DETECTION OF BTEX BY DIRECT AQEOUS INJECTION USING GC-FID

CHEM 4400

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Abstract

Benzene and its derivatives- toluene, ethylbenzene, and xylene-(BTEX) were analyzed in water samples using direct aqueous injection and analyzed using Gas Chromatography-Flame Ionization Detection (GC-FID). The method was able to separate BTEX compounds and detect in standards of ethanol and/or water. A sample preparation method was also developed to prevent loss of analyte and for more accurate results. A sample solution of 20% water sample and 80% ethanol was determined to produce the best results. A tap water sample was analyzed and the presence of BTEX was not detected.

Introduction

Benzene and its derivatives –toluene, ethylbenzene, and xylene –are major components of mineral oil products used as solvents in industrial processes. As water-soluble compounds in petroleum, they are usually found in the soil and groundwater near production sites and storage facilities[1]. Over 2000 facilities are involved with parts of the transportation, production, or storage of fuel in BC[2]. Additionally, benzene, toluene, ethylbenzene, and xylene (BTEX) can also be found in spill zones. These spill zones can leach into bodies of water such as rivers or lakes. Once BTEX is in bodies of water they can harm aquatic life or even humans. BTEX are volatile organic compounds (VOCs).

VOCs have short-term health effects, such as headaches and eye or nose irritation. Furthermore, VOCs can also have long-term health effects such as liver and kidney damage and benzene, specifically, has been proven to be a carcinogen[3]. Due to these health risks, it is imperative to develop a method that can directly analyze water samples for the presence of BTEX.

Traditionally, BTEX are analyzed using headspace Gas Chromatography-Mass Spectrometry (GC-MS). This is due to the volatile nature of the analyte and the difficulty of preserving them during sample processing[4]. In the present study, a method to detect BTEX by Gas Chromatography-Flame Ionization detector (GC-FID) in liquid form was developed. GC-FID was chosen for its ability to analyze VOCs. GC works by injecting a sample and converting it to gas form, which VOCs are naturally found in, then through a column to separate compounds

and finally to the flame ionizer for detection. The column used was a CP-Wax 57 CB, 25 m length, 0.25 mm id, 0.20 µm film thickness and was suitable for this study as ethanol could be used as a solvent.

Experimental

In this experiment, individual BTEX stock solutions were prepared. Then, standard solutions of BTEX were prepared and analyzed using GC-FID. Various methods were tested, and the most suitable one was determined and used to analyze a real sample.

Apparatus

An Agilent 8860 GC-FID/ECD (electron capture detector) was used in this study. The instrument parameters used are shown below in **Table 1.** The temperature program used in this study is shown in **Table 2.**

Table 1: Agilent GC conditions used in the study.

Injection Volume:	1 µL
GC Column:	CP-Wax 57 CB, 25 m length, 0.25 mm id, 0.20 µm film thickness
Injector:	Split/splitless injector that has a split/splitless liner
N_2 Carrier Gas flow:	0.8 – 1.0 mL/min
Injector Temperature:	200 ºC
Split Ratio:	50:1
Split Flow:	50 mL/min
FID Temperature:	250 ºC
Range:	10
ECD:	OFF

Table 2: GC oven conditions used in the study for Standards

Initial Temperature:	35 ºC
Temperature Program:	Hold at 35 ºC for 5 min
Hold time for Sample:	Ramp to 70 ºC @ 5 ºC/min
Total Run Time:	12 min

Stock and working standard solutions

Individual stock solutions of benzene, toluene, ethylbenzene, and m-xylene were prepared and dissolved in ethanol. Concentrations of stock solution are shown below in **Table 3.** Standards of various concentrations were prepared and analyzed. Some standards were dissolved in Ethanol, others were dissolved in TOC grade water. Standards and their compositions are shown in **Table 4.** Reagent-grade Ethanol was used to prepare standards.

Table 3: BTEX stock solution concentrations (mg/L)

Analyte	**Concentration**
	mg/L
Benzene	874
Toluene	867
Ethylbenzene	867
m-Xylene	864

Instrument Runs

The runs conducted in this study are shown in **Table 4.**

Sample

A sample was prepared using 20% tap water and 80% Ethanol. A spiked sample was prepared by adding 1.75, 1.74, 1.74, and 1.73 mg/L of BTEX, respectively to the sample solution. Tap water was taken from a tap inside the science building at Thompson Rivers University (TRU).

Table 4: Instrument Runs performed in the Study. Compositions of standards are also shown with concentrations in mg/L

Standard #	Analyte	Concentration mg/L	Dissolved in (% Ethanol)	Standard #	Analyte	Concentration mg/L	Dissolved in (% Ethanol)
1	Benzene	0.00	100	11	Benzene	0.44	0
	Toluene	0.00			Toluene	0.43	
	Ethylbenzene	0.00			Ethylbenzene	0.43	
	m-Xylene	0.00			m-Xylene	0.43	
2	Benzene	4.37	100	12	Benzene	1.75	0
	Toluene	4.34			Toluene	1.74	
	Ethylbenzene	4.34			Ethylbenzene	1.74	
	m-Xylene	4.32			m-Xylene	1.73	
3	Benzene	8.72	100	13	Benzene	1.75	0
	Toluene	8.68			Toluene	1.74	
	Ethylbenzene	8.68			Ethylbenzene	1.74	
	m-Xylene	8.64			m-Xylene	1.73	
4	Benzene	8.72	0	14	Benzene	1.75	100
	Toluene	8.68			Toluene	1.74	
	Ethylbenzene	8.68			Ethylbenzene	1.74	
	m-Xylene	8.64			m-Xylene	1.73	
5	Benzene	1.75	100	15	Benzene	1.75	50
	Toluene	0			Toluene	1.74	
	Ethylbenzene	0			Ethylbenzene	1.74	
	m-Xylene	0			m-Xylene	1.73	
6	Benzene	0	100	16	Benzene	1.75	100
	Toluene	1.74			Toluene	1.74	
	Ethylbenzene	0			Ethylbenzene	1.74	
	m-Xylene	0			m-Xylene	1.73	
7	Benzene	0	100	17	Benzene	1.75	50
	Toluene	0			Toluene	1.74	
	Ethylbenzene	1.74			Ethylbenzene	1.74	
	m-Xylene	0			m-Xylene	1.73	
8	Benzene	0	100	18	Benzene	1.75	90
	Toluene	0			Toluene	1.74	
	Ethylbenzene	0			Ethylbenzene	1.74	
	m-Xylene	1.73			m-Xylene	1.73	
9	Benzene	1.75	0	19	Benzene	1.75	80
	Toluene	1.74			Toluene	1.74	
	Ethylbenzene	1.74			Ethylbenzene	1.74	
	m-Xylene	1.73			m-Xylene	1.73	
10	Benzene	0.87	0	20	Benzene	1.75	0
	Toluene	0.87			Toluene	1.74	
	Ethylbenzene	0.87			Ethylbenzene	1.74	
	m-Xylene	0.86			m-Xylene	1.73	

Procedure

Preparation of Standards 1-3

- Using a 10 µL glass syringe, inject appropriate volumes of each BTEX stock into a glass vial.
- Fill the vial with Ethanol to 1 mL using the 500 µL glass syringe.
- Cap vial.
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Standard 4

- Using a 10 µL glass syringe, inject appropriate volumes of each BTEX stock into a glass vial.
- Fill the vial with tap water to 1 mL using a 1 mL repeater pipette.
- Cap the vial.
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Standards 5-8

- Using a 10 µL glass syringe, inject 10 µL of one BTEX stock into a glass vial per.
- Fill the vial with Ethanol to 1 mL using the 500 µL glass syringe.
- Cap the vial.

- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Standards 9-12

- Using a 10 µL glass syringe, inject appropriate volumes of each BTEX stock into a glass vial.
- Fill the vial with TOC grade water to 1 mL using a 1 mL repeater pipette.
- Cap the vial.
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Standards 13-20

- Add 1 mL of TOC-grade water or Ethanol into a glass vial. If needed, add varying amounts of Ethanol and TOC-grade water.
- Cap the vial
- Using a glass syringe, add appropriate amounts of BTEX stock through the cap of the vial.
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Sample

- Obtain a glass vial and add 200 µL of tap water using a repeater pipette. Then, using a glass syringe add 800 µL of Ethanol.

- Cap the vial
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Preparation of Spiked Sample

- Obtain a glass vial and add 200 µL of tap water using a repeater pipette. Then, using a glass syringe add 800 µL of Ethanol.
- Cap the vial
- Through the cap, use a 10 µL glass syringe to add 10 µL of each BTEX stock to the vial.
- Shake the vial by placing a finger on the cap and shaking vigorously back and forth.
- Analyze

Data and Results

Week 1

In week 1, a sample containing 100% Ethanol was analyzed (Figure 1.). Then, standards containing varying concentrations of BTEX with Ethanol were analyzed (Figure 2, 3), see Table 4 for concentrations of standards. 4 peaks were observed when BTEX was added. When concentration of BTEX increased, an increase in peak height was also observed. Finally, a standard containing BTEX with tap water was analyzed (Figure 4.). It was observed that the ethanol peak became much sharper at the base and the second BTEX peak was observed to have an improved baseline.

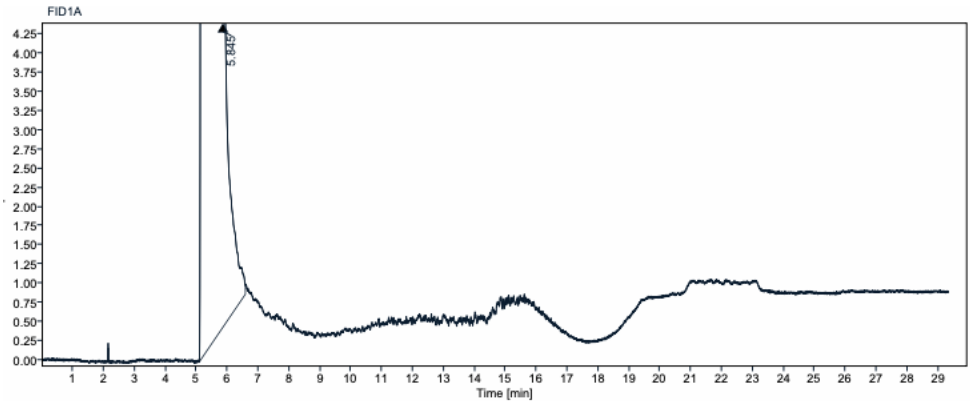


Figure 1: Chromatogram of Blank Standard obtained using GC-FID

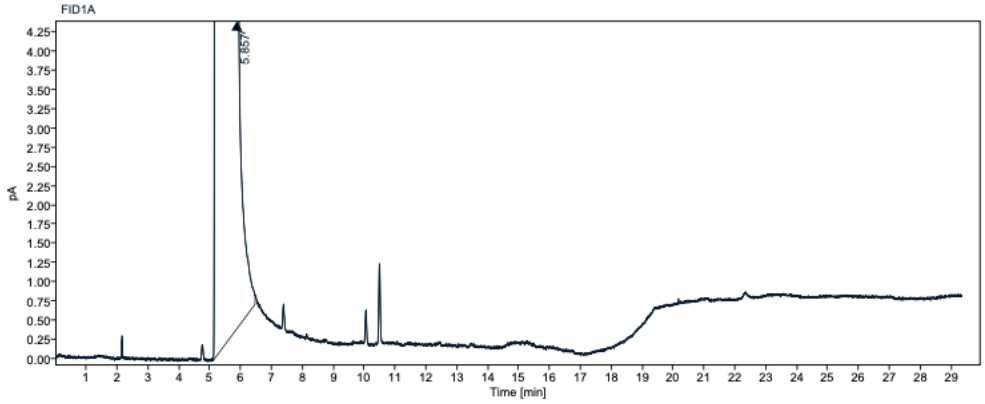


Figure 2: Chromatogram of Standard 2 obtained using GC-FID

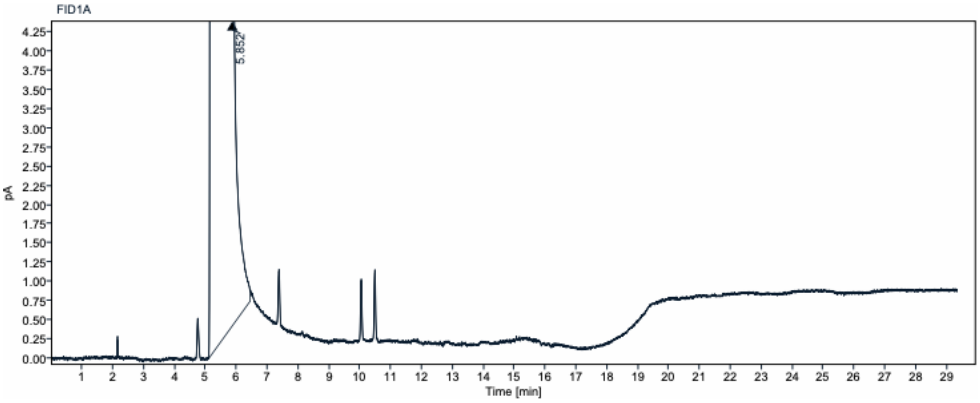


Figure 3: Chromatogram of Standard 3 obtained using GC-FID

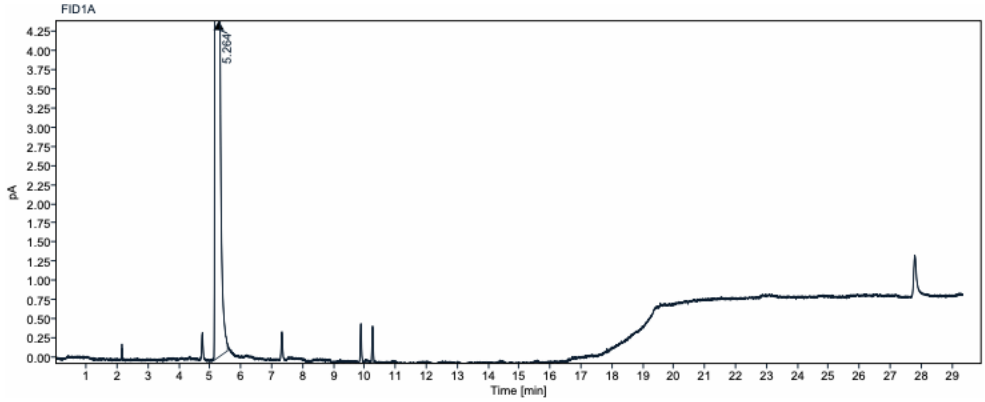


Figure 4: Chromatogram of Standard 4 obtained using GC-FID

Week 2

In week 2, retention times of BTEX were determined (Figures 5-8). Additionally, standards of decreasing concentrations were analyzed (Figures 9, 10). Finally, a sample preparation method for standards was developed (Figure 11-13).

Table 5: BTEX retention times as determined by using standards 5-8 and analyzing using GC-FID.

Analyte ID	**Retention Time (min)**
Benzene	4.726
Toluene	7.297
Ethylbenzene	9.855
m-Xylene	10.231

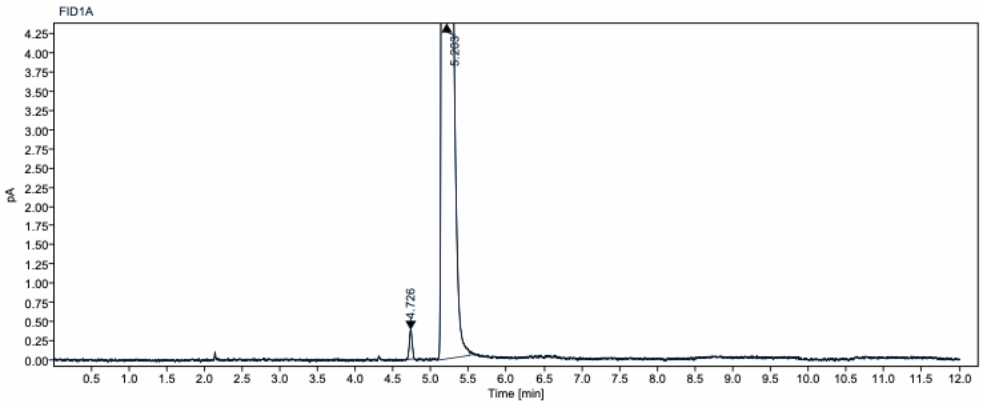


Figure 5: Chromatogram of Standard 5 obtained using GC-FID

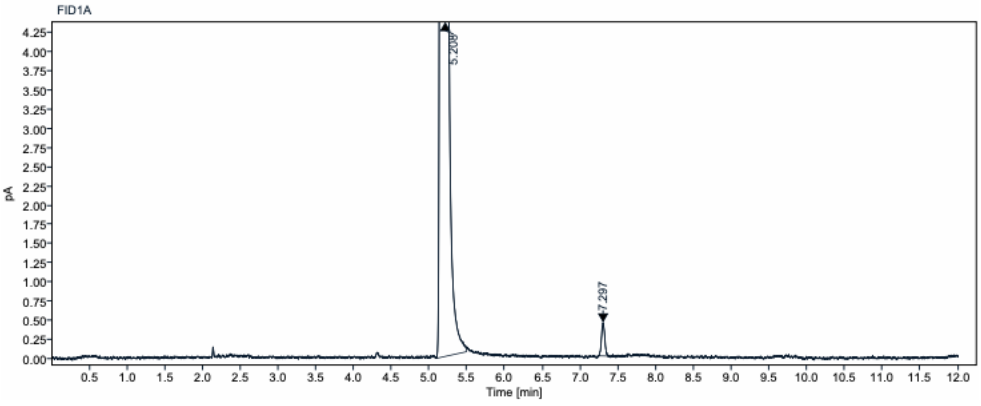


Figure 6: Chromatogram of Standard 6 obtained using GC-FID

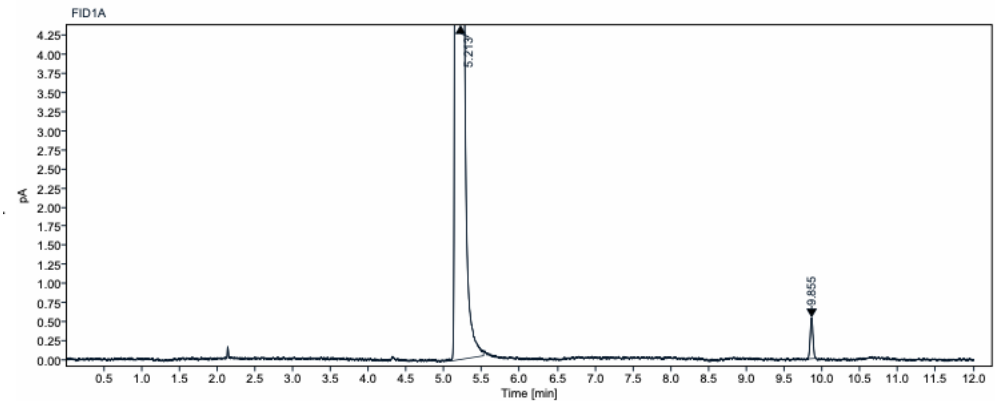


Figure 7: Chromatogram of Standard 7 obtained using GC-FID

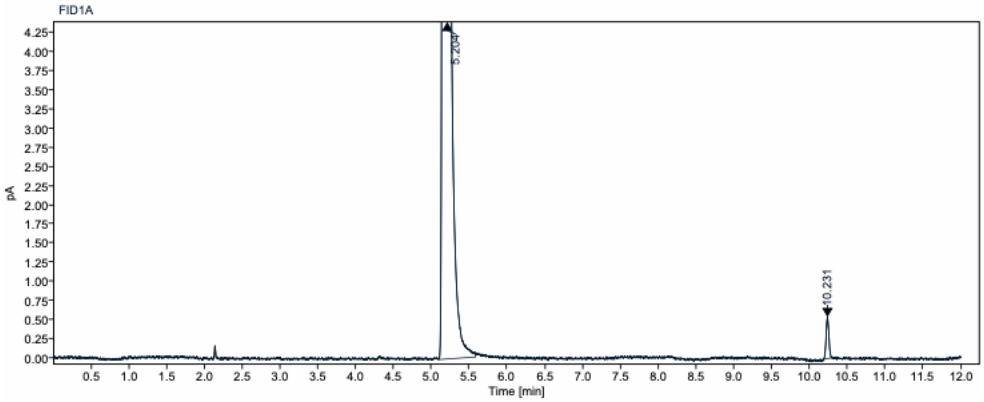


Figure 8: Chromatogram of Standard 8 obtained using GC-FID

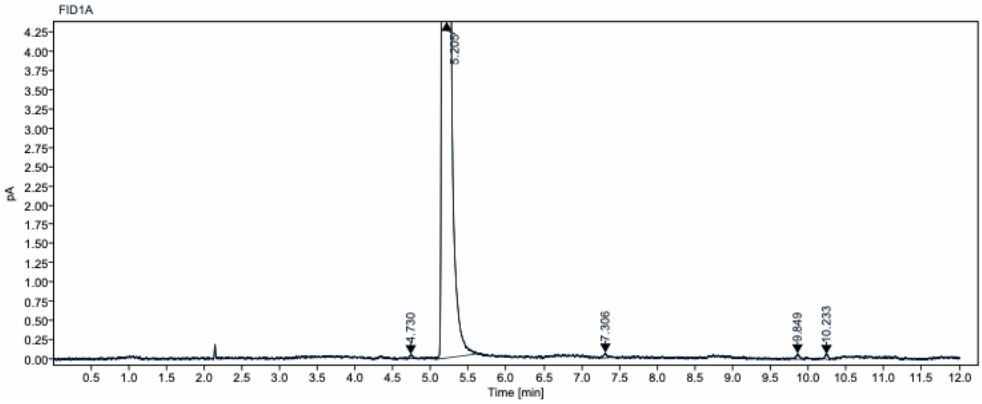


Figure 9: Chromatogram of Standard 9 obtained using GC-FID

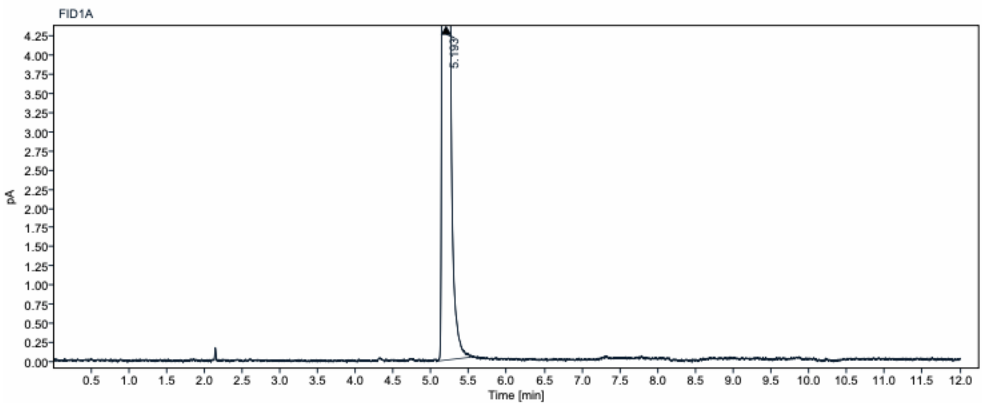


Figure 10: Chromatogram of Standard 10 obtained using GC-FID

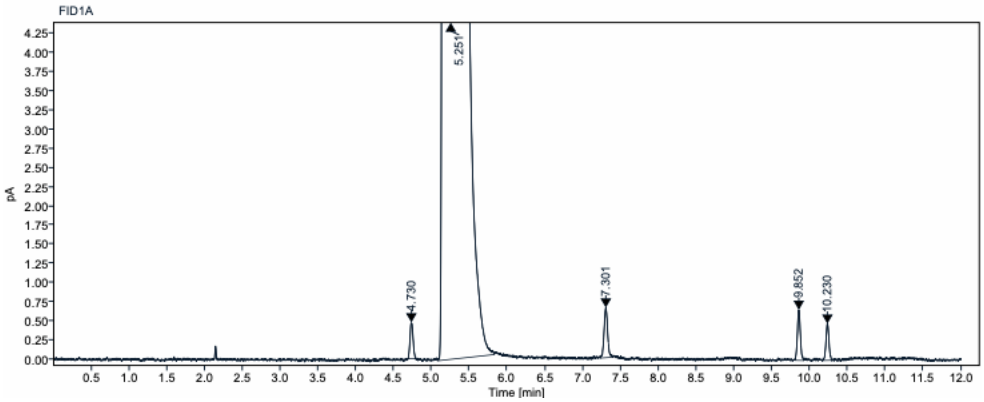


Figure 11: Chromatogram of Standard 12 obtained using GC-FID

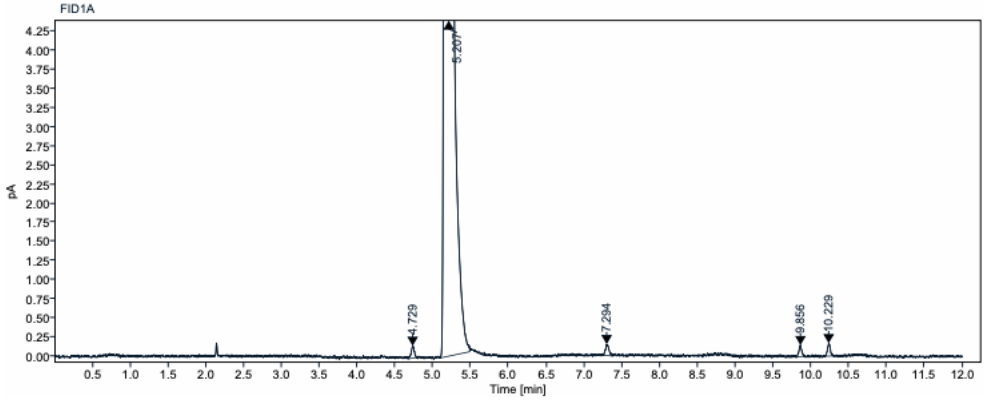


Figure 12: Chromatogram of Standard 13 obtained by GC-FID

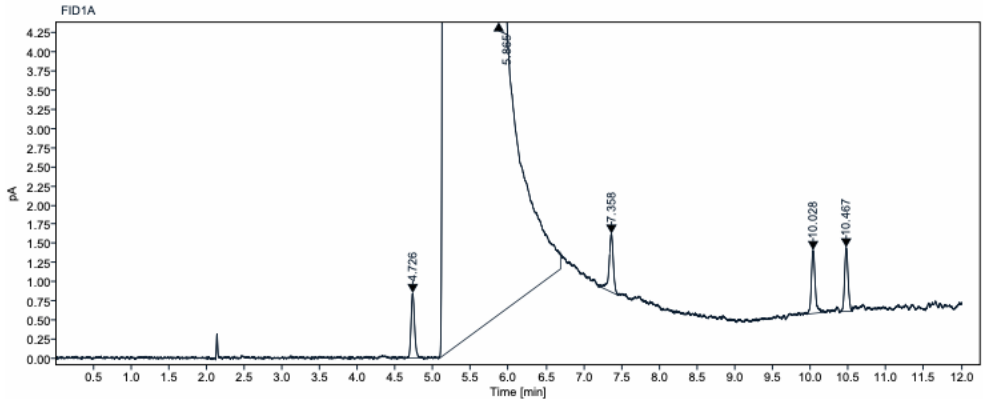


Figure 13: Chromatogram of Standard 14 obtained by GC-FID

Week 3

In week 3, standards with varying amounts of ethanol were analyzed for the lowest amount of ethanol required to contain the analyte (Figure 14-18). Table 6 shows the results tabulated. Then, the data from Table 6 was plotted (Figures 19-22) to obtain graphs to visualize data and select the best ratio of ethanol:water. The ratio of ethanol:water determined to be the best was used to analyze a real sample (Figure 23). A spike sample was produced and analyzed using the same ratio (Figure 24).

Table 6: Standards of varying concentrations of fraction ethanol and corresponding peak areas

Benzene			Toluene			Ethylbenzene			m-Xylene		
%ethanol	Rt	Area	%ethanol	Rt	Area	%ethanol	Rt	Area	%ethanol	Rt	Area
	(min)			(min)			(min)			(min)	
100	4.736	2.4617	100	7.363	2.5263	100	10.023	2.5768	100	10.46	2.2623
90	4.729	2.2503	90	7.342	1.9052	90	9.941	2.1931	90	10.401	2.2578
80	4.73	2.1529	80	7.345	2.0772	80	9.898	2.1348	80	10.341	2.4234
50	4.73	1.934	50	7.322	1.8828	50	9.859	2.0746	50	10.258	2.1266
0	4.733	1.5673	0	7.297	1.6363	0	9.85	1.5509	0	10.228	1.7924

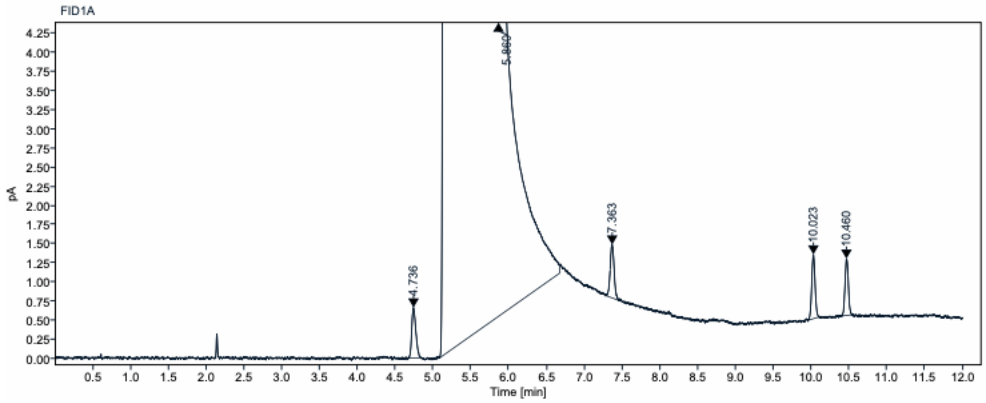


Figure 14: Chromatogram of Standard 16 obtained by GC-FID

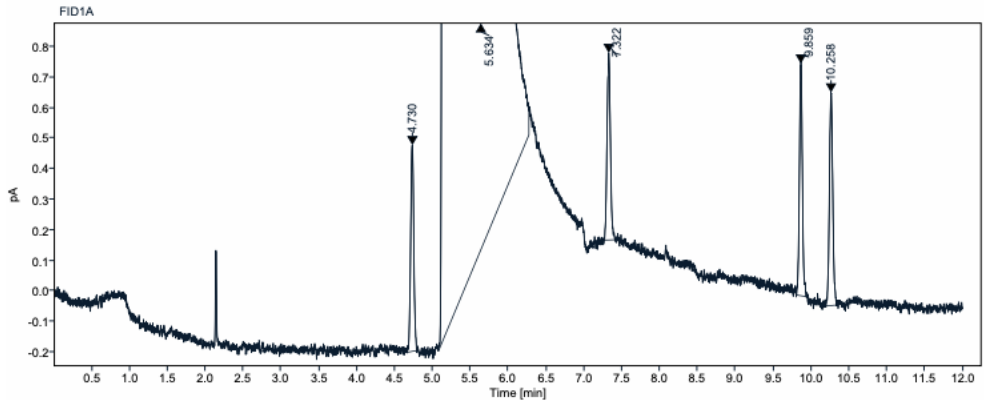


Figure 15: Chromatogram of Standard 17 obtained by GC-FID

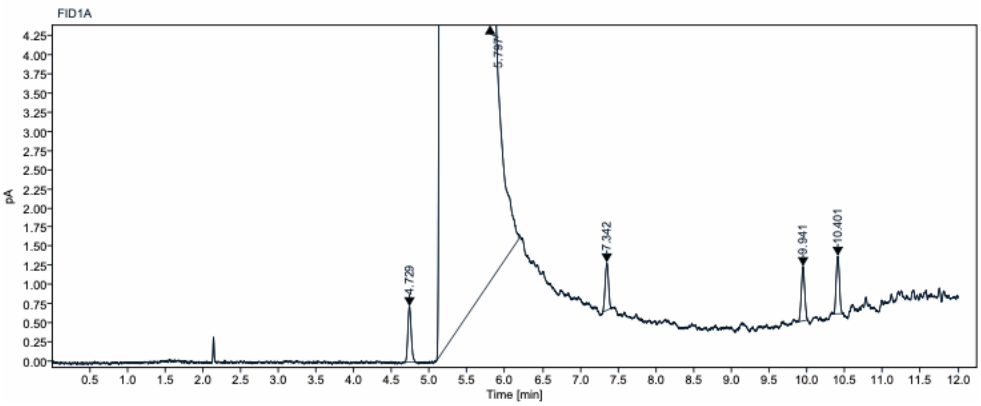


Figure 16: Chromatogram of Standard 18 obtained by GC-FID

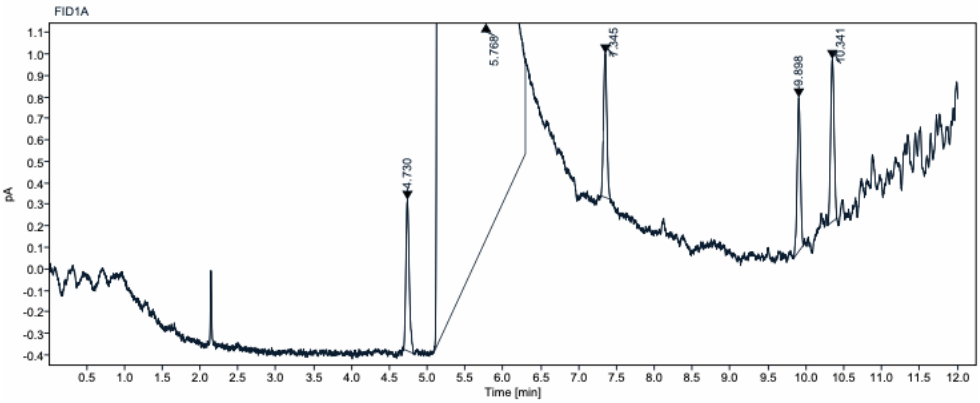


Figure 17: Chromatogram of Standard 19 obtained by GC-FID

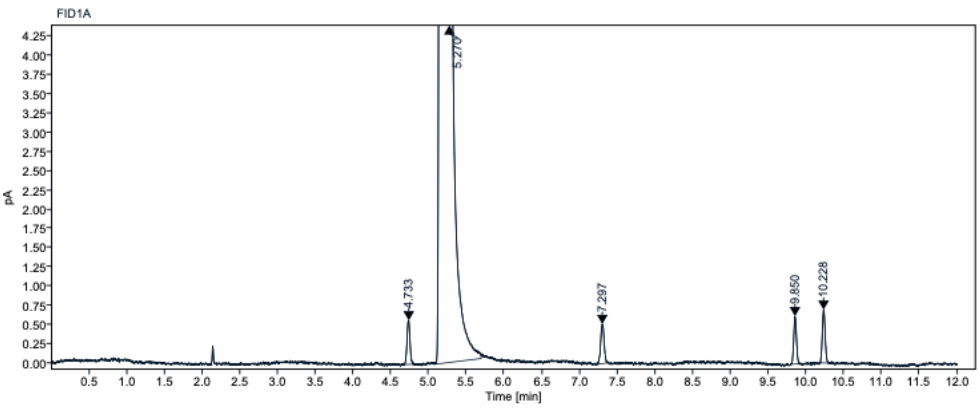


Figure 18: Chromatogram of Standard 20 obtained by GC-FID

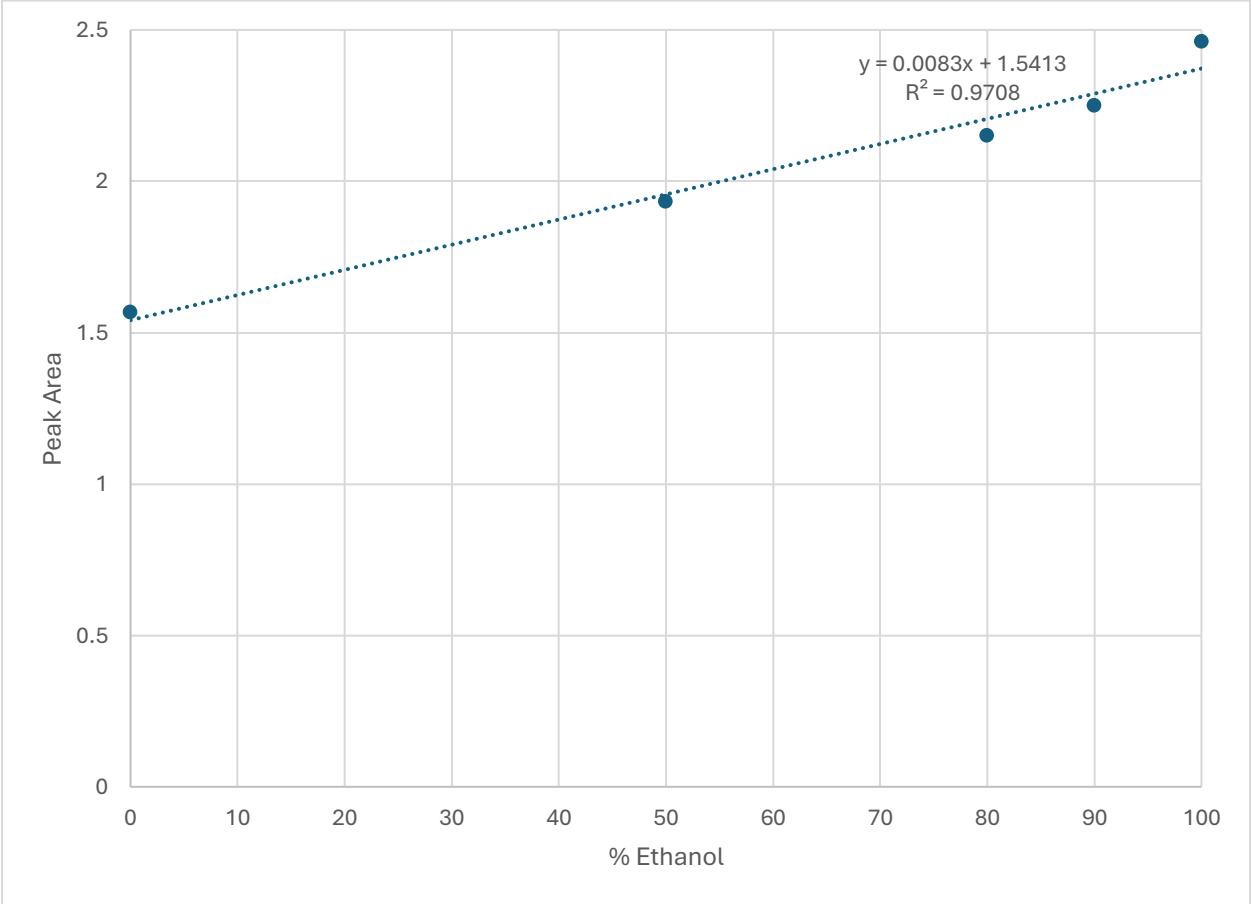


Figure 19: Plot of Benzene signals with varying fraction of Ethanol in BTEX standards analyzed by GC-FID

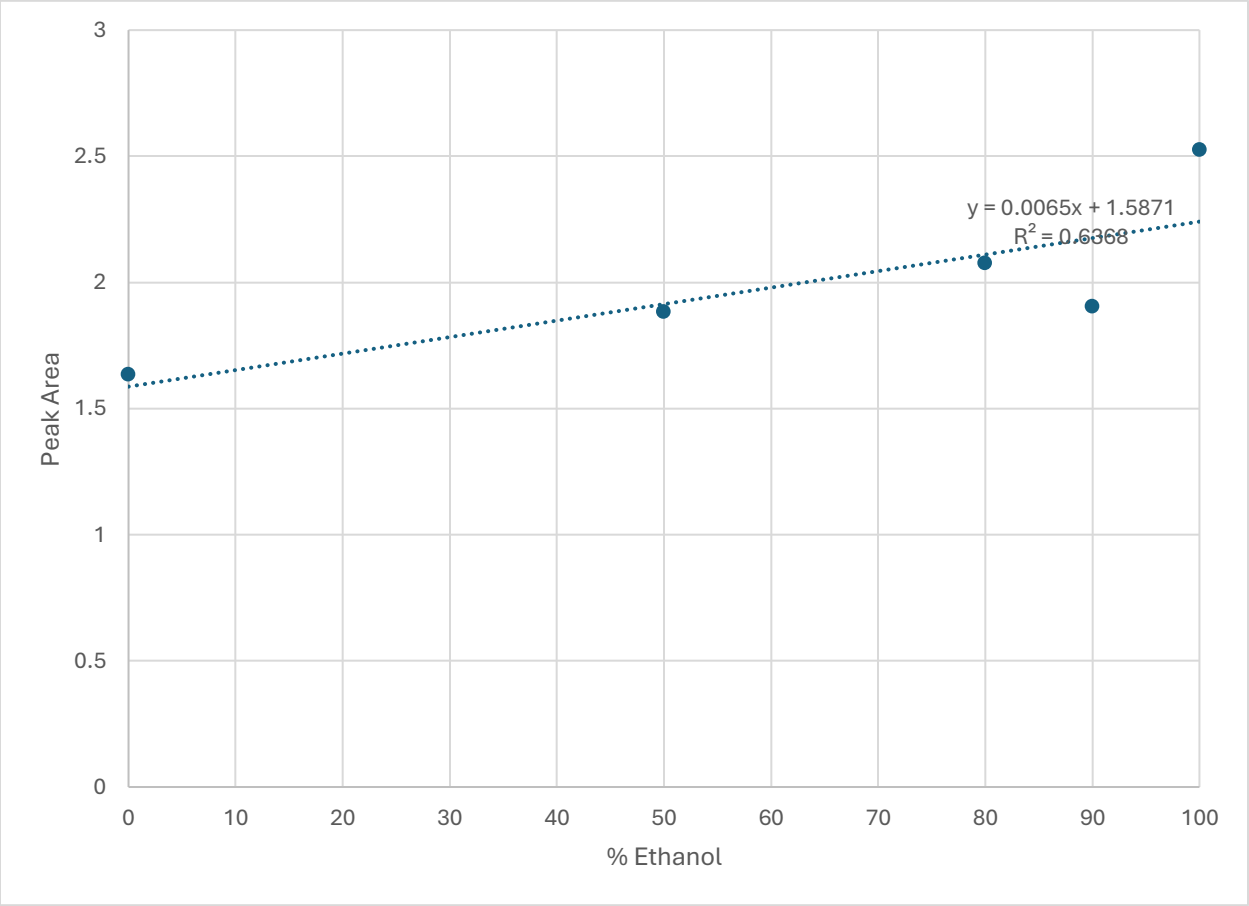


Figure 20: Plot of Toluene signals with varying fraction of Ethanol in BTEX standards analyzed by GC-FID

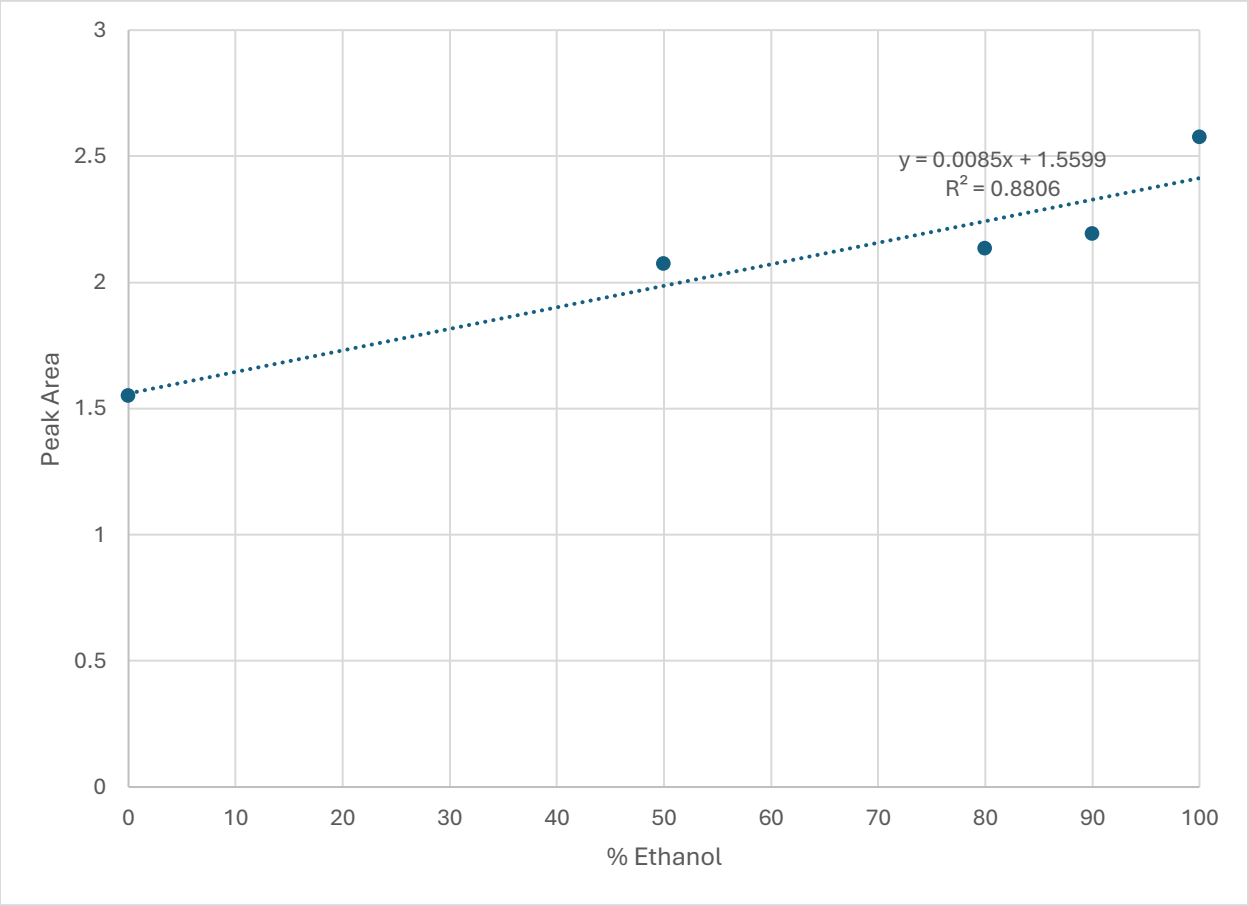


Figure 21: Plot of Ethylbenzene signals with varying fraction of Ethanol in BTEX standards analyzed by GC-FID

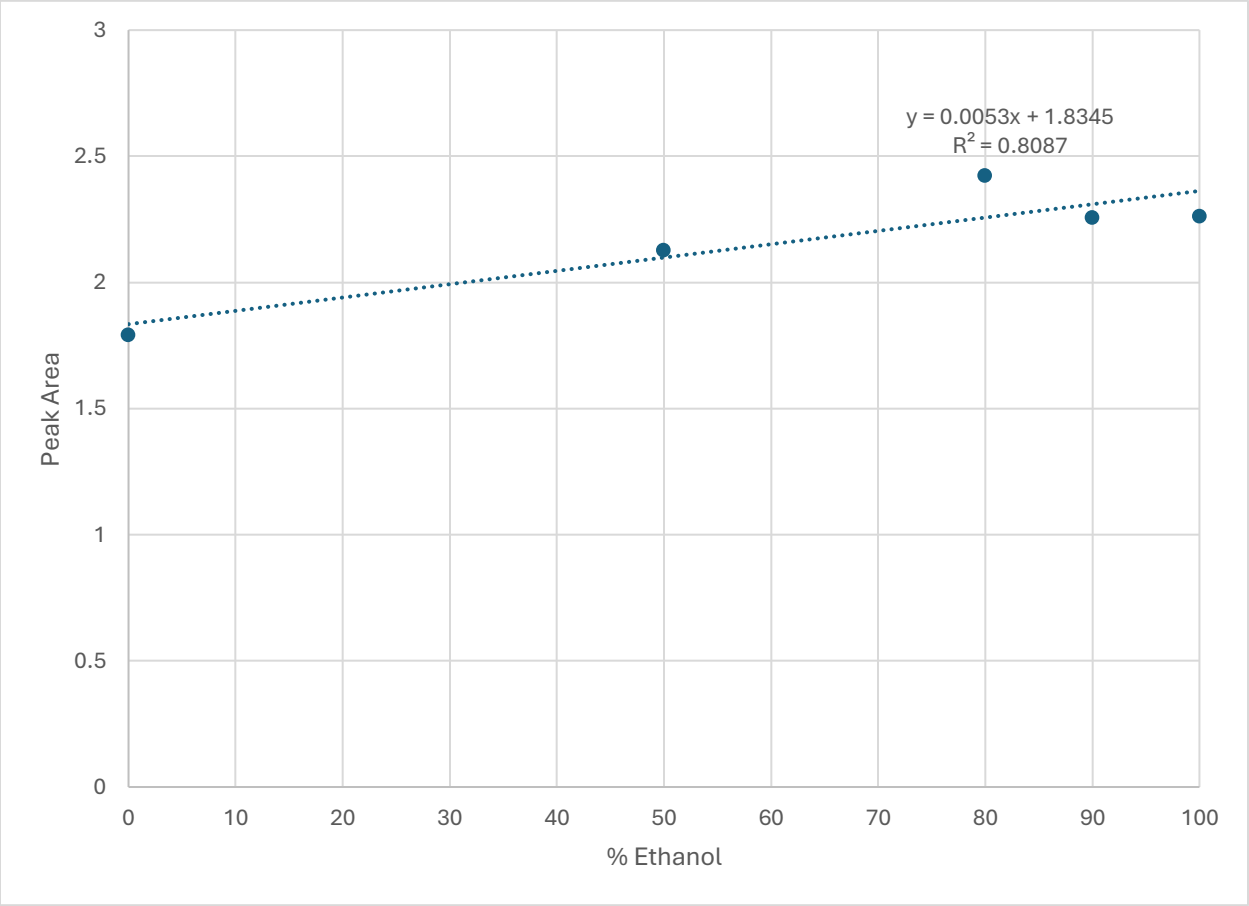


Figure 22: Plot of Xylene signals with varying fraction of Ethanol in BTEX standards analyzed by GC-FID

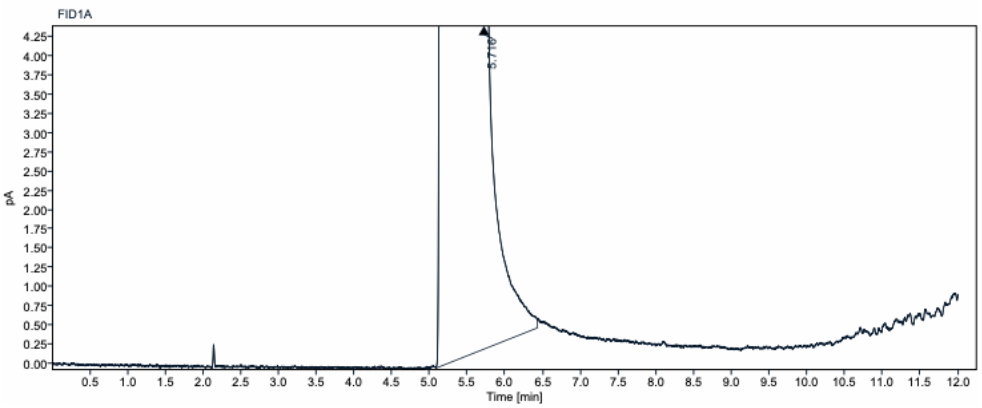


Figure 23: Chromatogram of Sample obtained by GC-FID

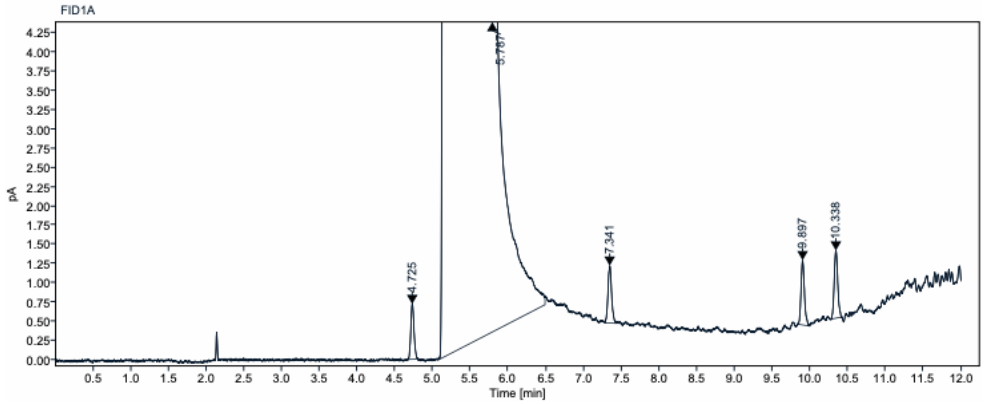


Figure 24: Chromatogram of Sample spiked with BTEX obtained by GC-FID

Discussion

Week 1

The goal for the first week of my project was to test a method obtained from the literature and see if it could detect the presence of BTEX. Using a method that is detailed in Table 2, with a total run time of 29 minutes on the GC-FID with parameters that are found in Table 1, I ran a blank and a standard containing BTEX.

First, a blank was analyzed (Figure 1.). In the blank, a peak at 2 minutes can be seen, this is likely due to impurities in ethanol. Then, a peak at 5 minutes is observed, this is determined to be the ethanol peak.

Next, two standards with different concentrations of BTEX were run (Figures 2 and 3). This showed that the method could, in fact, detect BTEX and was sensitive to different concentrations. This is proven by the appearance of 4 peaks that were not present in the blank. The methanol peak had a very large baseline and interfered with the second unknown peak that appeared. Therefore, I ran a standard that was made to 1 mL using tap water instead of ethanol as the previous two standards that were run. This sharpened the base of the ethanol peak, and the baseline for the second unknown peak was much clearer and visually looked better for quantitative purposes in the future. Some sources of error in the first week could be errors in preparing the sample and using tap water instead of TOC-grade water. Using tap water could introduce peaks as there is organic material present, whereas, in TOC grade water, there is no organic material, so it should prevent any unknown peaks from appearing. Additionally, having a

30-minute run time is wasteful for the environment when all my analytes are eluting within 12 minutes.

Week 2

My goal for week 2 was to identify the peaks as either benzene, toluene, ethylbenzene, or xylene. I also wanted to develop standards of decreasing concentration until I could no longer detect BTEX.

I was able to identify each peak as either benzene, toluene, ethylbenzene, or xylene. As seen in Figures 5-8, when running standards that contained only one of the analytes at a time, I was able to identify each peak. Additionally, as seen in Table 5, we can see that the elution order followed the BTEX name. When running standards of decreasing concentration, I was able to detect standards at the 1.7 mg/L level (Figure 9), and unable to detect standards at the 0.87 mg/L level (Figure 10).

During this process, an issue arose. The sample preparation process that was being conducted was not optimal. There was a lot of analyte loss occurring during my standard preparation. When the standard preparation process was adjusted, and a standard of the same concentration was run again, we can see the difference in signal (Figures 9 and 12). Then, this new process was used for a standard that was dissolved in ethanol (Figure 13). Here, we can see the largest signal. However, there is a large ethanol peak, which has a poor baseline. Additionally, having a sample in 100% ethanol is not realistic for real-world applications. Thus, the next goal was to determine the smallest amount of ethanol we could get away with while also obtaining a large signal.

Week 3

The goal for this week was to prepare standards with varying amounts of ethanol and then use the best ratio of ethanol:water and apply it to a real sample.

I examined various ratios of ethanol:water as shown in Table 4, standards 16-20. The results of the analysis shown in Figures 14-18, are summarized in Table 18. It was expected that at higher levels of ethanol the signal would be larger as the BTEX was able to be contained in ethanol better than in water. However, as shown in Figures 19-22, there was lots of variation in results between all 4 analytes in all 5 standards analyzed. More analysis needs to be done to get a better average. Additionally, the 80% ethanol, 20% water was the best ratio determined at the time and was used to analyze real samples.

My method was unable to detect BTEX in a real sample (Figure 23). I was able to detect BTEX when spiked (Figure 24).

Future Work

Developing a method using the GC-MS to detect static headspace in water samples should be investigated as it may allow detection of lower concentrations of BTEX. Integrating a purge and trap when preparing samples may allow the retention of VOCs to allow for more accurate analysis.

I would also like to create each standard in triplicate. This would allow me to test reproducibility in sample preparation. This would also allow me to have more accurate results that I can use to make better decisions.

Conclusion

This study was able to develop a method that involved direct aqueous injection to detect BTEX in standards. This method was also able to detect each BTEX individually and separate each compound. A sample preparation method was also developed for the prevention of loss of analyte and for more accurate results.

References

(1) Analysis of Benzene and Its Derivatives (BTEX) in Water by Gas Chromatography.

(2) *Facilities*. https://www.bc-er.ca/what-we-regulate/oil-gas/facilities/ (accessed 2024-10-29).

(3) *Volatile organic compounds (VOCs) | Minnesota Pollution Control Agency*. https://www.pca.state.mn.us/pollutants-and-contaminants/volatile-organic-compounds-vocs (accessed 2024-10-21).

(4) Mottaleb, M. A.; Abedin, M. Z.; Islam, M. S. Determination of Benzene, Toluene, Ethylbenzene and Xylene in River Water by Solid-Phase Extraction and Gas Chromatography. *Anal. Sci.* **2003**, *19* (10), 1365–1369. https://doi.org/10.2116/analsci.19.1365.

Appendix

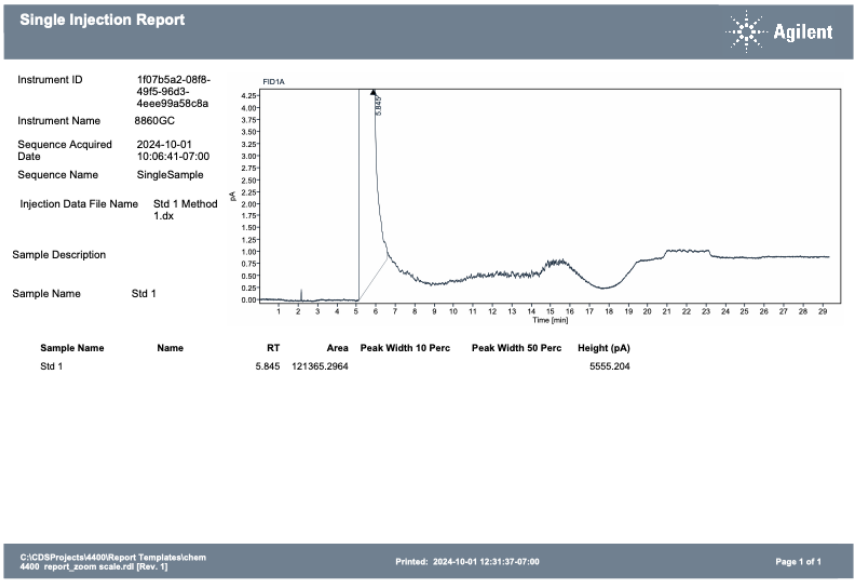


Figure 25: Chromatogram of Blank Standard obtained using GC-FID

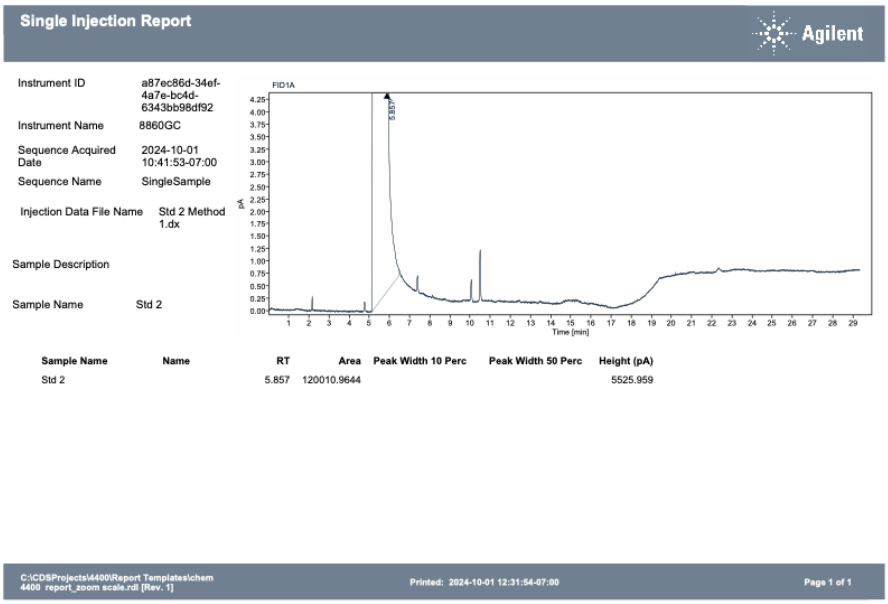


Figure 26: Chromatogram of Standard 2 obtained using GC-FID

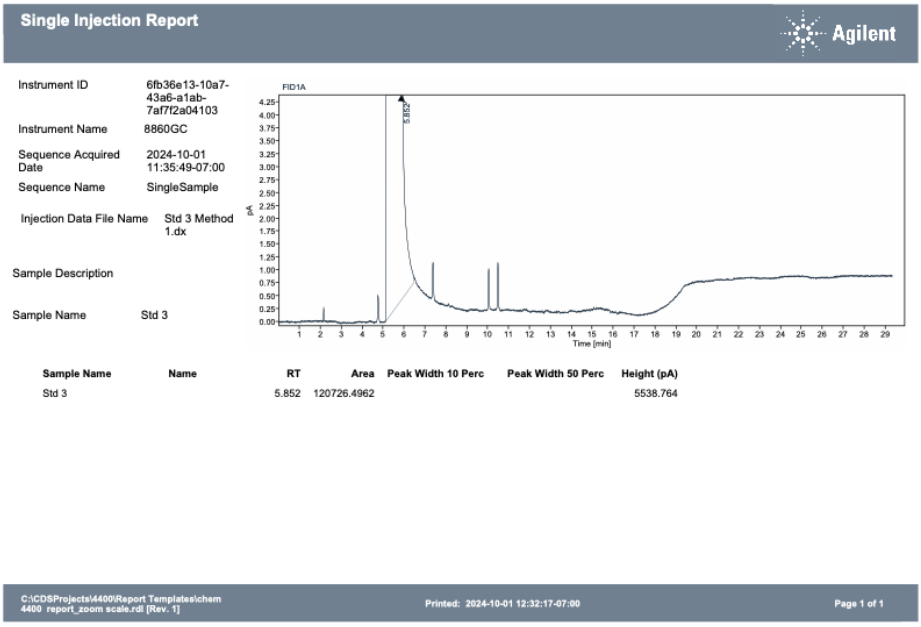


Figure 27: Chromatogram of Standard 3 obtained using GC-FID

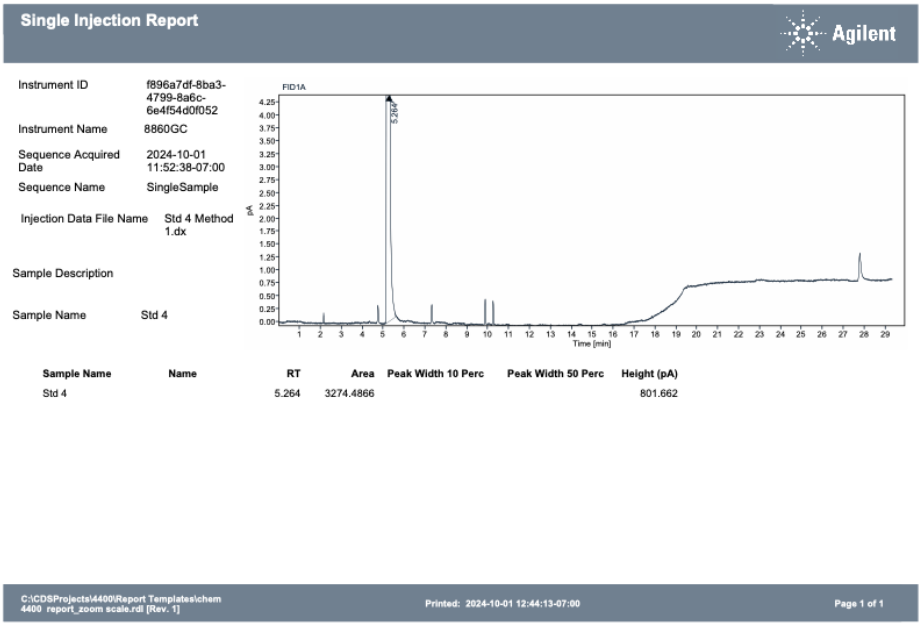


Figure 28: Chromatogram of Standard 4 obtained using GC-FID

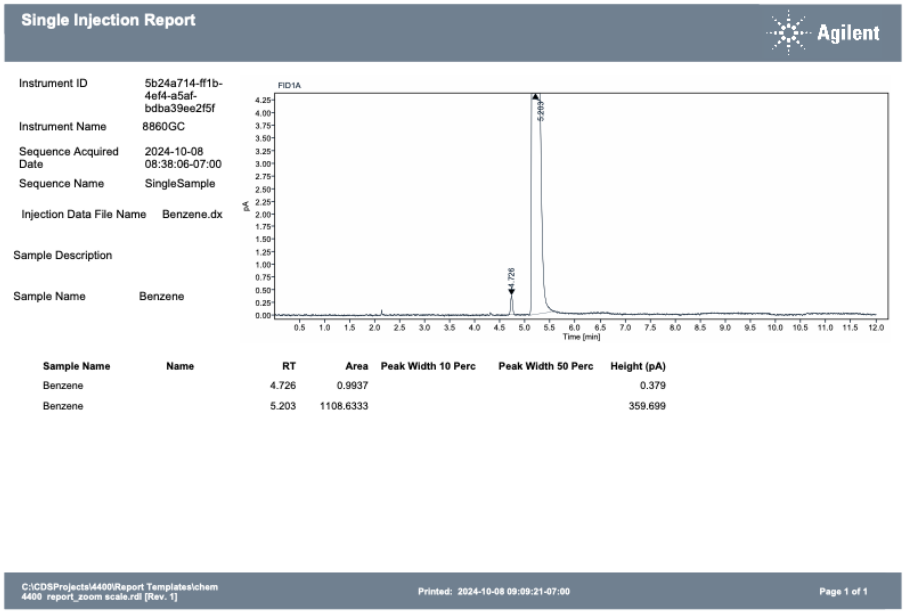


Figure 29: Chromatogram of Standard 5 obtained using GC-FID

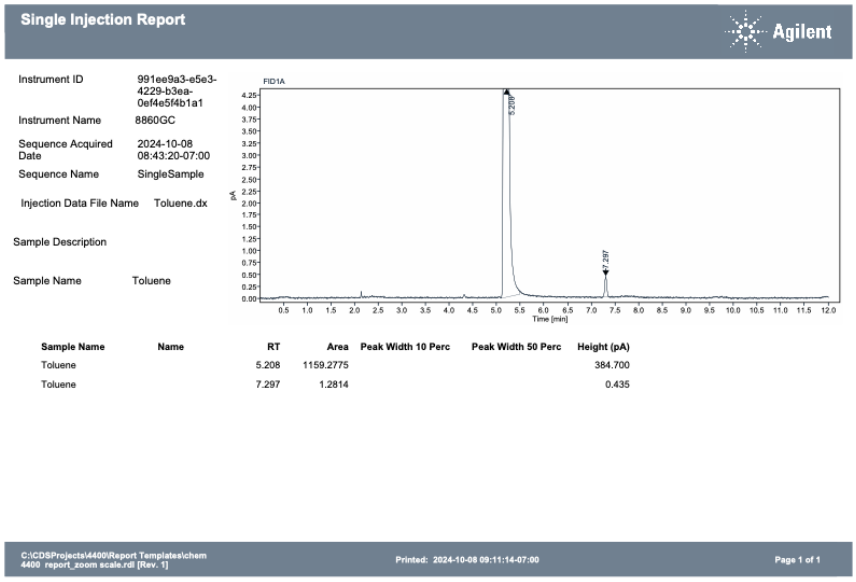


Figure 30: Chromatogram of Standard 6 obtained using GC-FID

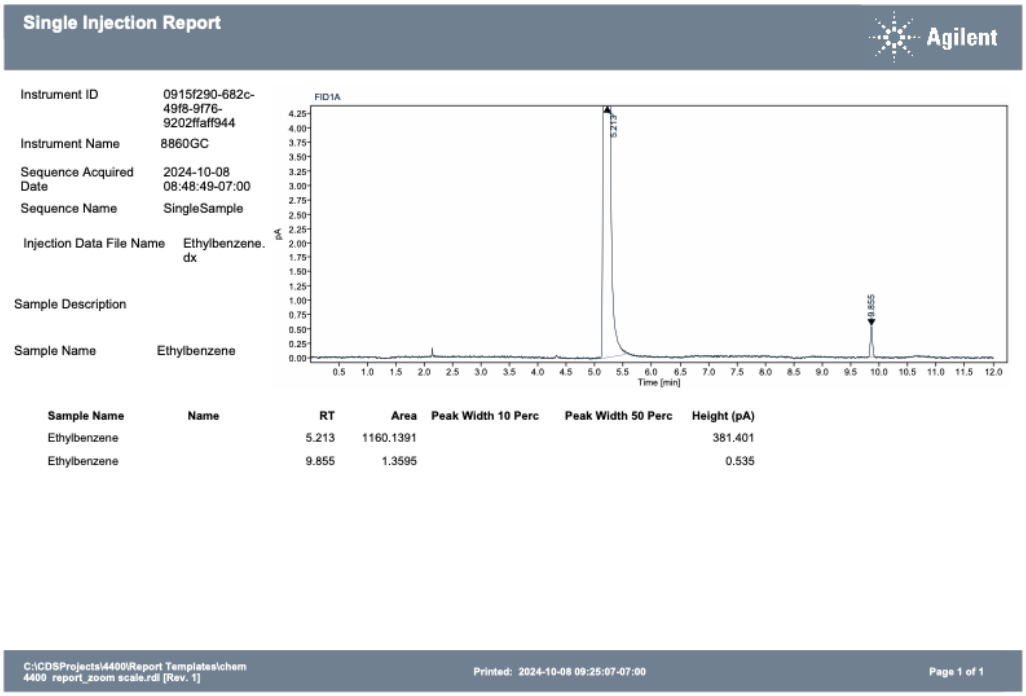


Figure 31: Chromatogram of Standard 7 obtained using GC-FID

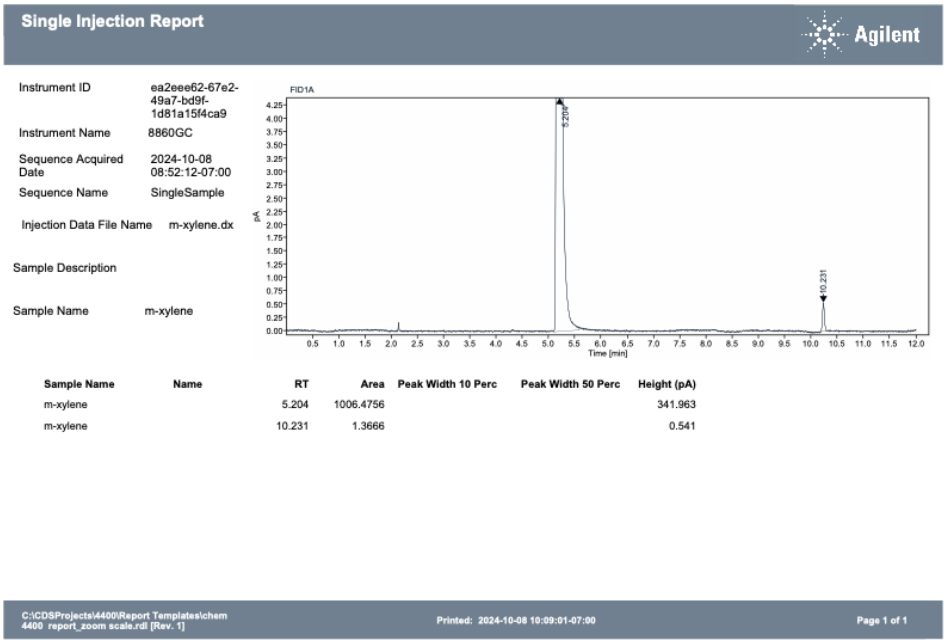


Figure 32: Chromatogram of Standard 8 obtained using GC-FID

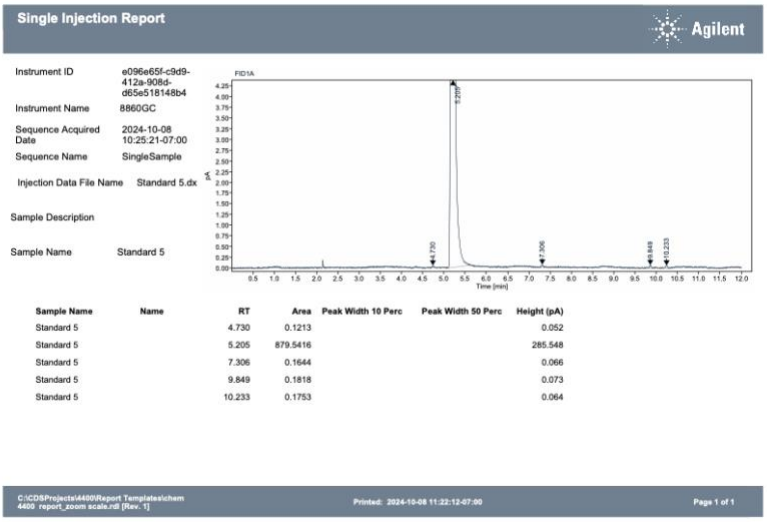


Figure 33: Chromatogram of Standard 9 obtained using GC-FID

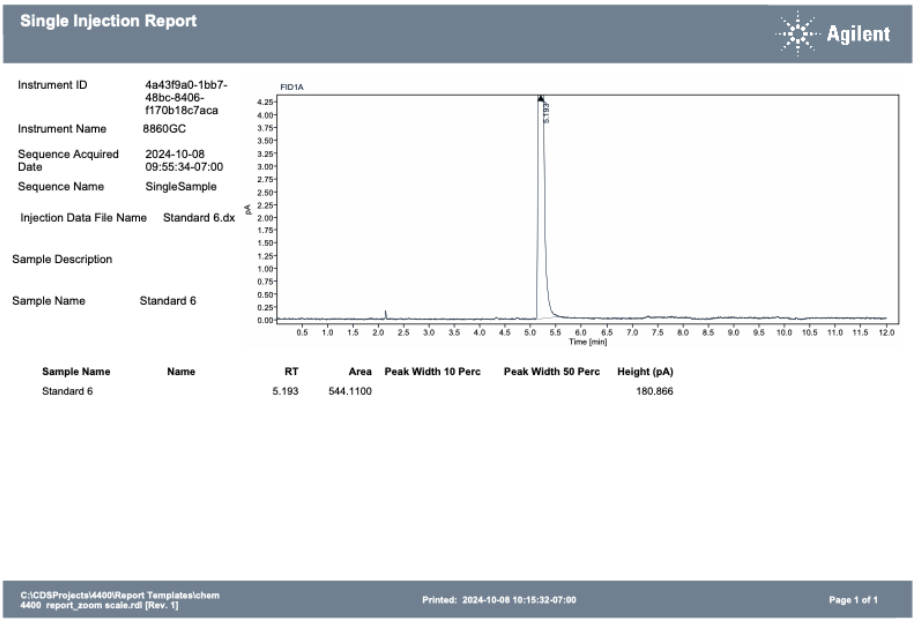
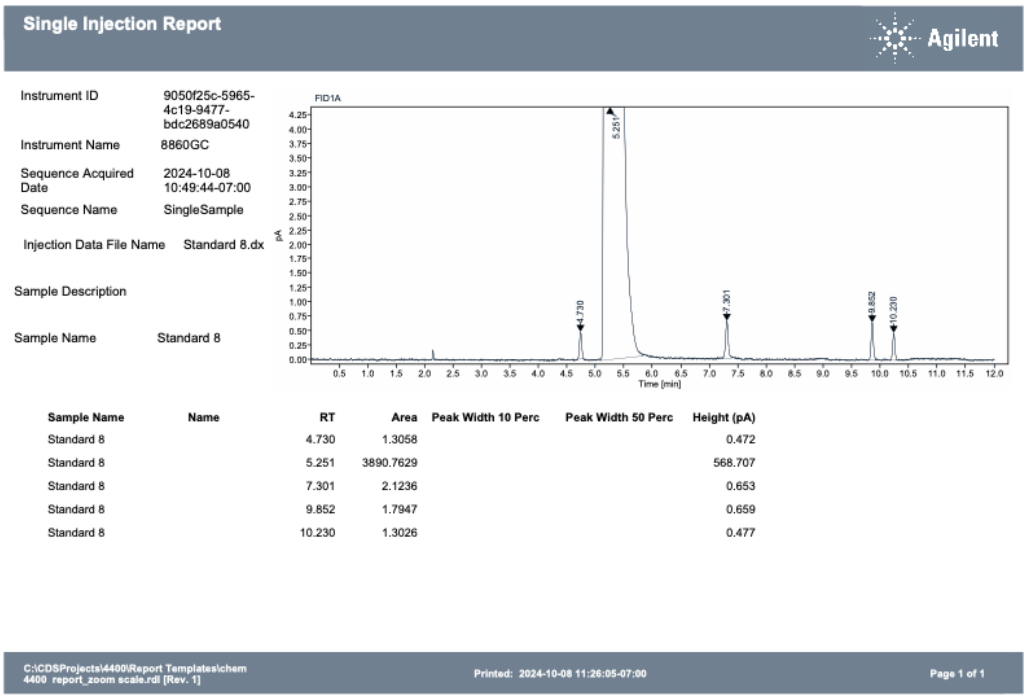


Figure 34: Chromatogram of Standard 10 obtained using GC-FID



Single Injection Report

Agilent

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Sequence Acquired Date	2024-10-08 10:49:44-07:00
Sequence Name	SingleSample
Injection Data File Name	Standard 8.dx
Sample Description	
Sample Name	Standard 8

Sample Name	Name	RT	Area	Peak Width 10 Perc	Peak Width 50 Perc	Height (pA)
Standard 8		4.730	1.3058			0.472
Standard 8		5.251	3890.7629			568.707
Standard 8		7.301	2.1236			0.653
Standard 8		9.852	1.7947			0.659
Standard 8		10.230	1.3026			0.477

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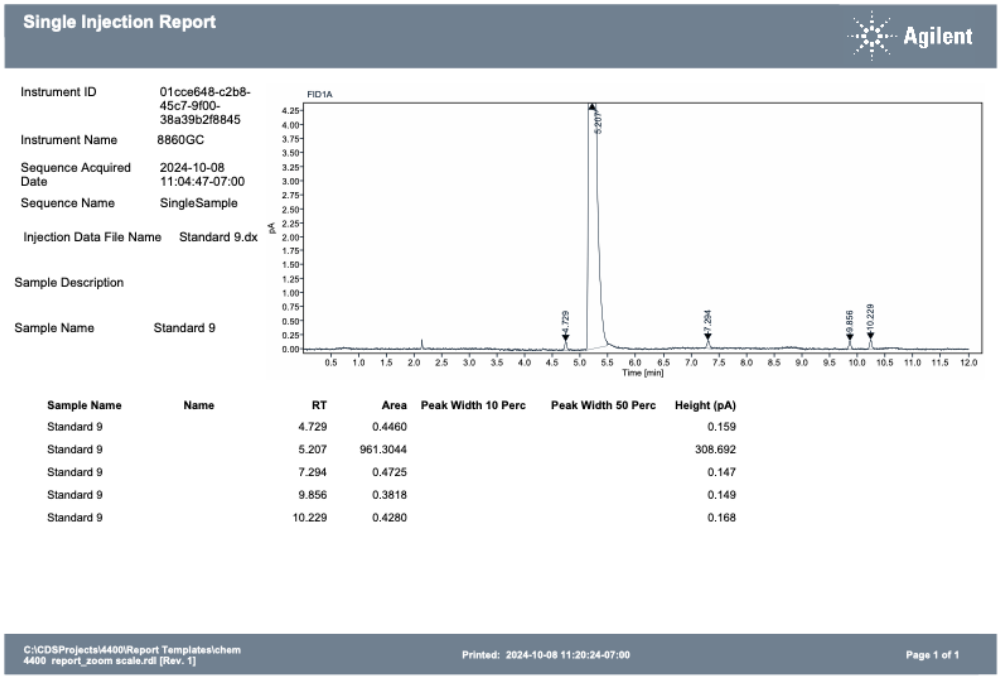
Figure 35: Chromatogram of Standard 12 obtained by GC-FID



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Sequence Name	SingleSample
Injection Data File Name	Standard 9.dx
Sample Description	
Sample Name	Standard 9

Sample Name	Name	RT	Area	Peak Width 10 Perc	Peak Width 50 Perc	Height (pA)
Standard 9		4.729	0.4460			0.159
Standard 9		5.207	961.3044			308.692
Standard 9		7.294	0.4725			0.147
Standard 9		9.856	0.3818			0.149
Standard 9		10.229	0.4280			0.168

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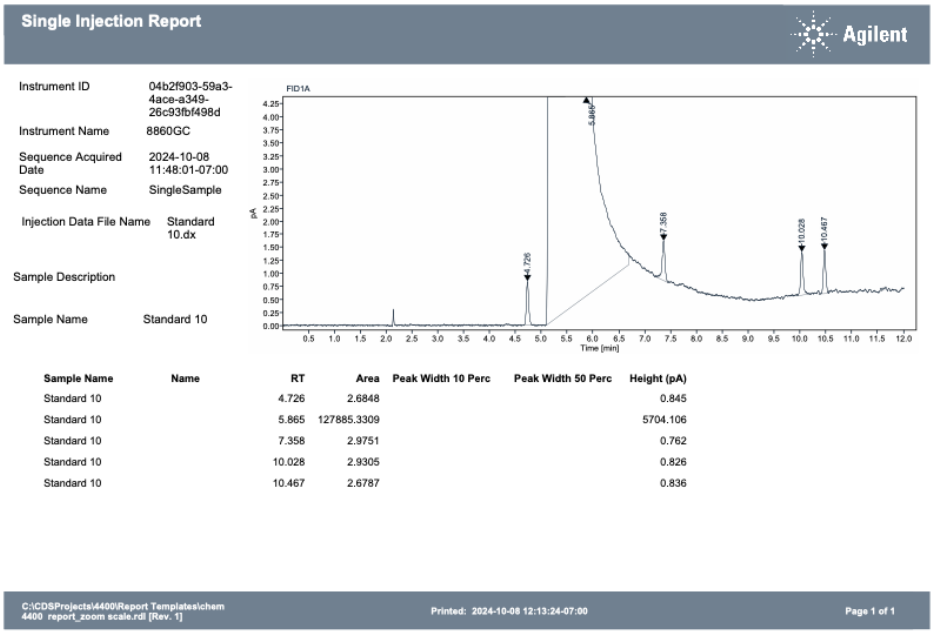
Figure 36: Chromatogram of Standard 13 obtained by GC-FID



Single Injection Report

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Sequence Name	SingleSample
Injection Data File Name	Standard 10.dx
Sample Description	
Sample Name	Standard 10

Sample Name	Name	RT	Area	Peak Width 10 Perc	Peak Width 50 Perc	Height (pA)
Standard 10		4.726	2.6848			0.845
Standard 10		5.865	127885.3309			5704.106
Standard 10		7.358	2.9751			0.762
Standard 10		10.028	2.9305			0.826
Standard 10		10.467	2.6787			0.836

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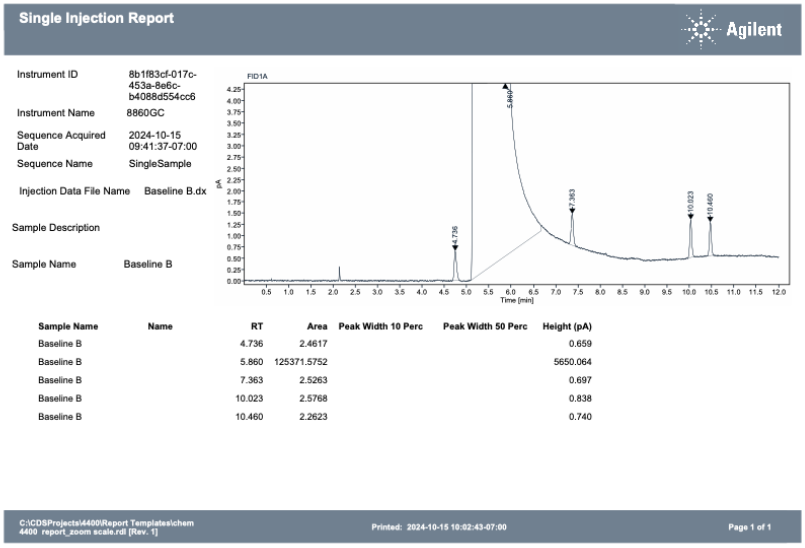
Figure 37: Chromatogram of Standard 14 obtained by GC-FID



Single Injection Report

Agilent

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Instrument Name	8860GC
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Sequence Name	SingleSample
Injection Data File Name	Baseline B.dx
Sample Description	
Sample Name	Baseline B

Sample Name	Name	RT	Area	Peak Width 10 Perc	Peak Width 50 Perc	Height (pA)
Baseline B		4.736	2.4617			0.659
Baseline B		5.860	125371.5752			5650.064
Baseline B		7.363	2.5263			0.697
Baseline B		10.023	2.5768			0.838
Baseline B		10.460	2.2623			0.740

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Figure 38: Chromatogram of Standard 16 obtained by GC-FID

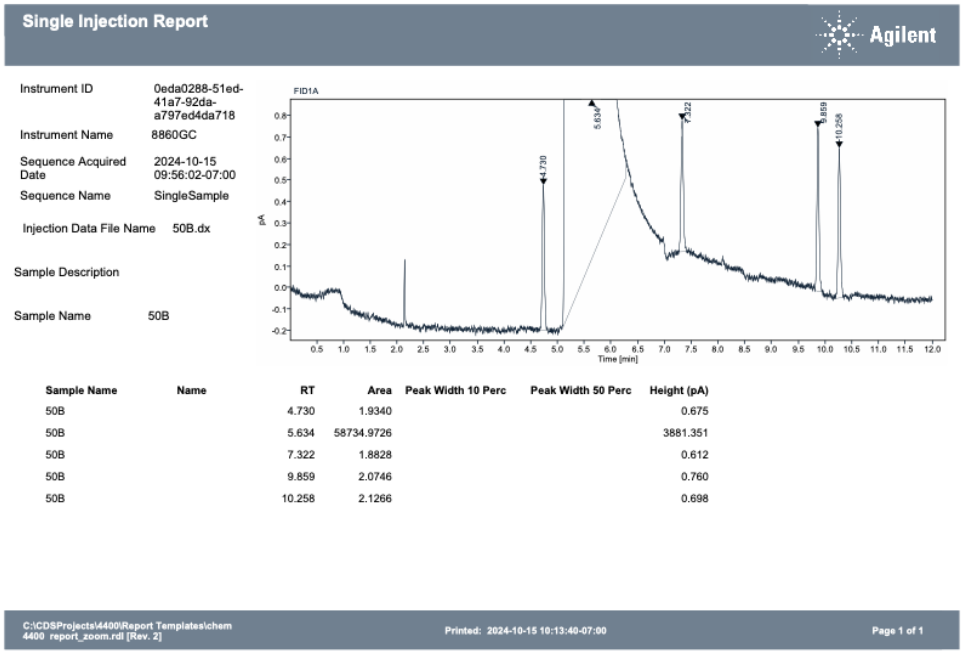

Figure 39: Chromatogram of Standard 17 obtained by GC-FID

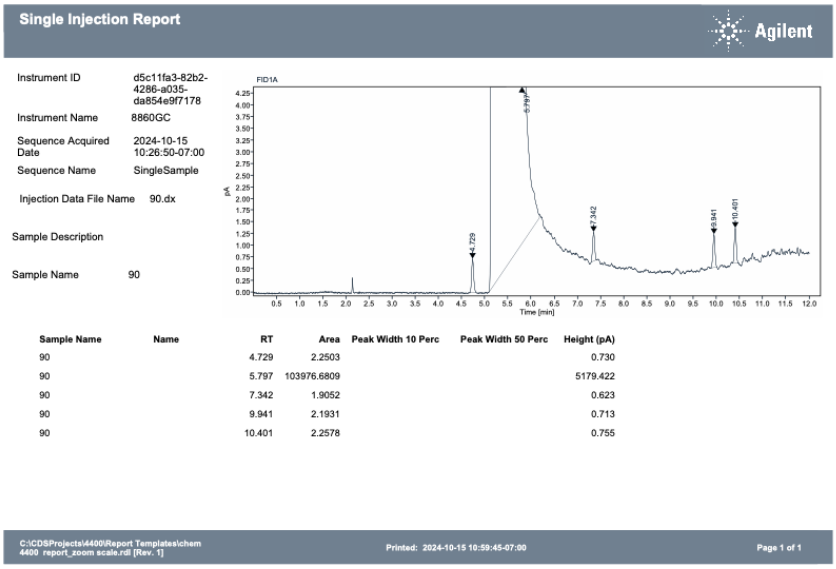

Figure 40: Chromatogram of Standard 18 obtained by GC-FID

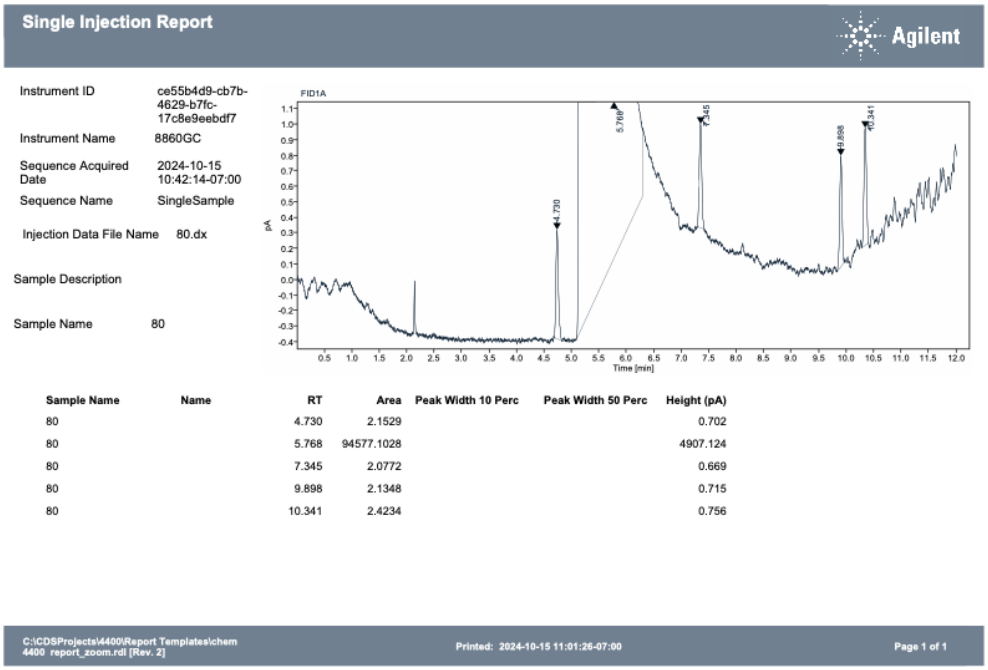

Figure 41: Chromatogram of Standard 19 obtained by GC-FID

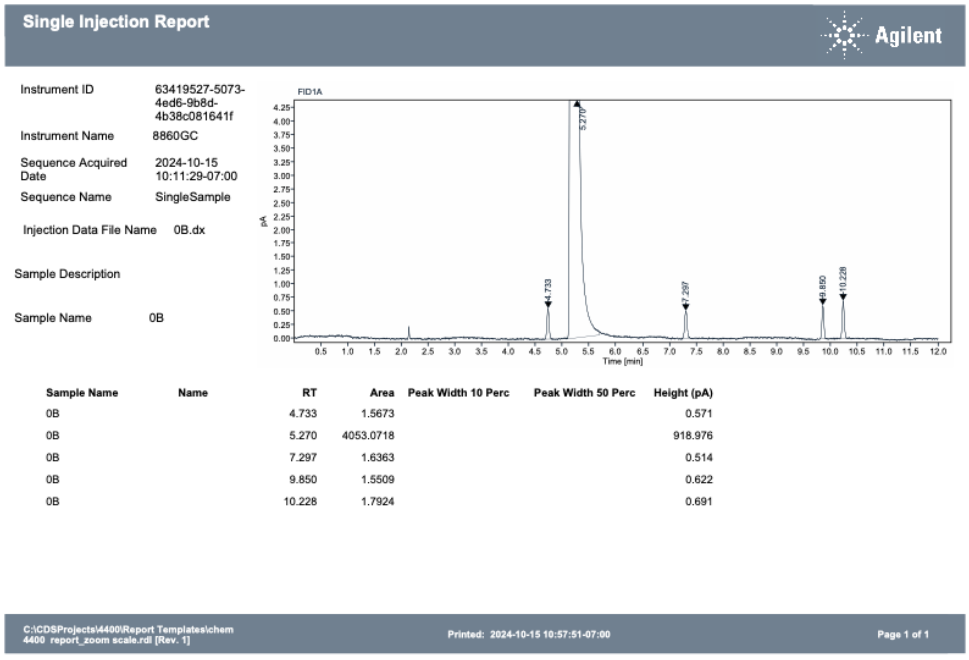

Figure 42: Chromatogram of Standard 20 obtained by GC-FID

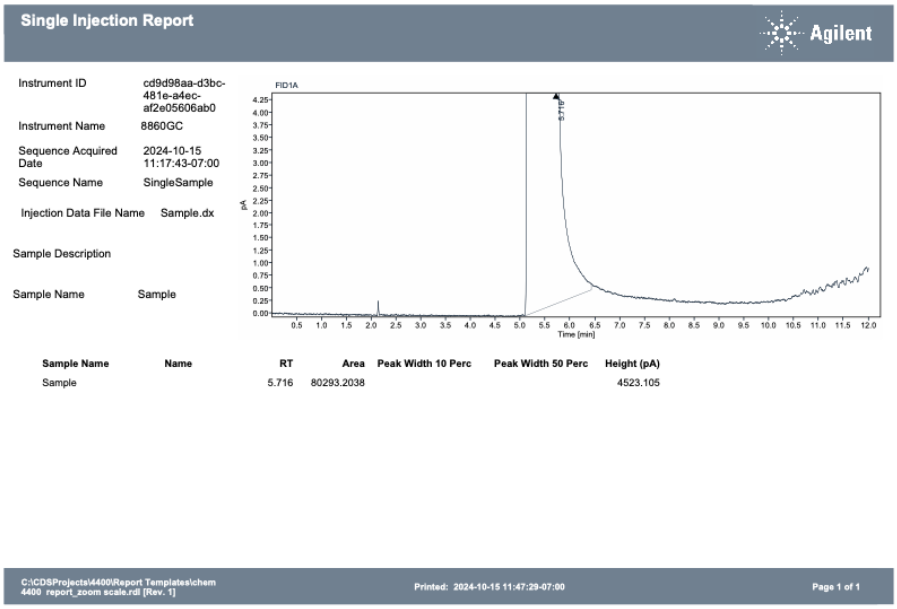

Figure 43: Chromatogram of Sample obtained by GC-FID

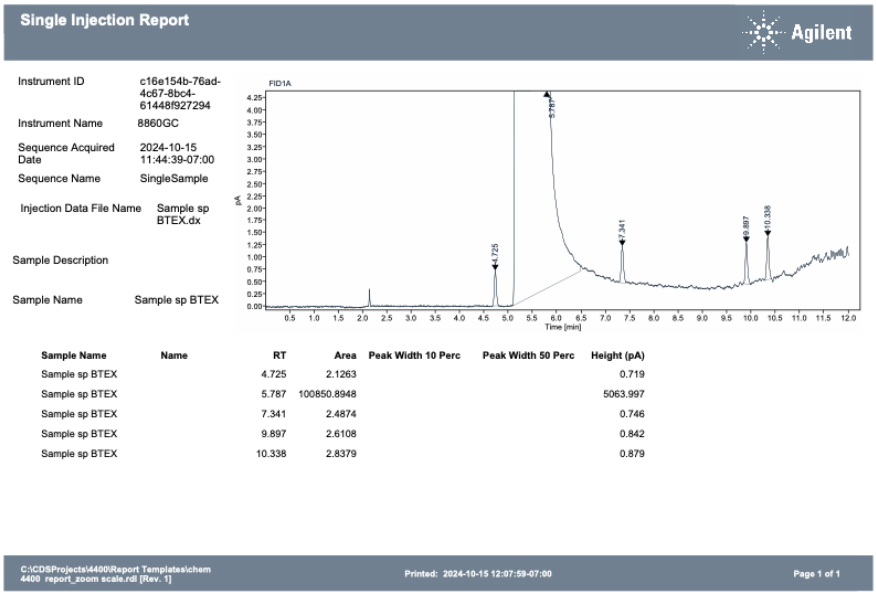

Figure 44: Chromatogram of Sample spiked with BTEX obtained by GC-FID