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Interactive comment on "Technical note: Determination of binary gas phase diffusion coefficients of unstable and adsorbing atmospheric trace gases at low temperature – Arrested Flow and Twin Tube method" *by* Stefan Langenberg et al.

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We thank the referee for reviewing and commenting our discussion paper. The remarks of the reviewer are marked like *this*. All symbols and equations used and cited herein refer to the discussion paper unless otherwise indicated. To the comments and questions we answer as follows:

In the experimental part, the authors shortly mention the limiting cases for each of the two methods. How many wall collisions do the diffusing molecules typically undergo?

The collision rate per unit area is given by

$$Z_w = \frac{1}{4} c \bar{v}$$

where

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

is the mean molecular velocity of the species under investigation. If the trace gas contact time τ is given, the (dimensionless) number of hits of an individual species molecule on the cylindrical surface can be estimated

$$N_{\text{hit}} = \frac{\tau \bar{v}}{2r}.$$

For the AF-method τ corresponds to the arrest time t_a. For the TT-method τ is the mean travel time of a molecule along the length l of the capillary. This yields

$$\tau = \frac{l^2}{2D}.$$

For ozone at 273.15 K $\tau = 14.4$ s is found for the TT-method. Thus, the number of hits is 9×10^6 for the AF-method at a arrest time of 100 s and 6×10^7 for the TT-method.

Since either reversible adsorption or chemical reaction are affecting the transport kinetics, the authors could elaborate the limiting first order loss rate coefficient and the limiting residence time on the surface to lead to a noticeable impact on the analysis of the detector signals for each method.

The AF-method is not affected by first order loss. However, most heterogeneous loss processes are not strictly first order. The TT-method *is* affected by lost processes. A tolerable upper limit for the uptake/reaction coefficient γ for enabling the TT-method is derived as follows: lets assume that the ratio between the reactive flow J_R to the surface and the diffusion flow through the capillary should not exceed 0.01. Thus, $J_R < 0.01 J_D$. The reactive flow the surface is given by

$$J_R = \frac{\bar{v}\gamma}{4l}\int_0^l \tilde{c}(z)\,\mathrm{d}z,$$

considering that the concentration $\tilde{c}$ is a linear function of the coordinate z along the capillary tube. We obtain

$$\tilde{c}(z) = c_0 + \frac{z}{l}(c - c_0).$$

This yields

$$J_R = \frac{1}{8}\bar{v}\gamma(c_0 + c).$$

Thus, it follows with Eq. (16)

$$\gamma < 0.08\,\frac{D}{\bar{v}l}\left(\frac{c_0 - c}{c_0 + c}\right) \approx 0.08\,\frac{D}{\bar{v}l}.$$

For ozone at 273.15 K with $\bar{v} = 347.1$ m s^{-1} $\gamma \ll 1.7\times10^{-7}$ is required for the successful application of the TT-method. Ozone destruction on similar quartz surfaces was already studied by Langenberg and Schurath (1999): $\gamma = 4.4\times10^{-7}$ was found for ozone at room temperature. Therefore, the TT-method is not suitable to determine the diffusion coefficient of ozone. In addition, further loss of ozone in other parts of the apparatus needs to be considered too.

Could the method in turn be used to measure the surface residence time of sticky but non-reactive molecules through their effective diffusivity?

The TT-method is not affected by non-reactive adsorption. However, the AF-method may be affected. The most simplistic model for adsorption is Henry's adsorption

isotherm: the surface concentration q as function of the trace gas partial pressure p is given by (Langenberg and Schurath, 2018)

$$q = K_H p.$$

The capacity ratio is defined as

$$k' = \frac{2RT}{r}K_H.$$

In case of adsorption it follows from the mass balance in the diffusion capillary

$$\left(\frac{\partial c}{\partial t}\right)_z = \frac{D}{1+k'}\left(\frac{\partial^2 c}{\partial z^2}\right)_t.$$

Therefore, the diffusion coefficient measured by the AF-method would be smaller than the actual diffusion coefficient. Thus, if the real diffusion coefficient D is known, measurement of the effective diffusion coefficients can be used to determine k' and K_H. However, it is much easier to determine k' using standard gas chromatography by measuring arrest times (first central moment) instead of measurement of peak broadening (second central moment).

Line 190: no need to decide whether ozone is adsorbing or non-adsorbing. Each molecule may adsorb. I suggest to simply mention chemical decay. Whether it undergoes reversible adsorption in addition seems not obvious (cf also previous comment) from the data but cannot be excluded.

We also tried to investigate the diffusion of NO$_2$ using the AF-method. However, adsorption gave rise to strong peak tailing which invalidated the AF-method.

References

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