



METHOD STATEMENT

Determinand:

Volatile organic compounds (VOCs) by headspace.

Matrix:

Ground waters, surface waters, landfill leachates and sewage and trade effluents

Principle of Method:

A 10ml aliquot of water sample, preserved to pH<2 with HCl, is placed in a septum vial together with 1ml 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) simultaneously operating in selected ion monitoring (SIM) and full scan modes.

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, the customer is to be informed and direction sought on how to proceed, if analysis is subsequently undertaken 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 between 3±2°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.

Performance of Method:

Range of Method: Typically MRL (Minimum reporting limit) to 250µg/l for each compound without dilution.

Precision, Bias and Limit of Detection

Name	LOD ug/L	MRL ug/L	Low Standard		High Standard	
			Bias	RSD	Bias	RSD
Dichlorodifluoromethane	0.118	1.0	6.2%	8.0%	3.8%	7.9%
Chloromethane	1.772	2.0	14.0%	18.4%	9.3%	11.8%
Vinyl Chloride	0.187	0.5	9.5%	6.0%	8.4%	7.5%
Bromomethane	0.710	1.0	7.7%	8.7%	7.2%	10.5%
Chloroethane	0.437	1.0	10.8%	6.0%	9.7%	7.7%
Trichlorofluoromethane	0.138	1.0	8.6%	6.1%	6.9%	9.9%
1,1-Dichloroethene	0.212	1.0	8.5%	5.1%	7.9%	7.7%
Dichloromethane	0.500	1.0	13.5%	10.2%	12.0%	12.1%



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Name	LOD ug/L	MRL ug/L	Low Standard		High Standard	
			Bias	RSD	Bias	RSD
MTBE	0.919	1.0	7.8%	14.4%	6.9%	8.5%
trans-1,2-Dichloroethene	0.313	1.0	9.5%	5.5%	9.0%	7.4%
1,1-Dichloroethane	0.536	1.0	11.7%	7.2%	10.7%	8.6%
cis-1,2-Dichloroethene	0.716	1.0	10.9%	8.3%	10.6%	9.2%
2,2-Dichloropropane	0.364	1.0	-6.6%	12.6%	-5.8%	9.3%
Bromochloromethane	0.947	1.0	12.9%	9.8%	10.6%	12.0%
Chloroform	0.792	1.0	12.1%	7.1%	10.6%	9.4%
1,1,1-Trichloroethane	0.328	1.0	8.8%	5.6%	7.5%	7.6%
1,1-Dichloropropene	0.215	1.0	6.7%	5.2%	7.9%	7.7%
Carbon Tetrachloride	0.244	1.0	8.1%	5.4%	7.5%	8.5%
1,2-Dichloroethane	0.616	1.0	14.1%	12.5%	13.7%	14.2%
Benzene	0.197	1.0	7.9%	4.9%	7.7%	7.9%
Trichloroethene	0.206	1.0	8.0%	6.2%	6.4%	10.2%
1,2-Dichloropropane	0.435	1.0	10.6%	6.1%	9.2%	7.5%
Dibromomethane	0.767	1.0	12.0%	8.4%	9.0%	9.0%
Bromodichloromethane	0.487	1.0	10.5%	5.6%	8.9%	8.4%
cis-1,3-Dichloropropene	0.398	1.0	6.4%	8.5%	6.5%	6.2%
Toluene	0.247	1.0	6.5%	4.7%	6.9%	8.0%
trans-1,3-Dichloropropene	0.508	1.0	6.1%	9.6%	6.8%	6.3%
1,1,2-Trichloroethane	0.506	1.0	11.5%	7.6%	9.3%	9.0%
Tetrachloroethene	0.241	1.0	6.0%	8.9%	4.8%	14.5%
1,3-Dichloropropane	0.389	1.0	8.7%	6.2%	9.1%	6.3%
Dibromochloromethane	0.391	1.0	10.6%	6.0%	8.4%	6.0%
1,2-Dibromoethane	0.461	1.0	12.4%	8.2%	8.2%	6.1%
Chlorobenzene	0.241	1.0	6.9%	4.6%	6.6%	6.9%
1,1,1,2-Tetrachloroethane	0.191	1.0	8.6%	4.4%	6.5%	6.8%
Ethylbenzene	0.080	1.0	3.7%	6.2%	6.7%	10.0%
m,p-Xylene	0.131	1.0	5.7%	6.8%	5.7%	10.2%
o-Xylene	0.127	1.0	4.6%	5.5%	7.2%	8.4%
Styrene	0.121	1.0	1.3%	7.2%	6.0%	7.0%
Bromoform	0.557	1.0	11.7%	6.8%	8.5%	6.6%
Isopropylbenzene	0.084	1.0	3.0%	8.3%	6.1%	11.7%
1,1,2,2-Tetrachloroethane	0.392	1.0	11.2%	7.0%	8.9%	6.6%
1,2,3-Trichloropropane	0.610	1.0	10.1%	6.9%	8.2%	6.7%
Bromobenzene	0.449	1.0	6.5%	5.6%	7.3%	5.8%
n-Propylbenzene	0.166	1.0	2.6%	8.4%	6.7%	11.8%
2-Chlorotoluene	0.256	1.0	5.2%	6.6%	6.8%	8.4%
1,3,5-Trimethylbenzene	0.181	1.0	3.3%	9.0%	6.1%	11.5%
4-Chlorotoluene	0.274	1.0	6.3%	6.3%	6.1%	8.6%
tert-Butylbenzene	0.195	1.0	1.5%	9.6%	6.3%	12.8%
1,2,4-Trimethylbenzene	0.183	1.0	2.6%	8.8%	5.3%	10.5%
sec-Butylbenzene	0.201	1.0	2.8%	10.6%	6.2%	14.1%
p-Isopropyltoluene	0.161	1.0	1.8%	11.0%	5.6%	13.8%
1,3-Dichlorobenzene	0.279	1.0	6.3%	6.2%	6.3%	8.0%
1,4-Dichlorobenzene	0.405	1.0	4.6%	5.0%	6.1%	7.2%
n-Butylbenzene	0.261	1.0	1.4%	10.2%	6.4%	13.7%
1,2-Dichlorobenzene	0.477	1.0	8.4%	5.9%	6.8%	6.8%
1,2-Dibromo-3-chloropropane	1.582	2.0	10.5%	8.1%	8.4%	8.9%



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Name	LOD ug/L	MRL ug/L	Low Standard		High Standard	
			Bias	RSD	Bias	RSD
1,2,4-Trichlorobenzene	0.826	1.0	3.9%	8.2%	6.7%	7.5%
Hexachlorobutadiene	0.641	1.0	3.4%	11.9%	0.4%	10.3%
Naphthalene	0.858	1.0	0.6%	12.3%	9.1%	5.7%
1,2,3-Trichlorobenzene	0.536	1.0	1.4%	8.1%	7.3%	7.9%

Matrix Spike Recoveries

Name	Groundwater		Surface Water		Landfill Leachate		Trade Effluent		Sewage Effluent	
	Recov.	RSD	Recov.	RSD	Recov.	RSD	Recov.	RSD	Recov.	RSD
Dichlorodifluoromethane	100.6%	10.9%	107.8%	16.3%	104.1%	6.5%	99.0%	8.7%	101.9%	6.4%
Chloromethane	107.8%	8.0%	113.9%	17.9%	103.1%	17.2%	105.8%	9.5%	111.0%	12.8%
Vinyl Chloride	107.4%	7.1%	111.1%	12.6%	107.2%	5.9%	103.3%	7.1%	106.5%	5.8%
Bromomethane	105.1%	7.2%	111.0%	12.4%	108.3%	7.4%	105.0%	6.6%	106.4%	8.7%
Chloroethane	108.6%	6.4%	112.3%	11.5%	109.7%	5.9%	106.4%	5.3%	107.8%	6.4%
Trichlorofluoromethane	107.4%	9.9%	110.0%	10.9%	106.7%	6.9%	106.2%	7.3%	106.0%	5.5%
1,1-Dichloroethene	108.0%	7.2%	110.1%	8.9%	107.6%	5.1%	106.4%	5.0%	106.9%	5.5%
Dichloromethane	110.7%	10.0%	114.6%	12.8%	112.8%	10.7%	108.9%	8.3%	108.9%	8.3%
MTBE	108.7%	9.6%	111.2%	11.0%	112.0%	10.5%	106.4%	8.6%	106.1%	9.4%
trans-1,2-Dichloroethene	108.8%	6.5%	110.9%	8.9%	109.2%	5.5%	107.2%	4.5%	108.0%	6.2%
1,1-Dichloroethane	110.1%	7.4%	112.6%	10.4%	110.9%	7.3%	107.8%	6.0%	109.1%	6.9%
cis-1,2-Dichloroethene	109.9%	8.0%	112.3%	10.1%	111.2%	8.1%	108.8%	5.7%	109.4%	7.3%
2,2-Dichloropropane	95.9%	10.0%	102.6%	11.0%	98.3%	9.2%	102.6%	9.1%	101.1%	10.0%
Bromochloromethane	110.6%	9.9%	114.0%	12.1%	112.6%	12.0%	109.1%	8.3%	109.1%	9.6%
Chloroform	109.6%	8.3%	112.8%	10.9%	111.3%	8.3%	108.0%	6.5%	109.4%	7.7%
1,1,1-Trichloroethane	107.6%	7.1%	109.1%	8.0%	107.5%	5.2%	106.6%	4.8%	106.5%	5.3%
1,1-Dichloropropene	108.5%	7.3%	108.8%	8.3%	107.8%	5.3%	107.3%	5.2%	107.2%	5.4%
Carbon Tetrachloride	108.3%	8.1%	108.7%	8.4%	107.2%	5.9%	107.3%	5.9%	106.8%	5.5%
1,2-Dichloroethane	112.1%	11.5%	115.7%	13.1%	113.7%	11.7%	110.2%	9.4%	111.6%	9.4%
Benzene	108.9%	7.5%	109.8%	9.1%	107.5%	5.9%	106.0%	4.6%	106.4%	4.9%
Trichloroethene	108.2%	10.2%	108.0%	9.0%	106.5%	8.4%	106.3%	8.1%	105.6%	5.6%
1,2-Dichloropropane	109.8%	6.8%	111.5%	9.9%	109.6%	6.7%	107.3%	4.8%	107.8%	5.5%
Dibromomethane	109.6%	7.5%	112.9%	11.8%	109.6%	8.6%	108.6%	6.1%	108.9%	7.9%
Bromodichloromethane	109.6%	6.8%	112.0%	10.2%	109.4%	7.0%	107.1%	5.2%	108.4%	6.6%
cis-1,3-Dichloropropene	106.7%	6.0%	108.4%	8.5%	106.6%	6.7%	105.4%	4.4%	105.8%	5.8%
Toluene	108.6%	7.8%	107.9%	8.7%	106.9%	6.7%	106.0%	5.7%	106.0%	4.9%
trans-1,3-Dichloropropene	107.5%	5.9%	109.4%	8.5%	107.1%	7.4%	105.9%	4.2%	106.4%	6.4%
1,1,2-Trichloroethane	109.2%	7.0%	112.4%	10.2%	110.4%	8.5%	107.8%	5.3%	108.6%	6.9%
Tetrachloroethene	106.9%	14.5%	105.6%	11.2%	104.0%	12.5%	105.6%	12.4%	103.5%	7.2%
1,3-Dichloropropane	108.8%	6.5%	112.7%	12.1%	109.1%	6.1%	108.3%	4.8%	107.8%	5.9%
Dibromochloromethane	108.2%	6.2%	112.7%	11.5%	108.7%	6.3%	107.7%	4.2%	107.6%	6.2%
1,2-Dibromoethane	107.8%	6.7%	112.2%	11.5%	108.3%	7.0%	108.0%	4.3%	107.5%	6.3%
Chlorobenzene	107.2%	6.6%	107.9%	8.1%	106.1%	5.6%	106.1%	5.1%	105.5%	4.9%
1,1,1,2-Tetrachloroethane	107.3%	6.9%	109.3%	8.5%	106.8%	5.8%	106.7%	5.1%	105.7%	5.2%
Ethylbenzene	107.9%	9.3%	106.4%	9.6%	106.1%	8.4%	106.4%	8.3%	105.7%	5.0%
m.p-Xylene	107.1%	10.2%	105.8%	10.4%	104.9%	8.4%	105.3%	8.0%	104.5%	5.0%
o-Xylene	107.7%	8.0%	107.5%	9.3%	106.6%	6.5%	106.6%	6.8%	106.2%	4.5%



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Name	Groundwater		Surface Water		Landfill Leachate		Trade Effluent		Sewage Effluent	
	Recov.	RSD	Recov.	RSD	Recov.	RSD	Recov.	RSD	Recov.	RSD
Styrene	107.0%	6.5%	106.8%	8.9%	106.3%	5.5%	103.6%	4.6%	106.0%	4.1%
Bromoform	108.4%	6.9%	112.4%	10.9%	108.9%	7.4%	108.3%	4.8%	107.6%	6.7%
Isopropylbenzene	107.5%	11.5%	105.2%	13.0%	105.1%	10.3%	106.3%	9.7%	104.8%	5.6%
1,1,2,2-Tetrachloroethane	108.3%	6.9%	113.2%	12.4%	109.5%	7.2%	108.6%	5.0%	108.1%	6.4%
1,2,3-Trichloropropane	107.9%	6.8%	112.8%	12.1%	109.3%	6.8%	108.2%	5.5%	107.8%	6.2%
Bromobenzene	107.4%	6.2%	110.3%	10.0%	106.0%	5.3%	106.0%	4.3%	106.2%	4.6%
n-Propylbenzene	108.0%	11.6%	106.0%	10.5%	104.3%	9.4%	105.8%	9.8%	105.3%	5.6%
2-Chlorotoluene	107.6%	8.7%	108.0%	8.0%	105.1%	6.5%	105.5%	6.5%	105.3%	4.6%
1,3,5-Trimethylbenzene	107.4%	11.2%	105.8%	10.1%	104.2%	8.7%	104.5%	8.8%	104.8%	5.3%
4-Chlorotoluene	107.1%	8.3%	107.6%	8.0%	105.2%	6.4%	105.4%	6.4%	105.3%	4.7%
tert-Butylbenzene	107.7%	12.5%	105.5%	11.7%	104.2%	10.4%	105.6%	10.2%	105.1%	6.0%
1,2,4-Trimethylbenzene	106.8%	10.1%	105.4%	10.1%	104.4%	7.8%	103.2%	7.4%	104.2%	5.1%
sec-Butylbenzene	107.8%	14.3%	104.8%	13.7%	103.9%	11.6%	105.8%	11.8%	104.8%	6.6%
p-Isopropyltoluene	107.4%	13.9%	104.1%	14.6%	103.9%	11.2%	104.9%	11.4%	104.4%	6.9%
1,3-Dichlorobenzene	106.8%	7.7%	107.3%	7.5%	105.1%	5.8%	105.0%	6.0%	105.0%	4.8%
1,4-Dichlorobenzene	105.8%	7.6%	106.4%	8.3%	103.7%	5.4%	104.2%	5.8%	104.6%	5.2%
n-Butylbenzene	108.3%	13.7%	104.4%	16.2%	104.4%	11.4%	106.0%	11.2%	105.1%	6.5%
1,2-Dichlorobenzene	107.5%	6.9%	108.8%	8.1%	106.1%	5.2%	105.8%	4.7%	105.8%	4.8%
1,2-Dibromo-3-chloropropane	107.6%	9.1%	109.7%	10.9%	108.1%	7.8%	108.0%	6.8%	106.5%	6.6%
1,2,4-Trichlorobenzene	107.4%	6.5%	106.5%	9.3%	104.6%	7.1%	105.7%	5.1%	105.2%	5.8%
Hexachlorobutadiene	104.0%	11.8%	104.9%	14.5%	102.9%	15.3%	105.5%	15.3%	103.3%	9.2%
Naphthalene	108.8%	6.8%	109.8%	8.1%	107.0%	7.3%	108.7%	5.0%	107.5%	6.0%
1,2,3-Trichlorobenzene	107.4%	7.3%	108.4%	9.1%	106.3%	7.5%	106.5%	5.3%	105.6%	5.9%

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 (%)	Name	Uncertainty (%)
Dichlorodifluoromethane	25.04	Dibromochloromethane	24.06
Chloromethane	38.85	1,2-Dibromoethane	25.76
Vinyl Chloride	23.74	Chlorobenzene	19.73
Bromomethane	26.79	1,1,1,2-Tetrachloroethane	20.87
Chloroethane	24.98	Ethylbenzene	23.92
Trichlorofluoromethane	22.99	m,p-Xylene	23.37
1,1-Dichloroethene	20.86	o-Xylene	22.19
Dichloromethane	33.14	Styrene	18.85
MTBE	30.93	Bromoform	25.11
trans-1,2-Dichloroethene	22.31	Isopropylbenzene	27.45
1,1-Dichloroethane	26.32	1,1,2,2-Tetrachloroethane	24.88
cis-1,2-Dichloroethene	28.00	1,2,3-Trichloropropane	25.21
2,2-Dichloropropane	28.67	Bromobenzene	19.09
Bromochloromethane	32.88	n-Propylbenzene	24.80
Chloroform	27.24	2-Chlorotoluene	19.92
1,1,1-Trichloroethane	19.92	1,3,5-Trimethylbenzene	22.61



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Name	Uncertainty (%)	Name	Uncertainty (%)
1,1-Dichloropropene	20.36	4-Chlorotoluene	19.23
Carbon Tetrachloride	21.58	tert-Butylbenzene	26.09
1,2-Dichloroethane	35.97	1,2,4-Trimethylbenzene	20.63
Benzene	20.39	sec-Butylbenzene	28.81
Trichloroethene	22.18	p-Isopropyltoluene	27.41
1,2-Dichloropropane	22.79	1,3-Dichlorobenzene	18.03
Dibromomethane	27.00	1,4-Dichlorobenzene	16.57
Bromodichloromethane	22.81	n-Butylbenzene	28.70
cis-1,3-Dichloropropene	19.18	1,2-Dichlorobenzene	18.27
Toluene	19.54	1,2-Dibromo-3-chloropropane	24.13
trans-1,3-Dichloropropene	21.27	1,2,4-Trichlorobenzene	18.32
1,1,2-Trichloroethane	25.15	Hexachlorobutadiene	31.23
Tetrachloroethene	29.26	Naphthalene	22.25
1,3-Dichloropropane	24.65	1,2,3-Trichlorobenzene	19.61

References:

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

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