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A Method for the Analysis of Halogenated Organic Compounds in Tap Water by Means of Mass Fragmentography of GC-MS

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A simple, sensitive and practical method for the halogenated organic compound analysis of tap water is reported. A pentane extraction procedure using a ten fold increase in concentration by volume (without further concentration) followed by mass fragmentography of GC-MS was used. As little as 0.05 ppb concentration of each compound was detectable. Five simple halogenated organic compounds, including CCl_4 and $CHBr_3$ whose concentrations are relatively small, were determined for tap water in Japan.

Recent years have seen an increasing concern[1,2] for levels of trace organic contaminants in water ultimately used for human consumption. In some cases less than 1 μg/l (1ppb) of the minimum detectable limit is required for specific compounds. This concentration is significant and all methods should approach this sensitivity requirement. Until now, procedures used for obtaining the required sensitivity have involved some sort of extraction procedure. Solvent extraction,[3–5] followed by further concentration for extreme trace concentration samples, has been commonly used. Although this method meets the sensitivity requirement, it suffers from serious interferences due to accumulation of solvent impurities as well as the informative substances.

However, solvent extraction without further concentration can be successfully applied to even extreme trace concentrations, when very high sensitive and specific detection is possible. Mass fragmentography[6] of GC-MS is a useful technique to meet the high sensitive and specific detection requirement, which provides specific information at a sensitive level that often surpasses that of the electron capture detector. I wish to report here a method for the analysis of halogenated organic compounds in tap water, utilizing mass fragmentography of GC-MS. A pentane extraction procedure without further concentration followed by mass fragmentography of GC-MS does not seem to have been reported.

Experimental

Apparatus. Gas chromatographic separation and mass spectrometric analysis were performed on a Finnigan 3300F gas chromatograph-quadrupole mass spectrometer equipped with multiple ion detector (Finnigan, PROMIM), by which mass fragmentography can be carried out. A selected mass can be quickly set with the aid of a digital mass marker display. The GC-MS interface utilizes an all glass jet-type enrichment device. A 3 m × 2 mm (i.d.) glass column packed with 5% SE-30 on 60/80 mesh Chromosorb W. AW. DMCS. (Johns-Manville) was used. Other conditions were: flow rate of helium carrier gas 30 ml/min, temperature of gas chromatograph injection port 200 °C, temperature of interface and transfer line 200 °C, pressure in the mass spectrometer 6×10^{-6} Torr, electron energy 70 eV, emission current 0.45 mA, electron multiplier 1450 volts.

Standard Solutions. A series of $CHCl_3$ standard concentrations in the range 0.5—400 ppb were made by successive dilution into special grade pentane (Wako pure chemicals) starting with pure $CHCl_3$ (Dojin chemicals). Calibration standards were made from pure reagents for each organohalide, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, and CCl_4 (Tokyo Kasei chemicals). Water used for recovery works was prepared by double distillation of ground water.

Procedure. Pretreatment of water samples was performed as follows, using pentane extraction procedure as a concentration technique. 10 ml of pentane was floated on 100 ml of water samples in a tightly closed container and agitated rigorously for 10 min. 10 μl injection of the extract was then made with a 10-μl Hamilton syringe (701-RN). At the start of each run the column was maintained at 40 °C for 7 min and programmed from 40 to 70 °C at 4 °C/min. The mass spectrometer was set to unit resolution (10% valley between adjacent nominal masses). The mass spectrometer was then set to monitor a specific mass of the examined compounds. The resulting ion currents were recorded on a strip chart recorder.

Positive identification of the compounds is supported not only by known retention times of the standards but also by the selectivity afforded by specific ion detection. The ions chosen to be monitored[7] include the chlorine and (or) bromine of each compound. Comparison of the expected ratio of isotope clusters with the observed ratio gives the permissible limit for analyzing unknown substances and determining whether they are free of coeluting impurities. Quantitative information was obtained using peak areas.

Results and Discussion

Detection Limit. Detection response (peak area) was linear over the range of standard solutions for each organohalide. The range was chosen to cover the concentrations likely to be found in various tap water samples. The detection limit of each compound (concentration of substance producing a peak five times higher than noise level) was found to be 0.5 ppb. Thus, water samples of 0.05 ppb concentration compound were determined by the extraction procedure using a ten fold increase in concentration by volume (10 ml of pentane per 100ml of water).

Recovery. Recovery was tested with amounts of the examined compounds similar to those which would be present in samples. A testing solution for recovery was prepared by mixing standard solutions of the compounds in treated and pretested water. The extraction was carried out as mentioned above. Recovery of each compound is given in Table 1. It is seen that efficient recovery was obtained for all tested substances, although a decrease in precision was observed at low concentration levels.

Table 1. Recovery of the halogenated organic compounds spiked into water

Compounds	Concentration added to water (μg/l)	Average[a] recovery (%)
$CHCl_3$	20	96±4
$CHCl_2Br$	1	94±8
$CHClBr_2$	1	93±7
$CHBr_3$	0.1	95±15
CCl_4	0.1	109±18

a) Average of five recovery works.

Table 2. Halogenated organic compounds in tap water

Compounds	Retention time (min)	Mass monitored (*m*/*e*)
$CHCl_3$	3.9	83,[a] 85
$CHCl_2Br$	7.2	83, 85, 127,[a] 129
$CHClBr_2$	10.8	127,[a] 129
$CHBr_3$	14.5	171, 173,[a] 175
CCl_4	4.9	117, 119[a]

a) Specific ions chosen for quantitative information of each compound.

Table 3. Halogenated organic compound concentrations (ppb) in tap water sample (July 8, 1976)

Location	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	CCl_4
Hanamuro[a]	22.5	0.6	0.24	undetectable	0.1
Kanamachi[b]	17.5	2.6	1.7	0.06	0.08
Hamura[c]	18.8	1.0	0.53	undetectable	0.05

a) Tsukuba Research Center. b) West Tokyo. c) East Tokyo.

Solvent. The pentane used as the diluent of the standard solutions and the solvent of the extraction was found to contain no detectable $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ with the exception of $CHCl_3$ and CCl_4. The presence of $CHCl_3$ (0.06 ppb to be estimated with exploration) and CCl_4 (0.05 ppb) as a trace contaminant in pentane limited the accuracy. However, there is no trouble with $CHCl_3$ since its amount is negligibly small to affect the signal. There is a much wider choice of solvents, such as the higher alkanes. However, these solvents obscure the volatile extraction components. It is more difficult to obtain them in sufficient purity. Pentane was found to be the most suitable solvent.

Tap Water Analysis. Many halogenated organic compounds have been found in tap water in the U. S.,[1,2,5,8–10] considerable interest in their determination being aroused. Analyses were made in an attempt to survey the amounts of five halogenated organic compounds in tap water in Japan. Table 2 summarizes their retention times and masses monitored. These compounds were major components of the halogenated organic compounds discovered in the U.S. water supplies. Figure 1 shows typical mass fragmentograms (*m*/*e* 83, 119, 127, 173), results of the analysis of tap water taken at Kanamachi in Tokyo. The results of measurements are given in Table 3. The $CHCl_2Br$ and $CHClBr_2$ concentrations were remarkably invariant. The related compound $CHBr_3$ was found in very low concentrations (0.06 ppb). The CCl_4 levels were very low. Individual samples of CCl_4 produced the same or a slightly higher peak than that of the trace contaminants in pentane. Quantitative values of CCl_4 were obtained by subtracting the amount of CCl_4 trace contaminants in pentane.

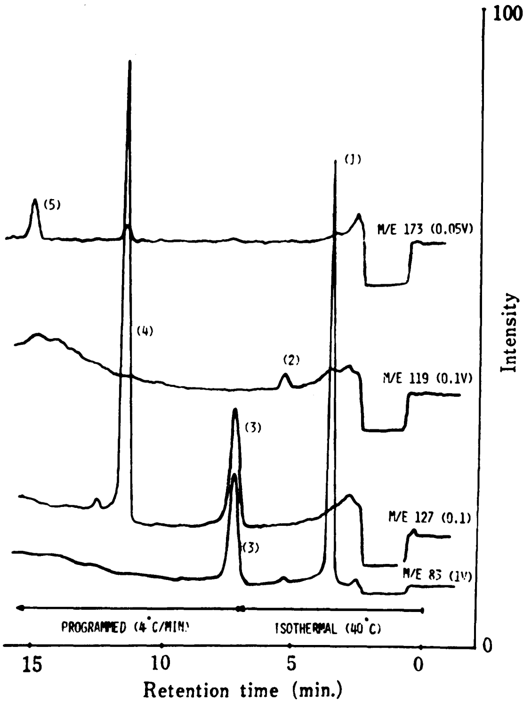

Fig. 1. Typical analysis of halogenated organic compounds in the tap water by mass fragmentography. A 10 μl injection.

Peaks are: (1) $CHCl_3$, (2) CCl_4, (3) $CHCl_2Br$, (4) $CHClBr_2$, (5) $CHBr_3$.

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