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Determination of biogenic and anthropogenic volatile halocarbons in sea water by liquid–liquid extraction and capillary gas chromatography

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ABSTRACT

A method is presented for the determination of fifteen biogenic and anthropogenic halogenated hydrocarbons, including brominated and iodated compounds, in sea water at concentrations below the nanograms per litre range. The method includes liquid–liquid extraction of the sea water with pentane, gas chromatographic separation and electron-capture detection. The separation was performed on two coupled fused-silica columns of different polarity and film thickness. In this way trichloroethene, bromodichloromethane and dibromomethane could be separated.

INTRODUCTION

The determination of anthropogenic halocarbons in environmental samples has become a standard procedure for many laboratories during the last 15 years, since they are regarded as indicators of pollution impact. Common methods usually include some kind of preconcentration step, either by a dynamic headspace technique combined with solid-phase adsorption or cold trapping[1,2], or by liquid–liquid extraction with organic solvents[3,4]. A typical procedure involves separation of the halocarbons by capillary gas chromatography on a non-polar silicone stationary phase and electron-capture detection (ECD). For sea-water samples with concentrations of volatile halocarbons in the lower nanograms per litre range, preconcentration is essential. Additionally, when dealing with sea water special problems are encountered, as a number of volatile halocarbons produced by marine organisms can be present in the sample and interfere with the determination of anthropogenic halocarbons[5–7]. Hence standard methods available for the determination of halocarbons in drinking water, waste water, etc., are often unsuitable for sea water, owing to differences as regards detection limits, separation properties, choice of standard mixtures, etc.

Liquid–liquid extraction with pentane has frequently been used for the determination of halocarbons in sea water[4,7–9]. The method produces reliable results in

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terms of precision, detection limits and contamination risks[3,8]. The technique is simple regarding instrumental set-up and the total analysis time is short.

Non-polar methyl or methylphenyl silicone phases, such as DB-1 or DB-5, are commercially available as bonded, cross-linked phases on fused-silica capillary columns. These columns, which provide a greater separation efficiency than packed columns, have frequently been used for the analysis of halogenated organic compounds[7,10–13], although their ability to separate halocarbons is limited[14,15]. For instance, the separation of trichloroethene, bromodichloromethane and dibromomethane from each other cannot be obtained on these stationary phases, and this problem also limits their use in sea-water analysis[16]. Mehran *et al.*[14] coupled two segments of capillary columns coated with two stationary phases of different polarity, 100% methylpolysiloxane (DB-1) and 14% cyanopropylphenylmethylpolysiloxane (DB-1701), and achieved the separation of eighteen mainly anthropogenic volatile halocarbons. Class *et al.*[17] used a similar combination of stationary phases (5% phenylmethylpolysiloxane, DB-5, and BP-10, equivalent to DB-1701) for the separation of halogenated trace compounds in marine air. A 6% cyanopropylpolymethylsiloxane-coated capillary column, DB-1301, has recently been introduced in the analysis of volatile priority pollutants by Mehran *et al.*[18], which seems to provide a new approach to the separation problems with halogenated compounds. The use of PLOT columns in the separation of volatile halocarbons has also been shown to be an attractive alternative to the widely used WCOT columns[19].

Our aim was to develop a method to determine biogenic and anthropogenic halocarbons in sea water. This required the separation of a number of substances which can be expected in sea water, including brominated and iodated compounds. The analytical procedure should be as simple and fast as possible, in order to allow the investigation of a large number of samples within a short time, both in the laboratory and under more primitive circumstances on-board ship. The standard substances were chosen according to results from algal extracts[5,6], sea water[7,8] and ambient air in marine environments[17,20,21].

EXPERIMENTAL

The following substances were evaluated and they were all pure (>98%; CH_2ClI >97%): $CHCl_3$ (Merck), CH_3CCl_3 (Fluka), (Merck), CH_3CHICH_3 (Fluka), $CHCl=CCl_2$ (Mallinckrodt), CH_2Br_2 (Merck), $CHBrCl_2$ (Fluka), $CH_3CH_2CH_2I$ (Fluka), CH_2ClI (Fluka), $CH_3CHICH_2CH_3$ (Fluka), $CHBr_2Cl$ (Fluka), $CCl_2=CCl_2$ (Merck), $CH_3CH_2CH_2CH_2I$ (Fluka), $CHBr_3$ (Merck) and CH_2I_2 (Fluka). Standard stock solutions were prepared in acetone (Merck).

The determinations were made with a Carlo Erba 4160 gas chromatograph equipped with a ^{63}Ni electron-capture detector (275°C). Sea water (100 ml) was extracted for 5 min directly in sampling bottles with 1 ml of distilled pentane, containing $CBrCl_3$ (Fluka) as internal standard, as this substance has never been found in natural sea water[3]. A 15-μl volume of the pentane phase was injected onto the column using an automatically driven liquid chromatography injection valve (Valco) with a 15-μl sample loop. Two fused-silica capillary columns were connected with a press-fit connector (Mikro Kemi), a 30 m × 0.32 mm I.D. DB-5 column of film thickness 1 μm (J&W Scientific) and a 25 m × 0.32 mm I.D. DB-1701 column of film thickness 0.1

μm (Nordion) in front of the DB-5 column. The hydrogen carrier gas flow-rate was 1.8 ml/min and the make-up gas (nitrogen) flow-rate was 30 ml/min.

During the separation the oven was held at an initial temperature of 40°C for 2 min and then raised to 100°C at 10°C/min. The chromatographic peaks were integrated using a Jones Model JCL 6000 chromatography system or a C-R5A Shimadzu integrator.

RESULTS AND DISCUSSION

Separation

With the combination of two columns of different polarity and different film thickness, separation was achieved for all fifteen substances studied (Fig. 1). The DB-1701 column caused a preseparation which made it possible to separate even trichloroethene, bromodichloromethane and dibromomethane. This separation could not be obtained if the DB-5 column was used separately. Large on-column injections for the determination of volatile halocarbons at extremely low concentrations have been described by Fogelqvist and Larsson[22]. With the arrangement described in this method, at least 15 μl of the pentane phase could be injected onto the column. This was not possible when using the DB-5 column only, because it resulted in peak deterioration. Hence the DB-1701 column acts both as a separation column and as a retention gap. The coupling of two columns did not result in a considerable increase in analysis time. The gas chromatographic run took 10 min and subambient cooling was not necessary. In principle, the coupled columns described here can be used in combination with a suitable purge and trap system.

Extraction efficiency

The extraction combines preconcentration with the transfer of the halocarbons to the organic solvent. The transfer of an individual compound is dependent on its

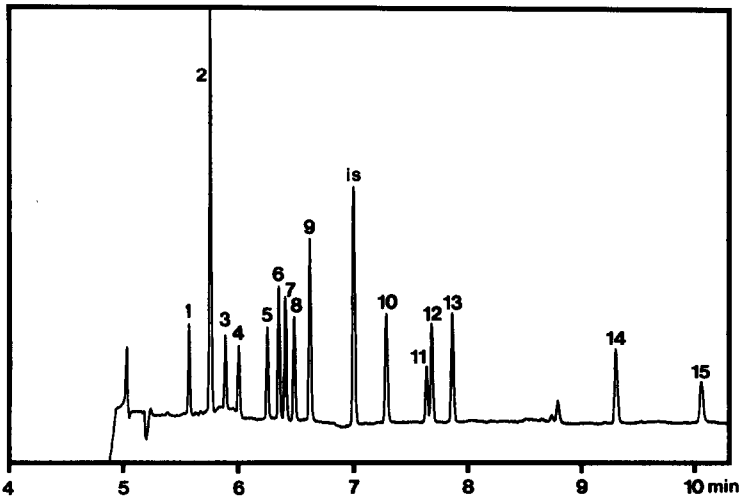

Fig. 1. Chromatogram of spiked sea water. The concentrations of the individual compounds vary between 4 and 110 ng/l. Peak integration was performed with a Jones chromatography system.

TABLE I

EXTRACTION YIELDS, PRECISION, RELATIVE RESPONSE FACTORS (R) AND DETECTION LIMITS FOR HALOCARBONS

No.	*Compound*	*Extraction yield (%)*	*Precision*[a] *(%)*	*Detection limit (ng/l)*	*R*
1	$CHCl_3$	48	9	2	0.05
2	CH_3CCl_3	80	8	0.2	0.4
3	CCl_4	84	10	0.05	1.3
4	CH_3CHICH_3	81	9	0.7	0.1
5	$CHCl=CCl_2$	75	8	0.4	0.18
6	CH_2Br_2	36	10	0.3	0.50
7	$CHBrCl_2$	52	10	0.2	0.61
8	$CH_3CH_2CH_2I$	79	7	0.2	0.28
9	CH_2ClI	41	3	0.03	1.3
10	$CH_3CHICH_2CH_3$	86	11	0.3	0.19
11	$CHBr_2Cl$	55	7	0.2	0.64
12	$CCl_2=CCl_2$	87	9	0.07	0.80
13	$CH_3CH_2CH_2CH_2I$	88	12	0.4	0.24
14	$CHBr_3$	59	5	0.2	0.22
15	CH_2I_2	55	7	0.4	0.15

[a] Relative standard deviation (n = 5).

partition coefficient and will influence the degree of preconcentration. The extraction efficiency was determined by consecutive extractions of spiked sea water for all compounds (Table I).

Precision and detection limits

The precision (relative standard devition, R.S.D.) was determined by calculating the amounts of halocarbons in spiked sea water samples (n = 5). For the low concentrations encountered in sea water, the R.S.D. is in the range 3–12% and the values for each compound are shown in Table I. The linearity down to concentrations as low as the detection limit was confirmed by correlation coefficients for the compounds of 0.996–0.999.

The detection limits, defined as a signal-to-noise ratio of 10:1 (blank signal plus nine standard deviations of the blank), were determined in natural sea water spiked with halocarbons. As can be seen from Table I, the detection limits are in the range of 30–700 pg/l, except for $CHCl_3$. The detection limit for $CHCl_3$ can be lowered if the phase ratio is increased[23]. The values given in Table I should be regarded as the limits of precise quantitative determination[24]. Depending on the chromatographic system, the integration system, the purity of the pentane and the matrix, it is possible to confirm the presence of a substance even at concentrations lower than the limits given here. The analysis of a large number of natural samples with concentrations of anthropogenic and biogenic halocarbons close to their detection limits showed good agreement with the values for detection limits and precision given in Table I.

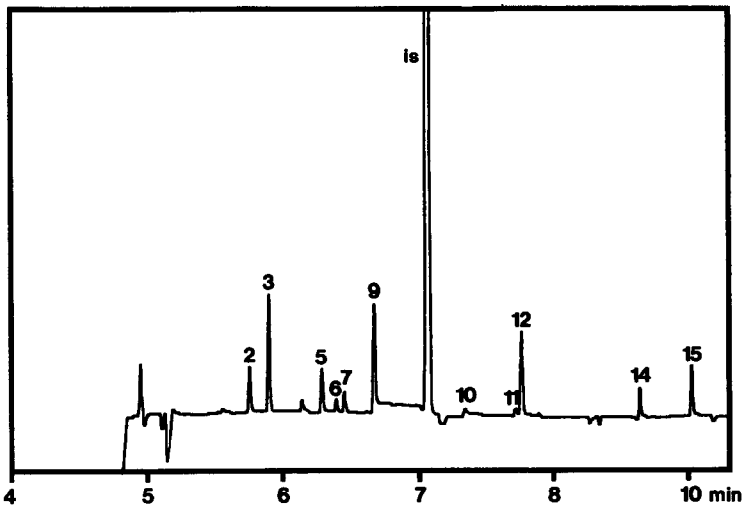

Fig. 2. Chromatogram of sea water, sampled in the central Skagerrak. 2 = CH_3CCl_3 (3.4 ng/l); 3 = CCl_4 (1.2 ng/l); 5 = $CHClCCl_2$ (7.1 ng/l); 6 = CH_2Br_2 (1.3 ng/l); 7 = $CHBrCl_2$ (1.3 ng/l); 9 = CH_2ClI (3.2 ng/l); 10 = $CH_3CHICH_2CH_3$ (0.55 ng/l); 11 = $CHBr_2Cl$ (<0.2 ng/l); 12 = $CCl_2=CCl_2$ (0.26 ng/l); 14 = $CHBr_3$ (6.5 ng/l); 15 = CH_2I_2 (19 ng/l). Peak integration was performed with a Shimadzu C-R5A integrator.

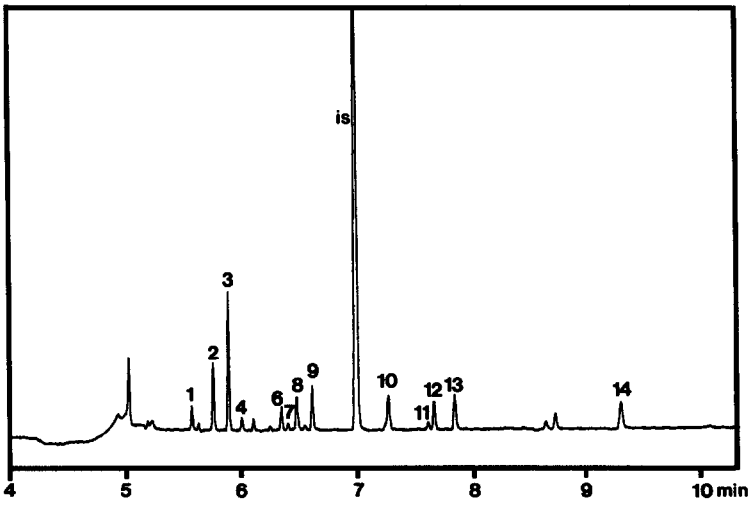

Fig. 3. Chromatogram of sea water sampled at S52°10′, W5°58′ on a cruise with R/V Polarstern, November 1989. 1 = $CHCl_3$ (9.3 ng/l); 2 = CH_3CCl_3 (1.8 ng/l); 3 = CCl_4 (1.2 ng/l); 4 = CH_3CHICH_3 (2.4 ng/l); 6 = CH_2Br_2 (1.3 ng/l); 7 = $CHBrCl_2$ (0.26 ng/l); 8 = $CH_3CH_2CH_2I$ (1.9 ng/l); 9 = CH_2ClI (1.1 ng/l); 10 = $CH_3CHICH_2CH_3$ (3.5 ng/l); 11 = $CHBr_2Cl$ (0.20 ng/l); 12 = $CCl_2=CCl_2$ (0.52 ng/l); 13 = $CH_3CH_2CH_2CH_2I$ (2.6 ng/l); 14 = $CHBr_3$ (4.5 ng/l). Peak integration was performed with a Jones chromatography system.

Application

The method described was specifically designed for the determination of biogenic and anthropogenic halocarbons at low concentrations in sea water. Emphasis was put on the separation of brominated and iodated compounds produced by marine algae and anthropogenic compounds that are detectable in almost all sea water samples. The method has been used successfully in the analysis of *ca.* 600 samples from the western coast of Sweden, from the Skagerrak and from the Antarctic. Figs. 2 and 3 show chromatograms of samples from the last two. As the iodated substances have not been determined in these areas before, it is not possible to compare the concentration levels with earlier studies. However, the values given are representative of water samples containing iodated substances in our investigations. In previous investigations on coastal waters in Sweden, no concentrations were given for dibromomethane and trichloroethene[7,9], since they could not be separated. For the other compounds the concentrations determined by us are in good agreement with these investigations.

The method described here can also be applied to the determination of volatile halocarbons in other water samples such as fresh water, drinking water and different types of waste waters.

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