Chapter 5 Homework

5-16. (a) For the fortification level of 22.2 ng/mL, the mean of the 5 values is 23.6_6 ng/mL and the standard deviation is 5.6_3 ng/mL.

$$\text{Precision} = 100 \times \frac{5.63}{23.66} = 23.8\%.$$

$$\text{Accuracy} = 100 \times \frac{23.66 - 22.2}{22.2} = 6.6\%$$

For the fortification level of 88.2 ng/mL, the mean of the 5 values is 82.4_8 ng/mL and the standard deviation is 11.4_9 ng/mL.

$$\text{Precision} = 100 \times \frac{11.49}{82.48} = 13.9\%.$$

$$\text{Accuracy} = 100 \times \frac{82.48 - 88.2}{88.2} = -6.5\%$$

For the fortification level of 314 ng/mL, the mean of the 5 values is $302._8$ ng/mL and the standard deviation is 23.5_1 ng/mL.

$$\text{Precision} = 100 \times \frac{23.51}{302.8} = 7.8\%.$$

$$\text{Accuracy} = 100 \times \frac{302.8 - 314}{314} = -3.6\%$$

(b) Standard deviation of 10 samples: $s = 28._2$; mean blank: $y_{\text{blank}} = 45._0$

Signal detection limit $= y_{\text{blank}} + 3s = 45._0 + (3)(28._2) = 129._6$

$$\text{Concentration detection limit} = \frac{3s}{m} = \frac{(3)(28._2)}{1.75 \times 10^9\ \text{M}^{-1}} = 4.8 \times 10^{-8}\ \text{M}$$

$$\text{Lower limit of quantitation} = \frac{10s}{m} = \frac{(10)(28._2)}{1.75 \times 10^9\ \text{M}^{-1}} = 1.6 \times 10^{-7}\ \text{M}$$

5-18. Mean = 0.383 μg/L and standard deviation = 0.0214 μg/L

$$\% \text{ recovery} = \frac{0.383\ \mu\text{g/L}}{0.40\ \mu\text{g/L}} \times 100 = 96\%$$

The measurements are already expressed in concentration units. The concentration detection limit is 3 times the standard deviation = 3(0.0214 μg/L) = 0.064 μg/L.

5-19. The low concentration of Ni-EDTA has a standard deviation of 28.2 counts for 10 measurements. The detection limit is estimated to be

$$y_{\text{dl}} = y_{\text{blank}} + 3s = 45 + 3(28.2) = 129.6 \text{ counts}$$

To convert counts to molarity, we note that a 1.00 μM solution gave a net signal of 1797 – 45 = 1752 counts. The slope of the calibration curve is therefore estimated to be

$$m = \frac{y_{\text{sample}} - y_{\text{blank}}}{\text{sample concentration}} = \frac{1797 - 45}{1.00\ \mu\text{M}} = 1.75_2 \times 10^9 \frac{\text{counts}}{\text{M}}$$

The minimum detectable concentration is

$$\frac{3\,s}{m} = \frac{(3)(28.2) \text{ counts}}{1.75_2 \times 10^9 \text{ counts/M}} = 4.8 \times 10^{-8} \text{ M}$$

5-22. *Comparison of Lab C with Lab A:*

First, use the F test to see if the standard deviations are significantly different: $F_{\text{calculated}} = s_C^2/s_A^2 = 0.78^2/0.14^2 = 31._0 > F_{\text{table}} = 3.88$ (with 2 degrees of freedom for s_C and 12 degrees of freedom for s_A)

Standard deviations are not equivalent, so use the following t test:

$$\text{Degrees of freedom} = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\dfrac{(s_1^2/n_1)^2}{n_1 - 1} + \dfrac{(s_2^2/n_2)^2}{n_2 - 1}} = \frac{(0.14^2/13 + 0.78^2/3)^2}{\dfrac{(0.14^2/13)^2}{13 - 1} + \dfrac{(0.78^2/3)^2}{3 - 1}} = 2.03 \approx 2$$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} = \frac{|1.59 - 2.68|}{\sqrt{0.14^2/13 + 0.78^2/3}} = 2.4_1$$

For 2 degrees of freedom, $t_{\text{table}} = 4.303$ for 95% confidence. Since $t_{\text{calculated}} < t_{\text{table}}$, we conclude that the difference between Lab C and Lab A <u>is not</u> significant.

Comparison of Lab C with Lab B:

$F_{\text{calculated}} = s_C^2/s_B^2 = 0.78^2/0.56^2 = 1.9_4 < F_{\text{table}} = 4.74$ (with 2 degrees of freedom for s_C and 7 degrees of freedom for s_A). The standard deviations are not significantly different, so we use the following t test:

$$s_{\text{pooled}} = \sqrt{\frac{0.56^2\,(8-1) + 0.78^2\,(3-1)}{8+3-2}} = 0.61_6$$

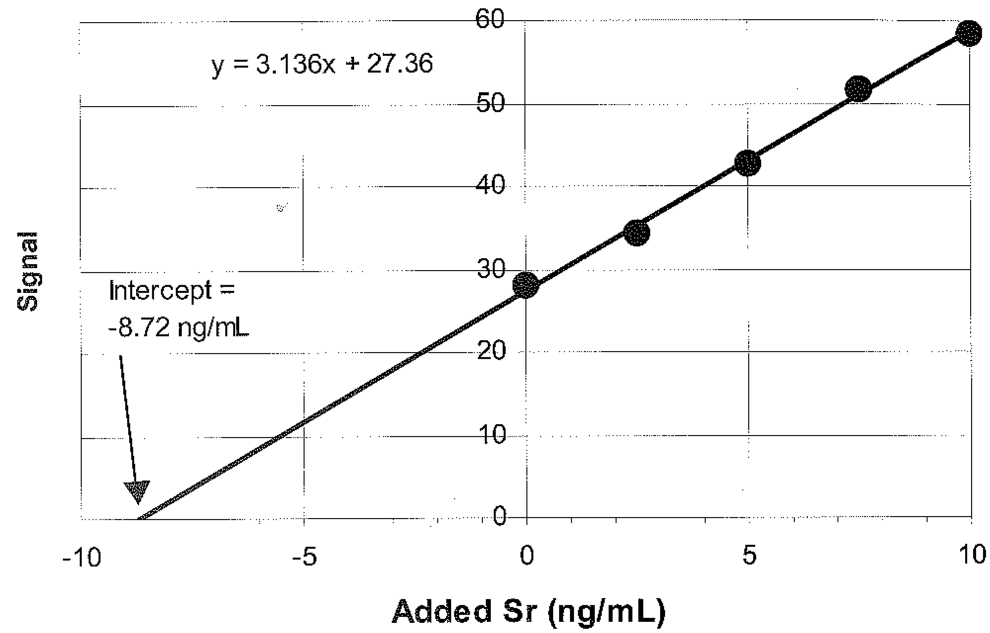
$$t_{\text{calculated}} = \frac{|1.65 - 2.68|}{0.61_6}\sqrt{\frac{8 \cdot 3}{8+3}} = 2.4_7$$

$t_{\text{table}} = 2.262$ for 95% confidence and $8 + 3 - 2 = 9$ degrees of freedom.

$t_{\text{calculated}} > t_{\text{table}}$, so the difference is significant at the 95% confidence level.

It makes no sense to conclude that Lab C [2.68 ± 0.78 (3)] > Lab B [1.65 ± 0.56 (8)], but Lab C = Lab A [1.59 ± 0.14 (13)]. The problem with the comparison of Labs C and A is that the standard deviation of C is much greater than the standard deviation of A and the number of replicates for C is much less than the number of replicates for A. The result is that we used a large composite standard deviation and a small composite number of degrees of freedom. The conclusion is biased by a large standard deviation and a small number of degrees of freedom. I would tentatively conclude that results from Lab C are greater than results from Labs B and A. I would also ask for more replicate results from Lab C. With just 3 replications, it is hard to reach any statistically significant conclusions.

5-25. (a) All solutions were made up to the same final volume. Therefore, we prepare a graph of signal versus concentration of added standard. The line in the graph was drawn by the method of least squares with the following spreadsheet. The x-intercept, 8.72 ppb, is the concentration of unknown in the 10-mL solution. In cell B27 of the spreadsheet (on the next page), we find the standard deviation of the x-intercept to be 0.427 ppm. A reasonable answer is $8.7_2 \pm 0.4_3$ ppb.



(b) Unknown solution volume = 10.0 mL with Sr = 8.72 ppb = 8.72 ng/mL. In 10.0 mL, there are (10 mL)(8.72 ng/mL) = 87.2 ng. Solution was made from 0.750 mg of tooth enamel. Sr (ppm) in tooth enamel is

$$\text{Concentration (ppm)} = \frac{\text{mass of Sr}}{\text{mass of enamel}} \times 10^6$$

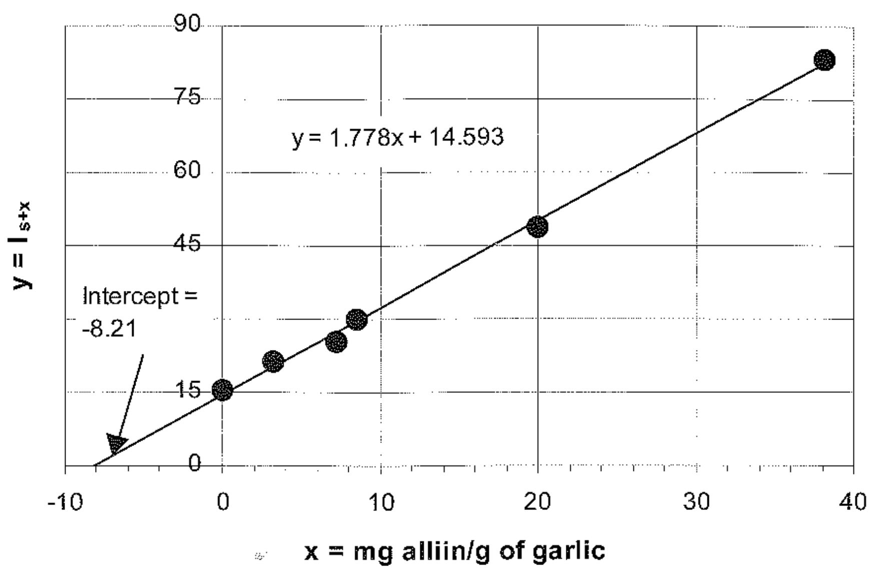
$$= \frac{87.2 \times 10^{-9}\ \text{g}}{0.750 \times 10^{-3}\ \text{g}} \times 10^6 = 116\ \text{ppm}$$

(c) Relative uncertainty of intercept is 100 × 0.43/8.72 = 4.9%, which leads to a 4.9% uncertainty in the concentration of Sr in the tooth enamel. 0.049 × 116 ppm = 5.7 ppm. Final answer: 116 ± 6 ppm.

(d) Student's t for $n - 2 = 5 - 2 = 3$ degrees of freedom and 95% confidence is 3.182. We found standard deviation = 5.7 ppm. 95% confidence interval is $\pm\, ts$ = (3.182)(5.7 ppm) = 18.1 ppm. Answer: 116 ± 18 ppm.

5-28.

	A	B	C	D
1	Standard Addition Constant Volume Least-Squares Spreadsheet			
2				
3		x	y	
4		Spike (mg/g)	I(s+x) =	
5		$[S]_f$	signal	
6		0.00	15.6	
7		3.12	21.1	
8		7.18	25.5	
9		8.48	30.0	
10		20.0	48.8	
11		38.2	83.4	
12				
13	B16:D18 = LINEST(C6:C11,B6:B11,TRUE,TRUE)			
14				
15		LINEST output:		
16	m	1.7776	14.5928	b
17	s_m	0.0449	0.8190	s_b
18	R^2	0.9974	1.4246	s_y
19				
20	x-intercept = -b/m =	-8.20906		
21				
22	n =	6	B22 = COUNT(B6:B11)	
23	Mean y =	37.40	B23 = AVERAGE(C6:C11)	
24	$\Sigma(x_i$ - mean $x)^2$ =	1004.7838	B24 = DEVSQ(B6:B11)	
25				
26	Std deviation of			
27	x-intercept =	0.62445		
28	B27 =(C18/ABS(B16))*SQRT((1/B22) + B23^2/(B16^2*B24))			



(a) In cells B20 and B27 of the spreadsheet, the negative x-intercept of the standard addition graph is 8.21 ± 0.62 mg alliin/g garlic.

(b) Two moles of alliin (FM 177.2) produce one mole of allicin (FM 162.3) in the assay. Therefore, the quantity of allicin in garlic is ½(162.3/177.2)(8.21 ± 0.62 mg/g) = 3.76 ± 0.28 mg allicin/g garlic or 3.8 ± 0.3 mg allicin/g garlic.

5-30. (a) $\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right) \Rightarrow \frac{3\,473}{[3.47\text{ mM}]} = F\left(\frac{10\,222}{[1.72\text{ mM}]}\right) \Rightarrow F = 0.168_4$

(b) $[S] = (8.47\text{ mM})\left(\frac{1.00\text{ mL}}{10.0\text{ mL}}\right) = 0.847\text{ mM}$

(c) $\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right) \Rightarrow \frac{5\,428}{[X]} = 0.168_4\left(\frac{4\,431}{[0.847\text{ mM}]}\right) \Rightarrow [X] = 6.16\text{ mM}$

(d) The original concentration of [X] was twice as great as the diluted concentration, so [X] = 12.3 mM.

5-32. Data in the following table are plotted in the accompanying graph. If the equation

$$\frac{\text{area of analyte signal}}{\text{area of standard signal}} = F\left(\frac{\text{concentration of analyte}}{\text{concentration of standard}}\right)$$

is obeyed, the graph should be a straight line going through the origin, which it is. The slope, 1.07_{57}, is the response factor. Over the concentration ratio analyte/standard = 0.10 to 1.00, the standard deviation of the response factor in the table is $0.06_{68} = 6._2\%$.

Sample	Concentration ratio $C_{10}H_8/C_{10}D_8$	Area ratio $C_{10}H_8/C_{10}D_8$	F = area ratio/conc. ratio
1	0.10	0.101	1.01_{27}
2	0.50	0.573	1.14_{61}
3	1.00	1.072	1.07_{24}
			mean = 1.07_{57}
			standard deviation 0.06_{68}
			relative standard deviation $6._2\%$