Chem 310
1st Homework Set Answers
Due Date: Jan. 27, 2004

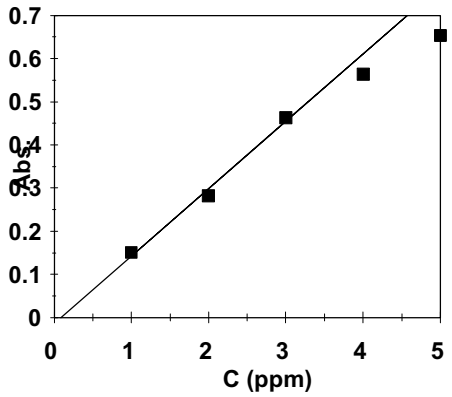
1. Sketch a calibration curve and show on the plot the data, the linear regression line, the linear dynamic range and the sensitivity.

The sketch should show a plot with Signal on the vertical axis and Concentration on the horizontal axis. Data points should show a linear and a nonlinear region. A linear regression line should be drawn through the linear points. The concentration axis should be marked to show the low and high conc. boundaries of the linear dynamic range. The slope of the linear regression line should be identified with the sensitivity.

2. A graphite furnace AA spectrometer was used to determine the copper (Cu) concentrations in drinking water. A large set of blank samples yielded a blank standard deviation of 0.015. The following data were obtained for a calibration curve.

[Cu] (ppm)	1.0	2.0	3.0	4.0	5.0
Absorbance	0.151	0.282	0.463	0.564	0.654

Using a spreadsheet, create a graph of the data using symbols only for the data points. Use your judgement to determine the dynamic range. Fit the data in the dynamic range to a linear regression line. Plot the line on the same graph and give the linear regression slope and intercept. If possible, give the standard deviations of the slope and intercept; these are also available from the spreadsheet (LINEST function). Make sure that the axes are labeled and that the data are plotted as symbols and the linear regression line is a solid line. Print the graph and attach it to your HW set.



Linear regression output: slope = 0.156 ± 0.014 ppm; *intercept = −0.013 ± 0.020.*
Answer the following questions.

(a) What is the dynamic range of the method? Hint: it is NOT the entire concentration range.

The linear dynamic range is 1-3 ppm. Higher concentration data clearly deviate from linearity.

(b) What is the sensitivity of the method? *sensitivity = slope = 0.156 ± 0.014 ppm*

(c) Calculate the LOD and LOQ for Cu.

LOD = 3(std.dev.blank)/sensitivity = 3*0.015/0.156 = 0.29 ppm.*
LOQ = 10(std.dev.blank)/sensitivity = 10*0.015/0.156 = 0.96 ppm.*

(d) A sample of water yielded an absorbance of 0.366. What is the concentration of Cu in the water? There are two ways to calculate the answer. Explain which way gives the more accurate answer.

Use linear regression parameters: C = (0.366 – (–0.013))/(0.156) = 2.3 ppm.
Use two points bracketing the sample signal:
C = 2.0 + (3.0 – 2.0)(0.366 – 0.282)/(0.463 – 0.282) = 2.5 ppm*
Both methods are equally accurate since the signal falls in the linear dynamic range and all the data points fall near the linear regression line.

3. A commercial analytical lab. received a vegetation standard from the National Institute of Standards & Technology and performed an analysis of a pesticide. They found a concentration of 8.4 ± 1.2 ppb. The NIST data sheet with vegetation standard stated that the concentration of the pesticide was 11. ± 1 ppb. The ±1.2 ppb is due to _*random*_ error and the difference between the measured conc. of 8.4 ppb and the true conc. of 11 ppb is due to _*systematic*_ error. Which type of error is correctable? *Systematic.*

4. A fish was caught in the Monongahela River just below the sewer treatment plant in Star City. The flesh was homogenized and analyzed for mercury. The following values were obtained: 51, 66, 63, 61 ppb. Calculate the mean, sample standard deviation, and RSD.
Mean = 60 ppb, s = 6 ppm, RSD = 6/60 = 0.1 or 10%. Note that the mean and standard deviation are rounded to the same # of significant figures as the data.

5. Convert 1 ppb Hg to the molar concentration of Hg. FYI, ppb = part per billion.
Definitions: 1 ppb = 1 g analyte per 10^9 g sample. To convert ppb to a molar concentration, you have to assume that your sample is a dilute aqueous solution (density of 1 g/mL). Then: 1 ppb Hg = 1 g Hg/10^9 mL = (10^{-9} g Hg/mL)(1 mol Hg/200.59 g)(1000 mL/L) = 5.0×10^{-9} M Hg

6. List 5 techniques for reducing matrix effects. Briefly describe each technique.
   (a) Matrix substitution: converting the sample to a phase more suitable for analysis, such as dissolving a metal sample in acid to get the elements into solution.
   (b) Separation: isolating the analyte from a complex mixture, usually by some form of chromatography.
   (c) Pre-concentration: collecting the analyte onto a surface or in a smaller volume to raise its concentration above the LOD or LOQ.
   (d) Derivatization: converting the analyte into a form more suitable for instrumental analysis, such as forming a colored metal complex.
   (e) Masking: converting interfering substances into a form that does not generate a signal in the instrument, such as forming colorless metal complexes.

7. Iron was determined by the method of standard addition using flame atomic absorption spectroscopy. A Fe sample and a Fe standard of 10.0 ppm were used to prepare the following solutions; each solution was diluted to a final volume of 100.0 mL. What is the concentration of Fe in the sample?

Sample (mL)	Standard (mL)	Absorbance
20.00	0.00	0.331
20.00	10.00	0.557

Note that fixed volumes of the sample and standard are diluted to a constant final volume.
(1) $0.331 = (m)(20.00/100.0)C$ (you must assume the blank signal is zero)
(2) $0.557 = (m)[(20.00/100.0)C + (10.00/100.0)(10.0\ ppm)]$
Substitute (1) into (2): $0.557 = 0.331 + (m)(1.0)$; $m = 0.226/ppm$
$0.331 = (0.226)(20.00/100.0)C$; $C = 0.331*5.000/0.226 = 7.32\ ppm$

8. The lead (Pb) levels in Finklea's home brew were determined by anodic stripping voltammetry. 30.0 mL of home brew was placed in the cell and analyzed. The signal (peak height of the stripping voltammogram) of 0.351 cm. Then 5.00 mL of a Pb standard containing 10.0 ppb Pb was added to the cell and mixed. The new signal was 0.583 cm. Calculate the Pb concentration in the home brew. State the assumption needed to do the calculations.
Note that the sample is diluted by the standard addition. You must assume that the signal is linear with concentration, and that the blank signal is zero.
(1) $0.351 = mC$
(2) $0.583 = (m)[(30.0/35.0)C + (5.00/35.0)(10.0\ ppb)]$
$m = 0.1975\ ppb^{-1}$; $C = 1.78\ ppb$

10. A 16-bit ADC is used to convert a signal between +2 V and 0 V to binary numbers. What is the resolution of the signal? What is the minimum RSD of the signal?
The range is 2 V. Resolution = range/2^{16} = (2 V)/(65536) = 3.05×10^{-5} V or 30.5 μV
Minimum RSD = $\pm$1 bit out of 2^{16} bits = 1/65536 = 1.5×10^{-5} or 0.0015%

11. Problem 20-26 (Chapter 20, problem # 26) in Harris.
$S/N = k\sqrt{N}$; $k = 8/\sqrt{1} = 20/\sqrt{N}$; $N = (20/8)^2 = 6.25$; round up to 7.

12. Problem 20-28 (Chapter 20, problem # 28) in Harris.
$S/N = k\sqrt{N}$; $k = 60/\sqrt{1000} = S/N/\sqrt{300}$; $S/N = 60*(300/1000)^{½} = 32.9$ vs 35.9 reported.
$S/N = 60*(100/1000)^{½} = 19.0$ vs 20.9 reported.
$S/N = 60*(1/1000)^{½} = 1.89$ vs 1.95 reported.

13. List the strategies for enhancing signal-to-noise in an instrumental method.
(a) Shield the experiment.
(b) Cool the detector.
(c) Use synchronous detection.
(d) Digitize the data and use computational methods (averaging or ensemble-averaging)

14. S/N for a FT-IR spectrum can be improved by ensemble averaging. How is this done?
Trigger the FT-IR spectrometer to acquire the spectrum repeatedly. Acquire the signal with respect to time. Store each digitized signal in a bin (memory location) corresponding to a particular time after the trigger. New data is added to old data every time the spectrum is triggered. The result is an ensemble-averaged spectrum with improved S/N.

15. In some sensitive spectrometers, the light detector is cooled well below room temperature. Why is this done?
To lower the Johnson noise in the detector. The detector is also subject to shot noise, but that is not reduced at lower temperatures.