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Pyrolysis Gas Chromatography-Mass Spectrometry of Polychlorinated Biphenyls On Sediment

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Polychlorinated biphenyls (PCBs) are common environmental contaminants which were freely employed for many years in numerous industrial applications but whose use has now been regulated. Many analytical schemes for monitoring these materials in environmental samples have been developed over the last decades, however, PCBs remain difficult analytical subjects (CAIRNS & SIEGMUND 1981a). Most protocols rely on a combination of wet chemical preanalytical isolation and purification whose complexity depends on the sample matrix. Wet chemistry is frequently followed by gas chromatography with an electron capture detector or other selective detector, or by combined gas chromatography/mass spectrometry Wet chemical manipulations are particularly involved for difficult matrices such as biological organisms, biological fluids, sediments and soils. These wet chemical procedures may include such steps as solvent extractions, solvent partitioning, column chromatography, high performance chromatography, and solvent evaporation to isolate PCBs, free them from interferring materials, and concentrate them to the degree required for ultimate analysis. The time required for these manipulations may greatly hamper efforts directed towards emergency cleanup of accidental or illicit contamination of the environment. Thus, a clear need exists for methods which will allow rapid analysis of relatively intransigent samples for PCB contamination. We would like to report preliminary experiments directed to assessing the use of pyrolysis/gas chromatography/mass spectrometry (PY/GC/MS) in determining PCB contamination of soils and sediments. In these experiments pyrolytic desorption at 1000°C during 10 sec was used to completely replace more lengthy wet chemical mainpulations.

METHODS AND MATERIALS

The top 6-8 in of sediment was collected from an area lake in approximately 5 ft of water using a grab sampler. Excess water was drained from the sediment which was dried for two days under flowing air in a fume hood. The resulting material was lightly ground in a mortar and pestle and passed through a 100 mesh screen to remove larger detritus. Portions of the resulting powder were extracted overnight in a continuous extractor with acetone--hexane and air dried. The material was spiked at approximately 1, 10, and 100 ppm levels using PCB in hexane solution. Spiked samples were thoroughly mixed by slow rotation of the container for 24 hours.

Samples were pyrolyzed in quartz boats using a Pyroprobe 120 (Chemical Data Systems, Oxford, PA), under an atmosphere of flowing helium (30 ml/min). The pyrolysis probe was inserted into the interface to the gas chromatograph, the sample was pyrolyzed, and the resulting vapors swept onto a cool gas chromatography column.

Pyrolyzates, cold trapped on the gas chromatography column (3%OV-1), 2 mm x 6 ft) at 80°C, were analyzed at a helium gas flow of 30 ml/min by temperature programming the column from the initial trapping temperature to 275°C at a program rate of 30°C/min for the first 5 min and 10°C/min thereafter.

The Hewlett-Packard 5985B combined gas chromatograph/mass spectrometer used in these studies was run using conditions generated by the instrument's computer controlled autotune program and an appropriate standard, except that electron multiplier voltage was set at 3000 volts for high sensitivity. Mass spectra were scanned between 200 and 500 amu.

RESULTS AND DISCUSSION

The total ion chromatogram and reconstructed gas chromatograms for three ions characteristic of PCBs containing 4, 5, and 6 chlorine atoms are shown in Fig. 1.

As may be seen, the total ion chromatogram (Fig. 1, A) displays a number of large and small peaks with retention times between _ca._ 3 and 10 min, while the reconstructed gas chromatograms (RCG) for ions of (B) m/z 292, (C) 326, and (D) 360 amu (ions characteristic for biphenyl substituted with 4, 5, and 6 chlorines, respectively) are primarily composed of incompletely resolved clusters of peaks with retention times between 7.5 and 10 min. The more rapidly eluting peaks between 3 and 7 min appear to originate from pyrolysis of non-PCB components of the sediment while the RCG clusters evident from retention time 7.5 to 10 min are derived from the Aroclor 1254 components. PY/GC/MS of extracted sediment spiked with Aroclar 1254 gave lesser amounts of the early eluting peaks, and analyses made on unspiked sediment showed the presence of the peaks from 3 to 7 min but gave little or no indication that PCBs were present.

The mass spectrum of the 360 amu RCG peak eluting at 9.5 min is given in Fig. 2. The two most notable features of the spectrum are the two molecular ion isotope clusters at 288-294 amu and 358-366 amu. These clusters (reflecting differing amounts of ^{35}Cl and ^{37}Cl isotopes in the molecular ion) are those expected for chlorinated biphenyls with 4 chlorine atoms (lower weight cluster) and 6 chlorine atoms (higher weight cluster). The rela-

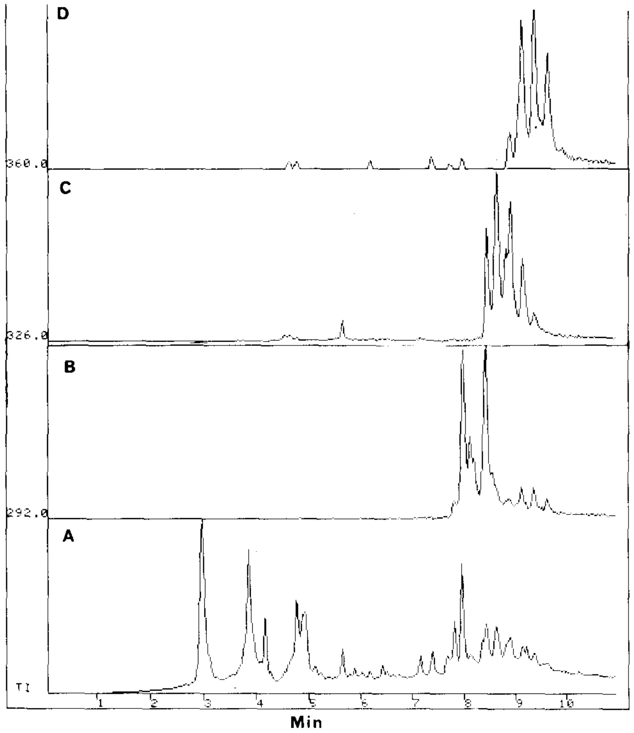

Figure 1. (A) Total ion chromatogram, (B) Reconstructed Gas Chromatogram (RCG) for m/z 292, (C) RGC for m/z 326 and (D) RCG for m/z 360 of PY/GC/MS of 5.0 mg sediment spiked with 11.8 ppm Aroclor 1254.

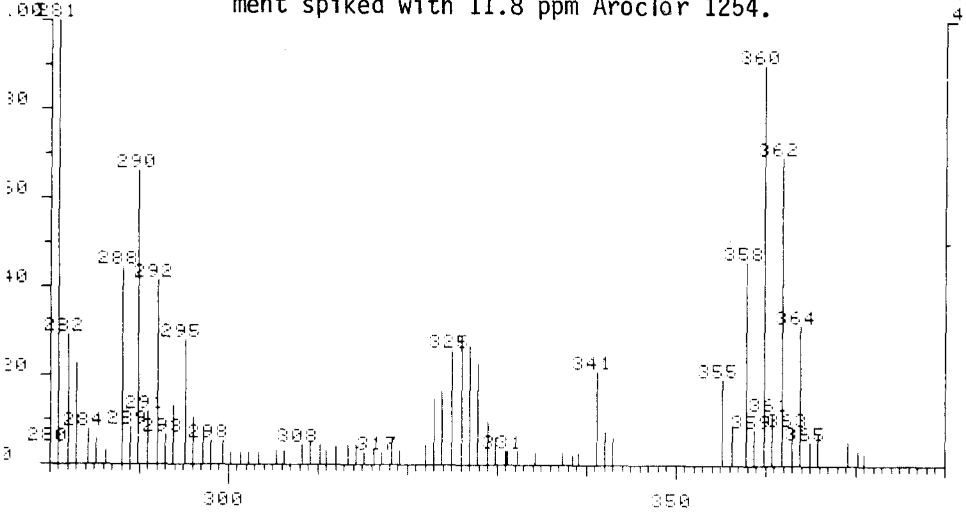

Figure 2. Mass spectrum derived from retention time 9.5 min peak of Fig. 1 D.

tive peak intensities expected for PCBs or other organic molecules with 4 and 6 chlorine substituents may be found in published accounts (WEBB & MCCALL 1973, CAIRNS and SIEGMUND 1981b) or in standard textbooks and references (MCCLAFFERTY 1973, SAFE & HUTZINGER 1973).

From the data presented above it is clear that PY/GC/MS is capable of demonstrating the presence of spiked PCBs on air-dried sediment at approximately 10 ppm level. No wet chemical manipulations were made on the spiked dried sediment. At present the limits of sensitivity of this method are not known. Attempts at using highly sensitive electron capture detectors during PY/GC/ have met with only limited success because of the large number of electron capturing substances released from the sediment during pyrolysis. One would expect that single ion monitoring mass spectrometry would decrease the minimal detectable level of PCBs on sediment to the low or mid ppb level. As described, however, this method offers the exciting promise of analyses of sediment and other solid materials for PCB contamination at low ppm levels with no lengthy sample work-up. Such a method might be very important during emergency situations when the extent of contamination of the environment by these substances needs to be known rapidly.

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