Abstract

Capillary electrophoresis often uses complexing agents since the interaction between the analyte and the complexing agent can result in achieving or improving the separation. Examples of such methods can be electrokinetic chromatography or affinity capillary electrophoresis (ACE).

ACE is used to determine the complexing parameters. In case of chiral separation, this issue gets complicated, since the parameters of the two analytes (enantiomers) are not completely independent to one another. Therefore, a procedure has been proposed in this thesis, that should always be used to evaluate the complexing parameters of two enantiomers. Statistical evaluation of these parameters was assessed as well. This work also proposes a method that allows to determine the relative migration order of two enantiomers in two different complexing separation systems.

The mathematical description of electrophoresis is based on continuity equations, that are inherently nonlinear. However, these equations can be linearized to obtain an approximate analytical solution. There was recently presented a generalized model, that enables inclusion of complete complexing equilibria in the theoretical description of electromigration. Thus, various phenomena, including nonlinear ones, associated with complexation can be predicted. This thesis is focuesed on description and experimental verification of these phenomena. Changes in the analyte and the system peak behavior were studied.

The nonlinear nature of the electrophoretic process causes a triangular peak shape. It is common practice to fit these peaks with Haarhoff-van der Linde (HVL) function, although the real peaks correspond to the shape of so-called HLVR function more. This work has proven by means of simulations that the HVLR function converges to the HVL function and thus fitting the experimental peaks with the HVL function is justified. HVL or HVLR function is an approximate solution to the continuity equations if the peak migrates separately from all other peaks. The issue of comigrating peaks has not yet been addressed in electrophoresis due to the nonlinearity. In our research group, an approximate solution for two comigrating analytes' peaks has been found (neglecting the diffusion). Simulations and experiments were designed and performed to successfully verify the theoretically described phenomena.