CHEMISTRY 447 **EXAM #1** **WINTER 2001**

Please answer all questions in a blue exam booklet and make sure you put your name on the cover. Good Luck!!

1. Please indicate the number that corresponds to the best response for each question statement below (3 points each).

a) With respect to operational amplifiers, in general it can be said that

       1. they exhibit very high output impedances
       2. they exhibit essentially zero output when there is zero input
       3. they exhibit infinite gain

b) Thermal or Johnson noise occurs within instruments as a result of

       1. random hopping of electrons across p-n junctions
       2. random jumps in temperature in the surrounding environment
       3. random movement of electrons in resistive elements of circuits

c) Felgett's advantage in fourier transform methods refers to

       1. The S/N enhancement that results from the ability to reduce noise by appropriate RC filters
       2. The S/N enhancement that results from all radiation of all wavelengths striking the detector at the same time
       3. The S/N enhancement that results from the ability to signal average multiple spectra acquired rapidly via the fourier transform method

d) Voltage follower circuits are commonly used as

       1. The initial input stage of high quality pH meters so that cell voltages arising from the glass pH electrode and associated reference electrode can be measured accurately
       2. Within conductivity meters often used as detectors in ion chromatography
       3. To determine the null point within a Wheatstone bridge arrangement

e) Modulation of analytical signals, especially in spectroscopy, is often employed to

       1. Reduce flicker noise arising from drift of amplifiers within instruments
       2. Reduce the noise associated with scattering from dust particles in the sample
       3. Enhance the signal by using high intensity bursts of radiation rather than a continuous beam of light

f) Analytical recovery studies are used to

       1. Determine whether given analytical method exhibits high precision
       2. Determine whether a given analytical method exhibits adequate selectivity to obtain accurate results
       3. Determine whether a given analytical method suffers matrix effects because the sensitivity toward analyte in standards is not the same as for the analyte in the sample

g) In Fourier transform instruments

       1. An array of detectors is used to obtain intensity information for a wide range of electromagnetic frequencies at the same time

2. A single detector is used and the intensity vs. time is recorded for all the frequency components at the same time

3. The fourier transform is required to convert the frequency domain spectrum into a time domain spectrum

f) The purpose of a lock-in amplifier in analytical instrumentation is to:

1. Amplify all high frequency signals within the analytical signal into DC signals that can be easily measured

2. Amplify and/or convert only an analytical signal, modulated at a specific frequency, into an easily measured DC signal.

3. Lock-in on only the analytical signal that has the greatest mean value.

2. Please answer the following questions about the circuit shown below (<u>note</u>: there are two separate voltage sources in this circuit!!!):

R1=1000 ohms

R3= 5000 ohms

R2=1000 ohms

Vs = 5 V

C = 10 uF

Vs = 5V
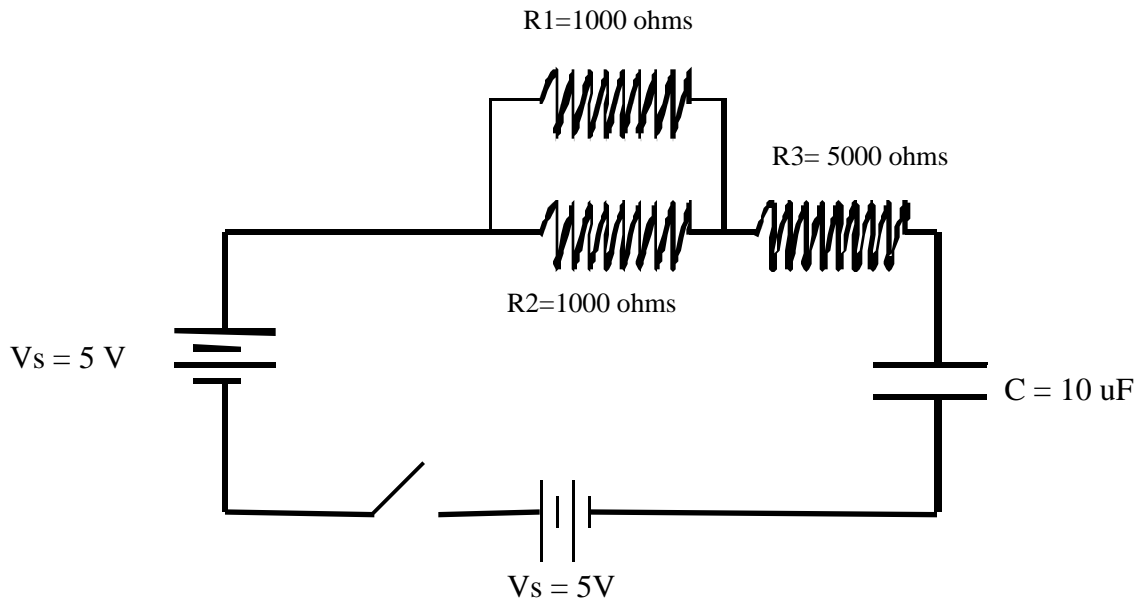
a) What is the potential across resistors R3 0.1 seconds after the switch is closed ?(8)

b) What is the % error in the measurement of the voltage across resistor R3 at t=0 immediately after the switch is closed if the voltmeter used had an internal resistance of 10 k . (8)

c) If the two voltage supplies were combined and made into a single AC source (and no voltmeter was present in circuit)---what would be the shape of the curve for plotting the output voltage across capacitor C (V_c) over the input voltage of the source as a function source voltage frequency. Put a value on the frequency axis to show where there would be the largest change in the output voltage as a function of input Vs frequency (5)

3. With regard to general quantitative instrumental analysis, concisely explain the difference between a standard addition technique and an internal standard method. Indicate the appropriate equations that relate to each method and explain under what circumstances each should be used to quantitate a given analyte in an unknown sample. (10)

4. Sketch a circuit configuration that would allow any operational amplifier to be employed to accurately measure an unknown voltage originating from a high impedance source without amplification of the value. What is this arrangement called? Explain why the output voltage from the amplifier could be measured with a relatively low impedance voltmeter and still accurately reflect the unknown voltage value? (10)

5. An electrochemical enzyme electrode can be used to monitor the concentration of glucose in whole blood. It is based on measuring the anodic current arising from the oxidation of hydrogen peroxide (H_2O_2), generated by an immobilized enzyme—called glucose oxidase---at the surface of a small platinum electrode. The current produced is linearly proportional to glucose concentration in the sample. However, certain other components in blood can interfere with the measurement, especially the drug acetaminophen (tylenol), which can also be oxidized at the platinum electrode to yield a current under the same experimental conditions. For a given glucose electrode, it was found that the response to 1 mM glucose was 100 nA (nanoamps) and the response to a separate solution of 5 mM acetaminophen was 75 nA. In the absence of either species, the current was found to be essentially zero. Based on this information, calculate the absolute and % error in the measurement of a blood sample containing 3 mM glucose, if the patient's blood also contained 5 mM acetaminophen (patient had a headache that day and ingested this drug!!!) (assume no matrix effects in terms of electrochemical response to species in blood vs. aqueous solutions). (10)

6. What is the mathematical/statistical meaning when it is stated that "the detection limits of a given instrumental method are 10 ppb (10 parts per billion) at a signal to noise (S/N) ratio of 3? If one defined the detection limit to occur when S/N = 2, would this mean your minimal detectable concentration of analyte was lower than when the criteria was S/N=3? Briefly explain! (10)

7. Briefly define the following terms (1-2 sentences!) (5 pt each):

   a) continuum source
   b) multiplex advantage
   c) incoherent source of radiation