GROUP QUESTION
Groups of 3-5 will have 10-20 minutes to discuss this problem TOGETHER and arrive at a solution. Then INDIVIDUALLY each member will explain the reasoning for that answer. Answer the question on this page, if you have room, adding pages as needed. Paper is provided. (There are 6 other questions on this exam).

1. (12 pts + 12 pts) As shown in the figure below, \( p \)-aminophenol is oxidized in solution to a quinoneimine. The quinoneimine then rapidly hydrolyzes to quinone. The quinone can be reduced to hydroquinone. The potentials given in the figure are versus the standard \( \text{Ag/AgCl/sat'd KCl} \) reference which is also the reference electrode used in the following experiment. Using a three electrode potentiostat a cyclic voltammogram was run on an aqueous solution containing 2 mM \( p \)-aminophenol and enough inert electrolyte to prevent iR drop problems. Sketch the voltammogram for a voltage scan initiated at 0.0 V, scanned to +1 V and then back to 0.0 V (one cycle) and explain your reasoning. You may ignore non-Faradaic currents in your sketch, but be sure to indicate the relative sizes, shapes, and positions of any Faradaic current features.

When the group has arrived at a decision, individually write an answer to the question. Be sure to explain your reasoning.

\[
\begin{align*}
\text{OH} & \quad \Leftrightarrow \quad 2 \text{e}^- + 2 \text{H}^+ + \quad \text{E}^+ \text{ vs Ag/AgCl} = 0.60 \text{ V} \\
\text{NH}_2 & \\
\text{O} & \quad \text{NH} & \\
\text{NH} & \quad \text{O} & \quad \text{OH}_2
\end{align*}
\]

fast hydrolysis, complete reaction

\[
\begin{align*}
2 \text{e}^+ + 2 \text{H}^- & \quad \Leftrightarrow \quad \text{E}^+ \text{ vs Ag/AgCl} = 0.38 \text{ V}
\end{align*}
\]
1. (12 group + 12 individual) Group question (on separate page).

2. (12 pts) Shot noise is a fundamental source of noise that is associated with semiconductor devices and phototubes. Can an RC filter be designed to effectively minimize this source of noise? Why or why not? (Do NOT design the filter.)

3. (12 pts) What problem can arise when using an amplifier with a low input impedance?

4. (14 pts) Dual slope analog to digital converters (ADC’s) are used for a variety of applications. Explain how this ADC works.

5. (12 pts) What is the difference between a method with a high sensitivity and a method with a low detection limit?

6. (12 pts) Why is voltammetry usually run in a quiet solution with a large excess of an inert supporting electrolyte?

7. (14 pts) What is $E_{out}$ for the circuit below? The resistors have tolerances of ±1%. Express your answer to the proper number of significant figures.

![Circuit Diagram]

I PLEDGE ON MY HONOR THAT DURING THE EXAM I HAVE NEITHER GIVEN NOR RECEIVED ASSISTANCE NOR HAVE I SEEN ANY DISHONEST WORK.

If you feel you can’t sign this, contact the instructor (e-mail or in person)
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2. (12 pts + 12 pts) You work in an environmental analysis lab and are assigned the task developing a method to analyze for \( p \)-nitrophenol in wastewater samples where concentrations of 1-10 ppm are expected. \( p \)-nitrophenol is colorless to slightly yellow in color, mp 113-114°C, readily sublimes. The nitro group reduces at \( E^\circ = -1.1 \) V and the phenol group oxidizes at \( E^\circ = +0.70 \) V.

Three instruments capable of doing the job are available: a GC with a thermal conductivity detector, an HPLC with a variable wavelength UV-vis detector, and a differential pulse electrochemical analyzer. Which method would you choose for this task? Explain why you would choose that method and why you would not choose the others. Consider such things as: performance characteristics, sample prep, ease of operation, disposal, reagents required, potential interferences, etc.
8. (12 group + 12 individual) Group question (on separate page).

9. (12 pts) What are the advantages and disadvantages of using a refractive index detector in HPLC?

10. (12 pts) What is the difference between adsorption and partition separation modes in chromatography?

11. (12 pts) In general why are mirrors the preferred optics in a spectrometer instead of lenses?

12. For each pair of conditions, which will produce the smaller (better) H in a chromatographic separation?
   a. (7 pts) A 46 mm diameter column packed with 5µm diameter particles or packed with 10 µm diameter particles of the same type of packing material? Explain your reasoning.
   b. (7 pts) Analytes with diffusion coefficients around $10^{-6}$ cm$^2$/s or analytes with diffusion coefficients around $10^{-3}$ cm$^2$/s? Explain your reasoning.

13. (12 pts) In capillary electrophoresis electroosmotic flow (flow of uncharged solvent) plays a significant role in effecting separations. However, pumps are not used in electrophoresis, so how are uncharged solvent molecules induced to flow?

14. Using the chromatogram below and the ruler supplied, calculate:
   a. (7 pts) the selectivity ($\alpha$) for the last two peaks.
   b. (7 pts) number of theoretical plates (N) using the last peak.

The first peak is the void volume peak (unretained). Show your measurements on the figure and your calculations on a separate page. Pay attention to significant figures as well.
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1. (12 pts + 12 pts) You are an employee in an analytical lab. Your boss is asked to prepare a bid to determine nitrate levels in South Dakota well waters for the state Department of Agriculture. A contract would require analysis of several hundred water samples from across the state that would arrive in lots of 10-20 samples at a time. You are to:
   a. Identify three possible instrumental methods that could be used and two advantages and two disadvantages for each.
   b. Recommend a method and explain why you chose it and why you did not choose the other two.
1. (12 group + 12 individual) Group question (on separate page).

2. (12 pts) Calmagite (an organic sulfonic acid) forms a 1:1 complex with Ca\(^{2+}\) that has a wine-red color in a pH 10 solution. A 100 ppm Ca(Calmagite)\(^{-1}\) solution is analyzed for Ca by flame atomic absorption spectroscopy (AA) and by UV-VIS absorption spectroscopy (Spec 20 or Ocean Optics type instrument). Both techniques utilize radiation in the UV region. The absorption bands (lines) observed in the AA are very narrow (<0.5 nm) but the bands in UV-VIS are very broad (>100 nm). What are the reasons for the big differences in the band widths?

3. (12 pts) In general, spectroscopic techniques involve either absorbance or emission of electromagnetic radiation. The names for spectroscopic techniques typically identify the portion of the electromagnetic spectrum involved in the technique. However, Nuclear Magnetic Resonance and Electron Spin Resonance do not mention the spectral region at all but do include the term “resonance.” What is it about NMR and ESR that make them different from the other spectroscopic techniques and what’s this “resonance” thing all about? (These questions are related and may be addressed together or separately - whatever way works for you).

4. (12 pts) Briefly explain how a photomultiplier tube is constructed and how it works.

5. (14 pts) Our FTIR has a triglycine sulfate detector. Explain how this detector works.

6. (14 pts) Explain how a Zeeman background corrector for an AA works.

7. (12 pts) Specular reflectance and attenuated total reflectance (ATR) are two techniques for obtaining IR spectra of solid samples. What is the difference between these two techniques?