Supporting Information

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State-Dependent Gas Chromatography Based on Flexible and Tunable Porous Coordination Polymers

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Dedicated to Renate and Roland Mertens.

Theoretical description of chromatographic separation processes

In the following the derivation of the temporal development of the analyte distribution in a capillary column is presented. The derivation follows the concept developed by M. Golay but uses a form based on the Laplace transformation presented by A. Pethö. The work carried out by A. Pethö relevant for the main article was unfortunately not published in a journal and is only available in German. Because of this reason, the derivation is here more or less repeated with additional intermediate steps to make it easier for the reader to follow and to understand the full derivation. [1]

The continuity equation for the capillaries reads

$$\iiint \left[-D\, div\, (grad(c)) + div(c\vec{u}) + \frac{\partial c}{\partial t} + Q \right] d\tau = 0 \tag{1}$$

($d\tau$ denotes here a volume element.)

The flow term Q describes the initial injection of the analytes and the transition to and from the stationary phase. Thus, after injection, the flow term is solely determined by the boundary condition for the analyte concentration between the gas and the stationary phase and describes the amount of analyte that is transferred between these phases.

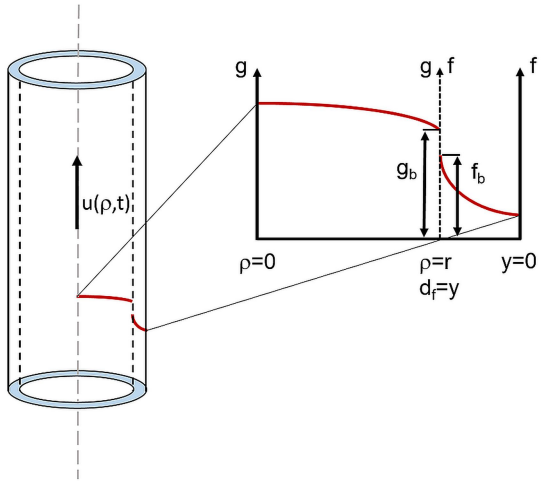

Figure 1: Analyte distribution in the column

After injection, it then can be expressed by

$$Q = \frac{A_s}{V_g}\left(k_a g_b - k_d f_b\right) = \frac{V_s}{d_s V_g}\left(k_a g_b - k_d f_b\right) \tag{2}$$

with g being the concentration in the gas phase, f the concentration in the stationary phase, A_s the surface between stationary and mobile phase per column length, V_g and V_s the respective volume per column length of the gasphase and the stationary phase, and k_a and k_d the adsorption and the desorption rate constants. By introducing the scaled concentration $f = aV_s/V_g$ and the partition coefficient $K = k_a/k_d$ and using the abbreviation $k = KV_s/V_g$ one obtains

$$Q = \frac{k_d}{d_f}\left(k g_b - f_b\right) \tag{3}$$

For the analysis that follows, the continuity equation for the gas and stationary phase is regarded separately, with the respective analyte concentrations labled g and f, coupled by the boundary conditions. In addition several assumptions are made:

1) u will only have a component in the direction along the capillary length and is considered to be constant.

$$\vec{u} = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = \begin{pmatrix} u_x \\ 0 \\ 0 \end{pmatrix} \tag{4}$$

$$\frac{\partial u_x}{\partial x} = 0 \tag{5}$$

2) D is concentration independent

3) In the following, the gas phase will be represented using cylindrical coordinates but the description of the stationary phase will be still in cartesian coordinates. In contrary, the stationary phase is so thin that the a radial change of its volume is neglected and the description of the concentration changes will still be in cartesian coordinates.

4) There is no flow in the stationary phase ($\Rightarrow\ f\vec{u} \equiv 0$).

From these assumptions, it follows that

$$D\Delta g - u\frac{\partial g}{\partial x} - \frac{\partial g}{\partial t} = 0 \tag{6}$$

$$D_f \Delta f - \frac{\partial g}{\partial t} = 0 \tag{7}$$

The transition to cylindrical coordinates reduces the problem to a two dimensional one because of the assumption that there is no variation of the concentration in respect to the azimuth angle ϕ because of the cylindrical symmetry of the problem.

For the gas phase:

$$D_g \left(\frac{\partial^2 g}{\partial x^2} + \frac{\partial^2 g}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial g}{\partial \rho} \right) - 2u\frac{\partial g}{\partial x}\left(1 - \frac{\rho^2}{r^2}\right) - \frac{\partial g}{\partial t} = 0 \tag{8}$$

and for the stationary phase with $r - d \leq \rho \leq r$

$$D_f \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial f}{\partial \rho} \right) - \frac{\partial f}{\partial t} = 0 \tag{9}$$

Initial and boundary conditions:

$$g(t=0) = 0\,;\, f(t=0) = 0 \tag{10}$$

$$g(x=0) = G_0(t)\ ;\ \left[\frac{\partial f}{\partial x}\right]_{x=0} = 0 \tag{11}$$

$$\left[\frac{\partial g}{\partial \rho}\right]_{\rho=0} = 0\ ;\ \left[\frac{\partial f}{\partial y}\right]_{y=0} = 0 \tag{12}$$

$$Q = -A_s D_g \left[\frac{\partial g}{\partial \rho}\right]_r = -\frac{2D_g}{r}\left[\frac{\partial g}{\partial \rho}\right]_r = \frac{k_d}{d_f}(k g_b - f_b) \tag{13}$$

and

$$Q = \frac{D_f}{d_f}\left[\frac{\partial f}{\partial y}\right]_{y=d_f} = \frac{k_d}{d_f}(k g_b - f_b) \tag{14}$$

In order to simplfy the problem, we shift the description from the total concentration to the deviation from the mean of the concentration. This will introduce a small quantity that will help to find suitable approximations.

The mean in cylindrical coordinates for the analyte concentration in the gas phase is given by:

$$G = \frac{\int_0^r g\rho d\rho}{\int_0^r \rho d\rho} = \frac{2}{r^2}\int_0^r g\rho d\rho \tag{15}$$

and for the stationary phase in cartesian coordinates by:

$$F = \frac{1}{d_f}\int_0^{d_f} f dy \tag{16}$$

The deviations from the mean are

$$\Delta G = g - G \tag{17}$$

$$\Delta F = f - F \tag{18}$$

If one stipulates that in the narrow tube the diffusional effects smooth out the concentration gradients across the capillary diameter comparably fast, the assumption

$$\Delta G \ll G$$

should be valid. The simplification of the analyte distribution dynamics by exploiting this relation-

ship is called the Taylor Golay approximation.

The application of the operator representing the averaging that ocurrs in Eq. 15

$$\frac{2}{r^2}\int \rho \ldots d\rho$$

allows to write the continuity equation for the mean concentration in the gas phase:
From the transition to the radial mean of equation 8) one obtains

$$\frac{2}{r^2}\int_0^r \left[D_g \left(\frac{\partial^2 g}{\partial x^2} + \frac{\partial^2 g}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial g}{\partial \rho} \right) - 2u\frac{\partial g}{\partial x}\left(1 - \frac{\rho^2}{r^2}\right) - \frac{\partial g}{\partial t} \right] \rho d\rho = 0 \tag{19}$$

$$D_g \left(\frac{\partial^2 G}{\partial x^2} + \frac{2}{r^2}\int_0^r \left(\frac{\partial^2 g}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial g}{\partial \rho} \right) \rho d\rho \right) - \frac{4u}{r^2}\int_0^r \frac{\partial g}{\partial x}\left(1 - \frac{\rho^2}{r^2}\right) \rho d\rho - \frac{\partial G}{\partial t} = 0 \tag{20}$$

The integral resulting from first term in the first integral kernel can be simplified using partial integration and the given boundary condition to

$$\int_0^r \frac{\partial^2 g}{\partial \rho^2}\, \rho d\rho = r \left.\frac{\partial g}{\partial \rho}\right|_r - (g(r) - g(0)) \tag{21}$$

and with

$$\int_0^r \left(\frac{1}{\rho}\frac{\partial g}{\partial \rho} \right) \rho d\rho = \int_0^r \left(\frac{\partial g}{\partial \rho} \right) d\rho = g(r) - g(0) \tag{22}$$

for the second term in this integral kernel one obtains for the complete integral:

$$\int_0^r \left(\frac{\partial^2 g}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial g}{\partial \rho} \right) \rho d\rho = r \left.\frac{\partial g}{\partial \rho}\right|_r = -\frac{r^2 k_d}{2D_g d_f}(k g_b - f_b) = -\frac{r^2}{2D_g} Q \tag{23}$$

Consequently, Eq. (20) reads:

$$D_g \frac{\partial^2 G}{\partial x^2} - \frac{4u}{r^2}\int_0^r \frac{\partial g}{\partial x}\left(1 - \frac{\rho^2}{r^2}\right) \rho d\rho - \frac{\partial G}{\partial t} - Q = 0 \tag{24}$$

In order to obtain a differential equation that captures only the dynamics of the small quantity ΔG, we subtract from the continuity equation of the complete concentration variable g (Eq. 8) the one dealing with the mean (Eq. 24). One obtains if g is replaced in it by $\Delta G + G$:

$$D_g \left[\frac{\partial^2 (G+\Delta G)}{\partial x^2} + \frac{1}{\rho} \frac{\partial \Delta G}{\partial \rho} + \frac{\partial^2 \Delta G}{\partial \rho^2} \right] - 2u \left(1 - \frac{\rho^2}{r^2} \right) \frac{\partial (G+\Delta G)}{\partial x} - \frac{\partial (G+\Delta G)}{\partial t}$$

$$- D_g \frac{\partial^2 G}{\partial x^2} + \frac{4u}{r^2} \int_0^r \frac{\partial (G+\Delta G)}{\partial x} \left(1 - \frac{\rho^2}{r^2} \right) \rho d\rho - \frac{\partial G}{\partial t} - Q = 0 \tag{25}$$

because $\Delta G \ll G$ all ΔG terms are neglected in the $G + \Delta G$ terms. This step is the major simplification step of the Taylor-Golay approximation. One obtains:

$$D_g \left(\frac{1}{\rho} \frac{\partial \Delta G}{\partial \rho} + \frac{\partial^2 \Delta G}{\partial \rho^2} \right) - u \left(1 - 2\frac{\rho^2}{r^2} \right) \frac{\partial G}{\partial x} + Q = 0 \tag{26}$$

This result is a linear differential equation of the independent variablen ΔG depending on ρ, which can be solved. The solution fulfilling the conditions

$$\left[\frac{\partial \Delta G}{\partial \rho} \right]_{\rho=0} = 0 \ , \ \int_0^r \Delta G \rho d\rho = 0$$

is given by:

$$\Delta G = g - G = \left(\rho^2 - \frac{\rho^4}{2r^2} - \frac{r^2}{3} \right) \frac{u}{4D_g} \frac{\partial G}{\partial x} - \left(\rho^2 - \frac{r^2}{2} \right) \frac{Q}{4D_g} \tag{27}$$

or

$$g = G + \left(\rho^2 - \frac{\rho^4}{2r^2} - \frac{r^2}{3} \right) \frac{u}{4D_g} \frac{\partial G}{\partial x} - \left(\rho^2 - \frac{r^2}{2} \right) \frac{Q}{4D_g} \tag{28}$$

Having expressed the g in terms of the integral quantity G allows to eliminate the factor $\frac{\partial g}{\partial x}$ from equation 20, the equation governing the evolution of the integral quantity G, by taking the derivative of the last equation in respect to x and to insert the result accordingly.

$$\left(D_g + \frac{u^2 r^2}{48 D_g}\right) \frac{\partial^2 G}{\partial x^2} - u \frac{\partial G}{\partial x} - \frac{\partial G}{\partial t} - \left(Q + \frac{u r^2}{24 D_g} \frac{\partial Q}{\partial x}\right) = 0 \tag{29}$$

Since it will be needed further down, we also list equation 28 for the boundary between the stationary and the gas phase:

$$g_b = G + \left(\frac{u r^2}{24 D_g}\right) \frac{\partial G}{\partial x} - \frac{r^2}{8 D_g} Q \tag{30}$$

The solution of the differential equation 29 for a given set of various initial and boundary conditions would give the development of the intgral analyte distribution along the capillary.

For the presented work only a delta peak injection of the analyte is assumed.

The boundary conditions that need to be obeyed are:

$D_f \frac{\partial^2 f}{\partial y^2} - \frac{\partial f}{\partial t} = 0 \;\; (0 \leq \rho \leq d_f)$

$f(t = 0) = 0$

$f(y = d_f) = f_b$

$G(t = 0) = 0$

$G(x = 0) = G_0(t_0)$

$G(x \to \infty) =$ limited

$[\frac{\partial f}{\partial y}]_{y=0} = 0$ (no flux boundary conditions to the tube walls)

$F = \int_0^{d_f} f dy / \int_0^{d_f} dy = \frac{1}{d_f} \int_0^{d_f} f dy$

$Q = \frac{\partial F}{\partial t} = \frac{2 D_f}{r d_f} \left[\frac{\partial f}{\partial y}\right]_{y=d_f} = \frac{2}{r} (k_a g_b - k_d f_b)$

In the following there will not be the attempt to solve this differential equation completely but to extract information about the solution, i.e. the spreading of the peaks as a function of their retention times. In order to regards the boundary conditions algebraically, the equations will be subjected to the Laplace transformation. The following abbreviations are used

$$\mathscr{L}G(t) = \Gamma(s) = \int_0^\infty e^{-st} G(t) dt$$

analogously

$$\mathscr{L}g = \gamma\,,\ \mathscr{L}F = \Phi\,,\ \mathscr{L}f = \varphi$$

In order to further proceed, and to solve the coupled system of the continuity equation in the stationary and mobile phase, we take the Laplace transformed of the continuity equation of the stationary phase which yields

$$\frac{d^2\varphi}{dy^2} - \frac{s}{D_f}\varphi = 0$$

with $\varphi(y = d_f) = \varphi_b$ and $\left[\frac{d\varphi}{dy}\right]_{y=0} = 0$.
the differential equation can be solved

$$\varphi = \varphi_b \frac{cosh\sqrt{sy^2/D_f}}{cosh\sqrt{d_f^2/D_f}}$$

From which Φ can be obtained if it is put in

$$\mathscr{L}\left(\frac{1}{d_f}\int_0^{d_f} f dy\right) = \frac{1}{d_f}\int_0^{d_f} \varphi dy = \varphi_b \frac{tanh\sqrt{sy^2/D_f}}{\sqrt{sy^2/D_f}}$$

and one obtains for

$$s\Phi = \frac{k_d}{d_f}(q\Gamma - \varphi_b)$$

$$s\Phi = \varphi_b \frac{D_f}{d_f^2}\sqrt{sd_f^2/D_f}\, tanh\sqrt{sd_f^2/D_f}$$

and

$$s\Phi = k\Gamma \left[\frac{d_f}{k_d} + \frac{1}{\left(\frac{D_f}{d_f^2} \sqrt{sd_f^2/D_f} tanh \sqrt{sd_f^2/D_f} \right)} \right]^{-1} = k\Gamma\psi$$

This equation allows to eliminate Φ from the respective Laplace transformed continuity equation for G. The variable Γ in previous equation couples the fields in the stationary and the mobile phase. As an approximation we replace Γ, the $\mathscr{L}$-transformed averaged analyte field by the value of g by the $\mathscr{L}$-transformed of its value at the boundary between the stationary and mobile phase, g_b, which is labeled as γ_b. This quantity is given by the the $\mathscr{L}$-transform of 30 which is

$$\mathscr{L} g_b = \gamma_b = \Gamma + \frac{ur^2}{24D_g} \frac{\partial \Gamma}{\partial x} - \frac{r^2}{8D_g} s\Phi$$

After having carried out the replacement the equation for Φ reads

$$s\Phi = k\psi \left(\Gamma + \frac{ur^2}{24D_g} \frac{\partial \Gamma}{\partial x} \right) \left(1 + \frac{kr^2}{8D_g} \psi \right)^{-1} \tag{31}$$

Laplace-transforming equation 29 using $Q = \frac{\partial F}{\partial t}$ yields

$$\left(D_g + \frac{ur^2}{48D_g} \right) \frac{\partial^2 G}{\partial x^2} - u \frac{\partial G}{\partial x} - s\Gamma - s \left(\Phi + \frac{ur^2}{24D_g} \frac{\partial \Phi}{\partial x} \right) = 0 \tag{32}$$

The variable Φ can now be eliminated using equation 31. The resulting differential equation is of the form

$$P_* \frac{\partial^2 \Gamma}{\partial x^2} + R_* \frac{\partial \Gamma}{\partial x} + S_* \Gamma = 0 \tag{33}$$

With

$$P_* = \left(D_g + \frac{ur^2}{48D_g} \right) - k\psi \left(1 + \frac{kr^2}{8D_g} \psi \right)^{-1} \left(\frac{ur^2}{24D_g} \right)^2$$

$$R_* = \left[1 + k\psi\left(1 + \frac{kr^2}{8D_g}\psi\right)^{-1}\frac{r^2}{12D_g}\right]u$$

$$S_* = s + k\psi\left(1 + \frac{kr^2}{8D_g}\psi\right)^{-1}$$

The differential equation Equation 33 needs to be solved obying the Laplace transformed boundary conditions $G(x=0) = G_0$ and $G(x\to\infty) =$ limited which ist $\Gamma(x=0) = \Gamma_0$ and $\Gamma(x\to\infty) =$ limited. As can easily be checked, the solution is given by:

$$\Gamma = \Gamma_0 exp\left[\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}x\right] = \Gamma_0\Gamma_*$$

.

For the derivatives in respect to s we obtain:

$$\Gamma_*' = x\left(\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}\right)'\Gamma_*$$

$$\Gamma_*'' = \left(x^2\left[\left(\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}\right)'\right]^2 + x\left(\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}\right)''\right)\Gamma_*$$

.

At $s=0$ one obtains $\psi(s=0) = {}_0\psi = 0$ and with it the following relations hold:

$${}_0P_* = D_g + \frac{u^2r^2}{48D_g}\ ;\ {}_0R_* = u\ ;\ {}_0S_* = 0$$

and ${}_0\Gamma_* = 1$.

Using ${}_0\psi' = 1$ at $s=0$ as well as ${}_0P_*' = k\left(\frac{ur^2}{24D_g}\right)^2 \quad ; \quad {}_0R_*' = \frac{kr^2u}{12D_g} \quad ; \quad {}_0S_*' = 1+k$, the first derivative of Γ at $s=0$ is given by

$${}_0\Gamma_*' = x\left(\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}\right)'_{s=0} = -\frac{1+k}{u}x$$

.

Taking into account

$$ {}_0\psi'' = -\frac{-d_f}{k_d} - \frac{2d_f^2}{3D_f} $$

for

$$ {}_0R_*'' = \frac{ur^2}{12D_g}\,{}_0S_*'' $$

and

$$ {}_0S_*'' = -k\left(\frac{2d_f}{k_d} + \frac{2d_f^2}{3D_f} + \frac{kr^2}{4D_g}\right) $$

to obtain ${}_0\Gamma_*''$ at $s = 0$ one arrives at

$$ {}_0\Gamma_*'' = \left(\frac{1+k^2}{u}\right)x^2 + x\left(\frac{R_* - \sqrt{R_*^2 + 4P_*S_*}}{2P_*}\right)''_{s=0} $$

Filling in all terms leads to

$$ {}_0\Gamma_*'' = \left(\frac{1+k}{u}\right)^2 x^2 + \left[\frac{2D_g}{u} + \frac{1+6k+11k^2}{24(1+k)^2}\frac{ru^2}{D_g} + \frac{2k}{(1+k)^2}\frac{d_f u}{k_d} + \frac{2k}{3(1+k)^2}\frac{d_f^2 u}{D_f}\right]\left(\frac{1+k}{u}\right)^2 x $$

The star as the index in above's expressions, indicates the development of the Γ from the Γ of the initial distribution, which is given by Γ_0, thus the relation $\Gamma = \Gamma_*\Gamma_0$ holds. Having derived ${}_0\Gamma, {}_0\Gamma'$, and ${}_0\Gamma''$ for an (here initial) analyte distribution function, the moments of this distribution can be calculated by using

$$ \tau = -{}_0\Gamma^{(1)}/{}_0\Gamma^{(0)} \text{ and } \tau^2 + \sigma^2 = {}_0\Gamma^{(2)}/{}_0\Gamma^{(1)} \tag{34} $$

.

These equations result from the definition of the moments of the distribution G which are given by:

$$M^{(i)} = \int_0^\infty t^i G(t) dt \tag{35}$$

$$\tau = M^{(1)}/M^{(0)} \tag{36}$$

$$\sigma^2 = \int_0^\infty (t-\tau)^2 G(t) dt / M^{(0)} = (M^{(2)}/M^{(0)}) - \tau^2 \tag{37}$$

$$\mathscr{L}G(t) = \Gamma(s) = \int_0^\infty e^{-st} G(t) dt \tag{38}$$

with

$M^{(i=0)} = \Gamma(s=0) = {}_0\Gamma^0$ the index 0 on the left side indicates $s = 0$, in the following a right hand sided index equal to zero will indicate that the quantity is considered at $(x = 0)$.

For $i > 0$ there is

$$M^{(i)} = (-1)^i \left[\frac{d^i \Gamma}{dt^i}\right]_{s=0} \equiv (-1)^i {}_0\Gamma^{(i)} \tag{39}$$

.

Furthermore the following relations also hold:

$$\tau = \tau_0 + \tau_* \tag{40}$$

$$\sigma^2 = \sigma_0^2 + \sigma_*^2 \tag{41}$$

$$\tag{42}$$

From which the development of the theoretical plate height can be obtained.

$$H = x\left(\frac{\sigma_*}{\tau_*}\right)^2 = x\frac{\sigma^2 - \sigma_0^2}{(\tau - \tau_0)^2} \tag{43}$$

Linker synthesis

The linker synthesis started from the commercially available 2,5 dihydroxy-1,4-benzenedicarboxylic acid (Sigma Aldrich 98 %) which was esterificated in MeOH with $BF_3{\cdot}Et_2O$ as catalyst and water scavenger under reflux for 8 h, to yield the dimethyl ester dimethyl 2,5-dihydroxy-1,4-benzenedicarboxylate. The product was then dried in vacuum. The actual synthesis of the final linker 2,5-diethoxy-1,4-benzene dicarboxylic acid compounds was carried out as Williamson etherification described in Ref.[2]

(872 mg, 4.15 mmol) dimethyl 2,5-dihydroxy-1,4-benzenedicarboxylate and (2.76 g) K_2CO_3 were suspended in 35 mL N,N-dimethylformamide (DMF). Subsequently, 0.746 mL ethyl bromide were added dropwise, the solution heated to 85 °C and kept at this temperature for 3 h. Afterwards, the solvent was removed by applying laboratory vacuum (10^{-1} mbar) the remainder was mixed with 40 mL H_2O and 0.4 g NaOH. The solution was heated an kept under reflux for 4 h. After subsequent cooling to room temperature, 23 mL conc. hydrochloric acid were added. The product was washed with H_2O (20 mL) filtered off and dried at 80 °C for 1.5 h and recrystallized in THF (yield 85 %).

The coating of chromatographic capillaries with a pillar-layered metal-organic framework ($[Zn_2(DE\text{-}bdc)_2(dabco)]_n$)

For the coating of the capillaries liquids were pumped by standard polyethylene syringes (1 mL) throug the capillaries. The coating of a fused silica capillary (CS Chromatographie-service, inner

diameter 0.32 mm, length 16 m) starts with its activation by filling the capillary with 1 M aqueous KOH solution. After 30 min the capillary was emptied by pressing air through it. Afterwards the procedure was repeated followed by neutral (water) rinsing, i.e. pressing water through the capillary until the the outflowing water reaches pH 7. The preparation proceeds by filling the capillary with 1 M hydrochloric acid and applying it for 30 min followd by another neutral rinsing cycle and letting the capillary dry in a drying cabinet over night by flowing a stream of argon through it.

For the coating by liquid phase epitaxy, three solutions need to be prepared.
a) 102.98 mg (0.35 mmol) of zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$) was dissolved in 25 mL ethanol (precursor solution).
b) 26.31 mg (0.24 mmol) of (1,4-diazabicyclo[2.2.2]octane) (dabco) was dissolved in 25 mL ethanol (pillar solution).
c) 696 mg (3.24 mmol) of the prepared linker compound 2,5-bis(ethoxy)-1,4-benzenedicarboxylic acid (leading to the linker 2,5-bis(ethoxy)-1,4-benzenedicarboxylate, DE-bdc) was dissolved in 25 mL of a 1:1 mixture (by volume) of ethanol and DMF dimethylformamide (linker solution).

One coating cylce consists of injecting 0.5 mL of precursor solution, followed by injecting 0.5 mL air (air plug) separating the liquids. Subsequently, 0.5 mL of the linker solution are injected also followed by the injection of another air plug. One cycle ends with the injection of 0.5 mL pillar solution again followed by an air plug.
For the preparation of the capillaries, 25 of the described cycles were applied. Afterwards, the capillary was dried in a drying cabinet at the subsequent temperature levels of 60 °C, 80 °C, and 100 °C held at each temperature level for 2 h with a stream of argon flowing through the capillaries.[3]

The deposition of the MOF within the capillary has been carried out many time for dicarboxylate MOFs of the BDC IRMOF and BDC-DABCO paddle wheel pillar-layered MOFs even with large bulky alkoxy substituents.[4–6] The coating was carried out by the so called Controlled SBU Approach. By this method, preformed SBUs for example $Zn_4O(CH_3COO)_6$ in the case of the

IRMOF series[4,7] or $Zn_2(CH_3COO)_2 \cdot {}_2H_2O$ will be used in solution and brought to an exchange reaction with a solution of dicarboxilic acids in way that a network is created. Because of the small amount of deposited material, the thickness of the layer is in the range of microns and the diameter of the capillary is only 0.5 mm, it is not simply possible to perform XRD measurement of the material on the inner walls of the GC capillaries. The curvature of the surface further aggravates the problem. In order to see if the deposition is possible, on can perform the coating procedure in the same manner of a flat piece of fused silica and perform an XRD measurement with it, see Ref.[4] Carrying out the Controlled SBU Approach to deposit various pillar-layered BDC-DABCO MOFs with very bulky substituents has also been done.[6] Conduction the same procedure using BDC with much smaller ethoxy substituents leads to a dense layer of (MOF) crystals as can be seen in FigS2 and FigS3.

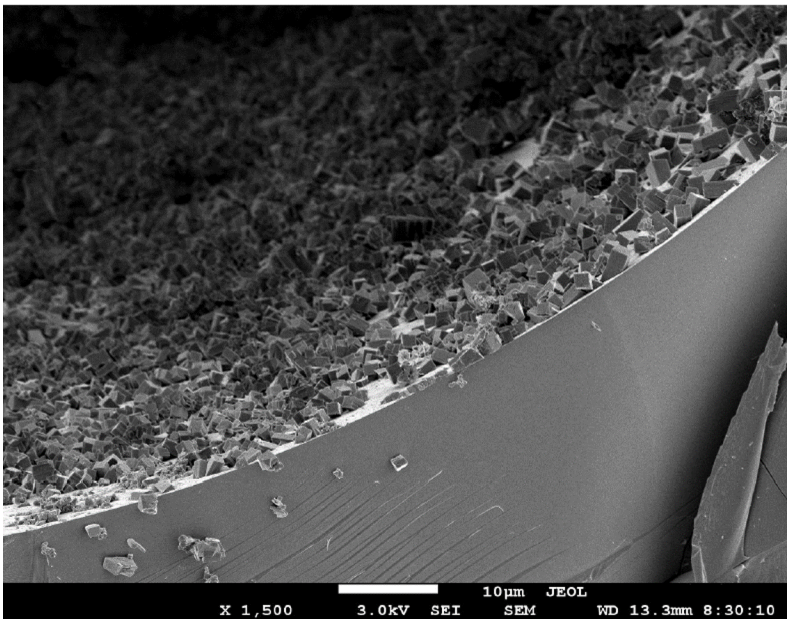

Figure 2: SEM image of material deposited by the Controlled SBU Approach on a capillary wall using the described procedure[3]

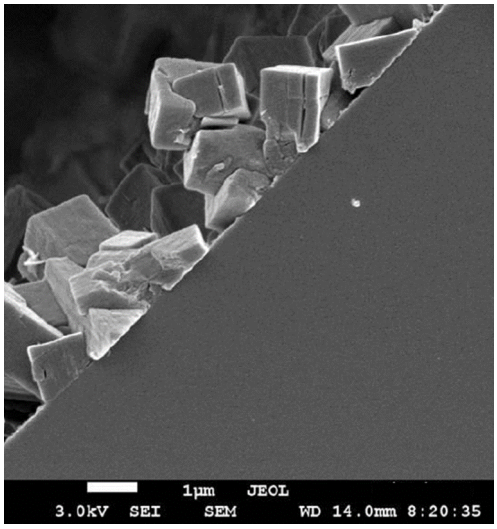

Figure 3: Magnified view of the capillary wall - MOF contact zone measured by SEM[3]

References

(1) Pethö, A.; Kühne, J. Über das dynamische Verhalten gaschromatographischer Vorgänge. *in Handbuch der Gaschromatographie, edited by E. Leibnitz, G. Struppe (Akademische Verlagsgesellschaft Geest & Portig KG, Leipzig* **1984**,

(2) Henke, S.; Schneemann, A.; Wütscher, A.; Fischer, R. A. Directing the Breathing Behavior of Pillared-Layered Metal-Organic Frameworks via a Systematic Library of Functionalized Linkers Bearing Flexible Substituents. *J. Am. Chem. Soc.* **2012**, *134*, 9464–9474.

(3) Schleicher, E. Untersuchung kinetischer Effekte von *Breathing Pillared MOFs* mittels inverser Gaschromatographie. *Bachelor Thesis, Technische Universität Bergakademie Freiberg* **2014**,

(4) Münch, A.; Seidel, J.; Obst, A.; Weber, E.; Mertens, F. O. High-Separation Performance of Chromatographic Capillaries Coated with MOF-5 by the Controlled SBU Approach. *Chem. Eur. J.* **2011**, *17(39)*, 10958–10964.

(5) Böhle, T.; Mertens, F. O. Two isoreticular pillared-layer frameworks as stationary phases for gas chromatographic applications - Unusual peak broadening in size exclusion chromatogra-

phy, determination of thermodynamic and kinetic data. *Microporous Mesoporous Mater.* **2015**, *216*, 82–91.

(6) Böhle, T. Pillared Paddle-Wheel Frameworks als stationäre Phasen für gaschromatographische Trennungen. *Dissertation, Technische Universität Bergakademie Freiberg* **2013**,

(7) Hausdorf, S.; Baitalow, F.; Böhle, T.; Rafaja, D.; Mertens, F. O. R. L. Main-Group and Transition-Element IRMOF Homologues. *J. Am. Chem. Soc.* **2010**, *132*, 0978–10981.