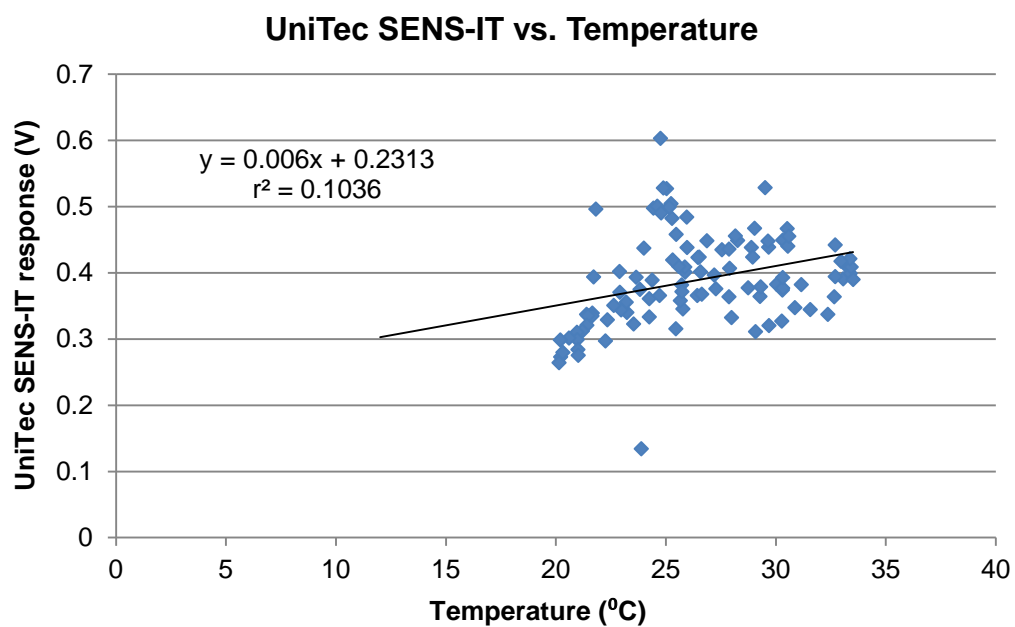


Figure 4.2.1-6. UniTec SENS-IT vs. temperature

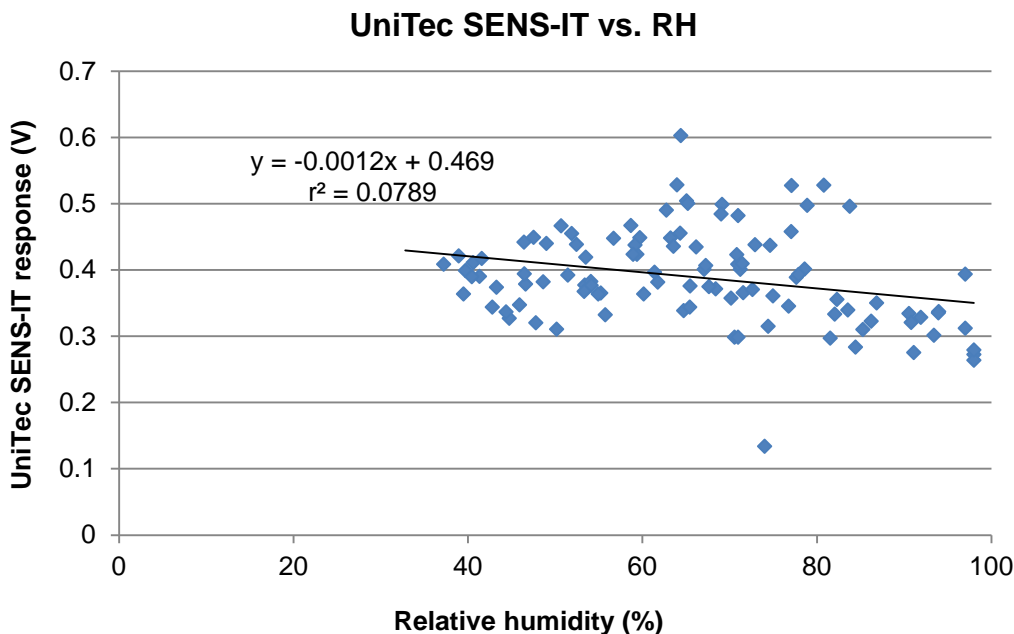


Figure 4.2.1-7. UniTec SENS-IT vs. RH

4.2.2 AirBase CanarIT

Figure 4.2.2-1 shows the AirBase CanarIT data over the course of the study. The data are very erratic with no observable pattern.

In Figure 4.2.2-2, data for the CanarIT have been split into blocks based on the hour the data were acquired. All data for a given hour were averaged in order to identify any daily cyclic trends. The concentrations begin rising at 06:00, peak at approximately 16:00, and return to baseline by 20:00. The cause of this pattern is currently unknown and cannot be determined without reference GC data and further investigation.

Figures 4.2.2-3 through 4.2.2-5 compare the AirBase CanarIT with the other sensors in the study. Only the ToxiRAE Pro shows any sort of correlation with the CanarIT. The correlation is low ($r^2 = 0.15$), however.

Figures 4.2.2-6 and 4.2.2-7 compare the AirBase CanarIT with temperature and RH as supplied by NRMRL, respectively, for which correlations ($r^2 = 0.37$ for temperature and $r^2 = 0.23$ for humidity) can be observed. It should be noted, however, that the reference temperature and humidity data were limited. Temperature might be related to the CanarIT response coincidentally since there is more traffic during the day. Still, a positive correlation with temperature might explain why the CanarIT reports a greater response for the evening commute than it does for the morning commute.

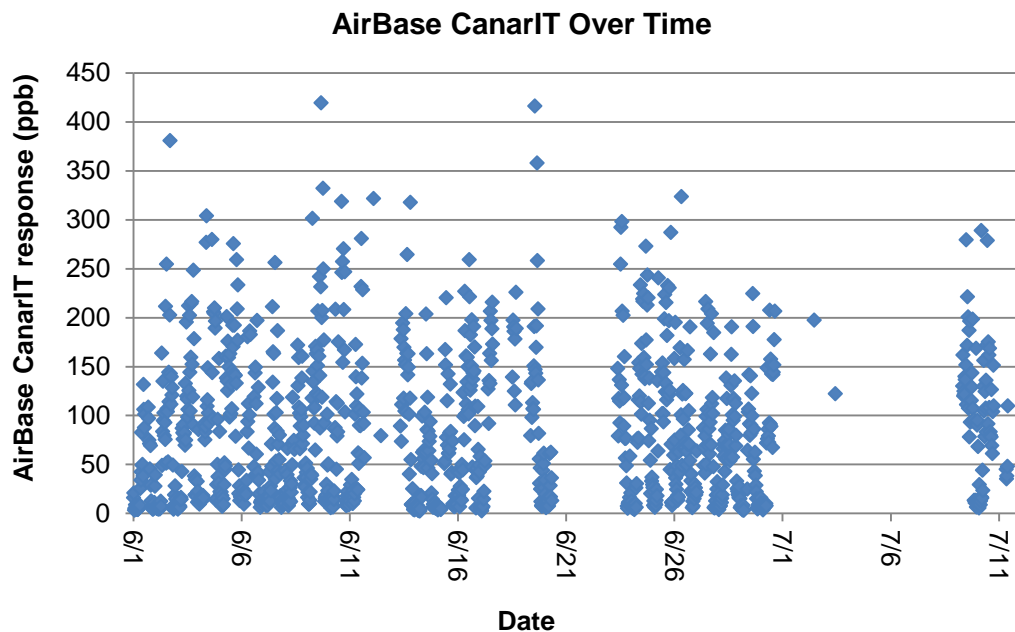


Figure 4.2.2-1. AirBase CanarIT field data over time

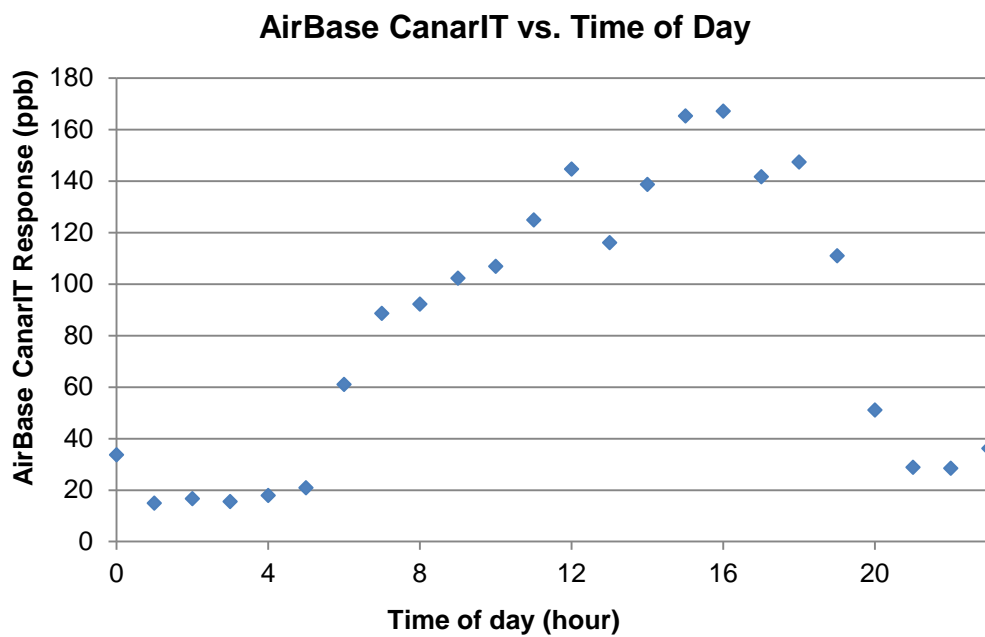


Figure 4.2.2-2. AirBase CanarIT vs. time of day

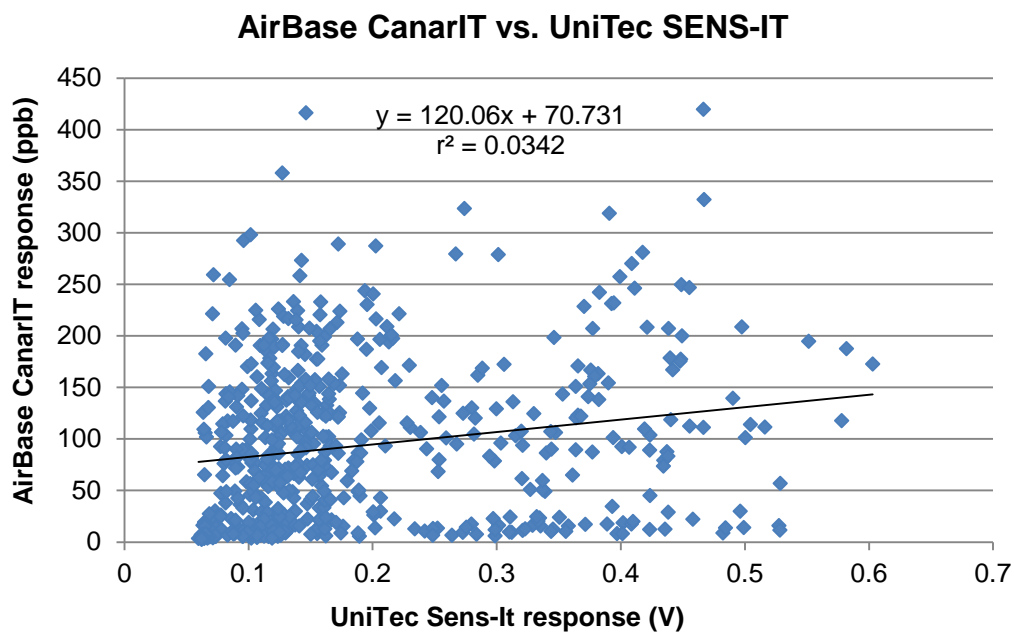


Figure 4.2.2-3. AirBase CanarIT vs. UniTec SENS-IT

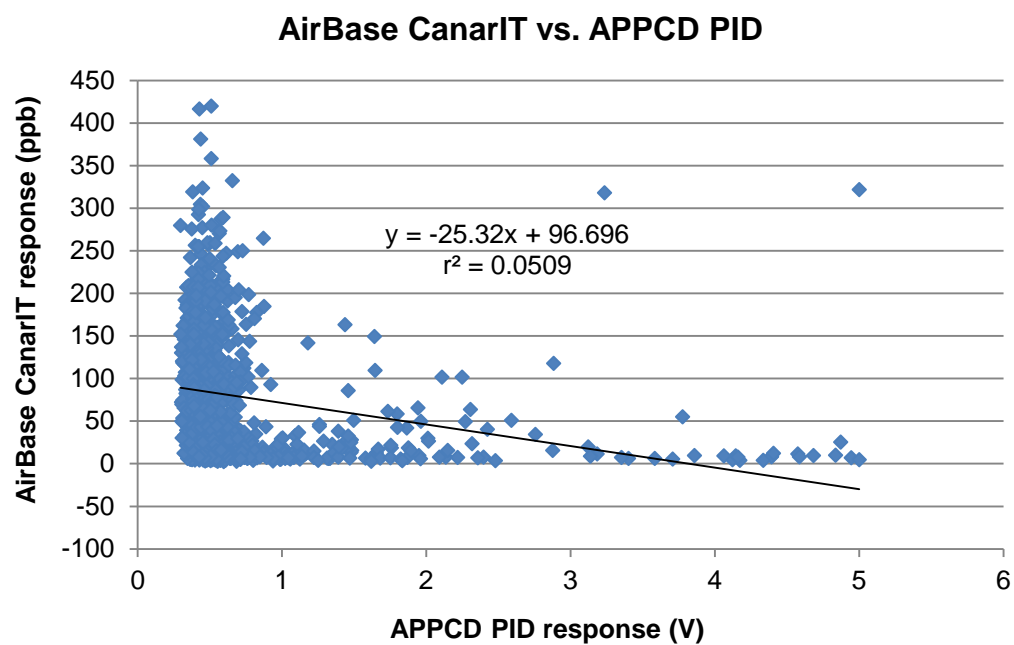


Figure 4.2.2-4. AirBase CanarIT vs. APPCD PID

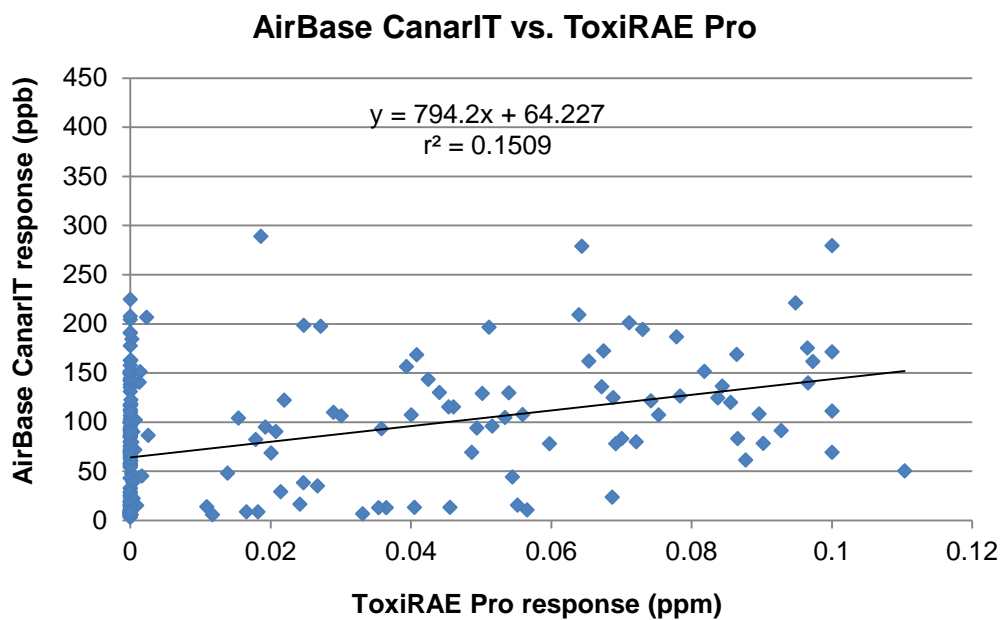


Figure 4.2.2-5. AirBase CanarIT vs. ToxiRAE Pro PID

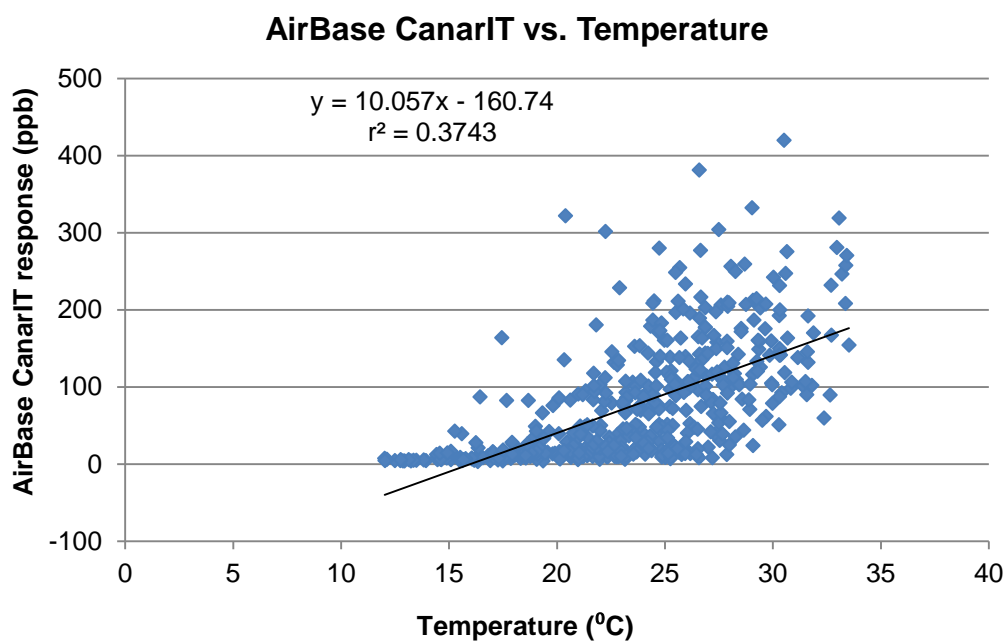
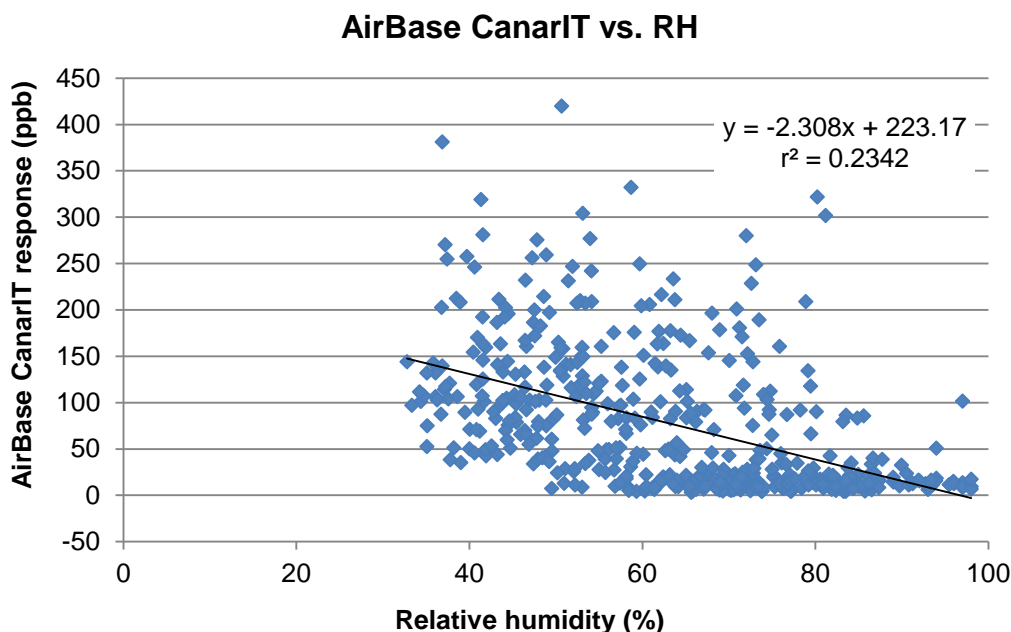


Figure 4.2.2-6. AirBase CanarIT vs. temperature



4.2.3 APPCD PID

Figure 4.2.3-1 shows the APPCD PID data over the course of the study. The data show a daily cycle of rising and falling. Approximately one-third of all days sampled showed a large spike in the data above 1.5 V.

In Figure 4.2.3-2, data for the APPCD PID have been split into blocks based on the hour the data were acquired. All data for a given hour were averaged in order to find any daily cyclic trends. Thus, the data point for 12:00 represents an average of all field data taken between 12:00 and 12:59. For the APPCD PID sensor, which measures data once per second, this is approximately 100,000 measurements in each block. The APPCD PID response peaks at approximately 07:00. The cause of this pattern is currently unknown and cannot be determined without reference GC data and further investigation.

Figures 4.2.3-3 through 4.2.3-5 compare the APPCD PID with the other sensors in the study. None of the other sensors show any correlation with the APPCD PID.

Figures 4.2.3-6 and 4.2.3-7 compare the APPCD PID with temperature and RH, respectively. Only a slight correlation is observed with RH ($r^2 = 0.12$).

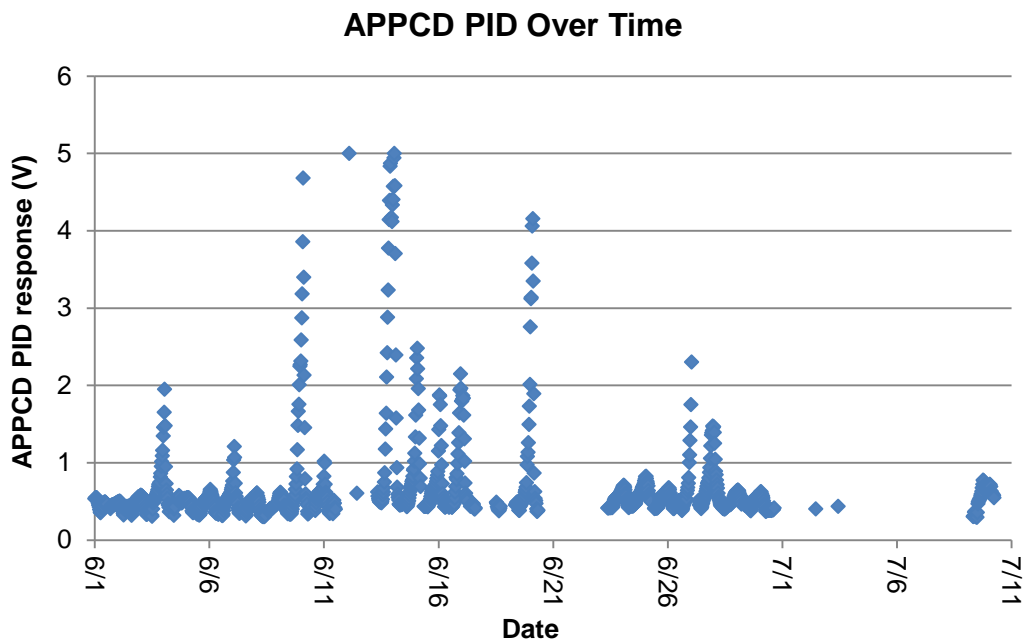


Figure 4.2.3-1. APPCD PID field data over time

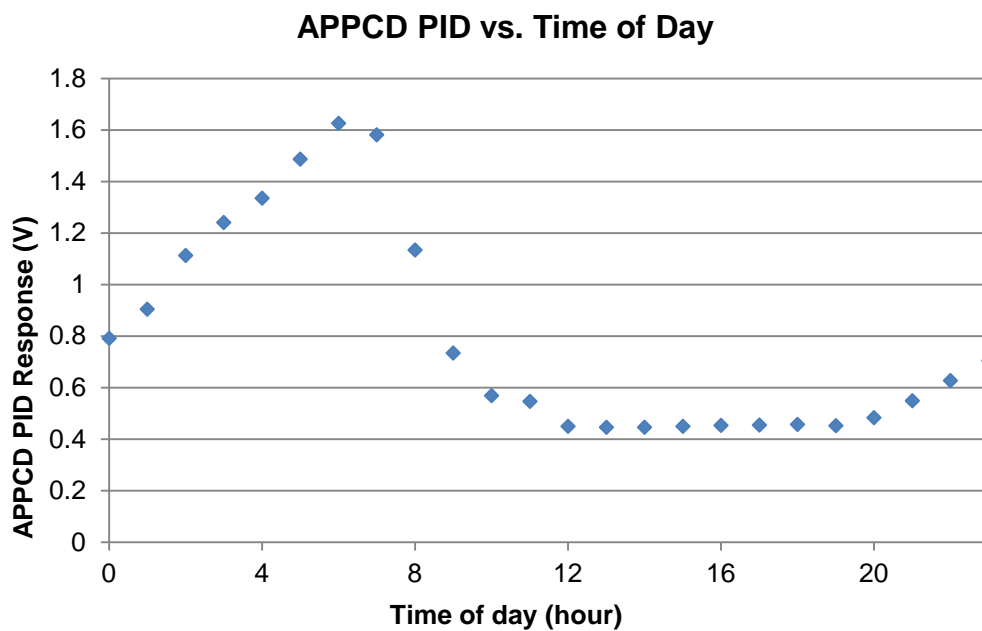


Figure 4.2.3-2. APPCD PID vs. time of day

APPCD PID vs. UniTec SENS-IT

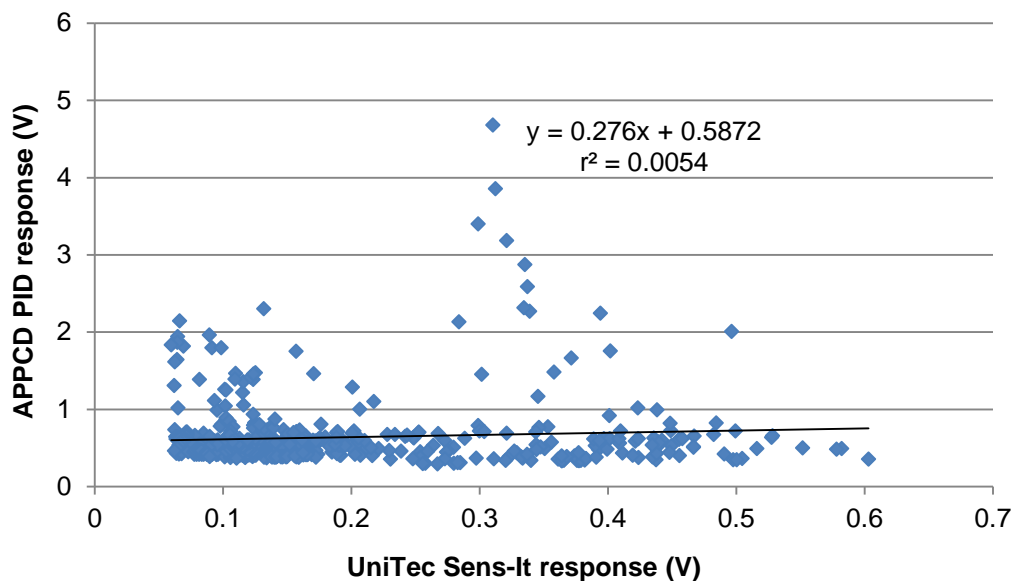


Figure 4.2.3-3 APPCD PID vs. UniTec SENS-IT

APPCD PID vs. AirBase CanarIT

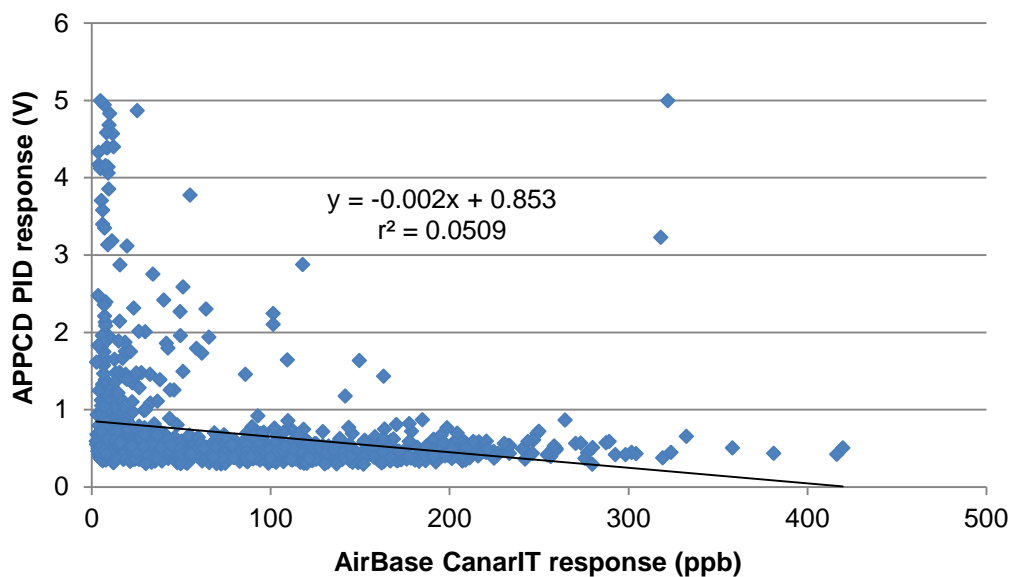


Figure 4.2.3-4. APPCD PID vs. AirBase CanarIT

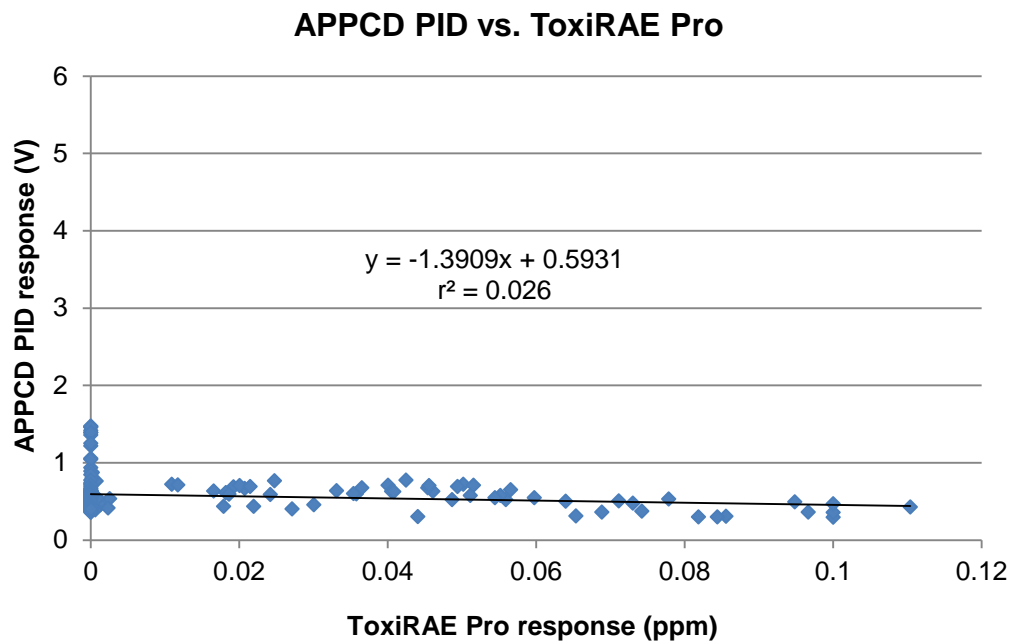


Figure 4.2.3-5. APPCD PID vs. ToxiRAE Pro

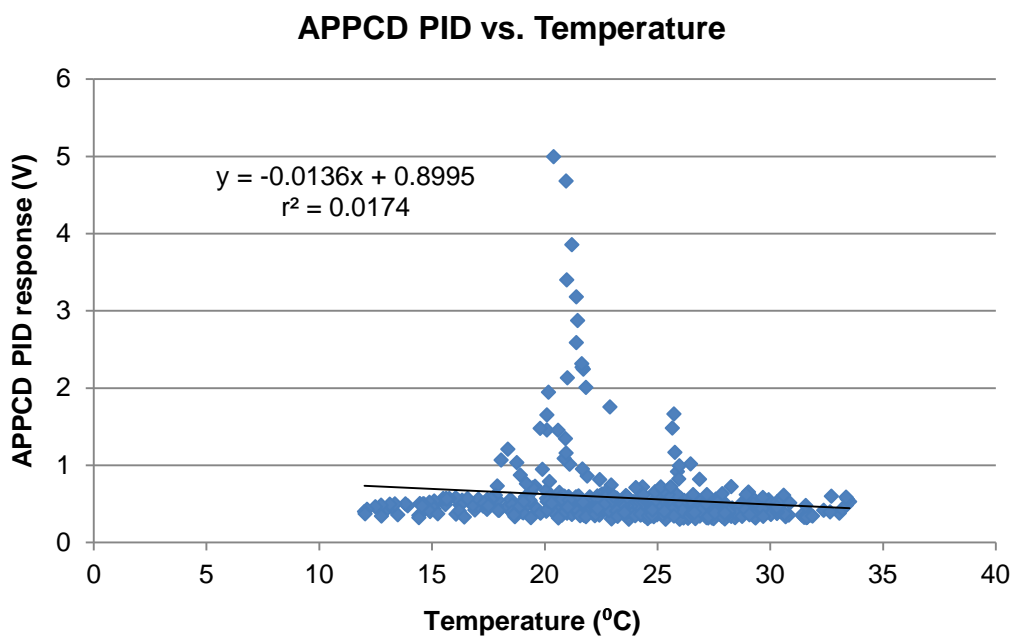


Figure 4.2.3-6. APPCD PID vs. temperature

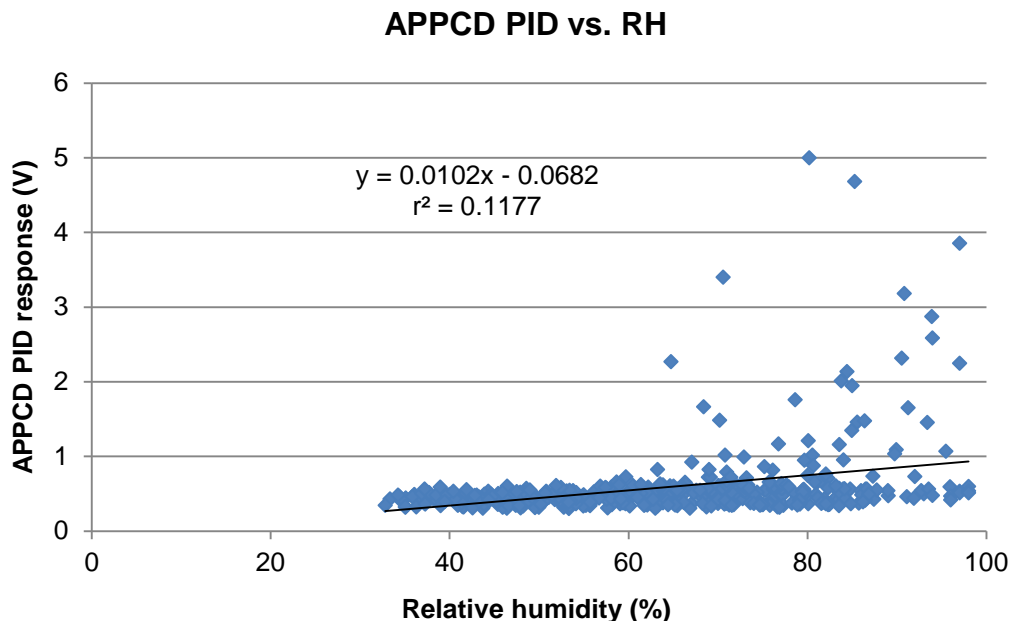


Figure 4.2.3-7. APPCD PID vs. RH

4.2.4 ToxiRAE Pro

Figure 4.2.4-1 shows the ToxiRAE Pro PID sensor data over the course of the study. Most of the data are less than 0.1 ppm, the reported limit of detection. This limit of detection is not the limit on the hardware, but rather a software limit for what the ToxiRAE is able to display and record. Data below this level are reported as 0.0. For this study, the data were compiled into 30-min averages. The values reported as less than 0.1 ppm are a result of averaging some data points at 0.0 and some at 0.1. For example, a value of 0.05 ppm might represent that half of the data taken in a 30-min average was approximately 0.1 ppm and the other half was less and therefore recorded as 0.

In Figure 4.2.4-2, data for the ToxiRAE Pro PID have been split into blocks based on the hour the data were acquired. All data for a given hour were averaged in order to identify any daily cyclic trends. Thus, the data point for 12:00 represents an average of all field data taken between 12:00 and 12:59. The ToxiRAE Pro data appear bell shaped with a peak at 12:00. The cause of this pattern is currently unknown and cannot be determined without reference GC data and further investigation.

Figures 4.2.4-3 through 4.2.4-5 compare the ToxiRAE Pro with the other sensors in the study. A slight correlation ($r^2 = 0.15$) is observed with the CanarIT. A much stronger correlation is seen between the ToxiRAE Pro and the SENS-IT ($r^2 = 0.57$), which suggests the two sensors have similar relative sensitivities to the VOCs present at the Triple Oaks sampling site.



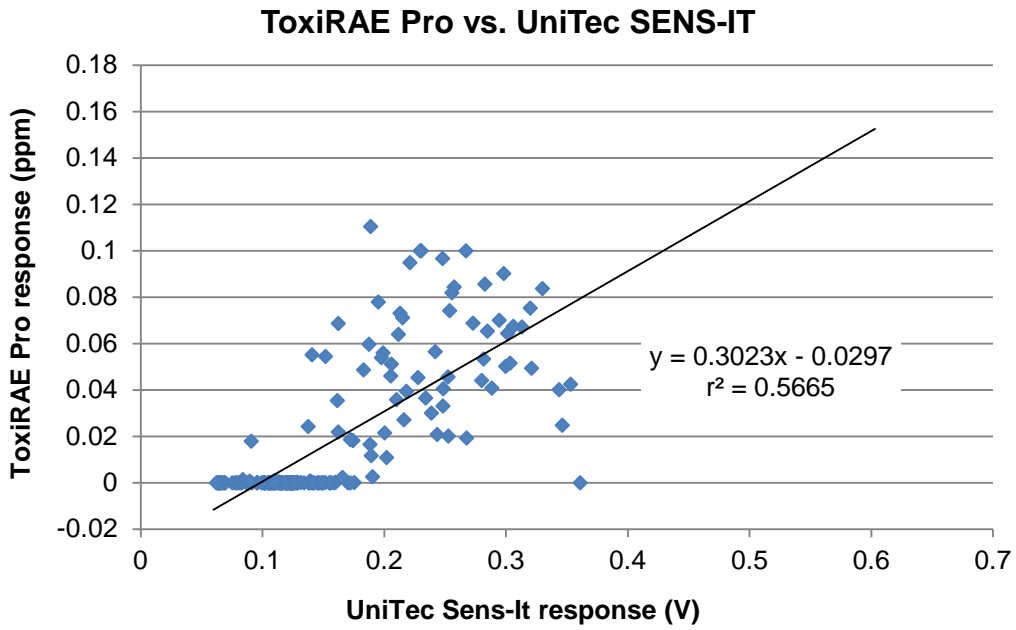


Figure 4.2.4-3. ToxiRAE Pro vs. UniTec SENS-IT

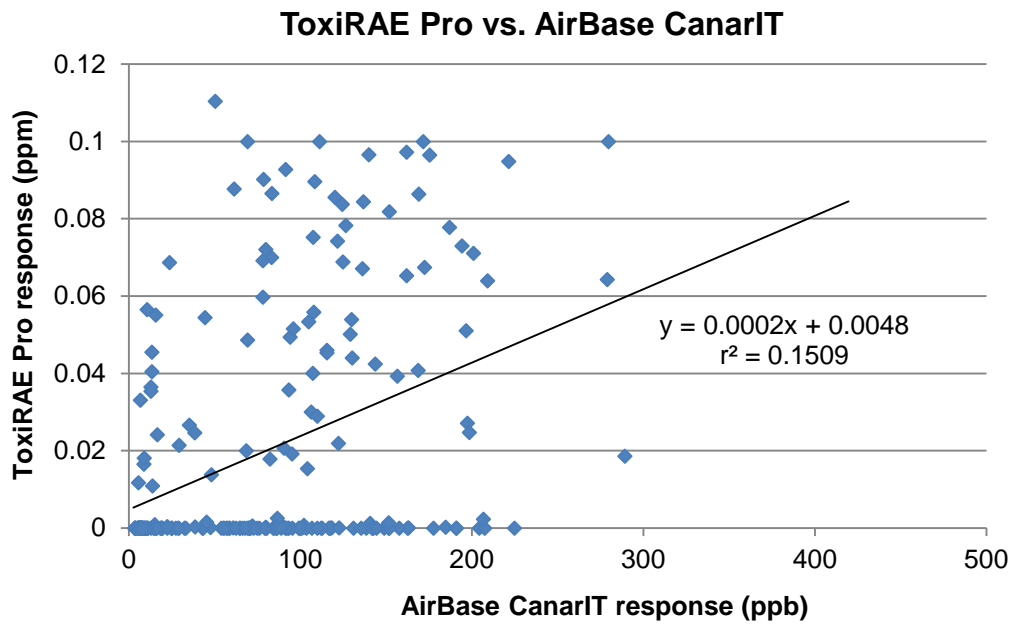


Figure 4.2.4-4. ToxiRAE Pro vs. AirBase CanarIT

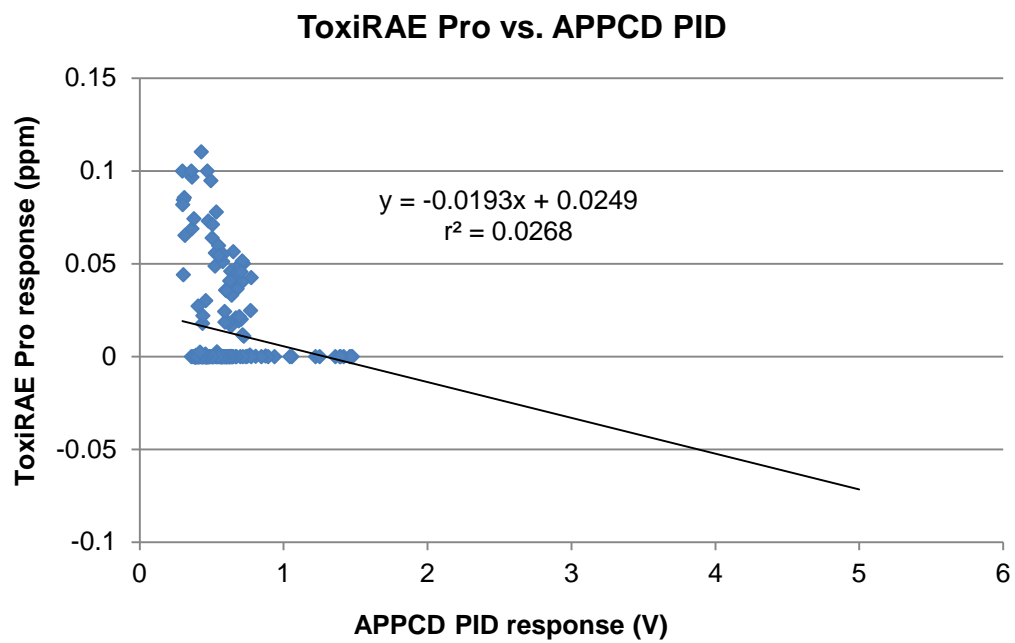


Figure 4.2.4-5. ToxiRAE Pro vs. APPCD PID

5.0 VOC Sensor Evaluation Summary

The performance of the VOC sensors tested in the laboratory is summarized in Table 5-1. The field evaluations are summarized in Table 5-2. Additionally, Figure 5-1 shows all total VOC sensors deployed in the field against time of day alongside one another. The terms used in the tables are as follows:

- Benzene r^2 : coefficient of determination; linearity of the sensor response for benzene only.
- Three-component r^2 : coefficient of determination; linearity of the sensor response for total VOCs in the three-component mix.
- RH: if a direct relationship exists between relative humidity and the sensor's signal, the r^2 of that relationship is displayed.
- Temperature: if a direct relationship exists between temperature and the sensor's signal, the r^2 of that relationship is displayed.
- Time resolution: the length of time between data points.
- Uptime: qualitative assessment by the operator about the frequency of data loss.
- Ease of installation: qualitative assessment by the operator about the level of effort required to bring the sensor to operational status in the field.
- Ease of operation: qualitative assessment by the operator about the level of effort required to operate the sensor, take data, and process the data.
- Mobility: qualitative assessment by the operator about the level of infrastructure required to operate the sensor in the field using the current operating procedure listed in Table 5-2. (Other procedures might have different requirements.)

Table 5-1. Summary of VOC Sensor Laboratory Performance

Sensor	Benzene r^2	Three-Component r^2	Benzene Response	Three-Component Response	Three-Component: Benzene Ratio
UniTec SENS-IT (V)	0.8973	0.9328	0.0081	0.0213	2.63
AirBase CanarIT (ppb)	NA	NA	NA	NA	NA
CairPol CairClip (ppb)	NA	NA	NA	NA	NA
APPCD PID (V)	0.7799	0.7912	0.0022	0.0060	2.73
ToxiRAE Pro (ppm)	NA	NA	NA	NA	NA

Table 5-2. Summary of VOC Sensor Field Performance

Sensor	Temp (°C)	RH (%)	UniTec SENS-IT (V)	AirBase CanarIT (ppb)	APPCD PID (V)	ToxiRAE Pro PID (ppm)	Time (s)	Uptime	Ease of install	Ease of use	Mobility
UniTec SENS-IT (V)	0.1036	0.0789	NA	0.0342	0.0054	0.5665	60	Poor	Poor	Very Good	Poor
AirBase CanarIT (ppb)	0.3743	0.2342	0.0342	NA	0.0509	0.1509	20	Excellent	Good	Excellent	Very good
APPCD PID (V)	0.0174	0.1177	0.0054	0.0509	NA	0.0268	1	Excellent	Poor	Good	Good
ToxiRAE Pro PID (ppm)	NA	NA	0.5665	0.1509	0.0268	NA	20	Fair	Good	Fair	Excellent

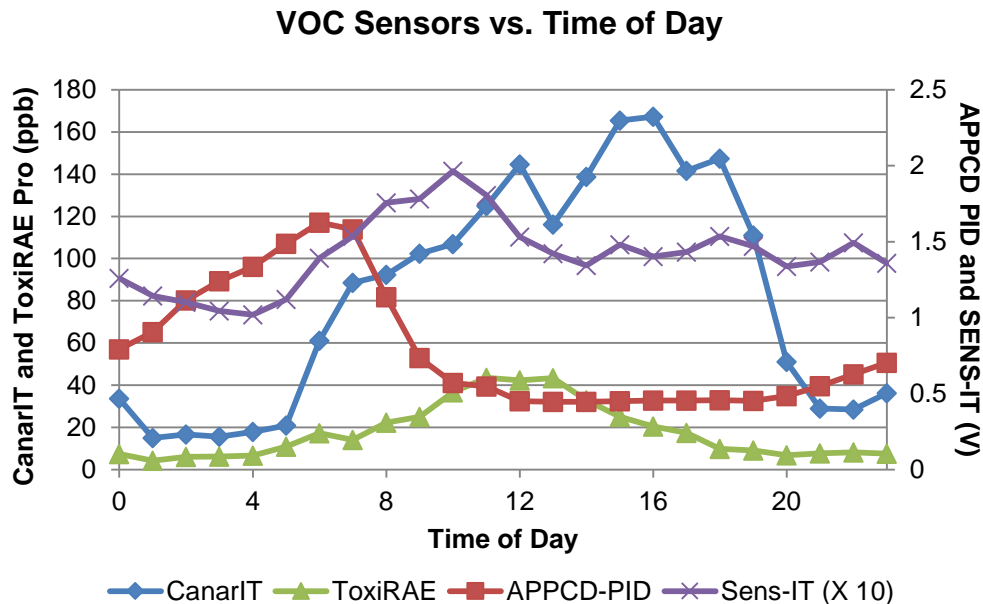


Figure 5-1. All total VOC sensors vs. time of day. Note that the UniTec SENS-IT data have all been multiplied by 10 to scale it to be more visible next to the other sensors

UniTec SENS-IT: The UniTec SENS-IT must be wired directly into power and a third-party data acquisition system, greatly reducing its mobility. This also necessarily increases the difficulty of initial setup. Data were recorded in tab-delimited 1-min averages for very simple processing. In the laboratory evaluations, there was evidence of both response to challenge and an 80-min cyclic signal. In the field evaluations, the SENS-IT was significantly correlated with the ToxiRAE Pro. This suggests the two sensors have similar sensitivity to the same mixture of VOCs.

AirBase CanarIT: Once the AirBase CanarIT has been set up, all it requires is power and the occasional reboot when it loses connection to the server. Even in the event connection is lost, the sensor continues recording and saving data for transmission once connection has been reestablished. In this round of testing the only interruption in field data collection was when a storm knocked out power to the sampling site. Upon restoration of power, the CanarIT automatically resumed taking data without incident. The requirement that it be furnished with a GSM SIM card and data plan adds a recurring expense to operations.

In laboratory testing the CanarIT data included the cyclic signal displayed by the SENS-IT but to a greater degree. This cyclic signal completely overwhelmed the response to challenges. In the field, the CanarIT showed some significant correlations with temperature and humidity and a minor correlation with the ToxiRAE Pro. The daily cyclic patterns to the field data do imply that the CanarIT was responding to real phenomena present at Triple Oaks. The CanarIT correlated most closely with the ToxiRAE Pro than with the other sensors.

CairPol CairClip: The CairPol CairClip NMVOC is light, portable, can run on battery power for 24 hours, and requires only a mini-USB connection for prolonged operation. However,

the unit tested in this study had apparent mechanical problems and no viable data could be gleaned from it.

APPCD PID: The installation of the APPCD PID sensor is hampered by the extremely large diameter of its cable and connector. Once installed, the device is robust and reliable. Data are transferred easily from the micro SD card in a usable format, but its 1-s time resolution leads to data files quickly becoming large and cumbersome. Because the data logger is not in any way weather shielded, care must be taken to protect it from water intrusion. This sensor also requires 110 V AC power. In this round of testing, the only interruption in field data collection was when a storm knocked out power to the sampling site. Upon restoration of power, the APPCD PID automatically resumed taking data without incident.

Laboratory testing demonstrated falling sensitivity over time as evidenced by decaying offsets on each subsequent day of testing. It is unknown if this is due to issues with the sensor itself. After compensating for the decreasing sensitivity, the linearity of the APPCD PID was extremely high at $r^2 = 0.9996$. Further research might be able to characterize, compensate for, or prevent this falling sensitivity, which would make the APPCD PID extremely precise. In the field, the only correlation with APPCD PID data was a minor ($r^2 = 0.1177$) correlation with RH. This suggests that the APPCD PID is sensitive to a different mixture of VOCs than the other sensors. The APPCD PID signal regularly peaked at approximately 07:00 each day. It is not currently known what this was indicating relative to its environment.

ToxiRAE Pro: Because the ToxiRAE was designed for industrial hygiene uses, its limit of detection and resolution are relatively high. It proved to be easy to install and simple to operate and can run for approximately 14 hours on a fully charged battery. It can also run continuously when plugged in to a power supply or outlet. Data are not well organized for processing or review of extended collection periods. The challenge conditions for laboratory trials were all below the limit of detection. In field testing, the ToxiRAE Pro correlated slightly with the AirBase CanarIT ($r^2 = 0.1509$). It had the strongest correlation in the entire study with the UniTec SENS-IT, suggesting that the ToxiRAE and the SENS-IT are both sensitive to the same mixture of VOCs.

The robustness of the sensor was less than expected based on previous testing. One difficulty with its operation was its tendency to slip out of the charging cradle, and frequent reseating of the sensor in the cradle caused the connection to break during the laboratory evaluation. The cradle had to be replaced. Later when being deployed for field trials, a fan error developed and the unit had to be sent for repair.

6.0 Study Limitations

6.1 Resource Limitations

It must be recognized and clearly stated that a variety of resource limitations influenced both the depth and overall dimension of the work performed and ultimately its conclusion. The findings of this report were limited to resources available to obtain NGAM VOC sensor technology and perform the necessary evaluation, especially that involving laboratory-based chamber efforts which incur greater overall research expense. To the greatest extent possible, attempts were made to leverage this effort with other ongoing ORD activities. This including the evaluation of the APPCD PID and use of an active VOC analysis system that was not designed specifically for this effort. Therefore, study staff had inherent limitations on both the availability of equipment and some of the operating parameters that had to be observed.

6.1.1 *Intra-sensor Performance Characteristics*

With the exception of the UniTec device, no replicate analyses to determine intra-sensor precision was possible. Resource limitations prevented direct purchase of replicates as well as the fact that such efforts were beyond the ability of the resources in conducting the more costly laboratory evaluations. Therefore it should be recognized that these data represent a snap shot of potential performance characteristics of the devices evaluated and are not to be considered definitive.

6.1.2 *Test Conditions*

The test conditions were limited in both their scope and depth. As examples, we limited the range of testing to cover only the 0 to 25 ppb range. This was due to the fact we believe such a range to be generally reflective of urban concentrations of relevance for target pollutants like benzene. Of course, there could be industrial and even other hot spot situations where VOC concentrations in the ppm range might be evident and where some of the devices evaluated here might have shown more potential. We also limited laboratory testing to a narrow range of both temperature and relative humidity (~ room temperature) because resources were not available to fully examine the wide range of environmental conditions that might be possible. It was planned that the collocated field tests would provide some benefit in investigating RH and temperature impact upon sensor performance but as stated elsewhere, ultimately reference data were not available as originally planned.

6.1.3 *Sensor Make and Models*

The findings reported here are limited to a very narrow window of NGAM VOC devices. Only a total of five (5) devices were obtained as these appeared to cover a range of some of the most commercially available types of products associated with the low cost tier (<\$2500). While literature review indicated that some of the more exotic devices such as those involving advanced nanotechnologies might be more prevalent, market review did not support that being

the case. PID technology still appears to be the primary sensor element of choice for this component of the market and with some of the same inherent benefits/limitations that PID technologies can provide. The benefits include the PID ability to respond to a wide variety of VOCs but simultaneously offering a lack of specificity.

7.0 Research Operating Procedures and Related Quality Assurance Documents

1. Alion Science and Technology (Alion). 2013. Quality Assurance Project Plan: PM and VOC Sensor Evaluation, QAPP-RM-13-01(1), November 14, 2013. Research Triangle Park, NC.
2. U.S. Environmental Protection Agency (EPA). July 2013. Quality Assurance Project Plan: Raleigh Multi-Pollutant Near-Road Site: Measuring the Impact of Local Traffic on Air Quality. Research Triangle Park, NC.
3. EMAB-153.0. 2013. Research Operating Procedure for the UniTec SENS-IT Air Sensor.
4. EMAB-154.0. 2013. Research Operating Procedure for the APPCD PID Sensor.
5. EMAB-155.0. 2013. Research Operating Procedure for the ToxiRAE Pro PID Sensor.
6. EMAB-156.0. 2013. Research Operating Procedure for the CairPol CairClip NM-VOC Air Sensor.
7. EMAB-161.0. 2013. Research Operating Procedure for the AirBase CanarIT PM and VOC Sensor.