

AN APPARATUS AND METHOD FOR DETERMINING TRACE  
LEVELS OF PENTACHLOROPHENOL IN AMBIENT AIR

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LEVELS OF PENTACHLOROPHENOL IN AMBIENT AIR

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## PREFACE

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## CHAPTER I

### INTRODUCTION

Pentachlorophenol is most commonly used as a wood preservative and termite treatment in construction. It is an ingredient in a number of processes and other products which include: moth proofing fabrics; mold and slime control in food processing plants; mildew control in shampoo; and as a fungicide/bactericide in adhesives, oils, paints and rubber (1).

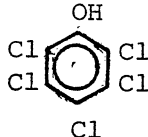
Pentachlorophenol is described as highly toxic (1,2). The compound may enter the body by dermal absorption, ingestion, and by inhalation. Although it is ubiquitous in human urine and a suspected cause of fetotoxicity and teratogenicity (2), there is little hard data to quantify the expected human and/or domestic animal exposure, specifically potential inhalation exposure, to the compound under normal use. The threshold limit value of pentachlorophenol in air has been established by the American Conference of Government Industrial Hygienists (3) at 0.5 microgram per cubic meter. This level is based on a 8 hour day of a 40 hour week. The exact dosage required to produce illness in man is not known.

Chemically, pentachlorophenol is a fully chlorinated phenol, illustrated by the structural formula in Table I. This white to buff colored crystal is produced by chlorination of molten phenol. Pure pentachlorophenol is practically insoluble in water but soluble in



TABLE I  
PROPERTIES OF PENTACHLOROPHENOL

---

Structure:	
Name:	Pentachlorophenol
Formula:	$C_6Cl_5OH$
Molecular Weight:	266.36 g/mole
Melting Point:	190°C
Boiling Point:	293°C
Description:	Buff-colored crystal
Specific Gravity:	1.9
Density:	1.987 g/mL
Vapor Pressure:	0.00017 (20°C)

---

Sources: Bevenue (1) and the Federal Register (2).

most organic solvents and oils. It is also quite stable, heating to temperatures below its boiling point will not cause decomposition. Table I contains a list of pentachlorophenol properties.

#### Early Studies in Airborne Pentachlorophenol Determinations

Analytical methods to date for the determination of pentachlorophenol in air have been, for the most part, developed in response to industrial needs. In these applications, concentrations of airborne pentachlorophenol were typically found to be in the milligram to microgram per cubic meter range (see Table II for methods summary). Therefore, bubblers, impingers, and/or flasks containing suitable solvents were used as collection media with relatively low volumes of air sampled (4-8).

Bencze (4) was one of the earliest to attempt to determine pentachlorophenol levels in air. Two bubblers in series each containing 5 milliliters of distilled water were used to strip air of pentachlorophenol. Samples were collected for 10 minutes at a flow rate of two liters per minute. After work-up which included color development, the sample was analyzed spectrophotometrically, with a lower detection level of 150 nanograms per liter.

Akisada (5) monitored the atmosphere in a manufacturing plant by pumping air through a flask containing fifty milliliters of a sodium hydroxide solution to collect pentachlorophenol. The average amounts of the compound found in the air ranged from 3.32 to 14.04 milligrams per cubic meter. Pentachlorophenol was determined spectrophotometrically following color development.

Gebefügi and co-workers (6) determined airborne pentachlorophenol

TABLE II  
SUMMARY OF EARLY STUDIES IN AIRBORNE PCP DETERMINATIONS

Reference	Trapping Medium	Method of Analysis	Lower Detection Reported ( $\mu\text{g}/\text{m}^3$ )
Bencze (1963)	10 mL $\text{H}_2\text{O}$	colorimetric	150
Akisada (1965)	50 mL 0.014N NaOH	colorimetric	3,000
Gebefügi (1976)	100 mL 0.1F $\text{K}_2\text{CO}_3$	GC	1
NIOSH (1977)	15 mL ethylene glycol	HPLC	265
Dahms (1979)	$\text{K}_2\text{CO}_3$ soln.	GC	0.05

in a specially constructed enclosed area. Gas scrubbers in series containing 0.1 formal  $K_2CO_3$  solutions were used as the collection apparatus. Pentachlorophenol, extracted from these solutions with hexane and determined gas chromatographically, ranged in concentrations from 1 to 160 micrograms per cubic meter.

In 1977, the National Institute for Occupational Safety and Health (NIOSH) reported (7) a liquid chromatographic method for the determination of airborne pentachlorophenol. This method utilized a membrane filter in tandem with a bubbler containing ethylene glycol to differentiate between analyte on particulate matter and that in a vapor state. The NIOSH method was used in sampling up to 180 liters of air at 1.5 liters per minute with a reported detection limit of approximately 0.3 milligrams per cubic meter.

Dahms (8) reported detection limits of 0.05 micrograms per cubic meter for pentachlorophenol in air using a bubbler containing a solution of  $K_2CO_3$ . In this study, pentachlorophenol was derivatized with acetyl chloride prior to quantitative determination with gas chromatography.

#### State of the Art in Sample Volume Measurement

The literature is filled with air sampling data that are based on incorrect measurements of air volume (9). This is primarily due to the fact that commonly available sampling devices operate over relatively long intervals and rely on precalibration of pumping speeds. Many factors can change during the process of sampling which may significantly alter pumping speeds and ultimately determination of total volume sampled; these include humidity, viscosity, sample loading, friction, plugging due to dust or particulate accumulation, supply voltage

changes, etc. In fact, recent reviews suggest that inaccurate sample volume measurement may be one of the largest single sources of error in any given validated method for trace components in air (9,10). Assumption of constant flow rate following accurate pump calibration and/or frequent monitoring will still allow error into the volume totalization.

It is recommended that a pump's sampling rate be known with  $\pm 5\%$  for each collection media (7,10). In ideal sampling situations (constant flow rate) the error in sample volume calculation will be five percent or less. Generally this is not the case, and knowledge of pre-sampling flow rates ( $\pm 5\%$ ) does not mean the calculated sample volume is within 5% of the actual value. In most cases the error could be larger. If the sample volume is large even five percent uncertainty could be significant. Error is minimized when flow rates are constantly and dynamically measured with a high degree of accuracy and these measurements used to totalize volume. Such a system is not commercially available even though sample volume is an important measurement. A recent automated, accumulative, sequential sampler with air flow rate measurement and totalization capability has been reported by Gearhart and co-workers (11). That device was designed to totalize volume through analog integration of the direct current signal from an air mass flow rate transducer. The circuit design was characteristically adaptable to sequential sampling with variable volume programming over relatively short term sampling intervals.

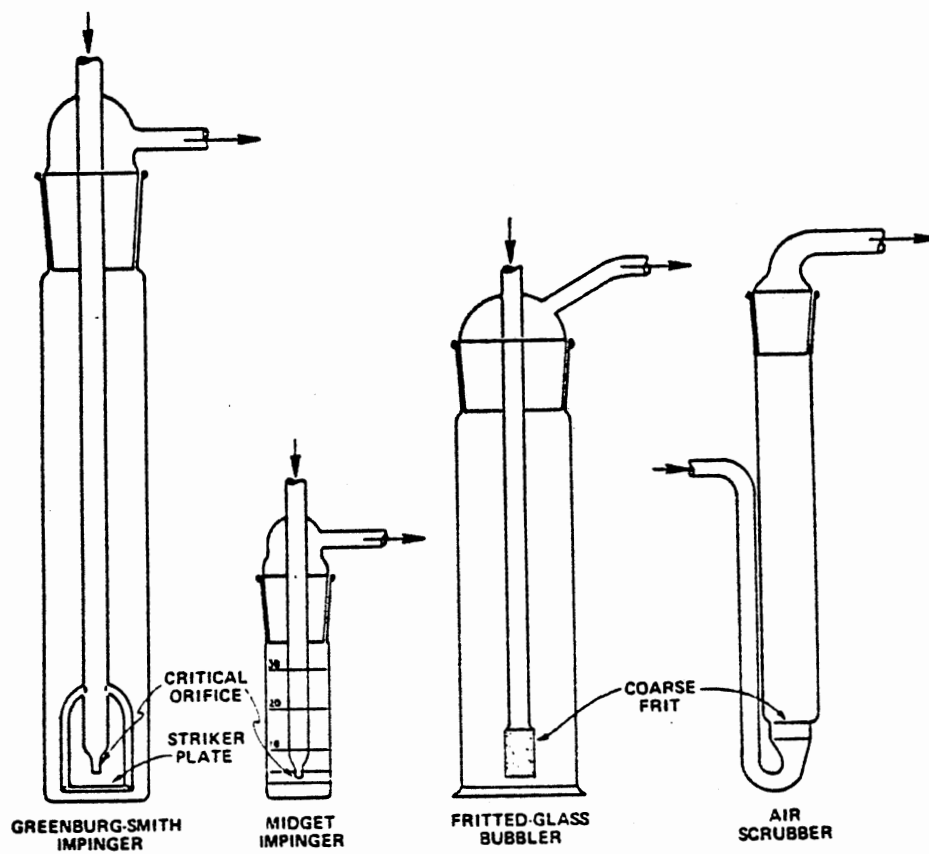
#### Airborne Analyte Collection and Concentration Methods

Pesticide sampling devices are classified as either accumulative, reactive, grab, or continuous. Accumulative samplers collect pesti-

cide vapors by entrapment and concentration from an air stream over some time interval. Reactive samplers operate in the same manner, but the pesticide vapor is chemically altered by the collection medium. Grab samples are obtained directly by filling an evacuated chamber with air. Continuous air samplers are designed to give a real time measurement of a pollutant's concentration in air. The two latter types are typically suitable only when airborne pesticide concentrations are relatively high approximately milligram per cubic meter. The two former types are suitable, depending upon specific detection limits of the overall method, for trace levels at or below microgram per cubic meter.

#### Liquid Collection Media

Liquid impingers and bubblers (Figure 1) have been employed as accumulative samplers more than other trapping mechanisms or designs. The widely used Greenburg-Smith impinger is illustrated in Figure 1. Air samples are pulled into the liquid filled cylinder by a pump connected to the outlet. The stream of air strikes the plate below the inlet tube restriction and produces small bubbles having a large interface with the liquid. Collection efficiency depends on solvation of the analyte and is altered by parameters that fluctuate during sampling such as: solvent viscosity, temperature and humidity. Evaporation of the solvent is a serious problem when sampling large volumes. Relatively long sampling periods, which are required for the determination of trace (approximately parts per billion) levels of organic volatiles in air, lead to sample loss and change in inherent collection efficiency in impingers. The need for immobility, orientation stability, and small sample sizes make impingers impractical for the potentially hostile environments of domestic domiciles with trace levels of analyte.



Source: Lee (9).

Figure 1. Air Samplers Designed for Liquid Collection Media.

### Solid Collection Media

Various reviews (9,12) on sampling techniques for airborne analytes have indicated that solid sorbents or standard GLC packings in small precolumns or sampling tubes are efficient in collecting and concentrating certain organic volatiles from pumped air streams (see detail, page 14). Solid sorbents used with accumulative samples are potentially less susceptible to certain parameters which limit the utility of liquid collection media to low air through-put volumes. Sample vapors are stripped from the pumped air stream as they interact with the sorbent in the sampling tube. This process resembles frontal analysis gas chromatography operating at ambient temperatures with air as a carrier gas. Solid sorbents which exhibit large gas chromatographic net retention volumes for the analyte at elevated temperatures are chosen as the trapping media. Since net retention volumes are longer at ambient temperatures, and sample loss occurs only when analyte elutes from the tube exit, solid sorbents effectively quantitatively collect vapors until the volume sampled approaches the net retention volume.

### Evaluation of Sorbent/Solvent Systems

Characterization of collection and desorption efficiency are important criteria for evaluation of methods which collect organic pollutants with solid sorbents followed by desorption with a suitable solvent and analysis. Once airborne pentachlorophenol is concentrated on a solid sorbent it is necessary to recover a known portion of the analyte in a solvent. This fraction has been called the desorption efficiency. Compounds are partitioned between the solid adsorbent and the desorption solvent according to the equation:



$$\frac{1}{D} = K \frac{\text{milligram sorbent}}{\text{milligram solvent}} + 1 \quad (1)$$

where D = desorption efficiency; K is a distribution ratio (13). If the sorbent/solvent ratio is not varied, desorption efficiency is constant when measured under equilibrium conditions.

Any solid sorbent used as a trapping/concentrating medium for organic volatiles in air has a potential limitation due to differential migration of the analyte through the packed bed under the influence of the moving air stream (10,14,15). With a steady flow of most organic vapors into a sampling tube bed, the tube will exhibit one hundred percent collection efficiency for a time. Eventually the analyte deposited from air onto the bed migrates as more air is sampled, accumulation along with other factors cause the analyte front to advance. Breakthrough occurs when the analyte first elutes in the pumped air stream at the exit of a packed sampling tube (10,14,15,16).

Several methods have been used to estimate the breakthrough volume and thus a safe sampling volume. For volatile compounds an artificially generated atmosphere of known concentration can be sampled, and the eluant of the sampling tube monitored for the compound of interest. Low vapor pressures of some compounds pose problems in generating atmospheres of known concentration. Breakthrough volume has been related to the retention volume in a gas chromatographic system. Plots showing Log (net retention volume) versus reciprocal degrees Kelvin are used to determine what the retention volume of the compound is at ambient temperatures (16). A safe

sampling volume is some fraction of the measurable breakthrough volume and can be determined with the appropriate mathematical model (17).

#### Direction of Research

The determination of pesticides in air involves two measurements, volume of air sampled and quantity of analyte collected. In determining trace levels of pentachlorophenol in homes and other domestic buildings, meaningful contributions to both these measurements were possible. Therefore, this paper will describe, in separate sections, the results of two projects.

First, sample volume measurement has been improved by continuous electronic monitoring of sampling flow rates. The need to precalibrate pumping speeds is eliminated by totalizing, with a high degree of accuracy, the actual sample volume. A new air sampler specifically designed for programmed volume totalization with short term to very long sampling time intervals is described. The sampler operates in a single-sample mode and is designed to dynamically measure sampled air mass flow rates. The details of its design and operation are reported (18).

In the second project a direct method for determination of trace levels of airborne PCP was developed. This method is simpler than others reported (Table II) in that it eliminates pH adjustments, derivatization, color development, sample concentrations, and problems associated with liquid collection media. The detection limits are lower in comparison with other similar methods. The development and evaluation of this analytical method for the quantitative determination of airborne pentachlorophenol at approximately one microgram per cubic meter levels is reported. The method utilizes solid sorbents as concentrating media together with the precision air sampler (18). Analyte recovery is done using a batch solvent extraction technique, with quantitative

determination of pentachlorophenol done by gas chromatography/electron capture detection techniques.

The analytical method reported for airborne pentachlorophenol therefore is characterized by high sensitivity, low detection limits, high and uniform collection efficiency, and good analyte recovery. The sample collection method together with the air sampling device (18) preclude the need for immobility and/or orientation stability during sampling. These factors collectively result in an analytical method for airborne pentachlorophenol which is particularly useful in measuring potential human inhalation exposure to low levels of pentachlorophenol within homes, workplaces, etc.

## CHAPTER II

### EXPERIMENTAL

#### Pneumatic Circuit Description

The gas flow pattern through the sampler is shown in Figure 2. An air sampling pump (MINIDIA-VAC model) was purchased from Air Dimension, Incorporation, Lansdale, Pennsylvania. It operates from 115 V, 60 Hz at 118 W, has a maximum vacuum of 21 inches of mercury, and has a maximum flow of 0.6 cubic feet per minute (0.0 in Hg). The construction (head) is stainless steel with a Teflon-coated diaphragm. An alternate, double head model is available from the same manufacturer with a maximum flow of 1.2 cubic feet per minute (0.0 in Hg). The stainless steel mass flow transducer is a Model 8163 (Matheson Gas Products, East Rutherford, New Jersey) calibrated over a 0-10 standard liters per minute range. It is available with flow ranges up to 0-400 standard liters per minute (Model 8164), if required. An external manifold was fabricated by using 0.25 in Ultra-TORR fittings (Cajon Company, Solon, Ohio) to facilitate sample tube and/or other concentrating trapping device connections. Figure 2 details the manifold with a packed 3 in. x 0.25 in. glass tube in place. Typical flow rates observed with packed tubes ranged between 1 and 4 standard liters per minute, depending upon the packing weight and particle diameter.

#### Electronic Circuit Description

The flow transducer, Model 8163, was calibrated to provide an out-

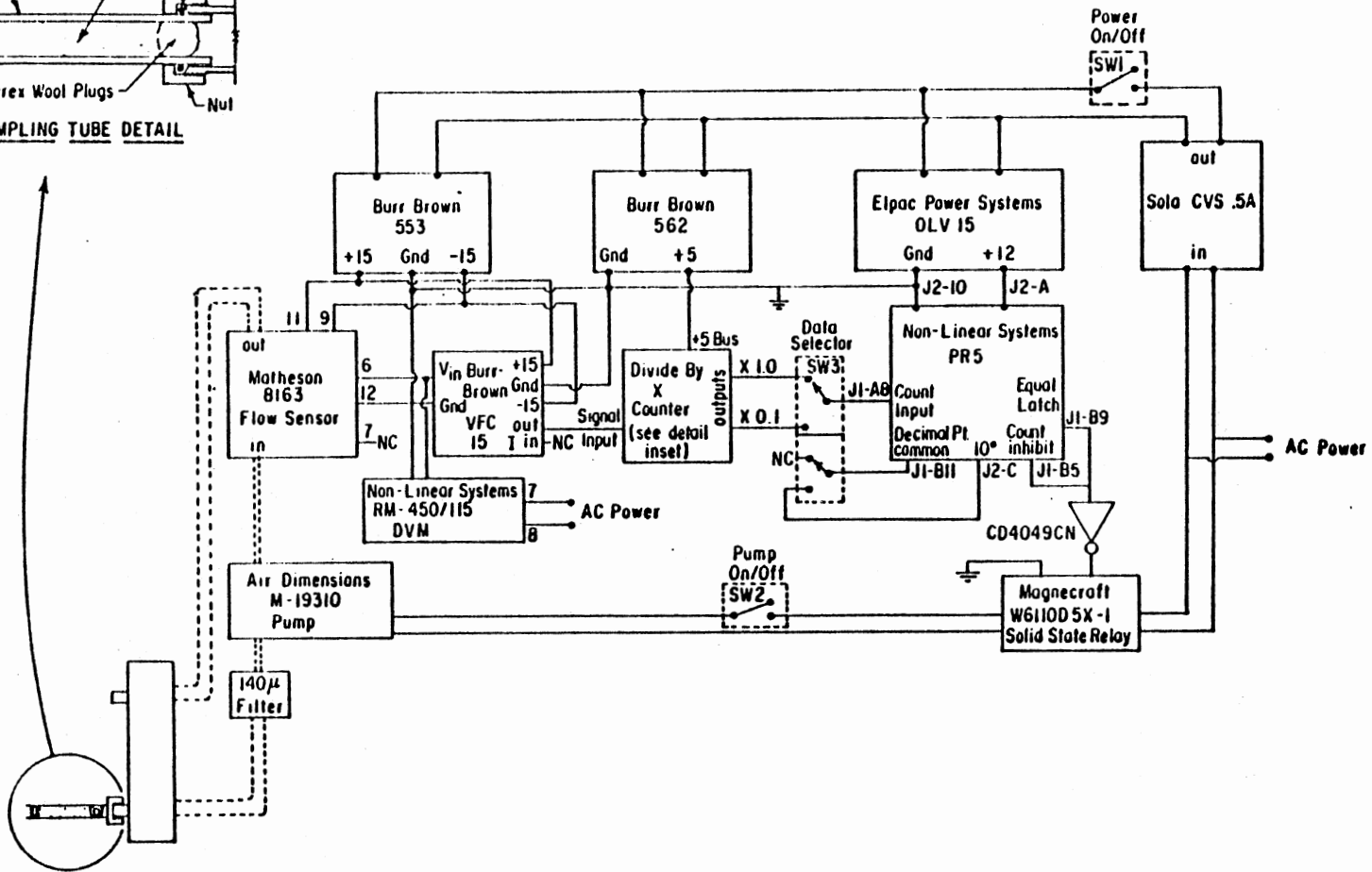
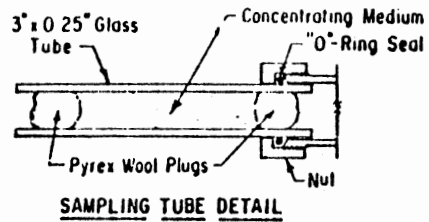


Figure 2. Electronic and Pneumatic Circuit Diagram for Air Sampler.

put voltage (0-5.0 V dc) proportional ( $\pm 1\%$ ) to mass flow rate (0-10 standard liters per minute). A VFC 15 (Burr-Brown, Tucson, Arizona) voltage to frequency converter was used which was factory calibrated to provide linear response (0.005% linearity) at 9.900 kHz per 10,000 V dc. This converter provided excellent temperature stability (10 ppm/ $^{\circ}$ C max gain drift). A TTL scaler circuit (detailed in Figure 3) was used to divide the VFC 15 output frequency by a factor of 30303 (demical) or 765F (hexademical) to give an output pulse rate corresponding to liters sampled. An additional integrated circuit (74193 in Figure 3) provided an output corresponding to liters x 0.1 sampled. This optional counting range provides increased resolution for low total volume samples. A Model PR-5 preset frequency counter (Non-Linear Systems, Del Mar, California), provided readout and preset input counts of five digits, respectively. A CMOS integrated circuit chip (CD4049, National Semiconductor, Santa Clara, California) was used for logic level conversion and inversion between the scaler circuit and the PR-5. A Model RM-450/115 digital volt meter (Non-Linear Systems) was used for continuously monitoring mass flow rate of sampled air. To ensure electronic stability high-performance power supplies were used. Models 553 and 562 (Burr-Brown, Tucson, Arizona) provided  $\pm 15$  V dc and +5 V dc, respectively. The OLV 15 provided +12 V (ELPAC Power Systems, Santa Ana, California). A Sola CVS, 0.5 A/115 V ac constant voltage transformer (Sola Electric, Elk Grove, Illinois) was used for ac input voltage (see detail in Figure 2).

#### Sampler Operation

Operation is initialized by providing ac power with all switches in the off position. The power ON/OFF switch (SW1, Figure 2) enables the constant voltage ac power to reach the power supplies.

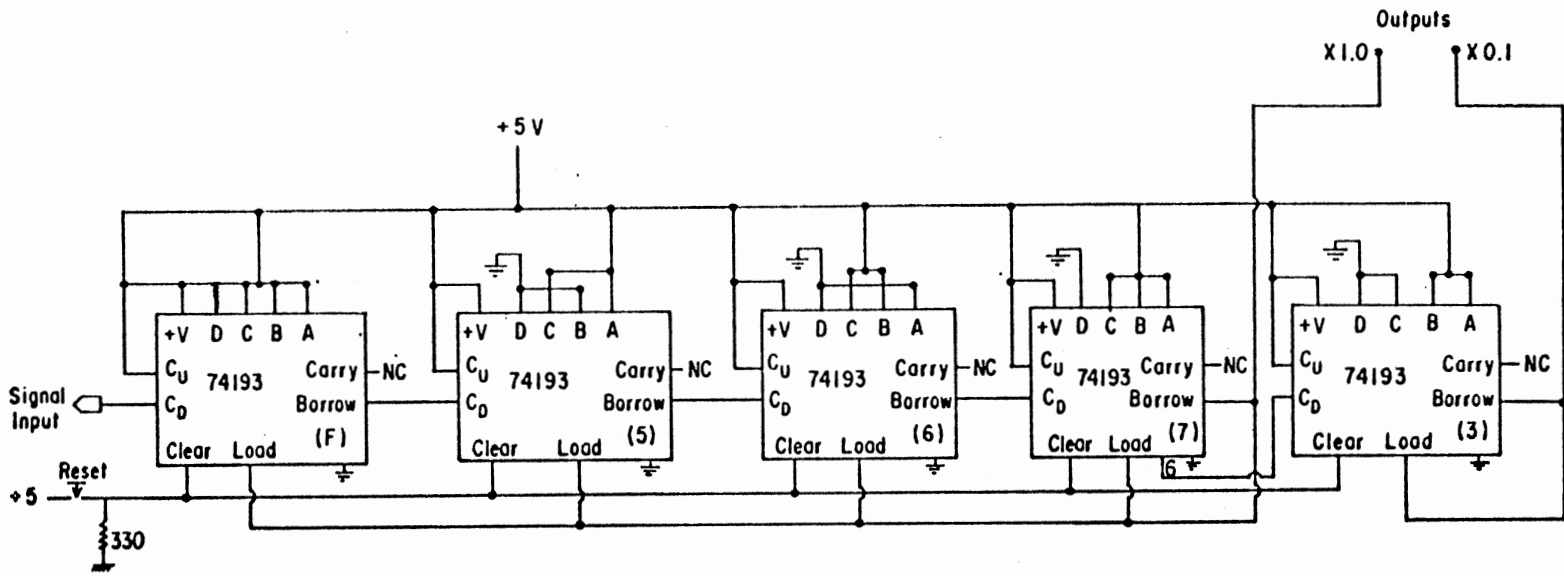


Figure 3. Electronics Circuit Diagram Detailing Frequency Count Scaler Elements.

An initial warm-up period of 30 min is recommended to allow the mass flow transducer output to stabilize. During this time a sample tube should be inserted into the intake manifold. The desired volume to be sampled is selected on the PR-5 front panel. The TTL scaler circuit is reset by a front panel push button (see Figure 2) which brings the CLEAR pin of each 74193 briefly to +5 V. The PR-5 totalizer front panel RESET button is depressed to initialize the count at zero.

The pump ON/OFF switch (SW2, Figure 2) is enabled and the pump begins sampling air. The mass flow transducer output voltage is converted to a train of pulses by the VFC 15. The TTL circuit scales the pulses. The scaling factor is simply changed with jumpers to allow matching different transducer output and frequency converter input characteristics. A single DPDT switch (SW3, Figure 2) allows the user to totalize in tenths of liters or liters. This switch also simultaneously sets the position of the decimal point on the PR-5 display.

Input pulses to the PR-5 are totalized and displayed. When the count reaches the preset value the EQUAL LATCH (pin J1-B9) changes from 0.0 to > 10 V. This level change is routed to the COUNT INHIBIT input (pin J1-B5) which holds the display at the preset count. The EQUAL LATCH signal is also fed to a CMOS level conversion inverter (CD4049CN). The high logic level is shifted from > 10 V to +5 V and the output logic is inverted. In normal operation the input of the CD4049CN is grounded and the output goes to the high level of +5 V. The output of the CD4049CN drives a MAGNECRAFT W6110DSX-1 solid-state relay (Newark Electronics, Oklahoma City, Oklahoma). When the inverter outputs +5 V the relay is turned on and the air pump operates. When the preset count is reached, the EQUAL LATCH goes high (> 10 V), the inverter grounds its output, the relay is disabled, and the air



pump shuts off. It will remain in this state with the pump off and the sampled volume displayed until reset or powered down.

#### Reagents and Chemicals

All glassware was silanized with 20% solutions (v/v%) of dichlorodimethyl silane in toluene (Mallinckrodt, St. Louis, Missouri). Following overnight drying in an oven at 200°C, the glassware was submerged in the silane solution for at least 20 minutes. The silanization process was stopped by first rinsing thoroughly with toluene and finally the reaction was completed by a methanol (Mallinckrodt, Paris, Kentucky) rinse.

Calibration was accomplished by syringe injection of PCP (certified 99% + purity, Aldrich Chemical Company, Milwaukee, Wisconsin) standards. 100.0 mg of PCP was placed in a 100 mL volumetric flask and the given solvent was added to volume. Aliquots of this stock solution were used to make solutions of 100, 50, 20, 10, and 5 ng/μL PCP. The solvents used were reagent grade or better. Silica gel and charcoal were obtained pre-packed in absorption tubes; Tenax, 80/100 mesh, a GC packing material was purchased in bulk quantity (Supelco, Bellefonte, Pennsylvania).

#### Gas Chromatographic Systems

All analytical determinations of PCP were made using a Hewlett-Packard (Hewlett-Packard Co., Avondale, Pennsylvania) Model 7620A Research Chromatograph equipped with a <sup>63</sup>Ni electron capture detector. Silanized glass columns (4 ft. x 1/4 in o.d.) were packed with 1% SP 1240 DA on 100/120 Supelcoport (Supelco, Inc., Bellefonte,

Pennsylvania). Analytical columns were conditioned at 190°C for at least 3 hours using a He carrier gas flow rate of 40 mL He/min, purified by in-line oxygen and hydrocarbon traps (Scientific Galss Engineering, Austin, Texas).

Calibration plots were done with PCP standard solutions (1-2 µL) syringe injected directly into the injection port held at 185°C. The oven temperature was isothermal at 170°C; and the detector, with a pulse interval of 15 µsec, was maintained at 310°C. The purified He carrier had a flow rate of 40 mL/min. The detector purge gas, a 90:10 mixture of Argon and Methane (Matheson Gas Company, East Rutherford, New Jersey) was set at a flow rate of 110 mL/min to obtain optimum response from the electron capture detector. GC operating conditions are summarized in Table III.

GC retention time studies for PCP on Tenax were done using a HP 5710 gas chromatograph equipped with a model 3385A Automation System (Hewlett-Packard). The flow rate of carrier was 25 mL He/min. and the injection port temperature was set at 250°C for these experiments. The column was made using 300 mg of Tenax enclosed in a nickel steel tube (4 in. x 1/4 in. o.d.) plugged with silanized glass wool and silver soldered at either end to lengths of 1/8 in. tubing fitted with vespel ferrules.

#### Special Experimental Apparatus

A cold trap was constructed by combining the Model 5710 gas chromatograph described earlier with a custom designed thermostated block (Figure 4). Tenax packed glass tubes (8 in. x 1/4 in. o.d. x 4 mm i.d.) were connected to the injection port of the chromatograph with graphite ferrules and Swagelok fittings, and conditioned for 1 hour at

TABLE III  
TYPICAL GAS CHROMATOGRAPHY OPERATING CONDITIONS

---

Electrometer Settings:

Function	EC
Pulse interval	15
Suppression	Low
Range	10
Attenuation	16

Temperatures ( $^{\circ}\text{C}$ ):

Injection port	185
Column oven	170
Electron capture detector	310

Gases:	Tank Settings (psi)	Approximate Flow Rate (mL/min)
Helium carrier	40	40
Argon methane	60	110

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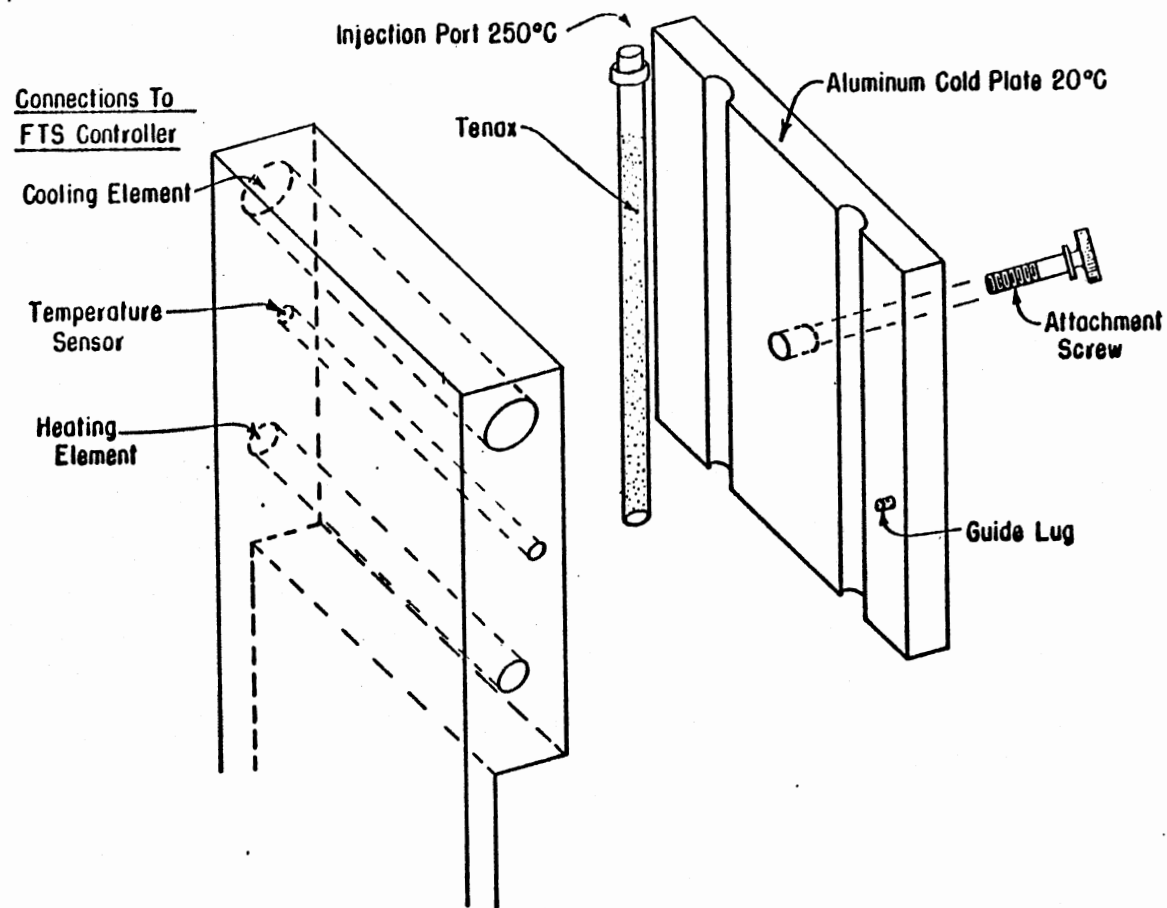


Figure 4. Diagram of Thermostatted Aluminum Block Designed for Collection of PCP Vapor With Packed Sampling Tubes.

300°C and a carrier flow rate of 40 mL He/min. The glass tube extending below the injection port and containing the trapping media was inserted into an aluminum block. Isothermal temperatures of 20°C for the thermostated block were provided by Model FC 2020P1 proportional temperature controller (FTS Systems, Stone Ridge, New York).

Simulated breakthrough studies were simplified by the use of an air sampler specifically designed for programmed volume totalization described previously by Gearhart et al. (18). This precision sampler was utilized to monitor pumped air flow rates (~1-3 L/min) and measure total volume sampled.

#### Air Sampling Procedure

Sampling tubes for collection of PCP from ambient air should be made from glass tubes (4 in x 1/4 in o.d. x 4 mm i.d.) packed with 100 mg of 80/100 mesh Tenax and plugged at either end with silanized glass wool. It is best to arrange the solid sorbent in 3 or 4 separate segments, each containing equal amounts of sorbent, which are isolated with silanized glass wool plugs, if it is desirable to look for evidence of breakthrough with each sample.

Following collection of each sample, the contents of each packed tube are placed in a 4 mL vial equipped with teflon lined septum caps (Supelco, Bellefonte, Pennsylvania). A 2 mL volume of methanol is added to the contents of the vial while simultaneously rinsing the tube's inner wall. Batch extraction is carried out for a 1 hr period on an oscillating mixer (Universal Oscillating Shaker, Labline Instruments, Melrose Park, Illinois). A 1.0 µL aliquot of liquid is removed from the vial using a 5 µL syringe, and this is injected into the chromatographs (conditions and column described previously).

## CHAPTER III

### RESULTS AND DISCUSSION

The results will be presented and discussed in two parts. The development of the analytical method by evaluation of the sorbent collection efficiency and the solvolytic analyte recovery will be reported later. The air sampler's contribution and characteristics will be presented first.

#### Air Sampler

The design of the air sampler demonstrates a very important advantage over various others reported previously. Comparable refinements in flow sensing and volume totalization, exhibited by this sampler, are not commercially available. It dynamically monitors fluctuations in sampling rate and totalizes the volume of air sampled accordingly. The phenomenon of varying pumping speed during sampling is illustrated by experimental results shown in Figure 5, where a 3 inch 0.25 inch glass tube containing 160 milligrams of silica gel was used as a collecting/trapping medium with the air sampler described for a 1000 liter air sample. An observed loss in pumping speed of approximately ten percent occurred over the sampling interval. The shape of the curve suggests a near exponential decay of air throughput rate versus

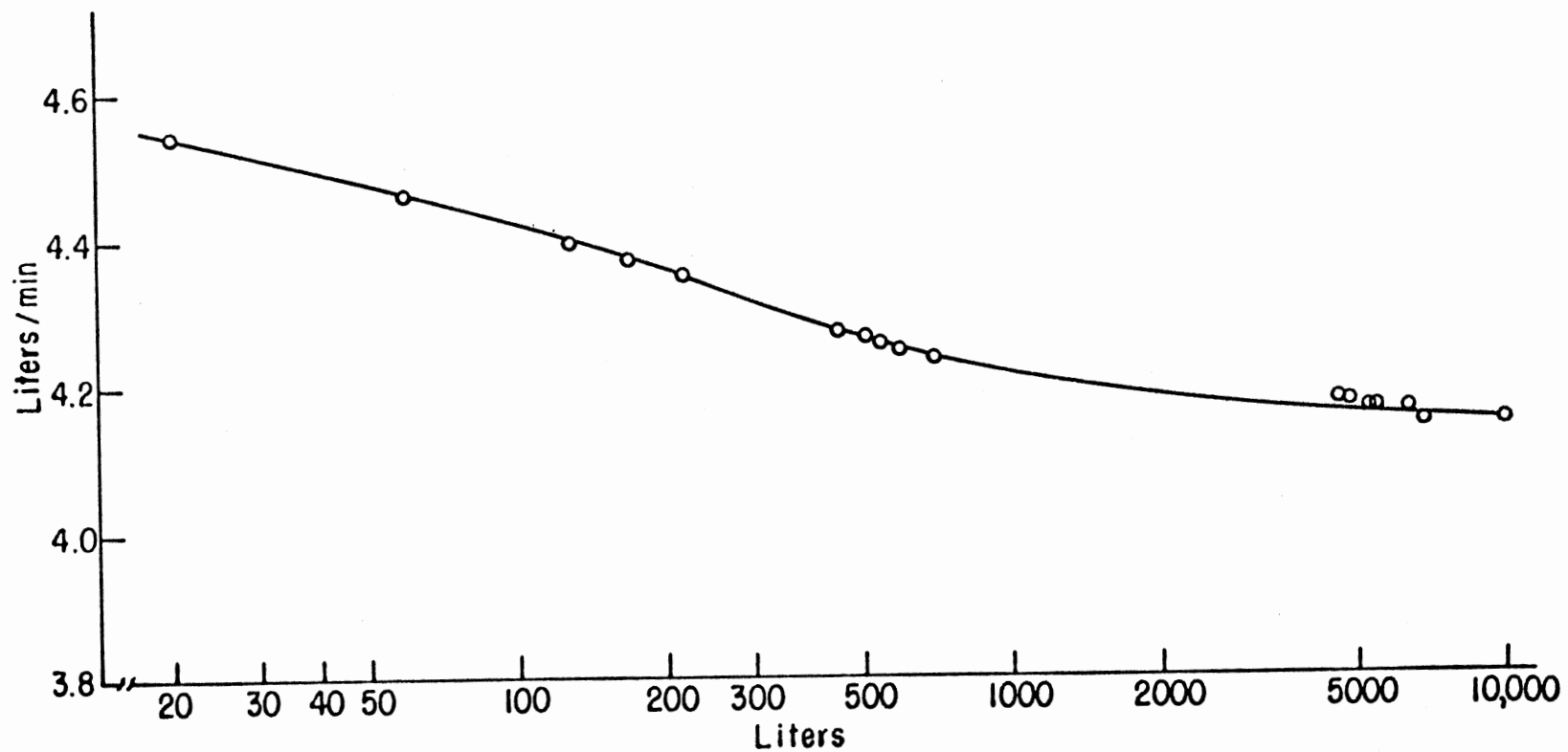


Figure 5. Plot of Sampling Flow Rate (L/min) Versus Log of Volume Sampled (L).

time. Similar but more drastic results were observed by using a 3 inch times 0.25 inch glass tube filled with Tenax (80-100 mesh), where an approximate twenty-five percent reduction in pumping speed occurred for a 10,000 liter air sample. These results clearly indicate the important contribution this sampler's design makes to the field of trace level determination of airborne pesticides and/or other classes of airborne pollutants, where the error in sample volume measurement may be virtually eliminated (i.e., reduced to approximately one percent) by using a mass flow transducer and a volume totalizer.

The sampler has an inherently simple design based on air flow to voltage to frequency conversion. Volume totalization is accomplished by scaled frequency counting. The electronics package design, as illustrated in Table IV, provides exceptionally low drift characteristics and a low temperature coefficient making the flow measurement and totalization process accurate and quite stable over relatively long sampling times (e.g., several days or more). The components used in the sampler's construction are commercially available, the design is simple to build, and it is adaptable to a very wide range of pumping speeds which individual situations might dictate. This air sampler is versatile in that it may be used with a wide variety of concentrating/trapping media including impact filters, liquid impingers, reactive beds, and/or porous polymer filled tubes. The sampler is designed to dynamically measure sampled air mass flow rates. It will pump a preselected volume of air (up to a maximum of 99,999 liters) through the concentrating/trapping medium, at which time it will turn the pump off and hold the measured volume readout in a visual display.



TABLE IV  
OPERATING CHARACTERISTICS OF SAMPLER COMPONENTS

	Flow Transducer	Voltage Converter
Temperature range	5 - 43°C	-25 - +85°C
Accuracy	± 1%	±0.005% FSR
Linearity	± 0.5%	±0.005% FSR
Output	0 - 5 VDC	0 - 5000 Hz

## Analytical Method Evaluation Procedures

Three commercially available solid sorbents, all used widely in air sampling applications were evaluated, together with two solvents (hexane and methanol) to determine an overall system exhibiting a high pentachlorophenol collection efficiency from a pumped air stream as well as good analyte recovery characteristics in the subsequent batch solvent extraction procedure. Silica gel, charcoal, and the porous polymer, Tenax, were considered, because of their well known sorption properties (14,15,19). Hexane and methanol were evaluated as solvents, because they both show minimal response with the electron capture detector. The two solvents also have quite dissimilar polarities and solubility parameters, suggesting a contrast in comparative extraction efficiencies.

### Desorption Efficiency

Desorption efficiencies were measured at constant temperature (25°C) using the phase equilibrium technique (13). Known concentrations of pentachlorophenol were prepared in methanol and hexane. Aliquots of these solutions were equilibrated with a measured weight of each sorbent. The system is agitated during equilibration and the solution analyzed when a steady state is obtained. The dissolved pentachlorophenol is expected to partition between the two phases according to the Equation 1.

$$\begin{aligned} \frac{1}{D} &= K \frac{(\text{weight sorbent in milligrams})}{(\text{weight solvent in milligrams})} + 1 \\ &= \frac{\text{weight pentachlorophenol in solution}}{\text{weight pentachlorophenol in system}} \end{aligned}$$

where: D = desorption efficiency

$$K = \frac{\text{weight of pentachlorophenol per mg of adsorbent}}{\text{concentration (wt./wt.) of pentachlorophenol in solvent}}$$

True equilibrium conditions are verified by measuring D while varying the amount of pentachlorophenol introduced into the system and maintaining the sorbent/solvent weight ratio constant. D is actually a ratio, of the total weight of pentachlorophenol equilibrated in a given system and the weight of pentachlorophenol found in a 1.0 microliter aliquot of liquid phase (the latter is determined using a gas chromatographic calibration curve technique and standard pentachlorophenol solutions).

The efficiency of one milliliter of hexane to desorb 50 micrograms of pentachlorophenol from charcoal, silica gel and Tenax was measured (Table V). The weights of sorbents used were those in the commercially available sampling tubes in the cases of charcoal and silica gel. Packed sampling tubes 3 inches times 1/2 inch outer diameter contain 100 milligram of Tenax. Table V shows the measured desorption efficiency and the standard deviation when calculatable. The desorption efficiencies determined for the charcoal/hexane system, zero percent, and the silica gel/hexane system, three percent, are unacceptable for trace analytical work. Hexane (one milliliter) desorbs nearly seventy-five percent of total pentachlorophenol present from Tenax. Tenax, therefore, is the most desirable sorbent when considering recovery of pentachlorophenol by hexane extraction.

Table VI summarizes results of the desorption efficiency measurements made using 50 microgram per milliliter pentachlorophenol solutions (in hexane and/or methanol) equilibrated in the various sorbent/solvent combinations considered. A measured quantity of each sorbent was equilibrated in two milliliter aliquots of the methanol/pentachloro-

TABLE V

<sup>1</sup>PCP DESORPTION EFFICIENCY WITH VARIOUS SORBENTS  
AND ONE MILLILITER HEXANE

	Charcoal	Silica Gel	Tenax
Repetitions	4	8	8
Desorption Efficiency	0	3	73
Standard Deviation	-	0.3	1.9

<sup>1</sup>All systems were equilibrated with 50 micrograms of pentachlorophenol.

TABLE VI

<sup>1</sup>PCP DESORPTION EFFICIENCY WITH VARIOUS SORBENTS AND SOLVENTS<sup>2</sup>

Sorbent: Solvent:	Charcoal <sup>3</sup> Methanol	Silica Gel <sup>3</sup> Methanol	Tenax Methanol	Tenax Hexane
Number of repetitions	4	8	8	4
Desorption Efficiency (%)	0	100	100	94
Weight of sorbent (mg)	150	195	100	100

<sup>1</sup>All systems were equilibrated with 0.1 mg PCP.

<sup>2</sup>The volume of solvent was 2 ml in each case.

<sup>3</sup>Sorbent quantities were preweighed in commercially available sampling tubes.

phenol solution, respectively. Also, a hexane/pentachlorophenol solution was used for the Tenax sorbent. As shown in Table VI, essentially no pentachlorophenol was found in the liquid phase for the charcoal/methanol system. High desorption efficiencies (approximately one-hundred percent) were measured for pentachlorophenol in both the silica gel/methanol, the Tenax/methanol, and the Tenax/hexane systems.

Pentachlorophenol appears to be irreversibly adsorbed by charcoal or at least unextractable with the solvents used. Charcoal has been successfully desorbed with carbon disulfide for a number of analytes (15). Carbon disulfide's need for hooded handling, the short shelf life of standards (two to three days) and the standards' refrigeration requirements complicates the analysis.

A total collected weight of pentachlorophenol in the range of approximately 0.2 to 200 micrograms was anticipated to occur under actual field sampling conditions. Therefore, the existence of true equilibrium conditions were tested by measuring percent D's for systems composed of 100 milligrams Tenax, two milliliter of either hexane or methanol. Additionally, the systems contained various weights of pentachlorophenol ranging between 0.2 and 200 micrograms total. Break-through studies, discussed later, eliminated the silica gel/methanol system from further consideration. Two milliliters of solvent was used to adequately cover the solid media. As can be seen from examination of the data presented in Figure 6, true equilibrium conditions were apparently achieved only for the Tenax/methanol/pentachlorophenol system.

Figure 6, a plot of desorption efficiency (measured by the phase

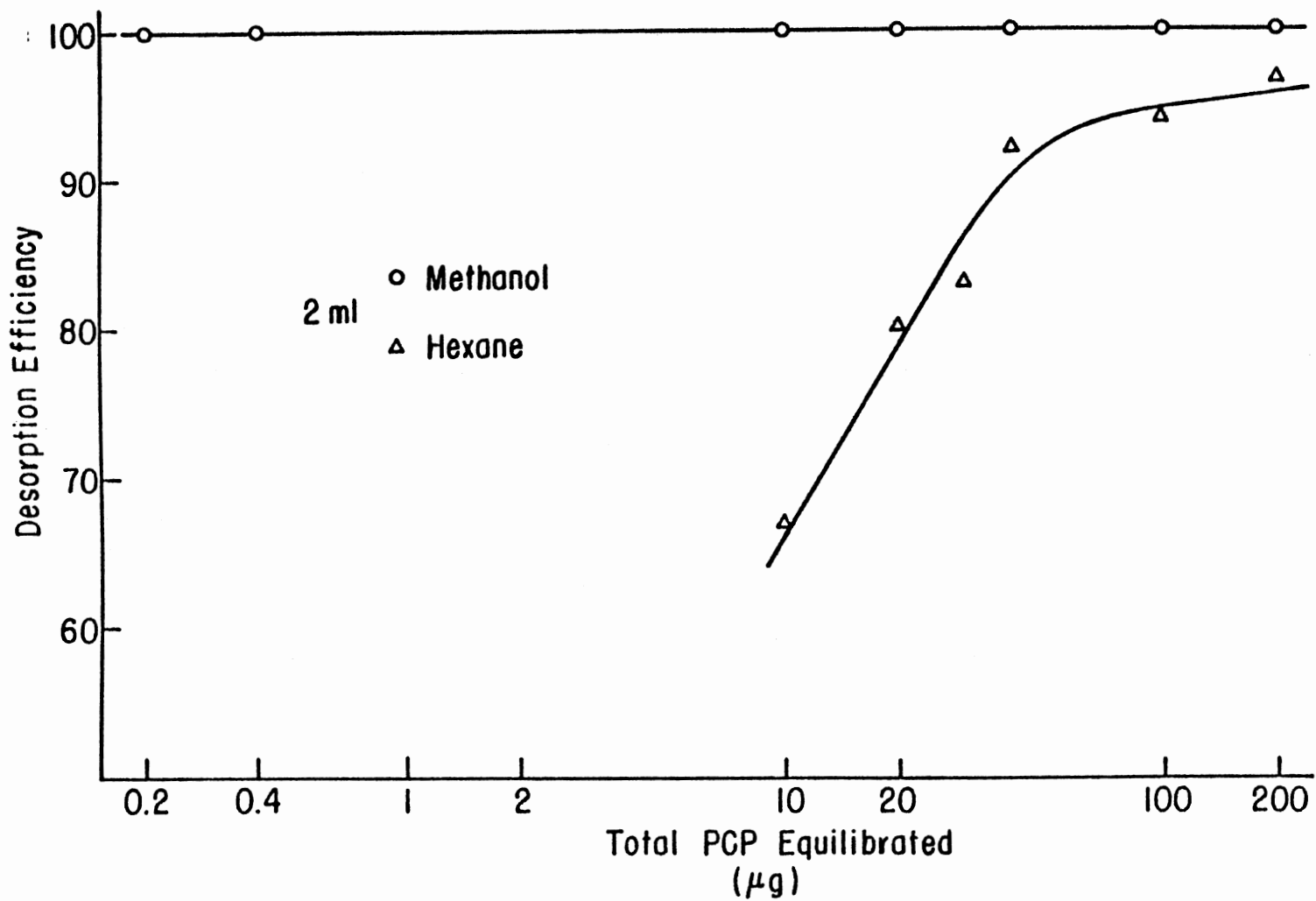


Figure 6. Plots of %D Versus Total Weight of PCP Equilibrated With 100 mg Tenax and 2 mL of Methanol and Hexane.

equilibrium technique) versus total weight of pentachlorophenol in the system, shows desorption efficiency may vary with concentration of solute. The effect is seen dramatically in the line representing hexane at low concentrations of pentachlorophenol. A slow diffusion controlled process with inefficient mixing or inadequate equilibration time could produce similar data (10). Switching from ultrasonication to a more violent mechanical oscillator for mixing improved extraction efficiencies only slightly (two to three percent). The general trend of the curve was the same. Longer equilibration periods (12 hours) and more highly inert containers to eliminate solute adsorption on glass vials, also had no noticeable effect.

The observed results are reasonable, considering the relatively polar methanol being present in excess (relative to pentachlorophenol) competes more favorably than hexane for available surface sites and more effectively displaces the highly polar pentachlorophenol solute from the polymer phase. The shape of the isotherm for the Tenax/hexane/pentachlorophenol system in Figure 6 was fit to the Freundlich equation below, with a correlation coefficient of 0.84.

$$D = \cdot K[\text{PCP}]^x \quad (2)$$

where:  $K = 60$

$$x = .116$$

$D$  = desorption efficiency

$[\text{PCP}]$  = concentration pentachlorophenol (micrograms per microliter)

The above result suggests an interesting physiochemical phenomenon, but it also precludes the use of such a system as a reliable analyte recovery method for pentachlorophenol. The Tenax/methanol/pentachloro-



phenol system, on the other hand, represents a nearly ideal situation in this regard, where essentially quantitative desorption efficiencies were achieved under apparently true equilibrium conditions.

#### Collection Efficiency

Characterization of the efficiency which the media has for trapping and retaining pentachlorophenol was obtained by studying breakthrough. Breakthrough volume has been related to the elution volume in a chromatographic system (16,17,20,21,22). With the log of net retention volume ( $\log V_n$ ) plotted versus reciprocal degrees Kelvin ( $1/T$ ), the breakthrough volume of pentachlorophenol was estimated to be  $1.3 \times 10^5$  liters at  $25^\circ\text{C}$  and 25 milliliters per minute. Helium flow for a 1/4 inch outer diameter by 3 inch tube packed with 300 milligrams of Tenax. The affinity pentachlorophenol has for Tenax is obvious from this, but the conditions do not represent those encountered in a sampling environment. We need to know the safe sampling volume for pentachlorophenol in conditions other than the purified helium carrier, thermally stable and low controlled flow rates available in gas chromatography. The flow rates should reproduce two to five liters per minute experience in field trials. Breakthrough is a function of sample loading, humidity, temperature, and flow rate. Pentachlorophenol will migrate differently in a sampling situation that includes peristaltic pump air flow, varying average flow rate, co-adsorption, ambient air (having water and carbon dioxide) and temperature which changes in a normal daily cycle.

To quantitatively measure pentachlorophenol breakthrough and collection efficiency in sorbent sampling tubes, a simulated elution

profile was determined for pentachlorophenol vapor in segmentally packed sampling tubes. These measurements avoided the problem of an artificially generated atmosphere of known concentration (9,10,23). This procedure was necessary due to the relatively low vapor pressure of pentachlorophenol under normal ambient conditions ( $1.7 \times 10^{-4}$  millimeters of mercury). The segmentally packed tubes were constructed from 8 inches by 0.25 inches outer diameter pyrex tubes packed with four separate segments each containing 25 milligrams of solid sorbent (Tenax) particles and isolated with silanized glass wool plugs.

The four inch long open section of the packed tube was inserted into the heated injection port of a chromatograph. The packed portion of the tube extending into the gas chromatography oven was inserted into a thermostatted block. A measured amount of a pentachlorophenol standard was volatilized and the vapors collected on the sorbent packing using a conventional syringe injection technique (see cold trapping method described in Chapter II). The tube was then removed from the heated GC injection port and a measured volume of ambient lab air ( $25^{\circ}\text{C}$ , relative humidity unknown) was pumped through the tube. The amount of PCP was determined in each individual packing segment by sequentially removing the packing segments, recovering the analyte with the methanol extraction procedure, and GC/ECD analysis. Results are summarized in Table VII. The total weight of PCP introduced into each sample tube is shown in the table and corresponds to an upper limit (or near limit) anticipated to be collected in a packed sample tube during field studies. It can be seen (Table VII) that under laboratory conditions, 50 milligrams of the Tenax porous polymer packed in a 0.25 inch outer diameter pyrex tube (air flow rate: two liters per minute) will ade-

TABLE VII

PROFILE OF PCP MIGRATION IN SAMPLE TUBES AS VOLUME OF AMBIENT AIR SAMPLE IS VARIED

Concentrating Sorbent: Packing Segment:	Total Volume of Air (L)	<sup>1</sup> Percentage of Total PCP Injected Recovered					
		Silica Gel		Tenax <sup>®</sup>			
		a	b	a	b	c	d
<sup>2</sup> Weight of PCP Injected (µg)							
30	500	95	5	---	---	---	---
30	1000	---	---	100	0	0	0
30	3000	13.4	4	100	0	0	0
30	5000	3.7	3.7	100	0	0	0
100	5000	---	---	96	4	0	0

<sup>1</sup>The weight of PCP recovered in each segment is reported as a percentage of the total PCP injected.

<sup>2</sup>The weight of PCP cold trapped on the sample tube.

<sup>3</sup>Segments are labeled a, b, c, etc. such that the segment adjacent to the tube inlet is "a", the 2nd segment "b" and so on.

quately retain 100 micrograms of PCP for a total of 5000 liters pumped through the tube. It should be noted at this point (see Table VII) that the silica gel sorbent system exhibited extremely non-ideal breakthrough characteristics for PCP in the simulated experiment described above. For example, only 17% and 8% of the total weight of PCP introduced into the sampling tubes was recovered after pumping total air volumes of 3000 and 5000 liters, respectively.

Table VII results may be further qualified by considering the following:

a. Breakthrough varies with concentration of the analyte; this is illustrated when the weight of pentachlorophenol deposited was increased to 0.1 milligrams.

b. Breakthrough generally is a function of humidity and possible coadsorption, however researchers have found Tenax adsorption of some organics is independent of water content of air (14). Silica gel has a well known affinity for carbon dioxide and water, both abundant in air.

c. Breakthrough is in part a function of flow rate. Sampler flow rates of 1.7 to 1.0 liters per minute were observed with tubes containing 80/100 mesh Tenax. Flow rates for the coarser silica gel were 4.5 to 3.5 liters per minute. The effect of flow rate alone is not responsible for the differences in Tenax and silica gel's collection efficiency in Table VII.

Several "rule of thumb" percentages have been suggested for determining a safe maximum for the final 1/3 weight of the sampling tube. No more than twenty percent of total analyte weight should be in the back section of 150 milligram charcoal tubes (15). Sample loss is probable if the back 1/3 contains greater than twenty-five percent, no significant analyte loss occurs if less than ten percent

of the total weight is found in the back segment (10).

From Table VII silica's breakthrough volume is considerably lower than that of Tenax. At a volume of 500 liters the back 1/3 section of silica gel shows a significant amount of pentachlorophenol. In the case of Tenax, breakthrough volumes are much higher. If the 25 milligram sections are considered as 1/3 weights of a 75 milligram sampling tube then analyte found in segment (d) would represent the amount of sample loss by breakthrough. Obviously if a larger quantity of Tenax is used (100 milligrams) it will increase its capability to hold the analyte and thus its breakthrough volume. Although silica gel and Tenax give a quantitative yield of pentachlorophenol when extracted with methanol, the greater retention of pentachlorophenol for longer sampling periods by Tenax makes it a more suitable sorbent for trace analysis.

It is understood that the simulated breakthrough experiments were highly idealized and that variables expected to influence breakthrough include: concentration of analyte in the influent air stream, temperature, humidity, packing particle diameter, air flow rate, etc. To determine possible effects resulting from extreme conditions, air inside a domestic building (partially constructed of pentachlorophenol pressure treated wood) was sampled over a 3-day period. During this period, daytime temperatures reached or exceeded 100°F. Total air volume sampled was 4,500 liters at a flow rate of 1.4 to 1.1 liters per minute. It was found that 2% of the total weight (15 micrograms) of pentachlorophenol collected was found in the last 1/3 segment of packing in the sampling tube. The tube was constructed in a similar fashion to those described in Table VII, except that the 100 milligrams of porous polymer media was

TABLE VIII  
SAMPLED AIR VOLUME SELECTION GUIDE

Total Sample Volume (L)	Minimum Ambient Content ( $\mu\text{g}/\text{m}^3$ )	Maximum Ambient Content ( $\mu\text{g}/\text{m}^3$ )
500	0.400	320
1000	0.200	160
3000	0.067	53
5000	0.040	32

1. The practical limit of detection is 100 pg for GC analysis (ECD).
2. Syringe injections of 1  $\mu\text{l}$  are assumed.
3. Sample tubes contain 100 mg Tenax . PCP is extracted with 2 mL of methanol.
4. Electron capture detector pulse interval is 15 microseconds.
5. Minimum ambient level detectable with 5000L sample using method is 40  $\text{ng}/\text{m}^3$ .

arranged into 3 segments, each containing 1/3 of the total weight.

Sample Collection/Gas Chromatography (Electron  
Capture Detector) Operating Parameters

The expected ambient PCP content should be considered when choosing sampling volumes, such that the quantity of PCP ultimately injected into the GC following the collection/concentration and solvent extraction steps will fall within the linear dynamic range (LDR) of the GC/ECD system. Using the GC/ECD conditions previously described, the LDR for PCP was determined to extend over slightly more than 2.5 orders of magnitude (see Figure 7). The upper limit of the LDR was measured at 80 ng, and the minimum detectable quantity (MDQ) was determined to be 80 picograms (signal:noise = 3:1). Table VIII provides a guide from which to select total volumes of air to be sampled in order to insure the amount of analyte ultimately injected into the GC will fall within the LDR. The minimum ambient level of PCP detectable (assuming the conditions given in Table VIII) is 40 nanograms per cubic meter. Lower limits of detection can be achieved with the system described by increasing either the sampled air volume, the injected liquid volume, or the pulse interval of the ECD. Of these parameters, the ECD pulse interval is probably the most direct and effective means of decreasing the MDQ, since variation of the total air volume sampled and the liquid volume injected affect the MDQ arithmetically while the pulse interval has a near logarithmic effect. It should be noted that the upper limit of the LDR is decreased more or less in proportion to the MDQ with changes in pulse interval. The parameters given in Table VIII are unique for the system described and a similar evaluation should be performed for each given instrument

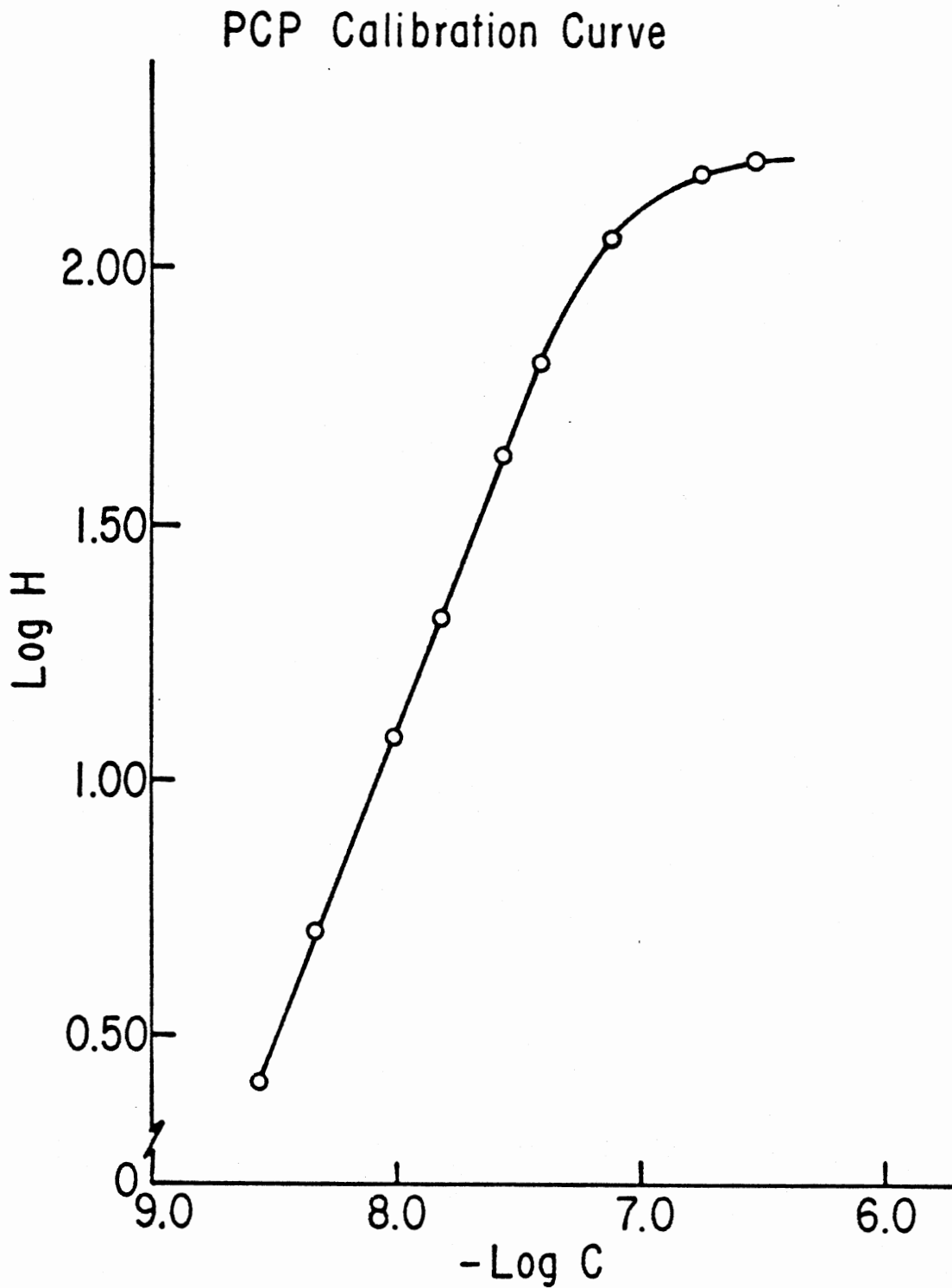


Figure 7. Electron Capture Detector ( $^{63}\text{Ni}$ ) Calibration Curve for Pentachlorophenol.



prior to adoption of the described method for determining trace levels of PCP in air.

Figure 8 is a chromatogram from analysis of a typical air sample and represents an injection of 10 nanograms of PCP.

The gas chromatograph was configured for large sample throughout to facilitate the evaluation of desorption efficiency, and other experiments (see Table III). When more efficient separation is desired longer columns (6-8 feet) and lower oven temperatures offer the most direct path to increased retention times for pentachlorophenol. No peaks adjacent to pentachlorophenol have been observed which interfere with quantifying the analyte in field studies.

#### Preliminary Field Studies

Results of the air sampling study for trace levels of airborne PCP within the buildings which were sampled during study are given in Table IX. Building 4 was studied extensively during the August, 1980 period primarily because it had given the highest airborne PCP levels during an earlier 1979 study (24). For Building 4, the Tenax/hexane system was used. Three samples, each concentrating PCP vapors from ~5,000 liter air volumes were taken. These samples were collected at approximately 1 liter per minute and were accumulated over a time span of about 48 hours. Daytime temperature maxima were all in excess of 100°F. Nighttime temperature minima were all greater than 70°F. The building remained closed during the sampling intervals. Values for PCP in air were measured at 3.21, 3.91, and 2.42 nanograms per liter on the three separate occasions. Since microgram quantities were being collected on 100 mg of Tenax in each air sample concentrated, the trapping efficiency of

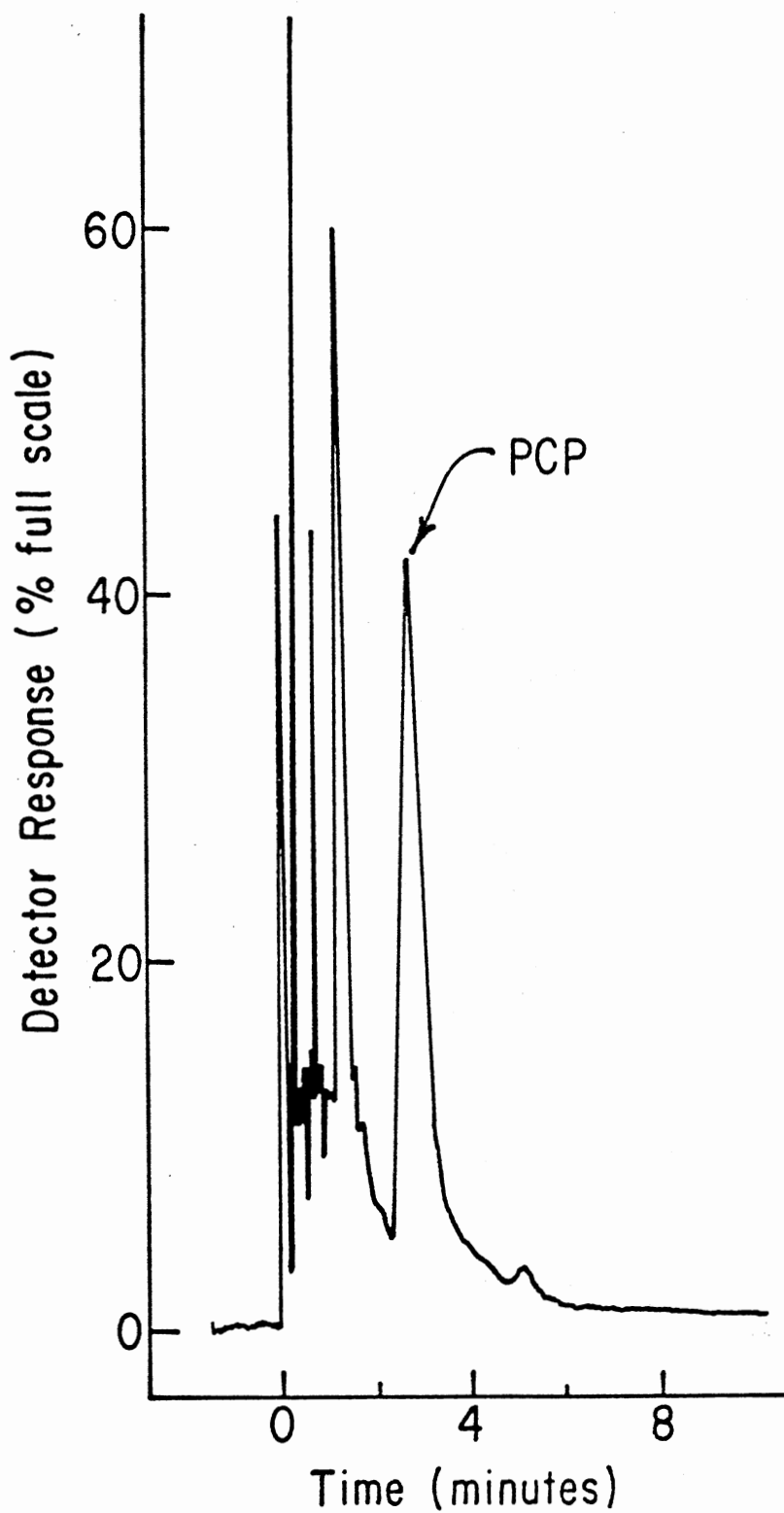


Figure 8. Chromatogram of a Typical Air Sample.

TABLE IX  
PRELIMINARY FIELD STUDY RESULTS

Building	Samples	PCP Level (ng/L)			Average
		a	b	c	
1	1	0.74	----	----	0.74
2	1	1.45	----	----	1.45
3	3	0.68	0.51	0.21	0.47
4*	3	2.42	2.91	3.21	2.87

\* Samples from Building 4 were extracted with hexane. The values are reported as minimum ambient content.

the system was measured using a Tenax backup column located between the trap and the air pump. Recovery of PCP from the backup column was determined to be 2% of that found in the trap.

Buildings 1-3 were studied during July/August, 1981. Methanol was used to extract trap pentachlorophenol from Tenax. The Ambient temperatures, flowrates, and sampling times in this study paralleled those of the 1980 study. Only one valid sample was taken in the present study for Buildings 1 and 2. Figure 8 is the chromatogram which resulted from analysis of air in Building 2. PCP levels found in Building 3 during this (1981) study were larger than those reported for the earlier study (24). The 1979 report indicated the average value for Building 3 was 0.26 nanogram per liter.

Since the vapor pressure of PCP varies approximately 20 fold over the temperature range from 20<sup>o</sup> - 50<sup>o</sup>C (1,2), it was expected that a significant increase in airborne PCP levels would be found in the buildings under study if sampling was done during hot summer months (in contrast to previous data measured during October-November, 1979 when ambient temperatures during sampling were less than 20<sup>o</sup>C). Results available at the present time indicate an approximate 2 to 6 fold increase in airborne PCP levels for the airspace within the structure(s) studied (24). This is more or less consistent with what one would expect, since equilibrium saturation levels of PCP (2.4 µg/L) (24) are probably never achieved in the situations studied (primarily because of existing levels of ventilation from passive sources). The temperature difference between the data taken during the 1979 study and that reported here is about 18<sup>o</sup>C. It should also be noted that the data presented here was integrated over about 48 hours while the data reported in the 1979 study

was taken over about 1/2 hr intervals. At any rate, the levels of airborne PCP found are approximately 100 times below the TLV (threshold limiting value) time weighted average of 500 ng/L for human inhalation during exposure over an 8 hr work day, 40 hr work week (3).

#### Conclusion

Comparable refinements in flow sensing and volume totalization, exhibited by the sampler, are not commercially available. Accurate sample volume totalization, high collection efficiency on Tenax, quantitative methanol desorption, and gas chromatography/electron capture detector analysis combine to yield a simple, accurate method for determination of underivatized pentachlorophenol. The recovery of near 100% of pentachlorophenol, as illustrated in Table VII, should be expected when sampling conditions are such that no breakthrough occurs. Batch extraction with methanol can provide repetitive data for each sample. This method achieves minimum detectable quantities for pentachlorophenol lower than or comparable with, other similar techniques without pH adjustments, color development, derivatization, or concentration. The analytical method reported for airborne pentachlorophenol therefore is characterized by high sensitivity, low detection limits, high and uniform collection efficiency, and good analyte recovery. Collectively, these factors result in an analytical method for airborne pentachlorophenol which is particularly useful in measuring potential human inhalation exposure to low (trace) levels of PCP within domestic enclosures.

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