

Modelling the Effects of Gas Bypass on Flow Systems Working with mg-Scale Samples

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Flow systems are among the most common macroscopic techniques used to measure mass transport of gases in nanoporous adsorbents. Working with mg-scale samples of material highly reduces the chances of encountering undesired heat and external mass transfer resistances, essentially simplifying the system to a Continuously Stirred Tank Reactor (CSTR) and allowing for increased accuracy in the determination of kinetic properties. However, when using such small sample masses and working with relatively high flowrates one must be aware of the increased risk of a gas bypass, i.e., the formation of a preferential path with lower resistance for a portion of the gas to flow without coming into contact with the adsorbent.

In this work we carry out the first analysis of a gas bypass effect on diffusion-limited flow systems with small sample masses. The analysis is based on the study of two systems that can be described using a simple CSTR model: the Zero Length Column (ZLC) and the gravimetric flow system.

The ZLC is a chromatographic technique originally proposed to study intra-crystalline diffusion in zeolites ¹. The inspiration for its development came from the need to overcome the limitations of the conventional breakthrough experiments for strongly adsorbing species by shrinking the column to a monolayer consisting of only a few milligrams of sample. The working principle of a ZLC is quite straightforward and concerns the analysis of the desorption curve of a sample pre-equilibrated with a known concentration of adsorbate by monitoring the outlet gas concentration ². A bypass in a ZLC system is primarily caused by non-uniform packing and/or distribution of sample inside the column.

Gravimetric flow systems, if operated in carefully calibrated conditions, can also be used to measure gas transport kinetics. In this case, the amount of gas adsorbed is measured directly by monitoring the weight change of the sample as the concentration at the inlet is altered ³. Gravimetric systems often exhibit bypass due to the design of the gas flow around the crucibles.

In addition to presenting differing origins of bypass, the two systems offer two distinct methods for monitoring how the presence of a bypass influences the response of the system, i.e., the gas phase concentration (ZLC) and the adsorbed phase concentration (gravimetric). By adopting both approaches, we develop a mathematical model to illustrate how the presence of bypass alters the respective system response with emphasis on the change in the apparent diffusional time.

Furthermore, using the developed bypass model, we provide a systematic analysis of the effect a gas bypass has on the response of the aforementioned systems to changes in typical experimentally controlled model variables, such as the gas flowrate, full or partial adsorbent equilibration, and column temperature. This allows for the design of experimental protocols capable of distinguishing between the presence of bypass from more complex apparent mass transport resistances.

References

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