Appendix : Calculations and methods:

The extra-column pressure drop values, ΔP_{ext} were measured without the separation column.

The column pressure drop values, ΔP_{col} were calculated from the total pressure drop according to $\Delta P_{col} = \Delta P_{tot} - \Delta P_{ext}$.

The peak efficiency was calculated using the Dorsey-Foley equation:

$$N = 41.7 \times \frac{t_r^2}{w_{10\%}^2 \times (As_{10\%} + 1.25)}$$

where $w_{10\%}$ and $As_{10\%}$ are the peak width and the peak asymmetry at 10% respectively

The extra-column variance was measured without the separation column by calculating the second order moment (using internally developped program) for the peak of an injected solute.

The diffusion coefficient ratio was found out from the Wilke-Chang equation [21] and from viscosity values calculated with empirical equations giving the eluent viscosity as a function of both temperature and mobile phase composition:

The empirical equations of viscosity for water-methanol and water-acetonitrile mixtures are

$$\eta = 10^{\left(-2.429+\frac{714}{T}-1.859X_{MeOH}+\frac{912}{T}X_{MeOH}+1.859X_{MeOH}^2-\frac{968}{T}X_{MeOH}^2\right)} \quad \text{A1}$$

$$\eta = 10^{\left(-2.063+\frac{602}{T}+0.071X_{acn}+\frac{62}{T}X_{acn}+0.504X_{acn}^2-\frac{346}{T}X_{acn}^2\right)} \quad \text{A2}$$

were T is the temperature in Kelvin and X is the volumetric fraction of organic solvent in the mixture.

The diffusion coefficient ratio and the diffusion coefficient values were calculated using an expression derived from the original Wilke-Chang equation

$$\frac{D_{m,X_{org},T}}{D_{m,ref}} = \frac{\left(X \cdot \Phi_{org} M_{org} + 18\Phi_{water}(1-X)\right)^{1/2} \times T}{\eta_{X,T}} \times \frac{\eta_{ref}}{\left(X_{ref}\Phi_{org,ref} M_{org,ref} + 18\Phi_{water}(1-X_{ref})\right)^{1/2} \times T_{ref}} \times \left(\frac{V_m}{V_{m,ref}}\right)^{0.6} \quad \text{A3}$$

ϕ being the association factor of solvent (1, 1.9 and 2.6 for acetonitrile, methanol and water respectively), V_m the solute molar volume and here, X is the mole fraction. The subscript "org" indicates the organic solvent of the mobile phase and the subscript "ref" indicates reference conditions (temperature, organic solvent, association factor, mole fraction and solute molar volume) for which the solute diffusion coefficient is available in the literature. Here, the reference values were taken for the pentylbenzene in water at 20°C (D_m = 0.73 10^{-9} m²/s and η =0.001 Pa.s).