

Rapid Sub-ppb Headspace Analysis of Selected Red List Solvents & THMs in Water using the Agilent 5975 GC-MS

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Introduction

A headspace-sampling (HS) method has been developed for rapid quantitation of sub-ppb level contamination of selected red list solvents and trihalomethanes (THMs) in water samples. The 8.75 minute cycle time (the time between 2 injections) allows quantitation of all the compounds listed whilst retaining integrity of the data acquired in full-scan mode.

Confidence in drinking water analysis measurements is paramount to ensuring that the general public are certain that they are not unduly exposed to trace levels of harmful compounds. Such compounds of concern to the industry are ppb-levels of disinfection by-products (e.g. THMs) and red list solvents (e.g. MTBE, chlorinated benzenes) that can become dissolved within water. Both types of compounds are considered volatile organic compounds (VOCs), which make them ideal candidates for quantitation by HS-GC-MS.

This headspace method affords reliable and accurate quantitation of VOCs in water samples up to 20 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 productivity.

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 8.75 minutes. The GERSTEL MPS 2 with the Anatune Ltd. enhanced productivity tray has a capacity of up to 160 samples, enabling the system to run continuously for just over 23 hours. Hence, data presented here highlight the need for this capacity, coupled with the Agilent 5975 inert MSD system, for the rapid detection and quantitation of selected red list solvents and THMs in water.

Instrumentation and Methods

- Agilent 6890N Gas Chromatograph with 5975 inert MSD
- Agilent ChemStation
- GERSTEL Multi-Purpose Sampler (MPS 2XL) configured for headspace analysis
- Anatune Ltd. 160 position tray

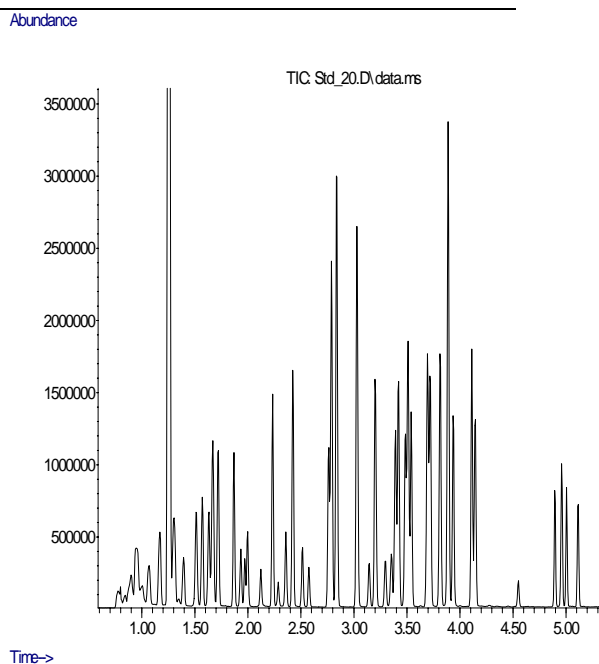


Figure 1: GC-MS total ion chromatogram of a calibration standard containing analytes at a concentration of 20µg/L

Compound List

Trihalomethanes:

Chloroform	Bromochloromethane
Dibromochloromethane	Bromoform

Red List Solvents:

t-Butyl Methyl Ether (MTBE)	1,2-Dichloroethane
1,1,1-Trichloroethane	Benzene
Trichloroethene	Toluene
Carbon Tetrachloride	Tetrachloroethene
m- & p-Xylene	o-Xylene
1,2-Dichlorobenzene	1,3-Dichlorobenzene
1,4-Dichlorobenzene	1,2,4-Trichlorobenzene
Hexachlorobutadiene	1,2,3-Trichlorobenzene

Internal Standard:

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.

1. Anhydrous sodium sulphate was pre-weighed into enough 20mL round-edged HS vials for the entire batch of samples to be analysed.
2. With the minimum disruption of the sample as possible, an aliquot of the aqueous sample was transferred into the vial.
3. Internal standard was spiked into the vial.
4. The vial was then capped with a magnetic cap fitted with a PTFE-faced chlorobutyl septum.
5. Steps 2 to 4 were repeated for each sample to be analysed.
6. The samples were loaded onto the MPS 2 for incubation and sampling.

Method Blanks & Calibration Standards:

Aqueous blanks were prepared as described above. Calibration standards were prepared by spiking method blanks with the required volume of VOC-Mix 20 and MTBE. Reproducible spiking was readily achieved using 10, 25 and 50 μ 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 8.75 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 sample 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 0.21-20ppb.

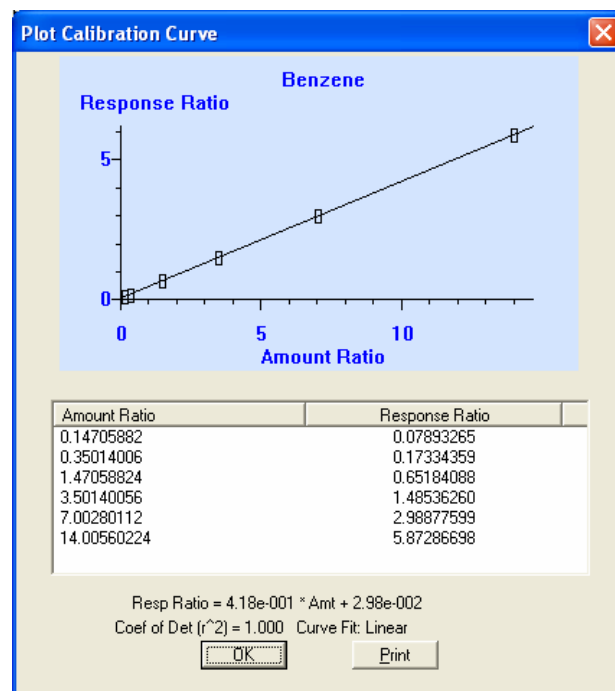


Figure 2: The calibration plot obtained for benzene.

The range of correlation coefficient obtained for all analytes listed above was between 0.999 and 1.000.

The reproducibility of the headspace sampling has also been examined. Table 1 shows a summary of the reproducibility results obtained from injecting ten spiked samples, with a concentration of 0.5 μ g/L, 5 μ g/L and 15 μ g/L in water.



	0.5ppb Water Samples (n=10)			5ppb Water Samples (n=10)			15ppb Water Samples (n=10)		
	MEAN	SD	%RSD	MEAN	SD	%RSD	MEAN	SD	%RSD
Internal Standard:									
4-Bromofluorobenzene	73347	2744	3.74	87644	5774	6.59	91573	2032	2.22
Trihalomethanes:									
Chloroform	0.37	0.02	5.18	4.82	0.21	4.31	15.26	0.33	2.18
Bromochloromethane	0.36	0.07	18.22	4.97	0.16	3.14	15.47	0.33	2.16
Dibromochloromethane	0.48	0.03	6.25	4.81	0.13	2.78	15.09	0.23	1.50
Bromoform	0.45	0.04	8.65	4.91	0.10	1.98	15.31	0.20	1.30
Red List Solvents:									
MTBE	0.43	0.07	15.50	4.68	0.12	2.66	14.90	0.21	1.40
1,2-Dichloroethane	0.35	0.07	19.12	4.82	0.15	3.12	15.20	0.31	2.06
1,1,1-Trichloroethane	0.43	0.02	4.85	4.78	0.25	5.33	15.21	0.41	2.66
Benzene	0.49	0.03	5.35	4.77	0.21	4.38	15.14	0.36	2.37
Trichloroethene	0.49	0.04	7.62	4.83	0.21	4.42	15.36	0.44	2.86
Toluene	0.67	0.02	3.14	4.60	0.22	4.78	16.69	0.50	2.99
Carbon Tetrachloride	0.41	0.04	10.36	4.83	0.29	6.00	15.22	0.35	2.30
Tetrachloroethene	0.47	0.04	8.10	4.81	0.28	5.88	15.23	0.43	2.83
m- & p-Xylene	0.53	0.02	3.66	4.69	0.24	5.20	15.36	0.32	2.10
o-Xylene	0.63	0.01	1.31	4.57	0.22	4.88	15.30	0.34	2.19
1,2-Dichlorobenzene	0.41	0.02	4.38	4.85	0.21	4.36	15.35	0.25	1.61
1,3-Dichlorobenzene	0.39	0.03	8.61	4.87	0.21	4.39	15.22	0.39	2.54
1,4-Dichlorobenzene	0.42	0.02	3.62	4.76	0.22	4.70	15.12	0.229	1.95
1,2,4-Trichlorobenzene	0.60	0.04	6.21	4.64	0.22	4.70	15.33	0.63	4.11
Hexachlorobutadiene	0.45	0.03	7.12	4.86	0.33	6.73	14.81	0.55	3.70
1,2,3-Trichlorobenzene	0.61	0.05	7.68	4.66	0.20	4.24	15.02	0.48	3.22

Table 1: Summary of the reproducibility data obtained by the analysis of 10 spiked samples at a concentration of 0.5µg/L, 5µg/L and 15µg/L.



The method has been demonstrated to be reliable and reproducible, but also sensitive enough to give high-ppt limits of detection (LOD). Figure 3 shows the extracted ion chromatogram for benzene in a spiked water sample at a level of 140ppt.

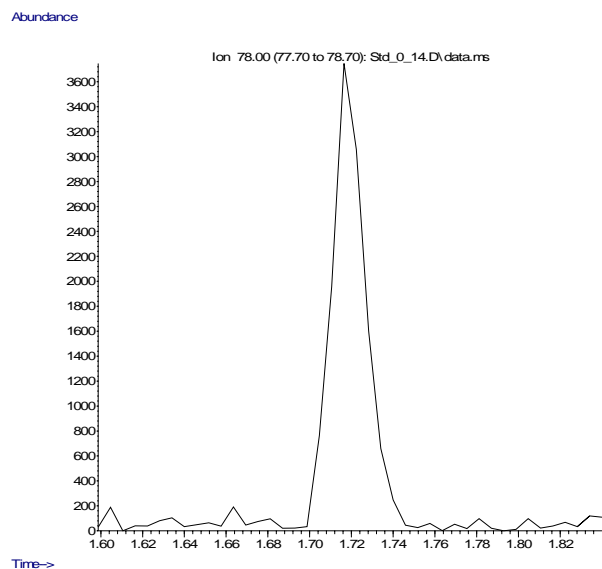


Figure 3: Chromatogram of the 78 ion used to quantitate benzene in a spiked water sample at a level of 140ppt.

Conclusions

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 selected red list solvents and THMs in water.

All analytes analysed had LODs of 0.14µg/L.

This system can thus be used as a rapid, cost effective and reliable method for the sub-ppb-level quantitation of selected red list solvents and THMs 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.