Chem 454 Name:_____
Instrumental Analysis Exam I
February 5, 1999 80 possible points

1] **5 points** Which of the following samples would be suitable for analysis by a calibration curve technique using a potentiometric device? Which would require a standard addition type of analysis in all likelihood?

a) Cd^{2+} in milk b) Cu^{2+} in distilled water c) Cl^- in blood

d) Ag^+ in a paint sample e) F^- in tooth paste f) Na^+ in tap water

2] **5 points** What is the dynamic range of the glass pH electrode?

3] **10 points** What are the principle interferences associated with the Cl^- sensitive electrode? Describe the chemical property that causes these species to be interferences.

4] **15 points** The F^- concentration of tap water in Moscow is maintained at 1.00 mg/mL. The response of a F^- selective electrode for this sample was measured at 0.320 volts. A sample of tap water from Pullman was measure with the same electrode at 0.360 volts. What is the concentration of F^- in Pullman water? The fluoride ISE has the following response.

$$E = \text{const} - 0.0592 \log[F^-]$$

5] **15 points** Calculate the standard potential for the following half-reaction, given the K_{sp} for $Pd(OH)_2$ is 3×10^{-28} and the standard potential for $Pd^{2+} + 2e^- = Pd(s)$ is 0.915 V.

$$Pd(OH)_2(s) + 2e^- = Pd(s) + 2OH^-$$

6] **20 points** Consider a solution consisting of 0.11 M Pd^{2+} and 0.23 M Ag^+ ions. If 1.0×10^{-6}M represents quantitative removal of the ions is it possible to electro-separated the two ions? If so what would be the sequence of removal. Also describe the electrode potentials require for each step.

$Ag^+ + e^- = Ag(s)$ $E^0 = 0.799$ V
$Pd^{2+} + 2e^- = Pd(s)$ $E^0 = 0.987$ V

Chem 454 Name:_____

Instrumental Analysis

Exam 3 April 19, 1999

Each Question is worth 10 points for a total of 80 possible points

---

1] When compared to HPLC, SFC has many advantages. Describe three of these in detail.

2] Describe how a transmission filter allows only a narrow bandwidth of radiation to pass. How does the destructive interference and constructive reinforcement work in this device?

3] What is a major source of the broadening of m/e peaks in magnetic sector mass analyzer? How does a double focusing mass analyzer overcome this shortcoming of the magnetic sector M.S.?

4] Describe the electro-osmotic flow action of capillary electrophoresis. What are the retention times trend for cations, anions, and neutrals?

5] Why do 4-level lasers hold an advantage over 3-level lasers?

6] Draw a sketch and describe each functional aspect of an electron impact ion source.

7] Sketch block diagrams for spectroscopic instruments involved in absorption and fluorescence. Why are there differences between the two types of instruments?

8] Fill in the blanks with a correct answer.

a) The dark current is the _____ of a PMT output.

b) PMT's require liquid nitrogen temperatures due to _____.

c) The Raman scattering involves a _____ in wavelength between the

_____ and scattered radiation.

d) The excited state lifetime of phosphorescence is _____ than fluorescence.

e) The electron multiplier is similar to the _____ photon detector in design.

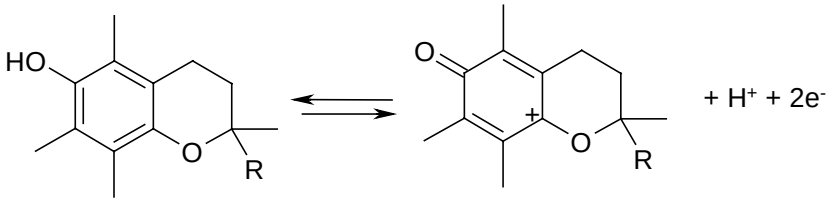
f) MALDI requires a _____ that absorbs_____ in order to efficiently ionize a sample molecule.

g) An example of a gas phase soft ionization technique is _____.

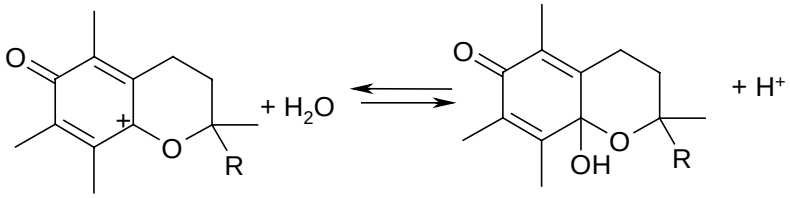
h) An example of a desorption method for M.S. is _____.

Chem 454 Name:_____
Instrumental Analysis Exam 2
March 10, 1999 80 possible points

1] **10 points** As described in the lecture notes, alpha-tocopherol (vitamin E) undergoes the following reaction.

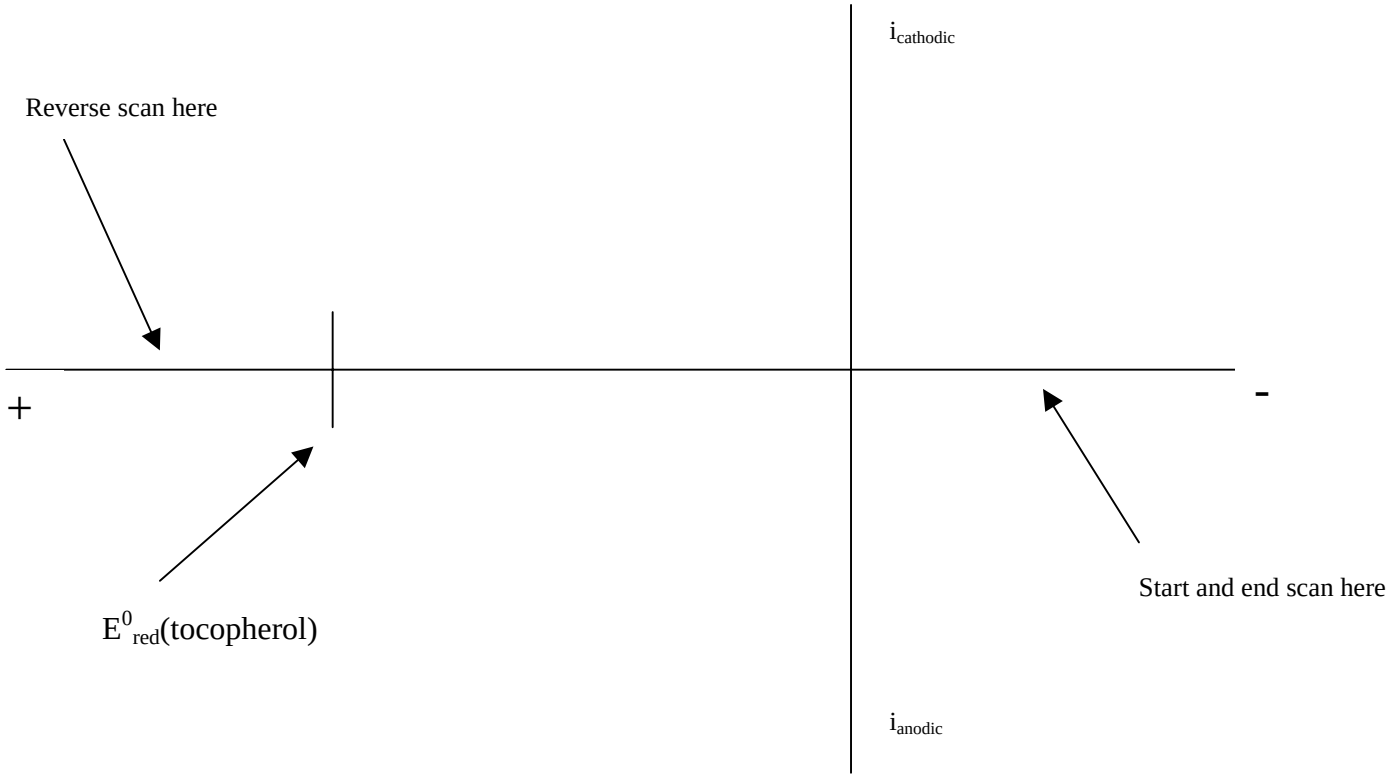


Compound 1 Compound 2



Compound 2 Compound 3

Assuming water is available in the electrolyte solution, draw a cyclic voltammogram that would be consistent with this mechanism.



2] **10 points** Discuss how tast polarography enhances the signal/background ratio relative to DC polarography.

3] **10 points** What are the advantages of capillary columns relative to packed columns in GC?

4] **10 points** Describe the principles that form the operational aspects of the electron capture detector. What type of species does it detect?

5] **10 points** Why are small stationary phase packing particles advantageous in the plate height characteristics in analytical LC column? What is the major drawback to decreasing the particle size?

6] **10 points** In the separation of nonpolar organics by gradient elution HPLC is best to begin with a polar or non-polar mobile phase when using a reversed phase C-18 column? Explain why.

7] **10 points** What is the suppressor column in IEC? Be sure to include why is it usually required and how it works in your discussion.

8] **10 points** Fill in the blank with a correct answer.

a) The capacity factor may be manipulated by _____ in gas chromatography.

b) In temperature programming a GC separation of analytes it is best to _____ the temperature so that the most volatile species elute first.

c) An example of a universal detector in GC is the _____

d) An example of a universal detector in HPLC is the _____

e) The FID in GC is sensitive towards _____

Chem 454 Final Exam
Instrumental Analysis May 12, 1999

NAME : _____

1] Below is an HPLC chromatogram for a single species taken at a mobile phase flow rate of 2.0 ml/min. In the space below sketch a chromatogram of the same species at a mobile phase flow of 1.0 ml/min. Be sure to include van Deemter type considerations in your chromatogram. (10 points)

2] Fill in the blanks with a correct answer.

(12 points)

a) The pH limits of the glass electrode are _____ and _____.

b) The chloride ion selective electrode suffers from interferences from _____ and _____ ions.

c) It is possible to increase chromatographic separation resolution by increasing column length but at a cost of _____ _____ effects.

d) The electron capture detector (ECD) is based on the high energy emission of _____ from a Ni-63 source.

e) A normal phase separation uses a _____ stationary phase.

f) The FID is sensitive for _____ containing compounds.

3] Answer correctly with True or False.

(14 points)

a) It is possible to achieve population inversion required for lasers by heating up the lasing medium. _____

b) Calibration curves always account for matrix effects of the analyte._____

c) UV-vis absorption analysis is a scattering effect. _____

d) Fluorescence involves singlet to singlet transitions. _____

e) Internal and external conversions are forms of radiationless decays. _____

f) Fluorescence emission wavelengths are always longer than the excitation wavelengths. _____

g) The TCD is sensitive only for fluoride sensitive detectors. _____

4] Spectrofluorometry can be more sensitive than spectrophotometry, why is this so?

(10 points)

5] From the cyclic voltammogram below which following mechanism would be most applicable to the observed system?

(10 points)

a) Forward $A + e^- \rightarrow A^-$ Reverse $A^- \rightarrow A + e^-$

b) Forward $A + e^- \rightarrow A^-$ Chemical Rxn $A^- \rightarrow B$ Reverse $B \rightarrow C + e^-$

c) Forward $A + e^- \rightarrow A^-$ Chemical Rxn $A^- \rightarrow B$ Reverse $A \rightarrow A^- + e^-$ & $B \rightarrow C + e^-$

d) none of the above.

For partial credit, justify you answer.

6] The van Deemter equation consists of three components. One of these is a mass transport related term. Explain how the term is affected by variations of the following variables in HPLC. Specifically answer the question as to whether band broadening increases or decreases with each of the following.

(20 points)

a) Increasing temperature

b) Decreasing stationary phase depth

c) Increasing diffusion coefficient of the solute

d) Decreasing mobile phase flow rate

7] Describe the electro-osmotic flow action of capillary electrophoresis. What is the retention time trend for cations, anions, and neutrals?

(10 points)

8] What is meant by soft ionization versus hard ionization? What types of information is obtain by each type of ionization?

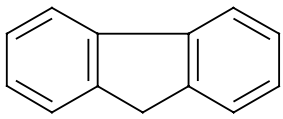
(10 points)

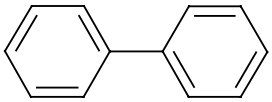
9] Beer's law ($A = \varepsilon bc$) fails under what sort of experimental conditions? Why is the non-linear region of limited analytical use?

(10 points)

10] Which of the following molecules would have a more efficient fluorescence yield and <u>why</u>?

(10 points)





11] What are the advantages of the ICP torch when compared to an acetylene/air flame in atomic emission spectroscopy? Are there any disadvantages to the ICP?

(10 points)

12] What are differences between atomic emission and atomic fluorescence spectroscopies? Why is the latter rarely used nowadays?

(10 points)

13] A sample was analyzed for a metal ion by adding 10 ml aliqouts of the unknown into five 50.0 ml volumetric flasks. To each flask was added a various volumes (0, 10, 20, 30, & 40 ml) of 12.2 ppm standard solution of this metal ion. Each flask was then diluted to 50.0 ml. Atomic absorption analyses was conducted on each sample. Absorbance was plotted versus standard addition volume. A linear regression analysis of the data yielded the following relationship.

$$y = 8.81 \times 10^{-3} x + 0.202$$

Calculate the concentration of the metal ion in the sample.

$$A = \frac{kV_s c_s}{V_t} + \frac{kV_x c_x}{V_t}$$

(15 points)

7] **10 points** Fill in the blank with a correct answer.

a) Concentration polarization is a form of _____

b) Charge-transfer polarization is also known as _____

c) An amperostat is a _____ device

d) Electrodes of the first kind are in equilibrium with a _____ in contact with a _____

e) Electro-separation of metal ions are accomplished by a controlled _____ electrolysis.