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ABSTRACT

Determination of
Pentachlorophenol in Wood
and Leachate from Discarded Treated Wooden Poles

by

Yan Zha

Pentachlorophenol(PCP) has long been used as a preservative in the wood industry. The disposal of the used treated wood poles in landfill is of an environmental concern.

The study presented in this paper was designed to determine the leaching of pentachlorophenol from treated aged wood. An analytical method for HPLC determination of PCP was developed and validated to perform the analysis of pentachlorophenol in samples of the oringinal wood and leaching solutions.

Further studies involved the description of the PCP distribution in wood poles, the estimation of the leaching rate of PCP and the factors which influence the leaching rate of PCP.

DETERMINATION OF
PENTACHLOROPHENOL IN WOOD
AND LEACHATE FROM DISCARDED TREATED WOODEN POLES

by
Yan Zha

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fullfillment of the Requirements for the Degree
of Master of Science
Department of Environmental Science
October 1992

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APPROVAL PAGE

Determination of
Pentachlorophenol in Wood
and Leachate from Discarded Treated Wooden Poles

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ACKNOWLEDGMENT

I wish to express my sincere thanks to Dr. Barbara B. Kebbekus, thesis adviror, for her guidance and encouragement throughout the implementation and writing of the thesis as well as her financial support.

Also I sincerely thank Dr. Somenath Mitra and Dr. Richard Trattner for reviewing this thesis.

In particular, I would like to express my appreciation to my husband for his support during the entire course of this thesis.

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CHAPTER 1
INTRODUCTION

1.1 Background of the Project

The purpose of this Project is to study the leaching characteristics of Pentachlorophenol(PCP) from treated utility poles which may be disposed of in landfill sites. Data collected during the study period will be available for developing the ground water transport model to be used to predict the level of PCP potentially reaching drinking water supplies. The ultimate objective is to assess the best way to dispose of these treated, aged wood poles at a reasonable expense without posing a health or environmental hazard.

The groups involved in this study represent both academic and industrial research communities: Hazardous Substance Management Research Center of Stevens Institute of Technology(SIT/HSMRS), Hazardous Substance Management Research Center of New Jersey Institute of Technology(NJIT/HSMRC), Bell Communication Research Center (Bellcore), and Electric Power Research Institute (EPRI).

1.2 Scope of Study

To determine the leaching characteristics of PCP from utility poles under laboratory conditions, the following studies will be involved:

1. Development of analytical method for determination of PCP in wood samples, and aqueous leaching solutions, which includes:

1) Optimization of instrumental conditions for PCP separation and measurements

2) Optimization of wood sampling procedures

3) Optimization of wood extraction and leachate concentration procedures by solid phase extraction

2. Determination of the leaching rate of PCP, which includes:

1) Selection of leaching solutions

2) Determination of the time intervals for leaching testing

3. Determination of the factors which influence the leaching rate of PCP:

The factors which influence the leaching rate of PCP are suggested as pH, temperature and ionic strength.

Three levels of these three factors will be varied in a "Latin Square" experimental design, which will require a minimum of 9 sets of experiments.

1.3. Literature Review

1.3.1. Chemical and physical properties

Pentachlorophenol is a fully chlorinated phenol. Its empirical formula is C_6Cl_5OH with a molecular weight of 266.36. It can be illustrated by the structure formula(I):

Pentachlorophenol, a white solid with needle-like crystals, has a melting point of 190-191°C, a boiling point of 293°C. It decomposes at 310°C. It is soluble in most organic solvents, oils, and petroleum hydrocarbons, but it has only limited solubility in water, 14-19 ppm at 20°C-30°C. In aqueous solution, it is weakly to moderately acidic ($pK_a = 4.73$), and it can be readily converted to the sodium salt as illustrated by the structural formula(II), which then is freely soluble in water. It is odorless unless heated, and its vapor pressure is 0.0011 mm Hg at 20°C [1,2].

1.3.2 Biological Effects and Industrial Application

Pentachlorophenol is a general cytotoxic agent due to its inhibitory properties upon oxidative phosphorylation[3].This unspecific and strong cytotoxic activity of PCP has led its use in a great variety of biocidal applications. The main use of PCP has been as a fungicide in wood preservation. Over 60% of wood utility poles were routinely treated with PCP in the wood industry [4-6].

The technical treatment of wood poles includes the selection of tree species, and selection of an EPA registered preservative. It is recognized that two types of trees supply most of the utility poles in the United States. Approximately 75% of the poles are southern pine and the remaining 25% are Douglas fir. These registered preservatives may be either pentachlorophenol-petroleum, creosote, or water-borne salts such as Chromated-Copper-Arsenate(CCA) type C.

A typical wood treatment process for southern pine involves two basic processes: conditioning and treatment. Steam conditioning is the preferred method for southern pine. The treatment process involves the impregnation of southern pine poles with the mixture of hydrocarbon solvent, type A and 5-9% pentachlorophenol. The treatment temperature is kept below 220°C, and the pressure is not allowed to exceed 175 psig.

The results of treatment are determined by the penetration of the preservative or the retention of the preservative. The southern pines having sapwood of 0.75 inch thickness are required be completely penetrated, and those poles having sapwood thickness greater than 0.75 inch are penetrated not less than 90% of the sapwood depth. The retention of dry pentachlorophenol as determined by lime-ignition assay shall not be less than 0.63 pound per cubic foot (pcf) of wood poles (or 1.7% by weight) when the sampling zone is 0-0.5 inch from the surface, and the retention of

PCP shall not be less than 0.43 pcf (or 1.1%) when the sampling zone is 0.5-2.0 inch depth.

1.3.3 Environmental Concerns and Related Regulations

Wood has long been used for such outdoor applications as utility poles and rail road ties. As the items age, they are removed from service in large numbers each year after their 20-35 years of installation [8].

The disposal of used wood poles in landfills, a method which was thought to be safe, is being reevaluated. The concern is that landfilled poles will potentially release toxic substances that eventually end up in the drinking water, despite the fact that PCP can be biodegraded in the soil, or photolyzed in the aquatic environments. The main metabolic and photolysis products of pentachlorophenol are very stable [9-12].

Pentachlorophenol, as a toxic waste material, falls under RCRA, the Resource Conservation and Recovery Act, which was promulgated by EPA in 1976, to regulate the disposal of hazardous wastes. RCRA requires EPA to identify the hazardous waste by developing two categories (1) those that are listed (2) those that exhibit one of four characteristics-ignitability, corrosivity, reactivity, and toxicity [13,14].

Of those, the test of toxicity was designed by extraction procedures (EP) in 1980. The EP test listed 14 toxic contaminants as hazardous waste. In 1990, the EP test was replaced by the toxicity characteristics leaching procedure(TCLP), which was designed to simulate the natural conditions that would occur in the landfill sites. The TCLP test added 25 new organic compounds to the list of analytes. Pentachlorophenol is among them. The regulatory level set for pentachlorophenol is 100 ppm [15,16].

The TCLP regulatory level set for pentachlorophenol is high enough that no problems are anticipated [17]. However, the future regulatory level for PCP may be lower based on new drinking water regulations. The TC will be based on Dilution Attenuation Factors (DAFs), derived from the EPA ground water transport model. The

model assumes that leachate is diluted 100-fold in ground water before reaching a drinking water well 500 feet away from the landfill. The allowable concentration of PCP is determined by multiplying the DAFs by the regulatory level for PCP in drinking water. So the future regulatory level for PCP will be 0.1 ppm [18].

Therefore, once EPA promulgates a new revised regulatory level for PCP, it could result in discarded PCP utility poles being declared as a hazardous waste. The disposal of PCP utility poles in landfill will have to be abandoned and the only way to get rid of these used treated wooden poles will be to burn them in incinerators. As a consequence, the cost could increase greatly.

1.3.4 Methods of Analysis

1. Quantitative methods of analysis

1) Standard methods of analysis of PCP in wood treatment

A number of methods have been used as standard methods for analysis of treated wood and treating solution, such as the lime-ignition titrimetric method, the copper-pyridine method and X-ray spectroscopy [19,20].

Of those, the lime-ignition assay is more used in wood treatment. It is specifically suitable for the determination of treating solution containing 1-10% pentachlorophenol, or treated wood containing less 2% pentachlorophenol. The Lime-ignition method is nonspecific because compounds other than pentachlorophenol may contribute chloride ion to the titrimetric procedures.

The copper-pyridine method is intended as an alternate for the lime-ignition method, when a method that is specific for chlorinated phenol is required.

X-ray spectroscopy is less used because of its high expense of equipment operation.

2) Chromatographic methods for analysis of trace PCP

A primary problem for trace PCP analysis by chromatography is the isolation and preconcentration of the target compound from extraneous matrix. Conventional liquid-liquid partitioning procedures have been widely used in the isolation of residue PCP in plants, animals, and human materials [20-23]. However, the use of a solid phase extraction of trace organic compounds from water has been studied and the advantage of such a technique over a liquid-liquid extraction is the possibility of more efficient and reproducible recoveries [24-26]

Many studies showed that GC-ECD has been recognized as the most sensitive method for trace PCP analysis. But it requires extensive amount of pretreatment-extraction, preconcentration and derivatization because the ECD does not respond as well to free PCP as to PCP ether. This requres PCP to be converted to its ether derivative with diazomethane [27,28]. Another technique for HPLC determination of PCP was also reported, which offers a rapid method for PCP analysis without the necessity of derivatization of PCP[29,30]. The problem resulting from the lower sensitivity of the UV detector could be avoided if an appropriate method of concentration were available.

Therefore, in this study, efforts have been made to develop a SPE/HPLC analytical method by concentration of PCP in leaching solution with a solid phase extraction, followed by high performance liquid chromatographic analysis.

2. Qualitative methods of analysis

Three techniques are commonly used to confirm the presence of pentachlorophenol. When a sufficient amount of sample is available for the collection of a GC or HPLC fraction of the suspected pentachlorophenol, the confirmation of identity may be obtained by ultraviolet and/or by infrared absorption analysis. The technique of GC/MS has rapidly become the preferred procedure for the more definite identification of PCP [31-34].

CHAPTER 2
METHOD DESCRIPTION

2.1 Method of Wood Analysis for Pentachlorophenol

2.1.1 Sample Acquisition

Three poles were selected for this test. The poles were treated by Escanbia Treating Company on September 5, 1978. The poles were Southern pine, treated in accordance with specification AT-7336, Issue 11, to a minimum retention of 0.43 pound/cubic foot in the 0.5 inch to 2.0 inch zone, with pentachlorophenol in hydrocarbon solvent type A. The posts were installed at the Bellcore Chester test site on October 31, 1978, and have remained there since.

Cross-section slices of poles, about 3 inch thick, were cut from each post approximately 1 foot above the ground, on March 8, 1991. (Pole number and the results of the PCP retention at the time of treatment are shown in Table 2.1)

2.1.2 Apparatus and Chemicals

1. Apparatus

1) High performance liquid chromatography (HPLC):

A Waters LC system equipped with a 600E pump, a 990 photodiode array detector and a 715 Ultra Wisp Sample Processor.

2) Solid State/Ultrasonic bath, FS-28 (Fisher Scientific)

3) Filter paper (Millipore Co. 0.45 micrometer, Type HV)

2. Chemicals

1) Hydrochloric Acid (Fluka, Reagent grade)

2) Acetonitrile (Fisher Scientific, HPLC grade)

3) Pentachlorophenol (Fluka, Cat.No. 76470)

2.1.3 Sample Preparation

The transverse slices of poles were drilled at one inch intervals, from the center of the pole to the surface. The samples were obtained using a hand drill, to avoid heating the material and losing pentachlorophenol by evaporation. Samples of wood powder of about 1 gram each were collected at each point as shown in Figure 2.1.

2.1.4 Analytical Procedures

1. Extraction

Each wood sample of about 1 gram is first acidified with 6N hydrochloric acid, to a pH about 2 or 3, then extracted ultrasonically for 25 minutes with 50 ml acetonitrile. The extracts are filtered through 0.45 micrometer HV filter paper, and analyzed by HPLC. The wood residues are repeatedly extracted ultrasonically with 25 ml acetonitrile and the extracts are analyzed by HPLC. Untreated Southern pine wood is extracted and analyzed following the same procedures, as a blank.

2 HPLC Operation Conditions

Column: C18 reversed phase column (15cm * 3.9mm), packed with 5 micrometer silica particles.

Mobile Phase: 1% Acetic acid : Acetonitrile

Operation temperature: ambient

Mobile phase running on a gradient program:

Time=0.0 min. 1% HAC: CH_3CN = 40:60

Time=4.0 min. 1% HAC: CH_3CN = 40:60

Time=14.0 min. 1% HAC: CH_3CN = 10:90

Time=17.0 min. 1% HAC: CH_3CN = 40:60

Time=25.0 min. 1% HAC: CH_3CN = 40:60

Flow rate: 1 ml/min

UV detection: 305 nm

Detector sensitivity: 0.2 absorbance units full scale.

Injection amount: 50, or 25 microliter

(An example chromatogam is as shown in Figure 2.2)

2.2 Method of Determination of the Leaching Rate of Pentachlorophenol Under Laboratory Conditions

2.2.1 Sample Acquisition (As described in section 2.1.1)

2.2.2 Apparatus and Chemicals

1. Apparatus

1) High performance liquid chromatography (HPLC):

A Waters LC system equipped with a 600E pump, a 994 photodiode array detector and a 715 Ultra Wisp Sample Processor.

2) Solid phase extraction equipment

Baker-10 extraction system (J.T. Baker Co.), using 1 ml disposable extraction columns, packed with reversed phase phenylsilicone bonded to silica gel.(40um APD)

3) B.Braun Melsungen Thermomix II (0-60 ^{O}C)

4) Analog pH meter, model 399

5) Filter paper (Millipore Co. 0.45 micrometer Type HA)

2. Chemicals

1) Hydrochloric acid, Sodium acetate, Sodium chloride, Acetic acid, and Calcium chloride (Fluka, Reagent grade)

2) Acetonitrile (Fisher Scientific, HPLC grade)

3) Pentachlorophenol (Fluka, Cat.No. 76740)

4) Stock standard solution: containing 200 mg PCP in 1000 ml acetonitrile

5) Leaching test solutions:

A) Distilled water (pH=6.4)

B) 0.15M Sodium acetate - 0.15M Acetic acid, allowing PH to be adjusted from 3.0 to 7.0 with addition of calcium chloride to adjust the ion strength of leaching solution.

2.2.3 Sample Preparation

Upon receipt of bulk transverse slices of poles, 1 inch cubes are cut from outer edge with a hand saw to provide subsamples of 1 square inch exposed outer surface and 5 square inches of fresh surfaces. This resulted in a consistent subsamples size of approximately 1 inch cube.(as shown in Figure 2.3)

2.2.4 Analytical Procedures

1. Preparation of the sample leaching conditions

The prepared 1 inch cubes are completely immersed in beakers of 200 ml leaching solutions, which is deionized water, or consists of 0.15M NaAC-0.15M HAC, with the pH adjusted to 3.0, 4.9, 7.0, and with the addition of calcium chloride at concentrations of 0, 0.001M and 0.01M. The test beakers are kept at different temperatures (10^oC, 20^oC, 30^oC) for 2 days to equilibrate. At 2 day intervals, the test solutions are replaced with fresh solution.

2. Sample Pretreatment

The leaching solutions are filtered through 0.45 micrometer type HA filter paper. The filtered solutions are first adjusted to pH=2 or 3 with 6N hydrochloric acid, then 10 grams of sodium chloride are added to each 100 ml test solution.

3. Sample Extraction- Solid phase extraction

The 1 ml Bakerbond SPE column is conditioned with 2 ml acetonitrile, followed by 5 ml 1N hydrochloric acid, with the vacuum off. The 50 ml reservoir is attached to the column with an adapter. During the addition of acetonitrile and 1N hydrochloric acid, it is essential that the column is not allowed to dry.

The aquous leaching solution is then poured into the column, and the vacuum is adjusted to achieve approximately 2 ml/min flow rate. The column is not allowed to go dry during the sample processing.

4. Sample Elution

After the entire sample solution of 100 ml volume has passed through, the column is washed with 5 ml 0.01N hydrochloric acid, then the reservoir and adapter are removed. The column is eluted with 2.5 ml acetonitrile 3 times, collecting the eluent in 10 ml volumetric flasks. Then the column is removed and the collected eluent is diluted to 10 ml.

5. HPLC Operation Conditions are as Mentioned in Section 2.1.4. An example HPLC Chromatogram is as shown in Figure 2.4

2.3 Method of Verification of the Analytical Method

2.3.1 Instrument

1. High Performance liquid chromatography (HPLC) with a 990 photodiode array detector

2. HP 5998 Mass Spectrometer coupled with HP 5890 Gas Chromatography

2.3.2 Sample Preparation

1. One of the samples chosen for method verification was the acetonitrile extract of treated wood.

2. The other sample was obtained from the effluent of HPLC by running the sample (1) several times and collecting the peak corresponding to the retention time of standard pentachlorophenol. The effluent was collected for 1.0 minute, dried with anhydrous sodium sulfate, and then concentrated under a slow stream of nitrogen.

3. Pentachlorophenol standard solution : 50 mg PCP in 1000 ml acetonitrile.

2.3.3 Analytical Procedures

In order to be certain there were no substances in the wood which would co-elute with the PCP, two techniques were used to confirm the identity of the investigated compound (PCP), and verify the analytical method as well.

First, sample(1) and PCP standard (3) as mentioned above, were run by HPLC with a photodiode array detector, which is able to scan the full range of UV wavelength from 200 nm to 900 nm, and give a spectrum of the compound found in each peak of the chromatogram. The results showed that the spectrum generated from the peak corresponding to the retention time of PCP in the wood extract was the same as that generated by the PCP standard. However, there still remained the possibility of an interference which could be caused by a compound with a similar spectrum. (UV spectra are shown in Figure 2.5, Figure 2.6)

Therefore, GC/MS was employed for further identification. The samples(2) mentioned above were run on a HP 5998 Mass Spectrometer coupled with HP 5890 Gas Chromatograph, using a 2 microliter sample(2) and the PCP standard. A 12 m methyl-silicone capillary column was used as the analytical column. The column temperature was programmed from 50 ^{o}C to 280 ^{o}C at 16 ^{o}C per minute. The mass spectral analysis of the sample(2) at 70 ev gave a molecular ion at M/e 266, which was also the base peak and other major peaks at M/e 230, 202, 165. These ion peaks generated from sample(2) were exactly the same as those generated from the PCP standard.

These results proved conclusively that pentachlorophenol quantitative determination was established beyond a doubt of false identification or of an interference in the wood extract. (MS spectra are as shown in Figure 2.7, Figure 2.8, Figure 2.9)

CHAPTER 3
RESULTS AND DISCUSSIONS

3.1 Quality Assurance

3.1.1 QA in Wood Analysis

1. Sampling system

The sampling method for wood analysis requires that

1) each transverse slice of wood pole for analysis be drilled in two different directions from the center of the pole to the surface, at one inch intervals.

2) a hand drill be used to avoid heating the material and causing the loss of pentachlorophenol.

3) each point of sample collected be accurately weighed using an analytical balance.

2. HPLC system

The HPLC performance requires that

1) The system be certified clean prior to sample analysis, through running a solvent blank with acetonitrile.

2) The daily cleaning of the HPLC system by 40% H_2O : 60% acetonitrile after sample analysis.

3) A daily calibration of the HPLC system.

3. Results of interlaboratory comparison

In the study of the content of pentachlorophenol, the collected wood samples were extracted twice. The average efficiency of the first extraction is about 91%, the standard deviation is 0.2 and the relative standard deviation is 15.3%.(The results are shown in Table 3.1)

Because of the inhomogeneous distribution of pentachlorophenol in wood pole, it is difficult to evaluate this analytical method by studying recovery, reproducibility, and extraction efficiency. It is also impossible to estimate the accuracy of the method without an appropriate standard in a similar matrix.

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However, the analysis data from wood poles of No.148 and No.154 showed that the mean value of PCP content(1.3%) obtained by HPLC from NJIT has a good agreement with that(1.2%) obtained by X-ray fluorescence from Bellcore despite differences of the absolute values due to the different points of sampling. It may suggest that HPLC method be regarded as reliable as the standard method recommended by AWPA. (Data are shown in Table 3.2)

3.1.2 QA in Leaching Rate Study

1. Sampling system

The sampling method for testing the leaching rate requires that

1) 1.0 inch cubes be cut from outer edge to provide 1 square inch of exposed outer surface, and 5 square inch of fresh surfaces.

2) A hand saw be used to avoid heating the material and causing the loss of pentachlorophenol.

3) Sample of 1 inch cube be weighed with the variance of 1.5 gram between samples.

2. HPLC system (As mentioned in 3.1.1.)

3. Recovery

To quantitatively determine the concentration of the leachate, the recovery of this method should be estimated first. Recovery studies were performed by adding a certain amount of PCP standard to the 100 ml of leachate, while another 100 ml of the same leachate were analyzed without addition of any standard.

From Table 3.3, the results showed that the recovery was as high as 95% when the PCP concentration of the leachate was within the range of 0.1 mg/L- 1.0 mg/L and the recovery was as low as 85% when the PCP concentrate of leachate was within the range of 0.01 mg/L- 0.05 mg/L. It was very likely that the loss of pentachlorophenol was due to the incomplete sorption and desorption of PCP during the solid phase extraction.

4. Reproducibility

Because of the inhomogeneity of the samples, it was very difficult to estimate the reproducibility by spiking the wood samples. Instead, 100 ml of distilled water was spiked with known quantities of standard and then concentrated by SPE and analyzed by HPLC. The measurements were repeated 7 times at three concentration level. The quantity of spike is equivalent to the PCP level in leachate solution. The reproducibility can be noted by the relative standard deviation, which is indicative of the spread in a set of observations. From Table 3.4, it was found that the larger amount of spiked PCP in 100 ml water has a better reproducibility than the smaller amount of spiked PCP in the same water solution.

5. Linearity and detectable limit

For the determination of linearity and detectable limit, PCP standard solution was prepared at six concentration levels by carefully and accurately diluting a certain volume of stock solution to 100 ml with water. Each standard solution was analyzed using the operation parameters and procedures described in section 2.2.4. The measurements were repeated three times. The results showed excellent linearity with concentrations ranging from 10 ug/l to 1000 ug/l. The concentration of standard solution below 10 ug/l was not reproducibly detected. Therefore, the detectable limit was approximately 10 ug/l (10 ppb).

3.2 Description of the Distribution Profile of PCP

To determine the distribution profile of pentachlorophenol in the wood poles, the treated wood poles were drilled from the center to the outer edge of transverse slices of the wood pole.

The analytical results showed that pentachlorophenol concentration ranged from 0.27% to 2.2% by weight along the radius of the wood pooles. The mean content of PCP derived from 24 sampling points of two utility poles is 1.3%, which is obviously

below the value (1.88%) analyzed when these poles were treated 13 years ago. Based on these limited sample data, an inspection of the mean concentrations of PCP may suggest a tendency of the loss of PCP from wood to the environment.

As shown in Table 3.2, there is variation in mean concentration of PCP between poles which can arise as a result of the differences of wood treatment, location of installation, section of sampling and analytical procedures.

Variation associated with the depth of the sample on a given pole was evaluated by subsampling at different depths of wood pole. Figure 3.1 showed that pentachlorophenol was distributed throughout the wood pole. The concentration of the outer edge(0-0.25 inch depth) is far less than those measured at the center(4.0 inch depth) and subsurface(0.5 inch depth) of the wood pole. It may indicate the possibility of PCP leaching from the outer surface of the wood poles during the period of service.

3.3 Estimation of the Leaching Rate of Pentachlorophenol Under the Laboratory Condition

3.3.1 Estimation of the Loss Rate of PCP from Wood to the Environment

By comparing the data of PCP retention at the time of treatment in 1978 with the present analysis data obtained from Bellcore and NJIT, it was found that approximately 30% of pentachlorophenol in the wood was lost during their 13 years of service. (Data are as shown in Table 3.2)

The loss of PCP in wood poles may result from the photolysis by sunlight, the biodegration by microorganism in soil or water, and the leaching from the wood to the environment. the loss rate of PCP from wood to the soil is calculated as 12.2 microgram per day per cubic inch.

3.3.2 Estimation of the Mobile Rate of PCP from Wood to the Leaching Solution

Leaching data has been completed for a span of 10 days, and no trend in the leaching rate has been shown in that time. The leaching tests will be continued, in order to reach a point at which it will be feasible to determine the rate of decrease in leaching with time. The amount of loss of PCP before the rate decreases should allow an estimation of the mobility of pentachlorophenol from wood to the leaching solution.

If the average mobile rate is also expressed in the unit of ug/day.cubic inch, then the formula of the calculation is as follows:

$$R_l = C_x V_o * 1000/D * V_c$$

R_l--- Average leaching rate of PCP (ug/day cubic inch)

C_x--- Actual PCP concentration of leachate (mg/L)

V_o--- Volume of leaching solution (L)

V_c--- Volume of wood samples(cubic inch)

D --- Time period of testing intervals

$$V_c = W_x / D_s$$

W_x--- Weight of wood sample (g)

D_s--- Density of southern pine wood (9.95g/cubic inch)

If the average leaching rate is expressed in the unit of ug/day square inch, then the formula of calculation is as follows:

$$R_l = Cx Vo * 1000/6.Vc^{2/3}$$

From the Table 3.5., it was found that the average concentration of PCP in leachate solution ranges from 0.134-5.78 mg/l, So the leaching rate of PCP from the wood can be estimated in the range of 9.16-445.68 microgram per day per cubic inch, or 1.24-62.47 microgram per day per square inch.

3.4 Discussion of the Influential Effects on the Leaching Rate of Pentachlorophenol

3.4.1 PH Effect on the Leaching Rate of PCP

The leaching rate of PCP is strongly dependent on pH because the pentachlorophenol is less soluble in acidic solution and more soluble in alkaline solution.

The effect of pH on the leaching rate was studied from 3.0 to 7.0 At pH=3, the leaching rate is lowest, at pH=7, the rate increases substantially.(The results are as shown in Table 3.5 and Figure 3.2)

3.4.2 Temperature Effect on the Leaching Rate of Pentachlorophenol

The temperature effect is as expected, with higher temperatures causing higher rates of leaching. Moreover, it was also found that the leaching rates increase linearly with the temperature increase which suggests the possibility of measurements of leaching rate at higher temperature to assess long term leaching. A series of runs at elevated temperature would accelerate the process, and the data could be extrapolated to ambient temperature.

(The results are as shown in Table 3.6 and Figure 3.3)

3.4.3 Ionic Strength Effect on the Leaching Rate of PCP

The study of the effect of ionic strength on the leaching rate was carried out by adding various amounts of calcium chloride in the leaching test solution. The concentration of the calcium chloride varies from 0 to 0.01M to adjust the ionic strength of the NaAC-HAC buffer system from 0.15M to 0.18M.

The formula for calculating the ionic strength of the leaching solution involved the consideration of the concentrations and electronic charges of calcium chloride and sodium acetate and the neglecting of HAC's ionization.

The results showed that at pH 3 and 7, the higher ionic strength of the leaching solution will lower the rate of leaching, which probably resulted from the solubility of PCP in water being lowered by adding salt. (The results are as shown in Table 3.7 and Figure 3.4).

CHAPTER 4
CONCLUSIONS

To study the leaching characteristics of PCP from utility poles under laboratory conditions, a method for determination of PCP in wood samples and in aqueous leaching solution by HPLC has been developed.

In the analysis of PCP content in wood poles, the collected samples were extracted ultrasonically with acetonitrile. It was found that these extraction procedures are quite efficient. The efficiency of first extraction was about 90%. The results of wood analysis of PCP obtained by HPLC has a good agreement with that by X-ray fluorescence spectroscopy.

In the analysis of PCP concentration in aqueous leaching solution, a solid phase extraction column was used to concentrate PCP prior to HPLC analysis. The QA results showed that the recovery of spiking PCP standard in leachate solution is greater than 85%. The standard deviation of the reproducibility is less than 22.2%. The detection limit is about 10 ug/L.

In the study of the PCP distribution in wood poles, it was found that there is a fairly even distribution throughout the wood pole except for the very outer edge of the pole, at least after the pole has been in service for a period of years. The PCP content of the outer edge(0-0.25 inch) is less than that measured at the center(4.0 inch) or subsurface of the wood pole(0.5 inch). This may indicate some mobility of the compound within the wood and some leachability of PCP from wood to the soil.

In the study of the leaching rate of PCP, it was found the quantity of PCP leaching from wood to aqueous solution varies from 9.16-445.68 microgram per day per cubic inch of wood under various leaching conditions. However, it is still uncertain that these data would be sufficient to determine the actual leaching rate of PCP from poles without further study.

In the study of the factors which influence the leaching rate of PCP, the results showed that the leaching rate of PCP is influenced by pH, temperature and ionic strength. The rate of leaching increases substantially as the pH rises. Increased temperature could cause higher rates of leaching. When pH is less than 7, higher ionic strength will lower the rate of leaching.

Table 3.4 Reproducibility study of leachate analysis

Conc of Std soln (mg/L)	No of replicate	Ave Conc(mg/L)	S.D	R.S.D (%)
0.10	7	0.09	0.02	22.2
0.50	7	0.47	0.07	14.9
1.00	7	1.10	0.10	9.10

Table 2.1 Data of treated wood poles selected for this study

pole number	Sample Depth	
	0.0- 0.5 inch	0.5-2.0 inch
154#	0.9194	0.4667
151#	0.9011	0.4927
148#	0.9697	0.4947

Table 3.1 Result of extraction efficiency

pole number	154#				148#			
sample depth (inch)	sample weight(g)	PCP Conc. 1st Ext(mg/L)	PCP Conc. 2nd Ext(mg/L)	Ext effeciency(%)	sample weight(g)	PCP Conc. 1st Ext(mg/L)	PCP Conc. 2nd Ext(mg/L)	Ext effeciency(%)
0-0.25	1.0000	90.4	20.2	91.2	1.0000	48.1	10.2	90.4
0.5	0.9992	237.3	64.8	87.9	0.8900	290.7	48.6	92.3
1.0	0.8818	196.6	43.7	89.7	1.0000	206.1	49.7	89.2
2.0	1.0574	239.1	54.5	90.2	1.0000	272.5	41.7	92.9
3.0	1.0000	192.1	40.5	90.4	1.0000	273.8	28.4	95.1
4.0	1.0000	396.7	81.1	90.7	1.0000	282.8	33.1	94.5

Table 3.3 Recovery study of leachate analysis

Exp#	No STD Added Conc (mg/L)	R.S.D.	AMT STD Added Conc (mg/L)	R.S.D	Recovery(%) Range	Ave	Averrage(%) R.S.D
7	0.01-0.05		0.05	15.8-20.4	82-91	85.1	19.8
7	0.05-0.10	25.5	0.10	12.6-16.4	90-95	93.5	15.7
7	0.10-1.00	18.9	0.50	9.8-13.5	>92	>95	11.9

Table 3.2 Data summary of wood analysis

Bellcore sample depth (inch)	PCP percent(%) when treated in 1978 bellcore 154	151	148	PCP percent(%) after 13 yr service Bellcore Data(XRF) 154	151	148	NJIT Data(HPLC) 154	148	NJIT sample depth (inch)
0-0.5	2.42	2.37	2.55	1.47	1.21	1.37	0.55	0.27	0-0.25
0.5-2.0	1.23	1.3	1.3	1.02	0.79	1.05	1.6	1.70	0.5
0-3.0				1.20	0.74	1.20	1.3	1.10	1.0
							1.5	1.40	2.0
							1.1	1.40	3.0
							2.2	1.50	4.0
	Average:1.88%			Average:1.20%			Average: 1.30%		

Table 3.5 Data summary of leachate analysis

| Exp# | leaching condition | | | | Time period of testing | | | | | | | leaching rate | |
	sample weight(g)	PH	Temp	CaCl2 Conc(M)	Day2	Day4	Day6	Day8	Day10	Ave Conc (mg/L)	Actual Conc(mg/L)	ug/hr.cube.inch	ug/hr.square.inch
1	14.1	3	10	0	2.09	1.48	1.51	0.77	0.84	1.34	0.134	9.16	1.24
2	16.6	3	10	0.001	3.59	2.62	2.12	3.05	2.11	2.69	0.269	16.08	1.91
3	16.7	3	10	0.01	3.81	3.84	3.37	3.78	3.45	3.65	0.365	21.84	2.58
4	14.7	4.9	20	0.001	5.50	4.33	2.50	2.36	2.11	3.36	0.336	22.80	2.93
5	15.9	4.9	20	0.01	8.90	7.69	7.20	5.10	6.27	7.03	0.703	43.92	5.36
6	16.7	4.9	20	0	5.47	4.53	5.03	3.65	4.01	4.54	0.454	27.12	3.20
7	17.6	7.0	30	0.01	29.56	35.90	22.67	33.65	34.05	31.2	3.12	176.4	20.10
8	16.9	7.0	30	0	6.84	8.07	7.31	10.69	8.51	8.28	0.828	48.72	5.70
9	12.9	7.0	30	0.001	80.71	60.50	41.51	48.93	57.67	57.8	5.78	445.68	62.47
10	13.1	D.W	10	0	2.49	2.21	2.53	2.60	2.42	2.45	0.245	18.72	2.59
11	16.4	D.W	20	0	5.61	4.33	2.93	3.57	5.06	4.3	0.430	26.16	3.69
12	17.1	D.W	30	0	2.14	2.18	1.43	1.78	1.80	1.88	0.188	11.04	1.28

Table 3.6 Effect of temperature on leaching rate

Sample Weight (g)	pH	Temp. (C)	Leachate Conc. day 2	day 4	day 6	Average conc.(mg/l)	Actual conc. (mg/l)	Leaching Rate ug/day.cube inch	ug/day.square inch
13.2	DW	10	0.56	1.69	1.85	1.37	0.137	10.32	1.45
13.6	DW	20	2.26	1.92	2.95	2.38	0.238	17.52	2.37
13.4	DW	30	3.35	2.70	3.92	3.32	0.332	24.72	3.38
14.1	4.9	10	2.60	1.00	1.29	1.63	0.163	11.28	1.47
14.6	4.9	20	5.71	2.22	2.76	3.56	0.356	24.24	3.13
14.2	4.9	30	8.93	3.23	3.22	5.13	0.513	35.76	4.70

Table 3.7 Effect of ionic strength on leaching rate

Sample weight(g)	pH	CaCl2 Conc.(M)	Leachate Conc. day 2	day 4	day 6	Average conc.(mg/l)	Actual conc. (mg/l)	Leaching Rate ug/day.cube inch	ug/day.square inch
13.2	3.0	0	3.15	3.03	3.59	3.26	0.326	21.60	2.73
13.6	3.0	0.001	2.75	2.82	2.29	2.62	0.262	17.04	2.14
13.4	3.0	0.01	2.77	2.45	1.33	2.18	0.218	14.16	1.77
14.1	7.0	0	8.64	7.36	12.4	9.47	0.947	61.20	7.60
14.6	7.0	0.001	7.08	8.92	8.70	8.23	0.823	52.08	6.40
14.2	7.0	0.01	8.63	8.23	6.06	7.63	0.763	48.00	5.88

Figure 2.1 Sample preparation for wood analysis

Figure 2.2 HPLC chromatogram of wood extract
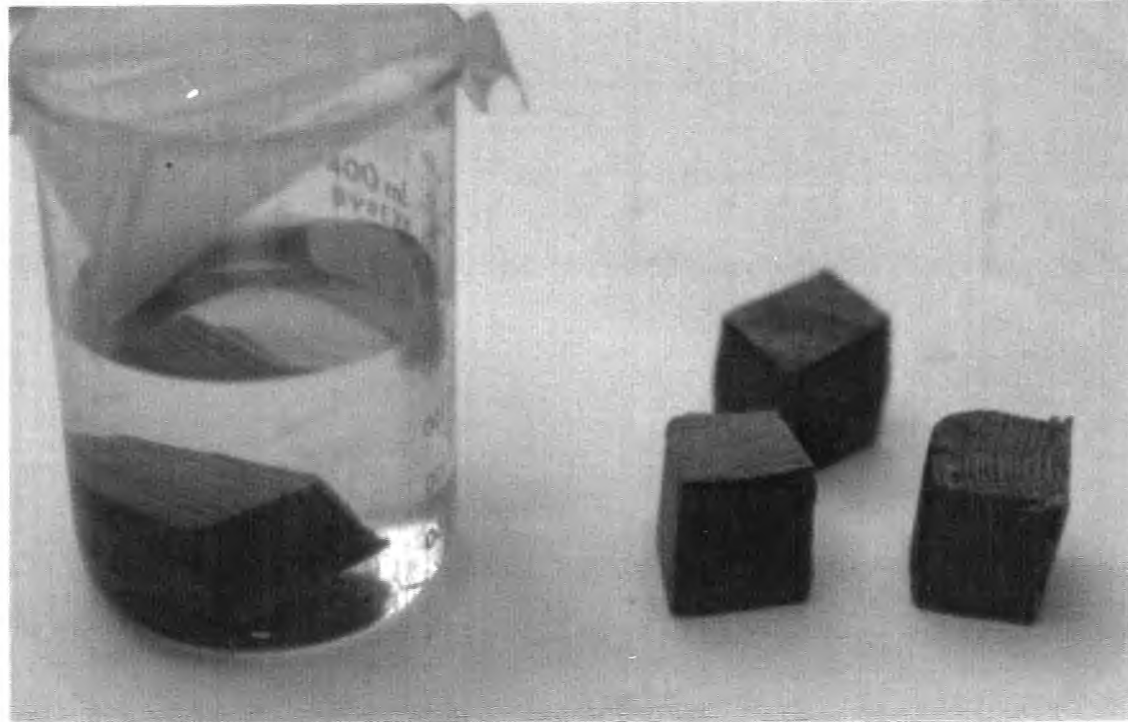
Figure 2.3 Sample preparation for leachate analysis

HPLC PDA Channels 3,4

LONG PLOT

Injection c: <YAN> 3 319SMP,7,1

Acquired on 19-Mar-92 at 16:22:51
Reported on 23-Mar-92 at 14:21:30
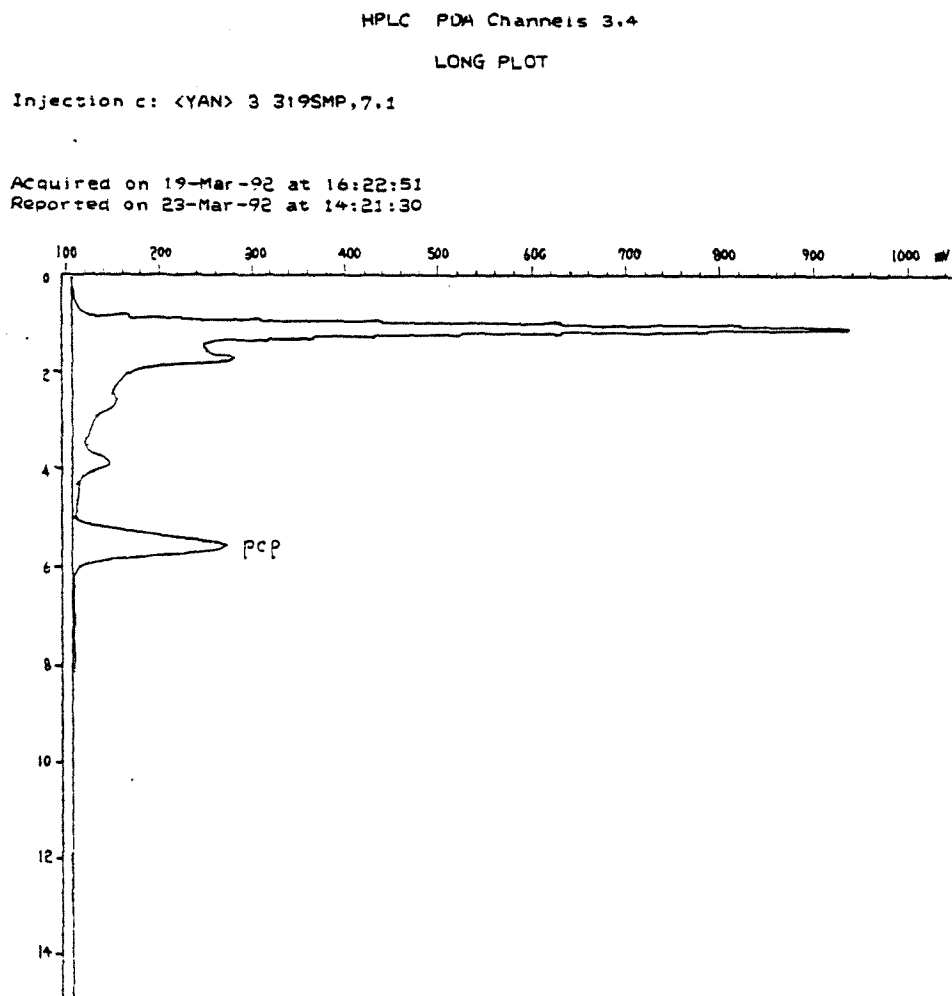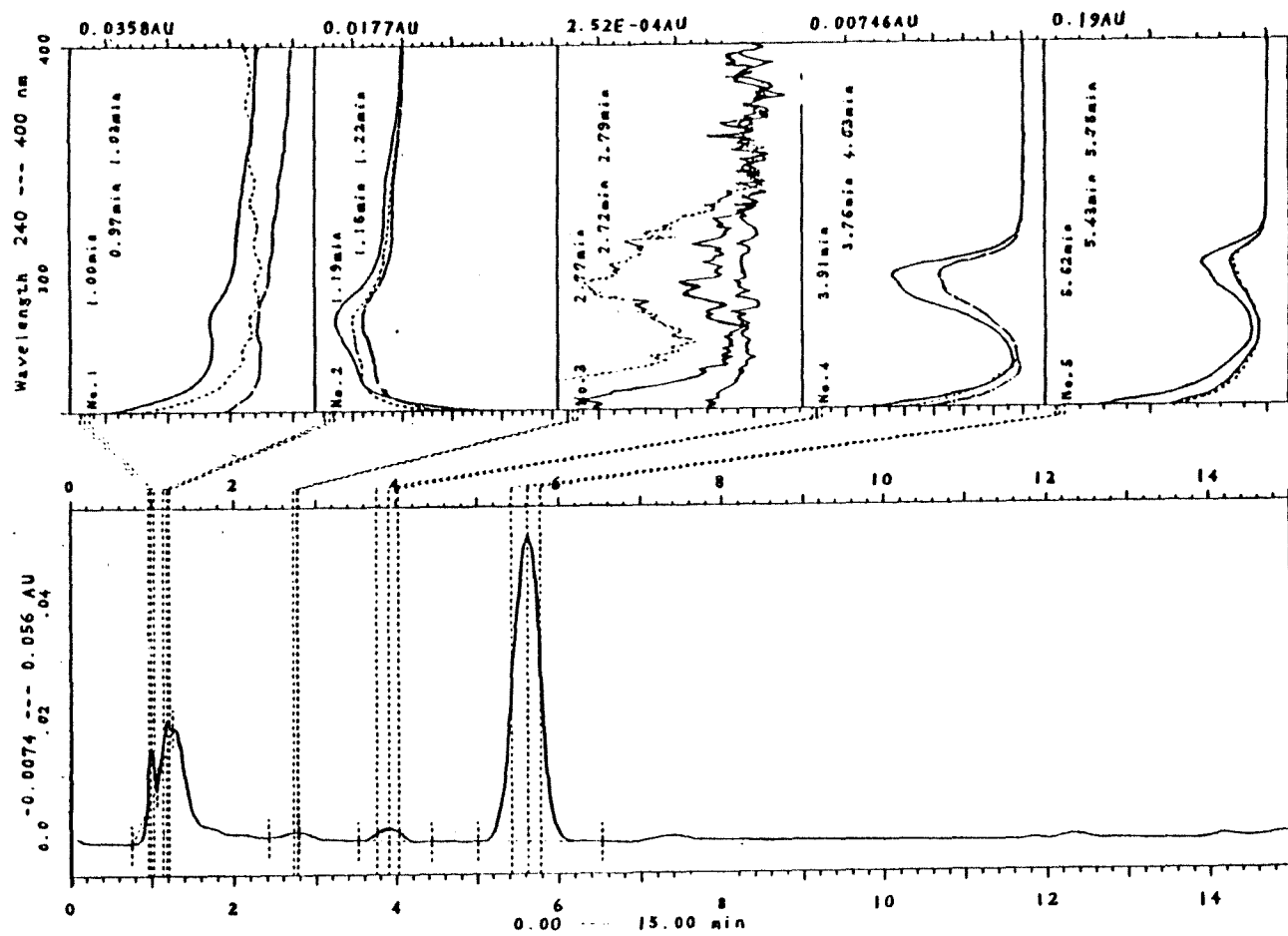

Figure 2.4 HPLC chromatogram of wood leachate

Figure 2.5 UV spectrum of wood extract
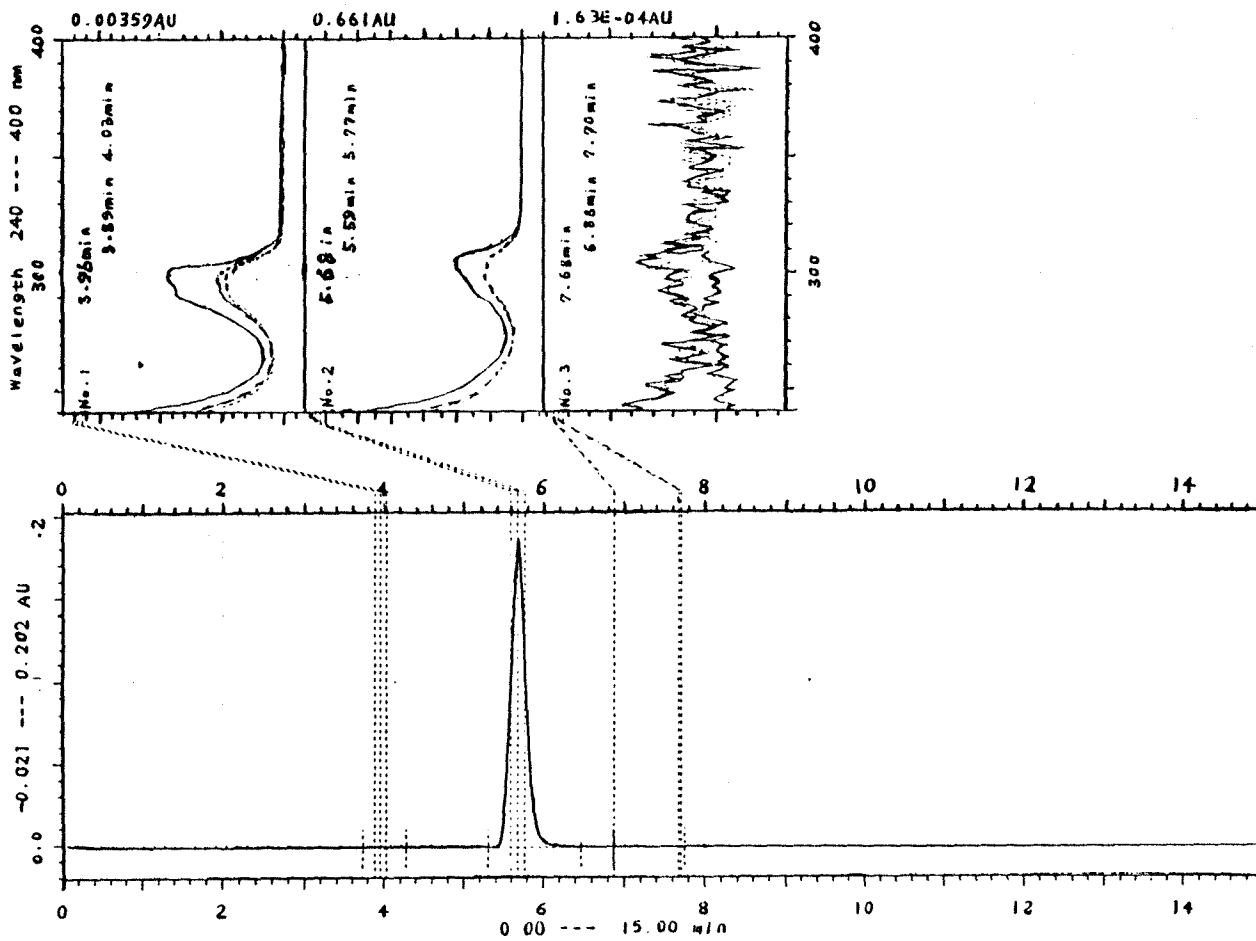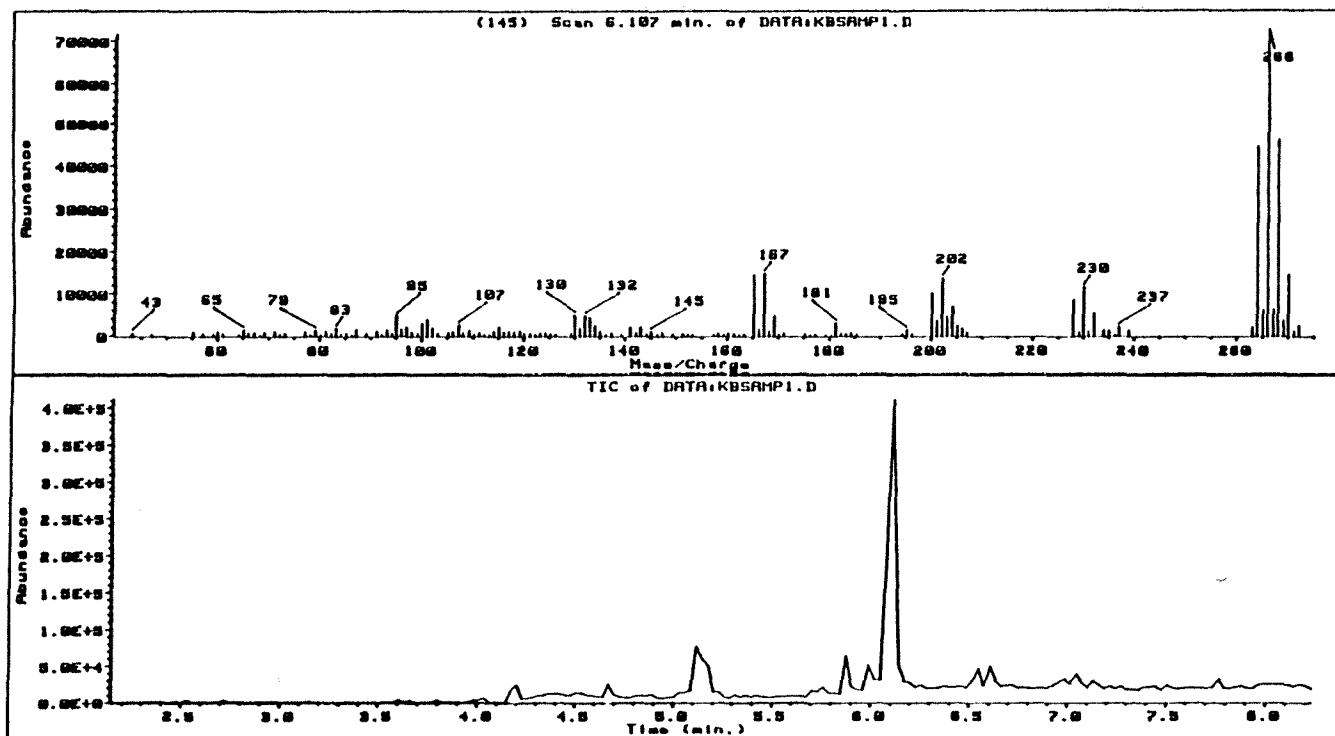
Figure 2.6 UV spectrum of PCP standard

Figure 2.7 GC/MS spectrum of wood extract
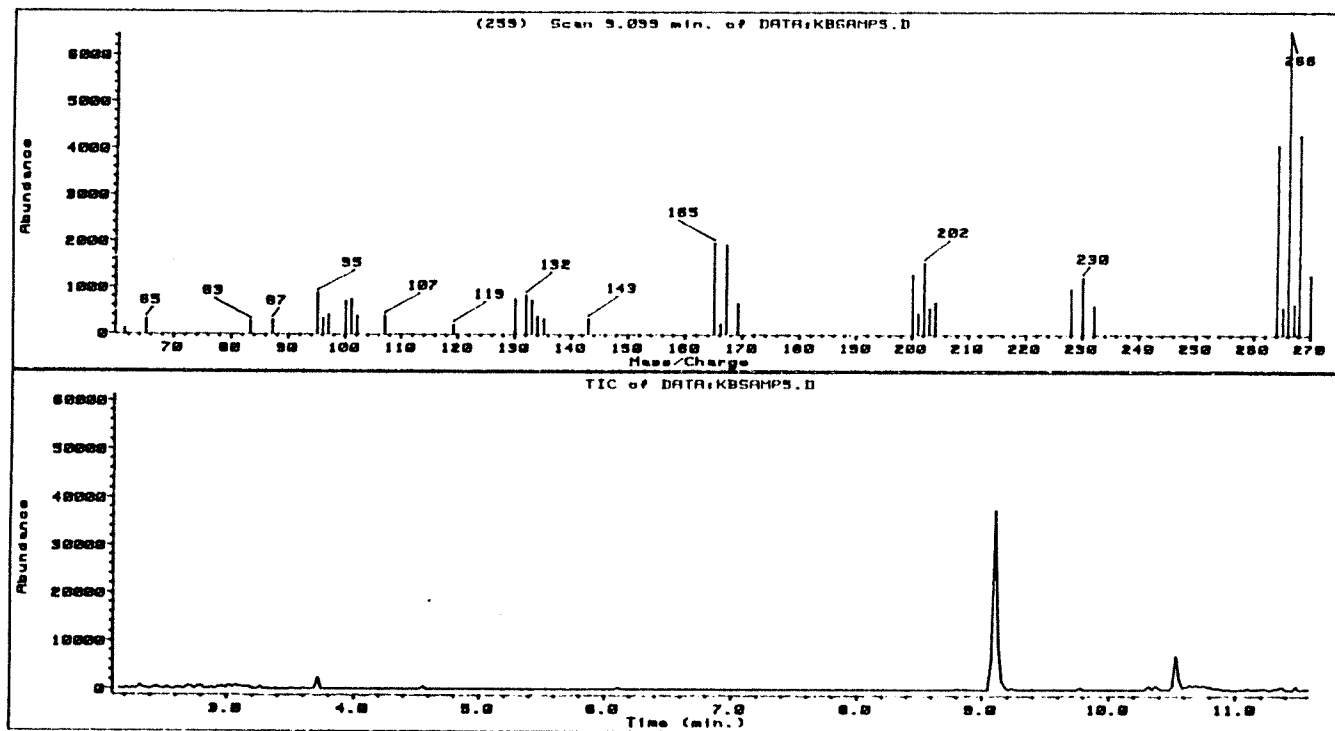
Figure 2.8 GC/MS spectrum of HPLC elute
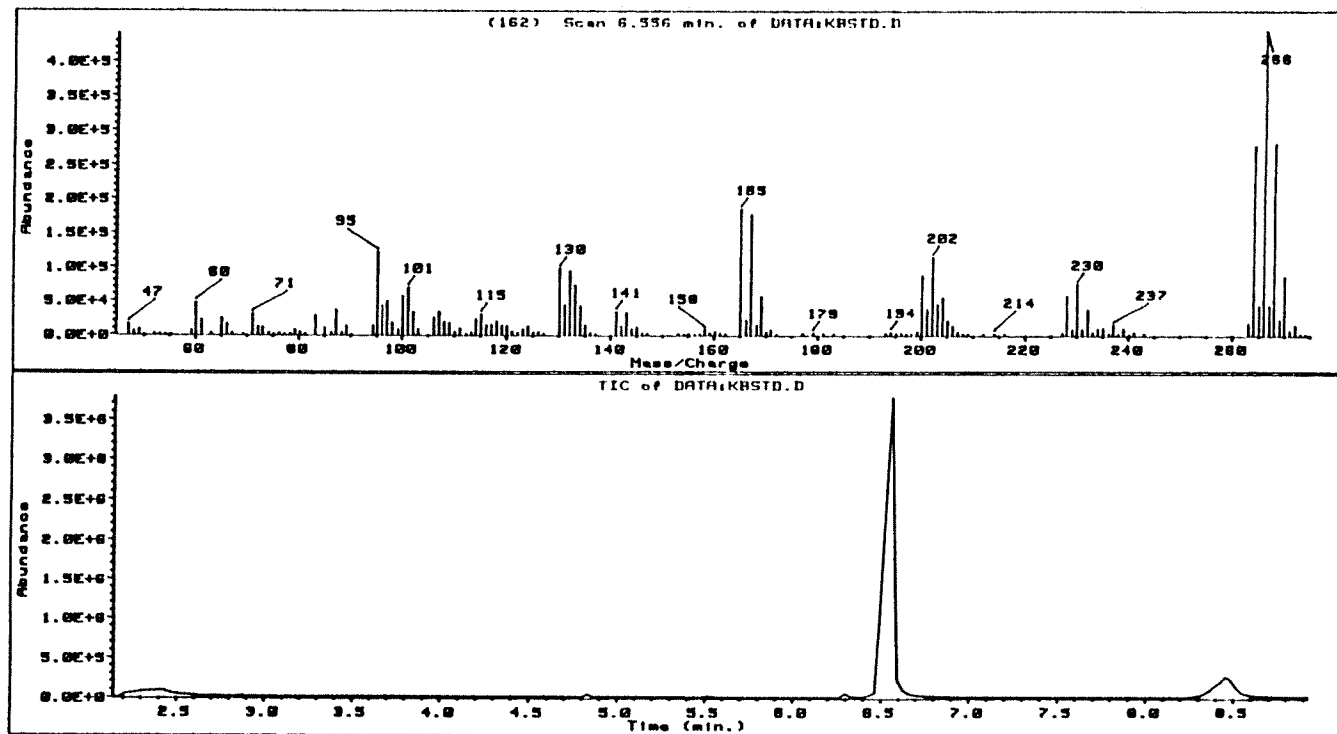
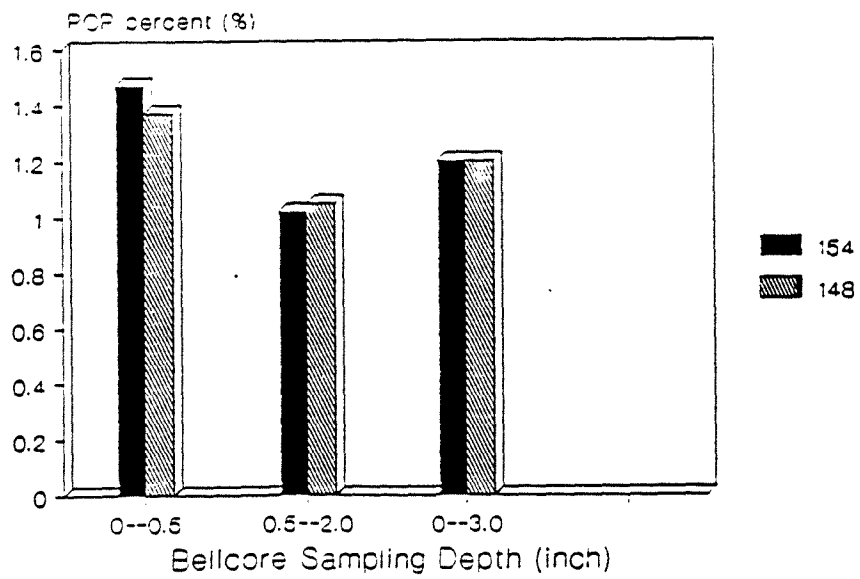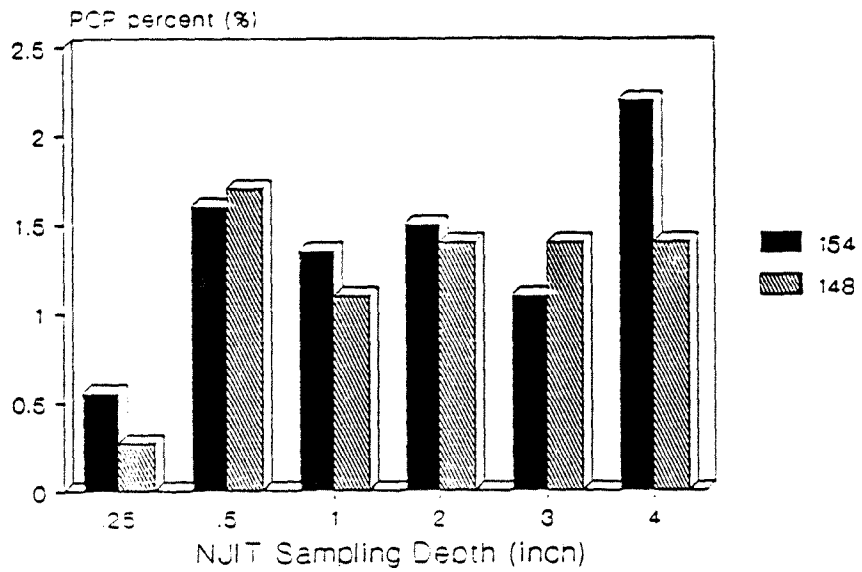**Figure 2.9** GC/MS spectrum of PCP standard

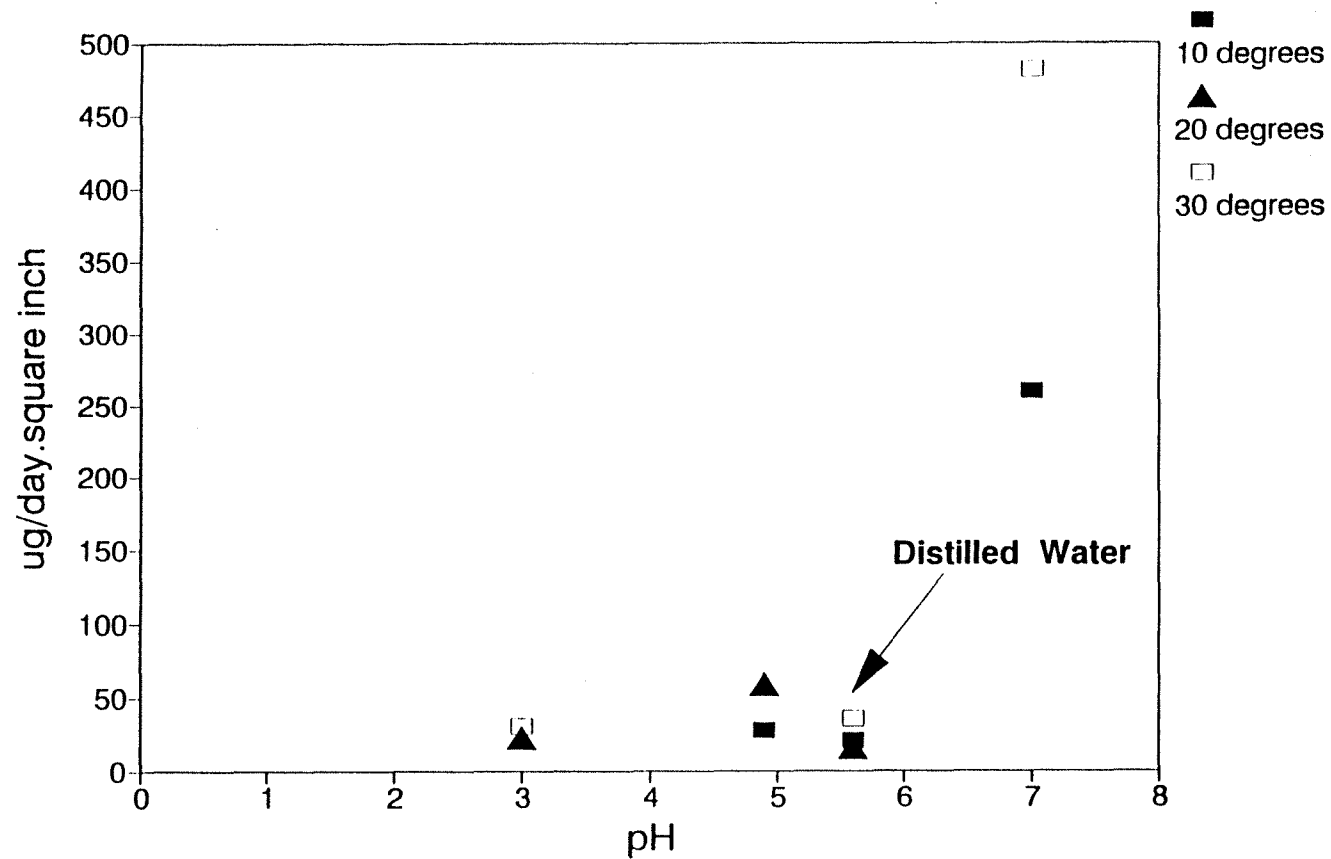Figure 3.1 Distribution of PCP in treated wood poles

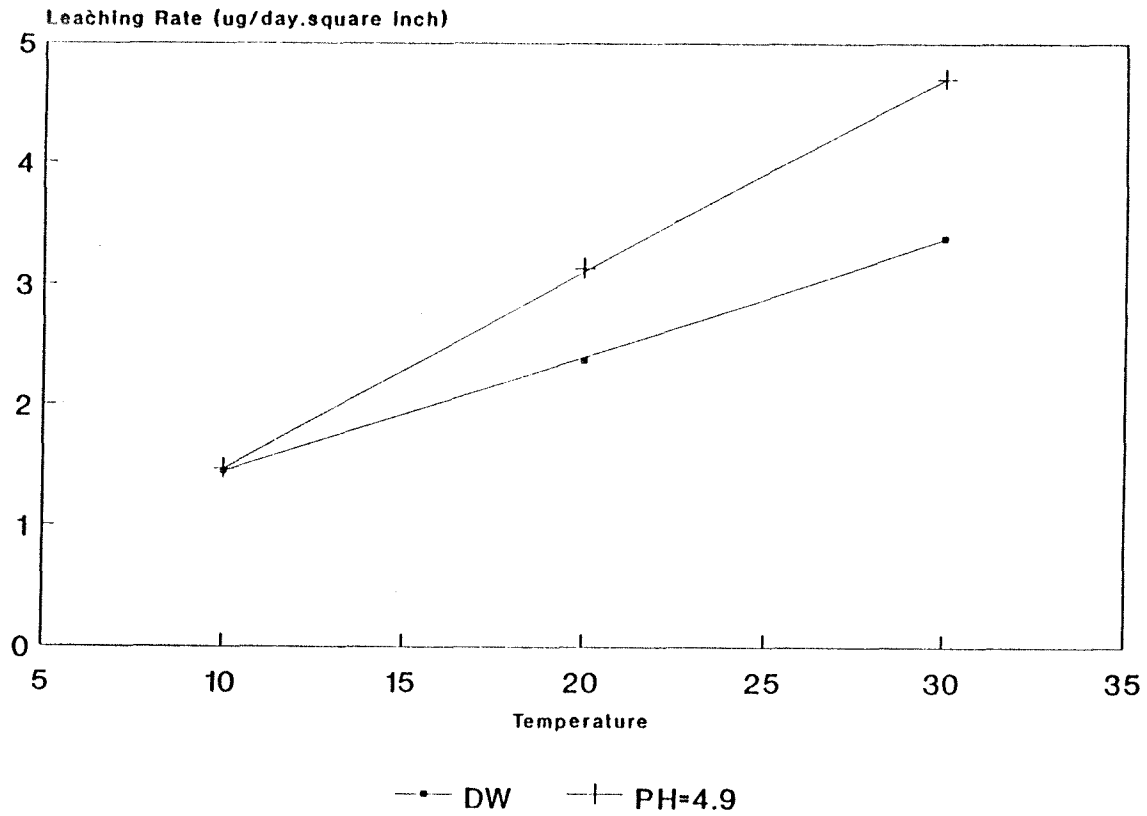**Figure 3.2** Leaching rate under different conditions

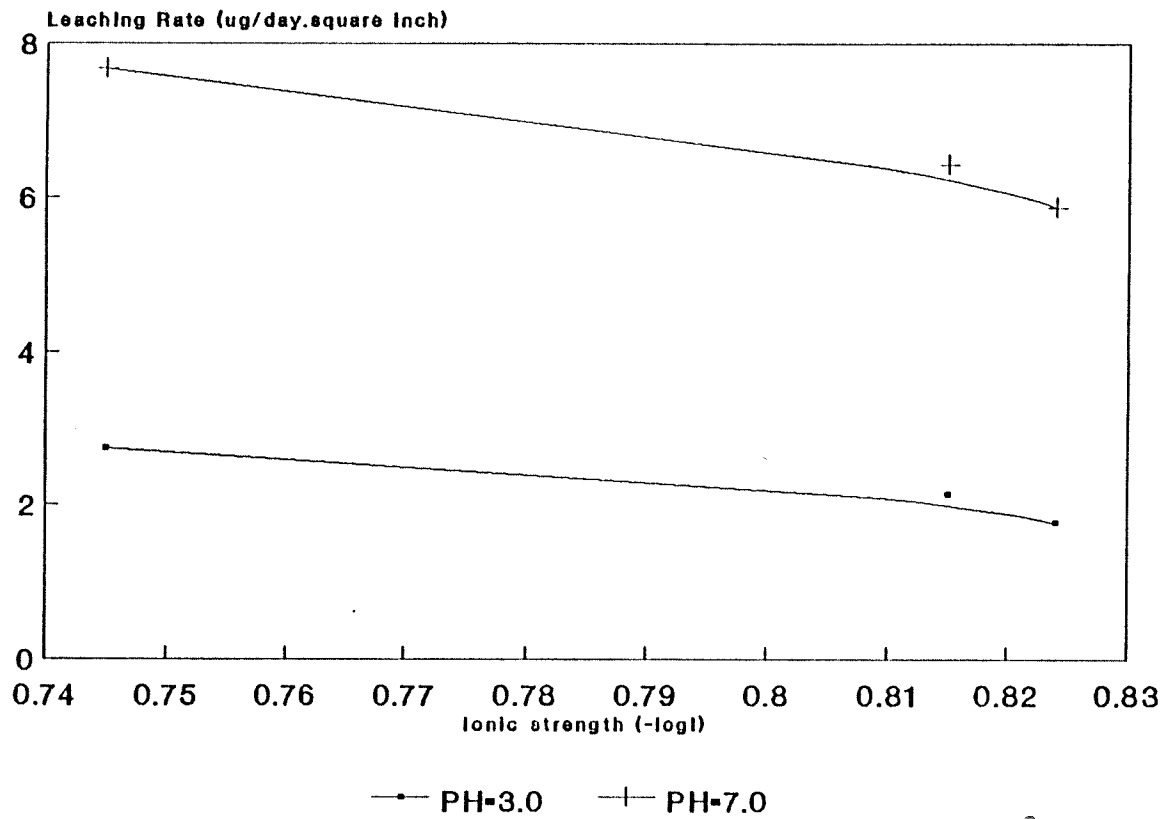**Figure 3.3** Effect of temperature on leaching rate

Figure 3.4 Effect of ionic strength on leaching rate

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