Appendix 1: Glossary of Terms

accuracy	measure of closeness of an experimental value to the 'true' value. Often expressed as % bias or % error.
aliquot	any portion of the 'bulk sample'
analyte	the particular element or chemical which is to be quantified
blank	a sample which is expected to contain no analyte
'bulk sample' (or sample)	the material (matrix) collected by the analyst or client and sent in for analysis.
calibration verification	a standard solution prepared from an independent source used to verify the calibration process.
determinate error	'systematic' error; created when a measurement is made incorrectly or made using a biased methodology (for example, not re-zeroing a baseline between samples; or having an incorrect concentration of stock solution).
field blank	a 'sample' of deionized water transported to the field and 'collected' at the time of sampling. the field blank is treated and handled in the same manner as the actual sample.
indeterminate error	'random' error; due to random variation in preparation and measurement (Gaussian distribution).
method spike	• a spike sample made up using the same sample preparation procedure as for your 'unknown' sample (i.e., all the steps required by the method). • contains all reagents, plus a known quantity of analyte
method blank	• a blank made up using the same sample preparation procedure as for your 'unknown' sample (i.e., all the steps required by the method). • only contains all reagents
QC sample	• a sample designed to confirm that the instrument, standards, method, and analyst are all working correctly! • may be a purchased or in-house certified/standard reference material (CRM/SRM).
quality control (QC)	refers to any actions taken to ensure that analytical results are accurate and precise.
precision	measure of the closeness of a series of replicate analysis. Often expressed as the standard deviation or relative standard deviation (RSD).

preservative	any material added to the collected sample to maintain the integrity of the analyte until analysis occurs.
sample spike	• an aliquot of 'unknown' sample, which has been spiked and carried through the same sample preparation procedure as for your 'unknown' sample (i.e., all the steps required by the method). • contains a known quantity of sample and an additional known quantity of analyte, plus all reagents etc.
sample	• contains an aliquot of the bulk sample, plus all reagents etc. Prepare duplicates. • any portion of the bulk sample, blank or spike that is being prepared for analysis
spike recovery	• the percentage of the added analyte that is 'recovered', i.e., measured. • note this can be greater or less than 100%!
spike	• refers to enriching a sample or blank with a known quantity of the analyte under investigation • the addition of a known amount of analyte (usually chosen to be from 50-100% of the expected sample analyte concentration)
standard blank	a blank made up using the same reagents as your standard curve
standard solution	any solution of known concentration.
standardization	the process of determining the precise concentration of a titrant
stock solution	a concentrated solution of known composition used to make a dilution series
titrant	solution of known concentration measured volumetrically (buret) until specified endpoint
tolerance	maximum determinate measurement error for equipment as reported by the manufacturer

Appendix 2: Basic Statistics Applied to Analytical Chemistry[1]

To be of any value, all analytical results must be reported with the associated units of measure (*e.g.*, µmole/L, mg/L, ppm) and uncertainties. It is therefore important to know how to express uncertainties in analytical chemistry. *There is error in every measurement.* Error arises due to limitations in the measuring device (ruler, pH meter, balance, etc.) and problems with equipment or methodology. The former are 'indeterminate' or 'random' errors and cannot be eliminated. Random errors limit the precision with which the final value can be reported. The latter are 'determinant' or 'systematic' errors. Analytical chemists continuously monitor for systematic errors in procedures. The fundamental hypothesis in statistics is the *Null Hypothesis*. The null hypothesis states that random error is sufficient to explain differences between samples. Statistical tests are designed to test the null hypothesis. If the null hypothesis is retained, there is insufficient evidence to show that there is a difference between the samples.

Significant Figures

In the absence of any reported experimental errors, the number of significant figures reported provides a rough guide to the level of precision. Keeping track of the number of 'sig-figs' in a calculation provides a simple, easy to use, 'quick and dirty' method of getting approximately the correct number of decimal places in the final value. Simple rules govern the propagation of sig-figs in mathematical operations:

Addition/Subtraction

- the number of decimal places to the right of the decimal point in the final answer is limited by the value with the least decimal places in the operation.

Multiplication/Division

- the number of sig-figs in the final result is limited by the value with the least sig-figs in the operation.

The correct and more time consuming method to determine the uncertainty in the final result is to consider the experimental uncertainty in each measured value and propagate the uncertainty through to each calculation leading to the final result. In summary;

Addition/Subtraction

- the absolute errors in the values are additive

Multiplication/Division

- the relative errors in the values are additive

To report the statistical uncertainty in a final value, the text could take the form, "Sample 123A has a lead content of (9.53 ± 0.22) ppm at the 95 % confidence level." Note that the uncertainty has the same number of decimal places as the final value. It is common to limit the uncertainty to one significant figure and therefore report this as (9.5 ± 0.2) ppm at the 95 % confidence level. Note also that the uncertainty is quoted at a specified confidence level.

[1] Adapted from UVic, Chem 212 Lab Manual; N. Taylor and J.Browning

Rounding

Keep extra digits through intermediate calculations, and don't round until the final answer is reached.

If the digits to be discarded are	Round the last digit to be kept	Example (rounded to three sig-figs)
less than 5	down	3.7249999 rounded to two decimal places is 3.72.
equal to 5	even	This depends on the preceding digit, and does not depend on any later digits. If even, round down. If odd, round up. For example, 3.7251 still rounds to 3.72.
greater than 5	Up	3.726000 rounds to 3.73.

Exact Numbers in Calculations

Some values are known or defined to be exact. For example:

- the ½ and 2 in $E_K = ½ \cdot m \cdot v^2$
- the stoichiometric coefficients and molecular formulae in chemical reactions such as
  - $C_3H_8 + 5 \cdot O_2 \longrightarrow 3 \cdot CO_2 + 4 \cdot H_2O$
- conversions such as 1 m^3 = 1,000,000 cm^3

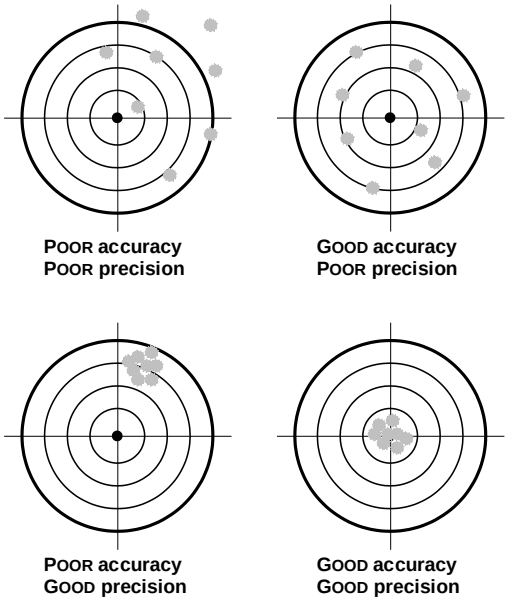
These numbers do not introduce or contribute to errors or uncertainties in a final calculated result.

Precision, Accuracy, and Tolerance

*There is no relationship between **precision, accuracy** and **tolerance**.*

Precision

Precision is observed as random error about the mean. *Every experimentally measured value has an associated error*. It is *impossible* to reduce this error to zero, even with an infinite number of observations. Random error has a gaussian (a.k.a. 'normal') distribution about the 'true' value. To encompass the true value with a desired confidence, the standard deviation is multiplied by a factor dependent on the number of observations and required confidence level.



A multitude of factors affect the precision:

- instrument noise (detector sensitivity, noise, etc.)
- experimental technique (pipetting, weighing, filling, etc.)
- sample inhomogeneity

Instrument noise is measurable by repeatedly measuring the same sample. Error in experimental technique is found by preparing replicates of a sample. An ANalysis Of VAriance (ANOVA) can be performed to determine the contribution to the uncertainty from various sources or steps in a method.

Average Values

When we are going to statistically treat a set of data, we need to calculate a representative value from our measurements. A representative value can be calculated as the mean, median, and mode. The most commonly used in analytical chemistry is the *mean* ($\bar{x}$), calculated as;

$$\bar{x} = \frac{1}{n} \cdot \sum_i x_i$$

The *median* is the middle data point after the data is sorted in ascending or descending order. If there is an even number of data points, the median is the mean of the center two data points. The *mode* is the most frequently observed value.

Measurements of Precision

Standard Deviation

For measurements where less than 20 replicates have been preformed ($n < 20$), the *sample standard deviation* (s_{n-1}, σ_{n-1}) is used to express the precision. Where n is the number of replicate measurements.

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

When greater than 20 replicates ($n > 20$) have been preformed, it is possible to calculate a true standard deviation as,

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n}}$$

For Precision Comparisons

The percent relative standard deviation (%RSD) can be used to evaluate the precision between different methods. When discussing precision, it is usually the %RSD that is quoted.

$$\%\ RSD = \frac{uncertainty}{average} = \frac{s}{\bar{x}} \cdot 100\ \%$$

Confidence Intervals

Reporting the uncertainty in an experimental result to ±1*s* (standard deviation) will be correct ~ 67 % of the time. To increase the confidence that a quoted result will reflect the true value (μ) within a quoted uncertainty, calculate a confidence interval using student t-values.

$$\mu = \bar{x} \pm \frac{t \cdot s}{\sqrt{n}}$$

where *t* is the two-tailed t-value from the table at a specified confidence level. Unless there is a reason to do otherwise, the two-tailed t-value is always used.

Example: Five samples of brass were analyzed for % copper and the results were determined to be: 93.42%, 93.86%, 92.78%, 93.14% and 93.60%. The mean is 93.36% and the sample standard deviation is calculated to be 0.417%. For five samples (i.e., four degrees of freedom) at the 95% confidence level, t = 2.776 and the confidence interval = 0.52%. The reported result of this experiment would state "The concentration of copper in the brass sampled was determined to be (93.4±0.5) % by mass at the 95% confidence level".

Rejecting Data Based on Imprecision – Grubbs Test for an Outlier

Before you calculate the mean of your sample data, you might want to examine your data for suspicious points that are abnormally far from the mean. The Grubbs test is recommended by the *International Standards Organization* and the *American Society for Testing and Materials* in place of the *Q*-test to reject outliers.

$$G_{calc} = \frac{|suspect\ value - \bar{x}|}{s}$$

where the numerator is the absolute value of the difference between the suspected outlier and the mean value.

Reject if $G_{calc} > G_{tab}$

If G_{calc} is greater than the critical *G* value (Table 1), the questionable point can be discarded at the specified confidence level. It should be noted that in order to continue to statistically treat your data after a point has been rejected, you should have at <u>least four values</u> to begin with. If you know a data point is suspect because of some faulty procedure (e.g., over-shot end point, spilled solution etc), it should be rejected without the need of any statistical test.

How to Discuss Precision

The replicate measurements made during any experiment can be used to calculate different precision values. Below are three estimates of precision, and the sources that contribute to each precision estimate.

1. Factors which contribute to the standard deviation in obtained from replicate sampling:
    - the volumetric technique of the analyst, including correct pipetting technique, and correct filling of volumetric flasks.
    - the random error in the instrument measurements.
    - random error in the method of sample introduction (*e.g.*, reproducibility of injection technique using the gas chromatograph).
    - random error in sampling, sample handling and transport.
    - inhomogeneity of sample.

2. Factors which contribute to the standard deviation in results obtained from different aliquots of the same sample (*i.e.*, unknown):
   - the volumetric technique of the analyst, including correct pipetting technique, and correct filling of volumetric flasks.
   - the random error in the instrument measurements.
   - random error in the method of sample introduction (*e.g.*, reproducibility of injection technique using the gas chromatograph).
   - homogeneity of the original sample.
   - precision of sample preparation.

3. Factors which contribute to the standard deviation in replicate analysis of the same aliquot of sample:
   - random error in the instrument measurements.
   - random error in the method of sample introduction.

4. Factors which contribute to the standard deviation in the linear regression of the standard curve:
   - the volumetric technique of the analyst, including correct pipetting technique, and correct filling of volumetric flasks.
   - the random error in the instrument measurements.
   - random error in the method of sample introduction (*e.g.*, reproducibility of injection technique using the gas chromatograph).

By using and comparing these three 'types' of precision, you may be able to isolate the biggest sources of error in your results; this will help you to improve your technique.
There is a more sophisticated way to determine the relative contributions to precision from several sources: *i.e.*, contributions from sampling, sample preparation, and from variations in the instrument. This technique of data analysis is called ANOVA (**AN**alysis **O**f **VA**riance).

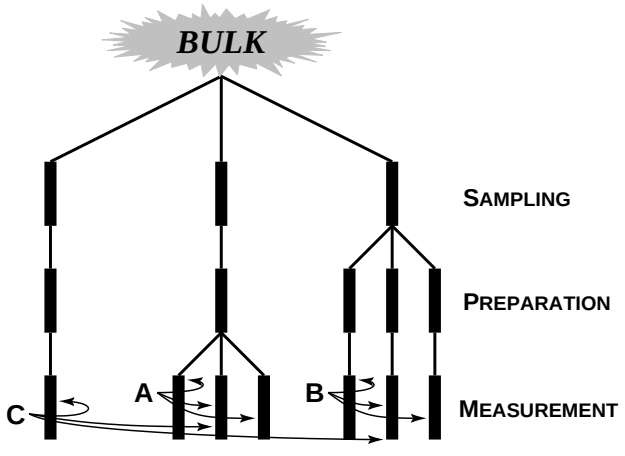
Sources of Uncertainty

The square of the standard deviation is the variance. Variance is additive for normal distributions, making it possible to determine the magnitude of various sources of error. This analysis is often called ANalysis Of VAriance (ANOVA).

$$V = s^2$$

The figure shows how a sample can be analyzed to determine the contributions from sampling, preparation, and measurement to the total uncertainty.

$$V_{\text{total}} = V_{\text{sampling}} + V_{\text{preparation}} + V_{\text{measurement}}$$



Each ▬ is an aliquot.

A. Observed variance is due to **Measurement**.
B. Observed variance is due to **Preparation** and **Measurement**.
C. Observed variance is the **TOTAL** variance.

Accuracy

Accuracy is a measure of the difference between the experimental value and the 'true' value. Differences are due to systematic errors. For example, a systematic error exists if a volumetric pipet is always blown out or an instrument not properly calibrated.

Accuracy can only be determined where the 'true' value of a sample is known, i.e., a reference. Certified or Standard Reference Materials (CRM's or SRM's) are substances that contain one or more analytes in a given matrix[2]. They have been exhaustively characterized by several laboratories using a number of analytical techniques to provide bias-free results. CRMs are expensive. A cheaper, less accurate, and widely used alternative is to prepare an in-house standard reference material.

Such reference standards are called quality control (QC) samples. The QCs are run at the same time as the unknowns. Since their concentration is known, systematic errors can be detected by comparing the experimental value with the known value.

Please note that the accuracy of the **method** may be good as indicated by the standards and QC values; but the accuracy of the **analysis** may be questionable due to poor sample homogeneity, or other sampling issues. This distinction may arise if you have an expected value for the sample (*e.g.*, a vitamin pill) which does not agree with your analysis value - but at the same time, the quality control results are accurate.

For Accuracy Comparisons

Accuracy (bias) can reported as the difference between an experimental and a 'true' or known value ($\bar{x}$ - μ), although it is common to express this as a percentage.

- *Percent Bias*

Percent bias is a calculation that measures deviation from the true value. Notice that there are *no absolute value brackets* in this equation; your experimental error will be either positive or negative, not both! Unlike the *t*-test, percent error provides information regarding the direction of a systematic error.

$$\%\ error = \left(\frac{experimental - actual}{actual} \right) \cdot 100\,\% = \left(\frac{\bar{x} - \mu}{\mu} \right) \cdot 100\,\%$$

- *The t-test*

To assess if an observed difference between an experimental result and a QC sample is statistically significant, the t-test can be used. Where μ* is the known or accepted value of the QC sample.

$$\left| \bar{x} - \mu^* \right| = \frac{t\,s}{\sqrt{n}}$$

If, $\left| \bar{x} - \mu^* \right| > \frac{t\,s}{\sqrt{n}}$, then the bias is statistically significant at the specified confidence level and systematic errors exist in the experimental method.

[2] NIST Standard Resference Materials, http://www.nist.gov/srm/, January, 2002.

Alternately, one can calculate a t-value;

$$t_{calc} = \left| \frac{\sqrt{n}}{s} \cdot \left(\mu^* - \bar{x} \right) \right|$$

If $t_{calc} < t_{tab}$, there is no statistical difference between $\bar{x}$ and μ^* and no systematic errors are observed at the specified confidence level. Equivalently, if μ^* is encompassed in the confidence range of $\bar{x}$, there is no statistical difference at the specified confidence level. When looking up a t value from a table, remember to look for the t-value for a certain number of *degrees of freedom*. The degrees of freedom will be the total number of replicates, minus one.

Example: A brass QC sample with a known copper concentration of (91.75±0.11) % was analyzed and found to contain (92.2±0.5) % copper at the 95% confidence level. Ignoring the uncertainty in the QC, t_{calc} is determined to be 2.413. Since t_{calc} is lower than t_{tab} (2.776), there is no statistical difference at the 95% confidence level. No systematic errors were observed, since the known QC value is encompassed within the confidence range: 91.7% to 92.7%.

Comparing Multiple Data Sets

If there is a specified uncertainty in the known QC value, or if we are comparing two experimental values, we use a different version of the t-test, explained in the section under comparing multiple data sets. In comparing two values with similar variances (s^2), the t-test is applied as above where between $\bar{x}_1$ and $\bar{x}_2$ are the two mean experimental values.

$$\left| \bar{x}_1 - \bar{x}_2 \right| = \frac{t\, s_{pooled}}{\sqrt{\frac{n_1 + n_2}{n_1 n_2}}}$$

$$\text{and } s_{pooled} = \sqrt{\frac{(n_1 - 1) \cdot s_1^2 + (n_2 - 1) \cdot s_2^2}{n_1 + n_2 - 2}}$$

Alternatively, calculate a t-value and compare to the tabulated values at a specified confidence level.

$$t_{calc} = \frac{\left| \bar{x}_1 - \bar{x}_2 \right|}{s_{pooled} \cdot \sqrt{1/n_1 + 1/n_2}}$$

If $t_{calc} < t_{tab}$, there is no statistical difference between $\bar{x}_1$ and $\bar{x}_2$ and no systematic errors are observed at the specified confidence level.

To determine if the *variances* of two data sets (*1* and *2*) are the same, use the F-test. Based on the results of the *F*-test, the *t*-test can be used to determine if the *means* of two data sets are the same.

$$F_{calc} = \frac{V_1}{V_2} = \frac{s_1^2}{s_2^2}$$ *1* and *2* are chosen so that $F_{calc} > 1$.

F_{tab} is then looked up for a specified confidence level. Again, look for the *degrees of freedom* in the numerator and denominator when finding an F_{tab} value. Unless there is a reason to believe otherwise, the two-tailed tabulated value is used. If $F_{calc} < F_{tab}$, then we can say, "There is no statistical difference between the distributions at the specified confidence level.", and can use a pooled standard deviation, s_{pooled}, (with degrees of freedom defined as simply $n_1 + n_2 - 2$) in further calculations. Otherwise, the degrees of freedom of t_{tab} must be calculated separately.

Passed F-test

$$s_{pooled} = \sqrt{\frac{(n_1 - 1)\cdot s_1^2 + (n_2 - 1)\cdot s_2^2}{n_1 + n_2 - 2}}$$

$$t_{calc} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}\cdot\sqrt{1/n_1 + 1/n_2}}$$

Failed F-test

$$t_{calc} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}}$$

$$d.f. = \left[\frac{\left(s_1^2/n_1 + s_2^2/n_2\right)^2}{\frac{\left(s_1^2/n_1\right)^2}{n_1 + 1} + \frac{\left(s_2^2/n_2\right)^2}{n_2 + 1}}\right] - 2$$

Example: To account for the uncertainty in the QC sample, first perform F-test to determine the similarity of variance. To calculate an F value we need to determine the standard deviation and the variance in the reported QC value, which was quoted as a 95% confidence interval. Assuming an infinite number of analysis were conducted (n > 20), the standard deviation is obtained by dividing the quoted confidence interval (0.11) by t (95%, ∞) = 1.960. Thus s for the QC known value is 0.056 and $F_{calc} = 0.417^2/0.056^2 = 55.4$. Since F_{calc} is greater than F_{tab} at the 95% confidence level, the two samples are not from the same population and t_{calc} is determined without pooling the standard deviations (see above under Failed F-test). Since the value of $t_{calc} = 2.413$ is lower than t_{tab} of 2.776, there is no statistical difference at the 95% confidence level.

Regression

The uncertainty arising from a result of a linear regression analysis (such as, linear calibration curves) can be calculated using formulas given in the text[3] and the Excel spreadsheet supplied in the lab. These formulas calculate the values of m (slope) and b (intercept) of the 'best fit' line as well as s_m and s_b the standard deviations in the slope and the intercept, respectively. They can also be used to calculate the uncertainty in an interpolated result (s_x) given the number of replicates used to generate a mean value for the sample. Uncertainty analysis for non-linear calibration curves is possible, but beyond the scope of this summary.

[3] D.C. Harris, Quantitative Chemical Analysis, 6th Ed., W.H. Freeman Pubs, 2002 p. 92

Detection Limits

The detection limit (DL) is defined as "the minimum result that can be distinguished from a suitable blank at a specified confidence level"[4]. In other words, a t-test between the blank and the sample must fail. Detection limits can be estimated in various ways. The US EPA (method 300.0) suggest using a low concentration sample predicted to be near the detection limit (3 to 5 times the estimated DL) and determining the standard deviation from seven replicate analysis. The detection limit is then calculated as t s, where t is the student t-value for a 99% confidence level (i.e., t = 3.14 for seven replicates) and s is the sample standard deviation.

Others suggest using the following formula for determining the detection limit.

$$x_{DL} = \bar{x}_{\text{blank}} + \frac{\text{t s}}{\sqrt{\text{n}}}$$

Tolerance

Tolerance is not a statistical parameter. For example, the tolerance of a 10.00 mL class A volumetric pipet is ± 0.02 mL. This means that the pipet is guaranteed to deliver between 9.98 mL and 10.02 mL. It *does not* mean that the pipet will deliver an average of 10.00 mL. A given pipet might routinely deliver 9.997 mL or 10.015 mL or 9.981 mL. Unlike precision, tolerance does not have a Gaussian distribution. Practicing analytical chemists calibrate their pipets. Analytical chemists can repeatable deliver within ± 0.002 mL with a 10.00 mL pipet: they gain an extra decimal place and reducing the associated uncertainty by a factor of 10!

It is a systematic error if you report the volume delivered by a 10 mL pipet as (10.00 ± 0.02) mL, the tolerance, when the pipet actually delivers (10.011 ± 0.004) mL.

Statistical Tables

Table 1: Critical values of ***G*** for rejection of outlier[5]

Number of observations (n)	*G* (95% confidence)
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176

[4] International Union of Pure and Applied Chemistry (IUPAC) Goldbook, http://www.iupac.org/publications/compendium/index.html, March, 2002.

[5] Values are for a one-tailed test as recommended by ASTM E 178-02 *Standard Practice for Dealing with Outlying Observations*, http://webstore.ansi.org; F.E. Grubbs and G. Beck, *Technometrics* **1972**, 14, 847.

Table 2. Tabulated values for the one and two-tailed *t*-tests.

D.F.	One-Tailed *t*-Test					Two-Tailed *t*-Test				
	68%	**90%**	**95%**	**98%**	**99%**	**68%**	**90%**	**95%**	**98%**	**99%**
1	0.635	3.078	6.314	15.894	31.821	1.819	6.314	12.706	31.821	63.656
2	0.546	1.886	2.920	4.849	6.965	1.312	2.920	4.303	6.965	9.925
3	0.518	1.638	2.353	3.482	4.541	1.189	2.353	3.182	4.541	5.841
4	0.505	1.533	2.132	2.999	3.747	1.134	2.132	2.776	3.747	4.604
5	0.497	1.476	2.015	2.757	3.365	1.104	2.015	2.571	3.365	4.032
6	0.492	1.440	1.943	2.612	3.143	1.084	1.943	2.447	3.143	3.707
7	0.489	1.415	1.895	2.517	2.998	1.070	1.895	2.365	2.998	3.499
8	0.486	1.397	1.860	2.449	2.896	1.060	1.860	2.306	2.896	3.355
9	0.484	1.383	1.833	2.398	2.821	1.053	1.833	2.262	2.821	3.250
10	0.482	1.372	1.812	2.359	2.764	1.046	1.812	2.228	2.764	3.169
12	0.480	1.356	1.782	2.303	2.681	1.037	1.782	2.179	2.681	3.055
14	0.478	1.345	1.761	2.264	2.624	1.031	1.761	2.145	2.624	2.977
16	0.477	1.337	1.746	2.235	2.583	1.026	1.746	2.120	2.583	2.921
18	0.476	1.330	1.734	2.214	2.552	1.023	1.734	2.101	2.552	2.878
20	0.475	1.325	1.725	2.197	2.528	1.020	1.725	2.086	2.528	2.845
25	0.473	1.316	1.708	2.167	2.485	1.015	1.708	2.060	2.485	2.787
30	0.472	1.310	1.697	2.147	2.457	1.011	1.697	2.042	2.457	2.750
40	0.471	1.303	1.684	2.123	2.423	1.007	1.684	2.021	2.423	2.704
50	0.471	1.299	1.676	2.109	2.403	1.004	1.676	2.009	2.403	2.678
75	0.470	1.293	1.665	2.090	2.377	1.001	1.665	1.992	2.377	2.643
100	0.469	1.290	1.660	2.081	2.364	0.999	1.660	1.984	2.364	2.626
200	0.468	1.286	1.653	2.067	2.345	0.997	1.653	1.972	2.345	2.601
500	0.468	1.283	1.648	2.059	2.334	0.995	1.648	1.965	2.334	2.586
∞	0.468	1.282	1.645	2.054	2.326	0.994	1.645	1.960	2.326	2.576

Table 3. Tabulated values for the two-tailed *F*-test.

95%		Degrees of Freedom: Numerator																							
		1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	25	30	40	50	75	100	200	500	∞
Degrees of Freedom: Denominator	1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.6	963.3	968.6	976.7	982.5	986.9	990.3	993.1	998.1	1001	1006	1008	1011	1013	1016	1017	1018
	2	38.51	39	39.17	39.25	39.3	39.33	39.36	39.37	39.39	39.4	39.41	39.43	39.44	39.44	39.45	39.46	39.46	39.47	39.48	39.48	39.49	39.49	39.5	39.5
	3	17.44	16.04	15.44	15.1	14.88	14.73	14.62	14.54	14.47	14.42	14.34	14.28	14.23	14.2	14.17	14.12	14.08	14.04	14.01	13.97	13.96	13.93	13.91	13.9
	4	12.22	10.65	9.979	9.604	9.364	9.197	9.074	8.98	8.905	8.844	8.751	8.684	8.633	8.592	8.56	8.501	8.461	8.411	8.381	8.34	8.319	8.288	8.27	8.257
	5	10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619	6.525	6.456	6.403	6.362	6.329	6.268	6.227	6.175	6.144	6.101	6.08	6.048	6.028	6.015
	6	8.813	7.26	6.599	6.227	5.988	5.82	5.695	5.6	5.523	5.461	5.366	5.297	5.244	5.202	5.168	5.107	5.065	5.012	4.98	4.937	4.915	4.882	4.862	4.849
	7	8.073	6.542	5.89	5.523	5.285	5.119	4.995	4.899	4.823	4.761	4.666	4.596	4.543	4.501	4.467	4.405	4.362	4.309	4.276	4.232	4.21	4.176	4.156	4.142
	8	7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.295	4.2	4.13	4.076	4.034	3.999	3.937	3.894	3.84	3.807	3.762	3.739	3.705	3.684	3.67
	9	7.209	5.715	5.078	4.718	4.484	4.32	4.197	4.102	4.026	3.964	3.868	3.798	3.744	3.701	3.667	3.604	3.56	3.505	3.472	3.426	3.403	3.368	3.347	3.333
	10	6.937	5.456	4.826	4.468	4.236	4.072	3.95	3.855	3.779	3.717	3.621	3.55	3.496	3.453	3.419	3.355	3.311	3.255	3.221	3.175	3.152	3.116	3.094	3.08
	12	6.554	5.096	4.474	4.121	3.891	3.728	3.607	3.512	3.436	3.374	3.277	3.206	3.152	3.108	3.073	3.008	2.963	2.906	2.871	2.824	2.8	2.763	2.74	2.725
	14	6.298	4.857	4.242	3.892	3.663	3.501	3.38	3.285	3.209	3.147	3.05	2.979	2.923	2.879	2.844	2.778	2.732	2.674	2.638	2.59	2.565	2.526	2.503	2.487
	16	6.115	4.687	4.077	3.729	3.502	3.341	3.219	3.125	3.049	2.986	2.889	2.817	2.761	2.717	2.681	2.614	2.568	2.509	2.472	2.422	2.396	2.357	2.333	2.316
	18	5.978	4.56	3.954	3.608	3.382	3.221	3.1	3.005	2.929	2.866	2.769	2.696	2.64	2.596	2.559	2.491	2.445	2.384	2.347	2.296	2.269	2.229	2.204	2.187
	20	5.871	4.461	3.859	3.515	3.289	3.128	3.007	2.913	2.837	2.774	2.676	2.603	2.547	2.501	2.464	2.396	2.349	2.287	2.249	2.197	2.17	2.128	2.103	2.085
	25	5.686	4.291	3.694	3.353	3.129	2.969	2.848	2.753	2.677	2.613	2.515	2.441	2.384	2.338	2.3	2.23	2.182	2.118	2.079	2.024	1.996	1.952	1.924	1.906
	30	5.568	4.182	3.589	3.25	3.026	2.867	2.746	2.651	2.575	2.511	2.412	2.338	2.28	2.233	2.195	2.124	2.074	2.009	1.968	1.911	1.882	1.835	1.806	1.787
	40	5.424	4.051	3.463	3.126	2.904	2.744	2.624	2.529	2.452	2.388	2.288	2.213	2.154	2.107	2.068	1.994	1.943	1.875	1.832	1.772	1.741	1.691	1.659	1.637
	50	5.34	3.975	3.39	3.054	2.833	2.674	2.553	2.458	2.381	2.317	2.216	2.14	2.081	2.033	1.993	1.919	1.866	1.796	1.752	1.689	1.656	1.603	1.569	1.545
	75	5.232	3.876	3.296	2.962	2.741	2.582	2.461	2.366	2.289	2.224	2.123	2.046	1.986	1.937	1.896	1.819	1.765	1.692	1.645	1.578	1.542	1.483	1.444	1.417
	100	5.179	3.828	3.25	2.917	2.696	2.537	2.417	2.321	2.244	2.179	2.077	2	1.939	1.89	1.849	1.77	1.715	1.64	1.592	1.522	1.483	1.42	1.378	1.347
	200	5.1	3.758	3.182	2.85	2.63	2.472	2.351	2.256	2.178	2.113	2.01	1.932	1.87	1.82	1.778	1.698	1.64	1.562	1.511	1.435	1.393	1.32	1.269	1.229
	500	5.054	3.716	3.142	2.811	2.592	2.434	2.313	2.217	2.139	2.074	1.971	1.892	1.83	1.779	1.736	1.655	1.596	1.515	1.462	1.381	1.336	1.254	1.192	1.137
	∞	5.024	3.689	3.116	2.786	2.567	2.408	2.288	2.192	2.114	2.048	1.945	1.866	1.803	1.752	1.709	1.626	1.566	1.484	1.429	1.345	1.296	1.206	1.128	1

Appendix 3: Tips on Writing Lab Reports

Example Title page

CHEM 311 Sample Lab Report Title Page

Volumetric Analysis of Alkalinity and Hardness in Ground and Surface Waters

Experiment Performed: Jan. 15th, 2003
Lab Report Due Date: Jan. 31st, 2003

For: Drs. Erik Krogh and/or Chris Gill
Prepared by: your name

UNKNOWN: ___none given___

SRM: Alkalinity SRM-501
Hardness SRM-500

Comments on Experimental Data and Results Tables

General:

Tabulations of data and results are the core of a good analytical chemistry lab report. They should be designed to be complete self-contained summaries that can stand alone to give the reader an appreciation of what was measured and some estimate of the uncertainties in those measurements.

Data Tables:
Data tables may be used to summarize lists of experimentally measured values and should include all relevant information required to repeat the observation, such as experimental conditions, operating parameters of instruments and estimates of individual reading errors. Since raw data is usually converted into results through some sort of calculation, other parameters needed in this calculation should be included either in the table or as a footnote to it.

Results Tables:
Results tables are used to summarize calculated results based on information given in data tables and should include some measure of the experimental precision (standard deviation among replicates), confidence intervals and final reported values. When a QC sample is included in a Results table, the known value and the observed bias should be noted.

Data and Results Tables:
For some experiments Data and Results can be combined into one table.

Things to remember to include:
1. Descriptive title
2. Appropriate headings (with units)
3. Individual measured values (with estimates of reading error)
4. Mean values (if replicates were preformed)
5. Sample standard deviations (where applicable)
6. 95% Confidence intervals (where applicable)
7. QC samples (if applicable)
8. Final reported values (quoted to an appropriate number of significant figures and an estimate of the uncertainty)

Data tables should also include footnotes that specify:
1. all information pertinent to experimental measurements, such as instrumental specifics, operating parameters, calibrations etc.

2. all pertinent information required to convert raw data into a calculated result, such as sample volumes, titrant concentrations etc.

Comments on Student Lab Reports

Principle of Method: Focus your attention on how the analyte conc. has actually been quantified. In this case, both alkalinity and hardness are determined volumetrically. Which means that the analyte conc. depends ultimately on the volume of titrant delivered. This only works because we know a) the stiochiometry of the reaction between titrant and analyte, b) the conc of the titrant and c) when to stop adding the titrant (ie the endpoint ~ equiv point). You do not need to reiterate all of the background information provided in the lab manual pre-amble (although some of it, such as the chemical equations that illustrate the reaction between titrant and analyte are essential).

You should comment on how the endpoint of your titrations was determined since this is crucial to the analysis (in principle, the endpoint will be close to the equivalence point – for a discussion of the difference between these terms see textbook, p. 149). In the first case, a pH meter was used (so briefly describe how it works). In the hardness determination, the endpoint was indicated when an indicator (calmagite) changed colour. Read up on EDTA in your textbook. You may want to include the structure of the EDTA-Ca complex and the value of the formation constant (K_f) from table 13.2. Find out what calmagite is and what makes it change colour when the number of moles of EDTA = the number of moles of metal ions ($Ca^{2+} + Mg^{2+} + \ldots$) present in the sample.

Calculations: Show calculations involving the analyte concentration and unit conversions. Include error analysis. There is uncertainty in every measured reading in the lab (see textbook sec. 2.4-2.6 for accepted uncertainties in standard labware) and rules for propagating this error through calculations (see textbook sec. 3.5). The accumulated reading error will be more or less the same for each set of measurements in a replicate set, so you need only perform this exercise once for each calculation. In experiments where replicates were preformed, there are two ways to calculate your errors - propagating individual measurement uncertainties and calculating standard deviations when replicate measurements have been made. In principle, these errors should be the same, however in practice the latter is often larger. When replicates have been preformed, express the error in your final result as the standard deviation and calculate the 95% CL.

Discussion: Explain what was being analyzed and discuss your values in the context of 'expected' or 'normal' values for the analyte. Various sources may be used for this (Cdn Drinking Water Guidelines, technical reports, internet sites etc.)

Conclusion: Report your experimentally determined values (including units) and quote the 95% Confidence Intervals.

Literature: Briefly summarize an alternative technique for the same analyte OR the use of the same technique for a different analyte.

Reference your sources of information using end note citations.

1. Author, Title of paper, *Name of periodical*, **year**, *vol*, page.

Where Students Loose Marks on Lab Reports

Layout and Organization
Title page missing information
Omitted Unknown # or SRM information

Principle of Method
Analyte not clearly defined
Method not clearly stated
Chemical reactions involving analyte not shown
Endpoint indicator not defined or described
Calibration/standardization method not described

Data
Vague entries or data not clearly labeled (i.e., Titrant Volume (transferred))
Data tables missing relevant information (i.e., sample volume and/or titrant conc. omitted)
Missing units
No estimates of reading errors

Calculations
Error calculations not shown or not done
Relative errors calculated and not converted back to absolute errors (with units)
95% CL not computed properly
Reporting too many significant figures especially with respect to error values
(i.e., 12.28 ± 1.25 mg $CaCO_3$/L should be 12 ± 1 or 12.$_3$ ± 1.$_3$ mg $CaCO_3$/L)
Reporting values and errors
(i.e., 0.00937 mol/L ± 0.00008 mol/L should be 9.37 (± 0.08) x 10^{-3} mol/L)

Discussion/Conclusion
Use of personal tense, such as "I", "we" etc.
Lack of focus on measured quantities
Comment on precision/accuracy omitted (Were replicates preformed? What was the RSD? Was the propagated reading error greater or less than the std dev? What measured quantity limited the experimental precision? Are there known or possible interferents than result in bias?)
Final results summary table omitted

Literature
Alternate method for the same analyte or alternate analyte for the same method omitted
Alternate method is a modification of the same method

All references cited in the report should be listed as numbered endnotes in the style adopted by the *American Chemical Society*.

Comments on the Results and Discussion for Calcium in Soils Lab

RESULTS: Results should be summarized in tables with descriptive titles and column headings, so that the reader knows what is being reported. Some of you included values in your Results tables that have appeared mysteriously without any indication of where they came from. Use footnotes on tables, if necessary. Any experimentally derived numbers that will be mentioned in the Discussion section should appear somewhere in the Results section.

Show a representative calculation used to convert measured quantities into reported results. Include calculations used to estimate uncertainties.

DISCUSSION: A good Discussion section has <u>three main components</u>.
An introductory paragraph that clearly states the analyte measured, the method employed and the actual result with a reported uncertainty. This should be followed by some statement to provide context for the magnitude of determined value (i.e., is it high, medium or low). Don't forget to round off your **uncertainties to one or two significant figures** and reference your sources of information. In this lab it might read something like. "The extractable calcium + magnesium from a garden soil; sample was determined to be 3200 +/- 100 μg/g as Ca by extraction with NH_4Cl followed by volumetric analysis with EDTA. This value is higher than that reported for typical coastal soils of 500 – 2000 μg/g as Ca (1)."

The second section should deal with precision and accuracy. In this lab there was the ability to discuss the precision of three different steps in the overall determination. The measurement precision was based on your ability to reproduce the titration step and was typically in the range of RSD = 0.5 – 2 %. This compares well with that reported by Standard Methods, which reports a 2.9% RSD when a sample was sent to 56 different laboratories who analyzed for Ca volumetrically. Using the fact that the variances from the different steps in this determination are additive, you could also report on the precision of the sampling and also the preparation steps. Most of you commented on the observation that most of the variance in this determination arose from <u>indeterminate errors</u> (lack of reproducibility) in the extraction and filtering steps and reported the relative amounts of variance from the three sources (i.e., $V_m/V_T \sim 5\%$, $V_p/V_T \sim 85\%$ and $V_s/V_T \sim 10\%$).

This should be followed by a comment about the accuracy of the determination, usually reported as a %bias using the SRM determination. Your results should again be compared to the value reported in Standard Methods (in this case, they report a bais of 0.8%). Remember to include your 95% CI when comparing your experimental value for the SRM to the true value. For instance, if you report the SRM to be 110 +/- 3 ppm $CaCO_3$ and the true value to be 113 ppm $CaCO_3$, do you have a significant bias.

The third section should report on the known interferences in the method (these can be found in Standard Methods among other places) and steps that can be taken to avoid or negate them. Remember, interferences usually lead to <u>determinate errors</u> not imprecision. In this lab, you carried out an endpoint correction by using a titration blank. Other interferents reported include, transition metals, which can be masked with a complexing agent MgCDTA and colloidal organic matter, which can be removed by combustion and redissolving the fixed solids.

Conclude with a clear final reporting of the results with 95% CL and *n* (# of replicates).

Canadian and International Drinking Water Guidelines for Selected Parameters

		CDWG		EU		WHO
Physical Parameters						
	colour	15 TCU	AO	1 TCU	GLO	15 TCU
	conductivity (specific)	700 (mS/cm)	AO	400 (mS/cm)		NS
	hardness*	500 mg/L $CaCO_3$	AO	NS		NS
	pH	6.5 - 8.5	AO	6.5 - 8.5	GLO	6.5 - 8.5
	solids (TDS)	500 mg/L	AO	NS		1000 mg/L
	turbidity	1 NTU	MAC	4 NTU	GLO	5 NTU
Inorganics		**(mg/L)**		**(mg/L)**		**(mg/L)**
	ammonia (as N)	NS		0.05	GLO	
	arsenic	0.025	IMAC	0.05	MAC	0.05
	barium	1	MAC	0.1	GLO	NS
	boron	5	IMAC	1	GLO	NS
	cadmium	0.005	MAC	0.005	MAC	0.005
	chloride	250	AO	25	GLO	250
	chromium	0.05	MAC	0.05	MAC	0.05
	copper**	1	AO	0.1	GLO	1
	cyanide	0.2	MAC	0.05	MAC	NS
	fluoride	1.5	MAC	NS		1.5
	iron	0.3	AO	0.05	GLO	0.3
	lead**	0.01	MAC	0.05	MAC	0.05
	manganese	0.05	AO	0.02	GLO	0.1
	mercury	0.001	MAC	0.001	MAC	0.001
	nitrate (as N)	10	MAC	6	GLO	10
	nitrite (as N)	1	MAC	0.1	MAC	NS
	phosphorous (as P)	NS		0.4	GLO	
	selenium	0.01	MAC	0.01	MAC	0.01
	sulphate	500	AO	25	GLO	400
	sulfide (as H_2S)	0.05	AO	NS		NS
	zinc**	5	AO	0.1	GLO	5
Organics		**(mg/L)**		**(mg/L)**		**(mg/L)**
	benzene	5	MAC	1	MAC	10
	carbon tetrachloride	5	MAC	3	MAC	3
	dichloromethane	50	MAC			
	2,4-dichlorophenol	0.3	AO			
	DDT (total isomers)	30	MAC			1
	ethylbenzene	2	AO			300
	lindane	4	MAC			3
	nitrilotriacetic acid (NTA)	400	MAC			
	pentachlorophenol	60	MAC			30
	phenol	2	MAC	5	MAC	NS
	toluene	24	AO			700
	trichloroethene	50	MAC			30
	trihalomethanes (TTHMs)	100	IMAC	100	MAC	100
	xylenes (total)	300	AO			500

CDWG Canadian Drinking Water Guidelines
EU European Union
WHO World Health Organization

AO Aesthetic Objective for the CDWG
GLO Guide Line Objective for the EU
IMAC Interim Max Acceptable Concentration
MAC Max Acceptable Concentration
NS No Standard Given

* hardness < 100 mg/L (as $CaCO_3$) are generally considered acceptable; levels higher than 200 mg/L are considered poor but can be tolerated; those in excess of 500 mg/L are normally considered unacceptable

** because first drawn water may contain higher concentrations of metals than are found in running water after flushing, faucets should be thoroughly flushed before water is taken for consumption or analysis

see further:
wlapwww.gov.bc.ca/wat/wq/Bcguidelines/approved.html#1
srmwww.gov.bc.ca/risc/pubs/aquatic/interp/index.htm
www.hc-sc.gc.ca/hecs-sesc/water/dwgsup.htm
w3.whosea.org/techinfo/water.htm
www.who.int/water_sanitation_health/dwq/guidelines4/en/
www.epa.gov/safewater/mcl.html#mcls

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.939	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (99)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0																
		57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0		
		89 **Ac** 227.0	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.1	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)		