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Determination of Pentachlorophenol Volatilized from Wood via Collection on Silica Gel

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The wood-preserving properties of pentachlorophenol (PCP) have been well-known for over forty years (CARSWELL & NASON 1938; CARSWELL & HATFIELD 1939). In general, wood treated with PCP has been limited to exterior applications. In recent years, PCP-treated wood products have been generally accepted for interior use. Because of the vapor pressure of PCP (0.00017 mm Hg at 20°C) (CARSWELL & NASON 1938), concern has been expressed about the levels of personnel exposure to PCP from treated wood in confined areas for prolonged periods of time.

Air concentrations of PCP have been measured in laboratory experiments (BENCZE 1963; HOBEN et al. 1976) and in treated buildings (CASARETT et al. 1969; GEBEFUGI et al. 1979). Impingers containing either 2,2,4-trimethylpentane, water, potassium hydroxide solution, or potassium carbonate solution were used to collect the airborne PCP. The method of analysis was either spectrophotometry or electron-capture gas chromatography (GC-ECD) after derivatization of the PCP. Collection apparatus composed of bulky glassware containing corrosive or flammable solvents severely limits the applicability to personnel or on-site monitoring.

In this paper we describe a convenient sampling method for PCP in air by employing silica gel collection tubes, desorption with benzene, and direct analysis by GC-ECD. Validation data demonstrating the collection and desorption efficiencies are presented. A simple laboratory reactor is described for use in collecting PCP volatilized from treated wood. Since this wood is treated with a technical grade of PCP which is a mixture of PCP and tetrachlorophenol (TeCP), both chlorophenols are measured in the air. In addition, various heavy metal and quaternary ammonium salt solutions were tested for effectiveness in suppressing the volatility of chlorophenols from treated wood.

MATERIALS AND METHODS

Instruments and Materials. Gas chromatograph: Varian 3700 with ^{63}Ni electron-capture detector. Gas chromatographic columns: 80 cm x 2 mm ID glass column packed with 1% SP 1240 DA on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA) or 20 m x 0.32 mm fused silica capillary coated with SE-54 0.25 µm film thickness (J&W Scientific, Inc., Rancho Cordova, CA). Portable battery operated pump capable of operating at flowrates of 50-200 mL/min (Sipin Model SPI, Anatole J. Sipin Co., Inc., New York, NY). Silica gel tubes, glass, containing 520 mg front section and 260 mg back section (Cat No. 226-15 Environmental Compliance Corp., Venetia, PA). Mechanical shaker, reciprocating (VWR Scientific Inc., Midland, MI).

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Laboratory reactor to generate and collect volatilized PCP constructed of a glass tube 3.5 cm (ID) x 45 cm fitted with 34/45 standard taper joints at both ends which reduce to 6 mm glass tubing. Diagram is shown in Figure 1.

Reagents. Benzene, methanol, (distilled in glass, Burdick and Jackson Laboratories, Muskegon, MI). Acetic acid, hydrochloric acid (J. T. Baker Co., Phillipsburg, NJ). Pentachlorophenol, 99% (Aldrich Chemical Co., Milwaukee, WI). Pentachlorophenol, technical (DP-2, Dow Chemical Co., Midland, MI). 2,3,4,6-Tetrachlorophenol (Pfaltz and Bauer, Inc., Stamford, CT). Penta WR, a formulation containing ~22% PCP in petroleum distillate and marketed by Chapman Chemical Co., Memphis, TN.

Gas Chromatographic Conditions. Packed column: column temperature, 150°C; injection port temperature, 200°C; detector temperature, 320°C; carrier gas, nitrogen; flowrate, 25 mL/min. Capillary column: column temperature, 190°C; injection port temperature, 230°C; detector temperature, 320°C; carrier gas, nitrogen; linear velocity, 17 cm/sec; split ratio, 35:1; injection volume, 2 µL.

Experimental.

The determination of the collection and desorption efficiencies for TeCP and PCP on silica gel was accomplished through the use of four different procedures. The phase equilibrium recovery method (PERM) (DOMMER & MELCHER 1978), the dynamic U-tube system (SEVERS et al. 1978), and the modified U-tube system (MELCHER et al. 1978) have been described previously. The fourth technique involved direct injection of known amounts of solutions of the chlorophenols onto the front sections of silica gel tubes, passage of air through the tubes, and finally desorption and analysis. The desorption of the chlorophenols from silica gel was accomplished by placing the silica gel in a 15-mL glass screw-cap vial, adding 200 µL of water and 10 mL of benzene or dry ice-chilled diethyl ether, and placing the mixture on a mechanical shaker for 2 h. The front and back sections of the silica gel tube were desorbed and analyzed separately. If PCP were found in the back section, breakthrough would have occurred and would indicate an invalid collection procedure.

Initial experiments were designed to determine a typical amount of PCP actually retained by various pieces of wood (southern yellow pine or white pine) after treatment with PCP solutions. The procedure employed for extracting PCP from the wood substrate has been reported previously (LAMPARSKI et al. 1980). The measurement of TeCP and PCP was accomplished by GC-ECD under either of the conditions described previously by using an external standard calculation method.

The laboratory reactor to generate and sample the air in contact with the PCP-treated wood is shown in Figure 1. Wood samples (90-200 cm^2 surface area) were placed in the reactor tube, silica gel tubes were placed on the entrance and exit ports, and laboratory air was pumped through the system at 175 mL/min. The system was allowed to equilibrate for 16 h, after which the silica gel tubes were replaced and known volumes of air were pulled through the collection tube for 2- to 4-h periods. Consecutive triplicate

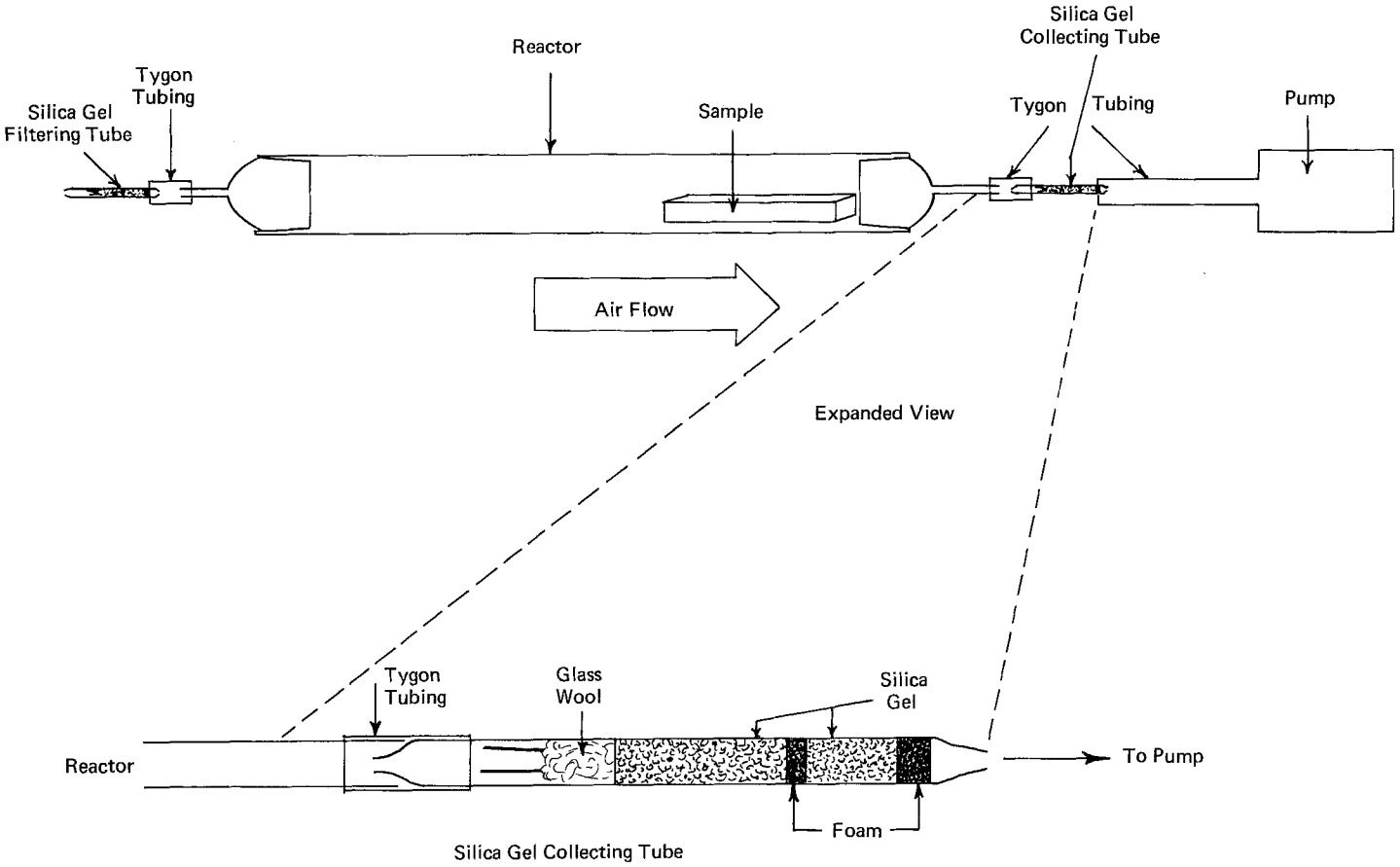

Figure 1. PENTACHLOROPHENOL VOLATILIZATION REACTOR

samples were collected over a 9-h period to ensure that a steady state condition had been achieved. The silica gel collection tubes were desorbed with benzene and analyzed by GC-ECD.

Two species of wood were treated with PCP solutions for subsequent experiments to determine both volatility and countertreating efficiency. Initial work was done on spruce wafers (5 x 3.5 x 0.5 cm) which had been pressure treated with a solution of technical PCP in either dichloromethane or mineral spirits according to the procedure described previously (LAMPARSKI et al. 1980). Later experiments were performed on southern yellow pine sapwood stakes (23 x 2 x 2 cm) which had been dip-treated in a 5% solution of technical PCP in mineral spirits and air-dried. This wood and treatment would typify the interior of a wooden dwelling.

The spruce wafers were pressure treated with aqueous solutions of the countertreating agents shown in Table 1. Countertreating the pine was accomplished by brush application of the aqueous solutions. The countertreated samples were air dried prior to volatilization experiments. Countertreated wood samples of equal surface area to PCP-treated samples were placed in the volatilization reactor and equilibrated, sampled, and analyzed as described above.

RESULTS AND DISCUSSION

The data obtained from the collection and desorption efficiency experiments are summarized in Table 2. Although this rigorous validation procedure was not implemented for 2,3,4,6-TeCP, preliminary experiments with 2,3,5,6-TeCP and 2,3,4,5-TeCP indicate that the overall recovery should be similar to that observed for PCP. Since each of the four recovery techniques demonstrated recoveries greater than 90% for PCP and since neither PCP nor TeCP were observed in any of the back sections of the collection tubes, it was judged that the values observed for PCP in collected air samples were indicative of the concentrations actually present.

During the determination of recoveries using the PERM technique, poor results were observed when air was not sampled through the silica gel tube. These poor recoveries could be improved either by sampling $\sim$ 10 L of air through the tube prior to desorption or by the addition of 200 µL of water to the desorption solvent. It is presumed that the water (vapor or liquid) deactivates the silica gel so that the PCP will be more readily desorbed by the solvent. Alternatively, a stronger solvent, such as 1% methanol in benzene, may be used. In general, the amount of water vapor present in the air sampled for PCP determinations should be sufficient for the deactivation of the silica gel, but the addition of a constant amount in the desorption solvent will ensure complete recovery.

The amount of PCP incorporated into the wood matrix during treatment was dependent upon the type of treatment and to a lesser extent the type of wood used. These data are shown in Table 3. The average PCP concentration is significantly lower for the dip-treated southern yellow pine than the pressure-treated southern yellow pine samples. The dip-treated white pine exhibited a greater PCP uptake than the dip-treated southern yellow pine.

Table 1. Chlorophenol Concentrations Volatilized from Countertreated Spruce and Pine

	Spruce, $\mu g/m^3$		Pine, $\mu g/m^3$	
Countertreatment	TeCP	PCP	TeCP	PCP
cupric acetate and silver acetate	2.1	12	--	--
zinc acetate and silver acetate	2.0	21	--	--
zinc acetate	1.0	10	--	--
magnesium acetate	2.3	12	33	58
didecyl dimethyl ammonium chloride	3.5	10	18	23
n-alkyl dimethyl benzyl ammonium chloride[a], octyl decyl dimethyl ammonium chloride, dioctyl dimethyl ammonium chloride, and didecyl dimethyl ammonium chloride	3.0	13	24	47
tetramethyl ammonium chloride	2.2	78	--	--
cetyl trimethyl ammonium chloride	1.2	6	--	--
N-(3-chloro-2-hydroxypropyl)-trimethyl ammonium chloride	2.4	45	--	--
methyldodecylbenzyl trimethyl ammonium chloride	2.8	14	--	--
n-alkyl dimethylbenzyl ethylbenzyl ammonium chloride[a]	1.8	6	--	--
bis(2-hydroxyethyl) dimethyl ammonium chloride	5.5	125	--	--
1-hydroxyethyl-1-benzyl-2-alkyl imidazolinium chloride	3.0	11	--	--
N-cetyl-N-ethylmorpholinium ethosulfate	3.5	15	--	--
dioctyl dimethyl ammonium chloride	6.4	22	--	--
n-alkyl dimethyl ethylbenzyl ammonium cyclohexylsulfamate[b]	1.6	9	-- --	-- --
didecyl dimethyl ammonium chloride and magnesium acetate	--	--	6	11

[a] n-alkyl group consists of a mixture of 40% C_{12}, 50% C_{14}, 10% C_{16}

[b] n-alkyl group consists of a mixture of 50% C_{12}, 30% C_{14}, 17% C_{16}, 3% C_{18}

Table 2. Recovery of Pentachlorophenol via Silica Gel Adsorption

µg Added	Recovery method	No. of samples	Mean % recovery and S.D.[a]
7 - 33	U-tube	6	89.7 ± 4.9
0.3 - 1	Modified U-tube	5	98.8 ± 2.9
0.1 - 1500	PERM	49	99.9 ± 7.4
0.2 - 33	Direct Injection	63	99.4 ± 6.3

[a] Standard deviation

Table 3. PCP Observed in Treated Wood

Wood type	Treatment	No. of samples	PCP range, %	Ave., %
Southern Yellow Pine	Dip	26	0.05-0.3	0.14
Southern Yellow Pine	Pressure	30	0.52-1.50	1.04
White Pine	Dip	19	0.31-1.80	0.89

Table 4. Chlorophenol Concentrations Volatilized From PCP-Treated Spruce and Pine

PCP Formulation		TeCP, $\mu g/m^3$	PCP, $\mu g/m^3$
None		N.D. (1)	1.5
None		N.D. (1)	1.5
None		3	3.0
5% PCP in CH_2Cl_2 (spruce)		35	580
		22	370
		30	430
		30	260
		24	330
		17	300
	Mean	26	380
5% PCP in mineral spirits (spruce)		40	290
		15	150
		40	240
		25	140
		20	140
		19	150
	Mean	26	180
20% Penta WR (~5% PCP) in mineral spirits (spruce)		110	350
		91	280
		26	140
		25	110
	Mean	64	220
20% Penta WR (~5% PCP) in mineral spirits (southern yellow pine)		270	240
		250	260
		130	160
		260	280
	Mean	230	240

Samples of southern yellow pine and spruce were subjected to the volatilization experiments using the apparatus shown in Figure 1. Reagent blanks were collected and analyzed before the experimentation began. These values are the first two listed in Table 4. After the final experiment using treated wood, a third reagent blank was collected to ensure that the system was sufficiently clean to permit measurement of countertreated samples. This blank showed low levels of TeCP and PCP. Although these concentrations may not have been significant compared to the levels in the wood, additional cleaning reduced levels of TeCP and PCP to the previous blank levels.

The results of the volatilization experiments conducted on the countertreated samples are summarized in Table 1. Although not all of the countertreatments investigated provided the same degree of reduction of volatilized PCP, comparison of Tables 1 and 4 shows that in every case a significant reduction was effected.

Conclusion.

We have described and validated a convenient procedure for the collection and measurement of airborne tetrachlorophenol and pentachlorophenol. This adsorption technique, employing silica gel collection tubes, is applicable to personnel or on-site monitoring; and the analysis procedure, consisting of desorption and direct analysis by electron capture gas chromatography, is amenable to automation for processing large numbers of samples.

In an application of the collection procedure, we have described experiments measuring the levels of TeCP and PCP volatilized from PCP-treated wood. PCP concentrations observed in our laboratory reactor at ambient temperature at ~50% humidity varied from 100-600 $\mu g/m^3$. After a brush application of ~5% solutions of many different quaternary ammonium salts, a significant reduction in the amount of volatilized PCP was observed. These preliminary experiments were intended to provide a screening procedure to test a wide variety of possible countertreatments. Further, more detailed experiments with a limited number of countertreatments and studying the lifetimes of such countertreatments are underway and will be reported at a later time.

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