Investigation of the Suitability of Dispersive Liquid-Liquid Microextraction with GC-MS to Determine Haloacetic Acids in Real Samples

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Abstract:

Haloacetic acids (HAAs) are disinfection byproducts potentially formed during the water treatment cycle, both in municipal water treatment and civilian water treatment. There are over thirty different forms of HAAs, many of which are labeled as suspected carcinogens, with only five being monitored annually in the Kamloops municipal treated water, these being monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid. HAAs can be time consuming and unwieldy to detect in real water samples using the standardized EPA method. This project investigated the applicability of dispersive liquid-liquid extraction combined with derivatization followed by GC-MS analysis for the determination of HAAs in water. The developed method was tested on local water samples (swimming pool, hot tub, and tap) and compared to guidelines and literature values which found 5 out of 6 samples to be over the Canadian guidelines.

Introduction:

When water is disinfected with chlorinated species, the interaction between the sanitizer and the organic material has the potential to form disinfectant byproducts (DBPs).[1] A subgroup of DBPs is haloacetic acids (HAAs). There are six main HAAs, being monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and bromochloroacetic acid (BCAA) as shown in Figure 1.

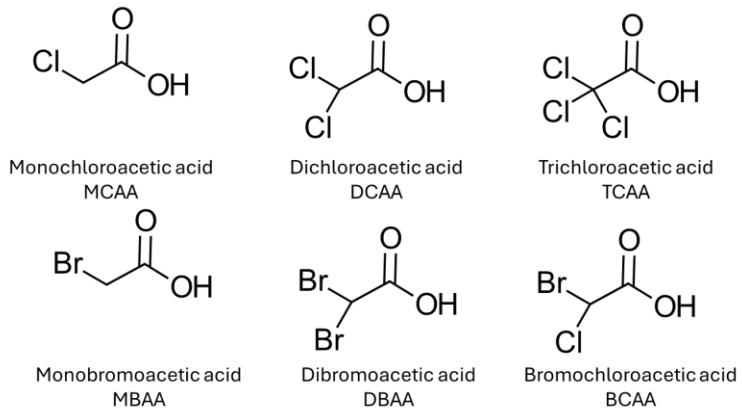


Figure 1. Structures of relevant HAAS.

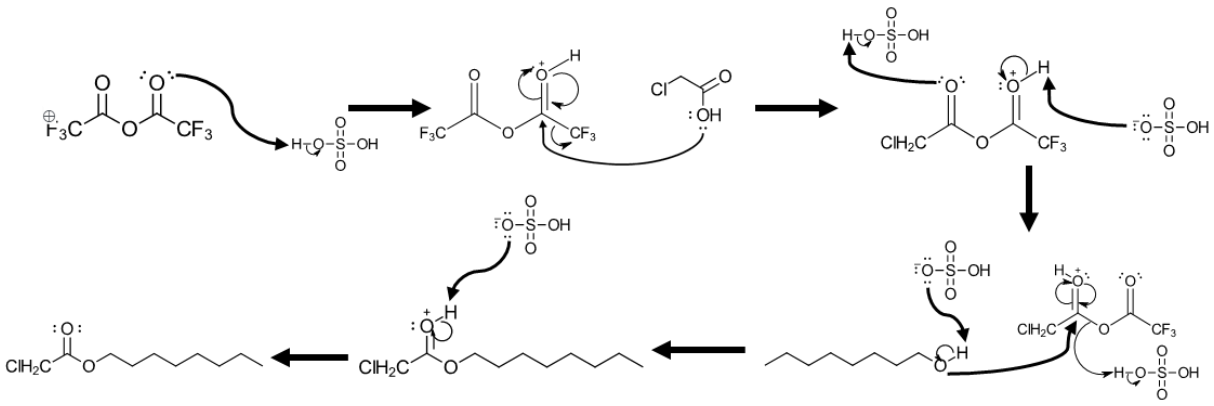
After water chlorinated to accomplish disinfection for either drinking water treatment, or to shock swimming pools and spas, there is residual chlorine left over. This residual free chlorine is available to interact with organic compounds that are present in the water after disinfection. Interactions between the free chlorine and acetic acid groups from the organic matter is the origin of the HAAs after disinfection.[1] The bromine variants of HAAs can still develop in chlorine treated water due to bromine contamination in the sanitizer used.[2]

These compounds are non-volatile, making them difficult to detect and analyze directly. The traditional EPA method uses GC-ECD to analyze samples along with a lengthy extraction and derivation process.[3] As the traditional EPA method can not be directly compared to the dispersive liquid-liquid microextraction method proposed, a GC-MS adapted EPA method was applied. The GC-MS adapted EPA method is near identical to the traditional EPA method, with the exception of the instrument used and the sample volume required.[3,6] The goal of this project was to investigate development of a method using dispersive liquid-liquid extraction combined with derivatization is suitable for the determination of HAAs in real Kamloops water samples. Dispersive liquid-liquid extraction combined with derivatization has the potential to be greener, faster, and safer compared to the current standard liquid-liquid microextraction method.[4,5]

There are several advantages to using a GC-MS based method compared to GC-ECD, which is mass detector that the EPA method suggests. To start, the standard method includes separate derivation and extraction steps, the base method we expanded on introduced a dual derivation and extraction which decreased the total amount of solvent needed.[4] More advantages include higher sensitivity for MCAA, cleaner baselines, and shorter run times.[4] Overall, this indicates in increase in greenness when compared to the EPA methods. To directly compare the EPA methods to this paper's updated method, the strategy from Chiavelli et al was applied to the GC-MS.[6] This allowed for a simple comparison between the Chiavelli et al method, which is a GC-MS adapted EPA method, and this updated method, specifically in the aspects of greenness.[6]

The HAAs were derivatized into respective octyl acetate complexes which are more volatile comparatively and can therefore be more reliably detected using GC-MS. Following Scheme 1, trifluoroacetic anhydride (TFAA) is attacked by the HAAs and the resulting compound is then attacked by 1-octanol to form the respective octyl acetate compound for each variety of HAA.[5]

In their *Report on Carcinogens*, the United States National Toxicology Program deemed that DBAA, BCAA, and DCAA were all labeled as "reasonably anticipated to be human carcinogens".[7] With the cancerous properties of these HAAs, having an accurate and straightforward testing method for treated water is essential for the safety of the citizens using such water. This is heightened by the scenario that the City of Kamloops tests for HAAs in their drinking water once a year. If introduced with a simpler method, it will present fewer challenges to encourage more frequent testing. By recommendation of Health Canada, the goal will be to prompt quarterly monitoring of HAAs.[8] Health Canada also promotes a limit on the combined concentration of the five HAAs listed prior, which is 80ppb.[8]



Scheme 1. Proposed derivatization mechanism to produce acetate complexes from HAAs and octanol in acid shown by the transition of MCAA to octyl chloroacetate.[2]

Table 1. Reactants used and products produced using various haloacetic acids using Scheme 1.

Reactants	**Products**
Haloacetic acid, found in sample	Octyl chloroacetate
Sulfuric acid	Octyl dichloroacetate
Trifluoroacetic anhydride	Octyl trichloroacetate
1-octanol	Octyl bromoacetate
	Octyl dibromoacetate
	Octyl bromochloroacetate

Experimental:

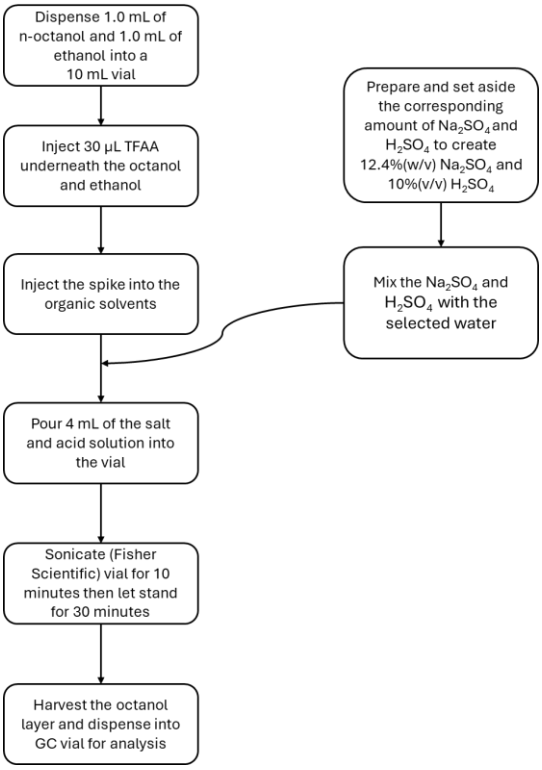
2.1. *Reagents and Chemicals*

Table 2. Reagents used for dispersive liquid-liquid microextraction and the adapted EPA method.

Reagent	**Manufacturer**
Haloacetic Acid Mix	Restek
99% 1-Octanol	Thermo Scientific
Octyl chloroacetate	Sigma Aldrich
Trifluoroacetic anhydride (1 g x 10)	Avantor
Trifluoroacetic anhydride (10 mL)	Sigma Aldrich
>99.9% Acetone	Sigma Aldrich
>99.5% Methyl-t-butyl Ether	Supelco
Anhydrous Ethanol	Commercial Alcohols
Sodium Sulfate	Caledon
99.8% Methanol	Ultrapure
99% Sulfuric Acid	Sigma Aldrich

2.2. *Preparation of Standards*

2.2.1 *Dispersive Liquid-Liquid Microextraction Standards*

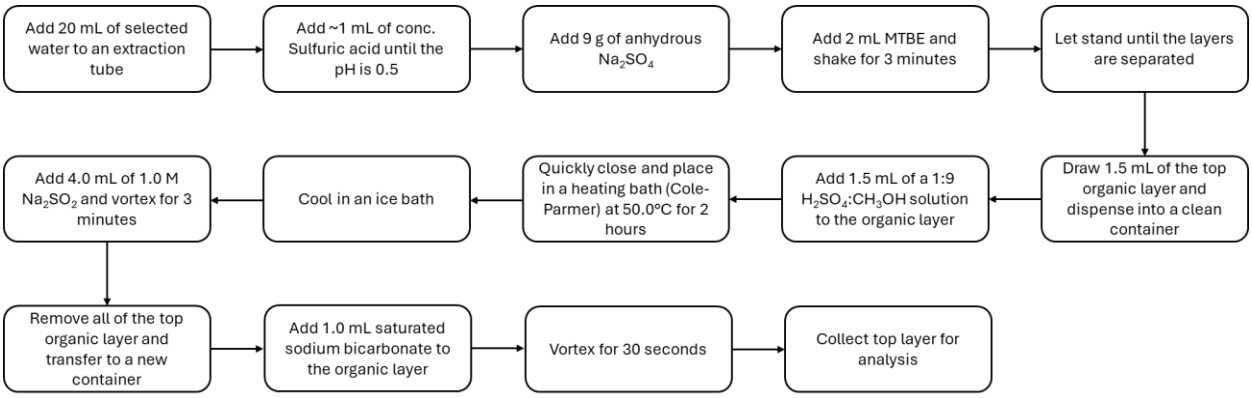


Scheme 2. The steps to create standards and samples for the dual extraction and derivation method.

2.2.2 *GC-MS Adapted EPA Standards*

From pure methyl dichloroacetate, an 82.9ppm stock was created by diluting in MTBE.

Using the purchased HAA mixture, a 20.0ppm stock solution was created by diluting in MTBE. This stock was used to spike LC-MS grade water before reacting following Scheme 3.



Scheme 3. The steps to create standards and samples for the GC-MS adapted EPA method.[6]

2.3. *Sampling Locations and Sample Collection*

2.3.1 *Tap Water Samples*

Two tap water samples were collected from varying locations across Kamloops, BC: a residential house in the Dallas neighbourhood and a residential house in the Aberdeen neighbourhood.

Before each sample was taken, the faucet head was wiped down with a clean disposable cloth and the water was turned on for 30 seconds before filling the sample bottle.

The residential tap water samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.3.2 *Swimming Pool Water Samples*

Two samples were collected from saltwater-based pools in the Dallas neighborhood of Kamloops, BC. These samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.3.3 *Spa Water Samples*

Two spa samples were collected from chlorine-based spas in Kamloops, BC, one in the Dallas neighbourhood and one in the Upper Sahali neighborhood. Both samples were preserved with ~12mg of ammonium chloride, filled to create zero headspace, and stored in a refrigerator immediately. These samples were analyzed after four days.

2.4. *Instrumentation*

The samples and standards were analyzed using the Agilent 7890B GC system paired with the Agilent 5977A MSD system along with a PAL liquid autosampler system.

2.5. *Method development*

2.5.1 *Dispersive Liquid-Liquid Microextraction Method*

The base of this method is from Al-shatri et al, with adjustments to the temperature program and the sample and standard preparation.[5]

On the GC-MS,a bakeout program was created and run between each sample to ensure no solvent carry-over as the octanol's retention time is less than a minutes from the HAA peaks.

The standard GC-MS method went through many iterations to optimize retention time and separation along with adjustments to the SIM ions selected for analysis. This was finalized with the following GC-MS method:

Table 3. GC-MS Method for dispersive liquid-liquid microextraction.

Inlet temperature	200°C
Ion source temperature	200°C
Carrier gas flow rate	2 mL/min
Carrier gas pressure	50 kPa
Injection volume	0.2 µL
Pre-washes with octanol	2
Post-washes with octanol	2
Temperature and hold #1	40°C for 1 minute
Ramp rate #1	25°C/min
Temperature and hold #2	180°C for 4 minutes
Ramp rate #2	30°C/min
Final temperature and hold	250°C for 2 minutes
Solvent delay	5.7 minutes
SIM	79, 95, 48, 76, 121, 123, 139, 36, 110, 127, 129, 131, 120, 122, 173
Scan range	35-230

To determine the retention time of octyl chloroacetate, the derivative of MCAA, standards were prepared by diluting the purchased chemical in acetone and octanol. This aided in determining the timing of the solvent delay as to not cut off any HAA peaks and identifying the retention time of MCAA product.

2.5.2 *GC-MS Adapted EPA Method*

This method was based on the procedure and temperature program listed by Chiavelli et al.[6]

Table 4. GC-MS Method for the adapted EPA method.

Inlet temperature	200°C
Ion source temperature	200°C
Carrier gas flow rate	2 mL/min
Carrier gas pressure	50 kPa
Injection volume	1 µL
Pre-washes with MTBE	2
Post-washes with MTBE	2
Temperature and hold #1	40°C for 1 minute
Ramp rate #1	2.5°C/min
Temperature and hold #2	65°C
Ramp rate #2	10°C/min
Temperature and hold #3	85°C
Ramp rate #3	20°C/min
Final temperature	205°C
Post run temperature	210°C for 7 minutes
Solvent delay	3 minutes
SIM	3 min(59, 64, 77), 8.3 min(59, 83, 85, 111), 10 min (59, 117, 119)
Scan range	35-230

To determine the retention time of methyl dichloroacetate, standards were prepared by diluting pure methyl dichloroacetate with MTBE. These standard concentrations were 0.55, 0.83, 1.1 and 10 ppm.

A 20.0ppm HAA stock in MTBE was used to spike LC-MS grade water to 0.025, 0.050, 0.100, and 5.00 ppm following Scheme 3.

2.6 *Ion Selection*

2.6.1 *Dispersive Liquid-Liquid Microextraction Ions*

The base for ion selection was based on the ions chosen by Saraji and Bidgoli with a few adjustments.[9] For methyl chloroacetate, the ions selected were 70, 79, 95 m/z. While 79 and 95

m/z were chosen as characteristic ions for MCAA, 70 m/z would produce a larger signal than either ion and act as a beacon.[9] Unfortunately, the octanol has a very similar structure and overpowered the MCAA peaks making it difficult to determine an exact retention time.

The ions selected to identify DCAA were 41, 43, 48, 56, and 76 m/z. While 48 and 76 m/z are used as characteristic peaks, the 41:43 m/z ratio were specifically useful to identify DCAA. There was also the 56:69 m/z ratio that was used to confirm the peak.

In the case of DBAA, there were multiple characteristic peaks that could have been used, but the 120:121:122 m/z ratio was the most helpful and reliable. TCAA was also simple to choose ions for, as the recommended ions, 110 and 121 m/z, were consistently prominent along with 57 m/z.[2] With a similar trend, the ions for BCAA were the recommended ions, 127, 131, and 129 m/z along with 57 m/z being used as a beacon.[9]

2.6.2 *GC-MS Adapted EPA Ions*

The ions for each molecule were selected from Chiavelli and Birch, focusing on the three chlorinated products.[6,10] For methyl chloroacetate, 59, 64, and 77 m/z were chosen. The 64 and 77m/z ions are characteristically not seen in the mass spectrum of MTBE, and therefore excellent identifiers. While 59m/z is seen within the mass spectrum of MTBE, it is at a significantly higher ratio in methyl chloroacetate and can still be used as character peak.

Methyl dichloroacetate compared four ions: 59, 83, 85, and 111m/z. The ratio between 83:85 m/z was immensely useful as characteristic ions as they could easily be compared to the reference mass spectrum.[11] Selecting the ions for methyl trichloroacetate used a similar logic with 59, 117, and 119 m/z as there is a characteristic ratio between 117:119 m/z and 59 m/z used as a beacon.

Results:

3.1 MS Peak Identification

Table 5. Average Retention Times for each octylated HAA.

Compound Name	Retention Time (min)
Octyl chloroacetate	Tentative
Octyl bromoacetate	6.945
Dichloroacetic acid octyl ester	7.809
Trichloroacetic acid octyl ester	9.333
Bromochloroacetic acid octyl ester	10.096
Dibromoacetic acid octyl ester	14.492

3.2 Real Sample HAA Concentrations

In the following tables, the term "ND" is defined as *non-detectable*.

Table 6. Final concentrations of MBAA in real water samples.

Sample Name	Peak Height	Peak Area	Concentration (ppm)	Retention Time (min)
Pool 1	ND	ND	ND	ND
Pool 2	ND	ND	ND	ND
Spa 1	6009	144579	16.6	6.957
Spa 2	4575	924561	106	6.957
Dallas Tap	752	126180	14.5	6.960
Aberdeen Tap	819	23075	2.66	6.957

Table 7. Final Concentrations of DCAA in real water samples.

Sample Name	Peak Height	Peak Area	Concentration (ppm)	Retention Time (min)
Pool 1	ND	ND	ND	ND
Pool 2	317	45155	0.610	7.827
Spa 1	1398	168681	2.73	7.814
Spa 2	80955	806313	13.7	7.803
Dallas Tap	2053	220518	3.63	7.718
Aberdeen Tap	2557	308063	5.13	7.828

Table 8. Final Concentrations of TCAA in real water samples.

Sample Name	Peak Height	Peak Area	Concentration (ppm)	Retention Time (min)
Pool 1	ND	ND	ND	ND
Pool 2	894	79805	1.230	9.302
Spa 1	3280	199228	4.080	9.265
Spa 2	29820	1005624	22.700	9.235
Dallas Tap	10140	426445	9.320	9.240
Aberdeen Tap	19096	664570	14.800	9.260

Table 9. Final Concentrations of BCAA in real water samples.

Sample Name	Peak Height	Peak Area	Concentration (ppm)	Retention Time (min)
Pool 1	ND	ND	ND	ND
Pool 2	107	7190	0.992	10.091
Spa 1	254	13331	2.480	10.076
Spa 2	1508	58984	13.60	10.058
Dallas Tap	580	21250	4.400	10.060
Aberdeen Tap	1021	338750	81.40	10.059

Table 10. Final Concentrations of DBAA in real water samples.

Sample Name	Peak Height	Peak Area	Concentration (ppm)	Retention Time (min)
Pool 1	26	1363	ND	14.508
Pool 2	2822	202777	2.030	14.465
Spa 1	8140	494461	5.490	14.455
Spa 2	36211	1702902	19.80	14.468
Dallas Tap	15839	503725	5.600	14.453
Aberdeen Tap	22859	754143	8.570	14.454

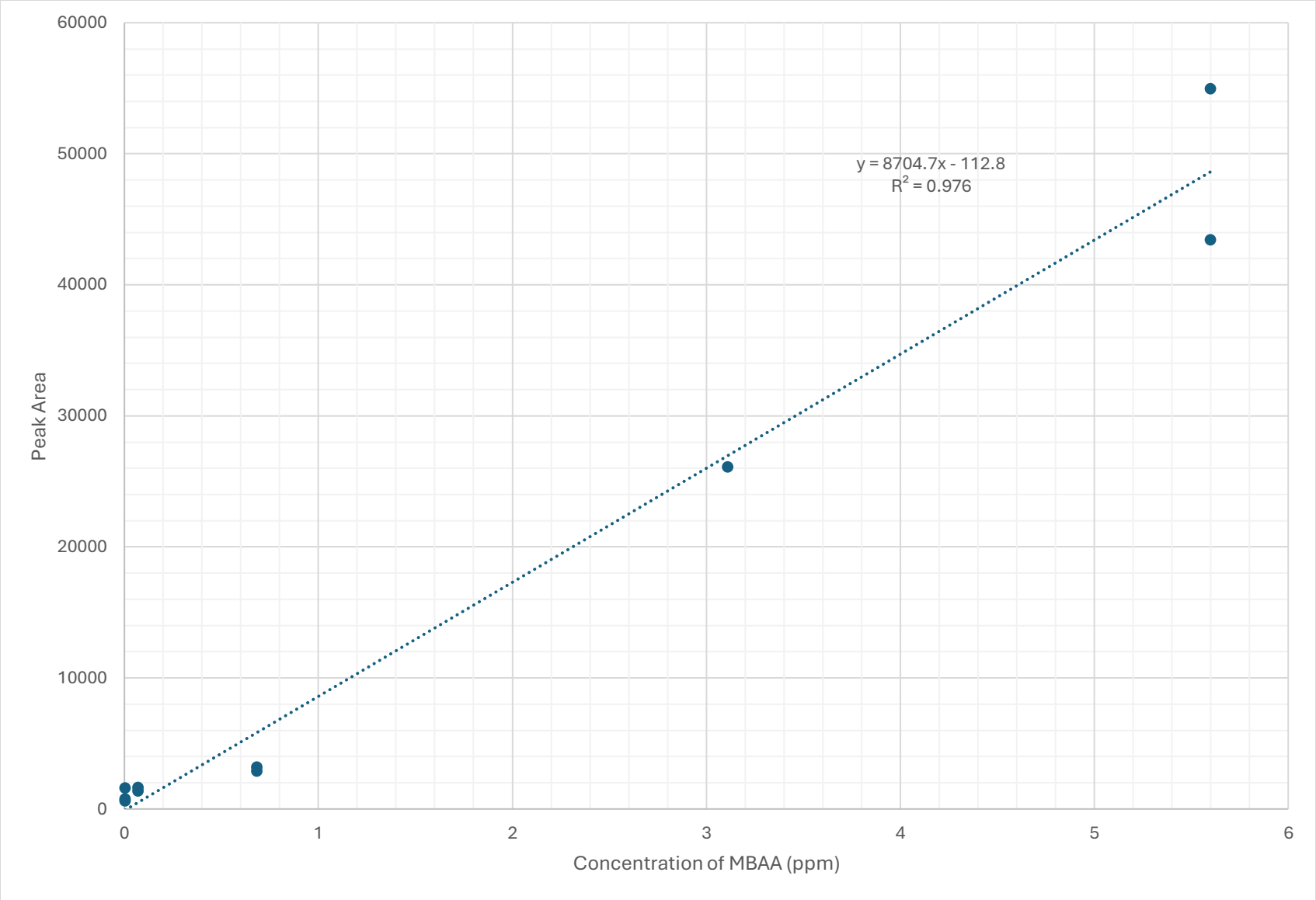


Figure 2: The concentration calibration curve of peak area for monobromoacetic acid.

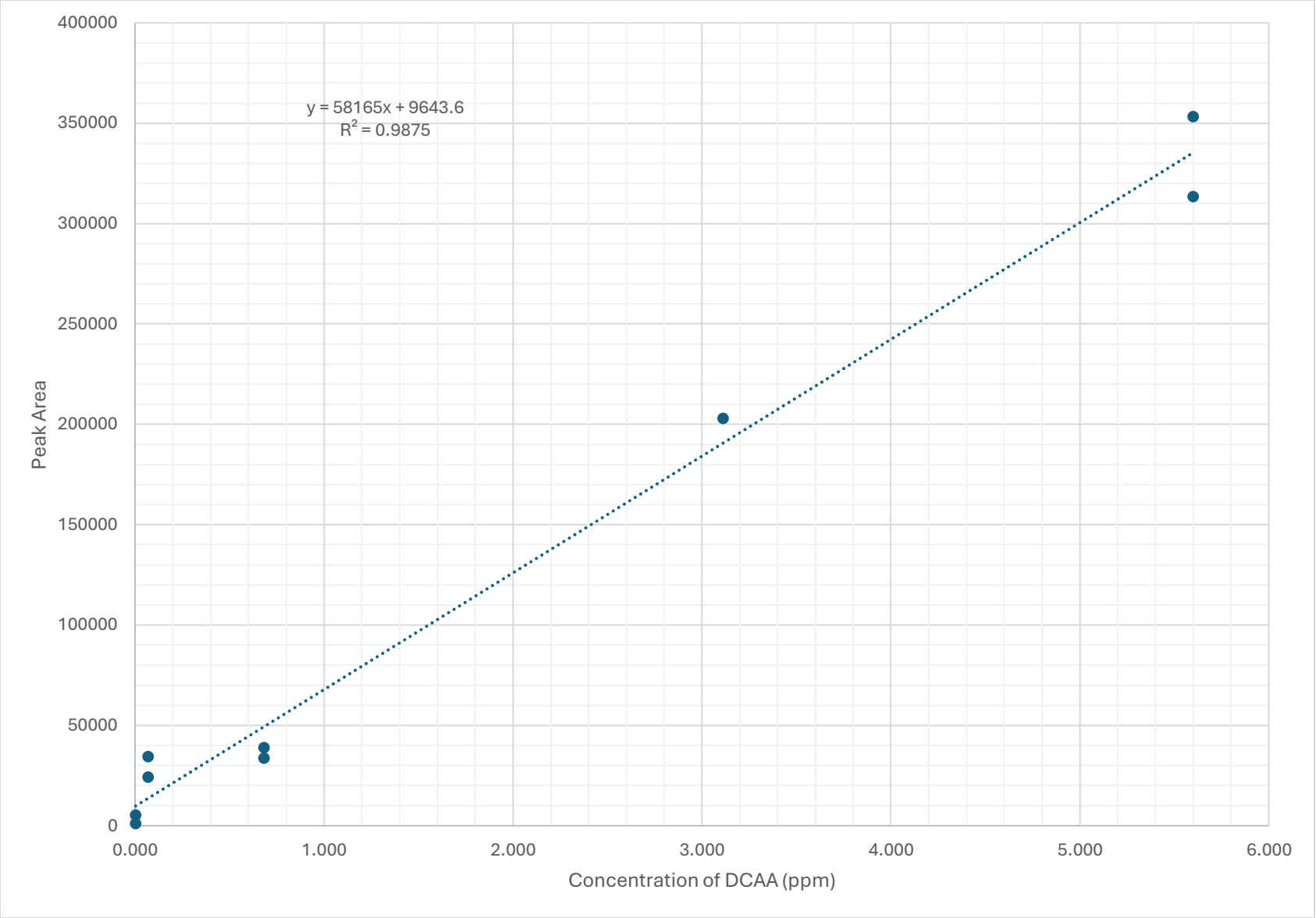


Figure 3: The concentration calibration curve of peak area for dichloroacetic acid.

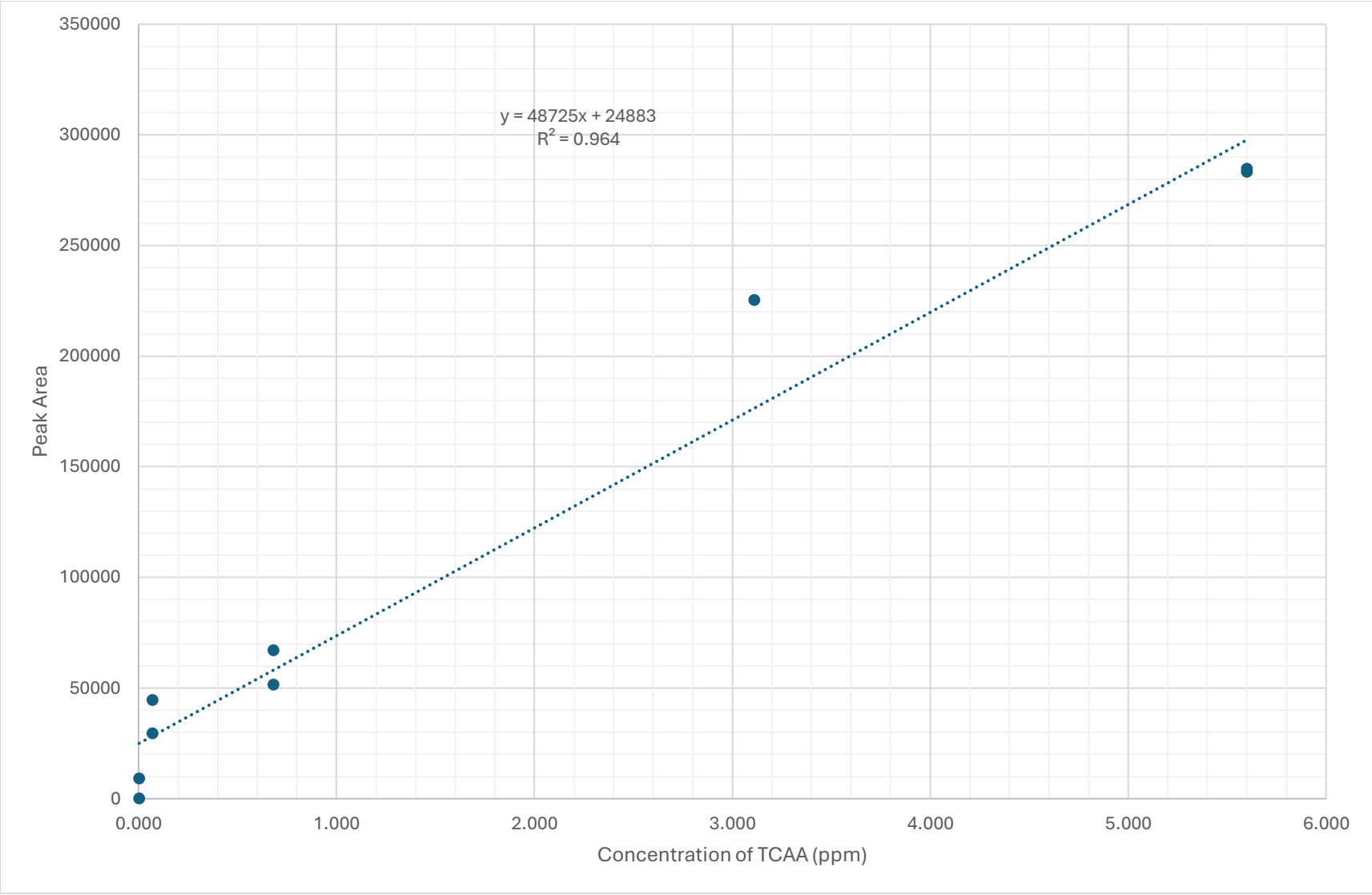


Figure 4: The concentration calibration curve of peak area for trichloroacetic acid.

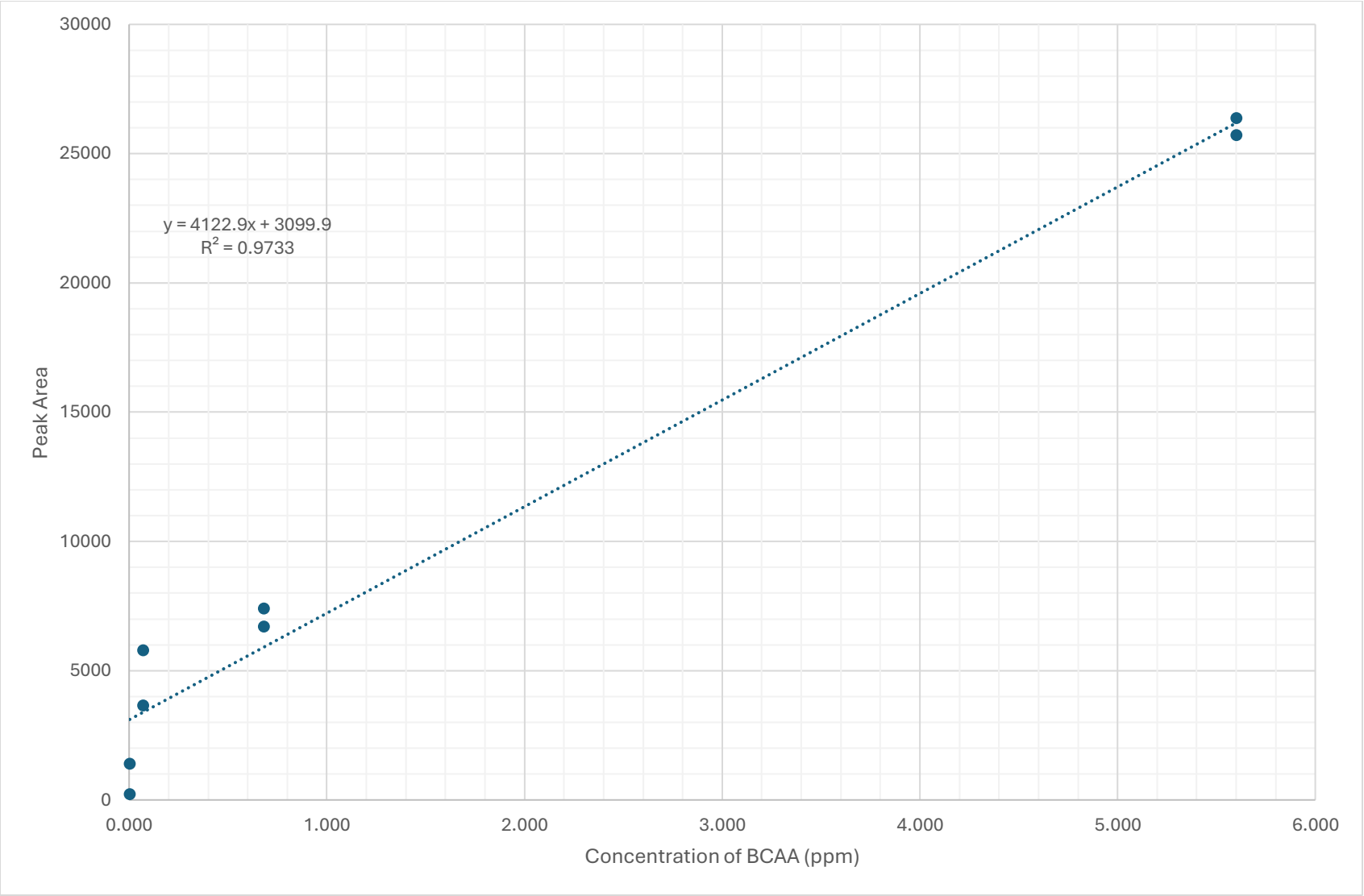


Figure 5: The concentration calibration curve of peak area for bromochloroacetic acid.

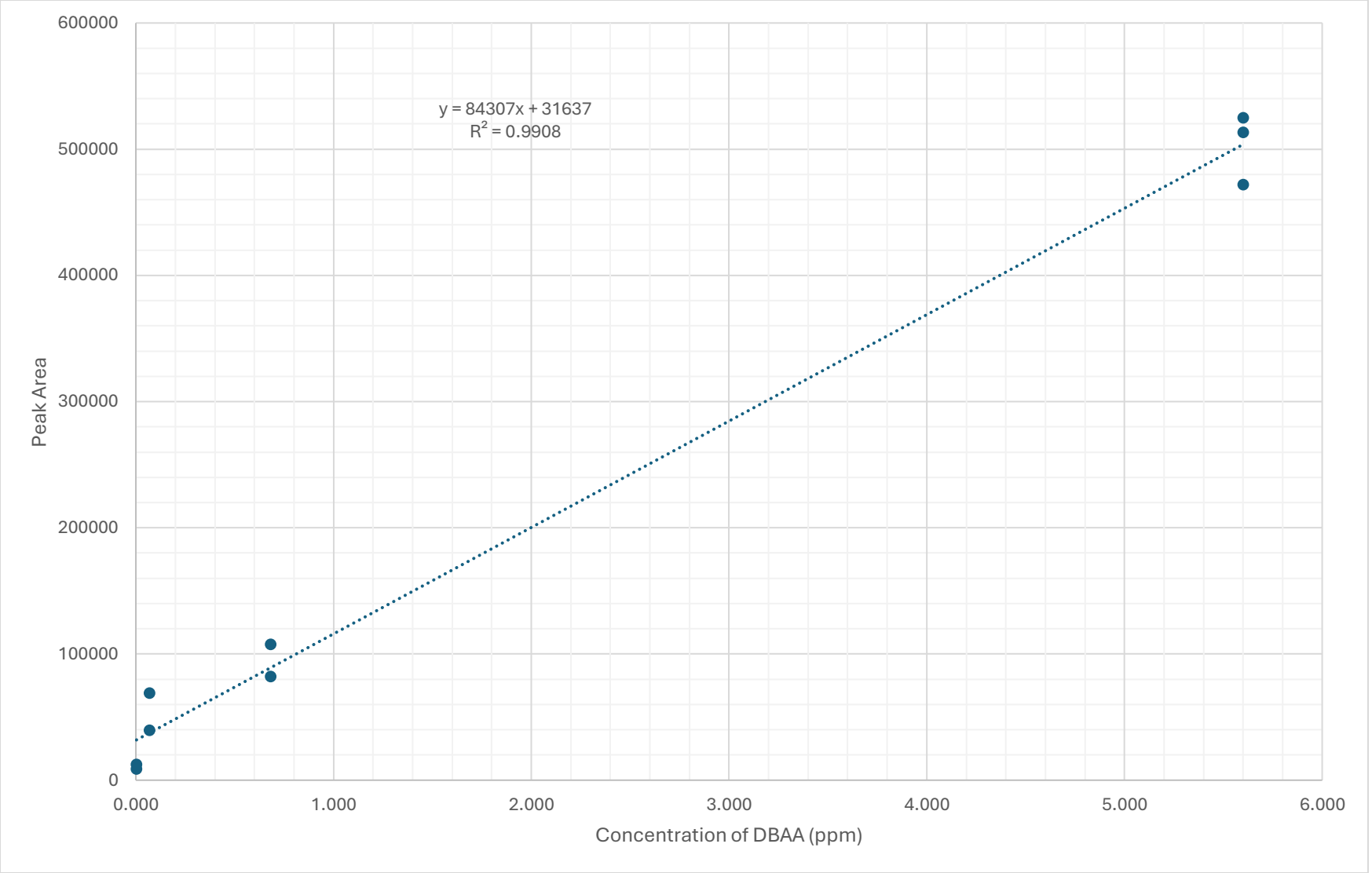


Figure 6: The concentration calibration curve of peak area for dibromoacetic acid.

Discussion:

3.1.1 Dispersive Liquid-Liquid Microextraction

To begin developing the temperature program, a set of standards with octyl chloroacetate, the octylated MCAA, diluted in octanol was formed. Unfortunately, due to the octanol, even with drastically increasing the concentration of the octyl chloroacetate, it was still overwhelmed by the octanol peak. To combat this, standards were created using acetone to replace the octanol. While this did show an identifiable peak, it could not be used as a base for the setting a calibration curve. As the octanol seemed to interfere with the magnitude of the product's ion peaks, a consistent baseline could not be met to confidently quantify the octyl chloroacetate. Due to this, the MCAA content in the water samples were not analyzed.

Each type of water sample had its own interesting qualities. Starting with the swimming pool water samples, it is important to note that Pool 1 had no detectable HAAS and Pool 2 had no detectable MBAA. In Pool 2, the highest HAA concentration was found to be DBAA at 2.029ppm and the lowest detectable HAA concentration was DCAA at 0.611ppm. This is puzzling as the concentration of free chlorine in the water should be higher than bromide due to the chloride salt sanitation method. It was predicted that the chlorine variants of the HAAs would be larger than their bromine counterparts due to the use of chlorine sanitation.

Hot tub water showed surprising high concentrations of all the HAAs detected. Hot tub 1 had the highest HAA concentration of all the water samples, with the highest being MBAA at 106.2pmm and the lowest being BCAA at 13.55ppm. Hot tub 2 possessed much lower, albeit still high compared to the recommended limit of 80ppb, HAA concentrations.[8] The highest was BCAA at 24.81ppm and the lowest was DCAA at 2.734ppm. The hot tubs followed the same trend as the swimming pools as the brominated HAAs were found at a higher concentration compared to the chlorinated HAAs.

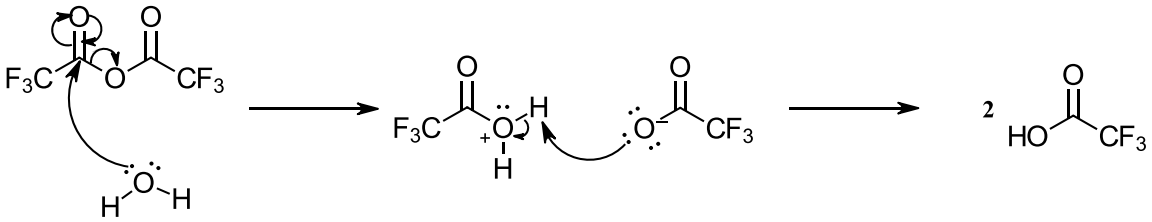
In the tap water samples, each sample had a different HAA with the highest concentration. In the Aberdeen tap sample, the HAA with the highest concentration was BCAA at 81.410ppm whereas the HAA with the highest concentration in the Dallas tap sample was MBAA at 14.509ppm. The lowest HAA for Aberdeen was then MBAA at 2.664ppm with the Dallas one being DCAA at 2.635ppm. This again shows the trend that the brominated products are higher than the chlorinated products.

Between all of the types of samples, the HAAs with the highest concentrations were always a brominated variant, which as mentioned above, is an unexpected result. As each of the water samples were sanitized with a chlorine product, it was expected that the chlorinated products would be at a higher concentration compared to the brominated products. While this was unexpected, it leads into many topics to research in the future.

An interesting turn of results was that the pool samples had lower concentrations of HAAs compared to tap water. While there is currently no concrete reason as to why this occurred, a possibility could be due to the constant filtration and circulation of the water. Both of the swimming pools had a filter media of sand, whereas the hot tubs had pleated cartridge filters, and the tap water's only extra filtration after being treated is only for debris.

Nearly all of the samples contained high levels of HAAs, especially when compared to the regulated limit allowed to be detected in Canadian drinking water. The maximum of combined HAAs concentration is indicated by Health Canada as 80ppm, which is drastically small when compared to the individual concentrations of each HAA detected.[8] While this was expected for the pool and hot tub water due to their open water and higher chlorination, the tap water samples exceeding the federal limits was unanticipated. The one exception was Pool 1, which had no detectable HAAS. While the first assumption as to why Pool 1 had such low levels of HAAs might be care of the water by the owners, this is disproved by the same owners maintaining Spa 2, which had the highest detected levels of HAAs. When later questioned, the owners stated that Pool 1 and Spa 2 were maintained on the same schedule together. Due to this, it is unknown as to why Spa 2 had such high levels of HAAs and why Pool 1 had such low levels of HAAs.

Throughout the development of the derivatization process, several challenges arose, such as in the earlier trials, the TFAA used was transferred into a smaller vial with a Teflon coated septum. The vial was evacuated and filled with nitrogen three times to reduce the degradation of the TFAA. This was necessary due to the original packaging including only a screw cap as the seal. If there was any air left over during the transfer, this could have caused the TFAA to degrade. After one use, the septum appeared to be contaminated. The TFAA then had to be transferred in a glove bag under nitrogen to smaller vials with Teflon coated septa. Each vial could only be used once, as once the septum was pierced, it was contaminated with TFAA and begun to degrade. In the case that the TFAA was degraded before it was used in the reaction, this could be the cause for the difficulty in detecting product peaks before the new TFAA arrived. Overall, the inert Teflon coated septa should not have reacted with the TFAA per Sigma Aldrich. This leads to the possibility that invisible drips landed on top of the septa after piercing or that in the case of the first vial, the septum was over punctured after being evacuated.



Scheme 4. The mechanism of TFAA in water.

When identifying each product, mass spectra from the National Institute of Standards and Technology (NIST) were used as the baseline. The sole exception was DCAA, as no certified mass spectrum could be found. For this compound, the experimental mass spectrum obtained by Bidgoli and Mohammad was used as the reference spectrum.[9]

The most noticeable challenge was the separation of the MCAA and octanol peaks. By using octanol as a rinse in the GC-MS, there was a significant shoulder left by the octanol that overrode the MCAA peak. When analyzing the selected ions, a tentative retention time of 6.15 min was selected due to the small 79 and 95 m/z peaks. These peaks were often overpowered by the octanol peak and proved difficult to pinpoint consistently. Due to the lack of confidence in the retention time of this peak, it was labeled as tentative.

3.1.2 Comparison to GC-MS Adapted EPA Method

When comparing the dispersive liquid-liquid microextraction method outlined in Scheme 2 to the GC-MS adapted EPA method, there are many factors to consider. The first aspect is the greenness of each method. There are twelve principles of chemistry outlined by the American Chemical Society: Prevention, Action Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstocks, Reduce Derivatives, Catalysis, Design for Degradation, Real-time analysis for Pollution Prevention, and Inherently Safer Chemistry for Accident Prevention.[12]

The most obvious improvement between the two methods is in the Catalysis section. In the dispersive liquid-liquid microextraction, TFAA is used as a catalyst to speed up the reaction time reducing it from 2 hours in a water bath to only 10 minutes in a sonicating bath.

The decrease in reaction time also leads into an increase in energy efficiency. Although, the water bath is not the only device that requires power in the EPA method, as it also required 3.5 minutes of vortexing.

Future Work:

There were many aspects that require a mention for future work. The first step would be to adjust the temperature program to reveal the MCAA peak from underneath the octanol peak. With a temperature program that can identify all the HAAs, the next focus would be to develop more specific calibration curves. With the range of concentrations being so broad, multiple calibration curves could be produced, one closer to the 500ppb range and the other covering the larger concentrations that ranged upwards of 100 ppm. With separate curves, it can make calculating the smaller concentrations more precise.

As mentioned in 3.1.1, the brominated HAAs were at a higher concentration than the chlorinated HAAs. In the future, it would be valuable to test the bromine and chlorine content in the sanitizing products as well as maintaining consistency by using the same sanitizing product for each water sample.

Another point of interest for the future is to extend sampling. This could include adding samples from public pools to compare to private pools, samples from chlorine puck pools, saltwater pools, and bromine pools, and also aligning the shock day of the pools and spas. This could also extend to analyzing the HAA content in the water over time, such as right after shocking to the next shock treatment.

To further asses the greenness of the developed method, a step forward would be to investigate and optimize the reaction's atom economy to reduce the amount of wasted reagents.[12]

Conclusion:

A method using GC-MS to determine the concentration of HAAs was developed, along with an increase in greenness compared to the standardized EPA method. This method is suitable to analyze many HAAs, including brominated variants. The real water samples assessed were determined to have higher concentrations of HAAs than the regulation limit of 80ppm with the exception of one swimming pool sample.

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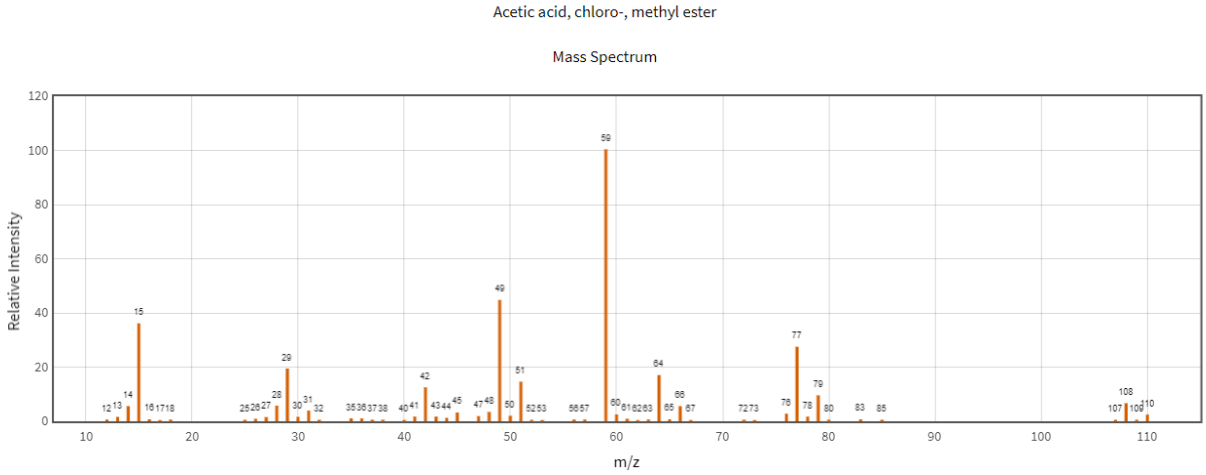
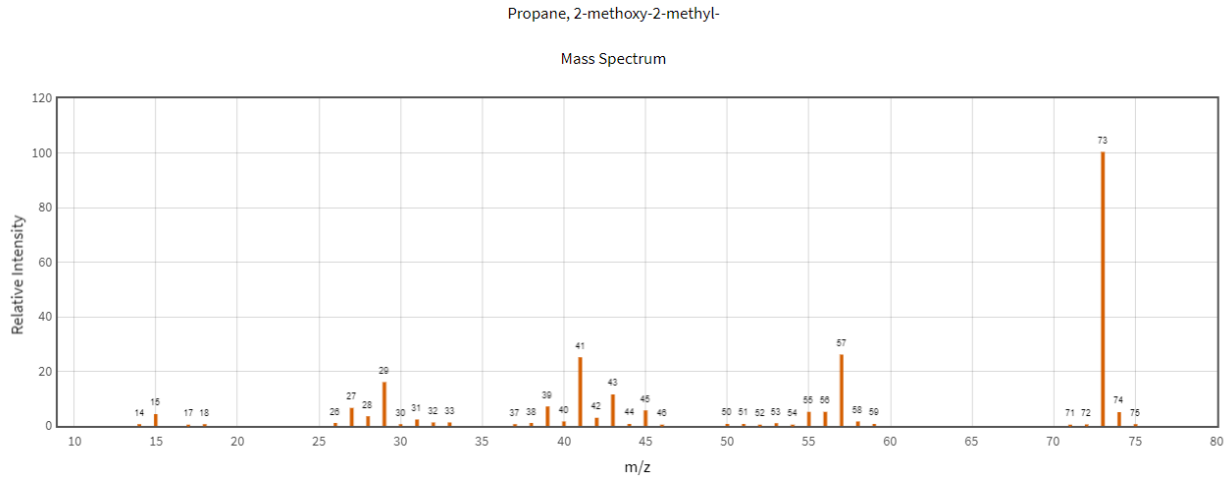
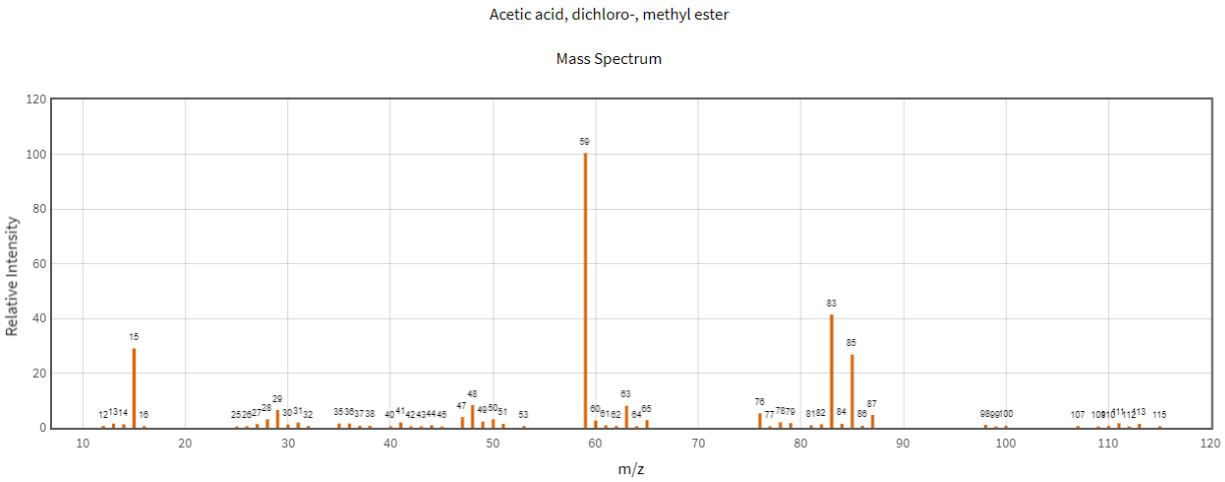
Appendix:



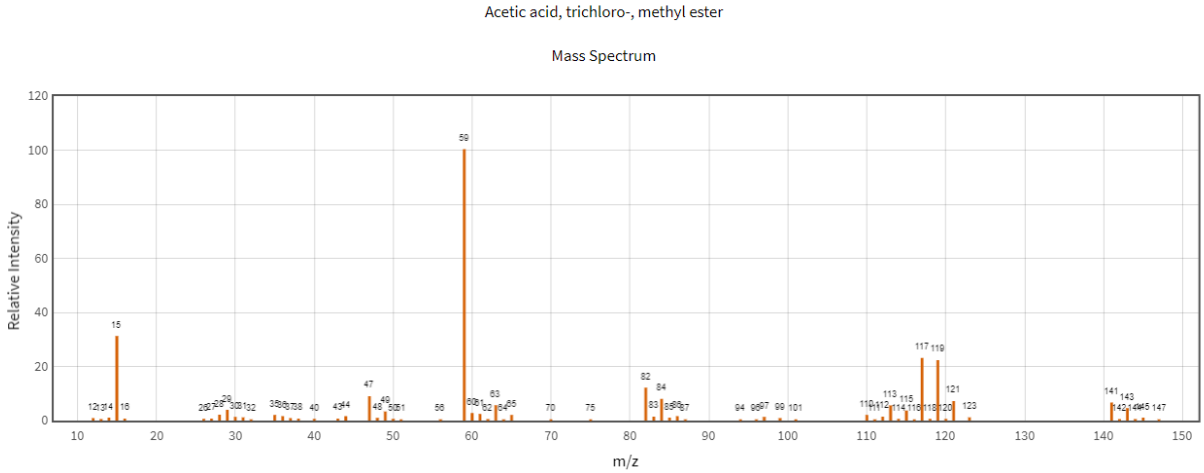
Reference mass spectrum for methyl chloroacetate from NIST.[13]



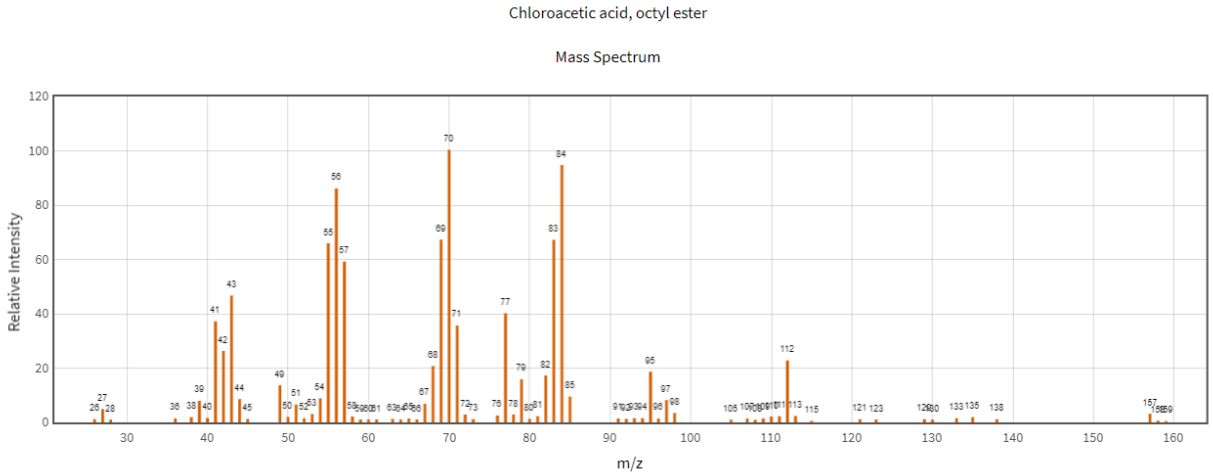
Reference mass spectrum for MTBE from NIST.[14]



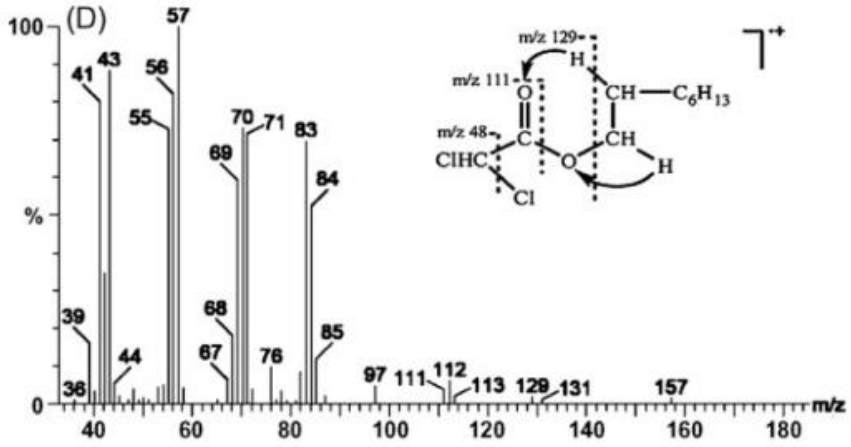
Reference mass spectrum for methyl dichloroacetate from NIST.[11]



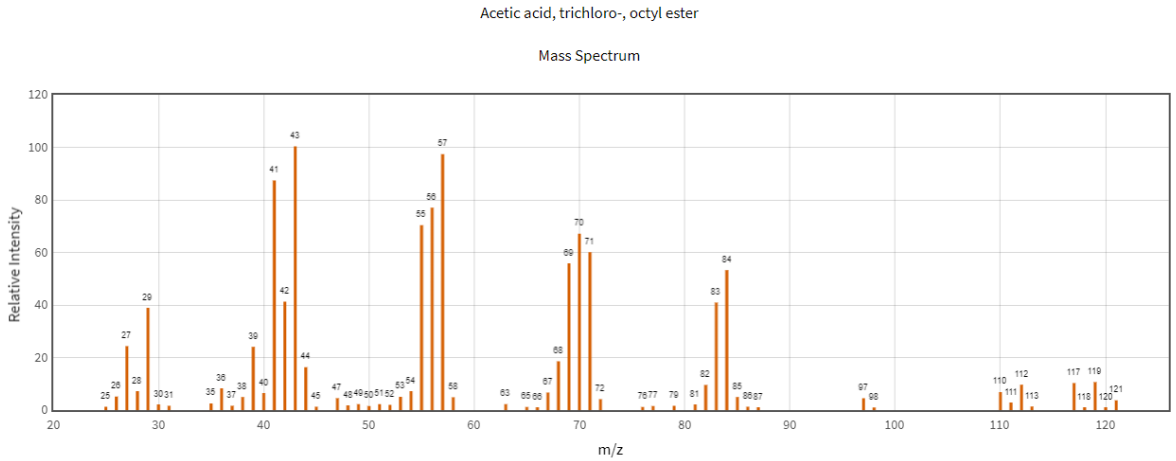
Reference mass spectrum for methyl trichloroacetate from NIST.[15]



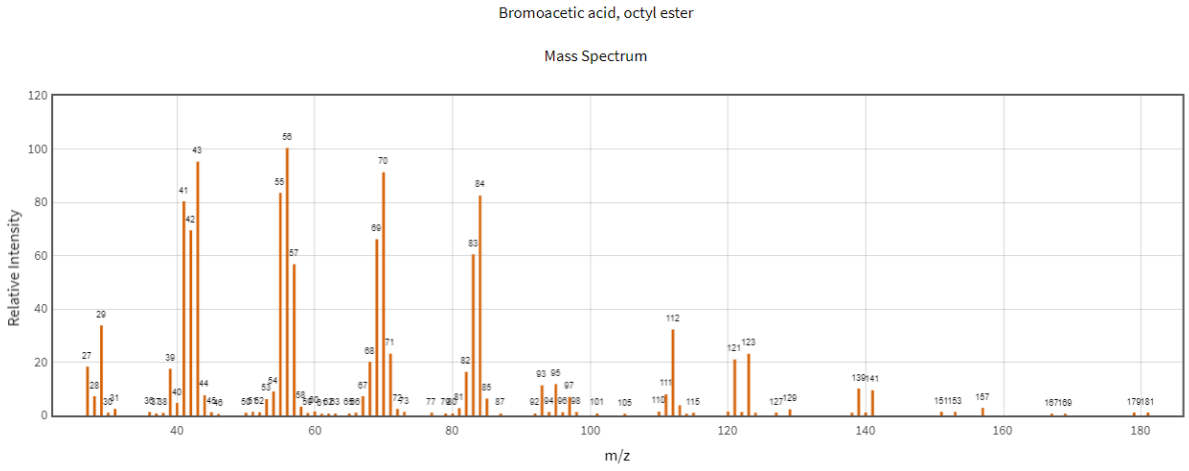
Reference mass spectrum for octyl chloroacetate from NIST.[16]



Reference mass spectrum for octyl dichloroacetate.[9]



Reference mass spectrum for octyl trichloroacetate from NIST.[17]



Reference mass spectrum for octyl bromoacetate from NIST.[18]

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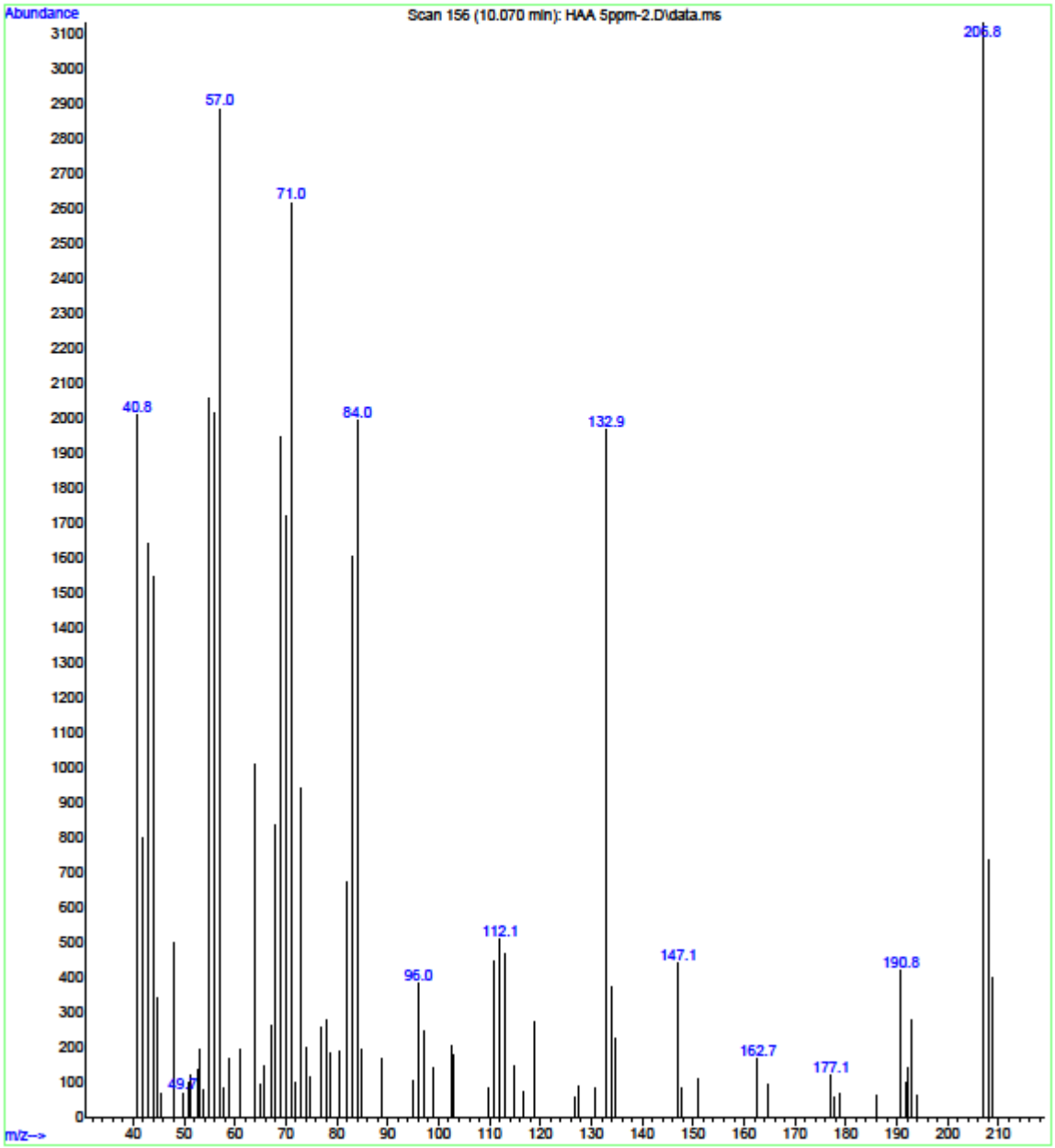

Experimental scan mass spectrum of BCAA.

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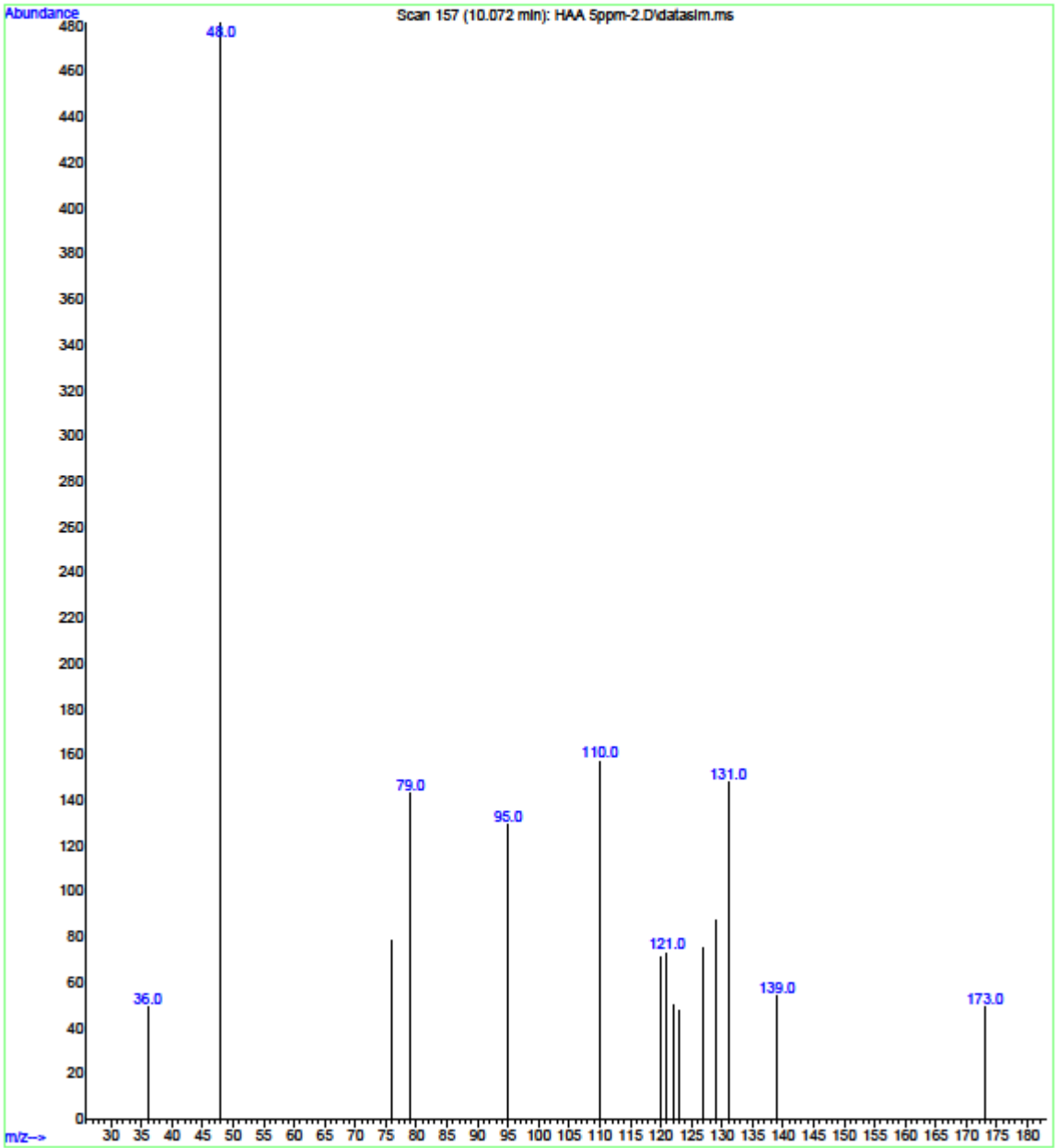

Experimental SIM mass spectrum of BCAA.

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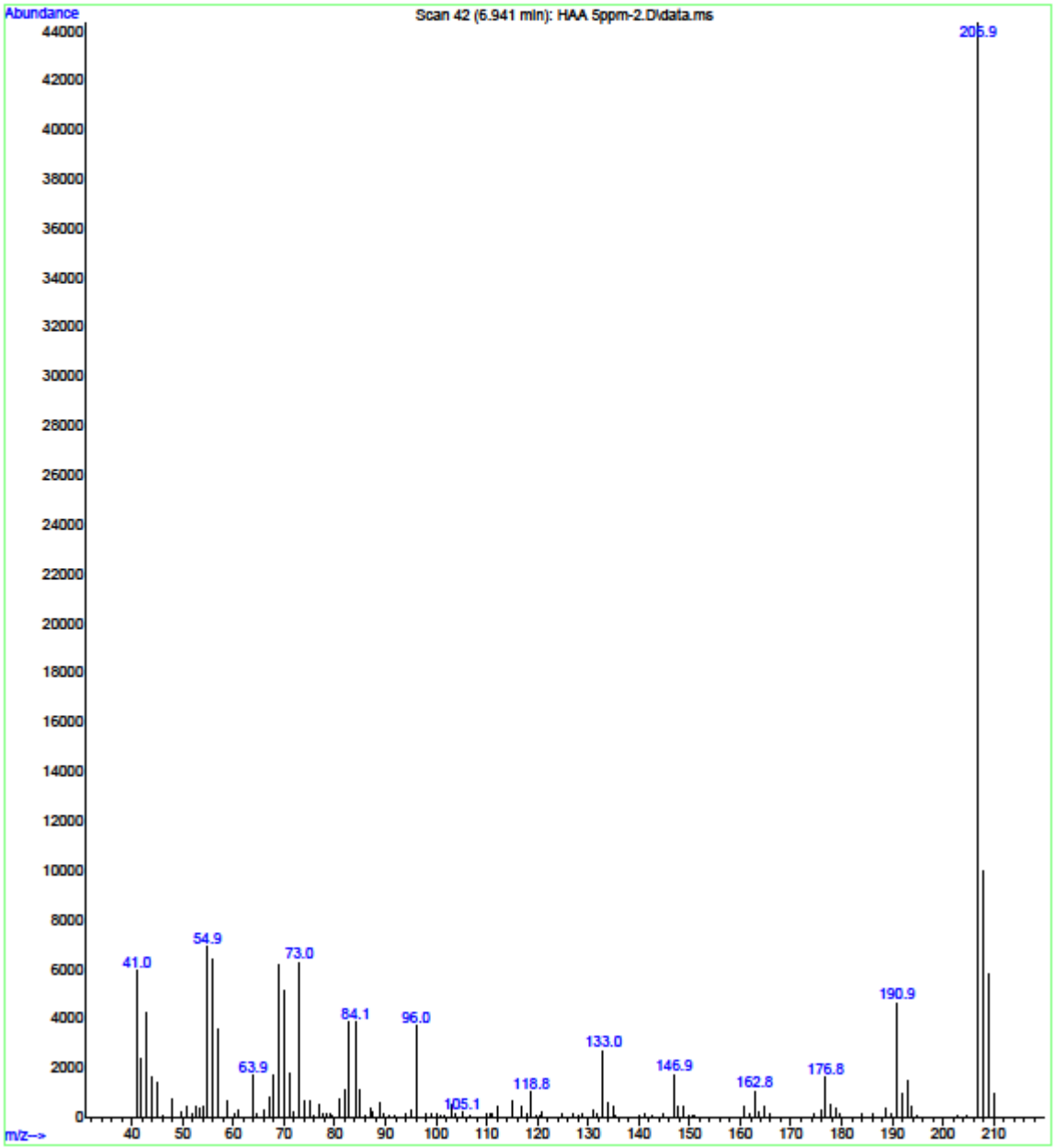

Experimental Scan mass spectrum of MBAA.

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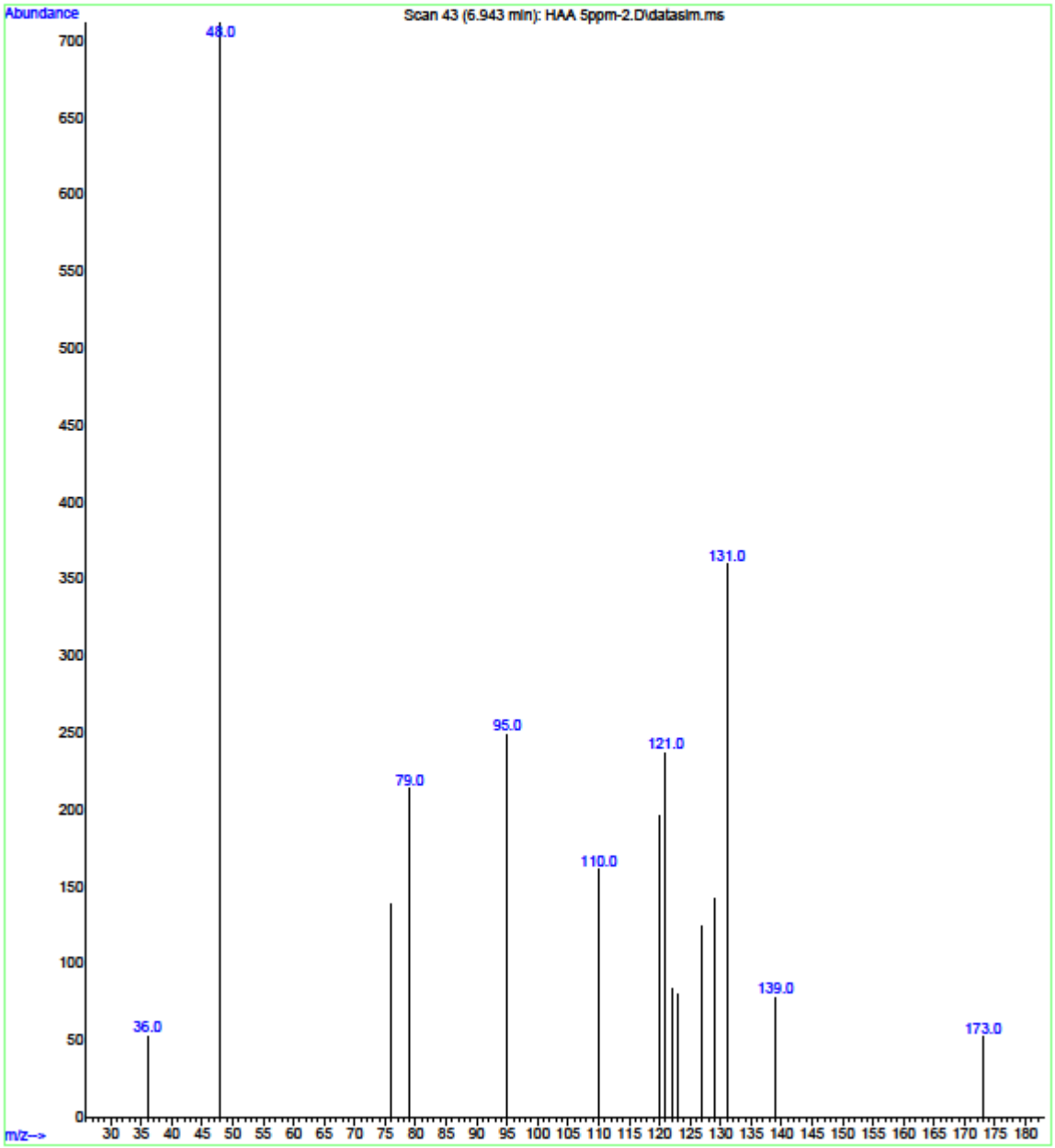

Experimental SIM mass spectrum of MBAA.

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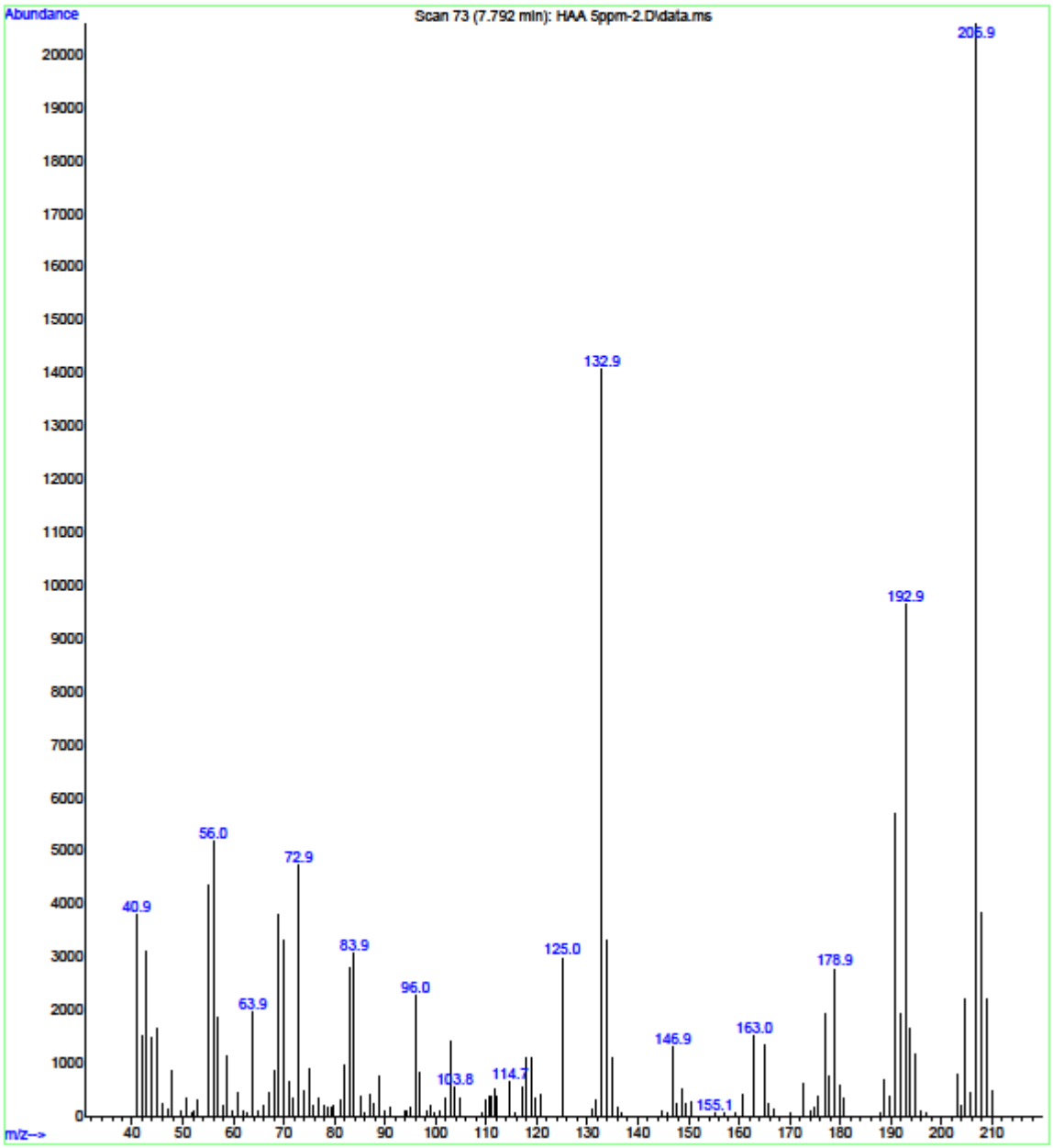

Experimental scan mass spectrum of DCAA.

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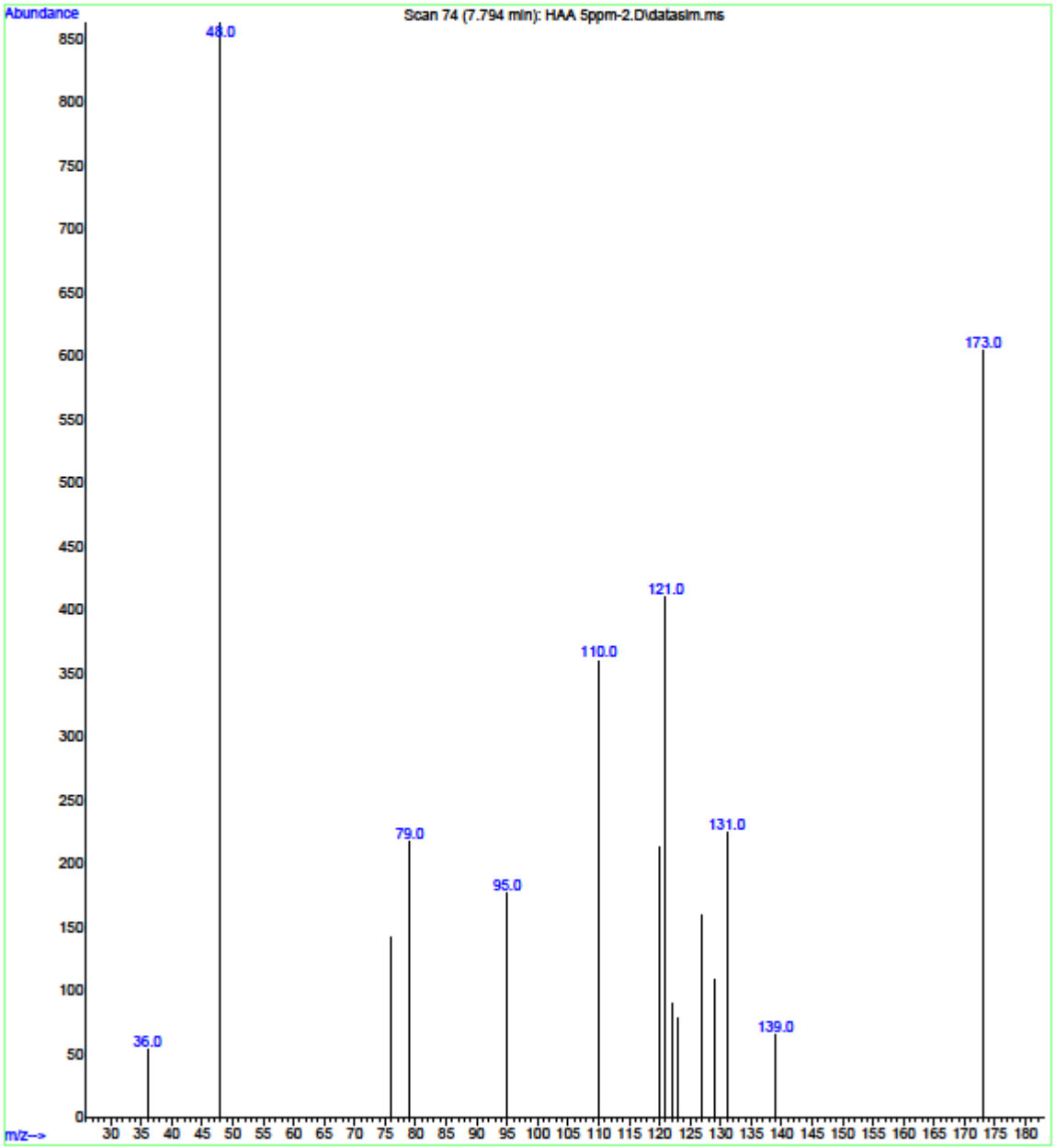

Experimental SIM mass spectrum of DCAA.

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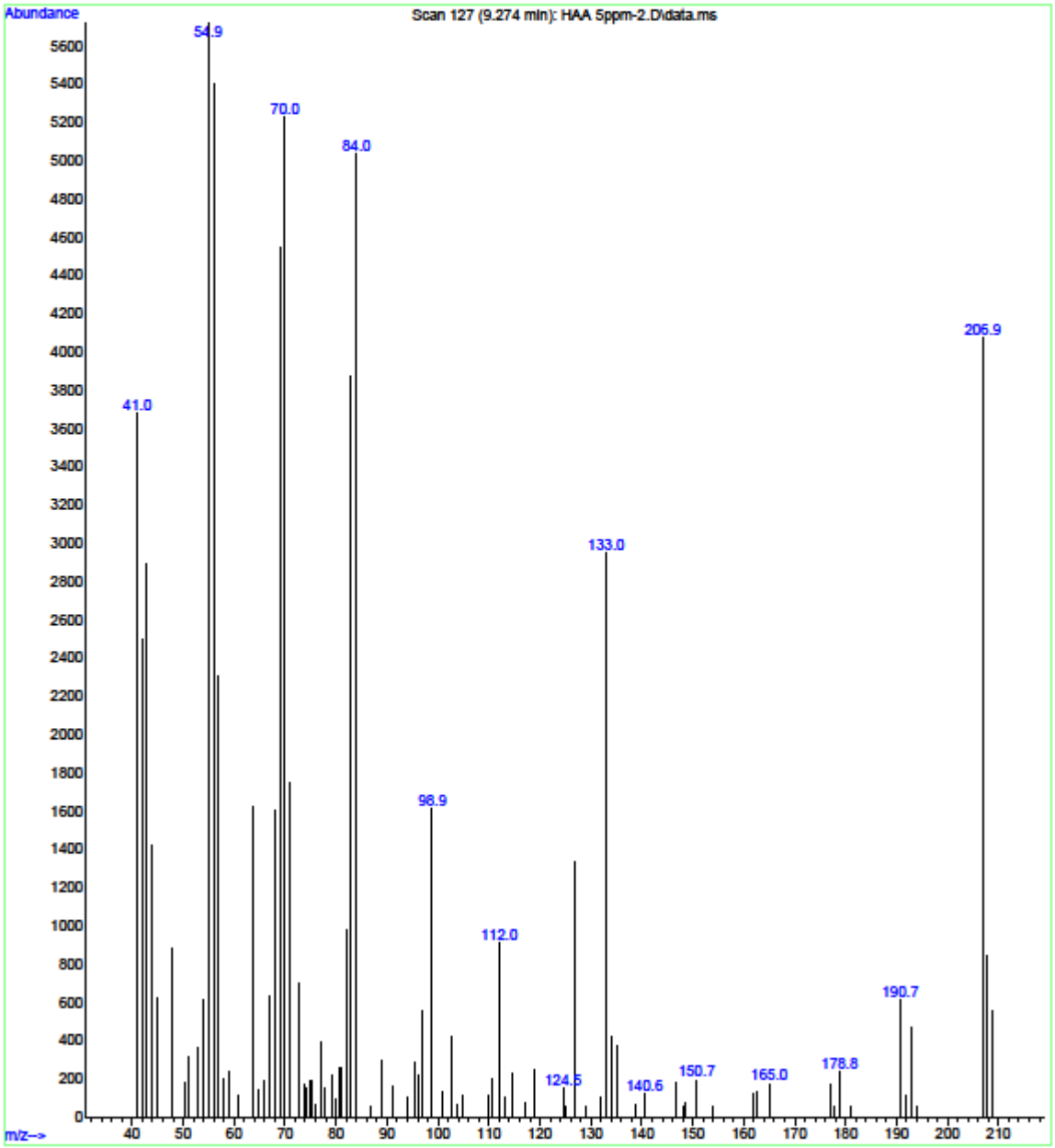

Experimental Scan mass spectrum of TCAA.

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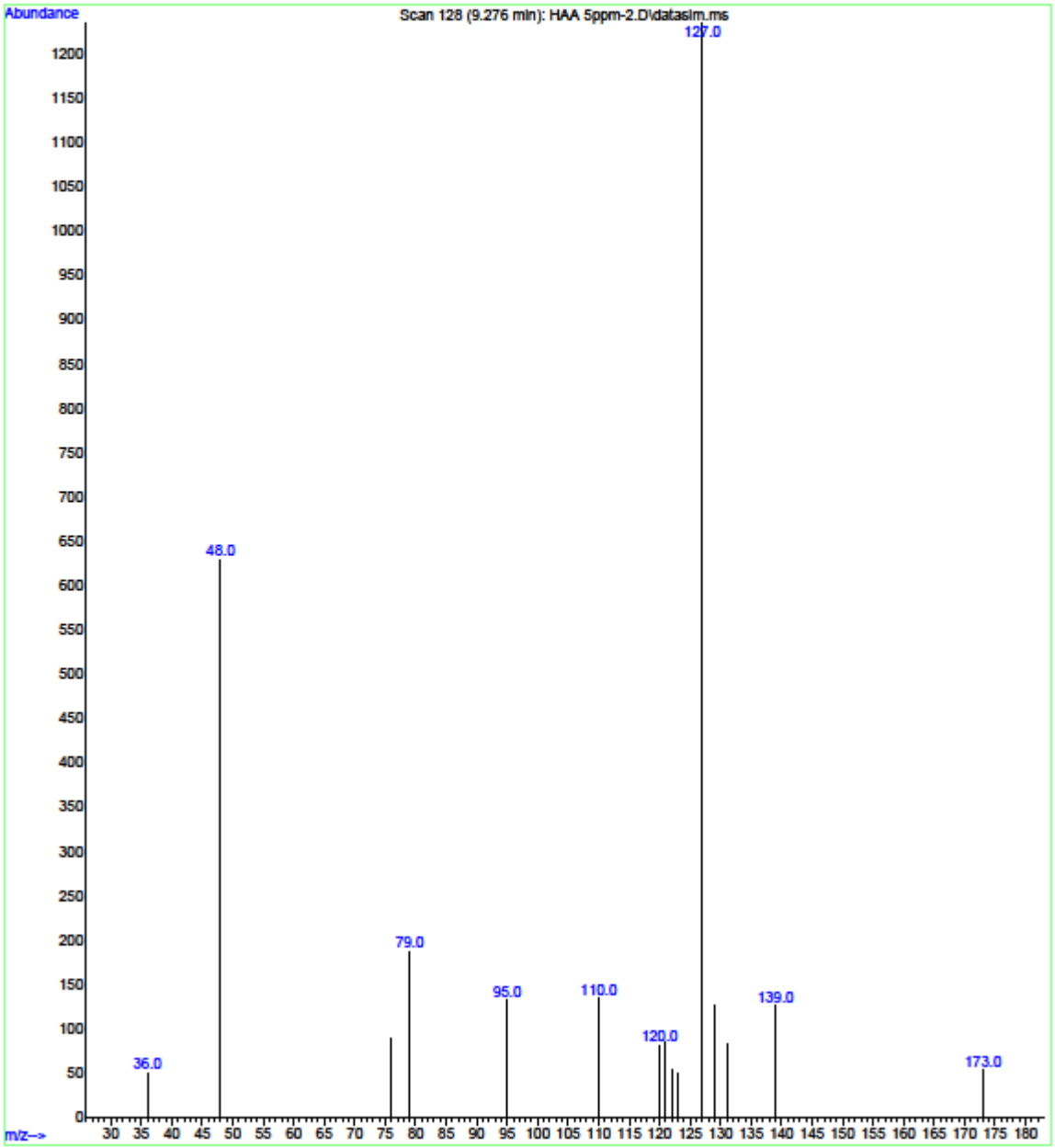

Experimental SIM mass spectrum of TCAA.

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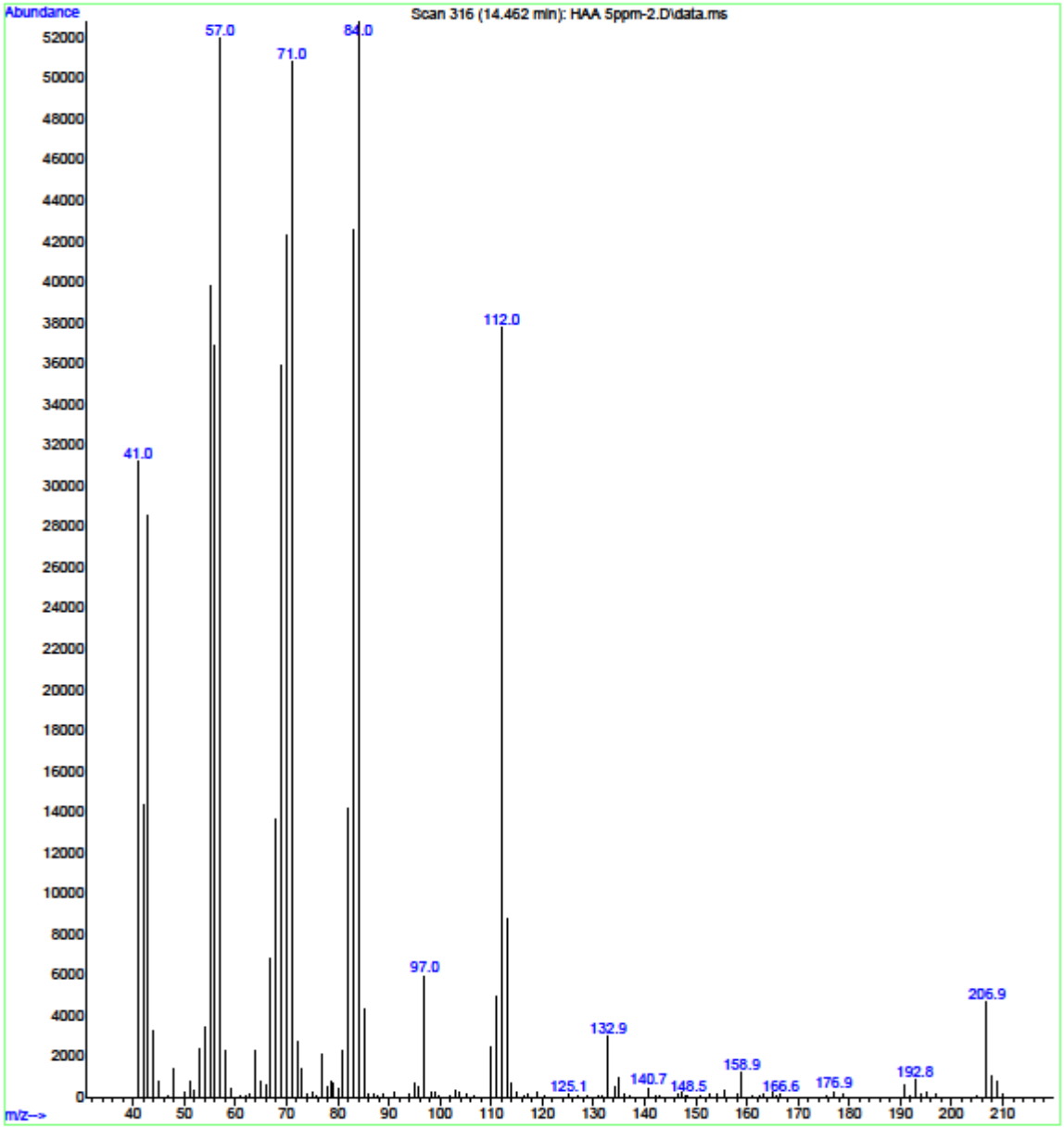

Experimental Scan mass spectrum of DBAA.

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Sample Name:
Misc Info  :
Vial Number: 6
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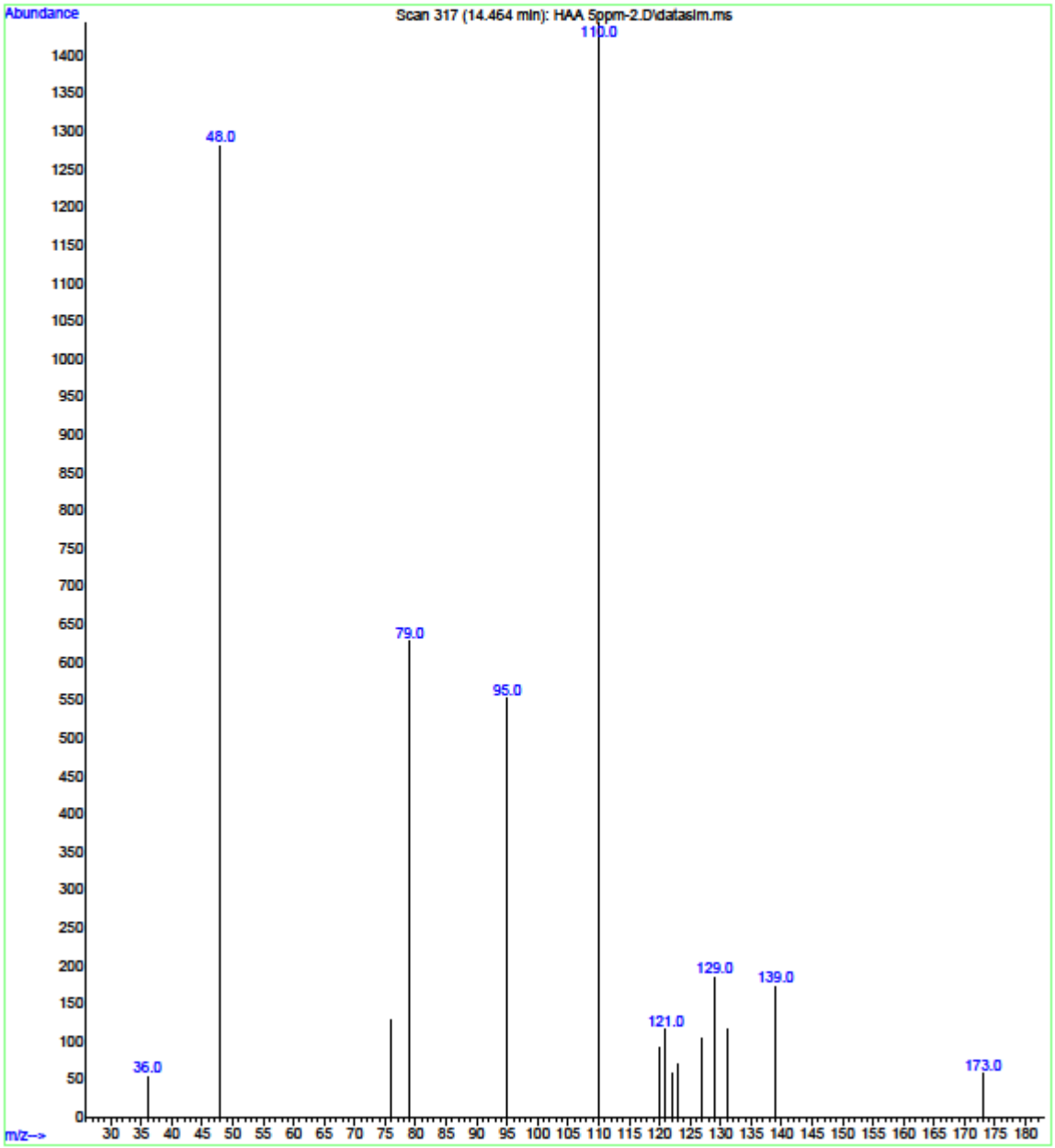

Experimental SIM mass spectrum of DBAA.