Methane Detectors Challenge

PHASE 1 TESTING REPORT

Revision 1

SwRI[®] Project No. 18.19910

Prepared for:

Environmental Defense Fund 1875 Connecticut Avenue N.W. Washington, D.C. 20009

December 9, 2014



SOUTHWEST RESEARCH INSTITUTE®

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EXECUTIVE SUMMARY

The Methane Detectors Challenge was initiated to expedite development and commercialization of low-cost methane detection technologies for applications in the oil and natural gas industries. The focus of the Challenge is to improve the speed and cut the costs associated with methane detection and monitoring. The initial applications are expected to be unmanned natural gas facilities, such as well pads and compressor stations. The Challenge commenced with laboratory testing ("Phase 1") of several sensors and will later expand to system testing and then pilot evaluation of selected technologies. The first step of this process was to perform controlled laboratory experiments of five technologies selected by The Environmental Defense Fund (EDF), participating oil and gas partners, and external technical advisors.

The technologies for the Phase 1 evaluation were a collection of methane detecting sensors from five different innovators selected by EDF and its partners. Some of these sensors were already integrated into stand-alone methane measurement systems, while others were sensors packaged with peripheral components for the purposes of this initial phase of testing.

A series of tests was performed in a controlled chamber to allow for the sensors to be evaluated against step changes in background methane levels. This testing was performed under a variety of environmental conditions. Testing was also performed in the presence of carbon monoxide, carbon dioxide, and ethane to determine if these gases would adversely affect sensor performance.

The purpose of this initial testing phase was to evaluate the various sensors against the technical conditions outlined in the Challenge's objectives and not to pick a "winner." Technology cost and other non-technical considerations were outside the scope of this testing. The primary metric for this testing is the ability to detect small changes in methane concentrations. Using that criterion, four of the five innovators met the testing objectives.

1. PROJECT BACKGROUND

1.1 Overview

The Methane Detectors Challenge was initiated to expedite development and commercialization of low-cost methane detection technologies. The intended application of the Challenge is to improve the speed and cut the costs associated with methane detection and monitoring from natural gas facilities, such as well pads and compressor stations, in order to reduce overall methane emissions. The Challenge commenced with laboratory testing ("Phase 1") of several sensors and will later expand to system testing and then pilot evaluation of selected technologies. The first step of this process was to perform controlled laboratory experiments of five technologies selected by EDF, participating oil and gas partners, and outside technical advisors. This document provides an overview of this testing.

1.2 Purpose

The purpose of this test was to investigate detection and operational limits of each sensor in a controlled environment as a means of establishing a performance baseline. The testing had two main points of emphasis:

- 1. To compare the performance of the sensors to the target specifications provided in the Challenge's Request for Proposal (RFP).
- 2. To contrast the various sensors to determine if future phases should concentrate on a down-selected subset of technologies most suitable for the intended application.

Although there is significant value in quantifying and characterizing methane leaks, it should be noted that the objective of the Methane Detectors Challenge was to evaluate the ability of a sensor to detect *that* an unintentional release or leak has occurred. From the Methane Detectors Challenge RFP:

The Challenge is not aimed at accurately quantifying methane flux rates. The Challenge is aimed at catalyzing commercial, low cost technology that can consistently detect leaks of methane over time and varying environmental conditions. The detection system is sometimes envisioned as akin to "a carbon monoxide alarm for methane." The ideal system will serve as a "smart" alarm, sending an alert to the operator when an increase in ambient methane is detected, one that reflects emissions beyond what would normally (be) expected to be seen and thus a high probability of a leak.

The results of this testing are provided to EDF and its assorted partners to use for vetting of the sensors for future phases of the Challenge.

1.3 Report Outline

This report is organized into several sections per the description in Table 1.1.

SECTION TITLE		CONTENTS
2	Innovator Technologies	Overview of each of the sensors that were used for testing.
3	Testing Overview	Description of the test setup and process.
4	Testing Results	Overview of the results from the sensor testing.
5	Summary	Testing conclusions and path forward.

	Table 1.1.	Report	Organization.
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2. INNOVATOR TECHNOLOGIES

2.1 Device Descriptions

The technologies tested were a collection of methane detecting sensors from five different innovators selected by EDF and its partners. Some of these sensors were already integrated into stand-alone methane measurement systems, while others were sensors packaged with peripheral components for the purposes of this initial phase of testing. The sensors tested were submitted by the following organizations:

- Dalian Actech
- Quanta3
- Oakland University
- SenseAir/Honeywell
- University of Colorado

The sensors submitted by each organization are briefly described and summarized in the following few sections.

2.1.1 Dalian Actech

The Dalian Actech device uses a tunable diode laser absorption spectroscopy (TDLAS) measurement technique to quantify methane concentration integrated over a path length in units such as ppm-meters. With knowledge of the laser's total path length, an absolute methane concentration can be directly calculated. In general, laser absorption-based measurement techniques measure the amount of laser light that is absorbed by the species of interest. The Dalian Actech device is open path, meaning it does not require a fan or pump to advect the methane-air mixture through the laser's path line. The system's laser path length is variable, ranging anywhere from 0.5 to three meters (the path was fixed at one meter for this testing). The tested prototype allowed for time-resolved measurements at 1 Hz over a range of one to 3,000 ppm-meters. Methane concentrations were provided by the Dalian software in ppmv, which is the average concentration over the sensor path length.

The tested prototype was calibrated once on site at SwRI by the engineers from Dalian Actech prior to testing. During calibration, the device was exposed to two equilibrium methane concentrations: ambient (approximately 2 ppmv) and 500 ppmv. The ambient concentration was used to "zero" the device, and the 500-ppmv concentration was chosen based on the range of concentrations that the device would be exposed to during testing. The calibration concentrations were manually entered into the Dalian software (at the time that the device was exposed to the concentrations), and the software performed the two-point calibration. It is important to note that any concentration could have been chosen for the second calibration point, and the accuracy of the device over a concentration range is dependent on the calibration points. Dalian Actech specifies that the device should be calibrated annually.

The Dalian software provided a real-time display of methane concentration as a function of time. The data logging rate, sensor path length, and laser settings could be adjusted manually within the software. The software was capable of writing data, including methane concentration, pressure, temperature, and absorption parameters, to a file at the rate (up to 1 Hz) specified by

the user. Figure 2.1 shows the Dalian Actech device. This system was powered using a peripheral power supply not shown below.



Figure 2.1. Dalian Actech System.

2.1.2 Quanta3

The Quanta3 is a sensor that also uses a laser absorption spectroscopy measurement technique. The laser path line is contained within the device's housing. As such, this system uses small fans to advect methane-air into the housing through the laser path line. The Quanta3 device also allows for time-resolved measurements at 1 Hz over a range of zero to 5,000 ppmv.

The device was calibrated prior to its arrival at SwRI, and it was not calibrated during the testing period. Quanta3 specifies that the instrument does not need to be calibrated frequently, but may require maintenance, such as the replacement of air filters. During testing, methane concentration measurements were gathered from the device display, which updated at a rate of 1 Hz. Data files were also stored on a USB drive inside of the device. Although the feature was not utilized during testing, data and the status of the instrument can be accessed wirelessly using handheld devices (tablet, smartphone, etc.). The Quanta3 device is shown in Figure 2.2. The device is approximately 17 in x 6 in x 6 in and requires a 110 VAC power connection.



Figure 2.2. Quanta3 Device.

2.1.3 Oakland University

The Oakland University system is comprised of a chemical sensor and signal generator/data acquisition combination analyzer unit. The analyzer applies a step function voltage excitation to the chemical sensor. This sensor outputs a current proportional to the methane concentration during the latter portion of the voltage excitation, while the analyzer measures this current output. A small pump is used to draw methane-air into the sensor housing where the excitation/reaction takes place. This system provides one measurement for every excitation cycle. For this phase of testing, a two-minute long excitation cycle was utilized. Oakland University reports that the system has a detection range of 5,000 to 500,000 ppmv. It should be noted that this range is far outside of the desired target range for this project. The Oakland chemical analyzer and sensor are shown in Figure 2.3.



Figure 2.3. (a) Oakland Chemical Analyzer and (b) Sensor.

2.1.4 SenseAir/Honeywell

The SenseAir (in collaboration with Honeywell) device uses a non-dispersive infrared (NDIR) sensor coupled with a long path length (LPL) platform. The LPL platform provides a 1.3-meter optical length that is contained in an eight-centimeter long package. This system measures infrared absorption through a sample gas (methane-air) and compares it against the absorption through a zero gas (ambient air). The tested prototype calibrates on a regular basis through a process noted as "zero calibration." This feature is controlled autonomously through software. Zero calibration performed at regular intervals minimizes the thermal sensitivity of the NDIR measurement technique. The concentration reading is updated after every zero calibration (approximately every five minutes) at a range of zero to 32,000 ppmv.

A Labview software program was used for the data acquisition and control of the SenseAir system. The program allowed for the adjustment of settings, such as the zero calibration period and sample gas period. After tuning the system at SwRI, SenseAir determined that a five-minute zero calibration period followed by a five-minute sample gas period would be sufficient for testing. The SenseAir system is shown in Figure 2.4. This system requires 110 VAC power.



Figure 2.4. SenseAir/Honeywell System.

2.1.5 University of Colorado

The University of Colorado provided three independent devices for testing. These systems integrate an array of off-the-shelf gas (including methane), humidity, and temperature sensors onto a single integrated circuit board. Specially-developed post-processing algorithms (developed in MatLab) are used to combine the individual measurements from these sensors to generate a single concentration reading. The working principle behind these sensors is that the resistivities of the sensing elements change in the presence of a given species, such as methane, carbon monoxide, carbon dioxide, or non-methane hydrocarbons. Colorado units #1 and #2, shown in Figure 2.5a and Figure 2.5b, respectively, are identical with the exception of desiccantfilled tubing attached to the inlet of unit #2 for drying out the sample gas. Unit #3, shown in Figure 2.5c, utilizes many of the same sensors as units one and two, but it has several additional features. The device draws a three-liter gas sample into a polyvinyl fluoride bag and samples from the bag for approximately 11 minutes. Half of the sample is directed to an array of sensors similar to those found in units #1 and #2, and the other half of the sample is directed through a catalyst. Units #1 and #2 provided a reading approximately every five minutes and unit #3 provided a reading approximately every 11 minutes. All units had a stated detection range of zero to 30 ppmv, though they were able to provide readings at levels orders of magnitude higher.



Figure 2.5. (a) Colorado Sensor #1 (b) #2, and (c) #3.

3. TESTING OVERVIEW

3.1 Tests

The primary purpose of the testing was to determine if the sensors would measure various changes in background levels of methane independent of background conditions. Sensors were exposed to the series of tests as noted in Table 3.1.

IESI	DESCRIPTION	
Ambient	Varying methane concentrations in air at ambient temperature and relative humidity level.	
Environmental	Varying methane concentrations in air at various temperatures and relative humidity levels.	
Contaminant	A matrix of mixtures containing various concentrations of air, methane, carbon dioxide, carbon monoxide, and ethane. Note: carbon dioxide, carbon monoxide, and ethane were used to simulate potential contaminants.	

Table 3.1. Overview of Tests Performed.

3.2 Test Setup

The general experimental configuration is illustrated in Figure 3.1 and shown in Figure 3.2. For all tests, the sensors were placed inside of a chamber constructed of a polycarbonate sheet on a metal frame. The chamber has multiple access points for gas injection, purging, and plumbing of reference measurements. Specified volumes of methane, carbon dioxide, carbon monoxide, and ethane gas were injected into the chamber using a mass flow controller. An explosion-proof fan was installed in the chamber for mixing and circulating test gas mixtures. In order to purge or reset the chamber gas composition, a panel on the chamber was hinged open and the mixing fan was activated to vent the methane. The 3.5 ft x 3.5 ft x 6 ft methane chamber was situated indoors in ambient conditions for the Ambient Test and Contaminant Test. For the Environmental Test, the chamber was placed inside of a walk-in environmental chamber. The hinged panel on the chamber was left open to equilibrate with the established environment within the environmental chamber. Once equilibrium conditions were reached, the hinged panel on the chamber for the short-duration test point.



Figure 3.1. Experimental Setup.



Figure 3.2. Testing Chamber With Instruments in Place.

3.3 Reference Measurements

A Picarro G2204 Cavity Ring-Down Spectroscopy (CRDS) gas analyzer was used to take methane reference measurements for all tests. The Picarro uses a vacuum pump to continuously draw in and analyze sample gas. Ports for the Picarro inlet and outlet sampling lines were installed at various locations on the testing chamber in order to allow for verifying that the contents of the chamber were well mixed. Although the accuracy specified by the manufacturer $(\leq 2.0 \text{ ppbv})$ is only guaranteed for the specified operating range of zero to 20 ppmv, the instrument is capable of taking measurements at much higher concentrations. Prior to testing, the accuracy of the Picarro in the range of zero to 1,000 ppmv was verified using a gas chromatograph flame ionization detector (FID). Six equilibrium methane concentrations in the range of zero to 2,000 ppmv were established inside of the testing chamber. For each concentration, samples were collected in polyvinyl fluoride bags to be analyzed by the FID and measurements from the Picarro were recorded. Table 3.2 shows the results from the verification testing. The Picarro results aligned well with the FID, especially considering the error that is introduced through the chromatograph sampling process. Near its specified operating range, the Picarro updated readings on the order of 1 Hz. However, at higher concentrations, the Picarro updated less frequently on the order of 0.1 Hz.

PICARRO (ppmv)	GAS CHROMATOGRAPH (ppmv)	PERCENT DIFFERENCE (%)
24.4	24	2
104.7	100	5
256.2	239	7
501.6	494	2
984.8	975	1
1,949.0	1,930	1

Table 3.2. Verification of the Picarro with Gas Chromatograph.

Once it was confirmed that the Picarro could be used for reference measurements, checkout tests on the experimental setup were conducted. The purpose of these tests was to determine important testing parameters, such as the amount of mixing time necessary to achieve a uniform concentration in the chamber. The uniformity of the gas within the chamber was verified by taking measurements with the Picarro at various locations.

3.4 Testing Approach

The general procedure shown below (Figure 3.3) was followed for the Ambient Test and Environmental Test. It is noted that the concentration steps could not be quickly incremented. Two of the systems (Innovator A and Innovator B) required five or more minutes of sampling at these conditions before the test could proceed to the next increment.

A variety of trials were performed during each test in order to gain an understanding of the capabilities of the sensors. Table 3.3 summarizes the four tests that were executed for the Ambient Test. Tests 1 and 2 focused on low methane concentrations with small incremental increases in concentration, while Tests 3 and 4 focused on high methane concentrations with large incremental increases in concentration.



Figure 3.3. General Test Approach for Tests 1, 2, and 3.

TEST	METHANE CONCENTRATIONS (ppmv)	# OF TRIALS
1	Amb., 5, 7, 9, 11, 13, 15	4
2	Amb., 5, 10, 15, 20, 25, 30	3
3	Amb., 40, 80, 120, 160, 200, 240	3
4	Amb., 500, 1,000, 1,500, 2,000, 2,500, 3,000	2

Table 3.3. Trials Performed for the Ambient Test.

Table 3.4 summarizes the four tests that were performed for the Environmental Test. The environmental testing was intended to investigate temperature/humidity level influence on each system. The intent was not to investigate a system's functional limits under extreme conditions. During Tests 5 and 6, the sensors were exposed to equilibrium methane concentrations in air at elevated temperatures and normal and high relative humidity levels, respectively. During Tests 7 and 8, the sensors were exposed to equilibrium methane concentrations in air at depressed temperatures and normal and low relative humidity levels, respectively. There was some variance in humidity levels, but it is suspected that the moisture was removed by those devices that desiccated the air prior to analysis. Also, it is noted that the chamber temperature typically increased by 3°C during a given trial due to heat transfer from the devices and stirring fan.

TEST	TEMP (°C)	R.H. (%)	METHANE CONCENTRATIONS (ppmv)	# OF TRIALS			
5	38	50	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	2			
6	38	80	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	2			
7	4	50	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	1			
8	4	30	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	1			

Table 3.4. Test Performed for the Environmental Test.

Two types of tests were performed for the Contaminant Test: incremented contaminant and background contaminant. In the first case, no methane was added to the test chamber. This test evaluated whether or not the systems would mistake the contaminant for methane. The same testing procedures for the Ambient Test and Environmental Test were used, with the exception that contaminants were incremented instead of methane. In the second case, a constant contaminant background concentration was maintained, while the methane concentration was varied. Again, the same testing procedures that were used for the Ambient Test and Environmental Test were used, with the exception that a contaminant was injected into the chamber at the beginning of the test in order to attain a background contaminant concentration. The tests that were performed for the Contaminant Test are summarized in Table 3.5 and in Table 3.6.

TEST	CONTAMINANT CONTAMINANT CONCENTRATIONS (ppmv)		# OF TRIALS
9	CO_2	Amb., 20, 100, 500, 1,000	1
10	CO	Amb., 20, 100, 500, 1,000	1
13	C_2H_6	Amb., 20, 100, 500, 1,000	1

Table 3.5. Tests Performed for the Contaminant Test.

Table 3.6. Tests Performed for the Contaminant Test.

TEST	CONTAMINANT	CONTAMINANT BACKGROUND LEVEL (ppmv)	CH₄ CONCENTRATIONS (ppmv)	# OF TRIALS
11	CO_2	1,000	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	1
12	CO	1,000	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	1
14	C_2H_6	1,000	Amb., 5, 10, 15, 20, 25, 30, 100, 250, 1,000	1

4. TESTING RESULTS

4.1 Results Discussion

The results for all systems are presented anonymously, meaning a system is referred by a letter (A, B, C, D, or E) as opposed to the innovator's true name.

4.1.1 Ambient Test

Figure 4.1 shows the Innovator A, Innovator B, Innovator C, and Innovator D sensor measurements as functions of the Picarro reference measurements for Tests 1 and 2 of the Ambient Test (ambient conditions). Data for Innovator E were not plotted, as that sensor did not provide readings over the range of concentrations in the plots. In all of the charts in this report, the various sensor readings are normalized to the initial background levels. Despite varying levels of accuracy and precision, all four sensors were able to detect small changes in methane concentration. This is apparent in Figure 4.2, which shows data from Tests 1 and 2 of the Ambient Test on a smaller scale. The Innovator C and Innovator D sensors showed the most repeatable data, and both were capable of consistently detecting changes in methane concentration on the order of two ppmv. The Innovator A and Innovator B sensors provide less repeatable data, but were still capable of detecting two ppmv changes in concentration.

4.1.2 Environmental Test

Figure 4.3 shows the results from the Innovator A sensor for the Ambient Test and Environmental Test. The sensor provided fairly accurate results (within 30% of the reference measurements) at ambient conditions despite repeatability issues. However, the accuracy of the sensor decreased when the temperature and relative humidity were varied in the Environmental Test. For high temperatures, the sensor consistently measured lower concentrations than were present in the chamber. For low temperatures, the sensor consistently measured higher concentrations than were present in the chamber. The Innovator A sensor was unable to predict (within reasonable error) concentrations above 30 ppmv.



Picarro Measurements (ppmv) Figure 4.1. Sensor Measurements for Tests 1 and 2 of the Ambient Test.



Picarro Measurements (ppmv) Figure 4.2. Sensor Measurements for Tests 1 and 2 of the Ambient Test.



Figure 4.3. Innovator A Measurements for the Ambient Test and Environmental Test.

Figure 4.4 and Figure 4.5 show the results from the Innovator B sensor for the Ambient Test and Environmental Test. The performance of the sensor was unaffected by the varying temperature and relative humidity in the Environmental Test. The majority of the measurements made by the sensor were within 30% of the respective Picarro measurements for lower concentration levels (Amb. to 30 ppmv) and within 10% of the respective Picarro measurements for higher concentration levels (up to 1,000 ppmv).



Figure 4.4. Innovator B Measurements for the Ambient Test and Environmental Test.



Figure 4.5. Innovator B Measurements for the Ambient Test and Environmental Test.

Figure 4.6 and Figure 4.7 show the results from the Innovator C sensor for the Ambient Test and Environmental Test. The data are displayed as sensor measurements as a function of Picarro measurements. The Innovator C sensor provided repeatable measurements for the concentration range that was tested, and the measurements were unaffected by temperature and relative humidity. Measurements taken by the Innovator C sensor were consistently 20-25% lower than measurements taken by the Picarro. Innovator C suspects that this offset is due to differences in the atmospheric pressure at the testing location and the location where the calibrations were performed. The innovator should further explore this discrepancy.



Figure 4.6. Innovator C Measurements for Ambient Test and Environmental Test 3.



Figure 4.7. Innovator C Measurements for the Ambient Test and Environmental Test.

Figure 4.8 and Figure 4.9 show the results from the Innovator D sensor for the Ambient Test and Environmental Test. The Innovator D sensor provided repeatable and accurate (within 10% of the Picarro) measurements at ambient conditions (Ambient Test). The sensor's accuracy decreased at lower concentrations (Amb. to 30 ppmv) when the temperature and relative humidity were varied in the Environmental Test. Changes in temperature and relative humidity in either direction from ambient appeared to have the same effect on the accuracy of the Innovator D sensor, causing it to measure lower concentrations than were present in the chamber. However, the accuracy of the sensor was unaffected by temperature and relative humidity at higher concentrations, as shown in Figure 4.9.



Figure 4.8. Innovator D Measurements for the Ambient Test and Environmental Test.



Figure 4.9. Innovator D Measurements for the Ambient Test and Environmental Test.

4.1.3 Contaminant Test

The first part of the Contaminant Test involved injecting contaminants into the chamber in order to determine whether the sensors would mistake the contaminants for methane. The key findings from this set of tests were:

- When the Innovator B, Innovator C, and Innovator D sensors were exposed to various concentrations of carbon monoxide and carbon dioxide with no methane (in addition to ambient concentrations) present, all of them continued to report baseline methane concentration measurements (i.e., the measurements were unaffected by the contaminants).
- The same results were seen for the Innovator C and Innovator D sensors when they were exposed to various concentrations of ethane. However, the Innovator B sensor measured significant methane concentrations when it was exposed to various concentrations of ethane with no methane (in addition to ambient concentrations) present, as shown in Table 4.1.
- The Innovator A system was unable to provide methane concentration measurements in the presence of contaminants.

ETHANE CONCENTRATION (ppmv)	INNOVATOR B METHANE MEASUREMENT (ppmv)
0	2
20	45
100	296
500	2,675
1,000	8,200

Table 4.1. Innovator B Methane Concentration Measurements when Exposed to Various Concentrations of Ethane.

The second part of the Contaminant Test involved injecting background levels of contaminants into the chamber prior to exposing the sensors to varying methane concentrations. The key findings from this set of tests were:

- The performances of the Innovator B, Innovator C, and Innovator D sensors were unaffected by the presence of 1,000 ppmv of carbon monoxide and carbon dioxide in the chamber as methane concentrations were varied.
- The same results were observed for the Innovator C and Innovator D sensors when 1,000 ppmv of ethane was present. However, the methane concentration measurements gathered by the Innovator B sensor were significantly different when 1,000 ppmv of ethane was present in the chamber as methane concentration was varied, as shown in Table 4.2.

4.2 Innovator E

Results from the Innovator E system must be assessed differently since the vast majority of tested methane levels were below this system's reported minimum of 5,000 ppmv. As a result of not having developed correlations for low concentrations, it should be noted that sensor output for the Innovator E system cannot be directly translated into a methane concentration reading.

It is uncertain whether this system is capable of detecting such low concentrations of methane. In other words, it is unknown if the performance at low concentrations is a physical limitation of the sensor or the inability to extrapolate results from higher concentrations. Figure 4.10 is a plot of the sensor output current versus the Picarro reference measurement for the zero to 30 ppmv range. This plot depicts data from the same sensor on two consecutive trials on the same day. At first glance, it seems that the sensor is reacting linearly to changes in methane concentration. However, it is known that this system has significant baseline drift, as can be seen by the higher overall output of Trial 2 compared to Trial 1. The increase in output seen may be merely a result of exciting the sensor system multiple times consecutively, not the result of methane reaction.

METHANE CONCENTRATION (ppmv)	INNOVATOR B METHANE MEASUREMENT (ppmv)
Amb. (No ethane)	1
Amb. (1,000 ppmv ethane)	8,450
5	7,750
10	6,940
15	6,450
20	5,565
25	5,115
30	4,770
100	4,775
250	5,020
1,000	6,740

Table 4.2.	Innovator B Methane Concentration Measurements in the Presence of	1,000 ppmv o	f
	Ethane.		



Figure 4.10. Innovator E Sensor Response Versus Reference Picarro Measurements, 0-35 ppmv.

In addition to the baseline drift previously illustrated, it is evident that the tested prototypes suffer from other non-stationary effects. Figure 4.11 is a plot of the sensor output current versus the Picarro reference measurement for the 0-250 ppmv range. This plot also shows the output for the same sensor used during two consecutive trials on the same day. As this graph shows, the sensor response is much more sensitive for Trial 2 compared to Trial 1. As before, it is uncertain whether this response is caused by methane exposure.



Figure 4.11. Innovator E Sensor Response Versus Reference Picarro Measurements, Zero to 250 ppmv.

Figure 4.12 illustrates the inconsistency between instances of the sensor. Note the logarithmic scale on the plot. The red points indicate the response at relatively low concentrations (~100 ppmv) and the blue indicate the response at methane concentrations an

order of magnitude larger (~1,000 ppmv). From this graph it is evident that the outputs, despite the large differences in methane concentration, are highly comparable. This also brings into question the ability for such a sensor to detect low methane levels. Also, it points out the sensor-to-sensor variation of the prototypes tested.



Figure 4.12. Comparison of Innovator E Sensor Output for Zero to 240 ppmv and Zero to 3,000 ppmv Tests.

A final set of tests was conducted to specifically investigate the Innovator E system. This testing used levels of methane far higher than levels previously tested (up to 15,000 ppmv) with the intent of exciting the chemical in the reported detection range. Figure 4.13 is a dual-axis plot illustrating the results, where the primary y-axis indicates nominal methane concentration, the secondary y-axis indicates sensor output, and the x-axis is the measurement number. The first eight measurements were taken at ambient conditions. As the output profile shows, the baseline was far from uniform and was scattered between 20 and $30 \,\mu A$. For the next eight measurements, the sensor was exposed to a 2,000 to 15,000 ppmv ramp followed by five consecutive excitations at 15,000 ppmv. While the sensor appeared to be responding to the methane, it is unclear if the response was a result of lag or drift in the measurement technique. The last four measurements were taken at ambient conditions. The output leveled off at this point, again illustrating the hysteresis issues.



Figure 4.13. Innovator E Sensor Output Compared Against Methane Concentration.

5. TESTING SUMMARY

5.1 Performance Summary

The purpose of this phase of testing was to evaluate the various sensors against the RFP conditions and not to pick a "winner." In revisiting the overall project objectives, the key point of evaluation is the ability of the sensors to detect small changes in methane levels. Table 5.1 provides an overview of how the various sensors performed regarding this metric. The primary metric from this testing is the ability to detect small changes in methane levels. Using that criterion, Innovators A, B, C, and D have met this objective.

Table 5.1 Summary of Ability to Detect Small Changes

INNOVATOR	ABILITY TO DETECT SMALL CHANGES
Innovator A	This sensor was, in general, able to capture small changes in background level, though with less consistency than some of the other sensors.
Innovator B	This sensor was able to capture very small changes in background level across all conditions.
Innovator C	This sensor was able to capture very small changes in background level across all conditions.
Innovator D	This sensor was able to capture very small changes in background level across all conditions.
Innovator E	This sensor was unable to provide repeatable results for concentration levels in the target range of <250 ppmv.

As previously noted, the ability of the sensor to lead to an accurate quantification of concentration is not a requirement for this project. However, such a capability would add value to the utilization of such a sensor. Table 5.2 provides an overview of how accurately each sensor was able to quantify the background levels.

Table 5.2. Summary of Ability to Quantify Concentration.		
INNOVATOR	ABILITY TO QUANTIFY CONCENTRATION	
Innovator A	This sensor provided a set of "ballpark" readings for concentrations below 30 ppmv,	
	but was less accurate than some of the more mature systems. The accuracy of the	
	sensor was negatively affected by deviations in temperature and relative humidity	
	from ambient conditions.	
Innovator B	This sensor provided fairly accurate readings, particularly at higher concentrations.	
	There was more inconsistency in quantification at lower concentrations than	
	compared to the Innovator C and Innovator D.	
	This sensor was very linear in its response. It was observed that the sensor read	
Innovator C	approximately 20% below actual concentrations. The innovator believes that this	
Innovator C	was due to a change in atmospheric pressure between the calibration facility and the	
	testing facility. The innovator believes this issue is easily correctable.	
Innovator D	This sensor was extremely accurate in quantifying the concentration over most	
	conditions. There was some observed drift at temperature extremes (likely the result	
	of a calibration issue).	
Innovator E	This sensor did not provide accurate or repeatable results over the test range of	
	interest. Drift in the sensor was observed over the course of testing.	

The sensors were also tested with a mix of contaminants (carbon dioxide, carbon monoxide, and ethane) to determine if other gases would impact the results of the testing. This

evaluation was done both by varying contaminant concentrations with fixed methane levels and by varying methane levels with a fixed (and elevated) background level of contaminants. Table 5.3 provides an overview of the performance of the sensors in the presence of contaminants.

INNOVATOR	PERFORMANCE IN PRESENCE OF CONTAMINANTS
Innovator A	The methane sensor was impacted by carbon monoxide, carbon dioxide, and
	ethane.
Innovator B	This sensor was not impacted by carbon monoxide or carbon dioxide, but was
	significantly impacted by the presence of ethane.
Innovator C	This sensor was not at all impacted by the presence of contaminants.
Innovator D	This sensor was not at all impacted by the presence of contaminants.
Innovator E	While the sensors should be able to separate methane from other contaminants,
	algorithms for processing the data have not been developed.

Table 5.3. Summary of Robustness Related to Contaminants.

5.2 Path Forward

The future trajectory of the Methane Detectors Challenge will involve field deployment of sensors through a pilot program. This Phase 1 testing was the first step necessary to vet various sensors that might be used in the pilot program. There is an intermediate testing set (Phase 2) that must be undertaken to further validate these technologies. The objectives of the Phase 2 testing include:

- Evaluating the leak detection "systems" that would be comprised of the sensors, power packs, electronics, required peripheral pumps, hardware, etc.
- Testing over the full range of Phase 2 testing requirements prescribed in the Challenge's RFP, including any subsequent refinements or clarifications.
- Closing any data gaps from Phase 1 through testing of sensors for which the innovators made improvements in the hardware after any Phase 1 shortcomings were identified.
- Performing rigorous testing at Technology Readiness Level 6 in order to determine which systems should proceed to the pilot phase.

The sensors utilized in Phase 1 were not necessarily stand-alone leak detection systems.

Phase 2 would require that the sensors be integrated into a system that, at a minimum, includes:

- Autonomous leak detection through various algorithms.
- Ability to self-power through a solar panel and battery pack.
- All peripheral equipment (pump, fans, tubes, etc.) fully integrated with sensor package.
- Full weatherization.
- Ability to communicate through a cell or wireless network (preferred, but not required).
- Meeting all safety requirements.

Additionally, some of the shortcomings of several sensors (temperature limitations, contaminant issues, etc.) need to be resolved prior to Phase 2.