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

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Introduction

The benefits of an efficient ion source were brought to bear on volatile organic analysis (VOA) of water. Although static headspace sampling is a widely accepted technique, response factors for the list of possible analytes vary widely. Due to the increased ion current created within the High Efficiency Source (HES) and associated improvement in sensitivity, results were obtained which suggest that a significant improvement in detection limits for VOA targets is possible. Method detection limits (MDL) for the majority of 48 target analytes were equal to or below 0.015 µg/L, or 15 ppt. Overall stability of the analysis was demonstrated by injecting replicates of local tap water to monitor some naturally occurring compounds.

Method

Analysis was performed in selected-ion-monitoring mode of a mixture of VOA compounds spiked into reverse osmosis water over a calibration range of 0.02 – 20 µg/L. To each headspace vial was added 10 mL water. 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. Nine replicate injections were made at 0.04 µg/L to assess the method detection limits (MDL). Tap water samples were injected 20 times, consecutively, in order to monitor stability of incurred volatile compounds.

	Headspace Parameters	Agilent 7697A Headspace Sampler
Instrument Settings	Loop Size	1 mL
	Transfer Line Type	Fused Silica, deactivated, (PN 160-2535-5)
	Transfer Line Diameter	0.53 mm
	HSS-GC coupling	Transfer Line Interface (G3520A)
	Carrier Control	GC Instrument
	Pressurization gas	Helium
	Vial standby flow	20ml/min
Temperature Settings	Oven Temperature	75 °C
	Loop Temperature	75 °C
	Transfer Line Temperature	110 °C
	Transfer Line Interface	115 °C
Timing Settings	Vial Equilibration Time	12 min
	Injection Duration	0.3 min
	GC Cycle Time	30 min
Vial and Loop Settings	Vial Size	20 mL
	Vial Shaking	Level 7
	Fill Pressure	10 psi
	Fill Time	0.2 min
	Loop Ramp Rate	20 psi/min
	Loop Final Pressure	7 psi
	Loop Equilibration Time	0.01 min
	Post Injection Purge	100 ml/min for 2 min
	Leak Check	Default, 0.2 ml/min
	Mode	Single Extraction

Method, cont.

New 5977B High Efficiency Source

5977B High Efficiency Source, magnet removed

More intense electron beam **x** Longer path length for electron beam/effluent interaction

= Up to 20x More Ions Produced

Gas Chromatograph Parameters	Agilent 7890B GC
Inlet Type	Split/Splitless Inlet (SSL)
Mode	Split
Inlet Liner	Straight, 2mm ID 250 µl (PN 5181-8818)
Heater	125°C
Column Flow	1.5 ml/min constant flow
Total Flow	25 mL/min
Septum Purge Flow	1.0 ml/min
Gas Saver	OFF
Split Ratio	15:1
Split Flow	22.5 ml/min
Column	Agilent VF-624 MS
Column Dimensions	60 m x 0.25 mm x 1.4 µm
Equilibration Time	0.25 min
Temperature Program	32°C (2 min), 12°C/min to 220°C (5 min)
Mass Selectice Detector Parameters	**Agilent 5977B**
Source Type	High Efficiency Source (HES EI)
Source Temperature	300°C
Quad Temperature	150°C
Transfer Line Temperature	280°C
Tune File	HES Auto Tune (HES_Atune.u)
Acquisition Type	SIM
Solvent Delay	3.95 min
Gain Factor	3

Better Method Detection Limits Means More Flexibility

The table below shows 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.

Selected Compounds Acquired: Retention Times in Minutes, Target Quantitation Ion (SIM), and MDL (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
trans-1,2-Dichloroethene	8.007	95.9	0.009	o-Xylene	14.664	91	0.018
1,1-Dichloroethane	8.554	63	0.004	Styrene	14.683	104	0.015
cis-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	n-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	tert-Butylbenzene	16.225	134	0.017
1,2-Dichloropropane	11.165	63	0.005	sec-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	0.02
cis-1,3-Dichloropropene	11.89	75	0.014	1,4-Dichlorobenzene	16.841	145.9	0.023
trans-1,3-Dichloropropene	12.506	75	0.013	n-Butylbenzene	17.194	134	0.02
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	0.01
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.

Excellent Linearity and Stability

An example of the linearity achieved over the concentration range 0.02 to 20 µg/L for two representative compounds is shown in the panels in Figure 1. Figure 2 is an overlay of nine extracted ion chromatograms (EIC), which shows stability obtained in the case of vinyl chloride, a particularly challenging analyte. Figure 3 represents the response over 20 injections of incurred dibromomethane (blue), bromochloromethane (red) and benzene, multiplied by 10 (green), in local tap water. Excellent overall system stability was achieved.

Figure 1. Excellent linearity from 0.02 – 20 µg/L

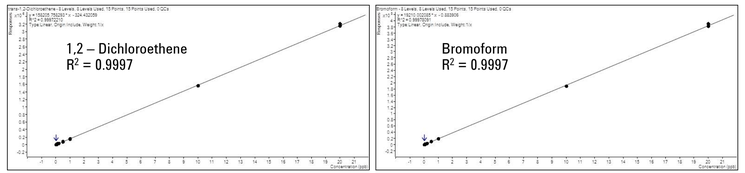


Figure 2. Overlay of the EIC for nine replicate injections of vinyl chloride at 0.04 µg/L.

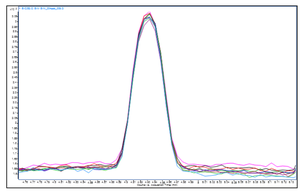
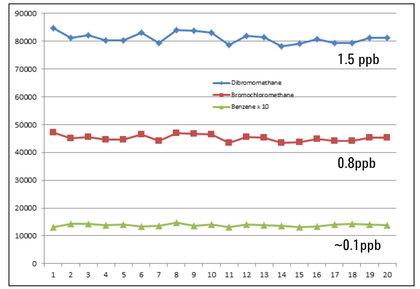


Figure 3. Response vs. number of injections of local tap water



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.