Determination of Aspirin using Back Titration

This experiment is designed to illustrate techniques used in a typical *indirect* or *back* titration. You will use the NaOH you standardized last week to back titrate an aspirin solution and determine the concentration of aspirin in a typical analgesic tablet. You will be graded on your accuracy.

Required Reading

D.C. Harris, Quantitative Chemical Analysis (7th ed., W. H. Freeman, NY, 2007) p. 121-122.

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: back titration, percent composition, the transition range of an indicator. You should be able to discuss the difference between a direct and a back titration, 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 clearly why we use a back titration for this particular analysis; i.e., why can't we just use the endpoint found from the initial NaOH titration?

Many reactions are slow or present unfavorable equilibria for direct titration. Aspirin is a weak acid that also undergoes slow hydrolysis; i.e., each aspirin molecule reacts with two hydroxide ions. To overcome this problem, a known **excess** amount of base is added to the sample solution and an HCl titration is carried out to determine the amount of unreacted base. This is subtracted from the initial amount of base to find the amount of base that actually reacted with the aspirin and hence the quantity of aspirin in the analyte.
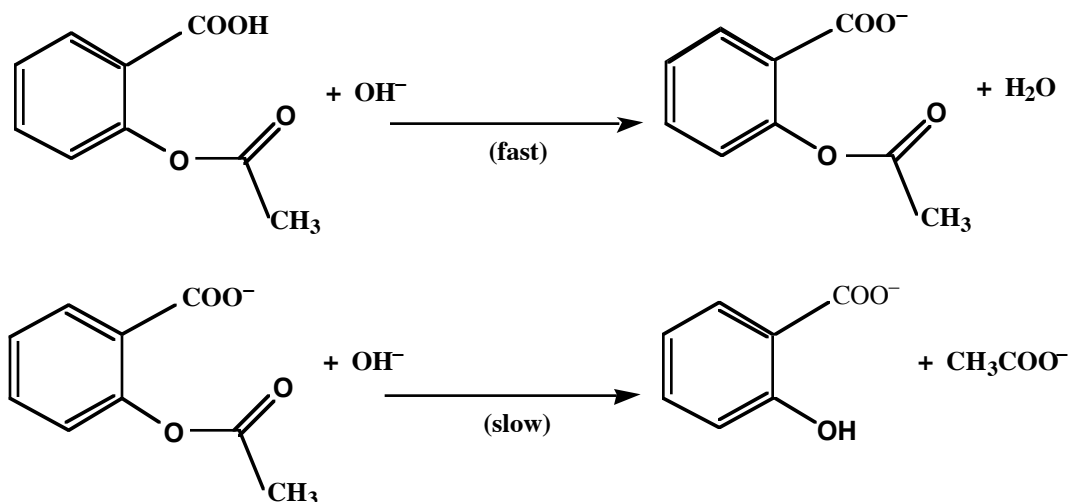
Chemicals and their Location

Balance Room
    Aspirin tablets

In the Hood
    Hydrochloric acid, conc., 37 wt %

on lab bench
    Ethanol
    Phenolphthalein, indicator soln

Your Drawer
    Sodium hydroxide, standardized soln

Equipment and its Location

Your Drawer
    Two Burets

    Weighing bottle

In the General Chem Lab
    Water bath

on lab bench
    Boiling chips, Mortar and Pestle

Safety Issues and Chemical Hazard Information

	Physical Hazards	*Health Hazards*
Aspirin	none	toxic, irritant, sensitizer
Ethanol	flammable	irritant
Hydrochloric acid	water-reactive, corrosive	toxic
Phenolphthalein	none	irritant
Sodium hydroxide	water-reactive, corrosive	toxic, irritant

Concentrated hydrochloric acid is highly corrosive. Be careful. Ethanol is flammable — keep away from heat, sparks, and open flames.

Procedure

There are various components to this procedure. If there is a delay at one step (e.g., all the water baths are in use), perform another section of this procedure while you are waiting.
Your instructor may suggest that half of the class work straight through the procedure, and the other half start at Step 4, returning to Steps 1 – 3 while waiting at Step 8, to reduce congestion in the lab.

Preparation of Approximate Acid Solution (~ 0.1M HCl)

1. Put ~100 mL distilled water into your other large bottle. <u>Before performing this experiment</u> (i.e., in your **prelab**), calculate the volume of concentrated HCl you will need to prepare 250 mL of 0.1M HCl. (Concentrated reagent grade HCl has a density of 1.188 g mL^{-1} and is 37 wt %. Check your answer with your TA before making this solution.) Measure approximately this volume of concentrated HCl using a graduated cylinder. Gradually add the acid to the water in your bottle, **mixing well** (remember, always add acid to water, not water to acid.). Add more distilled water, **mixing thoroughly** with each addition, until the total solution volume is ~ 250 mL. You do not have to measure the quantities accurately because you are going to standardize this solution in the next steps to determine its actual concentration.

Comparison of HCl to your standardized NaOH

2. Clean, rinse, and fill your burette with your ~0.1 M HCl solution. To each of three clean, labeled Erlenmeyer flasks, add 50 mL distilled water and three drops of phenolphthalein indicator. Use your HCl burette to add approximately 35, 40 and 45 mL of acid to flasks #1, #2 and #3, respectively, recording **exactly** how much acid is added to each flask within 0.01 mL. Swirl gently to mix.

3. Clean, rinse, and fill your second buret with the ~0.1 M NaOH solution that you standardized last week. Titrate the three HCl flasks with the NaOH to the phenolphthalein endpoint.

Sample Preparation

4. Accurately record the weight of a group of three aspirin tablets so that you can determine an average tablet weight. Use a mortar and pestle to crush enough tablets to produce ~ 1 g tablet powder.

5. Using a clean dry weighing bottle, weigh accurately, **by difference**, triplicate ~0.3 g samples of tablet, into labeled 250 mL Erlenmeyer flasks. To each flask, add 20 mL of ethanol (measure by graduated cylinder) and three drops of phenolphthalein indicator. Swirl gently to dissolve. (Aspirin is not very soluble in water — the ethanol helps the aspirin dissolve. Note that an aspirin tablet contains other compounds in addition to aspirin. Some of these are not very soluble. Your solution will be cloudy due to insoluble components of the tablet.)

Aspirin Titration with base

6. (If you were told to perform this step before Steps 1 – 3, clean, rinse, and fill a buret with the ~0.1 M NaOH solution that you standardized last week, before continuing.) Titrate the first aspirin sample with NaOH to the first permanent cloudy pink colour.

7. The aspirin/NaOH acid-base reaction consumes one mole of hydroxide per mole of aspirin. The slow aspirin/NaOH hydrolysis reaction <u>also</u> consumes one mole of hydroxide per mole of aspirin, and so for a complete titration **we will need to use a total of <u>twice</u> the amount of NaOH that you have already used, plus we will add some <u>excess</u> NaOH** to ensure that we really have reacted with all of the aspirin in your sample (adding excess reactant drives the equilibrium towards products — Le Chatelier's principle).

   Calculate how much extra NaOH you will need to add, following this reasoning: The volume of base to add for the hydrolysis reaction is equal to the volume of base you have already used to titrate to the acid-base endpoint in Step 6 <u>plus</u> an additional 10 mL of excess base. (For example: if you used 26 mL of base in the previous step, the volume of base you would add now would be 26 + 10 = 36 mL. Thus, you would have added a total of 26 + 26 + 10 = 62 mL of base.)

   Use your buret(not a graduated cylinder) to add the appropriate amount of extra NaOH to each of your three sample flasks. (Do not to allow the level of base in the buret to fall below the graduated markings; if necessary, record an intermediate volume and refill the buret to continue with your additions.) Record the <u>total</u> volume of NaOH added to each flask within 0.02 mL.

Heating the reaction to completion

8. Add two or three boiling chips to each flask and heat in a water bath to speed up the hydrolysis reaction. Avoid boiling, because the sample may decompose. While heating, swirl the flasks occasionally. After 15 minutes, remove samples from the water bath and cool for 5 minutes.

9. If the solution is colourless, add a few more drops of phenolphthalein. If it remains colourless, add 10!mL more of the base and reheat. (**Don't forget** to add this additional volume of base to the previously recorded total volume.)

Back titration with acid

10. The only base remaining in each flask will be excess base that has not reacted with the aspirin. Using your burette with your ~0.1 M HCl solution, titrate the excess base in each flask with HCl until the pink colour just disappears. The endpoint is best described as "cloudy white".

Shutdown procedures

IMPORTANT NOTE: Your NaOH solution **must be saved** upon completion of the experiment; you will use it again in future experiments. Save your HCl solution in case you find that something is wrong with your results from today's experiment.

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

13. Make sure you have recorded information on the sample you studied, including the manufacturer and brand name and the amount of aspirin reportedly in each tablet from the aspirin packet label.

Waste Disposal

Waste Chemicals	Waste Container	Location
Excess HCl, dilute or concentrated	Acid	Waste cabinet
Excess NaOH, dilute or concentrated	Base	Waste cabinet
Excess ethanol	Ethanol	Waste cabinet
Aspirin solutions after titration	Neutral	Waste cabinet
Aspirin solid waste	Solid waste	Balance room

Data Analysis

1. Using your NaOH molarity from last week, determine the molarity of your HCl solution from the volumes of NaOH needed to titrate your flasks of HCl, remembering that you designed it to be ~0.1!M. Report your standardized HCl concentration as the average of your three replicates with the standard deviation, %RSD, the 90% confidence interval, show example calcs.

2. Using the total volume of NaOH added to each, and the molarity of your NaOH standard solution, calculate the total number of moles of NaOH added to each sample.

3. Using the volume of HCl needed to back-titrate each aspirin flask and the average HCl concentration determined in Step One, calculate the number of moles of excess NaOH left in each flask after the reaction with aspirin.

4. From the total number of moles of NaOH added to the sample, and the number of moles of excess NaOH left after the reaction was complete, calculate the number of moles of base that reacted with aspirin.

5. Hence determine the number of moles of aspirin in each of your samples. (Don't forget the factor of two.)

6. Calculate the mass of aspirin in each of your samples. Using the mass of tablet you weighed into each sample, calculate the weight percent of aspirin in the tablets.

7. From the mass of the three tablets you weighed, calculate the average mass of a tablet. Use this value, and the weight percent of aspirin you have just calculated, to calculate the mass of aspirin in one of the original tablets. Apply the statistics described in 1. of the Data Analysis Section.

Discussion Questions

1. Why did you use your burette and not a graduated cylinder to add the excess NaOH?

2. What would be the consequence of competing equilibria, such as from other ingredients in the tablet, on your results? What if there were several pain relievers in the same tablet? How could the error from these interferences be minimized?

3. Ethanol was used in the solutions to help dissolve the acetylsalicylic acid. Ethanol is slightly acidic, and will react with NaOH. Describe a blank correction experiment; i.e., what experiment you might do to determine how much NaOH reacts with the ethanol in your solution. Once you have determined this, how would you use the results of a blank correction experiment in the data analysis?

Conclusions

As part of your conclusions for this experiment, compare the aspirin weight per tablet that you determined to the weight per tablet claimed by the manufacturer on the label.