

Achieving ppt Levels of Environmental Volatiles with a New Headspace Sampler

Application Note

Introduction

This study focuses on the Versa Automated Headspace Analyzer and its ability to analyze Volatile Organic Compounds (VOCs) in water at the part per trillion (ppt) level.

Experimental Conditions

The Versa Automated Headspace Analyzer in conjunction with a GC/MS system was used for this analysis. The parameters for these systems are displayed in Tables 1 and 2 respectively.



Parameters	Variable	Parameters	Variable
GC Cycle Time	32.00 min	Pressurize	12.0 psig
Valve Oven Temp	120 °C	Pressurize Time	1.00 min
Transfer Line Temp	120 °C	Pressurize Equil. Time	0.25 min
Platen/Sample Temp	70 °C	Loop Fill Pressure	9.0 psig
Sample Equil. Time	10.00 min	Loop Fill Time	0.30 min
Mixer	On	Inject Time	1.00 min
Mixing Level	Fast		
Mixing Time	10.00 min		
Mixer Stabilize Time	3.00 min		

Table 1: Versa Parameters

GC/MS Parameters	
Column	Rtx®-502.2, 30 m, 0.25 mm ID, 1.4 µm dF
Oven Program	35 °C for 1 min, 8 °C/min to 160 °C then 20 °C/min to 200 °C for 3 min, run time 21.63 min
Inlet:	Temperature 200 °C, Split Ratio 30:1, Constant Flow 1.0 mL/min
Transfer Line	Temperature 220 °C
Mass Spec	Start Time 1.65 minutes, Selected Ion Monitoring (SIM) Variable, Source Temperature 230 °C

Table 2: GC/MS Parameters

Standard and Sample Preparation

Stock standards from a 524.3 and a 502.2 commercially available mix were prepared in methanol at 5 and 50 parts per million (ppm). These stock standards were used to prepare working standards in distilled water for the calibration curve and MDL study. The compound list is presented in Table 3.

An internal standard solution containing 4 ppm of fluorobenzene, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4 were prepared in methanol. 5 µL of this standard was added to all samples and blanks for a final concentration of 2.0 ppb.

The headspace samples consisted of 10 mL of distilled water or the appropriate working standard.

Calibration Curves and MDL

The stock standard above was used to make a calibration curve from 0.020 to 20 ppb. MDL samples were prepared at .050 and 0.100 ppb.

Figure 1 is the total SIM chromatogram of a 0.5 ppb standard which is typically the lower detection limit standard used in scanning GC/MS. Figure 2 is a SIM chromatogram of the 0.020 ppb standard.

The data passed the current requirements of both methods with the majority detectable below the 0.020 ppb standard. The calibration curve from 0.020 ppb to 20 ppb for most of the compounds was <10% RSD, and the correlation coefficient was >0.995 for all compounds except 1,1,2,2-tetrachloroethane.

1,2-Dibromo-3-chloropropane and 1,1,2,2-tetrachloroethane were not detectable below 0.100 ppb with this method making their calibration range from 0.100 ppb to 20 ppb.

Table 3 presents the calibration data including %RSD for both the response factors Rf and using n=7 replicate samples for MDLs, correlation coefficients, and calculated MDLs. Styrene, toluene and methylene chloride are laboratory background contaminants.

1,1,2,2-tetrachloroethane did not pass the %RSD or correlation coefficient requirements when tested as an unmodified water sample. The newly released EPA Method 524.3 uses maleic acid as a dechlorinating agent and ascorbic acid as a preservative. 1,1,2,2-tetrachloroethane did pass these requirements when tested with the addition of these acids as a matrix modifying solution.

Minimum detection limits calculated from 0.050 ppb standards were below 0.020 ppb for all of the compounds except 1,2-dibromo-3-chloropropane and 1,1,2,2-tetrachloroethane. The MDL values for these two compounds were calculated from the 0.100 ppb level standards.

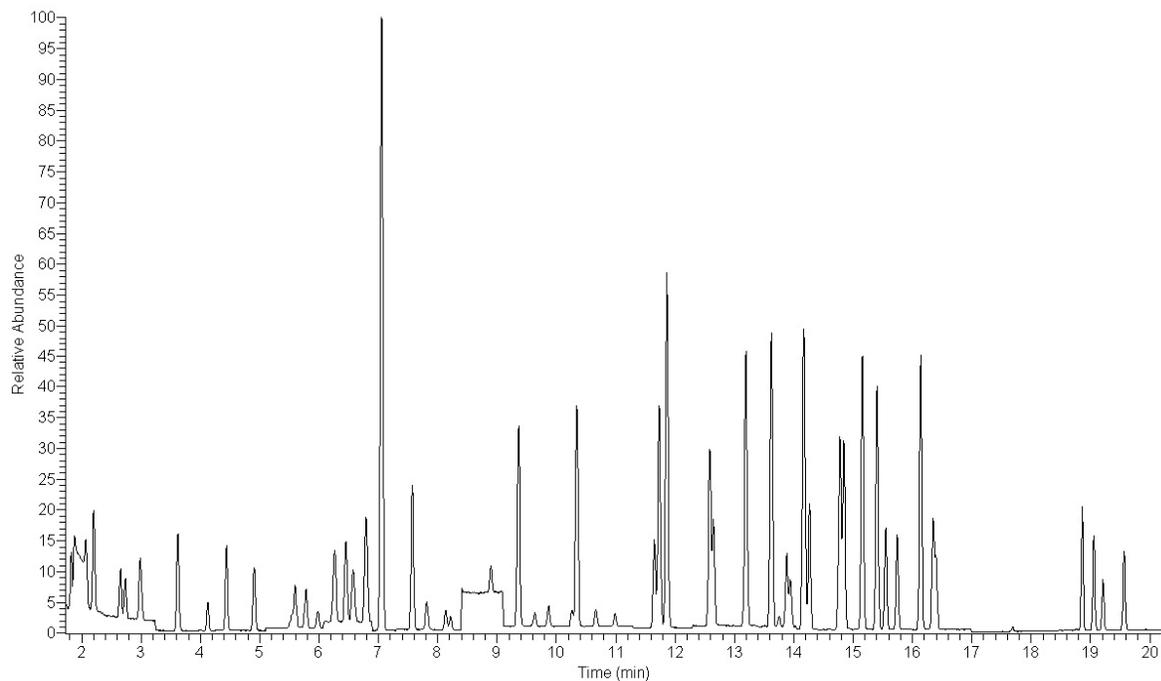


Figure 1: Chromatogram of the Summed Specific Ions of the 0.5 ppb Standard

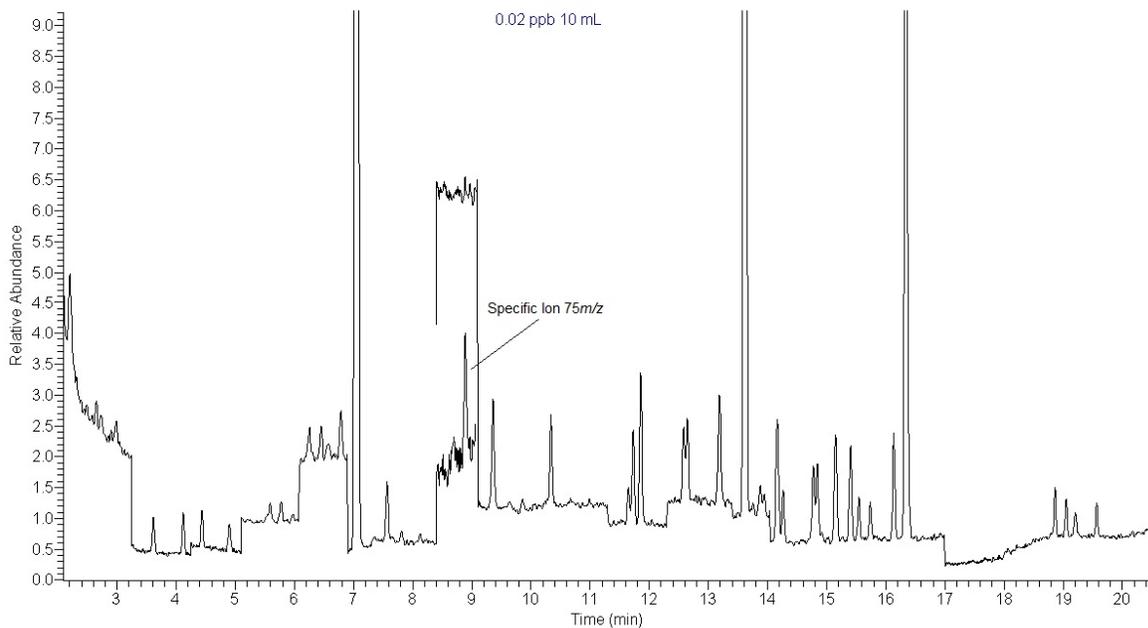


Figure 2: Chromatogram of the Summed Specific Ions of the 0.020 ppb Standard. The specific ion mass 75 m/z of cis-1,3-dichloropropene is inserted to display its peak area.

Compound	Quant Mass	Dwell Time	Confirm	Rf %RSD 0.02 -20	Linearity r ²	%RSD n=7 0.050 ppb	MDL 0.050 ppb
Dichlorodifluoromethane	85	30	101	8.1	0.9956	7.2	0.014
Chloromethane	50	30	52	6.8	0.9995	2.7	0.004
Vinyl Chloride	62	30	64	4.2	0.9990	4.5	0.008
Bromomethane	94	30	96	3.2	0.9999	8.2	0.013
Chloroethane	64	30	66	8.0	0.9998	7.3	0.012
Trichlorofluoromethane	101	30	66	9.3	0.9972	8.3	0.015
1,1-Dichloroethene	96	50	61	6.3	0.9989	6.1	0.010
Methylene Chloride	84	50	49	45.0	0.9999	5.1	0.009
trans-1,2-Dichloroethene	96	50	98	3.3	0.9998	7.2	0.011
1,1-Dichloroethane	63	50	65	3.3	0.9999	8.1	0.013
2,2-Dichloropropane (1)	77	50	79	9.8	0.9999	9.1	0.014
cis-1,2-Dichloroethene	61	50	98	5.0	0.9999	7.9	0.012
Chloroform	83	50	85	4.8	0.9999	7.0	0.011
Bromochloromethane	128	50	130	4.3	0.9999	4.4	0.006
1,1,1-Trichloroethane	97	30	99	4.8	0.9996	9.1	0.015
1,1-Dichloropropene	75	30	110	5.7	0.9995	5.0	0.008
Carbon Tetrachloride	117	30	119	9.8	0.9992	6.8	0.012
1,2-Dichloroethane	62	30	64	5.2	0.9999	3.0	0.005
Benzene	78	30	77	4.9	0.9999	5.9	0.010
<i>Fluorobenzene (IS)</i>	96	50	70	3.7			
Trichloroethene	95	50	130	7.1	0.9985	8.7	0.015
1,2-Dichloropropane	63	50	62	1.7	1.0000	6.1	0.010
Bromodichloromethane	83	50	85	6.3	0.9999	8.4	0.014
Dibromomethane	174	50	95	3.7	1.0000	4.8	0.009
cis-1,3-Dichloropropene	75	50	39	3.9	0.9998	8.9	0.012
Toluene	92	40	91	10.7	0.9998	6.0	0.010
trans-1,3-Dichloropropene	75	40	77	2.9	0.9999	8.5	0.012
1,1,2-Trichloroethane	97	40	99	5.8	0.9999	10.4	0.017
1,3-Dichloropropane	76	40	78	3.3	0.9997	6.7	0.010
Tetrachloroethene	166	40	164	2.9	0.9990	6.7	0.011
Dibromochloromethane	127	40	129	5.0	0.9999	6.5	0.010
1,2-Dibromoethane (EDB)	107	40	109	4.0	0.9999	8.8	0.014
Chlorobenzene	112	50	77	3.1	0.9998	5.2	0.008
1,1,1,2-Tetrachloroethane	131	50	133	2.8	0.9999	7.6	0.012
Ethylbenzene	91	50	106	3.0	0.9999	5.1	0.008
m-, p-Xylene	91	50	106	5.4	0.9999	5.7	0.017
o-Xylene	91	30	106	3.9	0.9999	6.2	0.010

Compound	Quant Mass	Dwell Time	Confirm	Rf %RSD 0.02 -20	Linearity r^2	%RSD n=7 0.050 ppb	MDL 0.050 ppb
Styrene	104	30	103	18.9	0.9998	6.8	0.010
Isopropylbenzene	105	30	120	5.4	0.9998	6.8	0.010
Bromoform	173	30	171	6.5	0.9999	4.6	0.008
1,1,2,2-Tetrachloroethane (2)	83	35	95	38.2 (3) 4.3 (3)	0.9880 0.9994	8.7 (4)	0.061 (4)
4-Bromofluorobenzene (IS)	95	35	174	4.6			
1,2,3-Trichloropropane	75	35	110	4.6	0.9999	6.9	0.011
n-Propylbenzene	120	35	92	6.6	0.9999	5.3	0.008
Bromobenzene	77	35	156	7.4	0.9999	8.8	0.011
1,3,5-Trimethylbenzene	105	50	120	6.8	0.9998	6.8	0.009
2-Chlorotoluene	126	50	128	7.4	0.9999	7.4	0.011
4-Chlorotoluene	91	50	126	6.8	0.9998	4.8	0.007
t-Butylbenzene	119	50	91	6.2	0.9998	7.9	0.012
1,2,4-Trimethylbenzene	105	50	120	5.8	0.9998	6.8	0.010
sec-Butylbenzene	105	40	134	8.0	0.9993	6.4	0.009
4-Isopropyltoluene	119	40	134	8.4	0.9995	5.9	0.009
1,3-Dichlorobenzene	146	40	148	3.4	0.9997	7.6	0.011
1,4-Dichlorobenzene	146	40	148	3.0	0.9998	4.6	0.007
n-Butylbenzene	91	40	134	9.7	0.9995	5.5	0.008
1,2-Dichlorobenzene-d4 (IS)	152	40	154	6.5			
1,2-Dichlorobenzene	146	40	148	2.6	0.9998	6.3	0.009
1,2-Dibromo-3-chloropropane (2)	157	70	75	5.9	1.0000	9.9 (4)	0.032 (4)
1,2,4-Trichlorobenzene	180	50	182	4.7	0.9996	3.7	0.006
Hexachlorobutadiene	225	50	227	4.8	0.9970	6.6	0.011
Naphthalene	128	50	127	4.8	1.0000	4.9	0.009
1,2,3-Trichlorobenzene	180	50	182	5.1	0.9997	7.1	0.012

Table 3: Mass Ion, Scan Rate, and Calculated Data for the VOCs Evaluated

1 – No peak detected at the 0.020 ppb levels.

2 – No peak detected at the 0.020 ppb or the 0.050 ppb levels.

3 – Upper data from the unmodified water standards. Bottom data from the ascorbic and maleic acid modified solution.

4 – MDL data calculated from the 0.100 ppb standards.

Conclusions

Versa, a static only headspace instrument, was evaluated to determine its capability of producing quantitative data for VOCs using SIM GC/MS at or below current water methods. These water methods include USEPA Method 524 and the 98/83/EC Directive. The data passed the current requirements for both methods with most of the compounds detectable below the 0.020 ppb standard. These detection limits are well below the current levels required by these methods.

References

1. USEPA Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, June 2009.