

Abstract

The dissertation thesis is focused on the physico-chemical characterization of interaction mechanisms of chiral stationary phases based on derivatized cyclofructans. Correct interpretation of retention and enantiodiscrimination processes substantially facilitates the development and optimization of new enantioselective methods using cyclofructan-based chiral stationary phases.

At first, the interaction mechanisms of three commercially available cyclofructan-based stationary phases were studied in normal-phase mode of liquid chromatography. Namely, systems using chiral stationary phases based on dimethylphenyl carbamate cyclofructan 7, *R*-naphthylethyl carbamate cyclofructan 6 and isopropyl carbamate cyclofructan 6 were studied. Linear free energy relationship model was used as a basic tool for characterization of interactions on the stationary phases. The mentioned model revealed that the main interactions contributing to retention in cyclofructan-based systems are hydrogen bond acidity and dipolarity/polarizability, while dispersion interactions cause decrease of retention. The impact of oligosaccharide skeleton of the cyclofructan selector on the enantioselectivity was elucidated by the comparison with seemingly analogous cyclodextrin-based chiral stationary phases. Cyclofructan-based chiral stationary phases performed unique enantioselectivity for binaphthol derivatives and various amines in normal-phase mode.

In the next step, the separation potential of cyclofructan-based chiral stationary phases, namely dimethylphenyl carbamate cyclofructan 7 chiral stationary phase, was studied under the conditions of supercritical fluid chromatography. Different distribution of retention interactions in both methods, liquid and supercritical fluid chromatography, was revealed by the linear free energy relationship model. The impact on chiral separations was also demonstrated.

Despite the fact that cyclofructan-based chiral stationary phases are mostly applied in normal-phase or polar-organic modes, the considerable separation potential in reversed-phase mode was demonstrated. The effect of the addition of Ba²⁺ to the mobile phase was studied. Changes in enantioselectivity of CF CSPs for some analytes were observed.

In order to demonstrate practical impact of the research carried out in the thesis, two methods for the determination of drugs enantiomers were developed, optimized and validated.