

A Simple Method for the Analysis
of Polychlorinated Biphenyls in
Ambient Air

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ABSTRACT

The development and utilization of a method to measure ambient polychlorinated biphenyls (PCBs) at ng/m³ level is presented. This procedure involves trapping the PCBs on a florasil absorbent at a flow rate of 15-25 L/min. Sampling time for the analysis will vary with the area under study. Trapping efficiency is greater than 95%. Samples are eluted with hexane. Concentration steps involve a Kuderna-Danish apparatus, 2 ball micro Snyder column, and a nitrogen evaporation to a volume not less than 50 ul. Confirmation is done with perchlorination by antimony pentachloride to decachlorobiphenyl (DCB). This procedure was used on an indoor area, an incinerator that was handling known PCB material, two capacitor manufacturers, and a landfill site. These results along with some correlation data with the polyurethane foam method are included in this report.

INTRODUCTION

Prior to 1971, PCBs were used as plasticizers, dielectric fluid in electrical transformers and capacitors, sealants, lubricants, hydraulic fluids, rubber, varnishes, inks, adhesives, etc. Today, they are still being used in closed electrical applications. Because of their broad extensive use and stable chemical properties, PCBs have been found at various levels throughout our environment. The biomagnification and toxicity of PCBs is well documented. Some induced effects are hepatomas (1,2), changes in hepatic microsomal enzymes (3,4), reproductive dysfunction (5), hepatic porphyria (6), lower gamma globulin level (7), and a possibility of tumorigenesis in the liver (8). The current OSHA health standard, U.S. Code of Federal Regulations, 1974, for an eight-hour time-weighted average is 0.5 mg/m for chlorobiphenyl (54%) and 1.0 mg/m for chlorophenyl (42%).

There are various methods for determining PCBs in ambient air. Basically, there are 3 modes of collection: first, impingers, using a liquid absorbent such as ethylene glycol (9); second, coated solid material such as glycerine on a glass fiber filter (10) or OV-17 on ceramic saddles (11); third, solid absorbents, such as florasil (12) or polyurethane foam (13). Florasil is inexpensive, accessible, and can be baked at elevated temperatures. There is no background problem with florasil. Less glassware and shorter time of analysis are achieved because no soxhlet apparatus is necessary for cleaning and extraction. Cleaning involves rinsing the florasil and baking it at 550°C. The PCBs are directly eluted with hexane. Routine laboratory pumps are used in the collection. Two important properties of florasil are the high trapping efficiencies and loading capacity for PCBs. This is a simple procedure that does not tie up its personnel and gives ambient level detectability.

METHOD

Reagents and Apparatus

- (A) PCB and DCB standards--U.S. Environmental Protection Agency, Quality Assurance Section, Research Triangle Park, N.C.
- (B) Specific chlorinated biphenyls--Analabs, Inc.
- (C) Antimony pentachloride--J.T. Baker Chemical Co., reagent grade.
- (D) Florisil--PR grade, 60-100 mesh, U.S. Environmental Protection Agency, Quality Assurance Section, Research Triangle Park, N.C.
- (E) Solvents--Burdick & Jackson Laboratory, distilled in glass.
- (F) Trap--150 ml, coarse, glass fritted funnel, ASTM 40-60.
- (G) Chromaflex column--Kontes, 7 mm, size 22.
- (H) Gas chromatograph--Varian 2100 equipped with a Ni63 electron capture detector. Chromatographic conditions for PCBs: 6 ft glass, 1.5% OV-17/1.95% QF-1 on 100-120 Gas Chrom Q, 190 C, 40 ml/min. Conditions for DCB analysis: 6 ft glass, 5% OV-210, 100-120 Gas Chrom Q, 210 C, 40 ml/min.
- (I) Gas chromatograph-mass spectrometer--Finnegan 1015 s/l with a glass jet separator coupled to a Digital PDP8. Conditions for DCB analysis: Gas chromatographic conditions, similar to (G) except the helium flow, 30 ml/min; mass spectrometer, mass scan range of 494-504 m/e, integration time, 1250 msec.

Procedure

Wash glassware with chromic acid, rinse with tap water, acetone, hexane, and then bake overnight at 550°C. Place 12 grams of florisil, that has been previously baked overnight at 550°C, in a 150 ml glass fritted funnel. Rinse twice with 50 ml of 15% methylene chloride in hexane and twice with 50 ml of hexane. Dry the traps with nitrogen. Controls and blanks are taken at this point. A control is a microliter volume of an aroclor standard in hexane onto the florisil. A blank consists of 3 rinses of 50 ml of hexane. Set aside the blanks until the collection

is completed. Dry the traps, including the controls, with nitrogen. Wrap the prepared traps in clean aluminum foil and place them in a dessicator for transport into the field. Any site suspected of high PCB concentration should have a back-up trap.

In the field, the sampler sets up the apparatus as outlined in Figure 1 (14). Perforate the aluminum foil covering the top of the trap. This is to prevent the wind from disturbing the florisil layer. Collect the sample at a rate of 15-25 L/min. Sampling time is variable depending upon the anticipated PCB concentration. Our normal sampling time is 4-6 hr. Monitor the flow rate hourly. After collection, wrap the traps again in clean aluminum foil and place in the dessicator to be transported back to the laboratory.

Extract the samples and controls with 3 rinses of 50 ml of hexane. Concentrate with a Kuderna-Danish apparatus and a 2 ball micro Snyder column to 1 ml. Usually, at this point, one goes directly to a micro florisil clean-up. Pack a chromaflex column with 1.6 gm of florisil (baked at 130 C) follow with 1.6 gm of sodium sulfate. Wash with 50 ml of hexane and elute the sample with 10 ml of hexane. Again concentrate with a 2 ball micro Snyder column to 1 ml. The sample is now ready for injection into the gas chromatograph. If needed, further concentrating can be done by nitrogen evaporation.

Perchlorination is used as a confirmation tool. Our procedure is similar to one recently published by Crist and Moseman (15). There are some differences in the two methods. In our procedure, the solvent exchange portion is 1-2 ml of chloroform. Perchlorinate a final volume of 0.2 ml at 150°C, overnight. Add 1 ml of 6N hydrochloric acid. Extract the DCB with 7 rinses of 5 ml of hexane, directly out of the hydrolysis tube. This number of rinses is used because some of the samples would jell in the extraction. Add 2 drops of methanol in the concentrating step.

RESULTS AND DISCUSSION

The degree of retention of PCBs in the florisil trap was determined by placing 2 pairs of florisil traps in series. Aroclors 1221 and 1242 were spiked onto the first traps using a microsyringe. No break-through was observed after a 2 hr operation. This was repeated for 13 hr using approximately 600 ng each of aroclors 1221 and 1242. No definite PCB peaks were observed. However there was a small amount of background, less than 5% of the PCB peaks. This may have been due to leakage at the junction between the 2 glass traps. Modification of this junction was done by sealing it consecutively with teflon tape, paper adhesive tape, and coating this with liquid plastic. As of the present, the largest quantity trapped in a single run is 1.6 ug and 0.05 ug of aroclors 1242 and 1254 respectively, collected over a 3.5 hr period at a rate of 27 L/min. No break-through was observed. This is illustrated in Figure 2. This back-up system is used routinely at sites of any suspected high concentrations.

Since one is usually dealing with ng levels of PCBs, any contamination will interfere with the pattern and chlorinate during perchlorination. There should be an organic trap on the nitrogen used for concentrating the sample. Our laboratory installed florisil filled pasteur pipettes on the end of the multi-concentrator. Besides contamination one should also be concerned with the loss of lower chlorinated biphenyls due to volatilization. We concentrated a standard solution of aroclor 1221 in hexane to near dryness volumes using some very narrow tapered tubes. Total volumes reduced to were approximately 10 ul and 20 ul with the recoveries of 60% and 90%, respectively. As a result, one should carefully control the nitrogen flow rate to prevent any splashing on the walls of the vessel, taper the bottoms of the hydrolysis tubes, and monitor the final volume.

With regard to perchlorination, a sample blank must be run to subtract out any background DCB (17). We run an extra control to check the perchlorination. With our procedure the average recovery values for these controls are; aroclor

Fig
1

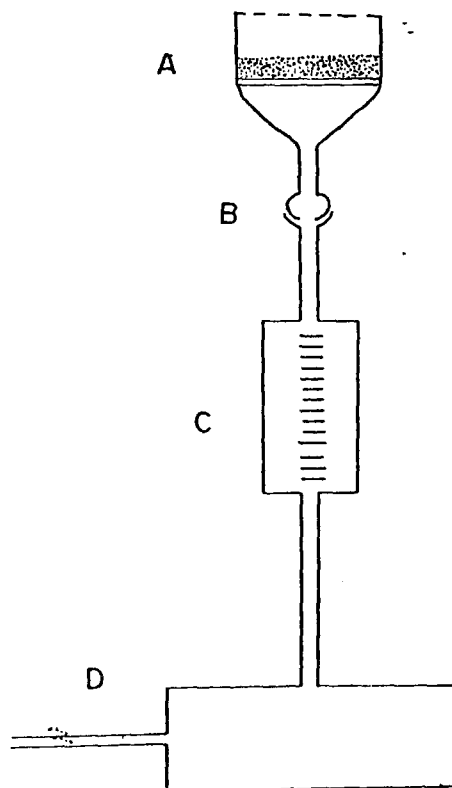
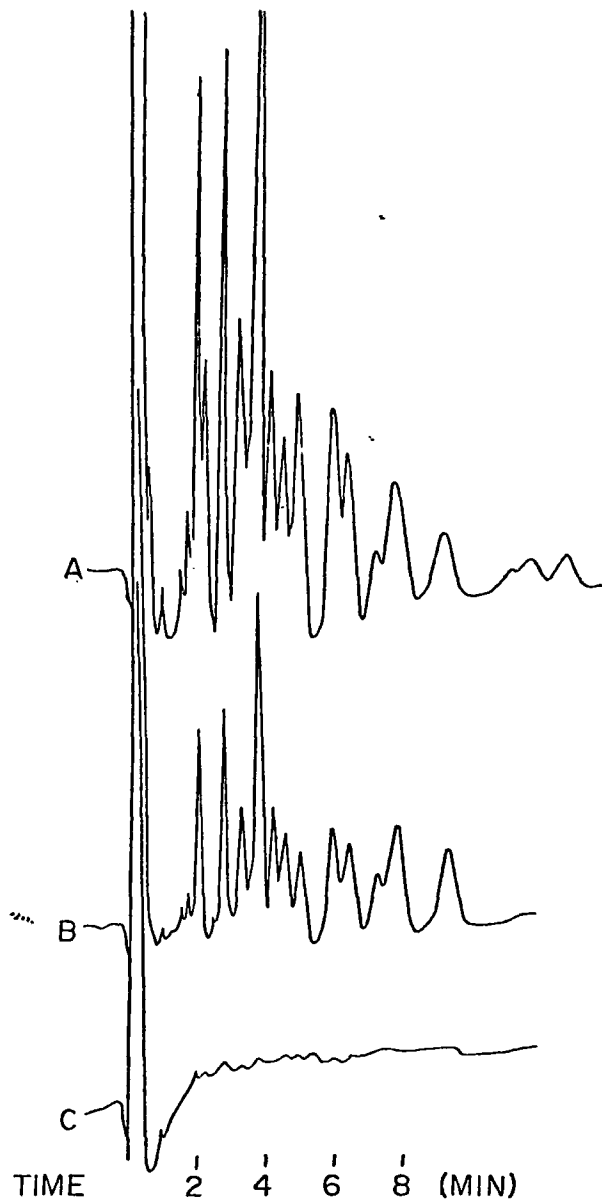


Fig
2



1016, 95%, 2, 5, 4' trichlorobiphenyl, 90%, and 4, 4' dichlorobiphenyl, 85%. Our recoveries for biphenyl, aroclor 1221, and 2 monochlorobiphenyl were low, approximately 50%, 60%, and 80%, respectively. A biphenyl standard in chloroform was perchlorinated directly, twice, with the same low recovery. So it is doubtful that these recoveries are totally due to volatility. In these biphenyl perchlorination chromatograms, there was only one major DCB peak. No sizable bromononachlorobiphenyl peak was found (16). The biphenyl may be involved with another competing side reaction besides antimony bromotetrachloride (17). This could be enhanced by our chromic acid wash leaving a chromium oxide residue. Unfortunately, this was not investigated. Data on the perchlorination method for confirmation of real air samples that were done in duplicate are listed in Table 1. All of these samples were aroclors 1016 or 1242. The DCB concentration was converted into a PCB concentration in the table for comparison. Most of the DCB samples were analyzed on the gas chromatograph. Two downwind samples from an incinerator had to be analyzed on the gas chromatograph-mass spectrometer. Even with the micro florisil clean-up, upon perchlorination the background level was too high. A micro-scale alkali treatment was attempted with little success (18). A mass spectrometer was used as a specific detector for this determination. Figure 3 is mass spectrum of DCB.

Application

Four examples are presented to illustrate the various PCB patterns that may be found. In most cases, the pattern appears to shift toward the more volatile, less chlorinated, components. Also, the difference between 1016 and 1242 is that 1016 has a smaller amount of pentachlorobiphenyls and hexachlorobiphenyls than 1242, see Figures 2 and 4. At low levels these were reported out as 1016/1242.

The first example is a sample that was done inside our laboratory during the month of November 1976, and in January 1977. Both analysis were done in duplicate. These samples were taken from the same room. Major differences are the locations

Table 1. Confirmation by Perchlorination (ng/m³)

Direct Injection	Perchlorination
38	28
58	55
150	208
240	202
20	20
40	20
110	83
226	95
441	499
529	650

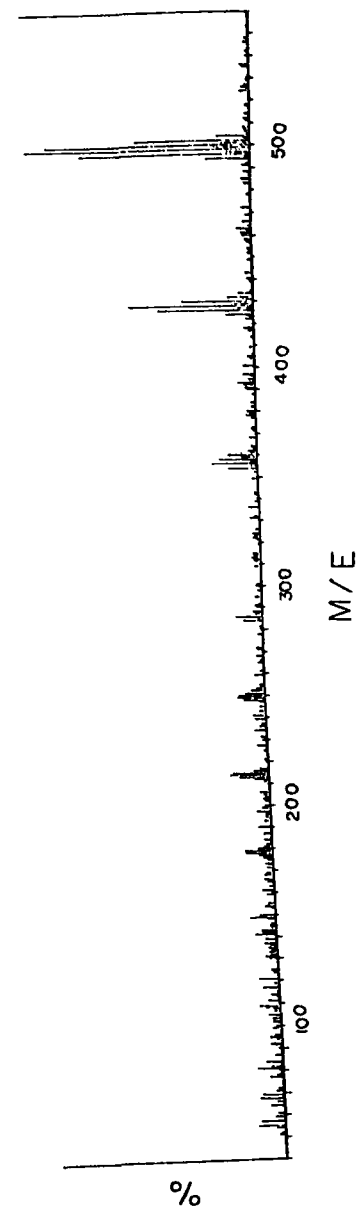
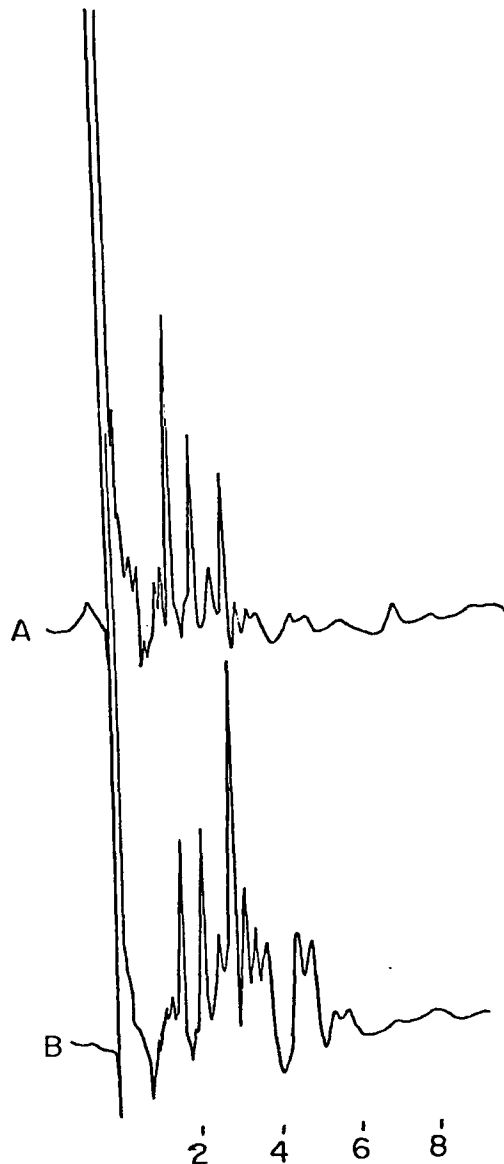


Fig
3



the room and the laboratory's heating during the month of January. November results were 236 and 284 ng/m³ and January values were 441 and 529 ng/m³. In all the PCB patterns there was a shift toward the more volatile components. This is illustrated in Figure 4.

Two electrical manufacturers that are known to be using PCBs were investigated in September 1978. The results are listed in Table 2 and the patterns are shown in Figure 5. Here the pattern is a close match to aroclor 1242.

A landfill that has received a large amount of PCB waste was tested in January 1978, and later in September 1978. These samples are interesting because of the changes in the patterns. The early Fall sample shows a shift toward the heavier, more chlorinated components as compared to the January sample. This would imply a relative depletion of the low chlorinated biphenyls at the landfill site along with the temperature influence on the pattern. These results are listed in Table 3 and the patterns are in Figure 6. The back-up at the landfill site for the September sampling shows no break through.

An incinerator handling known PCB waste was analyzed in the Winter of 1977. The pattern shows a slight shift toward the more volatile components. The values are listed in Table 4 and the patterns are shown in Figure 7.

There was some correlation work done with an independent laboratory using a polyurethane foam method of collection as described by Bidleman and Olney (19). The major problem here is the different sampling times. The polyurethane foam method uses the hi vol air sampler. Its sampling time is only a fraction of the time needed for the florisil method. For the data presented, the sampling times for the polyurethane and florisil methods are 15 min and 3-4 hr respectively. This data is given in Table 5. The result of 5 ng/m³ on the polyurethane foam method was a downwind sample and the corresponding upwind sample was 19 ng/m³. No florisil sample was taken at the upwind location. This could have been due to the short sampling time.

Table 2. Capacitor Manufacturer

PCB CONCENTRATION (ng/m3)		
Samples	1242	1254
Plant A		
Upwind	41	ND
Downwind	301*, 259	9*, 9
Back-up*	ND	ND
Plant B		
Upwind	18	ND
Downwind	743, 824	24, 38

ND--not detected

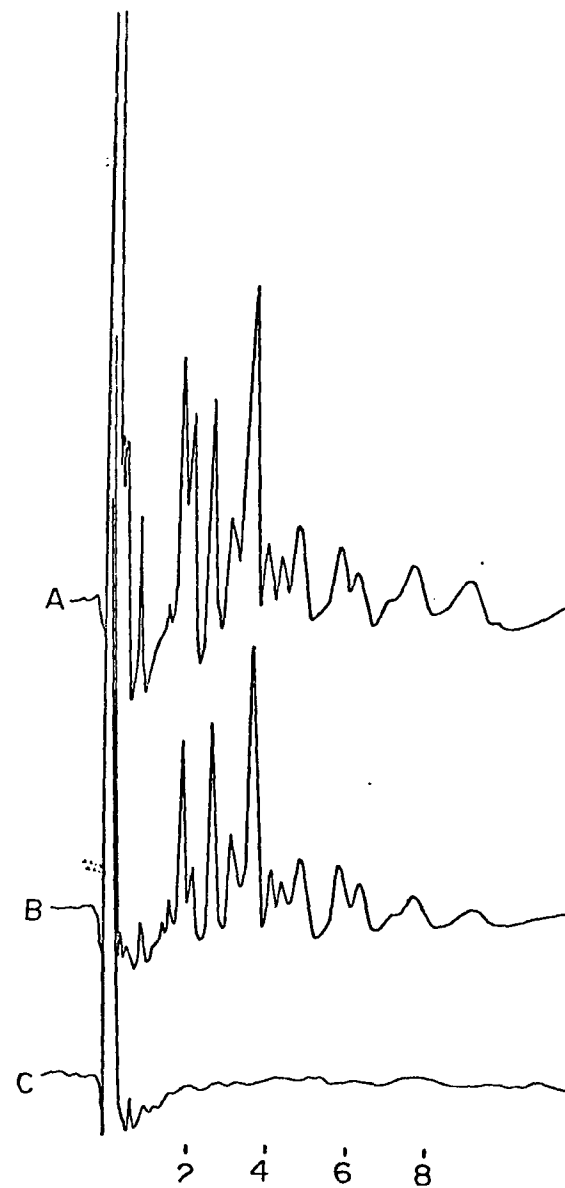


Table 3. Landfill Results

Samples	PCB CONCENTRATION (ng/m ³)	
	1016/1242	1254
January		
On Site	28, 24	ND, ND
Downwind	18, 12	ND, ND
September		
Upwind	27	ND
On Site	334, 703	33, 23
Downwind	18, 21	ND, ND

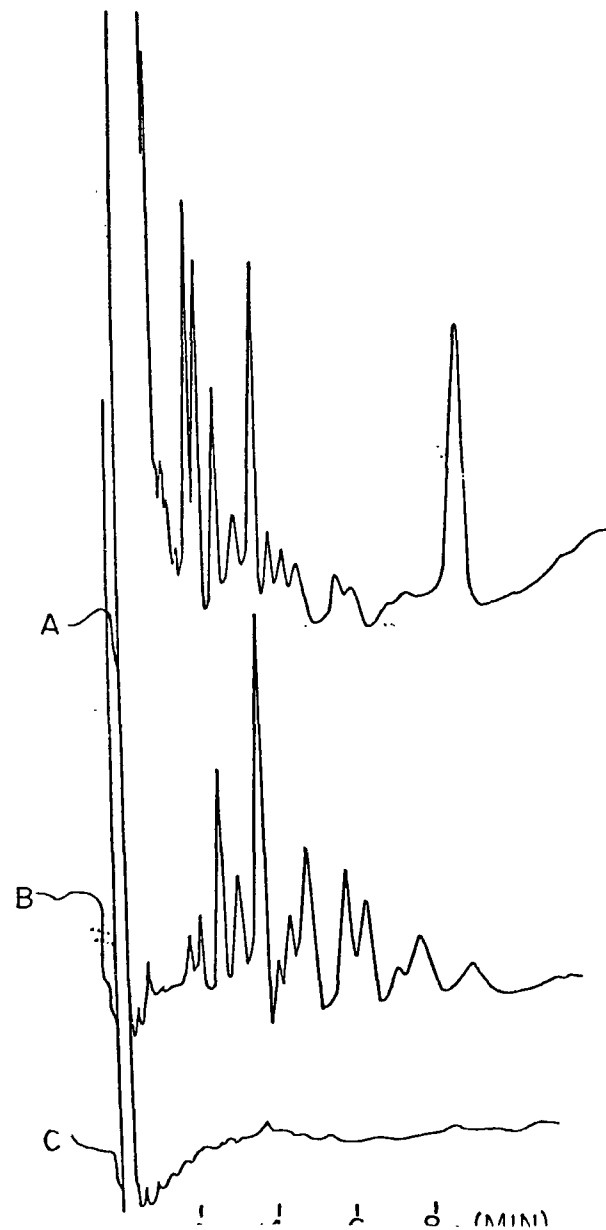
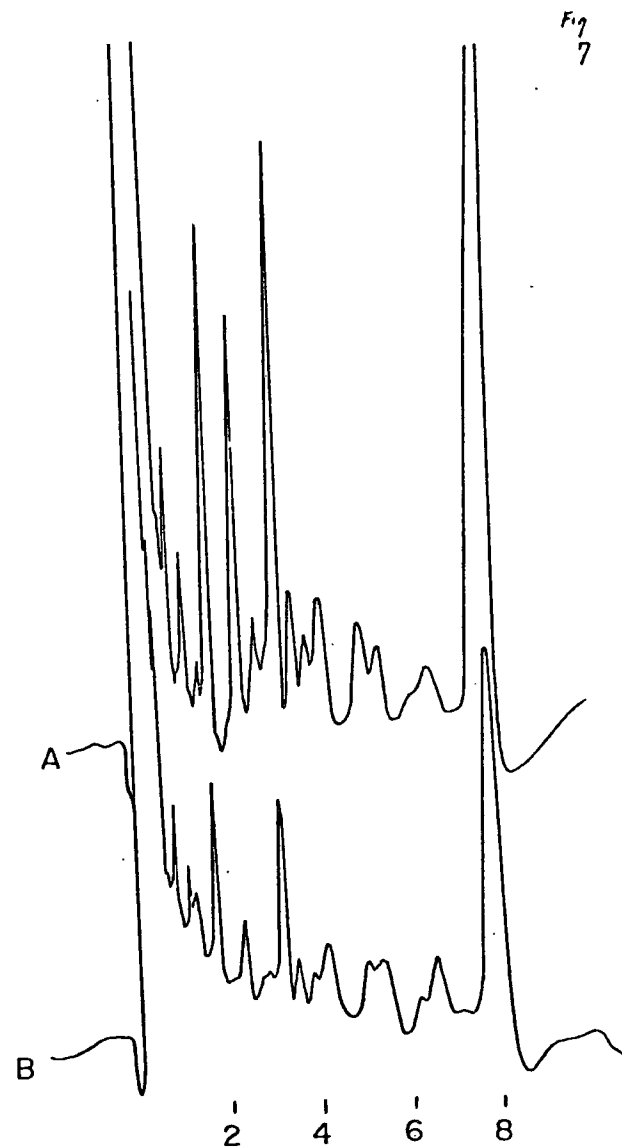


Table 4. Incinerator

Samples	PCB Concentration (ng/m ³)
Day One	
Upwind	38, 58
Downwind	150, 240
Day Two	
Upwind	20, 20
Downwind	110, 95



(FIGURE CAPTIONS)

Table 5. Comparison of
Florisil and Polyurethane Foam Methods (ng/m³)

Florisil	Polyurethane Foam
28, 24	21
18, 12	13
703, 774	490
30, 32	5

Figure 1. Florisil trap. (A) prepared trap with perforated aluminum foil
(B) ball and socket joint (C) rotometer (D) pump with exhaust
hose.

Figure 2. Trapping efficiency. (A) top trap (B) aroclor 1242 (C) bottom trap.

Figure 3. Mass spectrum of decachlorobiphenyl.

Figure 4. Indoor study. (A) laboratory room (B) aroclor 1016.

Figure 5. Capacitor manufacturer. (A) upward (B) downwind (diluted 7 x A,C)
(C) blank.

Figure 6. Landfill site. (A) January test (B) September test (diluted 7 x A,C)
(C) back-up to B.

Figure 7. Incinerator. (A) downwind (diluted 2 x B) (B) upwind.

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