Experiment 1

Determination of the Optimum Flow Rate and Van Deemter Parameters (A, B, and C) of a Capillary GC Column

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Background:

The chromatographic peak broadening is related to the kinetics and thermodynamics associated with the separation process. The peak broadening is attributed to the efficiency of the chromatographic system. Column efficiency is expressed as the number of theoretical plates N or as the height equivalent of a theoretical plate, H. H = L/N, where L is the length of the column. N can be estimated from the characteristics of the shape of the eluting chromatographic peak. If all other system parameters are held constant for a series of runs, except the carrier gas flow rate F it can be shown that H is related to the flow rate F (analogously to u) by the Van Deemter Equation.

$$H = A + \frac{B}{F} + CF$$

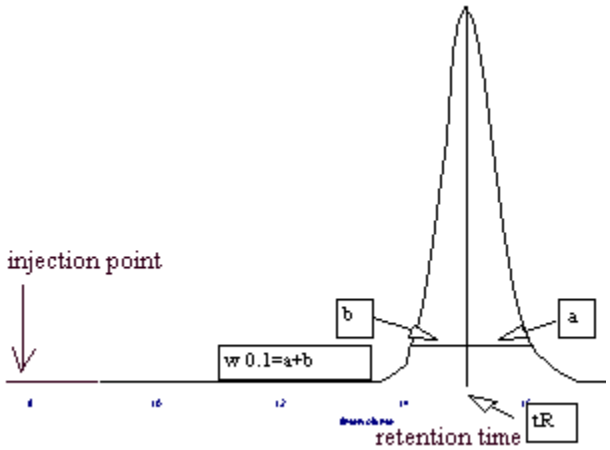
The constants A, B and C determine the efficiency variation of the column with flow rate. For the most general shape of the eluting peaks which are asymmetric efficiency N is calculable from (note the definitions of symbols on the figure) for both symmetric and asymmetric peaks as shown below.

For asymmetric peaks;

$$N = \frac{41.7(t/w_{0.1})}{(a/b + 1.25)}$$

For symmetric peaks;

$$N = \frac{5.55 t_r^2}{w_{1/2}^2}$$



The width at 10% height, $w_{0.10}$, of the peak from the base is used in the above equation for asymmetric peaks. Plot of H vs. F has a minimum in H at which point the flow rate is the optimum flow rate.

$$H = \frac{L}{N} = A + \frac{B}{F} + CF$$

$$F_{min} = \sqrt{\frac{B}{C}}$$

Apparatus:	Gas chromatograph, column - 30-m x 0.32mm capillary with 0.25 □m coating of poly(14% cyanopropylphenyl/86% dimethyl) siloxane (Supelco Equity 1701).
Chemicals:	Test sample – 50 uL Propiophenone in 50mL of methanol.

Procedure:

Familiarize with the operating instructions for the capillary column gas chromatograph. GC settings; He carrier gas inlet pressure 25 psi.; column temperature about 90^{o}C (~10^{o}C below the boiling point analyte), injector temperature 225^{o}C, detector temperature 225^{o}, split ratio 10:1, injection volume of 1uL. GC column length = 30m.

Generate the chromatograms for mobile flow rates from 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 12.0mL/min. for the isothermal runs. (Typical Run times for flow rates 1, 2, 4, 6, 8+ mL/min are 14, 8, 5, 4 and 3 min respectively.)

Export all peak data as an Excel files (.csv). Use Fityk to determine peak position and FWHM of each (Gaussian) peak if the peaks are symmetrical or (Split Gaussian) nearly symmetrical. If peak(s) is highly asymmetrical manually find the parameters a and b from the data in Excel spreadsheets. Perform calculations of H (see data treatment section) on a spreadsheet starting from the calculation of N (use the equation appropriate for the GC peaks generated, i.e. symmetric or asymmetric) for each flow rate F.

Record all GC parameters (column and operational) such as temperature(s) of the oven, detector and injector; *column length*, internal diameter, phases and pressures.

Data: Suggested Spreadsheet Format for fitting of the Van Deemter Plot:

Retention time, t_r (sec)	a (sec)	b (sec)	$w_{0.10}$ (sec)	$w_{1/2}$(sec)	N	U (cm/sec)	F (ml/sec)	H(mm)

Data Treatment and Analysis:

1. Calculate the number of theoretical plates for each chromatogram using the appropriate relationship between elution time, peak width data etc.
2. Using the column length, calculate the HETP at each flow rate.
3. Note the flow rate (F) in milliliters per minute for each setting of the flow rate control.
4. Construct the van Deemter plot (plot of H vs F) as the experiment is conducted, so that a sufficient number of well spaced points can be obtained.
5. Estimate the Van Deemter equation constants by regression analysis. (use Excel Solver)
6. Plot the experimental data points (as in 4) and overlay the best fit curve.
7. Report A, B, C and the optimum flow rate for the system.
8. Calculate the optimum flow rate (F_{opt}) and the HETP at that flow rate (H_{min}).