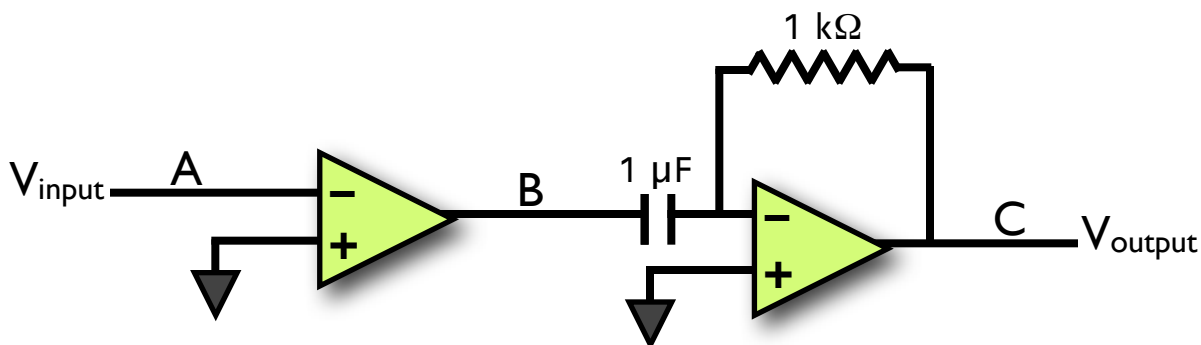


Chemical Instrumentation
CHEM*3440
Mid-Term Examination
Fall 2006
Tuesday, October 24

Duration: 2 hours. You may use a calculator. No additional aids will be necessary as a series of data and equation sheets are included as part of the examination.

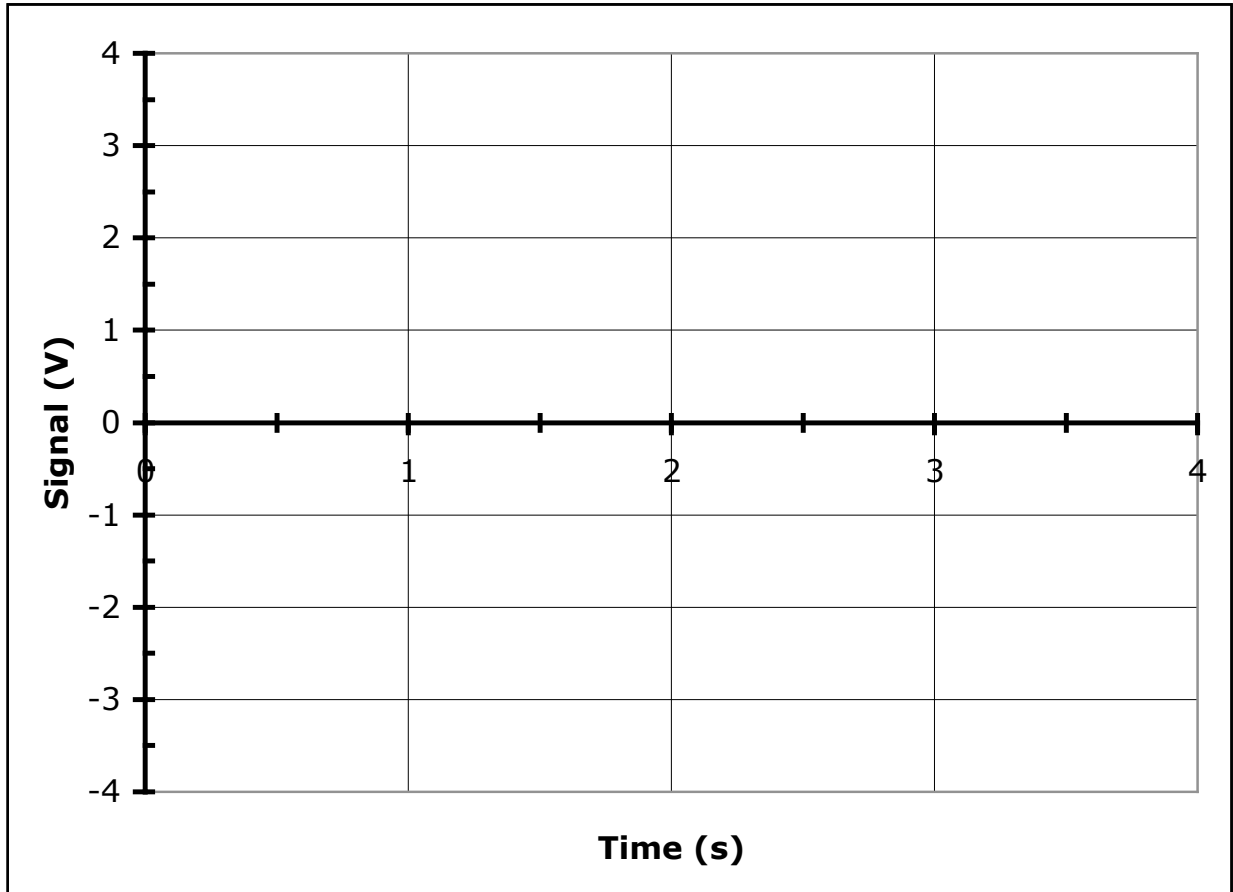
1. (10 points) Analyze the following operational amplifier circuit. The op amps are driven with a ± 3.00 V power supply.



The input signal is a sine wave whose behaviour is described by the following equation:

$$V_{in}(t) = 1.00\text{ V} + 1.50\text{ V} * \cos(2\pi t) \quad (t \text{ measured in seconds})$$

- What name describes the function of the first operational amplifier?
- What name describes the function of the second operational amplifier?
- On the accompanying graph (next page), carefully sketch and label the behaviour of the voltage at the three positions labelled A, B, and C. Overlay them on the graph and clearly label them. (Suggestion: Make B a dashed line and the three curves will be more clearly distinguishable.)
- A common assumption is that after 5 time constants, a circuit has essentially reached its final value. How long does it take for this circuit to settle to its final value following a change at the input?



2. (6 points) (a) Compare a Flash and a Staircase ADC (analog-to-digital converter). Discuss the relative complexity of construction, resolution, conversion times, and anything else you feel is pertinent.

(b) You have a 10-bit DAC operating over the range of 0 to +5V.

(i) In millivolts, what is the magnitude of an incremental step in the output voltage?

(ii) In volts, what is the output voltage corresponding to the number 291?

3. (12 points) Describe each of the following terms in a couple of sentences each.

(a) Conductivity

(b) Hyperchromic

(c) Drift

(d) White noise

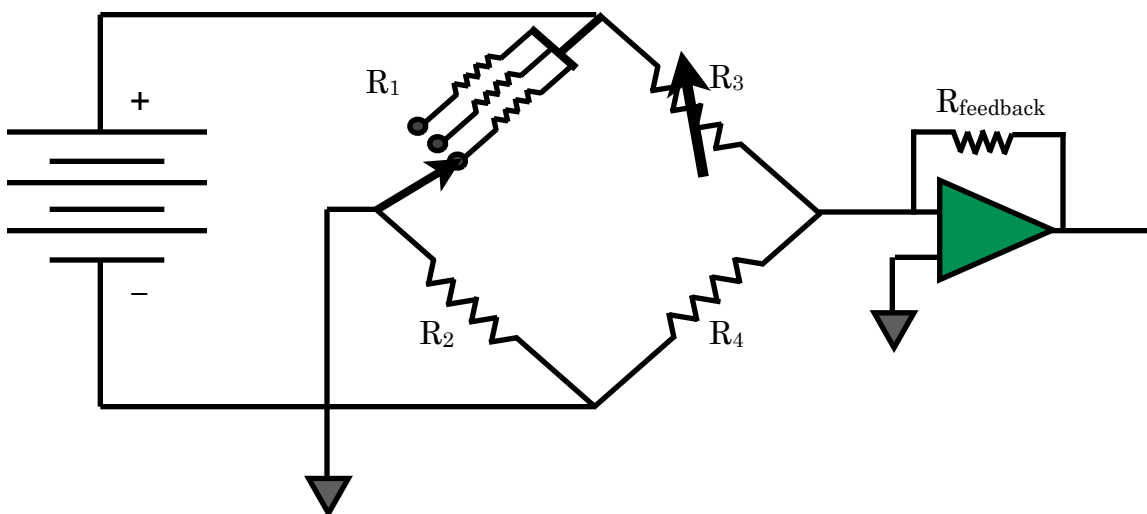
(e) Ensemble Averaging

(f) % Transmittance

4. (4 points) A resistance thermometer is a device whose resistance changes with temperature. Below is one used in a Wheatstone Bridge configuration with an error signal measurement. $R_2 = R_4 = 1.000 \text{ k}\Omega$. R_3 is the temperature sensor. R_1 is an adjustable precision resistor which can be adjusted to one of three positions $100 \text{ }\Omega$, $200 \text{ }\Omega$, or $500 \text{ }\Omega$ and thereby adjust the range setting for the instrument.

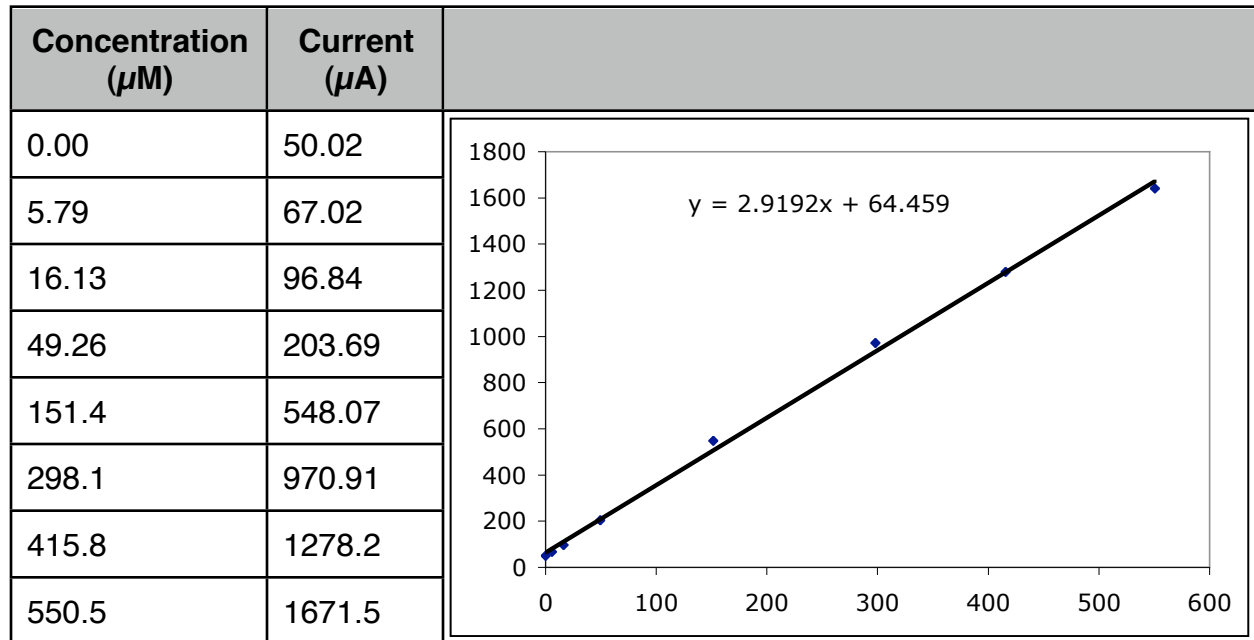
(a) At a particular temperature, the sensor has a resistance of $120 \text{ }\Omega$. To which resistor should R_1 be set for in order to give the best sensitivity to the instrument and why?

(b) If the error signal produces a current of $+10 \text{ }\mu\text{A}$, what should the value of R_{feedback} be in order to provide an output signal of -100 mV from the current-to-voltage amplifier?



5. (4 points) A substance with a molar absorptivity of $850 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm is found in a solution of unknown concentration. A cell with a path length of 1.00 cm is used in a spectrometer and the %transmittance found for the solution at 500 nm is 30% . What is the concentration of this compound in the solution?

6. (15 points) The following data were obtained in the calibration of an electrochemical sensor. Each data point in the calibration data is the average of three measurements. Also shown is the graph of the calibration curve.



The two fit parameters are y-intercept $b = 64.459 \mu\text{A}$ and slope $m = 2.9192 \mu\text{A}/\mu\text{M}$. Other fit data are the variance of the fit = $211.49 \mu\text{A}^2$ and the value of the determinant of the A matrix is $11959587.5 \mu\text{M}^2$. The sum of the concentration is $1486.98 \mu\text{M}$ while the sum of the squares of the concentration is $590445.71 \mu\text{M}^2$.

- What is the variance of the parameter b ?
- What is the standard deviation of the parameter m ?

An unknown sample was measured 5 times and the average signal was $683.6 \mu\text{A}$.

- What is the concentration of the unknown sample?
- What is the variance of the unknown sample?
- What are the 95% confidence limits for the concentration of this sample?

Equations

Statistics

$$\begin{pmatrix} b \\ m \end{pmatrix} = \mathbf{p} = \mathbf{A}^{-1} \mathbf{y} = \frac{1}{D} \begin{pmatrix} \sum x_i^2 & -\sum x_i \\ -\sum x_i & n \end{pmatrix} \begin{pmatrix} \sum y_i \\ \sum x_i y_i \end{pmatrix}$$

The parameter vector \mathbf{p} is solved in this matrix equation. Note that the determinant of \mathbf{A} is defined here as D .

$$\text{where } D = \det(\mathbf{A}) = n \sum x_i^2 - (\sum x_i)^2$$

$$s_{fit}^2 = \frac{\sum (y_i - y_{i,fit})^2}{\nu} = \frac{\sum (y_i - mx_i - b)^2}{n - 2}$$

This is the variance of the fit.

$$\mathbf{V} = s_{fit}^2 \mathbf{A}^{-1} = \frac{s_{fit}^2}{D} \begin{pmatrix} \sum x_i^2 & -\sum x_i \\ -\sum x_i & n \end{pmatrix}$$

This is the variance-covariance matrix and shown below are the diagonal terms which are the variances for the parameters.

$$s_b^2 = V_{11} = \frac{s_{fit}^2 \sum x_i^2}{D}$$

$$s_m^2 = V_{22} = \frac{s_{fit}^2 n}{D}$$

$$x_{CC} = \frac{(\bar{y} - b)}{m}$$

This expression finds the concentration of an unknown sample by using a calibration curve.

$$\begin{aligned} s_{x_{CC}}^2 &= \left(\frac{\partial x_{CC}}{\partial \bar{y}} \right)^2 s_{y, meas}^2 + \mathbf{d}_{CC}^T \mathbf{V} \mathbf{d}_{CC} \\ &= \frac{s_{fit}^2}{m^2} \left\{ \frac{1}{\bar{p}} + \frac{1}{D} (nx_{CC}^2 - 2x_{CC} \sum x_i + \sum x_i^2) \right\} \end{aligned}$$

This expression gives the variance for the concentration found for an unknown from a calibration curve experiment.

$$\text{Answer} = x_{\text{average}} \pm \frac{ts}{\sqrt{n}}$$

Here is how one can report a final answer and include confidence interval limits.

Student's t-factor Table

Degrees of Freedom	50%	90%	95%	99%	99.9%
1	1.000	6.314	12.706	63.656	636.578
2	0.816	2.920	4.303	9.925	31.598
3	0.765	2.353	3.182	5.841	12.924
4	0.741	2.132	2.776	4.604	8.610
5	0.727	2.015	2.571	4.032	6.869
6	0.718	1.943	2.447	3.707	5.959
7	0.711	1.895	2.365	3.500	5.408
8	0.707	1.860	2.306	3.355	5.041
9	0.703	1.833	2.262	3.250	4.781
10	0.700	1.812	2.228	3.169	4.587
60	0.679	1.671	2.000	2.660	3.460
∞	0.674	1.645	1.960	2.576	3.291

Electrical Properties:

Current Density: $J = I/A = Q/tA = nqv = nq^2Em = nqE\mu$ where $\mu = \text{mobility} = qm$

Conductivity: $\sigma = J/E = nq\mu$

Resistivity: $\rho = 1/\sigma$

Ohm's Law: $V = IR$ or $I = GV$

Conductance: $G = \sigma A/L$ Resistance: $R = \rho L/A$

Power: $P = IV = I^2R = V^2/R$

Voltage Divider Equation:
$$V_j = V_{total} \left[\frac{\sum_{j \neq i} R_j}{\sum R_i} \right]$$

Capacitance and Inductance:
$$i(t) = C \frac{dv(t)}{dt} \qquad v(t) = L \frac{di(t)}{dt}$$

Time evolution of RC circuit:
$$V_{output} = V_{max} e^{-t/\tau}$$

Time constant: $\tau = RC$

Reactance:
$$X_C = \frac{1}{2\pi fC} \qquad X_L = 2\pi fL$$

Impedance:
$$Z = \sqrt{R^2 + X^2}$$

RMS and P-P Signal-to-Noise:
$$N_{RMS} = \frac{1}{2\sqrt{2}} N_{p-p}$$

S/N:
$$\frac{S}{N} (\text{dB}) = 10 \log_{10} \frac{P_{\text{signal}}}{P_{\text{noise}}} = 20 \log_{10} \frac{V_{\text{signal}}}{V_{\text{noise}}} = 20 \log_{10} \frac{I_{\text{signal}}}{I_{\text{noise}}}$$

Thermal Noise:
$$V_{noise,rms} = \sqrt{4k_B T R B}$$

Shot Noise:
$$I_{noise,rms} = \sqrt{2q I_{dc} B}$$

Operational Amplifiers:

Current Amplifier: $V_{output} = -i_{input} R_{feedback}$

Voltage Amplifier: $V_{output} = - [R_{feedback}/R_{input}] V_{input}$

Integrator:
$$V_{output}(t) = -(1/R_{input} C_{feedback}) \int V_{input}(t) dt$$

Differentiator:
$$V_{output}(t) = -R_{feedback} C_{input} dV_{input}(t)/dt$$

Nyquist criterion: $f_{nyquist} = 1/2\Delta$ where Δ is the sampling interval

Spectroscopy

Photon Energy Units: $E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$

Transmittance: $T = P_{\text{sample}}/P_{\text{reference}}$

Absorbance: $A = \log_{10} [P_{\text{reference}}/P_{\text{sample}}]$

Beer's Law: $A = \log_{10}[P_0/P] = \epsilon bc$

Photometric Accuracy: $\Delta c = \frac{1}{\epsilon b} \Delta A = -(\log_{10} e) \frac{1}{\epsilon b T} \Delta T$

Grating Equations:

Fundamental equation: $\sin(\alpha) + \sin(\beta) = kN\lambda$

Angular Dispersion: $\frac{d\beta}{d\lambda} = \frac{kN}{\cos\beta}$

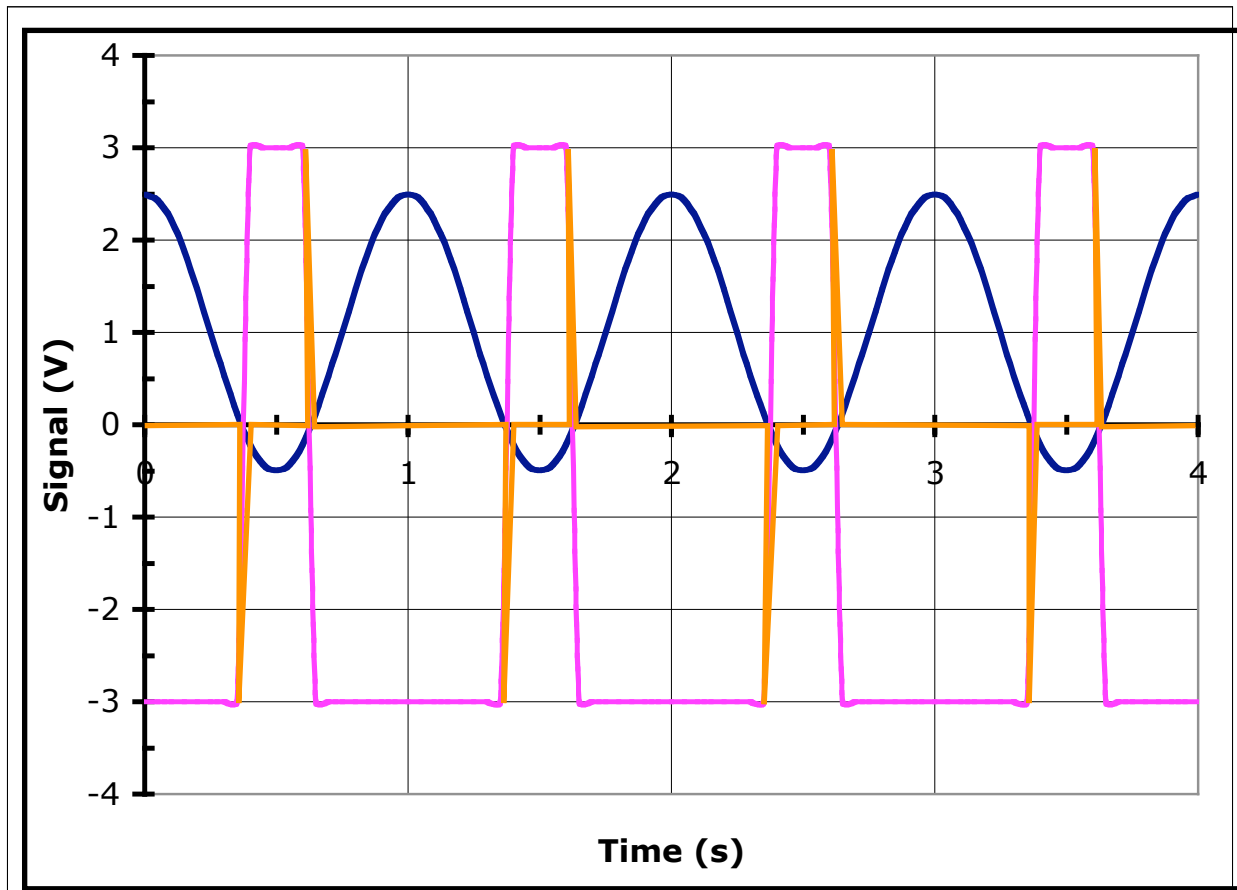
Linear Dispersion: $\frac{d\lambda}{dx} = \frac{\cos\beta}{kN L_{\text{exit}}}$

Resolving Power: $R = \frac{\lambda}{d\lambda} = kN W_{\text{grating}}$

SOLUTIONS

1. (a) The first op amp is a comparator.
- (b) The second op amp is a differentiator.
- (c) The input sine wave is asymmetric with a peak-to-peak amplitude of 3V and a period of 1 second. There should be four complete periods on the graph.

When passed through the comparator, it switches states at the zero-crossing (since the reference input is grounded on the comparator). The output is an almost square wave of opposite phase to the sine wave. It is also asymmetric; it is positive only during the small portion of time that the sine wave is below zero and it is negative for the rest of the time. My calculations put it at 25% positive.



The output of the differentiator is such that it has a large output when its input is changing and a zero output when its input is constant. Hence, we expect spikes when the square wave is changing state and zero otherwise. By making an assumption about the gain of the op amp (10^5) we can estimate the magnitude of the spike. You did not need to do this for the exam; any spike would do. However, a brief look at the sine wave, suggests that it will go through the $64 \mu\text{V}$ necessary to go from 0 to the maximum output of 3 volts in about $6 \mu\text{sec}$. The output of the comparator is changing 3 V during this time

so the rate is 500,000 V/sec. Put this in the expression for the output of the differentiator and we spike is calculated to have a magnitude of 500 V. But since the op amps can only output ± 3 V, the output reaches the maximum 3 V and then decays back to 0. The sign of the pulses is opposite to that taken by the square wave. The calculation in part (d) below indicates that it reaches 0 in about 5 msec. This is 1/200 of a second. This would not be observable on this graph. However, for our visualization purposes, I will accept any pulse that goes to the maximum 3 V or any voltage less and decays to 0 in some fashion. It should go in the opposite direction of the square wave. The peak should not go to infinity because the op amps are only powered to ± 3 V. The acceptable graph is shown above.

Point A is in deep blue, point B is in light pink, and C is in orange.

(d) It takes time to charge the capacitor to its final value and the feedback resistor puts a limit onto the magnitude of the current that can flow to accomplish that charging. The product RC is the time constant for that circuit.

$$\tau = RC = (1 \text{ k}\Omega) (1 \mu\text{F}) = (1000 \Omega) (0.000001 \text{ F}) = 10^3 \Omega \cdot 10^{-6} \text{ F} = 10^{-3} \text{ s} = 1.0 \text{ msec}$$

Five life times is, of course, 5.0 msec, the settling time for this circuit.

2. A staircase ADC sequentially increments the comparison voltage from the lowest value and increases it until a comparator changes state, indicating the value of the output voltage being equal to that of the test voltage. The conversion time depends upon the speed of the circuit to march through these values. It also varies with the size of the test voltage, larger voltages taking a longer time. If we seek higher resolution, we can decrease the size of the voltage steps, but that then increases the conversion time. Its advantages are in its relative simplicity. By contrast a flash ADC is more complex, requiring as many precision comparator circuits as there are levels of resolution. An 8 bit converter has $2^8 = 256$ resolution elements. This would require a precision voltage divider network to produce all 256 voltage levels and 256 comparator circuits to compare to the test voltage. All comparators below the test voltage will have one output state and all above will have the opposite output state. Then logic circuitry is employed to decode all 256 lines into the 8 bit word we seek. A 12 bit or 16 bit converter then would need 4096 or 65536 comparison units respectively. The virtue is that all voltages, large or small, are converted in a single processing step, making it very fast for all voltages, but the complexity is much greater.

(b) There are $2^{10} = 1024$ resolution elements. The 5 volt range is therefore divided into $5\text{V}/1024 = 0.00488 \text{ V} = 4.88 \text{ mV}$ steps. The 291 step is therefore $0.00488 \text{ V} \times 291 = 1.42 \text{ V}$.

3. (a) Conductivity. The transport of charge, whether as electrons or as ions, determines a material's conductivity. The mobility of the electrons or ions in the material and also the density of charge carriers together determine how well a substance can conduct electricity. A greater mobility or a greater number density both lead to a greater conductivity. Conductivity is a property of a given substance; conductance factors in the geometry of a given piece of material.

(b) Hyperchromic. The intensity of an absorption band is influenced by the solvent in which the absorber is found. If the absorption intensity increases by switching solvent, that solvent is said to be hyperchromic for that substance.

(c) Drift. The background output signal of an electrical device will change slowly with time. This is called drift. Is the DC component of $1/f$ noise.

(d) White noise. This arises from thermal noise sources and is characterized by having the same power at all frequencies, in contrast to $1/f$ noise which decreases in the reciprocal of frequency.

(e) Ensemble Averaging. When the same spectrum is acquired many times, the summing of all the spectra will need to increase in signal proportional to the number of scans n . However, the noise, because you get a randomly subtractive event, increases only as \sqrt{n} . The signal-to-noise improves as \sqrt{n} . This is a key noise reduction strategy.

(f) %Transmittance. Transmittance is the ratio of power of light reaching the detector in an absorbance experiment when the absorber is in the light path when compared to the power when no absorber is in the light path. Since the absorber will always take some light away from the transmitted beam, the ratio is always less than 1. Sometimes the ratio is taken between a reference beam, passing through similar cell holders and solvent but only without the absorber being tested, and the absorbing test cell. This ratio, multiplied by 100, is the percent transmittance.

4 (a) Setting to the 100 resistor would be most appropriate as it is closest in value to the test sensor. This would mean that the signal is smallest and therefore we can more accurately tell the difference between two magnitudes and therefore have a greater sensitivity. It is easier to tell the difference between 1 and 2 than it is to tell the difference between 101 and 102. The first demands 50% precision while the second requires 1% accuracy.

(b) The op amp is functioning as a current-to-voltage converter. The input current times R gives the output voltage. Therefore $R = 0.100 \text{ V} / 0.00001 \text{ A} = 10\,000 \, \Omega = 10 \text{ k}\Omega$.

5. This is a straightforward application of Beer's Law.

$$A = \epsilon cb = -\log T$$

$$T = 0.30 \quad A = -\log(0.30) = 0.523$$

$$c = A/\epsilon b = 0.523/(850)(1.00) = 6.15 \times 10^{-4} \text{ M}$$

6. Note that each of the 8 points on the calibration curve is really the average of 3 points. Therefore, $n = 24$ when we are dealing with properties of the calibration curve. I have calculated and given you all of the other necessary statistical values to fit directly into the expressions found on the equation page.

(a) The variance of b is given by

$$s_b^2 = \frac{s_{fit}^2 \sum x^2}{D} = \frac{(211.49)(590445.71)}{11959587.5} = 10.44 \, \mu\text{A}^2$$

(b) The standard deviation of m is given by the variance equation. Remember to take the square root to get the standard deviation.

$$s_m^2 = \frac{s_{fit}^2 n}{D} = \frac{(211.49)(24)}{11959587.5} = 4.244 \times 10^{-4} \, \mu\text{A}^2 / \mu\text{M}^2$$

$$s_m = \sqrt{4.244 \times 10^{-4}} = 0.0206 \, \mu\text{A} / \mu\text{M}$$

(c) Now we have measured an unknown 5 times (this is "p" in the equations). By finding the average of that distribution, we have set the number

of degrees of freedom to $p - 1 = 4$. The concentration is found straightforwardly from

$$x_{cc} = \frac{(\bar{y} - b)}{m} = \frac{683.6 - 64.459}{2.9192} = 212.1 \mu M$$

(d) The variance in this result comes from the expression near the bottom of the first equation page. Don't confuse n , the number of data points making up the calibration curve (which is 24 and not 8) with the number of data points contributing to the measurement of the unknown (which is 5). We have

$$\begin{aligned} s_{x_{cc}}^2 &= \frac{s_{fit}^2}{m^2} \left\{ \frac{1}{p} + \frac{1}{D} (nx_{cc}^2 - 2x_{cc} \sum x_i + \sum x_i^2) \right\} \\ &= \frac{211.49}{(2.9192)^2} \left\{ \frac{1}{5} + \frac{1}{11959587.5} (24(212.1)^2 - 2(212.1)(1486.98) + 590445.71) \right\} \\ &= 7.125 \mu M^2 \end{aligned}$$

(e) The confidence limits need to use the standard deviation (which is the square root of the above variance), Student's t-factor (taken from the tables, recalling that the degrees of freedom is 4 and we seek a 95% confidence), and the total number of data points for the unknown which is 5. From the table, we find the t-factor to be 2.776. The standard deviation is

$$s_{x_{cc}} = \sqrt{s_{x_{cc}}^2} = \sqrt{7.125 \mu M^2} = 2.67 \mu M$$

The confidence limits are then

$$C.L.(95\%) = \frac{ts}{\sqrt{p}} = \frac{(2.776)(2.67)}{\sqrt{5}} = 3.31 \mu M$$

So the final answer for the unknown concentration is $212.1 \pm 3.31 \mu M$ with 95% confidence.