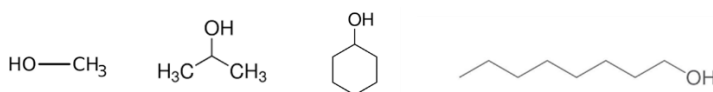


Name _____

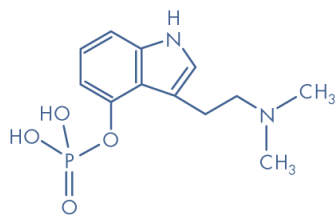
Chem 454 – Exam 3 – 4/27/22 – 90 points total. 10 points for each question.

1. Describe the chemical ionization technique for mass spectroscopy.¹
2. What is a TOF mass analyzer? What are its working principles? Sketch a diagram of the TOF.²
3. Outline the major components of the van Deemter equation and plot those relationships vs. mobile phase flow rate (u).³
4. What is an FID? Where is it used and describe its sensitivity to types of analytes.⁴
5. Why has the capillary column configuration overtaken packed columns in GC?⁵
6. Why are higher pressures required in analytical LC (HPLC)?⁶
7. Predict the elution order of the following analytes on a C-18 column.⁷



I II III IV

8. Explain the principles of electroosmotic flow. How does it conduct separation and what are the migration time trends for cations, anions, and neutral species?⁸
9. A hallucinogenic compound found in some mushrooms, psilocybin (below, MW 284.3) was analyzed by HPLC.⁹

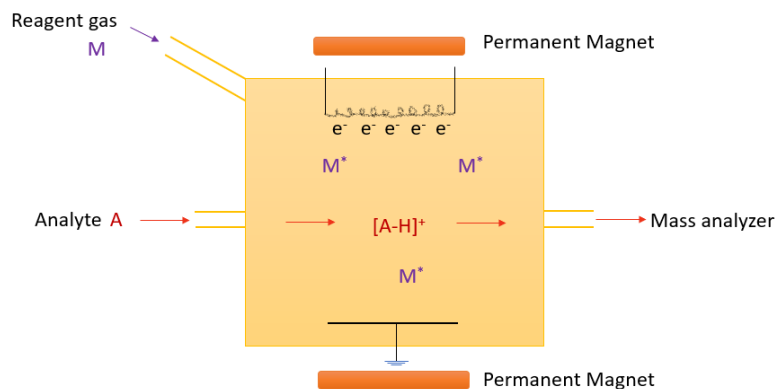


An internal standard used with detection by MS. The results are shown below.

	IS	psilocybin
Sample	3144	7502
10.2 ppm psilocybin std.	2982	8872

What is the concentration of psilocybin in the sample?

Name _____



A reagent gas is ionized (M^+) which undergoes charge-transfer processes that ionize the parent ion of the analyte (A) to $A-H^+$.

2 Time-of-Flight mass analyzer

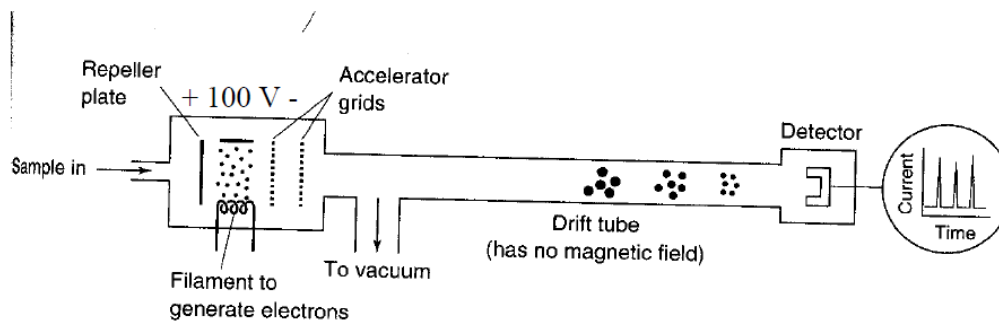


Figure 24-25 Time-of-flight mass spectrometer. Heavy ions are accelerated to a lower velocity than light ions are. The ions reach the detector in order of increasing mass.

Velocity follows as

$$v = L/t \text{ where } L \text{ is the length of drift tube}$$

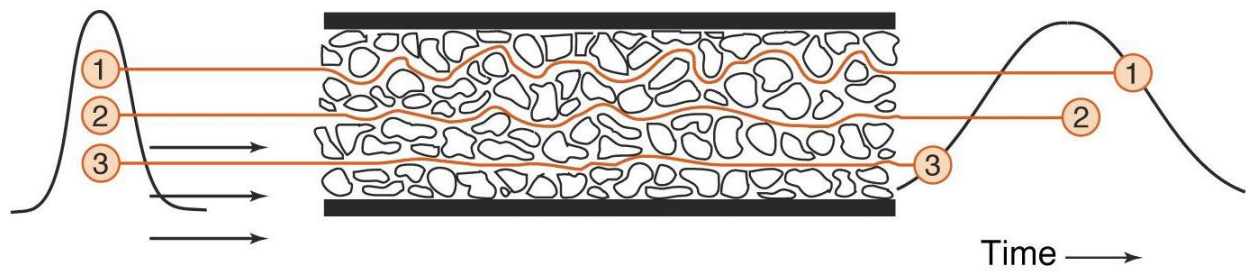
t is the time spent in the drift tube

All ions are accelerated to the same K.E. The drift tube allows the separation based on mass/charge where lighter ions emerge first.

$$^3 H = A + B/u + Cu$$

The plate height H is the variance per length (σ^2/L) of the separation column.

A – is the multiple path phenomenon where the solutes can take paths of various lengths through the column.

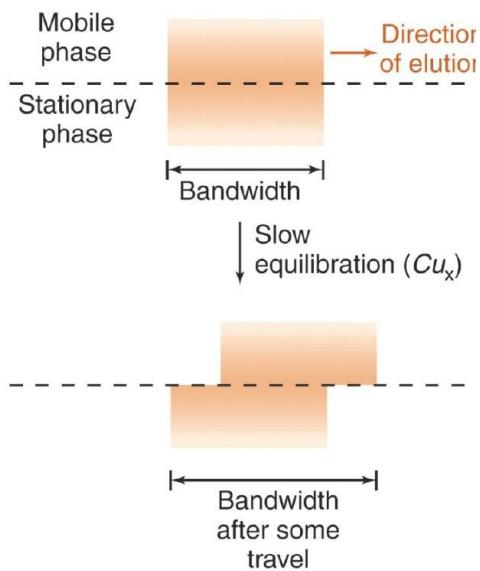


B/u is longitudinal diffusion, this is movement of particles from a more to less concentrated states. This is described by the

Einstein-Smoluchowski Eqn. $\sigma = (2Dt)^{1/2}$

One can see that the band spreading is proportional to $t^{1/2}$, where t is time spent in the column. The E-S equation reduces to B/u .

C_u is the mass transport issue between the s.p. and m.p.



Band spreading from this phenomenon increases with m.p. flow rate or C_u . Taken together the effects are shown below.

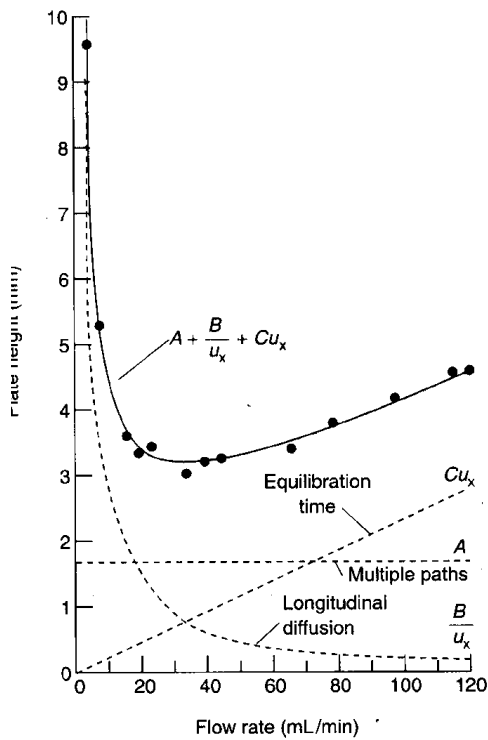


Figure 23-14 Application of van Deemter equation to gas chromatography. Experimental points are data from H. W. Moody, *J. Chem. Ed.* **1982**, 59, 291. Van Deemter parameters are $A = 1.65$ mm, $B = 25.8$ mm · mL/min, and $C = 0.0236$ mm · min/mL.

4

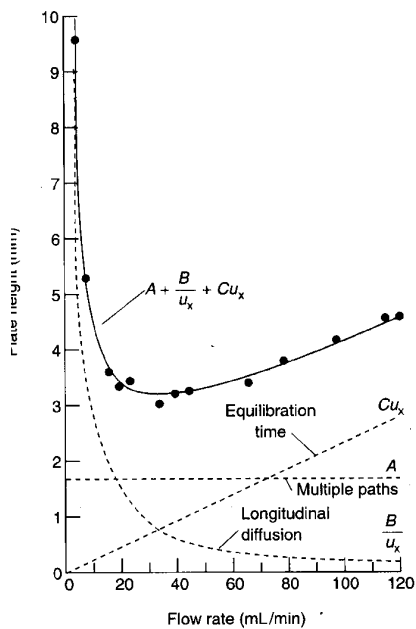


Figure 23-14 Application of van Deemter equation to gas chromatography. Experimental points are data from H. W. Moody, *J. Chem. Ed.* **1982**, 59, 291. Van Deemter parameters are $A = 1.65$ mm, $B = 25.8$ mm · mL/min, and $C = 0.0236$ mm · min/mL.

The GC column flow is introduced into the flame where organic radicals are produced. These radicals are reduced at cathode. The current is directly proportional to organic analytes in the flame.

Name _____

⁵ This gets back to v-D eqn considerations. The B/u, longitudinal diffusion term contributes most to band broadening in the gas phase. Capillary columns allow for the unobstructed and therefore faster flow of the gaseous m.p. over their packed counterparts.

⁶ In the v-D equation the MT effects predominate, i.e. Cu. Increasing the surface area/bulk ratio of the s.p. is a way to greatly improve the MT between the two phases. This requires small diameter supports for the s.p. The cost is the pressure required to squeeze the m.p. through the space between the smaller diameter particles at high pressures.

⁷ Elution sequence shortest to longest. I > II > III > IV

⁸ The electroosmotic flow is based on the flow of adsorbed cations to the -O- sites on the surface of the silica capillary. These cations will migrate towards the cathode dragging along with it a solvation sphere of water molecules (and thus neutrals) along with solvated anions. All three major types are pulled to the cathode with migration time trends of
t (cations) < t (neutrals) < t (anions)

⁹ $7502 (2982/3144) (10.2 \text{ ppm}/8872) = 8.18 \text{ ppm}$