CHARACTERIZATION OF ORGANIC CONTAMINANTS
IN SELECTED POTABLE WATER SUPPLIES
IN PUERTO RICO

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I. Introduction

In studies made in the early 1970's (1) about the water from the Ohio and Mississippi rivers, the presence of over 60 organic compounds was established, many of which are man-made and are considered hazardous, even in trace amounts. The first of these, concerning the municipal water supply of New Orleans, included not only the finished water but also the raw water derived from the lower Mississippi (2). It was suggested that the chlorination process used in water purification was partially responsible for the presence of halogenated organic compounds in potable water.

Further studies along these lines in Evansville, Indiana (3); Philadelphia, Pennsylvania, and Miami, Florida (4), have served to confirm the findings in the original study. Since these early studies were performed, numerous other researches have been done on the chemical water quality of practically all the municipal water supplies of major cities in the United States and in Europe.

The concern over the widespread presence of numerous synthetic organic chemicals in drinking water, with its probable implications for human health, spurred the United States Congress to enact legislation to assure the quality of natural and potable waters. The result of this action was the passage of the Clean Water Act in 1972 and the Safe Drinking Water Act in 1974. Most studies concerning the chemical water quality in the United States have been carried out under the auspices of the U.S. Environmental Protection Agency, which was charged by Congress with the implementation of the measures mandated by these Acts in order to preserve water quality in the Nation.

Because of the limited territorial extension of the Island of Puerto Rico, its rapidly growing chemically-related industries, and its overpopulation, it is believed that the same factors that contributed

toward the emergence of the water pollution problems in the mainland U.S. are operative in Puerto Rico, but probably in a magnified scale.

It was felt by the principal investigator of this project that a research of the chemical water quality of potable water in Puerto Rico was of utmost importance, in view of the experiences had in the continental U.S., in Europe and in other parts of the world.

The municipal water supplies selected for the study were those of some of the largest cities in Puerto Rico: San Juan, Ponce and Mayaguez. The principal objective of the study to be reported here was to investigate the extent of pollution by organic compounds of the aforementioned municipal water supplies. In order to achieve this goal, the identification of these compounds was necessary, along with some semiquantitative estimates of their concentrations. Furthermore, an examination of the raw water feeding the corresponding purification plants would be attempted whenever possible in order to determine whether the compounds found are present before purification or are formed as a result of the chlorination step in the purifying process.

II. <u>Methods and Materials</u>

The description of the analysis of water for organic contaminants can be divided conveniently into two conventional steps: extraction and concentration of the organic contaminants from the water samples and chemical analysis of the concentrated extracts for identification and quantitation purposes. While the chemical identification of the components of the extracts is mainly done by gas chromatography-mass spectrometry (GC/MS), there is a variety of methods in current use for the extraction step. Although sometimes a matter of preference, dictated by convenience, the selection of an extraction procedure is more often dictated by the particular class of compounds sought for.

It is generally agreed that no single extraction procedure will efficiently separate all types of compounds from the water; therefore, different schemes will have to be employed to extract non-volatile and volatile compounds from water. A further breakdown of non volatiles could be based on their acid-base properties.

In order to limit the scope of this research, a decision was made to analyze for volatile organic compounds, usually called Volatile Organic Analysis (VOA), after Bellar and Lichtenberg (5). Although the definition of "volatile organic compounds" has not been standardized, it is understood that the definition is implied in the method employed for this type of analysis. However, different methods are employed to analyze "volatile organics" in water; therefore, a significant uncertainty remains regarding the list of compounds that were analyzed for when any one of the methods in current use has been employed to look into a water sample.

A further restriction in the scope of the project became necessary because a realistic attempt at the identification of the numerous compounds present in water necessitates the availability of a computerized GC/MS

system. At the time of the project's conclusion, attempts to computerize our system were incomplete. Due to the selectivity of specific gas chromatographic (GC) detectors, it was decided to limit the volatile organic analysis to halogenated compounds, an interesting and important class which the electron capture (EC) detector is particularly well suited to detect. As a matter of fact, the Environmental Protection Agency has published (6) an alternate method to GC/MS for the analysis of halogenated volatile organics which involves the use of GC analysis on two different columns, using EC detection. This was the method adopted here for the identification of the water pollutants belonging to the volatile organo-halide class, the subject of this research.

A. Extraction Procedure

There are several alternative methods to effect the separation of volatile organics from water. These have been classified as liquid-liquid or liquid-gas extractions. The liquid-liquid extraction technique, popularized by Bellar (4) in the EPA laboratories is best suited for the extraction of non-volatile or low-volatility compounds. For medium-to-high volatility compounds, the purge and trap technique is generally estimated to be the best.

There are several techniques known collectively as "purge and trap", differing in the means employed to "sparge" the compounds out of the water, in the absorbing or "trapping" phase and in the methods used to extricate the compounds from the trapping medium for analysis. Of these, the "closed loop stripping analys" (CLSA) invented by Grob (7) was chosen for this research because its superiority for VOA has been amply demonstrated by studies in the U.S. and in Europe (7, 8, 9). In this method, a water sample is placed in a glass container, leaving an air headspace, which is circulated by means of a pump through a line containing an

activated carbon filter and back to the water sample, through which the
air is bubbled through a glass (or metal) frit. This process, operating
continuously for a number of hours, will eventually strip the water of the
medium-and-high volatility organics, trapping them in the carbon filter.
The filter is then disassembled and eluted with an appropriate solvent,
after which the extract, already concentrated, is subjected to GC analysis.

There were a number of modifications made to the original design of
Grob's CLSA apparatus (7). The most important one pertained to the
activated carbon filter design. Instead of using a glass filter, a
stainless steel (type 304) filter was designed and built in the Dept. of
Physics machine shop. A schematic diagram of the filter, including
dimensions, is given in Fig. 1. A matching filter holder of the same
material, was designed and built by suitable modification of a standard
1/4" Swagelok union. Its diagram is shown in Fig. 2 which includes its
relation to other system components. A critical part of the filter is
the wire mesh discs used to sandwich the activated carbon in place. These
were cut to give a close fit to the filter's I.D., using extra fine wire
stainless steel cloth, bought from Mc.Master-Carr Supply Corp., Chicago,
Illinois. Following Grob, 1.5 mg of activated carbon were used to prepare
the filter although recently we have used only 1.0 mg. The activated
carbon has a particle diameter range from 0.05 to 0.1 mm, and was prepared
according to Grob's specifications by Dr. Bender & Dr. Hobein AG, Zurich,
Switzerland from which it was acquired.

The sample container has a volume of 5 liters, connected to the
circulating pump by 1/8" SS lines. The pump is a Model M-118 stainless
steel bellows pump purchased from the Metal Bellows Corp., Sharon, Massa-
chusetts. The sample flask has a standard tapered ground joint (40/50)
that accommodates a matching hollow stopper. The connections to the

Fig. I ACTIVATED CARBON FILTER

.031"
.0525"
.250"
.1875"
.218"
.0835"
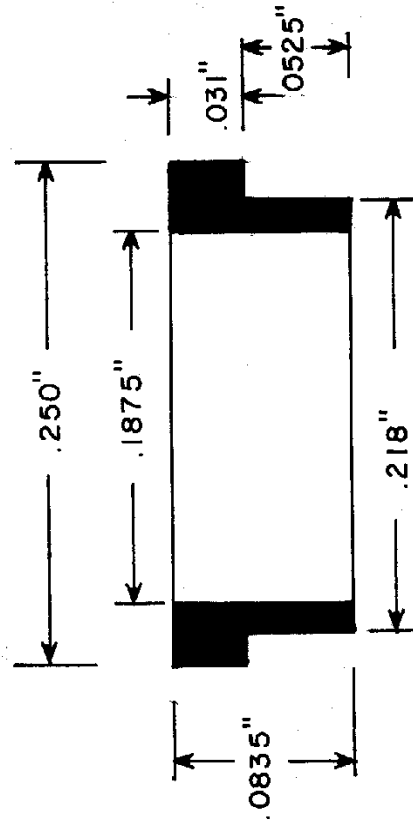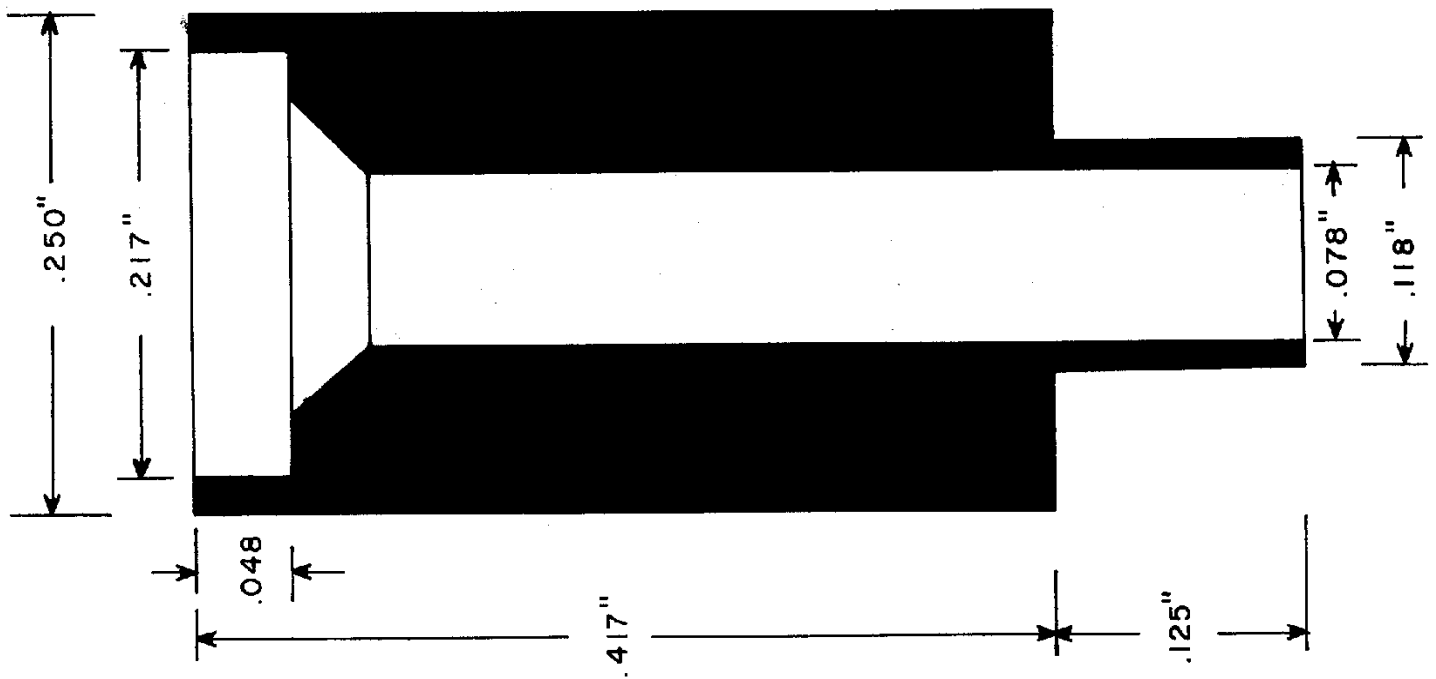
MATERIAL: Stainleess Steel

WIRE MESH SCREEN (DISK) DIAMETER : .218"

.250"
.217"
.078"
.118"
.048
.417"
.125"

Fig. 2 DIAGRAM OF FILTER HOLDER, FILTER, AND THEIR CONNECTION INTO THE SYSTEM.
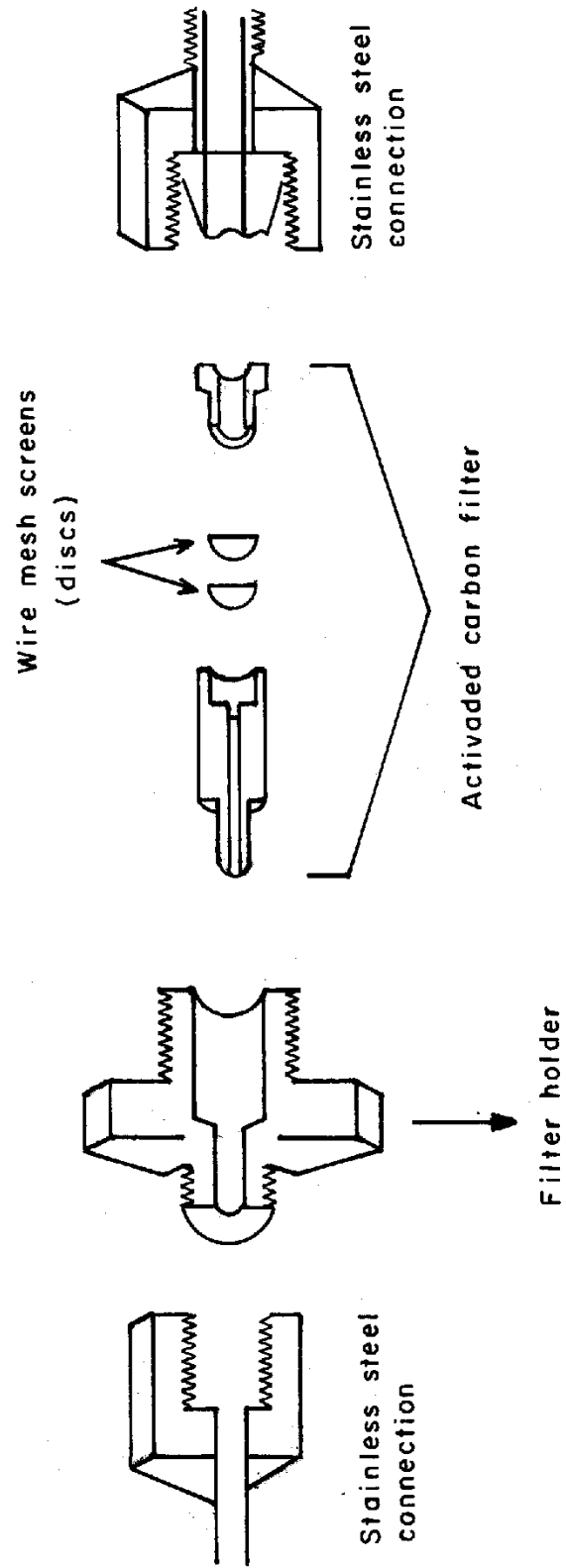
stopper were made of standard 1/4" glass-to-metal Kovar seals. All metal connections are demountable and made using Swagelok (SS) fittings. A glass tube projecting vertically downward from the glass stopper terminates in a medium porosity (porosity C) cylindrical glass frit. This acts as a dispersing element for the circulating headspace air to increase the gas-liquid interface area when the sample container is filled. Fig. 3 shows a schematic diagram of the complete CLSA system. It is made solely of glass and stainless steel to avoid contamination of the sample. In particular, the use of plastics, including PTFE, was avoided, because they are known to leach contaminants into the system, especially plasticizers (7).

In actual operation, 4,200 ml of water are added to the glass container, leaving a headspace of about 800 ml. The stopper is put in place after wetting the ground surfaces with a little glycerine to achieve a leaktight seal. The pump is turned on and the system can be left unattended for the required purge period. Although variable sparging times have been reported in the literature, down to a minimum of 2 hours, a period of 24 hours was generally used in the experiments. This long period was preferred because our system was left operating at room temperature (21-23°C) and maximum recovery was desired at this temperature. It was determined in trial runs that the percent recovery is a function of purging time; further recovery is insignificant after 24 hr. under these conditions.

After the purging period the pump is turned off and the filter is removed from the system for the extraction step.

Although activated charcoal is reported to be hydrophobic (10), a drying step was incorporated by using a water aspirator connected to a vial containing anhydrous sodium sulfate, where the filter was placed for several minutes.

Fig. 3 CLOSED CIRCUIT FOR STRIPPING WITH INERT GAS
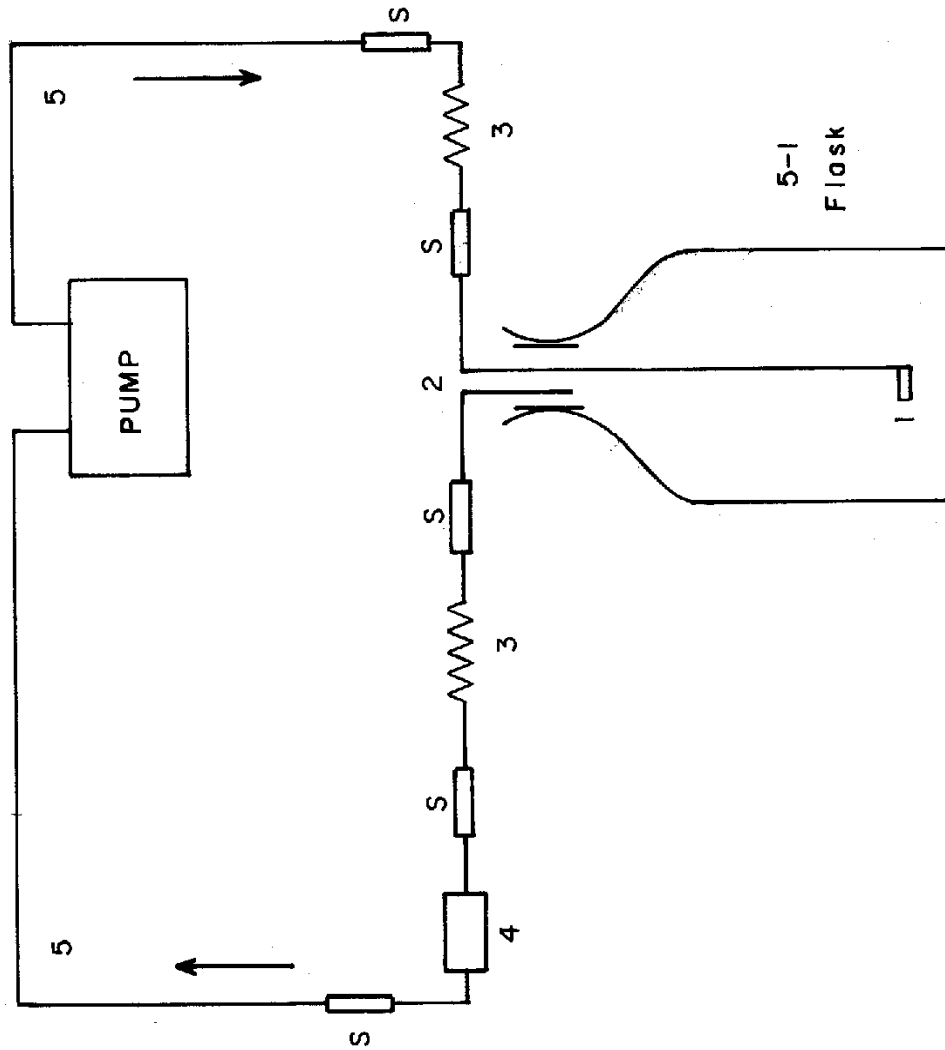
1. coarse glass frit
2. fused glass–metal connections
3. coiled steel tubing
4. filter holder
5. stainless–steel tubing
S. Swagelok fittings

A filter support made of aluminum is used to hold the filter in place during the extraction step. A microvial is placed under the filter in such a way that the latter rests squarely against to vial's lid, ensuring a relatively tight fit. The extraction is accomplished by adding 5 µl portions of solvent directly onto the activated carbon by means of a micropipette and moving the solvent drop up and down through the carbon by applying slight pressure or suction by means of a rubber bulb attached to the pipette's upper end. In order to accomplish this pumping action a PTFE sleeve is inserted over the filter's upper end; the pipette's lower end is inserted into the upper end of the sleeve, thus achieving a tight connection between the filter and the glass pipette. To avoid contamination from the rubber bulb in this step, a portion of activated charcoal is held in place between the rubber bulb and the pipette's body by means of a glass wool plug. A total of 10 washings were performed to ensure complete extraction. The combined washings were pooled as a single extract.

Different solvents have been used to elute organics from activated charcoal; among them, ethyl ether, acetone, methylene chloride, chloroform, hexane, pentane, dodecane, carbon disulfide, etc. After repeated trials with several of these we settled for pentane, distilled in glass, obtained from Burdick and Jackson, Muskegon, Michigan, and used without further purification. Although Grob (7) and Coleman (8) have found CS_2 quite satisfactory to elute organics adsorbed on activated carbon, this solvent gives a large peak in the EC mode of GC detection, completely masking early-eluting components. Furthermore, there are impurities which give other peaks at longer retention times, making it unsuitable as an eluant. Pentane gives five clearly defined peaks (the largest of them negative) in the chromatogram which are very reproducible. Only chloroform gives a peak

which coincides with one of pentane's peaks when one of the GC columns is used.

After the extraction procedure is completed, the combined extracts of about 20μl are taken immediately to the gas chromatograph for analysis in screw-capped microvials with PTEE-lined septa. When drawing a sample for injection the septum is not pierced, but rather, the whole cap is removed momentarily. This avoids the leaching of plasticizers from the septum's interior into the vial's contents.

Once the extraction process is over the filter is placed in methanol, where it is left to stand overnight. It was found that baking the filter in the oven at 200°C after this methanol washing did not significantly improve its performance; on the contrary, its life was appreciably shortened. At times it was possible to recognize one of the early-eluting peaks as due to traces of methanol remaining on the filter but this was a minor inconvenience. Although we have worked with one filter at a time, this would be a hindrance when many samples have to be processed; on the other hand, the recovery efficiencies of different filters would be different; thus, using the same filter is recommended for the complete analysis of a water sample, including the extraction runs on standard samples to determine percent recoveries.

After extraction of a water sample in the apparatus, the sample container is washed thoroughly, first with distilled, and then with doubly distilled water. Blank determinations were made every five samples. For this purpose, a sample of pure water was treated in the same way as the ordinary samples. Blank water was prepared by first passing it through a mixed-bed resin that retains organics, and then distilling it twice. The filter extracts obtained in this manner exhibited chromatograms identical to those of pure pentane.

B. Chromatographic analyses

The gas chromatograph used in the project was a Varian Model 2740-20, equipped with flame ionization(FID) and electron capture (EC) detectors. It was modified so that the carrier gas flow to each detector was independent of the other. Nitrogen (ultra high purity grade, Linde) was used for all determinations employing the EC detector. Two gas purifiers were used in series after the tank pressure regulator, one to remove traces of moisture and organics and the other to remove traces of oxygen, which is detrimental to some columns and a nuisance in the EC mode of operation.

The detector oven was held at the operating temperature for least 24 hours prior to any analysis. High-temperature septa which had been previously baked at 200°C for 24 hours were used throughout the experiments.

The chromatographic conditions for the analyses, including column selection, were optimized by repeated analyses of a standard mixture of volatile organohalides. All columns tried were packed columns; the column materials were stainless steel and nickel; the column lengths varied between 8 and 10 feet. It was found that column packings of a general type (non-polar)like SE-30 or OV-1 did not achieve adequate separation of these compounds. The columns and packings recommended by EPA (6) for the identification and quantitation of trihalomethanes were given special consideration. These were found to give the best chromatograms in terms of peak shapes and resolution; therefore, they were chosen as the analytical columns for the identification and quantitation of the volatile organo-halides in this research. The first one, packed with GP 20% 2100/0.1% CW 1500 on 100/120 mesh supelcoport, was obtained from Supelco, Inc., Bellefonte, Pennsylvania. The other column, packed with 0.2% Carbowax 1500 on 60/80 mesh Carbopack C, was purchased from the Regis Chemical Co., Morton Grove, Illinois. A description of the chromatographic

conditions employed for the analyses, including the columns, is given in Table 1.

As stated before, a positive identification of a given compound in a chromatogram is assumed when the retention times of a given standard, as measured in each of the chosen columns, coincide with those of the unknown, measured under the same conditions.

C. Sampling procedure

Water samples were taken directly from the tap in 1-gallon bottles provided with PTFE-lined screw caps. The bottles were washed with detergent and water, rinsed with tap water, then with distilled water, and finally dried in an oven at 200°C for 24 hours. When filled, care was taken to avoid trapping air bubbles that would provide a headspace where the volatile organics could accumulate. No quenching of residual chlorine with sulfite or thiosulfate was effected. Samples were transported to the laboratory the same day they were gathered; if sparging could not be started the same day, they were stored in a refrigerator at 4°C until processed. In no case was a sample stored for more than two days before analysis was begun. If any bubbles appeared during this period, the sample was discarded.

It should be noted that some investigators that have done drinking-water research have taken the samples directly from the water purification plant. As far as the director of this project knows, there are no reports in the literature where tap water analysis has been performed and compared with the composition of the water at the corresponding production site. Although this was not attempted in this project, it is suspected that a difference in composition might very well exist due to the residence time of the water in the pipes and the varying conditions,

Table 1. CHROMATOGRAPHIC COLUMNS AND CONDITIONS

COLUMNS

1. GP 20% SP 2100/0.1% CW 1500 on 100/120 supelcoport, 10 ft x 1/8" SS.

2. Eight ft stainless steel column (1/8 in OD. x 0.1 ID) packed with 0.2% carbowax 1500 coated on 60/80 mesh, carbopack C. preceded by a 1 ft stainless steel column (1/8 in OD. x 0.1 in ID) packed with 3% carbowax 1500 coated on 60/80 mesh Chromosorb W.

CONDITIONS

Carrier gas: Nitrogen at 45.2% ml/min

Column Temperature - 110°C

Injector Temperature - 150°C

Detector Temperature - 265°C

Electron Capture Detector - ^{63}Ni

Sample size: 1-2 ul

chemical and physical, to which it would be subjected therein. From the
human health standpoint, it is the composition of the tap water, delivered
at the homes (or other places where it is consumed) that really matters.
If a water sample is quenched at the plant, eliminating residual chlorine,
it might contain lower levels of trihalomethanes, upon analysis, than a
sample of the same water taken at the tap, several hours-or maybe days-
later.

III.   Results and discussion

For discussion purposes, the GP 20% SP 2100 column will be referred to as column 1, whereas the .2% Carbowax 1500 column will be referred to as column 2, in accordance with Table 1. The chromatogram obtained by extracting pure water using the CLSA apparatus and employing column 1 is shown in Fig. 4. The same extract, chromatographed by means of column 2 is shown in Fig. 5. The retention times of the different peaks are shown in both figures. The similarity in both chromatograms is apparent; however, column 1 shows better resolution. Furthermore, there is a reversal in elution time between the negative peaks and peak #2 in column 2 with respect to column 1. Peak #4 in Fig. 4 is not shown in Fig. 5 because of its low intensity: only 1 μl was injected to obtain Fig. 5 because in column 2 the size and shape of the negative peaks tends to obscure neighboring peaks if a larger volume is injected. Peak #1 in both figures is due to traces of methanol used to wash the filter. The negative peaks in EC chromatograms is a peculiarity exhibited by some compounds; under certain concentration conditions; otherwise, they are not important.

The chromatograms of the pure water extracts should be compared with the chromatograms of pentane using both columns. These are shown in Figs. 6 and 7. It should be noted that the chromatograms of n-pentane are identical with the corresponding ones of the pure water extracts. This shows that the purity of the water used in the blank determinations is adequate for our purposes.

A.   Identification of compounds in water samples

Fig. 8 shows the chromatogram of a typical water sample from Mayaguez. Besides the solvent peaks, it shows a number of peaks corresponding to organic contaminants, which are identified in the figure by
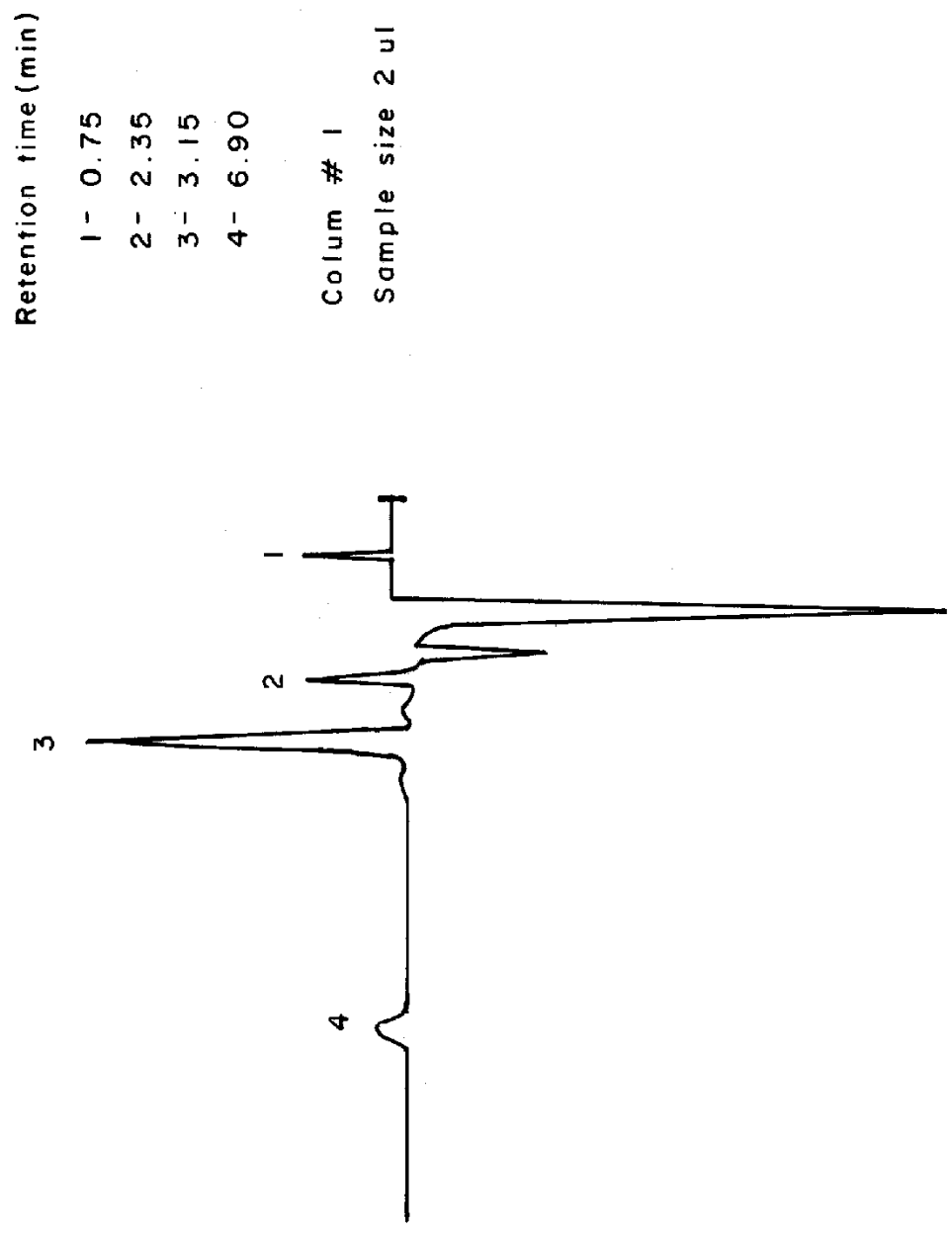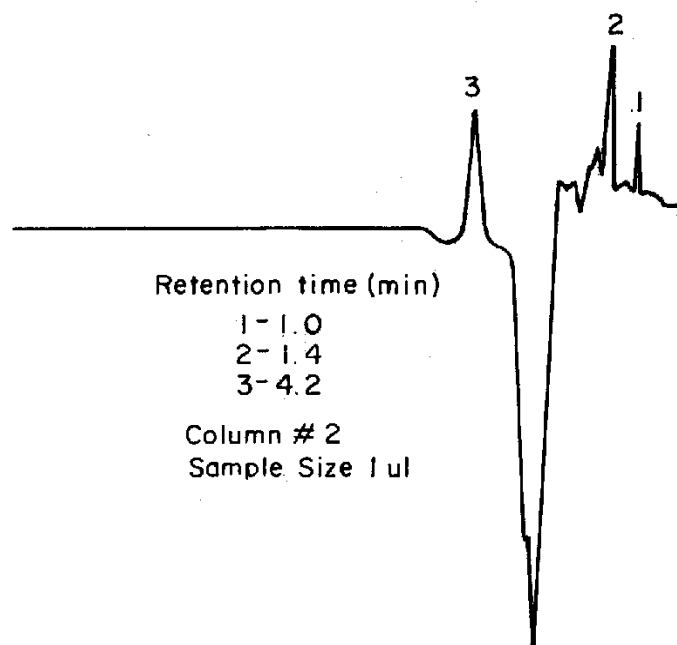
Fig. 4 REDESTILLED WATER CHROMATOGRAM

Retention time (min)

1- 0.75
2- 2.35
3- 3.15
4- 6.90

Colum # 1
Sample size 2 ul

Fig. 5 REDESTILLED WATER CHROMATOGRAM

Retention time (min)
1 - 1.0
2 - 1.4
3 - 4.2

Column # 2
Sample Size 1 ul

Fig. 6 n - pentane Chromatogram

Retention Time (min)

1 - 0.75
2 - 2.35
3 - 3.15
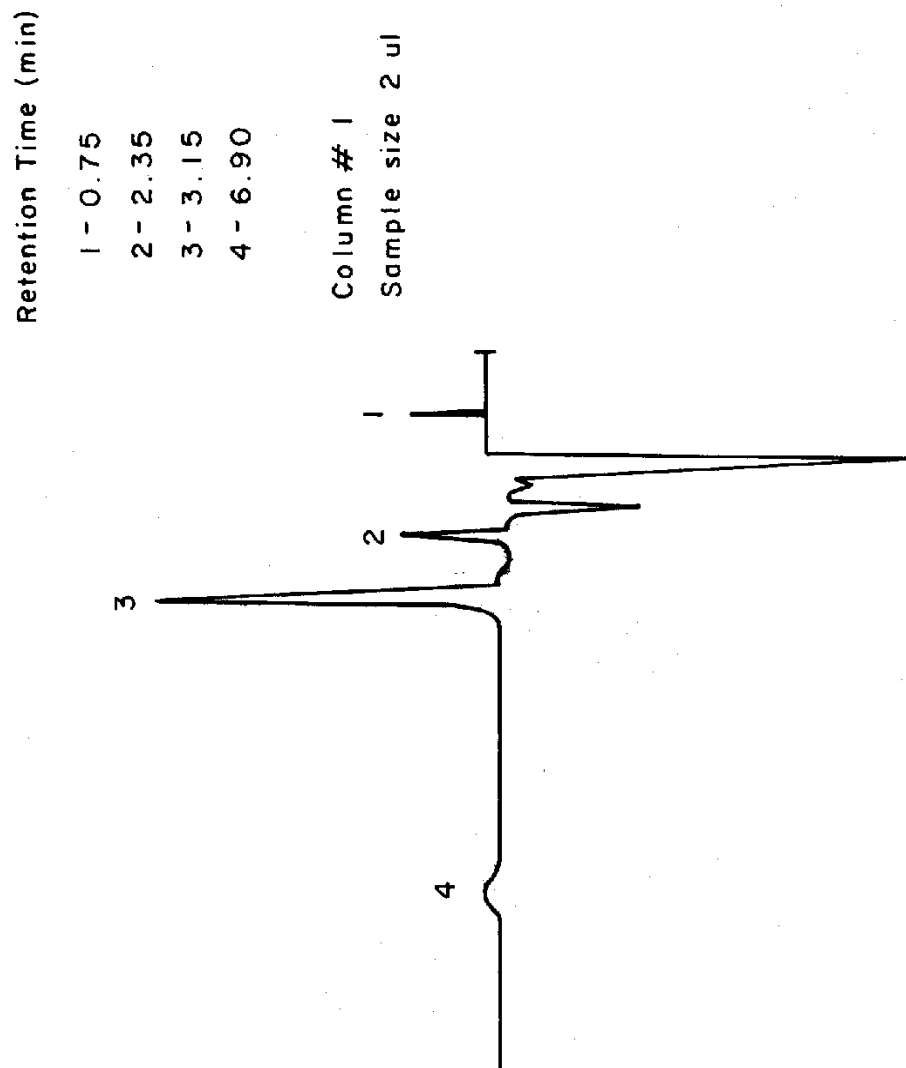4 - 6.90

Column # I
Sample size 2 ul

Fig. 7 n-pentane Chromatogram

Retention Time (min)

1 - 1. 0
2 - 1. 4
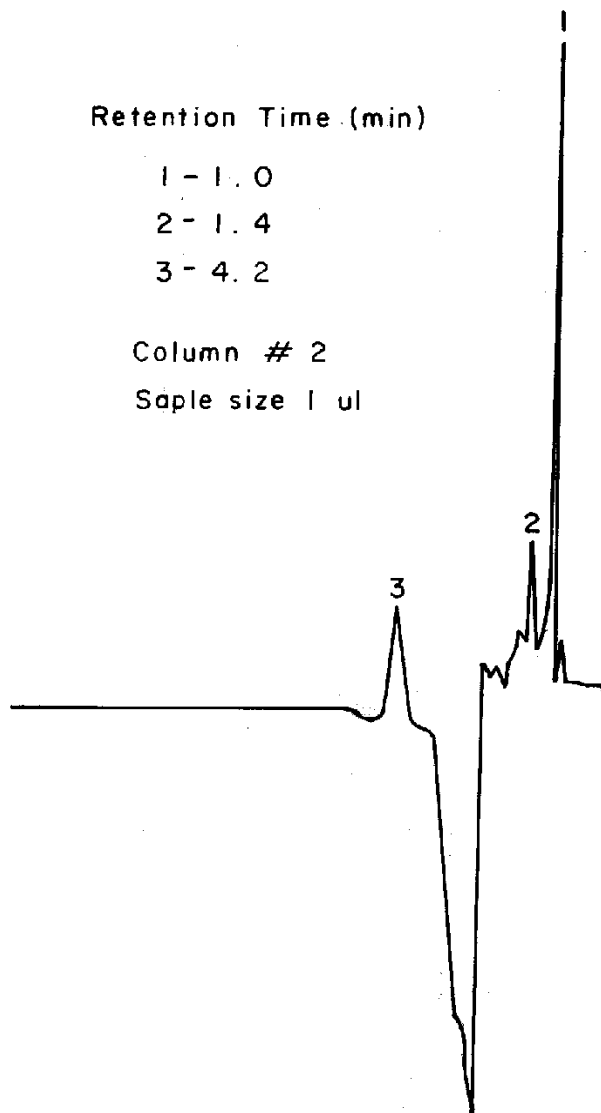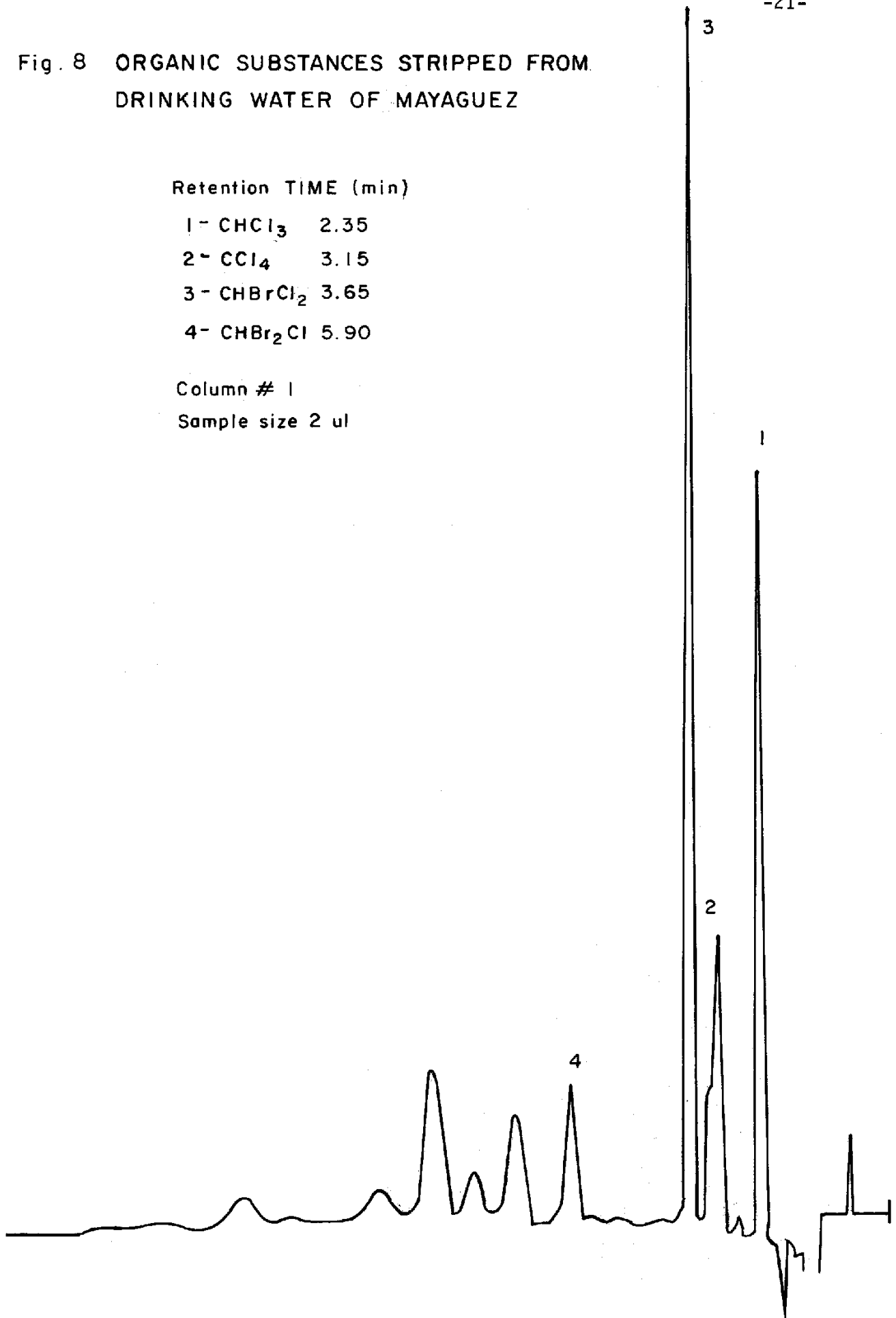3 - 4. 2

Column # 2
Saple size 1 ul

Fig. 8   ORGANIC SUBSTANCES STRIPPED FROM
DRINKING WATER OF MAYAGUEZ

Retention TIME (min)

1 - $CHCl_3$ 2.35

2 - CCl_4 3.15

3 - $CHBrCl_2$ 3.65

4 - $CHBr_2Cl$ 5.90

Column # 1

Sample size 2 ul

their retention times. There are still a number of them which have not been
identified; these have not been assigned any numbers in the chromatogram.
Fig. 9 shows a chromatogram of another sample extract from Mayaguez, passed
through column 2. In this chromatogram the notable feature is the absence
of the peak assigned to carbon tetrachloride in Fig. 8. All other
identified peaks are also present in the previous chromatogram. This
result confirms the findings of Coleman (9) and other investigators in the
sense that the composition of potable water is variable with time: a
contaminant that is present at a given time may be found to be present
at a different concentration or totally absent at another date. In some
instances, the discharge, accidental or otherwise, of a certain contaminant
into a water body that feeds a municipal purifying plant has been held
accountable for the sudden appearance of unusual chemicals in potable water.
It is uncertain whether the variations in the carbon tetrachloride con-
centration in the Mayaguez area are due to natural causes or are the
result of discrete, man-provoked inputs into the environment. The other
organohalides present in the Mayaguez water supply are the so-called
trihalomethanes, who have been found to be universal contaminants of water
supplies around the world where chlorination is used to desinfect the
water. The bromine derivatives are formed by substitution from the
chlorinated species by a mechanism that involves the HOBr species (12).
It is to be expected that natural waters rich in bromide would lead to
drinking water with relatively high levels of the brominated species.

Figure 10 shows a chromatogram of a standard mixture of halogenated
organics consisting of the trihalomethanes plus carbon tetrachloride,
all at a concentration of 1 ppm, along with their retention times.
Fig. 11 shows the corresponding chromatogram using column 2. The reten-
tion times obtained in this experiments were used to make the identifi-

Fig. 9 ORGANIC SUBSTANCE STRIPPED FROM
        DRINKING WATER OF MAYAGUEZ

Retention Time (min)

1 - CHCl$_3$ 2.8
2 - CHBrCl   4.65
3 - CHBr$_2$Cl   8.45

Column # 2
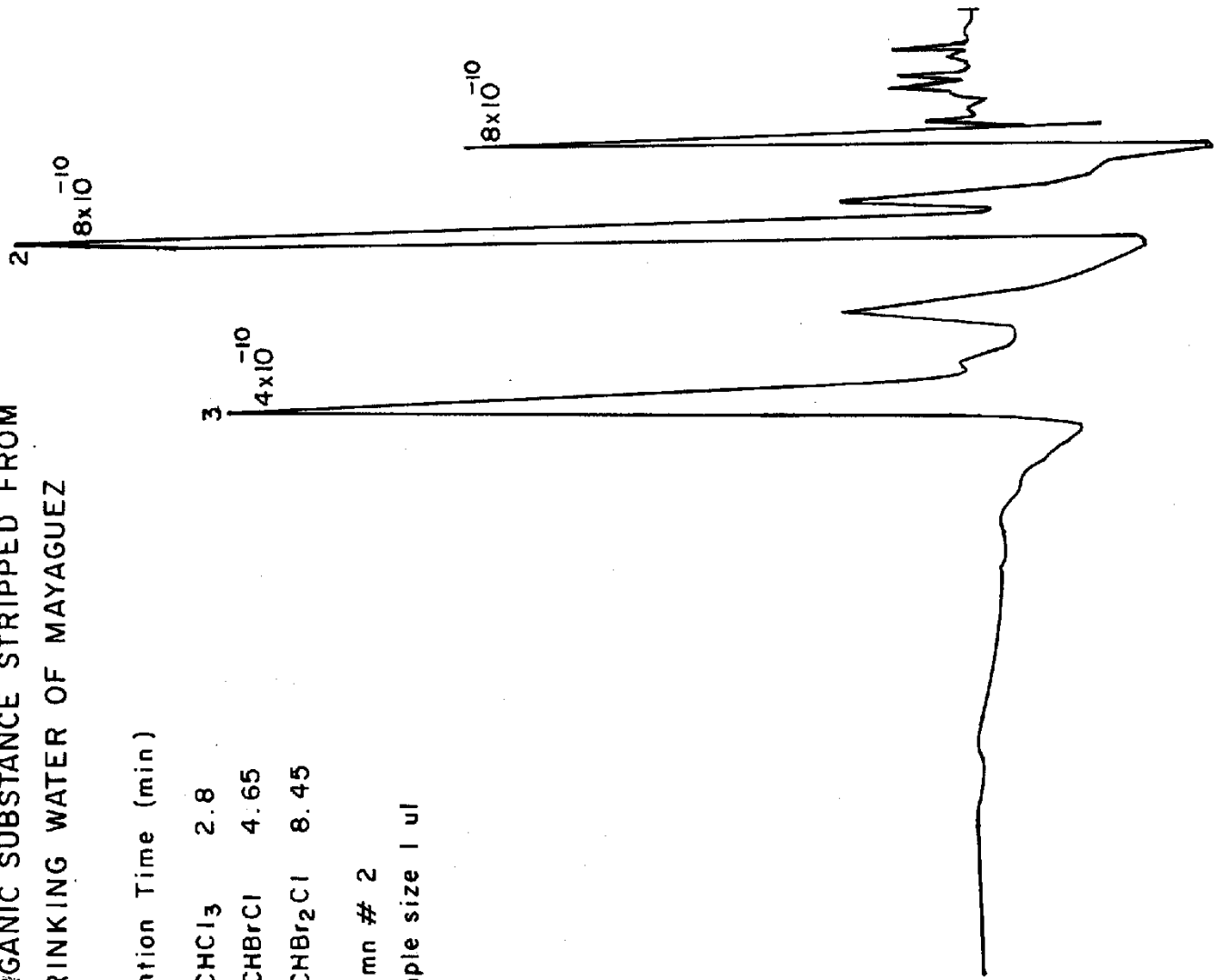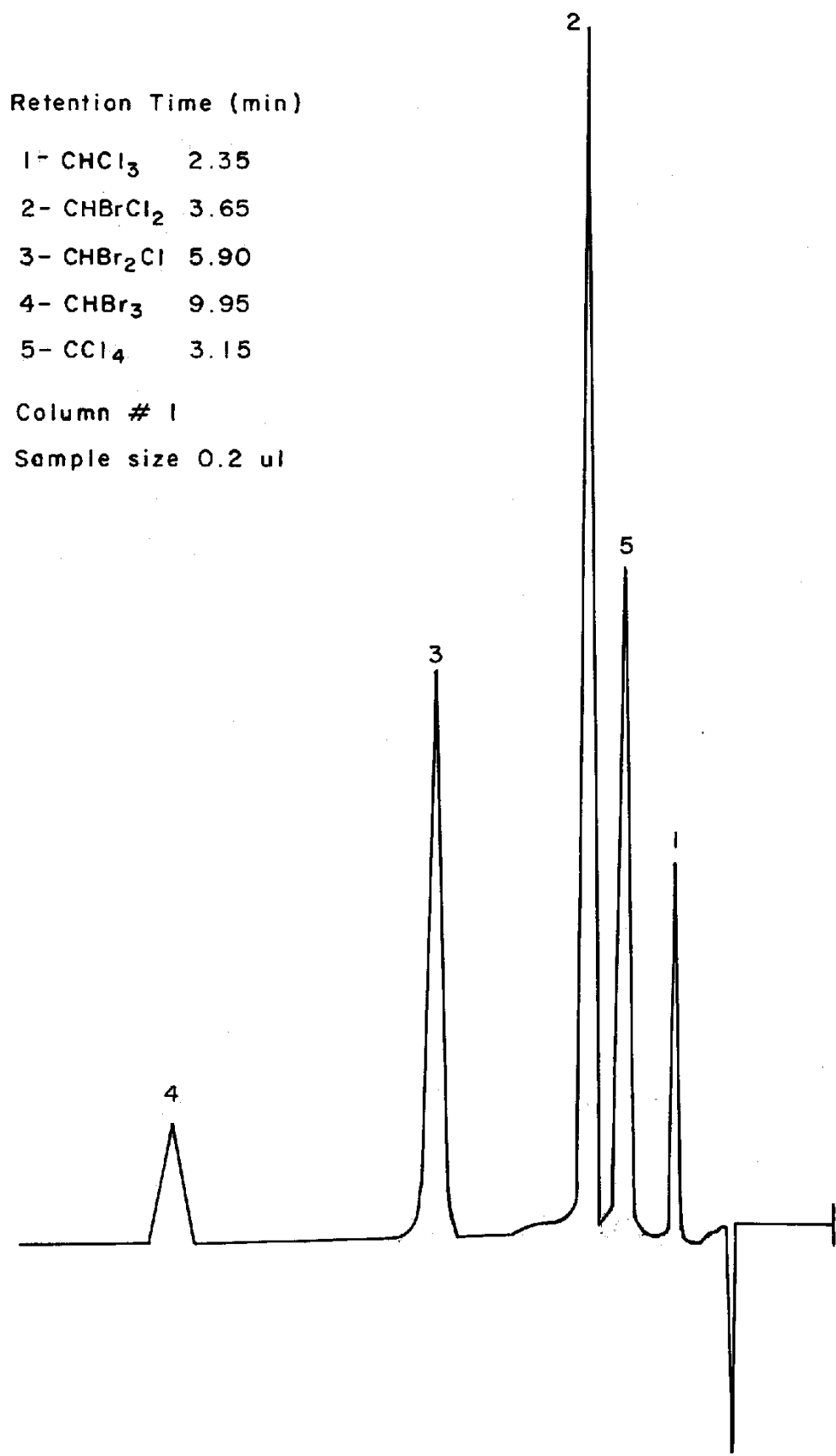Sample size 1 ul

Fig. 10 STANDARD COMPOND CHROMATOGRAM

Retention Time (min)

1- $CHCl_3$ 2.35

2- $CHBrCl_2$ 3.65

3- $CHBr_2Cl$ 5.90

4- $CHBr_3$ 9.95

5- CCl_4 3.15

Column # 1

Sample size 0.2 ul

Fig. 11 STANDARD COMPOUND CHROMATOGRAM

Retention Time (min)

1 – $CHCl_3$ 2.8
2 – CCl_4 4.2
3 – $CHBrCl_2$ 4.65
4 – $CHBr_2Cl$ 8.45
5 – $CHBr_3$ 15.65

Column # 2
Sample size .2 ul
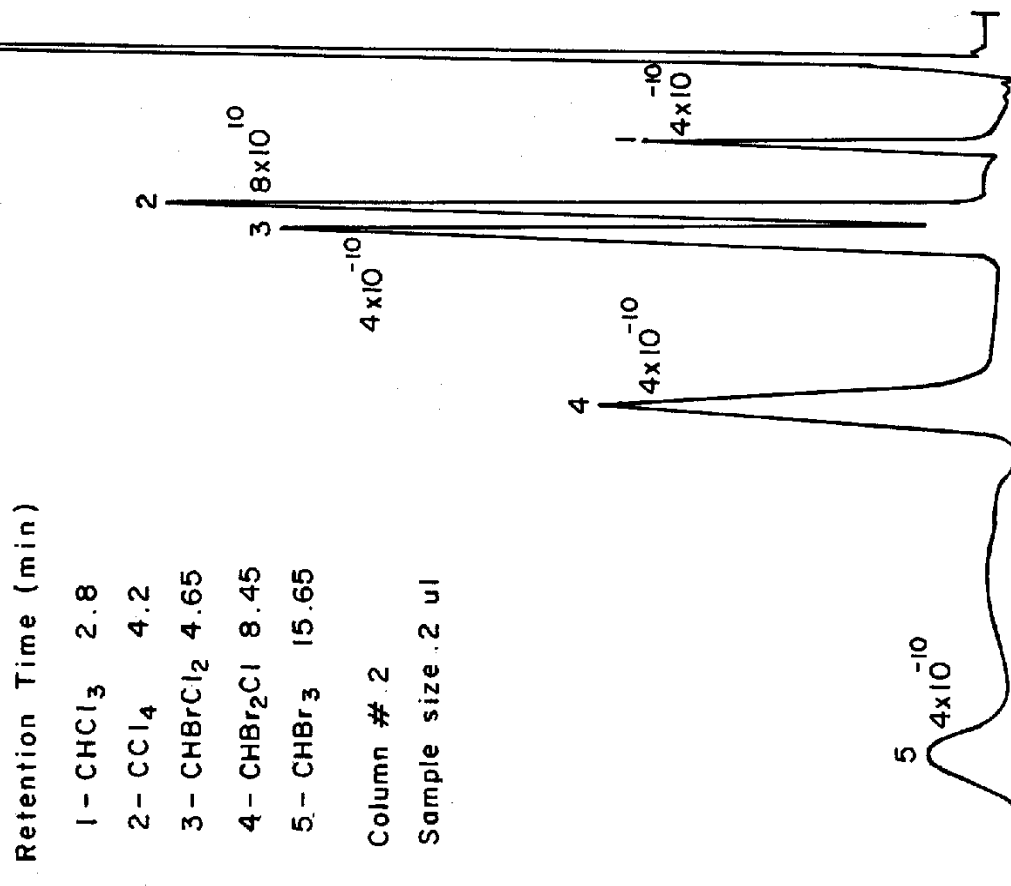
cations of the chromatographic peaks of all the water extracts.

Figure 12 shows a typical chromatogram obtained from a water extract from Ponce, using column 1. Its outstanding feature consists of the absence of the chloroform peak. Another salient feature of this chromatogram is the bromoform peak, which was absent in the Mayaguez water. Fig. 13 shows the chromatogram of another water extract from Ponce, using column 2. The chloroform peak is present here but at a very low intensity. As a matter of fact, these results were in line with the general trend in the composition of the Ponce drinking water: chloroform is the least abundant component, when present, and bromoform is always present. However, the bromoform concentration is variable. This could be attributed to the fact that Ponce has several water supplies, some deriving a substantial volume of their raw, water from deep wells. It has been implied (11) that groundwater may contain an appreciable concentration of bromides; if this holds true for the Ponce groundwater, then the high bromoform levels could be attributed to the reaction of HOCl formed from Cl_2 and H_2O with Br^- to form HOBr, which then reacts with chloroform to form $CHBr_3$. The low levels of $CHCl_3$ in Ponce seem to confirm this hypothesis.

Although Figs. 12 and 13 do not show other prominent peaks, later runs have shown the presence of another peak in the Ponce water which has been identified as tetrachloroethylene. There are no known natural sources of this compound; therefore, it is presumed that its presence is due to man-made pollution of either the surface or groundwater feeding the Ponce purification plants. It is more probable that this contamination is associated with the groundwater, since the rivers which feed the Ponce purification plants are dammed high up in the mountains, for away from industrial and commercial sources of tetrachloroethylene, a very prevalent solvent and degreaser. It is more reasonable to think that this

Fig.12 ORGANIC SUBSTANCES STRIPPED FROM
DRINKING WATER OF PONCE

Retention Time (min)
1 - CCl_4 3.15
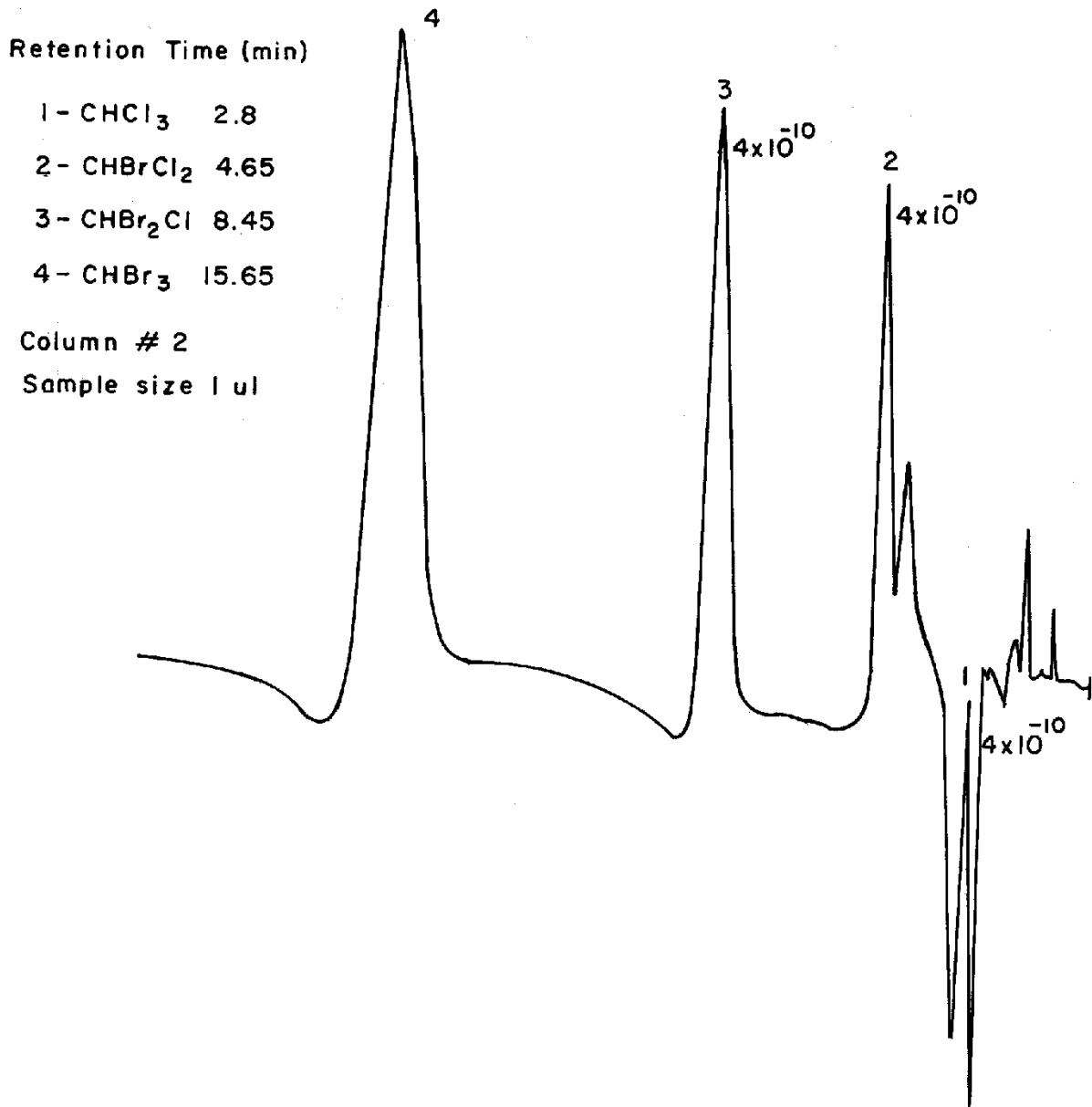2 - $CHBrCl_2$ 3.65
3 - $CHBr_2Cl$ 5.90
4 - $CHBr_3$ 9.95

Column # 1

Sample size 2 ul

Fig. 13 ORGANIC SUBSTANCES STRIPPED FROM DRINKING WATER OF PONCE

compound has found its way to the groundwater lying beneath the city by seepage through soil contaminated by the improper disposal of waste solvent.

Fig. 14 shows the resulting chromatogram of a typical water extract from the San Juan water supply. It should be mentioned that San Juan derives most of its raw water from lake Carraízo, a badly contaminated water body. It is not surprising, therefore, that all of the previously identified contaminants in the Island's water supplies are found in San Juan, including bromoform and tetrachloroethylene. As in some of the other chromatograms, there are a number of smaller peaks that had not been identified by the time this report was being written.

B. Quantitation of identified compounds

After the identification of the organic contaminants in a given water sample, there remains the task of assessing their concentrations before a realistic evaluation of their potential environmental hazard or health effects can be made and corrective actions implemented.

In order to calculate correctly the concentration of a given compound in a water sample, certain quantities need to be known in addition to the peak height or peak area in the chromatogram. These are:

a) The response factor for the compound, which can be defined as the area (in arbitrary units) or the peak height (arbitrary units) per unit mass (usually nanograms or multiples thereof). The mass is calculated as the product of the concentration (ppm or ppb) times the volume (usually microliters) used for injection into the gas chromatograph. Since different compounds have different response factors, the latter have to be determined for each compound by plotting

Fig. 14 ORGANIC SUBSTANCES STRIPPED FROM
DRINKING WATER OF SAN JUAN
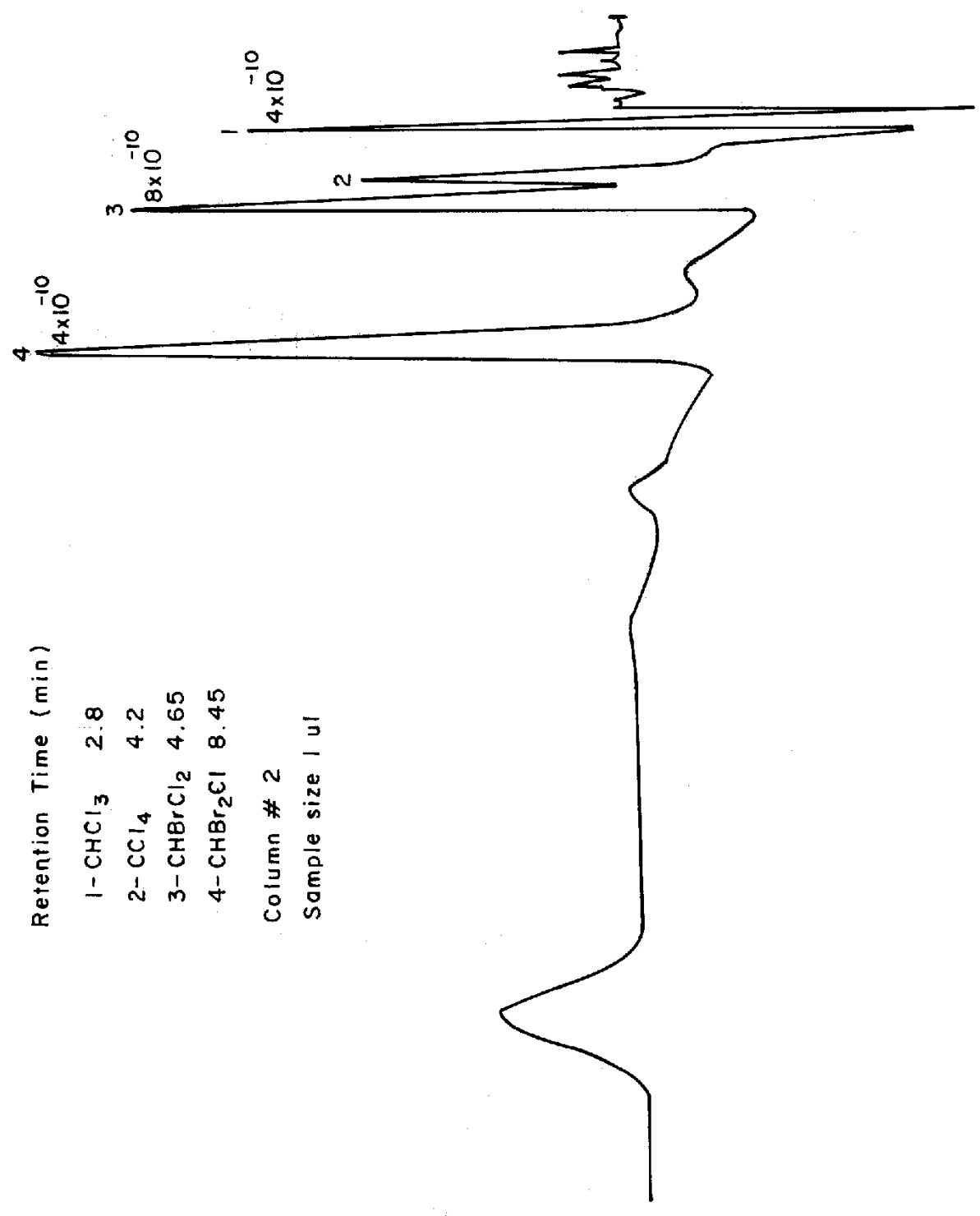
Retention Time (min)

1- $CHCl_3$ 2.8
2- CCl_4 4.2
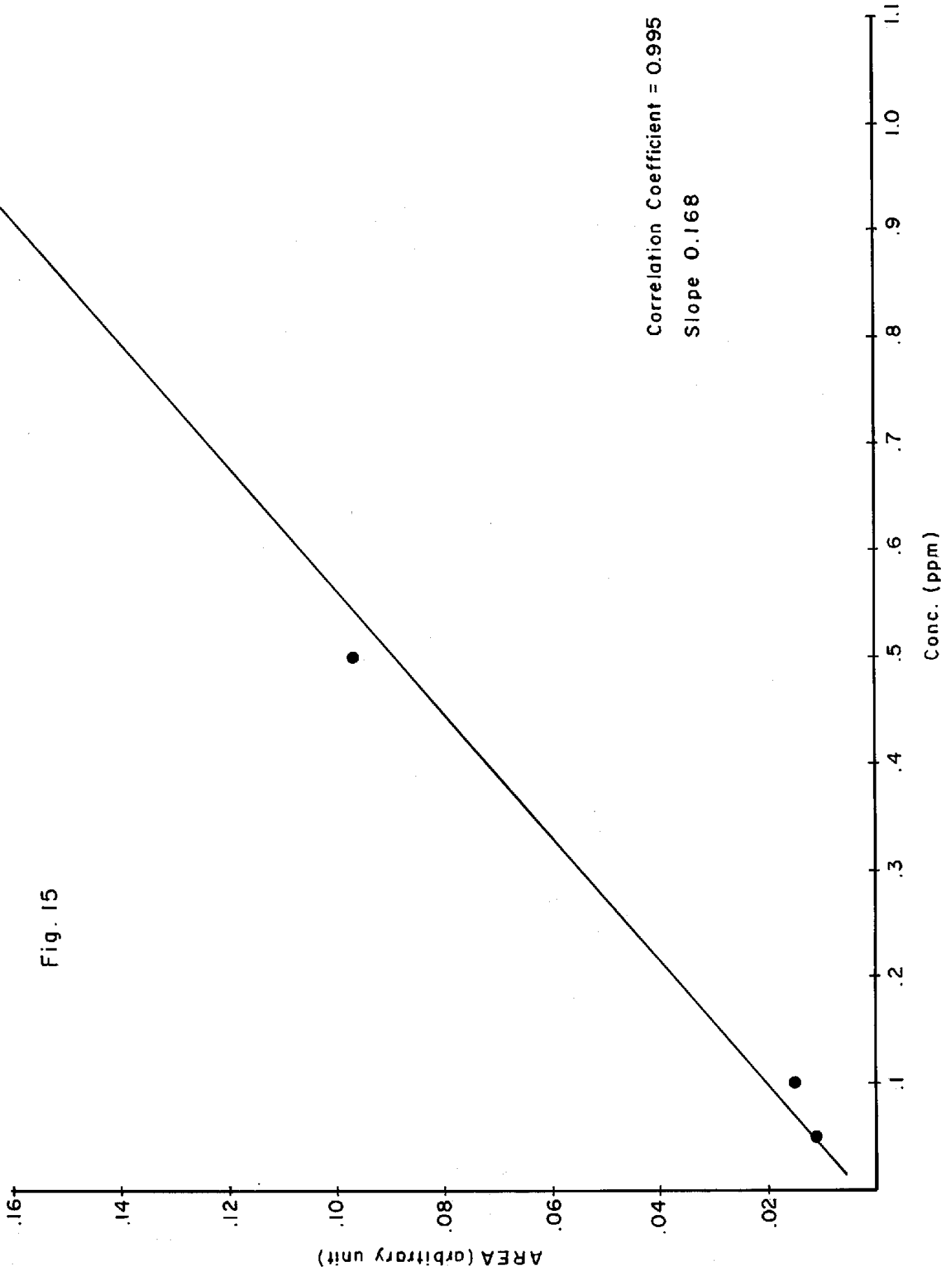3- $CHBrCl_2$ 4.65
4- $CHBr_2Cl$ 8.45

Column # 2

Sample size 1 ul

either the peak height (peak area) vs. concentration.
This was done for the various compounds confirmed to
be present in drinking water and is shown in Figs.
15 to 22. The correlation coefficient was calculated
for each regression line and is given for each plot.
All graphs are linear to a good degree, as evidenced
by the values of the correlation coefficients for the
various concentration ranges given. It should be
mentioned that the linear dynamic range of the EC
detector used is only about 50. Therefore, the
detector signal cannot be expected to correlate
linearly with concentration if the concentration
factor (maximum divided by minimum value) exceeds
this value. For example, the carbon tetrachloride
curve had to be divided into two parts, each of which
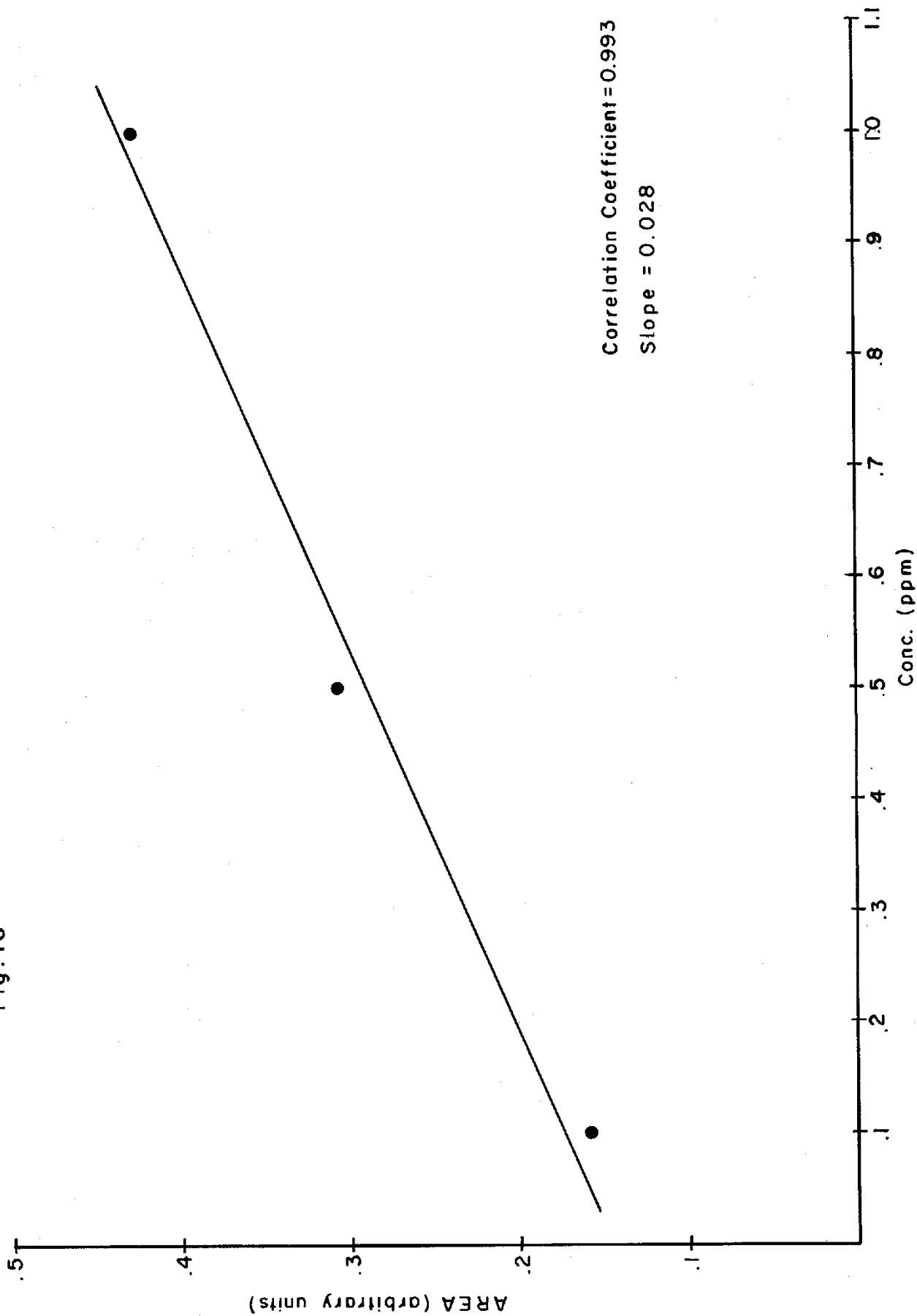is linear to a good approximation.

Through the use of these plots, constructed by
measuring the response to a series of standard solu-
tions, the external standard method can be employed
to determine the concentration of a compound in a
given water extract: the peak area of a given
compound in the chromatogram is matched against the
same value of the area in the standard curve and the
corresponding concentration is read off the graph's
concentration axis. In order to do this, equal
volumes of standard must have been used to construct
the curve as of water extract injected to obtain the
chromatogram.

Fig. 15

CCl₄ AREA vs CONCENTRATION (ppm)

Correlation Coefficient = 0.995
Slope 0.168

CCl$_4$ AREA vs CONCENTRATION (ppm)

Fig. 16

Correlation Coefficient = 0.993

Slope = 0.028

Conc. (ppm)

AREA (arbitrary units)

CHCl₃ AREA vs CONCENTRATION (ppm)

Fig. 17

Correlation Coefficient = 0.998

Slope = 0.245

Conc. (ppm)

ARE (arbitrary units)

CHCl₃ AREA vs CONCENTRATION (ppm)

Fig.18

Correlation Coefficient=0.999

Slope = 0.136

Conc. (ppm)

AREA (arbitrary units)

CHBrCl$_2$ AREA vs Concentration (ppm)

Fig. 19

Correlation Coefficient = 0.994
Slope = 0.344

Conc. (ppm)

AREA (arbitrary units)

Fig. 20
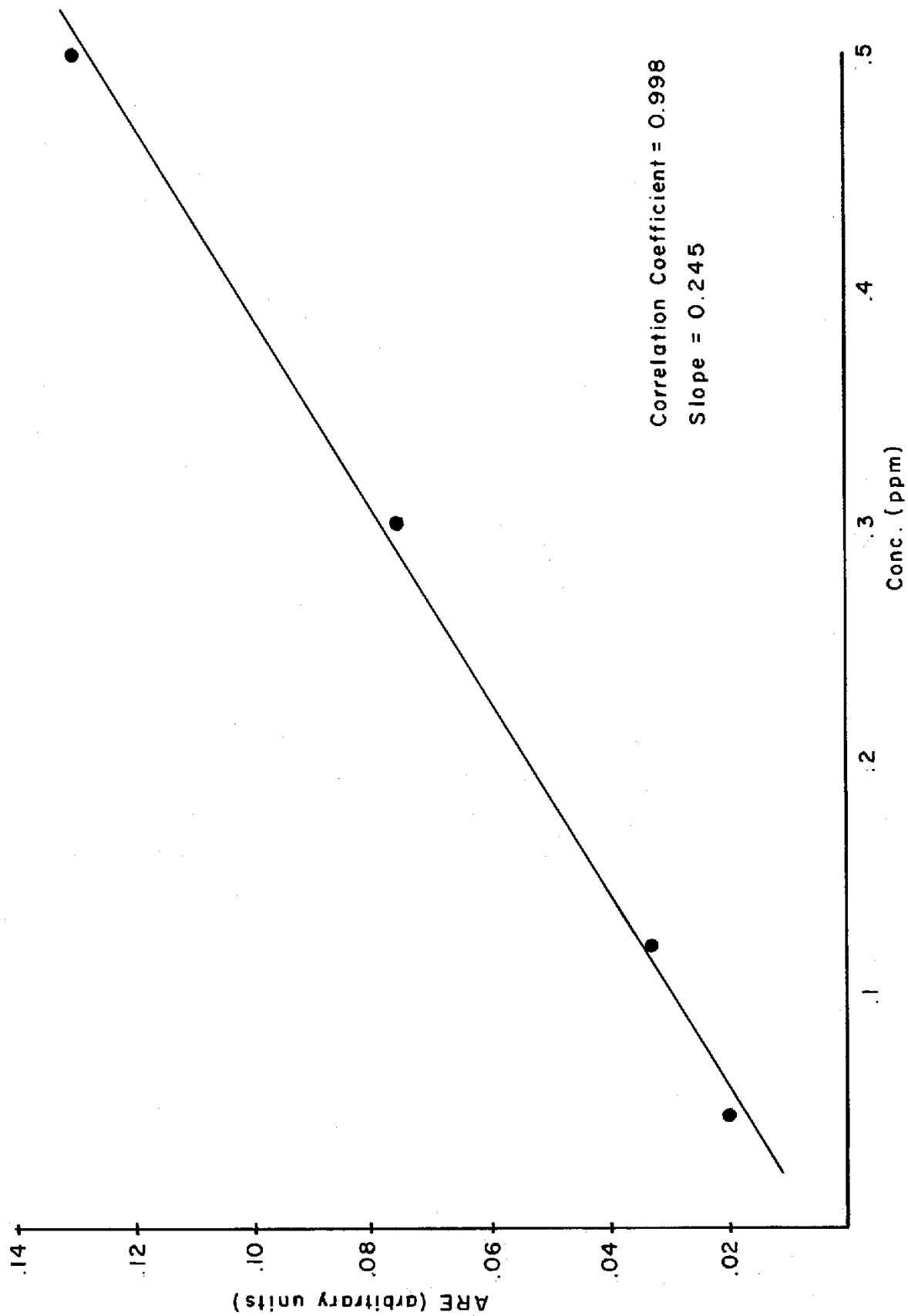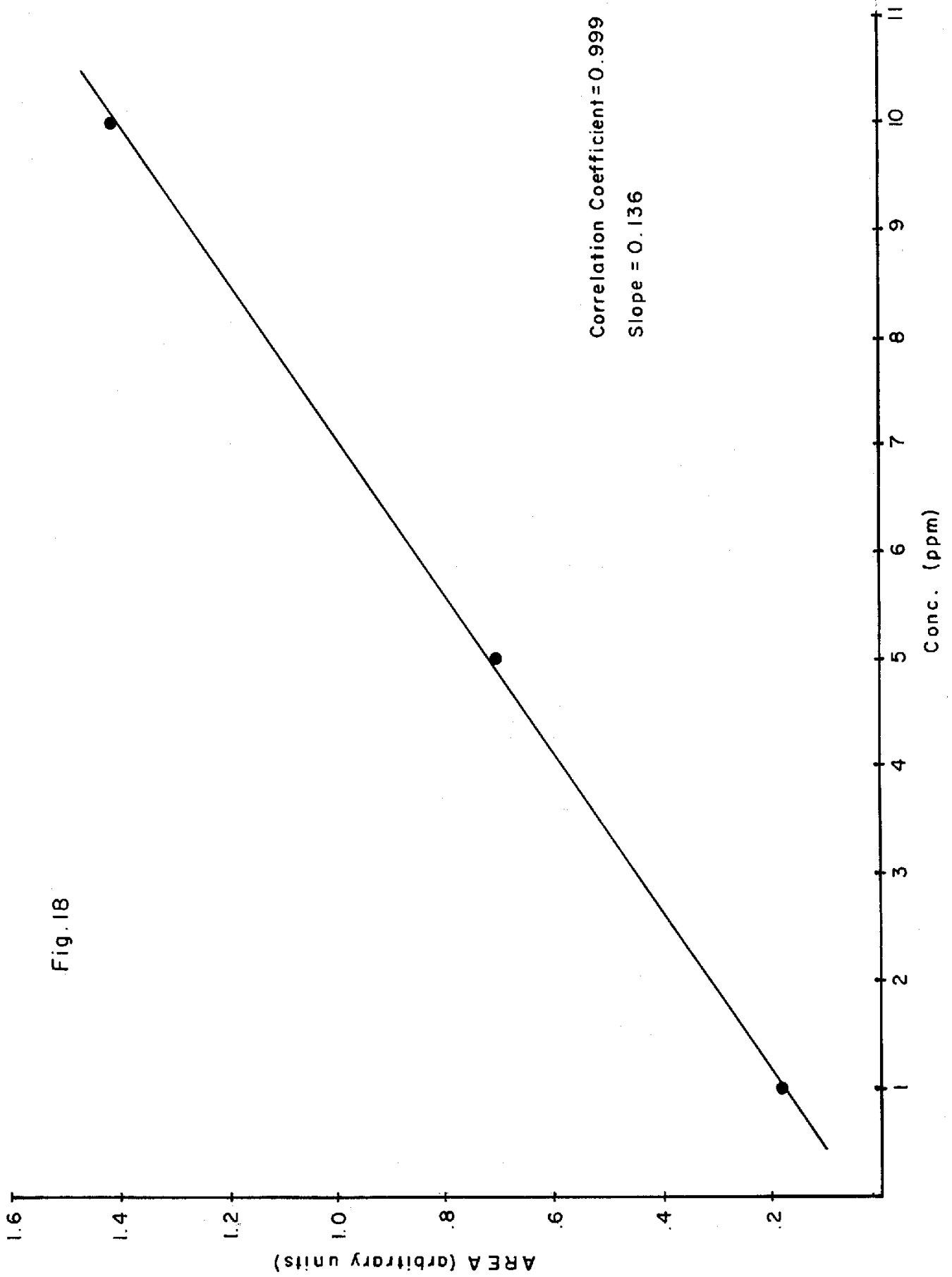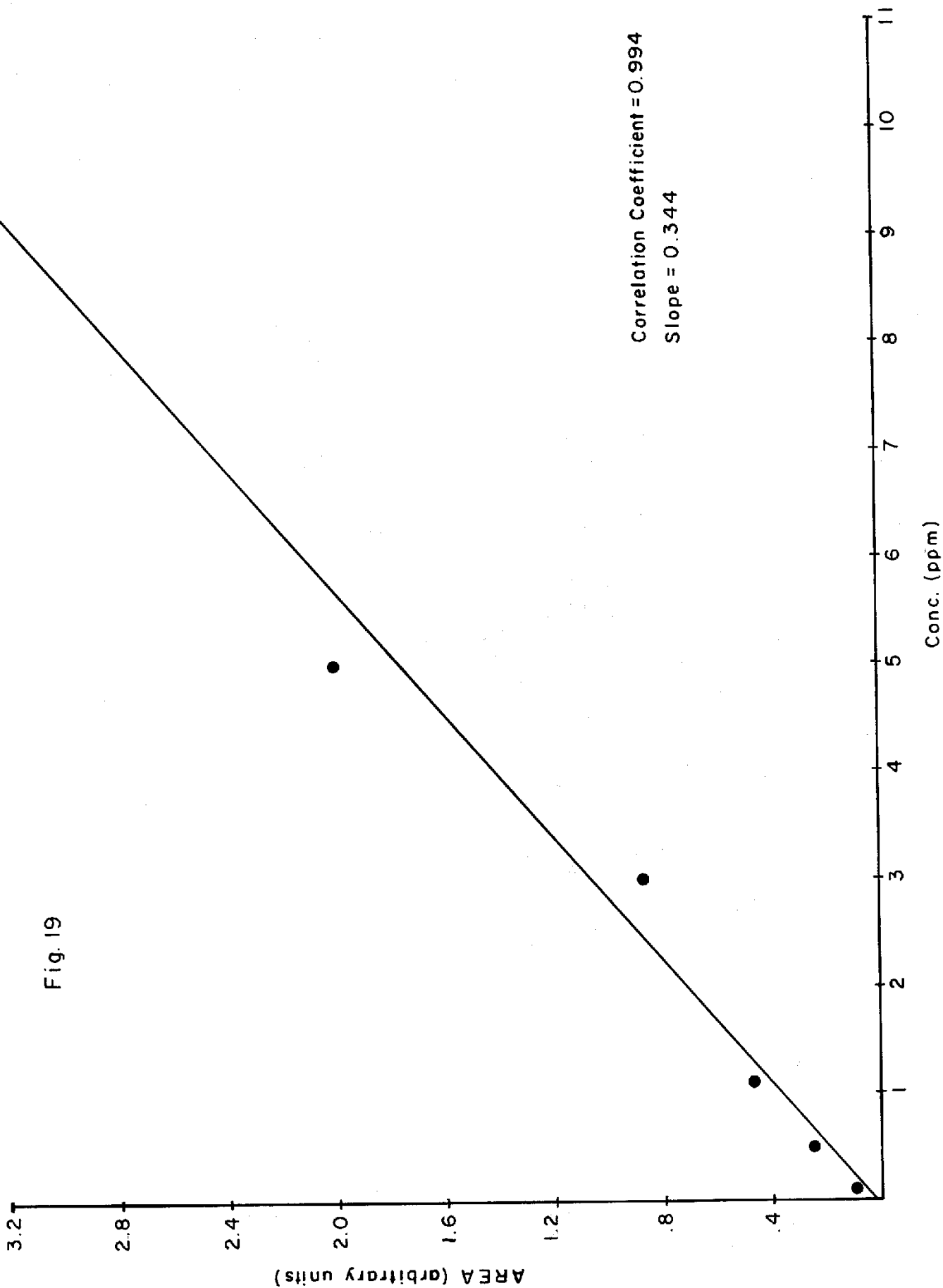
CHBr$_2$Cl   AREA vs CONCENTRATION (ppm)

Correlation Coefficient = 0.997
Slope = 0.303

Conc. (ppm)

AREA (arbitrary units)

CHBr₃ Area vs CONCENTRATION (ppm)

Fig. 21

Correlation Coefficient = 0.999
Slope = 0.057

Fig. 22
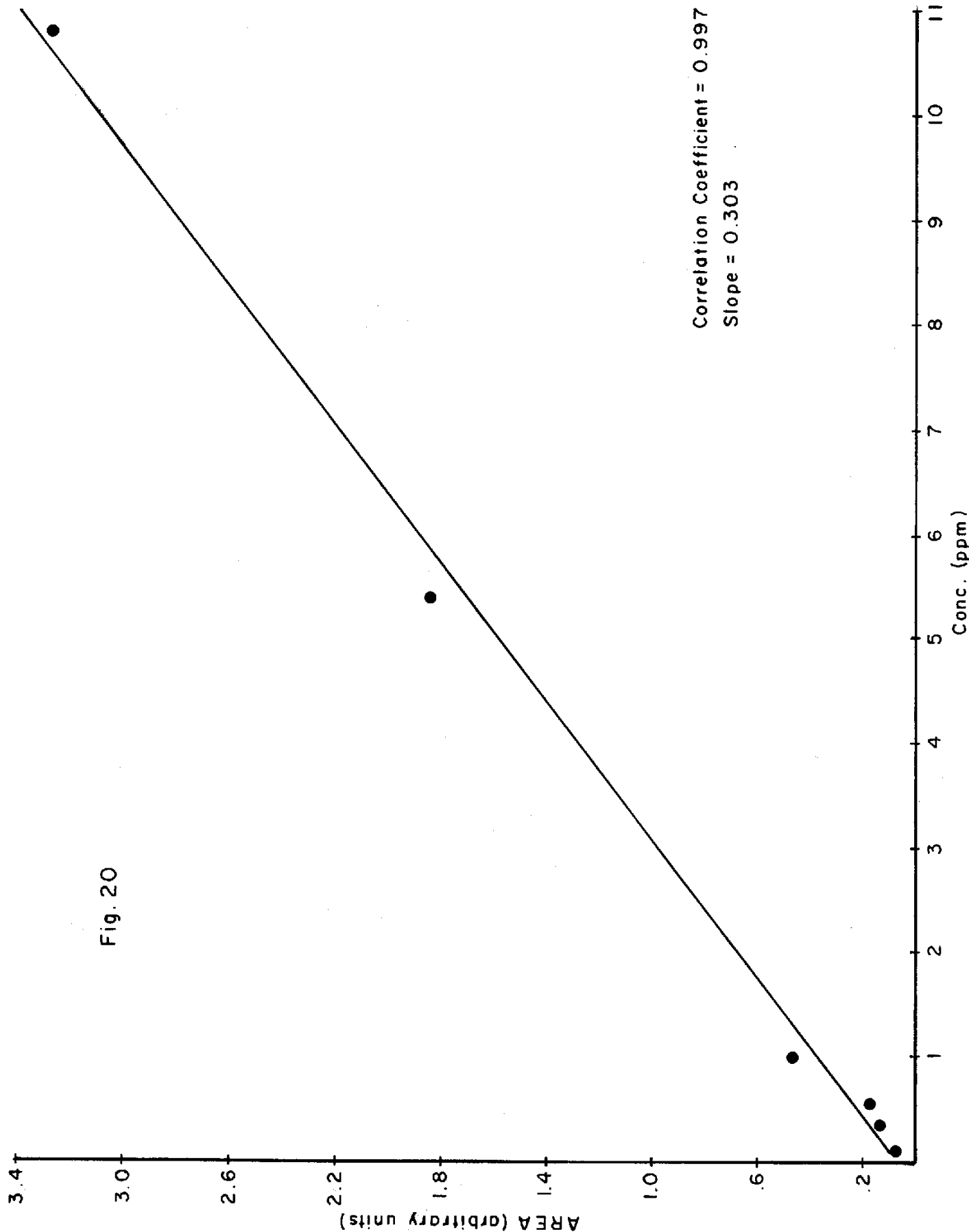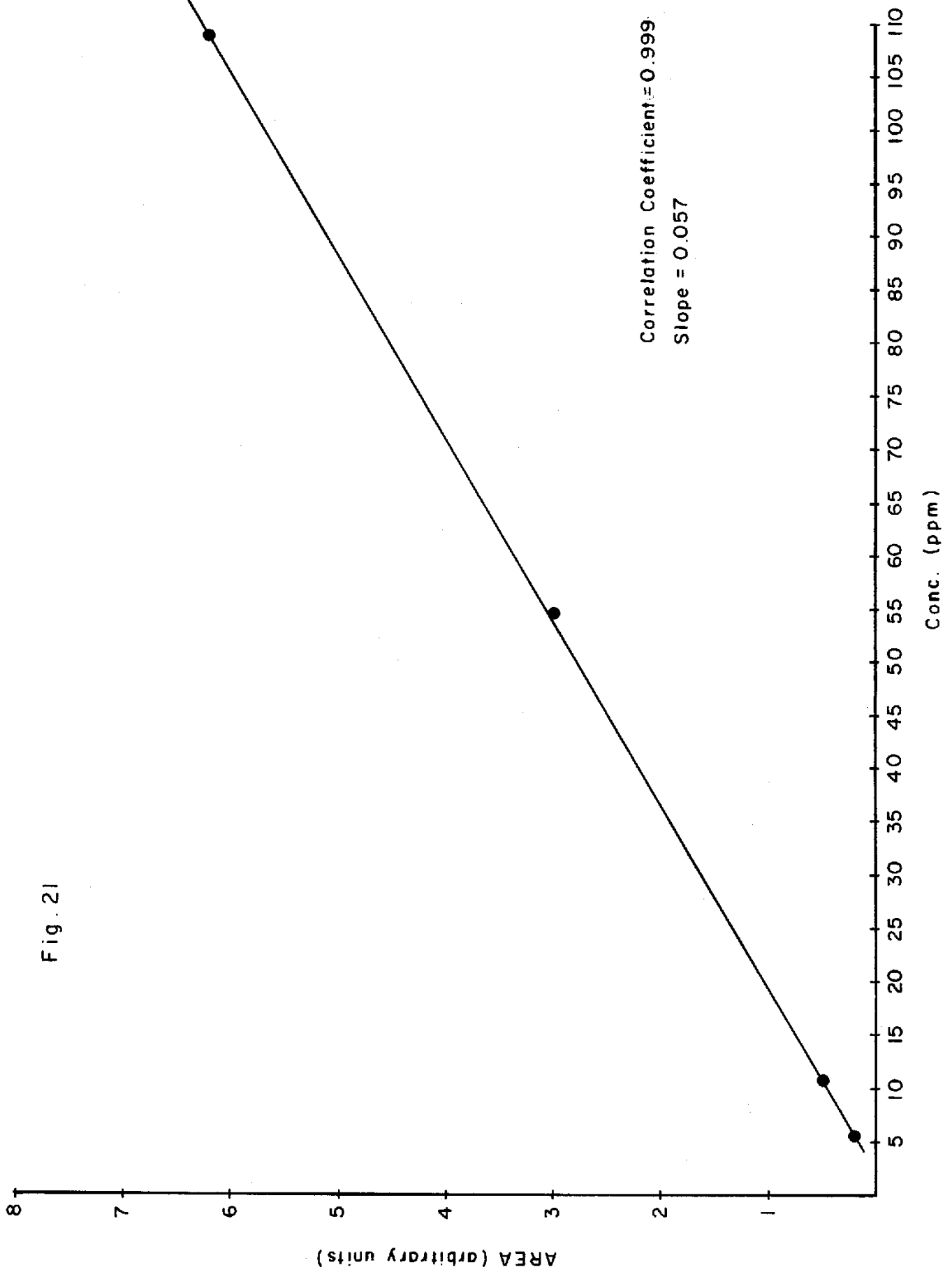
$CCl_2:CCl_2$ AREA vs CONCENTRATIO (ppm)

Correlation Coefficient = 0.998
Slope = 0.063

Conc. (ppm)

AREA (arbitrary units)
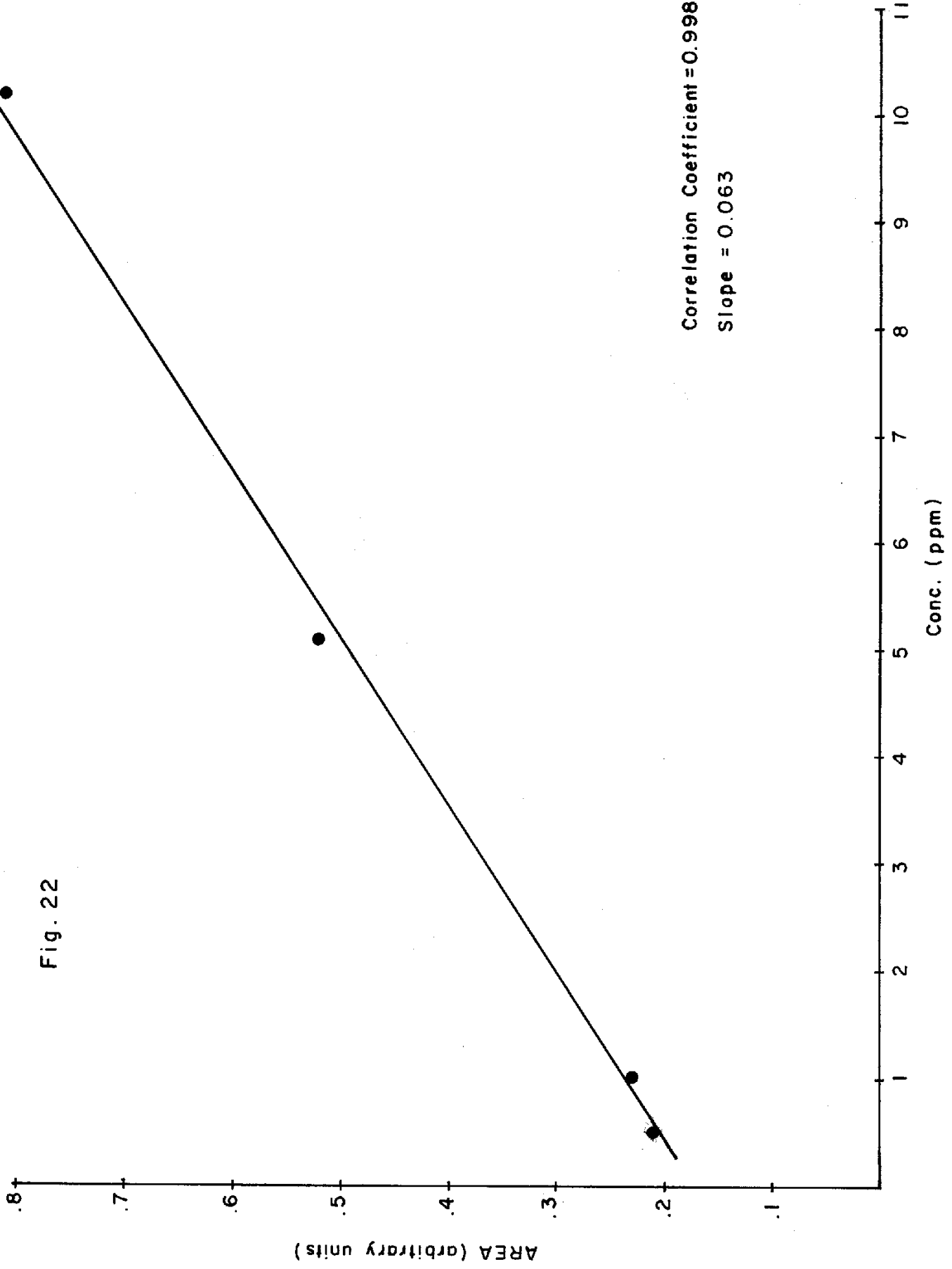
b)   Percent recovery (recovery efficiency), which can be
defined as the mass fraction (multiplied by 100) of a
given compound that is recovered in the whole procedure
(stripping, trapping, eluting) as measured by the
appropriate area in the chromatogram. This area must
be corrected for the response factor. The percent
recovery is a difficult parameter to measure and is
the source of the largest error in the quantitation
procedure. It is a function of sparging time, vapor
pressure of solute, solubility in water of solute,
adsorption capacity and amount of activated carbon in
the filter, among the best known factors. A critical
assumption made when calculating the percent recovery
by the method employed here is that elution of the
adsorbed compounds from the carbon filter is complete
with the amount of eluant employed. This assumption
has been made in all published reports using this method
(12, 13). However, using pentane as solvent, it has
been our experience that elution is not complete even
after 15 washings of the filter. In trial runs using
concentrations in water of a few parts for billion,
elution of the adsorbed compounds was incomplete even
after 25 washings of the carbon filter. Due to this
difficulty, a percent recovery could not be determined
for the compounds identified. Rather, a lower limit
was calculated for the concentration of each compound
using the following procedure.

Repeated washings of the filter were made and the eluting

portions stored individually in microvials. Each washing produced
approximately 20 microliters of extract. These extracts
were chromatographed using 2 µl injections. The peak
area was plotted vs "washing number" Some of these
plots are shown in Figs 23 to 27. It is seen that a
definite trend exists regarding the way a slute is
desorbed by repeated (equal volumes) washings with
pentane. The curves pass through a maximum and then
decrease toward zero slowly. In order to establish the
lower concentration limit, a line was drawn that passed
through the first and last ordinate (1st and 15th washing)
and extrapolated to zero concentration. A triangle was
drawn using this line, the first ordinate, and the
horizontal (concentration) axis. It is clear that the
area of this triangle underestimates the area correspond-
ing to the amount of compound present in the washings,
since it does not pass through the maximum ordinate.

The concentration of a given compound was calculated
from the peak area associated with the first washing,
then multiplied by the area of the triangle in order
to correct for the quantity remaining on the filter
after this washing.

Before the final calculation is obtained, a factor
of $\dfrac{20\ \mu l}{4,200\ ml} = 4.8 \times 10^{-6}$ had to be multiplied by the concen-
tration found in the extract in order to account for
the concentration factor achieved in the purge and
trap procedure.

ELUTION OF CHCl$_3$ FROM CARBON FILTER
BY REPEATED WASHINGS USING PENTANE

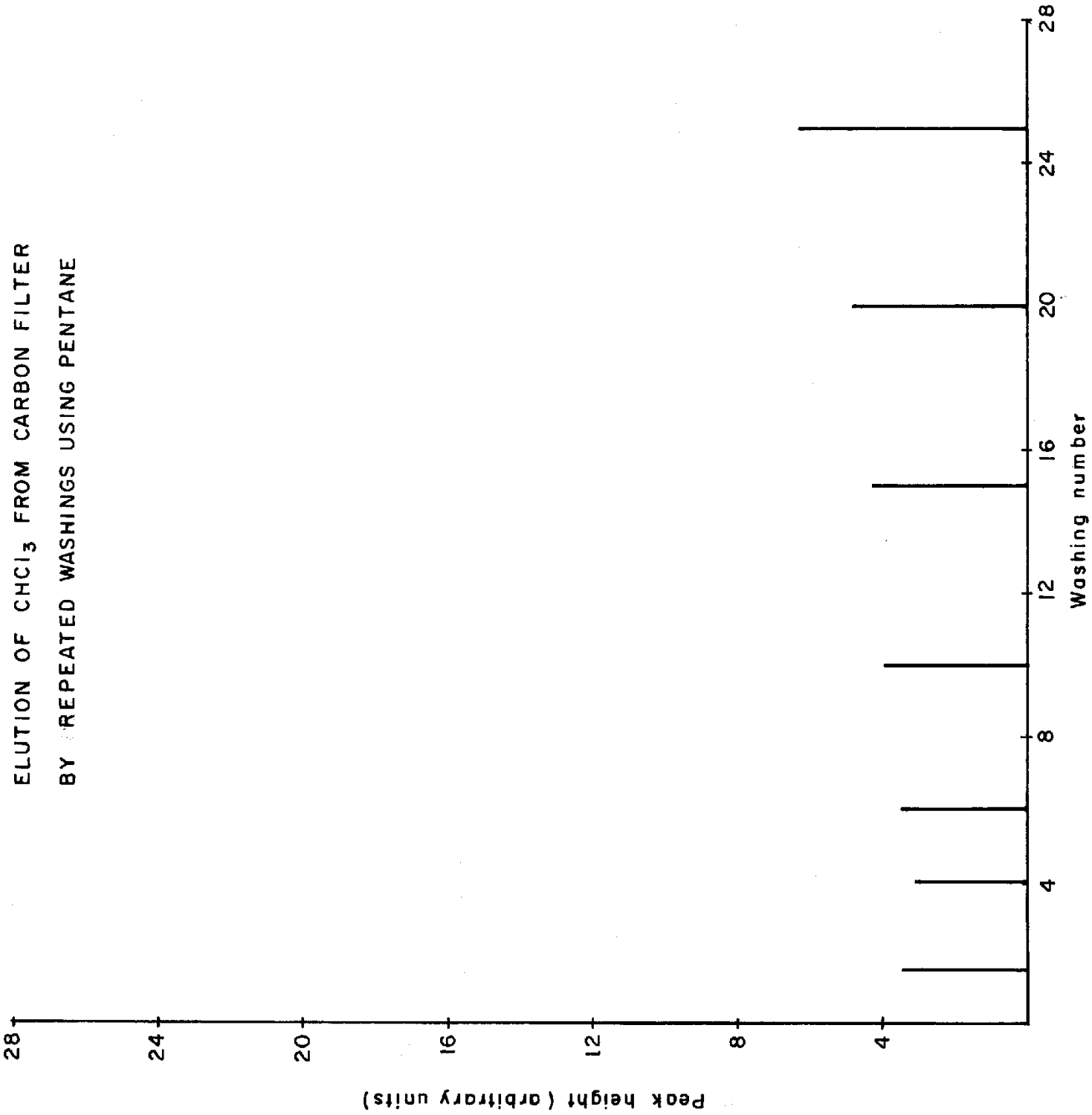Washing number

Peak height (arbitrary units)

FIG. 23

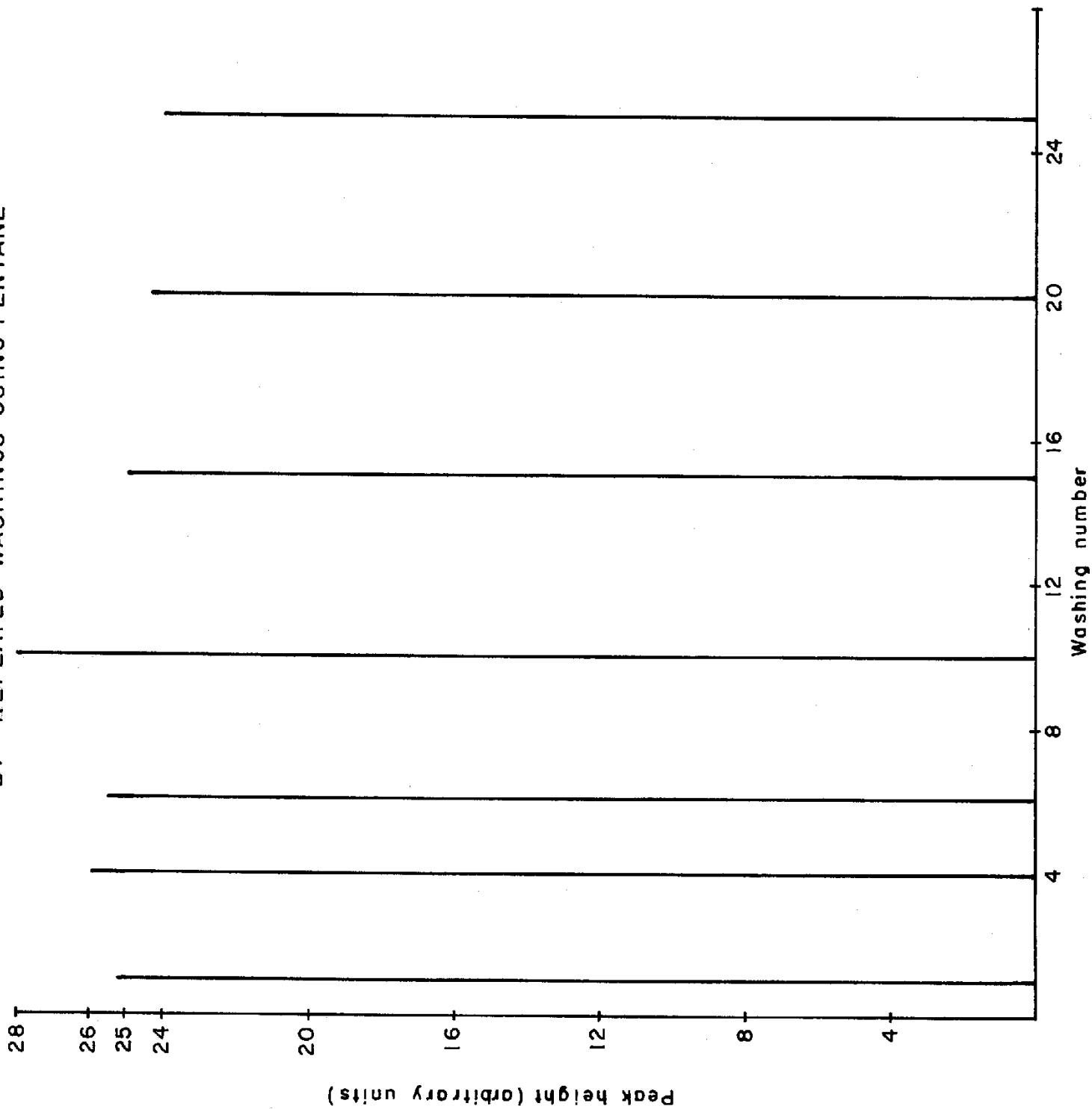ELUTION OF CCl$_4$ FROM CARBON FILTER BY REPEATED WASHINGS USING PENTANE

FIG. 24

ELUTION OF CHBr₃ FROM CARBON FILTER
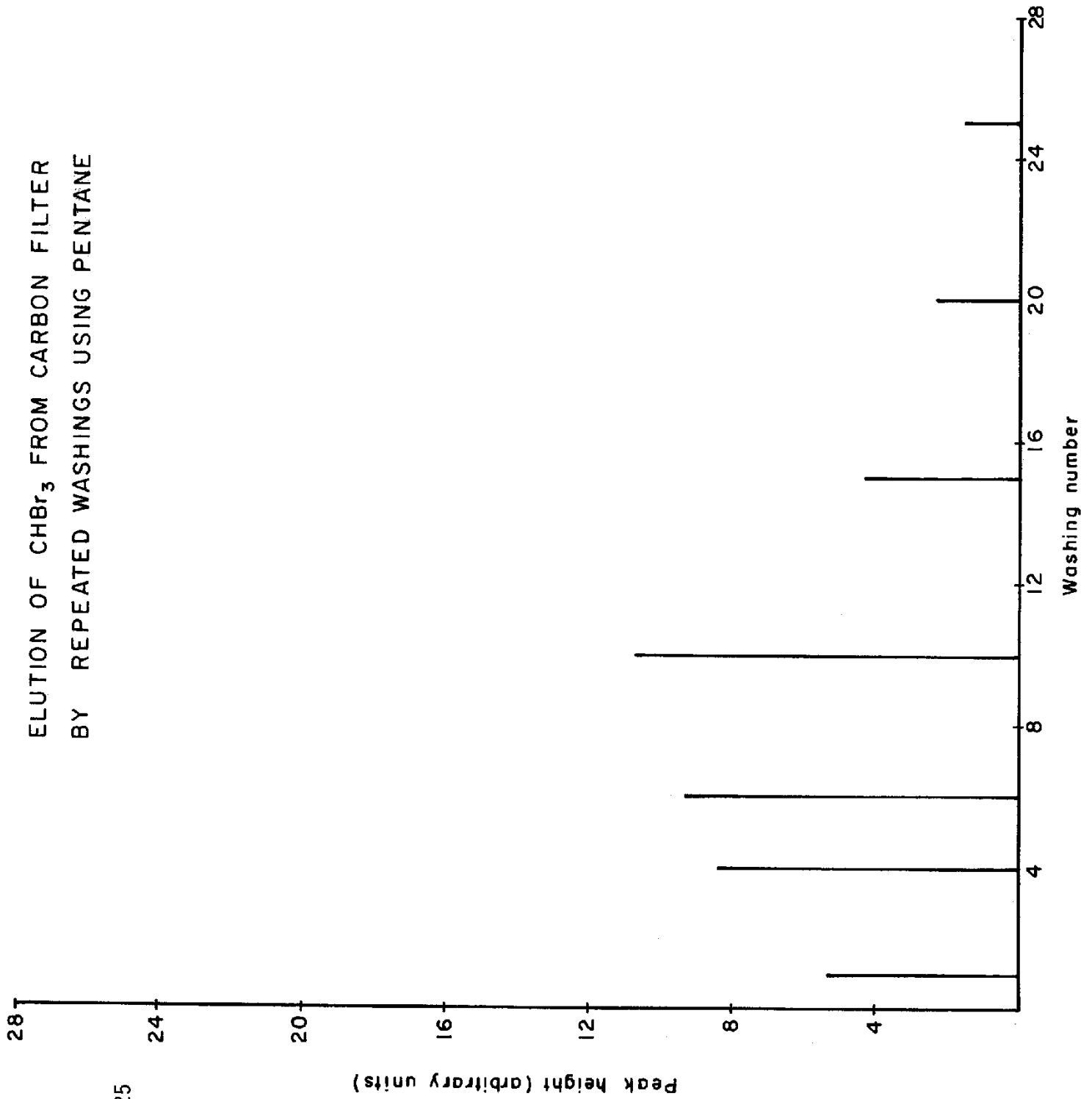BY REPEATED WASHINGS USING PENTANE

FIG. 25

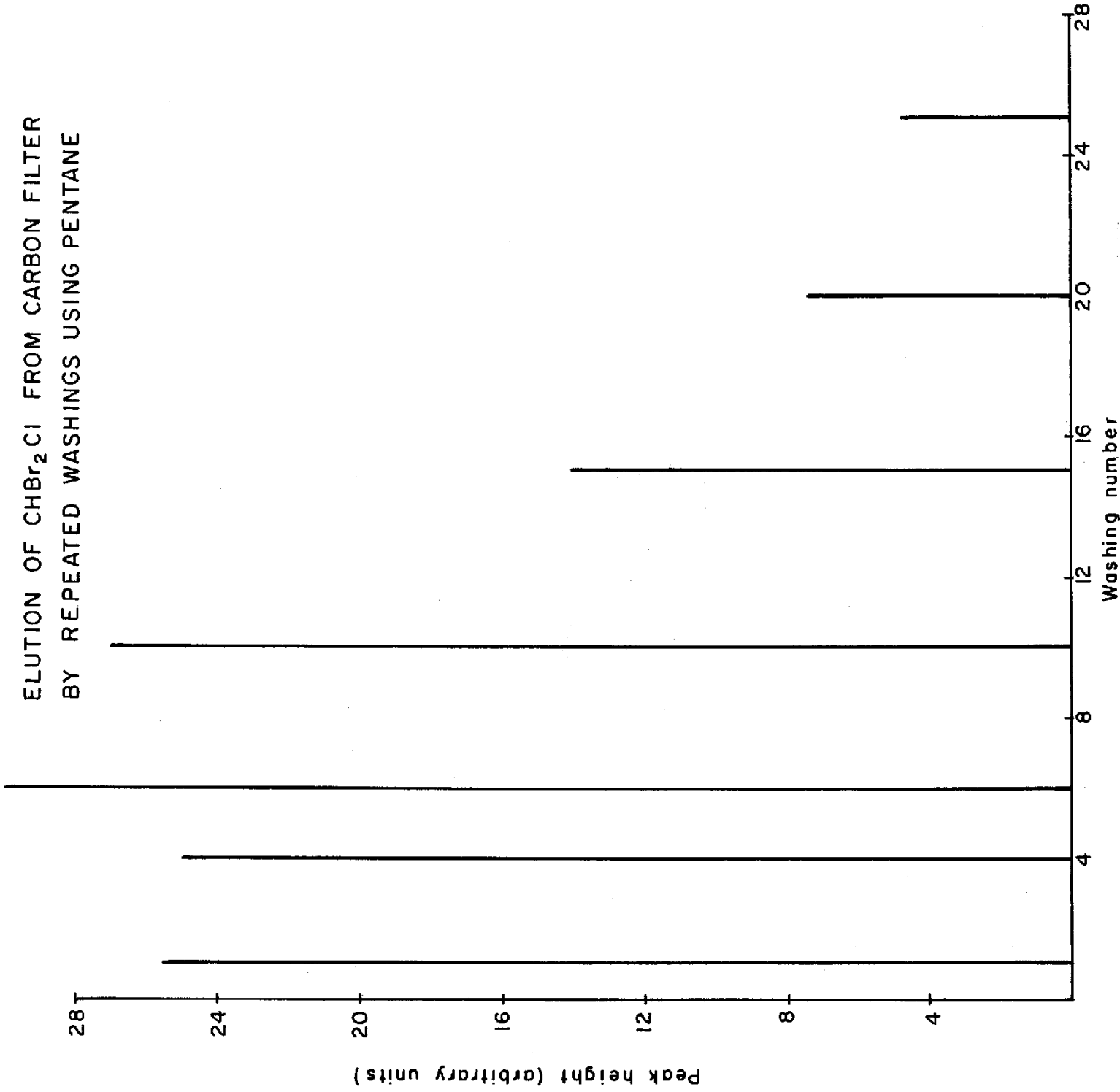ELUTION OF CHBr₂Cl FROM CARBON FILTER BY REPEATED WASHINGS USING PENTANE

FIG. 26

FIG. 27

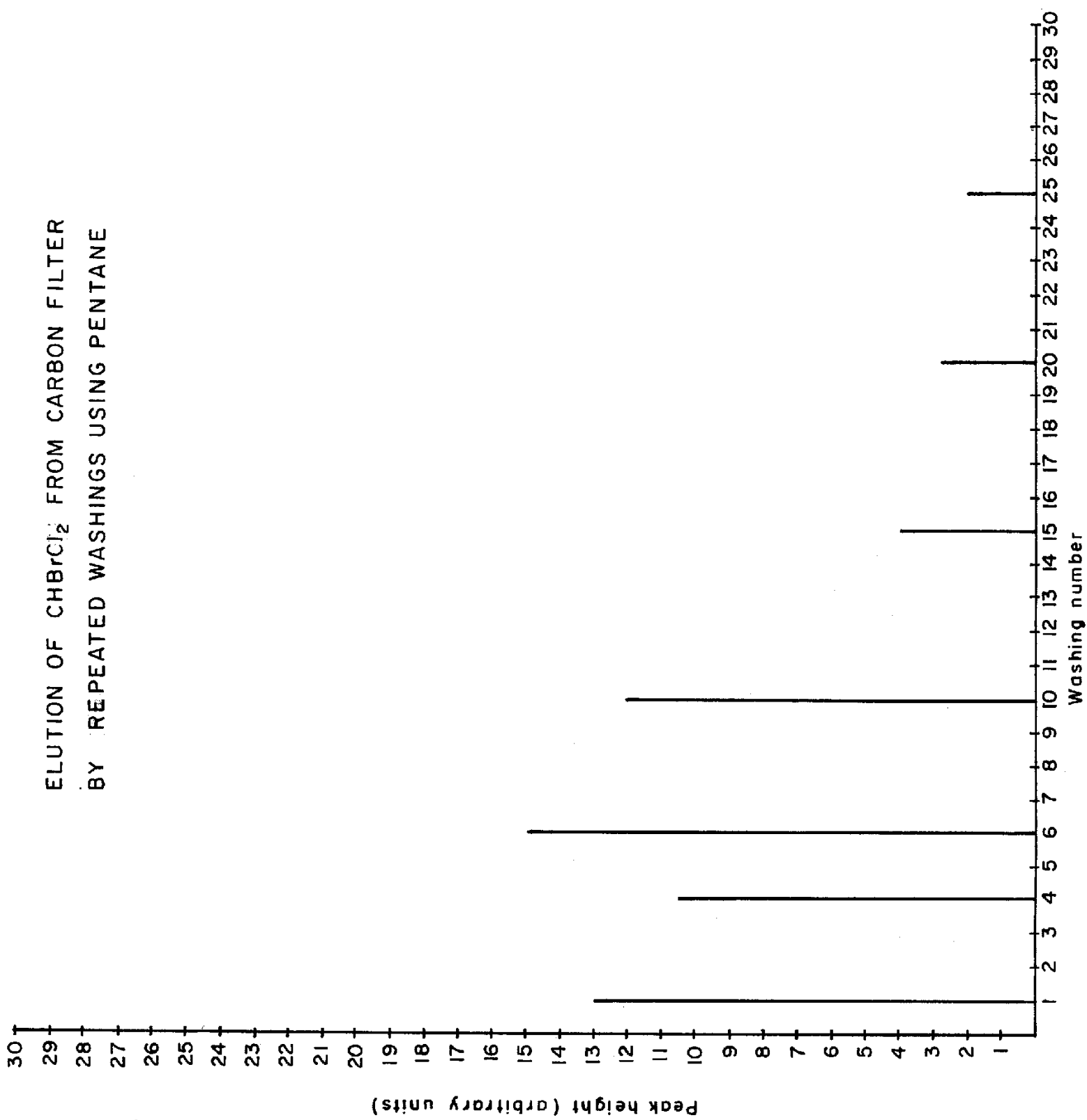ELUTION OF CHBrCl$_2$ FROM CARBON FILTER
BY REPEATED WASHINGS USING PENTANE

It has to be emphasized that in order to get correct results, the same filter (presumably with the same adsorption efficienty) has to be employed to trap the volatile compounds from the samples as to determine their recovery factors. Furthermore, the time period allowed for the stripping must be the same in all instances.

There are no clues in the published reports using the CLSA procedure to analyze water, to whether the elution of the organics adsorbed on carbon was complete after only one washing, particularly when only about 10 microliters of solvent were employed. In several of these studies (7, 9) carbon disulfide was used as eluant instead of pentane; it is not clear, however, why is the former so much more efficient than the latter in extracting the same compounds. Our experiments to verify the eluting capacity of carbon disulfide were hampered by impurities present in this solvent which were almost irreversibly adsorbed on the carbon filter.

Nevertheless, the researchers using CS_2 as eluant have used the internal standard method of quantitation, which would minimize the errors due to incomplete elution of the adsorbed compounds using only one washing. It is interesting that Coleman (8) reports very low recovery efficiencies for the trihalomethanes, ranging from 4%. to 12%.

This might be an indication that these compounds are incompletely desorbed by one washing employing 10 μl or less of carbon disulfide. It is estimated that further research along these lines is needed.

Table 2. Organohalides Found in Drinking Water in Puerto Rico

Compound:	$CHCl_3$	CCl_4	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	C_2Cl_4
San Juan	4.3	0.9	6.1	6.1	VS	36
Ponce	1.2	VS	3.2	6.8	96	29
Mayaguez	11	VS	11	11	ND	VS

Concentration (part per trillion)

VS: very small
ND: not detected

The estimated concentrations of the various organohalides found in the drinking water of Mayaguez, Ponce and San Juan are presented in Table 2. The values found agree well with those reported in similar studies in the United States and in Europe, which range in the ppt level. However, it should be kept in mind that the levels reported are lower limits and will have to be revised upwards when better estimates of the recovery efficiency are obtained in our laboratory. Even thinking in terms of revised figures, it would be difficult at this time to anticipate that the standard of 100 ppb for the total content of trihalomethanes in drinking water, set by the EPA (14) would be exceeded in any of our municipal water supplies. This would require a ten-fold increase in the total concentration of trihalomethanes, which is deemed improbable, unless some form of man-made pollution increases significantly in the future. Nonetheless, it is believed that monitoring of driking water in Puerto Rico for organics should be conducted on a continuous basis. The concentration found for bromoform in Ponce, 96 parts per trillion, the highest of the investigated supplies, suggests the need for a closer scruting of the conditions leading to the formation of this compound whose health effects are considered harmful, though inconclusive. Furthermore, the presence of tetrachloroethylene in the water supplies of San Juan and Ponce might indicate that improper disposition of this and other solvents and degreasers may be taking place.

Another point to be mentioned is the variations found in the concentrations of these compounds for given water utility as a function of time. Analyses performed in our laboratory do not show a definite trend because they were not made at sufficiently close intervals of time. Researchers in the United States have postulated seasonal variations that correlate with the amount of humic material in the raw waters; however, seasonal variations should be minimal in Puerto Rico. Thus, the changing trihalomethane levels must be the result of other active factors, whose mades of action are not presently understood.

IV. Conclusions

The main conclusions that can be derived from this research can be summarized as follows.

1. Before the CLSA method of water analysis can be used routinely with accurate and consistent results, a trial period of several months is needed to get acquainted with some of the subtleties of the method and of trace analysis in general. The accurate determination of trace amounts of volatile pollutants in water cannot be performed in haste, particularly by the uninitiated.

2. Once the CLSA technique is understood and mastered, together with the all-important gas chromatographic methods and procedures, the water analyst has at his command the best available means to determine a wide range of organic volatile compounds in water. The limitation of the method must be kept in mind: it is applicable to high-to-medium volatility substances having law-to-medium boiling points; however, this includes some compounds having as many as 12 carbon atoms. Again, the method can be very convenient from an operational standpoint once the experimental setup is ready.

3. There are a number of halogenated organic pollutants present in the municipal water utilities of the cities of San Juan, Ponce and Mayaguez, all of which have been included in the priority pollutant list of the Environmental Protection Agency. These are: chloroform, carbon tetrachloride, chlorodibromomethane, dichlorobromomethane, bromoform, and tetrachloroethylene. Although there are

other halogenated species present in drinking water, these are present in lesser amounts and have not yet been identified.

4. The concentrations of these pollutants range in the low parts-per-trillion range, which is the same order of magnitude found in similar studies done in the United States and Europe. These concentrations vary with time due to factors that have as yet not been definitely identified, like the presence of organic contaminants in the chlorine used in the disinfection step of water purification.

5. Al least one of the contaminants present in the Ponce and San Juan tap water, tetrachloroethylene, is not known to have a natural origin; therefore, its source is very likely the undue disposition of waste solvents and degreasers.

6. The other compounds are known to be generated when chlorine reacts with the traces of humic material that remains in the water after the sedimentation and filtration steps. To test this hypothesis, a few tests were made on water from lake Carraízo and from the Río Añasco, which individually supply most of the raw water to two of the municipal water utilities studied. The concentration of trihalomethanes in all raw waters was undetectable, lending credence to the aforementioned hypothesis.

7. Lastly, but very important, is the conclusion that while the present levels of organhalides in drinking water do not pose an imminent health threat, the monitoring of drinking water for these compounds should be established by the pertinent authorities on a continuous basis. Also,

the list of monitored substances should be expanded to

include other well known or suspected health hazards,

like pesticides, herbicides and the organic phthalates.

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