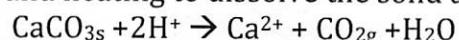


Exam 1

Name: key

Be sure to show ALL your work, write CLEARLY, and put your answers in the boxes.  
 For this exam, you are allowed the exam, a provided equation sheet, and an nonprogrammable graphing calculator.

1. Limestone consists of mainly the mineral calcite,  $\text{CaCO}_3$  (FM=100.87 g mol<sup>-1</sup>). The carbonate content of 0.5413g of powdered limestone was measured by suspending the powder in water, adding 10.00mL of 1.396 M HCl, and heating to dissolve the solid and expel  $\text{CO}_{2\text{g}}$ :



The excess acid required the addition of 39.96 mL of 0.1004 M NaOH for neutralization. Find the weight percent calcite in the limestone.

1-46, 1-34, 1-11

moles  $\text{CaCO}_3$  will be equal to moles  $\text{H}^+$  = moles NaOH divided by two. Thus,

$$\frac{1.396 \text{ mol HCl}}{\text{L}} \times \frac{10.00 \text{ mL}}{1} \times \frac{\text{L}}{1000 \text{ mL}} = 0.01396 \text{ mol H}^+$$

$$\frac{0.1004 \text{ mol NaOH}}{\text{L}} \times \frac{39.96 \text{ mL}}{1} \times \frac{\text{L}}{1000 \text{ mL}} = 4.0198 \times 10^{-3} \text{ mol NaOH}$$

$$0.01396 \text{ mol H}^+ - 4.0198 \times 10^{-3} \text{ mol NaOH} = 9.9402 \times 10^{-3} \text{ mol H}^+$$

$$9.9402 \times 10^{-3} \text{ mol H}^+ \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol H}^+} = 4.9701 \times 10^{-3} \text{ mol CaCO}_3$$

$$4.9701 \times 10^{-3} \text{ mol CaCO}_3 \times \frac{100.87 \text{ g CaCO}_3}{1 \text{ mol}} = 0.5013 \text{ g CaCO}_3$$

$$\frac{0.5013 \text{ g CaCO}_3}{0.5413 \text{ g limestone}} \times 100\% = 92.41\%$$

Wt % $\text{CaCO}_3$ in limestone	
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## 2. Errors in the laboratory

State the characteristics of Random error

- always present
- random direction & magnitude
- no assignable cause
- 

How is random error quantified?

- precision of replicate measurements
- standard deviation

Define Systematic error

- physical cause
- always affects data in same direction & magnitude

List at least 4 ways that systematic error can be detected.

- standard reference materials
- blank measurements
- calibration checks
- interlaboratory / method comparison

a. A 25 ml pipet consistently delivers  $24.78 \pm 0.09$  mL

Error type	Magnitude	Explanation
Random	$0.09\text{mL}$	the volume the pipet delivers varies by an st. dev. of $0.09\text{mL}$
Systematic	$0.22\text{mL}$	the pipet delivers on average $0.22\text{mL}$ less than it is supposed to

3. Propagation of error. To prepare a solution of  $\text{Ba}(\text{NO}_3)_2$  ( $\text{FM}=261.32 \text{ g mol}^{-1}$ ), you weigh out  $5.732 \pm 0.002 \text{ g}$  and dissolve it in a volumetric flask whose volume is  $100.00 \pm 0.08 \text{ mL}$ . Express the molarity of the solution, along with its absolute and percent relative uncertainty. Express your answer with a reasonable number of significant figures and follow the table method of keeping track of error shown in class for full credit.

$$5.732 \pm 0.002 \text{ g Ba}(\text{NO}_3)_2 \times \frac{\text{mol}}{261.32 \text{ g Ba}(\text{NO}_3)_2} = 0.021934 \pm 7.65 \times 10^{-4} \text{ mol Ba}(\text{NO}_3)_2$$

$$\frac{0.021934 \pm 0.000008 \text{ mol Ba}(\text{NO}_3)_2}{100.00 \pm 0.08 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 0.219347 \pm \frac{\text{mol}}{\text{L}}$$

$e_1$	$e$	$e/y$	$y \cdot e$	$y \cdot e^2$
	$7.65 \times 10^{-4}$	$3.489 \times 10^{-4}$	$0.0349$	$1.2175 \times 10^{-3}$
$e_2$	$0.08$	$8 \times 10^{-4}$	$0.08$	$+ 6.4 \times 10^{-3}$
$\Delta e$	$1.91 \times 10^{-4}$	$8.727 \times 10^{-4}$	$0.087$	$7.6175 \times 10^{-3}$

$\uparrow$   
absolute  
uncertainty

$\uparrow$   
% relative  
uncertainty

[NaCl] (M)	0.2193
Absolute uncertainty	$2 \times 10^{-4}$
Relative percent uncertainty	0.09

4. One of the principle goals of this class is for students to be able to critically evaluate data. Consider the dataset to the right listing the analytical results for the total sulfur content in mine tailings by two different methods. Your objective with this problem is to compare data collected by replicate measurements of the same sample by two methods to see if they yield statistically similar results.

Define a Confidence Interval.

a statistical measure of certainty  
the larger the stated range,  
the more likely the real answer will lie within the stated range

	Method 1	Method 2
1	12.4	14.3
2	13	13.8
3	12.7	14.1
4	12.8	13.6
5	13.1	14.3
6	12.5	13.8
7	12.3	13.4
8	15.0	14.0
9	13.2	13.9
10		14.2
11		13.9
12		14.5
	Mean=13.0 <sub>0</sub>	Mean= 13.9 <sub>8</sub>
	St. dev=0.8 <sub>1</sub>	St. dev= 0.3 <sub>2</sub>
	N= 9	N= 12

What specific statistical test can be used to compare the data sets? <sup>two</sup> shown?

- a. F-test, Case 1
- b. F-test, Case 2
- c. Grubbs test
- d. T-test, Case 2
- e. T-test, Case 3

b. Before performing the statistical test selected above, begin by looking over a dataset. Do you see anything concerning? If yes, describe what.

one of the values in method 1 is higher than the rest. Method 1, measurement 8

b. What statistical test can be used to determine if a data point can be thrown out? Grubbs  
Apply this test as needed.

$$G_{\text{calc}} = \frac{| \text{questionable value} - \bar{x} |}{s} = \frac{15 - 13.00}{0.81} = 2.469$$

$$G_{\text{table}} = 2.110$$

$G_{\text{calc}} > G_{\text{table}}$ ,  $\therefore$  reject the datapoint

c. Were you able to eliminate any of your data? Circle the answer:  Yes No  
IF YES, please see me for a new mean and standard deviation.

$$\bar{x} = 12.75$$

$$s = 0.333$$

$$n = 8$$

d. Continue to compare the data to determine if the two data sets are statistically different at the 95%CI.

This is a case 2 t-test, meaning that an F-test is required to determine if the standard deviations are statistically similar. This will guide the selection of t-test equations.

### F-test

$$F_{\text{calc}} = \frac{(0.3338)^2}{(0.3157)^2} = \frac{0.1114}{0.0996} = 1.118$$

$$F_{\text{table}} (n_1 = 8; n_2 = 12) = 2.85$$

$F_{\text{calc}} < F_{\text{table}}$ , no statistical difference @ 95% CI

### T-test

$$S_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-2)}{n_1+n_2-2}} = \sqrt{\frac{0.774 + 1.096}{18}} = 0.3225$$

$$t_{\text{calc}} = \frac{112.75 - 13.98}{0.3225} \sqrt{\frac{8+12}{20}} \underset{\tau_{2,19}}{=} \frac{1.23}{0.3225} \cdot 2.19 = 8.36$$

$$t_{\text{table}} (\text{DOF} = n_1+n_2-2=18) = 2.086$$

used  $n=20$

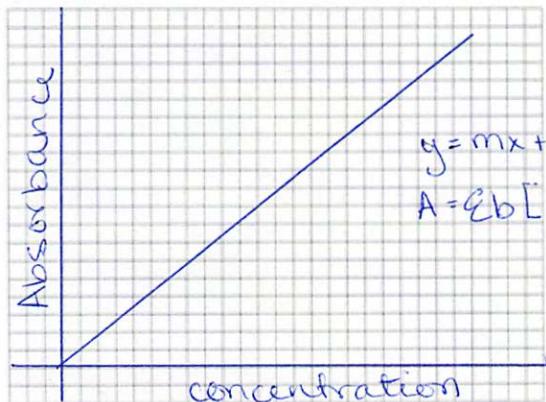
$t_{\text{calc}} > t_{\text{table}}$  ∴ means are statistically different

5. When is standard addition preferable relative to calibration curve.

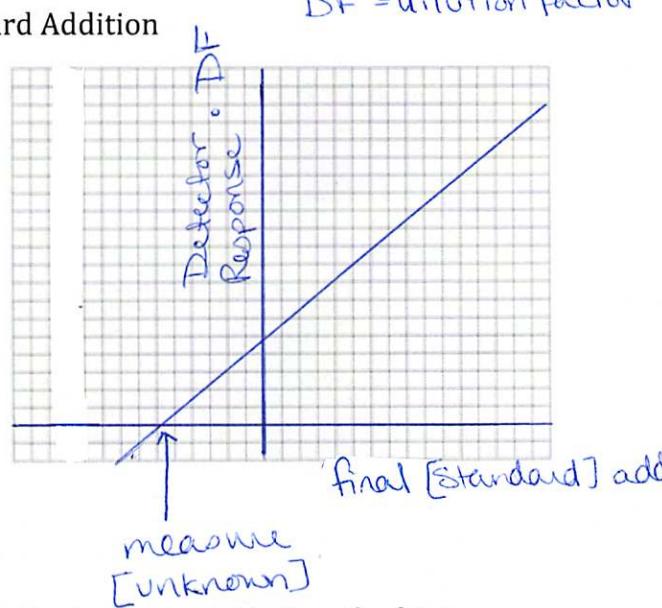
When matrix effects may distort the results.

Draw an example calibration curve and standard addition plot. On the standard addition plot, indicate where the concentration of an unknown can be measured.

Calibration Curve



Standard Addition



6. Beginning with a science question, the next step in developing an analytical method is to determine what use objectives defining what the data will be used for. List at least 5 criteria that can be used to determine if your method is suitable to addressing your science question

- # samples
- accuracy & precision
- rate of false results
- selectivity
- sensitivity
- Detection limit
- Range
- Robustness/ruggedness

6. Chloroform is an internal standard in the determination of the pesticide DDT in a polarographic analysis in which each compound is reduced at an electrode surface. A mixture containing 0.500 mM chloroform and 0.800 mM DDT gave signals of 15.3  $\mu\text{A}$  for chloroform and 10.1  $\mu\text{A}$  for DDT. An unknown solution (10.0 mL) containing DDT was placed in a 100 mL volumetric flask and 10.2 mL of 0.500 mM chloroform ( $\text{FM} = 119.39 \text{ g mol}^{-1}$ ) were added. After dilution to the mark with solvent, polarographic signals of 1.49 and 8.7  $\mu\text{A}$  were observed for the chloroform and DDT, respectively. Find the concentration of DDT in the original unknown solution.

5-31 Find response factor

$$F = \frac{\frac{A_{\text{DDT}}}{[{\text{DDT}}]}}{\frac{A_{\text{CHCl}_3}}{[{\text{CHCl}_3}]}} = \frac{\frac{10.1 \mu\text{A}}{0.800 \text{ mM}}}{\frac{15.3 \mu\text{A}}{0.500 \text{ mM}}} = \frac{12.625 \frac{\mu\text{A}}{\text{mM}}}{30.6 \frac{\mu\text{A}}{\text{mM}}} = 0.4126$$

2 Find  $[\text{CHCl}_3]$  in final soln

$$M_1V_1 = M_2V_2 \quad 0.500 \text{ mM} \cdot 10.2 \text{ mL} = M_2 (\text{mM}) \cdot 100 \text{ mL}$$

$$M_2 = 0.051 \text{ mM CHCl}_3$$

3 Find  $[\text{DDT}]$  in final soln

$$\frac{8.7 \mu\text{A}}{[{\text{DDT}}]} = 0.4126 \cdot \underbrace{\frac{1.49 \mu\text{A}}{0.051 \text{ mM}}}_{2.054}$$

$$[{\text{DDT}}] = 0.721 \text{ mM}$$

4. Calculate the  $[\text{DDT}]$  in the original solution

$$M_1V_1 = M_2V_2 \quad 0.721 \text{ mM} \cdot 10 \text{ mL} = M_2 100 \text{ mL}$$

$$[{\text{DDT}}] = 7.21 \text{ mM}$$