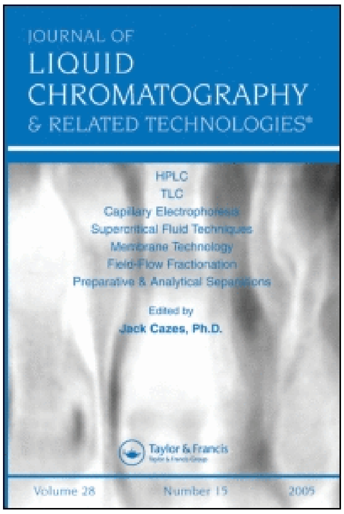

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ANALYSIS OF POLYCHLORINATED BIPHENYLS, DIBENZODIOXINS AND DIBENZOFURANS BY ON-LINE COUPLED MICROCOLUMN HPLC CAPILLARY GC-MS

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ABSTRACT

A multi-dimensional µLC-GC-MS system was developed and used to analyze a sample containing chlorinated aromatic solutes. The electron-acceptor stationary phase, 5-µm 2,4-dinitrophenylmercaptopropylsilica (DNPMP), was packed into a 0.32-mm x 400-mm microcapillary liquid chromatography (µLC) column. Aromatic fractions eluted from the µLC system at 12 µL/min and were then diverted to the gas chromatograph mass spectrometer (GC-MS) by a ten-port switching valve with 50 and 7.6-µL loops. Concurrent cosolvent evaporation occurred in a 0.32-mm x 3-m precolumn ahead of a 0.25-mm x 30-m DB-5 analytical column. Solvent vapors exited through an open-split interface. The µLC-GC-MS system was demonstrated through the analysis of a sample containing polychlorinated biphenyls, 2,7-dichlorodibenzodioxin and 3,6-dichlorodibenzofuran. The precision for the quantitative transfer of an analyte from the µLC to the GC-MS was 16.9% RSD.

INTRODUCTION

Polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have been designated among the most toxic

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anthropogenic compounds in existence [1]. There are 209 possible congeners of PCB, 75 congeners of PCDD and 135 congeners of PCDF.

The complexity of these samples has mandated selectivity and sensitivity available only with capillary high-resolution mass spectrometry (Rs > 10,000). There are interferences in the mass-spectral determination of PCDF and PCDD from PCB [2], 4,4'-DDT [3], chlorinated diphenylethers [4-7], polychlorinated phenols [7-9] and their methyl ethers [7].

Most of the isolation and concentration steps involve multiple-step open column techniques with silica, alumina and Florisil® (magnesium silicate) [2,7,10-12]. The PCDF and PCDD are eluted as a fraction between a fraction containing PCB and polychlorinated diphenylethers, and a fraction containing polar compounds like the phenols [11,12]. High performance liquid chromatography has also been used in the cleanup of PCDD and PCDF fractions prior to GC-MS analysis. Most of these techniques used silica and alumina columns [13-17], and some used reversed -phase HPLC [17,18]. The preferred technique is still to collect all PCDD or PCDF as a group with later analysis of selected isomers [19].

An interesting approach to this class separation was the separation of PCDD and PCDF, which have planar structures, from nonplanar PCB in an open column containing carbon coated on glass fibers [20]. Electron-acceptor phases have demonstrated some potential in resolving polycyclic aromatic solutes based upon the "flatness" of the molecule [21]. Based upon work performed in this laboratory, it appeared that 2,4-dinitrophenylmercaptopropylsilica (DNPMP) would be a good electron-acceptor bonded stationary phase for the separation of PCB, PCDF and PCDBD in normal-phase HPLC [22]. Individual isomers of PCDD have recently been separated on *p*-nitrophenylethylsilica in reversed-phase HPLC [23].

Electron-acceptor stationary bonded phases, packed in microcapillary liquid chromatographic (μLC) columns, have recently been coupled with GC-MS in a multidimensional separation scheme [24]. The specificity and resolving power from coupled μLC-GC-MS typically is far greater than that obtained from each independent technique [25-28]. This paper describes the μLC-GC-MS analysis of a sample containing polychlorinated biphenyls, 2,7-dichlorodibenzodioxin and 3,6 -dichlorodibenzofuran.

EXPERIMENTAL

Electron-acceptor μLC-GC-MS system

The preparation of 5-μm Dinitrophenylmercaptopropylsilica (DNPMP) [21], preparing and slurry packing fused-silica μLC columns [24,29,30] and interfacing them to a GC-MS system [24] have been previously described. Briefly, 0.2-μL aliquots of sample were injected into a 0.32-mm ID x 400-mm DNPMP column. The effluent was monitored with an on-column detector enroute to a switching valve. Fractions of the effluent were collected and diverted to a 0.32-mm ID x 3-m fused-silica precolumn located outside the GC oven. Inside the GC oven, the precolumn was attached to a 0.25-mm x 30-m DB-5 capillary column.

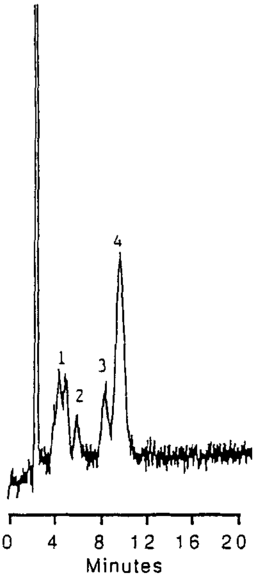

FIGURE 1. HPLC Chromatogram of PCB(1), DCDBD(2), DCDBF(3), OCDBF(4) in pentane and 5% toluene. 0.2 µL injected onto a 0.32 x 300 mm column packed with 5-µm 2,4-dinitrophenylmercaptopropylsilica. The mobile phase was 10% heptane in pentane at 10 µL/min. Fractions were diverted to the precolumn of the GC-MS at the indicated locations.

The GC column was connected to a Finnigan 4000 mass spectrometer via an open-split capillary interface as previously described [31]. Electron-impact (70 eV) mass spectra were recorded from 45 to 450 m/z at 0.5 s/scan.

Fly ash analysis by LC-GC-MS

A sample of fly ash was obtained from a power-generating station via Dr. Carol Strommen, Center for Great Lakes Studies, U. of Wisconsin, Milwaukee. Surrogate samples were generated by adding Aroclor® 1254 (ca. 30 mg/kg), 2,7-dichloro-*p*-dioxin (DCDBD) (ca. 35 mg/kg), 3,6-dichlorodibenzofuran (DCDBF) (ca. 20 mg/kg) and octachlorodibenzofuran (OCDBF) (ca. 40 mg/kg) (The Foxboro Co., North Haven, CT). Samples of spiked fly ash (20-g each) were extracted in a Soxhlet apparatus with toluene and hexane for 8 hours each. Following the toluene extraction, a Snyder concentrator column was placed on the flask, and the toluene was concentrated to around 4 mL. Hexane was poured back into the flask through the Snyder column and the extraction process continued. After the hexane extraction, the hexane was concentrated to around 4 mL with the

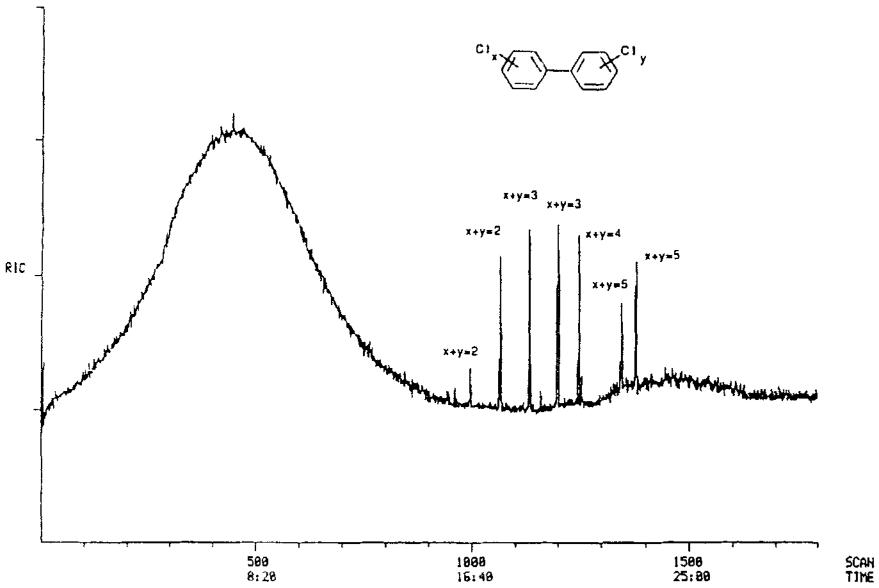

FIGURE 2. GC-MS chromatogram generated from the HPLC fraction (#1) of the front half of PCB peak.

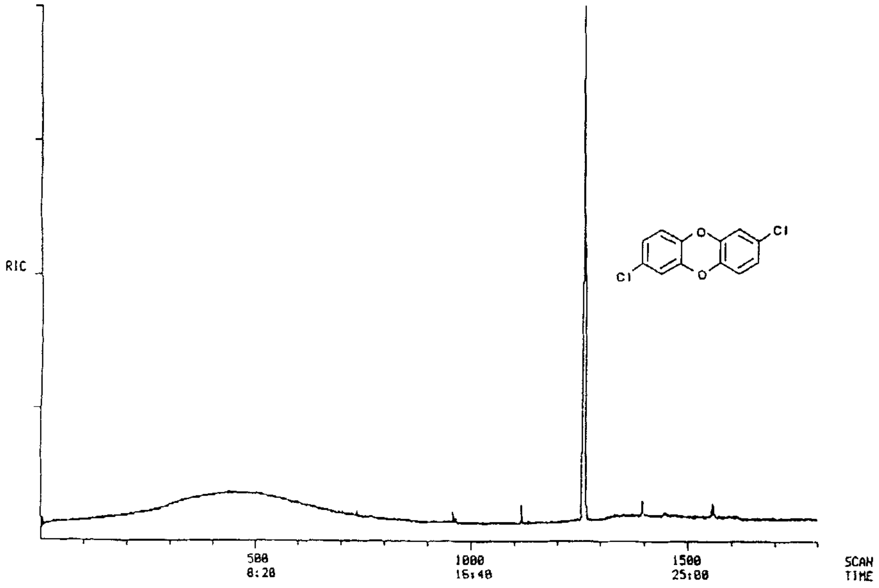

FIGURE 3. GC-MS chromatogram generated from the HPLC fraction (#2) corresponding to the DCDBD peak.

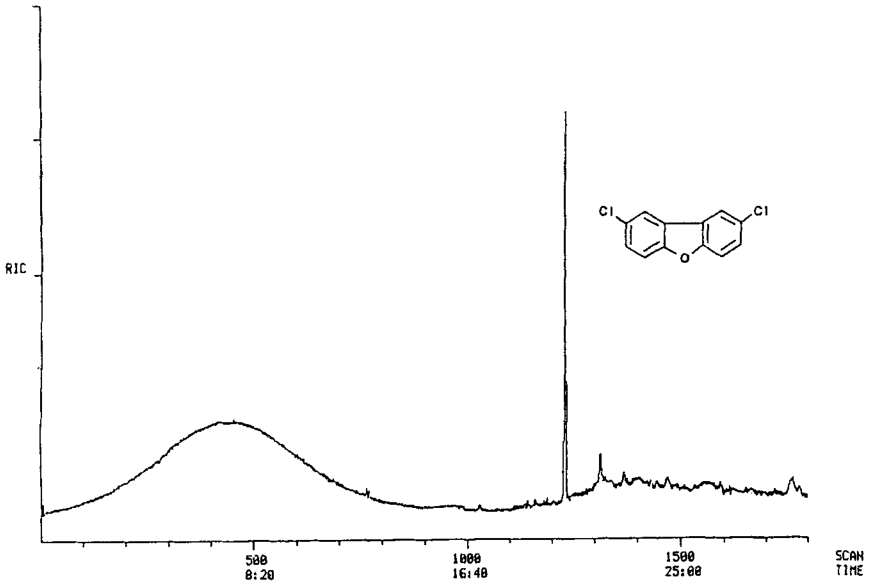

FIGURE 4. GC-MS chromatogram generated from the HPLC fraction (#3) corresponding to the DCDBF peak.

Snyder column and finally to 1 mL in a graduated centrifuge tube. Example μLC-GC-MS analyses of PCB, DCDBD, DCDBF were performed by operating the system as described above.

RESULTS AND DISCUSSION

The μLC separation of PCB, DCDBD, DCDBF and OCDBF is shown in Figure 1. A fraction was transferred to the GC-MS from the front of the PCB peak. The GC-MS chromatogram for this fraction is shown in Figure 2. The back of the PCB peak was also examined to see if a greater abundance of ortho-substituted PCB were in the leading edge of the PCB peak; but, a definitive difference between the components of each fraction could not be confirmed. The dioxin fraction yielded a single peak for DCDBD (Figure 3) confirmed by its mass spectrum. The GC-MS chromatogram for the peak at the front of the dibenzofuran band appears in Figure 4; the mass spectrum confirmed its identity as DCDBF.

The analysis of the three fly ash samples by HPLC yielded extraction efficiencies of 98% ±5%, 91% ±5% and 56% ±6% respectively for PCB, DCDBD, and the combination of OCDBF and DCDBF. To investigate the precision of quantitative transfer of analyte from the HPLC to the GC-MS, a standard of biphenyl and dibenzofuran was repetitively injected into the μLC-GC-MS system. The dibenzofuran fraction was transferred to the GC-MS, and the chromatographic peak area produced by the extracted ion current profile of 168 m/z was measured. After 5 injections and transfers, the %RSD for the measured HPLC peak area for dibenzofuran was 13.0%. The peak area measured by the GC-MS system had an RDS of 16.9%.

This limited data supports the supposition that electron-acceptor phases, as part of a μLC-GC-MS system, could be usefully applied to PCB, PCDD and PCDF characterization and quantitation in environmental samples. The data indicates that both qualitative and quantitative information can be obtained. An important feature of this system is that whatever is injected onto the microcolumn can be transferred, as a fraction, to the GC-MS. The addition of retention markers to the sample would make HPLC fraction selection more reliable when applying the method to authentic samples that may contain concentrations of aromatics below the detection of the HPLC detector. The addition of deuterated analogs as internal standards would improve the precision of the GC-MS quantitation.

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