Analysis of Volatile Organic Compounds and Odorants in Drinking Water via HS-SPME Arrow-GC-MS

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Abstract

Volatile organic compounds are commonly tested in drinking water to ensure safety for consumption. Additionally, odorants, like methylisoborneol (MIB) and geosmin, are of interest due to their off-putting aromas. It is of interest to combine these methods, which are typically run separately, into one method to achieve higher sample throughput. Solid-Phase Microextraction (SPME) using the SPME Arrow is of great interest due to its ability to combine sample preparation and sample introduction into one device. The SPME Arrow's ability to be automated using a rail-type autosampler lends itself to creating an even greater advantage in minimizing time spent preparing samples. The present method utilizes a simplified sample preparation workflow combined with Headspace–Solid Phase Microextraction–Gas Chromatography–Mass Spectrometry (HS-SPME-GC-MS) to determine VOCs and odorants in drinking water. This method shows a span of calibration ranges achieving r^2 values of 0.923-0.999 (average: 0.998); % residual standard errors (%RSEs) of 2–27% (average: 6%); analytical precisions of 2–15% RSDs (average: 4% RSD); and limit of quantification (LOQ) values of 0.0029–3.033 ng/mL (ppb, average: 0.223 ng/mL).

Related Products

- *1.10 mm SPME Arrow (cat.# 28903)*
- *Rtx-VMS capillary column (cat.# 19915)*
- *Topaz straight/SPME inlet liner (cat.# 23280)*
- *Geomin & 2-MIB (cat.# 30608)*
- *1,4-Dioxane-d8 (cat.# 30614)*
- *Fluorobenzene (cat.# 30030)*
- *4-Bromofluorobenzene (cat.# 30026)*
- *Leak detector (cat.# 28500)*

Introduction

Volatile organic compounds (VOCs) are commonly tested for in water due to their known toxicity and impact on human health. While odor compounds, like 2-methylisoborneol (MIB) and geosmin, do not pose a health risk, they are commonly tested for due to their off-putting, earthy, and musty taste and odor [1]. The analysis of VOCs and odor compounds is typically separated into two different analyses. By combining these methods, higher throughput and laboratory efficiency can be achieved. An approach to determine the presence of these compounds in water is Headspace–Solid Phase Microextraction–Gas Chromatography–Mass Spectrometry (HS-SPME-GC-MS) is presented here.

Experimental

Preparation of VOCs and Odor Solutions

Restek's Drinking Water Odor Standard (cat# 30608) and a custom VOC standard (see Restek's custom reference standards at www.restek.com/customstandards) were used for method development. Additionally, three internal standards (ISTDs) were selected: fluorobenzene (cat# 30030); 1,4-dioxane-d8 (cat# 30614); and 4-bromofluorobenzene (cat# 30026). Individual working solutions were prepared in methanol for each calibration point for both the VOCs and Odors and Method Detection Limits (MDL) were determined. The final sample size for this method was 5 mL in a 20 mL HS vial. After identifying the concentrations for the calibration and MDL, the working solution concentrations were calculated for making a 10 µL addition to reach the desired final concentrations. See Tables I & II for working solution concentrations and their corresponding calibration concentrations.

Table I: VOC Calibration and Working Solutions Concentrations

VOCs		
Level	Calibration Concentration (ppb, ng/mL)	Working Solution Concentration (ppb, ng/mL)
1	0.2	100
2	0.5	250
3	1	500
4	2	1000
5	5	2500
6	10	5000
7	25	12,500
8	75	37,500
9	200	100,000

Table II: Odorants Calibration and Working Solutions Concentrations

Odorants		
Level	Calibration Concentration (ppb, ng/mL)	Working Solution Concentration (ppb, ng/mL)
1	0.001	0.5
2	0.002	1
3	0.004	2
4	0.008	4
5	0.016	8
6	0.032	16
7	0.064	32
8	0.128	64
9	0.256	128

A working solution of the three selected ISTDs was prepared in methanol. The working solution was prepared at 10 µg/mL (ppm). Once calibration and MDL samples were prepared, the samples were then spiked with the 50 µL of the working solution to reach a final concentration of 100 ng/mL (ppb) in the final sample.

MDLs for each compound were determined similar to method detection limits per the procedure as dictated by the U.S. Environment Protection Agency (EPA) [2]. In following this procedure, seven replicate injections were made at low-level spikes (VOCs at 0.002 and 2 ng/mL, Odors at 0.008 ng/mL). See Table III for MDL spike concentrations. The standard deviation of these results was then multiplied by the student's t-value of 3.143 to determine the MDL. The limit of quantification (LOQ) for each compound was determined as 10 times (10x) the standard deviation of the MDL samples.

Table III: MDL Spike Levels

#	Compound	MDL Concentration (ng/mL, ppb)
1	Chloroethene	0.2
2	1,1-Dichloroethene	0.2
3	Dichloromethane	2
4	*trans*-1,2-Dichloroethene	0.2
5	MTBE	0.02
6	*cis*-1,2-Dichloroethene	0.02
7	Chloroform	0.02
8	Carbon Tetrachloride	0.02
9	1,1,1-Trichloroethane	0.02
10	Benzene	0.02
11	1,2-Dichloroethane	0.02
12	Trichloroethene	0.02
13	1,2-Dichloropropane	0.02
14	Bromodichloromethane	0.02
15	1,4-Dioxane	2
16	*cis*-1,3-Dichloropropene	0.02
17	Toluene	0.02
18	Tetrachloroethene	0.02
19	*trans*-1,3-Dichloropropene	0.02
20	Dibromochloromethane	0.02
21	*m,p*-Xylene	0.02
22	*o*-Xylene	0.02
23	Bromoform	0.02
24	1,2-Dichlorobenzene	0.02
25	2-Methylisoborneol	0.008
26	Geosmin	0.008

HS-SPME Arrow-GC-MS Parameters

All results were obtained using HS-SPME Arrow-GC-MS. HS-SPME Arrow, GC, and MS parameters can be found in Table IV, V, and VI respectively.

Table IV: HS-SPME Arrow Parameters

CTC PAL Parameters	
Sampling Mode	Headspace
SPME Device	1.10 mm SPME Arrow (cat.# 28903)
SPME Phase	120 µm CWR/PDMS
Vial Penetration Depth	45 mm
Injector Penetration Depth	50 mm
Incubation Temperature/Time	30 °C/120 s
Extraction Temperature/Time	30 °C/120 s
Desorption Temperature/Time	280 °C/1 min
Conditioning Temperature	280 °C
Preconditioning	1 min
Post Conditioning	0 min

Table V: GC Parameters

Agilent 7890B/5977B GC-MS Parameters	
Column	Rtx-VMS– 330 m x 0.2 5mm x 1.40 µm (cat# 19915)
Injection Mode	Split (15:1)
Inj. Vol.	See CTC PAL Parameters
Liner	Topaz 1.8 mm ID Straight/SPME Inlet Liner (cat# 23280)
Inj. Temp.	280 °C
Purge Flow	3 mL/min
Oven	35 °C (hold 3 min) to 60 °C at 8 °C/min (hold 0 min) to 280 °C (hold 3 min) at 30 °C/min; Total Time = 16.46 min
Carrier Gas	He, constant flow
Flow Rate	2.0 mL/min
Detector	HES - MS
Mode	SIM
Transfer Line Temp.	260 °C
Source Temp.	325 °C
Quad Temp.	200 °C
Acquisition Range	29 - 300 amu
Rate	5.1 scans/sec

Table VI: MS SIM Parameters

5977B MS SIM Parameters		
Group #	**Start Time**	**Mass, Dwell Time**
Group 1	0 min	(62, 30) (64, 15)
Group 2	1.8 min	(61, 15) (96, 30)
Group 3	2.3 min	(49,30) (57, 30) (61, 30) (73, 30) (84, 30) (96, 30)
Group 4	3.5 min	(61, 30) (96, 30)
Group 5	4.3 min	(47, 30) (61, 30) (82,30) (83, 30) (97, 30) (117,30)
Group 6	4.9 min	(52 ,30) (78, 30)
Group 7	5.3 min	(49, 30) (62, 30) (70, 30)
Group 8	6.2 min	(63, 30) (76, 30) (83, 30) (129, 30)
Group 9	6.75 min	(57, 15) (64, 15) (88, 15) (96, 15)
Group 10	7.1 min	(65, 30) (75, 30) (91, 30) (110, 30)
Group 11	7.6 min	(75, 30) (79, 30) (110, 30) (129, 30) (166, 30)
Group 12	8.4 min	(91, 30) (93, 30) (106, 30) (173, 30)
Group 13	9.1 min	(95, 30) (174, 30)
Group 14	9.6 min	(111, 30) (146, 30)
Group 15	10.5 min	(95, 30) (107, 30) (135, 30)

Results and Discussion

The separation of VOCs and odor compounds is shown in Figure 1. Method performance can be seen in Table VII. The calibration for the VOCs spanned from 0.2–200 ng/mL, while the odors calibration ranged from 0.001–0.256 ng/mL. The calibrations were assessed for each targeted compound, leading to different calibration ranges depending on the compound of interest. These differences are attributed to the SPME Arrows phase capacity and the extraction rate of each compound by the SPME Arrow phase.

The calibration r^2 values ranged from 0.923-0.999 (average: 0.998). A better assessment of each calibration is evaluating the % Residual Standard Error (%RSE), which tests each calibration level to the respective calibration curve. The %RSE across all compounds ranged from 2–27% (average: 6%). The two outliers being dichloromethane and 1,4-dioxane with %RSE values of 18% and 27%. All other compounds fell between 2–10% RSE. Method precision was evaluated from the seven replicate injections, showing %RSDs (Relative Standard Deviation) ranging from 2–15% (average: 4%). This falls within the typical method acceptance criteria of +/- 30%. Finally, the LOQs ranged from 0.0029–3.033 ng/mL (ppb, average: 0.223 ng/mL).

Figure 1: Analysis of VOCs and Odors in Drinking Water via HS-SPME-Arrow-GC-MS

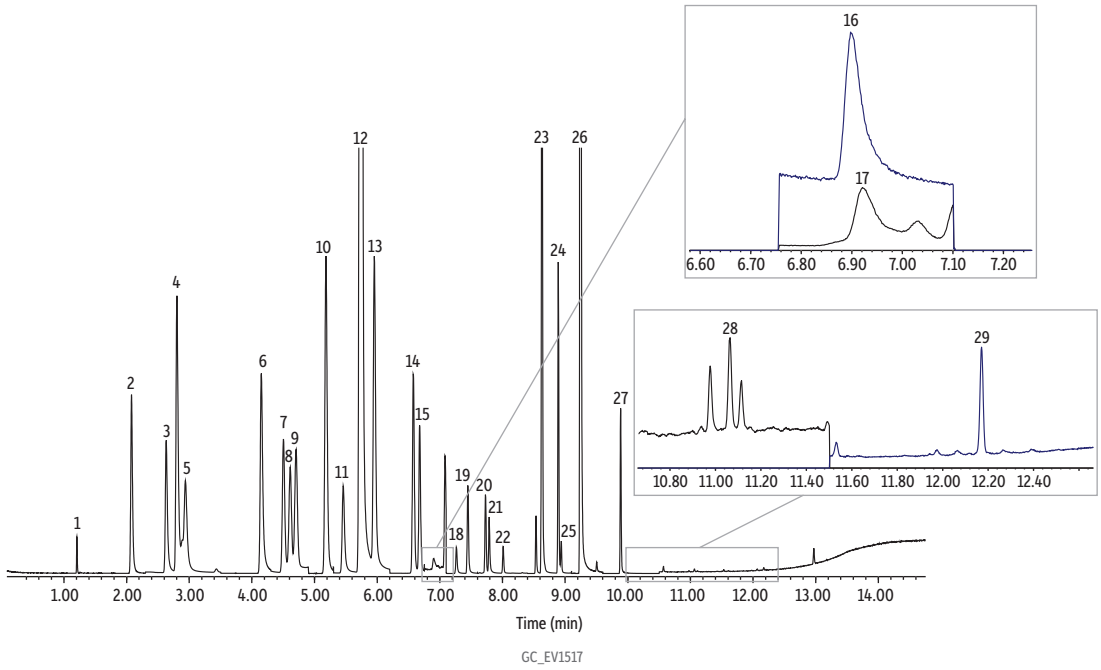

Table VII: Method Performance

Peak #	Compound	Retention Time (min)	Calibration Range (ng/mL, ppb)	Calibration Fit and Weighting	r^2	Calibration (%RSE)	LOQ	Method Precision (%RSD)
1	Chlorethene[1]	1.20	0.2-25	Quadratic, $1/x^2$	0.999	4%	0.078	4%
2	1,1-Dichloroethene[1]	2.07	0.2-25	Quadratic, $1/x^2$	0.991	9%	0.124	6%
3	Dichloromethane[1]	2.63	2-200	Quadratic, $1/x^2$	0.999	18%	3.033	15%
4	*trans*-1,2-Dichloroethene[1]	2.80	0.2-25	Quadratic, $1/x^2$	0.999	2%	0.035	2%
5	MTBE[1]	2.94	0.2-10	Quadratic, $1/x^2$	0.999	3%	0.059	3%
6	*cis*-1,2-Dichloroethene[1]	4.15	0.2-25	Quadratic, $1/x^2$	0.999	4%	0.056	3%
7	Chloroform[1]	4.50	0.2-25	Quadratic, $1/x^2$	0.998	5%	0.063	3%
8	Carbon Tetrachloride[1]	4.61	0.2-25	Quadratic, $1/x^2$	0.999	4%	0.058	3%
9	1,1,1-Trichloroethane[1]	4.70	0.2-25	Quadratic, $1/x^2$	0.997	8%	0.06	3%
10	Benzene[1]	5.18	0.2-75	Quadratic, $1/x^2$	0.998	5%	0.004	2%
11	1,2-Dichloroethane[1]	5.46	0.2-25	Quadratic, $1/x^2$	0.999	4%	0.009	4%
12	Trichloroethene[1]	5.96	0.2-75	Quadratic, $1/x^2$	0.999	4%	0.097	5%
13	1,2-Dichloropropane[1]	6.58	0.2-75	Quadratic, $1/x^2$	0.996	9%	0.05	2%
14	Bromodichloromethane[1]	6.68	0.2-75	Quadratic, $1/x^2$	0.999	4%	0.05	2%
15	1,4-Dioxane[2]	6.76	2-200	Linear, $1/x^2$	0.923	27%	0.895	3%
16	*cis*-1,3-Dichloropentane[1]	7.27	0.2-200	Quadratic, $1/x^2$	0.997	5%	0.041	2%
17	Toluene[1]	7.45	0.2-25	Quadratic, $1/x^2$	0.999	3%	0.123	6%
18	Tetrachloroethene[1]	7.73	0.2-25	Quadratic, $1/x^2$	0.999	2%	0.042	2%
19	*trans*-1,3-Dichloropropene[1]	7.79	0.2-200	Quadratic, $1/x^2$	0.997	5%	0.058	3%
20	Dibromochloromethane[3]	8.01	0.2-25	Quadratic, $1/x^2$	0.999	2%	0.047	2%
21	*m,p*-Xylene[3]	8.63	0.4-20	Quadratic, $1/x^2$	0.999	5%	0.564	14%
22	*o*-Xylene[3]	8.89	0.2-10	Quadratic, $1/x^2$	0.999	4%	0.139	7%
23	Bromoform[3]	8.94	0.2-75	Quadratic, $1/x^2$	0.998	4%	0.056	3%
24	1,2-Dichlorobenzene[3]	9.89	0.2-25	Quadratic, $1/x^2$	0.999	2%	0.045	3%
25	2-Methylisoborneol[3]	11.07	0.004-0.256	Quadratic, $1/x^2$	0.997	10%	0.005	9%
26	Geosmin[3]	12.17	0.004-0.256	Quadratic, $1/x^2$	0.996	10%	0.003	5%

ISTD Reference – Fluorobenzene[1], 1,4-Dioxane-d8[2], *p*-Bromofluorobenzene[3]

Conclusion

HS-SPME Arrow-GC-MS offers a simple approach for the determination of VOCs and Odorants in drinking water. This method shows the SPME Arrow's capabilities of quantifying a range of different compounds at various detection limits. Notably, the odorants were able to be detected at low part per trillion levels proving this is a viable sampling and testing method for the determination of their presence in drinking water. Future considerations for method optimization would be to select a more appropriate ISTD for the MIB and Geosmin.

References

1. Cobb County-Marietta Water Authority (CCMWA), Geosmin and methyl-Isoborneol (MIB), online article, 2023. https://www.ccmwa.org/education/geosmin-and-methyl-isoborneol-mib
2. United States Environmental Protection Agency (U.S. EPA), Definition and procedure for the determination of the method detection limit, revision 2, December 2016. https://www.epa.gov/sites/default/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

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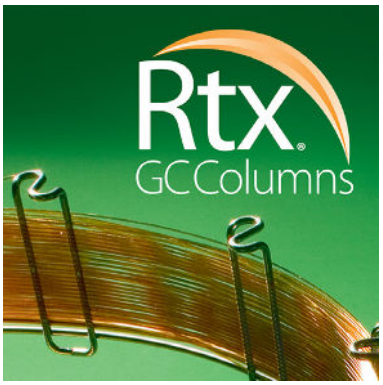

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Catalog No.	Product Name	Units
30614	1,4-Dioxane-d8 Standard, 2000 µg/mL, P&T Methanol, 1 mL/ampul	ea.

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Catalog No.	Product Name	Units
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