GC-QToF Analysis of Taste and Odor Compounds & Disinfection Byproducts in Water

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I. Outline

- Context of the study: Taste and Odor
- Objective of the study
- Sampling campaign
- Sample preparation and analysis
- Data processing for sample profiling
- Conclusion & Perspectives

Objective

Known Precursor + **Disinfectant** → **Known Precursor & Targeted and Untargeted Disinfection Byproducts**

Problem: Limited analytical platforms available that can determine the fate of known contaminant precursors and disinfection byproducts formed from treatment processes.

Objective: To use the high resolution GC-QToF to develop a method that can identify (with confidence) the products of known contaminants after disinfection and determine the mechanism in their formation.

Taste and Odor Compounds

Aesthetics

Taste

Odor

Not regulated, <u>only</u> consumer preference

Taste and Odor Compounds

- T/O compounds give water an earthy and musty taste[1]
- Shown to be recalcitrant to conventional water treatment methods[2]
- 16% of a total 377 utilities in the U.S. reported serious T/O problems[3]
- Low odor threshold (< 10 ng L^{-1} for 2-MIB and Geosmin) [4]

Customers associate odor & bad taste with contaminated water.

[1]Wnorowski et al., 1992; [2]Nerenberg et al., 2000; [3]Suffet, I.H. et al., 1996; [4]Ding, Zhen et al., 2014

Taste and Odor Compounds

Algae blamed for bad odor and taste in city of Houston water supply

Story | Comments

Posted: Wednesday, June 25, 2014 9:14 am

By Y.C. OROZCO

League City officials say they will be increasing city-wide flushing activity in response to temporarily odorous water issues.

A blue-green algae occurring in the Lake Livingston Reservoir and Trinity River has been blamed for a foul odor and metallic taste in the water for residents in cities which obtain their primary water supply from Houston, including League City.

Advertisement

"It's absolutely safe and has been through all of the processes," city spokesperson Kristi Wyatt said.

The complaints began last week, with residents reporting an unpleasant odor and taste in the water.

League City Water Department officials contacted the city's main water source, the city of Houston.

"The city of Houston began an investigation and the in meantime, their customers started complaining (about the water)," said Wyatt.

League City received a letter from the city of Houston stating that the algae did not pose a health or safety threat to the public.

The algae, Houston city officials said, were naturally occurring, was properly treated and regulatory compliant, but that it did cause an 'earthy, musty taste and odor.'

According to a statement posted on the League City website and Facebook, the algae bloom is most likely due to recent rainfall in the Lake Livingston and Trinity watersheds. The odor and taste may occur, it said, in the water system "until the bloom cycles through the raw water supply."

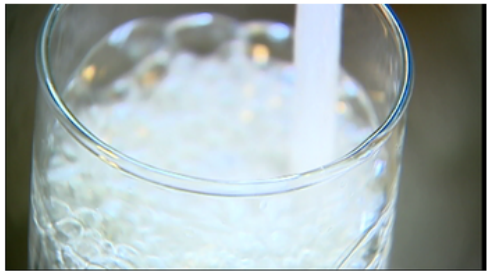
The Houston city officials has estimated that the condition could last up to two more weeks.

Neighbors Complain Water Smells, Tastes Bad

By Gabrielle Komorowski BIO »

Published 4:30 PM EDT Jun 16, 2014

Text Size: A A



VIEW LARGE »

ANDERSON COUNTY, S.C. — Many people living in Anderson County have contacted WYFF News 4 over the past few days and told us their water smells and tastes bad.

WYFF News 4 looked into this on Monday.

No one from the city or from Anderson Regional Joint Water System wanted to do an on-camera interview about the water. WYFF News 4 was directed to a statement posted on the city of

SNOHOMISH

ABOUT THAT FUNKY ODOR AND TASTE OF THE TAP WATER

July 02, 2014

Water photo by de:Benutzer:Alex Anlicker/Wiki Commons

(SNOHOMISH, WA) -- Late last week the city of Everett notified the Snohomish City staff that there were some "taste and odor issues" in the tap water occurring for some residents of Snohomish due to seasonal changes with the source water in Lake Chaplain.

The water customers that were affected live in the area north of Tenth Street, or the "North Zone," according to a statement by city officials.

Everett officials said that during the week of Monday June 30 a number of water systems - including Everett, Alderwood, and the PUD - had received several calls from consumers about taste and odor in their water.

"The water filtration plant staff observed a die-off taking place in the plankton populations in Lake Chaplain early last week (a normal occurrence). This change appears to have resulted in the release of some taste and odor causing compounds into the source water," said the Everett city statement.

Bottom line: some of the compounds appeared to be reacting with chlorine to cause a bitter or metallic taste.

Others seem to cause a musty or fishy taste and odor. The city says those compounds however do not present a health issue, but customers who have a "sensitive sense of taste and smell may notice the change."

The plant staff was continuing to monitor the conditions, and the city said it expected that the condition would pass this week.

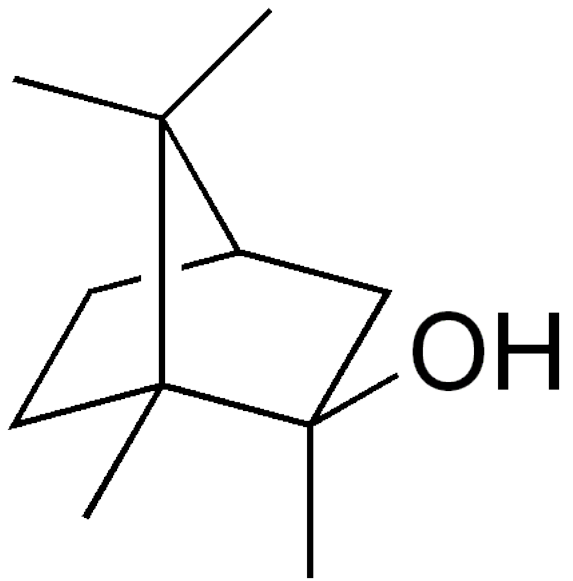
The area of Snohomish affected is supplied with water purchased from the City of Everett and is delivered directly to customers. It is stored in a 2.7 million gallon reservoir located off of Terrace Avenue.

If you have questions or concerns about your water you're asked to call Ann Ray, Water Quality Control Specialist at 360-568 7070 x232 or ray@snohomishwa.gov.

This change is a result of the presence of blue-green algae in Lake Hartwell. Water from Lake Hartwell, the sole source of drinking water for the City, is treated and submitted to over 200 water quality tests each day to ensure that all water quality regulations are met and that the water is safe for all uses. Unfortunately, the growth cycle of the blue-green algae in contact with the lake water produces Geosmin and Methylisoborneol (MIB) compounds. These compounds are completely harmless, but do create an earthy taste and smell which can be unpleasant at elevated levels.

2-MIB

2-methylisoborneol (2-MIB)



1,2,7,7-tetramethylbicyclo[2.2.1]heptan-2-ol

Algal-derived compounds (cyanobacteria)

Released upon organism death

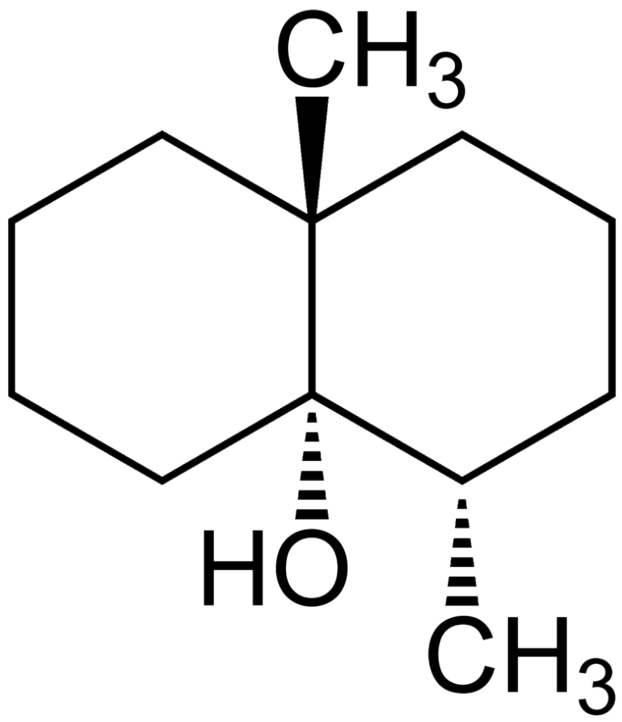
MW= 168.28 g/mol

Boiling Point= 208.7 °C

Henry's Constant=$2.68e^{-6}$ atm•m^3 •mol^{-1}

Geosmin

Geosmin



(4S, 4aS, 8aR)-4,8a-Dimtheyl- 1,2,3,4,5,6,7,8-octahydronaphthalen-4a-ol

Derived from gram positive bacteria

(Actinobacteria)

Released upon microorganism death

MW= 182.30 g/mol

Boiling Point= 270 °C

Henry's Constant=3.15e^{-6} atm• m^{3} •mol^{-1}

Literature Search

ENVIRONMENTAL ANALYSIS

MONITORING FOR 'TASTE AND ODOUR COMPOUNDS' INCLUDING GEOSMIN AND MIB IN POTABLE WATER USING THE AGILENT 7000 TRIPLE QUADRUPOLE GC/MS

Solutions for Your Analytical Business
Markets and Applications Programs

Solution Note

Author
Nick Davies
Dŵr Cymru Welsh Water, Newport, UK

Abstract

A target based screening method for a variety of 'taste and odour' compounds has been developed on an Agilent 7000 Triple Quadrupole GC/MS. There are 20 target compounds in this analytical suite, which includes Geosmin, 2-Methyl Isoborneol, Phenols, Anisoles, Pyrazines as well as 2-EMD and 2-EDD. This method is capable of achieving detection limits of 1 ng/L for all compounds and the range of application is up to 50 ng/L.

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Analytica Chimica Acta 548 (2005) 79–85

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Simultaneous determination of 22 volatile organic compounds, methyl-*tert*-butyl ether, 1,4-dioxane, 2-methylisoborneol and geosmin in water by headspace solid phase microextraction-gas chromatography–mass spectrometry

Sadao Nakamura *, Shigeki Daishima

Yokogawa Analytical Systems Inc., 9-1 Takakura-cho, Hachioji-shi, Tokyo 192-0033, Japan

Received 10 March 2005; received in revised form 27 May 2005; accepted 31 May 2005
Available online 14 July 2005

1 ng/L Detection Limit

Desalination 335 (2014) 47–54

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Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Performance of an integrated process combining ozonation with ceramic membrane ultra-filtration for advanced treatment of drinking water

Xiaojiang Fan [a], Yi Tao [a], Lingyun Wang [a], Xihui Zhang [a,*], Ying Lei [a], Zhuo Wang [a], Hiroshi Noguchi [b]

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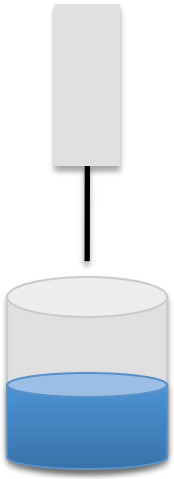
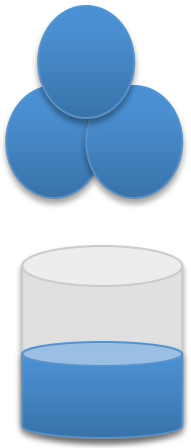
[b] *Meidensha Corporation, Meiko Building, 5-5-5 Osaki, Shinagawa-ku, Tokyo 141-8616, Japan*

Sampling Campaign & Treatment





Collection

Water was collected from Colorado River through the Central Arizona Project (CAP)

Sample spike

Samples were diluted to 2 mg L^{-1} TOC and spiked with 500 ng L^{-1} 2-MIB and Geosmin.

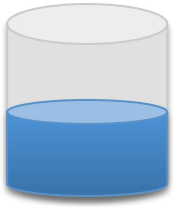
Ozonation

Spiked samples were ozonated at 3 doses & 3 time durations and then quenched with 50 mg L^{-1} sodium sulfite.

3 Doses	3 Time Durations
1 ppm	0.5 min
2 ppm	1 min
3 ppm	2 min
Control (No ozone)	

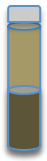
Work Flow

1



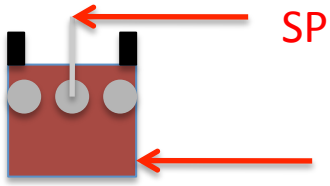
Water Sample
(No extraction step required)

2



10 mL of each blank, standard and sample was transferred to a 20-mL amber glass vial

3

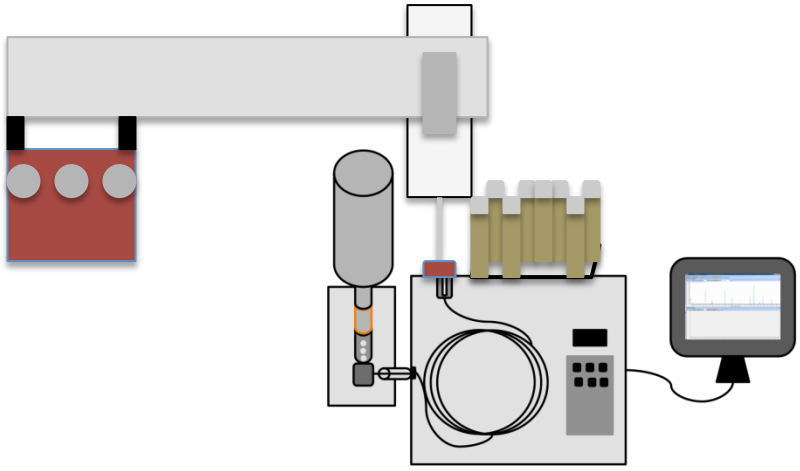


Fiber was inserted into sample for extraction.

4

Fiber was inserted into injector for desorption.

5



Samples were analyzed by GC-QToF

Sample Analysis

Advantages of GC-QToF

- Better Mass Accuracy enables identification of gas phase unknowns
- Higher Resolution compared to conventional techniques (ie. GC-ECD, GC-MS, GC-QQQ) that have unit resolution
- Ability to use QToF techniques to obtain fragmentation information (both electron impact and MS/MS) to identify unknowns
- Fast scanning of full spectrum
- Compatible with headspace and solid phase microextraction (SPME) units

Sample Analysis

Agilent 7890A GC/7200 QToF MS

MS Conditions

Ionization Mode- EI (70eV)
Type of Data Acquisition- MS Only
Source Temp- 230℃
Quad Temp- 150℃
Transfer Line Temp- 250℃
Emission Current- 35A°
Acquisition Mode- 2 GHz
Acquisition Range- 40-200 amu
Acquisition Speed- 5 spectra/ second

Figure. Shown above is the Agilent 7200 GC/Q-TOF. It is equipped with the headspace-SPME autosampler.

Sample Analysis

Agilent 7890A GC/7200 QToF MS

GC Conditions

Column

DB-5 MS UI (30m x 250µm x 0.25µm)

Injector Mode

Splitless

Inlet Temperature

250 °C

Carrier Gas/ Flow

Helium 1.0 mL/min

Oven Program

50℃ Hold 1 min; 10℃/min to 200℃, Hold 1 min; 20℃/min to 220℃, Hold 1 min

Purge Time

5 min

SPME Conditions

Fiber Type

85 µm Carboxen/ Polydimethylsiloxane

Cycle

SPME 04-V2

Incubation Temperature

65 ℃

Agitation Speed

250 rpm

Extraction Time

1800 sec

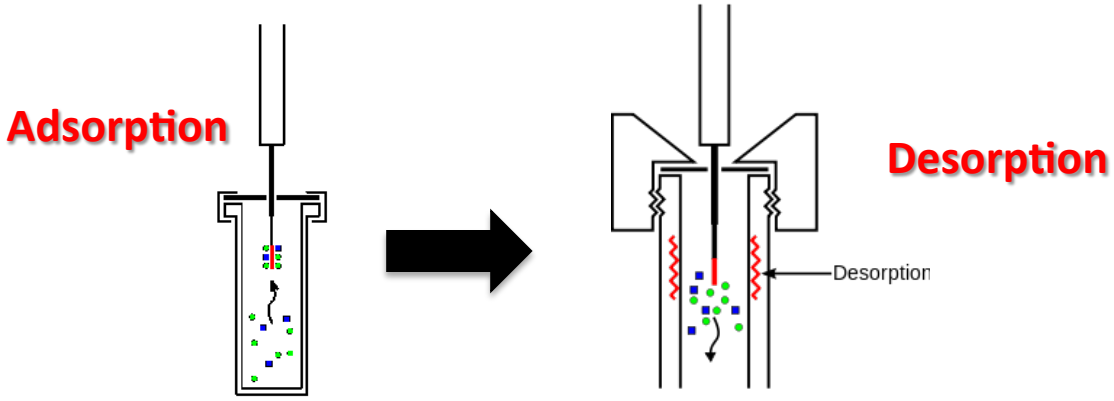
Desorption Time

300 sec

SPME

Solid Phase Microextraction (SPME)

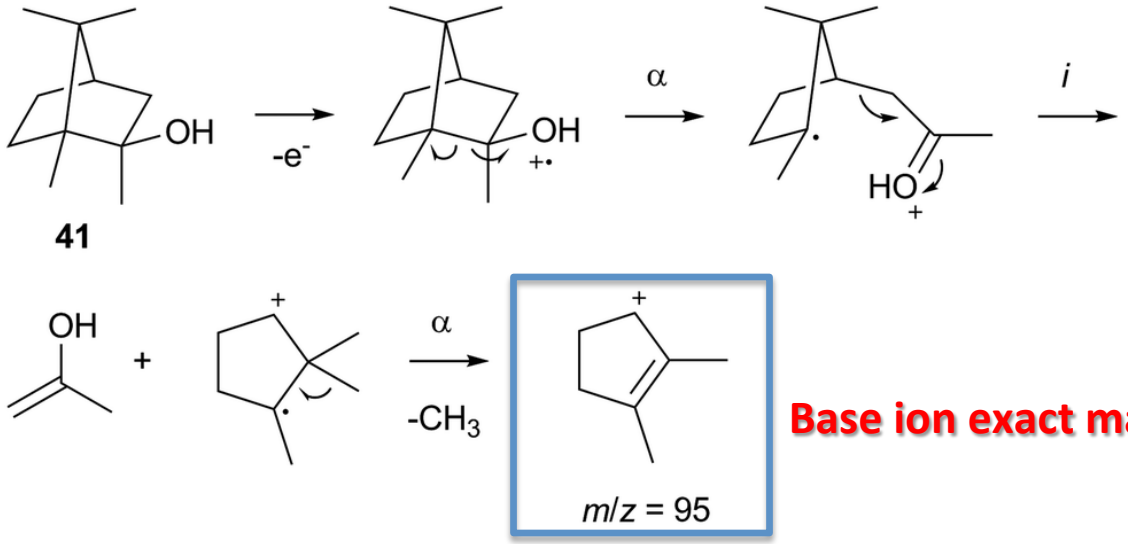
- Supelco 85 m Carboxen/ Polydimethylsiloxane selected
- Suitable for polar gases and low molecular weight (30-225 amu) compounds
- Used for trace organics
- Adsorption of analytes from liquid sample by immersion or headspace and desorption from the fiber by exposing fiber in the heated injection port.



2-MIB and Geosmin are low molecular weight, polar compounds

Positive Electron Impact Fragmentation

2-MIB



Base ion exact mass 95.0855

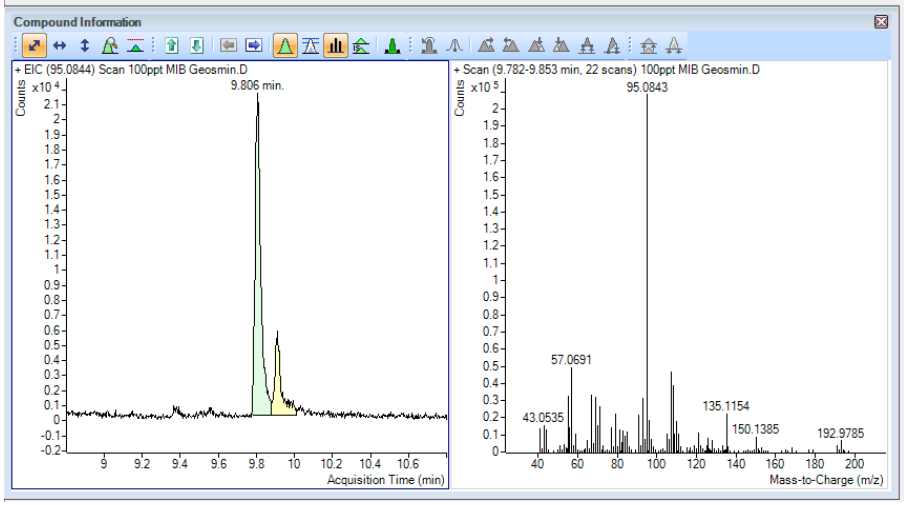
Schematic. Fragmentation mechanism of 2-MIB

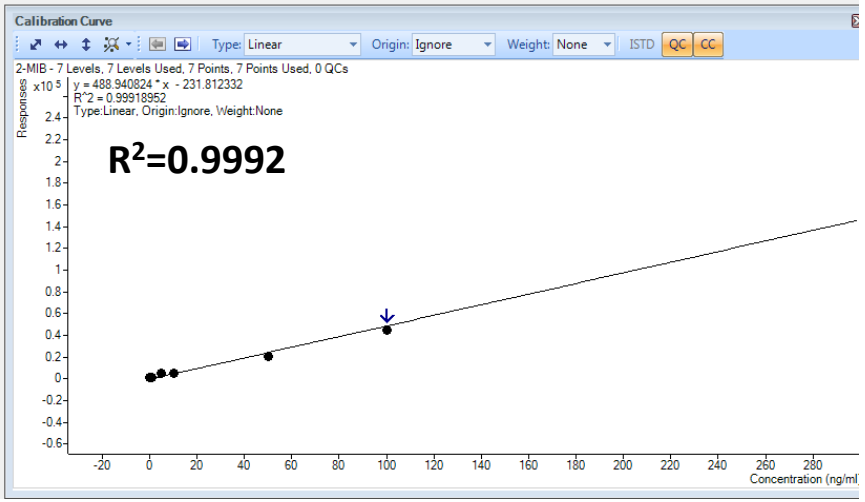
J.S. Dickschat et al., 2014

Chromatography and MS spectra

2-Methylisoborneol

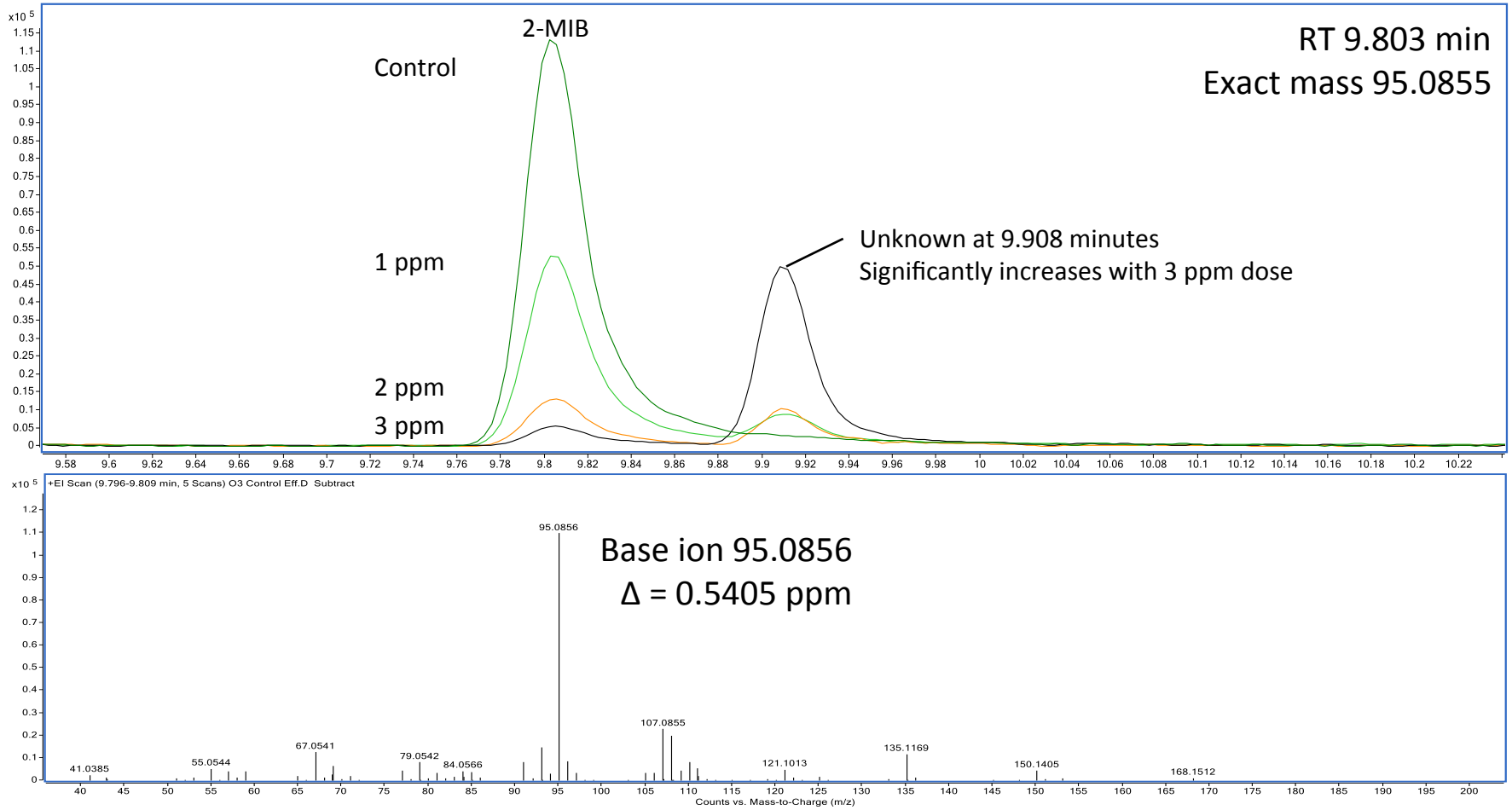
Sample						2-MIB Me...	2-MIB Results				
		Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.
		0_1ppt MIB Geosmin	0_1ppt MIB Geosmin.D	Cal	1	4/12/2014 10:25 AM	0.1000	9.805	1199		2.9271	2.9271
		1ppt MIB Geosmin	1ppt MIB Geosmin.D	Cal	2	4/12/2014 11:02 AM	1.0000	9.816	1230		2.9895	2.9895
		5ppt MIB Geosmin	5ppt MIB Geosmin.D	Cal	3	4/12/2014 11:39 AM	5.0000	9.800	5435		11.5910	11.5910
		10ppt MIB Geosmin	10ppt MIB Geosmin.D	Cal	4	4/12/2014 12:16 PM	10.0000	9.800	4957		10.6133	10.6133
		50ppt MIB Geosmin	50ppt MIB Geosmin.D	Cal	5	4/12/2014 12:53 PM	50.0000	9.805	211...		43.7518	43.7518
		100ppt MIB Geosmin	100ppt MIB Geosmin.D	Cal	6	4/12/2014 1:30 PM	100.0000	9.806	448...		92.1065	92.1065
		500ppt MIB Geosmin	500ppt MIB Geosmin.D	Cal	7	4/12/2014 2:07 PM	500.0000	9.803	245...		502.1208	502.1208





Overlay of ion chromatograms

SPME-headspace/GC-QTOF analysis of ozone-treated effluent samples

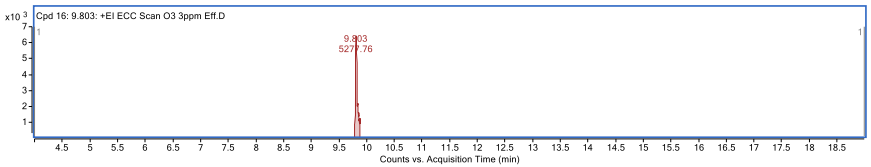


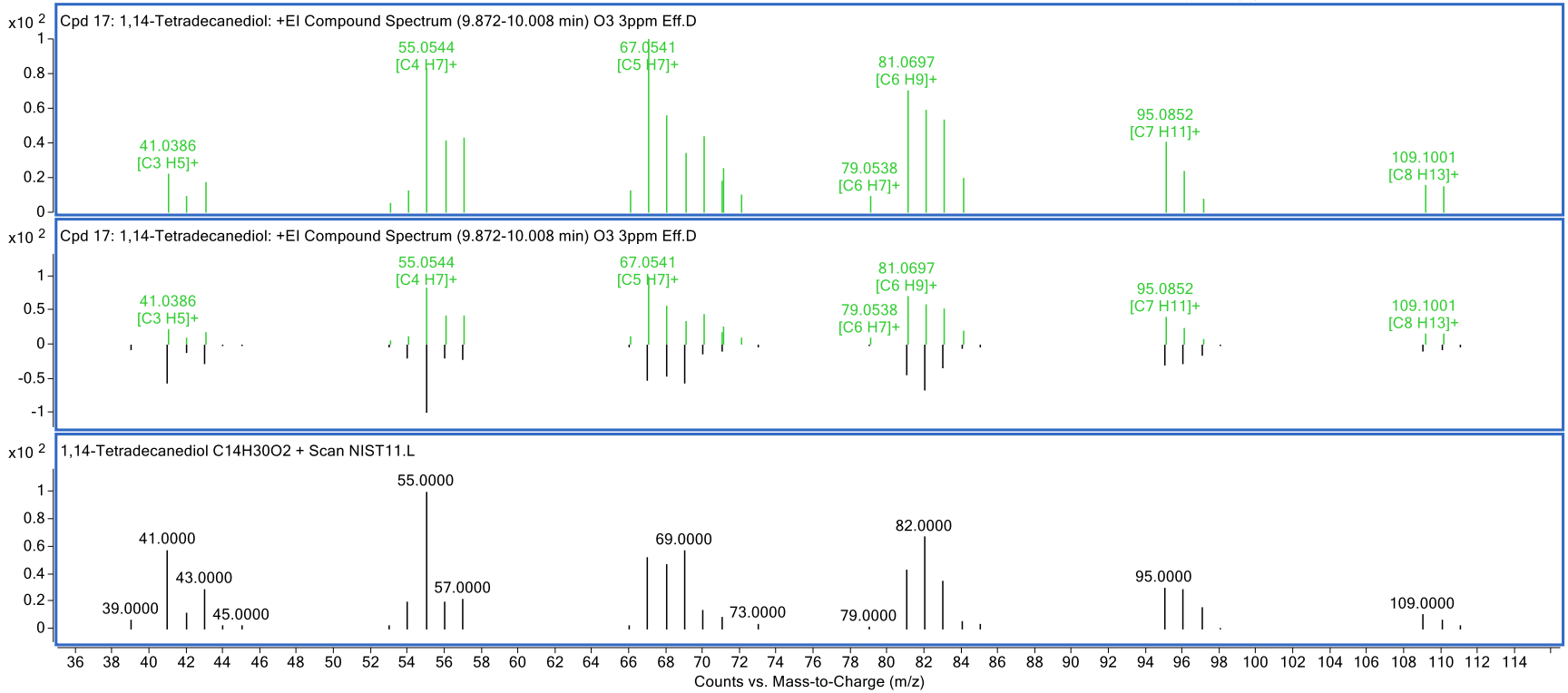
Putative ID of unknown at 9.908 minutes

MassHunter deconvolution, NIST11 Library search suggests:

a. 1,14-tetradecanediol, Match score > 92

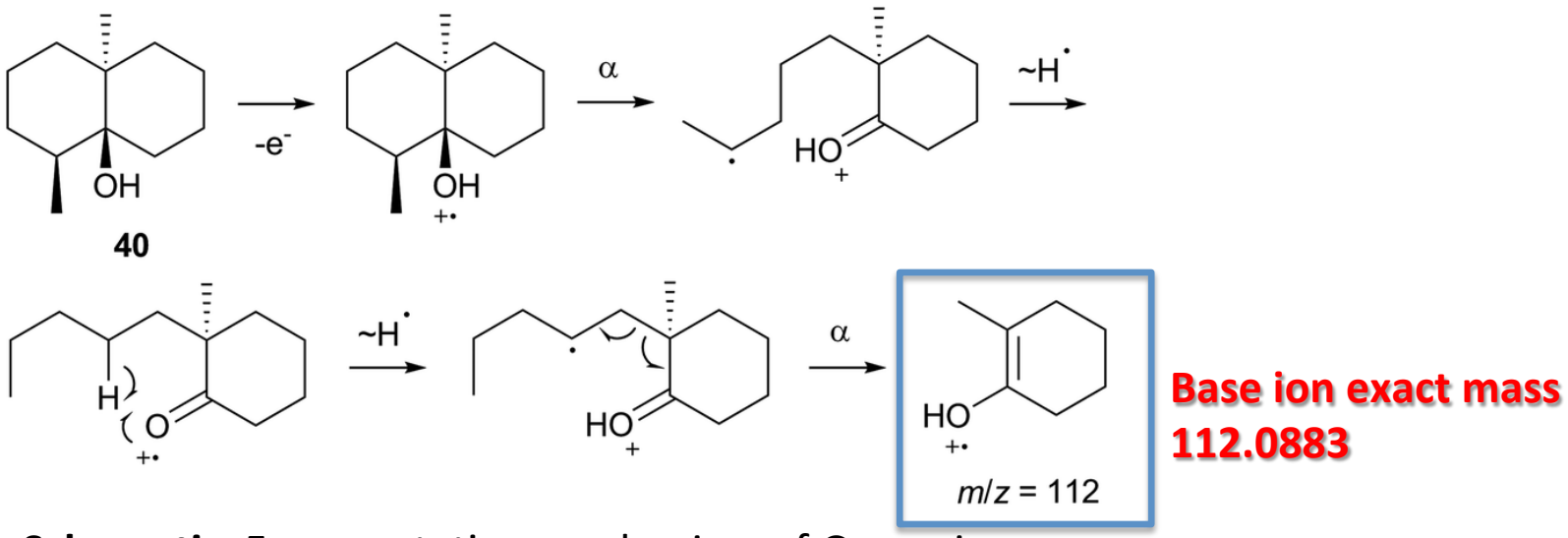
b. 1,10-decanediol, Match score > 91





Positive Electron Impact Fragmentation

Geosmin



Base ion exact mass 112.0883

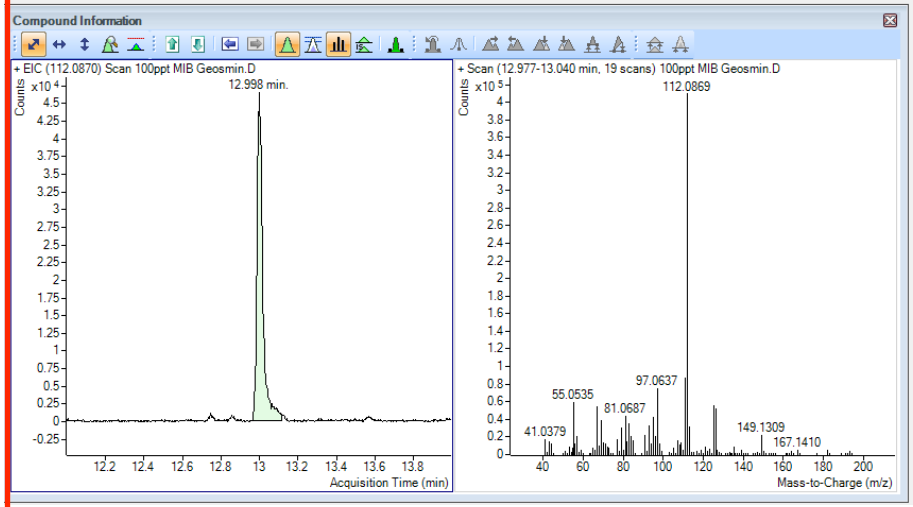
Schematic. Fragmentation mechanism of Geosmin

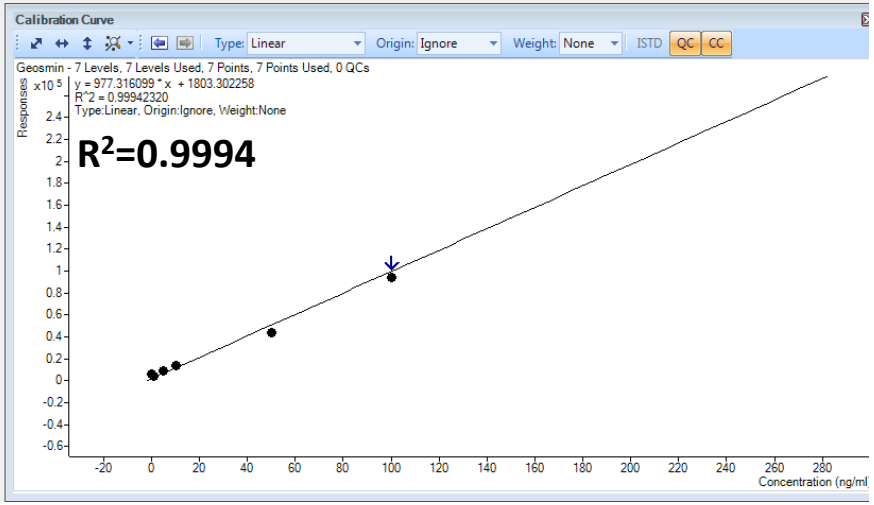
J.S. Dickschat et al., 2014

Chromatography and MS spectra

Geosmin

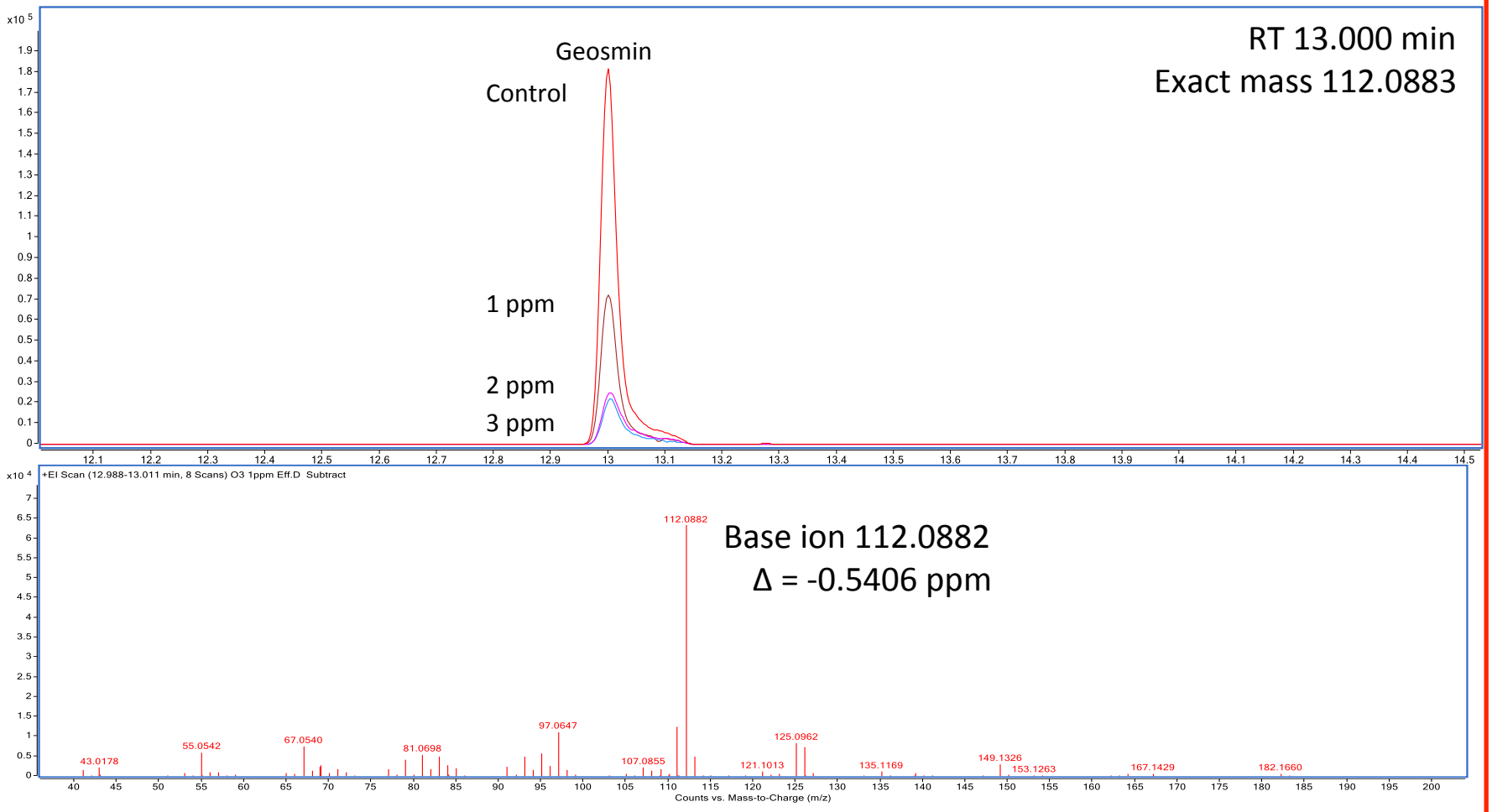
Sample						Geosmin...	Geosmin Results				
		Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.
		0_1ppt MIB Geosmin	0_1ppt MIB Geosmin.D	Cal	1	4/12/2014 10:25 AM	0.1000	13.0...	6484		4.7895	4.7895
		1ppt MIB Geosmin	1ppt MIB Geosmin.D	Cal	2	4/12/2014 11:02 AM	1.0000	13.0...	3991		2.2384	2.2384
		5ppt MIB Geosmin	5ppt MIB Geosmin.D	Cal	3	4/12/2014 11:39 AM	5.0000	13.0...	9335		7.7070	7.7070
		10ppt MIB Geosmin	10ppt MIB Geosmin.D	Cal	4	4/12/2014 12:16 PM	10.0000	13.0...	134...		11.9608	11.9608
		50ppt MIB Geosmin	50ppt MIB Geosmin.D	Cal	5	4/12/2014 12:53 PM	50.0000	12.9...	435...		42.7586	42.7586
		100ppt MIB Geosmin	100ppt MIB Geosmin.D	Cal	6	4/12/2014 1:30 PM	100.0000	12.9...	946...		94.9891	94.9891
		500ppt MIB Geosmin	500ppt MIB Geosmin.D	Cal	7	4/12/2014 2:07 PM	500.0000	13.0...	492...		501.6566	501.6566





Geosmin:
Overlay of Extracted Ion Chromatograms

SPME-headspace/GC-QTOF analysis of ozone-treated effluent samples



Proposed Degradation Mechanisms

Degradation mechanism

- The intermediates of Geosmin and 2-MIB that are formed by UV or oxidation degradation are not completely known.
- Alkanes, aldehydes, fatty acids, and hydrocarbons are formed.
- A mechanism for Geosmin was proposed.
- No published mechanism for 2-MIB.
- **No ozonation studies. Similar Mechanism??**

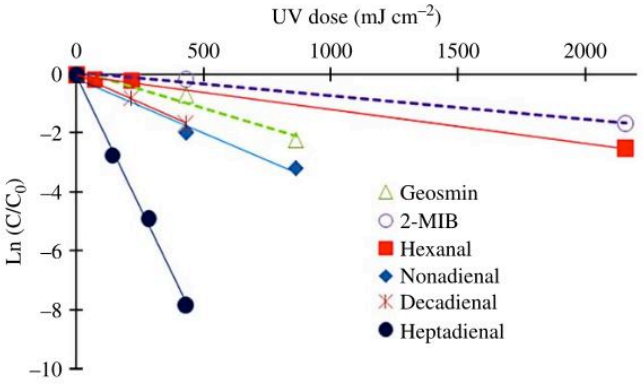
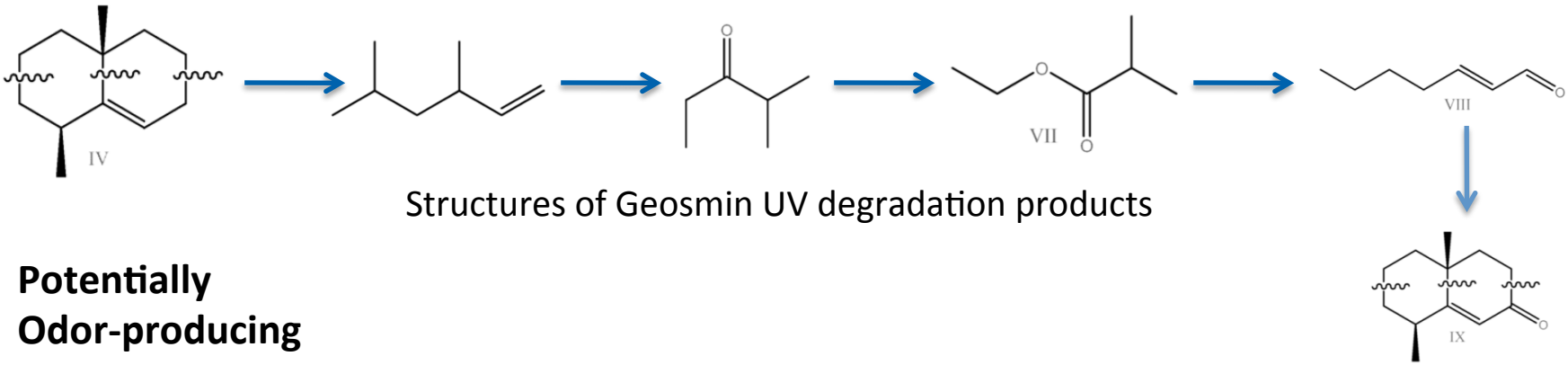


Figure 2 | Log removal of odorants with UV dose (6 mg l^{-1} H_2O_2).



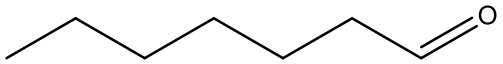
Structures of Geosmin UV degradation products

Potentially Odor-producing

Emomotimi E. Bamuza-Pemu et al., 2011 Chang Hyun Jo et al., 2009

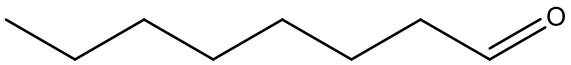
Proposed Geosmin Degradation Products

Heptanal



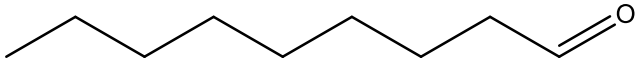
Chemical Formula: $C_7H_{14}O$
Exact Mass: 114.1045

Octanal



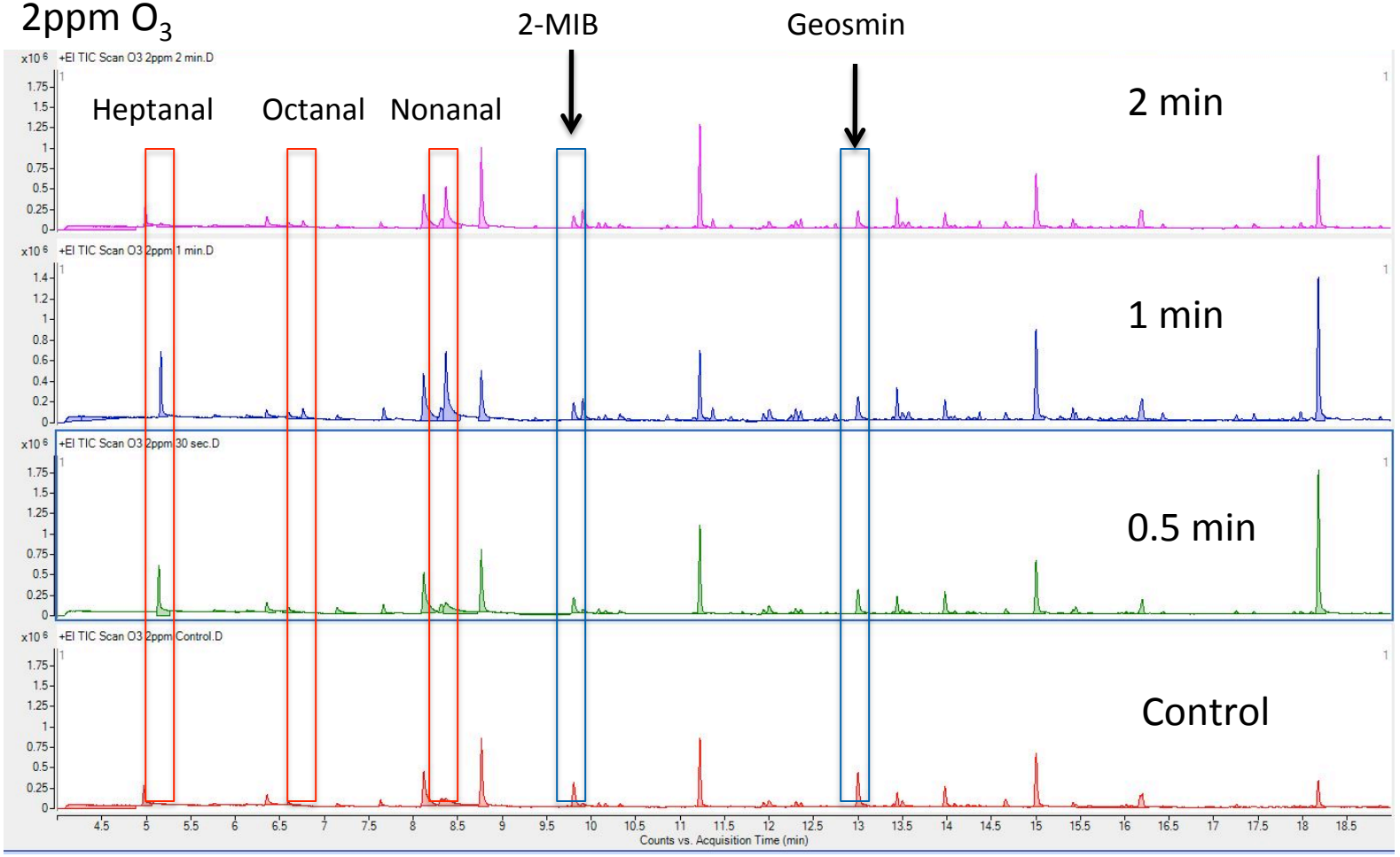
Chemical Formula: $C_8H_{16}O$
Exact Mass: 128.1201

Nonanal

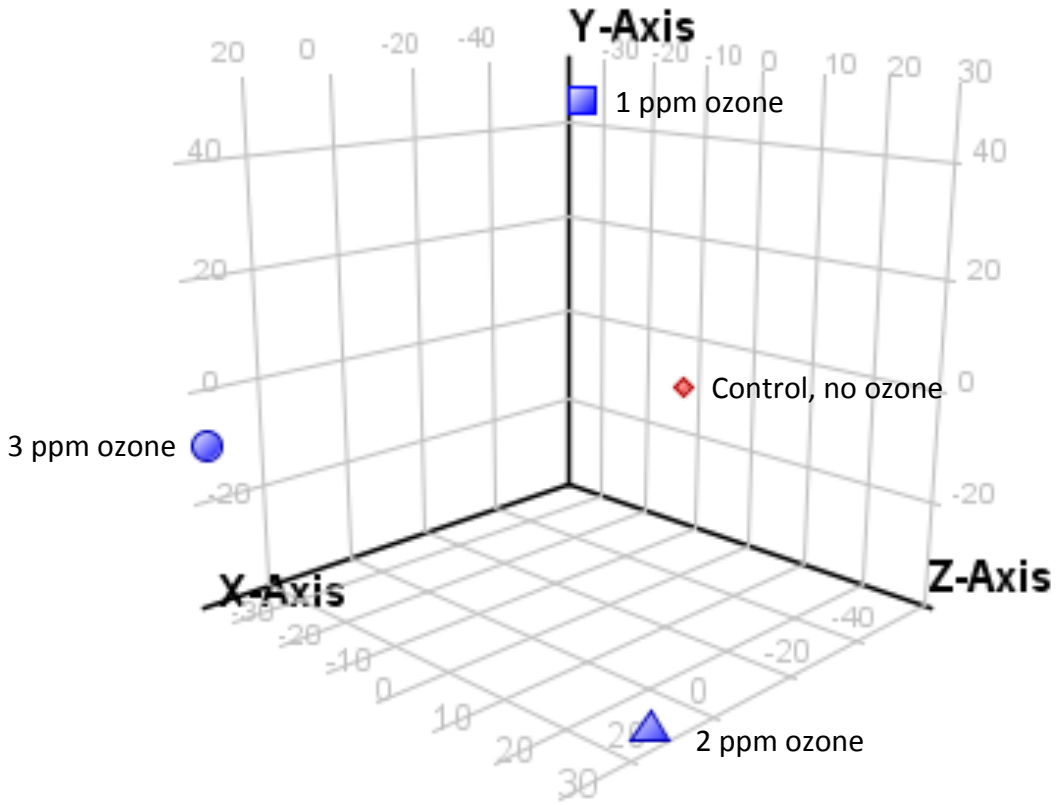


Chemical Formula: $C_9H_{18}O$
Exact Mass: 142.1358

Water samples after increasing time exposure to Ozone



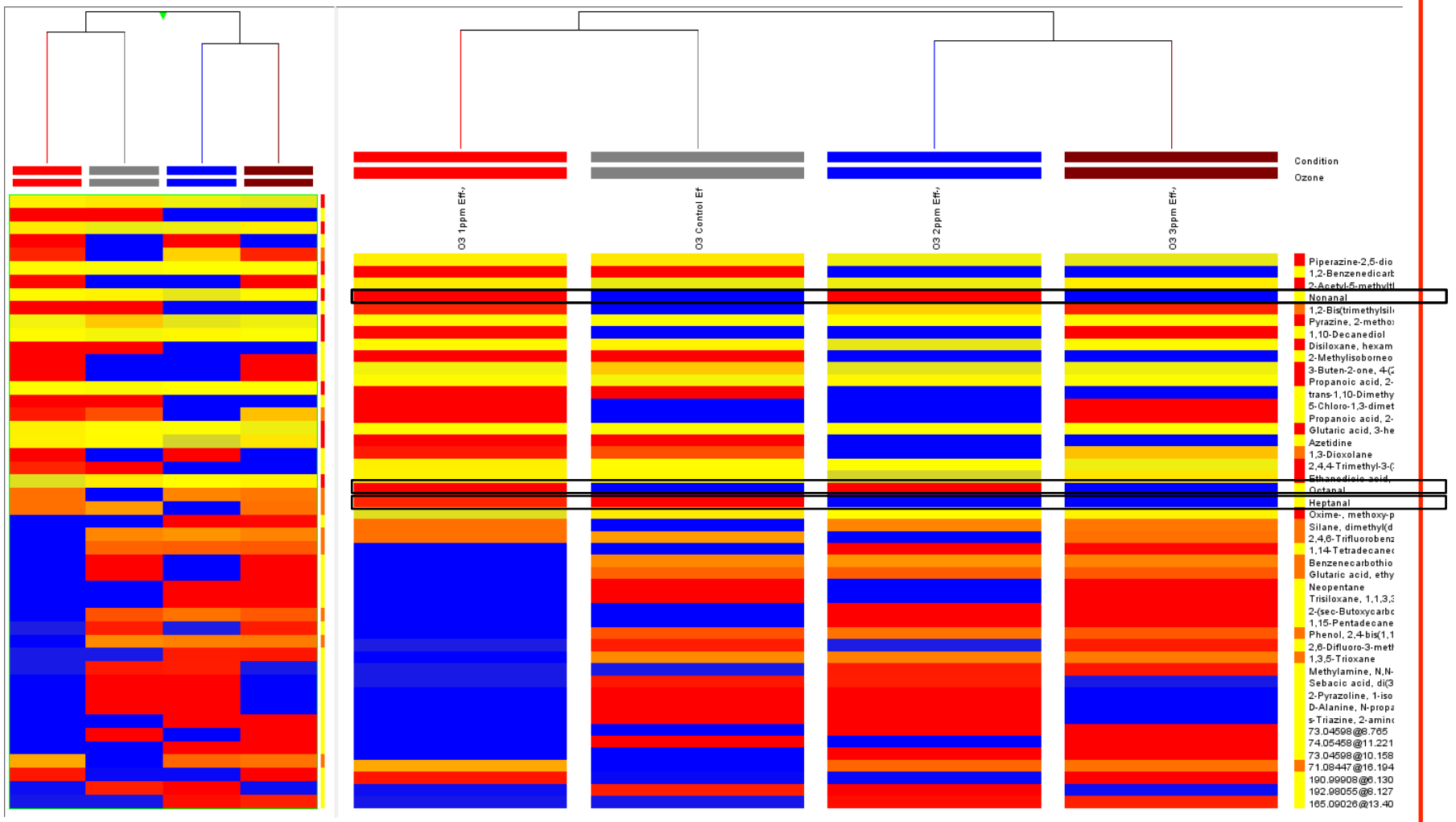
PCA shows each sample as unique
1 ppm closest & 3 ppm most distant from control



X-Axis Component 1 ... Y-Axis Component 2 ... Z-Axis Component 3 ...

Hierarchal Clustering

Heptanal, Nonanal and Octanal show no clear dose-response relationship in this dataset



Conclusion & Perspectives

- Headspace-SPME coupled to GC-QToF was able to detect 2-MIB and Geosmin in real water samples down to the lower ppt level.
- It is possible that new odor-producing compounds are generated with ozonation.
- The accurate mass spectra will allow identification of low level pollutants
- Additional Research
- Characterization of targeted compounds with various polarity SPME fibers
- Further investigation with both CI and EI sources and using MPP to identify the untargeted byproducts

II. Outline of DBPs Study

- Context of the study: DBPs
- Objective of the study
- Sample preparation and analysis
- Data analysis
- Conclusion
- Perspectives

Disinfection Byproducts (DBPs)

Disinfectants such as chlorine react with organic matter to produce new, sometimes more harmful, products.

Most Common Classes of DBPs

Trihalomethanes (THMs)
Haloacetic Acids (HAAs)
Haloacetonitriles (HANs)
Haloacetamides (HAms)
Nitrosamines

Mutagenic to both human and aquatic life

Developmental and reproductive toxins

Some are proven carcinogens

EPA's Disinfectants and Disinfection Byproduct Rule- regulates DBPs with a maximum contamination level

Disinfection Byproducts

Trihalomethanes (THMs)

Chemical	Ion	Boiling Point (°C)	Henry's constant ($atm \bullet m^3 \bullet mol^{-1}$)
Trichloromethane (Chloroform)	82.9448	91	$3.67e^{-3}$
Tribromomethane (Bromoform)	172.8434	167	$5.35e^{-4}$
Bromodichloromethane	82.9451	117	$2.12e^{-3}$
Dibromochloromethane	77.0048	142	$7.83e^{-4}$

- **Highly volatile compounds**
- **Exposure recreationally in pools, food, drinking, water**
- **Causes liver and kidney toxicity**
- **Carcinogenic, adverse reproduction and developmental effects**

THMs are formed during disinfection treatment processes- chlorine or bromine react with organic matter.

The four THMs listed above are presently regulated by the USEPA. However, there are additional THMs that are monitored by laboratories.

THM Sample Analysis

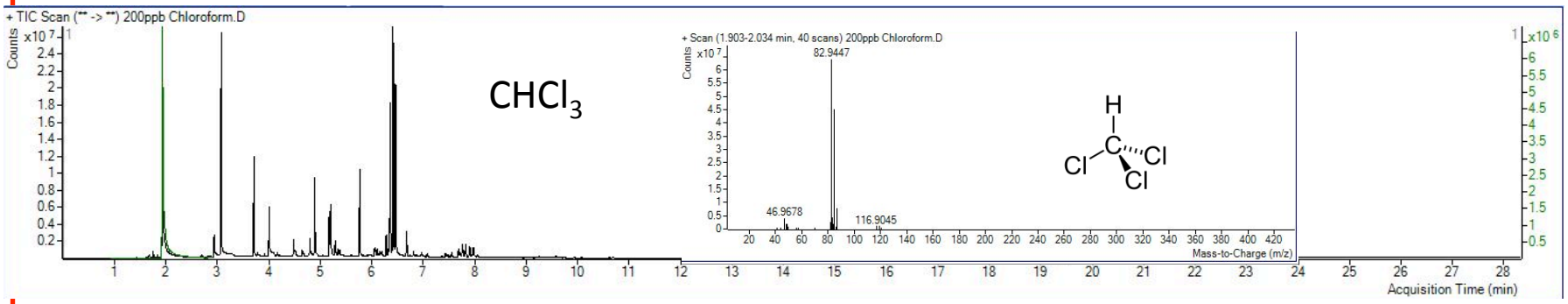
Acquisition Method- SPME/ GC Conditions			
Fiber Type	85 µm Carboxen/ PDMS	**Cycle**	SPME-04-V2
Agitation Speed	250 rpm	**Extraction Temp**	65 °C
Extraction Time	1800 sec	**Desorption Time**	300 sec
Column	DB5-MS UI (30m x 250 um x 0.25 um)		
Carrier Gas/ Flow	1.0 mL/min Helium	**Purge Time**	10 min
Oven Program	Initial	50 °C	Hold 1 min
	10 °C/min	62 °C	Hold 0 min
	5 °C/min	80 °C	Hold 0 min
	35 °C/min	260 °C	Hold 0 min
Injector Temp	280 °C	**Injector mode**	Splitless

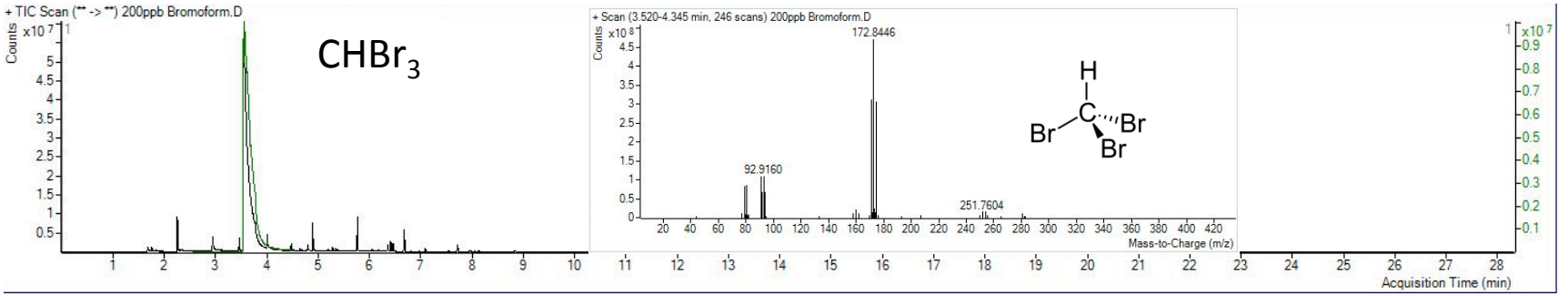
MS Conditions

Ionization Mode
EI (70eV)
Data Acquisition
MS Only
Source Temp
230℃
Quad Temp
150℃
Transfer Line Temp
260℃
Emission Current
35A°
Acquisition Mode
2 GHz
Acquisition Range
40-400 amu
Acquisition Speed
5 spectra/ second

Trihalomethane

Trihalomethanes

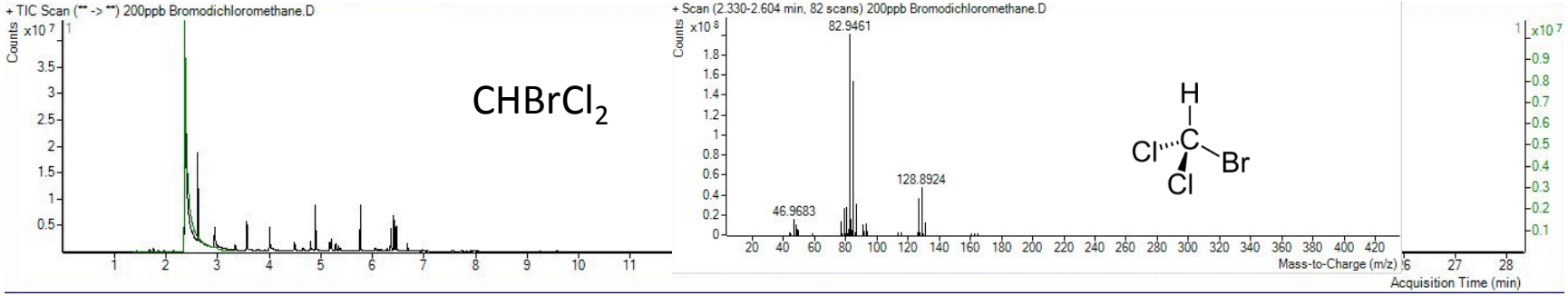


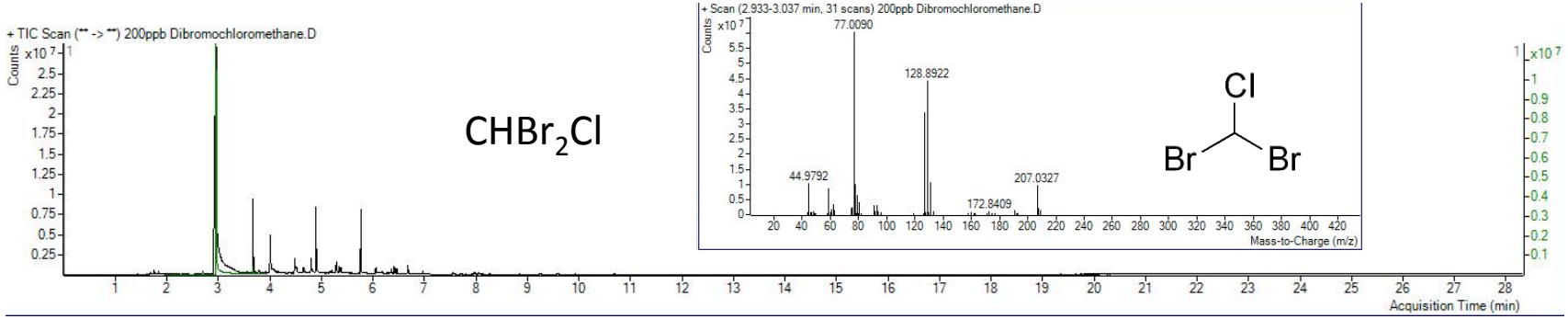


Chemical	RT (min)	Exact Mass of base peak
$CHCl_3$	1.930	82.9448
$CHBr_3$	3.544	172.8434

Trihalomethanes

Trihalomethanes





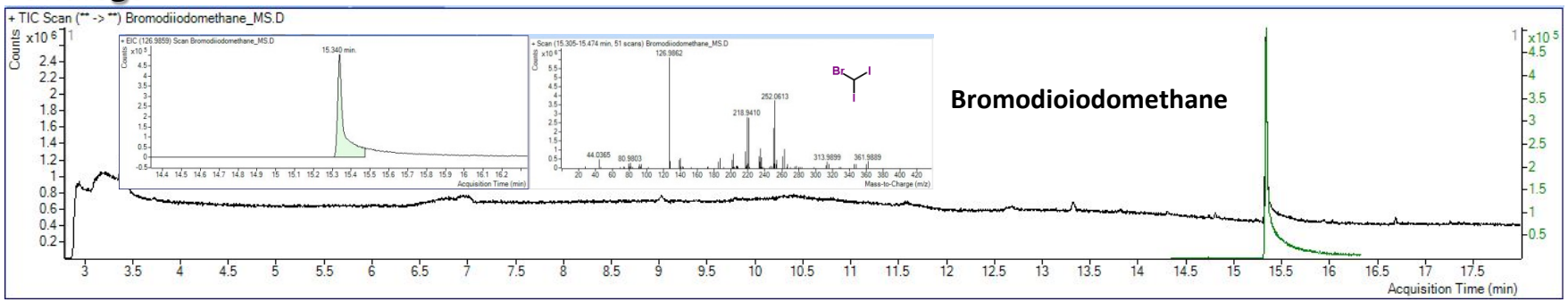
Chemical	RT (min)	Exact Mass of base peak
$CHBrCl_2$	2.363	82.9451
$CHBr_2Cl$	2.953	77.0048

Iodinated Trihalomethanes

Iodinated Trihalomethanes

Chemical	Ion	Boiling Point (°C)	Henry's constant ($atm \bullet m^3 \bullet mol^{-1}$)
Bromodiiodomethane	126.9859	225	$4.73e^{-5}$
Chlorodiiodomethane	174.9785	204	$1.45e^{-4}$
Iodoform	266.9368	252	$3.06e^{-5}$

Unregulated, but more genotoxic and carcinogenic than the brominated and chlorinated analogs

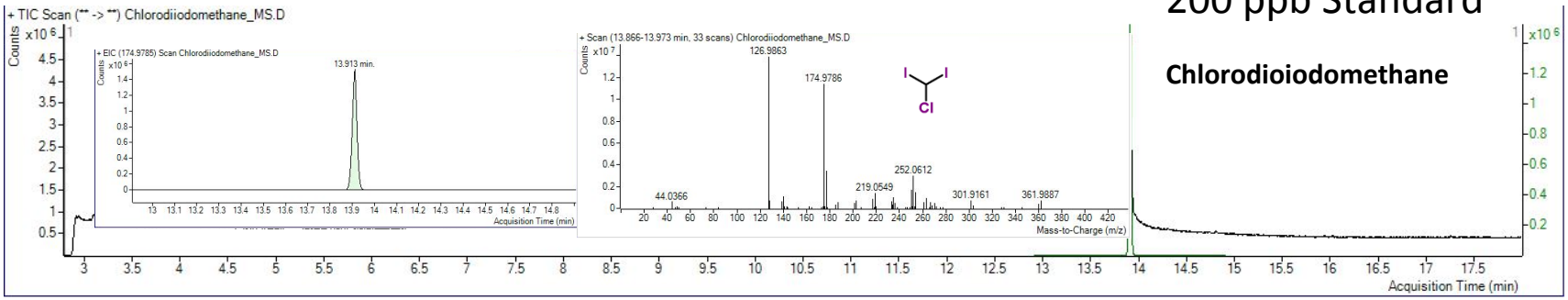


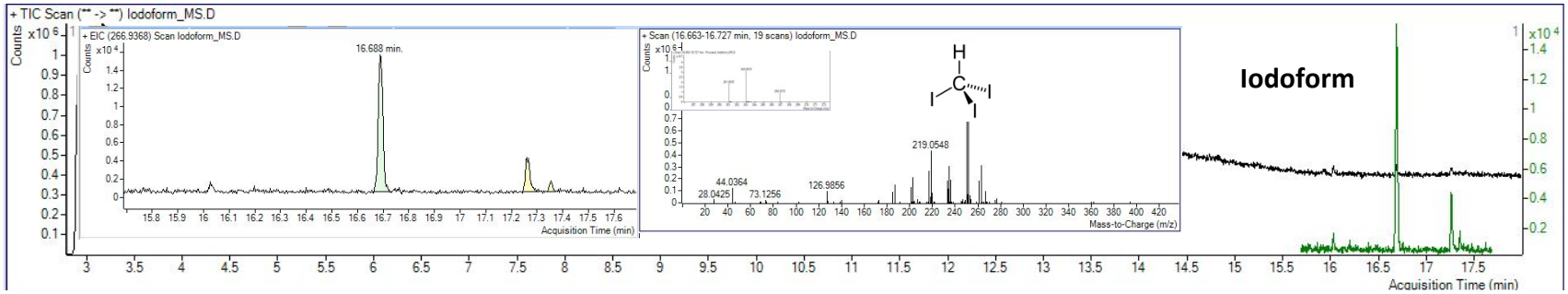
Chemical	RT (min)	Exact Mass of base peak
$CHBrI_2$	15.340	126.9859

Richardson et al., 2008

Iodinated Trihalomethanes

200 ppb Standard





Chemical	RT (min)	Exact Mass of base peak
$CHClI_2$	13.913	174.9785
CHI_3	16.688	266.9368

Conclusion & Continuing Research

- Headspace-SPME/GC-QToF can detect regulated and unregulated trihalomethanes with high mass accuracy.

Additional Research

- Investigate other iodinated THMs.
- Analyze real water samples following treatment and determine the pathway for the formation of THMs.
- Study other common disinfection byproducts (i.e. Nitrosamines)

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Questions??