A Flow-thru Method for the Separation of PAHs, PCBs and PCDDs/PCDFs from a Single Extract of an Environmental Sample

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are four related classes of toxic organic chemicals which are frequently present together in a variety of environmental samples.

Two coupled HPLC (high-peformance liquid chromatography) columns have been used to separate the four classes of organic compounds[1]. The first column, containing an amino-bonded phase, was used to separate the PAHs from the PCBs and PCDDs/PCDFs. Fractions containing planar and non-planar PCBs and PCDDs/PCDFs were then obtained from a porous graphitic carbon column. In our laboratory, cleanup of PCDDs/PCDFs in extracts from environmental samples is carried out using a semiautomated low pressure liquid chromatography system containing two alumina columns and a carbon column[2]. We find that cross-contamination is minimized in this system since the adsorbents are replaced between samples. In this study, we have investigated the collection of PCBs as a separate fraction from the semiautomated system. We have also determined that the PAHs can be separated from the PCBs and PCDDs/PCDFs in a preliminary step. Two columns were investigated for this purpose, an intermediate particle size (13-24 microns) silica gel column and a charge-transfer HPLC column containing tetrachlorophthalimidopropyl (TCPP) bonded to silica.

Methods

The silica gel used for the initial separation of the PAHs from the PCBs and PCDDs/PCDFs was 13-24 micron particle size LPS-1 (Whatman Inc.). The adsorbent (7 g) was packed into a Michel-Miller (Ace Glass Inc.) glass column (8 mm i.d. x 25 cm) attached to a second Michel-Miller column as a solvent reservoir. The column and reservoir were pressurized with nitrogen and the solvent flow was controlled with a manual valve (Hamilton Inc.). The PCBs and PCDDs/PCDFs were eluted with hexane which had been dried by passing through acid alumina activated at 450°C. The PAHs were subsequently eluted with 20% methylene chloride/hexane. The second column used for this separation was a preparative HPLC charge-transfer column (1 cm i.d. x 25 cm) containing TCPP (Shandon Scientific Ltd.).

The semiautomated-chromatography system consists of an acid alumina column coupled to a graphitized carbon column (Anderson AX21) which is in turn coupled to a second alumina column. In this study, PCBs were obtained in the wasteline eluent from the first alumina column which consisted of the solution in which the sample was loaded on the system (100 ml 10% toluene in hexane) and a subsequent wash solution (35 mL 3% methylene chloride in hexane).

The 16 Priority Pollutant PAHs and tetra-octa CDDs/CDFs were determined by capillary gas chromatography (GC)/low resolution mass spectrometry (MS) using ten ^{13}C-labeled PCDDs and PCDFs and sixteen deuterated PAHs as internal standards. The PCBs were determined by capillary GC with detection by electron capture[3].

Results and Discussion

The PCB formulations, Aroclors 1016, 1221, 1254 and 1260 contain the range of PCB congeners found in environmental samples in the USA. Initial experiments showed that more than 90% of the PCBs in a 1:1:1:1 mixture of these formulations could be recovered in the waste solvents from the first alumina column in a semiautomated chromatography system for the cleanup PCDDs/PCDFs from environmental samples. However, it was not possible to recover PAHs in a single fraction from this system (Table 1). In fact most of the PAH compounds were irreversibly adsorbed to the graphitized carbon column. Therefore, a preliminary chromatographic step was required to separate the PAHs from the PCBs and the PCDDs/PCDFs.

Experiments were carried out to achieve the separation using large particle-size (>100 microns) silica gel and silica derivatized with polar groups (amino and hydroxyl). However, even with the adsorbent which gave the best separation, a diamino propyl silica, several of the lower molecular weight PAHs were eluted with hexane prior to the last eluting TCDD isomer pair (1,2,6,7/1,2,8,9). When a smaller particle size (13-24 micron) silica gel was used, only naphthalene was eluted prior to the 1,2,6,7/1,2,8,9 TCDD isomer pair using dry hexane as an eluent (Table 2). It was found that solvent flow rates of 1.5 ml/min could be achieved with this particle-size silica using pressures of 20 psi. This pressure is below the upper pressure limit of the pump and glass columns used in the semiautomated chromatography system. Electron acceptor (EA) adsorbents were also investigated as alternative adsorbents for the same separation since the PAHs are strong electron donors (EDs)[4] while the PCDDs are weak EDs and interact with EA phases primarily by dipole forces[5]. The data in Table 2 show that a HPLC column containing the electron acceptor TCPP could also be used to separate TCDD isomers from the 16 Priority Pollutant PAHs. The separation techniques developed in this study have been applied to the analysis of PAHs, PCBs and PCDDs/PCDFs in biological samples and sediments.

References

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Table 1. Recoveries (%) of PAHs in Wastelines from a Semiautomated Cleanup System and in the PCDD/PCDF Sample Collection Flask.[1]

Compound	WL-1	WL-2	WL-3	Sample
Naphthalene	100	24	0.9	0.0
Acenaphthylene	0.6	0.0	0.0	0.0
Acenaphthene	1.0	0.0	0.0	0.0
Fluorene	0.0	85	0.6	1.1
Phenanthrene	0.0	0.0	4.8	90
Fluoranthene	0.0	0.0	0.0	69
Pyrene	0.0	0.0	0.0	7.6

[1] Anthracene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(123*c*,*d*)pyrene, benzo(*g*,*h*,*i*)perylene, dibenz(*a*,*h*)anthracene were not found in any fraction.

Table 2. Separation (%) of the Most Retentive TCDD Isomers from Priority Pollutant PAHs on LPS-1 Silica Gel and TCPP Electron Acceptor Columns.

	LPS-1		TCPP	
Compound	F-1	F-2	F-1	F-2
Naphthalene	100	0.4	57	0.0
Acenaphthylene	2.6	72	0.0	67
Acenaphthene	11	83	0.0	70
Fluorene	0.0	96	0.0	76
Phenanthrene	0.0	90	0.0	77
Anthracene	0.0	89	0.0	73
Fluoranthene	0.0	73	0.0	79
Pyrene	0.0	170	0.0	78
Benzo(*a*)anthracene	0.0	110	0.0	84
Chrysene	0.0	84	0.0	73
Benzo(*b*)fluoranthene	0.0	99	0.0	90
Benzo(*k*)fluoranthene	0.0	73	0.0	83
Benzo(a)pyrene	0.0	82	0.0	73
Indeno(123*c*,*d*)pyrene	0.0	130	0.0	68
Benzo(*g*,*h*,*i*)perylene	0.0	93	0.0	61
Dibenz(*a*,*h*)anthracene	0.0	120	0.0	78
1267/1289-TCDD	92	0.3	77	0.0
			75	0.0

F-1: 35 ml dry hexane (LPS-1), 18 ml 50% toluene/hexane (TCPP)

F-2: 20 ml 20% CH_2Cl_2/hexane (LPS-1), 42 ml CH_2Cl_2 (TCPP)