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Determination of Low ng/L Levels of Polychlorinated Biphenyls in Drinking Water by Extraction with Macroreticular Resin and Analysis Using a Capillary Column

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Polychlorinated biphenyls (PCB's) are usually extracted from water by solvent extraction (INLAND WATERS DIRECTORATE; analytical methods, 1974). However, the relatively small sample size, ca. 1-2 L, that can be handled restricts the quantitation limits of PCB's analyses. Recently charcoal (CHRISWELL et al. 1975) polyurethane foams (MUSTY & NICKLESS 1974), Carbowax-undecane on Chromosorb W (MUSTY & NICKLESS 1976), as well as macroreticular resins (CHRISWELL et al. 1977, MUSTY & NICKLESS 1976, LAWRENCE & TOSINE 1976, COBURN et al. 1977) have been used to isolate PCB's from water. Amberlite XAD-2 and XAD-4 macroreticular resins have been used by several workers (CHRISWELL et al. 1977, MUSTY & NICKLESS 1976, COBURN et al. 1977) to analyse PCB's from a variety of water sources but on relatively small sample size (1-2 L) and recovery studies were carried out at relatively high fortification levels (ca. 250 ng/L). However, COBURN et al. (1977), suggested that the XAD-2 method could be used to sample large volumes of water to decrease the quantitation limits for PCB's analysis.

Because of our interest in the analysis of a municipal well water supply that was suspected to be at risk from contamination by Aroclor 1016, we have extended the XAD-2 macroreticular resin method for use at low ng/L levels of Aroclor 1016. The general applicability of the method was also evaluated for Aroclors 1232, 1242 and 1254.

EXPERIMENTAL

Reagents

a) Solvent - Distilled in glass (Caledon Laboratories, Georgetown, Ontario). Re-distill in an all glass system.
b) PCB Standards - Analytical standards were obtained from Monsanto Co., St. Louis, MO (Aroclor 1016, 1242, and 1254) or from Supelco (Supelco Inc., Bellefonte, Pa. 16823) (Aroclor 1232). Prepare stock solution of each Aroclor at 1000 ug/mL in hexane. Prepare spiking solutions at 10 and 1 ng/uL in acetone and standard solution for GC analysis at 0.4 and 0.1 ng/uL in 2,2,4-trimethylpentane.
c) Macroreticular resin - Amberlite XAD-2 (Rohm and Haas through BDH Chemical Co., Toronto, Ontario). Purify as previously described (McNEIL et al. 1977).

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d) Anhydrous sodium sulfate - Reagent grade, granular. Heat at 400°C overnight. Cool and successively wash with methylene chloride, acetone and hexane. Store in bottle with Teflon-lined cap.
e) Purified water - Pass Millipore Super-Q system water through XAD-2 cartridge at ca. 150 mL/min. Collect and store in clean glass bottles.
f) Glass wool - Wash with methylene chloride, acetone and hexane. Store in clean glass jar with Teflon-lined cap.
g) Florisil - Heat at 275°C overnight. Cool and deactivate with purified water (2% w/w).

Apparatus for PCB's analysis

a) Mini-Florisil column - Custom made 10 cm x 10 mm id column connected to #2 Teflon stopcock and a 100 mL round bottom flask as reservoir.
b) Gas Chromatograph - Perkin-Elmer Model 910 equipped with ^{63}Ni electron capture detector; standing current setting 2.0; electrometer setting X64 - X128. Operating conditions: Temperatures (°C) - injector 250, interface 270, detector 300, oven programmed from 160 (hold 2 min) at 4/min to 220 (hold 5 min), post program 225 (hold 5 min); carrier gas-nitrogen at head pressure of 15 psig; make-up gas-nitrogen at 45 mL/min. The glass capillary column was a 11 m x 0.25 mm id WCOT, OV-17 from Perkin-Elmer contained in a cage connected to oven injector and detector ports with 0.3 mm id glass lined 1/16 in od stainless steel tubing. The transfer lines in the GC interface were also 0.3 mm id glass lined tubing. The injection port was modified by a splitless injection system (S.G.E. through Mandel Scientific, Montreal, Quebec) with a removable 0.75 mm id glass lined injector tube and a septum purge valve. The sample was injected using a Hamilton syringe with a 3 in needle.

Sampling with macroreticular cartridges

Prepare cartridge and sample tap water as previously described (LEBEL et al., 1979). Elute as previously described, except further rinse sodium sulfate drying columns with 2 x 10 mL each of methylene chloride, acetone and hexane respectively prior to percolating the XAD-2 organic layer eluate. Concentrate filtrate and rinsings to near dryness on a rotary flash evaporator (water bath 37°C). Transfer solution with several 1 mL hexane rinsings to a small graduated centrifuge tube and concentrate to 1 mL with a gentle stream of dry nitrogen.

Florisil column chromatography

The clean-up method described earlier (BAILEY et al. 1978) was modified as follows: insert plug of clean glass wool into mini column and pack with 3 g of deactivated Florisil (ca. 8 cm deep), topped by ca. 0.5 cm anhydrous sodium sulfate. Wash Florisil

column with ca. 25 mL hexane. Stop flow when hexane just reaches top of sodium sulfate. Place a clean 15 mL graduated centrifuge tube under column as receiver and transfer concentrated extract with clean disposable pipet to head of column. Resume flow. Rinse tube that contained extract with 2 - 1 mL hexane washes, successively adding rinsings to column when previous rinse just reaches Na_2SO_4 layer. Elute with hexane, collecting ca. 13 mL eluate as determined by calibration run to elute PCB's. Add 1 mL 2,2,4-trimethylpentane to eluate and concentrate to ca. 1 mL under a gentle stream of nitrogen. Make up to required volume (2 - 5 mL) with 2,2,4-trimethylpentane.

Analyse extract by capillary column GC-EC.

Field samples

Pass tap water through cartridge at a steady flow of 140 mL/min (ca. 3 bed volume/min) until 200 L has been sampled as determined by calculation or by passing effluent through a volumetric measuring counter (LEBEL et al. 1979).

PCB's recoveries

Fortification procedures similar to those previously described (LEBEL et al. 1979, BENOIT et al. 1979) were followed to give equivalent spiking levels of 1 and 10 ng/L.

RESULTS AND DISCUSSIONS

COBURN et al. (1977) have shown that XAD-2 macroreticular resin can be successfully used to analyse PCB's in 2 L natural water samples fortified at the 250 ng/L level. In order to extend this method to the sampling of larger samples of water, two factors were considered. These were the procedural blank value and the interference from other organic materials in the water sample. Contributions to the procedural blank came from the solvents, Florisil, sodium sulfate and glass wool used in the method. Low procedural blank values, equivalent to 0.04 ng/L for a 200 L potable water sample were attainable only by using doubly distilled solvents and by exhaustively washing all materials and glassware with these solvents. A gas chromatogram of a procedural blank is shown in Figure (2B).

GC analysis of concentrated extracts of potable water samples without Florisil column clean-up gave off-scale peaks at instrument settings suitable for low ng/L PCB's analysis. However, fractionation of the extract by Florisil column chromatography gave a PCB fraction sufficiently clear of interfering organics to permit PCB analysis at the 1 to 10 ng/L. The GC analyses were done on a relatively short (11 m) capillary column, thus providing a compromise of short analysis time and good resolution with minimum interferences from other substances present in the water extract.

Several methods can be used to quantitate PCB levels in environmental samples such as perchlorination (BERG et al. 1972), electron capture response factor to various isomer (WEBB & McCALL

1973, SAWYER 1978), use of specific isomer as a monitor (ZELL et al. 1978) etc. In our method, quantitation of recovery runs was by comparing peak heights of selected peaks from the samples extracts with the corresponding peaks from standard PCB solutions.

Low organic content Millipore Super Q water or laboratory tap water, after passage through XAD-2 resin, was used for fortification studies. Recoveries of Aroclors 1232, 1016, 1242 and 1254 from water samples fortified at the equivalent of 1 and 10 ng/L for a 200 L sample are reported in Table 1. Recoveries at the 10 ng/L fortification level ranged from 86 to 99% and at the 1 ng/L fortification level ranged from 91 to 110%.

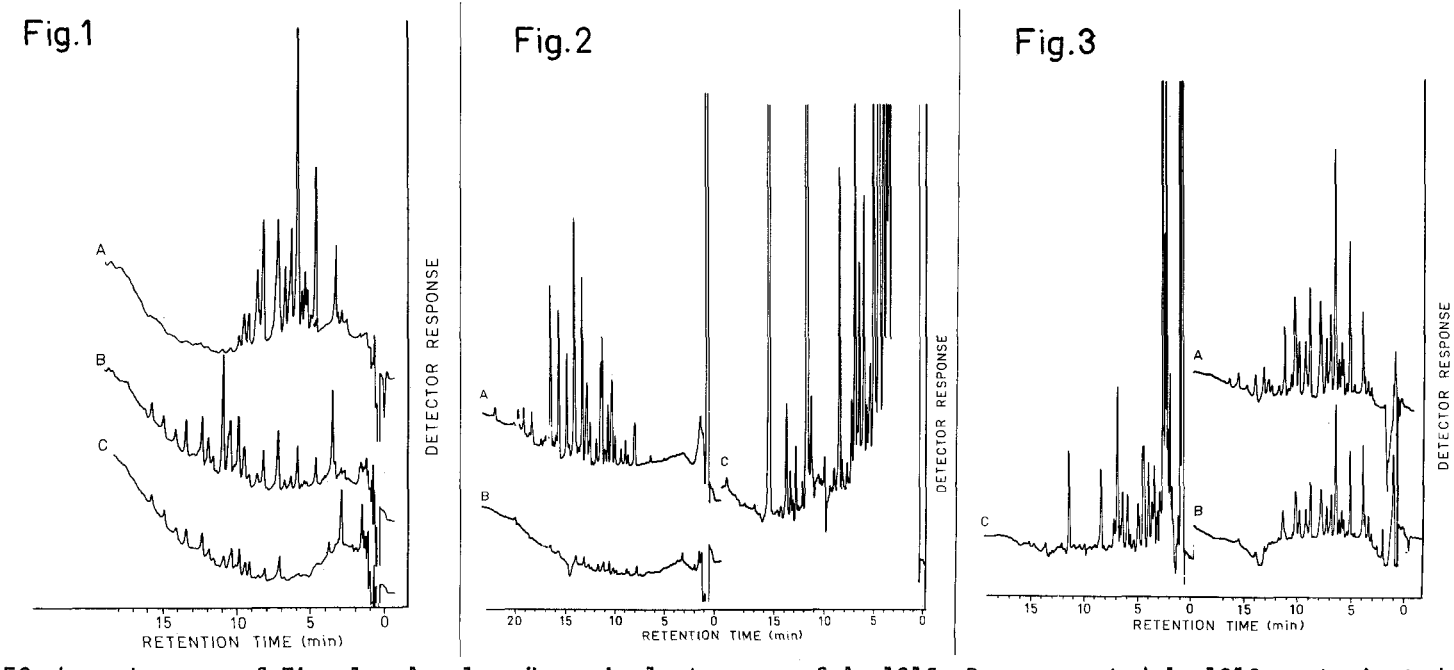
TABLE 1

Recoveries of PCB's from treated XAD-2 resin extract[a].

PCB's	Fortification level ng/L	Recoveries
Aroclor 1254	10	89, 99
	1	100, 110
	1[b]	91
Aroclor 1242	10	86, 98
	1	94, 96
	1[b]	92
Aroclor 1016	10	88
	2	91
Aroclor 1232	10	97, 96
	1	-
	1[b]	109

a) - XAD-2 filtered tap water as water source (Ref. 11).
b) - XAD-2 filtered Millipore Super Q system water as water source.

The analysis of 200 L potable water samples from three well water sources, suspected of contamination by Aroclor 1016, are reported in Table 2 and illustrated in Figure 1B. The interfering compounds were minimal except for an amplified series of peaks similar to the 2-fold concentration procedural blank shown in Figure 1C. The higher background was due to analysis before the method was fully optimized for minimum interferences. Quantitation of the Aroclor 1016 was done by comparing peaks from the interference-free region between retention times 3-7 min, where several of the Aroclor 1016 components (Figure 1A) are eluting. The detection limit was estimated to be ca. 0.04 ng/L of Aroclor 1016 from this source of water with Aroclors 1232, 1242 and 1254 having similar level of detection.



GC-EC chromatograms of Fig. 1: A - 1 ng/L equivalent conc. of Ar 1016, B - suspected Ar 1016 contaminated well water extract, C - 2X conc. of blank; Fig. 2: A - 1 ng/L equiv. conc. of Ar 1254, B - blank on regenerated XAD-2 resin cartridge, C - Ottawa tap water at 1 ng/L conc. level; Fig. 3: A - 10 ng/L equiv. conc. of Ar 1242, B - 10 ng/L equiv. conc. of Ar 1232, C - Ottawa tap water extract at the 10 ng/L conc. level.

TABLE 2

PCB's levels in drinking water samples.

Source	PCB's ng/L
Ottawa tap water	N.D.
Ground water #1	0.2[a]
#2	0.1[a]
#3	0.1[a]

a) Calculated as Aroclor 1016 (Suspected Contaminant).

When this method was applied to potable water from a river source, the interference in the GC-chromatogram (Figures 2C and 3C) from other organic compounds present in the sample made quantitation difficult at the 1 ng/L level. Aroclor 1254 would still be detectable at the 1 ng/L level (Figures 2A, 2C) but 1 ng/L levels of Aroclors 1232, 1016 and 1242 would not have been distinguishable from the background peaks. However, at the 10 ng/L level, it was possible to distinguish peaks due to Aroclor 1232 (Figure 3B), Aroclor 1242 (Figure 3A) and Aroclor 1016 from the background chromatogram from other organics (Figure 3C).

The analysis of a 200 L sample of potable water from a river source showed no detectable levels of Aroclor 1254 (< 1 ng/L) or of Aroclor 1232, 1242 or 1016 (< 10 ng/L).

It can therefore be concluded that the XAD-2 macroreticular resin method can be used to analyse large volumes of potable water for low ng/L levels of PCB's. The detection limits, however, are limited by the interference from other organics in the water sample but are typically in the 1 - 10 ng/L range from potable water from a river source and ca. 0.04 ng/L from underground water sources low in organic content.

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