The Retention Gap Effect

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In this month's "GC Connections," the author examines the effects on retention times and peak shapes when a retention gap is added to a capillary column.

A reader sent me the following question by e-mail:

As I read the recent article about the anatomy of a peak,[1] I had to ask the following question: "How does an inert precolumn influence the calculation of, for example, the plate height?" Let's assume the main column has an inner diameter of 0.25 mm and a length of 25 m, the inert precolumn has an inner diameter of 0.25 mm and is 5 m long. Do you then take 25 m or 30 m for calculating the plate height? I have never found this situation mentioned in a gas chromatography book.

This and some related issues arise whenever using a precolumn, which is also called a retention gap. Retention gaps serve as depositories for non-volatile residues that escape from the inlet system, as well as provide a means for consolidation of over-long or uneven injection profiles; the name comes from this second application. They protect the column from contamination as well as sharpen peaks from splitless or on-column injections. Chromatographers can trim the beginning of a retention gap as it becomes contaminated or simply replace it altogether instead of having to trim or replace the analytical column itself, thereby extending column life.

In practice, a retention gap can be used with either isothermal or temperature-programmed elution. In the situation of splitless injection, the column is nearly always temperature-programmed, but in many other applications, isothermal operation is acceptable. I have limited this discussion on retention gaps to isothermal operation, but the conclusions should be valid for temperature programming as well. Many labs will determine the apparent plate height of a peak or peaks in a quality-check mixture as part of standard operating procedures. By monitoring the plate height as well as related performance measures such as peak tailing and peak-to-peak resolution, analysts can track column degradation and anticipate failures before they occur.[1] To compute the plate height, however, the length of the column must be known. The reader's question thus arises when adding a retention gap.

The question can be expanded to encompass the following: What are the effects of a retention gap, if any, on the theoretical plate height and other column metrics? Is there any significant reason to include the retention gap length in plate height calculations from observed peaks?

Deciding on the best way to compute the minimum plate height involves consideration of how peaks disperse as they move along the uncoated precolumn and the main column. The effect of the plate height calculation on column suitability is another consideration. The related question of what happens to retention times also provides some interesting insights. To better understand what is happening, we will need to recall some gas chromatography (GC) theory and develop a model for a retention gap–column ensemble.

Measuring the Height of One Theoretical Plate

Before wandering off into the forests of GC theory, let us review some chromatogram measurements that will help evaluate the effects of adding a precolumn. Peak widths, the number of theoretical plates, the height equivalent to one theoretical plate, and some retention parameters such as the average carrier gas linear velocity, retention times, retention factors and the unretained peak time are all useful parameters that chromatographers can measure or calculate easily from a chromatogram. With this information in hand, we can proceed to discuss the effects of adding an uncoated precolumn.

Virtual chromatography: In this instance, GC theory should provide a suitable answer to the questions. Going into the lab and performing a series of experiments would no doubt give a better answer, but here we will have to make do with computer simulations of example chromatograms with and without a retention gap. Figure 1(a) shows such a chromatogram with four peaks: one at the unretained peak time, one midway along, and two that are adjacent but fully resolved from each other. The peaks' measured metrics are listed in Table 1a. These peaks represent typical isothermal chromatography on a 25 m $\times$ 0.25 mm capillary column with a thin 0.25 μm stationary-phase film but without an uncoated precolumn.

The first peak in Figure 1 represents an unretained peak, such as methane, that occupies only the mobile phase during its passage through the column. From its retention time t_M and column length L, we can determine the average carrier gas linear velocity $\bar{u}$

$$\bar{u} = \frac{L}{t_M} \qquad [1]$$

To simplify this discussion, we will keep the average velocity constant at 40 cm/s when adding the retention gap.

The average velocity is calculated from the total time that an unretained peak takes to be eluted. However, the carrier gas velocity is not the same along the entire length of the column. It starts out slower at the entrance and speeds up towards the exit. Measuring the exit or entrance

velocities directly is not simple. I do not know of anyone who has tried it. Instead, chromatographers measure the average value from the unretained peak time and then calculate the localized carrier gas velocity as desired. The velocities at several points along the column are relevant to this discussion; at the inlet, at the outlet and at the retention gap–column junction. These values, plus some other information, will allow us to calculate the effects of the retention gap on retention and peak shapes.

The unretained peak time and the retention times t_R of each of the peaks enter into the calculation of the retention factor k:

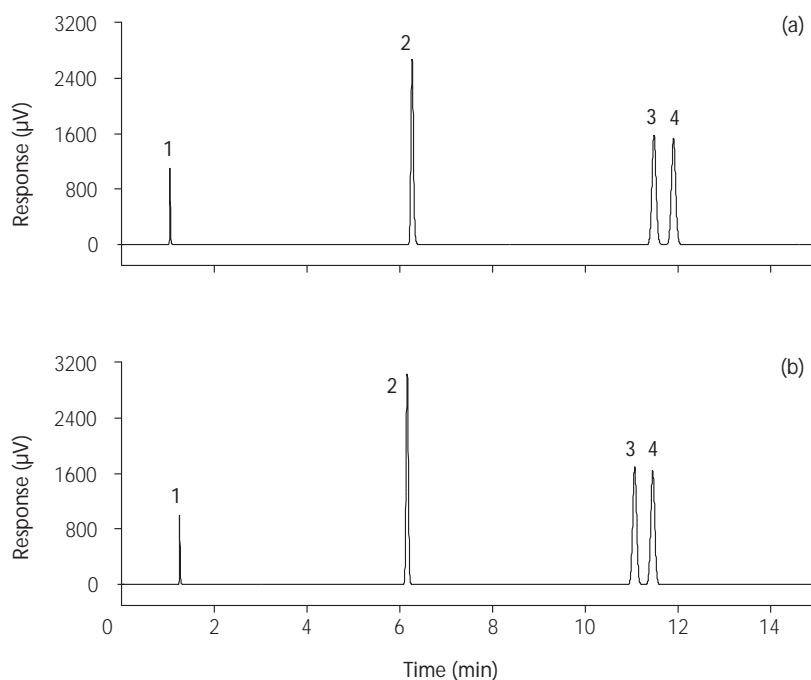$$k = \frac{t_R - t_M}{t_M} \qquad [2]$$

The retention factor is the number of multiples of the unretained peak time that a retained peak spends in the stationary phase as it transits through the column. The retention factor is independent of the unretained peak time and gas velocity and makes it easier to compare results between columns of different length or with different carrier gas conditions. However, retention factors do depend strongly upon the type of stationary phase, the column temperature and the amount of stationary phase relative to the gas volume of the column. I will keep the temperature and the analytical column stationary-phase film thickness constant for the purpose of this discussion. Adding the uncoated restrictor will change the ratio of stationary phase to gas volume, so k values should be expected to change.

In addition to retention-related metrics, GC users also measure peak widths and calculate some data about their shapes and their resolution relative to other peaks. The peak width at half-height w_h is measured the most often and is the easiest way to determine peak-shape metric. The peak width at half-height does not signify anything by itself, but in concert with retention time information, it can tell us how many theoretical plates N_{exp} are observed experimentally.

$$N_{exp} = 5.545 \left(\frac{t_R}{w_h}\right)^2 \qquad [3]$$

From the number of theoretical plates and the length of the column L, we can calculate the measured height — the length along the column — equivalent to one average theoretical plate H_{exp}:

Figure 1: Effect of a retention gap on retention and peak shape. (a) 25 m × 0.25 mm, 0.25 μm d_f column, 17.75 psig inlet pressure and (b) same column as (a) with a 5 m × 0.25 mm uncoated retention gap added to the beginning, 21.6 psig inlet pressure. Conditions for (a) and (b): helium carrier gas, 40 cm/s, 100 °C. Peak profiles calculated from theoretical H values assuming 83% coating efficiency.

$$H_{exp} = \frac{L}{N_{exp}} \qquad [4]$$

Finally, we can determine the resolution R_S between two adjacent peaks from their retention times and widths at the half-height:

$$R_{s,3:4} = 1.177 \frac{t_{R,4} - t_{R,3}}{w_{h,4} + w_{h,3}} \qquad [5]$$

In Equation 5, the subscripts 3 and 4 refer to the third and fourth peaks in Figure 1. A resolution of greater than 1.5 is considered baseline resolution. See reference 1 for a more detailed discussion of the significance of N, H and R. Table 1a lists these values as measured for the peaks in Figure 1(a).

Adding the Gap

Consider what happens to the observed performance when a retention gap is added to the front of the column, ignoring for the moment the peak focusing that the operator might invoke deliberately. By definition, the retention gap will not retain any of the peaks: they will all fly through the retention gap in the same time period.
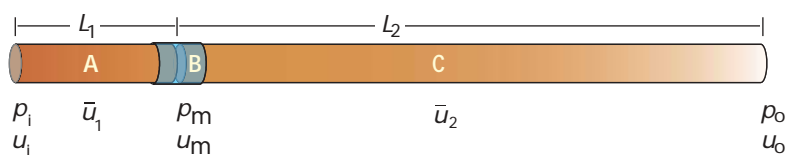
As they pass through the retention gap, they will experience some degree of broadening, then they will all encounter the analytical column at the same time.

One approach to answering the retention gap question considers the retention gap and the analytical column as acting separately but in series. We can model the overall ensemble behaviour and compare it with the column alone by computing the peaks' retention and broadening behaviours on the retention gap first and then feeding the peaks to the analytical column entrance as they exit from the retention gap.

Retention times: The issue under discussion here is whether to use the length of the column alone or the total length of the retention gap–column ensemble for plate-height calculations. First, I will take a look at the effect of a retention gap on retention times because there are some trends that run counter to intuition. Along the way, some pressure and velocity parameters will be developed that are essential to modelling peak broadening in column segments.

Figure 2 illustrates some characteristics of the retention gap–column ensemble. A retention gap A with length L_1 is joined to

Figure 2: Retention gap and analytical column ensemble. A = retention gap, B = zero dead volume connection and C = analytical column.

the analytical column C with length L_2 by a zero dead-volume connector B. The ensemble has inlet pressure p_i and outlet pressure p_o, as well as midpoint pressure p_m. By definition, $p_i > p_m > p_o$. Also shown are the inlet, midpoint and outlet carrier gas velocities, for which the velocities fall in the order $u_i < u_m < u_o$. Finally, both the retention gap and the analytical column have characteristic average carrier gas velocities $\bar{u}_1$ and $\bar{u}_2$, respectively.

It is intuitive to state that adding a length of uncoated precolumn as a retention gap to the front of an analytical column, while keeping the average carrier gas velocity constant, at 40 cm/s in the present example, will increase the retention times of all of the peaks. However, this is not entirely correct. Peaks that have small retention factors do gain in retention time, but peaks with larger retention factors are actually eluted *earlier* with a retention gap than without one, as seen by comparing Figures 1(a) and 1(b). To understand this effect, we will need to do some retention time calculations on the retention gap and the analytical column separately and then

combine them to find retention times on the ensemble.

I can rearrange and combine equations 1 and 2 to express retention time in terms of the retention factor, the average linear velocity and the column length:

$$t_R = \frac{L}{\bar{u}}\ (k+1) \qquad [6]$$

I can use Equation 6 to calculate retention times on the retention gap and the analytical column separately if I know their lengths, average velocities and the retention factors of the peaks in question. Then I can add the two times together to find the total retention time of the ensemble.

The lengths of the retention gap and column are known: 5 and 25 m, respectively. I also know the retention factors: $k = 0.0$ on the retention gap, and k has the values from Table 1a for the analytical column. The problem now is to determine the average carrier gas velocity in the two parts of the ensemble separately. One part of the calculation of the velocities involves finding the pressures

at the ensemble entrance p_i and also at the junction point p_m. The outlet pressure p_o remains at 1 atm. Although I could write equations and solve them for the pressure drops, most of this work has already been done for me by the GC manufacturers.

To set the inlet pressure of the ensemble, I went into the lab and used a gas chromatograph with electronic pressure control. I set the column length to 30 m, the inner diameter to 0.25 mm, the film thickness to 0, the average linear velocity to 40 cm/s, the oven temperature to 100 °C, and the carrier gas to helium. Setting a film thickness of zero in this instance will not affect the calculations because the 0.25 µm film has no significant effect on the pressure drop. The gas chromatograph selected an inlet pressure of 21.6 psig with an outlet pressure of 1 atm. This is slightly higher than the 17.8 psig needed to drive the carrier gas at 40 cm/s through the shorter analytical column alone, as would be expected.

Calculating the midpoint pressure of a column ensemble is beyond the capability of a standard lab gas chromatograph, but the relationships required to perform the calculations are found in GC textbooks [2,3]. I derived the carrier gas velocities at the inlet, midpoint and outlet as well as the average gas velocities in the retention gap and the analytical column, all of which are listed in Table 2. These calculations are more complex than will fit in the available space here, so I have placed them in an on-line supplement to this article for interested readers to review. Others might wish to use this material as a soporific. The supplement is located on the internet at http://www.lcgceurope.com.

The carrier gas expands during its passage through the column, but the rate of expansion is not proportional to the distance along the column. Rather, the gas expands more toward the end of the column than the beginning. As a result, although the average gas velocity from entrance to exit is 40 cm/s in both instances, the average velocity across the analytical column, where peaks are retained, is higher (42.5 cm/s) when it is preceded by a retention gap than when the retention gap is absent. This non-linear carrier gas expansion causes peaks to traverse the analytical column portion in less time with the retention gap attached. For this particular example, peaks with $k > 3.5$ end up being eluted sooner than on the analytical column alone, as shown in the retention times in Table 1b for the peaks in Figure 1(b), with the retention gap

Table 1: Metrics obtained from the peaks in Figure 1. (a) 25 m × 0.25 mm i.d. × 0.25 mm column. (b) Same column as (a) with a 5 m × 0.25 mm i.d. uncoated retention gap added to the beginning (peak 1 is an unretained peak).

Peak	1		2		3		4	
Metric	a	b	a	b	a	b	a	b
Retention time (t_R, s)	62.5	75.0 (= t_M)	375	369	688	663	713	687
Retention factor (k)	0.0	0.0	5.0	3.91	10.0	7.82	10.4	8.13
Width at half-height (w_h, s)	1.3	1.3	3.5	3.5	6.0	5.9	6.2	6.1
Measured plate count (N_{exp})			64 000	62 000	73 000	70 000	74 000	70 000
Measured plate height (H_{exp}, mm)			0.39	0.40	0.34	0.36	0.34	0.36
L = 25 m (column only) L = 30 m (column + retention gap)				0.48		0.43		0.43
Resolution (R_S)			Resolution between peaks 3 and 4				2.43	2.30

attached. This retention gap effect on retention time varies considerably with different column and retention gap lengths and diameters.

Peak shapes: To calculate the composite effect of the retention gap and analytical columns' peak broadening, we can add the peak variances σ^2 from each section taken separately:

$$\sigma^2 = \sigma_1^2 + \sigma_1^2 \qquad [7]$$

The subscripts 1 and 2 refer to the retention gap and analytical columns, respectively. The theoretical variance of a peak is a function of the column length, the plate height, and the retention time:

$$\sigma^2 = \frac{H \cdot t_R^2}{L} \qquad [8]$$

To find the theoretical variance of a peak on the retention gap and on the analytical column then, we must know its retention time and theoretical plate height on both. With that information, we can compare the variances contributed by the retention gap and the column to better understand the effects of the retention gap and to decide how best to measure the plate height.

To find the individual plate heights for the retention gap and the analytical column, we need to access some more theory. The Golay equation and its modifications that account for the columns' pressure drops give a fairly accurate assessment, but this derivation and the calculations are also too lengthy to include in print. They have been placed in the second part of the supplement to this discussion, located at http://www.chromatographyonline.com.

Table 3 shows the theoretical peak dispersion for each peak (in seconds) attributable to the individual sections and to the overall column or ensemble both with and without a retention gap. The retention gap contribution is the same for all peaks. This makes sense because they are not retained there and should experience only gas-phase broadening, which is assumed to be the same for all peaks. For the unretained peak, about 40% of the ensemble dispersion is caused by the retention gap and 60% to the analytical column. The retention gap affects the second peak slightly, but it does not have any kind of significant affect on the last two peaks' theoretical shapes at all.

To include or not to include: The degree

of band broadening that occurs on the analytical column, as measured by the calculated peak dispersions, is similar with and without the retention gap. For the later-eluted peaks 3 and 4, less broadening occurs on the analytical column with the retention gap in place. Peak 4, for example, has a dispersion of 2.43 s from the analytical column alone, while adding the retention gap decreases the dispersion from the analytical column to 2.38 s. These differences are because of the slight shift of the later peaks to earlier retention times, as described in Equation 8, and not to a real performance shift.

Overall, the earlier retention times and slightly smaller variances with the retention gap in place cause a net decrease in the resolution between peaks 3 and 4, as shown in Table 1. The theoretical plate count is not impacted in any meaningful way, however. The resolution loss is not significant and is likely to be less than the error associated with the theoretical calculations used to derive it and less than the accuracy of chromatogram measurements performed to determine it.

Table 1 clearly shows that including the retention gap length in the calculations increases the apparent plate heights, yet the number of theoretical plates and the peak widths do not change appreciably. Therefore, the retention gap length should not be included when determining analytical column plate heights.

Conclusion

This has been a long journey through a theoretical quagmire in quest of an answer to the question of how best to calculate observed theoretical plate heights when a retention gap is used. For the particular example chosen here, peaks with a retention factor of five or greater do not show a significant contribution to their shape from the retention gap. Theoretical plate numbers do not change and only a negligible resolution loss might occur. Therefore, it seems valid to conclude that the length of a retention gap as long as 5 m can be ignored when measuring analytical column performance.

Table 2: Pressures, velocities and retention times for a column ensemble. (a) 25 m × 0.25 mm i.d. × 0.25 mm film analytical column alone. (b) 5 m × 0.25 mm i.d. uncoated retention gap and analytical column in series. Helium carrier gas at 40 cm/s, 100 °C.

	a	b
Inlet pressure (p_i, psig)	17.8	21.6
Midpoint pressure (p_m, psig)	—	18.98
Outlet pressure (p_o, psig)	14.7	14.7
Flow-rate (F_c, mL/min)	1.98	2.17
Inlet velocity (u_i, cm/s)	30.4	29.8
Midpoint velocity (u_m, cm/s)	—	32.1
Outlet velocity (u_o, cm/s)	67.2	73.5
Retention gap average velocity ($\overline{u}_1$, cm/s)	—	30.9
Analytical column average velocity ($\overline{u}_2$, cm/s)	40	42.5
Ensemble average velocity ($\overline{u}$, cm/s)	—	40
Retention gap unretained peak time (t_{M1}, s)	—	16.2
Analytical column unretained peak time (t_{M2}, s)	62.5	58.8
Ensemble unretained peak time (t_M, s)	—	75

Table 3: Theoretical peak dispersion. (a) 25 m × 0.25 mm i.d. × 0.25 mm column. (b) Same column as (a) with a 5 m × 0.25 mm i.d. uncoated retention gap added to the beginning (peak 1 is an unretained peak).

Metric	Peak Location	1 a	1 b	2 a	2 b	3 a	3 b	4 a	4 b
Dispersion (σ, s)	Retention gap		0.10		0.10		0.10		0.10
	Analytical column	0.141	0.166	1.24	1.23	2.35	2.29	2.43	2.38
	Ensemble		0.194		1.24		2.29		2.38

References

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For an on-going discussion of GC issues with John Hinshaw and other chromatographers, visit the Chromatography Forum discussion group at http://www.chromforum.com