Chloro- and Bromo-Trihalogenated Methanes in Water 1980

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters and Associated Materials

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. Hence this method mentions the actual materials used for the evaluation tests. This in no way endorses these materials as superior to other similar materials. Equivalent materials are acceptable, though it must be understood that the performance characteristics may be different, and can vary with batch. It is left to the senior supervising analyst to evaluate and choose from the appropriate brands available.

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

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; and 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

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. It cannot be too strongly emphasised 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 radiochemical 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.

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. 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.

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About This Series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains 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, has 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 individual methods, 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 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 analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsiblity 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 one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine 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
2.0 Instrumentation and on-line ayalysis
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
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

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 for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. 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 the booklet.

T A DICK
Chairman

L R PITTWELL
Secretary

4 December 1980

Chloro and Bromo Trihalogenated Methanes in Water 1980

1 Performance Characteristics of the Method
(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results, also published in this series)

1.1	Substances determined	Chloroform (trichloremethane) Bromodichloromethane Dibromochloromethane Bromoform (tribromomethane)
1.2	Type of sample	Waters abstracted for potable supply and potable waters
1.3	Basis of method	Extraction into petroleum ether (b.p. 30-40°C) followed by gas chromatography with electron capture detection.
1.4	Range of application	Up to 100 μg/l of each trihalomethane.
1.5	Calibration curve (a)	Range of linearity depends on the detector used, typically Chloroform — linear up to 0.1 ng (100 μg/l) (b) Bromodichloromethane — linear up to 0.1 ng (100 μg/l) Dibromochloromethane — linear up to 0.1 ng (100 μg/l) Bromoform — linear up to 0.1 ng (100 μg/l)

(a) Results obtained at the Water Research Centre, Medmenham, England.
(b) Concentration figures in brackets assume a 1 μl injection into the gas chromatograph.

1.6 Total standard Deviation (c)

Trihalomethane	Standard Deviations of Standards in Distilled Water (μg/l)	
	Test Level	
	5 μg/l (4 degrees of freedom)	100 μg/l (4-9 degrees of freedom)
$CHCl_3$	0.2 to 0.8	0.9 to 12.3
$CHBrCl_2$	0.1 to 0.8	0.2 to 9.6
$CHBr_2Cl$	0.1 to 0.8	0.5 to 7.7
$CHBr_3$	0.1 to 1.1	1.2 to 8.6
Total Trihalomethanes (Sum of above)	0.5 to 2.6	0.4 to 40.4

Trihalomethane	Standard Deviation of Samples (μg/l) (4 degrees of freedom)			
	Upland Water		Lowland Water	
	Mean	Std Dev	Mean	Std Dev
$CHCl_3$	16.0	0.2 to 0.6	36.1	0.4 to 1.7
$CHBrCl_2$	3.02	0.03 to 0.9	30.4	0.4 to 3.2
$CHBr_2Cl$	0.49	0.01 to 0.4	21.9	0.3 to 1.7
$CHBr_3$	0.09	0.02 to 0.6	3.65	0.06 to 1.6
Total Trihalomethanes	18.7	0.2 to 1.3	89.2	0.9 to 3.9

1.7 Limits of Detection (c)

In the inter-laboratory exercise most blank values were returned as zero, due to the variability being less than the minimum discrimination used in the laboratory. Based on the non-zero figures returned, the following limits of detection were calculated (each with 5 degrees of freedom).

$CHCl_3$ 0.6 to 1.3 μg/l
$CHBrCl_2$ 0.04 to 0.7 μg/l
$CHBr_2Cl$ 0.2 to 1.1 μg/l
$CHBr_3$ 1.1 μg/l

The above figures tend to overestimate the limits of detection regularly achieved using the method. Where all zero figures were returned it can be argued that the minimum discrimination used by the laboratory represents a conservative estimate of the 95% confidence limits for the variability of blank values. Based on this premise the following limits of detection were calculated.

$CHCl_3$ 0.08 to 0.9 μg/l
$CHBrCl_2$ 0.06 to 0.5 μg/l
$CHBr_2Cl$ 0.03 to 1.2 μg/l
$CHBr_3$ 0.03 to 1.4 μg/l

(c) Results obtained in an inter-laboratory calibration exercise in which nineteen laboratories participated.

1.8 Sensitivity

Dependent on the detector used, but typically (d) 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%

$CHCl_3$	5 pg
$CHBrCl_2$	1.4 pg
$CHBr_2Cl$	3.3 pg
$CHBr_3$	12.5 pg

1.9 Bias (c)

In the interlaboratory test there was no evidence of bias in the analysis of a standard solution of the four trihalogenated methanes.

1.10 Inter-laboratory bias in the analysis of samples

In an inter-laboratory bias test (see footnote c) in which nineteen laboratories participated eleven laboratories used this method and eight laboratories similar methods involving solvent extraction and electron-capture gas chromatography. In some laboratories blanks, particularly for chloroform, were higher than recommended in the method (<1μg/l), these results were rejected in preparing the tables of results of the exercise given below. The results of the text are as given in the tables.

Difference between the mean value recorded by the laboratory and the mean of all laboratories (μg/l)
(5 results each laboratory)

Trihalomethane	Upland Water		Lowland Water		No. of laboratories
	Mean	Bias	Mean	Bias	
$CHCl_3$	16.0	−3.4 to +1.4	36.1	−3.9 to +5.3	4
$CHBrCl_2$	3.02	−1.57 to +1.69	30.4	−2.6 to +6.0	9
$CHBr_2Cl$	0.49	−0.48 to +0.46	21.9	−2.4 to +3.0	11
$CHBr_3$	0.09	−0.09 to +0.40	3.65	−1.4 to +0.2	10
Total Trihalomethanes	18.72	−4.0 to +2.4	89.20	−5.8 to +1.6	4

Maximum possible bias of the mean value recorded by the laboratory from the mean of all laboratories
(μg/l)
(4 degrees of freedom)

Trihalomethane	Upland Water		Lowland Water		No. of laboratories
	Mean	Bias	Mean	Bias	
$CHCl_3$	16.0	−3.9 to +1.7	36.1	−5.6 to +6.5	4
$CHBrCl_2$	3.02	−1.59 to +2.88	30.4	−3.7 to +6.4	9
$CHBr_2Cl$	0.49	−0.48 to +0.70	21.9	−3.7 to +3.4	11
$CHBr_3$	0.09	−0.09 to +0.40	3.65	−2.88 to +1.02	10
Total Trihalomethanes	18.72	−4.4 to +1.6	89.20	−7.9 to +5.5	4

(d) Anglian Water Authority Data using manual injection and manual processing of results.

1.11 Interferences

Any electron-capturing material which passes through the procedure and has similar gas chromatographic characteristics to the determinand (See Section 3).

1.12 Time required for Analysis (d)

(i) Minimum time to obtain a result from a sample received assuming all apparatus to be prepared, 30 min.

(ii) Time for batches of 10 samples including time for preparation of reagents and apparatus, 1 man-day.

2 Principle

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

3 Interferences

In theory, the many halogenated substances (e) commonly present in raw water are potential interferants. In practice, the concentrations of these substances seem to be sufficiently low (i.e. typically 1 μg/l (f)) not to interfere within the normal range of application of the method (1 to 100 μg/l). Some possible interferants have been identified (1 μg/l) these are:—

(trans) 1, 2 — dichloroethylene
trichloroethylene
dichloroacetonitrile
carbon tetrachloride
tetrachloroethylene
chlorobenzene

Dichloroiodomethane and bromochloroiodomethane have not been detected in raw water, but like other trihalogenated methanes, have been found in chlorinated water.

With a polar gas chromatographic column, such as that given in the method, and with a lower detection limit (1 μg/l), trichlorethylene could be an interference to chloroform in unchlorinated water where chloroform may occur at low concentration.

With a non-polar column system trichlorethylene and chloroform are adequately separated. However, the former could interfere with bromodichloromethane, and tetrachloroethylene with dibromochloromethane at 1 μg/l detection limits, especially in unchlorinated water. Chloroform elutes close to 1, 2 dichloroethylene.

Table 1 gives the retention times of the trihalomethanes and some potential interferants in their analysis, on a selection of gas chromatography columns.

4 Hazards

Methanol is toxic and flammable. 30–40° 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. Haloforms 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 oxidising agent and must not be allowed to come in contact with flammable materials.

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

(e) Water Research Centre data from gas chromatography — mass spectrometry

(f) Source: Survey of levels of trihalomethanes in UK potable waters and sources of potable water prior to treatment (1979 to 1981), carried out by Water Authorities at the request of the UK Department of the Environment.

5 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.

5.1 Water

The water used for blank determinations and preparation of standard solutions should have a trihalogenated methane content that is negligible in comparison with the smallest concentrations to be determined. This should be checked by analysis as in Section 8. Normally a blank water containing 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 procedure given below in Section 5.1.1 to 5.1.3. 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, where the data was derived from laboratories using all the water preparation methods in this section. 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.

5.1.1 *Activated Carbon Filtration*
Pass the water (distilled, deionized, tap or other source) through a column of granular activated carbon. The size and lifetime of the carbon will vary with the level of trihalogenated methanes to be removed and the grade of carbon used but a typical water treatment grade carbon (10 to 30 mesh) removed 100 μg/l total haloforms to acceptable levels from at least 100 bed-volumes of water using a contact time of 10 minutes.

5.1.2 *Solvent Extraction*
Extract the water (distilled, deionized, tap or other source) using the extraction solvent (5.2), a water to solvent ratio of 10:1 is usually satisfactory. Store under a layer of extraction solvent.

5.1.3 *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.

5.2 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 trihalomethanes from water. The main criteria are that the solvent should give a suitable blank (<1 μg $CHCl_3$/l solvent) and separate from chloroform under the gas chromatographic conditions used. 60 to 80°C petroleum ether, 30 to 40°C petroleum ether, hexane fraction from petroleum, n-hexane and n-pentane have all been used successfully (see note (c) p.2). 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.

5.2.1 *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 KOH pellets and the upper half with a fractionation column packing such as glass helices. If the original solvent contains <30 μg/l $CHCl_3$ then redistillation may not produce a satisfactory product.

5.2.2 *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 5l of satisfactory solvent can be produced from one column.

The whole of the adsorption procedure must be completed within a working day, and preferably without delay between steps. The heat-treated aluminium oxide can quickly pick up trihalomethane 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.

5.3 Methanol (Analytical reagent grade)

This must be checked by gas chromatography before use. It must contain <10 ng trihalogenated methanes/1 μl.

5.4 Standard Solutions in methanol

5.4.1 *Methanolic solution A*

To approximately 50 ml of methanol in a 100 ml volumetric flask add the following volumes:

chloroform	68 μl
bromodichloromethane	51 μl
dibromochloromethane	42 μl
bromoform	34 μl

(Figures based on densities given in reference 1). (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 (± 1.4%)/μl of each substance.

5.4.2 *Methanolic solution B*

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 (± 1.4%)/μl.

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

5.5 Sodium thiosulphate pentahydrate — Analytical Reagent Grade

5.5.1 Sodium thiosulphate solution 3% w/v. Dissolve 46 ± 0.2g sodium thiosulphate pentahydrate in 100 ± 5 ml water.

6 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.

6.1 Extraction using a separating funnel

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

6.1.2 *Pipettes*
1 and 25 ml.

6.1.3 *Glass stoppered bottles*
100 ml and 1000 ml capacity.

6.1.4 *Syringes*
1, 10 and 100 μl

6.1.5 *Volumetric flasks, glass-stoppered*
100 ml, 10 ml

6.1.6 *Conical (Erlenmeyer) flask, glass stoppered*
25 ml

6.2 Extraction using Septum Capped Vials

6.2.1 *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.

6.2.2 *as 6.1.2*

6.2.3 *Glass stoppered bottles*
1000 ml

6.2.4 *Syringes*
1 μl, 10 μl, 100 μl, 15 ml.

6.2.5 *Hypodermic syringe needle*
18 s.w.g.

6.2.6 *as 6.1.5*

6.3 Gas Chromatography

A gas chromatograph with electron capture detector. This should be operated in accordance with the manufacturer's instructions. Various columns are potentially suitable for the analysis. Glass columns of 1 to 3 metres in length packed with 5 to 10% of Carbowax 20 M or FFAP on 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 and the corresponding chromatogram in Figure 1.

Column	Glass 2.7 m × 6 mm OD, 3 mm ID; 5%FFAP on chromosorb HPW (100–120 mesh)
Detector oven temperature	350°C
Column oven temperature	100°C
Carrier gas	Nitrogen; 40 ml/min (Oxygen-free Nitrogen)
Chart speed	600 mm/hr
Injection volume	1 μl
Typical retention times (from injection)	*Min*
	Chloroform 1.5
	Bromodichloromethane 2.2
	Dibromochloromethane 3.8
	Bromoform 7.2

7 Sample Collection and Preservation

7.1 Separating funnel extraction

The sample is collected in a 100 ml glass-stoppered glass bottle by filling completely, discarding this water, refilling and stoppering so as to leave no headspace.

7.2 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.

7.3

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.

8 Analytical Procedure

CAUTION

BEFORE PROCEEDING WITH ANALYSES READ SECTION 4. HAZARDS AND SECTION 11.1 CONTAMINATION.

Step	Experimental Procedure	Notes
	Extraction	
8.1	Extract the sample using either procedure 8.1.1 or 8.1.2 below	
	Separating Funnel Extraction	
8.1.1	Pipette 25 ml of solvent into a 100 ml separating funnel (note a and b). Then add by pipette 25 ml of the sample (note a). Stopper the funnel and shake the mixture for 5 min. Allow the layers to separate (note c). Run off the aqueous layer carefully, including any interfacial emulsion, and discard. Collect the remaining solvent phase in a 25 ml conical (Erlenmeyer) flask and stopper (notes d, e and f).	(a) Neither the solvent nor the sample should be pipetted by mouth. (b) Sample to solvent ratios of up to 10 to 1 have given satisfactory results. Higher sample to solvent ratios can be useful if G.C. sensitivity is low or solvent blanks high. Recoveries should be checked. (c) Typically this should take about 5 min. With some raw waters a longer time may be necessary. (d) Extracts should be kept in the dark prior to GC analysis (e) Solvent extracts are stable for a 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 in a 50 ml glass bottle (PTFE stopper). 20 ml of solvent is then added to the bottle before shaking to extract. Perfomance data are not yet available.

Step	Experimental Procedure	Notes
	Septum Vial Extraction (note g)	
8.1.2	The vial should be full of sample. Insert a hypodermic syringe needle, through the septum, a distance of approximately 1 cm into the sample. Fill the 15 ml syringe (note h) with extracting solvent and adjust the volume to 10 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 10 ml of extraction solvent into the vial. 10 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).	(g) This method minimises headspace losses and possible sample contamination during transport and storage. (h) Syringes of 10 to 25 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 6). 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 10).
	Blank determination	
8.2	A blank must be analysed with each batch of samples. Step 8.1 is carried out but substituting water for the sample (see Section 5.1)	
	Calibration	
8.3	Duplicate calibration standards must be run with each batch of determinations. To 1000 ml of water (Section 5.2) in a glass stoppered 1000 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 trihalogenated methane is 100 μg/l. This solution is submitted to step 8.1.	
	Gas chromatography	
8.4	Set up the instrument according to manufacturer's instructions (see section 6.3).	
8.4.1	Run blank (note n) and determine peak height (B_1) for each trihalogenated methane peak. (Note o). (Set the instrument sensitivity to at least that required for measuring the smallest concentrations in the calibration range (see Section 9)).	(n) Injection volume will vary according to the instrument used but is typically 1 to 5 μl.
8.4.2	Run calibration standards and determine peak heights (C_1 and C_2) for each trihalogenated methane peak.	(o) The addition of an internal standard to solvent extracts of blanks, samples and standards is favoured by some laboratories. 1, 2-dibromo ethane, 1.2-dibromo propane and tetrachlorethylene have been used.
8.4.3	Run samples and determine peak heights (S) for each trihalogenated methane.	

Step	Experimental Prodecure	Notes

8.4.4 To check for any instrument variation repeat steps 8.4.1 and 8.4.2 and determine corresponding peak heights B_2, C_3 and C_4

Calculation of Results (notes p and q)

8.4.5 Calculate the concentration of each trihalogenated methane in sample as follows:

$$\text{Concentration (ug/l)} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 100\ \mu g/l$$

N.B. Peak heights are converted to the same instrumental sensitivity where

$$\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$$

$$\bar{B} = \frac{B_1 + B_2}{2}$$

(p) This calculation assumes a linear calibration curve. Linearity must be checked (see Section 9).
(q) If the trihalogenated methane concentration in the sample is likely to exceed 100 μg/l an appropriate dilution of the final solvent extract (produced in step 8.1) with solvent is necessary and the calculations in 8.4.5 modified appropriately.

8.4.6 The concentration of total trihalogenated methanes is calculated as the sum of the four individual compounds (note r).

(r) The concentrations of individual compounds must not be 'rounded off' nor should 'less than' figures be used. The calculated concentrations should be summed even if less than the limit of detection of the method.

9 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, this must be checked).

To each of a series of 1000 ml of water (Section 5.1) in 1000 ml glass stoppered bottles add methanol concentrates A and B in the following manner;

	Methanol concentration added	*Syringe Vol.*	*Concentration in water (ug/l)*
methanolic solution A	100 μl	100 μl	100
methanolic solution A	50 μl	100 μl	50
methanolic solution B	100 μl	100 μl	10
methanolic solution B	50 μl	100 μl	5
methanolic solution B	10 μl	10 μl	1

The concentrate is added just below the surface of the water and then the bottle is stoppered and shaken vigorously for 1 min.

Each standard solution is then submitted to the procedure outlined in steps 8.1–8.4 inclusive and a plot of peak height against μg/l trihalogenated methane constructed using linear ordinates.* Each standard must be used on only one occasion. If it is allowed to stand with a headspace the trihalomethane concentrations will change. The calibration curve is normally linear to at least 100 μg/l trihalogenated methane; 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 8.3 is not appropriate nor is the range given in section 1.4. In such a case the calibration standard chosen for step 8.3 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly.*

* 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.

10 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 of 82 to 104% were recorded (see footnote (c)). Recovery may be checked as follows:

(i) Prepare a standard solution in water as given in Section 9. Analyse as in Section 8. Let the concentration found be X μg/l of a trihalomethane.

(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 8.4.3 to 8.4.5, after mixing. Let the concentration found be Y ug/l of a trihalomethane.

(iii) Recovery $= \frac{X}{Y} \times 100\%$

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

11 Iodo Derivatives

Iodo-trihalogenated methanes have been detected in waters, especially dichloroiodomethane which can occur at higher concentrations than bromoform. These compounds can be detected and determined by this method; but the pure compounds are not readily available and standard solutions do not appear to be very stable. If their presence is suspected, it is suggested that small quantities be synthesized and used to calibrate the apparatus. A synthesis of dichloroiodomethane is given in reference [2], otherwise consult: Chemical Abstracts [3] and Beilstein [4].

12 Sources of Error

12.1 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. Tapwater will normally contain the substances to be determined, possibly at concentrations of over 100 μg/l.

12.2 Interfering substances

See Section 3. The effect of possible interfering substances may be determined by analysing samples spiked with trihalogenated methanes and various concentrations of the interfering substances. The degree of interference will be dependent on the gas chromatographic system used.

12.3 Volatility

Haloforms are volatile and of limited solubility in water. If a headspace is present over a solution of trihalomethanes in water then at equilibrium a significant loss of the determinands to the headspace will occur. The procedures in Section 8 have proved to give acceptably small losses of trihalomethanes, but care in techniques must be exercised and volatility borne in mind. HEADSPACE LOSSES HAVE NOT PROVED A PROBLEM WITH SOLUTIONS OF TRIHALOMETHANES IN ORGANIC SOLVENTS.

References

1 Water Research Centre, Medmenham. *Enquiry Report* No. 532, August 1977.

2 *Identification and Analysis of Organic Pollutants in Water*. Ed. L H Keith, p403 Ann Arbor, Ann Arbor, Michigan 1976.

3 *Chemical Abstracts*. American Chemical Society, Chemical Abstracts Service. Columbus, Ohio.

4 Beilstein, *Handbuch der Organischen Chemie*, Springer Verlag, Berlin.

TABLE 1. Retention times, relative to chloroform, of some halogenated hydrocarbons, on some gas chromatography columns which have been used for their analysis.

Compound \ Column and Conditions	10% Squalane on 80–100 mesh chromosorb W.AW. 78°C N_2flow 50 ml/min glass column 2.1m long 4 mm i.d.	10% FFAP on Diatomite AW 100°C, N_2 flow 80 ml/min Glass column 1.5m 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 mmid.	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	—

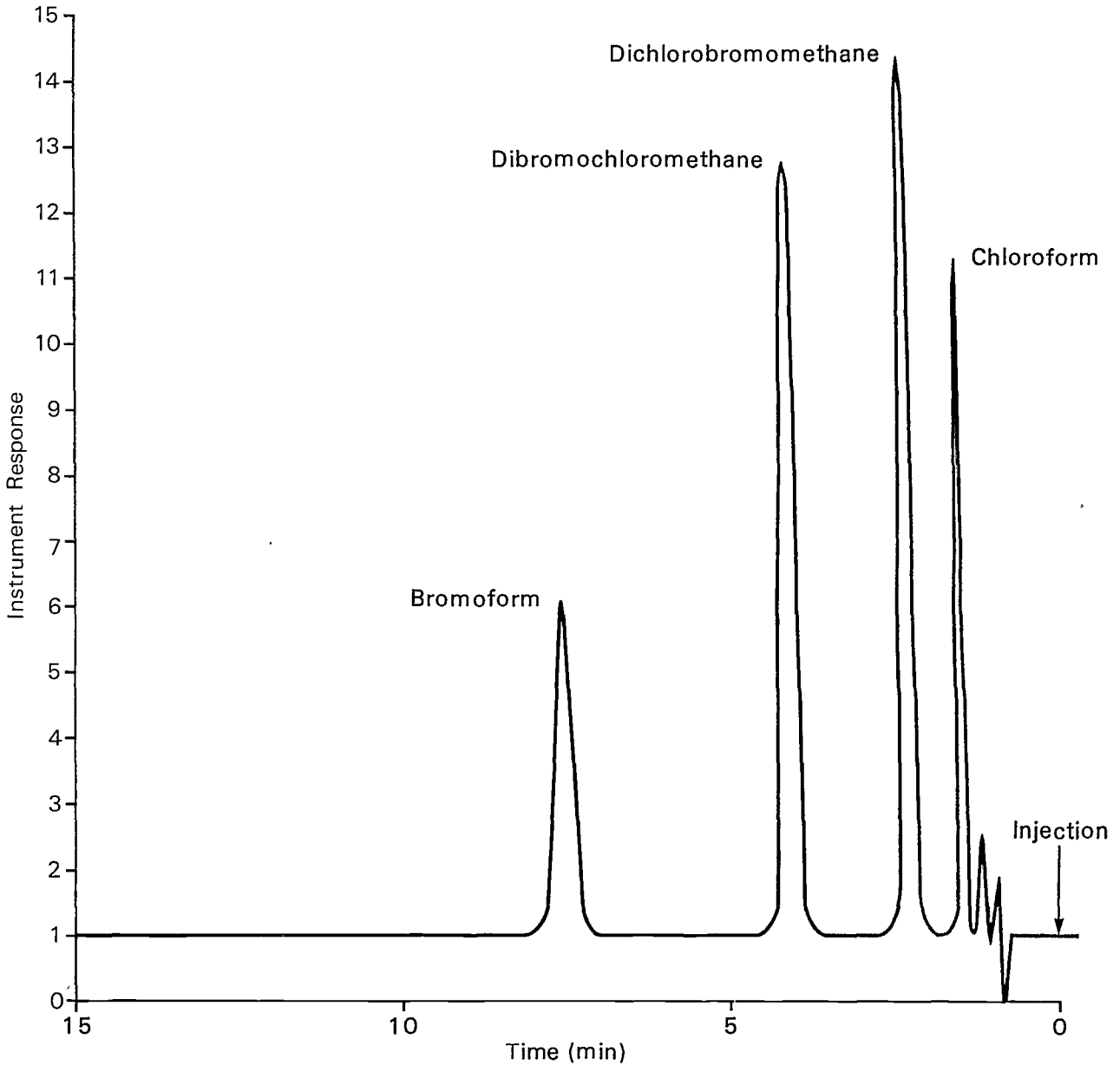

Figure 1. A Gas Chromatogram of the Four Chloro-Bromo-Trihalomethanes.

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