Determination of 2-Methylisoborneol and Geosmin in Water Using Solid Phase Micro Extraction

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ABSTRACT

The compounds 2-Methylisoborneol (2-MIB) and Geosmin are the primary source of the foul odor found in drinking water. Algal contamination is the principal cause of the formation of these compounds. Geosmin and 2-MIB have such a low odor threshold, that even the slightest amount can produce an unpleasant odor and taste in drinking water. Thus, developing a reliable sampling and analysis platform for very low level detection is important. Standard Method 6040D describes a procedure for the detection of 2-MIB and Geosmin using Solid Phase Micro Extraction (SPME) coupled with a Gas Chromatograph (GC) and Mass Spectrometer (MS). Selective Ion Monitoring (SIM) is used for compound detection down to part per trillion (ppt) levels. This examination will optimize the sampling and detection of 2-MIB and Geosmin.

INTRODUCTION

It has been found that the presence of blue green algae in water sources produces 2-MIB and Geosmin. Both Geosmin and 2-MIB are malodorous compounds that emit a musty earthy aroma. When the algae generates an abundance of these compounds in a drinking water reservoir, there are resulting taste and odor problems. Algae blooms are influenced by their climate, as a result, the formation of Geosmin and 2-MIB is more of a problem during the summer months and in warmer climates. Areas in the southwestern portion of the United States seem to have the most problems with 2-MIB and Geosmin.

Drinking waters are tested in order to determine water quality for prospective consumers. Two of the major complaints that water suppliers need to address are issues with taste and odor. Geosmin and 2-methylisoborneol (2-MIB), although non-toxic, both have very strong odors and can be detected at levels below 10ppt. Thus, developing a reliable sampling and analysis platform is important.

Standard Method 6040D addresses the sampling and analysis of 2-MIB and Geosmin utilizing SPME in conjunction with GCMS in Single Ion Monitoring (SIM) mode. The SPME fiber is placed in the headspace above the sample for a period of time and then the fiber is inserted into the GC injection port for analyte desorbtion onto the GC column. This application will develop and optimize Method 6040D experimental parameters for the determination of 2-MIB and Geosmin down to 5ppt.

EXPERIMENTAL

Headspace SPME is a non-exhaustive sampling technique so the experimental conditions required optimization in order to make the extraction technique both efficient and reproducible. For the automation of the sampling process, the EST Analytical FLEX autosampler was used. The FLEX suite software simplified the sample method development process with the ease of its drag and drop method builder.

The most efficient SPME fiber for this analysis was a Divinylbenzene/ Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) coated fiber with a 50/30µm film thickness. The Shimadzu QP2010 SE GCMS was run in SIM mode and was fitted with a SPME liner and a Restek Rxi-5 Sil MS column. The autosampler and GCMS experimental conditions developed for this analysis are listed in Tables 1 and 2.

Table 1: FLEX Autosampler Experimental Parameters

Autosampler	Flex
General	
Method Type	SPME
Gc Ready	Continue
Gc Cycle Time	21min
Constant Heat Mode	Yes/Continue
Sample Incubate Agitate	
Incubation Temp.	65°c
Incubation Time	1.0min
Extraction	
Fiber Guide Depth	45%
Sample Vial Fiber Depth	1Cm
Extraction Time	30.1min
Fiber Extraction Agitate	Yes
Agitation Type	Oscillate
Agitation Delay	0.1min
Agitation Duration	30.0min
Wait	
Wait On Input	Yes
Wait Input	GC Ready
Desorbtion	
Injection Port	A
Fiber Guide Speed	40%
Fiber Guide Depth	50%
Fiber Insertion Speed	75%
Fiber Insertion Depth	1cm
Fiber Desorbtion Time	3min
Injection Start Output	Start

Table 2: GC/MS Experimental Parameters

GC/MS	Shimadzu QP 2010 SE
Inlet	Split/Splitless
Inlet Temp.	270°C
Inlet Head Pressure	40.7kPa
Mode	Splitless
Injection Pulse Pressure	50kPa for 2.0 min
Carrier Gas Split Ratio	2
Desorption	3.0min at 270°C
Column	Rxi-5 Sil MS 30.0m X 0.25mm X 0.25µm
Oven Temp. Program	60°C hold for 2.0 min., ramp 8°C/min to 200°C, hold for 0.5min, 20min run time
Column Flow Rate	0.8ml/min
Gas	Helium
Linear Velocity	32.6ml/min
Source Temp.	220°C
MS Transfer Line Temp.	300°C
Acquisition Mode	SIM
SIM Ions 3.01 to 12.50min	95, 107, 108
SIM Ions 12.51 to 20.00min	112, 125, 126
Event Time	0.30sec
Solvent Cut Time	3.0min

The 2-MIB and Geosmin standard was ordered from Supelco while Sodium Chloride was purchased from Sigma Aldrich. A six point standard curve was prepared in water with a range of 5 to 100ppt. Ten milliliters of each curve standard was added to a prepared 20ml headspace vial and sealed. The prepared headspace vials contained 2.5g of Sodium Chloride. A linear curve was attained for each analyte, see Figure 1. After the curve was established, seven replicate samples of the 5ppt and the 50ppt standards were run in order to establish method detection limits and precision and accuracy data. Table 3 displays the experimental results and Figures 2 and 3 show chromatograms of both the 5 and 50ppt standards.

Table 3: Experimental Results Summary

Compound	Curve %RSD	Curve R^2	MDL (5ppt)	Precision (5ppt) %RSD	Accuracy (5ppt)	Precision (50ppt) %RSD	Accuracy (50ppt)
2-MIB	12.36	0.999	2.14	16.22	83.94	10.39	95.03
Geosmin	11.46	1.000	1.06	7.07	95.22	5.40	101.85

Figure 2: Chromatogram of 50ppt Standard

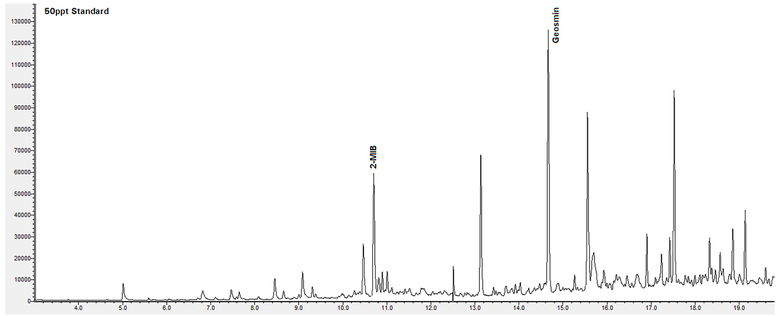
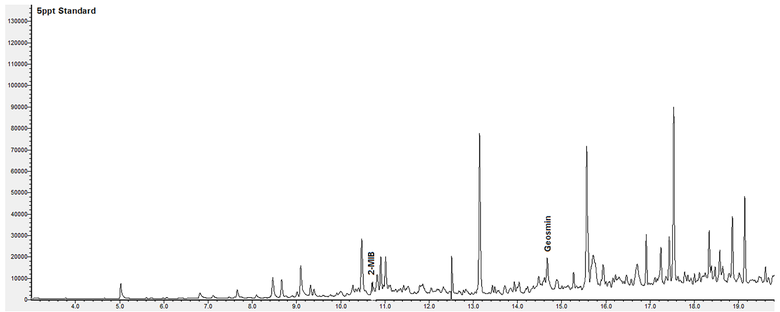


Figure 3: Chromatogram of 5ppt Standard



Conclusion

The SPME analysis of 2-MIB and Geosmin more than met the method requirements of Standard Method 6040D. The curve linearity from 5 to 100ppt had an R^2 of 0.999 or greater and a %RSD of better than 12.5. The resulting precision at 5ppt was about 16% for 2-MIB and 7% for Geosmin while the recoveries were 84% for 2-MIB and 95% for Geosmin. At 50ppt both compounds displayed improved precision and accuracy. Geosmin had 5.4% precision and 102% recovery while 2-MIB had 10.4% precision and 95% recovery. Once the optimum parameters were established the FLEX autosampler proved to be an exceptional system for the SPME sampling of drinking water samples.

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