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Abstract

Title	Retention Behavior on Surface-Modified Fibrous Stationary Phases in Microcolumn Chromatography

(800 words)

Miniaturization of analytical systems has been regarded as one of the most important projects in the field of separation science, because the miniaturized analytical systems enable to not only decrease resources and energy required for analysis but also perform the high-throughput and precise analysis. Liquid chromatography (LC) with microcolumn is a typical example for the development of microscale analytical system having a number of advantages. Downsizing the column also enables the employment of a unique stationary phase with a limited availability based on a preliminary synthesis.

In this thesis, the development of novel surface-modified fibrous materials as the stationary phase in microcolumn chromatography is described. Surface-modified fibrous materials were prepared either with a surface derivatization or a surface coating of fibrous materials, and the retention behavior of various aromatic compounds was studied on the resulting microcolumn packed with the surface-modified fibrous stationary phases. In Chapter 1, general introduction of this thesis including the aims and scope of the study is described along with the background of this work. Polymer-coated fibrous stationary phases were introduced as a stationary phase in microcolumn liquid chromatography (micro-LC) in Chapter 2. Typical polymeric materials such as polydimethylsiloxane and polyethyleneglycol that are conventional stationary phases of capillary columns in gas chromatography (GC) have been employed as the coating materials onto the surface of fine filaments. Packed longitudinally with a bundle of the polymer-coated filaments into a stainless steel capillary of 0.8 mm i.d., 150 mm length, several types of polymer-coated fiber-packed columns were prepared and the retention behavior of aromatic compounds on these columns has been studied. Introducing a polymer coating to fibrous polymeric support, the increased retention to the analytes was observed in all the polymer-coated fiber-packed columns prepared. A good linear correlation in the van't Hoff plots for the HR-17-coated fiber-packed column in the range between 0 to 200°C, showing a good thermal stability of the column and also enabling temperature-programmed separation based on the reproducible retention time in the temperature range. Taking advantage of the heat-resistant feature of the fibrous stationary phases, the separation of several test mixtures with temperature-programmed elution was studied, where a solvent gradient program was additionally introduced if needed. Separation was also carried out with pure water as the mobile phase using an appropriate temperature program. In Chapter 3, a novel fibrous poly(*p*-phenylene terephthalamide) (PPTA) material derivatized with aminoethyl group was studied, and the selectivity for several polar analytes was evaluated. Several experimental parameters in the derivatization reaction have been optimized, and the retention behavior of the surface-derivatized fibrous stationary phase has been investigated using various standard solutes, such as alkanes, alcohols and alkylbenzenes. By introducing aminoethyl functional groups onto the surface of the fibrous material, a specific selectivity for polar solutes has been observed. The retention factors for various sample probes has been compared with that observed on the parent fiber-packed GC columns. A certain selectivity improvement could be expected on the surface-derivatized filaments as the stationary phase, and the derivatized fibrous materials could be further applied as a support material for a novel GC stationary phase by introducing other functionalities and/or coating materials with the aminoethyl-group as the anchor. This two-step modification process will enable the development a novel stationary phase that could not be easily introduced to open-tubular columns. The results also suggest that the surface-derivatized fibrous materials could be applied to the extraction medium in solid-phase extraction, and thus allowing miniaturization of the sample preparation process. The future possibility of the short fiber-packed column has also been studied as a novel interface between two GC columns including particle-packed capillary columns. Other surface derivatization reactions for the application in microcolumn LC are introduced in Chapter 4, where, alkyl or perfluoroalkyl chains as functional groups were introduced to the surfaces of PPTA fibers. As one type of surface derivatization of synthetic fibers, alkyl or perfluoroalkyl chains as functional groups were introduced to the surfaces of PPTA fibers. When each functionalized fiber-packed column was used for LC, increases in retention power with respect to a variety of compounds were ascertained in comparison with that prepared by an untreated-fiber as the stationary phase. These results also demonstrated that the derivatization of the surface of PPTA fibers was successfully carried out. Furthermore, it was indicated that the perfluoroalkyl group introduced fibrous stationary phase showed a specific retention behavior with respect to halogenated benzenes. These derivatized fibers are expected to play roles as extraction media for specific compounds, although to obtain sufficient column efficiencies, further research is required with respect to appropriate conditions for separations of compounds, as well as the types and lengths of functional groups introduced on the PPTA fibers. Finally, the over-all conclusion of this thesis is summarized in Chapter 5.