Chemistry 222 **Name**_____
Spring 2021 **80 Points**
Exam 1: Chapters 1-5

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.

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

1. A solution was prepared by dissolving 1.795 grams of a solid sample containing an unknown amount of lead 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 lead concentration of 11.2 ppm. What was the percent lead 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 Pb as µg Pb/mL solution (or mg Pb/L solution). This isn't essential, but it makes the dimensional analysis a little more streamlined. There are several approaches to the answer, her is an example of one approach.

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

$$\frac{11.2\ \mu g\ Pb}{\cancel{mL\ C}} \times \frac{25.00\ \cancel{mL\ C}}{10.00\ \cancel{mL\ B}} \times \frac{100.00\ \cancel{mL\ B}}{5.00\ mL\ A} = \frac{560\ \mu g\ Pb}{mL\ A}$$

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

$$\frac{560\ \cancel{\mu g\ Pb}}{\cancel{mL\ A}} \times 100.00\ \cancel{mL\ A} \times \frac{10^{-6}\ g\ Pb}{\cancel{\mu g\ Pb}} = 0.0560\ g\ Pb$$

   Finally, determine %Pb:

$$\frac{0.0560\ g\ Pb}{\cancel{1.795\ g\ sample}} \times 100\ \% = \mathbf{3.12\ \%\ Pb}$$

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, 45.3, 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 = 1.1 ppm

With all of the other data bunched around 47 and 48 ppm, the point at 45.3 ppm should look a little odd and worthy of a Q-test. Q for 5 observations is 0.64

$$\frac{47.2-45.3}{48.1-45.3} = \frac{1.9}{2.8} =$$ **0.68 is > 0.64 so omit 45.3**

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

$$\frac{47.2-45.3}{1.1} = \frac{1.9}{1.1} =$$ **1.72 > 1.672 so omit 45.3**

Once the outlier is omitted, the average becomes 47.6 ppm with a standard deviation of 0.4 ppm. To determine whether systematic error is indicated, determine if the "true value" falls within the confidence interval. (using the 95% confidence level). For 3 degrees of freedom and 95%, t_{table} = 3.182

$$CI = 47.6 \pm \frac{ts}{\sqrt{n}} = 47.6 \pm \frac{3.182 \times 0.4}{\sqrt{4}} = 47.6 \pm 0.64$$

So, the confidence range is 47.6 ± 0.6 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:

$$t_{calc} = \frac{|\text{true value} - \bar{x}|}{s}\sqrt{n} = \frac{|45.4 - 47.6|}{0.4}\sqrt{4} = 11$$

Since $t_{calc} > t_{table}$ 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	32.1834±0.0002 g
Final mass of weighing bottle after sample was removed	30.9651±0.0002 g
Initial buret reading	2.83±0.02 mL
Final buret reading	39.45±0.02 mL
Molar mass of sodium carbonate	105.9885±0.0002 g/mol

Our reaction of interest is:

$$Na_2CO_3 + 2HCl \rightarrow H_2CO_3 + 2NaCl$$

Our general calculation is:

$$(m \pm e_m)\text{g } Na_2CO_3 \times \frac{1 \text{ mol } Na_2CO_3}{(MM \pm e_{MM})\text{g } Na_2CO_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Na_2CO_3} \times \frac{1}{(V \pm e_v)\text{L solution}} = [HCl]$$

We are given the molar mass and its uncertainty, but need to calculate the mass and uncertainty of Na_2CO_3 and volume and uncertainty of HCl solution.

Mass Na_2CO_3 = 32.1834-30.9651 g = 1.2183 g
Uncertainty in mass:

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

Volume HCl = 39.45-2.83 mL = 36.62 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

$$(1.2183 \pm 0.0002_8)\text{g } Na_2CO_3 \times \frac{1 \text{ mol } Na_2CO_3}{(105.9885 \pm 0.0002)\text{g } Na_2CO_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Na_2CO_3} \times \frac{1}{(37.16 \pm 0.02_8)\times 10^{-3}\text{ L solution}} = (0.62778 \pm e_M)\text{ M HCl}$$

$$e_M = 0.62778\sqrt{\left(\frac{0.0002_8\text{ g}}{1.2183\text{ g}}\right)^2 + \left(\frac{0.02_8\text{ mL}}{36.62\text{ mL}}\right)^2 + \left(\frac{0.0002\text{ g/mol}}{105.9885\text{ g/mol}}\right)^2} = (0.061866\text{ M})(0.00081)$$
$$= 0.000406\text{ M}$$

So, the HCl concentration is 0.6278 ± 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. You have been tasked with determining the limit of detection for a new instrumental technique for the determination of lead in drinking water. Describe how you would accomplish this task. Include a general description of the samples you would make and measure and how these measurements would be used to determine the LOD.

To find the LOD, you need to know the precision of the measurement and how the measurement response is related to concentration. Remember, LOD must have units corresponding to amount of analyte.

You process should include the following.

- You must prepare a series of solutions of known concentration, including a blank.
- You must measure the response of each of these solutions
- You must measure one of the solutions multiple times to determine the standard deviation of the response.
- You determine the signal at the detection limit by: $I_{LOD} = I_{blank} + 3s_{blank}$ where $I_{blank}$is the average signal of a blank measurement and s_{blank} is the standard deviation of the measurement.
- You determine the relationship between signal and concentration by plotting a calibration curve and fitting it (usually with a line)
- You then use the equation for the fit to convert I_{LOD} to concentration units.

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			
$\mathbf{(d - d_{average})^2}$	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:

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

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

Since $t_{calculated} > t_{critical}$ 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. You are working to determine the concentration of acetaminophen in an analgesic preparation by absorbance spectrophotometry. You prepare an unknown solution and series of standard solutions and measure the absorbance of each solution at 255 nm. The resulting data is shown below. Assuming a linear relationship between absorbance and concentration, describe how you would determine the 95% confidence interval for the acetaminophen concentration of the unknown. You DO NOT need to do any calculations, just clearly describe how you would go from the raw data to find the 95% confidence interval for the unknown. What key parameters will you calculate along the way? What value do you select for t?

[acetaminophen] (mM)	Absorbance at 255 nm
0.00	0.279
10.37	0.602
20.74	0.896
31.11	1.188
41.48	1.443
Unknown	0.785

To find the confidence interval, we need a measure of the concentration of the unknown and its uncertainty. To find these, we need to fit the data and calculate the uncertainty in an x value determined from the fit. Your process should include:

- Determine the least squares line for the data
  - Perform the requisite calculations to find slope and intercept
- Use the slope and intercept to find the concentration for the unknown.
- From the calibration data, determine the standard deviation about regression (s_y)
- Use s_y and the data to find s_x, the uncertainty of an x-value calculated from the line using an equation such as:
- Once $s_x$is determined, the confidence interval is *value* ± *ts* where t is determined by n-2 degrees of freedom. In this case, our number of degrees of freedom is (5-2 = 3), so the appropriate value for t is 3.182
- Note that there is no square root of n in the confidence interval calculation.

7. You have been given the task of teaching a quantitative analysis student, Al Thumbs, the proper preparation and 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

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

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