Determination of Very Low Concentrations of Hydrocarbons and Halogenated Hydrocarbons in Water 1984–5

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

This document contains 41 pages

Determination of Very Low Concentrations of Hydrocarbons and Halogenated Hydrocarbons in Water 1984–85

Methods for the Examination of Waters and Associated Materials

This booklet contains three methods, one for very low concentrations of hydrocarbons and two for halogenated hydrocarbon solvents.

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CORRECTIONS

Pages 13 and 14 (first method section 8 Analytical Procedure)

Delete the whole of the text in section 8.1 except for its title and step number and replace by the following text with extra step numbers as indicated. The notes in the notes section remain unchanged.

8.1.1 Weigh the stoppered sample bottle containing approximately 1 litre of sample and note the reading (w_1 g) to within 0.1 g.

8.1.2 Pour the sample into a 2 litre separating funnel and add 10 ± 0.5 ml of solvent, in such a manner as to cause least disturbance of the water. Stopper both the sample bottle and separating funnel immediately.

8.1.3 Weigh the bottle and stopper and note the reading (W_2 g) to within 0.1 mg.

8.1.4 Shake the mixture in the funnel for 3 minutes. Allow the layers to separate (note (a)).

8.1.5 Run off the aqueous layer into a 1 litre flask and stopper.

8.1.6 Collect the pentane layer in a separating funnel (50 ml) and stopper.

8.1.7 Pour a second 10 ± 0.5 ml aliquot of solvent into the sample bottle. Add 50 ± 10 ml of the water that was retained (8.1.5) (note (b)) and rinse the bottle with this mixture, which is then poured into the 2 litre separating funnel. The remainder of the retained water is added to the funnel as well. Stopper the funnel and shake for 3 minutes. Allow the layers to separate. Discard the aqueous layer and combine both the pentane extracts (8.1.6 and 8.1.7) in the 50 ml separating funnel and stopper.

Step 8.2 remains unchanged.

Step 8.3 first paragraph, amend to read as follows:

Concentrate the eluant to approximately 2.5 ml using the 305 mm column and flask and continue concentration to a volume of 0.3–0.5 ml with the smaller column (165 mm) and small flask. Transfer the concentrate to a 1 ml vial using a pasteur pipette.

The remainder of 8.3 is correct except in the last paragraph where the volume in the fifth line of the paragraph should read

1.00 ± 0.02 ml.

Department of the Environment
December 1987
LONDON: HER MAJESTY'S STATIONERY OFFICE

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About this series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has seven Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non metallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1986

Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, the Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO London.

It cannot be too strongly emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Determination of Very Low Concentrations of Hydrocarbons in Water 1984

Introduction

Hydrocarbons constitute a wide range of substances and a large number of individual compounds. The range is so diverse that no one analytical method can be expected to determine all possible hydrocarbons. Because of this diversity, the substances determined are defined within the methodology. In this method the range covers hydrocarbons extracted by pentane and boiling between 60°C to about 340°C. The method determines most of the hydrocarbon constituents in hydrocarbon materials such as petrol, paraffin, diesel oil, gas oil, petroleum solvents etc. Those not covered would be either very volatile or non-volatile constituents, which would be outside the range indicated.

The procedure outlined in this method is intended to provide quantitative data on hydrocarbons at low levels that, from experience, appear to be important. (It should be noted, however, that polycyclic aromatic hydrocarbons are covered by another method in this series). 'Total Detected Hydrocarbons' may be estimated but one should be aware of the following problem in applying this to such parameters. If the detection limit for individual hydrocarbons is xμg/l and for example, 10 hydrocarbons are present at 2xμg/l then the 'Total Detected Hydrocarbons' would be 20xμg/l. However, if 40 hydrocarbons were present at x/2 μg/l (below the detection limit) then the total present would also be 20xμg/l but would be undetected.

The manner in which the calibration curve has been constructed in this method was largely determined by the relatively short time of stability of the curve, and by the number of samples to be analysed in the production of performance data. It is possible that in practice the calibration curve is stable for sufficient time to enable it to be constructed differently, for example, construction of the curve on one day followed by the analysis of samples over several days. However, a change in the method of construction must be supported by satisfactory performance data.

The method forms part of a continuing series which when complete can be used as a general co-ordinated scheme of analysis. It is envisaged that it will be acceptable as a UK reference method for determination of hydrocarbons in drinking water under the EC Directive relating to the quality of water intended for human consumption (80/778/EEC) (limit of dissolved or emulsified hydrocarbons, after extraction by petroleum either, is 10 μg/l).

1. Performance Characteristics of the Method (See Ref. 2)

1.1	Substances determined	Hydrocarbons extracted by pentane under the conditions of the method which pass through a florisil column and are chromatographed and detected by GC-FID. Individual hydrocarbons and/or 'Total detected hydrocarbons' are determined.
1.2	Type of sample	Water abstracted for potable supply and potable water.
1.3	Basis of method	Solvent extraction with pentane; removal of non-hydrocarbons with florisil; concentration; and separation and detection by GC-FID.
1.4	Range of application	0–20 μg/l individual hydrocarbons.
1.5	Calibration curve	Linear over range of application.
1.6	Standard deviation	See Table 1.
1.7	Limit of detection	See Table 1.

Table 1 Performance Characteristics of the Method for the Determination of Hydrocarbons in Drinking Water

Hydrocarbon	Solution	True Concentration (μg/l) [1]	Mean Result (μg/l)	$S_W(5)$ (μg/l)	$S_T(4)$ (μg/l)	Limit of Detection (μg/l) [4]	Minimum Discernable Concentration (μg/l)	% Recovery	90% Confidence Limits (%)
Total	Low concentration standard	10	9.61	—	2.05				
	High concentration standard	200	191.33	[2] —	24.76	5.699 [5]	0.029		
	Tap water	—	1.66	1.45	—				
	Tap water + 100 μg/l spike	—	94.24	8.37	[3] —			92.6	±6.5
Benzene	Low concentration standard	1	0.84	—	0.42				
	High concentration standard	20	20.27	[2] —	5.12	1.580 [5]	0.066		
	Tap water	—	0.16	0.68	—				
	Tap water + 10 μg/l spike	—	10.65	2.40	[3] —			104.9	±27.1
Heptane	Low concentration standard	1	0.87	—	0.20		*		
	High concentration standard	20	19.51	[2] —	3.43	—	0.033		
	Tap water	—	−0.01	0.04	—				
	Tap water + 10 μg/l spike	—	10.86	1.07	[3] —			108.7	±10.2
Toluene	Low concentration standard	1	0.86	—	0.19				
	High concentration standard	20	18.82	[2] —	3.06	0.130 [5]	0.025		
	Tap water	—	0.02	0.03	—				
	Tap water + 10 μg/l spike	—	9.96	1.29	[3] —			99.4	±10.0
Octane	Low concentration standard	1	0.96	—	0.10		*		
	High concentration standard	20	19.12	[2] —	3.01	—	0.031		
	Tap water	—	0.00	0.00	—				
	Tap water + 10 μg/l spike	—	10.48	0.68	[3] —			104.8	±9.0
Ethyl Benzene	Low concentration standard	1	0.86	—	0.11				
	High concentration standard	20	18.63	[2] —	2.81	0.941 [6]	0.242		
	Tap water	—	0.24	0.35	—				
	Tap water + 10 μg/l spike	—	10.34	0.55	[3] —			101.0	±8.0
Iso-Propyl Benzene	Low concentration standard	1	0.94	—	0.04		*		
	High concentration standard	20	18.51	[2] —	2.60	—	0.026		
	Tap water	—	0.02	0.03	—				
	Tap water + 10 μg/l spike	—	10.35	0.86	[3] —			103.3	±7.3

(continued)

Table 1 ***(continued)***

Hydrocarbon	Solution	True Concentration (μg/l) [1]	Mean Result (μg/l)	S_W(5) (μg/l)	S_T(4) (μg/l)	Limit of Detection (μg/l)	Minimum Discernable Concentration (μg/l) [4]	% Recovery	90% Confidence Limits (%)
Decane	Low concentration standard	1	1.18	—	0.12		*		
	High concentration standard	20	19.53	[2] —	3.49	—	0.028		
	Tap water	—	0.02	0.07	—				
	Tap water + 10 μg/l spike	—	10.93	1.04	[3] —			109.1	±11.3
Naphthalene	Low concentration standard	1	1.09	—	0.08		*		
	High concentration standard	20	18.91	[2] —	2.29	—	0.214		
	Tap water	—	−0.01	0.07	—				
	Tap water + 10 μg/l spike	—	7.46	1.16	[3] —			74.7	±4.9
Tetradecane	Low concentration standard	1	1.34	—	0.29		*		
	High concentration standard	20	21.61	[2] —	6.50	—	0.045		
	Tap water	—	0.00	0.00	—				
	Tap water + 10 μg/l spike	—	10.36	3.13	[3] —			103.6	±17.3
Phenanthrene	Low concentration standard	1	1.02	—	0.58		*		
	High concentration standard	20	18.23	[2] —	1.11	—	0.024		
	Tap water	—	0.06	0.20	—				
	Tap water + 10 μg/l spike	—	2.037	1.77	[3] —			20.9	±6.4

S_W and S_T = Estimate of w batch and total standard deviation respectively. Figures in brackets ( ) indicate numbers of degrees of freedom.
[1] The true concentration of the tap water was unknown.
[2] There were no duplicate standards and therefore no within batch standard deviations could be obtained.
[3] Doubt existed as to the tap water's stability over the testing period and so an estimate of total standard deviation could not be entered.
[4] The minimum discernable concentration is useful in those specified cases (*) where the blank variation was insufficiently discernable to obtain a limit of detection.
[5] The limit of detection is calculated from 2.t. S_W + COD (where S_W is the within batch standard deviation of the blanks).
[6] The limit of detection is calculated from t.S_W + COD (where S_W is the within batch standard deviation of the tap water).

1.8 Sensitivity

Using a flame ionization detector, at a baseline noise level (peak to peak) of 0.5% full-scale deflection of the recorder, the following quantities of determinand produced a recorder deflection of 50%.

Ethyl Benzene	9.45 ng
Decane	9.91 ng
Naphthalene	6.83 ng

1.9 Bias

Potential interferences are given in Section 3. Since the determinand is defined by the method some aspects of interferences do not apply.

A reference mixture of 10 hydrocarbons is used to simulate the hydrocarbons that may be encountered. Some bias is possible but unknown.

		The determination of the calibration curve includes slight modification to the procedure for real samples, e.g. to take account of the small amount of acetone used to make the reference mixture spike; and an unavoidable headspace with spiked samples. These may lead to some bias.
1.10	Interference	Any non-hydrocarbons that are not eliminated in the sample processing and are separated and detected by GC-FID.
1.11	Time required for analysis	Preparation of reagants typically takes 12 hours in respect to elapsed time, with 3 hours operator time. Assuming all reagents are prepared, time to analyse one sample, including construction of the calibration curve, is 8 hours; to analyse 6 samples takes 2 days. This is elapsed time. Total operator time will be variable but approximately 15% less that of the elapsed time.

2. Principle

Hydrocarbons are extracted from a 1 litre sample using 2 × 10 ml of purified pentane. The extract is passed through a column of florisil which retains most non-hydrocarbons. The resulting extract is concentrated, separated and detected by capillary GC-FID. Individual hydrocarbons and 'Total detected hydrocarbons' are evaluated from a reference mixture using an integrator.

3. Interferences

In most, possibly all, methods for determining hydrocarbons in water, specific detection is not possible and specificity is usually introduced during sample processing. In this method a florisil column is used to retain non-hydrocarbons. The following classes of compounds were tested under the conditions of analysis, and were found to be sufficiently retained by the column: Esters, Alcohols, Ketones, Aldehydes, Ethers, Mercaptans and Phosphates.

Halogenated hydrocarbons are not retained satisfactorily. Thus halogenated hydrocarbons which are amenable to the method will interfere if present in the sample in sufficient amounts. In most drinking and related waters the potential interfering halogenated hydrocarbons, in relation to the sensitivity of the method, are bromodichloromethane, tribromomethane, trichloroethylene, 1,1,1-trichloroethane and tetrachloroethylene. Table 2 gives some relevant retention data.

4. Hazards

Pentane is flammable and highly volatile and possibly narcotic. Appropriate precautions must be taken in its use and spark-proofed refrigerators are essential for storage of solvents and solutions. Sulphuric acid is very corrosive and potassium permanganate is an oxidizing agent. Appropriate precautions are necessary, especially eye protection. Use of 'biological phosphate-free' detergents such as Decon 90 for cleaning glassware also demands eye protection.

5. Reagents

All reagents must be of sufficient purity that they do not give rise to significant interferences. Purity must be checked for each batch of material by running procedural blanks with each batch of samples analysed. Reagents may become contaminated via air and other materials, particularly plastic, or by degradation caused by the action of light. Reagents must be stored in dark, tightly-sealed all-glass bottles.

5.1 Water The water used for blank determinations and standards must have an individual hydrocarbon content which is negligible compared with the smallest concentration to be determined. This should be checked as in section 8.1–8.3. Normally water containing less than 0.2 μg/litre of individual hydrocarbons and less than 2 μg/litre 'Total detected hydrocarbons' will be sufficient. It is difficult to guarantee a suitable source of water. Distilled water or deionized water or even tap water may be satisfactory. Passing

deionized or tap water through activated carbon can be effective; however the following procedure is usually most appropriate.

5.1.1 Preparation of blank water Extract 5 litres of tap water twice with 500 ml of pentane. Distil the aqueous layer. Discard the first 500 ml of distillate and collect the following 4 litres. Store the water in glass-stoppered bottles in the dark. Recontamination can occur during storage and stocks should be checked regularly.

5.2 Pentane Analytical grade pentane is used. This should have, after concentration from 20 ml to 1 ml, less than 0.2 μg individual hydrocarbons detected per ml of concentrated solvent. To obtain such purity the following method was proved successful.

5.2.1 Purification of solvent Shake vigorously two litres of analytical grade pentane with 200 ml of concentrated sulphuric acid (CARE! see section 4). Remove the pentane layer and shake vigorously first with a further 200 ml of sulphuric acid and then with 200 ml of acidified potassium permanganate (5 g $KMnO_4$ in 200 ml water plus 20 ml concentrated sulphuric acid) until no further colour change occurs, usually within 15 minutes. Discard the lower layer. Distil the pentane layer; discard the first 500 ml, collect the next 1000 ml and discard the residue. Keep the solvent in the dark in glass-stoppered or PTFE lined screw-capped glass bottles. Pentane of this purity is commercially available from at least one specialist supplier.

5.3 Acetone (analytical reagent grade). This must be checked by GC-FID before use. It must contain less than 0.1 μg individual hydrocarbons or less than 0.1 μg total hydrocarbons detected per μl. Before GC-FID analysis the reagent needs to be diluted (1:500 acetone: pentane), because acetone alone would damage the GC column. This will give about 2% FSD for 2 μl with a noise of 0.5% FSD.

5.4 Standard solutions The standard solution comprises benzene, heptane, toluene, octane, ethyl benzene, iso-propyl benzene, decane, tetradecane, phenanthrene and napthalene, at a concentration of (each), 10 mg/10 ml in acetone. This solution is stable for a week if kept in the dark and in a freezer. For GC work (see Fig. 1) this solution is diluted in pentane (10 μl standard solution made up to 10 ml with pentane).

5.5 Florisil Heat florisil (60–100 mesh) to 600°C in a silica dish in a muffle furnace for 2 hr. Cool to 200°C in a furnace and to ambient temperature in a desiccator. Prior to use, store in the desiccator.

5.6 Dichloromethane (analytical reagent grade). This must be checked by GC-FID before use. It must contain less than 0.5 μg individual hydrocarbons or less than 5 μg of total hydrocarbons detected per ml after concentration of 20 ml to 1 ml.

6. Apparatus

All apparatus should be free from contamination. A suitable cleaning procedure for glassware is as follows: Wash glassware thoroughly with a biological phosphate-free detergent such as 'Decon 90' or equivalent and rinse thoroughly with distilled water. Air dry at 60°C and cool. Rinse thoroughly with acetone and then pentane immediately before use, and allow to drain.

6.1 General apparatus

Note: All separating funnel stopcocks should be grease free.

6.1.1 1 litre borosilicate glass-stoppered glass sampling bottles. (Amber bottles are recommended).

6.1.2 Glass-stoppered separating funnel, 2 l.

6.1.3 Measuring cylinders 50 ml, 25 ml and 5 ml.

6.1.4 Syringes 5 μl, 20 μl and 1 ml.

6.1.5 Kuderna–Danish apparatus including 10 ml concentrator, 250 ml flask, 305 mm column (with solvent recovery apparatus) and 165 mm column, (ground glass fittings) (see Fig. 2). (Screw-type fittings are available from various suppliers but have not been evaluated using this method).

6.1.6 Conical (Erlenmeyer) flask, 1 l.

Figure 1 Chromatogram of standard solution

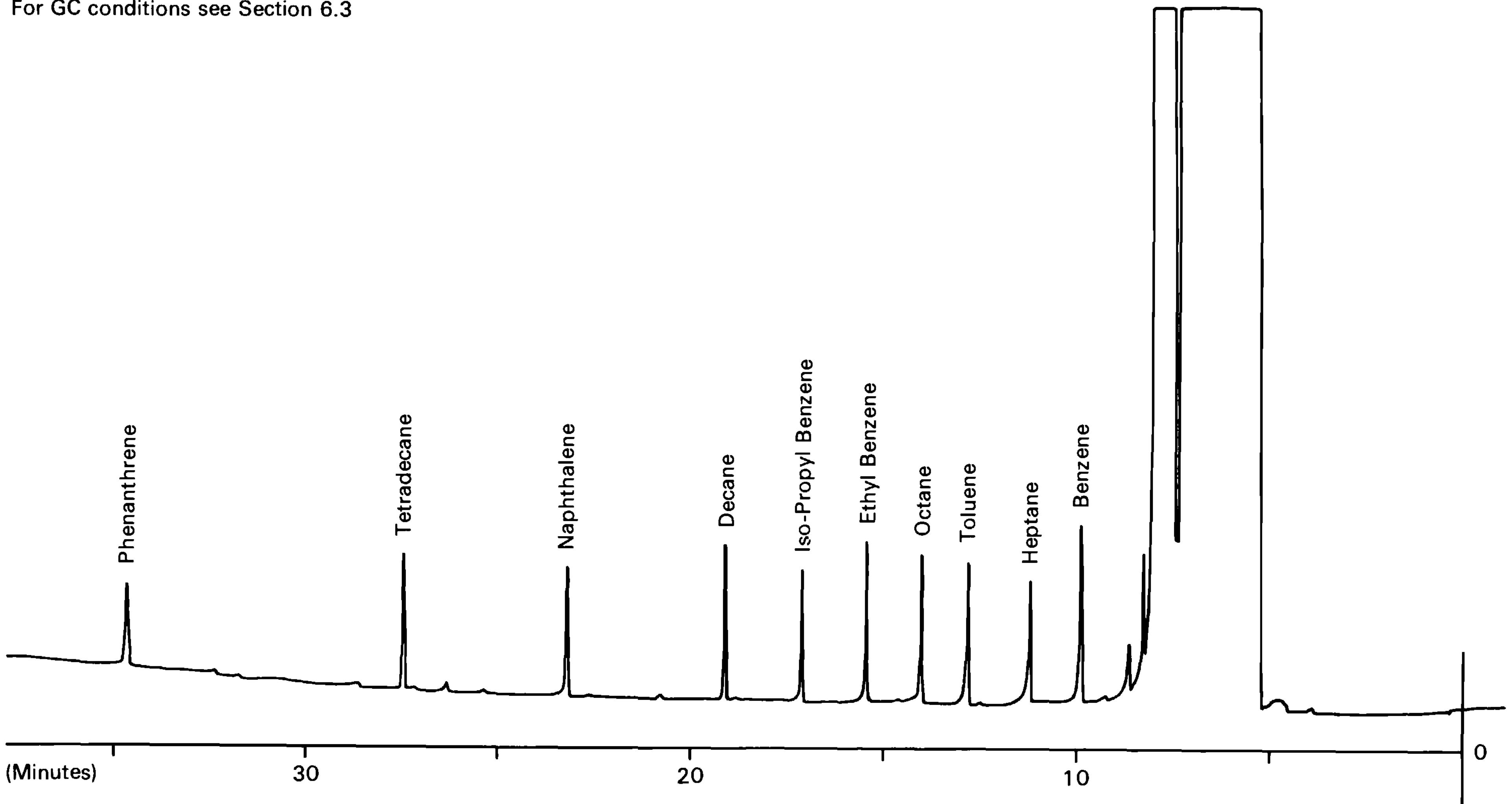


Figure 2 Kuderna-Danish evaporator with macro and micro columns

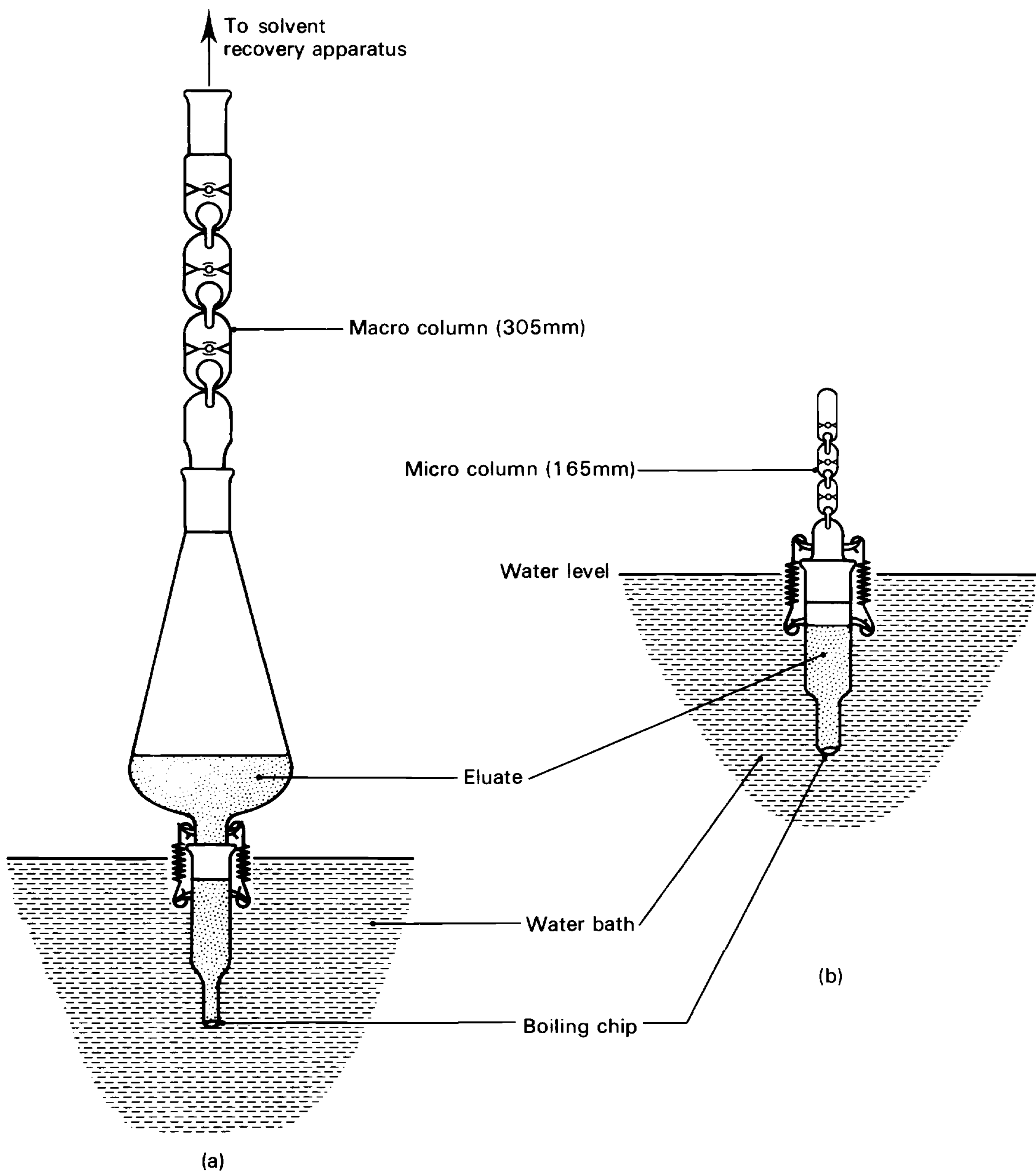
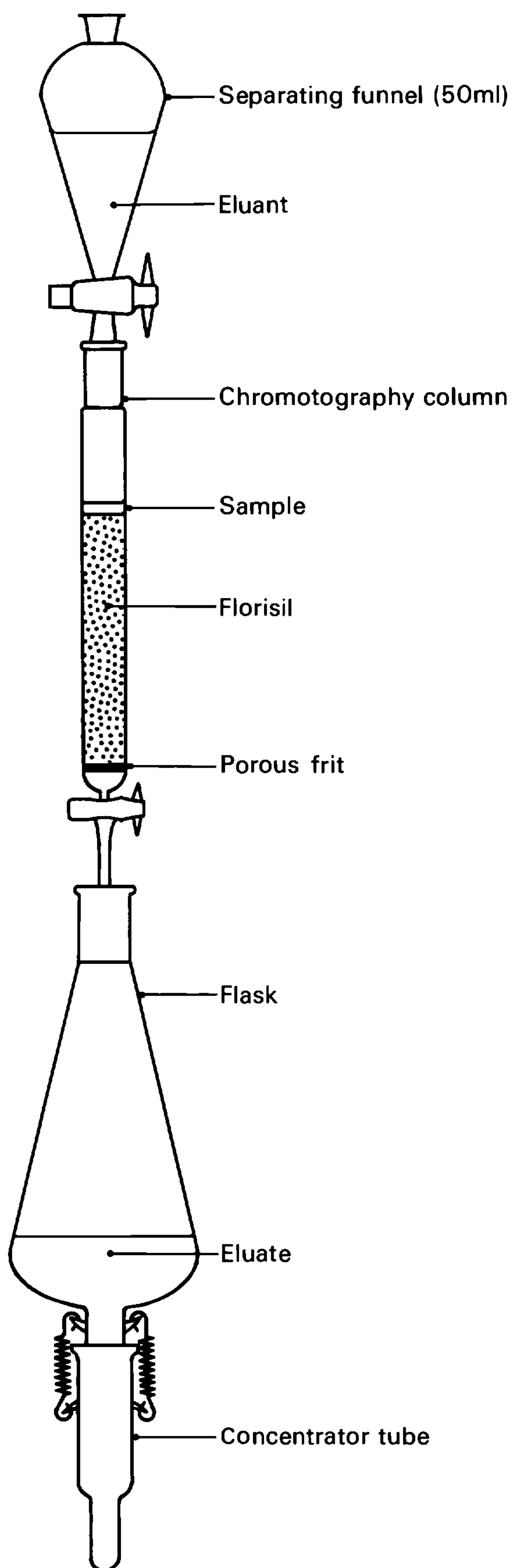


Figure 3 Sample clean-up apparatus



6.1.7 Pasteur pipettes, sterilized.

6.1.8 Chromatography column, 200 mm long by 10 mm ID. Ground glass stopcock. Sinter porosity of 1. (see Fig. 3).

6.1.9 Separating funnel, 50 ml with standard target joint. (Reservoir flask for column, see Fig. 3).

6.1.10 Septum-capped vials—graduated, 1 ml.

6.1.11 Nitrogen line—the supply of gas must be cleaned. The following procedure was found to be effective: Pass the gas through an impurity trap containing $\frac{1}{16}$ in pellets of type 13X molecular sieve and 15–40 mesh silica gel. The ensuing nitrogen line ends in a pressure valve. Attach flexible PTFE tubing to the outlet of this valve and insert a glass capillary column in the outlet of the PTFE tubing. The gas flowing from this column should be regulated by the valve to produce a flow just strong enough to indent the meniscus of the solvent being evaporated (typically 200 ml/min from a jet of internal diameter 0.5 mm at a distance of 20 mm from the liquid).

6.2 Special apparatus

6.2.1 Muffle furnace A furnace, capable of attaining temperatures in excess of 600°C, is required. (See section 5.5).

6.2.2 Florisil column The preparation of this column should be carried out immediately before use. (Relatively warm ambient temperatures may lead to some problems with formation of pentane vapour bubbles.)

To 3 g ± 0.2 g florisil (see section 5.5) add 5 ± 1 ml pentane to form a slurry. Pour all of this into the chromatography column (see section 6.1.8) and allow to settle. Drain off the excess solvent to just above the top of the florisil.

6.3 Gas Chromatography A Gas Chromatography suitable for use with capillary columns and equipped with FID and a sub-ambient cooling unit is required.

This should be operated in accordance with the manufacturer's instructions. For the development work and determination of performance characteristics a splitless injection system was used. However, other types of injector may be suitable, such as an on-column injector.

The following GC conditions have been found suitable (see Fig. 1);

Column:	OV-1 (or equivalent) silica, WCOT, 50 m, 0.2 mm I.D. A shorter (and cheaper) column may be used, for example 25 m.
Detector oven temp.:	300°C.
Column oven temp.:	20°C for 2 minutes. Temp. programmed at 8°C/min to 250°C and held there for 6 mins.
Carrier gas:	He, 1.5 ml/min.
Chart speed:	600 mm/hour.
Injector:	Splitless.
Integrator:	A GC computing integrator is required with capability of determining peak area, total peak area, retention time and with memory capable of handling up to 150 peaks (with sufficient sampling rate) from a complex capillary column chromatogram. Most modern integrators are suitable.

7. Sample Collection and Preservation

Sample bottles should be amber borosilicate glass with ground glass stoppers, cleaned in the manner described for glass apparatus (see section 6). Samples in clear glass bottles should be kept in the dark.

Collect the sample by rinsing the bottle with a small amount (less than 20 ml) of sample water. To the bottle, add 3.2 ± 0.2 ml of 4N hydrochloric acid to attain a pH of 2 (in the sample). Fill the bottle with the sample and stoppered so as to leave no head space.

The samples should be kept in the dark at or below normal temperatures and extracted as soon as possible. Normally samples are stable for up to 24 hours and possibly longer if stored in a refrigerator at 4°C.

8. Analytical Procedure

Caution: Before proceeding with analysis read section 4 Hazards and section 10 Contamination.

Step	Procedure	Notes
8.1	**Extraction**	
	Weigh the sample bottle containing approximately 1 litre of sample and stopper and note the reading (W_1g) to within 0.1 mg. Pour 10 ml ± 0.5 ml of solvent into a 2 litre separating funnel in such a manner as to cause least disturbance of the water. Stopper the sample bottle and separating funnel immediately. Weigh the bottle and stopper and note the reading (W_2g) to within 0.1 mg. Shake the mixture for 3 min. Allow the layers to separate (note (a)). Run off the aqueous into a 1 litre flask and stopper. Collect the pentane layer in a separating funnel (50 ml) and stopper.	(a) Separation of the layers is normally achieved within 5 mins.
	Pour a second 10 ml ± 0.5 ml aliquot of solvent into the sample bottle together with 50 ± 10 ml of the water that was retained (note (b)) and rinse the bottle with this mixture. It is then poured into the separating funnel and the remainder of the retained water is added to the funnel as well. Stopper the funnel and shake for 3 min. Allow layers to separate. Discard the aqueous layer and collect the pentane in the 50 ml separating funnel and stopper.	(b) The water is used to aid washing of the vessel with the pentane.
8.2	**Sample Clean-Up**	
	Prepare the florisil column as described in section 6.2.2. Load the extract onto the column (note (c)) and elute with 50 ml ± 1 ml of a 10% (v/v) dichloromethane in pentane mixture (see Fig. 3) at a rate of 1–2 ml/min. Collect the eluant in the concentrator tube (10 ml) and flask (250 ml) items of the Kuderna–Danish evaporator apparatus.	(c) Allow the extract on top of the column to penetrate the florisil. The meniscus should be kept just level with the surface of the bed. Add a small amount of the eluant (about 0.5 ml) to the column and allow this to penetrate the florisil as above. Add a further 0.5 ml and repeat the procedure above. Add the remaining 49 mls of eluant at the rate of 1–2 ml/min.
8.3	**Concentration**	
	Concentrate the eluant to approximately 2.5 ml using the 305 mm column and flask with the smaller column (165 mm), and continue concentration to a volume of 0.3–0.5 ml. Transfer the concentrate to a 1 ml vial using a Pasteur pipette.	
	The procedure for the Kuderna–Danish apparatus is as follows:	
	Rinse the larger and small columns with a small volume of pentane immediately before use. Place the apparatus in a water bath as depicted	

Step	Procedure	Notes
	in Fig. 2a. (A boiling chip must be used). The temperature of the water must be 45°C ± 3°C. This temperature produces an optimum reflux rate for the eluate (note (d)). After concentration to approximately 2.5 ml the Kuderna–Danish apparatus *must* be cooled. Run cold water over the concentrator tube and flask, (this condenses the solvent vapour, rinsing out the flask into the concentrator tube). Dry the outside of the apparatus with a paper towel. Remove the 250 ml flask swiftly, add a further boiling chip and connect the small column to the concentrator tube. Place the apparatus in the water bath as depicted in Fig. 2b. Proceed with final volume reduction.	(d) The balls in the column should chatter without flooding.
	Rinse the walls of the concentrator tube with 0.5 ml ± 0.1 ml of pentane and transfer the rinsings to the vial using a pasteur pipette. Adjust the volume of the concentrate to 1 ml ± 0.5 ml by either carefully concentrating (note (e)) to 1 ml by means of an oxygen-free nitrogen jet (see section 6.1.11), or, making up to 1 ml by the addition of pentane. Seal the vial with a PTFE faced septum cap.	(e) Do not concentrate to dryness.
8.4	**Blank Determination**	
	Analyse blanks with each batch of samples (see section 8.5). Carry out steps 8.1 and 8.3 but substitute cleaned water (see section 5.1) for the sample.	
8.5	**Calibration Curve**	
	A calibration curve must be constructed with each batch of samples. In order to analyse a reasonable number of samples in one batch, the determinations must be carried out over 2 days. This necessitates the construction of a calibration curve over 2 days to minimize any variance in the curve. The procedure is as follows:	

Day 1	**Day 2**
Blank (B_1)	Blank (B_2)
Calibration Standard 1 μg/l (C_1)	Calibration Standard 5 μg/l (C_5)
Calibration Standard 10 μg/l (C_{10})	Calibration Standard 20 μg/l (C_{20})
Sample 1 (S_1)	Sample 2 (S_2)

NB. A batch is that number of samples over which time the calibration curve holds constant. In the evaluation of this method, it was shown that the stability of the calibration curve was relatively short. The curve was therefore constructed during the time that the samples

Step	Procedure	Notes

were being analysed. This necessitated a 2-day batch period. Other procedures may be possible depending on the number of samples. At a minimum though, a standard must be run with each group of samples. The performance characteristics reported would then be irrelevant and would have to be recalculated for the new procedure.

To each of a series of 1000 ml ± 1 ml of water (see section 5.1) in 1000 ml glass-stoppered bottles add the acetone standards (see section 5.4) as follows:

Vol. of Spiking Solution Added (μl)	Syringe Volume (μl)	Concentration of Individual Hydrocarbons in Water (μg/l)	Concentration of Total Hydrocarbons in Water (μg/l)
1	5	1	10
5	20	5	50
10	20	10	100
20	20	20	200

Add the concentrate just below the surface of the water, stopper the bottle and shake vigorously for 2 min. Submit each calibration standard immediately to the procedure outlined in steps 8.1–8.4 inclusive (note (g)).

Such standards should be prepared immediately prior to extraction to prevent losses due to volatization into the headspace.

(g) As the calibration standards are made up to 1000 ml, it is not necessary to weigh the solutions.

8.6 **Gas Chromatography**

Set up the instrument according to manufacturer's instructions (see section 6.3). Set the integrator so as to commence immediately prior to elution of benzene in the standard (note (h)). Retention time, peak area, and total peak area must be recorded.

(h) The integration is started about 20 sec before the elution of benzene.

Hydrogen and air flows for the FID detector, and carrier gas flows, must remain the same for every GC run.

8.6.1 On Day 1 run blank, calibration standards (C_1, C_{10}) and samples (note (i)), and record the information indicated in section 8.6 using the integrator (note (j)).

(i) The injection volume is typically 2 μl for all extracts.

On Day 2 run blank, calibration standards (C_5, C_{20}) and samples, and record the same information.

(j) Due to the use of an integrator the GC attenuation is the same for all runs.

8.7 **Calibration of results (note (k))**

(a) Calibration Curve

The total peak area (TPA) is recorded for each standard and a plot of: (C_{1TPA}–B_{1TPA}),

(k) This calculation assumes a linear calibration curve. Linearity must be checked (see section 9).

Step	Procedure	Notes
	$(C_{10TPA}-B_{1TPA})$, $(C_{5TPA}-B_{2TPA})$, $(C_{20TPA}-B_{2TPA})$ against total concentration of hydrocarbon is constructed.	
	(b) Total Detected Hydrocarbons	(1) For practical purposes $1000\,g = 1000\,ml$
	Total hydrocarbons are determined as follows (note (1))	
	$$S_{TPA} - B_{TPA} \times \frac{1000}{W_1 - W_2} \frac{\mu g/l}{(g)}$$	
	where S (sample) and B (blank) are determined on the same day. The concentration, in $\mu g/l$, is read from the calibration curve.	
	(c) Individual Hydrocarbons	
	The determination of individual hydrocarbons depends on whether or not their identity is known. If the individual substances are unknown then a calibration curve based upon average standard response is plotted—concentration of individual hydrocarbons against average response e.g.	
	$$\frac{\text{Total Peak Area (Standard)}}{\text{Number of Standard Hydrocarbons (10)}}$$	
	Then,	
	$$S_{PA} - B_{PA} \times \frac{1000}{W_1 - W_2} \frac{\mu g/l}{(g)}$$	
	where PA—Individual Peak Area—is calculated and the concentration, in $\mu g/l$, read from the calibration curve.	
	If the hydrocarbon is known and in the standard, then the appropriate calibration curve can be plotted, e.g. for benzene $(C_{1BPA} - B_{1BPA})$, $(C_{10BPA} - B_{1BPA})$, $(C_{5BPA} - B_{2BPA})$, $(C_{20BPA} - B_{2BPA})$ against concentration of individual hydrocarbons.	
	where BPA = Peak area for benzene.	
	Then	
	$$S_{BPA} - B_{BPA} \times \frac{1000}{W_1 - W_2} \frac{\mu g/l}{(g)}$$	
	is calculated and the concentration, in $\mu g/l$, is read from the calibration curve.	
	If the hydrocarbon is known and not in the standard then a more appropriate standard can be made.	
8.7.1	**Correction for interferences**	
	The main interferences are likely to be halogenated hydrocarbons and in particular	

Step	Procedure	Notes
	those specified in section 3. Allowance for these interferences can be approached in the following way: The response (peak area/weight injected) and the retention time of these specified substances can be determined under the same GC-FID conditions. The potential presence of these compounds can be determined from the sample chromatogram (see 8.6.1) and the degree is unsatisfactory, e.g. greater than 10% of the total estimated hydrocarbons, then either of the following steps can be taken. (a) These specified substances can be estimated using a duplicate sample of the solvent extracts produced in this method, using the SCA method for trihalomethanes (1). A correction for the response is needed. (b) The solvent extracts produced in the method are readily amenable to gas chromatography-mass spectrometry (GC-MS) Analysis of the solvent extracts using a system with similar GC conditions enables the specified substances (and other non-hydrocarbons) to be identified and discounted from the total or individual peak areas as appropriate. GC-MS also enables identification of individual peak areas as appropriate. GC-MS also enables identification of individual hydrocarbons which then permits more accurate estimation by use of actual standards. Solvent extracts also permit the use of internal standards if desired.	

9. Checking the Linearity of the Calibration Curve

Refer to step 8.5. This procedure must be carried out on at least two independent occasions before application of the method to samples, and regularly thereafter.

10. Sources of Error

10.1 Contamination The analysis must be carried out in an environment sufficiently free of hydrocarbons. Hydrocarbons are very common constituents of various commercial products, such as paints solvents, adhesives and also the prime constituents of gasolines, fuel oils and petroleum products in general. They are also natural products and common atmospheric pollutants. Therefore constant checks (blank determinations) are essential.

10.2 Interfering substances See section 3. The effect of potential interfering substances can be studied by analysing samples spiked with hydrocarbons and various concentrations of the interfering substances. The degree of interference will depend on the nature and complexity of the hydrocarbons and the gas chromatographic system employed.

10.3 Volatility Hydrocarbons cover the whole spectrum of volatility. This method covers very volatile substances. Loss of very volatile hydrocarbons is possible if the procedures to minimize losses from the headspace above the samples are not followed. The use of the Kuderna-Danish evaporator is paramount in this respect.

11. Checking the Validity of Analytical Results

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of the reference hydrocarbons of suitable

concentration should be analysed at the same way as normal samples and calibration standards (see section 5.4 and step 8.5). The result obtained should then be plotted on the calibration curve, which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

Table 2 Retention Times, Relative to Toluene, of Potential Interfering Halogenated Hydrocarbons in Comparison to the Ten Hydrocarbons Used in the Standard Solution

Column: 50 meter BPl (equivalent to SE30 and OVl) Silica, WCOT, 0.20 mm I.D., 0.32 mm O.D., 0.25 um film.
(SGE Ltd., UK).

Hydrocarbon	Relative Retention Time	Halogenated Hydrocarbon	Relative Retention Time
Benzene	0.77	1,1,1-Trichloroethane	0.73
Heptane	0.88	Trichloroethylene	0.85
Toluene	1.00	Bromodichloromethane	0.85
Octane	1.09	Chlorodibromomethane	1.04
Ethyl Benzene	1.20	Tetrachloroethylene	1.14
Iso-propyl Benzene	1.32	Tribromomethane	1.22
Decane	1.47		
Naphthalene	1.78		
Tetradecane	2.09		
Phenanthrene	2.63		

Halogenated Hydrocarbon Solvents in Water 1985

A. Halogenated Solvents and Haloforms in Water Using a Static Headspace Technique

A1. Performance Characteristics of the Method (see Ref 2)

A1.1	Substances determined	Volatile halogenated solvents
A1.2	Types of sample	Drinking and river waters
A1.3	Basis of method	Equilibration of the sample with its headspace vapour under controlled conditions. Injection of sample of the vapour into a gas chromatograph fitted with an electron capture detector.
A1.4	Range of application calibration curve	The range of linearity depends on the detector and instrument in use. The range can be extended by injecting a smaller sample or by using the non-linear portion of the calibration curve.

Compound	Linear range μg/l	Useable range μg/l
1,1-dichloroethylene	0–15	0–80
1,1,1-trichloroethane	0–20	0–80
1,1,2-trichloroethane	0–15	0–50
tetrachloroethylene	0–10	0–20
1,1,1,2-tetrachloroethane	0–80	0–150
1,1,2,2-tetrachloroethane	0–50	0–100
carbon tetrachloride	0–5	0–15
trichloroethylene	0–20	0–80
chloroform	0–100	0–120+
bromodichloromethane	0–50	0–120+
dibromochloromethane	0–50	0–120+
bromoform	0–50	0–120+
pentachloroethane	0–10	0–40

A1.5	Standard deviation	See Table 3
A1.6	Limits of detection	

Compound	Limit of Detection μg/l
1,1-dichloroethylene	0.60
1,1,1-trichloroethane	0.60
1,1,2-trichloroethane	2.0
tetrachloroethylene	1.6
1,1,1,2-tetrachloroethane	0.57
1,1,2,2-tetrachloroethane	0.53
carbon tetrachloride	0.13
trichloroethylene	1.0
chloroform	0.66
bromodichloromethane	1.1
dibromochloromethane	0.45
bromoform	0.70
pentachloroethane	0.76

A1.7	Sensitivity	Dependent on the instrument in use. In these tests, to give a 50% FSD peak with a 0.5% baseline fluctuation the following approximate concentrations were required:

Compound	Sensitivity µg/l, for 50% FSD
1,1-dichloroethylene	2
1,1,1-trichloroethane	1
1,1,2-trichloroethane	3
tetrachloroethylene	0.4
1,1,1,2-tetrachloroethane	2.5
1,1,2,2-tetrachloroethane	5
carbon tetrachloride	0.2
trichloroethylene	5
chloroform	5
bromodichloromethane	1.5
dibromochloromethane	2
bromoform	10
pentachloroethane	3

A1.8	Bias	Contamination of the vials or syringe with commonly used solvents will lead to systematically high results.
A1.9	Interferences	Any compound which has a similar retention time to the determinand and which gives a detector response will interfere.
A1.10	Time required for analysis	Assuming that all the components sought will separate satisfactorily on a single column and that standards have been prepared 10 samples can be analysed in 4h.

A2. Principle

The sample is placed in a septum vial and allowed to equilibrate with its headspace vapour at 25°C. A sample of the vapour is injected with a gas-tight syringe into a packed column gas chromatograph fitted with an electron capture detector.

A3. Interferences and Contamination

Any compound which has a similar retention time to the determinand and which gives a detector response will interfere. Some of the determinands do not completely separate on a single GC column and the use of two or more columns is usually necessary.

Many laboratory atmospheres contain traces of chlorinated solvents (particularly chloroform and carbon tetrachloride) which give rise to high blank values. In these circumstances the samples can be taken directly into the sample vials or poured from the sample bottles in a nitrogen filled glove box. If circumstances permit, the samples may be poured in the open air, outside the laboratory. Syringes may also show a memory effect and it is necessary to move the plunger in and out in a contamination free atmosphere until the syringe is free from contaminants. Normally twelve times is sufficient.

The bottles of pure compounds should not be opened in the same laboratory as that in which the analyses are performed.

A4. Hazards

The pure compounds are toxic and narcotic. Several are suspected carcinogens. Acetone is flammable.

A5. Apparatus and Reagents

A5.1 Sampling vials: 30 ml glass screw capped tubes fitted with a Teflon-faced silicone rubber septum cap. (Pierce Chemical Company).

A5.2 Syringe: 1 ml pressure-lock gas tight syringe fitted with an open/close valve. (Dynatech Precision Sampling Corporation).

A5.3 Water bath: Capable of being maintained at 25 ± 0.2°C.

A5.4 Gas chromatograph: Packed column instrument operated isothermally and fitted with an electron capture detector.

Some suitable columns are:

1. 7 ft × ¼ inch glass column packed with 5% OV1 on AW DCMS treated Chromosorb W 100–120 mesh.
2. A similar column supporting OV7.
3. A similar column supporting Carbowax 20M.

The oven temperature is maintained between 30°C and 100°C depending upon the column and the compounds sought.

A6. Standards

A6.1 Stock solutions: Stock solutions of 5–20 mg/l of individual compounds are prepared in acetone using syringes after correcting for the density of each compound. These solutions are normally stable for up to two weeks if stored in a spark-proof refrigerator.

A6.2 Working standards: Inject appropriate quantities of the stock solutions into 20 ml of solvent-free water in a septum vial using microlitre syringes. Blanks are prepared by injecting the same volumes of acetone only. Standards must be freshly prepared with each batch of samples.

A7. Sample Storage and Preservation

Samples are unstable and should be analysed as soon as possible after receipt. If immediate analysis is impossible satisfactory results can be obtained if the samples are stored in a refrigerator for up to 24h.

A8. Analytical Procedure

Step	Procedure	Notes
A8.1	**Preparation of sample**	
A8.1.1	The sample (20 ml) is carefully poured into a septum vial avoiding turbulence and tightly sealed. Shake for 1 min.	(a) See notes on contamination, (Section A3).
A8.1.2	Place the vial in a water bath maintained at 25±0.2°C for 1–4h.	
A8.1.3	Prepare a range of standards and blanks by spiking, (Section A6) and place these in the water bath for the same time.	
A8.2	**Injection of samples**	
A8.2.1	Using a gas-tight syringe (A5.2), pierce the cap of the vial and withdraw 0.5 ml of the headspace vapour over a period of 15s. (Note (b)).	(b) It is not necessary to compensate for the removed vapour.
A8.2.2	As the syringe is withdrawn close the syringe exit valve. Depress the plunger until the gas volume is 0.05 ml.	
A8.3	**Chromatography**	
A8.3.1	Push the syringe through the chromatograph septum. Release the contents of the syringe by opening the valve and pushing the plunger fully home. (Note (c)).	(c) This procedure ensures minimum spreading of the peak.
A8.3.2	Repeat the preceding steps with the blanks and standards.	
A8.3.3	Plot a calibration graph of the concentration of standard injected versus peak height or peak area. (Note (d)).	(d) An integrator may be used.

Step	Procedure	Notes
A8.4	Calculation	
A8.4.1	From the calibration graph read off directly the concentration of the determinand in the sample.	

Table 3 Means and estimates of standard deviations

Compound	Spike µg/l	Water	Mean µg/l	S_W	S_b	S_t	Recovery %
1,1-dichloroethylene	1	Dist	1.0	0.13(5)	n.s.	0.21(6)	—
		Tap	1.24	0.16(5)	0.37(4)	0.40(5)	124
		River	1.07	0.17(5)	n.s.	0.22(7)	107
	10	Dist	10.0	0.63(5)	2.1 (4)	2.2 (4)	—
		Tap	7.84	0.21(5)	0.69(4)	0.71(4)	78
		River	8.03	2.3 (5)	n.s.	2.5 (9)	80
1,1,1-trichloroethane	1	Dist	1.0	0.13(5)	n.s.	0.17(7)	—
		Tap	1.04	0.05(5)	0.08(4)	0.09(5)	104
		River	1.07	0.10(5)	0 (4)	0.10(7)	107
	10	Dist	10.0	0.26(5)	0 (4)	0.26(7)	—
		Tap	10.8	0.33(5)	0.66(4)	0.74(5)	108
		River	9.8	0.47(5)	0 (4)	0.47(7)	98
1,1,2-trichloroethane	1	Dist	1.0	0.43(5)	n.s.	0.43	—
		Tap	1.02	0.21(5)	0.51(4)	0.55(5)	102
		River	0.76	0.09(5)	0.39(7)	0.40(4)	76
	10	Dist	10.0	1.26(5)	n.s.	1.61(7)	—
		Tap	7.57	0.37(5)	1.31(4)	1.36(4)	76
		River	9.01	2.22(5)	n.s.	3.88(6)	90
tetrachloroethylene	1	Dist	1.0	0.17(5)	0.28(4)	0.33(5)	—
		Tap	1.01	0.16(5)	0.31(4)	0.35(5)	101
		River	1.03	0.24(5)	n.s.	0.26(9)	103
	10	Dist	10.0	1.42(5)	n.s.	1.46(9)	—
		Tap	8.06	0.65(5)	1.89(4)	2.00(4)	81
		River	9.67	0.64(5)	1.55(4)	1.67(9)	97
1,1,1,2-tetrachloroethane	1	Dist	1.0	0.10(5)	n.s.	0.13(8)	—
		Tap	0.96	0.12(5)	n.s.	0.17(7)	96
		River	1.15	0.08(5)	n.s.	0.11(7)	115
	10	Dist	10.0	0.52(5)	0.78(4)	0.93(5)	—
		Tap	9.86	0.81(5)	n.s.	1.24(6)	99
		River	9.60	0.88(5)	1.32(4)	1.59(5)	98
1,1,2,2-tetrachloroethane	1	Dist	1.0	0.10(5)	n.s.	0.11(8)	—
		Tap	0.98	0.08(5)	n.s.	0.12(7)	98
		River	0.96	0.07(5)	n.s.	0.08(8)	96
	10	Dist	10.0	0.87(5)	n.s.	1.24(6)	—
		Tap	10.2	0.90(5)	1.31(4)	1.59(6)	102
		River	11.2	0.41(5)	0.92(4)	1.01(5)	112
carbon tetrachloride	1	Dist	1.0	0.01(5)	0.02(4)	0.03(5)	—
		Tap	1.06	0.07(5)	0 (4)	0.07(7)	106
		River	0.98	0.02(5)	0.05(4)	0.05(4)	98
	10	Dist	10.0	1.06(5)	n.s.	0.11(6)	—
		Tap	10.4	0.04(5)	0.12(4)	0.13(5)	104
		River	10.4	0.19(5)	0 (4)	0.19(9)	104
trichloroethylene	1	Dist	1.0	0.17(5)	0.19(4)	0.22(5)	—
		Tap	1.21	0.11(5)	0.22(4)	0.25(5)	121
		River	1.03	0.11(5)	0.17(4)	0.20(5)	86
	10	Dist	10.0	1.21(5)	n.s.	1.45(8)	—
		Tap	9.12	0.58(5)	n.s.	1.01(6)	91
		River	11.8	0.89(5)	2.46(4)	2.61(4)	118

Table 3 *(continued)*

Compound	Spike µg/l	Water	Mean µg/l	S_W	S_b	S_t	Recovery %
chloroform	1	Dist	1.0	0.12(5)	n.s.	0.14(7)	—
		Tap	0.87	0.07(5)	n.s.	0.08(9)	87
		River	1.05	0.10(5)	n.s.	0.18(6)	105
	10	Dist	10.0	0.43(5)	0.75(4)	0.86(5)	—
		Tap	9.23	0.79(5)	n.s.	1.10(7)	92
		River	10.5	0.55(5)	1.42(4)	1.51(5)	105
bromodichloroethane	1	Dist	1.0	0.09(5)	0.22(4)	0.24(5)	—
		Tap	0.86	0.05(5)	0.13(4)	0.14(5)	86
		River	0.83	0.11(5)	n.s.	0.16(6)	83
	10	Dist	10.0	0.04(5)	1.72(4)	1.83(5)	—
		Tap	9.39	0.69(5)	n.s.	1.18(6)	93
		River	8.99	1.01(5)	n.s.	1.13(8)	90
dibromochloroethane	1	Dist	1.0	0.07(5)	n.s.	0.10(8)	—
		Tap	0.83	0.09(5)	0.15(4)	0.18(5)	83
		River	0.57	0.09(5)	0 (4)	0.09(9)	57
	10	Dist	10.0	0.41(5)	n.s.	0.45(8)	—
		Tap	11.2	0.29(5)	0.57(4)	0.64(5)	112
		River	9.77	0.61(5)	n.s.	0.61(9)	98
bromoform	1	Dist	1.0	0.08(5)	0.15(4)	0.17(5)	—
		Tap	0.84	0.06(5)	n.s.	0.08(7)	84
		River	1.05	0.05(5)	0.09(4)	0.10(5)	105
	10	Dist	10.0	1.36(5)	n.s.	0.54(6)	—
		Tap	10.9	0.57(5)	0.84(4)	1.01(5)	109
		River	11.3	0.87(5)	0 (4)	0.87(8)	113
pentachloroethane	1	Dist	1.0	0.15(5)	n.s.	0.16(8)	—
		Tap	0.82	0.13(5)	n.s.	0.14(9)	82
		River	1.04	0.14(5)	0.20(4)	0.24(5)	104
	10	Dist	10.0	0.90(5)	1.55(4)	1.79(5)	—
		Tap	9.60	0.34(5)	1.90(4)	1.93(4)	96
		River	9.31	0.40	1.87(4)	1.91(4)	93

n.s. — not significant

Note: Other volatile chlorinated hydrocarbons can also be determined by this method. If there are unidentified peaks or if such less common substances are suspected, users should evaluate the method using synthetic and spiked samples containing substances of interest.

B. Halogenated Solvents in Water by Pentane Extraction, Electron Capture Gas Chromatography

B1. Performance Characteristics of the Method (see Ref 2)

B1.1	Substances determined	1,1-dichloroethylene 1,2-dichloroethane (poor sensitivity) Chloroform (trichloromethane) Bromodichloromethane Dibromochloromethane Bromoform (tribromomethane) Carbon tetrachloride Trichloroethylene Tetrachloroethylene 1,1,1-trichloroethane 1,1,2-trichloroethane 1,1,1,2-tetrachloroethane 1,1,2,2-tetrachloroethane Pentachloroethane Dichloromethane (very poor sensitivity)
B1.2	Type of sample	Waters abstracted for potable supply and potable waters.
B1.3	Basis of method	Extraction into petroleum ether (b.p. 30–40°C) followed by gas chromatography with electron capture detection.
B1.4	Range of application	See Table 9.
B1.5	Calibration curve (a)	Range of linearity depends on the detector used. The slightly curved section of the calibration may be used provided the curve is determined.
B1.6	Total standard deviation	See Tables 4–7.
B1.7	Limits of detection	See Table 8.
B1.8	Sensitivity	See Table 9.
B1.9	Bias	Mean recoveries are given in Table 10.
B1.10	Interferences	Any electron-capturing material which passes through the procedure and has similar gas chromatographic characteristics to the determinand (See Section B3).
B1.11	Time required for analysis	Time for batches of 10 samples including time for preparation of reagents and apparatus, 1 man-day.

Table 4 Standard Deviations of Distilled Waters Plus Low Spike

Compound	Spike Level μg/l	Mean conc found	Standard Deviation μg/l Sw	Sb	St	St%	Degrees of Freedom
1,1-dichloroethylene	2.00	2.24	0.042	0.117	0.124	5.6	4.5
1,1,1-trichloroethane	0.500	0.475	0.035	n.s.	0.037	7.9	8.6
1,1,2-trichloroethane	10.00	8.73	0.576	n.s.	0.576	6.6	8.5
tetrachloroethylene	0.500	0.635	0.027	0.068	0.074	11.6	4.6
1,1,1,2-tetrachloroethane	0.500	0.407	0.014	0.030	0.033	8.1	4.8

Table 4 *(continued)*

Compound	Spike Level µg/l	Mean conc found	Standard µg/l Sw	Deviation Sb	St	St%	Degrees of Freedom
1,1,2,2-tetrachloroethane	2.00	1.79	0.079	0.134	0.156	8.7	5.2
carbon tetrachloride	0.250	0.197	0.008	0.022	0.023	11.7	4.5
trichloroethylene	0.500	0.481	0.017	0.047	0.049	10.3	4.5
chloroform	2.50	2.12	0.085	n.s.	0.129	6.1	6.2
bromodichloromethane	2.50	1.80	n.s.	0.112	0.112	6.2	4.0
dibromochloromethane	2.50	1.80	n.s.	0.113	0.113	1.8	4.0
bromoform	2.50	2.24	0.031	0.177	0.180	8.0	4.1
pentachloroethane	0.500	0.212	0.014	0.085	0.086	40.4	4.1

Table 5 Standard Deviations of Distilled Waters Plus High Spike

Compound	Spike Level µg/l	Mean conc found	Standard µg/l Sw	Deviation Sb	St	St%	Degrees of Freedom
1,1-dichloroethylene	20.0	18.4	0.41	n.s.	0.44	2.4	8.5
1,1,1-trichloroethane	5.00	4.69	0.076	n.s.	0.140	2.2	6.8
1,1,2-trichloroethane	100.0	78.0	2.09	n.s.	2.09	2.7	8.7
tetrachloroethylene	5.00	5.22	0.079	0.143	0.163	3.1	5.0
1,1,1,2-tetrachloroethane	5.00	4.84	0.079	n.s.	0.089	1.8	8.1
1,1,2,2-tetrachloroethane	20.0	17.3	0.50	n.s.	0.50	2.9	9.0
carbon tetrachloride	2.50	2.52	0.019	0.072	0.074	3.0	4.3
trichloroethylene	5.00	4.92	0.050	0.180	0.187	3.8	4.3
chloroform	25.0	19.4	0.49	0.76	0.91	4.7	5.4
bromodichloromethane	25.0	21.2	0.10	0.80	0.81	3.8	4.1
dibromochloromethane	25.0	22.1	0.21	0.79	0.81	3.7	4.3
bromoform	25.0	22.4	0.25	1.15	1.18	5.3	4.2
pentachloroethane	5.00	4.45	0.079	0.19	0.210	4.7	4.6

Table 6 Standard Deviations of Tap Water Plus Low Spike

Compound	Spike Level µg/l	Mean conc found	Standard µg/l Sw	Deviation Sb	St	St%	Degrees of Freedom
1,1-dichloroethylene	2.00	2.09	0.149	n.s.	0.165	7.9	8.3
1,1,1-trichloroethane	0.500	0.453	0.029	n.s.	0.041	9.1	6.4
1,1,2-trichloroethane	10.00	8.18	0.285	n.s.	0.285	3.5	7.6
tetrachloroethylene	0.500	0.600	0.011	0.066	0.067	11.2	4.1
1,1,1,2-tetrachloroethane	0.500	0.385	0.019	n.s.	0.028	7.2	6.5
1,1,2,2-tetrachloroethane	2.00	1.68	0.072	n.s.	0.107	6.4	6.3
carbon tetrachloride	0.250	0.200	0.000	0.018	0.018	8.8	4.0
chloroform	2.50	2.15	0.016	0.133	0.133	6.2	4.1
trichloroethylene	0.500	0.479	0.016	0.047	0.050	10.4	4.4
bromodichloromethane	2.50	1.85	0.012	n.s.	0.181	9.8	5.8
dibromochloromethane	2.50	1.80	n.s.	0.112	0.112	6.2	4.0
bromoform	2.50	2.26	n.s.	0.238	0.238	10.5	4.0
pentachloroethane	0.500	0.215	0.011	0.102	0.102	47.6	4.0

Table 7 Standard Deviations of Tap Waters Plus High Spike

Compound	Spike Level µg/l	Mean conc found	Standard µg/l Sw	Deviation Sb	St	St%	Degrees of Freedom
1,1-dichloroethylene	20.0	18.4	0.52	n.s.	0.68	3.7	7.0
1,1,1-trichloroethane	5.00	4.72	0.100	n.s.	0.107	2.3	8.5
1,1,2-trichloroethane	100.0	77.2	3.23	n.s.	3.23	4.2	8.7
tetrachloroethylene	5.00	5.26	0.065	0.168	0.180	3.4	4.6
1,1,1,2-tetrachloroethane	5.00	4.85	0.108	n.s.	0.108	2.2	8.5
1,1,2,2-tetrachloroethane	20.0	17.1	0.68	n.s.	0.68	4.0	9.0
carbon tetrachloride	2.50	2.53	0.036	0.072	0.081	3.2	4.9
trichloroethylene	5.00	4.89	0.065	0.193	0.203	4.2	4.4
chloroform	25.0	19.5	0.19	0.93	0.95	4.9	4.2
bromodichloromethane	25.0	21.1	0.33	0.65	0.73	3.4	4.9
dibromochloromethane	25.0	22.3	0.30	0.51	0.81	3.7	5.2
bromoform	25.0	22.2	0.48	1.03	1.14	5.1	4.8
pentachloroethane	5.00	4.47	0.093	0.144	0.172	3.8	5.4

Table 8 Limits of Detection

Note

Ten samples of distilled water were spiked with a low level of each compound and analysis performed on one day. Spiking levels were such as to give a small peak which could easily be distinguished from the baseline and which was larger than the noise filter level of the integrator. The results shown in Table were calculated as $2\sqrt{2}t\ S_w$. (Where t is the appropriate Tennant' constant). (9 degrees of freedom)

Compound	Limits of Detection µg/l
1,1-dichloroethylene	0.026
1,1,1-trichloroethane	0.007
1,1,2-trichloroethane	0.64
tetrachloroethylene	0.012
1,1,1,2-tetrachloroethane	0.005
1,1,2,2-tetrachloroethane	0.030
carbon tetrachloride	0.009
trichloroethylene	0.037
chloroform	0.19
bromodichloromethane	0.022
dibromochloromethane	0.018
bromoform	0.079
pentachloroethane	0.014

Table 9 Retention Times and Detector Sensitivities

Compound	Retention times (min) (Columns see section B6.3) OV-7	Quantity of Compound ng	% fsd at a baseline noise level of less than 0.5%
1,1-dichloroethylene	1.76	0.2	19
1,2-dichloroethane	4.04	5.0	25
1,1,1-trichloroethane	3.50	0.05	46
1,1,2-trichloroethane	8.07	1.0	41
tetrachloroethylene	8.71	0.05	53
1,1,1,2-tetrachloroethane	11.04	0.05	51
1,1,2,2-tetrachloroethane	14.23	0.2	43
carbon tetrachloride	3.83	0.01	20
trichloroethylene	4.93	0.02	9
chloroform	3.12	0.1	43
bromodichloromethane	5.60	0.1	121
dibromochloromethane	9.24	0.1	73
bromoform	13.54	0.1	27
pentachloroethane	16.70	0.05	53
dichloromethane	1.96	1.0	8

fsd is full scale deflection

Table 10 Mean Recoveries of Solvents from Spiked Solutions

	% Recovery			
	Distilled Water		Tap Water	
Compound	High	Low	High	Low
1,1-dichloroethylene	92	112	92.2	105
1,1,1-trichloroethane	94	95	94	91
1,1,2-trichloroethane	78	87	77	82
tetrachloroethylene	104	127	105	120
1,1,1,2-tetrachloroethane	97	81	97	77
1,1,2,2-tetrachloroethane	87	90	86	84
carbon tetrachloride	101	79	101	80
trichloroethylene	98	96	98	96
chloroform	78	85	78	86
bromodichloromethane	85	72	84	74
dibromochloromethane	88	72	89	72
bromoform	90	90	89	90
pentachloroethane	89	43	89	42

Test Data above by Anglian WA

B2. Principle

The halogenated solvents are extracted into an organic solvent. The solution is then examined by gas chromatography with electron capture detection.

B3. Interferences

Any other compound with similar retention times to the compounds sought, extractable from water by 30–40°C BP Petroleum Ether, that will record with an electron capture detector. Change of column type may occasionally alter potential interference effects.

B4. Hazards

Methanol is toxic and flammable. 30–40°C Petroleum ether is flammable, highly volatile and possibly narcotic. Appropriate precautions must be taken in their usage including the use of sparkproof refrigerators for the storage of solvents and solvent solutions. Halogenated solvents may be carcinogenic, they should be handled with extreme caution. Their vapours should not be inhaled and they should not be allowed to come into contact with the skin. All handling should be within a fume cupboard. Magnesium perchlorate is a powerful oxidizing agent and must not be allowed to come into contact with flammable materials.

Electron-capture detectors contain radioactive materials. They must be used strictly in accordance with the manufacturer's instructions.

B5. Reagents

All reagents must be of sufficient purity that they do not give rise to significant interfering peaks in the gas chromatographic analysis of the solvent extract. Purity must be checked for each batch of material by the running of procedural blanks with each batch of samples analysed.

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

B5.1 Water The Water used for blank determinations and preparation of standard solutions should have a chlorinated solvent content that is negligible in comparison with the smallest concentrations to be determined. This should be checked by analysis as in Section B8. Normally a blank water containing less than 0.1 μg/l of each trihalomethane will be satisfactory.

It is impossible to guarantee a suitable source of water, but usually distilled or deionized water is satisfactory. Further purification, if required, may be achieved by the procedures given below in Section B5.1.1 to B5.1.3. Some workers have avoided the use of solvent saturated water and/or used water of the same or similar composition to the sample. These measures have not normally proved necessary to achieve the performance given in Section one. However, such measures may be necessary for some samples and may be achieved by the use of the appropriate procedures below. Recontamination of water during storage can be a problem and stocks should be checked regularly.

B5.1.1 Activated Carbon Filtration Pass the water (distilled, deionized, tap or other source) through a column of granular activated carbon. The size contact time and life of the column required to give acceptable levels will vary with the level and type of solvents to be removed and the grade of carbon used.

B5.1.2 Solvent Extraction Extract the water (distilled, deionized, tap or other source) using the extraction solvent B5.2), a water to solvent ratio of 10:1 is usually satisfactory. Store under a layer of extraction solvent.

B5.1.3 Evaporation Boil the water (distilled, deionized, tap or other source) to 50% of its initial volume. Should a water of approximately the same composition as the sample be required this can be achieved by mixing the sample or a similar water and distilled or deionized water, both evaporated to 50% volume, in equal quantities.

B5.2 Extraction Solvent Petroleum ether b.p. 30 to 40°C. Analytical reagent grade is recommended.

Various grades of predominantly aliphatic hydrocarbon solvents have proved suitable for the extraction of halogenated solvents from water. The main criteria are that the solvent should give a suitable blank and separate from the halogenated solvents under the gas chromatographic conditions used. 60 to 80°C petroleum ether, 30 to 40° petroleum ether, hexane fraction from petroleum, n-hexane and n-pentane may be suitable but recoveries should be checked. Some batches of solvent may give satisfactory blanks as supplied, but most will need pre-treatment to reduce chloroform blanks.

This may be achieved using one of the following procedures, but both may be required for some batches of starting material.

B5.2.1 Redistillation The most effective system is redistillation through a fractionation column at least 500 mm in length, the lower half of which is packed with Potassium hydroxide pellets and the upper half with a fractionation column packing such as glass helices. If the original solvent contains greater than 30 μg/l chloroform then redistillation may not produce a satisfactory product.

B5.2.2 Adsorption Heat aluminium oxide (basic, column chromatography grade) mesh size 70 to 230, at 500 to 550°C for 2 to 3 hours. Cool to approximately 200°C in the furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or an equivalent alternative desiccant. Using a suitable chromatography column dry pack a column of adsorbent of approximate dimensions 400 mm long by 20 mm diameter using the heat-treated aluminium oxide. The contaminated solvent is passed down the column, the first 100 ml ± 20 ml of eluate being returned to the top of the column. The capacity of the column for solvent purification will depend on the degree of contamination of the feedstock, but normally 2.5 to 5 l of satisfactory solvent can be produced from one column.

The whole of the absorption procedure must be completed within a working day, and preferably without delay between steps. The heat-treated aluminium oxide can quickly pick up contaminants from the atmosphere. The aluminium oxide may be heat-treated for re-use after removal of all traces of solvent.

The solvent should be stored in glass-stoppered glass bottles in the dark in an environment sufficiently free from volatile halogenated compounds. Usually, it can be kept for at least one week without deterioration of quality.

B.5.3 Methanol (Analytical reagent grade) This must be checked by gas chromatography before use. It must contain less than 1.0 ng halogenated solvents per 1 ul.

B.5.4 Standard solutions in methanol

B5.4.1 Methanolic solution A (1 μg/ul) To approximately 10 ml of methanol in a 100 ml volumetric flask add the following volumes:
70.2 μl 1,1-dichloroethylene
79.6 μl 1,2-dichloroethane
67.0 μl chloroform (trichloromethane)
68.2 μl carbon tetrachloride
68.4 μl trichloroethylene
61.6 μl tetrachloroethylene
74.1 μl 1,1,1-trichloroethane

(Figures based on densities given in reference 3).
If a single syringe is used it must be scrupulously cleaned between additions.

Make up to the mark with methanol to give a solution containing 1 μg/ul of each substance.

For other substances, if required, prepare 100 ml of a solution containing 0.1 g/l of the substance, calculate the volume to be added from the density. Use of microlitre range syringes is recommended.

B5.4.2 Methanolic solution B (0.1 μg/ul) To about 5 ml of methanol in a 10 ml volumetric flask add 1 ml ± 0.01 ml of solution A. Make up to the mark with methanol. This solution contains 0.1 μg/ul.

These solutions are stable for at least 2 weeks when stored in the dark, in a refrigerator, in a tightly stoppered container.

B5.5 Sodium thiosulphate pentahydrate—Analytical Reagent Grade
B5.5.1 Sodium thiosulphate solution 3% w/v. Dissolve 46.0 ± 0.2 g sodium thiosulphate pentahydrate in 100 ± 5 ml water.

B6. Apparatus

All glassware used should be washed with detergent and then either cleaned with chromic

acid solution, rinsed with deionized water and finally the extraction solvent or heated in an oven at 350°C overnight and cooled before use.

All syringes must be thoroughly cleaned and checked by GC before use. A separate set of glassware and syringes should be used for each level of concentration of calibration standards.

B6.1 Extraction using a separating funnel

B6.1.1 Glass stoppered separating funnel 100 ml, glass tap (no grease) or PTFE tap.

B6.1.2 Pipettes 1 and 25 ml.

B6.1.3 Glass stoppered bottles 100 ml and 1,000 ml capacity.

B6.1.4 Syringes 1, 10 and 100 μg.

B6.1.5 Volumetric flasks, glass-stoppered 1,000 ml, 10 ml.

B6.1.6 Conical (Erlenmeyer) flask, glass stoppered 25 ml.

B6.2 Extraction using Septum Capped Vials

B6.2.1 Septum capped vials approx 25 ml capacity (available from Pierce Chemical Co or equivalent). Septa must be coated with PTFE where they contact the sample or solvent.

B6.2.2 Pipettes 1 and 25 ml.

B6.2.3 Glass stoppered bottles 1,000 ml.

B6.2.4 Syringes 1 μl, 10 μl, 100 μl, 5 ml.

B6.2.5 Hypodermic syringe needle 18 s.w.g.

B6.2.6 As B6.1.5.

B6.3 Gas Chromatography A gas chromatograph with electron capture detector is used. This should be operated in accordance with the manufacturer's instructions. Various columns are potentially suitable for the analysis. Glass columns with acid-washed, silane-treated supports have proved most useful and are recommended. Columns should have an efficiency of better than 2,500 theoretical plates. A typical set of conditions is given below for resolution from high concentrations of haloforms.

Column	6/45–3.2 m × 3 mm i.d. 10% OV7 on Diatomite GLQ (100–120 mesh)
Temperature	Injection: 150°C, Detection 300°C
Programme	85°C (4 mins) 4°C/min 140°C (2 mins)
Gases	Argon/methane (40 mls/min)
Attenuation	×32
Chart speed	0.5 cm/min
Injection vol	5 ul
Injection cycle	28 mins (+1.5 mins autosample)
Area reject	1,000
Slope sensitivity	1

For information on other columns see Table 11.

B7. Sample Collection and Preservation

B7.1 Separating funnel extraction The sample is collected in a large glass-stoppered glass bottle (at least 1 litre is recommended) by filling completely, discard this water, refill and stopper so as to leave no headspace. If not used immediately, store upside down at between 4 and 0°C. Do not freeze.

B7.2 Septum vial extraction The vial is completely filled with sample. This water is discarded and the vial re-filled to give a convex meniscus on its top. The septum is then

slid sideways across the top of the vial in such a manner as to leave no headspace in the container, the vial cap is then screwed down to form a seal.

B7.3 If further reaction between free chlorine and organic matter in the sample, to produce trihalogenated methanes, is to be eliminated; an excess of sodium thiosulphate must be added to the sampling bottle or vial after rinsing the bottle but prior to filling with sample. The quantity of sodium thiosulphate added to the sample is not critical but must be sufficient to react with all the chlorine present. Normally 0.1 to 0.2 ml of a 3% w/v solution will be appropriate. For samples taken in the field it is convenient to add two or three drops of the above solution or a few crystals of the solid (sufficient to cover a microspatula tip).

Samples so taken can be kept in the dark at ambient temperature in an environment sufficiently free from trihalogenated methanes for at least 24 hours prior to analysis.

B8. Analytical Procedure

Caution—BEFORE PROCEEDING WITH ANALYSES READ SECTION 4. HAZARDS AND SECTION B11.1 CONTAMINATION

Step	Procedure	Notes
	Extraction	
B8.1	Extract the sample using either procedure **B8.**1.1 or **B8.**1.2.	
B8.1.1	**Separating Funnel Extraction.**	
B8.1.1.1	Pour sufficient sample carefully into a large glass stoppered bottle. Stopper the bottle and weight W_1g. (Note (f)).	
B8.1.1.2	Pipette 10 ml of solvent into a 250 ml separating funnel (Notes (a) and (f)).	(a) The solvent should not be pipetted by mouth.
	Then add the sample. (Note (a)). Stopper the funnel and shake the mixture for 5 mins. Allow the layers to separate (Notes (c) and (f)).	(b) Typically this should take about 5 mins. With some raw waters a longer time maybe necessary.
	Run off the aqueous layer carefully, including any interfacial emulsion, and discard.	(c) If a considerable amount of interfacial emulsion forms it may be difficult to separate sufficient extract for analysis in such cases the emulsion may be broken by centrifugation. CAUTION. The solvent is volatile and flammable, a spark-proof centrifuge must be used. The sample should be capped to avoid losses.
	Collect the remaining solvent in a 25 ml conical (Erlenmeyer) flask and stopper (Notes (c), (d), (e) and (f)).	
B8.1.1.3	Weight the empty sample bottle W_2g. Hence obtain the amount of sample taken $(W_1 - W_2)$g. (See Note (s)).	(d) Extracts should be kept in the dark prior to GC analysis.
		(e) Solvent extracts are stable for at least two weeks when stored in the dark and solvent evaporation prevented.
		(f) Extraction may also be performed in the sample bottle. Typically 20 ml of sample is withdrawn from a sample bottle (PTFE stopper). 10 ml of solvent is then added to the bottle before shaking to extract. Performance data are not yet available.
B8.1.2	**Septum Vial Extraction** (Note (g)) The vial should be full of sample. Insert a hypodermic syringe needle, through the septum, a distance	(g) This method minimizes headspace losses and possible sample contamination during transport and storage; but for the

Step	Procedure	Notes
	of approximately 1 cm into the sample. Fill the 5 ml syringe (Note (h)) extracting solvent and adjust the volume to 2.5 ml excluding any air bubbles. Insert the syringe needle, with syringe containing solvent attached, through the septum, as far as possible into the vial. Invert the syringe plus vial (vial now above syringe) and inject the 2.5 ml of extraction solvent into the vial. 2.5 ml of sample will be displaced via the open syringe needle. Both needles are then withdrawn and the vial shaken vigorously for 5 minutes (Notes (i) and (j)). Allow the layers to separate (Note (c)). Aliquots of the solvent layer for gas chromatographic analysis may be withdrawn through the septum using the appropriate micro-syringe (Notes (k), (l) and (m)).	determination of low concentrations may require large vials. (h) Syringes of 3 to 5 ml capacity have proved satisfactory. (i) Due to the absence of headspace, mixing with this technique is less efficient than using a separating funnel. Recoveries may be a little lower but are acceptable and reproducible. (j) Vial septa may be reused after heat cleaning (see Section B6). However, care must be exercised and some operators use a septum only once. (k) Care must be taken to avoid including any water. (l) Extracts, with water present, have proved stable for at least one week when stored in the vials, in the dark, in a refrigerator. (m) This method relies on the volume of the vials (approx. 25 ml) being reproducible. This has proved so in practice. Nevertheless each vial should be checked and its volume noted for use in recovery checks (see Section B10).
	Blank determination	
B8.2	A blank must be analysed with each batch of samples. Step B8.1 is carried out but substituting water for the sample (see Section B5.1).	
	Calibration	
B8.3	Duplicate calibration standards must be run with each batch of determinations. (See also Note (r)). To 1,000 ml of water (Section B5.2) in a glass stoppered 1,000 ml bottle add 100 μl of methanol solution A with a 100 μl syringe. This is injected below the surface. The bottle is stoppered and shaken vigorously for 1 min. The concentration of each halogenated solvent is 10 μg/l. This solution is submitted to step B8.1.	
	Gas Chromatography	
B8.4	Set up the instrument according to manufacturer's instructions (see Section B6.3).	
B8.4.1	Run blank (Note (n)) and measure peak height (B_1) for each determinand peak. (Note (o)). (Set the instrument sensitivity to at least that required for measuring the smallest concentrations in the calibration range (see Section B9)).	(n) Injection volume will vary according to the instrument used but is typically 1 to 5 μl. (o) The addition of an internal standard to solvent extracts of blanks, samples and standards is favoured by some laboratories.

Step	Procedure	Notes
B8.4.2	Run calibration standards and determine peak heights (C_1 and C_2) for each halogenated solvent peak. (See also Notes (n), (o), (p)).	1, 2-dibromoethane, or 1, 2-dibromopropane have been used.
B8.4.3	Run samples and measure peak heights (S) for each determinand. (Note (q)).	
B8.4.4	To check for any instrument variation repeat steps B8.4.1 and B8.4.2 and determine corresponding peak heights B_2, C_3 and C_4.	
	Calculation of Results (Notes (p), (q) and (r)).	(p) This calculation assumes a linear calibration curve. Linearity must be checked (see Section B9).
B8.5	Calculate the concentration of each halogenated solvent in the sample as follows: $$\text{Concentration } \mu g/l = \frac{S-B}{C-B} \times 10\,\mu g/l$$	(q) If the halogenated solvent concentration in the sample is likely to exceed 10 μg/l an appropriate dilution of the final solvent extract (produced in step B8.1) with solvent is necessary and the calculations in B8.5 modified appropriately.
	N.B. Peak heights are converted to the same instrumental sensitivity where: $$C = \frac{C_1 + C_2 + C_3 + C_4}{4}$$ $$B = \frac{B_1 + B_2}{2}$$ (see Notes (r) and (s)).	(r) If the calibration curve is non linear at the found concentration, prepare a curve using a series of four or more standard samples as required, correcting for the blank value. Deduct the blank value from the sample reading and read off the concentration from the curve. See Section B9. (s) If the sample size differs from the calibration standard size, proportionate accordingly. See also Section B10 for recovery efficiency correction.

B9. Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter. (Frequency will depend on instrument stability, which must be checked).

To each of a series of 1,000 ml samples of water (Section 5.1) in 1,000 ml glass stoppered bottles add methanol concentrates A and B in the following manner:

	Methanol concentration	Syringe Vol	Concentration in water (μg/l)
methanolic solution A	100 μl	100 μl	10
methanolic solution A	50 μl	100 μl	5
methanolic solution A	100 μl	100 μl	1
methanolic solution B	50 μl	100 μl	0.5
methanolic solution B	10 μl	10 μl	0.1

The concentrate is added just below the surface of the water and then the bottle is stoppered and shaken vigorously for one minute.

Each standard solution is then submitted to the procedure outlined in steps B8.1 to B8.4 inclusive and a plot of peak height against μg/l halogenated solvent constructed using linear ordinates*. Each standard must be used on only one occasion. If it is allowed to stand with a headspace the concentrations will change. The calibration curve is normally linear to at least 10 μg/l halogenated solvent, however the linearity of the curve

will depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve departs from linearity, the calibration standard in step B8.3 is not appropriate, nor is the range given in Section B1.4. In such a case the calibration standard chosen for step B8.3 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly*. Alternatively a curve may be plotted and quality assurance samples included in each batch (See B8.5 Note (r)).

B10. Checking the Recovery of the Solvent Extraction Stage

Although the calibration procedure given in this method compensates for bias due to non-quantitative recovery at the solvent extraction stage, recoveries should preferably be greater than 80% in order to minimize errors. In practice recoveries varied with compound (see Table 9). Recovery may be checked as follows:

(i) Prepare a standard solution in water as given in Section B9. Analyse as in Section B8. Let the concentration found be X μg/l of an halogenated solvent.

(ii) Inject the same quantity of the same methanol solution as used in (i) above directly into the same quantity of extraction solvent as used in (i) above. Analyse as in Section B8.4.3 to B8.4.5 after mixing. Let the concentration found be Y μg/l.

(iii) $\text{Recovery} = 100 \dfrac{X}{Y} \%$

Care must be taken to ensure that the results, especially in step (ii), are within the linear range of the method.

B11. Sources of Error

B11.1 Contamination The analysis must be carried out in an environment as free as possible from volatile halogenated compounds. Since the quantities measured by the GC system are minute (down to 10^{-12}g) the effect of chlorinated substances (such as solvents) used or present in neighbouring laboratories can be overwhelming. Constant checks (blank determinations) are necessary. Chloroform was a constituent (percentage levels) of toothpaste, cough lozenges and medicines and no doubt on occasions this has led to contamination problems.

Care needs to be taken when using water for blank determinations. Tap water will normally contain trihalogenated methanes possibly at concentrations of over 100 μg/l. (See B5.1.1–B5.1.3).

B11.2 Interfering Substances See Section B3. The degree of interference will be dependent on the gas chromatographic system used.

B11.3 Volatility Halogenated solvents are volatile and of limited solubility in water. If a headspace is present over a solution in water then at equilibrium a significant loss of the determinands to the headspace will occur. The procedures in Section B8 have proved to give acceptably small losses but care in techniques must be exercised and volatility borne in mind. HEADSPACE LOSSES HAVE NOT PROVED A PROBLEM WITH SOLUTIONS OF HALOGENATED SOLVENTS IN OTHER ORGANIC SOLVENTS.

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* Log-log ordinates are often used to plot gas chromatography detector calibration graphs. A straight line on log-log ordinates does not necessarily mean linear response.

Table 11 Retention Times, Relative to Chloroform, or some Halogenated Hydrocarbons, on some Gas Chromatography Columns which have been used for their Analysis

Column and conditions / Compound	10% Squalane on 80–100 mesh chromosorb W. AW. 78°C N_2 flow 50 ml/min glass column 2.1 m long 4 mm i.d.	10% FFAP on Diatomite AW 100°C, N_2 flow 80 ml/min glass column 1.5 m long 4 mm i.d.	5% FFAP on 80–100 mesh Gas Chrom Q. 100°C N_2 flow 40 ml/min glass column 3 m long 3 mm i.d.	20% E301 on 60–80 mesh celite 545 100°C, N_2 flow 40 ml/min glass column 3.0 m long, 3 mm i.d.
Chloroform	1.00	1.00	1.00	1.00
Bromodichloromethane	1.96	2.40	2.0	2.14
Dibromochloromethane	4.04	5.33	4.18	4.00
Bromoform	8.36	11.67	8.82	7.36
Bromochloromethane	0.96	—	—	—
1,1,1-Trichloroethane	1.28	0.47	0.64	1.43
Carbon Tetrachloride	1.56	0.47	0.64	1.71
Tetrachloroethylene	5.32	1.13	1.18	4.93
Dichloromethane	—	0.53	—	0.43
Trichloroethylene	—	0.93	0.91	2.14
1,2-Dichloroethane	—	1.40	—	1.50
Bromotrichloromethane	—	—	1.36	—

OV101 and SE54 were not found suitable.
Capillary columns may also be used for some analyses.

References

(1) Chloro- and Bromo-Trihalogenated Methanes in Water 1980 HMSO, in this series.
(2) General Principles of Sampling and Accuracy of Results 1980 HMSO, in this series.
(3) Handbook of Physics and Chemistry. Chemical Rubber Co.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. At the present time, though based on work in several laboratories, thorough test data is not available, hence the tentative status of the method. Additional test data would be welcomed. Users with information on this method are requested to write to:

The Secretary
The DOE Standing Committee of Analysts
The Department of the Environment
43 Marsham Street
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