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Development and evaluation of kinetic plot methods for SFC system performance prediction and comparison with hplc.

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To be able to estimate the true potential of SFC, kinetic plots for this technique should be constructed because, contrary to the van Deemter curves, the former bring into account the relationship between plate height, column permeability, particle size and column length in one type of curve. Kinetic plot construction in HPLC is performed by measuring the plate height as a function of mobile phase velocity on a column with fixed length and this information is then extrapolated to the kinetic performance limit values in order to obtain the kinetic plot. This extrapolation is not possible in SFC because the mobile phase is compressible and thus the retention factor (k') and diffusion coefficients (D_m) of the analytes vary with changing mobile phase velocity. As a result, the measured values for H do not truly show the evolution of the performance with the mobile phase velocity, because also the other parameters that influence H (k' and D_m) are not kept constant and extrapolation errors are made. In this work, an experimental method to construct van Deemter and kinetic plots is developed where the column length is not fixed but where the k' is kept constant as a function of flow rate by keeping the inlet and outlet pressure of the column (and thus the average pressure in the column) a constant. Because this fundamentally correct methodology is not practical, it is compared to a method where only the average pressure over the column is kept constant and a fixed column length is used to measure the H values (isopycnic method). It is shown that this isopycnic method delivers correct kinetic plots that can be used to compare the kinetic performance limits when different average pressures are applied. Also a correct comparison with HPLC is presented for the first time.