Analysis of the Polychlorinated Biphenyl Problem

Application of Gas Chromatography–Mass Spectrometry with Computer Controlled Repetitive Data Acquisition from Selected Specific Ions

James W. Eichelberger, Lawrence E. Harris, and W. L. Budde[1]

Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268

The polychlorinated biphenyls are a difficult-to-analyze class of environmental contaminants because of the large number of possible individual isomers and their physical and chemical similarity to the chlorinated hydrocarbon pesticides. Individual mass monitoring techniques were examined in search of a procedure which is sufficiently sensitive, but which eliminates the need for elaborate separations, and does not sacrifice too much of the qualitative information content inherent in a complete mass spectrum. Several sets of candidate masses were evaluated using PCB's mixed with certain pesticides which are likely to be in a solvent extract of an environmental sample. The method was also tested with a contaminated sediment sample from an Ohio lake and appears useful for both qualitative and quantitative analyses.

The polychlorinated biphenyls (PCB's) are widely discussed environmental contaminants which have been observed in air, water, sediment, and food chain samples (*1-3*). Qualitative and quantitative analyses of these mixtures of mono to perchloro position isomers are complicated by the large number of possible individual isomers and by the physical and chemical similarity of this set of compounds to the chlorinated hydrocarbon pesticides, *e.g.*, DDT, DDE, lindane, dieldrin. In an excellent review of the chromatographic and biological aspects of PCB's, Finkbein (*4*) points out the difficulty of analytical detection and separation of these materials. A suitable analytical method should combine high sensitivity with high qualitative information content in the response in order to obviate the need for elaborate separations and cleanup.

All reported analytical procedures for PCB's employ some type of separation of isomers and closely related compounds. Since most of these compounds are mildly polar non-ionic organic compounds, they are amenable to gas chromatography which has been employed widely. Several standard detectors respond to these compounds at environmentally significant levels, and the selective electron capture detector is capable of detecting these compounds well into the subnanogram level. However, it is now widely recognized that the qualitative information content in these detector responses is small and inadequate for analyses of mixtures of PCB's, chlorinated hydrocarbon pesticides, and other organic environmental pollutants.

The application of a mass spectrometer as a chromatographic detector generates the necessary qualitative information but with a substantial loss in sensitivity—perhaps a factor 10^3-10^5. A conventional mass spectrometer, which focuses on the detector each sequential ion in the required mass range of about 50-500 amu, spends only a very small fraction of the total scan time focusing ions of significant information content. Perhaps for as much as 95–99% of the total scan time, the spectrometer is not focusing ions on the collector or is focusing ions which do not contain relevant information. During these periods, significant information-containing ions are continuously generated in the ion source and literally discarded with the resultant wasted sensitivity. This occurs whether the spectrometer is operated in a continuously rescanning mode (*5*) or not.

Substantial gains in sensitivity have been reported (*6*) where it was possible to rapidly switch focusing between several ions of known significance to the problem. This was accomplished with a magnetic deflection instrument by a device which quickly modified the accelerating potential; however, the technique was limited to a maximum of three ions separated by a factor of 10% in mass.

The development of the digital computer controlled quadrupole mass spectrometer (*7*) opened the possibility of extensive use of program controlled data acquisition with sampling of specific ions, sequences of ions, and varying dwell times on each. Data acquisition from subsets of the ions used in conventional operations should enhance sensitivity without significant loss of information content. This technique is not the same as the "mass chromatogram" concept (*8*) which used conventional data acquisition, with the wasted ions, but displayed the change in abundance of selected ions under program control to facilitate interpretation.

The application of subset data acquisition techniques to the problem of analyses of PCB's is attractive because of the possibility of gaining needed sensitivity without sacrificing too much of the qualitative information content inherent in a complete mass spectrum. A major problem was to define which of the many ions from the large number of isomers it was most advantageous to utilize in the method.

This paper reports the results of our study of the use of subset data acquisition techniques with a minicomputer

[1] To whom correspondence should be addressed.

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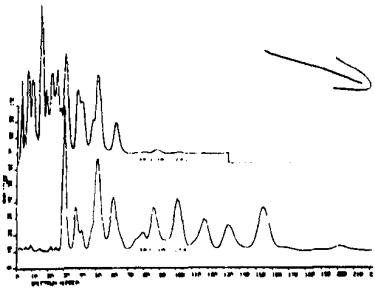

Figure 5. Ion abundance chromatograms from repetitive scans of the PCB subset masses. Upper chromatogram monitors a PCB mixture, Aroclor 1242. Lower chromatogram monitors Aroclor 1254

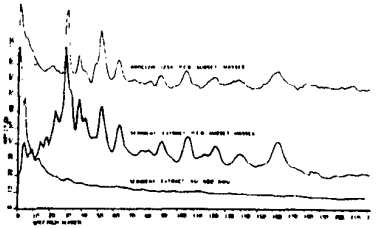

Figure 6. Ion abundance chromatograms from repetitive scans of the PCB subset masses and the mass range 40–400 amu. Lower chromatogram monitors 40–400 amu during sediment extract elution. Middle chromatogram monitors PCB subset during sediment extract elution. Top chromatogram monitors PCB subset during elution of a PCB mixture, Aroclor 1254

It would be desirable to develop a means of distinguishing between PCB compounds with different degrees of chlorination. It has been the practice to characterize PCB's found in environmental samples in terms of the commercial product mixtures and designations, *e.g.*, Aroclor 1248. While this approach has merit in pinpointing specific sources of pollution, it has several disadvantages: (a) less chlorinated biphenyl compounds are somewhat more biodegradable and environmental samples tend to become richer in the less degradable fractions; thus identification with a commercial product standard is precluded; and (b) different commercial mixtures mix in the environment and obscure identifications with standard samples. A scheme based on the relative amounts of mono-, di-, trichlorobiphenyls, etc. without regard to the specific position isomers is proposed as a meaningful way to represent PCB mixtures.

Subset mass scanning offers the possibility of a realistic method of measuring PCB's in terms of levels of chlorination. Table III shows a breakdown of the contributions to the integrated ion abundance data obtained during the chromatography of the seven pure PCB isomers with PCB subset mass scanning (Table I and Figure 2). As monochlorobiphenyl eluted, spectrum numbers 11–16, all of the integrated ion abundance was measured at mass 190. Ion abundance at other subset masses showed no significant deviation from base-line or background levels, as expected. As more chlorinated isomers emerged, interferences from fragment ions were apparent. For example, dichloro fragment ions were observed at mass 224 during the elution of tetrachlorobiphenyl isomers. However, selectivity was generally at least 80% in favor of the biphenyl actually eluting. This experiment is the basis for a method of assessing the levels of chlorination in a PCB mixture and it will be explored further in future work.

Quantitative Analysis. Quantitation of PCB's with ion abundance chromatograms from subset mass scanning is readily accomplished. For this experiment, the conventional approach was adopted and it was assumed that the PCB mixture was identified as one of the commercial mixtures. The sum of the relative ion abundance data from all the subset masses for all the PCB isomers was measured (total peak area) in three chromatograms obtained from three solutions containing 500, 300, and 100 ng, respectively, of Aroclor 1254. Each solution contained 40 ng of dimethylnaphthalene which served as an internal standard to normalize the PCB peak areas. A plot of total peak area against the amount of Aroclor 1254 was linear. Therefore, from this calibration, overall PCB concentrations could be calculated assuming the commercial mixture was correctly identified and the appropriate standards were used.

Table III. Percentage of the Integrated Ion Abundance Measured at Each Subset Mass

Compound eluting	Spectrum numbers	Subset masses						
		190	224	260	294	330	362	394
Monochloro	11–16	100	0	0	0	0	0	0
Dichloro	51–58	0	100	0	0	0	0	0
Trichloro	64–70	0	0	100	0	0	0	0
Tetrachloro	77–83	0	18	2	80	0	0	0
Tetrachloro	86–91	0	20	0	80	0	0	0
Pentachloro	112–119	0	0	18	0	82	0	0
Hexachloro	173–185	0	0	0	13	0	87	0

Application to an Environmental Sample. The PCB's like many of the persistent chlorinated hydrocarbon pesticides are water insoluble and accumulate in fatty tissue and are adsorbed on sediments beneath rivers and lakes. An extract of a sediment sample from Grand Lake St. Mary's, Ohio, was examined by GC/mass spectrometry using a conventional 40–400 amu repetitive scan. That ion abundance chromatogram is shown as the bottom trace in Figure 6. Examination of the mass spectrum at spectrum number 31 suggested the presence of a chlorinated biphenyl compound. The middle chromatogram in Figure 6 was generated by repetitive PCB subset mass scans using an identical amount of the same sample. A PCB pattern of peaks was clearly suggested. The top chromatogram was obtained by repetitive PCB subset mass scans during elution of 50 ng of Aroclor 1254.

CONCLUSION

The subset data acquisition technique with a computer controlled mass spectrometer is well suited to the analysis of PCB's in environmental samples. This technique is clearly adaptable to analyses of other environmental pollutants, *e.g.*, petroleum products, where the increased sensitivity has permitted the clear observation of molecular ions from saturated aliphatic hydrocarbons. The widespread application of computer controlled gas chromatography-mass spectrometry to problems of environmental research will no doubt result in a wide variety of other applications.

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