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Optimization of a Reversed Phase Partitioning Technique for the Analysis of Polychlorinated Biphenyls in Aqueous Samples by Gas Chromatography/Mass Spectrometry

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It has been previously demonstrated that carbowax 400 monosterate and n-undecane coated onto Chromosorb W is a suitable reversed-phase partitioning system for recovering organochlorine insecticides and polychlorinated biphenyls (PCBs) from water (MUSTY et al. 1976). This report details an effort to incorporate a commercially available C_{18} reversed-phase partitioning system into a preparative protocol for gas chromatography/mass spectrometry (GC/MS)analysis of PCBs in aqueous samples.

The C_{18} system chosen (Sep-Pak^R mfd. by Water Associates), and its usage procedure, have been marketed as a preparative procedure for liquid chromatography of PCBs (WATERS, applications insert). It will be shown that with minor technical alterations, these C_{18} systems can be used to quickly and easily, recover PCBs from an aqueous sample and prepare them for GC/MS analyses.

MATERIALS AND METHODS

The C_{18} partitioning cartridges (Sep-Pak^R) use in this study were purchased from Water Associates, Inc., Milford, MA 01757.

GC/MS analysis of the C_{18} -cartridge's background was carried out by adding the contents of a C_{18} -cartridge to 10.0ml of HPLC-grade dichloromethane in a 15.0ml screw-cap test tube. This mixture was vortexed for 10 min. and then centrifuged to clarification. A 5.0ml aliquot of the supernatant was then removed and taken to dryness. The resulting residue was redissolved in 40μl of dichloromethane; 1 μl was then removed for analysis.

The background eluting strength of various non-polar solvents was determined by eluting six cartridges with 5.0ml and 8.0ml volumes of HPLC-grade dichloromethane, methanol, or hexane. All eluents were collected and taken to dryness. The resulting residues were redissolved in 0.5ml of a solution of dichloromethane containing 100μls of bibenzyl/ml. A 1 μl aliquot of this solution was analyzed by GC/MS for each eluting solvent tested. The reported data represent an average of two samples using two different selected ions for integration.

Background comparisions between native and preconditioned cartridges were accomplished by first preconditioning a cartridge

by eluting it with 2.0ml of HPLC-grade methanol. Both preconditioned and native cartridges were then loaded with Arochlor 1248 by passing 50 ml of an aqueous solution containing 500ng/ml of Arochlor 1248 through them. These "loaded" cartridges were dried on a jet of dry filtered N_2 gas, and the Arochlor 1248 was eluted from each cartridge type with 2.0ml of methanol. These eluents were then dried and redissolved in 50.0 μl of HPLC-grade dichloromethane; 1μl aliquots of these concentrates were then analyzed.

To determine the optimal PCB elution solvent volume, a cartridge was loaded with Arochlor 1248 and then fractionally eluted with methanol. The cartridge was "loaded" by passing through it 25ml of an aqueous solution containing 4.0μg/ml of Arochlor 1248. The cartridge was then dried on a jet of dry, filtered N_2 gas. After drying, a flow restriction tip, made of drawn glass tubing, was applied to the exit port of the cartridge and this assembly was attached to the end of a 50.0ml buret. The buret was filled with 50.0ml of HPLC-grade methanol and 0.5ml elution fractions were collected as the methanol was passed through the cartridge. Each fraction was taken to dryness and residue and redissolved in 60μl of HPLC-grade hexane. A 1μl aliquot of the resulting hexane mixture was analyzed by GC/MS operating in a selected ion mode. The reported data represent an average of two analyses.

All GC/MS analyses were performed using a Hewlett-Packard 5985B GC/MS system containing a 10m OV101 fused silica WCOT column operating in splitless injection mode.

RESULTS AND DISCUSSION

It has been reported by KRUPCIK (1976), that mixtures of PCBs can be satisfactorily resolved with OV101 stationary phase on glass capillary (WCOT) columns. Comparable results have also been obtained using OV101 on a fused quartz capillary column (Fig. 1).

Using this column, the "background" material potentially elutable from commercial C_{18} cartridges with dichloromethane was determined. Figure 2 is a total ion spectrum of some of the major components of the "background mixture". The majority of this material was interpreted to be heavy organic methyl esters, high molecular-weight saturated and unsaturated aliphatic compounds, numerous phthalates, squalane, butylated hydroxy toluene, and the partitioning C_{18} phase itself. The majority of this mixture chromatographed at temperatures between 145° and 265°C of the programmed run, and would not interfere in in qualitative and/or quantitative PCB analyses employing gas chromatography with electron capture detection. These compounds, however, seriously impede the acquistion of reliable,

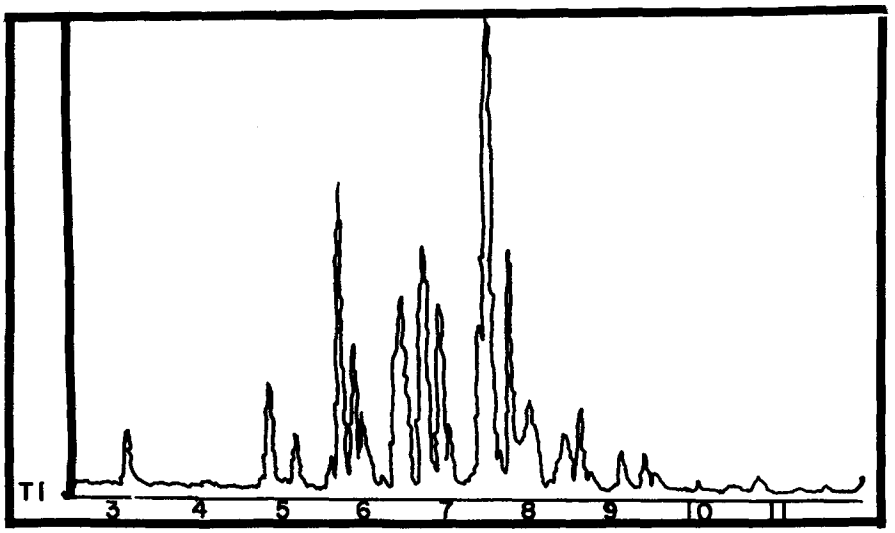

Figure 1. Total ion chromatogram of Arochlor 1242 chromatographed on a 10 meter OV101 fused silica WCOT column. Temperature program: 100° to 260° at 10°/min. (TI=time)

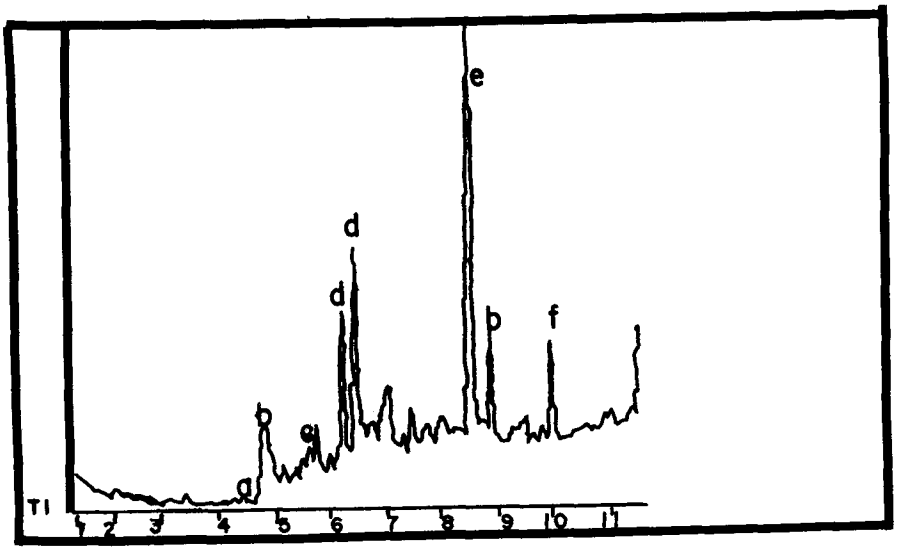

Figure 2. Total ion chromatogram of the background materials extracted into dichloromethane from the contents of a commercially available C_{18} partitioning cartridge. a=butylated hydroxy toluene; b=organic acid methyl esters; c=heavy hydrocarbons; d=phthalates; e=C_{18} phase breakdown; f=squalane; TI=time.

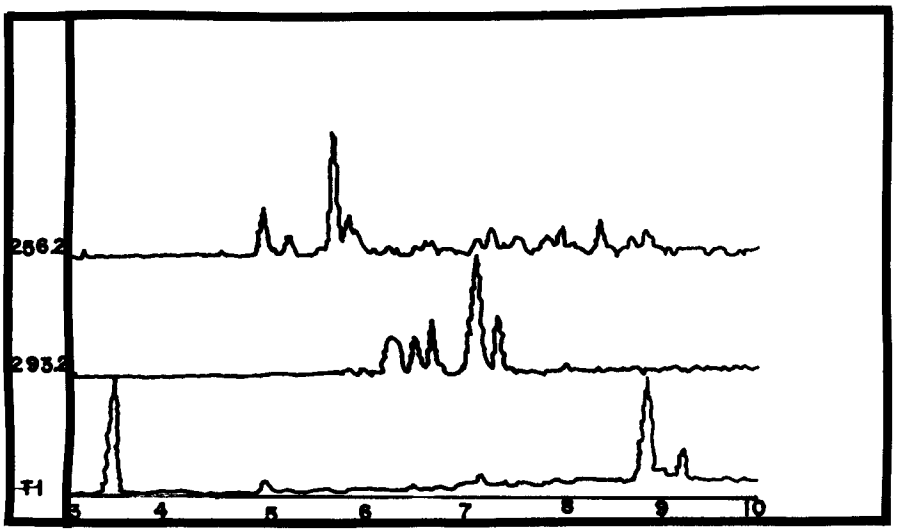

Figure 3. Total ion chromatogram of Arochlor 1248 extracted from water with normal commercially available C_{18} cartridges

Table 1. Relative Elution Strength of Selected Solvents *

Solvent	Background Elution Strength	C_{18} - Phase Stripping Strength
Dichloromethane	100%	100%
Hexane	65% ± 15	89% ± 5
Methanol	52% ± 18	72% ± 8

*All values are expressed as a % of the action of dichloromethane.

(Cont. Page 2)...total ion GC/MS data. Indeed, it has been determined that on the OV101 stationary phase, the C_{18} phase that is stripped from the partitioning system chromatographically coincides with the completion of the Arochlor 1248 fingerprint, and all other "background" substances of the C_{18} partitioning system would interfere with PCBs larger in % chlorine than 1248 (HUTZINGER et al., 1974).

In an attempt to at least control the problem of the high levels of "background" material eluting from the system, the background eluting strenghts of several solvents were tested. C_{18} cartridges were eluted with 5.0ml and 8.0ml volumes of dichloromethane, hexane, and methanol. These elutions were then analyzed by GC/MS with bibenzyl as an internal standard. Due to its great miscibility with most non-polar phases, dichloromethane was used as a reference solvent for evaluating the background-eluting strengths of dichloromethane, hexane, and methanol. These data, presented in Table 1, show that while hexane exhibits a slightly stronger affinity for the non-C_{18} background than methanol, this benefit

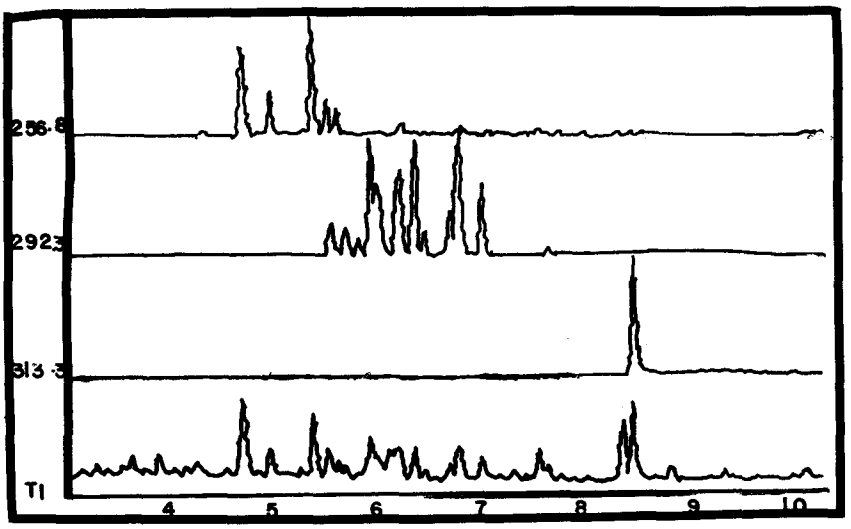

Figure 4. Total and selected ion chromatogram of Arochlor 1248 extracted from water with a C_{18} cartridge preconditioned with 2.0 ml of methanol.

(Cont. Page 4)... is offset by increased degradation of the stationary (C_{18}) phase.

Since even methanol can elute materials that give a high background signal, the need to precondition the C_{18} cartridge with methanol was evaluated. Total ion chromatograms of normal and methanol preconditioned C_{18} cartridges are presented in Fig. 3 and 4. A comparison of these chromatograms clearly shows that untreated cartridges yield a seriously high background signal. This signal is high enough to impose total ion normalization problems, and could potentially reduce capillary column resolution by overloading.

Finally, using methanol as the solvent and employing a methanol preconditioned cartridge, the effect of elution volume on recoverability was studied. In Fig. 5, PCB (Arochlor 1248) concentration is plotted as a function of elution volume. This figure illustrates that Arochlor 1248 is recovered in the first 2.0 ml of methanol. It also indicates that approximately 80% of Arochlor 1248 is recovered in the first ml of methanol.

The commercially available C_{18} cartridges evaluated in this study can be incorporated into experimental protocols employing GC/MS analyses of PCBs initially present in aqueous samples.

The following limitations on cartridge use, however, should be incorporated into the experimental design: (1) The native GC/MS background signal of the system is high[1], but can be greatly reduced by preconditioning with 2.0 ml of methanol; (2) of the solvents tested, methanol is the most suitable for removing PCBs from the

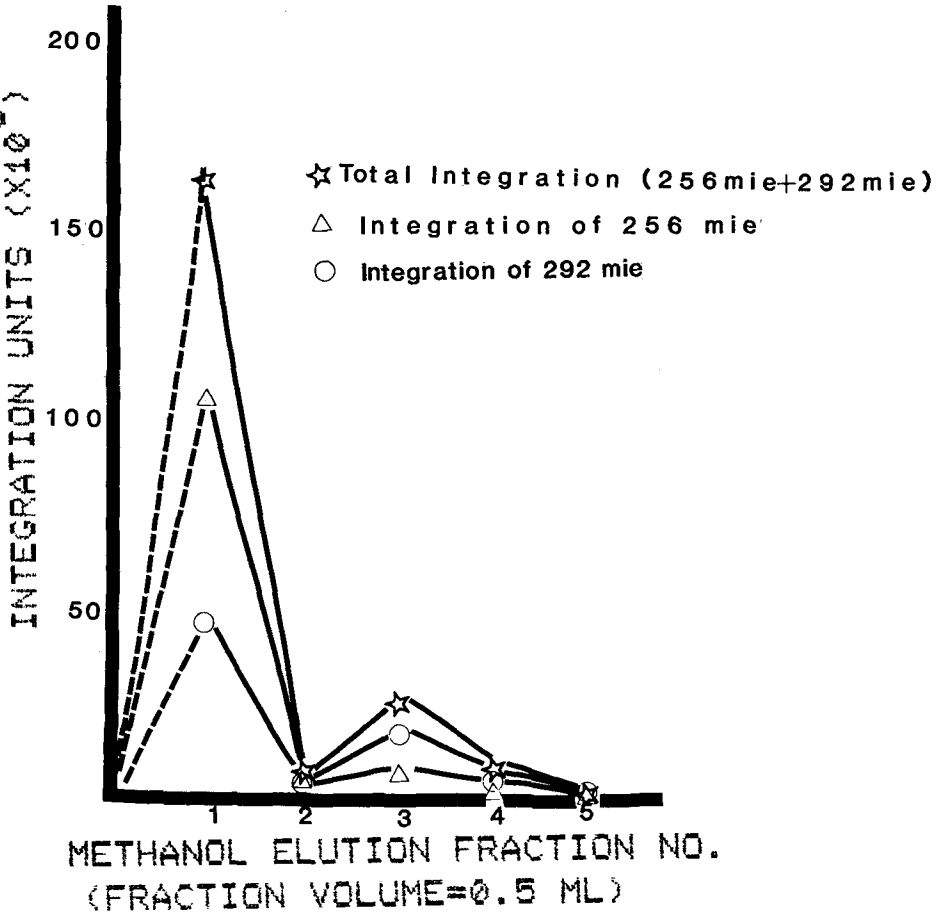

Figure 5. The effect of elution solvent volume on Arochlor 1248 recovery from the C_{18}cartridge system. Approximately 80% of the extracted PCB is eluted in the first milliliter of methanol.

stationary C_{18} phase; (3) Arochlor 1248 can be eluted from a cartridge with 2 ml of methanol: elution volumes greater than 2 ml only cause additional stripping of the C_{18} phase; and (4) the cartridge cannot be used to analyze PCBs with chlorine percentages larger than that of Aroclor 1248 due to unavoidable interference with the stripped C_{18} phase.

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WATERS ASSOC., applications insert.

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