Credit Hour System Health Engineering Management Program

Analytical & Lab Instruments (HEMN216) Exercise Sheet (3)

4. Boron gives a series of fluctuation bands due to the radical BO₂ that lie in the green portion of the spectrum of a FAES. Although the overlapping band systems present a problem in the measurement of the flame background, the minimum between adjacent band heads can be used. The results obtained are given in Table 1.

Table 1

Boron	Emission reading		
present (µg/mL)	518-nm peak	505-nm minimum	
0	36	33	
50	44	36	
100	52	39	
150	60.5	42.5	
200	68.5	45.5	

What are the concentrations of boron of the unknowns given in Table 2?

Table 2

Sample	518-nm peak	505-nm minimum
A	45	36.5
В	85	65
С	66	50

<u>Hint:</u> Use linear regression to construct a calibration model, assuming that the effective emission reading is the average of both readings.

- 5. A calibration curve for strontium, taken at 460.7 nm, was obtained in the presence of $1000 \mu g/mL$ of calcium as CaO and also in the absence of added calcium. These results are shown in Table 3.
 - a) Graph the calibration on a rectilinear graph paper and also on log-log paper.
 - b) What might be the cause of the upward curvature in the region of low concentrations on the rectilinear graph when calcium is absent?
 - c) Why does the addition of calcium straighten the calibration curve and increase the net emission reading for strontium?

Table 3

Strontium present (µg/mL)	Emission reading		
	No calcium Calcium adde		
0	0	13	
0.25	2	18.5	
0.5	6	24	
1.0	16	36	

2:5	44	70
5.0	94	125
7.5	150	181
10.0	200	238

- 6. To illustrate the effect of aqueous-organic solvents on droplet size coming out of a nebulizer, calculate the mean droplet diameter for
 - a) water
 - b) 50% methanol water
 - c) 40% glycerol -water.

Pertinent data follow.

System	Surface tension (dyne/cm)	Viscosity (dyne·s/cm²)	Density (g/cm³)	Velocity of aspirating gas (m/sec)	Qair/Qliquid
Glycerol, 40%	68.6	0.039	1.102	279	2540
Methanol, 50%	30.6	0.027	0.946	198	9540
Water	73	0.010	1.00	198	6400

The Sauter mean aerosol droplet diameter, d (in meters) is given by:

$$\sqrt{d} = \frac{585}{v} \left(\frac{\gamma}{\rho}\right)^{0.5} + 597 \left(\frac{\eta}{\sqrt{\gamma \rho}}\right)^{0.45} \left(\frac{Q_l}{Q_g}\right)^{1.5}$$

v = velocity difference between gas and liquid (m/s)

 γ = surface tension (N/m)

 ρ = liquid density (kg/m³)

 $\eta = \text{liquid viscosity (Pa·s)}$

 Q_l = liquid volume flow rate (m³/s)

 $Q_g = \text{gas volume flow rate (m}^3/\text{s})$

Neglect the velocity of the liquid in the nebulizer.

- 7. For (a) water and (b) 50% (v/v) methanol-water, plot the droplet diameters for solution flowrates ranging from 0.1 to 5 mL/min. As values for a typical nebulizer, assume the velocity of the aspirating gas to be 333 m/sec and Q_{gas} to be 8.5 liter/min. Other data are given in Problem 6.
- 8. In an atomic emission/ absorption flame photometer, the flame and aspirator have to be calibrated with lithium. The calibration circuit in Fig. 2 is adjusted, such that the voltage V_{OUT} is zero when a known concentration of Li is aspirated into the flame. In this case the lithium causes a photodetector output of +2 V. Calculate the fraction α needed to make $V_{OUT} = 0$, where the resistance of the potentiometer from the wiper arm down is $\alpha \cdot R_{OUT}$.

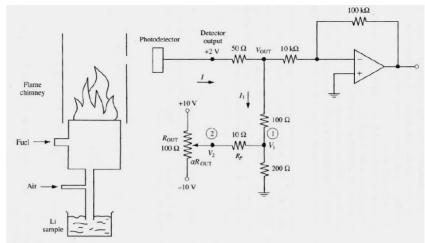


Fig. 2

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Analytical & Lab Instruments (HEMN216) Exercise Sheet (3) - Solved

4. We have to calculate the average emission reading between peak and minimum before applying linear regression analysis. Thus we should have:

Boron present (µg/mL)	Average emission reading
0	34.5
50	40
100	45.5
150	51.5
200	57

Also, the average readings for the unknown sample concentrations are given by:

Sample	Average emission reading		
A	40.75		
В	75		
С	58		

Now, for a given set of n data points (x_i, y_i) the linear regression model is given by:

$$y = mx + b$$

Where m & b can be calculated from

$$\begin{bmatrix} s_o & s_1 \\ s_1 & s_2 \end{bmatrix} \begin{bmatrix} b \\ m \end{bmatrix} = \begin{bmatrix} t_o \\ t_1 \end{bmatrix}$$

$$\therefore \begin{bmatrix} b \\ m \end{bmatrix} = \begin{bmatrix} s_o & s_1 \\ s_1 & s_2 \end{bmatrix}^{-1} \begin{bmatrix} t_o \\ t_1 \end{bmatrix}$$

$$s_o = n,$$
 $s_1 = \sum_{i=1}^n x_i,$ $s_2 = \sum_{i=1}^n x_i^2,$ $t_o = \sum_{i=1}^n y_i,$ $t_1 = \sum_{i=1}^n x_i y_i$

Now $s_0 = n = 5$

$$s_1 = 0 + 50 + 100 + 150 + 200 = 500$$

$$s_2 = 0 + 2500 + 10000 + 22500 + 40000 = 75000$$

$$t_0 = 34.5 + 40 + 45.5 + 51.5 + 57 = 228.5$$

$$t_1 = 0 \times 34.5 + 50 \times 40 + 100 \times 45.5 + 150 \times 51.5 + 200 \times 57 = 25675$$

Thus, the regression model is given by:

$$y = 0.113x + 34.4$$

For sample A:
$$y = 40.75$$

$$\therefore 40.75 = 0.113x + 34.4$$

$$\therefore 0.113x = 40.75 - 34.4 = 6.35$$

$$\therefore x = \frac{6.35}{0.113} = 56.2 \,\mu\text{g/mL}$$

For sample B: y = 75

$$\therefore 75 = 0.113x + 34.4$$

$$\therefore 0.113x = 75 - 34.4 = 40.6$$

$$\therefore x = \frac{40.6}{0.113} = 359.3 \,\mu\text{g/mL}$$

For sample C: y = 58

$$\therefore 58 = 0.163x + 35.9$$

$$\therefore 0.163x = 58 - 35.9 = 22.1$$

$$\therefore x = \frac{22.1}{0.113} = 195.6 \,\mu\text{g/mL}$$

5.a) The plots are shown in Fig. 1.(a) & (b)

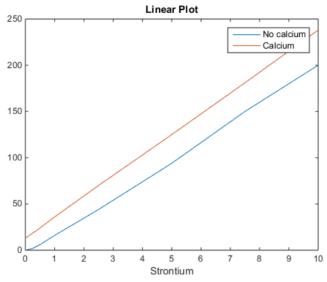
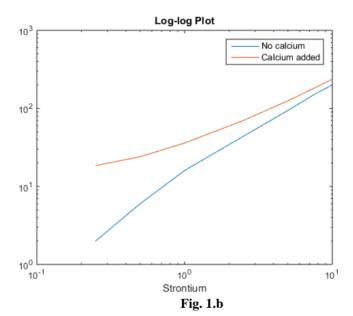


Fig. 1.a



- b) The upward curvature in the region of low concentrations on the rectilinear graph when calcium is absent is possibly because of low sensitivity of the atomic emission system to strontium.
- c) The addition of calcium straighten the calibration curve because more divalent atoms are introduced to the atomic emission system. (Ca and Sr are both divalent).

6. After converting the data to the SI unit system the table becomes

System	Surface tension	Viscosity	Density	Velocity	Q_{l}/Q_{g}
	(N/m^2)	(Pa·s)	(kg/m^3)	(m /s)	
Glycerol	0.0686	0.0039	1102	279	0.0003937
Methanol	0.0306	0.0027	946	198	0.00010482

We then compute the diameter from:

$$\sqrt{d} = \frac{585}{v} \left(\frac{\gamma}{\rho}\right)^{0.5} + 597 \left(\frac{\eta}{\sqrt{\gamma \rho}}\right)^{0.45} \left(\frac{Q_l}{Q_g}\right)^{1.5}$$

For glycerol:

$$\sqrt{d} = \frac{585}{279} \left(\frac{0.0686}{1102} \right)^{0.5} + 597 \left(\frac{0.0039}{\sqrt{0.0686 \times 1102}} \right)^{0.45} \left(3.937 \times 10^{-4} \right)^{1.5} = 0.01669 \,\mathrm{m}^{0.5}$$

$$\therefore d = 2.7851 \times 10^{-4} \,\mathrm{m} = 278.5 \,\mu\mathrm{m}$$

For methanol:

$$\sqrt{d} = \frac{585}{198} \left(\frac{0.0306}{946}\right)^{0.5} + 597 \left(\frac{0.0027}{\sqrt{0.0306 \times 946}}\right)^{0.45} \left(1.0482 \times 10^{-4}\right)^{1.5} = 0.016825 \text{m}^{0.5}$$

$$\therefore d = 2.8307 \times 10^{-4} \text{ m} = 283.07 \,\mu\text{m}$$

For water:

$$\sqrt{d} = \frac{585}{198} \left(\frac{0.073}{1000}\right)^{0.5} + 597 \left(\frac{0.001}{\sqrt{0.073 \times 1000}}\right)^{0.45} \left(1.5625 \times 10^{-4}\right)^{1.5} = 0.025263 \text{m}^{0.5}$$

$$\therefore d = 6.3824 \times 10^{-4} \text{ m} = 638.24 \,\mu\text{m}$$

7. The diameter is given by:

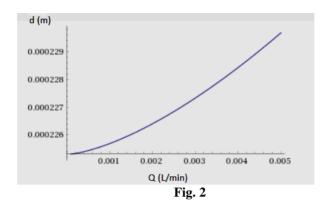
$$\sqrt{d} = \frac{585}{v} \left(\frac{\gamma}{\rho}\right)^{0.5} + 597 \left(\frac{\eta}{\sqrt{\gamma \rho}}\right)^{0.45} \left(\frac{Q_l}{Q_g}\right)^{1.5} = \frac{585}{333} \left(\frac{\gamma}{\rho}\right)^{0.5} + 597 \left(\frac{\eta}{\sqrt{\gamma \rho}}\right)^{0.45} \left(\frac{Q_l}{8.5}\right)^{1.5}$$
$$= 1.5768 \left(\frac{\gamma}{\rho}\right)^{0.5} + 24.09 \left(\frac{\eta}{\sqrt{\gamma \rho}}\right)^{0.45} Q_l^{1.5}$$

Where Q_l is measured in L/min.

a) For water:

$$\sqrt{d} = 1.7568 \left(\frac{0.073}{1000} \right)^{0.5} + 24.09 \left(\frac{0.001}{\sqrt{0.073 \times 1000}} \right)^{0.45} Q_l^{1.5}$$
$$= 0.01501 + 0.40982 Q_l^{1.5}$$

The plot is shown in Fig. 2.



For methanol: b)

$$\sqrt{d} = 1.7568 \left(\frac{0.0306}{946} \right)^{0.5} + 24.09 \left(\frac{0.0027}{\sqrt{0.0306 \times 946}} \right)^{0.45} Q_l^{1.5}$$
$$= 0.009992 + 0.78902 Q_l^{1.5}$$

The plot is shown in Fig. 3.

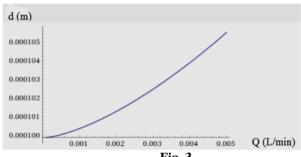


Fig. 3

8. Since V_{OUT} must be zero, we can calculate I = 2/50 A = 0.04 A. Because $V_{OUT} = 0$, the current through the 10-k Ω resistor is zero, so $I_1 = I = 0.04$ A. The voltage $V_1 = -I(100) = -4 \text{ V}$.

Then Kirchhoff's current law (KCL) at node (2) gives

$$\frac{V_2 - (-4)}{10} + \frac{V_2 - (-10)}{\alpha (100)} + \frac{V_2 - 10}{(1 - \alpha)(100)} = 0$$
 (1)

and KCL at node (1) gives

$$\frac{-4 - V_2}{10} + (-0.04) + \frac{-4}{200} = 0 \tag{2}$$

Solving Eqn (2) for V_2 gives $V_2 = -4.6$ V. Substituting this value in Eqn (1) gives

$$\frac{-4.6+4}{10} + \frac{-4.6+10}{100\alpha} + \frac{-4.6-10}{100(1-\alpha)} = 0$$
 (3)

Solving Eqn (3) for α we have

$$0.06 \alpha^2 - 0.260 \alpha + 0.054 = 0$$

$$\alpha = \frac{+0.260 \pm \sqrt{0.260^2 - 4(0.06)(0.054)}}{2(0.06)} = \frac{0.260 \pm 0.233752}{0.12}$$

 $\alpha = 0.2187$ or 4.1146

Since the root 4.1146 is greater than 1, it cannot be the correct value, so $\alpha = 0.2187$.

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Analytical & Lab Instruments (HEMN216) Exercise Sheet (4)

- 1. Consider HPLC. The time between sample introduction into the column and component elution is the retention time of the component and is symbolized t_r . The adjusted retention time, t_r' takes into account the time required for a non-retained solute to pass from injector to detector with no interactions. Let t_m be the time required for the un-retained solute to reach the detector.
 - a) Show that $t_r' = t_r t_m$
 - b) A circular cross-section column has a height h and an inner diameter D. Assuming that no retention takes place inside the column and that the mobile phase flows through the column only by means of gravity (starting from rest at the top of the column) derive an expression for t_m .
- 2. Under a given set of experimental conditions, an individual component has a characteristic capacity factor, k defined by

$$k = \frac{t_r'}{t_m}$$

The partition coefficient, K, of the solute (S) between the mobile and stationary phases is given by

$$K = \frac{[S]_{stationary}}{[S]_{mobile}}$$

Where $[\cdot]$ designates concentration.

a) If the relative volumes of stationary and mobile phases at equilibrium are given by V_s and V_m , respectively, show that

$$k = K \frac{V_s}{V_m}$$

b) Show that the relative retention of two components, α , may be expressed as

$$\alpha = \frac{t_{r2}'}{t_{r1}'} = \frac{k_2}{k_1} = \frac{K_2}{K_1}$$

- 3. A mixture consisting of two main protein components was subjected to chromatography, with pH 7.1, 0.05 M phosphate as the mobile phase and Sephadex G-100 as the stationary phase. An un-retained species, blue dextran, eluted in 2.6 min, while proteins X and Y eluted at times of 6.7 and 9.1 min, respectively.
 - a) Calculate the relative retention, α , of the two protein components.

- b) Which protein has a higher molecular weight?
- 4. A gel-filtration column prepared using Bio-Gel P-100 had a void volume of 5.0 mL and a stationary-phase volume of 50.0 mL. The column was calibrated using six proteins of known molecular weight, by measuring the elution volume of each peak (Table 1). An unknown protein was then applied to the column, and its elution volume was measured. Given the data in Table 1, determine the molecular weight of the unknown protein.

Hint: The elution volume, V_e is related to the void (mobile phase) volume, V_o and the gel (stationary phase) volume, V_g by the equation

$$V_e = V_o + K_{av}V_g$$

Protein

Aconitase

Unknown

Transferrin

 K_{av} , in turn, is related to the molecular weight, MW by means of

$$\ln \frac{K_{av}}{1 - K_{av}} = A - B \cdot \log(MW)$$

Table 1 MW (kDa) Elution Volume (mL) Cytochrome c 42.9 11.7 37.8 Myoglobin 17.2 23.5 Ig light chain 33.9 Ovalbumin 43.0 26.1

20.4 18.3

31.2

5.a) Use dimensional analysis to determine the SI physical units of the electrophoretic mobility.

66.0

77.0

?

The volume, V of a certain organic compound (measured in nm³) is related to its b) molecular weight, MW (in Daltons) by

$$V = (1.212 \times 10^{-3}) (MW)$$

Calculate the radius of an insulin molecule (MW = 5730 Dalton) assuming a spherical radius.

- For a certain capillary electrophoretic analysis the applied voltage is 25 kV, the c) capillary length is 50 cm, and the dynamic viscosity of the buffer is twice as much as water. Calculate the migration velocity of an insulin molecule, assuming that it has typically five positive charges.
- Calculate the migration time for the same molecule. d)
- 6. An experiment was performed using an open 50-mm diameter silica capillary, 50 cm long. A 5-mM carbonate buffer at pH 10 was used, with a separation voltage of 25 kV, following a 15 s, 1-kV electro-kinetic injection of an FITCderivatized amino acid mixture. Detection using laser-induced fluorescence showed that the mixture contained three main components, with elution times of 4.5, 6.3, and 10.2 min. How would these elution times be expected to change if
 - (a) The length of the capillary was increased to 1 m
 - (b) the separation voltage was increased to 50 kV
 - (c) a length of 1 m and a voltage of 50 kV were used?

Analytical & Lab Instruments (HEMN216) Exercise Sheet (4) - Solution

1.a) If the component passes un-retained, then $t_r = t_m$. In that case the relative retention time is given by $t_r' = 0$.

But if there is some retention, then $t_r > t_m$. Thus, t_r' would become

$$t_r' = t_r - t_m$$

$$t_m = \frac{h}{v_{av}}$$

where v_{av} is the average velocity of the mobile phase particles through the column.

Now the sample injected into the top of the column moves with the mobile phase from rest ($v_0 = 0$). Thus

$$v = v_o + gt = gt$$

$$\therefore v_{av} = \frac{1}{t_m} \int_0^t gt \cdot dt = \frac{g}{t_m} \int_0^t t \cdot dt = \frac{g}{t_m} \cdot \frac{t_m^2}{2} = \frac{gt_m}{2}$$

$$\therefore t_m = \frac{h}{gt_m} = \frac{2h}{gt_m}$$

$$\therefore t_m^2 = \frac{2h}{g} \Rightarrow t_m = \sqrt{\frac{2h}{g}}$$

2.a)Consider

$$K\frac{V_s}{V_m} = \frac{[S]_{stationary}}{[S]_{mobile}} \cdot \frac{V_s}{V_m} = \frac{M_s}{M_m}$$

Now, M_s is the mass partitioned in the stationary phase due to retention, and M_m is the mass partitioned in the mobile phase (i.e., the un-retained mass).

We can assume a linear relationship between the residence time in a compartment (stationary or mobile) and the partitioned mass, because the interaction processes are remarkably slow.

Thus,
$$M_m = c \cdot t_m$$
, $M_s = c \cdot t_r$

Where c is a proportionality constant.

3.a)
$$t_m = 2.6 \text{ min}, t_{r1} = 6.7 \text{ min}, t_{r2} = 9.1 \text{ min}$$

$$t_{r_1}' = t_{r_1} - t_m = 6.7 - 2.6 = 4.1 \text{ min}$$

 $t_{r_2}' = t_{r_2} - t_m = 9.1 - 2.6 = 6.5 \text{ min}$

$$\therefore \alpha = \frac{t_{r_2}'}{t_{r_1}'} = \frac{6.5}{4.1} = 1.585$$

b) Since low molecular weight species elute slower than high molecular weight species, we conclude that protein X has the larger molecular weight.

4.
$$V_e = V_o + K_{av}V_g$$
But $V_o = 5$ mL, $V_g = 50$ mL
$$\therefore V_e = 5 + 50K_{av}$$

$$\therefore K_{av} = \frac{V_e - 5}{50}$$
Let $R = \ln \frac{K_{av}}{1 - K_{av}}$

We construct the following table (Table 1), excluding the unknown

Table 1

MW (kDa)	$V_e (mL)$	K_{av}	R
11.7	42.9	0.758	1.141746
17.2	37.8	0.656	0.645519
23.5	33.9	0.578	0.314569
43	26.1	0.422	-0.314569
66	20.4	0.308	-0.809486
77	18.3	0.266	-1.015013

Now R = A - B(MW)

We then solve for A & B by linear regression

A & B can be calculated from

$$\begin{bmatrix} s_o & s_1 \\ s_1 & s_2 \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} t_o \\ t_1 \end{bmatrix}$$

$$\therefore \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} s_o & s_1 \\ s_1 & s_2 \end{bmatrix}^{-1} \begin{bmatrix} t_o \\ t_1 \end{bmatrix}$$

$$s_o = n, \qquad s_1 = \sum_{i=1}^n x_i, \qquad s_2 = \sum_{i=1}^n x_i^2, \qquad t_o = \sum_{i=1}^n y_i, \qquad t_1 = \sum_{i=1}^n x_i y_i$$

Where in that case $x_i = MW_i \& y_i = R_i$

Now
$$s_o = n = 6$$

 $s_1 = 11.7 + 17.2 + 23.5 + 43.0 + 66.0 + 77.0 = 238.4$
 $s_2 = 136.9 + 295.8 + 552.3 + 1849 + 4356 + 5929 = 13119$

$$\therefore \begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 6 & 238.4 \\ 238.4 & 13119 \end{bmatrix}^{-1} \begin{bmatrix} t_o \\ t_1 \end{bmatrix} = \begin{bmatrix} 0.599604 & -0.010897 \\ -0.010897 & 0.000274 \end{bmatrix} \begin{bmatrix} t_o \\ t_1 \end{bmatrix}$$

$$t_o = 1.1417 + 0.6455 + 0.3146 - 0.3146 - 0.8095 - 1.0150 = -0.0372$$

 $t_1 = 11.7 \times 1.1417 + 17.2 \times 0.6455 + 23.5 \times 0.3146 - 43 \times 0.3146 - 66 \times 0.8095 - 77 \times 1.0150 = -113.25$

Thus, the regression model is given by:

$$R = -0.0307 \cdot MW + 1.2117$$

Now that the elution volume of the unknown, $V_e = 31.2 \text{ mL}$

$$\therefore K_{av} = \frac{31.2 - 5}{50} = 0.524$$

Thus,
$$R = \ln \frac{0.524}{1 - 0.524} = 0.09607$$

Substituting, we obtain

$$0.09607 = -0.0307 \cdot MW + 1.2117$$

$$\therefore MW = \frac{1.2117 - 0.09607}{0.0307} = 36.34 \text{ kDa}$$

5.a)
$$[\mu] = \frac{[v]}{[E]} = \frac{LT^{-1}}{[V] \cdot L^{-1}} = \frac{L^2T^{-1}}{[V]} = \frac{L^2T^{-1}}{[W] \cdot Q^{-1}} = \frac{L^2T^{-1}}{[F] \cdot L \cdot Q^{-1}} = \frac{LT^{-1}}{[F] \cdot Q^{-1}} = \frac{LT^{-1}}{MLT^{-2} \cdot Q^{-1}} = M^{-1}TQ$$

Where the derived SI units are bracketed and given by: v = velocity, E = electric field, V = voltage, W = energy, F = force

The fundamental (unbracketed) SI units are given by:

$$M = \text{mass}, \quad L = \text{length}, \quad T = \text{time}, \quad Q = \text{charge}$$

Thus, μ is measured in Coul·sec/kg

b)
$$V = (1.212 \times 10^{-3})(MW) = (1.212 \times 10^{-3})(5730) = 6.945 \text{ nm}^3$$

But for a spherical model: $V = \frac{4}{3}\pi r^3$

$$\therefore r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3 \times 6.945}{4\pi}} = 1.1836 \text{ nm}$$

c)
$$v = \frac{E \cdot z}{6\pi \eta r}$$
But $E = \frac{V}{L} = \frac{25 \times 10^3}{0.5} = 50 \times 10^3 \text{ V/m}$

$$z = 5q = 5 \times 1.6 \times 10^{-19} = 8 \times 10^{-19} \text{ C}$$

$$\eta = 2 \times 0.001 = 0.002 \text{ Pa} \cdot \text{s}$$

$$r = 1.1836 \times 10^{-9} \text{ m}$$

$$\therefore v = \frac{50 \times 10^{3} (8 \times 10^{-19})}{6\pi (0.002) (1.1836 \times 10^{-9})} = 8.9645 \times 10^{-4} \text{ m/s} = 0.89645 \text{mm/s}$$

d)
$$t_m = \frac{L}{v} = \frac{0.5}{8.9645 \times 10^{-4}} = 557.5 \text{ sec} = 9.29 \text{ min}$$

6.
$$t_{m} = \frac{L^{2}}{\mu V}$$
So,
$$\frac{t_{m2}}{t_{m1}} = \frac{L_{2}^{2}}{\mu V_{2}} \cdot \frac{\mu V_{1}}{L_{1}^{2}} = \frac{L_{2}^{2}}{L_{1}^{2}} \cdot \frac{V_{1}}{V_{2}}$$
a)
$$L_{2} = 2L_{1}, \quad V_{2} = V_{1}$$

$$\therefore \frac{t_{m2}}{t_{m1}} = \frac{4L_{1}^{2}}{L_{1}^{2}} \cdot \frac{V_{1}}{V_{1}} = 4$$

Thus, the elution times become 18, 25.2 & 40.8 min, respectively.

b)
$$L_2 = L_1, \quad V_2 = 2V_1$$

$$\therefore \frac{t_{m2}}{t_{m1}} = \frac{L_1^2}{L_1^2} \cdot \frac{V_1}{2V_1} = \frac{1}{2}$$

Thus, the elution times become 2.25, 3.15 & 5.1 min, respectively.

c)
$$L_2 = 2L_1, \quad V_2 = 2V_1$$

$$\therefore \frac{t_{m2}}{t_{m1}} = \frac{4L_1^2}{L_1^2} \cdot \frac{V_1}{2V_1} = 2$$

Thus, the elution times become 9, 12.6 & 20.4 min, respectively.