Environmental Volatiles Using an Agilent 7697A Headspace Sampler, an Agilent 7890B GC, and an Agilent 5977A Series GC/MSD

Application Note

Environmental

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Abstract

The Agilent 7697A Headspace Sampler, Agilent 7890B GC, and Agilent 5977A Series GC/MSD system with extractor lens was used for the headspace analysis of environmental volatiles in water. EC reporting requirements, as outlined in the 98/83/EC Directive updated July 2009, were met for all compounds. Calibration was from 0.05 parts-per-billion (ppb)–20 ppb with excellent linearity. Peak shapes were very good for all compounds including the early eluting gases.

Introduction

Volatile organic compound (VOC) analyses is typically done by either purge and trap (P&T) or by headspace (HS), followed by GC/MS.

P&T is common to many USEPA methods and is also used outside the USA. It offers very good sensitivity as 5 or 25 mL of water are exhaustively extracted. The volatile analytes are concentrated on a packed trap, then backflushed into the GC. P&T can suffer from water carryover problems which can cause poor peak shape and reduced sensitivity. The hardware is more complicated than HS. There are a number of parameters to optimize, and samples can foam.

Analysis by HS extraction is a more direct approach for volatiles in water. Compounds are forced into the headspace above a sample in a sealed vial. This is done primarily by heating. Some analysts add salt to shift the equilibrium. The headspace is sampled and a portion delivered to the GC through a loop. HS extraction transfers less water to the GC, has fewer parameters to adjust, and is simple to implement.

Agilent Technologies

The 5977A Series GC/MSD has a new source with an extractor lens. This design provides greater ion throughput, higher abundance signals, and better sensitivity. Selected Ion Monitoring (SIM) is widely accepted for target compound analysis. Headspace can achieve part-per-trillion (ppt) levels using SIM and the 5977 MSD.

This application note details the use of a HS/GC/MSD Analyzer for Environmental Volatiles in Water. Calibration, limit-of-detection, reproducibility, and peak shape are addressed. Data analysis was accomplished using Agilent MassHunter software now available with the 5977A Series GC/MSD.

Experimental

Table 1 lists the recommended instrument operating parameters. These are starting conditions and may have to be optimized.

Table 1. *Headspace, Gas Chromatograph, and Mass Spectrometer Conditions*

GC	Agilent 7890B GC
Inlet	EPC Split/Splitless or MMI
Mode	Hot split
Heater	On 150 °C
Pressure	On 6.4 psi
Total flow	On 41 mL/min
Septum purge flow	Off
Run time	15.8 minutes
Gas saver	Off
Split ratio	40:1
Split flow	40 mL/min
Cryo	Off
S/SI Liner	Agilent 1.0 mm straight, no wool (p/n 5190-4047)
Oven	120 V or 240 V

Oven ramp	°C/min	Next °C	Hold minutes
Initial		30	0.30
Ramp 1	10	185	0.00

Total run time	15.8 minutes
Equilibration time	0.5 minutes
Oven max temperature	260 °C
Column	Agilent DB 5 MS UI (p/n 122-5533 UI)
Length	30.0 m
Diameter	0.25 mm
Film thickness	1.0 µm
Mode	Constant flow
Pressure	6.40 psi
Nominal initial flow	1.0 mL/min
Inlet	Front
Outlet	MSD
Outlet pressure	Vacuum

Headspace	Agilent 7697A Headspace Sampler, 111 Vial Sampler
Oven temperature	70 °C
Loop temperature	85 °C
Transfer line temperature	120 °C
Timing settings	
Vial equilibration (min)	10.00
Injection duration (min)	0.30
GC cycle time (min)	28.00
Vial and loop settings	
Vial size	20 mL
Vial shaking	Level 3
Vial pressurization	15 psi
Vial depressurization	4 psi
Loop size	1.0 mL
Extraction time	0.3 minute
Mode	Single extraction
Transfer line flow	> 20 mL/min
Transfer Line temperature	120 °C
Transfer line tubing	250 µm id uncoated deactivated fused silica
Vial size	20 mL p/n 5182-0837
Vial cap	Aluminum, PTFE/Si (p/n 5183-4477)
MSD	Agilent 5977A Series GC/MSD, Triple-axis detector trace ion detection enabled
Drawout lens	3 mm Standard aperture drawout lens
Solvent delay	0.0 minutes
SIM groups	19
SIM ions	3 to 15 ions/group
SIM dwell	20–100 msec/ion
Quad temperature	200 °C
Source temperature	250 °C
Transfer line temperature	190 °C
Tune type	Extractor etune.u and Autotune atune.u
EMV mode	Gain factor = 5

Calibration Standards

Calibration Mixes
- Two mixes, each at 2,000 ppm in methanol, were codiluted into methanol at 20, 2, 0.2, 0.1, and 0.05 ppm. Methanol dilutions spiked at 15 µL into 15 mL water, resulted in 20, 2, 0.2 0.1, and 0.05 ppb concentrations for calibration. Gases at 2x these values.

- 60 volatile compounds (p/n DWM-588)

- Six gases (p/n DWM-544) and three IS/SS compounds (p/n STM-320N), available from Ultra Scientific, North Kingstown, RI.

Split injection provides sufficient flow to flush the loop and transfer the analytes to the column in a short period of time. A split ratio of 40:1 gives good sensitivity while minimizing the amount of water on the column. A lower split ratio, such as 20:1, gives better sensitivity with some loss in peak shape for the early eluting gases. Split ratios lower than 20:1 showed significant peak shape loss due to water on the column and lack of analyte refocussing at 30 °C.

The straight bore 1.0-mm liner without glass wool resulted in the best peak shapes at the 40:1 split. Both 2-mm and 4-mm liners, with and without glass wool, gave the worst peak shapes for the earliest eluters. The transfer line, which feeds into the liner, was left with 35 mm protruding past the inlet septum. The column was left 30 mm above the ferrule, (24 mm if using S/SL), which is more than the typical distance. This positioned the column close to the transfer line and in combination with the narrow liner minimized peak broadening

The inlet top weldment was replaced with the accessory Agilent 7890A S/SL MMI Weldment for Headspace (p/n G3521A). This eliminates splicing the transfer line into the carrier line. The septum purge line exists, but the carrier is fed directly from the inlet EPC module to the headspace sampler.

The oven initial temperature is 30 °C. Higher initial temperatures result in broader early eluters and lower signal-to-noise (S/N). The 30 m × 0.25 mm, 1.0 µm DB 5MS UI column was chosen based on previous work [1]. Laboratories often use DB-624 type columns, which were also investigated. Peak shapes were worse for some compounds on the DB-624. All linearity data were identical for the two columns and only the DB 5MS UI results are reported here.

The headspace vial temperature was 70 °C, equilibrated for 10 minutes, with a pressurization of 15 psi, providing the necessary sensitivity and calibration range.

The standard 3-mm drawout lens was used for best sensitivity and sufficient linearity across the calibration range of 0.05–20 ppb.

A subset of compounds was taken from USEPA Method 524 and is typical of many EU methods. An exisiting data acquisition method, from E.02 MSD Chemstation, was loaded directly into the new revision F software and used with minor modification (Figure 1). All SIM acquisition groups, ions, and times were preserved.

Figure 1.   Agilent 5977A Series GC/MSD acquisition, after directly loading an Agilent 7890-5975 method.

A quantitation database of 60 compounds was converted, from an existing MSD Chemstation Classical DA method (Figure 2). ISTDs were added for calibration and quantitation to both the acquisition and DA methods.
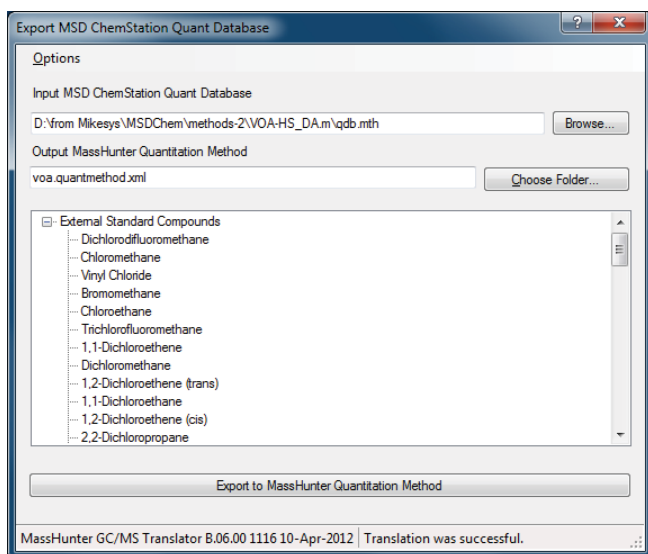

Figure 2. *Agilent MassHunter 5977 Data Analysis - Existing MSD Chemstation data analyses methods for are easily converted to MassHunter methods.*

Methanolic standards were codiluted from two 2,000 parts-per-million (ppm) commercially available standards, into methanol containing the 3 ISTDs at 2 ppm. The methanol standards were made at 20, 2, 0.2, 0.1, and 0.05 ppm. The highest methanol mixed standard at 20 ppm was stable for only a few days. All other levels had to be remade daily for reproducible performance of the early eluting gases. The calibration levels for the six gases are present at 2x greater concentration than that listed above.

A 15-µL spike into 15 mL water was used to achieve the calibration levels. The resulting concentrations in water were 20, 2, 0.2, 0.1, and 0.05 ppb, with the ISTDs at 2 ppb. All calibrations were done internal standard.

Results and Discussion

A total ion chromatogram (TIC) from a SIM acquisition of the lowest calibration level is shown in Figure 3. All 60 drinking water analytes elute in less than 16 minutes. Vinyl chloride is overlayed, with good peak shape and S/N.

The R^2 values for the five-level calibration are shown in Table 2. Excellent linearity is shown for all compounds with an R^2 range of 0.9997 to 1.0000.
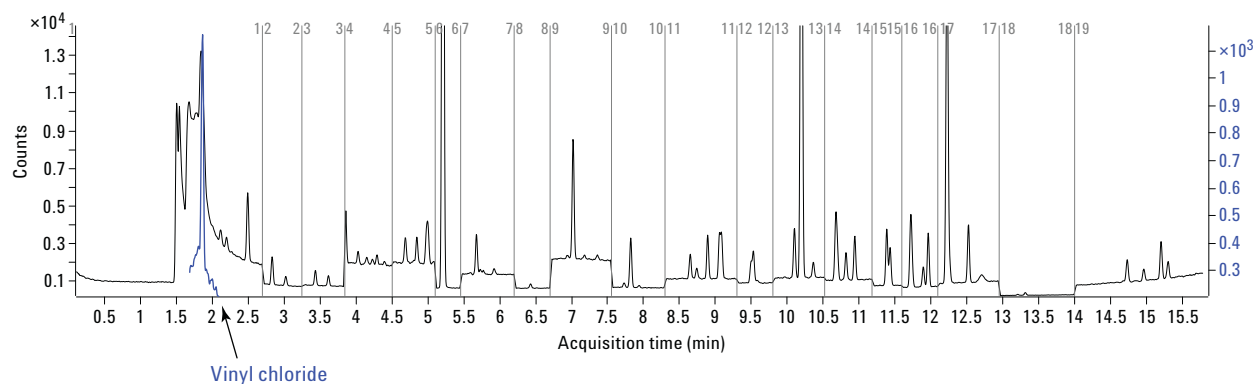

Figure 3. *SIM-TIC of volatiles standard lowest calibrator, 54 compounds at 0.05ppb, three ISTDs at 2 ppb and six gases at 0.10 ppb.*

Table 2.   Analytes and Linearity, R^2

Analyte	R.T	CAS#	Target	Q1	Q2	SIM group	R^2
Dichlorodifluoromethane	1.69	75718	85	87	101	1	0.9997
Chloromethane	1.81	74873	50	52		1	1.0000
Vinyl chloride	1.91	75014	62	64		1	0.9999
Bromomethane	2.12	74839	94	96		1	1.0000
Chloroethane	2.20	75003	64	66	49	1	1.0000
Trichlorofluoromethane	2.51	75694	101	103	66	1	1.0000
1,1-Dichloroethene	2.85	75354	61	96	98	2	1.0000
Dichloromethane	3.03	75092	49	84	86	2	1.0000
1,2-Dichloroethene (*trans*)	3.45	156605	96	98	63	3	1.0000
1,1-Dichloroethane	3.63	75343	63	65	83	3	1.0000
1,2-Dichloroethene (*cis*)	4.04	156592	61	96	98	4	1.0000
2,2-Dichloropropane	4.16	594207	77	41	79	4	1.0000
Bromochloromethane	4.24	74975	130	49	128	4	1.0000
Chloroform	4.31	67663	83	85	47	4	1.0000
1,1,1-Trichlorethane	4.70	71556	97	99	61	5	1.0000
1,2-Dichloroethane	4.81	107062	62	64		5	1.0000
1,1-Dichloropropene	4.86	563586	75	39	110	5	1.0000
Benzene	4.99	71432	78	77		5	1.0000
Carbon tetrachloride	5.01	56235	117	119	121	5	1.0000
Fluorobenzene (IS)	5.22	462066	96	70	50	6	
Trichloroethene	5.67	79016	95	130	132	7	0.9999
1,2-Dichloropropane	5.74	78875	63	62	41	7	1.0000
Dibromomethane	5.77	74953	174	93	95	7	1.0000
Bromodichloromethane	5.93	75274	83	85	47	7	1.0000
cis-1,3-Dichloropropene	6.43	10061015	75	39	77	8	1.0000
trans-1,3-Dichloropropene	6.95	10061026	75	39	77	9	1.0000
Toluene	7.03	108883	91	92	65	9	1.0000
1,1,2-Trichloroethane	7.19	79005	97	83	99	9	1.0000
1,3-Dichloropropane	7.35	142289	76	41	78	9	1.0000
Dibromochloromethane	7.74	124481	127	129	131	10	1.0000
Tetrachloroethene	7.83	127184	166	164	129	10	1.0000
1,2-Dibromoethane	7.95	106934	107	109	79	10	1.0000
Chlorobenzene	8.65	108907	112	77	114	11	1.0000
1,1,1,2-Tetrachloroethane	8.74	630206	131	133	117	11	1.0000
Ethylbenzene	8.90	100414	91	106	51	11	1.0000
m-Xylene	9.06	108383	91	106	105	11	1.0000
p-Xylene	9.09	106423	91	106	105	11	1.0000
Styrene	9.50	100425	104	103	78	12	1.0000
o-Xylene	9.54	95476	91	106	105	12	1.0000
Bromoform	9.59	75252	173	171	175	12	1.0000
1,1,2,2-Tetrachloroethane	9.97	79345	83	85	95	13	1.0000
Isopropylbenzene (cumene)	10.10	98828	105	120	77	13	1.0000
1,2,3-Trichloropropane	10.11	96184	75	110		13	1.0000

Table 2.   Analytes and Linearity, R^2 (continued)

Analyte	R.T	CAS#	Target	Q1	Q2	SIM Grp	R^2
4-Bromofluorobenzene (IS)	10.19	460004	95	174	176	13	
Bromobenzene	10.37	108861	77	156	158	13	1.0000
n-Propylbenzene	10.68	103651	120	92	65	14	1.0000
2-Chlorotoluene	10.70	95498	126	128		14	1.0000
4-Chlorotoluene	10.82	106434	91	126	125	14	1.0000
1,3,5-Trimethylbenzene	10.94	108678	105	120	77	14	0.9999
tert-Butylbenzene	11.39	98066	119	91	134	15	1.0000
1,2,4-Trimethylbenzene	11.44	95636	105	120	77	15	0.9999
sec-Butylbenzene	11.72	135988	105	134	91	16	0.9999
1,3-Dichlorobenzene	11.73	541731	146	148		16	1.0000
1,4-Dichlorobenzene	11.89	106467	146	148		16	1.0000
p-Isopropyltoluene (*p*-Cymene)	11.97	99876	119	134	91	16	0.9999
1,2-Dichlorobenzene-d4 (IS)	12.22	2199691	152	154	115	17	
1,2-Dichlorobenzene	12.26	95501	146	148	111	17	1.0000
n-Butylbenzene	12.53	104518	91	92	134	17	0.9999
1,2-Dibromo-3-chloropropane	13.21	96128	157	75	155	18	1.0000
1,2,4-Trichlorobenzene	14.73	120821	180	182	145	19	1.0000
Naphthalene	14.95	91203	128	127	129	19	1.0000
Hexachlorobutadiene	15.19	87683	225	227	223	19	1.0000
1,2,3-Trichlorobenzene	15.30	87616	180	182	145	19	1.0000

Table 3 shows the Instrument Detection Limit (IDL) for the EC named compounds. The IDL values are calculated from the standard deviation of seven replicate runs of the lowest calibration standard. Reporting levels are easily met based on these IDL values which demonstrates the excellent reproducibility of the system. All 60 compounds had IDL values < 0.10 ppb.

Table 3.   EC Directive Named Compounds and Instrument Detection Limits

2009 EC named compounds	R.T.	2009 EC reporting level (ppb)	5977 IDL (ppb)
Vinyl chloride	1.91	0.5	0.060
1,2-Dichloroethane	4.81	3.0	0.023
Benzene	4.99	1.0	0.020
Trichloroethene	5.67	10.0	0.021
Tetrachloroethene	7.83	10.0	0.017

Higher ion throughput is achieved using the new extractor lens source. Analytes with low background have improved S/N. The S/N, or sensitivity, improvement varies by compound and on the target ion used. Eight replicates of the lowest calibration standards were run, two with atune.u, two with etune.u, two with atune.u, and two with etune.u. Those run with etune.u used the extractor lens in the tune. Seventeen compounds were selected from those eight files for the S/N calculations.

The S/N values were averaged across the four like runs. Improvement ranged from a 2.7x increase in sensitivity, toluene, to no increase, vinyl chloride. In all cases, the ion abundances were higher using etune.u. There was no sensitivity dependence on retention time.

Peak shape is important for integration, accurate quantitation, and reproducibility. Figure 4 shows a screen capture from the new Mass Hunter Quantitation software for the 5977A Series GC/MSD. The earliest eluters can have peak shape problems due to their volatility and coelution with water. In this system, vinyl chloride, for example, has excellent peak shape even at the lowest calibration level.

The MassHunter Quantitation software allows for the rapid review of multiple datafiles, in this case the five calibration levels, as shown in Figure 4, at the top. Datafiles can be cycled through while leaving a single analyte displayed. Compounds can be reviewed either manually or by automation scrolling, functionally similar to Qedit in Classic Data Analysis.

Conclusions

The 7697A Headspace Sampler, Agilent 7890B GC, and Agilent 5977A Series GC/MSD system meets the EC requirements for volatiles in water as outlined in the 98/83/EC Directive updated 2009. Calibration from 0.05 ppb–20 ppb showed excellent linearity, as measured by R^2, for all analytes. Reproducibilty of replicate injections resulted in instrument detection limits of < 0.10 for the 60 analytes. Peak shapes were very good for all compounds including the early eluting gases as a result of using a narrow bore liner, and a 40:1 split ratio. Sensitivity, as measured by S/N, improved up to 2.7 fold using the extractor lens source in the 5977A Series GC/MSD.
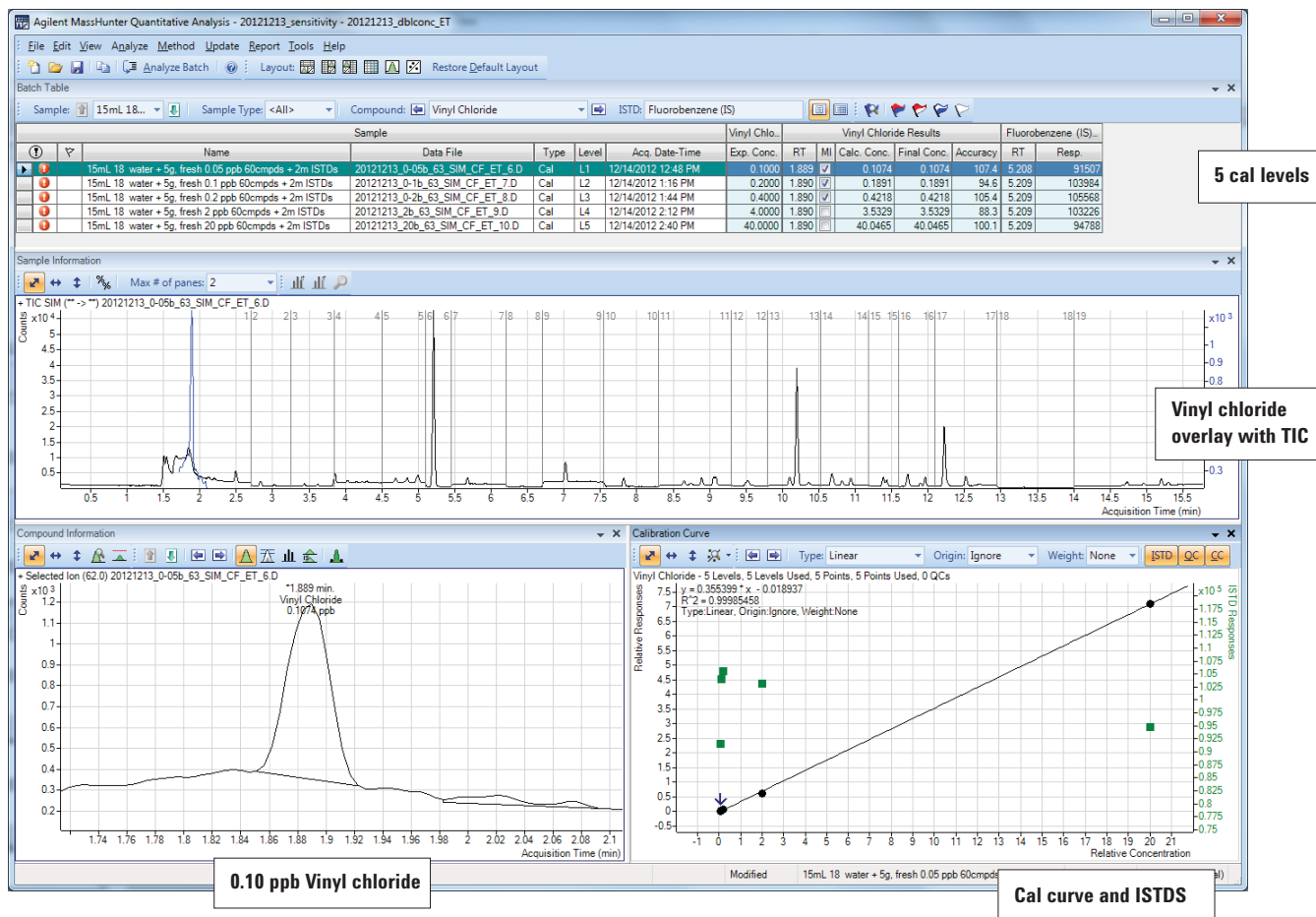

Figure 4.   Agilent MassHunter 5977 Data Analysis: vinyl chloride calibration from 0.10–40 ppb.

Reference

1. Mike Szelewski, "Environmental Volatiles using a Headspace-GC/MSD Analyzer", Agilent Technologies, Inc., Application Note, publication 5990-7907, www.agilent.com/chem

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

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