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NOVEL INTEGRATED NANO-SENSORS FOR ANALYSIS OF CHEMICAL
COMPOUNDS IN NATURAL GAS APPLICATIONS

A Capstone Experience/Thesis Project Presented in Partial Fulfillment
of the Requirements for the Degree Bachelor of Science
with Mahurin Honors College Graduate Distinction
at Western Kentucky University

By

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May 2020

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ABSTRACT

Semiconductor sensors have been important environmental gas detectors since the 1990s, and are commonly used to detect hydrogen, oxygen, alcohol vapor, and even harmful gases such as carbon monoxide. A gas chromatography approach is a well-proven and compact separation technique to identify and quantify multiple compounds in a complex background such as a true natural gas environment. Real time field monitoring implementing classical GC and standard sensors (FID, PID, etc.) have a lot of limitations due to its bulky size, heavy weight, and high maintenance. In this study, we developed a portable instrument through the utilization of novel solid-state sensors for real-time identification and quantification of target compounds in natural gas, which include hydrogen sulfide, benzene, mercaptans, ethylbenzene, toluene, xylene, vinyl chloride, and trimethylarsine. The initial phase of this project was devoted to the development of our portable device prototype, and its testing in methane background. Specific detection limits both in methane and in air for each of the gas components, together with the other specifications, were explored. The result of these first tests was the successful detection and quantification of our compounds of interest diluted in 99% methane. Now that the device has been tested in methane background, the goal of this project is to calibrate and test the prototype device in a true natural gas environment.

ACKNOWLEDGEMENTS

I would like to thank Dr. Vladimir Dobrokhotoy for his role as my first reader and research advisor. I would like to thank him in addition to Dr. Michael Carini and Dr. Gordon Emslie for forming my committee. I would like to thank Dr. Dobrokhotoy for his mentorship in the lab, as well as the Applied Physics Institute. Finally, I would like thank the WKU Department of Physics and Astronomy for their continuous support of my academic and professional endeavors.

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LIST OF ABBREVIATIONS IN THIS WORK

FID	flame ionization detector
PID	photoionization detector
GC	gas chromatography
ppm	parts per million
ppb	parts per billion
sccm	standard cubic centimeters per minute
VOC	volatile organic compound

INTRODUCTION

The detection and analysis of gases and vapors is an important part of the modern world. Gas sensing technologies improve the self-sustainability of our society, as well as the quality of everyday life. A variety of gas analysis techniques and gas detectors are regularly used to improve safety and establish more precise product quality control and process control.^{1,2} Some industrial sectors such as the food/medicine, automotive, heavy industry, environmental, security, and home appliances sectors have utilized gas analysis for a wide range of applications.³⁻⁶ This project is devoted to the development of a portable instrument for identification and quantification of target compounds in natural gas. The target compounds include hydrogen, sulfide, mercaptans, benzene, toluene, ethylbenzene, xylene, vinyl chloride, and trimethylarsine.

Gas chromatography is useful for separating different components in a mixture for identification and quantitative analysis.⁷ Classical GC with standard sensors (FID, PID, etc.) possess fundamental barriers and limitations due to its bulky size, high maintenance, heavy weight, and special carrier gases requirement. Special carrier gases require the use of bulky tanks, which attach to the instrument for operation. This is the major drawback of classical GC, because it limits portability. Natural gas contains trace amounts of impurities, and analytes targeted in this study were found at concentrations as low as 3 ppm. In several studies, the use of PID as gas sensors have shown less repeatable readings at lower concentrations, such as (<50 ppm) and even (<10 ppm).^{8,9} Therefore, the inability to consistently detect low concentrations of target analytes is a key flaw in PID.

In order to achieve sufficient portability and optimal sensitivity, this project utilizes a novel solid-state metal oxide detector with compact gas chromatography (GC) sampling

system. Relatively inexpensive compared to other sensing technologies, the key advantage of the novel solid-state metal oxide detector for portable real-time gas chromatography is the novel nanocomposite metal oxide MEMS sensors array.¹⁰ Nanostructures are defined as having at least one dimension between 1 and 100 nm, and are sought after for their unique chemical and physical properties compared to bulk counterparts.¹¹ Since the early 1960's, the sensing capabilities of metal oxides have been known.¹² The gas sensing process is strongly related to surface reactions, so the sensitivity of metal oxide materials will change with the factors influencing surface reactions, such as chemical components, surface modifications, temperature and humidity.¹³

The gas sensing process for our detector involves the following. A key component of any sensor is a chemiresistor, a device whose electrical resistance can be changed by absorption onto its surface. The changes in resistance are directly proportional to the partial vapor pressure in the atmosphere, so a chemiresistor converts the concentration of chemicals in the atmosphere into a measurable corresponding electrical signal.² Chemiresistors work as building blocks for integrated sensors, and metal oxides are common chemically sensitive materials. This study's multisensory detector utilizes metal-oxides for their unique sensing capabilities, and the catalytic reactions of gaseous species with oxygen sites on the surface induce charge transfer from the surface to the bulk, changing the electrical resistance of the device and therefore creating a signal.

The choice of materials for the detector was motivated by a long series of experiments conducted by Dr. Dobrokhotov's lab over ten years. In Phase IIB of this project, sensor characteristics such as the optimal operational temperature, response value (R_{air}/R_{gas}), time of response (T_{90}), and detection limit upon steady exposure to low

concentration of analytes were obtained. As a result of this study, a quasi-orthogonal array of sensors was developed, demonstrating high sensitivity, fast response and recovery times, and orthogonality of sensors in the detector for separation of chemicals.

This sensors array demonstrates outstanding performance for detection of ultra-low concentrations of gases and vapors, unlike classical GC with standard PID sensors. The detector utilizes air as the carrier gas for the GC column, which allows for easy portability because it is not burdened with the bulk of compressed zero grade gases required by more traditional gas chromatographs. Phase II of this project was devoted to the development of a portable device prototype and its testing in methane background. The outcome of Phase II was successful detection and quantification of compounds of interest diluted in 99% methane background. Phase III of this project is devoted to the calibration and testing of the device developed in Phase IIB in a true natural gas environment. The methodology was as follows.

Table 1. Types of background natural gas blends for testing of the device.

Component	Rich Gas	Lean Gas	Restek
Methane (%)	92	96	95
Ethane (%)	3.10	1.74	2.00
Propane (%)	0.44	0.19	0.75
i-Butane (%)	0.10	0.020	0.30
n-Butane (%)	0.11	0.030	0.30
i-Pentane (%)	0.080	0.010	0.15
n-Pentane (%)	0	0	0.15
n-Hexane (%)	0.060	0	0.10
n-Heptane (%)	0.040	0	0
n-Octane (%)	0.020	0	0
Total c6+	0.12	0	0
Nitrogen (%)	2.00	1.8	0
Oxygen (%)	0.10	0.010	0
Carbon Dioxide (%)	1.5	0.61	0
Benzene (ppmv)	95	0	X
Toluene (ppmv)	103	0	X
Ethyl Benzene (ppmv)	10	0	X

Ortho Xylene (ppmv)	43	0	X
Hydrogen Sulfide (ppmv)	1.0	0.20	0
Cyclopentane (ppmv)	29	0	0
Methylcyclohexane (ppmv)	5.7	0	0
Cyclohexane (ppmv)	68	0	0
Dimethylcyclopentanes (ppmv)	23	0	0
Methylcyclohexane	55	0	0
Trimethylcyclopentanes	9.5	0	0
H2O (lbs/mmscf)	7.0	0	0
BP Captan (lbs/mmscf)	1.0	0.20	0

METHODOLOGY

The specifications of gas composition blends were provided by NYSEARCH and the blends were purchased directly from third party vendors. The calibration for target analytes was conducted in clean dry air, calibration curves were obtained and verified, and the ability of the analyzer to conduct measurements in natural gas as tested in three different backgrounds as listed in Table 1. The initial testing was conducted in the RESTEK natural gas standard, followed by testing in the lean and rich gas. Using calibration curves, the target analytes were added to the standard background blends in known concentrations and then identified and quantified by the analyzer. The ability to detect and quantify target analytes in each of the three blends is summarized. The percent errors for every target analyte in each of the natural gas background blends were identified.

Device Calibration

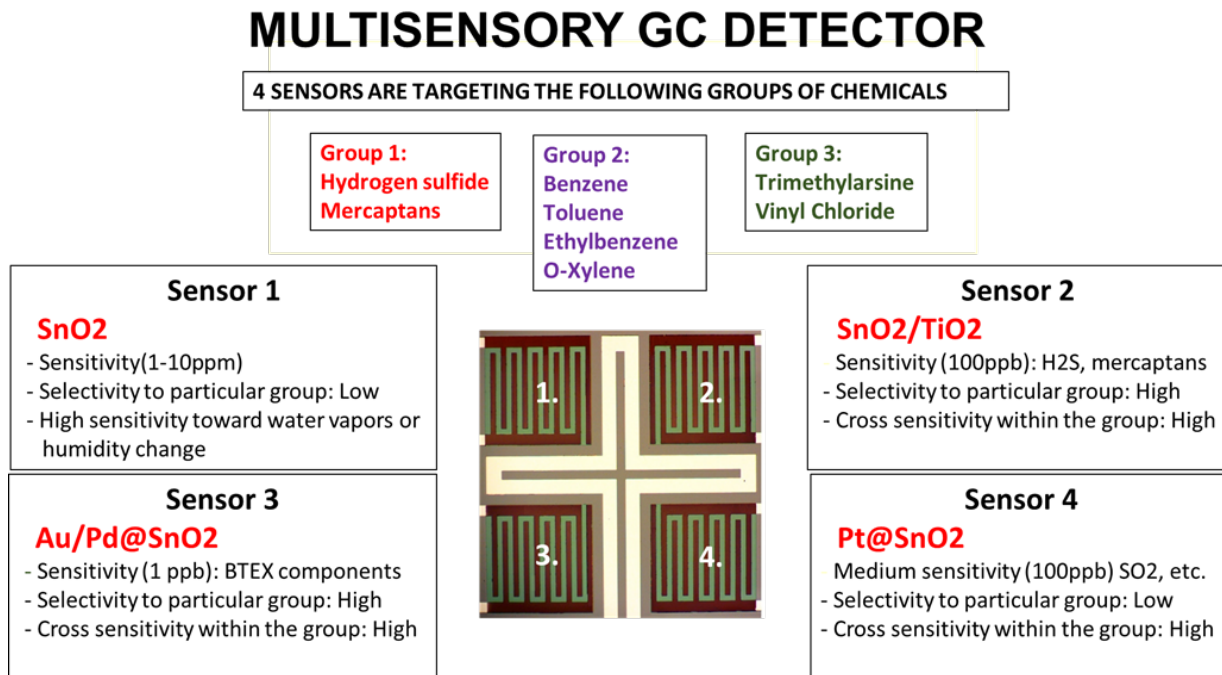


Figure 1. Chemical composition, sensitivity and specificity of the integrated detector.

The structure of the integrated detector is shown in Figure 1. In this project, the calibration was accomplished using the sensors as follows. Sensor 1 was only used as a background sensor. Sensor 2 was calibrated for hydrogen sulfide and ethyl-mercaptan (Group 1). Sensor 3 was calibrated for benzene, toluene, ethylbenzene and o-xylene (Group 2). Sensor 4 was calibrated for vinyl chloride and trimethylarsine (Group 3). All chromatogram plots are presented as R_{air}/R_{gas} vs time, where R_{air} is the initial value of resistance when zero air is flowing over the detectors. The integrated sensor's signal is the total area under the sensor's response (R_{air}/R_{gas}) curve for particular time interval associated with specific gas after the background is subtracted.

Before the calibration of target analytes, the instrument's background was analyzed by using zero grade air from AirGas (Figure 2). The flat background from all four sensors indicates there is no contamination inside the GC. The small peak between 350 and 400 seconds was identified as a water peak based on polarity, boiling point, and molecular mass.

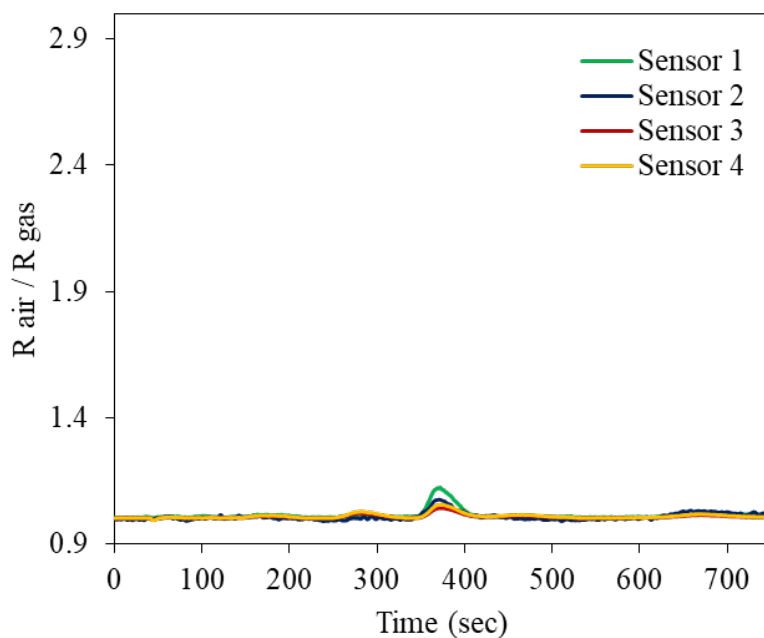


Figure 2. Detector's background signal obtained by analyzing ultra-zero grade air from AirGas

In gas chromatography, separation occurs when the sample mixture is injected into a mobile phase. In this experiment, the mobile phase was the carrier gas of the device (clean dry air). The mobile phase carries the sample mixture with different target analytes through a stationary phase, or the GC column. The mixture of compounds within the GC column interact with the stationary phase, and each analyte interacts at a different rate based on their adsorption characteristics and volatility. Those that interact fastest will exit the

column first, and vice versa. As the analytes are separated, they exit the column and enter a detector, which makes an electronic signal whenever the analyte is detected. The greater the concentration, the bigger the signal. The retention time is the time from when the injection occurs to when the analyte exits the GC column. After the background of the analyzer was recorded, the retention time for each gas was found (Table 2) from both theoretical calculations and experimental data collected under constant GC operational parameters: carrier gas (clean dry air) flow rate of 11 sccm and column temperature of 55 °C. The width of the integration window was also determined based on experimental data for maximum concentrations of detectable gases (Table 2). After the retention time and integration window for all detectable analytes were calculated, the calibration of the detector to specific gaseous components was performed.

Table 2. Retention time and the integration window width for target analytes.

Gases	Retention time (sec)	Integration window width (sec)
Hydrogen sulfide	44	17
Ethyl-mercaptan	61	29.
Benzene	140	70
Toluene	240	100
Ethylbenzene	410	120
O-Xylene	605	130
Trimethylarsine	54	15
Vinyl chloride	85	35

Calibration for Group 1 (Hydrogen Sulfide and Ethyl-Mercaptan)

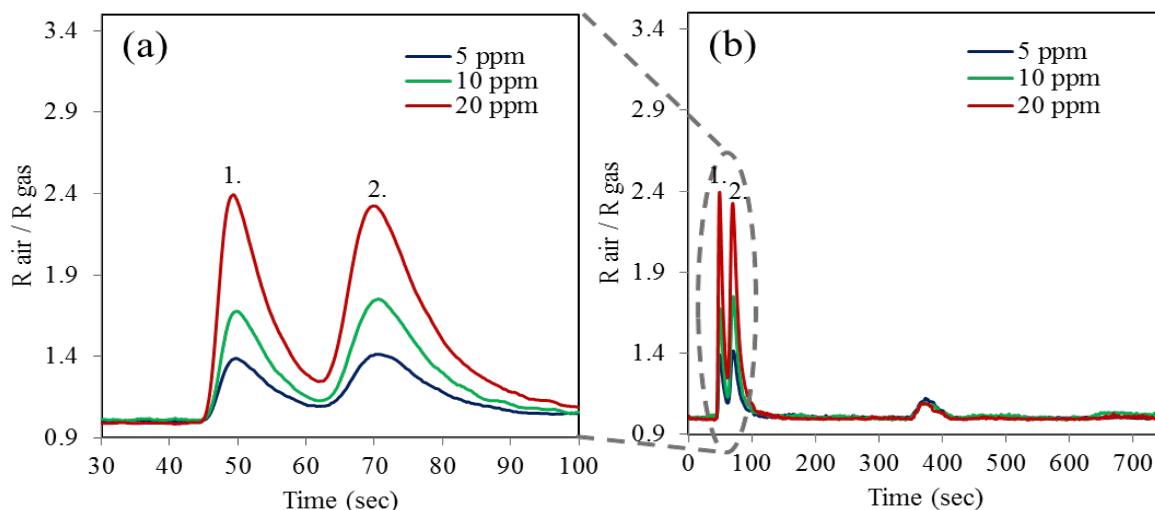


Figure 3. Gas chromatogram for 1. hydrogen sulfide and 2. ethyl-mercaptan (a) A detailed view of 1. hydrogen sulfide (5, 10 and 20 ppm) and 2. ethyl-mercaptan (5, 10 and 20 ppm) peaks and (b) full chromatogram over the time period of 750 sec.

Calibration cylinders of H_2S and ethyl-mercaptan at 200 ppm were used to generate the 5, 10, and 20 ppm gas samples used in this project. Figure 3 shows the chromatograms obtained on the same day for three different concentrations (5, 10, and 20 ppm) of hydrogen sulfide and ethyl-mercaptan in zero grade air by using Sensor 2 ($\text{SnO}_2\text{-TiO}_2$). The analysis of different concentrations of both analytes in Group 1 in zero grade air was repeated over five days. The integrated sensor response for hydrogen sulfide and ethyl-mercaptan was calculated by integrating the area under the curve over a specific time interval. In order to do that, a Gaussian fit was applied to the desired peaks. The peaks were identified, and the refraction windows were specified based off early experimental data (see Table 2 for integration window widths). A Gaussian fit was then applied, and if there were multiple overlapping peaks, as was the case for later tests in natural gas background, local maxima

were specified. This same process was used after calibration, during tests in natural gas background.

Table 3. Summarized results for detection of different concentration (5-20 ppm) of hydrogen sulfide and ethyl-mercaptan in zero grade air over five-day period.

Testing Day	Concentration (ppm)	Integrated signal (Hydrogen sulfide)	Integrated signal (Ethyl-Mercaptan)
1	5	3.0	5.8
1	10	5.1	11
1	20	10	18
2	5	3.1	5.5
2	10	5.8	11
2	20	12	19
3	5	3.5	6.1
3	10	6.0	11
3	20	11	17
4	5	3.5	6.2
4	10	6.0	11
4	20	11	17
5	5	4.0	5.8
5	10	6.0	9.7
5	20	11	17

The integrated response of Sensor 2 ($\text{SnO}_2\text{-TiO}_2$) was then plotted as a function of gas concentration in Figure 4. The response of Sensor 2 ($\text{SnO}_2\text{-TiO}_2$) to different concentrations of Group 1 analytes were found to be stable and repeatable over a five-day period. The average integrated signal was then calculated for each gas concentration of hydrogen sulfide and ethyl-mercaptan. The calibration curve for hydrogen sulfide and

ethyl-mercaptan in the range of 5-20 ppm is best expressed by linear approximation in Figure 5.

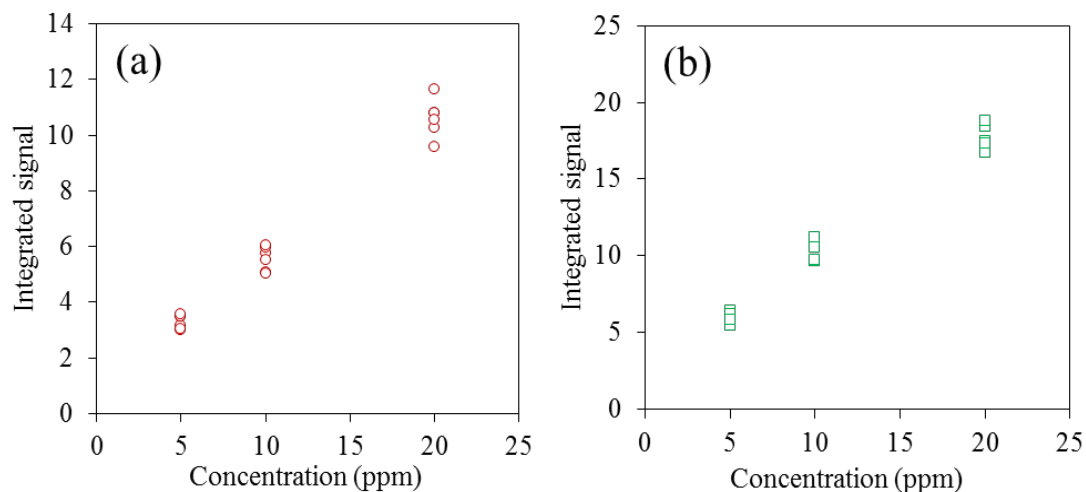


Figure 4. Graphs of integrated signal vs. corresponding gas concentration for (a) hydrogen sulfide and (b) ethyl-mercaptan collected over time period of 5 days.

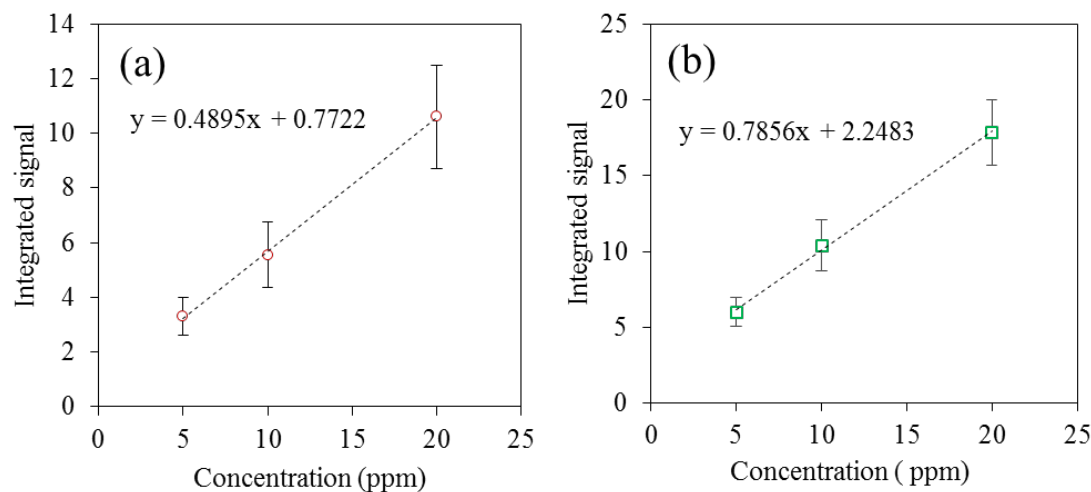


Figure 5. Calibration curves for detection of (a) hydrogen sulfide and (b) ethyl-mercaptan in a concentration range between 5-20 ppm in zero grade air.

Calibration for Group 2 (Benzene, Toluene, Ethylbenzene and O-Xylene)

Among VOCs (volatile organic compounds), BTEX is of immense concern. Even a small concentration of BTEX compounds has a significant negative impact on human health, and benzene is the most dangerous chemical among BTEX components due to its high carcinogenicity.¹⁴ Therefore, its detection in natural gas is of immense importance. Four different concentrations of BTEX components Mix. 1 – Mix.4 were used for calibration of Sensor 3 (Table 4). The analysis of the calibration standard (Mix 1) was first and the chromatograms from the sample were stored. Calibration concentrations (Mix. 2 – 4) with higher amounts of BTEX components were generated from liquid headspace concentrations of BTEX. The integrated signals for BTEX analytes were found by calculating the area under the curve of the chromatograms (Figure 6).

Table 4. Actual BTEX concentrations used for calibration of sensor 3.

Gas	Benzene Conc. (ppm)	Toluene Conc. (ppm)	E-Benzene Conc. (ppm)	O-Xylene Conc. (ppm)
Mix. 1	10	10	10	10
Mix. 2	54	57	6.6	18
Mix. 3	109	114	13	37
Mix. 4	163	171	20	55

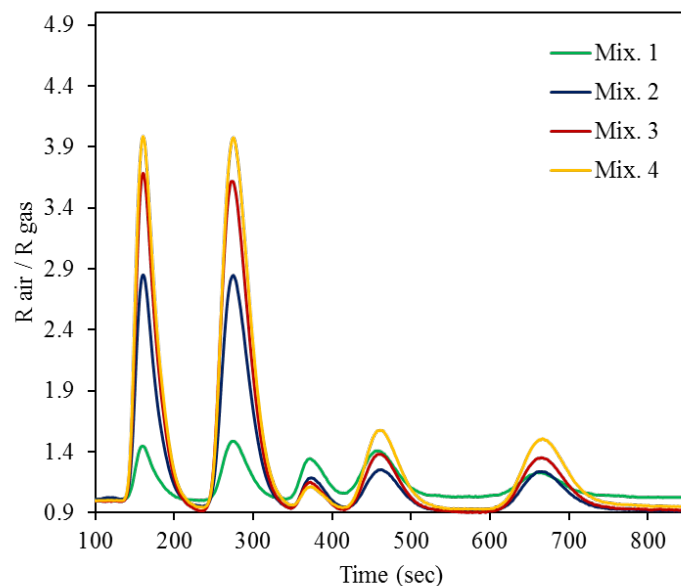


Figure 6. GC analysis of BTEX mixtures (Mix. 1 - Mix. 4) in zero grade air. Five consecutive peaks correspond to: 1. Benzene, 2. Toluene, 3. Water, 4. Ethylbenzene, and 5. O-Xylene.

Sensor 3's (Au/Pd@SnO₂) response to different concentrations of BTEX analytes were observed over a three-day period. The calculated values of the integrated sensor response for each gas are summarized and shown in Table 5.

Table 5. Summarized results for detection and quantification of different concentrations of BTEX components (Mix. 1- Mix.4) in zero grade air over three days.

Day	Concentration (ppm)	Integrated signal (Benzene)	Integrated signal (Toluene)	Integrated signal (Ethylbenzene)	Integrated signal (O-Xylene)
1	Mix. 1	13	19	23	18
1	Mix. 2	60	79	18	22
1	Mix. 3	85	111	24	30
1	Mix. 4	96	127	35	43
2	Mix. 1	14	20	24	19
2	Mix. 2	68	93	24	33
2	Mix. 3	89	118	27	37
2	Mix. 4	103	140	42	51

3	Mix. 1	14	20	23	19
3	Mix. 2	64	86	21	27
3	Mix. 3	87	115	26	33
3	Mix. 4	99	133	38	47

The calibration curves for benzene and toluene are shown in (Figure 7 a,b). Calibration curves for benzene and toluene analytes are non-linear, due to the range of expected concentrations in natural gas being quite large. Multiple runs were performed and variability is shown in the error bars on the curves. The calibration curves for ethylbenzene and o-xylene are best represented by a linear approximation (Figure 7 c,d).

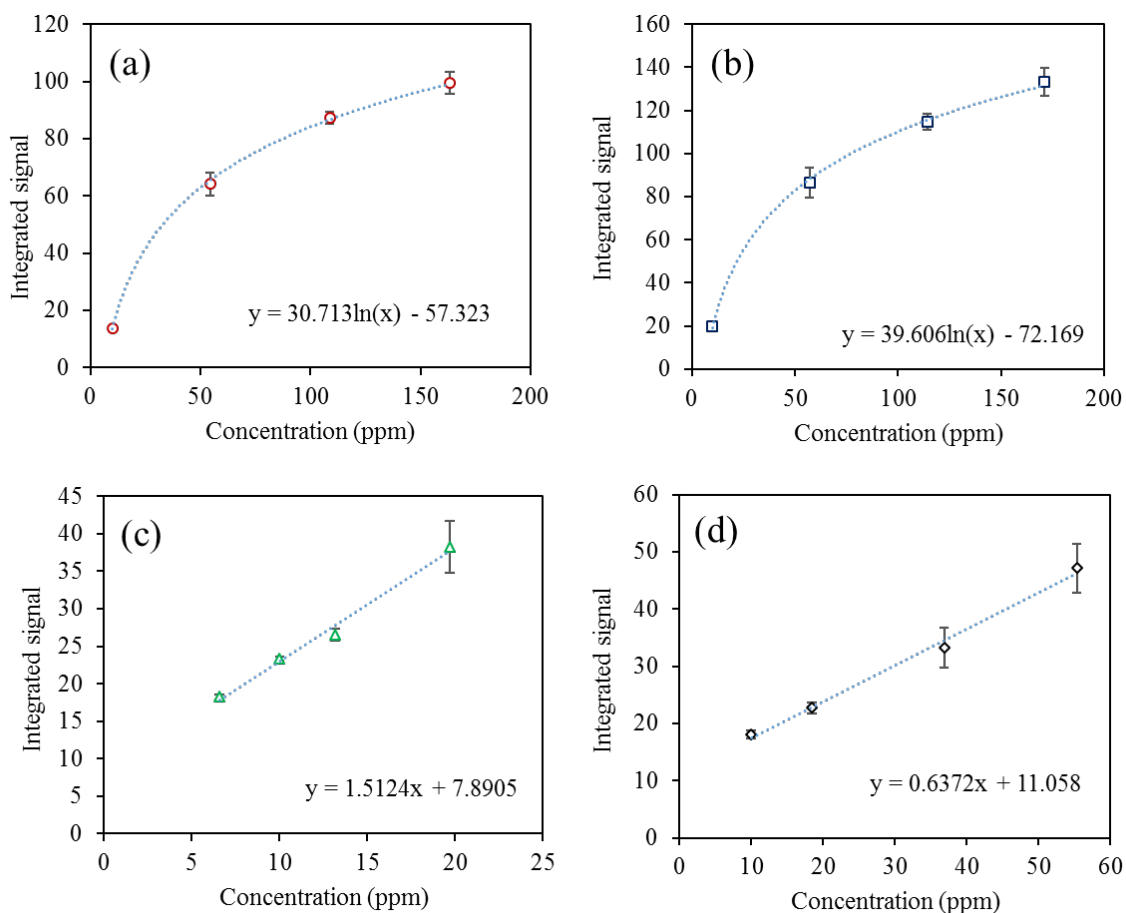


Figure 7. Calibration curves for (a) Benzene, (b) Toluene, (c) Ethylbenzene and (d) O-Xylene.

Calibration for Group 3 (Trimethylarsine and Vinyl Chloride)

Calibration cylinders of trimethylarsine and vinyl chloride were used to generate 1, 5, and 10 ppm samples used in this experiment. The chromatograms (Figures 8 and 9) were obtained over one day under analysis of three different concentrations (1, 5, and 10 ppm) of Group 3 analytes in zero grade air by using Sensor 4 (Pt@SnO₂).

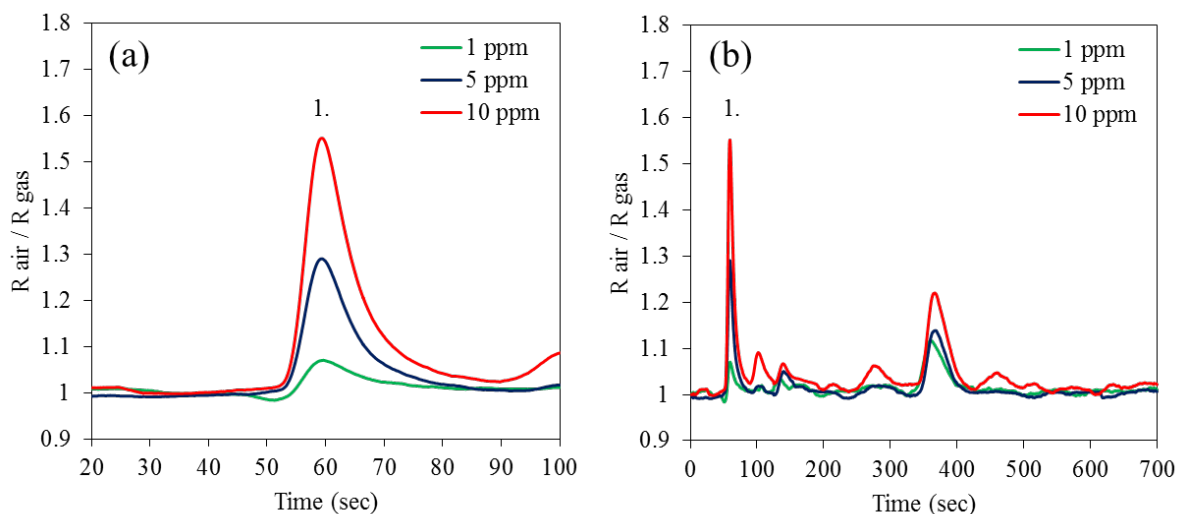


Figure 8 (a) Zoomed image of 1. trimethylarsine peak (1, 5 and 10 ppm) and (b) full chromatogram over the time period of 700 sec.

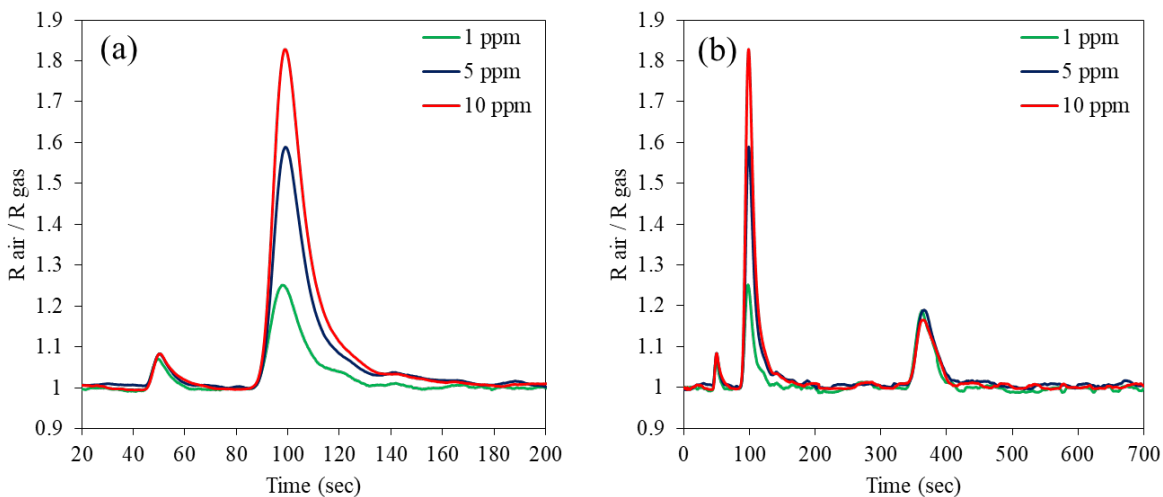


Figure 9 (a) Zoomed image of 2. vinyl chloride peak (1, 5 and 10 ppm) (b) full chromatogram over the time period of 700 sec.

The analysis of different concentrations (1, 5, and 10 ppm) of Group 3 in zero grade air was repeated over a span of three days. The integrated response signal for trimethylarsine and vinyl chloride was calculated by taking the area under the curve of the chromatograms over a specific time interval, and the final results are shown in Table 6.

Table 6. Summarized result for detection of different concentration (1-10 ppm) of trimethylarsine and vinyl chloride in zero grade air over three days.

Testing Day	Concentration (ppm)	Integrated signal (Trimethylarsine)	Integrated signal (Vinyl Chloride)
1	1	0.72	3.7
1	5	3.1	8.5
1	10	5.2	12
2	1	0.82	3.9
2	5	2.7	8.7
2	10	4.7	12
3	1	0.8	3.8
3	5	2.7	8.6
3	10	5.1	12

Then, the integrated response signal of Sensor 4 (Pt@SnO₂) was plotted as a function of gas concentration. The average of the integrated signal was then calculated for each gas concentration of Group 3. In Figure 10, the calibration curve for trimethylarsine and vinyl chloride from 1 – 10 ppm is best expressed by a linear approximation.

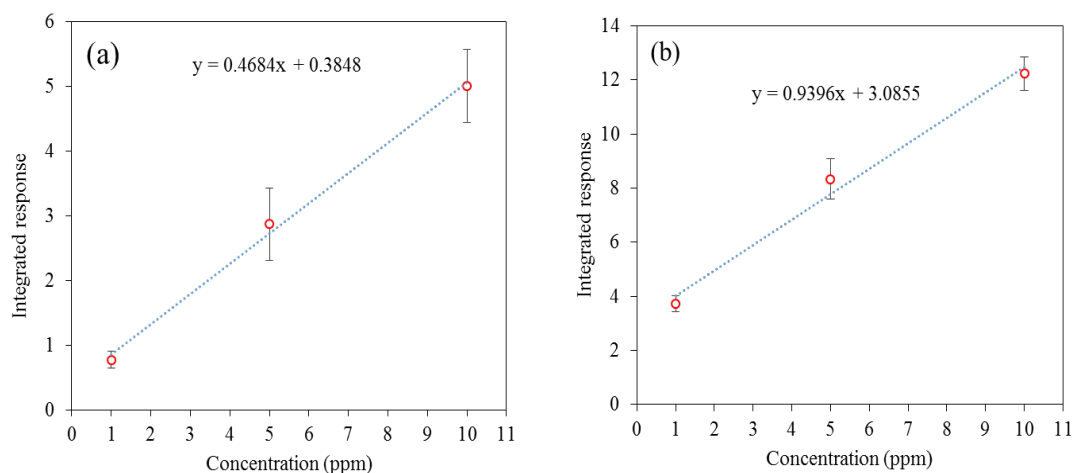


Figure 10. Calibration curves for detection of (a) trimethylarsine and (b) vinyl chloride in a concentration range between 1-10 ppm in zero grade air.

Testing in Natural Gas Background

Sample Preparation Procedure

For testing in Natural Gas background, calibration cylinders of hydrogen sulfide, ethyl-mercaptan, vinyl chloride, and trimethylarsine were used for this report. Calibration concentrations for BTEX were obtained from liquid headspace concentrations of benzene, toluene, ethyl benzene and o-xylene. A natural gas standard was purchased from RESTEK, MESA: Lean Natural Gas, and Rich Natural Gas.

Analytes of interest (hydrogen sulfide, ethyl-mercaptan, tenzene, toluene, ethyl benzene, o-xylene, trimethylarsine, and vinyl chloride) with known concentrations were added to 1L of rich natural gas mixture via gas tight syringes (Hamilton 1, 2.5, 10, and 50 mL) to obtain the requested concentrations for these analytes in natural gas mixture. The gas samples were mixed in 1L tedlar bags and attached to the sampling instrument using a Swagelok connector on the sampling system inlet port. The analyzers on the sampling pump were used to automatically sample the gases from the tedlar bag.

Testing in RESTEK Standard

Refer to Table 1 for the composition of RESTEK gas. The chromatogram is shown in Figure 11. Sensor 2 ($\text{SnO}_2\text{-TiO}_2$) has a very small response to light hydrocarbons, which allowed for an accurate quantification of the hydrogen sulfide and ethyl-mercaptan in highly concentrated hydrocarbons even if they are not completely separated in the GC column.

The RESTEK gas sample contained BTEX compounds according to the analysis, even though the composition provided by the vendor stated BTEX was not a part of the sample provided. This information regarding BTEX and the RESTEK gas sample was confirmed by the vendor, and was unable to provide us the exact concentrations of BTEX compounds present, citing them as “expected interferences.” Therefore, the concentrations of benzene, toluene, ethylbenzene and o-xylene in the RESTEK blend were calculated using the calibration curves generated for each analyte. The results are in Table 7.

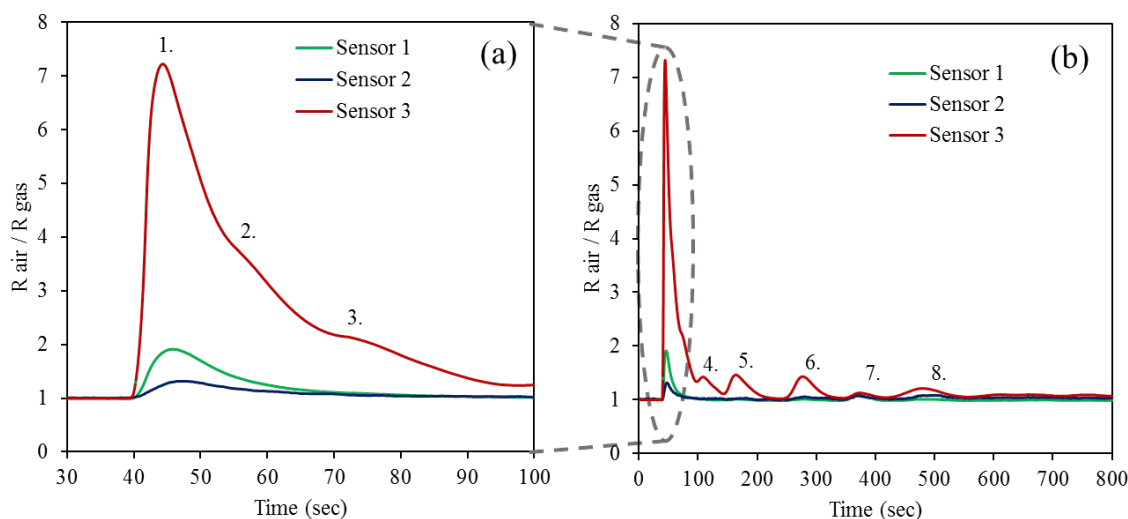


Figure 11. Gas chromatogram of Natural Gas (RESTEK) (a) magnified image of light hydrocarbons 1. methane, 2. ethane, 3. propane; and (b) full chromatogram with additional peaks corresponded to 4. butane, 5. benzene, 6. toluene, 7. water, and 8. ethylbenzene.

Table 7. Concentration of BTEX components in Natural gas (RESTEK).

Gases	Concentration (ppm)
Benzene	12
Toluene	9.8
Ethylbenzene	5.0
O-Xylene	0.97

Sensor 2 ($\text{SnO}_2\text{-TiO}_2$) has a very low sensitivity to hydrocarbons even at very high concentrations. However, Sensor 3 (Au/Pd@SnO_2) responds to light hydrocarbons in the RESTEK Natural Gas standard. At the same, Sensor 2 ($\text{SnO}_2\text{-TiO}_2$) has a high sensitivity to low concentrations of hydrogen sulfide and ethyl-mercaptan (Figure 12). After subtracting the background signal (natural gas signal) from the gas mixture (natural gas plus hydrogen sulfide and ethyl-mercaptans), the area under the curve was calculated for both gases. The corresponding concentration of each gas was found according to the calibration curve (Table 8).

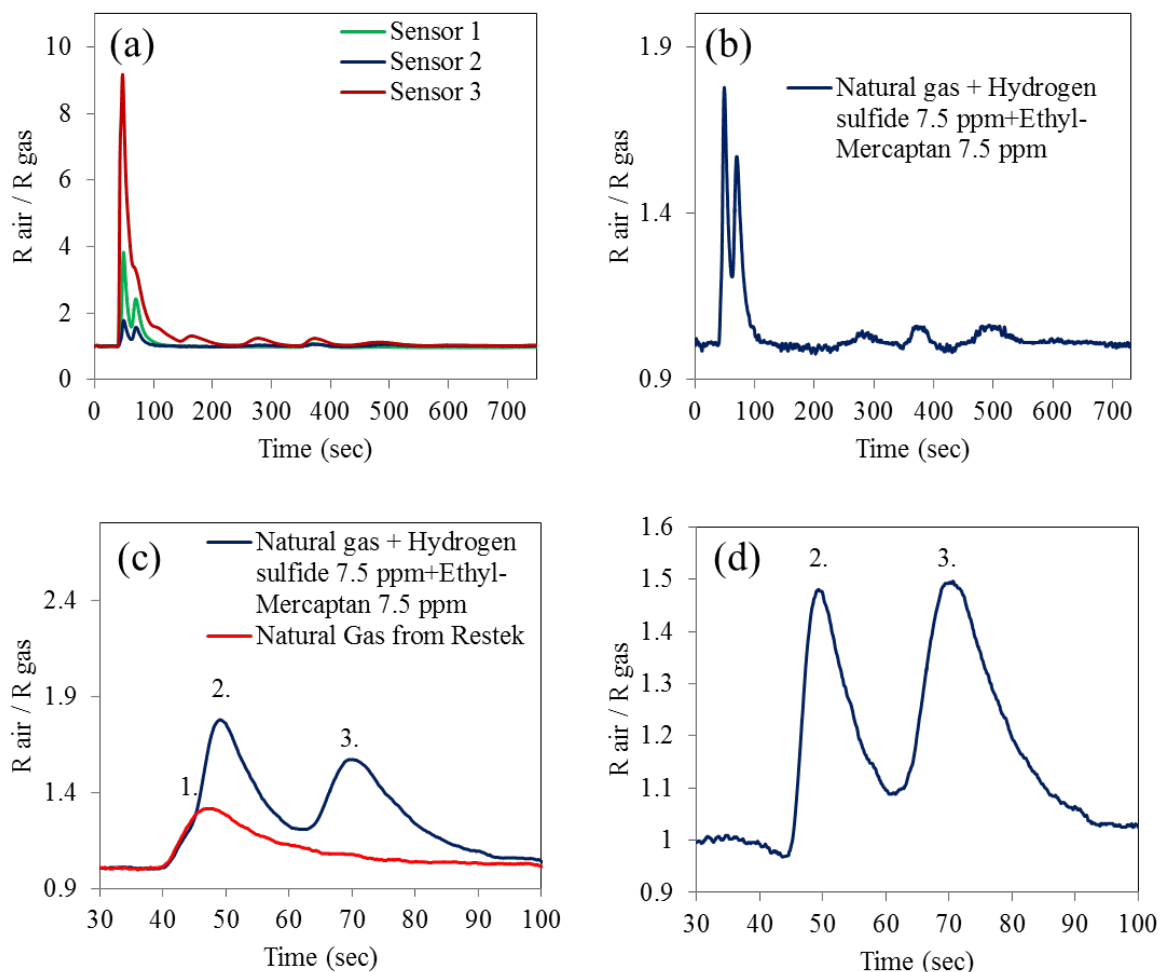


Figure 12. (a) Gas chromatogram obtained by analyzing Natural Gas (RESTEK) + hydrogen sulfide 7.5 ppm + ethyl-mercaptan 7.5 ppm with an array of sensors, (b) the chromatogram obtained from a single sensor (sensor 2), (c) the response of the sensor 2 to Natural gas (Red) (with a major peak corresponds to 1. methane) and Natural gas containing 2. hydrogen sulfide (7.5 ppm) and 3. ethyl-mercaptan (7.5 ppm) (Blue), and (d) the response of the sensor 2 to 2. hydrogen sulfide (7.5 ppm) and 3. ethyl-mercaptan (7.5 ppm) after subtracting the background.

Table 8. Detection of hydrogen sulfide and ethyl-mercaptan in Natural Gas.

Gases	Actual concentration (ppm)	Detected concentration (ppm)
Hydrogen sulfide	7.5	7.0
Ethyl-mercaptan	7.5	6.4

Following the detection of Group 1 analytes (hydrogen sulfide and ethylmercaptan), the procedure for sample preparation was followed and BTEX Mix. 2 was added to the RESTEK standard (Figure 13). Based on the measured concentrations of each BTEX component in the Natural Gas sample, the total error during the analysis was evaluated to be within +/- 10% of the actual concentrations of BTEX in the sample (Table 7 and 9).

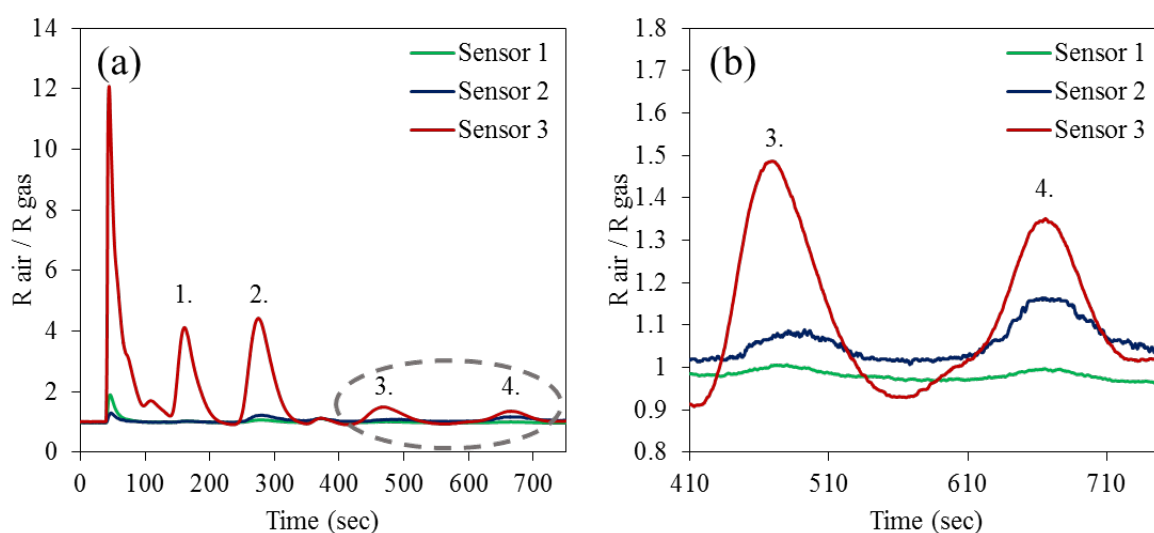


Figure 13. Gas chromatogram of the Natural gas sample with additional concentration (Mix. 2) of BTEX components: 1. Benzene, 2. Toluene, 3. Ethylbenzene and 4. O-xylene

Table 9. Detection of BTEX components in RESTEK Natural Gas

Gases	Actual concentration (ppm)	Detected concentration (ppm)
Benzene	121	113
Toluene	124	132
Ethylbenzene	18	19
O-xylene	38	39

Sensor 4 (Pt@SnO₂) was discovered to be sensitive to high concentrations of light hydrocarbons (methane, propane, ethane, and butane) in Natural Gas, as well as low

concentrations of trimethylarsine and vinyl chloride. Following sample loading procedure, after the background signal (Natural Gas signal) was subtracted from gas mixture (Natural Gas plus trimethylarsine and vinyl chloride), the area under the curve was calculated for both analytes. These concentration values were detected values. Then, the corresponding concentrations for each gas were found according to calibration curves (Tables 10 and 11). These concentrations were actual values. The corresponding chromatograms can be found in Figure 14.

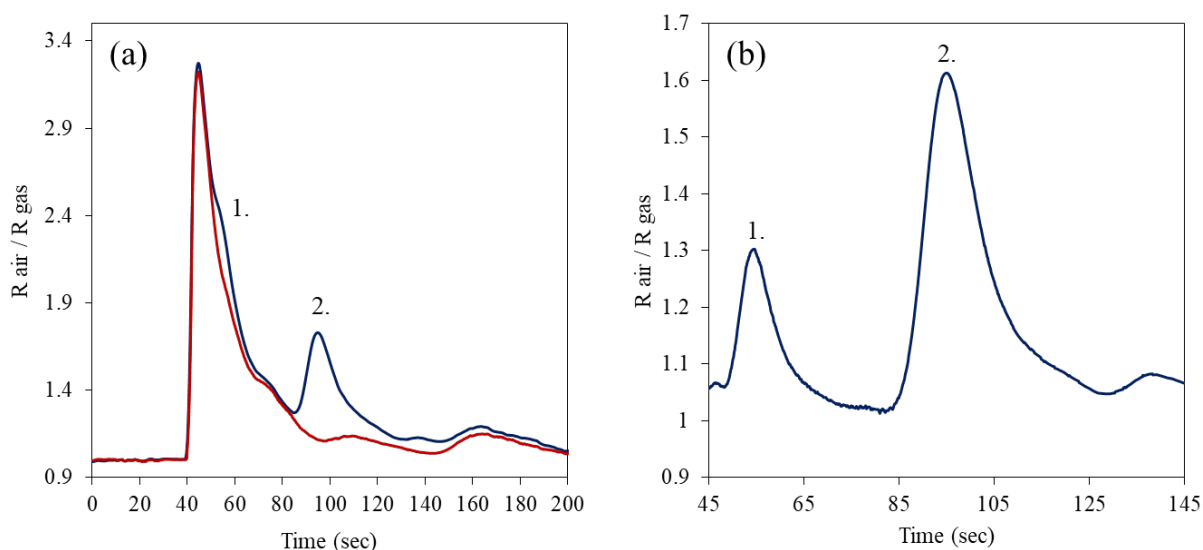


Figure 14. (a) Zoomed image of the gas chromatogram obtained by analyzing two mixes: Natural gas (Red) and Natural gas containing trimethylarsine (5 ppm) and vinyl chloride (5 ppm) (Blue) and (b) the major peaks detected after the background was subtracted (Red - Blue).

Table 10. Detection of trimethylarsine and vinyl chloride in Natural gas

Gases	Actual concentration (ppm)	Detected concentration (ppm)
Trimethylarsine	5.0	3.6
Vinyl chloride	5.0	6.8

Table 11. Detection of target analytes in RESTEK standard.

Gases	Calculated Conc. (ppm)	Actual Conc. (ppm)	% error
Hydrogen sulfide	7.5	7.0	7.5
Ethyl-mercaptan	7.5	6.4	15
Benzene	120	110	6.8
Toluene	124	130	6.6
Ethylbenzene	18	19	2.5
O-Xylene	38	39	4.2
Trimethylarsine	5.0	3.6	28
Vinyl chloride	5.0	6.8	36

A complete set of analytes of interest in RESTEK gas with detected concentrations and corresponding errors are shown in Table 9.

Testing in Lean Gas (MESA)

The composition of the lean gas is show in Table 1. The chromatogram for this background mix is shown in Figure 15.

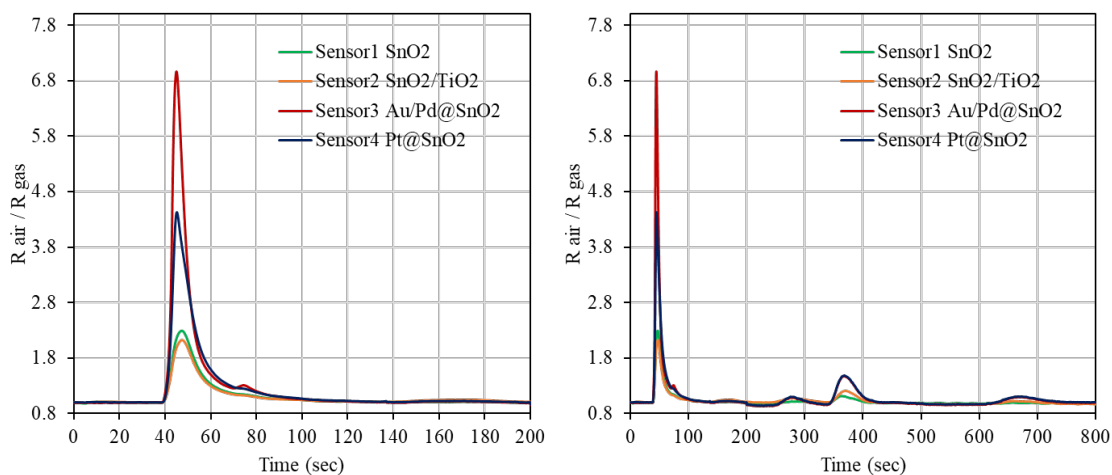


Figure 15. Chromatograms of lean gas background.

Following the procedure for sample preparation, the target analytes of known concentrations were added to the background lean gas, resulting in the chromatograms shown in Figure 16.

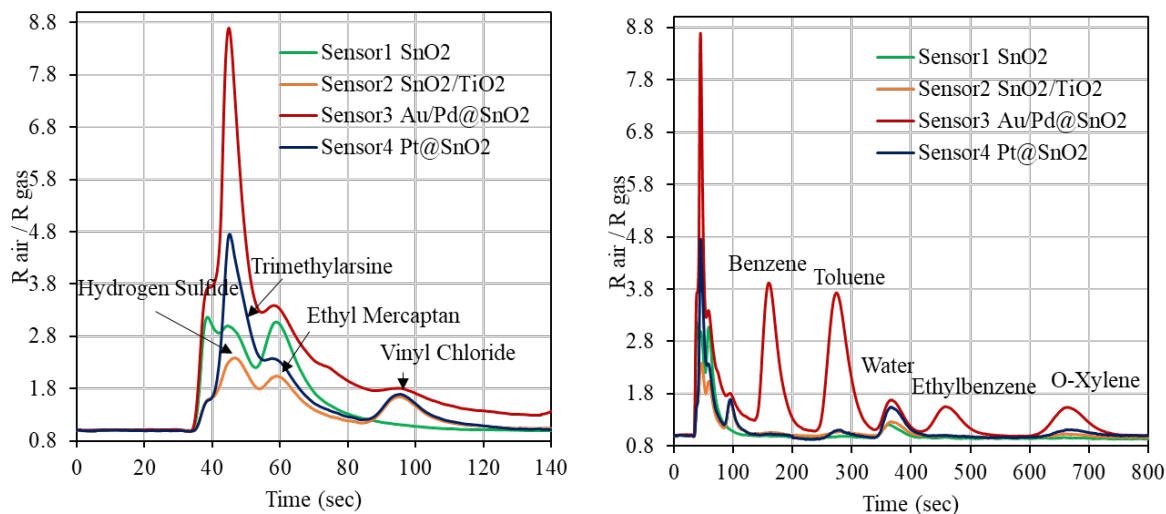


Figure 16. Chromatogram of the lean gas with added target compounds of known concentrations.

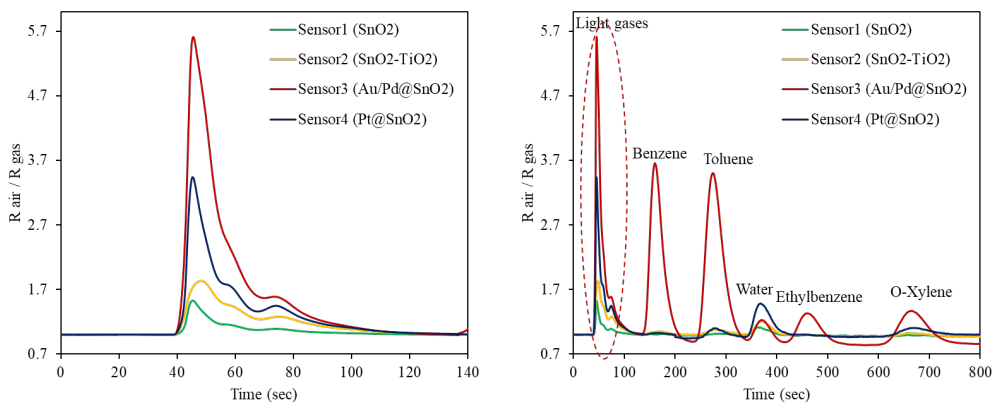
After subtracting the background signal (Natural Gas signal) from the gas mixture (Natural Gas plus analytes of interest) the area under the curve was calculated for all the compounds of interest. The corresponding concentrations for each gas was found according to their calibration curves (Table 12).

Table 12. Detection of target analytes in lean gas from MESA.

Gases	Integrated signal	Calculated concentration (ppm)	Actual concentration (ppm)	error %
Hydrogen sulfide	4.3	7.2	7.5	3.7
Ethyl-mercaptan	6.7	5.7	5.0	13
Benzene	94	136	125	8.7
Toluene	112	105	100	4.5
Ethyl benzene	31	16	15	3.6
O-Xylene	36	39	40	1.3
Trimethylarsine	12	24	10	140
Vinyl Chloride	10	7.9	7.5	4.6

Testing in Rich Gas (MESA)

Similar procedure was followed for testing with rich gas mixture. The composition of the rich gas background is shown in Table 1, and the chromatogram for this background mix is shown in Figure 17. Figure 18 consists of the chromatograms of rich gas background with added target analytes.

**Figure 17.** Chromatograms of rich gas background.

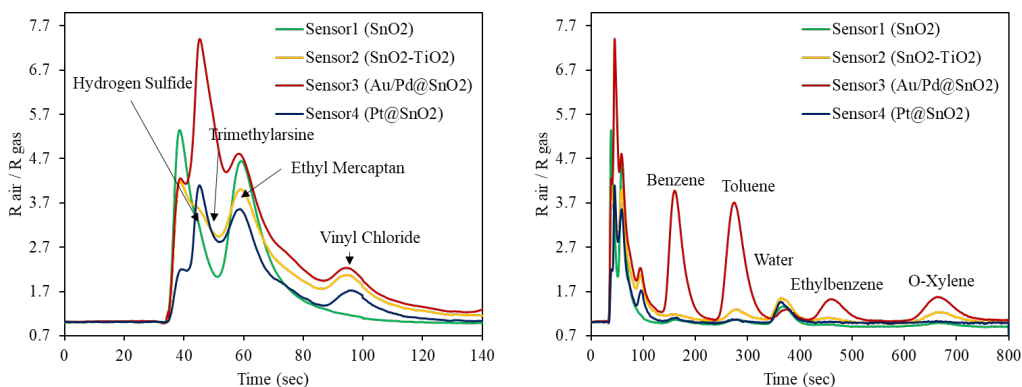


Figure 18. Chromatogram of the rich gas with added target compounds of known concentrations.

After subtracting the background (Natural Gas signal) from the gas mixture (Natural Gas plus compounds of interest) the area under the curve was calculated for all compounds of interest and the corresponding concentrations for each gas were found according to their calibration curves (Table 13).

Table 13. Detection of target analytes in rich gas from MESA.

Gases	Integrated signal	Detected Concentration (ppm)	Actual concentration (ppm)	% error
Hydrogen sulfide	31	62	7.5	728
Ethyl mercaptan	32.	38	5.0	667
Benzene	94	139	125	11
Toluene	111	103	100	2.7
Ethylbenzene	30	15	15	2.0
O-Xylene	40	45	40	12
Trimethylarsine	21	44	10	340
Vinyl chloride	9.9	7.3	7.5	3.2

DISCUSSION AND CONCLUSION

Based on the measured concentrations of each target analyte in the RESTEK gas mixture, the total concentration error was evaluated to be within $\pm 10\%$ of the actual concentration value of most of the compounds, except for ethyl-mercaptan (14.7%), trimethylarsine (27.8%) and vinyl chloride (36.4%). A $\pm 10\%$ error was also achieved in the lean MESA standard, and the exception of trimethylarsine (140.20%) and ethyl-mercaptan (12.89%). In the rich MESA standard, the total measurement error for benzene, toluene, ethylbenzene, o-xylene, and vinyl chloride remained within $\pm 10\%$. However, the percent error became very high for trimethylarsine, hydrogen sulfide, and ethyl mercaptan. Table 14 summarizes the outcomes of this project. Substantial errors in lighter compounds were a result of mixing all the target components together with the rich natural gas background, which makes the mix unstable. Individual components can react and form light reaction byproducts. There are two ways to overcome this problem and reduce the percent error.

One way is to introduce an additional chromatography column specifically targeting lighter compounds. This additional compound will improve the separation between the light compounds and will help to eliminate the unwanted reaction byproducts from the analyzed data. A second option involves applying a well-known mathematical technique of peak deconvolution, which will extract the informative part of the data and reduce error. The best results can be achieved by utilizing a complex approach that combines both methods.

Table 14. Summary of the errors in measuring each analyte for each one of the standards.

Gases	Natural Gas RESTEK % error	MESA Lean Gas % error	MESA Rich Gas % error
Hydrogen Sulfide	7.5	3.7	728
Ethyl Mercaptan	15	13	667
Benzene	6.8	8.7	11
Toluene	6.6	4.5	2.7
Ethylbenzene	2.5	3.6	2.0
O-Xylene	4.2	1.3	12
Trimethylarsine	28	140	335
Vinyl chloride	36	4.6	3.2

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