

**Analytical Chemistry**  
**Problem Set 4—due Monday, February 28, 2005**  
**-20% penalty per day if late**

1. (5 points) Harris 3-19
2. (4 points) Consider the following function of two independent variables,  $x$  and  $y$ :

$$z = 3x^3 + \sqrt{7y}$$

Derive an expression for the uncertainty in  $z$ ,  $e_z$ , in terms of the uncertainties in  $x$  and  $y$ ,  $e_x$  and  $e_y$ .

3. (20 points) You are using a mass spectrometer to determine methane in samples of air. First, you obtain the following calibration data for a set of CH<sub>4</sub> standards:

[CH <sub>4</sub> ] (ppm)						
0.000	0.062	0.122	0.245	0.486	0.971	1.921
Signal (millivolts or mV)						
9.1	47.5	95.6	193.8	387.5	812.5	1671.9

Then you make four replicate measurements on an unknown sample, and obtain an average (corrected) signal of 145.0 mV.

- (a) Construct an Excel spreadsheet like that shown in Harris Figure 5.9 and in the class handout. Use this spreadsheet to calculate the least squares parameters  $D$ ,  $m$ ,  $b$ ,  $s_y$ ,  $s_m$ , and  $s_b$  for the above calibration curve data. Remember to correct the signal measurements by subtracting the blank value, and fit your calibration curve to the corrected signals.
- (b) Plot the calibration curve, using the Add Trendline function to display the equation and the  $R^2$  value.

Be sure to include printouts of both your spreadsheet and calibration curve when you turn in this assignment. Be sure to save a copy of your spreadsheet; you will be using it to analyze your data for Experiments 2 and 3 as well!

- (c) Determine the mixing ratio of CH<sub>4</sub> (in ppm) in the unknown sample and determine the 95% confidence interval for the CH<sub>4</sub> mixing ratio using Harris Equation (5-14).
- (d) Determine the 95% confidence interval for the CH<sub>4</sub> mixing ratio of the unknown sample by using the error propagation formulas from Harris Table 3-1.
- (e) Compare the 95% confidence intervals you obtained in parts (c) and (d) and briefly explain any difference in the two values.

Problem Set 4 continues on the back.

4. (5 points) You are determining nickel concentrations using ion chromatography. A dilute sample known to contain  $\text{Ni}^{2+}$  gives the following measurements (in microamperes or  $\mu\text{A}$ ): 175, 104, 164, 193, 131, 189, 155, 133, 151, 176. Eight measurements on a blank give a mean signal of 45  $\mu\text{A}$ . A sample known to contain 1.00  $\mu\text{M}$   $\text{Ni}^{2+}$  gives an average uncorrected signal of 1797  $\mu\text{A}$ . Determine to two significant figures the signal and concentration detection limits for your experiment.