Chromatography Technical Note No AS138

Determination of VOCs in water using the new Anatune VOC Analyser

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Introduction

Static headspace extraction with Gas Chromatography-Mass Spectrometry (HS-GC/MS) is an established technique for the determination of volatile organic compounds (VOCs) in drinking water and waste water.
Anatune has many years of experience with headspace analysis for VOCs whereby many VOC analysers have been sold. Success stories at Severn Trent Water and Jones Environmental to name a few.

Within this application note, we show how VOCs quantification can be fully automated by using our new Anatune VOC Analyser.
Auto-spiking of internal standards is performed to achieve very good reproducibility. High through-put can be reached with the use of a 240 positions tray and the Prep. Ahead option in Maestro software along with a short GC run time.

Figure 1 shows the new Anatune VOC Analyser, set up with: a Gerstel MPS Dual Head (2.5 ml Headspace syringe and 100 µl syringe), an Agilent 7890B-5977 GC-MS and a 240 positions tray for 20 ml vials.

Figure 1: Anatune VOC Analyser

Instrumentation

Agilent GC 7890B and Agilent MSD 5977 inert with EI source
Gerstel MPS 2 XL-*xt*
Gerstel Headspace kit
Agilent MassHunter software (version B.07.00.1654)
Maestro software integrated (version 1.4.25.8/3.5)

Method

Headspace parameters:

15 ml water + sodium sulphate in 20 ml vials
Incubation for 17 minutes with an elevated temperature
Injection of 1 ml of headspace

GC-MS parameters:

Column: DB-624 30 m x 0.25 mm x 1.4 µm
GC cycle time: 14 minutes (GC run time = 9.08 minutes)
MS: EI source, SIM / Scan mode performed using two ions per analyte

Compound list:

Internal Standards

Pentafluorobenzene	1,4-Difluorobenzene
Chlorobenzene-d5	1,4-Dichlorobenzene-d4

System Monitoring Compounds

1,2-Dichloroethane-d4	Toluene-d8
4-Bromofluorobenzene	

Target Compound

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

For the suite of 58 compounds, a six point calibration was prepared in spring water at concentrations ranging from 0.1 µg/l to 20 µg/l, keeping the internal standards and surrogates consistent at 30 µg/l.

Calibration standards have been prepared with the use of the MPS, by auto-spiking the water with the suitable volume of stock solution. The only manual steps were adding the sodium sulphate and the water to the 20 ml vials.

Using this set up, one injection was performed every 14 minutes and in 24h , 97 samples could be run.

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Results

Good linearities, performed by auto-spike from the MPS, have been achieved with all correlation coefficients R^2 above 0.995.

Below (Figure 2) shows the calibration plot for chloroethane, carbon tetrachloride, chlorobenzene and naphthalene in spring water, corrected by internal standard. Correlation coefficients of 0.999 were achieved.

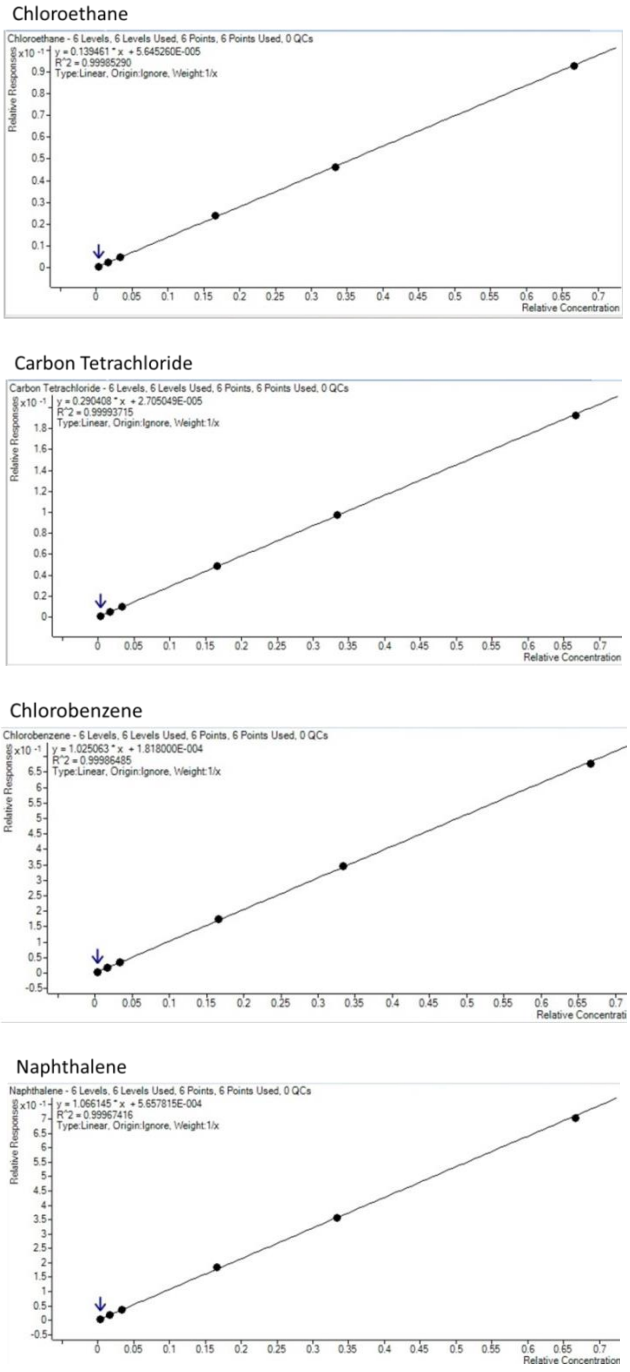

Figure 2: Linearity plots of chloroethane, carbon tetrachloride, chlorobenzene and naphthalene in spring water

Background of 0.1µg/l or less has been observed in our lab for these following analytes: dichloromethane, MTBE, chloroform, bromodichloromethane, toluene, ethyl benzene, m,p-xylene, o-xylene, bromoform, 1,2,4-trimethylbenzene, n-butylbenzene and 1,2,3-trichlorobenzene.
This could be resolved by running the analysis in a positive pressure laboratory.

Figure 3 shows a comparison between a blank and tetrachloroethene at 0.1µg/l.

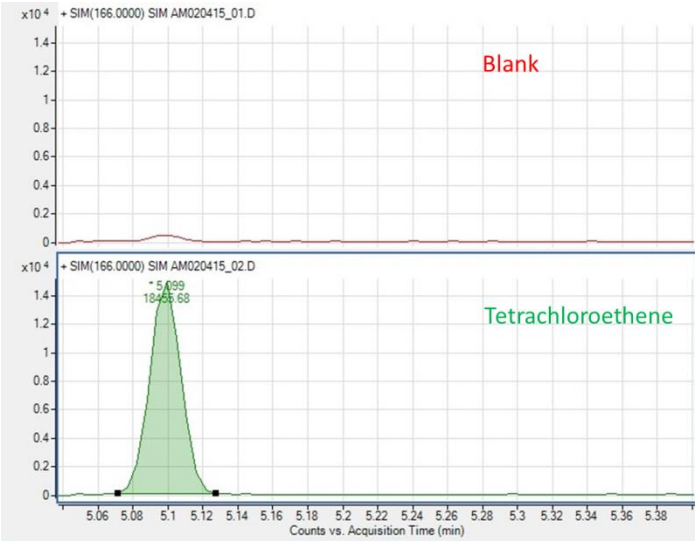

Figure 3: SIM chromatogram (ion 166) comparison of a blank and tetrachloroethene at 0.1 µg/l

Reproducibility experiments have been carried out on 6 aliquots of spring water auto-spiked at 4 µg/l and 16 µg/l. The CVs obtained are all below 10% and the recoveries, internal standard corrected, are between 92 and 107 %.

Table 1 shows the reproducibility data and the recoveries at these two levels for chloroethane, carbon tetrachloride, chlorobenzene and naphthalene.

	Chloroethane		Carbon Tetrachloride	
Amount spiked (µg/l)	**4.0000**	**16.0000**	**4.0000**	**16.0000**
Amount detected (µg/l)	3.9044	15.5161	3.9032	15.5761
	3.8031	15.7613	3.8891	15.6271
	3.9485	16.0213	3.9192	15.5233
	3.8760	15.4063	3.8805	15.4903
	3.8543	15.5026	3.9252	15.4709
	3.7679	15.3993	3.8688	15.3503
Mean	3.8590	15.6012	3.8977	15.5063
SD	0.0660	0.2441	0.0221	0.0955
%CV	**1.71**	**1.56**	**0.57**	**0.62**
% Recovery	**96.48**	**97.51**	**97.44**	**96.91**

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	Chlorobenzene		Naphthalene	
Amount spiked (µg/l)	4.0000	16.0000	4.0000	16.0000
Amount detected (µg/l)	3.9782	15.8103	4.0475	15.4151
	3.9989	15.8424	3.7855	15.5852
	4.0021	15.8653	4.0127	16.1090
	3.9835	15.8585	3.9302	15.2509
	4.0155	15.8687	3.9074	15.6987
	3.9890	15.6825	3.8947	15.5887
Mean	3.9945	15.8213	3.9297	15.6079
SD	0.0137	0.0713	0.0930	0.2915
%CV	0.34	0.45	2.37	1.87
% Recovery	99.86	98.88	98.24	97.55

Table 1: Reproducibility and recovery data for chloroethane, carbon tetrachloride, chlorobenzene and naphthalene in spring water

A comparison between an Agilent MS 5975 and our Agilent MS 5977 has been done. The extraction source of the 5977 was used and allowed to achieve better sensitivity.
Figure 4 shows this comparison at 0.5 µg/l for bromomethane and chloroethane (peaks of interest circled in green).

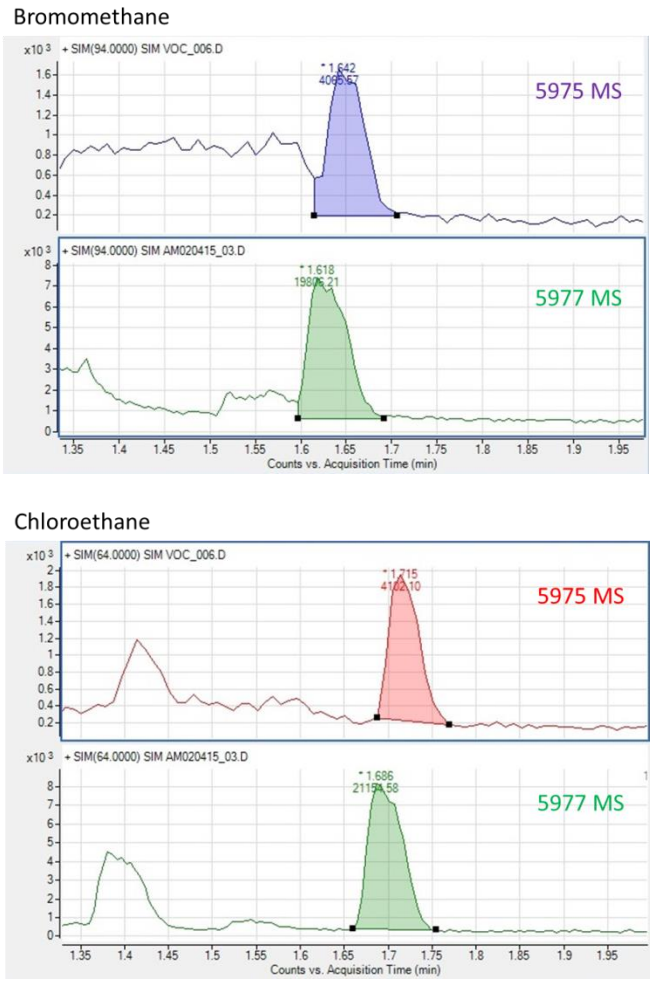

Figure 4: SIM chromatogram comparison between an Agilent MS 5975 and 5977 for bromomethane and chloroethane at 0.5 µg/l

LODs have been calculated from these above chromatograms:
On the 5975 MS, bromomethane got an LOD of 0.136 µg/l, chloroethane got an LOD of 0.087 µg/l.
On the 5977 MS, bromomethane and chloroethane respectively got an LOD of 0.085 µg/l and 0.029 µg/l.
For these two analytes, a 1.6 and 3 fold increase is noticeable from the 5975 MS to the 5977 MS.

Table 2 shows the LOD (µg/L) with two significant figures for the other analytes.

Compound	LOD (µg/L)	Compound	LOD (µg/L)
Dichlorodifluoromethane	0.017	1,2-Dibromoethane	0.0069
Chloromethane	0.039	Chlorobenzene	0.00083
Vinyl Chloride	0.0079	1,1,1,2-Tetrachloroethane	0.0039
Bromomethane	0.059	Ethyl Benzene	< 0.1 *
Chloroethane	0.023	m,p-Xylene	< 0.1 *
Trichlorofluoromethane	0.0048	o-Xylene	< 0.1 *
1,1-Dichloroethene	0.0087	Styrene	0.0011
Dichloromethane	< 0.1 *	Bromoform	< 0.1 *
MTBE	< 0.1 *	Isopropylbenzene	0.00098
trans-1,2-Dichloroethene	0.0069	1,1,2,2-Tetrachloroethane	0.023
1,1-Dichloroethane	0.0033	1,2,3-Trichloropropane	0.010
cis-1,2-Dichloroethene	0.0069	Bromobenzene	0.0022
2,2-Dichloropropane	0.018	n-Propylbenzene	0.00088
Bromochloromethane	0.0078	2-Chlorotoluene	0.0018
Chloroform	< 0.1 *	1,3,5-Trimethylbenzene	0.00087
1,1,1-Trichloroethane	0.0027	4-Chlorotoluene	0.0017
1,1-Dichloropropene	0.0025	tert-Butylbenzene	0.00089
Carbon Tetrachloride	0.0030	1,2,4-Trimethylbenzene	< 0.1 *
Benzene	0.0021	sec-Butylbenzene	0.00058
Trichloroethene	0.0013	1,3-Dichlorobenzene	0.0015
1,2-Dichloropropane	0.0051	p-Isopropyltoluene	0.0016
Dibromomethane	0.0046	1,4-Dichlorobenzene	0.0016
Bromodichloromethane	< 0.1 *	n-Butylbenzene	< 0.1 *
cis-1,3-Dichloropropene	0.0069	1,2-Dichlorobenzene	0.00080
Toluene	< 0.1 *	1,2-Dibromo-3-chloropropane	0.012
trans-1,3-Dichloropropene	0.014	1,2,4-Trichlorobenzene	0.0018
1,1,2-Trichloroethane	0.017	Hexachlorobutadiene	0.0016
1,3-Dichloropropane	0.0065	Naphthalene	0.0031
Tetrachloroethene	0.00078	1,2,3-Trichlorobenzene	< 0.1 *
Dibromochloromethane	0.0043		

* These results are due to the background observed in our lab

Table 2: LOD (µg/L) in spring water

Discussion

This application note shows how the VOC quantification can be fully automated,

Further work would need to be performed with vinyl chloride.
Method robustness and variability is due to be established on real samples from a variety of sources. A stability test and a short NS-30 will be carried out using the auto-spiking and will be detailed in another application note.

Acknowledgement

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