Mutah University
Faculty of Science
Department of Chemistry
General and Organic Chemistry Laboratory for Medicine Students (0303003)
First Semester 2022/2023

Instructor: Prof. Arab K. Qaseer

Time of Lecture: Sec. (3) Sundays 12 – 2 PM; Sec. (6) Tuesdays 10 – 12 PM; Sec. (9) Tuesday 12 – 2 PM

Office Hours: Sundays 11-12; Mondays & Wednesday s 9:30:10:30

Evaluation: Final Exam: 25%

Course Contents

Exp.#	*Experiment Name*	*Week*	*Date*
0	Completion of course addition and withdrawal	1	9/10 – 14/13
1	Basic Laboratory Operations	2	16/ 10 – 20/10
2	Identification of a Compound: Physical Properties	3	23/10 – 27/10
3	Identification of Compounds: Chemical Properties	4	30/10 – 3/11
4	Limiting Reactant	5	6/11 – 10/11
5	Acids and Bases	6	13/11 – 17/11
6	Antacid Analysis	7	20/11 – 24 /11
7	Recrystallization	8	27/11 – 1/12
8	Preparation of Aspirin	9	4/12 – 8/12
9	Functional groups (I): Reactions of Alkanes, Alkenes and Aromatics.	10	11/12 – 15/12
10	Functional groups (II): Reactions of Aldehydes, Ketones and Alcohols.	11	18/12 – 22/12
11	*Christmas and New Year's Holiday*	12	25/12 – 29/12
	Discussion and Prep. for the Final Exam	13	2/1/2023 – 5/1/2023
	Final Exam (January 9, 2023)	14	8/1/2023 – 12/1/2023

The End

EXPERIMENT 6

Antacid Analysis

All antacids, as weak bases, reduce the acidity of the stomach.

OBJECTIVE

- To determine the neutralizing effectiveness per gram of a commercial **antacid**

TECHNIQUES

The following techniques are used in the Experimental Procedure

INTRODUCTION

Various commercial antacids claim to be the "most effective" for relieving acid indigestion. All antacids, regardless of their claims or effectiveness, have one purpose—to neutralize the *excess* hydrogen ion in the stomach to relieve acid indigestion.

The **pH** of the "gastric juice" in the stomach ranges from 1.0 to 2.0. This acid, primarily hydrochloric acid, is necessary for the digestion of foods. Acid is continually secreted while eating; consequently, overeating may lead to an excess of stomach acid, leading to acid indigestion and a pH less than 1. An excess of acid can, on occasion, cause an irritation of the stomach lining, particularly the upper intestinal tract, causing "heartburn." An antacid reacts with the hydronium ion to relieve the symptoms. Excessive use of antacids can cause the stomach to have a pH greater than 2, which stimulates the stomach to excrete additional acid, a potentially dangerous condition.

Antacid: dissolved in water, it forms a basic solution

pH: negative logarithm of the molar concentration of hydronium ion, $-\log [H_3O^+]$ (see Experiment 6)

Appendix D

The most common bases used for over-the-counter antacids are:

aluminum hydroxide, $Al(OH)_3$	magnesium hydroxide, $Mg(OH)_2$
calcium carbonate, $CaCO_3$	sodium bicarbonate, $NaHCO_3$
magnesium carbonate, $MgCO_3$	potassium bicarbonate, $KHCO_3$

Milk of magnesia (Figure 17.1), an aqueous suspension of magnesium hydroxide, $Mg(OH)_2$, and sodium bicarbonate, $NaHCO_3$, commonly called baking soda, are simple antacids (and thus, bases) that neutralize hydronium ion, H_3O^+:

$$Mg(OH)_2(s) + 2\,H_3O^+(aq) \rightarrow Mg^{2+}(aq) + 4\,H_2O(l) \qquad (17.1)$$

$$NaHCO_3(aq) + H_3O^+(aq) \rightarrow Na^+(aq) + CO_2(g) + 2\,H_2O(l) \qquad (17.2)$$

The release of carbon dioxide gas from the action of sodium bicarbonate on hydronium ion (Equation 17.2) causes one to "belch."

To decrease the possibility of the stomach becoming too basic from the antacid, **buffers** are often added as part of the formulation of some antacids. The more common, "faster relief" commercial antacids that buffer the pH of the stomach are those

Figure 17.1 Milk of magnesia is an aqueous suspension of slightly soluble magnesium hydroxide.

Buffers: substances in an aqueous system that are present for the purpose of resisting changes in acidity or basicity

Table 17.1 Common Antacids

Principal Active Ingredient(s)	Formulation	Commercial Antacid
$CaCO_3$	Tablet	Tums®, Titralac®, Chooz®, Maalox®
$CaCO_3$, $Mg(OH)_2$	Tablet	Rolaids®, Di-Gel®, Mylanta®
$MgCO_3$, $Al(OH)_3$	Tablet	Gaviscon® Extra Strength
$Mg(OH)_2$, $Al(OH)_3$	Tablet	Gelusil®, Tempo®
$NaHCO_3$, citric acid, aspirin	Tablet	Alka-Seltzer®
$Mg(OH)_2$	Tablet	Phillips'® Milk of Magnesia
$Mg(OH)_2$	Liquid	Phillips'® Milk of Magnesia
$Mg(OH)_2$, $Al(OH)_3$	Liquid	Maalox®, Mylanta® Extra Strength
$MgCO_3$, $Al(OH)_3$	Liquid	Gaviscon® Extra Strength

containing calcium carbonate, $CaCO_3$, and/or sodium bicarbonate. A HCO_3^-/CO_3^{2-} buffer system[1] is established in the stomach with these antacids.

$$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3^-(aq) + H_2O(l) \quad (17.3)$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow CO_2(g) + 2\,H_2O(l) \quad (17.4)$$

Rolaids® is an antacid that consists of a combination of $Mg(OH)_2$ and $CaCO_3$ in a mass ratio of 1:5, thus providing the effectiveness of the hydroxide base and the carbonate/bicarbonate buffer. Some of the more common over-the-counter antacids and their major active antacid ingredient(s) are listed in Table 17.1.

In this experiment, the "neutralizing power" of several antacids is determined using a strong acid–strong base titration. To obtain the quantitative data for the analysis, which requires a well-defined **endpoint** in the titration, the buffer action is eliminated.

Endpoint: the point in the titration when an indicator changes color

The buffering component of the antacid is eliminated when an *excess* of standardized hydrochloric acid, HCl, is added to the antacid solution; this addition drives the HCO_3^-/CO_3^{2-} reactions in Equations 17.3 and 17.4 far to the right. The solution is then heated to remove carbon dioxide. At this point *all* moles of base in the antacid (whether or not a buffer is present) have reacted with the standardized HCl solution.

Back titration: an analytical procedure by which the analyte is "swamped" with an excess of a standardized neutralizing agent; the excess neutralizing agent is, in return, neutralized to a final stoichiometric point

The *unreacted* HCl is then titrated with a standardized sodium hydroxide, NaOH, solution.[2] This analytical technique is referred to as a **back titration.**

The number of moles of base in the antacid of the commercial sample *plus* the number of moles of NaOH used in the titration equals the number of moles of HCl added to the original antacid sample:

$$\text{moles}_{\text{base, antacid}} + \text{moles}_{\text{NaOH}} = \text{moles}_{\text{HCl}} \quad (17.5)$$

A rearrangement of the equation provides the moles of base in the antacid in the sample:

$$\text{moles}_{\text{base, antacid}} = \text{moles}_{\text{HCl}} - \text{moles}_{\text{NaOH}} \quad (17.6)$$

The moles of base in the antacid per gram of antacid provide the data required for a comparison of the antacid effectiveness of commercial antacids. If purchase prices for the antacids are available, a final cost analysis of various antacids can be made.

EXPERIMENTAL PROCEDURE

Procedure Overview: The amount of base in an antacid sample is determined. The sample is dissolved, and the buffer components of the antacid are eliminated with the addition of an excess of standardized HCl solution. The unreacted HCl is back titrated with a standardized NaOH solution.

[1] A buffer system resists large changes in the acidity of a solution. To analyze for the amount of antacid in this experiment, we want to *remove* this buffering property to determine the total effectiveness of the antacid.

[2] A standardized NaOH solution is one in which the concentration of NaOH has been very carefully determined.

At least two analyses should be completed per antacid if two antacids are to be analyzed to compare their neutralizing powers. If only one antacid is to be analyzed, complete three trials.

A. Dissolving the Antacid

1. **Determine the Mass of Antacid for Analysis.** If your antacid is a tablet, pulverize and/or grind the antacid tablet with a mortar and pestle. Measure and record the mass (±0.001 g) of a 250-mL Erlenmeyer flask. Add no more than 0.2 g of the pulverized commercial antacid (or 0.2 g of a liquid antacid) to the flask and measure and record the combined mass (±0.001 g).
2. **Prepare the Antacid for Analysis.** Pipet 25.0 mL of a standardized 0.1 *M* HCl solution (stomach acid equivalent) into the flask and swirl.[3] Record the actual molar concentration of the HCl on the Report Sheet. Warm the solution to a very *gentle* boil and maintain the heat for 1 minute to remove dissolved CO_2 . . . using a hot plate (Figure 17.2a) or a direct flame and a gentle swirl (Figure 17.2b). Add 4–8 drops of bromophenol blue indicator.[4] If the solution is blue, pipet an additional 10.0 mL of 0.1 *M* HCl into the solution and boil again. Repeat as often as necessary. Record the *total* volume of HCl that is added to the antacid.

B. Analyzing the Antacid Sample

Read Technique 16c closely

Read the buret to the correct number of significant figures

Obtain about 75 mL of a standardized 0.1 *M* NaOH solution. The solution may have been previously prepared by the stockroom personnel. If not, prepare a standardized 0.1 *M* NaOH solution, as described in Experiment 9. Consult with your laboratory instructor.

1. **Prepare the Buret for Titration.** Prepare a *clean* buret. Rinse the clean buret with two 3- to 5-mL portions of the standardized NaOH solution and drain through the buret tip. Record the actual molar concentration of the NaOH on the Report Sheet. Fill the buret with the NaOH solution; be sure no air bubbles are in the buret tip. Wait for 10–15 seconds, then read and record its initial volume, "using all certain digits *plus* one uncertain digit."

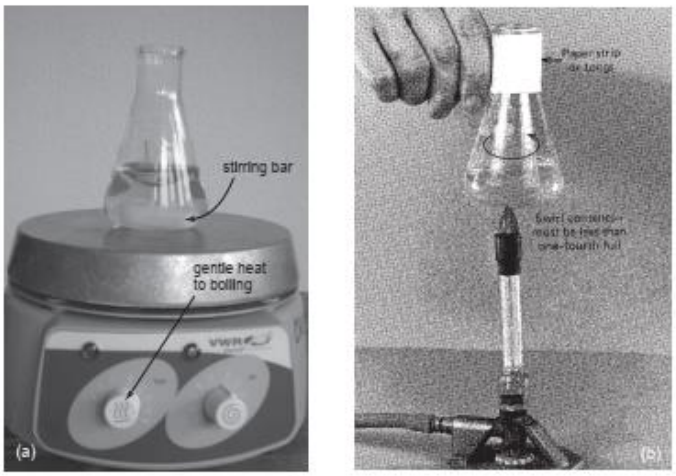

Figure 17.2 Gently heat the sample to remove CO_2 gas.

[3]If the sample is a tablet, swirl to dissolve. Some of the *inert* ingredients—fillers and binding agents used in the formulation of the antacid tablet—may not dissolve.
[4]Bromophenol blue is yellow at a pH less than 3.0 and blue at a pH greater than 4.6.

Be constantly aware of the use of significant figures that reflect the precision of your measuring instrument

2. **Titrate the Sample.** Once the antacid solution has cooled, titrate the sample with the NaOH solution to a faint blue endpoint. Watch closely; the endpoint may appear after only a few milliliters of titrant, depending on the concentration of the antacid in the sample. When a single drop (or half-drop) of NaOH solution changes the sample solution from yellow to blue, **stop.** Wait for 10–15 seconds and then read and record the final volume of NaOH solution in the buret.
3. **Repeat the Titration of the Same Antacid.** Refill the buret and repeat the experiment, starting at Part A.1.
4. **Analyze Another Antacid.** Perform the experiment, in duplicate, for another antacid. Record all data on the Report Sheet.

Disposal: Dispose of the test solutions as directed by your instructor.

CLEANUP: Discard the remaining NaOH titrant as directed by your instructor. Flush the buret several times with tap water and dispense through the buret tip, followed by several portions of deionized water. Dispose of all buret washings in the sink.

C. Calculations

1. Determine the number of moles of HCl added to the antacid sample.
2. How many moles of NaOH titrant were required to neutralize the *unreacted* acid?
3. Calculate the number of moles of base in the antacid sample.
4. Calculate the number of moles of base in the antacid sample *per gram* of sample.
5. (Optional) If the store-bought antacid and its purchase price are available, calculate its cost per gram. Complete a cost analysis—determine the best buy!

EXPERIMENT 6 *Prelaboratory Assignment*

Antacid Analysis

Date _____ Lab Sec. _____ Name _____ Desk No. _____

1. Write balanced equations for the reactions of the active ingredients in Gaviscon® Extra Strength with excess acid. See Table 17.1.

2. Identify the two most common anions present in antacids.

3. If the antacid for analysis (Part A.2) is known to be Phillips'® Milk of Magnesia, the solution does not need to be heated, but if the sample is Maalox®, the solution must be heated. Explain the difference in experimental procedures.

4. a. How much time should be allowed for the titrant to drain from the buret wall before a reading is made?

   b. What criterion is followed in reading and recording the volume of titrant of a buret?

   c. Bromophenol blue is the indicator used in detecting the endpoint for the antacid analysis in this experiment. What is the expected color change at the endpoint?

5. A 0.187-g sample of a CO_3^{2-} antacid is dissolved with 25.0 mL of 0.0984 *M* HCl. The hydrochloric acid that is *not* neutralized by the antacid is titrated to a bromophenol blue endpoint with 5.85 mL of 0.0911 *M* NaOH.
   a. Assuming the active ingredient in the antacid sample is $CaCO_3$, calculate the mass of $CaCO_3$ in the sample.

   b. What is the percent active ingredient in the antacid sample?

6. a. How many moles of stomach acid would be neutralized by one tablet of Regular Strength Maalox® that contains 600 mg of calcium carbonate?

   b. Assuming the volume of the stomach to be 1.0 L, what will be the pH change of the stomach acid resulting from the ingestion of one Regular Strength Maalox® tablet?

7. One tablet of Regular Strength Maalox® claims to contain 600 mg $CaCO_3$. If 7.25 mL of 0.100 *M* NaOH titrant is used to back titrate the excess 0.100 *M* HCl from the analysis of one-third of a Maalox® tablet, how many milliliters of 0.100 *M* HCl must have been initially added to the 200 mg of Maalox® sample?

EXPERIMENT

7 Recrystallization: Purification of Crystalline Organic Compounds

Impure crystalline substances can be purified by **recrystallization** from a suitable solvent. This process depends on two facts: Most compounds are more soluble in hot solvents than in cold ones, and impurities have solubilities different from those of the desired compound. The procedure involves (1) dissolving the impure material in a minimum amount of boiling solvent, (2) filtering the hot solution to remove insoluble impurities, (3) allowing the solution to cool slowly to deposit crystals of the compound, (4) filtering the crystals from the solution (called the **mother liquor**), (5) washing the crystals with a little cold solvent to remove the mother liquor, and (6) drying the crystals to remove the last traces of solvent.

This experiment illustrates recrystallization (a) from a single solvent (water) and (b) from a mixed solvent (ethanol-water).

1 General Principles

If recrystallization is to be effective, the solvent must be properly selected. A good recrystallization solvent should (1) dissolve a moderate quantity of the substance being purified at an elevated temperature, but only a small quantity at low temperature, (2) not react with the substance being purified, (3) dissolve impurities readily at a low temperature or not dissolve them at all, and (4) be readily removable from the purified product. This last requirement usually means that the solvent should have a fairly low boiling point and evaporate readily. If a single solvent cannot be found that meets all these requirements, a mixture of two solvents may be used.

Solvents suitable for recrystallizing a known compound are usually reported in the chemical literature. If none is reported, or if the substance is a new compound, several solvents can be tested in the following way. Place about 10 mg (a small spatula tipful) of the substance to be purified in each of several small test tubes, and add about 0.25 mL of a different solvent to each. Then observe the solubility of the sample in each solvent, when cold and when heated. Also note whether abundant, well-formed crystals are produced as the hot solution cools.

Caution Since many recrystallization solvents are flammable, do not use Bunsen burners to heat solutions unless your instructor indicates that you should do so. If you must use an open flame to heat a flammable solvent, follow your instructor's directions closely.

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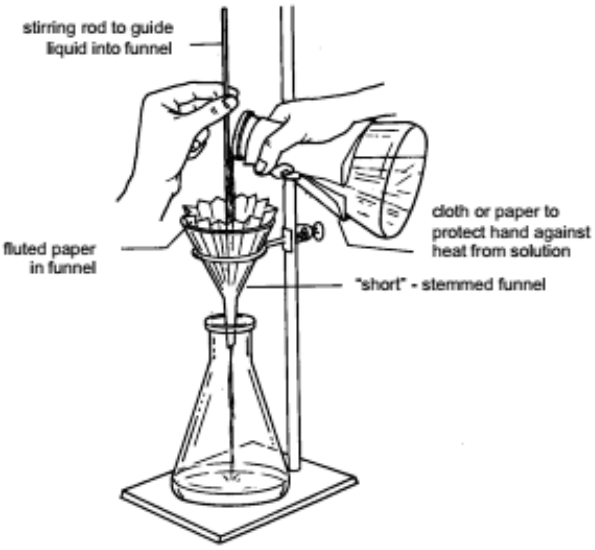

Figure 2.1 Filtration of a hot solution using fluted filter paper.

To obtain a good recovery of purified material, it is best to avoid using unnecessarily large volumes of solvent. Dissolving the substance in the smallest possible amount of hot solvent minimizes the amount of material lost by retention in the mother liquors. In practice, 3–5% more solvent than the minimum required is used so that the hot solution will be not quite saturated. This helps to prevent separation of the crystals and clogging of the filter paper during filtration of the hot solution.

Traces of coloring matter or resinous impurities can sometimes be removed with selective adsorbents, such as finely divided charcoal (Norit, Darco). To do this, add a small amount of decolorizing charcoal to the warm* solution before filtering it. Avoid using excess decolorizing agent, however, because it may also adsorb appreciable amounts of the substance being purified.

Some substances readily form supersaturated solutions, and crystallization may not occur spontaneously when the hot solution is cooled. In such situations, it is sometimes possible to initiate crystallization by scratching the walls of the vessel beneath the surface of the solution with a stirring rod. Though the effect of scratching the inside walls of the vessel in inducing crystallization is not well understood, two possible explanation are: (a) the fine glass particles produced through such scratching may act as nuclei on which crystallization may begin, or more likely, (b) small amounts of the solution drawn onto the sides of the vessel during scratching evaporate to produce dry solutes that are pushed back into the solution. These finely divided solute particles act as nuclei for crystallization to start. The best way to induce crystallization is to "seed" the cold solution with one or two crystals of the substance being purified. Although some compounds crystallize readily, others may separate from solution as oils, and it may take some time before they crystallize.

2 Apparatus for Hot Filtration and Vacuum Filtration

To remove insoluble impurities and decolorizing charcoal, it is necessary to filter the solution while it is hot. Otherwise, when the solution cools, crystals deposit prematurely. Rapid filtration can be accomplished by using fluted filter paper (paper folded with many pleats to give a large surface, Figure 2.1) or by using a vacuum to increase the filtration rate. Vacuum

*Do not add decolorizing charcoal to a hot solution. If a solution is at or near its boiling point, the addition of finely divided charcoal (which acts as thousands of boiling chips) will cause rapid boil over.

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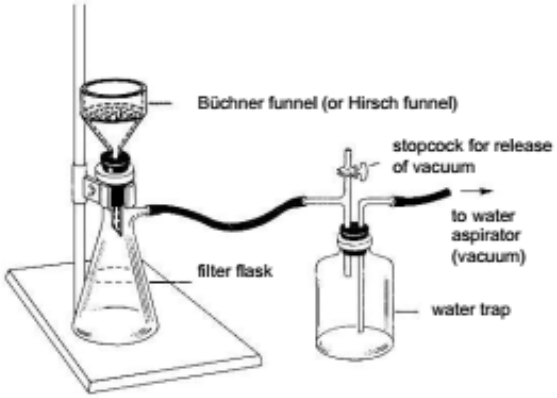

Figure 2.2 Apparatus for vacuum filtration.

filtration is generally used to remove soluble impurities and solvent from the crystals of the purified substance. Figure 2.2 shows the apparatus for vacuum filtration. A Büchner or a Hirsch funnel is fitted to a filter flask with a tight-fitting rubber stopper. A disc of filter paper just large enough to cover all the holes in the funnel is placed in the funnel and moistened with some of the solvent used in the recrystallization. The filter flask is then connected to the aspirator by thick-walled rubber tubing through a water trap, and vacuum is applied. When the filter paper is drawn tightly to the funnel, the solution and crystals are transferred to the funnel. The solution passes through the paper, while the crystals deposit on the paper.

3 Reflux Apparatus

It is sometimes necessary to heat a substance in a solvent for a long time without boiling away the solvent. This can be done by attaching a vertical condenser to the flask containing the boiling solution (Figure 2.3). The solvent vapor, upon cooling, condenses and returns as a liquid to the boiling solution. This process of continuous boiling, vaporization, cooling, and return of condensate is called **refluxing**. In recrystallizing, it is sometimes necessary to use a reflux apparatus to obtain a solution of the material to be purified because the dissolution process may be slow. We also use the reflux technique when recrystallizing large samples from volatile, flammable solvents (a sand, steam, or oil bath or an electric mantle is employed as the source of heat).

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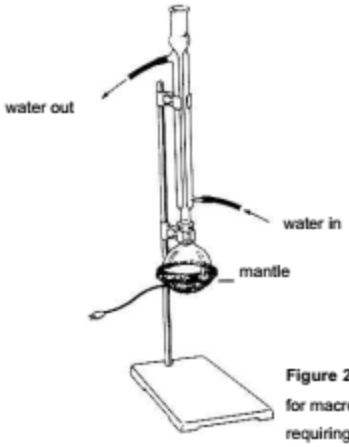

Figure 2.3 a Apparatus for macroscale reactions requiring reflux.

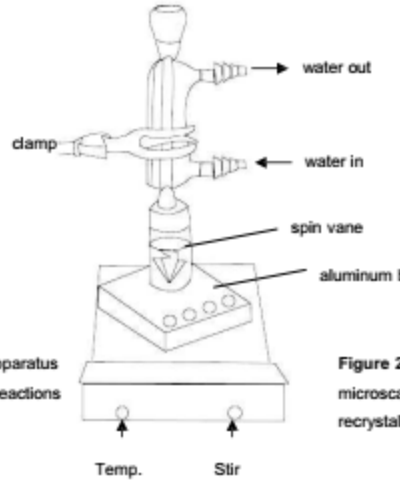

Figure 2.3 b Apparatus for microscale reactions or recrystallizations requiring reflux.

4 Recrystallization of Acetanilide

In this experiment a sample of impure acetanilide will be recrystallized from water. Pure acetanilide recrystallizes out as white leaflets from water. You will weigh the crude sample and the pure product and determine the melting point before and after recrystallization to illustrate the efficiency of the process.

Caution	Boiling water and steam can cause severe burns. Be very careful when handling vessels that contain hot water.

Macroscale Weigh out a 1.5-g sample of impure acetanilide and use a few milligrams to determine the melting point. Record the melting point on the report sheet. Place the rest of the acetanilide in a 100-mL round-bottomed flask, connect this flask to a reflux condenser (Figure 2.3 a), and start a slow stream of water through the jacket of the condenser. Add 35 mL of water to the flask through the top of the condenser, and bring the water to a boil by heating with a mantle. Adjust the mantle temperature so that the water refluxes steadily. Continue to heat until no more solid appears to dissolve. Then remove the heat source, allow the flask to cool a few moments after reflux stops to avoid boil over, remove the condenser momentarily, and add a small amount (about 0.2 g) of decolorizing charcoal to the contents of the flask (see footnote, p. 12). Replace the condenser and heat the solution at reflux for an additional 5 min.

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Meanwhile, set up the apparatus shown in Figure 2.1, using fast-flow fluted filter paper and a 125-mL Erlenmeyer flask as the receiver. Pour 15–20 mL of boiling water through the funnel to warm it and to wet the filter paper. Discard this water.

Remove the condenser and, using the clamp as a handle, filter the hot acetanilide solution without delay. If particles of charcoal pass through the filter paper, return the filtrate to the round-bottomed flask, heat the solution to boiling, and filter it again *through the same piece of filter paper.*

As the filtrate cools, crystals will begin to form immediately. Place the Erlenmeyer flask in a pan of ice to complete the crystallization. Meanwhile, set up the vacuum-filtration apparatus shown in Figure 2.2, using a 125-mL filter flask. Set a piece of filter paper in place, connect the flask to the aspirator, and turn it on. Pour 15–20 mL of cold water through the funnel to wet the filter paper. Discard this water. Reconnect the flask to the aspirator.

When crystallization is complete, collect the crystals by vacuum filtration. Rinse the crystals (with the vacuum on) with a few milliliters of ice-cold water. Use a clean spatula to press the crystals as dry as possible on the funnel. Then transfer the crystals to a piece of clean, white paper, spread them in a thin layer, and cover the crystals with a watch glass. Store them in your locker for drying until the next laboratory period.

Weigh the dried product and determine its melting point. Calculate the percentage recovery of pure material.* Turn in the purified acetanilide to your instructor with your report.

Microscale Obtain a small sample of impure acetanilide in a melting point capillary to determine the melting point range. Record the melting point range on the report sheet. Weigh out a 100-mg sample of impure acetanilide and place it in a 5 mL conical vial. Add 3 mL of water and a boiling stone** to the vial, place the vial on an aluminum block, attach a condenser (Figure 2.3 b), and heat the vial to bring the water to a boil.

During this time, set up a vacuum filtration apparatus (Figure 2.2) with a Hirsch funnel and a 10-mL filter flask.

Continue to heat the solution until no more solid appears to dissolve. Then remove the heat source and allow the vial to cool for about 30 s after reflux stops. Add a small amount (about 10 mg or one microspatula tipful) of decolorizing charcoal to the contents of the vial. Heat the vial for an additional 2 min. Use this time to wet the filter paper and apply vacuum to the filtration set-up made earlier.

Carefully and quickly remove the heat source and disassemble the reflux set-up so that the hot contents of the conical vial does not spill nor unduly cool. Filter the acetanilide solution without delay making sure that particles of charcoal do not pass through the filter paper.*** Transfer the filtrate into a 10 mL Erlenmeyer flask. If crystallization occurs during the transfer, use minimum amounts of hot water (not more than 1–1.5 mL) to wash the crystals into the Erlenmeyer flask and carefully heat the Erlenmeyer flask to redissolve the precipitate. Cool the Erlenmeyer flask to room temperature or even in a small beaker of ice to complete the crystallization.

Collect the crystals by vacuum filtration, using a Hirsch funnel. Rinse the crystals (with the vacuum on) with three 0.5-mL portions of ice-cold water. Use a clean microspatula to press the crystals as dry as possible on the funnel. Then transfer the crystals to a clean piece of filter paper, cover them with a small beaker, and allow them to air-dry in your drawer until

* The percentage recovery is calculated as follows: $\frac{\text{grams of purified product}}{\text{grams of crude sample}} \times 100 = \%$ recovery. The value should be less than 100%. If it is greater, your recrystallized material is wet or impure.

** The boiling stone (also known as a boiling chip or a Boileezer) is an inert material with small pores that provide sites where bubbles can form, thus inducing even boiling.

*** Use only the correct size filter paper that completely covers the inside of the Hirsch funnel.

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the next lab period. (Alternatively, the product may be dried for 20 min in a vacuum oven at 80°C. Transfer the crystals to a small (10 x 75 mm) weighed test tube, fashion a foil cap for the tube, and make several puncture holes in the cap before placing the tube in the oven. Allow the tube and contents to cool to room temperature before weighing.) Weigh the recrystallized product and determine the melting point range of the purified compound. Report the melting point range and the percentage recovery.

Waste Disposal Discard your used melting point tubes in the waste-glass container provided by your instructor. Place organic solids recovered on filter paper in a solid-waste container provided by your instructor. Pour the aqueous mother liquor solutions into an aqueous-waste bottle provided by your instructor.

5 Recrystallization of *p*-Dibromobenzene

This part of the experiment illustrates the technique of using a mixed solvent for recrystallization. *p*-Dibromobenzene is soluble in cold as well as hot ethanol. Therefore, ethanol alone is not a good recrystallization solvent for this substance. On the other hand, the compound has a very low solubility in hot or cold water. Therefore, water alone is also unsatisfactory as a recrystallization solvent for this substance. But because ethanol and water are miscible, it is possible to find a mixture of the two solvents in which *p*-dibromobenzene is soluble when hot but relatively insoluble when cold.

This experiment is also designed to acquaint you with the type of small-scale recrystallization that is commonly used to purify products you will prepare in later experiments in this manual.

Macroscale Procedure Weigh out 1 g of impure *p*-dibromobenzene and use a few milligrams to determine the melting point range. Transfer the solid to a 25-mL Erlenmeyer flask, add 5 mL of ethanol, and heat the mixture on a steam bath.

Caution	Ethanol is flammable; do not use an open flame as a heat source in this recrystallization.

Swirl or stir the solution until the solid dissolves. If any undissolved solid remains after several minutes of heating, filter the hot solution using fluted filter paper, a small stemless funnel, and a small Erlenmeyer flask. If, however, the solid dissolves completely, add water in 0.5-mL portions to the hot solution until it becomes cloudy or just fails to clear when stirred. Then add a little ethanol (0.5 mL or less) until the turbidity just disappears. If filtration is necessary, treat the hot filtrate with water and ethanol as just described.

Cool the flask in a pan of ice water for several minutes, and then collect the crystals by vacuum filtration (Figure 2.2). Rinse the crystals on the filter (with the vacuum off) with a few milliliters of ice-cold 50–50 ethanol-water. Stir the contents on the funnel (carefully) for just a few seconds; then turn the vacuum on. Repeat this operation until a white product is obtained or until most of the orange impurity is removed. Allow the pure crystals to air-dry on the filter (with the vacuum on) for a few minutes, and then transfer them to a clean sheet of filter paper for final drying.* After the crystals are dry, weigh the product, determine its melting point and the percentage recovery, and turn in the labeled sample to your instructor.

**p*-Dibromobenzene sublimes if left at room temperature too long.

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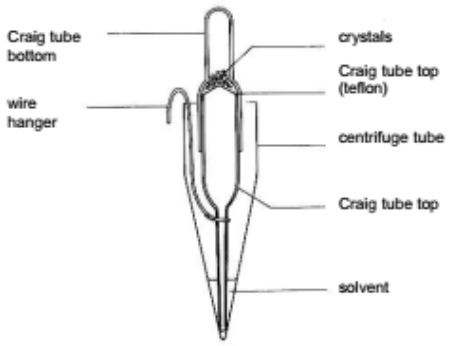

Figure 2.4 Use of the Craig tube in recrystallization.

Microscale Procedure

Obtain a small sample of impure *p*-dibromobenzene in a melting point capillary, determine the melting point range, and record it on the report sheet. Weigh out 50 mg of impure *p*-dibromobenzene and place the sample in a 10 x 75-mm test tube. Add 0.5 mL of ethanol and heat the mixture in a sand bath. Stir the solution with a microspatula until the solid dissolves. Transfer the hot solution with a Pasteur filter pipet* (this will remove any undissolved matter) to the bottom section of a weighed 1-mL Craig tube. Add hot water dropwise to the hot solution until it becomes cloudy or just fails to clear when stirred. Then add hot ethanol dropwise until the turbidity just disappears.

Place the top on the Craig tube, stand it in a small beaker, and allow it to cool to room temperature. Next place the Craig tube in a small beaker of ice water for a few minutes to ensure complete crystallization. Then remove the solvent by attaching a wire hanger to the stem of the Craig tube top, lowering a centrifuge tube over the top of the Craig tube until it fits snugly with the wire hanging out, inverting this assembly into a centrifuge, and centrifuging for 2–3 min (Figure 2.4).** The mother liquor will slip out between the loosely fitted top and bottom sections of the Craig tube, and the crystals will remain in the tube. The wire hanger allows the Craig tube to be retrieved easily from the centrifuge tube.

After removing it from the centrifuge, disassemble the Craig tube and scrape any crystals that cling to the upper section into the lower section. Wrap a piece of filter paper over the open end and allow the recrystallized product to air dry. (Alternatively, dry the Craig tube and contents in a vacuum oven at 60°C for 20 min. Be sure to place a small wedge of paper between the top and bottom halves of the Craig tube so that the tube can be evacuated.)

*A Pasteur filter pipet is constructed by taking a very small piece of cotton (about the size of a small grain of rice) and placing it in the large end of a standard Pasteur pipet. The cotton is tapped down to the drawn part of the pipet. A wire is used to push the cotton down until it forms a 2–3-mm plug that is flush with the end of the capillary. The plug should be loose enough so that it does not become wedged before reaching the end of the capillary. If the plug is too tightly wedged at the end, the pipet will not draw well.

**Craig tubes are fragile. They should be carried and stored in small beakers or Erlenmeyer flasks to avoid accidental breakage. Care should be taken to balance the centrifuge (pairs of students can put their Craig tubes in opposite slots, or a centrifuge tube containing water can be used as a balance). A high-speed centrifuge should not be used.

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Weigh the assembled Craig tube and contents, and determine the percentage recovery. Determine the melting point of the recrystallized product. Transfer the sample to a small labeled test tube and turn it in to your instructor.

Name_____ Section_____

Lab Instructor_____ Date_____

PRELAB EXERCISE EXPERIMENT 7

Recrystallization: Purification of Crystalline Organic Compounds

Consider the following statement to answer questions 1 and 2

Recrystallization of an impure solid must be carried out using a minimum amount of the required solvent(s) at or near its boiling point.

1. Why is it necessary to use only a minimum amount of the required solvent for recrystallization?

2. Why is it necessary to carry out the recrystallization at or near the boiling point of the solvent used?

3. How are insoluble impurities removed during recrystallization?

4. What purpose does the addition of finely divided charcoal serve during the recrystallization of impure solids?

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Experiment 8

Aspirin Synthesis and Analysis

Aspirin is a leading commercial pain reliever, first synthesized in a pure and stable form by Felix Hoffman in 1897.

OBJECTIVES

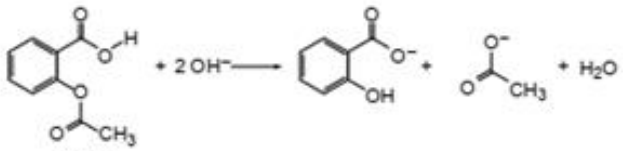
- To synthesize aspirin
- To determine the purity of the synthesized aspirin or a commercial aspirin tablet

TECHNIQUES

The following techniques are used in the Experimental Procedure

INTRODUCTION

Pure aspirin, chemically called acetylsalicylic acid, is both an organic **ester** and an **organic acid.** It is used extensively as a painkiller (analgesic) and as a fever-reducing drug (antipyretic). When ingested, acetylsalicylic acid remains intact in the acidic stomach, but in the basic medium of the upper intestinal tract, it forms the salicylate and acetate ions.



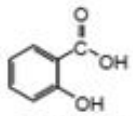
(19.1)

aspirin (acetylsalicylic acid) — salicylate ion — acetate ion

Ester: a  *grouping of atoms in a molecule*

Organic acid: a  *grouping of atoms in a molecule*

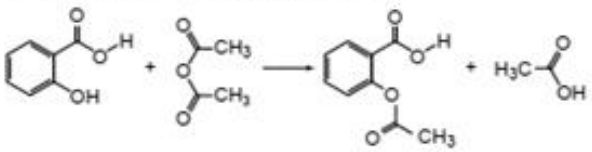
The analgesic action of aspirin is undoubtedly due to the salicylate ion; however, its additional physiological effects and biochemical reactions are still not thoroughly understood. It is known that **salicylic acid** has the same therapeutic effects as aspirin; however, due in part to the fact that it is an acid, salicylic acid causes a more severe upset stomach than does aspirin.



salicylic acid

Aspirin (molar mass of 180.2 g/mol) is prepared by reacting salicylic acid (molar mass of 138.1 g/mol) with acetic anhydride (molar mass of 102.1 g/mol). Aspirin, like many other organic acids, is a weak **monoprotic acid.**

Monoprotic acid: a molecule that provides one proton for neutralization

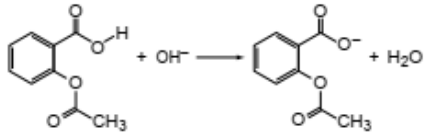


(19.2)

salicylic acid — acetic anhydride — aspirin (acetylsalicylic acid) — acetic acid

Qualitatively, the purity of an aspirin sample can be determined from its melting point. The melting point of a substance is essentially independent of atmospheric pressure, but it is always lowered by the presence of impurities (a colligative property of pure substances; see Experiment 14). The degree of lowering of the melting point depends on the nature and the concentration of the impurities.

Quantitatively, the purity of an aspirin sample can be determined by a simple acid–base titration. The acetylsalicylic acid reacts with hydroxide ion, from a standardized sodium hydroxide solution, accordingly.



(19.3)

Phenolphthalein: an acid-base indicator that is colorless at a pH less than 8.2 and pink at a pH greater than 10.0

A standardized NaOH solution titrates the acetylsalicylic acid to the **phenolphthalein** endpoint, where

$$\text{volume of NaOH (L)} \times \text{molar concentration of NaOH (mol/L)} = \text{mol NaOH} \quad (19.4)$$

According to Equation 19.3, one mole of OH^- reacts with one mole of acetylsalicylic acid; thus, the moles and mass of acetylsalicylic acid in the prepared sample are calculated. Knowing the calculated mass of the acid and the measured mass of the aspirin sample, the percent purity of the aspirin sample can be calculated:

$$\text{mol acetylsalicylic acid} \times \frac{180.2\ \text{g}}{\text{mol}} = \text{g acetylsalicylic acid} \quad (19.5)$$

$$\%\ \text{purity} = \frac{\text{g acetylsalicylic acid}}{\text{g aspirin sample}} \times 100 \quad (19.6)$$

In Part C, the analysis for the percent acetylsalicylic acid in an aspirin sample can be performed on the aspirin prepared in Part A *or* on a commercial aspirin tablet.

EXPERIMENTAL PROCEDURE

Procedure Overview: Crystalline aspirin is synthesized and then purified by the procedure of recrystallization. The melting point and the percent purity of the aspirin are determined, the latter by titration with a standardized NaOH solution.

A. Preparation of Aspirin

It is safest to prepare the aspirin in a fume hood. Set up a boiling water bath in a 400-mL beaker. Prepare about 100 mL of deionized ice water. Also, set up an ice bath.

1. **Mix the Starting Materials and Heat.** Measure about 2 g (±0.01 g) of salicylic acid (**Caution:** *this is a skin irritant*) in a *dry* 125-mL Erlenmeyer flask. Cover the crystals with 4–5 mL of acetic anhydride. (**Caution:** *Acetic anhydride is a severe eye irritant—avoid skin and eye contact.*) Swirl the flask to wet the salicylic acid crystals. Add 5 drops of conc H_2SO_4 (**Caution:** H_2SO_4 *causes severe skin burns.*) to the mixture and gently heat the flask in a boiling water bath (Figure 19.1[1]) for 5–10 minutes.
2. **Cool to Crystallize the Aspirin.** Remove the flask from the hot water bath and, to the reaction mixture, add 10 mL of deionized *ice* water to decompose any excess acetic anhydride. Chill the solution in an ice bath until crystals of aspirin no longer form, stirring occasionally to decompose residual acetic anhydride. *If* an "oil" appears instead of a solid, reheat the flask in the hot water bath until the oil disappears and again cool.

[1]A Bunsen flame may be substituted for the hot plate.

3. **Separate the Solid Aspirin from the Solution.** Set up a vacuum filtration apparatus and "turn it on." Seal the filter paper with water in the Büchner funnel. *Decant* the liquid onto the filter paper; minimize any transfer of the solid aspirin. Some aspirin, however, may be inadvertently transferred to the filter; that's O.K.
4. **Filter, Wash, and Transfer the Aspirin.** Add 15 mL of *ice* water to the flask, swirl, chill briefly, and decant onto the filter. Repeat until the transfer of the crystals to the vacuum filter is complete; maintain the vacuum to dry the crystals as best possible. Wash the aspirin crystals on the filter paper with 10 mL of ice water. Keep all of the filtrate until the aspirin has been transferred to the filter.

   If aspirin forms in the filtrate, transfer this filtrate and aspirin to a beaker, chill in an ice bath, and vacuum filter as before, using a new piece of filter paper.

Disposal: Dispose of the "final" filtrate as directed by your laboratory instructor.

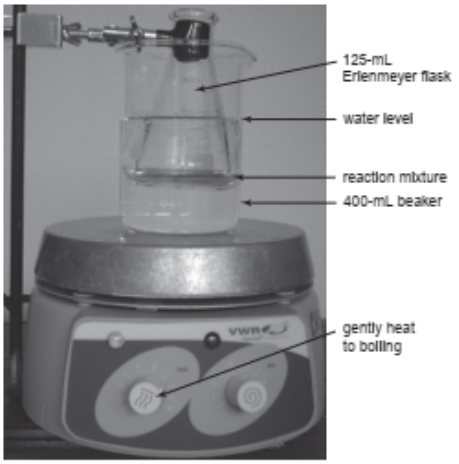


Figure 19.1 Boiling water bath for the dissolution of the acetylsalicylic acid crystals.

5. **Recrystallize the Aspirin.** Transfer the crystals from the filter paper(s) to a 100-mL beaker. Add repetitive small volumes of ethanol (e.g., 3-mL volumes) to the aspirin until the crystals *just* dissolve (≤20 mL is required). Warm the mixture in a 60°C water bath (**Caution:** *no flame,* use a hot plate or a hot water bath). Pour 50 mL of ~60°C water into the solution. If a solid forms, continue warming until the solid dissolves.

   Cover the beaker with a watchglass, remove it from the heat, and set it aside to cool slowly to room temperature. Then set the beaker in an ice bath. Beautiful needlelike crystals of acetylsalicylic acid form.

6. **How Much Did You Prepare?** Vacuum filter the crystals on filter paper, the mass of which has been previously measured (±0.01 g). Wash the crystals with two 10-mL volumes of *ice* water. Place the filter paper and aspirin sample on a watchglass and allow them to air-dry. The time for air-drying the sample may require that it be left in your lab drawer until the next laboratory period.

   Determine the mass of the dry filter paper and sample. Dispose of the filtrate as directed by your laboratory instructor.
7. **Correct for Residual Solubility.** The solubility of acetylsalicylic acid is 0.25 g per 100 mL of water. Correcting for this inherent loss of product due to the wash water in Part A.6, calculate the percent yield.
8. **What Do You Do with It?** Don't use it for a headache! Place the sample in a properly labeled test tube, stopper, and submit it along with your Report Sheet to your laboratory instructor at the conclusion of the experiment.

B. Melting Point of the Aspirin Sample

The melting point of the aspirin sample can be determined with either a commercial melting point apparatus (Figure 15.5) or with the apparatus shown in Figure 19.2 and described in Part B.1. Consult with your instructor.

1. **Prepare the Sample.** Fill a capillary melting point tube to a depth of 1 cm with the recrystalized aspirin prepared in Part A.6. See Figures 15.3 and 15.4. Attach the tube to a 360°C glass or digital thermometer with a rubber band (or band of rubber tubing).

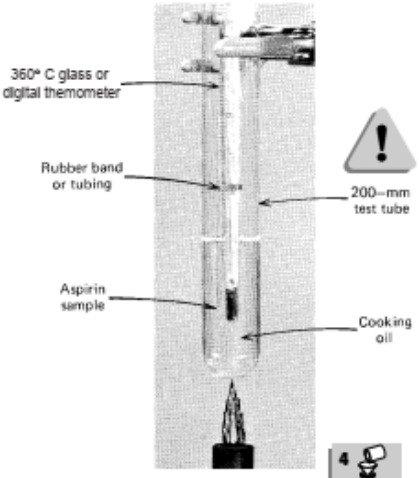


Figure 19.2 Melting point apparatus for aspirin.

Place the sample alongside the thermometer bulb (Figure 19.2) or thermal sensor. As the melting point for aspirin is greater than 100°C, a cooking oil must be used for the heating bath.

2. **Determine the Melting Point.** *Slowly* and *gently* heat the oil bath at a rate of ~5°C per minute until the aspirin melts. (**Caution:** *The oil bath is at a temperature greater than 100°C—do not touch!*) Cool the bath and aspirin to just below this approximate melting point until the aspirin in the tube solidifies; at a slower ~1°C per minute rate, heat again until it melts; this is the melting point of your prepared aspirin.
3. **A Purity Check of the Sample.** If the melting point of your prepared aspirin sample is less than 130°C, repeat Part A.5 to recrystallize the sample for the purpose of increasing its purity. After the recrystallization, repeat Parts B.1 and B.2.
4. **Repeat the Melting Point Measurement.** Again, cool the bath and aspirin to just below the melting point until the aspirin in the tube solidifies; at a 1°C per minute rate, heat again until it melts.

Disposal: Ask your instructor about the proper disposal of the oil. Be sure the oil is cool when handling it. Dispose of the capillary tube in the "Waste Glass" container.

C. Percent Acetylsalicylic Acid in the Aspirin Sample

Three trials are to be completed in the analysis of the aspirin. Prepare three clean 125- or 250-mL Erlenmeyer flasks and determine the mass of three aspirin samples while occupying the balance. Obtain a 50-mL buret.

1. **Prepare the Aspirin Sample for Analysis.** *Assuming* 100% purity of your aspirin sample, calculate the mass of aspirin that requires 20 mL of 0.1 *M* NaOH to reach the stoichiometric point. Show the calculation on the Report Sheet. On weighing paper measure the calculated mass (±0.001 g) of the aspirin you have just prepared (or a crushed commercial aspirin tablet) and transfer it to the flask. Add 10 mL of 95% ethanol, followed by about 50 mL of deionized water, and swirl to dissolve the aspirin. Add 2 drops of phenolphthalein indicator. Repeat for trials 2 and 3.
2. **Prepare the Buret for Titration.** Prepare a clean buret, rinse, and fill it with a standardized 0.1 *M* NaOH solution.[2] Be sure that no air bubbles are present in the buret tip. After 10–15 seconds, read and record the volume, and the *actual* molar concentration of the NaOH solution.
3. **Titrate the Sample.** Slowly add the NaOH solution from the buret to the dissolved aspirin sample until the endpoint is reached. The endpoint in the titration should be within one-half drop of a faint pink color. The color should persist for 30 seconds. Read and record the final volume of NaOH in the buret.

Disposal: Discard the test solution in the "Waste Acids" container or as advised by your instructor.

CLEANUP: Discard the NaOH titrant into a properly labeled bottle; rinse the buret with several 5-mL volumes of tap water, followed by two 5-mL volumes of deionized water.

The Next Step

The purity of an aspirin sample can also be determined spectrophotometrically. Research the Internet for the procedure and refer to Experiment 35 for details.

[2]You may need to prepare the 0.1 *M* NaOH solution using the procedure in Experiment 9, or the stockroom personnel may have it already prepared.

EXPERIMENT 8 *Prelaboratory Assignment*

Aspirin Synthesis and Analysis

Date _____ Lab Sec. _____ Name _____ Desk No. _____

1. A 0.421-g sample of aspirin prepared in the laboratory is dissolved in 95% ethanol, diluted with water, and titrated to the phenolphthalein endpoint with 17.3 mL of 0.114 *M* NaOH.
   a. How many moles of acetylsalicylic acid (molar mass = 180.2 g/mol) are present in the sample?

   b. Calculate the percent purity of acetylsalicylic acid in the aspirin sample.

2. Experimental Procedure, Part A.1. In the experiment 2.00 g of salicylic acid (molar mass = 138.1 g/mol) reacts with an excess amount of acetic anhydride. Calculate the theoretical yield of acetylsalicylic acid (molar mass = 180.2 g/mol) for this synthesis.

3. Experimental Procedure, Part C.1. Determine the number of grams of acetylsalicylic acid that will react with 20.0 mL of 0.100 *M* NaOH. Show calculation here and on the Report Sheet.

4. Experimental Procedure, Part A.5. What is the purpose of recrystallizing the aspirin?

5. Experimental Procedure, Part B.3. The melting point of the prepared aspirin in this experiment will most likely be less than (but not greater than) that of pure aspirin. Explain. See Experiment 14.

6. Where and why is Technique 14b used in this experiment?

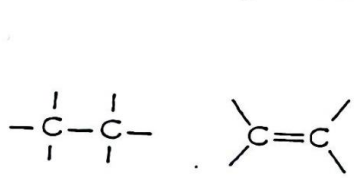
7. Describe the procedure for "seating" the filter paper in the funnel for a vacuum filtration.

8. Identify the five **cautions** cited in the Experimental Procedure for this experiment.

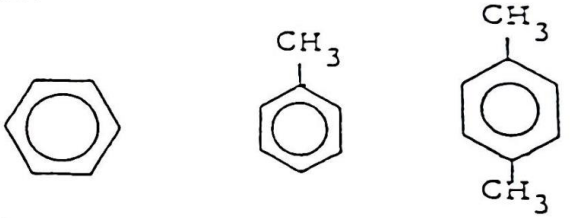
EXPERIMENT 9 REACTIONS OF THE FUNCTIONAL GROUPS I: ALKANES, ALKENES, AND AROMATICS

Organic compounds are divided into functional groups for the obvious reason that they have different chemical behavior. Each functional group responds or fails to respond to certain classes of chemical reactions. They vary from the reactive aldehydes to the relatively unreactive alkanes. In Experiments 6, 12, and 19, we shall examine the characteristic chemical behavior of the main organic functional groups. Experiment 17 (Organic Qualitative Analysis) shows how to use these reactions in differentiating between various compounds in qualitative analysis.

In this experiment, the characteristic reactions of alkanes, alkenes, and aromatic hydrocarbons are examined. Alkanes are saturated hydrocarbons in which each carbon has a maximum number of bonded atoms (four). All bonds are single bonds. Alkenes have one or more double bonds. Aromatic compounds include a variety of resonance stabilized substances, of which benzene is the most common. Because benzene has recently come under suspicion as causing leukemia, it will not be used here. It is added along with xylene and toluene to high-octane gasolines.



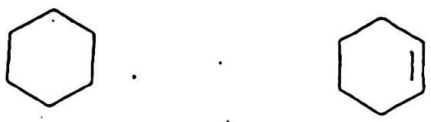
Alkanes Alkenes



Benzene Toluene p-Xylene

Aromatics

The following compounds will be used in most of the tests described in the procedures.



Cyclohexane Cyclohexene

The alkanes will betray themselves by their inactivity in almost any test we shall try. The alkenes, alkynes, and some aromatics dissolve in concentrated sulfuric acid (A), often with color. Alkenes and alkynes add bromine (B) readily and decolorize permanganate (C). Aromatics substitute readily with strong Lewis acid-type reagents,

such as test D using aluminum chloride and chloroform. Alkynes are rather uncommon and the best tests provide explosive compounds so they will not be tested here. The tests will be performed both on compounds that give positive reactions and on those that do not. Note and record any physical observations such as heat evolution, color change, formation of a precipitate, and formation or disappearance of layers.

PROCEDURE

A Sulfuric Acid

$$CH_3CH{=}CHCH_3 + H_2SO_4 \longrightarrow CH_3\text{-}CH_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\text{-}CH_3$$

With care, put about 1 ml of concentrated sulfuric acid in a 10 X 75-mm test tube. Add several drops of hydrocarbon to be tested and agitate carefully. Hold the tube with your left thumb and index figure at the very top. Gently strike the bottom of the tube with a downward motion with your right index finger. A little practice, using water, will teach you the technique of mixing without splashing.

Observe carefully whether or not the hydrocarbon is dissolving. A yellow-to-brown color indicates solution has taken place. The biggest problem is to note whether the hydrocarbon is dissolving or just hiding in the meniscus. Look very carefully, and perhaps add a few more drops of hydrocarbon to be sure. If the material does not dissolve, it is probably an alkane. If it also fails test C it is an alkane.

Try this test on cyclohexane, cyclohexene, and toluene.

B. Bromine in Carbon Tetrachloride

Alkane $\quad CH_3CH_2CH_2CH_3 + Br_2 \xrightarrow{\text{Light}} CH_3\underset{\displaystyle Br}{\underset{|}{CH}}CH_2CH_3 + HBr$

Alkene $\quad CH_3CH{=}CHCH_3 + Br_2 \xrightarrow[\text{or dark}]{\text{Light}} CH_3\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}CH_3$

Alkenes decolorize bromine rapidly and completely with a dilute solution of bromine in carbon tetrachloride, even in the dark. Alkanes react very slowly by substitution only in the presence of

ultraviolet light.

Put a little (1/2 ml of the hydrocarbon in a 10 X 75-mm test tube and add the dilute bromine in carbon tetrachloride solution drop by drop. If you add too much solution for the amount of alkene you have, the extra bromine will color the solution and mask the test. So observe carefully after each drop to determine whether or not the bromine is really adding.

Do the test on cyclohexane, cyclohexene, and chlorobenzene. (If you wish, you may take the cyclohexane and chlorobenzene tubes out in the sunlight, shake them, and observe.) HBr is produced in one tube and may be detected by carefully holding a strip of moist blue litmus down in the test tube.

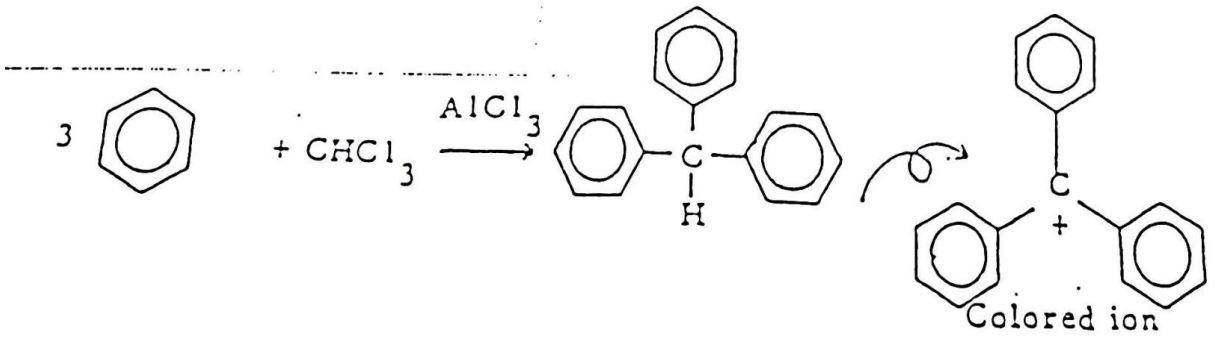
C. The Baeyer Test, Potassium Permanganate

$$\underset{\text{(purple)}}{MnO_4^-} + \text{alkene} \xrightarrow{OH^-} MnO_2 + \text{oxidation products}$$

Permanganate will react with double bonds forming diols, followed by more extensive oxidation. It will take place in either acidic or basic solution. In base, the purple color disappears, forming manganese dioxide. If concentrated enough, it will precipitate as a brown flocculent precipitate. If too much permanganate is used, the test may be masked by the intense color of the excess.

Place 1 ml of ethanol in each of three test tubes. Add 5 to 10 drops of cyclohexane to the first, cyclohexene to the second, and chlorobenzene to the third. Add a dilute solution of potassium permanganate dropwise and observe for an immediate reaction.

D. Aluminum Chloride and Chloroform

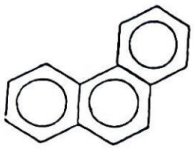


This is a complex reaction, involving several reactions ending in a colored product somewhat as illustrated above. Aromatic compounds produce colors whereas alkenes do not. Benzenes will give orange-to-red colors, naphthalenes will be blue, biphenyls and phenanthrenes will be purple, and anthracenes will be green.

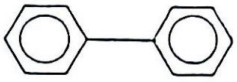
Benzene

Naphthalene

Anthracene



Phenanthrene



Biphenyl

You may wish to do the following test in a hood. Add a small spatula of solid aromatic compound to 1 ml of dry chloroform in a 10 X 75-mm test tube. Get a little anhydrous aluminum chloride on a spatula. (Keep the cover on the aluminum chloride as much as possible or it will pick up water and the test will fail.) Incline the test tube and wet the walls with the solution. Then while it is inclined, spill the aluminum chloride down the wet wall. Note the color on the wall and in the solution.

Try the test with one or more solid aromatics such as those suggested. Also try cyclohexane and cyclohexene.

E. Combustion

$$\text{Hydrocarbon} + O_2 \xrightarrow{\text{Flame}} CO_2 + H_2O$$

Saturated compounds burn cleanly, while unsaturated ones tend to produce soot.

Place a few drops of the compound to be tested on a watch glass or the inverted cover of a crucible. Ignite it with a match or a burner and note the character of the burning.

Try the test on cyclohexane, cyclohexene, and toluene.

Name _____ Date _____

Lab Instructor _____ Section _____

EXPERIMENT 9

Reactions of the Functional Groups I: Alkanes, Alkenes, and Aromatics

Observations; Results

Test Reagent	Cyclohexane	Cyclohexane	Aromatic (specify)
A. H_2SO_4			
B. Br_2/CCl_4			
C. $KMnO_4$			
D. $AlCl_3/CHCl_3$			
E. Combustion			

F. Results, Chlorobenzene, Phenol, and Aniline with Bromine Water

EXERCISES

Write reaction equations for all positive tests in parts A, B, C, E, and F.

EXPERIMENT 10 REACTIONS OF THE FUNCTIONAL GROUPS II: ALDEHYDES, KETONES, AND ALCOHOLS

Aldehydes and ketones are both characterized by the carbonyl group, $-C=O$. Aldehydes have at least one hydrogen bonded to the carbonyl carbon whereas in ketones, both bonds are to alkyl or aryl groups.

Aldehydes

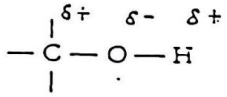
Carbonyl group

Ketones

Two types of chemical behavior will be tested here. First, in both aldehydes and ketones, the carbonyl group reacts well with many reagents to form derivatives. Secondly, aldehydes are readily oxidized by numerous mild oxidizing agents that do not react with ketones. Several special tests that work for methyl ketones will also be tried.

Structurally, alcohols have a hydroxy group bonded (usually) to a saturated carbon.

R-OH

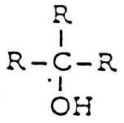


Alcohol

The reactions of alcohols involve the polar carbon-oxygen and oxygen-hydrogen bonds. Alcohols are classified as primary, secondary, or tertiary, and their rates of reaction frequently vary depending on the structure.

Primary (1°)

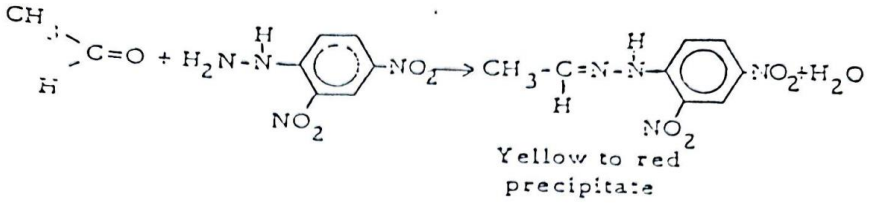
Secondary (2°)



Tertiary (3°)

PROCEDURE

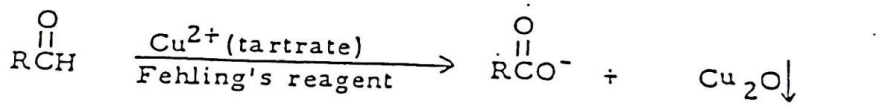
A. 2, 4-Dinitrophenylhydrazine



This orange-red solution of 2, 4-dinitrophenylhydrazine in sulfuric acid produces an immediate precipitate with most aldehydes and ketones, colored yellow to deep red. Recrystallization and determination of the melting point is a valuable clue to their identity.

Put 1 ml of the 2,4-DNP reagent (careful, it stains!) in a 10 X 75-mm test tube. Add 2 to 3 drops of the compound to be tested and shake carefully. Try the test with acetone, benzaldehyde, cinnamaldehyde, acetophenone, and cyclohexanol.

B. Fehling's Test



Fehling's solution is an alkaline solution of sodium tartrate, in which copper(II) ion is soluble because of complex formation. (Copper(II) ion is ordinarily insoluble in base.) This solution is a very mild oxidizing agent, sufficiently strong to oxidize aldehydes but not much else. In the reaction, the copper(II) ion is reduced to copper(I) and precipitates as a red solid, the copper(I) oxide. Enough reagent should be made at one time to handle all of your tests. The reagent reacts well at about 60 °C. You should, however, place one tube of the reagent without any test compound in the bath to make sure that any positive tests you may get are not simply the

decomposition of the reagent. When the reaction is positive, the deep blue solution of the reagent will turn to a murky olive-green suspension and the red precipitate will gradually collect on the bottom of the tube.

Take 5 ml of Fehling's A and 5 ml of Fehling's B and mix. Place 2 ml of this solution in each of three test tubes. Add 2 to 3 drops of the compounds to be tested to each tube and place the tubes in the warm-water bath. Also, place one tube in the bath that has only the reagent in it for a blank. Examine for any change in color or for a red precipitate on the bottom of the tube. Test on aqueous acetaldehyde and acetone.

C:- Tollens' Test

$$Ag^{+} + 2NH_3 \longrightarrow Ag(NH_3)_2^{+}$$

$$Ag(NH_3)_2^{+} + RCH \longrightarrow RCO^{-} + Ag\downarrow$$

This test is very similar to Fehling's test above in that Tollens' reagent is an ammoniacal solution of silver ion that is a very mild oxidizing agent. It produces silver metal, either as a fine black precipitate or as a mirror on the tube! This is how mirrors were made in the past; now they are made by evaporating aluminum metal onto glass. After we test for aldehydes, we shall make a mirror.

1. Test for Aldehydes

Put 5 ml of 0.1 M silver nitrate solution into a test tube. Add dilute ammonia dropwise until the brown precipitate that forms at first almost redissolves. Shake the tube between each drop so that you do not add too much ammonia. Place 1 ml of the solution in a 10 X 75-mm test tube and add 2 drops of the compound to be tested. You may warm it gently, but be careful as you may just decompose the reagent. You may test this by warming a sample of the reagent alone. With an aldehyde, you will observe a fine black precipitate, or if you are lucky and the tube is clean, you may silver the inside of the tube, giving a mirror that you can see from the outside. Try the test on the aqueous acetaldehyde and acetone.

2. Preparation of a Silver Mirror

Thoroughly clean a 90-mm watch glass and a 1 X 3-in. microscope slide by washing them with soap, rinsing with water and then acetone, and allowing to dry. Place 50 ml of water in a 400-ml beaker supported on a tripod or iron ring. Set the watch glass over the open end of the beaker and lay the microscope slide across the watch glass. Have a burner ready to heat the water.

Pour 25 ml of 0.1 M $AgNO_3$ into a small beaker. Add concentrated ammonia dropwise until the dark precipitate that forms after the first drop or so just disappears. Add a spatula (0.2 to 0.3 g) of glucose (grape sugar, blood sugar – the main energy source for animals; human blood contains 0.08% to 0.1% glucose). Stir or shake to dissolve the glucose and pour the solution into the watch glass. Bring the water in the 400-ml beaker to a boil. Remove the flame as soon as the first traces of mirror appear. Allow the plating to proceed for 3 to 5 min. With tongs, carefully remove the slide (handle on edges) and rinse with water and then with a little acetone. Place a piece of dark electrical or masking tape on the side with the better silver surface and rub the silver off the other side. Observe the mirror formed on the watch glass. The silver can be removed from the watch glass with a few milliliters of 6 N HNO_3.

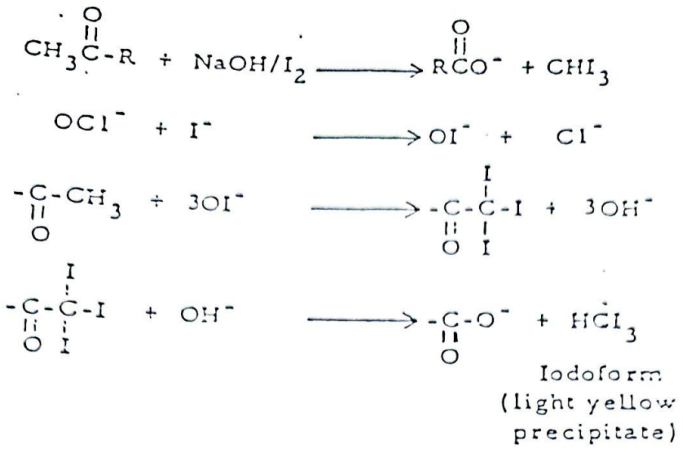
D. Iodoform Test

The iodoform test is positive for aldehydes and ketones, which have a methyl group directly connected to the carbon-oxygen double bond. It also is positive for primary and secondary methyl carbinols.

A methyl carbonyl A methyl carbinol

Put 2 to 3 ml of 10% potassium iodide solution (water/acetonitrile) in a 13 X 100-mm test tube Warm briefly on a steam bath or a boiling-water bath. Add 2 drops (no more) of the compound to be tested. Shake, then add 1 to 1.5 ml of Clorox . Agitate the solution. Look for the yellow precipitate, iodoform. Iodoform has a characteristic odor. You may have to filter the solution and isolate the iodoform to be sure the test is positive.

Secondary methyl carbinols are oxidized to methyl ketones and

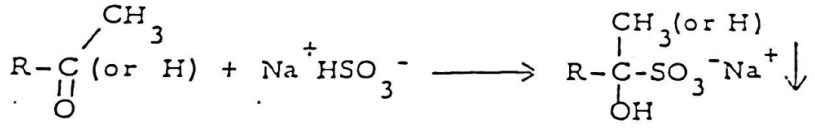


Iodoform
(light yellow
precipitate)

will therefore also give the test Try the test with acetone, 2-propanol, 3-pentanone, acetophenone, and propiophenone.

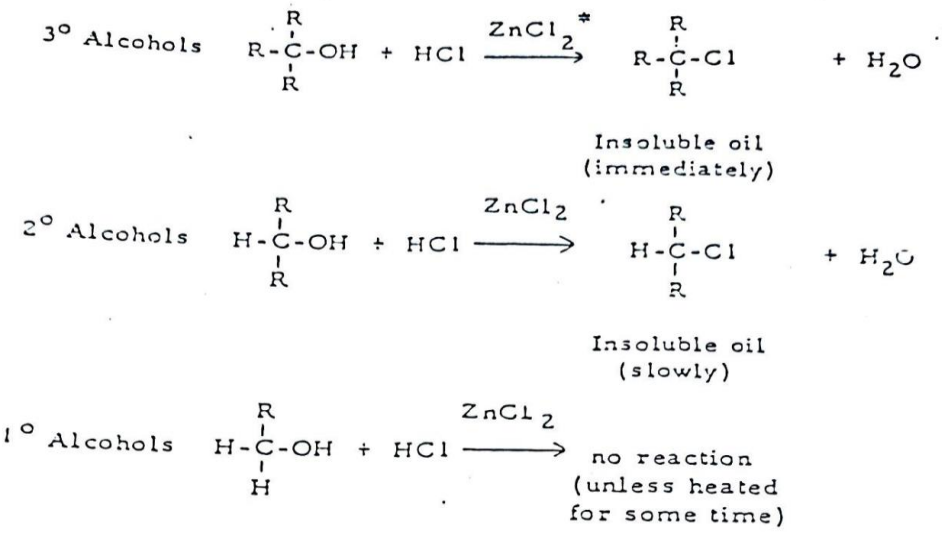
E. Sodium Bisulfite

Sodium bisulfite adds to aldehydes and methyl ketones to give crystalline addition products.



Shake 1 to 2 ml of a saturated solution of sodium bisulfite, $NaHSO_3$, (not meta-bisulfite) with a few drops of the compound to be tested. Aldehydes and methyl ketones give a precipitate of the addition product. Try the test with acetone, acetophenone, benzaldehyde, and cyclohexanol.

F. Lucas Test



The Lucas reagent replaces the hydroxyl group of an alcohol with a chloride The alcohol is usually soluble in the reagent, and the chloride is not. One therefore sees a clear solution become cloudy, and often a separate layer of the chloride will develop. Tertiary alcohol give the test immediately at room temperature. Secondary alcohols take 5 to 10 min at room temperature or a minute or two at 60 °C. Primary alcohols will react eventually but take much longer. Phenols and acids do not react. Since the reagent sometimes becomes weaker with age, you cannot rely on time alone. Always do the test with different kinds of alcohols simultaneously so that you can see the contrast.

Put 1 to 2 ml of the prepared Lucas reagent (anhydrous zinc chloride dissolved in concentrated hydrochloric acid) in a 10 X 75-mm test tube. Add 5 to 10 drops of the alcohol and shake briefly. Wait several minutes and then put the test tubes with no reaction into a beaker of water of 60 °C. The tertiary alcohols should react at room temperature and the secondary alcohols at 60°C; the primary alcohols won't react.

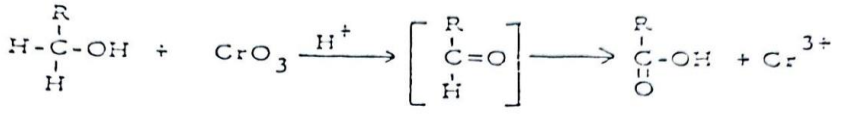
Try the test with 1-butanol, 2-butanol, and t-butyl alcohol. If desired, you may try a few drops of a 90% solution of phenol and a

*Does not have to be present for tertiary alcohols.

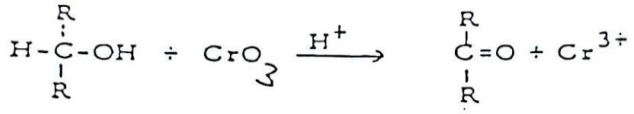
few drops of acetic acid in separate test tubes to perceive the nonreaction. Be extremely careful with phenol solutions. They are almost invariable strong vesicants (blisterers) or irritants. The irritant in poison oak is a phenol.

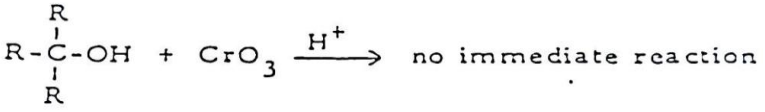
For contrast, repeat the tests with concentrated hydrochloric acid. Only the tertiary alcohol will react.

G. Chromic Anhydride — Oxidation of Alcohols

1° Alcohols 

Yellow orange — Aldehyde — Acid — Greenish blue (immediate)

2° Alcohols 

3° Alcohols 

Primary alcohols can be oxidized to aldehydes and then acids. Secondary alcohols are readily oxidized to ketones. Tertiary alcohols are not readily oxidized. Given just a little time, however, the tertiary alcohol will undergo changes such as unsaturation that will allow extensive oxidation. This hesitation is the basis of this test. Primary and secondary alcohols will react with this reagent within 2 sec. Tertiary alcohols hesitate for a few seconds, then react.

Add 1 to 2 ml of acetone to each 10 X 75-mm test tube. Add 1 to 2 drops of the compound to be tested and then add an equal amount of the chromic acid reagent. The yellow color should change immediately to the greenish blue of the chromic ion. If the solution remains yellow for 2 sec, the test is negative. Be sure to do a blank on the acetone. Test 1-butanol, 2-butanol, and t-butyl alcohol.

Name _____ Date _____
Lab Instructor _____ Section _____

EXPERIMENT 10

Reactions of the Functional Groups II: Aldehydes, Ketones, and Alcohols

Results; Observations

A. 2, 4-Dinitrophenylhydrazine
Acetone _____ Acetophenone _____
Cinnamaldehyde _____ Cyclohexanol _____
Benzaldehyde _____

Write reaction equations describing all positive reactions.

B. Fehling's Test
Acetaldehyde _____ Acetone _____
Reaction equation

C. Tollens' Test
Acetaldehyde _____ Acetone _____
Reaction equation

Results of silver mirror preparation

D. Iodoform Test

Acetone _____ 2-Propanol _____

3-Pentanone _____ Acetophenone _____

Benzaldehyde _____

Reaction equations for positive tests

E. Sodium Bisulfite

Acetone _____ Acetophenone _____

Benzaldehyde _____ Cyclohexanol _____

Reaction equations for positive tests

F. Lucas Test

1-Butanol _____

2-Butanol _____

t-Butyl alcohol _____

Reaction equations

G. Chromic Anhydride

1-Butanol _____

2-Butanol _____

t-Butyl alcohol _____

Reaction equations for positive tests

H. Reaction with Sodium Metal

1-Butanol _____ 2-Butanol _____

t-Butyl alcohol _____

Reaction equations for positive tests