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RAPID METHOD FOR THE ANALYSIS OF TRIHALOMETHANES IN WATER

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SUMMARY

A rapid and precise method for the analysis of trihalomethanes (THMs) in water is described. Samples are extracted with methylcyclohexane and analysed by gas chromatography using a short capillary column and electron-capture detection. THMs elute with baseline separation in 1.25 min, and detection limits of 1 μg/l are readily achievable using 100-ml samples and 2 ml of solvent. Standards are prepared in the same way as samples by extraction of aqueous solutions to compensate for the relatively low extraction efficiencies which result from the low solvent to water ratio used. Ascorbic acid is a more effective sample preservative than sodium thiosulphate.

INTRODUCTION

Although chlorination of drinking waters for disinfection has been carried out since 1908, the formation of trihalomethanes (THMs) through the reaction of chlorine with naturally occurring humic and fulvic materials has only recently been recognised[1,2]. In the presence of bromide ions, the THMs arising from this reaction include chloroform, dichlorobromomethane, chlorodibromomethane and bromoform.

The possibility of adverse health effects arising from the presence of THMs in drinking water is presently a major water quality issue. Chloroform has been found to be carcinogenic in rats and mice and may therefore be a human carcinogen[3]. As a consequence, a total THM limit of 100 μg/l has been set in the U.S.A.[4], and the World Health Organisation have recommended a limit of 30 μg/l for chloroform[5].

A number of methods for the analysis of THMs have been reported. These include purge and trap procedures[2], direct aqueous injection[6], headspace analysis[7], resin extraction[8] and solvent extraction[9,10]. Although sample preparation varies considerably, all procedures require gas chromatographic (GC) separation and quantitation of the individual THMs. The solvent extraction procedure is relatively simple and rapid, and has been further refined in this work by employing a short capillary column in the GC part of the procedure.

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EXPERIMENTAL

Reagents and materials

Chemicals used were analytical reagent or laboratory reagent grades. THM-free water was obtained by passing distilled water through a water purification cartridge (Barnstead Ultrapure) followed by purging with high purity nitrogen for several hours. Methylcyclohexane (Ajax, Unilab) was purified by distillation. An unchlorinated reservoir water was used in the preparation of standards for monitoring work.

Solutions

Stock solutions of individual THMs were prepared by dissolving 1 g of the THM in 50 ml methanol. A solution containing 100 mg/l of each THM was prepared by adding 1 ml of each THM stock solution to a 200-ml volumetric flask which was then filled to the mark with THM-free water. Standards for extraction were prepared by adding the requisite volume of the 100 mg/l solution to THM-free water in a 100-ml volumetric flask. In this way 100 μl in 100 ml gives a 100 μg/l solution, *i.e.*, 1 μl = 1 μg/l.

Sampling

Samples were collected in glass bottles (which had been washed with chromic acid and baked at 110°C) containing approximately 1 g ascorbic acid preservative.

Extraction procedure

A 100-ml volumetric flask was filled to the mark with sample, 2 ml of methylcyclohexane (containing 5 mg/l tetrachloroethane as internal standard) were added and the mixture was shaken vigorously for 90 sec. The phases were allowed to separate and the extraction solvent was removed to a stoppered centrifuge tube with a Pasteur pipette. Extracts were stable for several weeks if stored in a freezer.

Instrumentation

Analyses were conducted using a Varian 2700 gas chromatograph equipped with a 6 m × 0.2 mm I.D. SE-30 vitreous silica capillary column (Scientific Glass Engineering, Melbourne, Australia) and electron-capture detection (ECD). Nitrogen was used as carrier and make up gas. Flow-rates were 0.5 and 30 ml/min respectively. Split injections of 0.5 μl were used with a split ratio of 50:1. Column temperature was 50°C, injector 150°C and detector 300°C. Chromatograms were recorded using a Hewlett Packard 3390A integrator.

Quantitation

Concentrations of the THMs were determined by reference to the appropriate calibration curves.

RESULTS AND DISCUSSION

A single stage extraction using volumetric flasks is a convenient means of isolating THMs from aqueous samples as it minimises sample handling and helps to

avoid component losses and contamination. Methylcyclohexane was chosen as the extraction solvent because it is readily purified by distillation and has negligible ECD response. In addition, this solvent is relatively non-volatile and solvent losses during extraction and from sample extracts are minimal.

Rate of extraction from water

The rate of extraction of the THMs by methylcyclohexane was determined by spiking water samples with all four THMs at concentrations of 50 μg/l and 500 μg/l. Extraction for various times was followed by GC analysis of the extracts. Fig. 1, which gives the results for chloroform and bromoform at the 50-μg/l level, shows that the extraction is complete (or more correctly, the two phases are in equilibrium) within 90 sec. Results for the 500 μg/l levels were identical. The curves for dichlorobromomethane and chlorodibromomethane fall between those for chloroform and bromoform, indicating variable extraction rates for each THM. However, shaking for 90 sec is sufficient to equilibrate the four THMs between the two phases.

Extraction efficiencies

THM extraction efficiencies were determined by spiking water samples with THMs at six levels between 20 and 250 μg/l and comparing the THM concentrations

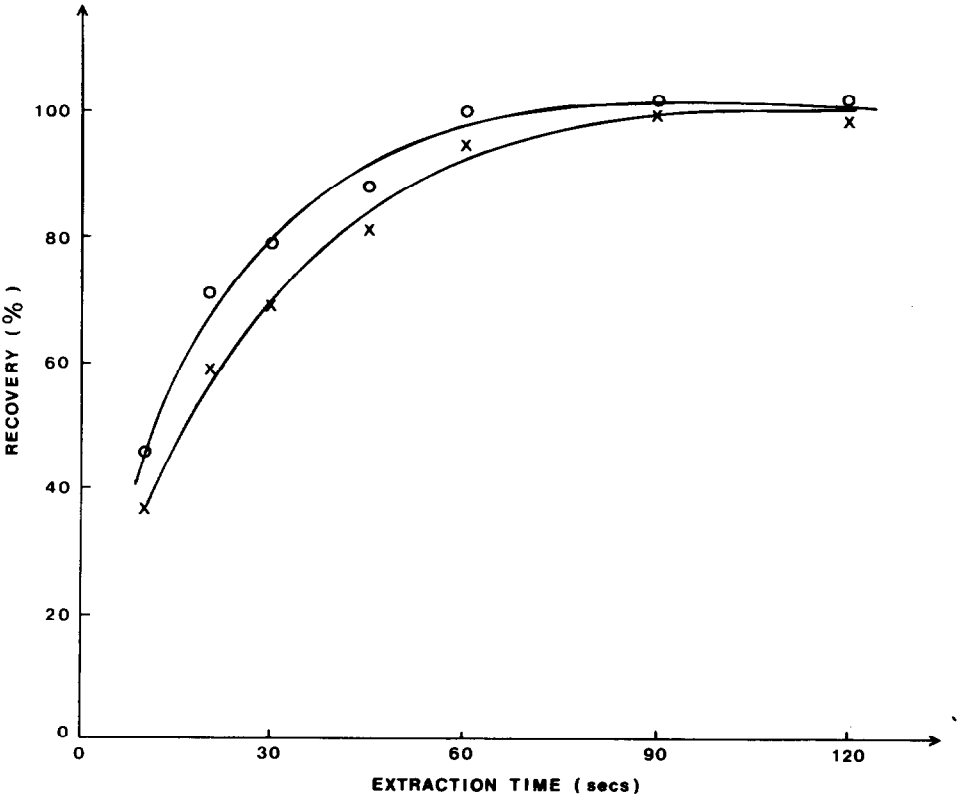

Fig. 1. Recovery *versus* extraction time for chloroform (O) and bromoform (×) at the 50-μg/l level (recovery relative to 5 min; extraction = 100%).

in the extracts with standards prepared directly in methylchlorohexane. The extraction efficiency was found to be independent of THM concentration (as indicated by the small standard deviation shown in Table I) but varied with the THMs.

The relatively poor extraction efficiency for chloroform results from the low solvent to water ratio used and may potentially be a source of error. In addition, some internal standard is lost from the solvent to the aqueous phase during extraction. However, there is no need for corrections if reference is made to aqueous standards extracted in the same way as samples[11].

The effect of water composition on extraction efficiency was determined by spiking a range of water types, including seawater, with THMs at levels between 50 and 500 μg/l and comparing the recoveries with those obtained from distilled water standards. It is clear from the results shown in Table II that water composition (at least for the waters samples tested) has little effect on THM extraction efficiency.

TABLE I

EXTRACTION EFFICIENCIES AND PARTITION COEFFICIENTS FOR THMs AT 20°C FOR A SAMPLE:SOLVENT RATIO OF 50:1

Compound	*Extraction efficiency (%)*	*Partition coefficient*
Chloroform	57 ± 1*	66**
Dichlorobromomethane	77 ± 2	170
Chlorodibromomethane	77 ± 2	170
Bromoform	80 ± 2	200

* The error is the standard deviation of extraction efficiencies obtained at six concentrations in the range 20–250 μg/l.

** The value of the partition coeffcient for chloroform (66) is in reasonable agreement with the value of 88 determined by Varma *et al.*[12].

TABLE II

CHARACTERISTICS OF WATER SAMPLES STUDIED AND THM RECOVERIES (RELATIVE TO DISTILLED WATER STANDARDS)

T.D.S. = Total dissolved salts, D.O.C. = dissolved organic carbon.

	Myponga reservoir	*Hope Valley reservoir*	*River Murray (Mannum)*	*Seawater*
pH	7.6	8.2	8.0	8.3
T.D.S. (mg/l)	370	600	500	38000
D.O.C. (mg/l)	10.8	6.9	5.5	2.1
Colour (Hazen Units)	42	9	15	4
Turbidity (NTU)	6.4	8.2	63.0	11.0
*Recoveries (%)**				
Chloroform	100 ± 1	99 ± 1	99 ± 2	103 ± 1
Dichlorobromomethane	102 ± 2	101 ± 1	101 ± 2	103 ± 2
Chlorodibromomethane	101 ± 2	100 ± 2	101 ± 2	99 ± 1
Bromoform	101 ± 2	101 ± 2	102 ± 2	101 ± 1

* Error is standard deviation of recoveries obtained at four concentrations in the range 50–500 μg/l.

Although it is not evident from the results in Table II, THMs are slightly more efficiently extracted from water samples with high ionic strengths, *e.g.* seawater. However, this effect is masked to some extent by the poorer extraction efficiency of the internal standard from the solvent into the aqueous phase. The real increase in THM extraction efficiency for seawater is of the order of 5% with respect to distilled water.

The preparation of THM stock solutions by direct addition to water involves several hours stirring of the mixture, and even then it is difficult to determine if solution is complete. These problems can be avoided by preparing standards from methanolic stock solutions.

The effect of methanol on THM extraction efficiency and reproducibility was determined by comparison of calibration curves resulting from methanolic and aqueous stock solutions. Standards prepared from methanolic stock solutions were found to give more reproducible calibration curves than those from aqueous solutions, which were consistently lower and tended to be more variable. The calibration curves for chloroform are shown in Fig. 2. The other THMs showed the same effect,

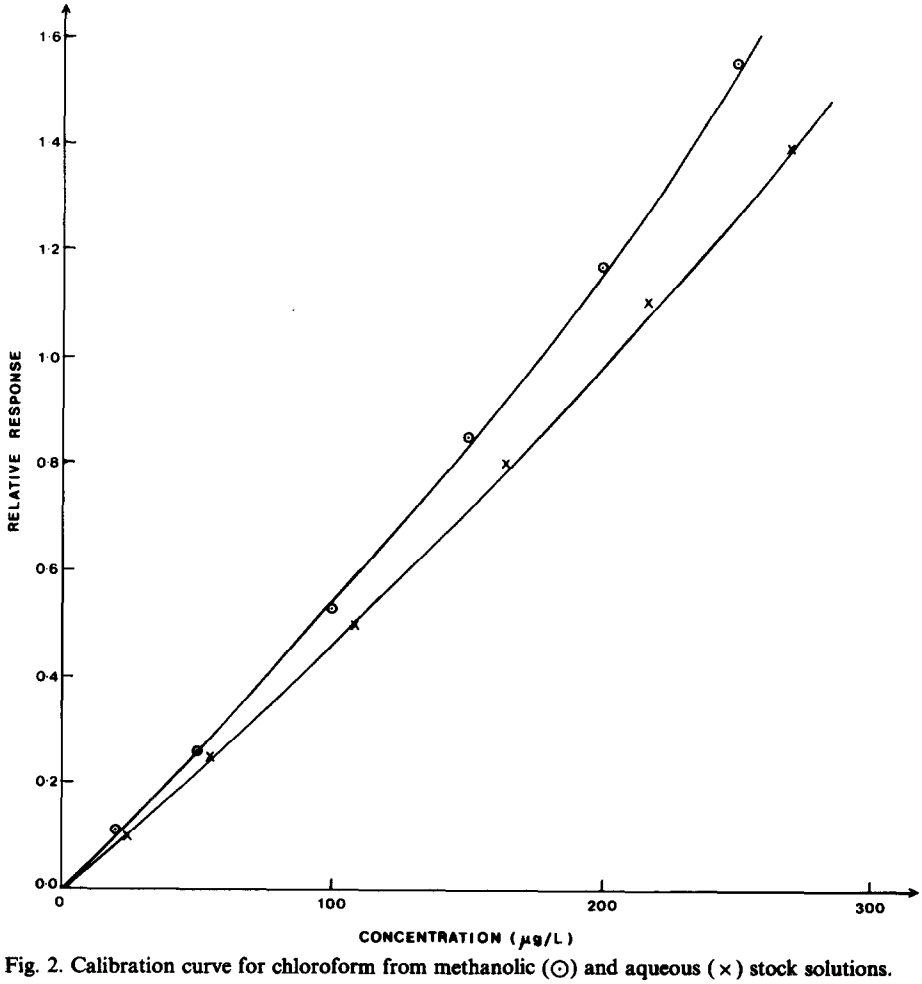

Fig. 2. Calibration curve for chloroform from methanolic (⊙) and aqueous (×) stock solutions.

of a standard containing 25 μg/l of each THM and 2.5 μg/l of carbon tetrachloride and trichloroacetone. Fig. 4 shows chromatograms for a drinking water supply before and after chlorination.

For the analysis of large numbers of samples, it was found more convenient to extract 5-ml samples with 1 ml solvent. Although more care had to be taken with blanks due to the lower THM concentrations in the extracts, more than one sample/solvent mixture can be shaken at a time.

Detection limit and reproducibility

Each of the THMs can readily be detected at the 1 μg/l level using this procedure, and lower detection limits can be obtained with cleaner solvents and by paying more attention to blanks. The precision of the method is excellent as shown in Table III.

TABLE III

THM LEVELS AND PRECISION OBTAINED FOR A TAP WATER SAMPLE (YORKETOWN, SOUTH AUSTRALIA)

THM	*Level obtained (μg/l)**	*Precision (%)*
Chloroform	58 ± 1	2
Dichlorobromomethane	86 ± 2	2
Chlorodibromomethane	127 ± 8	6
Bromoform	116 ± 4	3

* Average and standard deviation of five replicates.

Preservation of samples

THM levels in samples can increase during storage, and both sodium thiosulphate[15] and ascorbic acid[16] have been employed to prevent this by removing any chlorine residual. A study was conducted to determine the effectiveness of these two preservatives in chlorinated drinking waters. Samples were collected, analysed immediately, and again after one week, being stored with and without preservatives and at different temperatures. The results shown in Table IV indicate that without preservatives, THM levels can increase significantly with storage, even at 4°C. Ascorbic acid is a more effective preservative than sodium thiosulphate, enabling storage at 20°C for a week without significant changes in measured THM levels.

The preservative effect of ascorbic acid appears to be related in part to the stabilisation of trichloroacetone, a known intermediate in the haloform reaction. Besides removing residual chlorine, ascorbic acid reduces the pH of the sample and prevents hydrolysis of trichloroacetone to chloroform which occurs more rapidly in neutral or basic solutions[17].

sample, containing 100 μg/l of each THM, were equilibrated at various temperatures between 5 and 30°C and extracted normally. The THM recoveries from each aliquot were found to be identical within experimental error.

Application of the method

The relatively short capillary column employed gives good separation of the four THMs as well as carbon tetrachloride and 1,1,1-trichloroacetone, which are also detected by this method. These compounds elute with baseline separation in about 1.25 min, which is significantly shorter than the elution times obtained using more typical length capillary columns[11,14]. Fig. 3 shows a blank chromatogram and that

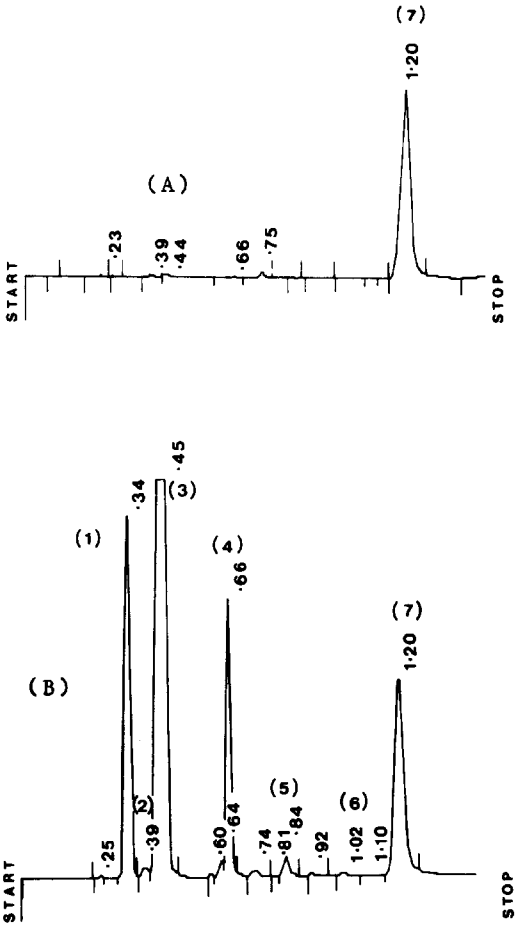

Fig. 4. Swan Reach/Stockwell Pipeline, South Australia, before (A) and after (B) chlorination. Identity of peaks as in Fig. 3. (A) Swan Reach, River Murray (THMs μg/l): chloroform, < 1; dichlorobromomethane, < 1; chlorodibromomethane, < 1; bromoform, < 1; carbon tetrachloride, < 0.02; 1,1,1-trichloroacetone, < 1. (B) Swan Reach/Stockwell Pipeline (2 km after chlorination): chloroform, 154; dichlorobromomethane, 78; chlorodibromomethane, 18; bromoform, 1; carbon tetrachloride, 0.28; 1,1-trichloroacetone, 8.

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TABLE IV

EFFECT OF SODIUM THIOSULPHATE AND ASCORBIC ACID ON STABILITY OF THM LEVELS

Sample	*Analysis time*	*Preservative*	*Temp. (°C)*	*Concentration (μg/l)*				
				Chloroform	*Dichloro-bromomethane*	*Chlorodi-bromomethane*	*Bromoform*	*Tri-chloroacetone*
A	Initial	–	–	18	44	82	38	<1
	1 week	None	4	19	46	85	40	<1
	1 week	Thiosulphate	4	19	47	85	40	<1
	1 week	Ascorbic acid	4	19	44	77	36	<1
	1 week	None	20	20	45	87	41	<1
	1 week	Thiosulphate	20	19	44	82	40	<1
	1 week	Ascorbic acid	20	18	42	72	33	<1
B	Initial	–	–	145	102	28	1	17
	1 week	None	4	171	108	29	1	12
	1 week	Thiosulphate	4	168	108	29	1	16
	1 week	Ascorbic acid	4	147	102	28	1	17
	1 week	None	20	185	106	29	1	4
	1 week	Thiosulphate	20	190	102	28	1	4
	1 week	Ascorbic acid	20	143	98	26	1	17
C	Initial	–	–	14	35	105	179	<1
	1 week	None	4	16	45	123	194	<1
	1 week	Thiosulphate	4	15	36	108	188	<1
	1 week	Ascorbic acid	4	15	38	103	173	<1
	1 week	None	20	20	57	147	209	<1
	1 week	Thiosulphate	20	15	35	105	188	<1
	1 week	Ascorbic acid	20	15	36	101	172	<1
D	Initial	–	–	137	61	10	<1	10
	1 week	None	4	178	70	12	<1	7
	1 week	Thiosulphate	4	170	64	10	<1	4
	1 week	Ascorbic acid	4	141	64	10	<1	12
	1 week	None	20	174	68	13	<1	<1
	1 week	Thiosulphate	20	180	62	10	<1	<1
	1 week	Ascorbic acid	20	137	59	9	<1	15

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