Potentiometric titration of a $HCl–H_3PO_4$ mixture

Potentiometry will be used to detect the endpoints of the titration of a mixture containing unknown amounts of hydrochloric (strong) and phosphoric (weak polyprotic) acids. Your standardized NaOH will be used as titrant. A good understanding of the experimental logic will be needed to simultaneously analyze two components of a mixture. You will use a more advanced mathematical treatment of data – using first and second derivative graphs – to aid in the detection of the endpoints. You will be graded on your accuracy. This experiment is performed in pairs.

Required Reading

D.C. Harris, *Quantitative Chemical Analysis* (6th ed., W. H. Freeman, NY, 2003) pp. 179–87, 204, 232–8, 139–40.
Pipettes, *Analytical Lab Manual*, pp. xxx–xxxii.
Volumetric Flasks, *Analytical Lab Manual*, pp. xxxii – xxxiii.
Graphical Analysis, *Analytical Lab Manual*, p. xxxvii.

PreLab Quiz Topics

In addition to being able to explain the purpose of your experiment, the general procedure steps, the use of all chemicals in this experiment and any specific hazards , your prelab quiz may include explanations of any of the following terms: strong and weak acid, polyprotic acid, pH, conjugate acids and bases, fraction of dissociation. You should be able to describe what you expect to see if you titrate a polyprotic acid with a strong base and know all relevant chemical reactions for this experiment. Describe the chemical and/or physical processes that will occur when you reach the endpoint of your titration. Explain how we can use first and second derivative analysis to determine the endpoints of your titrations. Explain how we can titrate a mixture and determine quantities of both components in a single titration.

There is a lot of data manipulation in the data analysis for this experiment — too much to do by hand, or with a calculator. We recommend you use Excel or a similar spreadsheet program. (It is difficult to use Kaleidograph to do this analysis.) **If you do not know how to use a spreadsheet, ask your TA to show you in office hours, before the day your report is due.** There are some helpful tutorials on Excel on the UT web at <http://www.utexas.edu/its/training/handouts/>.

Look up and record the three ionization steps of phosphoric acid in your notebook, along with their respective equilibrium constants. Because these equilibrium constants differ from each other by more than a factor of 10 000, there will be no more than two phosphate species present to any significant degree at any given pH. These two phosphate species will form a conjugate acid-base pair. As pH changes, protons are removed from (or added to) the phosphoric acid in a stepwise manner. The complete removal of each proton will be signaled by a distinct endpoint. We will observe two of the endpoints. These two endpoints are used to determine the phosphoric acid concentration by using the volume of standardized base

needed to get from: 1) the start to the first endpoint, 2) from the first to the second endpoint, and 3) from the start to the second endpoint.

If a second acid (in our case, the strong acid HCl) is present in addition to the phosphoric acid, it will also react with base according to its equilibrium constant. The HCl proton and the first proton of H_3PO_4 will react with base simultaneously (HCl actually reacts first, but no distinct endpoint is observed). The result is that the volume of standard base used to reach the first endpoint represents the sum of the HCl and H_3PO_4 concentrations, while the volume of base used to get from the first endpoint to the second is a measure of the H_3PO_4 concentration alone. From this information, the concentrations of both HCl and H_3PO_4 may be calculated. **This paragraph is important, if you don't understand it, read it again!**

The endpoints for this experiment cannot be easily detected using a visual (colour) indicator; however, the endpoints are clear when you measure the potential of a suitable electrode as a function of titrant volume. You will measure the pH of the solution as a function of the volume of titrant added, using a combination pH electrode consisting of a glass indicator electrode and a saturated calomel electrode. A pH meter measures *activity* (i.e., pA_{H^+}), which can be converted into the actual concentration of hydrogen ions; however, during a titration all we care about is the location of inflection points. Whether we measure pH or pA_{H^+}, the inflection points will occur at the same titrant volumes.

Chemicals and their Location

Stockroom

Unknown Hydrochloric – Phosphoric acid mixture

Balance Room

EDTA dihydrate, disodium salt

Your Drawer

Sodium hydroxide, standardized soln

Equipment and its Location

Stockroom

Burette
Magnetic stir bar
Weighing bottle
pH meter & electrodes

Above/on lab bench

Electrode holder
Magnetic stir plate

Safety Issues and Chemical Hazard Information

	Physical Hazards	*Health Hazards*
Hydrochloric acid	water-reactive, corrosive	toxic
Phosphoric acid	corrosive	none
Sodium hydroxide	water-reactive, corrosive	toxic, irritant

Both concentrated acids are highly corrosive. Be careful. Wear gloves while working with these chemicals.

Procedure

Preparation for your next experiment

1. **CH455 Water Hardness Prep (Required):** You need to make your standard EDTA solution that will be used for your experiment next week. It takes a while to dissolve, so start this preparation closer to the beginning rather than the end of today's lab session. If there is not a spare balance available, proceed with today's experiment, but remember to come back and make this solution some time today. Follow Steps 1 & 2 in the Water Hardness Procedure.
   CH456 Gravimetry Prep (Required): You need to finish the second section of the Gravimetry Procedure, in preparation for next week's experiment. Perform the *Crucible Cooling* steps before your potentiometry experiment, and the *Crucible Weighing* steps after your potentiometry experiment.
   CH456 Water Hardness Prep (Optional): Sometime in the next three weeks, you need to make your standard EDTA solution that will be used for your Water Hardness experiment. If you have spare time at the end of lab today, follow Steps 1 & 2 in the Water Hardness Procedure.

Set-up

2. Because of the limited number of pH meters, this experiment will be carried out in groups of two or three. Decide whose standardized NaOH solution you will use, yours or your partner's (choose based on volume available and reliability of the standardization). **Record the concentration of this solution**. (Your TA will let you know the correct value if your standardization was inaccurate.) Clean, rinse, and fill your burette with the NaOH. Record the initial reading of the burette to the nearest 0.02 mL.

3. Collect a pH meter from the Stockroom. Note that the electrode is stored in a solution that protects the electrode and keeps it functioning well. Do not leave the electrode exposed to air for any long periods of time, either have it in the storage solution, or in one of your experimental solutions. Whenever you change the solution the electrode is in, you should rinse the electrode well using your squeeze bottle of distilled water so that you do not cross-contaminate either the storage container or your solutions.

4. You will use beakers rather than Erlenmeyer flasks for this titration, so you can fit both the burette tip and the pH electrode into the titration container. Make sure you use a beaker that is large enough. Set up the apparatus using an empty beaker as a guide. The beaker sits on the stirplate with a stirbar inside it. Once you have solution in your beaker, you will use the electrode holder to position the electrode in the beaker so that the stir bar will not bump it and so that the electrode doesn't interfere with the titration process.

Sample Preparation

5. Obtain your unknown acid mixture from the Stockroom in a clean, dry, labeled 100 mL beaker and ask them which one you have received (it will have an identifying letter or number). Use your 25 mL

volumetric pipette to transfer 25.0 mL aliquots of your unknown solution into three clean, dry, labeled beakers. Dilute each sample with 40 mL of distilled water. No colour indicator is used for this titration.

6. Position the first beaker on the stirplate. Add the stirbar, and set the stirrer so it gently mixes the solution. You do not want a *whirlpool o' death*. Position the electrode and burette over the beaker.

Potentiometric Titration

7. This titration differs from previous experiments — in this case, you continue to add titrant **past** the endpoint. The endpoint position is determined later from your data. The pH of your solution will vary rapidly close to each endpoint, and be fairly constant in between endpoints. Titrate your first unknown, recording the burette reading and the pH after each addition. This titration should be fairly quick and approximate. You will not collect a lot of data, but you get an idea of the position of the two endpoints.

8. Now that you know the approximate positions of the endpoints, titrate your other two unknown samples. To get a good value for your endpoints you must obtain a **large number** of data points near the endpoints of the titration. Start titrating using relatively large aliquots of base (1–2 mL), recording pH and burette reading after each addition. As the pH starts to change, add enough titrant in a single step to change the pH by 0.1 units. Stop and wait for the stir bar to mix the solution well, before recording each data point. Continue titrating in this way, until you have passed both endpoints and a negligible pH change is observed for each additional mL of titrant added.

9. **CH456 Gravimetry Prep (Required):** Don't forget to perform the *Crucible Weighing* steps.

Shutdown procedures

IMPORTANT NOTE: Save your NaOH solution in case you find that something is wrong with your results from today's experiment.

10. Make sure you have recorded information for the sample you studied, in this case, the letter or number identifying your unknown.

11. Put all waste in the appropriate waste containers. Clean and dry all glassware. Clear up your work area. Return items to the Stockroom.

Waste Disposal

Waste Chemicals	Waste Container	Location
Unused HCl, dilute or concentrated	Acid	Waste cabinet
Unused NaOH, dilute or concentrated	Base	Waste cabinet
Excess unknown solution	Acid	Waste cabinet
All solutions after titration	Potentiometric Neutral	Waste cabinet

Data Analysis

Endpoint determination

1. Tabulate the data for each titration run in a spreadsheet. (See the sample spreadsheet shown below.) The first two columns will be the burette reading and the pH at each data point. The third column is the total volume of base added up to that point, found by subtracting the initial burette reading from the reading at each data point. Correct for cases where you had to refill your burette.

Sample Excel spreadsheet

	A	B	C	D	E	F	G
1	Burette	pH	Total Vol.	$\frac{DpH}{DVol}$	Average	$\frac{D^2pH}{DVol^2}$	Avg. avg.
2	reading		NaOH added		volume		volume
3	20.75	1.89	0				
4	25.35	2.01	=A4-A3	$=\frac{(B4-B3)}{(C4-C3)}$	$=\frac{(C4+C3)}{2}$		
5	29.12	2.21	=A5-A3	$=\frac{(B5-B4)}{(C5-C4)}$	$=\frac{(C5+C4)}{2}$	$=\frac{(D5-D4)}{(E5-E4)}$	$=\frac{(E5+E4)}{2}$

2. Make a single graph showing all three titrations, plotting the pH *vs.* Total volume added for each titration. Hide all data points and show just the line joining the points (see the ***Graphical Analysis*** section of this manual). The two endpoints for your titration occur where the pH is changing rapidly. Estimate the rough positions of the two endpoints as the midpoint of each vertical section of the graph (~9.8 mL NaOH in the Figure part *a*). **Label the endpoints** on your graph. If it is apparent from your titration plots that the first titration was too approximate and does not detect the endpoints as clearly, you may disregard the data from this run for the rest of this analysis. Determine a smaller volume range that expands the area of interest of the titration; i.e., includes both endpoints. Plot all graphs for the rest of your analysis over this shorter volume range, **using the same x-axis (volume) scale** for each graph so that they can be directly compared to each other.

3. Each endpoint falls at the point where the slope of the titration curve is the greatest. Mathematically, this can be described as the point where the derivative ($^{dpH}/_{dV}$) is maximized. Make a new column in your spreadsheet and calculate the first derivative of your data by dividing the change in pH between two consecutive readings, by the change in added volume between the two consecutive readings (giving the change of pH per mL of added base); e.g.,

Volume added (mL)	pH
9.01	3.18
9.12	3.24

$$\frac{dpH}{dV} = \frac{3.24 - 3.18}{9.12 - 9.01} = \frac{0.06}{0.11} = 0.545\ mL^{-1}$$

4. Make a new column in your spreadsheet and calculate an average volume to go with each derivative point, by finding the average of each pair of consecutive readings; e.g., for the data above

$$V_{av} = \frac{(9.01 + 9.12)}{2} = 9.065$$

5. Plot graphs of $^{dpH}/_{dV}$ *vs.* V_{av} for each titration run, hiding all data points and showing just the line joining the points, to give you a first derivative curve for each titration. The first derivative of a curve shows the slope of the curve. The slope of your titration curve should peak at each of the endpoints (~9.78 mL NaOH in the Figure part *b*). Determine the two endpoints for each titration from your first derivative curves. Label the endpoints on your graphs.

6. An alternative mathematical way to find the endpoints is to investigate the second derivative ($^{d^2pH}/_{dV^2}$), the rate of change for the slope of the curve. Make a new column in your spreadsheet and calculate $^{d^2pH}/_{dV^2}$ by dividing the change in $^{dpH}/_{dV}$ between two consecutive readings, by the change in the average added volume between the two consecutive readings; e.g.,

Volume added (mL)	pH	Average Volume (mL)	$\frac{dpH}{dV}$ (ml^{-1})
9.01	3.18	9.07	0.545
9.12	3.24	9.23	0.864
9.34	3.43		

$$\frac{d^2pH}{dV^2} = \frac{0.864 - 0.545}{9.23 - 9.07} = \frac{.319}{0.16} = 1.99\ mL^{-2}$$

7. Make a new spreadsheet column and calculate an "average average" volume to go with each second derivative point, by finding the average of each pair of consecutive average volumes; e.g.:

$$V_{avav} = \frac{(9.07 + 9.23)}{2} = 9.15$$

8. Plot graphs of $^{d^2pH}/_{dV^2}$ *vs.* V_{avav} for each titration run, hiding all data points and showing just the line joining the points, to give you a second derivative curve for each titration. The second derivative of a curve shows the rate of change of the slope of a curve, which should be equal to zero whenever the first derivative is at a maximum (or a minimum). At each endpoint, the second derivative should cross the x-axis, i.e., equal zero (~9.77 mL NaOH in the Figure part *c*). The second derivative graph should give the most accurate determination of each endpoint. Determine the two endpoints for each titration from your second derivative curves. Label the endpoints on your graphs. (A good titration will have only a single crossing of the x-axis at each endpoint. If you have multiple crossings, use your best judgment to determine what value to choose.)

9. Use your graphs to determine your end point volumes as precisely as possible and explain how you chose them.

Concentration determination

10. Go back and reread the introduction of this lab, to make sure you understand what is going on. The first endpoint is due to NaOH neutralizing both acids, but the second endpoint is due only to the neutralization of the phosphoric acid. (Note that both acids react 1:1 with NaOH.) For each titration run, use the volume of NaOH needed to titrate from the first endpoint to the second endpoint, to calculate the number of moles of NaOH that reacted with phosophoric acid at the second endpoint, and hence the number of moles of phosphoric acid in your unknown sample.

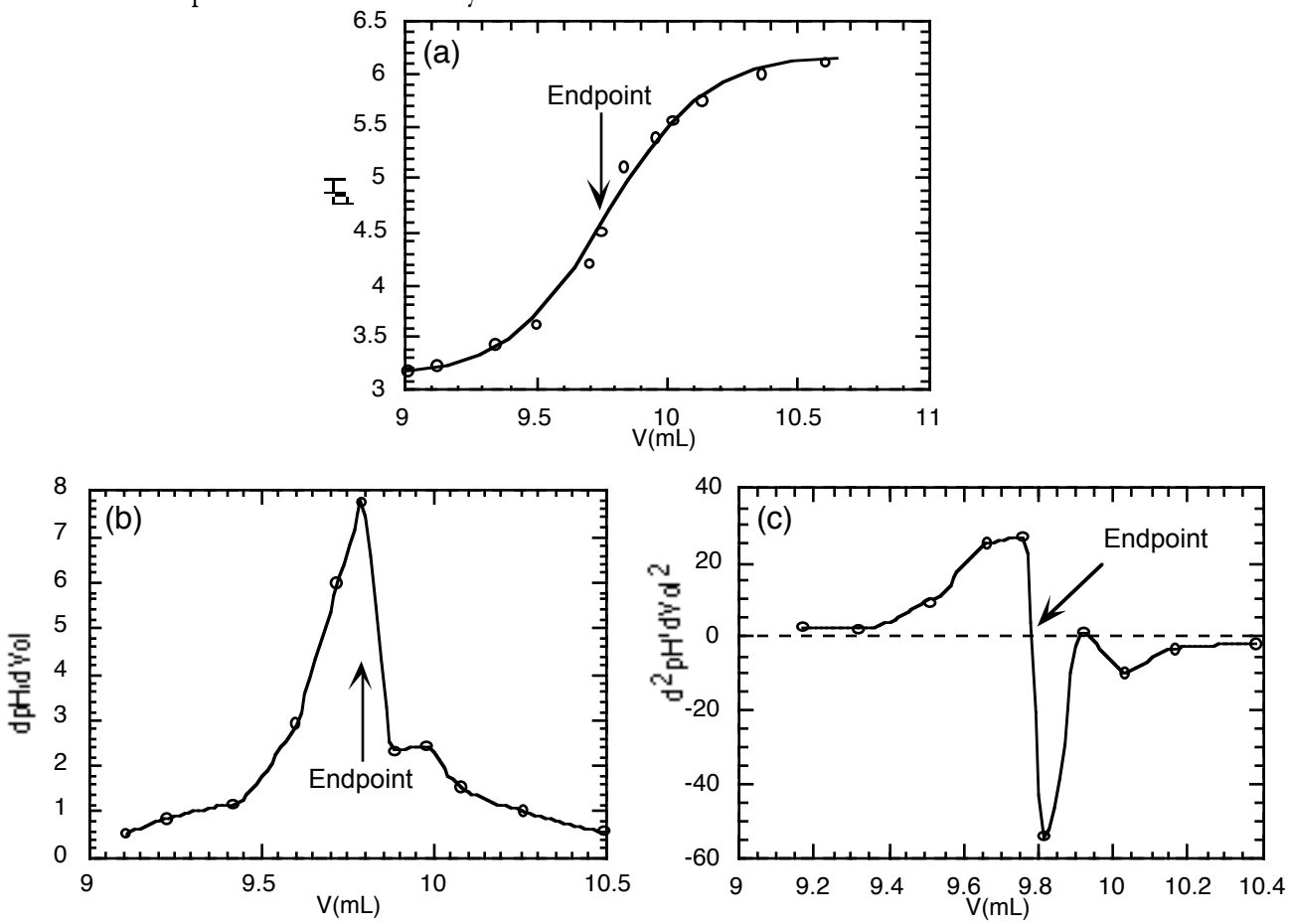
11. For each titration run, use the volume of NaOH needed to titrate to the first endpoint to calculate the number of moles of NaOH that reacted with both unknown acids at the first endpoint, and hence the total number of moles of acid in your unknown sample.

12. The amount of phosphoric acid is the same at both endpoints; i.e., the number of moles of phosphoric acid in your unknown found from the second endpoint will be equal to the number of moles of phosphoric acid in your unknown at the first endpoint. Thus, determine the number of moles of hydrochloric acid by subtracting the number of moles of phosphoric acid found from the second endpoint from the total number of moles of acid found from the first endpoint.

13. Knowing the volume of your unknown aliquot, and the number of moles of each of the two acids in your unknown aliquot, calculate the molarity of the two acids, HCl and H_3PO_4, in your unknown sample.

Discussion Questions

1. We didn't calibrate the pH meters before doing this experiment. Why doesn't this matter?
2. HCl has one proton and H_3PO_4 has three. We see only two endpoints. Which endpoints do we see and why don't we see four endpoints?
3. Explain clearly why we used a potentiometric titration for this analysis. Could we have used an indicator instead of a pH meter for this analysis?



Sample potentiometric titration data analysis: (a) raw data, (b) first derivative curve, and (c) second derivative curve.

From "Introduction to the use of Analytical Equipment"

Pipettes

Pipettes are used to transfer measured volumes of liquids between containers. You will be using TD pipettes; *to deliver* means that the pipette filled with solution will deliver the rated volume, with only the aid of gravity, not using a bulb to blow out the contents of the pipette. There are many types of pipettes, each designed for a specific function and mode of usage, three of which are listed below:

Transfer or Volumetric pipettes

These are used to transfer an accurately known volume of liquid from one container to another. They are shaped like a piece of tubing with a bulb and have one fiducial mark. If the bulb is centered, it is commonly called a *volumetric* pipette, while if the bulb is close to the delivery tip, it is called an *Ostwald-Folin* pipette. These are the **most accurate pipettes available** and range from 1 – 250 mL.

Measuring or Graduated pipettes

These pipettes are simply a piece of uniform diameter tubing drawn out to a delivery tip with graduations similar to those found on a burette. If the graduations extend all the way to the tip, they are called *serological* pipettes; if the graduations stop before the constriction for the tip, they are called *Mohr* pipettes. These are less accurate than transfer pipettes, but more accurate than graduated cylinders. The volume range of these pipettes is generally 0.1 – 25 mL.

Automatic Pipettes

These pipettes are equipped with a plunger that controls the delivery of fluid by the positive displacement of a plunger, and are equipped with disposable plastic tips. In some varieties, the delivery volume is variable, and controlled by a dial on the barrel of the pipette. The primary benefit of these pipettes is that they allow rapid, repetitive delivery of sample or reagent when multiple analyses are required. The volume of these pipettes range from 0.02 – 25 mL.

Using a volumetric pipette

For the best analytical results, pipettes should be used in a uniform manner. By always holding the pipette the same way, allowing the same amount of time for the pipette to drain, etc., errors in the volume will usually be minimized. The correct procedure for their use is as follows:

1. Clean your pipette and rinse with distilled water. Check the tip and return to the stockroom if damaged.
2. Rinse the inside of the pipette with the solution to be transferred to avoid dilution.
3. Use a pipette bulb to fill the pipette by suction to about 2 cm above the fiducial mark. If the bulb has filled with air, but your pipette is not yet full, remove the bulb from the pipette, replacing it with the tip of your forefinger. Squeeze the air out of the bulb and replace on the top of the pipette to continue filling.
4. Remove the pipette bulb, replacing it with the tip of your forefinger.

5. Using the thumb and other fingers, rotate the barrel of the pipette. Using your forefinger to control the flow of liquid out of the pipette, carefully lower the meniscus to the fiducial mark.

6. Touch off drops hanging from the pipette tip and wipe excess fluid from the outside of the pipette.

7. Move your receiving container close to your initial container. Transfer the pipette tip from one container to the other and allow the liquid to flow out of the pipette into the receiving container.

8. While draining, hold the pipette vertically. When flow stops, hold the tip against the inner wall of the container for a further 10 seconds to allow the final drops to exit.

9. A small volume of solution will be left in the pipette tip. This is normal.
   (a) if you are using a TD pipette (the only sort we have in our teaching labs), its volume is calibrated to take this into account; thus, this small volume should not be blown out; however,
   (b) if you were using a TC pipette, its volume is calibrated to include this small volume, and so the last bit of solution must be blown out from the tip.

From "Introduction to the use of Analytical Equipment"

Volumetric Flasks

Volumetric flasks are used to prepare exact volumes of primary standard solutions (e.g., EDTA) or exact dilutions of samples (e.g., unknowns). They are fragile and expensive. Do not heat solutions in a volumetric flask; it will not return to its original calibrated volume on cooling. Volumetric flasks are calibrated TC or *to contain* the stated volume when filled so that the bottom of the liquid meniscus is level with the fiducial mark on the neck of the flask. Since all the liquid cannot be removed from them (some always sticks to the sides), **they are not** suitable for "measuring out" volumes of liquids. There is **considerable** error if they are used in a *to deliver* manner.

When dissolving a solid in a volumetric flask, do not fill it to the mark until all the solid has dissolved. Solvation often results in a change of volume of the solution and this should be allowed to occur before the final volume adjustment is made. It is much easier to mix the contents of a flask before it has been filled to the mark. To mix the solution well, you should ensure the stopper is well seated before repeatedly inverting and shaking the flask.

When filling a volumetric flask, there is no margin for error. The typical operation is to add the substance to be diluted, mix well, fill the flask to the bottom of the neck with diluent and then add diluent slowly, using a Pasteur pipette, until the bottom of the meniscus reaches the mark. **Read the meniscus at eye level to avoid parallax errors.** The volumetric flask must be filled exactly to the mark, not just below or above it. If too much diluent is added, the process should be redone using more care. You should not simply remove the excess liquid above the fiducial mark.

From “Graphical Analysis”

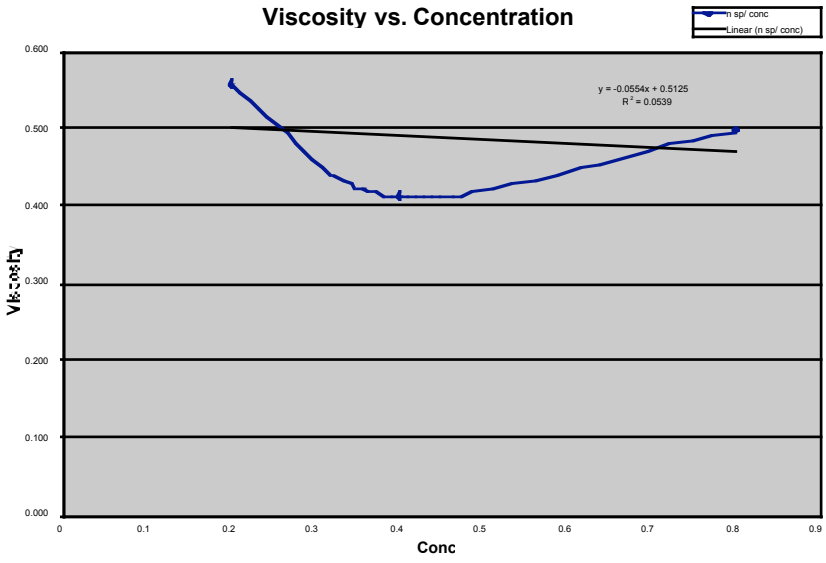
Formatting

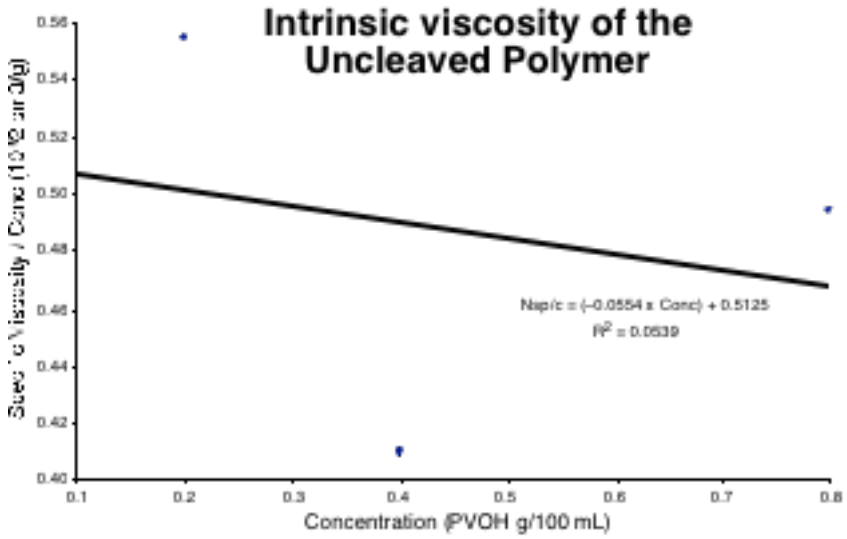
All graphs must be computer generated. All graphs must be of a suitable size, scale, and axes choice, so that the relevant features of the data are easily seen. Show units, have a title, label both axes, explain abbreviations, and have a legend identifying any symbols used if the graph shows more than one dataset. **Do not** have any shading in the graph background or gridlines (the Excel defaults). The title of your graph should be more descriptive than “Y” vs. “X”.

Some experiments use a computer to collect your experimental data. A plot of this data usually results in **a spectrum, voltammogram, chromatogram, cooling curve, or something similar whose shape is important.** In this case use the computer plot preferences to hide all data points, and just show the line. In Kaleidograph, use the Line Plot option; in Excel use the XY (Scatter) option and pick the appropriate chart sub-type (Do not use the Excel Line option, it will not allow you to specify the x axis).

Some experiments involve collecting a set of data that you will compare to a mathematical equation used to describe the phenomenon you were investigating. Data analysis of these experiments will involve plotting your data, finding the line of best fit, and deriving quantities from the slope and intercept of that line. **If your plot is a series of points that you hope show some relationship, such as a linear calibration curve**, then use the computer plot preferences to show the data points, and the line of best-fit. Do not draw any lines that “join the dots” — this is not good science. In Kaleidagraph, use the Scatter Plot option; in Excel use the XY (Scatter) option and pick the appropriate chart sub-type. Use the *Series* tab to *Add* a plot and select the appropriate cells for the X and Y axes.

Here are two examples of plots of the same dataset. The first was created using the default settings of Excel.





To make a more appropriate graph for a scientific report, the following changes were made to create the second plot: the grey background, grid lines, and legend removed; both axis ranges reduced so that data fills the entire graph and there isn't wasted "white space"; the fonts sizes were increased to be more legible; a more informative title and axis labels were added; units were added to the axis labels and their significant figures were fixed; the "join-the-dots" line was removed; the equation of the line of best fit was edited to include the names of the variables.

From "Determination of Water Hardness using Complexometric titration"

Chemicals and their Location

Balance Room

EDTA dihydrate, disodium salt

Equipment and its Location

Stockroom

One 250 mL volumetric flask, acid washed

Safety Issues and Chemical Hazard Information

	Physical Hazards	*Health Hazards*
EDTA dihydrate, disodium salt	None	irritant

Procedure

Important Note: Any metal ions present in your glassware will react with EDTA and lead to incorrect results. All glassware coming in contact with your EDTA solution has been cleaned for you by the Stockroom by rinsing with 50% nitric acid followed by a distilled water rinse.

At least one week before Lab

Standard EDTA Solution

1. The disodium salt of EDTA dihydrate $Na_2H_2Y{\cdot}2H_2O$ (the free acid is practically insoluble) is a primary standard. It is predried and kept in desiccators in the balance room. To minimize contamination, use the spatula provided in the desiccator. Using a clean dry weighing bottle, weigh accurately, **by difference**, ~0.25 g of disodium EDTA, into an acid-washed 250 mL volumetric flask. Use a clean dry funnel to ensure all of the accurately weighed solid is quantitatively transferred into the flask. Use a small amount of distilled water to carefully rinse the funnel to transfer any solid adhering to the funnel into the flask. Add ~200 mL of distilled water and swirl periodically until the EDTA has dissolved.
2. After the EDTA has dissolved, dilute to the mark and shake thoroughly. Rinse your clean polyethylene 500 mL bottle with three **small** portions of your EDTA solution, swirling to ensure the entire inner surface of the bottle has been rinsed, (to remove metals from the bottle's inner surface), and transfer the rest of your EDTA solution to the bottle for storage. (Polyethylene is preferable to glass for storage because EDTA solutions leach metal ions from glass containers, resulting in a change in the concentration of free EDTA.)