

Analytical Chemistry

Problem Set 3-due Monday, February 12, 2007 (at 4:00 p.m.)-Note Corrections to #4

Total Points for This Assignment = 41

1. (5 points) Harris 4-22. You are required to test at both the 90% and the 95% confidence levels. (Consult the table on back for the 95% calculation.)

2. (5 points) Harris 3-19. Use the data on the inside front cover of Harris (7th ed.).

3. (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 .

4. (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 CH₄ standards:

[CH ₄] (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. (There is no parameter "D" to calculate.) 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 CH₄ (in ppm) in the unknown sample, and determine the 95% confidence interval for the CH₄ mixing ratio using Harris Equation (4-27).
- (d) Determine the 95% confidence interval for the CH₄ 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 3 continues on the back.

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

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^a

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

^aIn this and the other accompanying tables, the newly generated or corrected values are indicated in boldface. ^bSample size.

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