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AN ARTIFACT IN THE GAS CHROMATOGRAPHIC DETERMINATION OF IMPURITIES IN PENTACHLOROPHENOL

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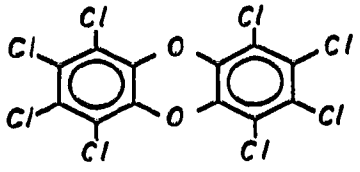
SUMMARY

Commercial samples of pentachlorophenol were analyzed by gas chromatography and mass spectrometry. The main impurity of higher molecular weight was found to be 3,4,5,6-tetrachloro-2-(2,3,4,5,6-pentachlorophenoxy)phenol. During gas chromatographic analyses this compound was found to undergo ring closure to give 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin, which may also be an impurity in the commercial samples. Other impurities found were two isomeric octachlorophenoxyphenols of unknown structure.

INTRODUCTION

Pentachlorophenol and its salts are used in large quantities as herbicides, slimicides in paper mills and wood preservatives. The annual world production is more than 20,000 tons. Technical grade pentachlorophenol contains as impurities up to 13% of other chlorophenols, mainly isomeric tetrachlorophenols.

Pentachlorophenol can be manufactured by alkaline hydrolysis of hexachlorobenzene at elevated temperatures and pressures[1]. From the preparation of other chlorinated phenols, it is known that this process can also result in the formation of chlorinated dibenzo-*p*-dioxins[2,3]. In the case of 2,4,5-trichlorophenol, which is prepared from 1,2,4,5-tetrachlorobenzene, the impurity was found to be 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, a compound with a high mammalian toxicity and teratogenic effect[4]. The analogous impurity from the preparation of pentachlorophenol is 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (I).



I

This compound has been reported as a pesticide[5], but no special biological effects seem to have been reported.

In connection with work on the photochemistry of pentachlorophenol, we were interested in identifying impurities other than tri- and tetrachlorophenols in technical pentachlorophenol. Therefore, conditions were chosen so as to separate compounds with molecular weights higher than that of pentachlorophenol.

EXPERIMENTAL

Materials

The pentachlorophenol used was "Dow technical grade" and Dowicide-7. The sodium pentachlorophenolate used was prepared by Xylo Chimie (France). All products behaved similarly. Diazomethane was prepared according to ARNDT[6].

Gas chromatography

A Pye-Unicam, Model 84, gas chromatograph was used. The column was packed with 1% of SE-30 on Chromosorb W, DMCS-treated, acid-washed, mesh size 100–120. After packing, the column was conditioned with three 10-μl volumes of Silyl 8 at 100°. The operating conditions were: inlet temperature, 275°; column temperature, 225°; and detector temperature, 250°. Helium was used as the carrier gas at a flow-rate of 25 ml/min. A flame-ionization detector was used. A volume of 1 μl of a 10% solution of a sample in mesitylene was injected.

Mass spectrometry

An LKB, Model 9000, mass spectrometer equipped with a Pye-Unicam, Model

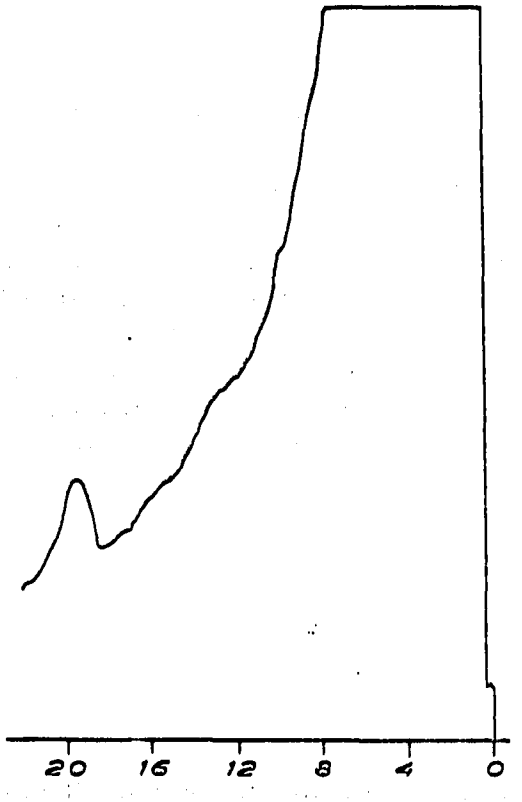


Fig. 1. Gas chromatogram of pentachlorophenol.

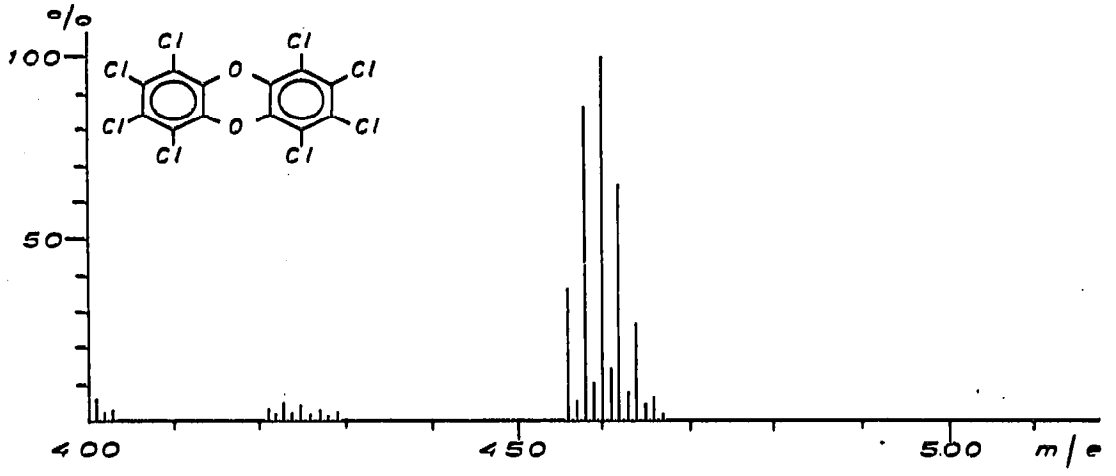


Fig. 2. Mass spectrum of the main impurity in the gas chromatogram shown in Fig. 1.

84, gas chromatograph was used. The operating conditions for the gas chromatograph were as above. The connection between the gas chromatograph and the mass spectrometer was maintained at 240°, the separator at 255° and the ion source at 270°. The ion source was operated at 70 eV.

The mass spectra given were calculated for $m/e > 400$. The most abundant peak in this region is assigned as 100%.

RESULTS

Fig. 1 shows a gas chromatogram of pentachlorophenol. In spite of tailing, the chromatogram indicates the presence of only one impurity with a longer retention time. This compound has the same retention time as an authentic sample of 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (I). The mass spectrum of this peak (Fig. 2) is identical with that of I. From this it seems feasible to assume that the main impurity in pentachlorophenol with higher molecular weight is the dioxin I, and the amount of this was estimated as 500 p.p.m.

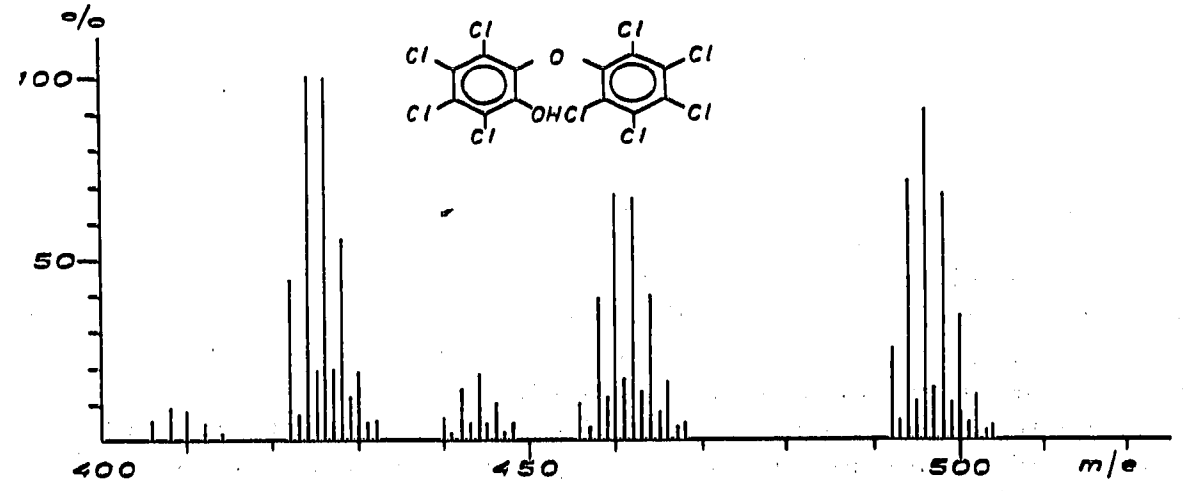


Fig. 3. Mass spectrum of pentachlorophenol obtained by using the direct inlet.

Pentachlorophenol was investigated by using the direct inlet of the mass spectrometer. The spectrum contained peaks at higher m/e values than was found in the authentic sample of I (Fig. 3). The peaks in the region m/e = 492–502 correspond to a compound with the empirical formula $C_{12}HCl_9O_2$. The pattern of the isotopic cluster is in accordance with a compound containing nine chlorine atoms.

Pentachlorophenol was treated with diazomethane, which reacts with free phenolic groups to give methoxy compounds but does not react with chlorinated dibenzo-*p*-dioxins. It can be assumed that it should be easier to separate methoxy ethers than phenols by gas chromatography.

The evaporated residue after the treatment with diazomethane gave a gas

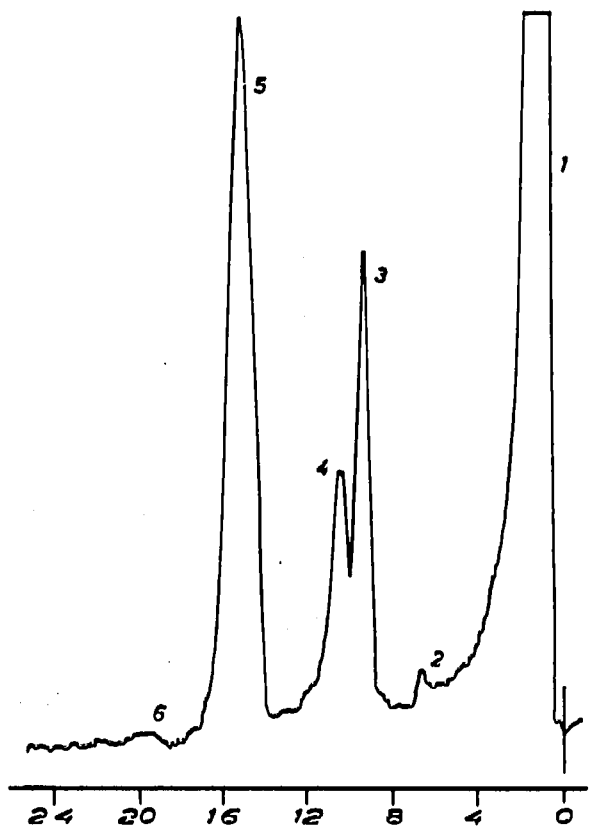


Fig. 4. Gas chromatogram of pentachlorophenol treated with diazomethane.

chromatogram with six peaks (Fig. 4). Peak 1 is pentachloroanisole and the solvent. The mass spectra of peaks 3, 4 and 5 are shown in Figs. 5, 6 and 7. Peaks 3 and 4 seems to consist of two isomers with clusters of eight chlorine atoms and a molecular weight of 472, corresponding to the empirical formula $C_{13}H_4Cl_8O_2$.

Peak 5 corresponds to the most abundant impurity. The mass spectrum indicates nine chlorine atoms and a molecular weight of 506. This corresponds to the empirical formula $C_{13}H_3Cl_9O_2$. This is the methyl derivative of the compound with the mass spectrum shown in Fig. 3, obtained from the direct inlet.

Peak 6 seems to be the octachlorodioxin I. This hypothesis was verified by the mass spectrum in which the peaks in the m/e = 456–466 region was about 10 times larger than those in the m/e = 506–516 region (Fig. 7). The amount of I in penta-

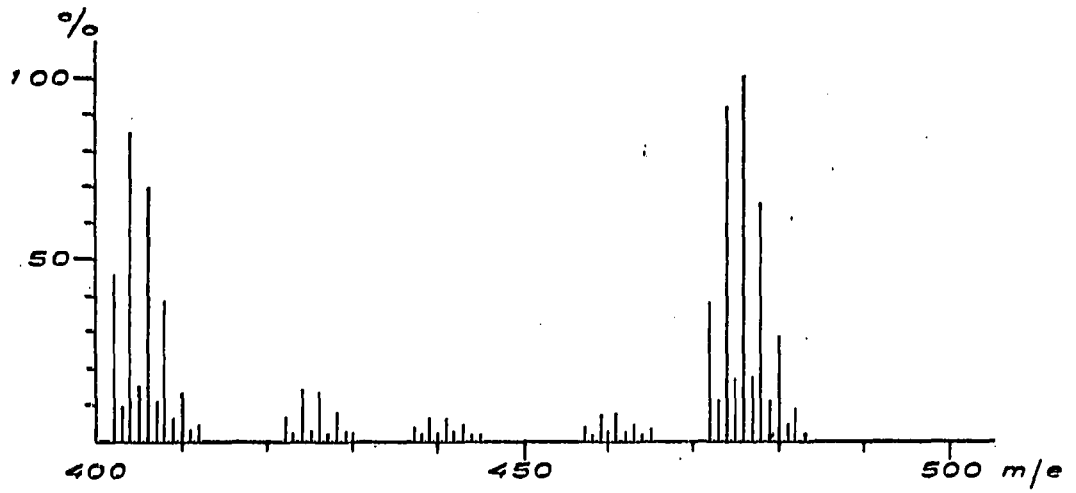


Fig. 5. Mass spectrum of peak 3 in Fig. 4.

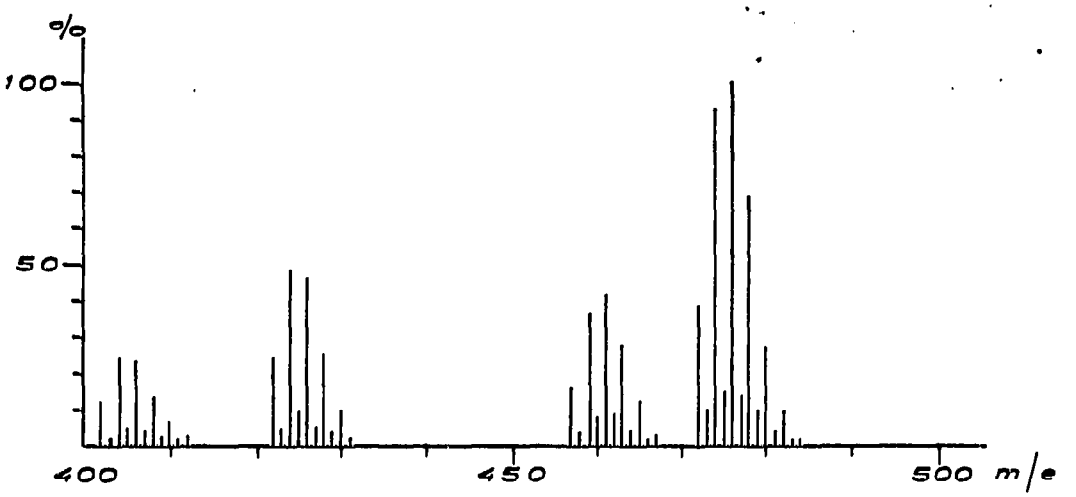


Fig. 6. Mass spectrum of peak 4 in Fig. 4.

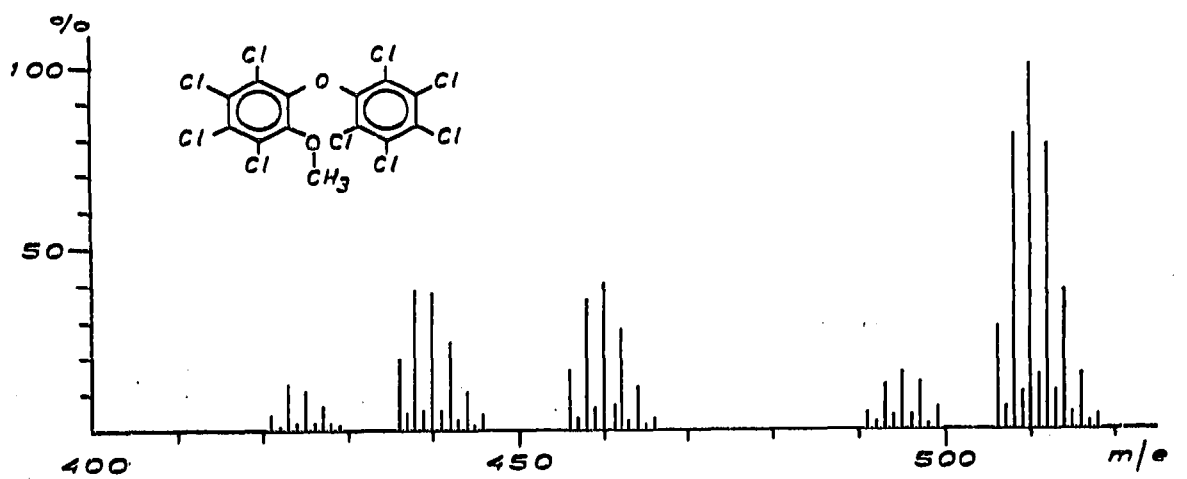
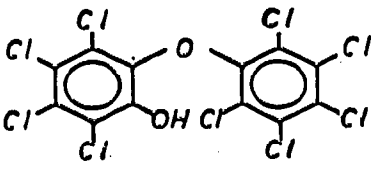


Fig. 7. Mass spectrum of peak 5 in Fig. 4.

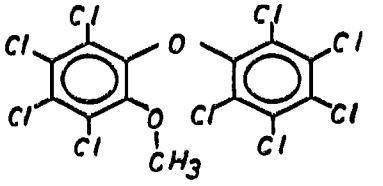
chlorophenol treated with diazomethane was estimated to be not higher than 10 p.p.m.

CONCLUSIONS

The best way to rationalize these contradictory results is to assume that the main impurity in pentachlorophenol is 3,4,5,6-tetrachloro-2-(2,3,4,5,6-pentachlorophenoxy)phenol (II).

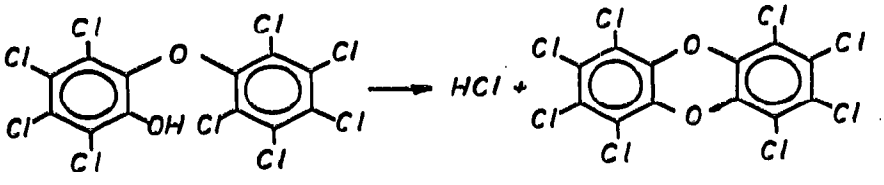


II



III

The mass spectral analysis of pentachlorophenol by using the direct inlet gave the spectrum of this compound, and probably of other compounds also (Fig. 2). The reaction with diazomethane gave the methyl ether of this phenol (III) (peak 5 in Fig. 4 and mass spectrum in Fig. 7). However, in the heated injection block of the gas chromatograph, a ring closure of II to the dioxin I took place:

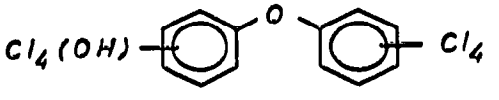


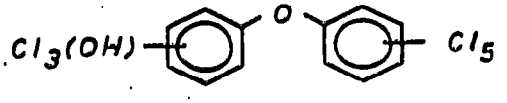
II I

This reaction can account for the much lower content of the octachloro-dioxin I in the methylated sample than in the unmethylated one.

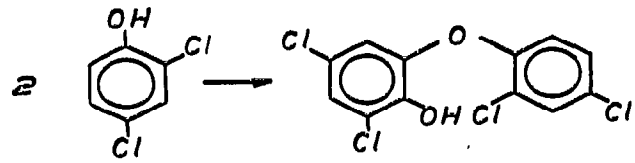
All attempts to synthesize the methyl ether III in a pure state have failed. Therefore, no quantitative determination of this compound has been made.

The impurities corresponding to peaks 3 and 4 in Fig. 3 are two or more isomers of octachloro-*o*-, *m*- or *p*-phenoxyphenol, of which there exist 21 possible isomers.





Chlorinated phenoxyphenols do not appear to have been observed before as impurities in chlorinated phenols. However, PLIMMER AND KLINGEBIEL[7] reported that the riboflavin-photosensitized oxidation of 2,4-dichlorophenol gave 4,6-dichloro-2-(2',4'-dichlorophenoxy)phenol (IV) and in a smaller amount an isomer of this compound. However, these authors did not observe any chlorinated dibenzo-*p*-



IV

dioxins, probably owing to a rapid photochemical breakdown of these compounds when formed.

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