SUPERCRITICAL FLUID EXTRACTION AND GAS CHROMATOGRAPHIC ANALYSIS OF PENTACHLOROPHENOL AND OIL FROM TREATED WOOD POLES

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Summary

A supercritical fluid extraction method has been evaluated for pentachlorophenol (PCP) and oil from a single treated-wood sample. Extraction efficiencies were determined for different fluid densities between 0.15 and 0.85 g/mL and temperatures of 40, 60, 80 and 120°C. Carbon dioxide and 2% methanol-modified CO_2 were used for these studies. The maximum extraction efficiency on a 0.3 g sample was found to be 75 and 90% for PCP and oil, respectively, at 120°C and 0.65 g/mL. The amount of organic solvent for class-fractionation of compounds was substantially reduced using a Florisil© adsorbent trap for selective recoveries. A new analytical method for the simultaneous determination of PCP and oil in a single gas chromatographic run is also presented which would provide more information about the composition of the oil. The potential of this method will be discussed.

1. Introduction

Pentachlophenol (PCP) was commercially introduced in Canada in the early 1950s as a chemical preservative to replace the creosote treatment of wood poles and leave them with a much cleaner appearance and a greater environmental acceptance. The PCP is dissolved in a diesel-type oil mixture (CAN/CSA-080.201-M89) and pressure-injected in the wood. The oil is not merely the carrier for PCP but also provides water-repellency characteristics and facilitates pole climbing by reducing wood hardness (Caroll-Hatch International, 1994). These properties have made it a popular wood treatment process for public utility poles. However, a pole in service is subjected to different climatic elements such as heat or rain, which tend to make the impregnated oil bleed into the immediate environment, carrying part of the dissolved PCP along with it. In order to tightly monitor the extent of this migration, analytical methods that are fast, easy, versatile and reliable are indispensable.

Several methods have in fact been developed for the analysis of pentachlorophenol in various matrices such as wood, soil or water. Early methods applied to wood samples were based on determining the chlorine content rather than the PCP molecule. They included X-ray fluorescence (Kressbach, Tang and Walker, 1987) and neutron activation analysis (NAA) (Slau and Meyer, 1973). Later, other methods were developed for the specific determination of PCP using high-performance liquid chromatography (e.g., Liu, Kapila and Nam, 1993; Goewie *et al.*, 1986), gas chromatography (e.g., Lee, Peart and Hong-You, 1992; Abrahamsson and Xie, 1984) and flow injection analysis (Rodriguez-Alcala, Yanez-Sedeno and Polo Diez, 1988). Few methods have considered determination of oil together with PCP from a single wood or soil sample (Sylvestre *et al.*, 1991; Besner *et al.*, 1994). In the simplest case, acetylated-PCP and oil are quantified by gas chromatography/electron capture detector (GC/ECD) and by Fourier transform infrared (FTIR) spectroscopy, respectively (Besner *et al.*, 1994). However, most of the methods cited so far use conventional organic-solvent extraction techniques (e.g. Soxhlet and sonication). They are known to be very tedious methods, which can often take several hours to be completed, and use large quantities of solvent that call for adequate disposal. Recently, supercritical fluid extraction (SFE) has proven to be an attractive alternative to conventional techniques for the recovery of organic analytes such as chlorinated pesticides and polyaromatic hydrocarbons from soils, sediment and wood (Lee, Peart and Hong-You, 1992; Hawthorne, 1990; Van der Velde, de Haan and Liem, 1992; Camel, Tambuté and Caude, 1993; Snyder *et al.*, 1992). In all cases, SFE has revealed itself to be a faster, less labor-intensive approach allowing a substantial reduction of extraction solvents.

This paper presents the development of a method for determining pentachlorophenol and oil from treated-wood samples based on supercritical fluid extraction. Overall recoveries are reported for extraction performed with pure CO_2 and methanol-modified CO_2. In order to increase the selectivity of the analysis, two approaches were studied: the first involves the use of solid sorbent phases, while the second consists of a gas chromatographic method that allows simultaneous analysis of PCP and oil from a single injection. The latter avoids the need to separate both analytical constituents prior to instrumental analysis.

2. Methodology

Theoretical considerations. The phase diagram of Figure 1 shows the relationship between the gaseous, liquid and solid states of a substance as a function of temperature and pressure. When the conditions of a gas-liquid system at equilibrium are modified toward the critical point (T_c and P_c), the higher pressure compresses the gas and the higher temperature expands the liquid. Their density will therefore change up to a point where they are both identical and no further distinction can be made between the gas and the liquid: the substance becomes a supercritical fluid. In these conditions, the fluid possesses properties that fall between those of liquids and gases, as can be seen in Table I. It follows that their use for the extraction of analytes from solid matrices can be beneficial in many ways compared to liquid extraction. First, extractive penetration is faster because of the higher diffusivity and lower viscosity of the fluids. As a result, quantitative SFE can be achieved in 10-60 min, whereas liquid extraction is usually performed over several hours, even days. Second, although the solvating power of these fluids is closer to that of liquids, their solvent strength can easily be adjusted by controlling the temperature and pressure parameters and, hence, the density. Third, many supercritical fluids are gases at ambient temperature. This property makes the concentration step easier and facilitates direct coupling of SFE with analytical instrumentation. Lastly, most of the supercritical fluids have the advantages of being relatively inert, non-toxic and inexpensive. Among the fluids listed in Table II, the choice for SFE is often restricted to CO_2 for practical and safety reasons (Westwood, 1993).

Instrumentation. A Hewlett-Packard unit (Palo Alto, CA), model 7680A, equipped with a reciprocating pump module, a controlled heated zone, a variable restrictor nozzle and a solid adsorbent trap was used for the supercritical fluid extractions. Figure 2 shows a schematic of the system. The nozzle of the restrictor was heated at 45°C during extractions and the trap was cooled cryogenically to -5°C with liquid CO_2. The initial tests were done using a trap filled with stainless steel beads. The SFE unit also has a second pump module to recover the trapped analytes with organic solvent. All extractions were performed in dynamic mode sweeping the equivalent of ten thimble volumes to ensure complete transfer of the analyte to the trap, compensating for dead volume. Extraction times varied from 5 to 15 min, depending on the density of the fluid. The extraction parameters were controlled by MS-Windows based SFE software, version 2.0, from Hewlett-Packard, running on an Intel-compatible 486 computer.

The PCP and oil were initially analyzed according to a procedure based on Besner *et al.*(1994) with the ultrasonication step replaced by SFE. The instruments used were: 1) a GC from Hewlett-Packard, model 5890, equipped with a ^{63}Ni ECD, an autosampler and a 25 m x 0.32 mm I.D. x 0.52 µm HP-Ultra 2 (cross-linked 5% phenyl methyl silicon) fused silica capillary column, and 2) a Nicolet 520 FTIR spectrometer (Nicolet Instrument, Madisson, WI). Later, the simultaneous analysis of PCP and oil was achieved with a Hewlett-Packard 5890 Series II equipped with an electronic pressure control board, an on-column injector, a flame ionization detector (FID) and a ^{63}Ni ECD. The capillary column was an HP-Ultra 1 (cross-linked 100% methyl silicon), 25 m x 0.32 mm x 0.17 µm, and the oven was programmed from 55 to 280°C at 20°C/min with the final temperature held for 8 min. The helium carrier gas was held constant at 1.5 mL/min by enabling constant flow mode. The on-column injector temperature was set 3°C above the column temperature by oven track mode. Automated injections were made with a HP 7673B equipped with a special tapered needle syringe for 0.32 mm on-column injections (Hewlett-Packard). Gas chromatographic instrumental control, acquisition and data processing were achieved using HPCHEM software for Windows (Hewlett-Packard), version 3.2.1, on an Intel-based 486 computer.

Chemicals. The helium (99.95%) carrier gas and 5% argon/methane ECD auxiliary gas were from Union Carbide (Toronto, Ont.). The liquid CO_2 and methanol-modified CO_2 (2% v/v) used for supercritical fluid extractions were SFE/SFC grade (Scott Specialty Gases, Plumsteadville, PA). The pentachlorophenol was purchased from Aldrich (Milwaukee, WI) and acetic anhydride from BDH (Darmstadt, Germany). The methanol, trichlorotrifluoro-methane (Freon©113), and hexane were all purchased from Fisher (Fair Lawn, NJ). The PCP solvent used is manufactured by Shell Canada (Sarnia, Ont.) under the label 645-900. Demineralized water obtained from a Milli-Q ultrafiltration system (Millipore, Bedford, MA) was used for all experiments. Solid-phase extraction (SPE) tubes were purchased from Supelco (Oakville, Ont.), and contained 1 g of 40 μm bonded or non-bonded phase silica packing material. The normal phase tubes tested were silica, magnesium silicate (Florisil©), aminopropyl, cyanopropyl and diol, which were treated before use with 6 mL of Freon©113. The phenyl reversed-phase tube used was treated with 6 mL of methanol.

Wood sample preparation. A stock of wood powder was prepared by chipping a PCP-treated red pine pole using an industrial shredder. The chips were ground in a Retsch SM1 (Brinkman Instruments, Rexdale, Ont.) equipped with a 2-mm mesh bottom sieve to obtain a powder which was further homogenized. The PCP and oil concentrations of this reference sample were established as 5.8 mg/g and 75 mg/g, respectively, using an alternative procedure (Besner *et al.*, 1994). For the SFE extraction experiments, samples of about 0.3 g of wood powder were weighed and put in 1.5-mL stainless steel extraction thimbles. During extraction, the analytes were collected on a cooled stainless steel bead packing trap. After supercritical fluid extraction, the trapped analytes were washed out either with methanol or Freon©113 into 1.5-mL screw-cap vials with a teflon-lined septum. The whole extraction and rinsing process is automated. Aliquots from these vials were then handled as described in Besner *et al.* (1994) for derivatization and instrumental analysis of PCP and oil.

3. Results and Discussion

Supercritical fluid extraction. Supercritical fluid extraction of PCP and oil from treated-wood samples was first investigated by adjusting the CO_2 solvating power. The temperature was fixed and the pressure varied to obtain the desired density for each extraction. Efficiencies were evaluated by comparing the recovered quantities with the established content in the reference sample. From Figure 3, it is obvious that PCP and oil are both extracted using pure supercritical CO_2 but with variable efficiencies. The recovery increases with the density of the fluid until it reached a plateau. A maximum of 65% PCP was recovered as compared to 75% for oil. The temperature also favorably influenced the extraction efficiency: equivalent quantities are extracted but at lower densities. However, the plateau is the same for all temperatures, except in the case of PCP at 120°C, which can be explained by interruption of some PCP and active polar site interactions. It is possible to retrieve the remaining bonded PCP fraction by adding a polar organic modifier to the CO_2 to compete with the matrix active sites.

Figure 4 shows the PCP and oil recovery values using 2% methanol in CO_2 as a polar organic modifier. The density was varied as in the preceding experiments and the extraction efficiencies were compared with the values obtained for pure CO_2 at 40°C and 120°C. At the lowest temperature, both compounds benefit from the presence of methanol in the extracting fluid. Pentachlorophenol has the greater increase in efficiency, namely 38% more at 0.65 g/mL. Overall, the maximum efficiency is 75% for PCP and 90% for the oil. However, there seems to be a decrease in efficiency toward the higher densities. It is especially visible at 120°C for PCP but also for oil at densities higher than 0.4 g/mL. This can be explained by the fact that the organic modifier itself can elute the target analytes from the trap during the SFE step, resulting in a low apparent recovery (Mulcahey, Hedrick and Taylor, 1991). The elution can be minimized by lowering the trap temperature or using a solvent trapping technique.

When comparing the behavior of pentachlorophenol and oil, it is important to keep in mind that oil is a complex mixture of branched and chained alcanes, aromatic and naphthenic hydrocarbons. In terms of boiling points, the mixture ranges from C_8 to C_{24} n-alcanes. Each species of this mixture therefore behaves differently under a particular supercritical fluid condition. Thus, when observing the extraction efficiency for oil, as in Figs. 3 and 4, it should be mentioned that this represents the net tendency of all oil constituents. Nevertheless, it is obvious that treated-wood samples can be extracted by SFE for PCP and oil determination, which considerably reduces the amount of organic solvent required, as compared to sonication and Sohxlet extractions. However, the analytes still need to be partitioned by a class-fractionation method prior to analysis because they are coextracted at all conditions studied. A selective recovery step from the SFE or a different instrumental method based on the selective detection of the compounds would even further simplify the PCP and oil analysis procedure. Both approaches are presented below.

Selective adsorbent recovery. In the experimental conditions used so far, both PCP and oil are recovered from the trap in a single solvent rinsing step. The inert stainless steel bead packing used to collect target analytes can be replaced by solid sorbent resin such as those used for SPE. Increased selectivity can thus be obtained from the solvent rinse recovery step after SFE, provided that the trap material exhibits interaction with one of the components. The analytes need only to be eluted one after the other with the appropriate solvent. In order to identify an adequate SPE adsorbent phase for selective recovery, several tube types were spiked with a solution of PCP and oil. The analytes were then eluted successively by rinsing the tubes, first with a portion of the same solvent used for spiking, methanol or Freon© 113, then with a solvent of reversed polarity. Figure 5 shows the selectivity of the recoveries. Some adsorbents, such as the amino, were too polar, making the PCP impossible to recuperate, while others such as cyano eluted all the target analytes at once. Among the SPE tubes tested, the Florisil© adsorbent seems to be the best candidate, since it allows unequivocal PCP and oil partition.

An SFE trap was filled with Florisil© adsorbent in order to perform selective recovery extractions of treated-wood samples using pure CO_2 at 120°C and 0.65g/mL. Methanol-modified fluids were rejected for these tests as they result in a selectivity loss due to the formation of a solvent film on the packing material. To avoid any crossovers, the trap was rinsed with three portions of 1.5 mL Freon©113 followed by three portions of 1.5 mL of methanol. Each portion was then analyzed as usual for PCP and oil. The resulting recoveries are shown in Figure 6, where it can be seen that, as expected, the oil is transferred in the Freon©113 without any trace of PCP. However, an oil fraction behaving like polar components is coeluted with PCP when methanol is used. This fraction, associated with the degraded oil components, does not interfere with PCP determination on the GC-ECD. Therefore, SFE of treated-wood samples followed by selective recovery from a Florisil© adsorbent trap completely eliminates the fractionation step necessary when existing GC and FTIR methods are used.

Dual-detector gas chromatography. Another approach that can be adopted to eliminate the PCP and oil fractionation step is through the use of a selective gas chromatographic detection method from a single sample injection. A schematic of the system is seen in Figure 7. Mass discrimination of heavy constituents is avoided by on-column injection of 0.5 µL of SFE wood extract. The split flow ratio from the column to the detectors is about 1:10 in favor of the FID. For better chromatographic peak shape and detection limit, PCP was derivatized from the wood extract as described in Besner *et al.*(1994). Typical chromatograms from a PCP/oil standard are shown in Figure 8. The ECD chromatogram is similar to what was observed previously but it is now possible to have an FID signal of the oil constituents at the same time. The n-alcane series is clearly visible, especially at higher retention times, along with major naphthalene derivative components. The baseline rise is due to the unresolved complex mixture of other hydrocarbons present in the sample. Oil quantitation is calculated from the area integrated under the chromatographic signal measured between 5 min and 30 min. Information not provided by the former FTIR method can thus be retrieved from the chromatographic pattern.

4. Conclusion

Pentachlorophenol and oil can be extracted from a treated-wood sample by supercritical fluid CO_2. Further simplification of the method is possible by selectively recovering the analytes from a Florisil© adsorbent trap. A new chromatographic method has been developed for the determination of PCP and oil in a single analysis using two types of detectors. This method provides additional information on the oil constituents which could be used for chromatographic pattern recognition.

5. Acknowledgments

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6. Literature

Abrahamsson, K. and J. Xie, 1983. *J. Chromatogr.*, **279**, 199-208.

Besner, A., R. Gilbert, P. Tétreault, L. Lépine and J.-F. Archambault, 1994. *Anal. Chem.*, accepted for publication.

Camel, V., A. Tambuté and M. Caude, 1993. *J. Chromatogr.*, **653**, 83-91.

Caroll-Hatch International, 1994. *Value Assessment of the Canadian Pressure Treated Wood Industry*, p.13.

Goewie, C.E., R.J. Berkhof, F.A. Maris, M. Treskes and U.A.TH. Brinkman, 1986. *Intern. J. Anal. Chem.*, **26**, 305-318.

Hawthorne, S.B., 1990. *Anal. Chem*, **62**, 633A-642A.

Kressbach, J.N., J. Tang and J.E. Walker, 1987. *Proc. of the 83rd Annual Meeting of the American Wood-Preservers' Association.*

Lee, H.B., T.E. Peart and R.L. Hong-You, 1992. *J.Chromatogr.*, **605**, 109-113.

Liu, M.H., S. Kapila and K.S. Nam, 1993. *J. Chromatogr.*, **639**, 151-157.

Mulcahey, L.J., J.L. Hedrick and L.T. Taylor, 1991. *Anal. Chem.*, **63**, 2225-2232.

Rodriguez-Alcala, M., P. Yanez-Sedeno and L.Ma. Polo Diez, 1988. *Talanta*, **35:8**, 601-604.

Slau, J.F. and J.A Meyer, 1973. *Wood Sci.*, **6:1**, 19-21.

Snyder, J.L., R.L. Grob, M.E. McNally and T.S. Oostdyk, 1992. *Anal. Chem.*, **64**, 1940-1946.

Sylvestre, P., J. Hawari, C. Beaulieu and R. Mayer, 1991. *Contaminated Soil Samples from Wood Preserving Plants in Québec: Extensive Analysis and Search for Remediation Technologies*, Conference Presented at the 1991 American Chemical Society, Division of Environmental Chemistry, New-York, August 25-30.

Van der Velde, E.G., W. de Haan and A.K.D. Liem, 1992. *J. Chromatogr.*, **626**, 135-143.

Westwood S.A., 1993. *Supercritical Fluid Extraction and its use in Chromatographic Sample Preparation*, CRC Press, Boca Raton, Fl.

Table I. Typical physical property values for gases, supercritical fluids and liquids.

	Density (g/mL)	Viscosity (mPa s)	Diffusion coefficient (10^4 m^2 s^{-1})
Gas	1 x 10^{-3}	(1-3) x 10^{-2}	0.1-0.4
Supercritical fluid	0.2-0.9	(1-9) x 10^{-2}	(0.2-0.7) x 10^{-3}
Liquid	0.6-1.6	0.2-3	(0.2-2) x 10^{-5}

Table II. Critical temperature, pressure and density of selected supercritical fluids (from Westwood, 1993).

Fluid	T_c (°C)	P_c (atm)	ρ_c (g/mL)
CO_2	31.3	72.9	0.47
N_2O	36.5	72.5	0.45
SF_6	45.5	37.1	0.74
NH_3	132.5	112.5	0.24
H_2O	374	227	0.34
n-C_4H_{10}	152	37.5	0.23
n-C_5H_{12}	197	33.3	0.23
Xe	16.6	58.4	1.10
CCl_2F_2	112	40.7	0.56
CHF_3	25.9	40.6	0.52

T_c : critical temperature
P_c : critical pressure
ρ_c : critical density

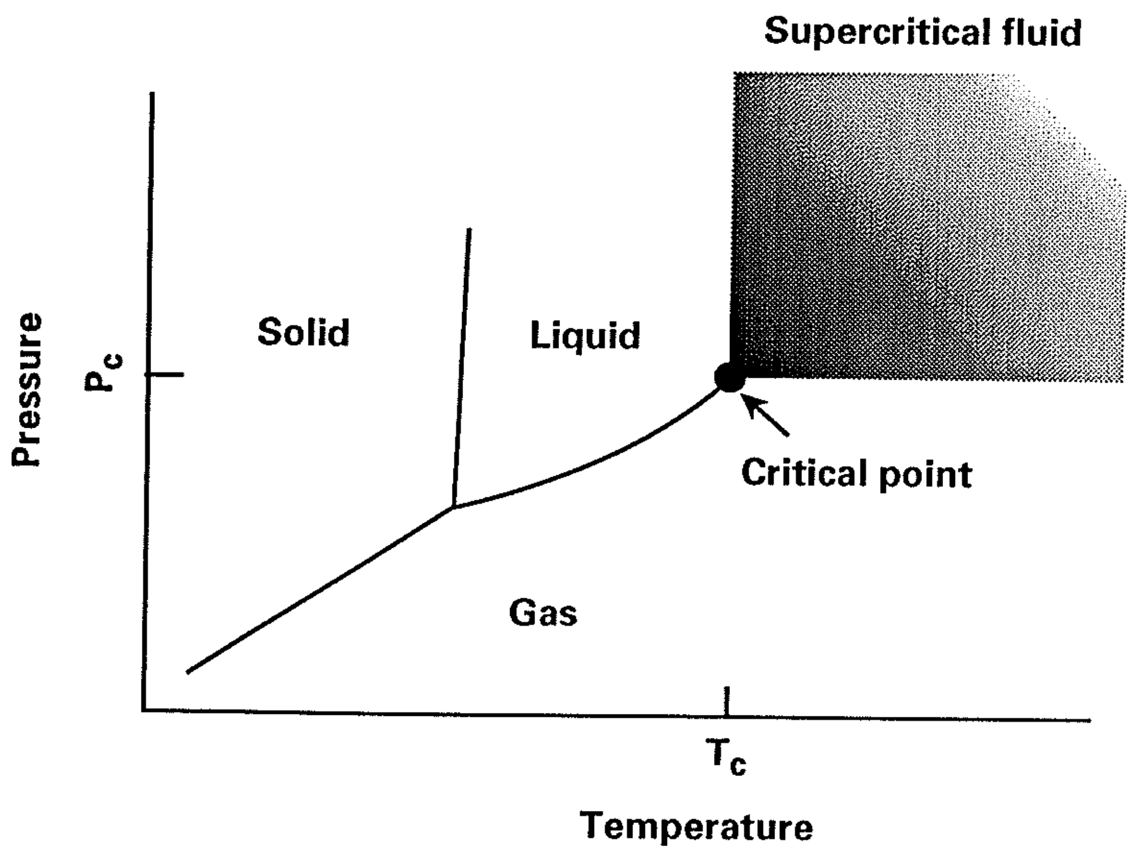

Figure 1. Phase diagram of a pure substance as a function of pressure and temperature.

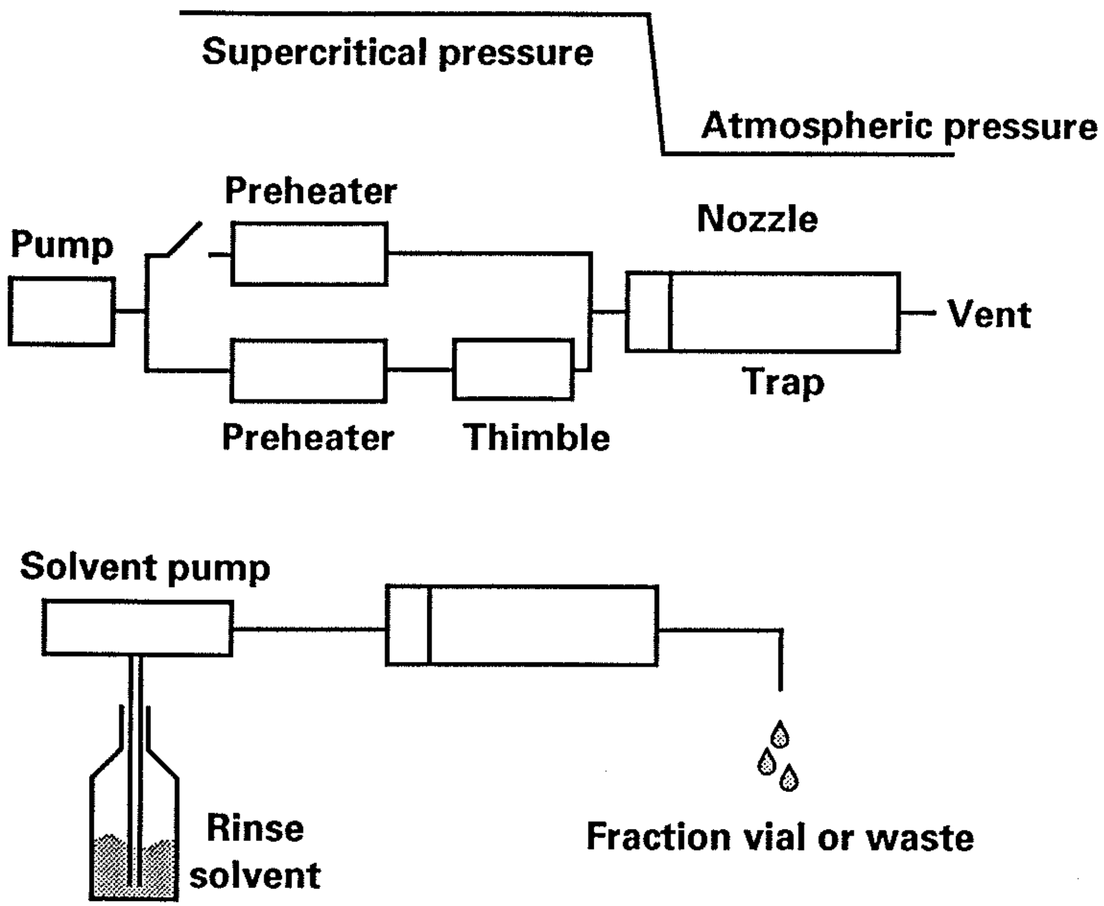

Figure 2. Schematic diagram of the SFE system.

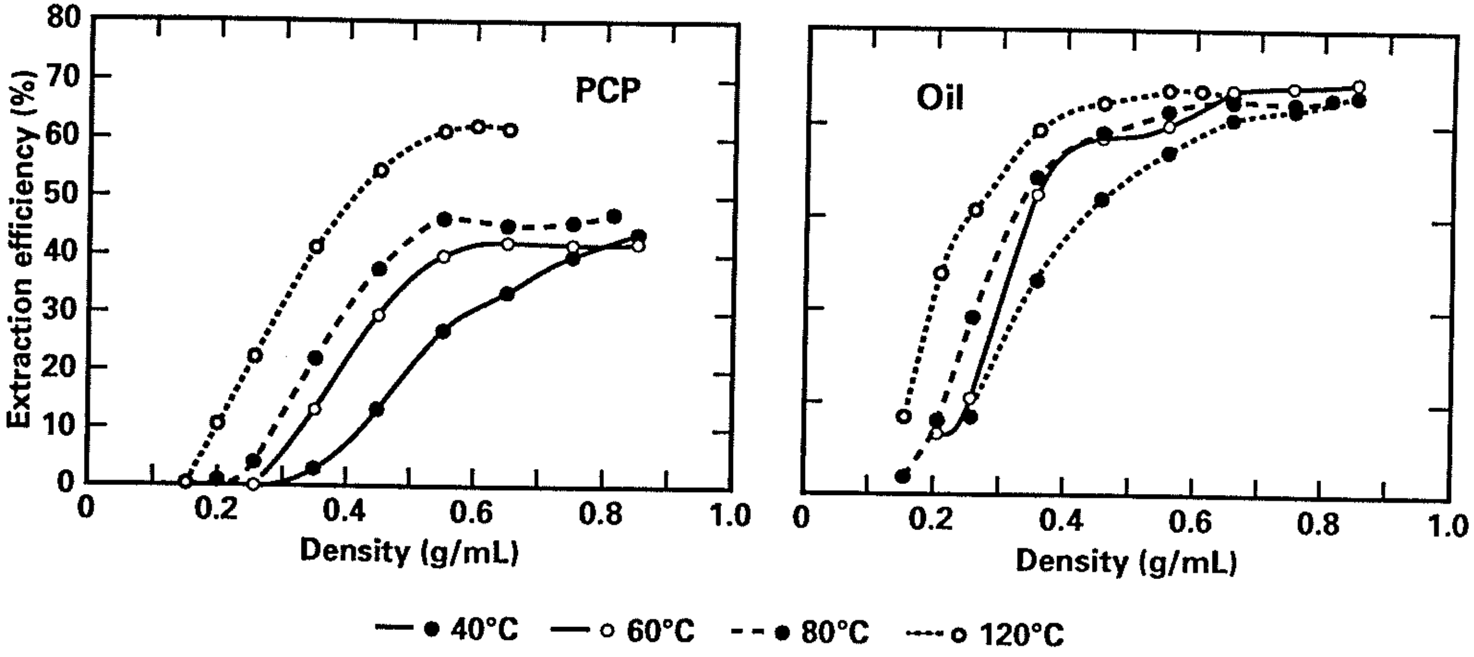

Figure 3. Extraction efficiency of pure CO_2 from treated wood samples at different densities and temperatures.

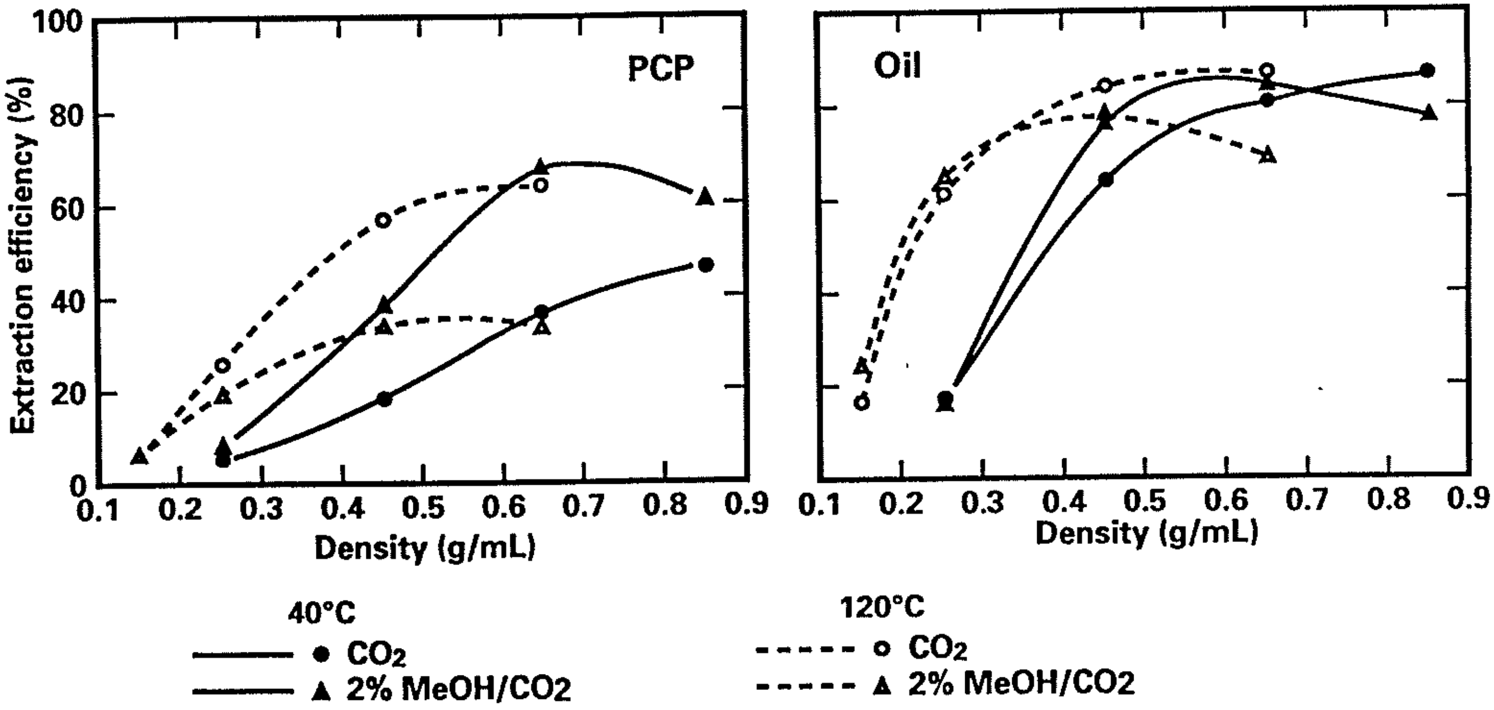

Figure 4. Extraction efficiency of 2% methanol/CO_2 from treated wood samples at different densities and temperatures.

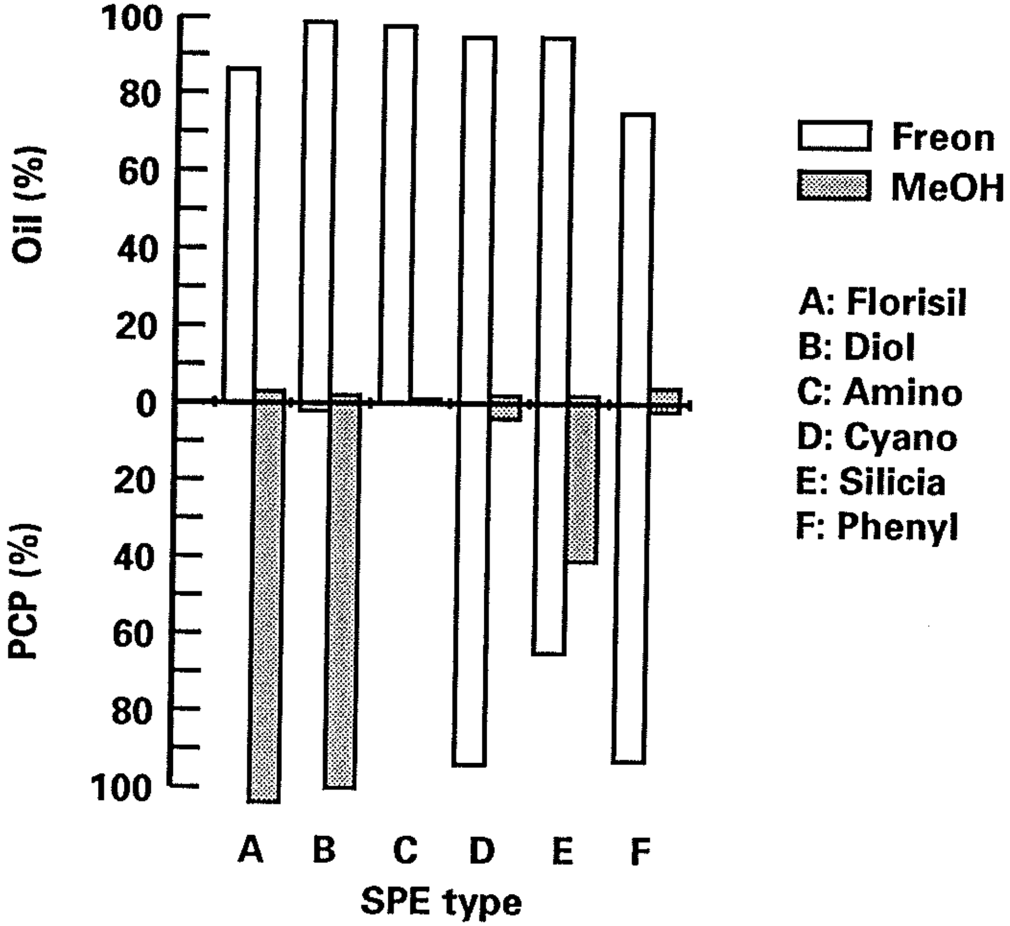

Figure 5. Selective recovery of PCP and oil from selected SPE packing materials.

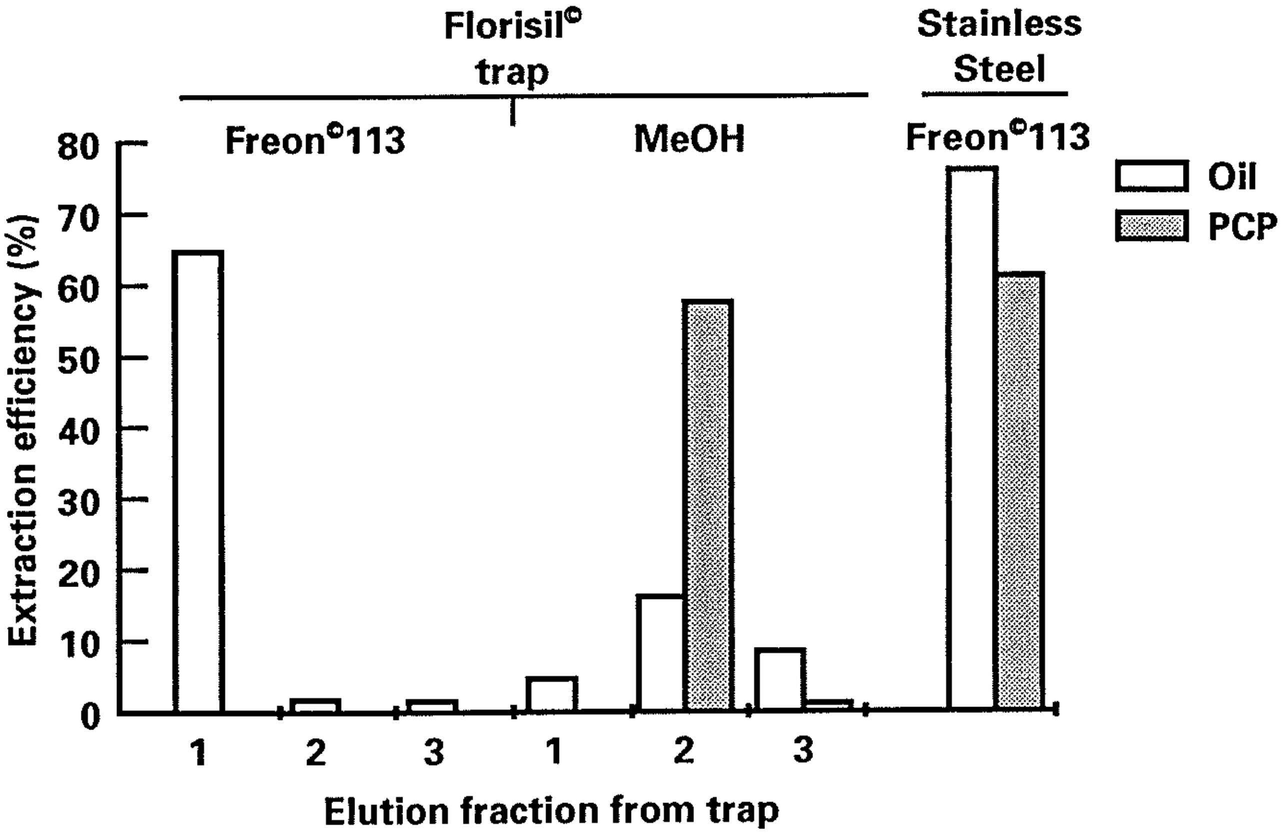

Figure 6. Selectivity of a Florisil adsorbant trap for SFE of treated wood.

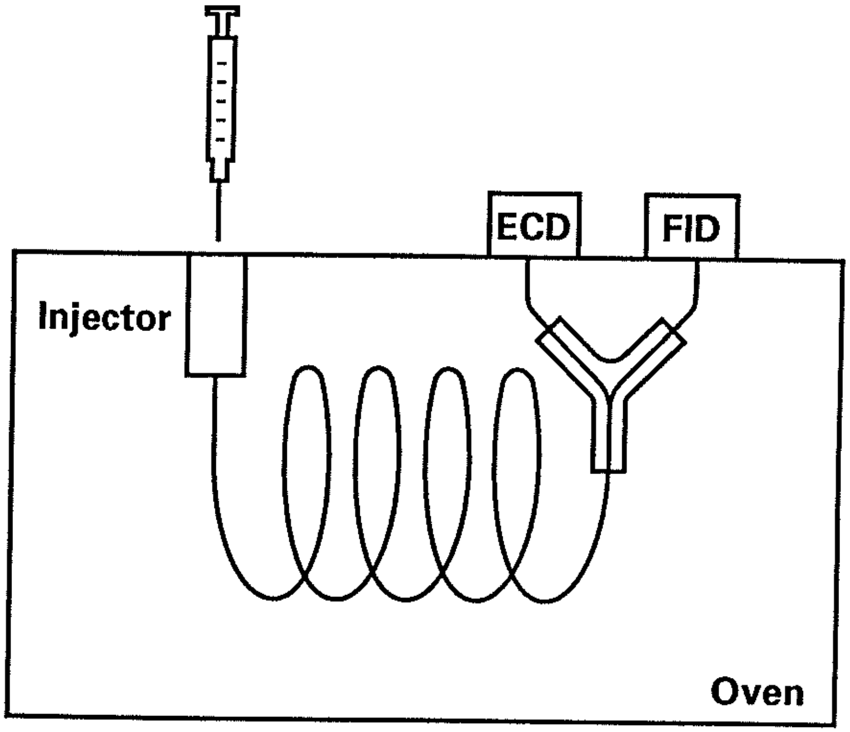

Figure 7. Schematic diagram of the dual-detector chromatographic system.

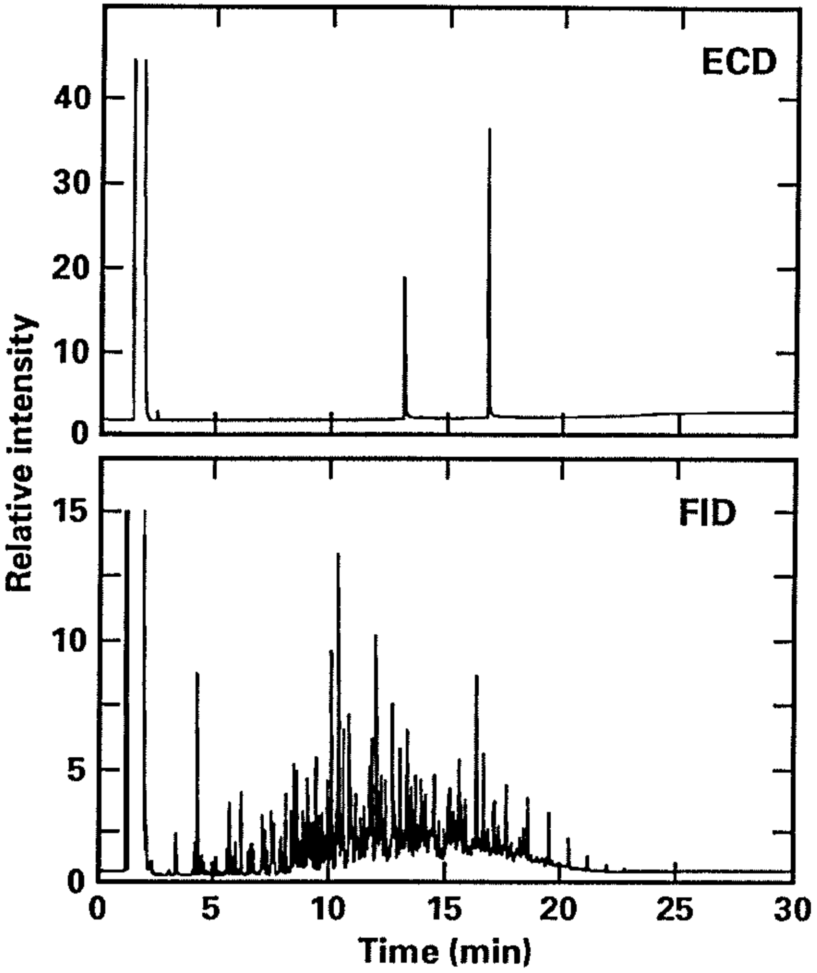

Figure 8. Simultaneous ECD and FID chromatograms from a PCP/oil standard.