

ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES : POLYCHLORONAPHTHALENES



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ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES: POLYCHLORONAPHTHALENES

by

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ABSTRACT

This research program was initiated to evaluate possible environmental contamination by polychlorinated naphthalenes (PCNs). The program included sampling and analytical method development and the collection and analysis of field samples.

Air, water, soil, sediment and biota were collected from sites near a PCN manufacturer, and six potential users. A glass fiber filter and two precleaned polyurethane foam plugs in tandem were used for PCN collection. Recovery of the PCNs from the foam and filter was accomplished by triple extraction with toluene. The concentrated extract was chromatographed on a silica gel column and the final volume reduced to 2 ml in a Kuderna-Danish apparatus. Samples were analyzed by gas chromatograph/quadrupole mass spectrometer/computer. The instrument was operated in the multiple ion detection mode which permitted the detection of <50 pg of a PCN isomer ($\sim 0.3 \text{ ng/m}^3$ in air, $\sim 0.2 \text{ }\mu\text{g/l}$ for water and $\sim 0.5 \text{ }\mu\text{g/kg}$ for soil). The presence of PCNs was confirmed from full scan mass spectra or by monitoring the chlorine isotope ratio. PCNs were found at all sites sampled although appreciable quantities were found at only three sites, near the manufacturer and two possible users.

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LIST OF ABBREVIATIONS

CDE	-	Cornell Dubilier Electronics Corporation, New Bedford, Massachusetts.
CDS	-	Cornell Dubilier Electronics Company, Sanford, North Carolina.
ECD	-	Electron Capture Detector.
FID	-	Flame Ionization Detector.
GC	-	Gas Chromatography.
GC/MS	-	Gas Chromatography/Mass Spectrometry.
GE-FE	-	General Electric Company, Fort Edwards, New York.
GE-HF	-	General Electric Company, Hudson Falls, New York.
GFF	-	Glass Fiber Filter.
K-D	-	Kuderna-Danish Evaporator
Koppers	-	Koppers Company, Incorporated, Koppers Chemical and Coatings Plant, Bridgeville, Pennsylvania.
Manning	-	Manning Paper Company, Green Island, New York.
MID	-	Multiple Ion Detection.
PCB	-	Polychlorinated Biphenyl.
PCN	-	Polychlorinated Naphthalene.
PPT	-	Parts per trillion.
PUF	-	Polyurethane Foam.
RMR	-	Relative Molar Response.
RSD	-	Relative Standard Deviation.
SD	-	Standard Deviation.
Sprague	-	Sprague Electric Company, North Adams, Massachusetts.
TIC	-	Total Ion Current.
VOA	-	Volatile Organic Analysis.

1.0 SUMMARY AND CONCLUSIONS

Polychlorinated naphthalenes (PCNs) are used principally as dielectrics in the capacitor industry. Due to their toxicity and chemical stability, their presence in the environment must be evaluated. Environmental samples were collected near several representative PCN manufacturing and use sites in the United States and analyzed by gas chromatography/mass spectrometry to assess the levels of PCNs near these sites. The objective of this research was to obtain a general assessment of PCN pollution, rather than detailed monitoring data.

Samples were collected near suspected PCN manufacturer (Koppers Chemical and Coatings Plant, Bridgeville, Pennsylvania), a suspected PCN-containing paper manufacturer: (Manning Paper Company, Green Island, New York), and five capacitor manufacturers: Cornell Dubilier Electronics Corporation, New Bedford, Massachusetts; Sprague Electric Company, North Adams, Massachusetts; General Electric Company, Fort Edward, New York; General Electric Company, Hudson Falls, New York; and Cornell Dubilier Electronics Company, Sanford, North Carolina). Two of the sites (Cornell Dubilier Electronics Corporation, New Bedford, Massachusetts and Sprague Electric Company, North Adams, Massachusetts) were designated as "secondary" sites and were sampled according to an abbreviated protocol. At the other five geographical sites, soil, sediment, biota, 24 hour integrated water and two consecutive 24 hour integrated air samples were collected, and analyzed for PCNs. In addition, miscellaneous related water samples were collected and analyzed where appropriate.

All sampling methods were developed, tested and validated prior to field sampling. An air sampler was developed in which PCNs were collected on a glass fiber filter (GFF) and two polyurethane foam (PUF) plugs in tandem. Suitable cleanup of the PUF was achieved using multiple washings with hot toluene. A flow rate of no more than about 60 l/min ($90 \text{ m}^3/24 \text{ hr}$)

sample) collected all but monochloronaphthalene efficiently. Higher flow rates substantially reduced the collection efficiency. Samples were collected at each site using four air samplers located along the arms of orthogonal transects of the plant site. The orientation of the transects and distance of the samples from the site were determined by meteorological, topographical, and other considerations.

Water samples were collected upstream and downstream using a peristaltic interval sampler or (where appropriate) by "grab" techniques. Three to ten core soil samples were collected within a 10-50 m location and composited for analysis. "Near" and "far" locations along each arm of the transects were sampled. In addition, "grab" soil samples were collected at locations suspected of contamination such as sanitary landfills, dumps, etc.

Evaluation of PCN solubility showed toluene to be a superior solvent to hexane which is customarily used in PCB analysis. Consequently, recovery of PCNs from PUF and GFF was best accomplished by triple extraction with toluene at 25°. Water samples were extracted by partitioning into toluene and soil samples were extracted using a mixture of acetone and toluene after first treating the soil with diethyl ether to loosen the PCNs from the matrix. The toluene extract volume was reduced without loss of PCNs using a Snyder column on a flat-bottom boiling flask and further reduced under a N₂ stream at 25°. The concentrated extract was chromatographed with hexane on a silica gel column and finally reduced to 2 ml using a Kuderna-Danish apparatus.

Sample analysis was accomplished by quadrupole gas chromatograph/mass spectrometry/computer (GC/MS/COMP) using an OV-101 column. To improve sensitivity and specificity for PCNs, the instrument was operated in the multiple ion detection (MID) mode, permitting detection of <50 pg of an individual PCN isomer or (for the volume of air sampled) about 0.3 ng/m³. The presence of PCNs was confirmed by either full scan GC/MS/COMP or by monitoring the chlorine isotope ratio using M and M + 2 or M + 4 mass ions.

Polychlorinated naphthalene levels in soil near Koppers Chemical and Coatings Plant, Bridgeville, Pennsylvania were found to be an average of 2400 µg/kg with a range of 480 to 5800 µg/kg. Air samples were found to

contain from 25-450 ng/m³ (avg. 150 ng/m³) on the first day and 120-2900 ng/m³ (avg. 1400 ng/m³) the second day. A small dead fish was found to contain 39 µg/kg and locally obtained apples, 90 µg/kg. Only trace amounts of PCNs were found in the water samples. All eight chloronaphthalene isomers were found in the air and soil samples, with mono-, di-, and trichloronaphthalene predominating in air and tri-, tetra-, and pentachloronaphthalene predominating in soil. The isomeric distribution is a significant parameter in evaluating the health effects of PCN contamination due to the varying toxicity of different isomers.

Samples collected near Manning Paper Company, Green Island, New York contained low-to-undetectable PCN concentrations with an average soil concentration of 10 µg/kg (range: undetectable to 34 µg/kg), an average air concentration of 1.5 ng/m³ (range: 0.3-2.5 ng/m³) and 1.4 ng/m³ (range: undetectable to 3.1 ng/m³) on two successive days, and generally undetectable amounts of PCNs in water.

A composite of the soil samples collected near Cornell Dubilier Electronics Corporation, New Bedford, Massachusetts was found to contain a total of 500 µg/kg PCNs. Water samples did not contain detectable amounts of PCNs.

Two composite soil samples collected near Sprague Electric Company, North Adams, Massachusetts were found to contain totals of 44 and 52 µg/kg PCNs. Water samples did not contain detectable amounts.

Air samples collected near General Electric Company, Ft. Edward, New York were found to contain an average of 3.1 ng/m³ (range: undetectable to 7.3 ng/m³) and 1.2 ng/m³ (range: undetectable to 4.9 ng/m³) total PCNs on consecutive days. Soil samples collected along the transects contained an average of 2.4 µg/kg (range: undetectable to 7.3 µg/kg) total PCNs. Grab soil samples contained an average of 7.0 µg/kg (range: undetectable to 21 µg/kg) total PCNs. Water collected by interval samplers did not contain detectable amounts of PCNs. Total PCN levels of undetectable, 0.6 µg/l and 5.5 µg/l were found in water collected by "grab" sampling.

Air samples collected near General Electric Company, Hudson Falls, New York were found to contain an average of 5.6 ng/m³ (range: 2.8-9.3 ng/m³) total PCNs. Soil samples were found to contain an average of 4.5

µg/kg (range: 0.3-12 µg/kg) total PCNs. Water samples did not contain detectable amounts.

Samples collected near Cornell Dubilier Electronics Company, Sanford, North Carolina contained an average of 19 ng/m³ (range: 9.8-33 ng/m³) on the first day and 17 ng/m³ (range: 9.8-33 ng/m³) on the second day in air, 240 µg/kg (range: undetectable to 470 µg/kg) in soil, and 0.6 µg/l in water downstream of the plant (undetectable in upstream sample). An amber-colored resinous solid collected near the plant was found to contain 920 µg/kg PCNs, mostly as the di-, tri-, and tetrachloronaphthalene.

For the sake of perspective, comparison of PCN concentrations in soil found in this study with those found in similar studies of PCNs and PCBs may be helpful. The first PCN concentrations reported for environmental samples in the United States were 1250-5000 µg/kg in sediment samples collected from a Florida drainage ditch.⁽⁶⁾ A nearby aircraft overhaul hanger was suspected as a possible source.⁽¹⁾ The values found in our study are lower than those reported for PCBs in soils near a PCB manufacturing site in Illinois where concentrations from 130-20,700 µg/kg with an average concentration of 3900 µg/kg were detected⁽⁹⁾ (about four times greater than our findings). These values are approximately ten times those reported for PCBs in bottom sediments of major drainage basins of the United States⁽¹⁰⁾ which ranged from 1.2-160 µg/kg with an overall average of 13.5 µg/kg. These results suggest that transport of PCN and PCBs by water over any significant distance is slight; a reasonable conclusion in light of their low solubility in water.

2.0 INTRODUCTION

Polychlorinated naphthalenes (PCNs) have recently come under suspicion as environmental contaminants because of their chemical and toxicological similarities to polychlorinated biphenyls (PCBs).⁽¹⁾ Marketed in the United States as Halowaxes[®] (2), PCNs are primarily used to impregnate capacitor tissue paper and as engine oil additives.⁽¹⁾

Occupational exposure to PCNs has resulted in dermal reactions (chlor-acne), liver damage^(1,2), and in a few cases, death.⁽¹⁾ Penta- and hexachloronaphthalene appear to be primarily responsible for the toxic effects of PCNs.^(1,4)

Polychlorinated naphthalenes have been detected in a variety of environmental media including dead cormorants in the Netherlands⁽⁵⁾, a drainage ditch in South Florida near an airport overhaul hanger (1250-5000 $\mu\text{g/kg}$)^(1,6) and in sediment from the Guadalupe River, California.⁽⁷⁾ These findings suggest a potential environmental hazard. It was the purpose of this research to develop analytical methods for collection and analysis of PCNs in ambient air and to apply these methods to study the occurrence of PCNs near five or more manufacture or user sites.

Polychlorinated naphthalenes and their environmental effects and toxicity have been recently reviewed.^(1,3,8)

3.0 METHOD DEVELOPMENT

3.1 SAMPLING

It was the objective of this research to collect samples of environmental media at various suitable sites to obtain a reliable assessment of environmental contamination by PCNs. To this end, sampling apparatus was developed or acquired and thoroughly tested, sampling sites were selected, and sampling protocols developed before embarking on any field sampling trips.

3.1.1 Apparatus

3.1.1.1 Air Sampler Design

A number of problems have been encountered with the impinger method for collecting pesticides and consequently it has been withdrawn as an EPA standard method. No other method has been substituted for this purpose. Substitute methods are currently being evaluated and the most promising of these is based upon polyurethane foam (PUF) as a sorbent.⁽¹¹⁻¹⁴⁾ The primary limitation of this material is a relatively high background. In order to compensate for this background, large samples at high flow rates have been collected for analysis. Hi-Vol samplers were modified to accept the sampling module (Figure 1) and a by-pass valve used to regulate the flow rate to ~300 l/min. The load on the pump motor plus the loss of ventilation resulted in overheating and occasionally total destruction of the pump motor. In addition to expense and inconvenience, such an occurrence has lead to sample contamination.⁽¹⁴⁾ In view of this problem the sampler was redesigned taking into account the particular constraints pertaining to this system.

The pressure drop imposed by the glass fiber filter and sorbent material is such that flow rates greater than 300 l/min are not practical.

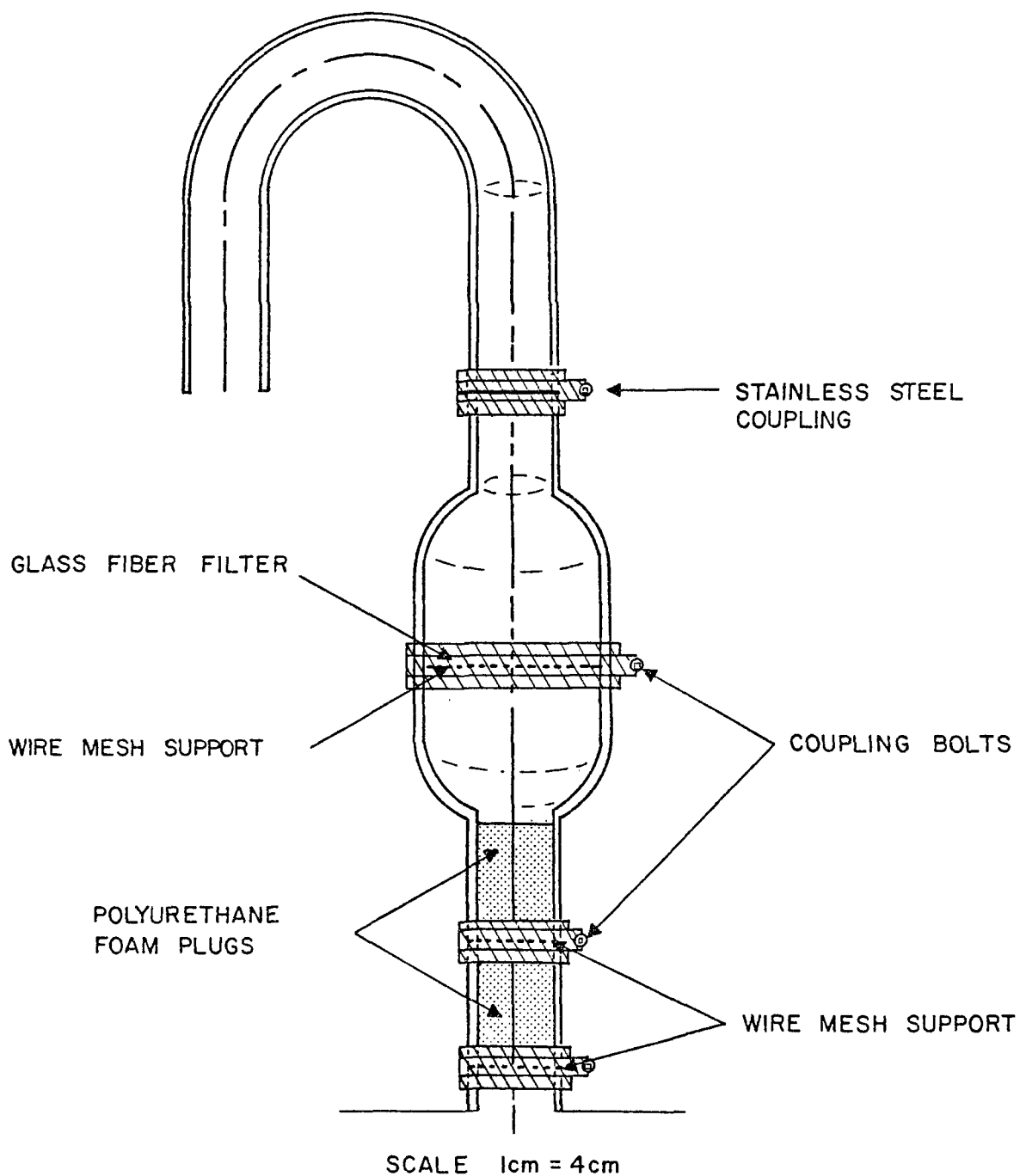


Figure 1. Sampling apparatus configuration for collection of polychlorinated naphthalenes.

For this reason pumps which could operate continuously at about 300 l/min with an estimated pressure drop of 130 mm of Hg were investigated. Gast rotary vane pumps satisfied this requirement.

Air samplers, custom designed by Nutech Corporation (Durham, NC), were used for the collection of chloronaphthalenes in ambient air. The sampler shown schematically in Figure 2 uses a Gast oilless rotary vane vacuum pump model no. 1022. This pump is rated to deliver 280 l/min air flow at no pressure drop and 250 l/min air flow at 130 mm Hg. The selection of this model was based in part on the fact that it has a motor mounted drive rather than belt drive which results in a more compact, lighter unit for field sampling.

The flow rate is monitored at the pump exhaust to avoid the problems associated with correcting for pressure changes during the sampling period. The pressure at the pump is monitored with a vacuum gauge which serves to signal possible malfunctions.

3.1.1.2 Clean-up Polyurethane Foam Plug

Previous workers using PUF to collect PCBs⁽¹¹⁻¹⁴⁾ have used hexane, acetone, and/or petroleum ether in a Soxhlet extractor to remove impurities prior to sampling. Initial tests with hexane-extraction showed no decrease in the level of impurities in the extracts after several successive extractions and it was further shown (vide infra) that in fact, PCNs were not readily soluble in hexane. Considerable effort was expended to find a method which would successfully clean up PUF for use in PCN sampling. The procedure finally developed involves manual extraction with hot toluene followed by drying in a vacuum oven. The complete standardized procedure is detailed in Appendix A. Details of the development of the procedure are discussed below.

When it was determined through initial extraction attempts with acetone and petroleum ether in a Soxhlet apparatus for 12 hours that an adequate removal of the electron capturing contaminants from samples of Olympic 4214[®] polyether type polyurethane foam (Olympic Products Company, Greensboro, NC) was not achieved, further development of PUF clean-up was pursued. In order to better estimate the mass of contaminants being extracted 100 to 200-fold concentrates of petroleum ether extracts were

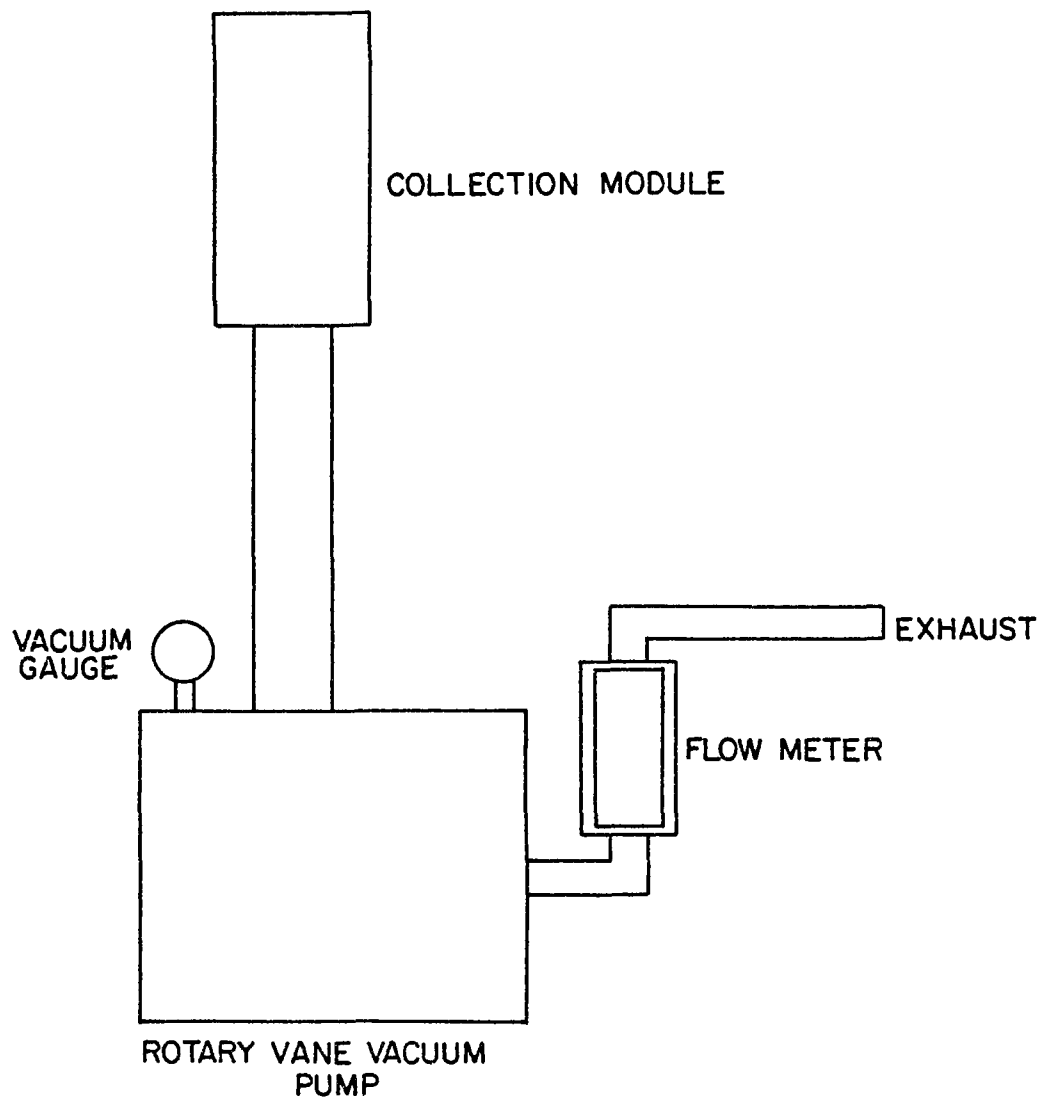


Figure 2. Air sampler.

analyzed by GC/Flame Ionization Detection (FID) which showed that most of these extracted materials were insensitive to FID. No improvement with additional petroleum ether extractions was observed. Similar extraction of a virgin piece of foam with toluene at 90° for 2 hr indicated a much higher degree of contaminant removal although no significant decrease in number or size of chromatograph peaks was observed with a second extraction. Subsequent extractions of this same piece of foam with hexane at 60° revealed smaller, but still substantial quantities of contaminants remaining.

In light of the solubility results, a 1 g piece of foam was manually extracted at 100° for 10 min with successive 50 ml volumes of toluene. Analysis by GC/ECD indicated the background contamination could be reduced to acceptable levels by five 10 min extractions. Chromatograms for the first, third, and sixth extractions are presented in Figures 3, 4, and 5, respectively.

Since it was necessary to prepare a large number of polyurethane foam plugs for field air sampling a study was made of the conditions required to remove electron-capturing interferences by extraction of several foam plugs simultaneously. Greatest success was attained by squeezing the foam in toluene at 100°C in the bottom of a four liter beaker with a one liter Erlenmeyer flask. Four extractions with redistilled toluene at 100° reduced the background contaminants to a level acceptable to GC/ECD. This procedure is faster and more efficient than Soxhlet extraction.

A higher-density and less-crosslinked polyurethane foam, Olympic 2315[®] (Olympic Products Co., Greensboro, NC) was selected as the adsorbent material for collecting chloronaphthalenes from ambient air primarily on the basis of lower background on GC/ECD. Foam plugs, 5 cm diameter x 13 cm long, were cut from sheets of polyurethane foam with an electric knife. Following five successive extractions with toluene at 100° for approximately 10 min per extraction the plugs were placed in individual 9 oz glass jars and dried in vacuo at 50°C for 12 hours. Upon removal from the vacuum oven, the jars were capped and wrapped with aluminum foil to prevent photodegradation of the foam. This cleanup procedure was followed for all foam plugs used in air sampling.

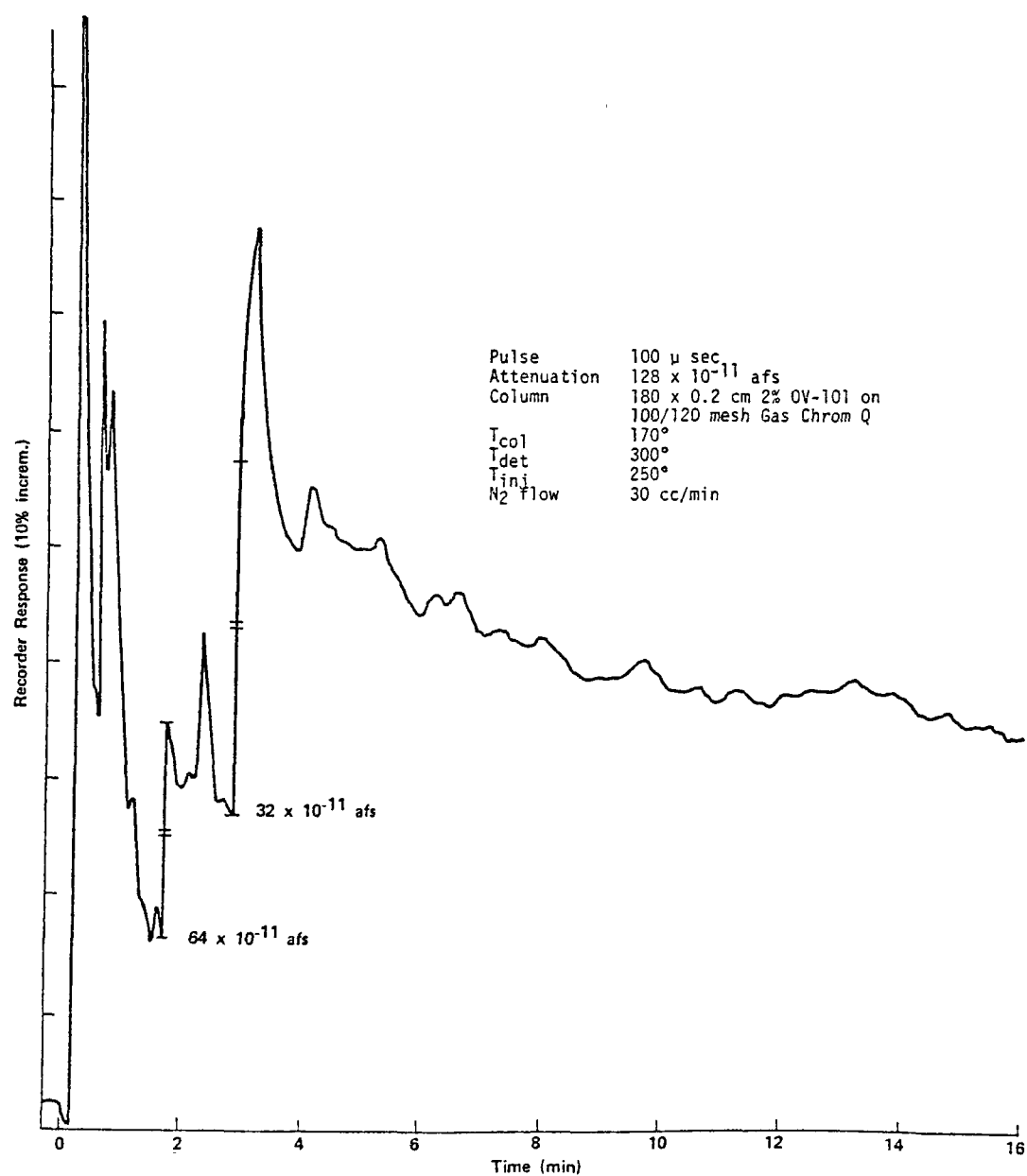


Figure 3. Gas liquid chromatography-electron capture detection (⁶³Ni) - foam clean-up; first toluene extraction.

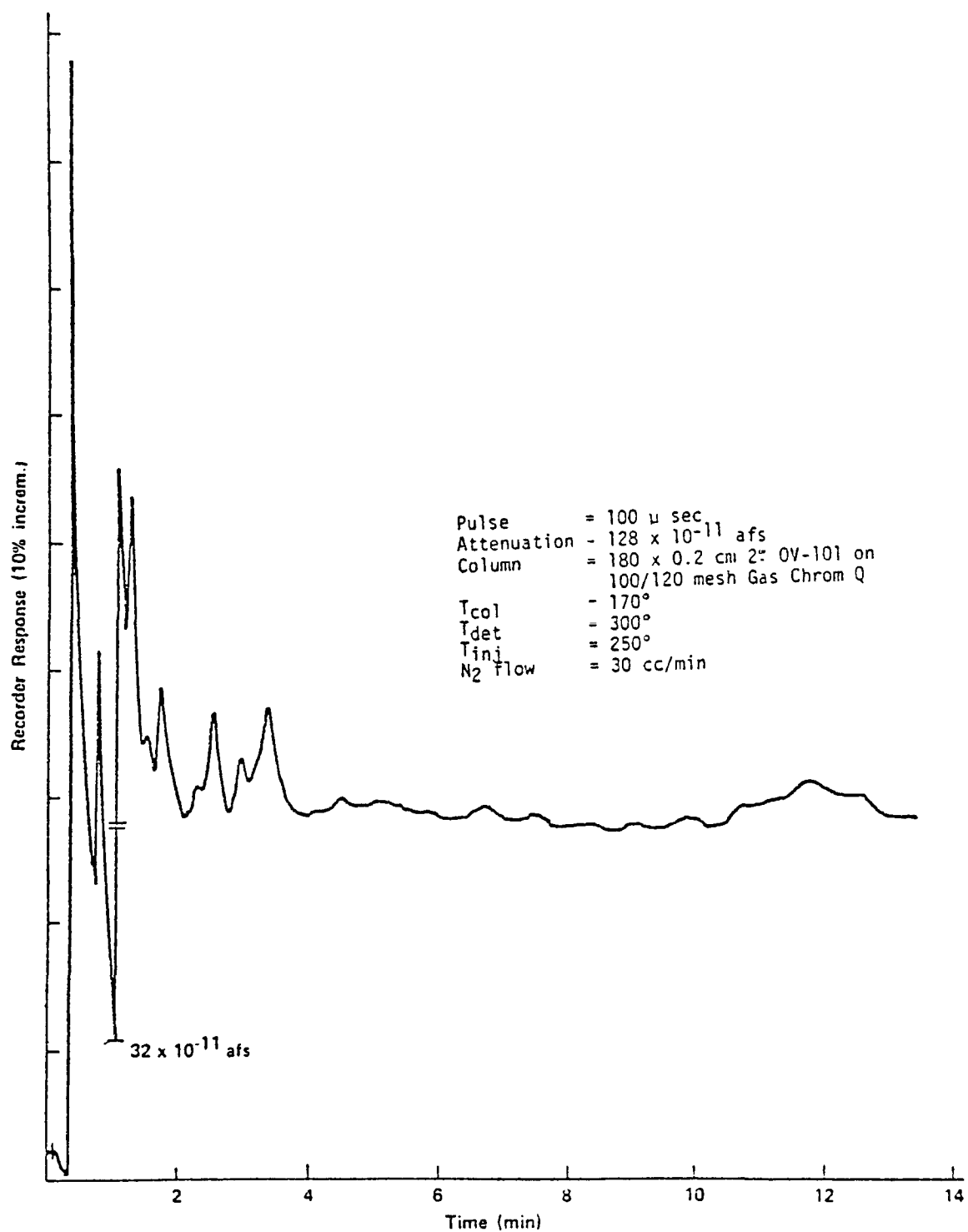


Figure 4. Gas liquid chromatography-electron capture detection (⁶³Ni) foam clean-up; third toluene extraction.

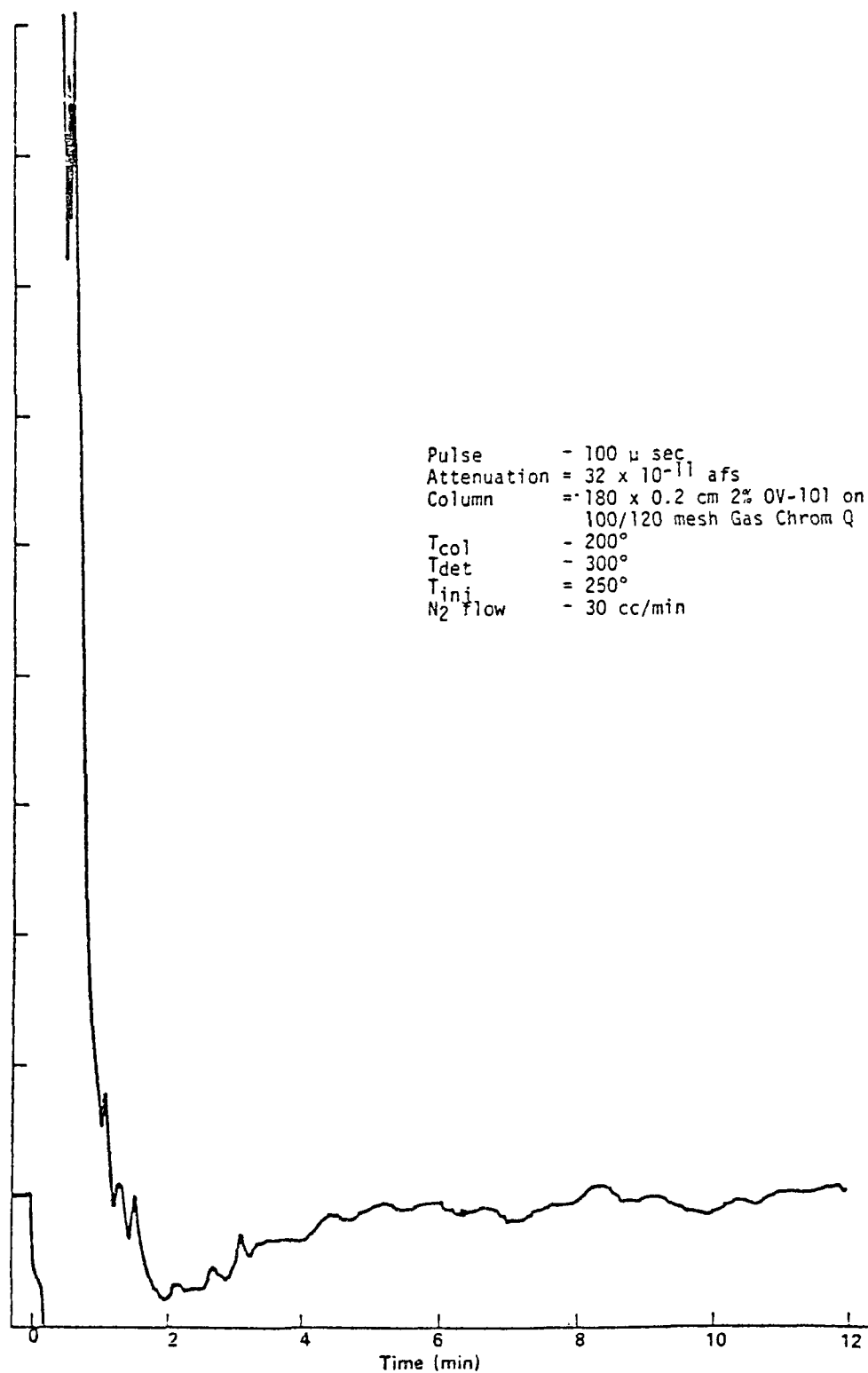


Figure 5. Gas liquid chromatography-electron capture detection (^{63}Ni) - foam clean-up; sixth toluene extraction.

Each of the five toluene extracts of the foam was analyzed by GC/MS, using the MID ions for the PCNs. Since the foam plugs were extracted in groups of four, simultaneously, the extracts contained contaminants from four plugs. The first extract contained large peaks in all channels, many with long retention times (greater than that for $C_{10}Cl_8$). Each successive extract contained fewer and less intense peaks. The fifth extract (Figure 6) contained three peaks in the 164 channel and three in the 196 channel. This background would not interfere substantially with the analysis of samples containing a total of ~ 200 ng or more of monochloronaphthalene. Dichloronaphthalene has a different retention time and was free of interference.

3.1.1.3 Collection of PCNs on Polyurethane Foam

The previous work on collection of PCBs using PUF^(12,13) indicated that it may be the most suitable medium for collection of PCNs. Investigations under this project determined that PUF is an acceptable collection medium for PCNs provided that the plugs are properly cleaned prior to use, the flow rate through the plugs is low enough to prevent breakthrough, and that some loss of lower chlorinated (particularly monochloronaphthalene) PCN isomers is acceptable.

The breakthrough volume and recovery of PCNs from PUF plugs was evaluated by treating a standard precleaned plug with 200 μ g of Halowax 1014[®] in toluene applied to one end of the foam plug, the solvent removed in vacuo, and the treated foam plug placed with the treated surface up in the air sampling train over a clean foam plug. Air was drawn through the two tandem foam plugs at 147 ℓ /min until 53 m^3 of air had passed through the sample. The two foam plugs were then extracted with toluene as above. Only 20% of the Halowax 1014[®] was found on the treated foam plug and none on the back-up foam plug. When this low recovery was encountered, an additional extraction with 200 ml of toluene at 80°C was made to make certain the problem was not incomplete extraction. No additional Halowax[®] was recovered in this extract. The profile of the Halowax 1014[®] extracted from the foam was distorted from the profile of the standard with the later eluting peaks being diminished. This is illustrated in Figure 7 which

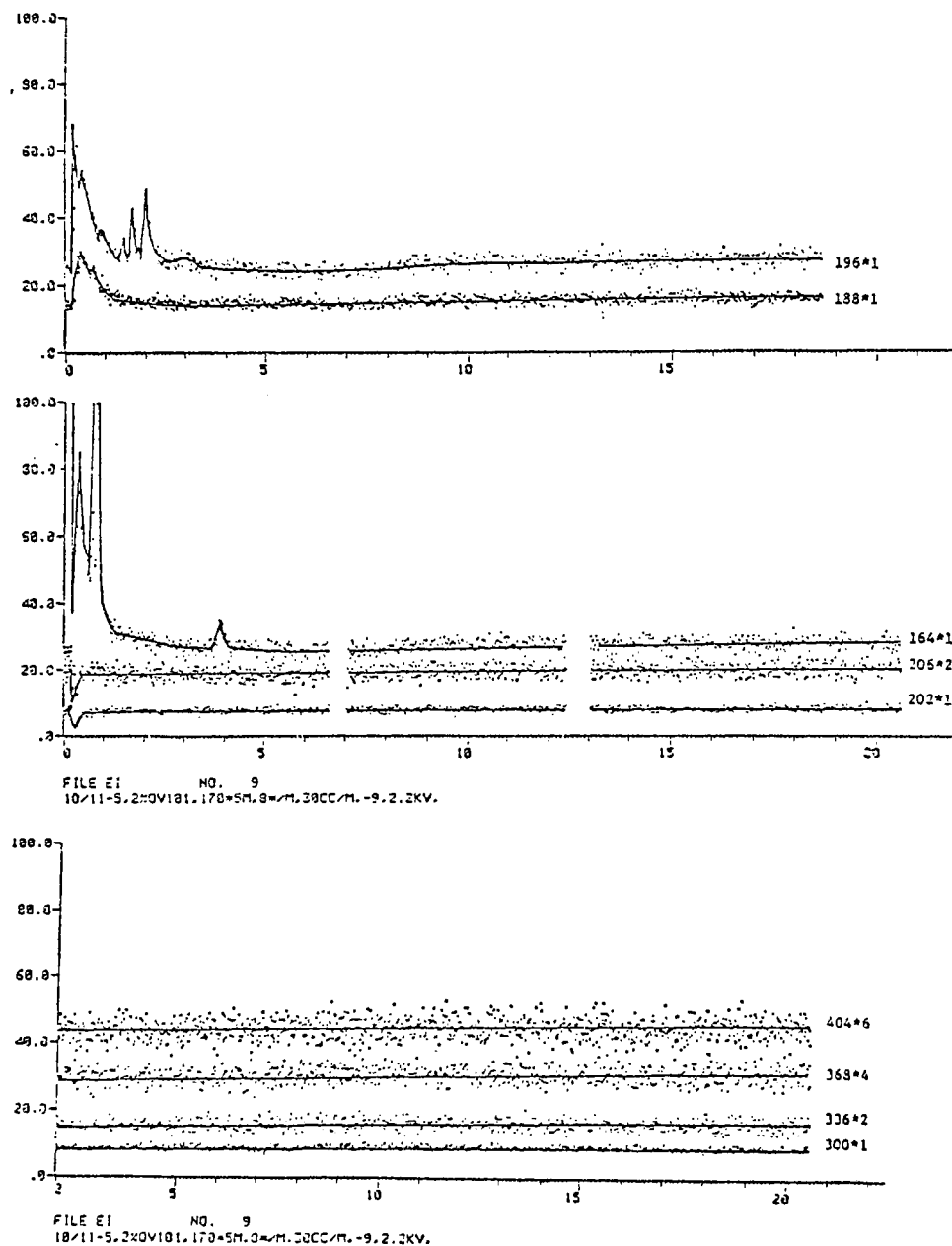


Figure 6. GC-MS analysis of the fifth toluene extract of a foam plug, multiple ion detection.

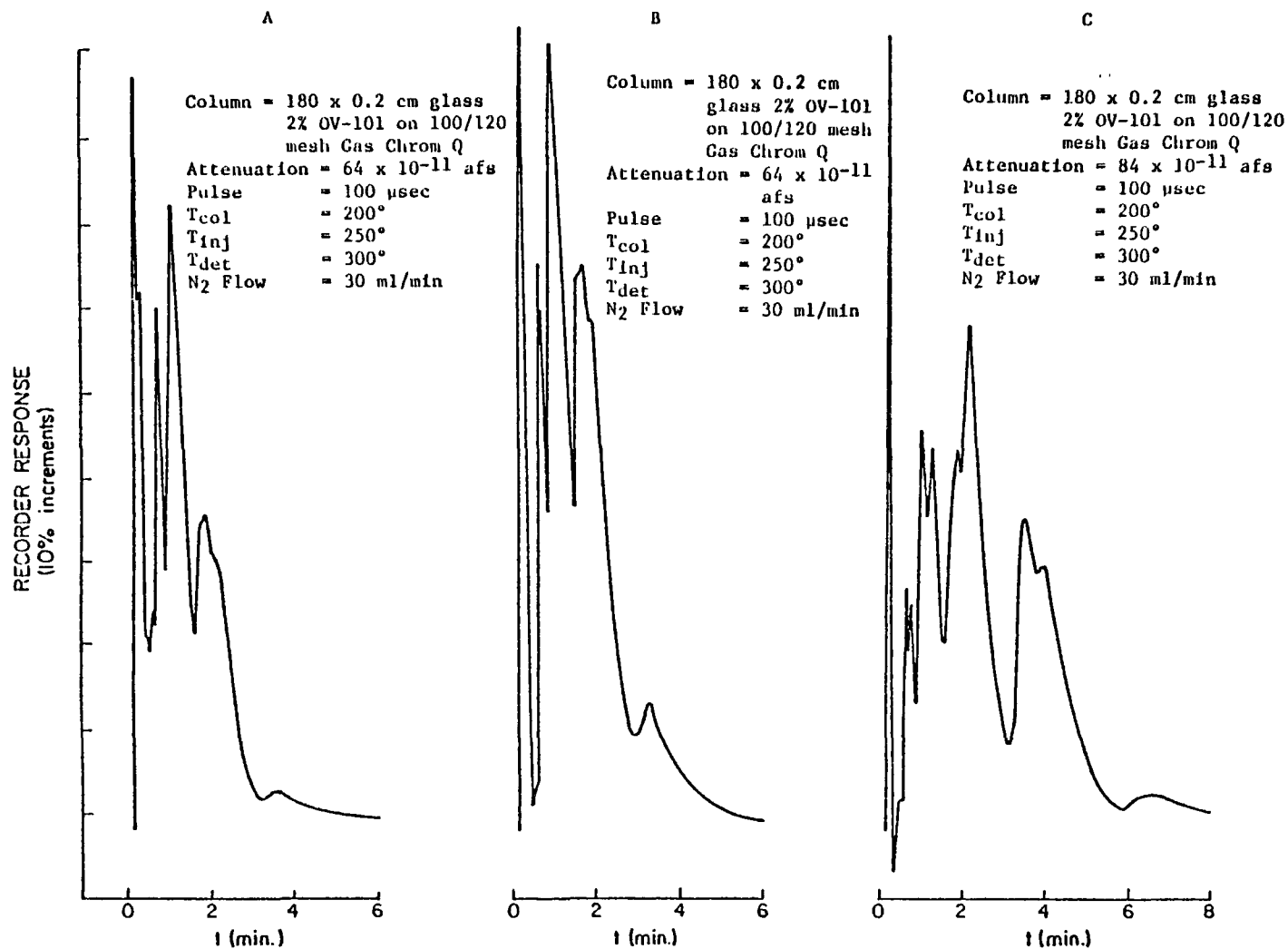


Figure 7. Gas chromatography-electron capture detection analysis of H-1014 recovered from polyurethane foam after air sampling and H-1014 standard. (A) Before column clean-up (1 μ l injection of a 30 ml sample); (B) After column clean-up (1 μ l injection of a 15 ml sample); (C) Halowax 1014 (5 ng injection).

contains chromatograms of the foam extract, before and after removal of interferences on a silicic acid column and a standard of Halowax 1014[®]. Vacuum stripping of the chloronaphthalenes from the foam was a possible explanation for the poor retention observed. Photodecomposition may also have been responsible for the significant loss of applied Halowax[®]. In fact a subsequent experiment in which two air sampling trains were run simultaneously implicated photosensitivity as the cause of some of this loss. In this experiment one sampling train contained two tandem plugs with 200 µg of Halowax 1014[®] applied on the top plug and the other contained a similarly spiked single plug. Both sampling units, shielded from sunlight by wrapping with aluminum foil, were run as previously described although a large difference in vacuum registered on the two pumps (<25 mm Hg for one plug; >180 mm Hg for two plugs) no major difference in retention of Halowax 1014[®] was observed. Seventy five percent recovery was observed for the two plug series and 64% recovery for the single plug. These results suggest that the chloronaphthalenes may be photosensitive and that retention is not only a function of the vacuum applied, but also a function of flow rate.

Flow rate through the air samplers was found to have a significant effect on the amount of Halowax[®] which could be recovered. Table 1 presents the results of several experiments at different flow rates. Experiment 1, indicates possible photodegradation of chloronaphthalenes. The only difference between Experiment 1 and the two plug series of Experiment 2 is that the plugs in Experiment 2 were shielded from sunlight. A study by Lewis et al.⁽¹⁵⁾ indicated that PCBs, particularly in the presence of diethylamine, are sensitive to sunlight. Lewis and co-workers actually employed this photosensitivity to facilitate determination of Mirex[®] in the presence of PCBs. Experiments 2, 3 and 4 show improved retention of chloronaphthalenes at lower flow rates even when the sampling period is extended to 24 hr. A 24 hr sampling period at 62 l per minute reflects a sampling volume of 90 m³. For an atmospheric PCN concentration of 1 part per trillion (ppt), 62 l/min would result in the accumulation of ~100 µg of Halowax[®] on the foam plug at 100% efficiency of collection. This flow rate was employed for field sampling.

Table 1. RETENTION OF HALOWAX 1014[®] AND 1051[®] ON OLYMPIC 2135[®]
POLYURETHANE FOAM DURING AIR SAMPLING.

Experiment	Plug	Flow Rate (l/min)	Sampling Period (hr)	Halowax Applied ^a 1014	1051	Halowax Recovered ^b 1014	1051	% Recovered 1014	1051	Notes
1	Top } Bottom }	150	6	232 µg 0		~27 µg 0		~12		Apparatus not shielded from sunlight
2	Top (only)	140	6	232		128		55		
	Top } Bottom }	140	6	232 0		143 6.6		62 3		
3	Top (only)	71	6	200		153		76		
	Top } Bottom }	71	6	200 0		170 0		85 0		
4	Top } Bottom }	62	24	232 0	222 0	220 0	215 0	95 0	97 0	
	Top } Bottom }	62	24	Blank	0	0 0	0 0	0 0	0 0	

^aHalowax applied by pipetting standard onto top surface of plug followed by vacuum drying.

^bHalowax recovered by three, 100 ml extractions with toluene at room temperature for 5 minutes.

One of the most important performance criteria for a sampling method is collection efficiency and knowledge of this parameter is essential to the interpretation of results in terms of atmospheric concentrations. To define this parameter, an experiment was conducted in which the apparatus illustrated in Figure 8 was employed. Halowax 1014[®] (464 µg) and Halowax 1051[®] (444 µg) were added to a slurry of 320 g of 3 mm glass beads in hexane. After evaporating the hexane the loaded beads were divided into 2 x 100 g and 2 x 60 g portions. Each of the 100 g portions was placed in sampling trains ahead of the glass fiber filter. Two PUF (Olympic 2315[®]) plugs were placed in the sampling module and the pump operated for 24 hr at 62 l/min. For four hours during this period the section housing the glass beads on one of the apparatus was slightly warmed with heating tape. Following the sampling period each of the foam plugs and glass bead portions was extracted with toluene and the extracts analyzed by GC/ECD. Each of the 60 g portions of glass beads was similarly analyzed to determine the actual loading of Halowax[®]. The loading was observed to be non-uniform hence no quantitative conclusions can be drawn for this experiment about the collection efficiency of chloronaphthalenes on foam, however, some interesting results concerning volatility were revealed. The components of Halowax 1014[®] were observed to be much more volatile than the components of Halowax 1051[®]. In general, volatility appeared to decrease with increasing chlorination, and is greatly increased by a slight rise in temperature. Semi-quantitatively speaking, chloronaphthalenes which were desorbed from the glass beads were proportionately adsorbed on the first foam plug. No chloronaphthalenes were detected on the second plug.

In a repeat experiment under more controlled conditions, 0.5 ml each of mono-, di-, tri-, tetra- and octachloronaphthalene standards were pipetted into a common vessel, the total volume reduced to 0.5 ml, and the PCNs quantitatively transferred to glass beads contained in the sampling apparatus displayed in Figure 8. This resulted in the application of 116 µg of 2-chloronaphthalene, 176 µg of 1,2-dichloronaphthalene, 208 µg of 1,2,3-trichloronaphthalene, 366 µg of 1,2,3,4-tetrachloronaphthalene and, 210 µg of octachloronaphthalene to the beads. After drawing ~90 m³ of ambient laboratory air through the samplers at 62 l/min the glass beads,

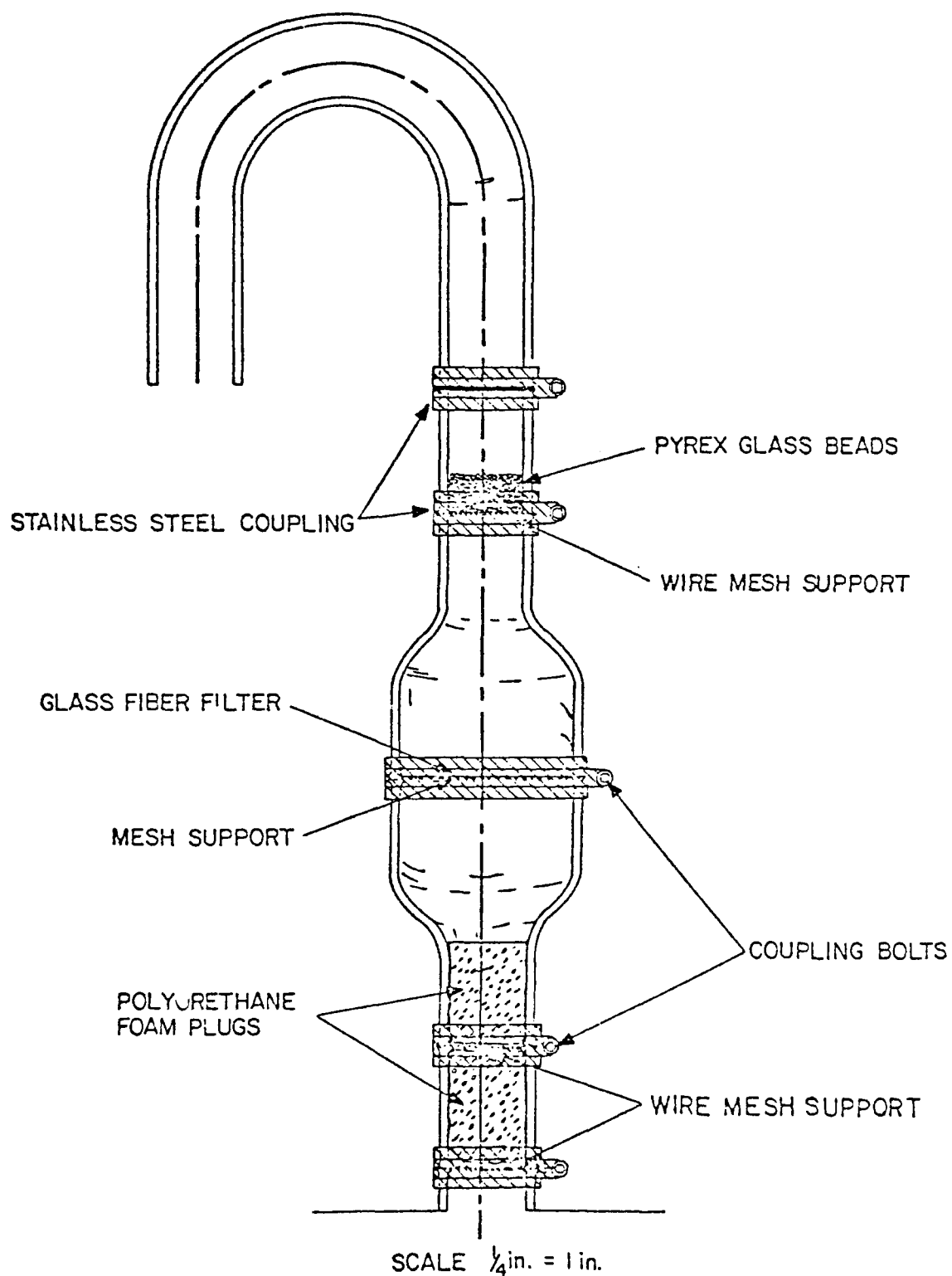


Figure 8. Sampling apparatus configuration for collection efficiency determination.

glass fiber filter and foam plugs were analyzed. The results presented in Table 2 reveals several interesting phenomena. Firstly, it appears that at the temperature (16°C) and flow rate (~62 l/min) of the sampled air monochloronaphthalene passes through both foam plugs. This is substantiated by the fact that 78-97% of dichloronaphthalene was found on the second foam plug and approximately 100% of trichloronaphthalene was found on the first foam plug. This is undoubtedly a result of decreasing volatility with increasing degree of chlorination. Although the lower air temperatures during field sampling would have reduced this volatility somewhat, concentrations of monochloronaphthalene observed in air samples must be regarded as minima. Secondly, only about one-half of the octachloronaphthalene was removed. The possibility of adsorption to glass surfaces prompted rinsing of interior surfaces of the glassware used in the sampling apparatus with toluene. However, no increase in recovery was observed. Photosensitivity of the higher chlorinated PCN isomers, a phenomenon suspected from previous experiments discussed above and reported as a destruction mechanism for PCBs^(14,15), may be responsible for this unexplained loss and prompted further investigation.

Table 2. COLLECTION EFFICIENCY OF POLYCHLORONAPHTHALENES

	% Recovered From Each Medium				
	m/e 164	m/e 196	m/e 230	m/e 266	m/e 404
Glass Beads	.47	1.36	6.88	26.6	55.2
Glass Fiber Filter	-- ^a	.06	.11	.17	--
PUF No. 1	.89	6.63	112.3	88.3	--
PUF No. 2	1.5	77.8	.73	.16	--
TOTAL	2.86	85.9	120.0	115.0	55.2
Glass Beads	.95	2.91	13.7	45.6	68.2
Glass Fiber Filter	.044	.067	.14	--	--
PUF No. 1	1.18	10.9	95.2	59.3	--
PUF No. 2	1.57	96.8	.286	--	--
TOTAL	3.75	110.7	109.3	104.9	68.2

^aNot detected

To assess photosensitivity a mixture of chloronaphthalenes (2-chloronaphthalene, octachloronaphthalene and Halowax 1014[®] -- about 500 µg/ml) in toluene was irradiated for eight hours with ultra-violet light from a germicidal lamp. The PCN mixture was analyzed by GC/MS before and after irradiation. No significant differences were observed and, therefore it does not appear that PCNs unaccounted for in collection efficiency and recovery studies were lost through photodecomposition.

3.1.1.4 Water Samplers

Water samplers were used without modification (vide infra). The efficiency of collection was tested to assure that PCNs were not adsorbed to the walls of the tubing.

The water sampling procedure was tested by sampling an aqueous solution spiked with Halowax 1014[®] and octachloronaphthalene (about 250 µg/l). The extracts of aliquots of water before and after sampling were analyzed by GC/MS and the integrated areas compared. The average concentrations were actually found to be greater in the sampled water than in the unsampled as shown in Table 3. Thus, loss of PCNs through adsorption to the tubing or other losses during sampling were assumed to be negligible.

Table 3. EFFECTS OF INTERVAL SAMPLING ON THE
CONCENTRATION OF PCNs IN WATER

Compound	Ratio (Sampled/Unsampled)
C ₁₀ H ₅ Cl ₃	0.83
C ₁₀ H ₄ Cl ₄	0.89
C ₁₀ H ₃ Cl ₅	1.03
C ₁₀ H ₂ Cl ₆	1.34
C ₁₀ HCl ₇	2.27
C ₁₀ Cl ₈	1.49
Mean	1.31
S.D.	0.54

3.1.2 Selection of Sampling Sites

Sites were selected to represent industries which manufacture and use PCNs. Use sites were selected within the electrical capacitor industry, both the manufacture of capacitor tissue and the capacitors themselves. To this end, a computer search (Predicast), Thomas Registry, Chem. Sources, Chemical Buyers Guide, two EPA reports^(8,1), Cramer Electronics Catalog, Pioneer Standard Electronics Catalog and the various state industrial directories were consulted. The sole domestic producer of PCNs^(8,1,3) is Koppers Company, Inc. at the Koppers Chemical and Coatings Plant, Bridgeville, PA, so this represented the manufacturing site for sampling. Manning Paper Co., Green Island, NY was selected as a representative capacitor tissue manufacturer. It is listed^(16,17) as a producer of electrical insulating papers. General Electric Company, Hudson Falls, NY; General Electric Co., Ft. Edward, NY; Sprague Electric Co., North Adams, MA, Cornell Dubilier Electronics Corp., New Bedford, MA; and Cornell Dubilier Electronics Co., Sanford, NC were selected as representative capacitor manufacturers. At these sites, a variety of capacitors ranging from automobile capacitors to electric power station capacitors are manufactured. With the exception of Koppers Company, Inc., there was no direct published evidence that any of the above listed manufacturers use PCNs. A detailed discussion of the known activities and other relevant information appears in the sampling and analysis section for each sampling site.

3.1.3 Sampling Protocol

The sampling protocol was developed to collect, air, water, soil, sediment, vegetation, and aquatic organism samples which would effectively assess the environmental contamination by PCNs near the suspected manufacturer and use sites. For all media, the prevailing philosophy of the sampling protocol was to collect samples which would be likely to yield positive results and which would reflect the extent of environmental contamination and its effect (either directly or indirectly) on humans.

3.1.3.1 Air

Sampling locations were selected within four quadrants around the sampling site. Selection of locations along transects of the suspected PCN source was made after surveying the site for wind speed and direction, air stability, terrain, population, and site accessibility. At each site four samplers were deployed along the arms of two orthogonal transects with two sets of air samples collected over consecutive 24 hr periods. During the entire collection time, meteorology was monitored continuously at a representative location for the entire site and intermittently at each sampling location.

3.1.3.2 Water

Where appropriate, water samples were collected using the interval samplers. Generally, samples were collected simultaneously upstream and downstream of the suspected PCN source. Suspected sources were identified by surveying the site for plant outfalls, local inquiries, inquiries at the wastewater treatment plant serving the plant, and in some cases, discussion with EPA Regional personnel. The samplers were deployed in the stream or river such that the inlet of the sampling tubing was well-removed from the river bank and in the main flow as much as possible. Water was generally collected from 10-30 cm beneath the surface with the samplers calibrated to pump 50% of a 15 min duty cycle for 24 hours. This resulted in the collection of about 4 l in 24 hours.

When interval sampling was inappropriate, 1 l grab samples were collected. These situations included mud puddles, stagnant ditches, ocean bays and streams which were not amenable to interval sampling.

3.1.3.3 Soil

Using the transects set up for air sampling, soil samples were collected at "near" and "far" locations along each of the four arms of the transects. Locations were selected according to meteorology, terrain, population, and accessibility. At each location, several core samples were taken within a 10-50 m radius which were representative of the location. Generally, attempts were made to obtain samples from high and low ground,

grassy and barren, under trees and in the open, etc. Every attempt was made to collect samples from areas which did not appear to have been recently disturbed. Each core sample was stored in a glass jar with a foil-lined cap and returned to the lab where the samples from each location were composited for analysis. During the first sampling trip (Koppers), ten core samples were collected at each location. It was the opinion of all personnel involved that this protocol was probably not necessary for obtaining a representative sample of the location, so on subsequent sampling trips only 3-5 core samples (at the discretion of the sampling personnel) were collected.

3.1.3.4 Miscellaneous

Sediment, garden vegetation, and aquatic biota were collected according to their availability. Sediment was usually collected in conjunction with water samples. At the discretion of sampling personnel, other samples of interest were collected -- generally industrial solid waste. Details of these samples and their collection are included in the sampling protocol for each site.

3.1.4 Meteorology

3.1.4.1 Measurements

The macrometeorology and micrometeorology were recognized as important factors in the transport of PCNs. With respect to air sampling, the specific meteorology of the site was important during the entire sampling period. Continuous measurements of temperature, wind direction and wind run were recorded on an MRI Mechanical Weather Station (MRI) at a central location throughout the sampling period. The strip chart record allowed subsequent reference to calm periods, wind direction shifts, etc., which could affect PCN transport in air. Intermittent measurements were made approximately six times daily at each sampling location. Humidity, temperature, wind speed, and wind direction were measured and noted along with general conditions (rain, snow, cloud cover, odors, etc.). Measurements at each location provided a cross-check with the MRI record.

3.1.4.2 Macrometeorological Data

Pertinent meteorological data for the sampling period were obtained from the nearest National Weather Service office. This data was used to augment that obtained at the sampling location.

Average annual and seasonal data were obtained from the National Climatic Center, Asheville, NC for construction of wind roses. The wind rose was used to correlate the theoretical PCN deposition with that found by sampling and analysis.

3.1.5 Sample Storage

The samples were preserved in the state in which they were collected as nearly as possible. To prevent degradation by microbial action or volatilization losses, all samples were kept cold. Solids (soils, foam plugs, etc.) were frozen and aqueous samples were stored at 5°C.

3.2 ANALYTICAL METHODOLOGY

The analysis of PCNs in environmental samples requires special methodology due to a number of factors. The volatility of PCNs spans a wide range and care must be exercised to prevent loss of lower chlorinated species. Because of the potential presence of a large number of chlorinated pesticides and PCBs in samples, the analytical method must remove as many interferences as possible and be sensitive to PCNs in the presence of inseparable interferences (notably PCBs). These factors were considered in the selection and development of all analytical procedures.

Samples were analyzed by GC/MS using multiple ion detection after extraction and cleanup. The specific methods used are detailed in Appendix A. All methods employed were tested and evaluated during the course of this project. Initially, perchlorination of PCNs followed by GC/ECD analysis was attempted. Perchlorination, a technique often used for PCB analysis, would involve conversion of all PCN isomers to octachloronaphthalene to yield a single GC peak with a long retention time, hopefully removed from that of interferences. Perchlorination was found to be fraught with difficulties including side reactions, low recoveries, and inconsistent reaction yields, and hence was abandoned. The GC/MS method ultimately

employed allowed positive identification of individual PCNs and permitted PCN identification even in the presence of much higher concentrations of PCBs.

The following discussion details the analytical method development and presents the results of method validation tests.

3.2.1 Apparatus, Instruments and Chemicals

3.2.1.1 Air Equipment

Air samples were collected on 5 cm diameter x 13 cm long polyether type polyurethane foam plugs cut from sheets of Olympic 2315[®] (Olympic Products Co., Greensboro, NC) using an electric knife. The foam plugs were preceded in the air stream by 11 cm diameter glass fiber filters (Gelman Type A-E). The sampling media were contained in an aluminum foil-wrapped glass module constructed of Kimax glass process pipe and fittings (Kimble Products, Toledo, OH). Air was drawn through the sampling module by a custom manufactured Nutech Corporation (Durham, NC) sampler which used a Gast oilless rotary vane vacuum pump Model No. 1022.

Air samples for collection of volatile and semi-volatile species were collected on Tenax GC cartridges using a Nutech Model 221A sampling pump (Nutech Corporation, Durham, NC) as described by Pellizzari.⁽¹⁸⁻²³⁾

3.2.1.2 Soil Equipment

Soil sample cores (5 cm diameter x 15-20 cm long) were cut using a common garden bulb planter. The samples were placed in labeled one-quart wide-mouthed jars with foil lined caps (Fisher Scientific).

3.2.1.3 Water Equipment

Unfiltered water samples were collected in amber four-liter bottles with teflon-lined caps using a S7576 AC Interval Sampler (Horizon Ecology Co., Chicago, Illinois) operated on a duty cycle of 7 1/2 minutes every 15 minutes (50%) at a flow rate of about 5 ml/min. Teflon tubing (3 mm id) was used, except for a short section of silicone tubing necessary for proper operation of the peristaltic pump. The pump and collection bottle were housed in a custom-built wooden box for security. A 24 hr sampling period was sufficient to nearly fill the sampling container.

In cases where interval sampling was inappropriate (e.g., mud puddles, lakes, etc.) grab water samples were collected in one-liter wide-mouthed bottles with foil-lined caps (Fisher Scientific).

3.2.1.4 Meteorological

Continuous meteorological measurements (wind run, wind direction, and temperature) were recorded using a MRI Mechanical Weather Station (Meteorological Research, Inc., Altadena, CA). Intermittent humidity and temperature readings were taken using a sling psychrometer (Taylor Instrument Co., Rochester, NY). Wind direction and speed were measured using an anemometer (Edmund Scientific Co., Barrington, NJ) and compass.

3.2.1.5 Chemicals

All solvents used were distilled in glass (Burdick and Jackson, Muskegon, MI) and used without further purification. Where purity was especially critical, solvents were redistilled in glass. Halowax[®] mixtures, Aroclor[®] mixtures, and pesticides were obtained from the Quality Assurance Section, Environmental Toxicology Division, EPA, HERL, Research Triangle Park, NC; individual PCN isomers were obtained from RFR Corp., Hope, RI; silica gel was obtained from Davison Chemical Division, W. R. Grace, Baltimore, MD and d₁₀-anthracene from Merck and Company, Rahway, NJ.

3.2.1.6 Analytical Instrumentation

Analysis of all samples for PCNs was accomplished using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer. Volatile and semi-volatile organics were analyzed using a Varian CH-7 GC/MS with a Varian 620/L computer. Gas chromatography-electron capture detection analyses were performed on a Fisher Victoreen Series 4400 gas chromatograph.

3.2.2 Sample Workup Procedures

3.2.2.1 Perchlorination Methods

Perchlorination has been successfully applied to the analysis of PCBs⁽²⁴⁻²⁶⁾, where all PCB isomers are converted to decachlorobiphenyl for GC/EC detection. The procedure is also reported to work for PCNs.⁽²⁵⁻²⁷⁾ In our laboratory, however, the methodology recommended by Analabs⁽²⁷⁾

using the procedure of Safe *et al.*⁽²⁸⁾ did not prove useful in perchlorination of Halowax[®] mixtures. Using the procedure of Armour⁽²⁵⁾, the reaction was observed to convert Halowax[®] mixtures to octachloronaphthalene ($C_{10}Cl_8$). However, this conversion was neither consistent nor complete with recoveries generally from 10-50%. After expending considerable effort on this technique with no foreseeable positive results, and with approval of the project officer, the perchlorination procedure in combination with GC/ECD was abandoned in favor of GC/MS. Details of the perchlorination efforts and results are included in Appendix B.

3.2.2.2 Extraction of PCNs from Water

Toluene was chosen as the extraction solvent based on PCN solubility studies conducted in this laboratory. The extraction procedure is as follows: In a separatory funnel, shake a 200 ml aliquot of the water sample with 25 ml toluene for five min. Repeat the extraction twice more (total toluene volume = 75 ml) and dry over Na_2SO_4 . Evaporate the solvent just to dryness, reconstitute the sample in 1.0 ml hexane and proceed with column chromatography clean-up. A detailed procedure is listed in Appendix A.

Several extractions of water samples spiked with PCNs were conducted to check recovery (Table 4). Polychlorinated naphthalenes were pipetted into 200 ml tap water in hexane or toluene solution (1.0 ml). After thorough mixing, the extraction was conducted as described previously. The mean extraction efficiency is 0.90 ± 0.19 (see Table 4).

Since it is often found that extraction of organic compounds from water samples is highly pH-dependent, the efficiency of extraction of PCNs from water at different pH values was tested. The results of this experiment are summarized in Table 5. The aqueous phase (2.0 ml) and 0.5 ml toluene containing $C_{10}Cl_8$ at 140 pg/ μ l were shaken together in a vial and equilibrated for four hours at 60°C with occasional shaking. The organic layer was then analyzed directly by GC/ECD. No significant dependence between recovery and pH was observed, indicating the extraction of water samples may be carried out without adjusting the pH. Consistent recovery of greater than 100% is attributed to solvent evaporation during the experiment.

Table 4. RECOVERIES OF POLYCHLORONAPHTHALENES FROM WATER

Sample No.	Spiked Substances	Amount Spiked (μg)	Extraction Solvent	Percent Extracted				Total
				First	Second	Third	Fourth	
K-I	C ₁₀ Cl ₈	0.28	Hexane					80
K-II	C ₁₀ Cl ₈	14	Toluene	60	9	2	2	72
K-III	C ₁₀ Cl ₈	14	Toluene	67.5	6	1	-	75
K-IV	H-1014	11.6	Toluene	117	<5	<2	-	~120
K-V	H-1051	11.1	Toluene	94	11	1	-	106
K-VI	H-1000	4.1	Toluene	71	12	6	-	<u>89</u>
							Mean	90.5
							SD	18.8
							RSD	20.8%

Table 5. EXTRACTION OF HALOWAX 1014 [®] FROM AQUEOUS SOLUTION WITH TOLUENE vs. pH

Aqueous Phase	% Recovery
0.5M NaOH	114
pH = 10.00 buffer	105
pH = 7.00 buffer	106
Distilled water (pH = 6.5)	119
pH = 5.08 buffer	104
3M HCl	123

To determine the efficiency of extracting chloronaphthalenes from natural aqueous media, one gallon of very turbid water was taken from a stream in Durham County, NC about one mile below a municipal waste water treatment plant outfall. To one 200 ml aliquot was added 400 µg of Halowax 1014 [®], to another was added 4.64 µg of Halowax 1014 [®] and 4.44 µg of Halowax 1051 [®]. After storage for 36 hours at 4°C, 86% recovery was observed at the high concentration and 83 and 118% recovery, respectively, at the low concentrations.

3.2.2.3 Extraction of PCNs from Soil

Prior to analysis, individual soil plugs were composited for each soil sampling location by combining one-half of the top 2.5 cm of each plug as illustrated in Figure 9. These semi-circular soil portions were subsequently broken into smaller pieces and pulverized by vigorous shaking. Fifty gram aliquots were removed from these composites for analysis. The soil extraction procedure was adapted from a method reported for pesticides, PCBs and PCNs⁽²⁹⁾, and tested for its applicability to this research project. Local soil samples were spiked with 20.4, 23.2 and 22.2 µg of Halowax 1000, 1014 and 1051 [®], respectively. The extraction of chloronaphthalenes from soil was accomplished using the procedure described in Appendix A with one modification: two parallel extractions were conducted, one using a hexane-acetone mixture and the other a toluene-acetone mixture. Following the

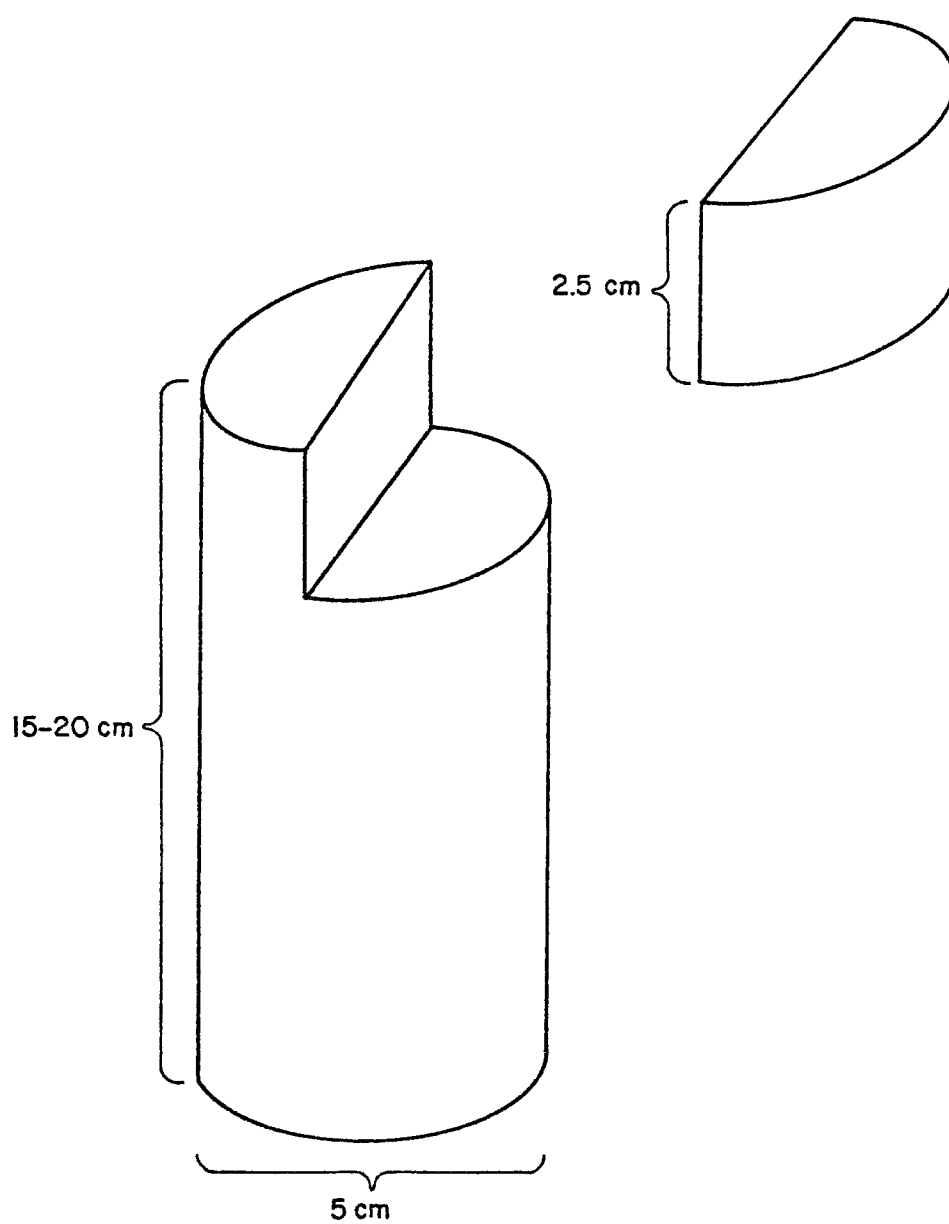


Figure 9. Sectioning of soil plugs.

extraction, quantitation was achieved using GC/ECD by comparison with standards. The results, presented in Table 6, indicate no appreciable difference in extraction efficiency between the two procedures. The toluene-acetone method was chosen for its consistency with methods employed for water and polyurethane foam.

3.2.2.4 Extraction of PCNs from PUF and GFF

Previous research on collection of airborne pesticides and PCBs on PUF used either petroleum ether^(28,29) or 5% ether in hexane⁽¹⁴⁾ to extract the chlorinated hydrocarbons from the foam. Initial efforts using hexane to clean-up the PUF (vide supra) were totally unsatisfactory, prompting further investigation. A test of the solubility of Halowax[®] and Aroclor[®] mixtures in hexane, acetone and toluene revealed by far the greatest solubility in toluene. Halowax[®] and Aroclor[®] mixtures (10 mg) were instantly soluble in 100 μ l of toluene whereas solvation by hexane and acetone was very slow and in some cases incomplete at room temperature.

Previous researchers have used Soxhlet extractors⁽¹²⁻¹⁴⁾ to extract PCBs from PUF. Early experiments in this research indicated that Soxhlet extraction was too time-consuming for the large number of PUF sampling plugs needed and a more efficient manual extraction was developed.

To this end, a pilot study of the extraction of Halowax 1014[®] from a 1 g piece of Olympic 4214[®] PUF was conducted by adsorbing 10 μ g (10 ml of a 1 μ g/ml solution) of Halowax 1014[®] onto a 1 g piece of foam which was pre-cleaned as described above. Solution not retained by the foam was drawn into the pores by compression and expansion of the foam. All solvent was removed by placing the foam, contained in a loosely covered beaker, in a vacuum oven at 40° for one hour. Extraction of the adsorbed Halowax[®] was accomplished with successive 30 ml portions of toluene at room temperature for 10 min. After concentration of the extracts to 10 ml, 1 μ l aliquots were analyzed at 200°C on the 2% OV-101 column using GC/ECD. Quantitation was attained by peak height comparison with a peak at 2.6 min for the Halowax 1014[®] mixture (0.2 mg/ μ l). The first, second and third extracts contained 6.07, 1.48 and 0.4 μ g, respectively, indicating a total recovery of 79.5%. Chromatograms of these extracts appear in Figures 10, 11, and 12, respectively. No losses have been attributed to concentration techniques.

Table 6. EXTRACTION EFFICIENCY OF CHLORINAPHTHALENES FROM SOIL

	Percent Recovery							Average
	$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	
Hexane-Acetone	64	77	-	160	66	86	83	90.6
Toluene-Acetone	84	46	-	115	79	122	105	95.7

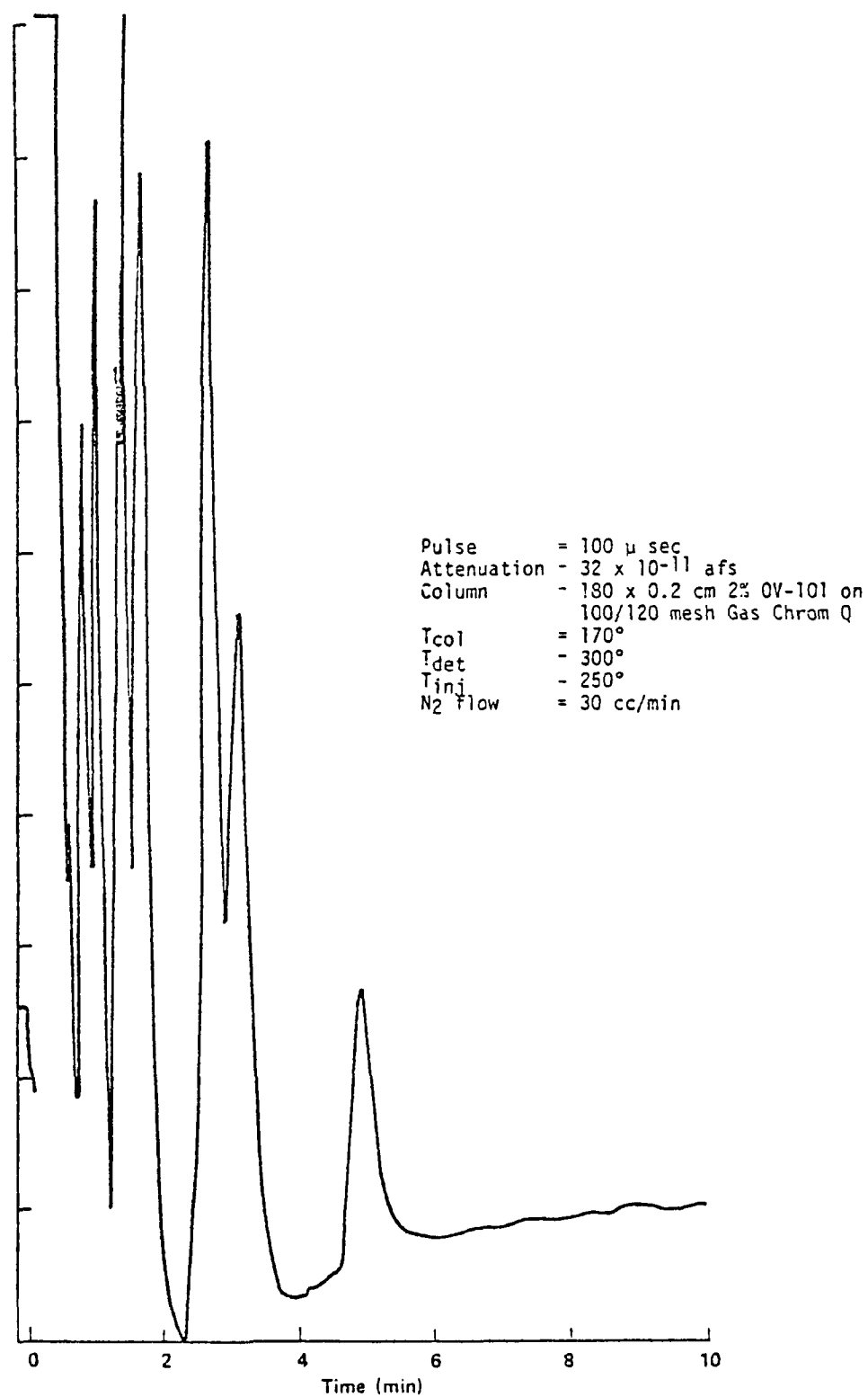


Figure 10. Gas liquid chromatography-electron capture detection (^{63}Ni) first extraction of Halowax 1014 from foam.

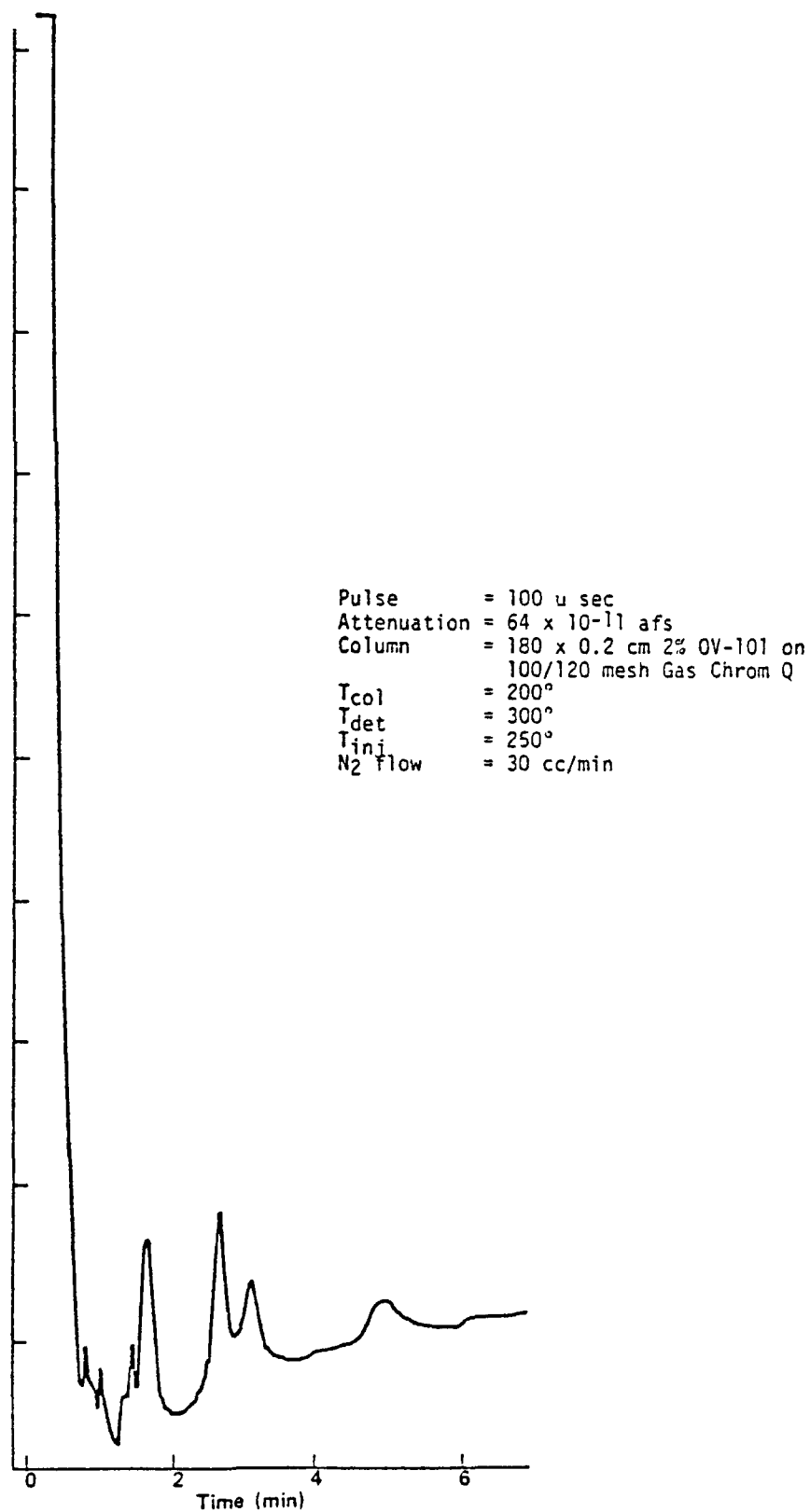


Figure 11. Gas liquid chromatography-electron capture detection (^{63}Ni) - second extraction of Halowax 1014 from foam.

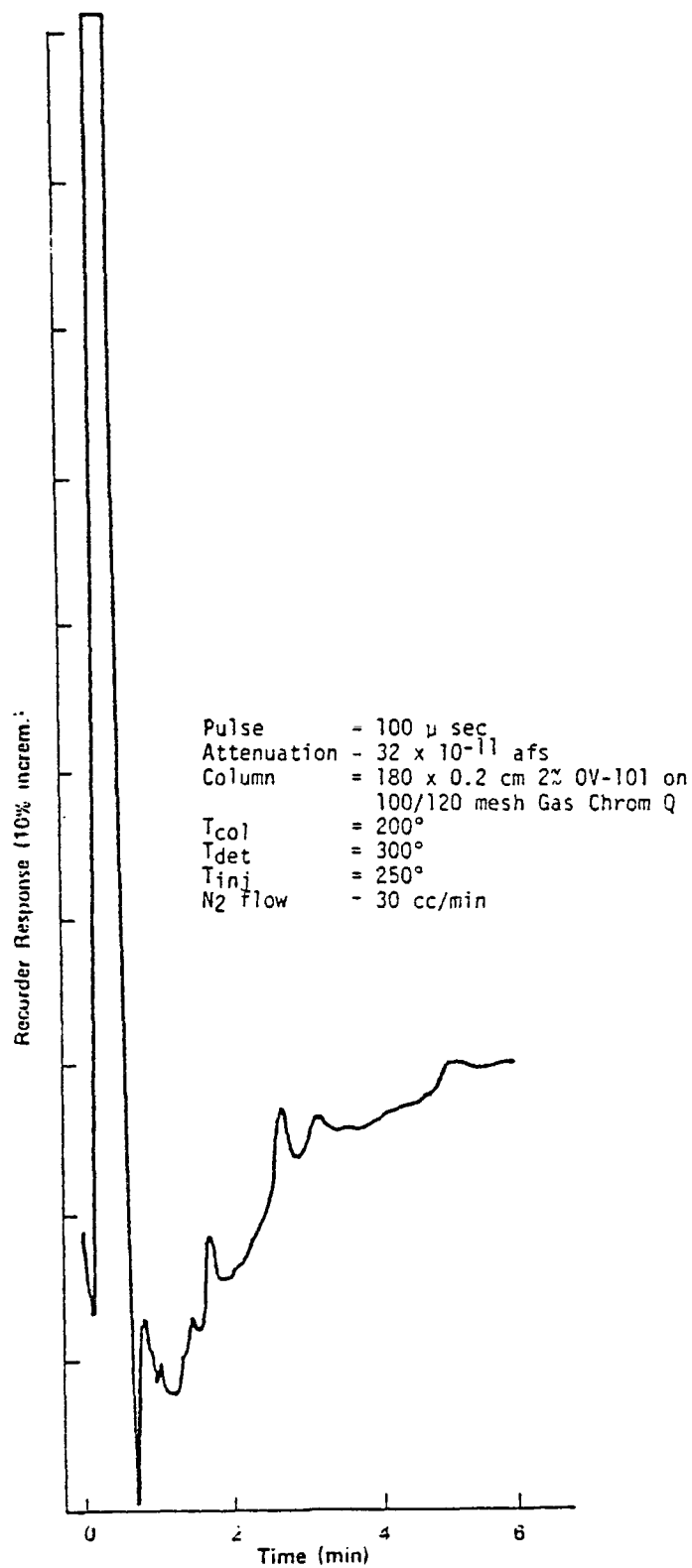


Figure 12. Gas liquid chromatography-electron capture detection (^{63}Ni) - third extraction of Halowax 1014 from foam.

Extending this evaluation to standard size plugs, the recovery of a 1.0 µg sample of Halowax 1014[®] applied to Olympic 2315[®] was found to be 100% when extracted four times for five min with 200 ml toluene. The sample was applied to the foam in toluene and the solvent removed in vacuo. It should be noted that all of the Halowax 1014[®] was removed in the first two extractions.

Another factor which may influence PCN recovery is the penetration of PCNs into the foam. The latter was evaluated by injecting Halowax 1014[®] into the center of a plug with a glass syringe. After drying in vacuo, 225 µg (97%) of the Halowax 1014[®] was recovered.

As used for the extraction of field samples, the PUF extraction procedure not only quantitatively recovered PCNs, but was quick, and required a minimum of glassware. To assure complete recovery of PCNs collected in the field, the GFF was analyzed in a manner similar to that for PUFs.

3.2.2.5 Column Chromatography

The column chromatography procedure used for cleaning up PCN extracts from foam plugs, water samples, and soil samples was adapted from that described previously.⁽²⁹⁾ The procedure is described in detail in Appendix A.

The results of several trials, summarized in Table 7, show that the column clean-up procedure easily removed most pesticides and polyurethane foam background without loss of PCNs. In addition to analysis of individual fractions by GC/ECD, the total hexane fractions were combined and analyzed to provide additional recovery data. The wide variance in results obtained from GC/ECD is due mostly to errors in the sample injection volumes. This column clean-up procedure removes all recognized potential interferents tested (see footnote "c", Table 7) except aldrin and PCBs.

3.2.2.6 Volatile Organics from Aqueous Samples (VOA)

A few water samples suspected of containing appreciable quantities of volatile organic materials were analyzed according to the modified VOA procedure outlined below.⁽³⁰⁻³²⁾ The volatiles were purged from the sample and adsorbed on Tenax GC. The Tenax was then analyzed by GC/MS/COMP using a Varian CH-7 interfaced with a high resolution glass capillary GC column.

Table 7. SUMMARY OF COLUMN CHROMATOGRAPHY CLEAN-UP EXPERIMENTS

Sample Number	Substance Chromatographed	Amount (μg)	Hexane Fraction	Volume (ml)	Analysis (μg)	Percent Recovery	Toluene Fraction	Volume (ml)	Analysis (μg)
KVII	C ₁₀ Cl ₈	28	1	17	22.3				
			2	22	3.2				
			3	10	0.1				
			4	<u>5</u>	<u>0.06</u>				
			Total	54	26.2	94			
			Combined	54	36.5	130			
KVIII	H-1014	23.2	1	5	0				
			2	13	7.9				
			3	10	7.9				
			4	10	1.2				
			5	10	0.1				
			6	<u>10</u>	<u>0</u>				
			Total	58	17.2	74			
			Combined		32.7	141			
KIX	H-1014 Concentrated Foam Extract	23.2	1	20	15.0				
			2	11	4.7				
			3	12	0.6				
			4	<u>12</u>	<u>0</u>				
			Total	55	20.2	87			
			Combined	55	24.8	107			
			Combined	55	17.3	75			
							1	10	a
							2	10	b

Table 7. (cont'd)

Sample Number	Substance Chromatographed	Amount (μg)	Hexane Fraction	Volume (ml)	Analysis (mg)	Percent Recovery	Toluene Fraction	Volume (ml)	Analysis (μg)
KX	H-1014	23.2	1	14	11.5				
			2	10.5	9.2				
			3	11	0.9				
			4	10.5	~0.3				
			5	<u>12</u>	<u>0</u>				
			Total	58	21.9	94			
			Combined	57	21.0	91			
KXI	Pesticide ^c Mixture	0.1-0.2 of each	1	10	0				
			2	10	0				
			3	10	54 ^d				
			4	10	42				
			5	<u>10</u>	<u>6</u>				
			Total	50	102	103	1	6.2	e
							2	11.9	f
							3	10.5	g
							4	5.6	o
KXII	H-1014 Pesticide Mixture	4.6 1-2	1	10.0	0				
			2	9.8	4.0 ^h				
			3	9.9	0.2 ^h				
			4	10.6	--- ⁱ				
			5	<u>10.7</u>	--- ⁱ				
			Total	51.0	4.2	91			
							1	10	j
							2	10	k
							3	10	l

Table 7. (cont'd)

NOTES

- ^aPeak at RRT = 0.95 from foam extract is eluting
- ^bIn addition to peak at RRT = 0.95, peak at 0.80 is observed. These two compounds are the most noticeable features of the foam extract.
- ^cPesticide Mixture Lindane (0.07 µg), heptachlor (0.11 µg), aldrin (0.10 µg), p,p'-DDD (0.20 µg), and p,p'-DDT (0.25 µg).
- ^dAldrin is only pesticide eluted with hexane.
- ^eSmall amount of heptachlor.
- ^fAll pesticides except aldrin.
- ^gSome dieldrin detected.
- ^hAldrin off scale, halowax present as measured.
- ⁱAldrin on scale, small amount of heptachlor.
- ^jAll pesticides except aldrin. Dieldrin concentration low.
- ^kDieldrin predominates. Some traces of other pesticides.
- ^lVery small amount of dieldrin.

In order to avoid contamination, all glassware used in the purging apparatus was washed and heated to 400°C in a glassware oven, with the exception of the fritted glass bubblers and the thermometers. Both were soaked in dilute HNO₃, then the thermometer rinsed well with distilled water and distilled water pulled through the bubblers. Clean Tenax GC cartridges (10 cm x 1.5 cm i.d.) were desorbed at 270°C for 20-30 min under a stream of helium to remove contaminants, then cooled to room temperature in a capped glass tube.

The sample (250 ml) was placed in a 250 ml round bottom, three-necked flask. The necks were occupied by a thermometer, a fritted glass bubbler and a condensor containing a small plug of oven-treated glass wool (see Figure 13). With the flow rate adjusted to 25 ml/min, the samples were purged at 40-45°C for 1.75 hour, including the time spent coming up to temperature. Loaded cartridges were stored in a freezer awaiting analysis by GC/MS.

This method has been validated by radioisotope recovery methods for a number of organic compounds including acetone, acetonitrile, benzene, toluene, phenol and dimethylbenzanthracene.⁽³²⁾

3.2.3 Instrumental Analysis and Data Reduction

3.2.3.1 GC/MS of PCNs

Analysis of all samples for PCNs was accomplished using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer. The 180 cm x 2 mm i.d. glass column, packed with 2% OV-101 on Chromosorb W was held at a temperature of 150° for three minutes, programmed to 230° at 8°/min and held isothermally until all peaks had eluted. The individual chloronaphthalenes were well resolved and the last peak (C₁₀Cl₈) eluted in approximately 18 min as illustrated in Figure 14. The flow rate was 30 cc/min, helium. The ionization voltage was nominally 70 eV and detector voltages were between 1.8 and 2.2 kV. Full scan spectra were obtained from m/e 110-500 and MID ions were set at the nominal masses discussed below. Exact mass settings were made using a standard PCN mixture which also served as an instrument check and as a cross-check on retention times.

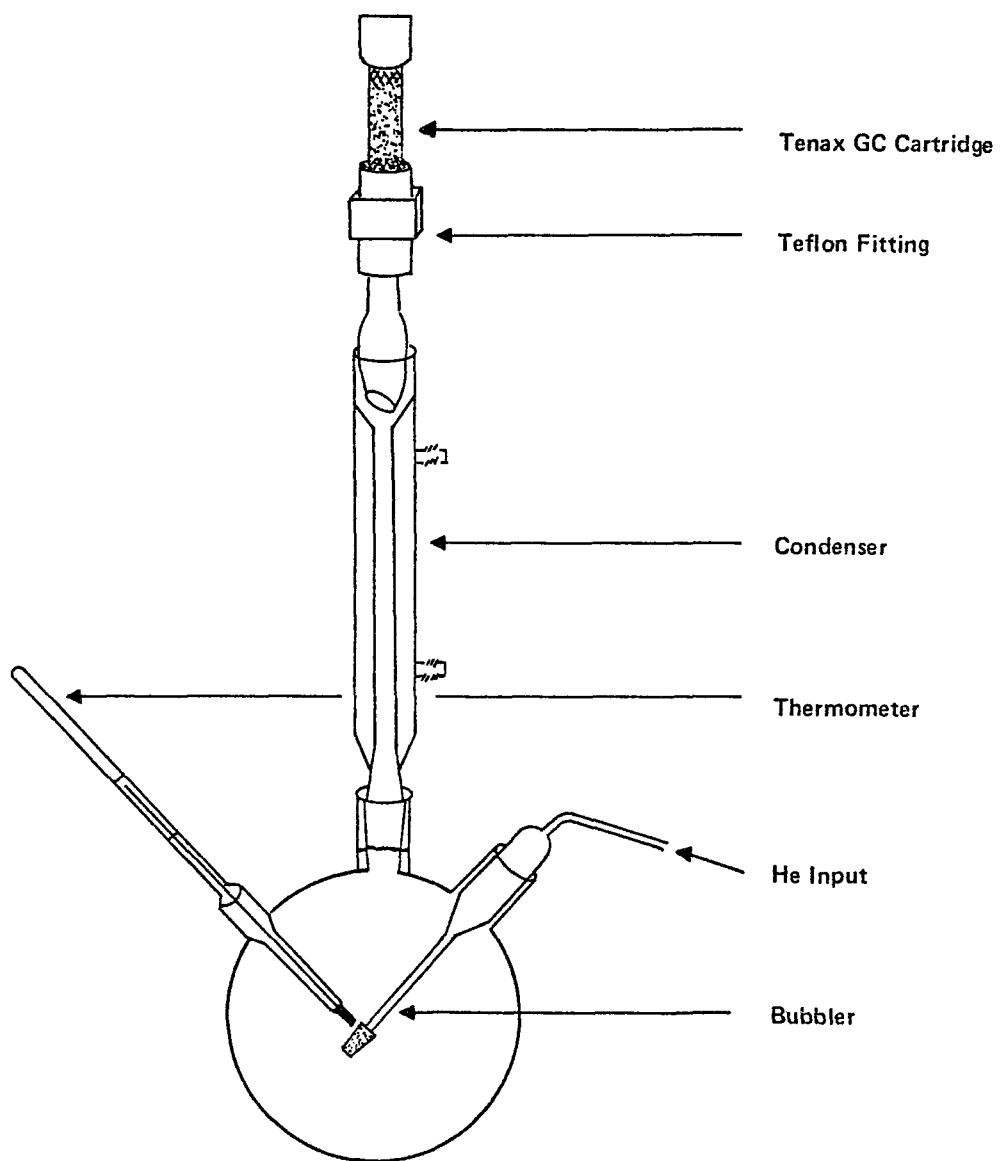
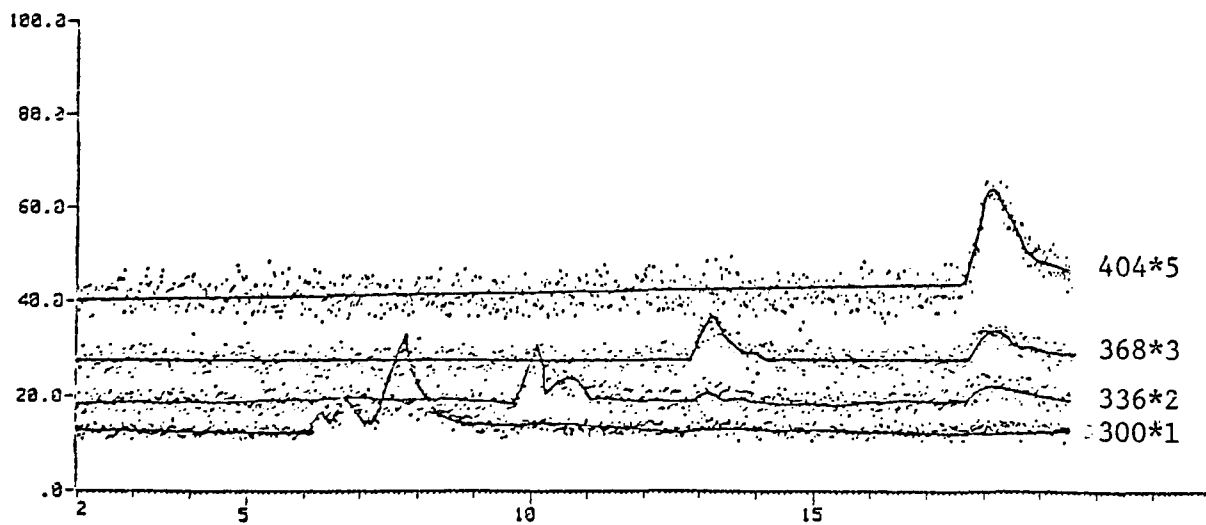
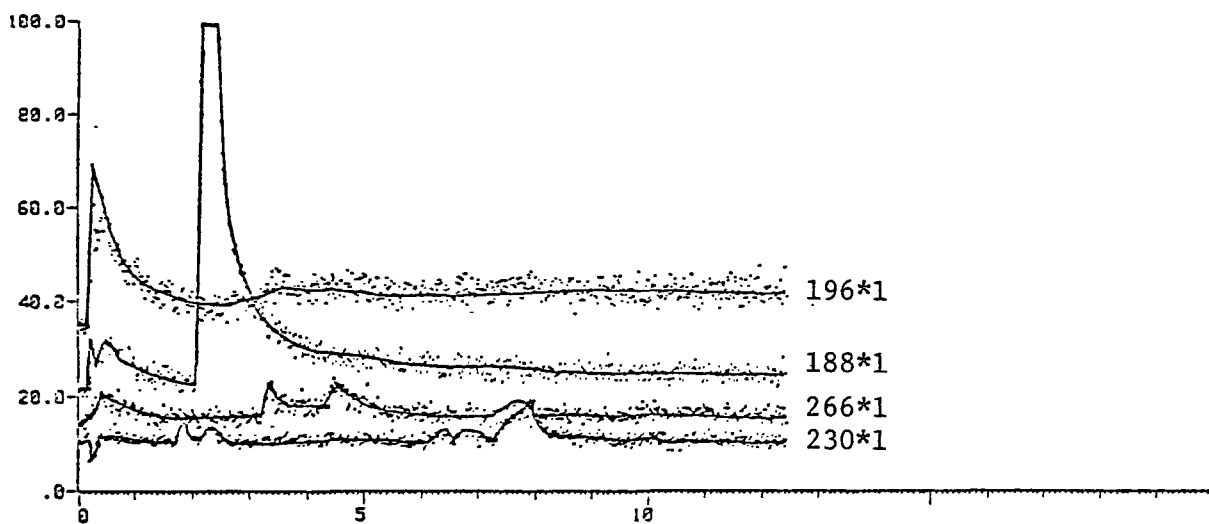


Figure 13. Apparatus for VOA purge.



FILE E1 NO. 5
MIX.2:0V101.170*5M.4*/M.-9.2.2KV.4NG/MCL.0CT26

Figure 14.. GC/MS of a Halowax 1014[®], Halowax 1051[®]
and d₁₀-anthracene mixture illustrating
temperature programming.

Analysis of PCNs by GC/MS provides positive identification of PCN isomers and allows analysis even in samples where interferences (such as PCBs) are present in much greater concentration. Gas chromatography/mass spectrometry represents state-of-the-art analytical methodology and is clearly the method of choice in terms of specificity and information content.

Samples were analyzed using the multiple ion detection mode to provide maximum sensitivity. The results were, in many cases, confirmed by measuring the chlorine isotope ratios by MID using different ions or (if the concentration was sufficient) by full scan mass spectrometric measurement. The details of the analytical method are discussed below and in Appendix A.

Multiple Ion Detection--Multiple ion detection is an operational mode for a quadrupole gas chromatograph/mass spectrometer where up to nine m/e values are monitored through the chromatogram. Preset voltages for each m/e value are step-jumped at short time intervals. Since this technique allows integration of ion intensity for a longer time period for the desired ions than in the customary full-scan mode, the sensitivity of the instrument is increased by approximately two orders of magnitude. By judicious selection of m/e values to be monitored, interference by unwanted compounds can usually be minimized.

Eight ions were selected for monitoring: one from the parent cluster for each of the eight chlorinated naphthalenes ($C_{10}H_7Cl-C_{10}Cl_8$). Although the parent ions were not necessarily the most intense, the probability of interference by PCN fragment ion or other contaminants was reduced. Ions were chosen from the M (parent), M + 2, or M + 4 m/e values (Table 8) according to an optimum combination of greatest intensity and least interference from PCBs and other PCNs. The ions selected are listed in Table 8. As expected, the MID scans of the Halowax[®] mixtures (ca. 4 ng) in Figures C-1-C-14 of Appendix C closely matched the total ion current (TIC) plots from normal GC/MS runs. Gas chromatography/mass spectrometry using MID is clearly sensitive to 4 ng of Halowax[®] mixture. This sensitivity is compared with the 200 ng amounts needed for good quality full scan spectra.

Interferences--MID scans of Aroclor[®] mixtures (ca. 20.0 ng) were obtained using the m/e values selected for PCN quantitation (Figures C-15-C-37

Table 8. POLYCHLORONAPHTHALENES PARENT ION AND MID ION (m/e) VALUES.

	M	M + 2	M + 4	MID Ion	"Double" MID	Theoretical Response Ratio
$C_{10}H_7Cl$	162	164	166	164	162, 164	100/33
$C_{10}H_6Cl_2$	196	198	200	196	196, 198	100/65
$C_{10}H_5Cl_3$	230	232	234	230	230, 232	100/98
$C_{10}H_4Cl_4$	264	266	268	266	264, 266	100/131
$C_{10}H_3Cl_5$	298	300	302	300	298, 302	100/106
$C_{10}H_2Cl_6$	332	334	336	336	332, 336	100/161
$C_{10}HCl_7$	366	368	370	368	366, 370	100/224
$C_{10}Cl_8$	400	402	404	404	400, 404	100/298

of Appendix C) to test the analytical specificity. For the most part, the PCBs are not detected, even at a 50-fold greater concentration than the PCNs, although several PCB peaks were observed in the 164 and 196 channels which represent fragments of higher molecular weight molecules. This represents a potential interferent in PCN detection, however comparison of retention times indicates the peaks are not at retention times for all isomers of mono- and dichloronaphthalenes.

Using the MID ions for PCNs, a mixture of chlorinated pesticides (lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, p,p'-DDD, and p,p'-DDT; 6-25 ng each) was analyzed and gave several early-eluting peaks which might interfere with PCN analysis (Figures 15-17). Since all of these compounds, except aldrin are removed by the silica gel column cleanup, the potential for interference is eliminated. Aldrin may present difficulties as it elutes early in the gas chromatogram and gives a sharp peak in most MID channels (Figure 17). This potential interferent in the analysis of field samples was noted, but not detected.

External Standard--An external standard, d₁₀-anthracene, was added to standard mixtures and samples for retention time correlation and quantitation. The d₁₀-anthracene was monitored in the MID mode at m/e 188, its parent ion. This compound eluted relatively early in the chromatogram and presented no potential interference. The results of an analysis of a mixture of Halowax-1014[®], Halowax-1051[®] and d₁₀-anthracene (Figure 14) illustrates this utility.

MID Response Linearity and Detection Limit--A mixture of 2-chloronaphthalene, Halowax 1014[®], octachloronaphthalene, and d₁₀-anthracene was prepared at several different concentrations and the MID responses measured. The response of each PCN isomer was calculated relative to that of the d₁₀-anthracene to normalize injection volume and instrumental variations. The results for the selected isomers C₁₀H₇Cl (m/e = 164), C₁₀H₅Cl₃ (m/e = 230), C₁₀H₂Cl₆ (m/e = 300), and C₁₀Cl₈ (m/e = 404) are plotted vs. concentration in Figure 18. Linear regression analysis (Table 9) indicates that, within experimental error, instrumental response is linear from <1 ng to at least 500 ng, which approaches the solubility limit of PCNs in hexane. The detection limit has not been specifically evaluated, but <50 pg of an

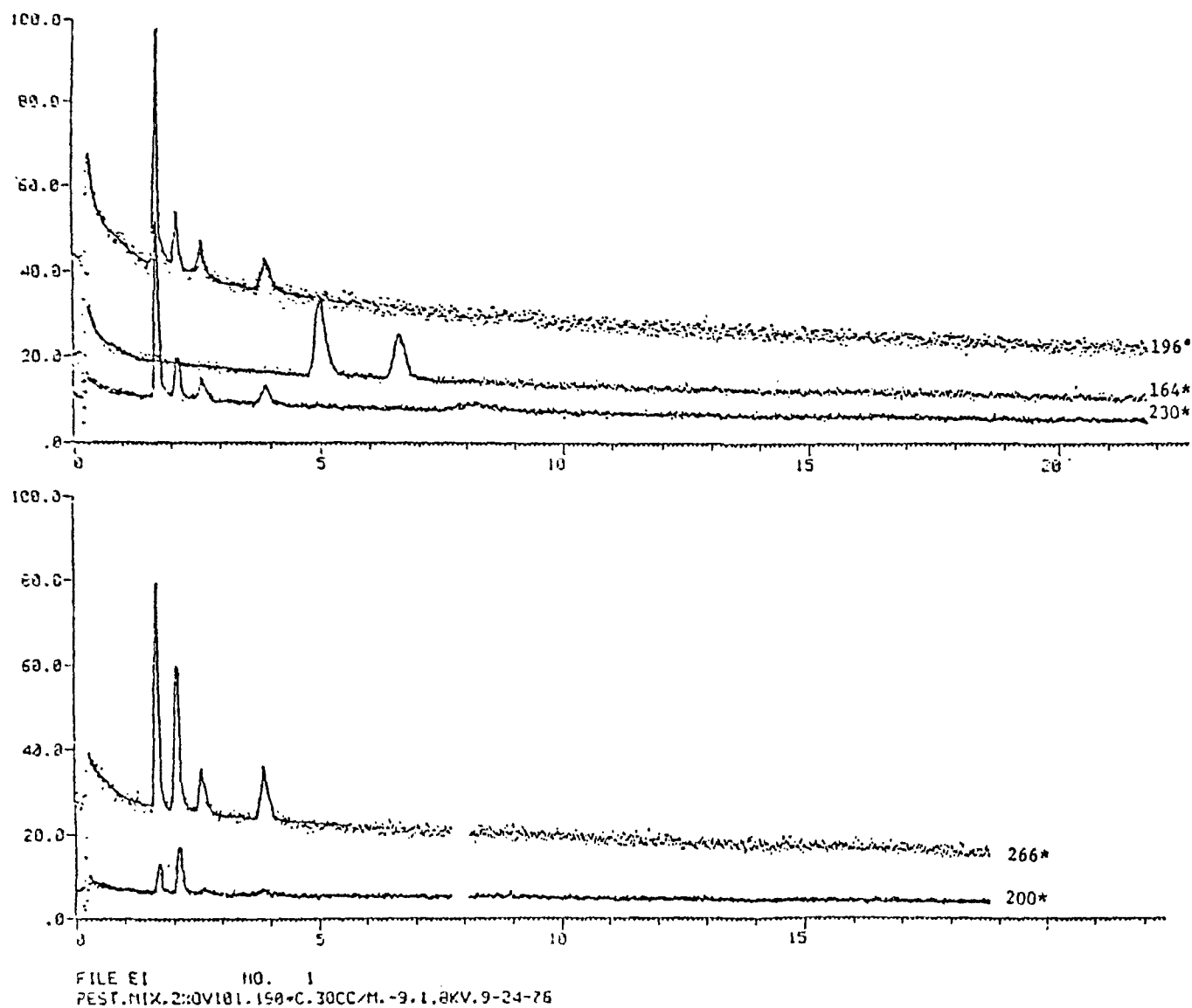


Figure 15. GC/MS analysis of a pesticide mixture using multiple ion detection with PCN ions.

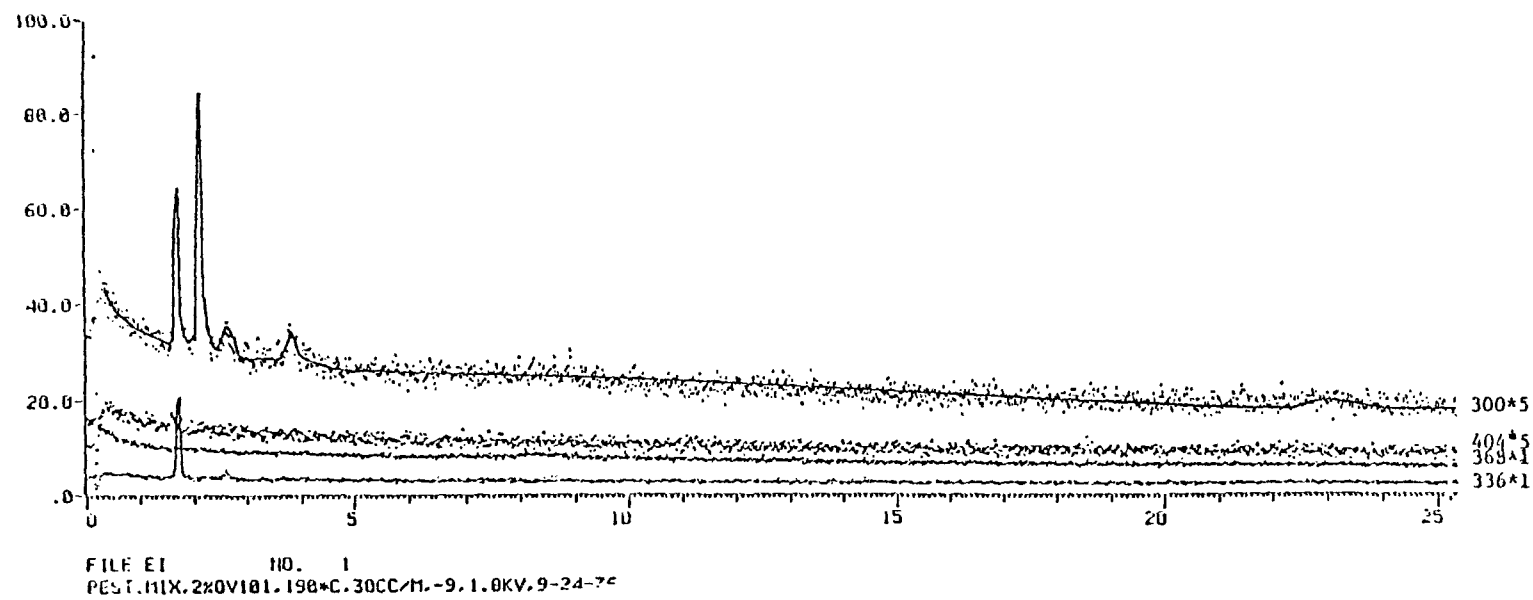
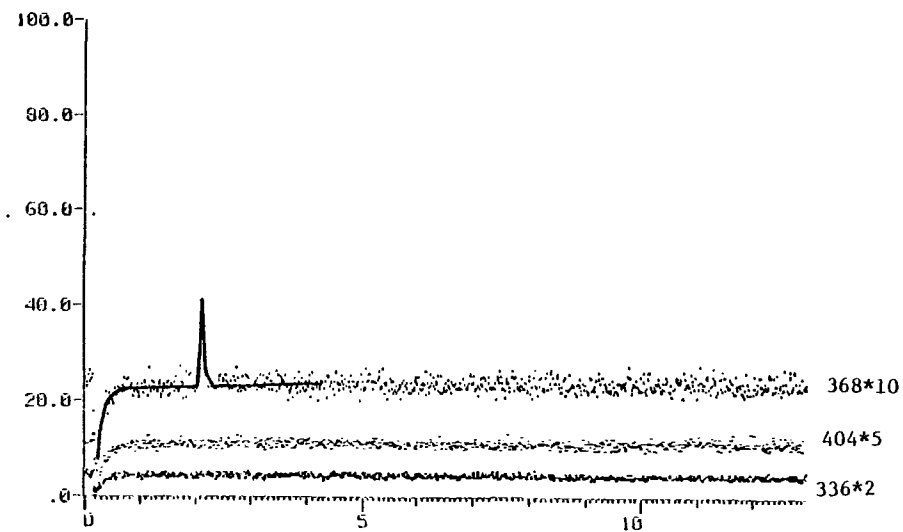
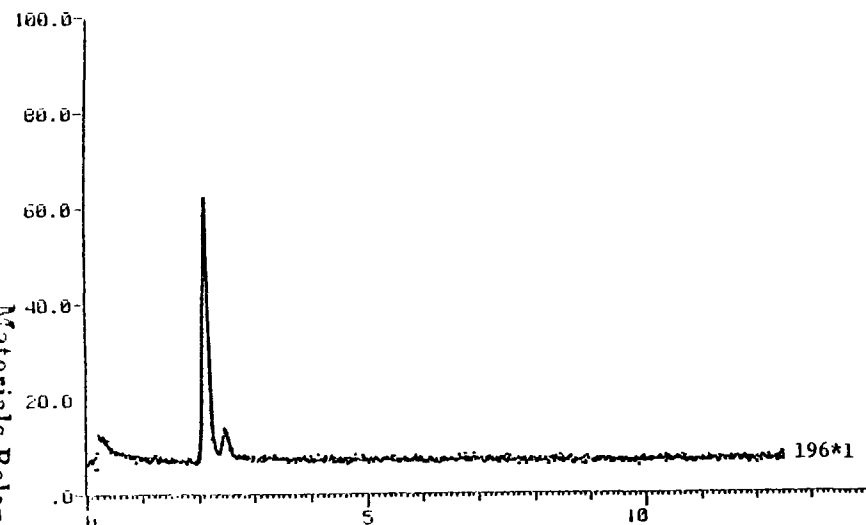
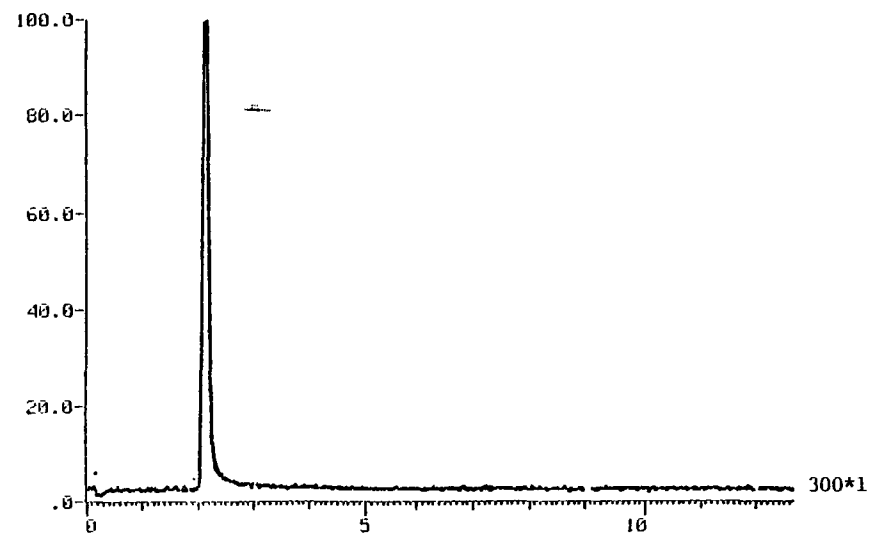
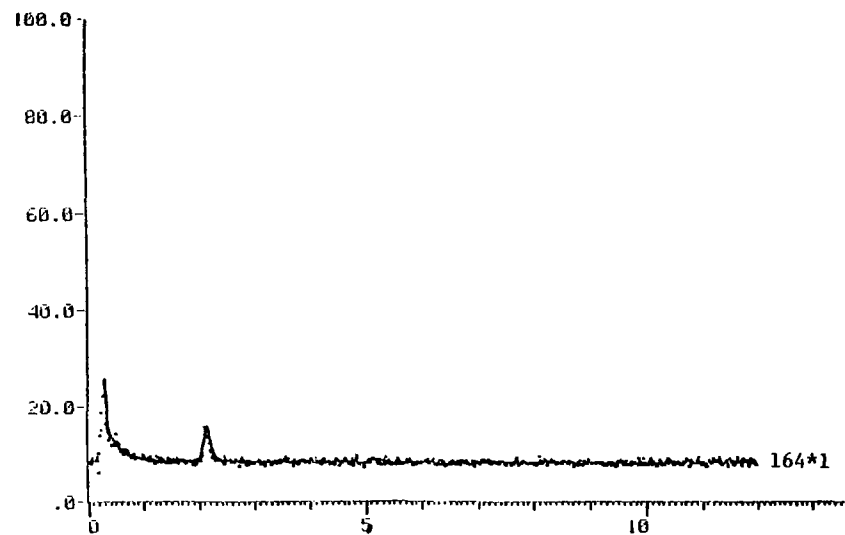


Figure 16. GC/MS analysis of a pesticide mixture using multiple ion detection with PCN ions.



FILE E1 NO. 1
ALDRIN: 20/101, 1904C, 300C/H, -9, 1.8KV, 10-06-76

FILE E1 NO. 1
ALDRIN: 20/101, 1904C, 300C/H, -9, 1.8KV, 10-06-76

Figure 17. GC/MS of Aldrin using multiple ion detection for polychloronaphthalene detection.

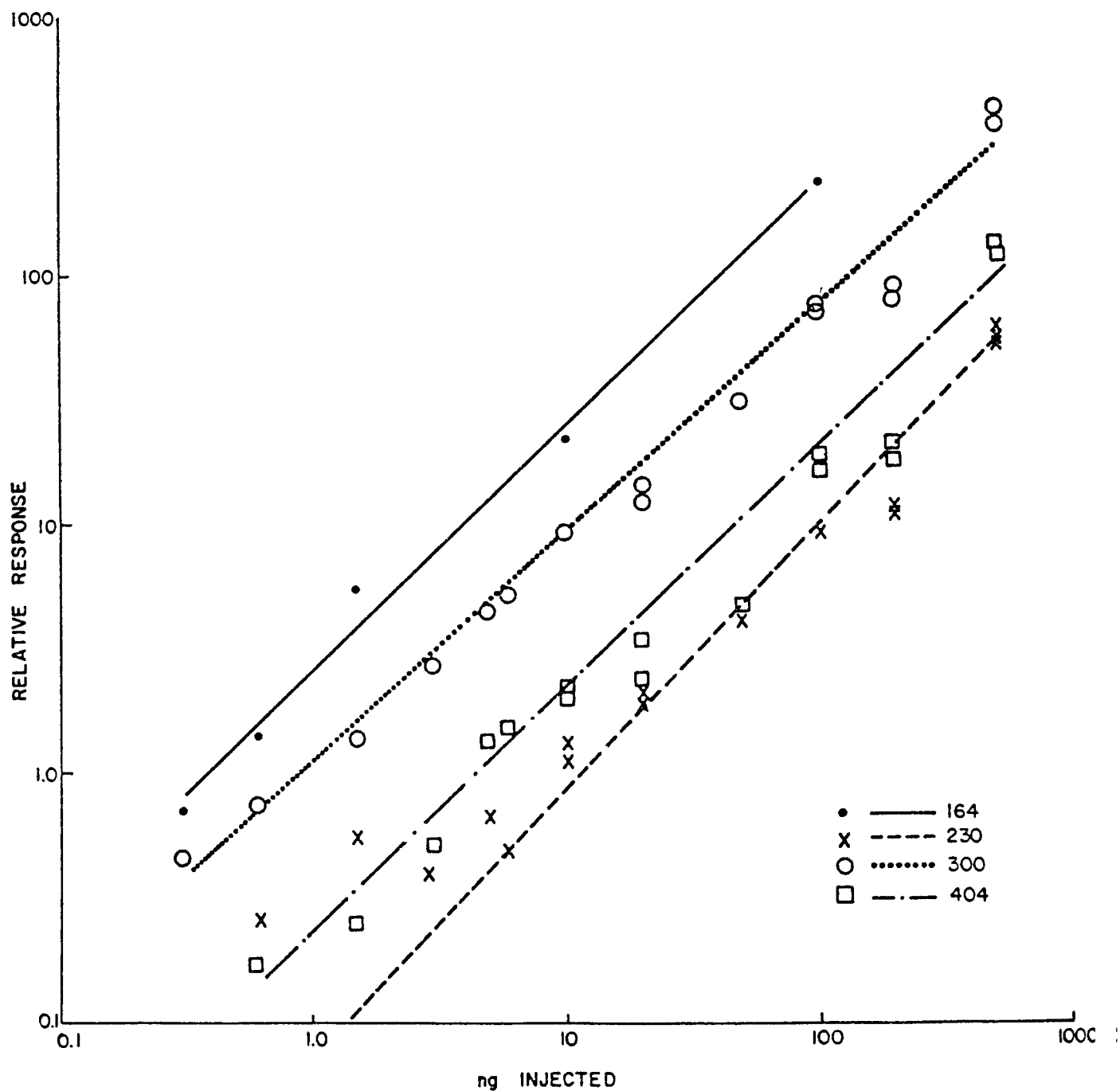


Figure 18. Gas chromatograph-mass spectrometric-multiple ion detection response relative to d_{10} -anthracene as a function of concentration for selected ions.

individual PCN has been reproducibly detected. This translates into an ultimate sample concentration of about 0.3 ng/m^3 for air (based on 90 m^3 sample), $0.2 \text{ } \mu\text{g/l}$ for water (based on 200 ml aliquot) and $0.5 \text{ } \mu\text{g/kg}$ for soil (based on 50 g aliquot).

Table 9. LINEAR REGRESSION RESULTS OF MID LINEARITY STUDY
FOR POLYCHLORONAPHTHALENES

Isomer	$\text{C}_{10}\text{H}_7\text{Cl}$	$\text{C}_{10}\text{H}_5\text{Cl}_3$	$\text{C}_{10}\text{H}_2\text{Cl}_6$	C_{10}Cl_8
m/e	164	230	300	404
Linearity	1.00	0.982	0.982	0.977
Slope	2.18	0.10	0.78	0.23
Y-intercept	0.365	-0.18	-8.85	-4.29
n	5	17	17	17

n = number of points in calculation

Determination of Relative Molar Response--The calculation of relative molar response (RMR) for the quantitation of sample components precludes the need for a calibration curve. The RMR is calculated as the integrated peak area of a known amount of the compound, A_{unk}° , with respect to the integrated peak area of a known amount of standard, A_{std}° (in this case d_{10} -anthracene), according to the equation

$$\text{RMR} = \frac{A_{\text{unk}}^\circ / \text{moles}_{\text{unk}}}{A_{\text{std}}^\circ / \text{moles}_{\text{std}}} = \frac{(A_{\text{unk}}^\circ) (\text{mw}_{\text{unk}}) (g_{\text{std}})}{(A_{\text{std}}^\circ) (\text{mw}_{\text{std}}) (g_{\text{unk}})} \quad (\text{Equation 1})$$

From this calculated value, the concentration of an identified compound in a sample is calculated by rearranging Equation 1 to give

$$g_{\text{unk}} = \frac{(A_{\text{unk}}^\circ) (\text{mw}_{\text{unk}}) (g_{\text{std}})}{(A_{\text{std}}^\circ) (\text{mw}_{\text{std}}) (\text{RMR})} \quad (\text{Equation 2})$$

The use of RMR for quantitation in GC/MS has proven successful in repeated application to similar research problems.⁽²¹⁾

The RMRs for the available PCN isomers were calculated from the numerical integrations of peaks observed in the appropriate MID channel. The RMRs listed in Table 10 are mean values of four injections of each of two concentrations (~ 1 ng and ~ 60 ng). The similarity of the values obtained at both concentrations is further indication of linear response and implies that the RMR values are valid at least over this range of concentrations. Since standards for isomers of $C_{10}H_3Cl_5$, $C_{10}H_2Cl_6$, $C_{10}HCl_7$ were not available, the RMR for each of these compounds was arbitrarily set at 0.75, the mean value for the five PCN isomers determined.

The randomness of the RMR with extent of chlorination is surprising, considering the change in ionization cross-section expected by systematically replacing hydrogens with chlorines. In addition, the small differences among the values (differing by no more than a factor of 3) is in marked contrast to ECD or FID detectors. For example, the sensitivity of ECD to decachlorobiphenyl is about 10^3 greater than the sensitivity to monochlorobiphenyl.⁽²⁸⁾

"Double" MID Confirmation--The identification of PCNs in samples was confirmed by "double" MID GC/MS analysis, wherein two ions of the parent cluster for each isomer were monitored (Table 8). The intensity ratio should agree with the isotopic abundance (Table 8). If the intensity ratio was incorrect (outside a 10-20% error margin), the results were assumed to be spurious and were entered in the final data tabulations as "not detected".

Full Scan Confirmation--In many cases, the PCN concentration found by MID analysis was sufficient to enable confirmation using the full scan mode of the mass spectrometer. This not only provided the needed confirmation, but also permitted identification of other components in the sample.

Volatile and Semi-volatile Organics Collected on Tenax--Tenax GC cartridges containing organic compounds were analyzed by GC/MS/COMP using a Varian CH-7 GC/MS with a Varian 620/L computer. Chromatographic separations were accomplished on a 0.35 mm i.d. x 100 m glass SCOT capillary column coated with OV-101 stationary phase and prepared in this laboratory. Using a custom-designed inlet-manifold⁽¹⁸⁻²¹⁾ the cartridges were thermally desorbed with the volatile components trapped in a liquid nitrogen-cooled nickel capillary and subsequently volatilized and injected into the

Table 10. RELATIVE MOLAR RESPONSES FOR POLYCHLORONAPHTHALENE ISOMERS

Low Concentration ^a Isomers	Amount (ng)	RMR ^b	SD ^c	RSD ^d
2-Chloronaphthalene	1.39	0.502	0.063	0.122
1,2-Dichloronaphthalene	1.06	0.937	0.068	0.072
1,2,3-Trichloronaphthalene	1.25	0.658	0.087	0.132
1,2,3,4-Tetrachloronaphthalene	1.10	1.024	0.088	0.086
Octachloronaphthalene	1.26	0.321	0.240	0.771
High Concentration ^a Isomers	Amount (ng)	RMR ^b	SD	RSD
2-Chloronaphthalene	69.6	0.439	0.046	0.106
1,2-Dichloronaphthalene	52.8	1.172	0.076	0.064
1,2,3-Trichloronaphthalene	62.4	0.805	0.037	0.046
1,2,3,4-Tetrachloronaphthalene	54.9	1.328	0.042	0.032
Octachloronaphthalene	60.0	0.330	0.026	0.077
Total ^e	Amount (ng)	RMR	SD	RSD
2-Chloronaphthalene		0.470	0.06	0.130
1,2-Dichloronaphthalene		1.054	0.14	0.135
1,2,3-Trichloronaphthalene		0.732	0.10	0.137
1,2,3,4-Tetrachloronaphthalene		1.176	0.17	0.147
Octachloronaphthalene		<u>0.326</u>	<u>0.14</u>	<u>0.442</u>
MEAN		0.752	0.36	0.484

^aFour injections

^bRelative Molar Response Standard = d₁₀-anthracene - 0.828 ng (0.276 ng/μl)

^cStandard Deviation

^dRelative Standard Deviation = SD/RMR

^eEight Injections

Varian 1700 gas chromatograph. Complete details of the system and its operation are included in Appendix A.

Data Handling and Interpretation--The data output of the GC/MS was screened at several levels and logged. After calculation, the results were recorded on summary sheets for each site. At that point, the results were evaluated and a decision made regarding the need for repeat analysis, confirmation by "double" MID, or confirmation by full scan analysis. The details of the data handling and interpretation are discussed below.

Data Output Format--The GC/MS/COMP system produced numerical data printout as illustrated in Table 11 for a representative sample. This is the raw data for a soil sample collected near Koppers Chemical and Coatings Plant, P2/C4/L11. The identification line contains the sample identification, GC oven temperature, programming conditions, attenuation, detector voltage, injection volume, and date of analysis. The nominal mass is printed in the first column; the precise mass of each channel (to five significant figures) is set daily to compensate for instrumental fluctuations. The peak intensity, retention time (MIN), integrated AREA, number of data points in the integration (PNTS), and background (BKGND) are printed in successive columns.

Table 11. GC/MS/COMP NUMERICAL DATA PRINTOUT

R23GABVLKOP-1-10, 150* 3M8*/M, -9, 1.8 kV, 1 MCL, J28					
MASS	PEAK	MIN	AREA	PNTS	BKNGD
164	40.98	0.916	258.86	42	28.84
196	52.80	1.882	646.10	84	11.72
230	47.62	3.799	916.46	103	05.54
188	02.68	4.599	54.20	65	13.64
266	26.10	7.116	1115.76	159	03.46
300	16.42	9.249	448.82	149	02.14
336	02.00	10.816	53.00	120	01.66
368	00.38	12.832	07.96	49	01.60
404	00.06	15.183	01.78	51	01.60

Calculation of Concentrations--Using the integrated peak area (numerical printout) for the RMR for each isomer (Table 10), concentrations of PCNs were calculated. The amount of trichloronaphthalene ($m/e = 230$) in a sample, for example, was calculated using the data in Tables 10 and 11 and Equation 2.

$$g_{\text{unk}} = \frac{(A_{\text{unk}})(mw_{\text{unk}})(g_{\text{std}})}{(A_{\text{std}})(mw_{\text{std}})(\text{RMR})} \quad (\text{Equation 2})$$

In this example,

$$\begin{aligned} A_{\text{unk}} &= 916.46 \\ A_{\text{std}} &= 54.20 \\ mw_{\text{unk}} &= 230 \\ mw_{\text{std}} &= 188 \\ g_{\text{std}} &= 0.276 \text{ ng}/\mu\text{l} \\ \text{and, RMR} &= 0.732. \end{aligned}$$

By substitution,

$$g_{\text{unk}} = \frac{(916.46)(230)(0.276 \times 10^{-9})}{(54.20)(188)(0.732)} = 7.80 \text{ ng}/\mu\text{l}.$$

The concentration in the actual sample was calculated from the volume of the extract, the recovery efficiency and from the volume of the sample or aliquot. For air samples, the volume of air sampled is listed for each sample in the sampling protocol for each location. For soil samples, a 50 g aliquot of the composited soil was analyzed; while for water samples a 200 ml aliquot was analyzed. For the sample cited above, the volume of the extract was 2.0 ml, so the total amount of trichloronaphthalene is 15,600 ng; dividing by 50 g soil extracted gives an original soil concentration of 310 ng/g or 310 $\mu\text{g}/\text{kg}$.

Assessment of Results--The calculated results were entered onto the appropriate summary sheet for that site. The results were also assessed for the need for confirmation by "double" MID or full scan GC/MS. Results which did not fit the prevailing isomeric distribution pattern, were unusually high or low, or were otherwise anomolous or interesting were subjected to confirmation.

3.2.3.2 GC/ECD of PCNs

Analysis using GC/ECD, limited to method development aspects of the project, involved a Fisher Victoreen Series 4400 gas chromatograph using a 180 cm x 2 mm i.d. glass column packed with 2% OV-101 on 100/120 mesh Gas Chrom Q at either 170° or 200° with a nitrogen flow rate of 30 ml/min. The

3.3 QUALITY CONTROL

To assure the validity of the results, careful quality control procedures were maintained throughout the project. These included validation and testing of all methods prior to use; logging of sampling protocol sheets, sample analysis progress, and GC/MS analytical results in multiple locations; analysis of blanks and controls; instrumentation control and error propagation. These procedures assured the quality (accuracy, precision, completeness, and representativeness) of the data with two exceptions: (1) poor recoveries were noted for PUF control samples stored with field samples. The percent recovery found was used as a correction factor to the air samples; (2) the collection efficiency of monochloronaphthalene (and to a lesser extent dichloronaphthalene) on PUF was found to be poor, so all values for monochloronaphthalene should be regarded as minima.

3.3.1 Method Validation

As previously discussed the analytical methods including GC/MS analysis, extraction of polyurethane foam plugs, soil, and water, column chromatography, and volatile organic purges were all validated and tested before use.

The sampling methodology, as discussed in a preceeding section was validated through a series of tests to check collection efficiency of the air and water samples. Under the sampling conditions used, the air samplers collected PCNs efficiently, except for mono- and dichloronaphthalenes which were only partially collected. The water sampling procedure was found to collect PCNs with no losses.

3.3.2 Controls and Blanks

Through the use of controls and blanks, contamination or loss of sample during storage was monitored. The recovery of PCNs from spiked

polyurethane foam plugs was found to be about 40%, so the analytical results were corrected by this factor. Blank polyurethane foam plugs were not contaminated during storage.

Control samples were prepared as part of the quality control program by spiking polyurethane foam plugs with known amounts of PCN mixtures and were stored with field samples. The plugs were extracted and analyzed after being stored for about as long as an average field sample from each of the three sampling trips. Table 12 summarizes the results of these experiments.

Parallel to the spiked polyurethane foam plugs, blank plugs were stored with field samples and analyzed after being stored for about as long as an average field sample. The results for these blanks are listed in Table 13. No PCNs were found in the blank samples.

3.3.3 Sample Log

At the time of collection of each sample, a sample protocol sheet (Figure 19) was filled out and stored in a loose leaf binder. Upon return to the lab, copies of these protocol sheets were stored in two separate locations to prevent accidental loss. In addition, a bound sample log book was kept with sample identification codes for a running record of analysis progress. Copies of the GC/MS analytical data were entered into the sample log book for archival purposes.

3.3.4 Instrumentation Control

To insure that the total operating system was calibrated and in proper working order, the Finnigan 3300 GC/MS was evaluated daily using a standard reference mixture of testosterone and cholestane under a set of reference criteria. In addition, a PCN reference mixture was subjected to GC/MS analysis under the identical operating parameters as those to be used for the analysis of field samples at the beginning of each working day. In this manner, the performance of the GC column, the sensitivity of the mass spectrometer, the calibration of the mass spectrometer and the performance of the computer system were monitored by evaluating the results of the reference mixture.

Table 12. RECOVERY OF CHLORONAPHTHALENES FROM CONTROL SAMPLES

Sample Code	Storage Time Days ^a	% Recovery								Mean	SD
		C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈		
PA-2 ^c	89	55.3	55.2	43.4	39.3	43.4	30.9	33.2	44.1	43.1	8.9
NY-1 ^d	72	--	26.5	23.0	24.2	27.0	22.3	22.0	18.5	23.4	2.9
NY-2 ^b	37	36.6	37.0	34.5	33.0	34.5	33.4	31.8	31.5	34.0	2.0
NC-1 ^b	37	13.6	68.9	59.1	59.7	64.3	63.2	70.0	58.0	57.1	18.1
Mean		35.1	46.9	40.0	39.1	42.3	37.5	39.3	38.0	39.8	3.5
SD		20.9	18.9	15.3	15.1	16.1	17.8	21.1	16.8	17.3	

^aIncluding storage on foam and storage awaiting analysis

^b116 µg Halowax 1014[®]; 111 µg Halowax 1051[®] applied to foam

^c232 µg Halowax 1014[®]; 222 µg Halowax 1051[®] applied to foam

^d11.6 µg Halowax 1014[®]; 11.1 µg Halowax 1051[®] applied to foam

Table 13. GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS OF BLANK SAMPLES

Sample Code	Storage Time ^a		$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	$C_{10}Cl_8$	Average
	Days										
PA-2	60		-	-	-	-	-	-	-	-	-
PA-3	60		-	-	-	-	-	-	-	-	-
NY-3	72		-	-	-	-	-	-	-	-	-
NY-4	72		-	-	-	-	-	-	-	-	-
NC-2	38		-	-	-	-	-	-	-	-	-

^aIncluding storage of extract prior to analysis

Date: _____

() () () () ()
Project No. Operator Seq. Sampler/Rationale State

Municipality _____ ()

Location _____

Site _____ ()

Sample Code _____

No.	Dimensions (cm)	Sorbent	Date/Analytical Procedure
_____	_____	(M)	_____
_____	_____	(M)	_____
_____	_____	(M)	_____
_____	_____	(M)	_____

DC Amps _____ Sampling Rate (LPM) _____ Vacuum ("Hg) _____

Rationale: Qual. Anal (F) _____ End: Time _____ ft³

Quant. Anal. (E) _____ Calibration (C) _____ Start: Time _____ ft³

Experimental: Lab (L) _____ Field (X) _____ Total: (min). _____ ft³

Remarks _____ Volume Air/Cartridge:

_____ 0.0283 (ft³) = _____ (M³)
No. Split

MAP:

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid _____ % Wind Dir./Speed _____ /
Cloud _____ Odor _____
Remarks _____

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid _____ % Wind Dir./Speed _____ /
Cloud _____ Odor _____
Remarks _____

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid _____ % Wind Dir./Speed _____ /
Cloud _____ Odor _____
Remarks _____

Time _____ Temp. Wet. _____ Dry _____
Rel. Humid _____ % Wind Dir./Speed _____ /
Cloud _____ Odor _____
Remarks _____

Figure 19. FIELD SAMPLING PROTOCOL FOR AMBIENT AIR

3.3.5 Data Evaluation and Quality Control

Gas chromatography/mass spectrometry data was screened by the instrument operator before printout and only peaks clusters near the appropriate retention time were included in the integration. The operator also screened the data for anomalous results. If the sum of the PEAK and BACKGROUND was ≥ 100 , the detector was saturated and the sample had to be re-run using a lower sensitivity or smaller injection volume.

In addition to preliminary screening by the operator, the data was also checked by the instrument supervisor to assure that the sample had been run as per the request sheet and that the output was of appropriate quality. The results were then released for interpretation.

Upon receipt of the GC/MS output, it was again checked for saturated peaks and for correlation in retention times with those of the corresponding known PCN isomers. The raw data was also added to the sample log book, which kept a running account of the status of each sample.

3.3.6 Confirmation of Results

Confirmation of representative samples were obtained by (a) full-scan GC/MS or (b) "double ion MID", where two ions of a chlorine isotope cluster are measured simultaneously as discussed in a preceeding section.

3.3.7 Archival Storage

All samples (e.g., remaining portions of soil samples) sampling protocol sheets, sample log books, notebooks, instrumental log books, spectra, GC/MS output, magnetic tapes, and other records were retained for archival purposes. After acceptance of the final report, the samples and magnetic tapes will be discarded but all hard copy records will be permanently archived.

3.3.8 Assessment of Error

The error of the entire analytical procedure is a function of the errors at each step. The major sources of error and their estimated magnitude are listed below.

3.3.8.1 Collection

The error involved in collection of soil and water sample resides primarily in the selection of a representative sample, however, the error in air collection involves the additional factor of collection efficiency of the GFF and PUF plugs. Studies of this efficiency indicate that a major error for monochloronaphthalene may result from collection as discussed in a preceeding section.

The error in measurement of the volume of air sampled is estimated at $\pm 10\%$, due to the sensitivity and stability of the flow rates.

Any error in volume for soil and water samples is derived from gravimetric and volumetric errors, respectively. An error of 0.2% for soils and 0.5% for water is estimated at this step. There is no dependable method for estimating the error or variability introduced by the selection of representative samples without an extensive sampling and analytical effort.

3.3.8.2 Extraction from Sampling Media

Based on the recovery of PUF control samples discussed above (Table 12), the average SD for the individual PCNs was $\pm 17.3\%$ which corresponded to $\pm 43.3\%$ (average RSD).

3.3.8.3 Column Chromatography

The average recovery of PCNs from the column clean-up step, as discussed above was 98.5%. Thus it may be assumed that the maximum loss at this step is 5%.

3.3.8.4 Addition of Standards

An error in addition of standard would affect the calculation of the amount of PCN in the sample. This error is that inherent in the volumetric and gravimetric manipulation of the sample. A balance error of $\pm 0.7\%$, volumetric error of $\pm 0.5\%$, dilution errors of $\pm 1\%$ for pipetting and $\pm 0.5\%$ for volumetric error, and a pipetting error of 1% upon addition of standard are estimated.

3.3.8.5 Final Volume of Sample

The sample is generally made up to a final volume of 2.0 ml. The error in this step is $\pm 5\%$.

3.3.8.6 RMR

The error in calculation of RMR can be estimated from the mean RSD in Table 10. The average RSD for the five RMR values is +19.9%.

3.3.8.7 GC/MS Analysis

The reproducibility of the GC/MS was checked using an actual sample and is summarized in Table 14. The average RSD of the five PCN isomers detected was 12%.

3.3.8.8 Total Error

The total error, S_T , associated with the reported PCN concentrations may be estimated by

$$S_T = \left\{ \sum_{i=1}^n S_i^2 \right\}^{1/2} \quad (\text{Equation 1})$$

where S_i is the error associated with the i^{th} source of error. This equation assumes that all sources of error are independent, which is a reasonable assumption in this case. The total error is listed for air, water, and soil samples in Table 15. Sediment, and other solid samples may be assumed to have errors similar to those listed for soil.

Table 15. TOTAL ESTIMATED ANALYTICAL ERROR

Medium	Propogated Error
Air	+ 50%
	- 51%
Water	+ 24%
	- 27%
Soil	+ 24%
	- 26%

Table 14. REPRODUCIBILITY OF GC/MS ANALYSIS OF SAMPLES FOR PCNs.
 REPLICATE INJECTIONS OF AN AIR SAMPLE EXTRACT - KOPPERS, P2/C1/L1 - FILTER

Injection	C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	Total
1	-	3.0	20.7	10.0	9.3	0.6	-	-	43.6 ng/m ³
2	-	3.2	25.3	12.1	11.5	0.7	-	-	52.9 ng/m ³
3	-	2.5	21.2	9.9	10.5	0.8	-	-	45.0 ng/m ³
Mean	-	2.9	22.4	10.7	10.4	0.7	-	-	47.2
SD	-	0.36	2.52	1.24	1.10	0.10	-	-	5.01
RSD	-	0.12	0.11	0.11	0.11	0.14	-	-	0.11

Average RSD = 0.12

4.0 SAMPLING AND ANALYSIS NEAR KOPPERS CHEMICAL AND COATINGS PLANT, BRIDGEVILLE, PA

Koppers Company, Inc., Pittsburgh, PA (Koppers) was selected for sampling since it is the sole U.S. producer of PCNs.^(1,8) The manufacture of PCNs takes place at Koppers Chemical and Coatings Plant, Bridgeville, PA⁽¹⁾ and they are distributed under the trade name Halowax®.

4.1 FIELD SAMPLING

Koppers is located in a southern suburb of Pittsburgh, PA in a deep (60-100 m) valley. The plant site is relatively large and old (roughly, 600 x 100 m), containing several main buildings and numerous smaller buildings. A high level of activity was inferred from the 30-50 plumes of steam and/or smoke observed at any one time. Several people indicated that a white "snow" occurred which was usually deposited in the night.

Based on the above discussions and on general sampling protocol, sampling locations were chosen both in the valley and on the hills surrounding the plant. The sampling protocol is summarized in Table 16.

4.1.1 Air

Two 24 hr air samples were collected at each of four points along the transects as shown in Figures 20 and 21. The MRI weather station was located at L3 (Figure 20). No adverse weather was noted, although wind direction and speed were highly variable.

4.1.2 Soil

Soil samples were collected along the transects according to the general protocol. One soil sampling site (L13, Figure 21) was in an area

Table 16. SAMPLING PROTOCOL FOR KOPPERS COMPANY, CHEMICAL AND COATINGS PLANT
BRIDGEVILLE, PENNSYLVANIA.

Period	Cycle	Location	Sampling Time	Sampling Volume	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
10/25/76 P1	C1 ^a	L1	1358-1432	91.8 m ³	APCN	8-4	93	SW/5-NW/13	slight rain, odor of benzophenone, naphthalene
		L2	1403-1435	93.0 m ³	APCN	8-4	93	SW/5-NW/13	slight rain
		L3	1350-1339	89.0 m ³	APCN	8-4	93	SW/5-NW/13	slight rain
		L4	1445-1404	89.2 m ³	APCN	8-4	93	SW/5-NW/13	slight rain
	C2 ^a	L5	1112-1125	2.7 ℓ	WPCN ^d	11 ^f		SW/5-NW/19	slight rain
		L6	1055-1125	2.6 ℓ	WPCN ^e	9 ^f		SW/5-NW/19	slight rain
	C3 ^b	L7	2120-2150	246 ℓ	AHC	7			mixed organic
	C1 ^a	L1	1446-1551	90.0 m ³	APCN	4-2	55	NW/13-W/4	odor of naphthalene
		L2	1510-1530	91.0 m ³	APCN	4-2	55	NW/13-W/4	
		L3	1355-1428	91.8 m ³	APCN	4-2	55	NW/13-W/4	
		L4	1420-1412	89.2 m ³	APCN	4-2	55	NW/13-W/4	
10/26/76 P2	C2	L5	1320-1328 ^a	2.4 ℓ	WPCN ^h	8 ^f		NW/15-W/4	
		L6	1330-1309 ^a	1.3 ℓ	WPCN ⁱ	9 ^f		NW/15-//4	
		L7	1050 ^c	0.8 ℓ	WPCN ^j				
	C3 ^c	L8	1425		apples				
	C4 ^c	L9	1800	12 cores ^g	SPCN	6		NW/11	odor of naphthalene
		L10	1830	10 cores	SPCN	6		NW/11	
		L11	1600	10 cores	SPCN	7		NW/13	
		L12	1630	6 cores	SPCN	7		NW/13	
		L13	1700	10 cores	SPCN	7		NW/11	
		L14	1730	10 cores	SPCN	6		NW/11	
		L15	0900	10 cores	SPCN	0		Calm	
		L16	0930	10 cores	SPCN	1		Calm	

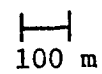
(continued)

Table 16 (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
10/26/76	C6 ^{c,k}	L17	0900	15 cm	fish				
	C7 ^{b,k}	L18	1048-1114	229 l	AHC			NW/6	cloudy
		L19	1048-1118	170 l	AHC	3		NW/6	cloudy, naphthalene
		L20	1126-1202	153 l	AHC	2	59	NW/6	cloudy, mixed organic
		L21	1217-1247	189 l	AHC			NW/6	cloudy

^a 24 hr. composite samples^b 30 mm survey samples^c grab samples^d ~10 m downstream from waste water out fall^e ~10 m upstream from waste water out fall^f water temperature^g 5 cm diameter x 13 cm depth^h ~100 m upstream from Koppers Chemical propertyⁱ same as Location 6, period 1^j drainage ditch^k 10/29/76

Key to Sample Type: APCN - polychloronaphthalenes, air
 AHC - hydrocarbons, air
 WPCN - polychloronaphthalenes, water
 SPCN - polychloronaphthalenes, soil



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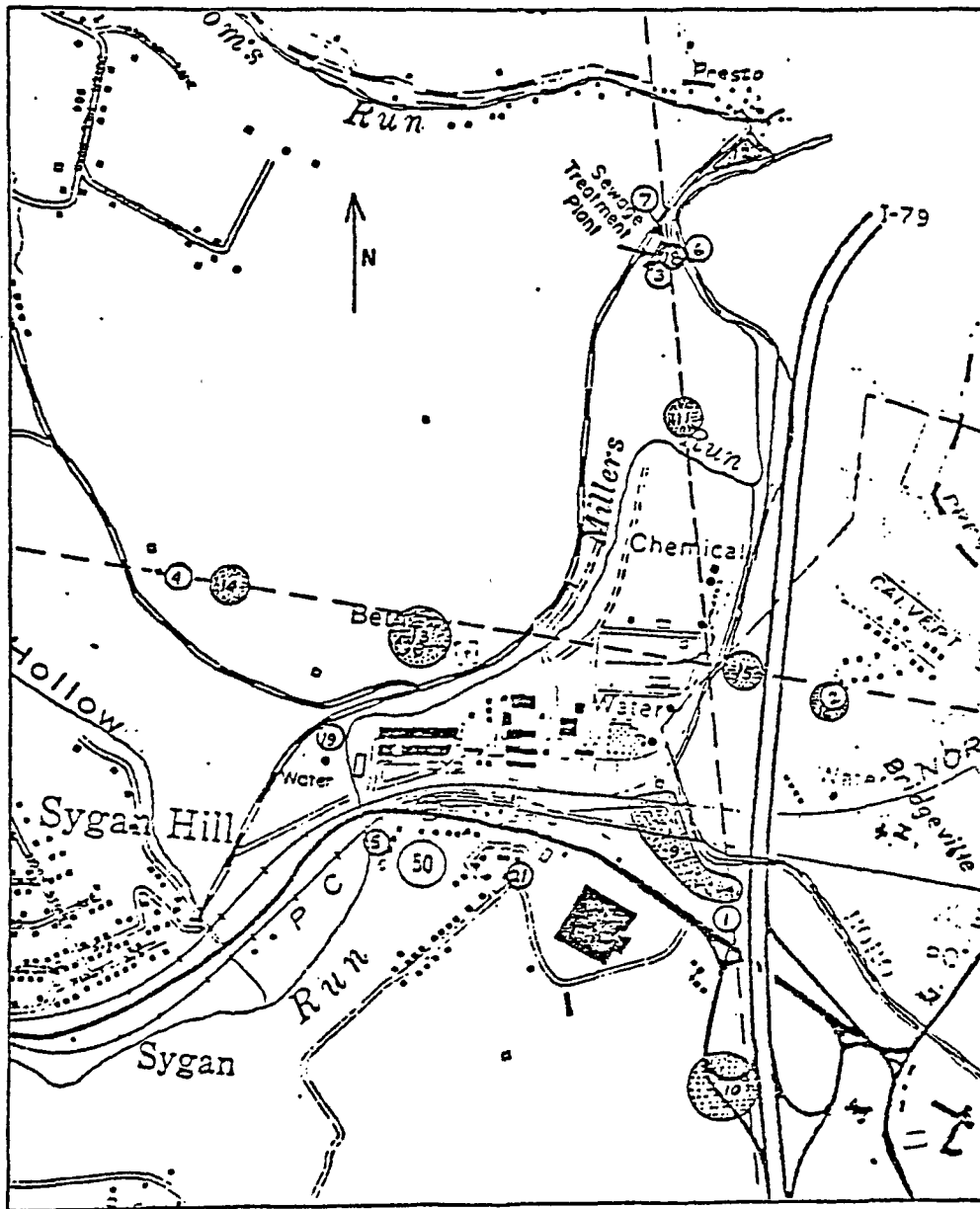


Figure 21. Map of Koppers with sampling locations for
P2 - 10/26/76.

which local sources said used to be a dumping ground for Koppers' solid waste.

4.1.3 Water

Interval samples were collected above and below the South Fayette Township Sewage Treatment Plant (P1, L5 and L6). The plant manager stated that Koppers did not use their system, but the proximity and possibility of leakage into the system prompted the decision to sample. Other composite samples were collected upstream (P2, L5) on Millers Run and downstream (P2 L6) on Chartiers Creek. A grab water sample (P2 L7) was collected from a small ditch which contained the runoff and/or leachate from the old dumping ground discussed in Section 6.1.2.

4.1.4 Miscellaneous

Several apples were collected from the apple trees on the farm at L4. A small dead fish (carp, 40 g, ~15 cm) was collected in Millers Run. No cause of death could be determined.

Five air samples were collected on Tenax. Both upwind and downwind samples were taken and attempts were made to be directly in the plume of the emissions from the plant for the downwind samples.

During the sampling period, a white flocculant crystalline material was observed as airborne particulates and adhering to low vegetation near sampling locations 9 and 10. This is presumably the "snow" noted by local residents. A sample was collected.

4.2 ANALYSES

Air, soil and water samples were analyzed according to the procedure detailed in Appendix A. The whole fish sample was homogenized in a blender and then extracted using the soil extraction procedure. The apples were likewise homogenized and also extracted according to the soil extraction procedure. The white flocculant crystalline material was analyzed by direct probe mass spectrometry (using the Finnigan 3300 instrument).

4.3 RESULTS AND DISCUSSION

The results of the analysis of samples collected near Koppers Company, Bridgeville, Pennsylvania are summarized in Table 17.

Table 17. RESULTS OF ANALYSIS OF SAMPLES COLLECTED NEAR KOPPERS CHEMICALS AND COATINGS, INC., BRIDGEVILLE, PENNSYLVANIA

Period ^a	Cycle ^a	Location ^a		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1	F ^c	-- ^d	--	--	--	--	--	--	--	--
			1	96	160	120	15	1.3	--	--	--	390
			2	49	1.3	5.2	--	--	--	--	--	55
			Total	140	160	130	15	1.3	--	--	--	450 ng/m ³
		L2	F	--	--	T ^e	--	--	--	--	--	T
			1	1.8	15	29	3.0	--	--	--	--	49
			2	--	--	--	--	--	--	--	--	--
			Total	1.8	15	29	3.0	--	--	--	--	49 ng/m ³
		L3	F	0.2	--	--	--	--	--	--	--	0.2
			1	--	25	59	5.0	--	--	--	--	89
			2	1.8	--	--	--	--	--	--	--	1.8
			Total	0.9	25	59	5.0	--	--	--	--	91 ng/m ³
		L4	F	--	--	--	--	--	--	--	--	--
			1	--	7.3	18	--	--	--	--	--	25
			2	--	--	--	--	--	--	--	--	--
			Total	--	7.3	18	--	--	--	--	--	25 ng/m ³
	C2 ^f	L5		--	--	0.5	0.5	0.4	T	T	T	1.4 µg/l
		L6		0.4	--	--	--	0.2	--	--	--	0.6 µg/l
P2	C1 ^b	L1	F	--	2.9	22	11	10	0.7	--	--	47
			1	230	610	750	99	30	--	--	--	1700
			2	130	--	--	--	--	--	--	--	130
			Total	360	610	770	110	40	0.7	--	--	1900 ng/m ³

(continued)

Table 17. (cont'd)

Period	Cycle	Location		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P2	C1	L2	F	--	1.8	22	7.2	3.2	0.2	--	--	35
			1	140	250	330	32	--	--	--	--	750
			2	42	--	--	--	--	--	--	--	42
			Total	180	250	350	40	3.2	0.2	--	--	830 ng/m ³
		L3	F	--	1.0	32	14	5.2	0.4	0.2	0.2	53
			1	970	860	920	83	1.0	--	--	--	2800
			2	45	--	--	--	--	--	--	--	45
			Total	1000	860	950	100	6.2	0.4	0.2	0.2	2900 ng/m ³
		L4	F	--	--	1.1	0.8	0.8	--	--	--	2.6
			1	5.5	32	62	11	1.0	--	--	--	110
			2	--	--	--	--	--	--	--	--	--
			Total	5.5	32	63	12	1.8	--	--	--	110 ng/m ³
	C2 ^f	L5		--	--	--	--	--	0.2	--	--	0.2 µg/l
		L6		--	--	--	--	--	--	--	--	--
		L7		--	--	--	--	--	--	--	--	--
		L8		62	8.9	13	7.3	h 25 µg/kg h		--h	--h	90 µg/kg
		L9		3.4	15	280	170	98	20	9.3	4.0	600 µg/kg
		L10		--	3.2	60	39	20	4.6	1.0	0.6	130 µg/kg
		L11		97	81	310	270	190	25	4.2	2.3	990 µg/kg

(continued)

Table 17. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total
			$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	$C_{10}Cl_8$	
P2	C4	L12	6.0	34	370	710	900	250	74	7.5	2300 µg/kg
		L13	9.6	75	880	760	310	55	16	5.2	2100 µg/kg
		L13A ^j	5300	>16000 ^k	>25000 ^k	18000	15000	11000	5200	760	>96000 µg/kg
		L14	1.6	15	86	49	26	6.3	1.5	0.7	190 µg/kg
		L15	--	57	260	230	200	30	6.8	3.1	780 µg/kg
		L16	--	8.8	180	130	79	18	5.6	--	440 µg/kg
	C6 ¹	L17	--	1.7	22	--	9.5	3.6	2.2	--	39 µg/kg

^aSee Table 16 for period, cycle and location designations in the sampling protocol

^b24 hour air samples

^cF = Glass fiber filter; 1 = Top PUF Plug; 2 = Bottom PUF Plug

^dNo PCN peak detected. Detection limit for air is about 0.3 ng/m³, for soil about 0.5 µg/kg, and for water about 0.2 µg/l.

^eTrace

^fWater samples

^gApples

^hInterferences prevented accurate quantitation - <5 µg/kg

ⁱSoil Samples

^jBlack crystalline component of sample L13

^kGC/MS detector saturated

¹Fish (whole, homogenized)

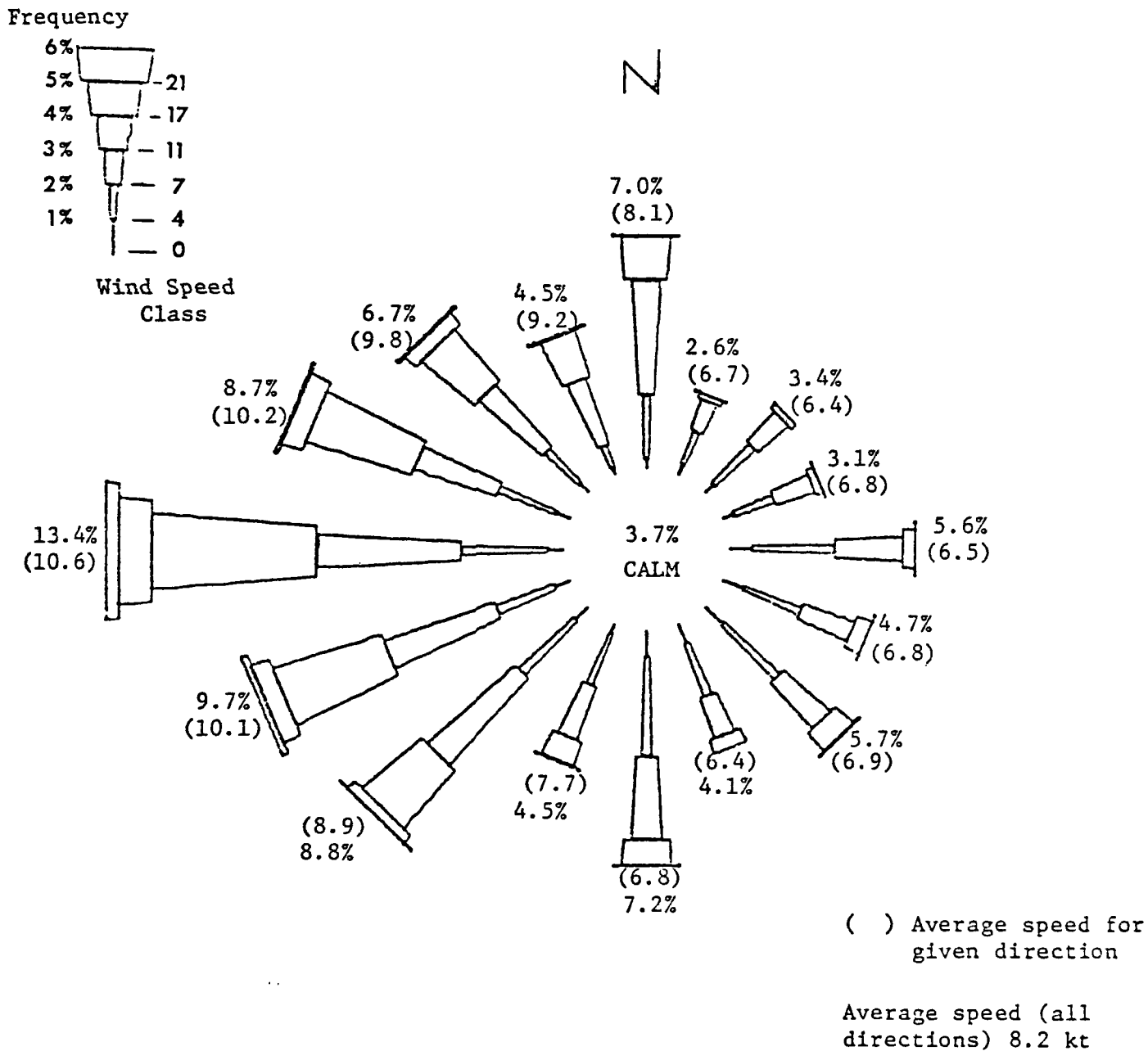
4.3.1 Air

The frequency of occurrence of wind speed classes having lower limits of 0, 4, 7, 11, 17 and 21 knots (1 kt = 0.5148 m/s) as a function of wind direction (of a 16-point compass) at the Greater Pittsburgh Airport is shown graphically in Figure 22. This distribution, called a wind rose is based on observations every three hours from January 1, 1970 to December 31, 1974. Westerly winds (WSW-WNW) occur most frequently with greater average speed and with infrequent low (<4 kt) wind speeds. Low wind speeds are more predominant in the southwest quadrant. Winds from the northwest quadrant are infrequent and are seldom over 10 kt.

Although wind rose data is useful in assessing long term trends in the macrometeorology, it does not always give insight to the ground level dispersion of an emission. This is especially true in the case of irregular terrain such as found near Koppers. In this case, the micrometeorology must be considered. These factors are included in the discussion below.

Total PCN concentrations for the air samples collected during Period 1 are presented in Figure 23, with detailed maps presented in Figure 24. Comparable data for Period 2 is given in Figures 25 and 26. The average concentration detected during the first 24 hr period was 150 ng/m^3 . The average concentration detected during the second 24 hr period was 1600 ng/m^3 .

Weather records from the Greater Pittsburgh Airport show that during Period 1 (10/25/76) light rain and fog was present with northerly winds at 11-15 km/hr until about 1830 EST. Visibility increased, the precipitation ended and wind speeds increased to 18.5-30 km/hr, gusting to 40 km/hr in the early evening. Skies remained cloudy overnight, keeping temperatures from falling more than 3°C . By sunrise of the following day, the skies cleared and northerly winds persisted at 20-26 km/hr throughout the day. An over-cast of shallow convective clouds formed during the late morning and lasted until late afternoon (Period 2). By evening, skies were clear with temperatures decreasing to 6°C by midnight and wind speeds decreasing to approximately 10 km/hr for the night. At midnight, low clouds returned and remained throughout the second sampling period.



ANNUAL WIND ROSE
PITTSBURGH, PENNSYLVANIA
1970-1974

Figure 22. The length of wind speed class proportional to its frequency of occurrence.

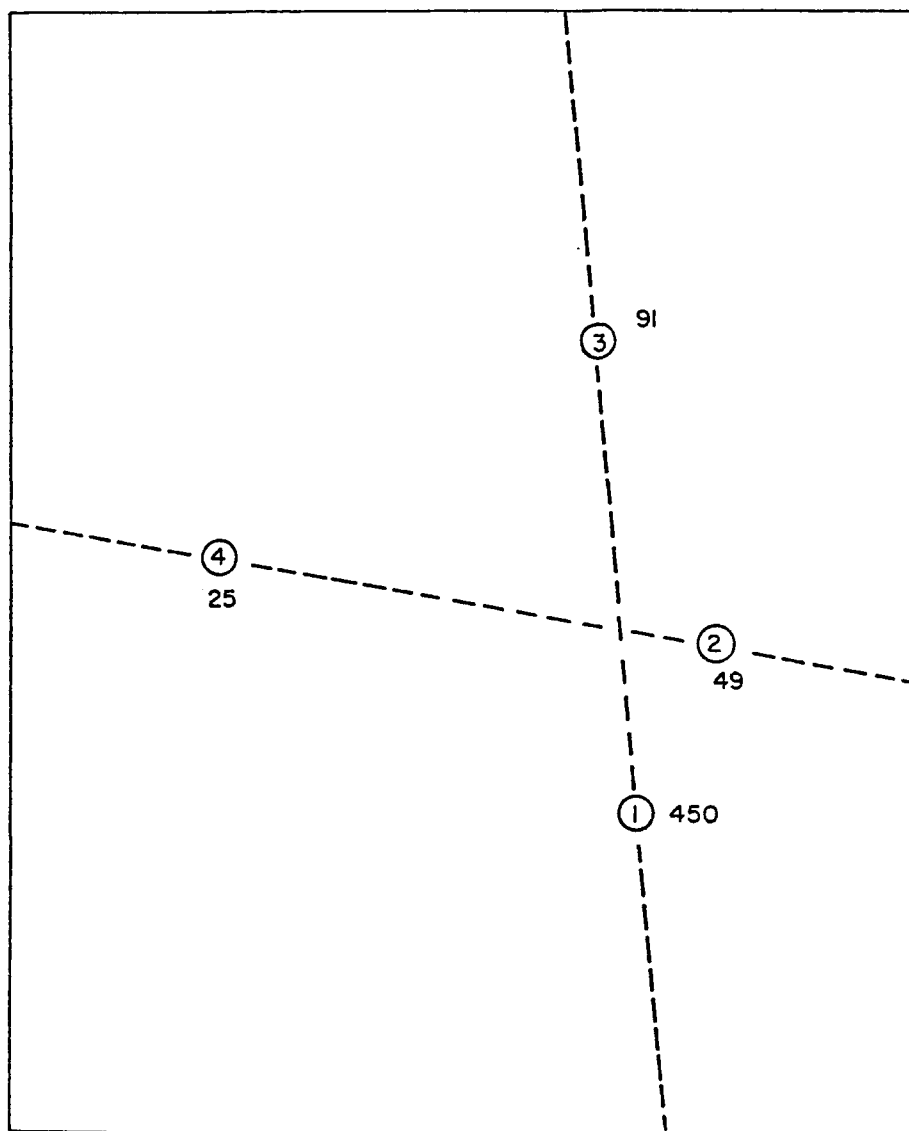


Figure 23. Total PCN concentrations (ng/m^3) in air near Koppers Chemical and Coatings Plant, Inc., Period 1.

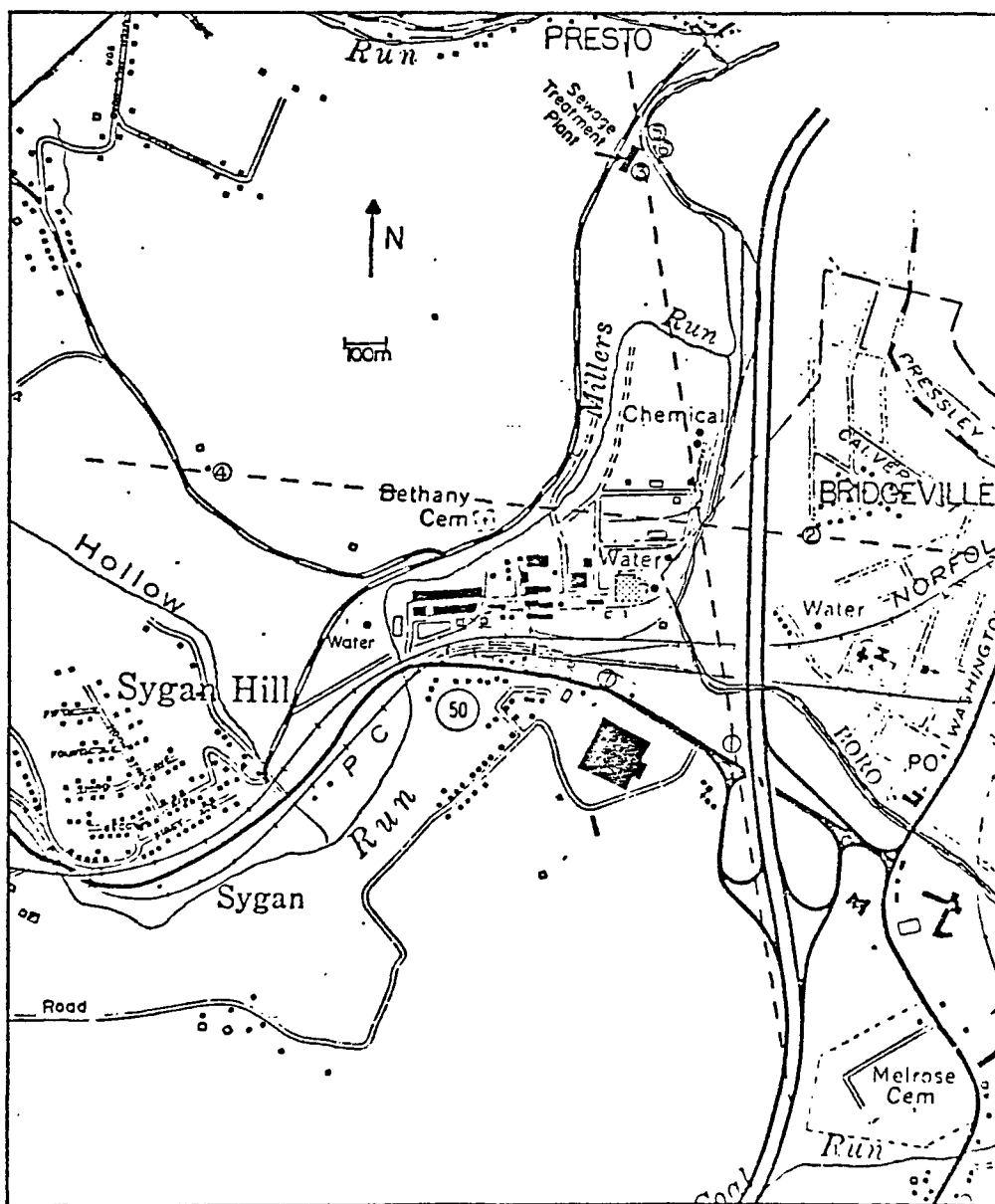


Figure 24. Map of Koppers with sampling locations (Period 1).

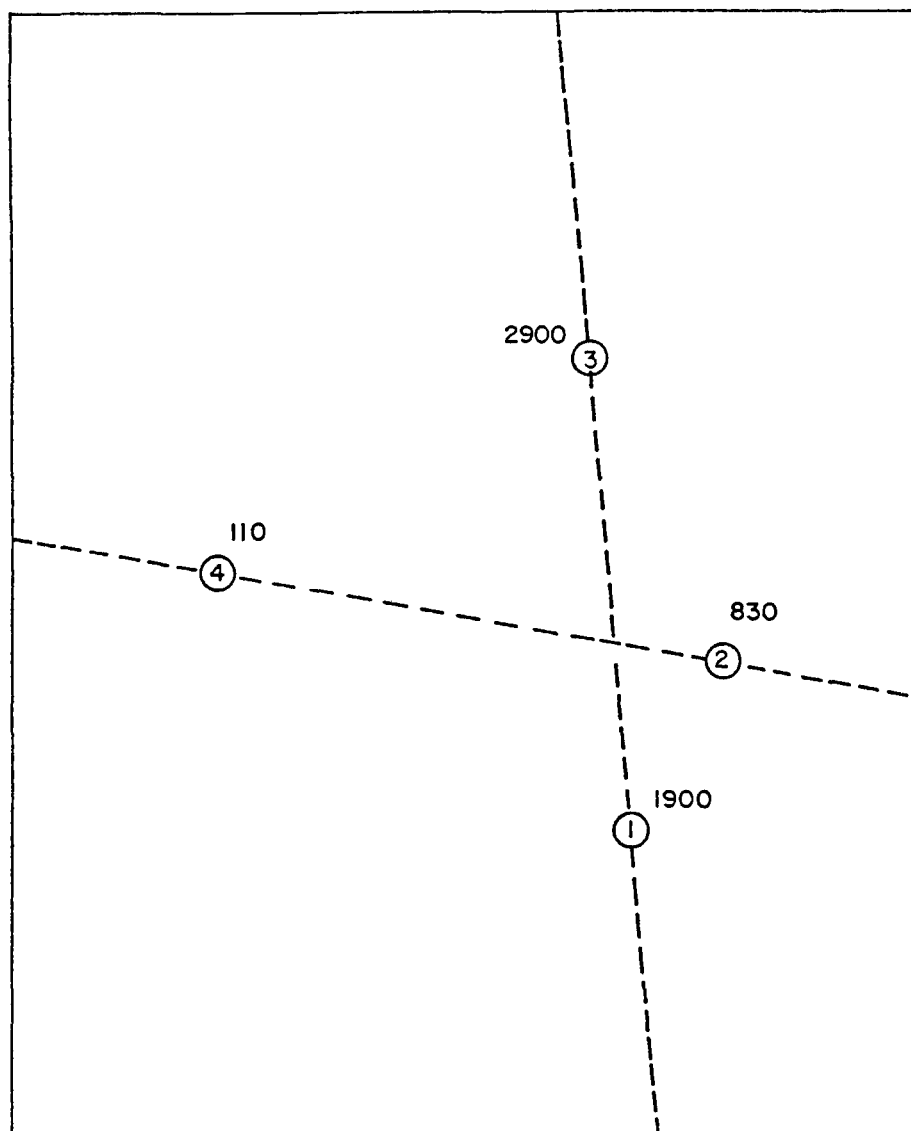


Figure 25. Total PCN Concentrations (ng/m^3) in air near Koppers Chemical and Coatings Plant, Inc., Period 2.

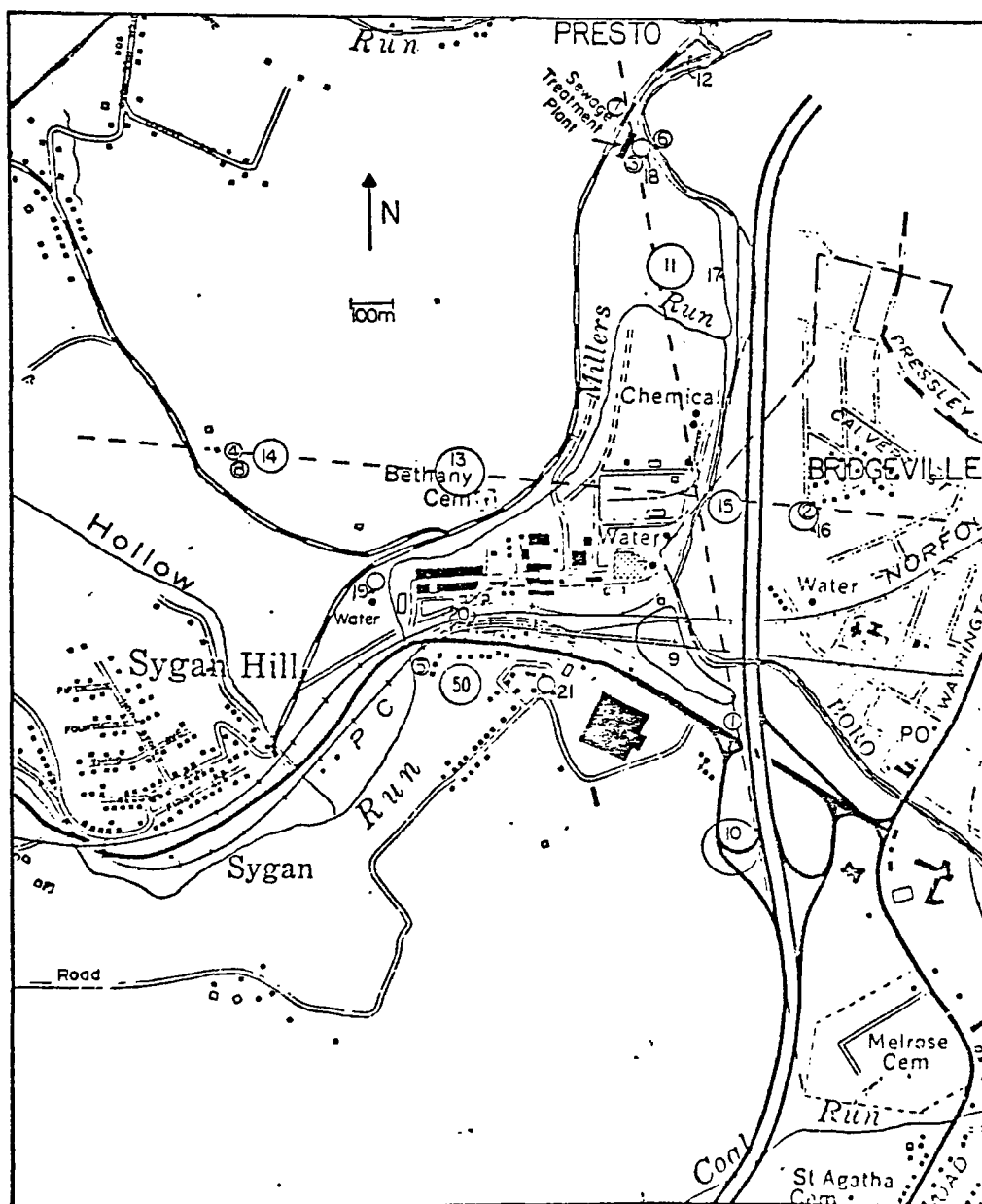


Figure 26. Map of Koppers with sampling locations (Period 2).

During the first sampling period, the brisk winds quickly diluted plant emissions as the air moved southward toward Location 1. Atop the hills to either side of the plant, at Locations 2 and 4, the winds were generally unfavorable for measuring emissions transported directly from the plant. Concentrations measured at these sites probably arose from horizontal and vertical diffusion of emissions during the period.

In Period 2, especially during the night of October 26-27, generalized meteorological conditions were extremely conducive to a localized wind circulation pattern which would transport emissions toward the wastewater treatment plant location. Clear skies and relatively dry air permitted the ground, hillside and high ground to cool by radiation. The cold air flowed toward lower elevation, accumulating as a cold air mass in the narrow valleys. As this mass of cool air deepened, warmer air was lifted aloft, creating a stable interface. Apparently, the mass of cool air deepened to such a height that the emissions had insufficient buoyancy to be lifted above the interface. The generally northerly wind flow was not strong enough to mix and dissipate this stable layer, so the emissions were trapped within the cold air mass. This cool air drifted very slowly down the Sygan Run and Millers Run Valleys, approximately in proportion to the slope of the land and contrary to the flow of air further aloft, toward the wastewater treatment plant sampling location. Anemometer records at that location indicated little movement of air during the night. With the vertical dispersion limited by the stable air aloft, horizontal dispersion confined by the valley walls, and very little movement of air past the emission location, the entire valley floor became an emission reservoir, giving a high concentration at sampling Location 3.

Although difficult to quantify, the depth of the cool air may have increased during the night to an altitude of 70 m above the valley floor, thereby affecting the hilltop monitoring locations. The PCN concentrations there are lower because of greater dilution as the depth of the cool air increased and because the samplers were probably above the stable interface at least for part of the sampling period.

The average distribution of the PCNs on the air sampling media is depicted in Figure 27. The bulk of the PCNs are collected on the first foam

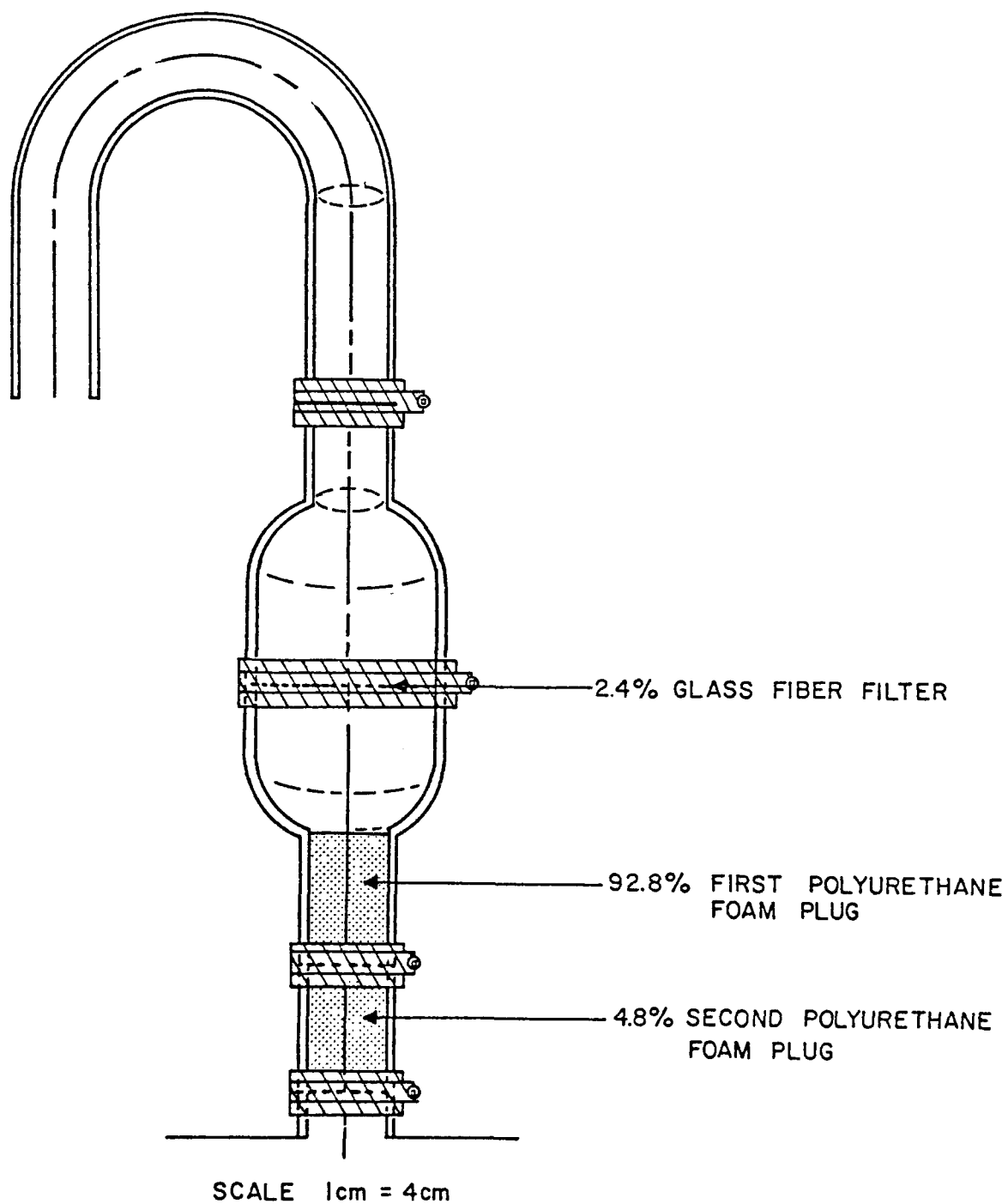


Figure 27. Average distribution of PCNs on sampling media.

plug; however a portion of the heavier isomers are collected by the glass fiber filter, indicating that they may be present in the air as particulates or aerosols. Only monochlorobiphenyl eluted, to any great extent, through the first foam plug to the second.

4.3.2 Soil

The soil analysis results are presented in Figure 28. The average concentration found was 950 $\mu\text{g/kg}$.

The concentration of PCNs detected generally decreased with increasing distance from the plant. The very high concentrations (2100 $\mu\text{g/kg}$) at Location 13 may not be due totally to air deposition. The samples comprising this composite were collected in an area which, according to local residents, was a place where Koppers has dumped solid waste. In fact, analysis of a black crystalline residue, collected at this site revealed >90,000 mg/kg total PCNs (where the exact value may be much higher since only the surface of this material was extracted).

The distribution of PCNs in the soil samples is consistent with airborne transport and subsequent deposition by climatological wind distribution and local circulation patterns, such as the drainage flow discussed previously. Prevailing southwesterly winds may be channeled to a more southerly flow by the Millers Run Valley. The northerly wind flow is likewise channeled up the valley, which would fail to reduce those wind speeds.

For an effective emission height of about 25 m the maximum relative concentration (concentration per unit emission per unit wind speed) should occur from 500 to 1000 m downwind of the emitter.⁽³³⁾ As the emission height increases, the downwind distance for the maximum increases. It is therefore feasible that the highest concentration would more likely be found farther away from the source (i.e., beyond the wastewater treatment plant) rather than nearer the source.

The average degree of chlorination of PCNs detected in samples collected nearer the plant is slightly lower than that of samples collected farther along the transect. This is illustrated in Figure 29. The mean degree of chlorination found for "near" samples was 3.75 while 4.33 was found for

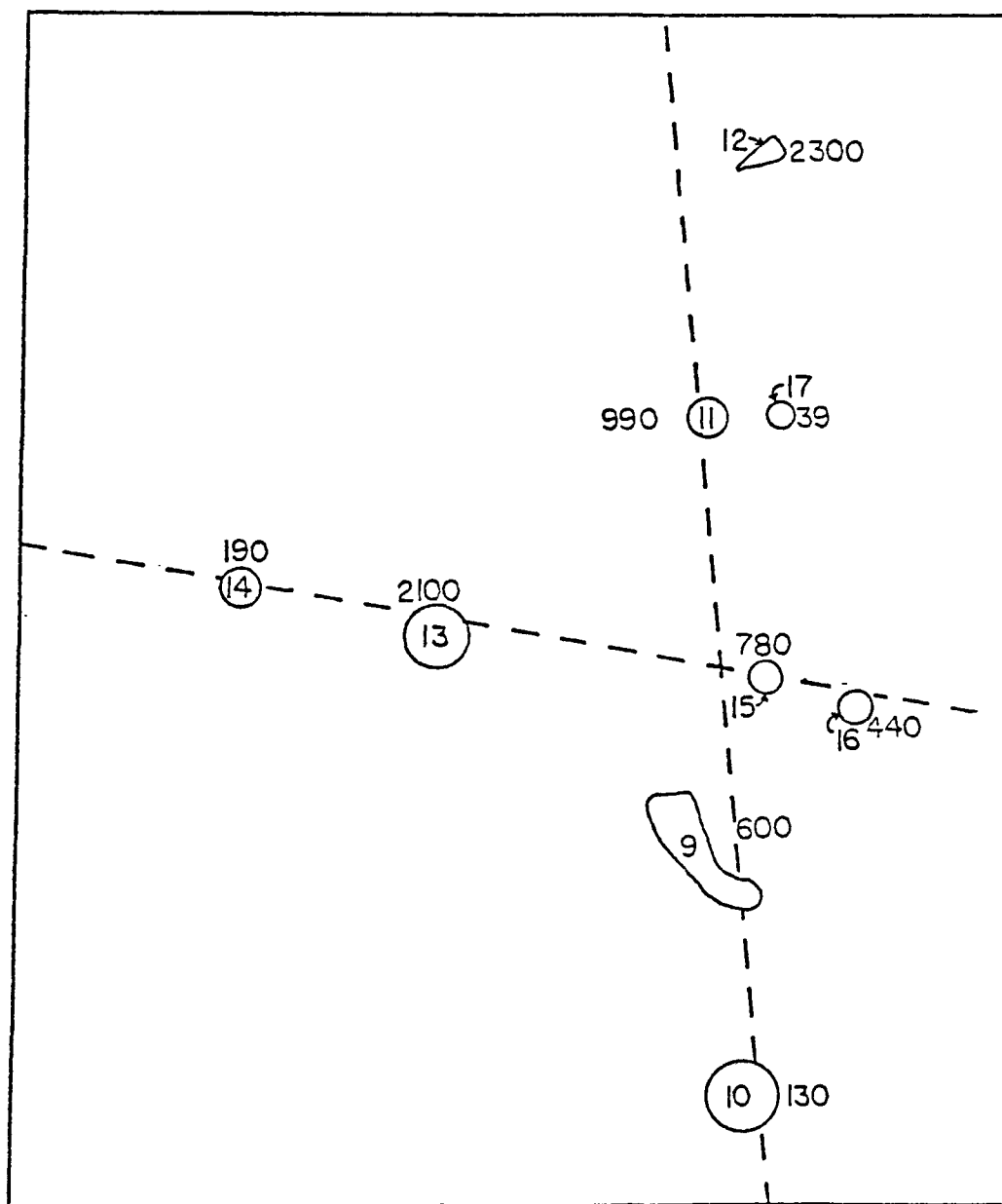


Figure 28. Total PCN concentrations (µg/kg) in soil near Koppers Company (Period 2).

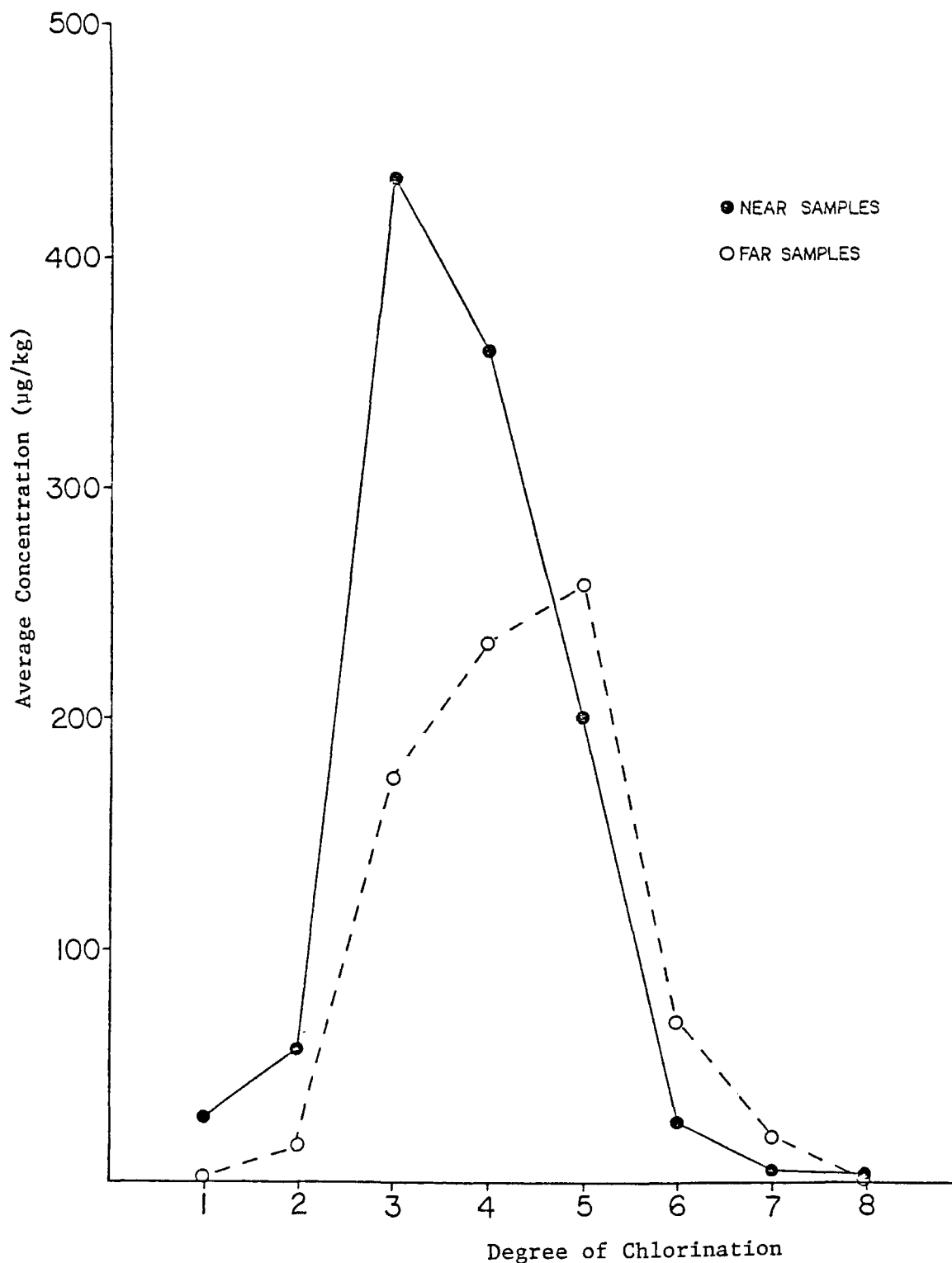


Figure 29. Distribution of PCNs on soil near Koppers Company.

"far" samples. No clear explanation is apparent for this slight difference other than differences in the physical properties of the various isomers, emission history and meteorological conditions.

4.3.3 Water

The water samples taken during Period 1 were from above (L6) and below (L5) the South Fayette Township Wastewater Treatment Plant outfall. This plant does not directly serve Koppers and hence only a very slight increase in PCNs is observed in water collected below the treatment plant outfall. The values are near the detection limit, but were confirmed by the "double MID" technique. The values therefore do not appear to be artifacts, but are nevertheless low.

Analysis of composited water samples collected during Period 2 above (L5) and below (L6) the Koppers plant reveals only a trace of $C_{10}H_2Cl_6$ in the upstream sample while no PCNs were detected downstream.

4.3.4 Miscellaneous Samples

The small dead fish (carp, 40 g, ~15 cm) retrieved from Millers Run was found to contain appreciable levels of PCNs (39.4 $\mu\text{g/kg}$ total) with approximately 57% accounted for by trichloronaphthalene. No other dead or living organisms were observed either upstream or downstream from the Koppers plant, consequently no cause of death can be assigned. In addition, it is not known whether the PCNs detected had been ingested by the fish or were adsorbed either before or after death.

Approximately one dozen red apples (variety unknown), obtained from the ground at Location 14, were found to contain a total PCN concentration of about 90 $\mu\text{g/kg}$.

The white flocculant crystalline material that was observed as airborne particulates was found to be phthalic anhydride. This conclusion was supported by a melting point of $\sim 128^\circ\text{C}$ (lit. 131.6°C).

Two of the five air samples collected on Tenax GC cartridges were selected for GC/MS analysis as the two most likely to produce positive results. The TIC chromatograms (Figures 30 and 31) were examined and the more interesting (Figure 32, P2/C7/L20) was selected for data output and

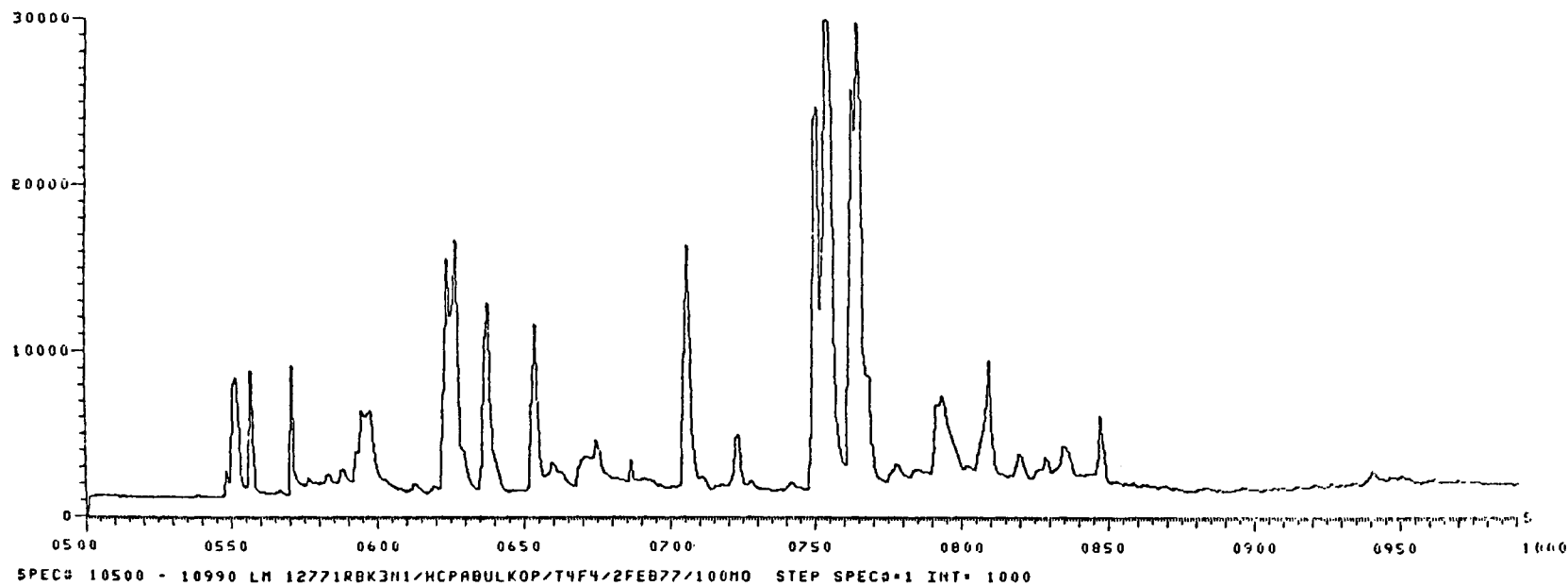


Figure 30. Total ion current chromatogram from gc/ms analysis of organics collected near Koppers Chemical Company, Bridgeville, Pennsylvania (P2/C7/L21).

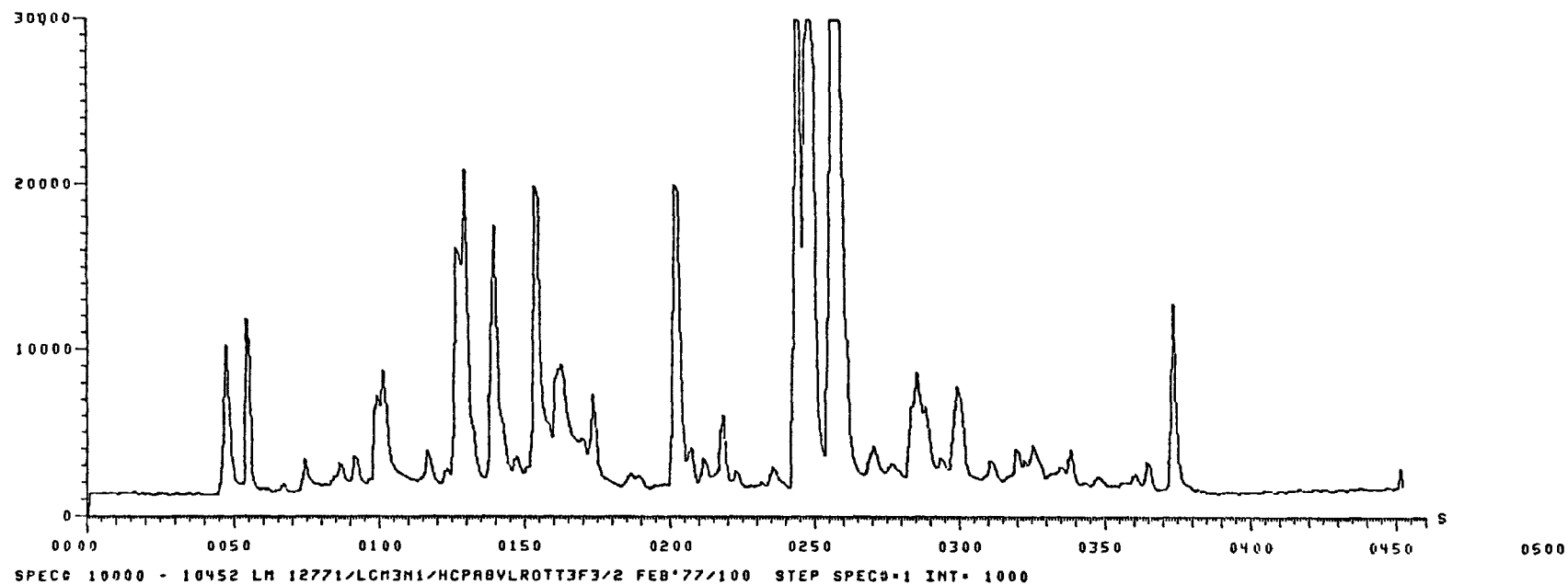


Figure 31. Total ion current chromatogram of gc/ms analysis of organics collected near Koppers Chemical Company, Bridgeville, Pennsylvania (P2/C7/L20).

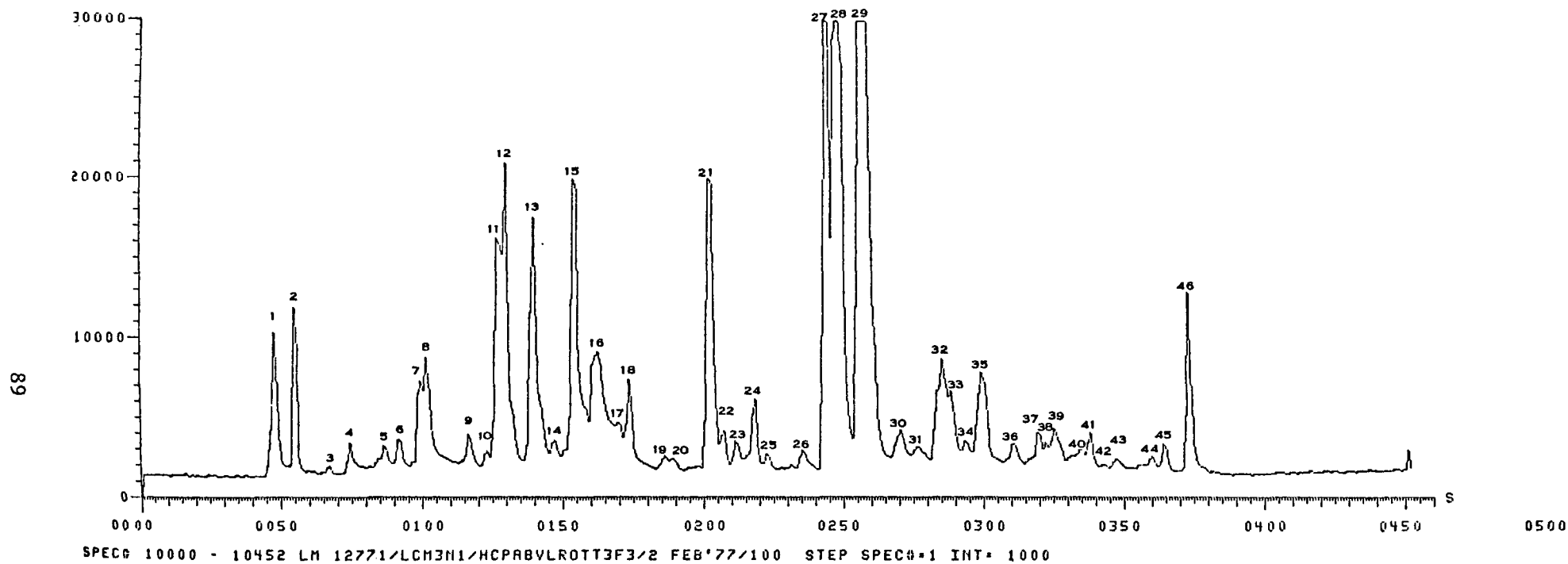


Figure 32. Gas chromatography/mass spectroscopic analysis of ambient air near Koppers (P2/C7/L20).

interpretation which involved plotting of 412 mass spectra and identifying the compounds from these spectra. The results of this identification are presented in Table 18. Although the styrene peak is very high relative to that normally seen in ambient air, the compounds identified were not directly relevant to this project, so further analysis and data interpretation of the Tenax cartridges was not pursued.

4.3.5 Isomeric Distribution of PCNs

All eight chloronaphthalenes were found to varying degrees in air and soil samples in the vicinity of the Koppers plant. As illustrated in Figure 33, the air samples contained predominantly mono-, di-, and trichloronaphthalenes, whereas the soil samples contained most tri-, tetra-, and pentachloronaphthalene isomers. This difference could be due to weathering and aging of the soils, or an average historical deposition of more highly chlorinated PCNs than was observed in the air during our sampling periods. Due to the poor collection efficiency (vide supra), the amount of monochloronaphthalene (and to a much lesser extent, dichloronaphthalene) may, in fact, be greater than that represented in Figure 33.

The knowledge of isomeric distribution and accompanying health effects information may be important to the assessment of the toxicological implications of this data. The toxicity of the chloronaphthalenes, similar to that of PCBs, is highly dependent on the organism exposed, the route of exposure, and the extent of chlorination.^(1,8) Humans are susceptible to physiological damage from PCNs and several occupationally related deaths have been recorded.⁽¹⁾ The clinical manifestations of PCN poisoning are liver necrosis and chloracne.⁽¹⁾ The effects of low-level exposure have not been reported. Individual PCN homologs exhibit markedly different toxicity levels. Mono- and dichloronaphthalenes are generally considered non-toxic; tri- and tetrachloronaphthalenes exhibit some toxicity, but the penta- and hexachloro analogs are responsible for the known cases of severe poisoning and are highly toxic.⁽¹⁾ Contrary to this trend, octachloronaphthalene is considered relatively innocuous. No information is available on the relative toxicities of the various positional isomers.

Table 18. COMPOUNDS IDENTIFIED IN AMBIENT AIR NEAR
KOPPERS CHEMICAL COMPANY (P2/C7/L20)

Chromatographic Peak No.	Compound
1	CO ₂
2	CF ₂ Cl ₂
4	<u>n</u> -propane
5	CCl ₃ F
7	CH ₂ Cl ₂
8	C ₂ Cl ₃ F ₃ (Freon 113, BKG)
9	acetone
10	C ₆ H ₁₄
11	3-methyl pentane
12	perfluorobenzene (standard)
12a	<u>n</u> -hexane
12b	chloroform
13	perfluorotoluene (standard)
14	methyl chloroform
15	benzene
15a	propyl acetate isomer
15b	2-methylhexane
16	2,3-dimethyl pentane
17	trichloroethylene
18	<u>n</u> -heptane
19	C ₇ H ₁₄
20	C ₇ H ₁₄
21	toluene
22	C ₈ H ₁₈
23	C ₈ H ₁₆
24	<u>n</u> -octane
25	tetrachloroethylene
26	C ₈ H ₁₆
27	ethylbenzene
28	<u>meta</u> - and/or <u>para</u> -xylene

(continued)

Table 18 (cont'd)

Chromatographic Peak No.	Compound
29	styrene
29a	<u>ortho</u> -xylene
30	isopropylbenzene
32	C ₃ -alkyl benzene
33	C ₃ -alkyl benzene
34	C ₃ -alkyl benzene
35	α -methylstyrene
35a	1,2,4-trimethylbenzene
36	1,2,3-trimethylbenzene
38	diethylbenzene
39	C ₃ -alkyl benzene (tentative)
40	C ₄ -alkyl benzene
41	<u>n</u> -undecane
42	C ₄ -alkyl benzene
43	C ₄ -alkyl benzene
44	C ₅ -alkyl benzene
44a	C ₁₀ H ₁₂
45	tetrahydronaphthalene
46	naphthalene

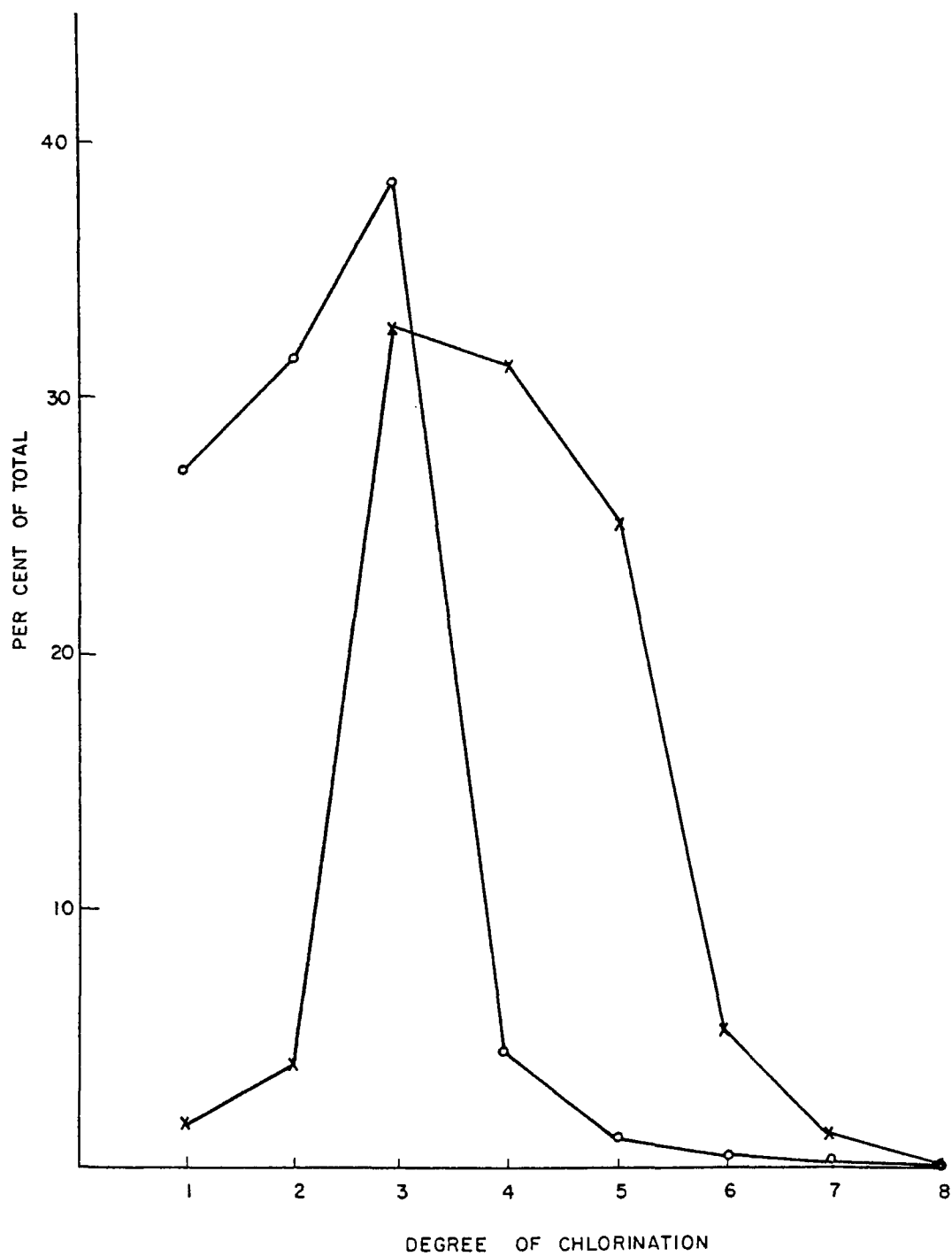


Figure 33. Isomeric distribution of PCNs between soil and air at Koppers. o - Air, x - Water.

5.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF MANNING PAPER COMPANY, GREEN ISLAND, NEW YORK

Samples were collected near Manning Paper Company, Green Island, New York on November 10-12, 1976. The samples collected were found to contain low-to-undetectable amounts of polychlorinated naphthalenes (PCNs). The sampling and analysis are discussed in detail below.

5.1 FIELD SAMPLING

Manning has 325 employees⁽³⁴⁾ and manufacturers rope, kraft papers⁽³⁴⁾, various grades and colors of paper for electrical insulation, filter paper, saturating paper and abrasive backing paper.⁽¹⁷⁾ Manning has been reported⁽¹⁶⁾ as a manufacturer of capacitor tissue paper and therefore a potential user of PCNs.

Manning began operation in 1914 and is presently housed in a compact two story facility in downtown Green Island, New York. The facility is bordered on three sides by a crowded mixed residential and commercial district and on the fourth by a lumber yard, railroad, small stream and Interstate highway immediately to the west. The plant appeared to be in operation 24 hours a day during the sampling period.

Green Island is a small (33,000) town in the Troy, New York metropolitan area. Most of the houses and businesses appear to be much as they were 30-50 years ago. Besides Manning, which is in the center of town, Bendix Friction Materials Division, Ford (radiators), and Zak, Inc. are large industries clustered about six blocks north of Manning. Troy, to the east; Watervliet to the Southwest; and Cohoes, to the northwest; are larger cities, but similar in their appearances. The attitude of the indigenous population was such that the procurement of secure sampling locations was difficult. Both home owners and businessmen warned of the danger of theft and vandalism.

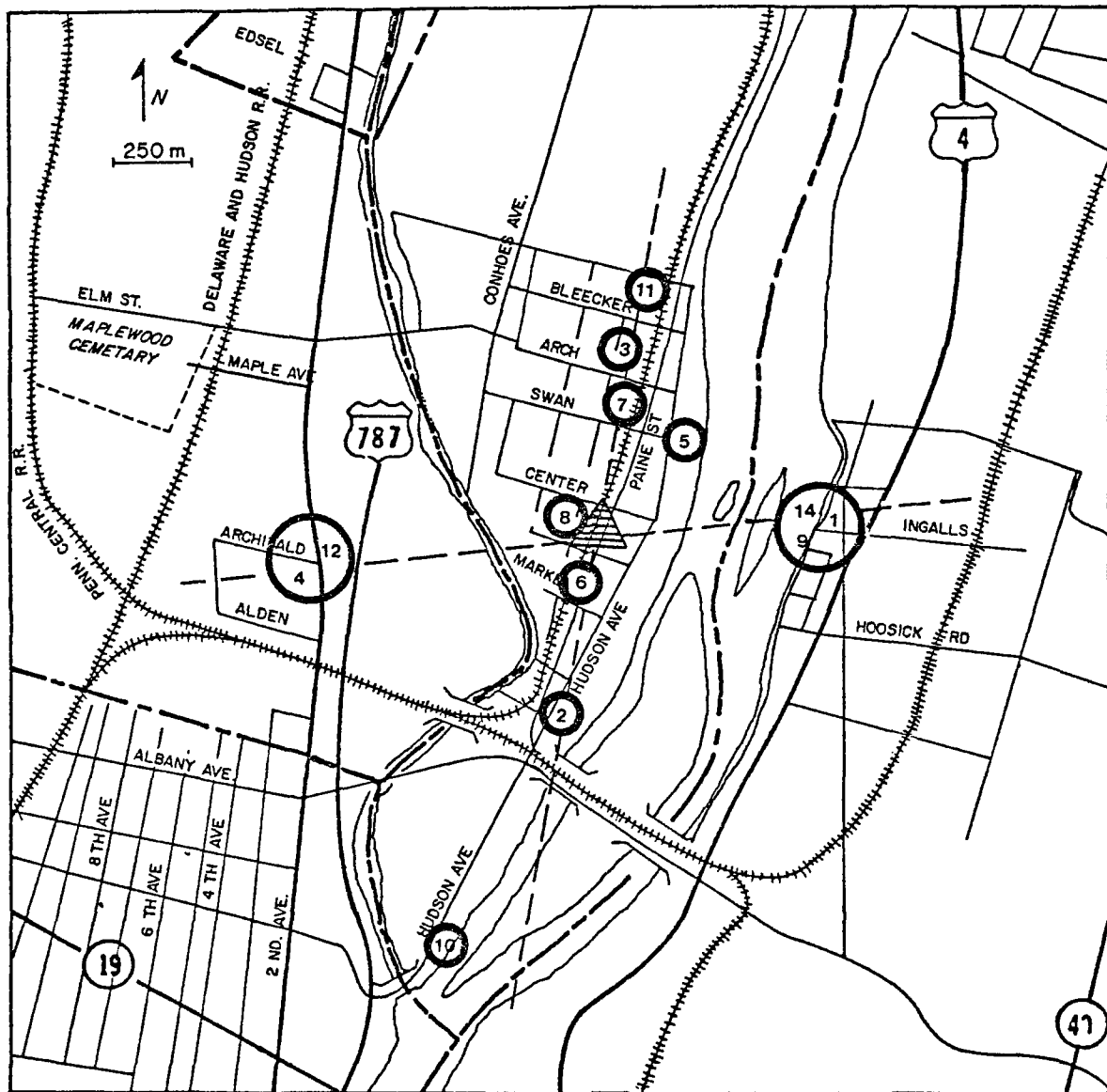


Figure 34. Map of Green Island and surrounding area with sampling locations for Manning - P1 - 11/10-11/76.



- Manning Plant Site

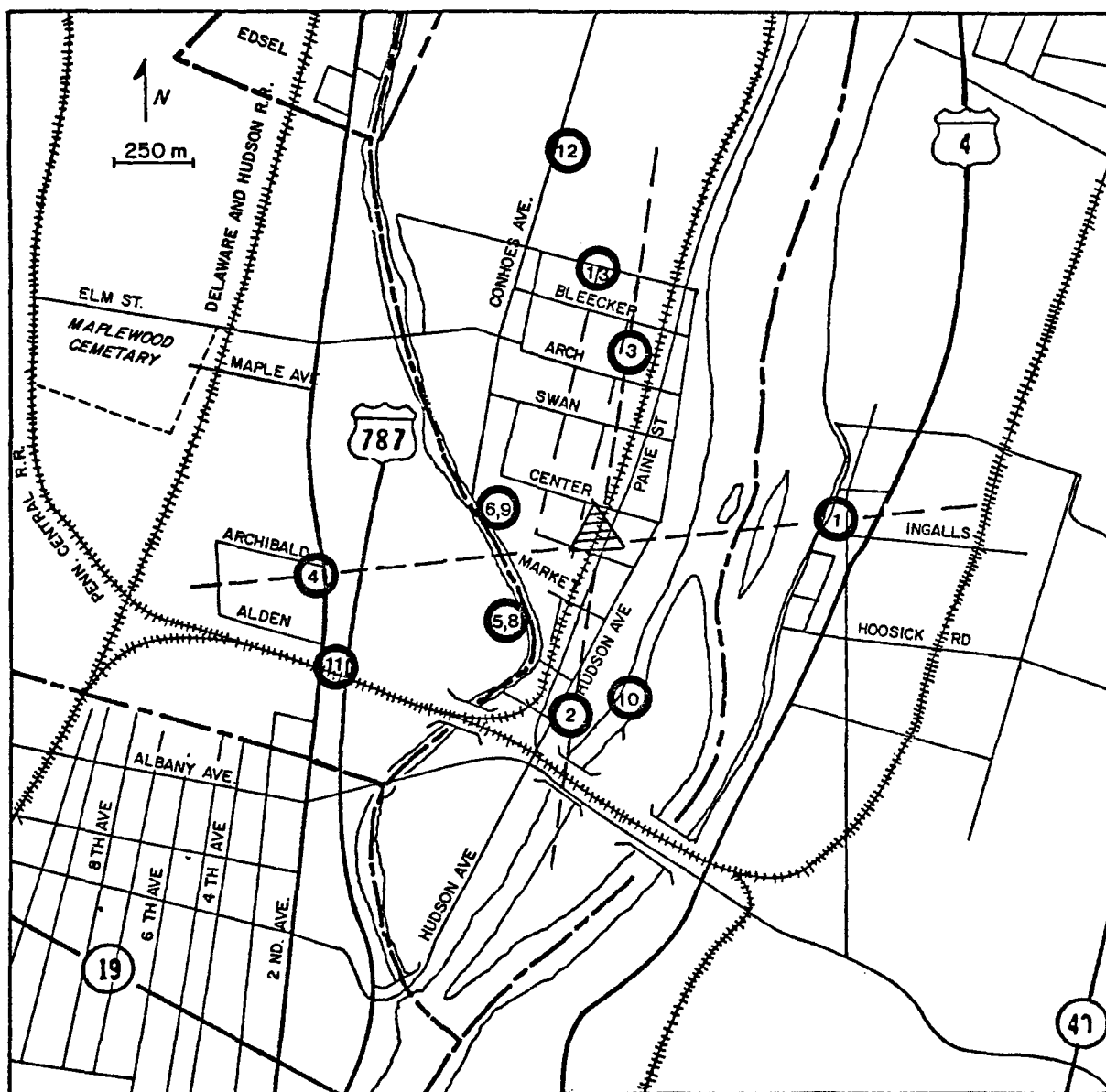


Figure 35. Map of Green Island and surrounding area with sampling locations for Manning - P2 - 11/11-12/76.



- Manning Plant Site.

5.1.1 Air

Despite initial difficulties, two 24 hour air samples was obtained along transects of the site as shown in Figures 34 and 35.⁽³⁵⁾ The air samplers were placed relatively far from the plant in order to optimize collection of emitted materials from a 50-70 m smokestack which occasionally belched forth black smoke.

The terrain of the area is generally flat, except for the Hudson, which flows in a 10 m deep channel and Interstate 787 which is 5-10 m above grade. After a 10 cm snowfall the first day (before samplers were set out), the weather was humid, overcast and calm. The temperature generally hovered slightly above freezing.

The sampling protocol data are summarized in Table 19.

5.1.2 Water

There was no evidence of sewage treatment facilities for Manning. In 1967⁽¹⁷⁾, the plant had no treatment facilities and was expected to tie into a municipal (North Albany) system when it was built. An employee of the Rensselaer County Wastewater Treatment Plant stated that Green Island was not hooked up to their plant and that he thought they dumped sewage directly into the Hudson. However, no outfalls were observed and no sign of water emission from Manning was detected.

Interval samplers were located upstream and downstream of Green Island. Upstream was near Location 1 and downstream at Rensselaer County Wastewater Treatment Plant about 3 km from Manning. One 24 hour sample was collected at each site. The only problem encountered was that the tide (1 m) came in after sampling had begun and almost inundated the samplers.

A grab water sample was taken from the west bank of the Hudson at about the middle of Green Island (downstream from Manning). Two grab water samples were obtained from the small (3 m wide) stream which marks the western boundary of Green Island. One was upstream from Manning and the other downstream. Again, no outfalls or other signs of pollution from Manning were noted, except that the stream flora appeared much denser and more varied.

Table 19. SAMPLING PROTOCOL FOR MANNING PAPER COMPANY,
GREEN ISLAND, NEW YORK.

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
11/10,11/76 P1	C1 ^a	L1	1630-1630	91,400	APCN	1-4	56-71	NW/0-1	Cloudy
		L2	1530-1530	85,900	APCN	1-4	52-91	W/0-1	slight rain in evening
		L3	1657-1555	85,800	APCN	1-4	52-91	W/0-1	snow in morning
		L4	1700-1510	82,800	APCN	1-4	50-81	C	snow in morning
	C2 ^b	L5	1545	3 cores ^c	SPCN				
		L6	1615	5 cores	SPCN				
		L7	1515	5 cores	SPCN				
		L8	1445	5 cores	SPCN				
		L9	1100	5 cores	SPCN				
		L10	1200	5 cores	SPCN				
		L11	1230	3 cores	SPCN				
		L12	1130	3 cores	SPCN				
	C3	L13	1200-2030	2.7	WPCN	1-4			
		L14	1250-2230	2.9	WPCN	1-4			
11/11,12/76 P2	C1 ^a	L1	1645-1540	85,600	APCN	-2-3	50-100	NW/0-7	Cloudy
		L2	1550-1641	92,800	APCN	-2-4	59-80	W/0-3	Cloudy
		L3	1610-1200	93,000	APCN	-3-4	51-88	W/0-3	Cloudy
		L4	1525-1728	97,300	APCN	-2-3	60-100	SW/0-3	Cloudy
	C2 ^e	L5	1100	1 ℓ	SPCN ^f				
		L6	1115	1 ℓ	SPCN ^g				
	C3 ^h C4 ^j	L7	1150	5 cores	SPCN ⁱ				
		L8	1100	1 ℓ	WPCN ^f				
		L9	1115	1 ℓ	WPCN ^g				
		L10	1115	0.95 ℓ	WPCN ^k				

(continued)

Table 19. (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (L)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
	C5	L11	1244-1309	190	AHC ^l	1.5		NE/0-3	
		L12	1157-1223	246	AHC ^m	1.5		N/0-5	
		L13	1157-1223	214	AHC ⁿ	1.5		N/0-5	strong odor of burning brake linings

^a 24 hour air samples on PUF^b Soil sampling along transects^c About 5 cm diameter, 13 cm depth^d Water samples taken at 100% sampling rate^e Grab sediment samples^f Small stream 100 m west of Manning, downstream^g Small stream 100 m west of Manning, upstream^h Grab soil samplesⁱ Representative sites around Colonie Landfill^j Grab water samples^k West bank of Hudson river, downstream from Manning^l Downwind of Manning, hopefully in plume from smokestack^m Upwind of Manning, upwind of Bendixⁿ Upwind of Manning, downwind of Bendix

Key to Sample Type: APCN - polychloronaphthalenes, air
 AHC - hydrocarbons, air
 WPCN - polychloronaphthalenes, water
 SPCN - polychloronaphthalenes, soil

5.1.3 Soil and Sediment

Three to five core samples were obtained at each of eight sites along the transects as shown in Figure 19. As nearly as possible, representative soils of each site were obtained. Multiple samples for each site were composited after return to the lab to yield eight samples for extraction and analysis.

Two sediment samples were obtained at the sites where grab water samples were collected in the stream west of Manning.

Six grab soil samples were collected at the Colonie Dump a few miles away. While this was cited by some natives as the only place where Manning would dump solid wastes, nothing at the dump was indicative of industrial paper wastes. These samples were composited in the lab to yield one sample for analysis.

5.1.4 Summary of Manning Sampling

The samples collected at Manning are summarized in Table 19. There are no subjective indications that Manning was producing PCN-impregnated paper. In fact, the plant was rather innocuous during our visit, with the exception of intermittent black smoke from the smokestack. During our upwind sampling near Bendix, there was a strong odor of burning clutch plates which is probably due to the phenolic resin being manufactured there.⁽³⁶⁾

5.2 ANALYSES

Air, soil and water were analyzed according to the procedure detailed in Appendix A.

5.3 RESULTS AND DISCUSSION

The results of sample analysis for samples collected near Manning Paper Company are summarized in Table 20.

The air samples collected contained low-to-undetectable PCN levels. Some of the values were confirmed by "double MID" GC/MS and do not appear to be artifacts. No pattern of geographic or isomeric distribution was observed. Because of the low levels found in the filter and first plug, the backup plug was not analyzed. This decision was made by the Project Officer.

Table 20. RESULTS OF ANALYSIS OF SAMPLES COLLECTED NEAR MANNING PAPER COMPANY,
GREEN ISLAND, NEW YORK.

Period ^a	Cycle ^a	Location ^a		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1	F ^c	-- ^d	--	--	--	--	--	--	--	--
			1	--	--	--	1.0	0.5	1.0	--	--	2.5 ng/m ³
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	--	1.0	0.5	1.0	--	--	2.5 ng/m ³
		L2	F	0.3	--	--	--	--	--	--	--	0.3
			1	--	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--	--
			Total	0.3	--	--	--	--	--	--	--	0.3 ng/m ³
		L3	F	--	--	0.6	0.2	--	--	--	--	0.8
			1	--	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	0.6	0.2	--	--	--	--	0.8 ng/m ³
		L3	F	--	--	0.6	--	--	--	--	--	0.6
			1	0.5	0.8	--	--	--	--	--	--	1.3
			2	0.5	--	--	--	--	--	--	--	0.5
			Total	1.0	0.8	0.6	--	--	--	--	--	2.4 ng/m ³
	C2 ^e	L5		--	--	--	--	4.9	--	--	--	4.9 µg/kg
		L6		--	--	4.6	--	--	--	--	--	4.6 µg/kg
		L7		--	2.2	9.5	11	11	--	--	--	34 µg/kg

(continued)

Table 20. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total
			$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	$C_{10}Cl_8$	
P1	C2	L8	--	--	--	4.0	--	--	--	--	4.0 µg/kg
		L9	--	--	8.1	2.0	5.2	1.8	0.9	2.3	20 µg/kg
		L10	--	--	3.6	1.6	1.3	0.4	3.2	1.4	12 µg/kg
		L11	--	--	--	--	--	--	--	--	--
		L12	--	--	--	--	--	--	--	--	--
	C3 ^f	L13	T ^g	--	--	--	--	--	--	--	T ^g
		L14	--	--	--	--	--	--	--	--	--
P2	C1 ^b	L1	F	--	--	--	--	--	--	--	--
			1	--	1.0	--	--	1.3	--	--	2.3
			2	--	--	--	--	--	--	--	--
			Total	--	1.0	--	--	1.3	--	--	2.3 ng/m ³
		L2	F	--	--	--	--	--	--	--	--
			1	--	--	--	1.8	1.3	--	--	3.1
			2	--	--	--	--	--	--	--	--
			Total	--	--	--	1.8	1.3	--	--	3.1 ng/m ³
		L3	F	--	--	--	--	--	--	--	--
			1	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--
			Total	--	--	--	--	--	--	--	--
		L4	F	0.2	--	--	T ^g	--	--	--	0.2
			1	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--
			Total	0.2	--	--	T ^g	--	--	--	0.2 ng/m ³

(continued)

Table 20. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
11/11/76 P2	C2 ^e	L5	--	0.6	--	--	--	0.4	1.1	--	2.6 µg/kg
		L6	--	--	--	--	1.1	0.7	--	--	1.8 µg/kg
	C3 ^e	L7	6.2	--	--	--	0.9	0.7	0.3	--	8.1 µg/kg
	C4 ^f	L8	--	--	--	--	--	--	--	--	--
		L9	--	--	--	--	0.2	0.1	--	--	0.3 µg/l
		L10	--	--	--	--	--	--	--	--	--

^a See Table 19 for period, cycle, and location designations in the sampling protocol.

^b Air samples

^c F = Glass fiber filter; 1 = Top PUF plug; 2 = bottom PUF plug (not analyzed at direction of Project Officer)

^d No PCN peak detected. Detection limit for air was about 0.3 ng/m³, for soil about 0.5 µg/kg, and for water about 0.2 µg/l.

^e Soil samples

^f Water samples

^g Trace

One of the three air samples collected on a Tenax GC cartridge was analyzed by GC/MS/COMP. Examination of the TIC chromatogram (Figure 36) and lack of relevant findings in the samples analyzed from other locations prompted the decision not to plot and interpret the mass spectra.

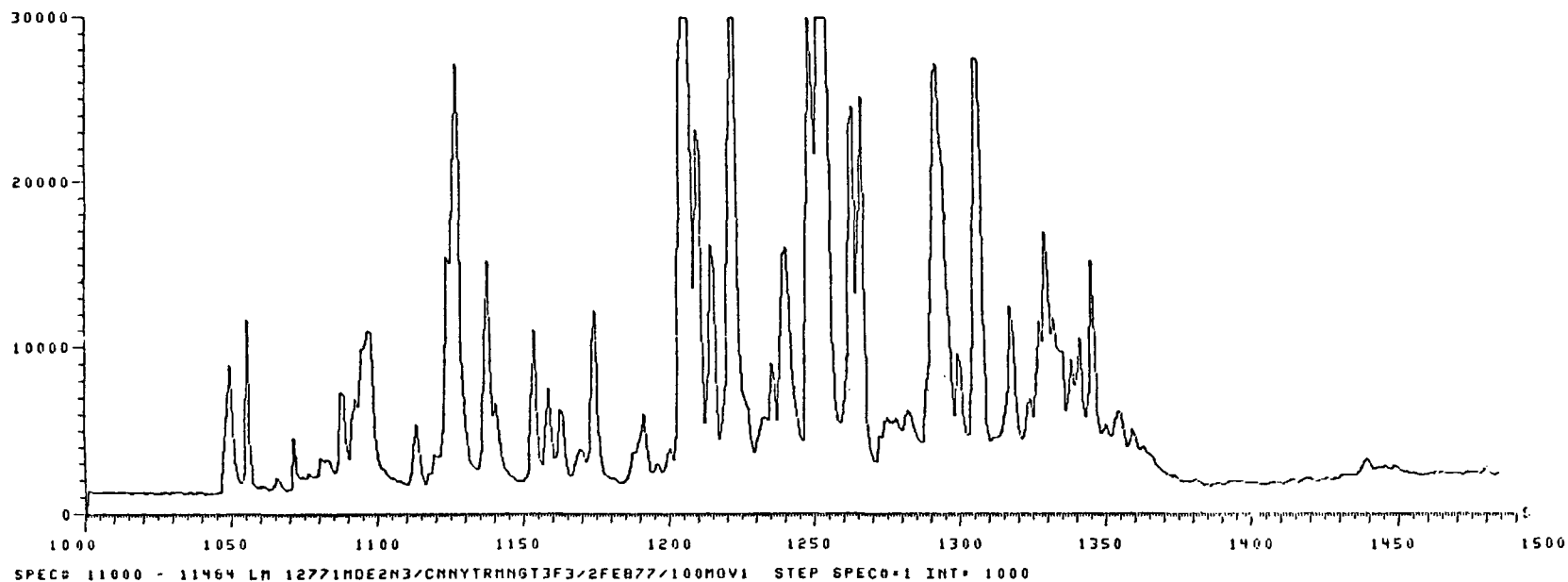


Figure 36. Total ion current chromatogram from GC/MS analysis of organics collected near Manning Paper Company, Green Island, New York (P2/C5/L11).

6.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF CORNELL DUBILIER ELECTRONICS CORPORATION, NEW BEDFORD, MASSACHUSETTS

Cornell Dubilier (CDE) has about 750 employees⁽³⁷⁾ and manufactures electronic components and capacitors. They are reported⁽³⁸⁾ to utilize PCN-impregnated paper in their processes.

The site was sampled on Saturday, November 13, 1976. A large number of cars in a small parking lot and on adjacent streets indicated the plant was operating. The plant is an old (1900-1920 vintage) three-story brick building. There are no major "industrial" features such as major plumbing or cooling towers. The plant is located on a peninsula (Figure 37)⁽³⁹⁾ called the "Ft. Area" at the south end of New Bedford. The area surrounding CDE on three sides is older residential and on one side is the mouth of the Acushnet River (at least 1 km wide, brackish water).

6.1 FIELD SAMPLING

During the sampling, the temperature was about 5°C, the wind generally from the northwest at 0-12 kmph, and the skies mostly clear. Details of samples collected are presented in Table 21.

6.1.1 Air

A faint white emission was observed from the main smokestack. An air sample was collected with a Tenax cartridge in a position on the sea wall such that the stack emission was coming down directly toward the sampler. An upwind air sample was taken at the corner of Cleveland and David Streets.

6.1.2 Soil

Six soil samples were collected from representative sites 0-5 blocks from the plant site (Figure 37). Samples were collected in a ditch, a vacant lot, the playground occupying the last half of the same block as CDE and some residential yards.

Table 21. SAMPLING PROTOCOL FOR CORNELL DUBILIER, NEW BEDFORD,
MASSACHUSETTS

Period	Cycle	Location	Sampling Time	Sampling Volume (l)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
11/13/77 P1	C1 ^a	L1	0940	1 core ^b	SPCN	5 ^c	54	NW/0-16	Clear, gusty wind
		L2	0945	1 core	SPCN				
		L3	0950	1 core	SPCN				
		L4	0955	1 core	SPCN				
		L5	1000	1 core	SPCN				
		L6	1010	1 core	SPCN				
	C2 ^d	L7	0940	1	WPCN	4.5	52	NW/0-19	
		L8	1000	1	WPCN				
	C3	L9	1008-1039	238	AHC ^e				
		L10	1047-1113	229	AHC ^f				

^aGrab soil samples

^bAbout 5 cm diameter x 13 cm depth

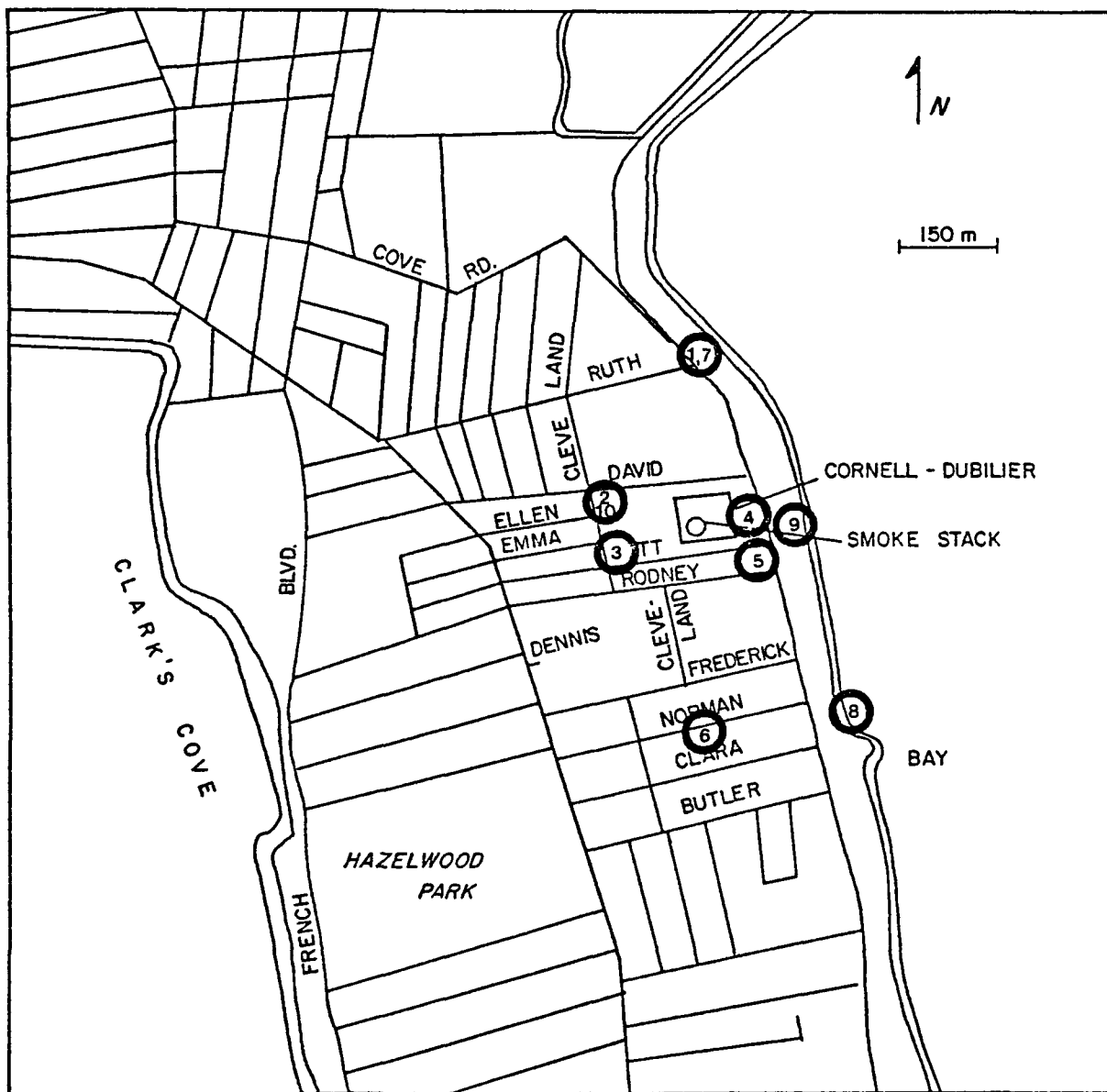
^cMeteorological conditions did not change noticeably from site to site during course of sampling, except for the wind velocity, which was gusting

^dGrab water samples

^eDownwind, in plume from smokestack, on seawall

^fUpwind

Key to Sample Type: SPCN - polychloronaphthalenes, soil
WPCN - polychloronaphthalenes, water
AHC - hydrocarbons, air



CORNELL-DUBILIER
NEW BEDFORD, MA.

Figure 37. Map of the area surrounding Cornell Dubilier, New Bedford, MA with sampling locations for P1 - 11/13/76.

6.1.3 Water

Two grab water samples were collected, one from standing water in a ditch about 300 m north of CDE and one from the brackish water at the edge of the bay. No streams or ponds were available for sampling.

6.2 ANALYSES

Soil and water samples were analyzed according to the procedures described in Appendix A. The two air samples were not analyzed.

6.3 RESULTS AND DISCUSSION

The results of the analysis of samples collected near Cornell Dubilier Electronics Corporation in New Bedford, Massachusetts are summarized in Table 25.

6.3.1 Soil

Due to the fact that CDE was a "secondary" sampling site, the six soil samples were composited into a composite sample. The PCN levels found (Table 22) were sufficient to warrant full scan GC/MS confirmation (Figure 38, Table 23). Tetra- and pentachloronaphthalene were confirmed and di- through octachlorobiphenyl were identified.

6.3.2 Water

No PCNs were found in the two water samples.

Table 22. RESULTS OF ANALYSIS OF SAMPLES COLLECTED IN THE VICINITY OF
CORNELL DUBILIER ELECTRONICS CORPORATION, NEW BEDFORD, MASSACHUSETTS

Period ^a	Cycle ^a	Location ^a	Degree of Chlorination								Total
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1-6 ^c	-- ^d	11	180	230	76	5.0	3.3	--	500 µg/kg
	C2 ^c	L7	--	--	--	--	--	--	--	--	--
		L8	--	--	--	--	--	--	--	--	--

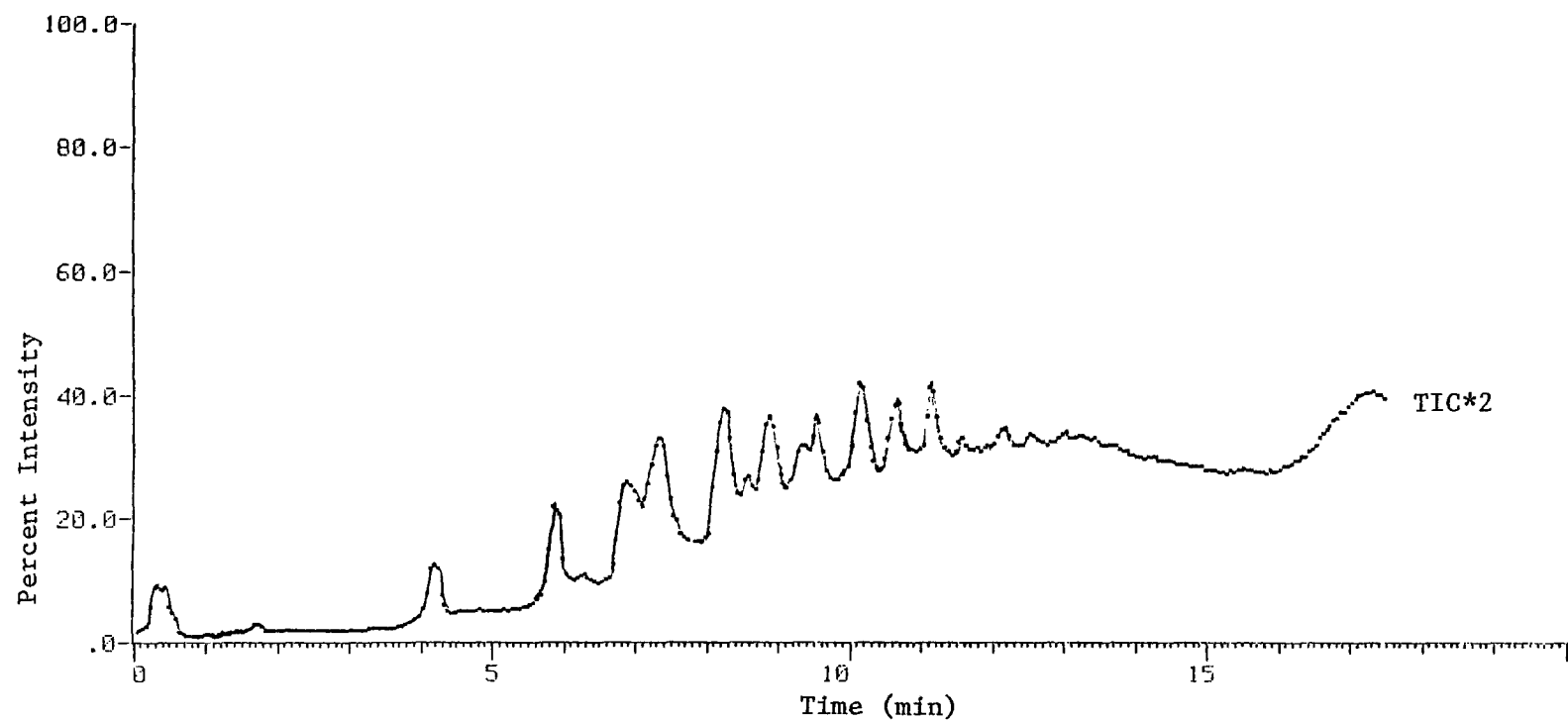
^aSee Table 21 for Period, Cycle and Location designations in the sampling protocol

^bSoil Samples

^cLocations 1-6 composited prior to sample workup

^dNo PCN peak detected. Detection limit for soil is about 0.5 µg/kg,
for water about 0.2 µg/l.

^eWater Samples



N3GSHBCD1-6.2%OV101.150*3M8*/M.-8.1.6.3-17-77

Figure 38. TIC chromatogram of GC/MS Analysis of CDE composited soil sample.

Table 23. RESULTS OF FULL SCAN GC/MS ANALYSIS OF CDE
COMPOSITED SOIL SAMPLE

Retention Time	Compound
3.34	$C_{12}H_8Cl_2$
5.74 - 5.89	$C_{12}H_7Cl_3$
6.24	$C_{10}H_4Cl_4$
6.79 - 8.54	$C_{12}H_6Cl_4$
7.29	$C_{12}H_7Cl_3 + C_{10}H_7Cl_4$
8.19 - 10.59	$C_{12}H_5Cl_5$
8.34 - 9.49	$C_{10}H_3Cl_5$
9.29 - 12.14	$C_{12}H_4Cl_6$
11.54 - 13.00	$C_{12}H_3Cl_7$
13.24	$C_{12}H_2Cl_8$

7.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF SPRAGUE ELECTRIC COMPANY, NORTH ADAMS, MASSACHUSETTS

Sprague Electric Company (Sprague), a 50 year-old company with over 1,000 employees, makes a wide variety of electrical components⁽⁴⁰⁾, including capacitors and foil.⁽¹⁶⁾ Sprague is a sprawling complex of old multi-story buildings in the center of town. On the main site are 5-10 buildings of varying size, the largest being three stories tall and over 100 m long. A second site ("Brown St. Plant"), two or three blocks west, consists of a single, large three story building, and a third site, about 1.5 km east is a large brick structure with five stories. All buildings appear to be at least 50 years old.

North Adams is a small city (20,000) in the Northwestern Massachusetts mountains. The city is in a deep, narrow valley running east-west, with a branch valley running south.

We sampled the site on Sunday, November 14, 1976 (see Table 24). There were less than five cars at each site, indicating the plant was not operating. No fumes, or other signs of activity were noted.

7.1 FIELD SAMPLING

7.1.1 Soil

Eleven soil samples were collected at various sites around Sprague as shown in Figures 39 and 40.⁽⁴¹⁾ A series of five samples were obtained in an array around the two plant sites downtown. Four soils were taken along transects at least 1 km from the plant. Two soil samples were taken near the plant on the east edge of town. Since Sprague was reported to dispose of their solid waste at the city landfill⁽⁴²⁾, one soil sample was taken at the landfill. No particular evidence of electrical manufacturing waste was observed.

Table 24. SAMPLING PROTOCOL FOR SPRAGUE ELECTRIC COMPANY,
NORTH ADAMS, MASSACHUSETTS.

Period	Cycle	Location	Sampling Time	Sampling Volume (l)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./Speed (kmph)	Other
11/14/76 P1	C1 ^a	L1	1420	1 core ^b	SPCN	6 ^c	43	W/O-16	Clear
		L2	1430	1 core	SPCN				
		L3	1440	1 core	SPCN				
		L4	1450	1 core	SPCN				
		L5	1455	1 core	SPCN				
		L6	1545	1 core	SPCN				
		L7	1630	1 core	SPCN				
		L8	1640	1 core	SPCN				
		L9	1705	1 core	SPCN				
	C2 ^d	L10	1500	1 core	SPCN				
		L11	1505	1 core	SPCN				
	C3 ^e	L12	1610	1 ^f	SPCN				
	C4	L13	1500	0.90	WPCN ^g				
		L14	1510	0.80	WPCN ^h				
		L15	1700	0.75	WPCN ⁱ				
		L16	1715	0.95	WPCN ^j				

^aSamples were taken along a transect of the main Sprague plant, as shown on the map.

^bAbout 5 cm diameter x 13 cm depth

^cDuring the sampling period, meteorological conditions were constant, except variable wind speed.

^dSamples were taken near Sprague plant on east edge of North Adams

Key to Sample Type: SPCN - polychloronaphthalenes, soil
WPCN - polychloronaphthalenes, water

^eLandfill, 5 km south of city

^fRepresentative soil collected

^gUpstream of all Sprague activity

^hDownstream of East plant, upstream of two downtown sites

ⁱDownstream of all Sprague plants, upstream of sewage plant outfalls

^jDownstream of Sprague plants and sewage plant outfall

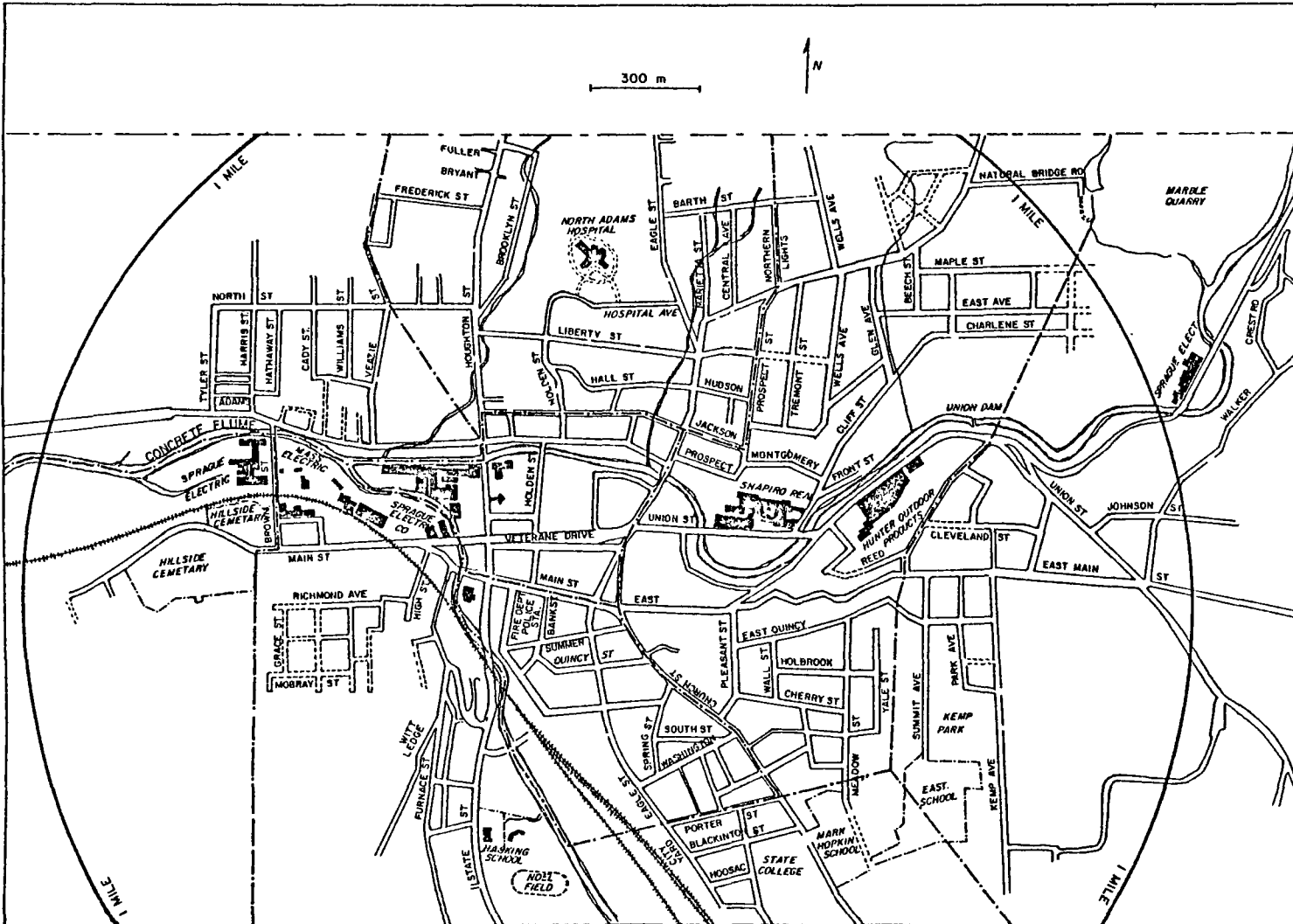


Figure 39. Map of the area surrounding Sprague Electric with Sampling Locations for P1 - 11/14/76.

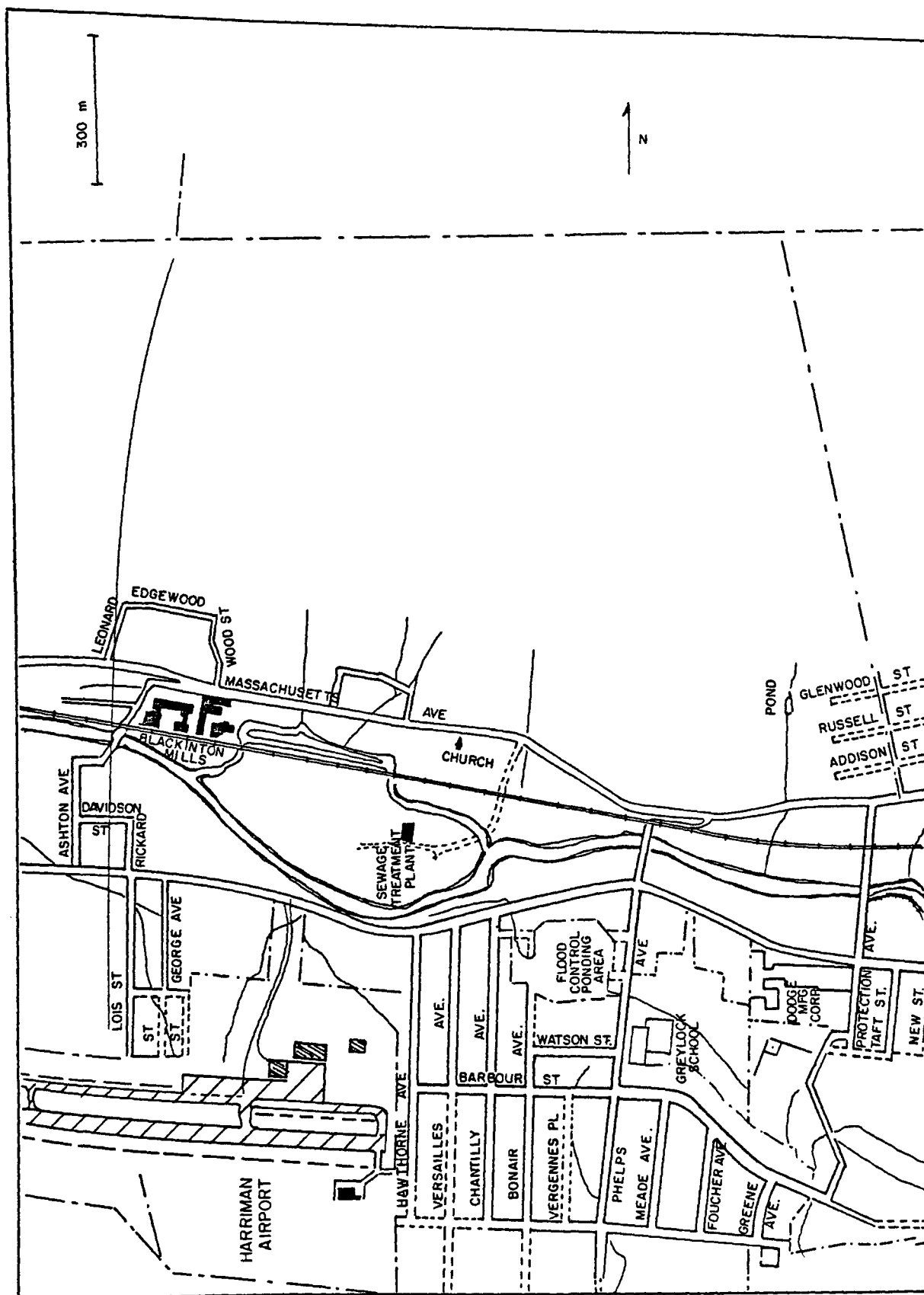


Figure 40. Map of the area to the west of Sprague Electric with sampling locations for P1 - 11/14/76.

7.1.2 Water

Four grab water samples were collected. One sample was obtained upstream of all Sprague sites (near the east plant location). A second sample, taken downstream of the eastern plant, served as the upstream sample for the two downstream sites. A third sample was obtained downstream of the downtown plants, but upstream of the sewage plant. A fourth sample was obtained downstream of the sewage plant.

No major effluent sources were noted, although two small (<10 cm) pipes drain from the main plant directly into an adjacent concrete flume (Hoosic River). It should be noted that Sprague's discharge situation is uncertain. Although reportedly⁽⁴³⁾ they discharge aluminum sulfates, their discharge permit application is being processed. In addition, the sewage system was about one or two weeks away from changeover from the old plant at North Adams to a newly constructed plant in Williamstown.⁽⁴³⁾

7.1.3 Summary of Sprague Sampling

The three large smokestacks at the main plant site were virtually idle (one stack was faintly emitting during the presampling site visit on October 26, 1976). No fugitive emissions were visible during either visit. Three local passersby said there was no smell or pollution from Sprague.

7.2 ANALYSES

Soil and water samples were analyzed according to the procedures detailed in Appendix A.

7.3 RESULTS AND DISCUSSION

The results of the analysis of samples collected near Sprague Electric Company in North Adams, Massachusetts are summarized in Table 25.

7.3.1 Soil

Due to the fact that Sprague was a "secondary" sampling site the 12 soil samples were composited into two composite samples representing six locations each (L1-L6 and L7-L12). The PCN levels found (Table 25) were judged sufficient to attempt full scan data on one of the samples, as shown in Figure 41 and Table 26. High background and low PCN levels prevented identification, although $C_{10}H_4Cl_4$ was tentatively identified at 7.09 minutes.

7.3.2 Water

No PCNs were found in the water samples.

Table 25. RESULTS OF ANALYSIS OF SAMPLES COLLECTED IN THE VICINITY
OF SPRAGUE ELECTRIC COMPANY, NORTH ADAMS, MASSACHUSETTS

Period ^a	Cycle ^a	Location ^a	Degree of Chlorination								Total
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1-6 ^c	-- ^d	--	9.4	18	8.7	4.5	3.8	--	44 ng/kg
		L7-12 ^d	--	--	13	25	12	1.2	--	--	52 ng/kg
	C4 ^e	L13	--	--	--	--	--	--	--	--	--
		L14	--	--	--	--	--	--	--	--	--
		L15	--	--	--	--	--	--	--	--	--
		L16	--	--	--	--	--	--	--	--	--

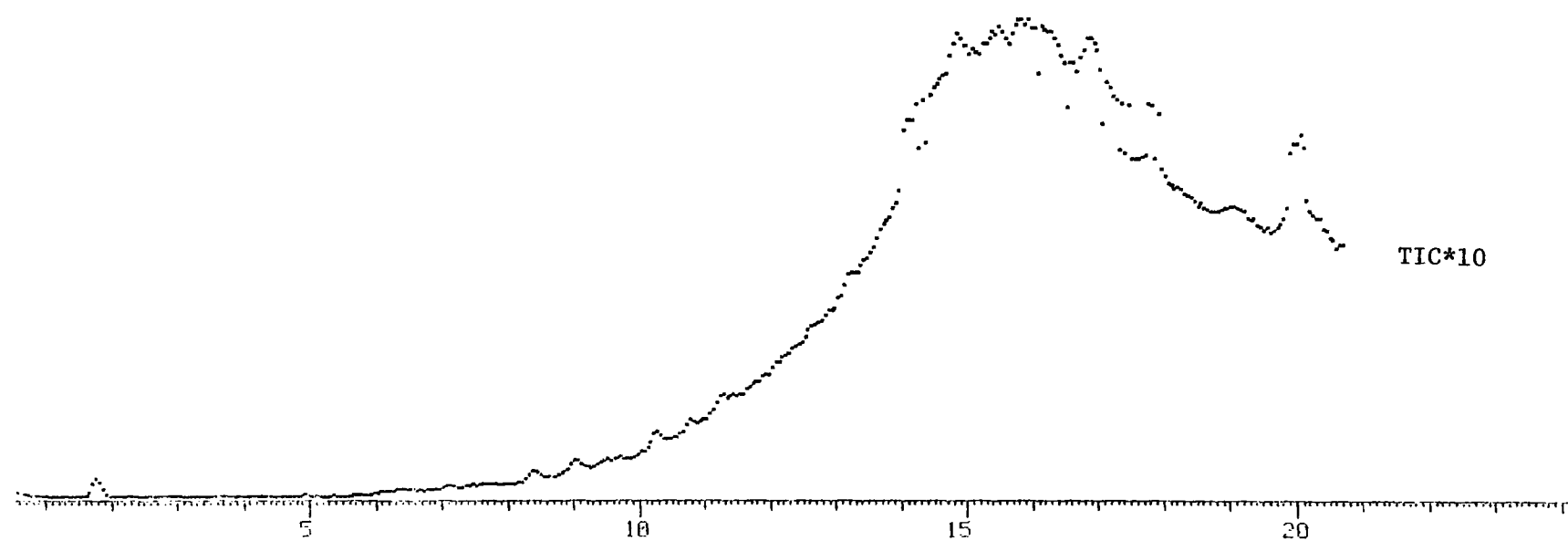
^aSee Table 24 for Period, Cycle and Location designations in the sampling protocol

^bSoil samples

^cLocations 1-6 and 7-12 composited into two samples prior to workup

^dNo PCN peak detected. Detection limit for soil is about 0.5 µg/kg, for water about 0.2 µg/l

^eWater samples



H4GSHASE1-6.2%OV101, 150*3MS*/M. -8.1.6.03-17-77

Figure 41. TIC chromatogram of GC/MS analysis of Sprague
composited soil sample (P1/C1/L1-6).

Table 26. RESULTS OF FULL SCAN GC/MS ANALYSIS OF SPRAGUE
COMPOSITED SOIL SAMPLE (P1/C1/L1-6)

Retention Time	Compound
7.09 - 8.39	$C_{12}H_6Cl_4$
7.09	$C_{10}H_4Cl_4$ (tent.)
9.04 - 10.24	$C_{12}H_5Cl_5$
10.24 - 11.19	$C_{12}H_4Cl_6$

8.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF GENERAL ELECTRIC COMPANY, FORT EDWARD, NEW YORK

General Electric (GE) operates two large capacitor plants in Hudson Falls, New York and Ft. Edward, New York. The plants, although in different villages, are only about 1 km apart. General Electric Company, Electronic Components, Capacitor Department employs 1,883 people distributed between the two plants in New York and a third in Lansing, North Carolina. Both plants appeared to operate two shifts daily, with a third shift for cleanup and maintenance according to local sources.

The Ft. Edwards plant (GE-FE), a relatively new facility (probably post-World War II), spreads over a site about 500 x 800 m and manufactures small capacitors, primarily for use in automobiles.⁽³⁶⁾ Several additions are apparent and, in fact, an addition at the southwest corner of the site was being started during our visit. This is reportedly a treatment plant to handle PCBs.⁽³⁶⁾

The vicinity of GE-FE was sampled on November 15-17, 1976. Nine air, five water, 18 soil, and two miscellaneous samples were collected. The sampling protocol is summarized in Table 27.

8.1 FIELD SAMPLING

8.1.1 Air

Four air sampling sites were selected on a transect and two 24 hour samples collected at each site (Figures 42 and 43).⁽⁴³⁾ Since there was no large smokestack, any emissions would most likely be fugitive. Therefore, sampling sites were selected fairly close to the plant.

Table 27. SAMPLING PROTOCOL FOR GENERAL ELECTRIC, FT. EDWARDS, NY.

Period	Cycle	Location	Sampling Time	Sampling Volume (l)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
11/15/76	C1 ^a	L1	0850-0914	90,800	APCN	-7-7 ^b	50-100	Variable, 0-3	Ranging from clear to overcast
		L2	0855-0930	91,800	APCN				
		L3	0907-0852	89,200	APCN				
		L4	0850-0947	93,200	APCN				
	C2 ^c	L5	1430	3 cores ^d	SPCN				
		L6	1240	4 cores	SPCN				
		L7	1400	3 cores	SPCN				
		L8	1200	3 cores	SPCN				
		L9	1500	3 cores	SPCN				
		L10	1000	3 cores	SPCN				
		L11	1530	3 cores	SPCN				
		L12	1215	4 cores	SPCN				
	C3 ^e	L13	1425-1630	4.0	WPCN ^f				
		L14	1512-1620	3.1	WPCN ^g				
	C4 ^h	L15	1130	1	WPCN ⁱ				strong odor of kerosene
		L16	1240	1	WPCN ^j				
		L17	1500	1	WPCN ^k				
	C5	L18	1600-1628	225	AHC ^l				

(continued)

Table 27. (cont'd)

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
11/16,17/76 P2	C1 ^a	L1	0926-1049	94,800	APCN	-5-6 ^b	51-89	NW/0-10	Variable, clear to overcast
		L2	0943-0912	87,700	APCN				
		L3	0909-0853	88,700	APCN				
	C2 ^m	L4	1245	~0.5	SPCN ⁿ				
		L5	1247	?	SPCN ^o				
		L6	1530	5 cores	SPCN ^p				
		L7	1535	~0.5	SPCN ^q				
		L8	1600	2 cores	SPCN ^r				
	C3 ^s	L9	1540		MPCN ^t				
		L10	1530	3 rolls	MPCN ^u				
		L11	1550	1 ℓ	MPCN ^v				
	C4 ^h	L12	1245	1 ℓ	WPCN ⁱ				
		L13	1530	1 ℓ	WPCN ^w				
		L14	1605	1 ℓ	WPCN ^x				
		L15	1600	1 ℓ	WPCN ^y				

Key to Sample Type: APCN - polychloronaphthalenes, air
 AHC - hydrocarbons, air
 WPCN - polychloronaphthalenes, water
 SPCN - polychloronaphthalenes, soil
 MPCN - polychloronaphthalenes, miscellaneous

Table 27. (cont'd)

- ^a24 hour air samples on polyurethane foam
- ^bMeteorological conditions monitored at centrally located MRI weather station. There were no perceptible local variations.
- ^cSoil samples collected along transects
- ^dAbout 5 cm diameter x 13 cm depth
- ^e24 hour water samples using interval samplers
- ^fUpstream of both GE-FE and GE-HF plants. Collection tubing froze up overnight, probably several hours of collection lost.
- ^gDownstream of both GE-FE and GE-HF plants. Collection tubing froze up overnight, probably several hours of collection lost.
- ^hGrab water samples
- ⁱCollected from GE-FE outfall into Hudson River
- ^jCollected in slough about 20 m from southwest corner of GE-FE fence
- ^kDownstream from GE-FE and GE-HF near downstream interval sampler. Green floating solid in the river was collected.
- ^lSample collected on bluff above GE-FE outfall (see footnote "i")
- ^mGrab soil samples
- ⁿSediment from edge of Hudson River about 50 m downstream from GE-FE outfall
- ^oBeige slime in GE-FE outfall. Sample scraped from rocks, leaves, etc.
- ^pCollected in valley about 10 m below old Ft. Edwards dump
- ^qCollected from capacitor-dumping area on top of old Ft. Edwards dump
- ^rCollected near capacitor dumping areas in new Ft. Edwards dump
- ^sMiscellaneous samples
- ^tSome water, foil, and paper chopped out of an open large capacitor
- ^uUnburned rolls of paper - probably capacitor paper
- ^vRepresentative small capacitor
- ^wCollected from 50 cm wide stream directly below (20 m) old Ft. Edwards dump
- ^xCollected from stream about 1 km west of old Ft. Edwards dump just above influence into Hudson River. Probably contains runoff from old Ft. Edwards dump
- ^yCollected from pond at new Ft. Edward landfill

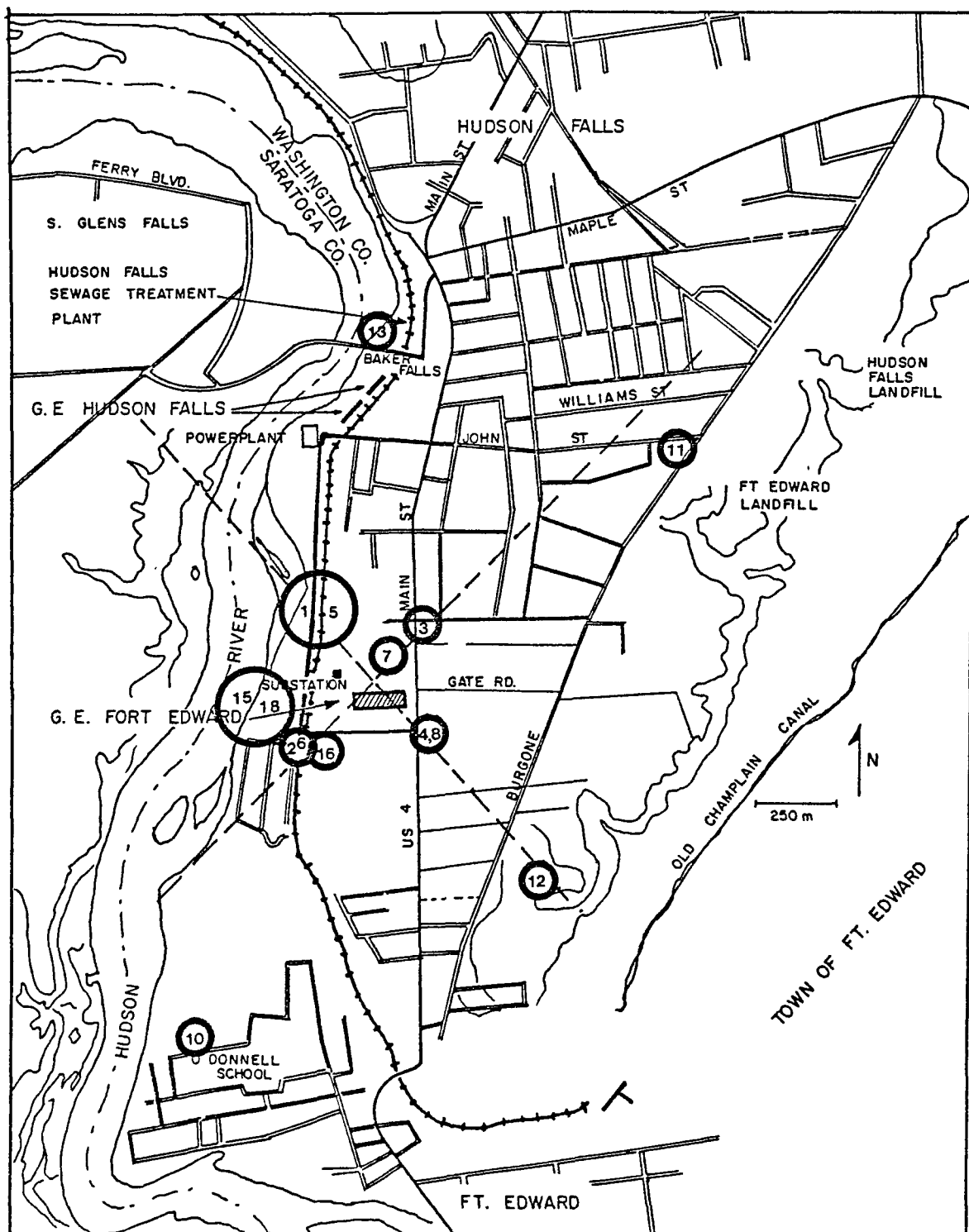


Figure 42. Map of the area surrounding General Electric - Ft. Edwards with sampling locations for P1 - 11/15-16/76.

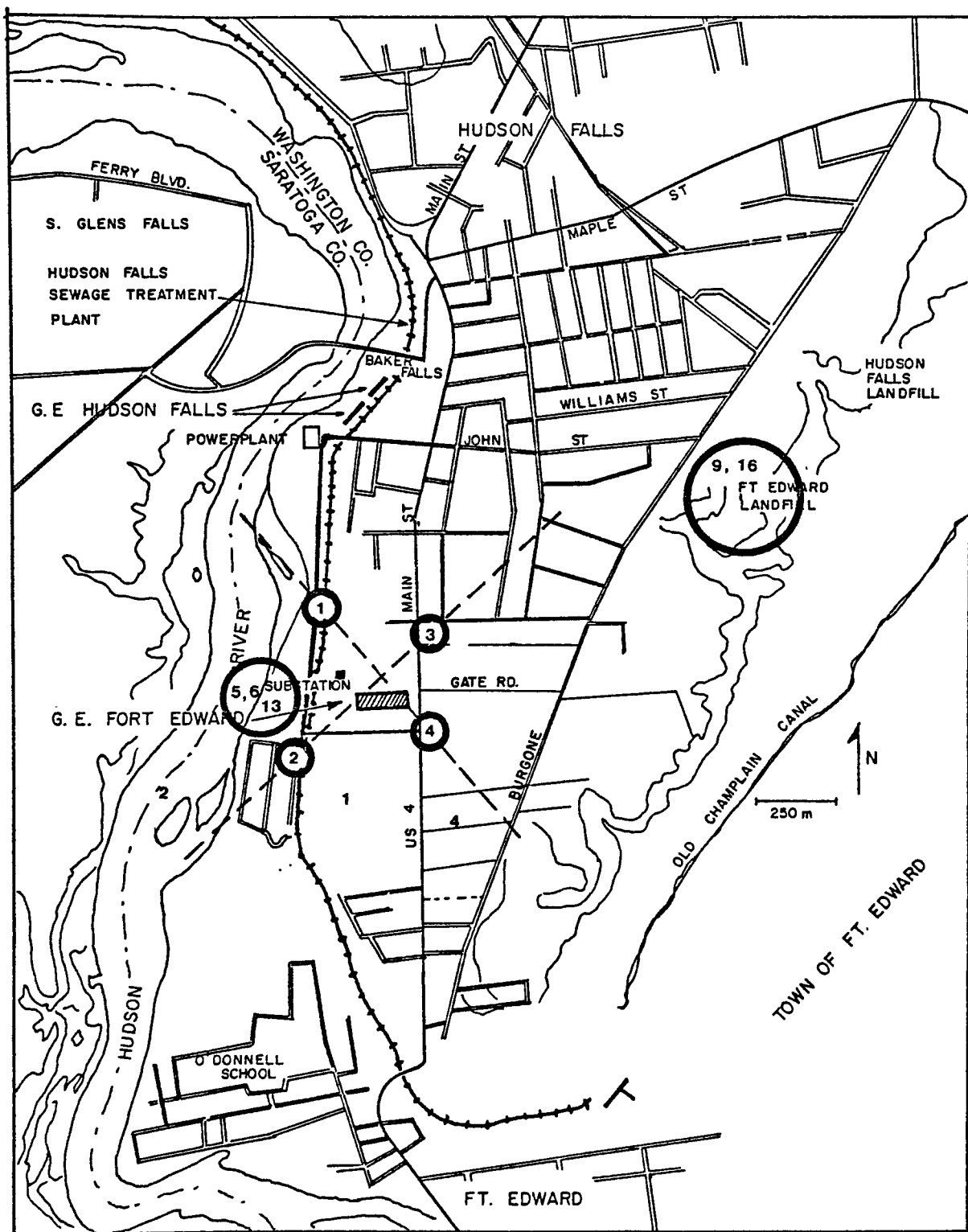


Figure 43. Map of the area surrounding General Electric - Fort Edwards with sampling locations for P2 - 11/16-17/76.

8.1.2 Soil

Three to five samples were collected at each of eight sites (a near and far site along each transect) as shown in Figure 42. An attempt was made to obtain soil samples representative of each site. The samples were composited upon return to the lab to yield eight samples for analysis.

8.1.3 Miscellaneous

Several grab soil samples were collected at three dump sites in the area (these could be considered to be either the Ft. Edwards or Hudson Falls site).

A visit to the old Ft. Edwards dump about 8 km south of town was very interesting. This dump was reportedly used from 1953-65 by GE for disposal of their solid wastes.⁽³⁶⁾ It is not currently used for any type of dumping. Hundreds of capacitors (assumedly) slightly smaller than a pack of cigarettes were strewn in several spots around the site. In one spot a dozen or more large (60 x 40 x 10 cm) capacitors were seen. A composite soil was taken downhill of the dump and another from the top near where many small capacitors lay.

A grab water sample was collected from a small (50 cm wide) stream flowing below the dump. Another water sample was taken from a stream (presumed to be the same stream) where it flowed into the Hudson.

The dump had been burned over, leaving small unburned rolls of paper. Since these were unburnable, it was supposed that they may be PCN-impregnated. A representative sample was collected. A sample of water, paper, and foil were collected from an open large capacitor. A small capacitor was also collected.

The new Ft. Edwards landfill was reportedly used by GE to dispose of solid waste from 1954 to 1975.⁽³⁶⁾ Again, both large and small capacitors were observed. Two representative samples of soil were obtained.

The Hudson Falls landfill was reportedly used by GE to dispose of solid waste from 1969-1975.⁽³⁶⁾ No samples were taken from this site.

8.1.4 Water

Because of the extremely steep bluffs overlooking the Hudson and the lack of electrical power near the river, a suitable sampling site between

the GE-FE and GE-HF plant could not be located. Therefore, we collected water samples from one site upstream and one downstream of both plants as shown in Figures 42 and 43. An upstream sample was collected near the Hudson Falls Sewage Treatment Plant, about 500 m upstream (north) of GE-HF. The river bank was about 10 m high and steep enough that a rope was a necessary aid in climbing up and down the bank. The downstream sample was collected under a highway bridge in Ft. Edwards. This location was the first available sampling site downstream. It was about 3 km south of GE-FE. During our first attempt at obtaining an integrated 24 hour sample, the Teflon lines froze on both samplers. Since subsequent nights were also well below freezing, samples were collected for 12.5 hours during above-freezing daylight hours.

8.1.5 GE-FE Discharge

Two grab water samples were collected on separate days from the outfall of the GE-FE discharge into the Hudson. This outfall was an 80-100 cm pipe which gushed forth a milky effluent with the distinct and overpowering odor of kerosene or turpentine. A sample of a beige slime which covered the rocks in the outfall, was collected, along with attached rocks, leaves, etc. A sample of the river sediment was collected about 30 m downstream from the discharge.

8.1.6 Summary of GE-FE Sampling

Subjectively, this site does not appear to be a "dirty" industry. Nearby residents complained of a glowing red emission from the stacks late at night, but we never observed this. One major exception to our impression of the site was the very foul discharge into the Hudson. The vapors were so dense at the outfall that eye glasses of the person collecting the samples steamed over, he became faint, and developed a headache. The only difficulty encountered was that of obtaining integrated water samples.

8.2 ANALYSES

Air, soil and water samples were analyzed by the procedures detailed in Appendix A. The grab water samples (P1/C4/L15, P1/C4/L16 and P1/C4/L17) were analyzed by the VOA procedure detailed in Section III.

8.3 RESULTS AND DISCUSSION

The analysis of samples collected at GE-FE are summarized in Table 28. Only low-to-undetectable amounts of PCN were found in these samples. One exception to this conclusion is a sample collected down an embankment below the old Ft. Edward dump. This sample (P2/C2/L7) contained appreciable amounts of most PCN isomers, indicating that these substances may be leaching from the materials in the dump.

8.3.1 Air Samples Collected on Tenax

Sample P1/C5/L18 from GE-FE, collected on a bluff above the outfall from the plant, was found to contain a large number of compounds as evidenced by the TIC chromatogram as shown in Figure 44. Mass spectra numbers 2240-2420 were plotted and interpreted (Table 29). Although the mass spectra were not interpreted in detail, the sample contains primarily hydrocarbons and alkyl aromatics, presumably kerosene components. No PCNs were detected.

8.3.2 Volatile Organics in Water

Three grab water samples collected at the outfall were purged for volatile organic analysis (VOA) and analyzed by GC/MS/COMP using the Varian CH-7. The TIC chromatograms are presented in Figures 45-47. Since the composition of these samples appeared similar to that found in the air sample taken on the bluff above the outfall [(P1/C5/L18), Figure 44], these samples were not interpreted.

Table 28. RESULTS OF ANALYSIS OF SAMPLES COLLECTED NEAR
GENERAL ELECTRIC COMPANY, FORT EDWARDS, NEW YORK

Period ^a	Cycle ^a	Location ^a		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1	F ^c	0.3	-- ^d	--	--	--	--	--	--	0.3
			1	--	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--	--
			Total	0.3	--	--	--	--	--	--	--	0.3 ng/m ³
		L2	F	--	--	--	--	--	--	--	--	--
			1	--	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	--	--	--	--	--	--	--
		L3	F	--	--	1.8	1.4	0.6	--	--	--	3.8
			1	--	--	2.0	1.5	--	--	--	--	3.5
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	3.8	2.9	0.6	--	--	--	7.3 ng/m ³
		L4	F	--	--	--	--	--	0.3	--	--	0.3
			1	--	--	--	--	1.8	1.3	1.5	--	4.6
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	--	--	1.8	1.6	1.5	--	4.9 ng/m ³
	C2 ^e	(L5) — beige slimes in outfall		--	--	--	2.5	4.8	--	--	--	7.3 µg/kg
		L6		--	--	--	--	--	--	--	--	--
		L7		1.6	--	--	5.1	--	--	--	--	6.7 µg/kg
		(L8) — new A.E. capacitor dump		--	--	--	--	--	--	--	--	--
		L9		0.3	0.1	--	--	--	--	0.6	1.4	2.4 µg/kg

(continued)

Table 28. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total
			$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	$C_{10}Cl_8$	
P1	C2	L10	--	--	--	--	--	--	--	--	--
		L11	--	--	--	--	--	--	--	--	--
		L12	--	--	--	--	--	--	--	--	--
	C3 ^f	L13	--	--	--	--	--	--	--	--	--
		L14	--	--	--	--	--	--	--	--	--
	C4 ^g	L15	3.6	1.2	--	0.7	--	--	--	--	5.5 µg/l
		L16	--	--	--	--	--	--	--	--	--
P2	C1 ^b	L17	--	0.6	--	--	--	--	--	--	0.6 µg/l
		L1	F	--	--	--	--	--	--	--	--
			1	--	--	--	--	--	--	--	--
			2	1.0	--	--	--	--	--	--	1.0
			Total	1.0	--	--	--	--	--	--	1.0 ng/m ³
		L2	F	--	--	--	--	--	1.0	2.9	3.9
			1	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--
			Total	--	--	--	--	--	1.0	2.9	3.9 ng/m ³
		L3	F	--	--	--	--	--	--	--	--
			1	--	--	--	--	--	--	--	--
			2	--	--	--	--	--	--	--	--
			Total	--	--	--	--	--	--	--	--

(continued)

Table 28. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total	
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈		
P2	C1 ^b	L4	F	--	--	--	--	--	--	--	--	--
			1	--	--	--	--	--	--	--	--	
			2	--	--	--	--	--	--	--	--	
			Total	--	--	--	--	--	--	--	--	
	C2 ^e	L7	old P.P. E capaci for dump	1.0	1.7	6.6	3.0	4.5	2.4	2.2	--	21 µg/kg
			L9	--	--	0.3	--	--	--	--	--	0.3 µg/kg
	C4 ^g	L13	stream below old dump	--	2.6	--	--	--	--	--	--	2.6 µg/l
			L14	--	--	--	--	--	--	--	--	--
			L15	--	--	--	--	--	--	--	--	--
			L16	--	--	--	--	--	--	--	--	--

^aSee Table 27 for Period, Cycle and Location designations in the sampling protocol

^b24 hour air samples collected on polyurethane foam and glass fiber filter

^cF = Glass fiber filter; 1 = Top PUF plug; 2 = bottom PUF plug (not analyzed as per directions from Project Officer).

^dNo PCN peak detected. Detection limit for air is about 0.3 ng/m³, soil about 0.5 µg/kg and water about 0.2 µg/l.

^eSoil samples

^f24 hour water samples

^gGrab water samples.

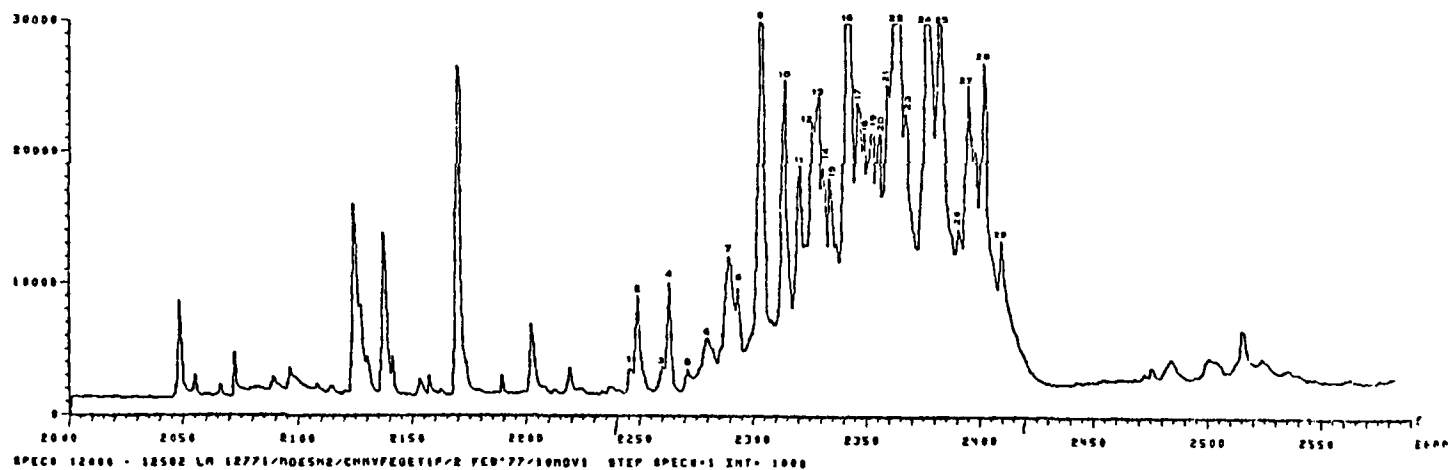


Figure 44. Gas chromatography/mass spectroscopic analysis of air samples collected above water outfall at General Electric Company, Ft. Edwards, New York (P1/C5/L18).

Table 29. COMPOUNDS IDENTIFIED IN AIR ABOVE OUTFALL
AT GENERAL ELECTRIC COMPANY, FT. EDWARDS, NEW YORK

Chromatographic Peak No.	Compound
1	C ₂ -alkyl benzene
2	C ₂ -alkyl benzene
3	C ₂ -alkyl benzene
4	C ₃ -alkyl benzene
7	C ₃ -alkyl benzene
8	C ₃ -alkyl benzene
9	C ₁₀ H ₂₂
9a	C ₄ -alkyl benzene
10	C ₁₁ H ₂₄
11	C ₁₁ H ₁₆
14	C ₁₀ H ₁₆
15	C ₁₁ H ₂₄
16	C ₅ -alkyl benzene
16a	C ₁₂ H ₂₆
22	C ₁₂ H ₂₆
24	C ₁₂ H ₂₆
23-29	C ₁₃ -alkane isomers

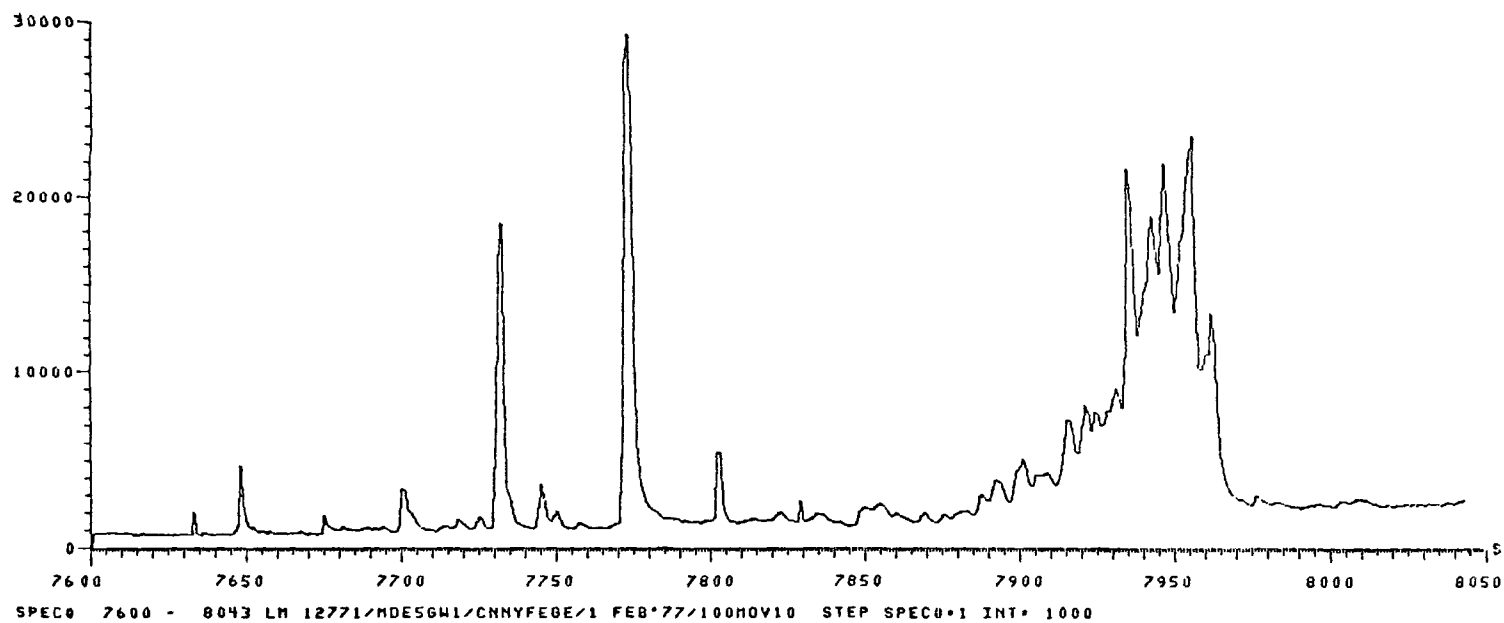


Figure 45. Total ion current chromatogram from gas chromatography/mass spectroscopic analysis of organics purged from water samples collected in outfall stream near General Electric Company, Ft. Edward, New York (P1/C4/L15).

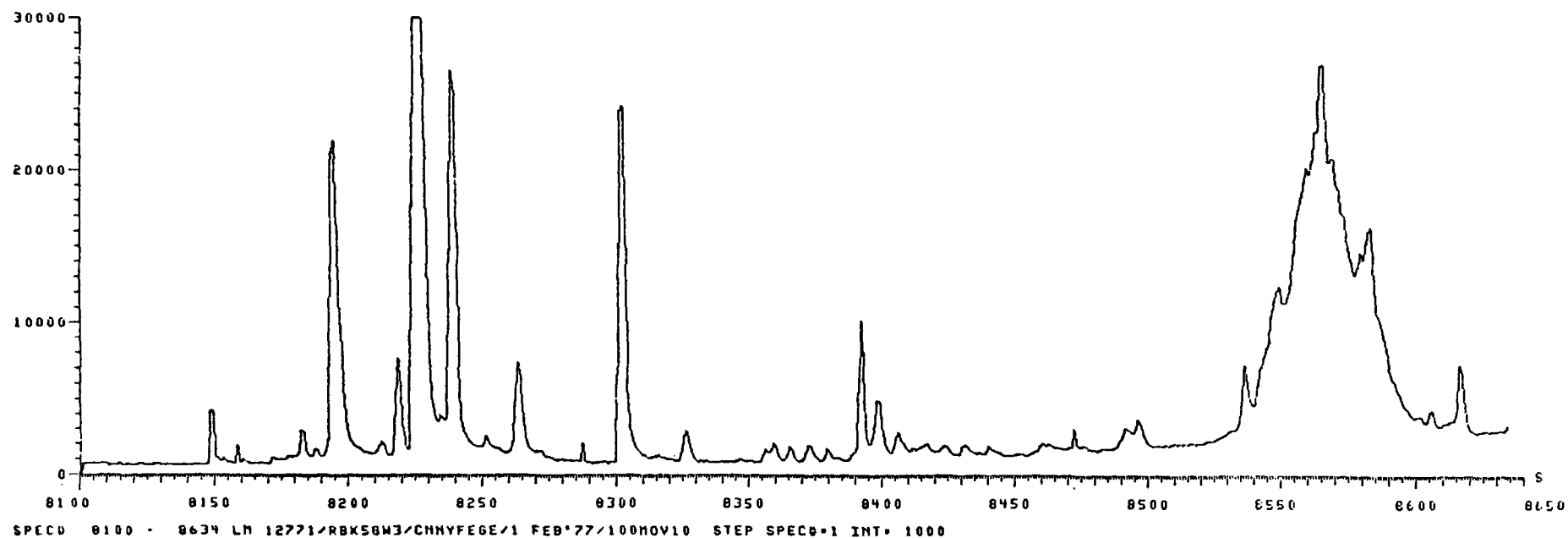


Figure 46. Total ion current chromatogram from gas chromatography/mass spectroscopic analysis of organics purged from water samples collected in outfall stream near General Electric Company, Ft. Edward, New York (P1/C4/L14).

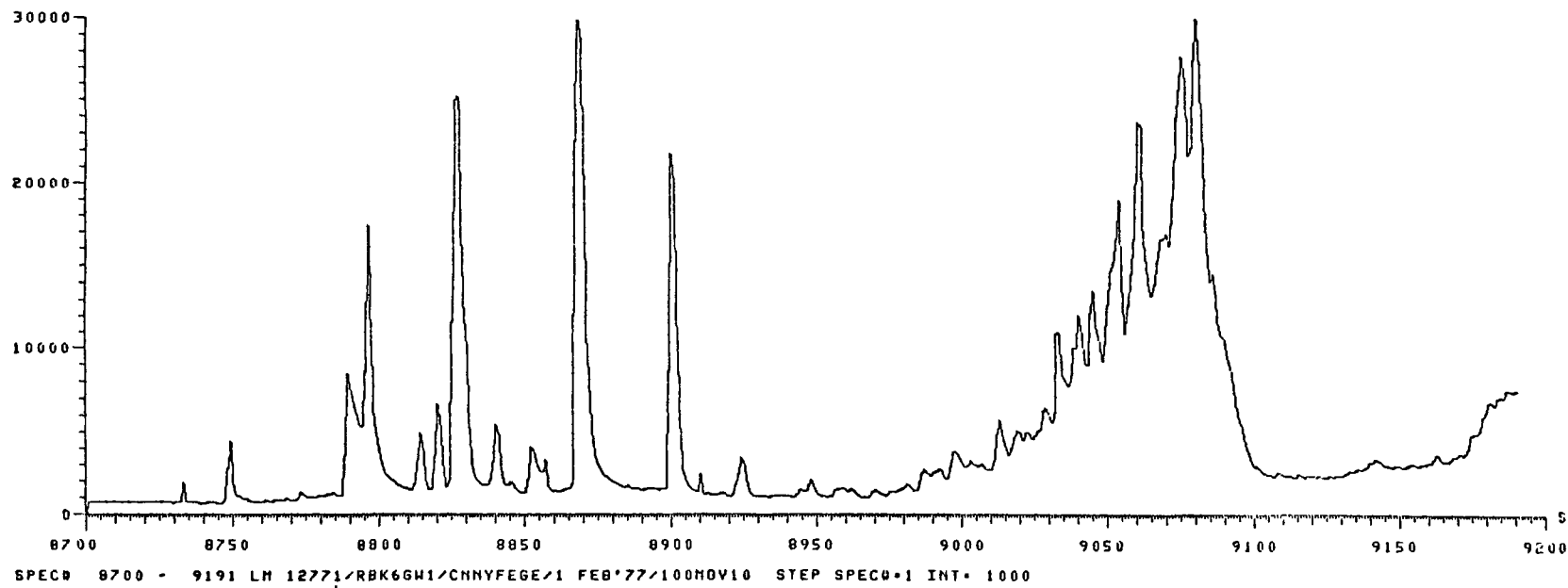


Figure 47. Total ion current chromatogram from gas chromatography/mass spectroscopic analysis of organics purged from water samples collected from Hudson River below outfall stream near General Electric Company, Ft. Edwards, New York (P2/C2/L5).

9.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF GENERAL ELECTRIC COMPANY, HUDSON FALLS, NEW YORK

Hudson Falls (Figure 48) is a village of 8,000 people located on the Hudson River in upstate New York. Ft. Edwards, located directly south of Hudson Falls has 3,700 residents. The terrain of the area is generally flat, except for the Hudson which flows in a 20-40 m deep channel with very steep banks.

The Hudson Falls plant (GE-HF) is considerably older than the Ft. Edwards plant. It consists of 8-15 buildings (depending on how one differentiates interconnecting structures) tightly packed into a small site on the edge of the Hudson River. The major building along Sumpter Street is 30 x 150 m and three stories high. Judging from the materials in the storage yard, this plant manufactures large capacitors for use in electrical substations.

To the north of the plant is the Hudson Falls Sewage Treatment Plant. To the east is a residential neighborhood. To the south is an older manufacturer, Sandy Hill, which appears to make steel shafts, etc. To the west is the Hudson River.

The site was sampled on November 16-19, 1976. Eight air, three water, and seven soil samples were collected. The sampling protocol is summarized in Table 30. Because of the proximity of this plant site to that of General Electric Company, Ft. Edwards, New York and certain sampling difficulties, some of the samples were taken from common locations.

9.1 FIELD SAMPLING

9.1.1 Air

Air samples were collected on November 17-19, 1976. A transect was set up and sites selected fairly far away (Figures 48 and 49)⁽⁴³⁾ from GE-HF because of the large (at least 50 m) smokestack.

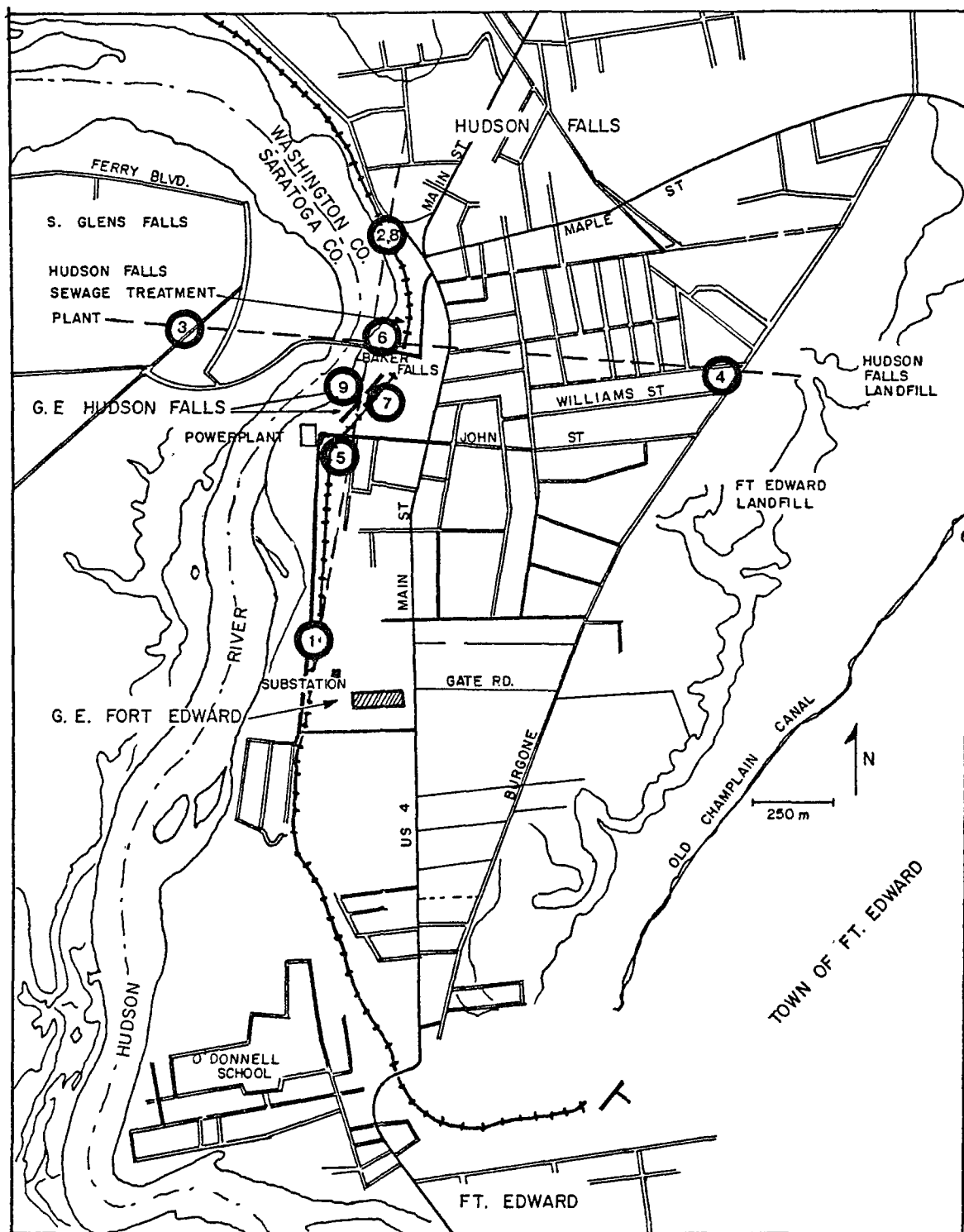


Figure 48. Map of the area surrounding General Electric - Hudson Falls with sampling locations for P1 - 11/17-18/76.

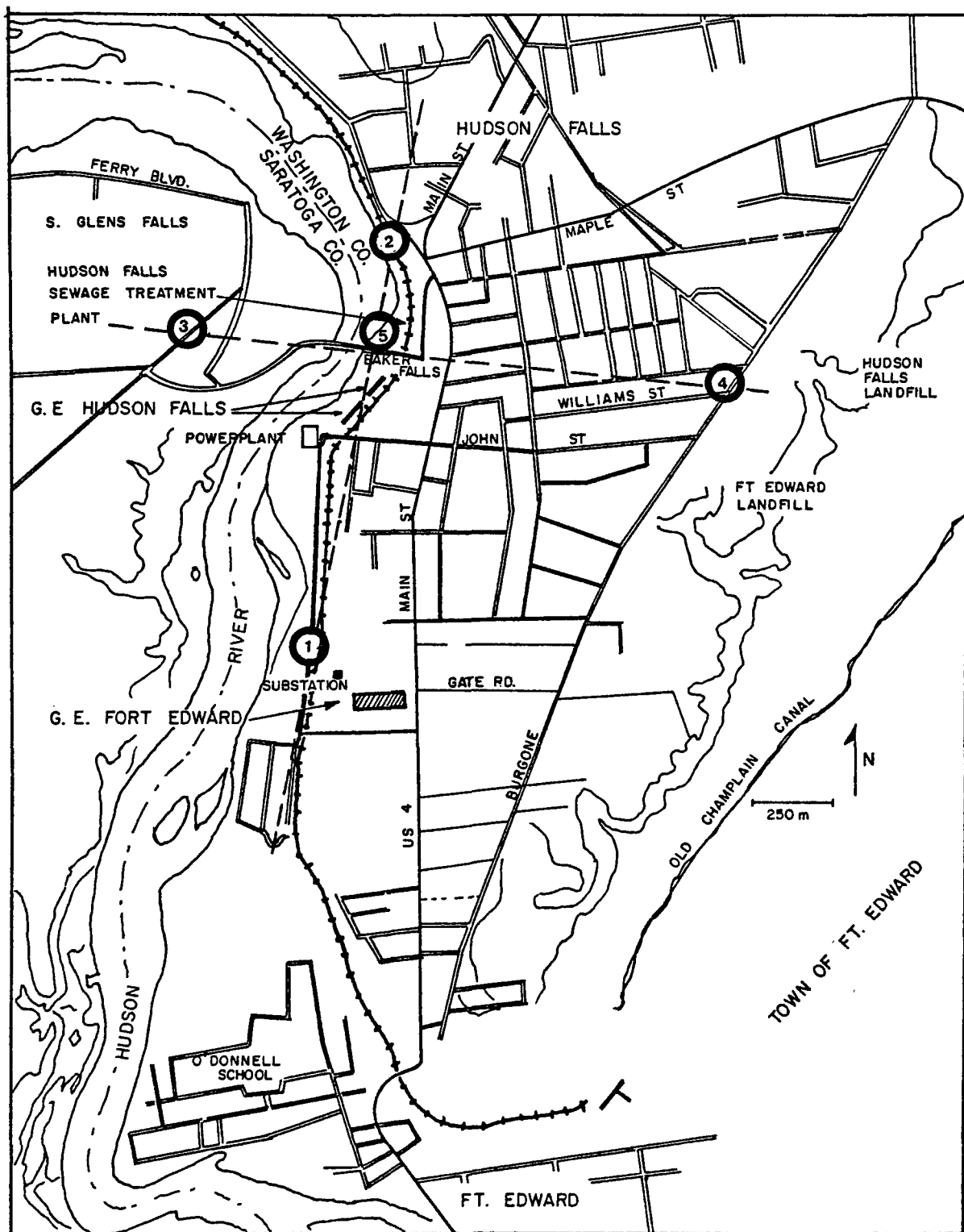


Figure 49. Map of the area surrounding General Electric - Hudson Falls with sampling locations for P2 - 11/18-19/76.

Table 30. SAMPLING PROTOCOL FOR GENERAL ELECTRIC, HUDSON FALLS, NEW YORK

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meteorological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
11/17,18/76 P1	C1 ^a	L1	1100-0931	84,100	APCN	-3-8 ^b	60-81	variable 0-10	Overcast
		L2	1115-1023	86,400	APCN				
		L3	1035-0957	87,300	APCN				
		L4	1135-1045	86,500	APCN				
	C2 ^c	L5	1225	3 cores ^d	SPCN	0-7 ^b	56-75	variable 0-10	variable cloudiness
		L6	1120	3 cores	SPCN				
		L7	1210	3 cores	SPCN				
		L8	1135	3 cores	SPCN				
	C3		1250	0.8	WPCN ^e				
11/18,19/75 P2	C1 ^a	L1	0951-1024	91,700	APCN				
		L2	1035-0941	86,300	APCN				
		L3	1010-1006	89,400	APCN				
		L4	1058-0920	83,600	APCN				
	C2 ^f	L5	0900	3.4	WPCN ^g				
		L6	0827-2109	4.0	WPCN ^h				

Key to Sample Type: APCN-polychloronaphthalenes, air
WPCN-polychloronaphthalenes, water
SPCN-polychloronaphthalenes, soil

Table 30. (continued)

- ^a24 hour air samples on polyurethane foam.
- ^bMeteorological data monitored on MRI weather station. No perceptible local variations.
- ^cSoil samples collected along transect. Note: Several soil samples from GE-FE sampling protocol are on GE-HF transect and thus were not duplicated. Samples collected on 11/16/76.
- ^dAbout 5 cm diameter x 13 cm depth.
- ^eGrab water samples collected from puddle in Sumpster Street, about 3 m from edge of GE-HF main manufacturing building. Collected on 11/15/76. On 11/18/76, the area was asphalted.
- ^f24 hour water samples using interval samplers. Sampler located upstream of GE-HF and GE-FE as in GE-FE protocol.
- ^gWater lines had clogged with no sample collected. Grab sample was collected.
- ^hSamples downstream of both GE-HF and GE-FE as in GE-FE protocol. Sampler was run at 100% sampling rates to keep lines from freezing.

9.1.2 Water

An integrated water sample was collected at L6, about 3 km downstream of GE-HF (also downstream of General Electric Co., Ft. Edward, New York). The corresponding upstream sampler became clogged during sampling, so a grab sample was collected at the end of the sample period. A grab water sample was collected from a puddle in Sumpter Street about 5 km from the main manufacturing building. This water may have been seeping up from some underground source. Three days later the area was asphalted over. A large outfall from the plant into the Hudson River was observed but not sampled because of the necessity of scaling a cliff on GE property.

9.1.3 Soil

Soil samples were collected in four locations along the GE-HF transect. The other four locations were also on the GE-FE transect and samples from this protocol will be used to complete the set.

9.1.4 Summary of GE-HF Sampling

No particular difficulties were encountered during the sampling of GE-HF, except a clogged water collection line and those imposed by the presence of the Hudson River.

9.2 ANALYSES

Air, soil, and water samples were analyzed according to procedures detailed in Appendix A.

9.3 RESULTS AND DISCUSSION OF SAMPLES COLLECTED NEAR GENERAL ELECTRIC, HUDSON FALLS, NEW YORK (GE-HF)

The analyses of samples collected near GE-HF are summarized in Table 31. As with GE-FE, the results are almost all near or below the detection limit, although two soil samples (P1/C2/L7 and P1/C2/L8) contained PCNs in concentrations about an order of magnitude higher than at other locations. On advice of the Project Officer, the air samples from P2 were not analyzed, since the values obtained from P1 were low.

Table 31. RESULTS OF ANALYSIS OF SAMPLES COLLECTED NEAR
GENERAL ELECTRIC COMPANY, HUDSON FALLS, NEW YORK

Period ^a	Cycle ^a	Location ^a		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1	F ^c	-- ^d	--	--	--	--	--	--	--	--
			1	0.8	2.0	--	--	--	--	--	--	2.8
			2	--	--	--	--	--	--	--	--	--
			Total	0.8	2.0	--	--	--	--	--	--	2.8 ng/m ³
		L2	F	--	--	--	--	--	0.5	--	--	0.5
			1	--	3.5	--	--	--	--	--	--	3.5
			2	--	--	--	--	--	--	--	--	--
			Total	--	3.5	--	--	--	0.5	--	--	4.0 ng/m ³
		L3	F	--	--	--	--	--	--	3.4	--	3.4
			1	--	0.3	2.5	--	--	--	--	--	2.8
			2	--	--	--	--	--	--	--	--	--
			Total	--	0.3	2.5	--	--	--	3.4	--	6.2 ng/m ³
		L4	F	--	--	--	0.8	--	--	--	1.5	2.3
			1	--	--	4.8	--	--	1.3	1.0	--	7.0
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	4.8	0.8	--	1.3	1.0	1.5	9.3 ng/m ³
	C2 ^e	L5		1.0	--	--	--	--	--	--	--	1.0 µg/kg
		L6		--	0.3	--	--	--	--	--	--	0.3 µg/kg
		L7		--	--	6.8	3.5	1.6	--	--	--	12 µg/kg
		L8		1.9	--	--	--	--	--	1.5	1.3	4.7 µg/kg
	C3 ^f	L9		--	--	--	--	--	--	--	--	--

(continued)

Table 31. (cont'd)

Period ^a	Cycle ^a	Location ^a	Degree of Chlorination								Total
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P2	C2 ^f	L5	--	--	--	--	--	--	--	--	--
		L6	--	--	--	--	--	--	--	--	--

^aSee Table 30 for Period, Cycle and Location designations in the sampling protocol

^b24 hour air samples

^cF = Glass fiber filters; 1 = Top PUF plug; 2 = Bottom PUF plug (not analyzed as per directions for Project Officer)

^dNo PCN peak detected

^eSoil samples

^fWater samples

10.0 SAMPLING AND ANALYSIS OF POLYCHLORINATED NAPHTHALENES IN THE VICINITY OF CORNELL DUBLIER ELECTRONICS COMPANY, SANFORD, NORTH CAROLINA

Cornell Dubilier Electronics, Sanford, North Carolina (CDS) employs between 500-1000 people and manufactures "fixed capacitors".⁽⁴⁴⁾ Since this plant purchases capacitor tissue, foil, and chemicals⁽⁴⁴⁾, it is a potential user of PCNs.

Cornell Dubilier began operations at this site in 1953 and currently occupies a one story 50 x 200 m building in an industrial park at the southern outskirts of Sanford, North Carolina. To the northwest is a small housing development. To the northeast and southeast are widely spaced mixed commercial and residential buildings. To the west and southwest is an industrial-commercial area with small textile companies, a shopping center, and miscellaneous small businesses.

Sanford is a town of 12,000 located in the central Piedmont region of North Carolina where prominent industrial products are textiles and bricks.⁽⁴⁴⁾

10.1 FIELD SAMPLING

10.1.1 Air

Two 24-hour air samples were collected at each of four points along a transect as shown in Figures 50 and 51.⁽⁴⁵⁾ The plant is low, there are no large smokestacks, and the terrain is fairly flat, so the samplers were placed relatively close (275-900 m) to the plant. A water tower at the south corner of the plant served as a landmark. Weather conditions were constantly monitored by the MRI weather station which was set up in a secure area at Location 3 (Figure 50).

During the collection of the air samples, two short puffs of black smoke were observed emitting from a smokestack at the plant. A light

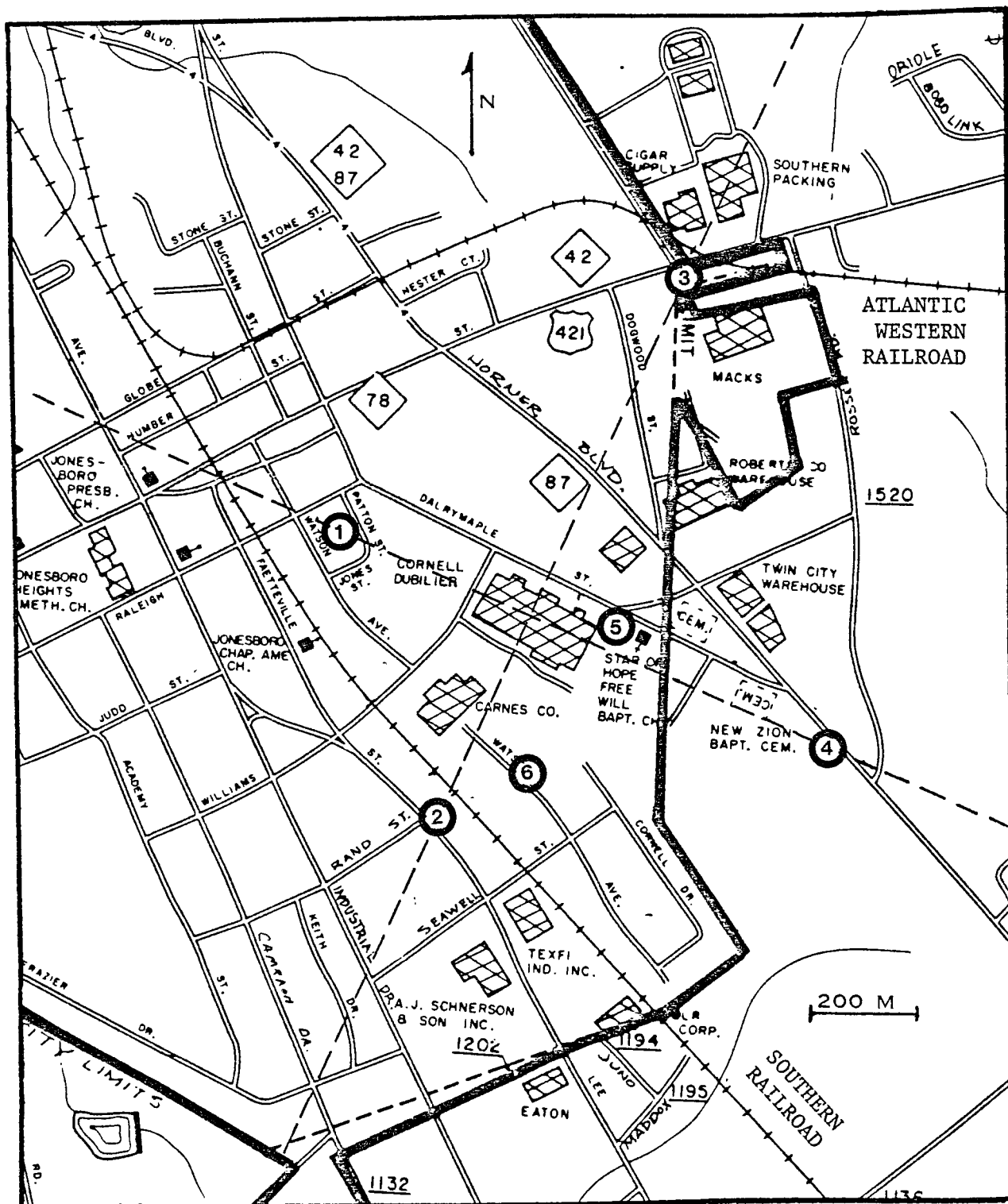


Figure 50. Map of the area surrounding Cornell Dubilier, Sanford, NC showing sampling locations for P1 - 12/7-8/76.

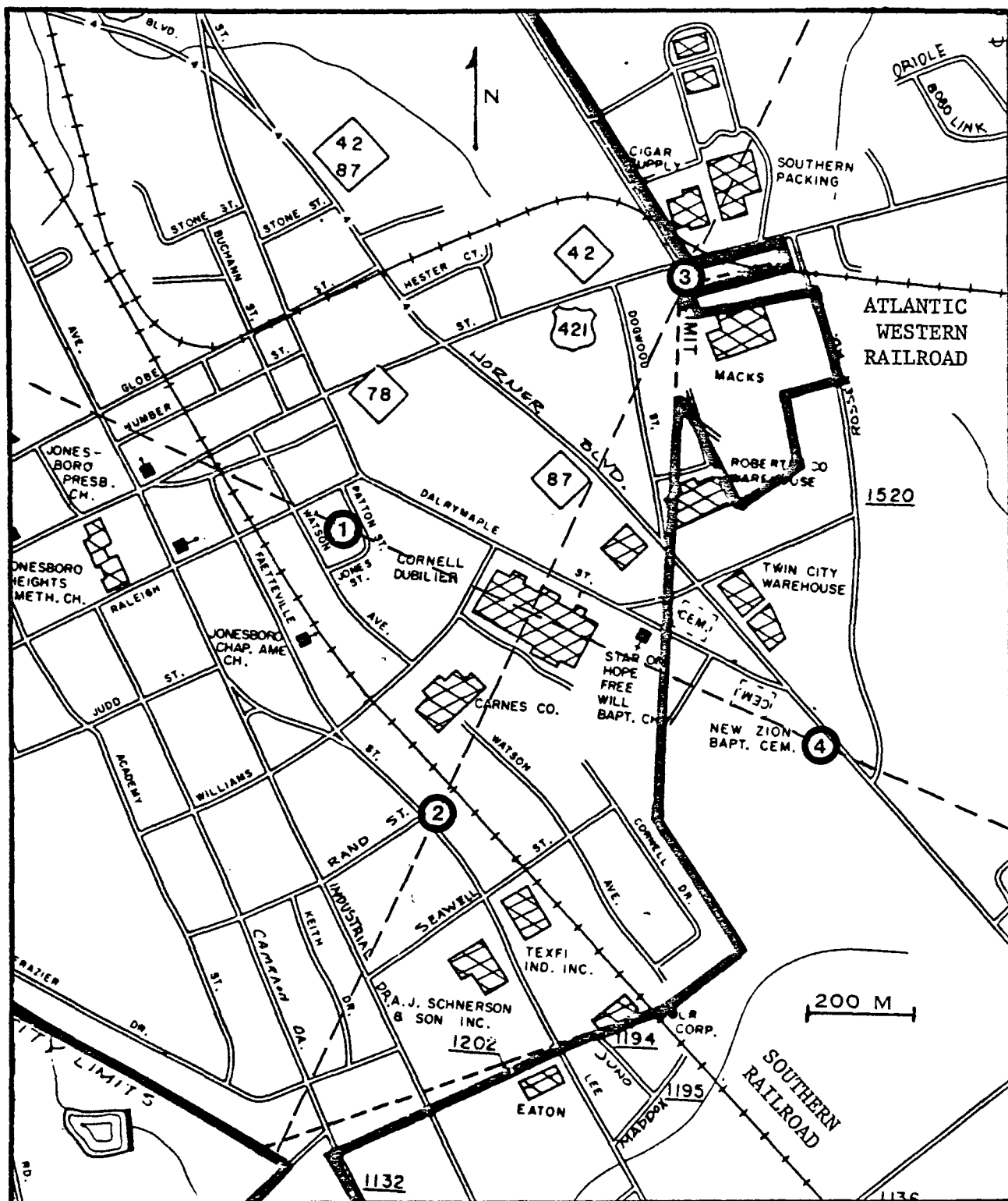


Figure 51. Map of the area surrounding Cornell Dubilier, Sanford, NC showing sampling locations for P2 - 12/8-9/76.

steady snow/rain during the first sampling period resulted in a total of 1.6 cm of precipitation. The sampling protocol is summarized in Table 32.

10.1.2 Water

Upstream and downstream water samples were obtained from a small stream which runs along the southern edge of the CDS plant site (about 10 m from the plant itself). The stream was about 0.5-1.6 m wide above the plant and widens out into a swampy lagoon beside the plant. The downstream sample was collected near a culvert which channels the stream under a dirt lane. The flow of water appeared to be significantly greater (about 3-4 fold) below the plant than above. The sampling protocol is summarized in Table 32.

10.1.3 Soil

Three soil samples were collected at each of eight locations surrounding CDS as shown in Figure 52 (L1-8). The samples were combined after returning to the lab to yield eight composite samples for analysis. Four samples were collected within 50 m of the CDS plant (although not on company property) along each side of the plant. The other four samples were collected 800-1000 m from the plant on each of the transects. The sampling protocol data is summarized in Table 32.

10.1.4 Miscellaneous

Several chunks of an amber-colored resinous material were observed near the CDS plant. A sample (about 20 cm diameter, 5 cm thick) was collected.

10.1.5 Summary

Due in part to the cooperation of the people at the sampling locations, the sampling of air and water went very smoothly. The weather refused to be cooperative, and the bulk of the sampling was accomplished under a light, intermittent rain or snow. Due to the weather and other factors, the soil sampling was delayed. When the soil samples were collected, the sampling was accomplished with ease. The plant appeared relatively innocuous, although occasional puffs of black smoke were observed. Several residents stated that they had never smelled any emissions from the plant.

Table 32. SAMPLING PROTOCOL FOR CORNELL DUBILIER ELECTRONICS COMPANY,
SANFORD, NORTH CAROLINA

Period	Cycle	Location	Sampling Time	Sampling Volume (ℓ)	Type of Sample	Meterological Conditions			
						T (°C)	% RH	Wind Dir./ Speed (kmph)	Other
12/7-8/76 P1	C1 ^a	L1	1431-1418	88,000	APCN	10-1 ^b	90	SW/3-6	1.65 cm precipitation during 24 hour period
		L2	1446-1434	88,900	APCN				
		L3	1413-1350	88,200	APCN				
		L4	1509-1451	89,000	APCN				
	C2 ^c	L5	1325-1508 ^d	4.0	WPCN				
		L6	1450-1515 ^d	4.0	WPCN				
12/8-9/76 P2	C1 ^a	L1	1450-1400	87,800	APCN	8-1 ^b	40	N/3-11	Intermittent Snow
		L2	1445-1416	87,800	APCN				
		L3	1407-1445	9,200	APCN				
		L4	1502-1432	87,800	APCN				
1/6/77 P3	C1 ^e	L1	1230	3 cores	SPCN				
		L2	1245	3 cores	SPCN				
		L3	1300	3 cores	SPCN				
		L4	1315	3 cores	SPCN				
		L5	1330	3 cores	SPCN				
		L6	1400	3 cores	SPCN				
		L7	1415	3 cores	SPCN				
		L8	1430	3 cores	SPCN				
	C2	L9	1445	amber colored resinous solid					

^a24 hour sample on PUF

^bTemperature and wind continuously monitored by MRI at L3. Conditions at other locations were not significantly different

^cInterval water samples collected at 50% sampling rate

^dSampling period was 25.5 hours

^eSoil sample collection delayed due to weather and other problems

Key to Sample type:

SPCN - polychloronaphthalenes, air
WPCN - polychloronaphthalenes, water
SPCN - polychloronaphthalenes, soil

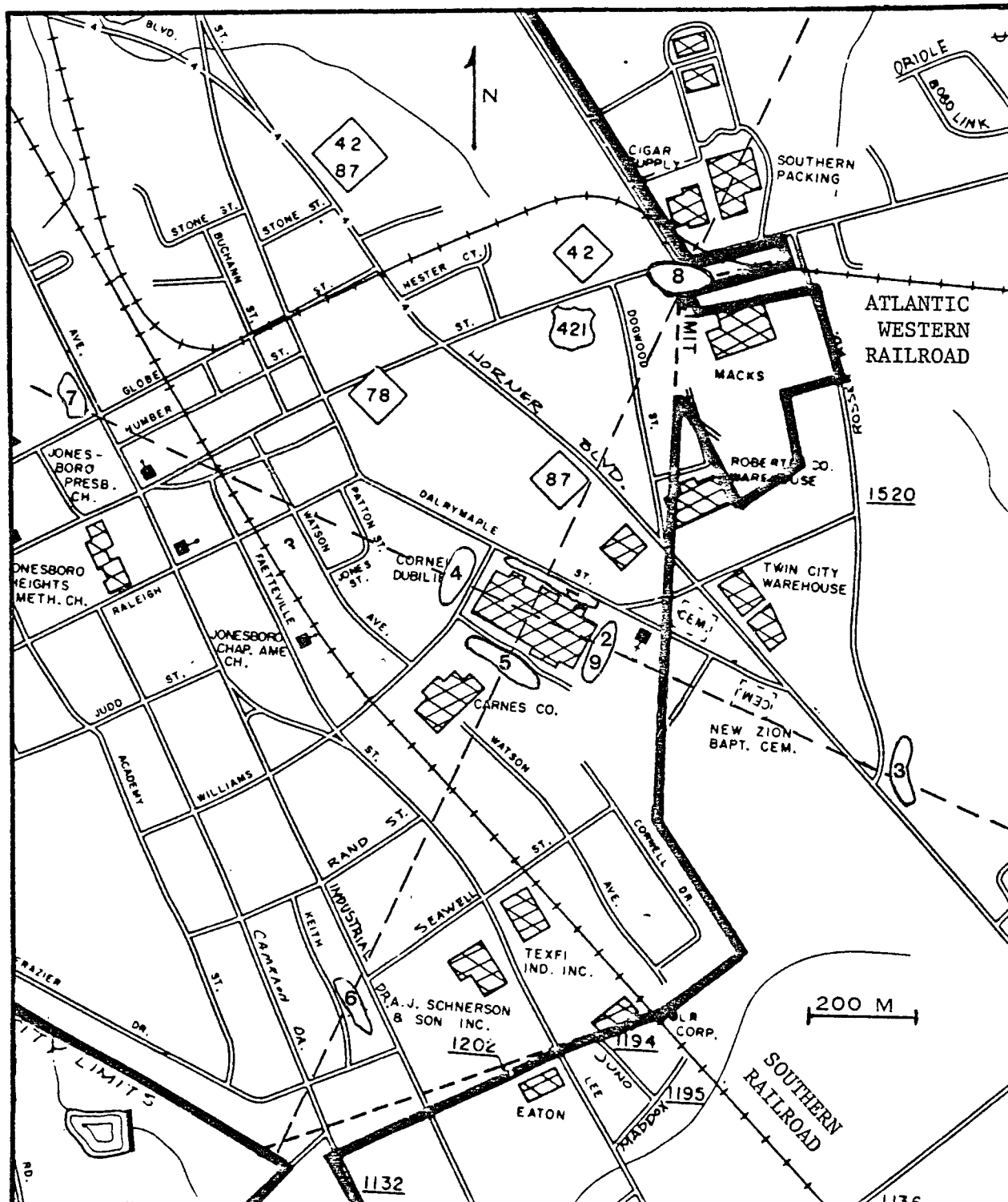


Figure 52. Map of the area surrounding Cornell Dubilier, Sanford, NC showing sampling locations for P3 - 1/6/77.

10.2 ANALYSES

Air, soil, and water samples were analyzed by the procedures detailed in Appendix A. The amber-colored resinous soil sample (P3/C3/L9) was analyzed by refluxing a 5 g piece for 15 min with toluene. The toluene extract was then concentrated and chromatographed as all other samples.

10.3 RESULTS AND DISCUSSION

The results of analysis of samples collected near Cornell Dubilier Electronics Company in Sanford, North Carolina are summarized in Table 33.

10.3.1 Air

The air samples all contained PCNs in amounts significantly greater than the background. The average concentration found was 19 ng/m^3 with a range of $9.8\text{--}31 \text{ ng/m}^3$ for the first sampling period and 17 ng/m^3 (from $9.8\text{--}33 \text{ ng/m}^3$) the second day. No significant pattern is discernible, neither with respect to isomeric distribution nor distribution along the transects as illustrated in Figures 53 and 54.

10.3.2 Water

The water samples contained low-to-undetectable PCN concentrations.

10.3.3 Soil

Total PCN concentrations for the soil samples collected during P3 are presented in Figure 55 with a detailed sampling map in Figure 56. The average PCN concentration found in soil was about $240 \text{ }\mu\text{g/kg}$. Two samples, L2 and L5 are roughly an order of magnitude higher than the other samples. Air-borne deposition does not appear to be the cause of these high concentrations, since, as illustrated in Figures 57 and 58, the annual and fall wind roses for the area indicate predominant northeasterly and southwesterly winds. These wind patterns are not concurrent with the soil PCN concentrations found. The area at L2 had been graded within the past several years and is near where the amber resinous solid (P3/C2/L9) was found. Since this sample contained higher than average concentrations of PCNs, it is possible that other solid wastes which may have been mixed into the soil during grading to account for this high concentration. The sample at L5 was obtained along the bank of a small ($\sim 1 \text{ m}$ wide) stream which flowed along

Table 33. RESULTS OF ANALYSIS OF SAMPLES COLLECTED NEAR
CORNELL DUBILIER ELECTRONICS COMPANY, SANFORD, NC

Period ^a	Cycle ^a	Location ^a		Degree of Chlorination								Total
				C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
P1	C1 ^b	L1	F ^c	-- ^d	--	--	--	--	--	--	--	--
			1	0.3	0.8	2.5	13	3.3	--	5.8	--	25
			2									
			Total	0.3	0.8	2.5	13	3.3	--	5.8	--	25 ng/m ³
		L2	F	--	--	--	--	1.1	1.9	1.6	6.3	11
			1	--	0.5	2.8	--	4.3	3.0	3.0	6.3	20
			2									
			Total	--	0.5	2.8	--	5.4	4.9	4.6	13	31 ng/m ³
		L3	F	--	--	--	--	--	--	--	--	--
			1	Te	1.8	6.0	2.0	--	--	--	--	9.8
			2									
			Total	T	1.8	6.0	2.0	--	--	--	--	9.8 ng/m ³
		L4	F	--	--	--	--	0.5	0.4	0.6	1.4	2.9
			1	0.3	0.5	4.0	--	2.0	1.0	--	--	7.8
			2									
			Total	0.3	0.5	4.0	--	2.5	1.4	0.6	1.4	11 ng/m ³
	C2 ^f	L5		--	--	--	--	--	--	--	--	--
		L6		--	--	0.5	0.1	--	--	--	--	0.6 µg/l

(continued)

Table 33. (cont'd)

Period	Cycle	Location		Degree of Chlorination								Total
				$C_{10}H_7Cl$	$C_{10}H_6Cl_2$	$C_{10}H_5Cl_3$	$C_{10}H_4Cl_4$	$C_{10}H_3Cl_5$	$C_{10}H_2Cl_6$	$C_{10}HCl_7$	$C_{10}Cl_8$	
P2	Cl ^b	L1	F	--	--	--	--	--	--	--	--	--
			1	--	--	7.5	1.5	0.8	--	--	--	9.8
			2	--	--	--	--	--	--	--	--	--
			Total	--	--	7.5	1.5	0.8	--	--	--	9.8 ng/m ³
		L2	F	--	0.8	--	--	1.0	1.7	1.5	--	5.0
			1	--	0.8	5.0	--	--	--	--	--	5.8
			2	--	--	--	--	--	--	--	--	--
			Total	--	1.6	5.0	--	1.0	1.7	1.5	--	11 ng/m ³
		L3	F	--	--	--	--	--	--	--	--	--
			1	0.8	0.8	1.0	2.3	--	--	1.5	--	15
			2	--	--	--	--	--	--	--	--	--
			Total	0.8	0.8	1.0	2.3	--	--	1.5	--	15 ng/m ³
		L4	F	--	--	--	--	--	--	--	--	--
			1	--	3.8	16	--	--	--	6.3	6.5	33
			2	--	--	--	--	--	--	--	--	--
			Total	--	3.8	16	--	--	--	6.3	6.5	33 ng/m ³
P3	Cl ^g	L1		--	0.4	10	15	6.8	1.3	--	--	34 µg/kg
		L2		--	4.8	210	170	39	3.0	25	--	470 µg/kg
		L3		--	--	--	--	--	2.1	2.3	7.1	12 µg/kg
		L4		--	0.7	2.0	--	--	--	--	--	2.7 µg/kg

(continued)

Table 33. (cont'd)

Period	Cycle	Location	Degree of Chlorination								Total
			C ₁₀ H ₇ Cl	C ₁₀ H ₆ Cl ₂	C ₁₀ H ₅ Cl ₃	C ₁₀ H ₄ Cl ₄	C ₁₀ H ₃ Cl ₅	C ₁₀ H ₂ Cl ₆	C ₁₀ HCl ₇	C ₁₀ Cl ₈	
		L5	--	1.3	52	130	55	5.3	3.3	5.8	250 µg/kg
		L6	--	--	--	--	--	1.0	1.3	2.6	4.9 µg/kg
		L7	11	--	2.5	2.3	2.4	1.3	1.7	8.7	30 µg/kg
		L8	--	--	--	--	--	--	--	--	--
	C2 ^h	L9	15	71	660	160	18	--	--	--	920 µg/kg

a. See Table 32 for period, cycle and location designations in the sampling protocol.

b. Air sample

c. F = glass fiber filter; 1 = top PUF plug; 2 = bottom PUF plug; (not analyzed at direction of Project Officer).

d. No PCN peak detected. Detection limit for air is about 0.3 ng/m³, soil about 0.5 µg/kg, and water about 0.2 µg/l.

e. Trace

f. Water samples

g. Soil samples

h. Amber-colored resinous solid.

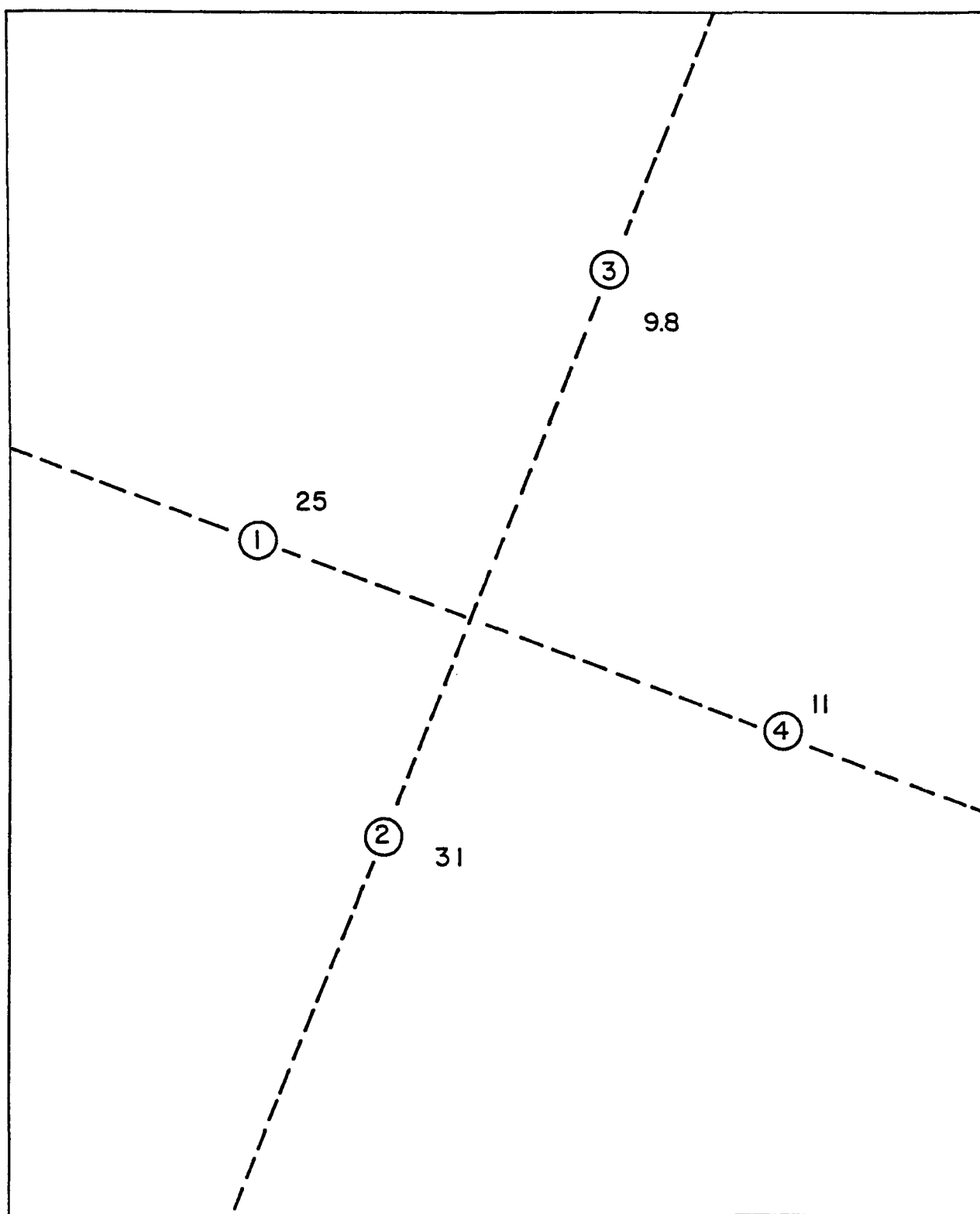


Figure 53. Total PCN concentration (ng/m^3) in air near Cornell Dubilier Electronics Company, Sanford, NC (Period 1).

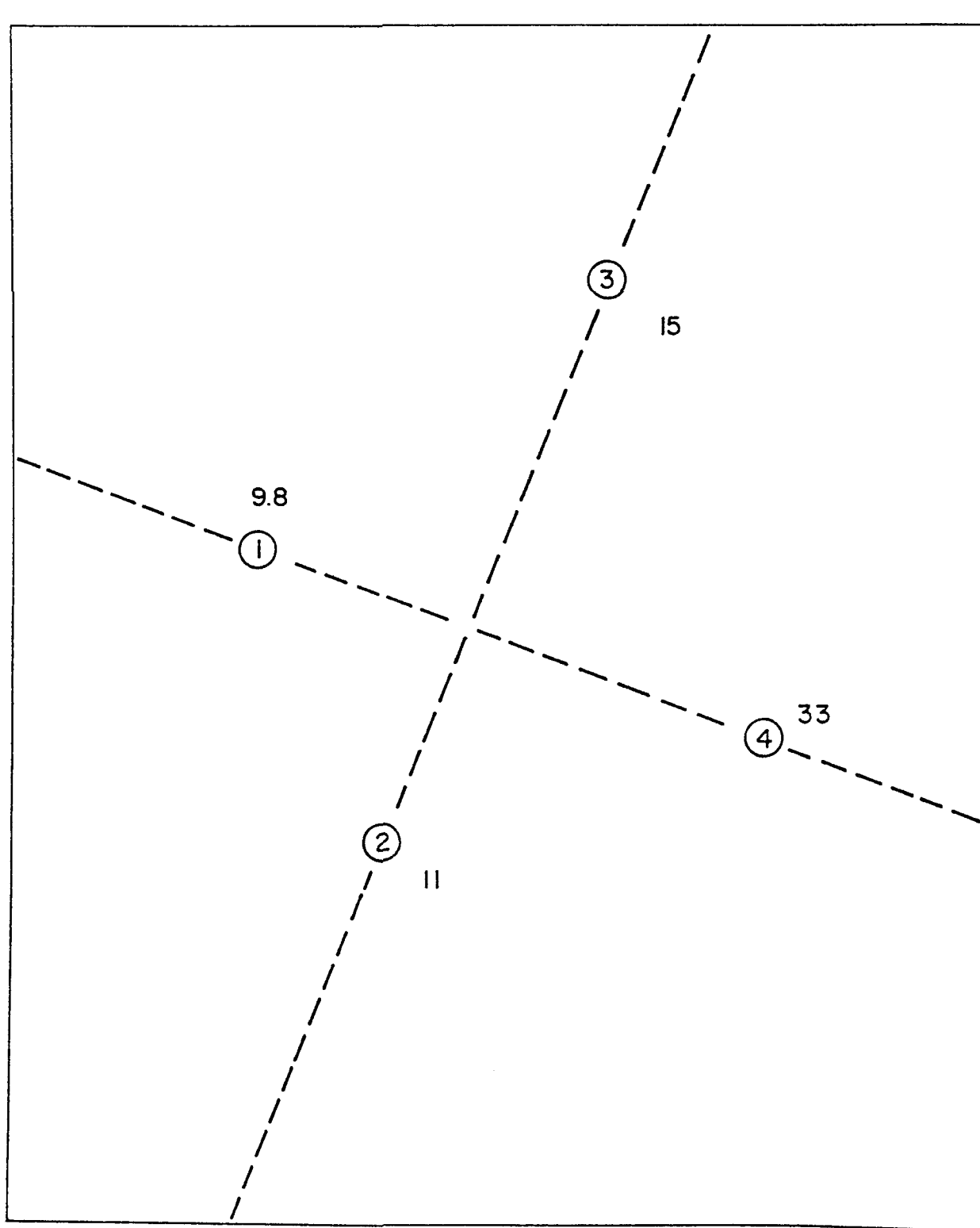


Figure 54. Total PCN concentration (ng/m³) in air near Cornell Dubilier Electronics Company, Sanford, NC (Period 2).

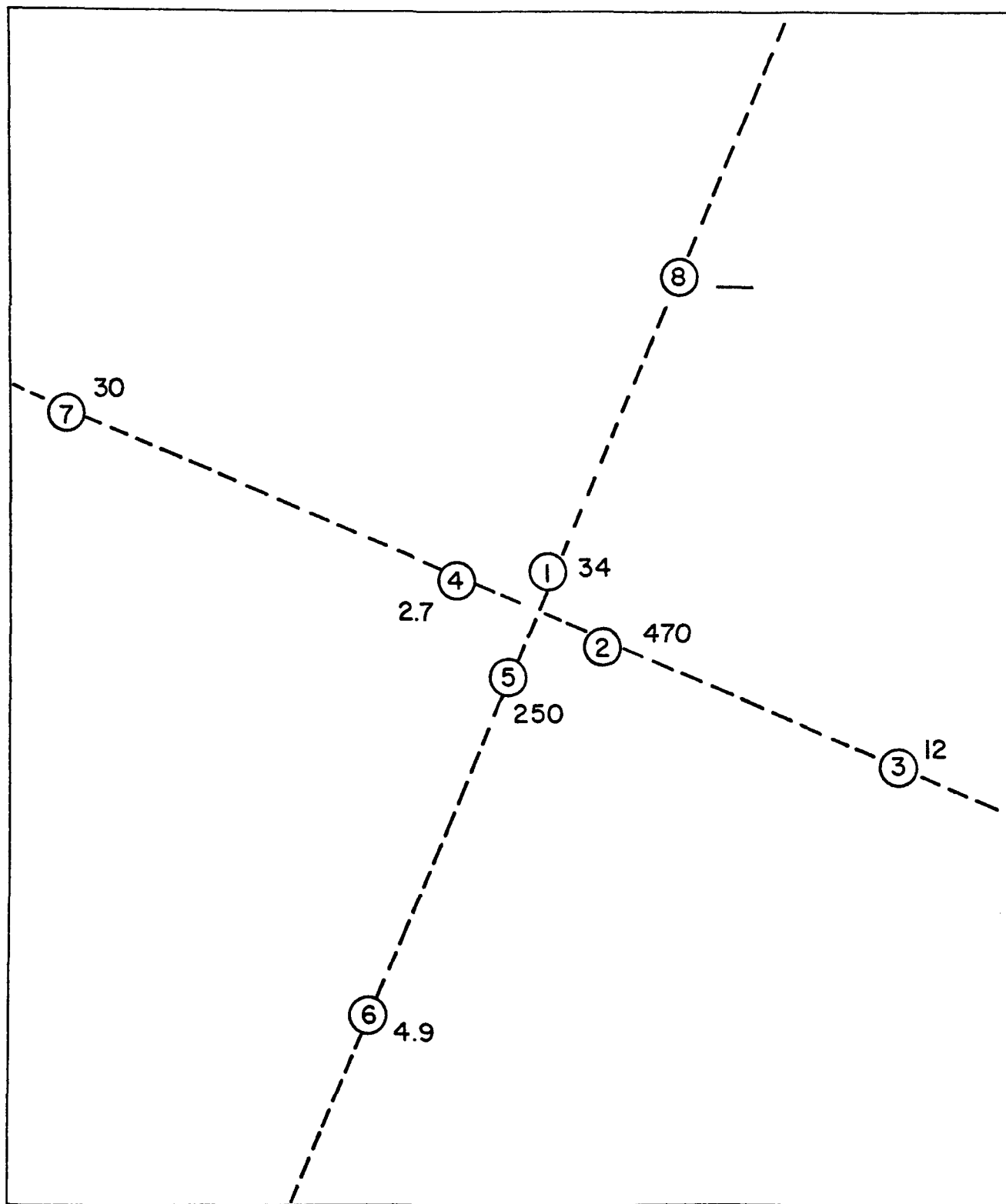


Figure 55. Total PCN concentration (µg/Kg) in soil near Cornell Dubilier Electronics Company, Sanford, NC (Period 3).

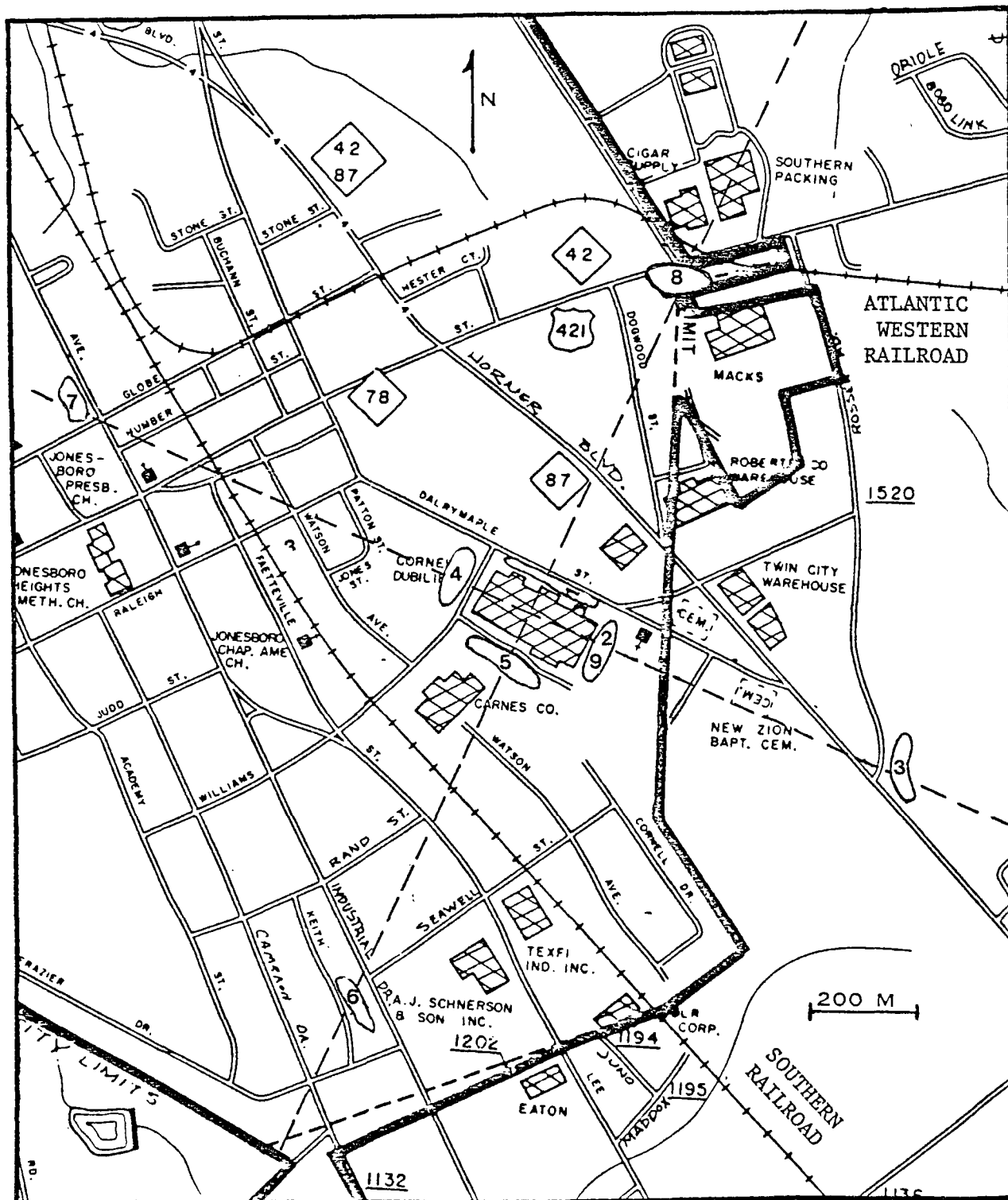
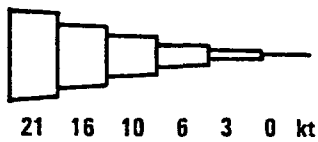


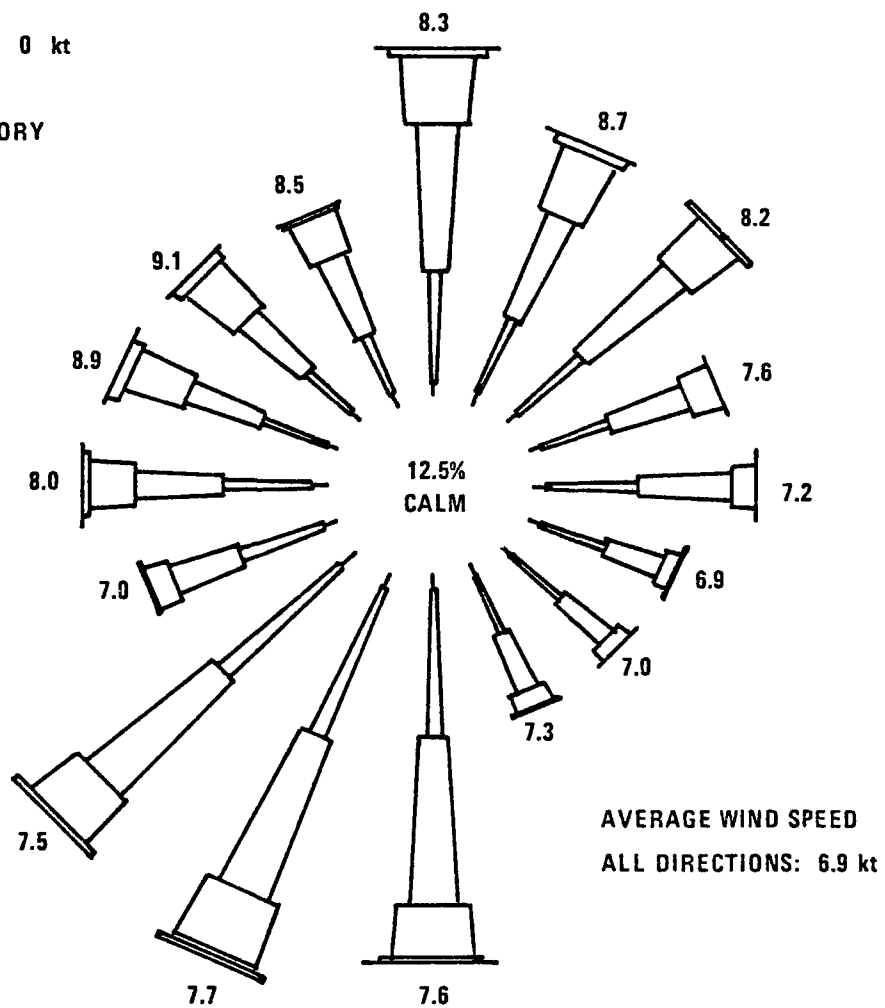
Figure 56. Map of the area surrounding Cornell Dubilier, Sanford, NC showing sampling locations for P3 - 1/6/77.

% FREQUENCY SCALE

0 1 2 3 4 5 6



WIND SPEED CATEGORY

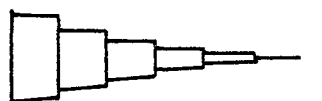


ANNUAL WIND ROSE

Figure 57. RALEIGH-DURHAM AIRPORT, NORTH CAROLINA
1955-1964

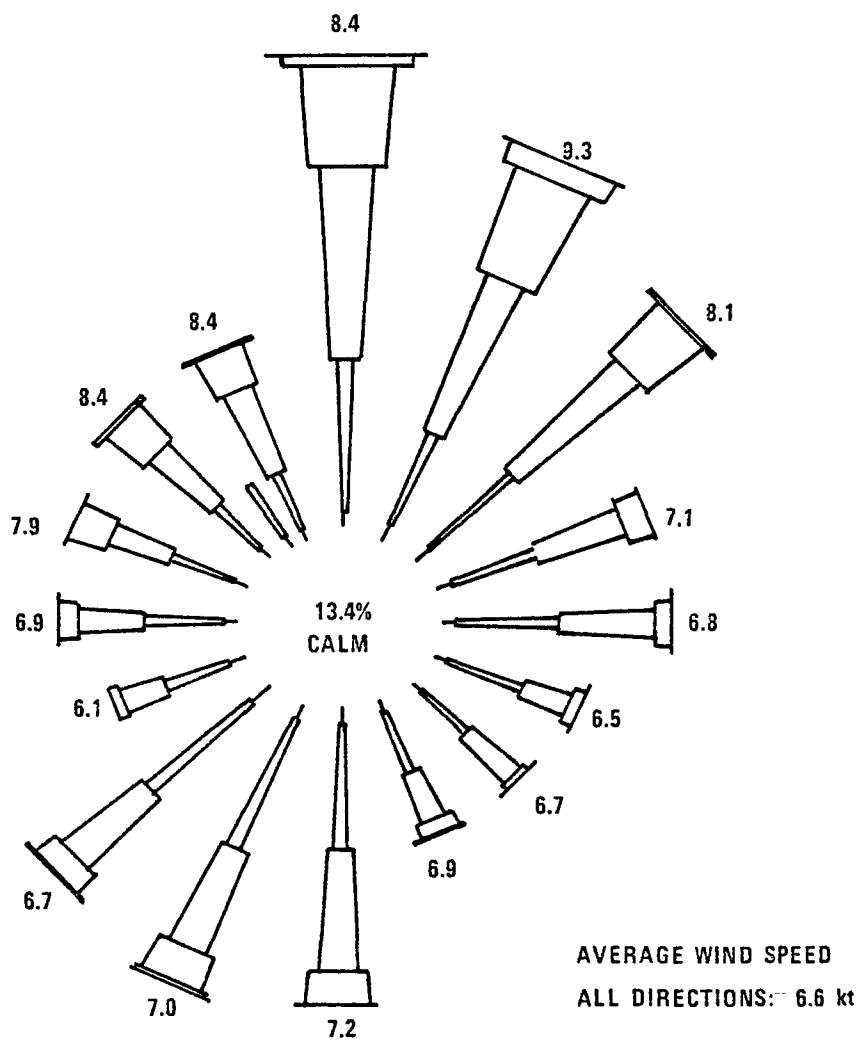
% FREQUENCY SCALE

0 1 2 3 4 5 6



21 16 10 6 3 0 kt

WIND SPEED CATEGORY



FALL WIND ROSE

Figure 58. RALEIGH-DURHAM AIRPORT, NORTH CAROLINA
1955-1964

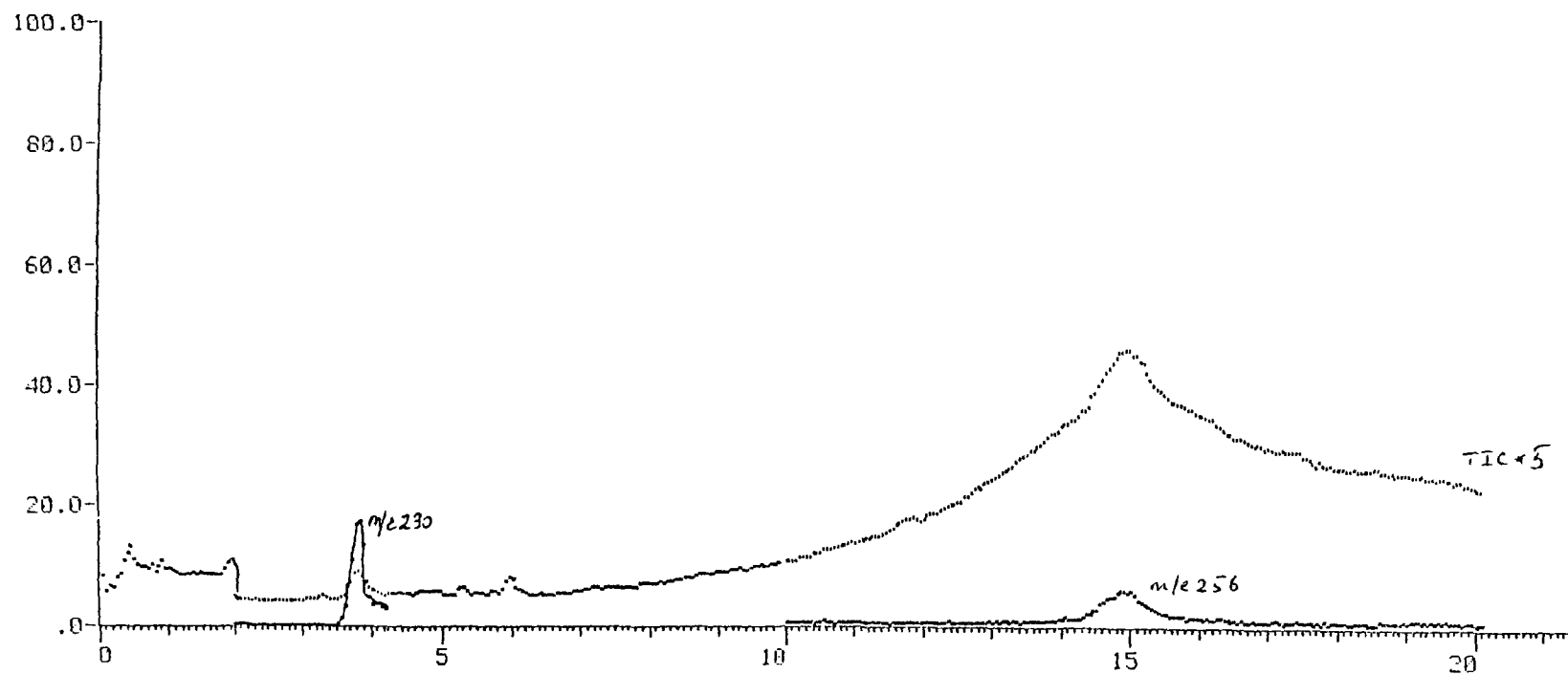
the edge of an area used to store old production equipment and other materials. It may be that the PCNs found at this site were either deposited or leached from the storage area.

10.3.4 Amber-Colored Resinous Solid Sample

This sample (P3/C3/L9) was found to contain 920 µg/kg PCNs, which was confirmed by "double MID" analysis and also by full scan GC/MS as shown in Figure 59 and Table 34. The large diffuse peak at about 15 minutes is not identifiable, but is probably due to constituents of the "plastic". The presence of trichlorobenzene and tetrachlorobenzene, while not relevant to this project may be of interest.

Table 34. RESULTS OF FULL SCAN GC/MS ANALYSIS OF AMBER-COLORED RESINOUS SOLID COLLECTED NEAR CORNELL DUBILIER, SANFORD, NORTH CAROLINA (P3/C3/L9)

Retention Time	Compound
0.44	trichlorobenzene
0.89	tetrachlorobenzene
1.84	dichloronaphthalene
4.69	trichloronaphthalene



B3GS15NFCD, 2%OV-101, 150° 3m8°/m-8, 1.8 kV, 03-17-77

Figure 59. TIC chromatogram of GC/MS analysis of amber-colored resinous solid collected near Cornell Dubilier Electronics Company, Sanford, NC (P3/C3/L9).

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APPENDIX A
ANALYTICAL METHODS FOR POLYCHLORINATED NAPHTHALENES

PROCEDURE FOR CLEANUP OF POLYURETHANE FOAM PLUGS

1. Cut 5 cm diameter x 13 cm long plugs from sheet of Olympic[®] 2315 polyurethane foam.
2. Mark each plug with an identification number in the top using a hot wire.
3. Place four plugs in bottom of clean four liter beaker, add 500 ml hot toluene (100°C).
4. Compress the plugs 10 times using a one liter Erlenmeyer flask.
5. Let sit five minutes on steam bath.
6. Repeat Steps 4 and 5.
7. Compress the plugs and decant the toluene.
8. Add 250 ml fresh, hot toluene and repeat steps 4 through 7.
9. Repeat Step 8 three times (total of five extractions).
10. Using clean tweezers, transfer each plug into a foil-wrapped wide-mouthed jar and cover loosely with a foil-lined cap.
11. Dry in vacuo at 50° for 12 hours.
12. Remove from oven, tighten cap and store away from potential contaminants.

PROCEDURE FOR EXTRACTION OF CHLORONAPHTHALENES FROM POLYURETHANE FOAM PLUGS AND GLASS FIBER FILTERS

1. Using cleaned tongs, remove foam plugs and filters from storage jars and place them in 400 ml beakers.
2. Add 150 ml of toluene to beakers containing foam plugs and 50 ml toluene to beakers containing filters.
3. Compress the foam plug 10 times to the bottom of the beakers with a 125 ml Erlenmeyer flask, soak for five minutes and compress an additional 10 times.
4. Squeeze the toluene out of the plug and decant into a flat bottom boiling flask. Similarly decant the toluene from the glass fiber filter into a separate flask.
5. Repeat Steps 2 through 4 two more times.
6. Concentrate in a flat bottom boiling flask topped with a Snyder column to approximately 15 ml.

7. Transfer concentrate to 1.5 x 120 mm culture tube, assuring quantitative transfer with small portions of petroleum ether. Blow down under N_2 at $\leq 25^\circ C$ just to dryness.
8. Dilute to approximately 1 ml with hexane and proceed with column cleanup.
9. Concentrate column eluant with a Kuderna-Danish (K-D) apparatus to 2.0 ml.

PROCEDURE FOR EXTRACTION OF WATER SAMPLES

1. Record total water volume.
2. Take 200 ml aliquot.
3. In separatory funnel, shake 5 min with 25 ml toluene.
4. Repeat Step 3 two times (total extract volume is ca. 75 ml).
5. Dry the combined toluene layers with ~ 2 g of Na_2SO_4 .
6. Reduce volume of combined extracts in flat-bottom boiling flask topped with a Snyder column to approximately 15 ml. Transfer concentrate to 15 x 120 mm culture tube, assuring quantitative transfer with small portions of petroleum ether.
7. Blow-down under N_2 just to dryness.
8. Reconstitute the sample in a small amount of hexane and proceed with column chromatography cleanup procedure.

PROCEDURE FOR EXTRACTION OF POLYCHLORONAPHTHALENES FROM SOIL SAMPLES*

1. Weigh 50 g of soil into a 1 quart screw cap jar.
2. Add 50 ml of diethyl ether, shake and allow to stand overnight.
3. Remove diethyl ether in vacuo at room temperature.
4. Add 5 ml of distilled-deionized water to dampen soil.
5. Add 40 ml of acetone and shake for 20 minutes.
6. Add 80 ml of toluene and shake an additional 10 minutes.
7. Decant acetone-toluene extract through glass wool into a one liter separatory funnel.
8. Repeat Steps 5 through 7 two more times.
9. Extract combined organic fractions with 500 ml water.

*-----
 * Procedure adapted from D. F. Goerlitz and L. M. Law, J. Assoc. Offic. Anal. Chem., 57, 176-181 (1974).

10. Back extract water three times with 25 ml portions of toluene.
11. Dry combined organic extracts with sodium sulfate.
12. Concentrate to 15 ml in a flat bottom boiling flask topped with a Snyder column. Transfer concentrate to 15 x 120 mm culture tube, assuring quantitative transfer with small portions of petroleum ether.
13. Blow-down under N_2 at $\leq 25^\circ C$ just to dryness.
14. Dilute to approximately 1 ml with hexane and proceed with column cleanup.

COLUMN CLEANUP PROCEDURE

1. Silica gel (Davison Chemical Division, W. H. Grace, Baltimore, MD), Grade 923, 100-200 mesh is washed with toluene, followed by hexane, dried at 130° for 16 hr and stored in a sealed amber bottle.
2. Using a 1.0 x 30 cm glass column, pack with a plug of glass wool, silica gel in a hexane slurry to 10 cm height, and 1.0 cm Na_2SO_4 .
3. Wash column with 50 ml hexane to settle the bed and clean any residual contaminants.
4. Transfer sample to column in 1.0 ml or less solvent (preferably hexane) with washing.
5. Elute the PCNs with 50 ml hexane.
6. The foam background and pesticides are eluted with toluene.
7. Concentrate hexane eluate in K-D apparatus, followed by nitrogen blow down if necessary to achieve a detectable concentration.
8. Analyze by GC/ECD or GC/MS as described elsewhere.

GAS CHROMATOGRAPH/MASS SPECTROMETER ANALYTICAL CONDITIONS

Instrument: Finnigan 3300 Quadrupole gas chromatograph/mass spectrometer with PDP/12 computer.

Column: 180 cm x 2 mm i.d. glass.

Column Packing: 2% OV-101 on Chromosorb W HP.

Oven Temperature: 150° , 3 min, $8^\circ/\text{min}$ to 230° , Hold.

Flow Rate: 30 cc/min, helium.

MID Ions: 164, 188, 196, 230, 266, 300, 336, 368, 404 (nominal).

Full Scan: 110-500 m/e.

Ionization Voltage: 70 eV (nominal).

Detector Voltage: 1.8 - 2.2 kV.

DESCRIPTION OF GAS CHROMATOGRAPH/MASS SPECTROMETRY/COMPUTER INSTRUMENTATION

Varian MAT CH-7

The Varian MAT CH-7 is a low resolution magnetic sector single focusing instrument. A resolution of 1,000 (10% valley definition) is attainable by the instrument using low resolution slits; a resolution of 3,000 (10% valley definition) may be attained by use of high resolution slits. Scan speed is variable from approximately one sec/mass decade to 18 hr/mass decade. Calibration of the system is routinely performed with perfluoro-kerosene.

The Varian 620/L computer is on-line with the CH-7 system. Long-term storage of data is on line-track, IBM-compatible magnetic tape. The computer system subsequently treats the stored data in several different ways to facilitate interpretation: (a) a reconstructed gas chromatogram (the abscissa is spectrum number) is routinely made in order to correlate the GC peaks (observed in the analog mode) with scan number; (b) any given mass spectrum or the entire series of scans is corrected for background signal (column bleed, other contaminants); (c) plots of intensities of specific ions (mass fragmentography) are made from the scan data. This information is often useful, when correlated with retention time data, in simplifying the identification of particular compounds; (d) normalized mass spectra are plotted using different types of normalization or amplification factors in order to facilitate identification; (e) hard copy output of normalized data in digital form, with various forms of background correction, is also available.

The GC system on the CH-7 mass spectrometer is a Varian Aerograph 1700 gas chromatograph. Glass capillary columns (~100 m, prepared in house) are used on this system. The capillary column is interfaced to the ion source through a single-stage glass jet separator. The system is equipped with a specially designed thermal desorption injection system⁽¹⁻⁵⁾

to allow injection of volatiles desorbed from a Tenax cartridge onto the capillary as a discrete-fine band.

The Varian 620/L computer interfaced with a MAT CH-7 mass spectrometer consists of a 12K central process with teletype, high speed paper tape reader/punch, and Statos-31 electrostatic printer/plotter. Its principal bulk storage device is a DEC IBM-compatible magnetic tape unit. The computer is also fitted with a hardware multiply/divide card and a dual disc system to speed up mass spectral data processing.

The mass spectrometer interface to the computer consists of a hardware multiplexer which allows the sampling of the multiplier output as well as the total ion current monitor and a Hall effect generator which is fitted in the CH-7 to sample the magnetic field. These signals, appropriately coded, are entered into the computer during data acquisition time. Peak time and intensities are computed on-line and stored, along with Hall probe and TIC information, on magnetic tape. In the continuous scanning mode, spectra are acquired every 6-7 seconds for the entire duration of the GC run. Using 600 ft tape reels, there is no difficulty in acquiring sets of over 2,000 scans for any run, if needed.

After acquisition of the entire GC run, a complete TIC profile can be generated and plotted on the Statos-31 recorder directly from the raw data. This plot serves to indicate the quality of the GC run, and may also be used to identify the scans of interest in the run. Generally, the mass spectral data must be converted from time information to mass information at this time. This is normally done by obtaining calibration constants from a standard perfluorokerosene run produced before or after a given series of unknown runs. Standard calibration curves are stored in the computer's core memory.

Finnigan 3300 GC/MS with PDP/12 Computer

The Finnigan 3300 mass spectrometer has a mass range of 1000, with unit resolution over the entire range. Calibration of the system is routinely performed with FC-43 for lower mass ranges and tris(perfluoroheptyl)-a-triazine in the higher ranges.

The PDP/12 computer is on-line with the Finnigan system. Long term storage of data is on LINC tapes or removable disc packs. The computer can

subsequently treat stored data in several different ways to facilitate interpretation: (a) a reconstructed gas chromatogram is routinely made to obtain retention times; scan number for a given gas chromatographic peak is obtained by operator interaction with a CRT display; (b) any given mass spectrum or an entire series of scans are corrected for background signal (column bleed, septum bleed, etc.); (c) plots of intensities of specific ions (mass fragmentography) are made from the scan data. This type of information is often useful, when correlated with retention time data, for simplifying the identification of particular compounds. Peak areas are also readily obtainable from these mass chromatograms and can be used to provide quantitative information; (d) normalized mass spectra are plotted, using different types of normalization or amplification factors in order to facilitate identification; (e) hard copy output of normalized data in digital form, with various forms of background correction, is also available.

The GC system in use on the Finnigan mass spectrometer is a Finnigan 9500.

The basic hardware of the PDP/12 consists of an 8K central processor fitted with a teletype, random access disc, CRT display and electrostatic printer/plotter. The interface to the mass spectrometer was custom-designed and built and consists of both analog to digital as well as digital to analog interfaces. The latter involves several unique concepts in interface design, since by using this system it is possible to put the entire mass spectral scanning operation under computer control. Since the data acquisition phase of the spectrometer operation is controlled entirely by the computer, a large number of different types of acquisition protocols have been implemented. For example, in the multiple ion detection mode, up to nine individual peaks can be selected within the entire mass spectral range, and acquired for varying time intervals as selected by the operator. In the repetitive scanning mode, scan intervals down to one scan per second are possible with entire scans recorded either on LINC tapes or disc.

All data processing operations are carried out interactively by means of programs stored on the small computer.

GC/MS ANALYSIS OF AIR SAMPLES COLLECTED ON TENAX

Volatile compounds were thermally desorbed from the Tenax GC collection cartridge, trapped in a cooled capillary and then injected onto the gas chromatograph. The inlet-manifold used for thermally recovering vapors trapped on cartridges is shown in Figure A-1.⁽¹⁻⁵⁾ For analysis by GC/MS/COMP, a Varian 1700 gas chromatograph was used to house the glass capillary column which was connected to the inlet-manifold (Figure A-1). A Varian MAT CH-7 mass spectrometer with a resolution of 2,000 equipped with single ion monitoring capabilities was used in conjunction with the GC. The mass spectrometer was interfaced to a Varian 620/L computer.

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with OV-101 stationary phase and benzyl triphenylphosphonium chloride (surfactant) was used for effecting the resolution. The capillary column was conditioned for 48 hours at 230°C and 1.5-2.0 ml/min of He flow. The operating parameters selected for the inlet-manifold GC/MS/COMP system are given in Table A-1.

Table A-1. OPERATING PARAMETERS FOR GC/MS/COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	350°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+180°C
thermal desorption time	4 min
GLC 100 m glass SCOT-OV-101	
50 m glass SCOT-Carbowax 20M or DEGS	20-240°C, 4°C/min
	80-240°C
carrier (He) flow	~3 ml/min
transfer line to MS	240°C
MS	
scan range	m/e 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 µA
multiplier	6.0
ion source vacuum	~4 x 10 ⁻⁶ torr

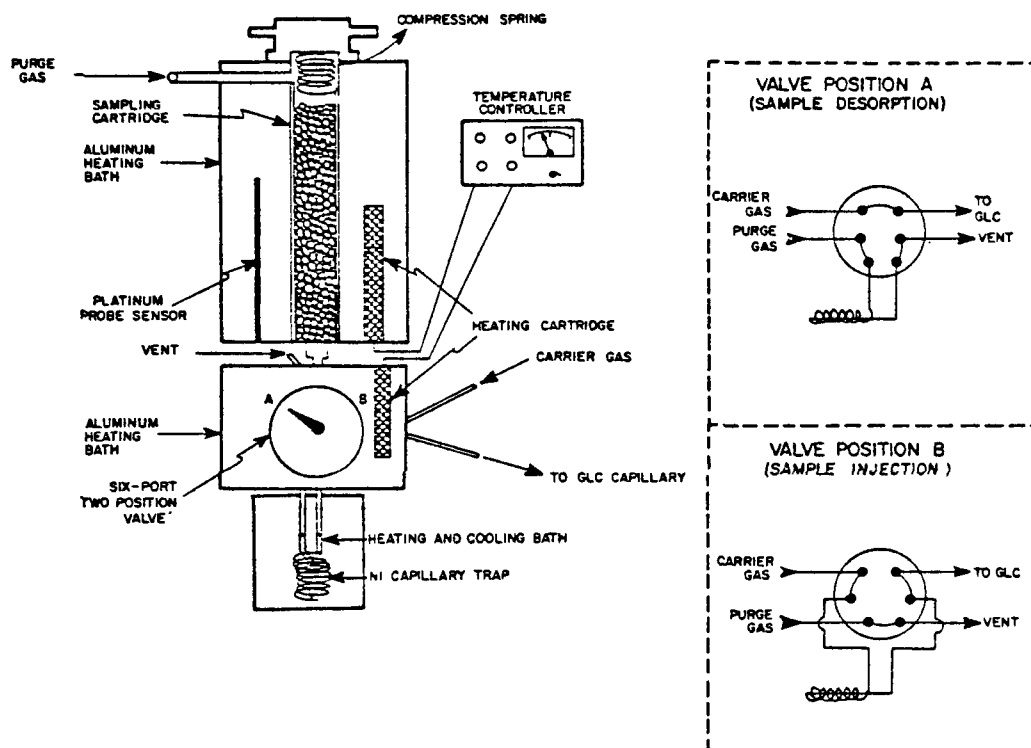


Figure A-1. Thermal desorption/high resolution interface manifold for gas chromatography.

At the beginning and throughout the chromatographic run the mass spectrometer was set to operate in the repetitive scanning mode. In this mode, the magnet was automatically scanned exponentially upward from a preset low mass to a high mass value (m/e 25-300). The scan is completed in approximately three seconds. At this time the instrument automatically resets to the low mass position in preparation for the next scan, and the information accumulated by an on-line 620/L computer and stored on magnetic tapes or the dual disk system. The reset period require approximately three seconds. Thus, a continuous scan cycle at six seconds/scan maintained and repetitively executed throughout the chromatographic run. The result is the accumulation of a continuous series of mass spectra throughout the chromatographic run.

Prior to running unknown samples, the system was calibrated with a standard substance, perfluorokerosene, to determine the time of the appearance of the known standard peaks in relation to the scanning magnetic field. The calibration table which was thus generated was stored in the 620/L computer memory. This procedure served to calibrate the masses over the scanning range.

With the magnet continuously scanning, the sample was injected and automatic data acquisition initiated. As each spectrum was acquired by the computer, each peak which exceeded a preset threshold was recognized and reduced to centroid time and peak intensity. This information was stored in the computer core while the scan was in progress. In addition, approximately 30 total ion current values and an equal number of Hall probe signals were stored in the core of the computer as they were acquired. During the three second period between scans this spectral information, along with the spectrum number, was written sequentially on disks or magnetic tape, and the computer is reset for the acquisition of the next spectrum.

Upon completion of the entire GC run, 300-1,000 spectra will have been recorded. Depending on the information required, the data may either be processed immediately or additional samples may be run, stored on magnetic tape and the results examined at a later time.

The mass spectral data were processed in the following manner. First, the original spectral data were read and the total ion current (TIC) information extracted. Then the TIC information was plotted against the spectrum number on the Statos-31 recorder. The next stage of the processing involved the conversion of spectral peak times to peak masses which was done directly via the dual disk system. The mass conversion was accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally one set of the calibration data was sufficient for an entire day's data processing since the characteristics of the Hall probe are such that the variation in calibration is less than 0.2 atomic mass units/day. A typical time required for this conversion process for 1,000 spectra was 20 minutes.

Interpretation of Data: Compound Identification

After the spectra were obtained in mass-converted form, the full spectral scans from the GC run was recorded on the Statos-31 plotter. The TIC information available at this time was most useful for deciding which spectra were to be analyzed. At the beginning of the runs where peaks were very sharp, nearly every spectrum was inspected individually to determine the identity of the component. Later in the chromatographic run when the peaks were broader, only selected scans were analyzed.

Identification of resolved components was achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra. Since the OV-101 SCOT capillary separates primarily on the basis of boiling point, particular note was made of the boiling point of the identified compound for comparison with the elution temperature of the standard.

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APPENDIX B
SUMMARY OF PERCHLORINATION REACTION DEVELOPMENT EFFORTS

Perchlorination was attempted under a variety of conditions. In a typical experiment approximately 1 µg each of Halowax 1051[®], Halowax 1014[®], Aroclor 1248[®] and a CHCl₃ blank were pipetted into separate reaction vessels and the solvent evaporated under a nitrogen stream. About 1.0 ml SbCl₅ (Cerac-Pure) was pipetted into a cold reaction vessel and immediately capped. After overnight heating at 170° in an aluminum heating block, the reaction tubes were cooled in ice. The reaction was quenched with 2 ml 25% HCl, and the SbCl₅ hydrolyzed at 60° for 20 min. If the yellow color persisted, additional HCl was added and the hydrolysis carried out at 100°. Following the hydrolysis, the aqueous phase was extracted with 4 x 1 ml benzene, the extracts eluted through a column of Na₂SO₄, combined, blown down to dryness under a N₂ stream and reconstituted to a known volume using benzene. The sample was then analyzed by GC/ECD.

In lieu of a pure standard for C₁₀Cl₈, Halowax 1051[®] was initially used to calibrate the retention time (RT) for C₁₀Cl₈. The gas chromatogram of Halowax 1051[®] on 2% OV-101 (Figure B-1, top) contains 2 major peaks with RT = 5 min and 9 min. The early eluting peak (RT = 5 min) was identified by GC/MS/COMP (Finnigan 3200) as C₁₀HCl₇ and the latter peak as C₁₀Cl₈.

There was an interfering peak in the chromatogram (Figure B-1, bottom) which caused problems because its RT is the same as that of C₁₀HCl₇. The interfering peak was traced to a septum problem and was solved by changing from a 2% OV-101 (200°) column packing to 2% OV-17 (230°). Figure B-2 illustrates the shift of this peak relative to C₁₀HCl₇.

The reaction consistently perchlorinates the Aroclor[®] polychlorobiphenyls (PCB) mixture with little or no by products (Figure B-3), although recovery is low (~10-20% -- no quantitation was performed). The Halowaxes[®] did not consistently perchlorinate. It had been thought that C₁₀HCl₇ was being formed in many of the trials, but discovery of the interference mentioned above (Figure B-2) negated these results. With a change of GC columns, it was found that perchlorination was not being achieved using the above conditions and that in fact no detectable compounds were present. Several possible causes of this loss were investigated. The possible loss during nitrogen blow-down was shown to be negligible. No perceptible change was noted in the Halowax 1014[®] fingerprint pattern in a reconstituted

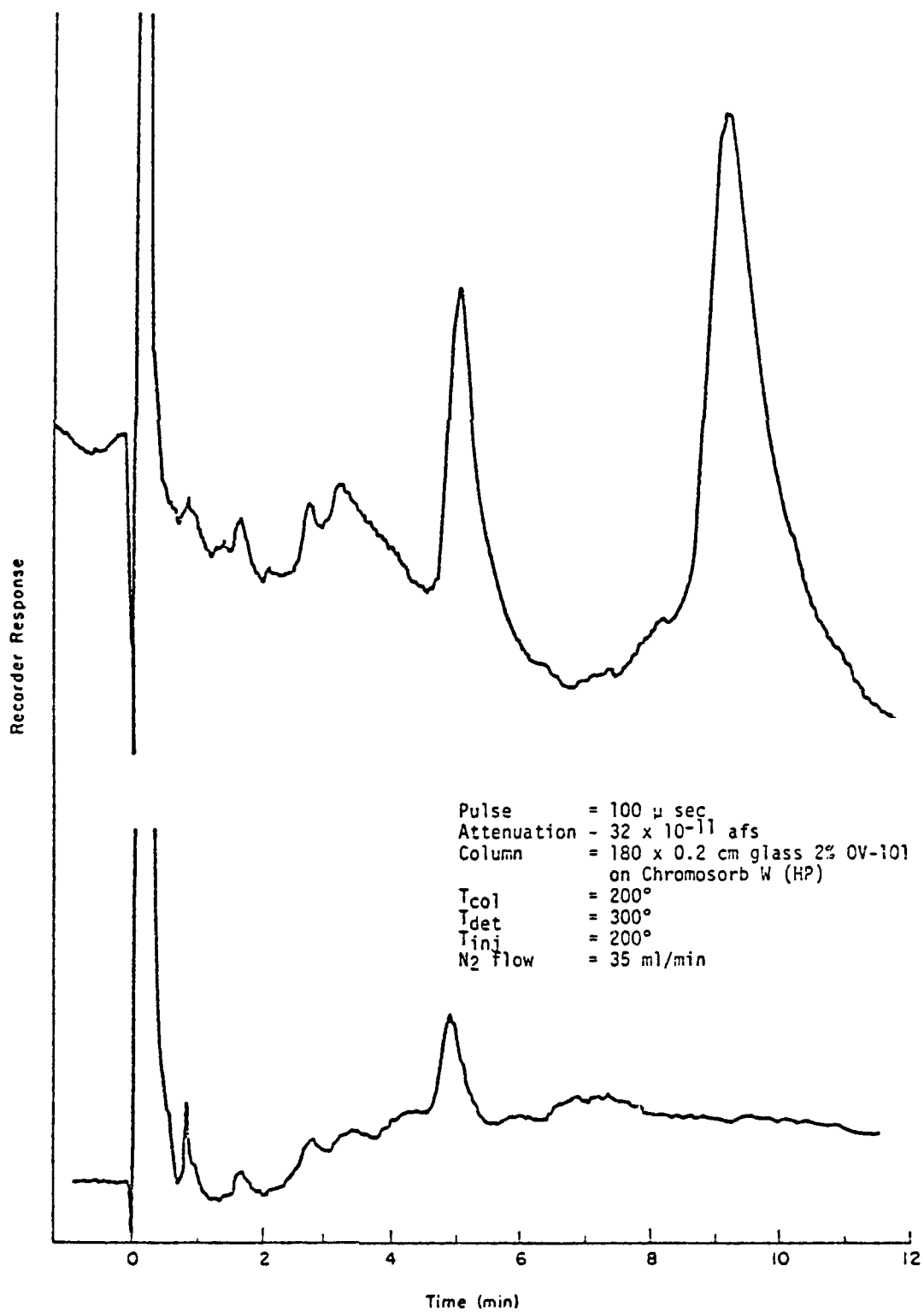


Figure B-1. Halowax 1051[®] and interfering peak.

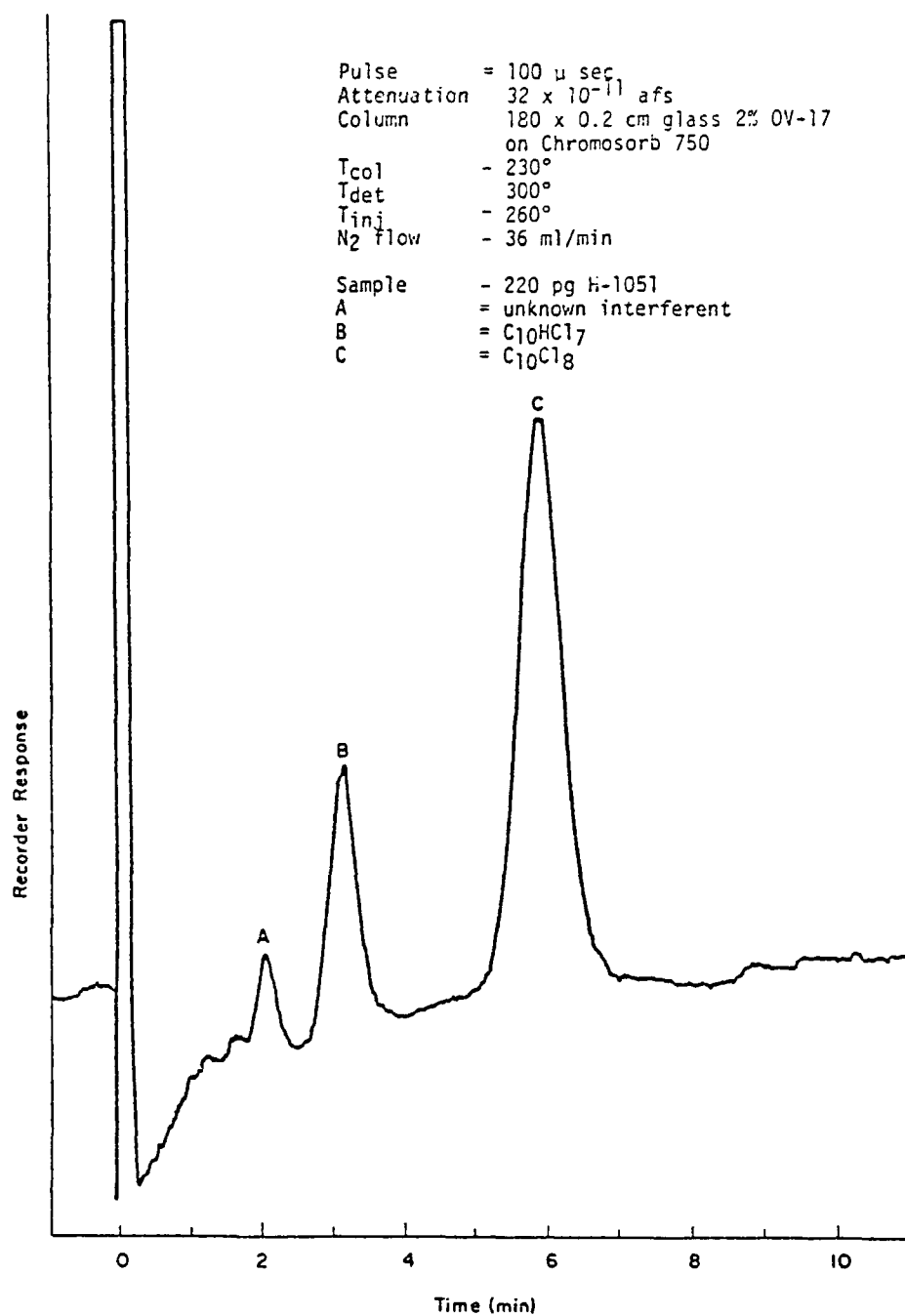


Figure B-2. Halowax 1051 [®] on 2% OV-17.

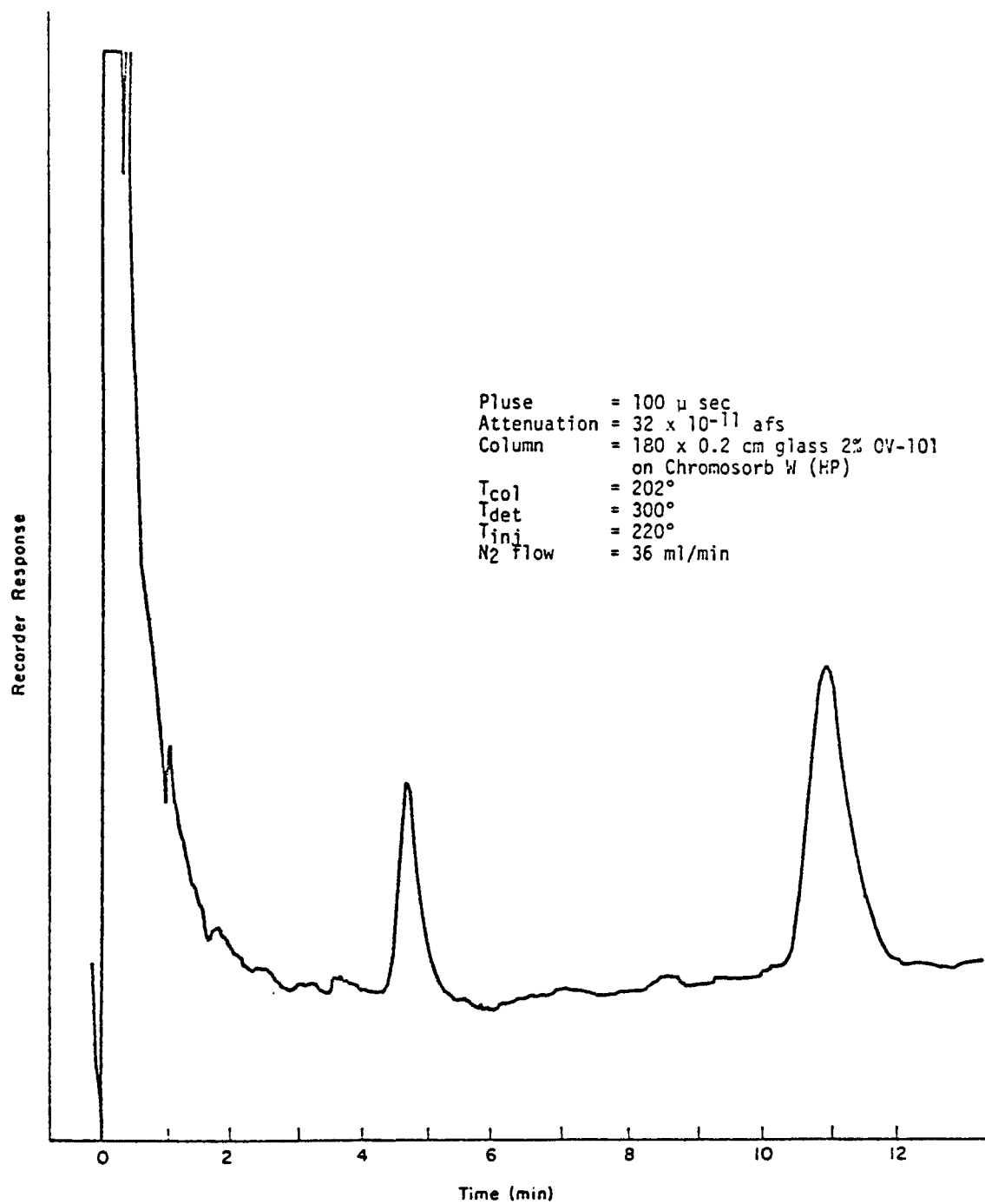


Figure B-3. Perchlorinated Aroclor 1248[®].

solution after 30 min of N_2 stream blowing through the sample tube at 35° . The possibility of loss due to adsorption on the Na_2SO_4 column was ruled out after an experiment showed that the Halowax[®] concentrate was the same before and after passage through the column. It is apparently important that a tightly sealed, inert reaction vessel be employed to prevent loss or contamination of the Halowax[®] at 170° . Hydrolysis vials (Regis), 5 ml reaction vials (Kontes), 17 x 150 mm screw cap culture tubes (Kimble), and vacuum hydrolysis vials (Pierce) were used as reaction vessels in these experiments. None was totally satisfactory.

The purity of $SbCl_5$ from various sources was investigated by running solvent blanks through the above procedure. All samples of $SbCl_5$ tried were found to contain some impurities, which elute early in the chromatogram. Antimony pentachloride from Cerac-Pure was the purest, followed by that from Ventron and then PCR. A blank sample prepared using Cerac-Pure $SbCl_5$ was analyzed by GC/MS. Very small amounts of C_6Cl_6 , C_6Cl_5Br and $C_6Cl_4Br_2$ (on the order of 0.1 ppm) were identified. These amounts were not great enough to interfere significantly with PCN analysis.

The use of both benzene and hexane as solvents for extraction of $C_{10}Cl_8$ from the hydrolyzed reaction mixture was investigated, and benzene was found to be more efficient.

In order to extend the range of conditions evaluated for the perchlorination of PCNs, milder conditions, e.g. lower temperatures and shorter times, were investigated. These conditions proved more satisfactory, although two problems with the reaction have not been solved to date: (1) apparent reaction by-products were observed even under the mildest of reaction conditions; (2) recovery of the products was poor, generally less than 50%. Several experiments were conducted in unsuccessful efforts to correct these problems.

Table B-1 summarizes the perchlorination trials conducted to demonstrate effects of time and temperature. At lower reaction temperatures, the vaporization of PCNs did not appear to be a problem nor did leakage from reaction vessels due to high internal pressures.

Accordingly, the requirement of carefully sealing the reaction vessel when two at higher temperatures was no longer so rigid. Screw cap culture

Table B-1. PERCHLORINATION REACTION RESULTS

Reaction Number	Reaction Vessel	Reagent	Temp.	Time (hr)	Starting Material	Amount Reacted (ug)	Analysis	% Recovered	Comments
I	H ^a	Hexane (1 ml)	210°	15	H-1051	1.2	No reaction	166%	Hexane Solvent may have evaporated to yield high recovery
II	H	CHCl ₃ (1 ml)	90°	15	H-1051	1.2	No reaction	101%	Rxn worked up by evaporating CHCl ₃ , reconstituted in hexane
III	H	SbCl ₅	23°	0	H-1051	1.2	No reaction	66%	
IV	H	SbCl ₅	90°	0.75	H-1051	1.2	C ₁₀ Cl ₈ = 0 C ₁₀ Cl ₇ H = 18%		Very large peak at RRT ^c = 0.36
V	H	SbCl ₅	90°	3.0	H-1051	1.2	C ₁₀ Cl ₈ = 0 C ₁₀ Cl ₇ = 12%		Peak at RRT = 0.36 has increased markedly at expense of C ₁₀ Cl ₇
VI	H	SbCl ₅	98°	73	H-1051	1.2	Nothing observed in chromatogram		
VII	H	SbCl ₅	23°	42	H-1051	1.2	Several small peaks, RRT ≠ PCNs		
VIII	H	SbCl ₅ /SO ₂ Cl ₂	23°	42	H-1051	1.2	C ₁₀ Cl ₈ is only PCN observed	19%	First extraction only
IX	H	SbCl ₅ /SO ₂ Cl ₂	23°	42	H-1014	118	C ₁₀ Cl ₈ is about 13 times C ₁₀ Cl ₇	52%	Small amount of early-eluting peaks.
X	H	SbCl ₅	23°	42	H-1014	118	C ₁₀ Cl ₈ , C ₁₀ Cl ₇ H approx. equal Many early eluting peaks		

(continued)

Table B-1. (cont'd)

Reaction Number	Reaction Vessel	Reagent	Temp.	Time Starting (hr)	Material	Amount Reacted (μg)	Analysis	% Recovered	Comments
XI	H	CHCl ₃ (1ml)	23°	42	H-1014	118	No reaction. Fingerprint similar to standard	71%	
XII	C	SbCl ₅	70°	0 ^d	H-1014	1.2	C ₁₀ Cl ₈ + C ₁₀ Cl ₇ H already forming	- ^e	
XIII	C	SbCl ₅	70°	0.25	H-1014	1.2	$\frac{C_{10}Cl_8}{C_{10}Cl_7H} \approx 7$	60%	No other PCN peaks
XIV	C	SbCl ₅	70°	0.50	H-1014	1.2	C ₁₀ Cl ₈ is only peak observed	48%	
XV	C	SbCl ₅	70°	1.0	H-1014	1.2	C ₁₀ Cl ₈	21%	Small "Char" peak at RRT = 0.59
XVI	C	SbCl ₅	70°	2.0	H-1014	1.2	C ₁₀ Cl ₈	4%	"Char" peak at RRT = 0.59 increasing
XVII	C	SbCl ₅	70° 170°	2.0, 9	H-1014	1.2	C ₁₀ Cl ₈	-	"Char" peak at RRT = 0.59 much larger
XVIII	C	SbCl ₅ ^f	55°	0 ^d	H-1014	1.2	C ₁₀ Cl ₈ + C ₁₀ Cl ₇ H are already quite prominent		
XIX	C	SbCl ₅	55°	0.5	H-1014	1.2	C ₁₀ Cl ₈ predominates, 21% C ₁₀ Cl ₇ H \sim 1/7 C ₁₀ Cl ₈		

(continued)

Table B-1. (cont'd)

Reaction Number	Reaction Vessel	Reagent	Temp.	Time (hr)	Starting Material	Amount Reacted (μ g)	Analysis	% Recovered	Comments
XX	C	$\text{SbCl}_5/\text{SO}_2\text{Cl}_2$	55°	0.5	H-1014	1.2	$\frac{\text{C}_{10}\text{Cl}_8}{\text{C}_{10}\text{Cl}_7\text{H}} = 0.85$	29%	
XXI	C	SbCl_5	55°	1.0	H-1014	1.2	C_{10}Cl_8 is only product	9%	
XXII	C	$\text{SbCl}_5/\text{SO}_2\text{Cl}_2$	55°	1.0	H-1014	1.2	C_{10}Cl_8 is only product	17%	Unknown peak at RRT = 0.52
XXIII	C	SbCl_5	50° ^g	1.0	C_{10}Cl_8	0.28	Char peak at RRT = 0.73 about 0.25 that of C_{10}Cl_8	47%	
XXIV	C	SbCl_5	50°	1.0	H-1051	1.2	C_{10}Cl_8 only product	38%	
XXV	C	SbCl_5	50°	1.0	H-1014	1.2	$\text{C}_{10}\text{Cl}_8/\text{C}_{10}\text{Cl}_7\text{H} = 9$	37%	
XXVI	C	SbCl_5	50°	1.0	H-1099	0.8	Traces of $\text{C}_{10}\text{Cl}_7\text{H}$ and lower PCN's	10%	
XXVII	C	SbCl_5	50°	1.0	A-1232	1.2	$\text{C}_{12}\text{Cl}_{10}$ peak slightly - increased over standard. Very little reaction.		
XXVIII	C	SbCl_5	-78°	0	H-1014	1.2	C_{10}Cl_8 and $\text{C}_{10}\text{Cl}_7\text{H}$ are already quite prominent		ⁱ "Char" peak at RRT = 0.81 visible as small bump

(continued)

Table B-1. (cont'd)

Reaction Number	Reaction Vessel	Reagent	Temp.	Time (hr)	Starting Material	Amount Reacted (μg)	Analysis	% Recovered	Comments
XXIX	C	SbCl ₅	23°	0.75	H-1014	1.2	C ₁₀ Cl ₈ is largest peak C ₁₀ Cl ₇ H is quite prominent other PCN's still present	19% 14%	ⁱ "Char" peak at RRT = 0.81 Visible as small bump
XXX	C	SbCl ₅	23° 40°	0.75 1.0	H-1014	1.2	C ₁₀ Cl ₈ predominates C ₁₀ Cl ₇ H not detected Some early-eluting peaks present	15%	"Char" peak is ~10% of C ₁₀ Cl ₈
XXXI	C	SbCl ₅	23° 40°	0.75 2.6	H-1014	1.2	Similar to XXX	9%	"Char" peak is ~27% of C ₁₀ Cl ₈
XXXII	C	SbCl ₅	23° 40°	0.75 2	H-1014	1.2	Very little early elutes observed	25%	"Char" peak is ~27% of C ₁₀ Cl ₈
XXXIII	C	SbCl ₅	23° 40°	0.75 2.6	A-1232	1.3	Very little reaction observed		
XXXIV	C	SbCl ₅	23° 40°	0.75 2.6	C ₁₀ Cl ₈	0.28	No Charing	8%	

^aH = Pierce Chemical Co. - Vacuum Hydrolysis Tube
C = Screw Cap Culture Tube with double Teflon liners

^bSbCl₅ added in 0.1 ml aliquots: SbCl₅/SO₂Cl₂ added in 0.1/0.4 ml ratio.

^cRRT = Relative Retention Time. RRT of C₁₀Cl₈ = 1.00

^dt=0 means reaction quenched immediately after addition of SbCl₅.

^eQuant. of Samples XII-XVI is for first extract only.

^fFor samples XVII-XXII, SbCl₅ added to tubes at 0° in ice bath.

^gReagent added at room temperature for reactions XXIII-XXVII.

^hReagent added to tubes in dry ice/acetone bath for reactions XXVIII-XXXIV.

ⁱRecoveries for XXVIII-XXXIV are for one extraction only.

*Values are for C₁₀Cl₈ found as percent of theoretical calculated from amount reacted. Reactions I-III.

H-1014 = Halowax-1014 [®]
A-1232 = Aroclor-1232 [®]

tubes or centrifuge tubes with double Teflon liners proved the most advantageous, both in terms of cost and ease of handling. Samples I, II and XI illustrate the good recoveries obtained from tightly sealed samples under typical reaction conditions.

Several results are worth special note from Table B-1. It appears that the presence of SO_2Cl_2 tempers the action of SbCl_5 and gives better yield and fewer unwanted by-products (compare reactions VII and VIII, IX and X, XIX and XX, and XXI and XXII). Further experiments would be needed in this area before definite conclusions could be drawn. The yield of the reactions at higher concentrations (IX-XI) is greater than normal, possibly indicating that the use of smaller amounts of SbCl_5 would yield better recoveries.

It appears that even with the addition of SbCl_5 to the reaction vessel in a dry ice-acetone bath and slow heating that the conditions may be too severe. Possibly dilution of the SbCl_5 with SO_2Cl_2 (mentioned above), C_6F_6 or other suitable solvent may be a solution.

Figures B-4-B-6 are examples of the more successful perchlorination attempts for three Halowax[®] mixtures. Note that all of the chromatograms contain early-eluting peaks which are attributed to unreacted material for Figures B-5 and B-6. There are no peaks attributable to Halowax 1051[®] with relative retention time (RRT) = 0.12 ($\text{C}_{10}\text{Cl}_8 = 100$), so the large, early-eluting spike is unidentified.

The effects of the use of SO_2Cl_2 are illustrated in Figures B-7 and B-8. While the percent conversion to C_{10}Cl_8 is greater with SO_2Cl_2 (Figure B-8), the presence of a large peak at RRT = 0.5 (RRT \neq $\text{C}_{10}\text{HCl}_7$) indicates either partial reaction or by-products.

The effects of time and temperature on the reaction are illustrated in Figures B-9-B-13. Figure B-9 is a chromatogram of Halowax 1015[®] standard for retention time comparison. The two large peaks at 4.5 min and 8.5 min in Figure B-10 (XXVII) show that the concentrations of $\text{C}_{10}\text{HCl}_7$ and C_{10}Cl_8 , respectively, have grown markedly even at dry ice temperatures. After 45 min at 23° (Figure B-11), the $\text{C}_{10}\text{HCl}_7$ and C_{10}Cl_8 peaks are even more pronounced, and the by-product peak at 6.9 min (RRT = 0.82) is clearly evident. In Figure B-12 the by-product peak has increased in prominence, while the

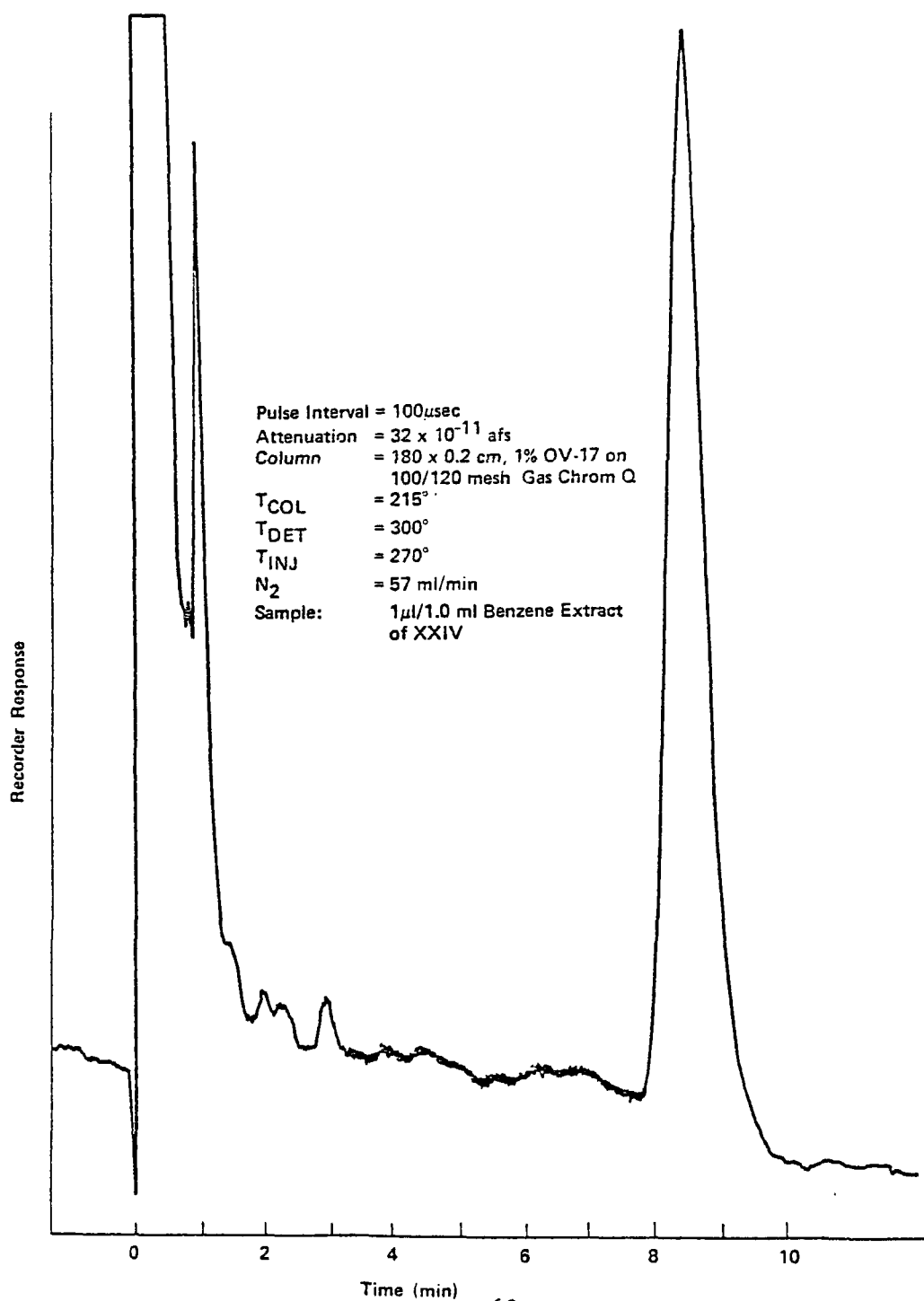


Figure B-4. Gas chromatogram (^{63}Ni electron capture detection) of perchlorinated Halowax 1051 $\text{\textcircled{R}}$.

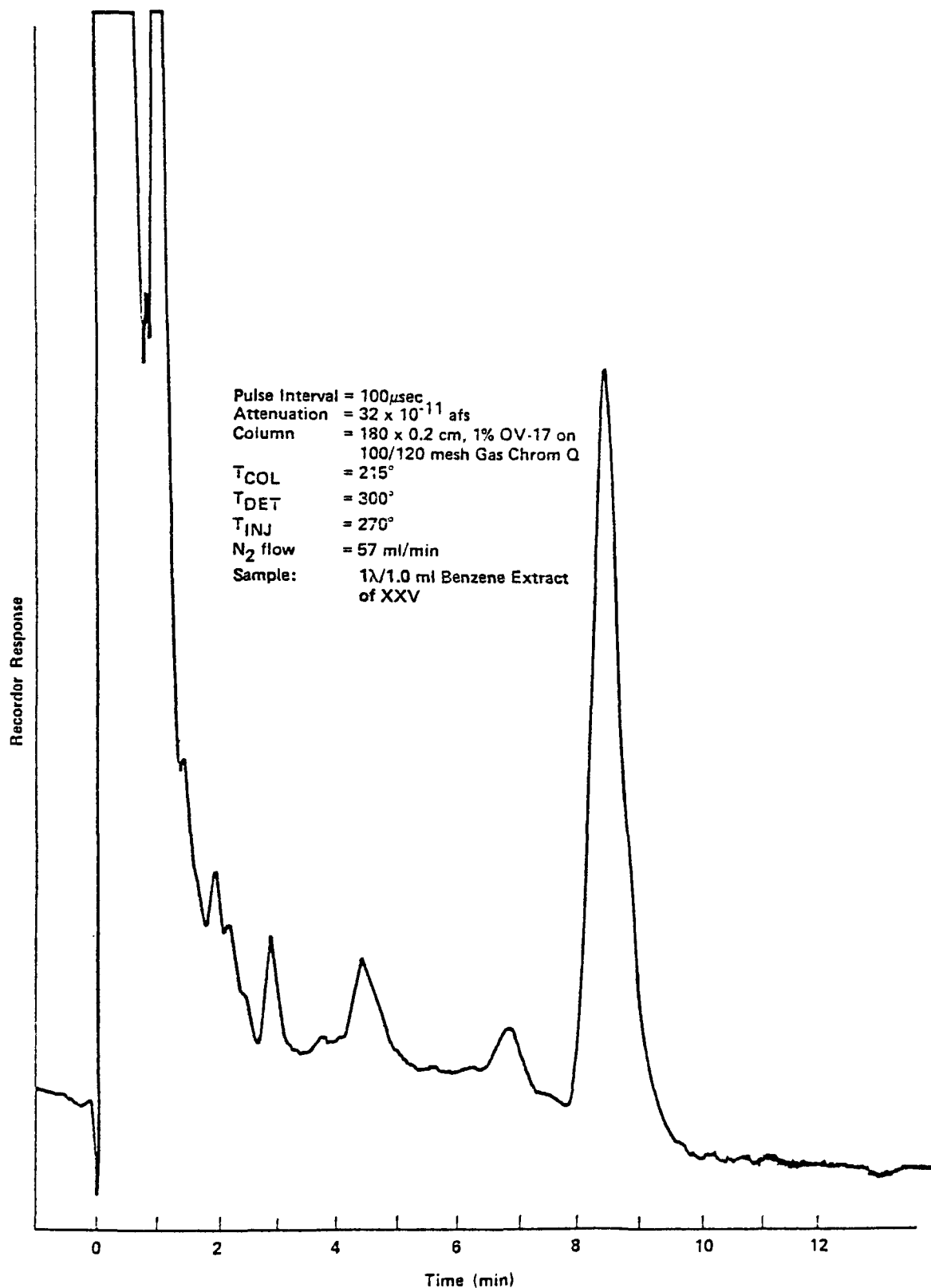


Figure B-5. Gas chromatogram (^{63}Ni electron capture detection) of perchlorinated Halowax 1014 $\text{\textcircled{R}}$.

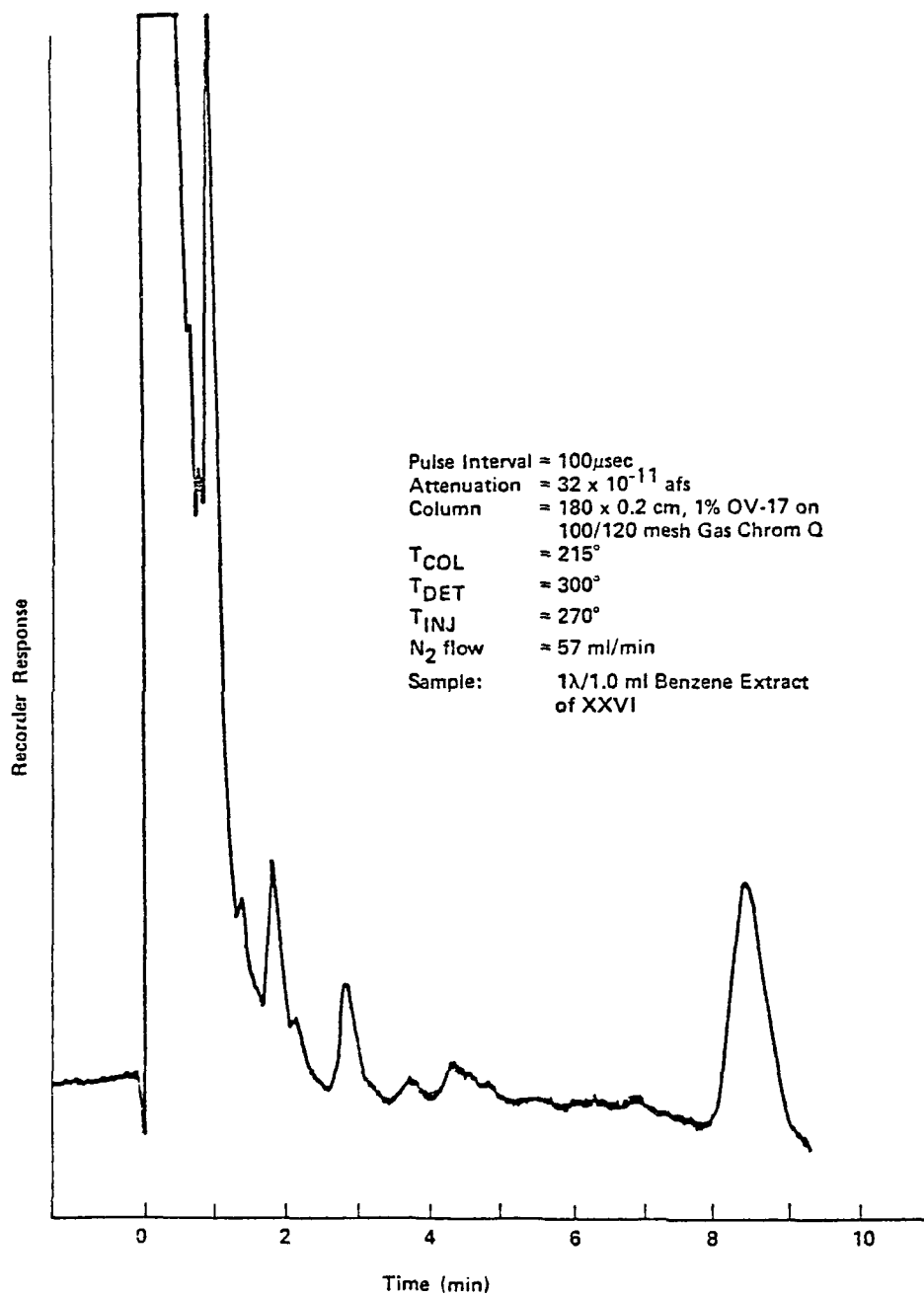


Figure B-6. Gas chromatogram (^{63}Ni electron capture detection of perchlorinated Halowax 1099 $\text{\textcircled{R}}$).

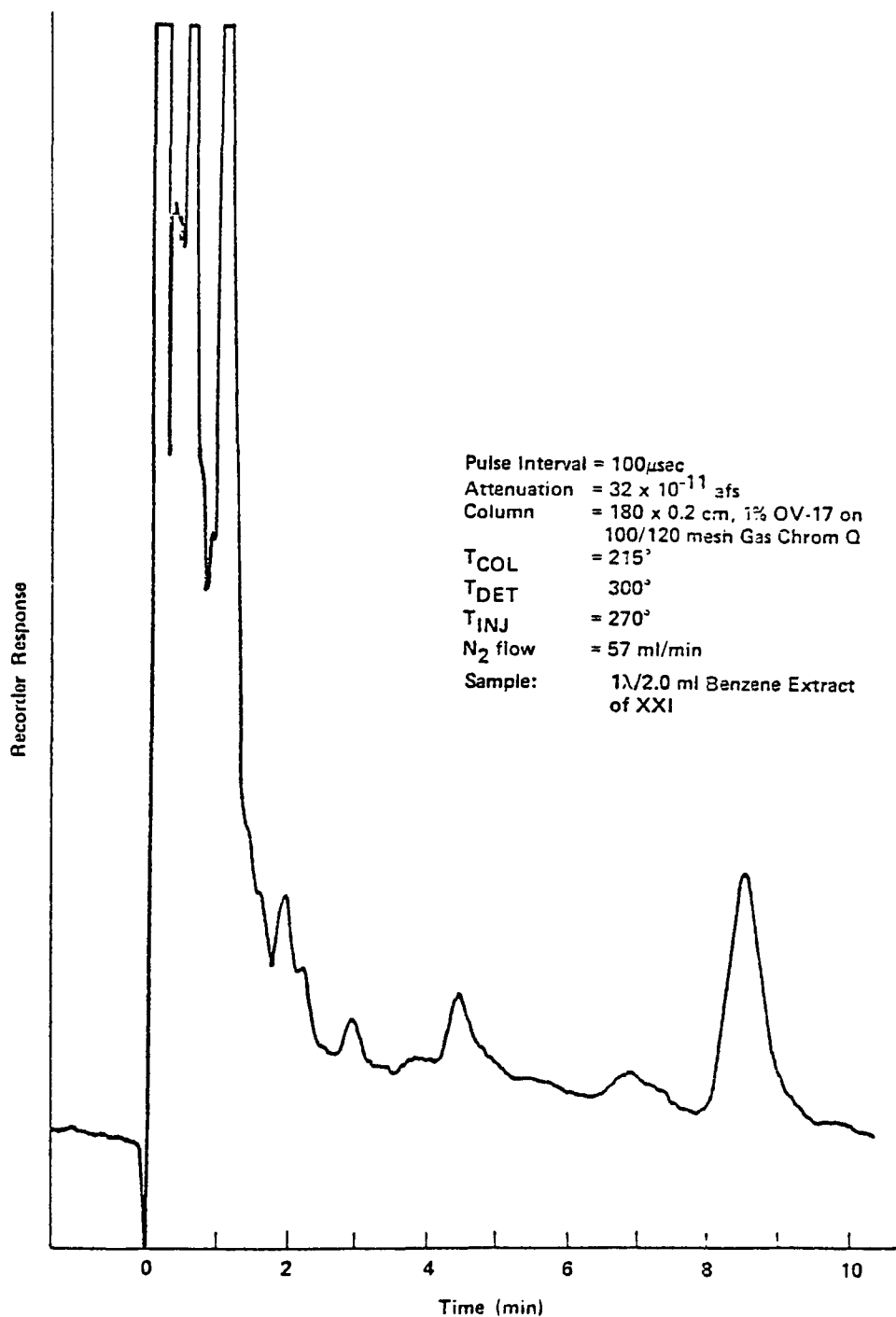


Figure B-7. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014[®] perchlorinated using antimony pentachloride.

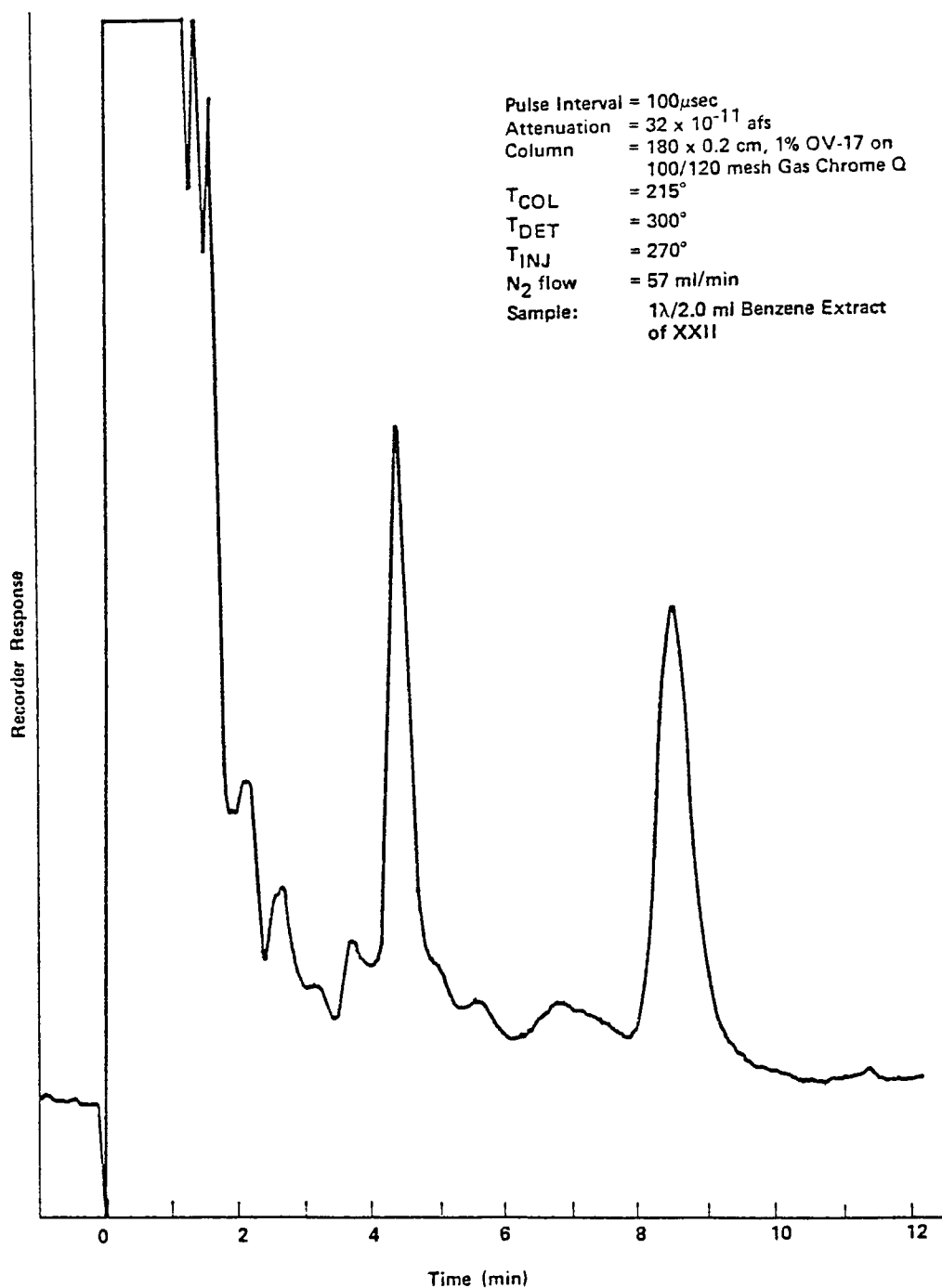


Figure B-8. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014[®] perchlorinated using antimony pentachloride and sulfuryl chloride.

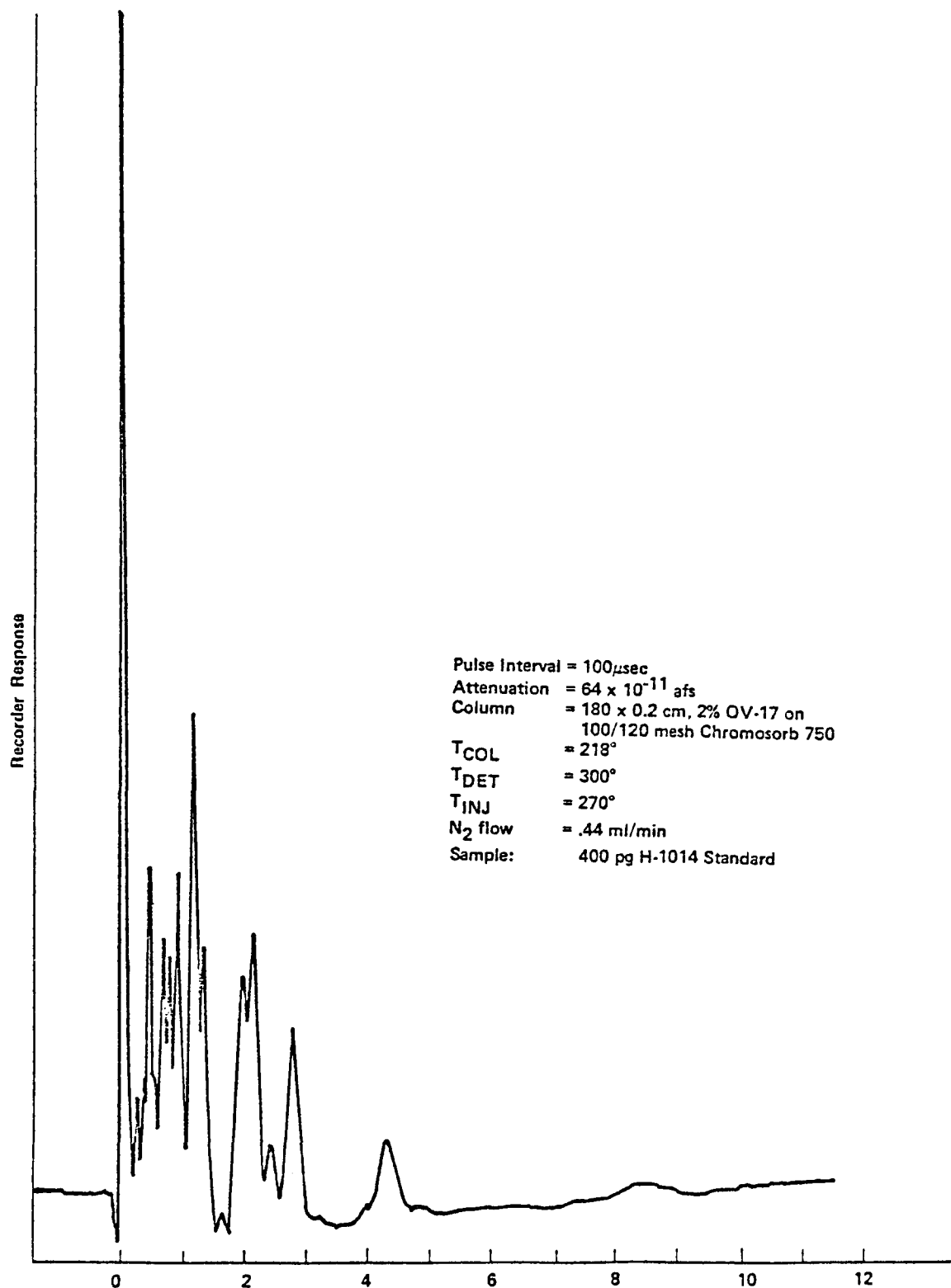


Figure B-9. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014 $\text{\textcircled{R}}$ standard.

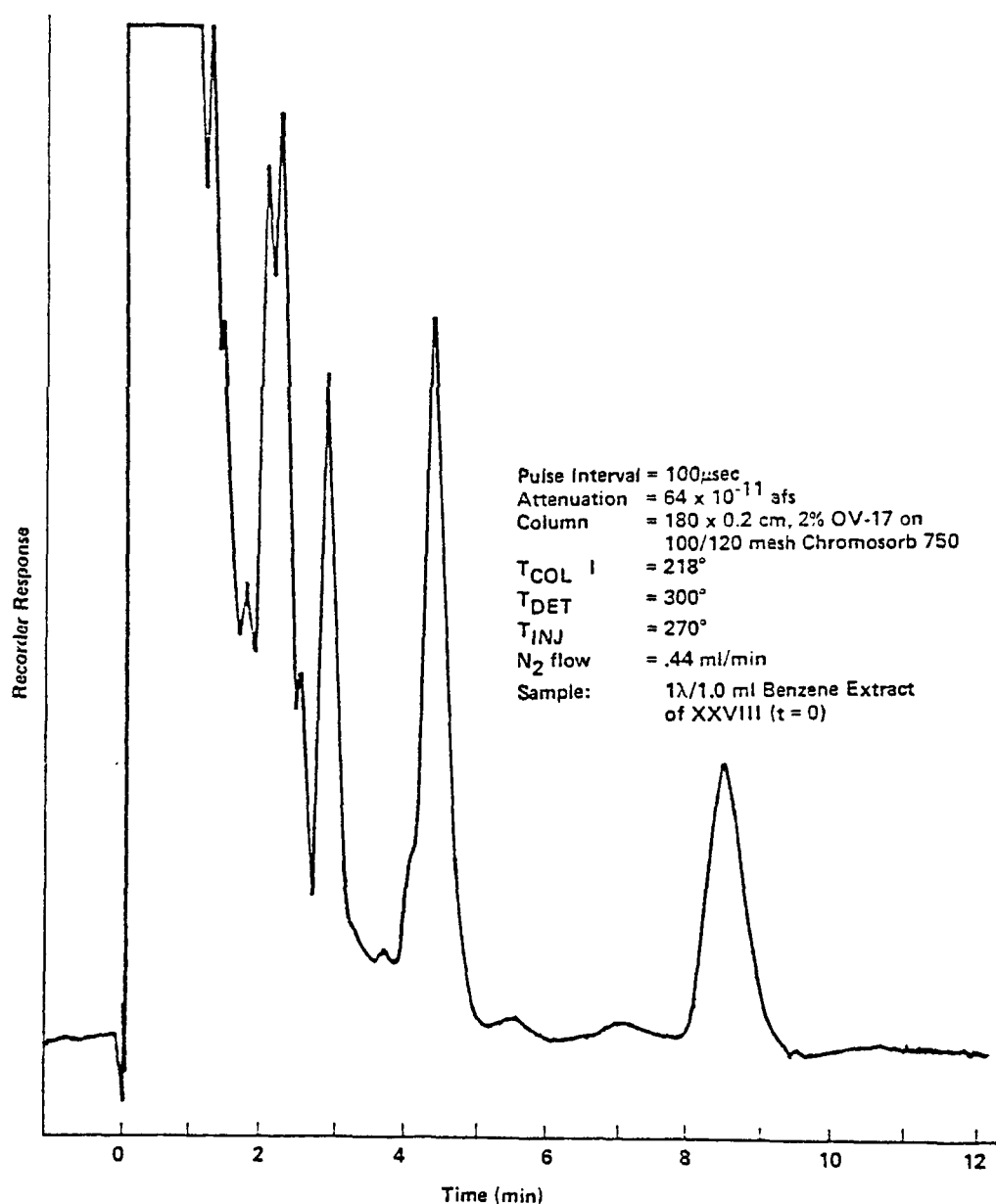


Figure B-10. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014[®] perchlorination reaction. Reaction quenched immediately after addition of antimony pentachloride at -78°.

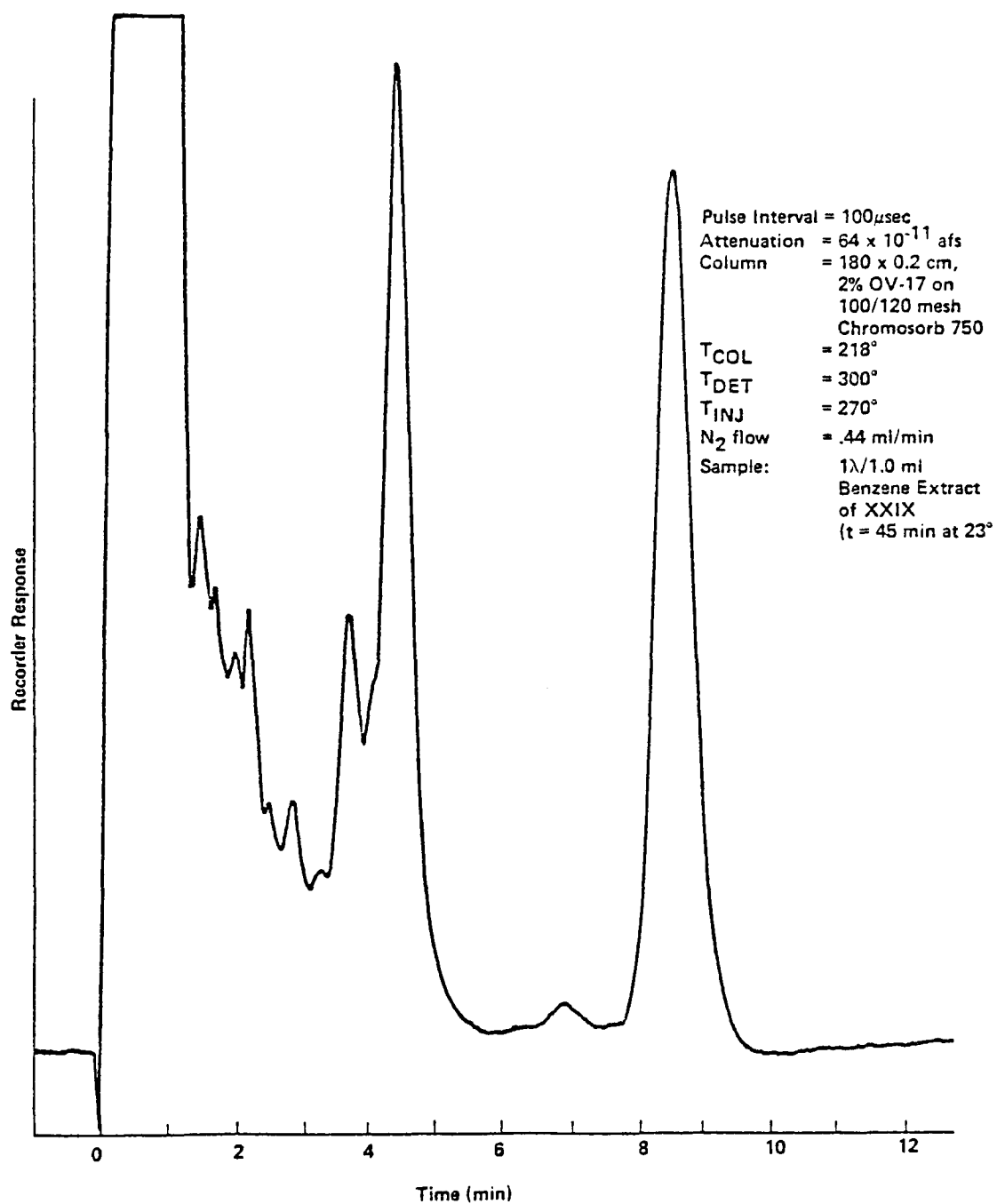


Figure B-11. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014[®] perchlorination reaction. Reaction quenched after 0.75 hour at room temperature.

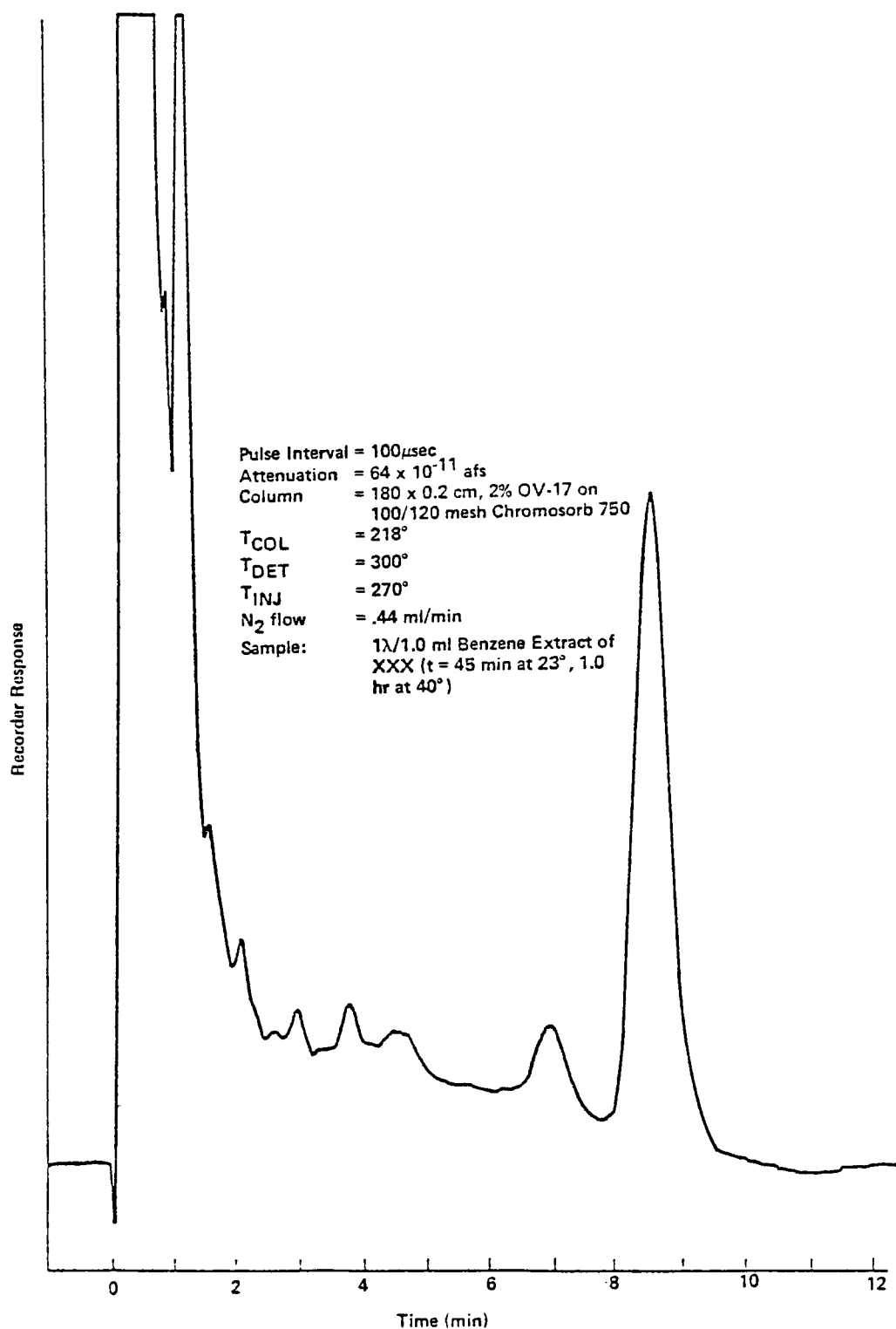


Figure B-12. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014 ® perchlorination reaction. Reaction quenched after 0.75 hour at room temperature and 1.0 hour at 40°.

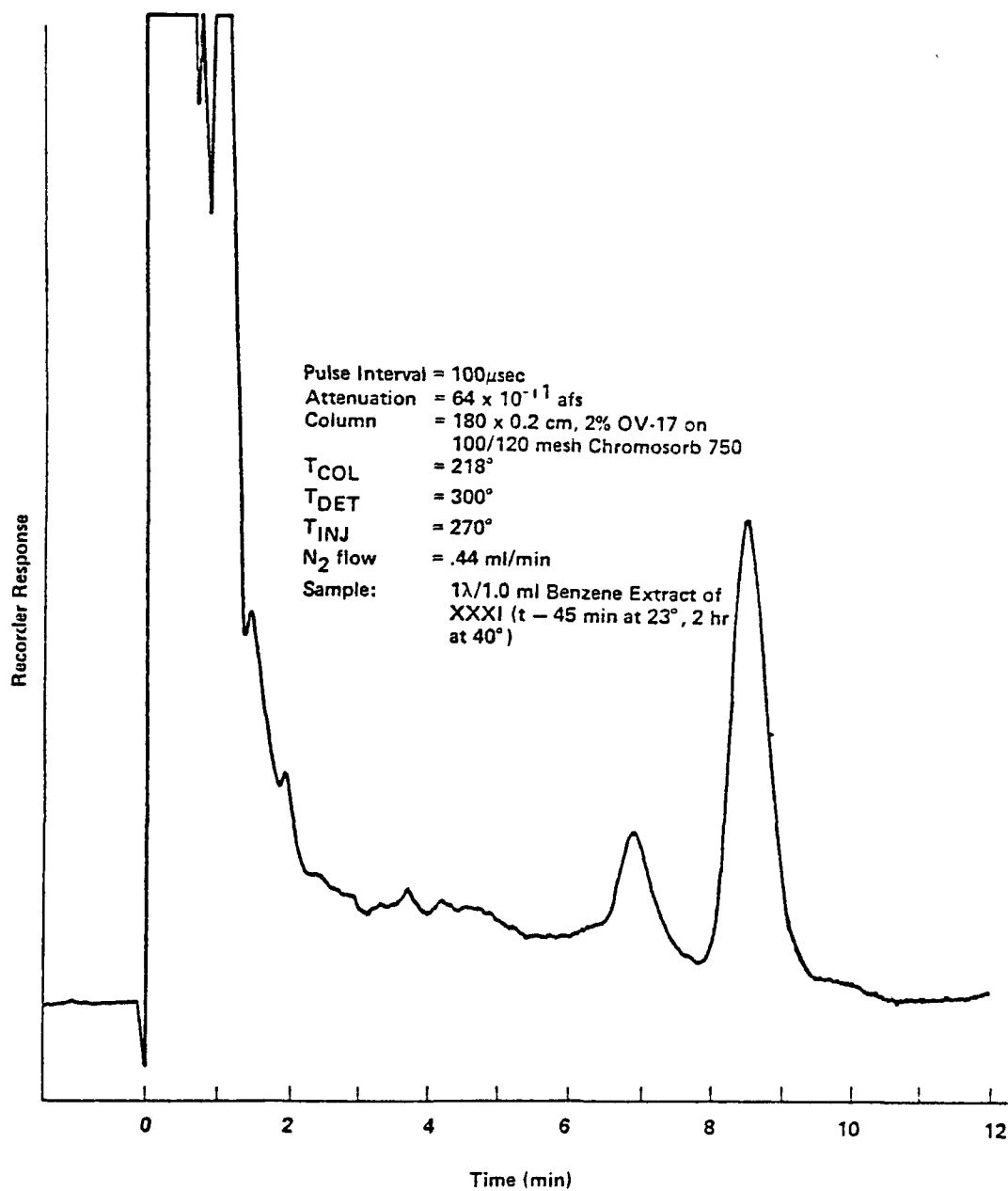


Figure B-13. Gas chromatogram (^{63}Ni electron capture detection) of Halowax 1014[®] perchlorination reaction. Reaction quenched after 0.75 hour at room temperature and 2.0 hour at 40°.

$C_{10}HCl_7$ peak has virtually disappeared. After 2.0 hr (Figure B-13), the by-product peak continues to increase, and the $C_{10}Cl_8$ peak is diminished.

At these mild perchlorination conditions the PCB mixtures examined were not perchlorinated significantly as illustrated in Figures B-14 and B-15. It does not appear from these results that suitable conditions will be found for perchlorination of PCNs and PCBs in the same sample.

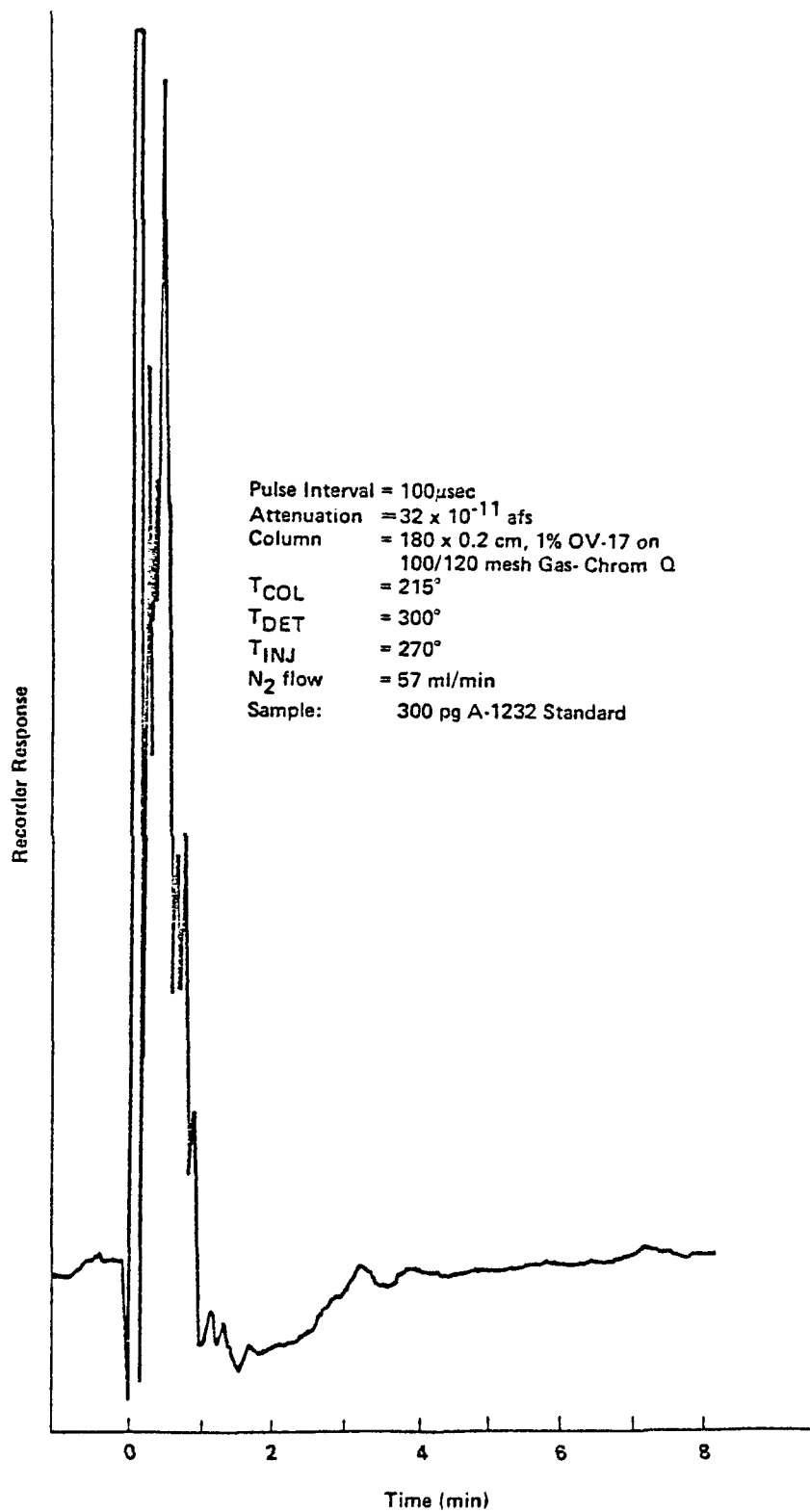


Figure B-14. Gas chromatogram (^{63}Ni electron capture detection) of Aroclor 1232 $\text{\textcircled{R}}$ standard.

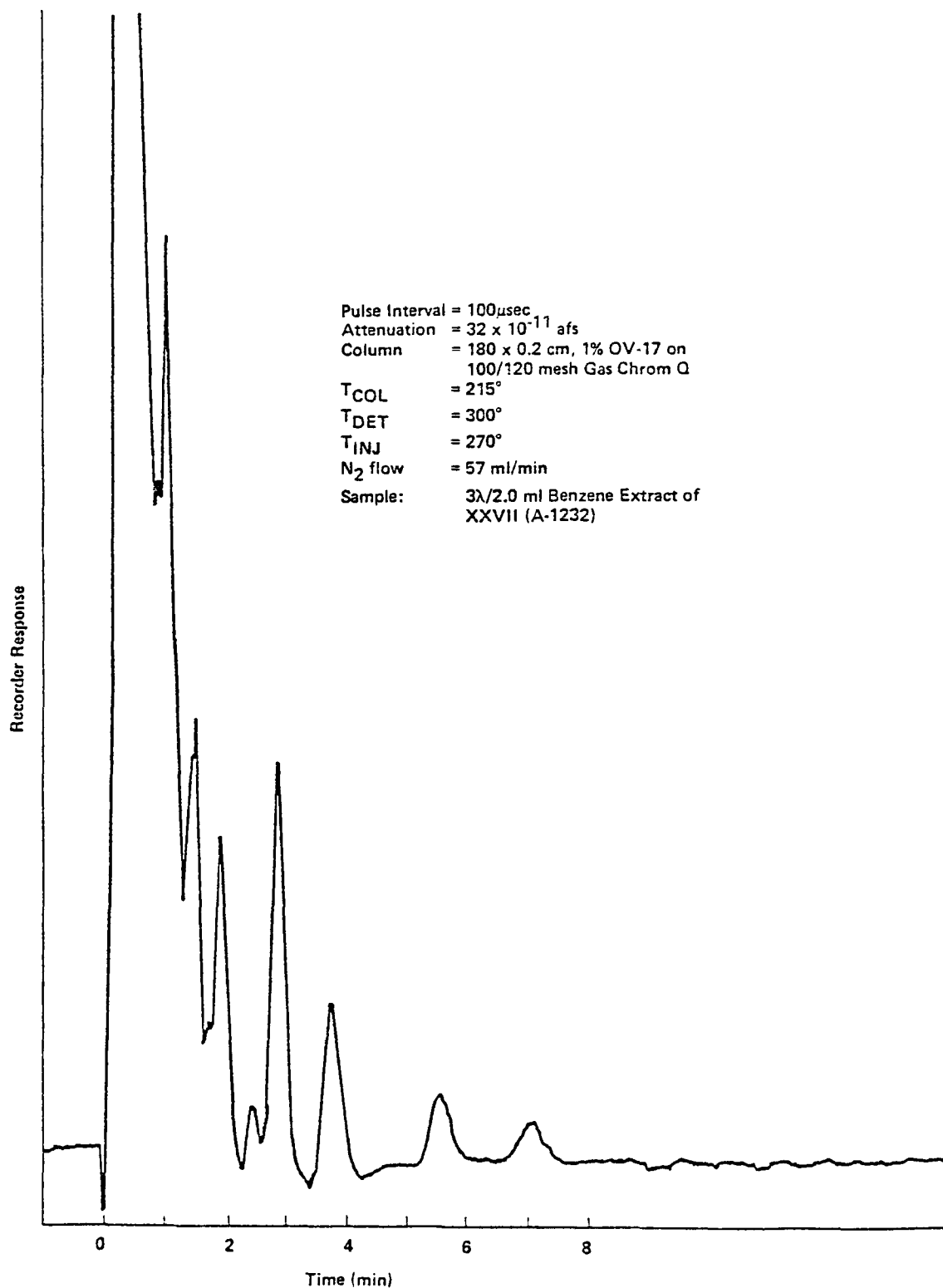


Figure B-15. Gas chromatogram (^{63}Ni electron capture detection) of Aroclor 1232 $\text{\textcircled{R}}$ reacted under Halowax perchlorination conditions.

APPENDIX C

GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF
HALOWAXES[®] AND AROCLORS[®]

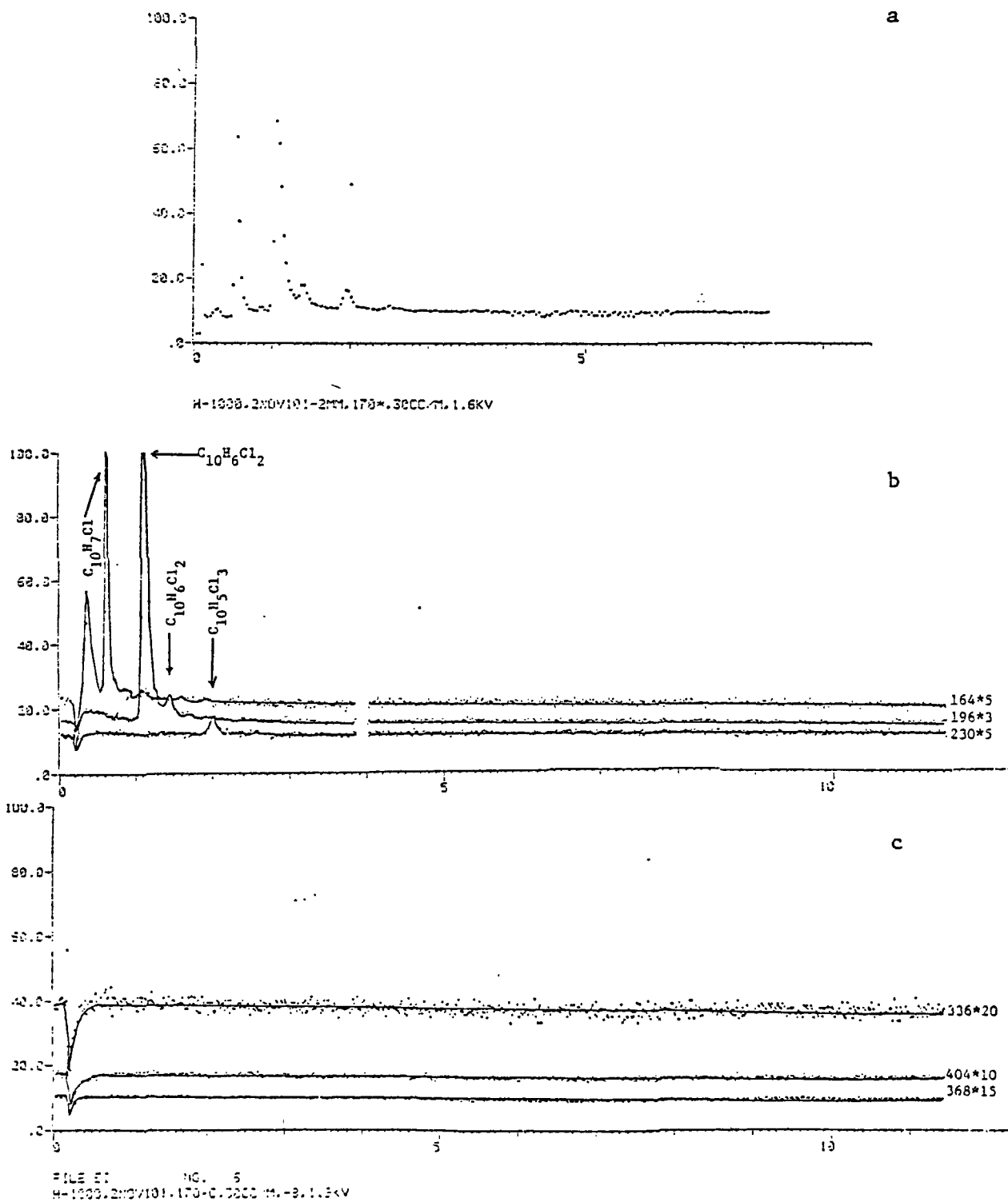


Figure C-1. Gas chromatographic-mass spectrometric analysis of Halowax-1000[®];
a. Total ion current (204 ng)
b. Multiple ion detection (4.08 ng)
c. Multiple ion detection (4.08 ng)

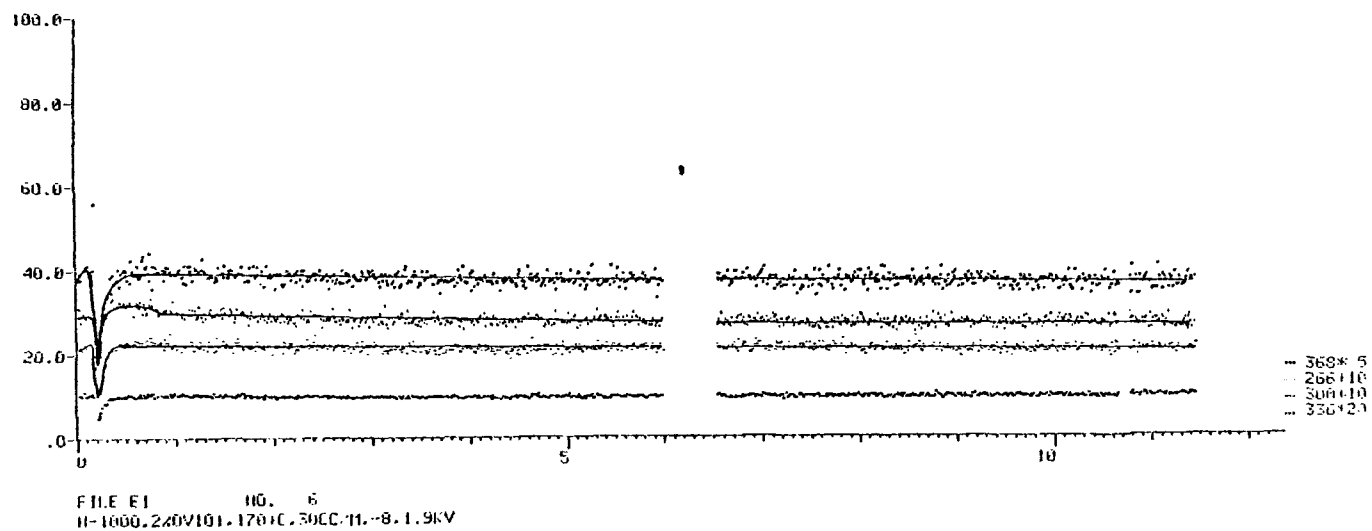


Figure C-2. Gas chromatographic-mass spectrometric analysis of Halowax-1000[®]; multiple ion detection of 4.08 ng.

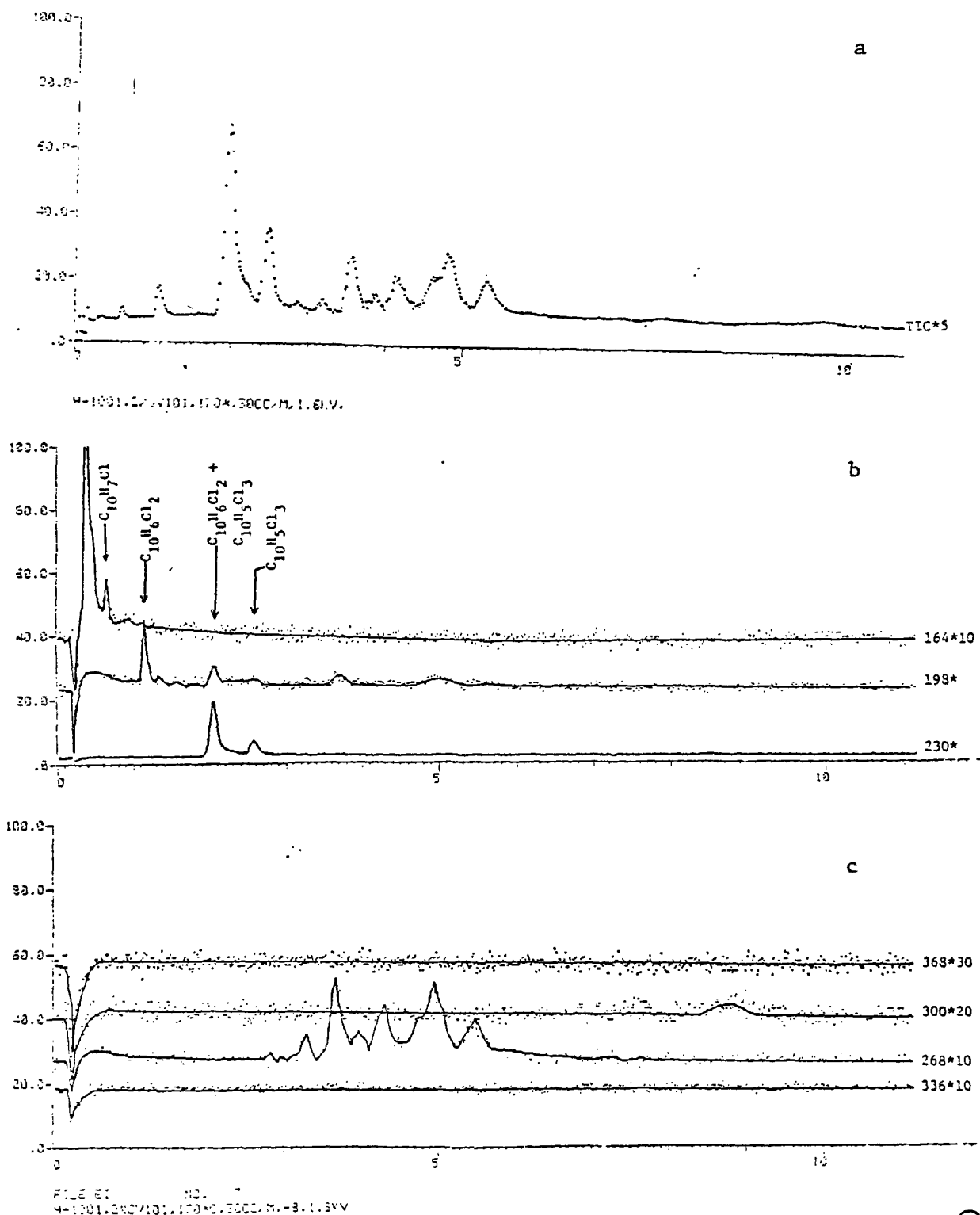


Figure C-3. Gas chromatographic-mass spectrometric analysis of Halowax-1001[®];
 a. Total ion current (208 ng)
 b. Multiple ion detection (4.10 ng)
 c. Multiple ion detection (4.10 ng)

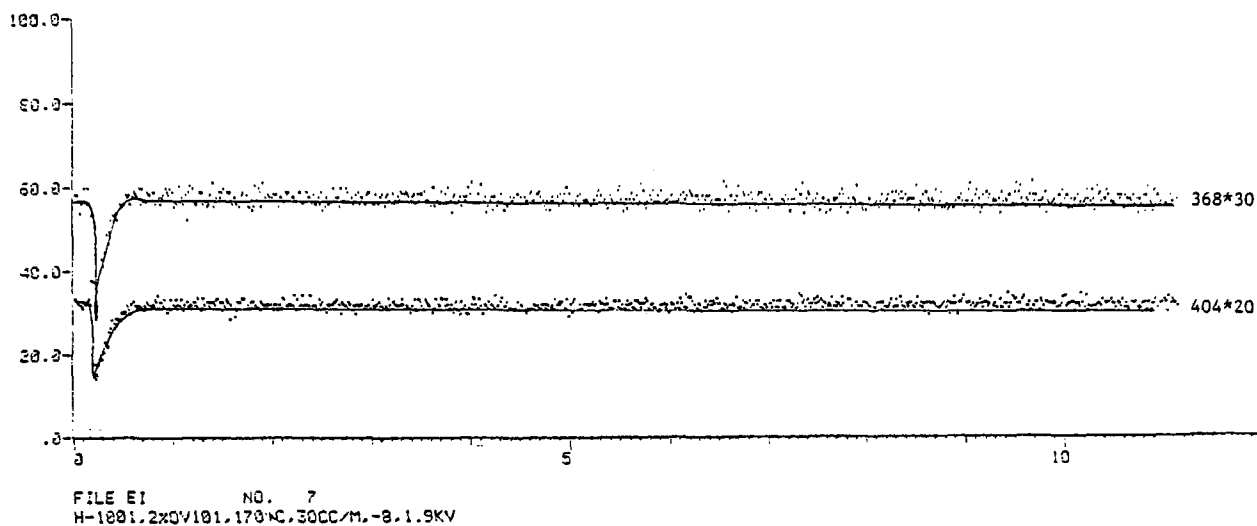


Figure C-4. Gas chromatographic-mass spectrometric analysis of Halowax 1001[®]; multiple ion detection (4.10 ng).

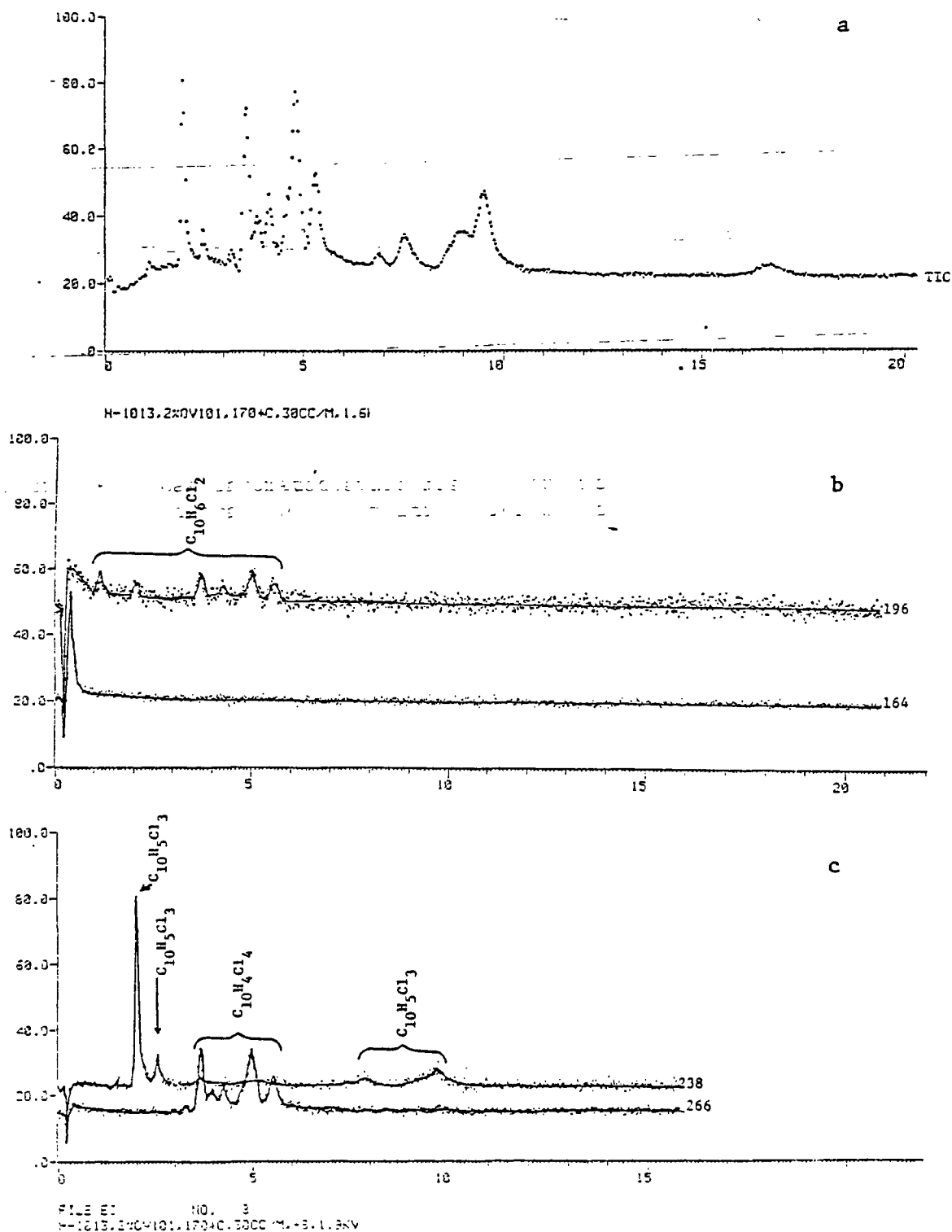


Figure C-5. Gas chromatographic-mass spectrometric analysis of Halowax-1013[®];
 a. Total ion current (180 ng)
 b. Multiple ion detection (3.76 ng)
 c. Multiple ion detection (3.76 ng)

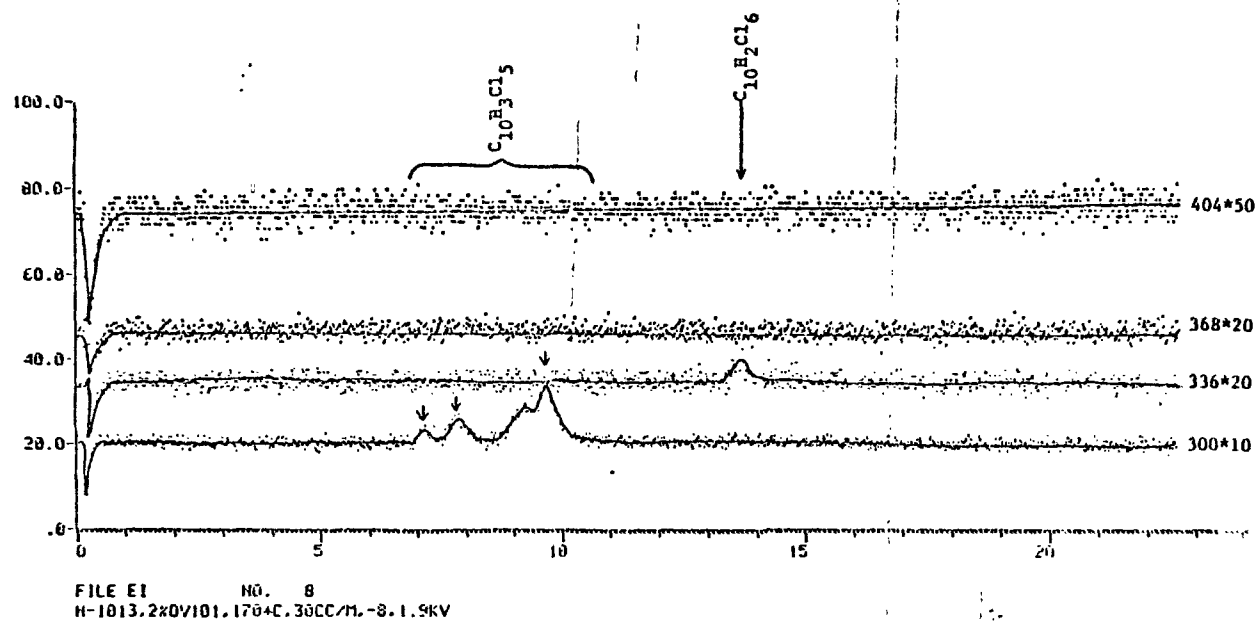


Figure C-6. Gas chromatographic-mass spectrometric analysis of Halowax-1013[®]; multiple ion detection (3.76 ng).

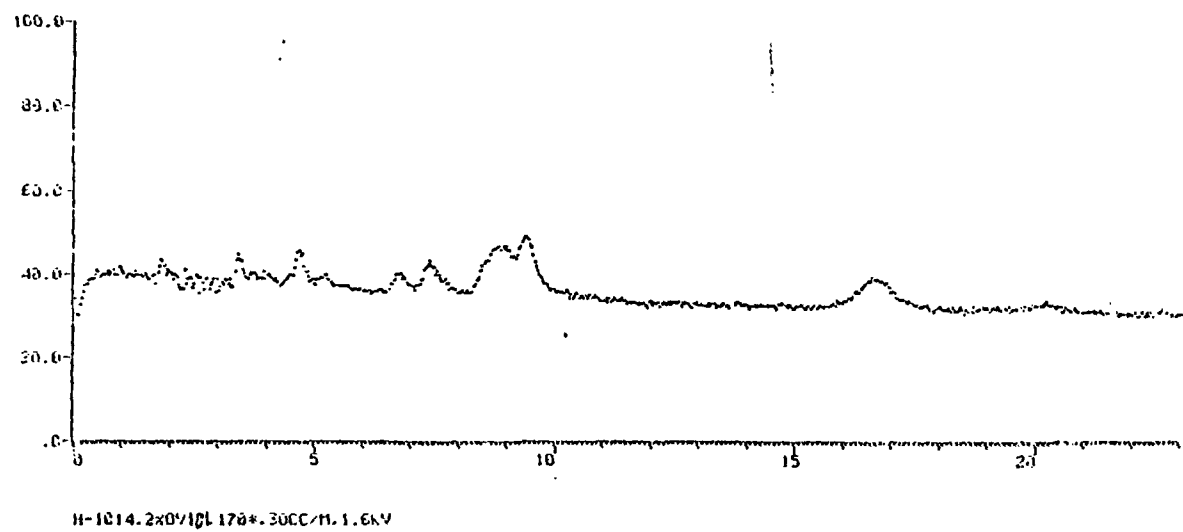


Figure C-7. Gas chromatographic-mass spectrometric analysis of Halowax-1014[®]; total ion current (232 ng)

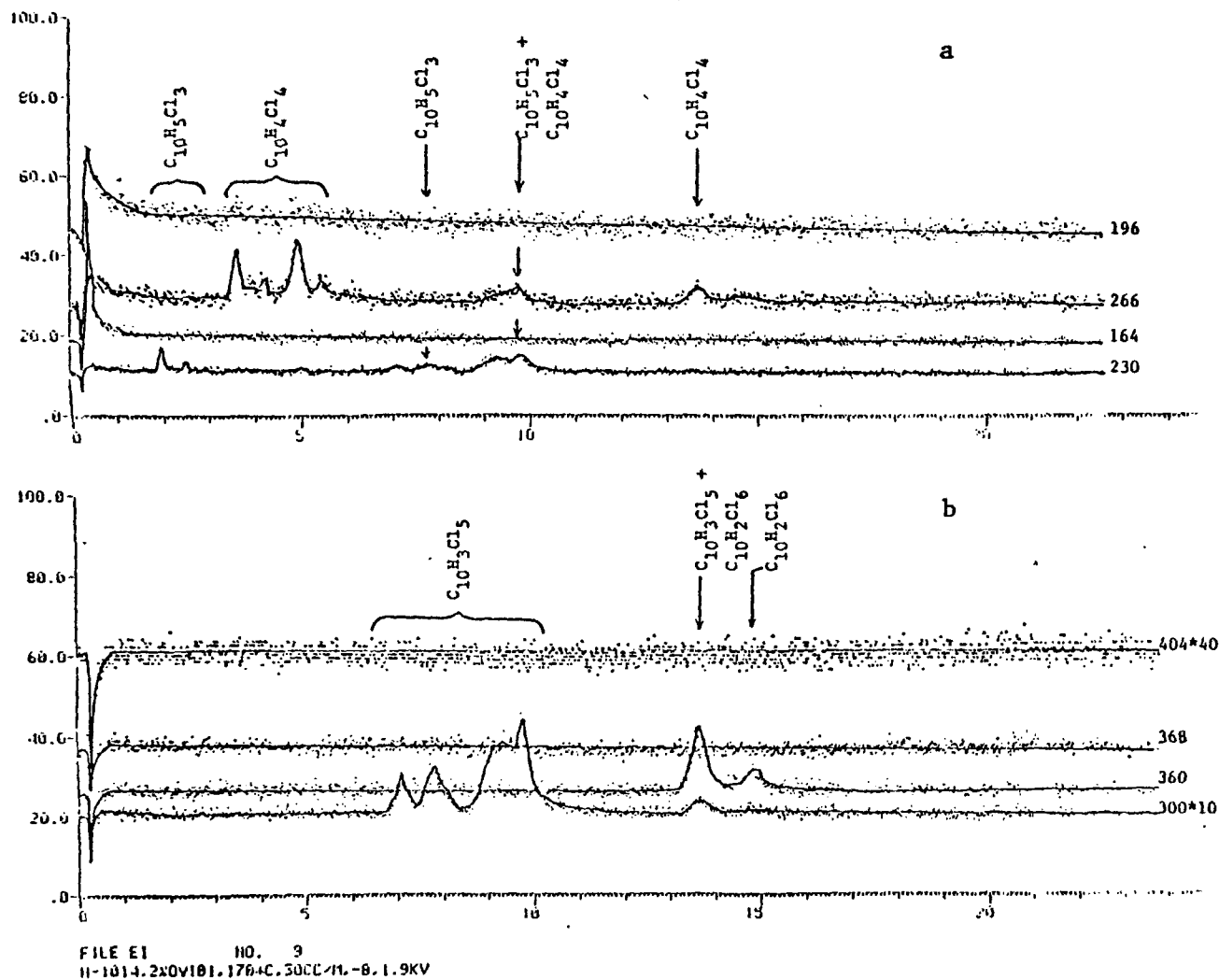


Figure C-8. Gas chromatographic-mass spectrometric analysis of Halowax-1014[®];
 a. Multiple ion detection (4.64 ng)
 b. Multiple ion detection (4.64 ng)

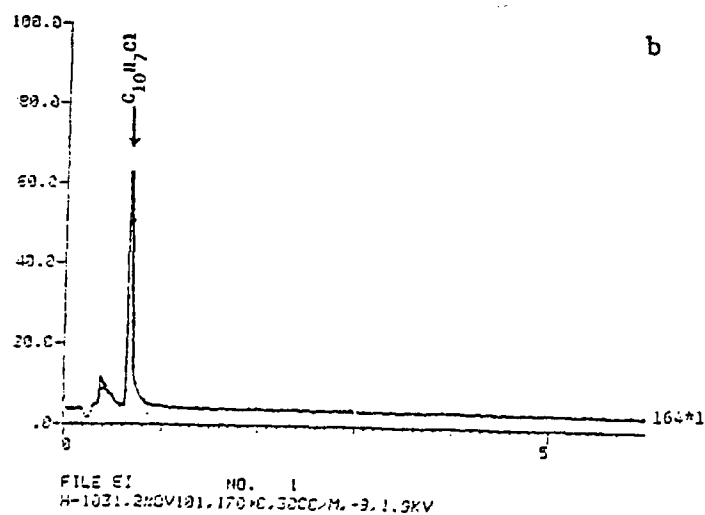
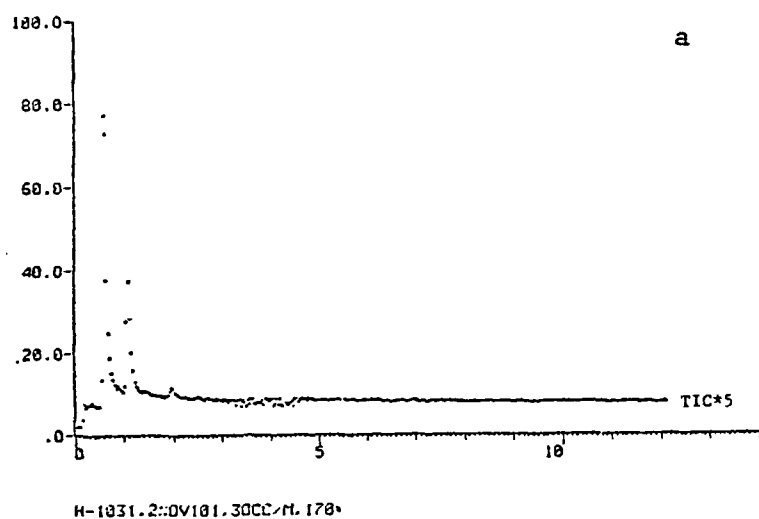


Figure C-9. Gas chromatographic-mass spectrometric analysis of Halowax-1031[®];
 a. Total ion current (218 ng)
 b. Multiple ion detection (4.36 ng)

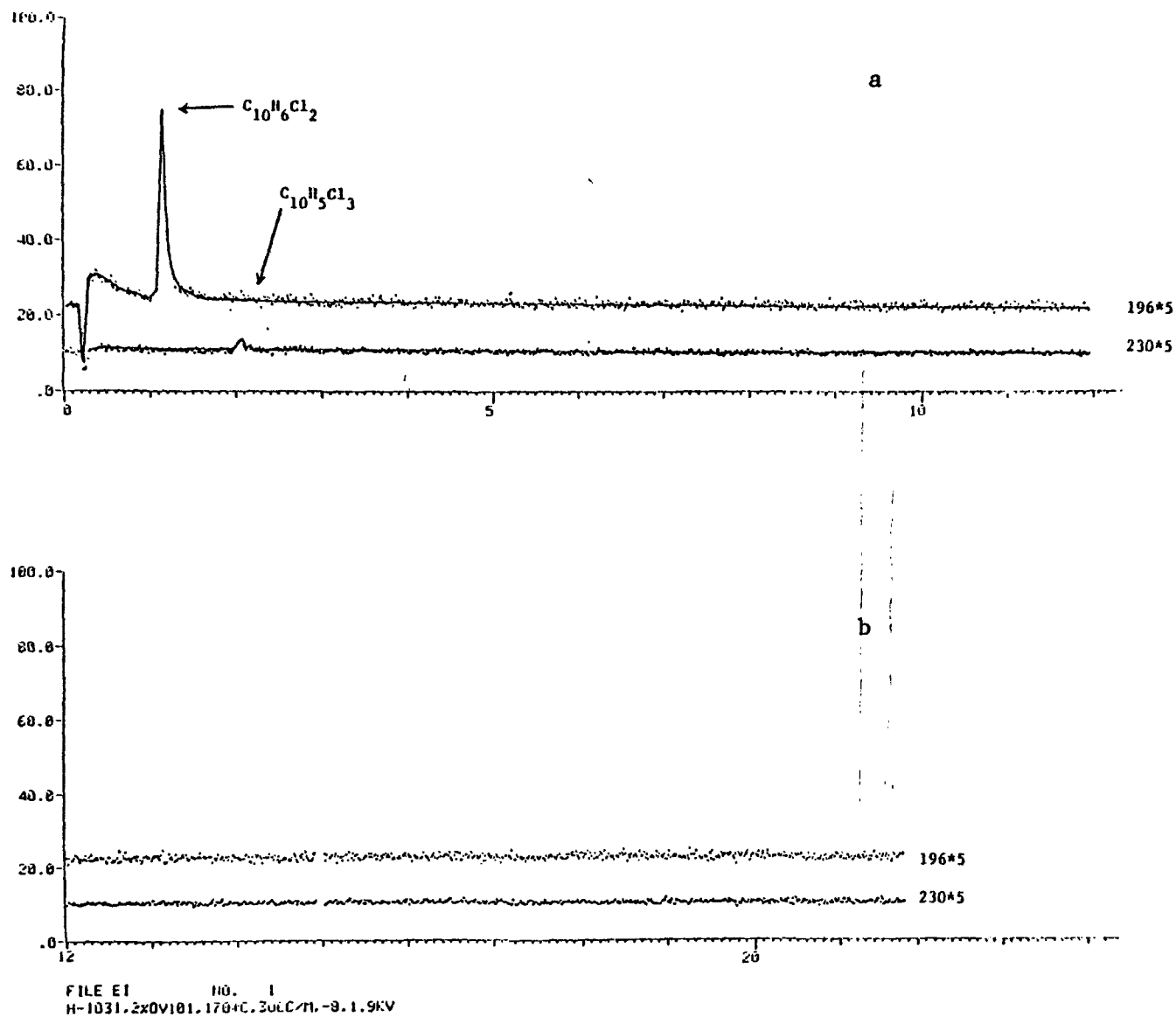


Figure C-10. Gas chromatographic-mass spectrometric analysis of Halowax-1031[®];
 a. Multiple ion detection (4.36 ng)
 b. Multiple ion detection (4.36 ng)

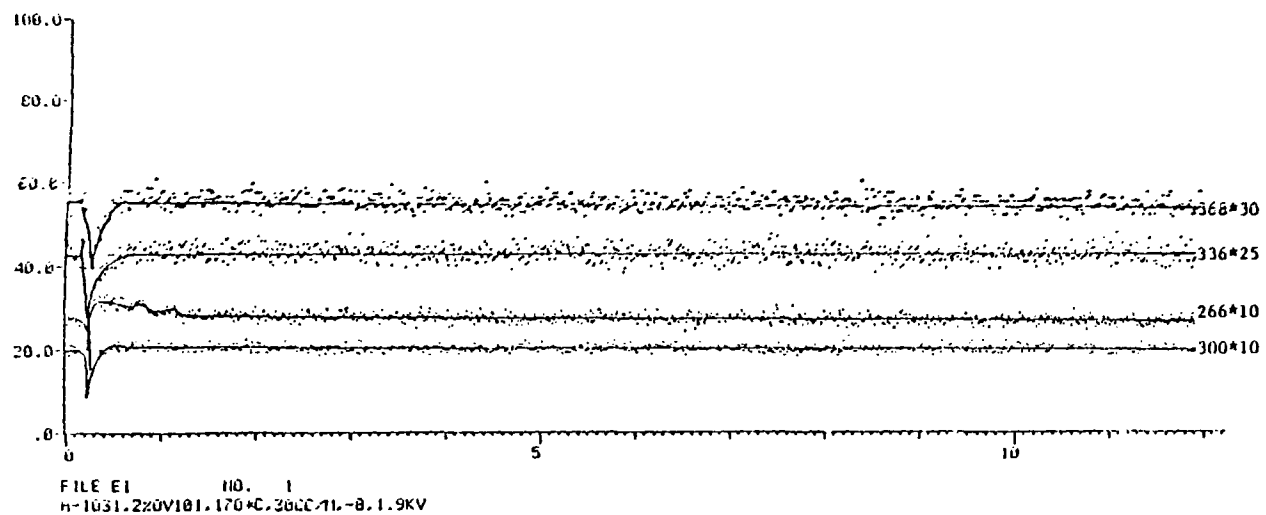


Figure C-11. Gas chromatographic-mass spectrometric analysis of Malowax-1031[®]; multiple ion detection (4.36 ng)

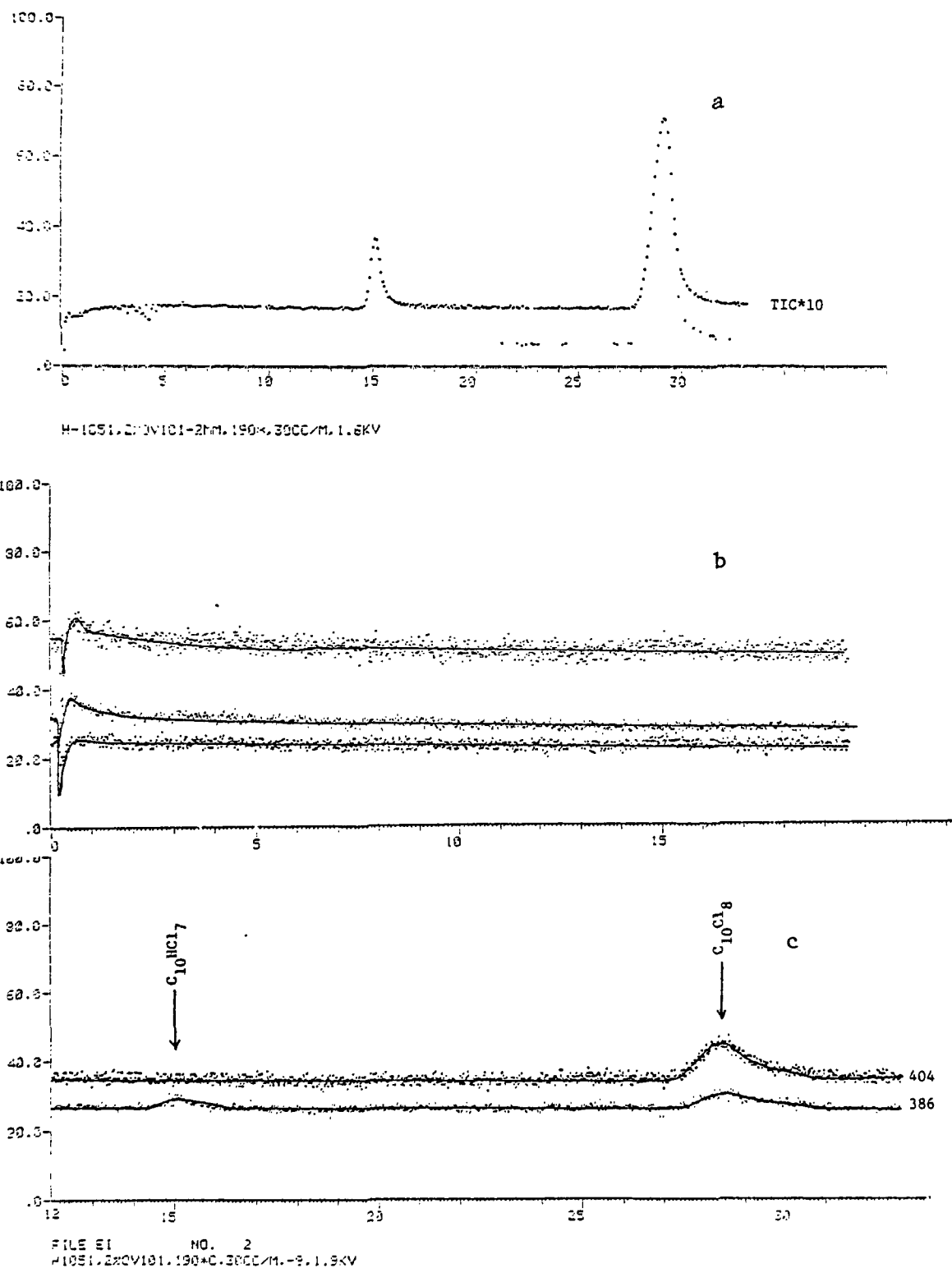


Figure C-12. Gas chromatographic-mass spectrometric analysis of Halowax-1051®;
 a. Total ion current 230 ng)
 b. Multiple ion detection (4.60 ng)
 c. Multiple ion detection (4.60 ng).

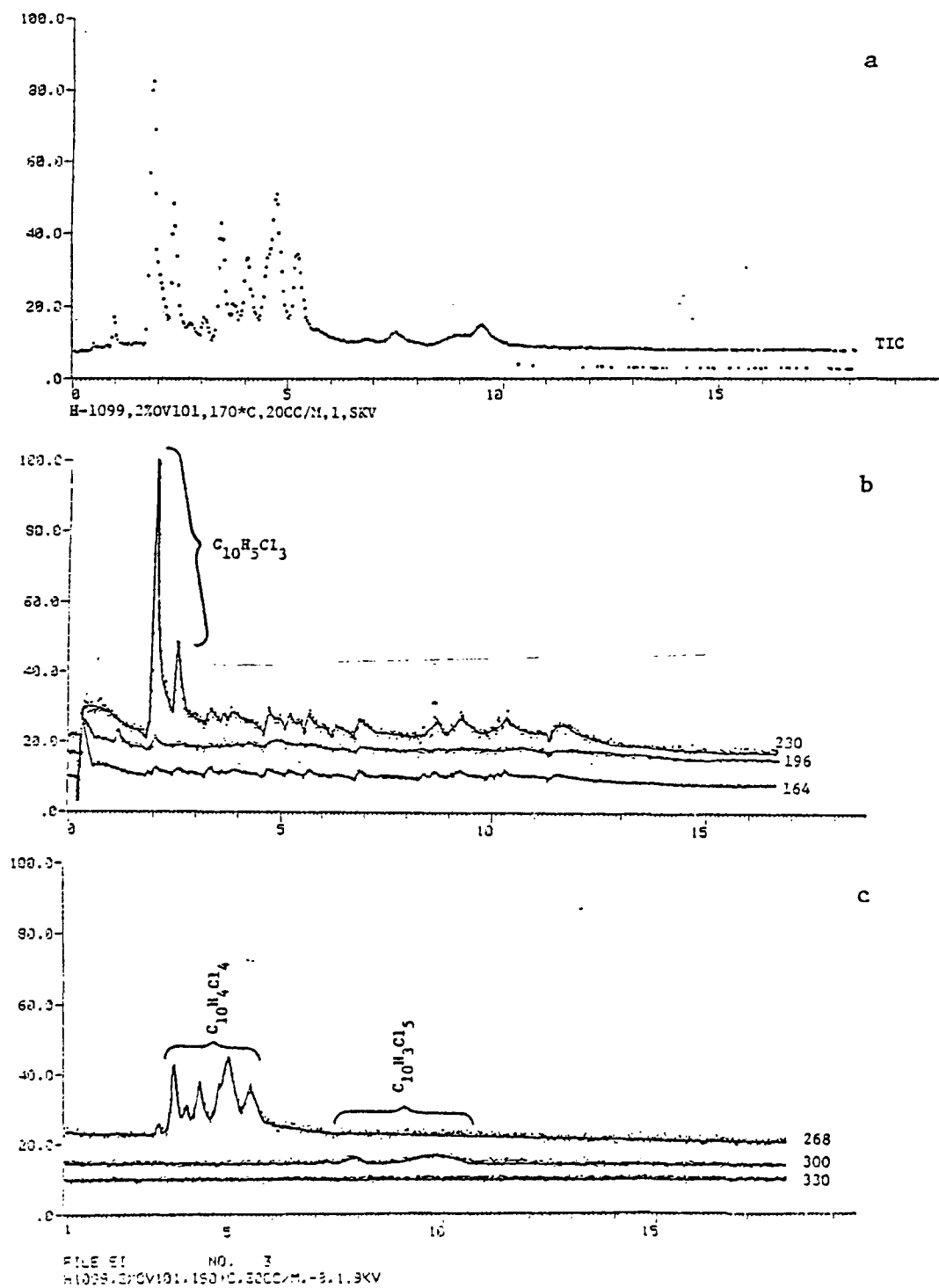


Figure C-13. Gas chromatographic-mass spectrometric analysis of Halowax-1099[®];
 a. Total ion current (222 ng)
 b. Multiple ion detection (4.44 ng)
 c. Multiple ion detection (4.44 ng)

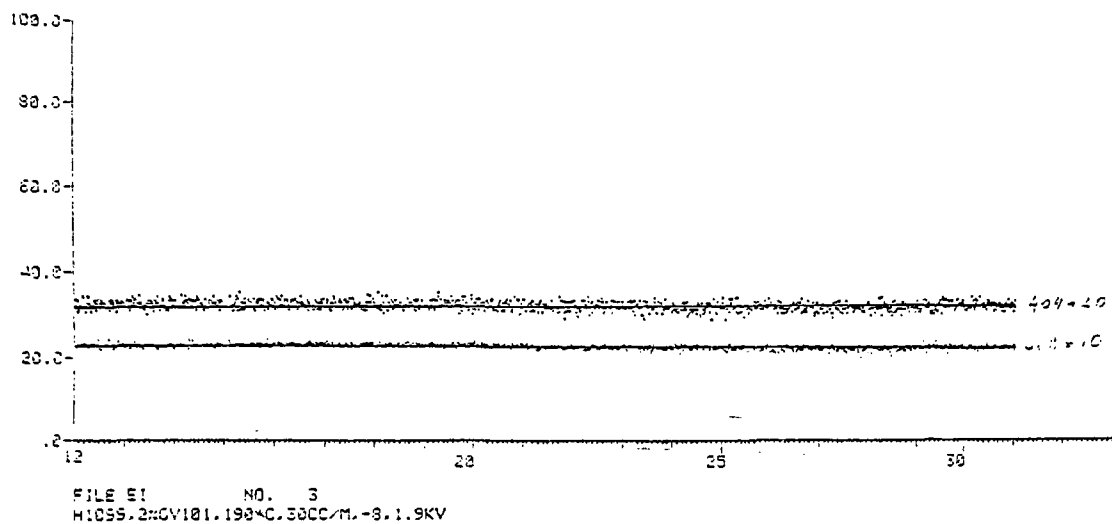


Figure C-14. Gas chromatographic-mass spectrometric analysis of Halowax-1099 ®; multiple ion detection (4.44 ng).

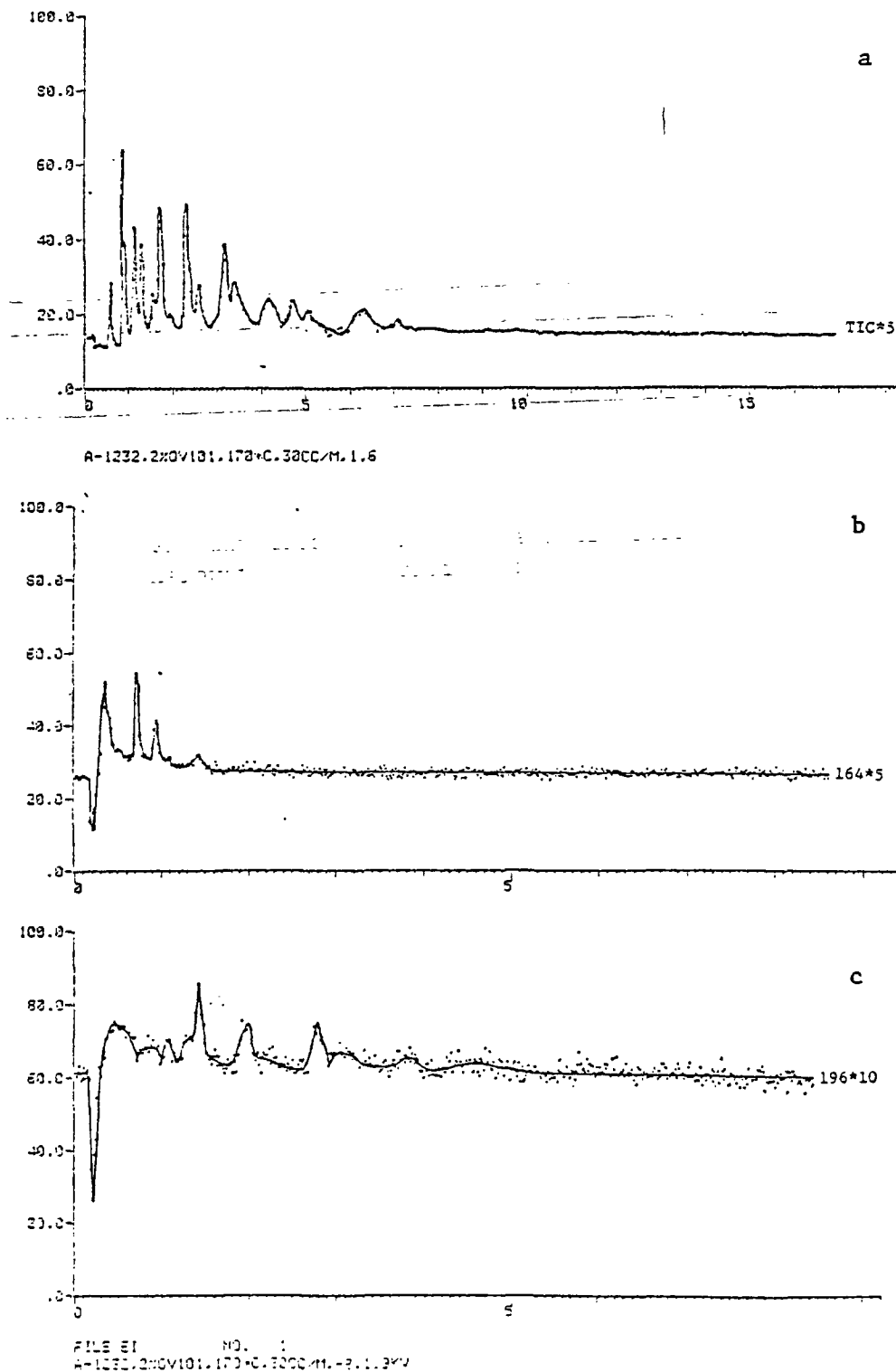


Figure C-15. Gas chromatographic-mass spectrometric analysis of Aroclor-1232[®];
 a. Total ion current (248 ng)
 b. Multiple ion detection (248 ng)
 c. Multiple ion detection (248 ng)

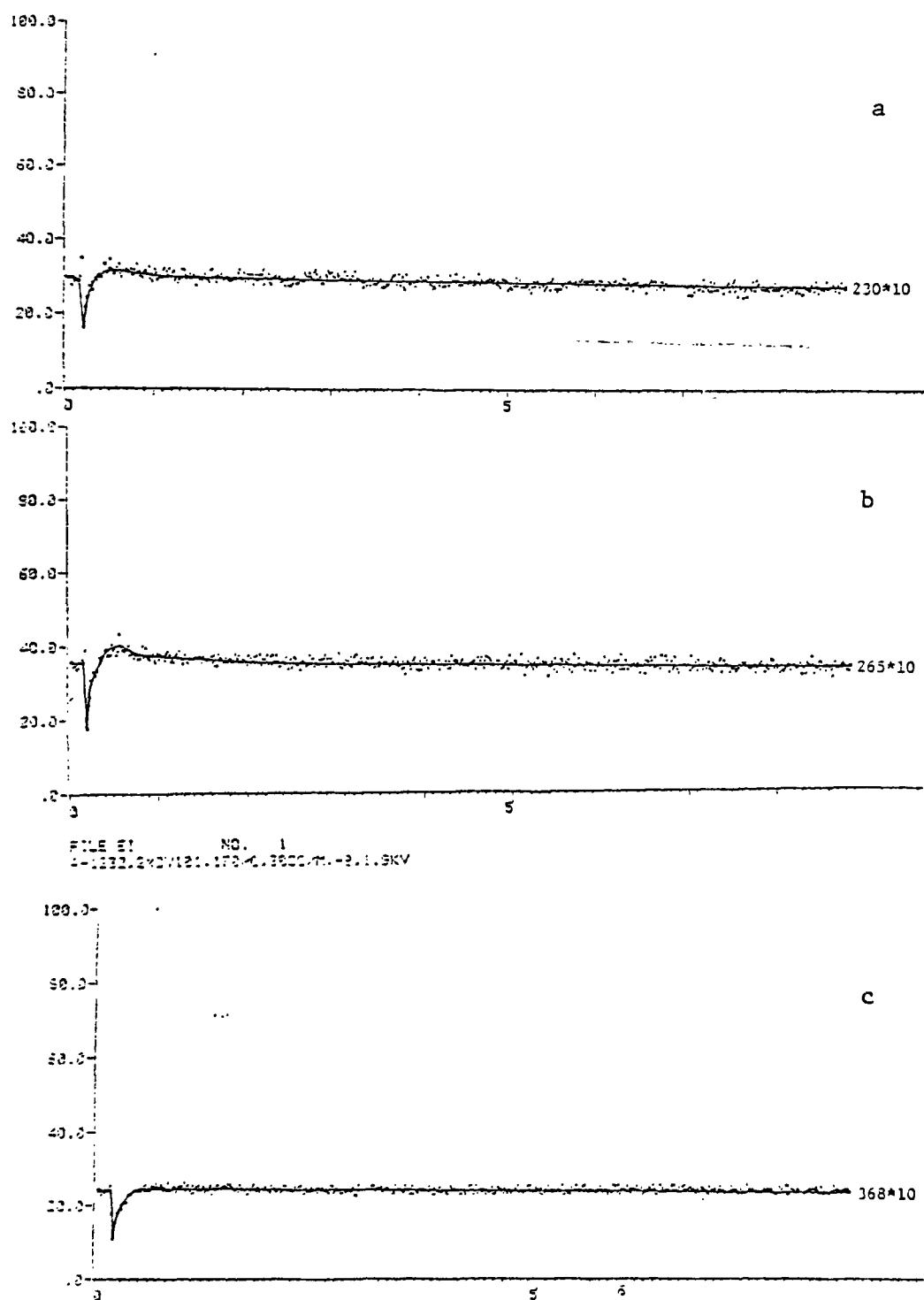


Figure C-16. Gas chromatographic-mass spectrometric analysis of Aroclor-1232[®];
a. Multiple ion detection (248 ng)
b. Multiple ion detection (248 ng)
c. Multiple ion detection (248 ng)

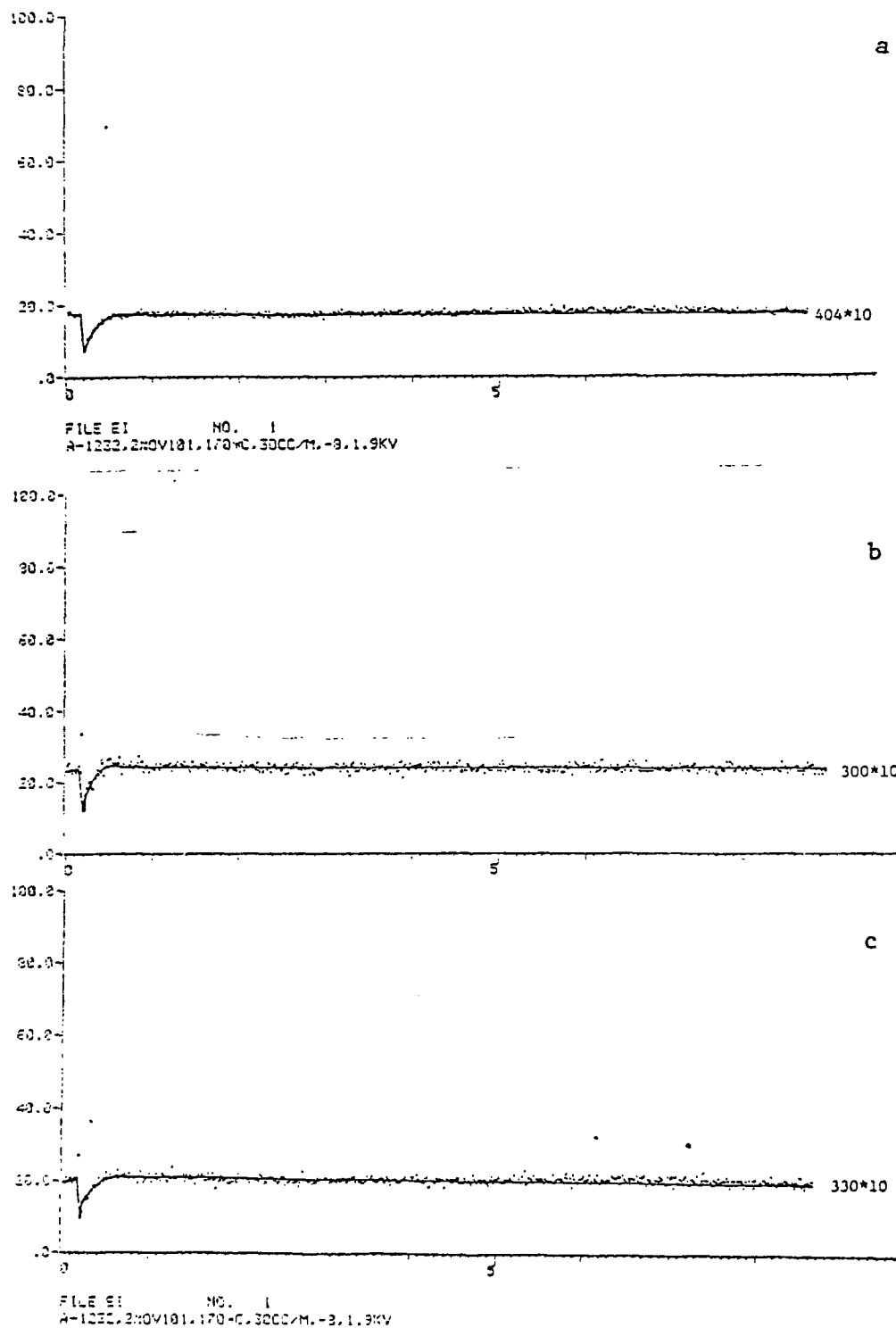


Figure C-17. Gas chromatographic-mass spectrometric analysis of Aroclor-1232[®];

- a. Multiple ion detection (248 ng)
- b. Multiple ion detection (248 ng)
- c. Multiple ion detection (248 ng)

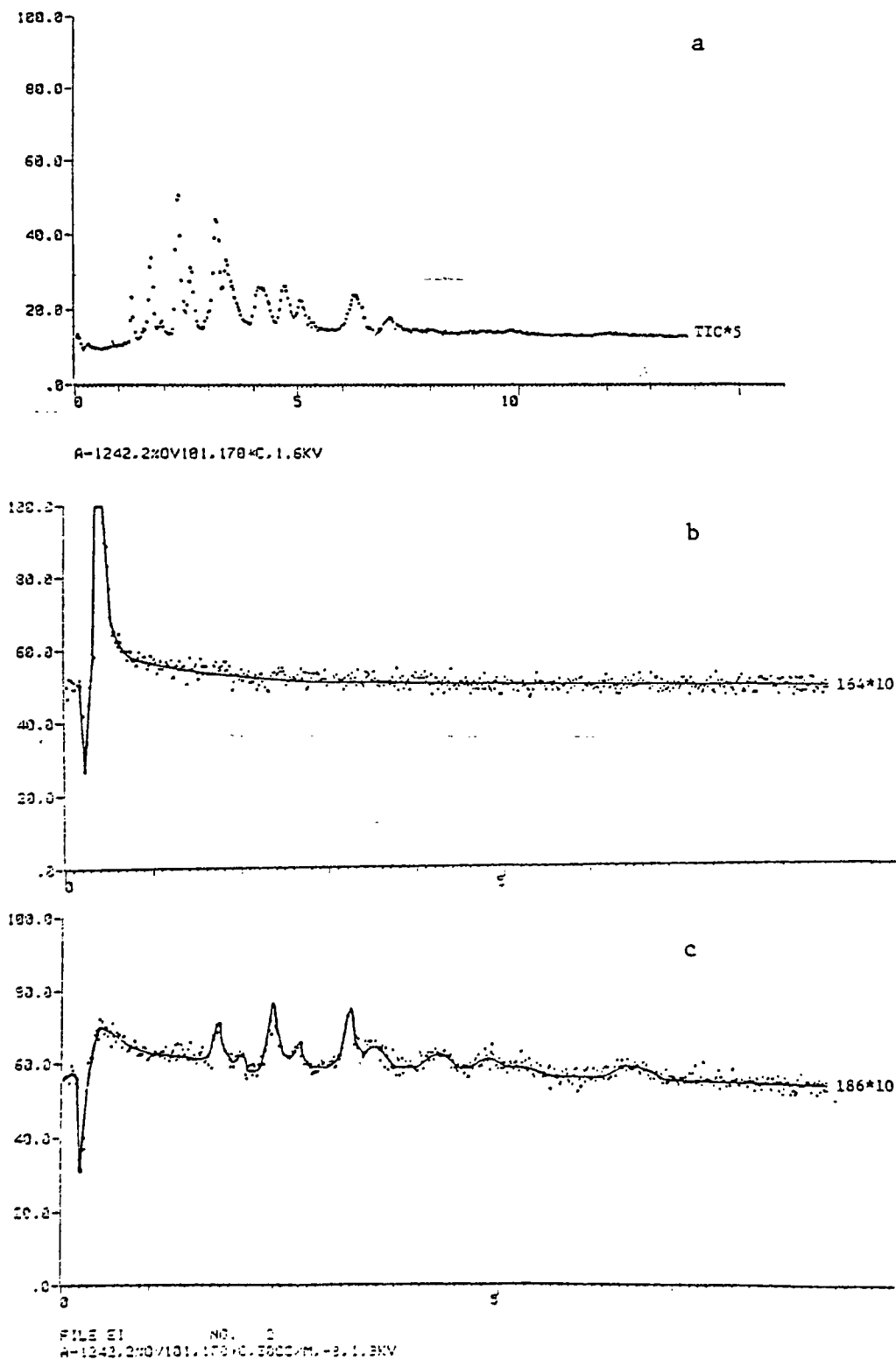


Figure C-18. Gas chromatographic-mass spectrometric analysis of Aroclor-1242[®];
 a. Total ion current (192 ng)
 b. Multiple ion detection (192 ng)
 c. Multiple ion detection (192 ng)

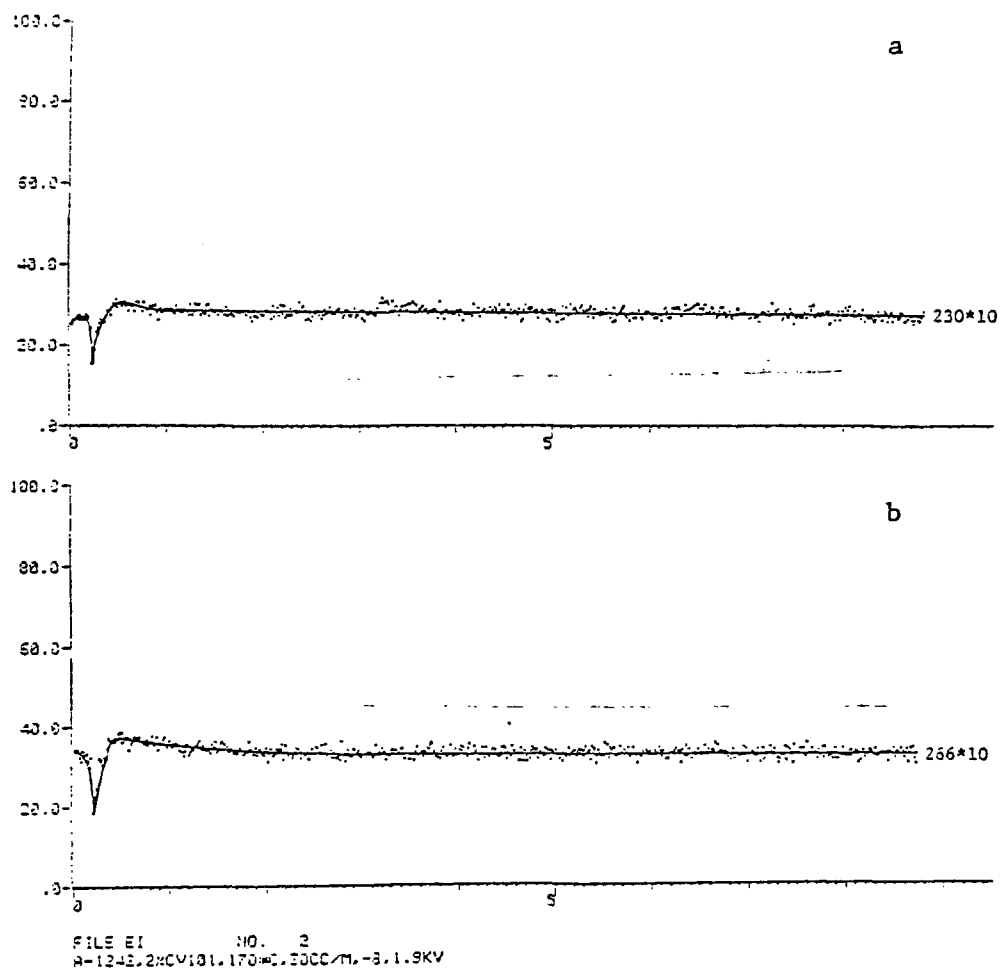


Figure C-19. Gas chromatographic-mass spectrometric analysis of Aroclor-1242[®];

a. Multiple ion detection (192 ng)

b. Multiple ion detection (192 ng)

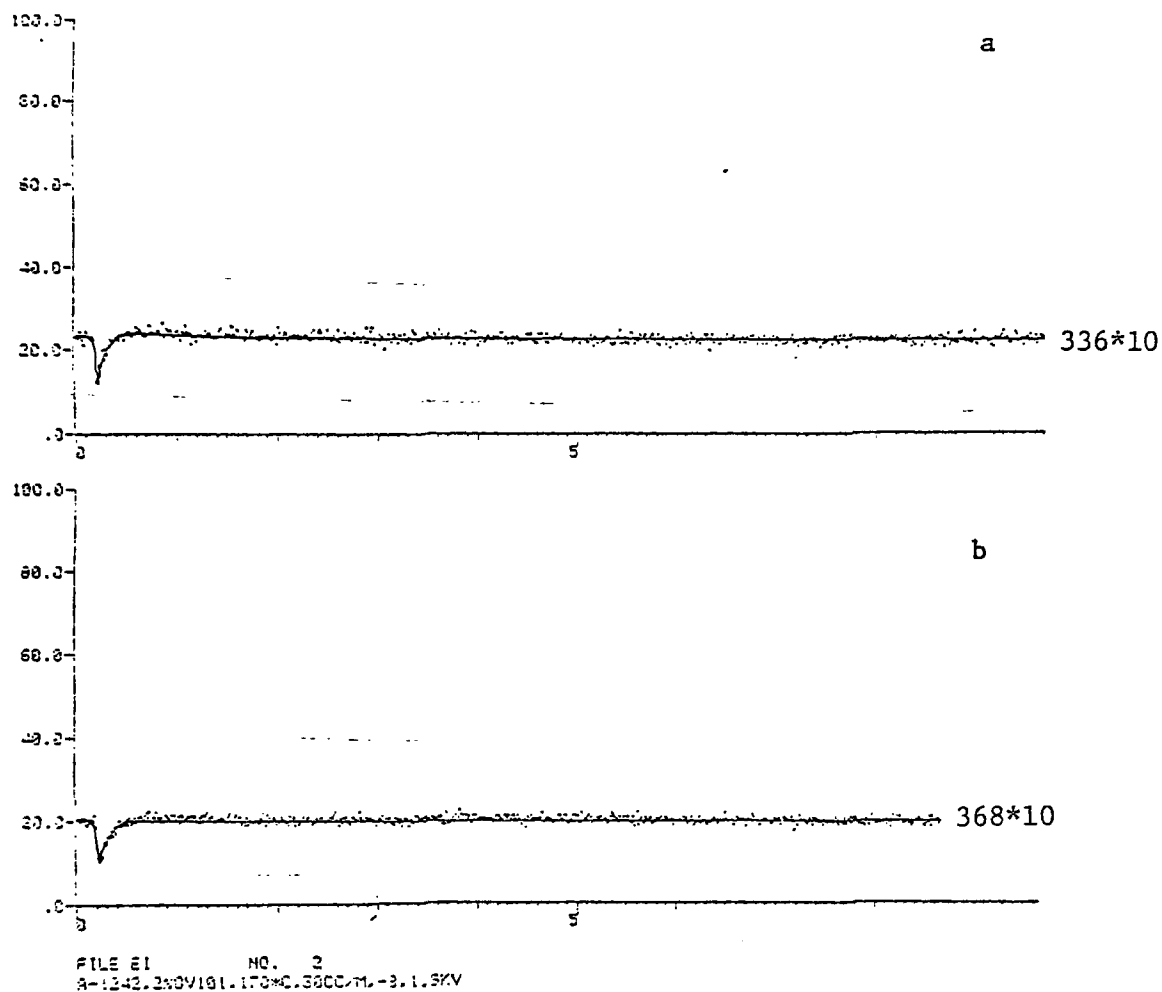
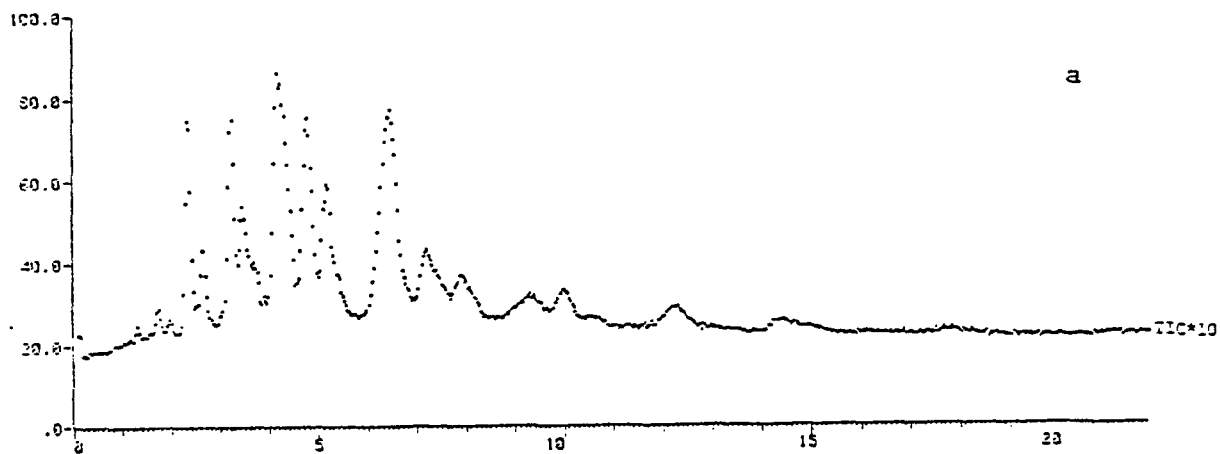
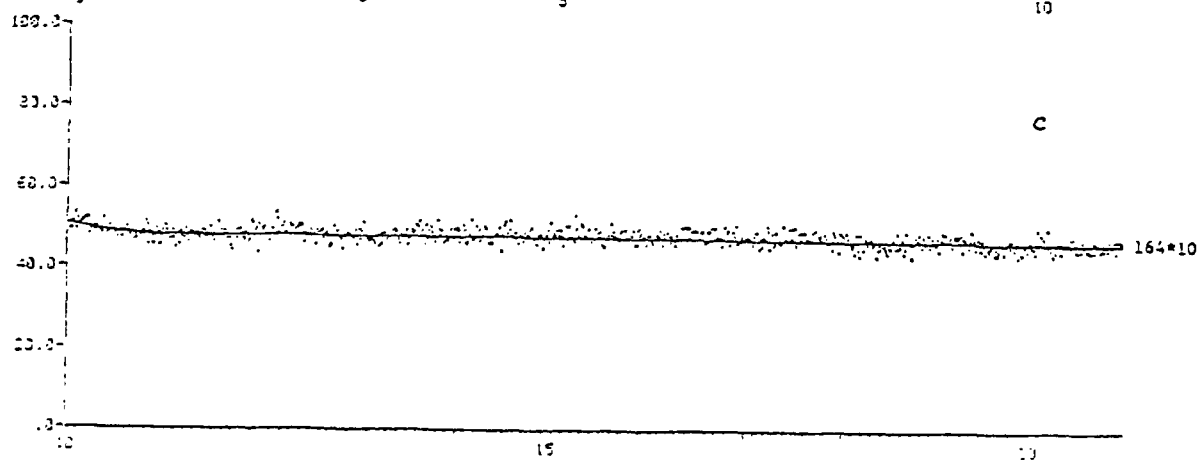
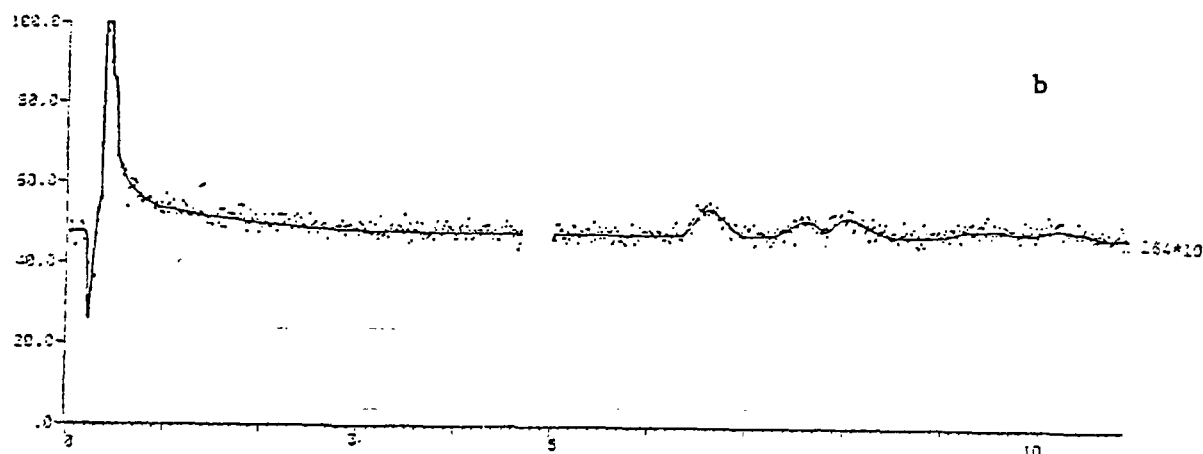


Figure C-20. Gas chromatographic-mass spectrometric analysis of Aroclor-1242[®];
a. Multiple ion detection (192 ng)
b. Multiple ion detection (192 ng)



A-1248-200V101.170-C.0000/M.-9.1



FILE 21 NO. 3
A-1248-200V101.170-C.0000/M.-9.1.3-V

Figure C-21. Gas chromatographic-mass spectrometric analysis of Aroclor-1248 Q ;

- a. Total ion current (192 ng)
- b. Multiple ion detection (192 ng)
- c. Multiple ion detection (192 ng)

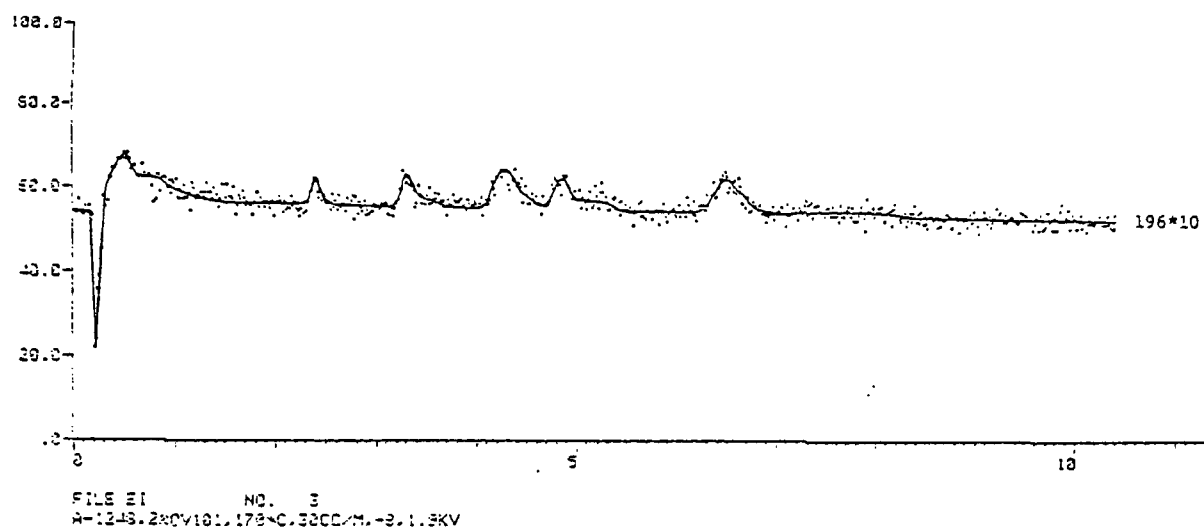


Figure C-22. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®]; multiple ion detection (192 ng)

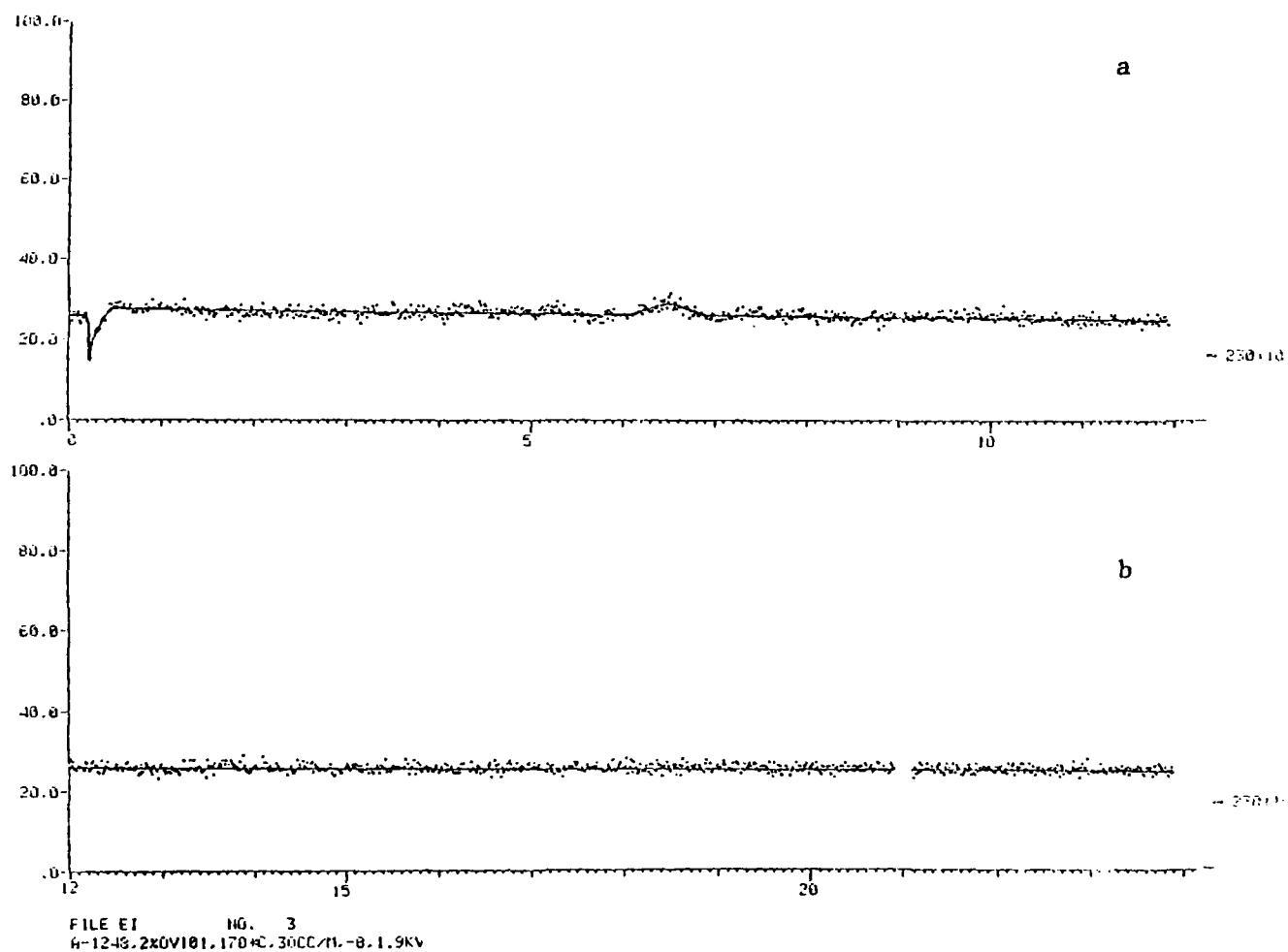


Figure C-23. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®];
a. Multiple ion detection (192 ng)
b. Multiple ion detection (192 ng)

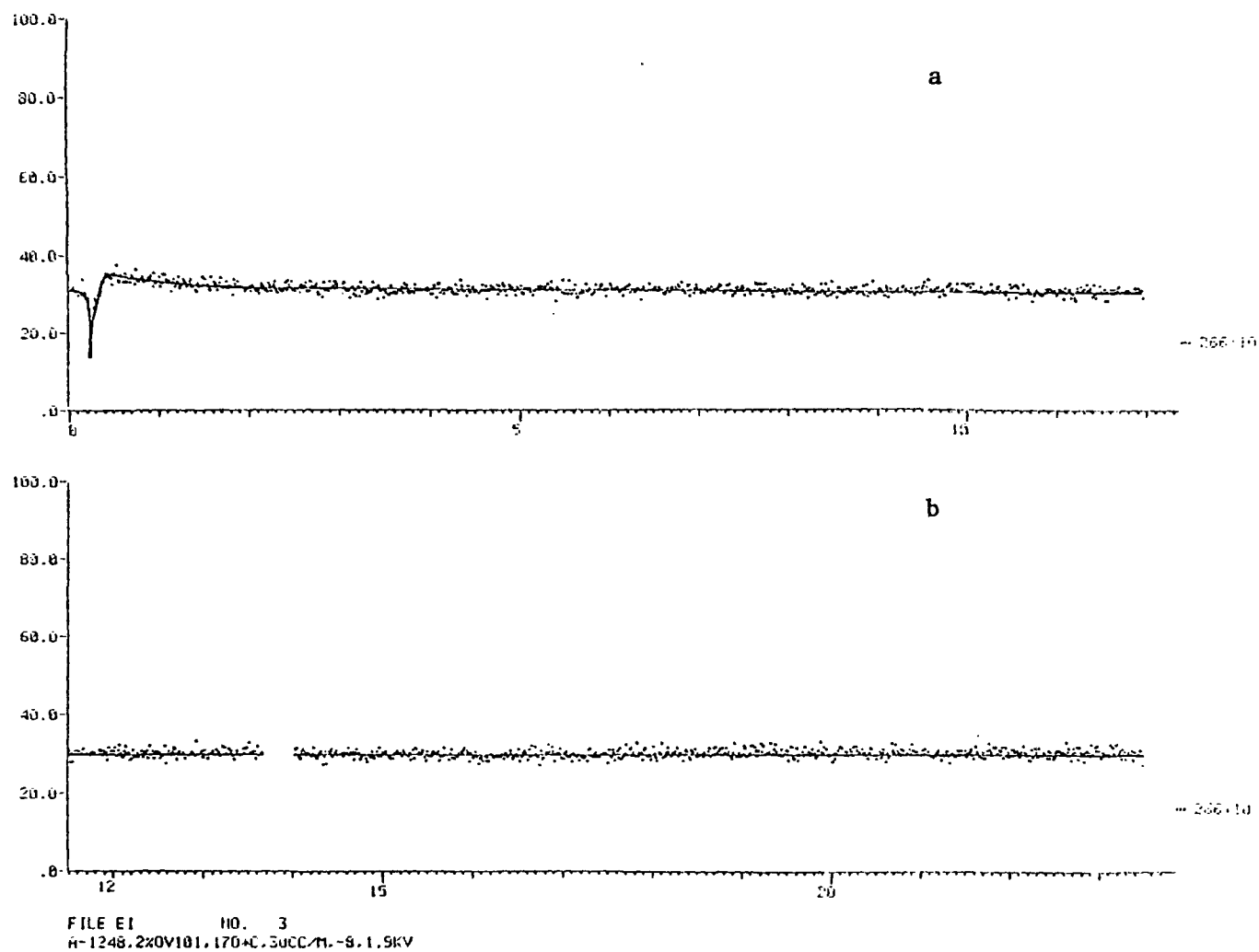


Figure C-24. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®];
 a. Multiple ion detection (192 ng)
 b. Multiple ion detection (192 ng)

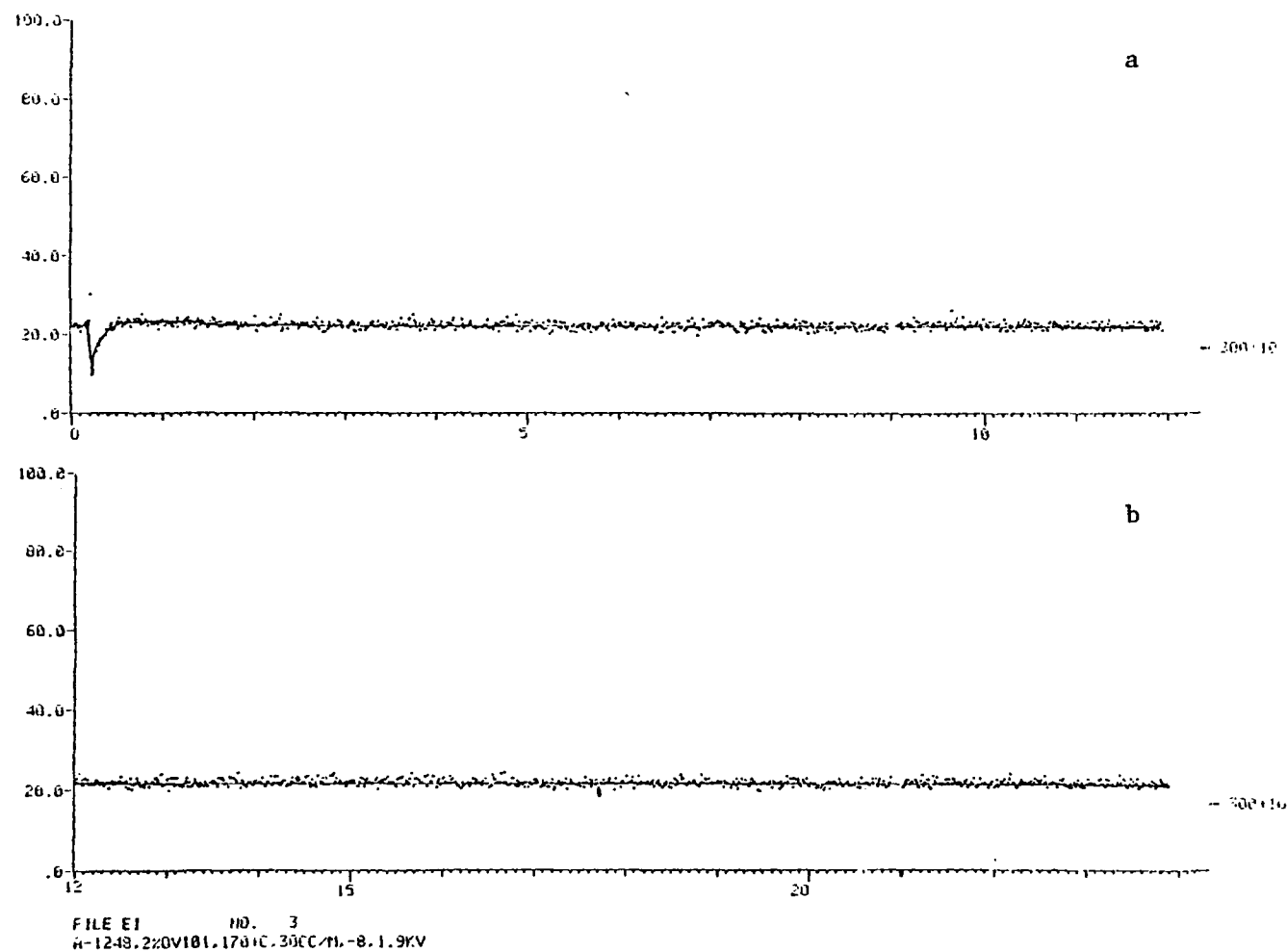


Figure C-25. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®];
a. Multiple ion detection (192 ng)
b. Multiple ion detection (192 ng)

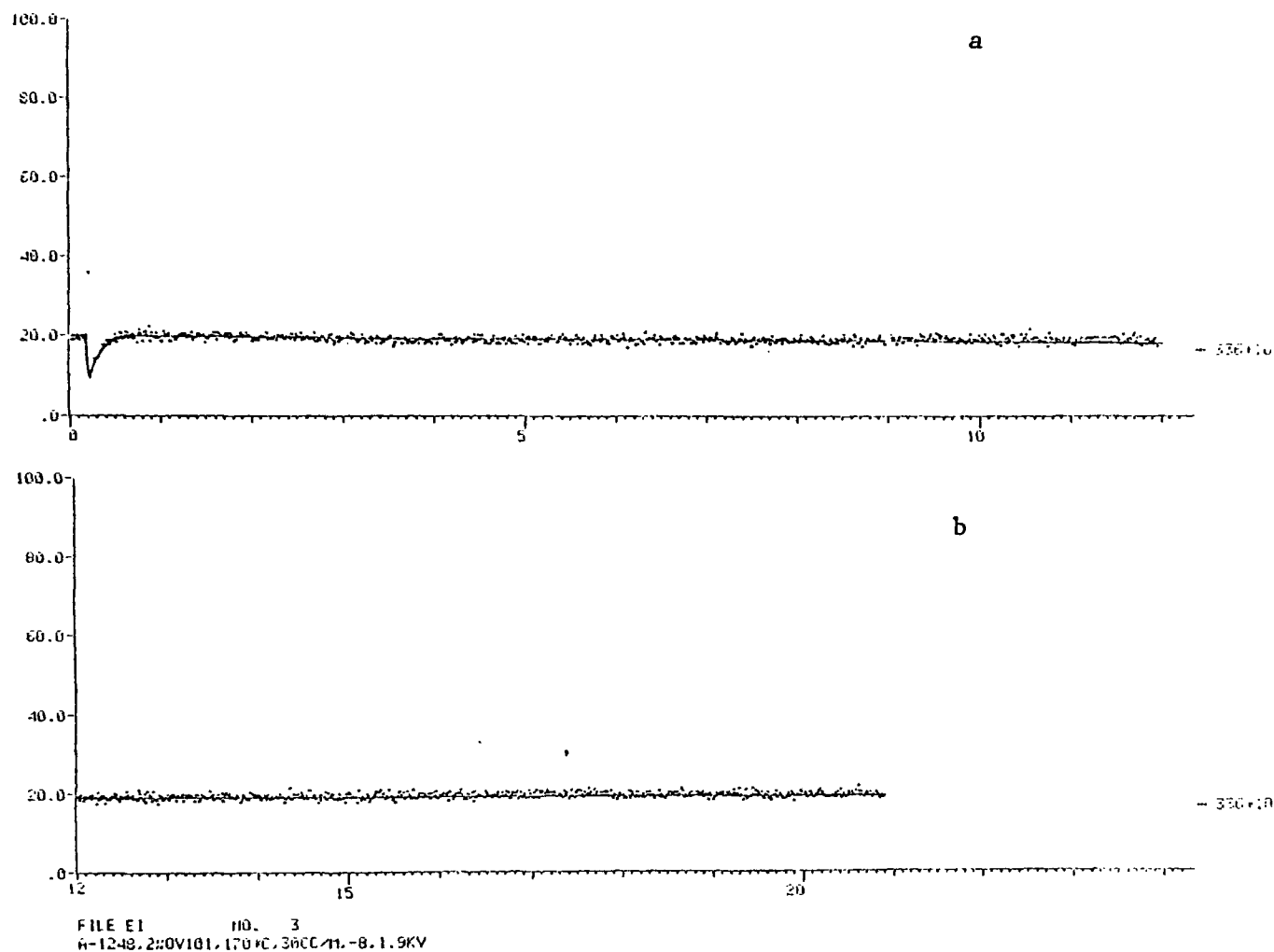


Figure C-26. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®];
a. Multiple ion detection (192 ng)
b. Multiple ion detection (192 ng)

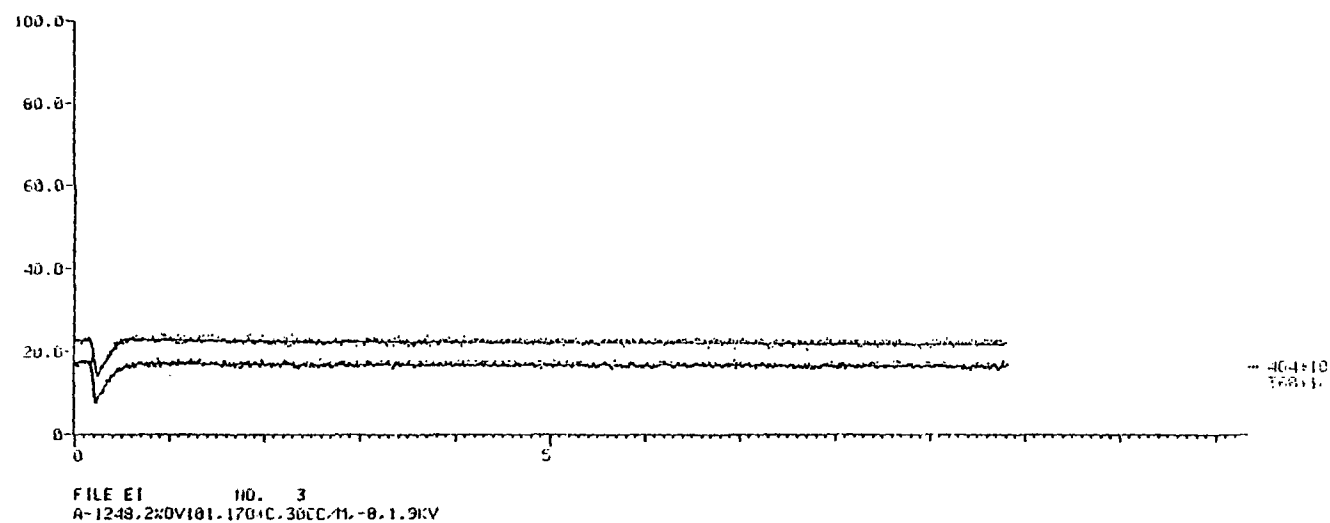


Figure C-27. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®]; multiple ion detection (192 ng)

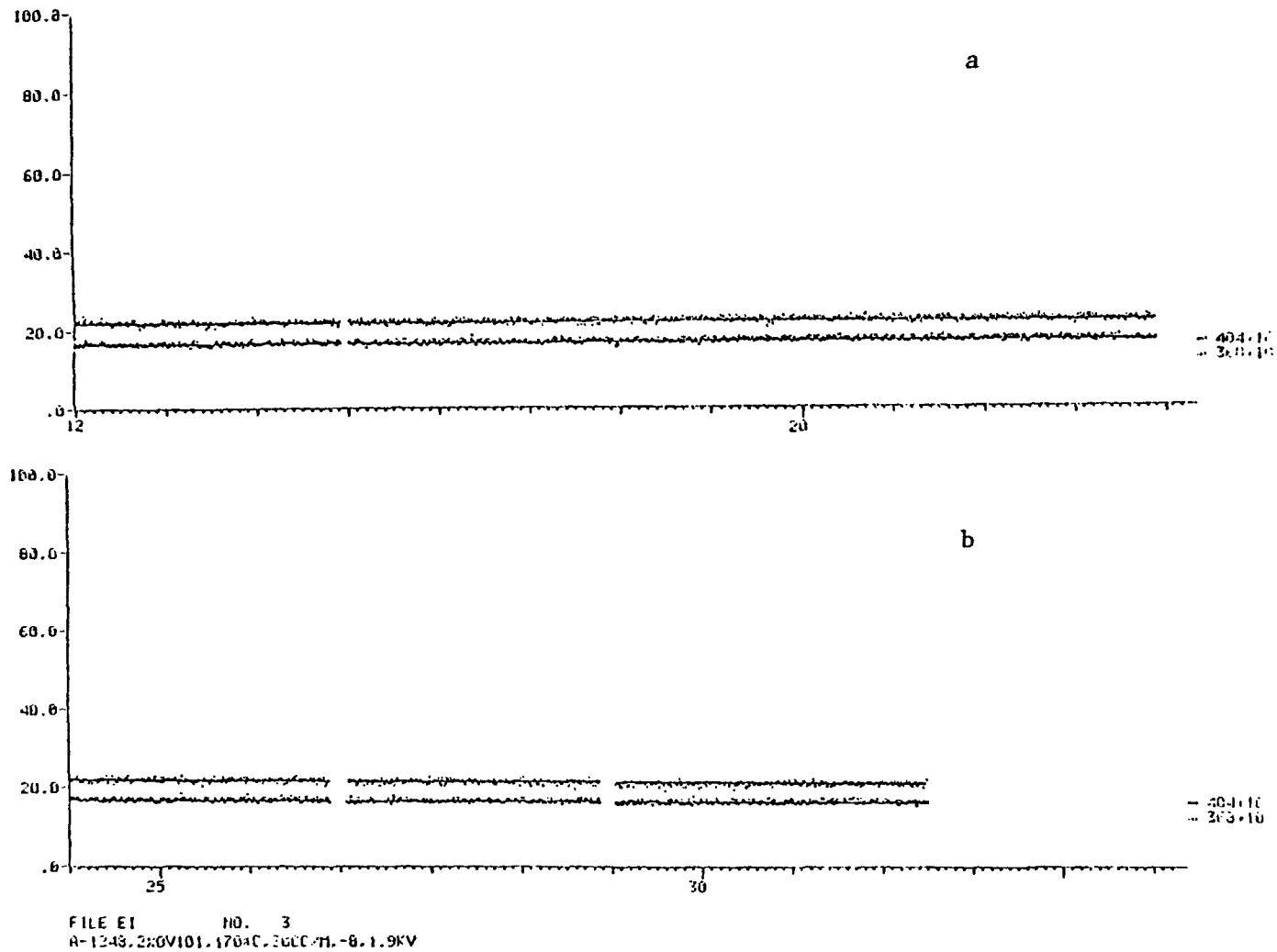


Figure C-28. Gas chromatographic-mass spectrometric analysis of Aroclor-1248[®];
 a. Multiple ion detection (192 ng)
 b. Multiple ion detection (192 ng)

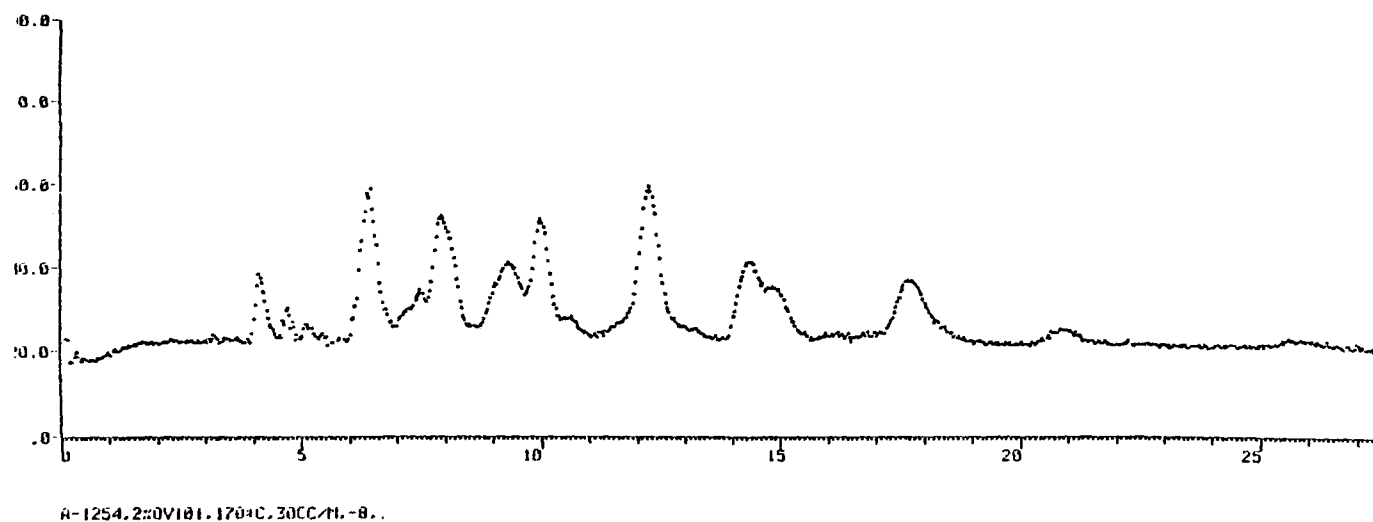


Figure C-29. Gas chromatographic-mass spectrometric analysis of Aroclor-1254[®]; total ion current (198 ng).

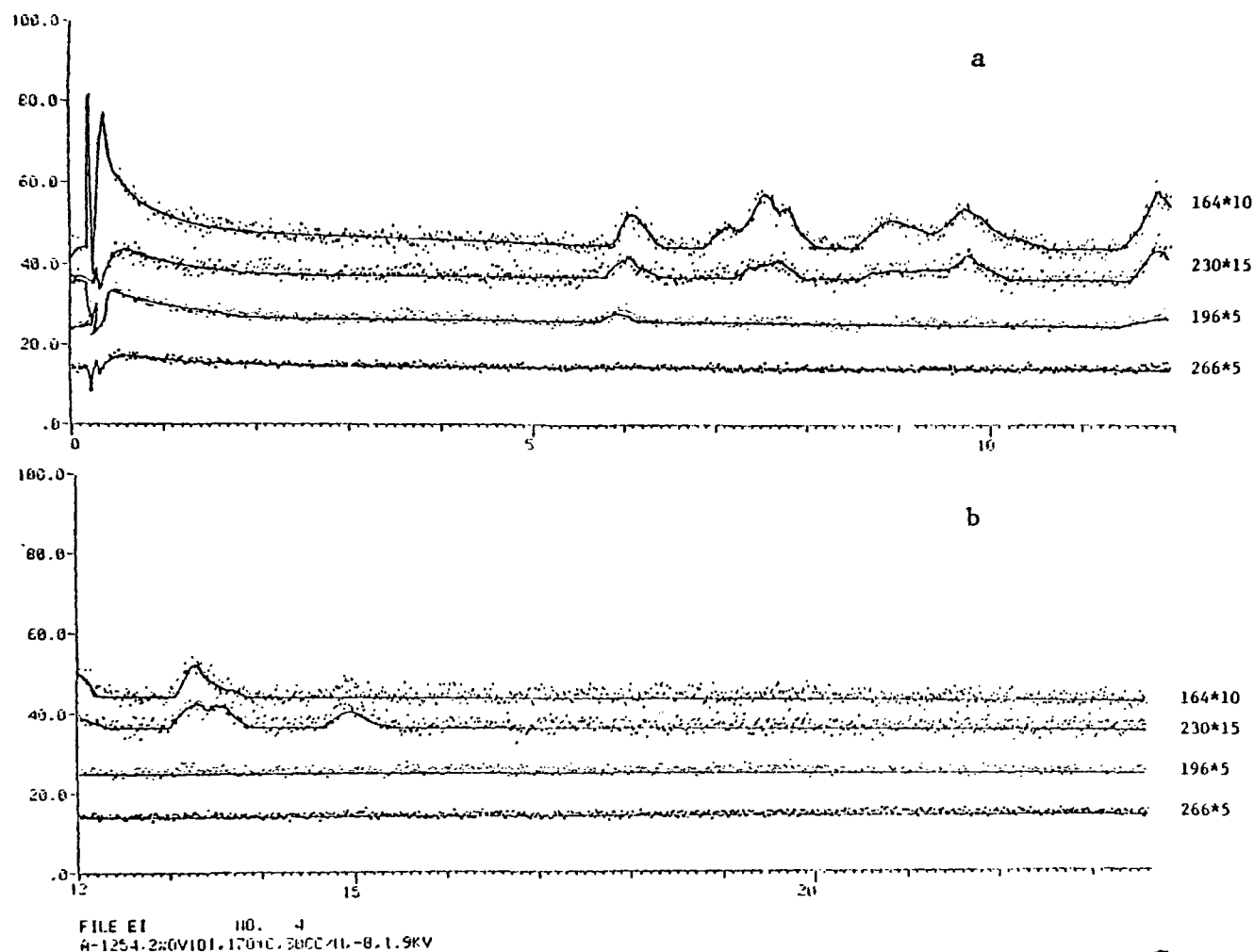


Figure C-30. Gas chromatographic-mass spectrometric analysis of Aroclor-1254[®];
 a. Multiple ion detection (198 ng)
 b. Multiple ion detection (198 ng)

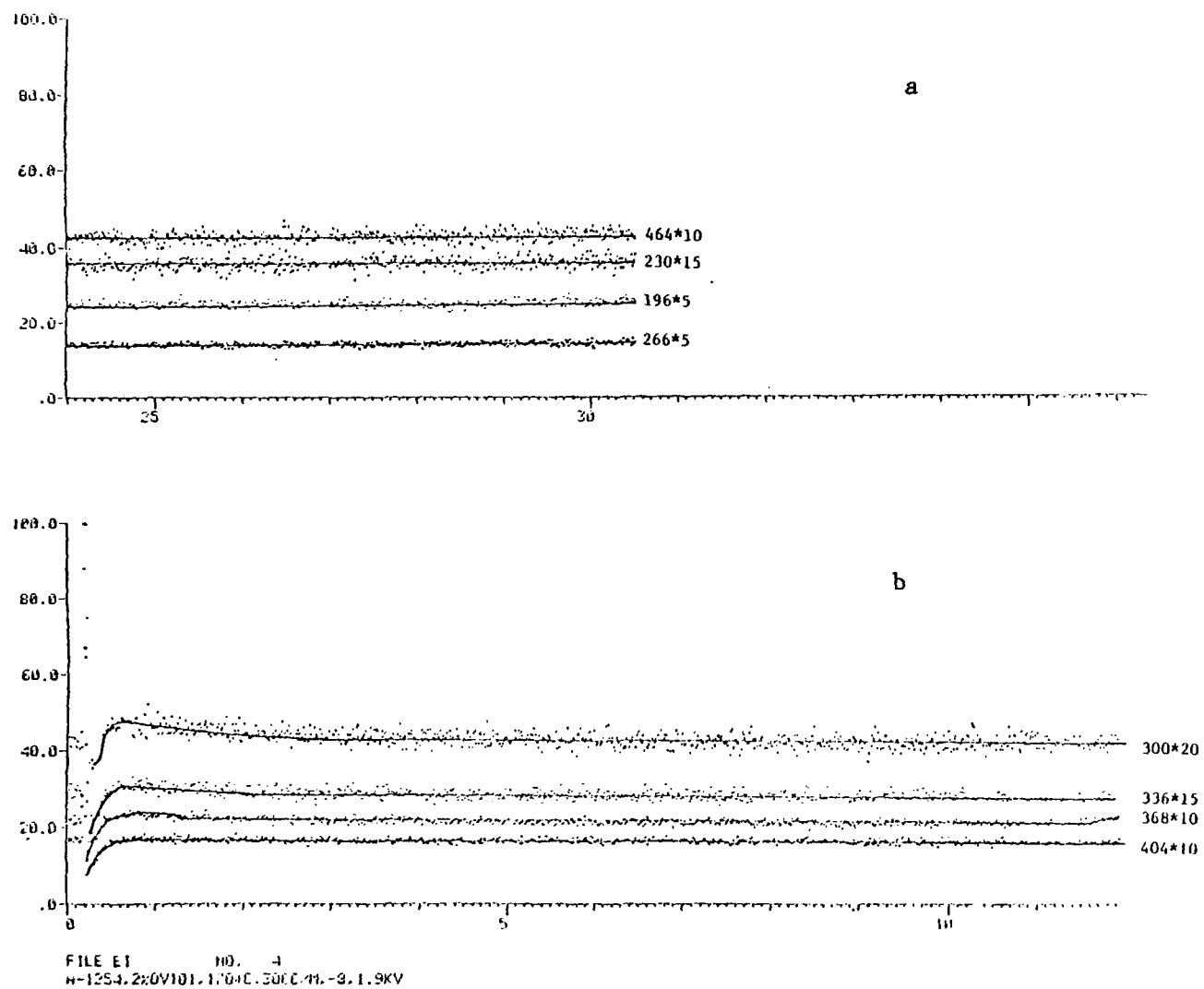


Figure C-31. Gas chromatographic-mass spectrometric analysis of Aroclor-1254[®];
 a. Multiple ion detection (198 ng)
 b. Multiple ion detection (198 ng)

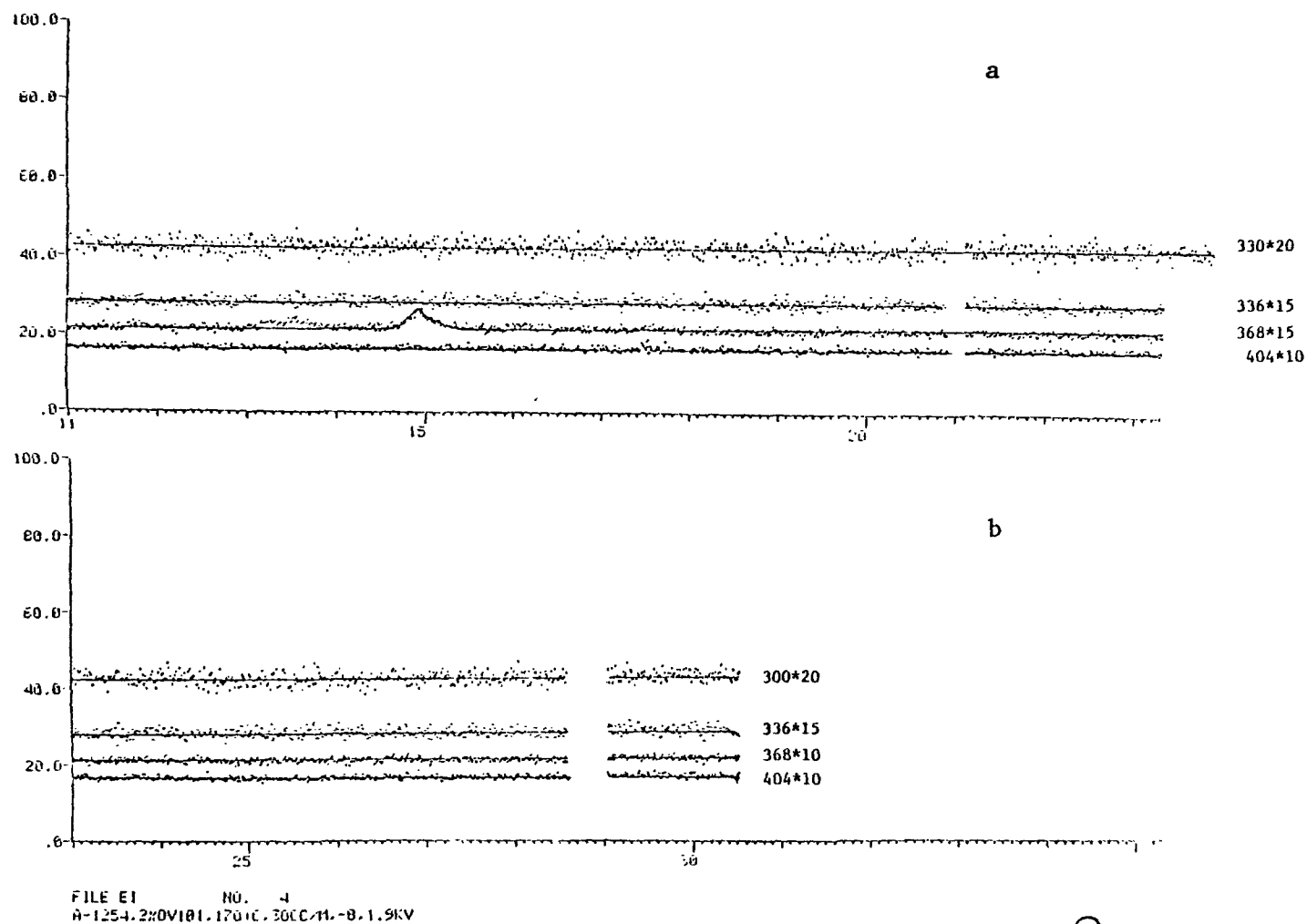


Figure C-32. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®];
 a. Multiple ion detection (198 ng)
 b. Multiple ion detection (198 ng)

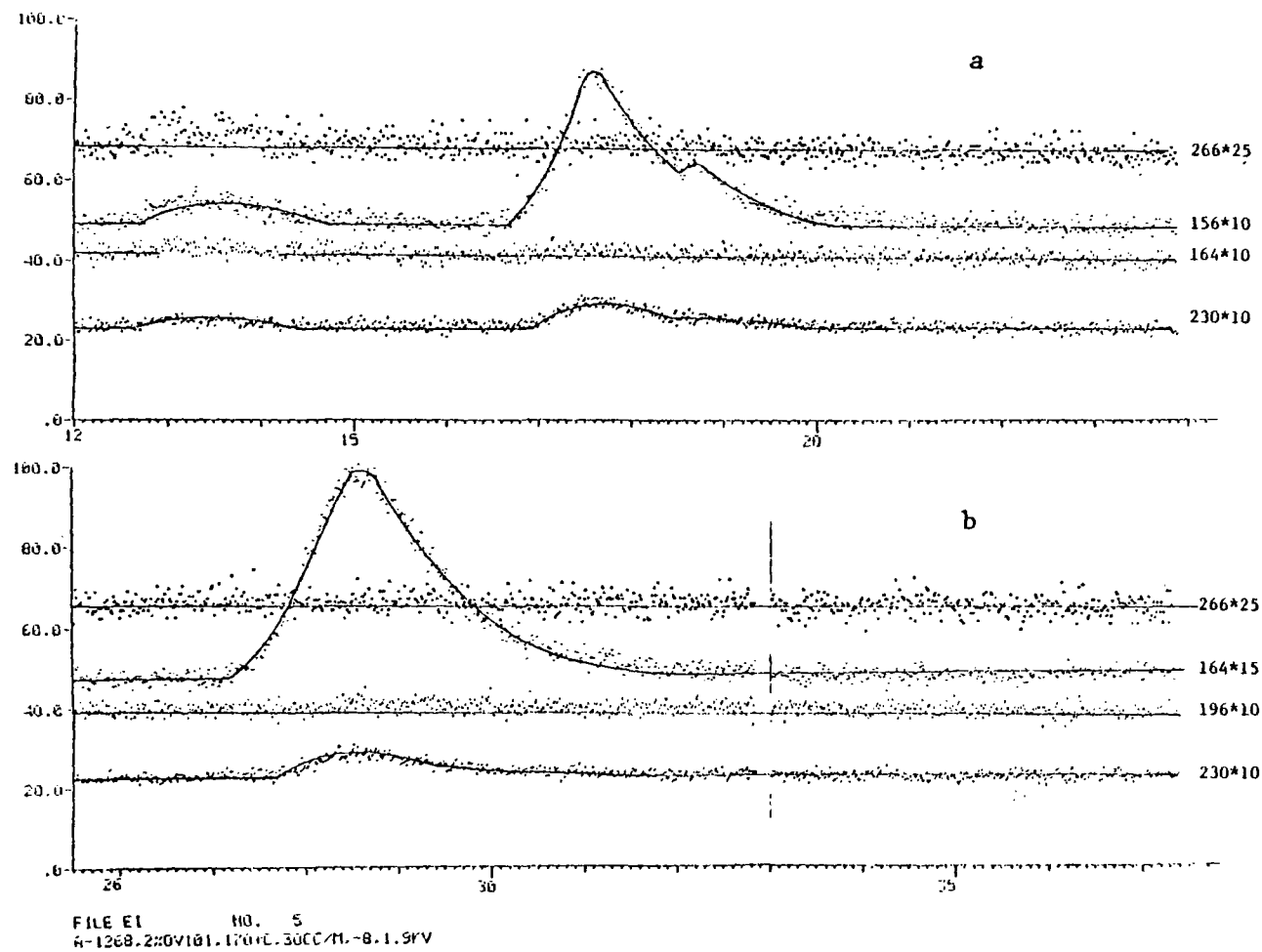
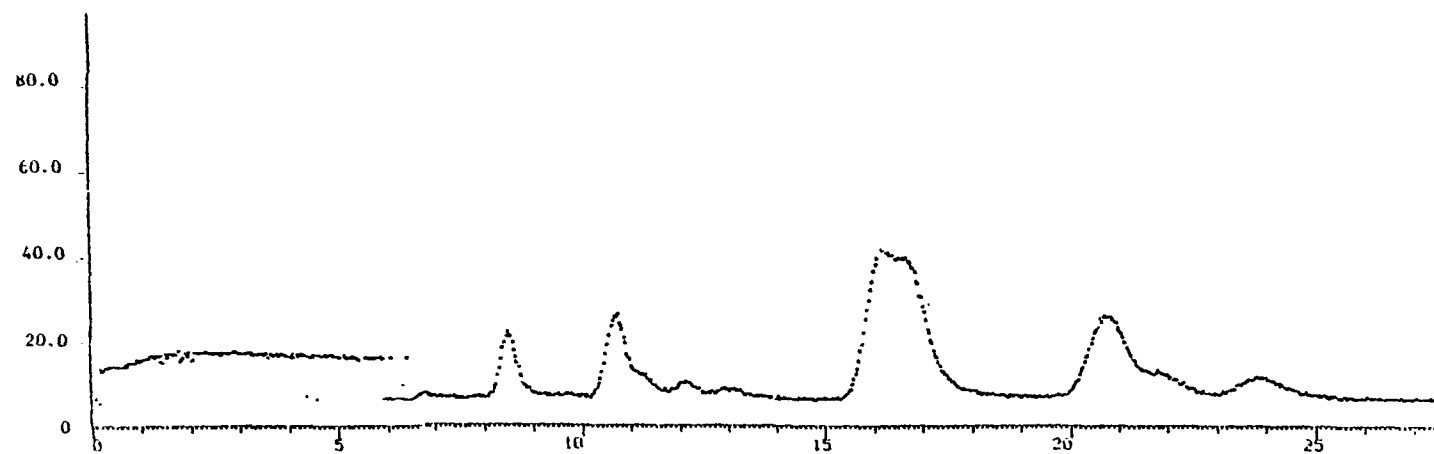


Figure C-33. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®],
 a. Multiple ion detection (180 ng)
 b. Multiple ion detection (180 ng)



10-1205, 270V101, 190°C, 300C/1L-9.

Figure C-34. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®]; total ion current (180 ng)

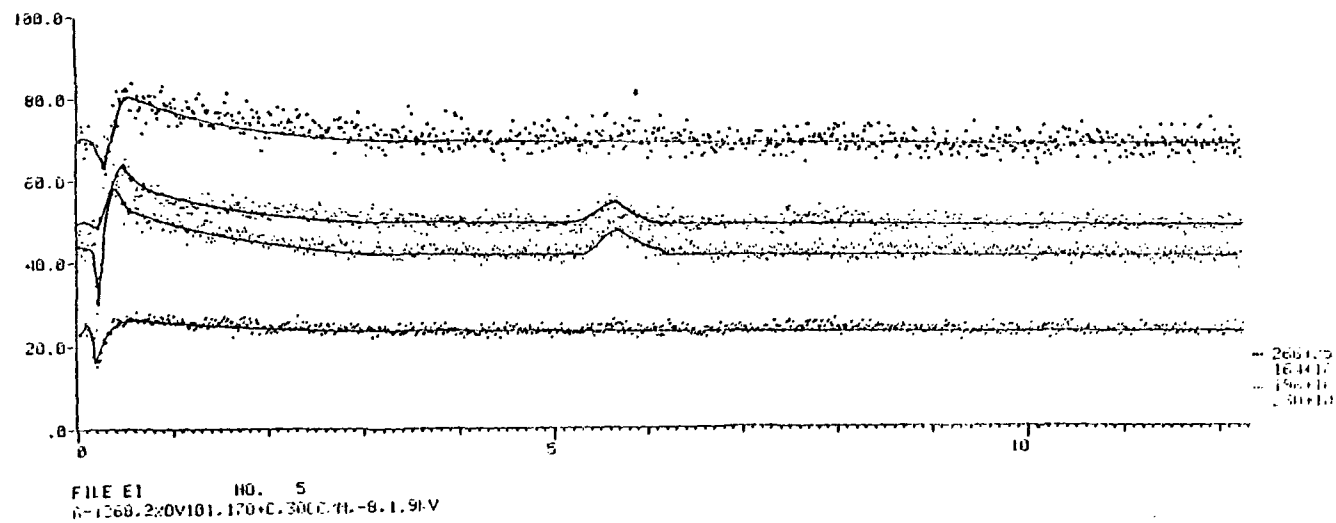


Figure C-35. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®]; multiple ion detection (180 ng)

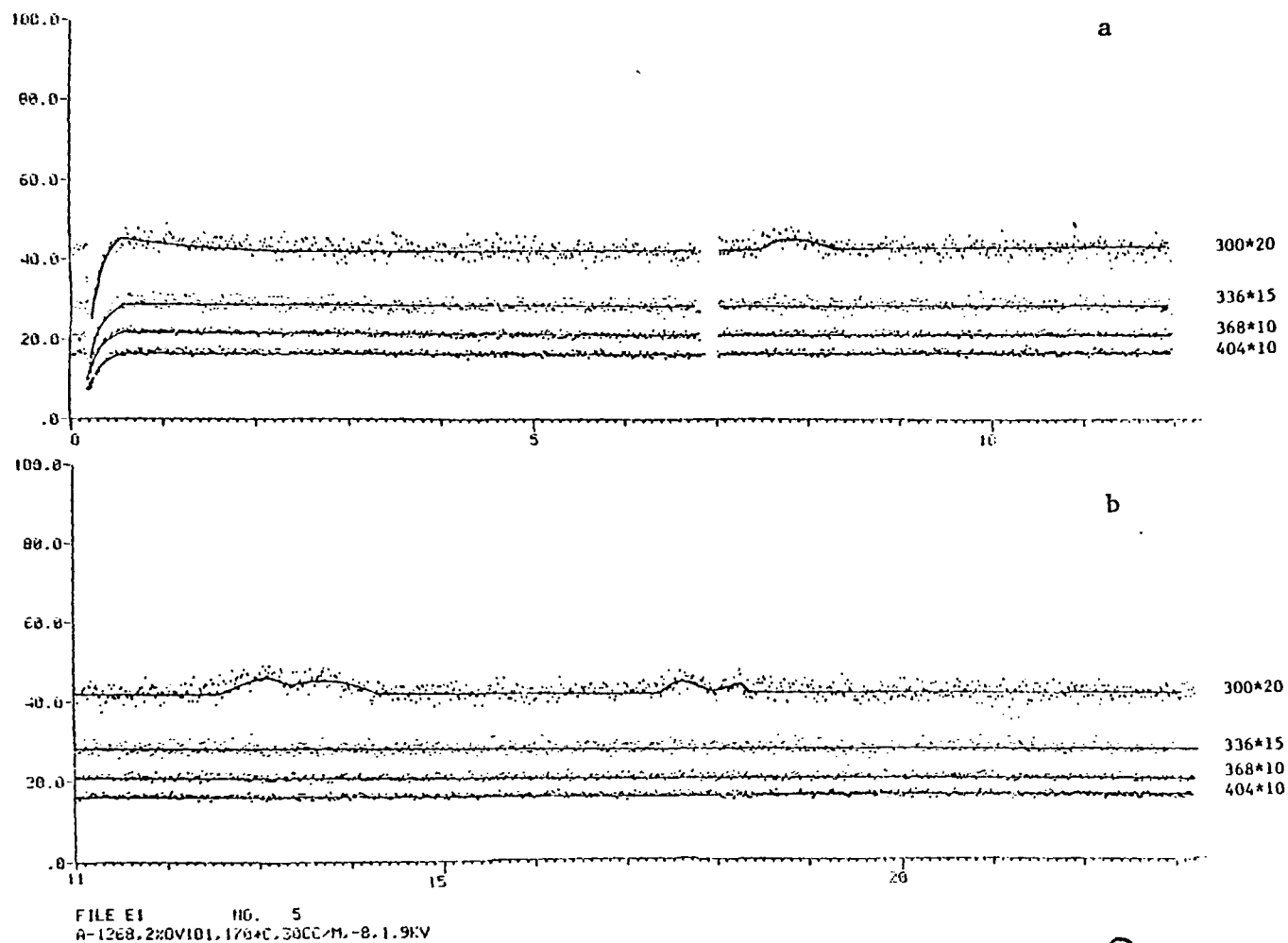


Figure C-36. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®];
 a. Multiple ion detection (180 ng)
 b. Multiple ion detection (180 ng)

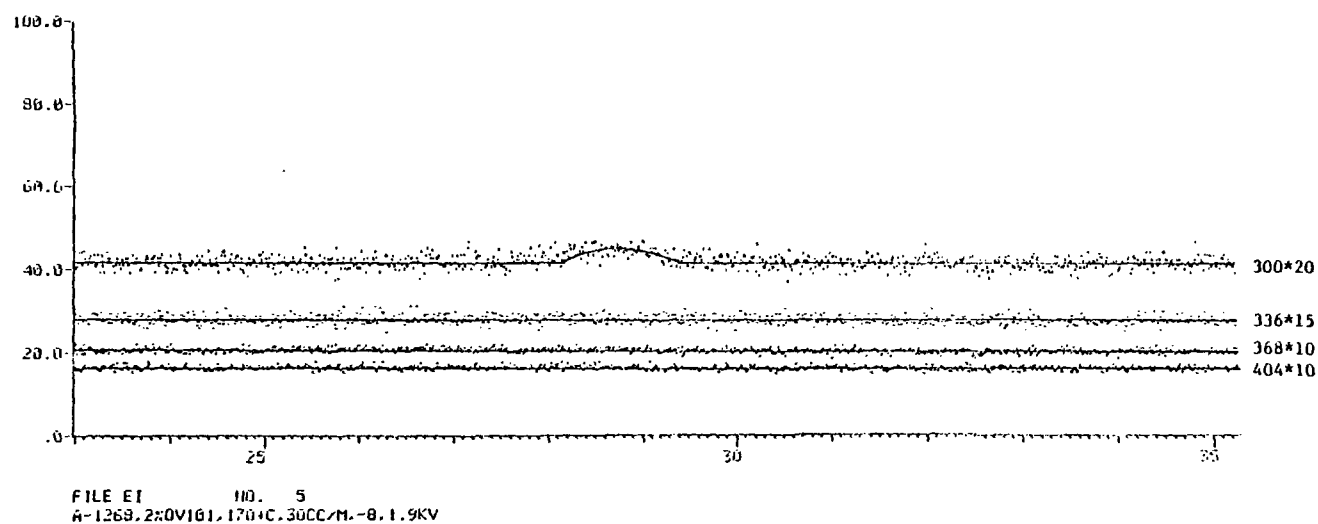


Figure C-37. Gas chromatographic-mass spectrometric analysis of Aroclor-1268[®]; multiple ion detection (180 ng)

TECHNICAL REPORT DATA

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1. REPORT NO.		2.		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Polychlorinated naphthalenes in Air, Water and Soil				5. REPORT DATE June, 1977	
				6. PERFORMING ORGANIZATION CODE	
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16. ABSTRACT This research program was initiated to evaluate possible environmental contamination by polychlorinated naphthalenes (PCNs). The program included sampling and analytical method development and the collection and analysis of field samples. A glass fiber filter and two precleaned polyurethane foam plugs in tandem were used for PCN collection. Recovery of the PCNs from the foam and filter was accomplished by triple extraction with toluene. The concentrated extract was chromatographed on a silica gel column and the final volume reduced to 2 ml in a Kuderna-Danish apparatus. Samples were analyzed by gas chromatograph/quadrupole mass spectrometer/computer. The instrument was operated in the multiple ion detection mode which permitted the detection of <50 pg of a PCN isomer ($\sim 0.3 \text{ ng/m}^3$ in air). The presence of PCNs was confirmed from full scan mass spectra or by monitoring the chlorine isotope ratio. Air, water, soil, sediment and biota were collected from sites near a PCN manufacturer, and six potential users. PCNs were found at all sites sampled although appreciable quantities were found at only three sites, near the manufacturer and two possible users.					
17. KEY WORDS AND DOCUMENT ANALYSIS					
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Polychlorinated naphthalenes (PCNs) Air Water Soil Fish Biota					
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