2,3,4,6-TETRACHLOROPHENOL

Method no.:	45
Matrix:	Air
Target concentration:	0.5 mg/m^3
Procedure:	Samples are collected by drawing a known volume of air through a sampling device consisting of two specially prepared XAD-7 adsorbent tubes which are connected in series. Following desorption with methanol, the samples are analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.
Recommended air volume and sampling rate:	48 L at 0.2 L/min
Reliable quantitation limit:	0.003 mg/m^3
Standard error of estimate: (Figure 4.7.1.)	6.65%
Special requirements:	The special sampling device as represented in Figure 4.2. must be obtained from the laboratory. It contains two XAD-7 adsorbent bed sections which are used for trapping vapor components; a glass fiber filter for trapping aerosols, and a XAD-7 "cap" section. The XAD-7 "cap" tube is used as a precautionary measure to prevent the loss of volatile components which may have collected on the filter during sampling. The "cap" tube must be removed from the front section of the sampler prior to sampling and reattached at the end of the sampling period.
Status of method:	A sampling and analytical method which has been subjected to established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1. Background

1.1.1. History

This air sampling and analytical procedure for 2,3,4,6-tetrachlorophenol (TCP) is essentially the same as OSHA Method 39 for pentachlorophenol (PCP) and is designed for the simultaneous collection and analysis of both of these analytes since they are used together in the wood industry (Ref. 5.1.). Only minor changes in sample tube design and in the analytical conditions have been made from the PCP method. Although there are three isomers of tetrachlorophenol, the industrial production of TCP from the chlorination of phenol produces primarily the 2,3,4,6-isomer with PCP as a contaminant since phenol is an ortho-para-director. (Ref. 5.2.) All evaluations in this method were performed with the 2,3,4,6-isomer, both in the presence and absence of PCP. For future reference, TCP will refer to the 2,3,4,6-isomer unless otherwise indicated.

The sampling tubes for PCP and TCP as represented in Figure 4.2. consist of two laboratory prepared XAD-7 sampling tubes connected in series with a small glass fiber filter disc mounted ahead of the resin bed in the front tube. The filter is used to trap any small aerosol particles of the analytes which are capable of penetrating through the sampling tube in its absence (Section 4.5.). A backup section is included to detect any analyte breakthrough. An additional XAD-7 tube is included with the sampling device and this is used to cap the front section of the sampler tube following collection to prevent possible loss of volatile analyte from the filter.

XAD-7 has been selected over the other possible adsorbents as a collection medium for these analytes because it has a very high capacity and its sampling performance, unlike silica gel, is not adversely affected by high humidity conditions.

The air sampling evaluations for TCP were performed with an aerosol generation system described in Section 4.5. Technical grade TCP containing 15-20% PCP was used for these studies although a purified TCP standard was prepared for use as an analytical standard. A majority of the atmosphere generated by the aerosol system was in the vapor phase because of the high volatility of both TCP and PCP; however, a measurable aerosol component was also produced.

The effectiveness of this sampling device in sampling an atmosphere of TCP/PCP was demonstrated by collecting side-by-side samples of XAD-7 tubes and bubblers containing isopropanol or 0.1 N NaOH. The average recovery of TCP from the XAD-7 tubes was 99% relative to the IPA bubblers and 89% compared to the 0.1 N NaOH bubblers. Similar high recoveries for the PCP component in the atmosphere were also obtained. (Section 4.8.)

A large number of GC methods have been published for the analysis of chlorophenols; however, many of these methods require precolumn derivatization (Ref. 5.3.). Several methods have been recently published for the direct analysis of TCP by HPLC (Refs. 5.1., 5.4. - 5.8.) and one by GC (Ref. 5.9.).

The HPLC analytical conditions employed for this analysis using a UV detector at 210 nm and a Zorbax ODS reverse phase column do not differ greatly from many of the previous HPLC methods. These conditions differ somewhat from those described previously for the PCP method; however, the analysis can be performed adequately using either procedure.

1.1.2. Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy)

Although the toxic effects of TCP have not been as well studied as PCP, based on LD_{50} data, TCP has a comparable acute toxicity. For the rat, LD_{50}'s range from 130 mg/kg to 210 mg/kg depending on the mode of administration (Ref. 5.10.). Oral LD_{50}'s for each tetrachlorophenol isomer and for PCP have been determined by one laboratory for rats. LD_{50} values for 2,3,5,6-; 2,3,4,6-; 2,3,4,5-TCP, and PCP of 109, 131, 400, and 74 mg/kg respectively were reported (Ref. 5.11.).

Acute exposure to TCP in animals produces symptoms common to the lower chlorinated phenols and some symptoms common to PCP. Convulsant activity, a characteristic of exposure to the lower chlorinated phenols, and signs of inhibition of oxidative

phosphorylation which are characteristic of PCP exposure, are observed (Ref. 5.12.). Accelerated respiration, elevated blood pressure and hyperpyrexia (elevated body temperature), which are all symptoms of oxidative phosphorylation inhibition can be anticipated upon acute exposure to TCP.

TCP is a strong irritant and can produce skin and eye irritation upon contact. Like PCP, TCP is readily absorbed through the skin and can produce systemic effects. Although a literature search did not reveal any human cases of acute exposure to TCP, it is widely used in the wood industry.

Exposure to TCP as a contaminant of PCP also occurs since technical grade PCP contains from 5-12% TCP (Ref. 5.13.). Widespread exposure of the general population to TCP is evidenced by the analysis of urine samples from the general population. Low ppb levels of 2,3,4,6-TCP which are approximately 1/5 to 1/3 the PCP levels are reported for twelve samples from the general population (Ref. 5.14.). Low ppm levels of both TCP and PCP are reported in the urine of exposed Finnish workers (Ref. 5.3.). Since skin exposure is a significant route of exposure for both TCP and PCP, biological monitoring through urine analysis is desirable.

Although no reports of a mutagenic or a teratogenic effect from TCP were found in the literature, the possibility of such an effect from polychlorinated dioxin and polychlorinated dibenzofuran contaminants must be considered. Trace levels of these contaminants in the blood of exposed workers have been measured (Ref. 5.15.).

1.1.3. Potential workplace exposure

TCP is used almost exclusively in the wood industry to treat wood. A dilute aqueous solution of mainly sodium tetrachlorophenate with lesser amounts of the pentachlorophenate salt is sprayed on newly milled wood surfaces to prevent the wood from darkening during the aging process (Ref. 5.4.). The pressure treatment of lumber with PCP dissolved in oil is also a potential source of exposure since TCP is a major contaminant. It is not known if TCP alone is used in this manner.

1.1.4. Physical properties (Ref. 5.16.)

CAS no.:	58-90-2
molecular weight:	231.89
melting point:	70°C
boiling point:	150°C (15 mm Hg)
soluble in:	alcohol, benzene, chloroform, petroleum ether
physical state:	white to tan crystalline solid
synonyms and trade names:	TCP, Dowicide 6

1.2. Limit defining parameters (The analyte air concentrations listed throughout this method are based on an air volume of 48 L and a solvent desorption volume of 2 mL)

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 1.5 ng per injection. This is the amount of the analyte which will give a peak whose height is approximately 5 times the height of the baseline noise. (Section 4.1.)

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 0.15 µg per sample (0.003 mg/m^3) for TCP. This is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 0.15 µg per sample (0.003 mg/m^3) for TCP. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (1.96 SD) of ±25% or better. (Section 4.2.)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4. Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.5 to 2 times the target concentration based on the recommended air volume is 101,610 area units per µg/mL. The sensitivity is determined from the slope of the calibration curve. The sensitivity may vary with different instruments or instrumental conditions. (Section 4.4.)

1.2.5. Recovery

The recovery of TCP from samples used in a 17-day storage test was 102% when the samples were stored at ambient conditions in the dark. This is the percent recovery at 17 days determined from the linear least squares line from the storage data. The recovery of the analyte from the collection medium during storage must be 75% or greater. (Section 4.7.)

1.2.6. Precision (analytical procedure only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.011. (Section 4.3.)

1.2.7. Precision (overall procedure)

The precision at the 95% confidence level for the 17-day storage test is ±13% for TCP. The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level. (Section 4.7.)

1.2.8. Reproducibility

Six liquid-spiked samples and a draft copy of this method were submitted to the OSHA laboratory for analysis by a chemist unassociated with this evaluation. The samples were analyzed approximately two weeks after preparation. The average recovery for the six samples was 94.0% with a percent standard deviation of 3.9%. (Section 4.9.)

1.3. Advantages

1.3.1. The two solid sorbent sampling tubes in series represent a convenient method for sampling both TCP and PCP.

1.3.2. The analysis is rapid, sensitive, and precise.

1.4. Disadvantages

1.4.1. The method has not been field tested.

1.4.2. The sampling tubes are not commercially available.

2. Sampling Procedure

2.1. Apparatus

2.1.1. A constant flow personal sampling pump is used which can be calibrated to within ±5% of the recommended 0.2 L/min flow rate while the sampling train is in line.

2.1.2. The sampling tubes, as represented in Figure. 4.2., consist of two 50-mm by 8-mm o.d. (6-mm i.d.) glass tubes which are each packed with approximately 175 mg (15-mm tube length) of XAD-7 resin held in place with two silanized glass wool plugs and small Teflon-support rings made from narrow slices of 6-mm o.d., 4-mm i.d. Teflon tubing. These Teflon rings, when cut at one point across their circumference, provide a flexible ring which can be easily inserted into the tube to provide support for the resin bed and the filter disc. The tubes are butted together using a connector made from a 9/32 inch diameter

plastic cap from which the closed end has been removed. The first sampling tube in the series also contains an 8-mm glass fiber filter disc as a precautionary measure to trap any aerosols of the analyte. A number 4 cork borer is used to cut out the discs from Gelman (Ann Arbor, Michigan, USA) Type A 35-mm glass fiber filters. The glass fiber filter is placed ahead of the resin bed and sandwiched between two Teflon-support rings by simply tapping the over-sized filter onto the surface of the Teflon ring with a glass rod or similar object and then placing an additional Teflon ring on top of the filter. In order to retain any volatile components which may have collected on the front filter section of the sampling device during sampling, an additional XAD-7 packed tube is included with the sampling device. This tube is used to cap the front section of the sampling device following sampling and must be removed prior to sampling and replaced at the end of the sampling period. Amberlite XAD-7 resin (Rohm and Haas, Philadelphia, PA, USA) 20-50 mesh size which was purchased from Sigma Chemical (St. Louis, MO) lot no. 61F-0150 was used in this study. The resin was first rinsed with methanol to remove fines and then Soxhlet extracted overnight with HPLC grade methanol. The resin was taken to dryness on a rotary evaporator and then dried for 12 h at 35°C under vacuum.

2.2. Reagents

None required

2.3. Technique

2.3.1. Properly label all three sections of the sampling device prior to sampling.

2.3.2. Before sampling, remove and save the front glass tube section containing XAD-7 resin which will serve as a cap following completion of sampling.

2.3.3. Attach the sampling tubes to the pump using a section of flexible, plastic tubing so that the adsorbent tube containing the glass fiber filter serves as the front sampling section. Do not place any tubing ahead of the sampling device. Attach the sampling device in the workers breathing zone in such a manner that it does not impede work performance.

2.3.4. After sampling for the appropriate time, remove the sampling device from the pump, cap the front end of the device with the resin-filled glass tube and cap the back end of the device with a plastic cap. Insure that the caps are well fitted and label the sampling tubes with OSHA seals (Form 21).

2.3.5. Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.

2.3.6. Any bulk samples submitted for analysis must be shipped in separate containers to avoid contamination of the air samples.

2.3.7. List any potential interferences on the sample data sheet.

2.4. Breakthrough

Since XAD-7 resin has a very high capacity for TCP, the determination of the amount of analyte which can be collected from an atmosphere before breakthrough occurs was found to be experimentally difficult to determine and of little practical value. Two studies were performed, however, to demonstrate the high capacity of the resin for the analyte.

In the first study, an XAD-7 sampling tube with a glass fiber filter insert was used to sample a 4.9 mg/m^3 atmosphere of TCP which was generated by an aerosol generation system. No breakthrough to the backup sampling tube was observed after 354 L of dry air was sampled at 1 L/min for 5.9 h. (A more complete description of the experiment and the aerosol generation system is discussed in Section 4.5.)

In the second study, the ability of a XAD-7 sampling tube to collect TCP vapors was investigated under high humidity conditions. No breakthrough was observed after sampling 438 L of a 4.3 mg/m^3 atmosphere of TCP at 1 L/min with an XAD-7 sampling tube containing a glass fiber filter. (Section 4.5.)

2.5. Desorption efficiency

The average desorption efficiency over the range of 0.5 to 2 times the target concentration was 95.4% for TCP and 99.8% for PCP. The percent recovery ranged from 91.2% for 2 times the target concentration to 99.7% for the 0.5 times target concentration for TCP. Similarly, PCP recoveries ranged from 95.5% to 105% over the same range. The variability in desorption efficiency with amount loaded on sample is not understood but may be a function of the spiking technique.

In the course of this evaluation, it was also observed that the desorption efficiency from XAD-7 was dependent on the drying temperature. XAD-7 resin dried at 105°C under vacuum following rotary evaporation and spiked at the PEL resulted in an 87% recovery for TCP and 91% recovery for PCP. This contrasts to resin which was dried by rotary evaporation alone which resulted in recoveries of 105% for TCP and 110% for PCP.

The desorption efficiency of the resin that was dried at 105°C under vacuum and of the resin similar to the one used in this study was not affected by humidity.

These variations in desorption efficiency for XAD-7 resin, depending on preparation technique, emphasize the need for careful quality control. (Section 4.6.)

2.6. Recommended air volume and sampling rate

A 48-L air sample obtained by sampling at 0.2 L/min for 4 h is recommended for TCP. If necessary, the sensitivity of the analytical method will permit a sampling period as short as 15 min at 0.2 L/min for determination of the analyte at the target concentration. Higher flow rates can also be employed if necessary.

2.7. Interference

There are no known interferences to the sampling procedure.

2.8. Safety precautions

2.8.1. Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2. Follow all safety practices that apply to the work area being sampled.

3. Analytical Procedure

3.1. Apparatus

3.1.1. A high performance liquid chromatograph equipped with sample injector, ODS bonded phase HPLC column, UV detector, and chart recorder are needed for the analysis. A Waters 6000A pump, a Waters WISP 710 auto sampler, a Dupont UV detector and a Zorbax 25-cm × 4.6-mm i.d. ODS-bonded phase column were used in this study.

3.1.2. An electronic integrator or other suitable means of measuring detector response is required. The Hewlett-Packard 3354 data system was used in this study.

3.1.3. Various sizes of volumetric glassware and pipettes are needed for sample and standard preparations.

3.1.4. Three-milliliter (or larger) screw-cap or crimp-type vials are needed for desorbing the XAD-7 sampling adsorbent. Four-milliliter Waters WISP vials were used in this study.

3.1.5. Small brown glass bottles fitted with inert cap liners are needed to store standard solutions.

3.1.6. A repetitive dispenser capable of accurately delivering the desorption solution is needed.

3.2. Reagents

3.2.1. HPLC grade methanol and acetonitrile.

3.2.2. Reagent grade phosphoric acid.

3.2.3. HPLC grade water. Water obtained from a Milli-Q reagent grade water system (Millipore, Inc. Bedford, Mass.) was used in this study.

3.2.4. Eighty-five percent pure 2,3,4,6-TCP containing PCP contaminant was purchased from Fluka Chemical (Hauppauge, NY, USA) for preparation of a purified standard. A semi-preparative HPLC technique which utilized a (8-mm i.d. × 25 cm) Zorbax ODS column and aqueous mobile phase of 80% acetonitrile 0.1% phosphoric acid with a 2.5 mL/min flow rate was used to prepare a purified standard. Repetitive 130-µL injections of a 1 mg/µL (130-mg injections) in methanol of the unpurified TCP were made onto the column. The peak fraction containing TCP which eluted at 7 min and was fully resolved from the PCP contaminant was collected. These TCP-containing fractions were pooled following verification of their purity by HPLC and the acetonitrile portion was removed by rotary evaporation. The remaining aqueous portion was then acidified to pH 1 with concentrated HCl and extracted with HPLC grade methyl t-butyl ether. The ether fraction was dried with anhydrous sodium sulfate and the purified 2,3,4,6-TCP was recovered following evaporation of the ether. The melting point of the white crystalline substance was 67°C and no PCP peak was evident upon HPLC analysis.

3.3. Standard preparation

Prepare a stock solution of TCP by accurately weighing approximately 32 mg of the standard in a 100-mL volumetric flask and diluting to volume with methanol. Prepare 1/50, 1/25, and 2/25 dilutions of this stock solution to obtain standards which correspond to approximately 0.5, 1 and 2 times the target concentration for the recommended sampling conditions.

3.4. Sample preparation

Prepare samples for analysis by transferring the entire contents of the sampling tube including the Teflon-support rings, both glass wool plugs, the XAD-7 resin and the glass fiber disc into a 4-mL vial. Considerable care must be exercised in transferring the samples to the vials to avoid sample loss from static build-up on the XAD-7 beads. The transfer is best accomplished if the Teflon support rings and the glass fiber filter are first transferred to the sample vial by using a small wire hook to remove them. Then with front glass wool plug partially removed, invert the sampling tube into the vial and use a small glass rod or similar object to force the contents of the tube into the vial. Rinse the inside of the sampling tube into the vial with two 1-mL portions of methanol using a 1-mL repetitive dispenser. Cap the vials and shake vigorously for a minimum of 10 s. The backup tube and the cap tube, which are analyzed separately, are handled in the same manner.

3.5. Analysis

3.5.1. Prepare a high performance liquid chromatograph for sample analysis using the HPLC conditions listed below:

column:	Zorbax 25 cm × 4.6-mm i.d. ODS bonded phase
mobile phase:	25/75 (v/v) acetonitrile/water containing approximately 0.1% by volume of phosphoric acid
flow rate:	1.3 mL/min
UV detector:	210 nm
injection volume:	20 µL
retention time:	4.6 min

3.5.2. Analyze the front and back sampling tubes and the sample cap tube separately. Verify that the sample responses lie within the range of the responses observed for the standards.

3.5.3. Since column to column variations do occur, it is important to ensure that TCP is separated from PCP. The injection of a TCP/PCP mixture should produce baseline separation if the analytical conditions are properly selected.

3.6. Interferences

Any compound which has the same retention time as 2,3,4,6-TCP is a potential interference. Under the analytical conditions outlined, 2,3,5,6-TCP and 2,3,4,6-TCP are not resolved. However, since only the 2,3,4,6 isomer of TCP is used industrially, and the response factors for these two isomers are very similar at 210 nm, no significant error would be introduced in determining TCP content under these conditions (Figure 4.10.). A complete separation of the three isomers of TCP in 30 min has been performed using gradient reverse phase HPLC conditions (Ref. 5.2.). A normal phase

separation of the isomers using a silica column and a GC separation have also been reported in the literature (Ref. 5.8.). These alternative methods are useful for sample confirmation. GC/Mass spectrometry may also be a useful method of sample confirmation.

3.7. Calculations

Prepare a standard calibration curve of area response versus concentration for TCP by determining the least squares fit equation for the curve. Calculate the amount of analyte (µg/mL) in the samples, preferably by entering their response values into the equation and solving for the sample concentration. Add the results from the backup and cap tubes to that of the front tube. Sample air concentrations are calculated as follows:

mg/m^3 = (µg/mL)(2 mL)(1 mg/1000 µg)/(air vol. m^3)(desorp. effic.)

To convert to ppm at 760 mm and 25°C:

ppm = $(mg/m^3)(24.46)/(MW)$ where 24.46 = the molar volume
MW = 231.89

3.8. Safety precautions

3.8.1. Minimize exposure to TCP by performing standard preparations in a well ventilated hood.

3.8.2. Avoid all skin contact with TCP.

3.8.3. Restrict the use of solvents to hoods which provide adequate ventilation.

3.8.4. Wear safety glasses in laboratory areas at all times.

4. Backup Data

4.1. Detection limit for analytical procedure

The detection limit for the analytical procedure is 1.5 ng for TCP. This is based on a 20-µL injection of a 0.075 µg/µL standard, and represents approximately 5 times the baseline noise (Figure 4.1.).

4.2. Detection limit of the overall procedure and reliable quantitation limit

The detection limit of the overall procedure and the reliable quantitation limit are both 0.15 µg per sample (0.003 mg/m^3) for TCP.

Six XAD-7 sampling tubes were spiked with 8 µL of 40.4 µg/mL TCP in methanol, then capped and stored overnight in a laboratory drawer. Assuming complete recovery, this amount of analyte is equivalent to the detection limit of the analytical procedure. The following day the samples were desorbed in 2 mL of methanol and analyzed. The percent recoveries (corrected for 95.4% desorption efficiency) are reported below in Table 4.2.

Table 4.2.
Detection Limit Data

% recovery	statistics
98.8	
98.8	$\bar{X}$ = 98.4
99.8	SD = 1.60
95.2	1.96 SD =3.14
98.8	
98.8	

4.3. Precision of the analytical method

The pooled coefficient of variation for TCP is 0.011 over a range of 0.5 to 2 times the target concentration. This value was determined from multiple injections of three standard solutions. The results are listed in Table 4.3.

Table 4.3.
Precision Data

× target conc.	0.5×	1×	2×
µg/mL	5.98	11.97	23.94
area counts	599574	1198240	2355190
	600337	1193360	2333730
	600090	1189100	2410920
	612430	1207610	2380600
	614097	1208830	2411150
	612310	1208540	2371280
$\bar{X}$	606473	1200947	2377145
SD	7123	8596	30693
CV	0.0117	0.00716	0.0129
$\overline{CV}$ = 0.011			

4.4. Sensitivity

The slope of the calibration curve over the range of 0.5 to 2 times the target concentration for the analysis represents the sensitivity of the method. The sensitivity determined in this manner is 101,610 area units per µg/mL for TCP (Figure 4.4.).

4.5. Breakthrough

Breakthrough studies were performed using a sub-micron aerosol generation system consisting of a TSI (St. Paul, MN) atomizer used in the non-recirculating mode, an aerosol electrostatic neutralizer, a sampling chamber, and a TSI Model 3203 Particle Mass Monitor.

Submicron aerosols of TCP/PCP, less than 0.3 microns in diameter, were generated by pumping a 1.5 mg/mL isopropanol solution of technical grade 2,3,4,6-TCP containing PCP into the atomizer with a Waters (Milford, MA) Model 6000A pump at a 0.7 mL/min flow rate. A fine aerosol spray is produced in the atomizer as the TCP solution passes into a high velocity jet air stream which consists of dry laboratory air supplied at a flow of 3.5 L/min. The large droplets of the aerosol, which produce large particles, impact on the wall of the atomizer and are drained to a waste container and do not enter the air stream. The submicron aerosol that is produced by the atomizer is then passed through an electrostatic neutralizer before it is diluted with 25 L/min of dry laboratory air and drawn into the sampling chamber.

The sampling chamber consists of a 9 in. by 20 in. clear acrylic plastic cylinder equipped with a diffuser plate at the top, and at the bottom are mounted 3.75-in. outlet lines attached to a flow-controlled vacuum pump that is used to maintain a 20 L/min air flow through the chamber. A separate vacuum pump attached to a manifold is used in conjunction with critical orifices to sample from six sampling ports positioned at the base of the chamber. Attached to a seventh sampling port in the base is a TSI particle mass monitor for measuring the total aerosol concentration of the chamber.

A simple experiment demonstrating the importance of the glass fiber filter in sampling a submicron aerosol was performed with the described apparatus. A glass fiber filter mounted in a glass sampling tube and placed ahead of the particle mass monitor reduced a 1.71 mg/m^3 TCP/PCP aerosol to background levels (0.034 mg/m^3) indicating that the filter alone was effective in trapping the aerosol. However, an XAD-7 tube without a glass fiber filter permitted approximately 50% of the same aerosol to pass through the tube (0.929 mg/m^3). Insertion of a filter ahead of the tube immediately reduced the aerosol concentration to background levels.

In other studies, breakthrough of TCP and PCP was observed upon analysis of backup sections from sampling tubes not equipped with a glass fiber filter which were taken from an aerosol test atmosphere.

These results differ from those observed for samples collected from 2.2 µm PCP aerosol generated by a TSI monodisperse generator. For these larger size aerosol particles, a sampling tube alone was completely effective in trapping the aerosol.

Although it is clear that TCP and PCP are quite volatile and exist largely as a vapor in test atmospheres, the potential for an aerosol component exists in the work environment. Penetration of a packed sampling tube by small aerosols, which has been demonstrated here and is reported in the literature can occur in the work atmosphere and does represent a potential source for loss of sample (Ref. 5.16.). Under these laboratory conditions, no sample breakthrough was observed for the sampling tube as designed.

Tests of the capacity of the XAD-7 sampling tube for sampling high concentrations of TCP were also performed with this apparatus. After sampling a 6 mg/m^3 TCP (1 mg/m^3 PCP) for 5.3 h, no breakthrough of either analyte was observed at the time the experiment was discontinued.

In order to test the effects of humidity on the sampling device, a crude vapor generation system was devised. This system consisted of a syringe drive pump which delivered 0.01 mL/min of 4 mg/mL technical grade 2,3,4,6-TCP in methanol into one end of a glass tee which was wrapped with heat tape and packed with silanized glass wool. A Rheostat set at 20% of full scale was used to heat the sampling tee. Air at 80% relative humidity and ambient temperature was drawn through the tee at 1 L/min and into an XAD-7 sampling tube (equipped with a glass fiber filter) which is attached to the other end of the tee. No breakthrough was observed during the 7.3 h sampling period. The total amount of TCP found on the sampling tube was 20 mg, which corresponds to a 4.6 mg/m^3 average concentration for TCP over the entire sampling period.

4.6. Desorption efficiency

Amberlite XAD-7 resin 20-50 mesh size which was purchased from Sigma Chemical (St. Louis, MO) lot # 61F-0150 was used in this study. The resin was first washed with methanol to remove fines and then Soxhlet extracted overnight with HPLC grade methanol. The resin was then taken to dryness with rotary evaporation and dried for 12 h at 35°C under vacuum.

Three sets of six sample tubes packed with this XAD-7 resin were each spiked with 1.25, 2.5 and 5.0 µL, respectively, of a stock TCP/PCP mixture (10.04/10.02 mg/mL) in methanol corresponding to 0.5, 1 and 2 times the target concentration. The samples were capped and stored overnight and analyzed the next day. The desorption efficiencies are reported below in Tables 4.6.1. - 4.6.2.

Table 4.6.1.
Desorption Efficiency (TCP)

× target conc.	0.5×	1×	2×
µg/sample	12.55	25.1	50.2
desorption efficiency, %	98.4	93.8	92.1
	99.2	92.1	91.3
	98.5	91.3	91.1
	99.2	93.0	91.0
	99.7	102.0	90.5
	102.9	100.2	91.0
$\bar{X}$	99.65	95.4	91.2
$\bar{\bar{X}}$ = 95.4			

Table 4.6.2.
Desorption Efficiency (PCP)

x target conc. µg/sample	0.5x 12.52	1x 25.05	2x 50.1
desorption efficiency, %	104.0	99.1	95.5
	105.6	98.0	98.0
	103.6	98.7	95.5
	104.4	99.4	94.8
	105.4	100.2	94.3
	107.0	98.5	94.7
$\bar{X}$	105.0	99.0	95.5

$\bar{\bar{X}}$ = 99.8

In order to test the effect of elevated drying temperatures of the adsorbent on desorption efficiency, a new portion of XAD-7 resin was prepared as above and dried under vacuum in 12-h increments at temperatures ranging from 50°C to 105°C. The desorption efficiencies for each step of the treatment are reported below in Table 4.6.3. for a 2.5-µL spike of six sample tubes of the stock TCP/PCP mixture.

Table 4.6.3.
Effect of Adsorbent Drying Temp. on Desorption Efficiency

XAD-7 lot no.	treatment	average % recovery TCP (% SD)	PCP (% SD)
103A	methanol extraction, to dryness with rotary evaporation	105(2.2)	110(1.6)
103B	103A plus 12 h at 50°C	105(1.9)	110(1.7)
103C	103B plus 12 h at 65°C	104(2.6)	109(2.5)
103D	103C plus 12 h at 80°C	88.1(4.8)	94.4(6.7)
103E	103D plus 12 h at 105°C	87.4(0.8)	92.6(0.5)

The effects of humidity on the dried XAD-7 resin were evaluated for lot 103C and lot 103E. For each test six sample tubes were spiked with 2.5 L of the stock TCP/PCP mixture. The percent recoveries for each test are reported below in Table 4.6.4.

Table 4.6.4.
Effect of Humid Air on Desorption Efficiency

XAD-7 lot no.	treatment	average % recovery TCP (% SD)	PCP (% SD)
103E	138 L of humid air (80% RH) sampled after spike	84.7(1.3)	89.3(1.7)
103E	control, no air sampled (four samples)	87.0(0.9)	90.7(1.0)
103C	60 L of humid air (80% RH) sampled after spike	97.8(1.3)	104(1.3)
103C	control, no air sampled (four samples)	102.(1.3)	107(1.3)
103C	80 L of humid air (80% RH) sampled spike	99.1(1.4) 99.9(2.0)	103(1.4) 103(1.8)

4.7. Storage test

No storage problem was observed for either the ambient or the refrigerated storage samples which were generated with the submicron aerosol generation system described in Section 4.5. Total air concentrations of TCP in the 1.2 - 1.7 mg/m^3 range were generated by using a 1.5 mg/mL solution of the technical grade TCP metered into the atomizer at a 0.7 mL/min flow rate. All other conditions for the aerosol system were the same as described in breakthrough. For storage, seven sets of six samples each were collected from the aerosol system at sampling rates ranging from 0.8 to 1.0 L/min. The individual sampling rates for each sample were determined both before and after collection with the sample tube in line. A 25-min collection period was used for all seven sets of storage samples. Since there was some variability in the air concentration of TCP generated in the aerosol chamber from one sample set to the next, one sample from each set was selected as a control and analyzed immediately. Of the remaining total of 35 samples generated for storage, three samples were discarded because of clogged sampling orifices, two were randomly selected for zero-day storage and analyzed immediately, and the remaining 30 samples were randomly split into equal-sized ambient and refrigerated groups for storage. All of the stored samples were capped and stored in the dark either at ambient conditions on a laboratory shelf or in a refrigerator at 5°C prior to analysis. Since variability in the air concentration of TCP occurred during the generation process, the percent recoveries reported below in Table 4.7. for each sample are determined relative to the concentration of TCP of the control sample for that set. A plot of percent recovery of TCP versus days stored for both ambient and refrigerated samples is shown in Figures 4.7.1. and 4.7.2.

Table 4.7.1.
Storage Samples

(set 1) sample	mg/m³	days stored	% recovery
1	1.28	control	100
2	1.13	10 (A)[1]	88.3
3	1.34	17 (R)[2]	105
4	1.30	7 (R)	102
5	1.33	14 (A)	104
6	1.32	0	103
$\bar{X}$	1.28		
CV	0.061		

(set 2) sample	mg/m³	days stored	% recovery
1	1.25	control	100
2	1.23	3 (R)	98.4
3	1.35	14 (R)	108
4	1.34	7 (R)	107
5	1.27	14 (A)	102
6	1.33	10 (A)	106
$\bar{X}$	1.295		
CV	0.039		

(set 3) sample	mg/m³	days stored	% recovery
1	1.46	control	100
2	1.51	10 (R)	103
3	1.50	7 (A)	103
4	1.46	0	100
5	1.48	10 (A)	101
6	1.52	17 (A)	104
$\bar{X}$	1.49		
CV	0.017		

(set 4) sample	mg/m³	days stored	% recovery
1	1.46	control	100
2	1.51	3 (A)	103
3	1.50	17 (A)	103
4	1.42	14 (A)	97.3
5	1.56	17 (A)	107
6	1.52	7 (A)	104
$\bar{X}$	1.50		
CV	0.033		

(set 5) sample	mg/m³	days stored	% recovery
1	1.64	control	100
2	1.62	7(R)	98.8
3	1.61	10 (R)	98.2
4	1.63	3 (A)	99.4
5	1.61	3 (R)	98.2
$\bar{X}$	1.62		
CV	0.008		

(set 6) sample	mg/m³	days stored	% recovery
1	1.66	control	100
2	1.64	10 (R)	98.8
3	1.63	7 (A)	98.2
4	1.72	3 (A)	104
5	1.62	14 (R)	97.6
$\bar{X}$	1.65		
CV	0.024		

(set 7) sample	mg/m³	days stored	% recovery
1	1.67	0	100
2	1.64	3 (R)	98.2
3	1.64	14 (R)	98.2
4	1.67	17 (R)	100
5	1.70	17 (R)	102
$\bar{X}$	1.66		
CV	0.015		

[1]ambient conditions [2]refrigerated conditions

4.8. Comparative sampling data

Comparative sampling of a TCP/PCP atmosphere was performed with XAD-7 sampling tubes and both isopropanol and 0.1 N NaOH bubblers. The test atmosphere was generated with the submicron aerosol generation system described in Section 4.5. A 1.8 mg/mL technical grade TCP solution in isopropanol containing PCP was metered into the atomizer at a 0.7 mL/min flow rate for comparative sampling with IPA bubblers. For the NaOH bubbler tests, the TCP concentration was reduced to 1.2 mg/mL.

Four sets of six samples were collected from the test atmosphere over several days using three XAD-7 sampling tubes and three IPA bubblers. Sampling rates were 1 L/min and the sampling time was 48 min for each set. The XAD-7 tubes were analyzed according to the procedure described in this method and the IPA bubblers were analyzed simultaneously by direct injection. The results are listed in Table 4.8.1.

The overall average recovery of the XAD-7 tubes relative to the IPA bubblers was 99% for TCP. For PCP, the average recovery was 115%. PCP comprised approximately 17% of the total weight of PCP and TCP sampled. This is approximately the content of the PCP contaminant in the TCP technical grade standard injected into the system.

Table 4.8.1
Comparison Sampling with IPA bubblers and XAD-7 Tubes

sample set 1	mg/m³ (TCP)		mg/m³ (PCP)	
XAD-7 - 1	1.25		0.26	
- 2	1.26	$\bar{X}$ = 1.26	0.33	$\bar{X}$ = 0.30
- 3	1.28		0.31	
IPA - 1	1.19		0.22	
- 2	1.25	$\bar{X}$ = 1.22	0.24	$\bar{X}$ = 0.23
- 3	1.21		0.24	
sample set 2	**mg/m³ (TCP)**		**mg/m³ (PCP)**	
XAD-7 - 1	1.29		0.30	
- 2	1.24	$\bar{X}$ = 1.26	0.29	$\bar{X}$ = 0.29
- 3	1.24		0.28	
IPA - 1	1.31		0.26	
- 2	1.33	$\bar{X}$ = 1.33	0.26	$\bar{X}$ = 0.26
- 3	1.34		0.27	

continued

Table 4.8.1 (continued)

sample set 3	mg/m³ (TCP)		mg/m³ (PCP)	
XAD-7 - 1	1.48		0.33	
- 2	1.60	$\bar{X}$ = 1.53	0.21	$\bar{X}$ = 0.29
- 3	1.50		0.32	
IPA - 1	1.68		0.32	
- 2	1.60	$\bar{X}$ = 1.62	0.30	$\bar{X}$ = 0.30
- 3	1.58		0.29	
sample set 4	**mg/m³ (TCP)**		**mg/m³ (PCP**	
XAD-7 - 1	1.23		0.22	
- 2	1.37	$\bar{X}$ = 1.34	0.29	$\bar{X}$ = 0.29
- 3	1.41		0.36	
IPA - 1	1.32		0.24	
- 2	1.30	$\bar{X}$ = 1.31	0.25	$\bar{X}$ = 0.24

For the comparative sampling with NaOH bubblers, four sets of six samples were sampled from the test atmosphere over several days using four XAD-7 tubes and two 0.1 N NaOH bubblers. The flow rate of the bubblers was approximately 0.5 L/min to avoid frothing of the collection solution. The flow rates for the XAD-7 tubes were varied from 0.2 to 1 L/min. Sampling times for each set ranged from 93 to 232 min. The XAD-7 samples were analyzed according to the procedure described in this method and the 0.1 N NaOH bubblers were analyzed directly by HPLC following acidification with concentrated HCl. The results are reported in Table 4.8.2. The overall average recovery of the XAD-7 tubes relative to the 0.1 N NaOH bubblers was 89% for TCP. For PCP the average recovery was 100%.

Table 4.8.2.
Comparison Sampling with NaOH Bubblers and XAD-7 Tubes

set 1	sampling rate (L/min)	TCP (mg/m³)		PCP (mg/m³)	(sampling time 93 min)
XAD-7-1	0.920	0.63		0.17	
-2	0.213	0.62	$\bar{X}$ = 0.62	0.16	$\bar{X}$ = 0.17
-3	0.197	0.56		--	
-4	1.02	0.68		0.19	
NaOH -1	0.480	0.73		0.17	
-2	0.490	0.67	$\bar{X}$ = 0.70	0.18	$\bar{X}$ = 0.175

continued

Table 4.8.2. (continued)

set 2	sampling rate (L/min)	TCP (mg/m^3)		PCP (mg/m^3)	(sampling time 152 min)
XAD-7-1	0.902	0.70		0.15	
-2	0.212	0.67	$\bar{X}$ = 0.675	0.17	$\bar{X}$ = 0.16
-3	0.196	0.66		0.16	
-4	0.980	0.67		0.15	
NaOH -1	0.475	0.78		0.18	
-2	0.470	0.66	$\bar{X}$ = 0.72	0.17	$\bar{X}$ = 0.175

set 3	sampling rate (L/min)	TCP (mg/m^3)		PCP (mg/m^3)	(sampling time 232 min)
XAD-7-1	0.905	0.77		0.17	
-2	0.211	0.84	$\bar{X}$ = 0.78	0.17	$\bar{X}$ = 0.17
-3	0.203	0.75		0.17	
-4	0.199	0.76		0.16	
NaOH -1	0.466	0.76		0.15	
-2	0.445	0.82	$\bar{X}$ = 0.79	0.18	$\bar{X}$ = 0.165

set 4	sampling rate (L/min)	TCP (mg/m^3)		PCP (mg/m^3)	(sampling time 202 min)
XAD-7-1	0.896	0.70		0.17	
-2	0.211	0.67	$\bar{X}$ = 0.68	0.14	$\bar{X}$ = 0.16
-3	0.196	0.70		0.16	
-4	0.201	0.65		0.15	
NaOH -1	0.448	0.80		0.18	
-2	0.63	0.78	$\bar{X}$ = 0.79	0.15	$\bar{X}$ = 0.165

4.9. Reproducibility

Six sample tubes, each spiked with 3 µL of a 10.75 mg/µL (79% pure) TCP standard in methanol. This resulted in a sample loading of 25.5 µg. The samples, along with a blank sample, were capped, labeled and submitted to an OSHA laboratory service branch, with a draft copy of this method, for analysis. The samples were analyzed approximately two weeks after preparation by a chemist not associated with this evaluation. The percent recoveries for the six samples were: 97.3, 99.9, 90.5, 93.5, 92.0, and 90.5. The average is 94.0 and the standard deviation is 3.9.

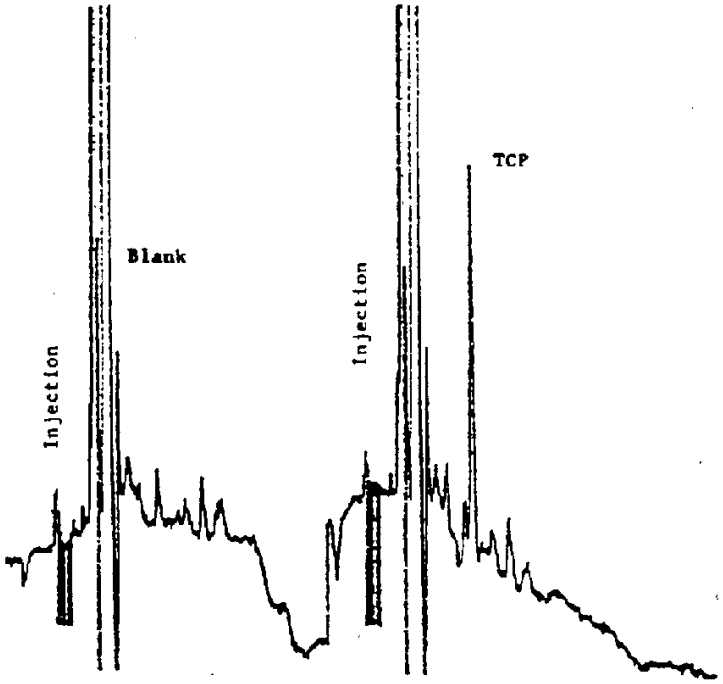

Figure 4.1. Detection limit for TCP.

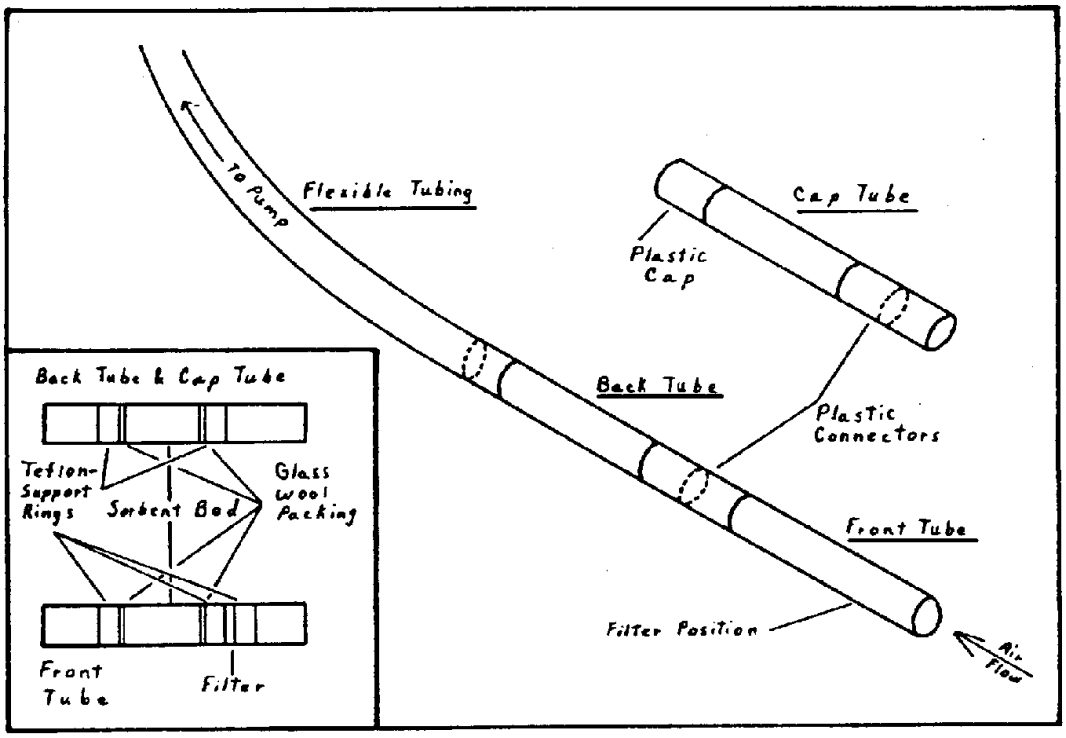

Figure 4.2. Sampling device for tetrachlorophenol.

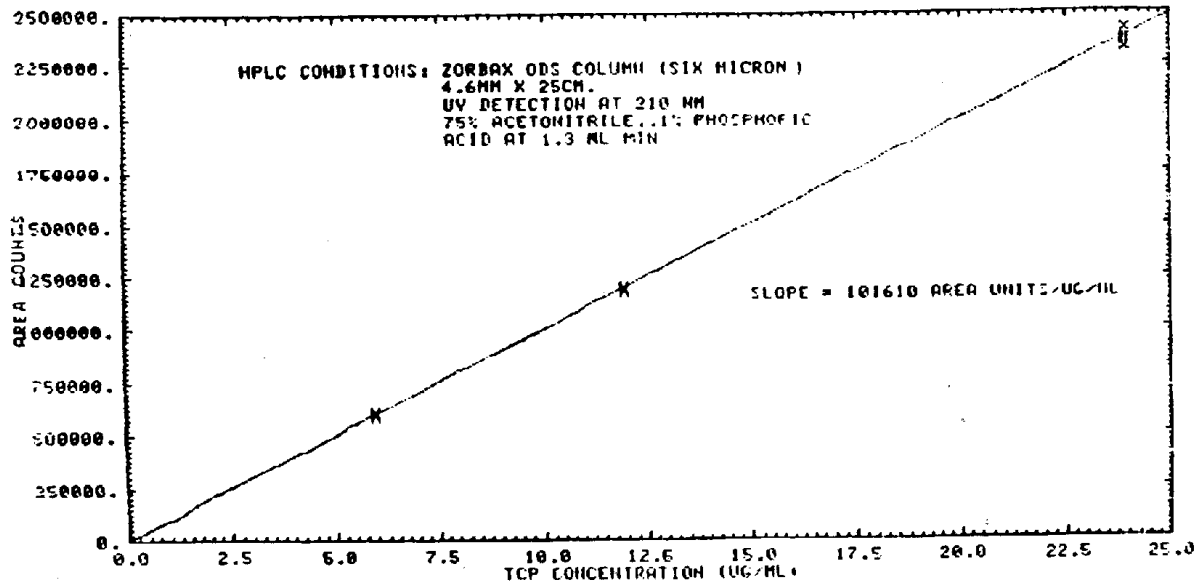

Figure 4.4. Calibration curve for TCP.

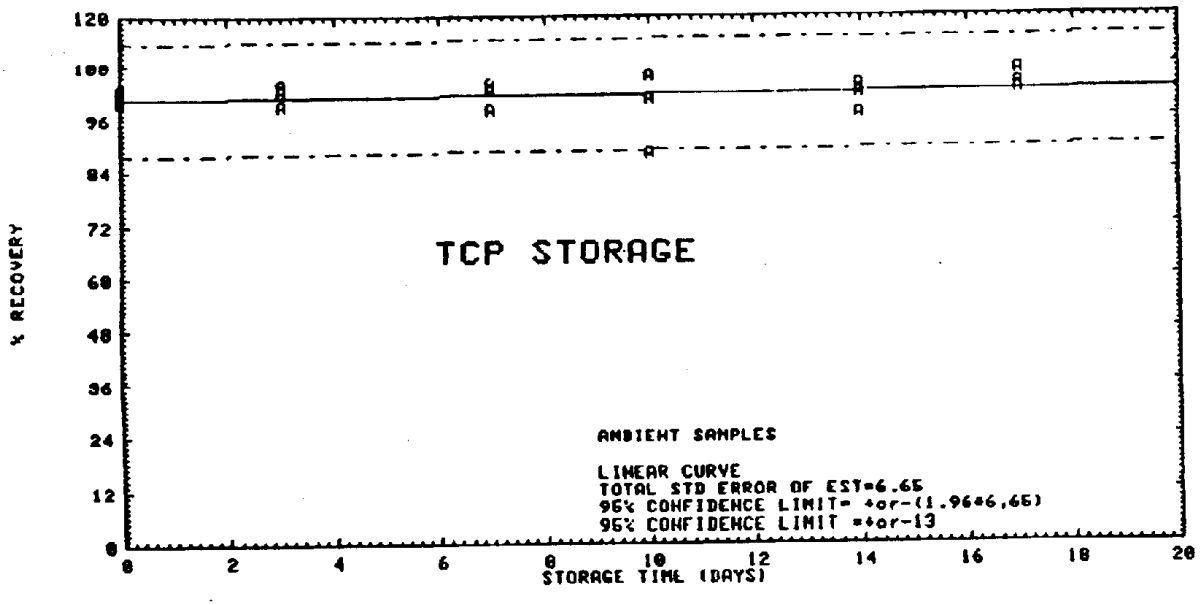

Figure 4.7.1. Ambient storage for TCP.

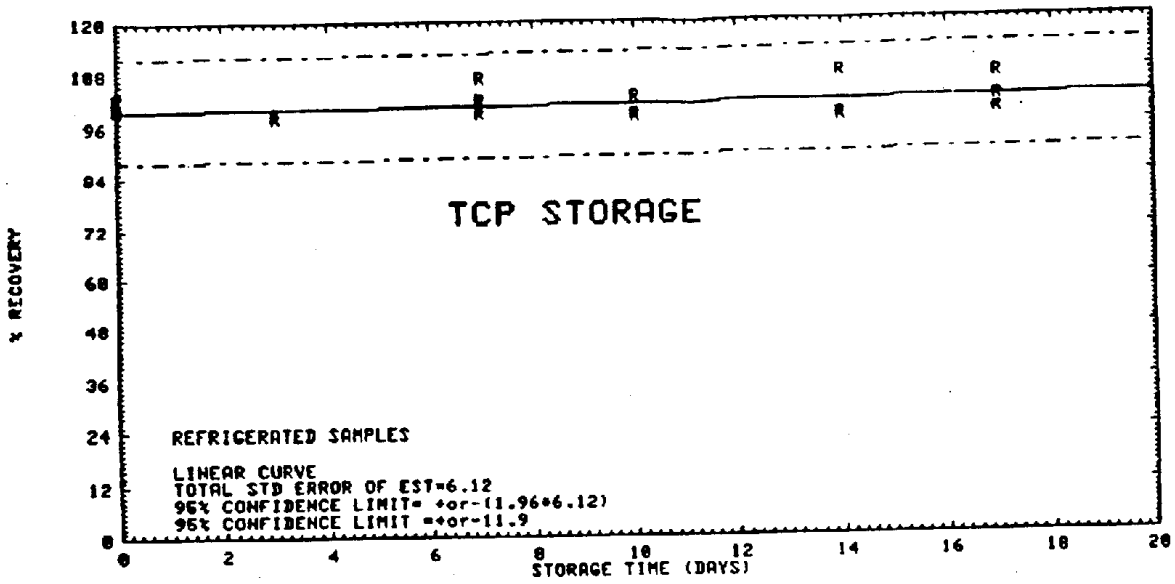

Figure 4.7.2. Refrigerated storage for TCP.

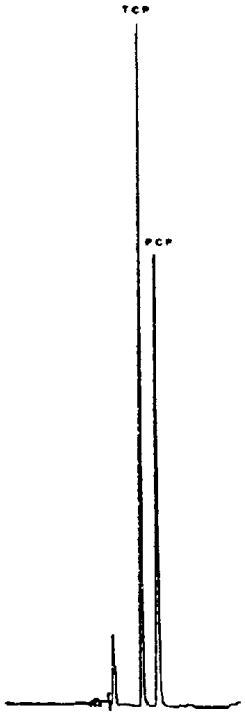

Figure 4.9. Analysis of TCP in presence of PCP.

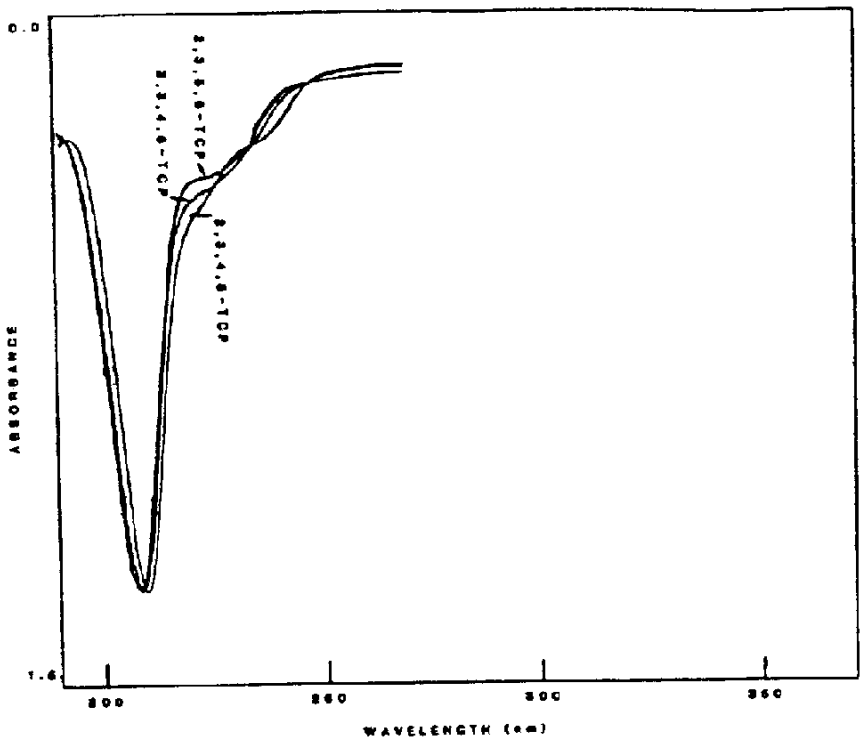

Figure 4.10. UV scan of TCP isomers in mobile phase solution.

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