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Note

Gas chromatographic determination of polychlorinated dibenzo-*p*-dioxins in wood preservatives

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Xylamit żeglarski, Xylamit stolarski and Antox, the most popular wood preservatives in Poland, were analysed. These oily liquids contain 5–6% of technical pentachlorophenol (PCP), dissolved in 1-chloronaphthalene, in resins or in chlorinated light coal tar. Technical PCP is commonly used as a wood preservative in the Xylamit formulation. Significant amounts of polychlorinated dibenzodioxins (PCDDs) have been found in technical PCP, chlorobenzenes and other chlorinated aromatic compounds[1–4].

Technical PCP has been shown to be contaminated by tetra- to octachlorodibenzodioxins. Recently obtained data on the concentrations of PCDDs in technical PCP indicate that concentration of dioxins varies from 361 to 1723 ppm for octa-(OCDD), from 119 to 562 ppm for hepta-(HPCDD) and from 1 to 38.5 ppm for hexachlorodibenzodioxins (HXCDD)[4].

EXPERIMENTAL

Apparatus

An N-504 gas chromatograph equipped with an electron-capture detector, an SE-30 capillary column (50 m × 0.3 mm I.D.) was used with nitrogen as the carrier gas and helium as make-up gas, a split–splitless injector and a TZ-4620 analog recorder.

A KB-5101 high-performance liquid chromatograph with an ODS (10 μm) column (250 × 4 mm I.D.) was equipped with a 254-nm UV detector.

The pyrolysis reactor for PCDD isomers was based on the design described by Nestrick *et al.*[5]. A glass tube (10 mm I.D.) was inserted in a temperature-controlled furnace (280–300°C, 1°C accuracy). Amounts of 20 mg of potassium pentachlorophenate solutions were injected onto a 2-cm glass plug and processed as described[6] for hexachlorodioxins.

A TH-24 haematological thermostat was obtained from DHN, Poland.

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PCDD standards

A 2,3,7,8-Tetrachlorodibenzodioxin (TCCD) standard solution for quantitative analysis (10 μg/ml) in toluene was obtained (from Supelco (Bellefonte, PA, U.S.A.). Additionally, the compound was synthesized by pyrolysis of 2,4,5-trichlorophenol and reversed-phase high-performance liquid chromatographic (RP-HPLC) purification as described[5,7].

Octachlorodibenzodioxin standard was synthesized by pyrolysis of analytical-reagent grade pentachlorophenol (Aldrich Milwaukee, WI, U.S.A.), purified by precipitation from a crude benzene extract, recrystallized twice from benzene and determined by weighing 10.2 mg OCDD. Then the sample was dissolved in toluene and analysed by capillary gas chromatography with electron-capture detection (GC–ECD).

Heptachlorodibenzodioxin standard was synthesized by photolytic degradation of OCDD standard solution and RP-HPLC separation from lower chlorinated PCDDs. This solution of two HPCDD isomers was treated as a quantitative standard.

Chemicals

Analytical-reagent grade chemicals were used unless indicated otherwise.

Silica gel (50–100 mesh) for chromatography (Suchardt, Munich, F.R.G.), was processed as described by Miles *et al.*[4] and stored in a desiccator over phosphorus pentoxide.

Alumina for chromatography, basic, activity I, was obtained from POCH (Gliwice, Poland). It was Soxhlet extracted with *n*-hexane and methylene chloride, dried and stored under the same conditions as the silica gel.

Anhydrous sodium sulphate (POCH) was purified by the same procedure as for alumina. Sulphuric acid, hydrochloric acid, potassium hydroxide and sodium hydroxide (POCH) were used without further purification. *n*-Hexane (Reachim, U.S.S.R.) was washed with concentrated sulphuric acid and water, refluxed with sodium, and distilled in glass. Methylene chloride, benzene, toluene and methanol were distilled in glass.

The preparations of 22% and 44% concentrated sulphuric acid on silica gel, 33% 1 M sodium hydroxide on silica gel and activated 10% silver nitrate on silica gel were described by Lamparski *et al.*[8]

Procedure

All the samples of Xylamit wood preservatives and three samples of technical PCP were obtained from the Building Research Institute (Warsaw, Poland). For the determination of PCDDs in Xylamit samples, all glassware and parts of the apparatus that could come into contact with any solution were cleaned as described by Lamparski and Nestrick[9]. Immediately before use they were rinsed twice with methylene chloride. The procedure for the determination of PCDDs in Xylamit samples was based on the method described by Hagenmaier and Brunner[10].

Xylamit samples analysis

Two 5-g portions of each kind of Xylamit (Xylamit stolarski, Xylamit żeglarski and Antox) were weighed into 50-ml beakers. After addition of 30-ml portions of

n-hexane, one portion was spiked with native 2,3,3,8-TCDD, HPCDDs and OCDD at concentrations corresponding to 10 ppb[a], 25 ppm and 50 ppm, respectively. Each pair of Xylamit solutions was analysed according to the following procedure.

The solution was passed through the chromatographic column (30 cm × 2.0 cm I.D.) filled with *ca.* 30 g of basic alumina, freshly prewashed with 50 ml of *n*-hexane. When the sample solution had drained, an additional 100 ml *n*-hexane and 200 ml of methylene chloride-*n*-hexane (2:98) were introduced into the column. The column effluent was discarded. Polychlorinated dibenzo-*p*-dioxins were removed from the alumina column by elution with 250 ml of methylene chloride–*n*-hexane (50:50). This effluent was collected in a beaker and concentrated to 5 ml under a stream of specially purified nitrogen[8].

The concentrated dioxin solution was passed through a combined clean-up column to remove potential interferences. This column was filled, from bottom to top, with a glass-wool plug, 2 g of silica gel, 5 g of 33% 1 *M* sodium hydroxide on silica gel, 2 g of silica gel, 10 g of 44% sulphuric acid on silica gel, 10 g of 22% sulphuric acid on silicagel and 2 g of silica gel. After preparation, the column was prewashed with 25 ml of *n*-hexane immediately before use. When the concentrated dioxin solution had drained, the column was rinsed with 50 ml of *n*-hexane and the effluent was concentrated to *ca.* 2 ml under a stream of nitrogen and passed through a silver nitrate column[8]. When it had drained, the column was eluted with 10 ml of *n*-hexane.

The silver nitrate column effluent was evaporated to approximately 2 ml under a stream of purified nitrogen and introduced into another basic alumina column (150 mm × 6 mm I.D.) containing a 1.5-g bed of freshly activated alumina on top of which was a 1-cm layer of sodium sulphate. When the effluent had drained, the column was rinsed with 20 ml of methylene chloride–*n*-hexane (2:98) and the effluent was discarded. PCDDs were eluted with 20 ml of methylene chloride–*n*-hexane (50:50) and collected in a 25-ml conical test-tube.

The methylene chloride–*n*-hexane (50:50) PCDD fraction was evaporated to dryness under a stream of purified nitrogen. During evaporation the tube containing the solution was gently heated to *ca.* 70°C in a TH-24 haematological thermostat. The residue in the tube was dissolved in 5 ml of toluene, transferred to a PTFE-sealed glass vial (Supelco) and stored in a refrigerator until the GC–ECD analysis.

PCP analysis

Three different technical PCP samples (NZPO Organika-Rokita, Dolny Brzeg, Poland, typical components in the Xylamit formulation, were processed as described below.

A 5-g amount of PCP was dissolved in 500 ml of 0.5 *M* potassium hydroxide and the solution was extracted twice with 100-ml portions of *n*-hexane. The *n*-hexane solutions were combined and washed with redistilled water. After drying with sodium sulphate and evaporation in a stream of purified nitrogen to a volume of *ca.* 5 ml, the concentrate was inserted in a basic alumina column (150 mm × 8 mm I.D.) filled with 5 g of freshly activated alumina. This column was first eluted with 50 ml of methylene

[a] Throughout this article, the American billion (10^9) is meant.

chloride–*n*-hexane (2:98) and the effluent was discarded. Subsequently the PCDDs were eluted with 60 ml of methylene chloride–*n*-hexane (50:50) and collected in a 75-ml calibrated conical tube.

This solution was concentrated to 20 ml in a stream of nitrogen, and transferred to a PTFE-sealed amber-glass bottle and stored in a refrigerator as a stock PCDD–PCP solution. A 1-ml volume of this solution was evaporated to dryness in a stream of purified nitrogen and the residue was dissolved in 4 ml of toluene. Additionally, a 5-g portion of PCP spiked with 2,3,7,8-TCDD to a concentration corresponding to 10 ppb was processed.

Selective separation of 2,3,7,8-TCDD

The separation of 2,3,7,8-TCDD from other chlorinated dibenzodioxins and dibenzofurans was carried out using the method described by Hagenmaier *et al.*[2].

Samples of 5 g of Xylamit were dissolved, spiked with 2,3,7,8-TCDD and PCDDs were isolated as described above. The PCDD residue was dissolved in 10 ml of benzene. The 2,3,7,8-TCDD from this solution and from a solution of technical PCP were separated and processed following Hagenmaier *et al.*'s procedure.

The benzene solution was introduced into a column filled with 2.5 g of alumina Woelm B Super I and 2 g of sodium sulphate on the top of the column. A 30-ml volume of methylene chloride–*n*-hexane (20:80) was passed through the column and the effluent was discarded. 2,3,7,8-TCDD was eluted from the alumina column with 25 ml of methylene chloride–*n*-hexane (50:50). This fraction was evaporated to dryness under purified nitrogen and the residue was dissolved in 50 μl of chloroform (Merck, Darmstadt, F.R.G.). This solution was injected into an ODS HPLC column (250 × 4 mm I.D.). The column was eluted with methanol at 2.75 ml/min at 25°C. The retention time of 2,3,7,8-TCDD was 12 min 30 s. The fraction between 11 min 50 s and 13 min 10 s was collected and 2,3,7,8-TCDD was extracted with 2 ml of *n*-hexane. This solution was dried and 100 μl of toluene were added. After evaporation to approximately 50 μl, this sample was analyzed by capillary GC–ECD.

Gas chromatography

Sample aliquots of 1–2 μl in toluene were injected onto the column using the splitting technique (1:120). The oven temperature was programmed from 180°C (held for 2 min) at 5°C/min to 250°C (held) for 2,3,7,8-TCDD analysis or isothermally at 250°C for HPCDD and OCDD. The detector temperature was 300°C and the injector temperature 240°C. The carrier gas was chromatographic-grade nitrogen (ZLE Róży Luksemburg, Warsaw, Poland) and the make-up gas was helium. Retention times were 17.2 min for 2,3,7,8-TCDD and 80.6 min for OCDD. The limit of detection for 2,3,7,8-TCDD (standard solution) was 100 pg and that for HPCDDs and OCDD was 750 pg.

RESULTS AND DISCUSSION

The three wood preservative samples contain a 5–6% solution of technical PCP in light coal tar. The PCDD analytical data for each sample are given in Table I. The 1-ppb limit of detection for 2,3,7,8-TCDD was defined as 2.5 times the peak-to-valley noise close to the 2,3,7,8-TCDD retention time.

The limits of detection of HPCDD and OCDD were not calculated because of their very high concentrations in all of the samples.

The recoveries of 2,3,7,8-TCDD from the Xylamit and PCP samples were 45% and 65%, respectively, and those of HPCDD and OCDD isomers were 70% for Xylamit samples and 90–95% for PCP. This evaluation was carried out by GC–ECD determination of these compounds in each of the spiked and non-spiked final extracts by comparing the peak-height responses at their retention times with those of standards injected after the injection of the extract.

Gas chromatograms of the three Xylamit formulations are given in Fig. 1a–c and for technical PCP in Fig. 1d.

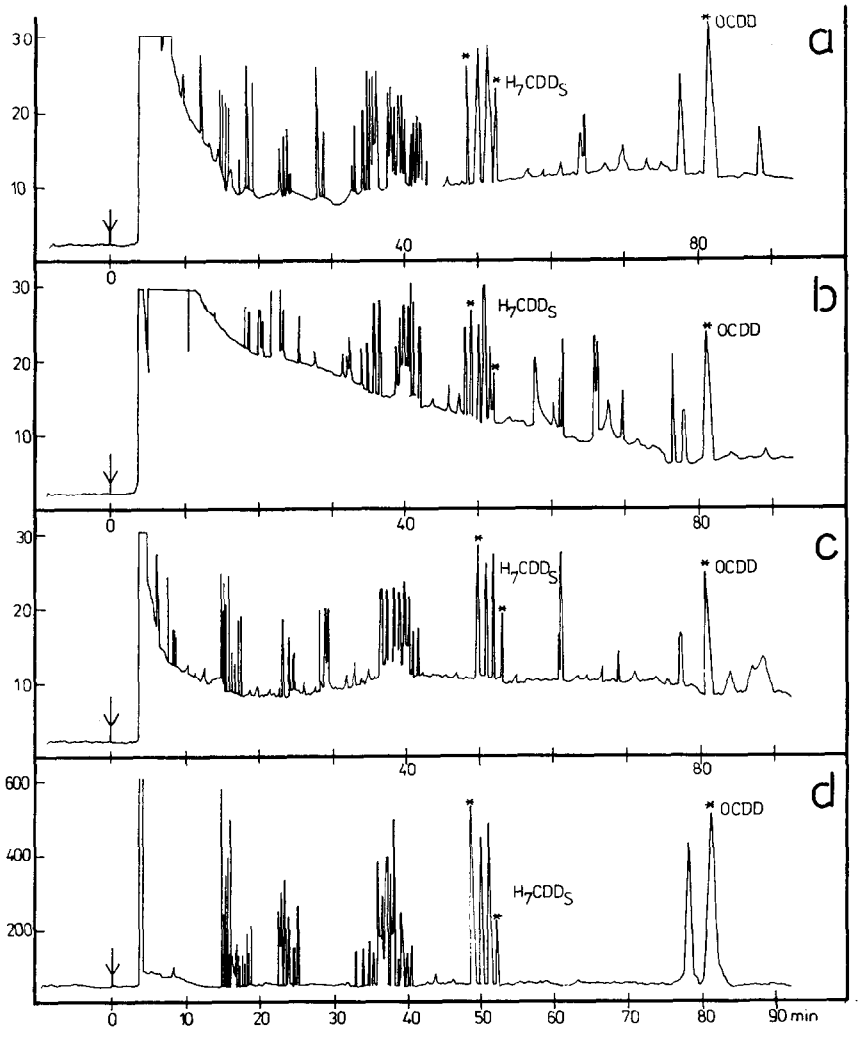

Fig. 1. Gas chromatograms of PCDD–polychlorinated dibenzofuran (PCDF) fractions from: (a) Xylamit stolarski, (b) Xylamit żeglarski, (c) Antox and (d) technical PCP.

TABLE I

RESULTS OF GC ANALYSIS OF WOOD PRESERVATIVE SAMPLE

Results are from three parallel analyses.

Sample	*2,3,7,8-TCDD*[a]	*HPCDDs (ppm)*	*OCDD (ppm)*
Xylamit stolarski	n.d.	9.2– 13.1	27.8– 33.9
Xylamit żeglarski	n.d.	7.7– 12.9	17.4– 21.8
Antox	n.d.	8.5– 10.1	19.9– 23.7
PCP 1	n.d.	166.1–236.2	547.3–712.0
PCP 2	n.d.	188.8–277.0	590.3–606.1
PCP 3	n.d.	117.3–119.3	435.6–486.9

[a] n.d. (Not detected) indicates that the compound was not detected within a detection limit of 1 ppb.

[b] HPCDDs is the sum of 1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin.

OCDD was the main PCDD isomer obtained in all the Xylamit and technical PCP samples. Two HPCDDs were determined as a sum. Polychlorinated dibenzofurans and some other unknown compounds that were found were not determined.

The results of the capillary GC–ECD analysis of the Antox 2,3,7,8-TCDD

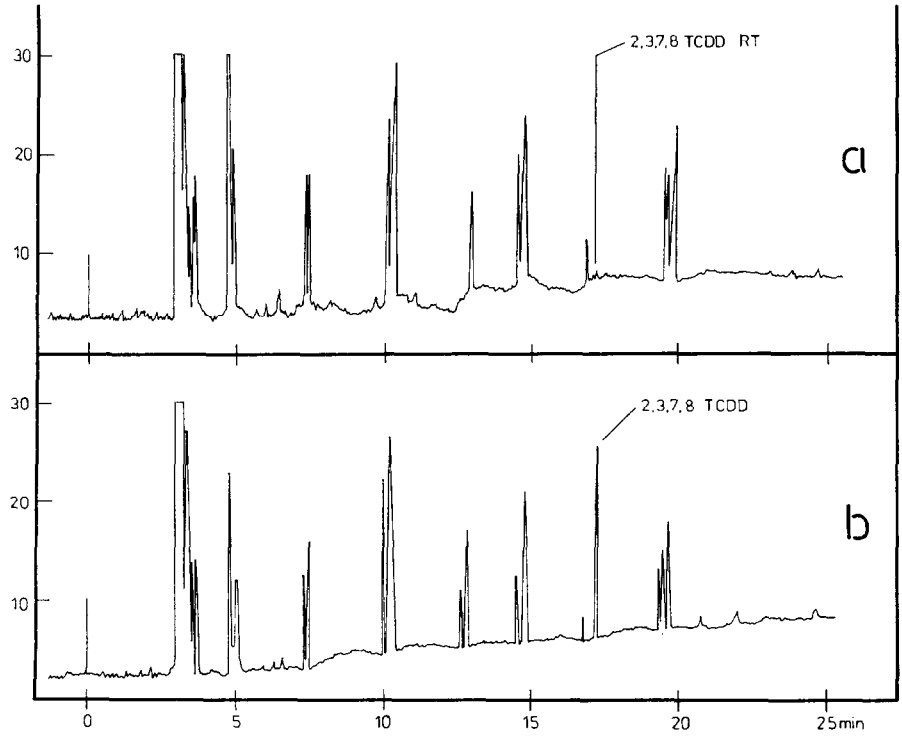

Fig. 2. Gas chromatograms of (a) Antox 2,3,7,8-TCDD fractions from alumina Woelm B Super I and (b) the same sample spiked with 2,3,7,8-TCDD standard solution to a concentration of 10 ppb. RT = Retention time.

fraction from alumina Woelm B Super I are shown in Fig. 2a and those for an Antox sample spiked with 2,3,7,8-TCDD standard solution (to obtain a concentration of *ca.* 10 ppb) in Fig. 2b.

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