The Use of Molybdenum Disulfide for Column Chromatography in Dioxin Methods

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INTRODUCTION

Graphitized carbon materials have been used extensively for column chromatographic separation of diphenyl ethers from chlorinated dibenzo-*p*-dioxins and dibenzofurans. Graphitized carbon posseses a lattice-layer molecular structure in which parallel sheets of atoms are held together by Van der Waals forces with no formal chemical bonding occurring between atoms in adjacent sheets. The effectiveness of carbon in separating diphenyl ethers from dioxins and furans is believed to be due to the ability of the diphenyl ethers to assume nonplanar configurations. These configurations allow them to "worm" their way through the space between the sheets of carbon atoms, whereas the rigid and planar dioxins and furans can do so only with difficulty. Therefore, it is possible that other materials possessing similar lattice-layer structures also could be effective in separating planar from nonplanar molecules.

To test this hypothesis, we studied the elution behavior of radiolabeled (^{14}C) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) on columns packed with other materials having lattice-layer structures. One of these materials (molybdenum disulfide) behaved in a manner similar to carbon with respect to retention and elution of TCDD when this material was eluted with the series of solvents specified in EPA Method 8290. Based on these results, further experiments were conducted to characterize the behavior of molybdenum disulfide with respect to the separation of chlorinated dioxins and furans from diphenyl ethers and its utility for the cleanup of extracts from environmental samples.

This paper describes these activities and the results obtained. Since the experiments conducted were of a limited nature and do not represent a statistically designed study, the results provide only an indication of this material's utility for the cleanup of samples for dioxin and furan analyses.

EXPERIMENTAL APPROACH

Appropriate amounts of molybdenum disulfide were mixed with Celite 545 to produce loadings of 1%, 5%, 10%, 20%, 30%, 40%, and 50% by weight. The mixtures were tumbled for 8 hours with occasional manual shaking and activated overnight at 130°C. To prepare each column, a glass wool plug was inserted in a 4-in section of a 10-mL disposable serological pipette, 0.55 g of packing material were added, followed by a second glass wool plug. Duplicate columns were prepared for each percent loading. The columns were preeluted with 5 mL of toluene, 2 mL of a methylene chloride:methanol:toluene mixture (75:20:5), 1 mL of a methylene chloride:cyclohexane mixture (50:50), and 5 mL of hexane.

Two milliliters of a standard solution containing four chlorinated furans (2,3,7,8-TCDF, 1,2,3,8,9-PeCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF), two chlorinated dioxins (2,3,7,8-TCDD and OCDD), and three chlorinated diphenyl ethers (2,4,4′,5-TCDPE, 2,2′,4,4′,5-PeCDPE, and DeCDPE) were added to the top of each column. One microgram of each component was added, with the exception that 0.8 μg of 2,3,7,8-TCDF was added.

The columns were eluted with two 2-mL portions of hexane, 2 mL of a methylene chloride:cyclohexane mixture (50:50), and 2 mL of a methylene chloride: methanol:toluene mixture (75:20:5). The columns were inverted and eluted with 20 mL of toluene. All fractions were retained. Each toluene fraction was reduced to approximately 1 mL using a rotary evaporator. The remaining liquid was quantitatively transferred with the aid of methylene chloride rinses to small vials, and the volume was reduced to approximately 100 μL under a stream of nitrogen. One hundred microliters of tridecane were added to each vial, and the samples were reduced to constant volume under a gentle stream of nitrogen. The remaining fractions were reduced to approximately 250 μL under a nitrogen stream and transferred to ½ -dram vials with the aid of two hexane rinses. After the sample volume was further reduced to approximately 100 μL, a tridecane keeper (100 μL) was added to each vial, and the samples were reduced to constant volume under a gentle stream of nitrogen.

Analysis was conducted on a high-resolution gas chromatographic/mass spectrometric system (Varian MAT 311 double-focusing, magnetic-sector) using a 30-m x 0.22-mm id DB-5 fused silica capillary column. All hexane and toluene fractions were analyzed. Intermediate fractions were analyzed as needed to complete the elution profile.

Cleanup of Contaminated Soil Samples

Two soil samples known to be contaminated with chlorinated dioxins, furans, and diphenyl ethers were extracted, cleaned up, and analyzed to determine the efficacy of the molybdenum disulfide column as compared with Carbopak C and AX-21 carbon columns. Both samples were Soxhlet extracted, cleaned up on silica and alumina columns, and split into three fractions. Each was cleaned up on one

of the test materials, which allowed a direct comparison of column efficiency among the three column types by direct comparison of the resulting chromatograms. The test columns were 40% molybdenum disulfide, 18% Carbopak C, and 8% AX-21 carbon, all coated on Celite 545. The forward elutions for each column were two 2-mL portions of hexane, 2 mL 50:50 methylene chloride:cyclohexane, and 2 mL 75:20:5 methylene chloride:methanol:toluene. The columns were inverted and eluted with 20 mL of toluene. The toluene fractions were reduced to a volume of approximately 1 mL using a rotary evaporator, and then reduced to approximately 100 µL under a nitrogen stream. After 100 µL of tridecane were added, the fractions were reduced to constant volume.

The sample extracts were analyzed by isotope dilution using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) according to standard procedures based on EPA Method 8290.

RESULTS AND DISCUSSION

Elution Profile for Chlorinated Dioxins and Furans

Figure 1 shows the results of the column elution profile experiments for the chlorinated dioxins and furans. The data points are the average of two determinations. Two distinct groups within these analytes exhibit different behaviors. The penta, hexa, hepta, and octa isomers exhibit quantitative recovery with column loadings of 10% or more. The tetra isomers exhibit recoveries directly proportional to the percent loading, with no obvious plateau reached within the range of 1% to 50%. For the 1% loading, the tetra isomers are essentially recovered in the hexane fraction. This indicates that they are not retained on the column. A loading of 10% shows no recovery of the tetra isomers in the hexane fraction, which indicates retention on the column. The balance of the tetra isomers are distributed among the remaining fractions, including the intermediate fractions. This distribution indicates that, although the tetra isomers were retained by the column at the 10% loading level, they migrate to a sufficient extent that the intermediate solvents cause them to elute.

Diphenyl ethers were found to be essentially quantitatively recovered in the hexane fractions for all column loadings with no traces found in any of the toluene fractions. This behavior demonstrates that molybdenum disulfide provides complete fractionation of the diphenyl ethers from the dioxins and furans.

Contaminated Soil Samples

Quantitative results for these determinations are not included in this paper. In general, the results obtained for the 2,3,7,8-substituted dioxins and furans using the three materials are comparable. However, the molybdenum disulfide extracts contained no diphenyl ether interferences to prevent quantification of the 2,3,7,8-substituted dioxins and furans. Interferences were present for Hx-CDF and Hp-CDF for the Carbopak C column and Hp-CDF for the AX-21 carbon column. Aside from

its effectiveness in removing diphenyl ethers, molybdenum disulfide was found to remove other interferences that were not removed by the AX-21 carbon and Carbopak C columns. In particular, molybdenum disulfide was found to be effective in the removal of hexachlorobiphenyl isomers and interferences tentatively identified as hydroxylated PCBs.

CONCLUSIONS

Molybdenum disulfide was found to be efficient in the removal of chlorinated diphenyl ethers and, in the proper proportion, yielded essentially quantitative recovery of the chlorinated dioxins and furans. Based on the limited number of experiments, 40% molybdenum disulfide on Celite 545 was selected for application to an environmental matrix. The results indicate that molybdenum disulfide may be useful for the cleanup of extracts for dioxin analysis.

Extracts from two contaminated soil samples cleaned up on 40% molybdenum disulfide and analyzed by HRGC/HRMS were found to contain no interferences for the chlorinated dioxins and furans. Extracts of the same soil samples, cleaned up on Carbopak C and AX-21 carbon columns, contained interfering diphenyl ethers and, possibly, polychlorinated biphenyls and hydroxylated polychlorinated biphenyls.

Preliminary work with brominated dioxins and furans, not described in this paper, indicates that molybdenum disulfide is also a promising material for use with these analytes. However, additional work is needed to further evaluate this material for use with the brominated species.

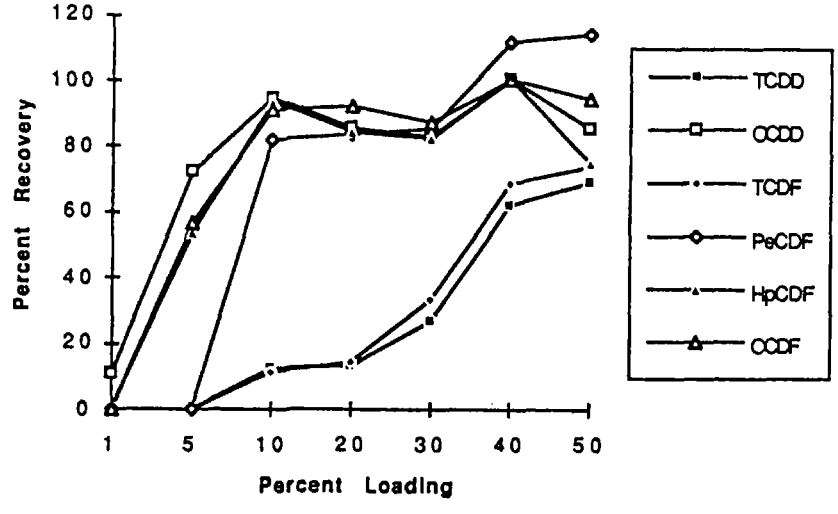

Figure 1. Recovery of dioxins and furans in toluene fractions from molybdenum disulfide.