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Mass Spectrometric Identification of Mirex Residues in Crude Extracts and in the Presence of Polychlorinated Biphenyls [a,b]

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Abstract

Mass spectrometry using 10 eV electron impact was employed in the analysis of Mirex residues in the presence of PCB's. Low voltage MS is a useful complementary tool for positive identification of both Mirex and PCB residues in organic extracts.

The MS patterns of pure 2,4,5,2',5'-pentachloro and 2,5,2',5'-tetrachlorobiphenyl and of mixtures of PCB isomers in Aroclor 1254 and 1260 are simple and distinguishable from the MS spectrum of Mirex. There is no overlapping of ions (molecular or fragment) of PCB's with those of Mirex. Each pure chlorobiphenyl has its base peak at the molecular ion (M) in contrast to Mirex which exhibits the intense M/2 ion (m/e 270) as base peak. In mixtures of PCB's, peak clusters, 34 mass units apart, correspond to $C_{12}H_{10-x}Cl_x$ where x = 4 to 9.

A mixture of 500 µg of Mirex and 500 µg of Aroclor 1254 added to 5 g of pork fat was detected by low voltage MS in the crude recovery extract. A probe temperature of 90 or 100°C was satisfactory for identification of each component in the mixture. However, when the probe temperatures reached 140°C or above, interference by extraneous peaks became more serious and most of Mirex and PCB's were depleted. The presence of these extraneous peaks indicated that the treatment of fat extracts by either 24-hr stirring in concentrated H_2SO_4 or by a single florisil column chromatography did not remove fatty residues satisfactorily. Thus, "standard" techniques of Mirex residue cleanup may be inadequate.

Introduction

The world-wide industrial use of polychlorinated biphenyls (PCB's) (4) has made them major potential pollutants. They concern environmental scientists because their toxicological properties are of a chronic nature. In addition, their chemical characteristics

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[b] Correspondence should be addressed to CMH.

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create substantial difficulties in pesticide residue analysis (2, 6, 9). For example, some of the GLC peaks of Aroclor 1254 and 1260 overlap or coincide with Mirex peak when analyzed on QF-1 + DC-200 column (3) or on QF-1[c] or on OV-210[d] (our laboratory). Mass spectrometry is a means of positively distinguishing Mirex from PCB's. Mass spectral patterns of Mirex and Kepone have been reported (10). The present paper reports the progress of our study of analytical methodology pertinent to the confirmation of Mirex residues in biological samples containing PCB's.

Experimental

Sample preparation

One, 5, 20, and 500 µg of Mirex[e] and of Aroclor 1254[f] were added to 5 g of pork fat. The sample was ground in a mortar and pestle with the aid of purified sand in 4 portions of 5 ml of benzene. The benzene fractions were combined and treated with an equivolume of concentrated H_2SO_4. A modified Craig countercurrent distribution cell[2](1) was used for the H_2SO_4 treatment by phase partition. Overnight stirring of the benzene extract with H_2SO_4 was also tested. The benzene layer was then separated, filtered over glass wool-Na_2SO_4 into a conical-bottom centrifuge tube, and carefully concentrated with a stream of dry air. When the volume was at about 0.5 ml, the benzene was carefully washed into a Pasteur pipette that had the tip cut and sealed off to allow the concentration to less than 5 µl. The residue was transferred into a melting point capillary tube which was then cut to 20 mm to fit the mass spectrometer probe. The tube was plugged with spectroscopically inert, fine mesh glass wool. Other samples of pure Mirex, pure chlorobiphenyl isomers, or mixtures of Mirex and Aroclors were put directly into glass capillary tubes cut to 20 mm length, and plugged with spectroquality glass wool.

Mass Spectrometry

A Bell-Howell/CEC model 21-490 mass spectrometer was used. All samples were introduced into the ionization

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[c] 3% QF-1 on Chromosorb G, AW-DMCS, 80-100 mesh.

[d] 3% OV-210 on Supelcoport, 100-120 mesh.

[e] Poly Science Corp., Evanston, Ill. 60201

[f] Monsanto Co., St. Louis, Mo. 63166

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chamber by means of a probe that can be heated independently of the source. Mass scans were taken at various probe temperatures for reasons discussed below. The source temperature was at 240°C and the sample pressure at about 1.5×10^{-5} Torr. The bombarding energy was set at 10 eV since it gives simple mass spectra of Mirex suitable for identification (10). The mass spectral pattern of Mirex was used as reference in combination with isotopic ratios due to ^{37}Cl to facilitate peak identification.

Results and Discussion

The fragmentation pattern of Mirex has been discussed previously (10). The mass spectral property of 2,4,5,2',5'-pentachlorobiphenyl is presented in Figure 1. Unless otherwise specified, ion clusters due to chlorine isotopes (^{35}Cl and ^{37}Cl) are identified in the figures and discussion only by the m/e of parent peaks (P), i.e., peaks due to ^{35}Cl, and molecular ions are referred to as M. Under 10 eV electron impact, 2,5,2',5'-tetrachlorobiphenyl showed breakdown process similar to that of 2,4,5,2',5'-pentachlorobiphenyl. Both compounds produced 2 fragments by losing 1 Cl (M-Cl fragment) and 2 Cl (M-2Cl fragment). Whether the molecule lost 1 and 2 Cl simultaneously or the M-Cl ion lost its second Cl ([M-Cl] - Cl) is not clear. No other ion of significance was observed. Other chlorobiphenyl isomers (hexachloro, heptachlorobiphenyl, etc.) apparently have similar fragmentation property as mass scans of the Aroclor 1254 or 1260 produced no peaks other than those corresponding to the molecular ion, the M-Cl, and the M-2Cl ions of the chlorobiphenyls. Biros, Walker, and Medbery (2) reported comparable results of trichloro, hexachloro, and heptachlorobiphenyl if peaks other than the aforedescribed ones are disregarded. Though not mentioned, the authors obviously used much higher electron energy.

The relative abundance of molecular ions of various isomers produced by successive mass scans with a gradual increase of probe temperatures indicated that the major components of Aroclor 1260 are tetrachloro, pentachloro, hexachloro, heptachloro, octachloro, and a small amount of nonachlorobiphenyls. Under similar conditions, Aroclor 1254 produced similar mass spectra but negligible amounts of heptachloro and the absence of octachloro and nonachlorobiphenyls.

When a mixture of Mirex and Aroclor was analyzed, their mass spectral patterns (produced by 10 eV electron impact) were completely separated from each other as

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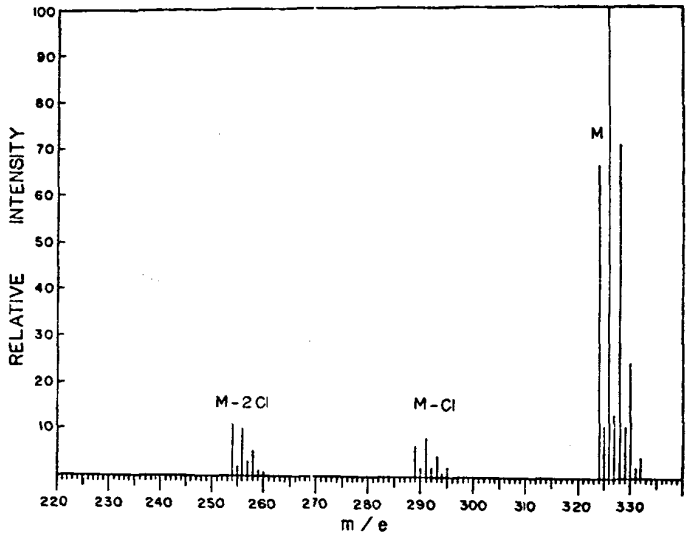

Figure 1. Mass spectrum of 2,4,5,2',5'-pentachlorobiphenyl under 10 eV electron bombardment. M is the molecular ion. There are no other peaks of significance.

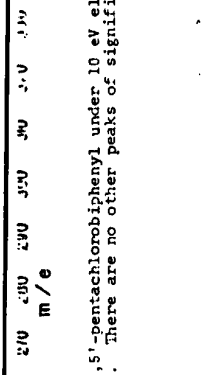

Figure 1. Mass spectrum of 2,4,5,2',5'-pentachlorobiphenyl under 10 eV electron bombardment. M is the molecular ion. There are no other peaks of significance.

shown in Figure 2. There were no peaks of importance pertaining to any of the components below m/e 200. Further differences in fragmentation behavior between Mirex and PCB's are that the former has its characteristic base peak at M/2 cluster (m/e 270) and quite small molecular ion peak (M), while PCB's have intense molecular ions as base peaks; the latter property is due to the 2 benzene rings (8).

Recovery of a mixture of 500 µg of Mirex and 500 µg of Aroclor 1254 added to 5 g pork fat was easily detected by low voltage MS in the crude extract after it was treated with concentrated H_2SO_4. The most favorable probe temperatures for obtaining good, clearly recognizable mass spectra were at 90-100°C as illustrated in Figure 3. Despite numerous extraneous peaks from the fat particularly at m/e below 200, mass scans in this temperature range showed minimum interference with ions of Mirex and/or PCB's except at the following masses: 237.5, 241.5, 256.5, 270.5, 271.5, 360.5, and 361.5. Nevertheless, peak clusters due to Cl isotopes at the aforementioned m/e regions remained clearly recognizable. The presence of extraneous peaks proved that the treatment of pork fat extracts with H_2SO_4 either by simple binary phase partition or by continuous overnight stirring did not eliminate organic impurities. One sample from florisil column chromatography showed similar incomplete cleanup of organic contaminants.

The results presented here show the feasibility of concentrating pesticide residue extracts, to µl-volume for positive confirmation by mass spectrometry. For relatively stable compounds with low vapor pressure such as Mirex, the sample in organic solvent such as benzene can be introduced into the glass capillary tube plugged with glass wool 1 to 2 weeks in advance before mass spectrometric testing. Thus, the sending of prepared samples to other laboratories where a mass spectrometer is available could be done without affecting the analysis. Thus, crude residues can be quantitated by EC-GLC then confirmed by mass spectrometry.

Analytical sensitivity remains a problem since we were unable to detect the presence of Mirex and/or Aroclor 1254 in sample extracts containing 1, 5, or 20 µg of each chemical. However, a standard preparation of 3.5 µg of pure Mirex gave highly satisfactory mass spectra during 5 repeated scans for about 5 min. Depending on the types of biological materials, better techniques of sample cleanup and of concentration to µl-volume would certainly improve the sensitivity of mass spectrometric analysis. Hutzinger and Jamieson (5) reported the analysis of 1 ppm of 2,6-dichloro-4-nitro-aniline (apparently a total amount of 100 µg) in

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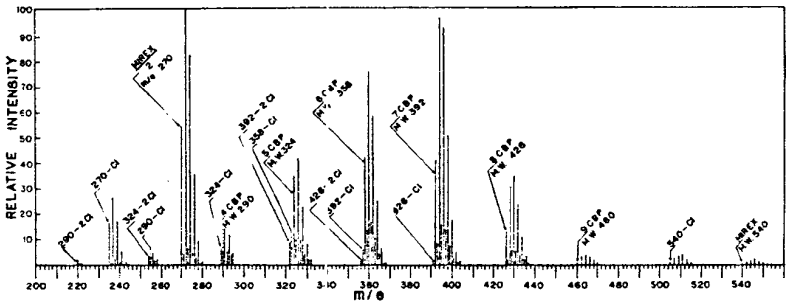

Figure 2. Mass spectra of a mixture of Mirex and Aroclor 1260 under 10 eV electron impact. Tetrachloro, pentachlorobiphenyl, etc., are referred to as 4 CBP and 5 CBP, etc. Fragments are designated as M.W.-Cl. The Hexachlorocyclopentalene ion of the Mirex fragment is called Mirex/2 at m/e 270. There are no peaks of importance below m/e 200.

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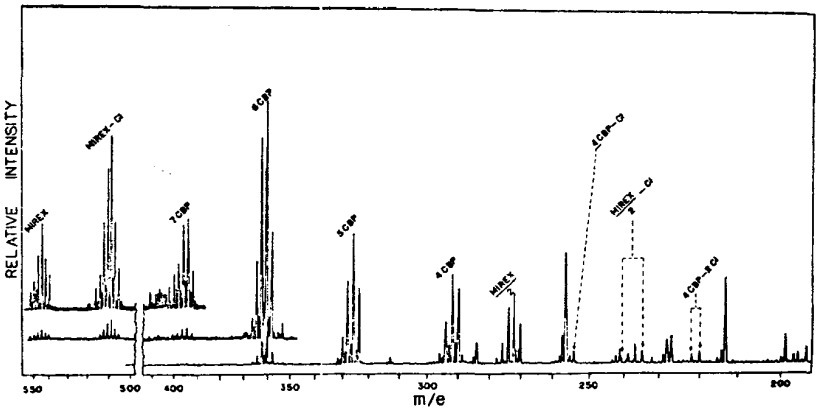

Figure 3. Partial galvanometer trace of mass spectra of pork fat extract spiked with 500 mg of Mirex and of Aroclor 1254 at probe temperature of 90°C. Peaks and peak clusters not labelled are due to interfering materials in the extract. There are numerous peaks below m/e 200, but none pertain to Mirex or Aroclor.

crude peach extract with low resolution mass spectrometry.

Low voltage mass spectrometry (10 eV or lower, i.e., slightly above ionization potential) should be a very useful complementary technique in the analysis of multiple pesticide residues as it produces, rather simple spectra. We also found that, under 10 eV, Dieldrin and DDE produced mass spectra easily distinguishable from each other as well as from those of Mirex and PCB's (unpublished data). Low voltage mass spectrometry in organic analysis has been briefly discussed by Roboz (7) who gave references to further details.

Acknowledgments

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