

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. We tend to ignore the contribution of buoyancy in virtually all of the mass measurements we make in the laboratory. How can we get away with this? Identify one situation where we would be unable to ignore buoyancy-introduced error.

The buoyancy correction accounts for the varying volume of air displaced when a sample is weighed compared to the volume displaced when the balance was calibrated with calibration weights. When the density of the sample being weighed is similar to the density of the balance weights (8 g/mol), the error due to buoyancy is minimal (remember the plot we discussed in class). In general buoyancy errors are minimal because we have been weighing solid samples and because we do our critical weighing **by difference**. If we were to weigh samples of very low density (like water or organic solvents or especially gases), we should account for buoyancy errors.

2. Describe a situation when the calculation of s_{pooled} would be necessary. How does this situation differ from one where s_d would be calculated?

The pooled standard deviation is used in situations where you have multiple measurements of a single sample run on two methods. The calculation using s_d is performed when single measurements of multiple samples are run on two methods.

3. What do the terms TD and TC stand for? What types of volumetric glassware are typically labeled TD? What types of volumetric glassware are typically labeled TC?

TC stands for "To Contain". Volumetric flasks are typically TC

TD stands for "To Deliver". Volumetric pipets and burets are typically TD

4. Whenever we use a confidence interval to represent the proximity of our results to the “true” value, we are forced to make an important assumption. What assumption must be made to use such a statistical analysis to reflect the accuracy of a measurement? Why is this assumption necessary?

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.

5. Outline the process that would typically be used in lab to perform a standard additions experiment. (*hint: you will need more than two solutions*)
 - Prepare a series of solutions, each containing the same amount of your unknown solution and "spiked" with a different (and known) concentration of analyte (including "0")
 - Perform analysis using each solution
 - Plot signal vs. added analyte concentration
 - Calculate least-squares line
 - Extrapolate the line to the x-intercept. The unknown concentration in the measured solution corresponds to the value at the x-intercept.
 - Account for any dilutions to determine the analyte concentration in your original unknown solution.

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

6. 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:

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

7. Low concentrations of thallium near the detection limit gave the following dimensionless instrument readings: 211.3, 178.9, 168.3, 180.3, 225.3, 166.1, 229.1, 207.7, 140.7, and 211.5. Ten blanks had a mean reading of 43.9. The slope of the calibration curve is $1.10 \times 10^9 \text{ M}^{-1}$. Estimate the detection limit for thallium.

The average of the measurements is: 191.9₂

The standard deviation is: 29.1₇. We assume the standard deviation of the blanks is the same

So, the signal at the detection limit is:

$$y_{\text{LOD}} = y_{\text{blank}} + 3s_{\text{blank}}$$
$$y_{\text{LOD}} = 43.9 + 3(29.1_7) = 131.4$$

We can use the slope to convert this to a concentration:

$$\text{LOD} = 131.4 / (1.10 \times 10^9 \text{ M}^{-1}) = \mathbf{1.19 \times 10^{-7} \text{ M}}$$

8. 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, 48.4, 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.

9. 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 Na_2CO_3 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 $0.5976 \pm 0.0005 \text{ M}$

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.

Atomic 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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