FIELD APPLICATION REPORT

Gas Chromatography

VOCs in Water Using Static Headspace GC/MS

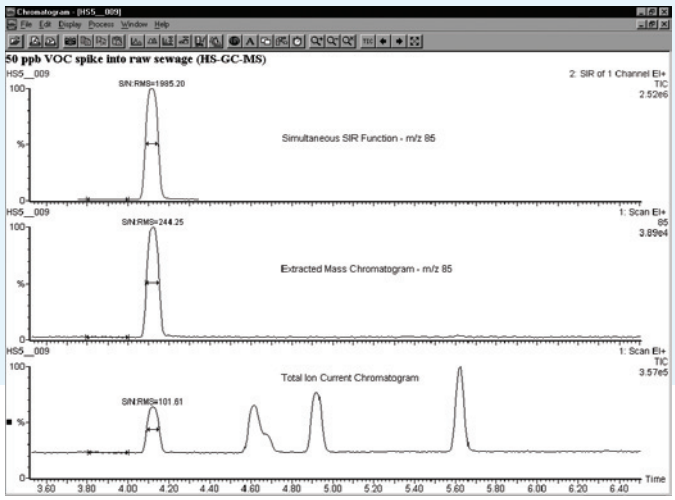

Figure 1. Sensitivity enhancement (50 ppb level) – Simultaneous Full Scan/SIR.

Introduction

The combination of static headspace sample introduction and gas chromatography/mass spectrometry (HS/GC/MS) provides the analyst with a powerful, fully automated technique for the determination of trace volatile organic compounds (VOCs) in water. Samples may be hermetically sealed in the headspace vial at the point of sampling. This approach avoids errors due to glassware cross-contamination and loss of volatile components during liquid sample transfers.

Precision is highly dependent on the reproducibility of the thermostatting and sampling procedure. On the PerkinElmer® HS 40XL automated headspace sampler used here, the samples are intelligently queued in an oven that is machined from a solid metal block to provide unparalleled temperature stability. Samples are transferred to the head of the capillary column via an inert fused-silica transfer line using a pressure-balanced sampling system. This unique approach to headspace sampling, which has been a feature of PerkinElmer systems for some 30 years, avoids contact of the sample components with materials used in valve rotors and sample loops.

There is also a link between precision and detection limits. By definition, it is difficult to get excellent reproducibility for analytes present at or near the limits of detection. Anything that improves the detection limits (signal-to-noise ratio) of the analytical method is also likely to prove beneficial in terms of precision.

The PerkinElmer TurboMass™ mass spectrometer utilizes MS methods that are composed of "scan functions." No restrictions exist to prevent mixing full-scan functions and the monitoring of specific ions using Selected Ion Recording (SIR), also called Selected Ion Monitoring (SIM). Under normal full-scan conditions, it is likely that any particular mass (for example, m/z 78) is only being monitored for 1 to 2 milliseconds in each scan. Adding a SIR function lasting for 0.02 to 0.05 seconds to the same run increases the scan duration by only a few percent. However, this same SIR function means that the specific mass is being monitored for a dedicated 20 to 50 milliseconds, yielding a dramatic increase in the signal-to-noise ratio and, thus, sensitivity.

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Table 1. **Instrument Conditions:** The following conditions can be used with any recent model PerkinElmer GC/MS-Headspace Sampler system (Autosystem XL/TurboMass with HS 40XL or Clarus® 500 GC/MS with TurboMatrix™ HS).

Gas Chromatograph			
Gas chromatograph	AutoSystem XL™ Gas Chromatograph		
Column	50 m x 0.32 mm x 1.0 µm film thickness, 5%-phenyl, methyl silicone		
Carrier	Helium, 4 mL/min for 0.25 min, then 8 mL/min down to 2 mL/min and hold		
Oven temperature	50 °C for 3 min, 10 °C/min to 180 °C, hold for 2 min		
Injector temperature	180 °C, PSS (Programmable Split/Splitless) with narrow bore liner		
Split flow	10 mL/min		
Headspace Sampler			
Headspace sampler	HS 40XL Automatic Headspace Sampler		
Oven time	30 min with shaker on		
Pressurization time	3.0 min		
Inject time	0.06 min		
Oven temperature	60 °C		
Needle temperature	110 °C		
Transfer-line temperature	120 °C		
Mass Spectrometer			
Mass spectrometer	TurboMass Mass Spectrometer		
Transfer-line temperature	225 °C		
Ion-source temperature	150 °C		
Mode	EI, Full Scan with Selected Ion Recording		
Full-scan function (1)	m/z 45 to 200 in 0.40 sec with 0.05 interscan delay		
SIR functions (2-8)	One to three ions monitored		
	Dwell time = 0.02 sec		
	Interchannel delay = 0.01 sec		
	Span = (Daltons) 0.5		
Monitored Masses	**Masses**	**Function Number**	**Analyte Name**
	83	2	Chloroform
	97	3	Trichloroethane
	62	3	1,2-Dichloroethane
	78	3	Benzene
	130	4	Trichloroethylene
	91	5	Toluene
	166	6	Tetrachloroethylene
	91	7	Ethyl Benzene, m,p & o-xylene, propyl benzene
	104	7	Styrene
	105	7	1,2,4-Trimethyl Benzene
	180	8	1,3,5 & 1,2,4 & 1,2,3 Trichlorobenzene

Results

In the following example, a raw sewage sample was spiked with a VOC standard at both the 50 ppb and 5 ppb level. The samples were then analyzed using HS/GC/MS under the conditions shown in Table 1. Figures 1 and 2 demonstrate the sensitivity enhancement obtained using simultaneous acquisition of full-scan and SIR data for the two spiked samples. Figure 3 shows the precision obtained for seven runs of the 50-ppb spiked sample. The data in Table 2 illustrate the retention time and area repeatability obtained for both samples. These results demonstrate that combining full scan functions and the monitoring of specific ions using SIR increase sensitivity, while maintaining excellent repeatability. In this example, an approximately 8-fold improvement in signal-to-noise was obtained. Larger improvements are possible with longer SIR dwell times.

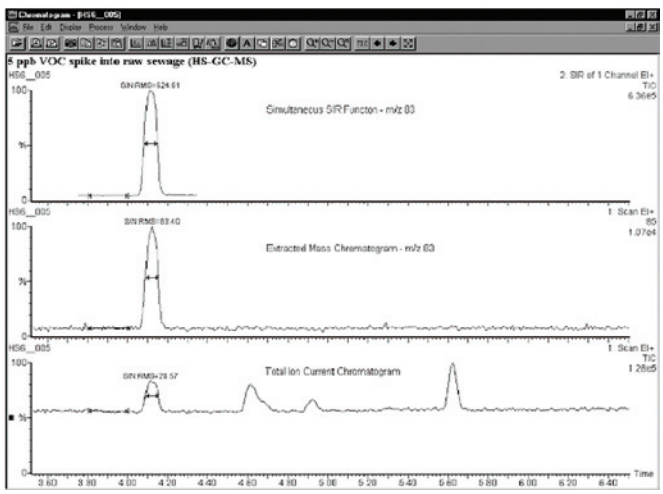

Figure 2. Sensitivity enhancement (5 ppb level) – Simultaneous Full Scan/SIR.

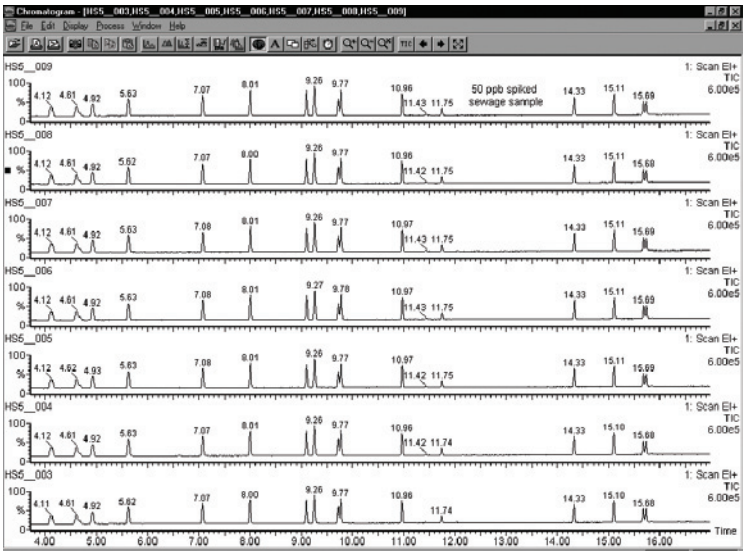

Figure 3. Precision using Headspace GC/MS – Simultaneous Full Scan/SIR.

***Table 2.* Precision Summary for Seven Runs each of a 5-ppb and 50-ppb Spike of VOCs in Raw Sewage.**

50-ppb Spike Compound	5-ppb Spike RT SD	Area %RSD	RT SD	Area %RSD
Chloroform	0.004	2.91	0.004	0.96
Trichloroethane	0.003	2.40	0.005	0.90
1,2-Dichloroethane	0.000	3.08	0.000	1.52
Benzene	0.004	3.01	0.004	8.58*
Trichloroethylene	0.000	2.08	0.001	1.50
Toluene	0.004	2.14	0.003	13.54*
Tetrachloroethylene	0.004	1.18	0.004	1.42
Ethyl Benzene	0.004	2.29	0.004	1.10
m- and p-Xylene	0.005	2.45	0.005	1.18
Styrene	0.004	2.25	0.005	2.97
o-Xylene	0.005	2.52	0.004	1.52
Propyl Benzene	0.003	1.97	0.004	0.87
1,2,4-Trimethylbenzene	0.004	1.61	0.004	2.57
1,3,5-Trichlorobenzene	0.004	1.21	0.004	0.97
1,2,4-Trichlorobenzene	0.004	0.80	0.004	1.85
1,2,3-Trichlorobenzene	0.004	0.77	0.030	2.08

**Subject to adsorption/biological degradation by solid matrix present in the sample.*

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