BNWL-SA-6266

CONF-7708108--1

INVESTIGATION OF TRACE ORGANIC COMPONENTS IN CHLORINATED NATURAL WATERS USING GLASS WCOT COLUMNS

R. M. Bean, P. W. Ryan and R. G. Riley

Battelle, Pacific Northwest Laboratories

P. O. Box 999

Richland, Washington 99352

To be published in:

The proceedings of the Symposium on High Resolution Gas Chromatography of the American Chemical Society, August 28 - September 2, 1977, Chicago, IL, Academic Press.

DISCLAIMER

INVESTIGATION OF TRACE ORGANIC COMPONENTS IN CHLORINATED NATURAL WATERS USING GLASS WCOT COLUMNS

R. M. Bean, P. W. Ryan and R. G. Riley

Battelle, Pacific Northwest Laboratories
P. O. Box 999
Richland, Washington

Glass wall-coated open tubular column chromatography has been used for the separation of organic components in fresh and saline waters after treatment with chlorine at concentrations approximating those in power plant cooling waters. Examination of the organic constituents isolated from water samples using an XAD-2 resin column has revealed that a complex mixture of electron-capturing components are produced by chlorination. The analytical scheme for the study of halogenated components consists of clean up steps performed by high speed liquid chromatography followed by gas-liquid chromatography on glass WCOT columns using flame ionization and electron capture GC detectors. Capillary GC/MS was also employed, using electron impact and chemical ionization techniques. Significant problems arose with respect to retaining the identity of hundreds of component peaks as they emerged from different chromatographic columns in different instruments using the different detection systems. Therefore, it was necessary to use procedures for insuring the reproducibility of retention times in different GC detection modes, and where this was not possible, to develop intercalibration techniques. Concentrations of nonpolar and presumably lipophylic, halogenated components formed by the chlorination of relatively uncontaminated natural waters appear to be very low (in the ng/l range), with the exception of the haloforms.

INTRODUCTION

Concern about the presence of halogenated organic compounds in water has been growing since Dowty, et al[1] detected volatile organochlorine compounds in a New Orleans area municipal water treatment facility. This report was rapidly followed with evidence adduced by Rook[2], Glaze and Henderson[3], Jolley[4], and others that the presence of a wide variety of organohalogen compounds in drinking waters and wastewater effluents is a consequence of current chlorination treatment practices. Halogen-containing organic compounds have been reported to adversely affect aquatic biological species through direct toxic action[5], as well as through indirect mechanisms, such as interference with reproductive success[6], and interference with photosynthesis[7]. Further, a number of halogenated organic compounds have been found to concentrate in the tissues of aquatic organisms[8,9], which in the case of food fish, increases the hazard of these compounds to human health.

In 1975, about 100,000 tons of chlorine were used in the treatment of cooling water for electricity generating plants[10], many of which use natural riverine or estuarine waters for once-through cooling. The number of power plants can be expected to grow rapidly as the nation copes with increasing energy demands, with accompanying increases in chlorine admitted to the environment through cooling water treatment. The studies reported here are part of an integrated research program to characterize the halogen-containing products which may arise from cooling water treatment, and to determine their toxicity and biological availability to aquatic life.

Initial analytical development has concentrated on the extraction, concentration, separation, and identification of volatile, lipophylic organohalogens formed from chlorination of both fresh and marine waters. Extraction and concentration of

nonpolar organics from water for the analysis of municipal wastewater were adapted from a procedure used by Glaze and Henderson[3]. In this procedure, the water sample is forced through a column of XAD-2 resin, the resin extracted with ether, and the concentrated ether extract analyzed by gas chromatographic and GC/MS techniques. Departures from the procedures of Glaze and Henderson were necessary because of the low concentrations of organic components found in these natural waters, and because of the exceedingly complex nature of the samples examined. The procedures used for this work would not be expected to detect more polar components in water, such as the halogenated derivatives of phenols, amines, or nitrogen heterocycles. Although these more polar types have been reported in chlorinated waters[3,4], the procedures used herein would specifically exclude these from the analysis.

EXPERIMENTAL

Chlorinated water samples were obtained using the Battelle-Northwest biological laboratory facilities at Sequim, Washington (seawater from Sequim Bay) and at Richland, Washington (fresh water from the Columbia River). Both water systems are relatively free from organic industrial pollutants. Chlorination of the water samples at between one and two mg/l chlorine as NaOCl was carried out in a continuous-flow apparatus. Residence time from chlorine addition to sampling was about two hours.

Both chlorinated and unchlorinated natural waters were sampled by pumping through 1/2" x 9" stainless steel columns filled with 15 to 18 ml of XAD-2 resin. The XAD-2 resin (Supelco chromatographic grade) was cleaned prior to use with the soxhlet extraction method of Junk et al.[11]. The pump used was a variable flow, positive displacement device capable of pumping against a pressure of 100 psi. Pumping rates ranged from 50 to 75 ml/min. Ceramic, fluorocarbon, and 316 stainless

steel were the only materials in contact with the water. For these initial studies, residual oxidant was not destroyed by sulfite addition, nor was there any attempt to control pH prior to column absorption. Instrumentation is being developed for accomplishing this on a continuous basis. The volume of water extracted using the XAD-2 adsorption technique varied considerably but generally ranged between 200 and 500 liters. The XAD-2 columns were kept at 4°C after sampling was completed.

The columns were extracted with 125 ml ether preserved with 2% ethanol (J. T. Baker, "Resi-analyzed") following the procedure of Junk et al.[11]. All other solvents used in these procedures were Burdick and Jackson "distilled in glass." The ether extracts were evaporated under a stream of dry nitrogen, the solvent changed to benzene. Those samples which were not directly investigated by gas chromatography at this point were subjected to the separation scheme described below.

The benzene solution of the ether extract was evaporated to 100 µl volume and injected into two 3/8" x 12" µ-Styragel^{R} columns (Waters Associates) connected in series. The columns were eluted with benzene at a flow of 1.0 ml/min using a Waters high pressure liquid chromatograph. The fraction eluting between 13 and 25 ml was collected for further study. Under the same conditions, polypropylene glycol (MW 800) has a retention volume of 10.8 ml and cholestane (MW 386) has a retention volume of 13.6. The fraction collected from 13-25 ml is thus designated as the <800 MW fraction. The <800 MW fraction was evaporated to 100 µl, and was further separated on a 3/8" x 12" deactivated silica gel column (MCB SX 144-7, 10% water deactivated) using 20 ml hexane at 2 ml/min to elute a nonpolar fraction (Fraction A), followed by 20 ml of a mixture of 16% ethanol-free ether in hexane, also at 2 ml/min, to elute a more polar fraction (Fraction B). The uneluted material was back-flushed from the column using a 40/60

ether/hexane mixture. Fractions A and B were evaporated to a volume of ca. 50 µl and stored in tapered-bottom 0.3 ml vials.

Gas chromatography of ether extracts and subfractions was carried out using a Hewlett-Packard Model 5840 equipped with cryogenics, flame ionization detector (FID) and electron capture detector (ECD). The chromatographic column and splitter assembly used for this work were purchased from J&W Scientific, Inc. The 30 m column used for this work was found to have 101,000 effective theoretical plates at k = 17.03 and was one-half of a 60 meter OV-101 capillary. The other half of the column was used to perform the GC/MS analyses.

Chromatographic conditions were as follows: Helium carrier gas flow, 1.30 ml/min at 16 psig; split ratio, 6.7 to 1; program, 4 min at 65°C followed by 4°C/min to 250°C and 20 min hold; injector temperature, 310°C. The above conditions were constant regardless of the detector used. When the column was connected to the electron capture detector (ECD), the following conditions obtained: detector temperature, 350°C; argon/methane flow to detector, 30 ml/min; detector attenuation, 8; slope sensitivity, 28. Samples were normally evaporated to a suitable volume such that the detector attenuation for the ECD was 8. Subsequent evaporation of the sample to somewhat less than half that volume permitted analysis of the sample using the following FID conditions: detector temperature, 310°C; nitrogen make-up to detector, 20 ml/min; detector attenuation, 2; slope sensitivity, 0.2.

Changing the column from ECD to FID is a simple procedure that takes less than 10 minutes. The oven is cooled to 30°C and the column, securing nut, and graphite ferrule moved to the other detector and locked in place being careful not to touch with fingers the portion of the column inserted into the detector base. This procedure is followed by changing the signal, attenuation, and slope sensitivity appropriate for the detector used.

The computerized GC/MS instrument used in this work was a Hewlett-Packard 5982A system which includes a HP 5710 gas chromatograph. The GC injection port was fitted with a splitter identical to that used with the EC/FID instrument and was operated as nearly as possible under identical flow and temperature conditions. The back end of the column was connected directly to the standard transfer line intended for chemical ionization GC/MS operation, so that effluent passed directly into the ion source. In CI operation, preheated reagent gas, usually methane, was added at the column exit, in a manner similar to the addition of make-up gas in conventional capillary chromatography. The 30 m OV-101 WCOT column used in this work was matched with the column used in the EC/FID instrument as described above. GC resolution obtained with this system was very nearly the same as on the other instrument, with most differences attributable to the different injection port heaters, geometries, and pressure differences. Chromatographic conditions were identical to those used for the EC/FID instrument, using a split ratio of about 6 to 1. Mass spectra were recorded every 0.9 sec, scanning over a mass range of 40-400 (EI) and 100-460 (CI). The data were stored on disk for off-line data reduction.

DISCUSSION

Preliminary studies of concentrated ether extracts from the XAD-2 resins indicated that large samples would be required in order to obtain sufficient material for characterization. At present, water samples of between 200 and 400 liters are being processed. Preliminary chromatography of these large volume samples produced an immediate analytical result: A series of electron-capturing peaks was observed in the ether extracts of unchlorinated Columbia River water (Figure 1). This pattern was found to be identical in relative peak intensities and relative retention times to that of Aroclor 1254, a well-known polychlorinated biphenyl (PCB) mixture (Figure 2). The concentration of

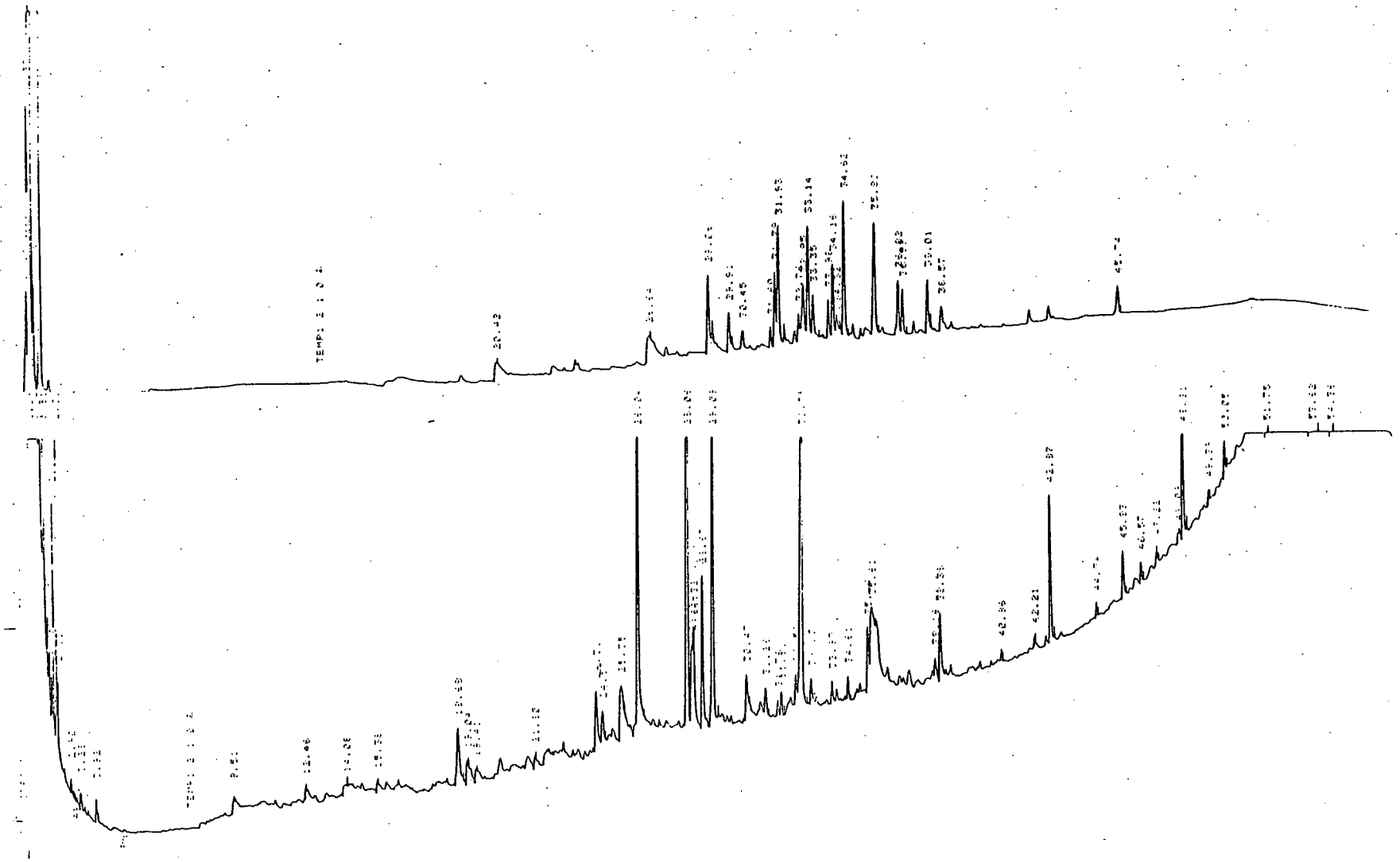

FIGURE 1. Above, electron capture chromatogram of the extract from several hundred liters of unchlorinated Columbia River water. Below, corresponding flame ionization chromatogram.

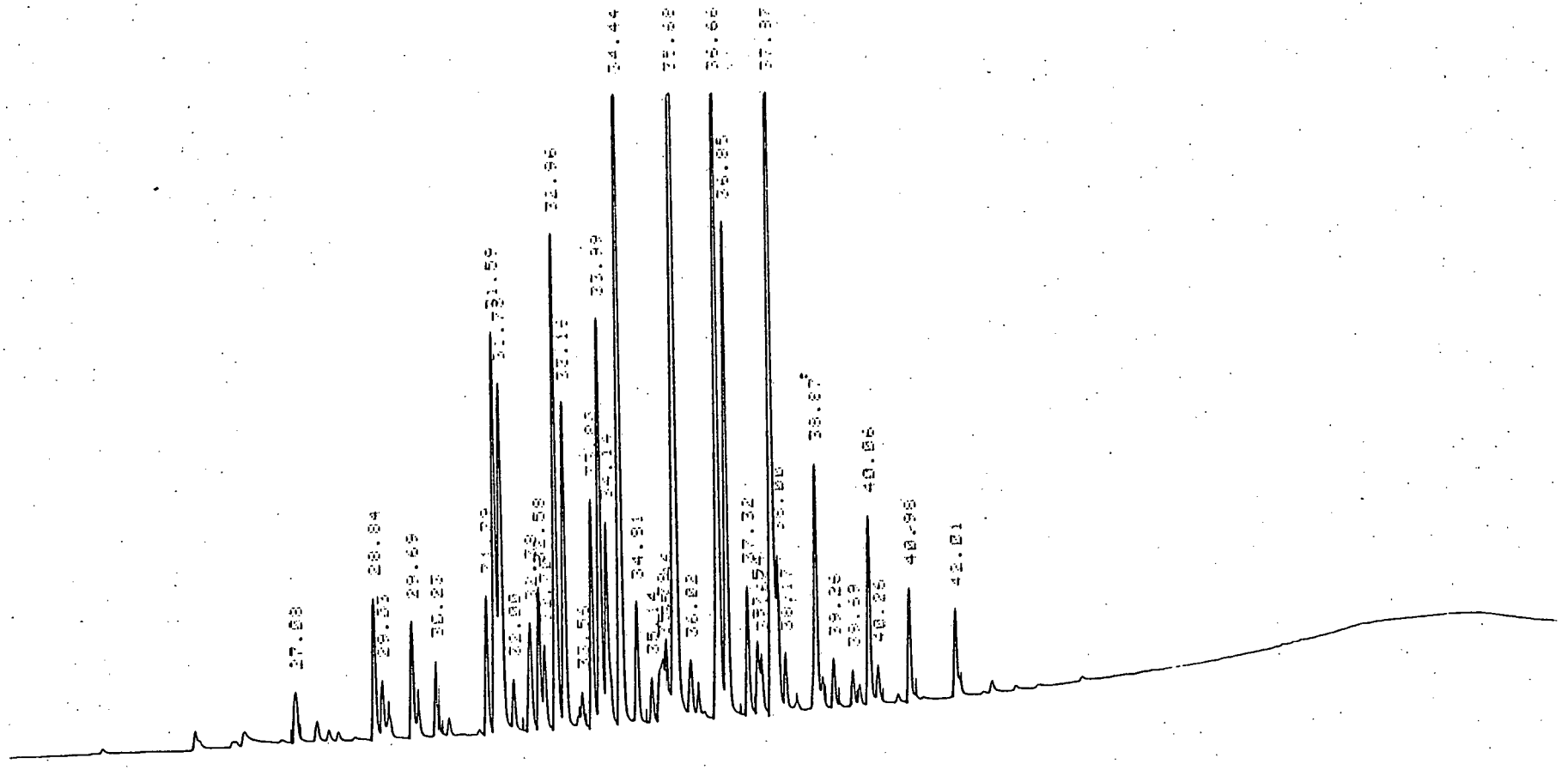

FIGURE 2. Electron-capture chromatogram of Aroclor 1254, showing similarity of relative peak heights and retention times to Figure 1. Absolute retention times differ because of slightly different chromatographic conditions.

Aroclor found in the Columbia River sample was in the ng/l range. In the corresponding chlorinated Columbia River sample (Figure 3) the Aroclor pattern remains identifiable, even in the presence of many other electron-capturing components, and indicates that while chlorination may have produced additional chlorine-containing components, significant additional PCB chlorination did not occur. The power of capillary chromatography is well illustrated here, in that this observation could not have been made with these samples using conventional chromatography.

Figures 1 and 3 also serve to illustrate some of the difficulties in working with the unrefined ether extracts of natural waters. In general, attempts to analyze the crude ether extracts directly on the gas chromatograph were not successful. It was evident from the dark greenish-brown appearance of the extracts that significant quantities of high molecular weight material were present. Thus, there was the likelihood that artifacts would be produced from pyrolytic reactions occurring in the injection port of the chromatograph. From inspection of the chromatograms obtained, we have formed the qualitative judgment that these types of reactions were occurring; however, this was not investigated in detail, since only a few of the crude extract samples could be run before the chromatographic column became plugged at the injection port end. This problem could be temporarily rectified by breaking off as much as one meter of column length. Inspection of the sealed capillary under magnification showed that, in addition to dark material within, the liquid phase had pulled away from the capillary wall. The glass liner of the injection port accumulated a black residue of carbonaceous material.

Another problem associated with the crude ether extracts was the complexity of the samples. The samples were sufficiently complex that most components could not be resolved on the capillary column. Thus, flame ionization chromatograms of the

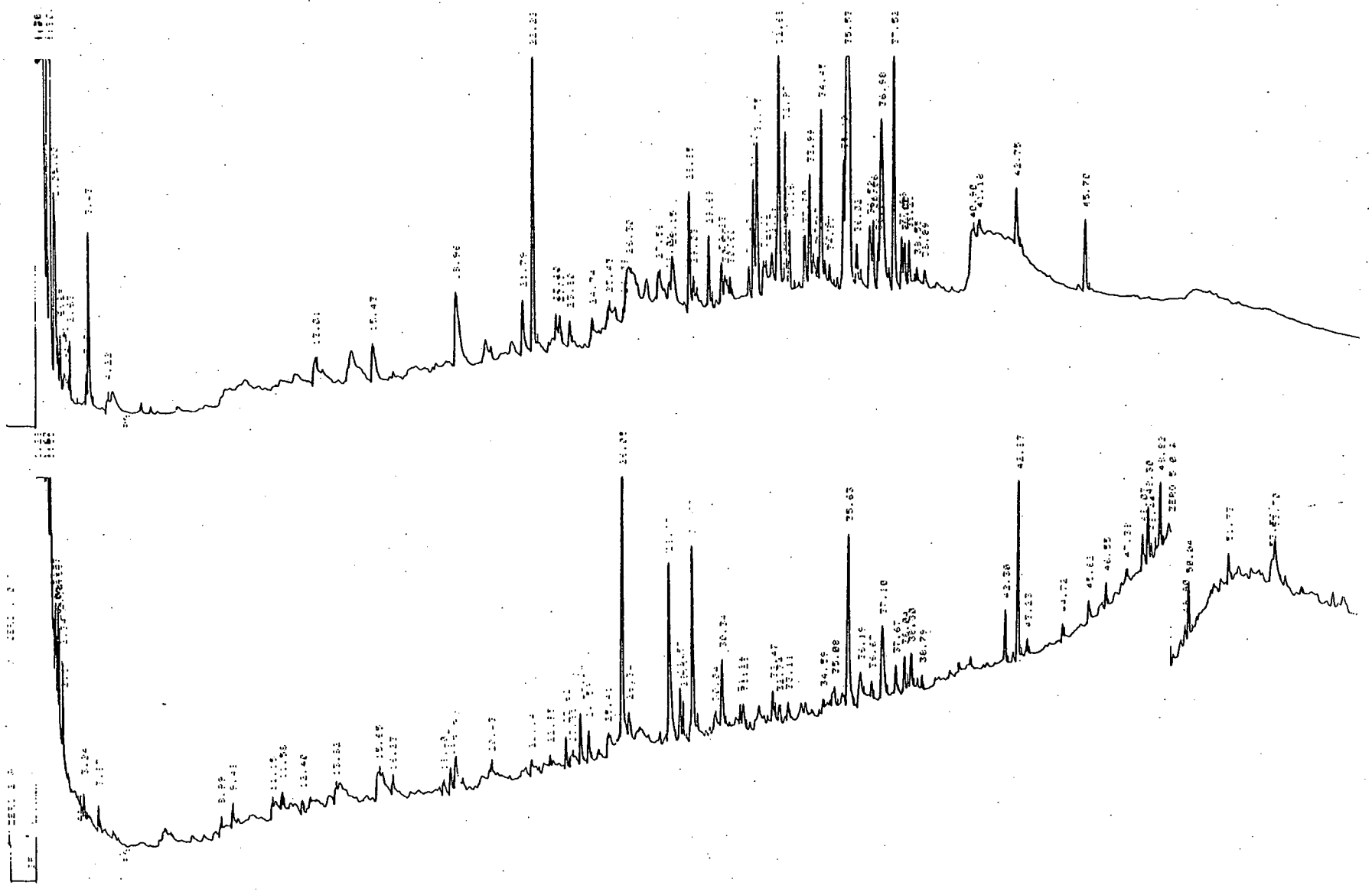

FIGURE 3. Above, electron capture chromatogram of the extract from chlorinated Columbia River water. The chlorinated sample was obtained simultaneously with the unchlorinated sample (Figure 1). Below, corresponding flame ionization chromatogram.

extracts were principally unresolved envelopes. The largest significant peaks were phthalate esters. Electron capturing components, being fewer in number, were better resolved from each other; however, there was little observable correspondence between peaks in electron capture chromatograms and those in the flame ionization chromatograms. Investigation of the samples by GC/MS was also unfruitful, since clean spectra could not be obtained. Single mass chromatograms generated from the spectral data were almost as complex as the total ion chromatograms for all masses investigated.

The above experiences serve to emphasize the importance of adopting sample cleanup techniques in the analysis of environmental samples for trace constituents in order to avoid artifacts and to reduce sample complexity. The separation of the sample by gel permeation chromatography permitted the rejection of all material in excess of 800 molecular weight. A chromatogram obtained from a seawater extract after the molecular weight separation step is shown in Figure 4. Fractionation of the sample over deactivated silica gel permitted the isolation of the relatively nonpolar, more lipophylic compounds of interest. Gas chromatography of both Fraction A (hexane elution from silica gel) and Fraction B (16% ether in hexane) could be accomplished with baseline separation of most components even after the samples had been evaporated to as little as 10 µl. A comparison of electron capture chromatograms of Fraction A obtained from chlorinated and unchlorinated seawater samples (Figure 5) clearly shows the enhancement of electron capturing activity introduced by chlorination. The chromatographic results obtained from Fraction B of the same water sample are shown in Figure 6.

The plan of attack for identification of halogenated components by GC/MS was to obtain FID and ECD chromatograms prior to the GC/MS analysis. Correspondence in retention times of peaks in both detection systems would be evidence that the eluting

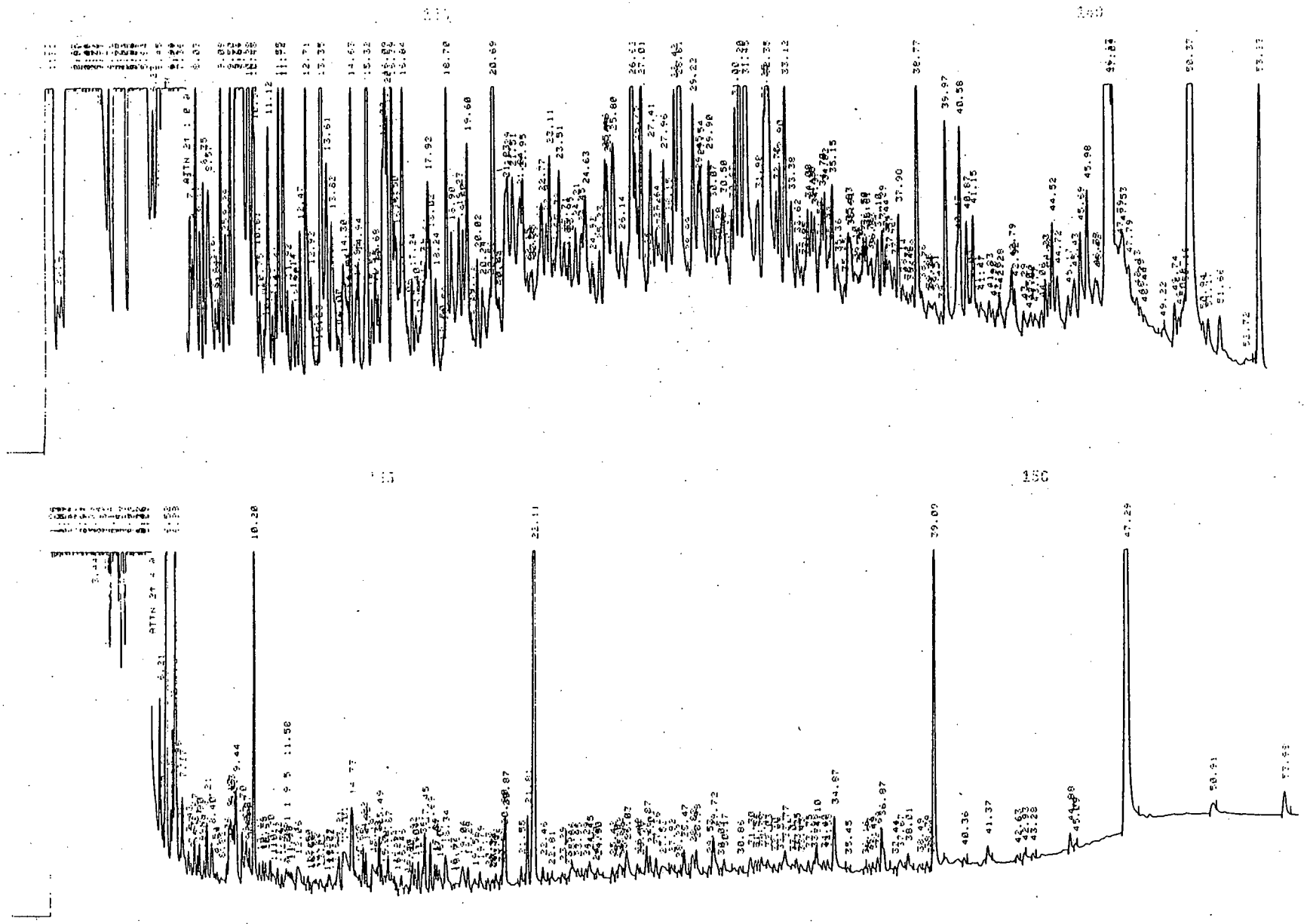

FIGURE 4. Above, electron capture chromatogram of an extract from Sequim Bay seawater after removal of material in excess of 800 molecular weight by gel permeation chromatography. Below, corresponding flame ionization chromatogram.

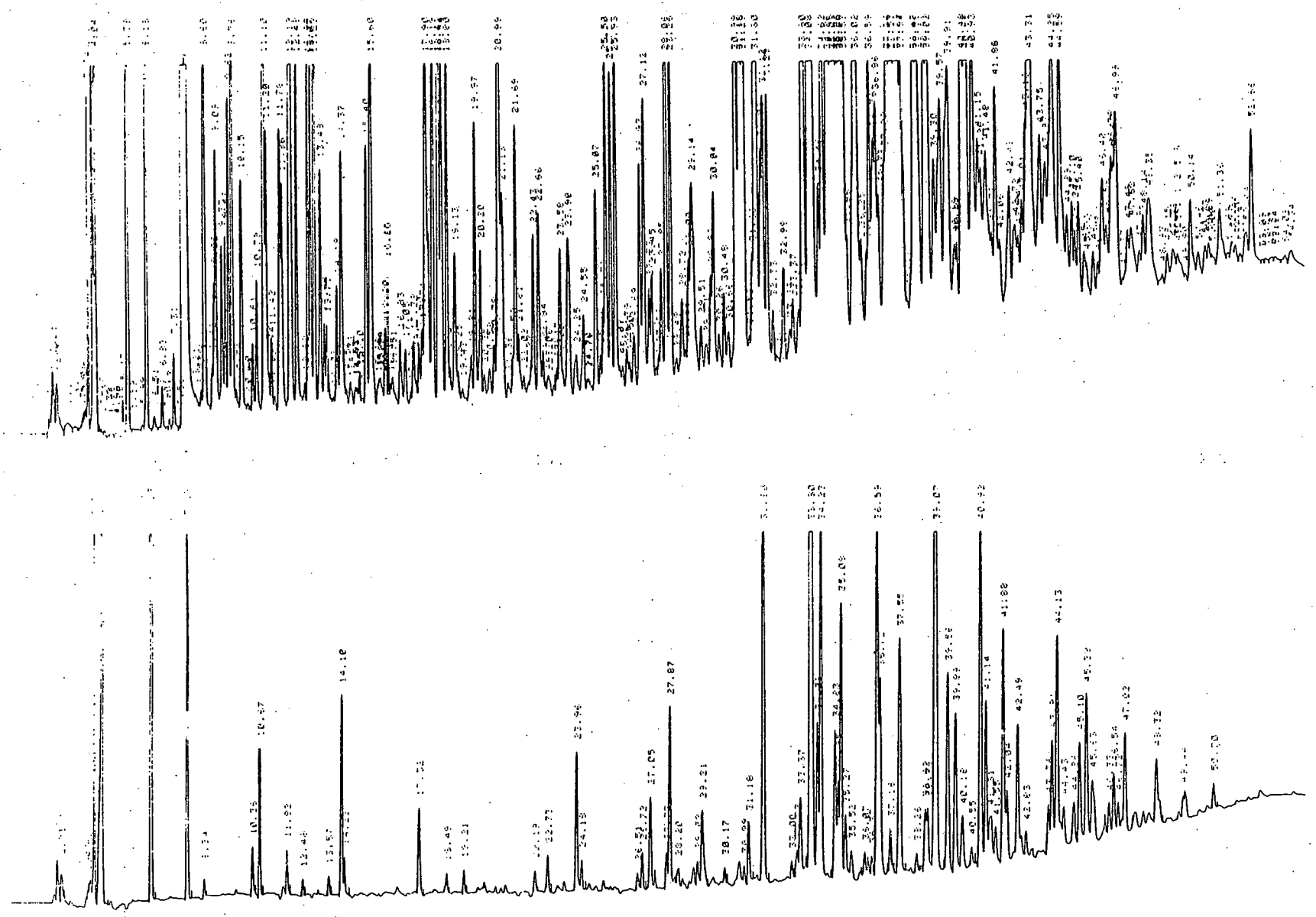

FIGURE 5. Above, electron capture chromatogram from Fraction A of a chlorinated seawater sample. Below, electron capture chromatogram from unchlorinated sample.

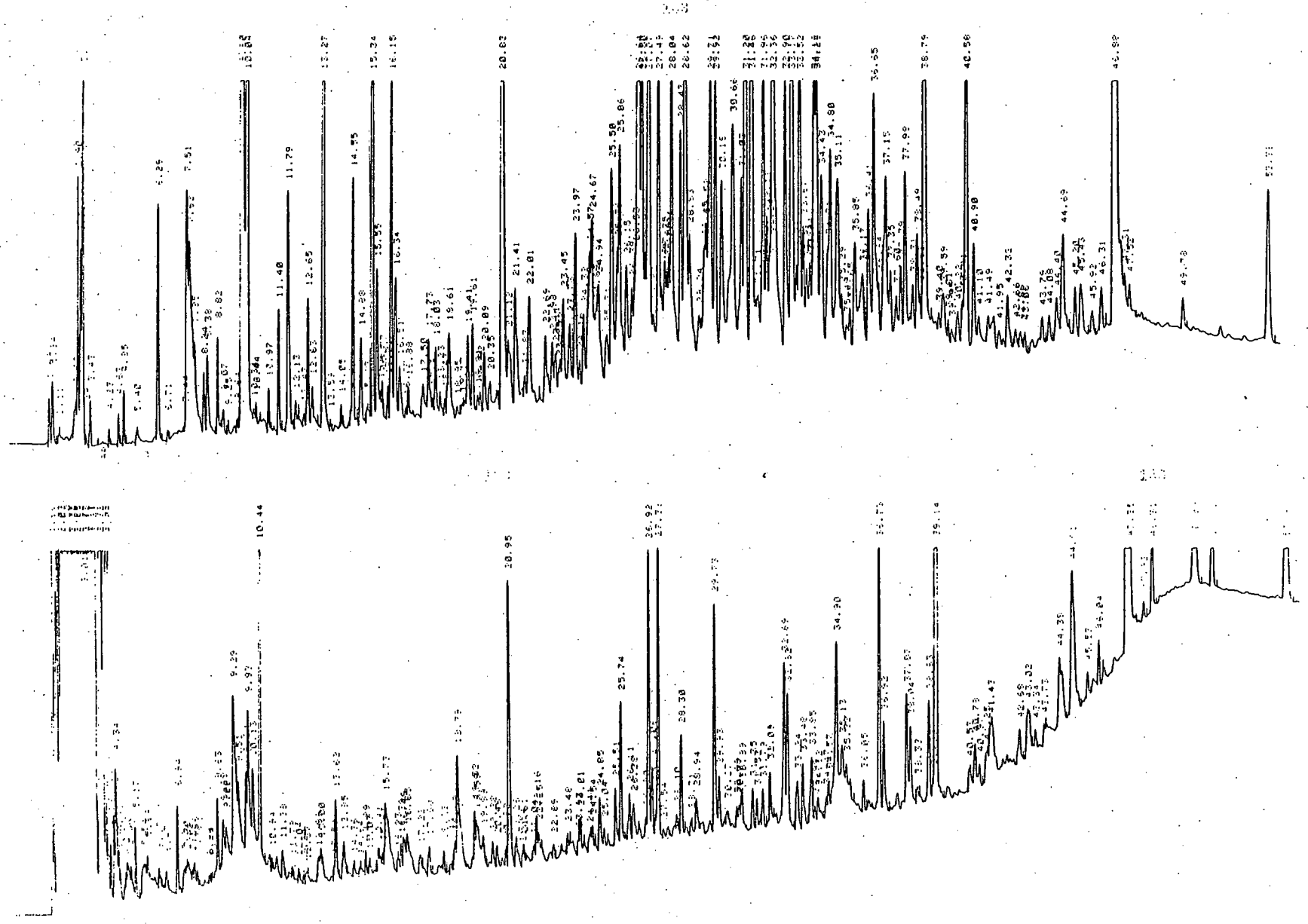

FIGURE 6. Above, electron capture chromatogram from Fraction B of a chlorinated seawater sample. Below, corresponding flame ionization chromatogram.

component contained halogen, and was present in sufficient quantity for GC/MS analysis. Identification of halogen compounds prior to GC/MS analysis could considerably reduce the time required on the mass spectrometer. As the initial results revealed almost no correspondence between ECD and FID peaks, a series of 1-chloroalkanes was separated on the column using both detection systems. Initial results revealed that, under the conditions used, the emergence times of these components were as much as 0.30 min longer when the flame detector was used than for the ECD. The lengthening of retention times was a result of back-pressure generated in the detector at high make-up nitrogen flow rates. Raising the carrier gas pressure and lowering the nitrogen make-up pressure and flow resulted in satisfactory correspondence between peaks obtained in FID and ECD modes of operation. Table 1 shows the data obtained from six FID and six ECD chromatograms obtained over a period of four days.

In other experiments conducted over a period of one day, the reproducibility of retention times was somewhat better, averaging ±0.04 min and ±0.05 min for FIC and ECD, respectively.

TABLE I. Correspondence Between Retention Times Obtained Using Flame Ionization and Electron Capture Detectors

Component	FID Retention Time Min ± s.d.	ECD Retention Time Min ± s.d.	FID-ECD Difference ± s.d.
1-Cl C_8	12.78 ± 0.054	12.66 ± 0.087	0.12 ± 0.10
1-Cl C_9	16.43 ± 0.063	16.38 ± 0.090	0.05 ± 0.11
1-Cl C_{10}	20.08 ± 0.058	20.07 ± 0.077	0.01 ± 0.10
1-Cl C_{16}	39.23 ± 0.059	39.26 ± 0.074	-0.03 ± 0.09
1-Cl C_{18}	44.44 ± 0.061	44.48 ± 0.075	-0.04 ± 0.10
1-Cl C_{20}	49.23 ± 0.060	49.25 ± 0.078	-0.02 ± 0.10

The general lack of correspondence initially obtained between ECD and FID peaks was primarily due to sensitivity differences between the two detectors, rather than retention time differences. The flame ionization detector was not sensitive enough to detect halogenated components giving large peaks from the ECD until samples were concentrated to about 20 µl prior to injection.

The GC/MS instrument available for this work could not be exclusively dedicated to this program, since it is a general service instrument shared by a wide variety of research programs. It is physically located several miles from the laboratory in which the samples are generated and investigated using FIC and ECD gas chromatography. Although the use of matched columns insured that comparable resolution and similar chromatograms were obtained for both instruments, retention times obtained on the two instruments varied by as much as three minutes. It thus became necessary to calibrate both GC/MS and EC/FID instruments for retention time in order to retain the identity of separated components.

The extremely small sample sizes mitigated against the use of an internal standard for retention time calibration. The procedure adopted was to chromatograph a series of normal alkanes with carbon numbers ranging from C_8 to C_{28} prior to analysis of the sample in either GC or GC/MS instruments. Using the retention times obtained for the standards on each instrument, the retention time of an environmental sample component peak on one instrument was calculated by linear interpolation. Thus:

$$P_B = C_{XB} + \frac{P_A - C_{XA}}{C_{(X+1)A} - C_{XA}} \left[C_{(X+1)B} - C_{XB} \right] ;$$

where C_X refers to the retention time of n-alkane of carbon number X, C_{X+1} refers to the retention time of the next highest

n-alkane, and P refers to the peak of interest occurring at a retention time intermediate to C_X and C_{X+1}. A and B refer to instrument A and instrument B.

In principle, one would like to use the ECD chromatogram to locate possible halogenated components, find the corresponding peak in the MS chromatogram and identify the electron capturing compound on the basis of this mass spectrum. In practice, the MS is so much less sensitive and less selective than the ECD that many ECD peaks cannot be detected in the GC/MS runs and the mass spectrum at the appropriate retention time may be due exclusively, partially, or not at all to the electron-capturing material. The most successful approach was a somewhat less direct one. The GC/MS data was first scrutinized for indications of halogenated species, the ECD chromatogram inspected for confirmation and for major omissions, then corresponding mass spectra examined for identification if possible.

The presence of Br and Cl is most clearly indicated in the mass spectrum by clusters of mass peaks with relative intensities characteristic of the halogen isotope ratios. But unresolved interferences, complex fragmentations and vagaries of the computer peak detection algorithm at low intensities can either distort real clusters or create misleading patterns. Hence, the ECD activity was required for identification of halogenated species.

Table II and Figure 7 give results obtained for the non-polar fraction (Fraction A) derived from several hundred liters of seawater from Sequim Bay. The darkened peaks in the EC/FID chromatograms in Figure 7 correspond to compounds which <u>both</u> chemical ionization GC/MS and electron capture GC indicate are halogen containing. Electron capturing components which did not give mass spectra having isotope characteristics of chlorine or bromine were rejected. Table II lists bromine-containing components identified using the dual-detection criteria discussed

TABLE II. Comparison of Retention Times Obtained for Bromo-organic and Aromatic Hydrocarbon Components on GC/MS and FID/ECD Instruments, Nonpolar Fraction from Chlorinated Seawater Extract

Component (or mass of characteristic Br-containing ion)	GC/MS Retention Time, Min	Calculated Retention Time on FID/ECD, Min	Actual FID Retention Time, Min	Actual ECD Retention Time, Min
$CHBr_3$	4.80	7.41	7.48	7.52
149	5.12	7.80	7.80	7.83
149	6.25	8.97	8.95	8.98
149	7.62	10.27	10.36	10.39
Trimethylbenzene	8.28	10.90	10.92	--
149	8.85	11.45	11.56	11.64
163	9.92	12.51	12.56	12.64
Naphthalene	15.00	17.56	17.63	--
Bromotrimethyl-benzene	18.55	21.13	21.11	21.08
169	19.55	22.14	22.14	22.13
Biphenyl	21.88	24.53	24.47	--
Bromomethyl-naphthalene	28.60	31.42	31.55	31.59
Bromomethyl-naphthalene	29.08	31.91	31.93	31.95
Bromomethyl-naphthalene	29.18	32.02	32.06	32.16
249	30.70	33.61	33.60	33.72
235	31.01	33.93	34.01	34.02
219	31.32	34.26	34.35	34.32
249	31.82	34.78	34.88	34.85
251	31.98	34.95	35.16	35.09
Bromodimethyl-naphthalene	32.21	35.19	35.38	35.31
235	32.64	35.65	35.82	35.80
Bromotrimethyl-naphthalene	35.66	38.76	38.86	38.70
Pyrene	41.10	44.41	44.58	--

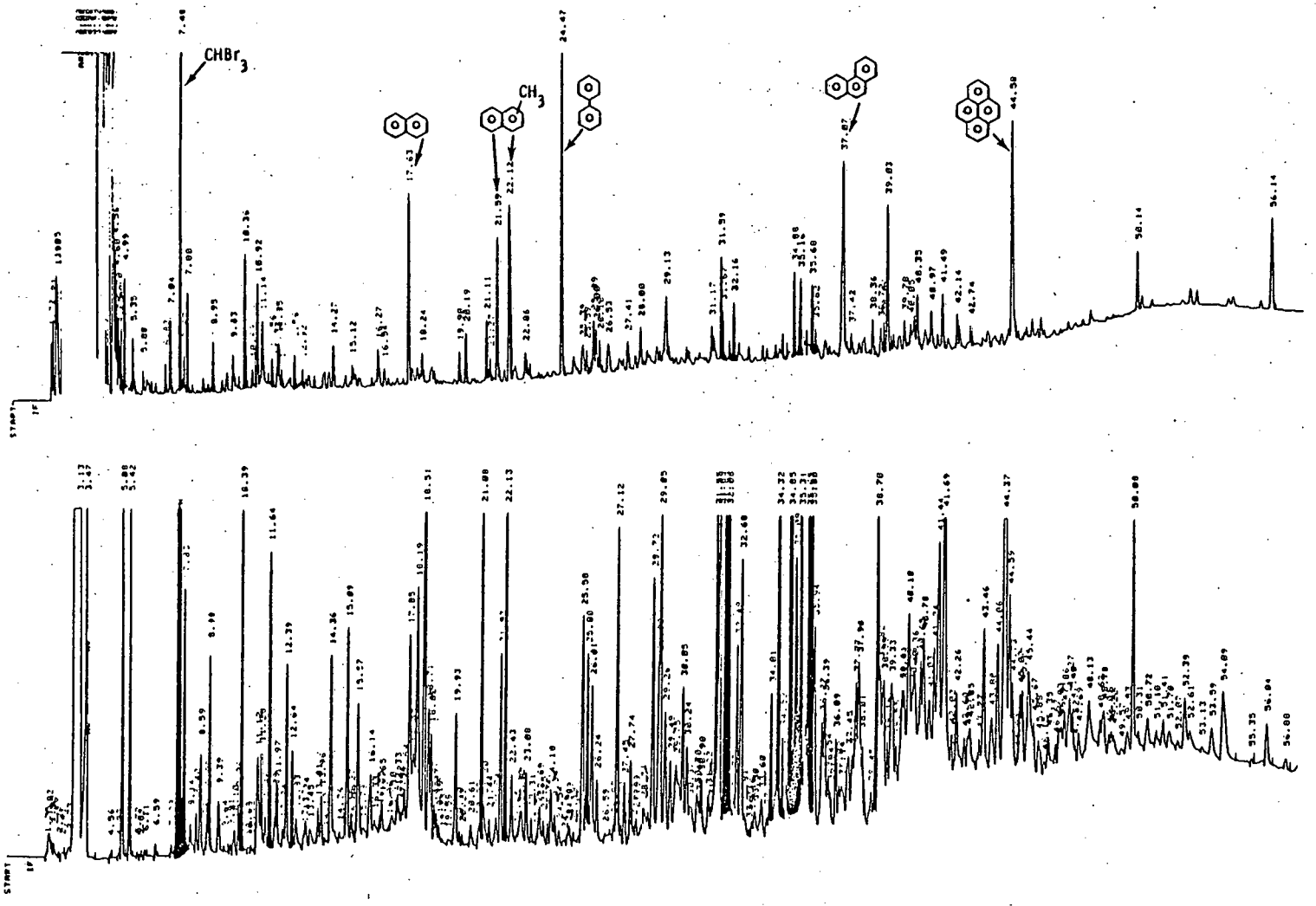

FIGURE 7. Above, flame ionization chromatogram of Fraction A from Sequim Bay seawater. Below, corresponding electron capture chromatogram. Darkened areas indicate those peaks arising from brominated organic compounds.

above, plus some aromatic hydrocarbons found to be present. The observed retention times for the components in both EC and FID detection modes in general are in good agreement with the retention times calculated by interpolation from the GC/MS analysis.

The fragmentation of halogenated species under electron impact conditions frequently involves a primary loss of X or HX, so that the isotope cluster information is lost from the mass spectrum. For this reason, we have relied heavily on chemical ionization mass spectrometry, which produces much less fragmentation and increases the probability that halogen-containing ions will contribute their characteristic clusters to the spectra. The high ionization efficiency of CI and its tendency to concentrate the entire ion current into a small number of mass peaks are additional advantages. Following the ECD and CI analysis to locate compounds of interest, the remainder of the sample was used to obtain EI spectra which contain structural information complementary to the CI data.

Sample complexity and the generally low concentrations of the components of interest force us to work with spectra of uncertain quality. The results have been mixed. Experience has shown that available libraries contain very few spectra which are similar to those which we attribute to possible halogenation products, and the combination of EI and CI data has been our most powerful tool. In many cases, a number of possible identities have been obtained, but with no reference spectra, no standards for retention time confirmation, and no a priori reason to expect any given species, the peaks are at present left unassigned.

A number of halogenated components have been identified in the samples thus far investigated. The principle halogenated products are the haloforms. Under the conditions employed, about 30 µg/l of bromoform is formed in seawater. It is quite likely, however, that many of the compounds are formed as a

result of secondary reactions of excess halogen with sample impurities. Although the XAD-2 resin is soxhlet extracted scrupulously with three different solvents, aromatic hydrocarbons have appeared in all samples investigated thus far. These hydrocarbons (naphthalenes, phenanthrenes, pyrene) are present as impurities in the uncleaned resin, but are not found when the cleaned column is extracted and the extract treated as a procedural blank. It is likely that these components are released from the XAD polymer matrix during the sampling of the water when the resin fractures under the fairly high back pressures produced. These components can then be halogenated during sampling, and indeed, brominated derivatives of these hydrocarbons are found in the seawater samples. Interestingly, few chlorinated aromatic hydrocarbons are found in fresh water samples even though the corresponding unchlorinated hydrocarbons were present.

It is apparent from the results obtained that with the exception of the haloforms, the quantity of nonpolar halogenated organics formed during the chlorination of natural waters is exceedingly low in the relatively pristine natural waters thus far investigated. Sample concentration factors are on the order of 10^6, and we still are approaching the limits of detection by GC/MS (on the order of one μg/ml). This corresponds to individual component concentrations in the parts per trillion range. At these concentrations, problems with experimental artifacts are major obstacles, since a number of substances are practically ubiquitous in the environment at these levels[12].

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the support of the Nuclear Regulatory Commission for the conduct of this work. Thanks are given to Mr. Gary Minnoch of Hewlett-Packard Corp. for suggesting solutions to some experimental problems. Brand

names are given to assist in replication of the analysis and use does not constitute endorsement by Battelle Memorial Institute.

REFERENCES

1. B. J. Dowty, D. R. Carlisle, and J. L. Laseter, Env. Sci. & Tech 9, 762 (1975).

2. J. J. Rook, J. Water Treat. Exam 23, 234 (1974).

3. W. H. Glaze and J. E. Henderson, J. Water Pollut. Contr. Fed. 47, 2511 (1975).

4. R. L. Jolley, J. Water Pollut. Cont. Fed. 47, 601 (1975).

5. G. Roesijadi, S. R. Petrocelli, J. W. Anderson, C. S. Giam, and G. E. Neff, Bull. Env. Contam. & Toxicol. 15, 297 (1976).

6. C. W. Gehrs, L. O. Eyman, R. J. Jolley, and J. E. Thompson, Nature 249, 675 (1974).

7. R. W. Eppley, E. H. Renger, and P. M. Williams, Est. and Coast. Mar. Sci. 4, 147 (1976).

8. R. W. Risebrough, B. W. DeLappe, and T. T. Schmidt, Mar. Pollut. Bull. 7, 225 (1976).

9. V. Zitko and O. Hutzinger, Bull. Env. Contr. & Toxic. 16, 665 (1976).

10. G. C. White, Proceedings of the Conference on the Environmental Impact of Water Chlorination, R. L. Jolley, ed., National Technical Information Service, Springfield, VA p. 7.

11. G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder, J. Chrom. 99, 745 (1974).

12. J. A. Singmaster III and D. G. Crosby, Bull. Env. Contr. & Toxic. 16, 291 (1976).