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NS30 and Stability Tests 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.

A previous application note (AS138) shows 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.

In this application note, you will find the promising results of 3 batches of NS30 procedure for VOC analysis in soft, medium, hard and surface water and a 7-day stability trial in spring water.

The NS30 - A Manual on Analytical Quality Control for the Water Industry defines validation and quality control criteria. For a full procedure, 11 batches are run to ensure that the required degrees of freedom are met.

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. water.

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 Compounds

Chloromethane	Benzene
Bromomethane	Trichloroethene
Chloroethane	Bromodichloromethane
Trichlorofluoromethane	Tetrachloroethene
Chloroform	Dibromochloromethane
Carbon Tetrachloride	Bromoform

The tests have been carried out for these 12 selected compounds but, the method can be applied on the suite of 58 compounds used in the previous application note AS138.

Before analysis of each batch (NS30 or stability batch), the 5977 MS was tuned, using the extraction source, and a calibration was run.

For the 12 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 30µg/l.

Calibration standards were 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.

The NS30 batches were as follow, run in a random order:

(nb replicates)	Sample	Low Spike	High Spike	LOD
Spring Water	-	2	2	2
Soft Water	2	2	2	-
Medium Water	2	2	2	-
Hard Water	2	2	2	-
Surface Water	2	2	2	-

Table 1: NS30 Batch

With: Sample = only internal standards and surrogate spiked
Low spike = 20 % of the range = 4 µg/l
High spike = 80 % of the range = 16 µg/l
LOD = Standard 1 = 0.1 µg/l

The stability trail has been carried out for 8 compounds: chloroform, carbon tetrachloride, benzene, trichloroethene, bromodichloromethane, tetrachloroethene, dibromochloromethane and bromoform.

A bulk solution containing the 8 analytes was prepared manually on Day 0, using a THM and VOA mix, and stored in the fridge.

Due to the volatility of the compounds, some degree of loss was expected during the spike preparation. However, the concentrations obtained were satisfactory for the purpose of the stability trial.

The target concentrations were as followed:

Compound	PCV (µg/L)
Benzene	1
Carbon Tetrachloride	3
Tetrachloroethene	5
Trichloroethene	5
Chloroform	25
Bromoform	25
Bromodichloromethane	25
Dibromochloromethane	25

Table 2: Target Spike Concentrations

Day 0 concentrations, lower than the targets, were therefore taken for reference of the following days results.

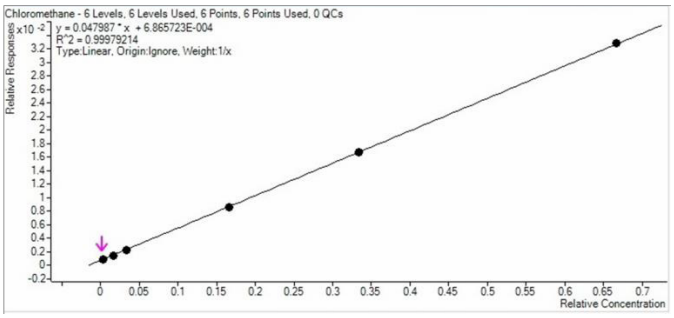
An additional calibration point at 30 µg/l was performed for chloroform, bromoform, bromodichloromethane and dibromochloromethane.

Results

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

Figure 2 below shows the calibration plot from the NS30 batch 1 for chloromethane and chloroethane, in spring water, corrected by internal standard. Correlation coefficients of 0.999 were achieved.

Chloromethane



Chloroethane

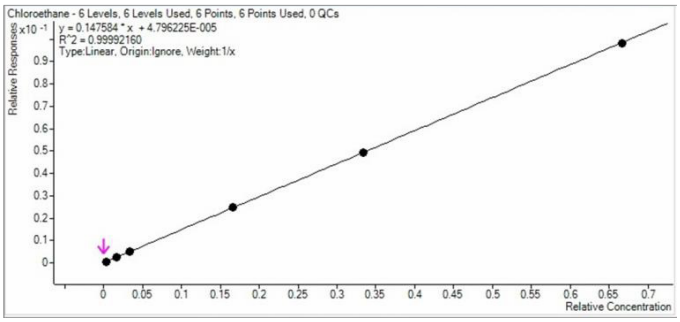


Figure 2: Linearity plots for Chloromethane and Chloroethane in spring water

NS30 procedure:

The 12 target compounds passed the NS30 test (3 batches assessed).

The tables below show the results for carbon tetrachloride in the different waters: spring, soft, medium, hard and surface water.

Carbon Tetrachloride in Spring Water				
Batch	Replicate	LOD	20% Spike	80% Spike
1	1	0.087	4.180	15.670
	2	0.094	4.061	15.752
2	1	0.101	3.976	15.873
	2	0.096	4.189	15.762
3	1	0.095	4.069	15.424
	2	0.097	4.217	15.058
Predicted Concentration (µg/L)		0.100	4.000	16.000
Mean		0.087	4.115	15.590
Relative SD (St)		2.56%	2.82%	1.14%
Recovery		96.67%	102.88%	97.44%

Table 3: Carbon Tetrachloride NS30 Results in Spring Water

Carbon Tetrachloride in Soft Water				
Batch	Replicate	Sample	20% Spike	80% Spike
1	1	nd	4.168	15.926
	2	nd	4.196	15.998
2	1	nd	4.260	15.525
	2	nd	4.119	15.073
3	1	nd	4.064	15.648
	2	nd	4.158	15.589
Predicted Concentration (µg/L)		0.000	4.000	16.000
Mean		-	4.161	15.627
Relative SD (St)		-	1.69%	1.28%
Recovery		-	104.02%	97.67%

Table 4: Carbon Tetrachloride NS30 Results in Soft Water

Carbon Tetrachloride in Medium Water				
Batch	Replicate	Sample	20% Spike	80% Spike
1	1	nd	4.1127	15.4969
	2	nd	4.0730	15.9410
2	1	nd	3.9972	15.8021
	2	nd	3.9457	16.1000
3	1	nd	4.2531	15.6320
	2	nd	4.0628	15.3487
Predicted Concentration (µg/L)		0.000	4.000	16.000
Mean		-	4.074	15.720
Relative SD (St)		-	2.02%	1.57%
Recovery		-	101.85%	98.25%

Table 5: Carbon Tetrachloride NS30 Results in Medium Water

Carbon Tetrachloride in Hard Water				
Batch	Replicate	Sample	20% Spike	80% Spike
1	1	nd	4.1073	15.4231
	2	nd	4.1831	15.8374
2	1	nd	4.1279	15.6616
	2	nd	4.0213	15.4803
3	1	nd	4.1008	15.7476
	2	nd	4.1961	15.5456
Predicted Concentration (µg/L)		0.000	4.000	16.000
Mean		-	4.123	15.616
Relative SD (St)		-	1.60%	1.29%
Recovery		-	103.07%	97.60%

Table 6: Carbon Tetrachloride NS30 Results in Hard Water

Carbon Tetrachloride in Surface Water				
Batch	Replicate	Sample	20% Spike	80% Spike
1	1	nd	4.2153	15.3940
	2	nd	4.1024	15.5433
2	1	nd	4.0948	15.8585
	2	nd	4.1709	15.5146
3	1	nd	4.1136	15.3965
	2	nd	3.9770	16.2379
Predicted Concentration (µg/L)		0.000	4.000	16.000
Mean		-	4.112	15.657
Relative SD (St)		-	1.91%	2.40%
Recovery		-	102.81%	97.86%

Table 7: Carbon Tetrachloride NS30 Results in Surface Water

Stability trial:

10 replicates of the VOC bulk solution, auto spiked with internal standard and surrogates on the day of analysis, have been run on Day 0, Day 4 and Day 7. Day 0 concentrations were taken for reference of the following days results.

The CVs obtained are below 10% for the 8 analytes. Table 8 shows the calculated concentrations, with internal standard correction, and reproducibility results over 7 days for benzene and chloroform.

	Chloroform			Benzene		
	Day 0	Day 4	Day 7	Day 0	Day 4	Day 7
Cal. Conc. (µg/L)	23.6702	22.4545	23.4429	0.8749	0.8146	0.8293
	21.9460	22.3803	23.6275	0.8623	0.7929	0.8283
	22.3230	22.5794	23.7194	0.8665	0.8253	0.8230
	21.9159	22.6898	23.1190	0.8589	0.8051	0.7956
	21.6321	25.0342	22.2612	0.8459	0.8464	0.8149
	22.6616	24.0269	24.2675	0.8513	0.8365	0.8389
	23.0743	23.0018	24.1953	0.8644	0.8240	0.8462
	22.6190	24.1428	24.0591	0.8626	0.8360	0.8410
	23.4269	23.1799	22.5385	0.8704	0.8249	0.8432
	22.7079	25.8616	24.5033	0.8710	0.8574	0.8640
Mean	22.5977	23.5351	23.5734	0.8628	0.8263	0.8324
SD	0.6649	1.1931	0.7461	0.0090	0.0191	0.0189
%CV	2.94	5.07	3.17	1.04	2.31	2.26

Table 8: Concentration and Reproducibility Data for Benzene and Chloroform Over 7 Days in Spring Water

To pass the trial, calculated concentrations had to stay within a range of +/- 20 % of the Day 0 concentration. Table 9 below shows the percentage change in concentration with respect to Day 0: the 8 analytes passed the 7- day stability trial.

	Day 4	Day 7
Chloroform	4.15	4.32
Carbon Tetrachloride	-7.85	-9.93
Benzene	-4.23	-3.52
Trichloroethene	-9.46	-14.52
Bromodichloromethane	1.88	3.42
Tetrachloroethene	-12.81	-15.22
Dibromochloromethane	2.36	1.88
Bromoform	4.45	5.40

Table 9: Percentage Change in Concentration with Respect to Day 0

The average calculated concentrations from Table 8 are displayed in Figure 3 and Figure 4. The standard deviations are represented by the error bars.

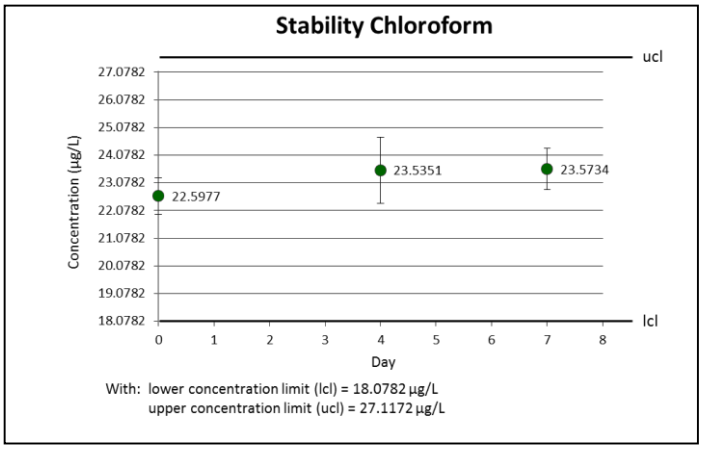


Figure 3: Average Calculated Concentrations for Chloroform over 7 Days

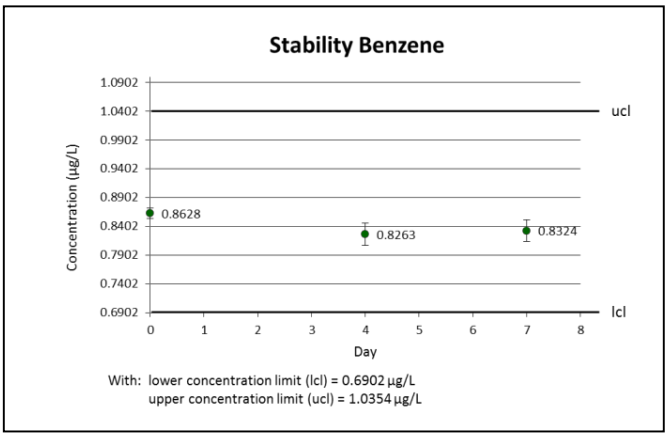


Figure 4: Average Calculated Concentrations for Benzene over 7 Days

Discussion

This application note shows how the VOC quantification can be fully automated and validated.

If you would like to discuss this further, please do not hesitate to contact us, either by emailing enquiries@anatune.co.uk, or call us now on +44 (0)1223 279210.

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