Florida International University
Department of Chemistry & Biochemistry
Instrumental Analysis
CHM-4130 Fall 2010

2nd Midterm Exam
PRACTICE TEST

Part I Definitions (2 points each)

Using one or two sentences define or explain the construction and function: (use graphs or formulas if you need)

1) Pneumatic nebulizer

2) Inductive Coupled Plasma Source

3) Monoisotopic mass of an element

4) X-ray Florescence spectrometer

5) Molecular absorptivity coefficient

6) Chromophore

7) $\sigma \rightarrow \sigma^*$ transition

8) Intersystem crossing from S1 to T1 energy levels.

9) Stokes Shift

10) $A+B \rightarrow C^* + D \quad C^* \rightarrow C + h\nu$

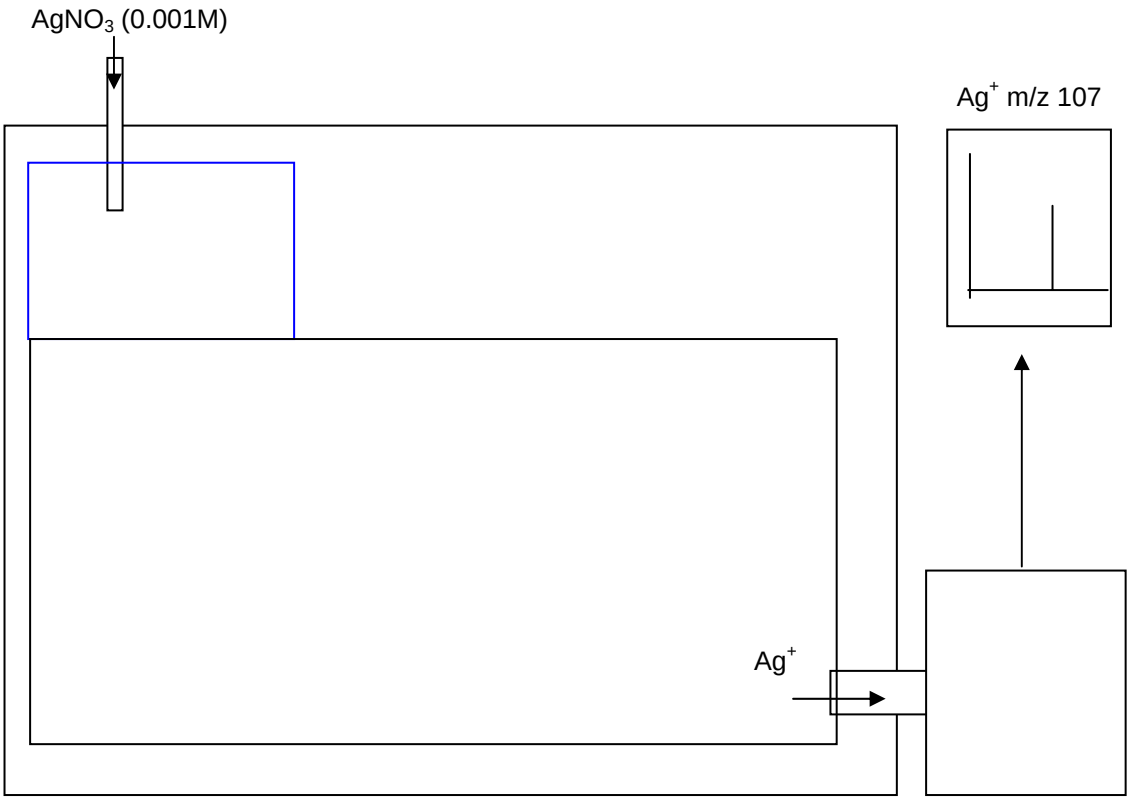
Part II Short Essay/Short Problems: (10 points each)

1) Explain at least two techniques that can be used for the simultaneous detection of multiple elements in aqueous samples. Show a diagram of the proper instrumentation.

2) Define the terms on Beer's Law and name two factors that contribute to deviations from it.

3) Give a detailed explanation using energy diagrams for the processes involved in the following electronic transitions: $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$. Use a generic formaldehyde molecule to show the electrons involved. Which transitions are favored in the visible range of 380-700 nm?

4) Fill in the diagram with anything you need to detect Silver Ions from a solution of 0.001M silver nitrate. Justify your selections and be careful with the geometry of the diagram.


AgNO3 (0.001M)
Ag+ m/z 107
Ag+

Part III Problems:

1) A photometric titration curve is a plot of absorbance vs volume of titrant. Propose what equipment should be used, and show the results you expect for the following titrations:

   a) Titration of a non-absorbing species to a non-absorbing product with a colored titrant ($\varepsilon_s = \varepsilon_p = 0$, $\varepsilon_t > 0$)
   b) Formation of a colored product from colorless reactants ($\varepsilon_s = \varepsilon_t = 0$, $\varepsilon_p > 0$)

   Make sure you draw the titration curves and explain them and show the equivalency point.

3) Please pair electronic transitions with the following molecules. Elaborate on their possible λmax and ε's. They may be multiple answers!

Transition

$\sigma \rightarrow \sigma^*$

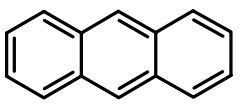
$\pi \rightarrow \pi^*$

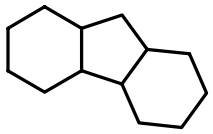
$n \rightarrow \sigma^*$

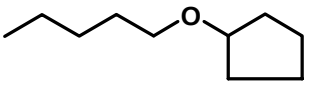
$n \rightarrow \pi^*$

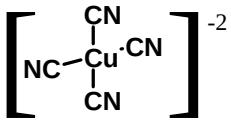
$d \rightarrow d^*$

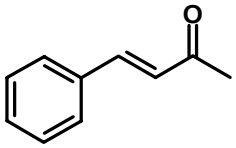
$f \rightarrow f^*$.



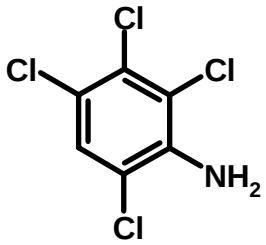








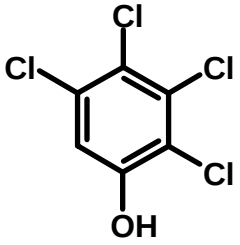
2) Here is a real life analytical challenge! You have to analyze a sample for these two compounds :



(1) 2,3,4,6-Tetrachloroaniline

K_b 3.8 x 10^{-10}

λ max : 252 nm
ε max: 1000



(2) 2,3,4,5-Tetrachlorophenol

K_a 1.3 x 10^{-10}

λ max : 254 nm
ε max: 1000

They are highly soluble in most organic solvents and the dissolve in water to a lesser extent. You also know that when a solution of compound (1) is measured at pH 4 the maximum of its absorption spectra shows a hypsochromic (blue) shift from 252 to 220 nm. In contrast, when a solution of compound (2) is measured at pH 10, a bathochromic (red) shift is observed and the absorption maximum appears now at 287 nm instead of 254 nm. The ε_{max} of the new peaks are not affected by the shift. Given this findings and the data on Table 1 answer the following questions:

a) How will you manage to determine both compounds in the same sample/solution?
b) What reactions/transformations/transitions/electrons are involved?
c) Which solvent would you choose to do the analysis and why?
d) If you decide to change the pH of the solution how would you do it ?
e) What will be your sequence of events?

Table 1. Solvents for UV-Visible Analysis

Solvent	Approximate Transparency minimum (nm)
Water	190
Ethanol	210
n-Hexane	195
Cyclohexane	210
Benzene	280
Diethyl ether	210
Acetone	330
1,4-Dioxane	220

Study Guide

Chapters covered 8 Introduction to Optical Atomic Spectrometry to (included) 14 Applications of UV-VIS Molecular Absorption Spectrometry

NOT INCLUDED:
8A-2, 8A-3
11B-1, 11-F
12B-4, 12C-3, 12D-3, 12E
13C-2
14D-3, 14F, 14G

Important concepts

Atomic energy diagrams
Difference between neutral atoms and ions in the diagram
Emission, Absorption and Fluorescence spectra
Nebulizers, flame compositions and temperature
Atomization for liquids, solids and gases
The processes leading to formation of an atom in the gas phase
Radiation sources (HCL, EDL) and instrument configurations (single vs double beam)
The ICP torch and its applications (MS, OES)
Single element vs multielemental
Polychromators
General terms in mass spectrometry m/z nominal mass, isotopes etc
Generic mass spectrometry
Mass analyzers (be able to define 2)
ICP-MS with multiple sample introduction techniques
Performance of ICP-MS vs ICP-OES , Flame AA and GFAA
Other sources for Atomic mass spectrometry
Generation of x-rays
The x-ray emission and absorption spectrum
Uses of Bragg's Law
Difference between energy and wavelength dispersive instruments
XRD, XRF
Beer's Law
%T, A, losses and limitations
Soectral resolution
Components of UV-Vis instruments
Be prepared to produce a diagram of a typical UV-VIS system
The jablonsky diagram, electronic states, transitions and chromophores
Shifts (hypo, hyper, batho, hypso)
Produce or interpret colorimetric titration curves based on the absorptivity of reactant, titrant and product