

**Analytical Chemistry**  
**Problem Set 3**  
**Due Monday, February 16, 2009 (at 4:00 p.m.)**  
Total Points for This Assignment = 41

Test 1, covering Problem Sets 1, 2, and 3, will be on Thursday, February 19

1. (5 points) Harris 4-14
2. (5 points) Harris 4-22. You are required to test at both the 90% and the 95% confidence levels. (Consult the table on the back for the 95% calculation.)
3. (5 points) Harris 3-19. Use the data on the inside front cover of Harris.

4. (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  $e_y$ .

5. (22 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  $\text{CH}_4$  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 4.13 and in the class handout. Use this spreadsheet to calculate the least squares parameters  $m$ ,  $b$ ,  $s_y$ ,  $s_m$ , 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  $\text{CH}_4$  (in ppm) in the unknown sample, and determine the 95% confidence interval for the  $\text{CH}_4$  mixing ratio using Harris Equation (4-27).
- (d) Determine the 95% confidence interval for the  $\text{CH}_4$  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.

**Table I. Critical Values of Dixon's  $r_{10}$  ( $Q$ ) Parameter As Applied to a Two-Tailed Test at Various Confidence Levels, Including the 95% Confidence Level<sup>a</sup>**

$N^b$	confidence level					
	80% ( $\alpha = 0.20$ )	90% ( $\alpha = 0.10$ )	95% ( $\alpha = 0.05$ )	96% ( $\alpha = 0.04$ )	98% ( $\alpha = 0.02$ )	99% ( $\alpha = 0.01$ )
3	0.886	0.941	<b>0.970</b>	0.976	0.988	0.994
4	0.679	0.765	<b>0.829</b>	0.846	0.889	0.926
5	0.557	0.642	<b>0.710</b>	0.729	0.780	0.821
6	0.482	0.560	<b>0.625</b>	0.644	0.698	0.740
7	0.434	0.507	<b>0.568</b>	0.586	0.637	0.680
8	0.399	0.468	<b>0.526</b>	0.543	0.590	0.634
9	0.370	0.437	<b>0.493</b>	0.510	0.555	0.598
10	0.349	0.412	<b>0.466</b>	0.483	0.527	0.568
11	0.332	0.392	<b>0.444</b>	0.460	0.502	0.542
12	0.318	0.376	<b>0.426</b>	0.441	0.482	0.522
13	0.305	0.361	<b>0.410</b>	0.425	0.465	0.503
14	0.294	0.349	<b>0.396</b>	0.411	0.450	0.488
15	0.285	0.338	<b>0.384</b>	0.399	0.438	0.475
16	0.277	0.329	<b>0.374</b>	0.388	0.426	0.463
17	0.269	0.320	<b>0.365</b>	0.379	0.416	0.452
18	0.263	0.313	<b>0.356</b>	0.370	0.407	0.442
19	0.258	0.306	<b>0.349</b>	0.363	0.398	0.433
20	0.252	0.300	<b>0.342</b>	0.356	0.391	0.425
21	0.247	0.295	<b>0.337</b>	0.350	0.384	0.418
22	0.242	0.290	<b>0.331</b>	0.344	0.378	0.411
23	0.238	0.285	<b>0.326</b>	0.338	0.372	0.404
24	0.234	0.281	<b>0.321</b>	0.333	0.367	0.399
25	0.230	0.277	<b>0.317</b>	0.329	0.362	0.393
29	0.227	0.273	<b>0.312</b>	0.324	0.357	0.388
27	0.224	0.269	<b>0.308</b>	0.320	0.353	0.384
28	0.220	0.266	<b>0.305</b>	0.316	0.349	0.380
29	0.218	0.263	<b>0.301</b>	0.312	0.345	0.376
30	0.215	0.260	<b>0.298</b>	0.309	0.341	0.372

<sup>a</sup>In this and the other accompanying tables, the newly generated or corrected values are indicated in boldface. <sup>b</sup>Sample size.

(Rorabacher, D.B. *Analytical Chemistry* **1991**, 63, 139.)