The determination of volatile organic compounds in waters and complex matrices by purge and trap or by headspace techniques 1998

Methods for the Examination of Waters and Associated Materials

The methods in this booklet are designed for the determination of volatile organic compounds by direct purge and trap analysis using gas chromatography with mass spectrometric detection, and by direct headspace analysis using gas chromatography with electron capture detection. Performance data are available from several laboratories.

Because of the volatility of the determinands and the nature of the purge and trap and headspace procedures, considerable care needs to be taken at all stages of the methods. This will ensure that losses caused by evaporation, or contamination of equipment or samples as a result of working in a contaminated atmosphere, are reduced. A number of precautions are described within the methods to help minimise these problems.

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of materials and apparatus used. Whilst the methods report the use of materials actually used in the evaluation tests this does not endorse these materials as being superior to others. Equivalent materials are acceptable and it should be understood that the performance characteristics may differ when others are used.

The performance data for the methods represent typical data obtained under the experimental conditions used by the laboratories which undertook the performance evaluation. It is essential for users to evaluate these methods in their own laboratories.

Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, groundwater, river and seawater, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests reported for most parameters. These methods should be capable of establishing within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors), systematic error (bias), total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of the publication on whether or not the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets in the series 'Methods for the Examination of Waters and Associated Materials' and their continuous revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage treatment methods and biodegradability
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods and the more important parameters and topics is available from HMSO (ISBN 0 11 752669 X).

Every effort is made to avoid errors appearing in the published text. If, however, any are found please notify the Secretary.

Dr D Westwood
Secretary

February 1998

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and any regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 (SI 1988/1657). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety, and these should be consulted and be readily accessible to all analysts. Amongst such publications are those produced by the Royal Society of Chemistry, namely 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', 5th edition, 1992; by Member Societies of the Micrbiological Consultative Committee, 'Guidelines for Microbiological Safety', 1986, Portland Press, Colchester; and by the Public Health Laboratory Service 'Safety Precautions, Notes for Guidance'. Another useful publication is produced by the Department of Health entitled 'Good Laboratory Practice'.

A The determination of volatile organic compounds in waters by purge and trap using gas chromatography with mass spectrometric detection

A1 Performance characteristics of the method

A1.1 Substances determined. See Table A1.

A1.2 Type of sample. Potable, river, ground, saline and some waste waters.

A1.3 Basis of method. The determinands are purged from water with an inert gas, trapped on a solid adsorbent and then thermally desorbed. The released determinands are analysed by gas chromatography (GC) with mass spectrometric (MS) detection.

A1.4 Range of application. Typically up to 120 $\mu g l^{-1}$ of each component, but this range may vary with different instruments. The upper limit may be extended by dilution of the sample. Systems should be validated across the range of concentrations to be measured. The performance characteristics obtained in Table A1 are based on a sample volume of 5 ml.

A1.5 Calibration curve. This will be dependent on the dynamic range of the instrument.

A1.6 Standard deviation. See Tables A1 and A3.

A1.7 Limits of detection. See Tables A1 and A3.

A1.8 Bias. See Tables A1 and A3.

A1.9 Interferences. Any purgeable substance having similar chromatographic and mass spectral properties to any of the determinands will interfere. Excess water vapour, if transferred to the trap, may adversely affect the mass spectrometer. Care should be taken to avoid contamination from organic vapours arising from within the laboratory. Care should also be taken with samples of unknown origin. Contamination of the instrument may occur with highly contaminated samples.

A1.10 Time required for analysis. Ten samples, including full calibration, control and blank solutions, can be prepared and analysed in a 24 hour period. This assumes the use of automatic purging and injection equipment. Data handling will require additional time. The minimum time to analyse a single sample is approximately 4 hours.

A2 Principle

An aliquot of sample is purged with an inert gas. Volatile compounds are subsequently adsorbed onto a suitable column of adsorbent material. The column material is then heated to desorb the volatile components, which are then separated by capillary GC, utilising temperature programming, and MS detection. The data are acquired in full scan mode so that the spectra may be matched against those of known standard compounds. Quantification is carried out using selected ions with characteristic m/z values for each determinand; for example see Table A2.

The method is not suitable for non-purgeable substances and some polar compounds.

A3 Interferences

In principle, any purgeable compound which elutes at the same chromatographic retention time and produces an identical, or very similar, mass spectrum to any determinand under investigation will interfere. In practice, this is unlikely as the spectra of most of the determinands are characteristic. With retention time data and the availability of the spectrum over a wide mass range, the possibility of mis-

identification is quite small. Co-eluting peaks with ions with common m/z values might cause interference, but quantification ions can be chosen to preclude this, although para- and meta-xylene are not resolved.

Suppression of the mass spectrometer sensitivity can occur when a component elutes when present at a high concentration. This is commonly observed for water where the presence of detergents in the sample can increase the amount of water vapour purged from the sample. This suppression can cause under-reporting, or over-reporting, of the determinand concentration.

To minimise contamination of samples and blanks from the atmosphere, extreme care should be taken in laboratories where extraction solvents are commonly in use. Contamination can arise within the laboratory, or from an adjacent laboratory area with a shared ventilation system, and can lead to airborne contamination of sample vials and equipment. Particular care should be taken in areas where samples are handled and transferred, and during the preparation of concentrated standard solutions.

A4 Hazards

Skin contact or inhalation of all reagents and their solutions specified in this method should be avoided. Methanol is toxic, narcotic and flammable. Several halogenated hydrocarbons are suspected carcinogens. Standard solutions should always be prepared in a fume cupboard. Always ensure adequate ventilation and work in a flame- and spark-proof area. Spark-proof refrigerators should be used to store standard solutions. Appropriate safety procedures should be followed.

A5 Reagents

All reagents should be of sufficient purity that they do not give rise to interfering peaks in the gas chromatographic analysis. Freshly prepared standard solutions can be checked against previously prepared standard solutions to ensure, and check for, standard integrity. This should be checked with each batch of material by analysing procedural blank solutions with each batch of samples. High performance liquid chromatographic grade solvents and analytical reagent grade materials in the case of other reagents are normally suitable unless otherwise specified. Reagents may become contaminated by contact with air and/or other materials, particularly plastics, or by degradation caused by the action of light. Reagents should be stored in all-glass containers or other vessels found to be suitable, and kept in the dark if necessary.

A5.1 **Methanol.**

A5.2 **Water.** Water known to be free from contamination, for example raw underground water. This is used for blank and quality control determinations and for preparing standard solutions and making dilutions.

The water used for blank determinations and preparation of standard and analytical quality control (AQC) solutions should show negligible interferences in comparison with the smallest concentration to be determined.

Sufficient water from the same batch should be available to complete each batch of analyses, including all preparations.

A5.3 **Sodium thiosulphate pentahydrate.**

A5.4 **Standard solutions.** Owing to the volatility of some gases and the more volatile compounds listed in Tables A1 and A3, great care is required in the preparation of standard solutions; losses may occur in the headspace of the vessel used to prepare standard solutions. Vials (completely filled) have been used or other appropriate systems devised to minimise headspace losses. It may be advisable, and more appropriate, to use commercially available standard solutions. Intermediate standard solutions should be stored below 4°C and allowed to reach room temperature before use.

Whilst the following procedure is given as an example, users may wish to prepare their own standard solutions by an alternative procedure which is shown to produce equivalent results.

A5.5 **Stock calibration standard solution (200 mgl^{-1}).** A solution of a mixture of volatile organic compounds (VOC) is commercially available.

A5.6 **Intermediate calibration standard solution (5 mgl^{-1}).** Using a 250 µl syringe, add to approximately 8 ml of methanol in a 10 ml volumetric flask, a quantity (250 ± 5 µl) of the VOC stock calibration standard (A5.5). Make up to the mark with methanol and mix well.

A5.7 **Internal and surrogate standard solutions.** Typical internal and surrogate standards which have been used include:

fluorobenzene	pentafluorobenzene
4-bromofluorobenzene	benzene-d_6
toluene-d_8	1,2-dichloroethane-d_4
dibromofluoromethane	ethylbenzene-d_5
chlorobenzene-d_5	bromochloromethane
1,4-dichlorobenzene-d_4	2-bromo-1-chloropropane
1,4-difluorobenzene	1,4-dichlorobutane
naphthalene-d_8	

Laboratories should choose internal and surrogate standard solutions which are appropriate to the suite and range of determinands being analysed.

A5.8 **Working standard solutions.** The following procedure was used in the production of the performance data shown in Table A1. Equivalent procedures may be used.

Using a microlitre syringe, add 50 ± 1 µl and 150 ± 2 µl respectively of VOC stock calibration standard (A5.5) to two separate 250 ml portions of interference-free water (A5.2). Inject the stock standards below the water surface and shake to mix. See table below.

Using microlitre syringes, as appropriate, add 50 ± 1 µl, 250 ± 5 µl and 500 ± 10 µl of the intermediate calibration standard (A5.6) to three separate 250 ml portions of interference-free water (A5.2). Inject the intermediate standards below the water surface and shake to mix. See table below.

A portion of unspiked water is set aside for use as an analytical quality control (AQC) blank.

Portions of all the working standard solutions prepared as above should be transferred to suitable containers fitted with polytetrafluoroethylene (PTFE) faced silicone discs within one hour of preparation and sealed. Working standard solutions should be prepared fresh on the day of analysis.

Working standard	STD 1	STD 2	STD 3	STD 4	STD 5
Spiking solution	A5.6	A5.6	A5.6	A5.5	A5.5
Volume of spiking solution (µl) added to 250 ml of water	50	250	500	50	150
Concentration (μgl^{-1})	1	5	10	40	120

A6 Apparatus

A6.1 **Purge vessels.** A variety of purge vessels are commercially available. Cleaning of the purge vessels should be carried out on a routine basis. The frequency of cleaning will depend on the frequency of use of the vessel and, more importantly, on the nature of the sample that has been analysed. For samples where high concentrations of volatile compounds have been found, the purge vessel should be removed from service and cleaned thoroughly. In case of continued contamination, the vessel should be discarded. This ensures that contamination or carry-over is minimised or eliminated. Vessels incorporating a glass frit are liable to cause cross-contamination. Procedures for cleaning purge vessels are given in Appendix A1.

A6.2 **Sample containers.** Screw-cap containers fitted with PTFE-faced silicone discs. Septa should not be re-used.

Typically, for systems fitted with an autosampler, nominal 44 ml screw cap septum vials fitted with PTFE-faced silicone discs are commercially available.

A6.3 **Purge and trap desorption apparatus.** This method has been validated using a commercially available automated purge and trap system. Other devices may be suitable but should be subjected to appropriate testing to ensure that satisfactory performance is demonstrated.

A6.3.1 **Purge and trap operation.** Refer to the manufacturer's instructions. The operating conditions used to generate the performance data shown in Table A1 were:

Purge time:	11 minutes.
Desorb pre-heat:	245°C.
Desorb:	5 minutes at 250°C.
Bake:	15 minutes at 260°C.
Trap stand-by temperature:	less than 30°C.
Carrier gas:	helium.
Column adsorbent material:	Vocarb 3000 (10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001)

Note: It should be understood that not every volatile organic compound referred to in Appendix A2 will be determined using a single adsorbent material. A range of materials will need to be considered. Purging of a volatile compound is usually carried out at ambient temperature. The response of some compounds may be improved by elevation of the purge temperature. A constant temperature heating jacket may be used to reduce the variation in the absolute amounts of compounds purged.

Care should be taken with systems without moisture control modules, as purged water vapour may pass into the mass spectrometer, causing a decrease in sensitivity.

A6.4 **Gas chromatograph-mass spectrometer.** Fitted with a temperature programmer and suitable analytical column. The GC operating conditions used to generate the performance data shown in Table A1 were as follows:

Column:	Fused silica WCOT, 60 m x 0.32 mm internal diameter, 1.8 µm film thickness coated with DB624.
Carrier gas:	Helium, 1 ml min^{-1}.
Column temperature:	Programmed, 35°C for 5 minutes, 6°Cmin^{-1} to 125°C, 15°Cmin^{-1} to 240°C. Hold for 7.5 minutes at 240°C.

The mass spectrometer should be capable of operating across the mass range of interest and incorporate a data system capable of quantifying ions using selected m/z values. See Figures A1-A3 for typical chromatograms.

A7 Sample collection and preservation

Samples should be collected directly into suitable containers (see A6.2), leaving no headspace. Without rinsing, the sample container should be completely filled to exclude any headspace (even small bubbles). In the case of glass vials this can be achieved by filling to give a convex meniscus before capping. Any samples found to have free air space should be considered suspect. It may be considered advisable to take two samples; one to be retained in the event of a repeat analysis being required. A crystal of sodium thiosulphate (A5.3) should be added to the container prior to sampling. The analysis should be performed as soon as possible after sample collection. If immediate analysis is not practicable, samples should be stored at 1-4°C, protected from direct sunlight and analysed within 14 days unless stability data show otherwise.

Care should be taken if subsamples are taken with a syringe, as a partial vacuum may be formed resulting in a change to the concentration of volatile components in the sample.

A8 Analytical procedure

This procedure refers specifically to the instrument used to generate the performance data shown in Table A1. Similar procedures may be applicable to other instruments and it should be recognised that different performance data may be produced.

Step	Procedure	Notes
A8.1	**Preparation for analysis**	
A8.1.1	Set up the instrument in accordance with the manufacturer's instructions with the mass spectrometer in full scan mode.	
A8.1.2	If fitted, load the autosampler with sample, standard and blank solutions (notes a and b)	(a) The samples, blanks and AQC samples for each batch should be randomised appropriately within the sequence. (b) Due consideration should be given to the likelihood of carry-over for samples subsequent to those containing high concentrations of volatile compounds.
A8.2	**Addition of internal and surrogate standards**	
A8.2.1	Add internal standard (for quantification) and surrogate standard (to assess instrument performance) solutions (A5.7) to aliquots of thesamples and blank and standard solutions (A5.8) prior to analysis. Cap to leave no headspace (notes c and d)	(c) Some commercially available instruments automatically add the internal and surrogate standard solutions to the sample prior to analysis. (d) A consistent technique for the addition of internal and surrogate standard solutions should be devised by each laboratory.

A8.3 Blank solutions

A8.3.1 For blank solutions, water (A5.2) should be used in place of the samples (note e).

(e) Adequate blank values should be obtained before analysing sample Blank corrections are not normally required.

A8.4 AQC

A8.4.1 Carry out the whole procedure using water (A5.2) spiked at an appropriate level with the compounds of interest.

A8.5 GC-MS analysis

A8.5.1 Perform a five point calibration by analysis of each working standard solution (solutions STD 1 to STD 5 in table shown in section A5.8) (notes f and g).

(f) Quantification is achieved by integrating selected ions for each compound and measuring the response. Typical ions used for quantification are given in Table A2.

(g) Verify that the response limits for the standards are within those set by the laboratory. If not, then it may be necessary to repeat the calibration or investigate the source of the problem.

A8.5.2 Analyse blank, sample and calibration standard solutions and additional standard solutions as required (note h).

(h) After the samples have been analysed, a calibration check standard should be run to ensure that the calibration has not drifted.

A8.5.3 Obtain a spectrum of each of the peaks corresponding to each determinand of interest (note i)

(i) A compound is identified if the spectrum and the retention time match the data in the calibration. See section A10 for details of data interpretation.

A8.5.4 If quantification of determinands is required, measure the response (ie peak area or height) of the peak of interest, including those of the internal standards. Check the response of the surrogate standards (note f).

A8.5.5 For each compound of interest, construct a calibration graph of calibration standard:internal standard response ratio versus concentration of calibration standard solution (note j).

(j) Some matrices can lead to interference with the response of the internal standard.

A8.5.6 Calculate the determinand: internal standard response ratio for each compound in the sample, and from the calibration graph, determine the concentration present in the origina factor sample (note k).
See also section A9.

(k) If the concentration of any analyte exceeds the calibration range, a replacement sample should be diluted and analysed, and the appropriate dilution used in the calculation.
The duplicate sample, if taken, should be used.

A9 Calculation

The total concentration of each volatile organic compound is given by

$C = S / m \quad \mu g l^{-1}$

where C = concentration of the volatile organic compound in the original sample ($\mu g l^{-1}$);

S = the determinand:internal standard response ratio;

m = the slope of the calibration line (response ratio divided by concentration of calibration standard solution obtained from the graph of concentration (x-axis) versus calibration standard:internal standard response ratio (y-axis).

Alternative methods of calculation may be used provided that they give equivalent results.

The calculations are more easily performed using a laboratory data system to integrate the relevant peaks and calculate the results automatically.

A10 Data interpretation

A10.1 **Qualitative analysis.** For qualitative screening of samples, the reconstructed total ion chromatogram (TIC) can be generated and peaks of interestselected. A check should be made to ensure that a peak selected from the sample is not present in the blank solution at a similar intensity.

A representative spectrum of each peak in turn should be examined, after background subtraction if necessary, and submitted to a library search. Any matched comparisons should be interpreted with caution to ensure the validity of the process.

If the library match is considered to be unequivocal, the identification can be reported.

If the isomer specificity is unclear or not certain, but elemental composition is considered unequivocal, the comparison can be reported without specific isomer identifiers.

If the compound type is unequivocal, but specific compound identification is not possible, then the compound class can be reported.

If library comparisons are considered to be unreasonable or inconclusive, then the component can be designated as unknown.

A10.2 **Semi-quantitative analysis.** The qualitative analysis described in section A10.1 may be extended to provide 'semi-quantitative' determination of concentrations. This may be carried out by addition of internal standards at known concentrations. Quantification for each determinand detected can be achieved using the ratio of the total ion current for the determinand and that of the closest eluting internal standard.

A10.3 **Quantitative analysis.** Quantitative analysis for any determinand is undertaken as described in section A8.5.

Table A1 Performance data for borehole drinking water

Number	Compound	Deionised water		Sample	Sample spike		High standard		Low standard		
		S_t	LOD	S_t	S_t	Rec	S_t	Bias	S_t	Bias	LOD
4	dichlorodifluoromethane	0.0089	0.041	0.0115(21)	4.22	153	7.02(14)	-7.53	0.0806(10)	2.32	0.227
5	chloromethane	-	-	-	2.51	104	2.49(10)	-2.16	0.367(18)	16.94	0.178
6	vinyl chloride	-	-	0.0013(21)	2.29	101	2.40(14)	-0.98	0.040(17)	2.03	0.114
9	trichlorofluoromethane	0.0059	0.025	0.0064(21)	0.553	104	1.88(11)	-0.17	0.0447(21)	-0.70	0.074
10	1,1-dichloroethene	0.0081	0.038	0.0775(21)	1.84	100	1.84(15)	-1.30	0.0326(19)	-1.18	0.101
11	dichloromethane	4.28	1.36	0.223(11)	3.89	83	10.41(16)	0.55	0.114(11)	54.52	0.358
12	trans-1,2-dichloroethene	0.0090	0.042	0.0098(21)	1.85	100	1.45(14)	-1.23	0.0341(19)	0.24	0.093
13	1,1-dichloroethane	0.0038	0.018	0.0037(21)	1.85	100	1.67(14)	0.21	0.0338(19)	0.48	0.091
14	2,2-dichloropropane	0.0036	0.001	0.0013(21)	2.55	77	12.93(10)	-17.6	0.210(21)	-23.30	0.115
15	cis-1,2-dichloroethene	0.0086	0.040	0.0056(21)	0.323	104	1.36(15)	-1.43	0.0293(20)	0.11	0.088
16	bromochloromethane	0.0042	0.020	0.0165(21)	1.92	103	1.75(11)	-0.69	0.0448(21)	-5.54	0.056
17	chloroform	0.0156	0.39	0.0999(10)	0.42	100	1.12(11)	-1.07	0.0951(20)	10.76	0.103
18	1,1,1-trichloroethane	0.165	0.082	0.0238(14)	1.84	97	1.26(11)	-0.29	0.0749(20)	7.27	0.092
19	carbon tetrachloride	0.0024	-	-	0.322	106	1.69(13)	-2.19	0.0277(18)	0.23	0.067
20	1,1-dichloropropene	0.0066	0.031	0.0078(21)	2.49	95	1.67(13)	-1.92	0.0341(14)	1.33	0.085
21	benzene	0.0126	0.058	0.0094(21)	0.309	104	1.66(16)	-0.36	0.0327(14)	3.57	0.104
22	1,2-dichloroethane	0.0095	0.044	0.013(19)	1.9	98	1.65(11)	0.05	0.0484(18)	5.00	0.075
23	trichloroethene	0.0144	0.067	0.0141(21)	0.318	102	2.15(11)	6.15	0.0601(21)	12.88	0.100
24	1,2-dichloropropane	0.0048	0.022	0.0052(21)	0.362	106	1.18(11)	0.26	0.0385(21)	2.59	0.065
25	dibromomethane	0.0143	0.066	0.0130(20)	0.419	104	1.66(11)	-0.90	0.0653(14)	2.02	0.084
26	bromodichloromethane	0.0082	0.038	0.0063(19)	0.344	105	1.47(11)	-1.09	0.0384(17)	2.93	0.059
27	trans-1,3-dichloropropene	0.0119	0.055	0.010(19)	0.401	101	1.67(11)	1.09	0.0531(15)	-3.96	0.077
28	toluene	0.0771	0.063	0.0227(11)	0.356	101	1.04(12)	-0.28	0.0527(20)	11.82	0.103
29	cis-1,3-dichloropropene	0.0165	0.077	0.0145(20)	0.389	101	1.94(13)	-3.94	0.0567(13)	1.11	0.131
30	1,1,2-trichloroethane	0.0133	0.062	0.0105(21)	0.396	105	1.46(11)	-0.28	0.0493(20)	2.46	0.079
31	tetrachloroethene	0.0185	0.068	0.0135(21)	0.320	102	1.61(17)	-1.77	0.0346(18)	2.47	0.117
32	1,3-dichloropropane	0.0115	0.054	0.0105(20)	0.498	105	2.30(12)	0.94	0.0525(20)	4.23	0.093
33	dibromochloromethane	0.0088	0.041	0.0067(21)	0.398	105	1.47(11)	-0.94	0.0458(15)	2.62	0.056
34	1,2-dibromoethane	0.0147	0.068	0.0152(20)	0.456	104	1.81(13)	-0.23	0.0619(16)	5.52	0.137
35	chlorobenzene	0.0162	0.075	0.0139(21)	0.330	105	1.13(13)	0.77	0.0340(21)	4.09	0.084
36	1,1,1,2-tetrachloroethane	0.0090	0.042	0.0071(21)	0.327	106	1.32(11)	-0.16	0.0359(17)	2.86	0.058
37	ethylbenzene	0.0180	0.081	0.0160(20)	0.516	101	2.63(19)	0.48	0.0420(18)	3.44	0.169
38	m- and p-xylene	0.0409	0.145	0.0287(18)	0.722	105	2.21(15)	-0.54	0.0722(18)	4.78	0.207
39	o-xylene	0.0146	0.046	0.0146(17)	0.375	105	1.05(16)	0.28	0.0301(21)	3.88	0.094
40	styrene	0.0346	0.091	0.0161(20)	0.331	105	1.03(14)	-0.43	0.0482(21)	6.36	0.132
41	bromoform	0.0127	0.059	0.0123(21)	0.502	106	1.82(11)	-1.17	0.0606(15)	2.31	0.090

Table A1 Continued

Number	Compound	Deionised water		Sample	Sample spike		High standard		Low standard		
		S_t	LOD	S_t	S_t	Rec	S_t	Bias	S_t	Bias	LOD
42	isopropylbenzene	0.0144	0.067	0.0131(21)	0.336	104	1.75(12)	1.84	0.0422(20)	5.02	0.091
43	bromobenzene	0.0233	0.108	0.0218(21)	0.347	106	1.22(15)	0.77	0.0421(21)	5.92	0.128
44	1,1,2,2-tetrachloroethane	-	-	0.0030(21)	0.548	109	2.75(11)	-9.47	0.0986(13)	-10.40	0.120
45	1,2,3-trichloropropane	0.0453	0.211	0.0275(21)	0.637	107	2.02(13)	0.48	0.0758(15)	-1.37	0.170
46	n-propylbenzene	0.0111	0.050	0.0059(19)	0.499	103	1.42(15)	-0.59	0.0552(20)	3.77	0.160
47	2-chlorotoluene	0.0130	0.060	0.0088(21)	0.379	105	1.76(21)	1.38	0.0508(20)	7.82	0.236
48	4-chlorotoluene	0.0130	0.060	0.0118(21)	0.641	104	3.30(17)	1.25	0.0839(13)	13.20	0.291
49	1,3,5-trimethylbenzene	0.0108	0.047	0.0110(21)	0.347	105	1.29(21)	0.62	0.0419(20)	6.80	0.195
50	tert-butylbenzene	0.0118	0.055	0.0138(21)	0.370	105	1.31(19)	0.43	0.0421(20)	6.74	0.167
51	1,2,4-trimethylbenzene	0.0264	0.123	0.0157(20)	0.326	105	1.29(21)	0.37	0.0470(21)	11.26	0.218
52	sec-butylbenzene	0.0178	0.083	0.0161(21)	0.352	101	1.66(16)	-1.33	0.0394(17)	7.14	0.127
53	1,3-dichlorobenzene	0.0322	0.15	0.0251(21)	0.357	105	1.24(17)	0.36	0.153(21)	5.54	0.533
54	1,4-dichlorobenzene	0.0321	0.15	0.0264(21)	0.405	103	1.85(18)	-0.20	0.147(20)	4.81	0.557
55	4-isopropyltoluene	0.0293	0.14	0.0170(21)	0.404	104	1.83(16)	0.75	0.192(20)	2.98	0.623
56	1,2-dichlorobenzene	0.0537	0.25	0.0477(19)	0.382	104	2.24(18)	-0.66	0.192(21)	4.11	0.700
57	n-butylbenzene	0.466	0.22	0.0425(19)	0.565	100	3.21(19)	-3.91	0.238(18)	0.75	0.943
58	1,2-dibromo-3-chloropropane	0.0836	0.388	0.0801(21)	0.781	103	3.75(18)	-0.70	0.379(20)	3.11	1.39
59	1,2,4-trichlorobenzene	0.239	1.11	0.200(19)	0.513	100	1.33(20)	-0.70	0.218(19)	8.92	0.897
60	hexachlorobutadiene	0.134	0.62	0.118(20)	0.416	102	1.65(17)	-0.92	0.178(21)	4.67	0.604
61	naphthalene	0.381	1.77	0.308(21)	0.778	98	2.40(18)	-0.50	0.379(11)	10.76	1.40
62	1,2,3-trichlorobenzene	0.310	1.44	0.264(21)	0.598	102	1.61(18)	-0.56	0.291(18)	10.17	1.07
63	1,3,5-trichlorobenzene	0.195	0.81	0.167(18)	0.647	99	0.765(12)	0.50	0.207(6)	7.57	0.762

Units are expressed in μgl^{-1} except for recovery (Rec) and bias, which are expressed as a percentage.
LOD is limit of detection, calculated as 4.65 x S_w (ie the within-batch standard deviation).
S_t is total standard deviation.
Figures in brackets represent degrees of freedom.
Sample, high standard and low standard spiked at 8.0 μgl^{-1}, 40 μgl^{-1} and 0.8 μgl^{-1} respectively.
Data provided by AES Ltd.

Table A2 **Compounds, Retention times and Quantification ions**

Number	Compound	Retention Time (min:sec)	Figure	Selected ions Primary	Secondary
1	fluorobenzene (IS)	7:53	A1/A2/A3	96	77
2	4-bromofluorobenzene (SS)	17:29		95	174, 176
3	1,2-dichlorobenzene-d_4 (SS)	21:06	A2/A3	132	115, 150
4	dichlorodifluoromethane	1:21		85	87
5	chloromethane	1:30		49	51
6	vinyl chloride	1:36	A1	62	64
7	bromomethane	2:08		94	96
8	chloroethane	2:00		49	-
9	trichlorofluoromethane	2:14	A2	101	103
10	1,1-dichloroethene	2:46	A1	96	61, 63
11	dichloromethane	3:22	A1/A2/A3	84	86, 49
12	trans-1,2-dichloroethene	3:45	A1	96	61, 98
13	1,1-dichloroethane	4:25	A2	63	65, 83
14	2,2-dichloropropane	5:29	A1	77	97
15	cis-1,2-dichloroethene	5:31	A2	96	61, 98
16	bromochloromethane	5:58	A1	128	49, 130
17	chloroform	6:12	A3/B1	83	85
18	1,1,1-trichloroethane	6:30	A2	97	99, 61
19	carbon tetrachloride	6:50	A1/B1	117	119
20	1,1-dichloropropene	6:52	A3	75	110, 77
21	benzene	7:15	A1	78	-
22	1,2-dichloroethane	7:18	A2	62	98
23	trichloroethene	8:40	A1/B1	95	130, 132
24	1,2-dichloropropane	9:06	A2	63	112
25	dibromomethane	9:20	A1	93	95, 174
26	bromodichloromethane	9:47	A3/B1	83	85, 127
27	trans-1,3-dichloropropene	10:47	A2	75	110
28	toluene	11:30	A1	92	91
29	cis-1,3-dichloropropene	12:04	A2	75	110
30	1,1,2-trichloroethane	12:27	A2	83	97, 85
31	tetrachloroethene	12:43	A1/B1	166	168, 129
32	1,3-dichloropropane	12:48	A3	76	78
33	dibromochloromethane	13:17	A2/B1	129	127
34	1,2-dibromoethane	13:28	A1	107	109, 188
35	chlorobenzene	14:41	A2	112	74, 114
36	1,1,1,2-tetrachloroethane	14:56	A1	83	131, 85
37	ethylbenzene	15:02	A1	91	106
38	m- and p-xylene	15:20	A2/A3	106	91
39	o-xylene	16:16	A1	106	91
40	styrene	16:18	A2	104	78
41	bromoform	16:37	A1/B1	173	175, 254
42	isopropylbenzene	17:12	A1	105	120
43	bromobenzene	17:46	A1	156	77, 158
44	1,1,2,2-tetrachloroethane	17:58	A3	86	131, 85
45	1,2,3-trichloropropane	17:59	A2	75	77
46	n-propylbenzene	18:13	A3	91	120
47	2-chlorotoluene	18:19	A2	91	126
48	4-chlorotoluene	18:36	A1	91	126
49	1,3,5-trimethylbenzene	18:42	A3	105	120
50	tert-butylbenzene	19:28	A3	119	91, 134
51	1,2,4-trimethylbenzene	19:35	A2	105	120
52	sec-butylbenzene	20:01	A1	105	134
53	1,3-dichlorobenzene	20:09	A2	146	111, 148
54	1,4-dichlorobenzene	20:22	A1	146	111, 148

Table A2 continued

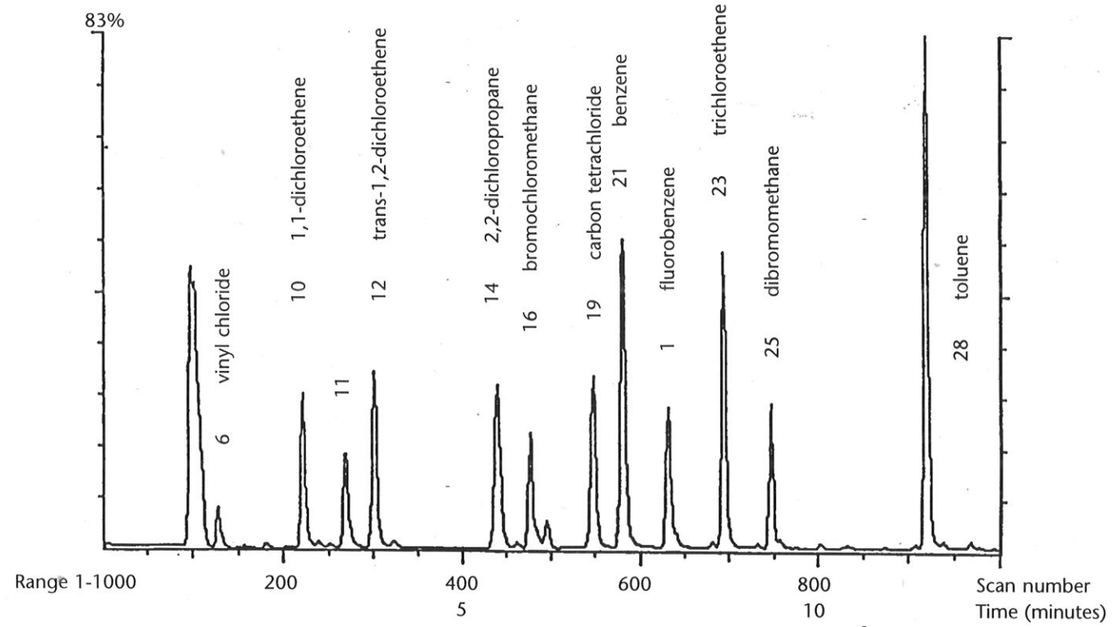
Number	Compound	Retention Time (min:sec)	Figure	Selected ions Primary	Secondary
55	4-isopropyltoluene	20:25	A3	119	134, 91
56	1,2-dichlorobenzene	21:08	A1	146	111, 148
57	n-butylbenzene	21:16	A3	91	92, 134
58	1,2-dibromo-3-chloropropane	22:35	A3	75	155, 157
59	1,2,4-trichlorobenzene	23:55	A1	180	182, 145
60	hexachlorobutadiene	24:13	A2	225	223, 227
61	naphthalene	24:15	A3	128	-
62	1,2,3-trichlorobenzene	24:37	A1	180	182, 145
63	1,3,5-trichlorobenzene	22.58		180	182, 145

Scan and retention times will vary with column age and replacement columns.
IS = internal standard.
SS = surrogate standard.

Table A3 **Performance data for river water**

Number	Compound	Standard RSD (%)	Bias (%)	LOD ($\mu g l^{-1}$)	Spiked sample RSD (%)	Recovery (%)
10	1,1-dichloroethene	11.0	2.1	0.23	15.2	108.7
12	trans-1,2-dichloroethene	11.5	1.4	0.15	9.3	102.0
13	1,1-dichloroethane	23.5	-4.9	0.19	13.2	101.1
14	2,2-dichloropropane	16.7	-23.5	0.36	25.5	71.1
15	cis-1,2-dichloroethene	12.1	-4.3	0.19	18.2	102.0
17	chloroform	10.5	0.1	0.15	9.8	103.4
18	1,1,1-trichloroethane	14.1	-0.9	0.17	17.5	104.5
19	carbon tetrachloride	13.9	-2.5	0.16	9.7	104.3
20	1,1-dichloropropene	7.9	-2.6	0.12	7.2	102.9
21	benzene	10.8	-0.7	0.14	11.7	103.8
22	1,2-dichloroethane	9.5	1.2	0.20	8.2	103.9
23	trichloroethene	9.4	0.1	0.14	7.0	105.9
24	1,2-dichloropropane	7.9	1.1	0.19	7.9	104.4
25	dibromomethane	10.4	-1.4	0.19	7.7	101.2
26	bromodichloromethane	11.1	-0.2	0.16	9.7	98.5
27	trans-1,3-dichloropropene	8.1	-3.2	0.17	10.9	101.5
28	toluene	13.4	1.2	0.15	8.8	103.8
29	cis-1,3-dichloropropene	7.3	-1.8	0.17	9.0	99.8
30	1,1,2-trichloroethane	8.3	0.4	0.21	7.3	102.4
31	tetrachloroethene	9.7	-1.1	0.13	7.9	102.4
32	1,3-dichloropropane	7.7	1.9	0.16	8.1	104.5
33	dibromochloromethane	10.8	0.4	0.18	5.9	103.9
34	1,2-dibromoethane	7.6	1.2	0.17	7.8	103.2
35	chlorobenzene	8.2	0.9	0.12	8.1	103.2
36	1,1,1,2-tetrachloroethane	8.2	-0.3	0.14	9.6	102.7
37	ethylbenzene	8.7	-0.4	0.13	10.2	103.0
38	m- and p-xylene	11.5	0.6	0.28	15.0	98.9
39	o-xylene	9.4	1.0	0.13	9.5	102.9
40	styrene	9.0	-0.3	0.13	9.1	102.0
41	bromoform	8.6	0.1	0.18	6.4	103.5
42	isopropylbenzene	9.4	0.4	0.12	8.3	102.4
43	bromobenzene	10.9	-2.2	0.37	7.6	99.9
44	1,1,2,2-tetrachloroethane	10.8	0.8	0.16	7.8	100.4
45	1,2,3-trichloropropane	13.9	2.2	0.16	9.3	102.0
46	n-propylbenzene	10.3	-0.3	0.13	9.6	100.9
47	2-chlorotoluene	10.4	-0.2	0.12	9.7	100.9
48	4-chlorotoluene	10.9	-0.2	0.13	10.8	101.3
49	1,3,5-trimethylbenzene	10.8	-1.1	0.10	10.7	99.6
50	tert-butylbenzene	11.8	-0.5	0.24	11.7	100.6
51	1,2,4-trimethylbenzene	12.6	0.8	0.09	10.9	101.3
52	sec-butylbenzene	12.5	0.6	0.10	10.6	101.4
53	1,3-dichlorobenzene	11.4	0.8	0.28	10.9	102.9
54	1,4-dichlorobenzene	10.1	-0.8	0.21	10.1	100.4
55	4-isopropyltoluene	12.9	-1.2	0.13	10.3	101.2
56	1,2-dichlorobenzene	10.0	1.7	0.28	11.5	102.2
57	n-butylbenzene	15.1	-0.6	0.16	16.8	94.0
58	1,2-dibromo-3-chloropropane	18.0	3.3	0.61	11.5	105.9
61	naphthalene	28.0	-3.3	0.32	30.2	78.3
16	bromochloromethane	9.9	-1.5	0.26	12.9	105.6
9	trichlorofluoromethane	14.2	-1.6	0.28	13.6	103.8
	tert-butylmethylether	10.2	-2.1	0.20	8.8	100.5

RSD is relative standard deviation.
LOD is limit of detection which is calculated on the standard solution.
Sample consisted of a spiked riverwater with typical hardness of 200 mgl^{-1} as calcium carbonate.
Results are based on 11 batches analysed in duplicate, ie with at least 10 degrees of freedom.
Standard and sample spiked at 9 μgl^{-1} and 6 μgl^{-1} respectively.
Data provided by Environment Agency, Leeds laboratory.



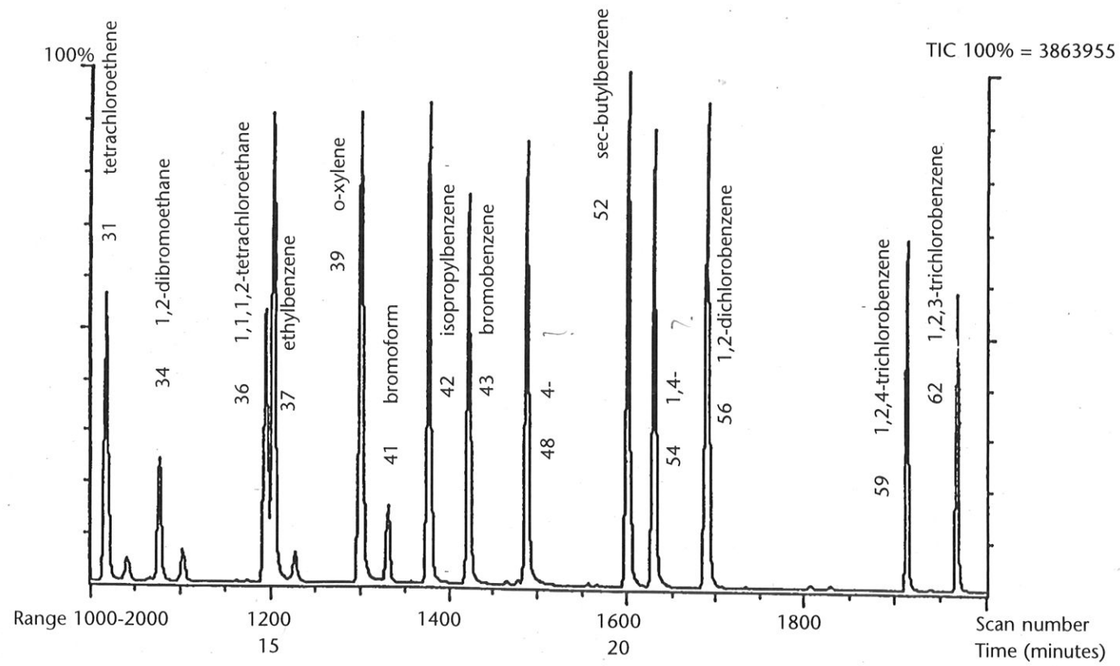
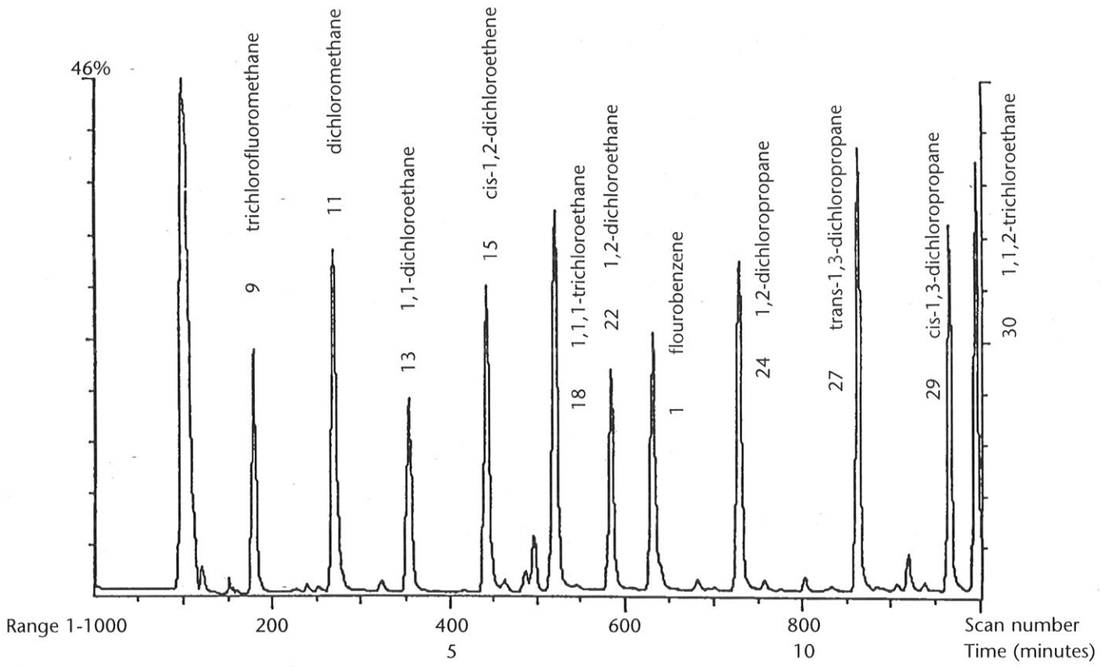
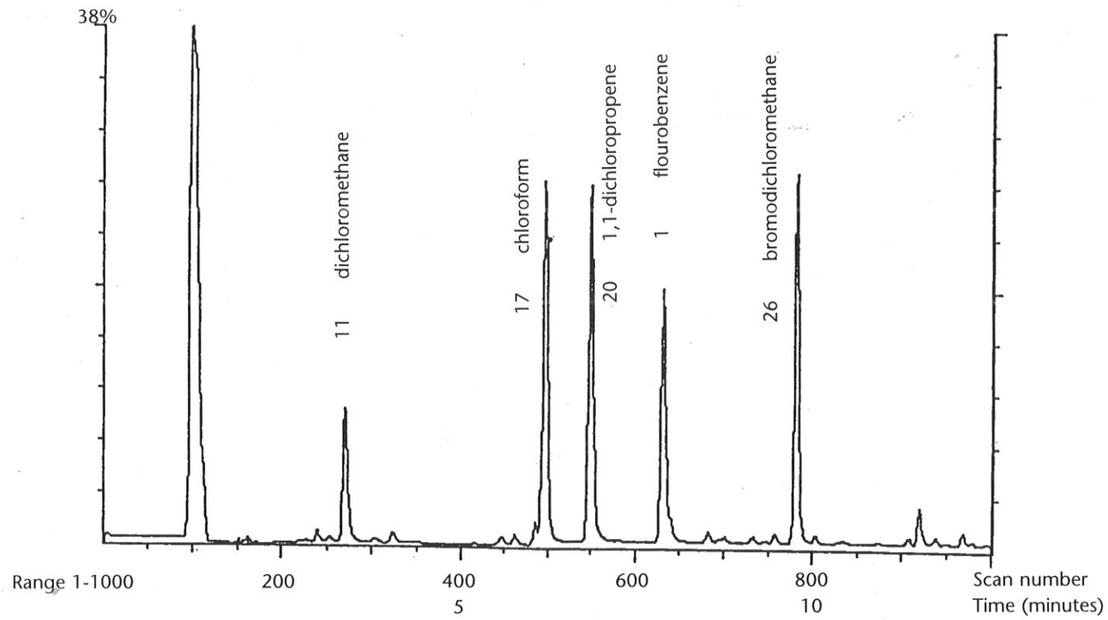


Figure A1 **Chromatogram of standard mixture (16 μgl^{-1})**





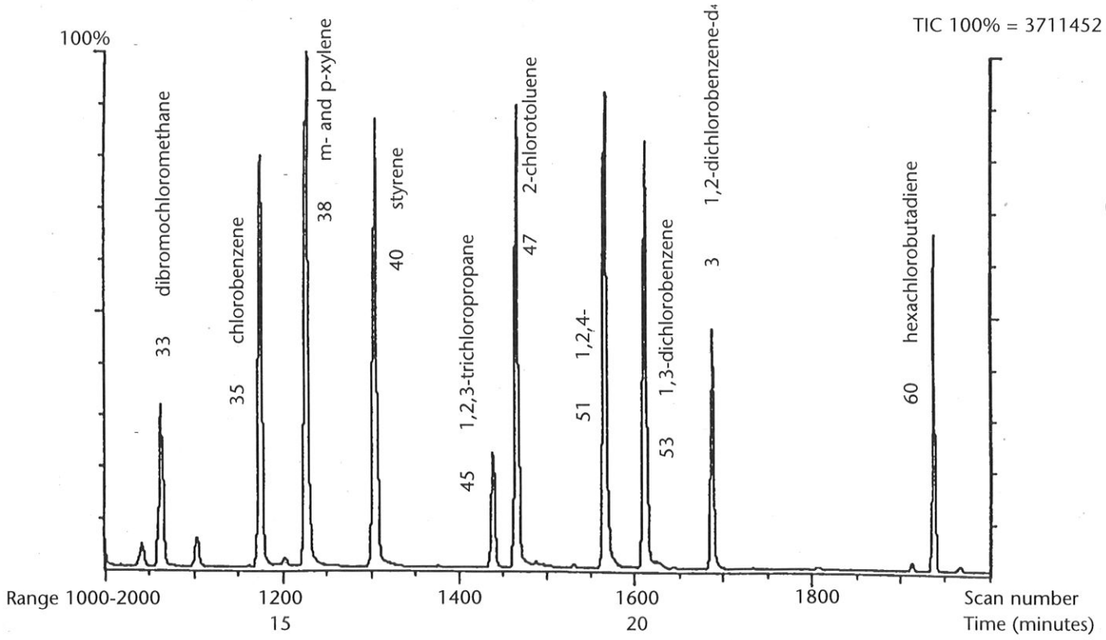


Figure A2 **Chromatogram of a standard mixture (16 µgl^{-1})**

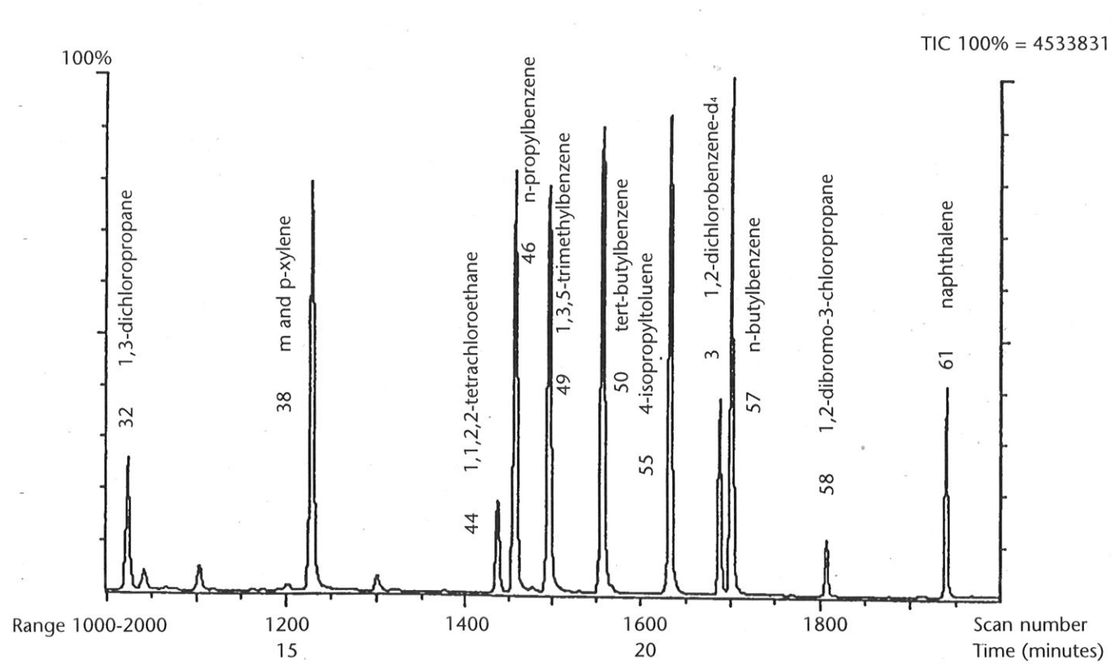


Figure A3 **Chromatogram of a standard mixture (16 µgl^{-1})**

APPENDIX A1

Routine cleaning

Procedures for cleaning purge vessels and glassware

Cleaning procedures will depend on the specific instrument being used. The following procedures have been shown to be satisfactory.

A1.1 Remove the purge vessel from the purge and trap instrument. Ensure that the PTFE ferrules are not damaged during this stage.

A1.2 Connect an open end of the purge vessel to a water pump and place the other end in a large beaker of clean water. Turn on the pump and draw water through the purge vessel in the direction of the gas purge flow. Flush the vessel in this way for approximately 1-2 minutes.

A1.3 Remove the water pump connection and place the purge vessel in a beaker. Fill the purge vessel with a further quantity of clean water, ensuring that the sample portion of the vessel is completely filled.

A1.4 Place the beaker in an ultrasonic bath and sonicate for a minimum of 20 minutes.

A1.5 Discard the water from the purge vessel and repeat steps A1.3 and A1.4, sonicating for another 5 minutes.

A1.6 Discard the water, dry the outside of the vessel and place immediately into an oven at a temperature of greater than 200°C. The vessels should be heated at this temperature for a minimum of 6 hours, or preferably overnight.

A1.7 After the purge vessels have dried, cool to 100°C and transfer immediately to an airtight storage container.

A1.8 The purge vessels should be fitted to the purge and trap system whilst still slightly above ambient temperature to minimise any adsorption of volatile compounds on to the glassware.

Glassware cleaning processes

For the analysis of samples containing volatile organic compounds in the low μgl^{-1} range, the preparation of scrupulously clean glassware is essential. Failure to do so can lead to problems in the interpretation of the final chromatogram due to the presence of extraneous peaks. The process of concentrating compounds of interest may similarly concentrate compounds resulting from contamination.

Basic cleaning steps include the following:

1 Remove surface residuals immediately after use. As soon as possible after glassware has come into contact with sample or standard solutions, the glassware should be methanol-rinsed before being placed in a hot detergent soak. If this is not carried out, the soaking process may serve to contaminate other glassware.

2 Hot soak the vessel to loosen most of the particulate material which may be present. The hot soak comprises a bath of a suitable detergent in water of 50°C or higher. The detergent should be entirely synthetic and not of a fatty acid base. Hard water scum possesses an affinity for many chlorinated compounds, and being almost wholly water-insoluble, may cause deposits to occur as a thin film on all glassware in the bath.

3 Rinse the vessel in hot water to flush away any particulate matter.

4 Soak the vessel in an oxidising agent to destroy traces of organic matter. The most common (and highly effective) oxidising agent for removal of traces of organic compounds is chromic acid solution made up of sulphuric acid and potassium or sodium dichromate. For maximum efficiency, the soak solution should be warm (40-50°C). Safety precautions should be rigidly observed in the handling of this solution.

5 Rinse the vessels in hot water to flush away loosened materials.

6 Rinse in distilled water to remove any metallic deposits.

7 Rinse with methanol to flush away any final traces of organic materials and to remove water.

8 Flush the vessels immediately before use with a suitable solvent and dry before use.

There is always a possibility that between the time of washing and subsequent use, the glassware may become contaminated from the atmosphere or by direct contact with volatile organic compounds. To ensure against this, it is good practice to flush the vessels immediately before use with a suitable solvent, for example methanoi.

APPENDIX A2

Compounds and groups of compounds determined by purge and trap using gas chromatography with mass spectrometric detection

Compounds determined by purge and trap using gas chromatography with mass spectrometric detection

benzene
bromobenzene
bromochloromethane
bromodichloromethane
tribromomethane (bromoform)
bromomethane
n-butylbenzene
sec-butylbenzene
tert-butylbenzene

tetrachloromethane (carbon tetrachloride)
chlorobenzene
chloroethane
chloromethane
2-chlorotoluene
4-chlorotoluene
1,2-dibromo-3-chloropropane
dibromochloromethane
1,2-dibromoethane
dibromomethane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
dichlorodifluoromethane
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
cis-1,2-dichloroethene
trans-1,2-dichloroethene

1,2-dichloropropane
1,3-dichloropropane
2,2-dichloropropane
1,1-dichloropropene
ethylbenzene
hexachlorobutadiene
isopropylbenzene
4-isopropyltoluene
dichloromethane
(methylene chloride)
naphthalene
n-propylbenzene
styrene
1,1,1,2-tetrachloroethane
tetrachloroethene
toluene
1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
trichlorofluoromethane
1,2,3-trichloropropane
1,2,4-trimethylbenzene
1,3,5-trimethylbenzene
vinyl chloride
1,2-dimethylbenzene (o-xylene)
1,3-dimethylbenzene (m-xylene)
1,4-dimethylbenzene (p-xylene)

Other compounds amenable to purge and trap analysis

acetone
acrolein
acrylonitrile
carbon disulphide
2-chloro-1,3-butadiene
2-chloroethyl vinyl ether
1,4-dioxane
ethyl methacrylate

2-hexanone
iodomethane
methacrylonitrile
methyl ethyl ketone (MEK)
methyl methacrylate
4-methyl-2-pentanone
vinyl acetate
aliphatic hydrocarbons
(pentane to decane)

BTEX

benzene
ethylbenzene
toluene

xylenes
(methyl tertiary butyl ether
(MTBE) is commonly analysed
within this suite).

Trihalogenated methanes (THM) and halogenated solvents

bromoform
bromodichloromethane
carbon tetrachloride
dibromochloromethane

chloroform
tetrachloroethene
trichloroethene
1,1,1-trichloroethane

The following volatile internal standards have been used in the quantification of the following determinands;

fluorobenzene

acetone
acrolein
acrylonitrile
bromochloromethane
bromomethane
2-butanone
carbon disulphide
chloroethane
chloroform
chloromethane
dichlorodifluoromethane

1,1-dichloroethane
1,1-dichloroethene
cis-1,2-dichloroethene
trans-1,2-dichloroethene
2,2-dichloropropane
iodomethane
methylene chloride
1,1,1-trichloroethane
trichlorofluoromethane
vinyl acetate
vinyl chloride

1,4-difluorobenzene

benzene
bromodichloromethane
bromofluorobenzene (surrogate)
carbon tetrachloride
2-chloroethyl vinyl ether
1,2-dibromoethane
dibromomethane
1,2-dichloroethane
1,2-dichloroethane-d_4 (surrogate)

1,2-dichloropropane
1,1-dichloropropene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
4-methyl-2-pentanone
toluene
toluene-d8 (surrogate)
1,1,2-trichloroethane
trichloroethene

chlorobenzene-d_5

bromoform
dibromochloromethane
chlorobenzene
1,3-dichloropropane
ethylbenzene

2-hexanone
styrene
1,1,1,2-tetrachloroethane
tetrachloroethene
xylenes

1,4-dichlorobenzene-d_4

bromobenzene
n-butylbenzene
sec-butylbenzene
tert-butylbenzene
2-chlorotoluene
4-chlorotoluene
1,2-dibromo-3-chloropropane
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
hexachlorobutadiene

isopropylbenzene
4-isopropyltoluene
naphthalene
n-propylbenzene
1,1,2,2-tetrachloroethane
1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
1,2,3-trichloropropane
1,2,4-trimethylbenzene
1,2,3-trimethylbenzene

B The determination of trihalogenated methanes and chlorinated solvents in waters by headspace analysis

B1 Performance characteristics of the method

B1.1 Substances determined. Bromodichloromethane, dibromochloromethane, tribromomethane (bromoform), trichloromethane (chloroform), tetrachloromethane (carbon tetrachloride), trichloroethene (trichloroethylene), tetrachloroethene (perchloroethylene), 1,1,1-trichloroethane. Other volatile chlorinated hydrocarbons may also be determined.

B1.2 Type of sample. Drinking water. The method may also be applicable to waste waters and effluents.

B1.3 Basis of method. Direct static headspace analysis of aqueous samples using capillary gas chromatography with electron capture detection (GC/ECD).

B1.4 Range of application. Dependent on the ECD response of the determinand. See Tables B3 to B5 for the range of concentrations tested.

B1.5 Standard deviation. See Tables B3 to B5.

B1.6 Limit of detection. See Tables B3 to B5.

B1.7 Bias. See Tables B3 to B5.

B1.8 Time required for analysis. Approximately one day to analyse a batch of 20 samples including preparation of standard solutions and apparatus.

B2 Principle

Samples of water contained in sealed vessels with sufficient headspace are allowed to reach equilibrium at a constant temperature. A portion of the headspace vapour is analysed directly by GC/ECD. Quantification is undertaken by comparison of the results obtained for samples with those for aqueous standards treated in an identical manner.

B3 Interferences

Any compound present in the headspace vapour which co-elutes with any of the determinands and which gives a response with the electron capture detector will interfere.

Care should be taken to ensure there is no contamination from the laboratory environment. Contamination can arise from within the laboratory, or from an adjacent laboratory with a shared ventilation system, and can lead to airborne contamination of sample vials and other equipment. Particular care should be taken in the area where samples are handled and transferred, and during the preparation of standard solutions.

B4 Hazards

Skin contact with, and ingestion or inhalation of, all reagents and their solutions specified in this method should be avoided. Methanol is toxic, narcotic and flammable. Several halogenated hydrocarbons are suspected carcinogens. Standard solutions should always be prepared in a fume cupboard. Always ensure adequate ventilation and work in a flame- and spark-proof area. Spark-proof refrigerators should be used. Appropriate safety procedures should be followed.

B5 Reagents

All reagents should be of sufficient purity that they do not give rise to significant interfering peaks during the gas chromatographic analysis. This should be checked for each batch of material and verified by running procedural blanks with each batch of samples analysed. High performance liquid chromatography (HPLC) grade solvents and analytical reagent grade materials are normally suitable unless otherwise specified.

Reagents may become contaminated by contact with air and/or other materials, particularly plastics, or by degradation caused by the action of light. Reagents should be stored in tightly sealed all-glass containers or other vessels found to be suitable and kept in the dark if necessary.

B5.1 Water. Water known to be free from contamination, for example ground water or certain commercially available bottled waters, is used for blank and AQC determinations and for preparing standard solutions and dilutions. Sufficient water from the same batch should be available to complete each set of analysis including all preparations and dilutions. The water used for blank determinations and preparation of control samples and standard solutions should show negligible interferences in comparison with the smallest concentration to be determined.

B5.2 Methanol.

B5.3 Sodium thiosulphate pentahydrate.

B5.4 Standard solutions. Owing to the volatile nature of the halogenated hydrocarbons, the preparation of standard solutions by routine weighing procedures may not always be sufficiently reliable. Provided the specific gravity of the halogenated hydrocarbon is known, standard solutions can be prepared using volume as a measure of amount present.

The ECD responds differently to different halogenated hydrocarbons. Hence, working standard solutions need to be prepared which contain different concentrations of the determinands of interest, but which show similar responses to all halogenated hydrocarbons present. These standard solutions are commercially available but can be prepared in the laboratory (see A5.4). For example, the following procedure may be used.

B5.5 Stock solutions of halogenated hydrocarbons. Because of the high ECD responses of certain halogenated hydrocarbons, for example tetrachloroethene and carbon tetrachloride, it is necessary first to prepare a preliminary solution of these halogenated hydrocarbons (see Table B1) for subsequent dilution.

Prepare individual stock solutions in methanol of pure or suitably certified halogenated hydrocarbons. In each case, add the appropriate amount of halogenated hydrocarbon, or preliminary solution, to approximately 85 ml of methanol in a 100ml volumetric flask and make up to the mark with methanol (see Table B1). If correctly stored (sealed, refrigerated and kept in the dark), stock solutions may be kept for up to two months.

B5.6 Working standard solutions. Prepare a series of mixed working standard solutions in water. These may be prepared directly from the stock solutions (B5.5). Alternatively, an intermediate standard solution may be prepared by dilution of suitable aliquots of the stock solutions (B5.5) with methanol. In either case, appropriate volumes of stock or intermediate standard solutions should be injected under the surface of the water and the solution mixed thoroughly after making up to volume.

A suitable series of halogenated hydrocarbon concentrations (see Table B2) can be prepared by adding 100 ± 1 µl, 75.00 ± 0.75 µl, 50.0 ± 0.5 µl and 25.00 ± 0.25 µl of the stock solutions to separate 490 ml volumes of water in 500 ml volumetric flasks, making up to the mark with water and mixing thoroughly.

Working standard solutions should be prepared fresh on the day of analysis. When correctly stored (sealed, refrigerated and kept in the dark), the intermediate solution may be kept for up to two weeks.

B6 Apparatus

Apparatus should be free from contamination before use. All glassware should be cleaned using detergent, and then thoroughly rinsed with water (B5.1) and allowed to dry.

B6.1 **Sample bottles.** Amber glass, 125 ml nominal capacity, fitted with glass stoppers. Clean bottles can be baked overnight in an oven at l05 ± 5 °C and allowed to cool before use.

Alternatively, sampling vials can be used (for example glass, 40 ml) fitted with PTFE-faced septum-lined screw-caps. To minimise contamination, the vials and septa may also be baked in the oven and allowed to cool before use.

B6.2 **General laboratory glassware.** Volumetric flasks, glass pipettes, syringes, etc of various sizes.

B6.3 **Headspace autosamplervials with crimp-on caps and PTFE-lined septa.** Borosilicate glass of, for example, 10 or22 ml capacity. Septa can be preconditioned by baking in the oven at 105 ± 5 °C for at least 2 hours before use.

B6.4 **GC equipment.** GC equipped with an autosampler for direct headspace analysis, electron capture detector and WCOT capillary column. Operate in accordance with the manufacturer's instructions. Operating conditions used to obtain the test data are given in Tables B3 to B5. A typical chromatogram of several halogenated hydrocarbons is shown in Figure B1.

B7 Sample collection and preservation

Samples should be collected directly into suitable containers (see B6.1), leaving no headspace. Without rinsing, the sample container must be completely filled to exclude any headspace (even small bubbles). In the case of glass vials this can be achieved by filling to give a convex meniscus before capping. Any samples found to have free air space should be considered suspect. It may be considered advisable to take two samples; one to be retained in the event of a repeat analysis being required. A crystal of sodium thiosulphate (B5.3) should be added to the container prior to sampling. The analysis should be performed as soon as possible after sample collection. If immediate analysis is not practicable, samples should be stored at 1-4 °C, protected from direct sunlight and analysed within 14 days unless stability data show otherwise.

Care should be taken if subsamples are taken with a syringe, as a partial vacuum may be formed resulting in a change to the concentration of volatile components in the sample.

B8 Analytical procedure

Step	Procedure	Notes
B8.1	**Preparation of samples**	
B8.1.1	Transfer a suitable aliquot of sample from the sample container to a headspace autosampler vial using a positive displacement pipette (note a). Immediately cap and tightly seal the vial (note b).	(a) The ratio of headspace volume to sample volume has been found to alter the performance characteristics of the method for some autosamplers. A Ratio of 10:1 headspace volume to sample volume has been found to produce satisfactory data. (b) Sufficient cap and septum sets should be prepared in advance. The septum must form a good seal with the top of the vial to prevent loss of determinands from the headspace.
B8.2	**Preparation of blanks and standards**	
B8.2.1	Using an identical procedure to that described under B8.1.1 prepare a series of vials containing laboratory air only (air blank), water (B5.1, water blank) and a range of working standard solutions (B5.6) (notes c and d).	(c) Normally a minimum of one air blank and two water blanks are analysed with each batch of samples. Sufficient standards should be included to establish and verify the calibration during the course of the analysis (see also note f). (d) The same batch of water should be used to prepare the blank and standard solutions.
B8.3	**AQC**	
B8.3.1	Undertake the entire procedure using purified water (B5.1) spiked at appropriate concentrations with the determinands.	
B8.4	**GC/ECD determination**	
B8.4.l	Set up the instrument in accordance with the manufacturer's instructions (note e)	(e) The conditions used to obtain performance data are given Tables B3 to B5.

B8.4.2 Analyse air and water blanks, samples and standard solutions by automatic injection. (note f).

(f) A typical analysis sequence would start with air and water blank solutions and calibration standard solutions, followed by samples, interspersed with standard solutions to check for drift. Air and water blank solutions should be used to check for contamination. The calibration should be checked at the end of the sequence. If unusually high blanks are obtained, the cause should be investigated and rectified before continuing the analysis. Use the duplicate sample if necessary.

B8.4.3 Measure the response of each of the peaks corresponding to halogenated hydrocarbons of interest.

B8.4.4 Using the results from the standard solutions, construct a calibration graph of peak response versus concentration of each of the halogenated hydrocarbons injected (μgl^{-1}).

B8.4.5 Use the calibration graph to calculate the concentration of each halogenated hydrocarbon in the original sample (see section B9) (note g).

(g) If the concentration of any halogenated hydrocarbon exceeds the calibration range, the duplicate sample (B7) should be diluted with water (B5.1) and analysed.

B9 Calculation

The concentration of each halogenated hydrocarbon is given by:

$C = S / m \quad \mu gl^{-1}$

where C = concentration of halogenated hydrocarbon in the sample (μgl^{-1});

S = peak response for the halogenated hydrocarbon in the sample (response units, ie peak area or height);

m = the slope of the calibration (response units, ie peak area or peak height, divided by concentration, $\mu g\ 1^{-1}$) obtained from the plot of concentration (x-axis) versus peak response (y-axis).

Alternative methods of calculation may be used provided they give equivalent results.

The calculations are more easily performed using a laboratory data system to integrate the relevant peaks and calculate the results automatically.

Table B1 Details for the preparation of stock standard solutions in methanol

Determinand	d_{20}	Volume of halogenated hydrocarbon (or preliminary solution) per 100 ml of solution	Concentration of solution
Preliminary solution			
tetrachloroethene	1.623	10.00 ± 0.02 ml	162 gl^{-1}
carbon tetrachloride	1.594	5.00 ± 0.02 ml	79.7 gl^{-1}
Stock solution			
bromodichloromethane	1.980	10.00 ± 0.01 µl	198 mgl^{-1}
dibromochloromethane	2.45	10.00 ± 0.01 µl	245 mgl^{-1}
bromoform	2.890	10.00 ± 0.01 µl	289 mgl^{-1}
chloroform	1.483	20.00 ± 0.02 µl	296 mgl^{-1}
carbon tetrachloride (P)		25.00 ± 0.05 µl	20 mgl^{-1}
trichloroethene	1.464	20.00 ± 0.02 µl	293 mgl^{-1}
tetrachloroethene (P)		50.00 ± 0.05 µl	81 mgl^{-1}
1, 1,1-trichloroethane	1.339	10.00 ± 0.01 µl	134 mgl^{-1}

d_{20} is density (gcm^{-3}) at 20°C.
As volumes of halogenated hydrocarbons are used to prepare the stock solutions, the temperature should be as close to 20°C as possible to minimise errors.
P is preliminary solution.

Table B2 Concentrations of working standard solutions in water

Volume of stock solution (µl)	100	75	50	25
bromodichloromethane	39.6	29.7	19.8	9.90
dibromochloromethane	49.0	36.8	24.5	12.3
bromoform	57.9	43.4	29.0	14.5
chloroform	59.4	44.6	29.7	14.8
carbon tetrachloride	3.98	2.99	1.99	1.00
trichloroethene	58.5	43.9	29.3	14.6
tetrachloroethene	16.2	12.2	8.10	4.05
1,1,1-trichloroethane	27.0	20.3	13.5	6.75

Concentrations are expressed in μgl^{-1}

Table B3 **Standard deviations, Recoveries and Limits of detection**

Determinand	High spike Conc.	S_t	Bias	Low spike Conc.	S_t	Bias	Sample Conc.	S_t	LOD	Recovery
bromodichloromethane	31.4	1.65(10)	-0.88	9.3	0.62(11)	2.29	7.11	0.42(12)	0.38	101
dibromochloromethane	38.7	2.03(11)	-1.19	11.7	0.68(11)	3.50	6.37	0.37(11)	0.34	102
bromoform	45.9	1.86(11)	-1.00	12.8	0.61(12)	-3.75	6.24	0.28(12)	0.46	102
chloroform	46.7	2.49(11)	-1.25	13.4	0.56(13)	-1.36	7.64	0.4(13)	0.65	103
carbon tetrachloride	3.20	0.30(11)	0.59	0.7	0.05(11)	-12.5	0.17	0.02(13)	0.05	103
trichloroethene	21.6	1.31(11)	-0.11	5.9	0.21(12)	-4.92	3.84	0.22(12)	0.41	102
tetrachloroethene	13.2	0.52(16)	1.87	3.6	0.23(11)	-2.88	0.92	0.25(10)	0.28	103
1, 1,1-trichloroethane	46.3	2.52(11)	-0.99	13.2	2.52(15)	-1.80	2.93	0.19(15)	0.79	99

Values expressed as μgl^{-1}, except for recovery and bias, which are expressed as a percentage.
S_t is total standard deviation.
LOD is limit of detection, calculated using 4.65 x S_w, ie the within-batch standard deviation.
Numbers in brackets represent degrees of freedom.

The following conditions were used for the determinations: Fused silica capillary 25 m x 0.32 mm internal diameter, phenylmethylsilicone BP 5, helium, 10 psi, column temperature programme 40°C for 5.5 min, 25°Cmin^{-1} to 163°C, hold for 8 min, injector temperature 150°C, detector temperature 300°C.

Headspace autosampler conditions:

Sample temperature	70°C.
Needle temperature	100°C.
Transfer temperature	120°C.
Injections per vial	1.
Thermostatting time	27 minutes.
Increment therm time	No.
Pressurisation time	1 minute.
Injection time	0.08 minutes.
Withdrawal time	1 minute.
Number of vents	1.

Data provided by Thames Water Utilities Ltd.

Table B4 **Means, Standard deviations, Recoveries and Limits of detection**

Determinand	High spike Mean	S_t	Low spike Mean	S_t	Sample Mean	S_t	LOD	Recovery (%)
bromodichloromethane	10.49(10)	0.7521	1.176(10)	0.1170	7.675(10)	0.5993	0.107	97.3
dibromochloromethane	9.884(10)	0.6474	1.051(10)	0.0856	12.28(10)	0.6312	0.055	98.2
bromoform	9.867(10)	0.3833	1.066(11)	0.1140	9.474(11)	0.4383	0.172	97.5
chloroform	9.889(11)	0.3483	1.092(11)	0.0836	6.191(11)	0.2489	0.122	98.9

Values expressed as μgl^{-1} unless otherwise stated.
S_t is total standard deviation. Sample consisted of a potable water from a surface water source.
Recovery based on spiked sample at 50 μgl^{-1}. High and low spikes at 10 μgl^{-1} and 1 μgl^{-1} respectively.
LOD is limit of detection, calculated using 4.65 x S_w, the within-batch standard deviation of a blank water spiked at 1μgl^{-1}.
Numbers in brackets represent degrees of freedom.

The following conditions were used for the determinations: Fused silica capillary (wide bore) 30 m x 0.53 mm internal diameter, DB 624 (3 µm film thickness), helium, approximately 8.0 $mlmin^{-1}$, column temperature programme 60 °C for 2 min, 11.5 °Cmin^{-1} to 120 °C, hold for 2 min, injector temperature 140 °C, split mode, flow rate 40 $mlmin^{-1}$. ECD temperature 325 °C.

Headspace autosampler conditions:

Injection volume	500 µl.
Incubation temperature	70 °C.
Incubation time	10 minutes.
Shaker speed	1600 rpm (run 15 sec, stop 5 sec).
Analysis run time	13 minutes.
Filling strokes	5 (delay time 2 sec).
Syringe heater	85 °C.
Syringe bake-out time	10 sec.
Syringe flush	20 sec.
Injection delay	5 sec post/5 sec pre.

Data provided by Anglian Water Services.

Table B5 **Standard deviations, Recoveries and Limits of detection**

Determinand	Tap water	Tap water spike			High standard			Low standard			Deionised water	
	S_t	Conc.	S_t	Recovery	Conc.	S_t	Bias	Conc.	S_t	Bias	S_t	LOD
chloroform	0.806	71.04	3.92	100	106.56	2.84	0.84	23.68	1.17	5.55	0.553	2.21
dibromochloromethane	0.532	35.70	2.21	103	53.55	2.64	0.76	11.9	0.798	-7.05	0.340	0.495
bromodichloromethane	0.520	29.4	1.89	105	44.1	1.84	3.63	9.8	0.432	-12.3	0.490	1.89
bromoform	0.669	35.28	1.87	96.7	52.92	1.44	-0.13	11.76	0.763	6.53	0.782	1.40
carbon tetrachloride	0.038	1.908	0.21	105	2.86	0.18	3.97	0.636	0.026	-4.06	0.031	0.137
trichloroethene	0.189	21.90	1.37	100	32.85	0.92	0.73	7.3	0.313	7.63	0.199	0.596
tetrachloroethene	0.096	6.804	0.56	102	10.21	0.44	2.22	2.268	0.333	0.980	0.058	0.246

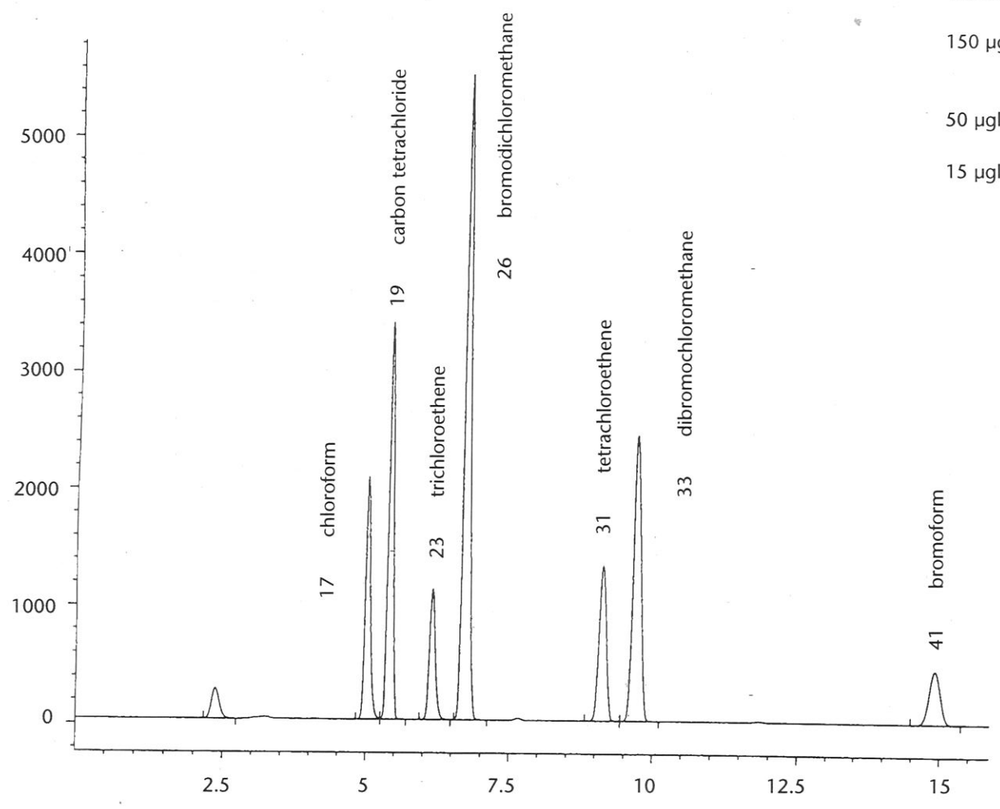
Values expressed as μgl^{-1} except for recovery and bias, which are expressed as percentages.
S_t is total standard deviation.
LOD is limit of detection, calculated using 4.65 x S_w, ie the within-batch standard deviation.
Results are based on at least 10 degrees of freedom.

The following conditions were used for the determinations: 30 m x 0.32 mm internal diameter, 6% cyanoprophenyl/94% dimethylpolysiloxane (1.80 µm film thickness), helium, 14 psi, column temperature programme 80 °C for 5 min, 7 $°Cmin^{-1}$ to 150 °C, hold for 2 min, injector temperature 150 °C.

Headspace auto sampler conditions :

Sample temperature	60 °C.
Needle temperature	100 °C.
Transfer tube temperature	120 °C.
GC cycle time	15 minutes.
Thermostatting time	61 minutes.
Pressurisation time	2.5 minutes.
Injection time	0.08 minutes.
Withdrawal time	0.3 minutes.

Data provided by AES.



Concentration

150 μgl^{-1}	chloroform, bromodichloromethane, dibromochloromethane, bromoform
50 μgl^{-1}	trichloroethene
15 μgl^{-1}	carbon tetrachloride, tetrachloroethene

Figure B1 **Chromatogram of a standard mixture**

C A note on the determination of volatile organic compounds in complex matrices

C0 Introduction

In order to analyse volatile organic compounds in complex matrices, the procedures described in Method A may require modification. Such matrices include sludges, soils, sediments, waste liquors and effluents. Although Method A may be used to quantify many volatile organic compounds which are insoluble or only slightly soluble in water, quantification limits for the more soluble compounds may be much higher because of poor purging efficiency. The purging efficiency may be improved by the addition of inorganic salts such as sodium chloride to the sample, and/or the use of longer purging times.

When undertaking the analysis of complex matrices, extra care will often be required to ensure that reliable results are obtained, especially when more manipulative operations are employed with non-aqueous matrices. Some of the difficulties which have been encountered during the analysis of such samples are highlighted below.

C1 Carry-over

Interference may occur when a sample which contains low concentrations of volatile organic compounds is analysed immediately after a sample which contains high concentrations of volatile organic compounds. To reduce this carry-over effect, the purging device, and any other equipment which has come into contact with the sample, should be rinsed with distilled water prior to commencing the next analysis. Hence, when a sample containing unusually high concentrations of volatile organic compounds is analysed, the results of subsequent samples may need to be considered suspect, and it may be necessary to repeat these analyses on duplicate samples if these are available.

Some samples may contain large amounts of water soluble materials, suspended solids, high-boiling compounds or high concentrations of volatile organic compounds. In these cases, it may be necessary between analyses to wash the purging device with a detergent solution, followed by a rinse with distilled water, which is followed by drying at 105 °C. Frequent 'bake-out' and purging of the entire system may also be advisable prior to subsequent analysis.

C2 Interference effects

Many interference effects occur because of high concentrations of compounds within the sample matrix. These effects may include suppression of the purging process, suppression of instrument response, and changing of retention times. In addition, samples which contain very high levels of volatile organic compounds may result in the saturation of the mass spectrometer, and cause overloading of the chromatographic column.

As a check to assess these effects, the peak areas obtained for the internal or surrogate standards added to the sample can be compared with the corresponding peak areas of the internal or surrogate standards added to the calibration standard solutions. Significant differences may suggest that these effects are apparent. Similar problems may also be highlighted by the results of recovery tests obtained using surrogate standards. For complex matrices, an appropriate number of internal and surrogate standards should be used which cover the whole elution range of the compounds of interest. See also section A3.

C3 Physical characteristics of the sample matrix

The purging of certain aqueous samples may result in foaming. This effect may cause part of the sample to migrate up the purge vessel into the purge and trap system, hence causing contamination of the system. To prevent this, it may be necessary to fit an additional glass foam-trap above the purge vessel, or to add a suitably based anti-foaming agent. If an anti-foaming agent is used, the same amount should also be added to the blank and calibration solutions to ensure that any nterference effects are taken into account with the determination of the target compounds.

For solid samples, the type and nature of the sample matrix should be taken into account. For example, with samples of a clay-like consistency, the purging process may be improved by mixing the sample with an inert granular material, for example quartz sand, which has previously been heated and allowed to cool. The mixing process should be undertaken as quickly as possible in order to reduce losses of the volatile compounds. The mixed sample should then be added to a quantity of interference-free water in the purging vessel. With such samples, needle sparging has been found to be less problematical than frit sparging.

The loss of volatile components from aqueous samples can often be more controlled than from solid samples, ie it is more difficult to avoid losses from solid samples, especially when solid samples involve additional manipulative treatments. To minimise these losses, the sample container should be completely filled and sealed immediately, and opened as infrequently as possible and only for short periods of time. As the number of manipulative operations used in the handling of the sample increases, then the loss of volatile components will become more significant.

C4 Water-immiscible liquid samples

It may be possible to extend the scope of Method A to include water-immiscible solvents by making an appropriate dilution of the sample with methanol. An aliquot of the diluted sample is then added to the water contained in the purge vessel and the analysis carried out in the normal manner. Alternatively, it may be more appropriate to use an adaptation of Method B or a direct injection technique.