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Optimizing Volatile Organic Compound Determination by Static Headspace Sampling

Application Note - Environmental

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Abstract

Volatile contaminants in drinking, ground and wastewaters are an ongoing environmental concern throughout the world. Testing for these contaminants is generally done using a Gas Chromatograph (GC) coupled to a Mass Spectrometer. However, sampling for these compounds is dependent on the environmental regulations of the country in which you are testing. The USEPA methods for extracting VOCs from environmental samples require purge and trap sampling. On the other hand, in Europe and Canada, it is common to use static headspace sampling for the measurement of VOCs.

Introduction:

Static headspace sampling has always been a viable option for the detection of Volatile Organic Compounds (VOCs) and is readily used in Europe and Canada for testing water samples. In order to detect low level contamination of water, it is essential for the static headspace sampling and GCMS analysis parameters to be enhanced. This paper will examine automated headspace sampling of VOCs in water using an innovative sampling system that performs sample preparation on top of the GC. The sampling and analysis will be optimized for better detection of volatile compounds at low concentrations and the final results will be compared with USEPA Method 8260 requirements.

Discussion:

Purge and trap sampling involves purging the VOCs out of the matrix and trapping the analytes onto an analytical trap, the trap is then desorbed to the GC/MS. This process has a number of pros and cons. On the positive side, purge and trap is more sensitive. It is also the recommended sampling technique for USEPA Methods. Furthermore, the advent of autosampling systems has simplified sample preparation. However, purge and trap does have some negatives, including active sites, worries about foaming samples, and trap degradation.

Static headspace sampling, on the other hand, is much simpler than purge and trap sampling. For this sampling technique, the sample is brought to equilibrium and a portion of the headspace is transferred to the GC/MS for separation and analysis. The simplicity of this technique is a definite pro. Moreover, this sampling process does not develop active sites, has no need for an analytical trap and the linear calibration range can be much higher than that of purge and trap sampling. Conversely, samples need to be manually prepped thus, losing their sample integrity. Additionally, the detection limits are higher for a number of compounds. Finally, some of the analytes do not partition into the headspace well enough and need method optimization.

In recent years, GC/MS systems have become much more sensitive. The advent of SIM/Scan acquisition techniques has made low level detection a much simpler proposition. This analysis will focus on the headspace sampling and analysis of over 50 volatile organic compounds.

Experimental:

The sampling system used for this analysis was the EST Analytical FLEX autosampler fitted with a 2.5ml headspace syringe. An Agilent 7890 GC and 5975 MS were used for separation and analysis. The GC was configured with a Restek Rxi 624 Sil MS 30m x 250mm x 1.4μm column and a SKY 2mm x 6.5 x 78.5 splitless inlet liner. The MS was run in SIM/Scan mode. Refer to Tables 1 and 2 for the analysis and sampling parameters.

Autosampler	FLEX
General	
Method Type	Headspace
Sample Incubate Agitate	
Incubation Temp.	60°C
Incubation Time	20min
Agitation Speed	80%
Agitation Delay	0.0min
Agitation Duration	19min
Sample Fill	
Syringe Temperature	60°C
Syringe Needle Depth	90%
Sample Depth Speed	20%
Sample Volume	1000μl
Sample Fill Rate	10%
Sample Fill Delay	Off
Injection	
Needle Depth Speed	30%
Needle Depth	90%
Injection Rate	40%
Injection Volume	1000μl
Pre-Injection Delay	Off
Post-Injection Delay	Off
Injection Start Input	Start
Sweep Needle	
Needle Temperature	150°C
Syringe Pumps	5
Syringe Pump Volume	1200μl
Syringe Pump Speed	20%

Table 1: FLEX Autosampler Experimental Parameters

GC/MS	Agilent 7890/5975
Inlet	Split/Splitless
Inlet Temp.	200°C
Inlet Head Pressure	12.153 psi
Split	5:1
Liner	Restek SKY Liner Splitless, 2mm x 6.5 x78.5
Column	Rxi-624 Sil MS 30m x 0.25mm I.D. 1.4μm film thickness
Oven Temp. Program	45°C hold for 2.0 min, ramp 15°C/min to 220°C hold for 1.33 min, 15 min run time
Column Flow Rate	1.0ml/min.
Gas	Helium
Total Flow	9ml/min.
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Solvent Delay	0.7 min
Acquisition Mode	SIM/Scan
Scan Range	m/z 35-265
SIM Ions: 50, 52, 62, 64, 66, 85, 87, 94, 96	0.70 to 2.12 min
SIM Ions: 61, 63, 96, 101, 103, 153	2.13 to 2.62 min
SIM Ions: 49, 61, 84, 86, 96	2.63 to 3.25 min
SIM Ions: 63, 64	3.26 to 3.69 min
SIM Ions: 52, 61, 62, 75, 77, 78, 83, 85, 96, 97, 98, 110, 117, 119, 128, 130. 168	3.70 to 4.84 min
SIM Ions: 41, 63, 76, 83, 85, 88, 93, 95, 112, 114, 130, 174	4.85 to 5.86 min
SIM Ions: 75, 77	5.87 to 6.19 min
SIM Ions: 91, 92	6.20 to 6.55 min
SIM Ions: 76, 78, 83, 85, 97, 107, 109, 127, 129, 164	6.56 to 7.45 min
SIM Ions: 52, 82, 91, 106, 112, 114, 117, 131, 133	7.46 to 8.09 min
SIM Ions: 78, 91, 104, 106, 173, 175	8.10 to 8.72 min
SIM Ions: 77, 83, 85, 91, 105, 120, 126, 156	8.73 to 9.40 min
SIM Ions: 105, 111, 119, 120, 134, 146, 150, 152	9.41 to 10.17 min
SIM Ions: 91, 111, 134, 146	10.18 to 10.80 min
SIM Ions: 75, 155	10.81 to 11.61 min
SIM Ions: 102, 128, 180, 182, 190, 225	11.62 to 15 min

Table 2: GC/MS Experimental Parameters

The 8260 standards were acquired from Restek. Next, several midpoint standards were made in order to determine the optimum experimental conditions. Ultimately, it was found that ten milliliters of standard added to two grams of sodium chloride provided the optimum analyte response. The most effective sampling and analysis conditions are listed in the previous two tables.

After the experimental conditions were established, a linear curve was run from 0.5 to 200ppb. Then, seven replicate low level standards were run in order to determine method detection limits.

Furthermore, a second set of replicate samples were run at the mid-level of the curve in order to ascertain the precision and accuracy of the sampling and analysis. SIM and Scan chromatograms of the curve midpoint can be found in Figures 1 and 2 and the experimental results are listed in Table 3.

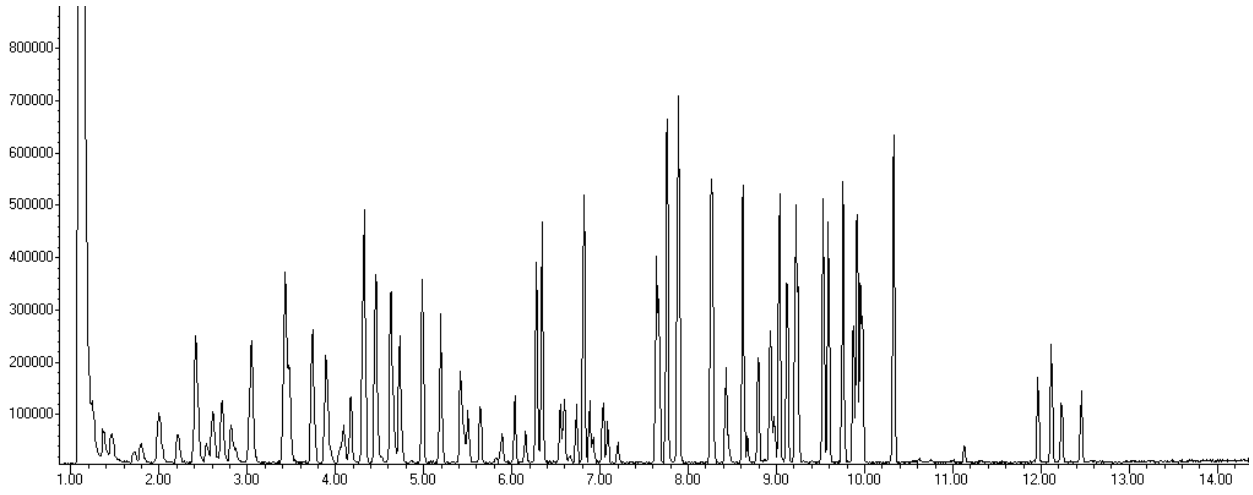

Figure 1: 50ppb Chromatogram in Scan

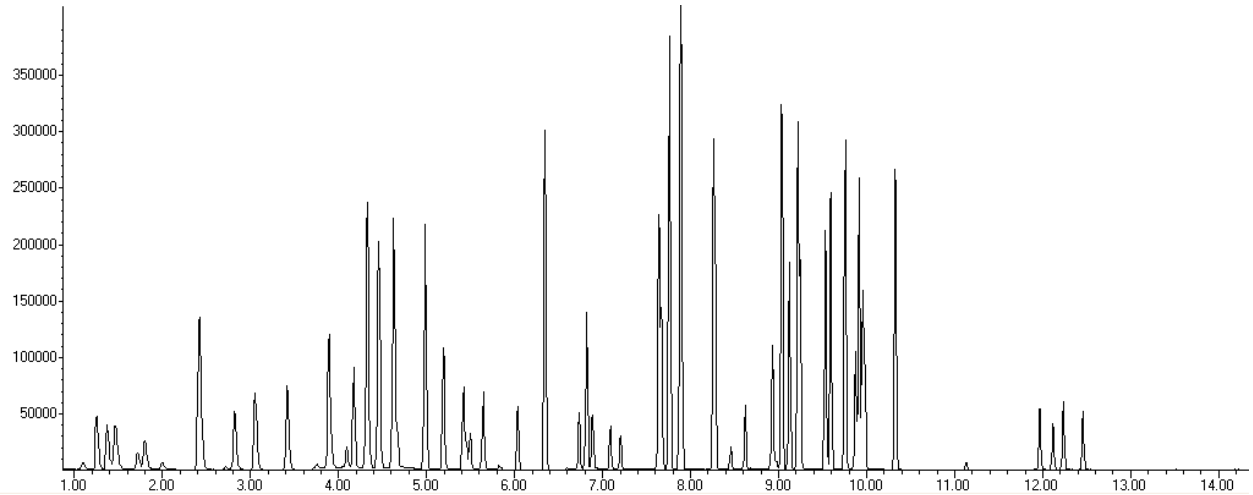

Figure 1: 50ppb Chromatogram in SIM

Compound	Curve %RSD	Ave. Curve RF	MDL	%RSD 50ppb	%Recovery 50ppb
Dichlorodifluoromethane	7.70	0.397	0.32	10.81	101.56
Chloromethane	11.17	0.356	0.39	10.03	109.17
Vinyl Chloride	11.57	0.423	0.26	8.45	114.23
Bromomethane	13.94	0.149	0.33	5.33	95.62
Chloroethane	10.15	0.269	0.23	8.41	102.60
Trichlorofluoromethane	9.26	0.423	0.28	9.94	97.13
1,1-Dichloroethene	6.44	0.356	0.17	8.49	101.55
Methylene Chloride	8.22	0.216	0.22	5.76	100.97
cis-1,2-Dichloroethene	8.29	0.314	0.13	5.42	103.09
1,1-Dichloroethane	10.22	0.667	0.21	7.45	105.25
trans-1,2-Dichloroethene	9.50	0.373	0.19	5.93	99.73
2,2-Dichloropropane	11.14	0.414	0.23	5.42	96.03
Bromochloromethane	6.32	0.103	0.16	3.34	98.29
Chloroform	7.36	0.537	0.17	6.14	102.71
1,1,1-Trichloroethane	8.63	0.650	0.25	7.59	99.53
Carbon Tetrachloride	7.61	0.544	0.26	8.73	100.03
1,1-Dichloropropene	9.15	0.618	0.28	7.80	101.56
Benzene	8.10	1.486	0.19	5.97	104.32
1,2-Dichloroethane	10.17	0.253	0.18	8.52	98.46
Trichloroethene	6.02	0.369	0.20	6.57	99.12
1,2-Dichloropropane	7.21	0.238	0.10	5.24	100.52
Dibromomethane	6.69	0.057	0.27	4.43	102.68
Bromodichloromethane	5.66	0.254	0.13	3.43	100.66
cis-1,3-Dichloropropene	6.08	0.273	0.15	3.92	100.12
Toluene	5.11	0.712	0.12	5.16	104.50
1,1,2-Trichloroethane	5.69	0.118	0.12	2.40	96.71
Tetrachloroethene	6.11	0.482	0.11	7.50	100.22
1,3-Dichloropropane	5.61	0.215	0.09	3.58	102.15
Dibromochloromethane	5.25	0.125	0.06	2.49	98.30
1,2-Dibromoethane	7.66	0.091	0.23	1.61	96.97
Chlorobenzene	4.33	0.891	0.09	4.26	100.53
1,1,1,2-Tetrachloroethane	5.80	0.290	0.10	4.60	99.10
Ethylbenzene	6.79	1.911	0.15	5.52	105.21
Xylene (m + p)	8.92	1.421	0.10	4.90	109.24
Styrene	11.04	0.885	0.10	3.47	110.98
Xylene (o)	8.65	1.341	0.08	4.22	108.33
Bromoform	11.09	0.089	0.34	3.80	93.60
Bromobenzene	7.58	1.176	0.10	5.34	99.46
1,1,2,2-Tetrachloroethane	6.71	0.326	0.10	5.10	94.44
n-Propylbenzene	8.91	4.871	0.19	5.79	105.37
2-Chlorotoluene	5.14	0.800	0.13	5.33	102.81
4-Chlorotoluene	5.11	0.808	0.15	3.69	103.71
1,3,5-Trimethylbenzene	10.07	3.039	0.16	5.12	106.84
tert-Butylbenzene	8.16	2.741	0.13	8.02	103.68
sec-Butylbenzene	8.99	0.832	0.16	9.16	104.84
1,2,4-Trimethylbenzene	9.87	2.907	0.21	3.94	107.61
1,3-Dichlorobenzene	5.29	1.380	0.14	3.46	99.16
1,4-Dichlorobenzene	6.09	1.330	0.09	2.52	98.15
1,2,-Dichlorobenzene	5.00	1.121	0.08	3.21	98.93
n-Butylbenzene	8.74	3.237	0.19	5.63	106.36
1,2-Dibromo-3-chloropropane	10.91	0.063	0.40	6.30	94.22
1,2,4-Trichlorobenzene	7.38	0.606	0.21	2.86	99.11
Naphthalene	6.75	0.955	0.13	2.94	95.02
Hexachlorobutadiene	12.36	0.543	0.25	10.71	97.42
1,2,3-Trichlorobenzene	12.38	0.486	0.09	3.56	97.42
Average	8.07	0.828	0.18	5.62	101.37

Table 3: Experimental Results Summary

Conclusions:

Static headspace sampling in conjunction with SIM/Scan acquisition proved to be a good alternative to purge and trap sampling for a number of USEPA Method 8260 compounds. The curve %RSD results showed the linearity of the curve to meet the USEPA Method 8260 requirement of 15% or better. The method detection limits of all the compounds tested also passed method requirements. Lastly, the precision and accuracy of the autosampling and analysis system was excellent, with the average precision at less than 6% RSD and the average %recovery at just over 101%.

References:

1. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); United States Environmental Protection Agency Method 8260B, Revision 2, December 1996.

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