INFORMAL COLLOQUIUM ON THE ANALYSIS OF ORGANIC MICROPOLLUTANTS IN WATER

Organized by the National Institute for Water Supply in cooperation with the W.H.O. International Reference Centre for Community Water Supply at Damsigt Building, Nieuwe Havenstraat 6, Voorburg, The Netherlands.

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Wednesday, February the 18th 1976.

GC/MS analyses of organic compounds in domestic waste water
Dr. A.W. Garrison, U.S. Environmental Protection Agency, Athens (presently consultant with I.R.C.).

Identification of the cause of odour nuisance in the neighbourhood of an industrial waste water site
Drs. C.T.H. Morra, National Institute for Water Supply, Voorburg

Organic micropollutants in the rivers Rhine and Meuse
Drs. W. van de Meent, K.I.W.A., Rijswijk

Considerations on precursors and formation of haloforms in water
Drs. J.J. Rook, Rotterdam Water Works, Rotterdam

Organic constituants of water, analysis by capillary gas chromatography
Dr. W. Giger, EAWAG, Dübendorf, Switzerland

The analysis of volatile organic compounds at different steps of drinking water processes
Dr. L. Stieglitz, Nuclear Research Centre, Karlsruhe

Drinking water contamination in The Netherlands, Methods, preliminary results and future programs
Ir. B.C.J. Zoeteman, G.J. Piet, National Institute for Water Supply, Voorburg

Qualitative and quantitative methods for the analysis of organics in surface water
Dr. J. Freudenthal, National Institute for Public Health, Bilthoven, The Netherlands

Identification of organic compounds in drinking water from thirteen U.S. cities
Dr. A.W. Garrison, U.S. Environmental Protection Agency, Athens

GC-MS Analysis of Organic Compounds in Domestic Wastewaters

by

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INTRODUCTION

In 1971 this laboratory began a program to identify extractable, volatile organic compounds in domestic wastewaters. Objectives were to develop analytical techniques for such analyses, to identify compounds being discharged into surface waters after secondary or advanced treatment, and to provide specific compound data that will help to determine waste treatment effectiveness. Knowledge of the specific compounds discharged is needed to study health effects of pollutants, to help determine the sources of compounds found in drinking water surveys[1], and to establish effluent guidelines. Finally, some parts of the world are concerned about the possible need to renovate domestic wastewater for human consumption[2,3], and the identification of hazardous compounds in such wastewaters is imperative for safe renovation.

Most previous studies of raw and treated sewage have been mainly non-specific characterizations of particulate and soluble fractions[4-7]. Organics were assigned to groups such as amino acids, carbohydrates, lipids, acids, proteins, surface active substances, tannins, fulvic acid, humic acid,

were identified. In the past few years, with the increasing concern over trace organics in all types of water, and with the availability of adequate analytical tools, more investigators are identifying and quantifying specific soluble organics in municipal effluents. Work in Israel[8] resulted in the identification by combined gas chromatography-mass spectrometry (GC-MS) of several fatty acids and aliphatic and aromatic hydrocarbons. Considerable work of this nature has been conducted in the United Kingdom[6,9]; specific optical brighteners, amino acids, carbohydrates, steroids, pesticides, and phthalates were identified. Earlier work of a less comprehensive nature resulted in the identification of volatile acids[10] and polycyclic aromatic hydrocarbons[11].

More recently, Burlingame[12] began to use high resolution GC-MS to analyze mixtures of organics extracted from treated municipal effluents, and has identified several specific compounds. Dunlap[13] is using accumulator columns for extraction and both electron impact and chemical ionization GC-MS to identify organics contributed to ground water by municipal solid wastes and septic tank effluents. Glaze[14] has identified more than 40 chlorinated compounds produced during wastewater chlorination. In work closely related to that reported here, Giger[15], in Switzerland, is

using capillary column gas chromatography (GC) and GC-MS to separate and identify compounds in municipal wastewaters; several aliphatic and aromatic hydrocarbons, chlorinated compounds, and alcohols have been identified.

It is generally agreed that the bulk of organic material--over 75% in most waters--is non-extractable, non-volatile, and mostly non-gas chromatographable. Municipal wastewaters are no exception[6]; but a group in the USA has made significant progress in identifying these materials, including those produced by chlorination, after separation by high pressure liquid chromatography[16-18].

Since the principal objective of our research was to identify extractable, volatile organics in representative raw and treated domestic wastewaters, the EPA's Advanced Waste Treatment Research Laboratory (AWTRL) at the Taft Center in Cincinnati was selected as the main sample source. Their pilot scale waste treatment plants have no industrial input, and their operation is well controlled and documented.

The activated sludge and physical-chemical pilot treatment plants take raw sewage from a common residential line (Figure 1). The activated sludge plant is a typical

biological treatment process depending upon bacterial action for most of the organics removal; the physical-chemical system relies mostly on removal of organics by carbon adsorption. Values for total pollution parameters (Figure 1) are highly variable, especially those for the raw sewage, mostly due to fluctuations in dilution of the organics by relatively unpolluted water. Since the pilot plants are enclosed within the AWTRL laboratory, the temperature varies little from day to day, but the averages does range from 12°C in winter to 20°C in summer.

Later, samples from the Blue Plains sewage treatment plant at Washington, D.C., were included in this project at the request of the Blue Plains plant manager. The EPA has a small research project at this plant where raw sewage is lime-clarified. Samples were collected, chlorinated, and extracted by Blue Plains personnel before being shipped to ERL-Athens for analysis.

EXPERIMENTAL

Sampling

Fifteen to twenty liter samples of raw sewage, activated sludge effluent, and physical-chemical effluent were collected in August 1972 and December 1973. In August 1972, three grab samples were collected at intervals corresponding to the retention time of each treatment system. Samples were collected in glass containers, adjusted to pH 4-5 with HCl as a preservative, and stored for one to three days at 4°C before extraction.

In December 1973, composite samples were collected at each sample point for 3.5 days while the glass sample containers were in a refrigerator at 4°C. Portions of each composite were transfered to polyethylene containers, frozen and stored for about two weeks until extraction.

Extraction and Fractionation

Samples were extracted manually in 3-liter batches using a liquid/liquid extraction scheme designed to separate sample components into acid, basic, and neutral fractions

(Figure 2). Pesticide grade methylene chloride was the extractant. All water used for reagents (HCl and NaOH solutions) was distilled and pre-extracted with methylene chloride. Before final evaporation, sample extracts were dried by passing through sodium sulfate that had been heated in a muffle furnace at 600°C for 2 hrs. A gentle stream of nitrogen was used for final evaporation of extracts to a known volume of appropriate concentration for GC analyses. Extracts were combined with those from other 3-1 batches and stored in glass vials with teflon lined septa at 4°C. The acid fractions were methylated with diazomethane in the presence of methanol[19]. A control was prepared for each sample set by taking appropriate amounts of solvents and reagents through the above extraction scheme.

One raw sewage sample was extracted into weak and strong acid fractions in addition to the usual extraction scheme. The first organic layer (Figure 2) was extracted with 5% sodium bicarbonate to extract strong acids, then with 5% sodium hydroxide for weak acids. Each extract was acidified, re-extracted with methylene chloride, and methylated (Figure 2). This fractionation was discontinued because only two compounds, phenols of very low concentration (<1 ppb), were recovered in the weak acid fraction.

Five hundred milliliter portions of some samples were distilled (Figure 2) by directly heating, using a water-cooled condenser. The first 25 ml of distillate was collected and re-distilled to collect the first 1 ml. During distillation of the raw sewage, several milligrams of waxy white material collected in the condenser. This was dissolved in methylene chloride, and methylated with diazomethane.

Chlorination

Lime-clarified raw sewage from the EPA-DC Blue Plains pilot plant in Washington, DC, was chlorinated and extracted at that facility. Chlorination was by addition of a sodium hypochlorite solution of such a pH that the final pH of the sample at "breakpoint chlorination" was between 7 and 7.5. The residual free chlorine in the sample was 3-5 mg/l. The chlorinated sample was allowed to stand for about 30 minutes before extraction. Extraction followed essentially the same procedure used at ERL-Athens (Figure 2). The extracts were delivered to ERL-Athens for final concentration, methylation, and analysis.

Ozonolysis

About 10 µl of the methylene chloride solution of the raw sewage acid fraction, previously esterified with diazomethane, was added with 2 ml of MeOH to the sample tube of an apparatus constructed after the design of Beroza[20]. After adjusting the oxygen flow to approximately 10 ml/min, the cold bath was brought into place, and ozonation began. At 2 min, the indicator solution detected excess ozone, but the generation continued for another 30 sec. After the system was flushed with nitrogen, 0.5 ml of dimethyl sulfide was added to the sample tube to reduce the ozonides. To insure complete reaction, the sample tube was left in the cold bath for 5 min, then placed in an ethanol/ice bath for 1 hr. Upon removal from this bath, the sample was shaken for 5 min, and the volume adjusted for GC analysis by gentle evaporation with a nitrogen stream.

Gas Chromatography

All extracts were analyzed by GC. Typical conditions were:

GC: Varian 1400, Perkin Elmer 990 or Tracor MT220

Column: 6 ft. x 1/8 in i.d. (1/4 in o.d.) glass

Packing: 3% SE-30 on 80/100 mesh Gas Chrom. Q.

Program: 50° for 2 min, then to 250° at 5°/min.

Carrier gas: helium at 50 cc/min.

Sample size: 2 µl

Detector: flame ionization

Some extracts were analyzed on a 3% SP-2100 column using similar GC conditions. This liquid phase is very similar to SE-30, but has a higher temperature limit. However, SP-2100 appeared to cause more tailing of early eluting peaks.

Aqueous distillates were analyzed by direct injection of 1 to 10 µl into a 10% FFAP GC column. (Temp. program: 150° for 2 min, then to 180° at 4°/min. Gas flow: 21 cc/min. Column: 6 ft x 1/4 in glass).

Other Instrumentation

A Finnigan 1015 mass spectrometer interfaced via a Gohlke separator to a modified Varian 1400 GC was used for GC-MS analysis[21]. A System Industries System 150 interfaced the GC-MS to a Digital Equipment Corp. PDP8/e computer for data acquisition, storage, and manipulation. Ionizing voltage was 70 eV.

Some low resolution GC-MS work was done on a Varian MAT CH5/DF system interfaced to a Varian 2740 GC via a Watson-Biemann separator and to a Varian MAT SS-100 Data System. This instrument was also used at a resolution of about 5000 for determination of possible empirical formulae of the major mass spectral peaks of some unknown biodegradation products in the activated sludge effluent.

The GC conditions for GC-MS analyses were similar to those used for GC analyses described previously.

Chemical ionization mass spectrometry was performed on selected extracts with a separate computerized Finnigan 1015 mass spectrometer interfaced to a Finnigan 9500 GC using methane as a carrier/reactant gas.

Combination gas chromatograph-infrared spectroscopy instrumentation was a computerized Digilab FTS-14D/IR Fourier transform spectrophotometer equipped with the Digilab GC/IR accessory and interfaced to a Perkin-Elmer 990 GC[22]. This instrument was used to confirm the presence of the clofibrate metabolite in the acid fraction of the activated sludge effluent collected in December 1973.

After tentative identification of pollutants by GC-MS, a Perkin-Elmer PEP-1 Data System, interfaced to a Varian 1400 GC operated under the conditions described above, was used for computerized quantitation and retention time measurements.

Identification of Compounds

Sample mass spectra stored on disks from the Finnigan GC-MS runs were compared via acousticoupler connection with standard spectra in the EPA-Battelle computer files at Battelle (Columbus). Sample mass spectra were also compared through a computer terminal and acousticoupler with standard spectra in the NIH Mass Spectral Search System in Bethesda, Maryland. Later a combination of these two search systems was used--the Mass Spectral Search System, handled by the Cyphernetics Corp., Ann Arbor, Michigan. This system contains about 40,000 reference mass spectra[23].

These computer-based searches were supplemented by manual searches of the Aldermaston Eight Peak Index of Mass Spectra[24]. Two publications were particularly helpful in interpreting the mass spectra of long-chain acids[25,26], and the clofibrate metabolite was first identified by matching its spectrum in the Archives of Mass Spectral Data[27].

Many compound identifications were confirmed (Table 1) by matching their GC retention times and mass spectra with those of standards. Standards of most of the acids were obtained in kit form from Applied Science Laboratories, Inc., State College, PA, or Supelco Inc., Bellefonte, PA.

RESULTS AND DISCUSSION

Raw Sewage Components

Total Methylene Chloride Extractables

Figure 3 shows the FID/GC peaks observed in all fractions of the methylene chloride extract of raw sewage collected from the AWTRL in December 1973. The acid and neutral fractions contained about the same amounts of gas chromatographable organic compounds, but the basic fraction contained much less. The methylated acid fraction produced a chromatogram that was typical of this fraction in all samples, even after treatment. Palmitic (C_{16}), stearic (C_{18}), and oleic ($C_{\overline{18}}$) acids predominated; the even-numbered straight chain acids and palmitoleic acid ($C_{\overline{16}}$) were at intermediate concentrations; and the odd-numbered straight

chain acids, branched chain acids, and miscellaneous acids were at lower concentrations (see Figure 4-8 for other compounds in acidic fractions).

Caffeine and nicotine produced the predominant peaks in the basic fraction chromatograms; no other components have yet been identified. Caffeine, α-terpineol, and several aliphatic and aromatic hydrocarbons were found in the neutral fractions. Most neutral fractions also contained cholesterol, coprostanol, phthalates, and several components that appeared to be long-chain alcohols and/or unsaturated hydrocarbons.

Raw Sewage Condensate

During distillation of the raw sewage sample of December 1973 as a means of concentration for analysis of volatile free acids, several milligrams of a waxy white solid collected in the condenser. This material was analyzed by GC-MS (Figure 9) after solution in methylene chloride and methylation. Limited mass range searches of the stored mass spectral data indicated the presence of three phthalates (m/e 149), and methyl palmitate and methyl myristate (m/e 74 and 87). The acid metabolite of the drug clofibrate was the most abundant component.

The main human metabolite of the drug clofibrate [ethyl 2-(4-chlorophenoxy)-2 -methylpropionate] has been shown to be 2-(4-chlorophenoxy)-2-methylpropionic acid (Figure 10). It is excreted in urine at 85% of the amount of the drug ingested[28]. Clofibrate is used by many older people in doses of 2 g/day to control atherosclerosis. It is not manufactured in this country, but is dispensed here.

Although the parent drug was never found in sewage, the metabolite was found in both August 1972 and December 1973 samples of the Cincinnati AWTRL pilot plant sewage, in Athens, GA, municipal sewage, and in sewage from Washington, DC, lime-clarified raw sewage (see Table 1 for concentrations). The metabolite identification was verified by comparison of mass spectra (Figure 10) and infrared spectra (Figure 11) of a standard with those of the sample component.

Effects of Physical Chemical and Activated Sludge Treatment

Treatment Effects on Acid Components

Comparison of chromatograms (Figure 4) showed the changes incurred during activated sludge and physical-chemical treatment of the raw sewage collected in August

1972. These chromatograms were reconstructed by the computer (RGC's) using the mass spectrometer as the detector, and were normalized on the most intense peak. Therefore, concentrations of the same components in different chromatograms were not comparable; only relative changes in components and concentrations were comparable. Measured concentrations of some components (Table 1) showed that there was a 3- to 5-fold decrease in concentration of the main components (C_{14}, C_{16}, C_{18}, C_{-18}) in raw sewage after activated sludge treatment, and a 10- to 100-fold decrease after physical-chemical treatment. These main components were present in about the same relative concentrations after treatment.

At least five new compounds with similar structures, based on their mass spectra, are present after activated sludge treatment (marked with a question mark in Figure 4). IR spectral evidence obtained on the GC-FTIR system, indicated that one of the larger unknown peaks was a LAS detergent biodegradation intermediate. This speculation correlated well with the sample history and with literature data on LAS degradation routes[29]. Although the low resolution GC-MS gave an unidentifiable spectrum, it did provide an apparent molecular weight. High resolution GC-MS, provided several possible molecular formulae for this

parent ion, one of which matched that of the speculated biodegradation product, p-hydroxy phenyldecanoic acid. A possible formula for one of the fragment ions also matched that of a logical fragment of the same compound. High resolution GC-MS also provided tentative structural information for two of the other possible biodegradation products.

Pentachlorophenol and the clofibrate metabolite were present only after activated sludge treatment. Their absence in the raw sewage is unexplained, but they could have been absorbed on activated sludge particulate matter from earlier raw sewage influents and partially desorbed during this sampling. (The clofibrate metabolite was found in the raw sewage of the December 1973 series of samples, but in relatively small concentration.) Since the drug clofibrate was not found in the neutral fraction of the raw or treated sewage, the acid metabolite probably was not produced during activated sludge treatment.

Palmitoleic acid (C_{16}) was present in relatively more abundance after physical-chemical treatment than in the raw sewage. The main changes after this treatment, however, are the formation of four β-hydroxy and three α-keto long-chain acids (Figure 4). The identities of these compounds have

not been confirmed, but their mass spectra, especially those of the β-hydroxy acids, are fairly distinctive. A limited mass range search of the disc-stored mass spectral data for m/e 103, which is distinctive for β-hydroxy acids, indicated their presence (Figure 5); a homologous series was indicated by the almost equal spacing of GC peaks (time of elution). These oxygenated acids were apparently formed during physical-chemical treatment, probably on the carbon column. Biological activity has been shown to occur on columns of activated carbon used for waste treatment[30]. In this case, the occurrence of oxidation was surprising, because the effluent smelled slightly of hydrogen sulfide, which indicated anaerobic conditions.

There was little difference in composition of the raw sewage acids in samples collected 16 months apart (Figure 6). Except for the two unsaturated acids, concentrations of the main components were higher in the first sample than in the second sample (Table 1). Palmitoleic acid (C_{16-}), was seven times more concentrated in the second sample, and the clofibrate metabolite (about 0.8 µg/l) was found only in the second sample.

Activated sludge treated effluents taken 16 months apart were also similar in acid composition (Figure 7). The

clofibrate metabolite concentration was about 1 µg/l in the first sample and 2 µg/l in the second sample. Pentachlorophenol was barely detectable in the second sample. The five unknown compounds previously discussed were present in both samples, but in different ratios. A sixth unknown compound with the same mass spectral structural characteristics appeared at spectrum number 195 in the second sample. Concentrations of the main (C_{16}, C_{18}, and $C_{\bar{1}8}$) components were lower in the second sample; this corresponded to their lower concentrations (except for $C_{\bar{1}8}$) in the second sample of raw sewage (Table 1).

Contrary to raw sewage and activated sludge treated acid components, the physical-chemical effluent acids were different in composition and concentration in the two samples taken 16 months apart (Figure 8). Although more components were identified and quantitated in the second physical-chemical treatment sample, all components were less concentrated in the second sample than in the first. The ratios of the main components (C_{16}, $C_{\bar{1}6}$, C_{18} and $C_{\bar{1}8}$) were also different; C_{16} was much more predominant in the second sample. Another striking difference was the complete absence of oxygenated fatty acids in the second sample. Most of these differences could be explained. The carbon, which is usually used eight months before changing, was

seven months old at the first sampling, but a different batch of carbon had been used only one month before the second sampling. The fresh carbon resulted in removal of more organics, and apparently was not old enough to allow establishment of bacterial colonies sufficient for biological metabolism of fatty acids.

Treatment Effects on Neutral Components

Many compounds were evident in chromatograms of the neutral fractions of raw and treated sewage (Figure 12). The total methylene chloride extractable neutral organics in the raw sewage were about 10 times more concentrated (perhaps 30 times for coprostanol and cholesterol) than in the activated sludge effluent, and at least 100 times more concentrated than in the physical-chemical effluent, according to these FID/GC measurements.

Relatively few of the neutral components have been identified (Figure 13), and none have been quantitated. (It is only possible in these RGC's in Figure 13 to compare ratios of compounds before and after treatment--not concentrations of the same compound in different chromatograms). Corresponding FID chromatograms of the December 1973 series were similar to those of the August

1972 series (Figure 12) in that almost no peaks showed up in the blank and few were in the physical-chemical effluent extract. The unsaturated or oxygenated hydrocarbons and α-terpineol are decreased in concentration relative to caffeine, the large unknown (*), and dioctyl phthalate after activated sludge treatment. Dibutyl phthalate predominates after physical-chemical treatment, but is probably at a very low concentration. These chromatograms were not programed to a high enough temperature to see coprostanol and cholesterol, which were observed in other chromatograms of the same samples.

Treatment Effects on Basic Components

In general, fewer chromatographable organics were observed in the basic extracts than in the neutral or acid extracts. The raw sewage from the AWTRL contained at least twenty times the amount of methylene chloride extractable bases as did the activated sludge effluent, and at least 100 times the amount in the physical-chemical effluent (Figure 14). Similar conclusions were drawn from chromatograms of the second series of samples (Figure 15), even though the chromatograms had a high noise level and baseline rise. Both series of chromatograms showed changes in composition after treatment, but there seemed to be less change in

concentration of some components after activated sludge treatment in December 1973.

Caffeine and nicotine were the only compounds identified thus far in the basic fractions. Caffeine was the principal component in the raw sewage and after activated sludge treatment (Figure 16); concentrations have not yet been measured. (The largest peaks in the corresponding chromatograms of Figure 15 are probably due to caffeine). Nicotine, the second most concentrated component in the raw sewage, was reduced in concentration, relative to caffeine, after activated sludge treatment. No caffeine or nicotine was observed after physical-chemical treatment (the detection limit was <1 µg/l).

Treatment Effects on Volatile Components

Volatile components of distillate from the raw sewage and treated effluent samples collected in August 1972 were analyzed by GC and GC-MS after direct aqueous injection of a 1 to 10 µl aliquot. Six volatile acids were identified in chromatograms of raw sewage and activated sludge samples (Figure 17). The concentrations of these acids were reduced 5 to 10 fold after treatment, but their ratios remained about the same, with valeric and isovaleric acids present in

most abundance. These compounds were verified by comparison of GC retention times of sample components with those of standards. GC-MS analysis of these free acids did not give discernible peaks on the RGC.

Other volatile components of the distillate from raw sewage and treated effluent samples were identified by GC-MS after direct aqueous injection and modification of the GC temperature program (Figure 18).

Most components were neutral oxygenated or halogenated materials, that were reduced in concentration or disappeared after treatment. One ketone increased in relative concentration after activated sludge treatment, and tetrahydrofuran was observed only after physical-chemical treatment.

Effects of Chlorination

Chlorination effects were determined by analysis of fractions before and after chlorination. Comparison of chromatograms of the neutral fractions of lime-clarified sewage from the Blue Plains waste treatment pilot plant before and after chlorination showed that some components

disappeared and some new compounds were formed during chlorination (Figure 19).

Caffeine, α-terpineol, and the compound peak marked "x" completely disappeared during chlorination; part of the largest peak marked "*" also disappeared. Some benzyl alcohol may have been oxidized to benzaldehyde, which was present only after chlorination. Two chlorinated compounds, chlorocyclohexane and 1,1,1,2-tetrachloroethane, were present only after chlorination.

Chromatograms of the basic fractions (Figure 20) of the same samples showed the same chlorination effects observed in the neutral fractions. Caffeine and nicotine completely disappeared upon chlorination; limited mass range searches for distinctive mass spectral ions failed to detect any trace of either compound after chlorination. One or two new GC peaks were observed after chlorination. Some of the benzyl alcohol observed in the neutral fraction carried over into the basic fraction, and was gone after chlorination. This could have contributed to the benzaldehyde, which was found only in the neutral fraction after chlorination.

The most pronounced effects of chlorination were observed in chromatograms of the acid fractions of the same

samples (Figure 21). Salicylic acid and all three mono-unsaturated fatty acids completely disappeared. Traces of the clofibrate metabolite were present in both chromatograms. Several new compounds (1,1,2,2-tetrachloroethane, pentachloroethane, hexachloroethane, and at least five unknown compounds) apparently were formed during chlorination. The presence of these neutral chlorinated compounds in the acid fraction cannot be explained at this time; they could be analytical artifacts, but were not seen in any other extracts.

Effects of Ozonolysis

Ozonolysis of the AWTRL raw sewage (Figure 22) had some of the same effects on acids as did chlorination of the Blue Plains lime-clarified raw sewage. The mono-unsaturated C_{16}^- and C_{18}^- acids and several minor components (probably unsaturated) reacted completely. Several new peaks, probably aldehyde reaction products, were formed. The ozonolysis reaction was different from the chlorination reaction in that the acids were methylated before reacting with ozone, and the reaction occurred in methylene chloride solution, not in the aqueous phase. This ozonolysis technique[20] was devised as an analytical tool to detect or confirm unsaturated compounds, and it proved useful for this

purpose. Although it was not designed to simulate waste treatment by ozonation, similar reaction with the unsaturated acids would be expected during such waste treatment.

CONCLUSIONS AND REMAINING WORK

Eighty specific volatile organic compounds were identified in raw and treated domestic wastewaters (Table 1), mostly by gas chromatography-mass spectrometry. A series of five or more similar unknown acids of relatively high concentration, were possibly detergent metabolites that were formed during activated sludge treatment of raw sewage; these need to be identified and quantitated. Only a few neutral compounds were identified in raw and treated domestic wastewaters; unsaturated and/or oxygenated hydrocarbons and many completely unknown compounds present in relatively high concentration have not been identified. While the basic fractions were less complex, several components remain unidentified.

Physical-chemical treatment (carbon adsorption) was more effective than activated sludge treatment in reducing

the concentration of specific volatile organic pollutants, but even in physical-chemical effluents, obvious components need to be identified and quantitated, especially in the neutral fractions.

Brief analytical studies on sewage before and after chlorination indicated important changes in some components. These changes need to be better defined by identification and quantification of compounds that react with chlorine and products that are formed by chlorination.

Identification of compounds is not enough. Their quantities must be measured before the significance of changes occurring during treatment can be assessed. Concentrations of only a few of the compounds identified in this study have been measured (Table 1). After qualitative and quantitative analysis of components in domestic wastewaters, toxicological studies will be necessary to determine the need for improved waste treatment methods.

These volatile, methylene chloride extractable compounds constitute only a small fraction (certainly less than 25%) of the total organic components of raw or treated domestic sewage. The next frontier in analysis of

wastewaters is identification and measurement of these non-volatile components.

ACKNOWLEDGEMENTS

The authors appreciate the advice and cooperation of personnel at the EPA's Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio. This research was not only condoned, but supported and encouraged by Mr. Jesse Cohen and Dr. Robert Bunch, of that laboratory. Dr. James Westrick and Mr. Richard Dobbs gave valuable technical advice and helped in obtaining samples. Mr. Thomas Pressley of that Laboratory's Blue Plains (Washington, DC) pilot plant suggested analysis of the chlorinated samples, and collected, chlorinated and extracted these samples.

At ERL-Athens, Mssrs. Mike Carter and Alfred Thruston and Ms. Ann Alford performed the GC-MS analysis, which consumed many man-months over a three year period. Dr. Leo Azarraga performed the GC-IR analyses. Dr. James Ryan at the EPA's pesticide analysis facility at Research Triangle Park, NC, performed some of the high resolution GC-MS analyses. Ms. Anne Elder did much of the drafting work.

DISCLAIMER

Mention of commercial products, trade names, and companies is for informational purposes only and does not imply endorsement by the U.S. Environmental Protection Agency or the Athens Environmental Research Laboratory.

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30. D. F. Bishop, T. P. O'Farrell, A. F. Cassel and A. P. Pinto, "Physical-Chemical Treatment of Raw Municipal

Wastewater" U.S. Environmantal Protection Agency Res. Rep. No. EPA-670/2-73-070, September 1973.

Table 1. Organic Compounds in Municipal Wastewaters

Compound by Class	Concentration in Wastewater, µg/l (+ = Present, not quantified)							
	Raw Wastewater		Activated Sludge Effluent		Physical-Chemical Effluent		Lime Clarified Raw Sewage	
	8/72	12/73	8/72	12/73	8/72	12/73	Before chlorination	After chlorination
Normal Chain Acids								
C_3 Propionic*	+		+					
C_4 Butyric*	+		+				+	
C_5 Valeric*	+		+	+				
C_6 Caproic*	+	0.4	+			+	+	
C_7 Enanthic*	+			0.5		0.2		+
C_8 Caprylic*	+	1.1		0.1		0.1	+	+
C_9 Nonanoic*	+	0.2		0.3		0.2	+	+
C_{10} Capric*	+	2.0		0.1		0.1	+	+
C_{11} Undecanoic*				+				
C_{12} Lauric*	0.5	1.7	0.3	0.1	+	0.1	+	+
C_{13} Tridecanoic*						+		
C_{14} Myristic*	1.3	0.7	0.5	0.2	0.1	0.1	+	+
C_{15} Pentadecanoic*	0.3	<0.1	0.3	0.2	+	0.1	+	+
C_{16} Palmitic*	28.0	7.1	6.0	2.0	0.6	0.2	+	+
C_{17} Margaric*	0.5	<0.1	0.2	0.4	+		+	+
C_{18} Stearic*	32.0	6.7	10.0	2.1	0.3	0.1	+	+
C_{19} Nonadecanoic	+							
C_{20} Arachidic	0.3	+						
C_{22} Behenic*			0.1					
Unsaturated Acids								
C_{16} Palmitoleic*	0.5	3.4		0.1	0.4	0.2	+	
C_{18} Oleic*	7.0	7.4	1.3	0.5	0.2	0.1	+	

Tab. 1 cont.

	Raw Wastewater		Activated Sludge Effluent		Physical-Chemical Effluent		Lime Clarified Raw Sewage	
	8/72	12/73	8/72	12/73	8/72	12/73	Before chlorination	After chlorination
Branched Chain Acids								
C_4 Isobutyric*	+		+					
C_5 Isovaleric*	+		+				+	+
C_{15} Anteisopentadecanoic†	+				+			
C_{17} Anteisomargaric†	+		+					
C_{17} α-Methyl Palmitic†					+			
C_{19} α-Methyl Stearic†					+			
Oxy-Acids†								
C_{10} β-Hydroxy acid					+			
C_{12} β-Hydroxy acid					+			
C_{14} β-Hydroxy acid	+				+			
C_{16} β-Hydroxy acid					+			
C_{18} β-Hydroxy acid	+							
C_{17} α-Ketomargaric					+			
C_{19} α-Ketononadecanoic					+			
Miscellaneous Acids								
Benzoic*						+	+	+
2-Ethylhexanoic		+		+		+		
Hexahydrobenzoic							+	
Phenylacetic*	+	+	+	+	+		+	+
Phenylpropionic	+						+	+
Alcohols								
Benzyl alcohol							+	+
Borneol							+	
2-Butoxyethanol	+							
2-Ethyl-1-hexanol				+				
1-Pentanol			+					
2-Phenoxyethanol							+	
α-Terpineol	+	+		+		+	+	
Phthalates								
Dibutyl		+	+	+	+	+		
Diethyl				+				
Dioctyl		+	+	+	+	+		

Table 1 cont'd.

	Raw Wastewater		Activated Sludge Effluent		Physical-Chemical Effluent		Lime Clarified Raw Sewage	
	8/72	12/73	8/72	12/73	8/72	12/73	Before chlorination	After chlorination
Chlorinated Compounds								
Chlorocyclohexane								+
Chloroform*		+				+		
Dichloromethane*		+		+				
Hexachloroethane*								+
Pentachloroethane*								+
Pentachlorophenol*			0.2	+				
1,1,2,2-Tetrachloroethane	+							+
1,1,1,2-Tetrachloroethane								+
Steroids								
Cholesterol		+		+				
Coprostanol		+		+				
Drugs and Drug Metabolites								
Caffeine	+	+		+			+	
2-(4-Chlorophenoxy)-2-methylpropionic acid* [Clofibrate metabolite]		0.8	1.0	2.0		<0.1	+	+
Nicotine		+		+			+	
Salicylic acid*	+	+					+	
Aromatic Hydrocarbons								
Dimethylbenzene isomer							+	
Dimethylnaphthalene isomer							+	
Ethylbenzene			+					
p-Methylstyrene			+					
Toluene			+					
Xylene				+				
Miscellaneous Organics								
Acetone		+		+		+		
Benzaldehyde							+	+
m-tert-Butylphenol*		+						
Carvone							+	
1-1-Diethoxyethane							+	+
Dioctyl Adipate					+			
Ethyl Acetate						+		
Indene			+					
p-Phenylphenol*		+						
Saccharin*		+					+	+
Tetrahydrofuran						+		

* Confirmed with standard; all others by mass spectral matching.

† Identified only by manual interpretation of mass spectra, except that the β-hydroxy acids matched GC retention times with standards. There is considerable possibility of error in identification of the α-keto and long branched chain acids.

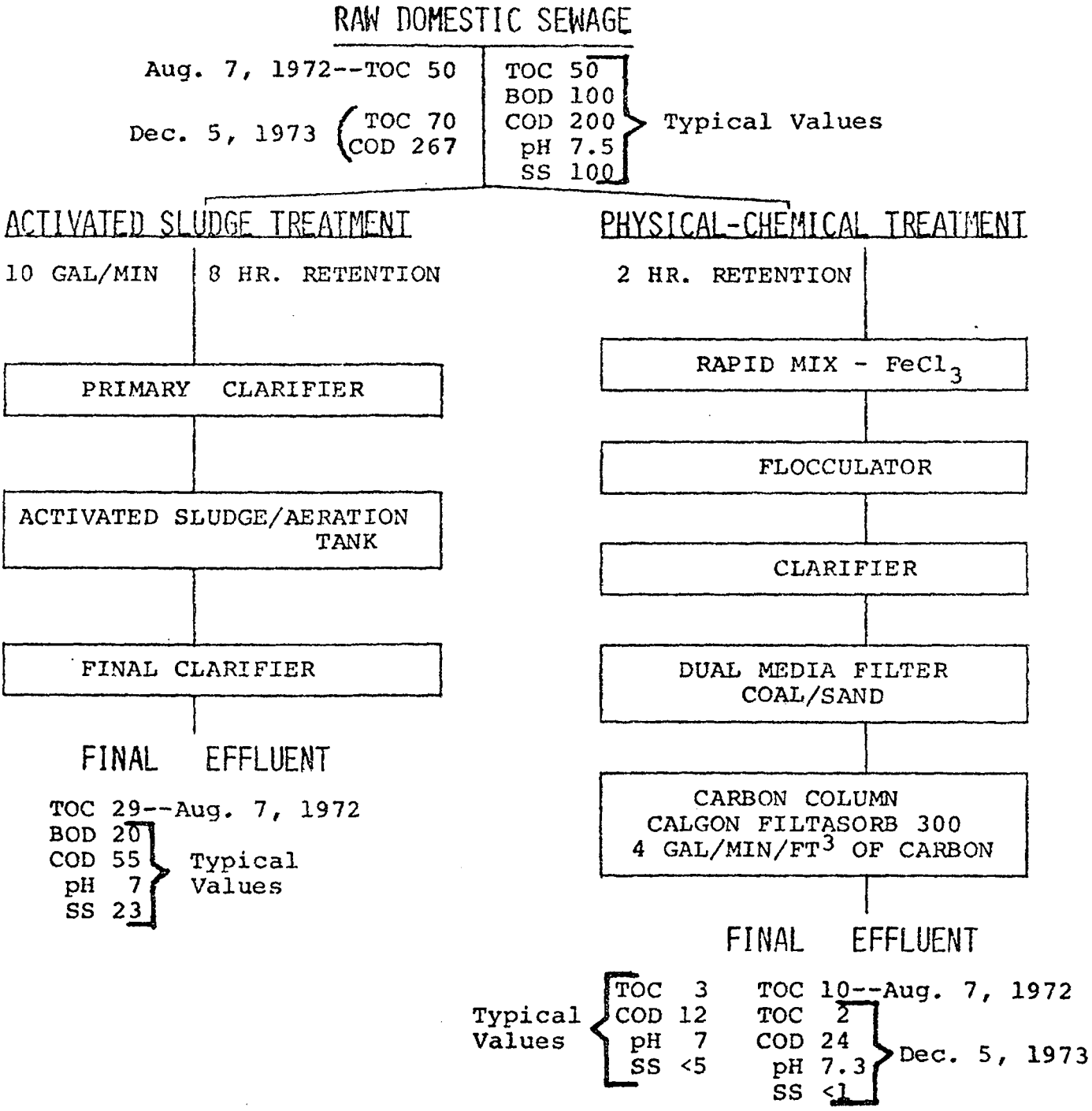
LIST OF FIGURES

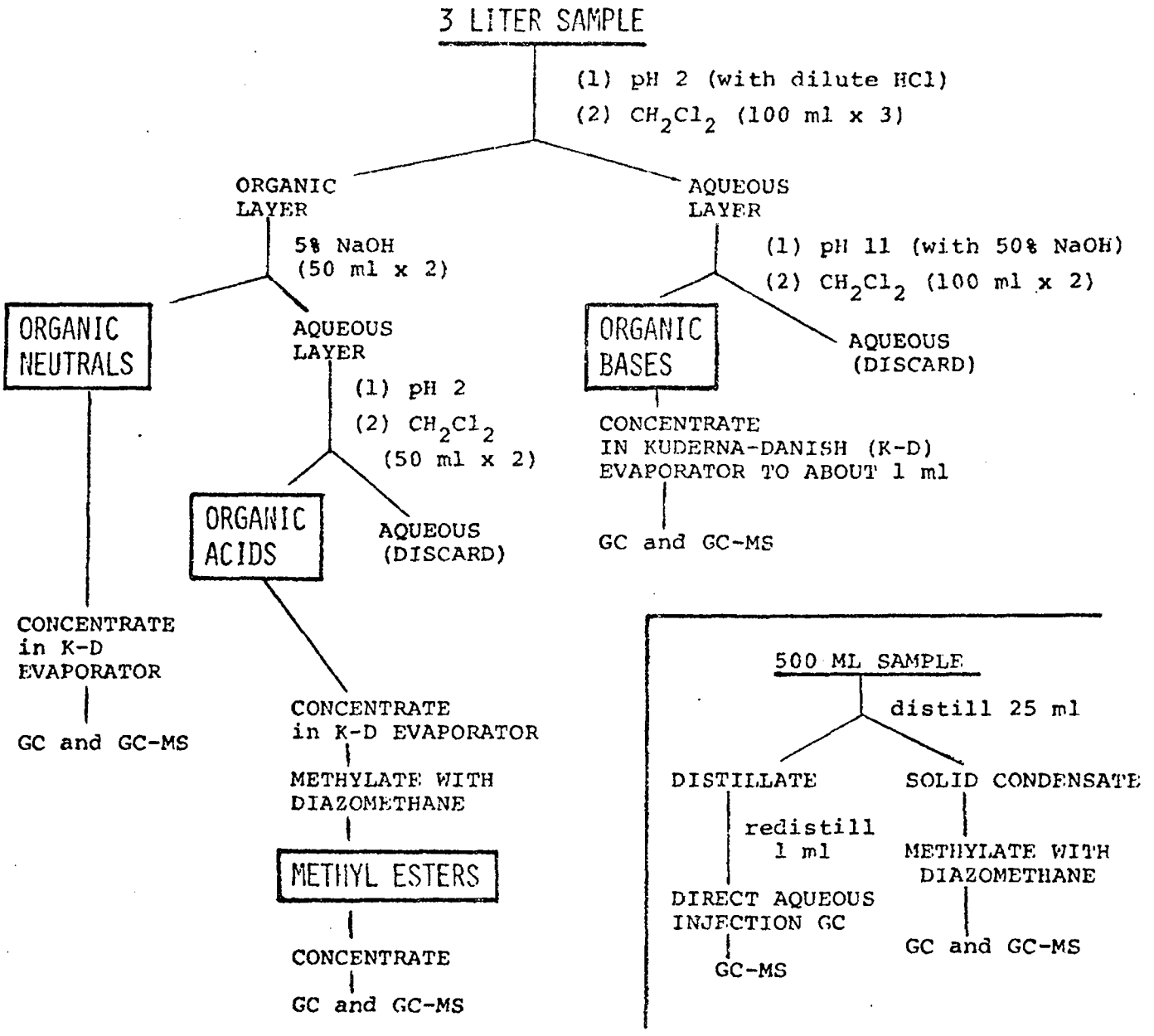
Number

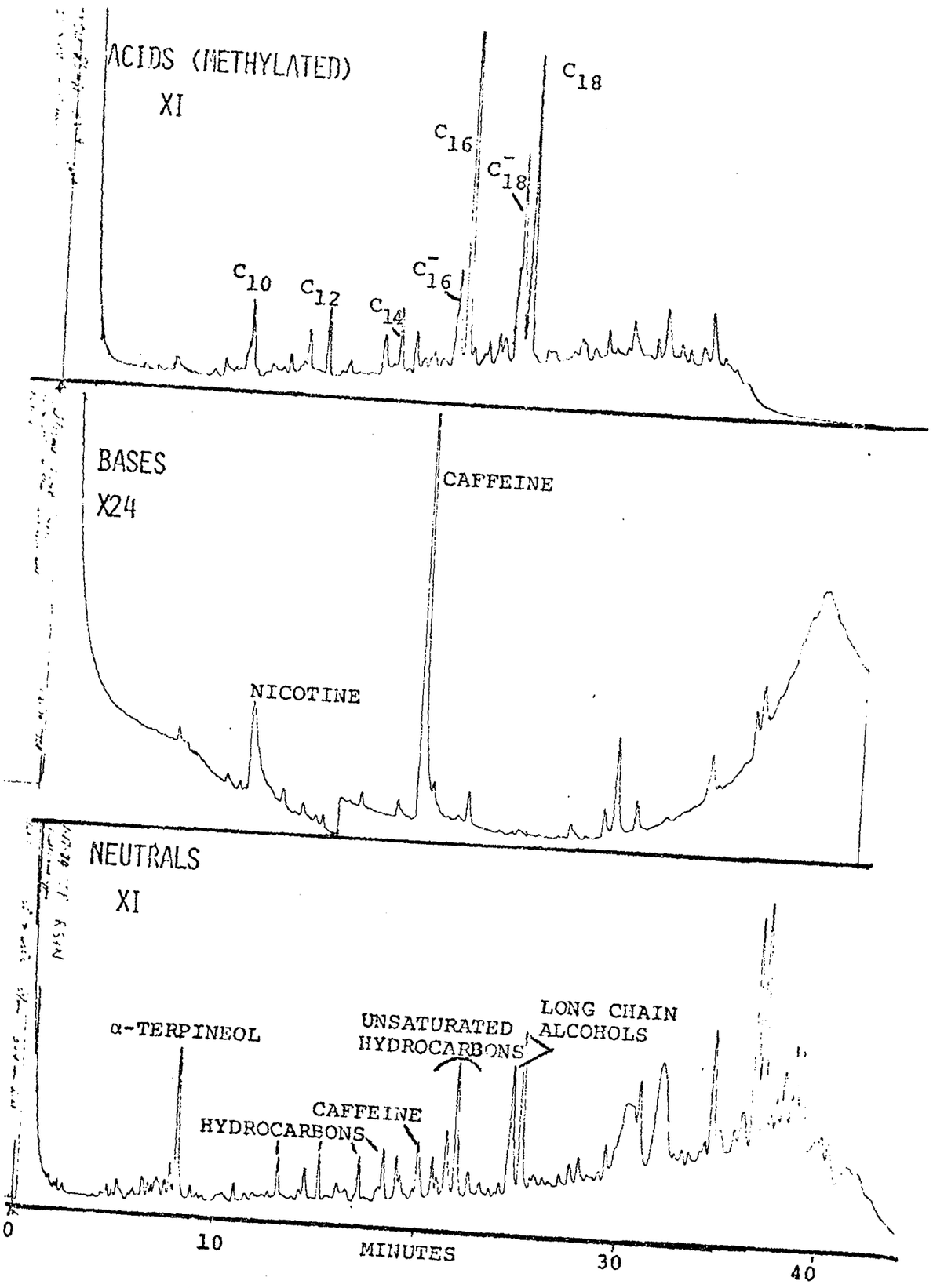
Number

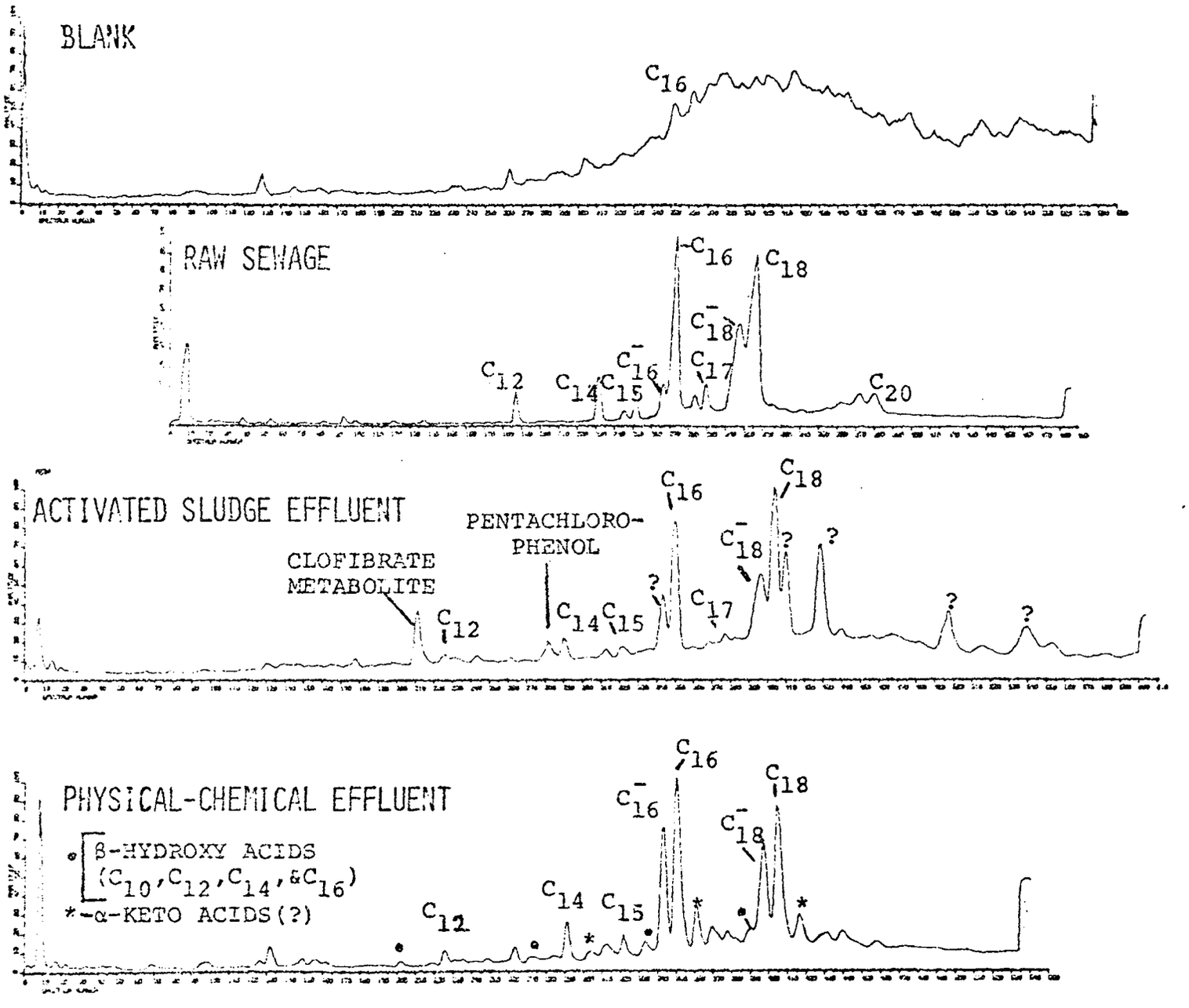
FIGURES (Cont'd)

Number

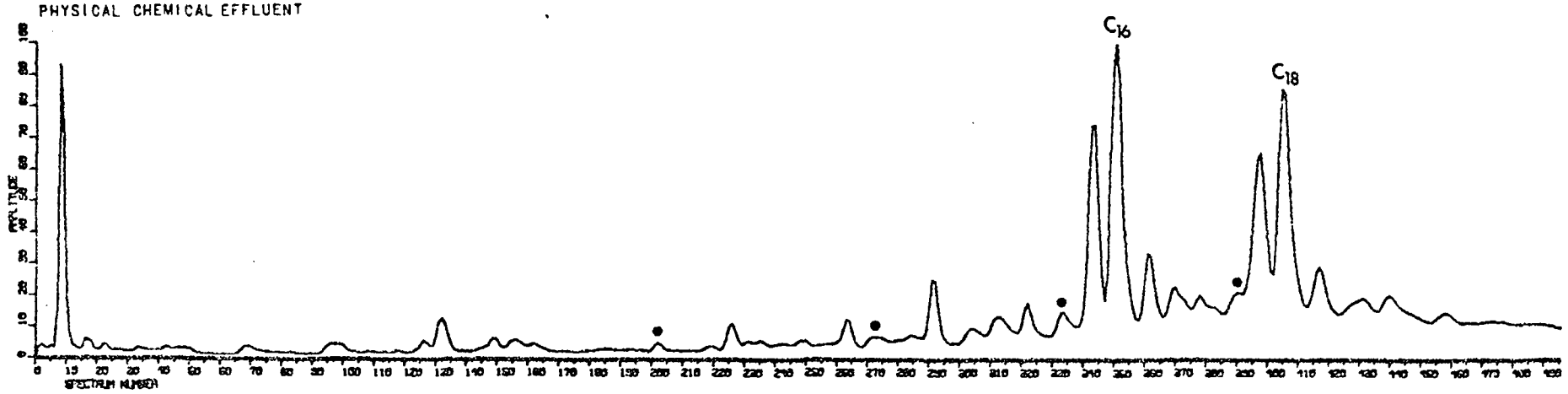

RAW DOMESTIC SEWAGE
Aug. 7, 1972--TOC 50
Dec. 5, 1973 TOC 70 COD 267
TOC 50
BOD 100
COD 200
pH 7.5
SS 100
Typical Values
ACTIVATED SLUDGE TREATMENT
10 GAL/MIN
8 HR. RETENTION
PRIMARY CLARIFIER
ACTIVATED SLUDGE/AERATION TANK
FINAL CLARIFIER
FINAL EFFLUENT
TOC 29--Aug. 7, 1972
BOD 20
COD 55
pH 7
SS 23
Typical Values
PHYSICAL-CHEMICAL TREATMENT
2 HR. RETENTION
RAPID MIX - FeCl3
FLOCCULATOR
CLARIFIER
DUAL MEDIA FILTER COAL/SAND
CARBON COLUMN CALGON FILTASORB 300 4 GAL/MIN/FT3 OF CARBON
FINAL EFFLUENT
Typical Values
TOC 3
COD 12
pH 7
SS <5
TOC 10--Aug. 7, 1972
TOC 2
COD 24
pH 7.3
SS <1
Dec. 5, 1973


3 LITER SAMPLE
(1) pH 2 (with dilute HCl)
(2) CH_2Cl_2 (100 ml x 3)
ORGANIC LAYER
AQUEOUS LAYER
5% NaOH (50 ml x 2)
(1) pH 11 (with 50% NaOH)
(2) CH_2Cl_2 (100 ml x 2)
ORGANIC NEUTRALS
AQUEOUS LAYER
ORGANIC BASES
AQUEOUS (DISCARD)
(1) pH 2
(2) CH_2Cl_2 (50 ml x 2)
CONCENTRATE IN KUDERNA-DANISH (K-D) EVAPORATOR TO ABOUT 1 ml
ORGANIC ACIDS
AQUEOUS (DISCARD)
GC and GC-MS
CONCENTRATE in K-D EVAPORATOR
GC and GC-MS
CONCENTRATE in K-D EVAPORATOR
METHYLATE WITH DIAZOMETHANE
METHYL ESTERS
CONCENTRATE
GC and GC-MS
500 ML SAMPLE
distill 25 ml
DISTILLATE
SOLID CONDENSATE
redistill 1 ml
METHYLATE WITH DIAZOMETHANE
DIRECT AQUEOUS INJECTION GC
GC and GC-MS
GC-MS

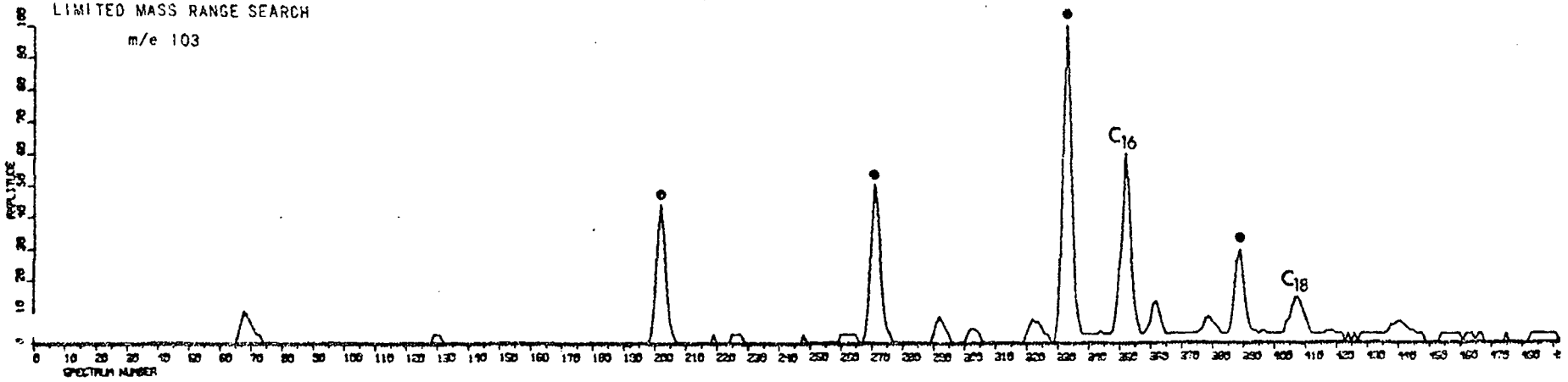

ACIDS (METHYLATED)
XI
C_{18}
C_{16}
C_{18}^{-}
C_{10}
C_{12}
C_{14}
C_{16}^{-}
BASES
X24
CAFFEINE
NICOTINE
NEUTRALS
XI
α-TERPINEOL
UNSATURATED HYDROCARBONS
LONG CHAIN ALCOHOLS
CAFFEINE
HYDROCARBONS
0
10
MINUTES
30
40

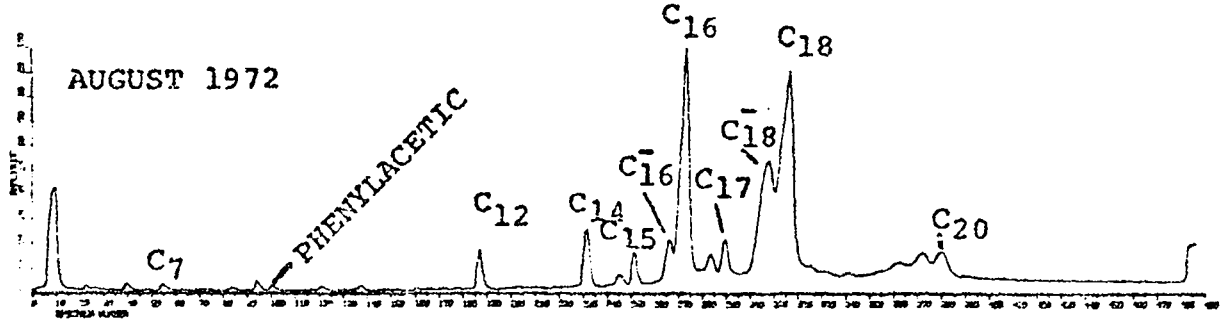

BLANK
C_{16}
RAW SEWAGE
C_{12}
C_{14}
C_{15}
C_{16}^-
C_{16}
C_{17}
C_{18}^-
C_{18}
C_{20}
ACTIVATED SLUDGE EFFLUENT
CLOFIBRATE METABOLITE
PENTACHLORO-PHENOL
C_{12}
C_{14}
C_{15}
C_{16}
C_{17}
C_{18}^-
C_{18}
?
PHYSICAL-CHEMICAL EFFLUENT
°[β-HYDROXY ACIDS (C_{10},C_{12},C_{14},&C_{16})
*-α-KETO ACIDS(?)
C_{12}
C_{14}
C_{15}
C_{16}^-
C_{16}
C_{18}^-
C_{18}

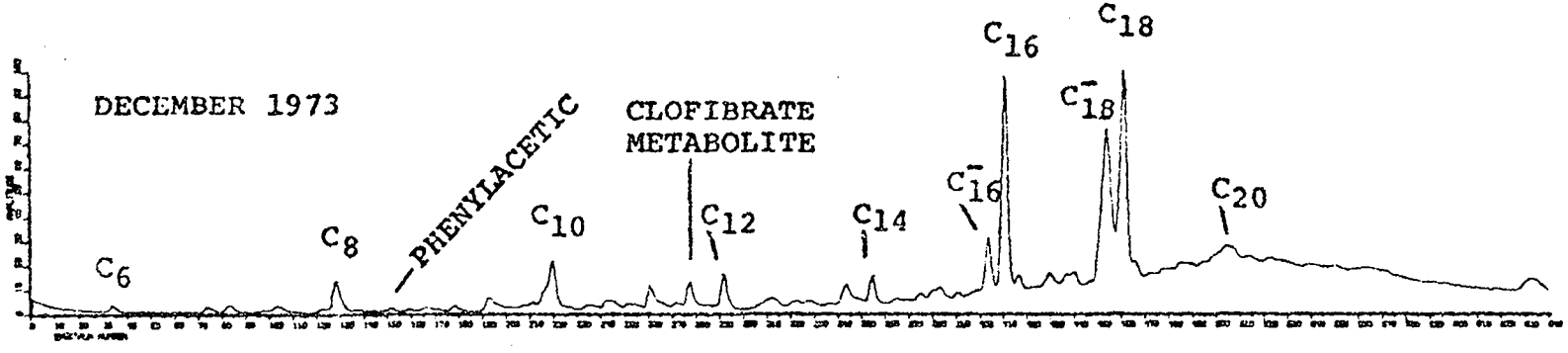
PHYSICAL CHEMICAL EFFLUENT

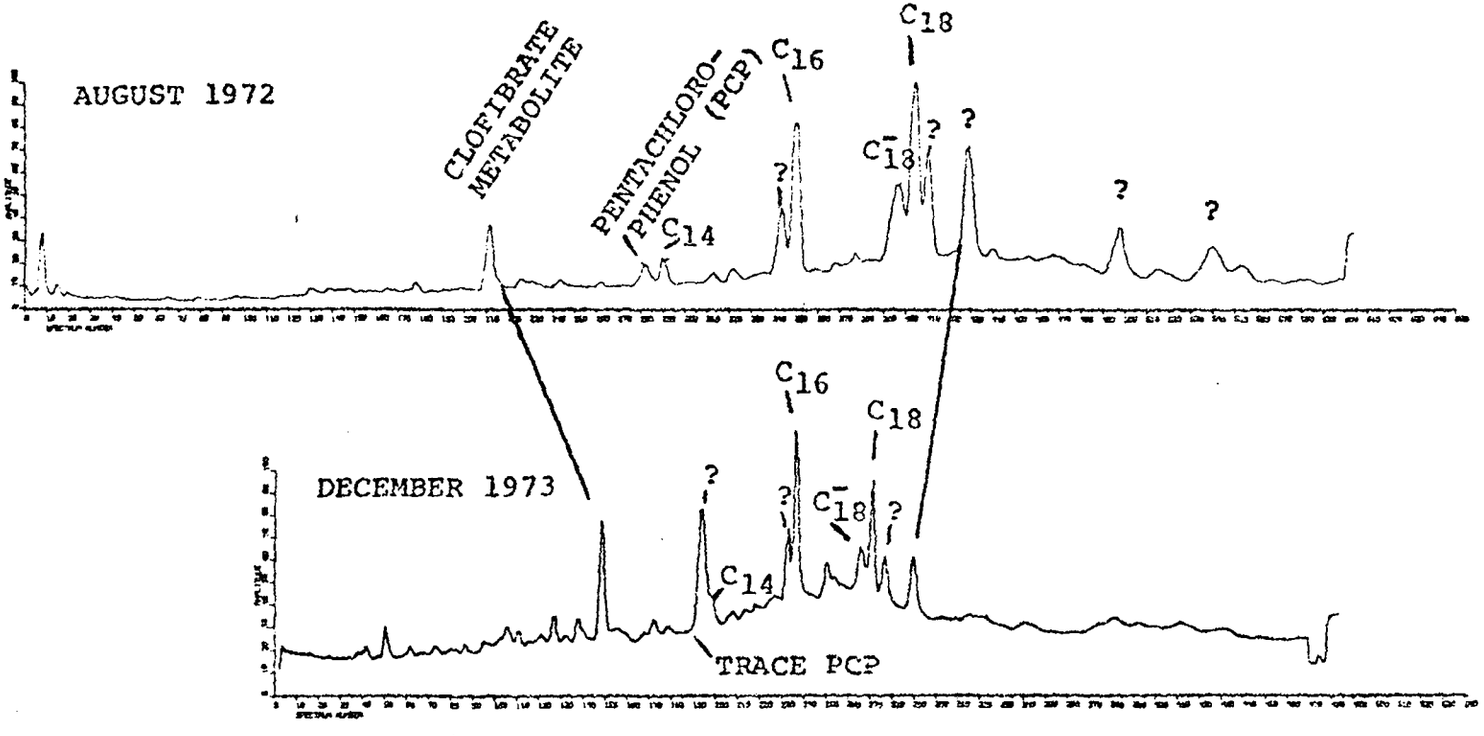


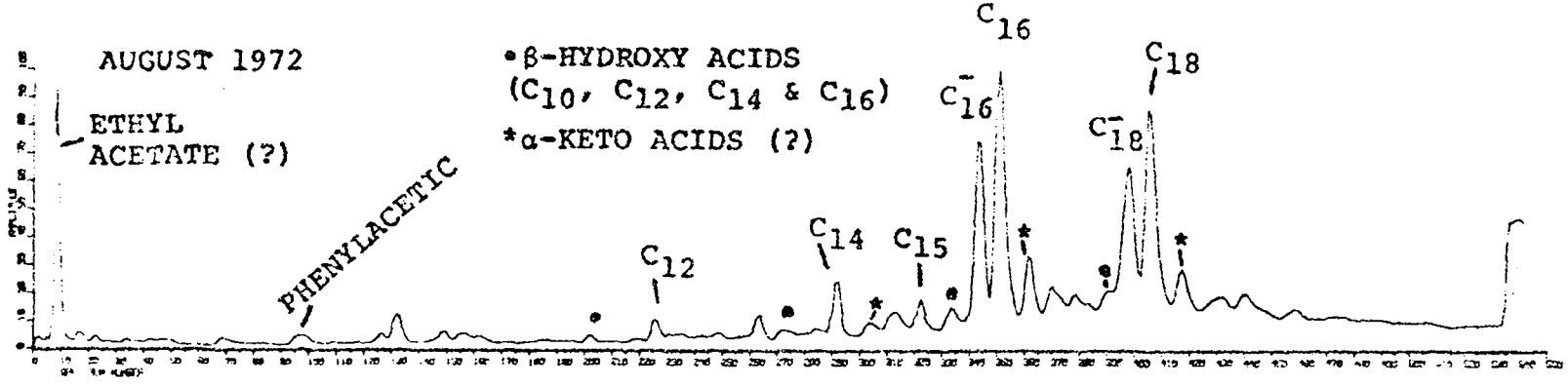
PHYSICAL CHEMICAL EFFLUENT
LIMITED MASS RANGE SEARCH
m/e 103

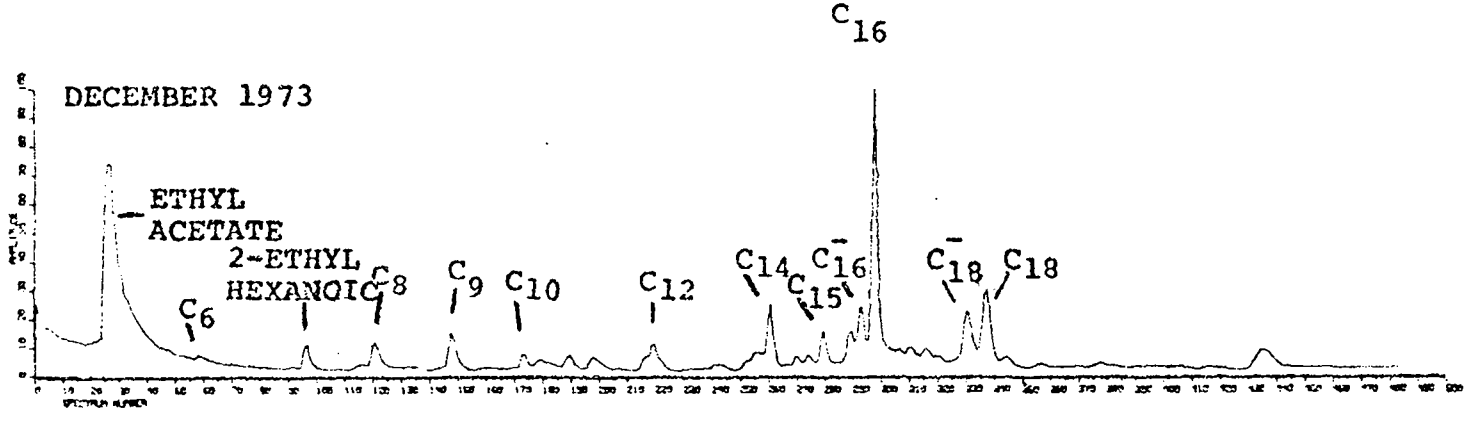


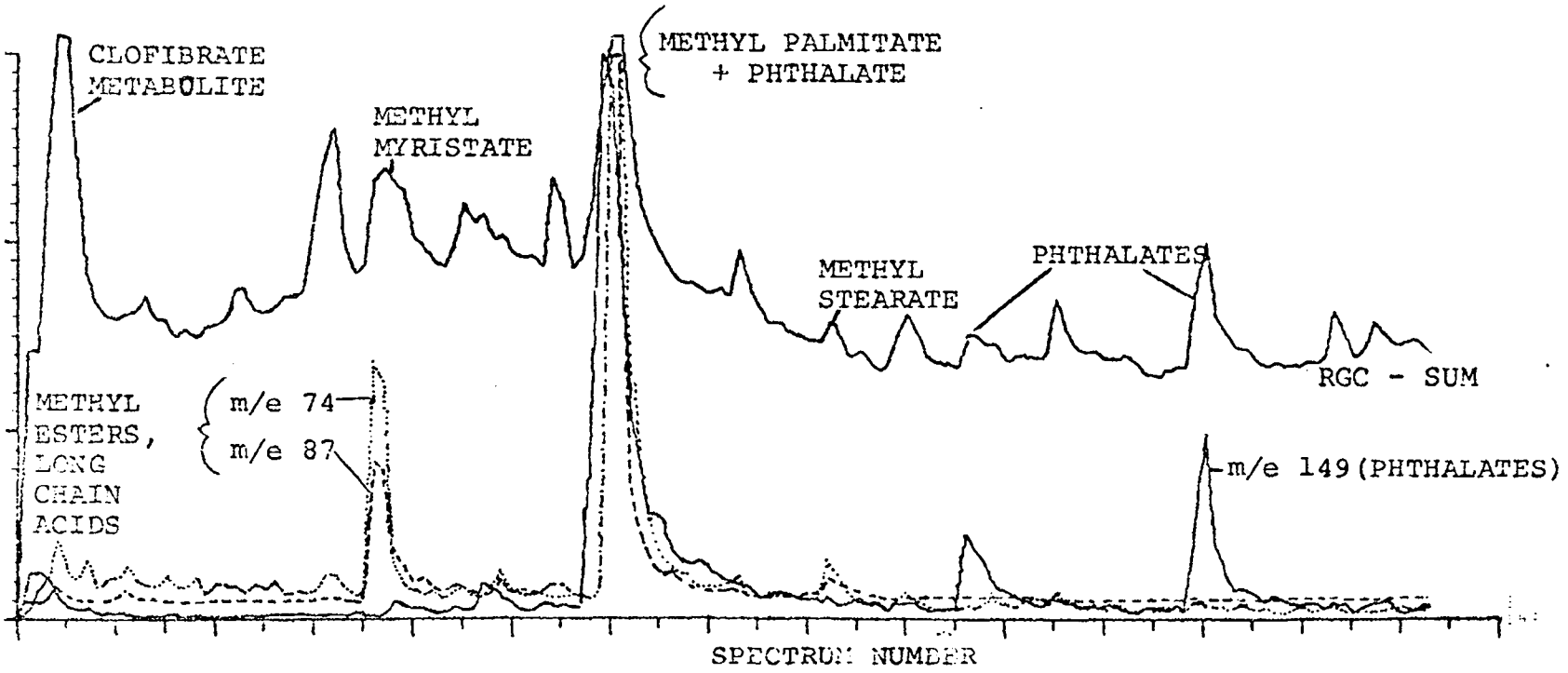

AUGUST 1972
PHENYLACETIC
C7
C12
C14
C15
C16
C16
C17
C18
C18
C20

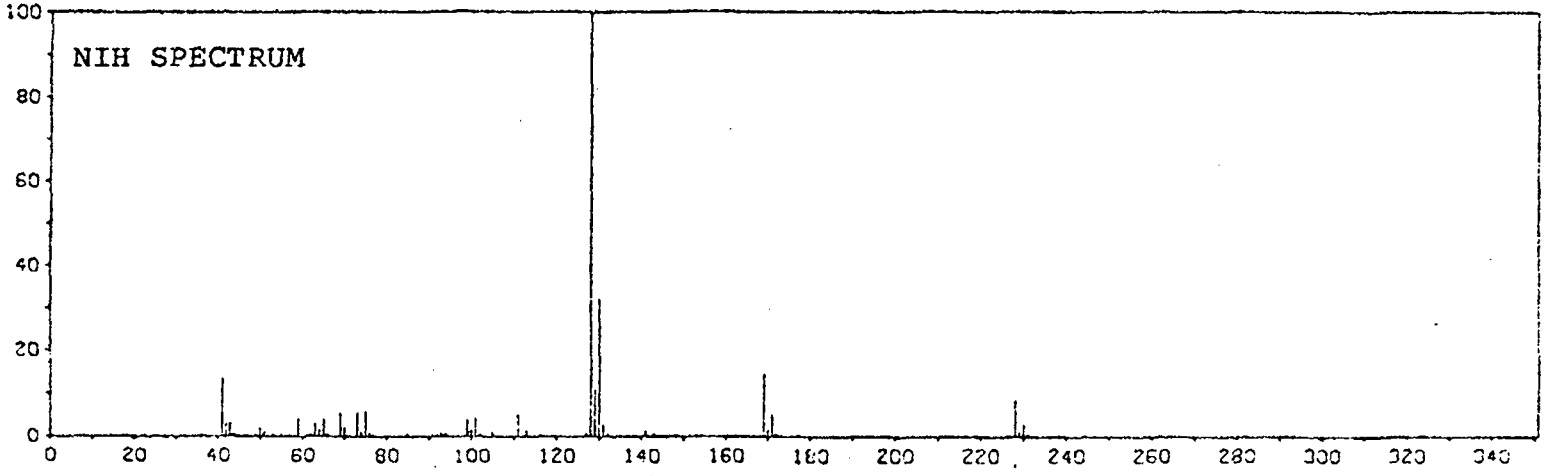

DECEMBER 1973
C6
C8
PHENYLACETIC
C10
CLOFIBRATE
METABOLITE
C12
C14
C16
C16
C18
C18
C20

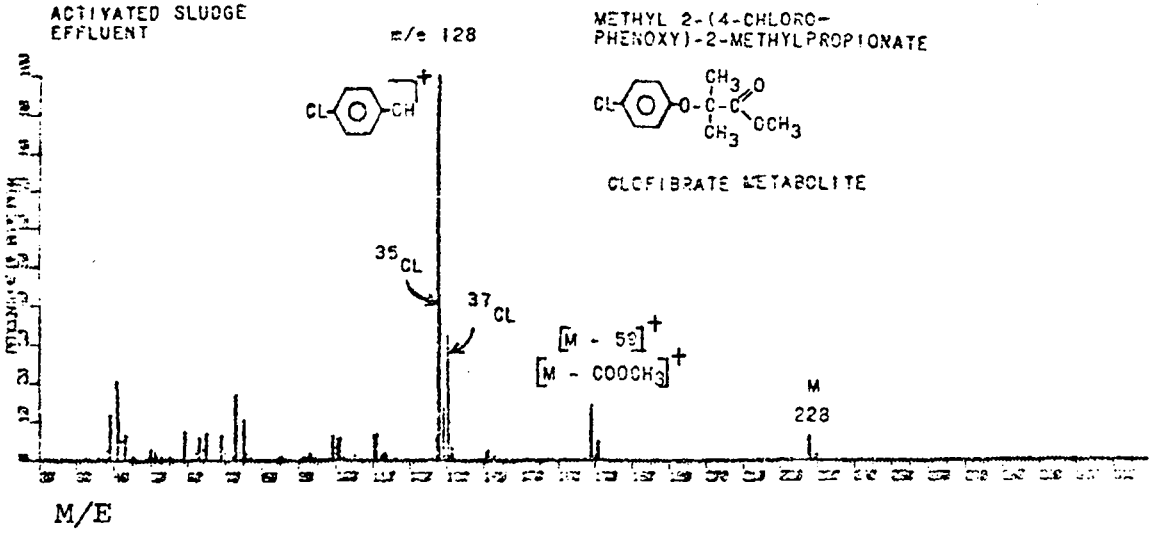

AUGUST 1972
CLOFIBRATE METABOLITE
PENTACHLORO-PHENOL (PCP)
C14
C16
C18
C18
?
?
?
?
?
DECEMBER 1973
C16
C18
C18
C14
?
?
?
?
TRACE PCP

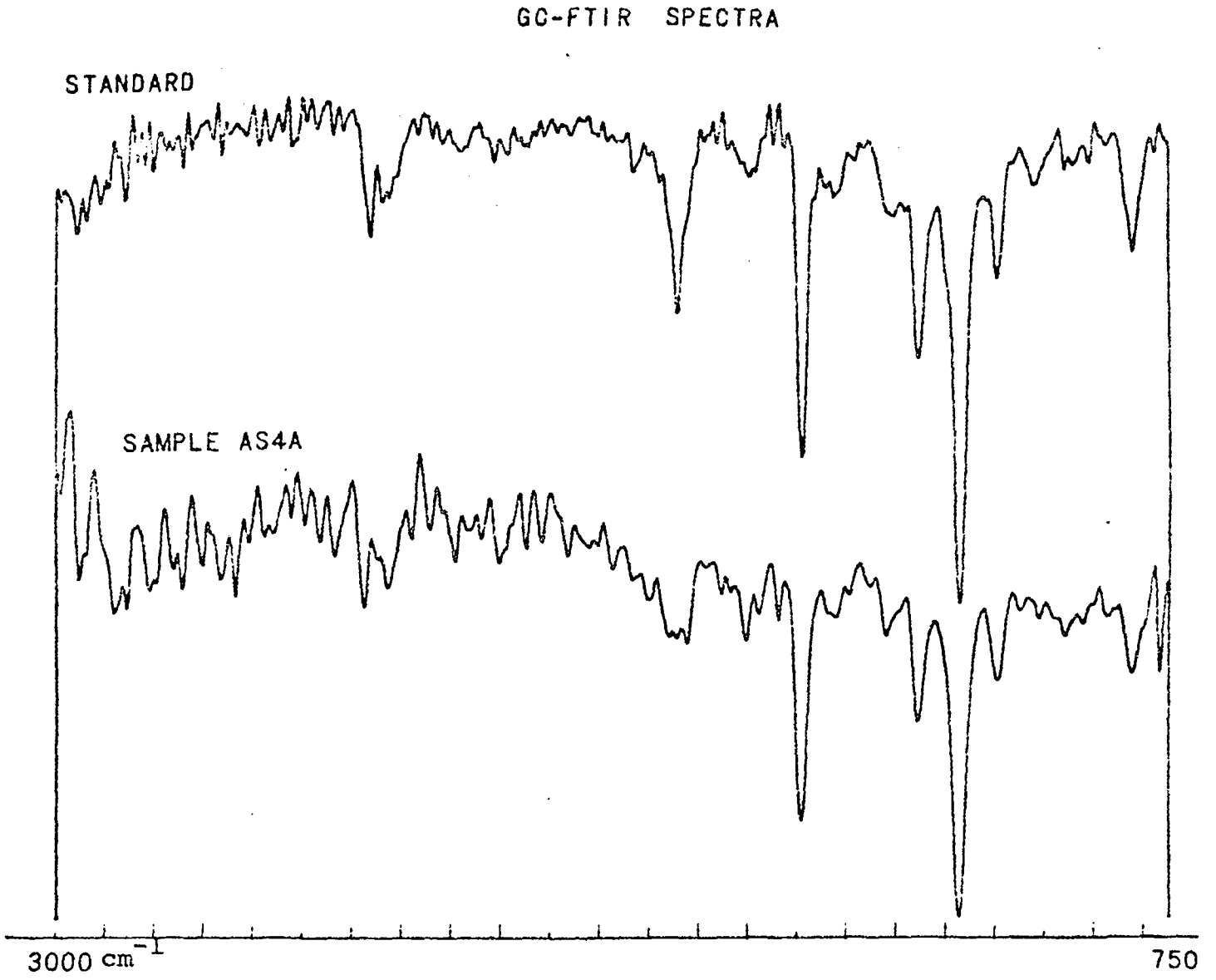

AUGUST 1972
•β-HYDROXY ACIDS
(C_{10}, C_{12}, C_{14} & C_{16})
*α-KETO ACIDS (?)
ETHYL
ACETATE (?)
PHENYLACETIC
C_{12}
C_{14}
C_{15}
C_{16}
$C_{\bar{1}6}$
C_{18}
$C_{\bar{1}8}$

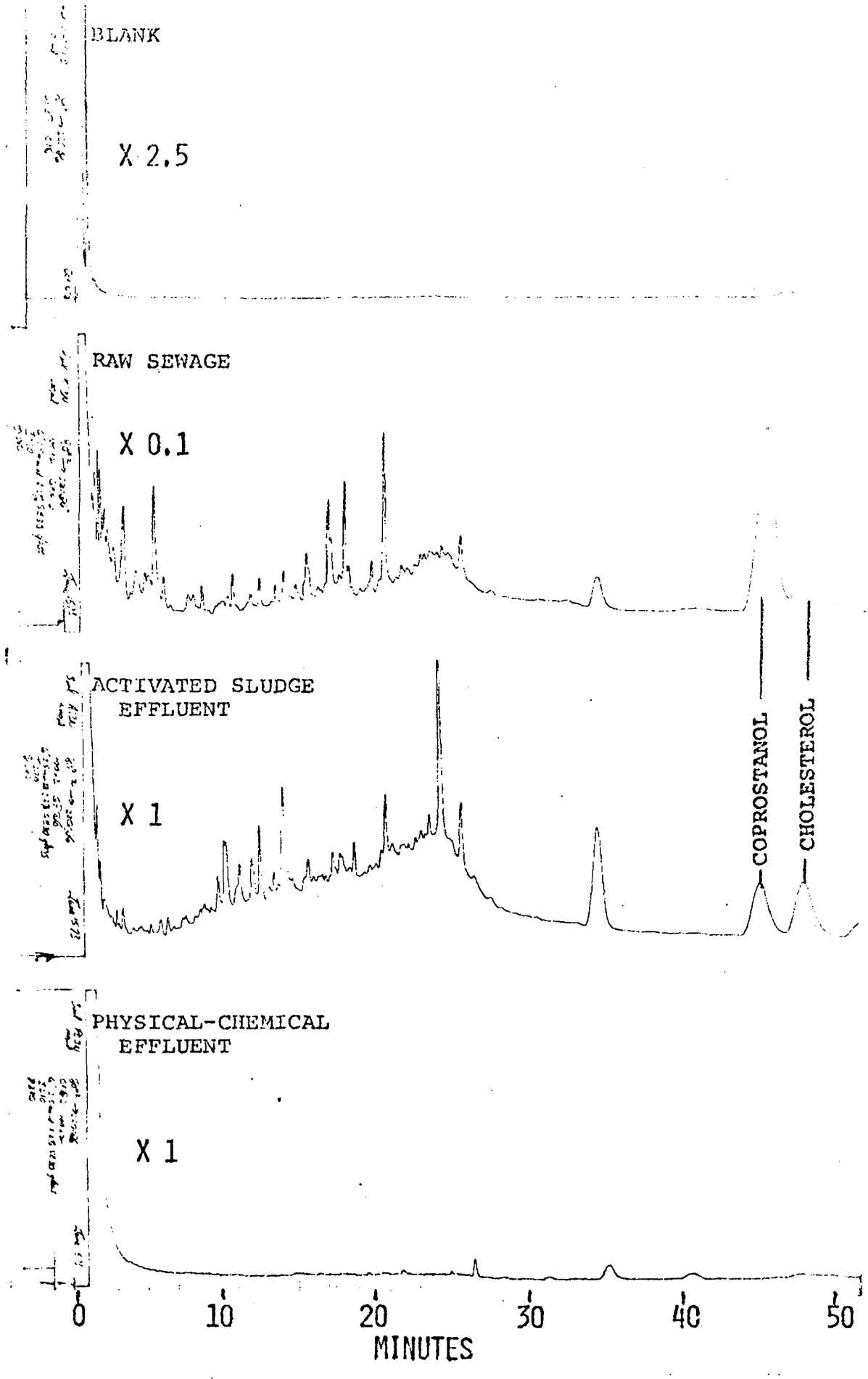

DECEMBER 1973
ETHYL
ACETATE
2-ETHYL
HEXANOIC
C_6
C_8
C_9
C_{10}
C_{12}
C_{14}
C_{15}
C_{16}
$C_{\bar{1}6}$
C_{18}
$C_{\bar{1}8}$

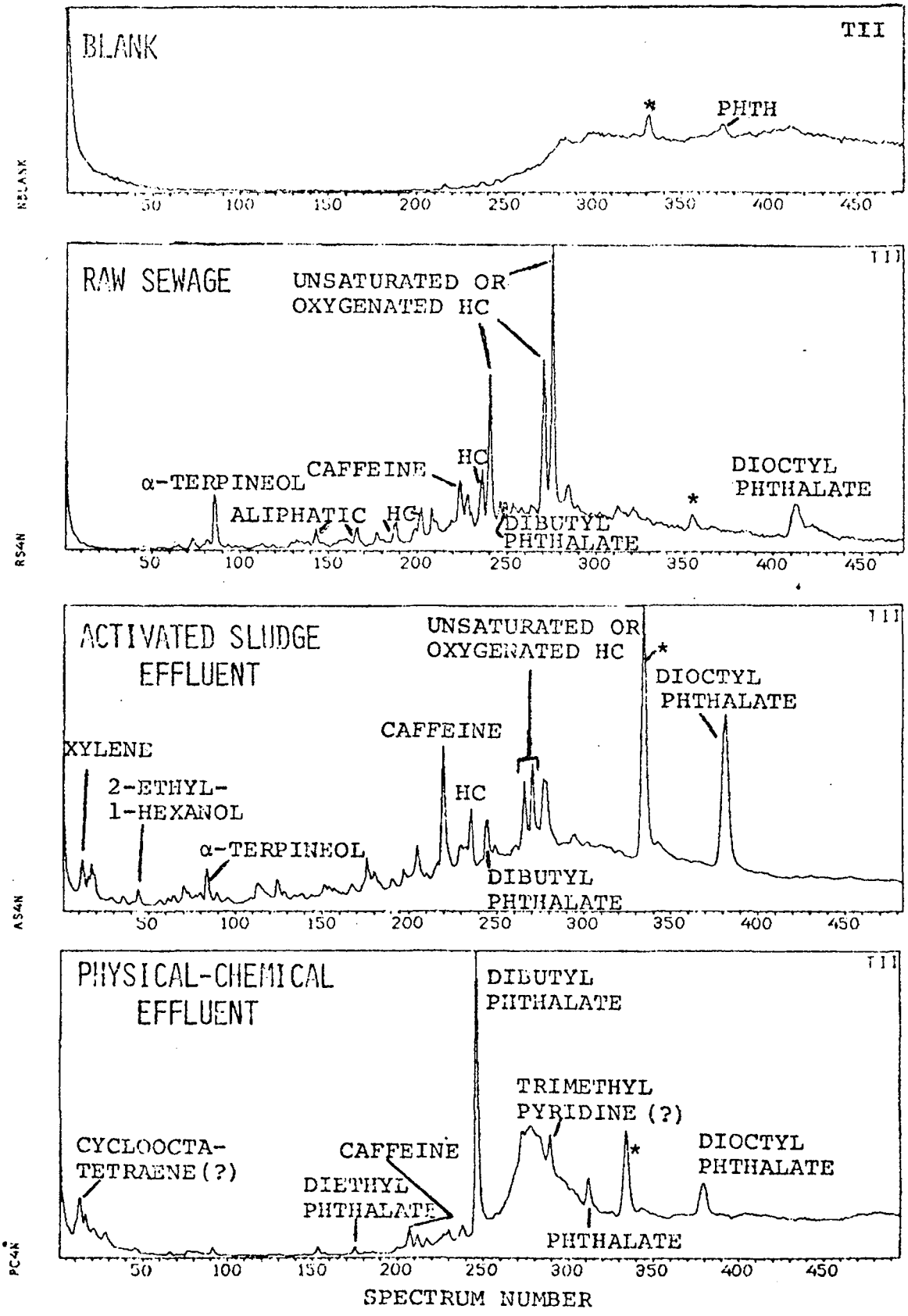

CLOFIBRATE METABOLITE
METHYL MYRISTATE
METHYL PALMITATE + PHTHALATE
METHYL STEARATE
PHTHALATES
RGC - SUM
METHYL ESTERS, LONG CHAIN ACIDS
m/e 74
m/e 87
m/e 149 (PHTHALATES)
SPECTRUM NUMBER

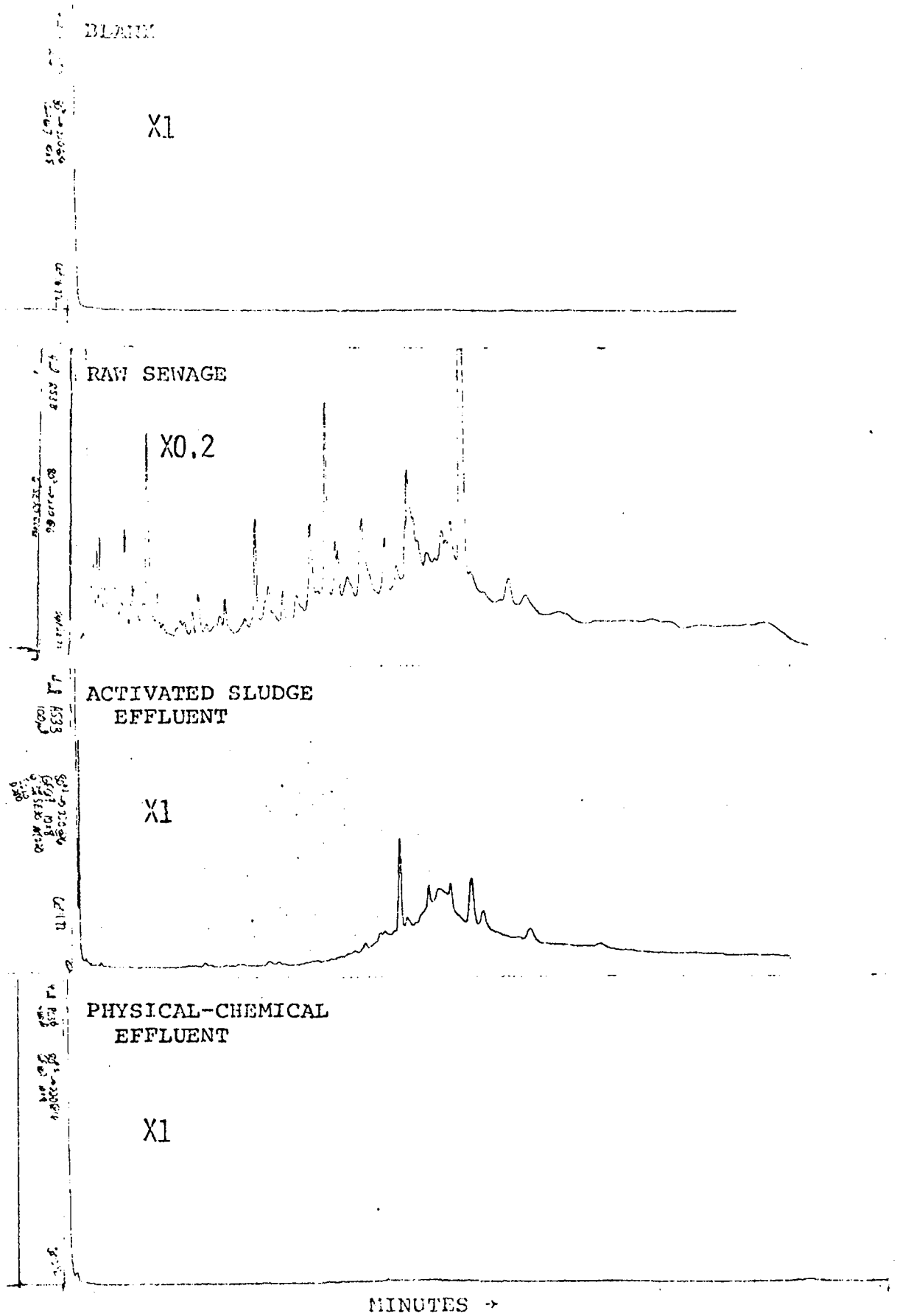

NIH SPECTRUM
100
80
60
40
20
0
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340

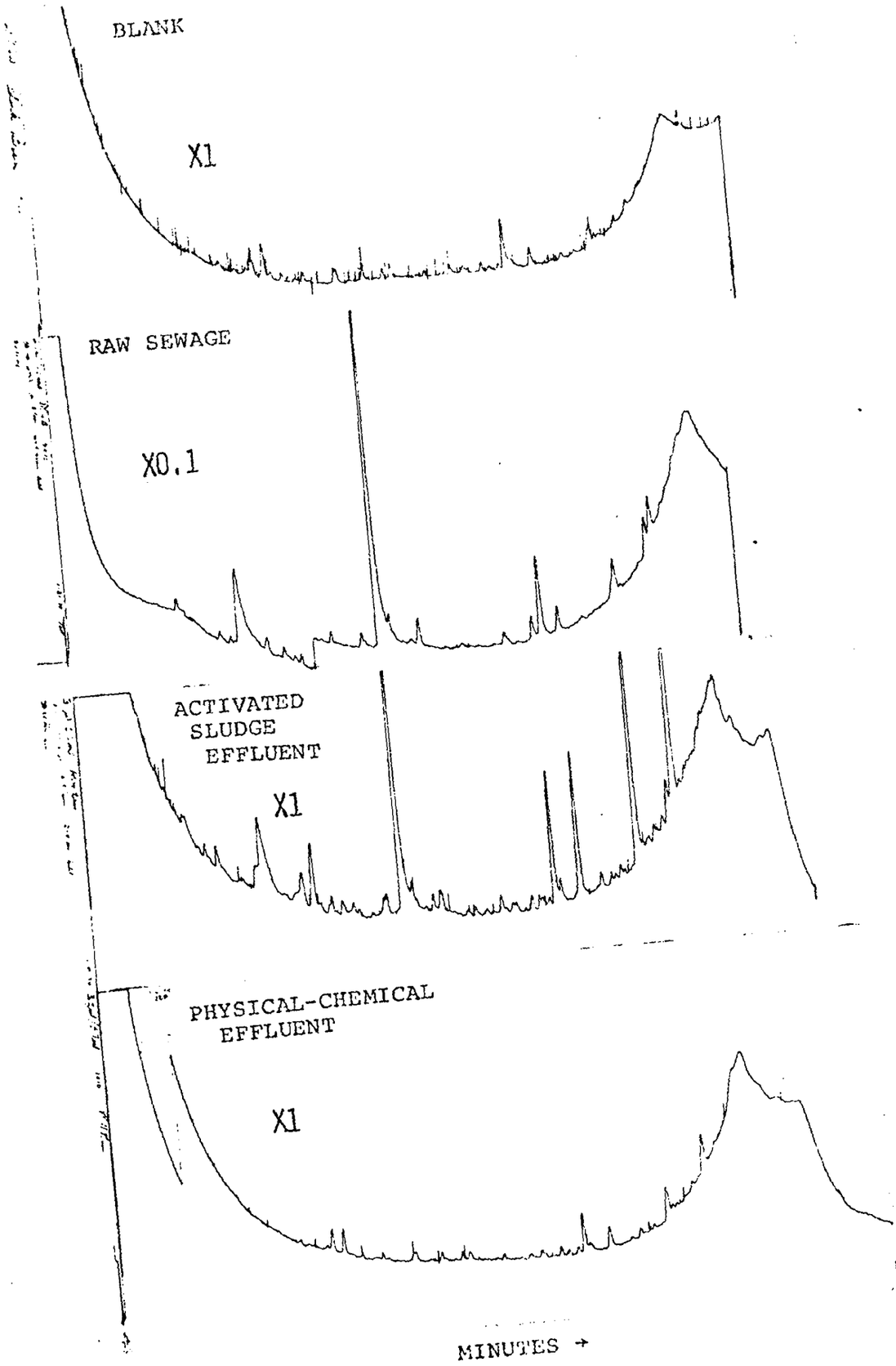

ACTIVATED SLUDGE
EFFLUENT
m/e 128
METHYL 2-(4-CHLORO-
PHENOXY)-2-METHYLPROPIONATE
CLOFIBRATE METABOLITE
35CL
37CL
[M - 59]+
[M - COOCH3]+
M
228
M/E

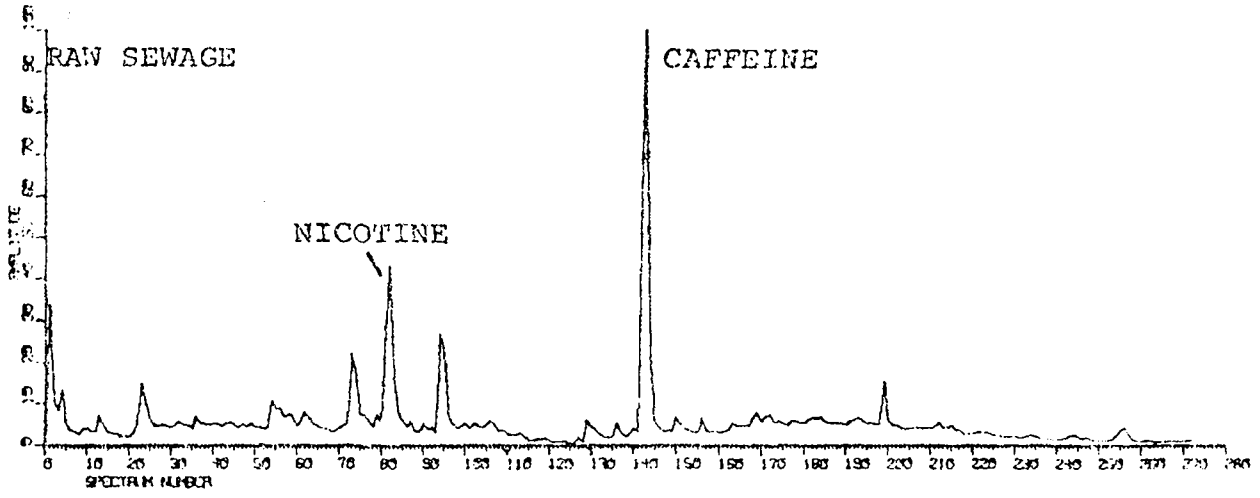

GC-FTIR SPECTRA
STANDARD
SAMPLE AS4A
3000 cm⁻¹
750

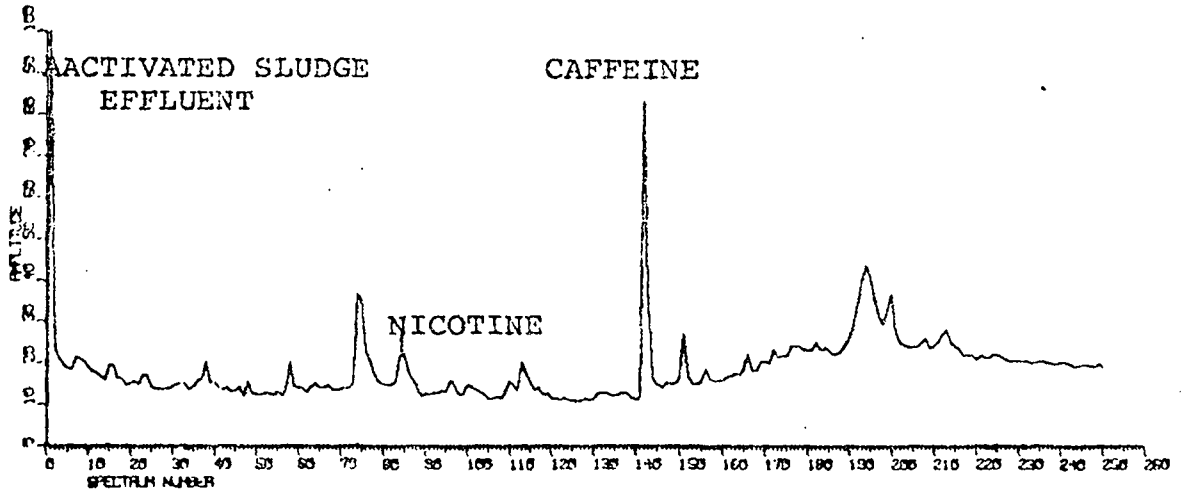

BLANK
X 2.5
RAW SEWAGE
X 0.1
ACTIVATED SLUDGE
EFFLUENT
X 1
COPROSTANOL
CHOLESTEROL
PHYSICAL-CHEMICAL
EFFLUENT
X 1
0
10
20
30
40
50
MINUTES

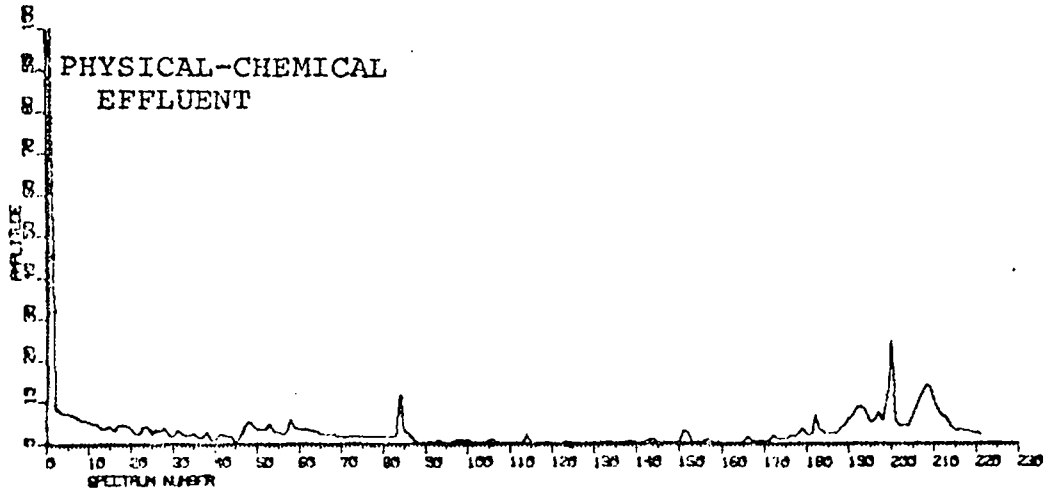

BLANK
TII
PHTH
BLANK
50
100
150
200
250
300
350
400
450
RAW SEWAGE
UNSATURATED OR
OXYGENATED HC
α-TERPINEOL
CAFFEINE
HC
ALIPHATIC HC
DIBUTYL
PHTHALATE
DIOCTYL
PHTHALATE
RS4N
ACTIVATED SLUDGE
EFFLUENT
UNSATURATED OR
OXYGENATED HC
DIOCTYL
PHTHALATE
CAFFEINE
XYLENE
2-ETHYL-
1-HEXANOL
HC
α-TERPINEOL
DIBUTYL
PHTHALATE
AS4N
PHYSICAL-CHEMICAL
EFFLUENT
DIBUTYL
PHTHALATE
TRIMETHYL
PYRIDINE (?)
CYCLOOCTA-
TETRAENE(?)
CAFFEINE
DIETHYL
PHTHALATE
DIOCTYL
PHTHALATE
PHTHALATE
PC4N
SPECTRUM NUMBER

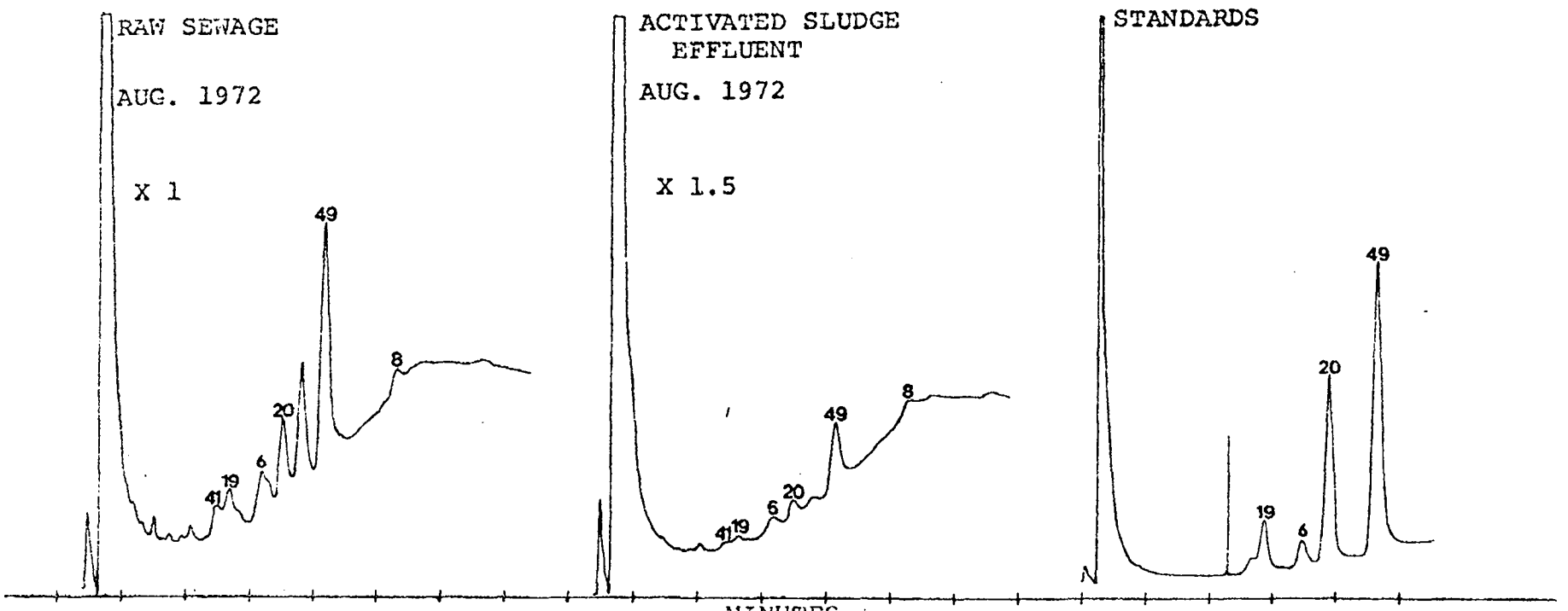

BLANK
X1
RAW SEWAGE
X0.2
ACTIVATED SLUDGE
EFFLUENT
X1
PHYSICAL-CHEMICAL
EFFLUENT
X1
MINUTES →


BLANK
X1
RAW SEWAGE
X0.1
ACTIVATED
SLUDGE
EFFLUENT
X1
PHYSICAL-CHEMICAL
EFFLUENT
X1
MINUTES →


RAW SEWAGE
CAFFEINE
NICOTINE
SPECTRUM NUMBER


ACTIVATED SLUDGE
EFFLUENT
CAFFEINE
NICOTINE
SPECTRUM NUMBER

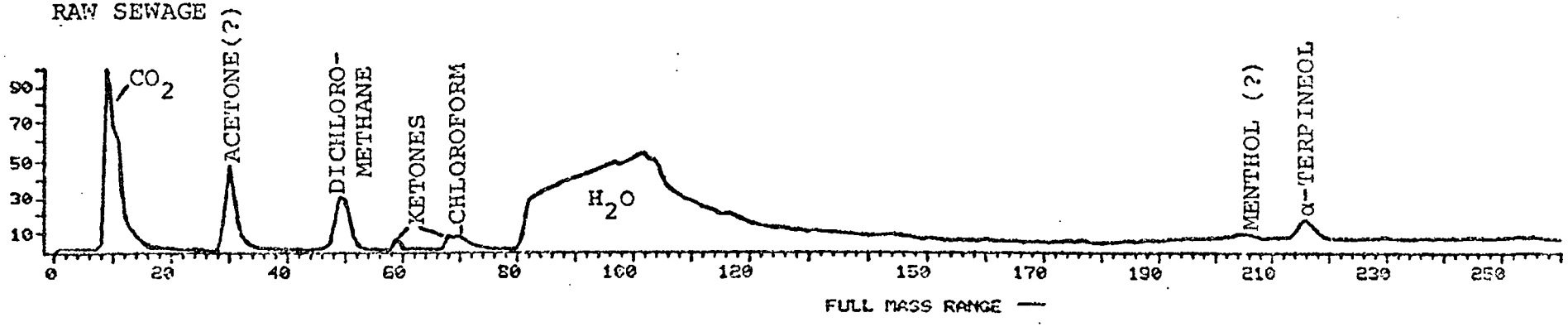

PHYSICAL-CHEMICAL
EFFLUENT
SPECTRUM NUMBER



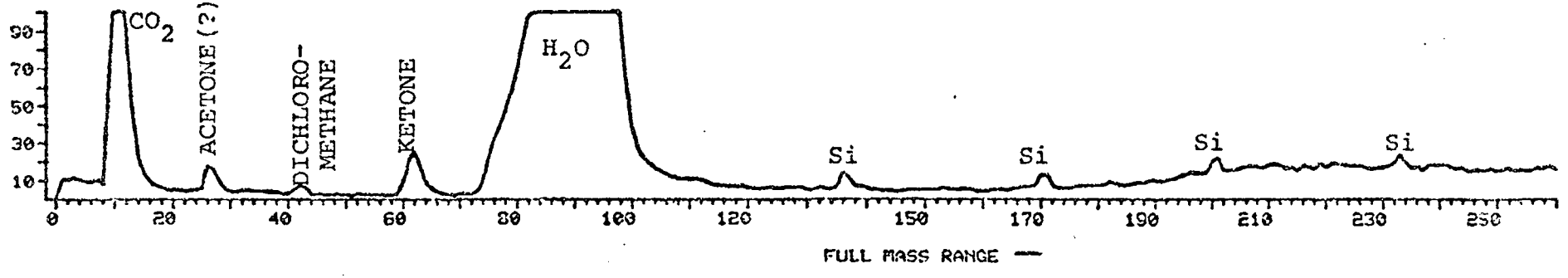
6 = BUTYRIC 19 = ISOBUTYRIC 41 = PROPIONIC

8 = CAPROIC 20 = ISOVALERIC 49 = VALERIC

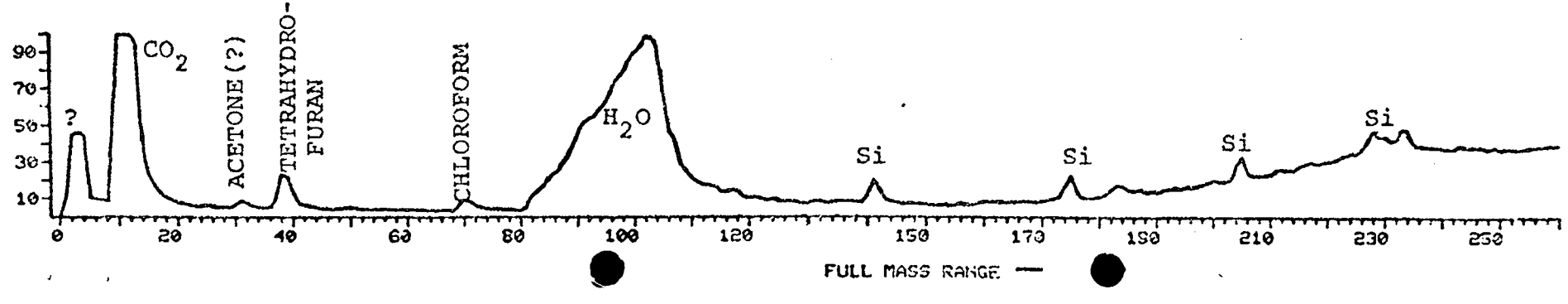
RAW SEWAGE



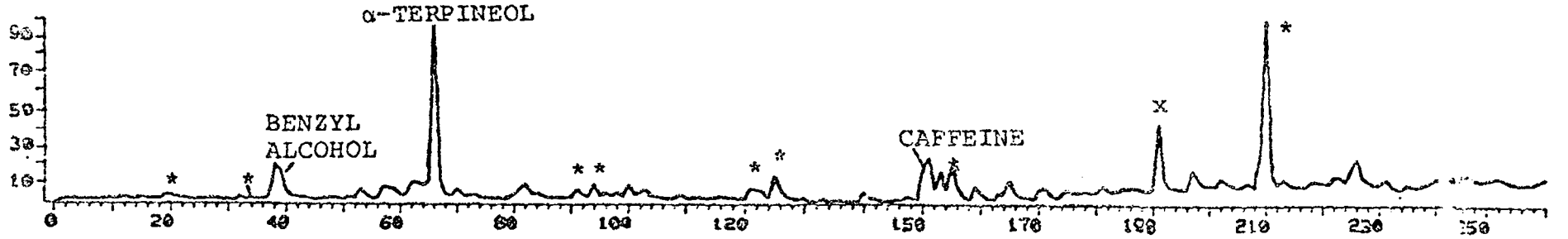
ACTIVATED SLUDGE EFFLUENT



PHYSICAL-CHEMICAL EFFLUENT



BEFORE CHLORINATION



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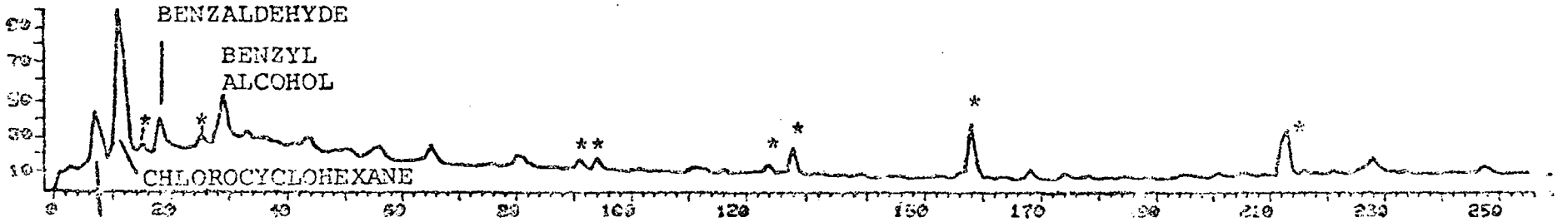

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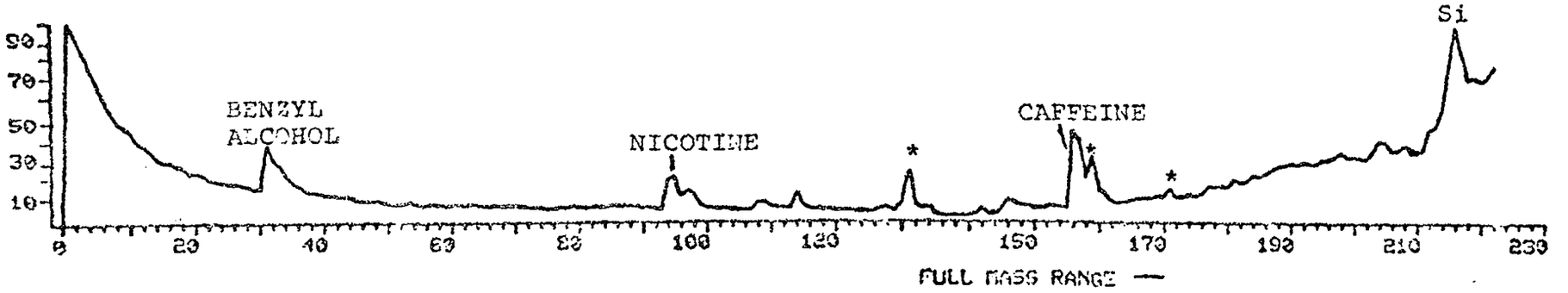

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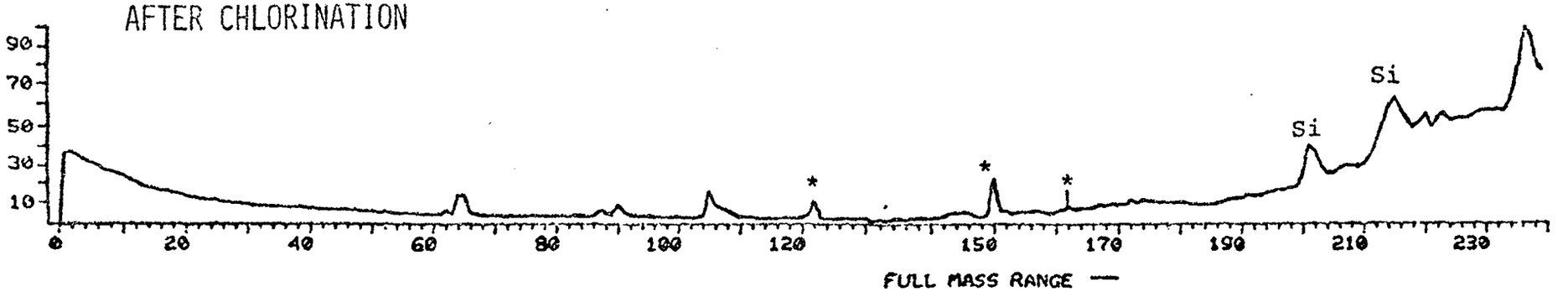
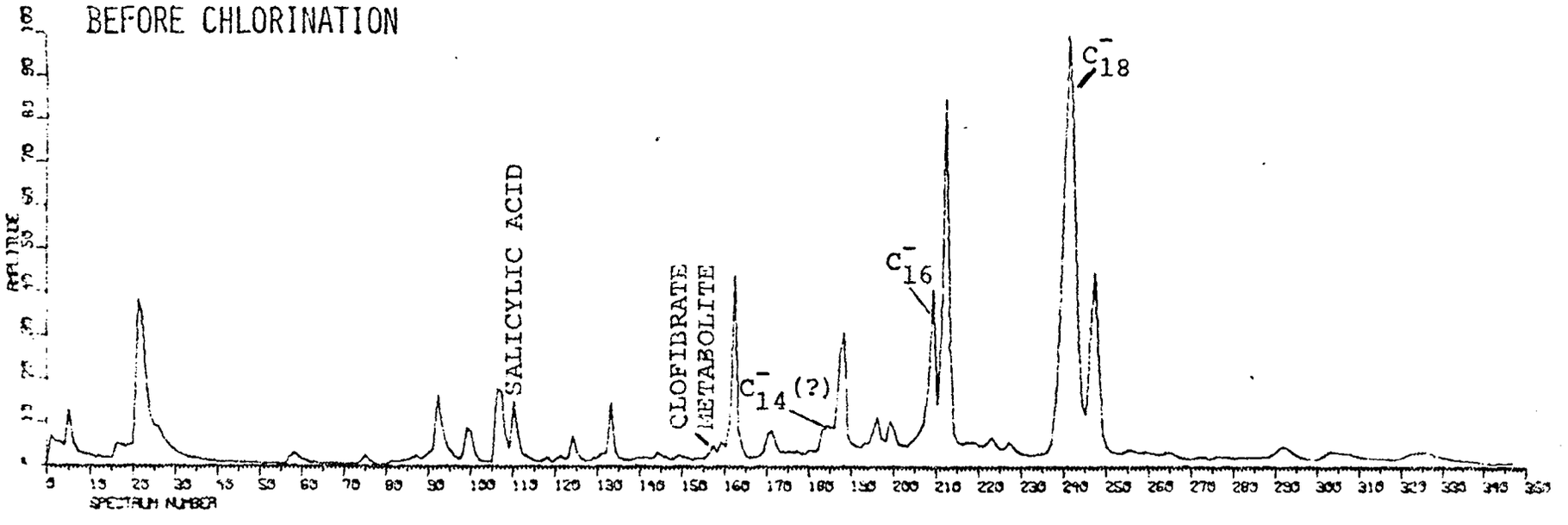
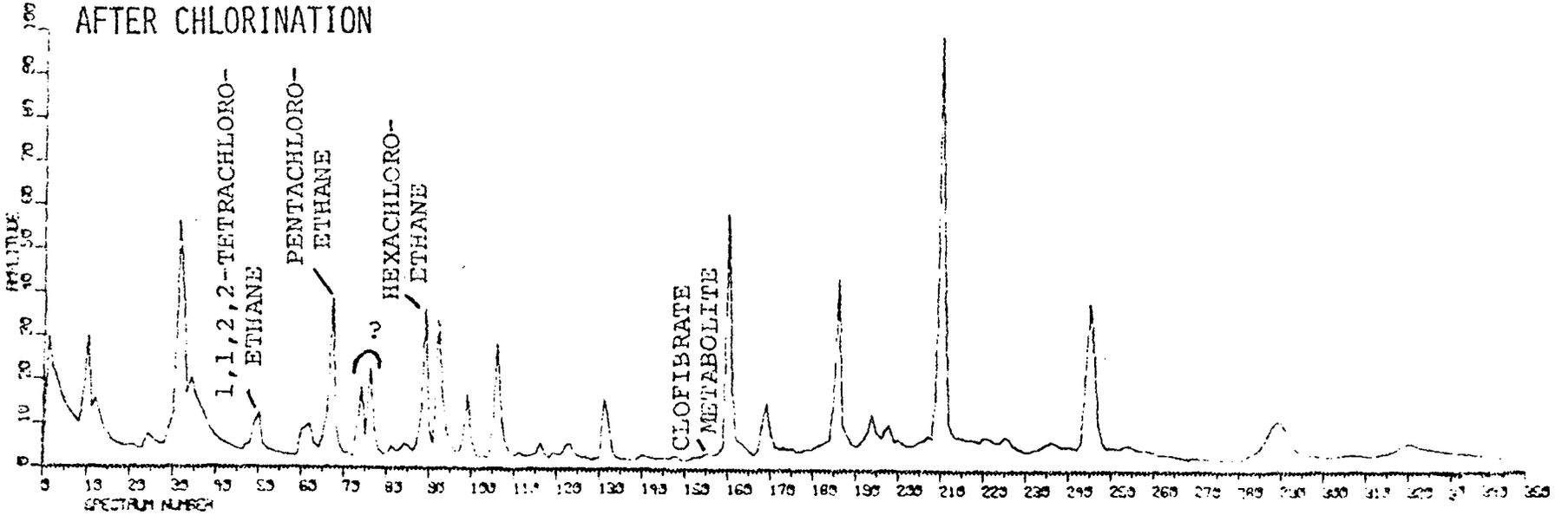
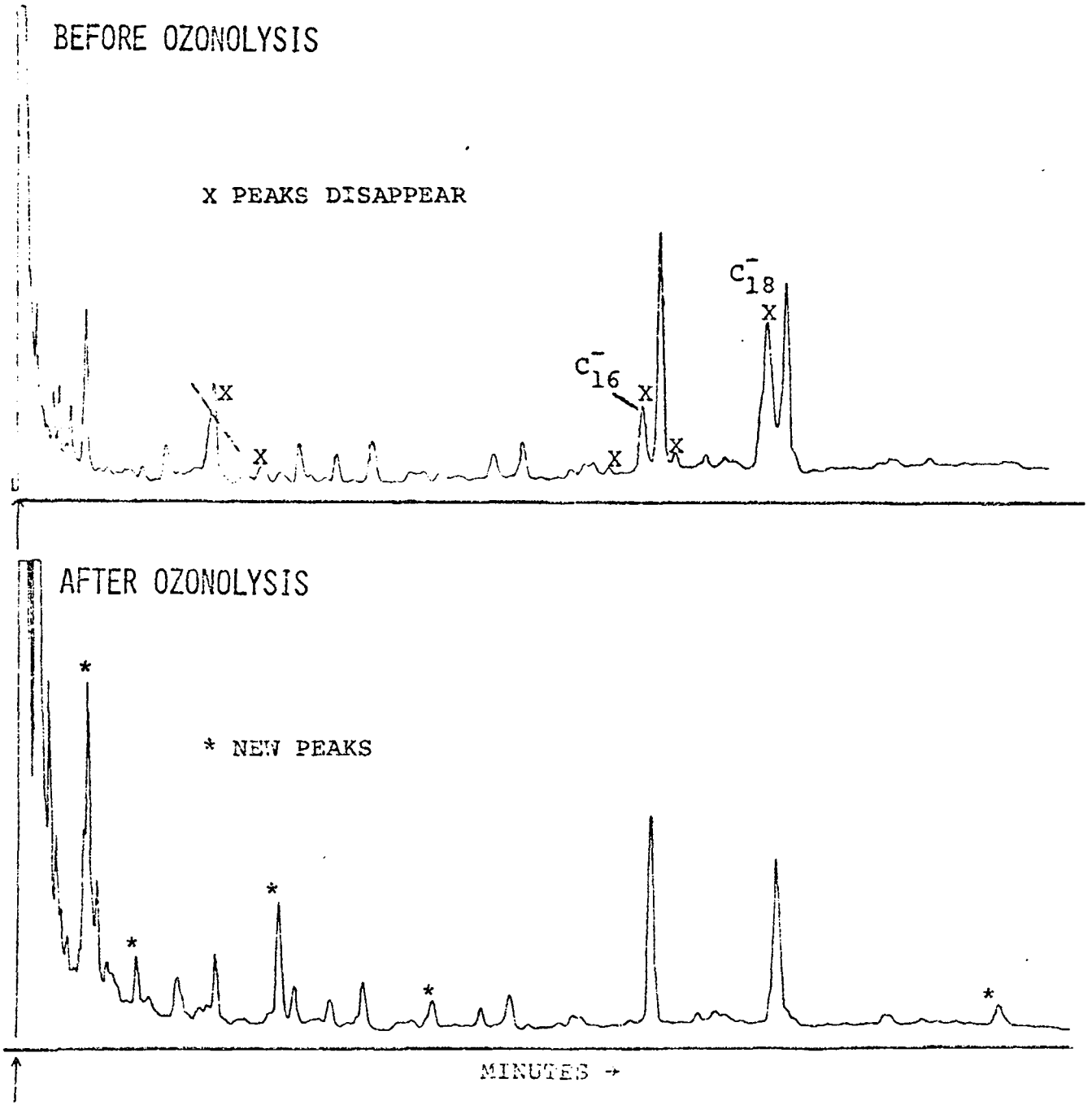



BEFORE CHLORINATION
SALICYLIC ACID
CLOFIBRATE METABOLITE
C 14 (?)
C 16
C 18
SPECTRUM NUMBER


AFTER CHLORINATION
1,1,2,2-TETRACHLORO-ETHANE
PENTACHLORO-ETHANE
?
HEXACHLORO-ETHANE
CLOFIBRATE METABOLITE
SPECTRUM NUMBER


BEFORE OZONOLYSIS
X PEAKS DISAPPEAR
C_{16}^-
C_{18}^-
AFTER OZONOLYSIS
* NEW PEAKS
MINUTES →

IDENTIFICATION OF THE CAUSE OF ODOUR NUISANCE IN THE NEIGHBOURHOOD OF AN INDUSTRIAL WASTE WATER SITE

Drs. C. Morra,
Drs. F. de Grunt,
Ing. A. de Boer,
Mr. G. Piet.

ABSTRACT

The odour nuisance caused by an effluent composed of several industral effluents and domestic sewage was examined to indicate (a) particular responsible polluter(s).
The effluent was examined by gaschromatography-mass spectrometry and the results were compared with organoleptic observations. Instrumental analysis as well as sensory evalution indicated both the responsible polluter, by which is demonstrated that sensory evaluation can be used as an usefull analytical tool.

1. INTRODUCTION:

The odour nuisance of a particular effluent could be caused by three suspected polluters, factory X and Y and domestic sewage from a city. The combined waste water is discharged into open surface water, at location Z, where a rapid dilution can take place. Factory X released about 100 times more waste water than factory Y.
When the effluent discharge started the population started complaining about odour nuisance. The type of smell was described as sewery-like, but more times complaints indicated an "industrial" odour. Recreation on the open surface water became restricted because of the odour nuisance.

An investigation was started in 1974 and the combined waste water at the location 2 was analyzed with G.C.-M.S. The polluter Y probably caused the odour at that time. The polluter Y changed its effluent treatment system but the local population kept complaining about odour nuisance, the character of the odour seemed to be somewhat different however.
In the summer of 1975 an orientation was made using sensory evaluation and instrumental analysis. Both methods indicated polluter X as the responsible one at this moment, A final investigation to establish the responsible polluter with ample evidence was started at the end of 1975.
At the time sufficient data were available about the type of components released by the individual polluters, while the waste water system was better known too. It should be kept in mind that chemical reactions of individual componentsoriginating from different sources could give chemical reactionsleading to the formation of odourous products.

2. DESCRIPTION OF THE INVESTIGATIONS

Samples were collected from the factories X and Y, from the domestic sewage outlet and from the effluent at Z.
The odour intensity and the odour character of the individual samples were compared with each other. The odour intensity is expressed as the number of equal volumes of pure water which are needed to dilute the original samples untill these are without odour for 50% of a panel of 10-15 odour judges. The results are presented in the following table.

Table 1.: Odour numbers of 4 effluent samples

Sample	Date	Odour number
Z	nov. 5	75.000
	nov. 7	50.000
	nov. 21	50.000
X	nov. 17	50.000
	nov. 20	50.000
Y	nov. 17	75.000
	nov. 20	75.000

The domestic sewage had a different odour character and the odour of the sample decreased rapidly because of very volatile components contributing to the odour.

As the volumetric contribution of X is much higher than Z (see figure 1), X probably had a major contribution of the odour nuisance according to these organoleptic determinations but further evidence had to be established. To this end the characters of the individual odours were compared and a scaling method was used by the odour panel. After this the samples were compared by using a gas-chromatograph with an odour outlet for the seperated components eluting from the gaschromatographic capillary column. The odour character of the individual components was described by two independent observers.
When this was established the samples were analysed by a G.C.-M.S. computer system, the components were identified and quantified and the contribution of the individual components was determined by using odour treshold concentration numbers (T.O.C.'s) known from literature. When the T.O.C.'s were doubtfull the panel varified the T.O.C.'s of the main suspected components by determining these again.

In this way a final report could be made indicating the responsible polluter.

3. RESULTS OF THE ORGANOLEPTIC RESEARCH

The evaluation of the character of the sample odour was made by comparing the effluent samples with each other and by comparing each sample with calibration substances.
A list of the calibration substances with their individual odour character and the results obtained with the scaling method is presented in table. 2.
The calibration substances were chosen in accordance with the odour of the samples.
0 = no resemblance
10 = full resemblance.

Some conlcusions can be drawn already
- There is an evident odour resemblance between X and Z.
- There is no evident odour resemblance between Y and Z.
- Ethyldisulfide is X more elevated at Z which suggests a certain contribution of domestic sewage, the odour disappears rappidly however, after 5-10 minutes the Z sample scores lower for ethyldisulfide while 6 and 7 become more elevated.

When the samples were compared with each other the following figures of resemblance were obtained, see table 3.

Table 3.: Scaling method to evaluate the resemblance of the odour character of the samples X, Y, Z compared with each other

	X	Y	Z
Z	6.5	2	9.5

0 = no resemblance
10 = full resemblance

The figures represent the averages of several samples determined in duplo by a panel of 10-15 observers.
It is clear that an evident resemblance exists between X and Z and that X is the main contributor to the odour of Z.

From the sensory evaluation it is demonstrated that the effluent

at Z has a certain contribution of domestic sewage, but the nuisance in the environment comes from an industrial effluent namely X. The domestic effluent's odour character is not really observed at location Z, but the "industrial" odour causes the problems.

4. IDENTIFICATION AND ODOUR EVALUATION OF THE INDIVIDUAL COMPONENTS OF THE SAMPLE

The samples were extracted with a cyclohexane-diethylether mixture (1:1) of 1% (1:100). The extracts were concentrated by means of a gentle pure nitrogen stream and a splitless injection of 1 µl was made on a capillary column. The elute of the column was fed to a flame-conization detector (10%) and the remaining was diluted with nitrogen and fed to an outlet where a odour observer was stationed. (see figure 2). The odour intensive peaks were marked and the odour characterized (see figures 3 and 4). The odour intensive peaks were particularly examined by G.C.-M.S. and a list of peaks of interest was made with a description of the odour character (figure 6, 7 and 8). After this a so called odourogram was set up where the concentration of a particular component was plotted in its ratio to the threshold odour concentration (1 means that the concentration = the odour threshold concentration as determined by a panel where 50% of the members observe the odour and 50% does not observe it). A component in a concentration ratio 1 will be noticed by 50% of a population and contributes to the odour of the samples (figure 9).
It is evident from the odourograms that X is the main contributer to the odour nuisance caused by the effluent at Z. Particularly naphtalene and the substituted naphtalens, besides indene, indanes, ethylbenzene, dimethylstyrene and acenaphtene are causing the odour nuisance at location Z.

5. INSTRUMENTAL ANALYSIS

A capillary column 50 m, OV, i.d. 0,32 mm was used for seperating the substances. A Dupont 492 mass-spectrometer was used for making the fragmentograms (scan time = 1 sec.decade) and a Interdata computer was used for the calculation and storage of the fragmentograms. Strongly polar components were not analyzed and organic sulfur components were not registered with the analytical systems.

The odour character of the substances identified however, were in accordance with the odour character of the samples of location Z causing odour nuisance.

DISCUSSION

Sensory evaluation coupled with advanced instrumental analysis is of great assistance in finding causes of odour nuisance. The human nose, when used in a right way, so that the observations are made in such a way that they are statistically reliable, is still a very valuable instrument in finding polluters. The factory X is evidently responsible for the odour nuisance as is proven by different independent methods and measures have to be taken to avoid this in the future. As oftentimes an expensive investment has to be made by polluters to treat their effluent before releasing these to open surface waters, clear evidence has to be established to demonstrate the source of the pollution. Instrumental analysis combined with sensory evaluation is a mighty tool to perform these difficult tasks.

Table 2.: Scaling method to evaluate the resemblance of the odour character of the samples X, Y and Z

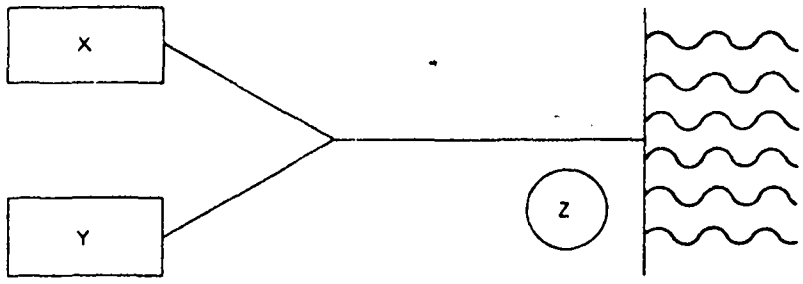
COMPOUNDS	ODOURS
1 IRONPOWDER	METALLIC
2 GUAIACOL	BURNT
3 ISOBORNEOL	EARTHY
4 ETHYLBISULFIDE	SULFIDY
5 PROPANOL	SWEET
6 NAPHTALENE • 1-OCTENE • MESITYLENE • ETHYLBENZENE	SHARP INDUSTRIAL
7 PETROL	PETROLIC
8 YEAST	YEAST

SAMPLE	1	2	3	4	5	6	7	8
X	1	1	2	1	1	9	5,5	0,5
Y	0,5	1	0,5	1	1	5	3	2,5
Z	1,5	1,5	1,5	2,5	1	6	3,5	1

SAMPLES OF X,Y AND Z COMPARED WITH COMPOUNDS WITH KNOWN ODOURS

FIGURE 1.

FLOW - SHEET

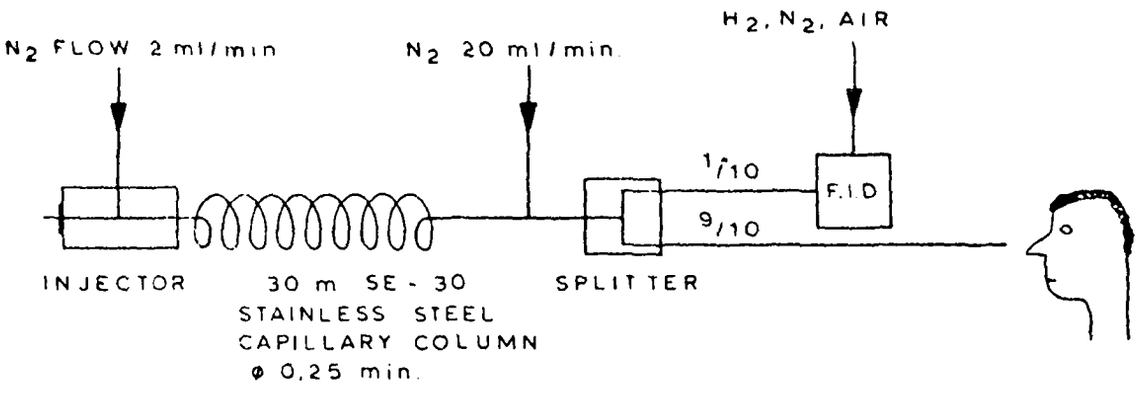


X, Y } WASTE WATER OF TWO FACTORY'S

Z TOWN NEAR THE OPEN SURFACE WATER

X : ± 250 m^3/h DRAINING
Y : ± 3 " "

FIGURE 2.



GASCHROMATOGRAPH FOR ODOUR - DETECTION AND ODOROGRAMS

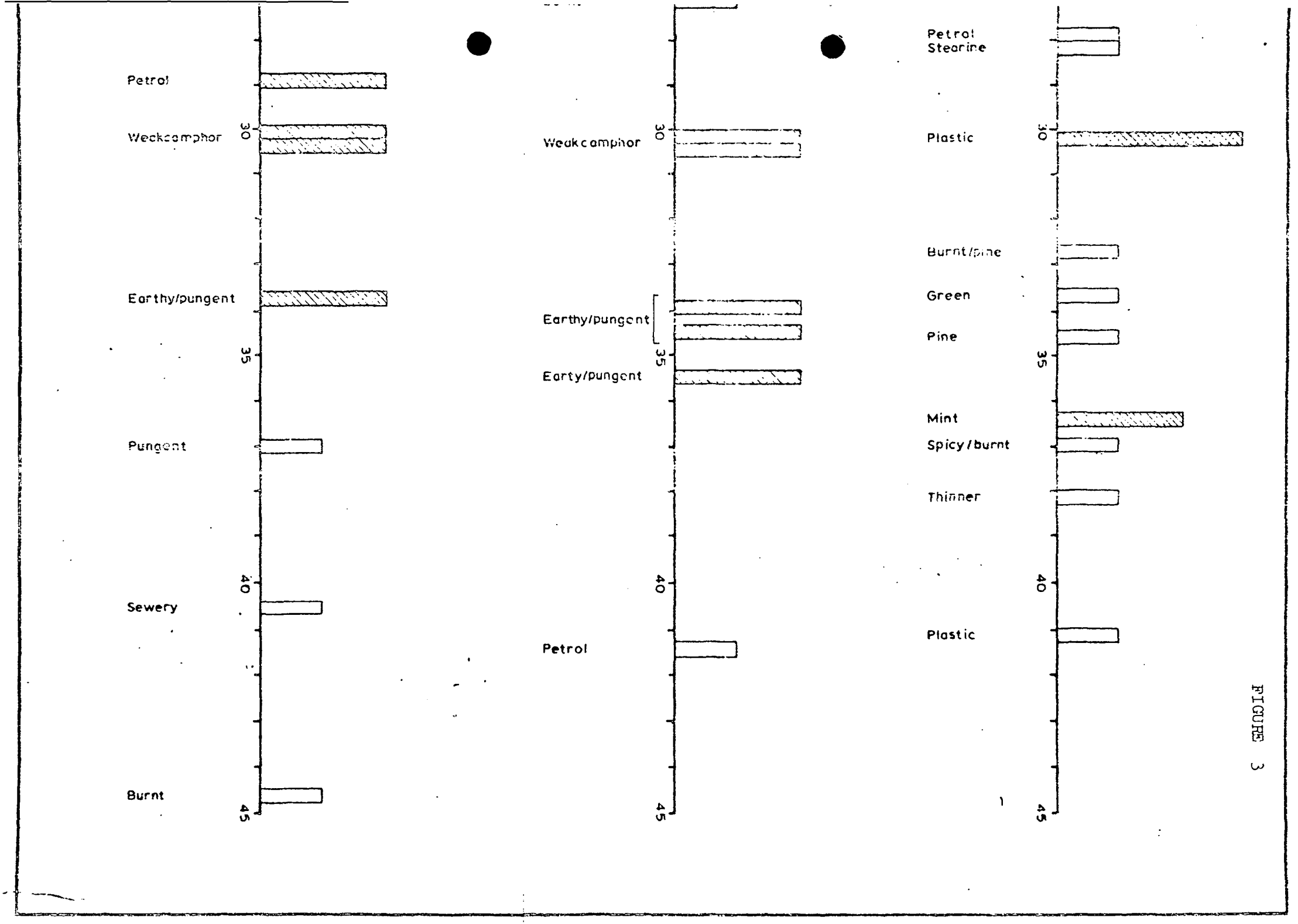
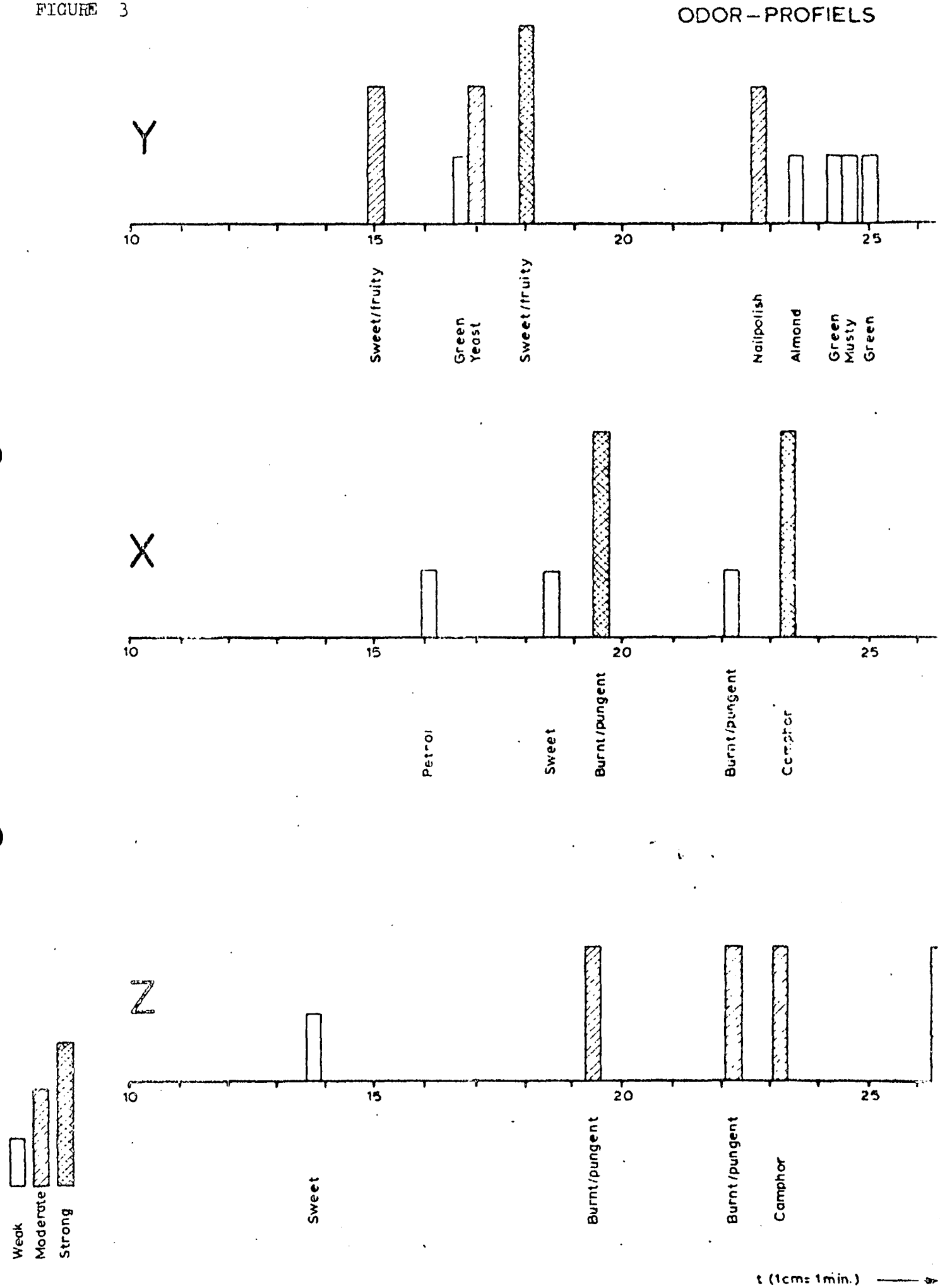

Petrol
Weakcamphor
Earthy/pungent
Pungent
Sewery
Burnt
30
35
40
45
Weakcamphor
Earthy/pungent
Earty/pungent
Petrol
Petrol Stearine
Plastic
Burnt/pine
Green
Pine
Mint
Spicy/burnt
Thinner
Plastic

FIGURE 3

FIGURE 3


ODOR-PROFILES
Y
10
15
20
25
Sweet/fruity
Green Yeast
Sweet/fruity
Nailpolish
Almond
Green Musty
Green
X
10
15
20
25
Petrol
Sweet
Burnt/pungent
Burnt/pungent
Camphor
Z
10
15
20
25
Sweet
Burnt/pungent
Burnt/pungent
Camphor
Weak
Moderate
Strong
t (1cm= 1min.)

ODOROGRAM OF TOWN Z

FIGURE 4.

FIGURE 5

ODOURDESCRIPTION	COMPONENTS IN		
	X	Y	Z
PLEASANT, SWEET		N - BUTYLACETATE	
PETROLIC		ETHYLBENZENE	
ETHEREAL	STYRENE	STYRENE	
BURNING, UNPLEASANT	INDENE		INDENE
BURNING, UNPLEASANT	METHYLINDENE		METHYLINDENE
CAMPHORIC, UNPLEASANT		BORNEOL	
CAMPHORIC	NAPHTALENE		NAPHTALENE
CAMPHORIC	METHYL NAPHTALENE		METHYL NAPHTALENE
CAMPHORIC (WEAK)	DIMETHYL NAPHTALENE		DIMETHYL NAPHTALENE
RESINOUS		CADINENE	
EARTHY, PRICKLED	TRIMETHYL NAPHTALENE		TRIMETHYL NAPHTALENE
PLEASANT, SWEET		UNKNOWN	

ODOUR - DESCRIPTION OF COMPOUNDS FOUND WITH G.C. IN SAMPLES X,Y AND Z

FIGURE 6

CHROMATOGRAMS OF Z

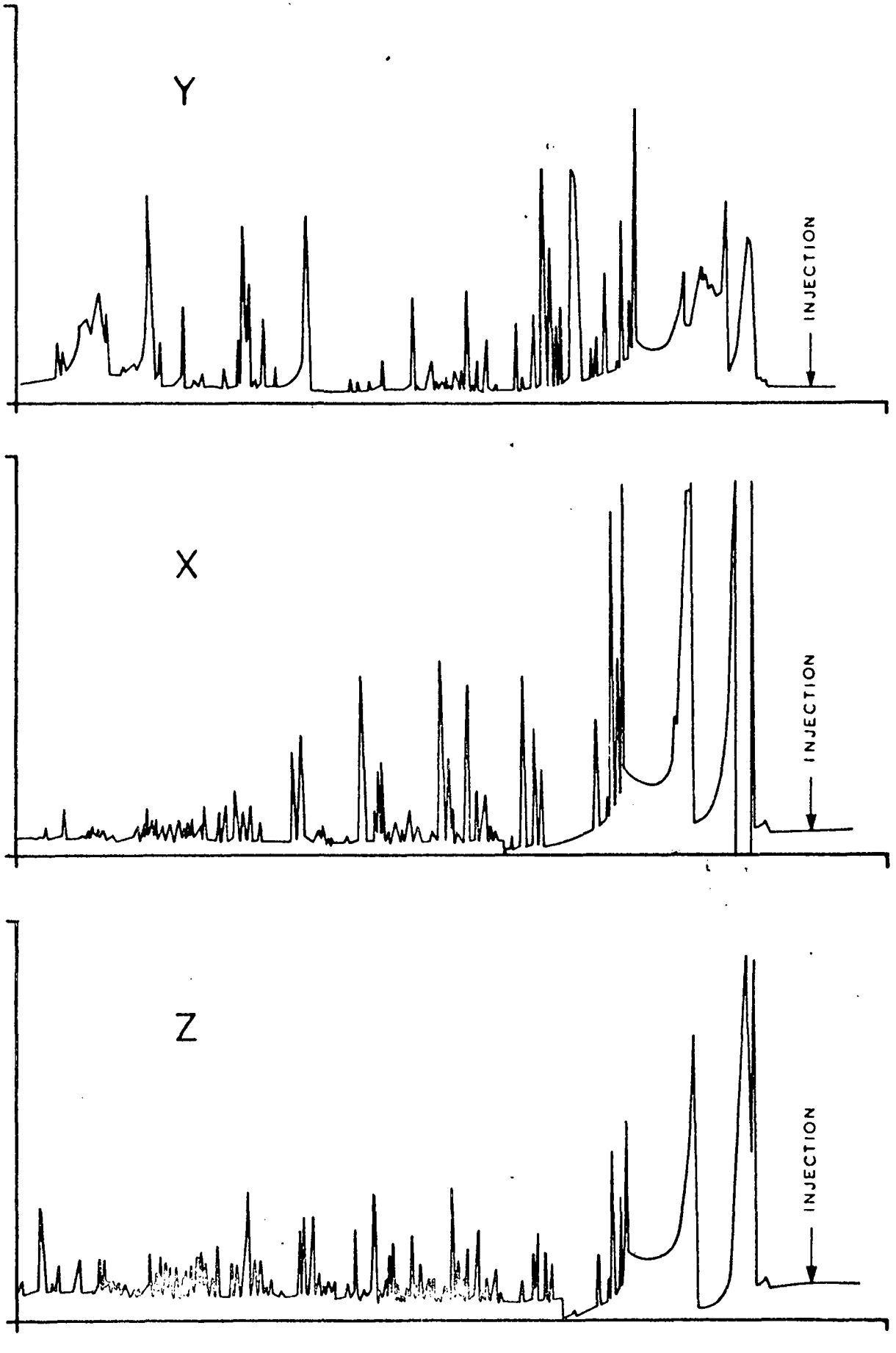


FIGURE 7.

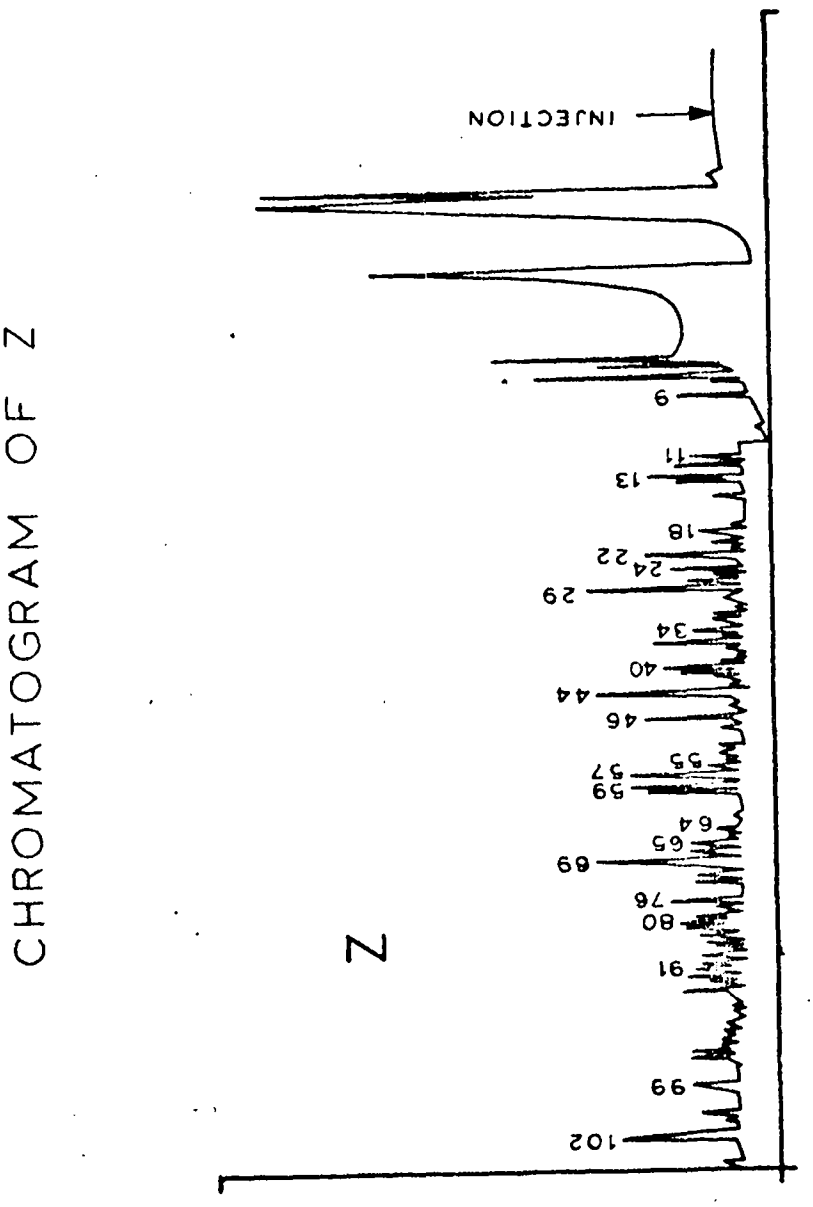
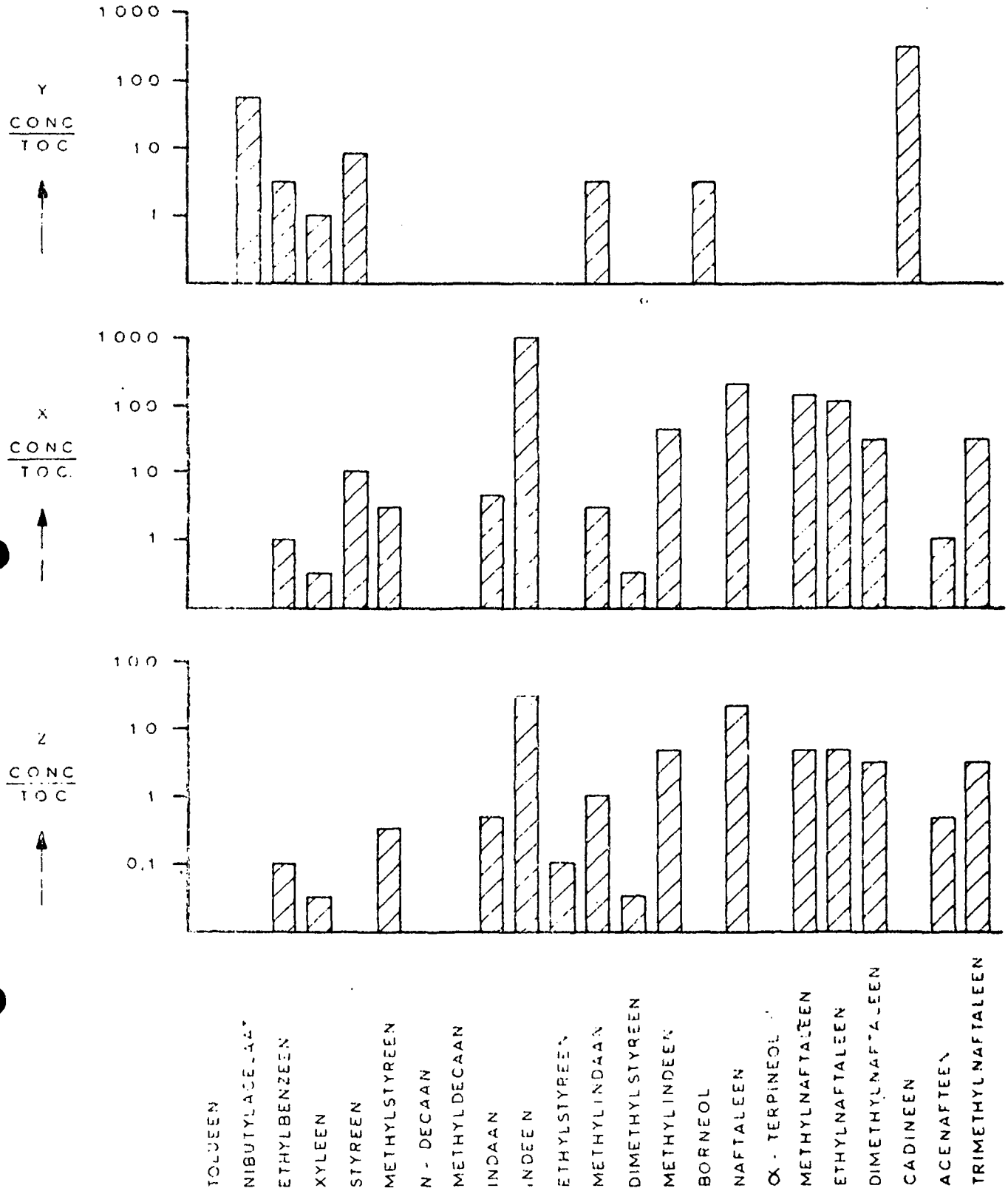

CHROMATOGRAM OF Z
Z
INJECTION
9
11
13
18
22
24
29
34
40
44
46
55
57
59
64
65
69
76
80
91
99
102

FIGURE 8

COMPONENTS OF Z

SC.NR.	NAME	SC. NR.	NAME
9	TOLUENE	46	DODECANE
11	ETHYLBENZENE	55	ANETHOL
12, 14	XYLENE - ISOMERS	57, 59	METHYLNAFTALENE - ISOMERS
17	N - PROPYL - BENZENE	61	TRIDECANE
18	1 - METHYL, 2 - ETHYLBENZENE	64	BIFENYL
20, 25	TRIMETHYLBENZENE - ISOMERS	65	ETHYLNAFTALEEN
22	METHYLSTYRENE	67, 70, 73, 75	DIMETHYLNAFTALENE - ISOMERS
24	N - DECANE	69	TETRADECANE
26	DICYCLOPENTADIENE	76	ACENAPHTENE
28	INDANE	80	1,5 DI(T)BUTYL, 2 - HYDROXY, 4 - METHYLBENZEN
29	INDENE	82	PENTADECANE
31, 32	DIMETHYLETHYLBENZENE	84 TO 89	TRIMETHYLNAFTALENE
33	ETHYLSTYRENE	90	FLUORENE
34, 39	METHYLINDANE - ISOMERS	91	DI - P - TOLYL
36	PENTYLBENZENE	99	ANTRACENE OR FENANTRENE
38	DIMETHYLSTYRENE	102	PHTALATE
40, 41	METHYLINDENE	105, 106	METHYLFENANTRENE
44	NAFTALENE	108	ELCOSANE

FIGURE 9



ODOUR NUISANCE PROFILES OF COMPONENTS IN SAMPLES X, Y AND Z.

DISCUSSION OF LECTURES OF GARRISON AND MORRA

Question Giger:
Did you find chlorinated aromatic hydrocarbons after sewage chlorination?
Answer Garrison:
No, we did not look especially for them - in this one- time experiment we should have seen them if they were present.

Question Piet:
Aldehydes could influence the odour, are there other aldehydes besides benzaldehyde indentified after chlorination?
Answer Garrison:
No.

Question Fielding:
As caffeine had gone after chlorination, is a chlorinated substance produced?
Answer Garrison:
8 chloro caffeine

Question Jeltes:
Is the source of the aromatic hydro carbons which cause odour nuisance known?
Answer Morra:
Yes, we can not mention it.
Comment Giger:
Alkylated benzenes and naphtalenes are found in the water soluable part of Diesel fuel.

Question Waggoth:
What working procedures did you use to recover quite volatile substances like acetone, tetrahydrofuran and tetra chlorethylene?
Answer Garrison:
They were present in pretty high concentrations and were not tatally lost by the destillationprocess. We did not quantify them.

ORGANIC MICRO POLLUTANTS IN THE RIVERS RHINE AND MEUSE

drs. W. van de Meent

Text of the lecture held at the Colloquium Analysis of Organic Micro pollutants in Water on 18th February 1976 at the National Institute for Drinkingwater supply

KEURINGSINSTITUUT VOOR WATERLEIDINGARTIKELEN KIWA N.V.

Organic Micro Pollutants in the River Rhine and Meuse.

Ever since 1973 the rivers Rhine and Meuse have been regularly tested by KIWA for the presence of organic micropollutants. This investigation (KIWA/RIWA project) is carried out in co-operation with those water companies forming the Rhine Committee of Watercompanies in the Netherlands having the aim of gathering information about the nature and appearance of organic compounds in surface water used for the public water supply.
During 1975 the investigations were continued at which much attention was paid to the identification of organic compounds and the quantification of certain interesting components. With the help of the following classification a view will be given of a part of the results obtained from the investigations carried out during 1975.

Sample Programme
Analytical Methods
View of identified Compounds
Organic Chlorine Compounds
Polynuclear Aromatic Hydrocarbons

Sample Programme.

Both the Rhine and the Meuse are important rivers in relation to the public water supply. In 1975 samples of 20 l were weekly taken from the Waal at Brakel and from the Meuse at Berg and at Heusden.
Fig. 1 shows the sampling spots. Thereupon the samples were transported to the KIWA/RIWA laboratory* at Bergambacht and put into work.
The mass-spectrometrical identification of the individual components was carried out in the KIWA laboratory at Rijswijk.

Analytical Methods.

The analytical procedure is schematically shown in fig. 2 and proceeds as follows:
The 20 l sample is exhaustively extracted with 2 l petroleum ether (PE) for 16 hours with the help of the so-called KIWA extractor.
This extraction procedure guarantees an almost complete recovery at a great variety of compounds, like these occur in polluted surface water.

*) KIWA is granted the hospitability of this laboratory by the Dune Water works of The Hague.

The petroleum ether extract is concentrated to 250 ml by means of evaporation 25 ml of this is reserved for the determination of the EOCl content (the fraction of the organic chlorine compound extractable from water by petroleum ether) faulty called TOCl (Total Organic Chlorine content).

This analysis is carried out by burning the sample in an oxygen furnace and by determining the chloride developed at that microcoulometrically.
The other part of the petroleum ether extract is washed with diluted hydrochloric acid in order to isolate the basic organic compounds.
The diluted hydrochloric acid is then extracted with diethylether (DEE) after which a gaschromatographic (GC) and/or gaschromatographic-mass-spectrometric (GS-MS) determinations of the aromatic bases follow.
The petroleum ether washed with diluted hydrochloric acid is concentrated to 5 ml by means of evaporation and column-chromatographically separated by means of a silicagel column in an aliphatic fraction, an aromatic fraction and a fraction containing polar organic compounds (oxys) such as alcohols, esters etc.
Except for the aliphatic fraction (oil) the occurring compounds are determined gaschromatographically and/or gaschromatographically-mass-spectrometrically.
According to the procedure described there is a possibility to isolate a large number of compounds from water and afterwards to separate them mutually, to identify them as well as to determine their quality.

Organic Micropollutants.

Tables I, II and III sum up all organic compounds found in the rivers Rhine (Waal) and Meuse and which were determined mass-spectrometricly during the period of 1972 to 1975 inclusive.
The compounds with a dotted line have only been indicated in the Meuse.
It will strike the attentive reader that the table includes compounds which do not belong under the heading of this table. (hexachlorocyclo hexane, limonene). The indications "Aromatics", "Aromatic Bases" and "Oxys" apply to most of the compounds occurring in the fraction in question. The fact that a matter might land in the "wrong" fraction can be explained by its physical chemical properties. The tables suffice with the name of the compound without mentioning which isomers were indicated.

One or more isomers have been found in the majority of the eligible compounds. This context will not go into this with the exeption of dichlorotoluene. Dichlorotoluene is present in both the aromat the oxy-fraction. In the aromatic-fraction the dichlorotoluene from 2 to 5 occurs whereas in the oxy-fraction this is the α, α-dichlorotoluene. The occurrence of phtalates in the base and oxy-fraction can be explained by an incomplete extraction when washing the petroleum-ether with diluted hydrochloric acid. The occurrence of a number of compounds (nitrotoluene, nitrobenzene, tetrachlorophenol) in the aromatic as well as the oxy-fraction is caused by an incomplete separation on the silicagel column. These compounds form the "transitional phase" between the aromatic and the more polar oxy-fraction.

Organic Chlorine Compounds.

During 1975 the analysis of organic chlorine compounds was appraoched from two sides, namely by means of the determination of the total organic chlorine content of the petroleum ether extract (see the analysis scheme) and the sum of the chlorine content of individual organic chlorine compounds from the different fractions.
Table IV shows a number of organic chlorine compounds indicated in Waal water. The contribution of the individual components to the total organic chlorine content calculated from the concentrations has been tabulated as well as the microcoulometrically determined EOCl content. These results have been plotted in fig. 3 and shows that the EOCl content of the Waal generally fluctuated from 10 to 20 µg/l.
The sum of the chlorine content of the components in the table fluctuated from 2 to 5 µg/l with the exception of the first quarter of that year. The results of the Meuse are shown in table V and fig. 4. The organic chlorine contents of the Meuse are generally between 5 and 15 µg/l. The sum of the chlorine contents of the individual components is smaller than 1 and has not been plotted in the figure.

When comparing the results of the Waal with the ones of the Meuse it is striking that the occurrence of organic chlorine compounds differs in both a qualitative and a quantitative respect. The contents of the Meuse are lower, yet in some cases remarkable values are found.
From the analytical point of view, the results show us that we are

not yet able to determine all individual parameters. Our research efforts will have to be directed to filling this lack of knowledge.

Polynuclear Aromatic Hydrocarbons.

The second group of organic compounds to be considered is formed by the polynuclear aromatic hydrocarbons in so far as thay can be determined by means of the applied gaschromatographical method. The concentrations of phenanthrene, fluoranthene and pyrene found in the Waal and Meuse in 1975 are given in tables VI and VII. The sum of these contents has been plotted in figures 5 and 6. These figures include the A1, A2 and A3 levels of the "Counsil Directive (June 1975)" concerning the required quality of surface water which is used for the preparation of drinking water in member States of the European Community. According to this directive the concentration of polynuclear aromatic hydrocarbons in the Waal is too high for drinking water purposes. The more so as in the calculation described only three polynuclear aromatic hydrocarbons are involved.

FIG. 1

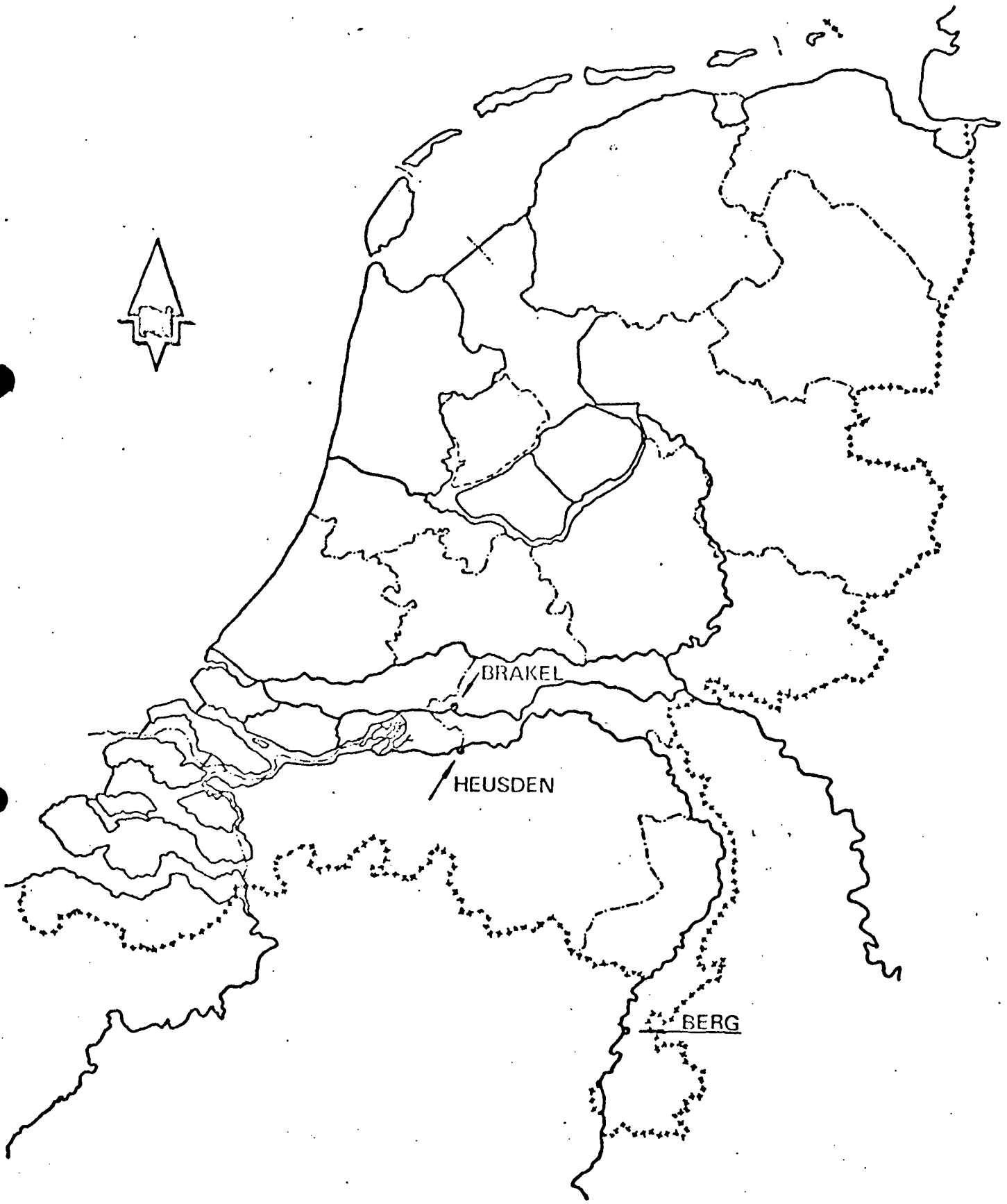


FIG. 2 Scheme of the Analysis.

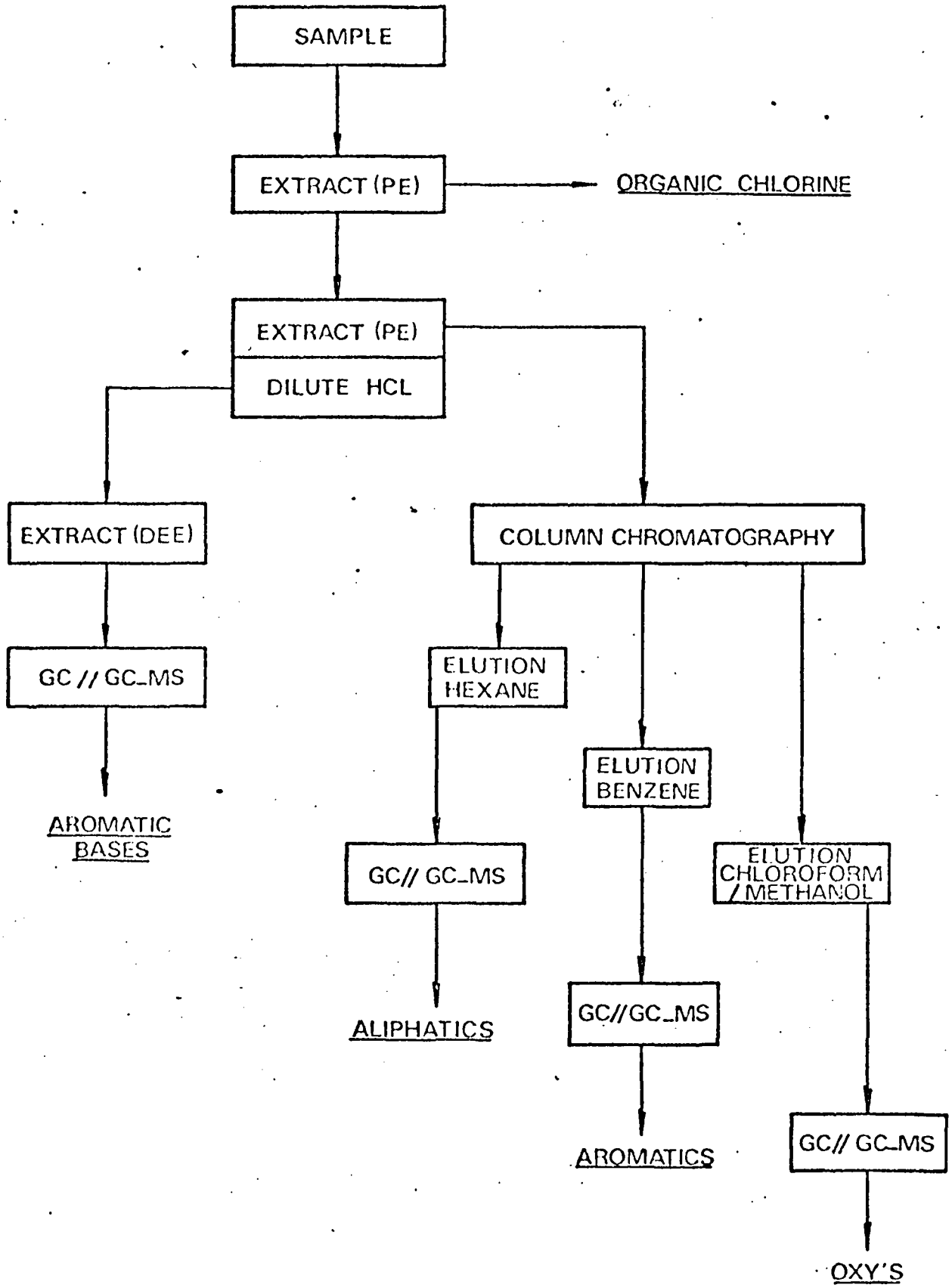


TABLE I

Identified compounds, AROMATIC FRACTION, Waal and Meuse*)
from 1972 to 1975 inclusive.

Alk(en)ylbenzenes.

ethylbenzene
propylbenzene
isopropylbenzene
C_4- benzene
C_5- benzene
C_6- benzene
C_7- benzene
dimethylbenzene
trimethylbenzene
diethylbenzene
diisopropylbenzene
styrene
ethyltoluene

Chlorobenzenes.

chlorobenzene
dichlorobenzene
trichlorobenzene
tetrachlorobenzene
chlorotoluene
dichlorotoluene
trichlorotoluene

Nitrobenzenes.

nitrobenzene
nitrotoluene
nitrobenztrifluoride
nitroxylene

Chloronitrobenzenes.

chloronitrobenzene
dichloronitrobenzene
chloronitrotoluene

Phenols.

diter. butylcresol
trichlorocresol
tetrachlorocresol
tetrachlorophenol
phenylphenol

Biphenyls.

biphenyl
ditolyl
dichlorobiphenyl
trichlorobiphenyl
tetrachlorobiphenyl

Di- and polynuclear aromatic hydrocarbons

naphtalene
methylnaphtalene
dimethylnaphtalene
trimethylnaphtalene
nitronaphtalene
acenaphtalene
methylacenaphtalene
fluorene

*) The underlines (- - - -) compounds are found in the river Waal only.

hydroxyfluorene
phenylfluorene
benzfluorene
phenantrene
methylphenantrene
dimethylphenantrene
anthracene
methylanthracene
fluoranthene
pyrene
methylpyrene
benzpyrene
chrysene

Miscellaneous.

acetophenone
dichlorophenylketon

phenylether
tolylether
dibenzofuran
methyldibenzofuran
dimethyldibenzofuran
diphenylamine
azobenzene
aminoethylcarbazole
phenyl-β-naphtylamine
benzthiophene
hexachlorocyclohexane
tetrachloro-di-isopropylether
tetrachloro-n-propylether
limonene
methylindan
terphenyl

Tble II

Identified Compounds, AROMATIC BASES FRACTION,
Waal and Meuse*, from 1972 to 1975 inclusive.

Alkylanalines.

aniline
3-amino benztrifluoride
O-toluidine
ethyltoluidine
3, 4-dimethylaniline
butylaniline
propyltoluidine
diethyltoluidine
dimethylethylaniline
diethyltoluidine
diethylxylidine
ditertbutylaniline
ditertbutyltoluidine

N-Alkylanilines

N, N-dimethylaniline
N-ethylaniline
N-ethyl-4-ethylaniline
N, N-dimethyl-p-toluidine
N-ethyltoluidine
N, N-diethylaniline
N-propylaniline

Quinolines.

Quinoline
isoquinoline
methylquinoline
ethylquinoline
benzquinoline
methylbenzquinoline

Pyridines.

dimethylpyridine
methylethylpyridine
dimethylethylpyridine
trimethylpyridine
diethylpyridine
phenylpyridine
trimethylpyridone

Chloroanilines.

N, N-dimethylchloroaniline
chloroaniline
chlorotoluidine
dichloroaniline
chloromethylaniline
dichlorotoluidine

Nitroanilines.

nitroaniline
nitrotoluidine

Indoles.

trimethylindole
trimethyloxindole
trimethylchloroindole

Anisoles.

anisidine
butylhydroxyanisole
nitroanisole

*) The underlined (- - - - -) compounds are found in the river Waal only.

Other N-compounds.

benzthiazole
octahydrophenazine

Organophosphates.

triethylphosphate
tributylphosphate
tri(chloroethyl)phosphate

Phtalates and adipates.

dimethylphtalate
diisobutylphtalate
dibutylphtalate
dioctylphtalate
dinonylphtalate
dioctyladipate

Miscellaneous.

ditert. butylhydroxybenzoic acid
phtalonitrile
phenylpropylether
phenylpropenylether

TABLE III

Identified compounds, Oxyfraction, Waal and Meuse*)
from 1972 to 1975 inclusive.

Alcohols.

hexanols
dimethylbenzylalcohol

Phenols.

chlorocresol
tertbutylcresol

dichlorophenol
trichlorophenol
tetrachlorophenol
pentachlorophenol
nitrophenol
nitrocresol
nitroxylenol
butylphenol
nonylphenol

Alifatics.

hexachloroethane
diethoxyhexane
diethoxydecane

Aromatics.

acetophenon
indanone
trimethyloxindole
anthraquinone
methylthiobenzothiazole
p, p-di(dimethylamino)benzophenone
dichlorotoluene
nitrotoluene
dinitrotoluene
nitrobenzene
chloronitroaniline

nitrobenzene
chloronitroaniline

Ethers.

bischloroisopropylether
tetrachloroisopropylether
dichlorobutylether
dibenzylether

Esters.

tri-isobutylphosphate
tri-n-butylphosphate
tri(2-chloroethyl)phosphate
ethylpalmitate
ethylstearate
hydroxyisooctylisobutyrate
dicyclohexyladipate
diethylphtalate
diisobutylphtalate
di-n-butylphtalate
dioctylphtalate
dinonylphtalate.

Acids.

myristic acid
palmitic acid
stearic acid
lauric

Steroids.

pregnandione
dihydroxypregnandione

(Table III)

Others.

terpenes

isophorone

cyclohexylcyclohexanone

terbutylcyclohexanone

TABLE IV

Organic Chlorine Contents (µg/l) Waal at Brakel 1975

Components	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Chlorotoluene	0.14	0.17	0.31	0.32	0.38	1.56	0.07	0.20	0.08	0.10	0.16	0.16
Dichlorobenzene	1.44	2.08	1.96	0.54	0.31	0.48	0.27	0.44	0.28	0.60	0.91	1.28
Dichlorotoluene	0.08	0.18	0.20	0.13	0.04	0.07	0.04	0.07	0.07	0.09	0.33	0.24
Trichlorobenzene	0.65	2.91	2.33	2.40	0.22	0.22	0.20	0.41	0.15	0.51	0.92	1.10
Chloronitrobenzene	0.25	0.51	0.64	0.28	0.20	0.16	0.04	0.15	0.09	0.26	0.33	0.27
Trichlorotoluene	0.18	0.41	0.26	0.15	0.04	0.09	0.06	0.14	0.08	0.07	0.10	0.20
Chloronitrotoluene	0.11	0.10	0.05	0.01	0.01	-	-	-	-	-	0.01	0.01
Dichloronitrobenzene	0.11	0.08	0.14	0.07	0.01	0.16	0.04	0.07	0.05	0.18	0.17	0.23
-chloroaniline	0.70	1.24	0.44	0.32	0.16	0.01	-	0.06	0.03	0.07	0.10	0.25
Chlorotoluidine	0.12	0.48	0.47	-	-	-	-	-	-	-	-	-
is-(chloroisopropyl)-ether	0.23	0.46	0.47	0.34	0.04	0.25	0.01	0.30	0.38	-	-	-
is-(dichloroisopropyl)-ether	0.31	0.27	0.75	0.21	0.61	0.52	0.16	0.03	0.06	-	-	-
otal	4.3	8.9	8.0	4.8	2.0	3.5	0.9	1.9	1.3	1.9	3.0	3.7
OCl	44	20	41	17	15	19	10	13	16	11	n.d.	n.d.

= not found

.b. = not determined

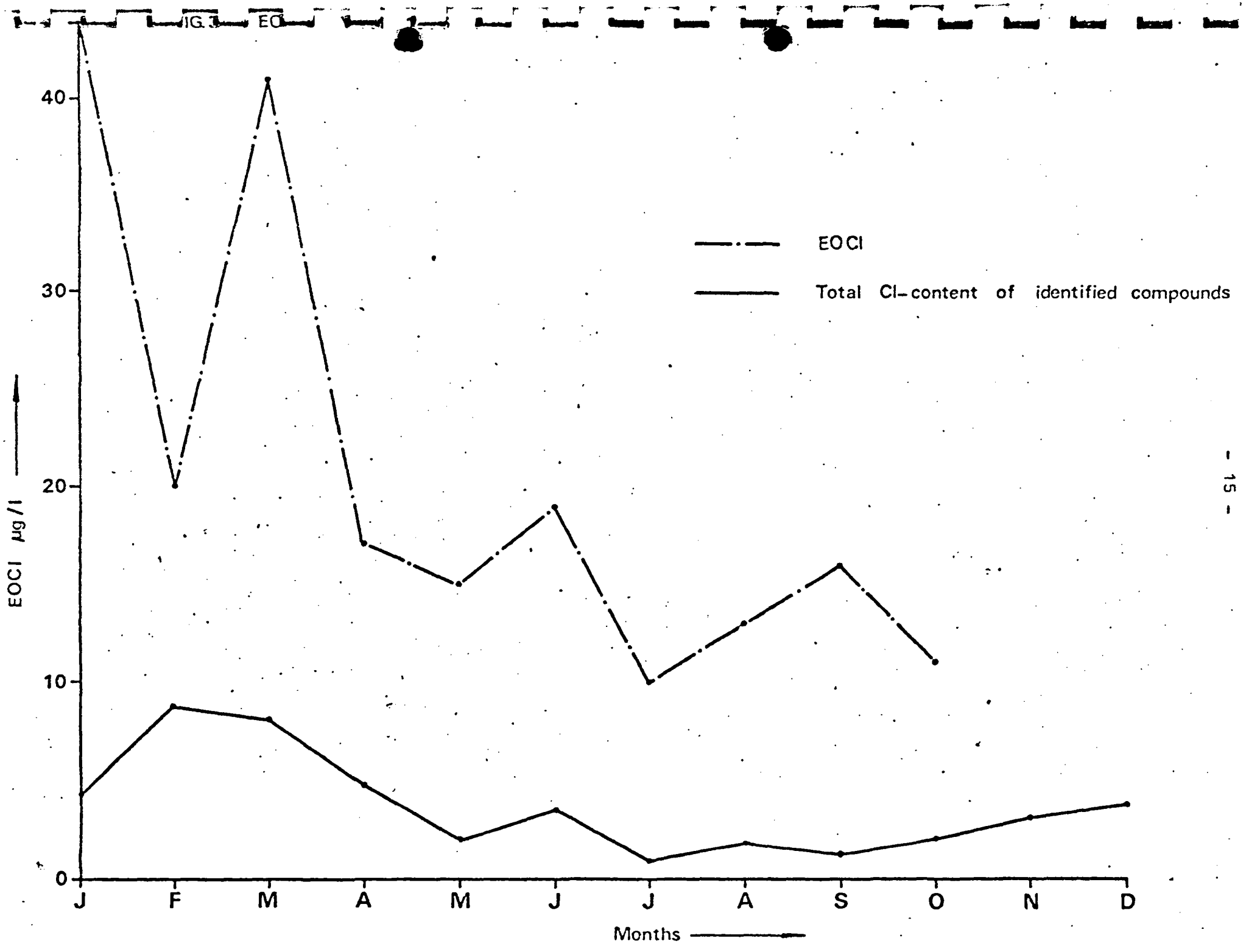

EOCl
Total Cl-content of identified compounds
EOCl µg/l
40
30
20
10
0
J
F
M
A
M
J
J
A
S
O
N
D
Months

TABLE V

Organic Chlorine Contents (µg/l) Meuse, Berg and Heusden 1975

Components	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Chlorotoluene	0.04	0.06	0.08	0.07	0.06	0.06	0.23	0.15	0.05	0.08	0.04	0.04
Dichlorobenzene	0.06	0.12	0.10	0.12	0.02	0.11	0.21	-	0.02	0.03	0.02	-
Dichlorotoluene	0.01	0.01	0.02	0.20	0.02	0.02	0.10	-	-	-	-	-
Trichlorobenzene	-	0.04	-	-	0.12	-	-	-	-	-	-	-
Chloronitrobenzene	-	-	-	0.01	0.04	-	-	-	-	-	-	-
Trichlorotoluene	-	-	-	-	0.02	-	0.09	0.08	0.06	0.04	0.03	0.06
Chloronitrotoluene	0.01	-	0.21	0.01	-	-	-	-	-	-	-	-
Dichloronitrobenzene	-	-	-	0.04	-	-	0.01	0.04	0.02	0.03	0.02	0.06
Total	0.1	0.2	0.4	0.5	0.3	0.2	0.6	0.3	0.2	0.2	0.1	0.2
EOCl	20	7	22	14	7	7	7	3	11	1.5	n.d.	n.d.

- = not found

n.d. = not determined

FIG. 4 EOCl Meuse Berg and Heusden 1975

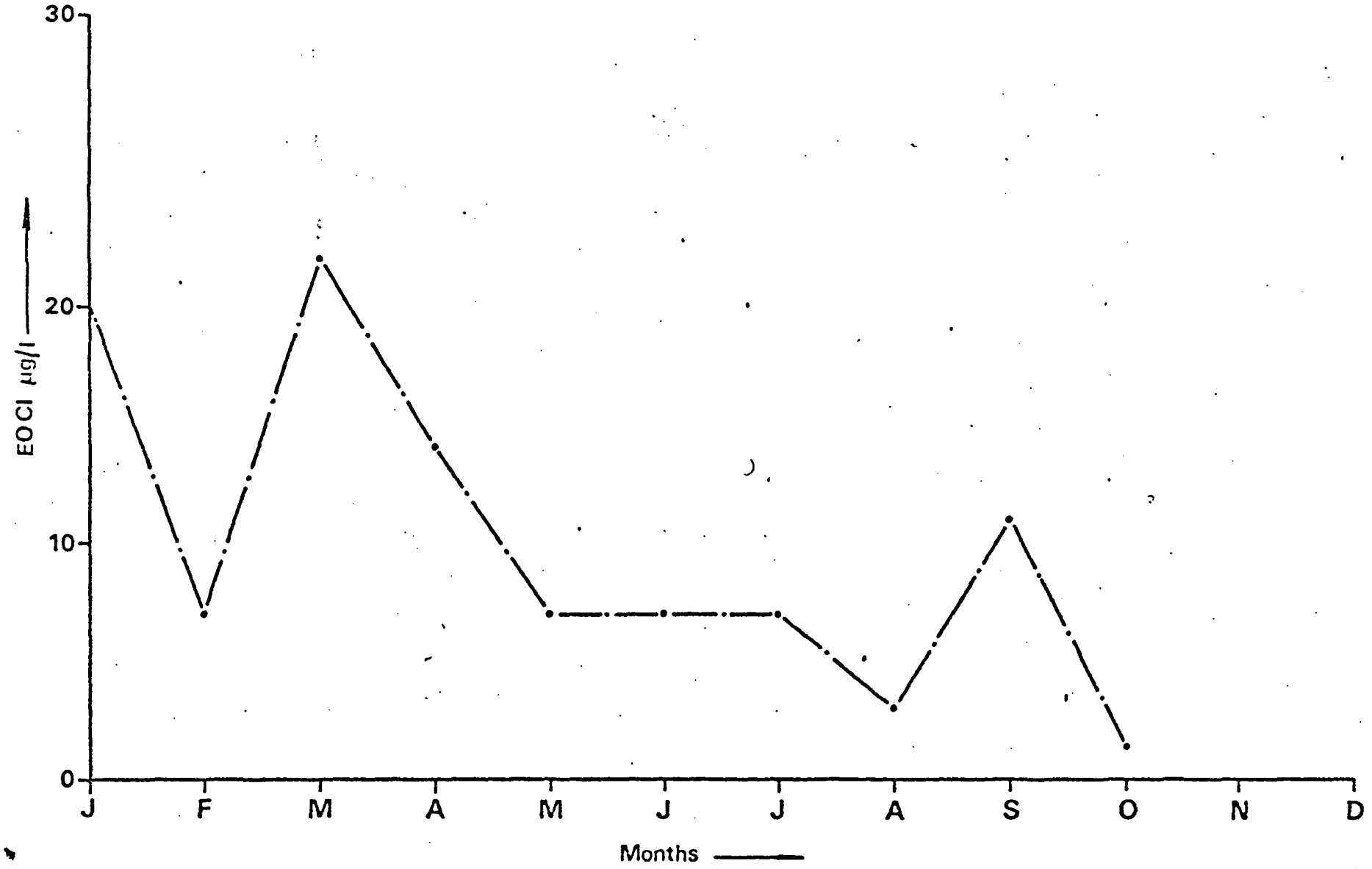


TABLE VI

Polynuclear Aromatic Hydrocarbons (µg/l) Waal at Brakel 1975

Components	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Phenanthrene	0.60	0.10	0.23	0.16	0.07	0.10	0.07	0.10	-	1.30	0.13	0.13
Fluoranthene	0.83	0.20	0.48	0.72	0.13	0.16	0.13	0.20	0.20	1.20	0.25	0.33
Pyrene	0.53	0.20	0.38	0.24	0.10	0.10	0.07	0.18	0.16	0.73	0.23	0.30
Total	1.96	0.50	1.09	1.12	0.30	0.31	0.27	0.48	0.36	3.23	0.61	0.76

TABLE VII

Polynuclear Aromatic Hydrocarbons (ug/l) Meuse, Berg and Heusden 1975

Components	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Phenanthrene	0.15	0.25	0.08	0.34	-	-	0.10	0.08	0.04	0.03	0.03	0.17
Fluoranthene	0.33	0.20	0.30	0.56	0.13	0.10	0.13	0.15	0.12	0.10	0.20	0.43
Pyrene	0.25	0.30	0.20	0.36	0.13	0.14	0.20	0.15	0.10	0.08	0.13	0.33
Total	0.73	0.75	0.58	1.26	0.26	0.24	0.43	0.38	0.26	0.21	0.36	0.93

- = not found

FIG. 5 Polynuclear hydrocarbons Waal, Brakel. 1975

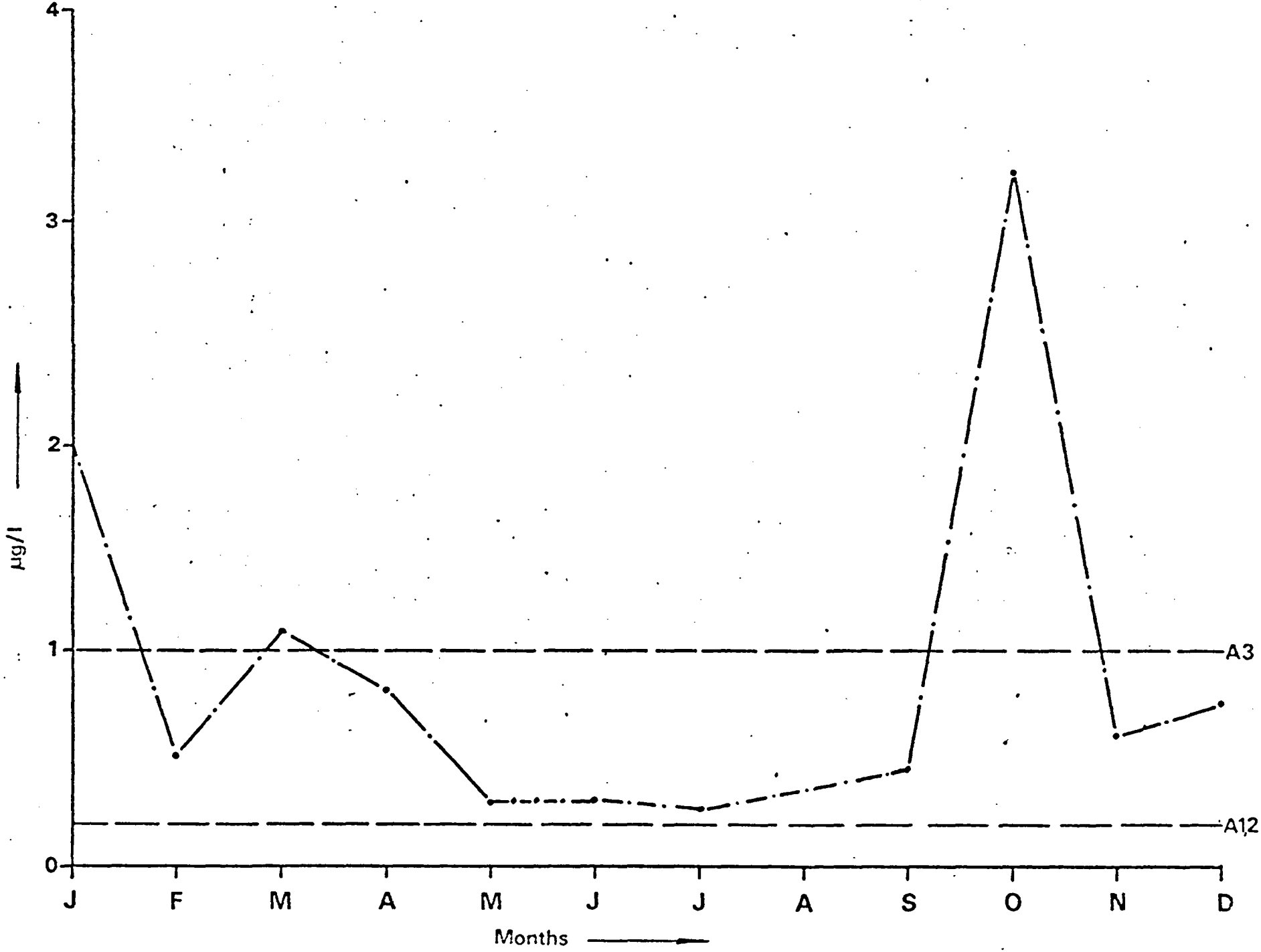
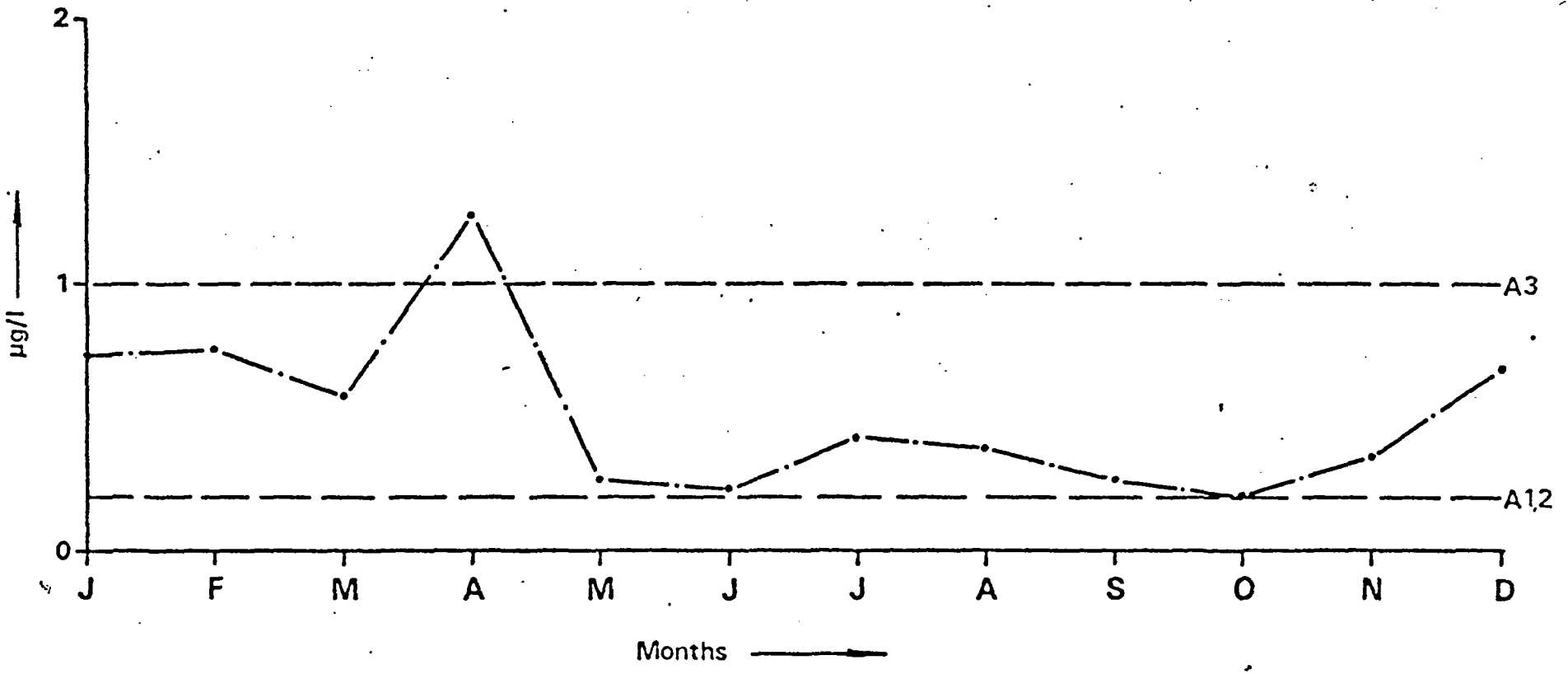


FIG. 6 Polynuclear hydrocabons Meuse, Berg and Heuden. 1975



CONSIDERATIONS ON PRECURSORS AND FORMATION OF HALOFORMS IN WATER

Drs. J.J. Rook,
Rotterdam Water Works, 1976.

In 1966 the analysis of volatile substances in the river Rhine was started in the Rotterdam Water Works Laboratory.
At that time the aim of the research was to locate the origin of bad odour and taste of the water. As the intake was situated at the lowest end of the river Rhine, biodegradable matter was not in the first place expected to impair taste and odour, but rather persistant substances, especially chlorinated solvents, benzene, derivatives and other bad smelling volatile compounds were supposed to be responsible for this adverse effect. Consequently we looked for a method which was specific for volatiles.
The analysis procedure was chosen in analogy with headspace analysis as already known from the brewery industry, but an enlarged bottle was necessary for water, see figure 1.
A 5 liter glass vessel was partly filled with 3.5 liter of water sample which was equilibrated with 2 liter of nitrogen gas.
The head-space gas was passed over a gaschromatographic pre-column, figure 2, cooled with dry ice. Magnesium-perchlorate was used as a drying agent.
The system was calibrated for the recovery of haloforms. Overall recovery was about 10% . For final analysis the pre-column was connected to an analytical column and flash-heated as shown in figure 3.

G.C. was performed on a 7 ft column, 1/4 inch, 10% TCP on Chromosorb P; carrier gas N_2, 40 ml/min; temperature programmed from 20° to $120^{\circ}C$. A typical headspace fingerprint of river Rhine is given in figure 4.
The normal purification treatment consisting of breakpoint chlorination, coagulation, sedimentation and rapid sand filtration did not remove headspace volatiles significantly. Only in the very volatile fraction the peaks of freons, butanes and pentanes diminished by 40%. A puzzling observation was the appearance of four new, large peaks which were clearly produced by chlorination, as shown by comparing the chromatograms of riverwater and chlorinated water in figure 5.

The four new peaks were identified with haloforms. Particularly chloroform was found in concentrations from 0,02 to 0,1 mg/liter. Also traces of tetrachloromethane, trichloroethylene and some aromatic hydrocarbons were detected.

Most of the volatile substances were reduced considerably by adding powdered activated carbon during the purification process.
Test runs with pilot filters of granulated activated carbon indicated that the small molecules of haloforms show a limited adsorption, and particularly chloroform, show break-through already after 4 to 5 days.
Analysis of the chlorine used for chlorination showed that chloroform was not an impurity of the chlorine. This meant that it was formed during the chlorination step. The identification of the other haloforms demonstrated the formation of $CHCl_2$, Br, $CHBr_2Cl$ and $CHBr_3$.

In the period of 1970-1973 the Rotterdam Water Works investigated the role of precursors of the haloforms. In the first approach we thought of the haloformreaction with acetone as precursor. It is wellknown that methyl ketones such as acetone produce haloforms after addition of halogenes.

$$CH_3 - \overset{O}{\overset{\|}{C}} - R + 3\ HOX \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - R + 3\ H_2O$$

followed by:

$$CX_3 - \overset{O}{\overset{\|}{C}} - R + H_2O \longrightarrow CHX_3 + R - \overset{O}{\overset{\|}{C}} - OH$$

The reaction rate is determined by pH. This is evident because the rate-determining step is the formation of an "enol" from the ketone.

$$CH_3 - \overset{O}{\overset{\|}{C}} - R \longrightarrow CH_2 = \overset{O}{\overset{\|}{C}} - R + H^+$$

In laboratory tests however, acetone reacted too slow to account for the concentrations of $CHCl_3$ produced (table 2). So a different precursor had to be found.
As the majority of possible volatile precursors of chloroform are removed in the storage reservoir of the Rotterdam Water Works (storage 3-4 months) before the chemical treatment is applied, the main precursors had to be a less volatile and non biodegradable substance.

By changing the rawwater supply from water of the river Meuse (TOC of about 3.5 mg/liter) which is much less contiminated with industrial micropollutants than the river Rhine, the chloroform formation did not decrease. This again supported the view that the precursor did not originate from industrial wastes.
Various uncontaminated groundwater samples were treated with chlorine to confirm the hypothesis that naturally colored substances were the cause of chloroform and bromoform formation.
Most groundwater samples had only chloroform contamination after chlorination. Bromoform was formed instead when 2-3 mg bromine was added to the water sample.
The bromide concentration of the riverwater (resp. 0,4 mg/l in the Rhine and 0,14 mg/l in the Meuse) decreased during chlorination

Table 1.: Decrease of bromide concentration by chlorination

Type of water	Bromide concentration (mg/l)	
	Before chlorination	After chlorination
Rhine (1972)	390	210
	136	57

The deficit in bromide ions after chlorination (0.18 ppm for river Rhine water and 0,08 ppm for Meuse water) is important. It means that more organic brominated compounds are formed than the volatiles CHX_3. The author suggests that heavier degradation products are formed. By the addition of chlorine, biomide-ions are oxidized to bromine, which than forms HBrO (or a BrO^- ion), which again brominates several organic substances, eg. phenols are easily brominated.
Acetone can be rejected as precursor of chloroform in the water purification because the yield of chloroform appeared to be only 0,1 % of acetone concentration 100 mg/l acetone after 4 hours chlorination at 10^oC as given in table 2.

The attention was now focused on fulvic and humic substances. Generally coloured water samples gave more chloroform production than uncoloured samples. Groundwaters, which were rich in fulvic substances i.e. more coloured, produced more chloroform formation than the less colored samples. When humic substances obtained by infusion of peat wered added to pure water samples, chloroform was formed. After addition of sodium bromide in an equivalent

concentration to surface water, all 4 haloforms were formed namely chloroform, dichlorobromomethane, dibromochloromethaan, and bromoform, figure 6.
Fulvic and humic substances are polycondensates of polyhydroxy-benzene, and other aromatics, as illustrated in figures 7 and 8. Resorcinol i.e. meta-dihydroxy benzene is a well known building block, which gives chloroform by chlorination in high yields, see table 2 and 3.

Conclusively a somewhat analogous mechanism in comparisson with the ketone reaction is suggested for the behaviour of hydroxy-aromatics. In the last case the formation of phenoxide-ions is to be considered to induce chloroform formation by activating the aromatic ring strongly in the ortho-positions.
The carbon atom between the OH groups in the meta-position seems to be readily attacked.

Fulvic- and humic acids still contain some OH groups in the meta-position, which act as active sites for chlorine to produce haloforms. When the humic acid concentration in water is reduced the chloroform formation decreases. Furthermore a competition between chlorination and ozonisation was observed. Ozonisation before chlorination lowered the chloroform production only when the time lag between the two dosing points was shorter than some minutes. This indicates that ozone and chlorine compete for the active sites with different reaction rates.
The original research focussed on the cause of odour and taste problems, has given valuable information about the cause of haloform production. It must be noticed however that chloroform in concentration, $>$ 100 µg/liter certainly contributes to bad odour and taste of drinking water.
To avoid risks in water purification the organic content of the raw water must be as low as possible. The W.H.O. as well as the E.P.A. recommend a T.O.C. of 5 mg/liter and if possible 1 mg/liter should be preferred when indirectly reused waste water is the raw water source for the drinking water supply.

Table 1.

Haloforms from precursors, 100 ppm concentration, 1000 ppm Cl_2, reaction during 4 hr, at 10°C.

	pH 7	pH 11
dimedone	90%	100%
1,3-indandione	6%	45%
1,3-cyclohexanedione	50%	70%
1,3-cyclohexanediol	0.6%	0.6%
1,2-cyclohexanedione	0%	0%
1,4-cyclohexanedione	0.8%	10%
resorcinol (meta)	40%	90%
hydroquinone (para)	1.5%	5%
catechol (ortho)	0.3%	5%
pyrogallol	0%	5%
phloroglucinol	0%	1.5%
phenol	0%	1%
acetone	0.2%	6.5%
ethanol	0%	0%

Table 2.

Yield of chloroform in mol. % (2 hr, 15°C).

	pH7	pH 11
dimedon	100%	100%
1,3-indandione	3%	45%
hydroquinone	2%	14%
quinone	1.5%	12.5%
resorcinol	36%	90%
phloroglucinol	0%	2%
phloroglucinolmonopentylether	10%	90%
orcinol	7%	32%
2,6-dihydroxytoluene	1%	6%

In the series of polyhydroxybenzenes the meta-dihydroxybenzenes give high yields: e.g. resorcinol and the related orcinol. Phloroglucinol with 3 OH-groups in meta-position was found desintegrate mainly into 3 molecules of dichloroacetic acid.

When we tested the mono-pentylether of phloroglucinol the ability for haloform formation was significantly enhanced, the monoether had remained the character of resorcinol. As OR-substituents do not differ much from OH-groups, both having -I +M effects, they are activating o- and p- substitutions. This phenomenon must be considered as blocking the formation of phenoxide ions. The phenoxide ion combines +I with +M effect; it activates strongly on ortho and para places.

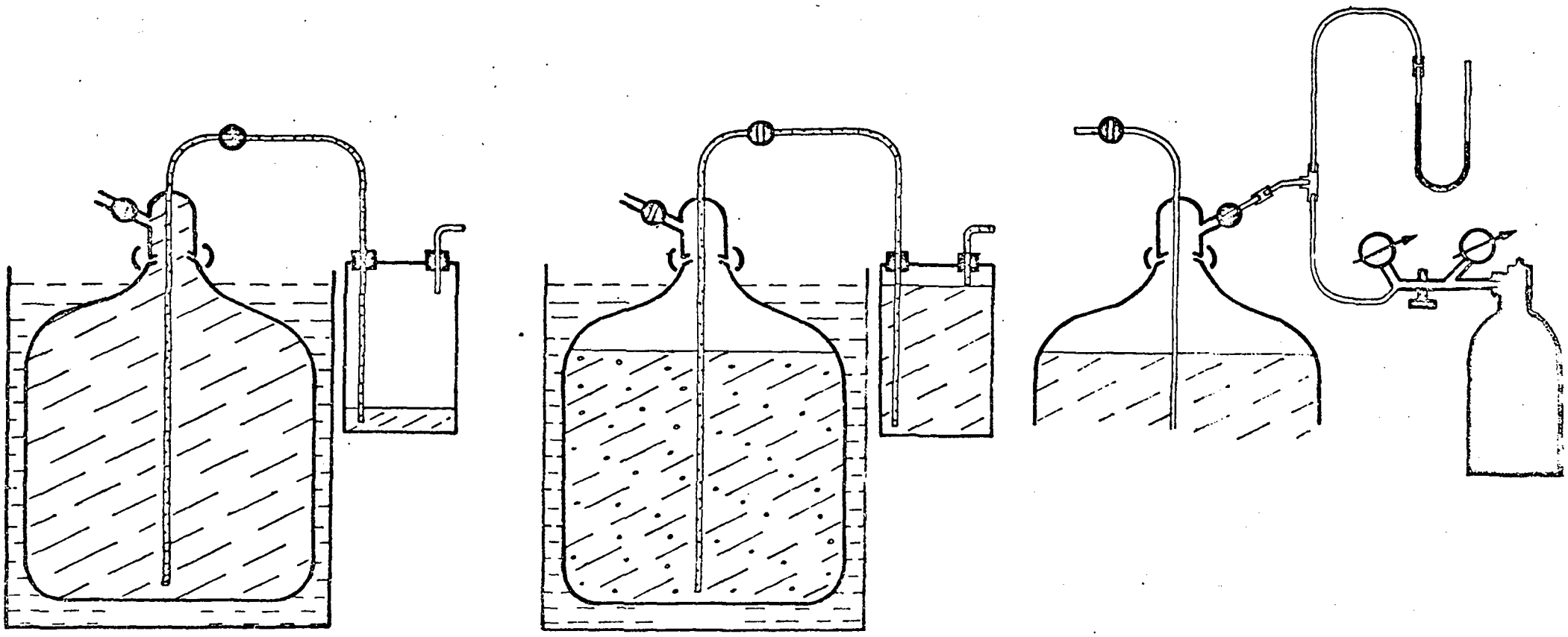


FIGURE 1.

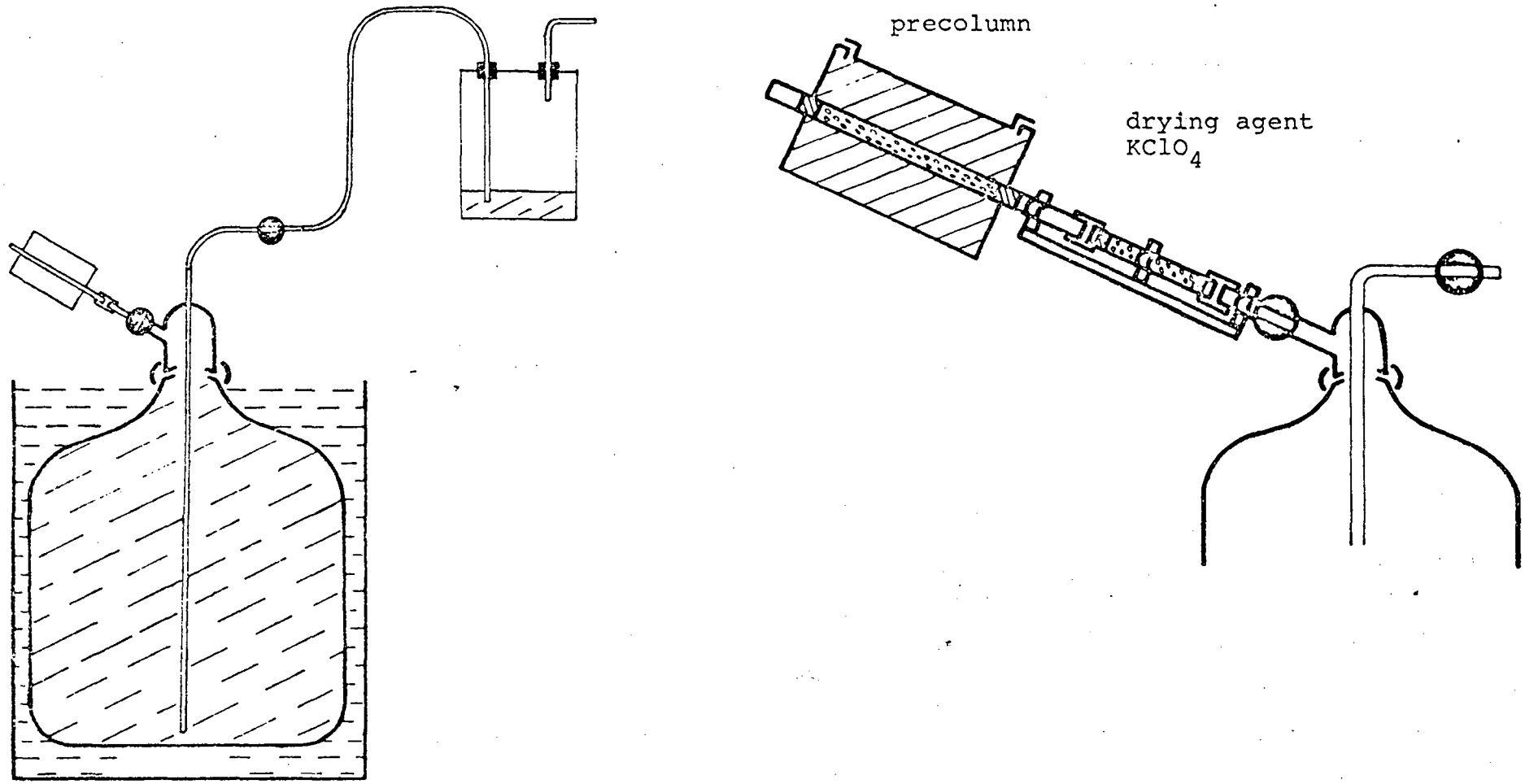


FIGURE 2

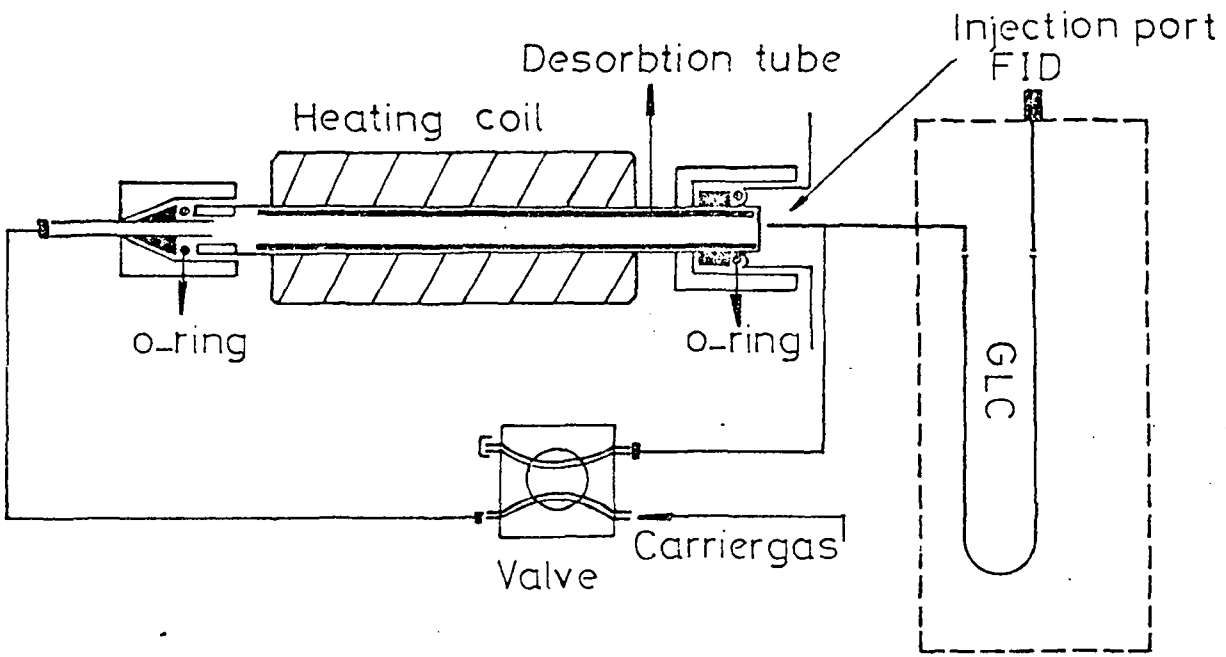


FIGURE 3: METHOD INJECTION HEADSPACE FROM PRECOLUMN

Rook

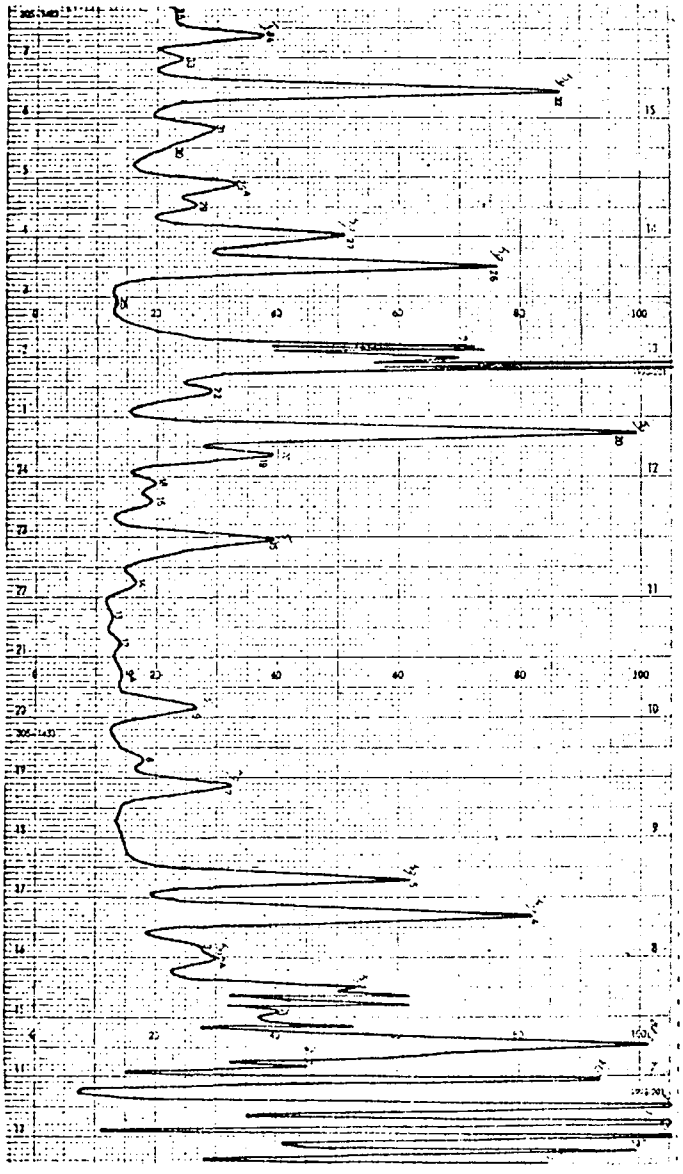


Figure 4.: Headspace Rhine at Ochten km. 906

Rook

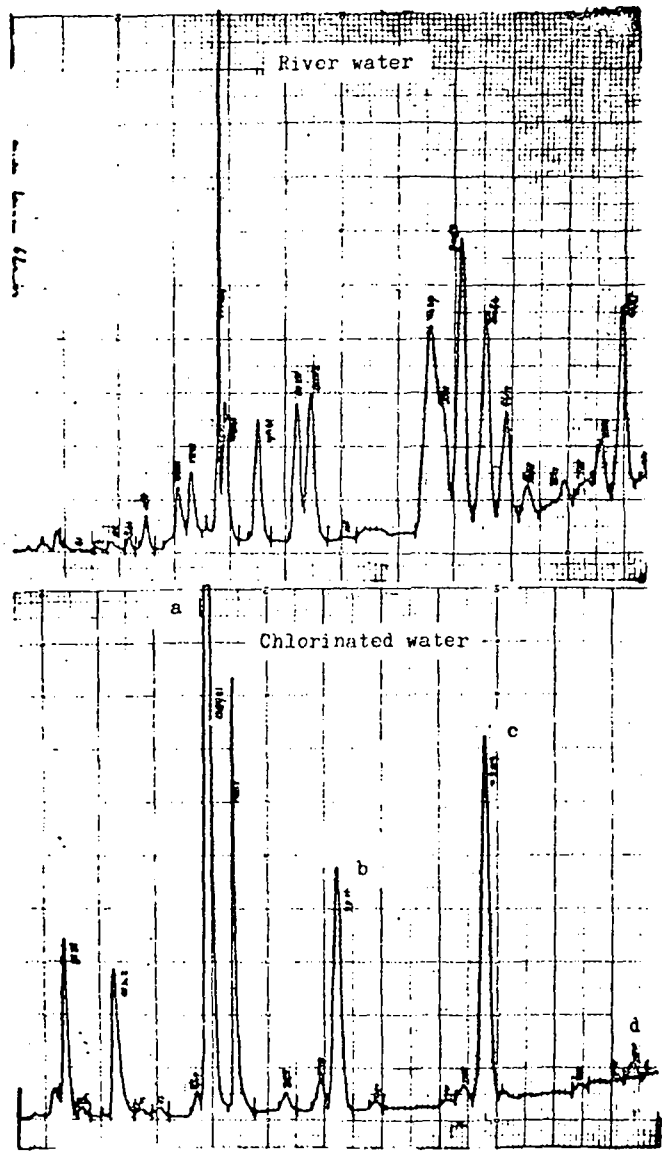


Fig. 5. Headspace chromatograms. Upper — river water; lower — chlorinated water (peaks a, b, c and d are haloforms)

Unsere heutigen Kenntnisse vom Bau eines „Huminstoffmoleküls" lassen sich in einem Strukturbild wiedergeben, das auf Vorschläge von *Flaig, Kickuth* und *Kleinhempel* zurückgeht:

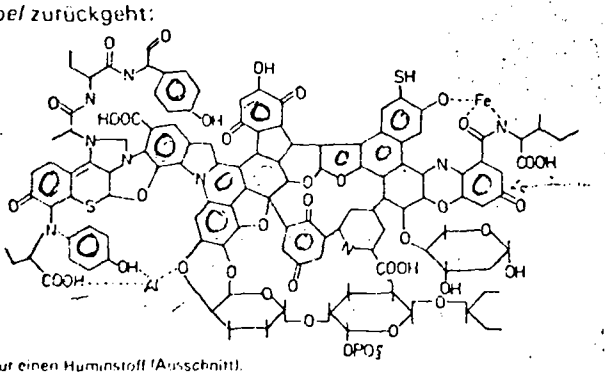


Abb. 2: Strukturbild für einen Huminstoff (Ausschnitt).

Figure 7: Humic acid according to Flaig, Kleinhempel

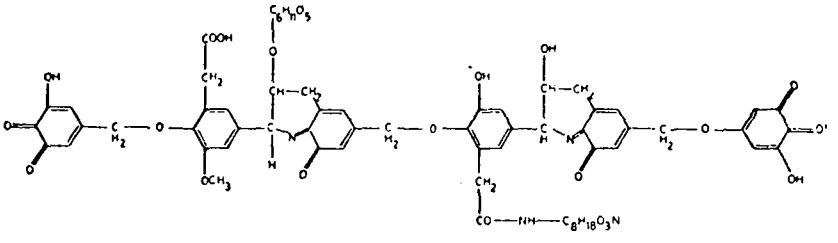


Fig. 8 Structure of humic acid molecule according to Dragunov

DISCUSSION OF LECTURES OF v.d. MEENT AND ROOK

Question Garrison:
Did you try to correlate turbidity of the water with chloroform production, Symons has found such a correlation?
Answer Rook:
Most water were groundwaters of very low turbidity, we found a direct correlation with T.O.C. and also with colour, high turbiditie correlated with higher amounts of humic substances adsorbed on mineral suspended solids, this is my hypothesis.

Question Hutzinger:
Have model substances been used closer in molecular weight to natural humic substances (e.g. commercial or prepared fulvic acids)
Answer Rook:
They all work.

Question Giger:
There is a big peak in the fluoranthene, phenanthrene pyrene concentration in october, do you know where it comes from? Are the PAH's adsorbed on solid matter or are they dissolved in the water?
Answer v.d. Meent:
There is no proof where it comes from we have no proof that PAH's are adsorbed on solid matter.
Comment Fielding:
We are convinced that the bulk of PAH's are associated with suspended particulate matter as we have seen in flood conditions.
Comment Piet:
We found correlation between PAH's and particulate matter in the Meuse when the flow suddenly increased.

Question Fielding:
What is the reason for monitoring the non-carcinogens instead of the known carcinogens of the PAH's?
Answer v.d. Meent:
It is just a matter of analytical procedure.

Question Piet:
There is about 15% of the "Total extractable organic chlorine" found back in individual components which were measured with G.L.C.

Is this due to the fact that much organic chlorine material is non-volatile or is also a part of the very volatile components lost?

Answer v.d. Meent:

Yes, both possibilities exist, another possibility is the interference of bromide, or iodide in the microcoulometric chloride determination.

Question Ott:

There are two marked big peaks for the organic chlorine compounds in Januari and March in the Waal and in the Meuse. Is there any explanation for this?

Answer v.d. Meent:

The sample frequency of once a week could be responsible for that. It is not tried to correlate concentrations with hydrological behaviour.

Question Stieglitz:

We also found nitrobenzotrifluoride, do you know where it comes from and what is the toxicity?

Answer v.d. Meent:

We have no further information about it.

Question v. Buuren:

Is there an important part of the TOCl remaining in the water phase after petroleum-ether extraction and what happens with the humic material?

Answer v.d. Meent:

Yes, referring to the work of Prof. Sontheimer I can say that chlorinated lignines and humic material is not determined in the procedure described. Adsorption on activated carbon can give higher results.

The analysis of volatile organic compounds present and formed during drinking water processing

Dr. L. Stieglitz, Institut für Heiße Chemie,
Kernforschungszentrum Karlsruhe

W. Leger, Lehrstuhl für Radiochemie der
Universität Heidelberg

In the last two years, special emphasis was put on the analysis of organic pollutants from water works. The objectives of the work are

1) Identification of volatile pollutants by GC-MS in water samples. The samples are taken at different processing steps of selected water works of the river Rhine.

2) Quantitative determination of the pollutants, in order to estimate the efficiencies of the different processing steps with regard to the individual compounds.

The work is part of a programme of the Engler-Bunte-Institut, Technical University Karlsruhe.

EXPERIMENTAL

Separation and Enrichment

From the various methods like solvent extraction, adsorption etc. first the gas stripping - gradient tube procedure by Kaiser was applied. The volatiles from the water sample are adsorbed in a gradient tube (Tenax packing), which is cooled by nitrogen. After complete adsorption, the pollutants are thermally desorbed, eluted unto the cooled separation column and analysed by temperature-programmed gaschromatography. The method was applicable to GC-MS, and first results were satisfying. With more detailed knowledge of the variety of pollutants it was however realized that the separation power of packed columns was to low, even for drinking water analysis, and the use of high resolution capillary columns obligatory.

In order to interface the capillary column with the gradient tube, a special condensation step had to be added, which made the whole procedure quite tedious: So the closed loop gas stripping method, as developed by Grob was acknowledged, which is now used as a standard method.

Gaschromatography - Massspectrometry

In the block diagramm (fig. 1) the set up for GC-MS-Analysis is shown. A Varian Aerograph gaschromatograph Model 1400 with a modified Grob type injector is used. The separation column is a 50 m narrow bore (0,25 mm) glas capillary column, coated with OV-101. The column is coupled via a platinum-iridium capillary to a MAT-112 low resolution mass spectrometer.

The instrument is run at a cyclic scan, which is controlled by the computer. The data are stored on magnetic tape and processed afterwards. The signal of the total ion current is fed to a recorder to have a visual control of the GC-run. The GC-peak areas are calculated by an electronic integrator and printed out.

Samples

Normally 2 l samples of water are taken for the outgasing. After 3 hours of gas stripping, the pollutants are extracted with CS_2.

For quantitative work two additional steps are added:

a) addition of known amounts of internal standard

As internal standard we use chlorododecane, which is not present as a pollutant, and which has a retention time different from the compounds to be investigated. The extraction is done in four steps. For the first two extraction steps a carbondisulfide is used with the standard added in a concentration of 74 ng/µl. The next further extractions are carried out with CS_2 without standard.

b) determination of response factors

As with the FID, the response of the mass spectrometer is also different for the various compounds. In order to account for these different responses calibration runs are made with CS_2-solutions containing known amounts of compounds such as chlorobenzenes, and other prominent pollutants. The concentrations are in the ppm range. The response factors are calculated refering to the response of the standard as unity.

In table 1 some of the response factors are listed.

Table 1 Response factors of pollutants for GC-MS-Analysis

$CCl_2 = CCl_2$	0,75
CBr_3H	1,55
CCl_4	1,45
$(ClC_3H_6)_2O$	0,9
C_6H_6	0,49
C_6H_5Cl	0,69
$C_6H_4Cl_2$	0,71
$C_6H_3Cl_3$	0,73
$C_6H_2Cl_4$	0,79
$C_6H_4(CH_3)_2$	0,60
$C_{12}H_{25}Cl$	1,0

With these data the concentrations may be calculated as

$$C_{comp.} = \frac{W_{STD}}{A_{STD}} \cdot \frac{A_{cpd}}{Vol.} \cdot f_{cpd} \quad (ng/l)$$

with W_{STD} weight of standard added

A_{STD} peak area of standard

A_{cpd} peak area of compound

Vol. volume of water sample

f_{cpd} response factor of compound

With the standard weight in nano-grams and the sample volume in liters the calculated concentration is in ng/l.

In this calculation the assumptions are made:

- that the stripping efficiency is 90 - 100 % and deviations are within the error limits of the method

- that no break-through or loss of the compounds from the charcoal filter takes place.

RESULTS

The application of the procedure is discussed with samples from a water work. At four strategic points samples were drawn over a period of November 1975 to January 1976.

point A: sample from river water
point B: sample after bankfiltration
point C: sample raw water with chlorination
point D: sample drinking water prior to chlorination and distribution

The samples were kept frozen until analysis.

Qualitative aspects

In fig. 2 to 3 the chromatograms of the four samples are shown. More than ninety percent of the peaks could be identified. The prominent compounds are listed in table 2. The comparison of the gas chromatograms shows the effect of bank filtration, viz. the decrease of variety and concentration of a substantial number of compounds. After

chlorination of the raw water additional peaks emerge, as already earlier pointed out by Dr. Rook, which are essentially dibromochlormethane and bromoform, but also bromotoluene, dimethylbromobenzene up to trimethylbromobenzene.

Quantitative aspects

With the quantitative determination of individual compounds, the fate of pollutants on their way through the different processing stages of the water work may be traced. In fig. 4 the change of concentrations of aromatic halogen compounds is illustrated. The following facts are obvious

- the concentration of chloroaromatics is decreased by the bank filtration
- a slight increase may be seen through the chlorination process
- bromotoluene (2 isomers), not present in the river water and bank filtrate is formed at a concentration of 150 ng/l in the chlorination step
- in the following purification processes of the water work the concentrations are decreased to 70 ng/l for dichlorobenzenes, and below 10 ng/l for all other aromatic halogen compounds.

In fig. 5 the behaviour of selected aliphatic compounds is shown. Noteworthy are the following relations:

- production of haloforms ($CHBr_2Cl$, $CHBr_3$) to concentrations of 2 - 2,5 µg/l in the chlorination step (Rook-Effect!)

- also increase of tetrachloroethylen by a factor of 2

- the over-all purification efficiencies are around 70 % for tetrachloroethylene and 30 % for trichlorethylene.

Table 2 List of pollutants in Rhine river water (Nov. 75 - Jan. 76) as identified after gas stripping (Grob method)

1) chloroform
2) di-isopropylether
3) hexene
4) 1.1.1 trichlorethane
5) benzene
6) carbontetrachloride
7) cyclohexane
8) trichlorethylene
9) heptane
10) dimethyldisulfide (artifact from CS_2 ?)
11) toluene
12) dimethyldioxane
13) tetrachloroethylene
14) methylamylketone (?)
15) chlorobenzene
16) chlorobenzotrifluoride
17) C_2-benzenes
18) styrene
19) dibutylether
20) tetrachloroethane
21) anisole
22) nonane
23) C_3-benzenes
24) chlorotoluenes
25) decane
26) dichlorobenzenes
27) terpenes
28) indene
29) nitrobenzotrifluoride
30) tetrachlorobutadienes
31) C_4-benzenes
32) hexachloroethane
33) nitrobenzene
34) undecane
35) dichlorotoluenes
36) pentachlorobutadienes
37) divinylbenzenes
38) trichlorobenzenes
39) naphthalene
40) hexachlorobutadien
41) dodecane
42) methylnaphthalenes
43) biphenyl
44) tridecane
45) tetradecane
46) tetrachlorotoluene
47) pentadecane
48) hexadecane
49) heptadecane

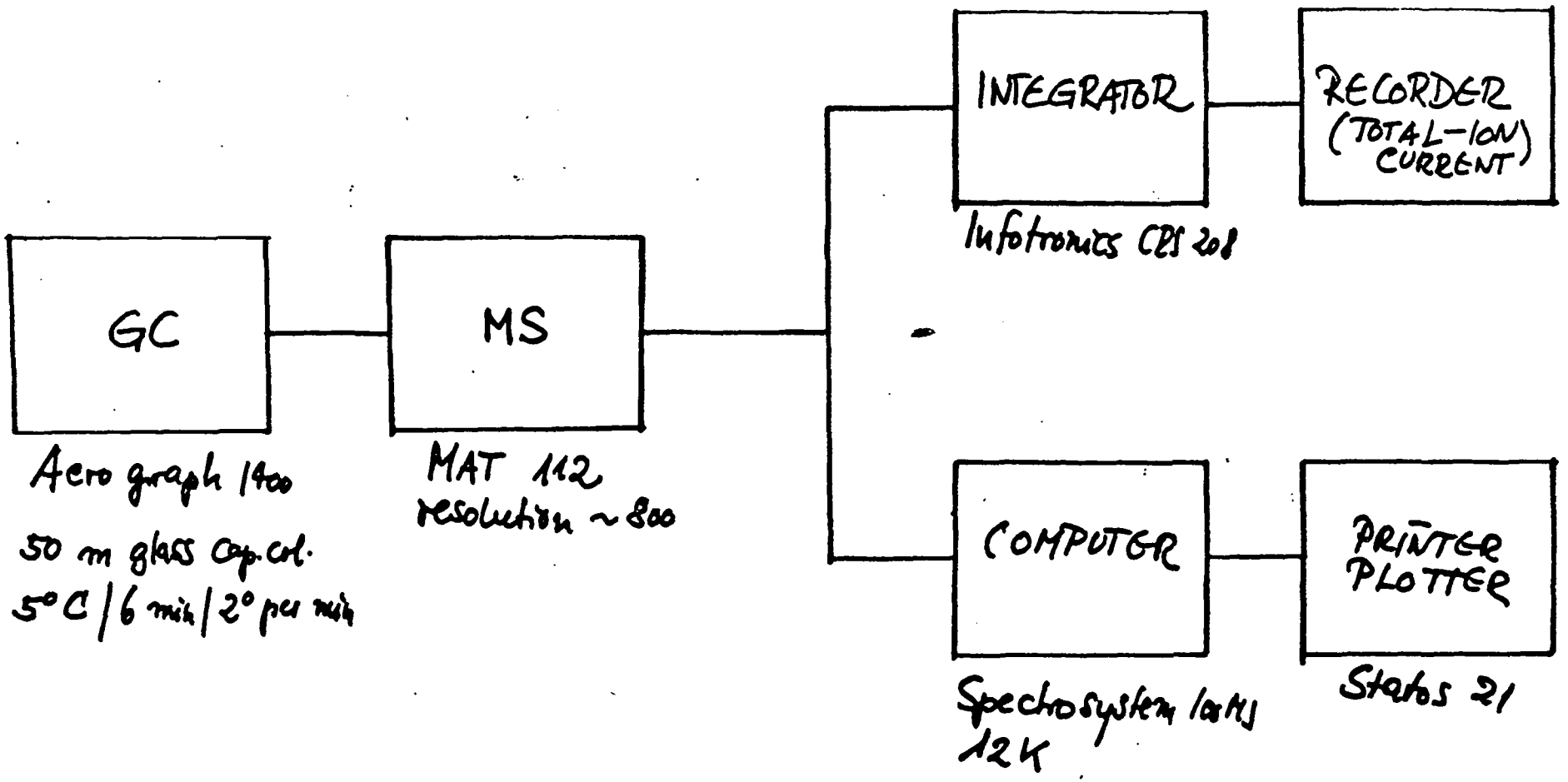
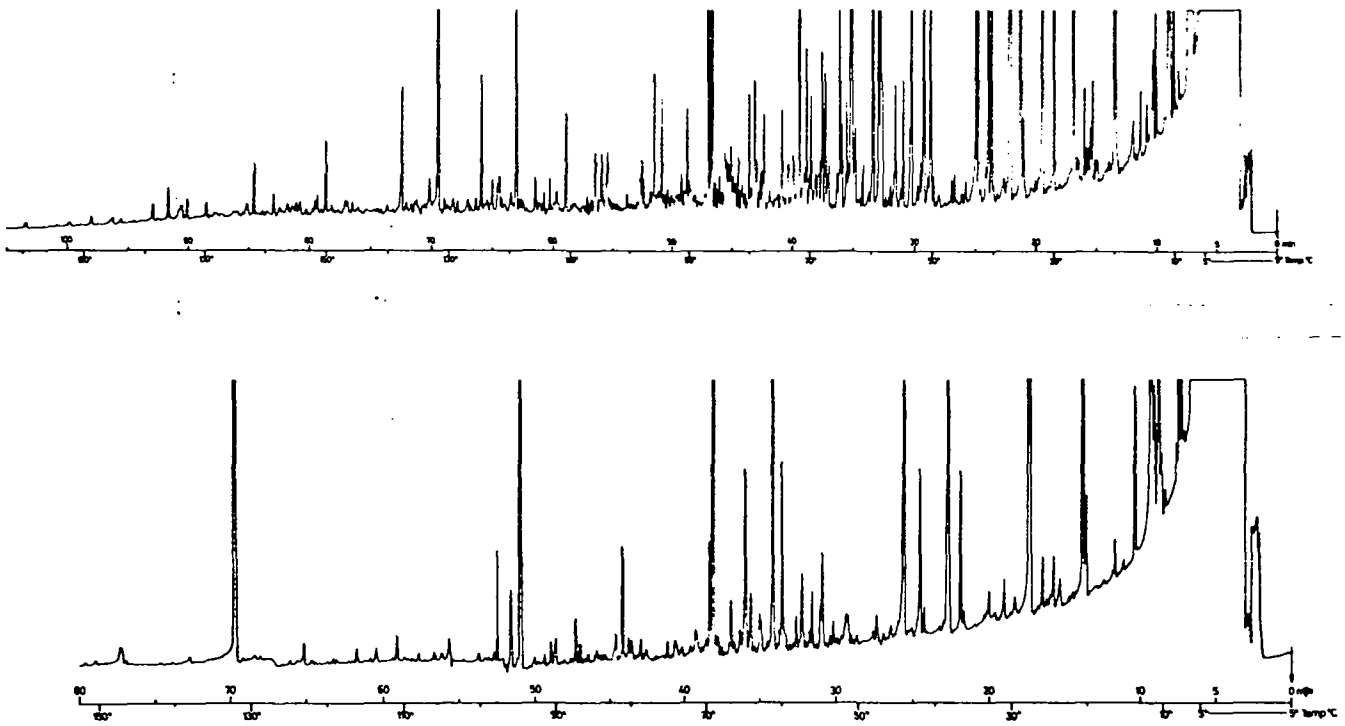


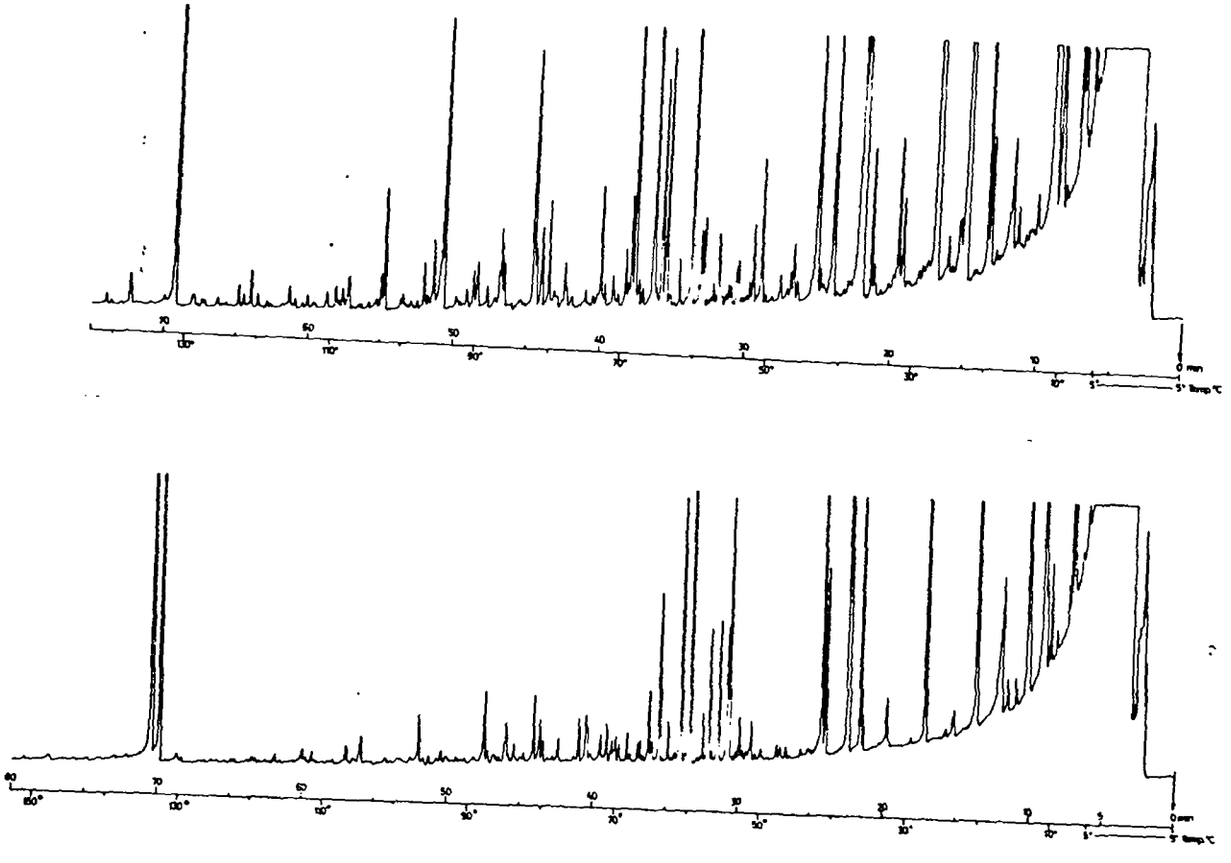
fig. 1 Block diagramm of GC-MS-combination



A

B

fig. 2 Total ion current chromatogramms of volatile organic pollutants
A river water
B bank filtrate



C

D

fig. 3 Total ion current chromatogramms of volatile organic pollutants
C raw water after chlorination
D drinking water prior to chlorination

fig. 4 Behavior of aromatic halogen compounds in drinking water processing

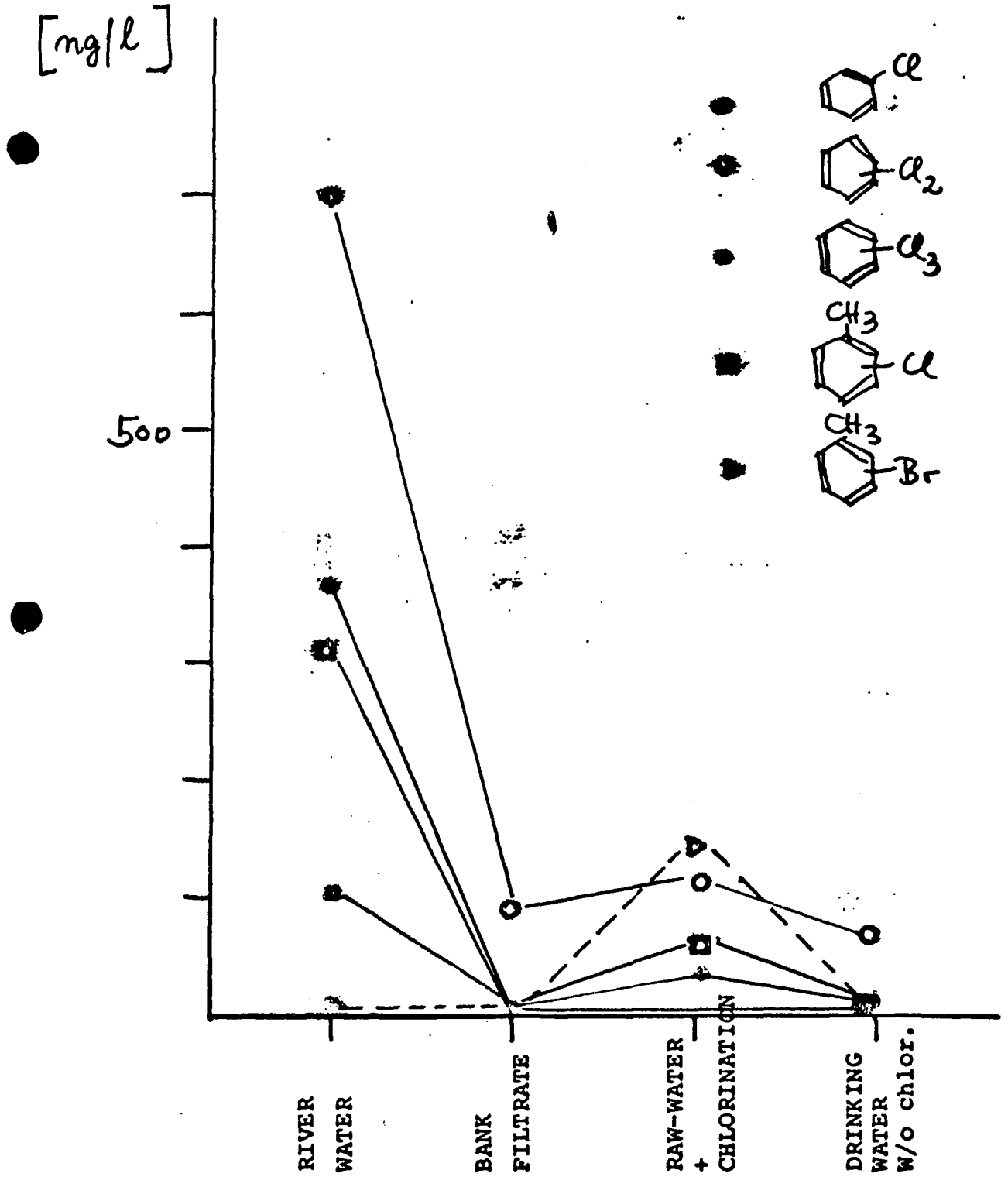
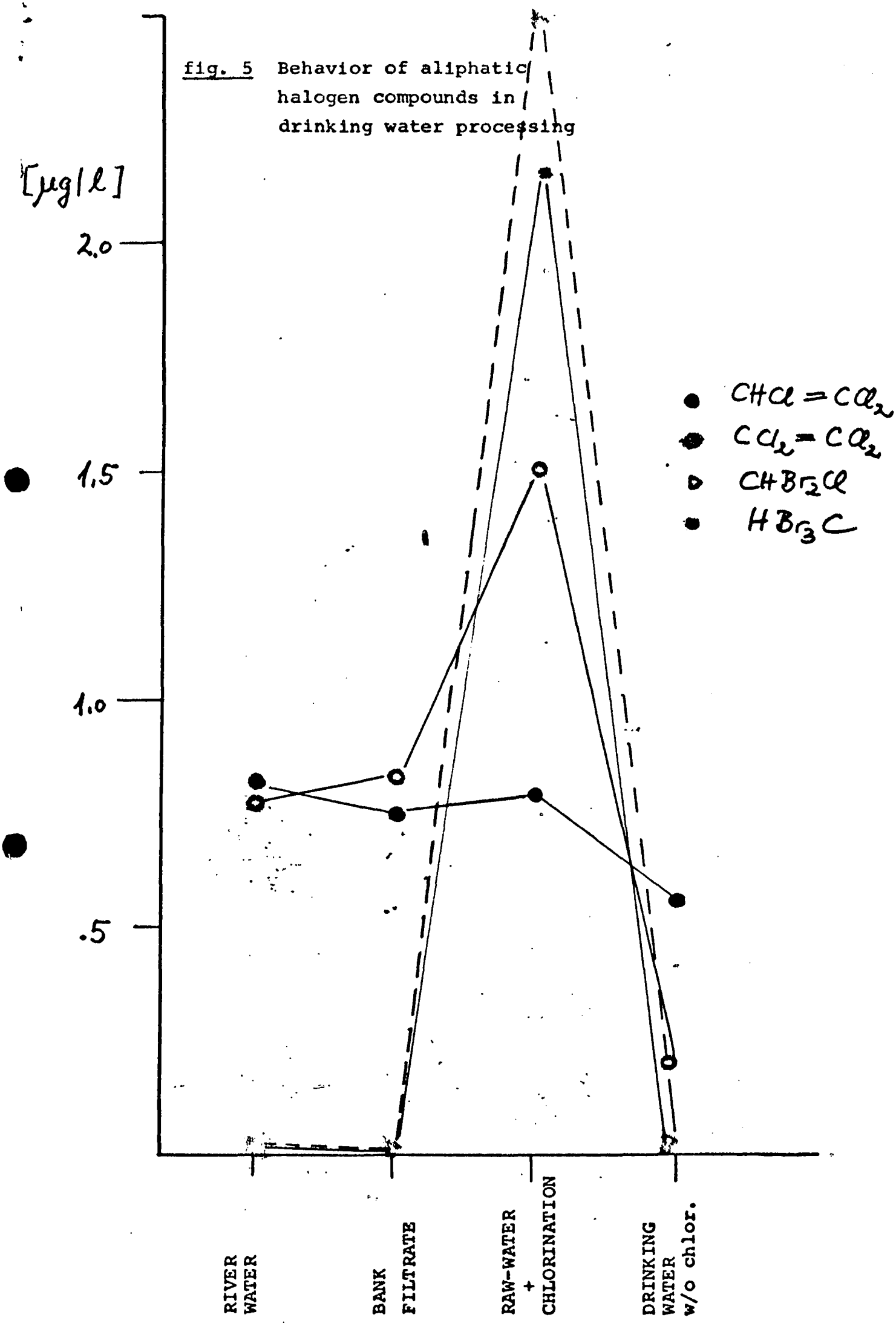


fig. 5 Behavior of aliphatic halogen compounds in drinking water processing



11

ORGANIC CONSTITUENTS OF WATER - ANALYSIS BY CAPILLARY GAS CHROMATOGRAPHY

by: Walter Giger,
Swiss Federal Institute for Water Resources and
Water Pollution Control (EAWAG)

INTRODUCTION

The impact of organic constituents on the aquatic environment is of growing concern for ecological and hygienic reasons. With a few exceptions routine assessments of water quality are based on collective parameters like total organic carbon or biological oxygen demand. But, since most biochemical reactions show a very pronounced structural dependence, studies on chemical ecology necessitate analyses for single constituents. Such investigations are hindered by two intrinsic properties of organic water constituents. Firstly, the organic assemblages in environmental samples are of an extraordinarily high compositional complexity, and secondly, single components occur in trace quantities only. Therefore, very efficient enrichment, seperation, and detection techniques are needed.

The seperation efficiency of capillary gas chromatography by far exceeds what presently is achievably by other methods. This analytical technique thus offers the best possibility to care with highly complex minimum of organic compounds. The limitations however, are given by the necessary limit volability and thermal stability of the components amenal to gas chromatography.

This paper reports an analyses of organic constituents in water utilizing gas chromatography with glass capillary columns. Detection and identifications are achieved by flame ionization, electron capture or computerized mass spectrometry. By applying two different enrichment procedures, namely closed loop gaseous stripping and liquid-liquid extraction, a bread variety of water samples can be studied. Analyses of primary and secondary effluents and river water. The results are discussed with respect to both possible sources and to the fate of organics in water treatment processes and in the aquatic ecosphere.

METHODS

Enrichment

Effluents of primary and secondary sewage treatment were filtered through a glass fritted funnel. The filtrates were then extracted by simple liquid-liquid partitioning into methylenechloride. The extracts were separated into three fractions by adsorption column chromatography on silica (1). The nonpolar constituents eluted with pentane and methylenechloride were analyzed by glass capillary gas chromatography after evaporative concentration. The more polar constituents were eluted with methanol, evaporated to dryness, and taken up in methylenechloride.

Volatile organic constitutents from river were enriched by a closed-loop gaseous stripping/adsorption/elution-procedure developed by Grob. The main advantage of this method is the high enrichment factor ($1 : 10^6$) which enables the detection of traces in the ng/l range. Since the gas chromatographic analyses can be performed without prior evaporation, low boiling components are quantitatively extracted as well.

It should be emphasized that no general method exists for enrichment of organics from water. The technique has to be chosen according to the type of water (e.g., total organic carbon content) and considering the properties of the components to be studied (volatility, polarity, etc.).

Gas chromatography

Gas chromatography was performed on Carlo Erba instruments equipped with glass capillary columns and Grob-type injectors. The glass capillaries, coated with OV-101 and Ucon HB were supplied by H.& G. Jaeggi, CH-9043 Trogen, Switzerland.

1-2 µl of the samples were injected without stream splitting onto the column at ambient temperature. After 30 sec. the split valve was opened, allowing the septum and injection port to be purged at a flow rate of 10-15 ml/min. Subsequent to the elution of the solvent, the oven temperature was raised with varying temperature programs. Hydrogen was used for carrier gas. In our GC-procedure we followed the description given by Grob.

The apparatus for simultaneous flame ionization and electron capture detection was kindly made available by Prof. Grob. The exit of the column is split, using the platinum capillary technique developed by Etzweiler and Neuner-Jehle. The low dead volume ECD was purchased from Brechbühler AG, CH-8902 Urdorf, Switzerland.

Gas chromatography - mass spectrometry

For mass spectrometric identifications and mass specific detection, a Finnigan GC-MS system (model 1015D) combined with an on-line computer (model 6000) was used. The glass capillary column was directly coupled to the mass spectrometer by means of a platinum capillary. Helium was used for carrier gas.

In environmental samples, specified substances or groups of substances usually are of interest. In simple cases they can be detected by tracing one specific ion (mass chromatography). The structure can then be elucidated by inspection of the corresponding mass spectra. If maximum sensitivity is needed, only a small number of preselected ions are detected, each mass with an optimum signal to noise ratio (mass fragmentography). As a result, much spectroscopic information is lost and the identification has to be based on the GC-retention data. The two methods can be combined by integrating certain masses of particular importance with maximum integration time during the cyclic acquisition of the spectra.

RESULTS AND DISCUSSION

Organic constituents of primary and secondary effluents

Steadily growing use of synthetic organic chemicals leads one to expect an increase load of such substances in sewage. Little is known about their behaviour in sewage treatment. One suspects that many of these man-made chemicals are sufficiently refractory to survive in conventional treatment. In an attempt to characterize the organic components in effluents from primary and secondary sewage treatment, glass capillary gas chromatography has been applied.

Table 1 lists mean values of TOC and of the various fraction weights. A noteworthy difference in elimination rates between TOC (73%) and the methylenechloride extractable material (83%), suggests a higher amount of nonextractable polymeric constituents in the secondary effluent. The pentane and methylenechloride eluates of the silica chromatography contain hydrocarbons predominantly of petroleum origin. The bulk of the extractable material is eluted with methanol and consists of more polar compounds which are only partly amenable to gas chromatography.

Table 1.: Weight distribution of organic constituents in primary and secondary effluents.

	Primary effluent mg/l	Secondary effluent mg/l	Elimination rate %
Total organic carbon	19.3	11.1	72
Methylenechloride extractable	12.0	2.0	83
Pentane eluate	0.44	0.05	89
Methylenechloride eluate	0.36	0.06	83
Methanol eluate	10.3	1.7	84

Data represent the mean values of three 96-hour composite samples. Total organic carbon was determined on a Beckman TOC analyzer after filtration through a glass fritted funnel. Weights of the extractable matter and the three fractions were measured by a Cahn electrobalance. Small aliquots (20-50 µl of 1-2 ml) were transferred with a 100-ul-syringe to the aluminum pan of the balance and weighed after air-drying.

In this report we focus on the two hydrocarbon fractions, aiming at a better understanding of the behaviour of petroleum constituents in activated sludge treatment.

The gas chromatograms of figure 1 characterize the aliphatic hydrocarbons in primary and secondary effluents, respectively. Before activated sludge treatment, a mixture of saturates that very much resembles the alkane distribution in No. 2 fuel oil is found. n-alkanes are dominant with a maximum abundance in the C_{11} to C_{14}-range. The pattern of branched hydrocarbons is closely related to the fingerprints often found in petroleum-derived hydrocarbon mixtures. In the secondary effluent, the distribution curve is shifted to a higher boiling range with its maximum at n-heptadecane. One possible explanation for this transformed ion would be the easier microbial degradation of hydrocarbons with shorter chain length.

However, the GC's reveal strong evidence that, at least in the C_{14}-C_{20}-range, allmost no biological degradation is taking place. It is a well established fact that branched and particularly isoprencidal hydrocarbons are more slowly degraded than straight chain alkanes. The ratios of n-heptadecane to pristane and n-octadecane to phytane can therefore be used as measures for the degree of microbiol degradation. As shown in figure 1, these ratios are not changed by the activated sludge treatment.

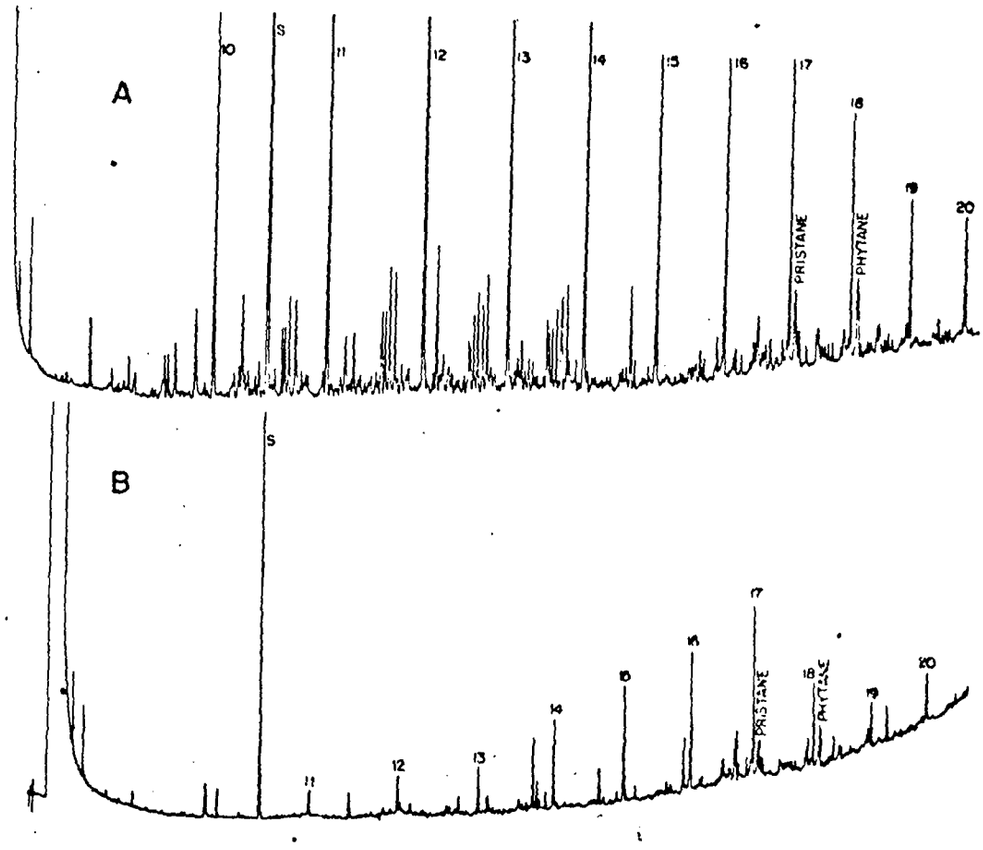


Figure 1.: Gas chromatogram of saturated hydrocarbon fractions.
A.: primary effluent
B.: secondary effluent
Column: OV-101 50m x 0.36 mm, 2.8°/min from 30 to 240°C,
4 ml H_2/min, FID
10-20: ^{n}C-number of n-alkanes, S: internal standard

Hence, it can be concluded that microbial degradation of C_{14} to C_{20}-alkanes is rather ineffective during this treatment.

Elimination by other mechanisms, such as gaseous stripping and adsorption, must prevail. Particularly lower boiling and non-polar components, such as lower alkanes, are probably stripped from the sewage during the aeration process. Adsorption on the sludge floc surfaces may be of importance as a removal mechanism for the heavier saturates.

Figure 2 shows the GC analyses of the aromatic hydrocarbon fractions. They mainly contain mixtures of alkylated benzenes as they are present in gasoline, diesel, fuel or No. 2 fuel oil In clear contrast to the alkane fraction, the low boiling constituents are not removed as efficiently. This may be explained by their better solubility in water, which decreases the stripping efficiency of the aeration.

p-Dichlorobenzene(peak No. 9) was found most abundant among the chlorinated benzenes of which the full series could be detected by mass chromatography and electron capture detection, respectively. In the higher boiling range a second group of components is present, but their structures could not yet be elucidated. According to the mass spectra, these compounds are not of aromatic hydrocarbon type. Preliminary results suggest that they are probably produced by the bacteria. Their concentrations increase after percolation through activated carbon filters which contain microbial populations (13). Concentration levels of major components are in the micro- and submicrogram-per-liter range for primary and secondary effluents, respectively.

The methanol fraction (see Table 1) has also been studied by capillary gas chromatography without derivatization. Among the major components found were a-terpineol, benzylalcohol, 2-phenylethanol, phenol and alkylated phenols, together with various phthalates and adipates. a-terpineol which is a widely used cheap synthetic flavour, proved to be easily eliminated showing an efficienty greater than 99%. In this case a rapid biodegradation is assumed.

Organic volatiles in river water

Recent analytical developments enable the detection of volatile organic compounds which are present in water as trace constituents (nanograms per liter). At this concentration level one finds organic volatiles in all natural water. The aim of this study was to characterize the strippable part of the organic material in the river Glatt which flows partly through a densely populated area. The input and fate of a few selected components are discussed on the basis of longitudinal concentration profiles.

Figure 3 represents a typical gas chromatogram of the volatile organics found in the river Glatt. Enrichment was performed by the closed-loop gaseous stripping procedure. Capillary gas chromatography reveals the tremendous complexity inherent to this fraction of the organic water constituents. GC-MS and in most cases co-injection of reference samples provided the identifications listed in Table IV. This particular sample was taken very close to the outflow from the Greifensee, the highly eutrophic lake which feeds the Glatt. While there is

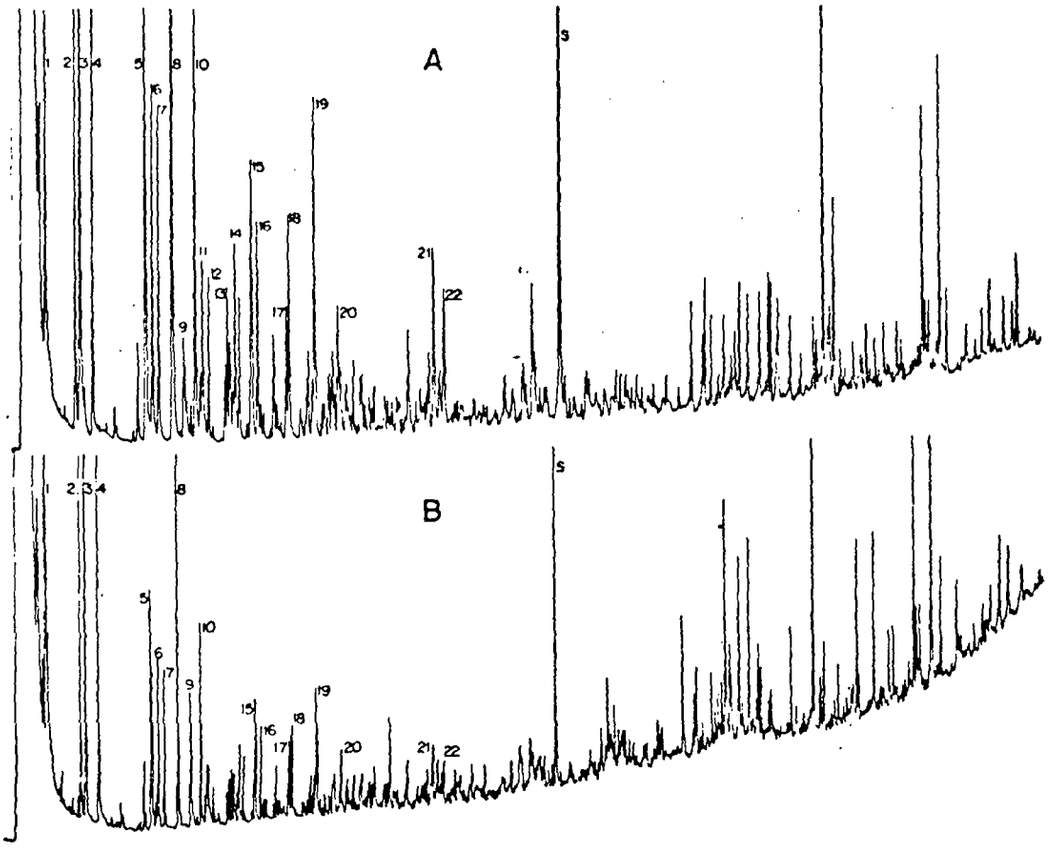


Figure 2.: Gas chromatogram of aromatic hydrocarbon fractions.
A.: primary effluent
B.: secondary effluent
Column: OV-101 50m x 0.36mm, 2.8°/min from 30 to 240°C, 4 ml H_2/min, FID.
1-22: identified constituents listed in Table II,
S: internal standard.

Table II: Aromatic hydrocarbons identified in primary and secondary effluents

1. Toluene
2. Ethylbenzene
3. m-/p-Xylene
4. o-Xylene
5. 1-Ethyl-4-methylbenzene/ 1-Ethyl-3-methylbenzene
6. 1.3.5-Trimethylbenzene
7. 1-Ethyl-2-methylbenzene
9. 1.4-Dichlorobenzene
10. 1.2.3-Trimethylbenzene
11. 1-Isopropyl-4-methylbenzene
12. Indan
13. 1.4-Diethylbenzene
15. 1.3-Dimethyl-2-ethylbenzene/ 1.3-Dimethyl-4-ethylbenzene
16. 1.2-Dimethyl-4-ethylbenzene
17. 1.2.4.5-Tetramethylbenzene
18. 1.2.3.5-Tetramethylbenzene
19. Tetralin
20. Naphtalene
21. 2-Methylnaphthalene
22. 1-Methylnaphtalene

Numbers refer to Figure 2.

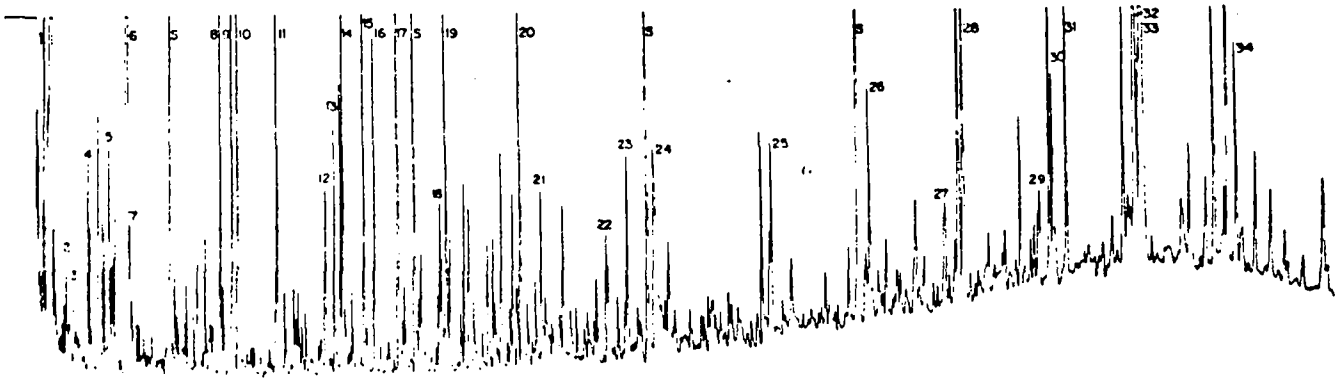


Figure 3.: Gas chromatogram of volatiles stripped from the river Glatt.
Column: Ucon HB, 50m x 0.32mm, 3°/min from 30 to 180°C, 2 ml H_2/min, FID
Sampling location close to the outflow from Greifensee.
1-34: identified compounds listed in Table III
S: internal standards

Table III: Compounds identified in river water.

1. Benzene
2. 1.1-Diethyoxy-ethane
3. cis-Dichloroethylene
4. Trichloroethylene
5. 1.2-Dichloropropane
6. Tetrachloroethylene
7. Toluene
8. Ethylbenzene.
9. p-Xylene
10. m-Xylene
11. o-Xylene/chlorobenzene
12. n-Propylbenzene
13. 1-Ethyl-3-methylbenzene
14. 1-Ethyl-4-methylbenzene
15. 1-Ethyl-2-methylbenzene
16. 1.3.5-Trimethylbenzene
17. 1.2.4-Trimethylbenzene
18. Diacetone alcohol
19. 1.2.3-Trimethylbenzene
20. 1.4-Dichlorobenzene
21. n-Nonanal
22. $C_{10}H_{18}O$
23. $C_{10}H_{18}O$
24. n-Decanal
25. n-Pentadecane
26. n-Hexadecane
27. Phistane
28. n-Heptadecane
29. Phytane
30. n-Octadecane
31. Tri-n-butylphosphate
32. n-Dibutylphtalate
33. Iso-Dibutylphthalate
34. n-Eicosane

Numbers refer to Figure 3.

no discharge of sewage into the Glatt between the Greifensee and the sample point, the Greifensee itself is subjected to a heavy sewage load. The mean residence time of water in the lake is about one year.

The identified components can be divided into the following groups:
A.: alkylated benzenes (No. 1,7-17,19)
B.: low-molecular-weight chlorinated hydrocarbons (No. 3-6,11,20)
C.: aldehydes (No. 21,24)
D.: aliphatic hydrocarbons (No. 25-30,34)
E.: miscellaneous

Groups A and B are ubiquitous in the environment and have been found in natural and treated waters. These components are presumably derived from human activity since they either occur in fossil fuels or are widely used organic solvents. A homologous series of n-aldehydes is considered to be of biogenic origin. This series extends from C_8-toC_{11}-aldehyde with its maximum at n-decanal. The aliphatic hydrocarbons appearing in the C_{15}-C_{20}-range may be either indigenous or petroleum-derived.

To get a better insight into the sources of these materials and their fate in the river, quantitative determinations were performed along the Glatt. Londitudinal concentration profiles of three components are shown in Figure 4. n-Decanol remains constant from the Greifensee to the Rhine. This leads to the assumption that the main source for n-decanal is the Greifensee. No change occurs in the well aerated river either because no elimination takes place or due to additional diffuse inputs. The other two components (tetra-chloroethylene and 1.4 dichlorobenzene) clearly demonstrate the influence of civilization. The water at station 1 contains significantly lower concentrations. The concentration profile for tetra-chloroethylene forms a distinct peak at station 2, suggesting a dominant point source between stations 1 and 2. This could be explained by the impact of the town of Dübendorf which is located above Station 2. Evaporation processes in the river are probably responsible for the concentration decrease after station 2. Dichlorobenzene, on the other hand, levels off after station 2 which might be explained by additional inputs along the river.

CONCLUSIONS

Capillary gas chromatography is a method of great potential for analyses of organic constituents, particularly in combination with appropriate enrichment and preseparation techniques. Complex mixtures of volatile organic components as contained in water are unraveled by this highly efficient separation technique. Specific detectors and directly coupled, computerized mass spectrometry further enhance the yield of information. Mass chromatographic methods enable a convenient screening for components of interest. It has to be stressed, however, that gas chromatography is capable of analyzing only a minor fraction of the organic matter in water samples. Comparisons with TOC values in the case of primary and secondary effluents show that only approximately 5% of the organics are amenable to analysis by gas chromatography. A similar relation probably holds for other types of water. Derivatization and high pressure liquid chromatography should be applied to widen the scope of organic analyses.

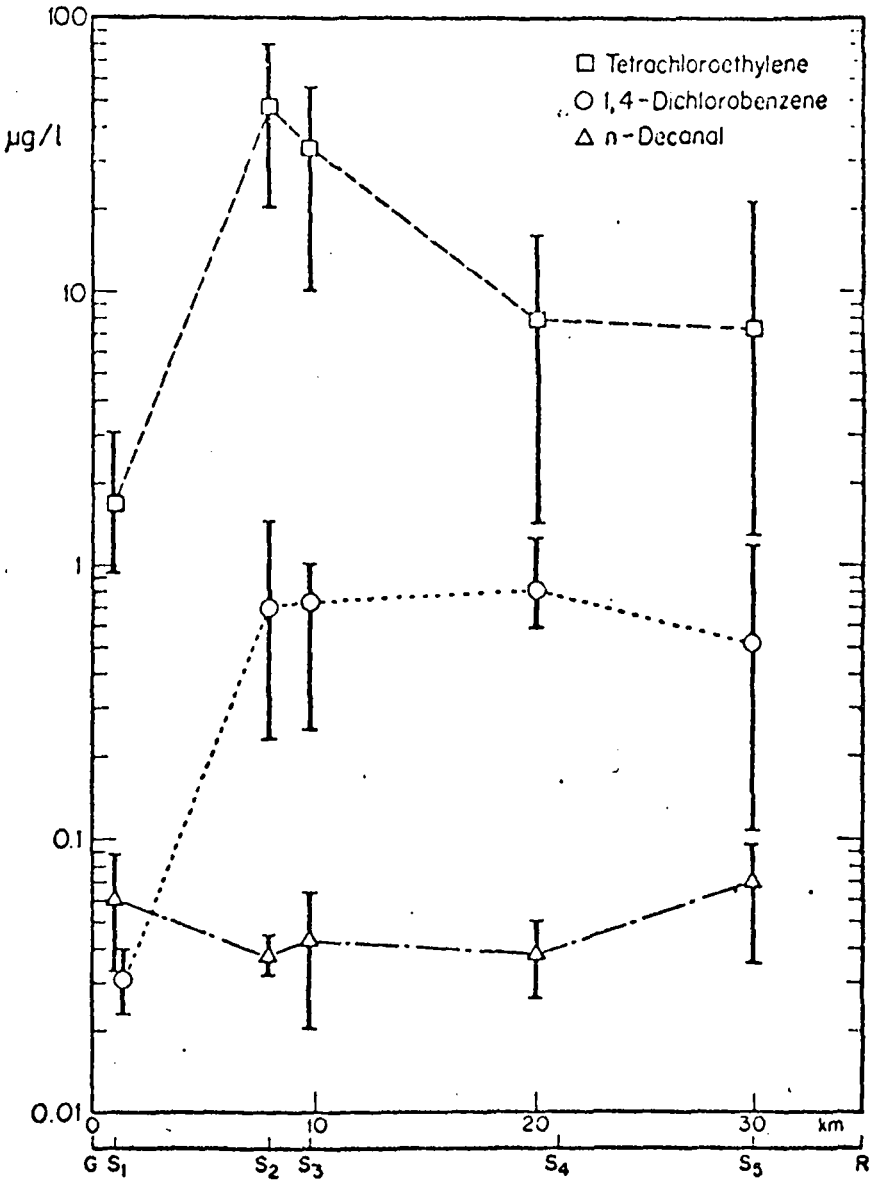


Figure 4.: Longitudinal concentration profiles of tetrachloroethylene, 1.2-dichlorobenzene and n-decanal in the river Glatt.

Mean values of 3-5 measurements and observed ranges are shown.

S_{1-5}: sampling locations, G: Greifensee, R: Rhine

For evaluating potential health hazards and ecological impacts of organic chemicals the direct interrelation between chemical structure and biological activity has to be considered. Consequently, it may be misleading to assess environmental quality by analyses with methods not achieving full separation and identification of specific compounds.

Complete resolution of organic constituents in environmental samples is extremely difficult, if not impossible. The better our analytical methods, the more we recognize the complexity of the mixtures present. Two approaches promise to provide valuable information. Firstly one can concentrate on a few selected constituents which are either of high ecological relevance or represent particular classes of compounds; the pathways and fates of these constituents would be investigated quantitatively. Secondly, monitoring changes in distribution patterns or fingerprints can describe qualitatively the behaviour of groups of components. The latter approach would be greatly improved by the development of computer methods for sophisticated processing of GC-MS data.

We plan to follow along both these lines to get better insight into the behaviour of organic constituents in water treatment processes and in the aquatic ecosphere.

This presentation is part of a paper which was presented at the Symposium on Identification and Analysis of Organic Pollutants in Waters, Mexico City, December, 1975.
The full paper:
"Analyses of organic constituents in water by high resolution gas chromatography in combination with computer-assisted mass spectrometry"
by Walter Giger, Martin Reinhard, Christion Schaffner and Fritz Zürcher will be published in
"Identification and Analysis of Organic Pollutants in Water", L.H. Keith, Editor, Ann Arbor Science, 1976.

Colloquium on the analysis of organic micropollutants in water.
Voorburg, The Hague.

CONTAMINATION OF DRINKING WATER WITH ORGANICS IN THE NETHERLANDS

by:
G.J. Piet
and
B.C.J. Zoeteman

18 februari 1976.

DRINKING WATER CONTAMINATION WITH ORGANICS IN THE NETHERLANDS

Methods

G.J. Piet and B.C.J. Zoeteman

1. INTRODUCTION

To evaluate the health effects and the contribution to odour of volatile organic compounds in drinking water, that means gas-chromatographable organics, the compounds have to be concentrated in a form where they can be easily subjected to a gaschromatographic analysis for identification and quantification.

The complexity of the organic constituents in drinking water from different sources is well known, so the analysis must be performed with high resolution gaschromatography, combined with a sensitive and fast mass-spectrometer. That means too a fast computer to sample the peaks of individual components or a mixture of organic components.

Low detection limits must be reached to reduce the volume of the water sample to be analyzed. It is almost impossible to transport or pretrent big volumes of drinking water without introducing contamination.

In general identification and quantification of the individual component is limited to a concentration of about 10 ppt in water. For instance, benz(a)pyrene, a very toxic substance can be allowed to a concentration of about 10 ppt in drinking water, according to W.H.O. recommandations (200 nanogram PAH's/liter). The same holds for very odourans compounds in water. Practically all organic compounds have a threshold odour concentration in water which is higher than 10 ppt.

2. CONCENTRATION TECHNIQUES,

Concentration of the volatile organic compounds in water(up to 25 catoms) is performed in several ways.

2.1. Closed loop stripping technique with an inert gas (Grob method) under standart conditions. Reproducibility of recovering and quantitative measurement of the organic compounds is achieved and controlled by adding an internal standard of e.g. butylcyclohexane.
In the standard procedure 5 liters of water sample are used in the stripped organic compounds are adsorbed on a very tin activated charbonfilter, which is eluted with 20 microliters of CS_2 or methylene chloride. No evaporation of the solvent has to be applied so no loss of very volatile components takes place.
The concentration step takes 15-20 minutes depending on the type of drinkingwater, this can be extended to 16 hours to recover high boiling or very polar compounds.
In general 20-90% of each organic component is recovered. A sample of tapwater of The Hague and of Dordrecht is shown, the gaschromatographic analysis took place with a 50 meter, 0,35 mm i.d. glass OV, capillary column.
The detection limit in capillary chromatography for most components is 0.04 nanogram, so in most cases 80 ml of drinkingwater is sufficient for detection, when the final concentrate of 20 µl CS_2 is evaporated to 2 microliters. 8 ml of drinkingwater is sufficient when each organic compound has a concentration of about 10 ppt. Extracts can be stored for several days without losses.

2.2. Macroreticular XAD resins.
In this case adsorption of the organics on the resin takes place in the water-phase, longer contact times are necessary because of the fact that about 80 ml of diethylether has to be used for the elution of the adsorbed compounds, bigger volumes of water have to be treated.
When no evaporation of the final extract is performed 320 liters of water have to be used for detection of the components with capillary gaschromatography at a detection limit of 10 ppt. When the final extract of 80 ml of diethylether is concentrated to a volume of 0,5 ml where allmost no loss of e.g. toluene takes place, this volume to be concentrated can be reduced to 20 liters of drinkingwater
A glass column of 30 cm length and 1.5 cm i.d. is filled with resin.
Recovery efficiencies for most components are between 20-60%.

2.3. Extraction techniques are used mostly in "analysis for specific compounds: PAH's, PCB's specific organo-chlorine compounds, oil" are concentrated in this way.

When the concentration of the compounds is about 10 ppt and the recovery efficiency is estimated at 50% 200 liters of water have to be extracted when the final extract can be reduced to 0.5 ml by evaporation. When reduction to 10 microliters can be applied only 4 liters of water have to be concentrated for detection. Disadvantages however are with capilairy chromatography loss of many very volatile compounds when the extract is couporated to 10 microliters and a more serious problem is the concentration of all impurities in the solvent which overshadows the organics in the drinkingwater itself.

2.4. Head space analyses.

This can be used for very volatile electro negative compounds in drinkingwater. No treatment of the sample has to take place. One milliliter of drinkingwater vapour under standard conditions is injected directly into a glass gaschromatographic column equiped with a 63 Ni electron-capture detector. Detection limits with a Tracor linearized E.C.D. are for chloroform 0,5 ppb and for trichloroethylene 0,1 ppb.
The analysis is very fast and introduction of errors by the treatment of the sample totally avoided.

2.5. Identification and quantification

As the seperated components leave a high resolution capillary column in 2-20 seconds depending on their character and the type of column a very fast scanning mass-spectrometer, like a quadrupole m.s. is coupled directly to the capillary column while the mass fragmentograms of the m.s. are sampled with a fast computer. Many peaks leaving a high resolution column are still not pure, which this often lines makes an identification impossible unless many spectra of one peak can be registered. The finnigan quadrupole can scan 6x/sec. In practice 2x/sec is used because of the limited store capacity of the magnetic disk where all fragmentograms of an analysis (4000-6000 scans) are stored. A calculated total ion current of a part of the analysis of The Hague tap water is shown, while too ion 57 is measured to select alkanes and parts of alkanes in organics. The results are plotted on a Varian Statos platter 31 or on a Tectronise 4014 visual display which is equipped with a head copy-unit. Sampling of the peaks in the fragmentograms takes place at a speed of 20.000 points per second. The software is develped by our own institute with the assistence of D.W.V. in München. All the work mentionned in this discourse is performed at our laboratory at this moment.

2.6. SUMMARY

In table 2.1 a survey is presented to show the amounts of drinking water to be concentrated for identification of compounds with the instrumental set-up as is discussed.

The calculations are based on an injection of 1-2 microliters in a capillary column with a Grob injector, a G.C.-M.S. combination (Finnigan) with an identification limit of 2 nanograms and a recognition limit of 0.2 nanograms.

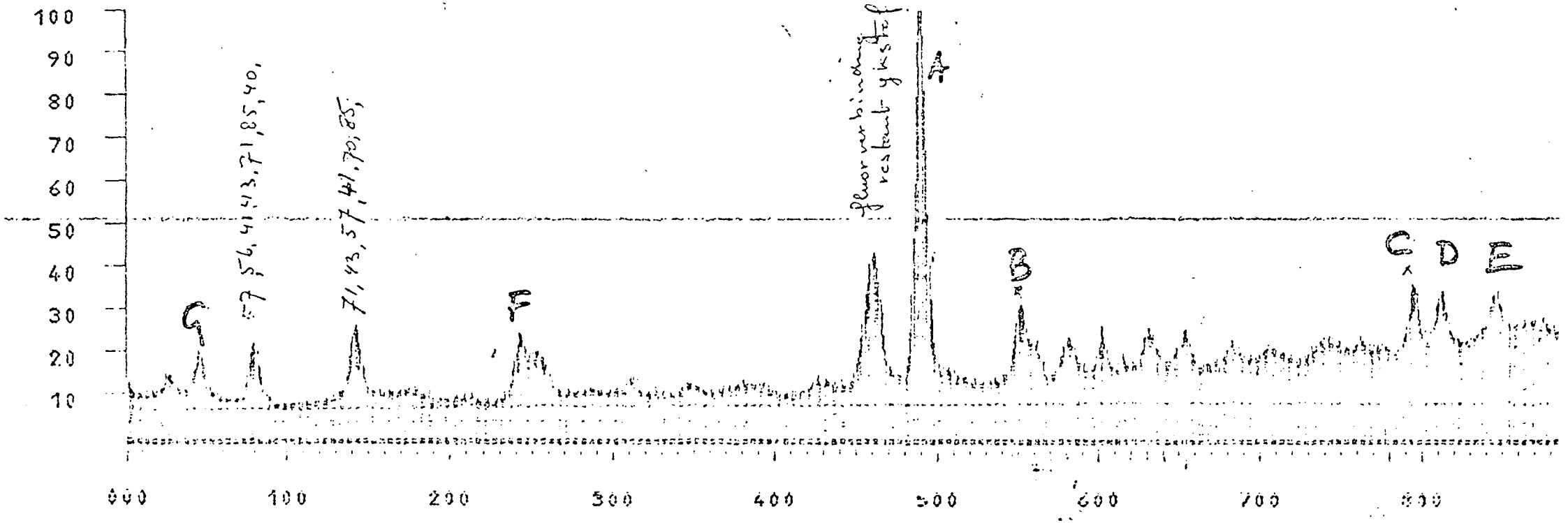
The table is further based on a concentration of 10 ppt or more of each component in the water.

Table 2.1: Volumes of drinking water needed for identification

Method (50% recovery efficiency assumed)	Liters of drinking water to be treated
Grob, without evaporation	4
Grob, with evaporation	0.4
XAD without evaporation	16.000
XAD with evaporation to o.5 ml	100
XAD with evaporation to 10 µl	2
Extraction with evaporation to 0.5 ml	200
Extraction with evaporation to 10 µl	4

MASS-CHROMATOGRAM

TAP WATER OF THE HAGUE



EXPERIMENT 10

MMAG 13/2/70 C02

4007 SCANS

1000 scans = 500 sec.

SCAN NR. 2001 TO 3000

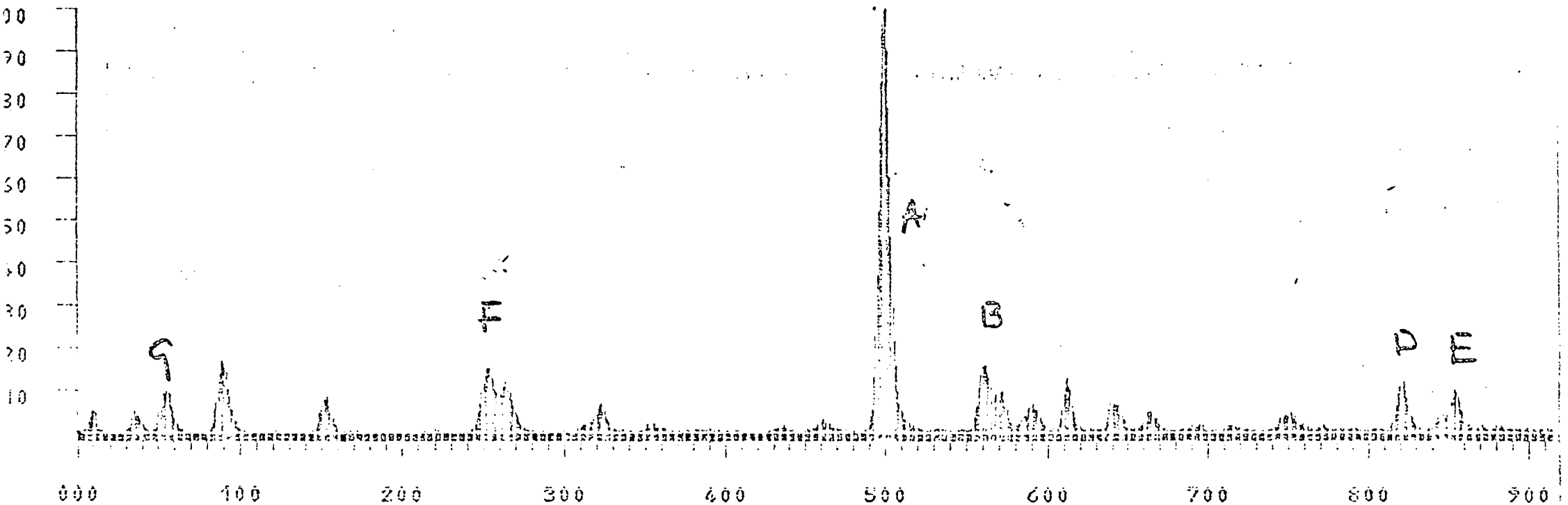
MASS 33 TO 400

Finnigan - Intelldata computer

50 m. glass-capillary OV,

MASS-CHROMATOGRAM

TAP WATER OF THE HAGUE



EXPERIMENT 10

HAAG 13/2/76 052

4007 SCANS

SCAN NR. 1971 TO 2990

MASS 57 TO 57

Finnigan - Interdata computer.
50m glass - capillary OV1

DRINKING WATER CONTAMINATION WITH ORGANICS IN THE NETHERLANDS

B.C.J. Zoeteman,

National Institute for Water Supply,
The Netherlands

1. PRESENT LEVELS OF CONTAMINATION

Up till now only very limited and preliminary data are available in The Netherlands on the presence of organic micropollutants in drinking water. At the laboratories of the waterworks, which derive their water from river water, determinations on some pesticides, phenolic compounds and detergents are carried out on a regular basis. Only very recently haloforms and polynuclear aromatic hydrocarbons have been analysed incidentally. The same applies to the analysis of drinking water for organics by means of G.C.-M.S. methods.

First some data on different categories of organic compounds will be presented, followed by a discussion of compounds determined by G.C.-M.S. techniques.

1.1. Polynuclear Aromatic Hydrocarbons

The highest levels of the sum of six PAH's in drinking water (Borneff's method) were up till now below 0.3 µg/l, which is slightly above the W.H.O. recommendation of less than 0.2 µg/l. Although fluoranthene is mostly the dominant compound among the six PAH's in surface water, in drinking water 1,12-Benzoperylene is also a major constituent of the PAH-group. The highest value for 3,4-Benzopyrene in drinking water was 15 nanograms/liter.

Table 1.1.1.: Polynuclear Aromatic Hydrocarbons in drinking water in The Netherlands

Compound	Concentration (µg/l)	
	Max.	Mean.
3,4 Benzofluoranthene	45	3
11,12 Benzofluoranthene	5	1
1,12 Benzoperylene	130	15
3,4 Benzopyrene	15	2
Fluoranthene	50	15
Indeno(1,2,3-c,d)pyrene	75	8
Totaal	300	45

The limited number of determinations can not be used to answer the question if there exists a P.A.H. problem in tapwater due to P.A.H. release by bitumibous pipe coatings.
On the other hand it is not likely that the riverwater contamination can lead to unacceptable high P.A.H. level- in conventionally treated drinking water.

1.2. Volatile halogenated compounds

Since the work of Rook on haloforms was published in 1974 the class of volatile organics in drinking water has suddenly received a great deal of attention. The main reason for this was the relatively high concentration of the volatile compounds which was in several cases closer to the p.p.m. level than to the normally found p.p.b. level for organics in drinking water. Furthermore the simple volatile substances can be rather toxic due to their high reactivity. Some compounds are particularly of interest because of their proven or possible mutagenic properties.
Examples are chloroform, tetra, vinylchloride, dibromoethane, tri-chloroethylene as well as some halo-ethers like bis-chloroethylether. All these compounds except vinylchloride, have been detected at levels of 1 nanogram/liter or substantally higher quantities in tapwater in The Netherlands. As the larger cities in The Netherlands are located in the water short western part of the country, they mainly depend on river water for their water supply. The drinking water of a large part (25%) of the Dutch population therefore has been treated with chlorine and contains halogenated compounds.

The following maximum and average concentrations have been found by our laboratory in tapwater of cities like Amsterdam, The Hague, Rotterdam, Dordrecht and Zwolle.

Table 1.2.1: Volatile halogenated organics in Dutch tapwaters

Name	Concentration (µg/l)		
	Max.	Mean	N
Chloroform	100	15	12
Di-chlorobromomethane + trichloroethylene	25	5	10
Bromoform	20	3	8
Dibromochloromethane	3	1	3
Bromoethane	1		1
Iodoethane	<0.1		2
1-chloro-2-bromoethane	<0.1		2
Dibromoethane	0.1		2
Dichloroethane	1		2
Dichloroethene	<0.1		1
Dichloropropane	<0.1		1
Tetrachloorethene	0.5	0.1	5
Hexachlorobutadiene			
Chlorobenzene	0.1		2
Iodobenzene	0.1		1
Chlorotoluene	0.1		1
o-Dichlorobenzene	1		3
m-Dichlorobenzene	0.1		2
p-Dichlorobenzene	3		5
2,2 Dichlorodiethylether	0.1		2
Monochlorodipropylether	0.1		1
Bis(3-chloropropyl)ether	0.1		3
Bis(2-chloroisopropyl)ether	10		10

1.3. Organics determined by G.C./M.S. techniques

Lists with organic compounds which have been identified in drinking water have been distributed the last 2 years on a frequent basis among research laboratories. The most recent version of the E.P.A. of January 1976 shows already about 300 different substances. Data on the present concentrations are still very limited. Quantitative information is however essential for the evaluation of health risks and organoleptic aspects related to the presence of the considered compounds. Besides the earlier mentionned haloforms, dichlorobenzenes e.o., main contaminants The Netherlands are compounds in drinking water derived from surface water with concentrations above ± 10 nanogram/liter like acetates and naphtalenes as well as some benzenes and alcanes like trimethylbenzene and decane. Furthermore everywhere phtalates like

diethylphtalate and dibutylphtalate are found in tapwater. Generally these compounds are not of interest from a toxicological point of view. However the taste and odour of the water can be influenced significantly. In this respect particularly dichlorobenzenes and naphtalenes are of importance, as table 1.3.1 illustrates.

Table 1.3.1: Some odour relevant tapwater contaminants in The Netherlands.

Name	Max. Detected Conc. µg/l	Thresh. Odour Conc. µg/l	Ratio conc/ Th.O.C
p-Dichlorobenzene	3	0.3	10
Geosmin	0.06	0.015	4
Naphtalene	10	5	2
o-Chlorophenol	2	2	1
1,3,5Trimethylbenzene	3	3	1
Dimethylnaphtalene	3	2,5	1
Chloroform	100	100	1
2-Methylthiobenzthiazole	1	7.5	0.2
Bis(2-chloroisopropyl) ether	10	100	0.1
Methylnaphtalene	0.5	5	0.1
Indene	0.1	1	0.1

2. PLANNED STUDY OF ORGANIC MICROPOLLUTANTS IN TAPWATER OF 20 CITIES IN THE NETHERLANDS

2.1. GENERAL ASPECTS

To improve the knowledge relating to the importance of the present types and concentrations of organic compounds in tapwater a study of tapwater in 20 Dutch cities is planned for 1976. The cities have been selected in such a way that all the surface water abstracting waterworks are included. Also those plants are considered that use groundwater which can be partially considered as bakfiltered riverwater. Furthermore 7 controle cities are included which use exclusively groundwater.

The aim of the investigation is not only to make an inventory of the present concentrations of organic micropollutants in tapwater, and particularly those with known mutagenic, carcinogenic and teratogenic potential, but also to study a possible relationship between the presence of organic pollutants and the perceived taste and odour by the population. The philosophy behind this is that a first sign for the consumer of water quality deterioration, due to higher levels of organic pollutants, will be reflected in the taste or smell of the tapwater. The smell may give him a very sensitive and usefull warning for an unwanted break-through of organic chemicals into the drinking water.

For the testing of the organoleptic properties of the water a national panel of about 50 selected consumers will be used. It is hoped that finally the presence of certain organic water contaminants can be related to a higher incidence of complaints about the taste and smell of certain types of water. It is also anticipated that the presence of certain organic pollutants can be correlated with mortality rates due to different types of desease, in the studied cities. Some more details of the planned study on sampling, chemical analysis and organoleptic testing are described in the following.

4.2. SAMPLING AND CHEMICAL-BIOLOGICAL MEASUREMENTS

The collection of a representative sample of the drinking water of a city is a difficult exercise. Furthermore the prevention of contamination of the sample with organic compounds from the atmosphere has been found to be a very important aspect, as well as losses of volatile compounds to the aim. In the national study individual samples of 10 taps in each city will be collected for the determination of haloform concentrations and for each city a mixed sample of 200 liters will be collected by adding 20 liter samples from 10 taps in a city into a stainless-steel container, which is specially developed for this purpose. All sampling is carried out by stainless-steel or teflon material under prevention of direct contact between the sampled water and the atmosphere. The mixed 200 liter sample will be used for organoleptic testing by a panel, for analysis on haloforms, P.A.H.'s and other organic compounds using as a concentration step the closed loop stripping method developed by Grob as well as concentration by adsorption on XAD-resin.
Both concentrates will further be analysed by a capillary G.C.-M.S. technique (using a Finnigan quadrupole mass-spectrometer, coupled with a W.D.V. computersystem).
Part of the XAD-concentrate, corresponding to a sample volume of 50 liters, will also be tested for mutagenic effects using a simplified version of the Ames'test with mutated Salmonella bacteria.

4.3. ORGANOLEPTIC TESTING

For the study of the influence of organic micropollutants in drinkwater on the perceived taste and odour a panel will be selected consisting of 2 citizens from each of the studied cities. The panel as a whole will be formed on the basis of equal numbers of males and females, a representative age distribution between 18-65 years and a representative sensitivity of the taste and smell organs. In relation to the latter the 50 panelmembers will be selected from a total number of 150 persons after testing their odour sensititvity for organic odorants in water.

The actual organoleptic testing of the water will take place in Utrecht in co-operation with the Psychological Laboratory of the

University of Utrecht. Wether or not this study will proof a relation between bad taste and smell of drinking water and insufficient treatment of drinking water for certain organic micropollutants, it is hoped that it will at least contribute to a better quantitative knowledge of the level of tapwater contamination with organic compounds in this country and it's significance from a toxicological point of view.
Thank you very much.

DISCUSSION OF LECTURES OF GIGER, STIEGLITS, PIET, ZOETEMAN

Question de Groot:
Is the possibility considered to install a capillary column on which an injection of an extract is made, in an analytical identification system to have that column used at an other laboratory to facilitate the exchange of information?
Answer Piet:
This is not yet considered.

Question Fielding:
Is there an optimum temperature in the Grob recirculating gas-stripping?
Answer Piet:
It is limited by the condensation that takes place in the system and on the carbon filter. High boiling and more polar compounds can be concentrated with the XAD adsorption. Different methods of concentration will give the right picture when these are combined

Question Fielding:
Giger did filter the water before using it in the recirculating gas-stripping procedure. Did you consider the less volatile components in this procedure?
Answer Giger:
No.

Question Rook:
Why is no drying agent, like magnesium perchlorate, introduced in the stripping method to be able to work at more elevated pressures?
Answer Piet:
In using the Kaiser Gradient tube we had to incorporate a drying agent to get rid of the water condensed, but we found losses in the organics comparing chromatograms with and without using a drying agent. In the nanogram level losses occur easily
Answer Giger:
The Grob stripping method is developed for nanograms of volatile components and for higher boiling components we have to use other concentration techniques, probably XAD or even extraction procedures.

Question Oskam:
The PAH content of drinking water in table 3.1.1 of Zoeteman is orders of magnitude higher than the levels in Rhine and Meuse as found by v.d. Meent. Is this because of release from bituminous lining in the distribution system?
Answer Zoeteman:
No, we have to make a correction in the table it should be nanograms/liter.

QUALITATIVE AND QUANTITATIVE METHODS FOR THE ANALYSIS OF ORGANICS IN SURFACE WATER

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Abstract

A new method for elemental analysis is described. It is based on destruction of the molecules by an electrodeless plasma and mass spectrometric investigation afterwards.

"Chlorograms" obtained with this method are given for a sewer sample and a sample of Rhine river water. The unknown compounds are identified.

The frequency of occurrence and the concentration range of the identified substances are checked in a system "mass spectral library of surface waters". A description of this system is given.

Qualitative and quantitative methods for the analysis of organics in surface water.

Element analysis.

Thousands of unknown compounds are present in the polluted surface water of e.g. the Rhine river (at the ppt and higher level). Therefore a choice is made for the identification of specific types of compounds. The choice is the group of halogenated organic compounds. In order to locate those compounds in the gas chromatogram, there is a need for a selective detector parallel to the mass spectrometer (fig. 1). Just after the gas chromatograph a splitter leads one fraction of the eluent into the selective detector and the other fraction into the mass spectrometer. This procedure is well known and several selective detectors are in use for this purpose.

For halogenated substances, the electron capture detector has been used frequently. This is possibly mainly because its excellent sensitivity and its simplicity in use. However, it responds not only to halogenated compounds. Furthermore the response of the detector is not proportional to the number of halogenes in the molecule. Therefore the detector is not a quantitative detector for the amount of halogene atoms in the molecules.

Other examples of selective detectors are the sulphur-phosphor detector and the coulometric detector.

Most of the detectors are only specific to one or more elements. It would be interested to have a tunable selective detector. Such a detector is the plasma emission detector. This type of detector was investigated by us. The sensitivity of it was good for metals. But for the elements Cl, Br, F, P, S, N and O the sensitivity was only in the nanogram range. Moreover, the response of the detector is matrix dependent; there is no linear response. Thus quantitative measurements were not possible.

Starting from the idea of the plasma emission detector, we developed a new type of detector: the plasma-mass spectrometer detector.

In this type of detector the molecules are being destroyed in an electrodeless microwave plasma. In the plasma the molecules are atomized and thereafter in a reaction they react with hydrogen. These molecules are then detected in a mass spectrometer.

The advantages of the system are the following:

1) The system is inexpensive, because one needs the mass spectrometer for the identification anyway.
2) There are no dead volumes between the GLC-capillary column and the mass spectrometer.
3) The system is sensitive; for chlorine for example the sensitivity is in the picogram range.
4) The system is quantitative, because of the absence of matrix effects.
5) The plasma can still be used for a simultaneous optical investigation.

In figure 2 the chlorogram of the water of a sewer is given. In table I the identified substances are given. From the chlorogram one can see that also all chlorinated compounds in that part of the chromatogram were identified. From table I follows that there are also chlorinated-brominated compounds. Therefore a bromogram was taken and the brominated compounds were identified (table II).

In figure 3 a part of the chlorogram of Rhine water is given. From this enormous number of compounds only a fraction is considered at first. In figure 4 the very first part of figure 3 is given (under other chromatographic conditions).

Results are given in table III.

The mass spectrometrical surface water library.

After the identification of an unknown compound in surface water, one wants to know whether the compound is a common one and in what concentration range the compound usually occurs. To get the information one can perform a lot of fragmentographic work on many samples. This is of course a time consuming operation. To avoid this, an other system was developed: "the mass spectral library of surface water".

On several places in the Netherlands (fig. 5) every 4 weeks in 1974 a sample of surface water was taken. A methylene chloride extract was made from this 3 litre sample. These extracts were run over a GC-MS-computer system. All the data were stored on the magnetic tape.

If one wants to know whether a certain compound occurs in the surface water one simply asks the computer to generate the fragmentogram for the specific compound. If the compound is there, the fragmentogram will show a response.

The advantage of the system is, that it costs just computer-time to know whether the compound is there or not and to make a semi-quantitative measurement.

Data are only generated when there is a need for those data. The limit of detection for our set-up of 1974 was 0.5 ppb. However, the limit can be made lower, if necessary. The runs are made from fresh extracts, deterioration of the data is impossible.

The system is further an historic representation. We observed for example an increase of pentachlorophenol in the last two years in the Rhine river water. A screening on hexachlorobutadiene for 1974 gave high values (an exact quantification has still to be done).

Fig. 1 A selective detector is placed parallel to the mass spectrometer. A splitter makes that a fraction of the eluent goes to the mass spectrometer and the other fraction to the selective detector.

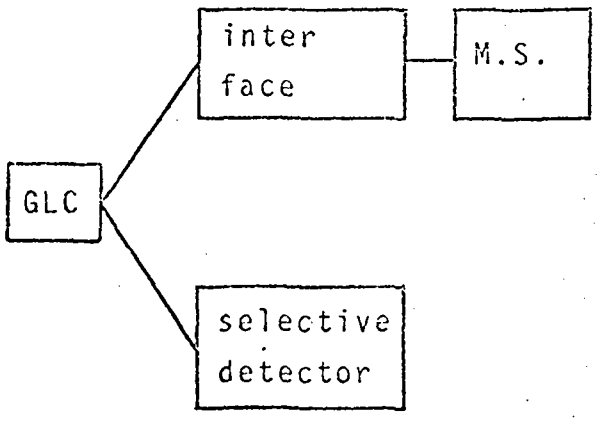


Fig. 2 A chlorogram of water of a sewer.

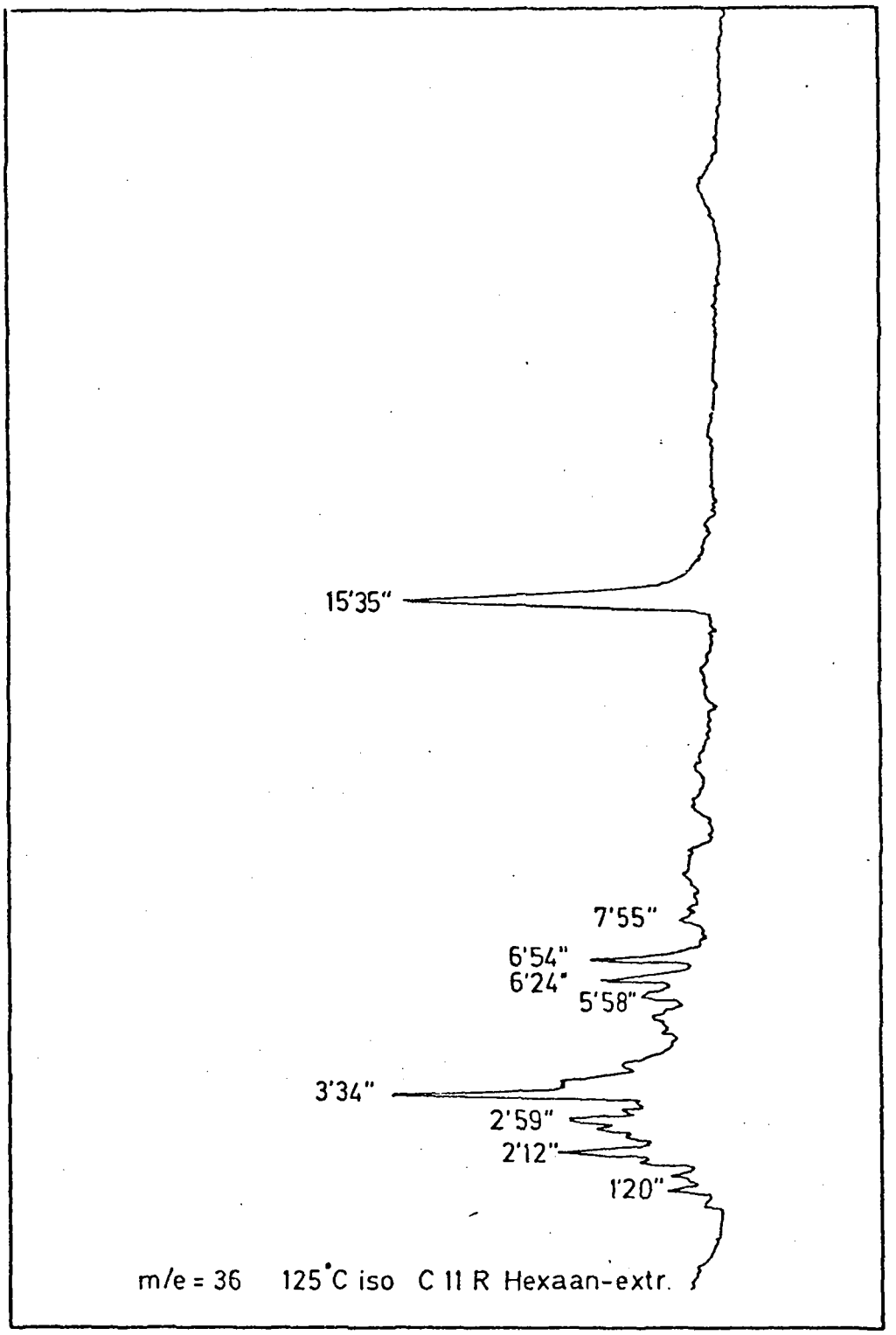


Fig. 3 A chlorogram of water of the Rhine River.
The gas chromatographic column was 30 m., and has an internal diameter of 0.45 mm. The phase was OV-101.

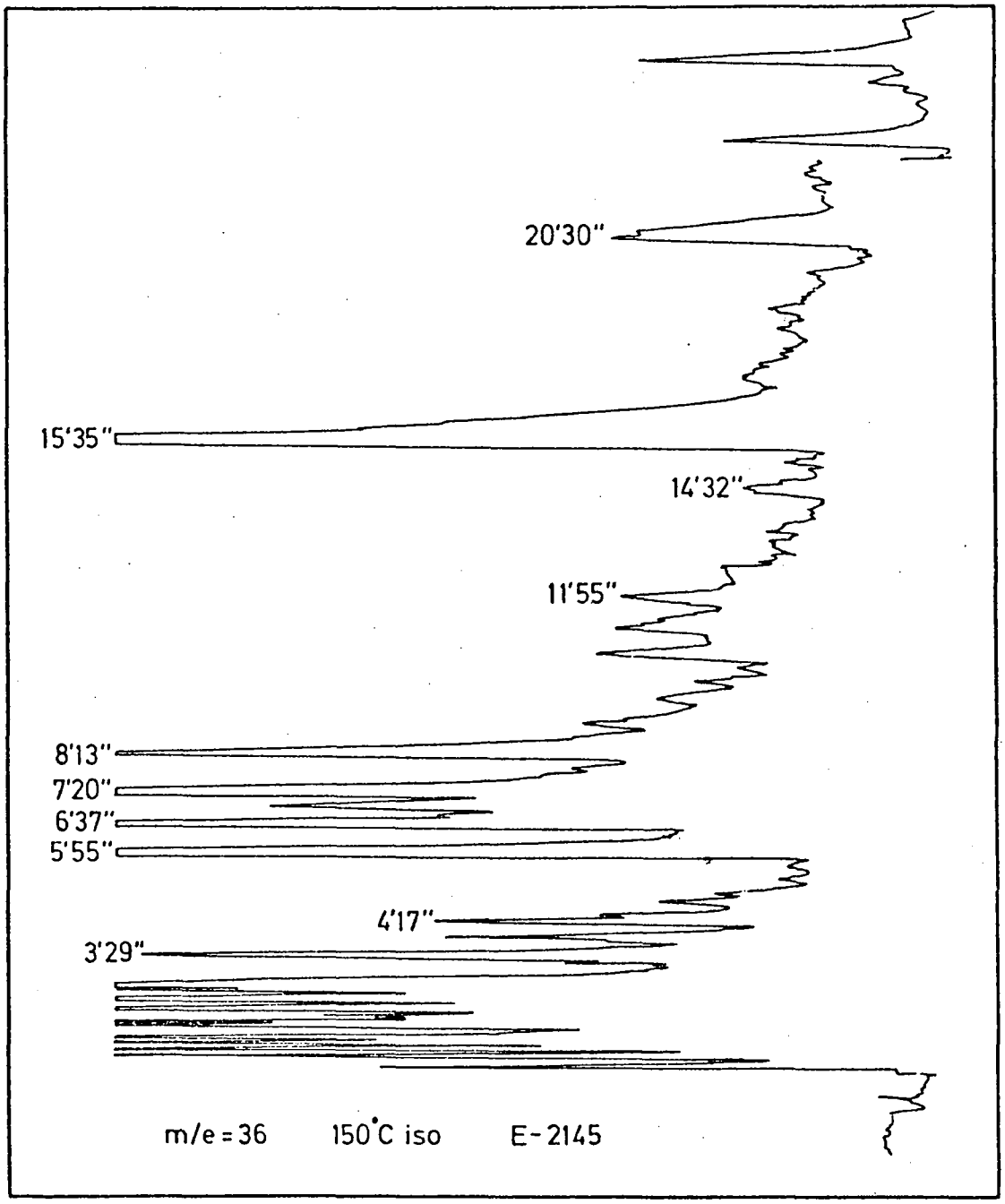


Fig. 4 A chlorogram of the same sample as in figure 3.
The chromatographic conditions were different; the temperature of the column was lower (100°C instead of 150°C). Only the first part of the chlorogram is observed here.

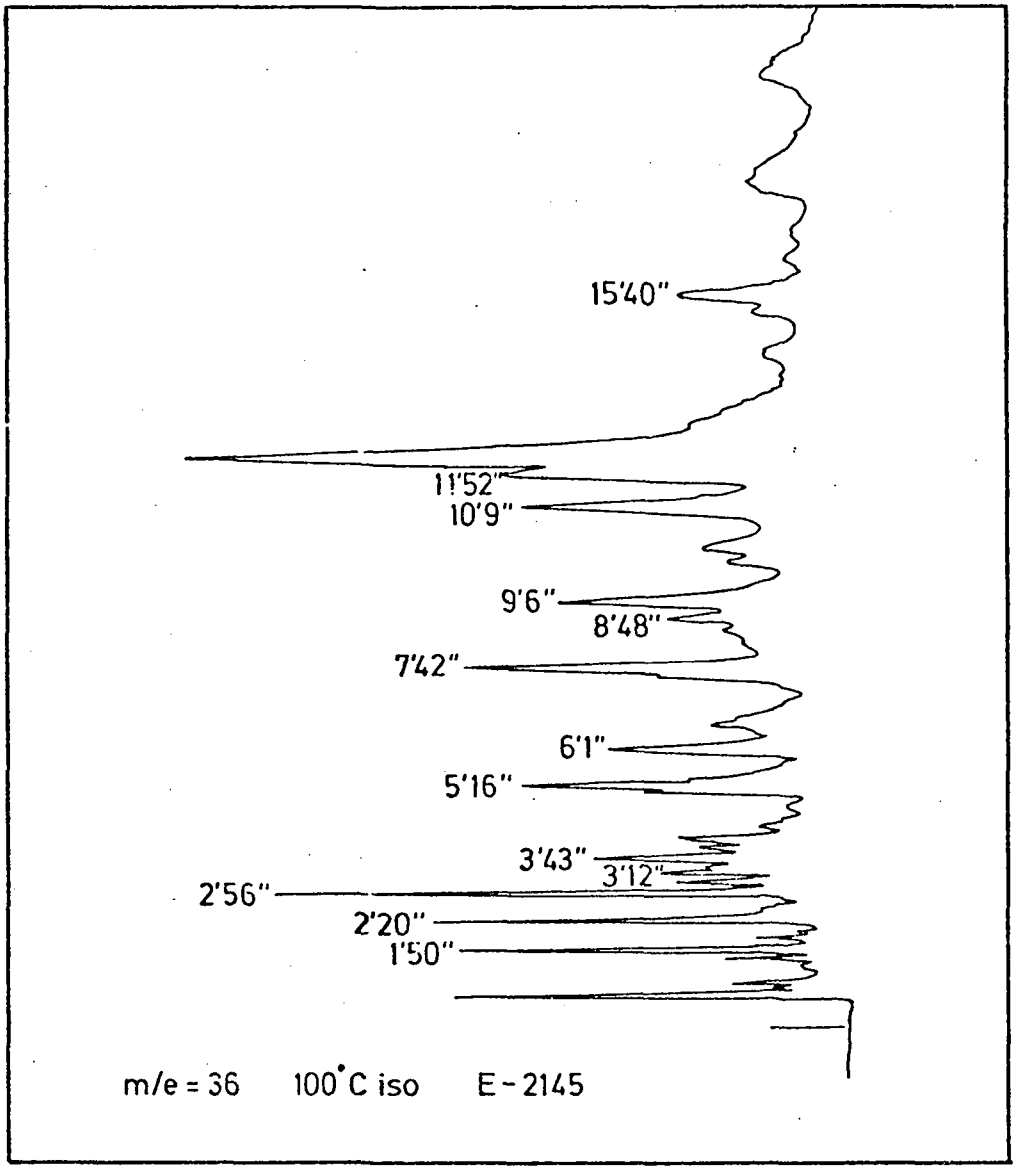


Fig. 5 Places in the Netherlands where samples were taken for the mass spectral library of surface waters.

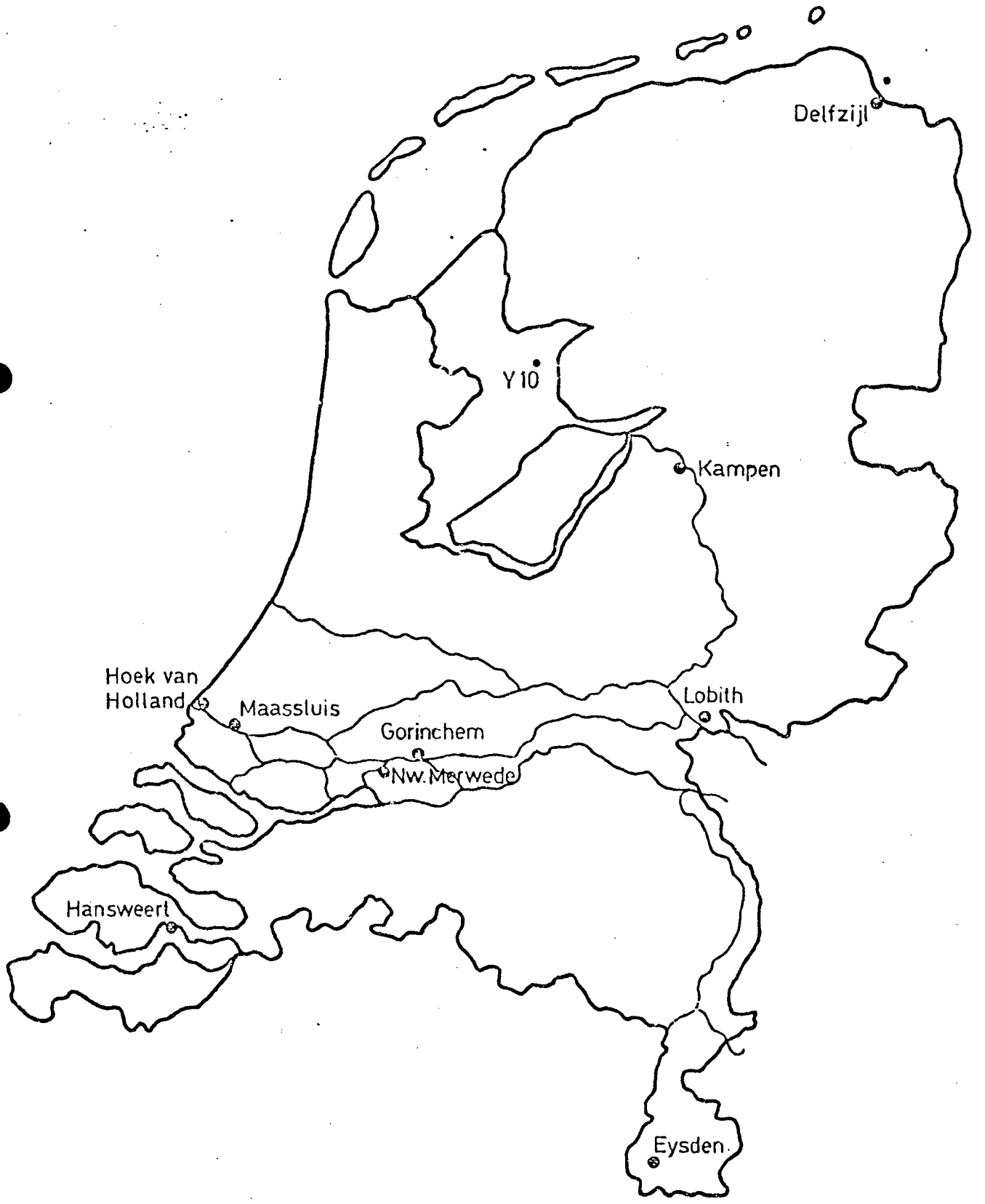


Table I

Chlorinated compounds identified from the chromatogram of the sewer sample (see also fig. 2)

C_6H_5OCl	chlorophenol (2 isomers)
$C_6H_3OCl_3$	trichlorophenol
$C_6H_2OCl_4$	tetrachlorophenol
C_6HOCl_5	pentachlorophenol
C_6HCl_5	pentachlorobenzene
$C_7H_5OHBrCl$	monochloro-monobromo cresol
C_6HOHCl_3Br	trichloro-monobromo phenol
C_6Cl_6	hexachlorobenzene
C_7H_6OHCl	monochloro cresol
C_8Cl_8	octachlorostyrene
C_8HCl_7	heptachlorostyrene (2 isomers)

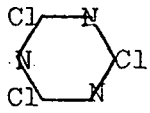
Table II

Brominated compounds identified from the chromatogram of the sewer sample (see also fig. 2).

$C_7H_5OHBrCl$	monochloro-monobromo cresol
C_6H_5OBr	monobromophenol (2 isomers)
C_7H_6OHBr	monobromo cresol
$C_6H_2OHBrCl_2$	monobromo-dichloro phenol

Table III

Chlorinated compounds identified from the chromatogram of the Rhine River (see also figures 3 and 4).

C_6H_6NCl	monochloro-aniline
$C_6C_3Cl_3$	trichlorobenzene
$C_6H_5NCl_2$	dichloro-aniline
$C_6H_2Cl_4$	tetrachlorobenzene
$C_6H_3OCl_3$	trichlorophenol
$C_7H_7NCl_2$	dichloro-toluïdine
$C_3H_6N_3Cl_3$ *	
$C_7H_5OCl_3$	trichlorocresol
C_6Cl_5H	pentachlorobenzene
C_6Cl_6	hexachlorobenzene
C_6H_6O	pentachlorophenol
C_4Cl_6	hexachlorobutadiene

* matched within 1 ppm.

Identification of Organic Compounds in Drinking Water from Thirteen U.S. Cities

by

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INTRODUCTION

The idea that it is desirable or necessary to specifically identify the individual organic compounds present in drinking water is rather recent. The embryo of this concept can be found in the records of a 1964 conference on pollution of interstate waterways of the Lower Mississippi River and its tributaries, called by the U.S. Secretary of Health, Education and Welfare. One of the recommendations of that conference was to establish a committee to direct and advise in the identification and abatement of all sources of pollution affecting the Lower Mississippi River. By 1967 consumer complaints of "oily" and "chemical" flavors in the drinking water of New Orleans and nearby communities were occurring with increasing frequency. Fish caught below Baton Rouge, LA were no longer saleable because of these same bad tastes. On March 23, 1967 Dr. Leslie L. Glasgow, Chairman of the Louisiana Stream Control Commission, wrote to the Commissioner of the U.S. Federal Water Pollution Control Administration requesting technical assistance in obtaining specific information on the effects of the presence of organic chemicals on water quality and aquatic life in the Mississippi and Calcasieu Rivers. The first step was to identify the compounds

present in the rivers. Work was begun in 1969 and culminated with a report[1] in 1972 in which forty-six organic compounds were listed as being present in the raw or treated water supplies from three water plants (Carrollton plant of New Orleans, Jefferson #2 at Marrero and the U.S. Public Health Service Hospital at Carville). An additional forty-four compounds not detected in the three water plants were identified in wastewaters from ten industrial plants that discharge into the Mississippi River just above New Orleans.

In July 1974, representatives of the State of Louisiana and the City of New Orleans requested the Region VI Environmental Protection Agency (EPA) administrator to undertake an analytical survey of the organic chemicals present in the finished water of three New Orleans area water plants (Carrollton, Jefferson #1, and Jefferson #2). Samples were taken in August 1974, extracted by EPA's R. S. Kerr Environmental Research Laboratory in Ada, OK, and analyzed by the Water Supply Research Laboratory, Cincinnati, Ohio and by the Analytical Chemistry Branch of the Athens, Georgia Environmental Research Laboratory. On November 8, 1974, a preliminary report[2] was released by the U.S. EPA that listed sixty-six organic chemicals identified in the finished water of the three New Orleans area water plants with concentrations that ranged in most cases from 0.01-5 ug/liter. The USAEC--Ames Laboratory at Iowa State University added six more compounds to the list, and through additional research at the Athens

Environmental Research Laboratory another twenty-eight compounds were identified, raising the total identifications to ninety-four.

Simultaneously with the release of the New Orleans preliminary report, the U.S. EPA announced plans for a National Organics Reconnaissance Survey (NORS) of water supplies of representative cities across the nation to determine the identity, concentrations and potential effects of chemicals in these drinking waters. Eighty cities were selected for analysis of six halocarbons in their raw and finished water supplies. Both raw and finished water were studied in order to correlate the presence of the haloforms with either the raw water source or the chlorination treatment. Ten of these same cities were chosen as sites for a more comprehensive survey of the organic content of finisned drinking waters. An interim report to Congress[3], discusses the preliminary results of the eighty city survey and five of the comprehensive analyses.

The Analytical Chemistry Branch of the Athens Environmental Research Laboratory analyzed the three New Orleans area carbon chloroform extracts (CCE's) in 1974 and the ten-city CCE's of the 1975 comprehensive National Organics Reconnaissance Survey. The results of the analyses from these thirteen water plant CCE's (Table 1) are the subject of this paper.

Table 1. Drinking Water Supply Sources

Source Character	Water Plants
Miss. R. at New Orleans	1. Carrollton (City of New Orleans) 2. Jefferson Parish #1 (east bank) 3. Jefferson Parish #2 (west bank)
Uncontaminated Upland Water	1. Seattle, WA. 2. New York, N. Y.
Ground Water	1. Miami, FL. 2. Tucson, AZ.
Contaminated by Agricultural Runoff	1. Ottumwa, IA. 2. Grand Forks, N. D.
Contaminated by Industrial Waste	1. Cincinnati, OH. 2. Louisville, KY.
Contaminated by Municipal Waste	1. Philadelphia, PA. 2. Terrebonne Parish, LA.

SOURCE

SAMPLING

Detailed descriptions of the sampling procedures appear elsewhere.[2,3] A variety of sampling procedures were used at New Orleans because this was the first place studied and because the best method of concentrating a wide variety of organic compounds present in trace amounts in water was not--and still is not--known.

At each New Orleans water plant, triplicate one liter samples of finished water were extracted in separatory funnels with two ml of tetralin. The extract was sealed in septum vials at the plant site. If extraction of very volatile components (e.g. chloroform, benzene) was quantitative, a 500 fold concentration factor would be achieved. A small peak from chloroform was detected. In EPA laboratories tetralin extraction has since been supplanted by the Volatile Organics Analysis (VOA technique because the latter is a superior method for concentrating trace amounts of very volatile organics from water.

Volatile Organics Analysis, accomplished by purging the water sample with helium, adsorbing the compounds on a small column of Tenax or Chromosorb 103 and then thermally desorbing them onto a gas chromatographic column, was carried out by the EPA's

Cincinnati Water Supply Research Laboratory and is covered in a later chapter.

Adsorption of the compounds in the New Orleans water supplies with XAD-2 resin was carried out by Mr. Gregor Junk, USAEC-Ames, Iowa State University, Ames, Iowa according to his established technique.[5] The eluates from these resin columns were analyzed at both the Athens and the Ames laboratories. Thirty-six of the ninety-four compounds identified were found in the resin eluates[6] and six of these were found only by Junk.

Three types of carbon adsorption units were used in the New Orleans study but only one--the CAM sampler--was used in the 10-city National Organics Reconnaissance Survey (NORS). The CAM sampler is a 3 inch diameter by 18 inch long glass cylinder that contains about 3/4 lb of granular activated carbon. In the New Orleans CAM samplers used for the "70 year" CCE's, the coarse carbon was used on each end of the column as a filter and holder for the fine mesh carbon. Two CAM samplers were always connected in series at each of the sites. The second type of carbon adsorption unit used was the Mega-sampler. It consisted of two large columns connected in series; each column holds about 22 pounds of carbon. The third type of unit used was the Mini-sampler, a

small polyvinyl chloride tube that holds about 70g (0.15 lbs) of 14 x 40 mesh activated carbon.

The Mega-sampler was only used at the Carrollton water plant; 300,000 gal of water was passed through it over a 7 day period. The CAM samplers were used at all three New Orleans water plants. A so-called "70-year" sample was collected over a 7 day period (25,500 liters) and represents the amount of water a person would theoretically drink in 70 years at the rate of 1 liter/day. The Mini-sampler was used at the three New Orleans water plants; a 2 month equivalent (60 liters) sample was collected over a 2 day period.

Sampling was much less extensive for the 10 cities in the NORS; 6000 liters of water were passed through two CAM samplers in series over a 7 day period.

Appropriate blanks were prepared for every method of sample concentration used, including separate adsorbent/solvent blanks for each of the carbon and resin extracts. These blanks were examined for interfering background components by both gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

carried to the Athens Environmental Research Laboratory in teflon bottles.

The Mini-samples were dried and extracted at EPA's Region VI Laboratory Facility in Houston, Texas. One half of these "2 month" CCE's were mailed to the Athens Environmental Research Laboratory.

Upon receipt of each of these extracts they were concentrated further in Kuderna-Danish and Micro-Snyder column evaporators (Figures 1 and 2); the final volume was adjusted with a gentle stream of nitrogen so that 1 microliter of the extract corresponded to 1 liter of water passed through the carbon or XAD resin filter (e.g. the NORS CCE's were concentrated to a volume of 6.0 ml since 6,000 liters of water was passed through the carbon filters). The extracts from the respective carbon and resin blanks and each of the solvent blanks were all concentrated to volumes equivalent to their corresponding sample extracts. An exception to this procedure was the Mini-samples. We received half of the "2 month" extracts and these were each concentrated to 0.3 ml so that 1 ul corresponded to 100 milliliters of water passed through the carbon filter. Blank extract volumes were adjusted accordingly.

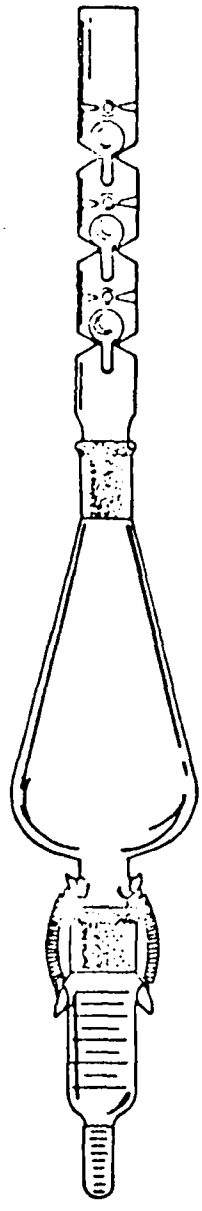


Figure 1. Kuderna-Danish Evaporator

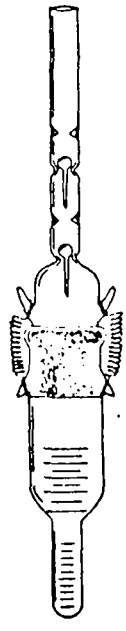


Figure 2. Micro-Snyder Column Evaporator

PRE-ANALYSIS FRACTIONATION

Organic analyses were performed using concentrated extracts from carbon and XAD-2 resin adsorption columns. Various attempts were made to fractionate the extracts to improve subsequent GC peak separation--most of these were unsuccessful. For example, TLC (silica gel : benzene) could be used to separate the mega-sample into three distinct fractions. However GC-MS of these separate fractions gave no identifications that were not also made by direct GC-MS of the original extract. The TLC separation had been attempted because it is particularly recommended for isolation of polynuclear aromatic hydrocarbons; in this case it was wasted effort.

Aliquots of the mega-sample CCE, the Carrollton "70-year" CCE, and their respective blanks were analyzed by the EPA organochlorine pesticide method.[7] This procedure involves fractionation by column chromatography on florsil with detection by electron capture GC. The presence of dieldrin and endrin, as determined by this technique, was confirmed by matching GC retention times with standards on two other GC columns of varying polarity. Further confirmation, as well as detection of chlordene,

α-chlordane, and pentachlorophenyl methyl ether, was obtained by GC-MS analysis of the appropriate fractions. With the exception of dieldrin, these compounds were present at concentrations too low for GC-MS detection using the total extracts. Dieldrin was detected in the total extracts only after searching for characteristic peaks by limited mass range mass spectral techniques. The Jefferson #1 and Jefferson #2 "70 year" CCE's were successfully analyzed by electron capture GC for the detection and measurement of endrin without prior fractionation.

Other attempts were made to improve GC peak separation by various types of fractionation. Steam distillation neatly separated the mega-sample CCE into volatile distillables and non-distillables, but did little to improve actual peak separation without major adjustment of GC conditions. Solubility extraction of the CCE into strongly and weakly acidic, basic, and neutral fractions served only to show that most of the compounds are neutral. Fortunately, extract fractionation was not necessary for qualitative or even quantitative analysis. Computer controlled GC-MS analysis, with computer manipulation of acquired data, allowed identification of compounds by direct injection of CCE's.

QUALITATIVE AND QUANTITATIVE METHODS

Instrumentation

Gas chromatography of the New Orleans CCE's was performed using a Varian 1400 GC with a flame ionization detector (FID). A 10 ft x 1/8 in I.D. glass column was packed with 3% SP-2100 on 80-100 mesh Supelcon AW/DMCS. Helium was used as a carrier gas at 20 ml/min and the temperature was programed from 40-280°C at 6°/min after an initial 6 minute hold at 40°. Similar conditions were used to obtain mass spectra on the Finnigan 1015 GC-MS system.

The "70 year" Carrollton CCE was rechromatographed on a 30 meter by 0.4 mm I.D. glass capillary column coated with Supelco SP-2100. The column was prepared at the Athens Environmental Research Laboratory. Replacement of the Gohlke separator in the Finnigan 1015 GC-MS with a 9 inch stainless steel capillary tube enabled direct connection of the glass capillary column with the mass spectrometer. Improved chromatographic separation (Figure 3) and enhanced sensitivity of this arrangement led us to use the capillary column with all the following CCE's from the 10-city comprehensive NORS.

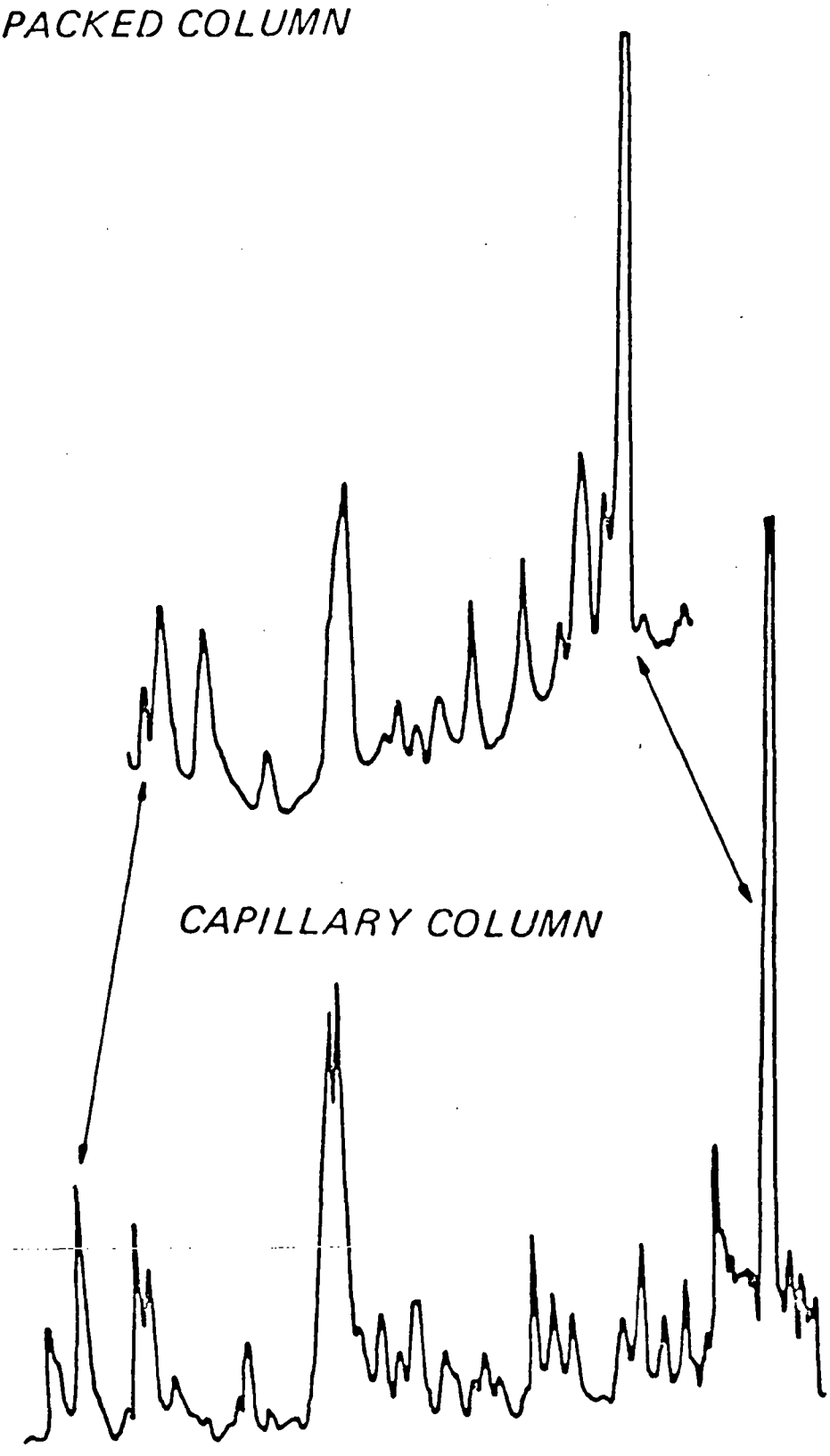


Figure 3. Comparison of a portion of the GC traces from the Carrollton "70 year" CCE using (Top) a conventional packed column and (Bottom) a glass capillary column. The stationary phase is SP-2100 in both examples.

Sample injection size was reduced from the 2.0 ul used with the packed column to 0.4 ul on the capillary column; no injection splitter was used with the latter. Chromatographic conditions for GC-MS analyses using the capillary column were modified and included multiple temperature and carrier gas (helium) flow programing. Injection was made with the GC oven door open, the column at room temperature (about 30°C), and the pressure in the mass spectrometer ion chamber at 1.5×10^{-5} torr. The GC oven door was closed 5 minutes after injection and the temperature was slowly increased to about 50°C over the next 6 minutes. At 11 minutes after injection the oven temperature controller was set at 60°C. Two minutes later temperature programming at 2°/min was started. Twenty-three minutes after injection (80°C) the temperature program rate was increased to 6°/min and carrier gas flow was increased to produce a pressure of 2.8×10^{-5} torr in the ion chamber (previously determined to correspond to a helium flow of 2 cc/min at room temperature). Thirty-three minutes after injection (130°C) the temperature program rate was increased to 10°/min. The final temperature of 250°C was maintained for 20 minutes.

Computer-controlled collection of mass spectral data was begun immediately after sample injection. To prevent

filament damage as solvent entered the MS, the ionization current was shut off 2.5 minutes after injection and turned on again 3.5 minutes after injection. Electron energy was maintained at 70 eV and filament current at 400 ua. The Finnigan 1015 mass spectrometer was connected by a System Industries System 150 interface to the PDP-8/e computer. A mass spectrum from m/e 41 to 350 was acquired approximately every 2.5 seconds under control of the computer.

Chemical ionization mass spectrometry (CIMS) was performed on selected components in the Carrollton "70 year" CCE with a separate computerized Finnigan 1015 mass spectrometer interfaced to a Finnigan 9500 GC using methane as the carrier/reactant gas. The same PDP-8/e computer was used for data acquisition.

Some initial GC-MS work was done on a Varian MAT CH5/DF system interfaced to a Varian 2740 GC via a dual Watson-Bieman separator and to a Varian SS-100 Data System. This instrument was later used in the New Orleans study for determination of empirical formulae of the major fragments in the mass spectra of alachlor and the alachlor chlorine homolog and for confirmation of the atrazine empirical formula.

A computerized Digilab FTS-14D/IR Fourier transform infrared spectrophotometer equipped with the Digilab GC-IR accessory and interfaced to a Perkin-Elmer 990 GC was used to confirm the presence of alachlor and atrazine in the Carrollton Mega-sample CCE.

Method of Identification

At the end of GC-MS data acquisition a computer-reconstructed gas chromatogram (RGC) is plotted. This is a recording of the ion current summation of each mass spectrum, i.e. the mass spectrometer is being used as a GC detector. The first step is to compare the RGC with the FID GC that was used to optimize chromatographic conditions. Although there is no correlation between the mass spectrometric ionization efficiency and the flame ionization response factors, correlation of the medium and large peaks in the two chromatograms is usually readily apparent. The RGC and FID chromatograms for the Carrollton "70 year" CCE are shown in Figure 4. Peaks are numbered to correspond with the alphabetical listing of compounds in Table 4.

Programs, raw data and reduced data are stored on Diablo discs. Mass spectra of interest are plotted, with

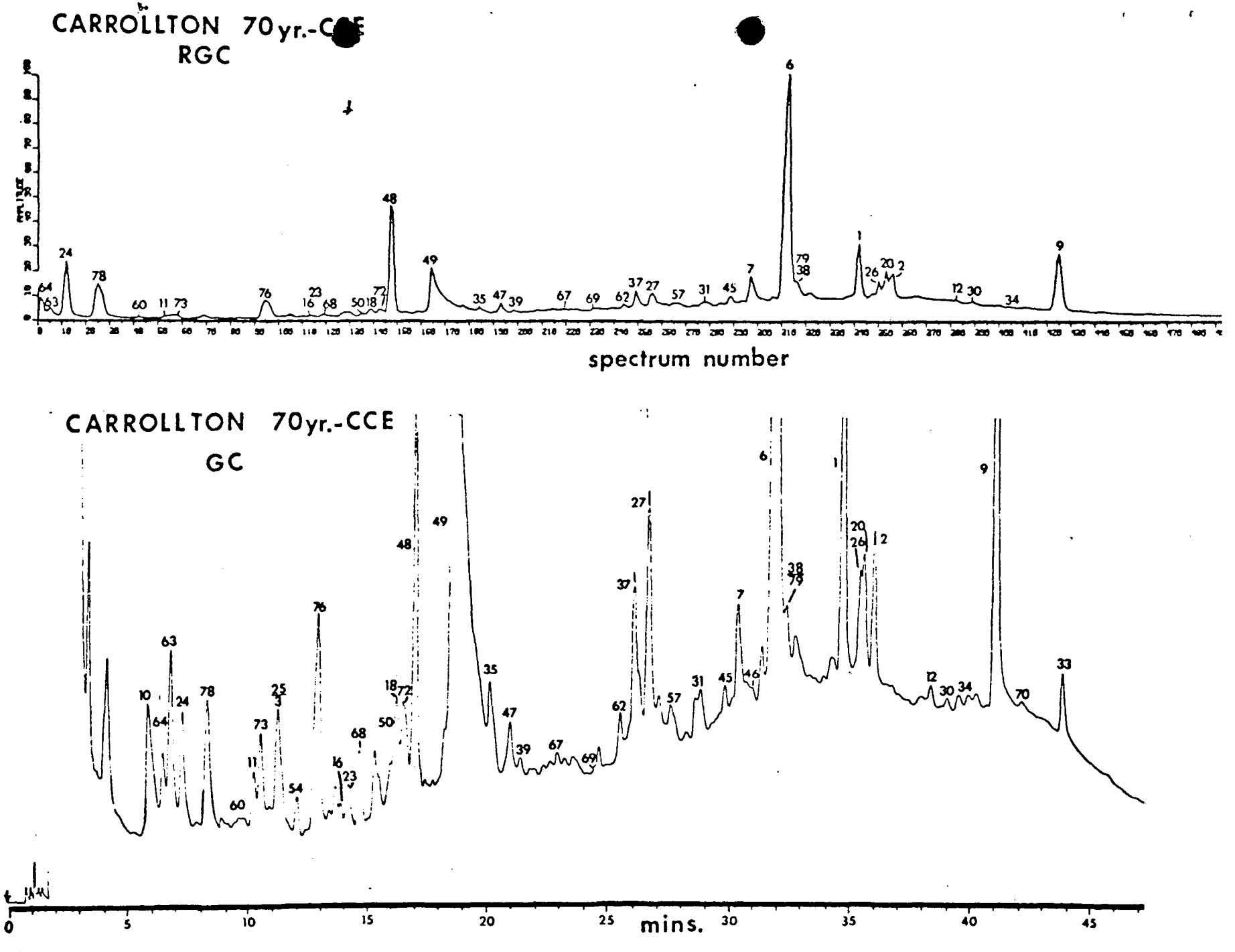


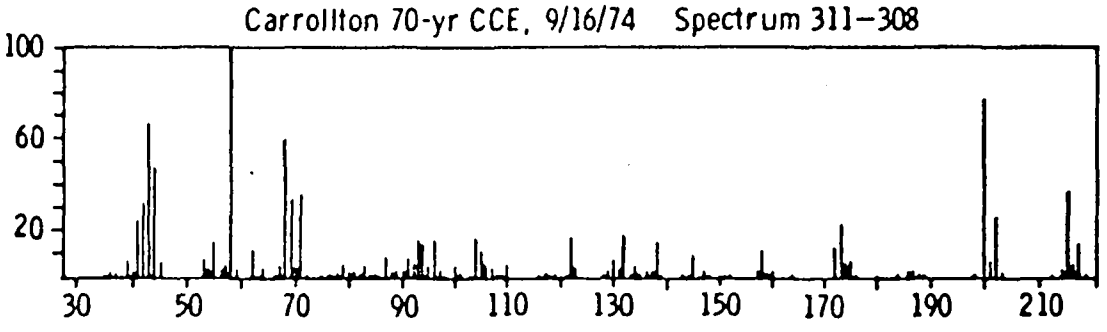
Figure 4. (Top) Reconstructed gas chromatogram (RGC) and (Bottom) FID gas chromatogram (GC) from the Carrollton "70 year" CCE. Numbers correspond to compounds in Table 4.

appropriate subtractions to remove background mass spectral peaks, using either a cathode ray tube (CRT) with an auxillary hard copy unit or a Houston plotter.

Since each environmental sample usually has large numbers of chromatographic peaks (often a hundred or more) computer matching of spectra is employed as the first method of identification. Computer-abbreviated spectra are sent via direct acousticoupler-telephone connection[8] to a larger computer that presently contains the EPA library of about 40,000 abbreviated mass spectra. The list of matches is returned within minutes with the best match presented first and the others following in descending order of Similarity Index (SI), which is a measurement of the degree to which the sample spectrum matches the library spectrum.

An example of this computer aided identification is shown in Figure 5. At the top is the plot of Carrollton "70 year" CCE mass spectrum No. 311 with No. 308 chosen as the background spectrum and subtracted from it (refer to compound number 6 in Figure 4-top). In the middle of Figure 5 is the computer match. There were only 3 hits (matches) with corresponding Similarity Indexes of 0.555, 0.122, and 0.103. Generally, a SI of 0.4 or greater is considered to be a fairly reliable tenative identification, especially

SAMPLE SPECTRUM



COMPUTER MATCHING

3 Hits
Atrazine (SEWL)
File key–8671
SI–0.555

Methyl 3-oxooctadecanoate 312 C19 H56 03
File key–6524
SI–0.122

1-Methyl-4-(1,2,3,4-tetrahydro-2-naphthyl)piperazine 230 C15 H22 N2
File key–4842
SI–0.103

Cost of search: 0.36

COMPUTER REFERENCE SPECTRUM

File key? 8671
2-Chloro-4-ethylamino-6-isopropylamino-6-triazine (Atrazine) (SEWL)-T6
N CN EnJ BMY CM2 FG-215 C8 H14 Cl N5 BSR 0186

m/e	INT	m/e	INT	m/e	INT	m/e	INT	m/e	INT
27	37	28	38	43	86	44	46	55	13
58	100	68	41	69	29	79	3	87	5
93	13	94	10	104	10	105	6	122	8
130	3	132	10	137	5	147	2	158	5
172	6	173	13	174	3	175	3	200	33
201	2	202	10	215	14	216	2	217	3

Figure 5. (Top) Mass spectrum of Carrollton "70 year" CCE, spectrum No. 311 minus No. 308; (Middle) computer match of this data -- 3 hits; (Bottom) print out of Atrazine's abbreviated spectral data that corresponds to the "best hit".

when, as in this instance, the next best match has a very low SI. The tentatively identified compound is always visually checked against a reference mass spectrum either from the data bank (as shown at the bottom of Figure 5), our files, other compilations of spectra (such as the Aldermaston Eight Peak Index of Mass Spectra[9]), or the scientific literature. However, the tentative identification is never considered confirmed until it has been verified by comparison of two different physical measurements of a standard (usually the GC-MS spectrum and GC retention time) obtained on our instruments under similar operating conditions. In this paper, compounds that have been confirmed by this definition are marked with an asterisk in tables where they are listed.

When there is no reasonable computer match (or when it has been determined that the sample compound does not correspond to any of the computer matches) the identification must be made by "manual" spectral interpretation. Often supplementary information from high resolution gas chromatography-mass spectrometry (GC HRMS), chemical ionization gas chromatography-mass spectrometry (GC CIMS) or gas chromatography Fourier transform-infrared spectroscopy (GC-IR) is necessary to make tentative identifications from spectral interpretations. Examples of

these identifications are discussed in a later section of this chapter.

Searches for compounds by mass spectral fragments that are specific, or at least indicative of them is a helpful routine. Figure 6 shows a portion of the Carrollton "70 year" RGC and a limited mass RGC (LMRGC) based on m/e 277, one of the fragments in a characteristic chlorine isotope cluster in the mass spectrum of dieldrin. The dieldrin peak in the RGC was so small that it could not be located until it was enhanced by the limited mass search.

Methods of Quantitation

Two methods of quantitation were used. The New Orleans samples were quantitated using GC peak areas and the NORS samples were quantitated using RGC peak areas. Each has advantages and disadvantages.

A Perkin-Elmer PEP-1 Data System, interfaced to a Varian 1400 GC operated under the conditions described above, was used for computerized GC quantitation and retention time measurements. Since atrazine was present in all extracts of New Orleans samples, it was chosen as an

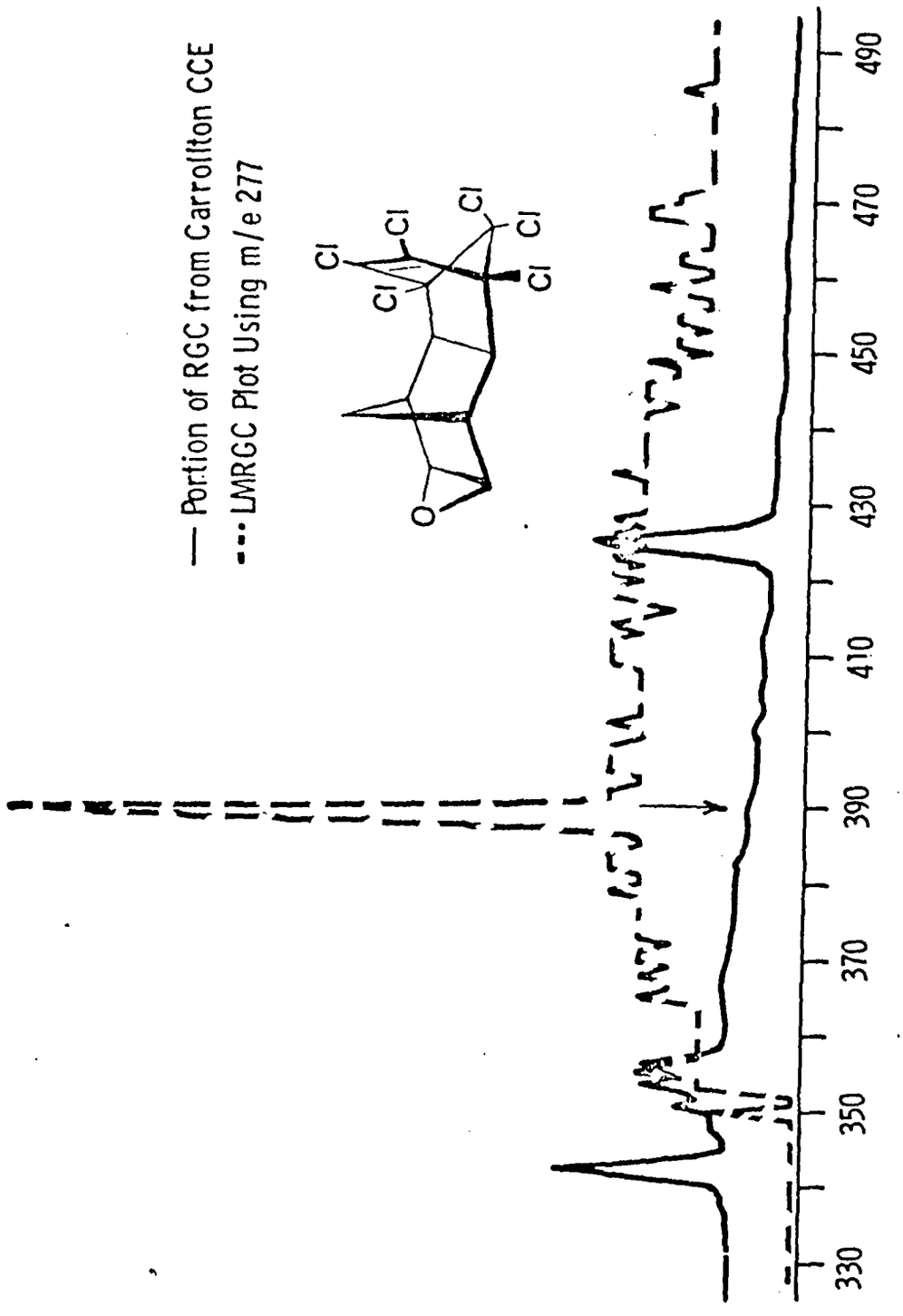


Figure 6. RGC of a portion of the Carrollton "70 year" CCE with an LMRGC of m/e 277, one of the characteristic ion fragments of dieldrin, superimposed above it. The dieldrin peak is greatly enhanced.

internal standard. A stock solution of 5 parts-per-thousand of atrazine (99.7% pure) in chloroform was the internal standard for quantitation of all identified pollutants for which standards were obtained. Solutions of known amounts of pure reference compounds were prepared and mixed with a known amount of the atrazine reference stock solution. Mixtures were designed so as to obtain good GC peak resolution. The atrazine was assigned a flame response factor (RF) of 1.000 and, since its concentration was known, the computer system was able to calculate the RF, as well as the relative retention time (to atrazine), of each standard.

After tentative identification of pollutants by GC-MS, a PEP-1 computer program was written for the GC-computer analysis of each extract, allowing the computer to use the known flame responses to calculate pollutant concentrations (Figure 7). The concentrations of the concentrated extract are expressed in g/liter which corresponds to µg/liter in the original water samples since the concentration factor is 1 million times. In some cases, the RF calculated for one standard was also used for other compounds of the same chemical class. The relative retention times, calculated for all pollutants and printed out by the computer, were then manually compared with those of the available standards. The blanks had to be dosed with atrazine as an internal standard, since atrazine was absent from them.

RUN 1 12: 37.9 9/ 9/ 74 CCE 1 CARROLTON

INST 4 , GC METHOD 42 , GC FILE 55 :

TIME	AREA	RRT	RF	C	NAME
3.48	1.4457	.107,	1.000,	.8987,	!
4.26	1.0659	.132,	1.000,	.6626,	!
5.40	.0066	.167,	1.000,	.0041,	!
5.95	.7198	.184,	1.000,	.4474,	!
6.59	.2873	.204,	1.319,	.2356,	112-TRICHLORØETHANE:
6.89	.7331	.213,	.214,	.0975,	TØLUENE:
7.38	.4588	.228,	2.380,	.6788,	CHLØRØDIBRØMEMETHANE:
7.99	.0368	.247,	1.000,	.0229,	!
8.42	.5926	.261,	2.500,	.9209,	DICHLOROIODOMETHANE
9.01	.0438	.279,	1.000,	.0272,	!
9.75	.0554	.302,	1.000,	.0345,	!
9.96	.0464	.308,	1.000,	.0288,	!
10.35	.1933	.320,	4.738,	.5694,	BRØMØFØRM:
10.64	.3883	.329,	.208,	.0502,	M- ØR P-XYLENE:
11.03	.0783	.342,	1.000,	.0487,	!
11.37	.6423	.352,	1.642,	.6556,	C2H2CL2BR2, Ø-XYLENE:
12.22	.1120	.378,	.184,	.0128,	NØNANE:
13.10	1.1664	.406,	1.000,	.7250,	UNK MW 145:
13.58	.0677	.421,	1.000,	.0421,	!
13.83	.1578	.428,	.217,	.0213,	P-ET TØL ØR PRØP BZ:
14.06	.0668	.435,	.957,	.0398,	BIS-2-CL-ET ETHER:
14.38	.1710	.445,	.184,	.0196,	BRANCHED DECANE:
14.85	.2593	.460,	.240,	.0387,	TRIMETHYL BZ ISØMER:
15.49	.3321	.480,	.184,	.0380,	DECANE, UNK ARØM:
16.15	.1760	.500,	.316,	.0346,	LIMØNENE:
16.39	.5249	.508,	.557,	.1817,	BIS-2-CL-1PR ETHER:
16.69	.5580	.517,	.184,	.0638,	BRANCHED UNDECANE:
17.18	1.5324	.532,	1.635,	1.5575,	HEXACHLØRØETHANE:
17.62	.0975	.546,	1.000,	.0607,	!
17.95	.0707	.556,	1.000,	.0439,	!
18.65	8.2608	.578,	.298,	1.5302,	ISØPHØRØNE:
20.32	.5689	.630,	.278,	.0983,	DIHYDRØCARVØNE:
21.16	.3025	.656,	.866,	.1629,	HEXACHLØRØBUTADIENE:
21.59	.0696	.669,	.184,	.0080,	DØDECANE:
21.95	.0418	.680,	1.000,	.0260,	!
22.54	.0380	.698,	1.000,	.0237,	!
22.80	.0557	.706,	1.000,	.0346,	!
23.09	.0980	.715,	.184,	.0112,	TRIDECANE:
23.42	.0692	.726,	1.000,	.0431,	!
23.75	.1090	.736,	1.000,	.0678,	!
24.36	.0017	.755,	1.000,	.0011,	3-M-3-Ø-6-H-TRIAZINE:
24.84	.0895	.770,	1.000,	.0556,	!
25.72	.2123	.797,	.184,	.0243,	TETRADECANE:
26.28	1.0357	.814,	.412,	.2653,	DIMETHYLPHTHALATE:
26.90	1.1325	.834,	.310,	.2182,	DI-T-BU-BENZØØUINØNE:
27.36	.2777	.848,	1.000,	.1726,	!
27.85	.2404	.863,	.184,	.0275,	PENTADECANE:
28.52	.0273	.884,	1.000,	.0170,	!
28.89	.1072	.895,	1.000,	.0667,	!
29.11	.1895	.902,	.314,	.0370,	DIETHYLPHTHALATE:
30.12	.2243	.933,	.416,	.0580,	CL7 NØRBØRNENE:
30.65	.7836	.950,	1.000,	.4871,	DE-ETHYL ATRAZINE:
31.65	.2206	.981,	.416,	.0571,	CL7NØRBØRNENE ISØMER:
32.25	7.7993	1.000,	1.000,	4.8480,	ATRAZINE:
32.66	.3798	1.012,	.314,	.0741,	DIPRØPYL PHTHALATE:
33.07	.3955	1.025,	1.000,	.2459,	!
33.64	.0662	1.043,	1.000,	.0412,	!
34.23	.0254	1.061,	1.000,	.0158,	!
34.54	.1663	1.071,	1.000,	.1034,	!
35.02	1.7922	1.085,	.715,	.7965,	LASSØ -- ALACHLØR:
35.76	.4150	1.108,	.314,	.0810,	DIBUTYL PHTHALATE:
35.91	.5095	1.113,	1.112,	.3522,	BLADEX:
36.34	.6254	1.126,	.715,	.2780,	LASSØ CL HØMØLØG:
36.84	.0641	1.142,	1.000,	.0398,	!
37.08	.1093	1.149,	1.000,	.0680,	!
38.31	.0644	1.187,	1.000,	.0400,	!
38.70	.1261	1.200,	.700,	.0549,	MACHETE:
39.37	.1122	1.220,	.613,	.0428,	DIELDRIN:
39.85	.1392	1.235,	.350,	.0303,	DIHEXYL PHTHALATE:
40.25	.1443	1.248,	1.000,	.0897,	!
40.56	.1976	1.257,	1.000,	.1228,	!
41.03	.0937	1.272,	1.000,	.0583,	!
41.37	3.1139	1.282,	.329,	.6368,	BENZYL BUTYL PHTHALA:
42.48	.7768	1.317,	.248,	.1198,	TRIPHENYL PHØSPHATE:
44.22	.4542	1.371,	.352,	.0994,	DI-2-ET HEXYL PHTHAL:

Figure 7. GC computer print-out for the Carrollton "70 year" CCE.

The advantage of the above method is that a standard is not needed for every compound identified. FID response factors for compounds with similar structures and functional groups are usually similar enough that a model compound can be used to determine response factors (e.g. once the response factor of 0.184 was determined for tridecane (Figure 7) it could be used for seven other normal and branched alkanes in the sample). Disadvantages of the above method are that careful correlation is required between the RGC and the FID GC peaks (sometimes a difficult task with minor components of complex mixtures) and a separate PEP-1 GC computer program must be generated for each sample.

A pair of System Industries GC-MS peak quantitation routines called QNTATE and QNTSET were used for the ten NORS samples. Data acquisition on standard compounds is made under the same conditions as data acquisition of the samples. A computer file containing information from the standard runs is established using the System Industries QNTSET program. The beginning, end and maximum of each peak (using spectrum numbers from the RGC), the quantity (expressed in nanograms) of the corresponding compound and its name are entered into the QNTSET file. Next, the QNTATE program is called into execution. The beginning, end and maximum spectrum numbers of the sample peak is specified along with information pertaining

to the standard peak in the QNTSET file with which the sample peak is to be compared. For each sample peak the computer prints out the name of the compound and the amount present (expressed in nanograms). Peak areas in both QNTSET and QNTATE programs are computed with baseline subtracted. The user specifies the spectral limits of the peak and the computer then assumes that the baseline connects the first spectrum before the starting value and the first spectrum after the terminating value.

Advantages to the QNTSET/QNTATE method of quantitation are ease and speed in setting up the standard files and direct comparison of the raw data in the computerized sample files with the same type of data in the standard files. Comparison of peaks from an RGC with peaks from a FID gas chromatogram is eliminated. Disadvantages are that sensitivity, calibration stability and base line may vary more over the time periods encountered between sample and standard runs (often several days) than these same parameters in a gas chromatograph. Also, the ionization efficiency of compounds of similar structure or with similar functional groups seems to vary more than the flame response factors using a FID.

Both methods require that standards and samples be run under identical conditions as far as possible. Best results

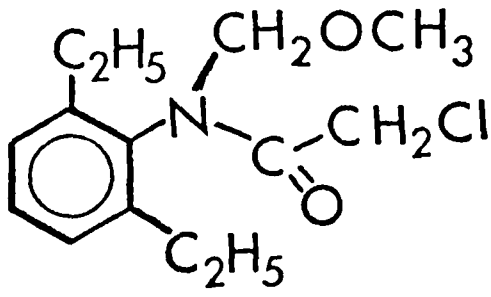
are obtained when samples and standards are run immediately after one another. In practice, of course, this is not usually feasable since standard runs cannot be made until the compounds in the sample are tentatively identified. Presumably once the standard mixture is prepared and run the sample could then be rerun. Since other factors in the overall analytical scheme such as efficiency of adsorption of the sample compounds onto the carbon and their desorption by chloroform were possibly of greater magnitude than the variation in quantitation conditions, this reanalysis was not considered to be worthwhile. The concentrations of the compounds reported are therefore only approximations and could vary from their true values by as much as a factor of 2. Since the adsorption, desorption and concentration steps are not likely to be 100% efficient most of the concentration values reported are probably lower than their true values.

RESULTS

Compound Identifications

Alachlor and its chlorine homolog

Alachlor (also known as Lasso and Lazo) is an acetanilide derivative introduced by the Monsanto Company in 1967 as a pre-emergence herbicide for use with soybeans, corn, cotton and peanuts. Its chemical name is 2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide (structure I). It does not give an easily discernible molecular ion by electron impact mass spectrometry (EIMS), and its spectrum was not in the computer data bank, which made its identification difficult.



I

The identification of this compound was particularly desirable since the size of its GC peak indicated that it was present in a relatively high concentration. Also, an associated peak in the gas chromatogram had a similar mass spectrum so one identification might lead to another. Chemical ionization mass spectrometry (CIMS), however, gave a characteristic molecular-ion-plus-one peak (m/e 270) (Figure 8). High resolution mass spectrometry (HRMS), obtained on the fly using the GC effluent, produced possible empirical formulae of the important mass fragments, including the molecular ion. These empirical formulae were correlated with reasonable fragmentation modes of the parent molecule, so that the most probable parent ion formula was deduced (Figure 8). Since other herbicides had been identified in the samples, a herbicide handbook[10] was searched for compounds having the appropriate molecular formula and structural characteristics. Alachlor was the only possibility. A standard of alachlor produced the same low resolution mass spectrum and GC retention time, confirming the identification.

The identity of alachlor was further confirmed by Fourier transform gas chromatography-infrared spectroscopy (see Figure 8), with a spectrum obtained on the fly from the Carrollton mega-sample extract. This spectrum matched that of the standard obtained in the same mode.

Ab Initio Identification of Alachlor

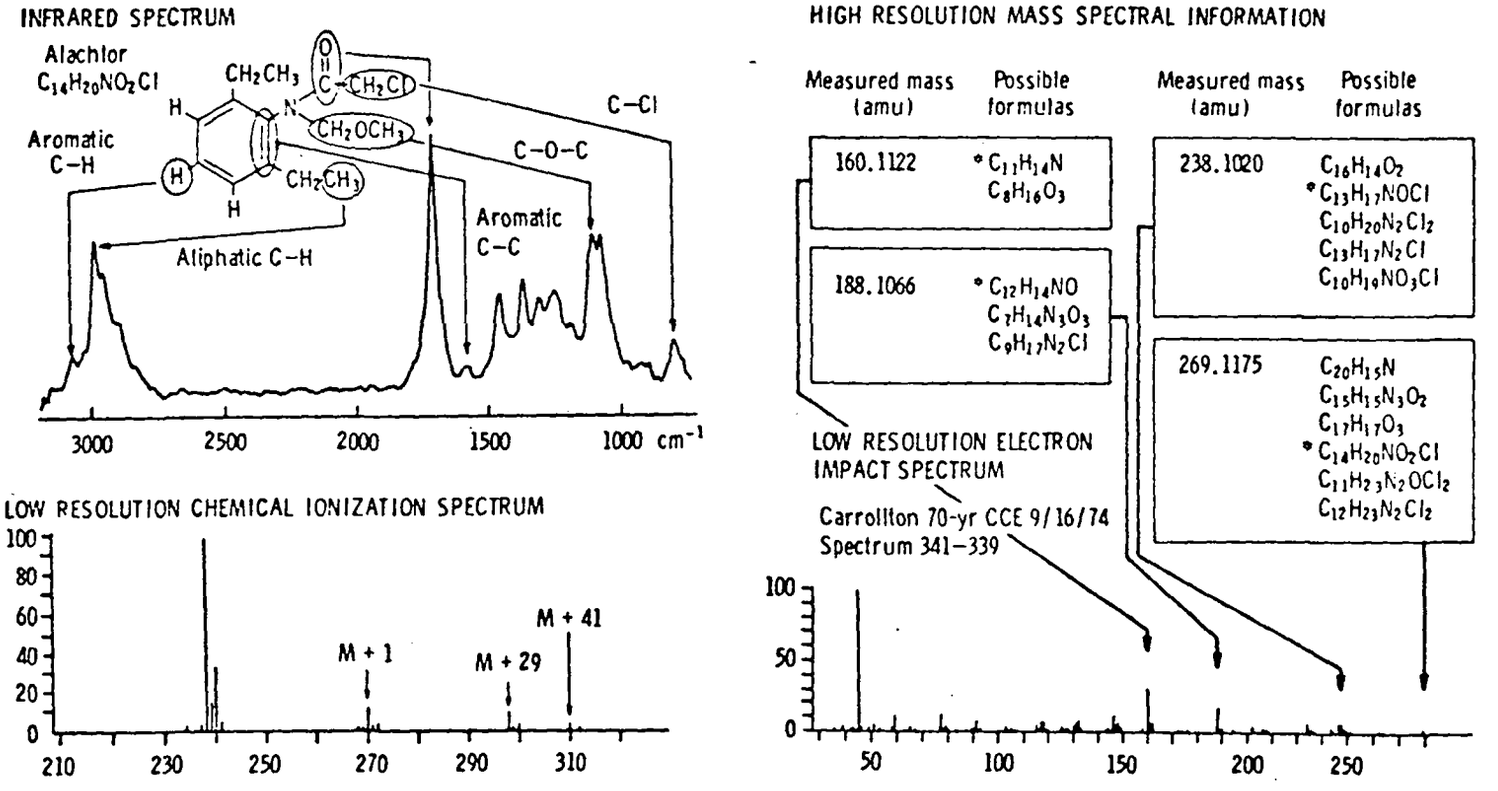
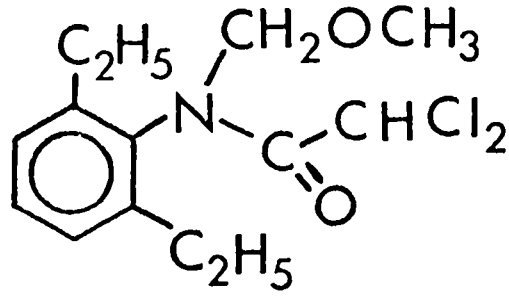


Figure 8. Spectra of alachlor in the Carrollton "70 year" CCE. Starred (*) formulas correspond to correct alachlor ion formulas.

The electron impact (EI) spectrum of the alachlor chlorine homolog (compound 2, Table 4) did not give a definitive molecular ion. Chemical ionization MS showed the molecular weight to be 303 and the chlorine isotope pattern indicated the presence of two chlorine atoms instead of one. Below m/e 188 the low resolution EI mass spectrum of this compound was similar to that of alachlor. The largest observable fragment was at m/e 272, which can be rationalized as loss of a methoxyl group as in the case of alachlor (Figure 9). The keys to the homolog's structure are the fragments at m/e 188 and 160. HRMS showed that they possessed the same empirical formulae as the m/e 188 and 160 fragments in alachlor's HRMS. The postulated structures giving rise to these alachlor fragments are shown in Figure 9. Loss of 84 mass units from fragment m/e 272 is caused by loss of CH_2Cl_2 and therefore identifies the position of the second chlorine atom as being on the same carbon as the single chlorine of alachlor. The Fourier transform GC-IR spectrum of this chlorine homolog was also very much like that of alachlor. On the basis of the above information the chlorine homolog was tentatively identified as 2,2-dichloro-2',6'-diethyl-N-(methoxymethyl) acetanilide (Structure II).



II

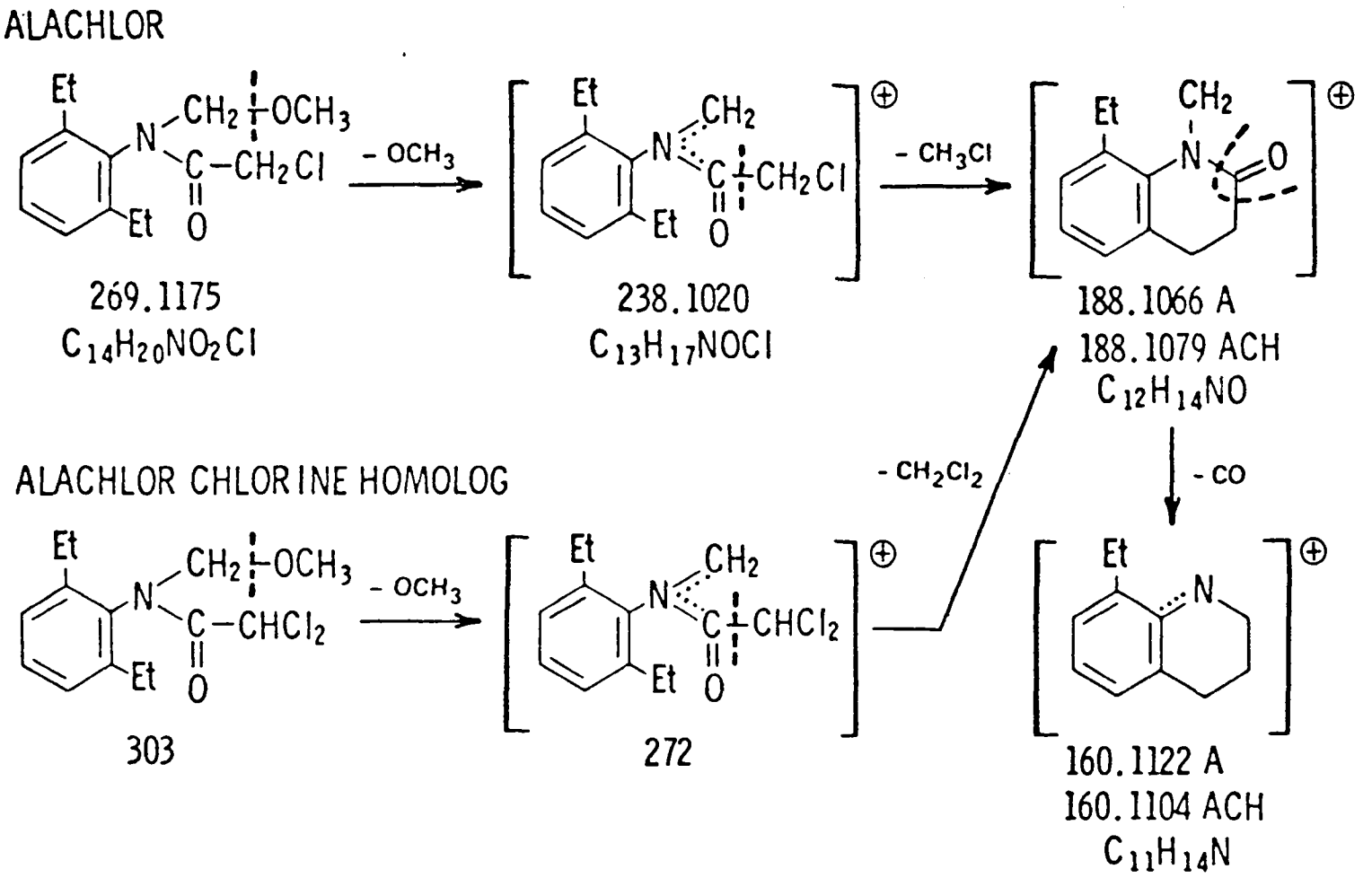


Figure 9. Proposed fragmentations of Alachlor (A) and Alachlor Chlorine Homolog (ACH).

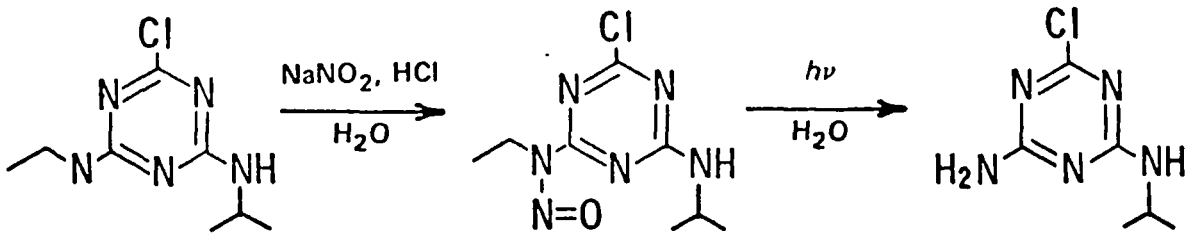
In an attempt to confirm the identification of the alachlor homolog and to determine whether it could have been produced during chlorination treatment of New Orleans drinking water, solutions of 5 mg/l alachlor in distilled water were treated with up to 138 mg/l of chlorine gas for 22 hours at room temperature. Two chlorinated compounds were formed, the concentrations of which were dependent upon the concentration of chlorine. The concentration of alachlor diminished correspondingly. The spectra of these compounds did not match that of the alachlor homolog found in the New Orleans water; they appeared to correspond to one and two chlorine additions to the aromatic ring of alachlor. Therefore the homolog is probably not formed by chlorination of alachlor in the New Orleans water supply; it could be a by-product of alachlor manufacture.

Deethylatrazine

Deethylatrazine (desethylatrazine) was found in New Orleans water only in samples collected by carbon adsorption, not in resin adsorption samples. Dealkylation appears to be the major mechanism involved in microbial degradation of alkyl substituted chloro-s-triazines.[11] However, microbial degradation produces both deethyl- and deisopropylatrazine. Similarly oxidative dealkylation by

free radicals produced both monoalkyl derivatives of atrazine plus the completely dealkylated products.[12,13] Limited mass range searches for the expected predominant fragments of deisopropylatrazine failed to yield any trace of this compound in the CCE's.

One possible explanation for the apparently exclusive formation of the deethyl product and none of the deisopropyl material was deduced from earlier experiments by other chemists at the Athens Environmental Research Laboratory.[14] Under synthetic reaction conditions involving atrazine (III) and sodium nitrite in water at 27°C with a low pH, only 2-chloro-4-(N-nitroso-N-ethylamino)-6-isopropylamino-s-triazine (IV, N-nitroso atrazine) was isolated. IV was stable in water at pH values greater than 4 and at 25°C. Surprisingly, it is highly photoreactive and was rapidly decomposed by UV light to deethylatrazine (V) and atrazine (III) in water. It was estimated that, near the surface of a water body, the half-life for photodecomposition of IV is less than 10 minutes throughout the United States. Experiments with IV under sunlight in both distilled water and water from a local river confirmed the calculated half-life.



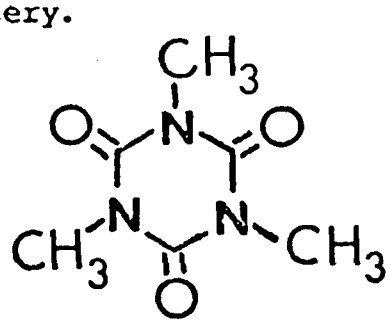
III IV V

Analysis for N-nitroso atrazine (IV) in the CCE samples by GC was unsuccessful since a standard of IV decomposed during gas chromatography under all conditions tried. Analysis for IV using limited mass range plots from the GC-MS data of the New Orleans CCE's was also unsuccessful. However, Fine et al. reported the possible presence of IV in the New Orleans CCE's on the basis of high performance liquid chromatography (hplc) chromatograms of the CCE's using a new Thermal Energy Analyzer (TEA) as a selective detector for N-nitroso compounds.[15] A N-nitroso atrazine (IV) standard matched the retention time of one of the twenty-four peaks in the hplc-TEA chromatograms of the New Orleans CCE's. Its concentration was estimated to be about 0.1 ug/l in the drinking water. An extract of water from the Mississippi River, although not concentrated as much as the CCE's, showed many of the same peaks in its hplc-TEA chromatogram including the one with the same retention time as IV. At present these data are only tenative and must remain so until the identity of each peak is confirmed. Preliminary analysis of the New Orleans CCE's by other chemists using liquid chromatography with a dual wavelength ultra violet (UV) detection system showed no detectable N-nitrosoatrazine (IV) down to the lower limit of 0.1 ug/l. It is possible that this is not contradictory to

Fine's tentative identification of IV since the estimated concentration was essentially at the threshold detection limit of the UV detection system. However, until the peaks observed with hplc-TEA are confirmed by unambiguous means (such as hplc-MS) the presence of N-nitrosoatrazine and other possible N-nitrosoamines should be considered with caution.

Trimethyl isocyanurate

A good computer spectral match (SI=0.509) for 1,3,5-trimethyl-2,4,6-trioxohexahydrotriazine (trimethyl isocyanurate, VI) was obtained for a small peak in the Carrollton CCE's. This same compound was also matched in the Cincinnati, Ohio CCE. No commercial source of VI was found so it was synthesized from cyanuric chloride by a published procedure.[16] The melting point, IR and mass spectra of the product matched reported values. The GC retention time and mass spectrum of VI matched the retention times and mass spectra of the tentatively identified compounds in the Carrollton and Cincinnati samples, thus providing confirmation of the identifications. At present the source of this compound in the two drinking water samples remains a mystery.



VI

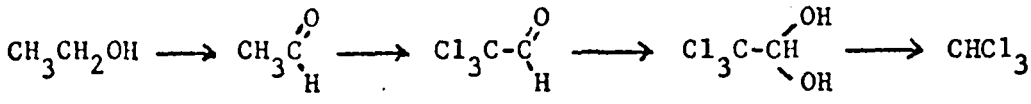
Chloral

Chloral (trichloroacetaldehyde) was found in the drinking water CCE's of six of the ten cities in the National Organics Reconnaissance Survey (Table 2). This frequent occurance leads to the postulation that its formation, like the haloforms, is from chlorination of other organic compounds during the addition of chlorine to the raw and/or finished drinking water. The reaction mechanism of chloral formation may be completely different from the predominant reaction mechanism of haloform production. An indication that chloral is a by-product of treatment rather than a contaminant in the raw water from industrial sources (it is a widely used monomer for copolymerizations) is its presence in the drinking water from the two cities that obtain their water supplies from uncontaminated upland water (New York City and Seattle). Chloral in water forms chloral hydrate.[17]

Chloral hydrate ("knockout drops") is a hypnotic drug sometimes used as a sedative and is considered "highly toxic".[18] The LD50 for oral injestion by rats is 285 mg/kg.[19] Chloral hydrate applied to the skin of mice (4-5% solutions in acetone) resulted in skin tumors in 4 of 20 of

the animals.[20] The highest concentration reported here for chloral in drinking waters is only 5 ug/l (Table 2).

Chloral can be synthesized by chlorinating ethanol, acetaldehyde, polyethylene glycol, ethylene chlorohydrin, chloroacetaldehyde and bis(2-chloroethyl) ether.[17] Bellar et al postulated the formation of chloral (VII) and chloral hydrate (VIII) as intermediates in the reaction mechanism involving conversion of ethanol to chloroform.[21]



Ethanol Acetaldehyde Chloral Chloral Hydrate Chloroform

VII VIII

Rook[22] has since demonstrated that chlorination of natural humic substances in raw waters (specifically structures containing the polyhydroxybenzene moiety) is the primary source of haloforms in drinking waters although the reaction mechanism remains to be explained.

Chloral was not identified in any of the NORS samples analyzed by the inert gas stripping technique refered to as Volatile Organics Analysis (VOA). To determine if chloral (which exists as chloral hydrate in water) could be stripped from water under conditions similar to those used for VOA[23],

Table 2. Concentration of Chloral Found in Drinking Water Supplies

Drinking Water	Conc. (µg/l)
Philadelphia, PA	5
Seattle, WA	3.5
Cincinnati, OH	2
Terrebonne Parish, LA	1
New York City, N. Y.	0.02
Grand Forks, N. D.	0.01

chloral hydrate was prepared at a concentration of 1 ug/ml in Ultra Pure Reagent Grade Water (New England Reagent Laboratory, East Providence, RI). Five ml of this solution was used to spike 500 ml of water previously stripped with nitrogen for 20 minutes at a temperature of 95°C. The spiked solution, containing chloral hydrate at 10 ug/l (twice the highest concentration of chloral found in the 13-city survey), was stripped again at 95° and the volatiles were trapped on Tenax resin.[23] Thermal desorption and analysis by GC-MS failed to reveal any trace of chloral, although chloroform was identified. Therefore, inert gas stripping is not a suitable technique for isolating and concentrating chloral from water prior to GC or GC-MS analysis.

Chloral hydrate is known to decompose in neutral, acidic and basic solutions to produce chloroform.[17] At a pH of 8 and temperature of 35°C its half-life is 2 days.[17] To determine if the failure to detect chloral by the VOA technique was due to its rapid decomposition rather than its high polarity, we conducted a kinetic study of chloroform formation from chloral hydrate in Ultra Pure Reagent Grade Water at 90°C. The results using direct aqueous injection/flame ionization detector are shown in Figure 10 and summarized in Table 3. After 24 hours only about 2% of

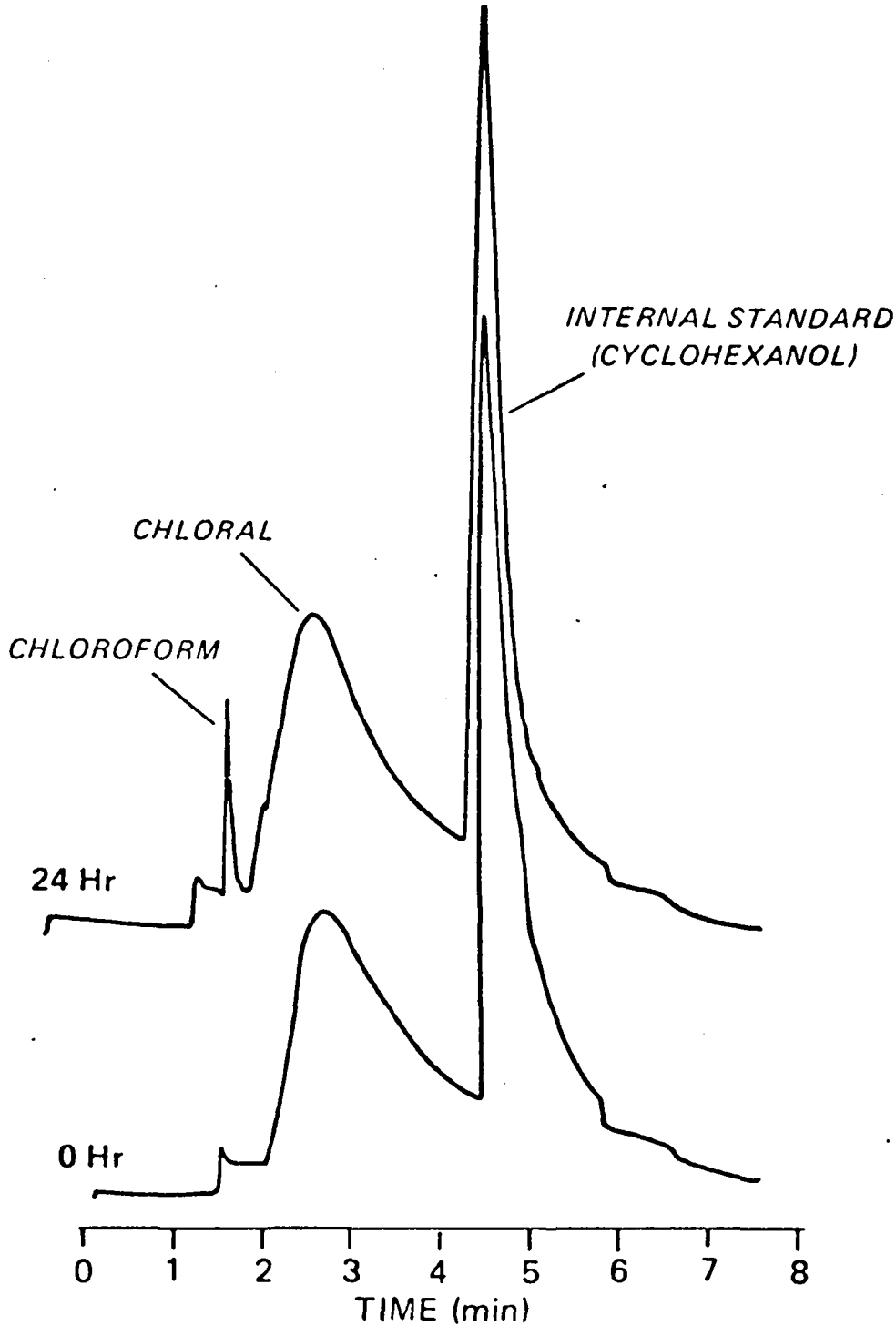


Figure 10. GC of aqueous chloral hydrate at 0 hours and after 24 hours at 90° C. GC conditions: direct aqueous injection, isothermal at 65° C, 30 m x 0.4 mm glass capillary column coated with SP-2100.

Table 3. Kinetic Study of the Formation of Chloroform from Chloral Hydrate

Time (hrs.)	Chloroform (mg/l)	Chloral (mg/l)
0	0.02	5.1
1-2	0.06	5.1
3-5	0.07	5.1
9-10	0.10	4.5
23-24	0.13	4.8

the chloral hydrate had decomposed to chloroform. Apparently chloral hydrate is so polar it simply doesn't appreciably strip out of aqueous solutions even at elevated temperatures.

Although these studies indicate a possible widespread distribution of chloral hydrate in drinking waters, a data base of thirteen samples is not sufficient to statistically confirm this distribution. Additional studies on the efficiency of chloral hydrate adsorption and desorption on both activated carbon and XAD resins, as well as its frequency of occurrance and its suspected production from chlorination treatment are needed.

Summary of Organic Compounds Found in CCE's of Thirteen Finished Drinking Water Supplies

Table 4 provides detailed information on the compounds identified in the three New Orleans area finished drinking waters. Table 5 lists the compounds identified in the 10-city National Organics Reconnaissance Survey CCE's. One hundred and nine different compounds were identified in the CCE's of these thirteen water supplies and eight more compounds were partially identified (e.g., alkylbenzene -C_4). Seventy percent of the identified compounds have been confirmed by comparison with standards.

A wide variety of chemical classes were present in these CCE's. Table 6 summarizes some of these.

Table 4. Compounds Identified in Carbon Chloroform and XAD Resin Extracts from Three New Orleans Drinking Water Plants.

(All concentrations are in ug/liter)

	COMPOUND	RRT[+]	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Notes
			70-Year[++] CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year[++] CCE	2-Month CCE	Resin Extract	70-Year[++] CCE	2-Month CCE	Resin Extract	
1	Alachlor* (Lasso®) [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide]	1.09	0.82	1.9	0.44	0.67	2.3	2.9	0.35	2.1	1.4	0.17	c,d,f,g,h,i,
2	Alachlor, one additional chlorine homolog [2,2-dichloro-2',6'-diethyl-N-(methoxymethyl) acetanilide]	1.14	0.28	1.7	0.18	0.21		P		0.05	P		d,f,gh i
3	Alkylbenzene-C_2 (m-xylene or p-xylene)	0.35	0.03	7.5	0.05			5.6			6.2		
4	Alkylbenzene-C_3 (p-ethyltoluene or n-propylbenzene)	0.42		2.4	0.01			1.9		0.03	2.2		
5	Alkylbenzene-C_4	~0.52	<0.1			J							g
6	Atrazine* (2-chloro-4-ethylamino-6-isopropylamino-s-triazine)	1.00	4.9	3.7	2.7	1.0	5.2	4.8	0.64	5.4	3.2	0.18	c,d,e,f,g,h,i,j
7	Atrazine, deethyl* (2-chloro-4-amino-6-isopropylamino-s-triazine) (desethylatrazine)	0.96	0.51	0.78	0.22		0.27	0.80		0.27	0.75		c,g

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT 70-Year++ CCE	CARROLLTON WATER PLANT 2-Month CCE	CARROLLTON WATER PLANT Mega-Sample CCE	CARROLLTON WATER PLANT Resin Extract	JEFFERSON #1 WATER PLANT 70-Year++ CCE	JEFFERSON #1 WATER PLANT 2-Month CCE	JEFFERSON #1 WATER PLANT Resin Extract	JEFFERSON #2 WATER PLANT 70-Year++ CCE	JEFFERSON #2 WATER PLANT 2-Month CCE	JEFFERSON #2 WATER PLANT Resin Extract	Notes
8	Benzaldehyde*	0.44			0.03								h
9	Benzyl butyl phthalate*	1.29	0.64	1.4	0.24		0.83	1.8		0.75	1.6	0.08	g,h
10	Bromodichloro-methane	0.18	P			<0.1			<0.1				b
11	Bromoform*	0.32	0.57										b,g
12	Butachlor* (Machete®) [2-chloro-2',6'-diethyl-N-(butoxymethyl)-acetanilide]	1.21	0.05		0.02	<0.1	0.06			0.05			g,h
13	Butyl octyl maleate*					J			J				
14	α-Chlordane				<0.1(T)								h
15	Chlordene*				<0.1(T)								h
16	bis-2-Chloroethyl ether*	0.44	0.04				0.16			0.12			g
17	Chloroform*												a,b
18	bis-2-Chloroisopropyl ether*	0.51	0.18		P		0.08			0.03			g,h
19	m-Chloronitrobenzene*					J			J				

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT 70-Year++ CCE	CARROLLTON WATER PLANT 2-Month CCE	CARROLLTON WATER PLANT Mega-Sample CCE	CARROLLTON WATER PLANT Resin Extract	JEFFERSON #1 WATER PLANT 70-Year++ CCE	JEFFERSON #1 WATER PLANT 2-Month CCE	JEFFERSON #1 WATER PLANT Resin Extract	JEFFERSON #2 WATER PLANT 70-Year++ CCE	JEFFERSON #2 WATER PLANT 2-Month CCE	JEFFERSON #2 WATER PLANT Resin Extract	Notes
20	Cyanazine* (Bladex®) [2-(4-chloro-6-ethylamino-s-triazin-2-ylamino)-2-methylpropionitrile]	1.13	0.35		<0.01		0.21			0.31			g,H
21	DDE*[2,2-bis-(p-chlorophenyl)-1,1-dichlorcethylene]					0.05(J)			0.05(J)				
22	n-Decane*	0.48		2.4	0.06			2.0			2.0		d
23	Decane, branched	0.44	0.02	5.8	0.03			5.4			5.2		
24	Dibromochloromethane*	0.23	1.1	<10	0.6	<0.1	0.4		<0.1	0.06	P		b,d,g
25	Dibromodichloroethane isomer	0.35	0.33		0.16					0.63			g
26	Dibutyl phthalate*	1.12	0.10		0.09	0.05	0.36		0.01	0.23		0.03	e,f,g
27	2,6-Di-t-butyl-p-benzoquinone*	0.84	0.22				0.21			0.25			
28	m-Dichlorobenzene*	0.46		<3					<0.1				f
29	Dicyclopentadiene*								J				
30	Dieldrin*	1.23	0.04		0.01	0.01(J)	0.07		0.01(J)	0.05			g,h
31	Diethyl phthalate*	0.91	0.03	0.24	0.02	J	0.03	0.10	0.03	0.01	0.18		e,f,g,h

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Notes
			70-Year++ CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	
32	Di-(2-ethylhexyl) adipate*	1.32			0.10								
33	Di-(2-ethylhexyl) phthalate*	1.38	0.10	0.40	11	0.05	0.46	0.50	J	0.27	1.2	0.16	d,f,g
34	Dihexyl phthalate	1.24	0.03			0.05						0.16	g
35	Dihydrocarvone	0.63	0.14				0.06			0.07			
36	Diisobutyl phthalate*	1.06		<1	0.59	<0.05							f
37	Dimethyl phthalate*	0.83	0.27	0.60	P		0.13	0.82		0.18	0.74		c,f,g
38	Dipropyl phthalate*	1.02	0.07		0.01		0.13			0.14			g
39	n-Dodecane*	0.67	0.01	0.10				0.40			0.37		
40	Endrin*	1.27 (1st peak)			0.004 (T)		0.008 (T)			0.006 (T)			
41	Ethyl acetate					P						P	
42	Ethylbenzene	0.32		2.3	0.02			1.6			1.8		
43	o-Ethyltoluene*	0.45					0.04			0.02			
44	m-Ethyltoluene*	0.42					0.05			0.02			

8h

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Notes
			70-Year++ CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	
45	1,2,3,4,5,7,7-Heptachloronorbornene*	0.94	0.06		0.03	0.02	0.07		0.04	0.07		0.01	d,f,g,h
46	Heptachloronorbornene isomer	0.98	0.06		0.02		0.04			0.04			g,h
47	Hexachloro-1,3-butadiene*	0.65	0.16	0.70	0.07	0.04	0.27		0.12	0.21		<0.01	d,e,f,g,h
48	Hexachloroethane*	0.53	4.3		0.39	0.03	0.19		<0.1	0.30			f,g,h
49	Isophorone*	0.60	1.6	2.9			2.8	<11		2.9	9.5		c,g
50	Limonene*	0.50	0.03										
51	Methyl benzoate*	0.58							<0.01				e
52	Methylnaphthalene								J				
53	Naphthalene*					J			J				
54	n-Nonane*	0.38	0.03	2.4				2.4			2.1		
55	Pentachloroethane*	~0.38				<0.1							
56	Pentachlorophenyl methyl ether				<0.1 (T)								
57	n-Pentadecane*	0.86	0.03					0.10	0.01		0.10	<0.01	

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Notes
			70-Year++ CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	
58	Propazine* [2-chloro-4,6-bis-(isopropylamino)-s-triazine]	~1.0			<0.1		<0.1			<0.1			
59	Simazine* [2-chloro-4,6-bis-(ethylamino)-s-triazine]	~1.0	<0.1			J	<0.1			<0.1			g
60	1,1,1,2-Tetrachloroethane*	0.30	0.04		0.11								
61	Tetrachloroethylene*	0.26		<1		<0.1	0.20	<5	<0.1	0.20	<5		b,g
62	n-Tetradecane*	0.80	0.02	0.10				0.10			0.12		
63	Toluene*	0.22		11	0.08		0.10	7.1	<0.01		12		b
64	1,1,2-Trichloroethane*	0.21	0.35	6.2	<0.2	<0.1	0.45	8.5	<0.1	0.41	6.4		
65	1,1,1-Trichloropropane	~0.07				<0.1							
66	1,2,3-Trichloropropane	0.36			<0.2								
67	n-Tridecane*	0.72	0.01	0.30				0.17			0.20		
68	Trimethylbenzene isomer	0.46	0.04	6.1	0.02	0.01		5.1		0.02	5.3		

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Note
			70-Year++ CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	
69	Trimethyl Isocyanurate*	0.73	0.01		0.01								c,g
70	Triphenyl phosphate*	1.31	0.12		0.03								h
71	n-Undecane*	0.58		2.5	0.03			<10			2.1		
72	Undecane, branched	0.52	0.06	5.3	0.04								
73	o-Xylene*	0.33	0.33	4.1	0.12			2.8			3.4		
74	Unknown chlorinated fluorinated hydrocarbon	0.78	<0.01			<0.1			<0.1			<0.1	
75	Unknown chlorinated fluorinated hydrocarbon	0.82	<0.01			<0.1			<0.1			<0.1	
76	Unknown compound, apparent MW 145	~0.40	<0.7		<0.3		<0.9			<0.9			g
77	Unknown dichlorinated compound MW 200	0.82			0.05								
78	Dichloroiodomethane	0.26	1.1		0.84		1.3			1.6			g,k
79	Unknown dichlorinated compound MW 249	~1.0	<0.04		<0.02		P			P			

Table 4 (continued)

	COMPOUND	RRT+	CARROLLTON WATER PLANT				JEFFERSON #1 WATER PLANT			JEFFERSON #2 WATER PLANT			Note
			70-Year++ CCE	2-Month CCE	Mega-Sample CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	70-Year++ CCE	2-Month CCE	Resin Extract	
80	Unknown phthalate	1.22			0.01								
81	Unknown phthalate	1.24			0.01								
82	Unknown phthalate	1.36			0.12								

* Confirmed by matching GC retention time and, in most cases, mass spectrum with that of a standard.

Blank spaces indicate that compound was not detected in that specific sample.

\+ Relative retention time (to atrazine); mostly determined by the GC computer system.

++ Concentration values for 70-year CCE compounds are sums of concentrations in CCE #1 (filter #1) and CCE #2 (filter #2).

J Detected only by Junk, USAEC-Ames Laboratory. Identified in the Carrollton or Jefferson No. 1 resin extracts by GC-MS, but not quantitated except for DDE and dieldrin. These compounds were not detected at SERL in the resin extracts.

P Present, usually in very low concentrations (<0.05 µg/l), but not quantitated due to interferences with other GC peaks or lack of a discernable GC peak (detected only by mass spectrometry).

T Detected only by Thruston at SERL by GC-MS after fractionation by column chromatography.

NOTES:

a Chloroform was identified at SERL only in the tetralin extract of the Carrollton water.
b These compounds were also identified at the Water Supply Research Laboratory, EPA, Cincinnati, by VOA analysis of the Carrollton water.
c Also identified in the Carrollton CAE.
d Also identified by Junk, USAEC-Ames Laboratory, in the Carrollton resin extract.

Table 4 (continued)

e Also identified by Junk, USAEC-Ames Laboratory, in the Jefferson #1 resin extract.

f Also identified by Melton at the Water Supply Research Laboratory, EPA, Cincinnati, by GC-MS analysis of a solvent extract of a 1 liter grab sample of the Carrollton water.

g Also identified by duplicate analysis of the Carrollton 70-year CCE using the Varian CH5/DF system.

h Also identified by GC-MS (Finnigan) analysis of the Carrollton mega-sample CCE after fractionation by TLC.

i Confirmed by high resolution mass spectrometry (only a structural indication in the case of compound #2).

j Confirmed by GC-Ft-IR.

k Identification based on a report received after this table was prepared (EPA Mass Spectrometer User's Group Newsletter No. 15, April 1975)--therefore not in alphabetical order.

® Registered trade names are given only as an aid to compound recognition, and do not indicate the source of the compound.

Table 5. Compounds Identified in Carbon Chloroform Extracts from Drinking Waters of 10 U. S. Cities.

(All concentrations are in ug/liter)

Compound	Cincinnati	Miami	Ottumwa	Philadelphia	Seattle	Grand Forks	Lawrence	N.Y. City	Terrebonne Parish	Tucson
1. Acetaldehyde*				0.1	0.1					
2. Acetone*					1.0					
3. Acetophenone*				1.0						
4. Atrazine*			0.1							
5. Bromodichloromethane*	1.0	4.5		1.0	0.1	0.6	0.6	1.3	2.0	
6. Bromoform*		1.5								3.0
7. t-Butyltoluene				0.01						
8. Camphor*	0.1	0.5	0.1		0.5					
9. Chloral* (trichloroacetaldehyde)	2.0			5.0	3.5	0.01		0.02	1.0	
10. Chlorobenzene*		1.0								
11. Chlorodibromomethane*	0.5	15		0.5		0.1	0.01	0.4	1.0	0.01
12. Chloropicrin* (trichloronitromethane)			0.05							
13. p-Chlorotoluene*		1.5								
14. Cumene* (isopropylbenzene)									0.01	
15. Cyclohexanone*			0.1							
16. Cymene isomer		0.1								
17. 2,6-Di-t-butyl-p-benzoquinone*		0.1								
18. Di-t-butyl ketone							0.02			
19. Di-n-butyl phthalate*		5.0	0.1	0.05	0.01		0.01		0.02	
20. o-Dichlorobenzene*		1.0								
21. m-Dichlorobenzene*		0.5								
22. p-Dichlorobenzene*		0.5								
23. Diethyl malonate*	0.01		0.1							
24. Diethyl phthalate*	0.1	1.0		0.01	0.01		0.04	0.01		
25. Di-(2-ethylhexyl) phthalate*		30		0.5			0.08		0.04	

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Table 5 Continued

Compound	Cincinnati	Miami	Ottumwa	Philadelphia	Seattle	Grand Forks	Lawrence	N.Y. City	Terrebonne Parish	Tucson
26. 1,4-Dioxane*							0.01			
27. Di-n-propyl phthalate		0.5								
28. 2-Ethylbutanal						0.02	0.04	0.05	0.01	
29. p-Ethyltoluene					0.05					
30. Hexachloro-1,3-butadiene*						<0.01				
31. Hexachloroethane*		0.5								
32. Isoamyl chloride								0.01		
33. Lindane* (γ-BHC)	0.01									
34. 2-Methyl-5-ethylheptane									0.01	
35. Methyl ethyl maleimide								0.02		
36. 5-Methylhexa-3-ene-2-one								0.07		
37. 3-Methyl-3-pentanal			1.0							
38. n-Nonane*								0.02		
39. n-Pentanal			0.5							
40. 2-Pentanone*			0.1							
41. n-Propylbenzene*	0.01	0.05								
42. n-Propylcyclohexane		0.2								
43. β-Santalene					0.01					
44. α-Terpineol*			0.5							
45. Tetrachloroethylene*	0.1	0.1				0.2	0.07	0.05		<0.01
46. 1,1,3,3-Tetrachloro-2-propanone* (tetrachloroacetone)	0.5	0.2		1.0						
47. Tetramethylbenzene isomer		0.2								
48. Tetramethyltetrahydrofuran isomer			0.5							
49. Tri-n-butyl phosphate*	0.05	0.5								
50. Trimethyl isocyanurate* (1,3,5-trimethyl-2,4,6-trioxo-hexahydrotriazine)	0.5									

* Identifications confirmed by matching mass spectrum and GC retention time of a standard with conditions identical to those under which data from the samples was obtained.

Table 6

Chemical Classification of Organics in the CCE's*

Chemical Family or Use	Compounds Present
Pesticides & associated compounds	8[a]
Herbicides & associated compounds	8[b]
Halogenated aliphatics	20
Chlorinated aromatics	7
Aliphatic hydrocarbons	10
Aromatic hydrocarbons	17
Plasticizers	14
Misc. compounds of industrial origin	21
Misc. compounds of possible natural origin	7
Partially identified compounds	5
Total	117

[a] α-Chlordane, chlordene, DDE, dieldrin, endrin, lindane, heptachloronorbornene and its isomer.

[b] Alachlor, alachlor chlorine homolog, atrazine, deethylatrazine, butachlor, cyanazine, propazine, and simazine.

* Also included in these data are the six compounds identified only by Gregor Junk and co-workers from XAD resin extracts of the New Orleans drinking water (DDE, butyl octyl maleate, m-chloronitrobenzene, dicyclopentadiene, napathalene and methylnaphthalene).

No polycyclic aromatic hydrocarbons (PAH's) or polychlorinated biphenyls (PCB's) were identified in any of these extracts. However, many of the compounds listed in Tables 4 and 5 have been identified previously in various industrial wastewaters.[24,25] It is our opinion that the majority of these chemicals come from industrial or municipal waste discharges although some of them may occur naturally in the water (e.g. acetone, dihydrocarvone, β-santalene); some may be produced by reaction of chlorine with other chemicals (e.g. chloroform, dichlorobromomethane, bromodichloromethane, bromoform, dichloroiodomethane and perhaps, chloral hydrate); and some may originate from agricultural runoff (e.g. dieldrin, endrin, lindane, atrazine, alachlor etc.).

Recovery Studies

Recoveries from Carbon Filters in Series

Quantitative results in Table 4 for the "70 year" CCE compounds are sums of the amounts recovered from two CAM carbon filters in series--filter #1 and filter #2. Table 7 gives for each compound that was present at a concentration $\geq$0.04 ug/l the percent of the total concentration that was recovered in each of the two filters for the Carrollton "70 year" sample.

Of the 29 compounds in Table 7, 24 were collected on filter #1 to the extent of 96% or more, indicating quantitative adsorption on carbon (but not necessarily quantitative recovery). These 24 include a wide variety of compounds, indicating a generally high degree of adsorption. However, there are exceptions. Three trihalogenated methanes or ethanes were adsorbed to the extent of only 64 to 85% on filter #1, and more hexachloroethane was found on filter #2 than #1.

Table 7.

Percent of Compounds Recovered from Carrollton Seventy-Year Filters No. 1 and No. 2 in Series

Compound	*Total concentration (µg/l)*	*Percent from Filter No. 1*	*Percent from Filter No. 2*
Alachlor	0.82	97	3
Alachlor homolog	0.28	100	0
Atrazine	4.9	98	2
Atrazine, de-ethyl-	0.51	96	4
Benzyl butyl phthalate	0.64	100	0
Bromoform	0.57	100	0
Butachlor	0.05	100	0
Cyanazine	0.35	100	0
Chlorodibromomethane	1.1	64	36
Bis-2-chloroethyl ether	0.04	100	0
Bis-2-chloroisopropyl ether	0.18	100	0
Dibromodichloroethane isomer	0.33	100	0
Dibutyl phthalate	0.10	80	20
2,6-Di-*t*-butyl-*p*-benzoquinone	0.22	100	0
Dichloroiodomethane	1.1	85	15
Dieldrin	0.04	100	0
Di-(2-ethylhexyl) phthalate	0.10	100	0
Dimethyl phthalate	0.27	100	0
Dipropyl phthalate	0.07	100	0
1,2,3,4,5,7,7-Heptachloronorbornene	0.06	100	0
Heptachloronorbornene isomer	0.06	100	0
Hexachloro-1,3-butadiene	0.16	100	0
Hexachloroethane	4.3	36	64
Isophorone	1.6	98	2
1,1,2-Trichloroethane	0.35	69	31
Trimethylbenzene isomer	0.04	100	0
Triphenyl phosphate	0.12	100	0
Undecane, branched	0.06	100	0
o-Xylene	0.33	100	0

*Including only compounds present in total concentration of 0.05 µg/l or greater.

Recoveries From Carbon Filters of Different Sizes

The two-month equivalent (mini-sample) CCE's contained much higher concentrations--up to 10 fold--of lower boiling compounds than did the 70-year and mega-sample CCE's, but about the same concentrations of the less volatile compounds. This may be seen by comparing the FID chromatogram of the Carrollton mini-sample CCE with that of the mega-sample, both in Figure 11, and with that of the "70 year" sample in Figure 4. Although the "70 year" sample was collected about ten days before the mini-sample, during which time the compound quantities in the river may have changed, the concentrations should not have changed as a function of volatility. These results may be an indication of organic overloading on the "70 year" carbon filter, although this explanation is contrary to most of the results shown in Table 7. Seventy grams of carbon were used to extract 60 liters of water in the mini-sample filters (0.9 l/g), while 230 grams were used for 25,500 liters in the "70-year filters" (75 l/g). This is an 83-fold difference in the water/carbon ratio.

Concentrations in the mega-sample CCE's were low relative to the "70 year" CCE's. Of 30 compounds quantitated in the Carrollton drinking water by both

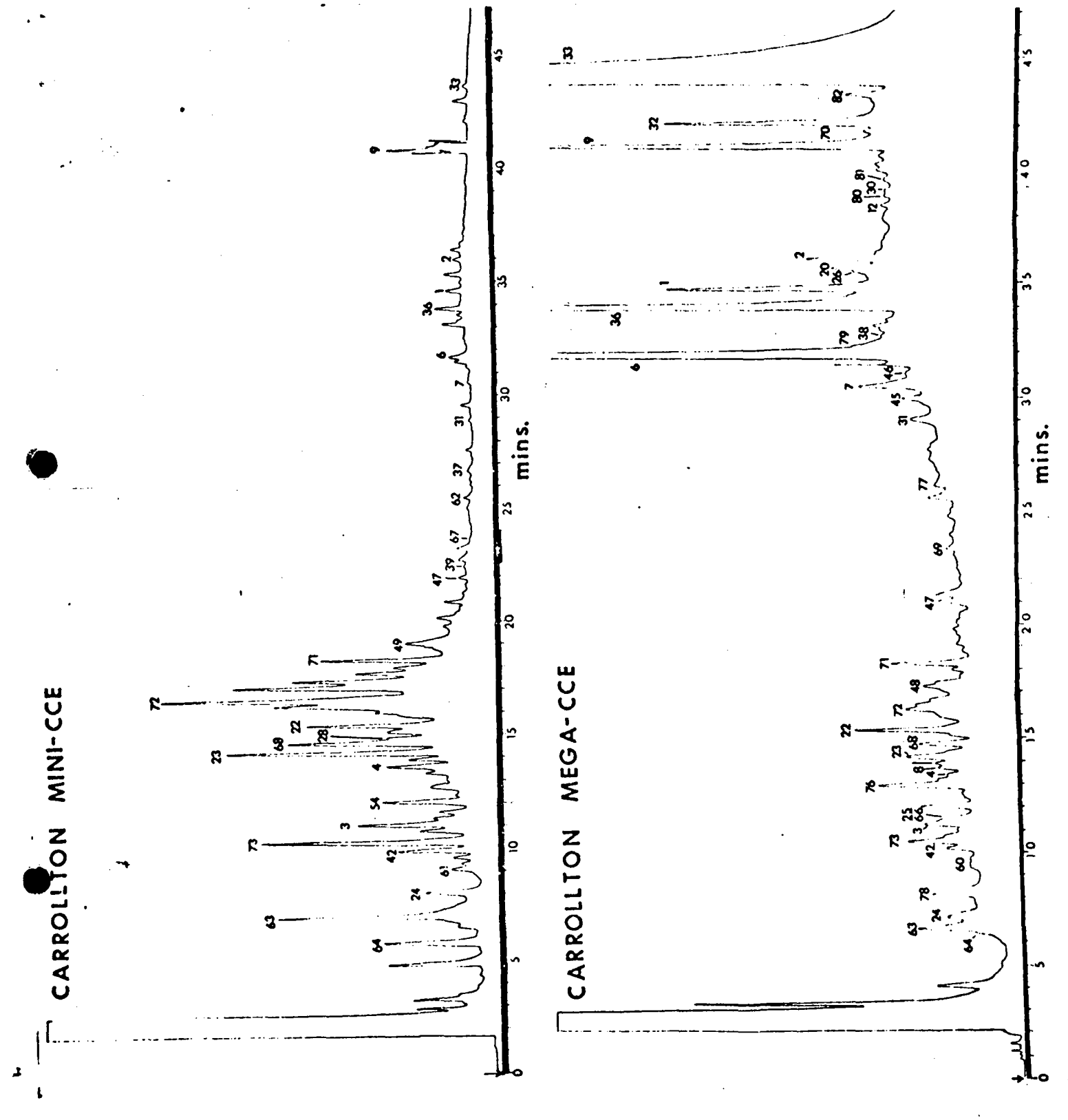

Figure 11. FID gas chromatograms of the Carrollton mini- and mega-CCE's. Numbers correspond to compounds in Table 4.

methods, the concentrations of 21 in the mega-sample were between 25 and 76% of that found in the "70 year" sample. The water/carbon ratio for the mega-sample was 57 l/g.

Several operational factors were biased against the mega-sample quantitations relative to those for the "70 year" sample. The mega-sample carbon was dried for 10 days before extraction, while the "70 year" sample carbon was dried for only 2 days. The first step concentration of the mega-sample CCE's was not as carefully controlled as it was with the "70 year" CCE's in that direct distillation of the chloroform was used for the mega-sample whereas vacuum evaporation at room temperature was used for the 70-year CCE's. However, recent quantitative studies by Webb[26] indicate that the first step concentration is not as critical as the final step concentration, which was the same with all of these samples.

Recovery from Resin

Not enough data are available from the New Orleans study to make a good comparison of XAD-resin vs. carbon extraction efficiencies. More compounds and higher concentrations were obtained from the carbon, but sampling circumstances were biased against the resin technique. A

well-designed comparison of these two accumulator techniques is needed.

Recovery Studies With Atrazine

Since several s-triazine herbicides were identified in the New Orleans CCE's the recovery of atrazine from water was studied to determine approximate recoveries that might be expected for the atrazine-type herbicides. Four extraction methods were tested using spiked samples:

(a) Liquid-liquid extraction--Two 1-liter tap water samples were spiked with 100 and 200 ug, respectively, of atrazine, allowed to stand 5 days in laboratory light, and extracted 3 times with 100 ml portions of methylene chloride. The extracts were evaporated to 1 ml using a Kuderna-Danish evaporator followed by final concentration with a slow stream of dry nitrogen, and then were analyzed by GC.

(b) Activated cocoanut charcoal (an incidental laboratory supply)--Five liters of tap water were spiked with 100 ug of atrazine and passed by gravity flow through a column of 11 grams (20-ml volume) of the charcoal (6-14 mesh). A control consisted of a similar charcoal column and

5 liters of unspiked water. For a direct recovery test, 100 ug of atrazine in 2 ml of chloroform was added directly to 11 grams of the same charcoal. The 3 charcoal samples were air-dried at room temperature overnight, then extracted with methylene chloride in a Soxhlet extractor for 6 hours. The extracts were evaporated to 1 ml as in experiment (a), and analyzed by GC.

(c) "Fine" mesh carbon (used at New Orleans)-- Experiment (b) was repeated with 3.5 grams (20-ml volume) of the "fine" mesh Nuchar 190 carbon used in the New Orleans study.

(d) "Coarse" mesh carbon (used at New Orleans)-- Experiment (b) was repeated with 10 grams (20-ml volume) of the "coarse" mesh carbon used for the New Orleans study. The results are summarized in Table 8.

The results are summarized in Table 8.

Table 8

Recovery Studies Using Atrazine-Spiked Solutions

Experiment Description		% Recovery
(a)	Methylene chloride extraction, 100 ug/l	98%
	Methylene chloride extraction, 200 ug/l	95%
(b)	Cocoanut charcoal/atrazine in water	29%
	Cocoanut charcoal/atrazine in $CHCl_3$	28%
(c)	Nuchar 190 fine mesh/atrazine in water	92%
	Nuchar 190 fine mesh/atrazine in $CHCl_3$	103%
(d)	Nuchar 190 coarse/atrazine in water	59%
	Duplicate of above	71%
	Nuchar 190 coarse/atrazine in $CHCl_3$	102%

From Table 8 it is seen that Nuchar 190 is an acceptable carbon for adsorption/desorption of atrazine--especially the fine mesh. Liquid-liquid extraction with methylene chloride would also be a good method of recovery for these herbicides. However, the cocoanut charcoal gave

very poor recoveries, probably because it was not desorbed efficiently by methylene chloride.

Carbon Variance

One of the disadvantages of using activated carbon for concentrating trace organics from water is the large variance in both its "activity" (adsorption/desorption characteristics) and its cleanliness. Table 8 provides an insight into how much various types of carbon can differ in their activities towards adsorbing/desorbing organic compounds.

The Nuchar 190 used for the New Orleans study was relatively free of background organic contaminants. Total organic peak area summation as measured on the PEP-1 system was 5.1 for the blank CCE. In contrast, the first carbon tried for the NORS gave a peak area summation of 61.6. The peak area summation for the chloroform solvent blank used in the NORS was only 0.25 so the organics were clearly eluting from the carbon. This carbon could not be used, but satisfactory results were obtained with Filtersorb 300 (although Nuchar C-190 was cleaner there was not a sufficient quantity on hand for the entire 10-city survey). Table 9 summarizes the results of these analyses.

Table 9

Peak Area Summations of Various CCE Blanks

CCE Source	Peak Area Summation
First NORS CCE blank	61.6
New Orleans Nuchar 190	5.1
Nuchar C-190	0.3
Filtersorb 300	1.2
Westvaco (sealed bag)	13.6
Westvaco (opened bag)	30.5

Probably the Westvaco open bag adsorbed organics from the air although this is not known for certain because the history of the bag is not known; the carbon was not from our laboratory.

A procedure needs to be developed for pre-cleaning carbon. Dunlap and Shew have experienced some success by boiling the carbon in organic free water with 5% hydrochloric acid followed by washing with organic free water and drying in a clean oven at 150°C for about 4 hours.[27]

CONCLUSIONS

Although we know much more now about trace organic contaminants in our drinking waters than we did one or two years ago, we still have a long way to go before we can feel confident about their quantities and distribution. computerized GC-MS has provided an efficient and cost-effective method of identifying these compounds, but we are still perfecting methods for concentrating and separating trace organics quantitatively and efficiently from water. Concurrently, we are just beginning to gather and organize data on trace organics so it can be computerized for output and assessment with useful correlations such as geographic location, type of water, etc. Concomitant with the availability of information pertaining to the identification of thousands of organic compounds in water there will be a surge of research efforts relating to the health and ecological effects of these compounds. At present there is little evidence either for or against significant health effects of most of these organic compounds at microgram per liter concentrations.

The results described in this and other chapters of this book are clearly the initial efforts of a relatively new trend in environmental chemistry--the qualitative and quantitative analysis of trace organic compounds in environmental samples.

Drinking water is but one of many kinds of samples where this information is sought. Awareness is finally increasing that we need to know what and how much of various chemicals are in our drinking waters in order to intellegently assess their significance. This same logic applies to our rivers, lakes and groundwaters which are the sources of our drinking waters. We expect to learn much more about the occurrance and distribution of these trace organic compounds--both natural and snythetic--in our environment over the next 10 years.

ACKNOWLEDGEMENTS

The authors thank Ronald G. Webb for the synthesis of chloropicrin and trimethyl isocyanurate used as standards for the confirmation of these two identifications. Thanks are also due Ann Alford for providing some of the GC-MS data and to Leo Azarraga and George Yager for GC-IR analysis of a alachlor and its chlorine homolog. Advice and help from William T. Donaldson and John M. McGuire is gratefully appreciated.

DISCLAIMER

Mention of commercial products and trade names is for informational purposes only and does not imply endorsement by the U.S. Environmental Protection Agency or the Athens Environmental Research Laboratory.

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DISCUSSION OF LECTURES OF FREUDENTHAL AND GARRISON

Question Greve:
To our experience the contribution of agricultural pollution of pesticides and herbicides is small in comparison with the industrial pollution unless airoplanes are used in spraying these substances. Is that also the experience in your country?
Answer Garrison:
According to the measurements of Junk in different locations of the U.S., industial contribution seems to be the most important. Arochlor probably comes from both sources.

Question Zoeteman:
What can be done with the data obtained by GC-MS in the survey of surface water?
Answer Freudenthal:
The frequency and concentration of several substances can be controled over different time periods, e.g. chlorophenols, when this is necessary.

Question Zoeteman:
What is the future work in the U.S. in the survey of drinking water?
Answer Garrison:
There is a list of about 20 compounds monitored for in the whole country and the survey analysis programm is extended to more cities A total organic chlorine determination may also be included in the survey.

Question Piet:
What is the detectable concentration of compounds in the complex mixture of surface water components analysed by GC-MS and stored in the computer and at what pressure is the plasma detector operated
Answer Freudenthal:
The plasma detector is operated at about 5-10 Torr. The quantification of organics in Rhine water can be done in the p.p.t. range but strongly depends on interference of other substances present.

Question Rook:
What is the cause of the difference in the levels of atrazine which are higher in the Mississippi than in the Rhine?
Answer Greve:
Atrazine has a limited use for specific purposes. From a toxicological point of vieuw it is not so important.

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CLOSING REMARKS

Ir. P. Santema
Director of the National Institute for Water Supply.

The director expresses his appreciation for the valuable contribution of the different speakers, the discussion and the chairman.

The proceedings of the symposium will be available as soon as possible and a similar symposium is planned in Amsterdam in the spring of 1977, as a collaboration of the Environmental Protection Agency (U.S.), The University of Amsterdam and The International Reference Center at The Hague.
The hope is expressed that the symposium may have stimulated future work and collaboration.