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Cosorption effect in gas chromatography: flow fluctuations caused by adsorbing carrier gases☆

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Abstract

Adsorbing carrier gases have a number of advantages in analytical and preparative gas chromatography, such as clearer detector signals and higher column efficiencies. This work shows that adsorbing carrier gases also may be useful because they cause the mobile phase flow rate to become unsteady after injecting a small amount of sample. This work shows that a 100 μL sample of helium can liberate enough carbon dioxide carrier gas from a zeolite 5A packed column at 373 K, that the departure from the steady-state flow rate had an upper lobe area of 586 μL of carrier gas. This was confirmed by coupling a modified Langmuir kinetic model with the Ergun equation.

Keywords: Carrier gas; Sorption effect; Thermal conductivity detection; Flame ionization detection; Ultraviolet absorbance detection; Signal amplification; Peak asymmetry; Langmuir kinetic model; Ergun equation; Nonlinear chromatography; Adsorption dynamics

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1. Introduction

Chromatographic separations rely on differences in multi-component adsorption dynamics. The science of multi-component adsorption has been studied since Langmuir and Brunauer, Emmett, and Teller [1]. However, as interest in more advanced separations and analyses increases, knowledge of multi-component adsorption in chromatography will become increasingly important. This work investigates the influence of multi-component gas adsorption dynamics on convective momentum transport in the mobile phase. In particular, this work examines how and when small perturbations in partial pressure can produce major variations in the effluent flow rate.

The assumption that the mobile phase flow rate remains constant after injection of sample is often appropriate in chromatography, especially if the sample is small and helium is the carrier gas. However, helium is not always selected for the mobile phase [2–11]. For example, humid nitrogen and carbon dioxide have been used as carrier gases to increase the retention of primary amines [8]; ammonia has been used as a carrier gas to increase the retention of organic acids of low molecular mass [9]; and binary mobile phases containing carbon dioxide have been used extensively in supercritical fluid chromatography (SFC) and high-performance liquid chromatography (HPLC) [12]. The choice of carrier gas is important because it dictates the column's efficiency [13,14], the sizes and shapes of detector signals [15–17], and the ease of downstream purification. This can be advantageous, but sometimes at the expense of this steady-flow assumption as shown in this paper.

Fluctuations in the mobile phase velocity and pressure have been studied previously. Bosanquet and Morgan examined changes in local flow velocity due to the sorption of sample [18] and are cited for terming this phenomenon the "sorption effect" [19,20]. Scott [21], Haarhoff and van der Linde [22] studied the local pressure changes in a column upon passage of sample. Peterson and Helfferich discussed changes

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in local, mobile phase velocity upon the arrival of a concentration band [23]. Buffham et al. measured such changes in flow rate and pressure [24]. Buffham and co-workers developed the method of sorption effect chromatography [25–27]. Yeroshenkova et al. [28], and Helfferich and Carr [29] noted how chromatograms can depend on the sorption effect. Jennings et al. [30], and Blumberg [31] explained the disparity of flow velocity in the column due to gas compression, whereas Shen and Lee [32] observed flow disparity caused by phase transitions. Many theories and methods that may deduce information about the stationary phase are based on the premise that there are differences in the linear velocity within the mobile phase. For example, the tracer-pulse technique [33] and sorption effect chromatography were developed to determine adsorption isotherms; they can be classified in the categories of perturbation gas chromatography and inverse gas chromatography [34–37]. The sorption effect continues to be used in gas–solid columns, but with the new focus of heterogeneous catalysis [38,39].

A common idea in these works is that a local stimulus (e.g., a change in the sample's concentration) can cause variations in the local flow velocity or pressure. This paper discusses a different kind of flow phenomenon: when an adsorbing carrier gas is used, a small amount of sample can affect the flow ahead of it, and perhaps behind it, by causing desorption of a larger amount of carrier gas—the sorption behavior of the carrier gas, rather than of the sample, affects the flow rate. This is complementary to the sorption effect and, for this reason, we call this phenomenon the cosorption effect. It can occur in the presence of a non-adsorbing sample such as helium, and may be useful in inverse gas chromatography or in applications where signal amplification is important.

Evidence for the cosorption effect arises in various applications, because it is an example of fundamental, multicomponent adsorption dynamics. In concentrated absorbers, significant increases in flow rates and entrainment occur while placing the system on standby operation [40]. This is the cosorption effect—placing absorbers on standby consists of replacing the feed stream with an inert stream, which can be considered an "injection" of a large sample. This effect can lead to mechanical damage and potentially dangerous and unacceptable exhausts to the environment [41]; and it causes premature and asymmetric breakthrough curves [42]. Furthermore, the pressure and flow transients can influence product formation in adsorptive reactors [43]. Here, the cosorption effect is discussed in the context of gas chromatography. Because it has not been explored in this context, it may be useful, and it can be very significant in analytical and preparative applications.

This paper demonstrates the cosorption effect in packed columns with carbon dioxide carrier and weakly-adsorbing samples; and it discusses how the effect is not limited to these systems. Consequently, the cosorption effect also is relevant to the science of SFC; which currently is exploring the effects of small amounts of helium in carbon dioxide carrier [44,45], and which has had a growing interest in developing packed-column SFC methods [46].

2. Fundamentals

The presence of sample can cause a flow fluctuation by influencing the sorption behavior of the carrier gas. After an injection of sample, fluctuations in the sample's and carrier's partial pressure occur as the sample passes each stage of the column. Consequently, the carrier desorbs and readsorbs at each stage with a net rate that is proportional to the slope of its isotherm. If the small amount of sample liberates large amounts of carrier while passing over the stationary phase, the cumulative amount of desorbed carrier can significantly alter the mobile phase flow rate. This effect is most significant in the presence of a non-adsorbing sample.

When both the sample and the carrier adsorb, the flow fluctuation depends on the difference between the rates of sample sorption and carrier sorption. The total pressure at each stage does not change if the sample is replaced immediately by an equivalent amount of carrier, and then vice versa. However, the total pressure increases at each stage if the rate of carrier desorption is greater than the rate of sample adsorption. As the sample passes the stages, the cumulative amount of desorbed carrier can be significant enough to change the effluent flow rate.

Fig. 1 demonstrates the cause of flow fluctuation in an activated-carbon column at 298 K when nitrogen sample is injected while using carbon dioxide carrier gas. In this illustration, it is assumed that the nitrogen and carbon dioxide adsorption isotherms are their pure fluid isotherms. If mass transfer is not rate-limiting, the decrease and increase of carbon dioxide's partial pressure will cause desorption and readsorption of carbon dioxide, respectively, as illustrated by the

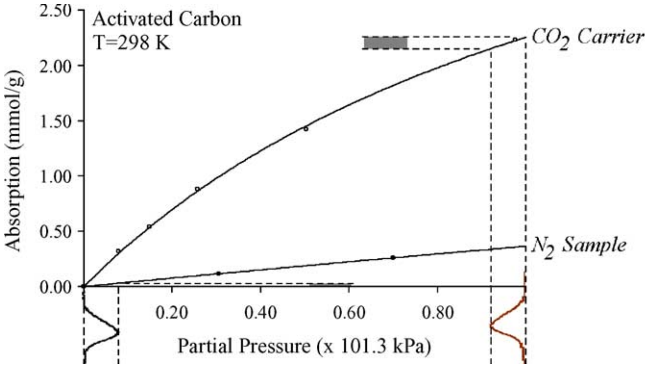

Fig. 1. Pure fluid adsorption isotherms of carbon dioxide and nitrogen on activated carbon [55]. An injection of nitrogen causes a perturbation in nitrogen's partial pressure, causing a complementary perturbation in carbon dioxide's partial pressure at the column's inlet—these perturbations are drawn below the horizontal axis. Consequently, the amounts of nitrogen and carbon dioxide adsorption change. The dashed lines indicate changes in the partial pressures and adsorption of both nitrogen and carbon dioxide. The relative sizes of the shaded sections emphasize that more carbon dioxide desorbs than nitrogen adsorbs, causing the flow fluctuation.