

Development of a Sensitive Headspace Gas Chromatography-Mass Spectrometry Method for Off-Flavor Compounds in Water

July 13, 2015

National Environmental Monitoring Conference

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Outline

- Off-Flavor Compounds (OFC)
 - Research Goal
 - Experimental Setup
 - Data Analysis
- Headspace-Trap Sampling
 - Preliminary Data
- Conclusions

Off-Flavor Compound Classification

Musty



Piney



Sulfury



Woody



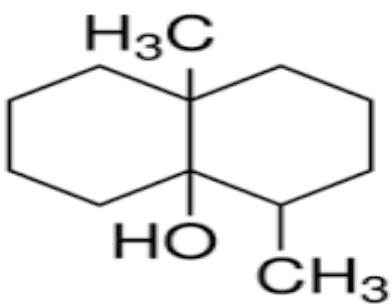
Rotten



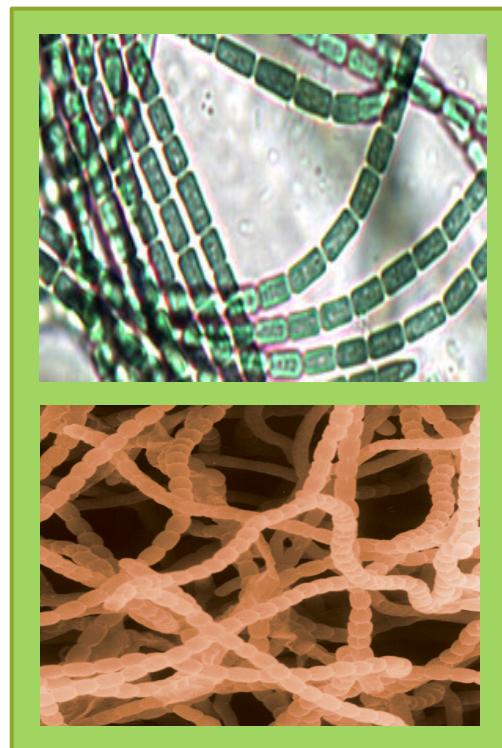
Grassy



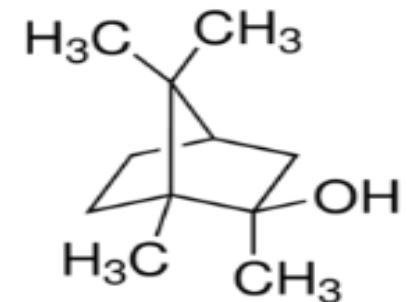
Common Compounds in Water



Min-Musty, Earthy Muddy
(10-dimethyl-*trans*-9-decalol)



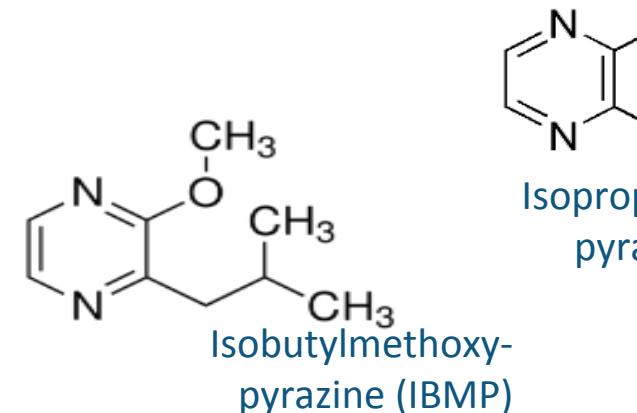
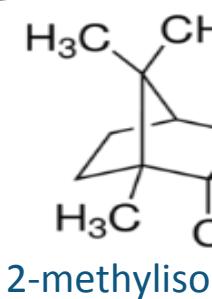
Cyanobacteria (top)
Actinomycetes (bottom)



MIB-Piney, Earthy, Muddy
(2-methylisoborneol)

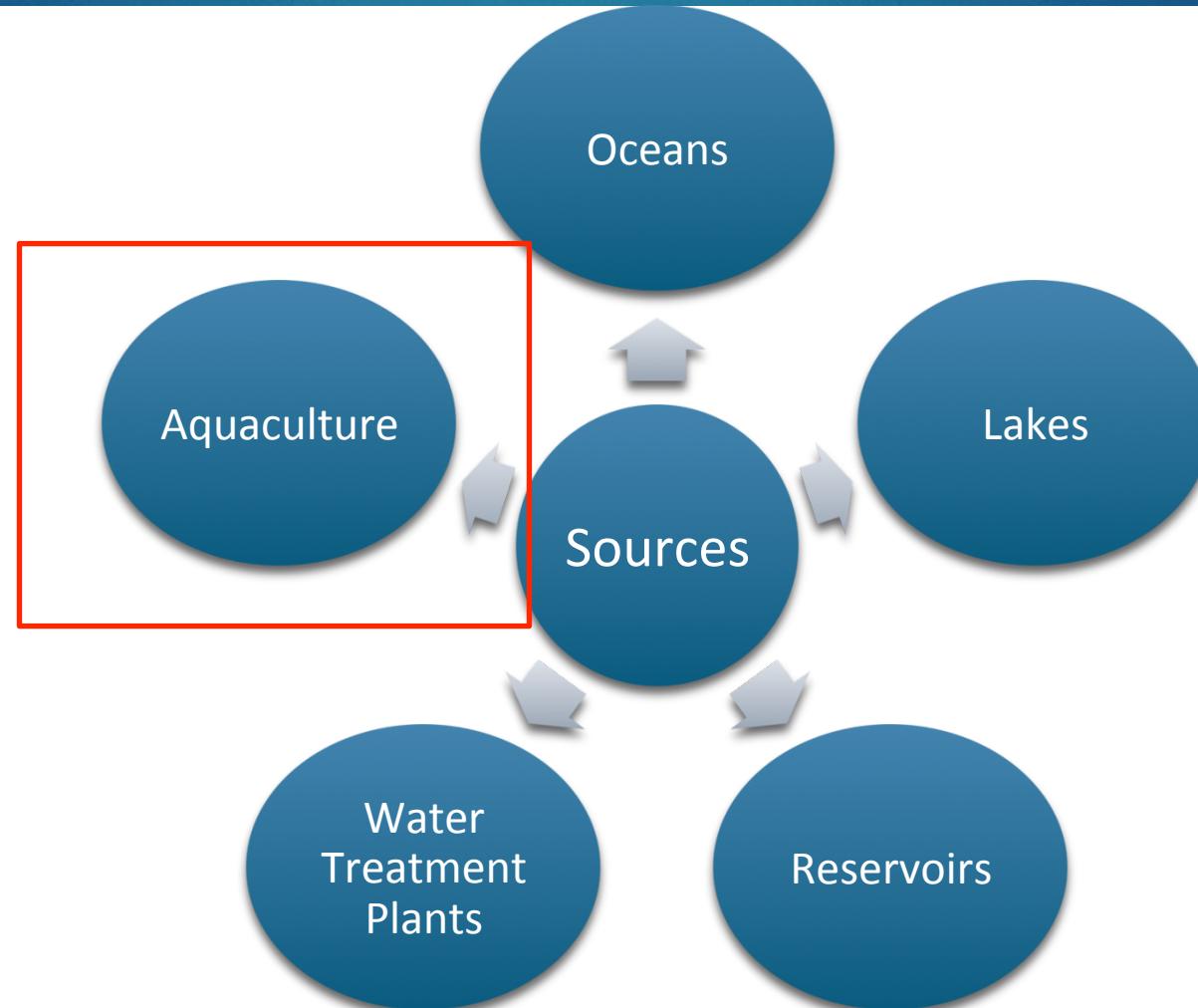
her “Off-Flavor” Compounds

Compound	Chemical Abbreviation	Threshold Concentration (parts per trillion)	Odor Description
2-dimethyl-ecalol	Geosmin (GSM)	1-10	Earthy-Musty (Old Books)
isobornol	MIB	6-42	Muddy-Piney
methoxy-	IBMP	1-16	Potato-Bin
dimethoxy-	IPMP	1- 16	Bell Pepper



Target Range \leq 1-42 ppt

Applications & Consequences of OFCs



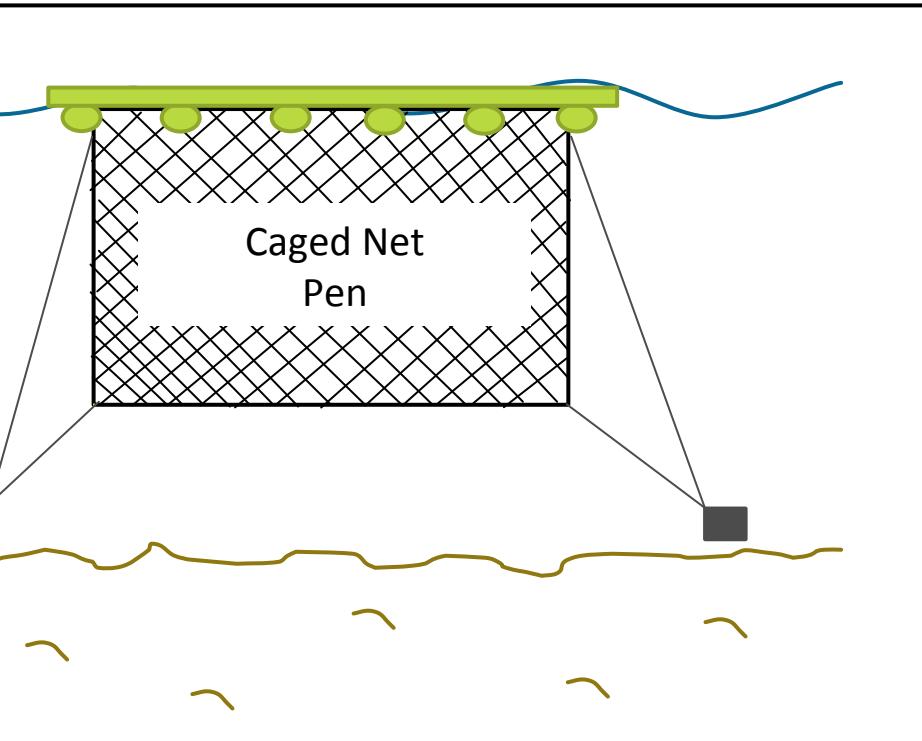
Factory odor, unpalatable, bothersome



COST

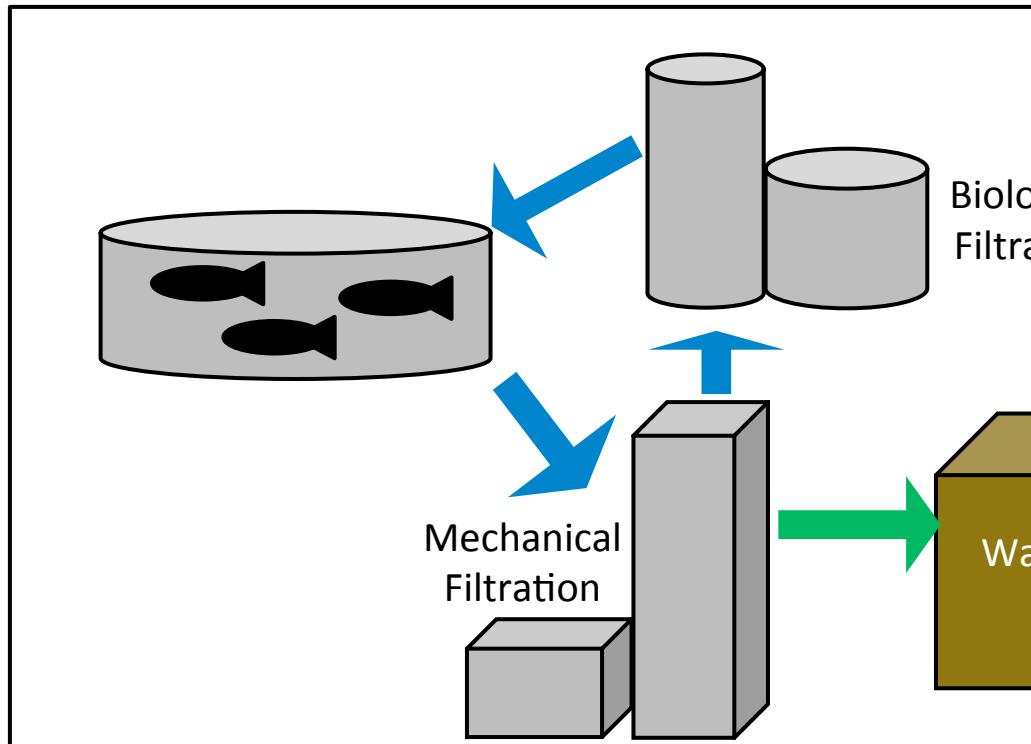
Aquaculture Systems

Traditional Aquaculture Systems



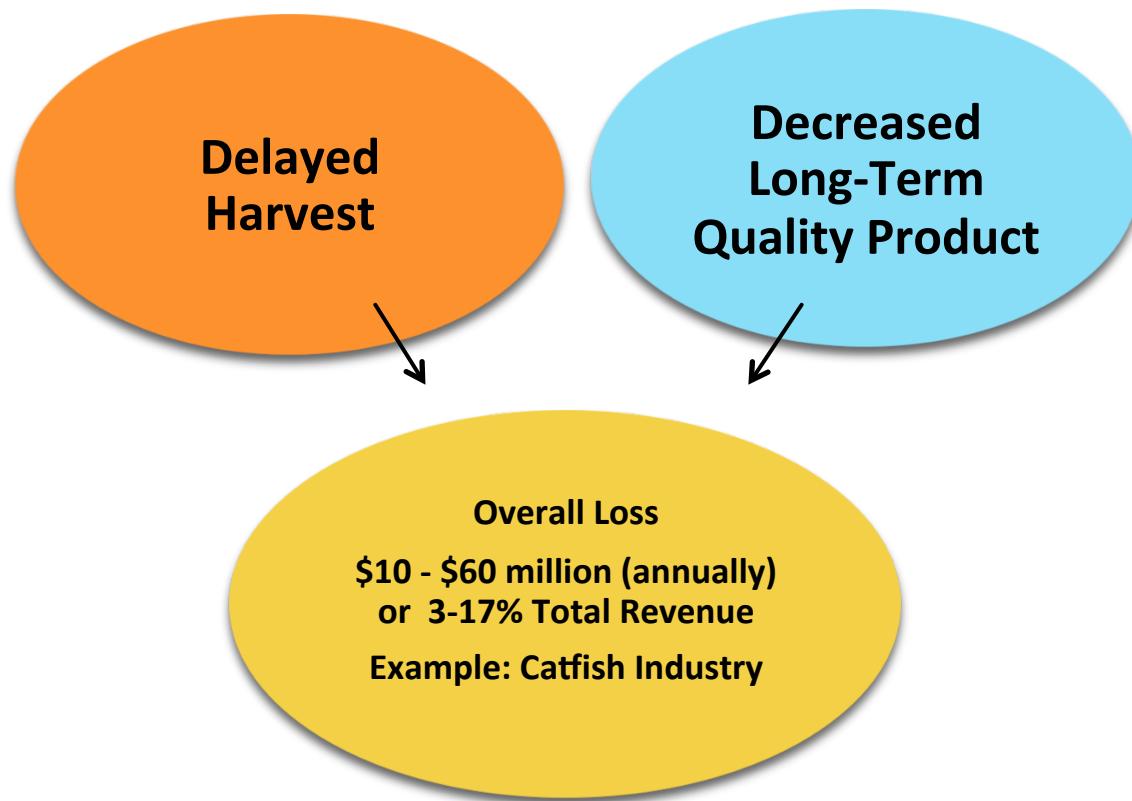
VS

Recirculating Aquaculture System



Economic Impact of Aquaculture

Aquaculture- culturing of aquatic organisms (finfish, mollusks, aquatic plants, turtles, etc.) in a large scale capacity
Challenge to control off-flavors
Aeration followed by deposition

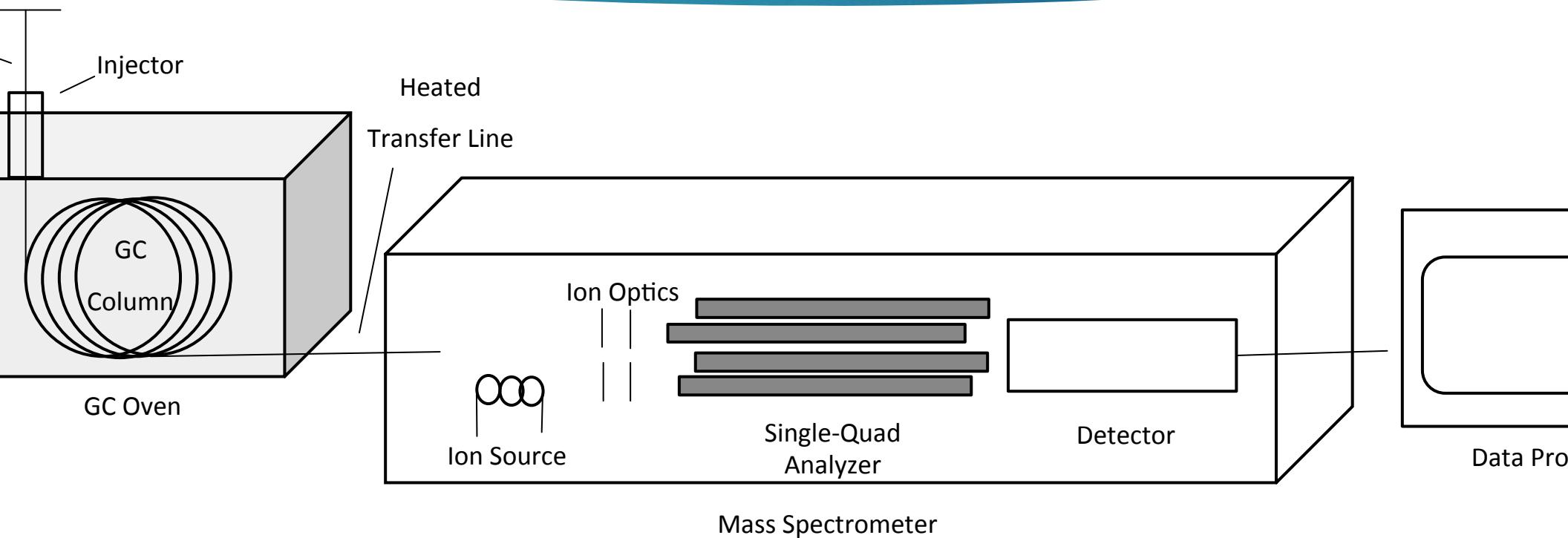


Research Question-*Can a method be developed to profile/map the OFCs within fully-contained recirculating aquaculture systems?*

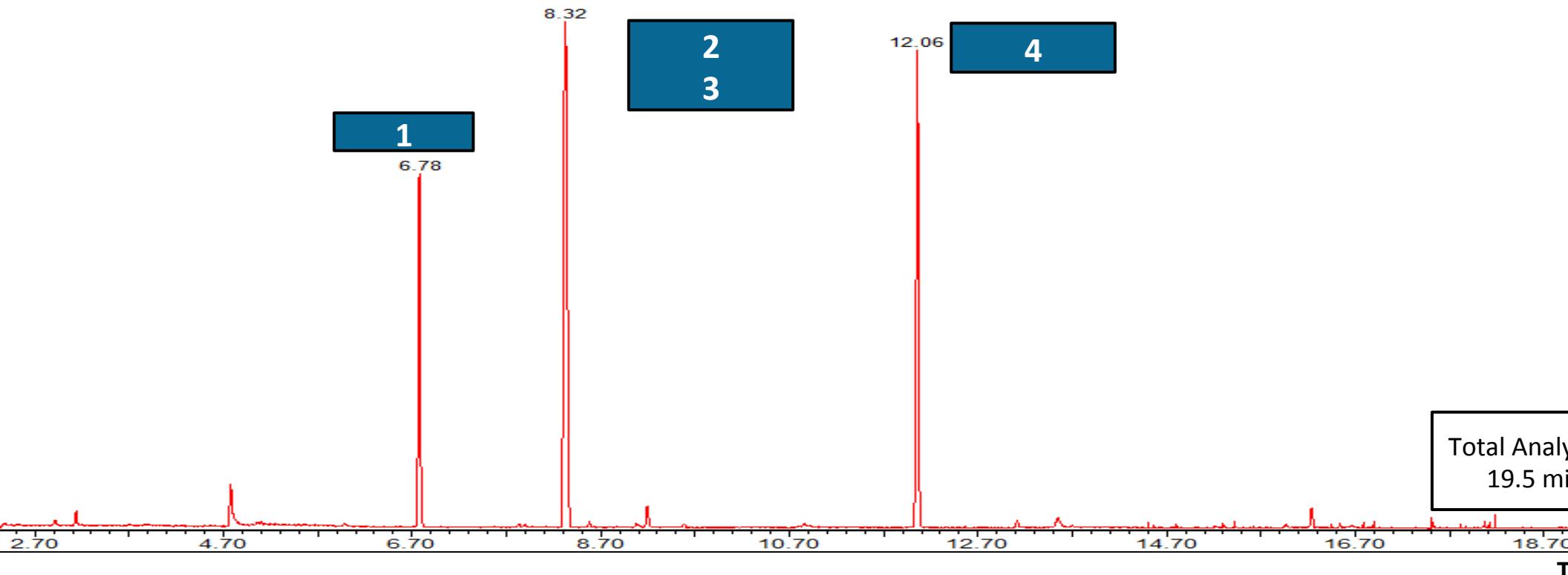
Goal of Study

Develop and optimize a sensitive GC-MS method for the quantitation of specific off-flavor compounds in water.

Gas Chromatography-Mass Spectrometry (GC-MS) Instrumentation

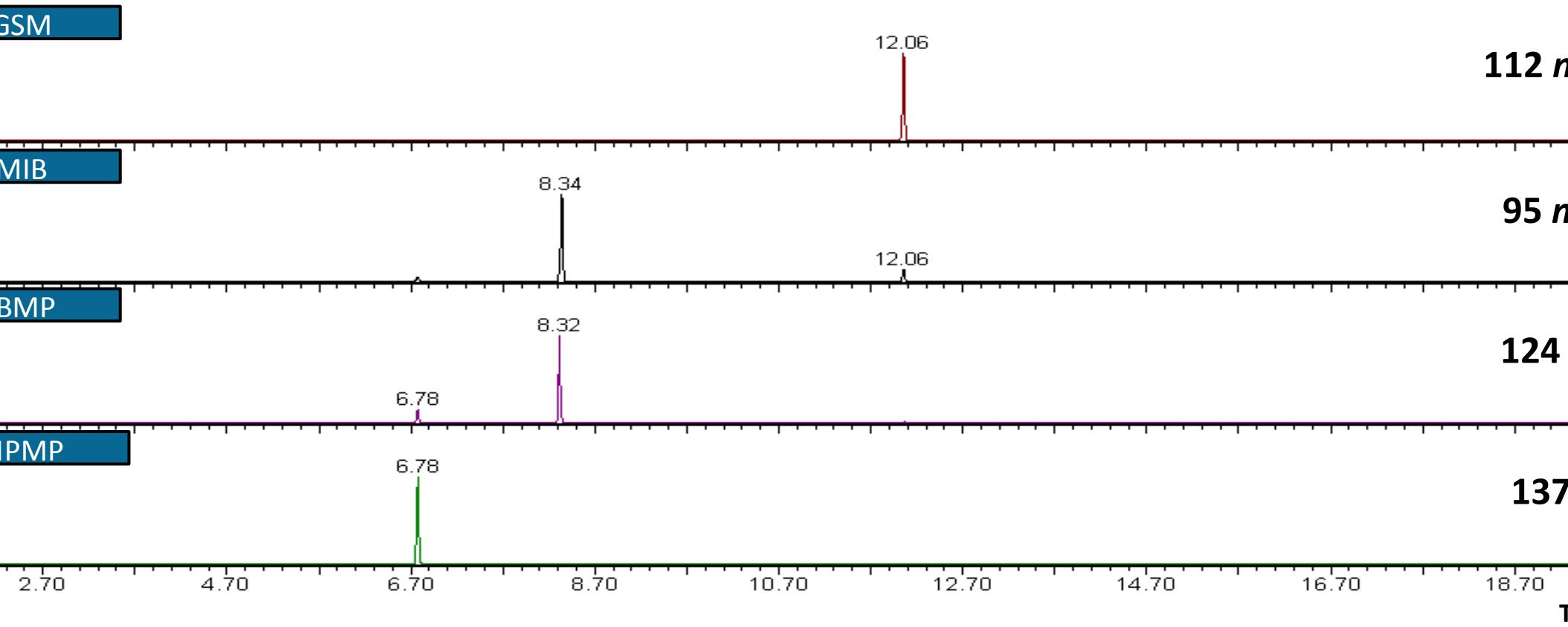


Initial Chromatographic Conditions



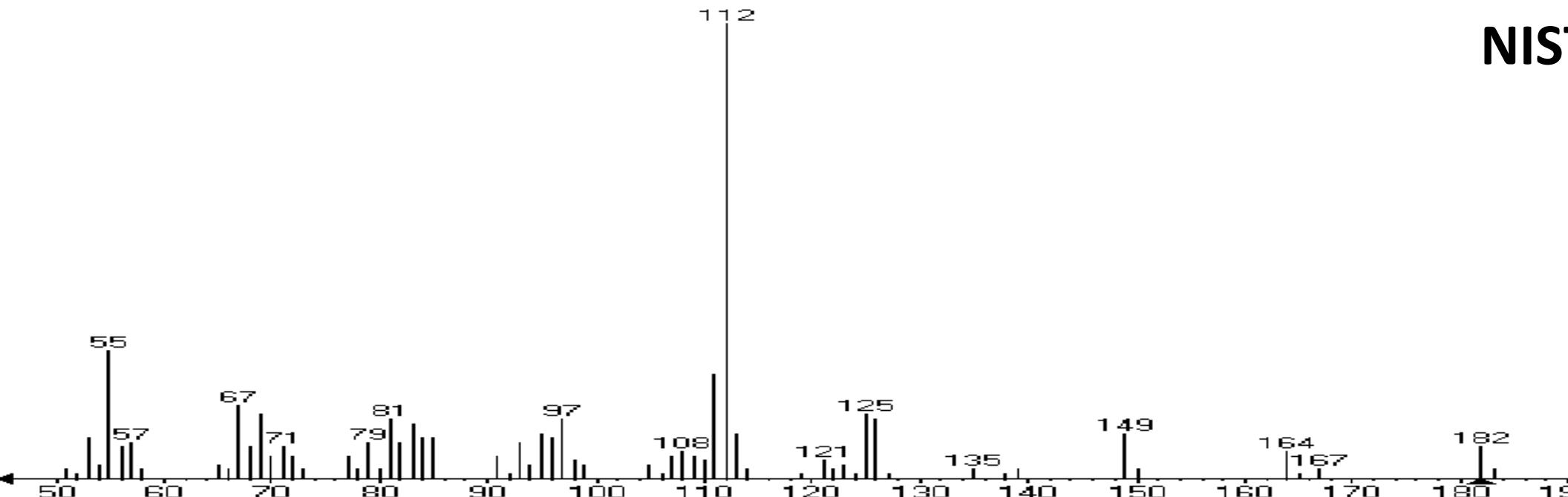
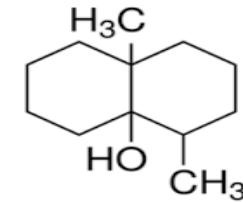
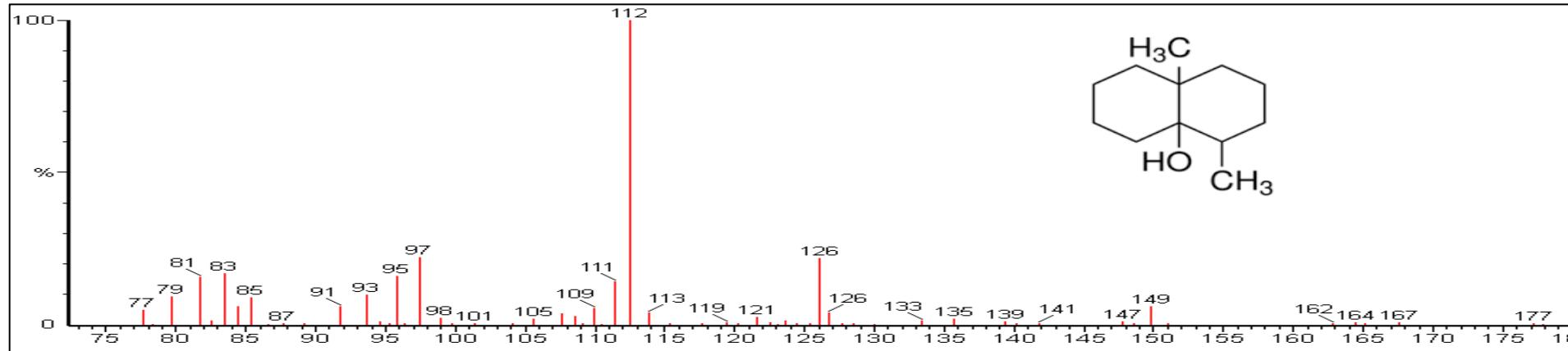
Chromatogram (TIC) of a standard mixture via GC-MS Direct Injection. 1)Isopropylmethoxy-pyrazine, 2)Isobutylmethoxy-pyrazine, 3)Isoborneol, 4) Geosmin. Experimental Conditions: 1 μ L OFC standard mixture in methanol; Injection Port Temp: 260°C; Temperature: Initial 60°C (2 minutes), 200°C (8°C/min); Flow Rate : 1.43 mL/min. (0.09 in³/min.); Carrier Gas: Helium.

Extracted Ion Chromatogram of Standard Mixture via Direct Injection



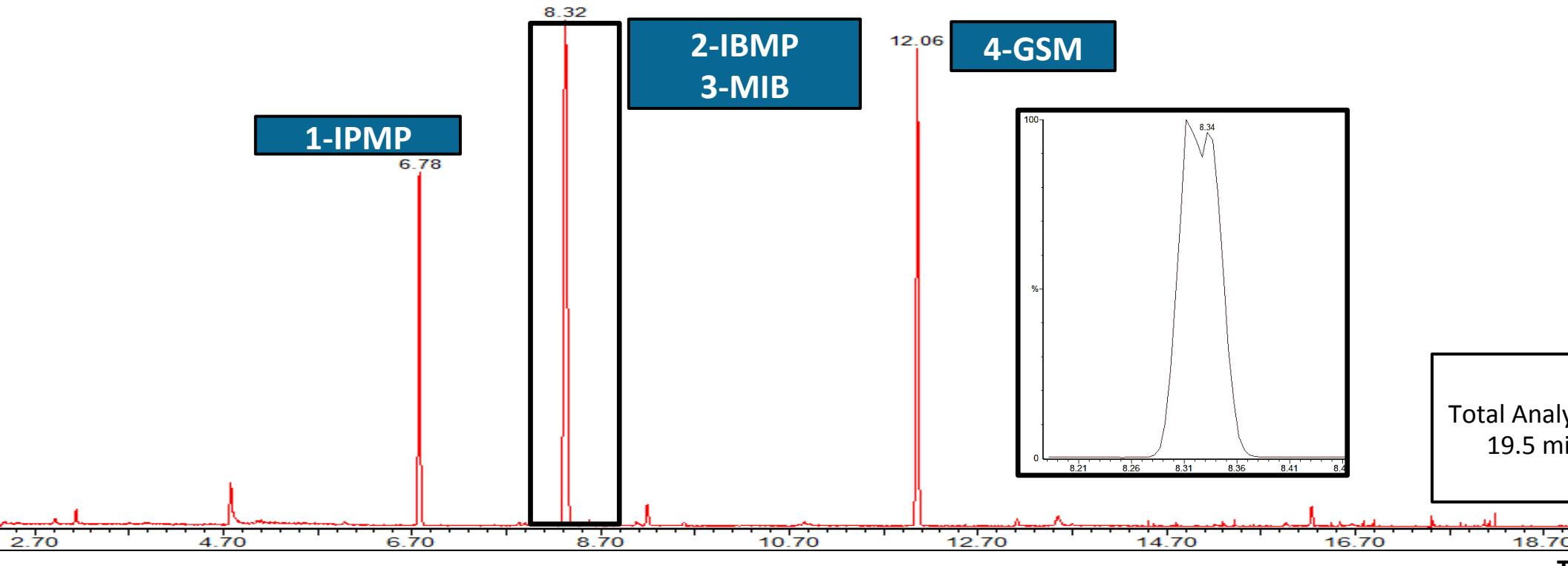
Extracted Ion Chromatogram (EIC) of a standard mixture via GC-MS Direct Injection. 1)Isopropylmethoxy-pyrazine, 2)Isobutylmethoxy-
cyclohexene, 3)Isobutylmethoxy-caryiosborneol, 4) Geosmin (GSM).

Compound Detection & Spectral Matching- Geosmin



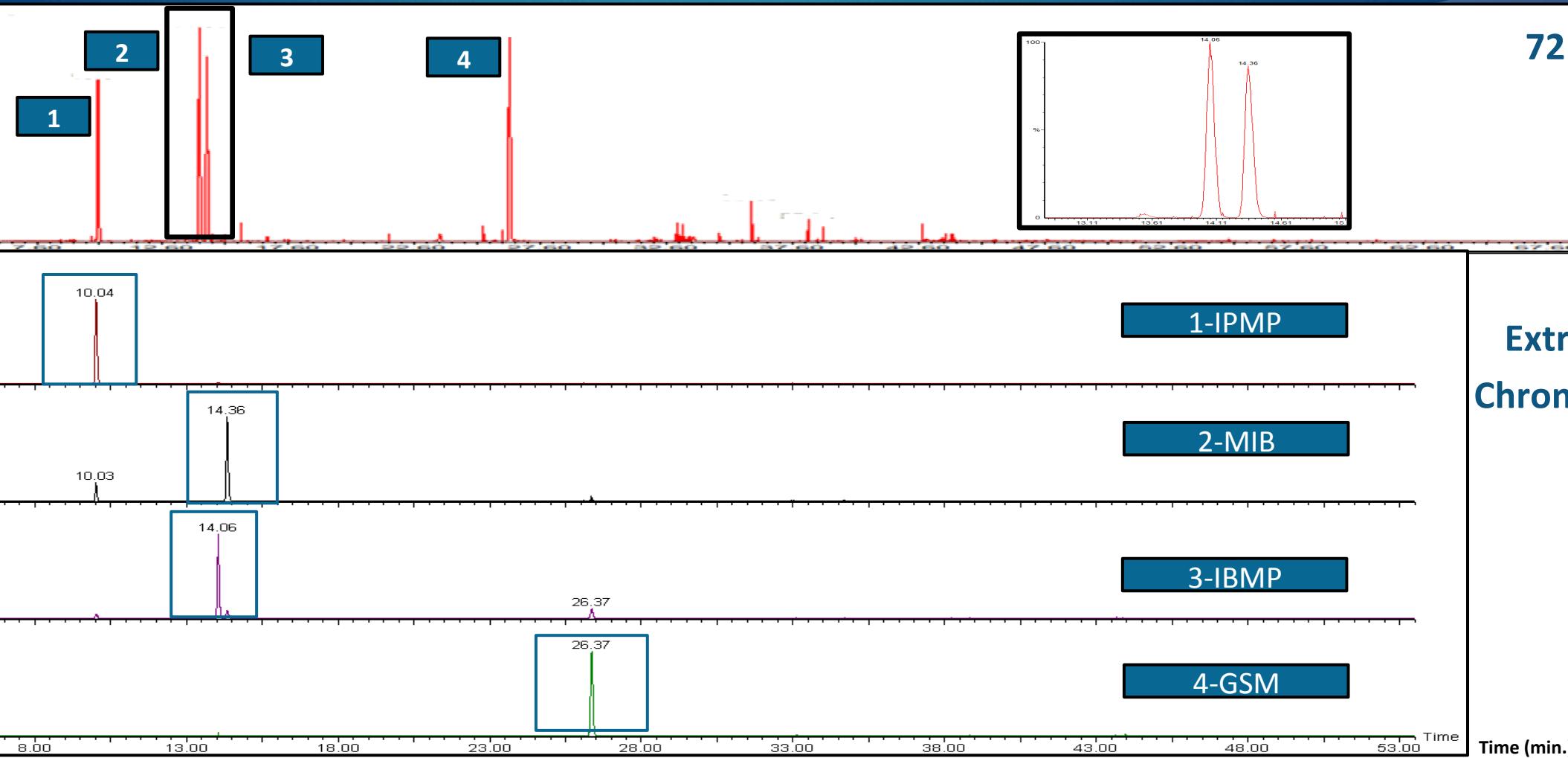
Mass Spectrum. Comparison to National Institute of Standards and Technology (NIST) Library spectra

-Elution from Initial Chromatographic Conditions

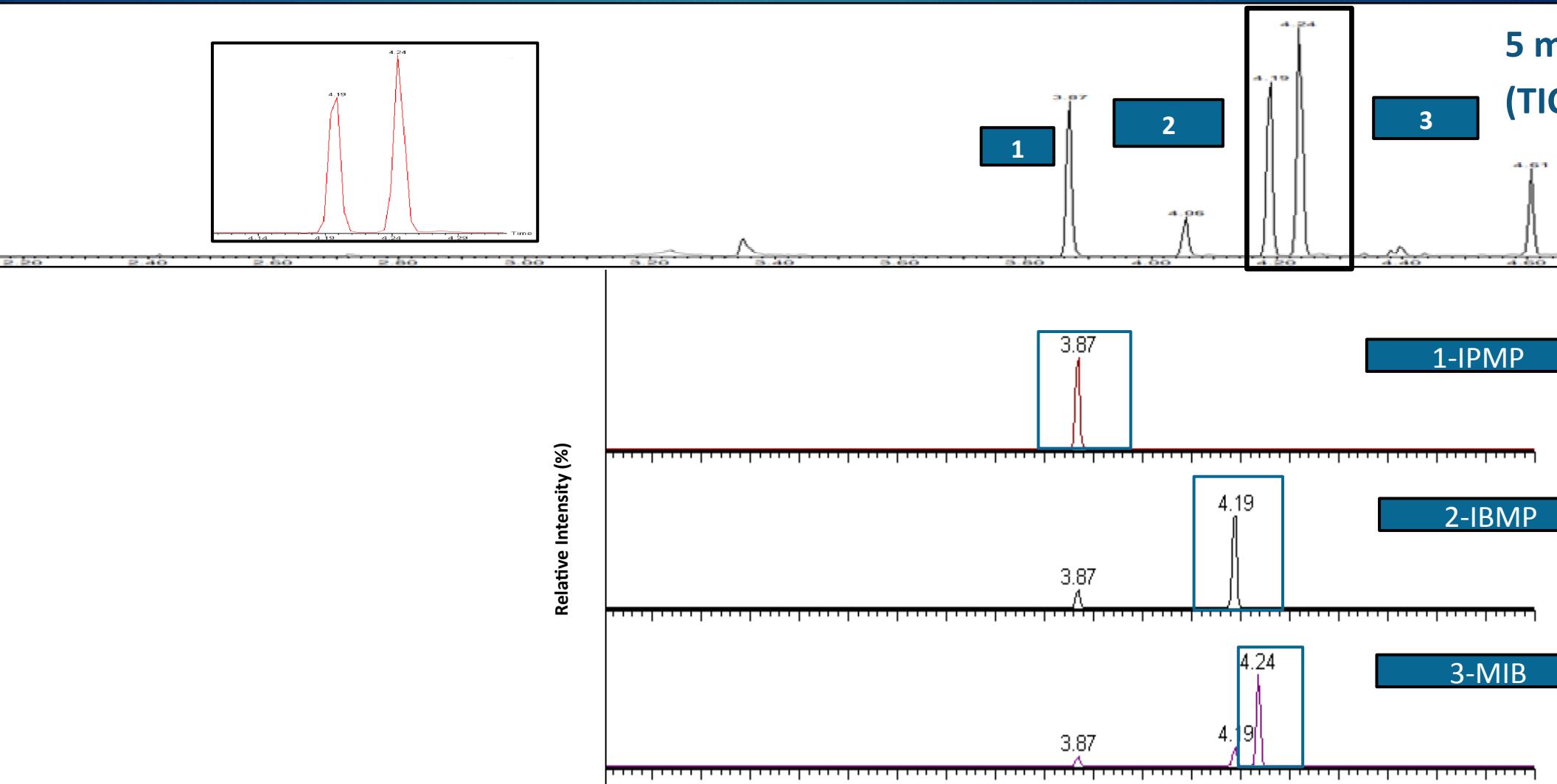


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Temperature Ramp at 2°C/minute

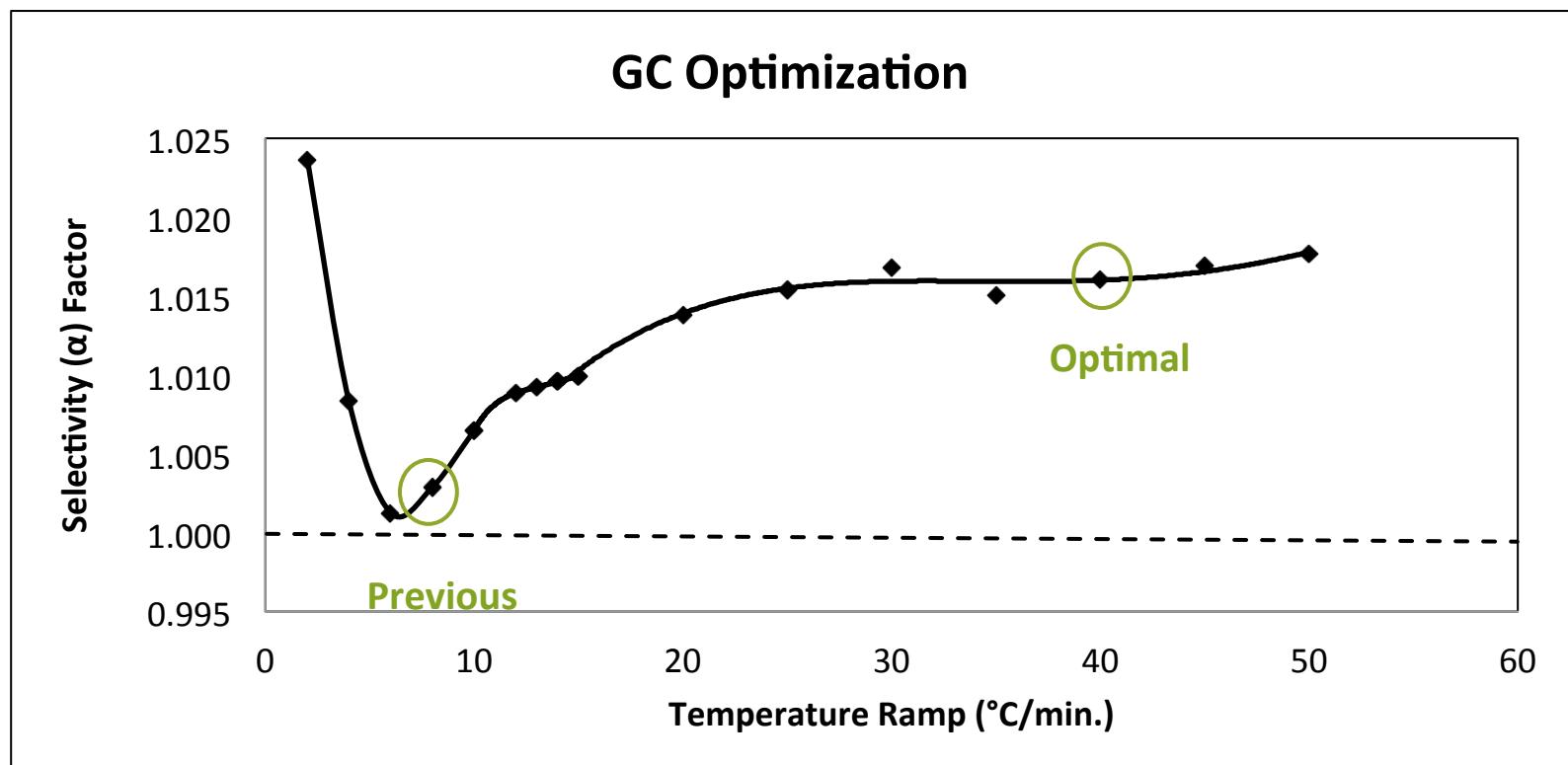


Temperature Ramp at 50°C/minute

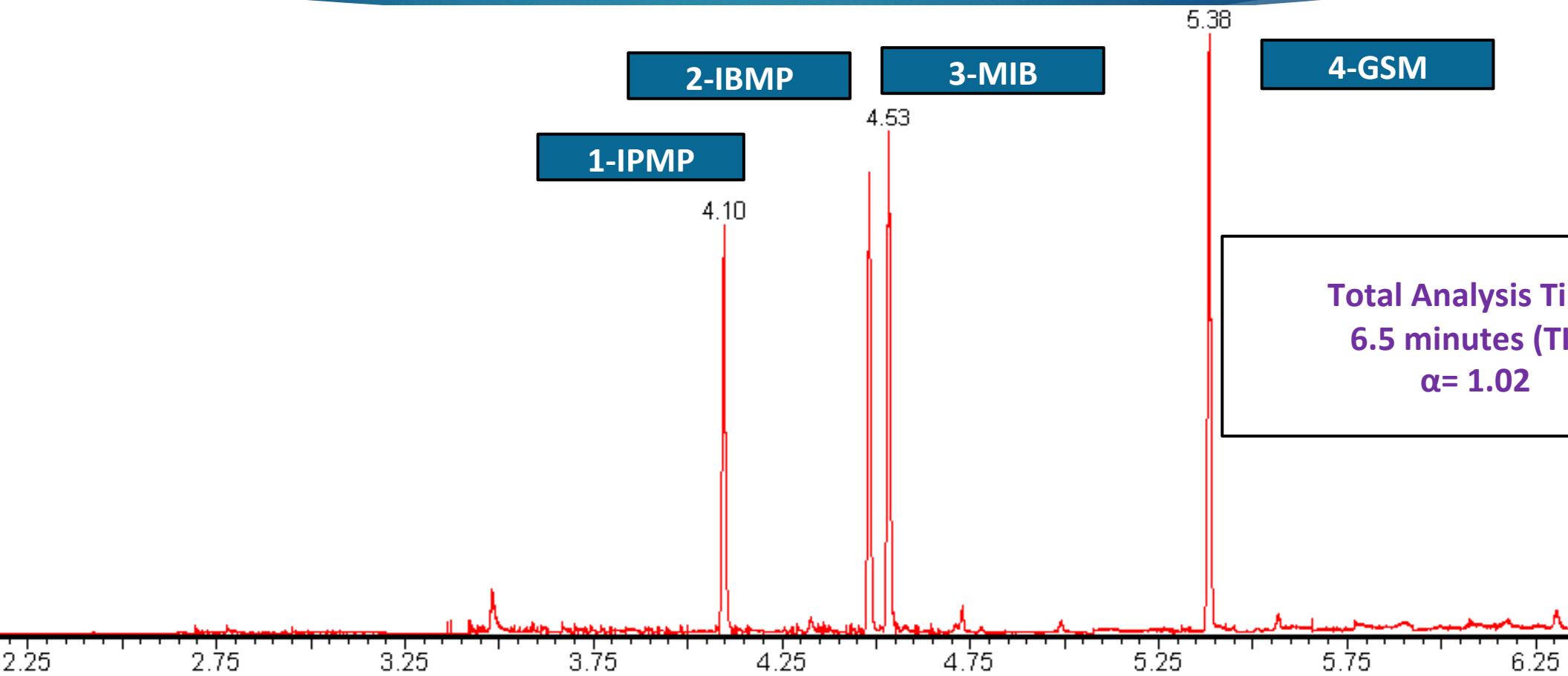


Method Optimization of Temperature Ramp

- Range 2-50 °C/min Temperature Ramp Cycle
- Total Analysis Times: 72 minutes – 5 minutes

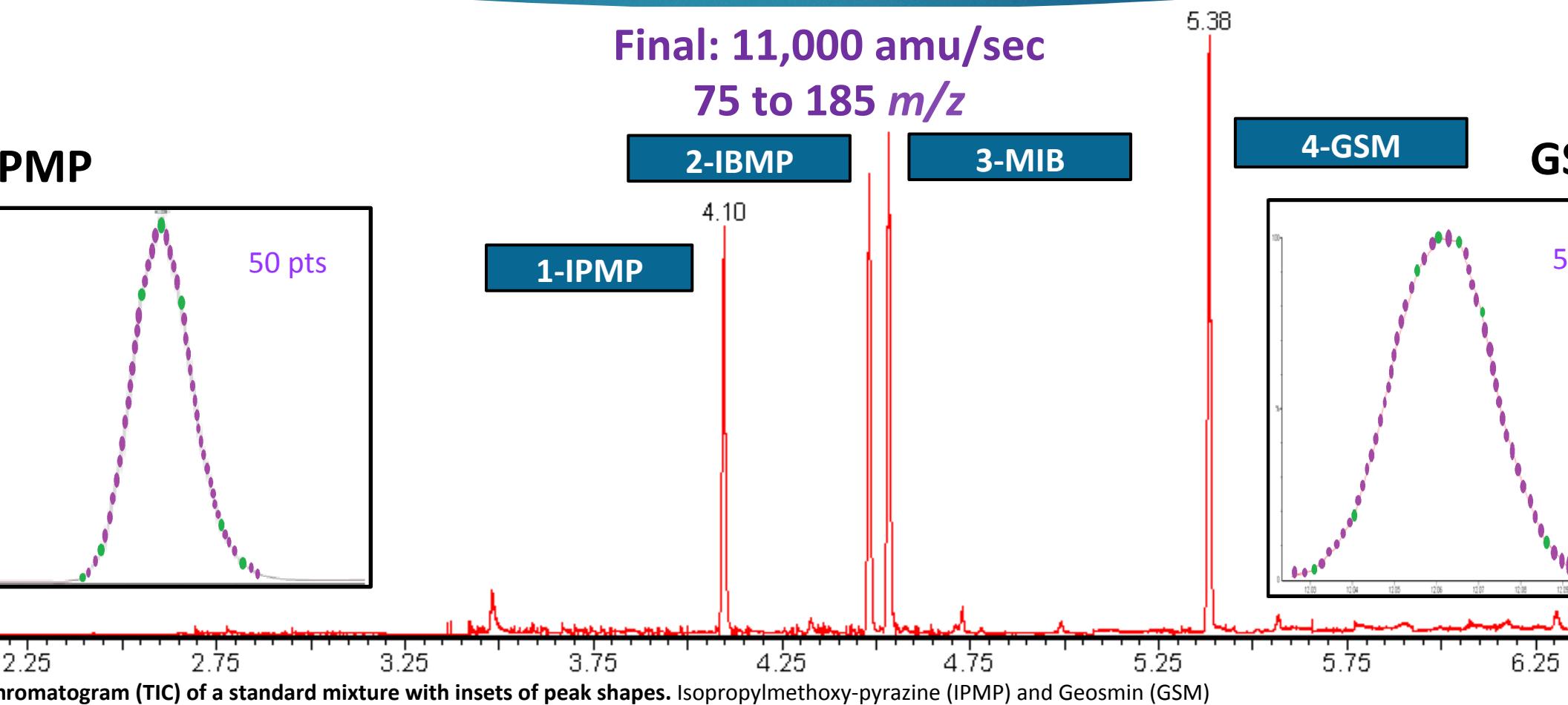


Optimal Separation Method at 40°C/minute



Chromatogram (TIC) of a standard mixture via GC-MS Direct Injection. 1)Isopropylmethoxy-pyrazine, 2)Isobutylmethoxy-pyrazine, 3)2-methylisoborneol, 4) Geosm

Optimal Separation Method at 40°C/minute

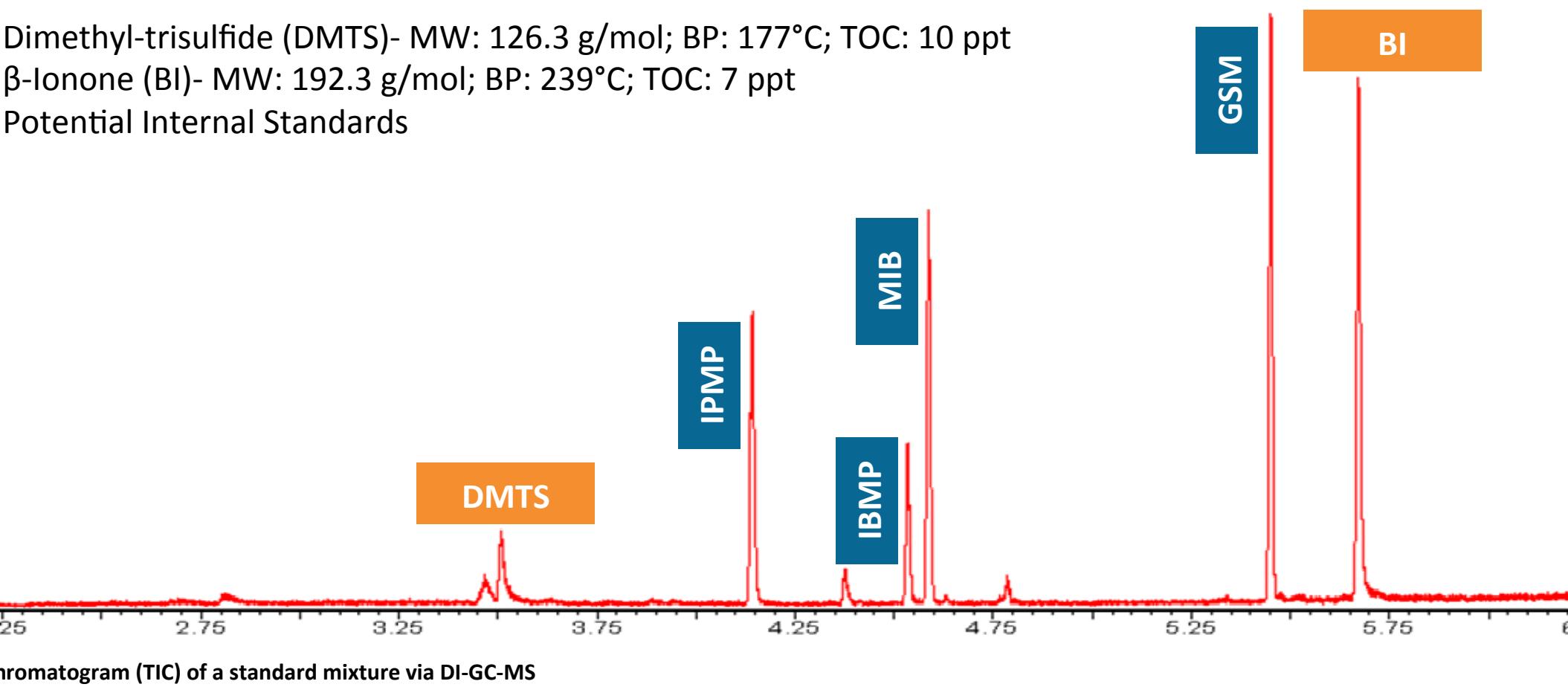


Additional Compounds for Standard Ladder

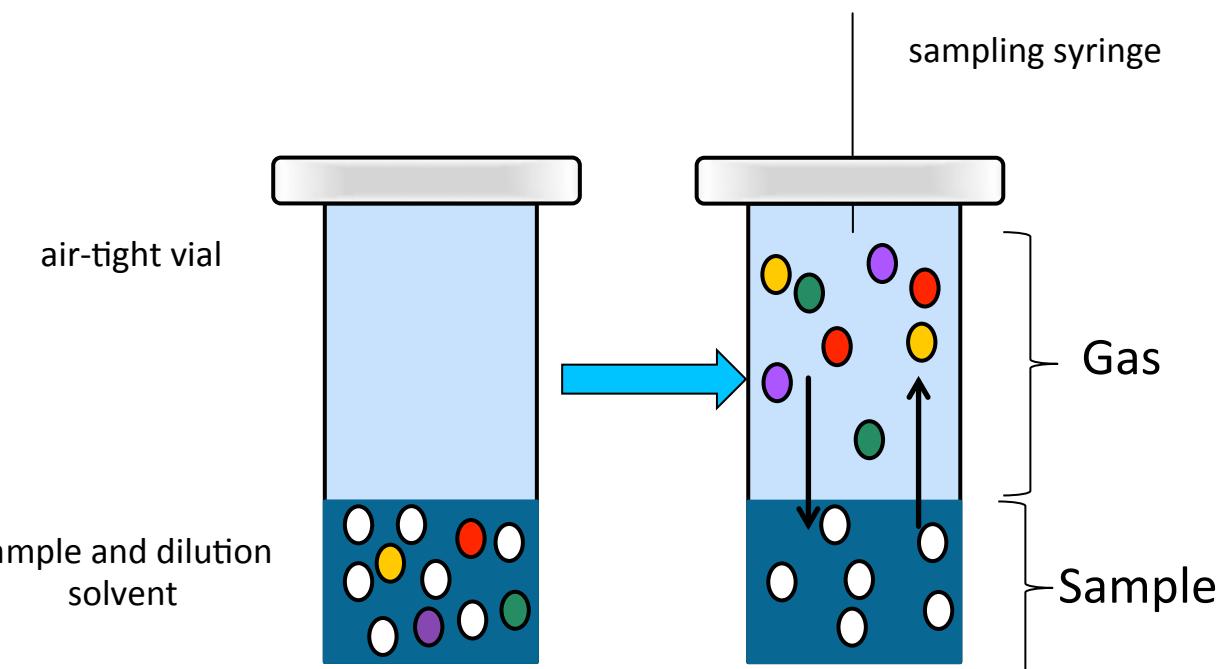
Dimethyl-trisulfide (DMTS)- MW: 126.3 g/mol; BP: 177°C; TOC: 10 ppt

β -Ionone (BI)- MW: 192.3 g/mol; BP: 239°C; TOC: 7 ppt

Potential Internal Standards



headspace Pre-concentration Technique



Principle of Headspace Sampling

- Equilibrium of Sample Matrix & Headspace
- Factors: Temperature, Sample Size, Solvent Addition
- Advantages: Trace Analysis, Simplicity, Independent of Matrix

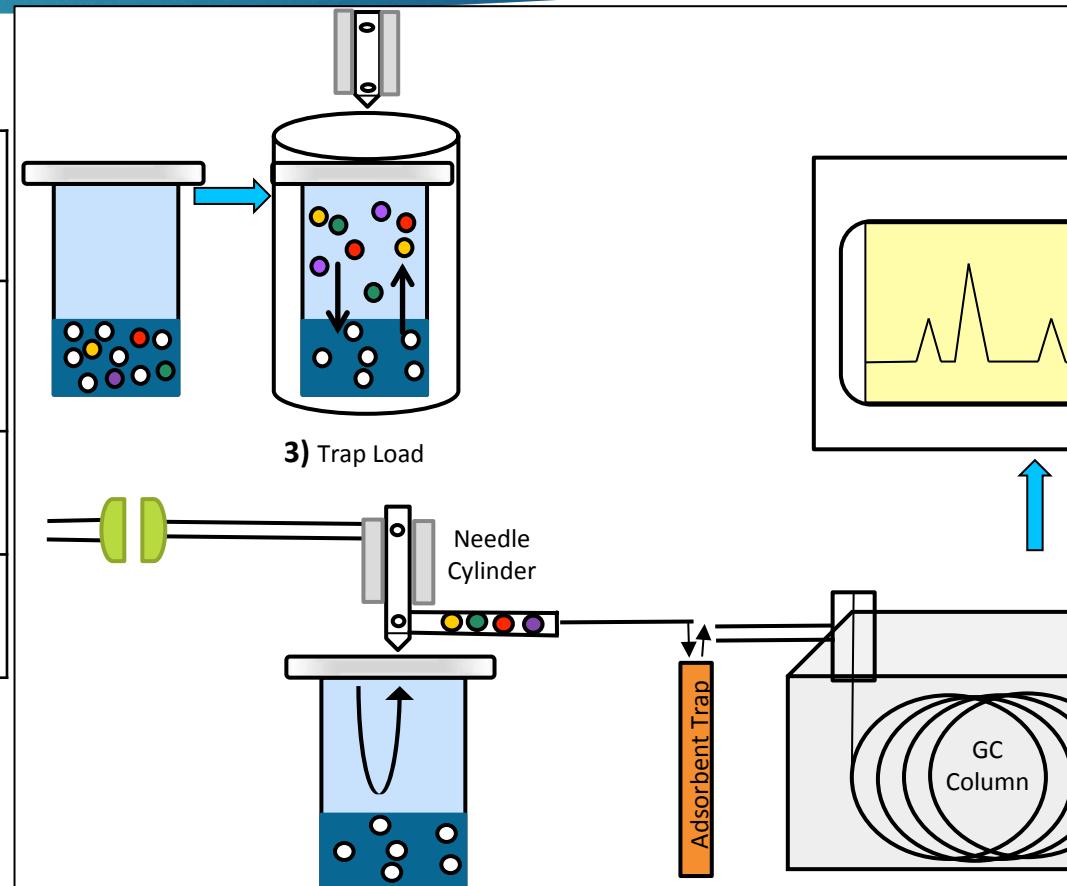
Existing Pre-concentration Methods

GC-MS Pre-concentration Method	Analysis Time	Drawbacks	Ref.
Solid Phase Extraction (SPE)	58-120 min (Pre-concentration) 19-37 min (Chromatography)	<ul style="list-style-type: none"> Poor Reproducibility Multiple steps Sample loss Internal Standard Complications 	Lloyd, et al. (1998); Watson, et al. (2000); Guttman, et al. (2012); Ding, et al. (2014)
Sample Purge & Trap (PT)	36-65 min (Pre-concentration) 29-56 min (Chromatography)	<ul style="list-style-type: none"> Prone to Carryover Multiple steps Interference from Water Vapor Required Cleaning steps 	Peterson, et al. (2011); Salemi, et al. (2006); Manickum, et al. (2012)
Sample Pretreatment w/ Inline Adsorbent	23 min (Pre-concentration) 7 min (Chromatography)	<ul style="list-style-type: none"> Prone to Carryover Peak Distortion 	Advantages: <ul style="list-style-type: none"> Minimal Steps Decreased Leaks Decreased Analysis Time

Vadspace w/ Inline Adsorbent Trap (HST) Specif

onal Parameters for HST Instrument

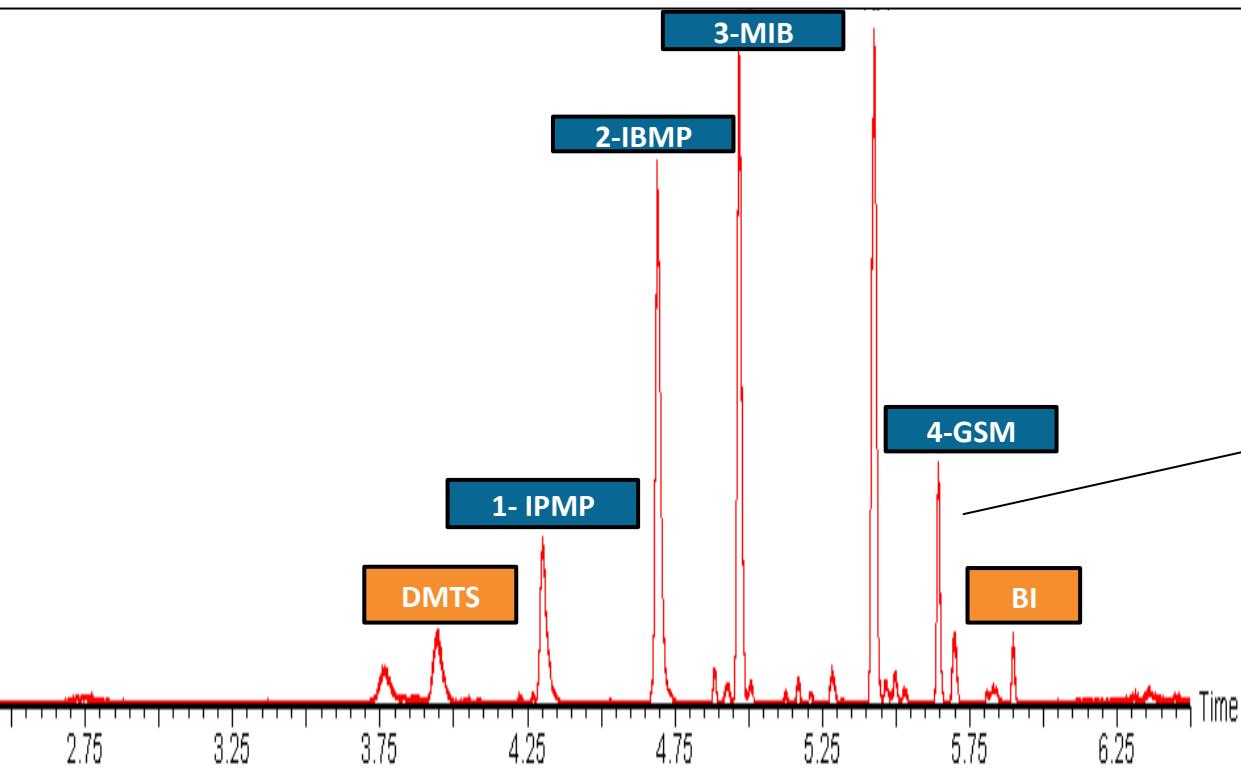
Trap	Carbonaceous Sorbents	Pneumatic Control	PPC
	132 mm	Water Management	Dry Purge
meter	3.5 mm	Transfer Line System	Deactivated Fused-Silica
eters	2.8/0.7	Transfer Line Temp	210°C



Schematic of Automated HST System

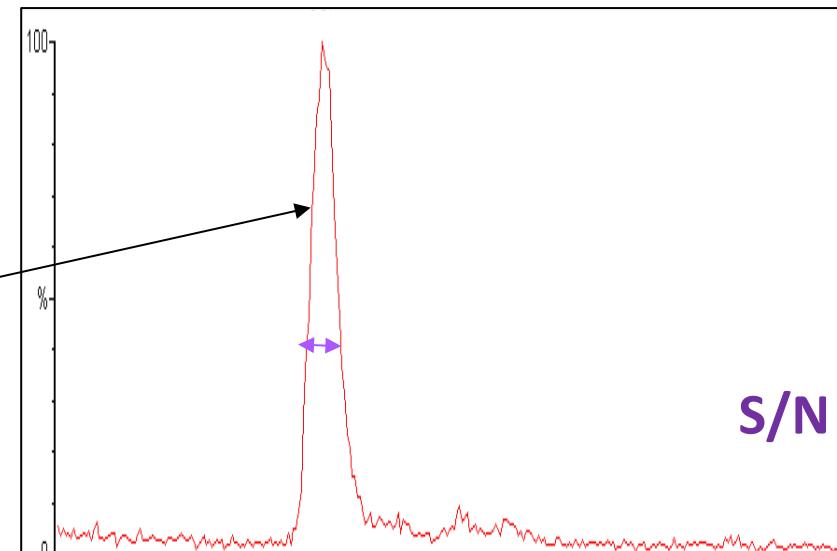
headspace w/ Inline Adsorbent Trap

Binary Data



Chromatogram (TIC) of a standard mixture via HST-GC-MS

Selective Ion Monitoring (SIM)



SIM of a 100ppt standard mixture via HST-GC-MS GC-MS

Conclusions & Future Work

Optimization of chromatography & detection methods using direct injection experimental parameters

Representative spectrum appropriate for future trace analysis

Preliminary confirmatory HST pre-concentration in water standards

Future studies to optimize trapping parameters

Extension of application to prepare water and alternative samples from aquaculture systems

Development of a Sensitive Headspace Gas Chromatography-Mass Spectrometry Method for Off-Flavor Compounds in Water

Overall Impact:

Eliminate Hurdle of OFCs

Support the Development of Aquaculture

Extension to Other Water Monitoring Analyses

Acknowledgements

Dr. William LaCourse, PI

LaCourse Lab/ Molecular Characterization and Analysis Complex (MCAC)

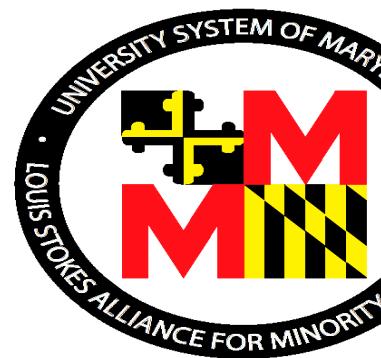
Meyerhoff Graduate Fellowship Program

Southern Regional Education Board (SREB) Doctoral Scholars Program

JMBC Department of Chemistry & Biochemistry



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QUESTIONS

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