

Complete two (2) of problems 1-3 and four (4) of problems 4-8. CLEARLY mark the problem 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 wrote a concentration on the board at 8:30 AM as he started class and said that the concentration would be an answer to one of the exam 1 questions. What concentration did he put on the board? **4.3 ppm**

Do two of problems 1-3. Clearly mark the problem you do not want graded. (10 pts each)

1. A Standard Reference Material is certified to contain 85.4 ppm of an organic contaminant in soil. You analyze this SRM to characterize a new method you are developing. Your analysis gives values of 88.6, 87.4, 83.6, 88.4, and 87.2 ppm. Do your results indicate the presence of systematic error in your method at the 95% confidence level? Justify your answer.

With all of the other data bunched around 87 and 88 ppm, the point at 83.6 ppm should look a little odd and worthy of a Q-test. Q for 5 observations is 0.64

$$\frac{87.2-83.6}{88.6-83.6} = \frac{3.6}{5} = 0.72 > 0.64 \text{ so omit } 83.6$$

*(The same conclusion is reached if a Grubb's test is used.)*

Based on the new dataset, the mean is 87.9 ppm, and  $s = 0.702$  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%,  $t_{\text{table}} = 3.182$

$$CI = 87.9 \pm \frac{ts}{\sqrt{n}} = 87.9 \pm \frac{3.182 \times 0.702}{\sqrt{4}} = 87.9 \pm 1.17$$

So, the confidence range is  $88 \pm 1$  ppm, which does not include the true value, therefore, there seems to be an indication of systematic error (at least a 5% chance).

*If you do not do the Q-test, the confidence range becomes  $87 \pm 3$  ppm*

2. Concisely describe how you would prepare 1.00 L of a 100.0 ppm  $\text{Pb}^{2+}$  solution from solid lead nitrate. You may assume a density of 1.00 g/mL for all solutions.

There are multiple ways to approach this problem. Here's one.

Since  $d=1.00\text{g/mL}$ , we can approximate ppm with mg/L

$$\frac{100.0 \text{ mg Pb}^{2+}}{\text{L solution}} \times \frac{1 \text{ mol Pb}^{2+}}{207.19 \text{ g Pb}^{2+}} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 4.82_6 \times 10^{-4} \text{ M Pb}^{2+}$$

From this concentration, we can find the mass of  $\text{Pb}(\text{NO}_3)_2$  needed.

$$\frac{4.82_6 \times 10^{-4} \text{ mol Pb}^{2+}}{\text{L solution}} \times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{1 \text{ mol Pb}^{2+}} \times \frac{331.2098 \text{ g}}{1 \text{ mol Pb}(\text{NO}_3)_2} = 0.159_9 \text{ g Pb}(\text{NO}_3)_2 \text{ per } 1 \text{ L solution}$$

So, to prepare 1 L of 100.0 ppm  $\text{Pb}^{2+}$ , dissolve 0.160 g of  $\text{Pb}(\text{NO}_3)_2$  in water and dilute to 1.00L.

3. Why do systematic (determinate) errors typically have a larger impact on the accuracy of a measurement than 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).

**Do four of problems 4-8. Clearly mark the problem you do not want graded. (15 pts each)**

4. The data below is for the determination of sodium in potato-chip samples using atomic spectroscopy. Least-squares analysis resulted in a line with slope of 0.016394 V/ppm and an intercept of 0.041373 V. Measurement of a single unknown sample resulted in a signal of 0.576 V. Calculate the concentration of sodium in the unknown, and its 95% confidence interval. The value for the D determinate is 9850.

Na Conc. x (ppm)	Signal y (V)	x <sup>2</sup>	y <sup>2</sup>	xy	y <sub>line</sub>	residuals d	d <sup>2</sup>	(x <sub>i</sub> - $\bar{x}$ ) <sup>2</sup>	
5	0.088	25	0.007744	0.440	0.1233	-0.03535	0.001249	676	
15	0.299	225	0.08940	4.485	0.2872	0.01171	0.000137	256	
30	0.560	900	0.3136	16.80	0.5332	0.02679	0.000718	1	
45	0.820	2025	0.6724	36.90	0.7791	0.04087	0.001671	196	
60	0.981	3600	0.9623	58.86	1.0250	-0.04404	0.001939	841	
<b>Sum (Σ)</b>	155	2.748	6775	2.0455	117.48	2.748	2.2x10 <sup>-16</sup>	0.005715	1970
<b>Average</b>	31	0.5496	1355	0.4091	23.497	0.5496	4.4x10 <sup>-17</sup>	0.001143	394

We first need to find the concentration corresponding to y = 0.576 V using the calibration relationship:

$$0.576 \text{ V} = (0.016394 \text{ V/ppm}) x + 0.041373 \text{ V}$$

Solving for x, we find  $x = (0.576 \text{ V} - 0.041373 \text{ V}) / (0.016394 \text{ V/ppm}) = 32.611 \text{ ppm}$

In order to determine the value for s<sub>x</sub>, we need a value for s<sub>y</sub>

$$s_y = \sqrt{\frac{\sum d_i^2}{n-2}} = \sqrt{\frac{0.005715}{3}} = 0.04365$$

$$s_x = \frac{s_y}{|m|} \sqrt{\frac{1}{k} + \frac{x^2 n}{D} + \frac{\sum x_i^2}{D} - \frac{2x \sum x_i}{D}} = \frac{0.04365}{|0.016394|} \sqrt{\frac{1}{1} + \frac{32.611^2(5)}{9850} + \frac{6775}{9850} - \frac{2(32.611)(155)}{9850}} = 2.917_9$$

95% CI (3 degrees of freedom, t = 3.182)

$$x = 32.611 \pm (3.182)(2.917) \text{ ppm} = \mathbf{33 \pm 9 \text{ ppm}}$$

5. A series of titrations have been run in order to determine the percent benzoic acid (molar mass  $122.123 \pm 0.002$  g/mol) in a solid mixture that contains benzoic acid and an inert compound. If it requires  $42.07 \pm 0.02$  mL of  $0.0997 \pm 0.0004$  M NaOH to neutralize the benzoic acid present in  $1.5835 \pm 0.0002$  grams of the sample, what is the percent benzoic acid in the unknown? Include calculation of the absolute uncertainty in your result. Benzoic acid is a monoprotic acid.

This is an exercise in error propagation. Start with the general calculation to determine the % Benzoic acid (HBz), then determine how the error will propagate (as absolute, relative, or both.)

$$42.07 \text{ mL} \times \frac{0.0997 \text{ mol-OH}^-}{\text{L}} \times \frac{1 \text{ mol HBz}}{1 \text{ mol-OH}^-} \times \frac{122.123 \text{ g}}{1 \text{ mol HBz}} = 512.2 \text{ mg HBz}$$

$$\frac{0.5122 \text{ g HBz}}{1.5835 \text{ g sample}} \times 100\% = 32.347\% \text{ HBz}$$

Since all of the operations are multiplication and division, the error will propagate as the relative uncertainties.

$$e_{\%}/\% = [(0.002/122.123)^2 + (0.02/42.07)^2 + (0.0004/0.0997)^2 + (0.0002/1.5835)^2]^{1/2}$$

$$e_{\%}/\% = 0.00404 = \mathbf{0.40\% \text{ relative uncertainty}}$$

$$e_{\%} = 0.00404 \times 32.347 = \mathbf{0.131\% \text{ absolute uncertainty}}$$
 (this number has percent units because our 32.347% has percent units)

**So, the percent HBz is  $32.3 \pm 0.1\%$**

6. While preparing for this exam, one of your classmates asks you why a confidence interval is used to describe the “quality” of a result, as opposed to a standard deviation alone. Clearly explain why a confidence interval is used and what types of information we can infer from the confidence interval about the quality of a result.

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 helps to account for this by adjusting the size of the confidence interval, depending on how well we have defined the scatter in the data (based on the number of data points). This allows a more realistic estimation of the measurement’s precision.

The confidence interval also allows us to make some inferences about the accuracy of a method, assuming only random errors are impacting our measurement.

7. The Au content (wt %) of a single ore sample was determined using two independent methods. The results for five replicate measurements of the same sample for each method are given the table below. Do the results indicate a significant difference at the 95% confidence level?

Measurement	1	2	3	4	5	Mean	s
Method A	0.0134	0.0144	0.0126	0.0125	0.0137	0.013 <sub>32</sub>	0.0007 <sub>92</sub>
Method B	0.0135	0.0156	0.0137	0.0137	0.0146	0.014 <sub>22</sub>	0.0008 <sub>81</sub>

This is a comparison of two methods, using several runs of a single sample to establish the uncertainty in each method. Since we have two means and standard deviations, use  $s_{\text{pooled}}$  to perform a t-test. Our ability to use  $s_{\text{pooled}}$  depends on the results of an F test verifying that our means are the "same"

$F_{\text{calc}} = (s_B^2)/(s_A^2) = 1.24 < F_{\text{table}} (6.39)$  so standard deviations are not different.

$$s_{\text{pooled}} = \sqrt{\frac{(0.00079)^2(4) + (0.00088)^2(4)}{5 + 5 - 2}} = 0.000838$$

$$t_{\text{calculated}} = \frac{0.014_2 - 0.013_3}{0.00083_8} \sqrt{\frac{25}{5 + 5}} = 1.698$$

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

Since  $t_{\text{calculated}} > t_{\text{table}}$ , the results **are not** significantly different

8. You have been given the task of teaching a quantitative analysis student, Al Thumbs, the proper laboratory techniques to obtain high quality quantitative results. Chose **one** of the two lab procedures below and clearly describe your instructions to this student, include reminders of common pitfalls Al should avoid.
- Handling and accurately massing solid samples
  - The proper use of a Class A buret for titrations

Your discussion for "a" should include the following:

- Drying solid samples to constant mass (what does "constant mass" mean?)
- Making mass measurements by "weighing by difference" (how?)
- Handle weighing bottles using lint-free and oil-free materials
- Cool solid samples before weighing
- Close balance doors before weighing
- Store samples in dessicator

Your discussion for "b" 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)
- Accounting for the width of the graduations in your reading of the buret
- Taking care to "cut" drops near the endpoint

## Blank Space if You Need Extra Room

**PERIODIC CHART OF THE ELEMENTS**

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	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 (256)	102 No (256)	103 Lr (257)
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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>
$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$	$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
$t_{\text{calculated}} = \frac{ \text{known value} - \bar{x} }{s} \sqrt{n}$	$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$
$t_{\text{calculated}} = \frac{ \bar{x}_1 - \bar{x}_2 }{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$	$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$
$t_{\text{calculated}} = \frac{\bar{d}}{s_d} \sqrt{n}$	$s_d = \sqrt{\frac{\sum_i (d_i - \bar{d})^2}{n-1}}$
$m = \left  \begin{array}{cc} \sum (x_i y_i) & \sum x_i \\ \sum y_i & n \end{array} \right  \div D$	$b = \left  \begin{array}{cc} \sum x_i^2 & \sum (x_i y_i) \\ \sum x_i & \sum y_i \end{array} \right  \div D$
$D = \left  \begin{array}{cc} \sum x_i^2 & \sum x_i \\ \sum x_i & n \end{array} \right $	$s_y = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n-2}} = \sqrt{\frac{\sum d_i^2}{n-2}}$
$s_m^2 = \frac{s_y^2 \times n}{D}$	$s_b^2 = \frac{s_y^2 \sum x_i^2}{D}$
$s_x = \frac{s_y}{ m } \sqrt{\frac{1}{k} + \frac{x^2 n}{D} + \frac{\sum x_i^2}{D} - \frac{2x \sum x_i}{D}}$	$s_x = \frac{s_y}{ m } \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y - \bar{y})^2}{m^2 \sum (x_i - \bar{x})^2}}$
$Q_{\text{calculated}} = \frac{\text{gap}}{\text{range}}$	$G_{\text{calculated}} = \frac{ \text{suspect value} - \bar{x} }{s}$
$F_{\text{calculated}} = \frac{(s_1)^2}{(s_2)^2}$	<p>Look both ways before crossing the street</p>

**Values of Student's t**

Degrees of Freedom	Confidence Level (%)			
	90	95	99.5	99.9
1	6.314	12.706	127.32	636.619
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
20	1.752	2.086	3.153	3.850
30	1.697	2.042	3.030	3.646
40	1.684	2.021	2.971	3.551
60	1.671	2.000	2.915	3.460
120	1.658	1.980	2.860	3.373
$\infty$	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
7	0.51
8	0.47
9	0.44
10	0.41

**Grubbs Test for Outliers**

# of Observations	$G_{critical}$ At 95% confidence
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176

**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
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98