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SUMMARY

In this thesis a design and prototype tests of a chip-like miniaturized integrated microfluidic system for hydrodynamic chromatography (HDC) are presented. The system is suitable for size characterization of large species such as particles or polymers.

Chapter 1 is a general introduction. First, the concept of miniaturized analytical systems is addressed. Then, the state-of-the-art of size-separation methods, specifically HDC, is discussed. The proposed layout of a chip for HDC is presented. Next, the microtechnology for the fabrication of the chip is briefly illustrated, and possibilities for the implementation of various microdetectors are discussed. Finally, fluidics and the computational fluid dynamics (CFD) simulation method used in the design are briefly explained.

In Chapter 2, theoretical aspects of the miniaturization of pressure-driven liquid chromatography and the specifics of HDC are addressed. First, approximate scaling rules are derived for different miniaturization schemes. Then, a more general concept of a time-efficiency parametric plot is introduced and extended to include all instrumental limitations related to kinetic parameters. Such plots allow an absolute and comprehensive evaluation of various column designs, i.e. packed, microcapillary and on-chip columns. This concept is then adapted for HDC, where a time-resolution plot is used because of the direct relation between column geometry and selectivity in this technique. It is concluded that a thin but wide on-chip chromatographic column enables fast, moderately resolved separations executed in practical detection volumes. Finally, an HDC chip of specific dimensions is theoretically evaluated.

The design and experiments on the first HDC chip prototype made of silicon and glass are presented in **Chapter 3.** Successful separations of fluorescently labeled latex nanospheres are demonstrated on a chip with a 1000 μ m wide and 1 μ m deep channel. Deviations from HDC retention and dispersion theories are found. The deviation in residence time is attributed to colloidal forces in aqueous solutions, the one in dispersion to a cross-sectional deformation of the channel due to a mismatch in thermal expansion coefficients of silicon and glass.

SUMMARY 146

Chapter 4 describes in detail the specific injection system that was used in this device. CFD simulation predictions obtained during its design are presented, and compared with injection experiments. A good correspondence is found.

In Chapter 5, a design of an optimized outlet transition structure between a wide flat separation channel and a narrow detection channel is presented. Classical fluidics is used, together with CFD, in order to choose a suitable shape. A flat nozzle with splitting structures, and a specifically shaped slit, both lead to low zone dispersion. A short depth transition structure from the flat nozzle into a deeper optical detection cell is suggested.

An HDC chip made of fused silica exclusively, with vertical through-chip UV detection in the optimized outlet channel, is presented in **Chapter 6.** With this device, separations of polystyrene latex nanoparticles standards are demonstrated. The influence of experimental conditions on particle retention is explored. A separation of proteins is also obtained. In addition, the influence of the channel width on the deformation of its cross-section in the silicon-glass chips, and the consequent crescent shape of the zone is studied. This deformation is found to be much smaller in the 500 μ m wide chips. With this smaller deformation, a transient form of side-wall effect on dispersion can be studied. A remedy is suggested in order to eliminate this effect.