EXPERIMENT 6: POTENTIOMETRIC TITRATIONS OF POLYPROTIC WEAK ACIDS

OBJECTIVES

- Use a pH probe to measure the pH during the titration of a weak acid.
- Confirm the identity of an acid through titration data
- Determine the molar mass of a known weak acid from titration data.
- Determine the K_a value(s) for a weak acid from titration data.
- Understand the reactions and the composition of a solution during a titration.

In this experiment, you will receive the following:

1. *A diprotic acid with equilibrium constant differing by at least four orders of magnitude.*
2. *A diprotic acid with equilibrium constants differing by much less than four orders of magnitude.*

INTRODUCTION (REPEATED FROM THE MONOPROTIC WEAK ACID LAB 16)

If we examine a solution of hydrochloric acid, we would find that the acid is completely dissociated, and is therefore a strong acid. On the other hand, careful observation of a solution of acetic acid shows that most of the acetic acid molecules do not dissociate and the acid is weak. Knowing the equilibrium constant and concentration of an acid is invaluable in determining the amount of dissociation observed. Similar observations can be made for bases.

For the titration of a weak acid, the initial pH is determined by the acid's concentration and the amount it dissociates. Pre-equivalence point pH values are determined from the quantities of undissociated weak acid and conjugate base left after the addition of a given volume of the standard base; at these volumes we have a buffer solution. At the equivalence point, the weak acid has been completely converted to its weak conjugate base, and the concentration and amount of dissociation of this base determines the pH. After the equivalence point, the pH is determined by the excess strong base that is added.

NOTE: In a solution containing several acids, the stronger will control the pH. A similar statement made be made about solutions of bases.

With this knowledge, one can determine the pH during a titration as a function of volume of titrant added; a plot of pH versus titrant added is called a titration curve. Understanding the shape of the titration curve assists in identifying the acid, selecting a visual indicator, quantitating the acid and even determining if a qualitative or quantitative analysis of the acid is even possible.

We mostly speak of the relative acidities of acids and bases based upon their pK_a which is defined by the equation: $pK_a = -\log K_a°$. Here $K_a°$ is the thermodynamic acid dissociation constant for the reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

In the following derivation, a_{A^-} , $[A^-]$, and γ_{A^-} represent, respectively, the activity, the molar concentration, and the activity coefficient of the conjugate base, A^-. Each species in the equilibrium will have similar quantities.

The thermodynamic acid dissociation constant can be written for this dissociation as:

$$K_a{}^o = \frac{a_{A^-} a_{H_3O^+}}{a_{HA}}$$

Since the activity of each species is dependent on its molar concentration and activity coefficient, e.g. $a_{A^-} = \gamma_{A^-}[A^-]$, it can then be shown that:

$$K_a{}^o = \frac{\gamma_{A^-}[A^-]\gamma_{H_3O^+}[H_3O^+]}{\gamma_{HA}[HA]} = \frac{\gamma_{A^-} \cdot \gamma_{H_3O^+}}{\gamma_{HA}} \cdot \frac{[A^-][H_3O^+]}{[HA]}$$

Since $pK_a° \equiv - \log K_a°$ we can write:

$$pK_a{}^o = -\left[\log(a_{A^-}) + \log\left(a_{H_3O^+}\right) - \log\left(a_{HA}\right)\right]$$

By definition we know that $pH = -\log\left(a_{A^-}\right)$

$$pK_a{}^o = pH + \log\left(a_{HA}\right) - \log(a_{A^-})$$

Rearranging using logarithm rules we get:

$$pK_a{}^o = pH - \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

After expanding the activity terms and collecting terms:

$$pK_a{}^o = pH - \log\left(\frac{[A^-]}{[HA]} \cdot \frac{\gamma_{A^-}}{\gamma_{HA}}\right)$$

We can now assume that $\frac{\gamma_{A^-}}{\gamma_{HA}} \cong 1$ and rearranging we get:

$$pH = pK_a{}^o + \log\left(\frac{[A^-]}{[HA]}\right)$$

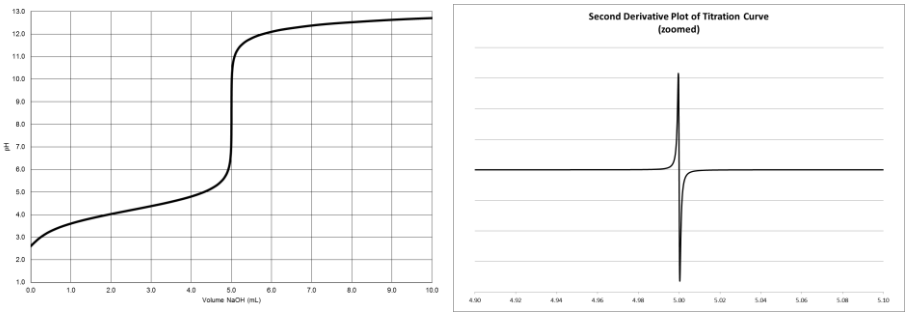
This is the famous Henderson-Hasselbalch equation. This equation can be applied to most (but not all!) buffer regions for titrations curves of 1) monoprotic acids, 2) polyprotic acids, 3) monobasic bases and 4) polybasic bases. A solution is a buffer is has the greatest buffer capacity when conjugate pairs are of similar concentrations. When the concentrations of conjugates are equal, the pH should equal the $pK_a°$. This value can be determined from the titration curve by taking the pH half-way to the endpoint or break. This, of course, also indicates that any equilibrium constant derived from the titration data will deviate from the listed values because these standard reference values represent thermodynamic constants at an ionic strength of zero. It is fraught with other assumptions as well, so be mindful of this.

TYPE OF ACIDS

The discussion now leads into some specifics relative to the identification of an acid from its titration data. Use this information to confirm the identity of your samples. You will need to prove the identity using multiple pieces of data, not just one.

A monoprotic acid:

A monoprotic acid titration curve is of sigmoidal shape and shows one endpoint or break. The endpoint volume for the titration is determined at the inflection point in the curve. The inflection point can be found by taking the second derivative of the titration curve $d^2(\Delta pH/\Delta V)$. Let's take the example of 10.0 mL of 0.1000 F benzoic acid, $K_a° = 6.3x10^{-5}$, being titrated with 0.2000 F NaOH:



The endpoint volume for this data is at 5.0 mL. You should confirm this by calculating it yourself!. Note that at the inflection point the derivative changes sign. If you take the highest point and the lowest point at the inflection point, you can find the x-value where the second derivative crosses the x-axis. This is done via linear interpolation. This is the endpoint. Given the mass of the acid and the volume of NaOH required to titrate it (the endpoint), you can calculate the acid's molar mass. The $pK_a°$ can also be extracted from the curve by realizing that at the 50% titrated point, 2.5 mL, the concentration of undissociated acid is equal to the concentration of the conjugate base. Assuming the ratio of activity coefficients is 1, we can see that the pH at this point will be equal to the $pK_a°$.

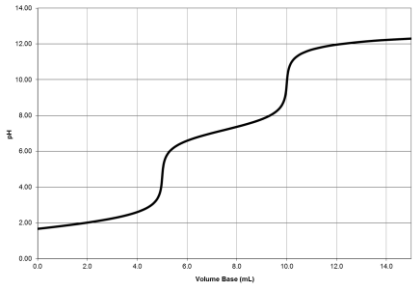
$$pH_{50\%} = pK_a{}^o + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a{}^o + \log(1) = pK_a{}^o$$

In this case it's about 4.2 which is close to the correct value.

Another characteristic of a monoprotic acid that distinguishes it between a diprotic acid with two distinct breaks is that the pH difference between 75% and 25% titrated is about 0.954 pH units and no more. The derivation of this can be found in the Appendix I.

A Diprotic Acid with two distinct breaks:

A diprotic acid titration curve also is of a sigmoidal shape, but can show one or two endpoints or breaks. Again, the endpoints for the titration are found at the inflection point(s) in the curve. Let's take the example of 10.0 mL of 0.0500 F sulfurous acid, $K_{a1}° = 1.7x10^{-2}$ and $K_{a2}° = 6.4x10^{-8}$, being titrated with 0.1000 F NaOH:



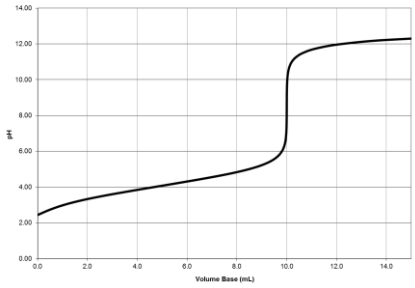
It is clear that the two protons from the acid are being titrated: the strongest from 0 to 5.0 mL (buffer region #1) and the second from 5.0 to 10.0 mL (buffer region #2). The endpoints are V_{e1} = 5.0 ml and V_{e2} = 10.0 mL, and it is noteworthy that V_{e2} is twice V_{e1}. This can only occur with a diprotic acid OR an equimolar mixture of monoprotic acids. It is obvious in this titration that the pH difference between 75% and 25% titrated for the titration of ***both*** protons is much greater than 0.954 (see monoprotic acid curve). However, if you look at 25% and 75% titrated for EACH proton the difference will be about 0.954 pH units (for instance, when titrated the second proton the difference in pH between 8.25 mL and 6.25 mL is ~ 0.954). This occurs in the buffer regions where two conjugates are present indicating that the $K_a°$ values of the two protons must differ by at least 10^3 to 10^4.

Either of the endpoint volumes can be used for quantitation, e.g. to find the mass of the acid present or its molar mass. Usually the clearest/sharpest endpoint is used and this can vary from acid to acid (see next example!), and depends on the relative $K_a°$ values. IMPORTANT: You have to consider the stoichiometry of the reaction based on the endpoint you select when you do these calculations.

The $pK_a°$ values can also be extracted from the curve by realizing that at the 50% titrated point in each buffer reaction (2.5 mL and 7.5 mL in this case), the concentration of conjugates making up the buffer are equal. Assuming the ratio of activity coefficients is 1, we can see that the pH at this point will be equal to the $pK_a°$ as with a monoprotic acid.

A diprotic acid with one apparent break:

As the $K_a°$ values of a diprotic acid approach each other you are less likely to see two distinct breaks. This can also happen if the second pK_a° approaches 10 or larger. This make identification much harder. Let's take the example of 10.0 mL of 0.0500 F isophtalic acid, $K_{a1}° = 2.8x10^{-4}$ and $K_{a2}° = 2.5x10^{-5}$, being titrated with 0.1000 F NaOH:



This is a diprotic acid, but it only has one endpoint at 10.0 mL. This can be easily mistaken for a monoprotic acid, but the molar mass will be incorrect. Plus, the difference between 75% and 25% titrated is much larger than 0.954. Nailing down the individual $pK_a°$ values is a challenge. How will you get any equilibrium constant data out of this titration curve? This behavior occurs when the acid's $pK_a°$s differ by less than 4 (4 orders of magnitude). The closer they are, the less distinct the first endpoint will be resulting in a curve with one endpoint or break.

Other diprotic variations can be observed. The shape of the curve will depend on the difference in the $pK_a°$ values and their values. It is difficult to see breaks that occur at very high pH values because the solution is becoming dilute and more error is introduced into measuring the pH by the glass electrode at these values.

You can take what you have learned with monoproticc and diprotic acids and apply it a titration analysis in the nest lab.

The astute student should also realize that the salt made from the conjugate of a monoprotic acid or a diprotic acid can also be titrated. Example include sodium benzoate, sodium sulfite, sodium hydrogen sulfite and sodium hydrogen carbonate. Note that the latter two are amphiprotic and can be titrated with an acid or a base!

ACID INDICATORS:

We will also add some indicators to the titrations you do and try to experimentally select the best visual indicator for each situation. Visual indicators are selected based on the pH at the endpoint of interest. It is usually best if the pH at the endpoint is within the color change range for the indicator.

PRE-LAB ASSIGNMENT:

As you make observations, enter them in your lab notebook.

Go to the lab eLC site and download the EXCEL file 'Diprotic Acid Titration Curve.' Open the file in EXCEL. You are presented with a titration curve for a monoprotic acid under the following initial conditions:

Acid Concentration:	0.0100 F	Acid Volume:	30.00 mL	$K_{a1}°$:	1.00E-2
				$K_{a2}°$:	1.00E-6
Base Concentration:	0.0100 F				

Ask yourself these questions:

1. Does the shape of the curve make sense for the diprotic acid condition shown? Explain.

2. From the graph what are the equivalence* point volumes? We have the equivalence point for the titration of the 1st proton, V_1, and overall equivalence point volume for the titration of both the 1st and 2nd protons, V_2. Not that the difference between these volumes equals V_1! Not that Do the calculation to make sure you understand.

   * We use equivalence point instead of endpoint because this curve is calculated in theory.

3. What species are in the solution at 0%, 50%, 100% and 110% titrated. Possible species include H_2A, HA^-, A^{2-}, H_3O^+, and OH^- (ignore water and other spectator ions).

4. Decrease the $K_{a2}°$ incrementally by an order of magnitude, i.e from 0.1 to 0.01. Does the overall shape of the curve change? Does the quality of each equivalence point (inflection point) break change? Explain.

5. Set the $K_a°$ values back to the starting values and change the acid concentration and observe. Then reset the acid concentration and change the base concentration and observe.

6. Does changing the volume of acid have a similar effect to any of the other variables?

Write any observations in your lab notebook.

PROCEDURE

- Attend a demonstration of the apparatus by your TA.

1. You will receive two samples: the first will be maleic acid and the second tartaric acid. Using the molar mass of each acid and the concentration of your standard NaOH solution, calculate the mass of each acid needed for **each** proton of the acid to react with ~10 mL of your standard base (i.e. the second endpoint should be 20 mL). Before you proceed to the next step, please show the calculations for both acids to your TA.

2. Using the information from the previous step, weigh 3 samples of maleic acid and 3 samples of tartaric acid into separate 250 mL beakers.

3. Dissolve the samples in ~30 mL of water. You have three different indicators, and each one should be tested on BOTH acids. You can add the indicators at this time. Make sure you account for the type of indicator in each flask.

4. While the acid samples dissolve, follow the steps in given in Appendix II to use Microlab pH probe and drop counter in your experiment.

5. Adjust a magnetic stirrer so that the stir bar does not hit the pH electrode immersed in the solution.

6. Start the experiment and write down the color of solution during the titration and note the volume of NaOH and pH of the solution.

7. You may stop your titration once you observe the pH plateauing above pH 10 or so. Ask your TA if you are unsure. Inspect your graph to make sure it is of good quality.

8. Save your data in a CSV format or text format from the MicroLab software.

9. On the eLC lab site download and then run the EXCEL file 'Decimate Titration Data for CurtiPlot'.

10. Load the CSV or text file you saved from the MicroLab software into EXCEL as well.

11. Follow the directions given in the Decimate Titration Data for CurtiPlot EXCEL file.

12. Once you have decimated your data, load CurtiPlot in EXCEL (when you load the file you may have to click the yellow Enable Editing button and then the Enable Content button).

13. Click on the Evaluation tab. Press the clear button at the top left of the sheet. Copy your decimated Volume and pH data into the Volume and pH columns on the Evaluation sheet in CurtiPlot.

14. Click the process button. If all endpoints do not show up, change the Detector Threshold down by 0.1 increments until you see all endpoints.

15. After processing, you are given the Volumes at each endpoint and the first and second derivative data (on the right of the sheet). You can copy this data and make a plot for yourself.

16. Repeat for all samples.

CALCULATIONS

To find the endpoint for each titration you will need to decimate the csv file from MicroLab. An EXCEL file called 'Decimate Titration data for Curtiplot1' is provided this purpose; it can be found under content in the 'Calculations/Titration Curve Simulations' folder on the lab eLC website. Directions on how to decimate are included in the EXCEL file.

When you have the data decimated for each titration, download the EXCEL file Curtiplot (on eLC in Content/Titration Curve Simulations). Run this program. You may have to enable macros.

Select the 'Evaluation' data sheet from the lower tab. The top of the sheet should say "Evaluation of Real and Simulated Titration Data by Derivatives and Interpolation." On the left-hand side of the sheet, look for the columns named Volume and pH. Delete any data in these first two columns starting at row 6 by clicking on the 'Clear' button or manual deleting the data. For one of your titration curves, copy the decimated volume and pH data into the Volume and pH columns of the Evaluation sheet.

Click on the "Process Smooth, interpolate and find inflections" button. Look at the Inflection auto-finder on the right side. You will see the volumes for each of your inflection points. You can also see the calculated and interpolated first and second derivative plot of the titration curve.

Use these volumes and your standard base concentration to find the molar mass of your acid. You can enter all of this data in the provided EXCEL file "Diprotic Acids Data Sheet." There will be one of these for each acid you analyzed. Repeat this for the other two replications of the acid, and use the EXCEL data sheet to help calculate the statistics. Raw data for each titration should be included in one of the sheets in this file.

You will also need to look at the titration curves and deduce the pK_a value of your acid.

You will repeat all of this for your second acid (use a fresh copy of the EXCEL file).

Don't forget to include data on from your indicator results and indicate which one would be best to use for that acid.

Use the instructions in Appendix III to properly plot your titration curves for presentation in the data sheet.

QUESTIONS

There are no questions for this experiment.

APPENDIX I

The theoretical curve for the titration of a weak acid with a strong base can be calculated from the equation shown below. This equation involves assumptions, which tend to break down near the beginning of the titration and near the equivalence point.

$$\left[H^+\right] = \frac{(C_a V_a - C_b V_b) K_a}{C_b V_b} \tag{18}$$

At 25 % titrated, $(C_aV_a - C_bV_b) = 3\ C_bV_b$, and we get

$$\left[H^+\right]_{25\%} = 3\,K_a \tag{19}$$

At 75 % titrated, $(C_aV_a - C_bV_b) = C_bV_b/3$, and we get

$$\left[H^+\right]_{75\%} = \frac{1}{3} K_a \tag{20}$$

Converting eq.19 and 20 to logarithms

$$pH_{25\%} = -\log 3 - \log K_a \tag{21}$$

$$pH_{75\%} = -\log(1/3) - \log K_a \tag{22}$$

Subtracting eq.21 from eq.22

$$pH = pH_{75\%} - pH_{25\%} = -\log(1/3) + \log 3 = 2 \log 3 = 0.954 \tag{23}$$

APPENDIX II

Instructions for Recording a Titration Curve with a MicroLab pH electrode manually

NOTE: The TA will show you how to calibrate your drop counter.

1) Prepare pH probe, 3 - 5 mL beakers, a medium sized beaker and a squirt bottle filled with DI water.
2) Fill the first beaker with pH 4 buffer (red), the second with pH 7 buffer (yellow), and the last one with pH 10 buffer (blue).
3) Make sure that the MicroLab box is powered on.
4) Open “MicroLab”, you will be presented with different types of experiments.
5) The default option will be “MicroLab Experiments”, press OK.

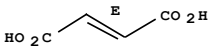
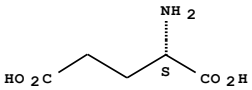
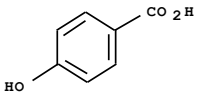
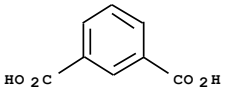
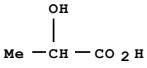
6) Press “Add Sensor” around the middle-left of your screen.
7) From the drop-down menu, choose counter.
8) Click on the red box overlaid on the image of the front of the box.
9) Click on the “Set counter options>” button. At the new dialog box select the “Continually increasing count minus 1 (use for titrations)” button.
10) Press “Finish.”
11) Press “Add Sensor.”
12) From the drop-down menu choose pH / D.O.
13) Plug in your pH probe into the BNC connection that is highlighted with red box.
14) Click on the red box.
15) Select pH from the radio buttons.
16) Press “Calibrate Sensor.”
17) Press “Perform Calibration.”
18) Submerge your pH probe into one of the pH buffers. Remember Red = pH 4, Yellow = pH 7 and Blue = pH 10.
19) Press “Add Calibration Point” on upper-left of the menu.
20) When the red bar under “Sensor History” stabilizes, write down the pH of your buffer into the “Actual Value” and press “OK”. Watch out for spikes in the data. Don’t press “OK” when it spikes!
21) Repeat procedure using the other two buffers.
22) You can right click on a data point to remove it.
23) Choose “First Order (Linear)” on the middle-left of the menu, confirm the validity of the calibration by checking the coefficient of variation value, R^2. Press “Accept and Save This Calibration”.
24) Save your calibration file on the desktop.
25) Press “Finish”.
    DROP COUNTER CALIBRATION
26) You will now calibrate your drop counter. Set up the drop counter and reservoir as indicated by your TA. Fill the reservoir with distilled water.
27) Weigh an empty dry beaker.
28) Drop about 100 drops through the drop counter. Get the exact number from the starting and ending count on the screen.
29) Weigh the beaker (no fingers on it!) and find the volume of water dispensed. Then calculate the volume (in mL) per drop.
    END OF DROP COUNTER CALIBRATION
30) Click “Add Formula.”
31) Click on the ‘Counter Cnt” in the variables box.
32) Click on the multiply, x, button.
33) Enter the value of the mL per drop you got when you calibrated your drop counter (if you skipped the calibration as indicated by your TA, use 0.037 mL per drop).
34) Enter the label “Volume” and units of “mL.”
35) Press “OK.”

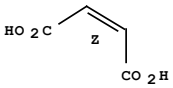
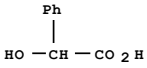
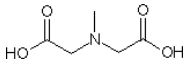
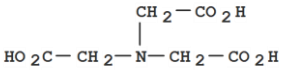
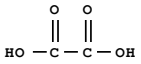
36) You should see 'Counter Cnt' under sensor on the top-left of the window. Click and drag 'Counter Cnt' to Column A of the spreadsheet table.
37) You should now see Volume under formulas (top-left of window). Click and drag the Volume to the X-axis of the plot. Click and drag it to column B of the table.
38) You should also see "pH" under "SENSOR" on the top-left of your screen. Drag the "pH" to the Y-axis of the plot. Also, drag it to column C, and blank box on the bottom-right of your screen.
39) You can now fill your drop counter reservoir with titrant and get the drop rate correct (see TA).
40) You should also be ready to the pH probe in your sample (with stir bar) under the drop counter.
41) In the lower left hand window you will see 'Experiment Steps.' Double click on the 'Repeat Every 0.500 seconds' step. In the dialog select 'Repeat when counter change' and press 'OK.'
42) Now everything is setup and ready to go!
43) Press "Start" on left-middle of your screen, it is under "Add Sensor".
44) Titrate your weak acid solution until the pH plateaus out somewhere above pH 10.
45) Press "Stop" when titration is complete.
46) Press "Analyze" under your graph and choose "Plot a Derivative (Rate of Change) [3rd choice].
47) Press "OK", and press "OK."
48) Repeat steps 30 and 31 but choose "Plot Second Derivative" [4th choice] instead.
49) Press and drag "DV" under your sensors onto column C.
50) Press and drag "DDV" under your sensors onto column D.
51) Press File -> Export data -> Comma-Separated-Value text file and save on the desktop
52) To repeat the titration, press "Repeat Experiment" next to the "Start" button, and choose "Repeat experiment without saving data" [3rd option].

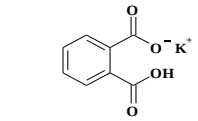
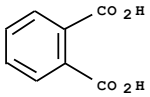
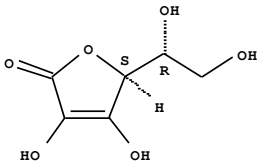
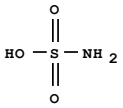
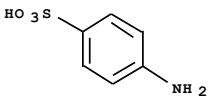
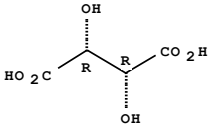
APPENDIX III:

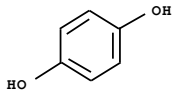
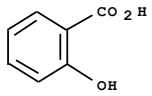
Instructions for Plotting Excel Titration Curves

1. Run Excel.
2. Go to the File menu and select Open. Select CSV as the file type. Then select a Microlab comma delimited (CSV) file containing your titration data. You can click through any dialog selections that appear and you may have to click Finish to load the file.
3. When you look at the data - Column A should have the drop number, Column B the volume and Column C the pH. You may also have a column with the calculated second derivative.
4. Save this file as an EXCEL workbook.
5. Highlight all the data in Columns B and C.
6. Click on the Insert menu and click on the Scatter plot icon.
7. Click on the smooth line type (scatter with data points connected by smooth lines with no markers).
8. A scatter plot will appear on the sheet. Right click on the plot and select 'Move to.'
9. Select 'New sheet', give it a name and press OK. The plot will appear as a new sheet in the workbook. You can tab back and forth between your data and the plot at will.
10. Double click on either of the axis labels and you can set the all of the axis options. Set these values to show off your data well.
11. When you are in a chart, the tool bar has a 'Chart Tools' section. Under layout, you can edit or add different things to your graph. You should add axis titles, a chart title and a legend. Please explore these options to make your graph look professional.
12. If you have more than one data series plotted, you can set the line style for each using the Layout menu as well. You can also add a legend. Just don't forget to name each data series (edited from the layout menu!)
13. Alternatively, you can select the plot, copy, and paste it into a "Word" document, and print the plot from within the word document.
14. Scaling a Plot - You may scale the plot to exhibit only those portions of a scan that are significant to your experiment.
15. You can have EXCEL print the chart alone using the print dialog.
16. You can also select the plot and copy it. You can then paste it into any other problem like Word as an EXCEL object or do 'paste special' an image (recommended).

Acid	**Structure**	**pK_a**	**M.W./g mol^{-1}**
Fumaric acid		3.03 4.44	116.07
L-(+)-Glutamic acid		2.19 4.25 9.67	147.13
Glutaric acid		4.34 5.41	132.11
p-Hydroxybenzoic acid		4.57	138.12
Iminodiacetic acid (IDA)		2.98 9.89	133.10
Isophthalic acid		3.54 4.60	166.13
Lactic acid		3.90	90.08

Maleic acid		1.92 6.22	116.07
Malonic acid		2.82 5.66	104.06
Mandelic acid		3.41	152.15
Methyliminodiacetic $CH_3N(CH_2COOH)_2$		2.12 9.65	147.13
Nitrilotriacetic acid (NTA)		1.65 2.94 10.39	191.14
Oxalic acid		1.27 4.27	126.07

Potassium hydrogen phthalate (KHP) $KHC_8H_4O_4$	 Potassium Hydrogen Phthalate (KHP)	5.51	204.23
Phthalic acid		2.95 5.41	166.13
Ascorbic acid		4.10 11.79	176.12
Succinic acid		4.21 5.64	118.09
Sulfamic acid		2.0	97.09
Sulfanilic acid		3.23	173.19
Tartaric acid		4.37	150.09

Hydroquinone		5.33	110.11
Salicylic acid		2.97 13.74	138.12
Sodium Citrate $Na_3C_6H_5O_7 \cdot 2\ H_2O$		3.08 4.74 5.40	294.10
Sodium Oxalate $Na_2C_2O_4$		1.27 4.27	134.00