Chlorinated Naphthalenes in Pesticide Analysis[1]

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Introduction

Chlorinated naphthalenes have been suggested as an additional source of interference in the gas chromatographic analysis of organochlorine insecticides (1). The chlorinated naphthalenes are manufactured for uses analogous to those of the PCB (polychlorinated biphenyl) compounds. The physical and chemical properties of both chlorinated biphenyls and chlorinated naphthalenes are similar (2,3). The chloronaphthalenes are manufactured in a range from the monochloro compound to the fully chlorinated octachloronaphthalene.

It is the purpose of this paper to show which of the chloronaphthalene isomers may possibly interfere with the gas chromatographic analysis of pesticides.

Experimental[2]

Hexane solutions of each of the commercially prepared chlorinated naphthalenes (Halowax ® 1000, 1013, 1014, 1031, and 1099) were analyzed by electron capture gas chromatography. Figures 1 and 2 show chromatograms pertinent to this study. It was necessary to show chromatograms of only two of the Halowaxes, 1013 and 1014, as they exemplify the chlorinated naphthalenes and isomers that appear in the other formulations. The gas chromatographic operating conditions are as follows:

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Gas chromatographic operating conditions for Figure 1

Varian Aerograph 204 electron-capture gas chromatograph
Column dimensions: 6' x 1/8" glass
Column packing: 100/120 mesh Gas Chrom Q coated 3 per cent by weight with OV-101
Column temperature: 180°C
Injection port temperature: 205°C
Detector temperature: 200°C (H^3)
Carrier gas flow: 37 ml/min N_2

Gas chromatographic operating conditions for Figure 2

Tracor MT-160 electron-capture gas chromatograph
Column dimensions: 6' x 1/4" glass
Column packing: An equal mixture of 1) 100/120 mesh gas Chrom Q coated 3 per cent by weight with OV-101 and 2) 100/120 mesh Gas Chrom Q coated 5 per cent by weight with OV-210
Column temperature: 175°C
Injection port temperature: 210°C
Detector temperature: 300°C (Ni^{63})
Carrier gas flow: 60 ml/min N_2

The chromatograms are arranged for direct comparison of the retention time region. Figure 1A shows the response obtained upon injection of 1.2 ng (10^{-9} g) of Halowax 1013. The chromatograms of Figures 1B and 2A were obtained upon injection of 2.0 ng of Halowax 1014. The amounts of insecticides analyzed were 0.064 ng lindane, 0.074 ng heptachlor, 0.068 ng aldrin, 0.11 ng DDE, 0.24 ng DDD, and 0.28 ng DDT.

Identification of the chloronaphthalenes was made by use of a Finnigan 150 computer controlled gas chromatograph-mass spectrometer system. Similar gas chromatographic columns and operating conditions were employed except helium was used as the carrier gas. The spectrum scans were controlled by the computer and the scan rate was stepped, from 2 milliseconds per atomic mass unit at the low end of the spectrum up to 33 milliseconds per atomic mass unit at the high end. Each spectrum was completed in 3.5 seconds and recorded on magnetic tape. Figures 3-7 show typical spectra of actual chromatographically separated chloronaphthalenes as plotted by the computer output device. Correlations of the spectra to the gas-chromatogram were also made by the computer. The chlorine number of each peak as assigned in Figures 1 and 2 was determined in this manner. The retention times, relative to aldrin, of selected pesticides and chlorinated naphthalenes are shown in tables 1 and 2. These retention times were obtained using the GC operating conditions and analytical columns previously stated. Peak numbers of the chlorinated naphthalenes refer to the numbered peaks in Figures 1 and 2.

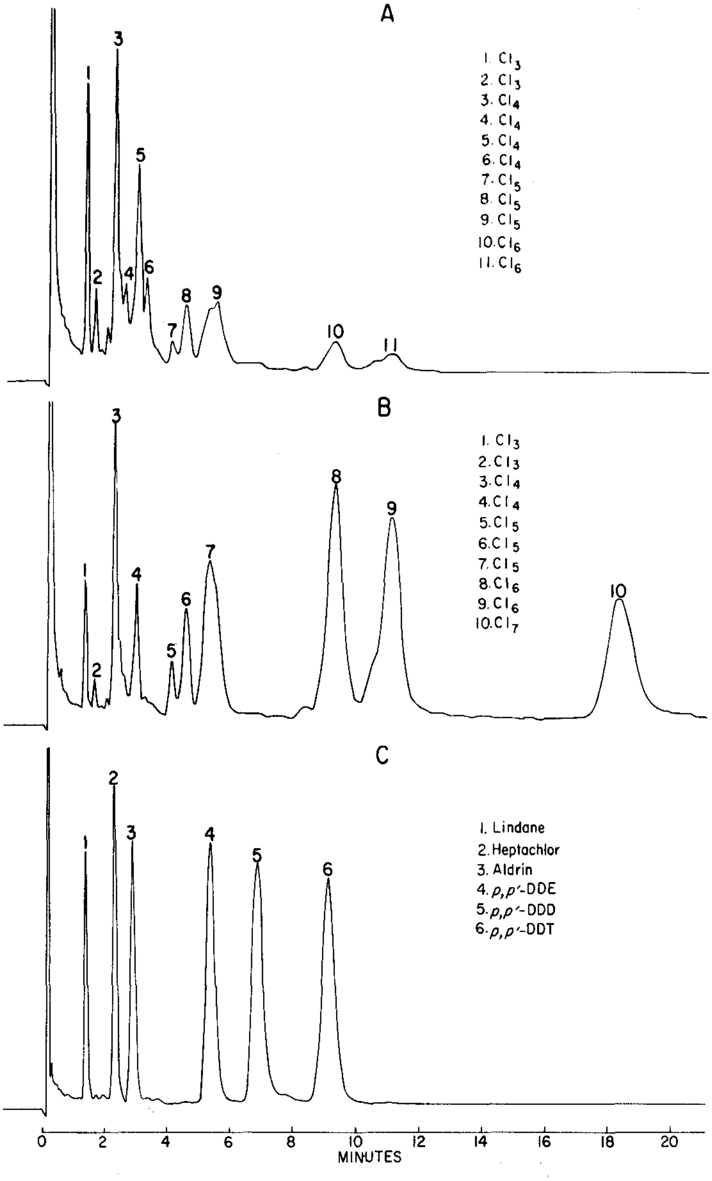

Figure 1. Gas chromatogram on OV-101 Column
A. Halowax 1013
B. Halowax 1014
C. Insecticide mixture

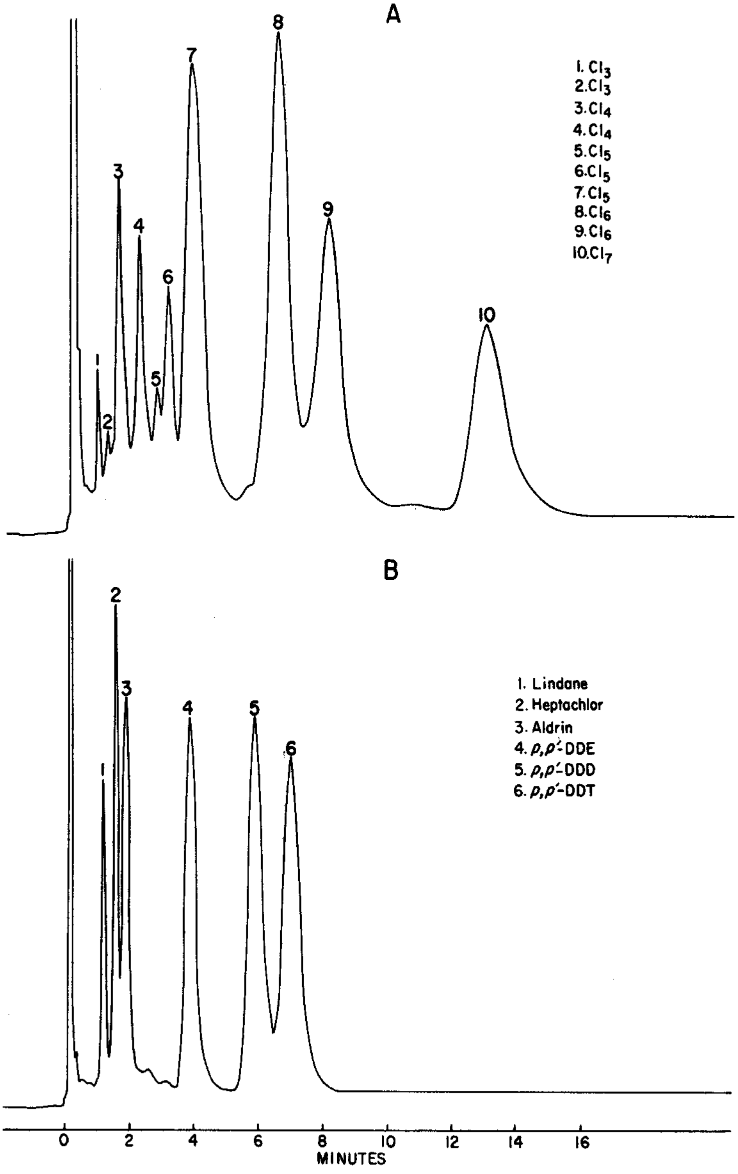

Figure 2. Gas chromatogram on OV-101/210 column
A. Halowax 1014
B. Insecticide mixture

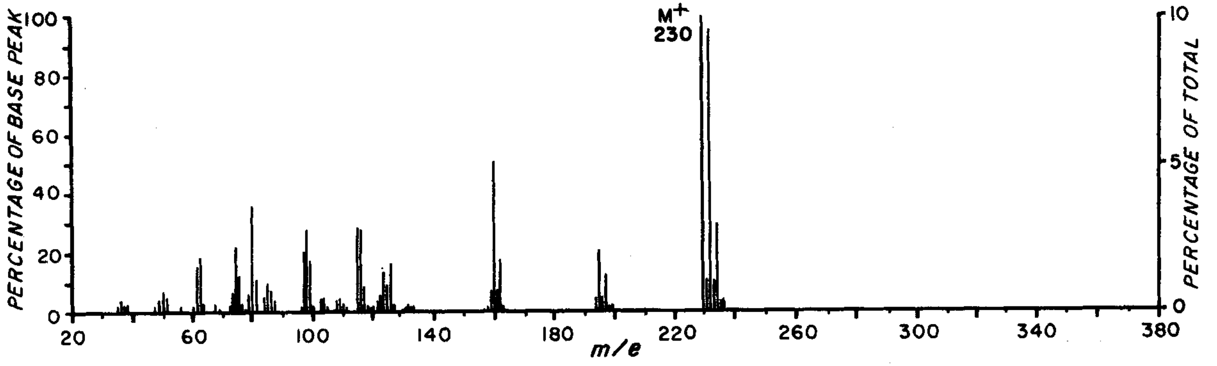

Figure 3. Mass spectrum of a trichloronaphthalene

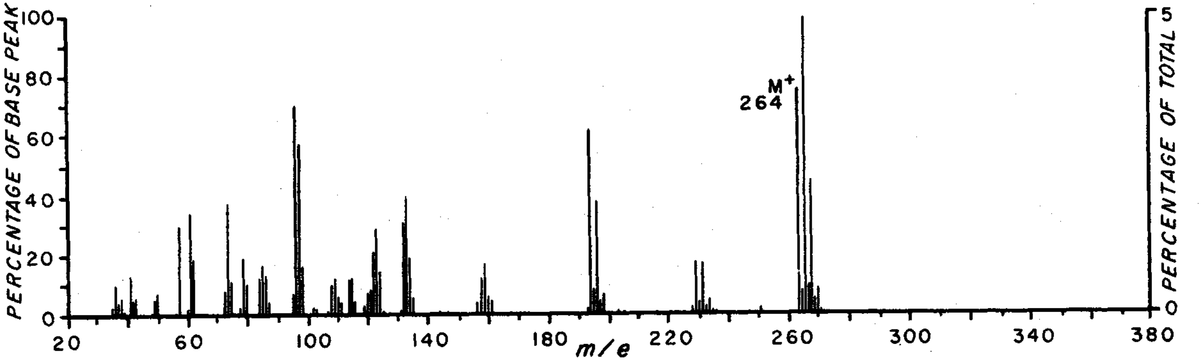

Figure 4. Mass spectrum of a tetrachloronaphthalene

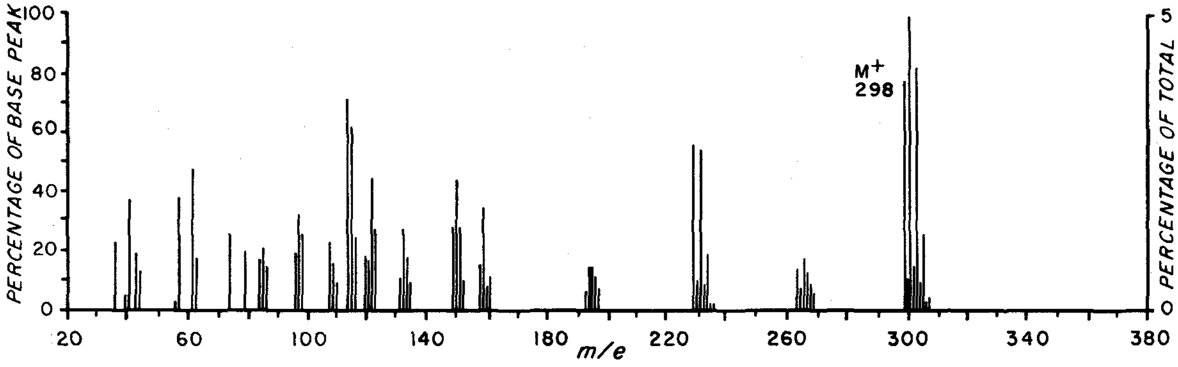

Figure 5. Mass spectrum of a pentachloronaphthalene

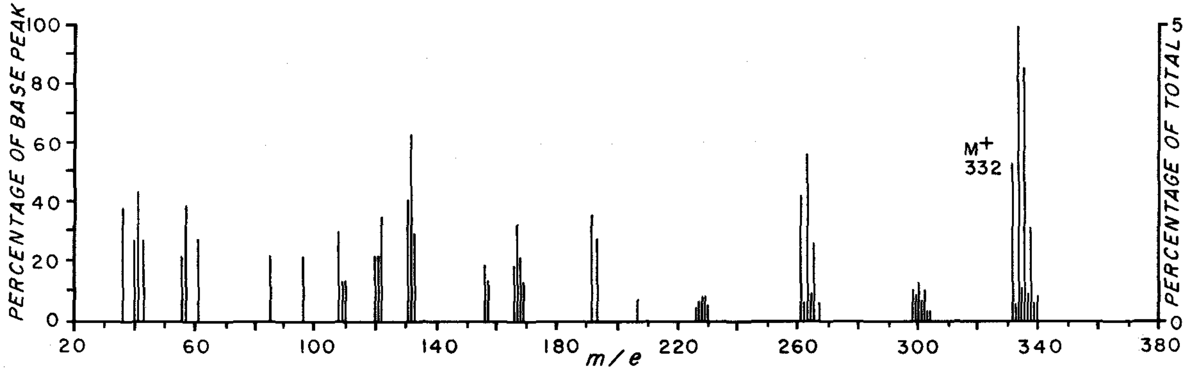

Figure 6. Mass spectrum of a hexachloronaphthalene

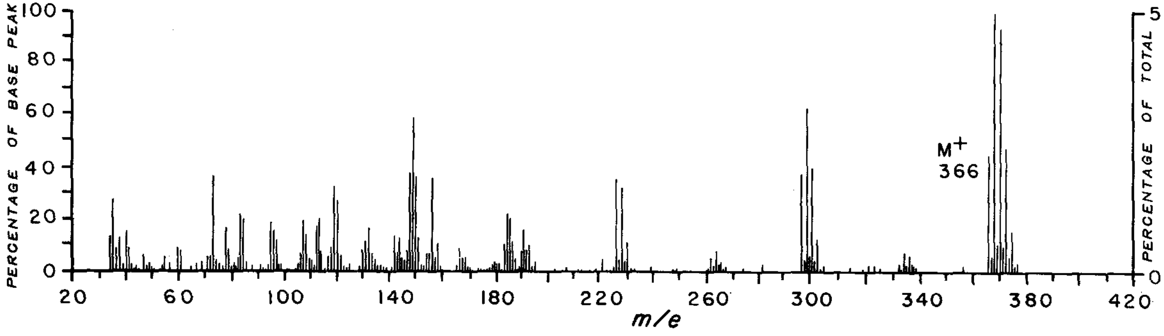

Figure 7. Mass spectrum of a heptachloronaphthalene

TABLE 1

Retention times of pesticides and chlorinated naphthalenes relative to aldrin (165 seconds absolute) on a 3% OV-101 column

		Halowax 1013		Halowax 1014	
Pesticides	RRT	Peak No.	RRT	Peak No.	RRT
		1	0.44	1	0.44
Lindane	0.44	2	0.56	2	0.56
Heptachlor	0.79	3	0.78	3	0.78
Aldrin	1.00	4	0.91	4	1.05
p,p'-DDE	1.93	5	1.05	5	1.48
p,p'-DDD	2.50	6	1.16	6	1.65
p,p'-DDT	3.32	7	1.45	7	1.94
		8	1.64	8	3.41
		9	2.02	9	4.08
		10	3.41	10	6.77
		11	3.99		

TABLE 2

Retention times of pesticides and chlorinated naphthalenes relative to aldrin (115 seconds absolute) on a 3% OV-101/5% OV-210 column

		Halowax 1014	
Pesticides	RRT	Peak No.	RRT
Lindane	0.63	1	0.53
Heptachlor	0.82	2	0.67
Aldrin	1.00	3	0.84
p,p'-DDE	2.01	4	1.10
p,p'-DDD	3.08	5	1.49
p,p'-DDT	3.66	6	1.67
		7	2.05
		8	3.45
		9	4.25
		10	6.81

Discussion

The pesticide analyst must be alert to the possible presence of chlorinated naphthalenes in addition to the chlorinated biphenyls. The pattern of compounds and isomers of a particular commercial chlorinated naphthalene preparation, as it appears on an electron-capture chromatogram, is not as characteristic or distinctive as PCB formulations. Consequently, one cannot readily assess the occurrence of chloronaphthalenes in previously analyzed samples by simply reviewing chromatographic records.

The insecticides lindane, heptachlor, aldrin, p,p'-DDE, p,p'-DDD and p,p'-DDT elute closely to major Cl_3, Cl_4, Cl_5 and Cl_6 chloronaphthalenes. In order to determine if chlorinated naphthalenes are interfering with the analysis it may be necessary to process each sample through some scheme such as detailed by Armour and Burke (1). Another approach is to compare the response of a component on electron capture and microcoulometric or conductivity detectors. If available, gas chromatographic-mass spectrometry offers an excellent method to distinguish chloronaphthalenes from pesticides and PCB compounds. Mass spectra of selected chlorinated pesticidal compounds have been presented by Damico et al. (4) and Sphon and Damico (5). The analyst is referred to the work of Bagley et al. (6), Biros et al. (7) and Bonelli (8) for the mass spectra of the polychlorinated biphenyl compounds. As with the PCB's, the base peak of chlorinated naphthalenes is typically found in the molecular ion cluster and the spectra are very characteristic. Until the problem is more clearly defined, consideration of some technique to detect or eliminate chloronaphthalenes should be given to future determinations of chlorinated hydrocarbon insecticides in environmental samples.

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