Chapter 4 Problems

4-3. (a) Mean = $\frac{1}{8}$(1.526 60 + 1.529 74 + 1.525 92 + 1.527 31 + 1.528 94 + 1.528 04 + 1.526 85 + 1.527 93) = 1.527 67

(b) Standard deviation =

$$\sqrt{\frac{(1.526\,60 - 1.527\,67)^2 + \cdots + (1.527\,93 - 1.527\,67)^2}{8-1}} = 0.001\,26$$

(c) Variance = $(0.001\,26)^2 = 1.59 \times 10^{-6}$

(d) Significant figures: $\bar{x} \pm s = 1.527_7 \pm 0.001_3$ or 1.528 ± 0.001.

4-4. (a) 1005.3 hours corresponds to z = (1005.3 – 845.2)/94.2 = 1.700.
In Table 4-1, the area from the mean to z = 1.700 is 0.455 4. The area above z = 1.700 is therefore 0.5 – 0.455 4 = 0.044 6.

(b) 798.1 corresponds to z = (798.1 – 845.2)/94.2 = –0.500.
The area from the mean to z = –0.500 is the same as the area from the mean to z = +0.500, which is 0.191 5 in Table 4-1.

901.7 corresponds to z = (901.7 – 845.2)/94.2 = 0.600.
The area from the mean to z = 0.600 is 0.225 8 in Table 4-1.

The area between 798.1 and 901.7 is the sum of the two areas:
0.191 5 + 0.225 8 = 0.417 3

(c) The following spreadsheet shows that the area from –∞ to 800 h is 0.315 7 and the area from –∞ to 900 h is 0.719 6. Therefore, the area from 800 to 900 h is 0.719 6 – 0.315 7 = 0.404 0.

	A	B	C
1	Mean =	Std dev =	
2	845.2	94.2	
3			
4	Area from -∞ to 800 =		0.3157
5	Area from -∞ to 900 =		0.7196
6	Area from 800 to 900		0.4040
7			
8	C4 = NORMDIST(800,A2,B2,TRUE)		
9	C5 = NORMDIST(900,A2,B2,TRUE)		
10	C6 = C5-C4		

4-9. Since the bars are drawn at a 50% confidence level, 50% of them ought to include the mean value if many experiments are performed. 90% of the 90% confidence bars must reach the mean value if we do enough experiments. The 90% bars must be longer than the 50% bars because more of the 90% bars must reach the mean.

4-11. $\bar{x} = 0.14_8, \quad s = 0.03_4$

$$90\% \text{ confidence interval} = 0.14_8 \pm \frac{(2.015)(0.03_4)}{\sqrt{6}} = 0.14_8 \pm 0.02_8$$

$$99\% \text{ confidence interval} = 0.14_8 \pm \frac{(4.032)(0.03_4)}{\sqrt{6}} = 0.14_8 \pm 0.05_6$$

4-13. (a) dL = deciliter = 0.1 L = 100 mL

(b) $F_{\text{calculated}} = (0.05_3/0.04_2)^2 = 1.5_9 < F_{\text{table}} = 6.26$ (for 5 degrees of freedom in the numerator and 4 degrees of freedom in the denominator).
Since $F_{\text{calculated}} < F_{\text{table}}$, we can use the following equations:

$$s_{\text{pooled}} = \sqrt{\frac{0.53^2(5) + 0.42^2(4)}{6+5-2}} = 0.48_4$$

$$t = \frac{|14.5_7 - 13.9_5|}{0.48_4}\sqrt{\frac{6 \cdot 5}{6+5}} = 2.12 < 2.262 \text{ (listed for 95\% confidence and}$$

9 degrees of freedom). The results agree and the trainee should be released.

4-14.

	A	B	C	D	E	F
1	Comparison of two methods					
2						
3	Sample	Method 1	Method 2	d_i		
4	A	0.88	0.83	0.05	= B4-C4	
5	B	1.15	1.04	0.11		
6	C	1.22	1.39	-0.17		
7	D	0.93	0.91	0.02		
8	E	1.17	1.08	0.09		
9	F	1.51	1.31	0.20		
10			mean =	0.050	= AVERAGE(D4:D9)	
11			stdev =	0.124	= STDEV(D4:D9)	
12			$t_{\text{calculated}}$ =	0.987	= D10/D11*SQRT(6)	
13			t_{table} =	2.571	= TINV(0.05,5)	

$t_{\text{calculated}} = 0.987 < 2.571$ (Student's t for 95% confidence and 5 deg of freedom)
The difference is <u>not</u> significant.

4-16. $F_{calculated} = s_2^2/s_1^2 = (0.039)^2/(0.025)^2 = 2.43$

$F_{table} = 9.28$ for 3 degrees of freedom in the numerator and denominator

Since $F_{calculated} < F_{table}$, the difference in standard deviation is not significant and we use Equations 4-8 and 4-9.

$$s_{pooled} = \sqrt{\frac{s_1^2\,(n_1-1) + s_2^2\,(n_2-1)}{n_1+n_2-2}} = \sqrt{\frac{0.025^2\,(4-1) + 0.039^2\,(4-1)}{4+4-2}} = 0.032\ 8$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}}\sqrt{\frac{n_1 n_2}{n_1+n_2}} = \frac{|1.382 - 1.346|}{0.032\ 8}\sqrt{\frac{4 \bullet 4}{4+4}} = 1.55$$

t_{table} $(4 + 4 - 2 = 6$ degrees of freedom$) = 2.447$

Since $t_{calculated} < t_{table}$, the difference is <u>not</u> significant.

4-22. (a) <u>Rainwater</u>:

$F_{calculated} = (0.008/0.005)^2 = 2._{56} < F_{table} = 4.53$ (for 4 degrees of freedom in the numerator and 6 degrees of freedom in the denominator). Since $F_{calculated} < F_{table}$, we use the following equations:

$$s_{pooled} = \sqrt{\frac{0.005^2(6) + 0.008^2(4)}{7+5-2}} = 0.006_{37}$$

$$t_{calculated} = \frac{0.069 - 0.063}{0.006_{37}}\sqrt{\frac{7 \cdot 5}{7+5}} = 1._{61} < t_{table} = 2.228$$

The difference is <u>not</u> significant.

<u>Drinking water</u>:

$F_{calculated} = (0.008/0.007)^2 = 1._{31} < F_{table} = 6.39$ (for 4 degrees of freedom in the numerator and 4 degrees of freedom in the denominator). Since $F_{calculated} < F_{table}$, we use the following equations:

$$s_{pooled} = \sqrt{\frac{0.007^2(4) + 0.008^2(4)}{5+5-2}} = 0.007_{52}$$

$$t = \frac{0.087 - 0.078}{0.007_{52}}\sqrt{\frac{5 \cdot 5}{5+5}} = 1._{89} < 2.306.$$ The difference is <u>not</u> significant.

(b) Gas chromatography:

$$s_{\text{pooled}} = \sqrt{\frac{0.005^2(6) + 0.007^2(4)}{7+5-2}} = 0.005_{88}$$

$$t = \frac{0.078 - 0.069}{0.005_{88}}\sqrt{\frac{7 \cdot 5}{7+5}} = 2._{61} > 2.228.$$ The difference is significant.

Spectrophotometry:

$$s_{\text{pooled}} = \sqrt{\frac{0.008^2(4) + 0.008^2(4)}{5+5-2}} = 0.008_{00}$$

$$t = \frac{0.087 - 0.063}{0.008_{00}}\sqrt{\frac{5 \cdot 5}{5+5}} = 4._{74} > 2.306.$$ The difference is significant.

4-24. Slope $= -1.298\,72 \times 10^4\ (\pm 0.001\,319\,0 \times 10^4)$

$= -1.299\ (\pm 0.001) \times 10^4$ or $-1.298_7\ (\pm 0.001_3) \times 10^4$

Intercept $= 256.695\ (\pm 323.57) = 3\ (\pm 3) \times 10^2$

4-29. Hopefully, the negative value is within experimental error of 0. If so, no detectable analyte is present. If the negative concentration is beyond experimental error, there is something wrong with your analysis. The same is true for a value above 100% of the theoretical maximum concentration of an analyte. Another possible way to get values below 0 or above 100% is if you extrapolated the calibration curve past the range covered by standards, and the curve is not linear.

4-30. Corrected absorbance $= 0.264 - 0.095 = 0.169$

Equation of line: $0.169 = 0.016\,30\,x + 0.004\,7 \Rightarrow x = 10.1\ \mu g$

4-31. (a) $x = \dfrac{y-b}{m} = \dfrac{2.58 - 1.3_5}{0.61_5} = 2.00$

$\bar{y} = (2 + 3 + 4 + 5)/4 = 3.5$ $\qquad \bar{x} = (1 + 3 + 4 + 6)/4 = 3.5$

$\Sigma(x_i - \bar{x})^2 = (1 - 3.5)^2 + (3 - 3.5)^2 + (4 - 3.5)^2 + (6 - 3.5)^2 = 13.0$

$$s_x = \frac{s_y}{|m|}\sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y-\bar{y})^2}{m^2\,\Sigma(x_i - \bar{x})^2}}$$

$$= \frac{0.196\ 12}{|0.615\ 38|}\sqrt{\frac{1}{1} + \frac{1}{4} + \frac{(2.58 - 3.5)^2}{(0.615\ 38)^2\,(13.0)}} = 0.38$$

Answer: $2.0_0 \pm 0.3_8$

(b) For $k = 4$ replicate measurements,

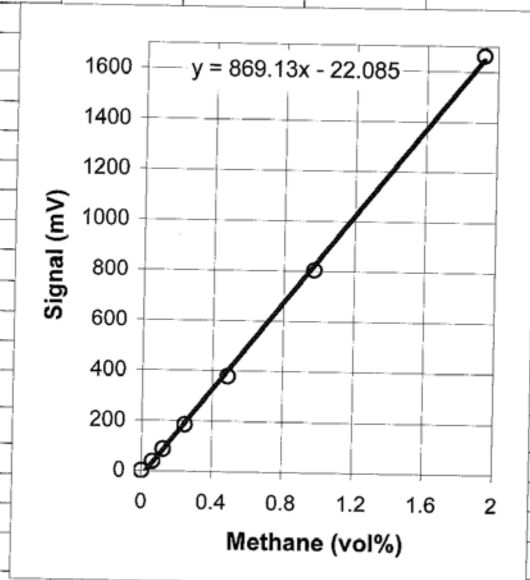
$$s_x = \frac{s_y}{|m|}\sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y-\bar{y})^2}{m^2\,\Sigma(x_i - \bar{x})^2}}$$

$$= \frac{0.196\ 12}{|0.615\ 38|}\sqrt{\frac{1}{4} + \frac{1}{4} + \frac{(2.58 - 3.5)^2}{(0.615\ 38)^2\,(13.0)}} = 0.26$$

Answer: $2.0_0 \pm 0.2_6$

4-33. (a)

	A	B	C	D
1	Least-Squares Spreadsheet			
2				
3		x	$y_{corrected}$	y
4		0	0	9.1
5		0.062	38.4	47.5
6		0.122	86.5	95.6
7		0.245	184.7	193.8
8		0.486	378.4	387.5
9		0.971	803.4	812.5
10		1.921	1662.8	1671.9
11				
12		LINEST output:		
13	m	869.13	-22.0852	b
14	s_m	10.6422	8.9474	s_b
15	R^2	0.9993	18.0527	s_y
16				
17	n =	7	B17 = COUNT(B4:B10)	
18	Mean y =	450.6	B18 = AVERAGE(C4:C10)	
19	$\Sigma(x_i$ - mean x$)^2$ =	2.87757	B19 = DEVSQ(B4:B10)	
20				
21	Measured y =	145.0	Input	
22	Number of replicate measurements of y (k) =	4	Input	
23	Derived x	0.19224	B23 = (B21-C13)/B13	
24	s_x =	0.0137	B24 = (C15/B13)*SQRT((1/B22)+(1/B17)+((B21-B18)^2)/(B13^2*B19))	



(b) Corrected signal = 154.0 – 9.0 = 145.0 mV

(c) Cells B23 and B24 give $[CH_4] = 0.19_2\ (\pm 0.01_4)$ vol%

4-36. For 8 degrees of freedom, $t_{90\%} = 1.860$ and $t_{99\%} = 3.355$.

90% confidence interval: $15.2_2\ (\pm 1.860 \times 0.4_6) = 15.2_2 \pm 0.8_6\ \mu g$

99% confidence interval: $15.2_2\ (\pm 3.355 \times 0.4_6) = 15._2 \pm 1._5\ \mu g$