

Flow Rate Fluctuations in Gas Chromatography

Gas chromatography is a widely used experimental method for the separation and analysis of multicomponent substances¹. To do this efficiently, one has to make the proper choices of column, carrier gas, and detector. The column is the heart of any gas chromatography experiment; it contains packed adsorbent, which is known as the stationary phase. Interactions between the stationary phase and mobile phase, the flowing gas mixture, are what allows the separation process.

The choice of detector is an important part of any chromatographic experiment. One common detector is the thermal conductivity detector (TCD). This detector is comprised of a hot filament that contacts the moving gas phase; it generates a signal when the filament temperature changes. Therefore, changes in gas composition or flow rate will generate signals². For this reason, the TCD is popular in gas chromatographs, mass flow meters, and flow controllers.

While the TCD has proven to be extremely useful in detecting components of gas mixtures, it is not without difficulties. For example, Figure 1 shows that anomalous signals arise in the detection of nitrogen injected into carbon dioxide using zeolite 5A as a stationary phase. These signals are caused by flow rate fluctuations. What needs to be addressed in this work are the origins of the fluctuations, their impact on the accuracy of composition measurements of the relative quantities of gasses present in the mixture, and the information that can be extracted about the surface of the adsorbent from these anomalous signals.

As can be seen from Figure 1, in the case of no post-column tubing the nitrogen signal masks the anomalous signal. This masking can introduce errors into a quantitative analysis. With the introduction of post-column tubing, the nitrogen signal moves to later time while the anomalous signal remains stationary. It becomes apparent that anomalous signals may be much more common than once thought; while they show up as distinctly non-Gaussian shaped peaks in experiments with post-column tubing, they are usually masked by the component's signal, making their contribution unnoticed.

The origin of flow rate fluctuations comes from adsorption and desorption behavior of both the carrier gas and the sample gas onto the stationary phase. Before the sample injection into the column, a certain amount of carrier gas is adsorbed onto the stationary phase, based on its adsorption isotherm. This is shown in Figure 2(a). After the sample is injected into the column, there is a local decrease in the partial pressure of the carrier gas, as shown in Figure 2(b). Following the isotherm in Figure 2(a), some of the carrier gas desorbs from the column packing, while the sample adsorbs. These amounts need not be the same. Any excess gas adsorbed (or desorbed) from the stationary phase will induce a change in total pressure, which

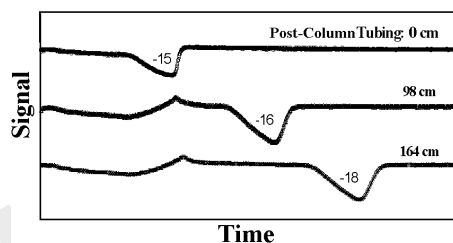


Figure 1: Gas chromatograms of nitrogen in carbon dioxide gas using zeolite 5A. As can be seen in the figure, with no post-column tubing, the signal looks distinctly non-Gaussian. However, with the introduction of 98 cm or 164 cm of post-column tubing, an anomalous signal can be filtered out, which leaves the column well before the sample signal.

alters the flow rate of the gas through the column³. This is the origin of the flow rate fluctuations. The change in flow alters the rate of heat removal from the filament in the TCD, and therefore shows up as a signal.

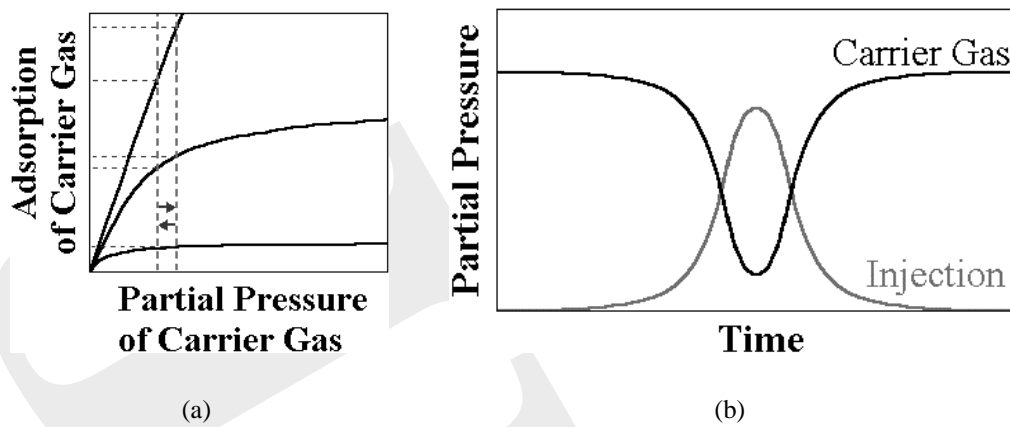


Figure 2: (a) The relationship between the adsorption of a gas and the partial pressure (the adsorption isotherm). The three lines represent the cases of strongly, moderately, and weakly adsorbing gasses. The most strongly adsorbing gas is represented by the steepest line. (b) The relationship between the partial pressure of a gas and time at a point inside the column.

It is possible to gain insight into the adsorption process and molecule-surface interactions by studying these flow rate fluctuations. This may allow for a new method of analyzing the adsorption of multicomponent gasses with the ultimate goal of obtaining information about heterogeneous surfaces. Furthermore, an understanding of these fluctuations will lead to corrections of some current experimental methods that have proven to be very difficult or error-prone⁴.

¹Fowles, I. A. *Gas Chromatography*, 2nd ed.; John Wiley & Sons: New York, 1995.

²Cowper, C. J.; DeRose, A. J. *The Analysis of Gases by Chromatography*; Pergamon Press: New York, 1983.

³Haarhoff, P. C.; van der Linde, H. J. *Anal. Chem.* **1965**, 36, 1455.

⁴Buffham, B. A.; Mason, G.; Yadav, G. D. *J. Chem. Soc., Faraday Trans.* **1985**, 81, 161.