

S1 The Temkin adsorption isotherm

This isotherm first reported by Temkin is valid at $\theta \approx 0.5$ in the way derived by Temkin. (Masel, 1996). However, this is not valid for our experiments, but the isotherm can be derived in another way, even valid for low surface concentrations: starting with Henry's adsorption isotherm, Eq. (3) is written as differential expression

$$\frac{dq}{dp} = K(q) \quad (S1)$$

But now it is assumed that K depends on q :

$$K(q) = K_T \exp(-q/\zeta). \quad (S2)$$

The vapor pressure at certain q can be evaluated by integration:

$$p = \frac{1}{K_T} \int_0^q \exp(q'/\zeta) dq' = \frac{\zeta}{K_T} [\exp(q/\zeta) - 1]. \quad (S3)$$

This rearranges into

$$q = \zeta \ln \left(1 + \frac{K_T p}{\zeta} \right). \quad (S4)$$

For $p \rightarrow 0$, Henry's adsorption isotherm is obtained: $q \approx K_T p$. For larger p , where $K_T p/\zeta \gg 1$, Eq. (S4) simplifies to

$$q = \zeta \ln \left(\frac{K_T p}{\zeta} \right) \quad (S5)$$

which is usually known as the Temkin isotherm (Foo and Hameed, 2010). With Van 't Hoff isotherm, it is obtained for the change of Gibbs free energy

$$\Delta G(q) = -RT \ln K(q) = \Delta G_0 + RT \frac{q}{\zeta}. \quad (S6)$$

S2 Simulation of peak shapes

Adsorption and transport in a chromatographic capillary column is described by a nonlinear partial differential equation. To solve this special equation, we use the package *ReacTran* (Soetaert and Meysman, 2012) of the open source software R (R Core Team, 2016). The package depends on another package *deSolve* (Soetaert et al., 2010) to solve partial differential equations. The default method LSODES is used as ordinary differential equations solver.

S2.1 1D model

On the basis of plate theory the column is described as a series of ideal phase mixers (Smit et al., 1980). In this most simplistic model, it is assumed that adsorption equilibrium is

instantaneously established. No radial transport limitation in the gas-phase is assumed, therefore the gas-phase concentration only depends on t and the coordinate of the column axis z . In a short section Δz the concentration change is given by

$$\left(\frac{\partial c_g}{\partial t} \right)_z + \beta \left(\frac{\partial c_s}{\partial t} \right)_z + u \left(\frac{\partial c_g}{\partial z} \right)_t = D_a \left(\frac{\partial^2 c_g}{\partial z^2} \right)_t \quad (S7)$$

where β is the phase ratio and D_a the axial dispersion coefficient (Jönsson and Lökvist, 1987). With k' as

$$k' = \beta \left(\frac{\partial c_s}{\partial t} \right)_z / \left(\frac{\partial c_g}{\partial t} \right)_z = \beta \left(\frac{\partial c_s}{\partial c_g} \right)_z = \left(\frac{\partial n_s}{\partial n_g} \right)_z. \quad (S8)$$

the concentration change in the gas phase is expressed as

$$\left(\frac{\partial c_g}{\partial t} \right)_z = \frac{1}{1+k'} \left[D_a \left(\frac{\partial^2 c_g}{\partial z^2} \right)_t - u \left(\frac{\partial c_g}{\partial z} \right)_t \right]. \quad (S9)$$

This partial differential equation is solved by *ReacTran*. For a capillary column k' is calculated from the Temkin isotherm of Eq. (S4) after applying Eq. (1):

$$k' = \frac{2RT}{r} \left(\frac{\zeta K_T}{\zeta + K_T p} + K_H \right). \quad (S10)$$

This expression does not fail for $p \rightarrow 0$. Note that for reasons of numerical stability, the dissociative Langmuir Model can not be used in the model, because then for $p \rightarrow 0$, $k' \rightarrow \infty$ is obtained. A reasonable assumption for K_T has to be made.

The flow of the tracer into the column injected as peak is described by a normal distribution. If the tracer is applied as concentration burst for the simulation of breakthrough curves, the tracer input is described by the cumulative distribution function of the normal distribution.

S2.2 2D model

This model extends the 1D model and includes slow diffusive uptake into the solid (stationary) phase with diffusion coefficient D_s . It is assumed that the uptake rate from the gas to the solid phase is limited by diffusion in the solid phase. The tracer concentration c_s in the solid phase can be expressed by the corresponding equilibrium gas phase concentration c_g linked together by Henry's-law

$$H = \frac{c_s}{c_g}. \quad (S11)$$

Thus, only the concentration in the gas phase and the equilibrium gas-phase concentration of the tracer in the stationary phase need to be considered further. It is assumed that gas phase diffusion is fast and therefore c_g is uniform over the column radius. The area of the solid-gas interface in a cylindrical geometry is given by $A_{sg} = 2\pi r l$. The volumes of the gas and solid phases are written as

$$V_g = A_{sg} \frac{r}{2}, \quad V_s = A_{sg} h. \quad (S12)$$

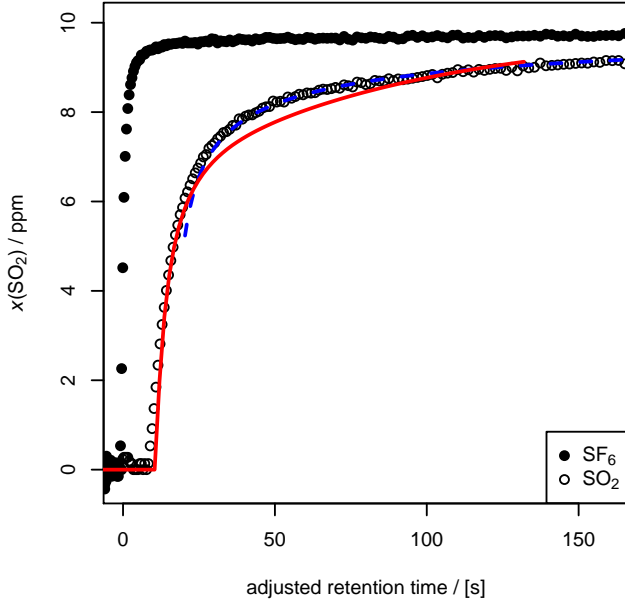


Figure S1. Breakthrough curves of 9.8 ppm SF₆ and SO₂ at 208 K and 2.8 μm ice film thickness. Carrier gas flow rate $\dot{n} = 7.8 \times 10^{-6} \text{ mol s}^{-1}$. The blue dashed line is a fit of Eq. (S16) to the tail of the SO₂ breakthrough curve. From this fit $H^2D = 5.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is obtained. The red curve is simulated using the 2D model with $H = 100$, $D = 5.2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. Further simulation parameters: $K_H = 5.2 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1}$, $K_T = 10^{-5} \text{ mol m}^{-2} \text{ Pa}^{-1}$.

respectively. In y-direction, the coordinate of the column radius, the first cell is used for the gas phase, cells 2 ... N_y are used for the solid phase:

$$\begin{array}{lcl} \text{gas phase} & z \rightarrow & c_{1,1} \quad c_{2,1} \quad \cdots \quad c_{N_z,1} \\ \text{solid phase} & y \downarrow & c_{1,2} \quad c_{2,2} \quad \cdots \quad c_{N_z,2} \\ & & \vdots \quad \vdots \quad \ddots \quad \vdots \\ & & c_{1,N_y} \quad c_{2,N_y} \quad \cdots \quad c_{N_z,N_y} \end{array}$$

The coordinate z of the column axis is discretized by

$$\Delta z = \frac{l}{N_z} \quad (\text{S13})$$

and the coordinate y is discretized by

$$\Delta y_1 = \frac{r}{2}, \quad \Delta y_{2 \dots N_y} = \frac{Hh}{N_y - 1}. \quad (\text{S14})$$

With rising H , the thickness of the solid phase is virtually increasing to fulfill mass conservation of the tracer.

Using this coordinate transformation for the solid phase, the effective diffusion coefficient applied in the model is H^2D_s . For the special case of gas-solid interface where the flux through the interface is limited by solid phase diffusion, the effective diffusion coefficient between cells 1 and 2 is set

to

$$D_{1,2} = \frac{H^2D_s}{2} \left[1 + \frac{r(N_y - 1)}{2hH} \right] \quad (\text{S15})$$

regarding the different sizes of Δy_1 and Δy_2 .

Langenberg (1997) measured a limited number of SO₂ breakthrough curves at 206 – 208 K. To validate the code, breakthrough curves are simulated and compared to the experimental breakthrough curves. A simple mathematical expression for breakthrough curves can be derived for the limit $t \rightarrow \infty$ (Huthwelker et al., 2001, 2006). The time-dependent mixing ratio of the tracer at the column exit is given by

$$x(t) = x_0 \exp \left(-\frac{2lH\sqrt{D_s}}{ur\sqrt{\pi t}} \right). \quad (\text{S16})$$

Using H^2D_s as fitting parameter, Eq. (S16) is fitted to the tail of the SO₂-breakthrough curve, see Fig. S1. From this fit $H^2D_s = 5.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is estimated. Using the 2D model several breakthrough curves are simulated with different values of D_s and H until a reasonable fit is achieved, see Fig. S1.

S3 Nomenclature

a_i	model fit parameter
A	area
c	concentration
D_a	axial dispersion coefficient
D_s	solid phase diffusion coefficient
h	ice film thickness
H	dimensionless Henry coefficient
ΔH_a	adsorption enthalpy
K_H	Henry's adsorption constant
K_L	Langmuir's adsorption constant
K_T	Temkin's adsorption constant
l	length of coated part of the column
\dot{n}	mass flow rate
\dot{n}	carrier gas mass flow rate
p	trace gas partial pressure
P	probability value
q	surface coverage
q_s	monolayer saturation capacity
r	column radius
R	gas constant
t	time
T	temperature
u	carrier gas velocity
v	column winding speed
V_m	molar volume
x	mole fraction
y	coordinate of column radius
z	coordinate of column axis
β	phase ratio

ν	column aging (binary variable)
ρ	density
σ	surface area density of an ice cloud
θ	surface coverage
ϑ	contact angle
ζ	parameter of Temkin isotherm

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