

Adsorption efficiency of a molecular sieve in low pressure

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DESCARTES is a balloon-borne grab-sampler instrument sampling stratospheric trace gases. Sampling and pre-concentration is done by adsorption traps and analysis by gas chromatography. In order to get good focusing for the chromatography the traps should be as small as possible and the lower limit is set by the breakthrough of the adsorbate during sampling. This study focuses on the adsorption behaviour of these traps under different circumstances. The results show that simple theory does not explain adsorption at high flow speed.

1. Introduction

DESCARTES is a lightweight grab-sampler instrument for measurements of long-lived stratospheric tracers from balloons and was built at University of Cambridge [Danis et al., 2000]. The instrument collects samples by letting a measured amount of air pass through a small trap containing carboxen adsorbent. The analysis of trapped species is done by direct desorption to a gas chromatograph. The traps thereby act as both sampler and pre-concentration step.

As the adsorbent is meant to give quantitative adsorption the ideal adsorbent would have infinite adsorption coefficient k_a and zero desorption coefficient k_d . The timescales for the adsorption and desorption processes is set by these constants. The adsorption is much faster and must happen on a timescale shorter than the time for an air parcel to pass the trap. The desorption is on a much longer timescale. This is used for the modelling of the desorption in the trap which is made in two steps according to these two physical processes.

In order to make direct injection to the gas chromatograph during the analysis without further pre-concentration steps the size of the adsorption bed should preferably be as small as possible. This must be balanced against the fact that the breakthrough of the trap has to be under control. The traps of the DESCARTES instrument is rather small and this study aims to investigate which sample sizes might be considered safe under different conditions including different flow rates and pressures.

Adsorption of gases to a surface is a competitive situation in that the molecules adsorb to the surface more easily than to other adsorbed molecules. For adsorption up to the limit where a mono-layer of adsorbed molecules is formed there is a theory that adsorption efficiency is proportional to the unoccupied area, called Langmuir theory. The adsorbents used are the hydrophobic molecular sieves Carboxen 569 and 1000. A molecular sieve is an adsorbent that has a large micro porosity with pore sizes of the same order of size as the molecules of interest. Smaller molecules will enter strong adsorption sites in the pores while larger molecules only can adsorb on the outer surface, the sieve effect. It is thought that the pore volume is the important parameter rather than the surface area [Harper, 2000]. According to Comes et al. [1993] concentration effects do not in practise become important until concentrations reach above 1 ppm, i. e. much higher than the levels considered here.

The parameter of investigation here is the critical volume of sampled air when the adsorbate is starting to bleed out of the trap. This is called the breakthrough volume and is defined in several different ways. To take samples in a safe

way different definitions on a safe sample volume have been proposed.

The breakthrough volume has been calculated from retention time determined by packed columns with the adsorbent. For higher concentrations the breakthrough volume is determined immediately by a chromatographic detector directly after a trap fed continuously with a sample [Harper, 2000]. Bertoni and Tappa [1997] developed a method for low concentrations by analysing the trapped amount in a trap and referencing a second species in the standard with much larger breakthrough volume. In the same article an indirect method for small samples is also developed based on a system with two traps in series where the sample is loaded to the first and after elution by a carrier gas both are analysed.

The breakthrough volume has been shown to be independent of flow speed up to a certain limit [O'Doherty et al., 1993b; Harper, 1993; Sturges and Elkins, 1993] while it is very pronounced for higher flows [Seshadri and Bozzelli, 1983; Sturges and Elkins, 1993]. Smaller tube diameter for the traps has been shown to increase trap efficiency below 6 mm inner diameter [Harper, 1993]. Unfortunately there are only a few [O'Doherty et al., 1993a, b] studies that have been done on such small traps as those investigated here.

2. Model description

The model developed models the trap by dividing it into bins and iteratively computing the distribution of CFC entering the trap and desorbing from the bins again and redistributes to new bins. Of course the fraction adsorbed in a bin must be small, i. e.

$$C_a \equiv \frac{\Delta x k_a}{v} \ll 1, \quad (1)$$

where Δx is the width of the bin, k_a the adsorption coefficient and v is the speed of the bulk flow. The incoming amount of CFC, N_{in} is distributed to the bins indexed n according to

$$N(n) = \frac{\int_{x_n - \frac{\Delta x}{2}}^{x_n + \frac{\Delta x}{2}} \Delta N_{in} e^{-\frac{x k_a}{v}} dx}{\int_0^\infty e^{-\frac{x k_a}{v}} dx} \quad (2)$$
$$= \left(e^{C_a} - 1 \right) \Delta N_{in} e^{-n C_a}.$$

This step is then iteratively altered with a step where a part

$$C_d \equiv k_d \Delta t \ll 1, \quad (3)$$

where k_d is the desorption coefficient and Δt the length of the time-step, is desorbed. This desorbed amount is then redistributed similarly to the incoming. The part of the distribution function extending outside the trap is monitored.

2.1. Model validity

There are several approximations made in this model. This also shows up in that the laboratory experiments can

not be reconstructed by the model. Further development will consider some of them.

According to Comes et al. [1993], the Langmuir isotherm does not have to be considered at concentrations lower than 1 ppm in adsorption beds of this kind. The method for low concentrations (ppb) by Bertoni and Tappa [1997] is also based on this assumption. The species of investigation here are sub ppb and thus do not affect each other by competition. There might well be other species in the air that is not caught in our analysis that can have larger concentrations. The calibration of the instrument is performed with both a synthetic standard of CFC in pure nitrogen and dried air. Which of these best represents the stratospheric air in this sense is not obvious. Further investigation includes looking at the possible effects of competing species.

There are reports that the trap efficiency drops considerable with high flow speed [Seshadri and Bozzelli, 1983; Sturges and Elkins, 1993]. These effects are very interesting for this study and form a target for further investigation.

It has been reported that the results depend on the geometry of the trap [Harper, 1993]; these mechanisms are poorly understood and are not included in the model. The adsorption bed consists of balls of Carboxen with small spacings; this is not considered in the model.

The dead volume between the traps in the double trap experiments is not included, but is found to be negligible.

The pressure difference and therefore the velocity difference in different parts of the traps is not considered. Neither is the temperature difference. None of these parameters is well known.

2.2. Numerical errors

There are always errors from the resolution of models. These are controlled both in time and position by comparison to high-resolution runs. The model is constructed in such a way that the amount of input is always conserved regardless of the binning. All distribution of molecules to new adsorption sites are thought to be immediate with no dependence of carrier velocity. Reemission is considered to appear from the geometrical centre of the bin. This is monitored and gives very little effect.

3. Results

The first lab test we need to recreate is the flow rate test performed by Roslin [2003]. The test was performed as a double trap experiment where a series of samples was taken through one trap. A second trap was changed for each sample to give a series of breakthrough values. The results presented in figure 1 show that similar sample sizes give widely different breakthrough values. This is to the largest extent due to the different reaction time available for adsorption. This is shown by the model run. As the relationship of the time and flow rate variables in the model to the absolute values is unknown, solutions with different combinations of these parameters are possible. Model runs with parameters that fitted to the highest breakthrough value are shown by black lines in figure 1. There is an infinite number of solutions of which three are shown. It is obvious that they have different success in describing the experiment. The model was then run with a flow that was 115/200 times the previous. The corresponding runs are plotted in gray corresponding line style. These are to be compared with the lower flow experiment. As indicated in the figure, all possible solutions overestimated the breakthrough for this flow. This shows that the reaction time can not fully explain the

flow rate dependence. The picture is consistent with even lower flow rates.

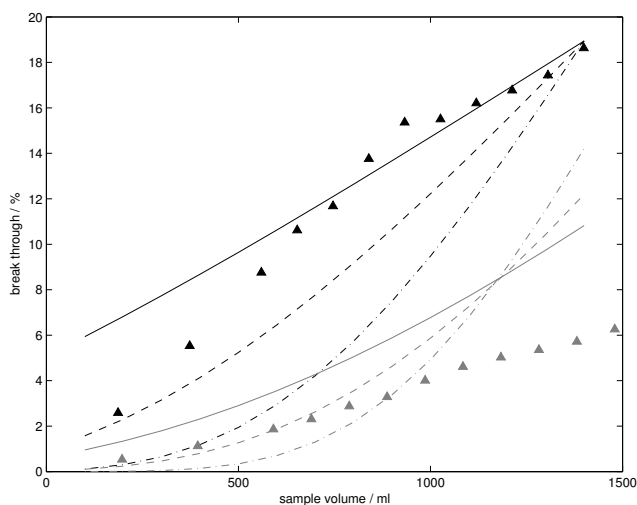


Figure 1. Breakthrough at different flow velocities, experimental values indicated by triangles, adopted from Roslin [2003], and simulations by lines. 200 SCCM in black and 115 SCCM in grey. The y-axis is the cumulative sum of the analysed amounts in the second trap divided by the known full input.

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