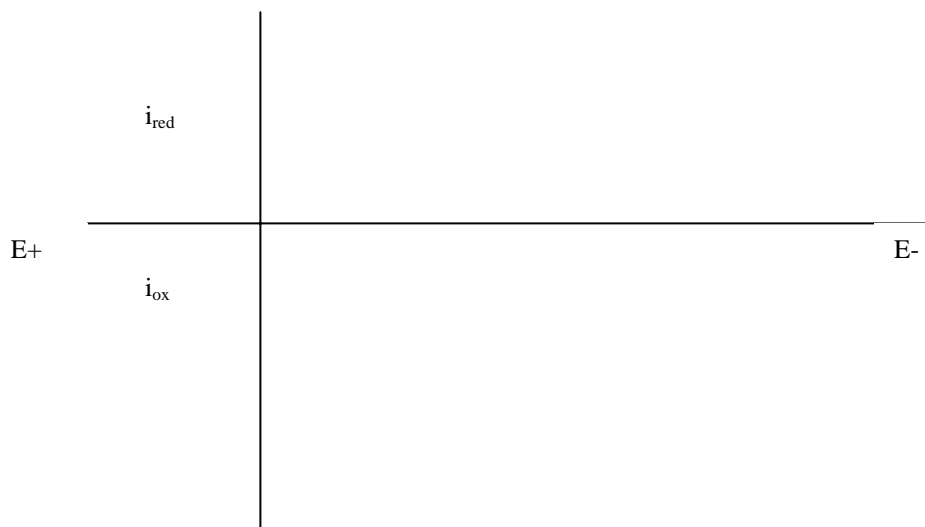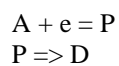1. Cyclic voltammetry involves the measurement of a diffusion controlled _____ at an electrode in which the _____ is controlled. (4 points)

2. (5 points) A. Sketch a cyclic voltammogram of a hypothetical reversible redox-couple: $A + e = A^-$
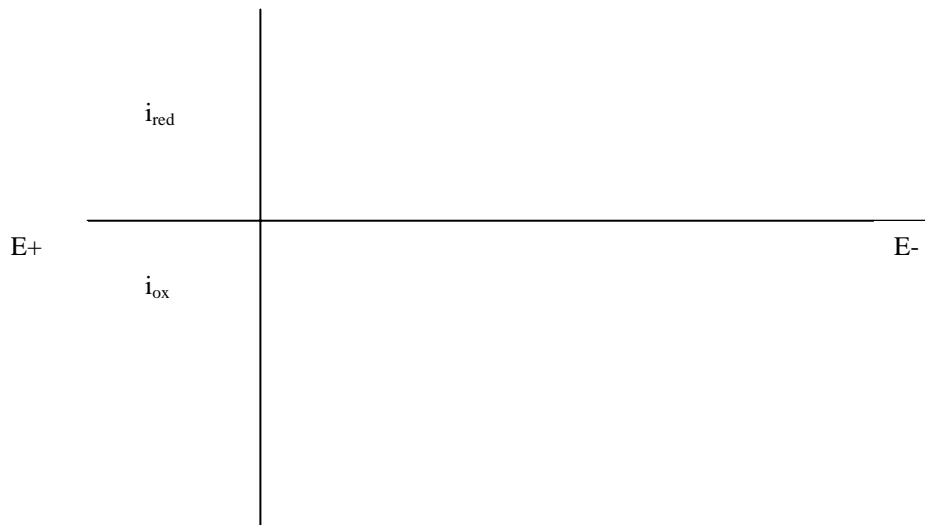
i_{red}

E+   E-

i_{ox}

2. (1 point) B. Indicate the approximate E^o_{red} of that redox species in part A on the graph above.

3. (5 points) Sketch a cyclic voltammogram in which the electrode product is consumed in a competing chemical reaction:
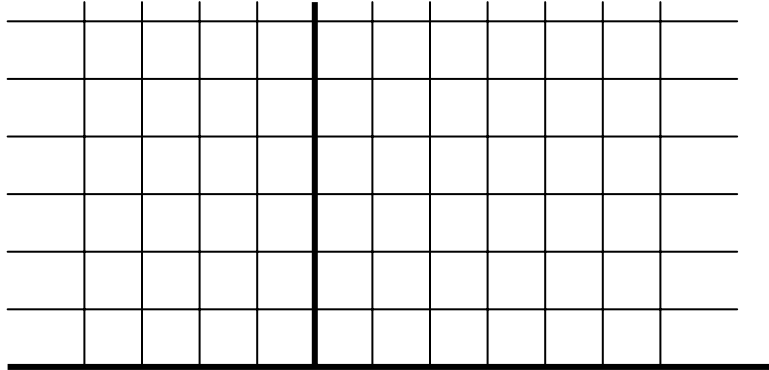
$$A + e = P$$
$$P => D$$

Assume that the product, D is not observed in any further electrochemical reactions.

i_{red}

E+   E-

i_{ox}

4. (5 points) Why is stripping voltammetry is the most sensitive of the polarographic techniques?

5. (10 points) A differential pulse polarogram gave a peak current of 10.1 μA for Cd^{2+} reduction for a 20.00 ml water sample. A spike of 0.0100 ml of 0.025 M of Cd^{2+} to this sample volume gives a current of 23.1 μA. What is the concentration of Cd^{2+} in the original sample?

   Hint: consider that the volume after that spike did not significantly change (20.00 vs 20.01 ml)

6. (5 points) Illustrate the power density spectrum for flicker, environmental, and Johnson/Shot noises below:

Power
Density
Watts/Hz

0

Frequency, Hz ⟶
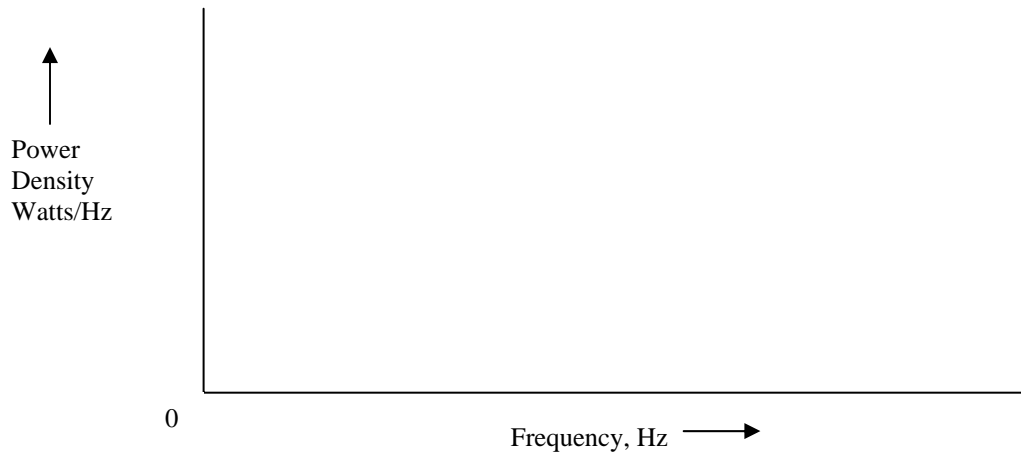
7. (5 points) Double-beam spectrophotometers are an improvement over single beam instruments because:

8. (5 points) Generally bands rather than lines are observed for molecular absorption spectra because:

9. (10 points) Label the transitions (the large letters) in the following diagram:
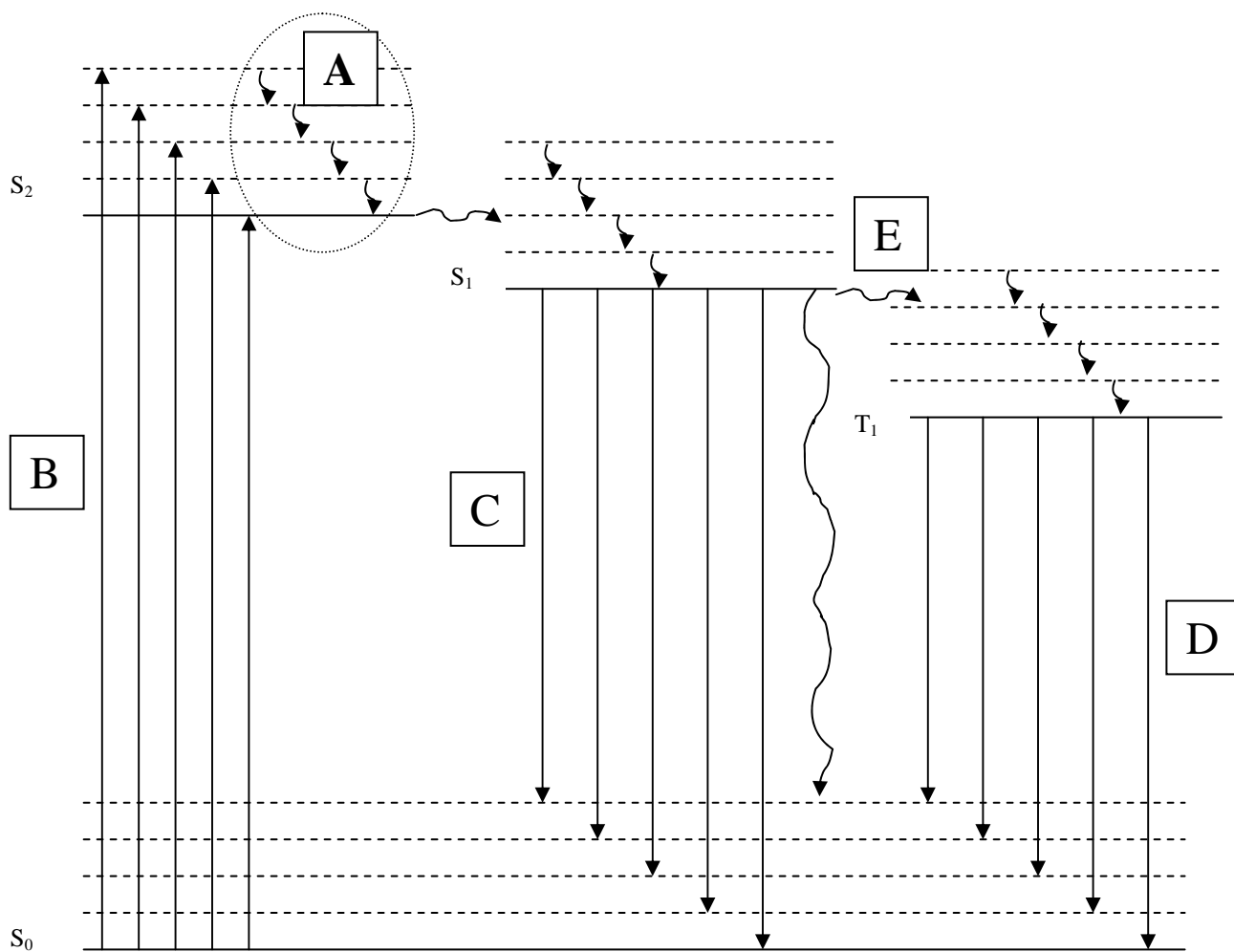
10. (4 points) The upper and lower pH ranges for the glass pH electrode are _____ to _____.
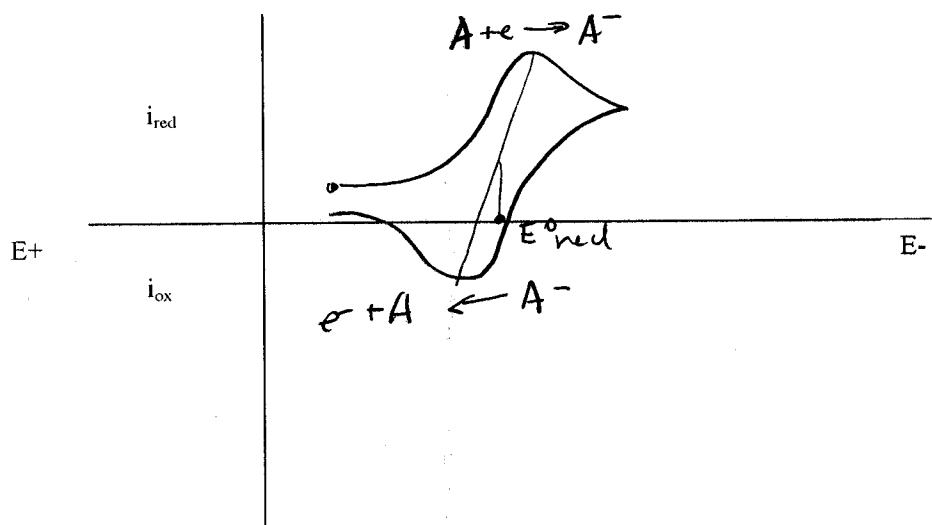
11. (6 points) The detection limit of an instrumental method is defined as a ratio of _____ (_____/_____)

12. (5 points) The lifetime of fluoresence is generally _____than that of phosphoresence.

13. (5 points) The wavelength of fluoresence is generally _____than that of the corresponding excitation.

14. (5 points) The background in voltammetry and polarography is attributable to _____ effects at the electrode.

15. (4 points) The electrode material in polarography is _____

16. (6 points) Beer's law is usually only obeyed if the analyte concentration is less than_____ or the absorbance signal is less than _____.

17. (10 points) You are investigating a new analytical method. A standard reference material of 4.41 % (masss/mass) is use to validate the new method. You find that using the new method four replicate measurements yields a mean analyte concentration of 4.83 % with a standard deviation of 0.38. Is that error truly random within a 95% confidence level? That level is 3.182 for 3 degrees of freedom (Table 4-2).

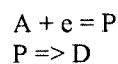$$\mu = \bar{x} \pm \frac{t_s \sigma}{\sqrt{n}}$$

1. Cyclic voltammetry involves the measurement of a diffusion controlled ___current___ at an electrode in which the ___potential___ is controlled. (4 points)

2. (5 points) A. Sketch a cyclic voltammogram of a hypothetical reversible redox-couple: $A + e = A^-$

$$A + e \rightarrow A^-$$

i_{red}

E^o_{red}

E+   E-

i_{ox}

$$e^- + A \leftarrow A^-$$

2. (1 point) B. Indicate the approximate E^o_{red} of that redox species in part A on the graph above.

3. (5 points) Sketch a cyclic voltammogram in which the electrode product is consumed in a competing chemical reaction:

$$A + e = P$$
$$P \Rightarrow D$$

Assume that the product, D is not observed in any further electrochemical reactions.

$$A + e^- \rightarrow P$$

i_{red}

E+   E-

i_{ox}

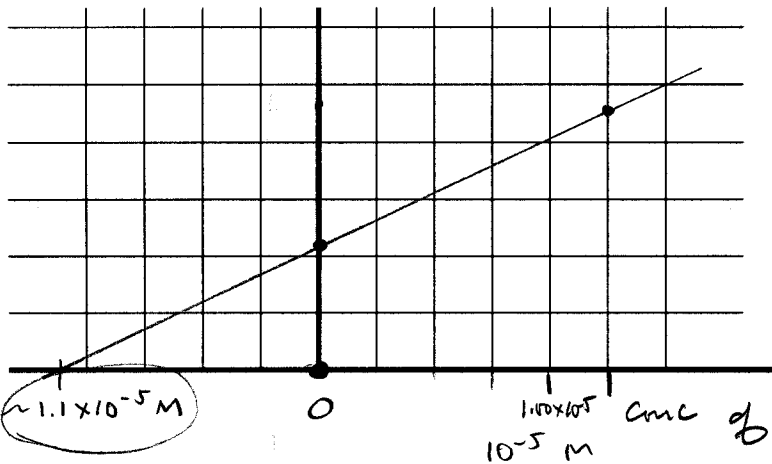No Oxidation peak because

$$P \rightarrow D$$
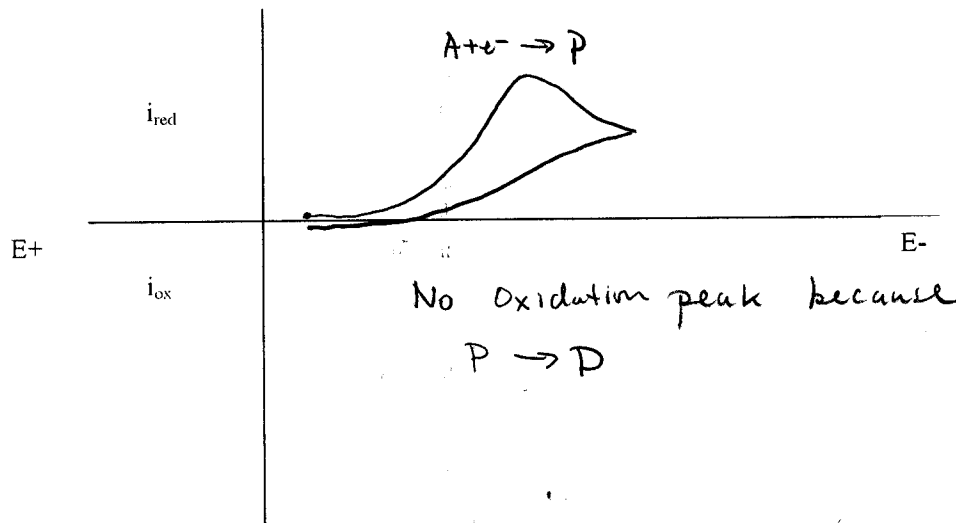
4. (5 points) Why is stripping voltammetry is the most sensitive of the polarographic techniques?

Because it accumulates analyte from the sample prior to analysis, i.e. it's a preconcentration technique.

5. (10 points) A differential pulse polarogram gave a peak current of 10.1 μA for Cd^{2+} reduction for a 20.00 ml water sample. A spike of 0.0100 ml of 0.025 M of Cd^{2+} to this sample volume gives a current of 23.1 μA. What is the concentration of Cd^{2+} in the original sample?

Hint: consider that the volume after that spike did not significantly change (20.00 vs 20.01 ml)

$$\frac{0.0100}{20.01} \, 0.025M = 1.25 \times 10^{5} \, M$$

conc of spike in sample

$\sim 1.1 \times 10^{-5} M$

1.10×10^{5}
$10^{-5} M$

Compare

$y = \frac{23.1 - 10.1 \mu A}{1.25 \times 10^{-5} M} \, X + 10.1 \mu A$

$0 = 1.04 \times 10^{6} X + 10.1 \mu A$

$X = 0.971 M$

6. (5 points) Illustrate the power density spectrum for flicker, environmental, and Johnson/Shot noises below:

Power Density Watts/Hz

environmental

60

120

180

Johnson/Shot

flicker

0

Frequency, Hz →
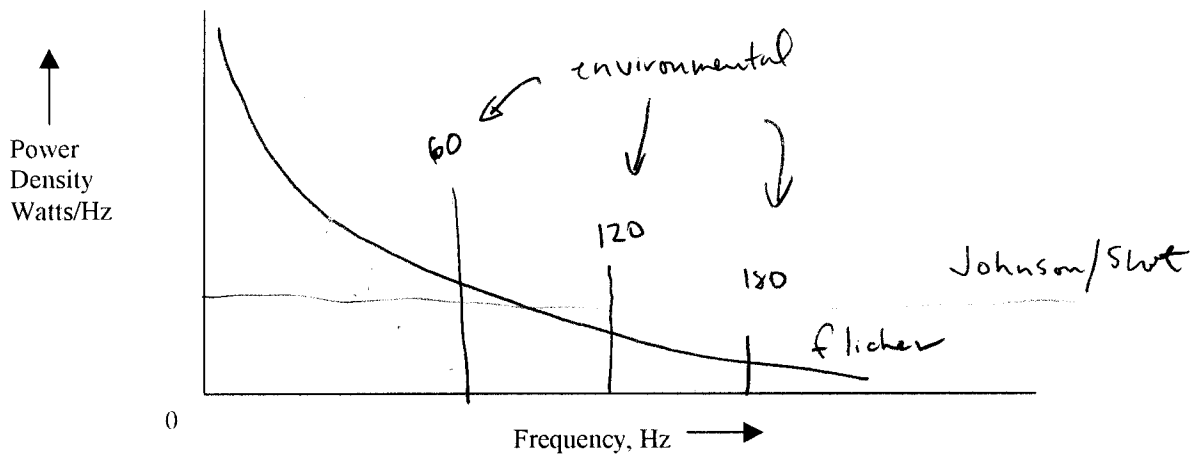
7. (5 points) Double-beam spectrophotometers are an improvement over single beam instruments because:

Adjusts for drift in source intensity & detector responses by measuring P_o then P. Also chopping the source beam effectively takes the frequency of the experiment from DC to higher and can compensate for flicker noise

8. (5 points) Generally bands rather than lines are observed for molecular absorption spectra because:

Electronic states are coupled to vibrational states (molecular) no vibrational states for atoms.

9. (10 points) Label the transitions (the large letters) in the following diagram:

A — Vibrational relaxation
Internal conversion

Intersystem Crossing

E

B — Absorption or excitation

C — fluorescence

T_1 external Internal conversion

phosphorescence

D

S_2

S_1

S_0

Relaxation
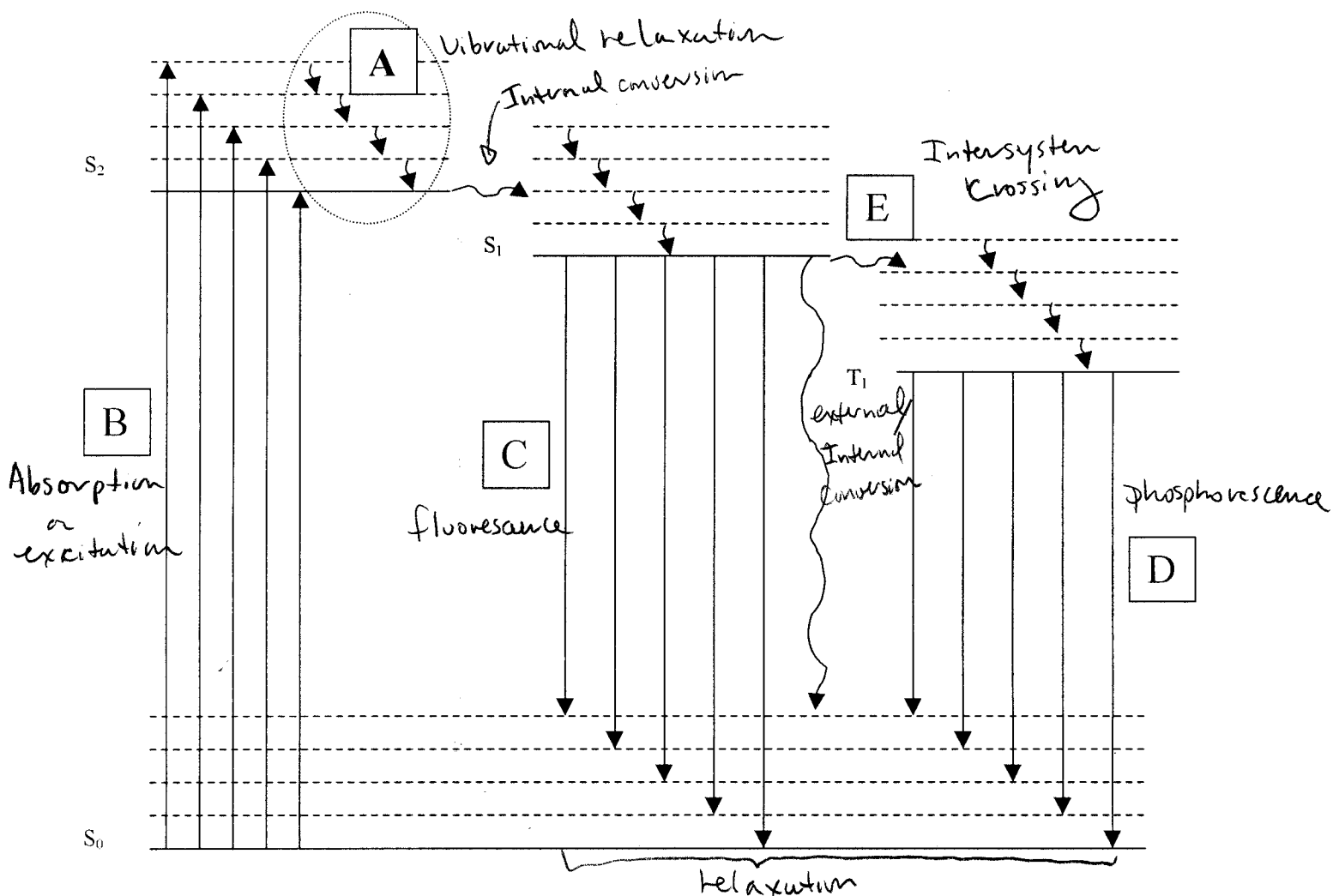
10. (4 points) The upper and lower pH ranges for the glass pH electrode are _____ 2 _____ to _____ 10 _____.

11. (6 points) The detection limit of an instrumental method is defined as a ratio of _____ 3/1 _____ (Signal / Background)

12. (5 points) The lifetime of fluoresence is generally _____ Shorter _____ than that of phosphoresence.

13. (5 points) The wavelength of fluoresence is generally _____ longer _____ than that of the corresponding excitation.

14. (5 points) The background in voltammetry and polarography is attributable to _____ Charging _____ effects at the electrode.

15. (4 points) The electrode material in polarography is _____ mercury _____

16. (6 points) Beer's law is usually only obeyed if the analyte concentration is less than _____ 0.010 M _____ or the absorbance signal is less than _____ 1 _____.

17. (10 points) You are investigating a new analytical method. A standard reference material of 4.41 % (masss/mass) is use to validate the new method. You find that using the new method four replicate measurements yields a mean analyte concentration of 4.83 % with a standard deviation of 0.38. Is that error truly random within a 95% confidence level? That level is 3.182 for 3 degrees of freedom (Table 4-2).

$$\mu = \bar{x} \pm \frac{t_s \sigma}{\sqrt{n}}$$

$$4.83 \pm \frac{t_s(0.38)}{\sqrt{4}} = 4.41$$

$$t_s = \frac{(4.41 - 4.83)\, 2}{0.38} = 2.21$$

Since 3.182 > 2.21 we can assume that the error is random and not significant

Name:_____

25 questions @ 4 points each

1] Describe the differences between phosphorescence and fluorescence.   Which would you expect to have the longer lifetime and why?

2] A GC analysis of trichloroethylene was conducted with a chlorobenzene internal standard. The 10.5 ppm trichloroethylene solution with 6.80 ppm chlorobenzene gave signals of 1,266 and 909 respectively. An unknow solution of trichloroethylene and 7.20 ppm chlorobenzene gave signals of 844 and 954 respectively. What is the concentration of trichloroethylene in that sample?

3] Label what you expect to be the excitation and emission spectra of anthracene below.
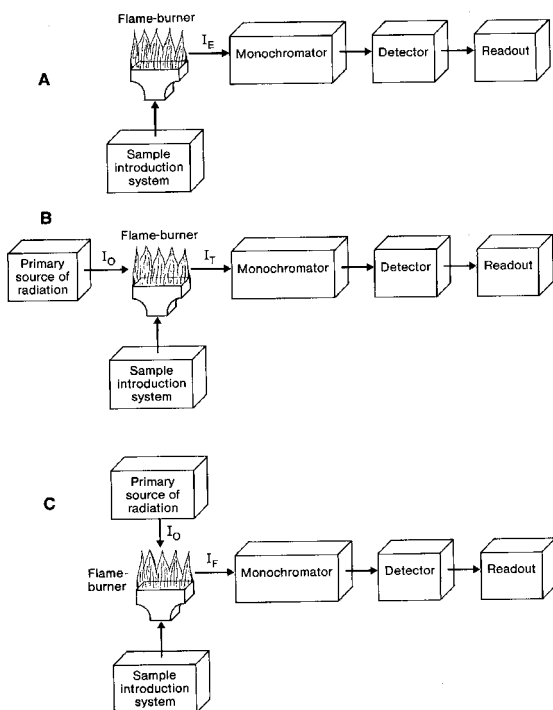

Wavelength, nm

4] Why you might expect anthracence to be efficient at fluorescence emissions.

    a. Because it consists of an organic backbone
    b. Because it has an extensive π-bonding backbone
    c. Because it has an extensive σ-bonding backbone
    d. Because it is a Lewis acid
    e. Because it is a high molecular weight compound

5] The block diagrams describe the instrumentation for atomic spectrometers. Label each for the technique normally associated with it.

A _____

B_____

C_____

6] What purpose or purposes does the flame serve in the techniques in question 5?

7] The Doppler phenomenon in atomic spectroscopies give is the basis for:

     a.   the background noise in AE
     b.   the maximum signal intensities
     c.   the detection limit
     d.   the line-broadening
     e.   the detector

8] Why does the graphite furnace hold an advantage over flame AA in terms of detection limit?

     a.   Because the atomic vapor plume formed by the furnace is more concentrated in atomic vapor than the constant feed of flame AA
     b.   Because the furnace runs at a cooler temperature
     c.   Because the flame contains flicker noise
     d.   Because the furnace has a larger dynamic range
     e.   Because of the emission intensities of the furnace

9] Describe how the "A" term of the van Deemter equation contributes to band broadening.

10] Describe how the "B/u" term of the van Deemter equation contributes to band broadening. Why is it inversely proportional to mobile phase flow rate?

11] Describe how the "Cu" term of the van Deemter equation contributes to band broadening. Why is it directly proportional to mobile phase flow rate?

12] The separation efficiency of capillary columns over packed columns in GC is attributable to

    a. lower operating temperatures
    b. higher sample loading
    c. B/u effects
    d. chemical inertness
    e. lower stationary phase volatility

13] The most common mobile phases in GC are

    a. Ar, N_2 and F_2
    b. N_2O, C_2H_2, and O_2
    c. H_2, Ar, and Ne
    d. He, Ne, and Ar
    e. H_2, He, and N_2

14] Split injections are required in GC capillary columns because

    a. they require cooler operating temperatures
    b. they are limited in terms of sample loading
    c. they increase the reproducibility of sample injections
    d. they require larger sample quantities relative to packed columns
    e. they are notorious for biting back

15] Hollow cathode lamps are

    a. broadband sources
    b. the basis for lasers
    c. used as a source for ICP
    d. used as a source for AE
    e. line sources

16] The ICP torch is based on

    a. a C_2H_2/air flame
    b. an electric spark
    c. Ar^+ in an RF magnetic field
    d. a CH_4/O_2 flame
    e. an electric arc

17] The resolution term in chromatographic separations is proportional to

    a. t_r
    b. k'
    c. H
    d. $L^{1/2}$
    e. $H^{1/2}$

18] The plate height in chromatography is best described as

   a. resolution per unit length
   b. variance per unit length
   c. k' per unit length
   d. t_r per unit length
   e. nausea per unit length

19] Assume that we using a very nonpolar stationary phase in GC we can guess that elution times for the four following analyte species can be ranked in terms of shortest to longest as:

   I. Benzene   II. Isopropanol   III. Ethanol

   a) I, II, III
   b) II, I, III
   c) I, III, II
   d) III, II, I
   e) III, I, II

20] The thermal conductivity detector, flame-ionization detector, and electron capture detector are respectively sensitive to

   a. electron withdrawing organics, all species, and organics
   b. organics, electron withdrawing organics, and all species
   c. all species, organics, and electron withdrawing organics
   d. organics, all species, and electron withdrawing organics
   e. electron withdrawing organics, organics, and all species

21] An example of a "hard" ionization source in mass spectroscopy is

   a. electrospray
   b. electron impact
   c. chemical ionization
   d. fast atom bombardment
   e. MALDI

22] The resolution required to distinguish between two ions of m/e ratios of 44.01 and 44.03 can be calculated as

   a. 10 x (44.03 – 44.01)
   b. 44.02/(44.03 – 44.01)
   c. (44.03 – 44.01)/1000
   d. (44.03 – 44.01) x 100
   e. (44.03 + 44.01)/44.02

23] In terms of highest to lowest resolution, the following mass analyzers can be ranked as:

   a. TOF, quadrapole, double focusing
   b. Quadrapole, TOF, double focusing
   c. Double focusing, quadrapole, TOF
   d. Double focusing, TOF, quadrapole
   e. Quadrapole, double focusing, TOF

24] The ion sources in EI and CI share a common feature, which is that both have:

     a.   the same reagent gases
     b.   the same detection systems
     c.   the same high voltage electron source
     d.   the same ionization characteristics
     e.   the same analyte ionization principles

25] If we were to rank nonvolatile ionization sources in term of highest to lowest analyte MW's the following ranking would be correct:

     a.   electrospray, FAB, field desorption
     b.   FAB, electrospray, field desorption
     c.   Field desorption, FAB, electrospray
     d.   Field desorption, electrospray, FAB
     e.   all are about the same

25 questions @ 4 points each

1] Describe the differences between phosphorescence and fluorescence. Which would you expect to have the longer lifetime and why?

Phosphorescence T => S transitions, spin forbidden, longer lifetimes

Fluorescence S => S transition

2] A GC analysis of trichloroethylene was conducted with a chlorobenzene internal standard. The 10.5 ppm trichloroethylene solution with 6.80 ppm chlorobenzene gave signals of 1,266 and 909 respectively. An unknow solution of trichloroethylene and 7.20 ppm chlorobenzene gave signals of 844 and 954 respectively. What is the concentration of trichloroethylene in that sample?

10.5 ppm/1266 = F (6.80 ppm/909);   F = 1.11

x/844 = 1.11 (7.20 ppm/954);   x = 7.07 ppm

3] Label what you expect to be the excitation and emission spectra of anthracene below.

Wavelength, nm
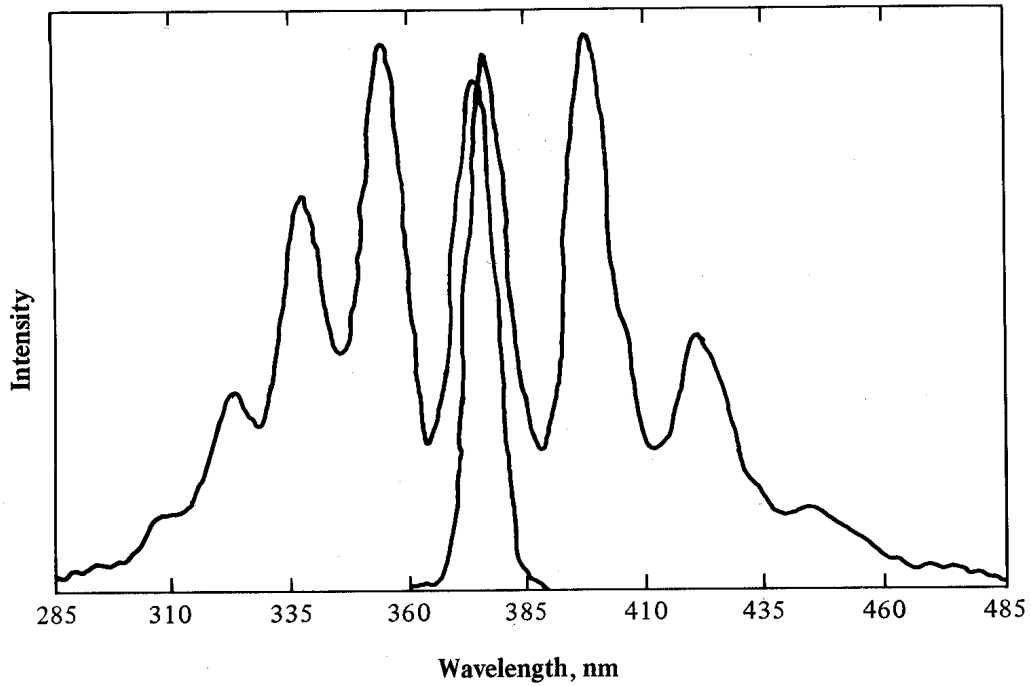
4] Why you might expect anthracene to be efficient at fluorescence emissions.

Because it has an extensive π-bonding backbone
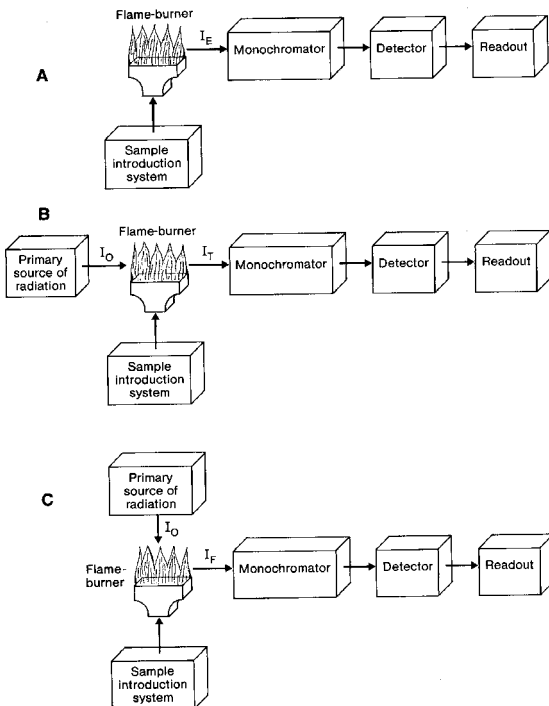
5] The block diagrams describe the instrumentation for atomic spectrometers. Label each for the technique normally associated with it.

A] AE

B] AA

C] AF

6] What purpose or purposes does the flame serve in the techniques in question 5?

Atomization for all three, also excitation for AE

7] The Doppler phenomenon in atomic spectroscopies give is the basis for:

     the line-broadening

8] Why does the graphite furnace hold an advantage over flame AA in terms of detection limit?

     Because the atomic vapor plume formed by the furnace is more concentrated in atomic vapor than the constant feed of flame AA

9] Describe how the "A" term of the van Deemter equation contributes to band broadening.

     Multiple paths – read notes

10] Describe how the "B/u" term of the van Deemter equation contributes to band broadening. Why is it inversely proportional to mobile phase flow rate?

     Longitudinal diffussion – read notes

11] Describe how the "Cu" term of the van Deemter equation contributes to band broadening. Why is it directly proportional to mobile phase flow rate?

     MT – read notes

12] The separation efficiency of capillary columns over packed columns in GC is attributable to

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13] The most common mobile phases in GC are

     H_2, He, and N_2

14] Split injections are required in GC capillary columns because

     they are limited in terms of sample loading

15] Hollow cathode lamps are

     line sources

16] The ICP torch is based on

Ar$^+$ in an RF magnetic field

17] The resolution term in chromatographic separations is proportional to

L$^{1/2}$

18] The plate height in chromatography is best described as

variance per unit length

19] Assume that we using a very nonpolar stationary phase in GC we can guess that elution times for the four following analyte species can be ranked in terms of shortest to longest as:

I. Benzene   II. Isopropanol   III. Ethanol

III, II, I

20] The thermal conductivity detector, flame-ionization detector, and electron capture detector are respectively sensitive to

all species, organics, and electron withdrawing organics

21] An example of a "hard" ionization source in mass spectroscopy is

electron impact

22] The resolution required to distinguish between two ions of m/e ratios of 44.01 and 44.03 can be calculated as

44.02/(44.03 – 44.01)

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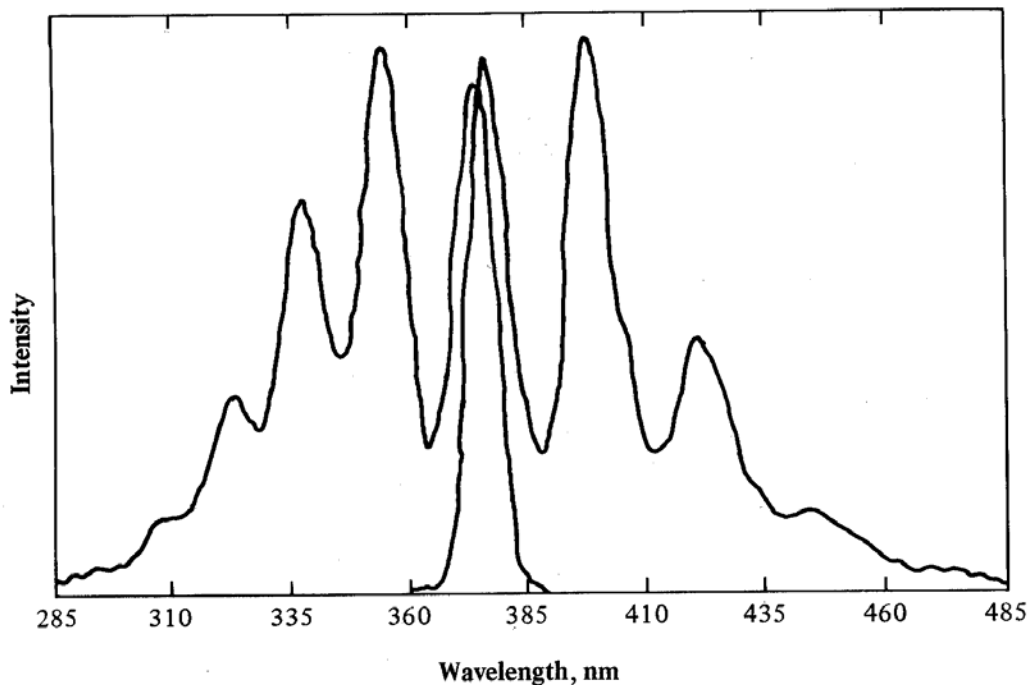
electrospray, FAB, field desorption

Name:_____

25 questions @ 4 points each

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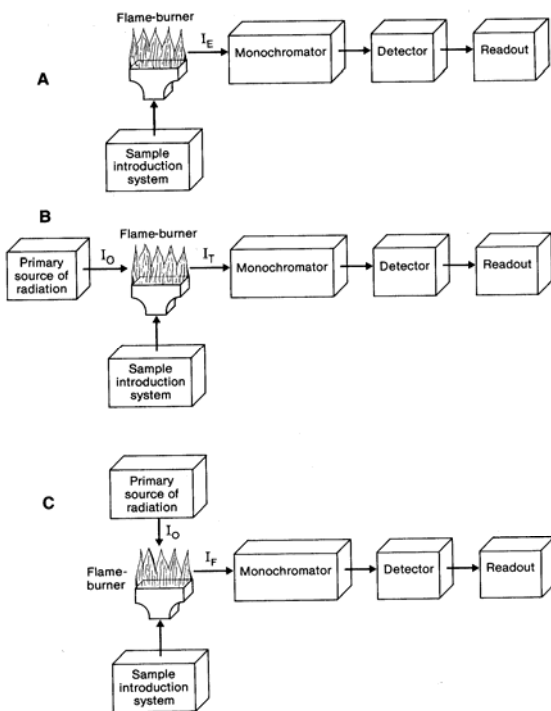3] Label what you expect to be the excitation and emission spectra of anthracene below.

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    c. (44.03 – 44.01)/1000
    d. (44.03 – 44.01) x 100
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23] In terms of highest to lowest resolution, the following mass analyzers can be ranked as:

    a. TOF, quadrapole, double focusing
    b. Quadrapole, TOF, double focusing
    c. Double focusing, quadrapole, TOF
    d. Double focusing, TOF, quadrapole

e. Quadrapole, double focusing, TOF

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a. the same reagent gases
b. the same detection systems
c. the same high voltage electron source
d. the same ionization characteristics
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25] If we were to rank nonvolatile ionization sources in term of highest to lowest analyte MW's the following ranking would be correct:

a. electrospray, FAB, field desorption
b. FAB, electrospray, field desorption
c. Field desorption, FAB, electrospray
d. Field desorption, electrospray, FAB
e. all are about the same