Polychlorinated Biphenyl (PCB) Analysis

In researching this subject one finds that the method presently recommended is a sound technical method based on gas chromatography with either electron capture or microcoulometric detectors. A method, however, highly sensitive but not highly specific. This GC method is presently being reviewed by ASTM Committee D-19.06 for acceptance as a standard method. This method and other GC procedures had been used for analyzing samples containing unknown PCB mixtures but the rise of a more specific yet less sensitive technique GC/MS (gas chromatography-mass spectrometry) (2)(3) has given identity to these PCB mixtures. GC/MS can identify and quantitate (4) the isomers of concern by determining the mass ion of a particular isomer at its known retention time. Several of the most abundant isomers are available commercially (5) with more being made available monthly. The work of Eichelberger et al. of the EPA (4) points out these problems and proposes a GC/MS procedure that is more sensitive than previous GC/MS methods.

The question is whether a regulation should be monitored by a method 10 to 1000 times more sensitive than GC/MS yet lacking the specificity of mass spectrometry. A combination of these techniques would be more ideal. Enough is known now, therefore, to use gas chromatography with electron capture or microcoulometric detection to analyze for individual isomers using the standards presently available and GC/MS to setup the method conditions and confirm selected samples.

In fact standardization with individual isomers will be more sensitive than with PCB mixtures where the standard response per unit weight is spread out over several isomers.

The following conclusions may be made.

(1) Present PCB method lacks specificity.

(2) GC/MS is specific but 10-1000-fold less sensitive.

(3) Using the present GC method for specific isomers confirmed by GC/MS will exceed the present method sensitivity.

The point, therefore, that must be emphasized is that the analytical technology of the compounds on the toxic pollutants list is a highly dynamic field and like the toxicological data must be kept up to date in our methodology.

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References

1. "Method for Polychlorinated Biphenyls (PCB) in Water", Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268.

2. Stalling, D. L. and Huckins, J. N., "Gas-Liquid Chromatography-Mass Spectrometry Characterization of Polychlorinated Biphenyls (Aroclors) and ^{36}Cl-Labeling of Aroclors 1248 and 1254", Journal of AOAC, Volume 54 #4, 801 (1971).

3. Fishbein, L., "Polychlorinated Biphenyls", J. Chromatography 68, 345 (1972).

4. Eichelberger, J. W., Harris, L. E., and Budde, W. L., "Analysis of the Polychlorinated Biphenyl Problem", Analytical Chemistry, Vol. 46 #2, 227 (1974).

5. Analabs Research Notes, Vol. 12 #2, 12 (1972).

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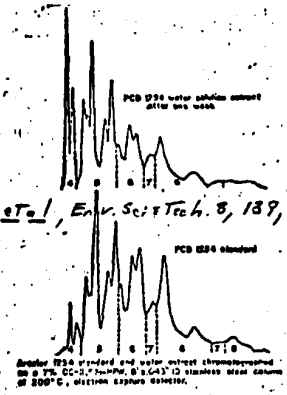
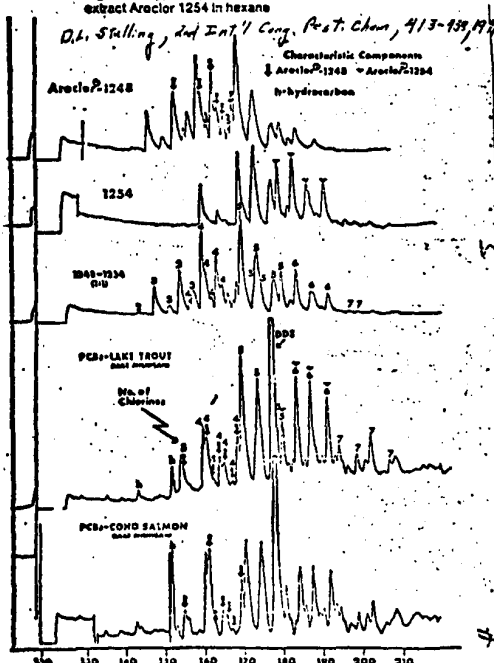


Haque et al, Env. Sci & Tech. 8, 139, 1974.

Figure 1. Typical gas chromatograms of standard and a water extract Aroclor 1254 in hexane

D.L. Stalling, 2nd Int'l Cong. Pest. Chem, 413-439, 1971



7. Composition of PCB residues in fish. Arrows and triangles designate the most characteristic peaks of the Aroclor. All numbered peaks in chromatograms of fish extracts are PCBs. These numbers designate the number of chlorine atoms in the compounds as determined by mass spectrometry. Temperature program rate, 4°C/min, He 3 psig, 50' x 0.020" i.d. SE-30 SCOT column, PE-2700 CC-MS.

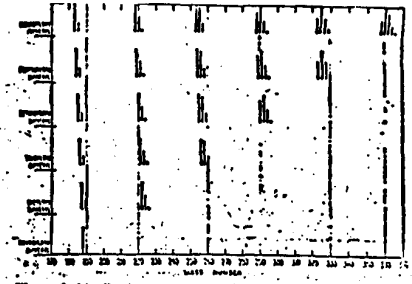


Figure 1. Idealized mass spectra of mono- to hexachlorobiphenyls above mass 180

Eichelberger et al, Anal. Chem. 46, 237, 1

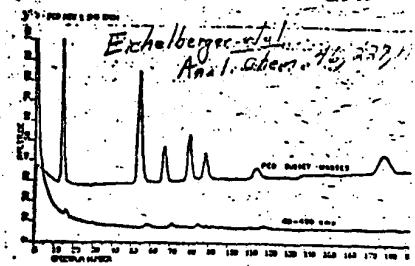


Figure 2. Ion abundance chromatograms of a mixture of 5 ng of each of seven pure PCB isomers. Lower chromatogram monitors masses 40–400; upper chromatogram monitors the PCB subset masses

Wallnofer & Koniger Analab Inc. Res Note 13, 3, 14, 15, Dec. 1973

TABLE 1

Solubility of chlorobiphenyls in water

Compound	Solubility (mg)	Solubility (ppm)
Monochlorobiphenyls		
2-	6.0	5.8
3-	3.35	3.6
4-	1.20	1.17
Dichlorobiphenyls		
2, 4-	1.40	1.40
2, 2'-	1.56	1.44
2, 4'-	1.90	1.85
4, 4'-	0.08	0.07
Trichlorobiphenyls		
2, 4, 4'-	0.085	0.085
3, 4, 2'-	0.075	0.080
Tetrachlorobiphenyls		
2, 2', 5, 5'-	0.046	0.046
2, 3, 2', 3'-	0.037	0.030
2, 3, 2', 5'-	0.170	0.170
2, 4, 2', 4'-	0.070	0.065
2, 4, 3', 4'-	0.055	0.060
2, 5, 3', 4'-	0.041	0.041
3, 4, 3', 4'-	0.175	0.175
Pentachlorobiphenyls		
2, 3, 4, 2', 5'-	0.021	0.023
2, 4, 5, 2', 5'-	0.035	0.028
Hexachlorobiphenyl		
2, 2', 4, 4', 5, 5'-	0.0058	0.0058

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