

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 STL53 are prepared prior to sending to samplers by the addition of 100 µL of sodium thiosulfate 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. Samples are assessed for suitability on arrival in the laboratory, by inversion of the vial, where the bubble covers approximately two thirds of the bottom of the vial this is approximately equivalent to a bubble of 2 mL. Any bubble larger than this (i.e. covers the full width of the vial) is deemed to be significant, and a deviating comment should be made against the relevant test.

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

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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 VOC Laboratory.

Performance of Method:

Range of Application:

Headspace Twister instruments	
Determinands	Operational Range
Trichloromethane	LOQ - 125 µg/l
Bromodichloromethane	LOQ - 125 µg/l
Dibromochloromethane	LOQ - 125 µg/l
Tribromomethane	LOQ - 125 µg/l
Tetrachloromethane	LOQ - 15 µg/l
Trichloroethene	LOQ - 25 µg/l
Tetrachloroethene	LOQ - 25 µg/l
1,1,1 - Trichloroethane	LOQ - 25 µg/l
1,2 - Dichloroethane	LOQ - 15 µg/l
1,2 - Dibromoethane	LOQ - 25 µg/l
MethylTertiary Butyl Ether (MTBE)	LOQ - 25 µg/l
TertAmylMethylEther (TAME)	LOQ - 25 µg/l
Benzene	LOQ - 5 µg/l
Ethylbenzene	LOQ - 25 µg/l
Toluene	LOQ - 25 µg/l
Para-Xylene	N/A
Meta-Xylene	N/A
Sum of Meta-Xylene + Para-Xylene	LOQ - 50 µg/l
Ortho-Xylene	LOQ - 25 µg/l
1,1-Dichloroethane	LOQ - 25 µg/l
Reporting Limits are the same as the LOQ	

Limit of Quantification:

Determinand	Det Code	LOQ Values (µg L ⁻¹)		
		WGCHS1	WGCHS2	Method*
Trichloromethane	A33	0.25	0.24	0.67
Bromodichloromethane	A2X	0.26	0.32	0.32
Dibromochloromethane	A2W	0.11	0.32	0.32
Tribromomethane	A30	0.10	0.29	0.31
Tetrachloromethane	A2Z	0.07	0.04	0.16
Trichloroethene	A32	0.05	0.05	0.40

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Determinand	Det Code	LOQ Values ($\mu\text{g L}^{-1}$)		
		WGCHS1	WGCHS2	Method*
Tetrachloroethene	A2Y	0.04	0.06	0.45
1,1,1 - Trichloroethane	A31	0.13	0.21	0.44
1,2 - Dichloroethane	A34	0.08	0.16	0.16
1,2 - Dibromoethane	AG4	0.09	0.06	0.32
MethylTertiary Butyl Ether (MTBE)	AEN	0.05	0.05	0.05
TertAmylMethylEther (TAME)	AG3	0.26	0.07	0.36
Benzene	A35	0.03	0.03	0.06
Ethylbenzene	AEK	0.02	0.03	0.04
Toluene	AG2	0.03	0.03	0.05
Meta-Xylene + Para-Xylene	AEL	0.05	0.06	0.08
Ortho-Xylene	AEM	0.03	0.04	0.04
1,1-Dichloroethane	AMT	0.08	0.06	0.27

Recoveries of Compounds and Uncertainty of measurement:

Determinand	WGCHS1		WGCHS2	
	% Recovery	Uncertainty %	% Recovery	Uncertainty %
Trichloromethane	97.53%	$\pm 17.78\%$	98.33%	$\pm 16.17\%$
Bromodichloromethane	96.05%	$\pm 13.38\%$	98.86%	$\pm 14.10\%$
Dibromochloromethane	94.02%	$\pm 20.30\%$	98.99%	$\pm 15.35\%$
Tribromomethane	95.26%	$\pm 24.46\%$	99.16%	$\pm 19.84\%$
Tetrachloromethane	99.73%	$\pm 19.28\%$	98.80%	$\pm 17.38\%$
Trichloroethene	104.71%	$\pm 13.73\%$	101.93%	$\pm 8.44\%$
Tetrachloroethene	101.46%	$\pm 13.37\%$	99.08%	$\pm 10.45\%$
1,1,1-Trichloroethane	102.46%	$\pm 12.88\%$	100.61%	$\pm 10.06\%$
1,2-Dichloroethane	98.28%	$\pm 8.45\%$	99.92%	$\pm 7.40\%$
1,2-Dibromoethane	96.59%	$\pm 12.53\%$	101.25%	$\pm 10.59\%$
MethylTertiary Butyl Ether (MTBE)	98.04%	$\pm 12.80\%$	97.58%	$\pm 10.08\%$
TertAmylMethylEther (TAME)	96.42%	$\pm 14.37\%$	97.68%	$\pm 9.93\%$
Benzene	95.02%	$\pm 15.12\%$	96.94%	$\pm 10.98\%$
Ethylbenzene	98.16%	$\pm 8.89\%$	98.35%	$\pm 10.44\%$
Toluene	95.43%	$\pm 12.55\%$	98.33%	$\pm 9.11\%$
Meta-Xylene + Para-Xylene	99.12%	$\pm 9.53\%$	98.88%	$\pm 9.19\%$
Ortho-Xylene	101.44%	$\pm 20.64\%$	100.51%	$\pm 14.18\%$
1,1-Dichloroethane	95.03%	$\pm 13.34\%$	97.67%	$\pm 14.57\%$

References:

In house method