

S. Langenberg & U. Schurath: Gas-Chromatography using ice-coated fused silica columns: Study of adsorption of sulfur dioxide on water-ice, acp-2017-800

This is an excellent piece of scientific work that fills a gap owing to the chosen temperature range of 205 to 265 K, a range which most studies do not explore. In addition, it uses a simple experimental technique that is rarely used in the present context despite its widespread use in separation sciences. I highly appreciate the present work as it corresponds to a thorough and thoughtful experimental study including random error and uncertainty estimates as well as the confrontation of experimental data with three models of SO₂ surface interaction at increasing complexity. It always appeals to compare different methods of experimental techniques for a given problem of some importance in order to gauge the possible existence of measurement artifacts or fallacies as a confidence building principle. The present study undertakes exactly this which contributes to its importance and value.

At this point I would like to raise a few questions that the authors should try to answer during the peer-review process in order to help the reader grasp the full significance of the work:

- The slow and inexorable "Degradation" of the ice film owing to the carrier gas decompression (pg. 3, lines 19 and 20, and equation (1)) should be explained in a bit more detail. Is this a temperature effect owing to adiabatic decompression across the length of the capillary? If one has a flow with an equilibrium amount of humidity in the carrier gas one loses this same amount at the exit to first order: What goes must come out at the end of the capillary. What you lose by sublimation is redeposited downstream, provided we are at steady-state and have a uniform temperature profile. What else is implied or important beyond that? Any unaccounted loss processes? Please explain the scientific basis or complications.

- I strongly suggest the addition of a qualitative explanation for the concentration dependence of the SO₂ retention time displayed in Figure 2. As far as I understand this effect it comes from the (partial) saturation of the SO₂ uptake (at equilibrium): The higher the SO₂ concentration the earlier the breakthrough because of vanishing interaction with the ice owing to surface saturation of the uptake following equation (11) (Langmuir dissociation, strong interaction) and (3) (Henry isotherm, weak interaction).

- The Temkin isotherm (equation (5)) seems to be a parametric treatment of the above behavior according to the derivation in the S1 section: Is there any scientifically rooted explanation to simply add algebraically both contributions (Henry + each of the stronger interactions) in all three models displayed in Table 1 as an "interpolation" or superposition scheme of two extremes? The molecular view (saturation to a variable degree depending on the SO₂ partial pressure) naturally arrives at the same result for purely kinetic reasons. Diffusion tube experiments under molecular flow conditions (T. Koch et al., JPCA 1998; C. Alcalá-Jornod et al., PCCP 2000; C. Alcalá-Jornod et al., JPCA 2004) arrived at the identical saturation behavior of salt and ice interfaces (without the presence of a carrier gas).

- What is the rationale for using "deactivated" (alkyl-silylated) Pyrex as a Substrate to grow the ice sample in the first place? I do not believe that a coating of several micrometers will let the SO₂ "feel" the underlying properties of the substrate. From our own studies of pure ice performing quartz crystal microbalance measurements on the evaporation rate of H₂O from pure ice films result in a value of 80 to 100 nm thick layer beyond which subsurface effects cease to be important. Beyond this thickness the kinetics of evaporation is unchanged up to several micrometer thickness of pure vapor-deposited ice which is believed to be less compact (lower density, more surface imperfections) than ice samples frozen from pure water. By the

same token, an interference of the silylated glass interface with ice at several micrometers thickness is highly unlikely (pg. 13, lines 30 and 31, and pg. 15, lines 15 and 16) unless the authors have solid evidence to the contrary.

- Regarding the strongly tailing peak shapes of the chromatograms for SO₂, and to a lesser extent for acetone: Is this a thermodynamic or kinetic effect? Is the equilibrium between adsorbed and gas phase SO₂ established at low concentrations of SO₂ at constant flow rate?

- As a general remark the units of K_H, K_L and q should be clearly included, at least once when mentioned in the text for the first time. One has to be aware that Henry's adsorption isotherm (K_H) is different from Henry's law solubility constant (gas-bulk partition coefficient)!

In addition, there are several minor technical points that may be raised:

- Regarding the square root dependence of the surface coverage (equation (15) and pg. 8, line 16) the requirement is that the active sites must be NEIGHBORING sites in order to yield the square root dependence.

- Pg. 2, line 30 and 31: sentence does not make sense!

- Pg. 3, line 20: "...ice film slowly but unavoidably..."

- Pg. 4, lines 15 and 16: Incomplete sentence.

- Pg. 8, line 5: I do not see a temperature effect in Figure 2b. It probably must be Figure 3b.

- Pg. 7, Figure 3: I do not see yellow data points, however there is a yellow (fitted) line.

- Pg. 10, bottom: "miscible".

- Pg. 12, Table 2: units of K_H: mol m⁻²Pa⁻¹.