HEATING TREATMENT AND EXFOLIATION OF KYNOL ACTIVATED CARBON AND ITS APPLICATION TO ABSORBENT FOR FRACTIONATION OF PCDDS, PCBS AND PESTICIDES BY COLUMN CHROMATOGRAPHY

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Introduction

The cleanup process for PCDDs determination, which consists of both extraction with sulfuric acid and fractionation by column chromatography is a time-consuming and tedious treatment where harmful eluting solvents such as dichloromethane and toluene are used in large quantity. To solve such problem, an absorbent having higher selectivity and adequate adsorptive activity for PCDDs must be desired as soon as possible.

Conventional graphite has a layer structure that may be suitable to discriminate the planar structure of PCDDs or coplanar PCBs, however, the layer spacing of the graphite is actually too narrow to incorporate such compounds. We therefore prepared exfoliated graphite which was intercalated with H_2SO_4 /HNO_3 1, and then was heated, and studied the separation property of the exfoliated graphite for PCDDs and PCBs 2.

In the present paper, we describe fractionations of PCDDs, PCBs and pesticides by chromatography on a column of silica gel mixed with absorbents that are prepared by heating and the exfoliation of carbon fiber and activated carbon fiber.

Methods and Materials

Materials:

Carbon fiber (Kynol CF 16BT) and activated carbon fiber (Kynol ACF 1603-15) were kindly donated from Gun-ei Chemical Industry Co., LTD.

Preparation of exfoliated carbon fiber column:

Finely cut carbon fiber was added stepwise with stirring to conc. H_2SO_4/HNO_3 in a three-neck flask cooled in ice bath, and allowed to stand in N_2 for 12h. After filtration of the reaction mixture with a membrane, the intercalated carbon fiber was heated in N_2 atmosphere. The exfoliated carbon fiber was mixed with silica gel. A glass column was packed with the silica gel / carbon fiber. A sample containing PCDDs, PCBs, and pesticides in hexane was applied on the column, firstly eluted with CH_2Cl_2/hexane (25:75, 200 cm^3), and secondly with toluene (200 cm^3); each fraction was volume was 10 cm^3. The concentrations of the organohalides in the fractions were determined by a Shimadzu GC-17A gas chromatograph equipped with an ECD.

Results and Discussion

Figure 1 shows a typical elution pattern of PCDDs, PCBs, and pesticides chromatographed on the activated carbon heated at 700 ℃ in air. CH_2Cl_2/hexane and toluene are used as eluents in Fr. 1-19 and in Fr. 20-34, respectively. Dieldrin, DDT, P_5CB, and H_7CB whose structures are low

molecular planarity are easily eluted with CH_2Cl_2/hexane. T_4CB and PCDDs are then rapidly eluted with toluene; their leak in CH_2Cl_2/hexane is not detected at all. In contrast, on commercially available active carbon-impregnated silica gel 3, complete elution for a part of PCBs needs larger volume of CH_2Cl_2/hexane. On the exfoliated fluorinated graphite that we have prepared previously 2, T_4CB was eluted through CH_2Cl_2/hexane and toluene fractions. Thus, the prepared absorvent can be applicable as one of the column in cleanup treatment, because the use of the absorvent allows to reduce the amount of a harmful solvent CH_2Cl_2. By electron microscopy, many holes of the surface (0.1-0.5 um) are observed as shown in Fig. 2 and may be responsible for the high absorption ability.

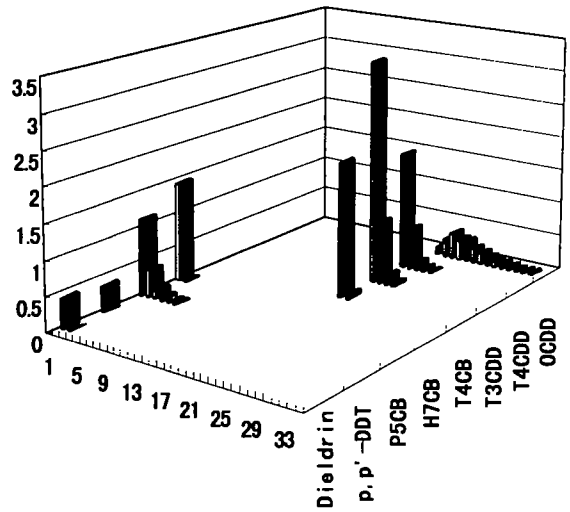

Fig. 1 Elution profiles by chromatography

The activated carbons active carbon. heated at 600 and 800 °C in air showed stronger absorption for P_5CB and PCDDs so that the elusion volumes were larger. The exfoliation treatment with heating at 400 and 700 °C also was not effective as to induce higher absorption ability superior to the activated carbon heated at 700 °C in air. Fortunately, the carbon fiber heated at 400 °C in N_2 or exfoliated showed low absorption ability and most of the organohalides were eluted even with CH_2Cl_2/hexane.
At present, the absorbents prepared at different heating temperature in air or N_2 atmosphere is being studied.

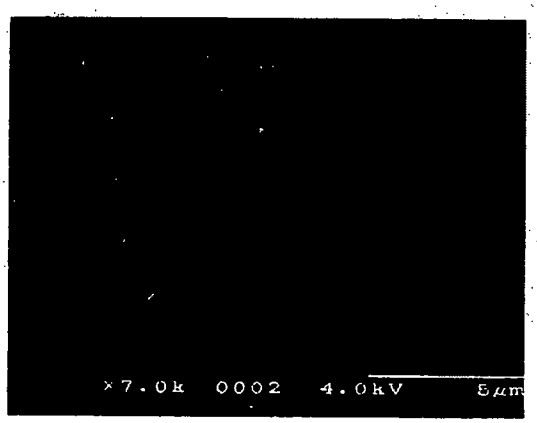

Fig. 2 Electron microscopy of the active carbon.

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