Chemical methods have been implemented to measure levels of polychlorodibenzo-p-dioxins, and polychlorodibenzofurans in pentachlorophenol solutions used in the Boulton treatment process. When normalized against the pentachlorophenol (PCP) concentration, the octachlorodibenzo-p-dioxin level was 34% higher in the recirculating PCP solution than in the fresh PCP solution, and in the sludge it was 90% higher. A smaller concentration increase was observed for the heptachlorodibenzo-p-dioxin in the recirculating solution, but a similar increase was observed in the sludge.

The determination of polychlorodibenzo-p-dioxins in pentachlorophenol and wood treatment solutions

J. LAMBERTON, D. GRIFFIN, B. ARBOGAST, R. INMAN and M. DEINZER
Environmental Health Sciences Center, Department of Agricultural Chemistry, Oregon State University, Corvallis, Oregon 97331

introduction

The United States production of technical pentachlorophenol (PCP) is around 50 million pounds per year. Most of the PCP is used in the wood products industry for protection against insects and fungus. Technical PCP may also be used as a slimicide, bactericide, and molluscacide, and it has frequently been added to paints for its biocidal properties.

Analysis of technical PCP shows that numerous contaminants are present in fairly high concentrations. These contaminants arise during the manufacturing process. The actual PCP content in the technical product ranges between 85%-90%. Tetrachlorophenol and trichlorophenol are present at 5%-12% and < 0.1% respectively. In addition there are chlorinated dibenzo-p-dioxins, dibenzofurans, diphenyl ethers, and a variety of hydroxypolychlorodiphenyl ethers. The extremely toxic 2,3,7,8-tetrachloro-p-dioxin has not been detected in PCP.

The presence of these impurities in technical PCP raises concerns about their possible health hazards. The acute toxicity of octachlorodibenzo-p-dioxin (OCDD) (LD50 < 1000 mg/kg) is much less than that of PCP (LD50 27-100 mg/kg) itself. The acute toxicity of hexachlorodibenzo-p-dioxin isomers (HCDD), however, has been reported to be about 100 μg/kg or about 10,000 times as toxic as OCDD. Teratogenic response in the pregnant rat is in the range of 100 μg/kg/day for HCDD, while OCDD showed embryo toxicity at 500 mg/kg/day and no teratogenic effects at this level.

Dioxins are readily formed from chlorophenols under basic conditions at elevated temperatures. Dioxins can also form from phenols: a) at elevated temperatures in the absence of base; b) from the corresponding copper salts; and c) under conditions which give rise to free radical species. The wood products industries frequently treat wood with 5% PCP solutions at elevated temperatures in the Boulton drying process. We were concerned whether these conditions, possibly under the catalytic influence of metallic surfaces, had caused the formation of additional quantities of chlorinated dioxins.

In the course of this study we implemented methods from the literature for determining polychlorodibenzo-p-dioxins (Clx-DBDIs) and polychlorodibenzofurans (Clx-DBFs), polychlorodiphenyl ethers (Clx-DPEs) in technical PCP as well as in solutions of PCP used in the treatment processes of wood.
products. The actual samples analyzed came from wood treatment plants and consisted of the starting and recirculated treating solutions which were 5% technical PCP in aromatic solvents. Sludge from the bottom of the recirculation tank was also analyzed. Ion exchange separation of PCP and hydroxy poly-chlorodiphenyl ethers (HO-Clx-DPEs) from the neutrals (Clx-DBDs, Clx-DBFs, and Clx-DPEs) prevented confusion between the HO-Clx-DPEs and Clx-DBDs during gas chromatographic analyses.

methods and materials

instrumentation

Because of a high level of interference from the aromatic solvents and wood residues in the solutions and sludge, a standard GLC system was not adequate. Therefore, a specially modified gas chromatographic system that could handle the solvents and various extractants was used for the analyses of the various fractions (Figure 1). A Varian Aerograph model 204 equipped with a Dohrman Division of Envirotech microcoulometric detector system consisting of a C-200-B microcoulometer, T-300-S titration cell, and S-400 furnace (Figure 2) was used. A precolumn vent assembly was installed in the gas chromatograph oven for venting the solvent (Figure 3). The inlet N\textsubscript{2} and exit valves were Clippard Minimatic No. MJV-2 electric solenoid operated valves. The solenoids were controlled by a Magnechart No. W 399ACQ SOX-2 delay timer adjustable from 0.1 to 2 minutes with a 10-turn 650 K\textOmega potentiometer. A delay of 1.75 min was normally used. The specially designed precolumn vent system allowed for venting of chlorinated solvents and
petroleum distillates from the gas chromatographic system during analysis for the chlorinated contaminants.

A 4’ × 1/8” glass column or a 5’ × 1/8” stainless steel column with 7% Dexsil® 300 GC (Dexsil Chem. Corp.) on 100/120 mesh acid-washed Chromosorb® W AW (Johns-Manville Corp.) was used for GLC analyses. The column oven was programmed from 200-350°C at 8°C/min with an initial 5 min program delay.

Mass spectral analyses were performed on a Varian CH-7 GC-MS with a System Industries 150 data system. The samples were introduced into the MS via a single stage glass jet separator from a Varian 1200 gas chromatograph using the columns previously described. The identity of the Cl<sub>x</sub>-DBDs, Cl<sub>x</sub>-DBFs, and Cl<sub>x</sub>-DPEs were confirmed by comparison to published spectra and spectra of authentic samples. The presence of HO-Cl<sub>x</sub>-DPEs was confirmed by GC-MS using the methyl ethers formed from the reaction with diazomethane.

Concentrations of Cl<sub>6</sub>-DBDs, Cl<sub>7</sub>-DBDs and Cl<sub>8</sub>-DBD were also determined by mass spectrometry. This was achieved by integrating the molecular ions of the Cl<sub>x</sub>-DBDs and comparing them to the integrated area of the Cl<sub>x</sub>-DBD molecular ion reconstructed gas chromatogram. This method is referred to as Selected Ion Summation Profile Analysis (SISPA).

**sample preparation**

Several methods commonly used to extract Cl<sub>x</sub>-DBDs in PCP were evaluated. An ion exchange method was adapted with some modifications. In order to reuse the ion exchange columns, the phenolic material was stripped from it, and the column was regenerated.

Samples were obtained from two local wood treatment plants. Several small pieces of the solid technical PCP weighing about 1 kg were ground in a ball mill, and 5 gm of the resultant powder was dissolved in 100 mL of benzene. Five milliliters of this solution or of the 5% PCP wood treatment solutions were used for analyses. Sludge samples (5-10 gm) were
<table>
<thead>
<tr>
<th>Sample</th>
<th>GC-MS Method</th>
<th>Microcoulometric Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clₓ-DBD</td>
<td>Clₓ-DBF</td>
</tr>
<tr>
<td></td>
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<td>Clₓ-DBF</td>
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</tbody>
</table>

*Concentrations are normalized against PCP content of the solutions.

Dissolved in 100 mL of methanol and filtered by suction through a Whatman no. 42 filter. The filter was rinsed with 100 mL of benzene and 200 mL of 1:1 benzene : methanol. This extract was evaporated to less than 100 mL and dried over anhydrous Na₂SO₄. The solution was then evaporated to dryness and dissolved in 5 mL benzene:methanol (1:1).

Dowex 21K ion exchange resin was converted to the hydroxide ion form using 100 mL 1N NaOH. Before loading each sample, the column was washed with 150 mL water, 100 mL methanol, and 50 mL benzene:methanol (1:1). The column was regenerated between samples using the same procedure but included a 400 mL 0.24 M HCl in benzene:methanol (1:1) and 1N NaOH washes before the water rinse. Five milliliters or less of sample solution noted above was added to a 100 mm × 19 mm column bed of the resin. The column was eluted with 75 mL of benzene:methanol (1:1). The collected benzene:methanol fraction containing the neutral compounds was then evaporated on a steam bath.

The residue from technical PCP was dissolved in 5 mL benzene without further treatment, but samples from the sludge or aromatic solvent required additional cleanup before column chromatography. These samples were dissolved in 25 mL benzene and shaken with 25 mL concentrated H₂SO₄. The benzene layer was removed by pipette, and an additional 25 mL benzene was used to reextract the acid. The benzene extracts were washed twice with 50 mL distilled water. Ten milliliters of 2% NaCl and 2 mL isopropanol were added after shaking to break the emulsion. The extracts containing aromatic solvent were then concentrated to approximately 5 mL while the sludge extract was concentrated to 2 mL. One-half of the extracts was placed on top of a 30 gm (19 mm I.D.) column, slurry-packed with activated alumina (Fisher A-540; 4 hr. at 450° C). Approximately 0.3 mL benzene and 10 mL pentane were used to rinse the sample onto the column. The column was eluted with 400 mL of pentane, 100 mL of 10% benzene in pentane, and 400 mL of 25% benzene in pentane. The ethers and aromatic petroleum solvent were found in the first two fractions, and the dioxins and furans were in the 25% benzene fraction.

**standards**

Standards for Clₓ-DBDs and Clₓ-DBDs were not available, so Cl₁-DBD standards were used. Temperature programs were set such that the retention times of the analytes of interest were as close as possible to the Cl₁-DBD standard. A correction factor was applied to account for the differences in percentage chlorine. The ratios of the molecular weight of Clₓ-DBD divided by eight to the molecular weights of Clₓ-DBD divided by “x” were used. Using the ratio method described above, comparison of a 1,2,3,4-Cl₁-DBD standard to Cl₁-DBD in the 100-200 ng range was within 5% of the expected value.

**results and discussion**

Complete separation of the neutral Clₓ-DBDs from the phenolic HO-Clₓ-DPEs which was required for quantitative gas chromatography was achieved by ion exchange chromatography. The Clₓ-DBDs were eluted from the Dowex 21K
column with 25 to 50 mL 1:1 benzene:methanol. When aromatic solvents were present some tailing occurred, and a total of 75 mL of solvent was used to assure complete elution of Clx-DBDs.

The separation of the Clx-DPEs from the Clx-DBDs and Clx-DBFs in the technical PCP was achieved by alumina column chromatography. Pentane containing 10% benzene was used as an eluting solvent to remove the Clx-DPEs. The gas chromatogram showed that very little Cl7-DBDs or Cl8-DBDs were present in this fraction. The absence of a molecular ion cluster based at (m/e 388) resulting from Cl8-DBDs in this fraction confirms that these compounds were also retained by the alumina column. Elution of the dioxins and furans was achieved subsequently by increasing the polarity of the solvent system to 25% benzene in pentane. The recovery for the analytical procedure was measured using Cl8-DBD and found to be 85%. The limit of sensitivity for the method is 10 ppb.

Since the microcoulometric detector response is based on the amount of chlorine present, the levels of chlorinated components were determined by comparing their response with that observed for Cl8-DBD. When PCP was measured against this standard the results obtained were in good agreement with those in which PCP was used as the standard.

Analysis of Clx-DBDs in PCP samples which were obtained from two Boulton wood treatment plants are shown in Table I. All the contaminants were measured relative to PCP. The chromatograms showed the presence of three Cl6-DBDs, two Cl7-DBDs, and one Cl8-DBD.

The interference from a Cl8-DBF in the determination of Cl8-DBDs gives a value that is about a two-fold factor high in the microcoulometric method when compared to the GC-MS method (Table II). The GC-MS is considered to be more reliable in the case of such interferences because it uses the molecular ion or other specific fragment ions of the compounds in the quantitative determination. These measurements are used for the Cl8-DBDs to make the comparison shown in Table I. Analyses of the other Clx-DBDs by GC-MS shows that Clx-DBFs are generally not resolved from the Clx-DBDs under our gas chromatographic conditions (Table II). However, the relative ratio of Cl7-DBFs to Cl7-DBDs is lower than the Cl8-DBFs/Cl8-DBDs ratio and lower still for Cl8-DBF/Cl8-DBD. All analyses for the Clx-DBDs, however, are somewhat higher when measured by the microcoulometric detector, and the sum of the Clx-DBD and Clx-DBF concentrations measured by GC-MS correspond more closely to the values measured by the microcoulometric detector.

When normalized against the PCP content, the Cl8-DBD level was 34% higher in the recirculating PCP solution than in the fresh PCP solution. The Cl8-DBD content of the sludge was 90% higher relative to the fresh solution and 42% higher when compared to the recirculating 5% PCP solution. Similarly, the Cl7-DBD levels were 18% higher in the recirculating PCP solution and 86% higher in the sludge when compared to the fresh PCP solution. Because replicate analyses were not performed for Cl6-DBD content in the three samples, not much can be said about their relative concentrations except that major differences were not observed between the samples.

In a similar study, it has been shown that an increase in the level of Cl8-DBD in the processing solution occurs. The present method, however, should be more accurate since a clean separation between the predioxin, 2-HO-Clx-DPE, and Cl8-DBD was achieved by ion exchange chromatography; thus, the use of a rather variable correction factor was not required to account for thermal conversion of the 2-HO-Clx-DPE to Cl8-DBD.

Interferences from Cl8-DBF can occur during gas chromatographic analyses of OCDD. This component, however, was determined to be <

<table>
<thead>
<tr>
<th>Chlorines</th>
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</tr>
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</table>

*From recirculated 5% treatment solution.

*Concentrations normalized against Pentachlorophenol (PCP) content in the solution.

*Gas Chromatography – microcoulometric detector.
1.5% of the OCDD by GC/MS/SISPA using the ion cluster based at m/e 440 which is the parent ion of Cls-DBF. The Cls-DBF ion cluster was compared to the Cls-DBD ion cluster at m/e 456 using the recirculated 5% treatment solution.

The apparent increase in the Cls-DBD and Cl/-DBD content in the recirculated PCP solution relative to the fresh solution could be due to conversion of the appropriate predioxins, 2-HO-Cl=/DPE and 2-HO-Cl=-DPE, during the wood treating process. It could also be due to other factors such as selective deposition of the PCP in the wood leaving a dioxin enriched solupion. The present data does not allow a distinction between these alternatives. The relatively higher levels of Cls-DBD and Cl/-DBD in the sludge suggests that these dioxins may tend to concentrate because of their low solubility in the petroleum distillates.

In contrast to these results for the Boulton process, it has been reported that the Cls-DBD/PCP ratio is 36/1000 in the sludge from the Cellon process compared with technical PCP where this ratio is about 1/1000. This dramatic difference in the relative level of Cls-DBD from the sludge of this process which uses a low volatile carrier vehicle, e.g. di-isopropyl ether, must again be viewed in terms of the possible roles of the chemical mechanisms of dioxin formation in these two processes, the relative solubility of the dioxin formation in these two processes, the relative solubility of the dioxin in each of the solvents, and the effects of the process with respect to the amount of dioxin incorporated into the wood. However, Cls-DBD accumulation in the sludge from either process appears to be significant, and the Cls-DBDs also accumulate in the sludge. The lower chlorinated and more toxic Cls-DBD isomers, on the other hand, appear not to concentrate in the sludge, and this could be due to the higher solubility of the Cls-DBD isomers which may also allow their impregnation into the wood.

acknowledgements
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references