Discrimination between PCB and DDT Residues by a Gas Chromatographic-Mass Spectrometric Technique

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Gas chromatography is the cornerstone of organic trace analysis in general and chlorinated hydrocarbon analysis in particular. Yet analyses based solely on gas chromatographic retention times have an inherent element of ambiguity. This is so because the possibility always exists that, for any given gas chromatographic system, two compounds will have indistinguishable retention times and thus be indistinguishable. In the analysis of chlorinated residues this possibility becomes a worrisome reality. Polychlorinated biphenyls (PCB's) (1), DDT and its metabolites(2), various cyclodiene pesticides(3), and chloronaphthalenes(4) all have quite similar retention times on the commonly used stationary phases. Numerous chemical(1,2) and chromatographic(5,6,7) procedures have been developed to differentiate among these classes of compounds.

Considerable effort has also been devoted to the development of combined gas chromatographic-mass spectrometric methods for analysis of trace amounts of organic materials(8,9) including organo-chlorine residues(10,11,12). Mass spectrometry is particularly useful in confirming gas chromatographic peak assignments of chlorinated organic species since such compounds give rise to characteristic multiplets in their mass spectra(13). In using mass spectrometry in conjunction with gas chromatography a considerable range of experimental variation is possible. No one approach is best for all analyses. Thus a procedure that inventories the major organo-chlorine constituents of a mixture(10) may be quite different from a procedure that assays picogram quantities of a specific compound(14).

This communication describes a gas chromatographic-mass spectrometric procedure for the confirmation of gas chromatographic analyses of PCB's, p,p-DDT and p,p-DDE in environmental samples. Part of this study has been to define a minimal level of instrumentation necessary for this work. Thus, the gas chromatograph used is a simple instrument. The mass spectrometer, although a machine capable of high performance, is operated at low resolution. Also, direct interfacing of the two instruments is not used.

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Simplicity of instrumentation has not meant a loss in sensitivity. The sensitivity obtained by this method is one to two orders of magnitude greater than that typically achieved by directly interfaced gas chromatograph-mass spectrometer systems(11,12). This procedure can certainly be refined and extended by the use of more sophisticated instrumentation, but in its current state, this is a useful basic protocol.

An Aerograph A90-P3 gas chromatograph has been used in this work. The operation parameters are: column, 1/8 inch by 6 feet aluminum tube packed with 8% SE-30 on Gas Chrom Q 100/120 mesh; carrier gas, helium, 30 ml/minute; temperature, oven-190°, injector-220°, detector-220°. To determine retention times for chlorinated compounds of interest a reference compound, benzil, is used. For a typical column, calibration showed that benzil has a retention time 0.28 that of p,p'-DDE and 0.155 that of p,p'-DDT. By using a reference compound, precise retention times for the chlorinated species can be calculated for the exact gas chromatographic conditions of temperature, flow rate and column condition that obtain on a given day. If a residue sample (prepared as for and typically previously analysed by electron capture gas chromatography(15)) being fractionated by gas chromatography contains PCB, pentachlorobiphenyl elutes at the retention time of p,p'-DDE and hexachlorobiphenyl elutes at the retention time of p,p'-DDT.

It is considered highly desirable that trace amounts of samples be collected from the gas chromatographic fractionation in such a way that transfer or concentration before mass spectrometric analysis is not required. To this end the following collector which can be transferred *in toto* to the mass spectrometer is used. The collector is a 65 mm length of pyrex glass tubing 3mm o.d. filled with 80/100 mesh glass beads which are held in place by plugs of brass gauze. This represents a modification of apparatus previously described by others(8,16). In use the glass beads are wetted with hexane and the entire assembly cooled with dry ice. At the appropriate moment the tube is connected to the collection port of the gas chromatograph, dry ice cooling being maintained. When the collection period is over the tube is removed from the gas chromatograph. Then the hexane and any condensed moisture are removed by exposure to vacuum for one minute at room temperature. At this point the tube can be introduced to the mass spectrometer (an AEI MS-9) via the direct insertion probe. Alternately the sample tube can be sealed in a glass ampule and kept at -10° until mass spectrometric analysis is convenient.

The mass spectrometer operating parameters are as follows: analyser slits, 50 microns; filament emission

current, 450 microamps; ionizing potential, 70 eV; electron multiplier, 2.9 kV; source temperature, 230°.

The mass spectromteric procedure for the analysis of the gas chromatographic fraction with the retention time of p,p'-DDE (which may also contain pentachlorobiphenyl) is as follows. The mass spectrometer is set to scanning repetitively (8 second scan followed by 8 second flyback) over a mass range approximately 315 to 330. Repetitive scanning of a selected mass range increases the mass spectrometer's sensitivity(11,17). A collection tube from the gas chromatographic fractionation is introduced through the direct insertion probe. Care is taken to ensure that the end of the tube which the gas chromatographic effluent entered is closest to the mas spectrometer's ion source. If p,p'-DDE is present, peaks are observed at M/e = 316, 318 and 320 of relative intensity 77:100:49. If pentachlorobiphenyl is present, peaks are observed at M/e = 324, 326 and 328 of relative intensity 62:100:65. If both p,p'-DDE and pentachlorobiphenyl are present, both sets of peaks are observed. This technique cannot distinguish among the possible chlorine substitution patterns of pentachlorobiphenyl(18) or even among any compounds of a given molecular weight and chlorine number.

Using the above procedure, one nanogram of p,p'-DDE or pentachlorobiphenyl from five nanograms of Arochlor 1254 (Monsanto's tradename for a commercial mixture of PCB's) can reproducably be detected. For detection of nanogram quantities of chlorinated hydrocarbons it is necessary to operate the mass spectrometer at a resolving power greater than one part in 3000. At such resolution peaks due to tetrachloride species are, because of the mass defect of chlorine, clearly resolved from unhalogenated organics.

A similar procedure is used to distinguish p,p'-DDT from hexachlorobiphenyl. Analysis is carried out as above except that the mass spectrometer scans the mass range 350 to 365. If p,p'-DDT is present, peaks are observed at M/e = 352, 354 and 356 of relative intensity 62:100:65. If hexachlorobiphenyl is present, peaks are observed at M/e = 358, 360, 362 and 364 of relative intensity 50:100:83:37. In this study it has been possible to collect nanogram quantities of p,p'-DDT only when a freshly fabricated column is used. A working hypothesis is that nanogram quantities of p,p'-DDT are degraded by alumina deposits that arise from oxidation of the column tubing. In this situation a limit of sensitivity for p,p'-DDT has not been determined. It is anticipated that the use of a glass column will eliminate this problem. Hexachlorobiphenyl can be detected from five nanograms of Arochlor 1254.

The use of this procedure to confirm the presence of PCB in plankton will be reported elsewhere. Other applications are in progress.

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