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DEVELOPMENT OF STANDARD OPERATING PROCEDURE WITH MODIFIED METHOD TO QUANTIFY BENZENE AND OTHER VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES USING GAS CHROMATOGRAPHY

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DEVELOPMENT OF STANDARD OPERATING PROCEDURE WITH MODIFIED
METHOD TO QUANTIFY BENZENE AND OTHER VOLATILE ORGANIC
COMPOUNDS IN AIR SAMPLES USING GAS CHROMATOGRAPHY

By

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Presented to the Faculty of the Graduate School of
Stephen F. Austin State University
In Partial Fulfillment
Of the Requirements

For the Degree of
Master of Science

STEPHEN F. AUSTIN STATE UNIVERSITY

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ABSTRACT

Stephen F. Austin State University (SFASU) Department of Environmental Science has recently invested in a gas chromatograph which can be used to analyze air samples for volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, and xylenes (BTEX). The goal of this project was to develop a standard operating procedure (SOP) and modify the current method for the detection of VOCs associated with oil and gas drilling activity to accommodate the equipment and capabilities of SFASU Environmental Assessment Lab. This study aims to provide the framework for future research in air quality monitoring in the Eagle Ford Shale area. An SOP has been developed for the SFA Environmental Assessment Lab and details materials, lab procedures, gas chromatograph (GC) analysis, field sample collection procedures, and operation and maintenance of the GC. A modified method of analysis for BTEX has been developed based on EPA Method TO14A and method validation parameters are discussed. Ambient air samples were collected from gas stations in Nacogdoches, Texas to evaluate whether the method is capable of detecting BTEX in air samples. Samples at the refueling level consistently had sufficient concentration of VOCs within the analysis capabilities of the current method parameters. Samples at the breathing level and property line levels consistently returned analysis results of less than the limit of quantitation

(LOQ). It was possible to see peaks in the respective retention windows on most breathing level chromatograms and some property line chromatograms, however the peaks could not statistically be differentiated from noise. Concentrations of toluene, ethylbenzene, and xylenes identified by the modified method of analysis were well below the National Institute for Occupational Health and Safety (NIOSH) recommended exposure limit (REL) and Occupational Safety and Health Association (OSHA) permissible exposure limit (PEL). The LOQ for these VOCs were also well below the respective protective levels. This indicated that the modified method was adequate for analyzing toluene, ethylbenzene and xylenes for protective purposes. Concentrations of benzene identified by the modified method of analysis were well above the NIOSH REL and OSHA PEL. The LOQ for benzene was above one of the protective levels. This indicated that the method may not be adequate for analyzing benzene for protective purposes.

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TABLE OF CONTENTS

ABSTRACT.....	i
ACKNOWLEDGEMENTS.....	ii
LIST OF FIGURES.....	vi
LIST OF TABLES.....	viii
LIST OF ACRONYMS.....	x
INTRODUCTION.....	1
OBJECTIVES.....	3
LITERATURE REVIEW.....	4
Hydraulic Fracturing.....	4
The Eagle Ford Shale.....	7
Effects of Benzene, Toluene, Ethylbenzene, Xylene on Human Health.....	9
Health and Regulatory Concentration Values.....	10
Gas Chromatography.....	13
Flame Ionization Detection.....	14
JUSTIFICATION.....	17
METHOD OF STUDY.....	18
Standard Operating Procedure.....	18
Sample Collection.....	19
Analysis Using Gas Chromatography.....	23
Quality Control and Quality Assurance.....	25
Method Validation.....	27

RESULTS AND DISCUSSION.....	39
Ambient Air BTEX Concentrations.....	39
Sample Statistical Analysis.....	39
CONCLUSIONS.....	47
LIMITATIONS AND FUTURE IMPLEMENTATION.....	48
REFERENCES.....	51

LIST OF FIGURES

Figure 1. Location map of Eagle Ford Shale formation in Texas, USA.	8
Figure 2. Sunoco Gas Station pump locations are identified within the sample location property boundary in Nacogdoches, Texas	21
Figure 3. Valero gas station pump locations are identified within the sample location property boundary in Nacogdoches, Texas.....	22
Figure 4. Representative chromatogram shows peaks for benzene, toluene, ethylbenzene, and xylenes analyzed during the calibration process. Each analyte had a retention window identified at the top of the chromatogram. Detector response was given on the y-axis in pA. Retention time was given on the x-axis in minutes.	24
Figure 5. Diagram of current equipment setup and flow of sample analysis using GC-FID.....	25
Figure 6. Calibration equation plots for benzene, toluene, ethylbenzene, and xylenes are given with confidence limits in red ($\alpha=0.005$). Yellow points indicate data point for selected injection and dotted lines indicate area and amount for selected data point.....	30

Figure 7. Distribution of average benzene, toluene, ethylbenzene, and xylenes concentration (ppm) in ambient air samples based on the gas station they were sampled from (Sunoco and Valero). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle. Diamond symbol inside box denotes the mean value. Line in the middle of the box represents the median value. Box upper and lower bounds represent the interquartile range (Q1 and Q3). Whiskers represent minimum and maximum values.43

Figure 8. Distribution of benzene, toluene, ethylbenzene, and xylenes concentration (ppm) in ambient air based on pump the sample was obtained. Gas pumps are denoted by their pump number (Pump 2, Pump 3, Pump 4, and Pump 5). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle. Diamond symbol inside box denotes the mean value. Line in the middle of the box represents the median value. Box upper and lower bounds represent the interquartile range (Q1 and Q3). Whiskers represent minimum and maximum values.45

LIST OF TABLES

Table 1. Regulatory values from the National Institute for Occupational Health and Safety (NIOSH) and Occupational Health and Safety Association (OSHA) for benzene, toluene, ethylbenzene, and xylenes (NIOSH 2010).....	13
Table 2. Typical retention time (minutes) for select volatile organic compounds (VOCs) associated with GC-FID analytical system (US EPA 1999).....	16
Table 3. Observed retention time (minutes) for select volatile organic compounds (VOCs) associated with GC-FID analytical system and modified method.....	16
Table 4. Calibration linear regression equations, R ² values, relative standard deviation (RSD), and calibration range are given for benzene, toluene, ethylbenzene, and xylenes based on calibration of GC analysis.....	29
Table 5. Known values of calibration standards and recovered measured values are used to calculate percent accuracy during calibration of GC analysis of benzene, toluene, ethylbenzene, and xylenes.....	36
Table 6. VOCs in ambient air samples at two gas stations in Nacogdoches, Texas. Refueling level of samples are indicated by REF. Breathing area level of samples are	

indicated by BRE. Property line level of samples are indicated by PRO. The number following level in Sample ID indicates the sample bag number. The day the sample was taken is indicated by D1, D2, D3. Sunoco gas station (S) and Valero gas station (V) are identified along with the respective pump number.....42

Table 7. Comparison of mean BTEX concentration (ppm) in ambient air samples between various pumps at two gas stations. Comparisons significant at the level $\alpha=0.05$ are indicated by ***. Gas pumps are denoted by their pump number (Pump 2, Pump 3, Pump 4, and Pump 5). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle.....44

Table 8. Average concentration (ppm) of benzene, toluene, ethylbenzene, and xylenes in ambient air based on the gas station (Sunoco or Valero). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle.....46

LIST OF ACRONYMS

ANOVA: analysis of variance
BTEX: benzene, toluene, ethylbenzene, and xylenes
FDA: Food and Drug Administration
FID: flame ionization detector
GC: gas chromatograph
LOD: limit of detection
LOQ: limit of quantitation
NIOSH: National Institute for Occupational Health and Safety
NIST: National Institute of Standards and Technology
OSHA: Occupational Safety and Health Association
PEL: permissible exposure limit
PSI: pounds per square inch
PTV: programmable temperature vaporizing
REL: recommended exposure limit
RSD: relative standard deviation
SFASU: Stephen F. Austin State University
SOP: standard operating procedure
TPY: tons per year
US EPA: United States Environmental Protection Agency
VOCs: volatile organic compounds

INTRODUCTION

Interest in natural gas as an energy source has seen a recent uptick because it is more efficient than coal or oil and recent developments in extraction technology have enabled this commodity to be produced and conveyed to the market efficiently. In regard to energy produced per carbon dioxide (CO₂) molecule, natural gas is 177% more efficient than coal and 140% more efficient than oil (Alvarez et al. 2012). Sharp growth in oil and natural gas production after 2008 was made possible by exploitation of shale and other low permeability geologic formations through improved horizontal drilling and hydraulic fracturing techniques. Operators have used hydraulic fracturing technology since the 1940's but the combination of fracking with horizontal drilling is what has caused an exponential increase in natural gas production since 2008. This increase in hydraulic fracturing techniques has the potential to add significant air emissions of volatile organic compounds (VOCs) in areas with drilling activity. The Eagle Ford Shale region is the second highest producing geologic formation in Texas, however this area is only monitored by two air monitoring stations. This underrepresentation of monitoring equipment could allow harmful quantities of VOCs commonly emitted from oil and gas activity, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) to affect populations that are not near an air monitoring station. Stephen F. Austin State University

(SFASU) has recently invested in a gas chromatograph for use in the Environmental Science division of the Arthur Temple College of Forestry and Agriculture. This machine can be used to analyze air samples for VOCs such as BTEX and may be able to identify other volatiles associated with oil and gas activity. The goal of this project was to develop a standard operating procedure and modify the current method for the detection of VOCs associated with oil and gas drilling activity, specifically BTEX. The existing standard method of analysis for BTEX has been modified in order to accommodate the equipment and capabilities of SFASU Environmental Assessment Lab. The standard method for BTEX analysis with gas chromatography begins with subatmospheric or pressurized sample collection with an evacuated stainless-steel canister. The sample is pumped from the canister for analysis and water vapor is reduced with a dryer, if available. The sample is concentrated with a cryogenically-cooled trap or other sorbent trap. Once concentrated on the trap, the sample can be revolatilized and pushed into the column and to the detector. The modified method will endeavor to achieve statistically similar results to the standard method without the use of evacuated stainless-steel canisters and cryogenically-cooled trap. The canister was replaced with a Tedlar bag and the cryogenically-cooled trap was replaced with a cryogenically-cooled Programmable Temperature Vaporizing (PTV) injection module. With this procedure and modified method, future air samples can be collected in the target area to determine if any human populations are exposed to unsafe concentrations of VOCs.

OBJECTIVES

1. Develop standard operating procedures (SOPs) for the analysis of benzene and other VOCs in ambient air using the newly acquired gas chromatograph – GC-FID system at the Division of Environmental Science, SFASU Environmental Assessment Laboratory.
2. Develop a modified method of analysis that can be used to detect low concentrations of VOCs in ambient air in a rural residential area near gasoline stations. This method validation will facilitate future analysis of air samples in Eagle Ford Shale region.

LITERATURE REVIEW

Hydraulic Fracturing

Background

Hydraulic fracturing is the process by which water, sand and chemicals are pumped under great pressure into oil and gas wells that crack the geologic formation and allow abundant natural gas to flow back to the wellhead. The energy industry has coupled hydraulic fracturing with vertical drilling for decades, but the technology was recently combined with horizontal drilling to create significant production increases. This relatively recent combination of horizontal drilling and high-pressure water hydraulic fracturing technologies has enabled the energy industry to take advantage of unconventional shale formations throughout the United States and produce record amounts of natural gas.

Hydraulic fracturing differs from conventional drilling mainly in that it requires millions of gallons of fluid, significantly more water than conventional vertical drilling, pumped at high pressures to create fractures in the rock formation that allow natural gas to flow from the fractures to the wellbore (US Department of Energy 2009). The fluid is comprised of water, chemical additives and sand, which are used to keep fractures open while the well is in flowback (US EPA 2010). 15-80% of flowback fluid is recovered at the wellhead in addition to produced water, which is highly saline water that originates

deep in the shale formation (Jackson et al. 2011). This waste is disposed in several ways, from wastewater treatment and release to waters of the United States to reinjection into the parent formation.

Air Emissions Sources

Air emissions are released from various sources at production sites during well development. Drilling mud, drilling cuttings, and temporary water storage ponds represent area sources of air emissions during the drilling phase. Fugitive and point emissions are potentially released from every piece of equipment on a developed well site, including generators, compressor engines, tanks, heater treaters, and loadout hookups. Every connection among pipelines has the potential to release fugitive emissions. Flaring is another contributor to air emissions during well development and production. Operators use flares to destroy excess associated gas at oil wells, especially where local infrastructure does not allow the gas to be profitably stored and/or transmitted for sale. Flares typically have very high destruction rates, usually assumed to be 98% (Caulton et al. 2014). One study observed high values of methane between flaring events, which was attributed to “unknown venting practices” (Caulton et al. 2014). Even minor variations in flaring destruction rates can lead to uncertain emission factors due to underreported flaring volumes (Willyard and Schade 2019).

Air Emission Estimates

Unknown venting practices and underreported flaring volumes are just a few examples of how estimated air emissions may be much lower than actual air emissions. In the scientific literature there are two methods of quantifying air emissions: top-down and bottom-up. Top-down measurements are taken by aircraft, satellites, or tower networks to infer overall methane emissions from all contributing sources across large areas. Bottom-up measurements generate regional, state, or national emission estimates by gathering measured emissions from individual pieces of equipment, operations, or facilities, using measurements made directly at the emission point or, in the case of facilities, directly downwind. These measurements are then used to extrapolate air emissions over large areas with a known number of facilities. Bottom-up measurements are the easier and more economically practical method to use when quantifying air emissions, but they have a tendency to underestimate total real emissions. A study published in 2018 estimated methane emissions from the US oil and natural gas supply chain by using ground-based, facility-scale measurements and validated with aircraft observations in areas accounting for ~30% of US gas production. What they found was that the top-down estimates are 60% higher than the bottom down estimates (Alvarez et al. 2018). The United States Environmental Protection Agency (US EPA) uses these bottom-up estimates to calculate country-wide emissions, therefore it is possible that their estimates for any VOCs are underestimated by up to 60%.

Eagle Ford Shale

The Eagle Ford Shale is a hydrocarbon-producing geological formation extending over 26 counties in south Texas. The formation ranges from the United States-Mexico border near Laredo to Northeast Texas near Waco. As of March 2020, this formation is second in Texas oil and natural gas production to the Permian Basin with 867,783 barrels per day of oil and 4,544 million cubic feet per day of natural gas (Railroad Commission of Texas 2020). The prolific production numbers are due the capability of conveying significant amounts of natural gas along with oil compared to traditional shale plays. While the Eagle Ford Shale formation may produce a smaller volume of oil and natural gas than the Permian Basin, it is in much closer proximity to major metropolitan areas, such as San Antonio and Houston, than the sparsely populated Permian Basin. It is important to consider human health when exposure to harmful contaminants is possible. Figure 1 shows a location map of the Eagle Ford Shale formation.

Eagle Ford Shale of Texas

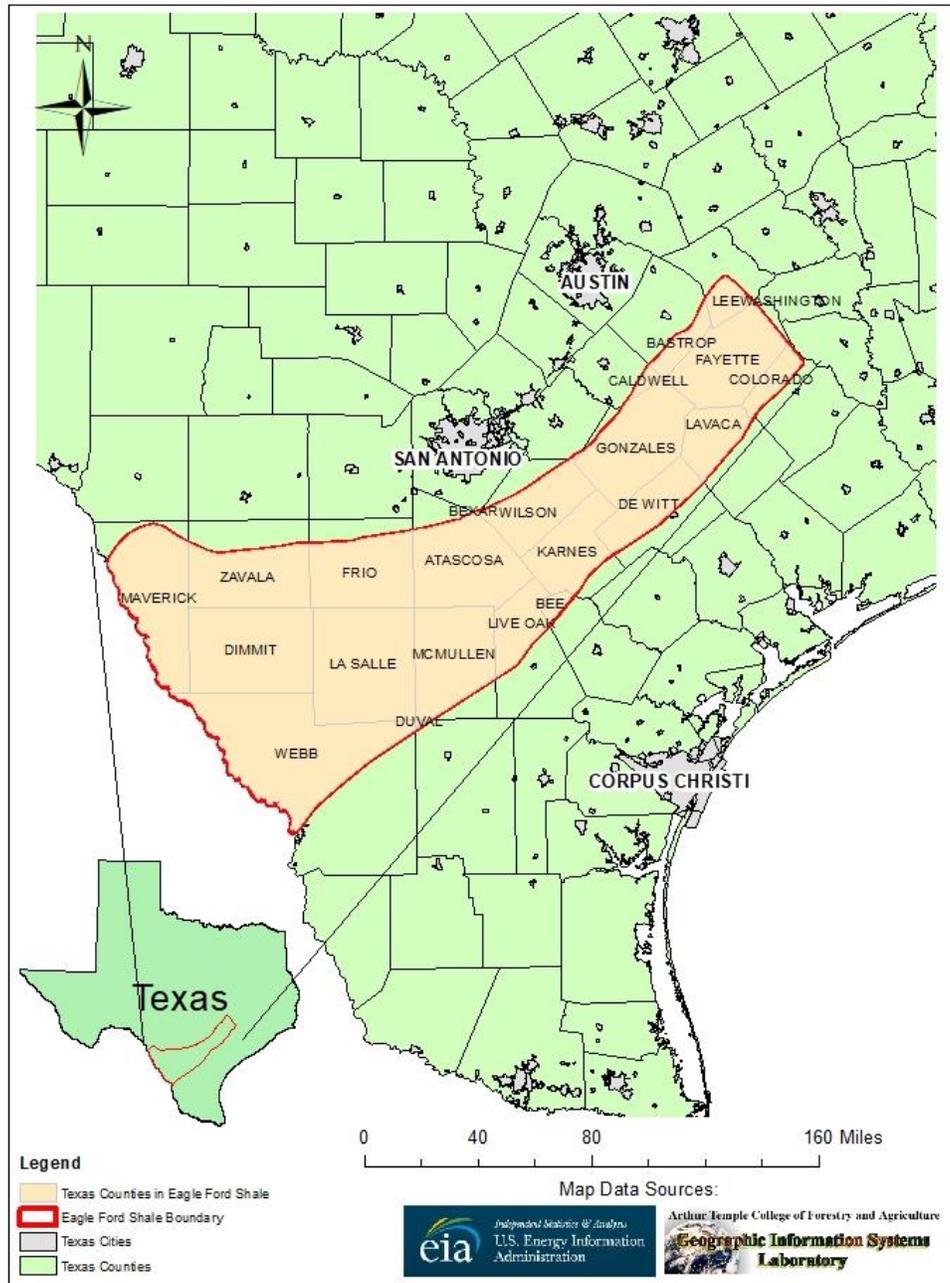


Figure 1. Location map of Eagle Ford Shale formation in Texas, USA.

Effects of Benzene, Toluene, Ethylbenzene, and Xylene on Human Health

BTEX is an acronym that groups four hazardous air pollutants from oil and gas-related activities: benzene, toluene, ethylbenzene, and xylenes. Hazardous air pollutants are known to cause cancer and other serious health impacts. The Clean Air Act requires the EPA to regulate toxic air pollutants emitted by industrial facilities.

Benzene is a volatile organic compound that is a natural chemical component of crude oil and natural gas. During the refining process, additional benzene can be added to fuel to increase octane. Benzene is emitted from a wide variety of sources including oil and gas wellheads, glycol dehydrators, petroleum refining, and gasoline marketing (US EPA 1998). These emissions can pose a risk to human health when significant concentrations are present in ambient air. Chronic exposure to benzene is associated with increased cancer risk in humans (Loomis et al. 2017). Exposure to benzene can lead to the following symptoms: irritated eyes, irritated skin, irritated nose, irritated respiratory system, dizziness, headache, nausea, staggered gait, anorexia, lassitude (weakness, exhaustion), dermatitis, bone marrow depression (NIOSH 2010).

Toluene is a chemical that is added to gasoline to improve octane (US EPA 2012). Exposure to toluene can lead to the following symptoms: irritated eyes, irritated nose, dizziness, headache, dilated pupils, muscle fatigue, insomnia, lassitude (weakness, exhaustion), confusion, dermatitis, liver and kidney damage (NIOSH 2010).

Ethylbenzene is another volatile organic compound that is a natural chemical component of crude oil and natural gas. Exposure to ethylbenzene can lead to the following symptoms: irritated eyes, irritated skin, irritated mucous membranes, headache, dermatitis, narcolepsy, and coma (NIOSH 2010).

Xylenes are a group of isomers of xylene (m-, o-, and p-xylene) which are found naturally in petroleum products but are also mixed and added to gasoline (ATSDR 1995). Exposure to xylenes can lead to the following symptoms: irritated eyes, irritated skin, irritated nose, irritated throat, dizziness, excitement, drowsiness, incoherence, staggered gait, corneal vacuolization, anorexia, nausea, vomiting, abdominal pain, and dermatitis (NIOSH 2010).

Severity of symptoms will depend on the concentration and duration of BTEX exposure.

Health and Regulatory Concentration Values

Different regulatory bodies are tasked with developing protective standards for human health in different exposure scenarios. While these standards may be developed independently, it is important to understand the different levels and why they may vary.

OSHA

The Occupational Safety and Health Association (OSHA) is mainly concerned with regulating and enforcing worker health standards. While these may not apply to directly to citizens who are not working with exposure to chemical hazards, they do provide

useful information regarding concentrations of BTEX that are considered threshold values and are useful in protecting human health. OSHA has developed permissible exposure limits (PELs) that dictate what concentration of hazardous chemical is allowed per exposure time. The National Institute for Occupational Health and Safety has joined with OSHA to develop recommended exposure limits (RELs). These threshold values are similar to the PELs but are often more conservative. These two limits of exposure show what concentrations of chemical hazards are considered without significant long-term effects (RELs) and what concentrations will lead to long-term health effects and trigger regulatory enforcement (PELs). RELs and PELs can vary depending on the amount of time a person is exposed to the chemical. Each limit has an acute concentration and a chronic concentration. Time-weighted average (TWA) “indicates a time-weighted average concentration for up to a 10-hour workday during a 40-hour work week” (NIOSH 2010). Short-term exposure limits (STEL) represent an acute exposure limit that cannot be exceeded in any 15-minute time period. OSHA regulatory values are conservative because it is expected that workers will be working in close contact with these chemicals and possibly for a large duration of the workday.

TCEQ/EPA

The Texas Commission on Environmental Quality (TCEQ) is the regulating entity for oil and gas related air emissions in Texas. These responsibilities are delegated from the United States Environmental Protection Agency (US EPA). TCEQ has two permanent air

monitoring stations in the Eagle Ford Shale, one in Wilson County and the other in the adjacent Karnes County. Each of these sites features an automated gas chromatograph which provides near-real-time data in the Eagle Ford Shale area. VOCs are regulated by air permits in terms of tons per year (TPY). A Permit by Rule will permit the emission of 25 TPY of VOCs per facility, which is an average of approximately 5.7 lbs per hour (30 TAC §106.4). This value is a much lower concentration than the OSHA regulation values because the TCEQ is mainly tasked with ensuring these chemicals do not have a negative impact on the general population and surrounding environment. The general population are typically much farther away from the equipment than workers and spend a very small amount of time in close proximity to the equipment.

When analyzing air samples for hazardous chemicals, it is important to understand how people, animals, sensitive plants species, etc. can be exposed and to what degree. This helps determine which regulatory values are appropriate to compare results to. Table 1 shows concentration limits set by NIOSH and OSHA for BTEX.

Table 1. Regulatory values from the National Institute for Occupational Health and Safety (NIOSH) and Occupational Health and Safety Association (OSHA) for benzene, toluene, ethylbenzene, and xylenes (NIOSH 2010).

Compound	Limit Type	Time Component	Concentration (ppm)
Benzene	NIOSH REL	TWA	0.1
		STEL	1.0
	OSHA PEL	TWA	1.0
		STEL	5.0
Ethylbenzene	NIOSH REL	TWA	100.0
		STEL	125.0
	OSHA PEL	TWA	100.0
		STEL	-
Toluene	NIOSH REL	TWA	100.0
		STEL	150.0
	OSHA PEL	TWA	200.0
		STEL	500.0
Xylenes	NIOSH REL	TWA	100.0
		STEL	150.0
	OSHA PEL	TWA	100.0
		STEL	-

- : indicates no established limit

Gas Chromatography

Gas chromatography is a common analysis method for testing air samples for volatile organic compounds. This method is specifically designed to identify volatile organic compounds by heating and separating different compounds by their boiling points and molecular weights. Gas samples are injected into the gas chromatograph by a canister with a pump attached or with a gas-tight syringe. The Programmable Temperature Vaporizing (PTV) injection port and oven are cryogenically cooled with a cooling agent

such as liquid nitrogen which causes the volatile compounds to condense, preventing them from escaping the machine before the analysis begins. Once the injection is complete, the oven begins to ramp up temperature until it reaches 250°C. During the heat ramp, different compounds are volatilizing at different times based on their respective boiling points. Compounds with lower boiling points elute through the column before compounds with higher boiling points. The compounds also move through the column at different rates depending on their molecular structure and weight. Once the compounds reach the end of the column, they encounter the detector. This study uses a flame ionization detector to identify volatile organic compounds.

Flame Ionization Detection

While the theory behind flame ionization detection was not fully understood when it was developed in 1958, it was proven to have: a low noise level, high sensitivity, and optimal response even when factors such as detector temperature and carrier gas flow rate vary. These characteristics have led to the widespread and reliable use of the flame ionization detector (FID) in gas chromatography, making it the most common detector (Holm 1999). Flame ionization detectors identify compounds in air samples by combusting volatile organic compounds to produce ions. The flame is fueled by a tank of hydrogen. The ions are detected by a set of electrodes which measure a potential difference. The ions moving across the electrodes generate a signal which is displayed by a graph, referred to as a chromatogram. The graph is generally displayed with retention time on

the horizontal axis and intensity of signal on the vertical axis. The detector reacts to the presence of the compounds and produces a graph that gives a peak for each analyte that has been detected. The area under the peak is proportional to the amount of analyte in the sample. Intensity of signal is used to calculate the concentration of analyte in a sample, based on the volume of sample injected into the gas chromatograph. The analyte that corresponds to each peak is determined by the time that the analyte elutes. Each analyte will elute at a predictable retention time (Table 2). Table 3 shows the observed retention times for the modified method. Many different method parameters can affect the time an analyte elutes, especially PTV and oven ramp settings. These settings define most of the duration of the instrument method. Once the GC is calibrated, it is automatically programmed to detect analytes within a method-specific window around their retention time. Retention windows were determined with high concentrations of BTEX standard (200 ppm). At this concentration and scale of response, noise is almost nonexistent to the point that only four peak are detected by the data processing wizard. It is clear which peaks are attributed to which analyte in this test. Some methods are specific enough to see separate peaks for the xylenes, however it is more common for the xylenes to co-elute. Analytes will always appear in established analyte windows for a specific instrument method and processing method. Any shift in analyte retention times not caused by a change in method may indicate that a calibration should be performed.

Table 2. Typical retention time (minutes) for select volatile organic compounds (VOCs) associated with GC-FID analytical system (US EPA 1999).

Compound	Retention Time minutes
Benzene	13.51
Toluene	16.17
Ethylbenzene	18.51
m,p-Xylene	18.72
o-Xylene	19.23

Table 3. Observed retention time (minutes) for select volatile organic compounds (VOCs) associated with GC-FID analytical system and modified method.

Compound	Retention Time minutes
Benzene	11.89
Toluene	16.47
Ethylbenzene	16.96
Xylenes	17.95

JUSTIFICATION

This study aims to provide the framework for future research in air quality monitoring in the Eagle Ford Shale area. Data from subsequent studies may identify the need for additional state agency air monitoring equipment to protect the health of Texas residents. Additionally, the development of these SOPs and method will provide an in-department resource for sample analysis which can support a wide variety of future research at SFASU.

METHOD OF STUDY

Standard Operating Procedure

The method for this project follows a modified version of the guidelines set in US EPA Method TO-14A: “Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography”.

Per Method TO-14A, each laboratory must develop a set of Standard Operating Procedures (SOPs) that is specific to their equipment and systems. These SOPs should describe and document the following:

1. Assembly, calibration, leak check, and operation of specific sampling systems and equipment used.
2. Preparation, storage, shipment, and handling samples.
3. Assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used.
4. All aspects of data recording and processing, including lists of computer hardware and software used.

A Standard Operating Procedure has been developed for the SFA Environmental Assessment Lab and can be found in Appendix A. This SOP details materials, lab

procedures, GC analysis, field sample collection procedures, and operation and maintenance of the GC.

Sample Collection

Initial testing of the GC-FID system was performed with BTEX liquid standard (n=18). Three injections were made for each level of concentration were obtained. BTEX gas standard was tested at six levels on concentration: 1 ppm, 1.5 ppm, 3 ppm, 5 ppm, 7 ppm, and 10 ppm. Some lower levels of concentration have less data points because the GC was not able to make a detection at that concentration. Because the PTV injection module is not currently cooling to the desired temperature, the GC was not able to detect VOCs in the ppb range and provide a quantitation. Initial screening for VOCs determined that ambient air samples collected at the refueling level may see levels of benzene up to and beyond 10 ppm. This initial screening was performed with an SKC Gastec colorimetric tube (No. 121L) for benzene only. Ambient air samples were also collected to test the GC-FID system method and to determine whether the current system and method are capable of detecting BTEX in ambient air concentrations.

Ambient air samples were collected near gas stations, due to the prevalence of BTEX in gasoline products. Three sampling excursions occurred at two gas station locations. The Sunoco gas station is located at 2830 North Street in Nacogdoches, Texas. Samples were collected at Sunoco gas station on June 21, 2021 and June 30, 2021. The Valero gas station is located at 2013 North Street in Nacogdoches, Texas. Samples were collected at

Valero gas station on June 28, 2021. Figure 2 and Figure 3 show location maps of the sample locations. Seven sample Tedlar bags were collected at each location on each of the three sampling days (two at refueling level, two at breathing level, two at property line, and one blank bag). Analysis was divided into three levels: refueling level (n=12), breathing level (n=12), and property line (n=12). Two subsamples were analyzed from each of the Tedlar sample bags. The blank samples are a variety of blanks: trip blank, field blank, and instrument blank. The trip blank samples determine whether there is any measurable contamination in the way the sample bags are transported or handled before, during, or after a sampling trip. The field blanks determine whether there is any measurable source of contamination in the way the bags are filled. The instrument blanks determine whether there is any measurable carry over due to the analytical method of the GC. There is no Tedlar bag associated with the instrument blank because there is no actual injection for an instrument blank. One Gastec tube was sampled on each of the three sampling excursions for comparison to measurements made by the GC (n=3). An SKC Vac-U-Chamber and SKC Quick Take 30 pump were used to inflate Tedlar bags with air samples. A portable Kestrel weather meter was used to monitor weather conditions during sampling. Table B in Appendix B shows weather parameters measured during each sampling day. Main weather parameters such as relative humidity, dew point, wind speed/direction, and barometric pressure remained adequately consistent during sampling excursions.



Figure 2. Sunoco Gas Station pump locations are identified within the sample location property boundary in Nacogdoches, Texas.



Figure 3. Valero gas station pump locations are identified within the sample location property boundary in Nacogdoches, Texas.

Analysis Using Gas Chromatography

With SOPs developed, the next step was to analyze liquid standards in order to calibrate the GC. Chromeleon 7 software was used to perform analysis. After the machine was calibrated, the ambient samples were analyzed. The analysis method consisted of an instrument method, sequence, and processing method. These methods were created in Chromeleon 7 with parameters based on US EPA Method TO-14A. Method parameter details are located in Appendix A.

The method begins by cooling the oven and the PTV injection port, each with a connection to liquid nitrogen tanks. The PTV should be connected to a 22 pounds per square inch liquid nitrogen tank (PSI). The oven should be connected to a liquid nitrogen tank with a pressure of 60-80 PSI. The oven was cooled to 0 °C and the PTV injection port was cooled to 15°C. These values are not as low as initially intended, due to a mechanical failure in the cryogenic cooling system of the PTV injection module. Once cooled, the injection phase of the method begins and the user has 5 minutes to inject sample into the PTV injection port. After injection phase, the oven ramps up heat to 250 °C and analytes elute through the column and are detected by the FID. The analysis runs for 39.8 minutes. The full analysis duration, including preparation events (oven cooling, PTV cooling, etc.) was approximately 55 minutes. The analysis output was a graph showing a peak for each analyte detected. A representative chromatogram from the analysis is provided in Figure 4. A processing method was applied to this graph; the analytes are identified by their retention time and concentrations calculated based on the

area under corresponding peaks. Figure 5 shows a basic diagram of the process of analysis with GC.

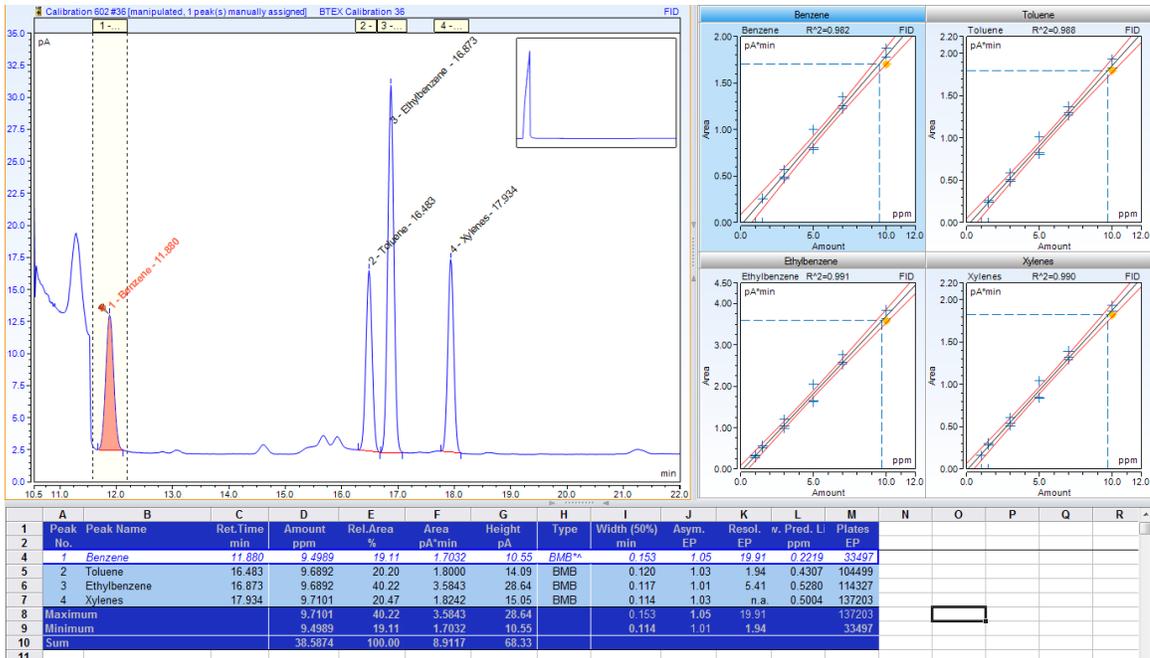


Figure 4. Representative chromatogram shows peaks for benzene, toluene, ethylbenzene, and xylenes analyzed during the calibration process. Each analyte had a retention window identified at the top of the chromatogram. Detector response was given on the y-axis in pA. Retention time was given on the x-axis in minutes.

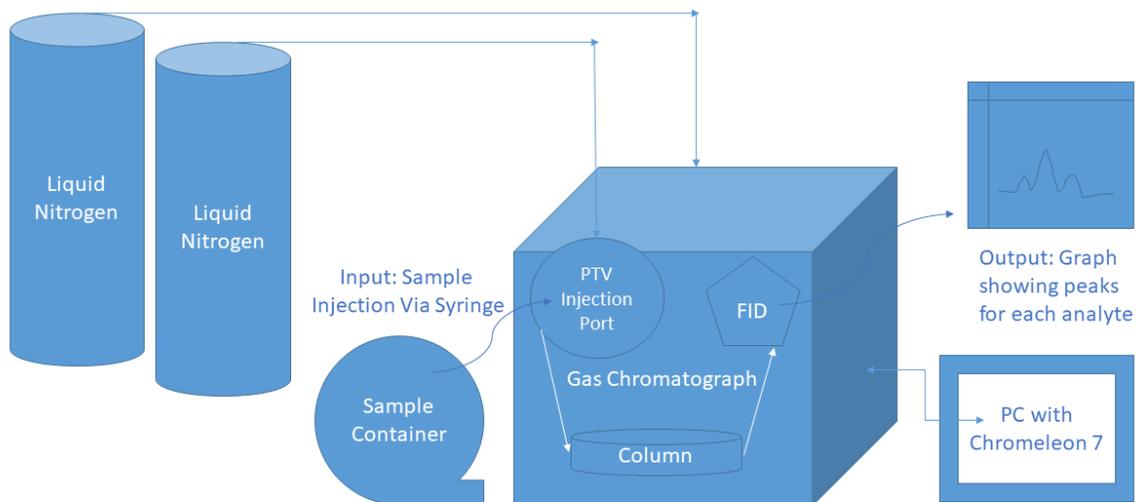


Figure 5. Diagram of current equipment setup and flow of sample analysis using GC-FID.

Quality Control and Quality Assurance

Certain cleaning methods are required for quality assurance. Tedlar sample containers were cleaned with zero air before sampling and passed an initial calibration gas certification with a percent recovery of greater than 90% by the manufacturer. In addition all calibration gases or liquid used were traceable to National Institute of Standards and Technology (NIST), the gas chromatograph analytical system had an initial calibration (method validation), and it was made sure that the GC-FID system had established retention windows for each analyte prior to sampling. Three types of blank sample were collected and analyzed to evaluate sources of contamination and ensure

quality control. A trip blank was tested to evaluate whether there were any measurable sources of contamination in the transportation process. A Tedlar bag was leak tested, filled with zero air, and was stored in the same manner as all other sample bags during the first sampling excursion. This sample was returned to the lab and analyzed with the GC using the same procedure as the ambient samples. A field blank was tested to evaluate whether there were any measurable sources of contamination in the field sampling process. A Tedlar bag was leak tested, filled with zero air in the field, and was stored in the same manner as all other sample bags during the second sampling excursion. This sample was returned to the lab and analyzed with the GC using the same procedure as the ambient samples. An instrument blank was tested to evaluate whether there were any measurable sources of carryover in the GC analysis. A blank run with no injection was performed after a high concentration field sample to determine if any analytes remained in the system after the previous analysis run.

Method Validation

Method validation is an essential part of method development. Validation is the act of proving that the process, instrumentation, experimental procedure, and lab conditions are appropriate for detection of the given analytes and can provide consistent, reliable, and accurate data (Peris-Vicente et al. 2015). Parameters such as selectivity, calibration curve linearity and calibration range, accuracy, precision, limit of detection (LOD), limit of quantification (LOQ), robustness, system suitability, and stability will help evaluate the quality and consistency of analytical results obtained from a method (Peris-Vicente et al. 2015).

Sample stability is a measure of how well the analytes in a sample will be preserved over time in the specified sample container under the specified storage conditions.

Measurements are typically taken to determine what extent of degradation or other analyte loss may occur over the sample stability period. A stability study on VOCs in Tedlar bags showed a 98% recovery after 48 hours for benzene, 92% recovery for toluene after 48 hours, and 83% recovery of p-Xylene after 48 hours (Coyne et al. 2011). Understanding sample stability ensures sample containers do not have significant loss of subject analytes before analysis. It may be prudent for future studies to perform an in-house sample stability study on Tedlar bags similar to the aforementioned studies. It was observed during the calibration procedure that liquid BTEX standards stored in 2 mL SureStop glass vials in the freezer begin to lose effectiveness one week after initial

mixing. Measured values from calibration standards began to decrease with time after one week. New mixtures of liquid standard were back to expected values.

A calibration curve is an equation that relates the area under the peak to the known concentration of the analyte. It is typically expressed in the format:

$$A = (b \pm s_b) [\textit{concentration}] + (a \pm s_a)$$

Where A= peak area, b= slope, s_b = standard deviation of slope, a= y-intercept, and s_a = standard deviation of the y-intercept (Peris-Vicente et al. 2015). A good calibration curve should have five levels of concentration with three data points for each level. Because the method was not able to quantify some analytes in the lower concentrations, the number of data points and range of calibration for each analyte varied. Linearity is first appraised visually by inspecting the least-square linear regression line to see if it follows a linear trajectory. Next, the coefficient of determination (R^2) value is calculated and should be greater than 0.990 (Peris-Vicente et al. 2015). R^2 values for ethylbenzene and xylenes were >0.990 but R^2 values for benzene and toluene were slightly <0.990 (0.9820 and 0.9881, respectively). Linearity is generally expressed as the confidence limit around the slope of the regression line (Bhardwaj 2016). Table 4 shows the calibration curve equations and R^2 values for each analyte. Figure 6 shows calibration equation plots for each analyte. R^2 values are based on 99.5% confidence level. Negative values for y-intercepts in calibration equations indicated that the calibrations are slightly under-recovering the given concentrations. This inherent bias in the model can be attributed to

matrix effect, systematic errors in calibration standard preparation, or a combination of both. Matrix effect should be evaluated when linearity, accuracy, and precision have been calculated based on standard solutions (Peris-Vicente et al. 2015). A blank sample (in this case air sample or standard air) should be analyzed and recovery compared to liquid standards that the calibration is based on. Recoveries of <100% indicate matrix effect and can be corrected using a correction factor (Peris-Vicente et al. 2015). Sample matrix effect analysis is outside the scope of this project. However, once the cryogenic cooling system of the PTV module has been repaired and an updated method has been validated it would be appropriate to test the sample matrix effect.

Table 4. Calibration linear regression equations, R² values, relative standard deviation (RSD), and calibration range are given for benzene, toluene, ethylbenzene, and xylenes based on calibration of GC analysis.

Analyte	Calibration Equation	R²	RSD %	LOQ ppm	Calibration Range ppm
Benzene	y= 0.1822x -0.0276	0.98198	7.1625	0.2219	1.5-10
Toluene	y= 0.1902x -0.0427	0.98809	6.4631	0.4307	1.5-10
Ethylbenzene	y= 0.3754x -0.0526	0.99122	7.1152	0.5280	1.0-10
Xylenes	y= 0.1892x -0.0134	0.99021	6.2450	0.5004	1.5-10

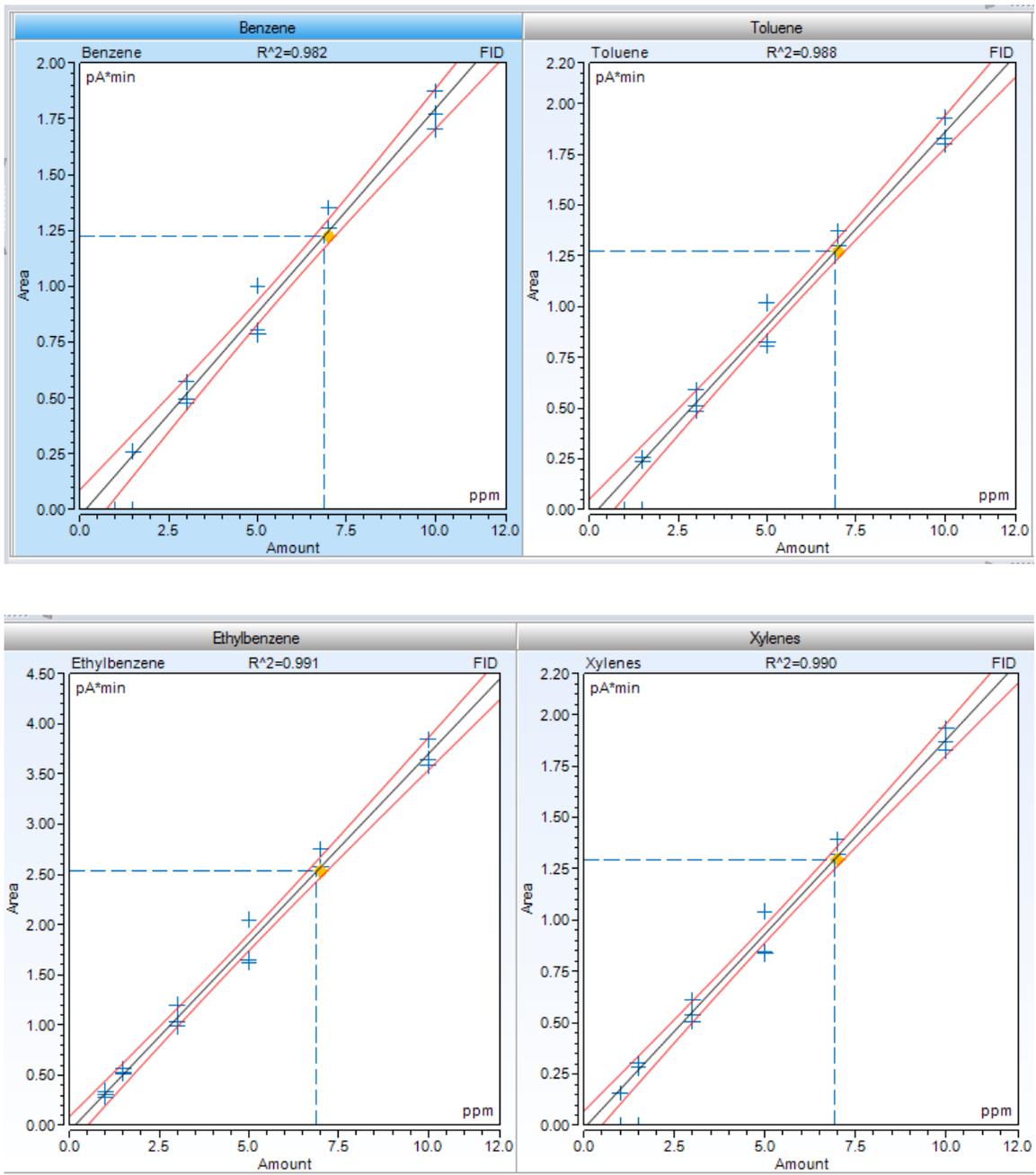


Figure 6. Calibration equation plots for benzene, toluene, ethylbenzene, and xylenes are given with confidence limits in red ($\alpha=0.005$). Yellow points indicate data point for selected injection and dotted lines indicate area and amount for selected data point.

In order to calculate measured amounts of BTEX in ambient air samples, there must be a calibration which produces a calibration curve. Chromeleon 7 software uses Equation 1 to calculate the amount in an unknown injection via external standards (Thermo Fisher Scientific Inc. 2015).

Equation 1:

$$Amount_{j,k} = f(Rsp_{j,k}) * \left(\frac{DilutionFactor_j}{Weight_j} \right) * Factor_k * InStd Factor_{j,k}$$

Where:

j, k: Indexes. Index j is used for any injections, k is used for components in the component table.

f: Inverted Calibration Function for a component in an unknown injection.

Rsp_{j,k}: Measured detector response of component k for injection j (area under the peak).

Dilution Factor: Injection-specific Dilution factor, as defined in the injection list.

Weight: Injection-specific Weight Factor, as defined in the injection list.

Factor_k: Scaling Factor as defined in the component table, for example, to compensate the differing absorption behavior; specific for each component.

InStd Factor: Correction factor for the Internal/External standard method. For the External standard method, this factor always equals 1.

The limit of detection (LOD) describes the lowest amount of analyte that will elicit a response from the GC but cannot necessarily be quantified. If a sample elicits a response from the GC but it is not able to be quantified, it will appear in the results as though it is not detected. The user may zoom in on the peak window in the chromatogram and observe a peak even though there is no detection reported. This indicates that the concentration of the analyte is above the LOD but below the limit of quantitation (LOQ). The LOD is estimated by the signal-to-noise ratio (3:1), where signal (s) is determined by $s = H/h$ (where H=height of corresponding peak and h=absolute value of largest noise fluctuation) (Bhardwaj et al. 2016). During the calibration testing process, gas samples as low as 100 ppb were injected into the GC and were able to elicit a response in the form of very small peaks in the retention windows for benzene, toluene, ethylbenzene, and xylenes. These peaks are not able to be quantified based on their small magnitude in relation to the noise in the baseline. It may be possible with method optimization to reduce the amount of noise in the baseline in order to quantify smaller concentrations of BTEX. The LOQ describes the lowest amount or concentration of analyte that can be quantified with a suitable precision and accuracy (Bhardwaj et al. 2016). The LOQ is estimated by the signal-to-noise ratio (10:1), where s is determined by $s = H/h$ (where H=height of corresponding peak and h=absolute value of largest noise fluctuation) (Bhardwaj et al. 2016). The Chromeleon 7 program refers to the LOQ as Lower Prediction Limit. Any analytes that were reported by the GC as “not detected” were

reported as <LOQ as is common practice in environmental sample reporting. LOQ for each analyte was reported in Table 4.

Precision is a measure of the closeness of agreement among a series of measurements of the same homogeneous sample, which is usually expressed as relative standard deviation (RSD) (Bhardwaj et al. 2016). Precision can also be defined as intermediate precision. Intermediate precision shows the method ruggedness when certain factors vary like analyzing samples on different days in the same lab (Bhardwaj et al. 2016). The calibration performed in this study incorporated elements of ruggedness because standard liquids were injected on different days to create a calibration curve. There were also two separate batches of calibration standards that were created during the calibration process. RSD was calculated by Equation 2.

Equation 2:

$$RSD = \frac{s}{\bar{x}} \times 100$$

Where s = sample standard deviation and \bar{x} = sample mean.

RSD for each analyte were between 6.2450-7.1625%. Acceptable RSD for method precision is less than 15-20% according to the Food and Drug Administration (FDA) (Peris-Vicente et al. 2015). RSD values for each analyte were given in Table 4.

Accuracy of the method was assessed by injecting VOC standards and calculating percent relative accuracy, as described in US EPA Method TO-14A (Equation 3).

Equation 3:

$$\% \text{ Relative Accuracy} = \frac{Y - X}{X} \times 100$$

Where:

Y= Concentration of the targeted compound recovered from sampler.

X= Known concentration value of VOC targeted compounds in the standard.

Table 5 shows known values of calibration standards and the recovered measured values were used to calculate percent accuracy during calibration using Equation 3. The accuracy is positive when the method overestimated the amount of analyte in the sample and negative when the method underestimated the amount of analyte in the sample.

Percent relative accuracy for benzene ranged between -10.272% and 10.373% with an overall average of 0.337% based on 13 data points. Percent relative accuracy for toluene ranged between -10.354% and 11.754% with an overall average of 0.331% based on 14 data points. Percent relative accuracy for ethylbenzene between 1 ppm and 10 ppm ranged between -10.402% and 12.133% with an overall average of 0.782% based on 18 data points. Percent relative accuracy for xylenes was between -9.518% and 11.84% with an overall average of 0.951% based on 15 data points. Calibration standards in the lower concentrations that did not report a measured value were considered not detected (ND).

The GC will extrapolate values below the calibration range (1.5-10 ppm) based on the calibration curves. Because accuracy cannot be calculated in these areas, it is prudent to treat samples that return low concentrations with skepticism.

Table 5. Known values of calibration standards and recovered measured values are used to calculate percent accuracy during calibration of GC analysis of benzene, toluene, ethylbenzene, and xylenes.

Calibration ID	Known Value		Measured Value				Percent Accuracy			
	Concentration PPM	Benzene PPM	Toluene PPM	Ethylbenzene PPM	Xylenes PPM	Benzene PPM	Toluene PPM	Ethylbenzene PPM	Xylenes PPM	
Cal 1 #1	1	ND	ND	0.999	0.975			-0.150	-2.530	
Cal 1 #2	1	ND	ND	1.084	ND			8.410		
Cal 1 #3	1	ND	ND	0.927	ND			-7.340		
Cal 2 #1	1.5	1.581	1.580	1.650	1.678	5.380	5.360	9.993	11.840	
Cal 2 #2	1.5	ND	1.487	1.540	1.560		-0.840	2.660	-3.987	
Cal 2 #3	1.5	ND	ND	1.510	ND			0.647		
Cal 3 #1	3	3.311	3.342	3.364	3.329	10.373	11.387	12.133	10.953	
Cal 3 #2	3	2.787	2.795	2.792	2.800	-7.090	-6.843	-6.930	-6.660	
Cal 3 #3	3	2.888	2.948	2.925	2.970	-3.747	-1.750	-2.487	-1.000	
Cal 4 #1	5	5.652	5.588	5.613	5.596	13.032	11.754	12.262	11.914	
Cal 4 #2	5	4.576	4.580	4.550	4.556	-8.474	-8.394	-8.994	-8.882	
Cal 4 #3	5	4.486	4.482	4.480	4.524	-10.272	-10.354	-10.402	-9.518	
Cal 5 #1	7	7.573	7.435	7.484	7.421	8.189	6.213	6.909	6.016	
Cal 5 #2	7	7.062	7.048	7.002	7.049	0.884	0.684	0.033	0.693	
Cal 5 #3	7	6.874	6.905	6.891	6.916	-1.807	-1.363	-1.560	-1.196	
Cal 6 #1	10	10.426	10.364	10.370	10.272	4.263	3.636	3.696	2.720	
Cal 6 #2	10	9.875	9.834	9.840	9.902	-1.255	-1.661	-1.602	-0.980	
Cal 6 #3	10	9.490	9.681	9.680	9.691	-5.098	-3.190	-3.201	-3.091	
Average						0.337	0.331	0.782	0.951	

Robustness is the ability of a method to remain unaffected by small, deliberate changes of the experimental conditions (Peris-Vicente et al. 2015). This parameter is outside the scope of this project. However, once the cryogenic cooling system of the PTV module has been repaired and an updated method has been validated it may be appropriate to test the robustness of the method during routine usage.

A system suitability test can be performed during a routine analytical assay to assess that the overall system (instrumentation, hardware, software, etc.) is running as required to carry out analysis (Peris-Vicente et al. 2015). The GC is capable of detecting when method parameters deviate outside a preset range and sometimes can even implement a remedy if programmed to do so. The GC does not currently have any programmed system suitability test cases. The GC will report that each injection “passed” the system suitability check for each injection during the calibration process and during sample analysis because there were technically no failures. It may be prudent for future research to set up system suitability test cases, especially on critical method components and processes.

Selectivity means that the method is capable of producing a response to a specific analyte without any interference from other analytes and the response is fully attributed to that analyte only. A method is considered selective if the analyte is completely resolved, there are no baseline distortions near the retention time, and there are no overlapping peaks

from other analytes (Peris-Vicente et al. 2015). Individual resolution is a measure of a peak's isolation from other nearby peaks, which can be calculated with Equation 4.

Equation 4:

$$r_i = 1 - \frac{w'_i}{w_i}$$

Where r_i = individual peak resolution, w_i = area of the peak, w'_i = area of the peak overlapped by other peaks. The value r_i should always equal 1 for adequate resolution (Peris-Vicente et al. 2015). There was no peak overlap in calibration injections or sample injections. Some methods are selective enough to separate m- and p-xylenes from o-xylenes but it is not necessary. Labs will typically report xylenes as one group (total xylenes), especially when they co-elute. Regulatory agencies concerned with these VOCs will typically publish regulatory values for individual xylenes and also total xylenes.

RESULTS AND DISCUSSION

Ambient Air BTEX Concentrations

Measured concentrations of BTEX in ambient air samples are provided in Table 6. Samples at the refueling level consistently had sufficient concentration of VOCs within the analysis capabilities of the current method parameters. Samples at the breathing level and property line levels consistently returned analysis results of <LOQ. It was possible to see peaks in the respective retention windows on most breathing level chromatograms and some property line chromatograms, however the peaks could not statistically be differentiated from noise. Gastec tube sample values are relatively similar to at least one refueling level benzene detection on the corresponding sample day. Gastec D1 was measured at approximately 3 ppm, which is relatively close to the REF 2 D1 values of 4.3371 ppm and 2.9041 ppm. Gastec D2 was estimated at approximately 0.5 ppm, which is relatively close to the REF 2 D2 values of 1.4487 ppm and 1.3997 ppm. Gastec D3 was estimated at >10 ppm, which is in agreement with the REF 2 D3 values of 16.2388 ppm and 18.8537 ppm.

Sample Statistical Analysis

Because samples were collected from two gas stations and data were insufficient for analysis of covariance in the property line and breathing area levels, a two-way analysis

of variance (ANOVA) was performed on the refueling level of data. The two-way ANOVA expresses sample variability based on two factors, the station the sample was collected at and the pump it was collected from (Zar 2014). The objective of this statistic was to determine whether ambient BTEX at gas stations was prevalent enough to be detected by the modified method and whether the results can produce useful statistics regarding the studied factors. A model was developed for hypothesis testing using two-way ANOVA as shown in Equation 5 ($\alpha=0.05$). A Tukey test was performed to investigate multiple comparisons of analyte concentration among different sampled gas pumps ($\alpha=0.05$).

Equation 5:

$$Y_{ijk} = \mu + \text{Station}_i + \text{Pump}_j + \text{Error}_{ijk}$$

Where:

Y_{ijk} : the kth replicate of the jth pump of the ith day

μ : the overall mean

Station_i : the ith station effect (fixed)

Pump_j : the jth pump effect (fixed)

Error_{ijk} : the random error, $\text{Error} \sim \text{NID}(0, \sigma^2)$

Gas station VOC average concentrations were significantly different as seen in Figure 7. Each sample pump is significantly different in terms of VOC average concentrations, except for S3-S5, see Table 7. Each analyte varies significantly based on the pump it was

sampled from, see Figure 8. Table 8 shows average concentration of BTEX in ambient air based on sampling day. Model assumptions were checked using residual plots. It is likely that results from analysis lack statistical significance based on a deficiency of systematic sampling of air samples rather than poor quality of data.

Table 6. VOCs in ambient air samples at two gas stations in Nacogdoches, Texas. Refueling level of samples are indicated by REF. Breathing area level of samples are indicated by BRE. Property line level of samples are indicated by PRO. The number following level in Sample ID indicates the sample bag number. The day the sample was taken is indicated by D1, D2, D3. Sunoco gas station (S) and Valero gas station (V) are identified along with the respective pump number.

Sample ID	Station/ Pump	Benzene PPM	Toluene PPM	Ethylbenzene PPM	Xylenes PPM
REF 1 D1	S5	34.9721	18.3382	19.7231	15.4144
	S5	34.2135	16.8652	17.0713	14.774
REF 2 D1	S2	4.3371	4.8588	7.5772	5.3293
	S2	2.9041	4.3014	6.6073	4.5756
REF 1 D2	V4	8.7214	3.5645	6.4538	5.522
	V4	5.2465	3.2347	4.6501	3.8606
REF 2 D2	V4	1.4487	0.493	0.735	0.6155
	V4	1.3997	<0.4307	0.561	<0.5004
REF 1 D3	S2	3.4706	14.5209	5.3633	17.1945
	S2	2.8627	15.1075	4.6136	18.8423
REF 2 D3	S3	16.2338	28.1895	5.9155	31.3443
	S3	18.8537	26.4933	6.9458	27.0466
BRE 1 D1	S7	<0.2219	<0.4307	<0.5280	<0.5004
	S7	<0.2219	<0.4307	<0.5280	<0.5004
BRE 2 D1	S7	<0.2219	<0.4307	<0.5280	<0.5004
	S7	<0.2219	<0.4307	<0.5280	<0.5004
BRE 1 D2	V3	<0.2219	<0.4307	<0.5280	<0.5004
	V3	<0.2219	<0.4307	<0.5280	<0.5004
BRE 2 D2	V1	<0.2219	<0.4307	<0.5280	<0.5004
	V1	<0.2219	<0.4307	<0.5280	<0.5004
BRE 1 D3	S2	<0.2219	<0.4307	0.629	<0.5004
	S2	<0.2219	<0.4307	<0.5280	<0.5004
BRE 2 D3	S7	<0.2219	<0.4307	<0.5280	<0.5004
	S7	<0.2219	<0.4307	<0.5280	<0.5004
PRO 1 D1	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
PRO 2 D1	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
PRO 1 D2	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
PRO 2 D2	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
PRO 1 D3	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
PRO 2 D3	-	<0.2219	<0.4307	<0.5280	<0.5004
	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D1	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D1	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D2	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D2	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D3	-	<0.2219	<0.4307	<0.5280	<0.5004
Blank D3	-	<0.2219	<0.4307	<0.5280	<0.5004
Gastec D1	S7	3	-	-	-
Gastec D2	V4	0.5	-	-	-
Gastec D3	S3	>10	-	-	-

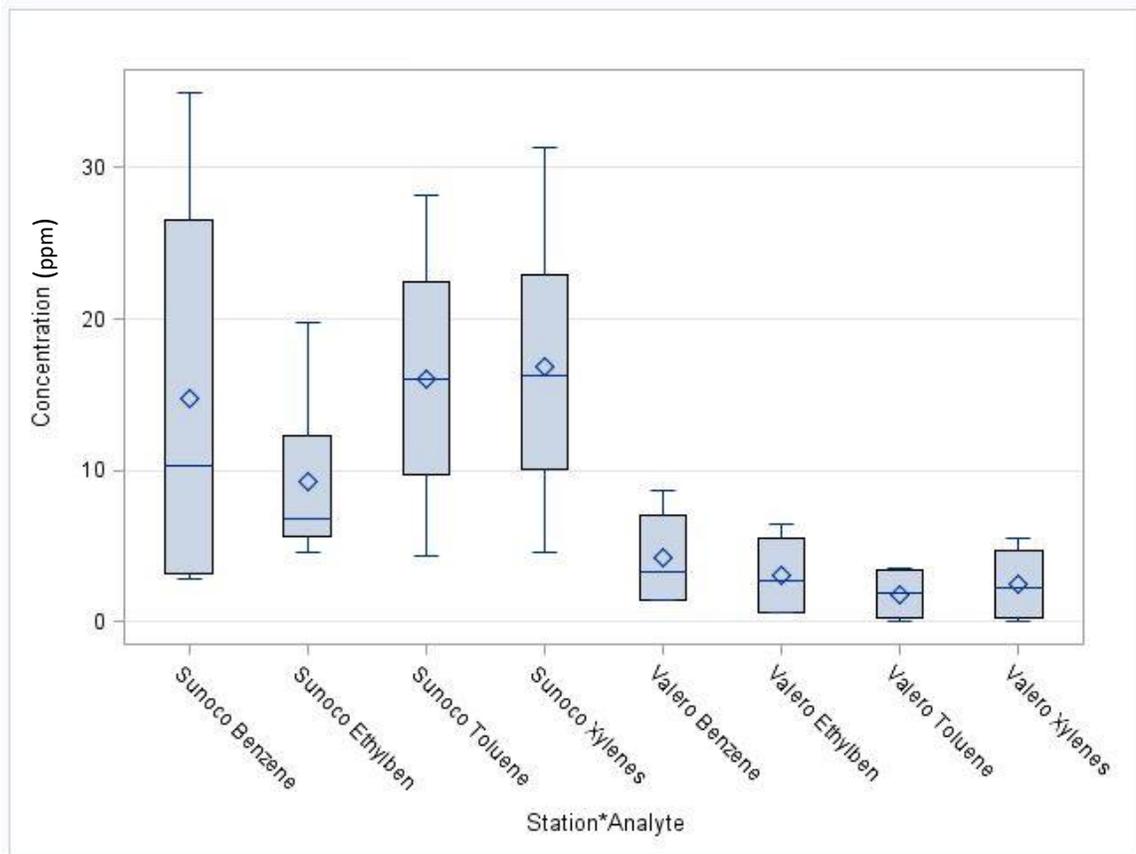


Figure 7. Distribution of average benzene, toluene, ethylbenzene, and xylenes concentration (ppm) in ambient air samples based on the gas station they were sampled from (Sunoco and Valero). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle. Diamond symbol inside box denotes the mean value. Line in the middle of the box represents the median value. Box upper and lower bounds represent the interquartile range (Q1 and Q3). Whiskers represent minimum and maximum values.

Table 7. Comparison of mean BTEX concentration (ppm) in ambient air samples between various pumps at two gas stations. Comparisons significant at the level $\alpha=0.05$ are indicated by ***. Gas pumps are denoted by their pump number (Pump 2, Pump 3, Pump 4, and Pump 5). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle.

Pump Comparison	Difference		
	Between Means (ppm)	Simultaneous 95% Confidence Limits (ppm)	
5 - 3	1.294	-3.480	6.067
5 - 2	13.767	9.634	17.901 ***
5 - 4	18.515	14.381	22.649 ***
3 - 5	-1.294	-6.067	3.480
3 - 2	12.474	8.340	16.607 ***
3 - 4	17.221	13.087	21.355 ***
2 - 5	-13.767	-17.901	-9.634 ***
2 - 3	-12.474	-16.607	-8.340 ***
2 - 4	4.747	1.372	8.123 ***
4 - 5	-18.515	-22.649	-14.381 ***
4 - 3	-17.221	-21.355	-13.087 ***
4 - 2	-4.747	-8.123	-1.372 ***

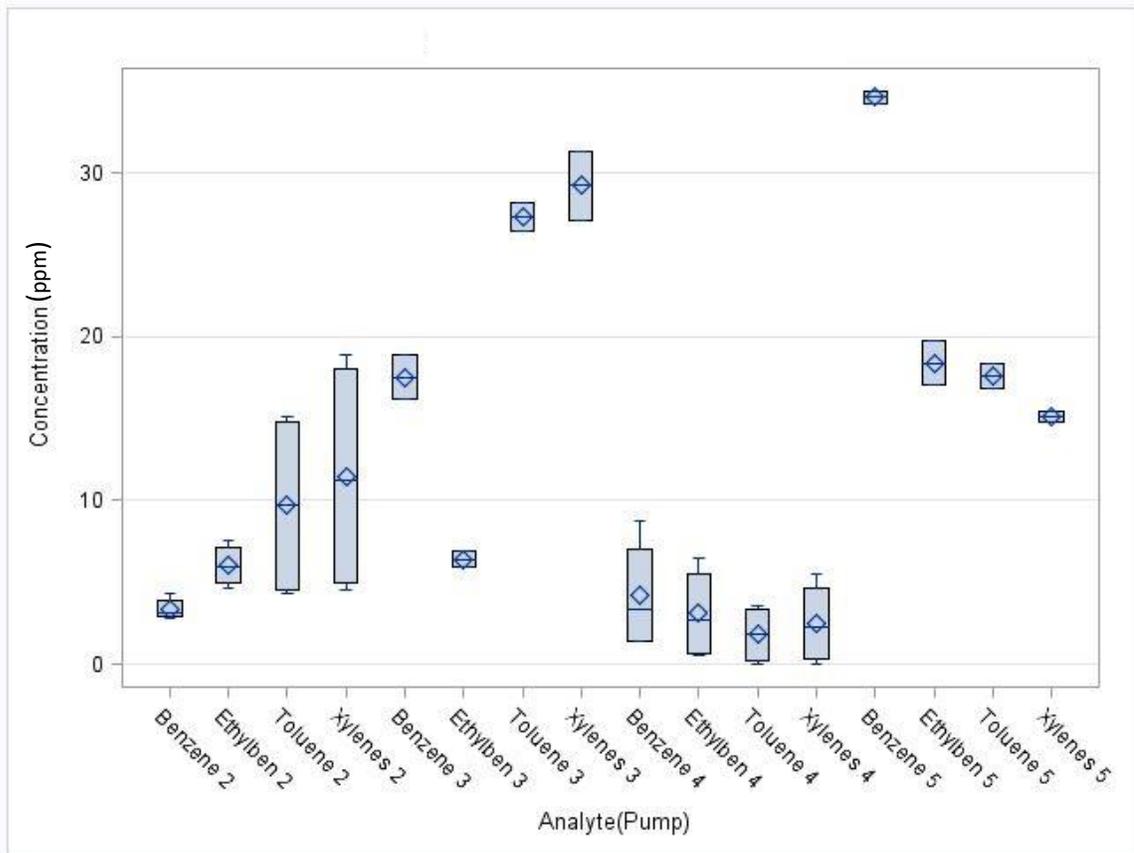


Figure 8. Distribution of benzene, toluene, ethylbenzene, and xylenes concentration (ppm) in ambient air based on pump the sample was obtained. Gas pumps are denoted by their pump number (Pump 2, Pump 3, Pump 4, and Pump 5). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle. Diamond symbol inside box denotes the mean value. Line in the middle of the box represents the median value. Box upper and lower bounds represent the interquartile range (Q1 and Q3). Whiskers represent minimum and maximum values.

Table 8. Average concentration (ppm) of benzene, toluene, ethylbenzene, and xylenes in ambient air based on the gas station (Sunoco or Valero). Ambient air samples were obtained at the refueling level adjacent to the fuel nozzle.

Station	Analyte	N	Concentration	
			Mean	Std Dev
Sunoco	Benzene	8	14.731	13.753
Sunoco	Ethylbenzene	8	9.227	5.778
Sunoco	Toluene	8	16.084	8.692
Sunoco	Xylenes	8	16.815	9.319
Valero	Benzene	4	4.204	3.509
Valero	Ethylbenzene	4	3.100	2.926
Valero	Toluene	4	1.823	1.836
Valero	Xylenes	4	2.500	2.632

CONCLUSIONS

Concentrations of toluene, ethylbenzene, and xylenes identified by the modified method of analysis are well below the NIOSH REL (ranging 100 ppm to 150 ppm) and OSHA PEL (ranging 100 ppm to 500 ppm). The LOQ for each of these VOCs are well below their lowest protective levels of 100 ppm. This indicated that the modified method was adequate for analyzing these VOCs for protective purposes. Concentrations of benzene identified by the modified method of analysis were well above the NIOSH REL and OSHA PEL. The LOQ for benzene was also above protective level of NIOSH REL (0.1-1.0 ppm) and OSHA PEL TWA (1.0 ppm) though it was below the OSHA STEL (5.0 ppm). This indicated that the modified method may not be adequate for analyzing benzene for protective purposes.

LIMITATIONS AND FUTURE IMPLEMENTATION

The main variation from the EPA method procedure is that the evacuated canisters used to collect and store air samples were replaced with Tedlar bags. The Tedlar bag is a common sample container used in air quality analysis (Lee et al. 2002). The Tedlar bag is recommended in EPA Method 18 to measure organic compounds in air samples by gas chromatography (Wang et al. 1996). Tedlar bags are considered to have good nonsorbing properties and are relatively inexpensive in comparison to stainless steel canisters (Wang et al. 1996). Samples from Tedlar bags are easier to analyze because they do not require the pressurization and cleaning procedures that stainless steel canisters require (Pau et al. 1991). Though cost-efficient and convenient, Tedlar bags have been shown to lose VOCs from samples when stored over time. Leaks are possible on improperly closed bags and the type of hardware attached to the bag can cause a significant loss of VOCs in a 12-24 hour period (Wang et al. 1996). This disadvantage can be controlled by analyzing samples within a short period of time after collection and ensuring the Tedlar bags are equipped with septum or Teflon coated valve. A stability study on VOCs in Tedlar bags showed a 98% recovery after 48 hours for benzene, 92% recovery for toluene after 48 hours, and 83% recovery of p-Xylene after 48 hours (Coyne et al. 2011). Because this study employed Tedlar bags as sample containers, the injection method was manual via gas-tight syringe.

Whole air sampling using evacuated canisters as described in US EPA. Method TO-14A does require the use of sample preconcentration either by cryotrap or a sorbent bed. The cryogenically cooled PTV injection port on the Trace 1300 is only capable of receiving an injected volume of air or liquid at approximately 2 milliliters. The US EPA. Method TO-14 requires approximately 490 milliliters of air sample to be concentrated and injected into the gas chromatograph in order to observe contaminant levels in the ppb range, which is the anticipated level of concentration in ambient air. The sorbent-based method concentrates analytes in ambient air samples by passing through a glass or metal tube packed with a material specifically designed to absorb the analyte. The concentrated analytes then go through a thermal desorption process that transfers the analytes to the GC column for analysis. Preconcentration using cryogens such as liquid nitrogen condenses analytes onto an inert solid surface. This method of sample preconcentration requires more sample preparation and is more time consuming (Lee et al. 2002). Without the use of a sample preconcentration unit, it is unlikely that the gas chromatograph will be able to detect analytes from small volume air samples in low ppb range with a high level of confidence.

Under the current operating parameters, the GC was able to detect VOCs in the ppb range, with an acceptable level of confidence. However, the LOQ of this study for benzene is greater than the NIOSH REL TWA of 0.1 ppm which means that there are ambient levels of benzene that exceed the REL that cannot confidently be detected by the current method parameters of the GC. Repair of the cryogenic cooling system of the PTV

injection port could allow cryogenic focusing of samples to recover analytes in samples less than the LOQ in this study.

Future study of VOCs with the modified method is not limited to oil and gas exploration air quality. Benzene and other VOCs are found in many other products of crude oil such as plastics. Benzene can also be naturally found in wildfire smoke. Particularly destructive wildfires can contaminate local drinking water sources with dangerous levels of benzene (Proctor et al. 2020). A simple calibration for other VOCs could facilitate a study of other outdoor air quality applications such as solvent utilization and waste management. The modified method could also facilitate indoor air quality studies, of which VOCs are a common contaminant.

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Appendix A
Standard Operating Procedure (SOP) for GC Analysis of BTEX

1. Purpose

The purpose of this document is to develop a Standard Operating Procedure (SOP) in accordance with the requirements of EPA Method TO-14A and good laboratory practices regulations. This SOP details how to analyze ambient air samples for concentrations of volatile organic compounds (specifically benzene, toluene, ethylbenzene, and xylenes) by use of the Thermofisher Trace 1300 Gas Chromatograph (GC) and related equipment in the Stephen F. Austin State University Environmental Assessment Lab.

2. Scope

This SOP covers general operation of the GC, preparations of standards, method calibration, sample collection, sample preparation, machine calibration, sample analysis, and routine maintenance. This SOP applies to all ambient air samples with VOCs processed in the Stephen F. Austin State University's Environmental Assessment Lab. The samples analyzed using this procedure will be collected by graduate students for the use in their thesis.

3. Responsibilities

Heather Hall is the primary researcher responsible for this SOP and the assays involved herein. Dr. Sheryll Jerez is also covered in this SOP.

4. Materials

Instruments and Consumables

1. Thermofisher Trace 1300 Gas Chromatograph
2. Thermofisher 10 ul Syringe
3. Hamilton 2.5 mL Gas-Tight Syringe
4. 10-liter Tedlar Bags (Cat. No. 231-10)
5. Vac-U-Chamber
6. SKC Quick Take 30 pump (Cat. No. 228-9530)
7. Various GC consumables referenced throughout the SOP, some for regular maintenance and some only on as-needed basis (septa, vials, column, column cutter, ferrule, leak detector etc.)
8. Laboratory Hood
9. Kestrel portable weather meter 5500

Chemicals

1. BTEX Liquid Standard 200 ug/mL (Restek Catalog # 30051)
2. Liquid Nitrogen tanks for cooling oven and PTV inlet (PTV = 22 PSI, Oven = 60-80 PSI)

Gases

3. Helium
4. Zero Air
5. Hydrogen
6. BTEX Gas Standard 100 ppb (Air Liquide Cat. No. 41901)

5. Lab Procedures

General Operation of the GC

1. The oven requires a nitrogen tank that can be at an optimal pressure of about 60-80 PSI, but no more than 100 PSI. You may achieve this by pressuring up a 22PSI tank to 60 PSI, or you may choose to take a higher PSI tank and vent the pressure down. On a 200 PSI tank (or greater), it is helpful to open the nitrogen vent as far as practical so that the pressure can drop quickly to reduce the waste of liquid nitrogen. The sound from the venting is quite loud (>100 decibels) so hearing protection is strongly recommended.
2. Once the PTV is repaired, the liquid nitrogen tank attached to the PTV should read 22 PSI. If the tank reads 22 PSI, there is no need to vent the tank. If a nitrogen tank was delivered at a higher pressure, it is advisable to replace it with a tank that is at 22 PSI. You may be able to run analysis with a tank at larger pressure, but the tank must be vented to 22 PSI to prevent damage to the GC. Turn "Vent" valve on liquid nitrogen tank counterclockwise until gas begins to vent out of the tank.
3. The first vent of a new set of tanks may last a few minutes and it may be wise to open the lab door and exterior door to allow air flow. There is a yellow O₂ meter attached to the hydrogen line. It will beep if the venting of the N₂ displaces the %O₂ in the room. It typically will stop beeping after about 30 seconds as air O₂ levels return to normal. If the beeping lasts significantly longer, it is advisable to ensure the N₂ vent is closed and leave the lab for fresh air until the beeping has ceased. If the tanks are used frequently, the subsequent venting may only take a minute or so for each nitrogen tank. When the tanks are installed it is helpful to point their vents towards the door. Vent one tank at a time and do not pass any body parts through vent gas.
4. Use a cloth, glove, or other insulating material to protect your hand from the cold of the knobs and valves on the liquid nitrogen tank. It will typically accumulate frost by the time venting is complete and should not be allowed to contact bare skin.
5. Turn on the desktop computer connected to the GC. The password is Trace133085. Do not leave any USB drive inserted into the computer during boot or the computer will attempt to boot from the USB rather than the hard drive. Ok to leave Chromeleon License Key.
6. The computer will request to update the .NET Framework. The .NET Framework must not be updated. The version of Chromeleon installed on the computer will not operate correctly if the .NET Framework is updated. The computer will also send a pop-up stating that the virus definition files are out of date. Close this pop-up. The computer must not be updated or it will no longer interface correctly with the GC.

7. Open the valves on the hydrogen gas, synthetic air, helium gas, and liquid nitrogen tanks that inlet to the GC. The pressure on all these tanks should be kept below 100 psi. Higher pressures could damage the gas inlets on the GC.
8. Flip the power switch located on the back of the GC to the “On” position. The lights on the front display of the GC should illuminate.
9. Open the Chromeleon Instrument Configuration Manager (Instrument Controller) software on the computer connected to the GC.
10. Click the “+” to open the FO133085 menu, click the “+” to open the Trace 1300 menu, then right click the column “Trace 1300 Series GC II” to open column properties.
11. Click ‘Get’ to retrieve the instrument configuration and establish a connection to the GC.
12. Several of the settings within the configuration will need to be altered in order to correctly connect to the GC if it has not been operated recently or if someone else has changed the settings. Sometimes it will appear that the settings have been maintained, but it is still vital to “Get” settings every time you start the GC to ensure proper analysis. Under the “General” tab, Cryo settings must be set to “LiquidNitrogen”. Under the “Oven” tab, the minimum temperature of the oven must be changed to -100 degrees Celsius. Under the “Front Inlet” tab, uncheck the ‘Installed’ box. Under the “Front Detector” tab the makeup gas should be ‘Helium’. Press OK. Check the instrument controller status feed. Once you have updated the properties, the controller will initialize the driver of the GC and do some internal checks. If everything went well, the latest status will say “New detailed run state: Waiting for prep run key”. That means that the GC is ready to begin analysis.
13. To save the configuration setting click “File” – “Save Installation”. The configuration steps from step 9 must be performed each time the GC is connected to the computer. Failure to follow all portions of step 9 will result in a variety of issues when working in the Chromeleon software. If you saved the installation, the “Save Installation” option in the “File” menu will be disabled (grey instead of black).
14. The GC will still attempt to connect to the autosampler even though the sampler is not currently enabled. You may receive a pop up that gives a warning that “More than one inject device is installed” and that’s ok, click close. Do not close the instrument controller window. Minimize the controller window so that during analysis you can see details regarding how the method, etc. are running.

Creating an Instrument Method

1. The Instrument Method creation process is very detailed and requires knowledge of the basic chemical properties of the analytes you will be sampling for and a thorough understanding of the analytical process of the GC. There is a lack of method development information on the internet, though there are people at Thermofisher who can assist with method development for a fee. You may have better luck discussing method development questions with local chemists at a lab who work with GC every day. Photos of method parameters can be found in Section 9 of this SOP.

2. A method for analyzing BTEX has been created and is named “Modified TO14A BTEX” in the Chromeleon software. If you ever start having an issue with a method, it is sometimes best to just create a new method file with all the same settings and that may solve your issue. The following instructions contain specific settings for the “Modified TO14A BTEX” method. You may wish to test and/or change these settings in the future, especially with equipment changes.
3. In the Chromeleon 7 software, click “Create” and “Instrument Method”.
4. The first step is to determine how long the method will run. If you are not sure, put 0 in the “Run Time” field. It will be calculated at a later step. Next.
5. Select Injector that you will use for this method “PTVInjection”. Next.
6. Select available inlet “BackInlet”, select available column “BackInlet (carrier settings)”, and select available detector “FID”. Next.
7. Back Inlet flow is suggested to be a constant flow of 2 ml/min. Next.
8. In the “BackInlet Options” there is a wide array of settings to be managed. Under “Temperature Settings”, check the box to “Enable Temperature Control”. This will allow you to change the set “Temperature” or initial temperature of the PTV inlet at the beginning of the method. The current recommended temperature is 15 degrees Celsius. Also check the box to “Enable Cryogenics” to Cool During “PrepRun”. This allows the flow of liquid nitrogen to cool the PTV inlet before the method begins analyzing the sample. It is important to cool the inlet to prevent VOCs from escaping before analysis begins. The PTV cryo system is currently not operational, however the cooling of the oven does allow the PTV to cool to an extent. If the oven is cooled to 0 degrees Celsius, it allows the PTV inlet to cool to 15 degrees Celsius. The Cryo “Threshold” should be set to 40 degrees Celsius. When the PTV temperature is above 40 degrees Celsius, the fan will cool the PTV. When the temperature reaches 40 degrees Celsius, the PTV will begin cooling with cryogen. “Timeout” can be set to how ever long you wish the machine to time out if it is not able to cool efficiently, recommended 30 minutes.
9. In the “Inlet Parameters” section choose “Splitless” operating mode. Enable “Split Flow Control” by checking the box. Recommended “Split flow” is 50 ml/min, “Split ratio” is 25, and “Splitless time” is 2 minutes. Splitless mode is recommended for low concentration samples. You still need split flow and purge available to clean out the PTV after injection phase. Check the “Display Phase Program Plot” to ensure you are not splitting or purging until after injection phase is complete. Enable “Purge flow control” by checking the box and set purge flow to 5 ml/min. Do not enable “Constant septum purge” but do stop purge for 2 minutes. This prevents purging during sample transfer to the column. Do not enable vacuum compensation and do not enable gas saver mode.
10. In the “PTV Ramp Settings” section, enable evaporation phase and clean phase by checking the respective boxes. Do not enable pressure ramps. Post cycle temperature should be set to “CoolDown”. The following settings are also included in the PTV Ramp Settings section:

PTV Ramp
Settings

	Pressure (kPa)	Rate (°C/s)	Temp (°C)	Time (min)	Flow (mL/min)
Injection	-	-	-	2	(50)
Evap	-	5	40	5	-
Transfer	-	5	250	5	-
Cleaning	-	5	250	1	50

11. You can “Display Phase Program Plot” and make sure that all of the settings are correctly enabled and follow a logical pattern. The “Vapor Volume Calculator” will help you calculate the amount of sample you can inject based on the solvent type, liner, temperature, and pressure settings of the method. The “Column Flow Calculator” will help you calculate what column flow is appropriate for your method based on several factors. Next.
12. In “GC Oven Settings” section, “Prep Run Timeout” can be set to 10 minutes. “Oven equilibration time” can be set to 0.10 minutes. “Ready delay” can be set to 0 minutes. Enable cryogenics by checking the box and set threshold to 40 degrees Celsius. Oven mode should be set to “Ramped Temperature” and the temperature ramp settings are:

No	Retention time (min)	Rate (°C/min)	Target value (°C)	Hold time (min)
1	0	-	-	-
2	0	0	0	0
3	11	5	40	3
4	23	5	100	0
5	27.167	12	150	0
6	38.833	15	250	5
	Total time = 38.9	-	-	-

13. In the “FID Options” section, the FID should be enabled by checking the “Detector active” box and acquisition can run the duration of the method or you may choose to only run the FID in the time frame when analytes are expected to elute. “Data collection rate” should be 15 Hz. Enable “Detector Temperature Control” by checking the box and set detector temperature to 250 degrees Celsius. Enable “Flame” and “Flameout retry” by checking the boxes. “Ignition threshold” should be set to 2.0 pA. “Peak Width” should be set to “Standard.” Enable “Air flow control” (350 mL/min), enable “Makeup gas flow control” (35 mL/min), and enable “Hydrogen flow control” (40 mL/min). Next.
14. No need for “FID Time Program.” Next.
15. No need for “Relay and Switching Valves Time Program”.

16. Add comments in the comments section. You may want to specify analytes that the method was developed for or changes you've made to this new method from an existing method. Finish.
17. In the top left corner, save the method by clicking the "Save Changes" icon. Save the method in the methods folder and give it a name.
18. You do not need to create a new method every time you analyze samples, as long as you are analyzing for the same analytes that the method was developed for.

Creating a Processing Method

1. In the Chromeleon 7 software, click "Create" and "Processing Method". A "Quantitative" method is recommended. A "Basic Quantitative" method will not have the capability to do certain calculations.
2. Save the processing method and give it a name. It is helpful to name the processing method in a similar way to the method that it is associated with.
3. The first time you calibrate and change processing parameters it will update the processing method so that every subsequent sample in that sequence that uses that processing method will be processed with the same settings.
4. In order to analyze samples and produce a measured amount based on a calibration, you must analyze samples in the same sequence that the calibration was performed. If you add the processing method to a new sequence, it will appear as if no processing has been performed.

Creating a Sequence

1. Create a new sequence for the samples to be analyzed. This is done in Chromeleon using the sequence Wizard. Choose "Create" – "Sequence" This should start the wizard.
2. In the new sequence wizard you are able to create a pattern for injection name. Each sample in the sequence will follow this pattern name. Choose the number of vials and the number of injections per vial. It is helpful to use your vials as samples and the injections per vial as replicates. For manual injections the start position is irrelevant. Each injection in a sequence must be the same volume, put that volume into the injection volume field. Click next.
3. Choose which instrument method you will use by browsing the methods saved in the files. If you have made changes to a method since your last sequence, it is important to browse and reselect that method so that the updated parameters will be used in the new sequence. Browse for a processing method, you will likely want to use a quantitative processing method. Browse for a report template, you will likely want the default template. Channel: FID. Click next.
4. Record any comments you have regarding the sequence that you are making. It is helpful to describe what you are analyzing, how many samples, the date, etc. Finish.
5. Give your sequence a unique name and make sure it is saved in the sequences folder. You will create a new sequence every time you need to recalibrate the GC or analyze new analytes.

GC Calibration

1. If any changes have been made to the processing parameters in the instrument method or if the GC has been through a period of disuse, it is important to perform a routine calibration of the GC.
2. When handling standard solutions with hazardous substances, please use appropriate safety equipment such as goggles, nitrile gloves, breathing protection (hood), etc.
3. A typical GC calibration sequence will have 14 samples. 5 calibration levels with at least one replicate (3 is best), two blanks, and one unknown sample with a replicate. The 5 calibration levels should span the expected range of sample concentrations that will be analyzed.
4. Example dilutions of a 200 ppm (ug/mL) stock standard BTEX solution are summarized in the table below:

Volume of BTEX Liquid (200 ppm)	Volume Solvent	Concentration
5 uL	1 ml	1 ppm
15 uL	1 ml	3 ppm
25 uL	1 ml	5 ppm
35 uL	1 ml	7 ppm
50 uL	1 ml	10 ppm

5. Once all injections are analyzed in the calibration sequence, you must give each calibration injection an appropriate type and level. The type is “Calibration Standard” and the level is 1-5 depending on the concentration of the injection. You should also designate a blank injection with a type “Blank.”
6. Once the calibration standards all have type and level designated, you can open the Studio by clicking the “Studio” button in the top left corner of the “Data” page. In this view you can see details of the selected injection such as chromatogram, calibration plot, peak results, and calibration properties to name a few.
7. Zoom in the chromatogram so that you can see the peaks with adequate resolution for processing. You should be able to see the peak and the tail delimiters that indicate where the peak starts and stops so you can insert peak windows. The elution times may vary slightly from injection to injection so give a little extra room in the window to accommodate that. Click on the chromatogram to bring up the “Chromatogram Tools” pane in the top left area of the window. In the “Scale” pane you may want to use the “Autoscale Signal” and “Autoscale Time” buttons to improve the appearance of the peaks for easier processing. In the “Processing Details” activate the “Peak Windows” button which will add a small bar at the top of the chromatogram. You will click inside the bar to drag out the windows that each analyte elutes in.

8. Dragging out the peak windows automatically adds a new default component to the Component Table. You may also consider “Run Component Table Wizard” to identify peak windows.
9. Edit each component name in the Component Table and set the concentrations for each level for each analyte. Be sure to include units. Click “Show Properties” and click on the Calibration tab to check calibration properties such as origin settings and confidence limit settings.
10. In the “Data Processing Home” pane, click the “Calibration Plot” to show the calibration plot. You can update the plot settings by right clicking inside the plot and click “Properties.” Under “Title” in the “Center Title” type “ $R^2 = \{\text{peak.rQuadrat}/100;$ “0.000”} to have the R^2 value displayed on the calibration plot. Save everything when you are done.

Sample Analysis

1. After you have turned on the GC and updated the instrument controller settings, open the Chromeleon 7 software. The GC connection bar should be green and the status on the screen should read “StandBy”.
2. Add the samples you intend to analyze to a sequence that has been calibrated. If you need to change the injection name or volume, you can do so manually once the injection has been added. Save the sequence before you start the sequence.
3. Start the sequence by selecting the “Start” button in the Chromeleon software. The oven and PTV will begin to cool to the appropriate temperature as determined by the method. The status of the GC will state “Waiting” and may list “Oven Temperature” and “Inlet Temperature”. The GC is waiting for these two components to reach their initial settings (temperature) as programmed by the method. [Note: When the oven or PTV are cooling, you will hear a clicking sound from the valve that controls the flow of liquid nitrogen through the module. Be familiar with the sound it makes when it is working properly, so that when it is not working properly and making a different sound you can identify it and correct the problem.]
4. Once the GC has cooled to the start temperature of the instrument method, the feed will say “Entered Stage Inject Preparation” and you should hear a small beep. The GC is ready for injection when it says “Waiting for inject response on Trace 1300”. It will wait for approximately 10 minutes before it times out.
5. If you are analyzing standards or samples with hazardous chemicals, such as benzene, it is advisable to draw up samples in the laboratory hood to help protect yourself from breathing any escaped vapors. You will want to return liquid standards to the freezer between samples but do return to the hood to perform the next injection. Use a syringe to puncture the septum of the 10-liter Tedlar sampling bag or glass vial with rubber septum cap. Pull back slowly on the plunger of the syringe until you have drawn the sample to

the desired value (no more than 2 mL). 2mL is the largest volume of air or liquid that the PTV injection port will accommodate. A typical liquid injection size is 1 uL.

6. Press the “Start/Stop” button on the front panel of the GC to start the run. The blue “Run” light will illuminate indicating that the method is running. You have one minute to inject the sample. [If that is not enough time, you can adjust in the method settings.]
7. Place the tip of the syringe into the back inlet of the GC. Push the tip past the septum but do not push it far enough to contact the column (approximately halfway). Push down on the plunger of the sample syringe until all of the sample is injected into the GC.
8. At the end of the injection phase the GC will begin to raise the temperature of the PTV and oven.
9. As individual analytes elute from the column the FID will graph a response on the graph display on the main Chromeleon screen.
10. Between injections, clean the syringe by clearing with zero air 5 times or cleaning with solvent (methanol, etc) 5 times, depending on whether the samples are air or liquid.
11. Next the report generated by Chromeleon must be interpreted to determine the concentration of each constituent.

6. Field Procedure

Preparing for Field Sampling

1. When handling samples with hazardous substances, please use appropriate safety equipment such as goggles, nitrile gloves, breathing protection, etc.
2. Ensure that the bag material and fittings are appropriate for the compounds to be sampled.
3. Using PTFE tubing will prevent sample loss by adsorption on tubing walls.
4. Before using sample bags, flush the bag thoroughly 3 times with purified air or nitrogen.
5. Tedlar bags have been leak-tested by the manufacturer, however it is wise to leak test the bags before you take them into the field. Fill bags no more than 80% full of purified air or nitrogen and leave them for 24-48 hours to observe whether they deflate or not.
6. Sample analysis should occur within 24-48 hours of sample collection. Long-term storage of air-contaminant mixtures in bags is not recommended.

Sample Collection

1. Ensure sample bags have been checked for leaks, cleaned, and labeled with Sample ID. Open sample bag inlet by rotating plastic lock two turns counterclockwise and then push the slim tube all the way down. Rotate the plastic lock 2 turns clockwise to lock the inlet in the open position. This will allow air to flow into the bag. Open Vac-U-Chamber and insert stainless steel inlet fitting of 10-liter Tedlar sampling bag into sample inlet tube inside the Vac-U-Chamber. Remove two loose tubes that are stored inside the Vac-U-Chamber.

2. Ensure the air pump has been calibrated and the flow rate has been recorded. Describe Rotameter procedure. For grab samples it is not as important to know the flow rate, other than to ensure the sample bags are not overfilled.
3. Two tubes should be connected to the corresponding inlets on the exterior of the Vac-U-Chamber. The tube with the brass fitting is connected to the “Vacuum” fitting on the exterior of the Vac-U-Chamber. Firmly insert the male fitting into the female fitting until it clicks and is locked in place. The opposite end of this tube is inserted onto the pump. The other tube does not have any fitting and it attached to the “Sample” inlet on the exterior of the Vac-U-Chamber.
4. Close the Vac-U-Chamber ensuring that the two plastic clasps on the outside of the Vac-U-Chamber have snapped shut.
5. Hold the inlet tube of the air pump at chest level. Switch the air pump on and collect sample until the Tedlar bag has sufficient sample but is not overfilled. It is important to know the flow rate and volume of the bag to determine what time the pump will need to run for. Consider filling the bag approximately 80% full to reduce the risk of rupture or leakage. You may observe the bag filling through the window in the Vac-U-Chamber.
6. Switch off the air pump.
7. Disconnect the Tedlar bag from the Vac-U-Chamber. To close the sample bag inlet, rotate plastic lock two turns counterclockwise and then pull the slim tube all the way up. Rotate the plastic lock 2 turns clockwise to lock the inlet in the closed position. This will prevent sample loss by leaking.
8. Disconnect the pump tubing from the Vac-U-Chamber by pushing the ring around the female fitting towards the chamber and pull the male fitting towards you.
9. Sample bags should be stored at room temperature and should be analyzed within 24-48 hours.

7. Operation and Maintenance

Daily Operation

1. Efficient operation of the GC requires careful monitoring of all instrument parameters. Daily maintenance of the instrument includes: monitoring of gas levels and ensuring there are no active leaks, inspection of injection port septum, glass liner, gold seal and column connections, and injection syringes. All consumables and their respective connections should be in good operating condition and without leaks.
2. Injection port cleaning and maintenance for our purposes is required less frequently because during a typical sample run, all or almost all of the sample is vaporized and pushed onto the column. If any tubing or fittings between the GC and tanks are hissing or dripping, then they are leaking and should be addressed. [Note: The only valve that is appropriate to “hiss/leak” is the pressure relief valve that prevents the liquid nitrogen canister from building excessive pressure and rupturing. This pressure relief valve will constantly hiss as long as there is liquid nitrogen in the tank.]

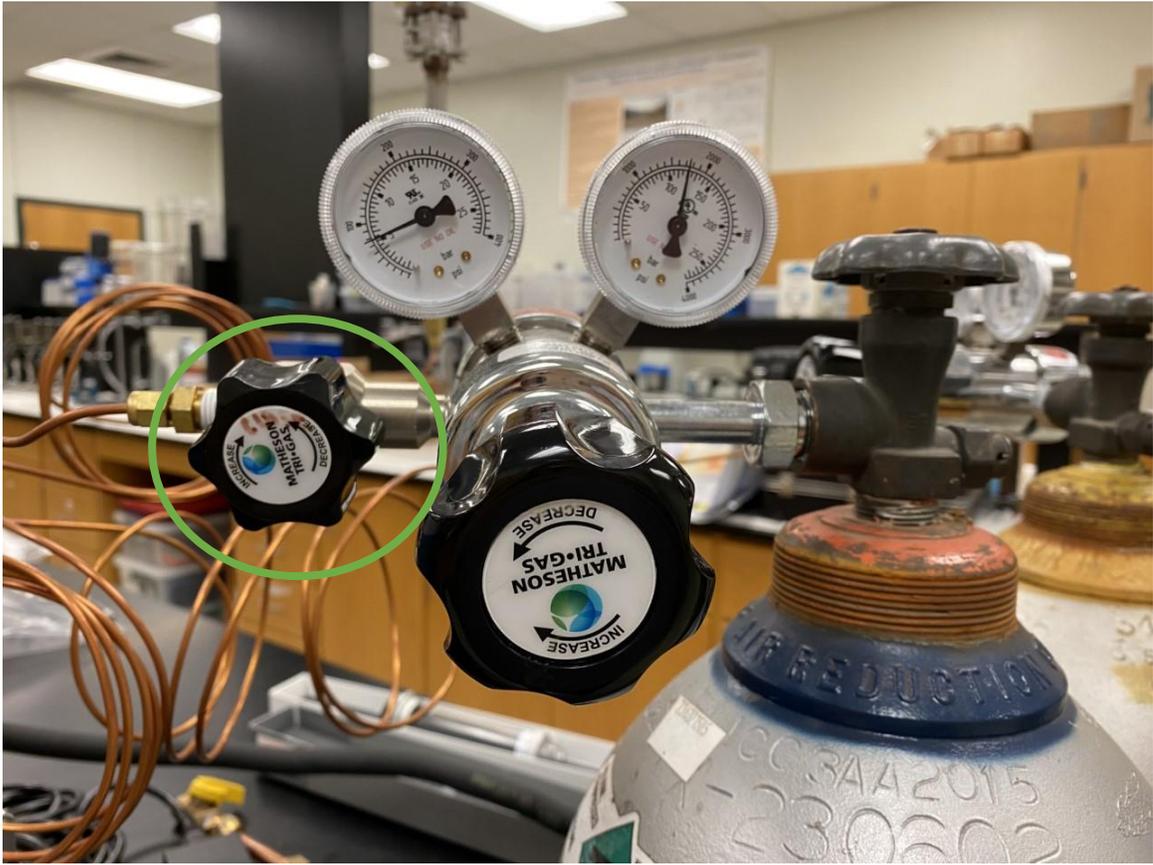
3. Some repairs will need a work order from the physical plant. It is ideal to have a photo and/or video of the issue to provide to the physical plant. Some repairs should only be made by a Thermofisher Technician. If you're not sure, consult the manual and/or call the Thermofisher Technical Support line: 1-800-532-4752.
4. Any variation from a consistent sample run could indicate the need for trouble shooting the instrument, indicated by retention time shifts, baseline movement, inconsistent injections, or improper standard and sample preparation.
5. Check syringe barrel for cracks and check syringe needle for burrs (beveled tip). Needle burrs can plug the needle with a small piece of septum. The cone tip syringe is much less prone to needle burrs. If the beveled tip syringe becomes plugged, do not pump the syringe at high pressure as it can crack the barrel. Using a solvent like acetone to soak a plugged syringe needle will help break down the rubber septum plug and facilitate plug removal.

GC Calibration

1. It is necessary to perform routine calibration any time a component of the system has been altered, changed, or replaced, if the machine has been idle for a long period of time, and if any parameters of the method have been altered.

Common Issues during Analysis

1. If the oven or PTV are not cooling, double check that you opened the valves to the liquid nitrogen.
2. If you receive an error that says "PTV carrier loss," you may need to open the valves to the helium tank. There is a small knob that opens and closes the regulator. It says "increase" and "decrease" when it should say "open" and "close." You should turn this knob counterclockwise to open the valve and clockwise to close the valve. See the knob circled in green in the following photos.





3. If you receive an error that says “FID carrier loss,” you may need to inspect the column for breakage or leak. Leak testing procedure is detailed in the manual.
4. If you receive an error that says “Waiting for front detector ready” during injection preparation phase, it is possible that the FID is not lit. The FID menu in the Instruments panel may show that the flow rate for makeup gas was good, but the flow rates for hydrogen and air were zero. The gas canisters were inspected and found to have appropriate amounts of gas and supplied pressure. This means that the FID failed to light. Typically, when the FID is attempting to light it will allow flow of the H₂ and Air but keep Makeup at 0. You may also hear a distinctive “pop” sound when the FID is attempting to light. You can observe the signal peaking from the typical baseline of 0.0900 above 2.5 pA when attempting to light. If the values go up near 4 pA and you observe all of the gases increase to their designated flows, then the FID is lit. Restarting the injection may solve FID lighting issues.
5. Sometimes you may receive an error that should not be happening upon further inspection. When this happens, end the run and restart. The next run might perform with no errors. Sometimes you just need to restart the method run or sometimes you need to shut the GC down fully and restart the whole system. This may resolve several types of errors.

8. Definitions

GC: gas chromatograph

FID: flame ionization detector

SOP: standard operating procedure

Cryo: cryogenic

PTV: Programmable Temperature Vaporizing injection module

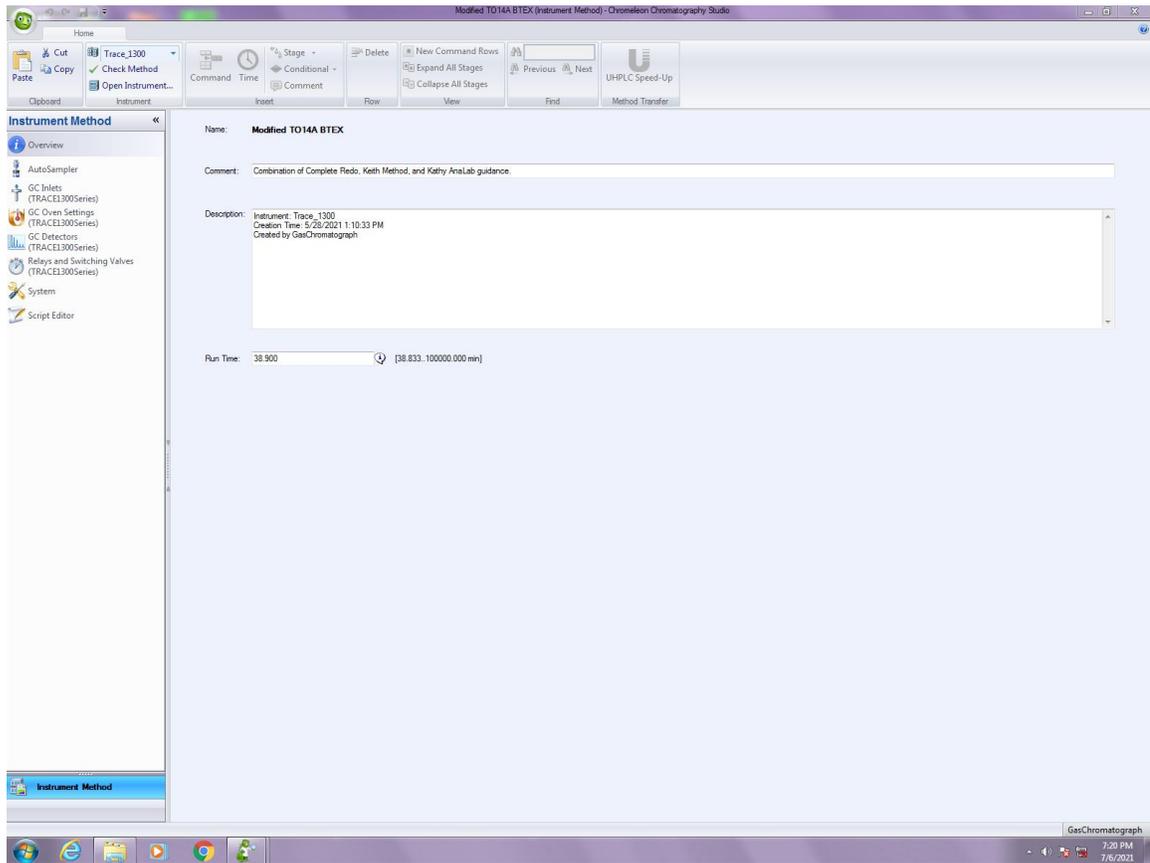
BTEX: Benzene, toluene, ethylbenzene, and xylenes (m-, o-, and p-) (Note: the xylenes are grouped together because they typically co-elute, but it is possible for them to elute separately.)

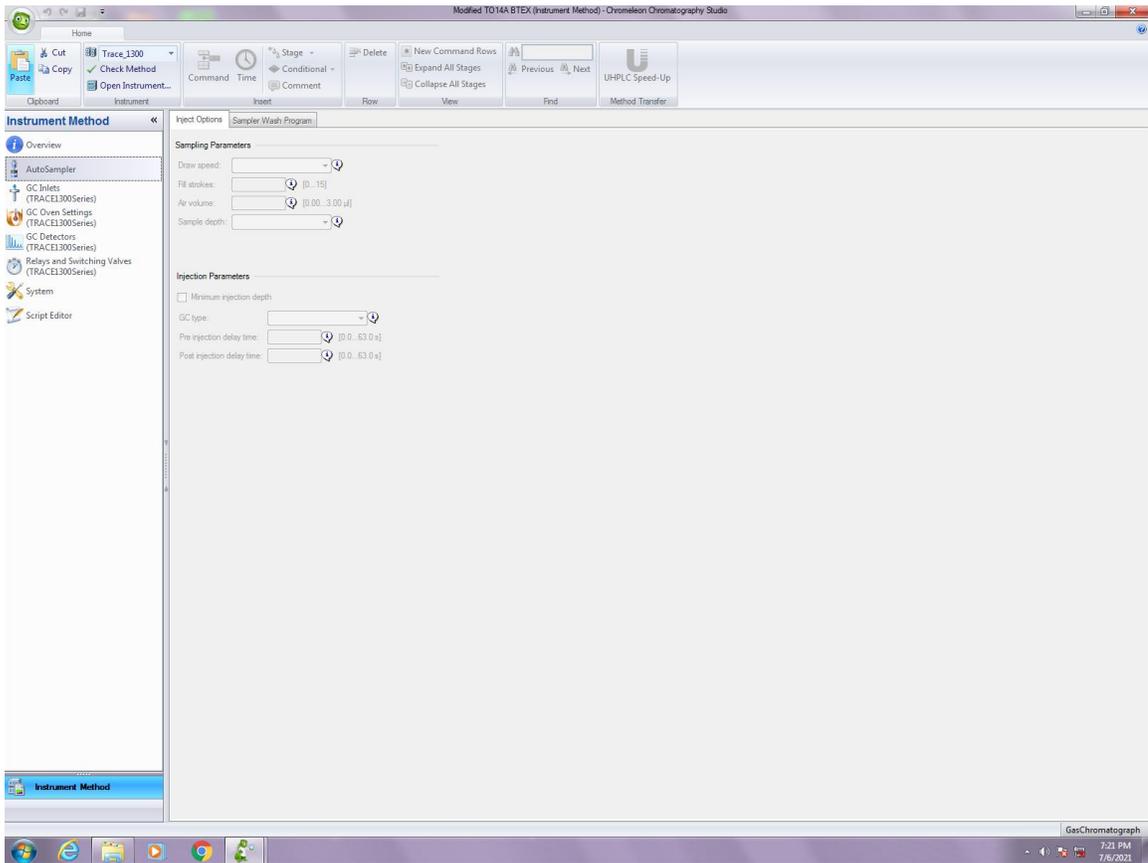
PSI: pounds per square inch

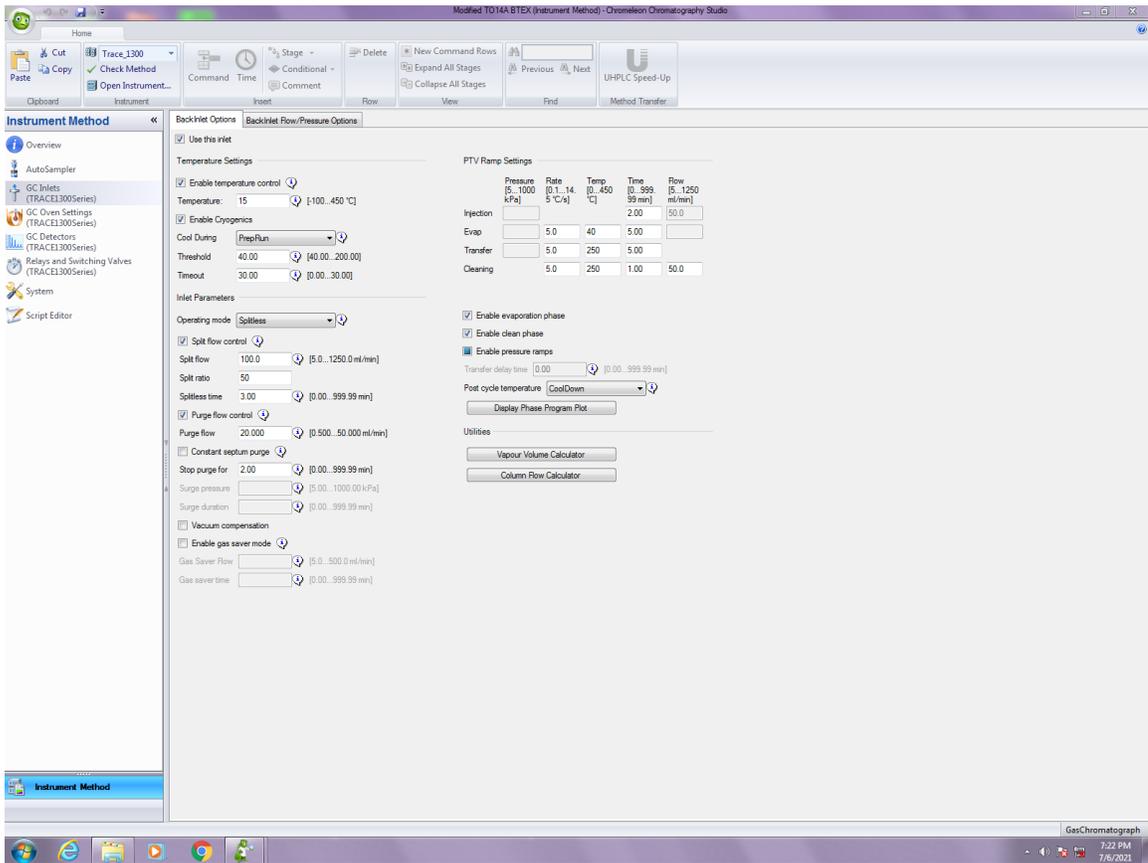
PTFE: polytetrafluoroethylene

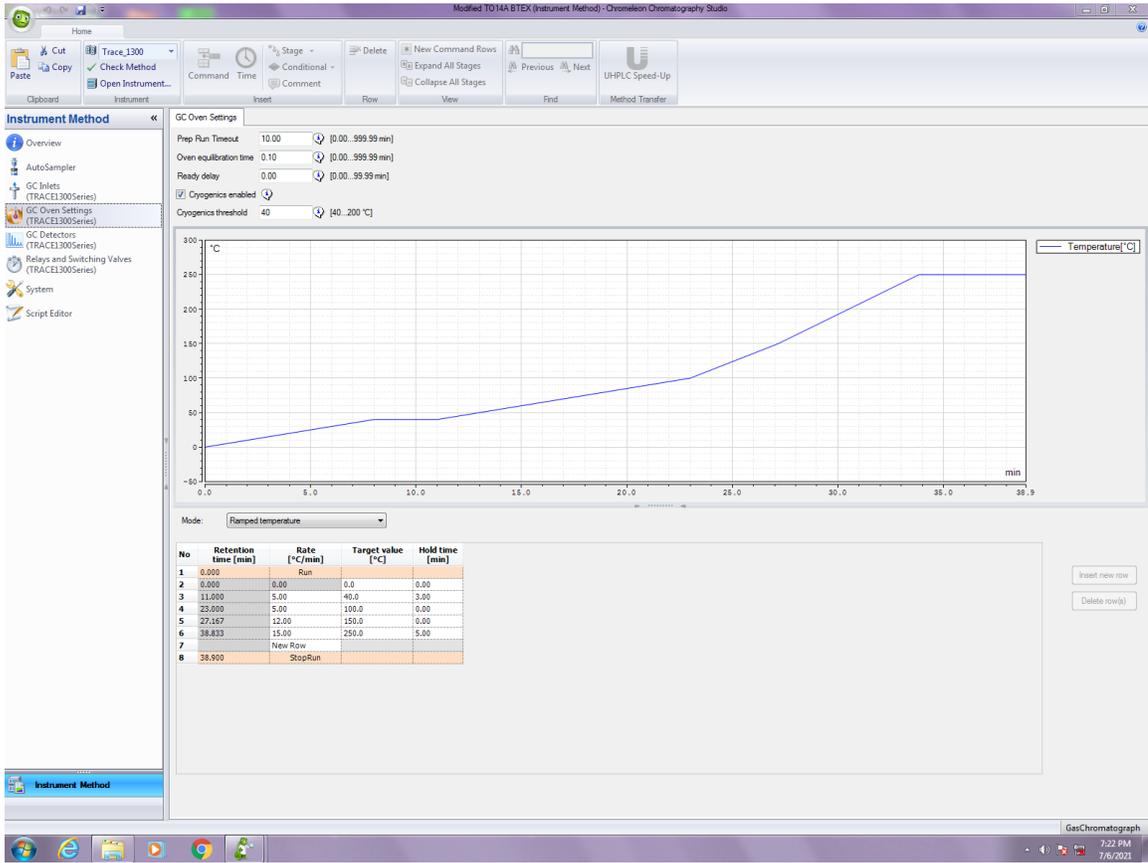
9. Method Parameters

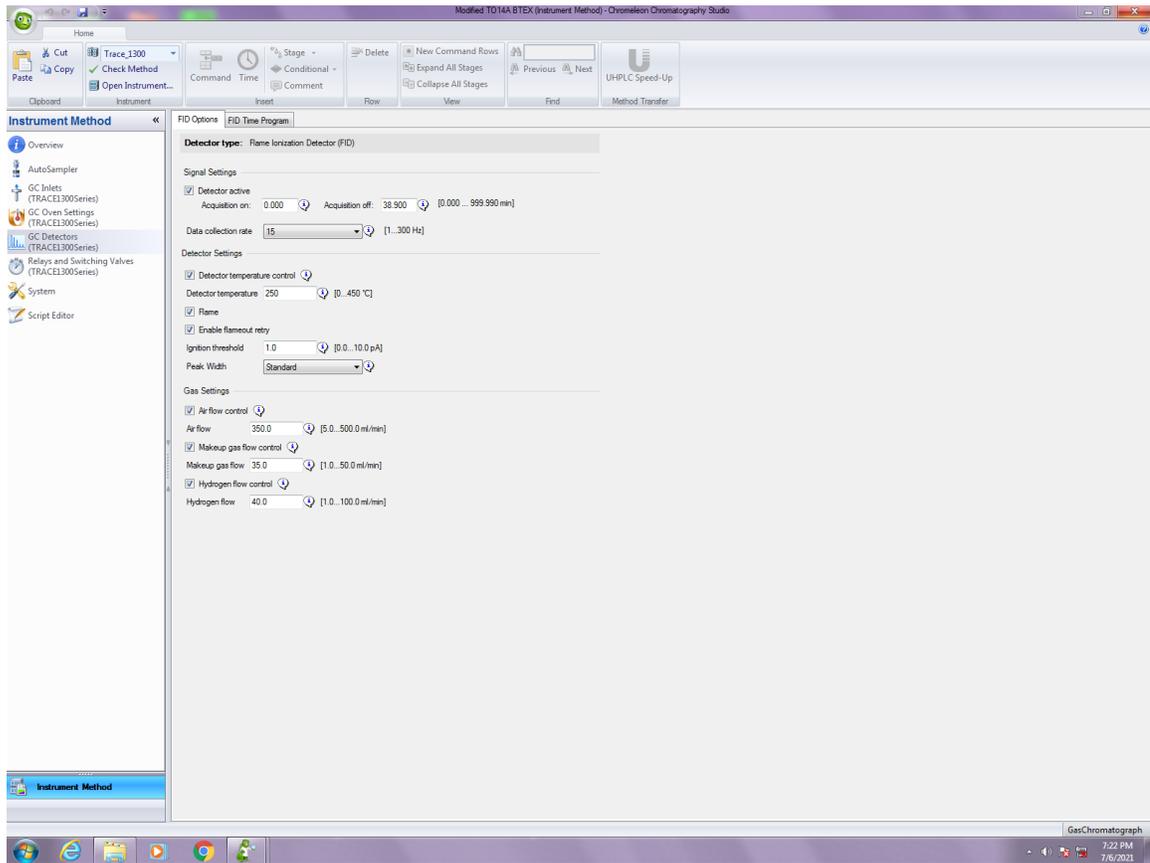
The following photos detail the Instrument Method parameters for “Modified TO14A BTEX” in Chromeleon 7.

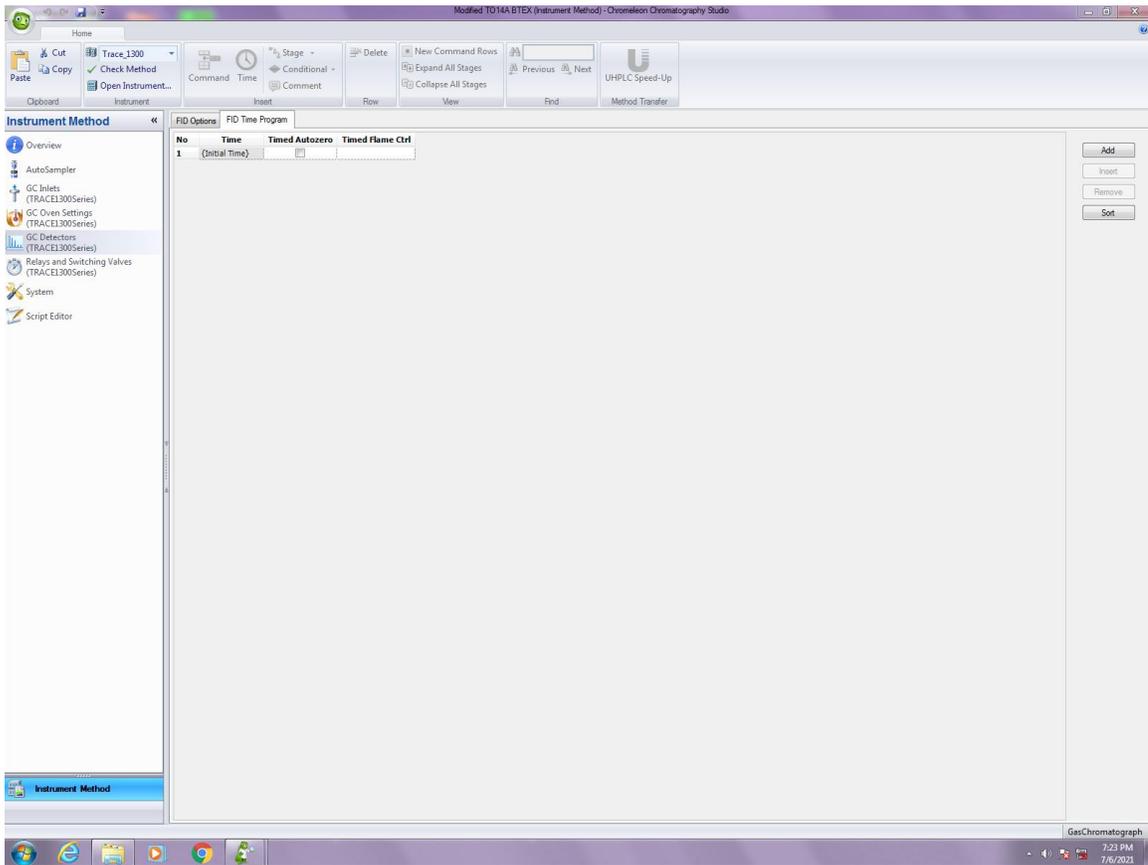


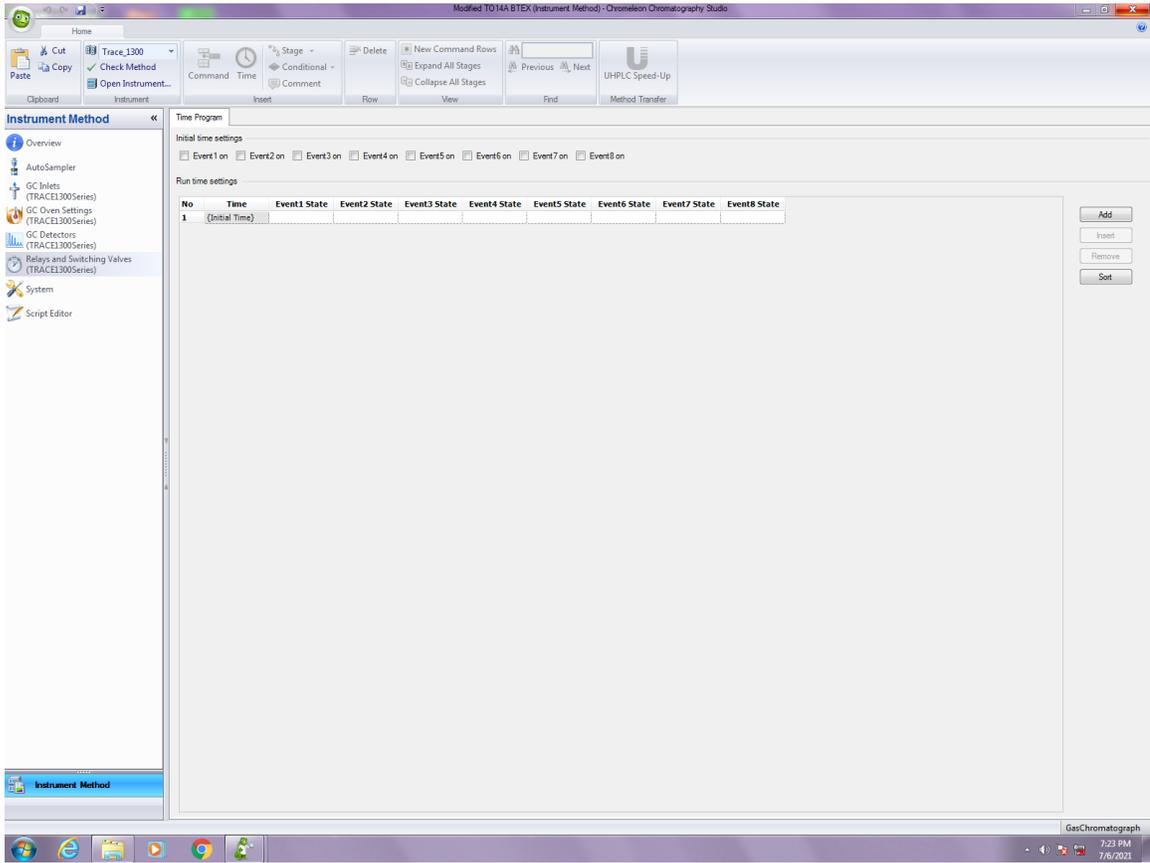


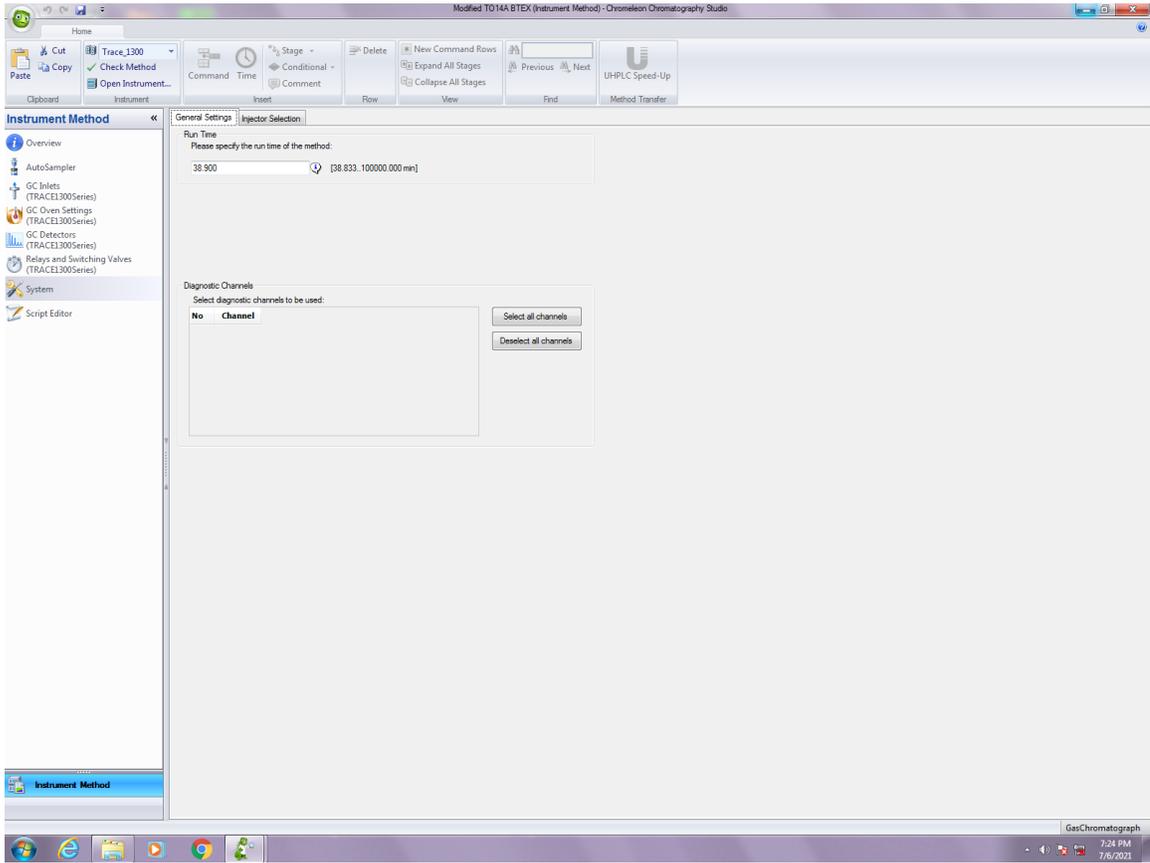


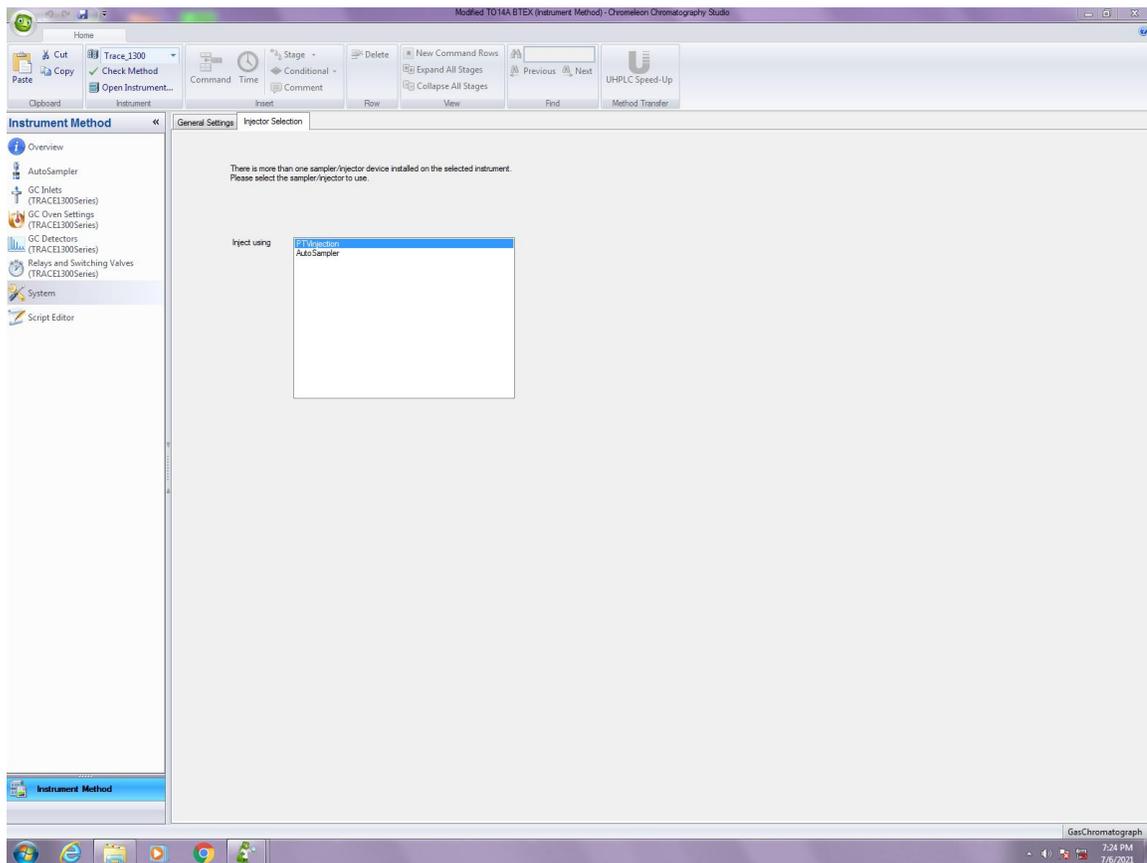












10. Versions

Update this document with the name of the modifier and date for each modification. It may be prudent to maintain records of old SOPs for reference.

Version 1.0 Author: H. Hall

Version 1.0 Date: 7/1/2021

Modified By:

Modification Date:

Appendix B
Field Sampling Weather Data

Table B. Field sampling weather data collected during sampling trips to measure VOCs in ambient air samples at gas stations.

	Sampling Day								
	21-Jun-21			28-Jun-21			30-Jun-21		
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average
Wind speed (m/s)	1.2	4.4	2.0	0.4	1.6	0.7	0.0	1.6	0.9
Wind direction (degrees)	136	226	189	76	309	193	80	185	143
Relative Humidity (%)	60.2	67.4	63.9	73.2	83.3	78.7	63.3	74.3	67.4
Dew Point (°F)	73.9	78.1	75.4	74.0	75.1	74.4	71.0	75.9	72.7
Ambient Temperature (°F)	87.6	91.8	89.2	78.1	83.9	81.4	82.2	85.8	84.6
Barometric Pressure (in Hg)	29.44	29.46	29.45	29.61	29.63	29.62	29.69	29.71	29.70

VITA

Heather Hall received her high school degree from Pine Tree High School in Longview, Texas. She graduated from University of Washington in Seattle, Washington with a Bachelor of Science in Environmental Science. In January 2019, she entered the Arthur Temple College of Forestry and Agriculture at Stephen F. Austin State University to pursue a Master of Science in Environmental Science.

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APA Style

This thesis was typed by Heather Hall.