

Complete five (5) of the following problems. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

Bonus (5 points):

One day last week, Dr. Lamp announced a concentration at 8:30 AM as he started class and said that it would be an answer to an exam 1 question. What concentration did he announce?

3.62 ppm

Do five of problems 1-7. Clearly mark the problems you do not want graded. (16 pts each)

1. A solution was prepared by dissolving 1.975 grams of a solid sample containing an unknown amount of mercury in a total of 100.00 mL of solution, which was labeled solution A. Before analysis, 5.00 mL of solution A was pipetted into a 100.00 mL volumetric flask, mixed and diluted to the mark to form solution B. Then 10.00 mL of solution B was pipetted into a 25.00 mL volumetric flask, mixed and diluted to the mark to make solution C. Analysis of solution C determined that it had a mercury concentration of 12.6 ppm. What was the percent mercury by mass in the original solid sample? You may assume a density of 1.00 g/mL for all solutions.

It is useful to think of ppm Hg as $\mu\text{g Hg/mL}$ solution (or mg Hg/L solution). This isn't essential, but it makes the dimensional analysis a little more streamlined.

We need to first account for each of the dilutions to determine the concentration of mercury in the original solution:

$$\frac{12.6 \mu\text{g Hg}}{\text{mL C}} \times \frac{25.00 \text{ mL C}}{10.00 \text{ mL B}} \times \frac{100.00 \text{ mL B}}{5.00 \text{ mL A}} = \frac{630 \mu\text{g Hg}}{\text{mL A}}$$

Now we can determine the mass of Hg in solution A:

$$\frac{630 \mu\text{g Hg}}{\text{mL A}} \times 100.00 \text{ mL A} \times \frac{10^{-6} \text{ g Hg}}{\mu\text{g Hg}} = 0.0630 \text{ g Hg}$$

Finally, determine %Hg:

$$\frac{0.0630 \text{ g Hg}}{1.975 \text{ g sample}} \times 100 \% = 3.19 \% \text{ Hg}$$

2. A Standard Reference Material is certified to contain 45.4 ppm of an organic contaminant in soil. You analyze this material to characterize a new method you are developing. Your analysis gives values of 47.8, 47.4, 45.6, 48.1, and 47.2 ppm. Evaluate the results for suspect data and determine whether your results indicate the presence of systematic error in your method at the 95% confidence level. Justify your answer.

Based on the full dataset, the mean is 47.2 ppm, and $s = 0.97$ ppm

With all of the other data bunched around 47 and 48 ppm, the point at 45.6 ppm should look a little odd and worthy of a Q-test. Q for 5 observations is 0.64

$$\frac{47.2-45.6}{48.1-45.6} = \frac{1.6}{2.5} = 0.64 \text{ is not } > 0.64 \text{ so retain 45.6}$$

If you choose to do the Grubb's test, G for 5 observations is 1.672:

$$\frac{47.2-45.6}{1.19} = \frac{1.6}{0.97} = 1.649 < 1.672 \text{ so retain 45.6}$$

To determine whether systematic error is indicated, determine if the "true value" falls within the confidence interval. (using the 95% confidence level). For 4 degrees of freedom and 95%, $t_{\text{table}} = 2.776$

$$CI = 47.2 \pm \frac{ts}{\sqrt{n}} = 47.2 \pm \frac{2.776 \times 0.97}{\sqrt{5}} = 47.2 \pm 1.20$$

So, the confidence range is 47 ± 1 ppm, which does not include the true value, therefore, there seems to be an indication of systematic error (at least a 5% chance).

You could also calculate a t value to compare to the tabulated t:

$$t_{\text{calc}} = \frac{|\text{true value} - \bar{x}|}{s} \sqrt{n} = \frac{|45.4 - 47.2|}{0.97} \sqrt{5} = 4.15$$

Since $t_{\text{calc}} > t_{\text{table}}$ there is a statistically significant difference.

3. Acid solutions can be standardized using primary standard sodium carbonate, much like base solutions can be standardized using pure KHP as we did in lab. Below is data from a titration of a sodium carbonate sample with a solution of hydrochloric acid of unknown concentration. In this titration, approximately 25 mL of distilled water was used to dissolve the sodium carbonate that was dispensed from the weighing bottle into an Erlenmeyer flask. What is the molarity of the hydrochloric acid solution with its absolute uncertainty?

Initial mass of weighing bottle and sodium carbonate	32.1384±0.0002 g
Final mass of weighing bottle after sample was removed	30.9615±0.0002 g
Initial buret reading	2.38±0.02 mL
Final buret reading	39.54±0.02 mL
Molar mass of sodium carbonate	105.9885±0.0002 g/mol

Our reaction of interest is:



Our general calculation is:

$$(m \pm e_m) \text{g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{(\text{MM} \pm e_{\text{MM}}) \text{g Na}_2\text{CO}_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Na}_2\text{CO}_3} \times \frac{1}{(V \pm e_v) \text{L solution}} = [\text{HCl}]$$

We are given the molar mass and its uncertainty, but need to calculate the mass and uncertainty of Na₂CO₃ and volume and uncertainty of HCl solution.

$$\text{Mass Na}_2\text{CO}_3 = 32.1384 - 30.9615 \text{ g} = 1.1769 \text{ g}$$

Uncertainty in mass:

$$e_m = \sqrt{(0.0002 \text{g})^2 + (0.0002 \text{g})^2} = 0.0002_8 \text{g}$$

$$\text{Volume HCl} = 39.54 - 2.38 \text{ mL} = 37.16 \text{ mL}$$

Uncertainty in volume:

$$e_v = \sqrt{(0.02 \text{ mL})^2 + (0.02 \text{ mL})^2} = 0.02_8 \text{ mL}$$

Now we can insert these values into our calculation

$$\frac{(1.1769 \pm 0.0002_8) \text{g}}{\text{Na}_2\text{CO}_3} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{(105.9885 \pm 0.0002) \text{g Na}_2\text{CO}_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Na}_2\text{CO}_3} \times \frac{1}{(37.16 \pm 0.02_8) \times 10^{-3} \text{ L solution}} = (0.5976 \pm e_0) \text{ M HCl}$$

$$e_0 = 0.5976 \text{ M} \sqrt{\left(\frac{0.0002_8 \text{ g}}{1.1769 \text{ g}}\right)^2 + \left(\frac{0.02_8 \text{ mL}}{37.16 \text{ mL}}\right)^2 + \left(\frac{0.0002 \text{ g/mol}}{105.9885 \text{ g/mol}}\right)^2} = (0.5976 \text{ M})(0.00079) = 0.0004_7 \text{ M}$$

So, the HCl concentration is 0.5976 ± 0.0005 M

4. Complete both parts in a few sentences. (8 pts each part)
- a. Why do systematic (determinate) errors typically have a larger impact on the accuracy of a measurement than random (indeterminate) errors?

By their nature, systematic errors (such as miscalibrated equipment), result in the experimentally determined value being offset from the true value by a constant amount. For example, a poorly calibrated volumetric pipet may deliver an extra 0.10 mL of solution, but it will reproducibly deliver this erroneous volume. Therefore every independent measurement will be skewed by the same amount, leading to poor accuracy.

Indeterminate (or random) errors involve both positive and negative deviations from the true value. While they may vary in size, the scatter is always around the true value. Therefore, as long as you collect a reasonable number of data points, the average should be close to the true value (good accuracy), although reproducibility may be poor (poor precision).

- b. How is the percent recovery of a spiked (fortified) sample determined and how is it useful in evaluating the accuracy of a method?

A percent recovery is accomplished by making two measurements, one of the sample itself and one with the sample spiked with a known additional quantity of analyte. Since a known quantity of analyte has been added, the change in response should correspond to the change in concentration. If it does not, there is an indication of systematic error.

5. You are working to develop a new method for the determination of the sulfur content in coal. If successful, your method has the potential to be very valuable. To validate your method, you decide to compare it to an established, "Industry Standard" method. The weight percent sulfur of four different coal samples (each containing different amounts of S) was measured by the two different methods. Does your method give results that are consistent with the Industry Standard at the 95% confidence level?

Sample	1	2	3	4
Industry Standard Method	1.157	1.538	1.795	2.284
Your Method	1.151	1.534	1.785	2.280

Since these values are for single measurements of multiple samples, we have to base our decision on the differences between the results for each sample. First we need to calculate an s_d :

Sample	1	2	3	4
Industry Standard Method	1.157	1.538	1.795	2.284
Your Method	1.151	1.534	1.785	2.280
d	0.006	0.004	0.010	0.004
Average d	0.006			
$(d - d_{\text{average}})^2$	0	$(0.002)^2$	$(0.004)^2$	$(0.002)^2$

$$s_d = \sqrt{\frac{(0)^2 + (0.002)^2 + (0.004)^2 + (0.002)^2}{4 - 1}} = 0.00283$$

Now we can calculate a t value:

$$t_{\text{calculated}} = \frac{\bar{d}}{s_d} \sqrt{n} = \frac{0.006}{0.00283} \sqrt{4} = 4.243$$

The critical value of t for 3 degrees of freedom is 3.182.

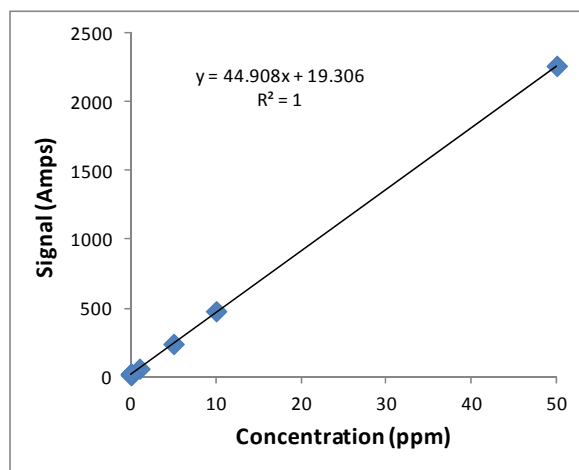
Since $t_{\text{calculated}} > t_{\text{critical}}$ there is a statistically significant difference between the two methods.

Since these are the results for individual measurements of different samples, it is not appropriate to use s_{pooled} which compares replicate results of a single sample on two methods.

6. As a recently hired analytical chemist, you have been tasked with determining the detection limit for an analytical measurement. You collect data for five blanks and four standard solutions. The data and the result of your calibration curve are below. Determine the detection limit for the measurement. You may ignore uncertainties in the slope and intercept.

Calibration relationship: $\text{Signal} = 44.91 \mu\text{A/pp}[\text{concentration}] + 19.31 \mu\text{A}$

Concentration (ppm)	Signal (microamps)
0 (blank)	15.6, 20.2, 13.8, 22.3, 23.9
1.00	60.3
5.00	240.2
10.0	478.2
50.0	2263.2



Recall that the signal at the detection limit is:

$$y_{\text{LOD}} = y_{\text{blank}} + 3s$$

where s is the standard deviation of the measurement. Since we have several measurements of the blank, we can use those to determine the standard deviation of the measurement:

For 15.6, 20.2, 13.8, 22.3, 23.9, the average blank signal is 19.16 microamps and the standard deviation is 4.32 microamps.

Therefore the signal at the detection limit is: $y_{\text{LOD}} = 19.16 + 3(4.32) = 32.12$ microamps

To find the detection limit we need to convert this signal to a concentration using the calibration relationship. We insert y_{LOD} as our y value and solve for x :

$$\frac{(32.12 - 19.31) \text{ microamps}}{44.91 \text{ microamps/ppm}} = \mathbf{0.2852 \text{ ppm}}$$

Therefore, our detection limit is $0.2_9 \text{ ppm} = \mathbf{0.3 \text{ ppm}}$

7. You have been given the task of teaching a quantitative analysis student, Al Thumbs, the proper use of a Class A buret for titrations in order to obtain high quality quantitative results. Clearly describe your instructions to this student, include reminders of common pitfalls Al should avoid.

Your discussion for should include the following:

- Procedure for cleaning the buret (and tip)
- Taking care to avoid air bubbles in the tip
- Being sure to allow time for the walls to drain and material to react before reading
- Reading the buret from the bottom of the meniscus, with the meniscus at eye level
- Estimating readings to 1/10 of the smallest graduation (0.01 mL on a 50 mL buret)
- Shoot for consistent endpoint color.
- Taking care to "cut" drops near the endpoint

Possibly Useful Information

$m = \frac{m' \left(1 - \frac{d_a}{d_w}\right)}{\left(1 - \frac{d_a}{d}\right)}$	<p>Density of air = 0.012 g/ml Density of balance weights = 8.0 g/ml</p>
$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$	$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
$e_C = \sqrt{e_A^2 + e_B^2}$	$e_C = C \sqrt{\left(\frac{e_A}{A}\right)^2 + \left(\frac{e_B}{B}\right)^2}$
$t_{\text{calculated}} = \frac{ \text{known value} - \bar{x} }{s} \sqrt{n}$	$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$
$t_{\text{calculated}} = \frac{ \bar{x}_1 - \bar{x}_2 }{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$	$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$
$t_{\text{calculated}} = \frac{\bar{d}}{s_d} \sqrt{n}$	$s_d = \sqrt{\frac{\sum_i (d_i - \bar{d})^2}{n-1}}$
$s_x = \frac{s_y}{ m } \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y - \bar{y})^2}{m^2 \sum (x_i - \bar{x})^2}}$	$s_y = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n-2}} = \sqrt{\frac{\sum d_i^2}{n-2}}$
$s_m^2 = \frac{s_y^2 \times n}{D}$	$s_b^2 = \frac{s_y^2 \sum x_i^2}{D}$
$y_{\text{LOD}} = y_{\text{blank}} + 3s$	$F_{\text{calculated}} = \frac{(s_1)^2}{(s_2)^2}$
$Q_{\text{calculated}} = \frac{\text{gap}}{\text{range}}$	$G_{\text{calculated}} = \frac{ \text{suspect value} - \bar{x} }{s}$

Values of Student's t

Degrees of Freedom	Confidence Level (%)			
	90	95	99.5	99.9
1	6.314	12.706	127.32	636.61
2	2.920	4.303	14.089	31.598
3	2.353	3.182	7.453	12.924
4	2.132	2.776	5.598	8.610
5	2.015	2.571	4.773	6.869
6	1.943	2.447	4.317	5.959
7	1.895	2.365	4.029	5.408
8	1.860	2.306	3.832	5.041
9	1.833	2.262	3.690	4.781
10	1.812	2.228	3.581	4.587
∞	1.645	1.960	2.807	3.291

Values of Q for rejection of data

# of Observations	Q (90% Confidence)
4	0.76
5	0.64
6	0.56

Grubbs Test for Outliers

# of Observations	G _{critical} At 95% confidence
4	1.463
5	1.672
6	1.822

Critical Values of F at the 95% Confidence Level

Degrees of freedom for s ₂	Degrees of freedom for s ₁								
	2	3	4	5	6	7	8	9	10
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES	
1 H 1.00797															1 H 1.00797	2 He 4.0026	
3 Li 6.939	4 Be 9.0122										5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183	
11 Na 22.9898	12 Mg 24.312										13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948	
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atonic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (258)	102 No (258)	103 Lr (257)
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