Chapter 1: End-of-Chapter Solutions

1.
In order from increasing to decreasing precision:
pipet (2 mm i.d.) - most precise
buret (1 cm i.d.)
graduated cylinder (2.5 cm i.d.) - least precise
The precision of the volume measurement increases as the diameter of the glassware gets smaller.

2.
a) $\%\text{-RSD} = \frac{0.02\ \text{mL}}{10.0\ \text{mL}} = 0.2\ \% \Rightarrow 0.00500 \pm 0.00001\ \text{M}$

b) $\%\text{-RSD} = \frac{0.1\ \text{mL}}{10.0\ \text{mL}} = 1\ \% \Rightarrow 0.00500 \pm 0.00005\ \text{M}$

c) $\%\text{-RSD} = \frac{1\ \text{mL}}{10.0\ \text{mL}} = 10\ \% \Rightarrow 0.0050 \pm 0.0005\ \text{M}$

3.
The calculations were very precise, they have to be since space travel is difficult. Unfortunately they were inaccurate due to a gross error in calculations that failed to convert values in metric units (newtons) with values in Imperial units (pound-force).

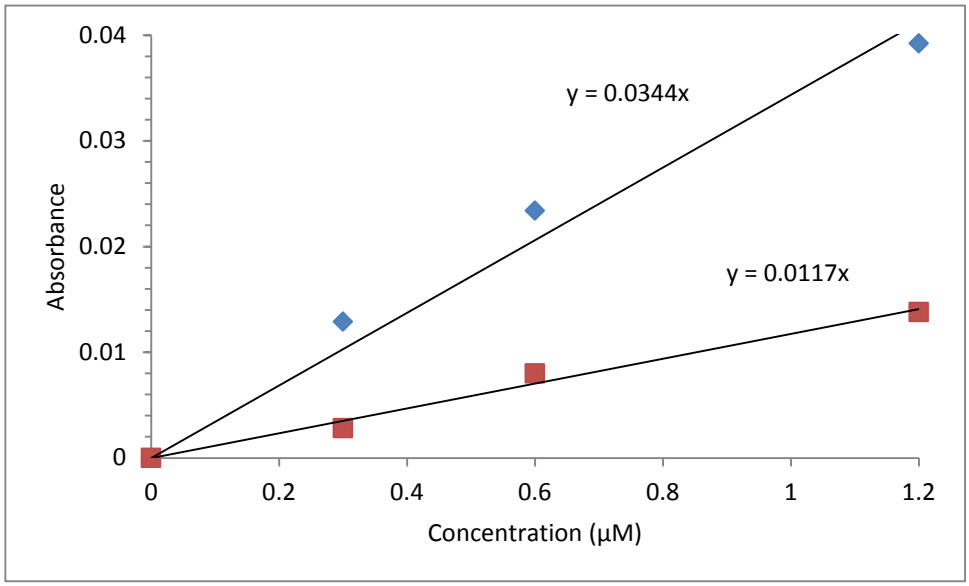
4.
The one-point calibration with pH=7 buffer is rapid and will be accurate for pH measurements near pH 7. The disadvantage of the one-point calibration is that measurements at low pH or high pH could be erroneous due to an incorrect slope in the calibration function of the pH meter. The two-point calibration is more time consuming, but will provide more accurate data over the full range of the pH meter. Figure 1.5 shows an example of the error introduced by extrapolating a one-point calibration.

5.

Plots of Table 1.11 data forcing trendline through zero.

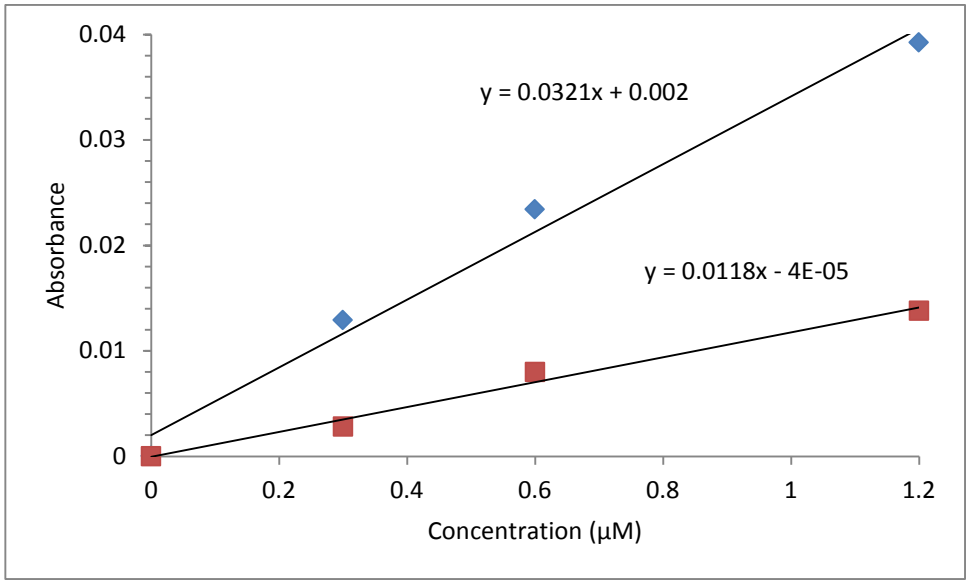
diamonds: 266 nm
squares: 440 nm

Note that the blank for the 266 nm data is obscured by the square marker in both charts.



Plots of Table 1.11 data as given.

diamonds: 266 nm
squares: 440 nm



Sensitivities:

	266 nm	440 nm
zero intercept	0.034 μM^{-1}	0.012 μM^{-1}
non-zero intercept	0.032 μM^{-1}	0.012 μM^{-1}

There is a 6-% difference in the slopes at 266 nm depending on whether or not the trendline is forced through zero. Looking at the data, the 1.2 μM point appears low compared to the trendline. The scatter in the 440 nm data points appears random. The take-home message is that calibration curves should be constructed from at least 5 or 6 measurements.

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6.
The individual volume measurements give a mean and standard deviation of:
1.022 ± 0.007 mL.

The density is:

$$\frac{2.3291\ \text{g}}{1.022\ \text{mL}} = 2.278\ \text{g/mL}$$

The RSD of the volume measurements is:

$$\frac{0.007\ \text{mL}}{1.022\ \text{mL}} = 0.0071$$

The final result should have the same RSD (2.278 g/mL × 0.0071 = 0.016 g/mL) to give:
density = 2.278 ± 0.016 g/mL (2.28 ± 0.02 g/mL is also correct)

7.
a) For either primary standard we need (0.1000 L)(0.150 M) = 0.0150 mol of Na.

- For NaCl (f.w. = 58.443 g/mol):
  (58.443 g/mol)(0.0150 mol Na) = 0.8766 g NaCl
- For $Na_2C_2O_4$ (f.w. = 133.998 g/mol):

$$133.998\ \text{g/mol}\ \frac{1\ \text{mol}\ Na_2C_2O_4}{2\ \text{mol Na}}\ 0.0150\ \text{mol Na} = 1.0050\ \text{g}\ Na_2C_2O_4$$

  (note an additional significant figure for the higher formula weight standard)

b) We need (0.05000 L)(0.0100 mol/L)(58.443 g/mol) = 0.0292 g Na. Since we can weigh to 0.0001 g, the uncertainty is

$$\frac{0.0001\ \text{g}}{0.0292\ \text{g}} \times 100\ \% = 0.3\ \%$$

c) We need (1.000 L)(0.500 M)(58.443 g/mol) = 29.2215 g of Na. Weighing will not be a limiting factor, so the volume measurement, 0.1 %, is the largest source of uncertainty.

d) A weight measurement equivalent to 0.1 % give that the balance weighs to 0.0001 g is:

$$0.1\ \% = \frac{0.0001\ \text{g}}{x\ \text{g}} \times 100\ \%$$

x = 0.1000 g
For NaCl (f.w. = 58.443 g/mol):

$$\frac{0.0001\ \text{g}}{58.443\ \text{g/mol}} = 1.711\ \text{mmol}$$

The volume needed to make 0.1 mM is:

$$0.100\ \text{mM} = \frac{1.711\ \text{mmol}}{x\ \text{L}}$$

x = 17.11 L
This result is a large volume, which shows why common lab practice is to make a concentrated stock solutions that can be diluted to the desired concentrations.

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8.
The actual volume delivered by the "10-mL" pipet is (10.021 g)/(0.99707 g/mL) = 10.050 mL. The error is 0.05 mL or

$$\frac{0.05\ \text{mL}}{10.050\ \text{mL}} \times 100\ \% = 0.5\ \%.$$

9.
a) There should be few if any interferences in drinking water, so blanks to check for contamination and a spike to check for detection limit should be sufficient.

b) "Field" blanks and field spikes are necessary due to the large number of sample prepa- ration steps that will be necessary for such a complicated sample matrix.

c) In addition to the usual blanks, a "field" spike will be very important to determine if there is any loss of analyte.

10.
a) There should be few if any interferences in drinking water, so a calibration curve using standards of lead in 0.1 M nitric acid should be sufficient.

b) The complexity of the sample matrix warrants using the standard addition method for calibration. Any matrix effects should affect the standard addition equally to the matrix effects of the unknown amount of Pb in the test solutions.

c) Given the possible loss of analyte during sample processing, using an internal standard will be the preferred method of calibration. An element similar to Pb that is not present in the sample should be chosen for the internal standard. Using an internal standard requires some knowledge of the sample composition.

11.
(a)
Your spreadsheet will look something like:

Data:	78.93	
	78.77	
	79.09	
	78.52	
mean =	78.8275	
std dev =	0.243088	
%-RSD =	0.308379	=(C9/C8)*100
std err =	0.121544	
95% C.I.	0.386753	=3.182*C9/SQRT(4)

Notes:

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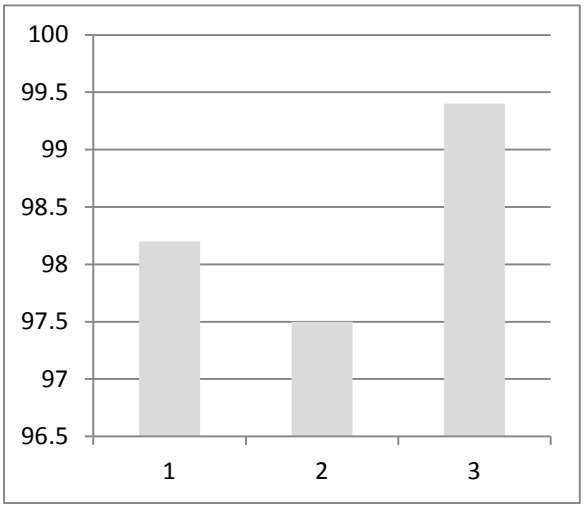
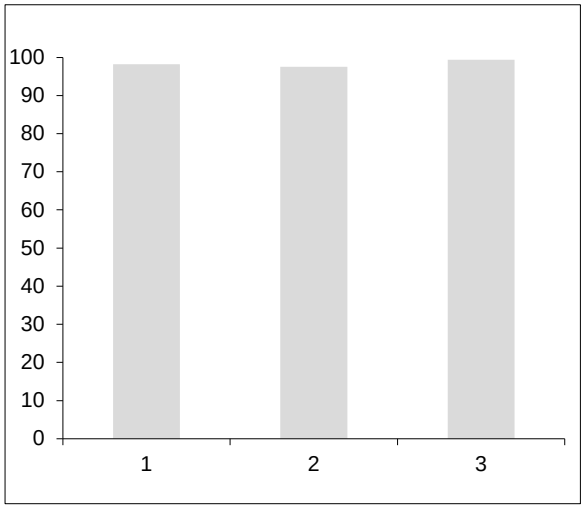
- To understand the formulas copied to the right of the results, cell C10 contains the standard deviation result and cell C9 has the mean.
- The mean can gain an additional significant figure due to the size of the sum of the data: 78.828. However, the standard deviation of 0.243 shows that extended significant figures in the result have little meaning.
- The result can be reported as 78.83 ± 0.24. or 78.8 ± 0.2.

(b)
In the following example, the formulas are written to accommodate up to 10 data points. It is not necessary to revise formulas if data is added to the set:

			Results	Formulas
Data:	78.93	N =	5	=COUNT(G$5:G$14)
	78.77	sum =	394.11	=SUM(G$5:G$14)
	79.09	mean =	78.82	=I6/I5
	78.52	std dev =	0.21	=STDEV(G$5:G$14)
	78.8	%-RSD =	0.27	=(I8/I7)*100
		std err =	0.09	=I8/SQRT(I5)
		95% C.I.	0.26	=2.776*I8/SQRT(I5)

12.
(a) The left figure is Excel's default scaling on the y axis. Note how it exaggerates the differences in the values compared to the right plot that is scaled from 0 to 100.





Mean and standard deviation: 98.37 ± 0.96 (an additional significant figure is gained due to the size of the sum of the data, but it can also be reported as 98.4 ± 1.0).

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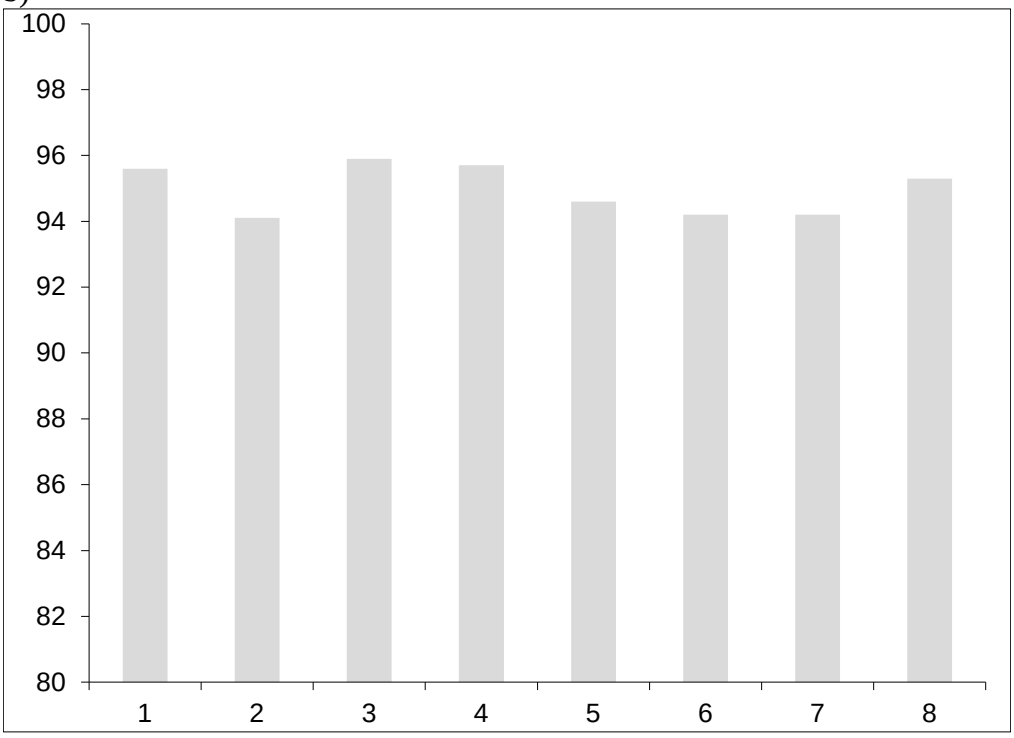
b)



Mean and standard deviation: 94.95 ± 0.75 (an additional significant figure is gained due to the size of the sum of the data, but it can also be reported as 95.0 ± 0.8)

c) Q (0.63 and 0.11) is less than Q_c for both cases, so the values must be retained. In the first case, N is small and the criteria for rejection is high. In the second case, the outlier is not very different from other data points.

d) As an example, if you must divide by a sum by N, it is more robust to use a spreadsheet's COUNT function to get N rather than entering it numerically since it might change on adding or removing data points.

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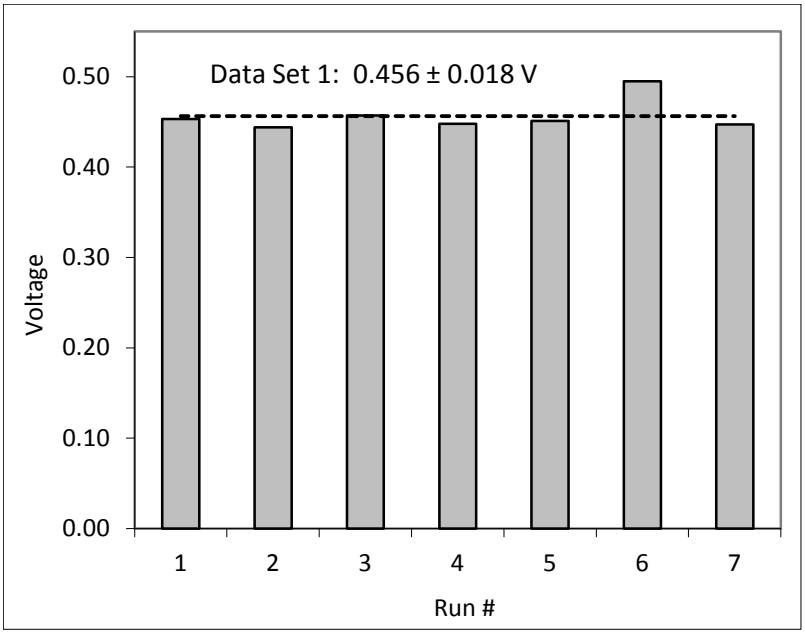
13.
a) Your spreadsheet might look something like the following screen capture:

Data Set 1			
Run #	Voltage	deviation	deviation^2
1	0.453	-0.0034	1.176E-05
2	0.444	-0.0124	1.545E-04
3	0.457	0.0006	3.265E-07
4	0.448	-0.0084	7.104E-05
5	0.451	-0.0054	2.947E-05
6	0.495	0.0386	1.488E-03
7	0.447	-0.0094	8.890E-05
N (#):	7	sum d^2:	1.844E-03
sum/N:	0.4564	std. dev.	0.0175
average:	0.4564	stdev:	0.0175

b) Note that the automatic scaling in spreadsheets will show approximately 0.4 to 0.5 on the y-axis, exaggerating the difference in the values compared to plotting the y-scale from 0 to 0.5:



(c)

Q=	**(outlier-closest) / (outlier-farthest)**		
Q=	**(0.495-0.457) / (0.495-0.444)**		
Q=	0.745098		
	Qc=0.57		
Q > Qc	so data point 6 may be discarded		

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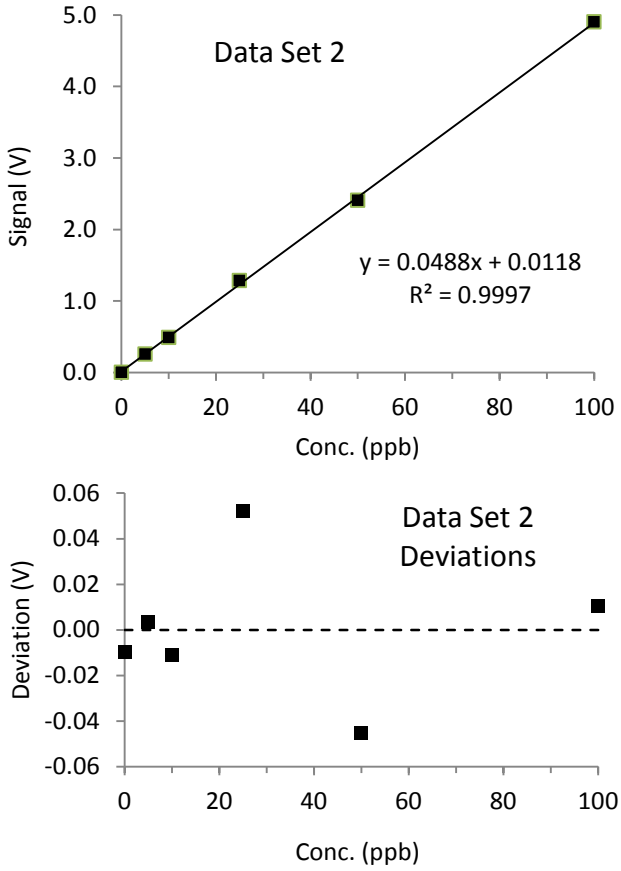
Q is 0.745, larger than Q_c of 0.57 for seven data points. The value may be rejected, and the new average is:

	mean	0.4500	V
	std. dev.	0.0046	V

0.450 ± 0.005 V is also correct.

14. (a)



Note that the randomness in the scatter of the residuals indicates a linear model is appropriate for this data.

(b) Below are two different ways to obtain this data:

					LINEST results	
	Conc. (ppb)	Signal (V)	deviation (d)	zero line	slope	intercept
	0.00	0.002	-0.010	0	0.04881	0.01176
	5.00	0.259	0.003	0	0.00042	0.01969
	10.00	0.489	-0.011	0	0.99971	0.03564
	25.00	1.284	0.052	0	13568.93	4
	50.00	2.407	-0.045	0	17.23112	0.00508
	100.00	4.903	0.010	0		
unknown signal:		0.999		unknown conc:	20.2	ppb
				estimated uncertainty:	± 0.3 ppb	

	Conc. (ppb)	Signal (V)	deviation (d)	x^2	x-d^2	y-d^2	(x-d)*(y-d)
	0.00	0.002	-0.010	0.00	1002.78	2.4191	49.25
	5.00	0.259	0.003	25.00	711.11	1.6857	34.62
	10.00	0.489	-0.011	100.00	469.44	1.1413	23.15
	25.00	1.284	0.052	625.00	44.44	0.0747	1.82
	50.00	2.407	-0.045	2500.00	336.11	0.7219	15.58
	100.00	4.903	0.010	10000.00	4669.44	11.1935	228.62
	sum(x)=	sum(y)=	sum(x^2)=	Sxx=	Syy=	Sxy=	sy=
	190.00	9.34	13250.00	7233.33	17.2362	353.04	0.0356
	N =	6					
	avg(x)=	avg(y)=				std.dev.	R.S.D.(%)
	31.67	1.56		m =	0.0488	0.0004	0.86
				b =	0.0118	0.0197	167.44

(c)

	unknown:	0.999	V	20.227	±	0.559	ppb
					±	2.76	R.S.D.(%)

Note that the units are not easy to show in the spreadsheets, they are:
slope = 0.0488 ± 0.0004 V ppb^{-1}
intercept = 0.0118 ± 0.0197 V

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