You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

The take-home least-squares problem will account for 15 possible points on this exam.

Do four of problems 1-5. Clearly mark the problems you do not want graded. (10 pts each)

1. A statistical analysis is an essential component in the evaluation of experimental results. In our discussion of statistics, I stated several times that statistics only tell us about the precision of a measurement, not the accuracy. Why is this so? If this is true, how can we use the confidence interval to predict how close our results are to a "true" or accepted value?

When we refer to quality of results, we are typically considering the accuracy and precision of a value. In terms of precision, statistics are a useful tool to evaluate how reproducible our data are, with a standard deviation serving as an estimate of the scatter of the data. The challenge comes in the fact that we typically have a very small data set and are forced to rely on that small set to approximate the standard deviation. The confidence interval also allows us to make some inferences about the accuracy of a method by taking the fact that we have a small data set into account; **assuming only random errors are impacting our measurement.** Therefore, we must rely on good experimental design to remove systematic errors to make an evaluation using the confidence interval reasonable.

2. Outline the process that would typically be used in lab to perform an <u>internal standards</u> experiment. (*hint: you will need more than two solutions*)

Internal standards are useful when variable sample sizes are used or when instrument fluctuations prevent the reliable use of a calibration curve. The material chosen for the internal standard must respond to the measurement but have a different identity than the analyte.

- 1. Select internal standard
- 2. Prepare a series of standards that contains varying amounts of the analyte, but constant amounts of internal standard.
- 3. Prepare unknown solutions that have the same amount of internal standard as the standard solutions contain.
- 4. Measure the response of each solution for the standard and the analyte
- 5. Prepare a calibration plot of the relative response of the analyte and internal standard as a function of analyte concentration.
- 6. Use the calibration curve to determine the concentration of analyte in the measured unknown solution.
- 7. Account for any dilution steps to determine the concentration of analyte in the original unknown solution.

3. In producing a calibration curve, raw data is typically subjected to a "linear least squares" analysis. Dissect the phrase "linear least squares" and describe qualitatively what is done in a linear least squares analysis. Why "linear"? "Least squares" of what? No calculations are necessary.

The goal of a linear least squares analysis is to determine the linear relationship (y = mx+b) that "best" describes the trend in a data set. In this analysis, "best" means that the calculated values for slope (m) and intercept (b) describe a line where the sum of the squares of the residuals (the difference between the actual y-values and those predicted by the line) is minimized. This is accomplished by setting the partial derivatives of the residuals calculation with respect to the slope and intercept to zero and solving for m and b. A key assumption in this analysis is that the x-values are known to a high degree of precision, while the y-values hold the most uncertainty.

4. The sensitivity of an analytical method is often confused with the limit of detection, even though they are not the same. Explain the differences between the sensitivity and limit of detection.

Your discussion should focus on the fact that sensitivity describes the ability of a method to distinguish between small changes in concentration (or amount) of analyte throughout the range of the measurement. The limit of detection describes the minimum concentration (or amount) of analyte that can be distinguished from the blank with some level of certainty. It is certainly possible for a method to be sensitive and not have a small limit of detection, and vice versa.

5. You have been given the task of teaching a new student, AI 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 AI 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

Do <u>three</u> of problems 6-9. Clearly mark the problems you do not want graded. (15 pts each)

 You need to prepare a 500.0 mL of solution that is 100.0 ppm calcium. Clearly describe how you would prepare this solution starting from the points below. Include the quantities of each starting material that you would need

a. starting with solid calcium nitrate

Remember, calcium nitrate is Ca(NO₃)₂ (FW = 164.088 g/mol)

 $\frac{100 \text{ mg Ga}^{2+}}{1 \text{ L}} x_{1} \frac{\text{mol Ga}^{2+}}{40.08 \text{ g}} x_{1} \frac{\text{mol Ca}(\text{NO}_{3})_{2}}{1 \text{ mol Ca}^{2+}} x_{1} \frac{164.088 \text{ g Ca}(\text{NO}_{3})_{2}}{1 \text{ mol Ca}(\text{NO}_{3})_{2}} x_{1} \frac{164.088 \text{ g Ca}(\text{NO}_{3})_{2}}{1 \text{ mol Ca}^{2+}} x_{1} \frac{1 \text{ mol Ca}(\text{NO}_{3})_{2}}{1 \text{ mol Ca}(\text{NO}_{3})_{2}} x_{1} \frac{164.088 \text{ g Ca}(\text{NO}_{3})_{2}}{1 \text{ mol Ca}(\text{NO}_{3})_{2}}} x_{1} \frac{164.088 \text{ g Ca}(\text{NO}_{3})_{2}}{1 \text{$

So, dissolve 0.2047 g Ca(NO₃)₂ in a small amount of water in a 500 mL volumetric flask, mix well, dilute to the mark and mix well again.

b. starting with a 0.100 M calcium nitrate solution

Since each mole of $Ca(NO_3)_2$ that dissociates liberates 1 mole of Ca^{2+} , a 0.100 M $Ca(NO_3)_2$ solution is also 0.100 M Ca^{2+}

$$\frac{100 \text{ mg } \text{Ga}^{2+}}{1 \text{ L}} \times \frac{1 \text{ mol } \text{Ga}^{2+}}{40.08 \text{ g}} \times 0.500 \text{ Lx} \frac{1 \text{ L}}{0.100 \text{ mol } \text{Ga}^{2+}} = 12.5 \text{ mL}$$

So, dilute 12.5 mL of 0.100 M CaCl₂ solution in a small amount of water in a 500 mL volumetric flask, mix well, dilute to the mark and mix well again. The 12.5 mL could be delivered by pipet or buret.

7. You have run a series of titrations to determine the unknown concentration of KHP in a solid sample. The results of titrations indicate KHP concentrations of 36.14%, 35.69%, 30.15%, 35.55%, 36.07%, 35.98%. The "true" value for KHP in this sample is 36.29%. Evaluate the data and determine if your results differ from the true value at the 95% confidence level.

Looking at the data, it appears that the value 30.15% is an outlier so try a Q-test or a G-Test:

$$Q_{calc} = \frac{35.55 - 30.15}{36.14 - 30.15} = 0.90$$
 $G_{calc} = \frac{34.93 - 30.15}{2.147} = 2.23$

 $Q_{table} = 0.56 < Q_{calc}$, and $G_{table} = 1.822 < G_{calc}$ so the data point should be rejected.

Based on the remaining data, the mean for the data set is $35.88_6\%$ with a standard deviation of $0.2_5\%$. Do a t-test:

$$t_{\text{calculated}} = \frac{|36.29 - 35.88_6|}{0.25}\sqrt{5} = 3.553$$

 t_{table} for 4 degrees of freedom is 2.776, since t_{calc} > t_{table} , the results do differ significantly.

(NOTE: if you do not do the Q-test, the standard deviation is large enough that is looks like the results do not differ. Always look at the data!)

Alternatively, you could have calculated the range determined by the confidence limit and shown that 36.29% lies outside this range. The 95% CI is $35.9 \pm 0.3\%$

8. Nitrite (NO₂⁻) was measured in rainwater and unchlorinated drinking water using replicate measurements of a single sample by an established spectrophotometric method. Based on the results below, does drinking water sample contain significantly more nitrite than rainwater sample (at the 95% confidence level)?

Replicate	1	2	3	4	5	mean	st. dev.
Rainwater (ppb)	55.1	59.6	63.1	66.4	71.5	63.1	6.28
Drinking Water (ppb)	74.6	81.0	87.3	91.8	93.2	85.6	7.77

This is a comparison of two methods, using several runs of a single sample to establish the uncertainty on each method. Since we have two means and standard deviations, use s_{pooled} to perform a t-test. Check the standard deviations with an F-test first:

$$\mathsf{F}_{\text{calculated}} = \frac{(\mathsf{s}_1)^2}{(\mathsf{s}_2)^2} = \frac{(7.77)^2}{(6.28)^2} = 1.53$$

Since $F_{calculated}$ is less than F_{table} (6.39), our "normal" equations will be fine.

$$s_{\text{pooled}} = \sqrt{\frac{(6.28)^2(4) + (7.77)^2(4)}{5+5-2}} = 7.06$$

$$t_{\text{calculated}} = \frac{85.2 - 63.0}{7.06} \sqrt{\frac{25}{5+5}} = 5.02$$

 t_{table} for (5+5-2) = 8 degrees of freedom is 2.306

Since $t_{calculated} > t_{table}$, the results **are** significantly different

9. The composition of a sample containing an unknown amount of sodium carbonate in combination with an inert material was determined by dissolving the sample in 20.0 mL of water and titrating the resulting solution with standardized nitric acid solution. Using the information below, determine the percent by mass of sodium carbonate in the original sample, with its absolute uncertainty. You may assume that the contribution of molar masses to the overall uncertainty is negligible.

Concentration of nitric acid standard	0.2026 ± 0.0006 M
Mass of carbonate-containing sample	0.9113 ± 0.0005 g
Initial buret reading	1.28 ± 0.05 mL
Final buret reading	29.74 ± 0.05 mL

 $Na_2CO_3 + 2HNO_3 \rightarrow H_2CO_3 + 2NaNO_3$

Uncertainty in the volume delivered by the buret:

 $(29.74 \pm 0.05 \text{ mL}) - (1.28 \pm 0.05 \text{ mL}) = 28.46 \pm e_1 \text{ mL}$ $e_1 = [(0.05)^2 + (0.05)^2]^{1/2} = 0.0707 \text{ mL}$

Concentration calculation: (DON'T FORGET THE STOICHIOMETRY!)

$$\frac{0.2026\pm0.0006 \text{ mol HNO}_3 \times 28.46\pm0.07 \text{mL } \times 1 \text{ mol Na}_2\text{CO}_3 \times 1 \text{ L}}{2 \text{ mol HNO}_3 \text{ 1000 mL}} = 0.002882998 \pm 2 \text{ mol HNO}_3 \text{ mol H$$

 $0.002882998 \pm ? \text{ mol } Na_2CO_3 \times \underbrace{105.988 \text{ g } Na_2CO_3}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{0.9113 \pm 0.0005 \text{ g sample}} \times \underbrace{100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x100\% = 33.530 \pm e_2 \%}_{1 \text{ mol } Na_2CO_3} \times \underbrace{1 \qquad x10$

e ₂ = 33.530 %	$\left(\frac{0.0006}{0.2026}\right)^2$ +	$\left(\frac{0.07}{28.46}\right)^2$ +	$-\left(\frac{0.0005}{0.9113}\right)^2$	= 33.530 M(0.00389) = 0.130 %
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 $e_2 = 0.130 = 0.1$ % so the percent sodium carbonate is 33.5 ± 0.1 %

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
$\mu = \overline{x} \pm \frac{ts}{\sqrt{n}}$	$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
$\mathbf{e}_{\mathrm{C}} = \sqrt{\mathbf{e}_{\mathrm{A}}^2 + \mathbf{e}_{\mathrm{B}}^2}$	$e_{c} = C_{\sqrt{\left(\frac{e_{A}}{A}\right)^{2} + \left(\frac{e_{B}}{B}\right)^{2}}}$
$t_{calculated} = \frac{ known value - \overline{x} }{s} \sqrt{n}$	$s = \sqrt{\frac{\sum_{i} (x_i - \overline{x})^2}{n - 1}}$
$t_{calculated} = \frac{\left \overline{x}_{1} - \overline{x}_{2}\right }{s_{pooled}} \sqrt{\frac{n_{1}n_{2}}{n_{1} + n_{2}}}$	$s_{pooled} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$
$t_{calculated} = \frac{\overline{d}}{s_d} \sqrt{n}$	$s_d = \sqrt{\frac{\sum (d_i - \overline{d})^2}{n - 1}}$
$s_{x} = \frac{s_{y}}{\left m\right } \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{\left(y - \overline{y}\right)^{2}}{m^{2} \sum \left(x_{i} - \overline{x}\right)^{2}}}$	$s_y = \sqrt{rac{\sum (d_i - \overline{d})^2}{n-2}} = \sqrt{rac{\sum d_i^2}{n-2}}$
$s_m^2 = \frac{s_y^2 \times n}{D}$	$s_b^2 = \frac{s_y^2 \sum x_i^2}{D}$
y _{LOD} = y _{blank} + 3s	$F_{calculated} = \frac{(s_1)^2}{(s_2)^2}$
$Q_{calculated} = \frac{gap}{range}$	$G_{calculated} = \frac{ suspect value - \overline{x} }{s}$

Values of Student's t

	Confidence Level (%)						
Degrees of Freedom	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 ₁								
Degrees of freedom for s ₂	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

INERT IIA IIIB IYB YΒ YIB YIIB YIII IB IIB IIIA YΑ YIA YIIA GASES IA IYA 2 1 H 1.00797 He н 1.00797 Li 9 4 10 6 Č В Be Ν 0 F Ne 12.0112 18.9984 6.939 9.0122 10.811 14.0067 15.9994 20,183 17 11 12 13 14 15 16 18 Na Mg 22.9898 24.312 Si Ρ **S** 32.064 CI 35.453 AI Ar 22.9898 26.981 28.086 30.9738 39.948 19 20 29 30 31 32 33 34 35 36 21 24 25 26 27 28 22 23 **K** 39.102 Sc 44.956 Ca 40.08 Ti 47.90 Cr 51.996 Co Cu 63.54 Zn 65.37 Se 78.96 v **As** 74.9216 Mn Fe Ni Ga Ge Br Kr 50.942 54.9380 55.847 58.9332 58.71 69.72 72.59 79,909 83.80 54 38 41 45 47 50 37 39 40 42 43 44 46 48 49 -51 52 53 **Sr** 87.62 Ag **Cd** 112.40 **Sn Sb** 121.75 Xe RЬ Y Zr NЬ Мο Τc Ru Rh Pd Тe I In 85.47 88.905 91.22 92.906 95.94 (99) 101.07 102.905 106.4 114.82 127.60 126.904 55 56 *57 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 Hg Hf w Pt Po At (210) Cs Ba La Re TΙ ΡЬ Bi Тα Os Ir Au Rn 132.905 137.34 138.91 180.948 183.85 190.2 192.2 195.09 196.967 200.55 204.37 207.19 (210) 178.49 186.2 208.980 (222) 87 88 **# 89** 105 108 109 104 106 107 110 111 112 ? ? ? **Rf** (261) **Sg** (266) Hs (265) Ra Άc Bh Mt Fr Db (277) (223) (226) (227) (262) (262) (266) (271) (272) Numbers in parenthesis are mass numbers of most stable or most * Lanthanide Series 59 60 58 61 62 64 66 67 68 69 70 71 63 65 common isotope. Ce Pr Nd Pm Sm 140.907 144.24 (147) Eu 151.96 Tb Dy Ho 158.924 162.50 164.930 Er Tm 167.26 168.934 Gd 157.25 YЬ Lu Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights. 173.04 174.97 +Actinide Series 90 91 92 93 94 95 96 97 98 99 100 101 102 103 The group designations used here are the former Chemical Np (237) Es (254) Pa Pu Cf Fm Md No Th U Am Cm Bk Lr Abstract Service numbers.

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