

CHEMISTRY 311 - ASSIGNMENT 2

Hand-in your answers in a neat and organized format to the appropriate number significant figures, showing chemical equations and calculations where appropriate.

Due date: Tuesday, Oct. 17th, 2017

1. Shown below are the results for the determination of acetaminophen (in mg) in ten separate tablets of Excedrin Extra Strength. Check for potential outliers and report the mean, standard deviation, coefficient of variation and the 95% confidence interval.

224.3 240.4 246.3 239.4 253.1 261.7 229.4 255.5 235.5 249.7

↑ potential outliers ↑

[Answer: mean = 243.53 mg

range = 37.4 mg

standard deviation = 11.9 mg

variance = 141 mg

95% CI = 8.5 mg]

mean and std dev. from calculator functions

$$\bar{x} = \frac{\sum x_i}{n} \quad s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

$$G_{\text{calc}}^{\text{low}} = \frac{224.3 - 243.5}{11.9}$$

$$= 1.61$$

$$G_{\text{calc}}^{\text{high}} = \frac{261.7 - 243.5}{11.9}$$

$$= 1.52$$

Since $G_{\text{calc}} < G_{\text{crit}}$, retain all values

$$95\% \text{ CI} = \frac{t s}{\sqrt{n}} \quad \text{where } df = n - 1 = 9$$

and $t = 2.262$

$$\therefore \text{CI} = \frac{(2.262)(11.88)}{\sqrt{10}} = 8.5 \text{ mg}$$

Using the 95% CI, the final value is reported as $244 \pm 9 \text{ mg}$ or $243.5 \pm 8.5 \text{ mg}$

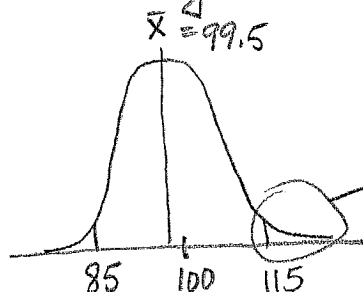
2. One of the methods used to evaluate procedures for digesting oysters and mussels prior to analyzing for the samples for cadmium involves measuring a spike recovery in which a known amount of cadmium is added to the tissue sample. The recovery is reported as the measured amount of cadmium relative to the amount added. Ideally, spike recoveries should fall within the range $100 \pm 15\%$. The results for one method are;

106% 108% 92% 99% 104% 101% 93% 93%

Assuming that the spike recoveries are normally distributed, what is the probability that any single spike recovery will be within the accepted range?

[Answer: 98.2%]

mean recovery = 99.5% $s = 6.30\%$



calculate area under normal distribution curve using Table 4.1

calculate $z \approx \frac{x - \bar{x}}{s}$ (see Section 4.1 text)

low tail; $z = \frac{85 - 99.5}{6.30} = -2.30$

area under curve at $z = 2.30$ is 0.4893

area under curve between $-\infty$ and $\bar{x} = 0.5000$

\therefore area between $-\infty$ and -2.30 is $0.5000 - 0.4893 = 0.0107$ (1.07%)

Similarly, for $\frac{115 - 99.5}{6.30} = 2.460$

area under curve = 0.4928

and betw ∞ and 2.460 = $0.5000 - 0.4928 = 0.0072$ (0.72%)

Therefore, total area outside 100 ± 15 is given by $1.07 + 0.72 = 1.79\%$

So probability of being with range is 98.2%

3. A 100.0 (± 0.1) mL water sample containing calcium and magnesium is volumetrically analyzed by titrating with $1.102 (\pm 0.003) \times 10^{-3}$ M EDTA. In the first titration the sum of calcium and magnesium concentrations is determined. A second titration is conducted after precipitating magnesium hydroxide at pH ~ 12 , such that the titration data yields only the calcium concentration. The concentration of magnesium is subsequently calculated by difference. If the uncertainty in each transferred titration volumes is ± 0.05 mL, calculate the molar concentration of both the calcium and magnesium and the relative uncertainty in each.

Titration 1: 48.16 mL (Ca + Mg)

Titration 2: 41.78 mL (Ca)

Solution:

The first titration gives the total hardness as;

$$\begin{aligned}
 [\text{Ca}^{2+} + \text{Mg}^{2+}] &= \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample}}} = \frac{((1.102 \pm 0.003) \times 10^{-3} \text{M}) (48.16 \pm 0.05 \text{ mL})}{(100.0 \pm 0.1 \text{ mL})} \\
 &= 5.307 \times 10^{-4} \text{M} \pm \sqrt{\left(\frac{0.003}{1.102}\right)^2 + \left(\frac{0.05}{48.16}\right)^2 + \left(\frac{0.1}{100.0}\right)^2} \\
 &= 5.307 \times 10^{-4} \text{M} \pm \sqrt{(7.4 \times 10^{-4}) + (1.1 \times 10^{-6}) + (1.0 \times 10^{-6})} \\
 &= 5.307 \times 10^{-4} \text{M} \pm [0.027] \text{ (relative error)} \\
 &= 5.3_1 (\pm 0.1_4) \times 10^{-4} \text{M} \text{ (absolute error)}
 \end{aligned}$$

The second titration at pH ~ 12 , gives the calcium hardness as;

$$\begin{aligned}
 [\text{Ca}^{2+}] &= \frac{M_{\text{EDTA}} \times V_{\text{EDTA}}}{V_{\text{sample}}} = \frac{((1.102 \pm 0.003) \times 10^{-3} \text{M}) (41.78 \pm 0.05 \text{ mL})}{(100.0 \pm 0.1 \text{ mL})} \\
 &= 4.604 \times 10^{-4} \text{M} \pm \sqrt{\left(\frac{0.003}{1.102}\right)^2 + \left(\frac{0.05}{41.78}\right)^2 + \left(\frac{0.1}{100.0}\right)^2} \\
 &= 4.604 \times 10^{-4} \text{M} \pm \sqrt{(7.4 \times 10^{-4}) + (1.4 \times 10^{-6}) + (1.0 \times 10^{-6})} \\
 &= 4.604 \times 10^{-4} \text{M} \pm [0.027] \text{ (relative error)} \\
 &= 4.6_0 (\pm 0.1_2) \times 10^{-4} \text{M} \text{ (absolute error)}
 \end{aligned}$$

The concentration of magnesium can therefore be determined by difference.

$$\begin{aligned}
 [\text{Mg}^{2+}] &= [\text{Ca}^{2+} + \text{Mg}^{2+}] - [\text{Ca}^{2+}] = [5.31 (\pm 0.14) \times 10^{-4} \text{M}] - [4.60 (\pm 0.12) \times 10^{-4} \text{M}] \\
 &= 0.71 \times 10^{-4} \text{M} \pm \sqrt{(0.14)^2 + (0.12)^2} = 0.71 \times 10^{-4} \text{M} (\pm 0.18) \text{ absolute error} \\
 &= 0.7_1 (\pm 0.1_8) \times 10^{-4} \text{M}
 \end{aligned}$$

Note that the relative error in the $(\text{Ca}^{2+} + \text{Mg}^{2+})$ is 2.7%, whereas that in the Mg^{2+} concentration is 25%. This is a direct consequence of the propagation of error which occurs when calculating a concentration by difference.

4. Six replicates for the determination of zinc in an individual's hair gave the following results (in ppm); 2.67 2.75 2.82 3.01 2.94 2.87
 After six months of taking zinc supplements, the study was repeated. The mean value was 3.03 ± 0.22 ppm (value \pm s) for five replicate samples. Is the difference between the two sets of data significant at the 95% confidence level?

$$\bar{X}_1 = 2.84 \text{ ppm} \quad s = 0.12 \text{ ppm} \quad n = 6$$

$$\bar{X}_2 = 3.03 \text{ ppm} \quad S = 0.22 \text{ ppm} \quad n = 5$$

$$\text{Use } |\bar{X}_1 - \bar{X}_2| = \frac{t_{\text{Spooled}}}{\sqrt{\frac{N_1 N_2}{N_1 + N_2}}}$$

$$\text{where } S_{\text{pooled}} = \left[\frac{(0.12)^2(5) + (0.22)^2(4)}{9} \right]^{1/2} = 0.172$$

$$t @ 95\% \text{ and } df = 6 + 5 - 2 = 9 \text{ is } 2.26$$

$$\begin{aligned} \text{rearranging for } t_{\text{calc}} &= \frac{|\bar{X}_1 - \bar{X}_2|}{S_{\text{pooled}}} \sqrt{\frac{N_1 N_2}{N_1 + N_2}} \\ &= \frac{|2.84 - 3.03|}{0.172} \cdot (1.65) = 1.82 \end{aligned}$$

Since $t_{\text{calc}} < t_{\text{tab}}$, there is no significant difference between \bar{X}_1 and \bar{X}_2 at 95% confidence

5. A 0.250 g sample of corn syrup was assayed for dextrose using a method that uses an enzyme assay. The sample was diluted in a volumetric flask to 100.0 mL. A 25 μ L sample was analyzed and gave an absorbance of 0.736 at 490 nm. When the same volume of a 200. mg/L dextrose standard was analyzed by the same method it gave an absorbance of 0.886 at the same wavelength. What is the concentration of dextrose (%w/w) in the original corn syrup?

[Answer: 66.46 mg/g dextrose or 6.646 %w/w]

0.250 g corn syrup into 100.0 mL

$$A_x = 0.736$$

external std containing 200. mg/L dextrose

$$A_s = 0.886$$

$$\frac{A_x}{A_s} = \frac{[X]}{[S]} \quad \text{and} \quad [X] = \left(\frac{0.736}{0.886} \right) \left(200. \frac{\text{mg}}{\text{L}} \right)$$
$$= 166.1 \text{ mg/L}$$

Therefore, in 100.0 mL flask

$$\text{we have } 0.100 \text{ L} \times 166.1 \frac{\text{mg}}{\text{L}} = 16.61 \text{ mg dextrose}$$

This all came from 0.250 g of sample

So mass percent dextrose in sample

$$= \frac{16.61 \text{ mg}}{0.250 \text{ g}} = 66.46 \frac{\text{mg dextrose}}{\text{g corn syrup}}$$

or 6.65% (wt/wt)

6. The following are relative peak areas for chromatograms of standard solutions of 2,3-butandione.

Conc (mM)	0.500	1.50	2.50	3.50	4.50	5.50
Peak Area	3.76	9.16	15.03	20.42	25.33	31.97

- a) Plot a calibration curve report the least squares linear expression.
b) Calculate the concentration of 2,3-butandione in a sample that yielded a relative peak area of 16.30 (based on the mean of four replicate analysis) and use EQN 4-27 (textbook) to calculate the standard deviation in your answer.

[Answer: a) $Peak\ Area = 5.570 [23BD] + 0.9017$

b) $[23BD] = 2.765\ mM; s = 0.047\ mM$

(see attached spreadsheet)

Least Squares Spreadsheet

number of points (n) =	x	y	xy	x ²	d	d ²
6	0.500	3.760	1.88	0.25	0.0733	0.0054
	1.500	9.160	13.74	2.25	-0.0967	0.0093
	2.500	15.030	37.575	6.25	0.2033	0.0413
	3.500	20.420	71.47	12.25	0.0233	0.0005
	4.500	25.330	113.99	20.25	-0.6367	0.4053
	5.500	31.970	175.84	30.25	0.4333	0.1878
	column sums					
	18.000	105.670	414.49	71.5		6.50E-01

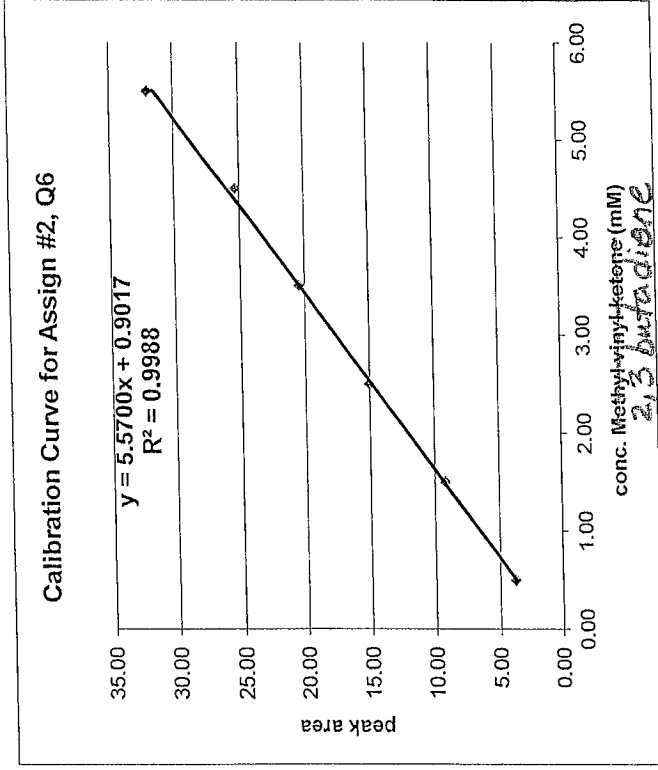
D=	s _y =	105	0.403
m=	s _m =	5.570	0.096
b=	s _b =	0.9017	0.333

F4=C4-\$A\$16*B4-\$A\$18
 A14=\$A\$5*E11-B11*B11
 A16=(D11*\$A\$5-B11*C11)/\$A\$14
 A18=(E11*C11-D11*B11)/\$A\$14
 B14=SQRT(G11/(\$A\$5-2))
 B16=\$B\$14*SQRT(\$A\$5/\$A\$14)
 B18=\$B\$14*SQRT(E11/\$A\$14)

Finding uncertainty in x with EQN 4-27 (Harris)

measured y=	16.30	input	number of replicate values of y measured (k)=	4
derived x=	2.765	output	uncertainty in derived x (s _x) =	0.047

A26=(A24-A18)/A16
 G26=(B14/A16)*SQRT((1/G24)+A26*A26*A5/A14+E11/A14-2*A26*B11/A14)



7. A standard solution was prepared containing 10.0 ppm of caffeine and 15.0 ppm of an isotopically labeled internal standard. Analysis of the sample by gas chromatography-mass spectrometry gave signals for caffeine and the internal standard of 1.55×10^3 and 2.33×10^3 (arbitrary units), respectively. Sufficient internal standard was then added to a sample to bring it to a final concentration of 15.0 ppm in the internal standard. Analysis by the same method yielded signals for caffeine and the internal standard of 2.74×10^3 and 1.98×10^3 , respectively. Report the concentration of caffeine in the sample.

[Answer: 20.80 ppm analyte]

Response factor

$$F = \frac{A_x/[X]}{A_s/[S]} = \frac{1.55/10.0 \text{ ppm}}{2.33/15.0 \text{ ppm}} = 0.9979$$

Sample

$$A_x = 0.274$$

$$A_s = 0.198$$

$$F = 0.9979$$

$$[S]_f = 15.0 \text{ ppm}$$

$$\frac{A_x}{[X]} = F \left(\frac{A_s}{[S]} \right)$$

$$\therefore [X] = \frac{A_x}{F} \cdot \frac{[S]}{A_s} = \left(\frac{0.274}{0.9979} \right) \left(\frac{15.0 \text{ ppm}}{0.198} \right)$$

$$= 20.80 \text{ ppm}$$

8. A urine sample is analyzed for copper by the method of standard additions as follows. Three 5.00 mL aliquots were taken from the same sample. Nothing is added to the first aliquot, 50. μL of a 100.0 mg/L Cu^{2+} standard was added to the second and 100. μL of the same standard was added to the third. The data is summarized below.

Sample	Volume of 100.0 ppm spike (μL)	Instrument Signal (a.u.)
1	0	0.205
2	50	0.320
3	100	0.426

- a) Ignoring the small volume change, calculate the conc of Cu^{2+} in the sample in mg/L.
 b) Determine the magnitude of the error introduced in part a) and indicate if this is a determinate or indeterminate error.

Answer: a) 50 μL spike \rightarrow 1.782 ppm Cu^{2+}
 100 μL spike \rightarrow 1.855 ppm Cu^{2+}
 Mean = 1.818 ppm Cu^{2+}

b) 50 μL spike \rightarrow 1.734 ppm Cu^{2+} ; determinant error +0.05 ppm Cu^{2+}
 100 μL spike \rightarrow 1.786 ppm Cu^{2+} ; determinant error +0.07 ppm Cu^{2+}
 Mean = 1.762 ppm Cu^{2+}

Solution:

a) In general for standard additions, we can write;

$$\frac{[X]_f}{[X]_f + [S]_f} = \frac{A_x}{A_{x+s}}$$

where $[X]_f$ and $[S]_f$ are the concentration of analyte in the unspiked sample and that resulting from the addition of spike, respectively and A_x and A_{x+s} are the measured signals from the unspiked and spiked samples, respectively.

In part a) we will assume that the relatively small volume change resulting from the addition of the spike does not significantly affect the result and can be ignored.

Thus, $[X]_f \approx [X]_i$

Using data from sample 1 and 2, we have;

$$[S]_f = \frac{(50. \times 10^{-6} \text{ L})(100.0 \text{ mg/L})}{(5.00 \times 10^{-3} \text{ L})} = 1.0_0 \text{ mg/L Cu}^{2+}$$

Hence,

$$\frac{[X]_i}{[X]_i + (1.0_0 \text{ mg/L})} = \frac{0.205}{0.320} = 0.640_6$$

$$[X]_i = 0.6406 ([X]_i + 1.00 \text{ mg/L}) = 0.6406 [X]_i + 0.6406 \text{ mg/L}$$

$$\text{and } [X]_i (1 - 0.6406) = 0.6406 \text{ mg/L}$$

$$\text{and } [X]_i = 0.6406 / (1 - 0.6406) = 1.7_{82} \text{ mg/L Cu}^{2+}$$

Similarly for the sample 1 and 3 (100 uL spike)
100 μL spike \rightarrow 1.85₅ ppm Cu^{2+}

Mean (part a) = 1.81₈ ppm Cu^{2+}

b) In part b), we will repeat the calculation taking into account the small dilution that occurs as a result of the spike addition.

$$[S]_f = \frac{(50. \times 10^{-6} \text{ L})(100.0 \text{ mg/L})}{(5.05 \times 10^{-3} \text{ L})} = 0.9901 \text{ mg/L Cu}^{2+}$$

$$[X]_f = [X]_i \frac{(5.00 \text{ mL})}{(5.05 \text{ mL})} = 0.9901 [X]_i$$

Substituting these into equation for standard additions using sample 1 and 2 yields;

$$\frac{[X]_i}{0.9901 [X]_i + (0.9901 \text{ mg/L})} = \frac{0.205}{0.320} = 0.640_6$$

$$[X]_i = 0.6342 [X]_i + 0.6342 \text{ mg/L}$$

$$\text{and } [X]_i (1 - 0.6342) = 0.6342 \text{ mg/L}$$

$$\text{and } [X]_i = 0.6342 / (1 - 0.6342) = 1.73 \text{ mg/L Cu}^{2+}$$

Comparing this result to that obtained in part a), we observe a determinant error +0.05 ppm Cu^{2+}

Similarly for the sample 1 and 3 (100 uL spike)

100 μL spike \rightarrow 1.78₆ ppm Cu^{2+} ; determinant error +0.07 ppm Cu^{2+}

Mean (part b) = 1.76₂ ppm Cu^{2+}

<i>Summary Table</i> Vol of spike added (uL)	Answer part a) (ppm Cu^{2+})	Answer part b) (ppm Cu^{2+})	% error*
50	1.782	1.734	2.8
100	1.855	1.786	3.9

* % error = [answer part a) – answer part b)]/answer part b)

Note:

Differences in the results between sample 2 and 3 are indeterminate (random), whereas those between part a) and part b) are determinate (systematic).