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Title : SOME RECENT ANALYTICAL DEVELOPMENTS IN RESPECT TO ORGANOCHLORINE COMPOUNDS IN THE ENVIRONMENT

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Summary : In a study of the residues of organochlorine insecticides occurring in two species of aquatic birds, the heron (Ardea cinerea) and the Shag (Phalacrocorax aristotelis), compounds interfering in the gas chromatography of the insecticides were noted. These compounds may be separated from γ BHC, heptachlor epoxide, dieldrin and endrin by liquid solid chromatography, but not from pp'-dichlorodiphenyltrichloroethane, pp'-DDT or its metabolite pp'-dichlorodiphenyldichloroethylene, pp'-DDE.

The Dohrmann microcoulometric detector and thin layer chromatography gave evidence that some of these compounds were halogenated and further their stability to strong acids and bases indicated that they were probably chlorinated aromatic compounds. By means of combined gas liquid chromatography - mass spectroscopy, these compounds were shown to be polychlorinated biphenyls.

The occurrence of such compounds in the environment present serious problems in the analysis of tissues of humans and animals for chlorinated insecticides.

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Text: Environmental pollution with organochlorine insecticides and their metabolites, particularly DDE, dieldrin, DDE and DDT, has been recognised for some years. Structural formulae of the most widely occurring compounds are given in Figure 1.

Recognition of the widespread occurrence of these compounds was chiefly due to the development of the electron capture detector in conjunction with gas-liquid chromatography. This technique provided a sensitive and semi-selective method for determination of these compounds (Figure 2). Samples provided by the U.K. Nature Conservancy in connection with a study of the effect of organochlorine insecticide residues on aquatic predatory birds, in particular the shag (Phalacrocorax aristotelis) and the heron (Ardea cinerea), gave, by electron capture detection, chromatograms in which other compounds interfered with the determination of the insecticides (Figure 3).

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However, microcoulometric detection following combustion when using silver ion in acetic acid solution as titrant (Figure 4) and thin layer chromatography indicated the presence of halogenated compounds.

Another group of chlorinated compounds widely used commercially as plasticisers and oil additives are the chlorinated biphenyls and following an isolated report of the occurrence of such compounds in the environment we obtained samples of these from Monsanto. The chlorinated biphenyls are produced by the chlorination of biphenyl to give varying percentages of chlorine in the product, e.g. Arochlor 1254 contains 54% chlorine, and as such they consist of a range of compounds containing 3 to 7 chlorine atoms per biphenyl nucleus. Since isomers occur there are obviously a large number of compounds which may be present and this is well illustrated by the number of peaks in the chromatogram of Arochlor 1254 shown in Figure 5. The relative retention volumes of some of the compounds closely correspond to those of some chlorinated insecticides (Figure 6).

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Two biological samples which contained chlorinated compounds in addition to insecticides have been examined in detail. These are herring oil and heron eggs. Chromatograms of these with both electron capture and microcoulometric detection are given in Figures 7 and 8 respectively. Since the compounds are present in concentrations of one part per million or less, further advance in their characterisation required the use of a combination of gas-liquid chromatography and mass spectrometry.

The samples were extracted with hexane and further cleaned up by partition with dimethyl formamide, liquid-solid chromatography on Florisil and finally by treatment with concentrated sulphuric acid. The resulting hexane solutions were examined by GLC - MS using SE 30 as the liquid phase in the chromatograph. The eluting gas was split 1:1, one half to a flame ionisation detector, the other half to an MS 12 mass spectrometer fitted with a Blomann separator.

The chromatogram of Arochlor 1254 showed 10 main peaks. (Figure 9). Part of the mass spectra for peak 2, $RRV_{DDE} = 0.5$ and peak 9, $RRV_{DDE} = 1.84$ respectively shows that peak 2 is due to a compound of mass 290 ($Cl = 35$) which contained 4 chlorine atoms and peak 9 is that of a compound of mass 358 containing 6 chlorine atoms (Figure 10). The chromatogram for the heron egg was likewise obtained (Figure 11). The mass spectra of peak 2 $R_{DDE} = 0.5$ and peak 8 $R_{DDE} = 1.84$ (Figure 12), show that the first compound contains 4 Cl and has a mass of 290 whilst the second contains 6 Cl atoms. A precise mass was not obtained for this compound. The herring oil chromatogram (Figure 13) was scanned on ten peaks. The mass spectra for peaks 4 and 10 $R_{DDE} = 0.81$ and 1.85 respectively are shown in Figure 14. Peak 4 is due to a mixture of 6 and 7 chlorinated compounds of masses 358 and 392 respectively.

A comparison of the relative retention times of these compounds occurring in herring oil and heron eggs (Figure 15) also supports the presence of chlorinated biphenyls as environmental pollutants.

From these investigations it is apparent that the pollution of the environment by organochlorine compounds other than insecticides and their metabolites makes the interpretation of gas-liquid chromatograms extremely difficult and further separation procedures will be required before the problem is solved. There is a strong possibility that chlorinated naphthalenes and hexachlorobenzene may also occur in the environment which would complicate the issue further. The problem is an extremely practical one since to quote but one example, herring oil is widely used in margarine manufacture and in some countries there are stringent regulatory limits as to the permitted levels of organochlorine insecticides in foodstuffs. Obviously with the type of pollution described it is virtually impossible to precisely determine the level of some organochlorine insecticides with the methods currently at the disposal of the pesticide residue analyst.