Flow model for coupled-column gas chromatography systems

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Abstract

One of the challenges in performing comprehensive two-dimensional gas chromatographic separations is being able to predict the average linear velocities of the carrier gas in the two columns, especially when they have different diameters. The problem is compounded for loop-type modulators, where two thermal trapping zones that switch from hot to cold and back simultaneously are separated by a delay loop. If the linear velocity in the loop is not tuned to the length of the loop and the modulation period, the dual-stage modulation may cease to work properly. A model has been developed that calculates the flow rates in the columns and predicts appropriate delay loop dimensions for a given set-up. Additionally, the model determines the pressure ramp that needs to be used in order to maintain constant average linear velocity within the modulator loop throughout the course of the separation.
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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a technique that is receiving more and more attention recently. It offers vastly improved separation power over conventional GC due to additional separation achieved in the second dimension column, characterized by different selectivity. The two columns must be coupled by a special GC × GC interface. A more detailed overview of the technique can be found in recently published reviews [1,2].

One of the problems facing GC × GC chromatographers is the difficulty with predicting the linear velocities of the carrier gas in the two separation columns, especially when they have different diameters (as is usually the case). If one wants to know the average linear velocity in the second dimension column, this parameter usually has to be determined experimentally. In the authors' laboratory, this is done by trapping a non-retained compound (such as propane) in the modulator, injecting it from the modulator onto the secondary column at a known time, and measuring the time it takes the non-retained compound to reach the detector. Depending on the

modulation system used (e.g. the type of coolant in cryogenic modulators), this approach may be difficult or even impossible to implement. Experimental determination of the average linear velocity in the primary column is even more difficult. As a result, in the majority of cases only the average linear velocity through the system is determined through the total system dead time, though this does not give an accurate picture of the velocities in either of the columns.

This problem is particularly severe for loop-type modulators introduced by Ledford et al. [3], including the liquid nitrogen single cryojet GC × GC modulator developed in our previous work [4]. These modulators use a single jet of cryogen and a loop of deactivated capillary that transports material past the jet two times, thus creating two cold spots for dual-stage modulation in the column train. One of the potential problems associated with the use of such modulators is that for a loop of a given geometry, the linear velocity of the carrier gas within the loop determines the range of modulation periods that can be used. For example, assuming that cooling the trapping capillaries from the oven temperature to the trapping temperature requires 0.5 s, while thermal desorption of the trapped bands requires 1 s, the minimum delay in the loop should be 1.5 s, so that breakthrough of the analyte band injected from the first cold spot to the second cold spot does not occur.

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To be able to choose the length of the delay loop that would accomplish such a delay, one should know the linear velocity of the carrier gas in the loop. In practice, this becomes the minimum length for the loop, and usually somewhat longer loops are used. However, the loop should not be too long either, as with a loop that is too long, it is possible for breakthrough to occur because a band arrives at the second cold spot too late, and the next desorption phase has already started. In this case, the band would pass straight through the second cold spot without being refocused. Similar phenomena may occur when the modulation period is changed without a corresponding change in the length of the delay loop. Additionally, if the loop is too long, multiple injections from the first cold spot could be present within the loop simultaneously, which increases the probability of running into breakthrough problems when modulation period is changed. Even if there are no problems associated with breakthrough, the primary retention times of the compounds would be artificially lengthened. This could pose problems with analyte identification in very complex mixtures. With all these possibilities, it becomes clear that setting up a loop-type modulator could be a challenge.

Presented here is a model for GC × GC systems using a loop modulator that determines the appropriate length for the loop capillary given a set of other initial parameters. Once the length has been found and the geometry of the column set fixed, the model then uses the desired oven-programming rate to determine the correct pressure ramp that should be used for the inlet in order to maintain a constant average linear velocity within the sample loop throughout the run.

2. Experimental

The model was tested by configuring a 6890GC (Agilent Technologies, Mississauga, Canada) with a 30 m × 0.25 mm, 1.0 μm VF-1MS column (Varian, Middelburg, The Netherlands) and a 1.55 m × 0.15 mm, 0.25 μm BP-20 column (SGE, Austin, TX, USA). The trapping capillaries were 12 cm segments of 0.10 mm deactivated fused silica tubing (Polymicro Technologies, Phoenix, AZ, USA). All connections were made using press-fit connectors (Chromatographic Specialties, Brockville, Canada). The model was then used to choose an appropriate length of 0.25 mm diameter tubing (Chromatographic Specialties) with the linear velocity of the carrier gas in the primary column being set to 30 cm/s at the initial oven temperature.

The testing was performed using a mixture of linear alkanes from *n*-pentane through *n*-tridecane in CS_2. Pentane was obtained from Sigma–Aldrich (Oakville, Canada). Hexane and CS_2 were obtained from Fisher Scientific (Toronto, Canada), and the remaining linear alkanes were obtained from PolyScience Corporation (Niles, IL, USA). Detection was performed with a flame ionization detector (FID) system at 100 Hz; the carrier gas was hydrogen. A liquid nitrogen-based, single-jet loop-type cryogenic modulator developed in the laboratory was used [4]. Data processing and modulator control were performed by in-house written software packages. Measurement of the flow rates was performed using an ADM2000 digital flow meter (Agilent Technologies, Mississauga, Canada).

3. Results and discussion

3.1. Theory

When performing a GC × GC separation, knowing flow rates and being able to predict appropriate pressure ramps to achieve the desired flow rate is crucial. In 1D GC systems or in GC × GC systems that use columns of identical diameters, the GC control software can determine the pressure as long as the column geometry is provided. A problem arises when one uses multiple columns of different diameters, as the commercial software might not be able to predict the appropriate pressure ramps. The problem can be somewhat alleviated if one enters an equivalent column dimension into the GC [5]. This will work for maintaining a constant volumetric flow rate of gas within the column set; however, this does not solve the problem of the modulator loop and allow a chromatographer to choose an appropriate length of the loop. To do this, the entire system must be modeled so that the linear velocities in the different segments of the column set are known.

In considering the flow through the column, one can use the Poiseuille equation, which describes the flow of an ideal compressible gas through a tube (Eq. (1) [6]):

$$F = \frac{dV}{dt} = \left(\frac{\pi r^4}{16\eta L} \right) \left(\frac{p_i^2 - p_o^2}{p_o} \right) \tag{1}$$

where $F = dV/dt$ is the volumetric flow rate of the gas, measured at the outlet of the capillary (cm^3/s), r the radius of the capillary (cm), η the viscosity of the carrier gas at the oven temperature (poise), L the length of the tube (cm), and p_i and p_o are the absolute inlet and outlet pressures (dynes/cm^2).

To account for temperature in the equation, one can simply relate the flow to standard conditions by using Eq. (2), which also includes a conversion factor of 60 to convert from ml/s to ml/min, a more standard measure in GC.

$$\frac{dV}{dt} = \left(\frac{60\pi r^4}{16\eta L} \right) \left(\frac{p_i^2 - p_o^2}{p_o} \right) \left(\frac{p_o}{p_{ref}} \right) \left(\frac{T_{ref}}{T} \right) \tag{2}$$

where T is the oven temperature (K), T_{ref} the reference temperature (K), and p_{ref} the reference pressure (dynes/cm^2). Changes in oven temperature will also affect the carrier gas viscosity and to account for this, curves were fit to the viscosity data in Table 1 [7]. The equations relating carrier gas viscosity to temperature for two typical carrier gases (helium and hydrogen) are:

$$\eta_{He} = -2.01786 \times 10^{-10} T^2 + 5.88964 \times 10^{-7} T$$
$$+ 4.13 \times 10^{-5} \tag{3}$$

	Gas viscosity (μPa s)					
	100 K	200 K	300 K	400 K	500 K	600 K
Hydrogen	4.2	6.8	9.0	10.9	12.7	14.4
Helium	9.7	15.3	20.0	24.4	28.4	32.3

$$\eta_{H_2} = -1.08929 \times 10^{-10}\, T^2 + 2.77964 \times 10^{-7}\, T$$
$$+ 1.59 \times 10^{-5} \tag{4}$$

where η is the viscosity (poise) and T the oven temperature (K). These equations allow us to calculate the flow through a capillary at a given temperature, for a given inlet and outlet pressure, adjusted to reference conditions. One other key equation is the equation for the outlet linear velocity, calculated as the outlet volumetric flow rate divided by the cross-sectional area of the column, or Eq. (1) divided by πr^2 [6].

$$u_o = \frac{r^2(p_i^2 - p_o^2)}{16\eta L p_o} \tag{5}$$

The outlet linear velocity of the column is useful, and in principle can be used to calculate the flow rate at any point along the column. However, what is more useful and more easily measured is the average velocity of the carrier gas through the column, calculated by dividing the length of the column by the dead time. As the carrier gas travels along the column, it depressurises, expands, and as a result it accelerates, reaching a maximum as it exits the capillary. The outlet velocity can be easily related to the average velocity by the gas compressibility factor, j [6]:

$$j = \frac{3p_o(p_i^2 - p_o^2)}{2(p_i^3 - p_o^3)} \tag{6}$$

By combining Eqs. (5) and (6), we obtain the equation for the average linear flow rate through a segment of capillary column, given its dimensions, the inlet and outlet pressures, and the viscosity of the carrier gas at the temperature of interest [6]:

$$\bar{u} = \left(\frac{3r^2}{32\eta L}\right)\left(\frac{(p_i^2 - p_o^2)^2}{(p_i^3 - p_o^3)}\right) \tag{7}$$

This equation should, in principle, allow us to calculate the linear velocity in the loop of the modulator (see Fig. 1); once the length of the loop is known, one can calculate the amount of time that it will take for a band to travel from one trapping zone to the other. The challenge comes in determining what the inlet and outlet pressures of the loop will be under the experimental conditions.
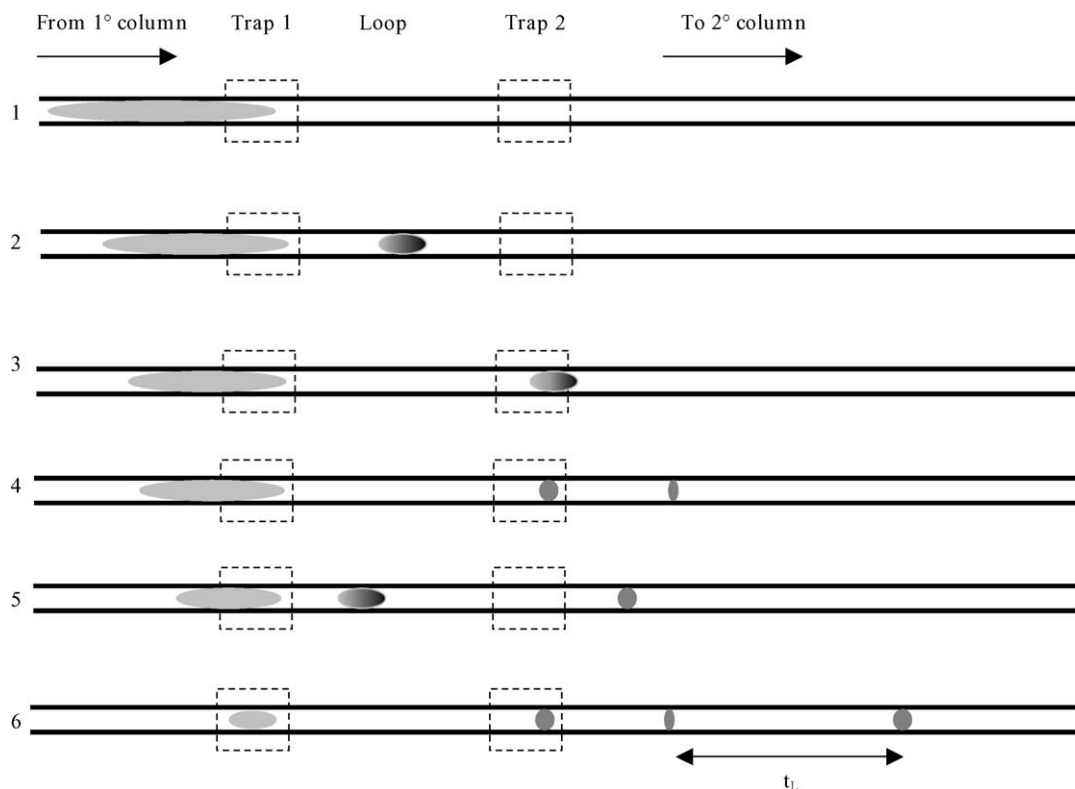

Fig. 1. Experiment with a loop that is intentionally made too short, allowing the measurement of the time that it takes a band to travel through the loop (t_L). (1) A band enters the first trap from the primary column, and a fraction is then injected to the loop (2). This fraction reaches the second trap as it is cooling down and a small portion breaks through to the secondary column (3 and 4). Upon the following modulation cycle (5) a fraction is released from each trap simultaneously; however, the loop is too short and a small portion from the first trap breaks through as before.

The approach that was taken to solve this problem was to choose dimensions for the primary and secondary columns, the trapping capillaries, and the diameter of the delay loop, and then set up a series of equations in Mathcad (Mathsoft, Cambridge, MA, USA). To perform the calculations, Mathcad requires that initial guesses are made as to the flow through the system under standard conditions and the length of the delay loop. Then, knowing the type of the carrier gas, the oven temperature, and the outlet pressure of the system (either atmospheric pressure or vacuum outlet conditions, depending on the detector), the inlet pressures of each column segment can be calculated, starting with the second dimension column. The following equation, which is a rearrangement of Eq. (2), can be used for this purpose:

$$p_i = \sqrt{F\left(\frac{T}{T_{ref}}\right)\left(\frac{16\eta L}{60\pi r^4}\right)p_{ref} + p_o^2} \qquad (8)$$

This equation makes it possible to calculate the pressure at the inlet of the secondary column required to achieve the specified flow rate, F, at the outlet of this column. Knowing that the volumetric flow rate as measured under standard conditions must be the same through the entire column train, it is obvious that the inlet pressure of the second dimension column is simultaneously the outlet pressure of the second trapping capillary. This then makes it possible to calculate the inlet pressure of the second trapping capillary, and so forth.

A series of equations was set up in Mathcad to perform this task and calculate the pressure at the inlet of the primary column at the starting temperature of the GC oven program. Then, a desired initial average velocity for the primary column and a desired dead time for the loop capillary were specified, and Mathcad solved the series of equations, adjusting the flow rate and the length of the loop to satisfy the boundary conditions.

Once the length of the loop at the initial oven temperature were determined and the geometry of the system became fixed, Mathcad was then used to solve this same set of equations to find the inlet pressure for the system as a function of time that would keep the linear velocity in the loop constant, given the oven temperature program. Though strictly speaking these equations are valid only for systems at a steady state and not for systems where there are dynamic changes in temperature and pressure, within the context of a GC × GC experiment, these equations can be used as typical pressure ramps and temperature ramps (on the order of 0.2 psi/min and 3–5 °C/min) are so slow that the system behaves almost as if it were at steady state.

3.2. Testing of the model

The initial test of the flow model was performed by using a simplified version that only modeled a single dimension column under vacuum and atmospheric outlet conditions for various oven temperatures and flow rates, and for helium and hydrogen carrier gas. Other carrier gases were not included in the model as they are not commonly used in GC × GC, though they could be added easily if one desired. The results from these predictions were compared with the results from the HP Flow Calculator software, available from the Agilent website [8]. This software uses standard gas flow equations implemented in a user-friendly way. Some results comparing the 1D model to the Flow Calculator results are shown in Table 2. It should be noted that in developing the model, numerous discrepancies were found. This turned out to be due to subtle errors in the viscosity data table in reference [6]. When this data was replaced with data taken directly from reference [7], the model agreed much more closely with the HP Flow Calculator software. The slight differences in the values for hydrogen as a carrier gas can most likely be attributed to slight differences in the viscosity data that were used with the two models.

In order to test the complete flow model, it was used to size a 0.25 mm I.D. delay loop for a system with a 30 m × 0.25 mm I.D. primary column, two 0.12 m × 0.10 mm trapping capillaries, and a 1.55 m × 0.15 mm secondary column. The model suggested using a 1.10 m long segment of capillary in order to have an average linear velocity in the primary column of 30 cm/s and a dead time in the loop of 2.5 s at 35 °C.

The model then predicted that a pressure ramp of 14.64–17.85 psi at 0.08 psi/min and then to 20.90 psi at 0.07 psi/min would maintain the average linear velocity in

Table 2
Comparison of 1D model with HP Flow Calculator software for various input parameters; p_o is the outlet pressure, F is outlet flow rate

Input parameters						Calculated inlet pressure (psi)		Calculated average linear velocity (cm/s)	
Carrier	T (°C)	L (m)	d (mm)	p_o (atm)	F (mL/min)	Model	Flow Calculator	Model	Flow Calculator
Helium	50	30	0.25	1	1.5	16.5	16.4	33.9	34.0
Helium	50	30	0.25	0	1.5	12.9	12.7	44.1	44.4
Helium	200	15	0.18	1	1	30.2	30.0	47.2	47.3
Helium	200	15	0.18	0	1	27.8	27.5	54.0	54.1
Hydrogen	100	10	0.10	1	1	48.5	50.7	88.7	85.7
Hydrogen	100	10	0.10	0	1	46.8	49.1	95.1	91.7
Hydrogen	300	60	0.25	1	1.5	30.0	31.4	44.6	43.4
Hydrogen	300	60	0.25	0	1.5	27.6	29.0	51.0	49.4

Table 3
Predicted and measured flow rates and dead times for a GC × GC column set at different temperatures

Temperature (°C)	Inlet pressure (psi)	Outlet flow (mL/min)		System dead time (s)	
		Predicted	Measured	Predicted	Measured
35	14.63	1.8	1.9	89	87
100	16.76	1.5	1.7	91	87
150	18.31	1.4	1.6	92	86
240	20.90	1.2	1.4	93	87

the loop at the same value throughout the analysis, so that the timing of the jet and the length of the loop would always work properly together for an oven programming rate of 35–240 °C at 2.5 °C/min. The two linear programming rates for the pressure were used to approximate the actual second-order pressure ramp equation as best possible within the limitations of the pressure control on the 6890GC.

Table 3 shows the pressures that were predicted at different temperatures along with the predicted and measured flow rates and dead times for the system. When conducting the experiments, only the predicted pressures were recorded for each temperature before making any measurements, and the flow rates and dead times were recorded with no knowledge of the predicted values to avoid any bias in the measurements. As can be seen, the numbers were in good agreement, with the minor discrepancies being easily attributed to minor differences between nominal lengths and diameters of column segments and their actual dimensions, and any influences from the press-fit unions used to join column segments which were not accounted for in the models.

A further example of how well the model worked can be seen in the results for an experiment where the delay loop was intentionally made too short. This experiment was designed such that when an injection band was launched from the first trapping stage, a small portion of it would break through the second stage. In that way, the amount of time that it took to travel through the delay loop could be easily measured, as illustrated in Fig. 1. For this experiment, the instrument was configured with a 30 m × 0.25 mm I.D. primary column, two 0.12 m × 0.10 mm trapping capillaries, and a 1.6 m × 0.15 mm secondary column. The model suggested using a 0.88 m long segment of 0.25 mm I.D. capillary in order to have an average linear velocity in the primary column of 35 cm/s and a dead time in the loop of 2.0 s.

The results from this experiment (Fig. 2) show that two peaks were formed in each modulation cycle, one from each trap. The difference in the retention times for the pairs of peaks shown in the figure represents the amount of time that it takes to travel through the loop. The results for all of the alkane peaks are summarised in Table 4. The difference between the retention times for all of the pairs of peaks generated in this way was 2.0 s, showing that the linear velocity in the loop was in fact constant throughout the entire analysis.
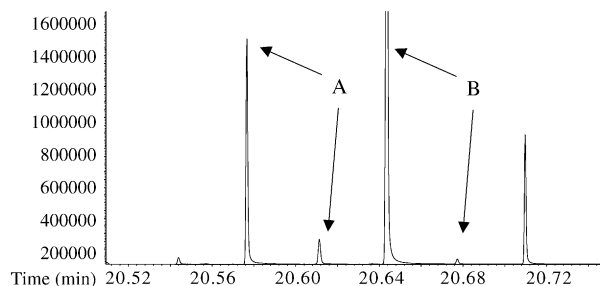

Fig. 2. Results from the experiment depicted in Fig. 1. The difference in the retention times of the pairs of peaks marked A and B indicates the amount of time it takes to travel the loop, in this case both were 2.0 s.

Table 4
Differences between the retention times of the original peaks and the breakthrough peaks, equivalent to the time it takes to travel the delay loop

Compound	t_L (s)
Pentane	1.92
Hexane	2.04
Heptane	2.10
Octane	2.07
Nonane	2.02
Decane	2.10
Undecane	2.01
Dodecane	2.04
Tridecane	2.04
Average	2.04

4. Conclusions

A model has been developed that allows the prediction of pressure programming ramps that can be used for generating specific flow rates within a GC × GC column train (or a column train used for other purposes). The model is able to predict the length of the delay loop for use in GC × GC experiments with loop-type modulators, such that the loop, modulation period and linear velocity of the carrier gas are all in accordance with each other for successful operation of the system.

As the model is designed and written in Mathcad, it is very flexible and can be quickly and easily modified by users with even a rudimentary knowledge of the software package to model the carrier gas flow rates in other systems, for example GC × GC systems without a loop-type modulator. It can also be modified for other purposes; for example, conditions can be determined for which the average linear velocity in the second-dimension column remains constant throughout the analysis. When fixed geometry GC × GC systems with loop-type modulator are used (i.e. the user does not want to change the delay loop), it can be determined which modulation periods and flow rates will work correctly.

Though the model has not yet been tested under vacuum outlet conditions or with helium carrier gas, there are no reasons to believe that it will not function equally well under these conditions, considering that the results produced by

the model for these scenarios agreed well with the HP Flow Calculator software when modeling 1D systems and in regular use in the laboratory the observed secondary retention times for primary column bleed agreed with the predicted secondary dead times from the model.

A tool such as this should help remove some of the guesswork from setting up a GC × GC column set, and can also be used to help diagnose problems in system performance, as it has the ability to predict linear velocities in each segment of capillary column in the column train. Interested readers may request a copy of the Mathcad worksheet from the authors.

Acknowledgements

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