



## METHOD STATEMENT

### Determinand:

Analysis of volatile organic compounds (VOCs).

### Matrix:

Ground waters, surface waters and saline waters.

### Principle of Method:

A 15ml aliquot of water sample, preserved to pH<2 with HCl, is placed in a septum vial together with 3ml of a sodium chloride based matrix modifying solution and allowed to equilibrate with its headspace vapour at 90°C. A sample of the vapour is injected using an automatic headspace sampler into a capillary column gas chromatograph (GC), the volatile organic compounds are separated and then identified and quantified using a mass spectrometer (MSD) operating in selected ion monitoring (SIM) mode.

### Sampling and Sample Preparation:

Water samples are to be supplied in 40ml screw top glass vials preserved with HCl. They must be taken without any significant headspace – that is filled at least up to the shoulder of the vial - and delivered to the laboratory. Where significant headspace is evident, analysis will be undertaken but the results must be accompanied by an analyst comment informing the client of the potential for losses to have occurred.

Samples are stored prior to analysis in a fridge at  $3 \pm 2^\circ\text{C}$ .

Samples should be preserved with HCl to pH<2.

Samples are stable for 14 days (Standard Methods: -ISBN 0-87553-161-X) from sampling.

### Interferences

Excessive amounts of a particular VOC may cause difficulty with the quantitation of others due to spectral interferences. TPHs are particularly prone to interfere; if this is the case then the reporting limit for the VOCs may be raised.

High concentration ( $\geq 10\mu\text{g/l}$ ) of Benzene may result in artificially high concentration of 1, 2-dichloroethane as a consequence of matrix interference due to relatively close retention times of both peaks. To address this, the reporting limit may be raised for 1, 2-dichloroethane whenever the concentration of Benzene is  $\geq 10\mu\text{g/l}$ .

### Performance of Method:

#### LOD, Precision and Bias

Name	LOD $\mu\text{g/L}$	LOQ $\mu\text{g/L}$	MRL $\mu\text{g/L}$	Low Standard		High Standard	
				%Bias	%RSD	%Bias	%RSD
Dichloromethane	0.1529	0.32	0.50	3.34	8.96	-0.39	8.47
trans-1,2-Dichloroethene	0.0466	0.10	0.10	2.39	9.12	1.02	8.81
1,1-Dichloroethane	0.0255	0.052	0.075	3.13	8.12	0.47	8.87
cis-1,2-Dichloroethene	0.0586	0.12	0.15	3.49	7.65	0.40	8.32
Chloroform	0.0442	0.075	0.075	4.94	5.80	0.10	8.38
1,1,1-Trichloroethane	0.0213	0.044	0.050	2.79	6.34	1.01	9.56
Carbon Tetrachloride	0.0267	0.054	0.075	1.55	7.21	1.32	11.25
1,2-Dichloroethane	0.0293	0.060	0.075	1.63	9.53	-1.46	9.18
Benzene	0.0252	0.052	0.075	-1.30	5.09	1.40	7.25
Trichloroethene	0.0217	0.044	0.050	1.58	5.25	1.93	7.50
1,2-Dichloropropane	0.0239	0.048	0.050	1.85	7.03	0.95	7.18
Toluene	0.0284	0.058	0.075	1.34	6.50	2.08	6.72



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Name	LOD µg/L	LOQ µg/L	MRL µg/L	Low Standard		High Standard	
				%Bias	%RSD	%Bias	%RSD
1,1,2-Trichloroethane	0.0605	0.14	0.15	1.55	5.84	0.37	7.21
Tetrachloroethene	0.0217	0.044	0.050	-1.40	11.43	1.26	9.30
Ethylbenzene	0.0233	0.048	0.050	0.65	5.64	1.16	5.78
m.p-Xylene	0.0447	0.090	0.100	-4.34	5.64	3.27	5.24
o-Xylene	0.0231	0.048	0.050	-1.18	4.95	1.92	5.22
Total xylene	0.0669	0.14	0.15	-3.29	5.33	2.82	5.23
Naphthalene	0.0496	0.10	0.10	6.12	8.54	0.10	5.06

### 20% Matrix Spike Recoveries

Name	Eddlestow Groundwater		Draycote Surface Water		Cleethorpes Saline Water	
	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
Dichloromethane	100.02	13.80	104.66	10.88	104.17	14.72
trans-1,2- Dichloroethene	100.92	13.82	104.80	11.61	103.13	14.76
1,1-Dichloroethane	101.46	13.64	106.89	10.25	108.77	15.08
cis-1,2-Dichloroethene	101.80	13.41	106.77	10.61	108.01	16.55
Chloroform	103.11	10.90	108.21	7.33	110.74	11.61
1,1,1-Trichloroethane	100.42	13.71	104.63	9.68	103.33	13.35
Carbon Tetrachloride	98.15	16.20	100.62	13.55	98.16	14.53
1,2-Dichloroethane	98.36	12.74	104.01	9.68	108.68	12.19
Benzene	97.51	8.61	99.28	7.50	96.79	9.14
Trichloroethene	100.74	9.79	101.44	8.10	96.68	9.59
1,2-Dichloropropane	101.08	8.64	104.24	7.36	102.88	8.73
Toluene	100.00	8.66	101.16	7.76	100.88	11.41
1,1,2-Trichloroethane	101.33	8.34	103.69	6.50	104.05	7.84
Tetrachloroethene	99.59	13.88	96.21	13.90	87.21	12.86
Ethylbenzene	99.55	8.40	100.01	9.16	95.18	9.67
m.p-Xylene	94.34	7.78	94.51	9.49	90.87	9.92
o-Xylene	97.08	6.31	98.50	8.14	94.04	9.63
Total xylene	95.26	7.22	95.84	8.95	91.93	9.76
Naphthalene	105.93	8.63	107.86	9.78	109.82	8.08

### 80% Matrix Spike Recoveries

Name	Eddlestow Groundwater		Draycote Surface Water		Cleethorpes Saline Water	
	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
Dichloromethane	99.01	7.39	102.76	6.83	105.66	10.31
trans-1,2- Dichloroethene	99.49	6.87	101.63	7.85	105.60	8.64
1,1-Dichloroethane	100.65	6.68	103.15	7.31	109.91	9.41
cis-1,2-Dichloroethene	99.90	6.60	103.11	7.33	109.65	10.06
Chloroform	100.35	6.64	102.95	6.67	110.14	9.39
1,1,1-Trichloroethane	100.76	6.88	100.69	9.34	104.43	9.18
Carbon Tetrachloride	100.22	8.22	98.63	10.06	100.59	9.40
1,2-Dichloroethane	98.83	8.38	102.53	8.73	110.33	11.58
Benzene	101.49	5.12	100.59	6.54	102.50	8.09



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Name	Eddlestow Groundwater		Draycote Surface Water		Cleethorpes Saline Water	
	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
Trichloroethene	102.26	5.12	99.87	7.74	99.29	7.73
1,2-Dichloropropane	101.53	5.95	101.50	4.96	105.02	8.58
Toluene	102.71	5.98	100.41	5.72	103.93	6.63
1,1,2-Trichloroethane	100.92	7.41	101.50	5.29	105.85	9.64
Tetrachloroethene	102.28	7.84	97.81	9.01	91.67	8.01
Ethylbenzene	102.25	4.27	98.48	6.54	100.42	5.78
m.p-Xylene	104.24	3.97	100.67	5.72	102.73	5.20
o-Xylene	101.95	4.06	99.86	4.84	99.36	5.40
Total xylene	103.48	3.94	100.40	5.42	101.61	5.24
Naphthalene	99.19	6.05	99.27	3.77	103.98	6.28

### Uncertainty of Measurement

The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

Name	Uncertainty of Measurement (%)
Dichloromethane	31.96
trans-1,2-Dichloroethene	26.97
1,1-Dichloroethane	28.95
cis-1,2-Dichloroethene	29.72
Chloroform	28.91
1,1,1-Trichloroethane	26.52
Carbon Tetrachloride	31.38
1,2-Dichloroethane	32.60
Benzene	19.66
Trichloroethene	16.05
1,2-Dichloropropane	18.67
Toluene	18.26
1,1,2-Trichloroethane	19.73
Tetrachloroethene	29.99
Ethylbenzene	17.88
m.p-Xylene	19.42
o-Xylene	16.61
Total xylene	18.19
Naphthalene	18.91

### References:

EPA SW846, Test methods for Evaluating Solid Waste, Physical/Chemical Methods, 3<sup>rd</sup> Edition, Update 111, Dec 1996.

ISBN 0-87553-161-X, Standard Methods for the Examination of Water and Wastewater.