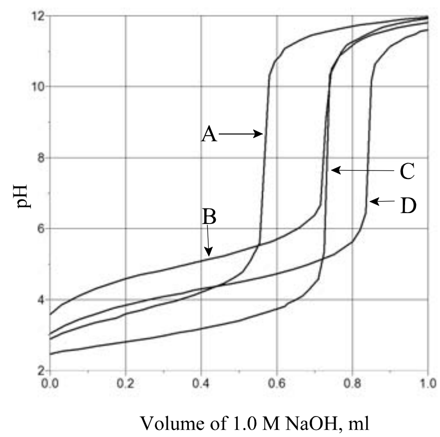
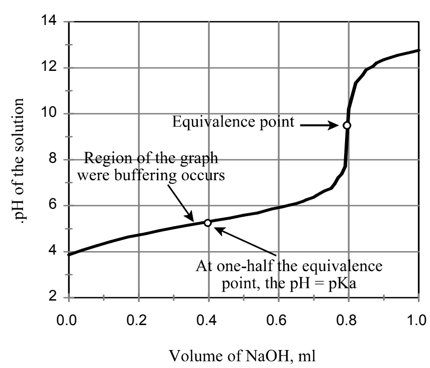
THE IDENTIFICATION OF A SOLID ORGANIC ACID

The volumetric procedure called a "titration" is a powerful tool in analytical chemistry. Not only does the process give the concentration of an unknown solution, but we can use it to determine the quality of a reactant, its molecular weight, its acid or base strength, and more. For example, the adjacent graph reflects the pH of equal masses of four different organic acids vs the volume of a NaOH solution. The first element of graph you might notice that each substance has a different equivalence point. That is, they require a different amount of base to neutral the sample. Moreover, they are all monoprotic acids as they exhibit only one area with a large inflection. The large slope and high pH at half the equivalence point tells you that each are relatively weak acids. We also note that the order of decreasing acid strength is C > A > D > B.



Other information we can obtain from the graph is the relative molecular weights. Since the same mass of each acid is reacted, acid A required the least number or moles of base and hence, it has the highest molecular weight. Using the same logic, acid D would have the lowest molecular weight as it required the greatest amount of base to neutralize the sample. Acids B and C have roughly the same molecular weight but are different acids as they have pKas.

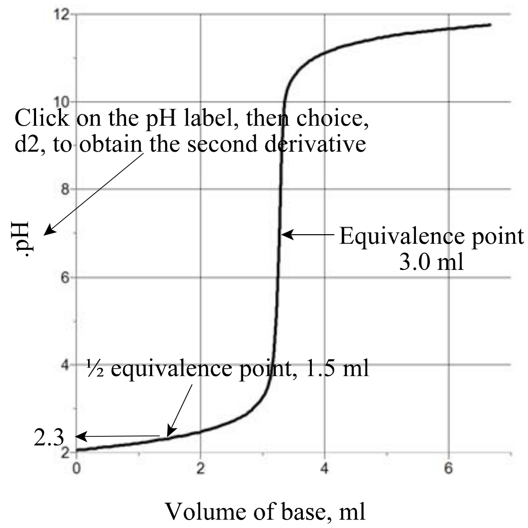
How do we know all this information? How can we determine it in this experiment? The key to these calculations is the "equivalence point" or the point on the graph where a known quantity base has exactly neutralize the acid sample. Recall that the moles of a substance equals volume of solution (in liters) times the molarity of the solution in moles per liter. At the equivalence point with a monoprotic acid, the moles of acid exactly equals the moles of base. Since we are titrating a base of know concentration, we can calculate the number moles of base reacted, and hence, the moles of the acid.

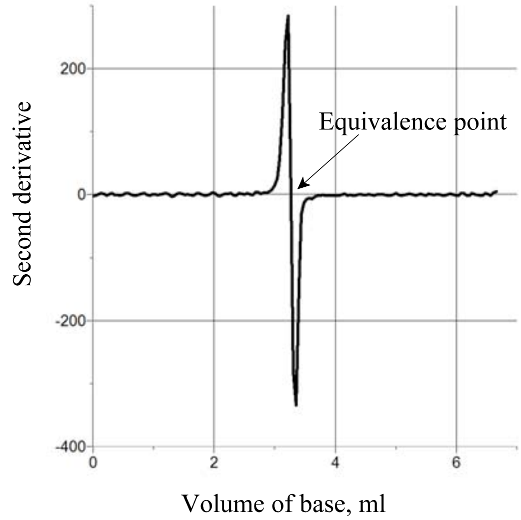


$$\text{moles of acid} = \text{moles of base}$$

$$\text{moles of base} = \text{volume (liters)} \times \text{molarity}\ \left(\frac{\text{moles}}{\text{liter}}\right)$$

The next piece of information which can be gleaned from the experiment is the relative strength of the acid as measured by the ionization or acidity constant, Ka, and pKa, the negative log of this constant. To determine this value, we must revert back to the equivalence point. First, how is it determined? Using computers as we will in this experiment, the equivalence point can be found from a graph of the second derivative of the pH vs the volume of titrant. The equivalence point is the center point on the graph where the pH abruptly changes. Note the graphs below:





To find the equivalence point using Vernier's Logger Pro software, click the "pH' label on the vertical or "Y" axis. Select the second derivative, d2, from the menu. Next, place your mouse arrow at the point on the graph where the plot exactly crosses "0." The "X, Y" mouse position coordinate read at the bottom lefthand portion of your graph provides you with "volume of base, and d2," in that order. The volume of NaOH obtained above is the volume of NaOH needed to exactly neutralize your sample of acid.

The next important value on your graph is at one-half the equivalence point. At one-half the equivalence point, exactly one-half of the acid has been neutralize yielding an equal amount of salt, also known the acid's conjugate base.

$$\text{acid + base} \rightleftarrows \text{salt + water}$$

or

$$\text{acid + base} \rightleftarrows \text{conjugate base + conjugate acid}$$

Applying the Henderson-Haselbach equation, one can determine the pKa of a solution from known concentrations of an acid and its conjugate base.

$$\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{at} \tfrac{1}{2} \text{ equivalence point} = [\text{base}] = [\text{acid}], \text{ or}$$

$$\text{pH} = \text{pKa} + \log \frac{[\cancel{\text{base}}]}{[\cancel{\text{acid}}]} = \text{pKa} + \log 1 = \text{pKa} + \log \text{"0"}$$

$$\therefore \ \text{pH} = \text{pKa}$$

Assuming the equivalence point in the sample graph above occurs at 3.0 ml, then ½ eq. pt. would occur at 1.5 ml. At 1.5 ml, the pH is roughly 2.3. Therefore, the pKa of the acid would be 2.3.

Another import quantity which can be determined once the equivalence point is known is the molecular weight of the acid. Assuming you weighed the acid sample before the reaction, then the molecular weight can easily be determined from the relationship:

$$\text{molecular weight} = \frac{\text{mass of acid}}{\text{moles of acid}}$$

If you recall from the discussion above,

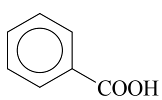
$$\text{moles of acid} = \text{moles of base} = \text{volume of base (liters)} \times \text{molarily of the base} \left(\frac{\text{moles}}{\text{liter}}\right)$$

Let's assume in the example above, we reacted 1.00 gram of our acid with 3.0 ml of 1.0 M base. Then,

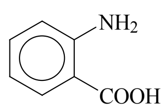
$$\text{moles of acid} = \text{moles of base} = 3.0 \times 10^{-3}\,\ell \times 1.0\ \text{M} \left(\frac{\text{moles}}{\text{liter}}\right) = 3.0 \times 10^{-3}\text{mol}$$

$$\text{molecular weight} = \frac{\text{mass of acid}}{\text{moles of acid}} = \frac{1.00\ \text{gram}}{3.0 \times 10^{-3}\text{mol}} = 333\ \text{g/mol}$$

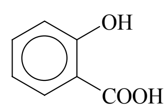
In this experiment, you will titrate standard 1.00 M sodium hydroxide solution against a sample of one of four unknown organic acids. From the data obtained, you will calculate the molecular weight of your acid and determine its pKa. Using this information, and the class discussion which follows, you will determine which of the four acids is the acid assigned to you.



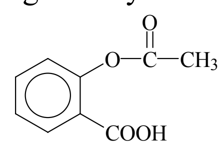
benzoic acid



2-aminobenzoic acid



salicylic acid



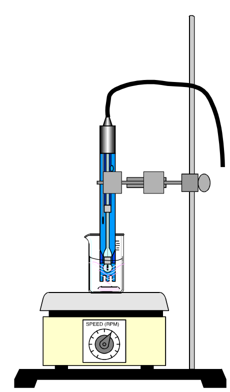
aspirin

Materials:

1.0 ml syringe w/tip extender
1.0 M sodium hydroxide
unknown acid
100-ml beaker
ring stand and clamp
magnetic stirrer w/stir bar

LabPro interface w/USB cable
computer with Logger Pro software
pH probe
50 ml graduated cylinder
ethanol

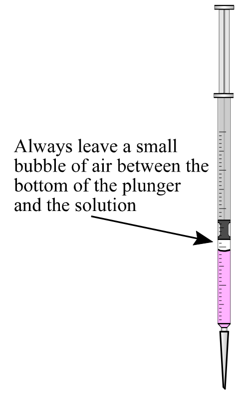
Procedure:



1. Prepare the pH sensor and LabPro for data collection.
   - Throughly rinse the pH electrode with tap water followed by distilled water.
   - Plug the pH electrode into channel #1 (CH1) of the LabPro.

C Connect the LabPro to the computer by means of a USB cable.
C Start the Logger Pro program on your computer. Open the file from the CIBA folder.

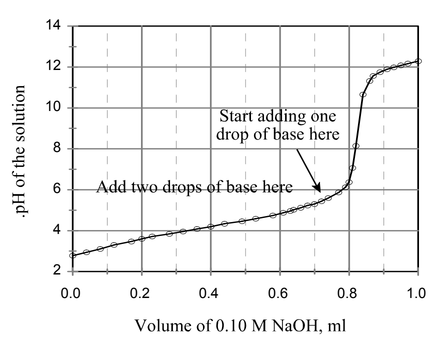
2. If necessary, attach the tip extender to the 1-ml hypodermic syringe. To prepare the syringe for the experiment; first rinse the syringe with distilled water by inserting the tip of the syringe below the surface and drawing in water completely filling the syringe. Expel the water and repeat this process a few times in insure that the syringe is clean. Remove the few remaining drops of water from the syringe by drawing in air and pushing it out rapidly several times. Next, rinse the syringe twice with the solution being reacted discarding the spent solution.



   Fill the syringe by inserting the tip of the syringe extender below the surface of the solution. Draw the solution into the syringe until the syringe piston reaches the top of the syringe. Always draw the solution slowly to prevent bubbles being formed. If you pull the plunger to quickly, air may be drawn into the syringe from the around the tip extender. If this happens, tighten the tip extender by pushing it firmly onto the syringe and try again. Adjust the volume of the solution in the syringe until the bottom of the concave meniscus rests on the 1.00 ml mark.

3. Tare a clean, dry 100-ml beaker. Add 0.100 gram of your unknown acid to the beaker and mass to the precision of your balance. Add 5 ml of ethanol to the solid and gently swirl to dissolve the acid. Finally, add a stirring bar and 45 ml of distilled water to the beaker.

4. Begin the titration:
   C Place the beaker containing your sample on a magnetic stirrer and add a stirring bar.
   C Set up a ring stand and clamp to hold the pH Sensor in place. Position the pH sensor in the beaker so that the tip of the probe is completely immersed.
   C Gently stir the dissolved acid/ethanol/water system.
   C Click the green “Collect” icon to begin monitoring the pH. When the pH stabilizes, click the “KEEP” icon next to the “COLLECT” icon. Enter “0" milliliter in the space provided and then press ENTER.
   C Add two drops of base. When the pH stabilizes, press KEEP and enter the volume of base in the syringe and again press ENTER. Note that the graduations are upside down. Subtract the volume read from 1.00 ml to obtain the volume of base added to the beaker. For example, if the volume reads 0.96 ml, that would mean that you’ve added 0.04 ml of base.
   C Continue to add base in two drop increments recording the pH and volume of NaOH until the pH starts to increase more rapidly. Note the adjacent graph. Continue the experiment by adding the NaOH in one drop increments until the data is above the equivalence point and begins to plateau. You can now add the base



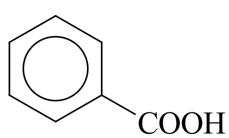
in two drop increments. Finally, when all the base has been added to the beaker, press the red “STOP” to stop collecting data.

C Dispose of the contents of beaker. Throughly all materials and return them to their designated area.

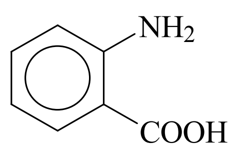
Questions and Calculations:

Q1. (a) What is the volume of base added to the beaker at equivalence point of your titration?
(b) Calculate the volume of base added at one-half the equivalence point.
(c) What is the pH of your solution at one-half the equivalence point? This value equals the pKa of your acid.

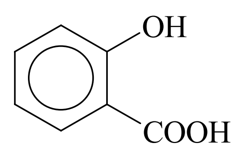
Q2. (a) Calculate the number of moles of base needed to exactly neutralize your sample of acid.
(b) Calculate the molecular weight of your acid from the mass of acid and the number of moles of base reacted.



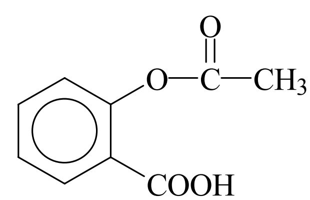
benzoic acid



2-aminobenzoic acid



salicylic acid



aspirin

Q3. Using the pKa and molecular weight of your acid, identify your unknown.

122 g/mol	137 g/mol	138 g/mol	180 g/mol
pKa 4.20	pKa 4.97	pKa 2.97	pKa 3.50

Q4. If an indicator was used what would be true about the pKa of the indicator ?

5. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

(a) What measurement(s) must be made to determine the number of moles of NaOH used in the titration?

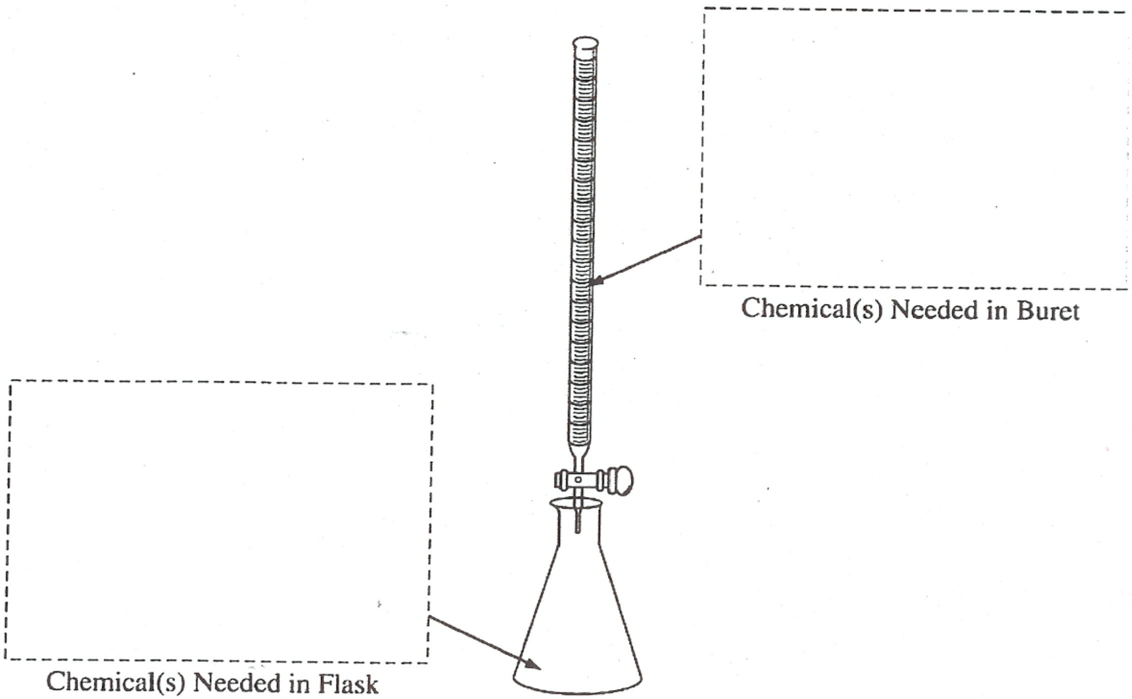
(b) Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.

(c) How can the number of moles of HA consumed in the titration be determined?

(d) In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA ?

(e) Write the mathematical expression that is used to determine the molar mass of HA.

(f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.



(g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

(ii) The procedure called for 25 mL of H_2O in the Erlenmeyer flask, but a student used 35 mL of H_2O.