

## Rapid Analysis of VOCs in Water, to 1-ppb, by HS-GC-MS to MCERTS Criteria using the Agilent 5975 GC-MS

Jonathan Angove, Anatune Ltd., Hardwick, Cambridgeshire, UK.  
Keith Summerhill, Anatune Ltd., Hardwick, Cambridgeshire, UK.

### Introduction

A headspace-sampling (HS) method has been developed for rapid quantitation of ppb-level contamination in water samples. The 8<sup>1</sup>/<sub>2</sub>-minute cycle time (the time between 2 injections) allows quantitation of >60 volatile organic compounds (VOCs).

This HS method affords reliable and accurate quantitation of VOCs in water samples up to 200 ppb, yet remains robust enough to be unaffected by samples containing ppm-level contamination, which can compromise purge and trap (P&T) systems. Samples with very high VOC concentrations (e.g. >5ppm) may cause carry-over into subsequent analyses, but the system will not require being taken offline for cleaning, thereby enhancing lab profitability.

Samples analysed by HS require minimal preparation and, after the initial 15-minute incubation, the HS-GC-MS system is capable of generating a full-scan chromatogram (Figure 1) every 8<sup>1</sup>/<sub>2</sub> minutes. The GERSTEL MPS 2XL robotic autosampler has a capacity of up to 128 samples, enabling the system to run continuously for almost 23 hours. Hence, data presented here highlight the need for the capacity of the GERSTEL MPS 2XL, coupled with the Agilent 5975 inert MSD system, for the rapid detection and quantitation of ppb-level VOCs in water samples to meet the MCERTS criteria.

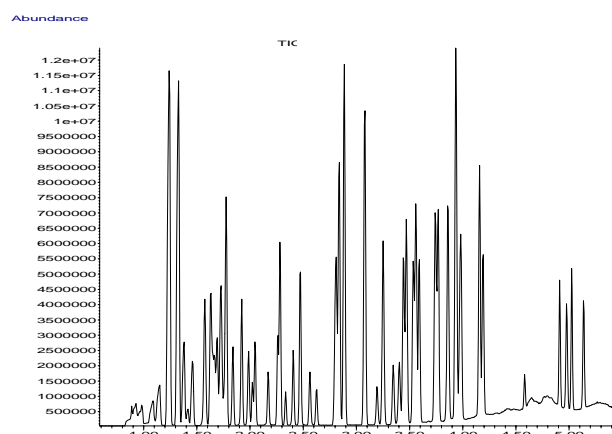


Figure 1: GC-MS total ion chromatogram of a calibration standard containing analytes at a concentration of 200µg/L

### Instrumentation and Methods

- Agilent 6890N Gas Chromatograph with 5975 inert MSD
- Agilent ChemStation
- GERSTEL Multi-Purpose Sampler (MPS 2XL) configured for headspace analysis.

### Compound List

Dichlorodifluoromethane	Chloromethane
Chloroethane	Bromomethane
Trichlorofluoromethane	1,1-Dichloroethene
1,1-Dichloroethene	trans-1,2-Dichloroethene
2,2-Dichloropropane	cis-1,2-Dichloroethene
Bromochloromethane	Chloroform
1,1-Dichloropropene	1,1,1-Trichloroethane
Benzene	1,2-Dichloroethane
Bromodichloromethane	Trichloroethene
Dibromomethane	Dibromomethane
Toluene	cis-1,3-Dichloropropene
1,1,2-Trichloroethane	trans-1,3-Dichloropropene
Tetrachloroethene	Carbon Tetrachloride
1,2-Dibromoethane	1,3-Dichloropropane
1,1,1,2-Tetrachloroethane	Dibromochloromethane
m,p-Xylene	Chlorobenzene
Styrene	Ethyl Benzene
Isopropylbenzene	o-Xylene
1,2,3-Trichloropropane	Bromoform
Bromobenzene	1,1,2,2-Tetrachloroethane
1,3,5-Trimethylbenzene	n-Propylbenzene
tert-Butylbenzene	2-Chlorotoluene
sec-Butylbenzene	4-Chlorotoluene
1,3-Dichlorobenzene	1,2,4-Trimethylbenzene
n-Butylbenzene	p-Isopropyltoluene
1,2,4-Trichlorobenzene	1,4-Dichlorobenzene
Naphthalene	1,2-Dibromo-3-chloropropan
1,2-Dichloropropane	Hexachlorobutadiene

### Internal Standards

Pentafluorobenzene  
1,4-Difluorobenzene  
Chlorobenzene-d5

### Surrogate Compounds

Dibromofluoromethane  
Toluene-d8  
4-Bromofluorobenzene

## Sample Preparation

Both crimp-capped and screw-capped round-edged vials have been tested for use with this method. As long as the type of vial used remains consistent, then either style of vial may be used.

### Method Blanks & Calibration Standards:

Aqueous blanks were prepared by weighing anhydrous sodium sulphate into a vial before adding the required volume of water. Calibration standards were prepared by spiking method blanks with the required volume of VOC-Mix 20. Methanol was added to the blanks and calibration standards to ensure that the overall amount of methanol added to each one was the same. Reproducible spiking was readily achieved using 10, 25 and 100 $\mu$ L syringes, ensuring that the tip of the needle was beneath the meniscus of the water within the vial.

## Headspace GC-MS Method

Given the relative simplicity of the sampling procedure, the GERSTEL MPS 2 is able to perform the fully automated headspace sampling in a high-throughput, "just-in-time" manner. This enables one sample to be running on the GC-MS whilst the next two samples are being agitated, the agitation being completed just after the GC-MS is ready for the next injection to occur. The vials are agitated for 15 minutes at a temperature of 60°C. After being agitated, a heated gastight syringe removes an aliquot of the headspace and injects the abstracted gaseous mixture into the GC inlet. Reliable transport of vials is achieved by the use of magnetic vial caps.

The GC-MS cycle time is 8 $\frac{1}{2}$ -minutes. The sample agitation time is 15 minutes; hence, on any occasion, up to three of the six agitator positions may contain vials at different stages of agitation. This rolling sample preparation feature is the key to the MPS 2 being able to conduct high-throughput analyses.

The 2.5mL gastight syringe used for sampling the headspace is heated to a temperature greater than that at which the sample agitation was done to help prevent cross-contamination of samples. The aliquot is introduced onto the GC column via a split/splitless inlet fitted with a wide bore liner (4mm id). The subsequent detection of the chromatographically separated compounds was achieved using an Agilent 5975 Inert MSD operating in full scan mode. Quantitation of the resultant chromatograms was performed using a multi-point calibration within ChemStation.

## Results

Linear calibration plots were obtained for all the compounds listed previously.

Figure 2 shows the calibration plot obtained for benzene throughout the calibration range of 2-200ppb.

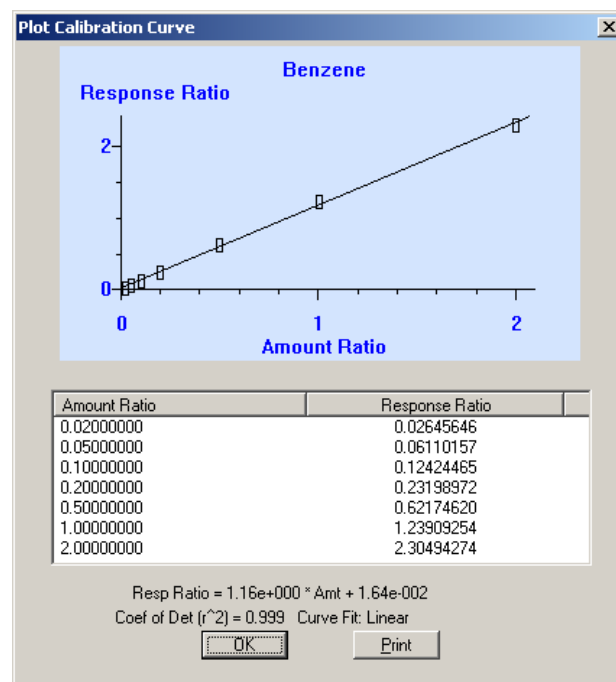


Figure 2: The calibration plot obtained for benzene.

The range of correlation coefficient obtained for all analytes listed above was between 0.995 and 1.000.

The reproducibility of the headspace sampling has also been examined and can be demonstrated to meet MCERTS criteria. These criteria state that the spiked samples' % RSD and bias must not exceed 15 and 30% respectively. Table 1 shows a summary of the reproducibility results obtained from injecting ten spiked samples, with a concentration of 40 $\mu$ g/L and 160 $\mu$ g/L in water.



Internal Standards	40ppb Water Samples (n=10)					160ppb Water Samples (n=10)				
	Range	MEAN	SD	%RSD	Bias (%)	Range	MEAN	SD	%RSD	Bias (%)
Pentafluorobenzene		810099	47927	5.92			805077	17645	2.19	
Difluorobenzene		1111388	64584	5.81			1105954	25315	2.29	
Chlorobenzene-d5		476186	25382	5.33			469220	12870	2.74	
1,4-Dichlorobenzene-d4		542362	32503	5.99			534780	19884	3.72	

#### Surrogate Standards

1,2-Dichloroethane-d6	70 - 130	101.41	3.50	3.45	1.41	70 - 130	101.88	1.07	1.05	1.88
TOLUENE-d8	70 - 130	99.76	0.66	0.66	-0.24	70 - 130	99.61	0.90	0.91	-0.39
4-Bromofluorobenzene	70 - 130	101.63	2.29	2.25	1.63	70 - 130	99.61	0.90	0.91	-0.39

Target Compounds	40ppb Water Samples (n=10)					160ppb Water Samples (n=10)				
	Range	MEAN	SD	%RSD	Bias (%)	Range	MEAN	SD	%RSD	Bias (%)
Dichlorodifluoromethane	28 - 52	42.94	2.14	4.98	7.36	112 - 208	171.29	4.82	2.82	7.06
Chloromethane	28 - 52	40.36	2.87	7.11	0.90	112 - 208	152.56	2.88	1.89	-4.65
Chloroethane	28 - 52	42.07	2.71	6.43	5.17	112 - 208	165.54	3.45	2.09	3.46
Bromomethane	28 - 52	41.27	2.21	5.36	3.16	112 - 208	163.51	2.62	1.60	2.19
Trichlorofluoromethane	28 - 52	43.09	2.55	5.93	7.72	112 - 208	175.40	2.28	1.30	9.62
1,1,-Dichloroethene	28 - 52	41.91	2.46	5.87	4.76	112 - 208	171.16	2.36	1.38	6.98
trans-1,2-Dichloroethene	28 - 52	42.86	2.62	6.11	7.14	112 - 208	171.73	2.33	1.36	7.33
1,1-Dichloroethane	28 - 52	42.80	2.05	4.80	7.00	112 - 208	170.17	2.28	1.34	6.36
cis-1,2-Dichloroethene	28 - 52	42.99	2.20	5.11	7.48	112 - 208	169.87	1.73	1.02	6.17
2,2-Dichloropropane	28 - 52	32.22	2.97	9.22	-19.46	112 - 208	113.81	7.25	6.37	-28.87
Chloroform	28 - 52	43.37	2.62	6.03	8.41	112 - 208	174.18	2.08	1.19	8.87
Bromochloromethane	28 - 52	44.01	2.39	5.43	10.03	112 - 208	175.68	2.69	1.53	9.80
1,1,1-Trichloroethane	28 - 52	43.12	2.21	5.12	7.80	112 - 208	176.83	2.46	1.39	10.52
1,1-Dichloropropene	28 - 52	43.04	2.31	5.38	7.60	112 - 208	171.60	2.49	1.45	7.25
1,2-Dichloroethane	28 - 52	43.49	2.24	5.16	8.71	112 - 208	173.20	3.11	1.79	8.25
Benzene	28 - 52	42.02	1.96	4.66	5.05	112 - 208	167.79	2.84	1.69	4.87
1,2-Dichloropropane	28 - 52	42.36	2.00	4.73	5.89	112 - 208	166.19	3.35	2.02	3.87
Trichloroethene	28 - 52	42.93	2.12	4.94	7.31	112 - 208	173.73	3.17	1.83	8.58
Bromodichloromethane	28 - 52	42.15	1.99	4.71	5.38	112 - 208	173.42	3.20	1.85	8.39
Dibromomethane	28 - 52	44.16	2.35	5.33	10.40	112 - 208	172.97	4.41	2.55	8.11
cis-1,3-Dichloropropene	28 - 52	40.54	2.19	5.40	1.35	112 - 208	157.07	4.65	2.96	-1.83
Toluene	28 - 52	42.18	1.79	4.25	5.44	112 - 208	169.78	3.03	1.79	6.11
trans-1,3-Dichloropropene	28 - 52	39.52	1.67	4.23	-1.20	112 - 208	151.77	4.99	3.29	-5.14
1,1,2-Trichloroethane	28 - 52	42.64	2.18	5.12	6.61	112 - 208	171.45	3.08	1.79	7.16
Carbon Tetrachloride	28 - 52	42.46	1.74	4.09	6.14	112 - 208	175.00	2.51	1.43	9.38
1,3-Dichloropropane	28 - 52	42.29	1.72	4.06	5.72	112 - 208	168.94	2.89	1.71	5.59
Tetrachloroethene	28 - 52	43.04	1.64	3.81	7.60	112 - 208	172.06	2.36	1.37	7.54
Dibromochloromethane	28 - 52	42.60	1.77	4.16	6.49	112 - 208	172.42	2.86	1.66	7.76
1,2-Dibromoethane	28 - 52	43.01	1.75	4.06	7.52	112 - 208	171.76	3.01	1.75	7.35
Chlorobenzene	28 - 52	42.30	1.73	4.10	5.75	112 - 208	172.18	2.08	1.21	7.61
1,1,1,2-Tetrachloroethane	28 - 52	43.57	1.93	4.44	8.93	112 - 208	176.26	2.72	1.54	10.16
Ethyl Benzene	28 - 52	42.55	1.55	3.65	6.37	112 - 208	172.99	2.70	1.56	8.12
m,p-Xylene	28 - 52	42.41	1.51	3.56	6.01	112 - 208	173.22	2.69	1.55	8.26
o-Xylene	28 - 52	42.63	1.44	3.38	6.57	112 - 208	173.83	3.60	2.07	8.64
Styrene	28 - 52	42.51	1.92	4.52	6.29	112 - 208	172.70	3.89	2.25	7.94



Target Compounds	40ppb Water Samples (n=10)					160ppb Water Samples (n=10)				
	Range	MEAN	SD	%RSD	Bias (%)	Range	MEAN	SD	%RSD	Bias (%)
Bromoform	28 - 52	42.46	1.33	3.12	6.16	112 - 208	175.12	3.47	1.98	9.45
Isopropylbenzene	28 - 52	42.90	1.56	3.63	7.24	112 - 208	177.24	4.18	2.36	10.78
1,1,2,2-Tetrachloroethane	28 - 52	42.40	1.56	3.69	6.01	112 - 208	170.70	5.59	3.28	6.69
1,2,3-Trichloropropane	28 - 52	44.62	2.39	5.35	11.54	112 - 208	181.82	5.36	2.95	13.64
n-Propylbenzene	28 - 52	42.61	1.49	3.51	6.53	112 - 208	176.31	5.33	3.02	10.20
Bromobenzene	28 - 52	43.53	1.86	4.28	8.81	112 - 208	177.17	4.88	2.75	10.73
2-Chlorotoluene	28 - 52	42.86	1.56	3.65	7.14	112 - 208	175.87	5.53	3.14	9.92
1,3,5-Trimethylbenzene	28 - 52	43.23	1.69	3.90	8.07	112 - 208	177.40	5.59	3.15	10.88
4-Chlorotoluene	28 - 52	43.38	1.41	3.25	8.45	112 - 208	175.45	4.06	2.31	9.66
tert-Butylbenzene	28 - 52	42.94	1.61	3.75	7.35	112 - 208	175.89	4.92	2.80	9.93
1,2,4-Trimethylbenzene	28 - 52	42.79	1.60	3.73	6.96	112 - 208	174.63	5.94	3.40	9.14
sec-Butylbenzene	28 - 52	43.57	1.74	4.00	8.94	112 - 208	174.89	3.61	2.06	9.30
p-Isopropyltoluene	28 - 52	43.13	1.59	3.68	7.82	112 - 208	172.43	4.49	2.60	7.77
1,3-Dichlorobenzene	28 - 52	42.74	1.91	4.46	6.85	112 - 208	172.75	5.09	2.95	7.97
1,4-Dichlorobenzene	28 - 52	42.38	1.48	3.50	5.95	112 - 208	171.31	2.24	1.31	7.07
n-Butylbenzene	28 - 52	42.61	2.04	4.79	6.52	112 - 208	172.52	3.09	1.79	7.82
1,2-Dichlorobenzene	28 - 52	42.40	1.83	4.31	5.9875	112 - 208	171.465	3.29	1.92	7.17
1,2-Dibromo-3-chloropropan	28 - 52	43.92	1.95	4.43	9.81	112 - 208	174.759	6.88	3.93	9.22
1,2,4-Trichlorobenzene	28 - 52	43.22	1.77	4.09	8.0425	112 - 208	173.511	7.21	4.16	8.44
Hexachlorobutadiene	28 - 52	46.99	2.61	5.55	17.48	112 - 208	176.50	8.20	4.65	10.31
Naphthalene	28 - 52	42.70	1.69	3.95	6.74	112 - 208	169.83	6.24	3.67	6.14
1,2,3-Trichlorobenzene	28 - 52	42.25	2.11	5.00	5.62	112 - 208	169.83	6.02	3.54	6.15

Table 1: Summary of the reproducibility data obtained by the analysis of 10 spiked samples at a concentration of 40µg/L and 10 spiked samples at a concentration of 160µg/L.



The method has been demonstrated to be reliable and reproducible, but also sensitive enough to give low-ppb limits of detection (LOD). Figure 3 shows the extracted ion chromatogram for benzene in a spiked water sample at a level of 1ppb.

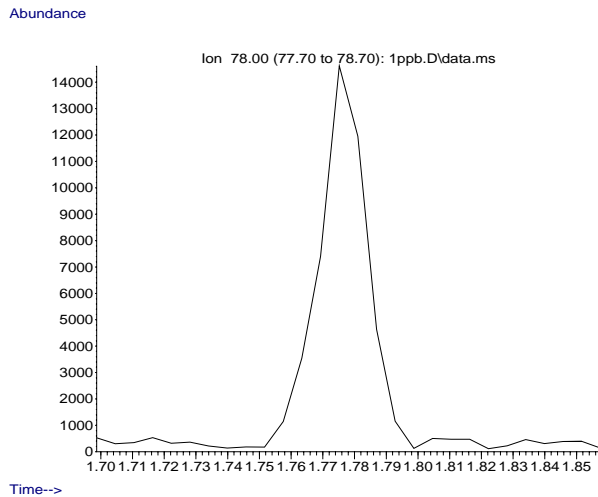


Figure 3: Chromatogram of the 78 ion used to quantitate benzene in a spiked water sample at a level of 1ppb.

## ***Conclusions***

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This evaluation has confirmed the suitability of the GERSTEL MPS 2 combined with the Agilent 5975 inert MSD for high-throughput screening and quantitation of VOCs in water.

All analytes analysed had LODs of 1µg/L and met MCERTS criteria

This system can thus be used as a rapid, cost effective and reliable method for the ppb-level quantitation of VOCs in water. The GC-runtime of 5.4 minutes affords sufficient separation of all compounds analysed, significantly increasing laboratory productivity when compared with SIM GC-MS or purge-and-trap methods delivering similar sensitivity.