ENVIRONMENTAL ANALYSIS

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN ENVIRONMENTAL WATERS USING THE AGILENT 7697A HEADSPACE AND 7890B/5977A GC/MS

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Solution Note

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Abstract

A retention time locked (RTL) method for the determination of trace level volatile organic compounds (VOCs) in environmental waters was developed on the Agilent 7697A Headspace and 7890B/5977A GC/MS. Analysis on the GC/MS was performed in simultaneous Scan/SIM mode. This method can determine 66 VOCs over a calibration range of 1 – 20 µg/L with some compounds being detectable at lower levels.

This method is therefore suitable for routine analysis, as part of a monitoring strategy that includes volatile organic compounds, as required by the Water Framework Directive (2000/60/EC) and detailed in the update to Annex I: Environmental Quality Standards for Priority Substances and certain other Pollutants [1].

Introduction

The analysis of volatile organic compounds (VOCs) in environmental water samples is usually performed by either headspace (HS) or purge and trap (P&T), with separation by gas chromatography (GC) and detection by mass spectrometry (MS).

The P&T technique uses a continuous flow of carrier gas to purge any volatiles from the matrix onto an adsorbant trap. The trap is then heated, releasing the adsorbed compounds onto the GC/MS for analysis. This technique offers very good sensitivity as the sample is exhaustively extracted. However, P&T systems are more complicated to run and maintain compared to HS systems. They can also suffer from water carryover problems which can lead to reduced sensitivity, loss of peak shape and cross-contamination. Environmental samples containing detergents can also suffer from foam formation issues.

The other approach is the HS technique, which uses a closed sample container and a sampling system. The water sample in the sealed vial is heated and agitated to help drive the volatiles from the sample matrix and into the gaseous headspace. An equilibrium is formed between the two phases. This equilibrium can be shifted by the addition of salt to the sample. After a specified time, a portion of the headspace is transferred onto the GC/MS via a valve with a sample loop. This technique is robust and experiences few carryover problems as less water is transferred to the GC/MS.

This application note details the use of an Agilent 7697A HS coupled to a 7890B/5977A GC/MS for the analysis of VOCs in environmental waters. The MS system features a new inert source with an extractor lens, which provides additional focus to the ion beam into the mass analyser, resulting in a significant increase in the number of ions analysed and better sensitivity of the instrument. The GC/MS was run in Scan/SIM mode and the data analysis was accomplished using MassHunter software.

Analytical Technique

Sample Preparation

Sample Preparation: 10 mL of sample and 2 g of salt were added to each vial. An aliquot of Stock Internal Standard (prepared in Methanol) was spiked into the solution and the vial sealed.

Standard Preparation: 10 mL water and 2 g of salt were added to each vial. An aliquot 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 1, 5, 10 and 20 µg/L, with 66 analytes and 3 internal standards at each level. Two sets of standards were prepared and run at the beginning and end of the sequence.

The Internal Standards used were D4- 1,2-Dichloroethane (CAS 17060-07-0), D8-Toluene (CAS 2037-26-5) and 4-Bromofluorobenzene (CAS 460-00-4). The method was retention time locked to D8-Toluene at 11.890 minutes.

Instrumentation

Agilent 7697A Headspace Sampler, Agilent 7890B Gas Chromatograph with an Agilent VF-624 MS 60m capillary column and an Agilent 5977A Mass Selective Detector with MassHunter workstation.

Results and Discussion

The method was developed using the 10 µg/L standard solution. The method is run in Scan/SIM mode, where selective ion monitoring (SIM) is used for quantitation and Scan could be used for identification purposes if necessary. To maximise sensitivity the run has been divided into 16 SIM groups, with 2 ions for each compound, one for quantitation, the other for qualitation. Figure 1 shows the Scan (Total Ion Chromatogram, TIC) and SIM traces for the 10 µg/L standard and Figure 2 the Scan and SIM traces for the 1 µg/L standard.

Calibration standards at 20, 10, 5 and 1 µg/L were analysed at the beginning and end of each sequence. Figures 3 and 4 show typical 8-point calibrations for bromochloromethane and 1,2-Dichloroethane. All VOCs could be detected in the 1 µg/L standard. Some compounds were even visible in the blanks, mostly at very low levels, indicating that the detection limits for some of the VOCs may even be below the 0.1 µg/L level.

A spiked surface water sample at the 1 µg/L level was prepared and analysed to assess reproducibility. Table 1 shows the relative standard deviation data for this solution (total number of samples = 5). With the exception of Vinyl chloride, all of the compounds tested for had RSDs of less than 3% at this level.

VOC Compounds

Compound	RT, min	CAS Number	Compound	RT, min	CAS Number
Dichlorodifluoromethane	3.387	75-71-8	Dibromochloromethane	12.981	124-48-1
Chloromethane	3.734	74-87-3	1,2-Dibromoethane	13.175	106-93-4
Vinyl chloride	3.980	75-01-4	Chlorobenzene	13.830	108-90-7
Bromomethane	4.390	74-83-9	1,1,1,2-Tetrachloroethane	13.939	630-20-6
Chloroethane	4.788	75-00-3	Ethylbenzene	13.934	100-41-4
Trichlorofluoromethane	5.202	75-69-4	m and p-Xylene	14.115	108-38-3 & 106-42-3
1,1-Dichloroethene	5.998	75-34-4	o-Xylene	14.669	95-47-6
Carbon disulphide	6.338	75-15-0	Styrene	14.699	100-42-5
Dichloromethane	6.701	75-09-2	Bromoform	14.994	75-25-2
Methyl tert-butyl ether	7.046	1634-04-4	Isopropylbenzene	15.183	98-82-8
trans-1,2-Dichloroethene	7.069	156-60-5	1,1,2,2-Tetrachloroethane	15.612	79-34-5
1,1-Dichloroethane	7.644	75-34-3	Bromobenzene	15.697	108-86-1
Ethyl tert-butyl ether	8.091	637-92-3	1,2,3-Trichloropropane	15.731	96-18-4
cis-1,2-Dichloroethene	8.353	156-59-2	n-Propylbenzene	15.793	103-65-1
2,2-Dichloropropane	8.370	594-20-7	2-Chlorotoluene	15.952	95-49-8
Bromochloromethane	8.656	74-97-5	3-Chlorotoluene	16.042	108-41-8
Chloroform	8.756	67-66-3	1,3,5-Trimethylbenzene	16.048	108-67-8
1,1,1-Trichloroethane	8.995	71-55-6	4-Chlorotoluene	16.133	106-43-4
1,1-Dichloro-1-propene	9.177	563-58-6	tert-Butylbenzene	16.526	98-06-6
Carbon tetrachloride	9.189	56-23-5	1,2,4-Trimethylbenzene	16.608	95-63-6
Benzene	9.440	71-43-2	sec-Butylbenzene	16.856	135-98-8
1,2-Dichloroethane	9.497	107-06-2	1,3-Dichlorobenzene	17.071	541-73-1
tert-Amyl methyl ether	9.540	994-05-8	4-Isopropyltoluene	17.077	99-87-6
Trichloroethene	10.232	79-01-6	1,4-Dichlorobenzene	17.220	106-46-7
1,2-Dichloropropane	10.576	78-87-5	1,2,3-Trimethylbenzene	17.231	526-73-8
Dibromomethane	10.699	74-95-3	n-Butylbenzene	17.689	104-51-8
Bromodichloromethane	10.884	75-27-4	1,2-Dichlorobenzene	17.761	95-50-1
cis-1,3-Dichloropropene	11.437	10061-01-5	1,2-Dibromo-3-chloropropane	18.949	96-12-8
Toluene	11.890	108-88-3	1,3,5-Trichlorobenzene	19.215	108-70-3
trans-1,3-Dichloropropene	12.165	10061-02-6	1,2,4-Trichlorobenzene	20.179	120-82-1
1,1,2-Trichloroethane	12.443	79-00-5	Hexachlorobutadiene	20.370	87-68-3
Tetrachloroethene	12.580	127-18-4	Naphthalene	20.604	91-20-3
1,3-Dichloropropane	12.673	142-28-9	1,2,3-Trichlorobenzene	20.922	87-61-6

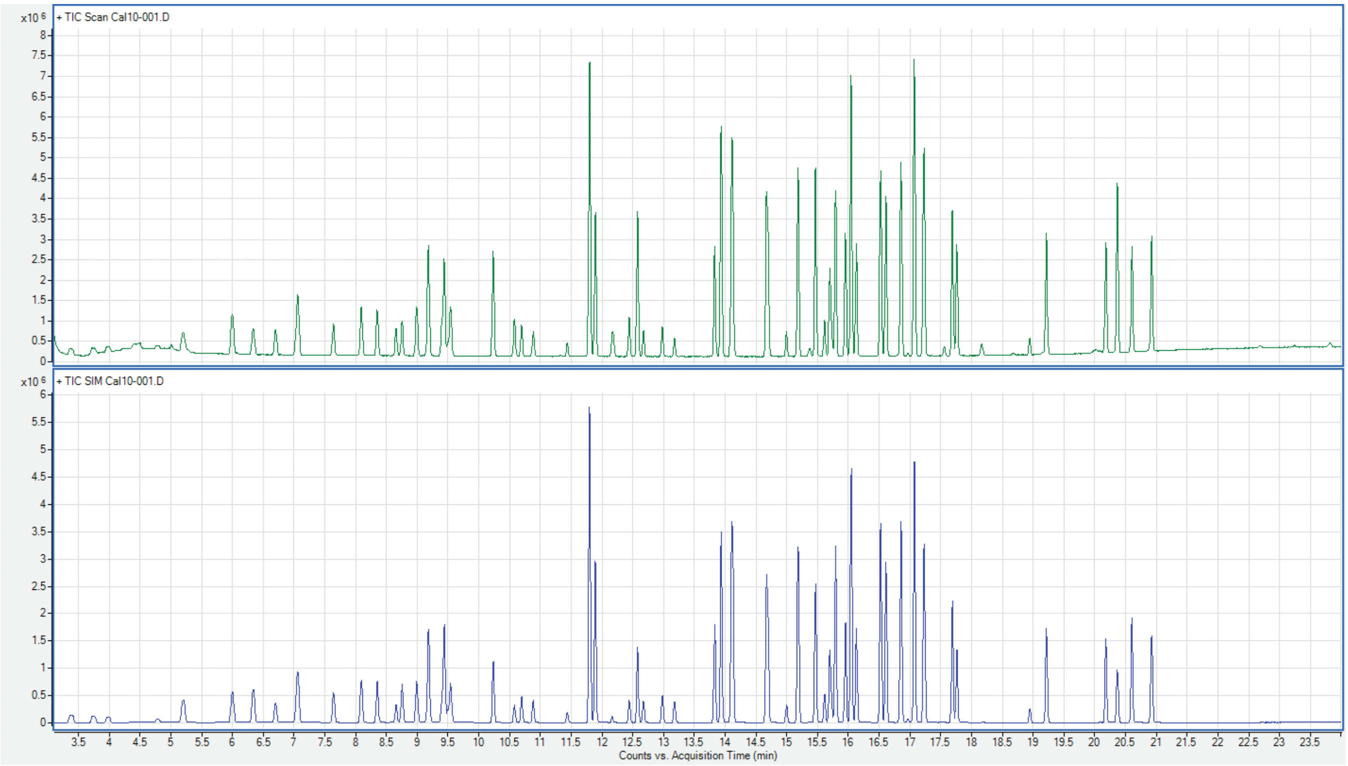

Figure 1: 10 µg/L VOC Standard Scan and SIM Traces.

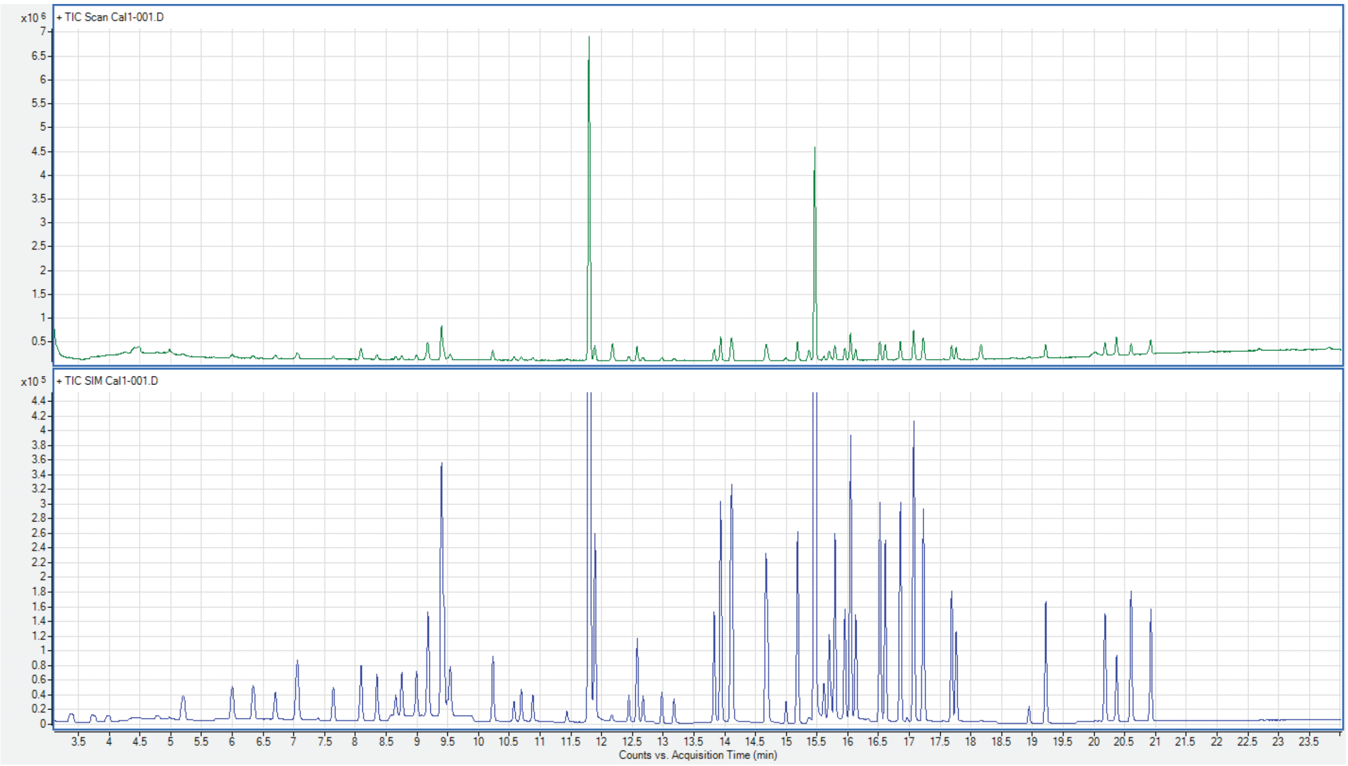

Figure 2: 1 µg/L VOC Standard Scan and SIM Traces.

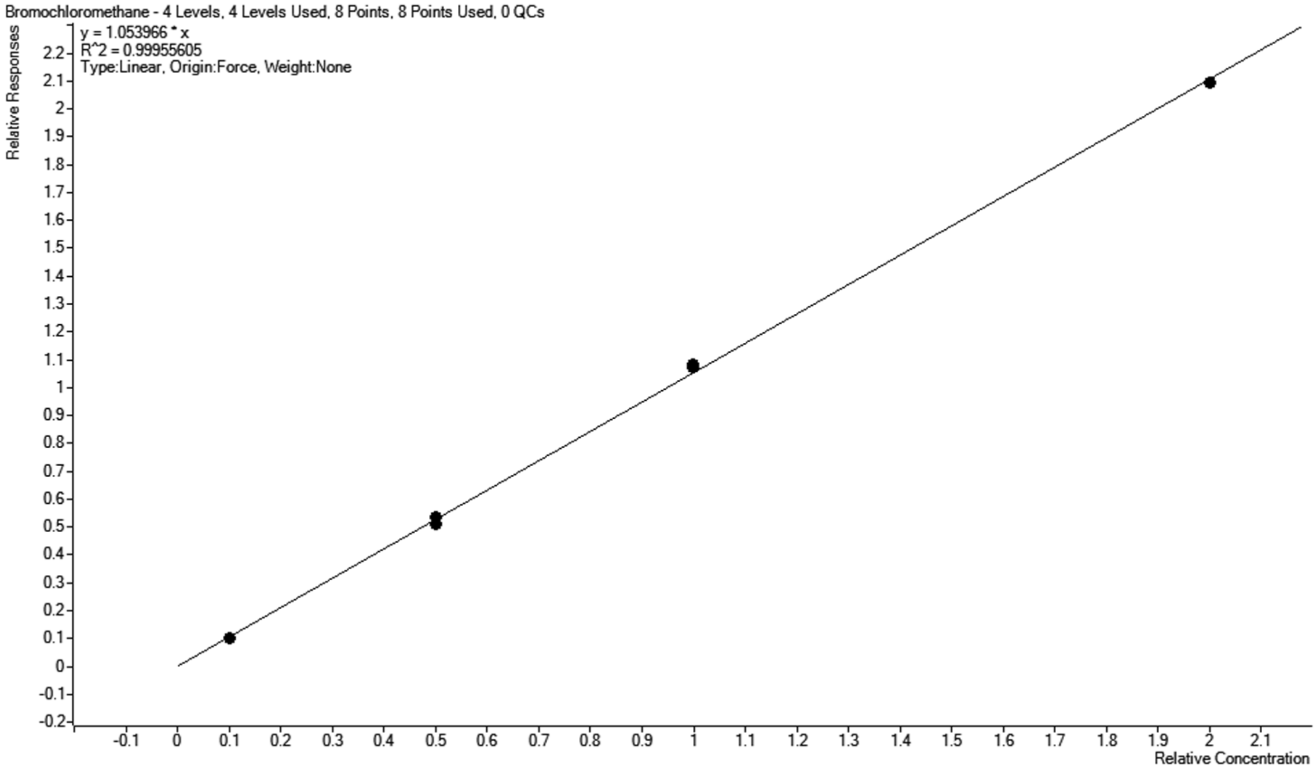

Figure 3: Bromochloromethane Calibration Curve.

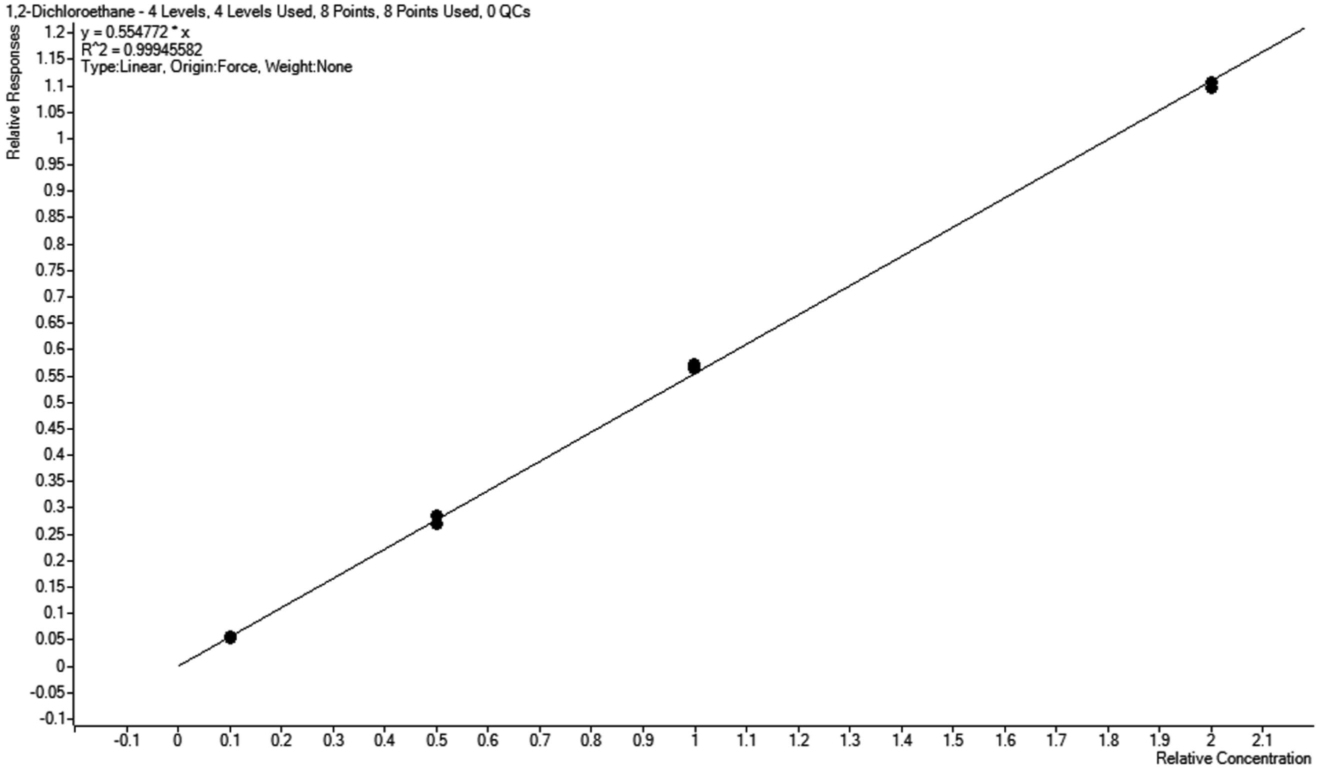

Figure 4: 1,2-Dichloroethane Calibration Curve.

Responses	Injection 1	Injection 2	Injection 3	Injection 4	Injection 5	Average	SD	% RSD
Vinylchloride	0.8984	0.9002	0.8151	0.8822	0.8344	0.8661	0.0390	4.50
Dichloromethane	1.0967	1.1210	1.0994	1.1181	1.0829	1.1036	0.0159	1.44
MTBE	1.1983	1.1919	1.1600	1.1393	1.1175	1.1614	0.0343	2.95
Benzene	0.9971	1.0000	0.9910	0.9989	0.9929	0.9960	0.0039	0.39
1,2-Dichloroethane	1.0135	1.0005	0.9993	1.0113	1.0030	1.0055	0.0065	0.64
Bromodichloromethane	0.9519	0.9602	0.9350	0.9447	0.9322	0.9448	0.0116	1.23
Bromoform	0.9468	0.9385	0.9240	0.9513	0.9198	0.9361	0.0138	1.48
1,2,3-Trichlorobenzene	1.0291	0.9815	0.9667	0.9887	0.9792	0.9890	0.0237	2.40

Table 1: Typical data from a Surface Water sample spiked at the 1.0 µg/L level.

Conclusions

A retention time locked method has been developed on the Agilent 7697A Headspace, 7890B/5977A GC/MS for the determination of VOCs in environmental waters. The GC/MS was run simultaneously in Scan/SIM mode, allowing for quantitation of the analytes whilst also providing a means of identifying any unknowns over a single run. This method demonstrated excellent sensitivity and is capable of determining 66 VOCs over a calibration range of 1 – 20 µg/L.

References

1. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water quality;
Official Journal of the European Union, L 226, Volume 56, 24 August **2013**.

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