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Advanced Development and Technology Transfer of a Methane/Natural Gas Microsensor (#506)

FINAL PUBLIC REPORT

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Executive Summary

Methane detectors are widely used by natural gas utility personnel as well as natural gas customers in order to detect the presence of natural gas. The most widely used sensors are those installed to sense a natural gas leak. Given that the lower flammability limit of methane in air is about 5% by volume, these sensors typically operate in the 0 – 5% range. Another set of applications is that of measuring the concentration of natural gas in order to determine the absence of other desirable or undesirable gases. These sensors typically require an operational range of 0 – 100% methane.

Given the continuous technological developments and new technologies and principles that are coming to light, new sensors come to the market at frequent intervals. One of these technologies is that by Applied Nanotech Inc. which is based on microresonator technology (MR). In early 2011, with funding from NYSEARCH/NGA, a feasibility study was completed that established the ability of the microresonator (MR) technology to be used as a methane/natural gas sensor by building a benchtop prototype and testing it in the lab. In a follow up Phase II, an engineering prototype sensor was built and tested extensively in the laboratory and in the field by NYSEARCH member companies. Following the success of this Phase II effort, NYSEARCH decided in June 2012 to fund further development of the sensor in order to seek further improvements and develop the specifications for a commercial detector and analytical tool. A major

advantage of the MR sensor is that it will not produce false alarms in the presence of other hydrocarbons and organic vapors. Upon the successful completion of this phase, the present work, cofunded by DoT/PHMSA and NYSEARCH/NGA, was initiated in order to carry out the design of the pre-commercial MR methane/natural gas sensor and to complete the development of the commercial system(s) prior to introducing to the market. The focus has been on building pre-commercial prototype devices in two versions - an analytical instrument “A” and a safety monitor sensor “S” (alarm only). The analytical methane and natural gas sensor/instrument will include all necessary outputs, alarm signal with a preset concentration level, LCD display, and operator setting of instrument parameters. The safety monitor sensor (detector) is based on the design approach developed for the full analytical instrument but with a number of functions and hardware elements removed. This safety sensor should have equivalent performance with the full analytical instrument but at reduced cost. Using a contract manufacturer, a beta-version of the detector (alarm only) was designed, built and tested prior to submittal to Underwriters Laboratories (UL) for certification. After initial submission to UL in late 2015, the detector is currently undergoing redesign and will be resubmitted for certification testing in mid- 2016. At the completion of the certification testing, the detector will comply with necessary standards and regulations and will be ready for field trials via a pilot testing program to be funded and executed by NYSEARCH.

1. INTRODUCTION

A highly accurate, robust new generation methane and natural gas sensor has several potential uses that are relevant to the PHMSA mission of improved safety as well as improved use of resources. The RA under which this program was funded included a request for development of Smart Leak Detection Systems*: Technology improvements are sought for pinpointing LDS on …and distribution systems. Such a project will develop and demonstrate robust and miniaturized sensing tools able to operate in the harsh oil and gas environments.* The subtopics of this area include *new development of sensor and instrumentation,* which correlated well with the work that was performed by an earlier NYSEARCH program.

Methane detectors are widely used by natural gas utilities personnel as well as natural gas customers in order to detect the presence of natural gas. Given the continuous technological developments and new technologies and principles that are coming to light, new sensors come to the market at frequent intervals. NYSEARCH has been interested and searching for many years for new miniaturized methane sensor technologies to adapt to LDC gas company needs. In this search, we found that an existing Applied Nanotech Inc. (ANI) technology presented the potential to serve as a methane sensor for the entire 0% to 100% natural gas in air range. This technology is based on a pair of tuning fork micro-resonators and is used in a commercial hydrogen sensor.

A number of sensors/instruments are available in the market that measure concentration of methane and/or combustibles. They vary in accuracy, range, price, and calibration needs. These sensors typically suffer from unacceptable levels of false positives. Table 1 below presents a summary of existing sensors and instruments in the market and their specifications and compares them to the sensor under development (ANI MR Sensor). A major advantage of the MR sensor is that it will not produce false alarms in the presence of other hydrocarbons and organic vapors.

Table 1: Specifications of commercially available natural gas/methane leak detectors compared to the ANI sensor.

Manufacturer	Unit	UL	ANI MR sensor	Heiman	EXTECH	Macurco	Kidde
Sensor Model			MS-10	HM-706	EZ40	GD-2A	KN-COEG-3
Retail cost (1 ea.)	$		99	<40	130	100	37
Upper detection limit	%		100		0.4 LEL		
Lower detection limit	%		0.25		50 ppm		
Alarm level(s)	LEL	0.25	0.2	0.1	0.1	0.25	0.25
Accuracy			0.25%	0.05 LEL			
Temperature min	C	0	-30	-10	0	0	4
Temperature max	C	49	50	50	50	49	38
Humidity min	%	0	0	0	10		5
Humidity max	%	95	95	95	90		95
Response time (t90)	s		3		2		
Voltage	V	<30	5	12 or 24	4.5	12	~120
Current	A		1			0.045	

Power supply			external	wired	8 hrs 3 C batteries	wired	Wired 9V backup
Interference			H2, He	HC	HC, CO, NH3	HC	HC, CO
Detection principle			microresonance	MOS	solid state	MOS	MOS
Sensor life	yr	3	5				7
Warranty	yr		2	5?	1	2	5
Weight			8 oz	<16 oz	18 oz	9 oz	24 oz
Sampling method			diffusion	diffusion	pump	diffusion	diffusion
O2 required			no	yes	yes	yes	yes
LCD			yes	no	no	no	yes - CO
Manufacturer	**Unit**	**UL**	**Universal**	**First Alert**	**Safe T**	**IMR**	**Safe T**
Sensor Model			MCN400B	GCO1CN	40-411	CD100A	HS80504
Retail cost (1 ea.)	$		33	40	37	140	45
Upper detection limit	%						
Lower detection limit			70 ppm CO			50 ppm	
Alarm level(s)	LEL	0.25	0.2	0.25	0.25		0.25
Accuracy	%						
Temperature min	C	0		4	-35	0	4
Temperature max	C	49		38	66	50	38
Humidity min	%	0		10	15		
Humidity max	%	95		95	93		
Response time (t90)	s		240		8		
Voltage	V	<30	~120	~120	12	9	~120
Current	A						

Power supply			9V backup	9V backup	2W transformer	5 hr from a battery	15 W
Interference			HC, CO	HC, CO	HC, VOC	HC	HC, CO
Detection principle						MOS	
Sensor life	yr	3	7	5			
Warranty	yr		5	5	3	1	5
Weight			7 oz	14 oz	13 oz	15 oz	12 oz
Sampling method			diffusion	diffusion	diffusion	diffusion	diffusion
O2 required			yes	yes	yes	yes	yes
LCD			yes - CO	yes - CO	no	no	no

In early 2011, with funding from NYSEARCH/NGA, a feasibility study was completed that established the ability of the microresonator (MR) technology to be used as a methane/natural gas sensor by building a benchtop prototype and testing it in the lab. This next generation sensor will be used in two ways. First, the sensor will be used as an analytical tool for in-line and off-line natural gas measurement in gas field operations. For in-line measurement, the instrument will be directly hooked up into a natural gas system to measure methane concentration, such is in the case of purging operations. For off-line measurement, the instrument will draw a sample from the ambient to determine presence of natural gas and at what concentration. This is a routine task of gas operations crews concerned with safety. Second, it will be used as an alarm/safety system to alert customers in case of a gas leak in residential, commercial and industrial applications. In a follow up Phase II, an engineering prototype sensor was built and tested extensively in the laboratory and in the field by NYSEARCH member companies. To date, for a full range of operating conditions (concentrations, pressure, temperature), positive NYSEARCH project test results have been recorded regarding performance, accuracy, impact of aging, reliability and cross sensitivity to consumer products, the sensor having met or exceeded all specifications. Following the success of this Phase II effort, NYSEARCH decided in June 2012 to fund further development of the sensor and seek a commercialization partner. Following a review of the laboratory tests carried out by ANI and by field tests conducted by NYSEARCH member companies, updated sensor specifications were developed and compared with those of methane sensors already in the market. This analysis helped us to understand if and how the ANI methane sensor design and specifications can be improved and whether there is further potential for cost reduction of the sensor. Ultimately, this work contributed to the definition of the commercial specifications.

2. OBJECTIVES

The objectives of this program were to:

- Complete the design of the pre-commercial MR methane sensor. The focus was on building pre-commercial prototype devices in two versions - an analytical instrument “A” and a safety monitor sensor “S” (detector; alarm only). The analytical methane and natural gas sensor/instrument includes all necessary outputs, alarm signal with a preset concentration level, LCD display, operator setting of instrument parameters, and dual power capabilities. The safety monitor sensor is based on the design approach developed for the full analytical instrument but with a number of functions and hardware elements removed. This safety sensor has equivalent performance with the full analytical instrument but at reduced cost,
- Complete the development of the commercial versions of the system using a contract manufacturer,
- Carry out tests to verify performance, and,
- Carry out UL certification.

3. TECHNICAL APPROACH

3.1 Description of background effort to the present effort

NYSEARCH/NGA was interested in developing a small, reliable, low cost methane (natural gas) sensor. The sensor would be used in detecting natural gas leaks and other applications. The sensor should be capable of measuring the methane concentration from 0% to 100% in air at different pressures, relative humidity levels and in a wide temperature range. The measurement range of primary interest corresponds to 0-100% Lower Explosive Limit (LEL) with the ability to measure gas concentrations up to 100%. [LEL for methane corresponds to approximately 5% gas concentration in air.]

Applied Nanotech, Inc. (ANI) proposed to develop a robust, low cost, miniature methane (natural gas) sensor based on MicroResonator (MR) technology. The sensor should have a detection limit and an accuracy of 0.25% natural gas concentration in air. The sensor should be capable of operating at various gas gauge pressures ranging from 30 to 110 kPa and temperatures of -20°C to 50°C. The response time of the sensor should be 1 second.

The sensor is based on measuring the viscosity of a gas mixture. The viscosity of methane is 11.2 kPa*sec, and that of air is 18.5 kPa*sec. This difference in the viscosity of over 60% gives rise to a change in the oscillation frequency of a tuning fork microresonator when it is placed in gas mixtures with variable gas composition. The methane sensor uses a pair of quartz tuning forks (see Fig. 1) oscillating at the resonance frequency of f_0. The frequency difference ($f - f_0$) between a measuring microresonator and a reference microresonator enclosed in a vacuum package is proportional to the methane concentration in a mixture of natural gas and air.

Figure 1: Quartz tuning fork: self-standing (left) and packaged (right)

Because the resonance frequency of a microresonator (MR) depends on the ambient pressure and, to a lesser extent, relative humidity (RH) of air, the MR sensor also incorporates a pressure sensor and RH sensor for compensation against variations in ambient conditions. For a permanently installed methane detector, the RH sensor may not be needed. A proprietary system provides the proper insensitivity to temperature variations. We demonstrated that the accuracy of the developed engineering prototype is better than ±0.25%. The digital outputs of the microresonators are connected to a flip-flop trigger in order to obtain a differential frequency signal. The RH and pressure sensors have their own digital output (I^2C) circuits. Outputs from all three sensory elements are connected to a microprocessor (controller) that calculates methane concentration (see the sensor block diagram in Fig. 2). Natural gas concentration is calculated based on this measurement, once a natural gas composition profile is programmed into the instrument.

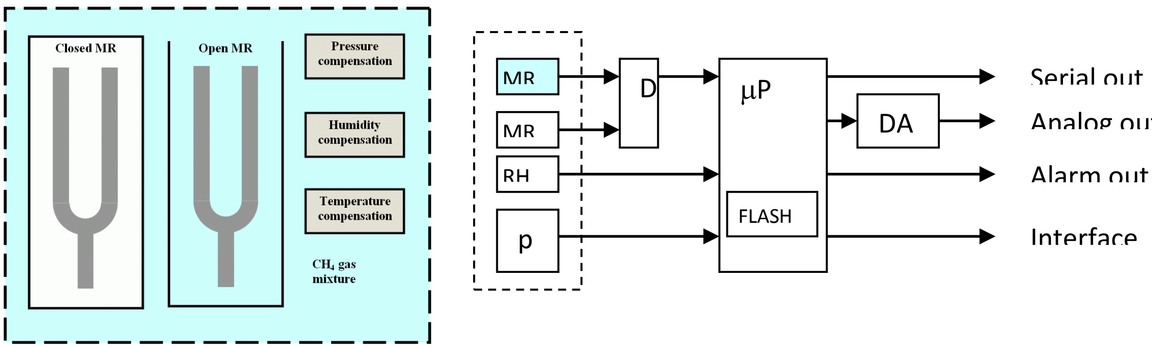

Figure 2. Sensor design diagram (left) and block diagram (right)

There are different design considerations for the two types of sensors. The safety sensor “S” (alarm monitor) will give a positive detection for methane or natural gas with alarms for concentrations at or below the 25% threshold of the Lower Explosive Limit (LEL) for methane in air, but will have no option for user control. It can be wired to a DC or AC power source, but could also be operated by battery. The entire device is anticipated to weigh less than 0.75 lbs. The size of the safety sensor can be as small as a deck of cards. The fully loaded analytical methane/natural-gas sensor “A” will allow user control, in order to specify operating parameters and record data in-real time, and will provide an optional output signal (alarm) indicating that the composition of the gas contains a certain amount of methane, as set by the operator.

Commercial microresonator sensor prototype specifications for the analytical instrument were determined based on the feedback from the contract funders and observations from earlier work. System peripherals such as alarms and the corresponding alarm concentration levels, master/slave communications to an external controller or PC, sensor functions, user selectable parameters, display information are all potential features of a commercial prototype (but not required). The user selectable parameters include the following: gas type (methane/NG), alarm ON/OFF, balance gas (N_2/air), zero calibration, operation mode, and others. Mechanical design of the engineering prototype is based on the overall device dimensions 1.5” x 3.5” x 5”. The sensor is powered from an external 5V adapter.

The sensor is based on a microprocessor and additional circuits capable of handling LCDs, user controls, and a larger code base. The prototype controller is capable of:

- receiving data from the sensor head (f - f_0, T, p, RH, calibration data, serial number).
- sending data to the sensor head (calibration data, serial number).
- sending data to LCD display
- sending data to serial port
- processing user controls and selections
- using real-time clock (RTC)

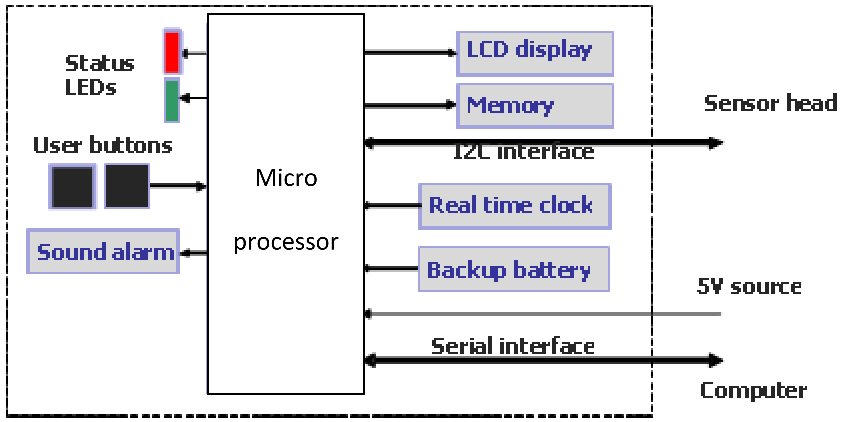

Figure 3: Sensor controller diagram

The engineering prototype of the analytical instrument built in the earlier effort is based on a two-line 2x16 ASCII LCD display with backlight, which is capable of indicating additional sensor parameters and user settings. The electronics of the sensor were finalized. Device operation and functionality were verified and debugged. The sensor controller boxes and sensor face plate were also developed. The face plate has two openings for red and green status LEDs above the LCD display. The sensor faceplate outline is shown in Fig. 4 below.

The MR based methane analytical instrument is powered using an external 110VAC/5VDC adapter. Battery operation capability was not implemented in the engineering prototype design. Sensor data output is performed via serial port using an RS232 adapter cable. A photograph of the analytical instrument with a built-in sensor head, power supply and a serial cable is shown in Fig. 5.

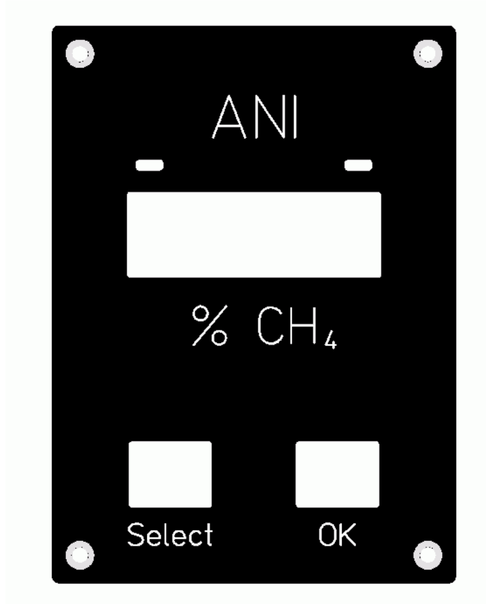

Figure 4: Sensor faceplate outline

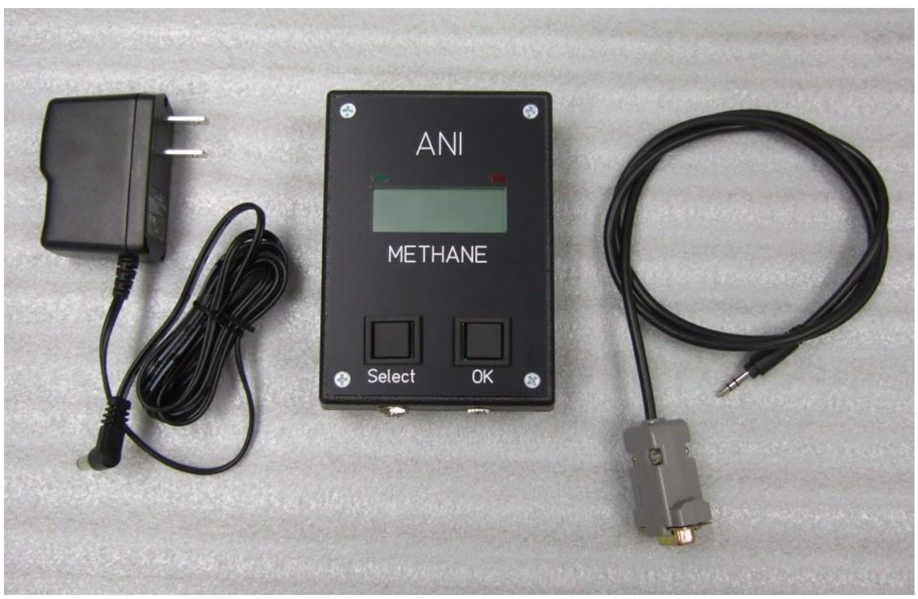

Figure 5: Methane sensor kit

It is envisioned that the commercial sensor will use a master/slave communication interface to transfer and receive data between the microprocessor in the sensor package and the controller's processor described above. The communications will be further extended to the PC via RS-232 interface. Detection algorithms were implemented to improve the signal-to-noise ratio as well as create distinct visual or audio alarms for different concentration levels.

Firmware functions of the engineering analytical instrument prototype enable the following:

a. stable and reliable I2C communication with the sensor head

b. calculation of the methane concentration based on the data from the sensor head

b. RS-232/USB serial port communication

c. control audio and visual alarms

d. query the user interface controls

e. process hardware errors

The software developed for the methane sensor is a PC console application for Windows which is capable of retrieving real time data from the sensor and saving them on a PC connected through the serial port, as well as synchronizing the real-time clock of the sensor and the connected computer. The saved data include a time stamp, sensor serial number, methane concentration, sensor temperature, relative humidity near the sensor head, atmospheric pressure, as well as service information.

Based on the test results of sensor performance in different environments, the design, hardware and algorithms of the sensor have been optimized. The optimization subtasks included the following:

1. Design a low-cost mechanical package.
2. Improve sensor accuracy.
3. Optimize user interface and available sensor control functions.

The sensor prototype performance was validated in the lab through the tests in the environmental chamber at selected gas composition mixtures for the five prototypes that were built (shown in Fig. 6 undergoing testing). The sensor was tested at 0%, 0.25%, 1%, 10% and 100% NG concentrations. We introduced variations in gas pressure, temperature, and relative humidity levels during the tests. Sensor heads were tested simultaneously in a single aluminum sensor chamber. No technical issues were found. Four out of five tested devices were delivered to NYSEARCH/NGA for field testing. The fifth sensor was tested on the roof of the ANI building for two months until it failed due to water condensation on contact pins followed by corrosion and damaging the sensor head. The results of the life test were used for corrosion mitigation.

Figure 6: A photograph of five devices tested simultaneously

3.2 Initiation of present effort

In August 2013, a proposal that had been submitted to PHMSA for funding the completion of the development effort for the MR Methane Sensor was approved for funding. Work was initiated in September 2013. The effort started with the development of the specifications of the alarm detector and the subsequent design, manufacturing and lab testing of a pre-commercial prototype. Improvements to the design of the sensor head were implemented that reduced power consumption and manufacturing cost. Once the detector had been developed, a pre-commercial version of the analytical tool was developed that incorporated the improvements of the detector system. When we tested the detector with common household and industrial chemicals, it was established that detector did NOT respond to these chemicals. This outcome contrasts with behavior of a series of commercial systems that do respond to household chemicals and therefore are compromised by false alarms. Testing of the detector by the potential commercializer followed, that were successful. As a result, we moved forward with the hiring of a contract manufacturer who designed and manufactured a commercial grade detector. This detector was then submitted to UL for the necessary certification. Following the identification of some issues with the detector, the detector was redesigned and is to be resubmitted shortly to UL for completion of the certification testing.

4. WORK PERFORMED

The work performed under this program is presented along the lines of the tasks presented in the proposal. Given that some of the material is proprietary, two final reports were submitted; one for public release and one confidential. This report is the public one. It contains he main body of the confidential report only, while the confidential report contains the main body plus the appendices.

Task 1.1-*A Finalize electronic design of S sensor commercial prototype*

In this Task, we will finalize the electronics design of the "S" sensor (alarm only sensor). Many functions and the related hardware such as LCD screen and serial port are not needed for leak detector and will be excluded from the final design.

At the time that this project was initiated the features and specifications were as following:

Operating Principle

- Micro-resonance effect
- Compensated solid state sensor

Features

Performance Features

- Fast response time
- Wide concentration range
- No chemical reactions involved
- Inherently safe
- Operates in air, nitrogen, and binary mixtures
- Measures temperature, pressure, and humidity
- Audible alarm

Applications

- LEL methane detectors
- Automotive applications
- Pipeline backfill monitor
- Natural gas storage and transfer
- Custom applications

Sensor Specifications

- Concentrations range: 0 – 100%
- Operating temperature: -20ºC to 50ºC
- Storage temperature: -40ºC to 90ºC
- Relative humidity:0-95%
- Ambient pressure:30 - 110 kPa
- Response Time (T_{90}): 1 sec
- Accuracy: 0.25% of full scale*
- Resolution:0.1% of full scale
- Sensor voltage: 5V DC**
- Sensor current: 1.1 A (maximum at -20C), 0.6A (average)
- Dimensions: Custom package

* Error may be higher in extreme environments. Sudden changes in the humidity or temperature may result in a temporary decrease in the sensor accuracy due to a longer humidity sensor response time.

** A wall plugged 110VAC/5VDC adapter will be used to power the sensor

Design

The heart of the methane sensor design is the MR sensor, which is built into the device. The sensor retrieves the data from the sensor head and performs necessary calculations for signal compensation. The engineering prototype analytical instrument also indicates measured data on an LCD display and transmits the data to an external computer via a serial port. The instrument has two connectors and two push buttons to select and confirm the display mode.

Standard Features

- LCD Display
- RS232 Port
- User control buttons (2)
- Audible Alarm

Optional Features

- Data logging capability
- Analog output
- RS485 or USB port

User Selectable Parameters

- Detected gas (Methane or natural gas)
- Ambient gas (Air or nitrogen)
- Reset Zero
- Alarm ON/OFF

Operating Modes

The sensor will continuously collect data: methane concentration, temperature, relative humidity and atmospheric pressure. The sensor display will indicate the measured parameter and the result of the measurement. Only one parameter will be displayed at a time, depending on the selected display mode.

Display modes can be changed by pressing the “Select” button. Every time the “Select” button is pressed, the sensor controller scrolls to the next display mode. The displayed parameters are the following:

- CH_4 - Methane concentration in %;
- Mm – Effective molar mass of gas mixture;
- TC - Temperature in degrees Celsius;
- RH - Relative humidity in %;
- Pa - Pressure in Pa.;
- Zc – Zero calibration (needs to be confirmed by pressing “OK” button).

Zero calibration of the sensor can be performed by user one time per year at standard conditions, where no methane is present in the atmosphere. It is recommended that the user perform zero calibration in any new environment or installation. Zero calibration is performed automatically on powering up the sensor.

Computer Interface

The sensor can be connected to a computer using an optional cable with DB-9 female connector. Windows’ program “Hyper Terminal“ can be used to view and capture data from the sensor. Once the controller box has been connected to the computer RS232 port, it sends lines of ASCII data to the computer at periodic intervals.

In this first task of this PHMSA-cofunded project, we developed the specifications and design of a “safety” only sensor (alarm only, “safety” or “S” sensor), i.e. a device that will be used only for alarm purposes to detect the undesirable presence of methane. Given that the engineering prototype already developed and tested in the earlier work was for an analytical grade tool, that prototype included capabilities that are not needed in the case of a sensor tailored to safety applications. The analytical tool capabilities include user controls and relevant software, serial port interconnection to a computer for data downloading, LCD display, and user selection of gas to be detected (methane vs. natural gas). In this task, we redesigned the analytical grade instrument to a tool that is for safety (detector) applications only. The following Table 3 provides a comparison of basic characteristics of the two tools.

Table 3: Basic configurations of the two systems developed

	“S” Design	“A” Design
Application	Residential - Safety	Industrial - Instrument
Compliance	UL 1484	UL 2075/ASTM
Usage	Wall/ceiling mount	Handheld/portable
Power	~120V + backup bat.	~120V + recharg. bat.
Indication	LED/Sound Alarm	LCD/Sound Alarm
Communication	-	RS232
Parameters	Fixed	User selectable
Other	RH sensor not needed	Micropump may be optional

The redesign involved removing many of the features inherent in an analytical tool, but not needed in an alarm sensor. Displays, serial port connections and user controls were eliminated. It also involved redesigning the various components of the system to minimize power consumption so it can meet battery operation requirements as per applicable codes. The most crucial element in this redesign was the heating element for the sensor, because it is the most power consuming component of the system.

Task 1.1-B ***Finalize firmware of S sensor commercial prototype***

In this Task, we will finalize the firmware of the commercial prototype "S" sensor following completion of Task 1.1-A. In addition, a high-pass filter in the detection algorithms developed in an earlier phase will be implemented for drift compensation and to create distinct visual or audio alarms at 25% LEL concentration level (1% CH_4 in air).

A review of the existing firmware on the engineering prototype for the analytical tool was carried out for the purpose of determining the components that could/should be removed in the case of the “S“ sensor. Final selection was based on “S” sensor final configuration after Task 1.1-A-1 was completed. Firmware associated with the serial port, the passing of data to the LCD screen and the control of the tool by user were eliminated. Another major firmware task was to introduce a high-pass filter in the detection algorithms for drift compensation (following the experience gained during field testing) and to create distinct visual or audio alarms at the alarm concentration level. With the selection of the “S” sensor final configuration in Task 1.1-A, the new firmware for the “S” sensor was designed and implemented. Some minor modifications to the firmware were made once the new PCB was received and implemented/tested. Once all components of the new design for the S-sensors were received, including the PCB of the commercial prototype of the “S” sensor, they were assembled and pre-tested. Six devices were built. The photographs of the sensors are shown in Fig. 7 below.

Figure 7: Photograph of (6) pre-commercial detector prototypes

The power consumption of the new design was evaluate through testing and was found to consume an amount higher than desired. A model of a new design indicated that theoretically we could achieve a four-fold reduction in power consumption. That design was implemented and that resulted in significant power consumption savings.

Task 1.1.-C Finalize *electronic design of "A" sensor commercial prototype*

In this task, we will finalize the electronics design of the "A" type sensor (analytical instrument). In addition, we will consider UL2075 Standard requirements during this effort. We will verify and debug the device operation and functionality. We anticipate that one or two design iterations may be needed.

With the finalization of the design of the sensor head in the “S” sensor and the positive test results, we initiated the work to redesign the “A” sensor (analytical instrument). The new design for the S-sensor head with the improved performance was also implemented in the “A” instrument, so that we can take advantage of the improved features of the new sensor head, i.e. lower power requirements and manufacturing costs. The specifications for the sensor were developed, reviewed and approved as follows:

- The sensor will be capable of handling the LCD, user controls, and a large code base. The commercial prototype design features of a single station portable device include:
- Handheld device with up to four built-in sensor heads, one of which is standard and other three are optional, and the circuits needed for the sensor heads operation, where the sensor heads include:
- Standard methane sensor head - design similar to "S" sensor head;
- Electrochemical dual CO/H2S sensor (4COHS type sensor from CiTicel);
- Electrochemical oxygen sensor (4OXV type sensor from CiTicel).
- The device should have a fixed PCB layout design, rather than modular design.

- The device will be powered off the external rechargeable Li/Ion battery such that the device operation time using the battery is at least 8 hrs, or external power supply.

- The device will have an internal fan for delivering the sampled air into the sensor box, while the air sample is drawn via a gooseneck probe attached to the sensor enclosure.

- The device will use an LCD display.

- The device should have a battery voltage indication.

- The device should be able to process hardware errors and display them on LCD.

- The device will have at least three user control buttons.

- The device should produce sound alarms at or below 25% LEL concentrations and hazardous CO (H2S) concentrations.

- The device will have an RS232 port.

- The test data from the device will include:

    a. troubleshooting mode - timestamp, 4 concentrations, T_pcb, RH, pressure, dF, T_head, PWM

    b. normal operation mode - timestamp, 4 concentrations, T_pcb, RH, pressure

    c. Serial numbers for all sensors, compensation parameters for CH_4 sensor, firmware version, user settings, etc., accessible via user interface.

- The data logging capability to store at least 100,000 lines 100 bytes each, recorded every second (or per user selected recording interval).

- User selectable gas mixtures.

- Real-time clock (RTC), external (have its own battery) .

The design of the "A" type device will comply with UL2075 Standard requirements and the UL requirements for other sensors used.

With the specifications set, the design of the electronic boards was undertaken and finalized. The following Fig. 8 shows the final PCB outlay.

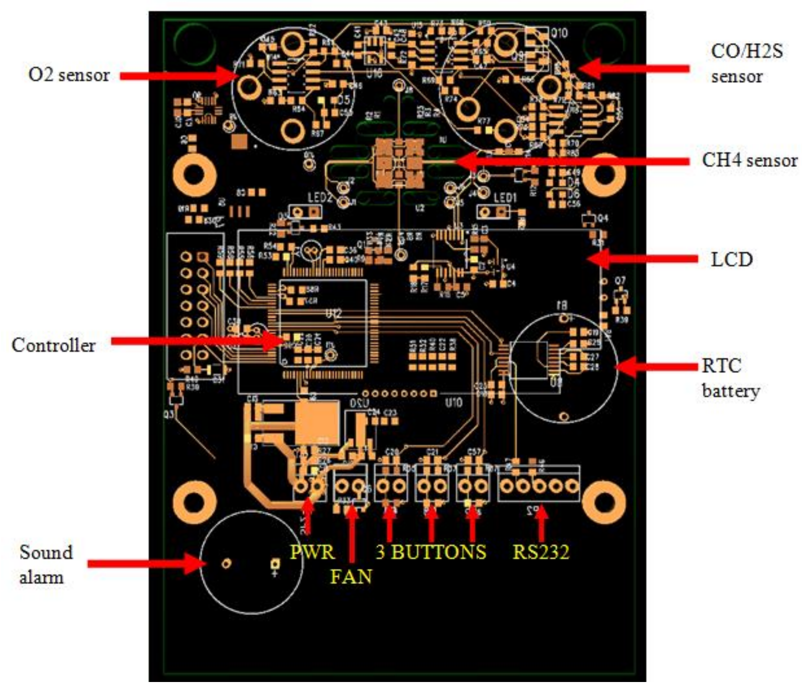

Figure 8: Layout of final “A” instrument

Task 1.1.-D ***Finalize firmware of A sensor commercial prototype***

The commercial prototype sensor will use a master/slave communication interface to transfer and receive data between the microprocessor, sensor head, and peripherals. The communications will be extended to the PC via RS-232 interface, dependent upon specifications being developed on the on-going work.

The firmware developed in the earlier phases of this program (not funded by PHMSA) was reviewed and modified to accommodate the new design. Given that a decision was made by earlier NYSEARCH member funders for the instrument to also have an option to include additional sensors (O_2, CH_4 and CO/H_2S), the firmware was modified to handle this additional capability.

Task 1.2-A ***Test the sensors per commercial specifications***

Prior to submitting the sensor for UL certification, the sensors will be pre-tested in the ANI lab. These tests will be conducted for both "A" and "S" sensor designs to pre-qualify the sensors for UL testing and certification, which will follow with a UL-qualified test laboratory

The “S” sensor was tested extensively in the laboratory as per applicable UL standards and met these standards. One “S” sensor was tested for immunity to short-term changes in ambient temperature by placing it in an environmental chamber at -20C and +40C. A characteristic “temperature change” time was on the order of one minute. Sensor firmware was also updated to adjust the sensor response and detect slow changes in sub-LEL levels of natural gas concentration. A minor bug in the sensor firmware which was related to the serial SPI interface to the internal pressure sensor was also fixed. This bug had been causing occasional spikes in the pressure sensor output.

In addition to these tests, we carried extensive testing to verify that the new sensor does not respond to common household and industrial chemicals, something that plagues most commercially available detectors. At the same time, we tested a leading methane detector in the market for comparison purposes. The results were very encouraging. The sensor under development did not respond to any of the gases/chemicals tested while the leading detector sensor did respond to some of them.

Task 1.2-B ***Accelerated sensor test at third party facilities***

The performance of the commercial sample will be validated through the tests by third parties (NGA members or commercialization partners) at their facilities.

Four of assembled and tested devices were given to a leading manufacturer of methane and other detectors for testing. We are in discussions with this manufacturer regarding potential licensing of this technology for commercialization purposes. Prior to shipping the units to the manufacturer, a minor software issue in the sensor firmware, which was related to the serial SPI interface to the internal pressure sensor, was fixed. This bug had been causing occasional spikes in the pressure sensor output.

Test results of the ANI methane safety sensor (detector) conducted by this manufacturer are summarized below. The manufacturer's report states: "…The ANI sensor shows significant promise as a superior replacement for the tin oxide sensor type, with a small sensitivity to humidity and no real sensitivity to temperature". It also states that "….the Applied Nanotech alarms display an impressive level of stability over the low RH regime". However, the power consumption appears to be higher than would be desired by this manufacturer. In addition there was "….. slight evidence of a memory effect in that the sensors do not return to their initial alarm points when returned to normal humidity. The effect is much less marked than for the tin oxide sensors". The report concludes with the statement that "…..the alarms provided by Applied Nanotech show very promising performance, but it will be necessary to obtain more information about the sensor itself…"

Task 1.2-C ***Optimize and finalize calibration procedure for mass production***

The sensor calibration, setting the "zero" and the "span", in mass production will be developed and finalized.

With the final design of the boards available, we finalized the calibration procedure, as follows (some details are not presented here):

1. The sensor PCB board is fabricated and populated. There are two sensors on the PCB, an active sensor and a reference sensor.
2. The active sensor needs to be exposed to the environment that it is sensing. The board is placed in an oven at a temperature of 80-deg C for 5 to 7 days in air for aging to stabilize the sensor.
3. A number of the sensor boards should be installed in a hermetically sealed chamber (Fig. 9) for pressure and concentration calibration tests. The chamber should have a gas inlet and a gas outlet ports. The chamber accommodating several PCBs should also have sealed connectors with at

least 4 digital I/O lines for RS232 data collection together with power feedthrough port (2 lines) per sensor. The RS232 lines should be connected to RS232 level converters (one per sensor) for compatibility with a PC RS232 voltage levels. Each converter is typically connected to a Serial to USB adapter attached to a PC. A HyperTerminal program is used to record the raw sensor data. A new data line is recorded every 10 seconds.

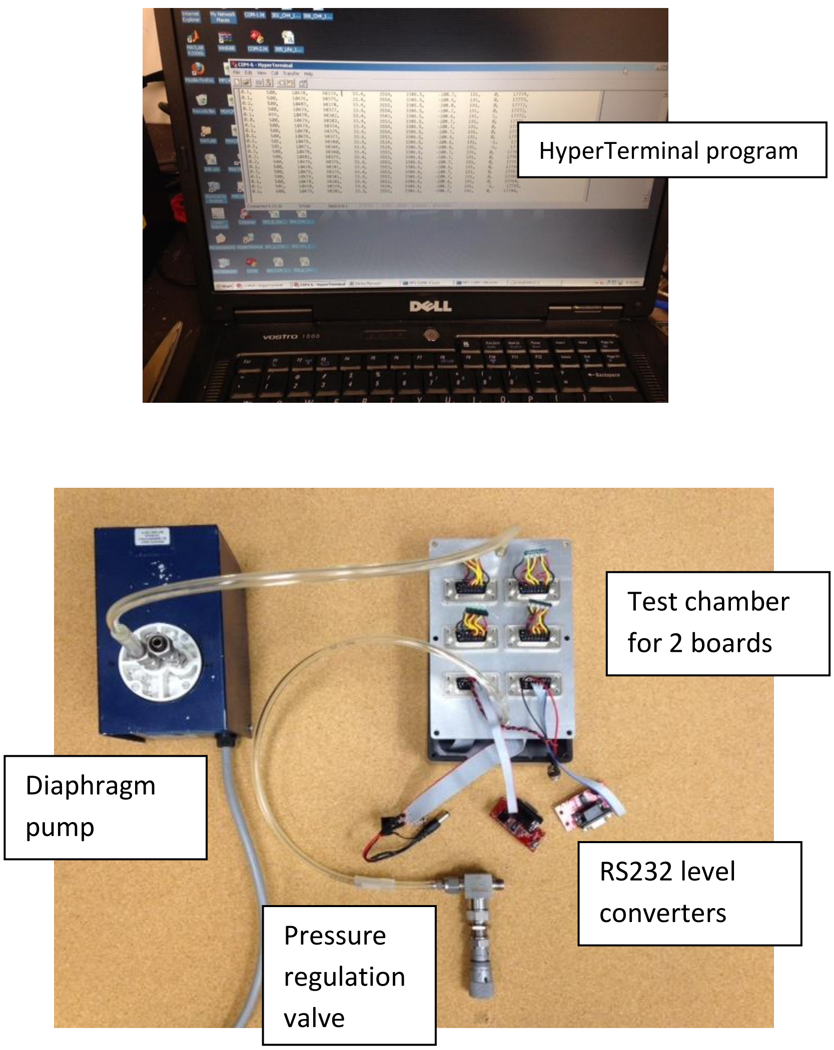

Figure 9: Pressure and concentration calibration set up

4. **Pressure calibration:** The first data file will collect data from the pressure test. In this test, the inlet and then outlet (low and high pressure side) of a diaphragm pump is connected to the inlet of the test chamber. The outlet of the test chamber is connected to valve which is used to adjust pressure inside the chamber by controlling air flow through the valve. First, the data are recorded at atmospheric pressure inside the chamber (the pump is off or the gas line is disconnected); then, the program will record sensor data at low pressure (the pump is turned on, or the line from the test chamber is connected to the pump). The pressure is set in the range of 70 kPa to 75 kPa using the control valve. Finally, at the end, the program will record sensor data at high pressure (the line is reconnected to the pump outlet). The pressure is set in the range of 110 kPa to 115 kPa using the control valve. After the test is complete, the data collection should be stopped.
5. **Methane concentration calibration:** The second data file will collect data from the concentration test. In this test, regulated methane flow is connected to the inlet of the test chamber. The outlet of the test chamber is connected to the exhaust line. First, the data are recorded in air at atmospheric pressure inside the test chamber; then the methane line is opened and the program will record sensor data at 100% methane. After the test is complete, the methane line should be closed and the data collection stopped.
6. The sensor PCBs should be assembled in the final plastic design (housing) before the temperature test.

7. **Temperature calibration:** The third data file will collect data from the temperature test. In this test, the sensors are placed inside an environmental chamber (EC, Fig. 10). The temperature tests are performed in air at atmospheric pressure. Four temperature set points should be tested. The sensors should be placed inside the EC at room temperature. The data cables will be pressed against the EC front wall by the rubber seal of the chamber door. The first temperature set point is applied. A specified temperature ramp should be used between the set points. The hold time at a given set point should be at least a preset number of minutes. After the last set point is completed, the sensors should be allowed to slowly reach room temperature to avoid water condensation. After the test is complete, the data collection should be stopped.

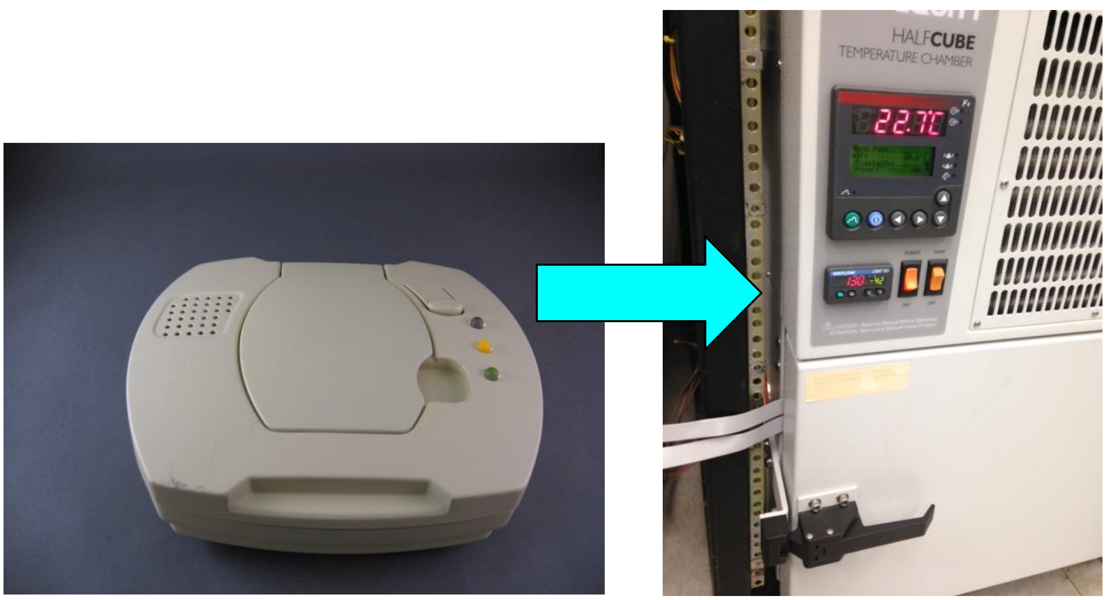

Figure 10: Environmental chamber for temperature calibration

8. The data from the three data files should be copied and pasted into the "calibration" Excel spreadsheet and the calibration coefficients (calculated from slopes and offsets of the data dependencies) data should be obtained using the embedded Excel procedures.
9. Once the calibration coefficients are obtained using the Excel spreadsheet, they are uploaded into the sensors individually via the RS232 port.

The calibration procedure was submitted to the EMS contractor (next task) and was eventually used to calibrate the units prior to UL certification.

Task 1.3-A ***Sensor design by EMS contractor***

The Electronic Manufacturing Services (EMS) contractor will develop a commercial prototype design in collaboration with ANI and the commercialization partner.

With the completion of the successful testing of the new S-sensor (detector) in the laboratory and by the potential commercializer, the design was submitted to an Electronics Manufacturing Services (EMS) contractor for design review and possible improvements. The EMS contractor is Ascendant Engineering Solutions of Austin, TX, whose task is to carry out the final design of a commercial prototype system for the "S" sensor (detector) and submit it to Underwriters Laboratories (UL) for certification. The design and operational characteristics of the detector are to satisfy the UL1484 standard, which is the standard specifying the operational and safety characteristics of residential detectors.

Ascendant carried out first a review of the final pre-commercial design completed by ANI in Tasks 1.1-A and 1.1-B above. Following the review, they developed a series of solutions to improve the design for the purpose of reducing the bill of materials (BOM), reduce manufacturing costs and ensure UL certification. A power analysis was carried out that resulted in modifications that saved ~35% of power during standby. All these changes resulted in a significant decrease of the electrical components listed in the bill of materials and dropped the System Failure Rate to less than 3.5 failures / million as required by UL standard.

Regarding the mechanical design of the housing certain changes were implemented to strengthen the housing and reduce its manufacturing cost. The

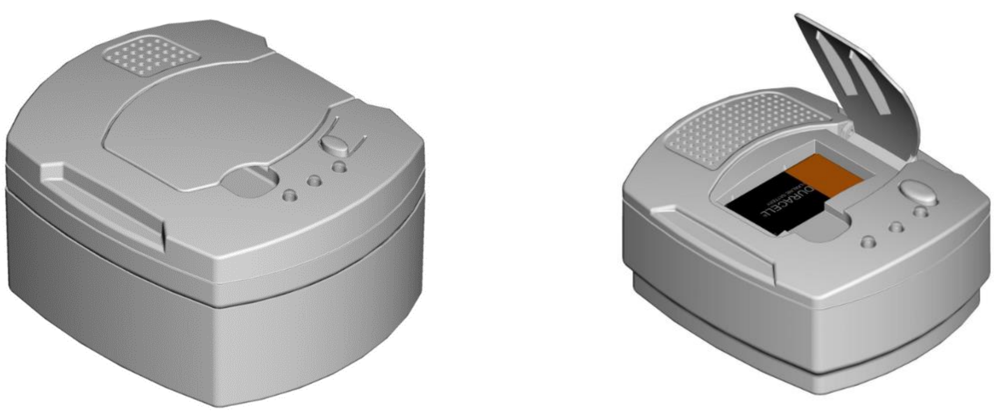

Figure 11: Initial (left) and final (right) housing design.

housing was extended downward to enclose the power supply, the package grew in the other 2 axes to maintain aesthetics, the number of vent holes above buzzer was reduced and the button configuration was modified to enhance strength. Figure 11 shows the initial and modified (final) designs of the housing. A top level assembly procedure was also developed and optimized to minimize manufacturing and assembly costs.

Ascendant completed the construction of (5) prototype boards in early May 2015 and delivered them to ANI for comprehensive testing to ensure that the manufactured detectors meet specifications. Tests identified two different issues with the electronic boards. The boards were returned to Ascendant, and the errors were corrected. The firmware on the prototypes and proper operation was checked. The boards were taken through the stabilization and calibration procedure (defined earlier). Final assembly and testing of the assembled detectors completed the effort.

Ascendant also developed the manufacturing flow diagram in preparation for submission of the detector to a contract manufacturer for construction and assembly of the 50 units to be submitted to UL. We have selected ACD in Dallas, TX, as our contract manufacturer for these 50 units.

The finalized design and performance requirements for the "A" design (analytical instrument) were also submitted to Ascendant Engineering for review and issuance of a quote for commercial system design, manufacturing and UL certification. The Finalized Design and Performance Requirements for the

Methane Sensor "A" design were developed. The project funders decided not to pursue the analytical instrument any further at this point in time but instead concentrate all efforts to the completion of the detector effort.

Task 1.3-B UL Certification and T*echnology licensing and transfer*

We envision signing an agreement or multiple agreements on the manufacturing of the sensor in "A" and "S" design configurations. Since the target users and applications of the sensors in these configurations are different (residential vs. industrial), it is possible that the sensors in different configurations will be produced and/or marketed by different business entities.

While finalizing the detector design, Ascendant initiated contact with UL to prepare the submission of the detector for certification. UL requires that all post-manufacturing processing also be performed at the manufacturing site. Given that ANI is not a UL-certified manufacturer and becoming one would be very expensive and time consuming, we will transfer all calibration and testing of the sensors to ACD, the contract manufacturer.

UL also requires a user's manual that will be included as part of the product to be submitted as part of the certification process. The manual was developed by ANI with significant input from the NYSEARCH Advisory Board for the project. In addition, UL requires that we supply the sensors in packaging that would be used to ship and sell the product. ANI developed the packaging.

UL requires the following units to be submitted for certification against the UL 1484 standard.

- 26 fully functional units that are calibrated and 'ready for sale' but not in packaging
- 2 fully functional units that have the alarm programmed to be 'on' all the time
- 2 fully functional units in retail packaging
- 2 fully functional units that have the EOL set to expire in 48 hours
- 4 fully functional units that have been acoustic tested and have the alarm programmed to be 'on' all the time (yes, different than the 2 listed above per Hugo)
- 4 fully functional units that have the alarm programmed to be 'on' all the time, but altered so the acoustic level is 10dB below the other set
- 8 back-up units

This totals 48 units. Units highlighted in yellow required some modification or reprogramming after the testing and calibration is completed at ACD (now Libra Industries). These modifications were performed by Ascendant.

Production of the longer term item, the detector housing, was completed in mid-August as were the electronic boards. Figure 12 shows the units produced by ACD.

Figure 12: Methane detector components produced by ACD for UL testing.

This was followed by the necessary testing needed to ensure the produced units met the specifications. A couple of minor issues emerged during testing (one related to the electronic boards and one with the packaging) that were resolved fairly easily. The detectors were then calibrated, following the necessary training by the lead project engineer at ANI. Figure 13 shows the ACD facilities involved in the testing and calibration efforts.

Figure 13: Calibration and testing of components at ACD/Libra.

The earlier version of the software did not support low battery level warning while plugged in. This was resolved. Current CCA design has a battery monitoring circuit that is picked up by the ADC. Software was added to read this input, and a fault alarm will sound when the battery drops below 7.5V (normal low battery point for 9V battery). This was added to code as UL programming was completed.

The required units were submitted to UL in November 2015 for Part 1 (out of 4) testing. At the same time we were working with UL on Part 2 testing that involves the alarm buzzer. Preliminary testing revealed a problem with the alarm level. The buzzer integrated onto the detector was supposed to provide sound at a level of 91 db. Test showed the resulting sound level to be around 84 dB (short of the 85 db required), results varying with the actual environment in which the test was carried out. An investigation ensued that identified the problem partially with the power supply to the buzzer. However, it appeared that the buzzer is also underperforming.

At that point in time, as Part 1 testing was completed, we froze the UL testing process to deal with the buzzer issue and a minor problem with the battery. We worked with UL to establish the best way to deal with the issues. This caused a significant delay in submitting the sensors to UL for Part 2-4 testing.

The battery issue was resolved with selection of a different battery and a minor redesign of the board and the software. The buzzer issue emerged as a major one in the sense that alternate buzzers could require the redesign of the electronics board and of the casing. We undertook a systematic study to identify a different buzzer that would meet the UL standards and minimize impact on budget and schedule. Various buzzers were integrated on the existing detector and tested in an acoustic chamber for performance. We finally selected a buzzer that should meet the UL standards but requires a redesign of the casing and the electronic size due to its larger size. The buzzer is rated at 106 db, which translates to 92 db as per UL standard (we need to meet a minimum of 85 db). This buzzer is a UL approved component, so there are no issues with its acceptance on the board.

Ascendant undertook and completed the redesign effort in mid-April 2016. At that point in time the drawings were send to the casing and electronic board manufacturers. The new detectors will be assembled by end of May 2016 and calibrated the first week of June 2016. At that point in time they will be resubmitted to UL for certification.

Regarding the commercialization of the detector and instruments, we contacted eleven (11) manufacturers and marketers of sensors and instruments for gas detection equipment. Three of them expressed initial interest and we pursued further discussions with them. Early on, one of the three decided not to continue discussions. We continued with the other two; one is a major manufacturer of methane and other detectors for residential and commercial applications and the other a major supplier of instruments to the gas industry. A number of meetings and/or conference calls followed. Following two meetings with the supplier of instruments and after providing them with prototypes of the instrument, the company decided not to pursue the opportunity further. We continued with the signing of a Non-Disclosure Agreement (NDA) with the major manufacturer of methane and other detectors after which we provided them with four prototype detectors. They carried out a series of tests for a first evaluation of the technology. The results, as discussed in Task 1.2-B, were positive. However, no further discussions took place following a change at the top management of this company. We are continuing to explore options and discuss potential licensing of the technology with interested parties.

5. RESEARCH FINDINGS AND DISCOVERIES

This research and development program, initiated in 2003, has proven that:

1. The methane sensor technology based on MicroResonator (MR) technology is a viable technology for the detection and measurement of methane.
2. The technology offers several advantages over existing technologies in terms of sensitivity to environmental factors and response to common household and industrial chemicals.
3. The sensors do not require humidity correction since it is inherently not sensitive to it.
4. Pressure correction is required to sustain acceptable accuracy.
5. Temperature effects are dealt with a proprietary system.
6. The sensor does not respond to common household and industrial chemicals. In comparative tests, the leading methane detector in the market responded to some of them.

The discoveries made in the course of this project are protected as know-how by the interested parties. Background intellectual property includes one patent. No new patent applications have been filed under this program.

6. CONCLUDING REMARKS

This project focuses on the completion of the development of a new methane sensor for natural gas applications. The effort was initiated in 2011 with funding from NYSEARCH and resulted in the development of an engineering prototype for an analytical instrument based on ANI's microresonator technology. This last phase of the program, with cofunding from PHMSA, focused on the design of the pre-commercial MR methane/natural analytical instrument, the development of an alarm sensor (detector) for residential and commercial applications based on the analytical instrument, and the design and manufacturing of commercial grade versions followed by UL certifications.

The new sensor has proven to be accurate, robust, and cost competitive. Its main advantage is the fact that it does not respond to common household and industrial chemicals thus, not generating false alarms, something that plagues the commercially available detectors. At the completion of this effort, the detector (alarm sensor) is about to be resubmitted to UL for certification.

7. REMAINING WORK

As mentioned above, the final testing of the detector by UL is to be initiated in June 2016 and completed by end of 2016. At the time of the writing of this report the 50 units to be submitted to UL for testing were being manufactured. Following receipt of UL certification, NYSEARCH will fund and execute a pilot testing program that will involve the deployment of about 150 units in the field in various parts of the US for final testing prior to commercialization.

8. DISSEMINATION OF RESULTS – PUBLICATIONS

A paper was presented at the 2016 NGA Fall Operations Conference , the prime event for NGA Operations people, held in Saratoga Springs in October 2015. The paper was very well received and many of the NGA member company representatives expressed interest in the technology.