Sidebar 1

Under gradient conditions, the retention factor k varies, and needs to be written in a differential form:

$$k = \frac{dt_s}{dt_m} \qquad \text{(S1.1)}$$

t_s is the time spent in the stationary phase, and t_m the time spent in the mobile phase. The elution pattern of a peak is obtained by integrating this equation over time:

$$\int_0^{t_r - t_0} \frac{1}{k} \cdot dt_s = \int_0^{t_0} dt_m \qquad \text{(S1.2)}$$

t_r is the retention time. The retention factor k changes with the solvent composition c, which in turn changes linearly with time t:

$$k = k_0 \cdot e^{-S \cdot \Delta c \cdot t / t_g} \qquad \text{(S1.3)}$$

Δc is the difference in the solvent composition over the gradient run time t_g. Inserting this relationship into equation S1.2, we obtain:

$$\frac{1}{k_0} \cdot \int_0^{t_r - t_0} e^{S \cdot \Delta c \cdot t / t_g} \cdot dt_s = t_0 \qquad \text{(S1.4)}$$

t_0 is the retention time for an unretained peak, also called the column dead time. The integral can be solved to yield:

$$\frac{1}{k_0} \cdot \frac{t_g}{S \cdot \Delta c} \cdot \left(e^{S \cdot \Delta c \cdot (t_r - t_0) / t_g} - 1 \right) = t_0 \qquad \text{(S1.5)}$$

Rearranging this equation results in the expression for the retention factor under gradient conditions k_g:

$$k_g = \frac{t_r - t_0}{t_0} = \frac{1}{S \cdot \Delta c} \cdot \frac{t_g}{t_0} \cdot \ln \left(k_0 \cdot S \cdot \Delta c \cdot \frac{t_0}{t_g} + 1 \right) \qquad \text{(S1.6)}$$