Public Final Report

Public Final Program Report

Submitted to:

PHMSA/DoT

Development and Field Testing of a Highly Sensitive Mercaptans Instrument

Period of Performance: October 1, 2010 to March 31, 2012

Final Report

Issued: July 25, 2012

Revised: October 15, 2012

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Public Final Report

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Executive Summary

Mercaptans are sulfur compounds that are used to odorize natural gas so that leaks are apparent. They are introduced into the gas stream at various locations in the natural gas distribution system. As per DoT's regulation 49 CFR 192.625, that addresses gas odorization, Local Distribution Companies (LDCs) need to monitor the level of mercaptans in their system, in order to ensure proper levels. Currently, there is no accurate, portable mercaptans instrument in the market that would allow LDCs to carry such a test on a routine basis and replace the prevailing sniffing test. Existing gas chromatographs are expensive and bulky for this purpose. Similarly, it is imperative to be able to measure the concentration of sulfur compounds in renewable and similar gases because their interaction with components of the infrastructure can result in corrosion and other undesirable effects. Currently, they can be detected only through the use of bulky and expensive gas chromatographs.

From the above, it is clear that the industry would greatly benefit from an instrument that would allow it to measure the concentration of mercaptans in natural gas and other related gases, in the field at the parts per billion level. The objective of this project was to build and field test a new portable, low-cost instrument for the measurement of hydrogen sulfites and mercaptans, routinely encountered in natural gas, renewable natural gas, biogas, landfill gas, etc. The instrument allows the detection and measurement of such compounds at the part per billion (ppb) level, thus serving as an artificial human nose that can enhance or replace the sniffing tests currently carried out by utility personnel, or be installed in-line at gas custody transfer facilities where mercaptans concentration is currently supposed to be measured.

Two engineering prototype units were designed, built, and tested, following the successful testing of a bench top unit in an earlier phase. The unit was designed for minimum size and weight, and for maximum operating performance. This unit is powered by line power (a battery powered unit is possible with some redesign of the power system). Extensive testing showed that the instrument can indeed measure mercaptans in natural gas and in air/methane mixtures down to the level of a few parts per billion, thus being able to serve as an artificial nose. Improvements and needed enhancements will be implemented in a follow-up, commercialization phase.

1. INTRODUCTION

Mercaptans are sulfur compounds that are used to odorize natural gas so that leaks are apparent. They are introduced in the gas stream at various locations in the natural gas distribution system. Currently, the human nose can detect odorant because it is sensitive to mercaptans at levels of a few parts per billion (ppb). DoT's regulation 49 CFR 192.625, that addresses gas odorization, states that - "*each operator shall conduct periodic sampling of combustible gases to assure the proper concentration of odorant in accordance with this section."* Thus, Local Distribution Companies (LDCs) need to monitor the level of mercaptans in their system, in order to ensure proper levels. Proper level is considered a concentration that allows the average person to detect a natural gas leak that has resulted in a concentration of natural gas in air of less than 1/10 of the lower flammability limit, which is 5% natural gas in air. LDCs have dedicated employees that periodically "sniff" samples of natural gas drawn from various parts of their system and measure the level of natural gas concentration in air at which detection is sensed. If that level is below the 0.5% (1/10th of 5%) limit, then the gas is considered to be properly odorized. Given the various levels of sensitivity to smell that individuals exhibit, the test is subjective. However, there is no accurate, portable mercaptans instrument in the market that would allow LDCs to carry such a test on a routine basis and replace the sniffing test. Existing gas chromatographs are expensive and bulky for this purpose.

While sulfur compounds are artificially introduced in natural gas by operators, they exist naturally in alternate supplies of natural gas, such a landfill gas, biogas, etc, in very small concentrations (from a fraction of a ppm to a few thousand ppm). As a result, they are considered "trace" compounds. In these cases, it is imperative to be able to measure their concentration in the gas because their interaction with components of the infrastructure can result in corrosion and other undesirable effects. Currently, they can be detected only through the use of bulky and expensive gas chromatographs.

From the above, it is clear that the industry would greatly benefit from an instrument that would allow it to measure the concentration of mercaptans in natural gas and other related gases in the field. The instrument needs to be less expensive than gas chromatographs,

portable, and accurate enough to detect mercaptans at the 1 ppb level. The size of the final instrument is expected to be that of a standard business briefcase.

The objective of this project was to build and field test a new portable, low-cost instrument for the measurement of hydrogen sulfites and mercaptans, routinely encountered in natural gas, renewable natural gas, biogas, landfill gas, etc. The instrument allows the detection and measurement of such compounds at the part per billion (ppb) level, thus serving as an artificial human nose that can enhance or replace the sniffing tests currently carried out by utility personnel, or be installed in-line at gas custody transfer facilities where mercaptans concentration is currently supposed to be measured. In this last case, this technology will replace much more expensive existing gas chromatograph systems, which measure the total amount of sulfur present in the gas and not individual mercaptans components. In addition, low levels of detection are needed in order to measure these compounds in alternative fuel gases where many times they exist as trace gases. In addition, such levels of detections are needed if the current practices involving the sniffing of natural gas by company employees are to be reduced. However, even in such low concentrations, these compounds can have profound effects on emissions as well as the integrity of systems handling these gases. In an earlier phase of this program (not funded by PHMSA/DoT), the underlying science was proven viable, i.e. detection levels of the order of one ppb in air were demonstrated and the various components of the final instrument were optimized for maximum performance. The focus of the present project was to build a prototype system, based on the already proven concept, and test this prototype instrument in the field. A follow-up phase will be needed to build a market-ready instrument and commercialize it.

Starting in early 2009, NYSEARCH funded Applied Nanotech Inc. (ANI) to develop a mercaptan instrument that is based on a combination of Gas Chromatography (GC) and Differential Mobility Spectroscopy (DMS). A schematic diagram of the basic principles behind the GC-DMS technology is depicted in Figure 1a below. A gas sample is introduced into the instrument. First, the gas flows through the GC column where the components of interest (mercaptans) are separated from the rest of the gas. These components of interest eluted by the GC then flow into the DMS unit (Figure 1b), where they first flow through an ionization region, where molecules are ionized. In the ion filter, the charged molecules are

filtered according to their "mobility", i.e. the speed with which they move in an electric field of certain strength. The selected ions, both positive and negative, are then detected by collector electrodes and identified based on their mobility (which is unique for each molecule and is experimentally determined). The elemental composition of the analytes is thus determined. The technology has demonstrated capability of measuring multiple analytes in the ppb range, or better, with a high degree of selectivity and can be made relatively small and portable.

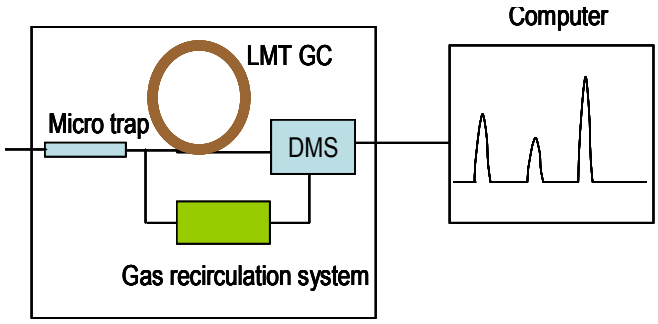


Figure 1a: Depiction of combined Gas Chromatography and Differential Ion Mobility (DMS) technology

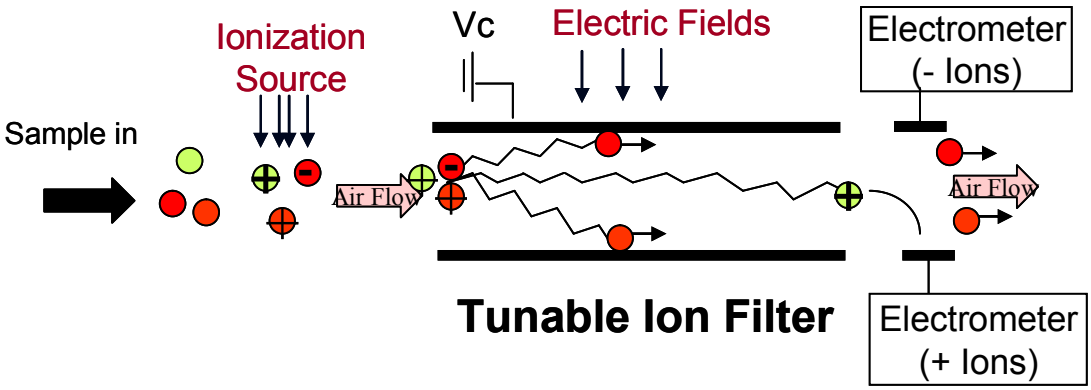
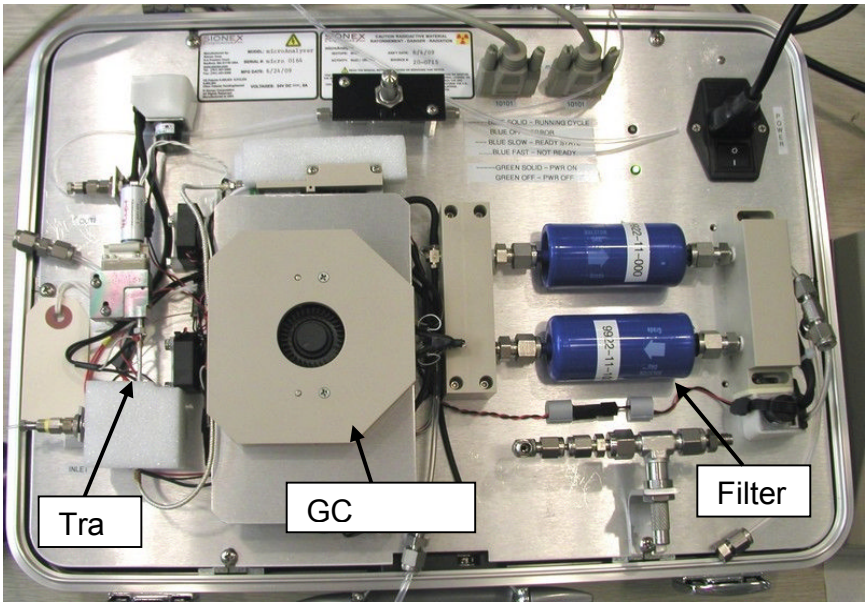


Figure 2b: Depiction of Differential Ion Mobility (DMS) technology

GC-DMS technology is included in this program (see Figure 2), which employs a standard gas ionizer (used for this and other ion mobility spectrometers) of radioactive Ni-63. Initial tests established the ability of the instrument to detect mercaptans at the ppb or near ppb level. However, a radioactive source-based instrument would impose additional regulatory requirements on the use of the instrument. As a result, a non-radioactive gas ionizer that was developed by ANI was then tested as part of the earlier NYSEARCH feasibility study, in which the GC-DMS technology with the ANI non-radioactive ionization source was benchmarked against the Ni-63 ionization source for mercaptan detection.

The earlier feasibility study focused first on establishing the ability of the technology to detect mercaptans at the ppb level. The Advisory Group for this program, consisting of experts from the NYSEARCH funding partners, chose the following mercaptans for this program: tert-butyl mercaptan (TBM), normal propyl mercaptan (NPM), iso-propyl mercaptan (IPM) and ethyl mercaptan (EtM). These mercaptans are the most widely encountered in the blends used by the natural gas industry. A GC-DMS unit, with a radioactive ionizer, was used to carry out the benchmarking of the mercaptans. The unit is configured so that components are readily accessible, allowing modifications to optimize the system.

Figure 2: GC-DMS unit. A laptop computer is used to run the data acquisition software.



Data was first collected using the Ni-63 GC-DMS unit for the four mercaptans listed above. In addition, a three component mixture of mercaptans in methane (IPM, NPM and TBM mixture) was tested. Various traps were used to identify the optimum one. However, other operational parameters, such a sample loading time and compensation voltage, were not varied to achieve optimum performance. All these tests were then repeated after replacing the radioactive ionization source with the non-radioactive one (NRI unit). Limits of detection (LOD) were calculated from the data obtained using the different traps. No data averaging or special processing was done at that point in time to reduce noise in the data, which can significantly improve the LOD.

The LODs for the Ni-63 source were of the order of 1 ppb, with some being below that and some above that. The LODs for the NRI Source were about one to two orders of magnitude higher than that with the Ni-63 source. These results were very encouraging given, again, that the GC/DMS unit had not been optimized at all to detect mercaptans. The same was true for the NRI source.

Given these very promising results a follow up phase was initiated to optimize the various system components and operating parameters to maximize the performance of the instrument, i.e. to improve the level of detection of all mercaptans below 1 ppb and to minimize the time it takes to carry out one test. This benchtop tool was the precursor to the engineering pre-commercial prototype that was built under this project.

The focus of this work was to redesign the benchtop instrument into an engineering prototype instrument. Work on the engineering prototype consisted of two primary tasks:

(a) Design, build, and test two engineering prototype units. With the components and testing parameters proven on the benchtop unit, the design process of the prototype instrument was simplified. The unit was designed for minimum size and weight, and for maximum operating performance. The portable unit is powered by line power (a battery powered unit is possible with some redesign of the power system). New electronics were designed as needed. Two units were built so that during field testing a spare unit was available. In addition, a second unit gave us the ability to implement

and test changes in operating parameters or make minor design changes in response to experience gained in the field.

(b) Field testing of the instrument. Extensive field testing took place within a NYSEARCH member company. The engineering prototype was delivered to that company and personnel were trained by ANI on the use of the instrument, sampling methods, and data analysis. The instrument was installed in-line at a receiving station in order to provide continuous live data of odorant concentrations in natural gas. ANI was available to provide field support at any point in time during the field testing effort. The experience gathered through this effort will be used to validate the system and provide us valuable information for the design of the final commercial unit (in a subsequent phase).

2. TECHNICAL DEVELOPMENT

Task A: Fabrication of Engineering Prototype

Task A Objectives

This task will take the information from the preceding program phases, and construct two engineering prototype tools for the in-line application using the non-radioactive ionizer. The units will be tested in the lab prior to field testing (Task B).

Construction of Mercaptan Sensor (non-radioactive ionization source)

The construction of the mercaptan sensor progressed from breadboard assemblies to benchtop to an integrated and packaged instrument. The sensor consists of two subsystems: DMS filter and detectors, and gas recirculation and sampling. The subsystems were constructed separately and then combined into the working instrument.

DMS filter and detectors

New DMS filter electronics and control electronics were designed and built. The microcontroller is the center of DMS system. This controller has:

1. a serial communications port;
2. two analog outputs to control RF amplitude and compensation voltage;
3. six analog inputs to measure RF amplitude, temperature, atmospheric pressure, and signals from positive and negative picoampere meters;
4. ability to supply a stable frequency signal for the RF generator.

Several electrical circuits were replicated from the benchtop tool. These circuits operated at set specifications.

Parts (filters, pumps, valves, pressure regulators, flow meters) were purchased for the prototypes. A 3-way valve allows changing the gas flow through the trap for sampling.

The measurements to be carried out by this instrument, requiring the recording of data during each step of the DMS filter DC voltage sweep, demand the use of picoampeters with the speed and stability in the sensitive measurement range required.

The controller software was installed into the microcontroller for the DMS filter operation. A breadboard system was then assembled consisting of the DMS filter, ion detectors, non-radioactive gas ionizer, system controller, and electronics.

Initial testing indicated that the system was functioning as expected. Dry air flowing through the sensor was ionized; the ions were filtered by the DMS filter and were detected by the picoammeters. *Figure* shows an oscilloscope trace for two different RF values. The oscilloscope is sweeping with the DC voltage and measuring the ion current. The ion peak position is shifted at the higher voltage.

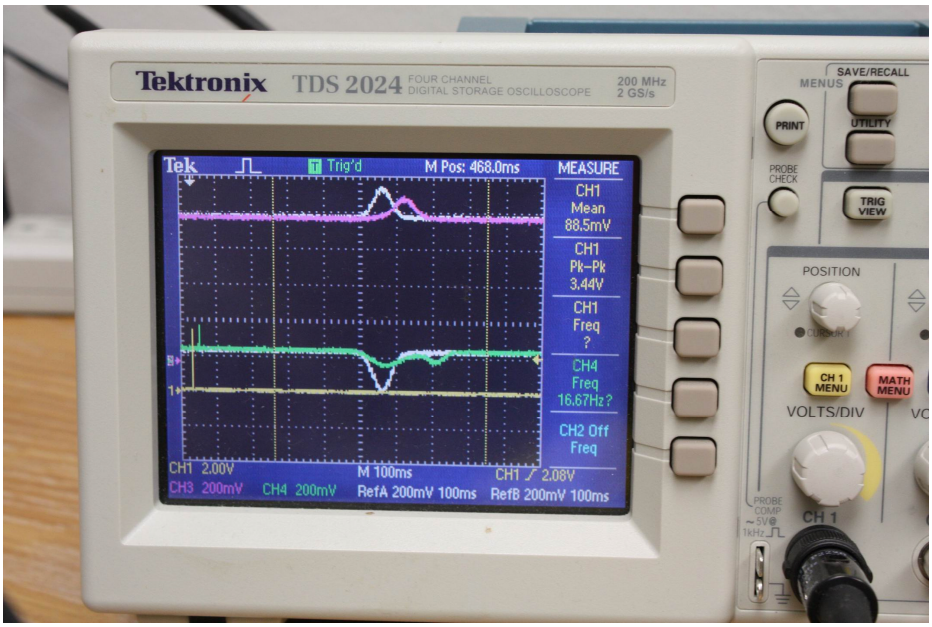


Figure 3: Oscilloscope showing DC sweep voltage and ion current detection. The shift is seen is due to different RF voltages.

After this initial successful testing, the breadboard electronics were made into printed circuit boards. The picoammeter boards are seen in Figure 4. The RF driver board is seen prior to installing the components in *Figure 5*, and with components attached in *Figure*. The boards were then assembled into a compact package for the tool (*Figure*).

The picoammeters for ion detection are very sensitive, and thus require shielding to prevent external interference with the signal. An early attempt to use a copper mesh to shield the picoammeter boards proved ineffective, and the signal was still unstable when the system was moved or an object moved nearby. After some experimentation, it was found that a solid metal shield was sufficient to shield the boards and prevent problems with interference.

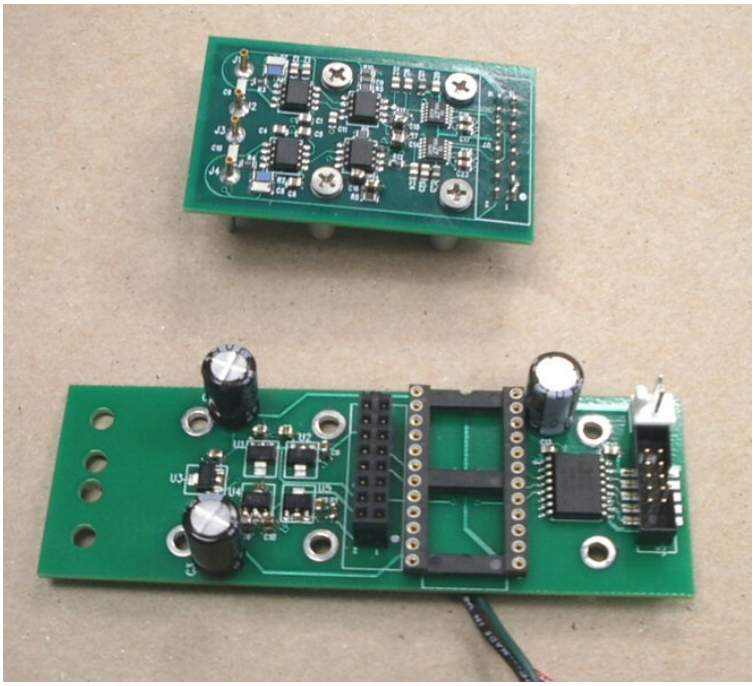


Figure 4: Picoammeter boards for ion detection.

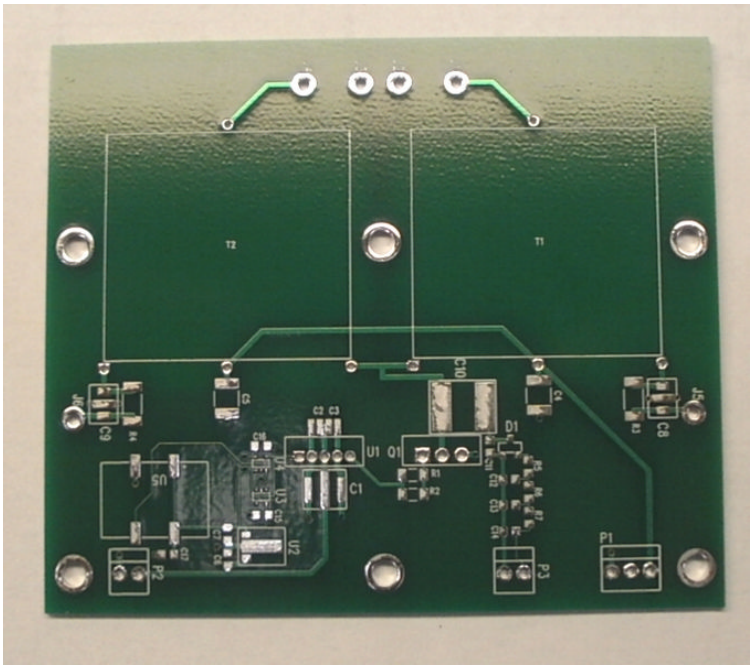


Figure 5: RF board prior to installing parts.

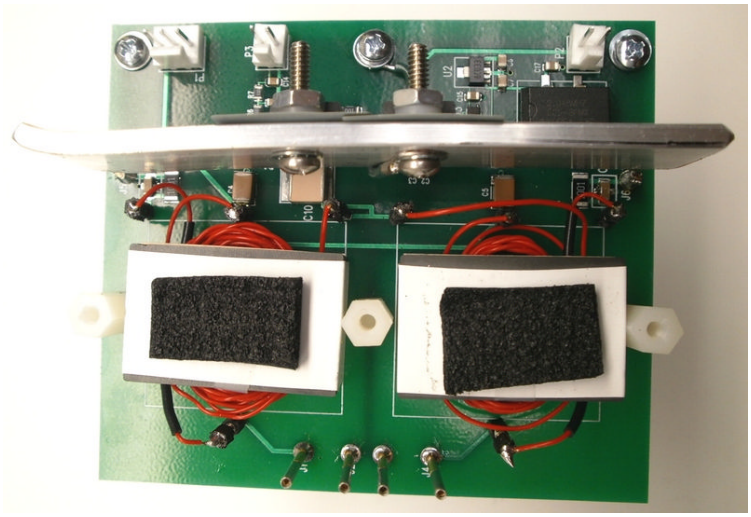


Figure 6: RF board with parts attached.

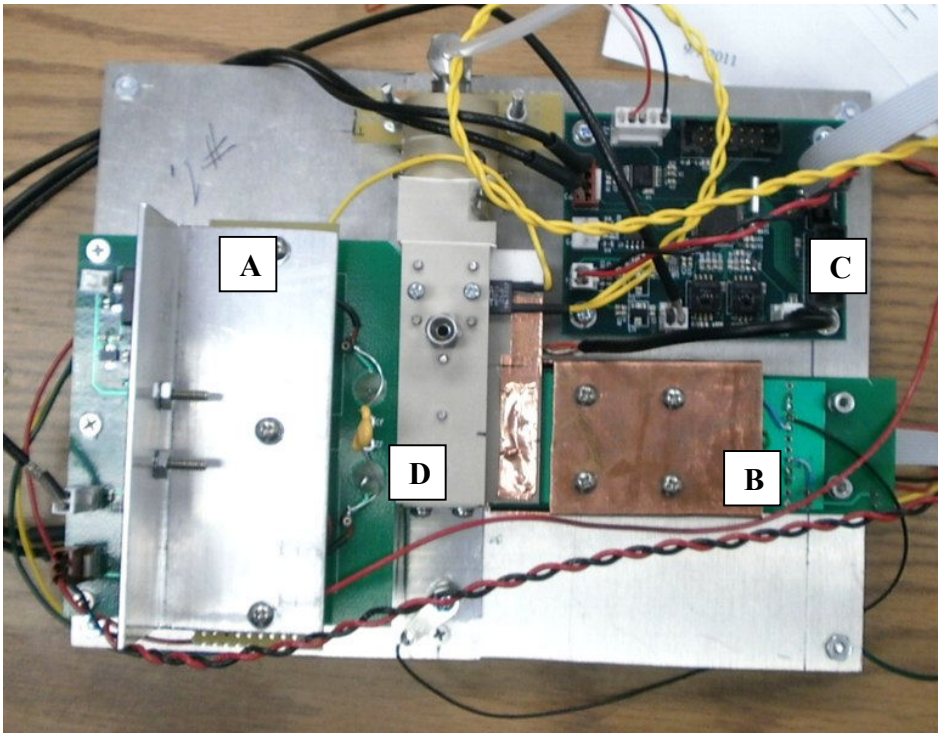


Figure 7: Assembled DMS unit. A) RF drivers, B) Picoammeters, C) Controller and D) DMS filter/sensor assembly.

Gas recirculation system

The GC column contains a custom Resistance Temperature Detector (RTD) for temperature measurement, each column requiring individual calibration for temperature control. The column was placed into an oven and the temperature was raised as the RTD resistance was measured. Over a small temperature range, the rate of change of resistance is nearly constant (see *Figure 8*). After calibration, the column was connected to the controller and the control capability was checked. *Figure* shows the plot of temperature ramp speed, settling and stability.

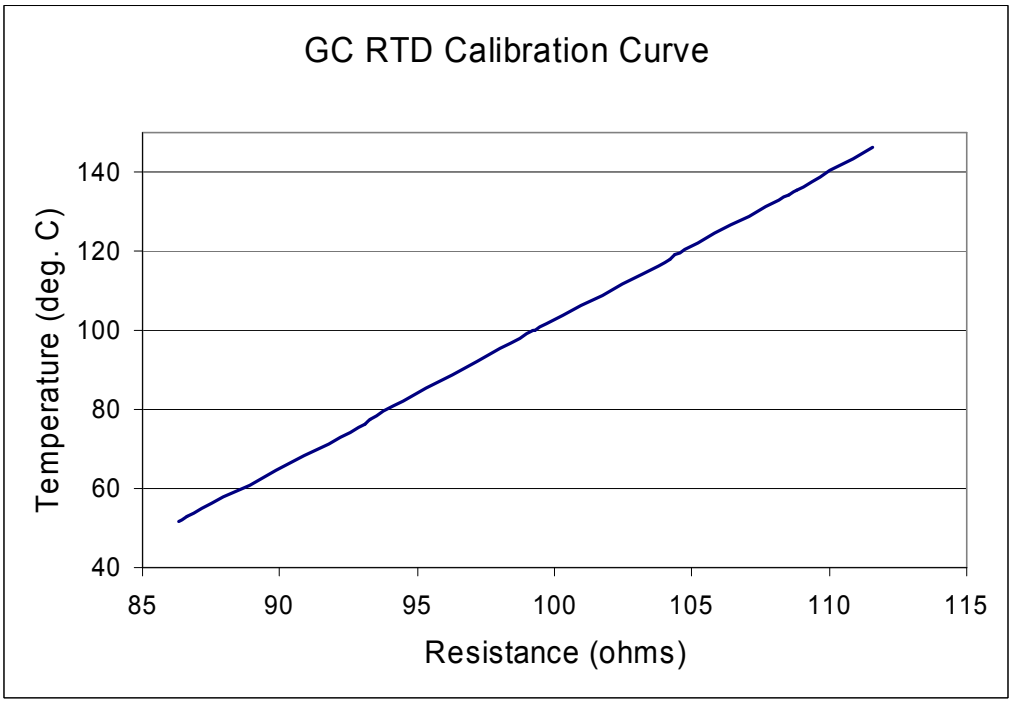


Figure 8: RTD calibration curve. The change in resistance is near linear for the temperature range of interest.

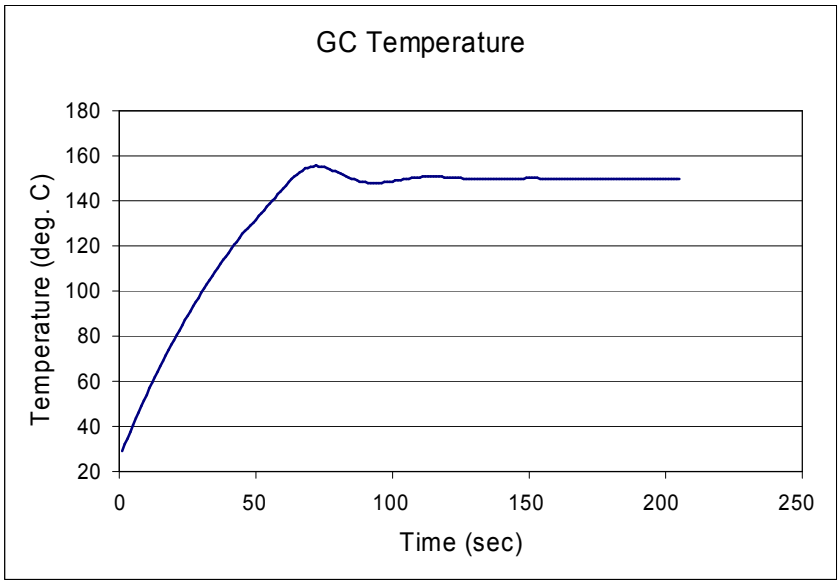


Figure 9: GC temperature control. The ramp speed, settling time and stability of the GC temperature is shown.

The recirculation system was then built as a benchtop unit and tested successfully. Once tested, the gas recirculation system was made more compact for installation into the final engineering instrument. A third filter was added to allow purging of the sampling system to reduce contamination of the carrier gas during natural gas sampling. The sample gas input and exhaust were connected through ¼" Swagelok connectors.

Instrument assembly

Once fully tested, the two completed subsystems were assembled into the two engineering prototype finished GC/DMS instruments.

Assembly of the first unit was completed in late 2011. The assembly of the second unit was completed in early February of 2012. A picture of the finished assembled instrument is shown in *Figure* .

Figure 10: Front panel of GC/DMS mercaptan sensor. All connections (power, computer control, gas input) are on the front panel.

Characterization for mercaptans

The mercaptan sensor was characterized for five mercaptans (selected by the project's Advisory Board) and a sampling protocol was finalized for an in-line application (i.e. an application where the instrument is directly sampling gas from a natural gas main or pipeline). The mercaptans tested are:

EtM: Ethyl Mercaptan

IPM: IsoPropyl Mercaptan

NPM: Normal Propyl Mercaptan

TBM: Tert-Butyl Mercaptan, and

THT: TetraHydroThiophene.

Mercaptans were purchased at a ppm level in methane gas. The methane was diluted with an artificial natural gas mixture to vary the mercaptan concentration in the test sample. A series of concentrations are tested and curves obtained for each mercaptan (Figure 11 for EtM). The curves can be used to find the concentration of mercaptan in an unknown sample gas by measuring the signal strength at the mercaptan peak location.

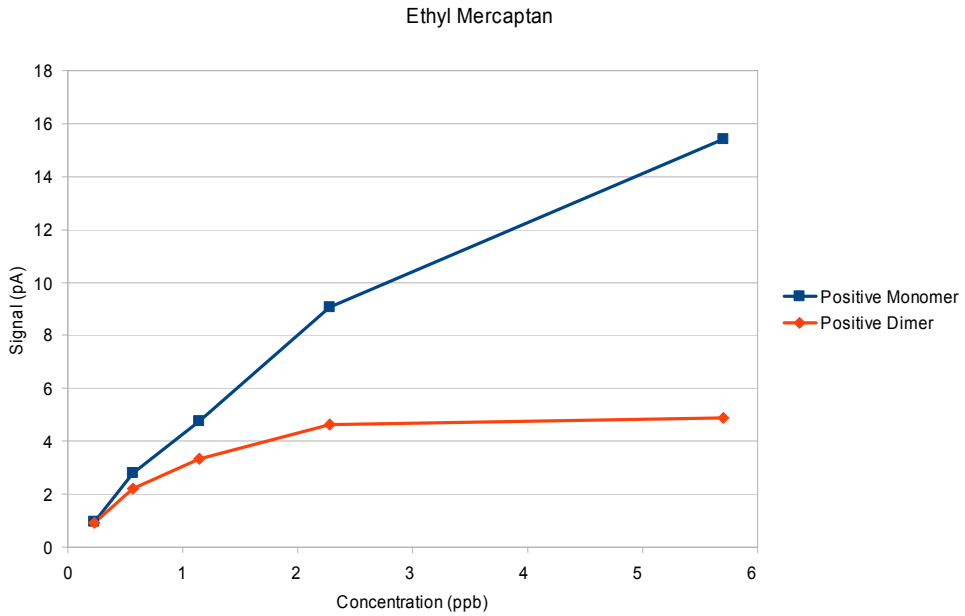


Figure 11: Ethyl mercaptan concentration curves.

Prior to field deployment another set of complete runs was made to establish the lower detection limit (LDL) of the engineering prototypes. All LDLs obtained were less than 10 ppb, as per instrument specifications.

Task B; Field Testing of Instrument

Task B Objectives

The Engineering prototype (with the non-radioactive ionizer) was field tested at a natural gas receiving facility of one of NYSEARCH's members in the northeastern US. User training, sampling methods, and data analysis was coordinated and provided as needed.

Field Test

A field test plan was drafted to outline the requirements for using the equipment for testing. The plan was made available to interested NYSEARCH companies. A company in the northeastern US was selected as the site for the first deployment of the instrument in a real-life environment.

The instrument was shipped to the designated site during the first week of January 2012. An ANI engineer travelled to the facility to install it and train the users during the second week of January.

The instrument arrived to the facility with some damage, and had to be returned to ANI for repair. Following the necessary repairs, it was returned to the site and testing commenced. Several issues arose concerning gas leaks and contamination of the system. These issues were addresses and are noted for implementation into the commercial version of the instrument.

The installation is shown in Figure 12*Figure* .

Figure 12: Mercaptan sensor installed at the natural gas receiving facility.

Data was returned to ANI from the users at the facility. Initial data showed strong sensing of the tert-butyl mercaptan in the gas line. The isopropyl and normal propyl mercaptans were not as easily seen since they are present in smaller amounts.

By increasing the sampling time, the propyl mercaptans can be measured. A change of sampling protocol, to include a short sampling period followed by a longer sampling period, allows detection of all mercaptans with a single data run.

The mercaptan content of the odorant used is known to be: TBM 75 – 80%, NPM 3 – 8%, IPM 13 – 18%. Using the mercaptan percentages and knowing the total sulfur content in the gas line measured by a titrator, the expected concentrations of mercaptans in ppm in the gas line are calculated as shown in Table 1. The graph in *Figure 13:* shows upper and lower expected levels of the mercaptan concentrations as well as the measured result.

Table 1: Comparison of measured concentrations and those encountered in the gas at the testing facility.

Mercaptan	**TBM**	**NPM**	**IPM**
Odorant % Min	75	3	13
Odorant % Max	80	8	18
Calculated ppm Min	2.092	0.099	0.429
Calculated ppm Max	2.231	0.264	0.594
Measured with Sensor	2.488	0.243	0.118

After the system had been running for several days, the measured values range near the expected values. However there is an instability of the data and the measured values are not stable or varying smoothly.

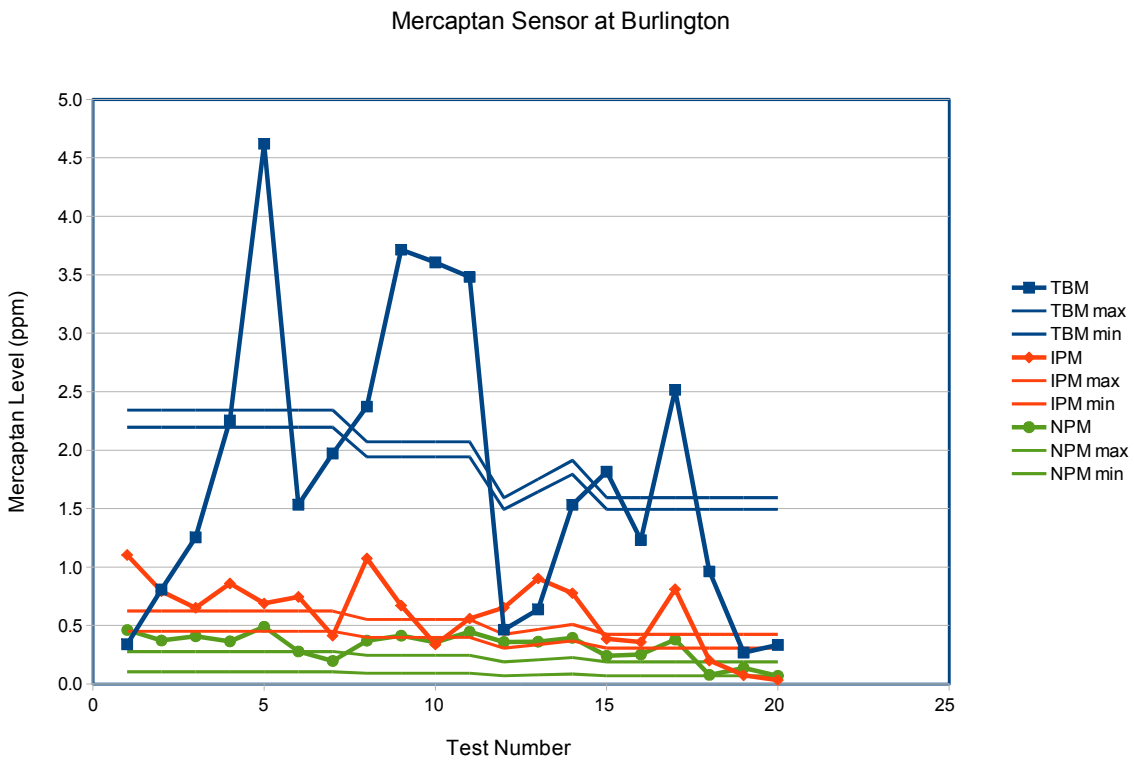


Figure 13: Graph of measured and expected mercaptan concentration in NG at the field test facility. The data points should fall between or close to the min and max lines.

A snapshot of the data is shown in Table 1. The TBM result is close to expected and the NPM is in the expected range. However the measured IPM level is less than expected. A better measurement can be made by increasing the sampling time.

During the field testing, an instability was discovered in the ionization source. The power level drifted causing a change in the ions available (from the ionized recirculated air) for ionizing the analyte. As the power level increases, more mono-nitrogen oxides (NOx) ions are generated decreasing the efficiency of the ionization process.

A graph of the current level in the ionized recirculating air (reactive ion peak, or RIP) in the positive channel over time, showing how the ionizer instability affects the ion current, is shown in Figure 14. After the ionizer is restarted, a drift upward is seen during the interval after the restart. Over longer periods of time, the current level in the positive channel drops,

due to the increase of NOx generated as the ionizer power drifts upward to higher power levels.

A power limiting control was implemented in the ionizer driver to prevent this power drift. The graph in Figure 15 shows the RIP current with the power limiting function active. The current level remains stable after restarting the ionizer and does not drift over longer time spans.

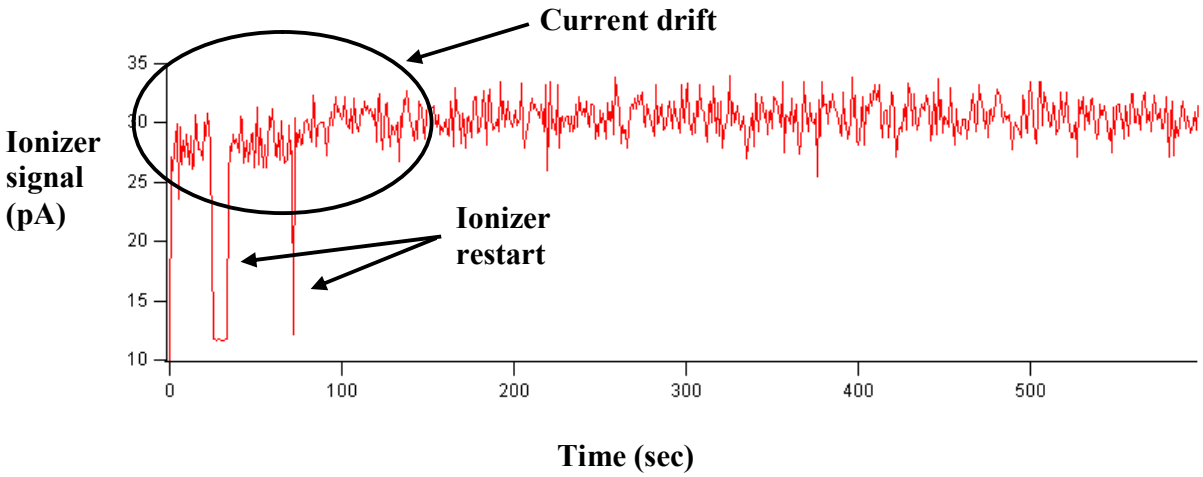


Figure 14: Current level of the ionized recirculated air (positive channel) before power stability implemented. The power drifts after the ionizer is restarted leading to a change in the ionization of the analytes.

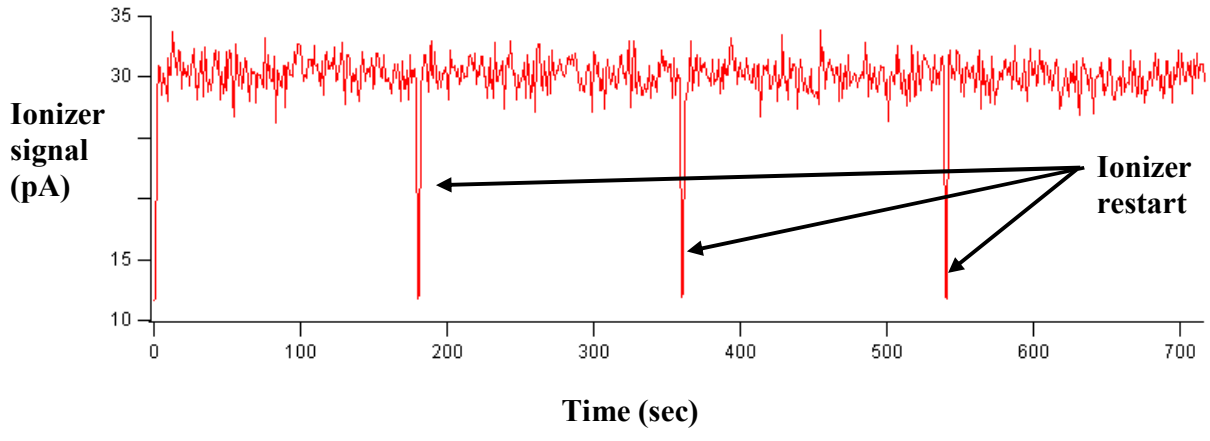


Figure 15: Current level of the ionized recirculated air (positive channel) after power stability implemented. The current stabilizes quickly after the ionizer is restarted providing a more consistent ionization of the analytes.

The issue of variations in the data is currently being examined in the lab at ANI. The second sensor unit is being used to test alternative sample and data run protocols. A solution has been identified and implemented in the tool in the lab and once verified it will be implemented in the tool in the field. The sensor in the field continues to take data for testing instrument operation.

Other features of the instrument were discussed with the group of users at the demonstration site and some suggestions were made for improving it during the commercialization phase:

1. Provide a simple output of results, showing a list of mercaptans and their respective concentrations.
2. Provide an electronic output so that the data can be automatically transmitted and recorded.
3. Modify system so that no laptop computer is required on the side.
4. Provide light indicators on the front panel that provides the user with an indication of the status of the system
5. Provide a screen on the front panel displaying the results.
6. Introduce self diagnostics for the system at power-up.
7. Provide some procedure for the periodic calibration of the system using a reference gas.
8. Provide an automatic valve for turning on and off the gas flow during the sampling period (there is no problem with flowing gas through the sensor to an exhaust, but it only needs to flow for a limited amount of time during sampling).

3. CONCLUSIONS

A program to develop and field test an engineering prototype of an instrument able to measure mercaptans concentrations in natural gas and related gases was completed successfully. Two engineering prototype units were designed, built, and tested, following the successful testing of a bench top unit in an earlier phase. The unit was designed for minimum size and weight, and for maximum operating performance. This unit is powered by line power (a battery powered unit is possible with some redesign of the power system). Extensive testing showed that the instrument can indeed measure mercaptans in natural gas and in air/methane mixtures down to the level of a few parts per billion, thus being able to serve as an artificial nose.

Following successful testing in the lab, one of the two units was deployed in the field at a facility operated by a NYSEARCH member company. A second unit gave us the ability to implement and test changes in operating parameters or make minor design changes in response to experience gained in the field. The engineering prototype was delivered to that company and personnel were trained by ANI on the use of the instrument, sampling methods, and data analysis. The instrument was installed in-line at a receiving station in order to provide continuous live data of odorant concentrations in natural gas. ANI was available to provide field support at any point in time during the field testing effort.

Overall the system operated satisfactorily. A number of issues arose that were dealt with successfully. One remaining issue, that of an apparent fluctuation of the signal after a substantial time of continuous operation, is being resolved and the identified solution will be implemented in a subsequent phase of the program, i.e. during the commercialization effort. The experience gathered through this effort will be used to implement a number of changes during that commercialization phase.