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Re-evaluation of solid-phase adsorption and desorption techniques for isolation of trace organic pollutants from chlorinated water

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ABSTRACT

Amberlite XAD resin and activated carbon columns were tested for their abilities to concentrate trace organic pollutants in chlorinated water. Both XAD-2 and XAD-7 resin columns (20 ml) were capable of adsorbing about 30% of total organic halogen (TOX) present in 20 l of drinking water (pH 7) containing about 100 μg/l of TOX, whereas the carbon column (10 ml) adsorbed over 90% of TOX. The adsorption capacity of XAD-7 resin was found to be strongly dependent on the solution pH, as compared with those of XAD-2 and carbon adsorbents. Soxhlet and sonication extractions were also evaluated for their abilities to recover the adsorbed organics from the adsorbents, by measurements of TOX, chromatographable compounds and mutagenicity in the eluates. Soxhlet extraction gave higher recoveries than sonication, as measured with the above indices, but these differences were generally small (*ca.* 20%), with exception of the carbon extracts. The XAD-2 and XAD-7 extracts of drinking water also showed about 3–4 times higher mutagenic activity than the carbon extracts.

INTRODUCTION

Chlorination is widely used in wastewater and water treatment plants to control harmful microorganisms in water, and in several bleaching steps in the pulp and paper industry. However, this is now considered as a major source of organic halogens, one class of which is called as purgeable organic halogens (POX), including trihalomethanes (THMs), and another non-purgeable organic halogens (NPOX), found in drinking water [1,2] and natural waters [3,4]. Although THMs are of concern, because of both their effects on health [5–7] and their significant levels in water, recent work has shown that the even higher levels of NPOX can be formed from chlorination of the organic compounds in natural water [8–13]. Because it has also been shown that the mutagenic character of drinking water is more closely associated with the concentrations of NPOX [7,14–16], it seems reasonable to consider not only the occurrence of THM but also of NPOX in chlorinated water. However, no simple and accurate method exists for the identification and determination of the major individual NPOX that are formed as the result of chlorination.

The potential health effects of organic contaminants in chlorinated water can be studied only after they have been isolated from the water and identified. However, because most of these compounds are present at micrograms per litre (ppb) levels or less in water, a concentration step is necessary prior to the identification of individual contaminants. Conventional techniques used for isolating organic compounds from the water for analytical purposes include liquid–liquid extraction [17–20], carbon adsorption [16,21–25] and resin adsorption [21,25–32]. These methods, like other concentration procedures, fail to provide a totally representative concentrate as one or more groups of organic compo-

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nents are not recovered effectively. Consequently, systematic evaluation of different extraction methods for several group parameters in water is important in developing an effective concentration procedure.

The aim of this study was to re-evaluate common solid-phase extractions for isolating trace organic pollutants from chlorinated water, using XAD-2 and XAD-7 resins and activated carbon. The adsorption capacity of these water pollutants on each adsorbent and the desorption efficiency of these compounds using Soxhlet and sonication extraction were evaluated by measurements of different indices such as TOX, chromatographable compounds and mutagenicity.

EXPERIMENTAL

Materials

Organic solvents (acetone, *n*-hexane, and methanol) were of analytical-reagent grade for pesticide residue analysis (Wako, Osaka, Japan). They were checked for purity by evaporating 100 ml to 100 μl followed by gas chromatographic (GC) and TOX analyses. High-purity water obtained from a Milli-Q purifier system (Millipore) was used throughout. Chlorinated humic solution as humus-rich model water was prepared by treatment with hypochlorite of humic acid (5 mg/l as total organic carbon; Fluka, Buchs, Switzerland) at a Cl:C molar ratio of 5 and at pH 7 for 24 h. The residual chlorine was removed by addition of an equivalent volume of sodium thiosulphate solution. The concentrations of TOX in the chlorinated humic solution were determined by with a TOX analyser.

The adsorbents, XAD-2 and XAD-7 resins (20–50 mesh) (Rohm and Hass, Philadelphia, PA, USA) and activated carbon (AMF QUNO), were commercially available. Fines were removed by decanting after slurrying in water. The resin and carbon adsorbents were washed in a Soxhlet extractor with acetone–*n*-hexane (50:50, v/v) for 24 h, in order to remove interferences from the adsorbents. During the cleaning, a portion of the solvent was evaporated and checked for interferences by GC. If necessary, the solvent washing in the Soxhlet extractor was repeated. When the blank chromatogram showed no interferences, the adsorbents were removed from the extractor. The solvent remaining on the adsorbents was then evaporated completely in a vacuum desiccator for 24 h. The purified adsorbents were stored under methanol.

Adsorption and desorption tests

The cleaned XAD-2 (20 ml), XAD-7 (20 ml) and carbon (10 ml) materials were separately packed in small-scale glass columns (15 cm × 2 cm I.D.) equipped with a No. 2 glass filter and a PTFE stopcock. Before processing a 20-l water sample, the column was washed with a 2 l of water. Drinking water or the chlorinated humic solution was introduced bottom-to-top into the column, which was connected directly to the water tap in the laboratory or to the water tank (20 l). Water samples were continuously passed through the column at room temperature at a flow-rate of 2 bed volumes/min. An SF-160 fraction collector (Toyo, Tokyo, Japan) was used for collection of water fractions to measure breakthrough curves. The adsorption efficiencies of the adsorbents were investigated by monitoring the concentrations of TOX in the effluent fractions.

After processing a 20-l sample of the chlorinated water, the column was washed with 500 ml of 0.08 *M* sodium nitrate solution to remove residual chloride ions on the adsorbent. The remaining water in the column was gently evaporated at room temperature under a light stream of dry nitrogen. Each adsorbent was removed from the column and the organic substances on the adsorbent were then extracted by sonication with 20 ml of acetone–*n*-hexane (50:50, v/v) for the small-scale column. The sonication extractions were repeated twice more with a fresh 20-ml volume of the solvent mixture. Soxhlet extractions were also performed using the same mixed solvent for 4 h, in order to remove the organic substances from each adsorbent. These extracts were dried over anhydrous sodium sulphate and evaporated to dryness by means of a rotary evaporator at 40°C. The dry concentrate was dissolved, as rapidly as possible, in 2 ml of diethyl ether or methanbol, producing a concentration factor of 10^4, and stored in a refrigerator at 4°C until the subsequent analyses were performed.

A large-scale glass column (16 cm × 4 cm I.D.) equipped with a No. 2 glass filter and a PTFE stopcock, which was packed with 200 ml of each cleaned adsorbent, was also used for the isolation of trace organic pollutants in drinking water [33], in order

to study their mutagenic activities and chemical characteristics.

Organic halogen determination

The activated carbon–microcoulometric method was carried out with a Mitsubishi Chemical TOX-10 organic halogen analyser to determine the TOX in the water samples and in the acetone–hexane extracts. The analytical procedures for TOX determinations in these samples were essentially the same as in a previous study [3]. The corresponding detection limits were *ca.* 5 μg/l for the carbon adsorption method and 2.5 μg/l for the mixed solvent extraction method.

Gas chromatography

The Soxhlet- and sonication-extracted organics were analysed using a Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector [33,34]. A glass column (2 m × 2 mm I.D.) packed with 2% OV-1 on Uniport HP (60–80 mesh) was employed. The temperature of the column oven was increased from 80 to 260°C at 5°C/min. The carrier gas (nitrogen) flow-rate was 40 ml/min. A Shimadzu Chromatopac-1A data system was used to determine the retention times and peak areas on the chromatograms.

Mutagenicity tests

The mutagenicity of the samples was tested according to the method of Ames *et al.* [35] with minor modifications. *Salmonella typhimurium* strain TA 100 was used through the experiments in the absence of metabolic activation, because most of the extracts of chlorinated water have been shown to be active in this system [25]. The samples were dissolved in methanol and pre-incubated with the strain at 37°C for 30 min (prior to plating). After addition of the test samples, the plates were incubated at 37°C for 2 days. The assay was performed in triplicate for each sample. The mutagenic activity is expressed as the mean value of mutagenicity ratios (revertants of sample/revertants of control).

RESULTS AND DISCUSSION

Comparison of the adsorption capacities of XAD resins and carbon

The adsorption of organic compounds from aqueous solution on XAD resins and activated carbon has been extensively used for the study of volatile organic compounds. Compounds evaluated in previous studies include pesticides [36–39], polycyclic aromatic hydrocarbons [40–43], polychlorinated biphenyls [44] and chlorophenols [45–47]. Although the recovery efficiency of these volatile organics by resin adsorption has been well established, little information is available on the non-volatile organics in chlorinated water, which are not amenable to GC. The capacities of XAD-2, XAD-7 and activated carbon to adsorb the non-volatile organics were therefore determined by TOX measurements in aqueous samples, because the concentrations of TOX have been shown to be closely associated with the mutagenicity of chlorinated drinking water [15,16].

Fig. 1 shows the breakthrough curves of TOX in chlorinated humic solution (pH 7) and drinking water (pH 7) on small-scale resin and carbon columns at a flow-rate of 2 bed volumes/min. The greater capability of the carbon column to adsorb TOX from the chlorinated humic solution (1000 μg/l of TOX) and drinking water (100 μg/l of TOX) was observed even after passing water sample of 20 l. In contrast, only 30% of the original TOX (100 μg/l) present in drinking water could be adsorbed on the two resin columns when a 20-l sample of water was passed through.

Because the XAD resins are non-ionic in nature, ionic organic compounds are adsorbed more efficiently on the resins at a pH at which ionization is suppressed, while neutral compounds are adsorbed independent of pH. Therefore, at normal drinking water pH, which is generally neutral, acidic organic compounds are ionized, whereas at pH 2, ionization is suppressed and they are retained more efficiently. In order to confirm this fact, subsequent experiments were conducted to determine the capacity of the resins and carbon columns to adsorb the organic halogens under the various pH conditions and using chlorinated waters containing 100 and 1000 μg/l of TOX.

Table I shows the influence of solution pH on the adsorption on the small-scale XAD-2, XAD-7 and carbon columns of TOX in 2 l of a chlorinated water sample after passing it through the column at a flow-rate of 2 bed volumes/min. A decrease in the solution pH resulted in an increase in the amounts

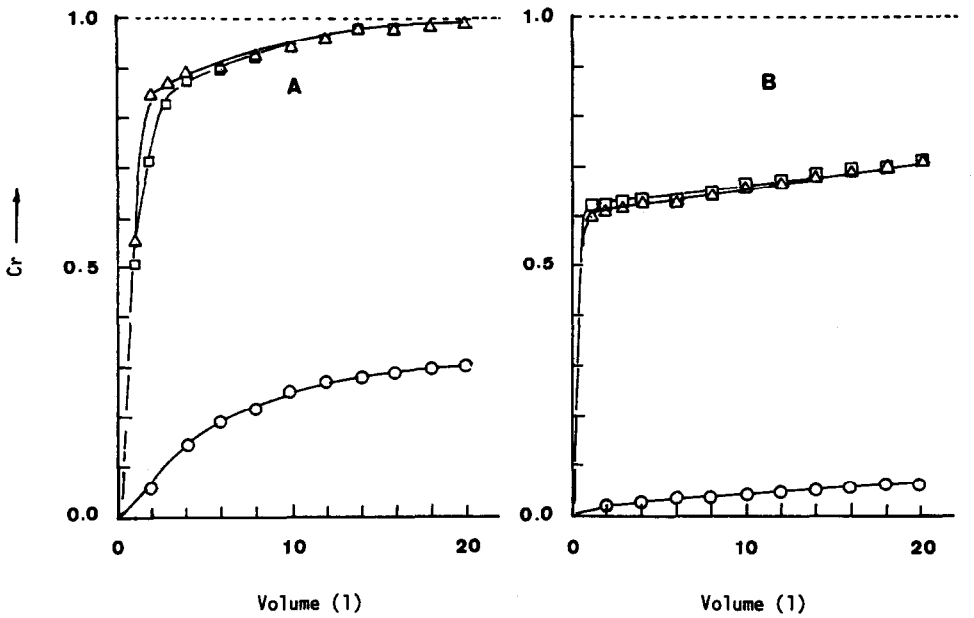

Fig. 1. Breakthorough curves of total organic halogen (TOX) on activated carbon (10 ml) and XAD resins (20 ml), measured as relative concentrations of TOX in aqueous effluent fraction. (A) Chlorinated humic solution (TOX = 1000 μg/l and pH 7); (B) drinking water (100 μg/l and pH 7). $C_r = C_e/C_i$, where C_e and C_i are the concentrations of TOX in the effluent and influent, respectively. △ = XAD-2; □ = XAD-7; ○ = carbon.

of adsorbable TOX on these adsorbents. Especially the capability of the XAD-7 column to adsorb TOX in drinking water was found to be strongly dependent on the solution pH, in contrast to those of XAD-2 and carbon adsorbents. About 90% of the original TOX present in the 2-l water sample was adsorbed on the XAD-7 resin at pH 2, whereas at pH 7 only 50% of the TOX was retained on this resin. This phenomenon agrees with the observation that certain mutagenic substances could be adsorbed on resins after acidification of water samples [26,30,32,48]. It is also known that XAD-2 has a

TABLE I

EFFECT OF THE SOLUTION pH VALUES ON ADSORPTION ON XAD RESIN AND ACTIVATED CARBON COLUMNS OF TOTAL ORGANIC HALOGEN (TOX) IN WATER

Volume of 2 l of chlorinated water samples were separately passed through each column at a flow-rate of 2 bed volumes/min at room temperature. The amounts of TOX adsorbed on each packing material were calculated from measurements of TOX concentrations in the effluent and influent.

Water sample	Packing material	Adsorption efficiency of TOX (μg per column)			
		pH 2	pH 4	pH 6	pH 7
Drinking water (100 μg/l of TOX)	XAD-2 (20 ml)	127 (63.5%)	119 (59.5%)	112 (56.0%)	100 (50.0%)
	XAD-7 (20 ml)	179 (89.5%)	153 (76.5%)	120 (60.0%)	100 (50.0%)
	Carbon (10 ml)	200 (100%)	198 (99.0%)	194 (97.0%)	190 (95.0%)
Chlorinated humic solution (1000 μg/l of TOX)	XAD-2 (20 ml)	1090 (54.5%)	1040 (52.0%)	920 (46.0%)	800 (40.0%)
	XAD-7 (20 ml)	1350 (67.5%)	1260 (63.0%)	1170 (58.5%)	960 (48.0%)
	Carbon (10 ml)	2000 (100%)	1980 (99.0%)	1940 (97.0%)	1900 (95.0%)

high affinity for non-polar compounds [26], whereas XAD-7 has been found to be more efficient in the recovery of polar compounds such as humic acids [49]. Hence it seems that 40% of the XAD-7 resin-adsorbable TOX present in drinking water at pH 2 consists of ionic organic halogens and about 50% non-polar halogenated organics.

Comparison of Soxhlet extraction and sonication techniques for isolation of organic substances from the adsorbents

The most popular method for the elution of adsorbed compounds is direct addition of diethyl ether to the wet column followed by a 10-min penetration period before drawing off the solvent. However, our experience showed that the in-column elution procedure with any organic solvent did not give uniformly high recoveries of organic materials from the adsorbents. Therefore, the classical Soxhlet elution method and sonication extraction for isolating the adsorbed organics on the XAD resins and carbon were performed using acetone-*n*-hexane (50:50, v/v) as the eluting solvent. The desorption efficiencies were evaluated for both extraction methods by measurements of TOX, chromatographable compounds and Ames mutagenicity of the eluates.

TOX. Table II shows the efficiency of recovery of the adsorbed organics on XAD-2, XAD-7 and activated carbon using the Soxhlet and sonication techniques, evaluated by measurements of TOX in the eluates. Before Soxhlet and sonication extractions are performed, 20 l of chlorinated humic solution containing 1000 μg/l of TOX were separately passed through the column at a flow-rate of 2 bed volumes/min. A low recovery efficiency of $< 10\%$ for the adsorbed TOX from these adsorbents was observed with both extraction systems. In particular, a poor recovery of the adsorbed TOX from the carbon adsorbent was observed when sonication extraction was performed. However, Soxhlet extraction was more effective in recovering the adsorbable TOX than the sonication technique, with the highest efficiency from XAD-7 resin. These results are in agreement with those reported previously [50].

Chromatographable compounds. On the basis of TOX measurements, subsequent investigations were performed to determine the chromatographable compounds in the Soxhlet and sonication extracts, using a packed column and flame ionization detection (FID). Fig. 2 shows the gas chromatograms of the sonication extracts from XAD-2, XAD-7 and carbon adsorbents after processing 20 l of the chlorinated humic solution containing 1000 μl/g of TOX. Over 40 compounds that respond to FID were detected in both resin extracts. In contrast, small numbers of compounds were found in the carbon extract even though the highest TOX content, most of which is likely to the chlorinated organic acids, had been detected in this extract (see Table II). Of note is the higher recovery of XAD resin-extractable organics with longer retention times in sonication extraction, as can be seen in Fig. 2.

Because of the complexity and the very low concentrations of these organic compounds, the exact nature of the individual compounds corresponding to each peak on the chromatograms was not estab-

TABLE II

EXTRACTION EFFICIENCY OF TOTAL ORGANIC HALOGEN (TOX) FROM XAD-2 (20 ml), XAD-7 (20 ml) AND ACTIVATED CARBON (10 ml) BY SONICATION AND SOXHLET TECHNIQUES AFTER PROCESSING OF 20 l OF CHLORINATED HUMIC SOLUTION (pH 7) CONTAINING 1000 μg/l OF TOX

The values are averages of three determinations.

Packing material	Amount of TOX (mg/per adsorbent)		
	Retained on the material	Sonication extractable	Soxhlet extractable
XAD-2	1.50 (100%)	0.05 (3.33%)	0.08 (5.33%)
XAD-7	1.60 (100%)	0.07 (4.37%)	0.12 (7.50%)
Carbon	12.80 (100%)	0.09 (0.70%)	0.34 (2.65%)

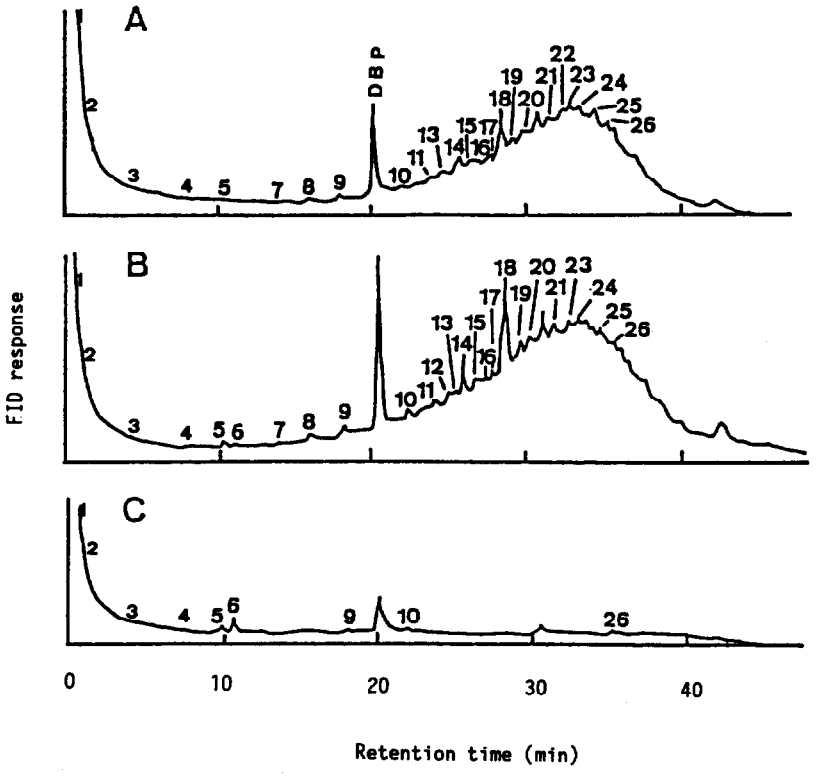

Fig. 2. Gas chromatograms (flame ionization detection) of acetone–*n*-hexane (50:50, v/v) extracts of chlorinated humic solution (1000 μg/l of TOX and pH 7) obtained through (A) XAD-2, (B) XAD-7 and (C) activated carbon adsorption and subsequent sonication extraction. Before the extraction, 20 l of the water sample were passed through the column at a flow-rate of 2 bed volumes/min. The temperature of the GC column (packed with 2% OV-1 on Uniport HP) was raised from 80 to 260°C at 5°C/min. A 5-μl volume of the extract, equivalent to 5 ml of chlorinated humic solution, was injected into the column. The numbered peaks were used for evaluation of each extract with respect to the concentrations of organic compounds in water.

lished. Consequently, the individual peak areas of compounds appearing on the chromatograms were measured using a Shimadzu Chromatopac-1A integrator and the amount of each compound in the extracts was then evaluated from the GC peak area, relative to the area of corresponding compounds in the XAD-7 extract.

Table III shows the extraction efficiency of the chromatographable compounds in chlorinated humic solution using XAD resin or activated carbon adsorption and subsequent Soxhlet or sonication desorption. The total amounts of chromatographable compounds in the XAD-7 extracts obtained by both Soxhlet and sonication extraction were found to be about 2 and 100 times greater than those observed for the XAD-2 and carbon extracts, respectively. Soxhlet extraction resulted in an increase in the amounts of chromatographable compounds, but the differences between Soxhlet and sonication extraction were not very large (*ca.* 20%), with the exception of the carbon extracts. Hence it seems that over 70% of the adsorbed organics obtained by Soxhlet extraction can be recovered from the XAD resins using sonication extraction.

Mutagenicity. On the basis of TOX and chromatographable compound analyses of the water concentrates, further experiments were conducted to determine the mutagenic acitvities of XAD-2, XAD-7 and activated carbon extracts obtained through Soxhlet and sonication extractions. Be-

TABLE III

EXTRACTION EFFICIENCY OF CHROMATOGRAPHABLE COMPOUNDS FROM XAD RESIN (20 ml) AND ACTIVATED CARBON (10 ml) COLUMNS

Before extraction, 20 l of chlorinated humic solution (pH 7) containing 1000 μg/l of TOX were passed through the column at a flow-rate of 2 bed volumes/min. The amount of each compound was calculated from the GC peak area relative to the area of corresponding compounds in the XAD-7–Soxhlet extract.

Compound		Amount detected (%)					
Peak no. in Fig. 2	Retention time (min)	XAD-7		XAD-2		Carbon	
		Soxhlet	Sonication	Soxhlet	Sonication	Soxhlet	Sonication
1	0.52	100	0	0	0	2	0
2	1.26	0	0	0	0	100	0
3	3.72	100	0	341	0	2655	0
4	7.77	100	0	100	0	146	0
5	10.16	100	63	65	17	70	15
6	10.87	100	23	132	5	58	43
7	13.96	100	33	77	25	59	0
8	15.79	100	100	79	76	69	0
9	17.96	100	81	84	57	21	3
10	22.06	100	18	100	29	44	6
11	23.89	100	77	69	41	14	0
12	24.56	100	0	0	0	71	0
13	25.19	100	100	97	61	0	0
14	25.73	100	88	54	39	12	0
15	26.42	100	89	67	56	8	0
16	26.86	100	93	61	50	9	0
17	27.46	100	77	73	40	43	0
18	28.56	100	86	48	47	1	0
19	29.12	100	94	41	29	9	0
20	29.76	100	96	40	35	1	0
21	31.39	100	100	54	54	0	0
22	32.26	100	89	53	30	2	0
23	32.89	100	100	70	68	0	0
24	33.33	100	100	40	40	1	0
25	34.39	100	92	100	90	0	0
26	35.26	100	48	100	52	59	15

TABLE IV

COMPARISON OF THE AMES MUTAGENIC ACTIVITY, TOX CONTENT AND GAS CHROMATOGRAPHABLE (GC) COMPOUNDS IN DRINKING WATER CONCENTRATES OBTAINED THROUGH SOLID-PHASE ADSORPTION AND SUBSEQUENT SONICATION EXTRACTION

A large-scale column packed with each adsorbent was used for the isolation of organic pollutants from 2000 l of drinking water at a flow-rate of 2 bed volumes/min. The values are averages of three determinations.

Packing material	Mutagenicity (revertants/l)	TOX content (μg/l)	GC compounds (GC counts/l)
XAD-2	138	2.17	84.7
XAD-7	134	3.25	97.2
Carbon	43	1.27	38.6

cause the extracts of the chlorinated humic solution showed a poor or scattered mutagenicity in the test strain, only drinking water concentrates obtained with a large-scale column were tested for their mutagenicities.

The Ames mutagenic assays and TOX and chromatographable compound determinations in the resins and carbon extracts of drinking water obtained by both Soxhlet and sonication extractions are summarized in Table IV. The recovery of mutagenicity from drinking water using XAD-2 and XAD-7 adsorption and subsequent sonication extraction was about 3–4 times greater than that of the carbon adsorption. The use of Soxhlet extraction provided an efficient recovery of mutagenicity from the activated carbon. However, the efficiency of recovery from the resins by Soxhlet extraction was not as high as that observed with the sonication technique. This can be explained in terms of the substantial destruction of mutagenic compounds on heating [25] and of the co-extraction of compounds that exhibits toxicity to the test strain during Soxhlet extraction procedure.

In connection with mutagenic activity in the drinking water concentrates, these extracts were also chromatographed using a packed column and FID. Fig. 3 shows the gas chromatograms of XAD resin and carbon extracts obtained through sonication extraction. A large difference between the compositions of chromatographable organics present in drinking water and chlorinated humic solution is seen in the chromatograms in Figs. 2 and 3. Several compounds with relatively shorter retention times were detected on the chromatograms of the resin

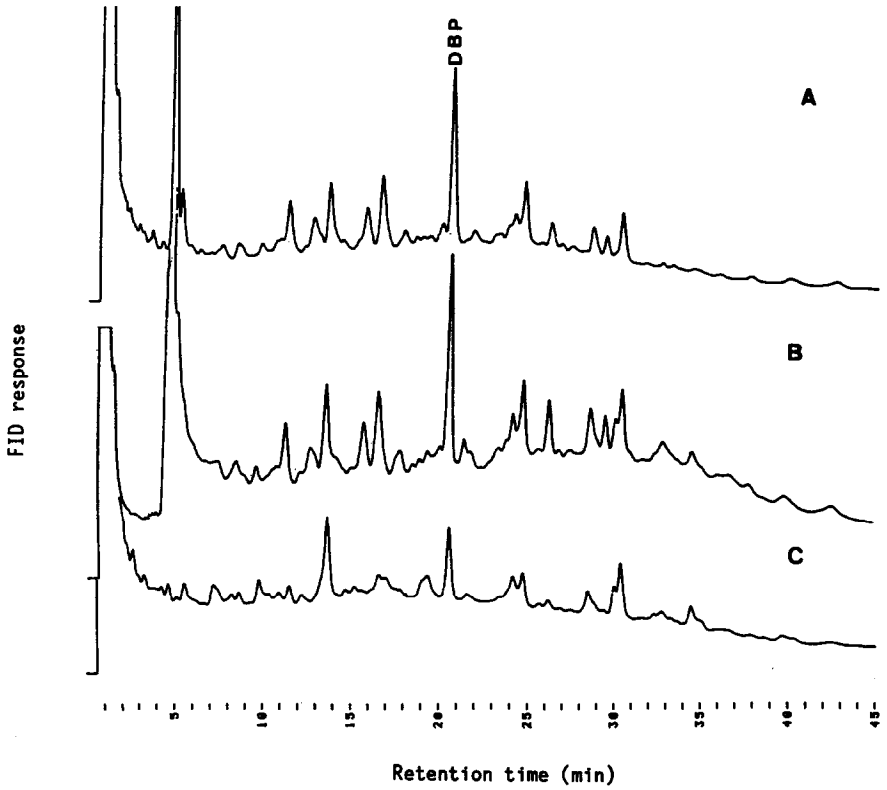

Fig. 3. Gas chromatograms (flame ionization detection) of acetone–*n*-hexane (50:50, v/v) extracts of drinking water (TOX = 100 μg/l and pH 7) obtained through (A) XAD-2, (B) XAD-7 and (C) activated carbon adsorption and subsequent sonication extraction. GC column temperature programme as in Fig. 2. A 5-μl of volume of the extract, equivalent to 5 l of drinking water, was injected into the column.

extracts of drinking water, whereas compounds with relatively longer retention times were present in the resin extracts of the chlorinated humic solution. This indicates the presence of not only naturally occurring organics, similar to humic acids, but also man-made chemicals in drinking water. The presence of synthetic compounds such as phthalate esters and polyaromatic hydrocarbons in the mutagenic resin extracts of drinking water has been reported previously [33].

In this work, common solid-phase extractions for the isolation of trace organic pollutants in chlorinated water were compared by measurements of some group parameters. Because various organic halogen compounds with a wide polarity range are present in chlorinated water, it is not surprising that low recoveries of TOX from the resin and carbon adsorbents by both Soxhlet and sonication extractions was obtained [51]. Recent studies [52–55] have demonstrated that chemically bonded silica and graphitized carbon black are effective for the solid-phase extraction of trace organic substances from water. Therefore, a further investigation will be conducted to determine and compare the extraction efficiencies of these adsorbents.

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