METHOD STATEMENT

Determinand:
The analysis of Trichloromethane, Bromodichloromethane, Dibromochloromethane, Tribromomethane, Tetrachloromethane, Trichloroethene, Tetrachloroethene, 1,1,1-Trichloroethane, 1,2-Dichloroethane, 1,2-Dibromoethane, MethylTertiary Butyl Ether (MTBE), TertAmylMethylEther (TAME), 1,1-Dichloroethane, Benzene, Toluene, Ethylbenzene and Xylenes (BTEX compounds).

Matrix:
Sample Type: Raw and Potable waters.

Principle of Method:
The water sample is placed in a septum vial and allowed to equilibrate with its headspace vapour at 60°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 with mass spectrometric detection (MSD) in selected ion monitoring (SIM) mode.

Sampling and Sample Preparation:
Amber sampling vials are prepared prior to sending to samplers by the addition of 100µl of Sodium Thiosulphate solution as specified in the sampling manual.
The vial is slowly and completely filled to exclude headspace in order to avoid loss of volatile determinands. When the water just begins to overflow the vial it is capped with the PTFE face of the septum in contact with the sample.
Storage – samples should be analysed as soon as possible after collection. When this is not possible they should be stored under refrigeration at 3 ± 2°C in the dark, until analysis can begin. The maximum permissible storage time prior to analysis is given below which is either derived from BS EN ISO 5667-3: 2003 "Water Quality – Sampling – Part 3: Guidance on the preservation and handling of water samples (BS 6068-6.3:2003) or from Wakefield Laboratory in-house data ["WL IHD"] which is held by the Quality section.

Determinand	**Maximum period of analyte stability prior to any extraction step (days)**	**Maximum period of analyte stability after to any extraction step (days)**	**Data is quoted from in-house data ["WL IHD"]**
Trichloromethane	21	N/A	WL IND
Bromodichloromethane	21	N/A	WL IND
Dibromochloromethane	21	N/A	WL IND
Tribromomethane	21	N/A	WL IND
Tetrachloromethane	21	N/A	WL IND
Trichloroethene	21	N/A	WL IND
Tetrachloroethene	21	N/A	WL IND
1,1,1 - Trichloroethane	21	N/A	WL IND
1,2 - Dichloroethane	21	N/A	WL IND
1,2 - Dibromoethane	21	N/A	WL IND
MTBE	21	N/A	WL IND
TAME	21	N/A	WL IND
Benzene	21	N/A	WL IND
Ethylbenzene	21	N/A	WL IND
Toluene	21	N/A	WL IND
Para-Xylene	21	N/A	WL IND
Meta-Xylene	21	N/A	WL IND

Ortho-Xylene	21	N/A	WL IND
1,1-Dichloroethane	21	N/A	WL IND

As the samples are analysed directly from the supplied sealed 'THM' vial, no data is available for stability in solvent.

The sample vials are checked for headspace prior to analysis and vials with significant headspace, >10% of the vial, are noted on the extraction log and an appropriate analyst's comment must be assigned to the sample when entering the sample results both onto the worksheet and onto the LaBS database

Interferences

Any compound, which passes through the extraction procedure, and has similar Gas Chromatographic and mass spectrometric properties to the analyte will cause interference. No bottles of reference materials are to be opened, and no stock, intermediate or spiking solution preparation is to be carried out in the Wakefield VOC Laboratory.

Performance of Method:

Range of Application:

Headspace Twister instruments

Determinands	Operational Range
Trichloromethane	LOQ - 200 µg/l
Bromodichloromethane	LOQ - 100 µg/l
Dibromochloromethane	LOQ - 100 µg/l
Tribromomethane	LOQ - 100 µg/l
Tetrachloromethane	LOQ - 10 µg/l
Trichloroethene	LOQ - 50 µg/l
Tetrachloroethene	LOQ - 20 µg/l
1,1,1 - Trichloroethane	LOQ - 20 µg/l
1,2 - Dichloroethane	LOQ - 20 µg/l
1,2 - Dibromoethane	LOQ - 50 µg/l
MethylTertiary Butyl Ether (MTBE)	LOQ - 50 µg/l
TertAmylMethylEther (TAME)	LOQ - 50 µg/l
Benzene	LOQ - 5 µg/l
Ethylbenzene	LOQ - 20 µg/l
Toluene	LOQ - 20 µg/l
Para-Xylene	N/A
Meta-Xylene	N/A
Sum of Meta-Xylene + Para-Xylene	LOQ - 40 µg/l
Ortho-Xylene	LOQ - 20 µg/l
1,1-Dichloroethane	LOQ - 20 µg/l

Reporting Limits are the same as the LOQ

Limit of Quantification:

Determinand	**Det Code**	**LOQ Values (µg L^{-1})**		
		Headspace	Twister	**Method**
Trichloromethane	A33	0.18	0.17	**0.18**
Bromodichloromethane	A2X	0.17	0.18	**0.18**
Dibromochloromethane	A2W	0.32	0.21	**0.32**
Tribromomethane	A30	0.31	0.30	**0.31**

Determinand	Det Code	LOQ Values (µg L^{-1})		
		Headspace	Twister	**Method**
Tetrachloromethane	A2Z	0.16	0.11	**0.16**
Trichloroethene	A32	0.40	0.15	**0.40**
Tetrachloroethene	A2Y	0.45	0.27	**0.45**
1,1,1 - Trichloroethane	A31	0.44	0.22	**0.44**
1,2 - Dichloroethane	A34	0.16	0.11	**0.16**
1,2 - Dibromoethane	AG4	0.32	0.29	**0.32**
MethylTertiary Butyl Ether (MTBE)	AEN	0.05	0.05	**0.05**
TertAmylMethylEther (TAME)	AG3	0.36	0.44	**0.44**
Benzene	A35	0.06	0.03	**0.06**
Ethylbenzene	AEK	0.04	0.05	**0.05**
Toluene	AG2	0.05	0.04	**0.05**
Meta-Xylene + Para-Xylene	AEL	0.08	0.07	**0.08**
Ortho-Xylene	AEM	0.04	0.06	**0.06**
1,1-Dichloroethane	AMT	0.27	0.06	**0.27**

Recoveries of Compounds and Uncertainty of measurement:

Determinand	Headspace	
	% Recovery	**Uncertainty %**
Trichloromethane	91.36%	± 46.86%
Bromodichloromethane	138.44%	± 58.44%
Dibromochloromethane	170.01%	± 90.42%
Tribromomethane	178.29%	± 99.46%
Tetrachloromethane	91.36%	± 24.99%
Trichloroethene	83.45%	± 31.19%
Tetrachloroethene	98.25%	± 12.08%
1,1,1-Trichloroethane	89.15%	± 23.07%
1,2-Dichloroethane	132.41%	± 50.18%
1,2-Dibromoethane	117.78%	± 34.74%
MethylTertiary Butyl Ether (MTBE)	151.95%	± 68.68%
TertAmylMethylEther (TAME)	114.79%	± 31.36%
Benzene	100.91%	± 7.88%
Ethylbenzene	99.09%	± 67.49%
Toluene	102.37%	± 52.52%
Meta-Xylene + Para-Xylene	130.02%	± 35.83%
Ortho-Xylene	106.36%	± 14.15%
1,1-Dichloroethane	137.58%	± 59.47%

Determinand	Twister	
	% Recovery	**Uncertainty %**
Trichloromethane	97.98%	± 10.77%
Bromodichloromethane	95.23%	± 12.54%
Dibromochloromethane	98.44%	± 9.83%
Tribromomethane	98.30%	± 11.81%
Tetrachloromethane	96.15%	± 16.94%
Trichloroethene	94.60%	± 13.26%
Tetrachloroethene	99.17%	± 11.11%
1,1,1 - Trichloroethane	98.85%	± 10.78%
1,2 - Dichloroethane	105.52	± 11.73%
1,2 - Dibromoethane	102.10%	± 10.39%

Determinand	Twister	
	% Recovery	Uncertainty %
MethylTertiary Butyl Ether (MTBE)	102.21%	± 8.28%
TertAmylMethylEther (TAME)	105.82	± 17.74%
Benzene	98.52%	± 7.47%
Ethylbenzene	102.33%	± 8.61%
Toluene	101.43%	± 7.33%
Meta-Xylene + Para-Xylene	101.14%	± 7.03%
Ortho-Xylene	102.33%	± 8.15%
1,1-Dichloroethane	103.82%	± 12.10%

References:
In house method