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PCB'S, PHTHALATES AND OTHER ORGANIC COMPOUNDS IN GROUNDWATER

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PCB'S, PHTHALATES AND OTHER ORGANIC

COMPOUNDS IN GROUNDWATER

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I INTRODUCTION

The effect of solid wastes on groundwater quality has been the subject of numerous investigations. The evaluation of the resulting water quality impairment had been based on such parameters as chloride concentration, mineral content, biochemical oxygen demand, total organic carbon and total organic nitrogen. The results obtained from studies of simulated and actual landfills show the presence of a high concentration of organic compounds in the leachate from these landfills.

Leachate is the aqueous solution formed when surface or subsurface water comes in contact with deposited refuse. This solution is rich in minerals, gases and other waste decomposition products capable of being leached out of the fill. Leaching can occur in several ways, the most significant of which are direct horizontal leaching by groundwater and vertical leaching by percolating water from rainfall or runoff. Contamination of the groundwater with the leachate occurs under the following conditions: the landfill site must be adjacent to or in an aquifer, there must be saturation within the fill, leached fluids must be produced, and the leachate must be capable of entering the aquifer.[1]

Previous studies[2] indicated that these conditions exist in the Norman Sanitary Landfill and it was therefore chosen as the site for this study. This study was undertaken to determine

the extent and nature of organic pollution occurring in the groundwater underlying the landfill. The specific objectives were to find evidence of groundwater contamination with polychlorinated biphenyls and other chlorinated hydrocarbons and to determine the major organic compounds polluting the groundwater.

The Norman landfill is located approximately one mile south of the city of Norman, Oklahoma on the east bend of the South Canadian River on section 18-T-8W-R2N, Cleveland County, Oklahoma. The landfill covers an area of 180 acres. It was originally operated by the city as a rubbish dump for a period of 38 years. There was no restriction concerning the type of material that could be deposited and open burning was also practiced. A large amount of refuse was deposited within the groundwater table which is only 2.5 feet below ground level. During flood periods, the fill was completely inundated with flood waters. Later, the deposited waste was covered with a cover material consisting of quarternary recent alluvium, composed of silt, clay, gravel and dune sand. All of this material is moderately to highly permeable.

During the past three years, the landfill has been operated privately with the following modifications. The refuse is now being deposited on top of an old refuse cell, compacted and covered with river sand. Some of the existing refuse cells are as deep as 15 feet and as much as eight feet into the water table in some sections.

One of the studies undertaken on the Norman landfill was

concerned with the determination of the direction and rate of groundwater flow, and the permeability of the soil underneath the fill.[2]

The direction of groundwater flow was determined as follows: Five eighth inch diameter holes were drilled around the landfill to a depth of two feet below the depth of two feet below the top of the water table. A survey was then conducted to determine the elevation of the top of the water table for each well plus the surface of the river water. This survey also included three already existing wells. The data from this study are shown below:

well no.	character of material	casing top elev.	water table elev.
1	5' coarse to fine sand	1088.22	1082.02
2	6' coarse to fine sand	1087.89	1028.51
3	Existing well at asphalt plant	1093.91	1082.89
4	2' coarse sand, 1' clay, 5' fine sand	1092.37	1084.70
5	1' coarse sand, 1' clay, 5' fine sand	1091.47	1084.47
6	1½' coarse sand, 1' clay, 4' fine sand	1091.77	1084.73
7	Existing well at naturizer	1094.70	1084.10
8	Existing well at sewage plant	1098.49	1089.00

Contours representing the water table elevation were drawn and are shown in Figure 1. The direction of flow of the groundwater was considered normal to these contours and determined to

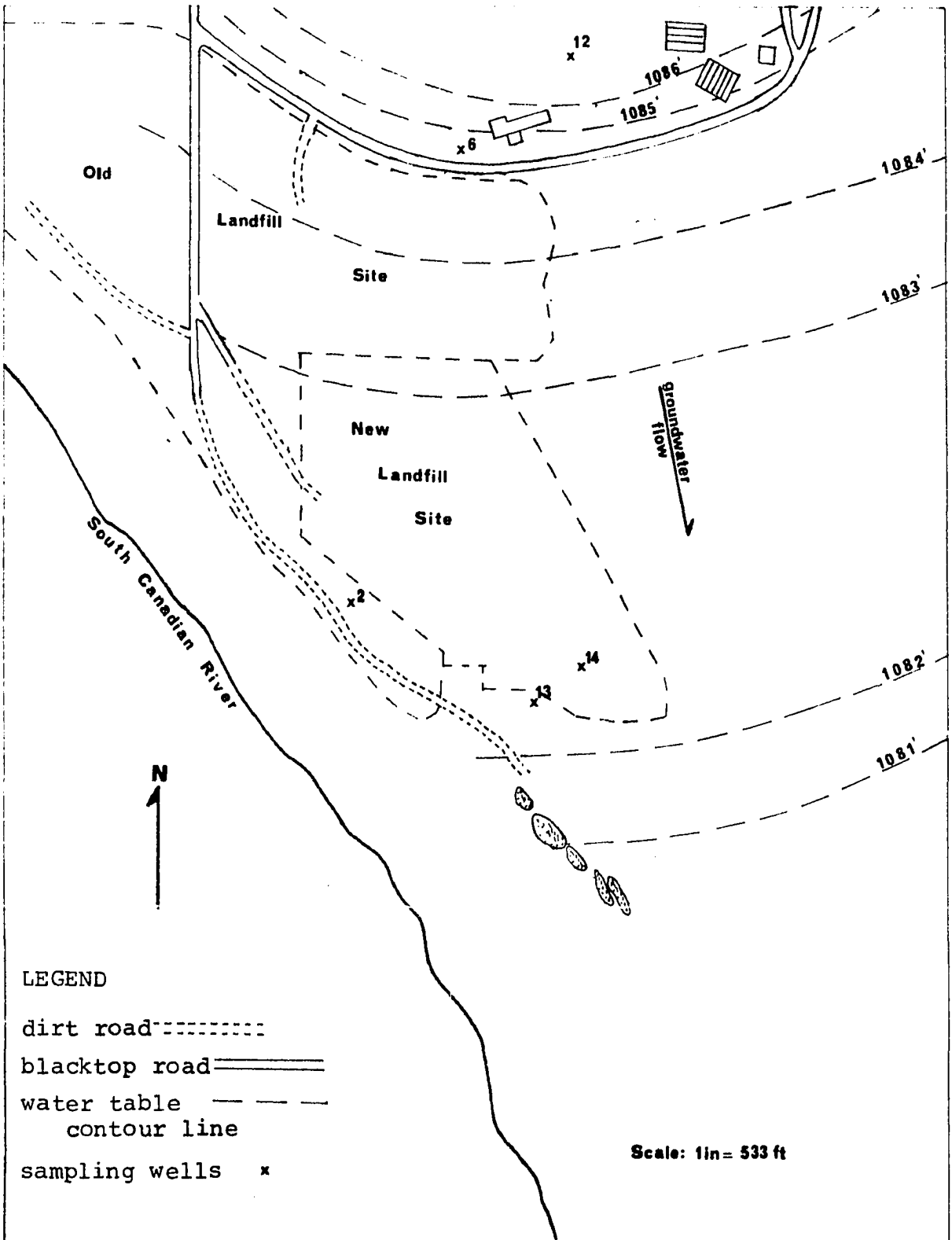


Figure 1. Well Locations at Norman Landfill.

be 7^{o} west of south.

Studies regarding the rate of flow of the groundwater were hampered by the loss of the dye used as a tracer. Uramine, used as the dye tracer was adsorbed on clay particles and the amount of the dye traveling with the downstream flow of groundwater was continuously decreasing. The available data, nevertheless, gave rates of 0.13 - 0.18 feet per day.

Soil samples from several wells were also analyzed for density and moisture content. These samples were also subjected to sieve and hydrometer analyses and the data were used to calculate the soil permeability which was obtained to be 6.3 - 9.99 feet/day.

In a landfill situated as in this case, where the groundwater table is close to the surface and in a geologic formation of considerable permeability, an appreciable amount of leaching can be expected to occur. Precipitation which averages 32 inches per year contributes significantly to the leaching process, percolating through the refuse and increasing the potential of groundwater contamination in the area.

II LITERATURE SURVEY

Leachates

Solid wastes contain mineral and organic substances capable of causing pollution of underground water. The decomposition of organic matter by bacteria either aerobically or anaerobically results in a variety of chemical and biochemical products capable of potential distribution in ground or surface waters. When contamination of ground water from leaching occurs in the vicinity of the solid waste disposal site, water as far as one thousand feet downstream can become polluted and rendered unfit for human or animal consumption.[3] Organic matter contributes significantly to this deterioration of water quality.

Organic matter is broken down by bacteria to substances which will no longer decompose even if allowed some more time. The complete breakdown of organic substances is represented by the following equations:

$$\text{organic compound} + O_2 \longrightarrow CO_2 + H_2O + \text{nitrates} + \text{sulfates}$$

(Aerobic breakdown)

$$\text{organic compound (nitrogenous, carbonaceous, sulfurous)} + H_2O \longrightarrow CO_2 + CH_4 + N_2 + \text{sulfides}$$

(Anaerobic breakdown)

The above equations are obviously simplified. The initial products of decomposition are organic acids, acid carbonates, humic components and others. The organic constituents of solid waste giving rise to these decomposition products come mostly from food wastes. Food wastes contain carbohydrates such as sugars and starches which are rapidly digested by bacteria. The fats and proteins in garbage are also readily attacked by bacteria. However, in anaerobic conditions, the breakdown of fats can go on for years.[4] Moisture and temperature affect degradation rate. This rate can be retarded or increased by allowing more or less water to pass through the fill.[1]

The organic matter in combustible rubbish such as the cellulose of wood and paper decomposes very slowly. Therefore, in a landfill which contains these wastes, the early decomposition products will only be those associated with the breakdown of carbohydrates, proteins and fats. If leaching occurs at the early stages, the initial decomposition products will be found in the underground waters. In addition, a portion of the organic matter found in the refuse can be leached out and extracted prior to decomposition.

The formation of the leachate depends entirely on the presence and movement of water through and within the fill.[4] Studies in Britain and in Riverside, California [4, 5] involving wet placement of refuse showed that this process represents the most serious condition with respect to ground water pollution. Deposited refuse was completely submerged and horizontal flow

of water through the refuse resulted in the maximum amount of leaching. High values of BOD, organic carbon and organic nitrogen occurred shortly after each new addition of refuse. These wet cells also gave higher amounts of chloride, sulfate and minerals. The absence of appreciable amounts of nitrate and sulfate observed indicates that the decomposition was proceeding anaerobically. In a separate study, refuse was deposited in an inactive mining area where the pits penetrated the high water table. The dissolved minerals were found to be three times greater than in areas not exposed to the landfill operations.[6]

Studies run on the Scholl Canyon landfill in Los Angeles produced a significant contrast between the values obtained for BOD and COD. The COD values were higher than BOD by 4500 ppm, indicating that a large portion of the organic carbon in the leachate is subject to chemical but not biological oxidation.[4] This is contrary to the result obtained from investigations involving sanitary landfills in Northeastern Illinois where BOD was higher than COD.[7]

Another example of the deleterious effect of organics in water is the discovery of taste and odors in a well downstream from the Mayflower landfill in Southern California.[4] F. M. Middleton also reports that serious taste and odors in drinking waters are usually associated with high recoveries of chloroform extractables in the water source.[8]

Organics in water are not only objectionable from the standpoint of taste and odors but they can cause deterioration

of anion exchange resins used in demineralization of some water supplies. Therefore, the ever increasing number of synthetic products that eventually wind up in a landfill multiplies the prospect of groundwater pollution with unknown, long-lived and possibly toxic organic substances.

Polychlorinated biphenyls

Some of the organic compounds that have been found in natural waters are numerous hydrocarbons, chlorinated pesticides, and a recently discovered chlorinated hydrocarbon called polychlorinated biphenyls or PCB's. The PCB's started to receive considerable attention in 1966 when they were found in fish by Jensen.[9] In addition to their widespread use, a source of concern about the PCB's have been their unusual stability and their structural similarity to the DDT family. The PCB's have, in fact, been found to interfere with the analysis of these well-known pesticide residues[10] and may have been falsely identified as such.

PCB's are manufactured in the U.S.A., France, Germany, Great Britain, Italy, Japan and Russia. The sole manufacturer of PCB's in the U.S.A. is Monsanto and these are marketed under the trade name Aroclor. The Aroclors are produced by chlorination of biphenyl to a given chlorine content.[11] The most commonly used ones are 21, 32, 42, 48, 54, and 60 percent chlorine by weight and are called Aroclor 1221, 1232, 1242, 1248, 1254 and 1260 respectively. It is obvious that each of these commercial products are mixtures of several compounds since there are ten possible sites of chlorination in the biphenyl moiety (Figure 2) and altogether 210 different theoretically

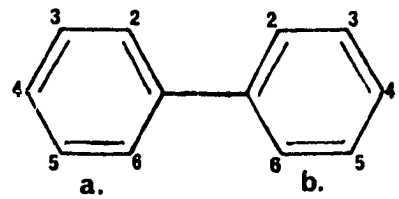


Figure 2. Biphenyl

possible chlorinated biphenyl structures. The presence of several components in an Aroclor sample is further indicated by the gas chromatograms of some standard commercial preparations (Figure 3).

It should be noted that the major peaks in Aroclor 1232 have longer retention times than those of Aroclor 1221, because this suggests that the higher numbered Aroclors contain a greater number of more highly substituted components. This is in fact shown by results obtained by Willis and Addison,[12] Sissons and Welti,[13] and Tas and DeVos[14] on the compositions of 1221, 1254, and 1260 respectively.

Aroclor 1221 was found to contain 92 percent by weight of biphenyl, monochloro biphenyls and dichloro biphenyls. The major components of Aroclor 1254 as reported by Sissons and Welti contained mostly tetrachloro biphenyls, pentachloro biphenyls and hexachloro biphenyls with the pentachloro biphenyls predominating.

Only four of the major peaks of Aroclor 1260 were identi-

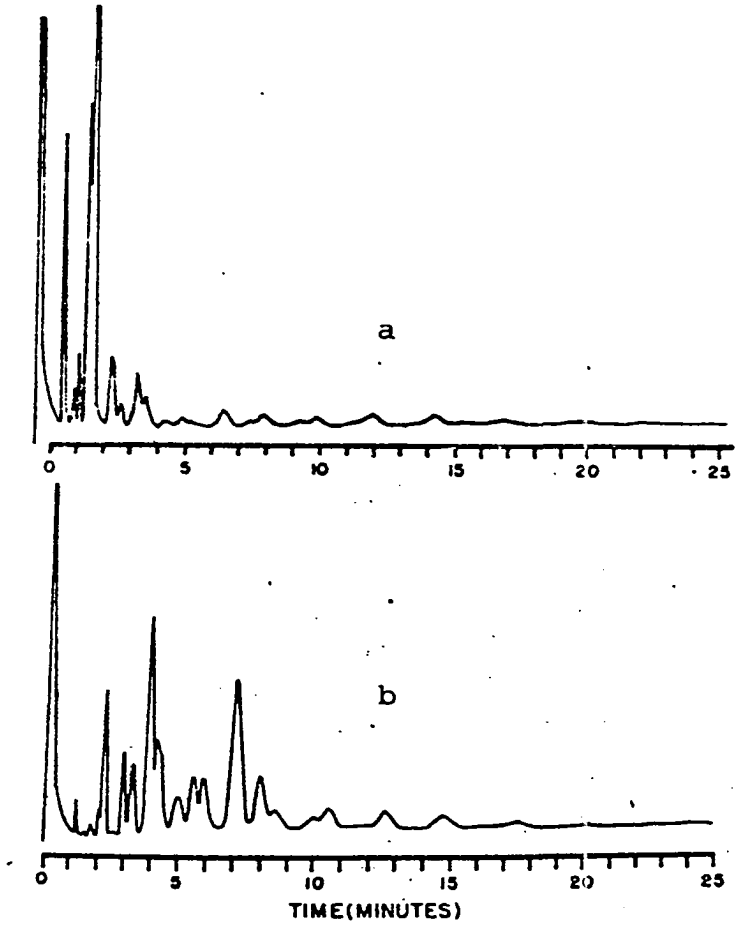


Figure 3. Gas chromatograms of PCB's. A is Aroclor 1221. B is 1232.

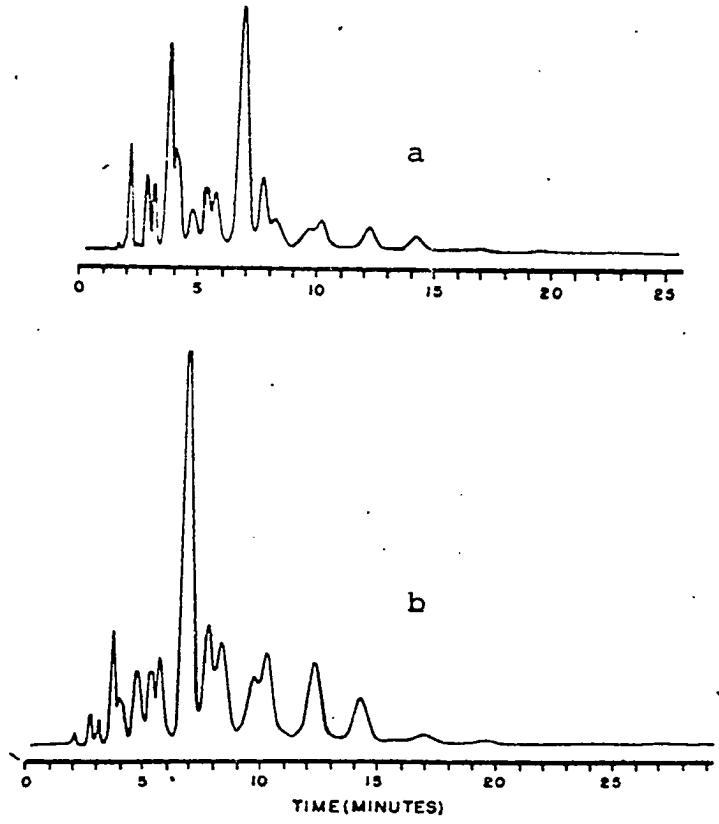


Figure 4. Gas chromatograms of PCB's. A is 1242 and b is 1248.

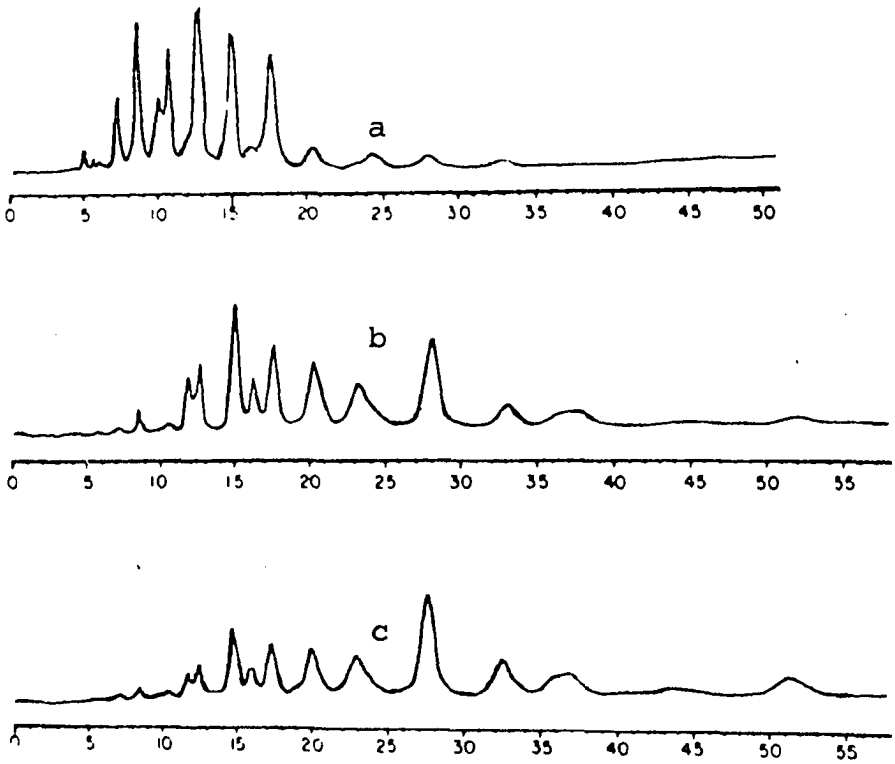


Figure 5. Gas chromatograms of PCB's. A is 1254, b is 1260 and c is 1262.

fied by Tas and DeVos and they include two hexachloro and two heptachloro biphenyls.[14] However, Koeman et al.[15] showed the presence of six pentachloro biphenyls, five hexachloro biphenyls and one octachloro biphenyl in the same PCB mixture.

PCB's are chemically inert, are not hydrolyzed by water and resist alkalies, acids and corrosive alkalies. They have low volatility ranging from 278^{o} for Arochlor 1221 to 415^{o} for Arochlor 1268. All are stable to prolonged heating at 150^{o}C and the lower Arochlors can be distilled at atmospheric pressure without appreciable decomposition. PCB's are insoluble in water but very soluble in hydrocarbon solvents. These properties would indicate that PCB's could persist and accumulate up the food chain[15] especially the higher numbered components.

The presence of PCB's in many environmental samples have been determined. Among these samples are fish,[10,16] birds,[10] food,[18] marine animals,[19] human adipose tissue,[20, 21, 22] and numerous water samples.[23, 24, 25]

The analytical methodology used in these investigations and others involving the detection and identification of organic compounds will be discussed on succeeding pages. The techniques involved range from thin layer chromatography[26] gas chromatography, and gas chromatography-mass spectrometry.[10, 27] Gas chromatograph-mass spectrometry developed as a very useful tool in the identification of PCB's in the presence of interferences from compounds having very similar retention volumes e.g. pesticide residues. The removal of interferences of other

chlorinated hydrocarbons in the analysis and identification of PCB's has been the subject of extensive cleanup procedures involving column chromatography on florisil according to the method of Reynolds[28] or on Silicic acid/cellite according to Armour and Burke.[29] Other g.c. detectors aside from flame ionization and electron capture had also been used for the selective detection of chlorinated insecticides in the presence of PCB's like the Coulson electrolytic conductivity detection used by Dolan et al.[30]

A technique that would not necessitate the careful separation of PCB's from pesticide residues in order to be identified involves a gas chromatograph-mass spectrometer technique called peak monitoring and involves the selective monitoring of selected mass ion peaks in a gas chromatogram. Identification of a compound is achieved by comparing its retention time to the presence of up to eight of its characteristic mass peaks at that retention time. Quantitation is achieved by comparing the area under one or more of the eight peaks to the area of a known amount of a standard.[31]

A number of studies on the toxicity of PCB's have been conducted and a summary of some findings is given by Veith and Lee[23] and J. G. Vos.[22]

The following tables give a good indication of the effect of different PCB preparations on some test animals.

Table 1 shows that the acute and subacute toxicity value for PCB's are high; but the semichronic oral toxicity and dermal and inhalation toxicity are quite significant.

Table 1. Acute and Subacute Oral Toxicity Studies of PCB Preparations[22]

Preparation	Animal	Treatment	Mortality	Liver Effects
Unknown	Mouse	single dose of approx. 2000 mg/kg	LD_{50}	
Aroclor 54%	Rat	single dose of 500 mg/kg	0%	Increase of weight and lipid; potentiation of CCl_4 toxicity
Aroclor 42, 54, 60, and 68% Cl	Mallard	single dose of 2000 mg/kg	0%	
42% Cl	Rat	20 daily doses of 138 mg	0% in 3 months	Hyalin bodies in liver cells
42% Cl	Guinea pig	2 doses of 69 mg 1 week apart	100% between 11 and 29 days	Fatty metamorphosis; central atrophy
65% Cl	Rat	6 daily doses of 300 mg	70% in 14 days	Increase of weight; cell swelling; hyalin granules

Table 2. Semichronic Oral Toxicity Studies of PCB Preparations.[22]

Preparation	Animal	Treatment	Mortality	Liver effects	Other effects
65% Cl	Rat	Doses of 50 mg every second day	60% in 5 weeks	33% weight increase; cell swelling; hyalin globules	
48% Cl	Cynomolgus monkey	From 641 mg in 40 days to 348 mg in 239 days	not given	Enlargement; SER proliferation	Main cause of death: pneumonia or diarrhea
48% Cl	Squirrel monkey	From 320 mg in 46 days to 67 mg in 48 days	not given	Enlargement; SER proliferation SER proliferation	Main cause of death: pneumonia or diarrhea; palpebral edema in 1 animal
48% Cl	Mouse	Daily doses of 0.001 ml for 13 to 26 weeks	0%	Enlargement; SER proliferation RER reduction; myelin figures; increase of microbodies, lysosomes and lipid	Skin: loss of hair, erosion and ulceration after 3 months
Aroclor 42% Cl	Chicken	100, 200, 400, and 1000 ppm in diet for 4 weeks	0, 0, 50, 90, and 90% respectively	Enlargement; damage at the higher levels	Edema formation from 200 ppm; at high levels internal haemorrhage and tubular dilatation in kidneys

Table 2. Continued

Preparation	Animal	Treatment	Mortality	Liver effects	Other effects
Aroclor 42% Cl	Chicken	200 and 400 ppm in diet for 3 weeks	0 and 12% respectively		Pronounced edema at 400 ppm; enlarged kidneys; small spleen; defeathering and dermatitis
48% Cl	Chicken	1, 5, 10, 25, 50, 100, 300, 600, 1200, 2400, and 4800 ppm in diet for 20 days	0% from 1 to 100 ppm; 100% from the 100 ppm level		Edema formation 100 ppm level
Aroclor 48% Cl	Chicken	10, 20, 30, 50, 100, and 150 ppm in diet for 4.5-5 weeks	After 3 weeks: 0, 0, 30, 30, and 20%; at the end 0, 0, 80, 60, and 80% respectively	Enlargement	General edema and depression of the secondary sexual characteristics from the 30 ppm level
Aroclor 54%	Chicken	250 and 150 ppm in diet for 6 to 13 weeks	250 ppm 100% between 3 and 10 weeks; 500 ppm some mortality at the end		500 ppm at end: comb weights 20-fold and testes weights 2-fold lower than controls
Aroclor 54% Cl	Bengalese finch	Estimated dose rate at 56 days of 254 mg/kg/day	50%		Hydropericardium in some birds
Phenoclor 60% Cl	Japanese quail	2000 ppm in diet	100% between 6 and 55 days		Hydropericardium

Table 3. Dermal Toxicity and Inhalation Studies of PCB Preparations.[22]

Preparation	Animal	Treatment	Mortality	Liver effects	Skin effects
42% Cl	Guinea pig	11 daily skin applications of 34.5 mg	100% between 11 and 21 days	Fat; central atrophy; perinuclear basophilic granulation; focal necrosis in a few animals	Occasional thickening of the epidermis
42% Cl	Rabbit	Skin application at alternate days, total dose from 946 to 1980 mg	100% between 17 and 98 days	Fatty degeneration; central atrophy	Thinning of prickle cell layer and thickening of outer cornified layers
Aroclor	Rabbit	Daily skin applications of 0.3, 0.6, and 0.9 g	High dose died before liver necrosis developed	Moderate doses: mottled liver, subacute yellow atrophy, fatty degeneration, and marked necrosis	Reddening; formation of small papules and blisters; finally desquamation of external epidermal layers
Aroclor 65% Cl	Rat	Inhalation of 0.57 mg/cubic meter for 16 hours for 37 to 134 days	0%	Pale and yellow; cell swelling; hyalin degeneration; potentiation of CCl_4 and C_2H_4OH toxicity	

The chlorinated biphenyls have two distinct actions on man: an acne-like skin disease and a toxic action on the liver. The lesion produced in the liver is an acute yellow atrophy. This hepatotoxic action appears to increase if there is exposure to CCl_4. At the same time the higher the chlorine content, the more toxic it is liable to be.[32] An epidemiologic investigation of epidemic in Western Japan showed the cause to be the ingestion of a brand of rice oil contaminated with PCB's[33] to the extent of 2000-3000 ppm Kanechlor 400 (48 percent Cl). The average amount of Kanechlor 400 ingested by a patient was estimated to be 2 g and the minimum dose consumed was estimated to be 0.5 g. The symptoms of the disease include eye discharge, swelling of the eyelids followed by acne-like eruptions, edematic swelling of the limbs, pigmentation of skin membranes and other neurological symptoms. To date 50 percent of the affected patients are still suffering from these symptoms. It should be noted however, that the PCB preparations involved in the above toxicity studies may contain other impurities which may or may not be responsible for some of the observed results.

PCB's have a wide variety of uses and are therefore a cause of major concern because of the great number of ways in which they could be introduced into environmental samples.

A summary of the present knowledge about production, uses and losses of PCB's is given by Nisbet and Sarofim.[34]

The breakdown by grade of the current uses of PCB is as follows:

current use: Aroclor 1016 - electrical capacitors

Aroclor 1242, 1254, and 1260 - electrical transformers

Aroclor 1248 and 1254 - vacuum pumps

Aroclor 1221 and 1242 - gas transmission turbine

former use: Aroclor 1232, 1242, 1248, 1254 and 1260 - for hydraulic fluids

Aroclor 1242 - for heat transfer systems

Aroclor 1248, 1254, 1260, 1262, and 1268 - for plasticizers - synthetic resins

Aroclor 1221, 1232, 1242, 1248, and 1254 - for adhesives

Aroclor 1221, 1232, 1242, 1248, 1254, and 1268 - for plasticizers and rubbers

Aroclor 1242, 1254, and 1268 - for pesticide extenders

Aroclor 1254 and 1260 - for dedusting agent

Aroclor 1254 for pesticide extender, inks, lubricants and cutting oil

Aroclor 1242 - for carbonless reproducing paper

An indepth discussion of several specific uses of PCB's, the required physical properties for each application and the advantages and disadvantages of PCB's is given by Broadhurst.[35] More importantly, the possibility of replacing PCB's with other materials for use in the following is considered:

1) dielectric fluids for capacitors and transformers
2) industrial fluid for hydraulic, gas and vacuum pumps

3) heat transfer uses

4) plasticizer and miscellaneous uses

There are a lot of ways by which PCB's are discharged into the environment. Possible routes into the environment include leaks, spills, manufacturing losses, leaching and waste disposal operations. These are illustrated by the following figure.[34]

It should be noted that most of these routes eventually end at waste disposal operations involving a sanitary landfill.

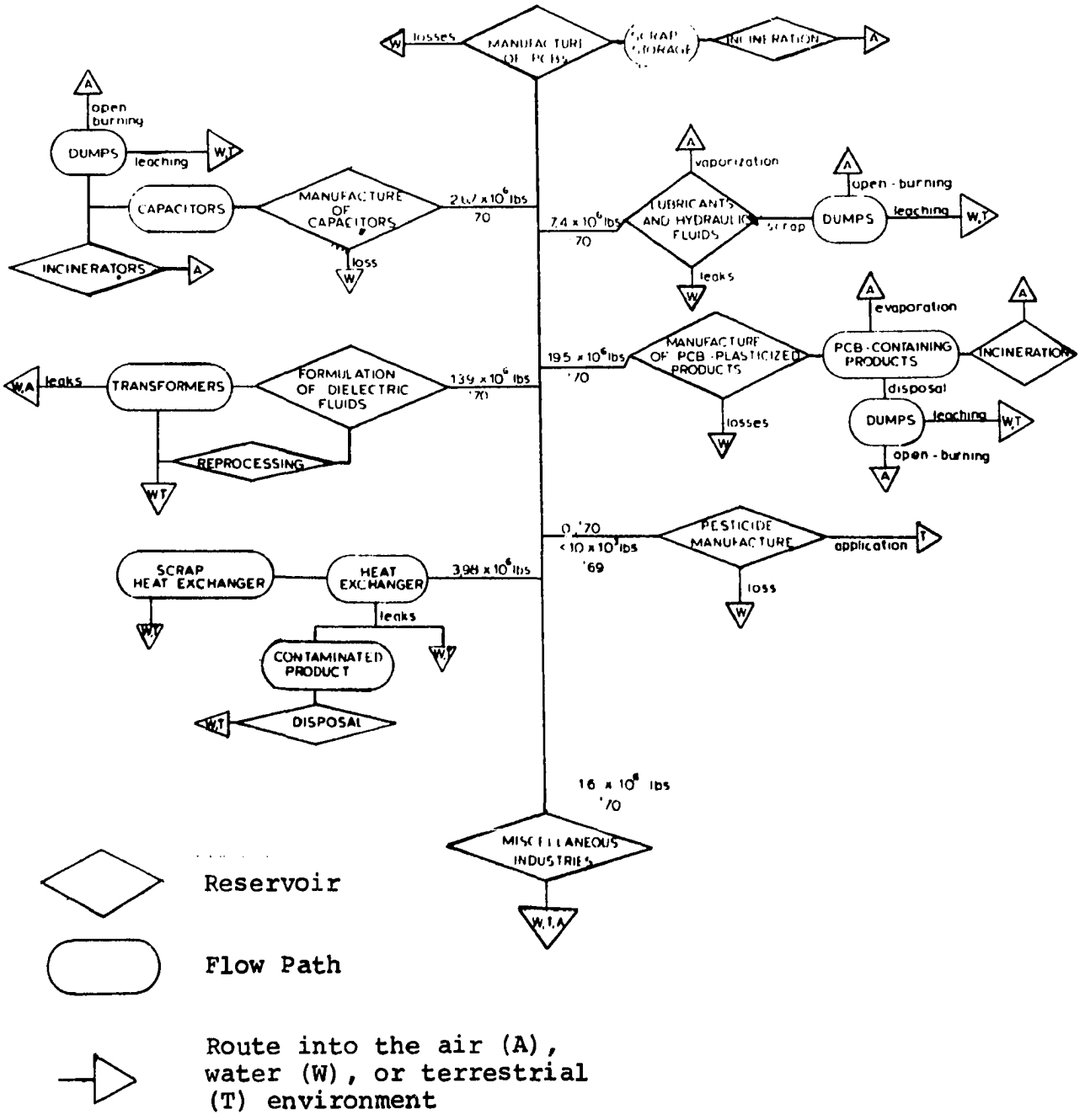


Figure 6. Routes of PCB's to Environment

Phthalates

In some of the samples examined for PCB's, peaks with longer retention times were observed and eventually identified as phthalate esters. Phthalate esters have been found in surface waters[36] and air samples[37] as well as in humans.[38]

Phthalate esters are produced by the reaction of phthalic anhydride and the appropriate alcohol (Figure 7).

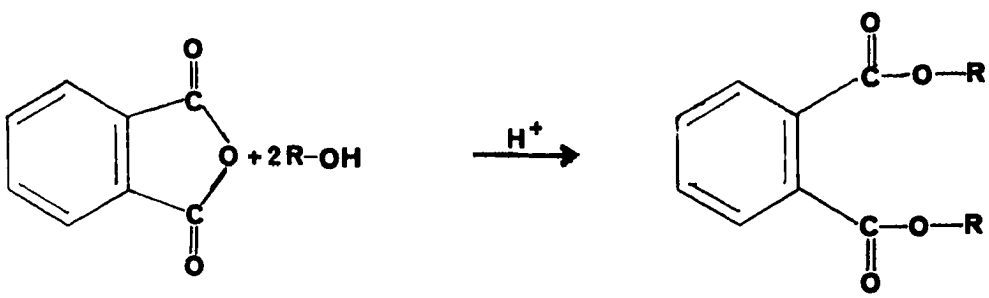


Figure 7. Reaction of phthalic anhydride and alcohol.

The yield of the ester is quantitative and with a purity greater than 99 percent. Some of the more common esters are the following:

$R_1 = R_2 = CH_2- CH_3$ diethyl phthalate

$= CH_2- CH_2- CH_2- CH_3$ di-n-butyl phthalate

$= CH(CH_3) - CH_2- CH_3$ di-isobutyl phthalate

$= CH_2- (CH_2)_6 - CH_3$ di-n-octyl phthalate (DOP)

$= CH(CH_2- CH_3) - CH_2- CH_2- CH_2- CH_3$ di-2-ethylhexyl phthalate (DEHP)

$R_1 = CH_2- CH_2- CH_2- CH_3$

$R_2 = CH_2- \overset{O}{\overset{\|}{C}}- O- CH_2- CH_2- CH_2- CH_3$

butylglycolbutyl phthalate (BGBP)

About 850 million pounds of phthalate esters were produced in 1970[39] and annual production still exceeds 900 million pounds a year. Greater than 95 percent of all phthalate esters produced end up in plasticizer uses as outlined below:

Building and construction; wire and cable, flooring, swimming pool liners

Home furnishings;furniture upholstery and wall coverings

Automobile upholstery; seatcovers, mats and tops

Apparel; footwear and outerwear

Food surfaces and medical products such as food wrap, film, medical tubing and intravenous bags

Estimates of the amount of plasticizer being used in each of these products are given by Graham.[40]

Approximately 75 percent of all phthalate esters used as plasticizers end up in vinyl products while 15 percent goes into synthetic rubber cellulose resins and other plastics.[43] The nonplasticizer uses of phthalate esters are as gasoline additives, synthetic lubricant, pesticide carriers, cosmetics, fragrances and insect repellants. Among the companies that manufacture phthalate in the U.S. are Enjay Chemical, Monsanto and Union Carbide.

The popularity of phthalate esters as plasticizers is due to their ability to impart a good balance of flexibility and

permanence to a polymer such as polyvinyl chloride (PVC). Diethyl-hexyl phthalate (DEHP), diisooctyl phthalate (DIOP) and diisodecyl phthalate (DIDP): all impart a good overall balance of properties. Diethyl-hexyl phthalate in particular has long been the industry's standard for general purpose uses.[41]

The environmental problems arising from the tremendous amount of phthalate esters used in all sorts of products are now a subject of considerable interest to investigators. The health and environmental implications of phthalate esters in particular was brought into focus by the discovery that blood stored in PVC plastic bags is capable of leaching the plasticizers into the blood. Since that time, other investigations into the amount and effect of plasticizers in the environment have multiplied. The presence of significant quantities of these esters in water samples have been reported by Hites[42] and Corcoran.[36] It is perhaps noteworthy that the production of phthalate esters is much larger than both DDT and PCB's which have been established as definite threats to the environment.

Among the phthalate plasticizers, DEHP is the most widely used. It is not therefore surprising to find that more toxicological studies on phthalate esters have been done on DEHP.

In general, the acute toxicity of phthalate esters is low. For example, a study involving oral administration of DEHP indicated an LD_{50} of approximately 30 g/kg in rats and rabbits, given a single dose.[43, 44] Ninety-day and two-year feeding studies in guinea pigs and dogs also indicated a low order of toxicity. These data resulted in the FDA approving DEHP for

use in plastic wrapping for food intended for human consumption.[45]

Summaries of the results of some acute toxicity studies involving several esters are given by Kraunshopf[43] and Gesler[44] and in a more recent review by Autian[46] from which the following acute toxicity data for butyl phthalate and octyl phthalate were taken.

Table 4. Summaries of Acute Toxicity Studies

	Animal	Route	LD_{50} g/kg
di-n-butyl phthalate	mouse	IP	4.0
	rat	IP	3.05
	rabbit	IP	8.0
	rabbit	dermal	20.0
diisobutyl phthalate	mouse	oral	12.8
	mouse	IP	4.5
	rat	IP	3.75
	guinea pig	dermal	10.0
dioctyl phthalate	mouse	oral	13.0
	rat	IP	50.0
	guinea pig	dermal	5.0
DEHP	mouse	IP	14.2
	rat	oral	26.0
	rat	IP	34.0
	guinea pig	dermal	10.0

Rubin and Jaeger[47] conducted extensive studies on the extraction, localization and metabolism of DEHP from plastic medical devices. It is reported that the amount of DEHP extracted by blood from PVC plastic storage bags increased linearly with time. When DEHP is introduced intravenously into rats, 79.1 percent of the total injected dose is recovered after 24 hours, with the liver and lung containing the largest total amount of the received dose. This study also indicates that rats do not metabolize DEHP or that it is metabolized to something other

than phthalic acid. The same investigators found, however, that another phthalate ester, butyl glycolyl butyl phthalate (BGBP) is metabolized to glycolyl phthalate (GP).[48]

Metcalf et al.[49] studying the uptake and fate of DEHP in aquatic organisms using (C^{14}) carboxyl labelled DEHP found that it is biodegraded slowly by algae, daphnea, mosquito larvae, snails and clams and more rapidly in fish by hydrolysis at the ester linkage to form monoethyl hexyl phthalate, phthalic acid, phthalic anhydride and a variety of polar metabolites and conjugates. DEHP closely resembles DDT in rate of uptake and storage and it is partitioned strongly in the lipids of plants and animals and is therefore concentrated through food chains.

Although the acute toxicity data on DEHP and other phthalates are low as mentioned earlier, chronic toxicity studies indicate several effects. For example, rats fed diets containing 0.01, 0.05, and 0.25 percent dibutyl phthalate showed no reaction after one year. However, of those fed 1.25 percent, half died during the first week. Rats administered DEHP in their diet at 0.375, 0.75, 1.5 and 3.0 percent for 10 days showed a slight decrease in growth at the highest three dose levels.[46] Mice exposed to DEHP vapors for one hour three times a week for twelve weeks showed signs of diffuse chronic inflammation in their lungs similar to a burn reaction.

Repeated administration of DEHP showed also a cumulative toxic effect. Several dose levels were administered intraperitoneally to mice 5 days/week for eleven weeks. At the end of the first week the LD_{50} for DEHP was 25.41 ml/kg. This

decreased to 3.06 ml/kg at the end of ten weeks, a factor of 8.31.

More subtle effects such as embryo toxicity and teratogenic effects of phthalate esters are also significant. All the esters studied[46] to some degree produced gross or skeletal deformities which are dose related. Rubin and Jaeger suggest that these effects plus behavioral effects and effect on the response to drugs might be a more realistic indication of the threat which phthalate esters pose to animal or human life.

III. ANALYTICAL TECHNIQUES

It is always difficult to classify or identify a complex mixture of organic compounds. Investigations involving water samples are further complicated by the inadequacy of samples obtainable from dilute aqueous solutions. The approach to the solution of this problem involves the application of systematic and effective separatory and analytical techniques. Fortunately, these techniques are available and have been utilized to some degree of success in other investigations of this nature.

For the isolation and recovery of organic compounds in water several techniques have been utilized. Among these methods are solvent extraction, steam distillation, freeze concentration and adsorption on a suitable adsorbent followed by desorption.

Solvent extraction makes use of a volatile organic solvent to take up the organic substances from aqueous solutions. This is based on preferential partitioning of the organic solute in the organic solvent. However, solvent extraction is only effective for fairly concentrated solutions. Since the solubility of organic compounds in water is very low, the operation would require large volumes of solvent to remove minute amounts of solutes from large volumes of water. The large quantity of organic solvent is difficult to evaporate and may leave a residue of impurities. Steam distillation is also limited to small

volumes of water and this restricts its usefulness in water related studies.

Freezing as a technique for concentrating organic compounds in water was investigated by Shapiro[50] and Baker[51] in 1961 and 1967. The advantages of the method were found to be the following: chemical structure was not altered, bacterial degradation is inhibited and loss of volatile compounds was reduced.

The most widely used method of recovering organic compounds from water solutions is adsorption on activated carbon. The method, called the carbon adsorption method (CAM), has been used in the measurement of gross contamination in the nation's rivers, recovering phenolic compounds from polluted waters, and concentrating organic compounds responsible for causing taste and odors in drinking waters. Reports on its use abound in the literature.[8, 52 through 59]

The CAM involves the controlled flow of the water sample through a glass column filled with activated carbon, followed by drying of the adsorbent then desorption with a non-polar solvent like chloroform and a polar solvent like ethanol. Both of the desorption processes are done under reflux.

The chloroform extract (CCE) contains mostly non-polar organic compounds while the alcohol extract contains the polar fraction (CAE). The ratio of the quantities of these extracts could serve as an indication of the types of organic compounds predominating in the water sample. In most instances, however, these extracts are subjected to further separations. Some specific chemical pollutants that have been isolated from the

chloroform extract are chlorinated insecticides and other industrial chemicals. The alcohol extractables have been synthetic detergents, carboxylic acids and humic materials which originate naturally or from the oxidized product of domestic or industrial wastes.

The efficiency of the CAM method has been evaluated by several authors. Booth[60] wrote that the reproducibility of the CAM is +10 percent and that the rate of adsorption varies inversely with flow rate. Hoak[52] reported that quantitative adsorption yielded only 70-80 percent recovery. About the same desorption efficiency 72.7 percent was found for phenol by another author,[61] using labelled (C^{14}) phenol as standard. The work of Baker[62] involving a mixture of n-butanol and n-amylacetate showed that activated carbon may preferentially adsorb certain organic compounds.

A summary of other findings about the CAM appears below:

1. Adsorption efficiency dropped rapidly when larger volumes of solution were passed through the column.[62]

2. Turbidity at natural pH did not affect qualitative results but removal of turbidity with prefilters improved the reproducibility of the results.[63]

3. Organic solutes are adsorbed as a multimolecular layer on the surface of the carbon.[64]

4. A two-stage countercurrent adsorption process is most useful.[65]

5. A flow rate of not more than 120 ml/min and a total volume of not more than 400 gallons is recommended.[60]

Another adsorbent which has shown promising results in the adsorption process is a new non-ionic polyacrylate resin called XAD. Using XAD-7 as adsorbent, organic compounds of the order of 1 ppb have been detected from water samples. Carboxylic acids, ketones, ethers and alcohols in the molecular range of 200-300 have been isolated. The reported advantages are: The drying process is eliminated thereby removing the possibility of loss of volatile compounds, the desorption process is more complete, structural changes do not occur on the adsorbent and the adsorbent can be regenerated.[66] The use of other amberlite resins like XAD-2 for the removal of organic substances from aqueous solutions have been reported as satisfactory.[67]

In spite of these advantages, the use of the resin in water quality investigations are still limited. The CAM is still the method used extensively. Moreover, one of the limitations of the CAM, that of possible loss of volatile compounds can be eliminated by removing the drying process.

The CAE and CCE obtained from the CAM are complex mixtures which require extensive separations if characterization of the components is attempted. Classical solubility separations are often used as a preliminary step to separate the acidic and neutral fractions.[68] Further separations of these fractions may be accomplished by thick layer chromatography, column chromatography, and gas-liquid chromatography. These techniques could be used independently or in conjunction with each other. In most cases, they are used in succession.

Thin or thick layer chromatography involves deposition of

a small amount of the sample on a layer of adsorbent like silica gel supported on a clean glass plate followed by elution of the sample with a suitable solvent by means of capillary action. The process could be one or two-directional. The components of the sample will move up the plate depending on the relative degrees by which each is adsorbed by the adsorbent. The position of each component can then be determined by several ways, one of which is the use of ultraviolet light. Once the individual spots are determined, they could be removed and extracted with a suitable solvent.

Column chromatography uses the same principle as thin layer chromatography, that is, differential adsorption. The more commonly used adsorbents are silica gel and alumina. The sample is introduced on top of the column then eluted successively with solvents of increasing polarity and fractions of a predetermined volume are collected. Each of the fractions is then evaporated and the weight determined to await further analysis.

The basis of separation of the components of a mixture by gas liquid chromatography (GLC) is the distribution of a sample between two phases. One of these phases is a stationary phase of large surface area and the other phase is a gas which percolates through the stationary bed. The stationary phase is a liquid spread as thin film over an inert support and the sample is partitioned in and out of the liquid film. The wide range of liquid phases with usable temperatures up to 400^{o}C make gas liquid chromatography the most versatile and selective

form of gas chromatography. Its use as a separatory tool involves collection of each component as it emerges at the end of the column.

Besides their use in separating a mixture of organic compounds, TLC, column chromatography and GLC are more valuable as analytical techniques for identification and quantitation of the components of the mixture. However, column chromatography has less applications in qualitative studies than GLC or TLC.

The identification of a compound by TLC is based on comparison of its R_f value with that of a standard. In some cases, specific color reactions with a well chosen reagent are utilized.

The latter technique was used in the determination of phenols in surface waters by Smith and Lichtenberg.[59]

Gas Liquid Chromatography, being a more refined technique affords better resolution and reproducibility. For this reason it found wider application as a qualitative tool. It has been used to identify volatile organic compounds which cause malflavors in drinking waters. The retention times of each component was used as the characterizing property. Many organic compounds have been identified by GLC in Chesapeake Bay. Among these were ethane, ethylene, propane and propylene, isobutane, n-butane, isopentane and normal pentane.[69] GLC has also been applied in studies involving petrochemical wastes,[70] and chlorinated hydrocarbon pesticides.[71]

Absorption spectroscopy is another valuable technique in structural studies. Ultraviolet, infrared and nuclear magnetic spectroscopy are among the important techniques that the organic

chemist now uses routinely to gain information about a particular substance.[72] The theoretical aspects and instrumentation involved in these techniques are discussed in many texts and will not be discussed here in any detail.

Interpretations of molecular spectra are based largely on empirical correlations with extensive compilations of data. A given absorption can usually be attributed with reasonable assurance to a particular group or arrangement of atoms within a molecule. When used in conjunction with classical methods, it can help elucidate molecular structure.

Absorption of ultraviolet light (220-800 mu) is caused chiefly by electronic excitation. The spectrum provides information about the type of bonding electrons present in the molecule.

Absorption in the infrared region (0.8-2.5 u near IR) (15-200 u far IR) is due to molecular vibration of one kind or another. The spectrum is generally very complicated. Many of the absorption bands cannot be assigned accurately, those that can however, provide a wealth of structural information about the molecule. Although the spectrum cannot distinguish between a pure and impure sample, in general, the spectrum of a pure compound will have fairly sharp and well resolved absorption bands while the spectrum of a crude sample will display broad and poorly resolved bands because of the many absorptions present.

The examination of the spectrum is useful in following the progress of chromatographic fractionation. Compilations of characteristic group absorptions are available in the literature and are very helpful in the interpretation of spectra. Answers

to structural questions as, does the sample contain a carbonyl group, acid or aldehyde can often be obtained.

The Nuclear Magnetic resonance (NMR) spectrum of a compound can usually be completely interpreted and provides information about the number, nature and chemical environment of the protons in the molecule. Because of this reason, NMR is a more powerful analytical tool than either UV or IR. The interpretation of the NMR spectrum is aided by proper choice of solvent, good resolution, and spin decoupling techniques.

A great deal of information concerning the structural formula of organic compounds and the composition of mixtures of organic compounds can be obtained by mass spectrometry.[73] It is used by the petroleum industry to determine the amount of various compounds present in volatile samples rapidly; geochemists use it to distinguish the place of origin of minerals by measurement of isotopic abundance ratios; and by other industries in the detection of an unsatisfactory product and by organic chemists in structural determination of organic compounds. Correlations of spectra and structure could be found in the literature.

The mass spectrum provides three different kinds of information about any positive ion:

1. The mass to charge ratio can be measured relative to that of ions of known mass to charge ratios.

2. The abundance of the ion can be measured relative to that of other ions in the spectrum.

3. Detailed information regarding the mode of formation of the ion from the sample can be obtained.

If the investigator is prepared to thoroughly study the effects of varying parameters under his control, such as the energy of the bombarding electrons, the amount of sample, the speed of examination, sensitivity and others, the mass spectrum can be very valuable in the solution of a structural problem. It is the single most important source of accurate information about the sample. In conjunction with the gas chromatograph, it is finding wide application in the analysis of a mixture of trace organic compounds obtained from water samples.

The gas chromatography-mass spectrometer system is a valuable tool which enables analysts to obtain the mass spectra of individual components of a complex mixture, as they are eluted off a gas chromatographic column. The recording of this vast amount of data is facilitated by the development of a mass-spectrometer-computer system developed by Hites and Bieman [74] Some of the features of this system are that spectra are recorded continuously regardless of the emergence of gas chromatographic fractions, peak centers and intensity. Calculations proceed while the spectrum is being scanned, secondary storage on magnetic disks allows space for practically an unlimited number of spectra; the spectra are correlated with the chromatogram by a plot of total intensity versus spectra index number and all spectra are presented in digital form (mass intensity table and/or plots) suitable for further analysis.

The interpretation of the large amounts of data thus collected presents a tremendous challenge to the investigators.

However, in most complex mixtures, several of the components are known and they could be identified by comparing the spectrum with that of the authentic sample. Recent developments enable one to make the comparison of the spectra of an unknown sample to a large file of reference spectra. Details of the process are discussed by Hites et al.[75, 76] and are welcomed by all investigators faced with the difficult task of deciphering the composition of some unknown sample.

IV. EXPERIMENTAL PROCEDURES

All solvents were distilled prior to use. All glassware was washed with detergent and chromic acid, and rinsed with water and acetone.

Infrared spectra were obtained as film on NaCl or NaBr disks using a Beckman FR-8 spectrophotometer. NMR spectra were obtained on a Varian A-60 instrument. The Gas chromatograph used was a Varian Aerograph 204 equipped with flame ionization and electron capture (Tritium, 250 mc) detectors. Mass spectra were obtained on a Finnigan mass spectrometer hooked up to a Varian Aerograph and a computer.

TOC's were obtained from a Beckman TOC analyzer on well samples filtered through a glass fiber filter, acidified to pH 2 with concentrated H_2SO_4 and purged with N_2 gas for 5-10 minutes.

Sampling. All samples were obtained by the CAM with the exception of one sample which was taken with XAD-2 for comparison of adsorption efficiency and selectivity.

The carbon column used consisted of a 3" i.d. x 18" glass column (Figure 8) packed with activated carbon (supplier : Herbert Chemical Co.) and plugged at both ends with glass wool. The column was attached to a teflon line that extended into the water table and groundwater was pumped through at a certain rate

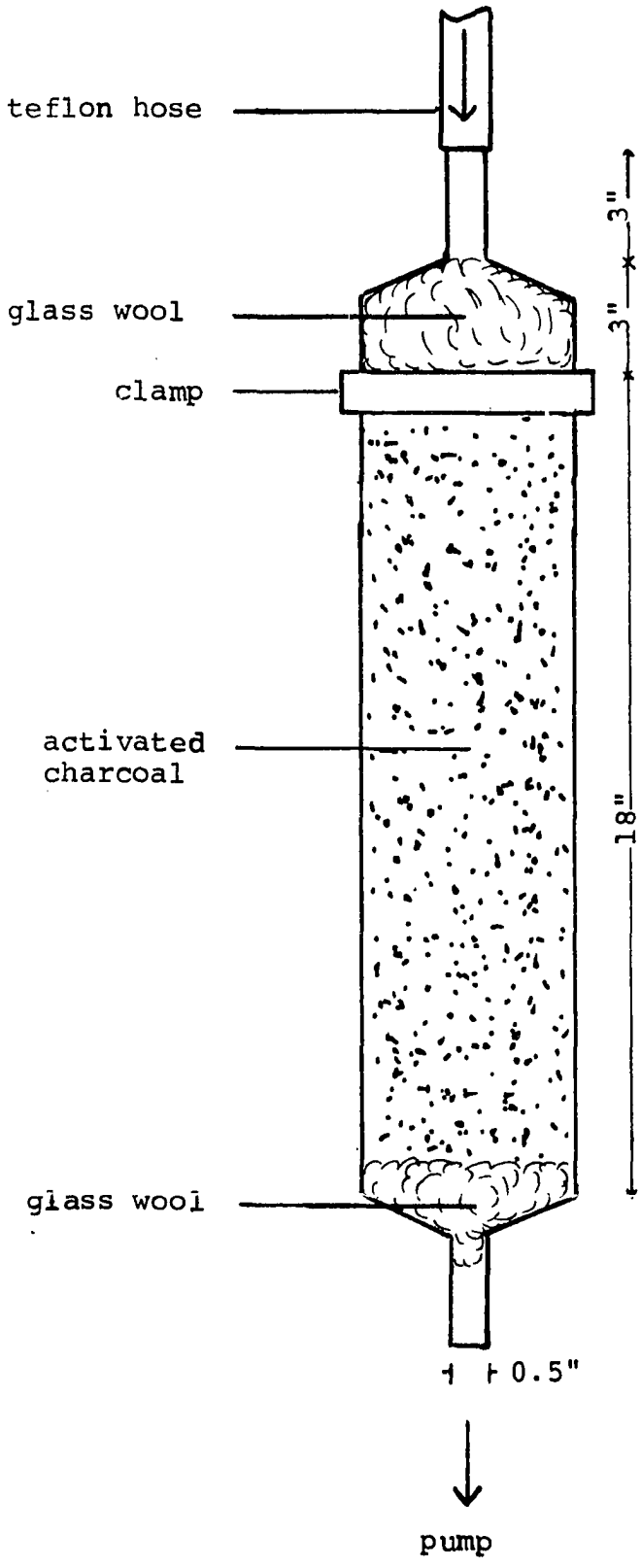


Figure 8. Carbon Adsorption Column

which was measured periodically. The pumps used were of the rubber impeller type that could be operated by a 12 volt battery or a 110 volt power source.

After the desired volume of water had passed through the column, the column was drained and dried by passing dry N_2 gas at a low rate with heating to a temperature not exceeding 65°C. Invariably the drying process took at least 24 hours and a cylinder of N_2 gas (2,300 psi).

The amberlite column used measures 30 cm x 3 cm i.d. and was packed loosely with XAD-2 which had been pretreated as follows. The resin (150 ml) was washed with several bed volumes of distilled water then extracted with acetonitrite (2 liters) for 18 hours. The extraction was repeated with fresh acetonitrite for another 18 hours. The acetonitrite was washed off with distilled water and was packed into the column which was plugged with glass wool at one end. Some glass wool was placed at the inlet end to act as a prefilter.

Desorption of organics from the adsorbent. The dried carbon was transferred to a modified Soxhlet extractor (capacity, 3 liters) and extracted with chloroform for a period of at least 36 hours. The $CHCl_3$ solution was dried by passing it through an anhydrous Na_2SO_4 column and concentrated or evaporated to dryness with the use of a rotary evaporator.

The XAD-2 column was drained, and the glass wool used as a prefilter was removed. Hot ethanol (200 ml) was passed through the column at full gravity flow followed by 500 ml of distilled water. The combined aqueous solution was then extracted with three

50 ml portions of hexane. The hexane extract was dried and concentrated to a volume of 5 ml.

Analysis of the extracts. Thin layer chromatography was performed on all CCE crude extracts to determine the separation of components on silica gel G. (supplier: Applied Science Laboratory). The developing solvents used were hexane, benzene, $CHCl_3$ and different mixtures of $CHCl_3$ and methanol. The position of TLC spots were determined with I_2 vapor or with chromic acid spray reagent (supplier: Applied Science Laboratories).

Column chromatography was accomplished on a dry column of silicar (60-100 mesh) of about 12 cm x 15 cm and topped with anhydrous Na_2SO_4. Elution was usually in 2-100 ml portions of the following solvents: hexane, benzene, chloroform and 1:1 $CHCl_3$-MeOH.

Gas chromatography of individual fractions obtained from the column chromatographic separation were done on the following columns: 5.3 percent DC-200 Gas Chrom Q, 1 percent OV-1 on Gas Chrom Q, and 10 percent QF-1 on Gas Chrom Q.

All chart speeds are 0.5 inches per minute, unless otherwise specified.

Quantitative Estimation of Phthalates. Plots of peak areas versus amounts of some standard phthalates such as diisobutyl phthalate, octyl adipate, di-2-ethylhexyl phthalate, and n-octyl phthalate were constructed and found to be linear (Figure 53).

The amounts of selected compounds were estimated by calculating the peak areas from the gas chromatogram and reading

the corresponding concentrations from the standard plots.

The CAM blank. A column-full (183 grams) of activated charcoal used as adsorbent was extracted with three liters of chloroform, dried over anhydrous Na_2SO_4 and evaporated to dryness with the use of a rotary evaporator.

The crude chloroform extract obtained was analyzed by gas chromatography-mass spectrometry then subjected to column chromatographic separation on silicar (10 cm x 1.5 cm). Each of the six 100 ml fractions were concentrated to a volume of $\simeq$ 1 ml and analyzed by gas chromatography.

V. RESULTS AND DISCUSSION

As a result of previous studies on the Norman Sanitary Landfill, a number of wells were already existing when this project began. Four of these existing wells were chosen to be used as sampling wells for determination of the gross organic concentration in the groundwater. These wells were originally designated numbers 6, 12, 13, and 3 in Figure 1 by another investigator.[2] In addition to these wells, a deep well (30 feet) was drilled at the south end of the landfill, (number 14, Figure 1) which is part of the new landfill. Approximately fifteen feet of refuse and eighteen feet of water was present in the well, and the bottom three feet of refuse appeared to be in the water table. These wells have been renumbered 1a, 1b, 2, 4, and 3 respectively.

The gross organic content of these wells were determined from measurement of COD and TOC and appeared to be lower than expected (Table 5). The COD's obtained indicate that the gross concentration of organic matter is highest in the groundwater from well number 3. The groundwater from well number 4 shows a much lower COD, which indicates that stabilization of the organics in this location proceeded to a greater extent. The COD data also shows a remarkable attenuation of the organic concentrations as the groundwater moves downstream. The TOC's obtained on 6/6/73 show the highest value for well number 3.

Table 5. COD and TOC Data (mg/ml)

Well No.	Location with respect to landfill	Depth (ft.)	Perforations	COD* (average) 11/28/72	TOC (filtered) 5/16/72	6/6/73	8/10/73
1a	upstream	10 (sand-point)	bottom 3 ft.		11.5		15.0
1b	upstream	40 (cased)	bottom 10 ft.	87.63		14.0	
2	50 feet downstream	40 (cased)	bottom 10 ft.	91.58	9.0	5.5	23.0
3	in the new landfill	30 (cased)	bottom 10 ft.	346.71		34.2	13.0
4	in the old landfill	35 (cased)		80.01	13.0	8.0	28.0

* Average of duplicate samples.

These data indicate that in general, the organic content of the groundwater increased in samples located within the landfill, and decreased again as it moved away from the landfill. The TOC data obtained on August 10, 1973, however, does not agree with this trend. The low TOC observed in well number three can be partly explained, however, by the fact that during the dry season, a minimum amount of leaching occurs as precipitation stops and the water table goes down. The increased organic concentration in well number two, downstream from well number three could be due to the fact that it is located at a much lower elevation than well number three and a nearby pond that feeds it still contains water but has been concentrated by evaporation. This was borne out by the following experiment. A shallow sandpoint (six feet) was put in place beside well number two. The depth was chosen such that only the perforated section of the pipe was in the water table. TOC obtained from this sandpoint was almost identical to that of the nearby pond which was 28 mg/l, only 5 mg/l above the sample obtained from well number two at a depth of forty feet.

For the determination of specific organic compounds in groundwater, especially the PCB's, it was decided to utilize wells numbers two and three, because these wells are located within the fill or in close proximity to it and would therefore be richer in organic pollutants. Moreover, the organic compounds present in these locations would reflect the biochemical processes taking place in these environments.

CAM samples were obtained from wells numbers 1b, 2, 3,

and 4, but only samples from wells numbers 2 and 3 were subjected to extensive analysis. Furthermore, since the determination of the PCB's was an important objective, the CCE was to be examined more closely. The samples isolated from the above sampling wells and the conditions under which they were obtained are listed in Table 6.

Table 6. Groundwater Samples

Well number	1	2	3	4
Location	naturizer	300 feet downstream from land-fill edge	in refuse cell	at asphalt plant
Sampling conditions carbon adsorption method	2 l/min. 374 gal.	a) 2 l/min. 187 gal. b) 400 ml/min. 99.68 gal.	175 ml/min. 42 gal.	300 ml/min. 85 gal.
weight (mg) of carbon chloroform extract	43.4 (.116 mg/l)	a) 55.7 (0.077 mg/l) b) 157.5 (0.41 mg/l)	75 (0.46 mg/l)	55.3 (0.65 mg/l)
weight (mg) of hexane fraction after column chromatography over Silicar		a) 1.9 b) 12.6	5.9	2.7
first benzene fraction		a) 3.9 b) 35.2	9.7	1.21
XAD-2 (mg) extract (5 gal. H_2O)			9.0	

As can be seen from the above table, the amount of organics adsorbed by carbon is dependent on flow rate and the total volume

of water passed as previously observed by Booth.[61] The variable flow rates obtained with each sampling run were due to the differences in the elevation of the water table at each well and also due to the changes in the capacity of the pumps used.

The use of XAD-2 amberlite resin as an adsorbent was tried on well number 3. As with the CAM sample obtained from the well, sampling could not be accomplished by direct flow of groundwater up the teflon line to the column with the use of a rubber impeller pump. Sampling had to be done by drawing groundwater into a 3.5 gallon glass carboy with the use of a vacuum pump and this water was allowed to flow into the column by gravity. Flow through the carbon columns was maintained without any difficulty. The XAD column on the other hand plugged after 1½ gallons of water had passed through. The sampling process had to be completed in the laboratory by first filtering the groundwater through a glass fiber filter, then letting it pass through the amberlite at full gravity flow. Even after the filtering operation which removes practically all the turbidity from the groundwater, the flow rate dropped from an initial 100 ml/min. to 60 ml/min., at the end of a 5-gallon sample. In spite of the difficulty, however, the quantity of sample obtained with the resin compares favorably with the CAM. Furthermore, since the drying process was eliminated, the loss of volatile compounds should be minimized. The gas chromatogram of the crude XAD-2 hexane extract from well number 3 is shown in Figure 9.

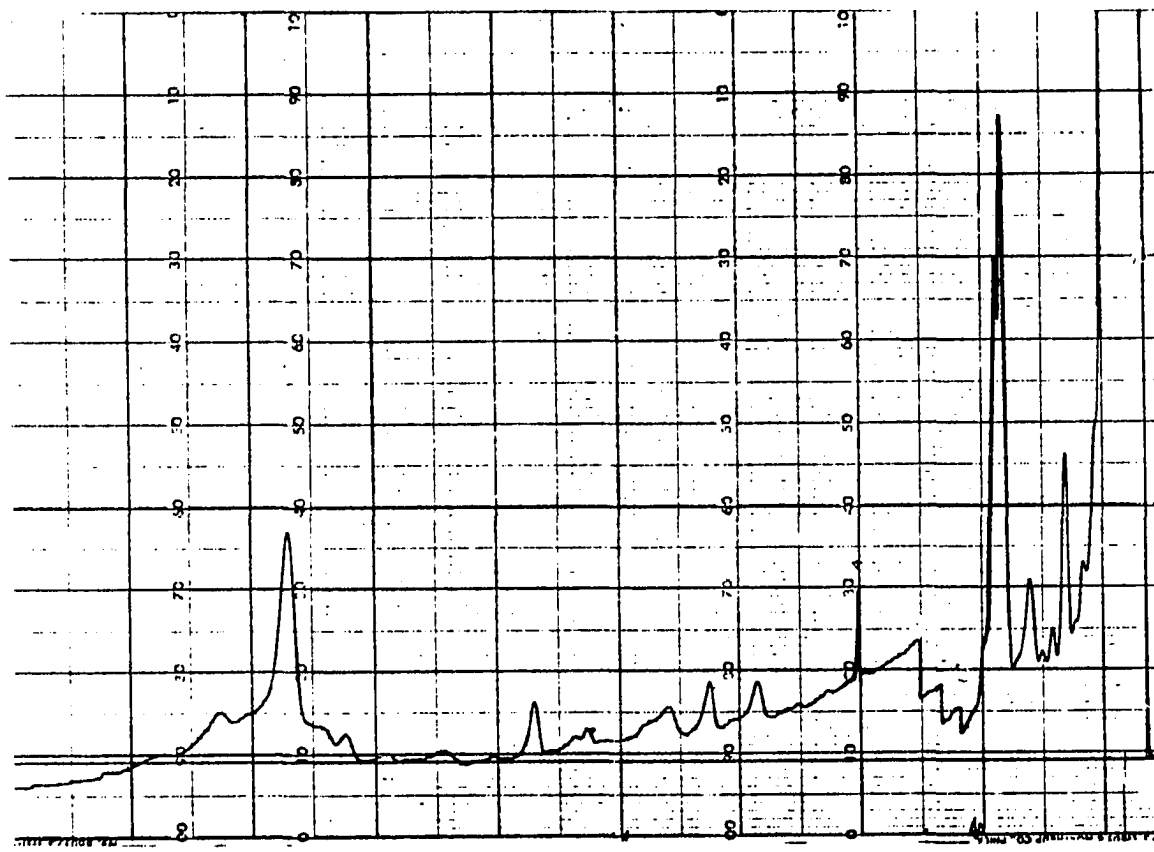


Figure 9. Gas Chromatogram for XAD-2 Sample, Well number 3.

Sample Analyses. Thin layer chromatography of the CCE extracts from well number 3 on silica gel plates showed the presence of several components. One of the major components moved very close to the solvent front (R_f value = 0.96 with benzene as the developing solvent) and was later isolated as a single spot by column chromatography on silicar using 100 ml of hexane as the eluent.

The same component was also obtained from the hexane fraction of the column chromatographic separation of the CCE from well number 2. The column chromatographic separation of both CCE samples was performed without prior solubility separation because it was desired to separate the aromatic fraction rapidly as this

would presumably contain most PCB's and/or chlorinated HC pesticides. The procedure followed the general separation scheme for the identification and measurement of chlorinated hydrocarbon pesticides in surface waters,[77] although the volume and number of fractions varied slightly.

Aliphatic Fractions. The hexane fractions from both wells gave identical gas chromatograms. The gas chromatogram of the hexane fraction from well number 2 (ICCE2 hexane) can be seen in Figure 10a. Some of the peaks in the chromatogram coincide with peaks in Aroclor 1232 (Figure 10b) and was thought to contain some of the PCB mixture in addition to the other major components. This thinking was encouraged by Reynolds' report[28] that PCB's tended to run toward the solvent front and that these compounds are eluted from florisil by 200 ml of hexane. Gas chromatography-mass spectrometric analysis of the hexane fraction from well number 3 (ICCE3 hexane)(Figure 11) gave mostly the typical spectra of aliphatic hydrocarbons. The spectra are not presented here, however, because as can be seen from the gas chromatogram the separation of components is not adequate. Nevertheless, the presence of the following compounds in the mixture is indicated (Table 7).

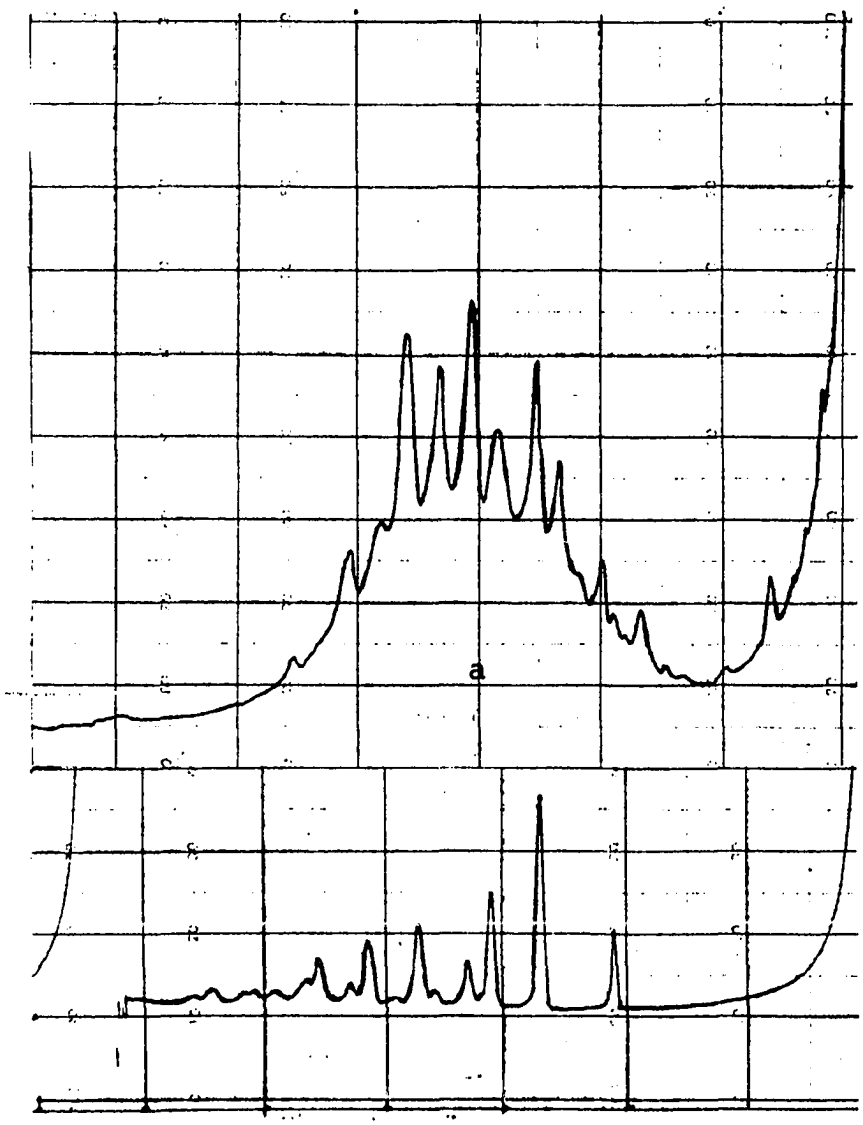


Figure 10. (a) Gas chromatogram of hexane fraction from well number 2 (ICCE2 hexane). (b) Aroclor 1232. (chart speed 0.5 in/min.)

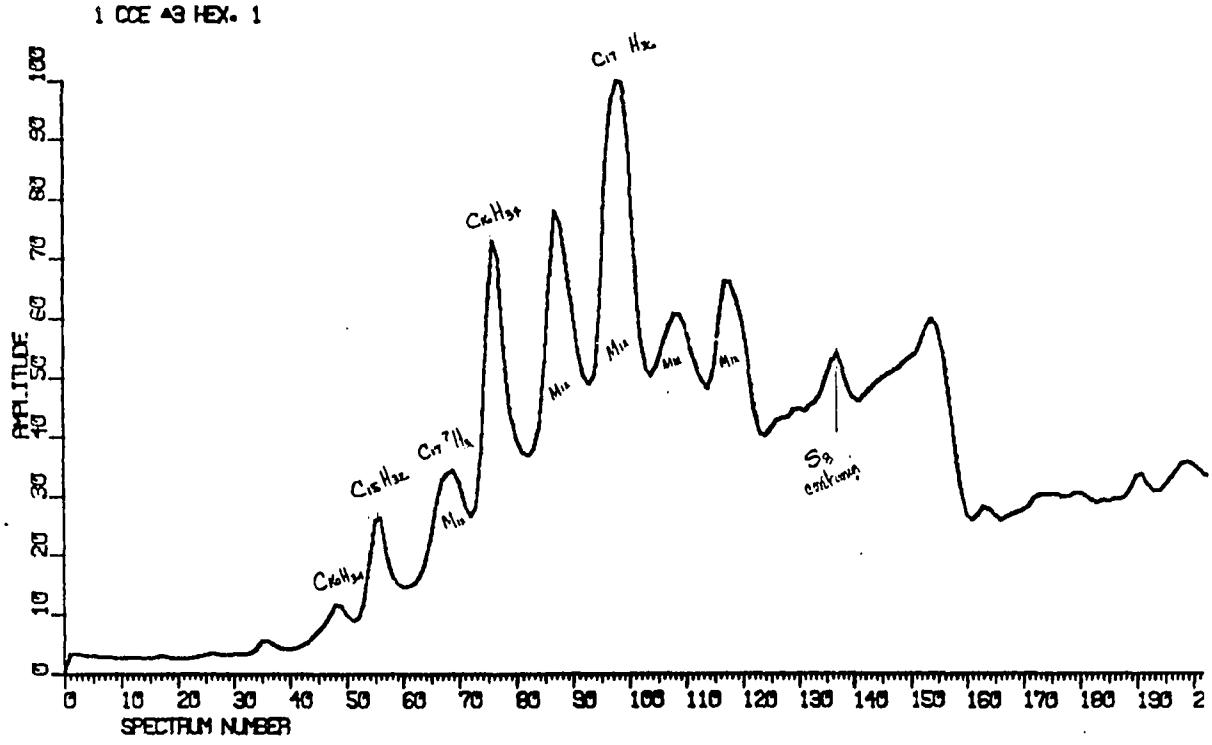


Figure 11. Gas chromatogram plot of hexane fraction of CCE 3. Column: 5.3% DC-200, Temperature 125° - 250°, 10°/min.

Table 7. ICCE-3 Hexane

Spectrum number	M^+	Molecular formula
48	226	$C_{16}H_{34}$
55	212	$C_{15}H_{32}$
69	240	$C_{17}H_{36}$
76	226	$C_{16}H_{34}$
87	254	$C_{18}H_{38}$
137	268	$C_{19}H_{40}$
137	256	S_8

There are two isomeric hexadecanes in the mixture (spectra numbers 48 and 76) and more compounds and their isomers could be possibly discerned if the separation of the component peaks was better. Spectrum number 137 (Figure 12) also shows the presence of two distinguishable components, a hydrocarbon with $M^+ = 268$ ($C_{19}H_{40}$) and sulfur in the form of S_8, the spectrum of which dominates the mixture.

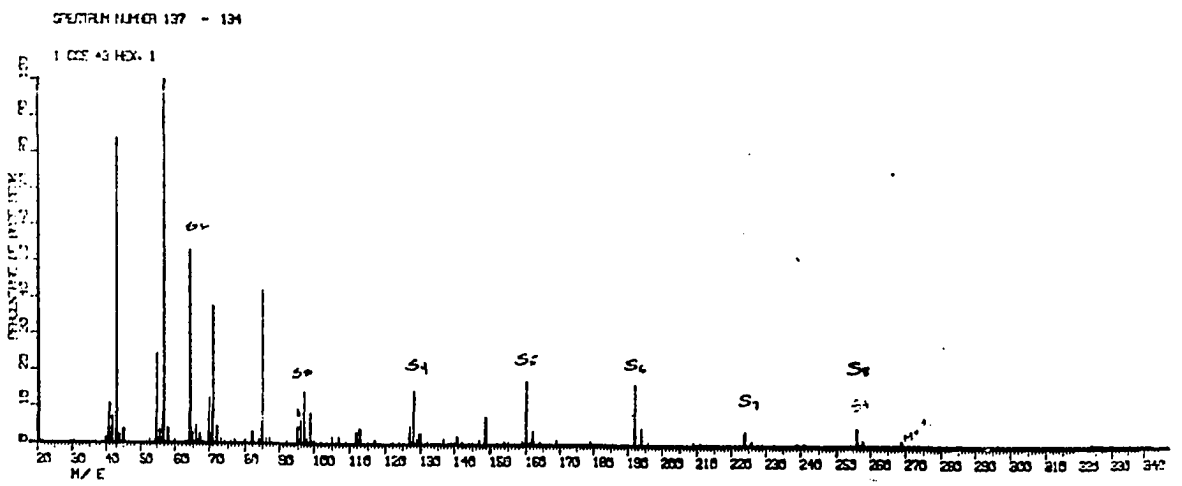


Figure 12. Mass spectrum of Hexane fraction, CCE-3.

The presence of sulfur in the sample indicates the fact that it is fairly soluble in chloroform and is therefore extracted together with the organics that had been adsorbed onto the carbon column. It also confirms that the conditions existing under the fill are indeed anaerobic and that bacterial reduction of sulfates to elemental sulfur takes place.

Aromatic Fraction: Search for PCB's. The identification of the components of the hexane fraction was not taken beyond this point because the aromatic fraction was of more interest to us. The benzene fraction was the next fraction obtained from the column chromatographic separation of the CCE. This fraction contained a large number of components which were adequately separated on a 5 ft. x 1/8 in. DC-200 column (Figure 13). The next fraction ($CHCl_3$ eluate) still contained compounds present in the benzene fraction (Figure 14) but the second $CHCl_3$ eluate shows a predominance of the compounds with lower retention times (Figure 15) which were present in smaller amounts in the benzene fraction.

Figure 16 is the gas chromatogram of the benzene fraction plotted during the gas chromatography-mass spectrometry (gc-ms) run on this sample. The major components of this mixture have longer retention times and start coming off the column at a temperature of 250°C and fifteen minutes after injection at a temperature of 110°C.

The use of Tritium as electron capture detector with a maximum operating temperature of 225°C would therefore not be advisable. However, if the column was changed to QF-1, the

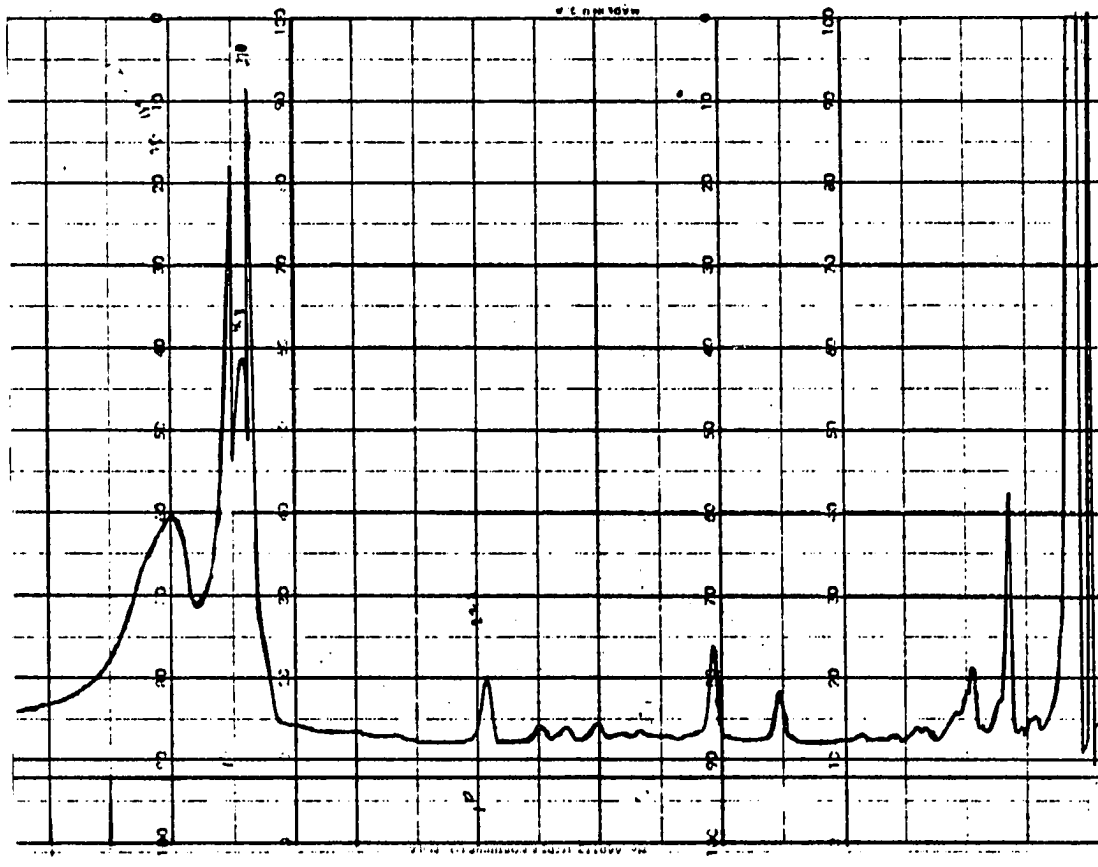


Figure 13. Gas chromatogram of benzene fraction, CCE-3
Column: 5.3% DC-200 on Gas Chrom Q
Temperature - 125° - 250°, 10°/min.

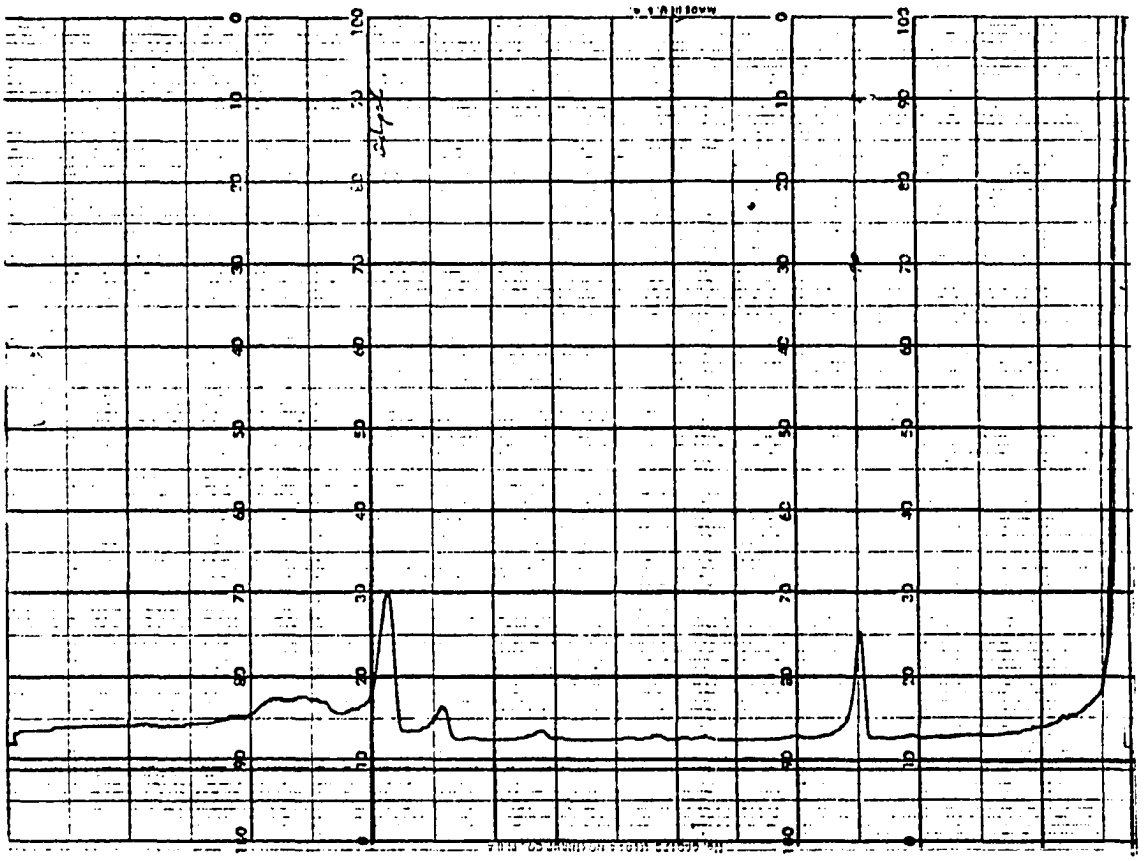


Figure 14. Gas chromatogram of $CHCl_3$ fraction of CCE-3
Column: 5.3% DC-200 on Gas Chrom Q,
Temperature - 150° - 260°, 10°/min.

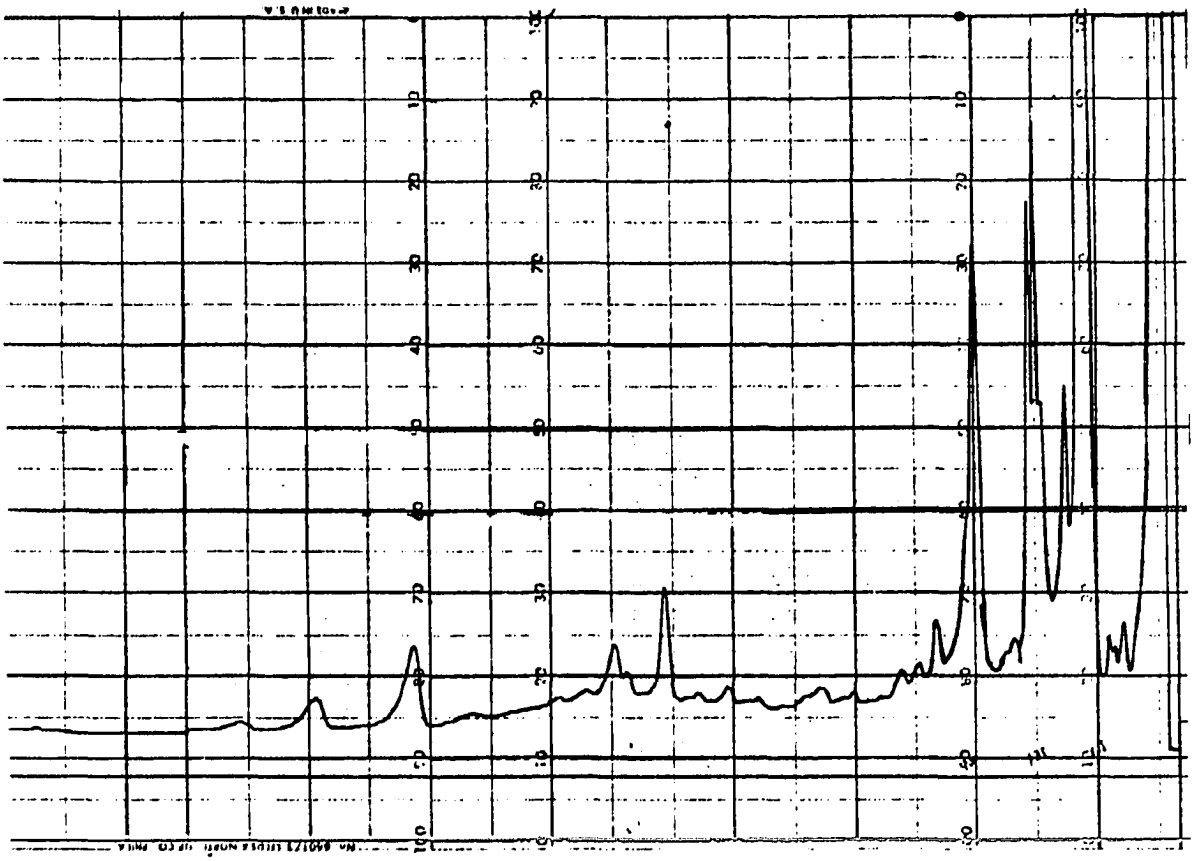


Figure 15. Gas chromatogram of $CHCl_3$ fraction CCE-3

Column: 5.3% DC-200 on Gas Chrom Q,
Temperature - 100° - 260°, 10°/min.

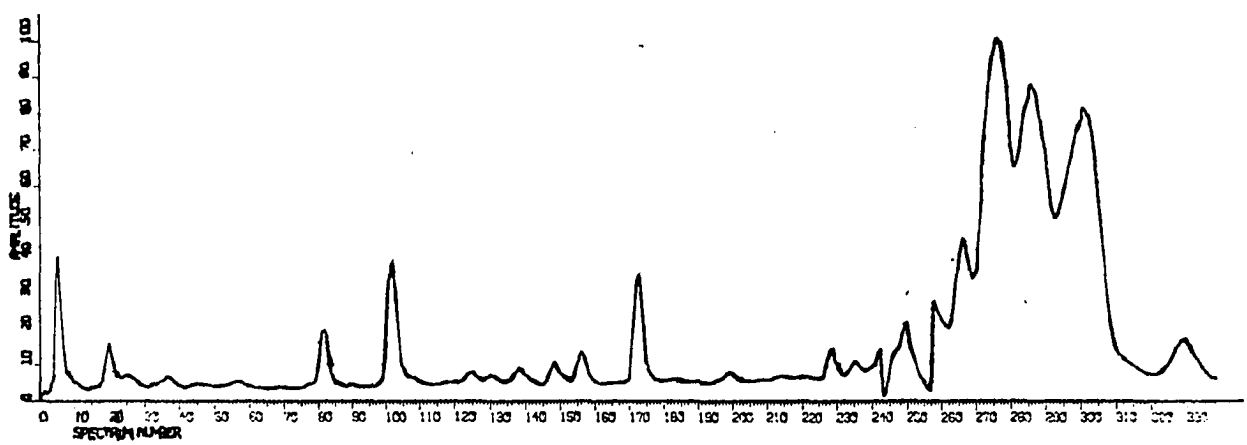


Figure 16. Gas chromatogram - mass spectroscopy of CCE-3

retention of these compounds and the operating temperature could be lowered considerably.

This fraction being the aromatic fraction was searched for the presence of PCB's. The gas chromatograms have components emerging off the DC-200 column at the same relative time and temperature at which the PCB's (Figures 17, 18, 19, and 20) come off although the quantitative similarity is not apparent. A subset scan (Figure 21) was therefore run on the recording gc-ms. This scanning technique is similar in principle to Bonelli's[31] discussed earlier but is mostly that developed by Eichelberger et al.[78] which involves program controlled scans with several specific ions of known significance to the compound of interest.

The application of subset scanning techniques to the analyses of PCB's enhances the sensitivity and yet does not sacrifice too much of the qualitative information inherent in a complete mass spectrum. Details of the application of the technique and rationale behind it are discussed by Eichelberger et al.[78]

The gas chromatogram in Figure 21 was obtained by repetitive scan of the PCB subset masses 190, 224, 260, 294, 330, 362, and 394 with the integration time adjusted such that each peak in the subset scan appears approximately at the same place on the spectrum number axis of the complete mass chromatogram scan, 0-350 atomic mass units (Figure 16).

The selected subset ions are the M^++2 ions of monochloro biphenyl, dichloro biphenyl, trichloro biphenyl, tetrachloro biphenyl, pentachloro biphenyl, hexachlorobiphenyl and heptachloro biphenyl respectively. It is obvious from Figure 21 that

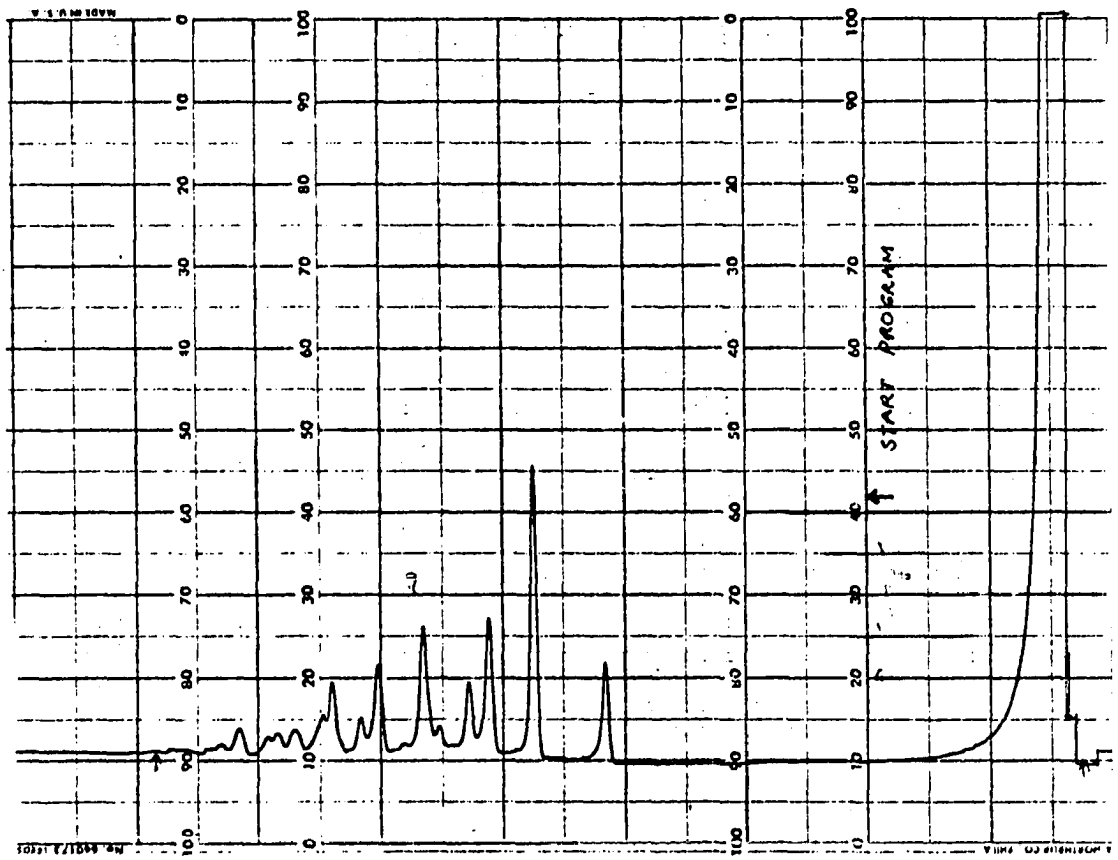


Figure 17. Aroclor 1232 on 5.3% DC-200 5' x 1/8"
Temperature - 120° - 250°, 10°/min.
N_2 flow - 20 ml/min.

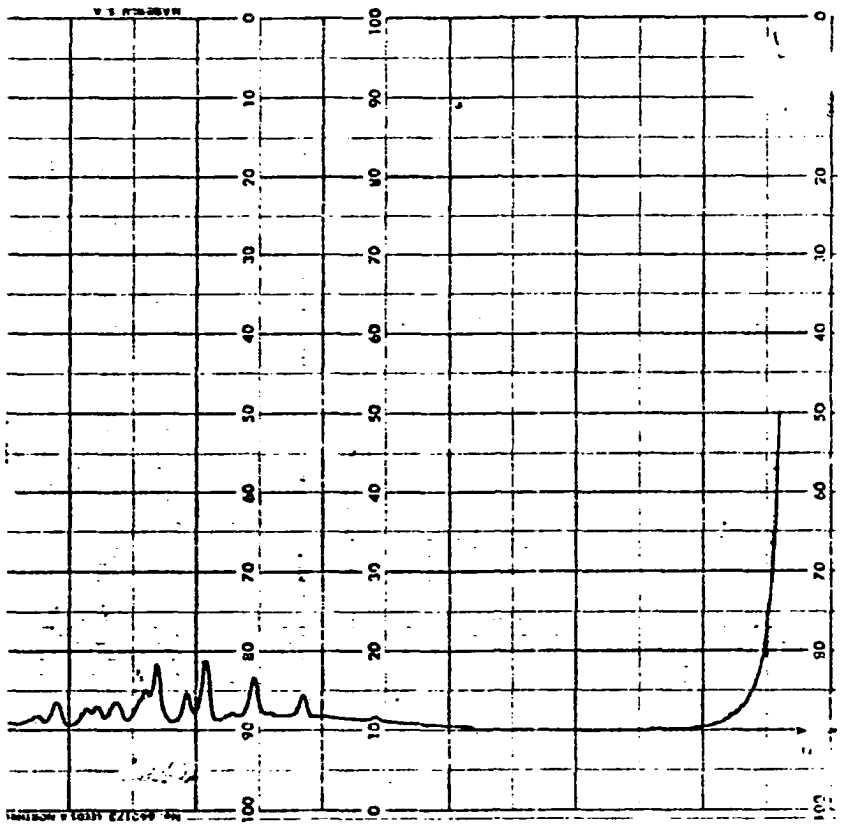


Figure 18. Aroclor 1242 (1ul)
Column: 5.3% DC-200 on Gas Chrom Q
Temperature - 120° - 250°, 10°/min.
N_2 flow 20 ml/min.

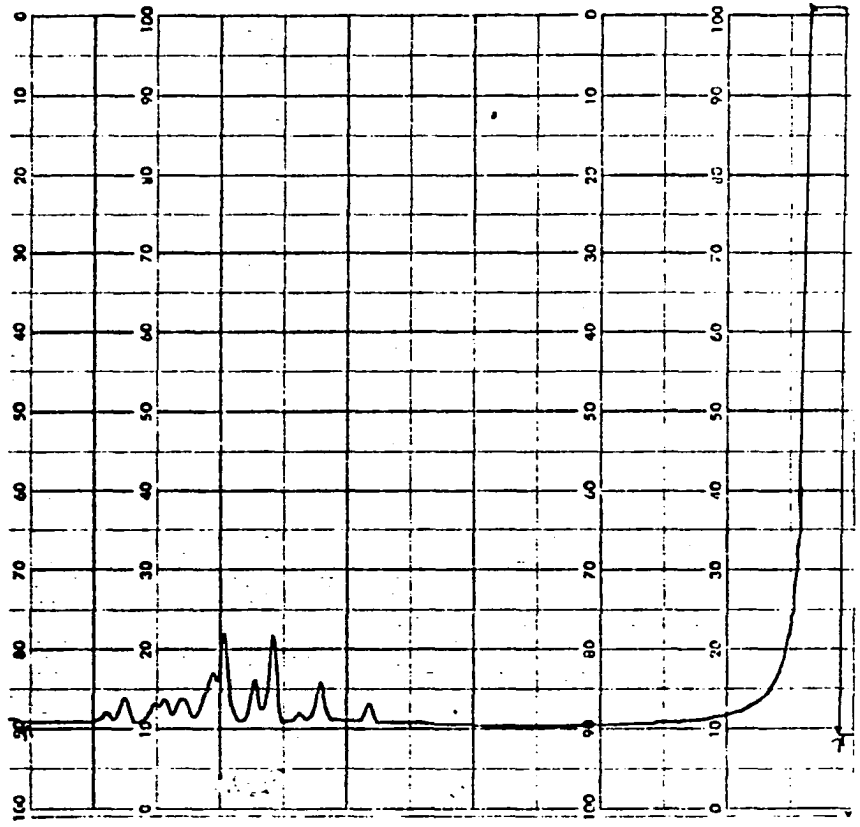


Figure 19. Aroclor 1248
Column: 5.3% DC-200 on Gas Chrom Q
Temperature - 120° - 250°, 10°/min.
N_2 flow 20 ml/min.

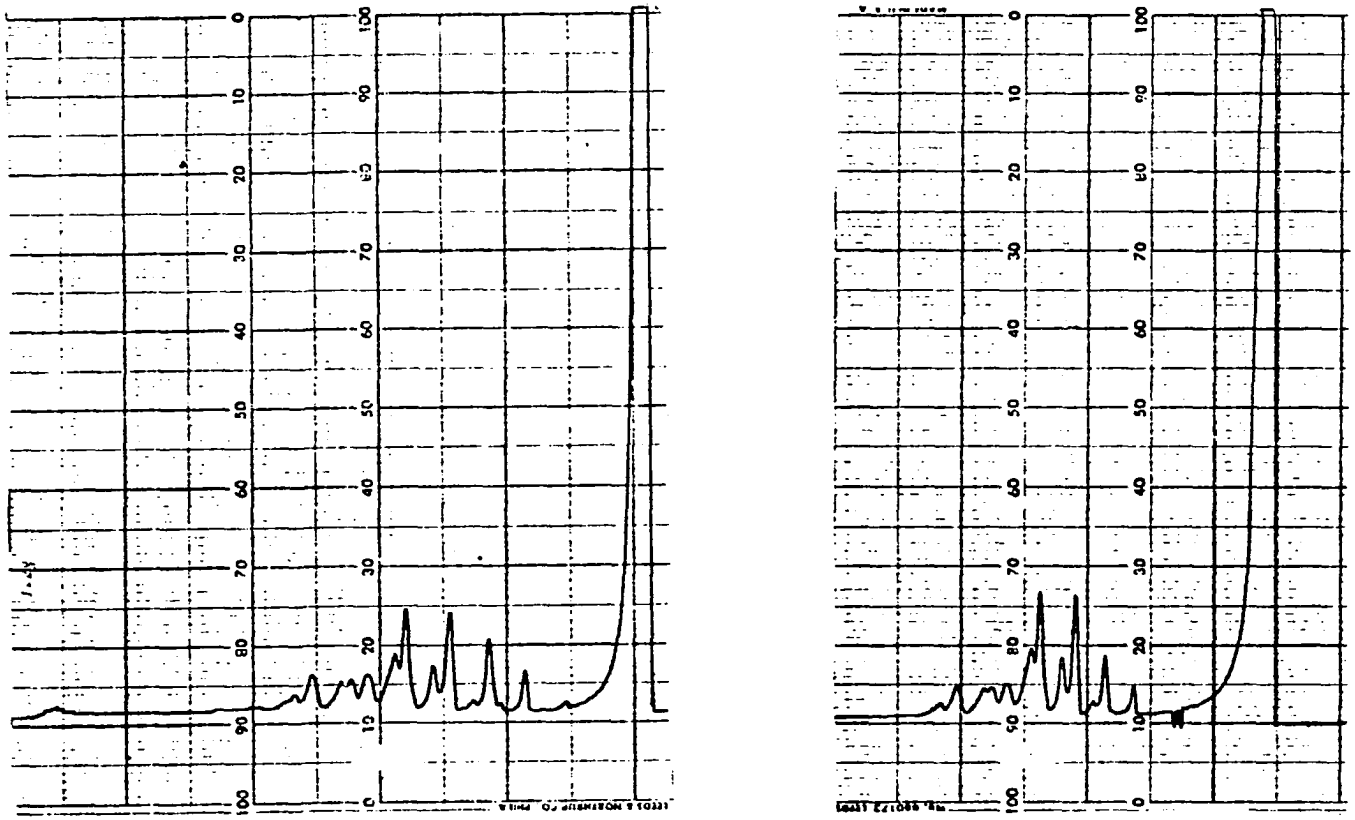


Figure 20. Aroclor 1242 (a) and 1248 (b) Column 3% OV-1 on Gas Chrom Q, 6' x 1/8" Temperature - 150° - 250°, 10°/min. N_2 flow $\simeq$ 25 ml/min.

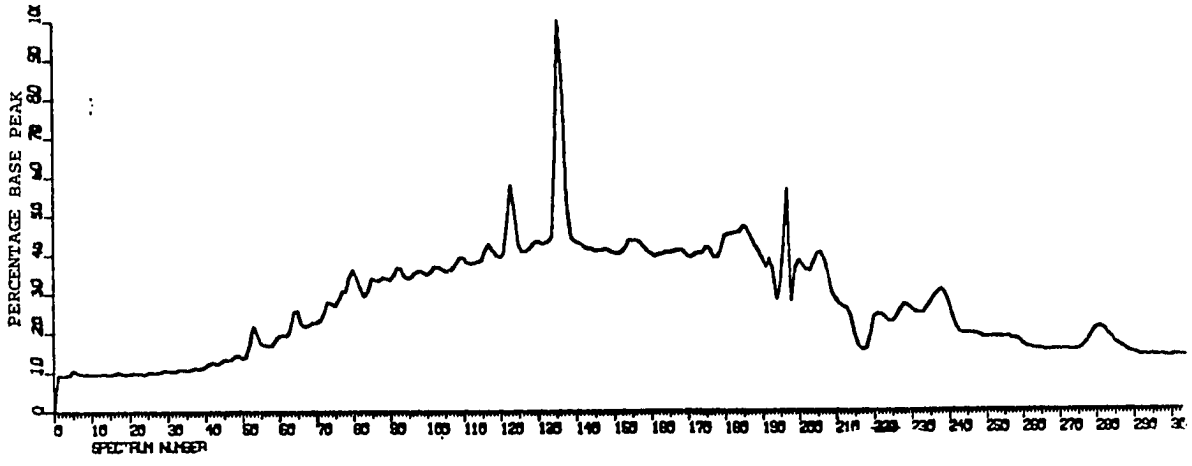


Figure 21. gc-ms Plot of Benzene Fraction CCE-3 Subset Scan, Column 5.3% DC-200 on Gas Chrom Q, Temperature - 110° - 250°, 10°/min.

there is indeed a gain in sensitivity from peaks which contain the selected subset masses. The presence of a PCB mixture in the sample would be indicated by the appearance of the subset gas chromatogram and confirmed by obtaining the complete mass spectrum on component peaks. The complete mass spectrum of the major components of this sample were obtained and are shown in Figures 22 through 35. None of these resemble the characteristic mass spectra of the polychlorinated biphenyls, some of which are shown in Figure 36.

Phthalates: Well number 3. The majority of these spectra, on the other hand, have base peaks at m/e 149 which are very characteristic of another group of environmental contaminants known as dialkyl phthalates. PCB's are known for their stability and also exhibit the same stability upon electron impact as evidenced by the presence of large molecular ion peaks. Often, the presence of a PCB mixture in an environmental sample is sufficiently indicated by the presence of those molecular ion

Figure 22. Spectrum number 4 - 2
ICCE3 Benzene 3

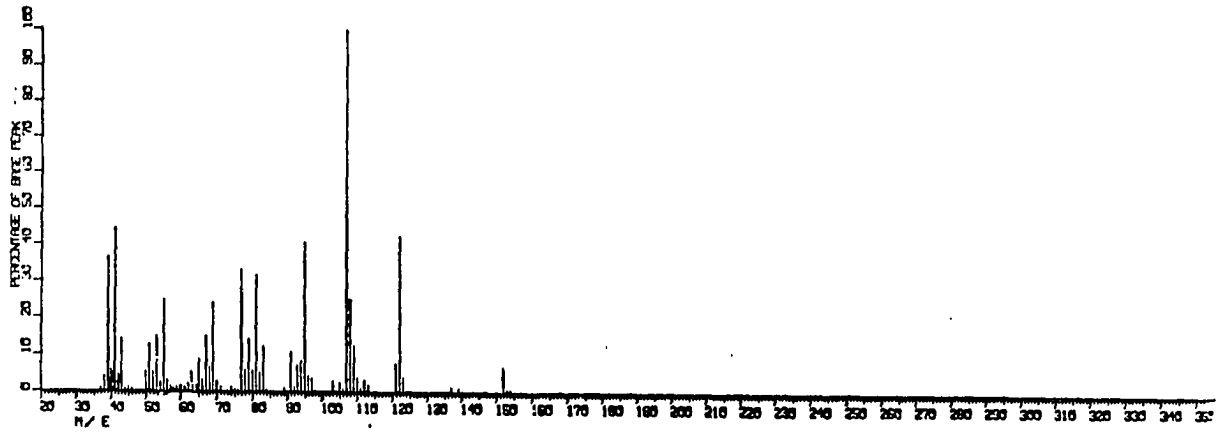


Figure 23. Spectrum 20 - 17
ICCE3 Benzene 3

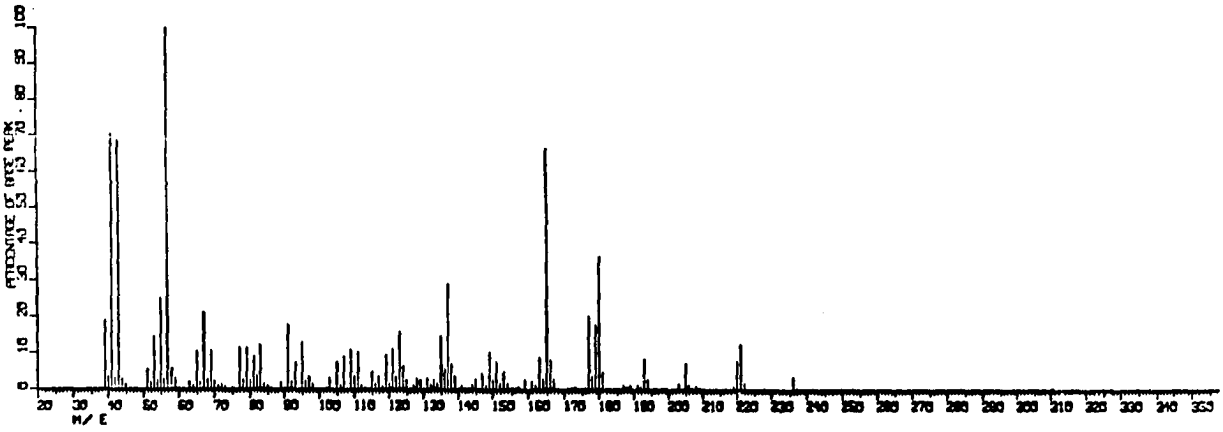


Figure 24. Spectrum number 81 - 78
ICCE3 Benzene 3

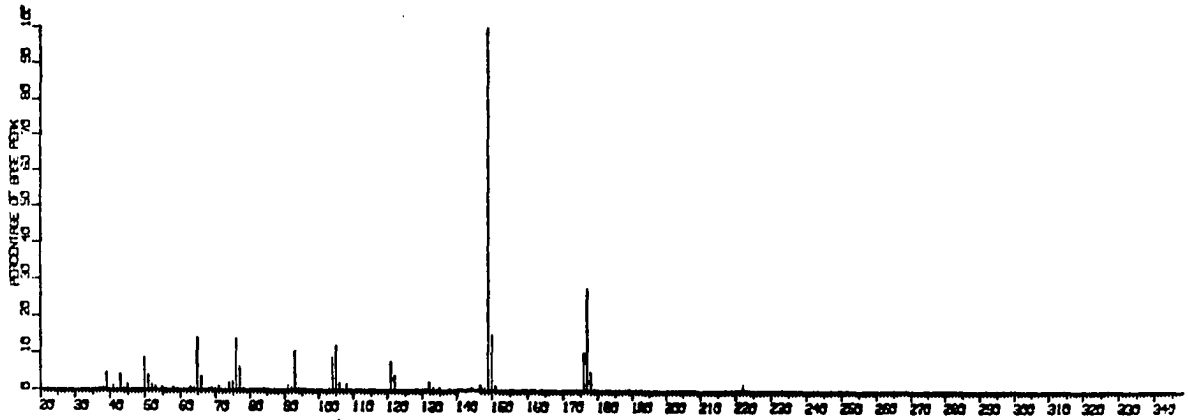


Figure 25. Spectrum number 101 - 98
ICCE3 Benzene 3

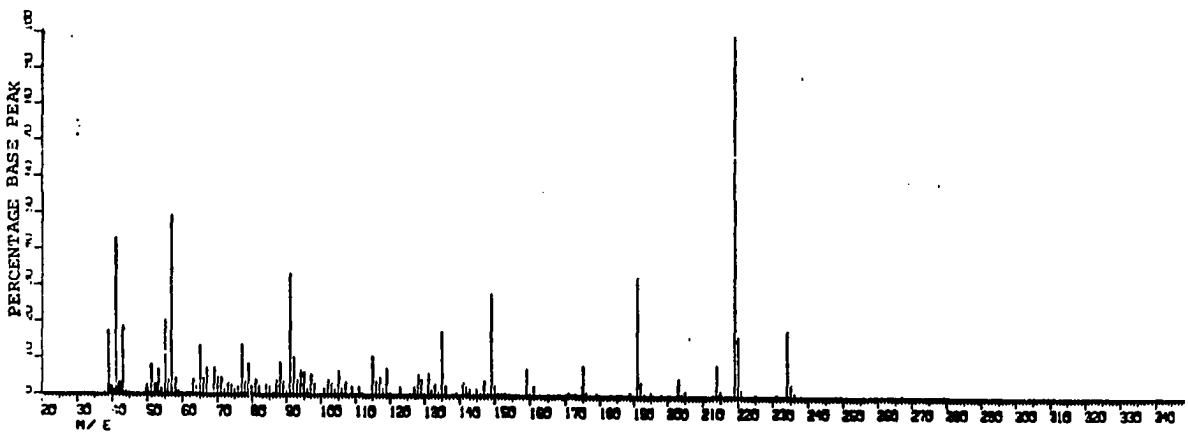


Figure 26. Spectrum number 138 - 135
ICCE3 Benzene 3

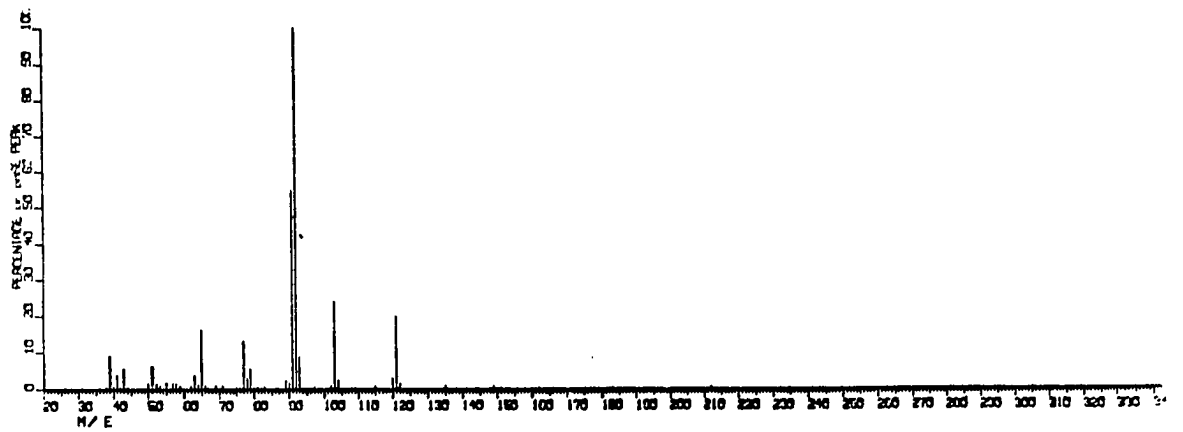


Figure 27. Spectrum number 148 - 145
ICCE3 Benzene 3

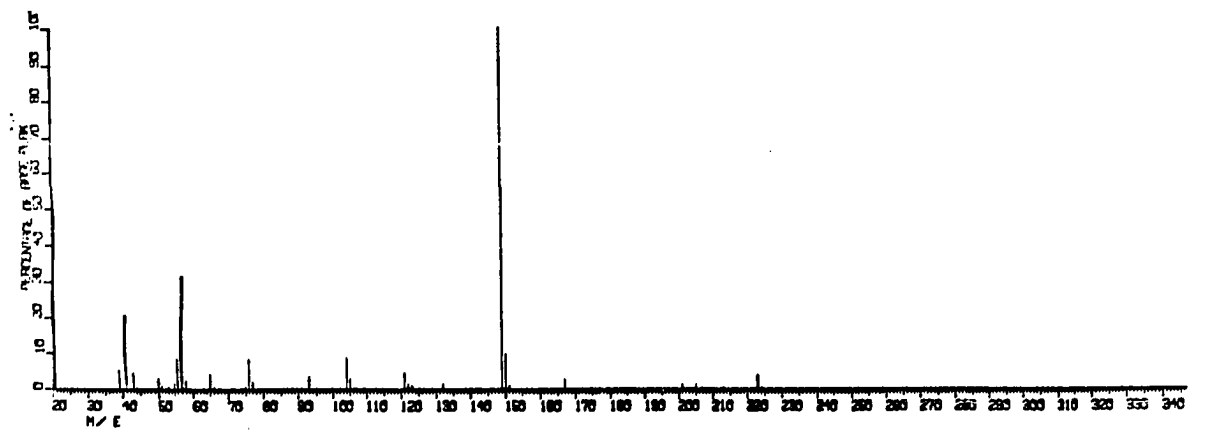


Figure 28. Spectrum number 156 - 153
ICCE3 Benzene 3

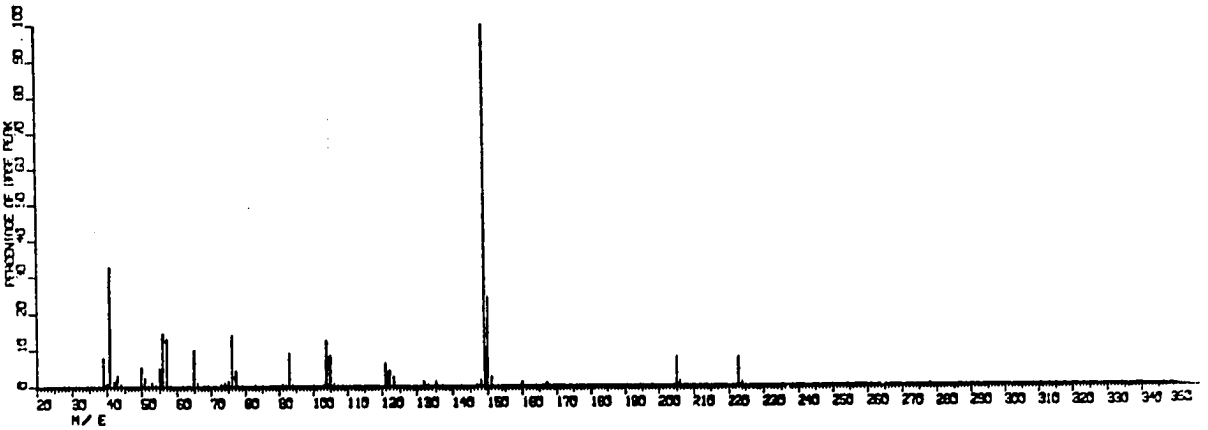


Figure 29. Spectrum number 172 - 169
ICCE3 Benzene 3

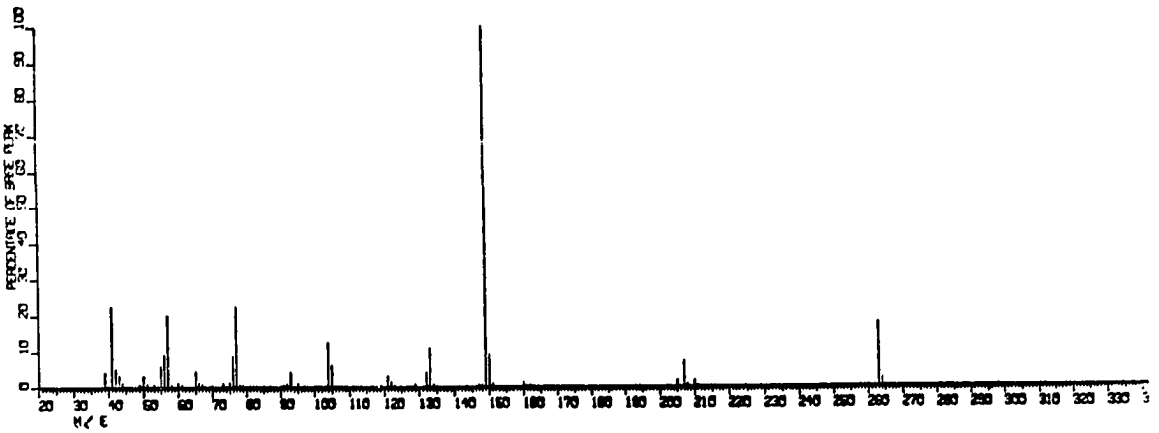


Figure 30. Spectrum number 228 - 225
ICCE3 Benzene 3

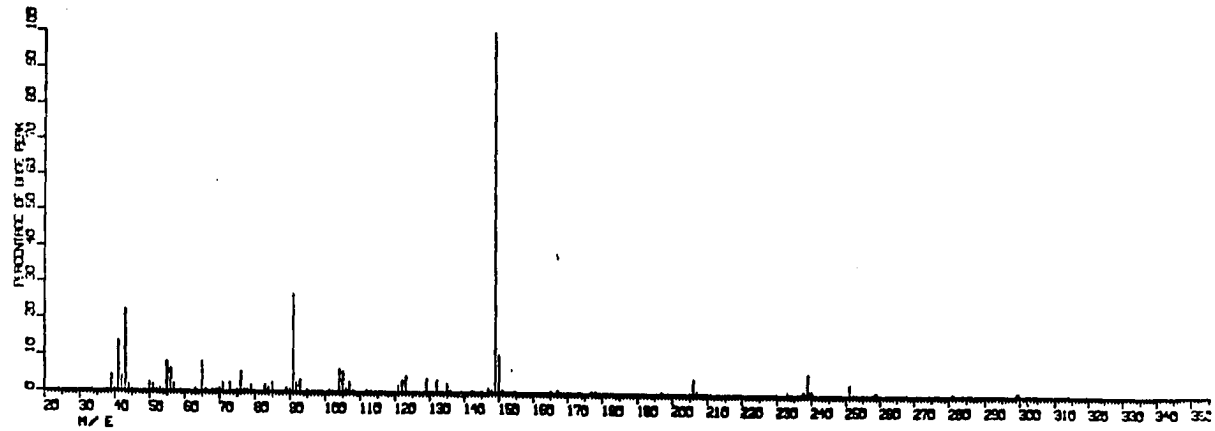


Figure 31. Spectrum number 235 - 232
ICCE3 Benzene 3

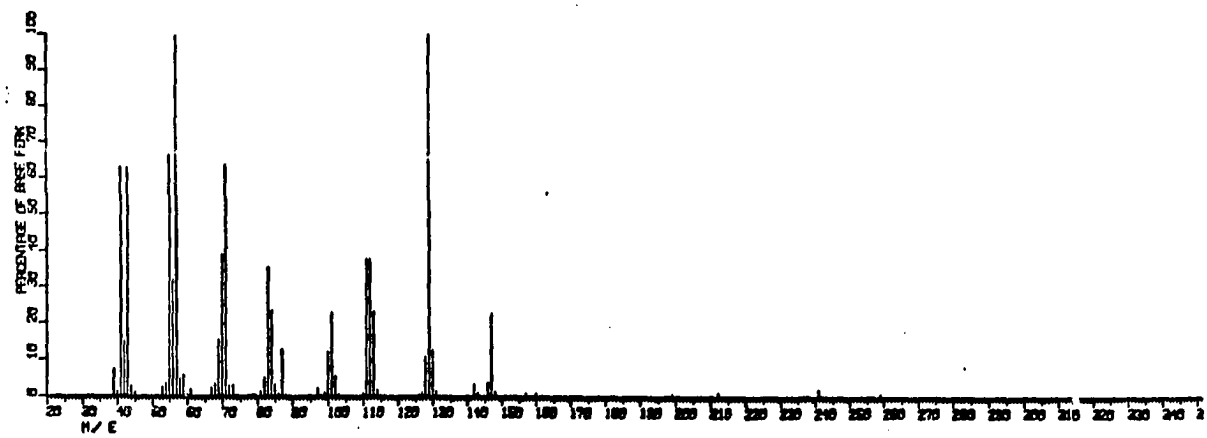


Figure 32. Spectrum number 244 - 241
ICCE3 Benzene 3

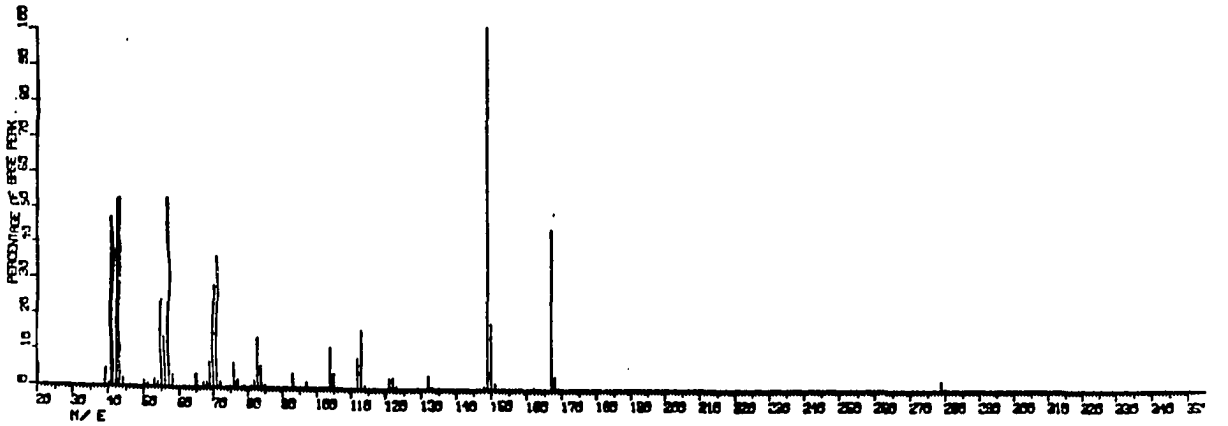


Figure 33. Spectrum number 272 - 267
ICCE3 Benzene 3

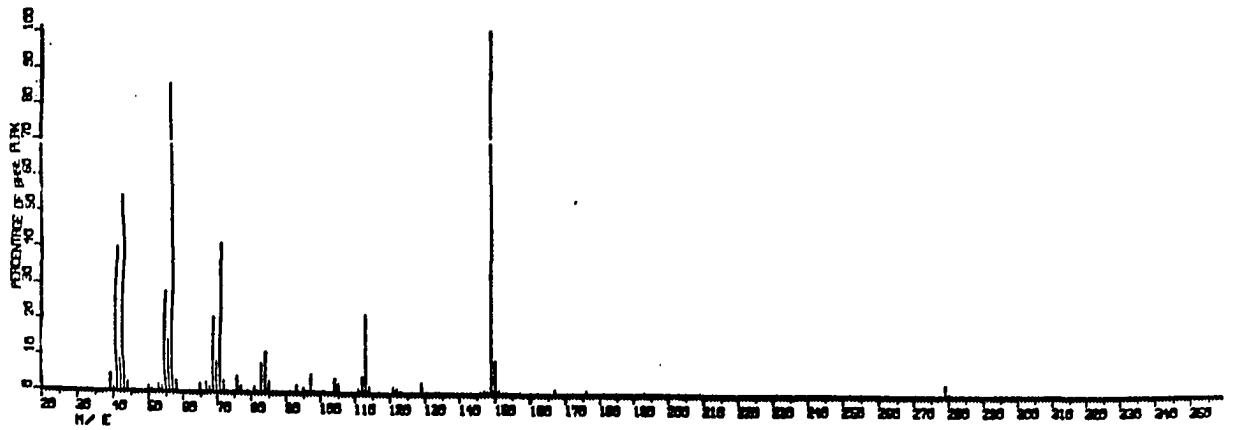


Figure 34. Spectrum number 282 - 279
ICCE3 Benzene 3

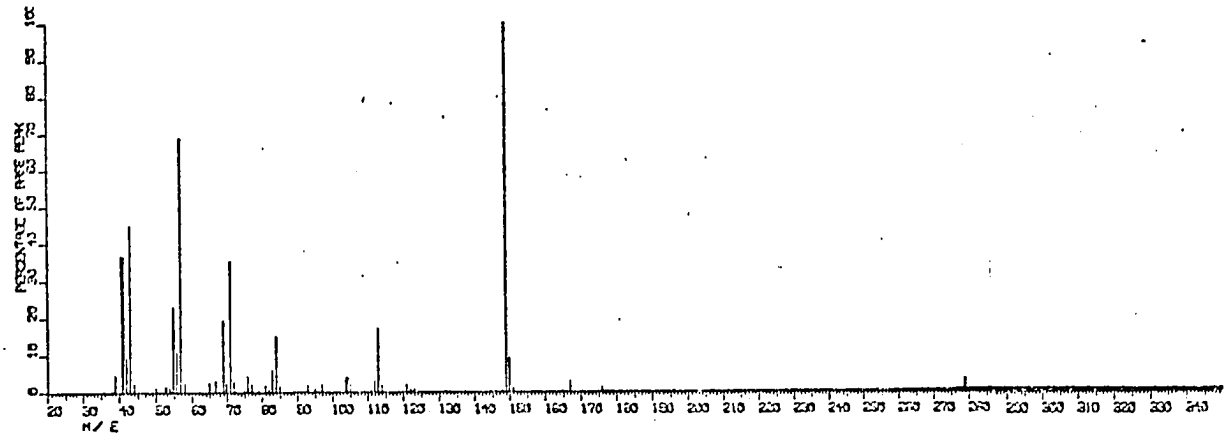


Figure 35. Spectrum number 297 - 290
ICCE3 Benzene 3

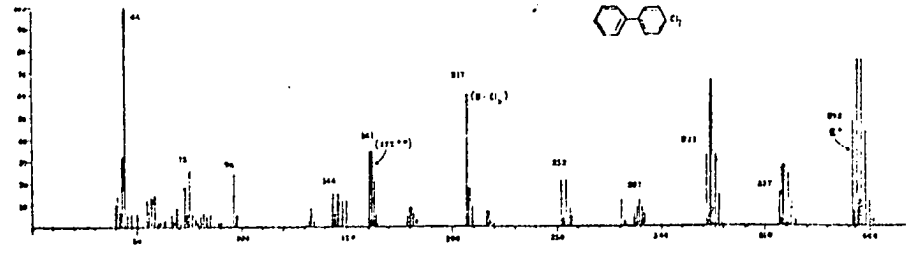


Figure 36a. Mass spectrum of a heptachloro biphenyl found in standard Aroclor 1260.

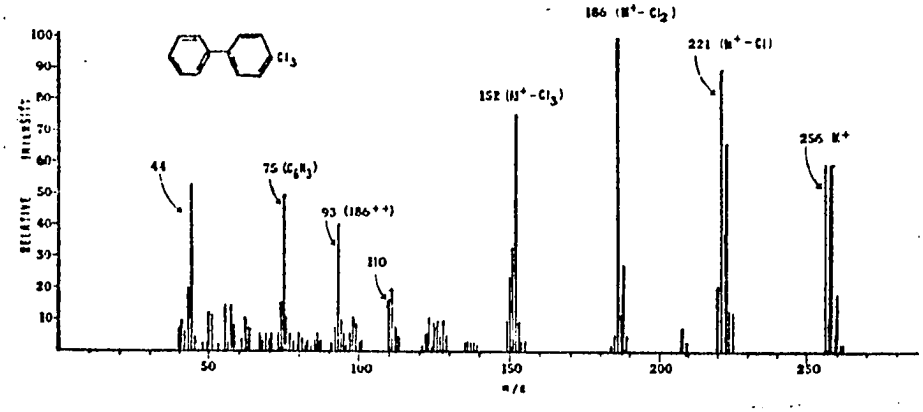
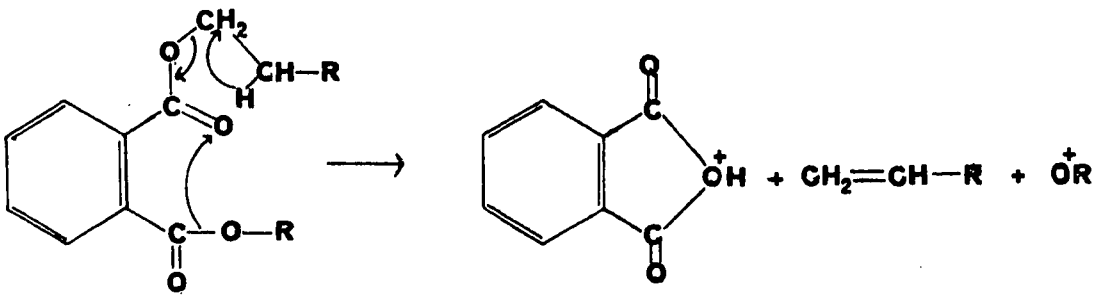


Figure 36b. Mass spectrum of a trichloro biphenyl contained in standard Aroclor 1232.

peaks in the gc-ms analysis of such samples. This was done by Koeman et al.[10] in his work on marine animals. The dialkyl phthalates, however, exhibit very weak molecular ion peaks, if at all, and their mass spectra are dominated by the m/e 149 peak corresponding to the very stable protonated anhydride ion. The origin of this ion has been postulated as involving a proton transfer from the B-Carbon of the alkyl group as follows:[79]



This mechanism explains why the mass spectra of dimethyl phthlate does not give this base peak.

Stepwise mechanisms toward the formation of this fragment ion are also given by others[42, 80] and one of the possible pathways is shown in Figure 37. For the smaller ions resulting from the subsequent fragmentation of the protonated phthalic anhydride, the following structures are also suggested.[80]

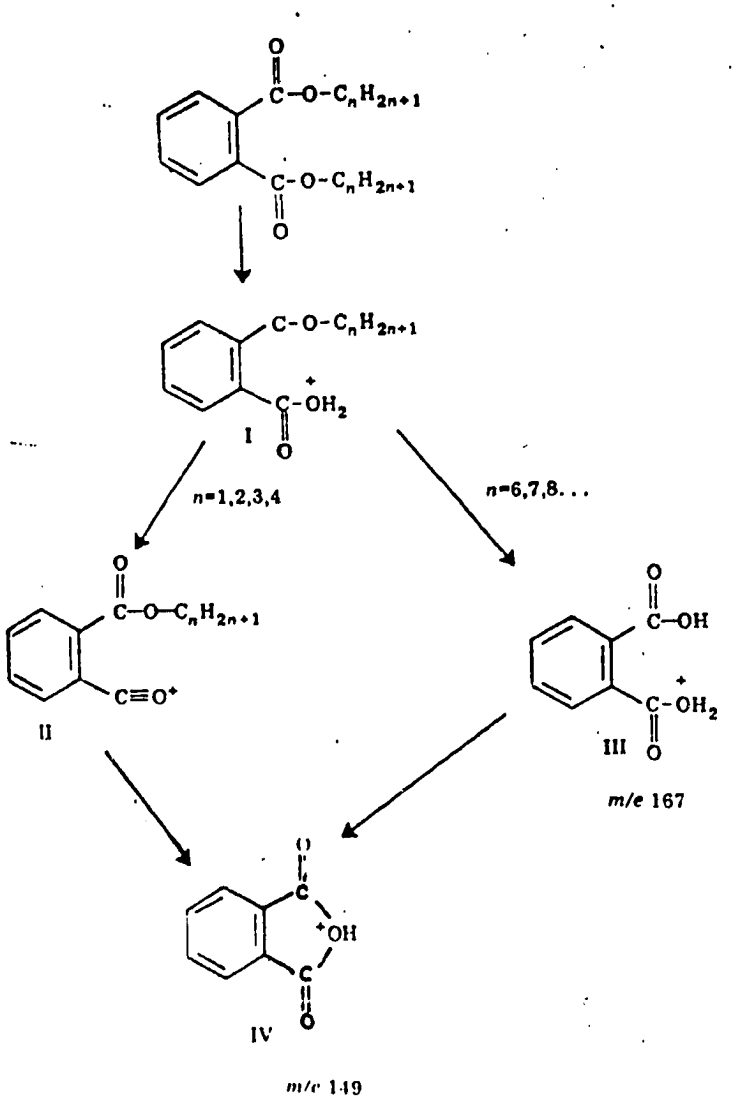


Figure 37. Partial fragmentation pathways for phthalate esters.

m/e	Structure
93	Ar-O
104	-Ar-C=O
105	Ar-C=O
121	Ar-COO
122	Ar-COOH

It can be seen from the above that irrespective of the nature of the alkyl group, a number of peaks will be common to all dialkyl phthalates so that the identity of the alkyl chain would be determined from the characteristic aliphatic fragment at 14 amu intervals usually predominant in the lower part of the spectrum. The mass spectra of some standard dialkyl esters are shown in Figures 38 through 42. Mass spectral data on these standard phthalates, including a related aliphatic diester, di-octyl adipate, are summarized in the following table.

Table 8. Mass Spectral Data of Standard Diesters

Diester	MW	Base peak
Ethyl phthalate	222	149
Diisobutyl phthalate	278	149
Di-n-butyl phthalate	278	149
Di-2-ethylhexyl phthalate	390	149
Di-n-octyl phthalate	390	149
Di-2-ethylhexyl adipate	370	129

The base peak of 129 produced by the fragmentation of di-octyl adipate is the analogous protonated anhydride of adipic acid and the mode of formation of this ion would be similar to the corresponding protonated phthalic anhydride (m/e 149).

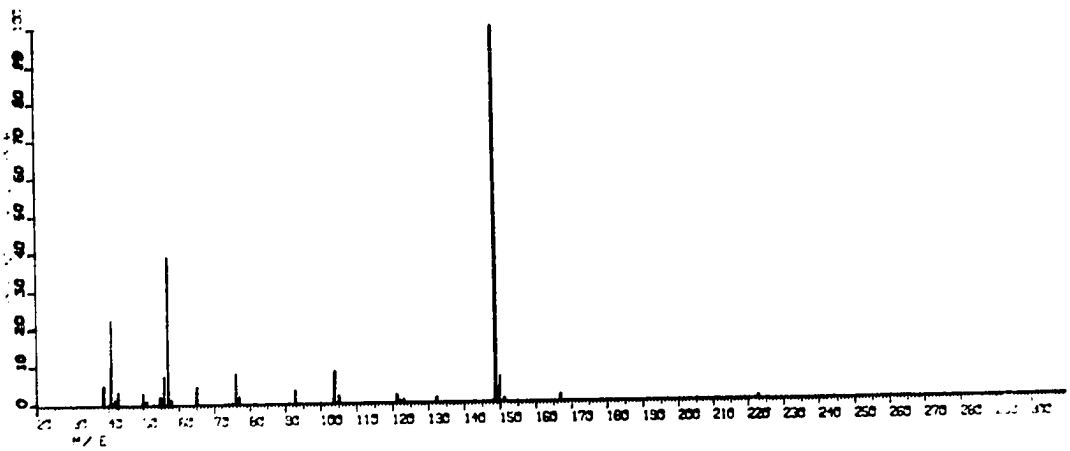


Figure 38. Spectrum number 72 - 66
Diisobutyl phthalate

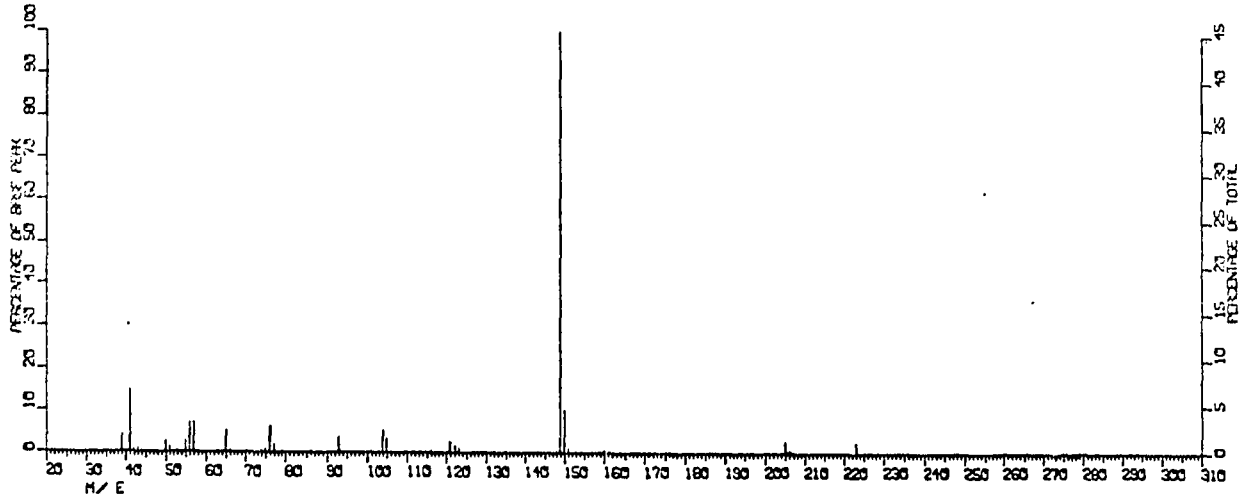


Figure 39. Spectrum number 141 - 136
Dibutyl Phthalate (GC)

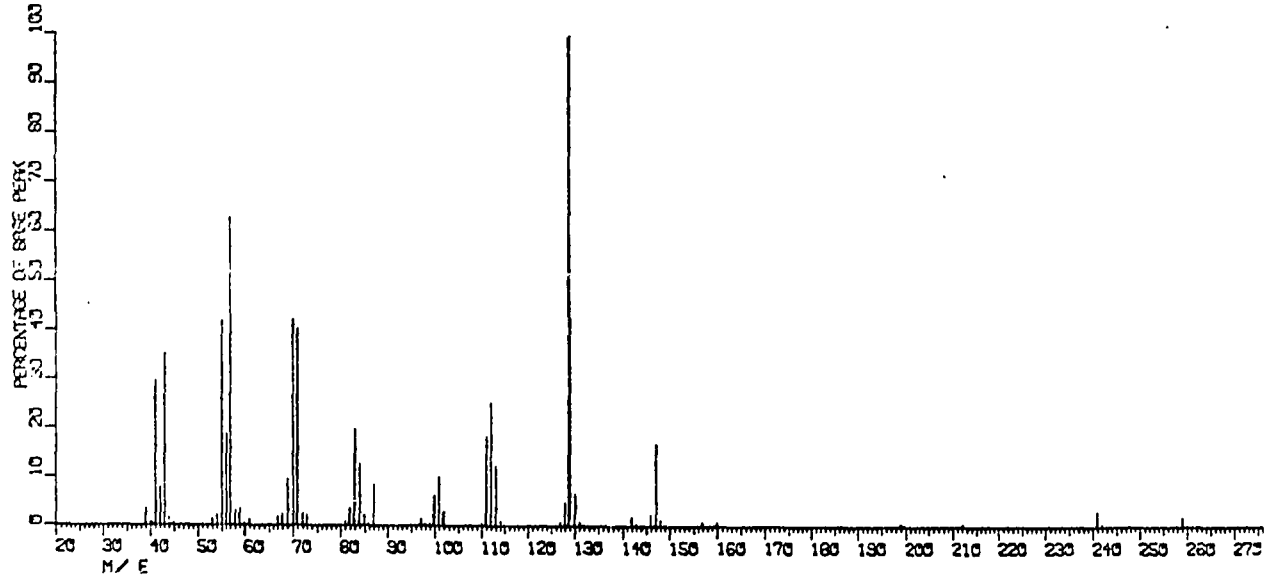


Figure 40. Spectrum number 50 - 46
Bis 2-ethylhexyl adipate (GC)

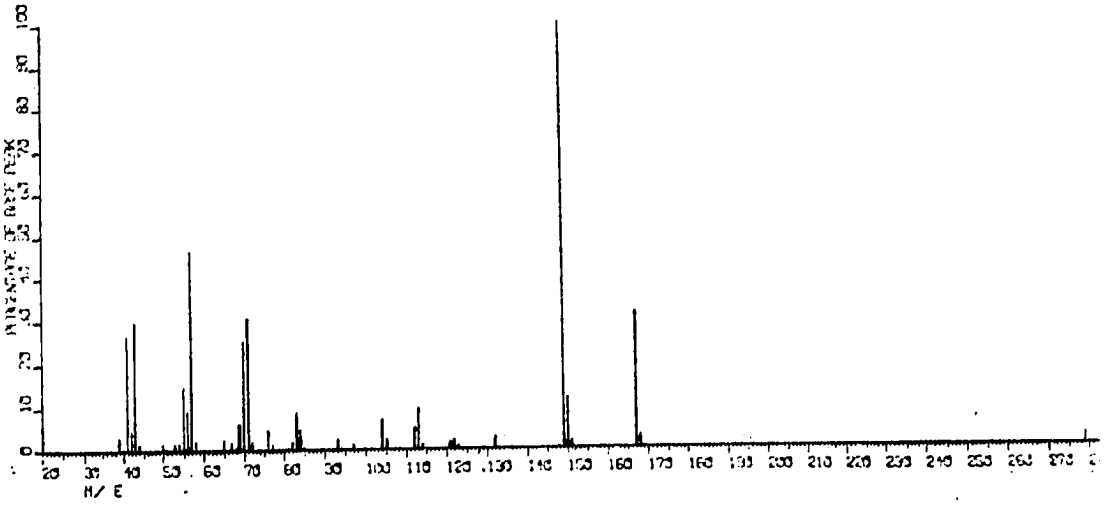


Figure 41. Spectrum number 74 - 70
Di-n-octyl phthalate (GC)

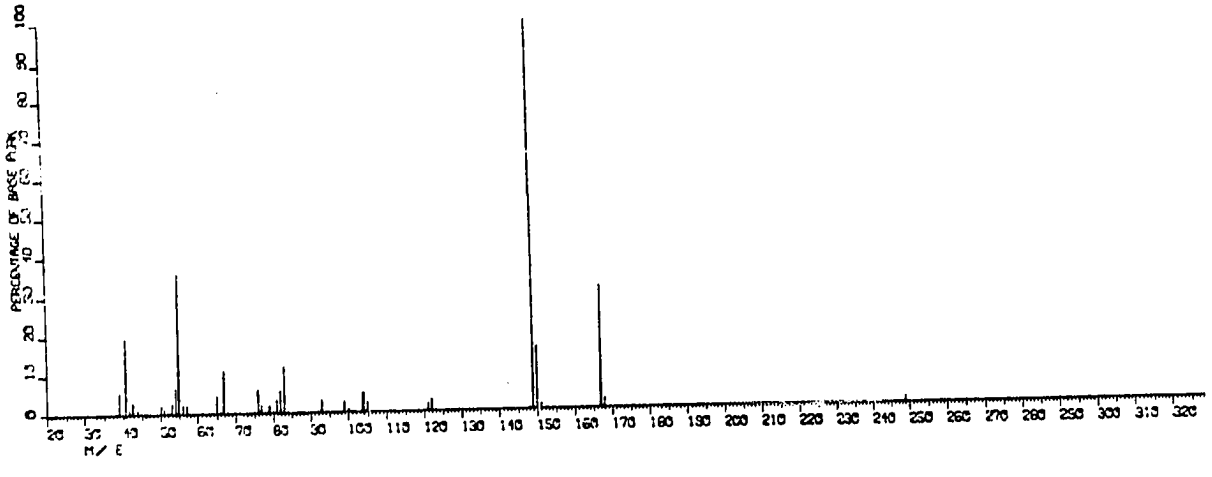
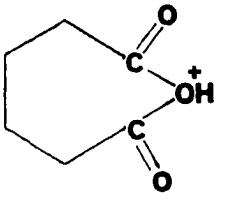


Figure 42. Spectrum number 64 - 59
Dicyclohexyl phthalate (GC)



protonated adipic acid anhydride m/e 129

The retention times of the dialkyl phthalates off a DC-200 column in general, vary directly with molecular weight. Isomeric phthalates, however, sometimes do not have the same retention time as can be seen from the data on the two isomeric dibutyl phthalates in Table 9, below. (See also Figure 43.)

Table 9. G.C. Data on Standard Diesters, Column: 5.3% DC-200 (5 ft. x 1/8 in.) on Gas Chrom Q, Temperature 110° - 270° at 10°/min. N_2 flow 18ml/min.

Diester	Retention Time (min.)
Ethyl phthalate	7
Di-isobutyl phthalate	9.5
Di-n-butyl phthalate	10.5
Di-2-ethylhexyl adipate	13.8
Di-2-ethylhexyl phthalate	14.8
Di-n-octyl phthalate	14.8

The two isomeric dioctyl phthalates, di-2ethylhexyl and di-n-octyl phthalate, are not separated under the conditions at which this chromatogram (Figure 43) was run, but were partially separated in the chromatogram of the ICCE-3 benzene sample (Figure 16) due to a lower carrier gas flow rate.

On the basis of the above gc-ms data, and also a search of the spectral reference file available to users of most gc-ms systems, the following diesters have been identified from the

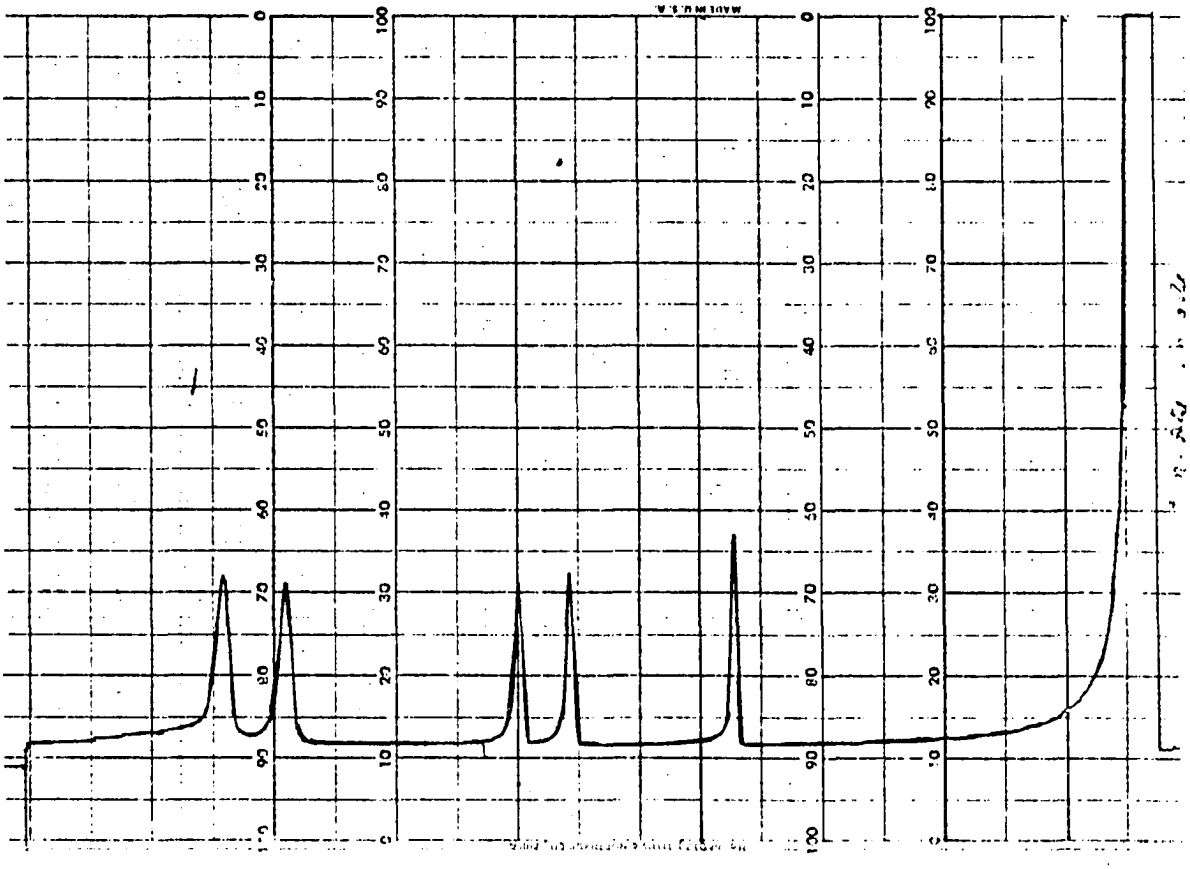


Figure 43. Gas chromatogram of standard phthalates: ethyl, diisobutyl, di-n-butyl, dioctyl adipate, di-2-ethylhexyl phthalate, and n-octyl phthalate. 5.3% DC-200, Temperature 110° - 270°, 10°/min. Flow 18 ml/min.

aromatic fraction of a CAM sample obtained from well number 3 (Table 10).

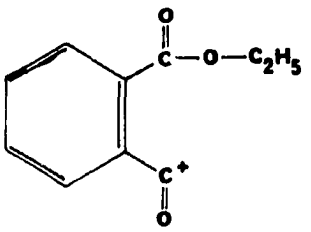
Table 10. Identification of Diesters From Aromatic Fraction of a CAM Sample From Well Number 3.

Spectrum number	Identity
101	Ethyl phthalate
156	diisobutyl phthalate
172	di-n-butyl phthalate
228	butyl glycolylbutyl phthalate
244	di-2-ethylhexyl adipate
272	di-2-ethylhexyl phthalate
282	di-octyl phthalate
297	Di-octyl phthalate

The spectra of the last four compounds (numbers 244 through 297) were obtained from a separate gc-ms run using a less concentrated sample.

The characteristic peaks in each of the above compounds and the fragment species responsible for them are readily seen from comparison of their spectra with those of standards and in discussions by many authors.[42, 73, 80, 81, 82]

Ethyl phthalate (spectrum 101) is the only diester among those present in the sample that has a discernable molecular ion (m/e 222). The other significant peaks occur at m/e 177 and m/e 149. m/e 149 is the protonated phthalic anhydride and m/e 177 is the ion fragment:



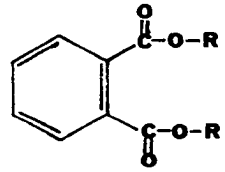
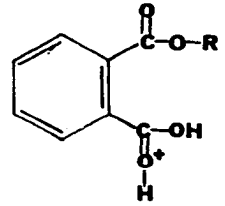
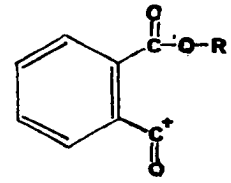
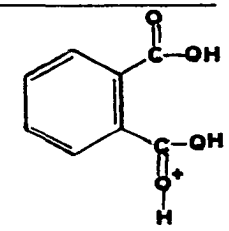
For a summary of the significant peaks appearing in the spectra of esters found in the samples, see the following table (Table 11).

As expected, the mass spectra of the isomeric esters are similar except with a variation of the abundance of fragment ions arising from the alkyl chain. For example, the spectrum of standard di-n-butyl phthalate (Figure 39) shows a lower intensity of the fragment at m/e 57 than the spectrum of diisobutyl phthalate. This is due to the relative stability of isobutyl carbonium ion compared to the n-butyl carbonium. The same relationship is also evident from the spectra of di-2-ethylhexyl phthalate and n-octyl phthalate. On this basis and also on the retention times of these compounds, it was determined that spectrum number 156 is diisobutyl phthalate, spectrum number 172 is n-butyl phthalate and spectrum number 272 is di-2-ethylhexyl phthalate. Due to the unavailability of the other isomeric phthalate, diisooctyl phthalate, however, spectrum 282 and 299 could not be differentiated and are therefore both designated as di-octyl phthalate.

Phthalates were also found from CCE samples obtained from well number 2. Although present in smaller amounts, relative to those found in well number 3, these compounds also make up the major portion of the aromatic fraction from this well. The gas chromatogram of this fraction (ICCE-2 benzene 2) on DC-200 is shown in Figure 44 and the gc plot of the subsequent gc-ms run is in Figure 45.

This fraction was also searched for the presence of PCB's

Table 11. Significant Peaks Appearing in Spectra of Esters Found in Samples.

Spectrum number				
101	222(2%)		177(30)	
156	278(0)	223(4)	205(2)	167(3)
172	278(0)	223(9)	205(9)	167(2)
228	336(0)		263(20)	
244	370(0)			147(25)
272	390(0)	279(3)		167(45)
282	390(0)	279(3)		167(2)
297	390(0)	279(3)		167(2)

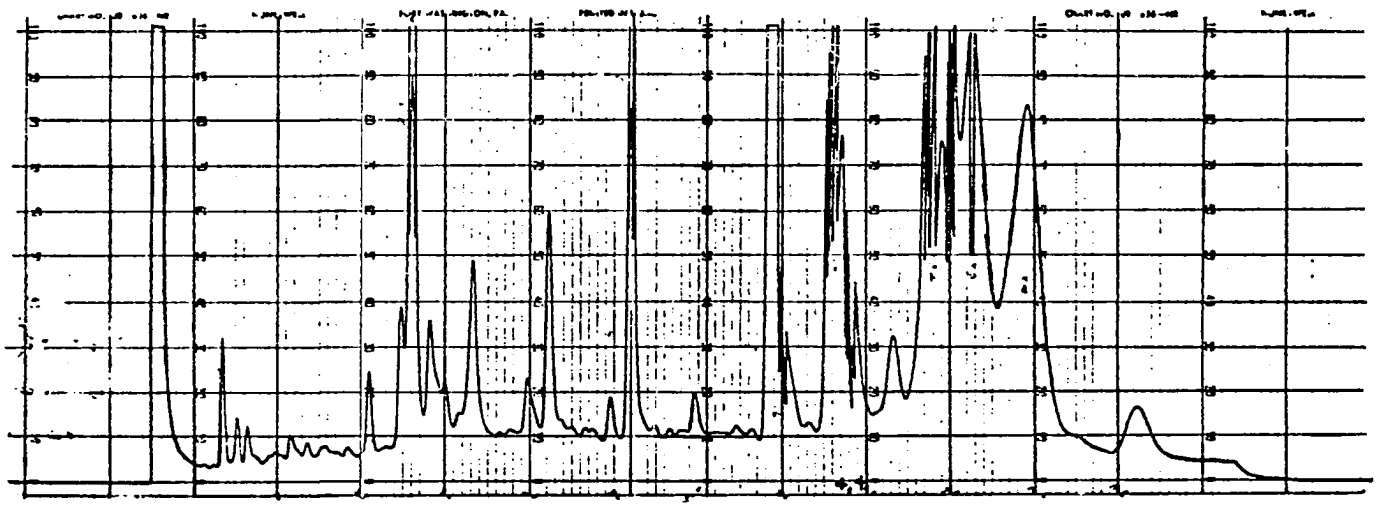


Figure 44. Benzene eluate from CCE of well number 2 Column DC-200 on Gas Chrom Q, Temperature - 110° - 250° 10°/min.

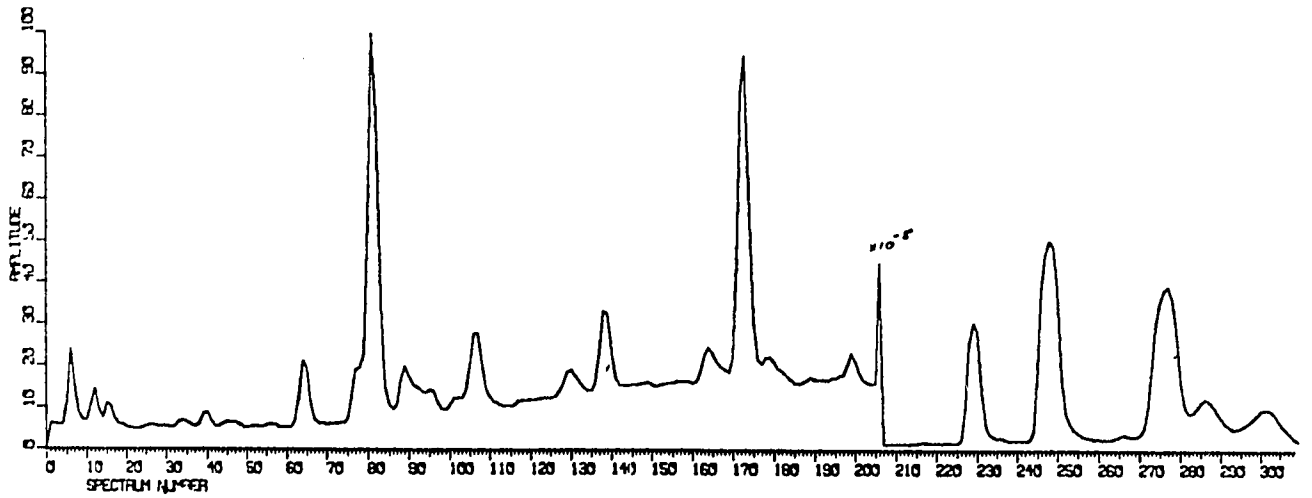


Figure 45. ICCE2 Benzene 2

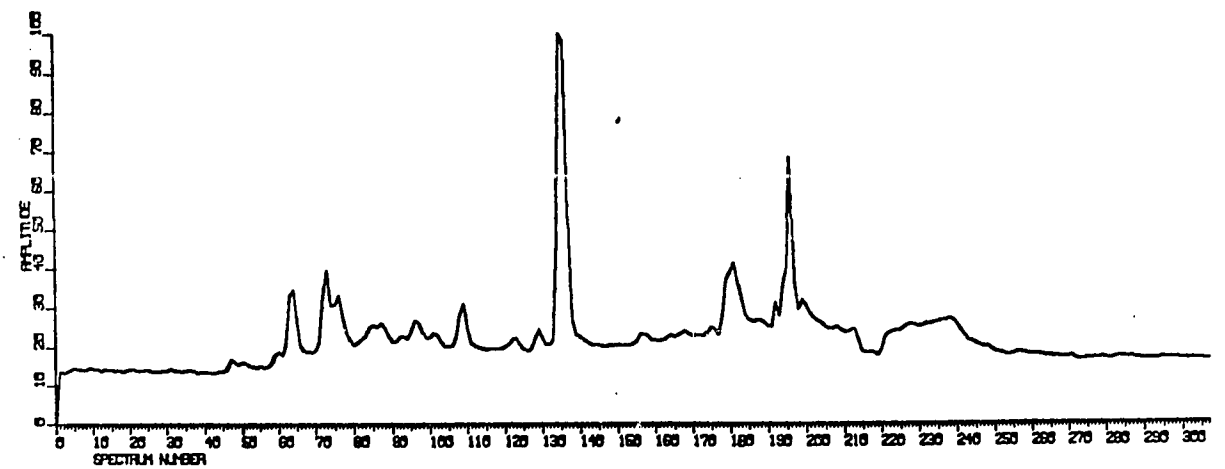


Figure 46. ICCE2 Benzene 2: Subset scan.

by the subset scanning technique previously discussed. The resulting subset scan plot is in Figure 46. As with the aromatic fraction from well number 3, the results were negative and the identification of the major components of this fraction was undertaken instead. The complete mass spectra of the major peaks were taken and after an analysis of the spectra and a search of available reference files, the identity of these peaks were determined as follows (Table 12).

Table 12. Phthalates Found in Well Number 2

Spectrum number	Phthalate
173	di-n-butyl phthalate
229	butylglycolylbutyl phthalate
248	dioctyl adipate
276	di-2-ethylhexyl phthalate
286	di-octyl phthalate
301	di-octyl phthalate

The significant peaks in the mass spectra of the above phthalates have been discussed earlier. Ethyl phthalate and diisobutyl phthalate which were found in well number 3 are only present here in small quantities as could be discerned from the gas chromatogram (Figure 45) at spectrum numbers 103 and 158 respectively.

Blank CCE. In the laboratory, there are several ways in which phthalates could contaminate environmental samples, the most common of which is the inadvertent use of tygon or rubber tubing in sampling or other operations. As was discussed previously phthalate esters are used in a wide variety of plastic and paper products. Therefore finding phthalate esters in these

samples is not at all unexpected.

At the outset of this investigation, it was decided to take all precautionary measures to minimize contamination with plasticizer compounds like PCB's and PAE's. This is why an all-glass all-teflon sampling system was devised. Furthermore, to insure that the phthalate esters found in the samples were not coming from elsewhere, a blank run was taken as follows. 182.9 g of activated charcoal was extracted with 3 liters of distilled chloroform, dried, and evaporated in the same manner as the CCE from the sampling wells. The blank CCE weighed 1.8 mg and its gas chromatogram on a 3 percent OV-1 column on Gas Chrom Q (Figure 47), showed the presence of one major peak and two smaller peaks. These were identified by mass spectrometry as diisobutyl phthalate, dicyclohexyl phthalate and di-n-octyl phthalate (Figures 48, 49 and 50).

The blank CCE was then subjected to column chromatography on silicar and subsequent gas chromatographic analysis showed that the phthalates were eluted with benzene. Figure 51 is the chromatogram of a 1 ul sample from a 1 ml solution of the benzene fraction in $CHCl_3$. Peak enhancement (Figure 52) with a mixture of six standard phthalate esters confirm the identity of diisobutyl phthalate (Spectrum number 103, Figure 48) and n-octyl phthalate (Spectrum number 251, Figure 50).

Quantitative Estimation of Some Phthalates. Standard solutions of ethyl phthalate, diisobutyl phthalate, di-2-ethylhexyl adipate, di-2-ethylhexyl phthalate and n-octyl phthalate were prepared and known concentrations were injected into the

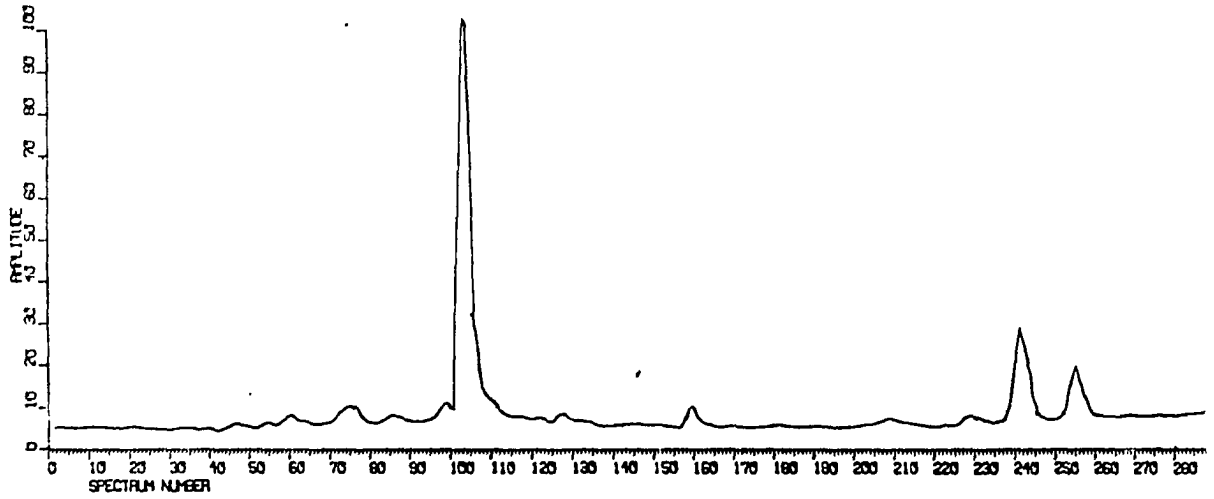


Figure 47. Blank carbon-chloroform extract
Column: 3% OV-1 on Gas Chrom Q

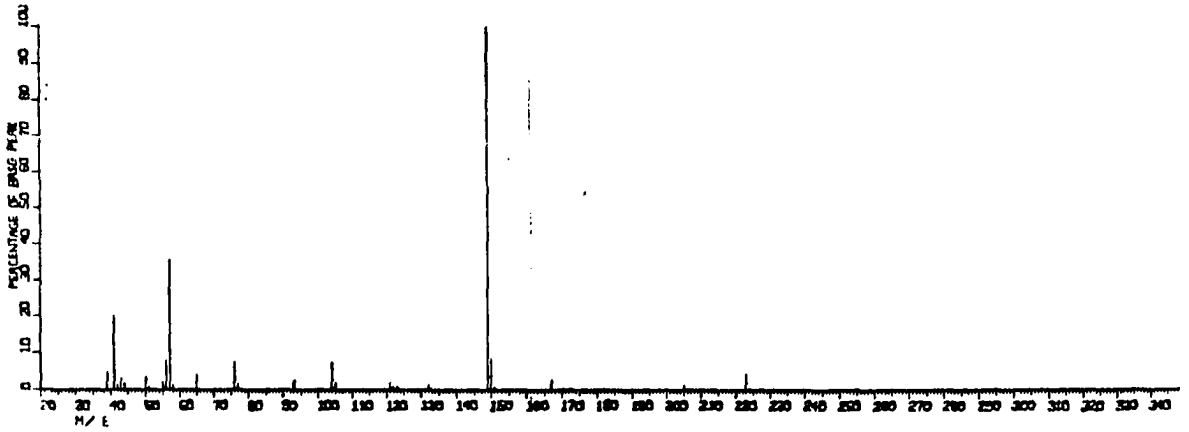


Figure 48. Spectrum number 103 from blank
CCE extract Column: 3% OV-1 on Gas Chrom Q

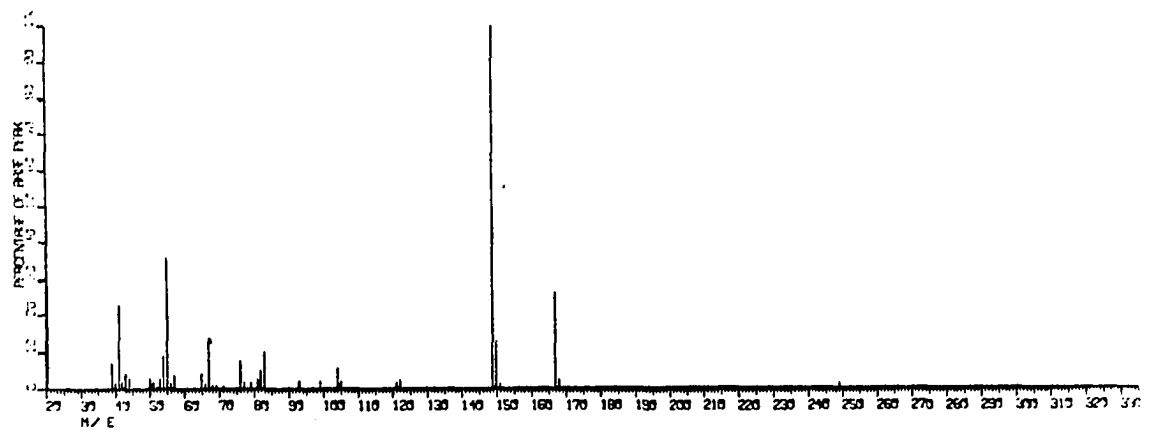


Figure 49. Spectrum number 241
CCE Blank

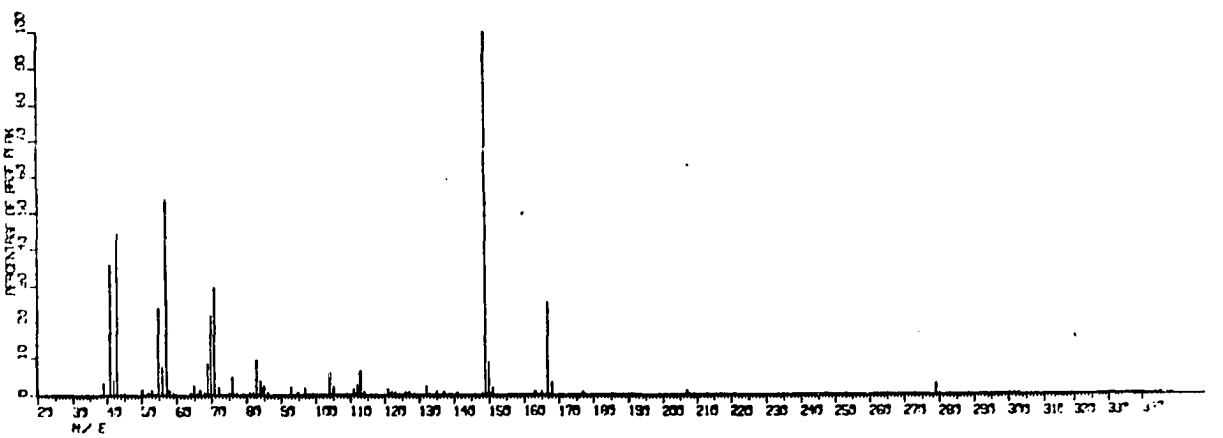


Figure 50. Spectrum number 256
CCE Blank

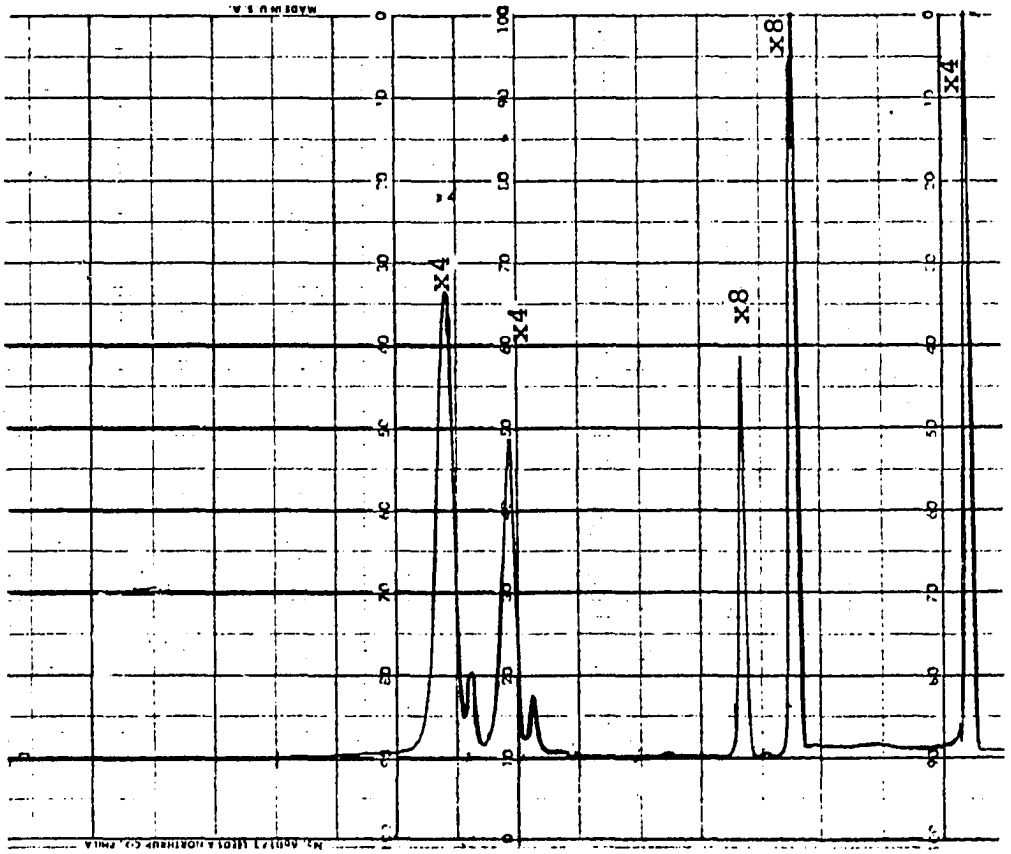


Figure 52. Carbon Blank number 2 benzene fraction + mixture of 5 standard phthalates.

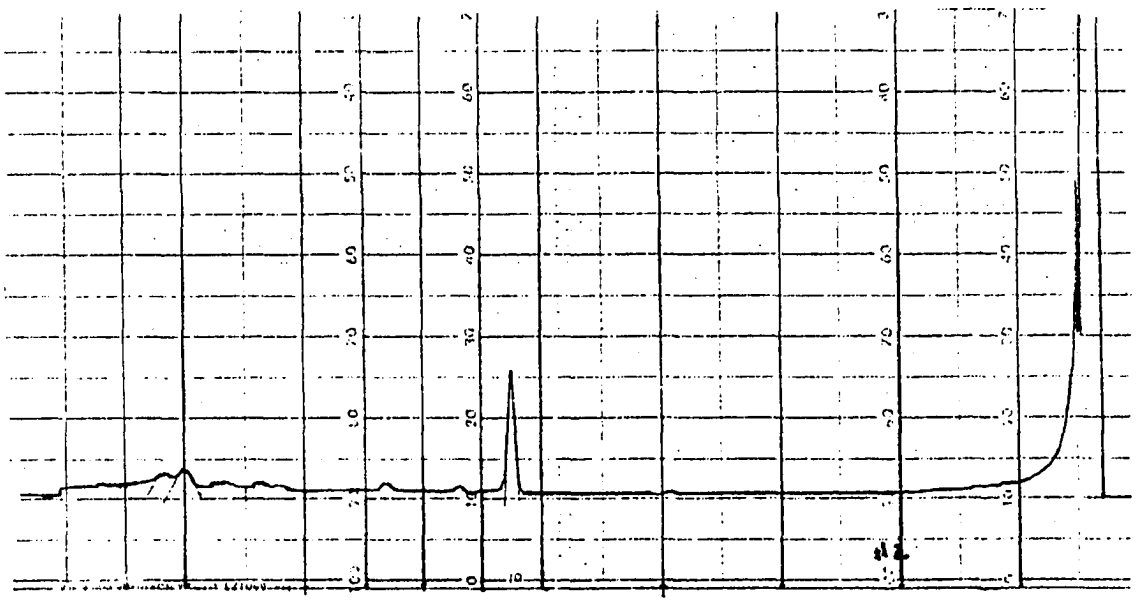


Figure 51. Blank CCE benzene fraction
Column: 5.3% DC-200 on Gas Chrom Q.

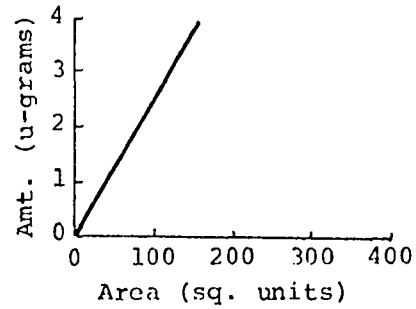
gas chromatograph. The peak areas were calculated and a plot of the peak areas versus the concentration in ug were drawn (Figure 53). Peak areas of known volumes of the benzene fractions from the blank CCE, CCE-2 and CCE-3 were then calculated and the corresponding concentrations read from the graph. The results are listed below (Table 13).

Table 13. Quantitative Estimates of Some Phthalates Found in the Aromatic Fraction Concentrations in ug/ul.

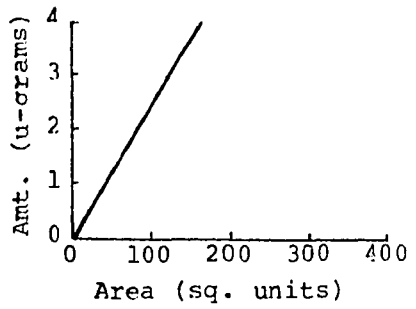
Phthalate	Blank	ICCE3	ICCE2
Diisobutyl phthalate	0.2	0.1	0.4
Ethyl phthalate		0.05	trace
Octyl adipate	0.0	15.2	8.8
Octyl phthalate (DEHP)	0.15	8.8	2.0

It is evident from the above figures that the phthalate esters found in the samples obtained from the groundwater exceeds that which might have been picked up from the carbon, silica gel, solvents and other sources encountered in the course of routine analytical prodecures.

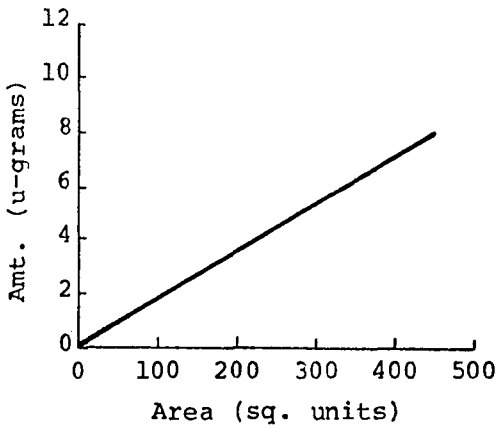
Compounds Other Than Phthalates Present in the Groundwater. There are a number of compounds aside from phthalates present in the groundwater which have also been identified. Several have not been identified due to complexity of the mass spectra and the lack of other supporting data. To determine the structures of all these compounds would involve more sophisticated separating techniques (e.g. preparatory gas chromatography) which this laboratory is not equipped to do. However, several of these compounds are definitely chlorinated and should receive further



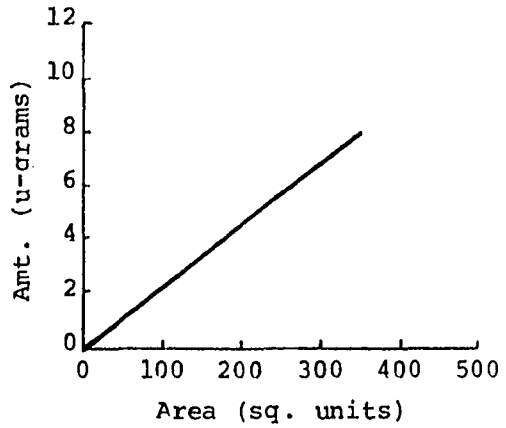
diisobutyl phthalate



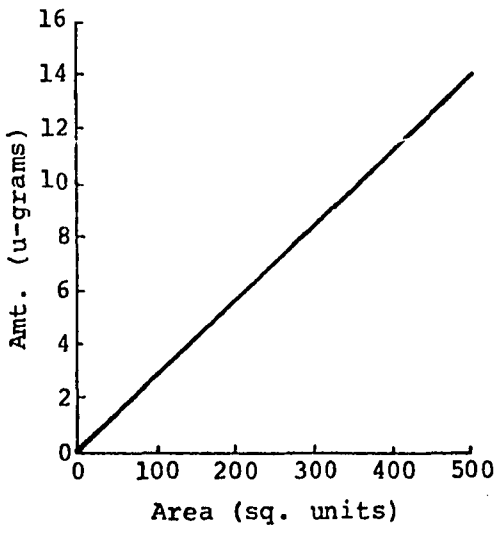
ethyl phthalate



n-octyl phthalate



DEHP



n-octyl adipate

Figure 53. Peak areas versus weight in ug of select phthalates.

study. One of these compounds has the mass spectra shown in Figure 54. This compound corresponds to spectrum number 6 of the aromatic fraction of well number 2. The mass spectrum indicates that the compound contains one chlorine atom. The isotopic ratio of M^+ and M+2 at m/e 151, 123, 107, and 95, is right for the presence of one chlorine in these fragments. Moreover, there is a peak at 49 which is undoubtedly due to a CH_2-Cl fragment. The absence of a molecular ion, however, makes the identification of this compound difficult. The application of chemical ionization mass spectrometry[82] to this problem would be very helpful.

While the minor peaks in the aromatic fraction of well number 2 are chlorinated compounds, those found in well number 3 were oxygenated. Two of these compounds come off the gas chromatographic column first as spectrum numbers 6 and 20 (Figure 16). The mass spectra of these substances are shown in Figures 22 and 23. Spectrum number 6 was identified as cresol or methyl-phenol but the positions of substitution cannot be ascertained. The molecular ion is present (m/e 108) but the base peak is at m/e 107 or M^+-1 which is due to the formation of hydroxy tropylium ion. Spectrum number 20 is apparently also a cresol although the mass spectra shows it to be in a mixture with another compound with M^+ of 152. The molecular ion of 122 corresponds to cresol plus a methyl group, and is therefore designated as methyl cresol or dimethyl phenol. This ion would lose a methyl group to give the peak at m/e 107 (M-15).

The finding of these phenolic type compounds is not sur-

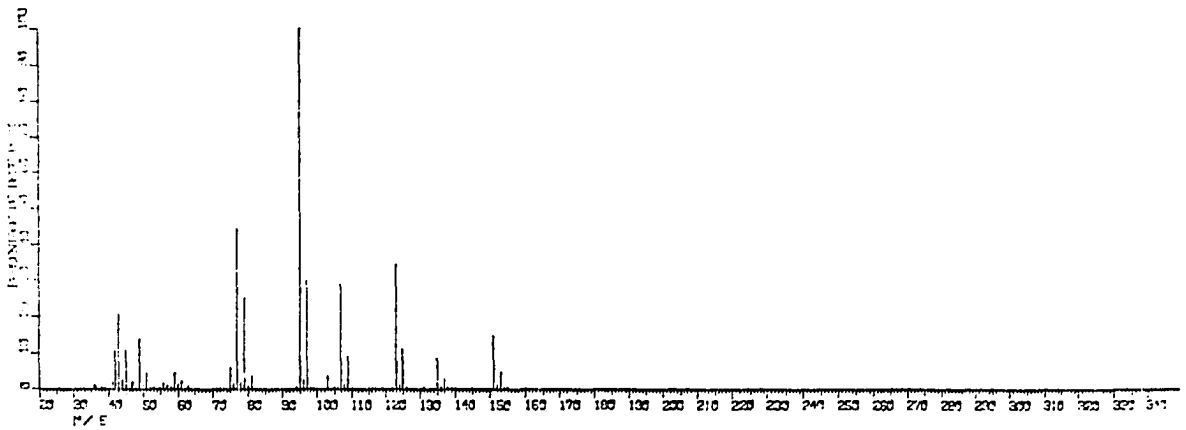
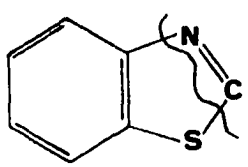


Figure 54. Spectrum number 6 - 4

ICCE2 Benzene 2

prising since methylated phenols like the cresols and the more highly substituted ones like ditertiary butylethyl phenol are commonly used as industrial preservatives. In addition, these phenolic compounds may also be of natural origin since the skeletal configuration of humic components contain these functional groups and are likely produced during their biological degradation.

The hexane fraction from both well numbers 2 and 3 contained a large number of unresolved peaks and probably peaks hidden underneath others (Figure 11). When the second sample from well number 2 (IICCE2) was obtained the hexane fraction was divided into two fractions to determine if the separation of the components improved. The gas chromatogram of the second hexane fraction is shown in Figure 55. This fraction was again searched for the presence of PCB's by subset scanning (Figure 56) and the result was negative. The presence of some phthalates was evident from the mass spectra. Another compound was also identified and its mass spectrum appears in Figure 57. The compound is benzothiazole. The mass spectrum of benzothiazole has the molecular ion (m/e 135) as the base peak and has a fragment ion at m/e 108 which is formed by cleavage of the C-N and C-S bond as follows:



resulting in the ejection of a neutral HCN molecule. The mass

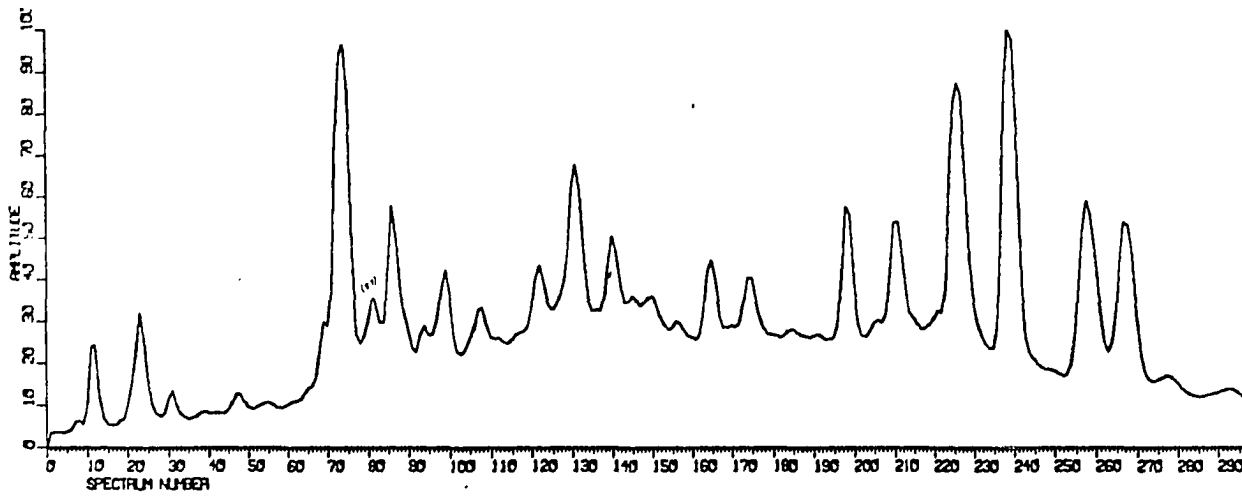


Figure 55. IICCE-2 Hexane 2

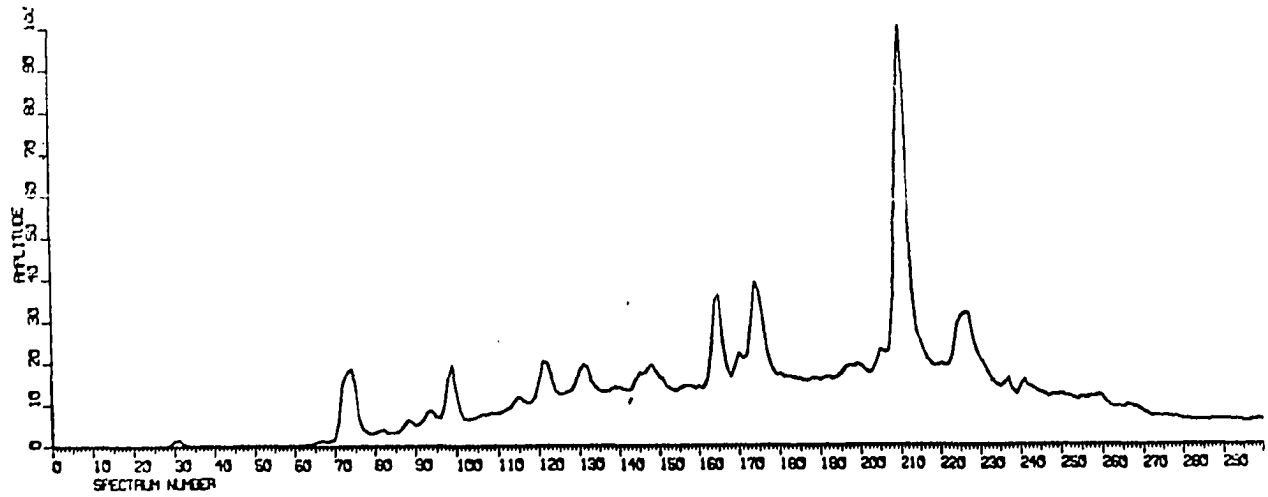


Figure 56. IICCE-2 Hexane 2
Subset scan.

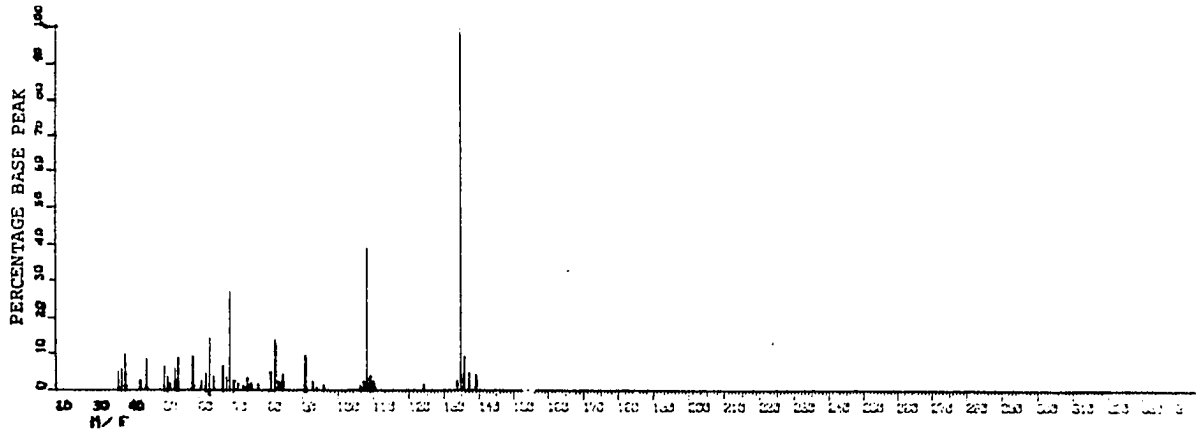


Figure 57. Spectrum number 23 - 18
IICCE-2 hexane 2

spectrum of standard benzothiazole obtained from the reference file of standard spectra matches that of this sample.

VI. SUMMARY AND CONCLUSIONS

The presence of organic compounds in natural waters is a problem of great interest in water quality investigations especially with respect to persistent organic compounds which also have deleterious physiological effects on living organisms. Groundwater gets its share of organic pollution from the leaching of organic substances present in solid wastes. This study was concerned with the chemical determination of the extent and nature of organic pollution occurring in the groundwater underlying the Norman Sanitary Landfill. The specific objectives of this study were to find evidence of contamination with polychlorinated biphenyls and chlorinated pesticides, and to determine the major organic compounds present in the groundwater.

Five sampling wells were selected; two upstream from the landfill (1a, 1b), two within the landfill (3, 4) and one 50 feet downstream(2). Initial measurement of COD and TOC from these wells indicated the presence of an appreciable amount of organic matter present in the groundwater. The concentration of these organic substances was accomplished with a modified carbon adsorption column using an all-glass, all teflon system to preclude contamination and/or interaction with plastic or rubber materials. Carbon chloroform extracts (CCE) obtained from four deep wells (1a, 2, 3, 4) ranged from 0.077 mg/l upstream

to 0.46 mg/l in groundwater located directly under a refuse cell, to 0.40 mg/l 40 feet downstream. These organic concentrations are lower than what was indicated by the COD and TOC data. However the CCE values do not include the amount of leakage through the carbon column which is considerable due to the high rates of flow and low retention times, and the alcohol extractables which would consist of the more polar compounds like the fatty acids.

Carbon chloroform extracts from wells 2 and 3 were subjected to a more extensive qualitative analysis since they were found to contain higher gross organic contamination. Moreover since they are located under a refuse cell (well 3) or in close proximity to it (well 2), the organic compounds present would reflect the biochemical process taking place in these environments.

The separation of the CCE's into an aliphatic fraction, aromatic fraction and oxygenated fraction was accomplished by column chromatography or a silica gel column. Each of these fractions was analyzed by gas chromatography on 3% OV-1, 5.3% DC-200 and 10% QF-1. The DC-200 column afforded the best separation of component peaks and was therefore used more extensively. IR and NMR spectra of these fractions were obtained and provided some qualitative information e.g. the presence of OH^-, -COOR, C-H, and aromatic absorptions. The identification of the components of the aliphatic and aromatic fractions was based mostly on gas chromatographic data and the mass spectrum of each component peak obtained by a continuously scanning gc-ms interfaced with a computer. The search for PCB's was immediately undertaken. Each

of the fractions whose gas chromatograms contained peaks emerging between 150° and 250° C on DC-200 columns at a program rate of 10°/min. was presumed to contain PCB's and confirmatory evidence was sought by the PCB subset scanning technique developed by Eichelberger et al.[78] The results were negative, which means that PCB's are either totally absent in groundwater or more likely that they are present in quantities below the concentration limit of the CAM and the detection limit of the gc-ms subset scanning technique. The latter was estimated by Eichelberger et al.[78] to be equivalent to $\simeq$ 5 ng of an aroclor mixture.

The major organic compounds extracted by chloroform from the groundwater were phthalic acid esters (PAE's). These compounds are widely used as plasticizers and their presence in groundwaters underlying a landfill strongly suggests that these compounds reach the groundwater by leaching from the many industrial products buried there, although PAE's may also be produced biosynthetically. The alkyl phthalates are not very water soluble but humic substances like the fulvic acids which are present in the soil can interact with the phthalate forming water soluble complexes.[83] This would explain why these plasticizers and not the PCB's were found to predominate in the groundwater. Another explanation arises from the fact that PAE's have a higher volatility than PCB's and are more apt to be released into the surrounding environment. Nisbett and Sarofim[34] offer the following assessment of the occurrence of PCB's in groundwater. The low water solubility and high specific gravity of the PCB's would make their transport through soil systems and into groundwater negli-

gible. PCB's will be mostly adsorbed on waterborne particles and the concentration of PCB's will be governed by solution and readsorption in the sediment and its partition coefficient between water and the sediment. The partition coefficient is obviously very low.

The esters identified in the samples were: ethyl phthalate, diisobutyl phthalate, butyl glycolyl butyl phthalate, di-2-ethylhexyl phthalate, n-octyl phthalate and di-2-ethylhexyl adipate. The blank contained primarily diisobutyl phthalate, and traces of di-2-ethylhexyl phthalate and dicyclohexyl phthalate. The mass spectra of these compounds are characterized by the presence of m/e 149 as the base peak corresponding to a protonated phthalic anhydride fragment.

In addition to the PAE's, the following substances also occur in the groundwater samples: aliphatic hydrocarbons, $C_{15}H_{32}$, $C_{16}H_{34}$, $C_{17}H_{36}$, $C_{18}H_{38}$, and $C_{19}H_{40}$; phenolic compounds, cresol and methyl cresol, benzothiazole and several chlorinated hydrocarbons still unidentified. Sulfur was also identified in the aliphatic fraction which indicates that active anaerobic decomposition of S-containing compounds or bacterial reduction of sulfate is taking place.

In conclusion, the results of this study show that:

1. Groundwaters underlying or in close proximity to landfills are contaminated with a significant variety of organic compounds, the most predominant of which are PAE's.

2. Groundwater sampling is made difficult by the variation in depth of the water table at different sampling sites and the

limited capacity of rubber impeller pumps. These factors cause variation in flow rates and consequently the quantity and to some extent the nature of organic compounds isolated.

3. Activated charcoal supplied by some chemical companies for use in the CAM contain traces of organics, mostly PAE's.

4. The possibility of contamination of samples with PAE's is great and extra precaution should be taken to eliminate and/or determine these sources. This also necessitates a blank determination.

5. Groundwater has an enormous capacity of attenuating the concentration of organic contaminants through the combined effects of dilution, soil adsorption and anaerobic stabilization of these compounds. These processes however, depend on the quantity of leachate produced and introduced into the groundwater and is expected to vary with time. The adsorptive capacity of the soil will also decrease with time and the degree of saturation.

6. PCB's in sanitary landfills are released very slowly and reach the groundwater in negligible amounts because of the containment offered by slowly decomposing containers and binders and the surrounding soil.

7. Groundwater is not a renewable resource and landfills which are situated such that considerable leaching occurs render the groundwater so affected unfit as a source of supply. Organic compounds contribute significantly to this deterioration of water quality and should be considered in making water quality evaluations.

8. In the Norman landfill, vertical leaching should be

minimized by the use of proper cover material and the maintenance of proper grading, and horizontal leaching should be eliminated by keeping refuse cells sufficiently above the groundwater table. For future consideration, the landfill site should not be located in a flood plain.

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