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DIRECT AQUEOUS INJECTION GAS CHROMATOGRAPHY–MASS SPECTROMETRY FOR ANALYSIS OF ORGANOHALIDES IN WATER AT CONCENTRATIONS BELOW THE PARTS PER BILLION* LEVEL

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SUMMARY

A rapid and precise method for the determination of organohalides in the concentration range of 0.1–50 ppb in water samples is described. The method involves the use of mass fragmentographic gas chromatography–mass spectrometry and direct aqueous injection of a large sample (100 μl) on the column (diglycerol as a liquid phase); no concentration or extraction is required. Tap water samples from five locations in Japan were found to contain numerous organohalides, the concentrations of which were determined.

INTRODUCTION

The determination of mixtures of organic compounds in water is a common analytical problem in studies of environmental contamination. The primary requirement is that detection should be sensitive and stable at maximum sensitivity, and gas chromatography–mass spectrometry (GC–MS) is a suitable technique. However, when the concentration of the individual substance to be determined in the practical water sample is low, GC–MS usually requires a concentration step. The concentration procedures now in use or reported in the literature, such as liquid–solid adsorption[1,2], batchwise or continuous liquid–liquid extraction[3], head-space[4,5], vacuum evaporation and gas-phase stripping[6,7], are laborious and inconvenient.

Recently, Harris *et al.*[8] proposed, to water analysis, a new approach of direct aqueous injection GC–MS which requires no pretreatment. However, the detection limit is not sufficient for relatively clean water, *i.e.*, drinking water or surface water, as the method involves no concentration step. Mass fragmentography meets the sensitivity requirements, surpassing the performance of the electron capture detector, and providing maximum sensitivity of the detectors currently in use.

This paper reports the extension of the direct aqueous injection GC–MS

* Throughout this article the American billion (10^9) is meant.

method to the use of large volume water samples and operation in the mass fragmentography mode, and provides a quantitative survey of organohalides in the Tokyo region drinking water.

EXPERIMENTAL

Apparatus

All analyses were performed on a Finnigan 3300F gas chromatograph–mass spectrometer equipped with a multiple ion detector and operated in the electron impact mode. The interface between the gas chromatograph and the mass spectrometer was an all-glass jet-type enrichment device. The mass spectrometer was set to unit resolution (10% valley between adjacent nominal masses). The resulting ion currents were recorded on a multichannel strip chart recorder. Other conditions held constant throughout the analysis were: helium carrier gas flow-rate (30 ml/min); temperature of the gas chromatograph injection port (200°); pressure in the mass spectrometer ($6 \cdot 10^{-6}$ Torr); ionizing voltage (70 eV); emission current (320 μA).

Column

A 90 cm × 2 mm I.D. metal straight main column was used, in simple conjunction with a 70 cm × 2 mm I.D. metal straight precolumn. The precolumn contained 10% diglycerol on 60/80 mesh Chromosorb W NAW (Johns-Manville, Denver, Colo., U.S.A.) and the main column 5% SE-30 on 60/80 mesh Chromosorb W AW DMCS (Johns-Manville) to allow each organohalide to appear before an overload water peak due to aqueous injection and to achieve the required separation. This situation was made possible by the very long elution time of water by the diglycerol precolumn in comparison to the elution time of the examined organic substances. The longer diglycerol precolumn should be selected in order to elute the higher boiling materials in the particular water sample before the water. Other columns capable of performing the required separation could be used for the main column, depending on whether any interfering substances are present in the sample.

A venting valve (three-way valve, Hoke 316SST), which was connected to the outlet of the main column, was positioned in the column oven to prevent high volume effluent water in the sample (eluting after informative components) from entering the mass spectrometer. Venting of the water allows continuous MS operation without the possibility of damage to the filament or electron multiplier.

The column temperature was maintained isothermally.

Standardization

A series of $CHCl_3$ standard concentrations from 0.1 to 50 ppb was made by successive dilutions into interfering organics-free water with a reagent-grade $CHCl_3$. A series of standard solutions of each organohalide was also made for calibration work. Water used as the diluent was prepared with the Milli-Q water purification system (Millipore, Bedford, Mass., U.S.A.) and then distilled twice. The CH_2Cl_2, $CHCl_3$, $CHBr_3$, CCl_4, $CHCl{=}CCl_2$, $CCl_2{=}CCl_2$, CH_2ClCH_2Cl, CH_3CCl_3, and $CH_2ClCHClCH_3$ used were reagent-grade chemicals (Wako, Osaka, Japan). The $CHClBr_2$ and $CHCl_2Br$ were purchased from Tokyo Kasei (Tokyo, Japan).

Procedure

Water analysis was performed as follows. A 100 μl water sample was injected directly with a 100 μl Hamilton syringe (Model 710). Positive identification of organohalides in the tap water samples is supported not only from known retention times of the standards but also from the selectivity afforded by selected ion monitoring. As the selected ion contains chlorine and/or bromine, isotope clusters were checked to confirm the absence of interferences. Quantitative information was obtained from peak heights.

Although all examined organohalides eluted in less than 6.5 min, this analysis normally required *ca.* 60 min, as the column was maintained at 100° for at least 50 min so that water and less volatile materials would be removed before the next analysis. The short- and long-term stability of the GC–MS system was good throughout the analysis period.

Fig. 1 illustrates typical mass fragmentograms of specific ions of $CHCl=CCl_2$

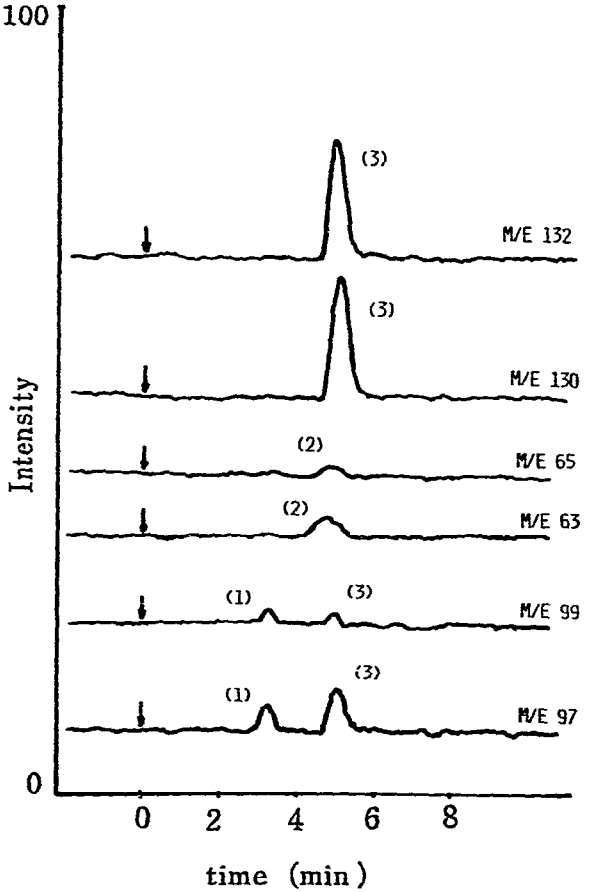

Fig. 1. Six-channel mass fragmentograms obtained from a 100 μl sample of the tap water collected at Tokorosawa near Tokyo. The gas chromatographic effluent is analysed by the mass spectrometer operated in the mass fragmentography mode. The two specific ions in the mass spectrum of each organohalide were monitored. Peaks are: (1) CH_3CCl_3, 0.5 ppb; (2) $CH_2ClCHClCH_3$, 0.8 ppb; $CHCl=CCl_2$, 0.9 ppb.

CH_3CCl_3 and $CH_2ClCHClCH_3$ in a certain tap water, showing no interference from other organics.

RESULTS AND DISCUSSION

Detection limit

Trace components are not easily determined when they appear on the tail of an overload water peak. However, use of a column from which water elutes much later than the organic substances of interest, and injection of very large (100 μl) samples, lead to an extension of the detection limit. As 100 μl of standard solution was injected, it was possible to obtain a clean (signal to noise ratio 3 or greater) mass fragmentogram from each organohalide standard solution of the less than ppb level. Table I summarizes the examined organohalides, the GC–MS conditions, the retention times and the detection limit of each (concentration of single substance producing a peak three times higher than noise level).

TABLE I

ORGANOHALIDES DETECTED IN THE TAP WATER SAMPLE

Organohalide	*Retention time (min)*	*Column temperature (°C)*	*Masses monitored*	*Detection limit (ppb)*
CH_2Cl_2	2.4	50	84, 86	0.2
$CHCl_3$	4.1	50	83, 85	0.1
$CHCl_2Br$	1.8	70	83, 85, 127, 129	0.2
$CHClBr_2$	3.1	70	127, 129	0.1
$CHBr_3$	6.5	70	171, 173	0.2
CCl_4	4.3	50	117, 119	0.8
$CHCl=CCl_2$	5.0	55	130, 132	0.2
$CCl_2=CCl_2$	3.4	70	164, 166	0.1
CH_2ClCH_2Cl	4.8	50	62, 64, 98, 100	0.5
CH_3CCl_3	3.2	55	97, 99	0.4
$CH_2ClCHClCH_3$	4.8	55	63, 65, 97, 99	0.8

Linear concentration range

Detection response was linear over the chosen range of 0.1–50 ppb standard solutions for the organohalides. A plot of six concentrations of each substance in distilled water ranging from 0.1 to 50 ppb against their corresponding peak heights produced a straight line with an intercept at the origin.

Accuracy and precision

The accuracy of the method was determined by making measurements on spiked tap water samples at various concentrations of $CHCl_2Br$ (Table II).

The precision of the method was determined from replicate analyses (five times) of the standard sample at 1 ppb concentration of $CHCl_2Br$, when the standard deviation was 0.14 and the coefficient of variation 4.2% using peak height (mm). These figures are close to the generally accepted best performance of a microlitre

TABLE II

ACCURACY OF MEASUREMENTS ON SPIKED TAP WATER SAMPLES WITH VARYING AMOUNTS OF $CHCl_2Br$ ADDED

$CHCl_2Br$ added (ppb)	*$CHCl_2Br$ found (ppb)*	*$CHCl_2Br$ recovered (ppb)*
0	4.0	0
4	8.1	4.1
6	9.8	5.8
10	14.2	10.2

syringe in the hands of an experienced operator. Similar results were obtained for all compounds examined, although a decrease in precision was observed at near the detection limit. Direct aqueous injection of relatively large quantities on the diglycerol precolumn had no significant effect on the precision.

Application to tap water sample

Numerous organohalides have been discovered in the drinking water supplies of many major U.S. cities[2,3,6,7,9,10]. As the method described has proved to be sensitive, accurate and precise for the analysis of organohalides in water samples, it was applied to the analysis of organohalides in the Tokyo region tap water.

Table III summarizes the substances determined in the drinking tap water of five locations near Tokyo. $CHCl_3$ was the major component with concentrations in the low ppb range which represented a very large peak in the mass fragmentograms. The profiles obtained from various tap water samples showed similar patterns, although variations in the total concentration were large. Other researchers[3,11] have confirmed the hypothesis that nearly all of these compounds are generated only during water treatment, and possible mechanism for their formation are being studied. As

TABLE III

ORGANOHALIDE CONCENTRATIONS (ppb) IN JAPANESE TAP WATER SAMPLES (11 DECEMBER 1976)

Organohalide	*Tokorosawa**	*Fussa***	*Tsuchiura****	*Urawa†*	*Hanamuro††*
CH_2Cl_2	0.3	—	—	—	—
$CHCl_3$	10.2	2.6	13.0	2.7	17.2
$CHCl_2Br$	6.4	1.6	10.5	2.3	4.0
$CHClBr_2$	3.2	0.6	4.0	1.4	0.6
$CHBr_3$	0.5	—	0.4	0.3	—
CCl_4	1.2	—	—	—	—
$CHCl{=}CCl_2$	0.9	—	0.7	—	—
$CCl_2{=}CCl_2$	0.6	0.2	0.2	0.2	0.2
CH_2ClCH_2Cl	0.9	—	—	—	—
CH_3CCl_3	0.5	—	—	—	—
$CH_2ClCHClCH_3$	0.8	—	—	—	—

* Located 30 miles NE of Tokyo.
** Located 30 miles E corner of Tokyo.
*** Located 40 miles W of Tokyo.
† Located 20 miles N of Tokyo.
†† Located in Tsukuba Research Center.

the above method is capable of monitoring the products, these mechanisms will be studied successively.

CONCLUSION

This study has demonstrated that direct aqueous injection GC–MS is an effective and practical method for the measurement of organohalides in water samples. High sensitivity (less than 1 ppb detectable) and precision were afforded by the large water sample injection and operations in the mass fragmentography mode. The diglycerol precolumn has an extremely long retention time for water in comparison to that of many organic substances, so that the latter appear before a large peak due to water in the sample. This method is not applicable to all trace organic compounds in water; those which elute later than water cannot be determined. However, it is versatile and convenient and can be applied to relatively volatile compounds, such as phenols, alcohols, ketones, hydrocarbons and amines. Vinyl chloride is one compound of considerable interest that can be determined by this method.

Direct aqueous injection GC–MS could be further modified, perhaps by the aqueous injection of large quantities on cross-linked porous polymer packed columns, from which water elutes very quickly, with concentrated significant organics retained for measurement.

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