

cently, 2,3,4,6-tetrachloroanisole has been identified in eggs and broiler chickens, apparently through absorption from litter shavings obtained from wood impregnated with polychlorophenols as antifungal agents (Engel *et al.*, 1966). These chlorophenols are reported to be converted into the corresponding anisoles through microbiological methylation in the litter (Curtis *et al.*, 1972). The same authors mention the extremely low odor thresholds of 2,3,6-trichloroanisole and 2,4,6-trichloroanisole in aqueous solution.

In connection with our discovery of 2,4,6-trichloroanisole, the use of 2,4,6-trichlorophenol (Dowicide 2S) as an antimicrobial agent should be mentioned. However, the difference in geographic location and subsequent agricultural practice, and the difference in plant family and in shipping containers used make it difficult to explain the external introduction of 2,4,6-trichloroanisole into the essential oil. Its absence in such oils as bergamot, cinnamon leaf, lavandin, and spearmint absolves practices used after the oils have left the original containers.

Examination of old essential oil samples antedating the era of wide use of chlorinated industrial chemicals may shed further light.

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Chlorodibenzo-*p*-dioxin Contamination of Two Commercially Available Pentachlorophenols

A comparison was made of chlorodibenzo-*p*-dioxin contamination in a technical and an analytical grade of commercially available pentachlorophenols. Hexa-, hepta-, and octachlorodibenzo-*p*-dioxin were found in both samples. The technical product was more contaminated than the analytical one by factors of 1400, 600, and 539 for the hexa-, hepta-, and octachlorodibenzo-*p*-dioxin, respectively. Tetrachlorodibenzo-*p*-dioxin was not found. Results were determined by gas chro-

matography and confirmed by infrared spectrophotometry and mass spectrometry. Mass spectral analysis indicated the presence of polychlorodibenzofurans and polychlorodiphenyl ethers. A distinction was made, using gas chromatography-mass spectrometry, between the chlorodibenzofurans observed as original constituents of the pentachlorophenol and those derived from the fragmentation of chlorodiphenyl ethers.

Recent research has shown that some chemicals receiving widespread use in the environment contain contaminants which are more toxic than the major compound (Goursaud *et al.*, 1972; Vos *et al.*, 1970; Woolson *et al.*, 1972). Studies should be conducted to determine the acute and chronic effects of the major compounds both with and without the toxic contaminants.

It is established that the conditions of manufacture for pentachlorophenol (PCP) can give rise to the toxic contaminants chlorodibenzo-*p*-dioxins (CDD's) (Higginbotham *et al.*, 1968; Jensen and Renberg, 1972). The toxicities of some of the compounds in this series have been reported (Higginbotham *et al.*, 1968; Rowe *et al.*, 1971; Williams *et al.*, 1972).

This paper reports an assessment of the levels of contamination of two commercially available PCP's: a technical product containing 86% PCP and a product of analytical grade containing 99+% PCP.

EXPERIMENTAL SECTION

The CDD's were extracted with hexane from an aqueous solution of the sodium pentachlorophenate and the extract was chromatographed on alumina columns according to the method of Firestone *et al.* (1972). Although four fractions were collected from alumina, only fractions III and

IV were subjected to sulfuric acid cleanup (Firestone, 1971) and, subsequently, analyzed.

CDD concentrations in fractions III and IV were determined by gas chromatography (gc) coupled with electron capture (EC) ⁶³Ni, Coulson conductometric (CC), and flame ionization (FI) detectors. A Tracor 550 gas chromatograph was equipped with a ⁶³Ni EC detector and a 6 ft × ¼ in. o.d. glass column packed with 3% OV-1 on 80/100 mesh Supelcoport. The column temperature was 220°, and the nitrogen flow was 135 cm³/min at 60 psi.

A Micro-Tek 2000 with a FI detector was used with a 6 ft × ¼ in. o.d. stainless steel column packed with 3% SE-30 on 100/120 mesh Chromosorb W, DMCS treated, AW. The column temperature was 220°. With a head pressure of 40 psi, the flow rates in cm³/min are as follows: nitrogen, 80; oxygen, 31; air, 39; and hydrogen, 181.

A Micro-Tek 2000 was also used with a CC detector. A 6 ft × ¼ in. o.d. glass column was packed with 3% OV-1 on 70/80 mesh Chromosorb G, DMCS treated, AW. The column temperature was 220°. Helium flow was 65 cm³/min at 40 psi.

Under these conditions, the limits of sensitivity for tetraCDD on EC, FI, and CC are 1.0, 10.0, and 2.0 ppb, respectively. Gas chromatograms were compared qualitatively and quantitatively to those of standard CDD solu-

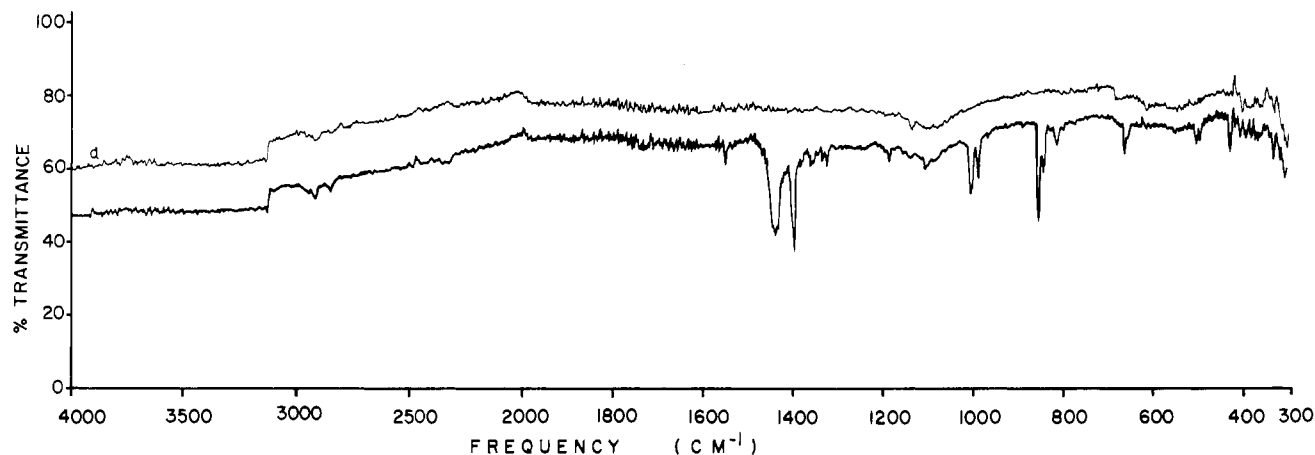


Figure 1. Infrared spectrum of a precipitate from fraction III of the technical PCP extract. a = blank.

Table I. Dioxin Concentration Found by gc Analysis in ppm

Sample	Detector	Hexa-CDD	Hepta-CDD	Octa-CDD
Technical (86% pure)	EC	42.00	24.07	10.78
	FI	42.08	20.37	7.12
	CC	32.75	19.03	7.52
Analytical (99+% pure)	EC	0.03	0.04	0.02
	FI	0.03	0.09	0.03
	CC	0.02	0.06	0.03

tions 1 and 2. Solution 1 contained di-, tri-, and tetraCDD. Solution 2 contained hexa- (four isomers), hepta- (two isomers), and octaCDD. All quantitation was based on peak heights.

A precipitate from fraction III of the technical product was analyzed by infrared spectrophotometry using a Perkin-Elmer 521 and a multiple internal reflection apparatus (Wilks Scientific Corporation, 1965).

Mass spectral analysis of fraction III of the technical product was accomplished using an LKB 9000 equipped with a mass marker (± 0.3 mass unit) and interfaced to a 10 ft \times $\frac{1}{4}$ in. o.d. coiled pyrex glass column packed with 3% SE-30 on 60/80 Chromosorb G, DMCS treated, AW. The column was maintained at 230° with a helium flow of 70 cm³/min at 12 psi. Under these conditions the 2, 3, 7, 8-tetraCDD had a retention time of 9.5 min.

RESULTS AND DISCUSSION

The data obtained by gc analysis of fractions III and IV from the technical and pure PCP extracts are summarized in Table I. Although fractions III and IV and the precipitate were analyzed separately, the data are combined in Table I. Values are reported for the three modes of detection used. The highest CDD level was found in the technical grade PCP, where the order of decreasing concentrations of the CDD's present was hexa-, hepta-, and octaCDD. In the pure sample of PCP, heptaCDD was higher in concentration than hexa- or octaCDD. The technical product was more contaminated than the analytical one by factors of 1400, 600, and 539 for the hexa-, hepta-, and octaCDD, respectively.

An infrared spectrum of the precipitate from the technical product fraction III is presented in Figure 1. The spectrum of this residue is superimposable on the spectrum of an octaCDD standard (Woolson *et al.*, 1972). Gas chromatographic analysis showed this residue to be predominantly octaCDD.

Mass spectral analysis confirmed the presence of the reported CDD's. TetraCDD, the most toxic of the CDD's, was not found in the PCP's analyzed. The minimum detectable limit was 0.4 ppm.

Mass spectral analysis also revealed the presence of several chlorodibenzofurans (CDF's) and chlorodiphenyl ethers (CDE's). Hexa-, hepta-, and octaCDF and hexa-, hepta-, and octaCDE were found as original constituents of PCP. The mass spectra of the hexa- and heptaCDE contained additional ions of 304 and 338, which correspond to the masses of tetra- and pentaCDF, respectively. Multiple scans of these two CDE's indicated that tetra- and pentaCDF were formed subsequent to the loss of two chlorines from the parent CDE's. It is conceivable that *o,o'*-substituted CDE's could rearrange to CDF's upon fragmentation.

Gas chromatography-mass spectrometry indicated that the CDD's were not completely resolved from the CDF's and CDE's. Consequently, the calculations of CDD levels, which were based on CDD standards alone, may be slightly high. HexaCDD showed more interference from CDF and CDE than did hepta- and octaCDD.

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