CHROMSYMP. 244

ANALYSIS OF TRACE HALOCARBONS IN NATURAL WATERS BY SIMPLIFIED PURGE AND CRYOTRAP METHOD

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SUMMARY

A simplified purge and cryotrap method for the analysis of trace aqueous halocarbons is described. The usual Tenax®* adsorption trap is replaced with a cryoloop preceded by a permeation dryer which selectively removes water vapour and thereby prevents freezing in the cryoloop. This "one-step" method reduces potential contamination and is highly sensitive when coupled with capillary electron capture detector analysis of the purged volatiles. Using this method several previously unreported halocarbons have been observed in natural waters. Furthermore, Henry's law constants can be calculated directly by analysing both water and ambient air samples collected at the same time.

INTRODUCTION

Halocarbons of both natural and industrial origin completely pervade the global environment. The concentrations, sources, and sinks of the major atmospheric halocarbons have all been investigated. Furthermore the lifetimes of the principal anthropogenic halocarbons have been established from long-term atmospheric measurements[1–6]. The distribution of halocarbons in natural waters, and in particular their degree of saturation with respect to the overlying air, is less well established. In view of their very low concentrations most atmospheric halocarbons can be expected to behave like ideal gases and partition between the air and water phases according to their Henry's law constants. Recent measurements[7,8] confirm that the surface sea-water is very close to saturation with respect to the atmospheric concentrations of trichlorofluoromethane and carbon tetrachloride. Thus to ascertain if any disequilibrium exists measurements of both the dissolved halocarbons and their concentrations in the overlying air need to be determined experimentally.

In most natural waters halocarbon concentrations are extremely low and either large volumes of water must be taken for analysis or concentration methods using adsorption traps or solvent extraction must be employed. Existing methods for determining organohalides in aqueous samples include headspace analysis[9–14], solvent extraction[15–20], direct aqueous injection[21–25], closed loop stripping[26–30], and the

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* Tenax is a registered trade-mark of the Enka Research Institute.

widely used purge and trap technique[31–38]. With many of these methods there is a high risk of contamination. This paper reports on a simplified purge and cryotrap method which eliminates the usual Tenax adsorption trap and reduces sample handling to a minimum. A selective permeation dryer is used to remove water vapour which would ordinarily complicate the cryotrapping process.

EXPERIMENTAL

The basic experimental arrangement (Fig. 1) consists of a glass purging device, permeation dryer, and sampling valve with small volume loop (30 μl) for cryogenic concentration (liquid nitrogen) of the purged volatiles. A heated (150°C) stainless-steel transfer line (15 cm × 0.25 mm I.D.) connects the sample valve directly to a thick film DB1 silicone capillary column (30 m × 0.32 mm I.D.; J&W Scientific, U.S.A.). All samples were analysed with a Hewlett-Packard 5880 gas chromatograph equipped with ^{63}Ni electron-capture detector maintained at 320°C. For the majority of analyses the column was operated isothermally at 50°C and with nitrogen carrier gas at an average linear flow velocity of 20 cm/sec. Purified nitrogen was used as the detector make-up gas at a flow-rate of 30 ml/min.

Several precautions are necessary to exclude the risk of contamination from adventitious halocarbons. Purified nitrogen carrier gas (< 5 ppm O_2) was further purified by passing through a mixed bed adsorbent containing activated charcoal,
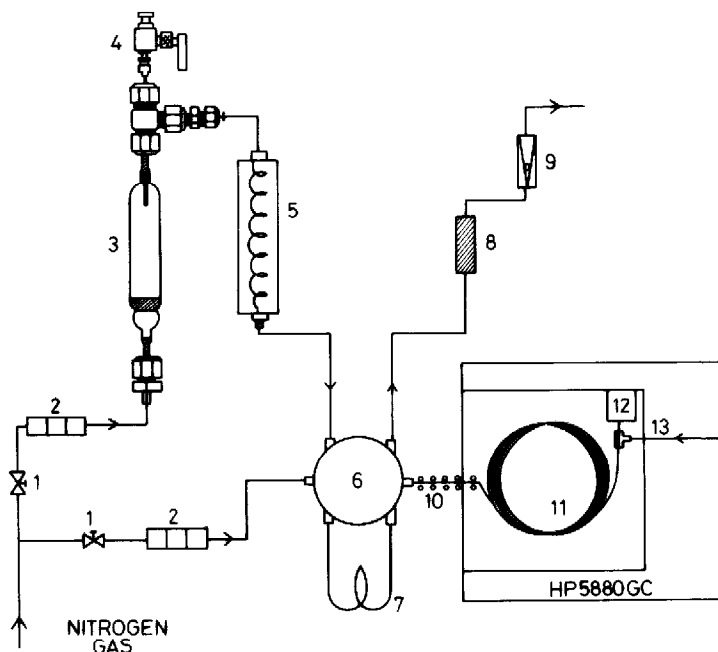

Fig. 1. Schematic of purge and cryotrap apparatus. 1 = Flow control valve; 2 = mixed bed adsorbent; 3 = glass purging tube; 4 = Hamilton two-way valve; 5 = permeation dryer; 6 = Valco six-way valve; 7 = 30-μl sample loop; 8 = 13 × sieve adsorption trap; 9 = rotameter; 10 = heated capillary transfer line (150°C); 11 = DB1 silicone capillary column; 12 = electron-capture detector; 13 = nitrogen make-up gas (30 ml/min).

13X and 5A molecular sieves. The entire apparatus was purged continuously with this purified nitrogen and 500-ml volumes were concentrated routinely through the cryoloop as system blanks.

Water samples (5 ml) were introduced from a precision glass syringe to the purging device through a small valve (Hamilton, Reno, NV, U.S.A.) connected to a hypodermic needle which passed through the neck of the purge tube. Volatiles were efficiently purged with a nitrogen flow-rate of 25 ml/min through a fine porosity glass sinter sealed in the base of the purging device. As the purge gas is saturated with water vapour this must be selectively removed before cryotrapping occurs otherwise there is a serious risk of ice formation plugging the sample loop.

The Nafion®* permeation dryer consists of two parallel 1-m lengths of Nafion® polymer tubing (Type 815, 1.14 mm I.D., wall thickness 0.127 mm) sealed within an acrylic tube. This tube was filled with freshly activated 5A molecular sieve (≈ 175 g) which serves as an external desiccant[39]. The dewpoint of the gas leaving the dryer was monitored with a minihygrometer (Shaw Instruments, U.K.) and was always less than $-40°C$. The six-port gas sampling valve (Valco Instruments, U.S.A.) was fitted with a 30-μl stainless-steel sample loop (35 cm $\times$ 0.33 mm I.D.) with a 1-cm central section packed with 100-mesh glass beads to assist condensation of the volatiles[40]. Volatiles were released from the cryotrap by immersion of the sample loop in a small dewar containing near boiling water. Gas samples were also analysed on the same apparatus either by injection through the Hamilton valve or via a second gas sampling valve (not shown in Fig. 1) mounted just before the purging device.

Halocarbons used to prepare standards were all reagent grade obtained from Aldrich Chemical Co. Standard solutions of halocarbons were prepared by carefully adding 1-5 μl of the pure compounds to methanol in a 40-ml glass vial sealed with a PTFE-faced septum so as to leave no headspace. 5-μl aliquots of this standard mixture were then added to 40 ml of halocarbon-free water in a second glass vial. Further serial dilutions were prepared to give aqueous halocarbon standards in the range 0.1-10 ng/l. Gas standards were prepared by injecting 1-μl aliquots of the standard methanol solution into an evacuated 800-ml stainless-steel cylinder and then pressurised to 200 p.s.i.g. with purified nitrogen. Weighing the gas bottle before and after filling with nitrogen established the volume of gas in the cylinder and hence the dilution factor.

Purging efficiency tests

To test the purging efficiency of the system a three-way switching valve was installed between the purging device and the Nafion® dryer. 5-ml aqueous standards were stripped of volatiles as in previous experiments for either 5 or 10 min. The three-way valve was then switched to close the purging line and seal the water sample under nitrogen. During analysis of this first cryotrapped sample purified nitrogen was supplied to the same three-way valve and vented through the dryer to prevent any back diffusion of air. Following analysis of the first purge the valve was again switched to continue purging for an additional 20 min before volatilization and analysis. The purging efficiency was determined for individual halocarbons by calculating

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* Nafion® is a registered trade-mark of the DuPont Company.

the ratio of the peak areas in the first purge to the sum of the peak areas in the first and second purge.

RESULTS AND DISCUSSION

   Experiments to determine the precision of the purge and cryotrap method are reported in Table I. The precision of analysis for the majority of the halocarbons is reasonably good with a relative standard deviation (R.S.D.) of better than 5%. However, the precision for bromoform (17.4%), 1,2-dibromoethane (12.1%), iodomethane (9.5%), and dibromochloromethane (8.8%) is less satisfactory. When gas standards containing the same halocarbons are analysed by injection of 5-ml calibrated volumes using a gas sampling valve placed ahead of the empty purging device the precision is considerably improved with a mean R.S.D. of 3.6%. As the gas standard follows the same flow path as the volatiles stripped from the water sample, it appears likely that inefficient purging of the more soluble and less volatile halocarbons, such as bromoform, is responsible for their lower analytical precision.
   Results of the purging efficiency tests are summarised in Table II. As no peaks or only very small peaks were observed in the second purge, it was assumed that purging was essentially complete for the majority of halocarbons. In fact, most compounds are quantitatively purged from the 5-ml sample after 10 min, and even 5 min is adequate for complete removal of certain halocarbons. As might be expected the more water-soluble halocarbons with relatively low vapour pressures, such as bromoform and 1,2-dibromoethane are incompletely purged, even after 30 min.

TABLE I

PRECISION OF PURGE AND CRYOTRAP METHOD

Compound	% R.S.D.*	
	Gas standard	Water standard
1,1,2-Trichlorotrifluoroethane	2.5	3.9
Iodomethane	2.4	9.5
Chloroform	2.8	4.3
1,2-Dichloroethane	3.8	4.8
1,1,1-Trichloroethane	3.9	4.5
Carbon tetrachloride	1.8	3.1
1,2-Dichloropropane	2.6	3.4
Trichloroethylene	1.9	3.2
Iodopropane	5.8	2.7
1,1,2-Trichloroethane	4.3	5.1
1,3-Dichloropropane	5.1	3.6
Dibromochloromethane	4.7	8.8
1,2-Dibromoethane	5.6	12.1
Tetrachloroethylene	1.5	5.7
Bromoform	5.1	17.4
Mean	3.6	6.1

   * Per cent relative standard deviation calculated from two replicate analyses of the gas standard, and three analyses of the water standard.

TABLE II

PURGING EFFICIENCIES (%)

Calculated from 5-ml water standards.

$$\% \text{ efficiency} = \frac{A}{A + B} \times 100$$

where A = peak area first cryotrap, B = peak area second cryotrap.

Compound	5 min	10 min
1,1,2-Trichlorotrifluoroethane	100	100
Iodomethane	98.7	100
Chloroform	100	100
1,2-Dichloroethane	96.6	99.5
1,1,1-Trichloroethane	100	100
Carbon tetrachloride	100	100
1,2-Dichloropropane	93.4	96.0
Trichloroethylene	98.2	100
Iodopropane	98.0	99.3
1,1,2-Trichloroethane	100	100
1,3-Dichloropropane	92.4	97.6
Dibromochloromethane	90.6	96.2
1,2-Dibromoethane	84.1	92.4
Tetrachloroethylene	96.4	100
Bromoform	79.0	82.5

TABLE III

ANALYSIS OF HALOCARBON STANDARD WITH AND WITHOUT NAFION DRYER

Mean $\bar{X}$ is calculated from peak areas from two replicate analyses with and without Nafion® dryer.

Compound	Mean $\bar{X}$ (σ)		$\dfrac{\bar{X} \text{ with Nafion}}{\bar{X} \text{ without Nafion}}$
	With Nafion	Without Nafion	
1,1,2-Trichlorotrifluoroethane	427.8 (10.7)	452.1 (13.6)	0.95
Iodomethane	593.6 (14.2)	568.3 (23.8)	1.04
Chloroform	1824.3 (51.1)	1767.6 (47.7)	1.03
1,2-Dichloroethane	1865.5 (70.9)	1782.5 (94.4)	1.05
1,1,1-Trichloroethane	711.3 (27.7)	716.5 (25.8)	0.99
Carbon tetrachloride	1652.4 (29.7)	1638.6 (37.7)	1.01
1,2-Dichloropropane	731.5 (19.0)	685.1 (17.1)	1.07
Trichloroethylene	1297.7 (24.6)	1242.2 (23.6)	1.04
Iodopropane	986.5 (57.2)	916.6 (40.3)	1.08
1,1,2-Trichloroethane	933.3 (40.1)	927.5 (44.5)	1.01
1,3-Dichloropropane	945.1 (48.2)	998.8 (38.9)	0.95
Dibromochloromethane	1403.8 (66.0)	1408.9 (74.7)	0.99
1,2-Dibromoethane	904.2 (50.6)	921.4 (64.4)	0.98
Tetrachloroethylene	1213.5 (18.2)	1122.1 (19.1)	1.08
Bromoform	1102.2 (56.2)	1146.9 (53.2)	0.96

It is therefore not too surprising that these compounds also give the lowest precision during replicate analyses of the aqueous standards. Nevertheless, this does not entirely account for the overall lower precision obtained with water samples. Adsorption losses in the glass sample bottle or small differences in sample size would also introduce random errors into the measurements. In fact, using 1,1,2-trichloro-
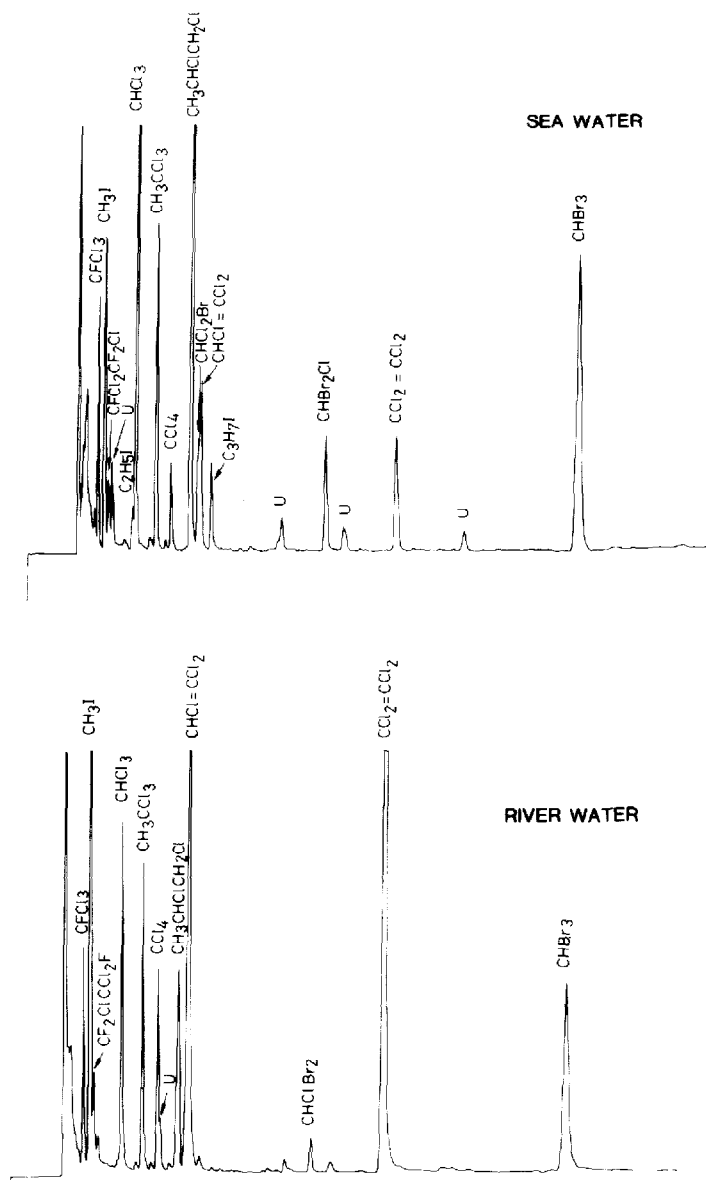
Fig. 2. Analysis of volatiles purged from 5-ml samples of sea-water and river-water (Hampshire, Avon, U.K.). Capillary column: 30 m × 0.32 mm I.D.; isothermal *ca.* 50°C. U = unidentified peak.

ethane as an internal standard makes a small but significant improvement (mean R.S.D. with internal standard = 5.4%, *versus* 6.1% without internal standard) in the overall precision and presumably corrects for any sample volume differences.

One other possible source of error is losses of halocarbons during the selective removal of water vapour by the permeation dryer. Previous work has demonstrated that non-polar compounds such as halocarbons, and hydrocarbons are quantitatively transmitted through the Nafion® tubing used to construct the dryer[39,41]. To extend these early results to the broader range of halocarbons used in this work, gaseous
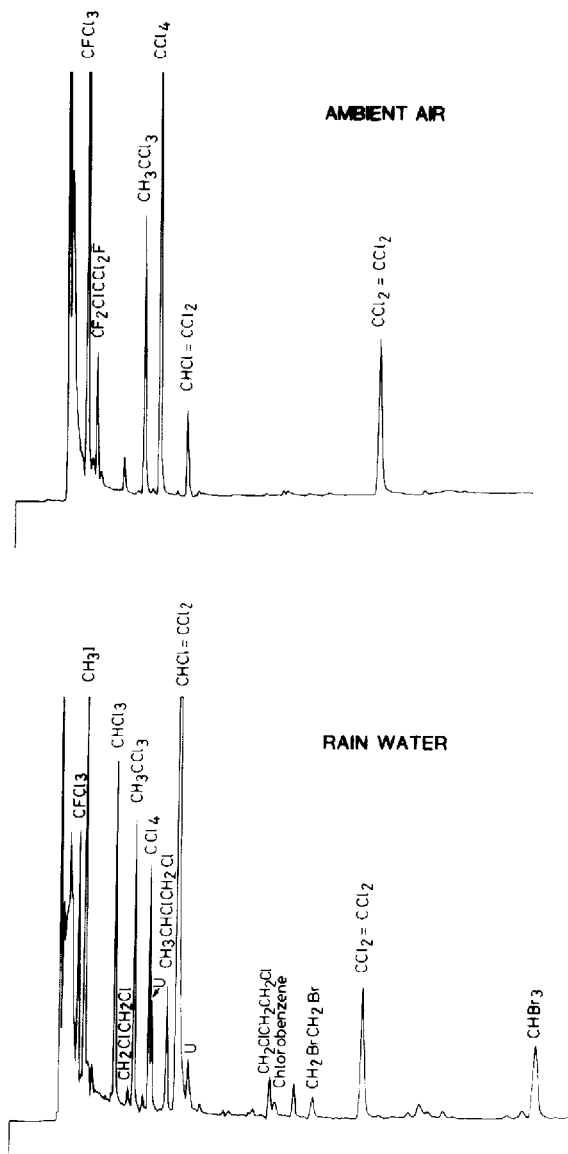

Fig. 3. Analysis of volatiles purged from 5 ml rain-water (collected June 16th, 1983), and 15 ml ambient air (collected June 21st, 1983). Conditions as in Fig. 2.

halocarbon standards were analysed without the Nafion® dryer. These results are listed in Table III where the ratio of the peak area means, computed from replicate analyses with and without the dryer, are compared. Although a ratio of less than one might imply losses through the Nafion® tubing, most of the ratios are spread randomly about unity, and are generally within the precision of the method. It is reasonable to conclude that the Nafion® dryer transmits all of the halocarbons studied here without any significant loss.

The analysis of halocarbons in natural waters is illustrated in Figs. 2 and 3. Fig. 2 is the analysis of a local river and sea-water, while Fig. 3 compares the analysis of rain-water and ambient air. Most striking in these chromatograms is that many additional halocarbons are observed in all of the water samples compared with the ambient air. The concentrations of individual halocarbons are summarised in Table IV. It is important to note that while identification for most of the major peaks ($CFCl_3$, CH_3I, CF_2ClCCl_2F, $CHCl_3$, CH_3CCl_3, CCl_4, C_2HCl_3, and C_2Cl_4) have been confirmed by gas chromatography–mass spectrometry (GC–MS) the smaller peaks have only been assigned on the basis of retention data and their identifications are therefore at present only tentative. Of interest is the observation that many of the minor peaks are halocarbons of industrial origin which have only been observed previously by concentrating large volumes of ambient air[42]. Their presence, especially in the rain-water samples, implies a substantial preconcentration effect which is most probably related to their higher water solubility.

One of the objectives of this research was to establish a method for comparing the distribution of halocarbons between air and water. Henry's law constants, H, have therefore been calculated from the analysis of water and corresponding air samples collected at the same time. In Table V data are compared with either published Henry's law constants[7] or values of H calculated from solubility[43], and saturated vapour pressure data[44,45]. Only for very few halocarbons does equilibrium exist between the water and overlying air, in most cases the water samples are su-

TABLE IV

CONCENTRATIONS OF HALOCARBONS (ng/l) IN NATURAL WATERS

Compound	Frome river	Avon river	Rain-water**	Rain-water***	Sea-water
$CFCl_2CCl_2F$	1.35	0.92	1.93	0.68	0.62
CH_3I	0.16	0.63	0.70	0.12	0.19
$CHCl_3$	2.4	2.6	3.8	1.06	5.25
CH_3CCl_3	20.6	9.7	4.4	1.4	1.04
CCl_4	0.71	1.1	1.2	0.68	0.68
$CH_2ClCHClCH_3$*	37.8	56.5	33.6	13.6	180.0
$CHCl=CCl_2$	14.0	15.2	0.45	15.0	2.5
CH_2ClCCl_2H*	–	–	–	2.6	4.5
$CHBr_2Cl$	0.97	0.98	0.69	1.9	3.4
CH_2BrCH_2Br*	–	–	4.4	3.2	1.0
$CCl_2=CCl_2$	109.0	14.7	0.73	1.1	1.9
$CHBr_3$*	17.4	20.5	7.7	3.6	31.0

* Identified only on the basis of retention data.
** Collected Sept. 1st, 1983.
*** Collected June 16th, 1983.

persaturated. In fact, in all water samples analysed carbon tetrachloride is the only halocarbon in which the water/air phases are close to equilibrium. Methylchloroform is apparently close to equilibrium in rain-water, also trichlorofluoromethane is in equilibrium with sea-water. For the majority of other halocarbons the water is clearly supersaturated.

The presence of surprisingly large concentrations of industrial halocarbons in two rivers, which flow through predominantly rural areas is most probably due to contamination from local industry and dry cleaning establishments. Of perhaps greater interest is the higher than expected levels of iodomethane and bromoform which strongly suggests that freshwater rivers are a source of these halocarbons. Furthermore, the concentrations of iodomethane and bromoform in both these river-waters and sea-water are roughly comparable (see Table IV). As both halocarbons have been observed previously in sea-water[19,46,47] it seems likely that both freshwater and marine biota are capable of synthesizing these compounds in significant quantities. Rain-water has been found to contain several halocarbons which have not been observed previously in rainfall samples, although their concentrations are generally very low. Bromoform, 1,2-dibromoethane, and dibromochloromethane were all detected at concentrations of approximately 1–10 ng/l. 1,2-Dibromoethane is used primarily as fumigant and petroleum additive, and has been measured in the atmosphere

TABLE V

HENRY'S LAW CONSTANTS CALCULATED FOR HALOCARBONS IN NATURAL WATERS

Values of H are calculated at $ca.$ 20°C:

$$H = \frac{\text{equilibrium concentration in gas phase (g per cm}^3 \text{ of air)}}{\text{equilibrium concentration of unionised dissolved gas in liquid phase (g per cm}^3 \text{ of water)}}$$

Compound	H	Frome river	Avon river	Rain-water*	Rain-water**	Sea-water
$CFCl_3$	3.17	1.6	1.7	1.9	1.98	4.57 (4.06)***
CF_2ClCCl_2F	–	0.14	0.18	0.27	0.88	1.87
CH_3I	0.16§	0.08	0.02	0.02	0.02	0.01 (0.24)***
$CHCl_3$	0.12	0.009	0.03	0.03	0.02	0.02 (0.15)***
CH_3CCl_3	0.42§	0.06	0.14	0.43	0.39	0.34 (0.68)***
CCl_4	0.77§	0.81	0.78	0.76	0.74	1.17 (1.19)***
$CHCl=CCl_2$	0.35	0.01	0.01	0.04	0.02	0.31
$CCl_2=CCl_2$	0.83	0.003	0.02	0.53	0.37	0.53
$CHBr_3$§§	0.017	0.005	0.001	0.002	0.005	0.0005
$CHBr_2Cl$§§	–	0.009	–	0.01	0.009	0.003
CH_2BrCH_2Br§§	0.02	–	–	0.005	0.01	0.02
$CH_2ClCHClCH_3$§§	0.03	0.002	0.002	0.004	0.009	0.0006

* Collected Sept. 1st, 1983.

** Collected June 16th, 1983.

*** Values of H are for sea-water at $ca.$ 18°C (ref. 7).

§ Values of H are for distilled water at $ca.$ 18°C (ref. 7). *NB.* Purging temperatures for water samples are: Frome (20°C); Avon (19°C); Rain* (18°C); Rain** (18°C); sea-water (18°C).

§§ Henry's constants for these compounds have been estimated by assuming a peak area of unity as no peak was observed for these particular halocarbons in ambient air.

of several U.S. cities[42]. Bromoform is now confirmed as a constituent of both fresh and marine waters. It is also produced in drinking water supplies during chlorination, as is dibromochloromethane. Since all three brominated halocarbons have significant water solubilities (≈ 0.4 wt. %) it is reasonable to expect them to be removed from the atmosphere by wet deposition.

A compound with a retention time equivalent to 1,2-dichloropropane was found not only in the two rain-water samples but also in the river- and sea-waters. Although 1,2-dichloropropane has been observed in the atmosphere, albeit at very low concentrations (≈ 0.02 ppb)[42], its apparent presence in natural waters at concentrations exceeding 10 ng/l is surprising and emphasizes the need for more positive identification, especially as both methylene dibromide and trichlorobromomethane have retention times very similar to 1,2-dichloropropane on the column used in these experiments.

In addition to those compounds reported in Table IV, traces of 1,2-dichloroethane, chlorobenzene, and 1,3-dichloropropane have also been observed with concentrations generally below 1 ng/l. While rain-water is approximately saturated with respect to the atmospheric concentrations of both carbon tetrachloride and methylchloroform almost all of the other halocarbons found in rain-water are present at concentrations exceeding those predicted from their calculated Henry's constants (see Table V). For example, there is 7 times more iodomethane, 3–5 times more chloroform, and 8–17 times more trichloroethylene than expected from equilibrium between rain-water and the ambient air. Wet deposition would therefore appear to be an efficient mechanism for scrubbing these compounds from the atmosphere. It also seems reasonable to expect that many of these trace halocarbons will be absorbed onto particulates which will also be removed from the atmosphere during precipitation.

Additional experiments are now underway to further improve the sensitivity of the method and to attempt to confirm the identifications of the ultratrace halocarbons present in natural waters by GC–MS.

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