



# Improved Volatiles Analysis Using Static Headspace, the Agilent 5977B GC/MSD, and a High-efficiency Source

## Application Note

Environmental

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### Introduction

A preliminary assessment of environmental volatiles in water using static headspace analysis was performed using the Agilent 7697A Headspace Sampler, Agilent 7890B GC, and the Agilent 5977B GC/MSD system with high efficiency source (HES). The revolutionary design of the HES produces a higher ion current yield for many compounds (greater sensitivity), which allows flexible approaches to sample analysis such as lowering detection limits, reducing sample size, speeding up analysis, and so forth.

Volatile organic analysis (VOA) by static headspace is a widely applied technique, but it is also particularly challenging as the response factors for the many potential analytes vary widely. This application note presents a survey of select compounds of environmental interest as an indication of what may be achieved with the 5977B GC/MSD in this approach.

Analysis was performed in selected ion monitoring mode of a mixture of VOA compounds spiked into reverse osmosis (RO) water over a calibration range of 0.02–20 µg/L. Replicate injections were made at 0.04 µg/L to assess the method detection limits (MDL). A study of replicates of local tap water was used to demonstrate long-term stability for some naturally occurring compounds.



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## Materials and Methods

### Sample preparation

A 10 mL volume of water was added to each vial. Aliquots of Stock Standard (prepared in methanol) and Stock Internal Standard (prepared in methanol) were spiked into the solution and the vial sealed. Standards were prepared at 0.02, 0.05, 0.1, 0.2, 0.5, 1, 10, and 20 µg/L.

Table 1 presents a summary of the instrumental acquisition conditions.

Table 1. Headspace Conditions and MS Conditions

Headspace parameters	Agilent 7697A Headspace Sampler	GC parameters	Agilent 7890B GC
<b>Instrument settings</b>		<b>Inlet</b>	
Loop size	1 mL	Inlet type	Split/Splitless Inlet (SSL)
Transfer line type	Fused Silica, deactivated (p/n160-2535-5)	Mode	Split
Transfer line diameter	0.53 mm	Inlet liner	Straight, 2 mm id, 250 µL (p/n 5181-8818)
HSS-GC coupling	Transfer line interface (G3520A)	Heater	125 °C
Carrier control	GC Instrument	Column flow	1.5 mL/min constant flow
Pressurization gas	Helium	Total flow	25 mL/min
Vial standby flow	20 mL/min	Septum purge flow	1.0 mL/min
<b>Temperature settings</b>		Gas saver	OFF
Oven temperature	75 °C	Split ratio	15:1
Loop temperature	75 °C	Split flow	22.5 mL/min
Transfer line temperature	110 °C	<b>Oven</b>	
Transfer line interface (Aux1)	115 °C	Column	Agilent VF-624 MS
<b>Timing settings</b>		Column dimensions	60 m × 0.25 mm, 1.4 µm
Vial equilibration time	12 minutes	Equilibration time	0.25 minutes
Injection duration	0.3 minutes	Temperature program	32 °C (2 minutes), 12 °C/min to 220 °C (5 minutes)
GC cycle time	30 minutes	<b>Mass Selective Detector parameters Agilent 5977B</b>	
<b>Vial and loop settings</b>		Type	High Efficiency Source (HES EI)
Vial size	20 mL	Source temperature	300 °C
Vial shaking	Level 7	Quad temperature	150 °C
Fill pressure	10 psi	Transfer line temperature	280 °C
Fill time	0.2 minutes	Tune file	HES Auto Tune (HES_Atune.u)
Loop ramp rate	20 psi/min	Acquisition type	SIM (see Table 2)
Loop final pressure	7 psi	Solvent delay	3.95 minutes
Loop equilibration time	0.01 minutes	Gain factor	3
Post injection purge	100 mL/min for 2 minutes		
Leak check	Default, 0.2 mL/min		
Mode	Single Extraction		

## Results and Discussion

Table 2 gives the results of an MDL study performed at 0.04 µg/L, with nine replicate analyses. Note that all MDLs are below 0.025 µg/L or 25 ppt with the exception of two compounds, which have MDLs below 30 ppt. The majority of compounds produce MDLs below 0.015 µg/L, including some compounds with relatively low response.

Table 2. A Summary of Selected Compounds Acquired Stating Retention Times in Minutes, Target Quantitation Ion (SIM), and MDL Calculated for Nine Replicates at 0.04 µg/L

Name	RT	Quant ion	MDL	Name	RT	Quant ion	MDL
Vinyl chloride	4.934	62	0.004	1,2-Dibromoethane	13.427	106.9	0.006
Bromomethane	5.611	93.9	0.003	Chlorobenzene	13.969	112	0.015
Chloroethane	5.806	64	0.003	Ethylbenzene	14.03	91	0.014
1,1-Dichloroethene	7.007	95.9	0.008	1,1,1,2-Tetrachloroethane	14.049	130.9	0.005
<i>trans</i> -1,2-Dichloroethene	8.007	95.9	0.009	<i>o</i> -Xylene	14.664	91	0.018
1,1-Dichloroethane	8.554	63	0.004	Styrene	14.683	104	0.015
<i>cis</i> -1,2-Dichloroethene	9.19	95.9	0.011	Bromoform	14.975	170.8	0.006
2,2-Dichloropropane	9.208	77	0.013	1,1,2,2-Tetrachloroethane	15.45	82.9	0.041
Bromochloromethane	9.47	127.8	0.004	1,2,3-Trichloropropane	15.567	110	0.007
1,1,1-Trichloroethane	9.769	96.9	0.005	Bromobenzene	15.573	155.9	0.017
1,1-Dichloro-1-propene	9.921	75	0.012	<i>n</i> -Propylbenzene	15.63	91	0.017
Carbon tetrachloride	9.94	116.9	0.003	2-Chlorotoluene	15.768	91	0.016
Benzene * (blank issue)	10.165	78	0.009	1,3,5-Trimethylbenzene	15.84	105	0.018
1,2-Dichloroethane	10.202	62	0.006	4-Chlorotoluene	15.914	91	0.018
Trichloroethene	10.848	129.9	0.009	<i>tert</i> -Butylbenzene	16.225	134	0.017
1,2-Dichloropropane	11.165	63	0.005	<i>sec</i> -Butylbenzene	16.499	105	0.016
Dibromomethane	11.275	173.8	0.006	4-Isopropyltoluene	16.67	119	0.017
Bromodichloromethane	11.421	82.9	0.005	1,3-Dichlorobenzene	16.719	145.9	0.020
<i>cis</i> -1,3-Dichloropropene	11.89	75	0.014	1,4-Dichlorobenzene	16.841	145.9	0.023
<i>trans</i> -1,3-Dichloropropene	12.506	75	0.013	<i>n</i> -Butylbenzene	17.194	134	0.020
1,1,2-Trichloroethane	12.762	96.9	0.011	1,2-Dichlorobenzene	17.316	145.9	0.021
Tetrachloroethene	12.884	163.8	0.009	1,2-Dibromo-3-chloropropane	18.334	154.9	0.010
1,3-Dichloropropane	12.963	76	0.009	1,2,4-Trichlorobenzene	19.493	179.9	0.028
Dibromochloromethane	13.238	126.8	0.004	Hexachlorobutadiene	19.651	224.8	0.006

\*Blanks showed some low-level contamination for benzene.

Figure 1 shows an example of the linearity achieved over the concentration range 0.02 to 20 µg/L for several representative compounds. Figures 2 and 3 show the system stability for a few compounds of interest. It is noteworthy that these preliminary results do not benefit from the use of internal standard corrections (that is, external standard calibration, and so forth), which can be expected to greatly improve all aspects of the analysis.

## Conclusions

These preliminary results suggest a significant improvement in detection limits is possible in VOA applications through the HES of the Agilent 5977B GC/MSD. The signal improvement provided is not complicated by interferences, and results in clear enhancements in detection.

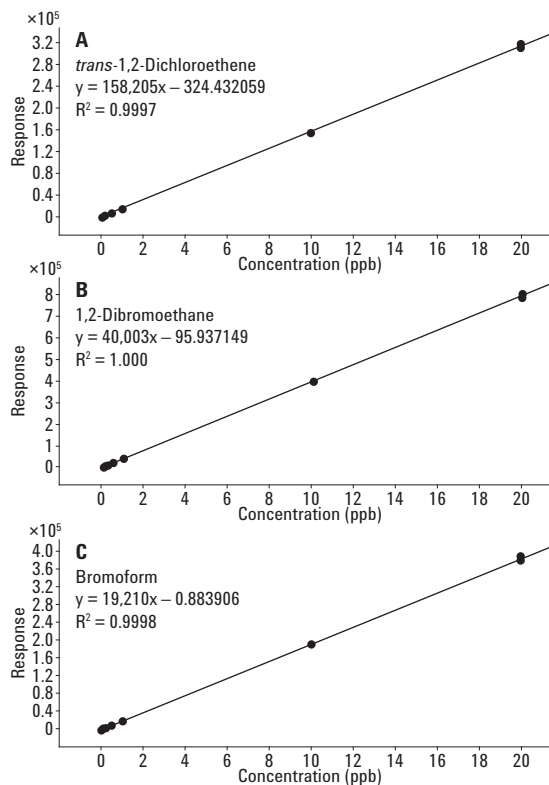


Figure 1. Linearity to 20 µg/L (external standard) for *trans*-1,2-dichloroethene (A), 1,2-dibromoethane (B), and bromoform (C).

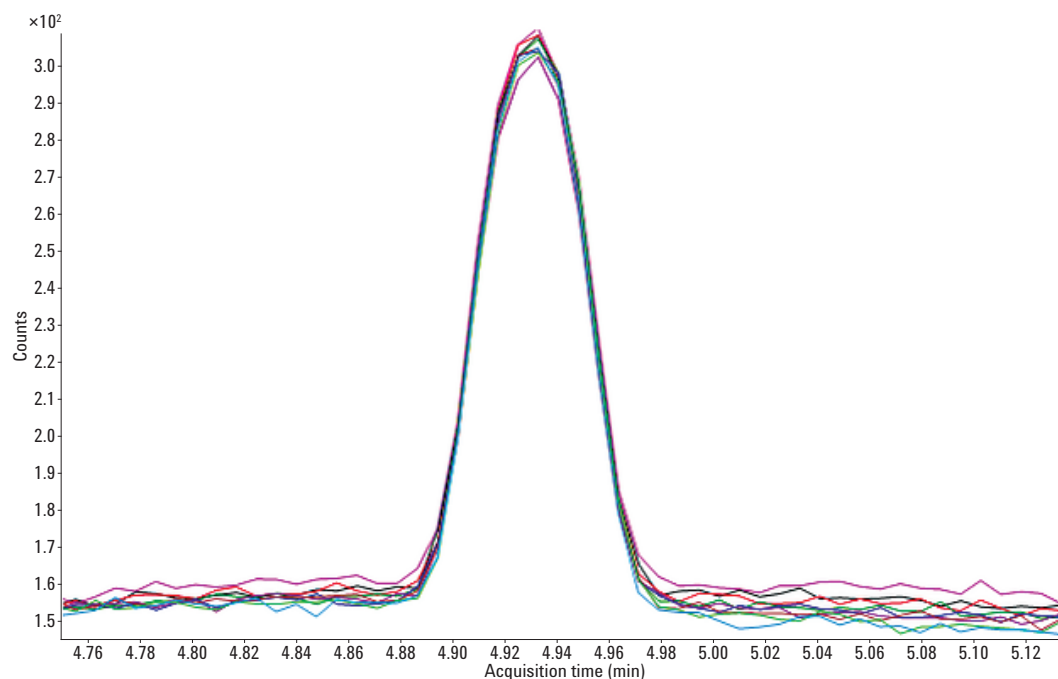


Figure 2. Overlay of the EIC for nine replicate injections of vinyl chloride at 0.04 µg/L.

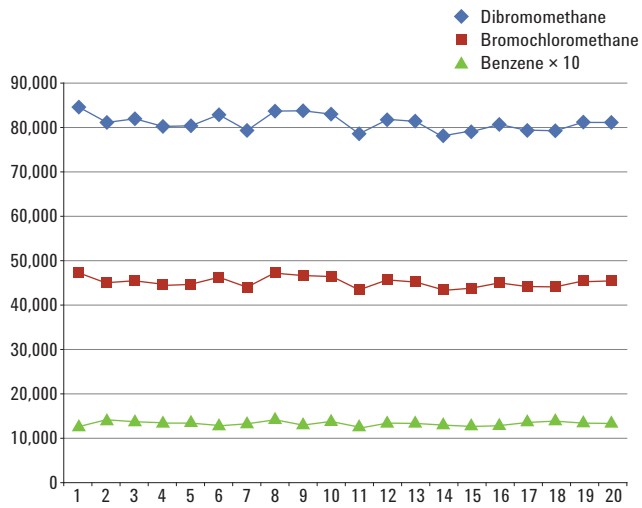


Figure 3. Response as peak areas for replicate injections (n = 20) of selected compounds showing system stability in time: benzene ~0.01 ppb, dibromomethane 1.5 ppb, and bromochloromethane 0.8 ppb.

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Printed in the USA  
January 7, 2016  
5991-6539EN



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