Exam 3 * Chem 454 * April 24, 2019

Name_____

1. In general, rank the CCD, PMT and PDA systems for photon detection from lowest limit of detection from lowest (best) to highest (worst). [1]

	Best LOD				Worst LOD
a]	PDA	>	CCD	>	PMT
b]	PMT	>	CCD	>	PDA
c]	CCD	>	PMT	>	PDA
d]	CCD	>	PDA	>	PMT

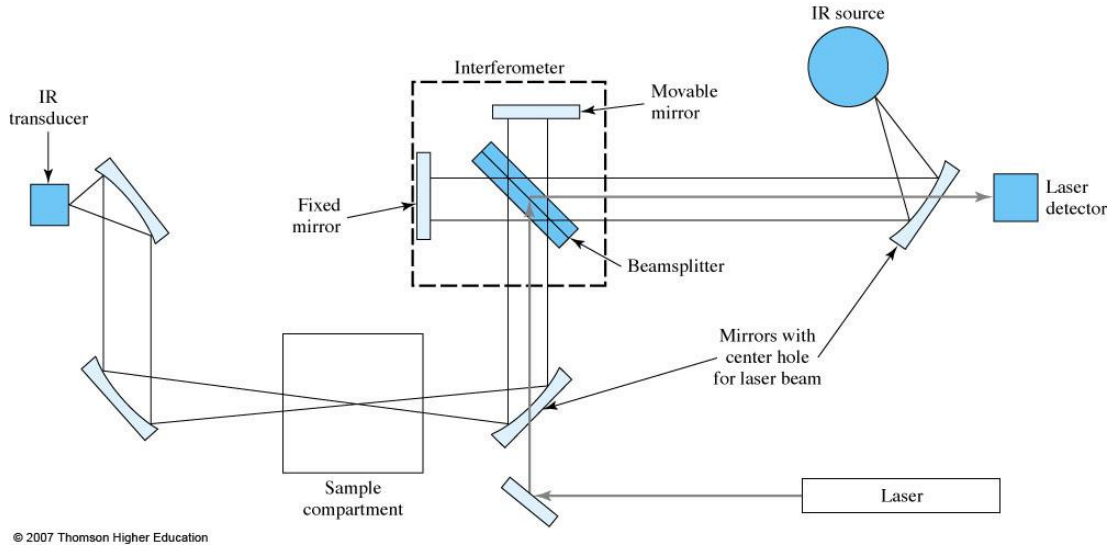
2. Using CO_2 as an example sketch <u>one</u> IR and Raman active vibrational mode each. [2]

3. Two GC injections were made and the respective detector responses are below.

	Analyte Response	Internal Std. Response
Sample X + IS	111,332	97,677
432 ppm Analyte + IS	144,089	107,612

What is the analyte concentration in Sample X? [3]

4. Below is a block diagram for what type of instrument? Why is the laser used in this device? [4]



5. Describe the radiation source for flame atomic absorption spectroscopy. Is it a line or broad-band source? [5]

6. How does the graphite furnace AA spectrometer achieve a lower limit of detection than the flame AA one? [6]

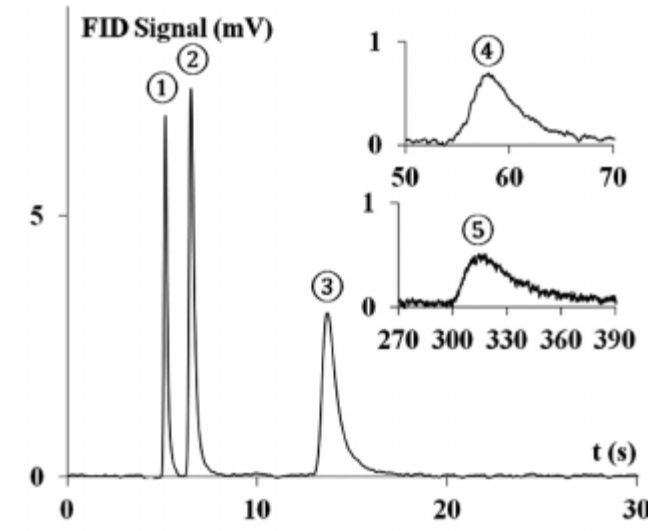
7. Plate height, H in chromatography expresses which of the following? [7]

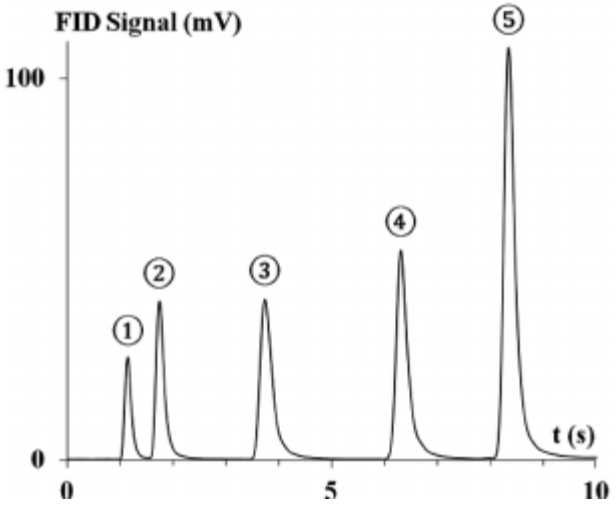
   a) Standard deviation per unit length, σ/L
   b) Flow rate, u in ml/min
   c) Variance per unit length, σ^2/L
   d) Retention time, t_r
   e) Flow rate per unit time, u/t

8. Which of the three terms in the van Deemter equation most applicable in GC? Explain why and why capillary columns are used in GC. [8]

9. What is an FID and how does it work? What types of analytes does the FID respond to? [9]

10. Which chromatogram is likely used temperature programming in the GC separation? Top or bottom? Why are solutes 4 and 5 broader in the top chromatogram? [10]


FID Signal (mV)
1
2
3
4
5
1
0
50
60
70
1
5
0
270 300 330 360 390
t (s)
0
0
10
20
30


FID Signal (mV)
5
100
4
2
3
1
t (s)
0
0
5
10

Answers

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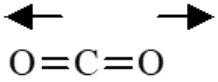
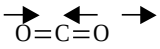
[1] c] CCD > PMT > PDA

B & D ½ credit

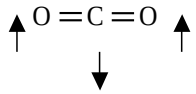
[2] Raman Active:



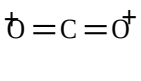
Several IR active modes:



Asymmetrical stretching
2350 cm^{-1}, active



Bending (in plane)
666 cm^{-1}

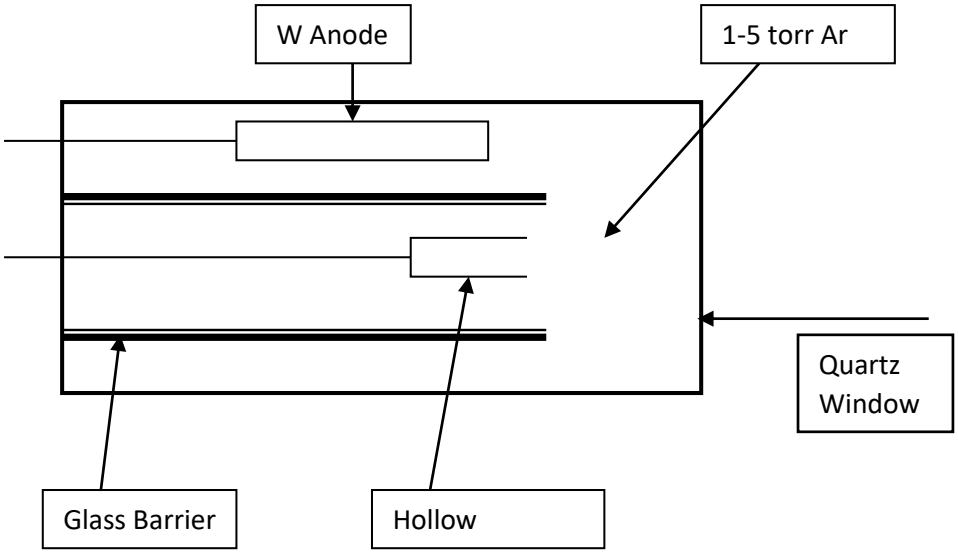


Bending (out of plane)
666 cm^{-1}

[3] 111,332 * (107,612/97,677) * (432/144,089) = 368 ppm

[4] This is an FT-IR. The laser is used to accurately measure the position of the mirror for the optical path difference with the fixed mirror.

[5] This device is known as a hollow cathode lamp. It consists of a hollow cup of a cathode constructed from the analyte element(s) the sample, and anode in a low pressure Ar atmosphere



- 300 – 400 V is applied which allows for the passage of 3-25 mA of current
- Current creates excited state atoms at the cathode which causes emission at the element's characteristic λ. <u>The HCL is a line source.</u>

  $Ne(g) => Ne^{+}(g) + e -$

  $Ne^{+}(g)$ strikes the cathode

  vaporizes some of the metal cathode into excited state M*(g)

  $M^*(g) => M + h\nu$

  - Disadvantage of the HCL is that you need a lamp for each analyte element. Many lamps are multi-element.

[6] *It is based on the GFAA creating a nearly instantaneous plume of concentrated analyte as opposed to the flame AA which requires a constant feed of sample solution into the flame.*

[7] C

[8] H = A + B/u + Cu

A, multiple paths this has some bearing in GC as a capillary column offers only one, vs. a packed column.

B/u, Longitudinal diffusion. This is the force that moves particles from higher to lower concentrations. The long the solute spend in the column the more the band spreading from this effect. Therefore faster flow rate is minimizes B/u effects. A capillary column offers faster flow as there is less resistance to flow than a packed column.

Cu, mass transfer effects. While this effect contributes less than B/u it is minimized by using a thin stationary phase. This allows the solute to diffuse in and out more rapidly than a think one.

[9] The flame ionization detector (FID) for GC is based on the formation of organic radicals, CH and CHO^+ within a flame. These radicals are reduced at a cathode and the current flow is proportional roughly to the number of organic carbons in the analyte. The flow or effluent from the separation column is fed to a flow air and fuel (H_2) where the analytes are combusted. A cathode is further upstream from the flame. The FID is responsive only to organic carbons.

[10] The bottom chromatogram is the obvious one for a temperature programmed gas chromatogram. Much better separation efficiency and note that the solutes 4 and 5 elute in 6 and 8 mins in the bottom vs. 60 and 320 minutes in the top. The peaks are broader for 4 and 5 in the top as they spent more time in the column and are subject to more longitudinal diffusion (B/u) band broadening effects.