

CHEM*3440
Instrumental Analysis
Mid-Term Examination
Fall 2004

Duration: 2 hours

1. (10 points) An atomic absorption experiment found the following results for a series of standard solutions for dissolved palladium metal ion. The data were plotted in Excel and from the LINEST function, the following values of the parameters were obtained:

$$m = 0.1674 \quad b = 14.17 \quad s_m = 0.00051 \quad s_b = 0.101 \quad s_r = 0.1267$$

[Pd] ppm	Instrument Signal
0	14.1
80	27.7
205	48.4
325	68.6

- Determine the concentration (in ppm) of an unknown Pd sample whose average signal was 56.5.
- Calculate the standard deviation of this result, given that the above average was the result of 5 measurements.
- What is the 95% confidence interval for this result?

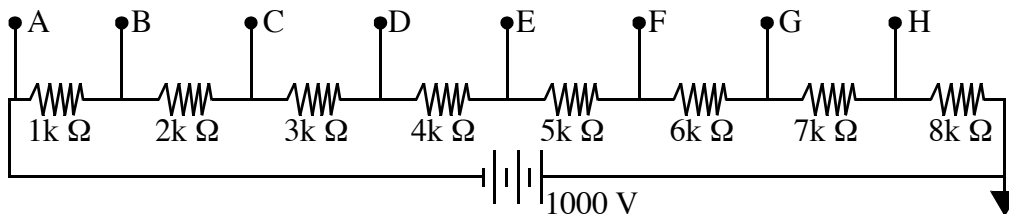
2. (10 points) The following data arose out of a determination of Cr in water. The protocol specified to run a blank, the sample and the sample with a series of added standards. Assume that the added standards did not substantively affect the solution volume.

Solution	Added Cr (ppm)	Run #1	Run #2	Run #3
Blank	0.000	0.005	0.009	0.006
Unknown	0.000	0.537	0.548	0.531
Addition 1	2.000	0.666	0.659	0.667
Addition 2	4.000	0.790	0.784	0.805
Addition 3	6.000	0.912	0.901	0.935

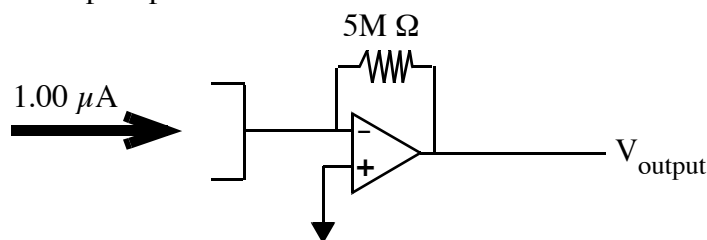
Using a graphical approach, calculate the concentration of Cr in the unknown sample.

3. (5 points) A signal is sampled at a frequency of 15.000 kHz. The signal actually consists of three sinusoidal signals at 6.301 kHz, 11.244 kHz, and 32.863 kHz. If no filtering is applied, at what frequencies would the signals appear due to signal aliasing?

4. (7 points) Below is a voltage divider network used in a photomultiplier tube. The resistors shown give an increasingly large potential step to the next dynode in the chain, assuring that the large volume of electrons are successfully accelerated to it. Calculate the potential at each step (B - H) as indicated, given that the potential at step A is that of the potential source: -1000 V.



5. (5 points) The output of the above PMT is an electron current which reaches the Faraday cup and is carried to the non-inverting input of an op amp, configured as given below. When the input current is $1.00 \mu\text{A}$, what is the voltage at the output of the op amp?



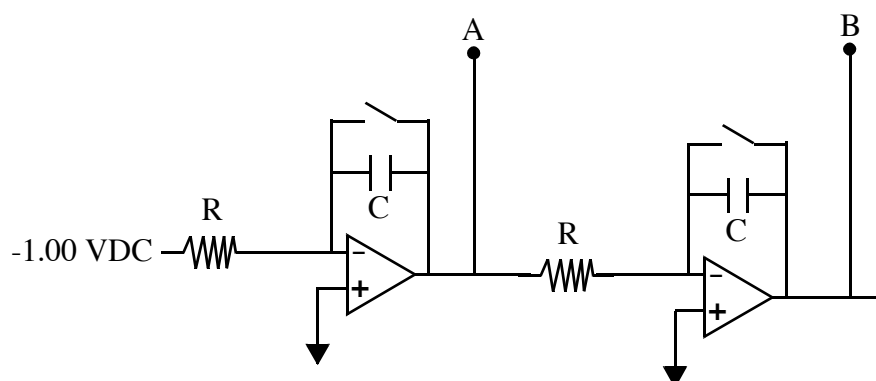
6. (8 points) A photometer with a linear response to light gave a reading of 685 mV with a blank in the light path and 179 mV when the blank was replaced by an absorbing solution. Calculate

- the percent transmittance of the sample solution.
- the absorbance of the sample solution.
- the percent transmittance expected if the solution concentration was $1/2$ of the original concentration.
- the signal (in mV) expected if the light path were doubled.

7. (9 points) Explain and relate the following collection of terms:

- Reactance, resistance, and impedance.
- Thermal noise, shot noise, and flicker noise.
- Bathochromic, Hyperchromic, and Auxochrome.

8. (8 points) Carefully draw graphs of the time vs. voltage at each of the two points labelled A and B in the accompanying operational amplifier circuit. Both resistors have the value of $100 \text{ k}\Omega$ and both capacitors have the value of $10 \mu\text{F}$. The input voltage is -1.00 V DC . Graph the evolution of the voltages for 2 seconds, assuming that the reset switches clear the potentials simultaneously at the start.



Statistics

$$\bar{x} = \frac{\sum x_i}{N} \quad s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$$

$$RSD = s/\bar{x} \quad s_{mean} = s/\sqrt{N}$$

$$S_{xx} = \sum x_i^2 - \frac{(\sum x_i)^2}{N}$$

$$s_{calc} = \frac{s_r}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_{unk} - \bar{y}_{calib})^2}{m^2 S_{xx}}}$$

$$\text{Confidence Limits: } \pm \frac{s_{calc} t}{\sqrt{N}}$$

$$\text{Analytical Sensitivity: } \gamma = \frac{m}{s} \quad \text{LOD} = 3 s_{bl} \\ \text{LOQ} = 10 s_{bl}$$

$$E = h\nu = hc/\lambda = hc\bar{\nu}$$

$$1 \text{ eV} = 8065.6 \text{ cm}^{-1} = 1.602 \times 10^{-19} \text{ J} = 241.8 \text{ THz}$$

$$A = -\log_{10} T = \log_{10} (P_o/P_T)$$

$$A = \epsilon b c$$

Photometric Accuracy

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

Noise

$$N_{RMS} = \frac{1}{2\sqrt{2}} N_{p-p}$$

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

$$\text{Thermal noise } V_{\text{noise,rms}} = \sqrt{4k_B TRB}$$

$$\text{Shot noise } I_{\text{noise,rms}} = \sqrt{2qI_{dc}B}$$

$$q = 1.602 \times 10^{-19} \text{ C} \quad k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$\text{Current Amplifier } V_o = -i_i R_f$$

$$\text{Voltage Amplifier } V_o = -\frac{R_f}{R_i} V_i$$

$$\text{Integrator } V_o(t) = -\frac{1}{R_i C_f} \int V_i(t) dt$$

$$\text{Differentiator } V_o(t) = -R_f C_i \frac{dV_i(t)}{dt}$$

Standard Addition

$$\text{Two-point } c_x = \frac{S_1}{(S_2 - S_1)} \frac{V_s}{V_x} c_s$$

$$\text{Multi-point } c_x = \frac{b}{m V_x} c_s$$

$$\Delta = \frac{1}{f_{\text{sampling}}}$$

$$f_{\text{Nyquist}} = \frac{1}{2\Delta}$$

Grating Equations

$$\sin \alpha + \sin \beta = k N \lambda$$

$$\frac{d\beta}{d\lambda} = \frac{k N}{\cos \beta} \quad \frac{d\lambda}{dx} = \frac{\cos \beta}{k N L_{\text{exit}}}$$

$$R = \frac{\lambda}{d\lambda} = k N W_{\text{grating}}$$

Electricity

$$\text{Ohm's Law } V = IR$$

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

$$X_C = -\frac{1}{\omega C}$$

$$X_L = \omega L$$

$$Z^2 = X_C^2 + X_L^2 + R^2$$

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SOLUTIONS

1. (a) We need only use the least squares parameters and solve for the unknown quantity.

$$y = m x + b$$

$$\frac{y - b}{m} = x = \frac{56.5 - 14.17}{0.1674} = 253 \text{ ppm}$$

(b) We use the equation for computing the standard deviation for a calibration curve. We have to calculate the term S_{xx} first and we need to realize that there are 5 averaged results for the unknown and 4 data points on the calibration curve. We also need the average value for the y-values used in the calibration curve. This term accounts for the fact that the closer our measurement is to the middle of the calibration curve, the more confidence we can have in its result.

$$S_{xx} = \sum x_i^2 - \frac{(\sum x_i)^2}{N} = 154050 - 93025 = 61025$$

$$\bar{y}_{calib} = \frac{\sum y_i}{N} = 39.7$$

$$s_{calc} = \frac{s_r}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_{unknown} - \bar{y}_{calib})^2}{m^2 S_{xx}}} = \frac{0.1267}{0.1674} \sqrt{\frac{1}{5} + \frac{1}{4} + \frac{(56.5 - 39.7)^2}{(0.1674)^2 (61025)}} = 0.594$$

(c) We look up the t-value from the student's t-table, and use the expression for confidence limits. Since there are 5 data points averaged to find the estimate, we have 4 degrees of freedom. Therefore, from the table, $t = 2.776$. We find

$$\text{Conf. Limits} = \pm \frac{s_{calc} t}{\sqrt{N}} = \pm \frac{(0.59)(2.776)}{\sqrt{5}} = 0.73$$

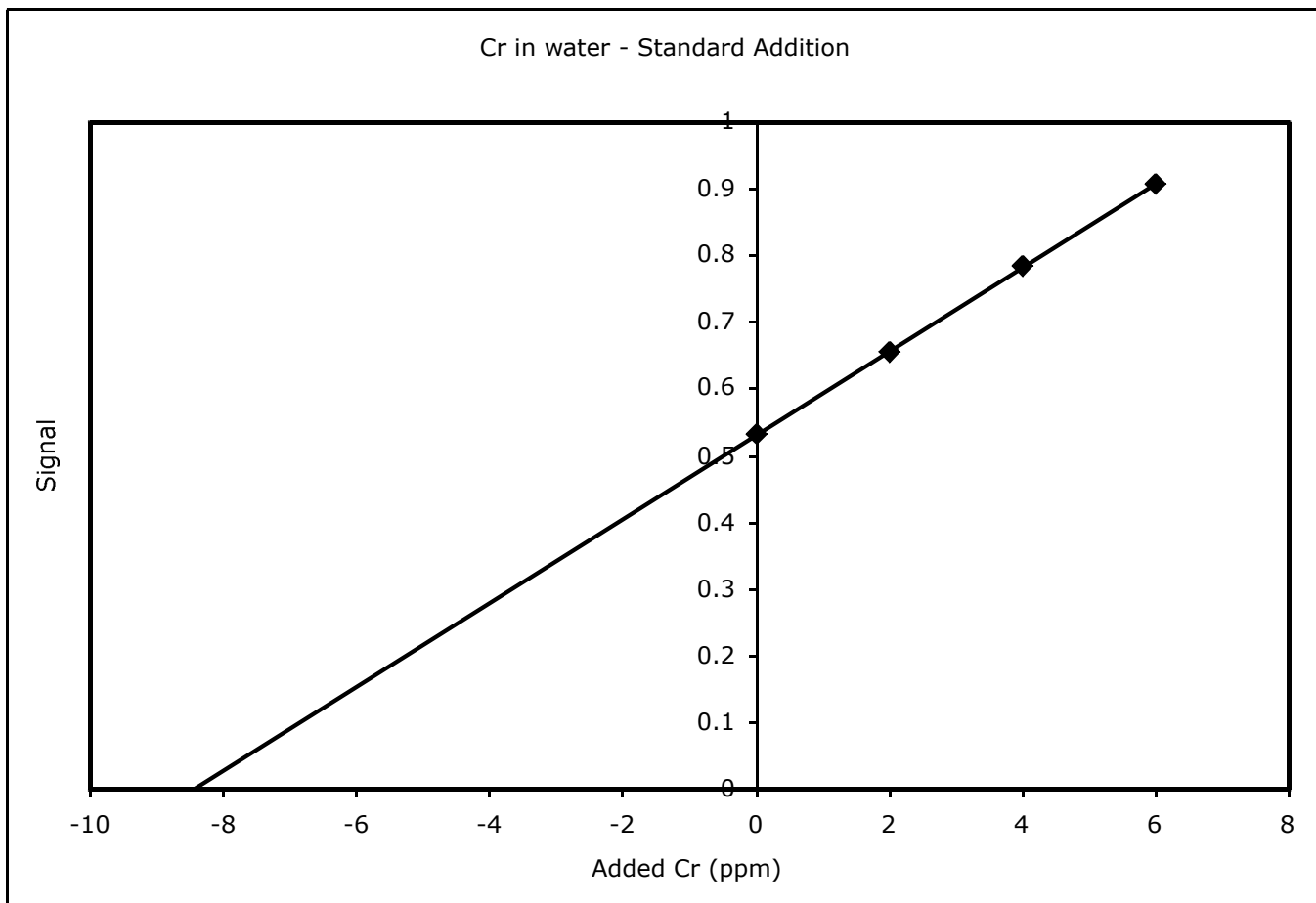
The final answer would be reported as 253 ± 1 ppm.

2. We first find an average value for the five solutions: blank, unknown, and unknown + the three additions. We obtain the data given in table.

Solution	Added Cr (ppm)	Average Signal
Blank	0.000	0.0067
Unknown	0.000	0.539
Addition 1	2.000	0.664
Addition 2	4.000	0.793
Addition 3	6.000	0.916

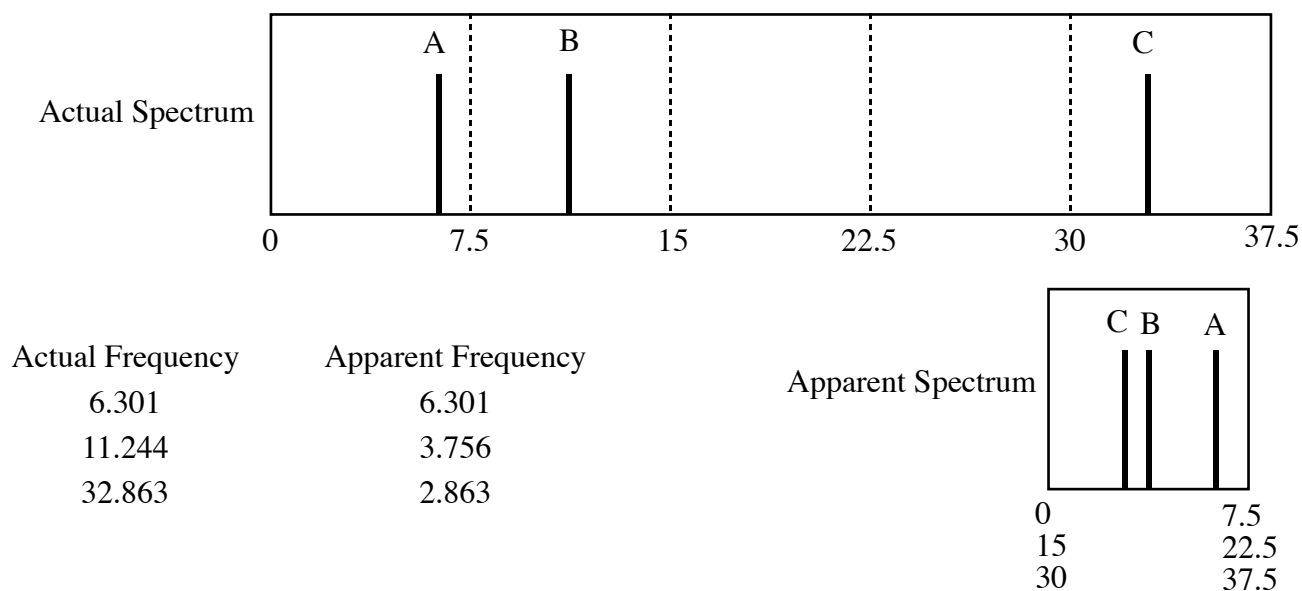
We first subtract the blank from all of the values and then graph the four values against the amount of added Cr. The graphical solution to this problem is to extrapolate back to the x-axis. In this case, it will give the concentration of the unknown directly in ppm.

Solution	Added Cr (ppm)	Average Signal (blank)
Unknown	0.000	0.532
Addition 1	2.000	0.657
Addition 2	4.000	0.786
Addition 3	6.000	0.909



The x-intercept is at about ~ -8.5 ppm. Therefore, the unknown concentration is around 8.5 ppm. An analytic solution gives a more accurate value of about 8.72 ppm, but anything in this ballpark will be accepted.

3. We need to note that the Nyquist frequency is $1/2$ of the sampling frequency, namely 7.5 kHz. The spectra will “fold-over” at multiples of this frequency. Think of z-fold paper; the spectra folds over just like that.



4. The fraction of resistance that remains in a circuit at a given point can be used to calculate the potential at that point. The total resistance is the sum, which equals 36 k Ω . Below is a table, showing the fraction and the voltage at each point.

Point	Fraction	Voltage
A	36/36	-1000
B	35/36	-972
C	33/36	-917
D	30/36	-833
E	26/36	-722
F	21/36	-583
G	15/36	-417
H	8/36	-222

5. The output voltage must be sufficient to perfectly balance the incoming current so that it sums to zero.

$$V = IR = (1.00 \times 10^{-6} \text{ A}) (5 \times 10^6 \text{ W}) = 5 \text{ V}$$

But the output is inverted; it must be a negative voltage. The output potential is -5.00 V.

6. (a) The blank signal correlates to the incident power without an absorbing medium; it is proportional to 685 mV. The absorbing sample reduces that light so that the transmitted power is proportional to 179 mV. This ratio is transmittance. $\times 100$ is the percent transmittance.

$$T = \frac{P}{P^0} = \frac{179}{685} = 0.261 \quad \%T = 26.1\%$$

(b) The absorbance is the negative log of the transmittance.

$$A = -\log_{10} T = -\log_{10}(0.261) = 0.583$$

(c) Remember that it is, according to Beer's law, absorbance that is proportional to concentration, not transmittance. Determine absorbance differences and then determine the transmittance from that.

$$A = \epsilon bc \quad \frac{A}{c} = \epsilon b$$

$$\frac{A_1}{c_1} = \frac{A_2}{c_2} \quad c_2 = \frac{1}{2} c_1$$

$$A_2 = \frac{c_2}{c_1} A_1 = \frac{0.5 c_1}{c_1} (0.583) = 0.291$$

$$T = 10^{-0.291} = 0.512 \quad \%T = 51.2\%$$

(d) Same as above but now you have to go a step further to find the expected signal response, and it is just that fraction of the blank signal.

$$A_2 = \frac{b_2}{b_1} A_1 = \frac{2b_1}{b_1} (0.583) = 1.166$$

$$T = 10^{-1.166} = 0.0682 \quad \%T = 6.82\%$$

$$\text{Signal} = 0.0682 \times 685 \text{ mV} = 46.7 \text{ mV}$$

7. (a) Reactance is the frequency dependent force opposing the flow of current in a circuit. It can be either capacitive or inductive in origin. A capacitive reactance will tend to lag behind the driving signal while an inductive reactance will tend to lead the driving signal. By contrast, resistance is the frequency-independent force opposing the flow of current in a circuit. Impedance is the vector sum of these quantities. Its magnitude is given by

$$Z = \sqrt{X_L^2 + X_C^2 + R^2}$$

(b) Thermal noise: arises because of collisions between electrons and vibrating nuclei (phonons). It increases with increasing temperature.

Shot noise: arises from the quantized nature of charge carriers. Their randomly timed arrival at a detector will impose the minimum noise level.

Flicker noise: Origin is uncertain. It has a $1/f$ dependence. As such, it is worst for DC currents. It is the source of drift in electrical systems. We modulate signals to get around flicker noise.

(c) Bathochromic refers to solvents which shift the absorption wavelength of a given transition in a molecule.

This specifically refers to shifts towards the red, or in other words, longer wavelengths.

Hyperchromic refers to solvents which shift the intensity of absorption wavelengths, specifically increasing their intensity.

Auxochrome refers to a molecular substituent which itself is not optically active but nevertheless has an effect on a neighbouring group by shifting its absorption position and intensity.

8. Both of these op amps are configured as integrators and are given the same time constants. The inputs both go into the inverting inputs so that the signal direction will shift each time. The value for R and C makes for a time constant of

$$\tau = RC = (100,000 \Omega) (0.000010 \text{ F}) = 1.0 \text{ s}$$

The first stage then integrates the constant input voltage, which, of course, produces a straight line, rising slope. The output voltage is just

$$v_{out} = -\frac{1}{RC} \int v_{in} dt = -\frac{1}{1.00 \text{ s}} (-1.00 \text{ V}) \int dt = t$$

This is the input to the second integrator. We see that the output depends quadratically on time and don't forget that the inverting input causes it to become more negative in time also. We have

$$v_{out} = -\frac{1}{RC} \int v_{in} dt = -\frac{1}{1.00 \text{ s}} \int t dt = -\frac{1}{2} t^2$$

The two output curves are thus given as

