Appendix A: Precision and Accuracy of Experimental Data

Reading Scales

All measurements must be determined and recorded to the highest possible precision and accuracy. One of the skills to be mastered in this course is the estimation of fractional scale divisions. On many instruments (e.g., thermometers, burettes, voltmeters, etc.), the smallest scale division is several millimeters wide. This spacing is much wider than the smallest spacing that the human eye can see. In everyday applications, (e.g., bathroom or kitchen scales and room thermometers) it is usually sufficient to read the scale to the nearest full division.

In the laboratory, you will have to estimate to the tenths and fifths of a scale division. This is simple if you take advantage of the fact that the human eye is much better at estimating ratios than absolute lengths. In reading a thermometer marked off in units of 1 °C, for example, look at the mercury level and compare the distance to the mark below with the distance to the mark above. Thus, for a temperature of 25.1 °C, the ratio of the distances is 0.1/0.9 or 1:9. For 25.3 °C, the ratio is 0.3/0.7 or 1:2.33. Such ratios are different enough to be easily distinguishable. If the scale divisions are very close on the other hand, the width of the scale mark itself is no longer negligible, and you will have to account for that.

Significant Figures

Accuracy in scientific work refers to the agreement between a measurement and the accepted value of the measured quantity. Precision refers to the agreement of several measurements of a measured quantity, independent of the accepted value. Scientists indicate the degree of precision in their observations through the number of significant figures. Significant figures include all known (certain) digits plus one estimated (uncertain) digit.

In general, all non-zero digits are considered significant. A digit of zero may or may not be significant depending on where it appears in a measurement. Use the following rules to determine whether or not a zero is significant.

- Leading zeros are never significant.
- Zeros located between non-zero digits are significant.
- Zeros located after a decimal point are significant.
- If there is no decimal point, trailing zeros may or may not be significant. You must be given additional information to determine their significance.

Refer to your textbook for more details on significant figures.

Consider an example dealing with the mass of an object. If a mass is recorded as 2.835 g, the measurement has a total of four significant figures. This quantity may also be written as 0.002835 kg or 0.000002835 Mg. Regardless, all of the measurements are physically the same and each carry four significant figures. In other words, the "roaming" decimal point does not change the number of significant figures in a measurement, consistent with the first "zero rule" listed above.

If a mass is recorded as 4.3 g, the measurement has two significant figures. If the mass was recorded as 4.300 g however, the measurement has four significant figures; the zeroes behind the nonzero digits are significant, consistent with the third "zero rule" listed above. Do not be

tempted to drop off trailing zeros the way most calculators and Excel do – those trailing zeros may be significant if you read them directly off of a high precision instrument!

When you write 4.3 g for a measurement, it implies that you are stating an uncertainty of ±1 in the last digit, meaning the value is between 4.2 g and 4.4 g. Similarly, a measured value of 4.300 g implies that the value lies between 4.299 g and 4.301 g. Between the two measurements, 4.300 g is considered much more precise than the measurement of 4.3 g because the spread of likely measurements is much smaller.

Because significant figures are used to indicate the precision of a measurement, they apply only to measured or experimental quantities. Some mathematical values are exact numbers that are treated as if they have an infinite number of significant figures (i.e., they are known exactly). For example, in some formulae such as the volume of a sphere

$$V = \frac{4}{3}\pi r^3 \tag{A.2}$$

the numerals 4 and 3 are not measured values but exact numbers and do not limit the number of significant figures your result should carry.

Mathematical Operations and Significant Figures

When measured numbers with different amounts of significant figures are added, the resultant is considered no more precise than the least precise number. For example, when a measured length of 1.345 m is added to 2.1 m, the result should be 3.4 m, not 3.445 m. It makes sense that you shouldn't be more certain of the sum than you are of one of the original measurements. When a measured length of (1.345 ± 0.004) m is added to (2.1 ± 0.1) m the result is 3.4 ± 0.1 m. Similar rules apply to subtraction, multiplication, and division of numbers with significant figures. The following examples show you the result you would expect from your calculator and the result stated with the proper number of significant figures.

$$2.6843004 + 1.56 + 0.0434 = 4.2877004 \tag{A.3}$$

The correct result is 4.29.

$$2.6843004 - 1.56 = 1.1243004 \tag{A.4}$$

The correct result is 1.12.

$$2.6843004 \times 4.26 = 11.4351197 \tag{A.5}$$

The correct result is 11.4.

$$268.43004 \div 1.56 = 172.07054 \tag{A.6}$$

The correct result is 172.

Estimation of Uncertainty

It is often quite helpful to record some estimate of the uncertainty in your primary data in your notebook. In the previous section, it was assumed that unless explicitly stated, all of the uncertainty was ±1 in the last reported digit. In practice, a more precise measurement may

require better estimate of this uncertainty. For example, a recorded measurement may be (3.654 ± 0.003) cm. In this example the estimated uncertainty is ±3 in the last recorded digit. A good measurement often requires such a statement of uncertainty. Keep in mind that the uncertainty should be reported to only **ONE** significant figure.

Experimental Errors

When a measurement is made, experimental error may be imbedded in the data. The validity of a measurement and agreement between experiment and theory is largely dependent on the practical consideration of the theory and the experimental precision. Experimental errors should be considered and properly treated to achieve a correct understanding of a measurement.

Experimental errors are classified as either systematic errors or random errors. Systematic errors refer to errors that cause a measurement to be either consistently too high or too low due to some defect of equipment or some measuring procedure, including calibration errors, and failure to apply environmental corrections. Random errors refer to those errors from some irregular or unpredictable fluctuation in a measurement.

Systematic errors can often be reduced or corrected by comparing your results to those from alternative instruments and experimental procedures. In addition, you can eliminate all unjustified assumptions in your measurement process. On the other hand, random errors may be reduced by careful experimental procedure but never be eliminated completely. You can try to reduce these errors as much as possible to obtain the best possible values of measurement by repeating the measurement several times. In this way, you can arrive at your best guess at the "true" value of your measurement by calculating the average of your readings and describe the random errors in each measurement as fluctuations around the "true" value of measurement.

When multiple measurements are made, you can describe a single value for the measurements in one of three ways.

Mean

The mean is the most common way to present a single value for a set of measurements. The mean is simply the arithmetic average of all measurements:

$$\overline{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad \text{(A.7)}$$

where N is the total number of data points and x_i represents the i^{th} measurement in your data set.

Median

The median is the middle value of a set of measurements. It has an equal number of data points above and below it.

Mode

The mode is measurement that occurs most frequently in a set of measurements. It is the most probable measurement value.

The most useful statement of a measurement from the above list depends on the type of measurement. A correct description needs careful consideration of the specific measurement process. In the case of measurements with asymmetric random errors, it may be true that all measurements are needed to describe the true measurement.

You can report the magnitude of the fluctuations in a set of measurements by determining the sample standard deviation of the measurements. The sample standard deviation, s_x, is defined as

$$s_x = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - \overline{x}\right)^2} \tag{A.8}$$

and your final measurement is reported in the form:

$$\overline{x} \pm s_x \tag{A.9}$$

When reporting your value this way, the average is your best guess of the "true" value and the standard deviation is a measure of the uncertainty in that guess. Again, keep in mind that the reported standard deviation should have only **ONE** significant figure.

Appendix B: Washing Glassware

Rinse dirty glassware with tap water several times in the lab sink. There is no need to use detergent solution unless you want to dislodge solid particles or get the surface so clean that water wets it uniformly, which is important when performing volumetric analysis. Finally, rinse the surface with deionized water. You may want to use a wash bottle to get into tight spaces. Keep in mind that washing with several small volumes of solvent (e.g., water) is more efficient than washing one time with the same total volume.

Appendix C: The Analytical Balance

In many experiments, you will need to determine accurate masses of various samples. For this purpose, you will use an analytical balance, an instrument capable of determining the mass with a sensitivity of ±0.1 mg (±0.0001 g).

The balance you will be using is an electronic balance. Make sure the balance has been on for at least ten minutes before using it to ensure the electronic components of the balance have stabilized. Press the tare button or bar to clear and zero the display. Open one of the balance doors, place the item to be massed on the pan, and close the door. When the reading has stabilized, record all of the digits for the mass.

Mass by difference

Mass by difference is the technique you will use to find the mass of most samples you'll encounter in the laboratory. Typically, a container of sample is placed on the balance and its mass recorded. Then, the container is removed from the balance, and some of the sample is dispensed to another container for use. The sample container is placed back on the balance and its new mass is recorded. The difference between the *before mass* and the *after mass* is the mass of material dispensed. Similarly, the mass of a sample can be found by recording the mass of an empty container, filling it with sample, recording the mass and determining the difference between the two values.

The net mass of a sample can also be found directly by initially taring the mass of the container. Before placing the empty container on the balance, close the door, and clear and zero the display by pressing the tare button. The display will now indicate zero grams. Leave the empty container on the balance, add some of the sample to it, and then read the mass directly. The mass of any material added to the container hereafter will be directly shown on the display.

The first method—measuring the mass of sample *removed* from a container—is the most common method you will use in the laboratory because it usually gives the smallest relative uncertainty in your measurement.

Appendix D: The Centrifuge

When you place a test tube in the centrifuge rotor, always place another test tube of the same size filled with water to about the same to counterbalance it. If the centrifuge operates unbalanced, the bearings and spindle of the machine could be seriously damaged. Also unbalanced centrifuges can "walk" across a table. If the angular momentum of a centrifuge is allowed to become linear momentum by, say, springing off a bench and landing on the rotor, the centrifuge will become a ten-pound missile. If you see a centrifuge wobbling and moving across a bench, shut it off *immediately*.

Use a disposable pipette to remove the supernatant liquid (i.e., the liquid above a solid) from a test tube. Unless instructed otherwise, do not attempt to pour the liquid off. Always wash a centrifuged precipitate with several portions of distilled water if it is to be used further on in the procedure. In washing, the precipitate must be thoroughly mixed with the wash water before centrifuging again. This might require you to break up the solid after centrifuging the first time.

It will seldom be necessary to transfer a precipitate out of the bottom of a test tube because you can usually dissolve the precipitate with a reagent that will be used later in the procedure.

Label test tubes with a lab marker only. Do not use paper labels. Such labels invariably stick inside the test tube holders of the centrifuge.

Appendix E: Graphing Techniques

In many facets of your professional (and personal) lives you will have to deal with data. It is important that you learn to present data in a clear, precise manner so that you and other people can easily interpret and use those data.

The presentation of quantitative data can take on several different forms. Two of the most common forms are tables and graphs. Tables have the advantage that your data, in the form of actual numbers, are readily seen, whereas graphs are better at visually showing trends and changes. Graphs also make it easier to interpolate (estimate a value between two data points) and extrapolate (estimate a value beyond points already measured.)

Here are some rules to follow when creating a graph:

- Use Excel to create all of your plots.
- Plot the dependent variable along the vertical axis (*y* axis) and the independent variable along the horizontal axis (*x* axis). When measuring two variables, you usually vary one condition and measure its effect on some other condition. The variable associated with the changed condition is the independent variable, and the quantity you observe as a result of the change in the independent variable is the dependent variable. For example, if you were to measure your body temperature each hour for 12 hours, time would be the independent variable and temperature the dependent variable.
- Both axes must be clearly labeled and include the unit of measure. In the previous example, the vertical axis would be labeled "Body Temperature (°F)" and the horizontal axis would be labeled "Time (hr)".
- Scale values should be reasonable, uniform values. Each square should represent a whole number of units.
- The data points must be easily distinguished from the line or curve drawn through the points. Small dots are not acceptable data points. Commonly used representations are ●, X, O, and +.
- The data should cover as much of the area between the axes as possible.

The instructions below will guide you through the process of generating a simple plot and performing a linear regression to determine the slope and intercept of the best possible straight line through the data set in Excel, first for the Windows operating system followed by a list of slight differences for the macOS operating system. The data set used in this sample can be found in Table E.1. Here, time will serve as the independent variable, and temperature will be the dependent variable.

Table E.1. Sample data for plotting in Excel

Time (min)	Temperature (°C)
0	50
5	59
10	71
15	80
20	88
25	99

Open Excel and select a new blank worksheet. As shown in Figure E.1, type in the column headers to remind you of the type of data each column contains and the data. Note that independent data is typed into column A in this example. Even though we describe plots as "*y* vs. *x*," the independent variable data must be selected **first** when plotting in Excel. If the data are not in adjacent columns or in the reverse order, you can highlight non-adjacent columns by holding down the Ctrl key while clicking and highlighting.

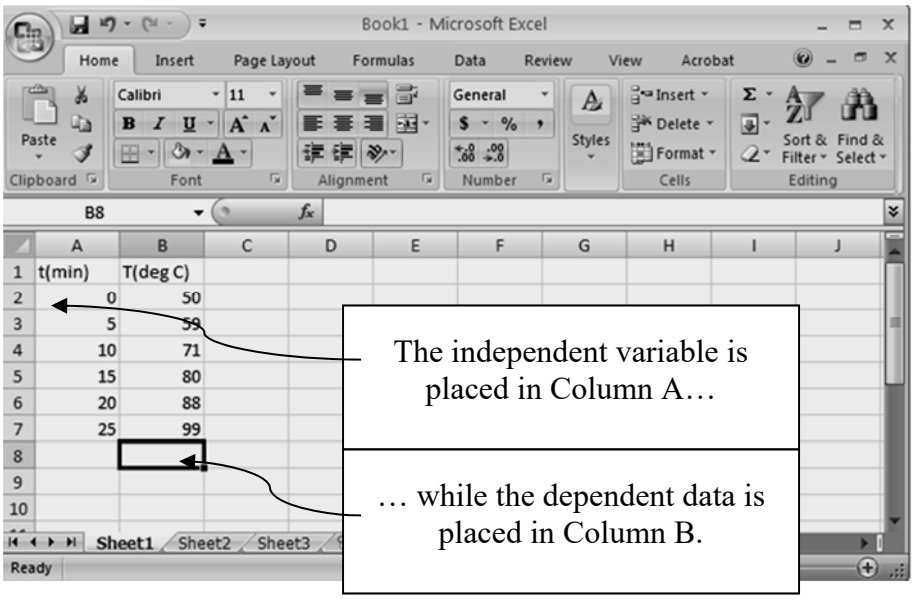


Figure E.1. Raw sample data with column headings. Note that, when constructing a plot of temperature vs. time, the independent variable data (time) are in Column A.

Once the data have been typed in, use the mouse to highlight the data as shown in Figure E.2, then click on the Insert tab. In the Chart window, select the option without connecting lines under Scatter.

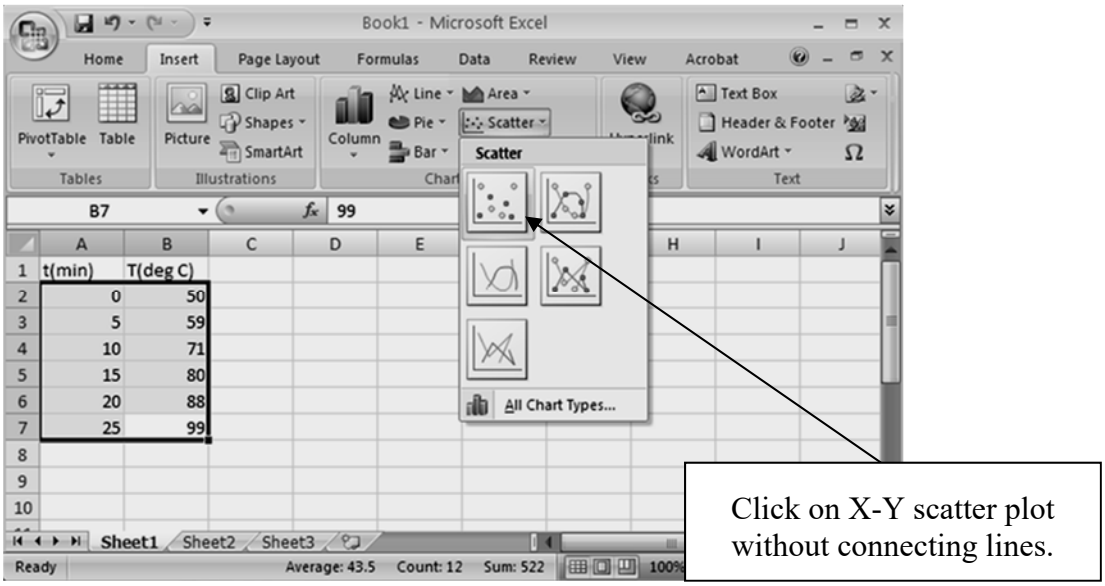


Figure E.2. Location of scatter plot command in Excel.

A plot for the selected data is automatically generated as an object in Sheet 1 (Figure E.3).

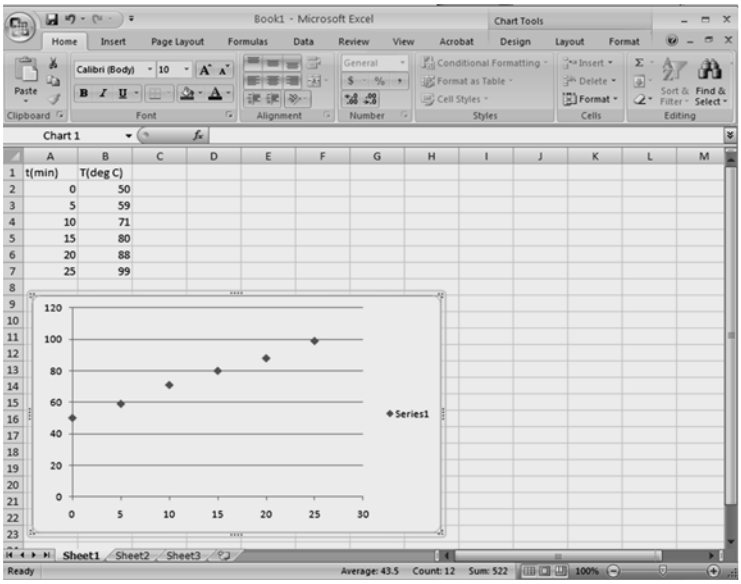


Figure E.3. Result of clicking on scatter plot in Excel.

Now you need to format the plot correctly before using it as a figure in your lab report. An easy way of doing this is by starting with a template. Under the Chart Tools tab, select Layout 1 in the Chart Layout window, which will display the chart and axis titles.

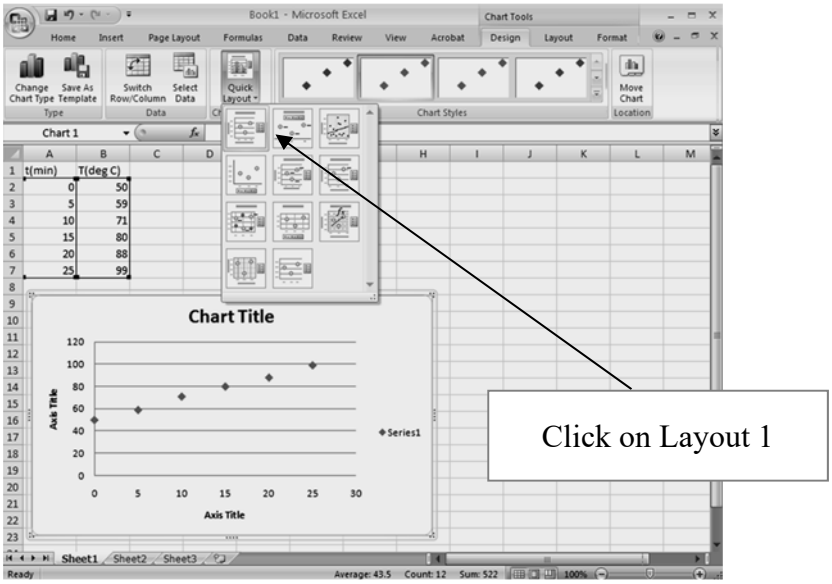


Figure E.4. Result of clicking Layout 1 under Chart Tools.

Alternatively, the various layout options can be accessed through "More Primary Horizontal/Vertical Axis Options" under the Layout tab in the Chart Tools tab (Figure E.5).

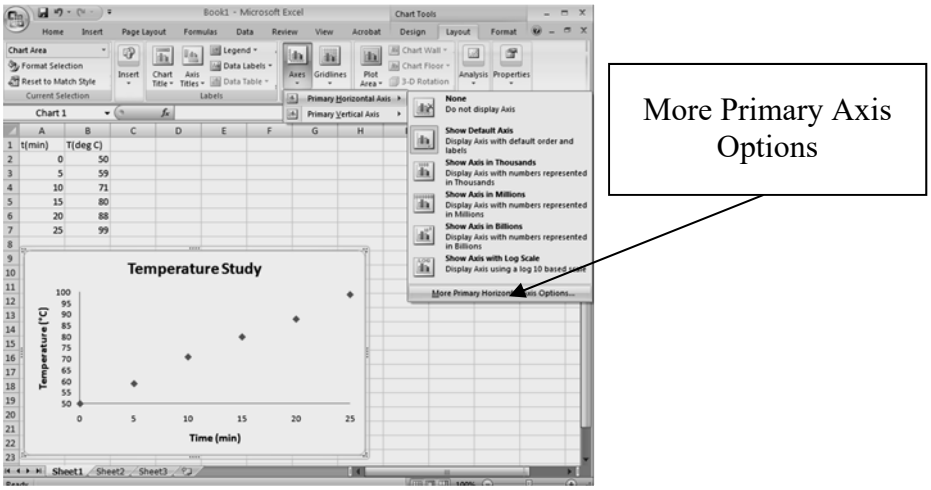


Figure E.5. Location of axis options dialog box under Chart Tools.

The axis titles can be modified by clicking on the text boxes and typing the desired text, including the appropriate units. The chart title text box should be deleted, as figure titles are not written directly on the figure.

Legends are used to help the reader identify different data sets plotted on the same graph. When only one data set is plotted, as in this example, the relationship between the variable is evident and no legend is needed. Therefore, in this case, the legend should be deleted as well.

The gridlines should also be deleted, which can be done by simply clicking on one of them to highlight all of the gridlines in that direction, and pressing delete.

In order to change the scaling on the *x* and *y* axes click on the Axes button in the Chart Tools tab and select More Primary Axis Options. Ordinarily, you want the data to be spread out as much as possible on your graph. If the Auto option does not maximize the plot area, you need to type in appropriate values for the minimum and maximum axis values in the dialog box (Figure E.6).

Figure E.6. Axis Options dialog box.

For this horizontal axis of this plot, change the minimum to 0 and the maximum to 25 to match the data range, and then click on Close. Repeat the same operation for the *y* axis, with a minimum of 50 and a maximum of 100. When you are finished, your graph should look like the one in Figure E.7:

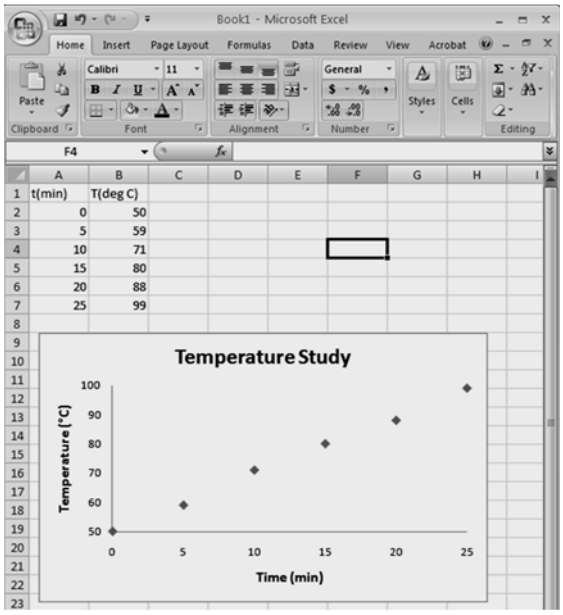


Figure E.7. Sample data plot with new axis ranges.

Excel has a built-in feature to draw a line of best fit through the data points. Click on the Analysis button in the Layout tab of the Chart Tools toolbar and select Trendline (Figure E.8) or right-clicking on a data point in the plot and selecting Add Trendline in the pop-up menu.

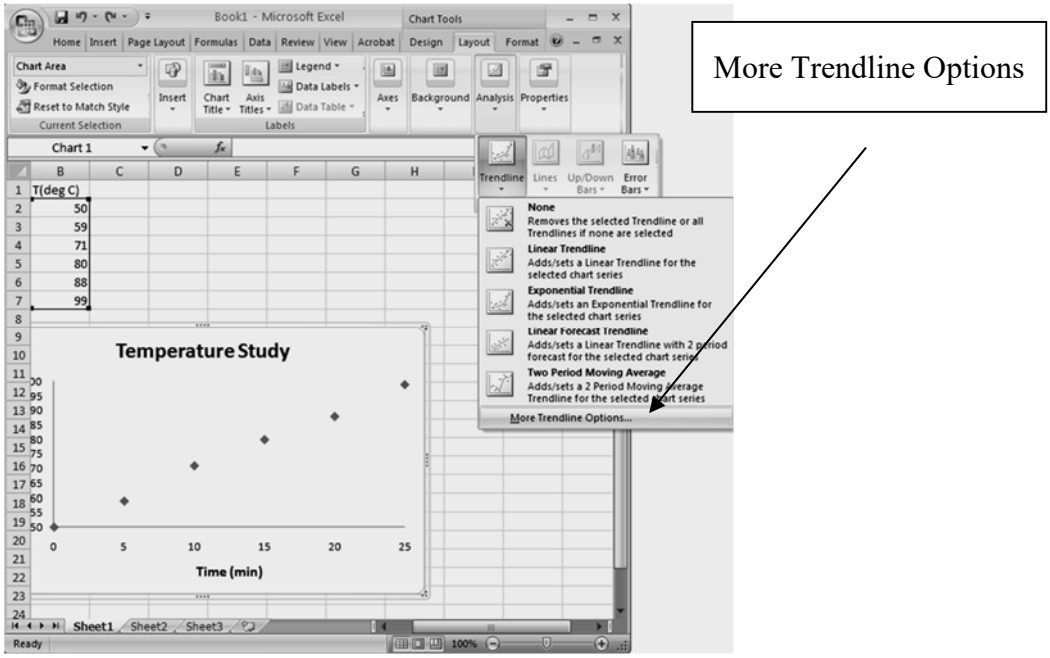


Figure E.8. Location of Trendline menu in Excel.

If you select More Trendline Options a dialog box will appear (Figure E.9). Select the appropriate fit function (usually linear) and select the Display Equation on chart option.

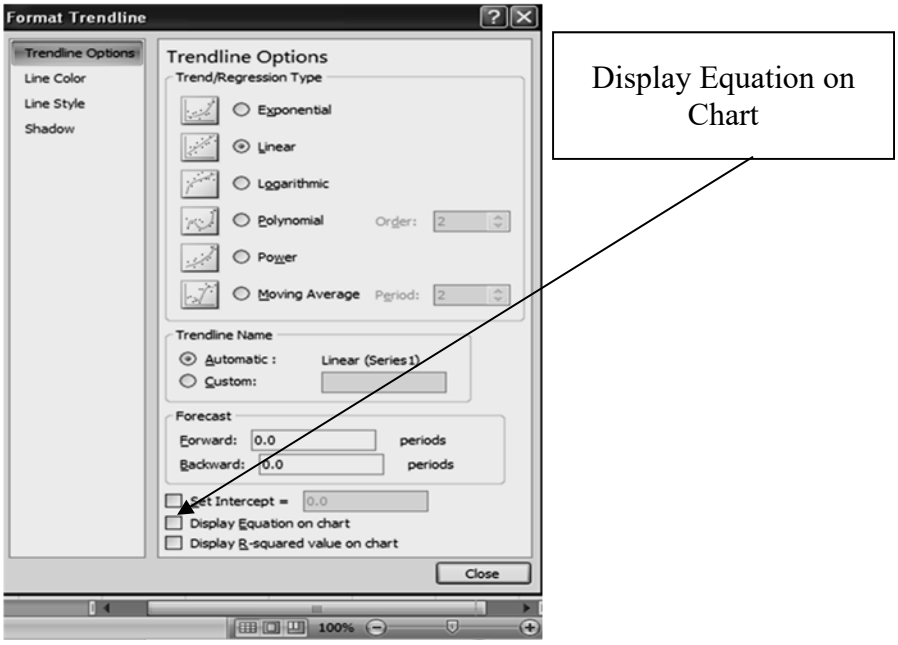


Figure E.9. More Trendline Options dialog box in Excel.

This set of operations will not only draw a line through the data points, but also display the equation of the line (Figure E.10). The equation may overlap other areas of the graph, but you can click on it to highlight it and then move it within the plot area so it is easier to read.

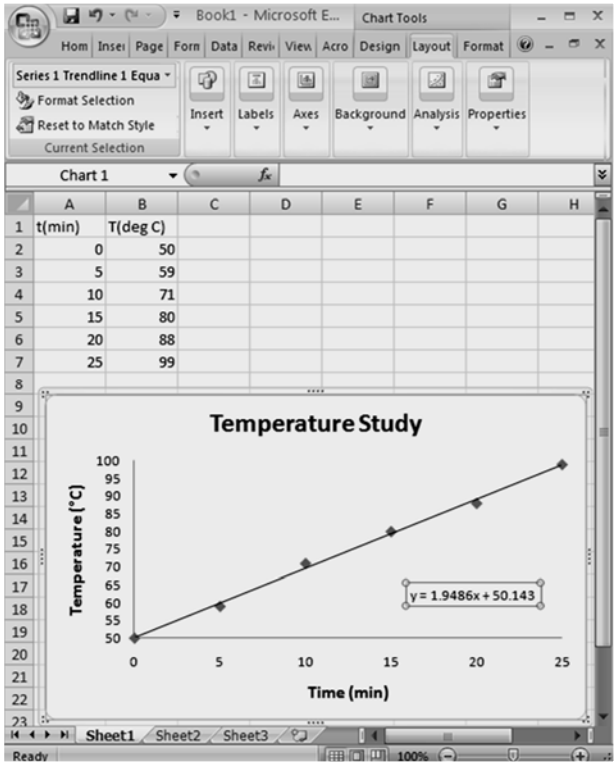


Figure E.10. Sample plot with line of best fit and corresponding equation.

As you can see, the slope of this line is 1.9486 °C·min^{-1} and the intercept is 50.143 °C. Note that Excel will *not* show you the units, the correct number of significant figures, or the appropriate variables to use in your equation! You must determine all of these on your own and include them in your equation of best fit.

You will usually be told how many significant figures belong in your fit parameters. (If you're not sure, ask your instructor.) Oftentimes the equation Excel presents will not have enough digits for you to report those values to the correct precision. In that case (and a better idea in every case, for that matter), you will need to use the SLOPE and INTERCEPT functions on the data directly.

Once you write down the equation, click on it, and press the Delete key to delete it. The equation of the line should never be on the graph itself; it should be reported in the figure caption.

Continue to format the plot according to the requirements listed in the Lab Report Guidelines document (see the D2L page for your lab section). When you are finished making formatting changes, copy and paste the graph into the body of your report in Word. Right-click somewhere in the blank area surrounding the axes, and select Copy from the pop-up menu (or Ctrl-C on the keyboard). This will place you graph on the clipboard. Next, switch to Word and move the cursor in the document you are editing to where you want to insert the graph. Then, right-click in that location and select Paste from the pop-up menu (or Ctrl-V on the keyboard). Your graph should now be in your document. You may need to resize the figure or center it, if it isn't already. Figure E.11 show the final result of this operation for the sample data given.

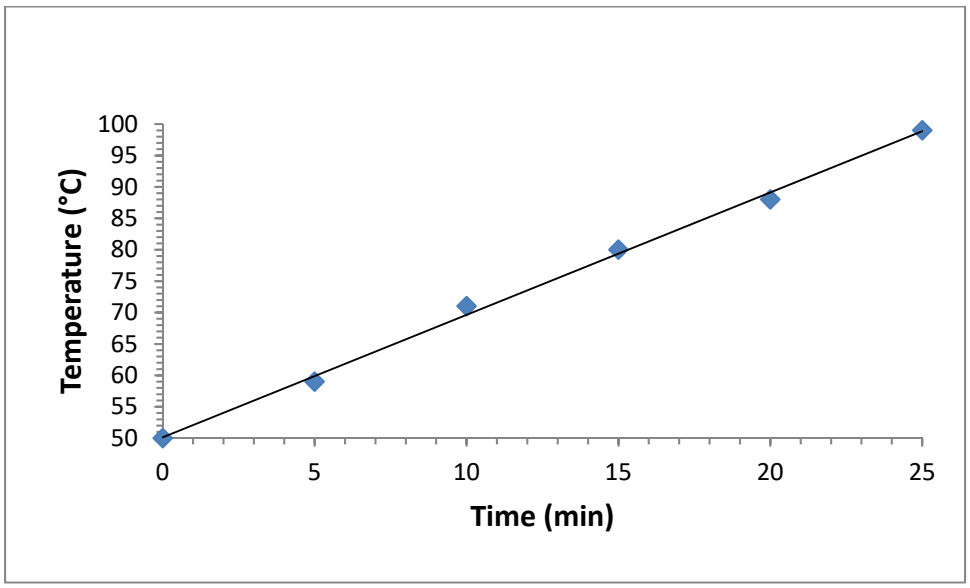


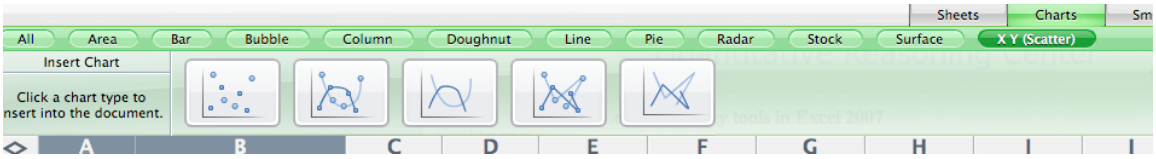
Figure E.11. Final version of the sample plot.

Graphing Information for macOS Users

Much of the process is the same for Mac users as for PC users. Some of the key combinations or menu locations are different, though. The biggest difference is the use of Command (or Apple) key instead of Ctrl.

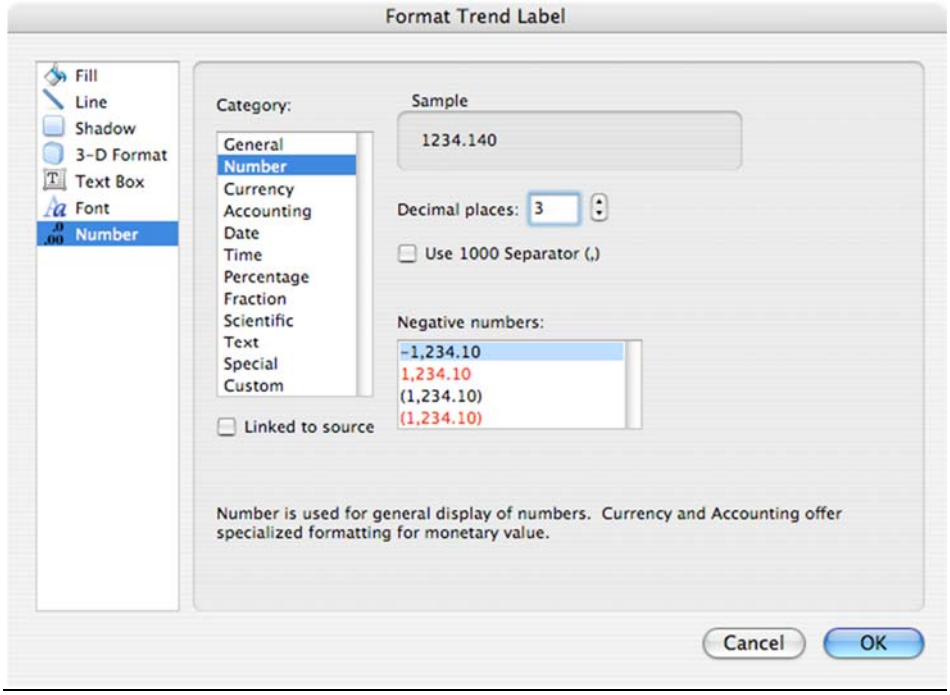
Below is a set of instructions from an older version of Excel for Mac for reference.

Creating a Graph: Select the data to be graphed. Unless told otherwise, Excel will assume that the independent variable (plotted on the x-axis) is in the left-most column, whereas the dependent variable (plotted on the y-axis) is in a column to the right. To highlight non-adjacent cells, highlight the first column of data then hold the **Apple command** key while you highlight the second column of data. Click on "Insert" and then choose "Chart…" Select the group **XY (Scatter)** and choose "Marked Scatter" (the first option).

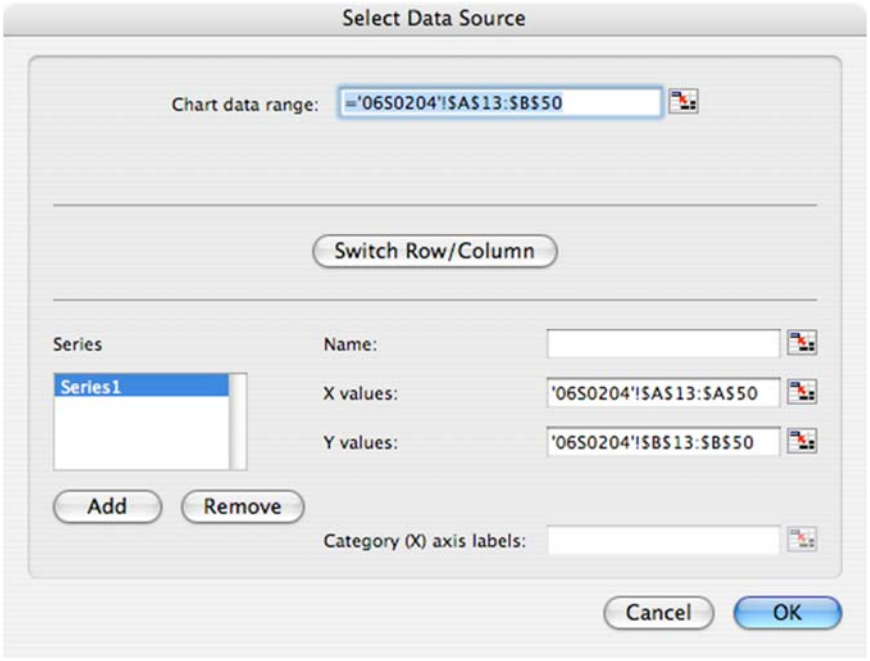


Adding Graph and Axis Titles: Click on the graph to activate it. (Then click on the **Toolbox** button from the top menu if the Toolbox is not already open. Select the **Formatting Palette** from the **Toolbox**.) In the **Formatting Palette** window, expand the **Chart Options** section. Under **Titles**, use the drop-down menu to select Chart Title or an axis. Below the drop-down menu, click **here to add title**, and then type a title. You can also remove the legend by looking under **Other Options** and using the drop-down menu to select None for Legend.

Changing Decimal Places on Axes: Double click on the axis. In the new dialog box, select **Number**, uncheck "Linked to source" if it is checked, and change the number in the "Decimal places" box.

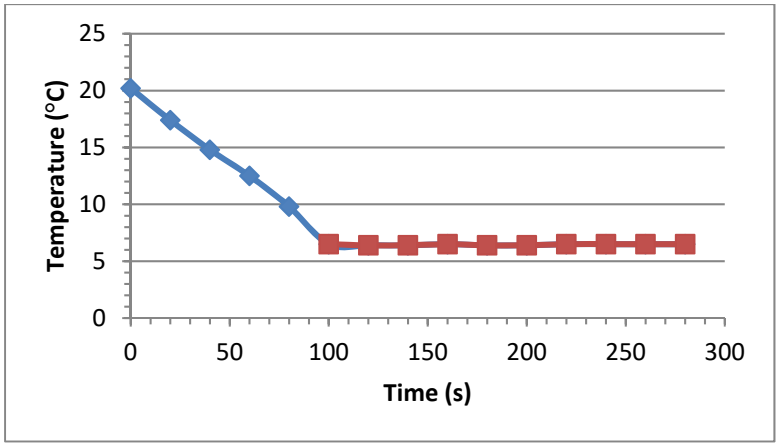


Adding a Trendline: Click on your graph to activate it. From the drop-down box under the **Chart** menu at the top of the screen, select **Source Data**. A new dialog box will appear.

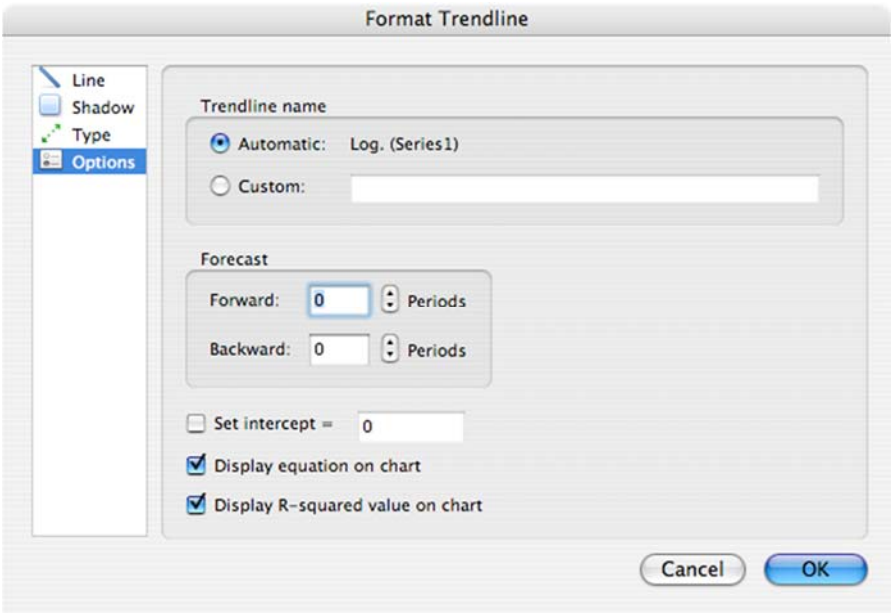


Under **Series** select the **Add** button. Click in the **X values** box, then use your cursor to select the appropriate x-values for your localized trendline. Repeat with the **Y values** box and click **OK**. When you are finished, there will be a new series of data overlaid on the end of the existing data series.

Your graph should look something like this:



Click on one of the new points to activate them, then from the drop-down box under the **Chart** menu at the top of the screen, select **Add Trendline**. A new dialog box will appear.



From the menu on the left side, select **Type** and make sure that "Linear" is selected. Select **Options**. To extend the best-fit line beyond the points selected, type "4" in the "Forward" and "Backward" boxes in the **Forecast** section. Check the box for "Display equation on chart" and click **OK**.

Appendix F: Volumetric Analysis

Analytical chemistry comprises qualitative and quantitative analyses. Qualitative analysis aims to identify the elements in a compound or mixture without regard to amount. Quantitative analysis deals with the next step: given the elements in a sample, what are their proportions? This is important not only when determining the formula of a new compound but also when using a commercial chemical for precise work (no chemical is ever 100% pure!). A more common application is the analysis of solutions or mixtures (e.g., tap water, alloys, rocks, foods, bodily fluids, etc.).

Quantitative analysis is built on two axioms (law of definite composition and conservation of mass) and one special skill: the ability to steer a sample through a maze of chemical operations without losing more than 0.1% or 0.2% of the sample at each step. This requires attention to detail, neatness, cleanliness, dexterity, and a sixth sense for tracking bits of sample or reagent that are trying to slip away. These skills are useful not only in chemistry but also in biology and medicine.

Traditional quantitative analysis is divided into gravimetric and volumetric analyses. However, examples of more recent branches are colorimetric, chromatographic, electrochemical, spectroscopic, and mass spectrometric analyses.

The accuracy attainable in volumetric analysis is 0.2% − 0.5%. This means that you have to worry about volumes of a drop or less. Sample or reagent volumes are typically about 25 ml, so one drop (0.05 ml) of water in the wrong place can cause an error of about 0.2%. For this reason, it is essential to learn quantitative techniques, especially the proper care and use of volumetric glassware.

Definitions

Volumetric analysis, also known as titration, involves slow addition of a measured volume of solution 1 (titrant) to solution 2 (sample or analyte). Solution 1 is chosen so that it reacts quickly and stoichiometrically with solution 2.

The titrant is contained in a burette, which is a long, graduated, cylindrical glass tube with a stopcock and delivery tip at the bottom. With a burette, additions of 0.02 mL can be easily measured, and the total volume in a titration can be determined to within a few parts per thousand. The sample is measured out by a volumetric pipette, which delivers a fixed, accurately known volume.

The key problem in a titration is to recognize the stoichiometric equivalence point. This is where the titrant has just consumed all of the solute in solution 2, but it is not yet present in excess. Sometimes the equivalence point can be recognized directly (e.g. one solute may be colored). More commonly, an indicator must be added. Indicators are substances that have different colors in the presence of excess solute 1 or 2 and, hence, change color at the equivalence point. Actually, some small excess of titrant must be present for the color to be perceptible (whether from the indicator or the titrant itself), and so, in practice, the titration is carried to this "endpoint" rather than to the equivalence point. This excess is called the indicator blank. It is generally kept small by using very intensely colored indicators at the lowest possible concentration, just enough to give a delicate pastel shade. In precise work, the indicator blank is actually measured with a suitable blank solution of similar composition and ionic strength (e.g. NaCl for a titration of NaOH with HCl), and is subtracted from the gross volume of titrant consumed.

To help recognize even light color changes, a piece of white paper is placed under the titration flask. Additionally, a reference solution corresponding to the correct endpoint is prepared and the sample is titrated until its color exactly matches that of the reference solution.

The concentration of the titrant is usually expressed in units of molarity, or moles of solute per liter of solution. The product of molarity and volume of titrant needed to reach the equivalence point equals the number of moles of solute 1 that reacted with solute 2. Given a balanced chemical equation that states in what proportions solutes 1 and 2 react, we can find the number of moles of solute 2.

Volumetric glassware is calibrated either "to contain" (TC) or "to deliver" (TD) the specified volume. In the latter case, the liquid that stays behind on the walls and in the burette/pipette tip, which is constricted to ensure complete and reproducible drainage, is *included* in the stated value. Accordingly, you should never use the pipette bulb to "blow out" the liquid remaining behind in the tip.

Tolerances, or permissible limits of error, for volumetric glassware are set by the National Bureau of Standards. They are typically 0.1% for the most common sizes but range from 0.2% to 0.3% for small pipettes and from 0.03% to 0.05% for large volumetric flasks. For very accurate work the glassware is calibrated by weighing the amount of water delivered. If the laboratory is not at the calibration temperature specified for the glassware (25 °C or 20 °C), then corrections for thermal expansion of aqueous solutions (about 0.025% per °C) must also be applied.

Before using a communal piece of volumetric glassware, verify that it is of the right size! Once in a while it happens that a 25 mL pipette finds its way into a box of 20 mL units or a 200 mL flask into a box of 250 mL units!

Burette

Burettes are available in many different sizes. Typically, you will be using a 50 mL burette that is divided into 0.1 mL divisions. Using a burette reading card (a thick black line on a white sheet of paper), you are expected to determine the liquid level to the nearest 0.02 mL. Your laboratory instructor will show you how. The burette is clamped in a burette holder to make sure it is properly aligned and stable.

Like all volumetric glassware, the burette must be scrupulously clean and free of grease so that water wets the walls and drains in a smooth film. This is an unending battle, as traces of oil from air or reagents settle onto the walls and make them water-repellent. To check your burette, place a beaker beneath the delivery tip and open the stopcock so that the water drains from the burette. Watch the wall a few cm above the meniscus as the burette is being emptied. If the thin film of water remaining on the inner wall breaks up into droplets, the burette is dirty and must be cleaned. If so, drain the burette completely and close the stopcock. Remove the burette from its holder and pour in a small amount of detergent solution. Using a burette brush, scrub the inside of the burette. Remove the brush and drain the detergent solution. Thoroughly rinse the burette, first with tap water and then with distilled water. Fill it with distilled water and recheck the water drainage. If the burette is still dirty, check with your laboratory instructor or use the cleaning solution.

Before filling the burette with titrant, you'll have to flush out all traces of water so that it does not dilute the titrant. This process is referred to as "priming" the glassware. Drain the burette completely and close the stopcock. Using a small beaker, add several mL of titrant. Remove the burette from its holder. Holding the burette in a nearly horizontal position, simultaneously rotate

and tip it so that the solution wets the entire inside surface (without pouring out the top!). Turn the burette upside down and drain the solution. Do this again with another portion of the titrant and again drain completely. Now the liquid film stuck to the glass should have the same composition as the titrant. Place the burette in its holder and fill it to above the 0 mL mark. Open the stopcock and allow the solution to flow into the delivery tip. Make sure that no air bubble is trapped immediately below the stopcock. If it is, you can usually get rid of it by running the burette full blast for a few seconds. Drain the titrant to slightly below the 0 mL mark, but do not fuss to get it to 0.00 mL. (As the net volume is the difference between the initial and final readings, there is no need to start exactly at 0.00 mL. In fact, starting at 0.00 mL increases the uncertainty in your measurement because there is no scale division mark above 0.00 mL that you can use to estimate the hundredths place.). Remove any droplets adhering to the outside of the tip. Note that you can control the flow rate by proper control of the stopcock. You can add one drop (and even fractions of a drop) of the titrant at a time. Your laboratory instructor will demonstrate the proper technique.

A puddle of liquid beneath the burette indicates either a spill or a leak. To check for the latter, wipe up the puddle. Make sure the stopcock is fully closed, dry any hanging drops from the burette tip, and check again in a few minutes for any signs of leakage. If the burette leaks, report it to your laboratory instructor, who will either fix it or give you a new one.

You must check for any stubborn air bubbles in the burette before starting your experiment. Bubbles are most likely formed just below the stopcock and may not be flushed out when the burette is run full blast. If you start your titration with an air bubble in the burette, you cannot use those data and will need to completely restart that trial with a new sample. This is why it's imperative to check that all bubbles are flushed out before starting. Check with your lab instructor before delivering the titrant to make sure you are all set. If not, the instructor will either fix the problem or get you a new burette.

During an analysis, you can deliver the titrant quickly at the start of a titration and then slow it down as the endpoint is approached, finally adding only a drop or even a fraction of a drop to reach the endpoint. The walls of the flask containing the analyte often retain some unreacted sample from the early stages, especially if your swirling becomes less vigorous as time progresses. Throughout the titration, rinse the walls of the flask with distilled water; if the color fades, there was indeed sample caught on the walls and you are not at the true endpoint. Titrate with fractional drops until you again get a color change. This should be the true endpoint.

Sample sizes and titrant concentration are generally chosen so that the titration requires between 15 and 40 mL of titrant. Smaller volumes give a larger relative error, since all contributing errors are constant (reading errors 2×0.02 mL, calibration error 0.05 mL, endpoint error 0.02 mL to 0.1 mL, etc.). Larger volumes may require 2 fillings of the burette and 4 readings, resulting in some loss of time and accuracy. To avoid this, refill the burette with titrant before starting each new trial.

Pipette

The volumetric (or transfer) pipette consists of three segments: a delivery tip, an enlarged bulb, and a narrow tube bearing the calibration mark. Like the burette, the volumetric pipette must be clean. To check the cleanliness of your pipette, hold the top (not the bottom) segment of the pipette in your nondominant hand. Hold the rubber bulb in your dominant hand, squeeze it, and then press it against the top of the pipette to create a seal. While holding the bulb to the pipette, place the tip into a beaker containing distilled water and fill the pipette by gradually releasing the

pressure on the rubber bulb. When the liquid level rises above the calibration mark, quickly remove the bulb and place your (dry) fingertip (of your nondominant hand) over the top of the pipette to hold the liquid in place. You can slowly drain the contents of the pipette by decreasing the pressure applied by your fingertip or quickly drain it by removing your finger completely. In this case, lift your finger and let the water drain freely into a beaker. If the water film breaks and droplets appear on the inside surface, the pipette is dirty.

A dirty pipette must be cleaned with a cleaning solution. Draw up the cleaning solution to slightly above the calibration mark, leave it at that level for about a minute, and then let the solution drain into a waste beaker. (Be careful not to get this solution onto your hands or clothes; carry the empty pipette with its tip in a beaker. Do not drip the cleaning solution on the floor.) Thoroughly rinse the pipette, first with warm tap water (rinse the outside, then draw water from a beaker slightly above the level reached by the cleaning solution and let drain; repeat three times, changing the water in the beaker each time). For the fourth rinse, use distilled water. The trickiest part of this procedure is to get the cleaning solution out of the top segment of the pipette. Ideally, you should draw each wash a little higher than the previous one, but without getting any water into the rubber bulb. (If liquid enters the bulb at any point, let your instructor know so the bulb can be cleaned and dried thoroughly. Wet bulbs should never be used, and bulbs should be checked for internal liquid before use.). This is tricky, and you should therefore squirt some distilled water into the top of the pipette after each wash. Do not try to shorten the above cleaning procedure by simply rinsing the pipette under the tap; the tip orifice is too small for sufficient water to get inside. Also, the pipettes are fragile and easily break when being washed in a sink.

Like the burette, the pipette must be primed with the solution to be measured. Dry the outside of the pipette tip with a Kimwipe so as not to contaminate the solution to be sampled. Using the procedure described above, partially fill the pipette. Hold the pipette in a nearly horizontal position and simultaneous rotate and tip it so that the entire inside surface gets rinsed. Place your fingertip over the top and turn the pipette upright. Hold a beaker at an inclined angle beneath the pipette tip so that the tip touches the inside wall of the beaker. Now let the contents drain into the beaker. Note that a drop remains in the pipette tip. This is expected, as the pipette has been calibrated to deliver a known volume with this amount of liquid left in the tip. But if you had not touched the tip to the inside wall of the beaker, another drop or two would have stayed behind.

Wipe the outside of the tip with a Kimwipe, and rinse and drain a second time. Again dry the outside of the tip. Fill the pipette to above the calibration mark, then seal with your fingertip. Place the pipette in a nearly horizontal position and dry the outside of the tip. Turn the pipette upright and hold a waste beaker beneath the tip, inclined at an angle so that the tip of the pipette touches the inside wall of the beaker. By controlling the pressure of your fingertip on the top of the pipette, let the liquid drain slowly until the bottom of the meniscus coincides with the calibration mark. Remove the beaker and place the sample container under the tip, again inclined so that the tip touches the inside wall. Remove your finger and allow the solution to flow freely into the container. Allow enough time (about 30-40 seconds) for the pipette to properly drain under the force of gravity. Never push the liquid out of the pipette using the bulb. This procedure is called “taking an aliquot of a solution".

Standard Solutions

A solution with an accurately known concentration of solute is called a standard solution. For a solute available in pure form, a standard solution can be prepared by accurately obtaining the mass of a known amount of solute and dissolving it in a known amount of solvent. Normally the

solute is quantitatively transferred (i.e., making sure every speck of solute is transferred) to a volumetric flask, which is a piece of glassware calibrated to contain a definite volume of liquid. The volumetric flask should have a small amount of solvent already present to start dissolving the solute. Solvent is added to the flask in small amounts and then swirled around to ensure adequate mixing and dissolution of any remaining solute. Make sure all of the solute is dissolved before reaching the calibration mark of the flask. More often than not, the solute required for a titration is not available in a pure state, so its exact concentration in solution must be determined by analysis. A solution of approximately the desired concentration is made up and is analyzed by titration against a primary standard, which is a well-behaved, non-hygroscopic solid that is readily available in very pure form (>99.95%). (A hygroscopic solid is a solid that absorbs water directly from the atmosphere.) Through this standardization process, the exact concentration of the titrant is determined.

Accuracy of Reagent Mass

"Is this close enough?" You will often encounter seemingly contradictory directions such as "accurately obtain 0.8 g of sample." This simply means that the amount of sample you used should be in the neighborhood of 0.8 g (say ±10-20%). There is absolutely no point in trying to get exactly 0.8000 g; if you have a bit more (or less) sample, then it just means you'll need more (or less) titrant. However, the amount of sample you do measure out must be known to the full accuracy of the balance (i.e., to ± 0.0001 g), so make sure to write down all of the digits from the reading on the balance. It doesn't matter that you don't get exactly 0.8000 g on the balance, but it does matter (a lot) that you obtained 0.7635 g of sample.

Mass by difference

Rarely are samples placed directly on the balance pan. Instead, the sample mass is found as the difference between the mass of the sample container before and after removing the amount you need. This method for obtaining the mass is known as mass by difference and consists of the following steps.

Place the sample bottle containing excess sample on the balance pan and record the mass.

Transfer the sample from the bottle to a flask or beaker. You may pour the sample directly into the vessel by slightly rotating the bottle, or by using a clean, highly polished spatula, but in either case, your marksmanship must be good. Everything that comes out of the bottle must go into the receiving vessel. If some spills, you will need to start over to obtain an accurate mass. It is better to transfer too little than too much on the first try because more material can always be added, whereas a reverse transfer from the vessel back into the bottle is impossible.

Obtain the mass of the sample bottle again. The difference between the two readings is the mass of the sample taken out of the bottle. If you were careful not to spill any, it is also equal to the mass of sample transferred to the receiving vessel.

An alternative method involves the use of a small transfer container (beaker, weigh bottle) or a sheet of weighing paper to transfer the sample quantitatively to a larger vessel. For most solid samples, this is a fast, convenient, moderately reliable method. The difficulty, as with the indirect method, is the quantitative transfer of the solid. In general chemistry lab, we will not be using this method.

Drying Glassware

All glassware should be clean and rinsed with deionized water before use. In some cases it is essential that a container also be dried before it is used to hold a particular liquid. In other cases, the drops of water left behind from rinsing do not affect the outcome of the experiment. Therefore, you may be able to save some time and use the glassware without drying it. The manual will tell you so in the beginning. Later in the term, it will be the student's responsibility to decide if a container must be clean and dry, or just simply clean, before being used in an experiment.

Does the residual water in the glassware affect the result of the measurement? Frequently chemists need to measure a specific volume of a solution that has a specific concentration of material dissolved. Any water remaining on the inside of a wet piece of glassware will combine with the solution of interest and contribute to the volume measured. As a result, the concentration of the solution will change. Therefore, the chemist has measured a known volume of solution but changed the concentration in the process. This decreases the accuracy and precision of the experiment. Examples of glassware that must be free of any residual water before use are pipettes, burettes, any container that will hold a solution of precisely known concentration.

It is a tedious task to sufficiently dry the inside of a burette or pipette. This is why these items are primed with a small amount of the solution to be delivered instead.

Appendix G: Laboratory Safety

You should read through the DePaul University Chemical Hygiene Plan for detailed information on safety practices in the university's laboratories. Students must complete laboratory safety training before being they can be allowed into the laboratory. This training must be completed once each academic year they are enrolled in a lab course. Your laboratory instructor will provide information on how to find the necessary training and related safety quiz.