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Chromatographic Retention Times Using Mixture Pulses of Different Compositions

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Abstract. This work is concerned with how gas chromatographic (GC) retention times are determined for adsorption measurements. The standard way is to add a pulse (slug) of one of the pure gases using either an injection valve or a syringe. A chromatographic detector is used to determine the time taken for the pulse to travel through the column. The whole procedure is then repeated using a pulse of the other pure gas. Experience from other workers would suggest that the two retention times are not the same. We take a novel approach. We add pulses of the same size but of *different* composition. That is, we use *mixture* pulses. Our investigation involves the ethane-helium-13X zeolite system at 50°C and we consider only one main (carrier) flow. Our results show that there is a linear variation between the composition of the pulse and the retention time. Indeed, it is not sufficient to simply add the retention times for the two pulses and take the average. The standard GC detector is based on thermal conductivity measurements (TCD). In a novel development, we also show how a detector based on the measurement of viscosity can be used to determine these retention times.

Keywords: adsorption, chromatography, retention time, binary mixtures

Background

Gas chromatographic (GC) methods provide an alternative to conventional gravimetric or volumetric methods in the determination of adsorption isotherms. In general, GC methods are low-cost and are characterised by short experimental times. For a GC method, an adsorption column is packed with mass W of adsorbent. The carrier gas has composition (y_A, y_B) and volumetric flow rate Q through the column. At time zero, a pulse of gas of different composition is added to the carrier gas. The (retention) time taken for the pulse to pass through the column (t_r) is measured by a suitable composition detector. These quantities are related to the two isotherm (w is the amount adsorbed per unit mass of adsorbent) gradients by Peterson and Helfferich (1965):

$$K = (t_r - t_g)\frac{Q}{W} = y_B\frac{dw_A}{dy_A} + y_A\frac{dw_B}{dy_B} \qquad (1)$$

where the time t_g is the time taken for a *non-adsorbed pulse* to travel through the column. The variable K

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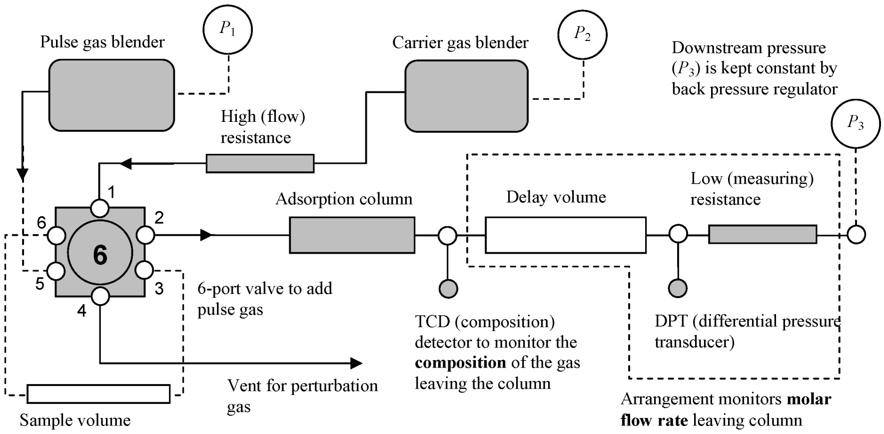

Figure 1. Experimental arrangement to determine pulse retention times.

is often termed the binary equilibrium constant. According to the form of the equation, the retention time should be independent of the composition of the pulse. The validity of this equation requires that the pulse size is low enough, so that equilibrium can be assumed to be linear. One problem with this equation is that the two retention times obtained from using the pure gases (A and B) often do not agree and can differ significantly (Tezel et al., 1992). This is often checked by reducing the pulse size and taking the retention time in the limit as the volume tends to zero. Here, we have taken a different approach. Rather than use pulses of different volumes, we use a single volume and different compositions.

Theory

For a pulse experiment, a quick approximation can be obtained from measuring the time difference between the injection time and the time to the peak height (t_{peak}) of the signal $s(t)$. However, this is sufficient only for symmetrical peaks. For skewed peaks, it is necessary to calculate the first moment of the peak (t_{firstm}) from:

$$t_{\text{firstm}} = \frac{\int_0^\infty t[s(t) - s_{\text{base}}]\,dt}{\int_0^\infty [s(t) - s_{\text{base}}]\,dt} = \frac{A_1}{A_2} = \frac{(\text{mV s}^2)}{(\text{mV s})} \quad (2)$$

The area A_2 is simply the area under the peak. The quantity A_1 also involves the elapsed time after switching the valve. There can be problems with the first moment if the baseline value s_{base} varies with time.

Experimental

Figure 1 shows a schematic of the experimental arrangement. The flow rate of the main (carrier) gas is determined by the upstream (P_2) and downstream (P_3) pressures and is typically around 30 mL/min. The area surrounded by the dotted line is used to monitor the molar flow rate of the gas leaving the column. The purpose of the delay volume (about 8 m of 1/4 inch o.d. nylon tubing) is to ensure that the DPT signal is not affected by viscosity variations. This will be shown in the results section. The column has a volume of around 2 mL and contains around 1 g of 13X zeolite. The sample volume has a value of around 0.1 mL. Initially the main gas flows from port 1 to port 2, while the pulse gas flows from port 5 to port 6 through the sample loop, back into the valve at port 3, then through port 4 and then to vent. An experiment is conducted by switching the 6-port valve, which directs the main flow through the sample volume, pushing a plug of pulse gas through the system. The two detector signals are monitored using a data acquisition system, and a spreadsheet is used to process the data. Another experiment is carried out by changing the composition of the pulse gas.

Results

Figure 2 shows the composition (TCD) and column outlet flow rate (DPT) signals for adding a helium pulse to the carrier gas of 40% ethane. The DPT record in Fig. 2 shows that the valve is switched at a time of around 106 seconds. There is a negative spike at this point because as the valve is switched, there is a temporary interruption in the carrier gas entering and leaving the column.

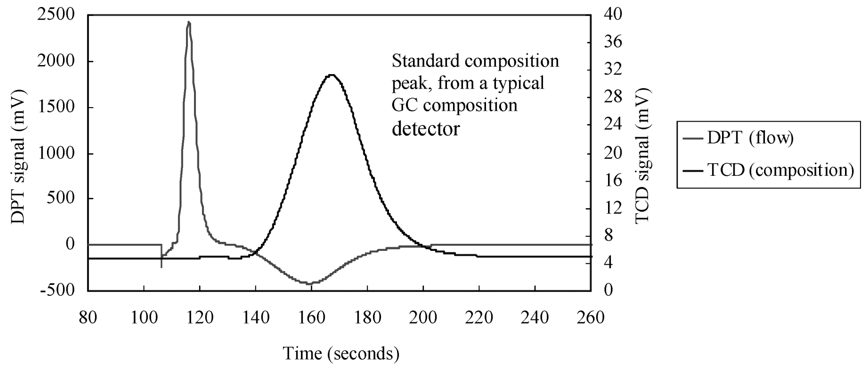

Figure 2. Initial TCD and DPT records for the addition of a helium pulse to a carrier of 40% ethane.

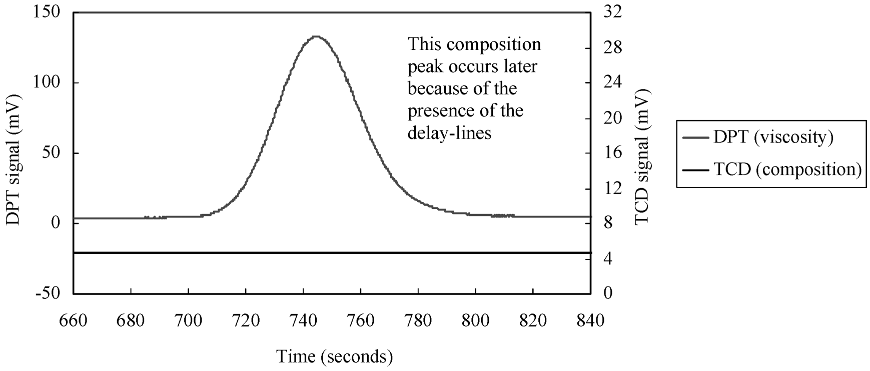

Figure 3. Later TCD and DPT records for the addition of a helium pulse to a carrier of 40% ethane.

The flow rate variation is a consequence of the pulse causing desorption. The composition (TCD) peak is typical of what would be expected from a GC detector. Figure 3 shows what is recorded some time later. Note that the DPT is now recording changes in viscosity. The delay of this "viscosity" peak is caused by the presence of the delay line. Note that the "viscosity" peak has a similar shape to the thermal conductivity peak in Fig. 2. The whole procedure is then repeated for pulses of different compositions. Figures 4 and 5 show the results of superimposing the TCD and DPT (viscosity) peaks.

Figures 4 and 5 show clearly that the retention time of the peak clearly depends on the composition of the pulse. The peak caused by the helium pulse arrives much later than the peak caused by the ethane perturbation. We can quantify these retention times in two different ways. First, we can measure the time difference to the peak maximum. Second, we can measure the first moment using Eq. (1). This depends on evaluating the two areas A_1 and A_2. This is tricky because an important parameter is the baseline value c_{base}. The integrations were carried out over various time spans and

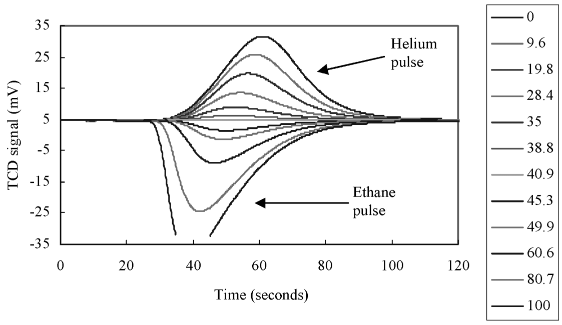

Figure 4. Composition (TCD) records for adding pulses of various compositions to a carrier gas of 40% ethane.

the ratio of the areas calculated as a function of time. This is a useful procedure because it helps to identify any possible drifting in the baseline. The results of the calculations are summarised in Table 1. Note that there are no entries in A_1 and A_2 for the pulse composition of 40.9%. This is because the pulse and carrier compositions are so close that the signal is almost indistinguishable from the noise.

Table 1. Complete set of peak areas, heights and retention times for the TCD data.

Pulse gas (% ethane)	Time to peak maximum (s)	Peak height (mV)	Peak area A_2 (mV s)	Area A_1 (mV s^2)	First moment t_{firstm} (s)
0	61.0	26.7	783	49230	62.9
9.6	58.8	20.9	595	36694	61.7
19.8	56.6	14.0	414	25071	60.5
28.4	54.2	8.8	238	14072	59.1
35.0	52.8	4.2	112	6515	58.3
37.4	52.0	2.5	65.8	3780	57.4
38.8	51.8	1.5	40.9	2343	57.3
39.8	51.0	0.83	21.6	1224	56.5
40.9	–	−0.05	–	–	–
45.3	50.0	−3.24	−84.6	−4784	56.5
49.9	49.0	−6.03	−156.3	−8758	56.0
60.6	46.6	−13.6	−345.4	−18631	54.0
80.7	42.2	−29.2	−740.3	−37756	51.0
100	40 (?)	–	–	–	–

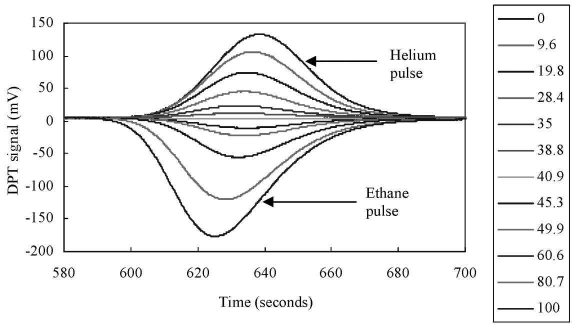

Figure 5. Viscosity (DPT) peaks for adding pulses of various compositions to a carrier gas of 40% ethane.

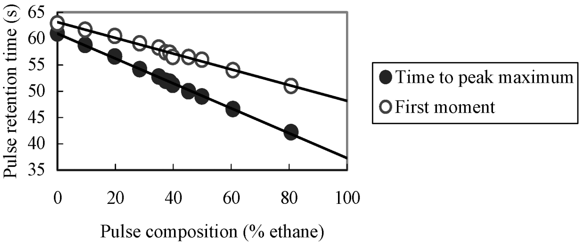

Figure 6. Variation of the retention time with the composition of the pulse gas. The values are taken from Table 1.

Discussion

For a (hypothetical) linear isotherm (of constant gradient), the pulse retention time should be *independent* of the pulse composition and the two lines in Fig. 6 would then be horizontal and coincident. This is evidently not the case in Fig. 6. From Fig. 4, the composition peak for the helium pulse is fairly symmetrical, and that for the ethane pulse is significantly skewed. This explains the increasing deviation between the times to the peak maximum and the first moment shown in Fig. 6. The linearity of both lines in Fig. 6 over the entire composition range, however, is interesting. The variation is presumably due to the non-linearity of the isotherm with the large changes in concentration caused by adding pulses, and so the *true* retention time (corresponding to the actual isotherm gradients at the carrier composition) is that for which the pulse composition approaches that of the carrier gas. Figure 6 shows that this is *not* simply the average of the two retention times for the ethane and helium pulse experiments. Figure 6 would suggest that the required value is a weighted average of the ethane and helium pulse experiments according to the composition of the carrier gas. The suggested way of dealing with potential non-linearity of an isotherm is to use sample volumes of reducing size. However, it can be a problem finding tubes of known and small volume. By using mixture pulses, it is possible to reduce to a much smaller size the concentration change caused by the pulse. This is advantageous when dealing with isotherms with a high degree of non-linearity.

Let us now consider the viscosity peaks shown in Fig. 5. Certainly, it can be seen that these peaks suggest the same type of variation in retention time with the composition of the pulse. It should, of course, be borne in mind that these viscosity peaks have had to travel through about 8 m of $^1/_4$ inch tubing before reaching the DPT. Nevertheless, the results do suggest that this is a possible alternative to the conventional thermal conductivity detector (TCD), especially for systems in which the components have similar thermal conductivities, for example oxygen-nitrogen and ethane-ethylene. Monitoring the flow rate also has the advantage that one can determine the exact time at which the valve is switched. The results also show that it is preferable to use a valve to add the slug. Using a syringe would give a large momentary increase in flow rate, causing a large spike in the DPT record.

One problem with the TCD is that the signal is affected (albeit only slightly) by changes in flow rate. This is because the TCD is typically a semi-diffusion type and a fraction of the carrier flows over the heated wires. One advantage with the DPT is that the composition (viscosity) changes occur well *after* the flow rate changes in the column have ceased. The problem is that it is necessary to subtract the time taken to pass through the delay lines from the time scale shown in Fig. 5 in order to make direct comparisons with Fig. 4. One elegant solution might be to re-plumb the TCD so that the outlet flow from the delay line passes through the second port of the TCD. This would cause a second peak (in the opposite direction) in the TCD record. The time between the two TCD peaks would correspond to the delay time caused by the delay volume.

Conclusions

The problem with adding pulses of gas to determine chromatographic retention times is that one cannot be sure exactly what happens as the pulse passes through the column. This is likely to violate the important assumption that the concentration change caused by the pulse should be *small*. Ideally, the composition of the pulse should be as close as possible to the composition of the carrier gas. However, in this case the composition (TCD) peak would be very small and the retention time difficult to determine. Our results would suggest that it is not good practice to take a simple average of the pulse retention times for the two pure components, unless the carrier composition is close to 50%. Otherwise, the *true* value should be obtained using a *weighted* average of these two retention times. For example, for a carrier composition of 90% (component A), the true value is much closer to the pure-A retention time than it is to the pure-B retention time.

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