Chemistry 350

Organic Chemistry I

Procedures Only
Laboratory Manual 2019-21

(104 pages
or 90 pages without Safety Section)

Athabasca University

CHEM 350 Procedures Only Lab Manual Contents

Safety

General

In 1975, a survey carried out by Her Majesty's Inspectors of Schools showed that of the 70,000 accidents reported in British schools, only two per cent occurred in a science laboratory. Although Athabasca University students are not attending laboratory sessions in Britain, and are more mature than most school-children, this statistic is relevant to the laboratory component of *Chemistry 350*. The figures suggest that, although a laboratory is a potentially dangerous place to work, the chances of an injury-causing accident are relatively low. This situation exists because of the strict safety rules that are applied to students working in laboratories, and because of a willingness of both students and instructors to look out for unsafe practices and possible hazards at all times.

Some people will approach the laboratory component of their Athabasca University chemistry course with a certain amount of trepidation. In a sense, this is a good thing—no one can afford to adopt a complacent attitude towards laboratory safety. However, you should realize that you could well face a greater chance of being killed or injured as you drive to the laboratory session than you will while you are working in the laboratory. Most of the hazards that you are likely to face while performing the experiments in this laboratory are relatively minor and easily avoided. They include:

minor cuts—most cuts can be avoided if a student never uses broken or cracked glassware, and is particularly careful when carrying out potentially dangerous operations, such as inserting glass tubing into a rubber stopper.

burns—burns usually occur when a student forgets that something which has just been heated on a hot-plate or in a heating mantle may be very hot.

chemical spills—spills can usually be avoided if students pay particular attention to the technique used when pouring chemicals from a container, and injury caused by spills can be minimized if students wear the appropriate protective clothing: safety glasses, gloves, and lab coat or apron.

Another possible danger is the presence of hazardous gases or vapours in the air. In this course, we have kept the use (or production) of such materials to a minimum. Where eliminating such materials is not practical, you will be advised to work in a fume hood, which will protect both you and your co-workers from exposure to undesirable concentrations of toxic or otherwise unpleasant vapours.

When designing the laboratory component of this course, we found it necessary to strike a balance between minimizing possible hazards and exposing you to a full range of techniques. By its very nature, chemistry often necessitates the handling of dangerous substances; if chemistry students are never exposed to such situations, we would never have any fully trained chemists. Having said this, perhaps we should reassure you that, provided you follow the safety rules that follow, we do not anticipate that any problems will arise.

Safety Rules

1. **Safety glasses must be worn in the laboratory at all times.** Wearers of prescription glasses may wear their own spectacles, but should be aware of the possibility that chemicals or flying glass could enter the eye through the gap between the temple and the frames of the glasses. Thus, in potentially hazardous situations, wearers of spectacles are advised to wear safety goggles or a safety mask over their prescription glasses. Contact lenses must *not* be worn in the laboratory.

   Note 1: Safety glasses will be provided by Athabasca University and must be worn at all times—even when you are not actively using chemicals and glassware. Remember that injury could result through carelessness on the part of one of your fellow students.

   Note 2: Contact lenses are not permitted for two reasons.

   a) If a chemical is splashed into the eye of a person wearing contact lenses, neither the normal tearing mechanism nor external irrigation (with water) is effective in removing chemicals from under the contact. The contact must first be removed before tearing and irrigation is effective; however, the contact may be difficult to remove because of the tight squeezing shut of the eye that occurs in response to the chemical in the eye. Since time is of the essence with a chemical burn, a delay caused by the necessity of removing a contact lens could have serious consequences.

   b) Soft contact lenses present an additional hazard. Any chemical (including vapours) that comes into contact with such a lens can diffuse into the interior of the lens, which then acts as a reservoir that can create additional exposure, even if the lens is removed and rinsed.

Note 3: The correct emergency treatment for chemicals that enter the eye is to wash the injured eye thoroughly with plain water for 15 minutes. Medical attention should be sought for all eye injuries. An eye-wash fountain should be available in the laboratory; make sure that you are aware of its location.

2. **A lab coat should be worn at all times.** You must purchase a lab coat in order to participate in the laboratory component of this course. A lab coat will not only make you look and feel like a chemist, but will also protect you and your clothes in the event that you inadvertently spill a chemical.

   While we are on the subject of clothes, dress sensibly. It can become very hot in the laboratory and you will not be comfortable working all day with a three-piece suit worn underneath your lab coat. Similarly, clothes worn in the laboratory tend to acquire a "chemical odour", and it may be advisable to leave your more expensive shirts and sweaters at home.

3. **Protect your feet by wearing "sensible" shoes.** Bare feet, open-toed sandals, etc., are not permitted. Spilling concentrated sulfuric acid on your big toe, or cutting your foot on a piece of broken glass would result in a trip to the hospital. Avoid high-heeled shoes; remember that you will be "on your feet" for up to eight and one-half hours on any given lab day.

4. **Tie back long hair.** Long hair can be a fire hazard. Also, when you bend over to inspect the contents of a beaker containing a chemical, long hair can easily fall into that chemical. Not only could this damage your hair, but it could also ruin your experiment!

5. **Never run in the laboratory, and never be tempted to become involved in practical jokes or other horseplay.**

6. **On no account attempt an unauthorized experiment.**

7. **Never work in the laboratory when the supervisor is not in attendance.** Our regulations require that at least one qualified supervisor be present in the laboratory whenever a student is working there.

8. **Eating, drinking and smoking are not permitted in the laboratory.** Food and drink may become contaminated by toxic substances. Smoking is a fire hazard. When you leave the laboratory, wash your hands, particularly before eating.

9. **In the event of fire:**

a. do not panic; many small fires can be extinguished without the use of a fire extinguisher, simply by cutting off the air supply. For example, when a flammable liquid 'catches' fire in a beaker, the fire can quickly be put out by placing an asbestos pad or watch-glass over the beaker.

b. if the use of a fire extinguisher is necessary, leave it to the supervisor and concentrate on getting yourself to the nearest exit.

c. in the event that your instructor is incapacitated (e.g., through injury), be prepared to extinguish a fire, especially if human life is in danger. To do so, you must know the location of the nearest fire extinguisher and how to use it. Most of the extinguishers that you will encounter are of the ABC type, which means they are effective on fires involving trash, wood or paper (Class A), liquids and grease (Class B), and electrical equipment (Class C). These extinguishers are not effective on Class D fires. (i.e. those involving active metals such as sodium and potassium). Fires involving the latter substances are unlikely to occur during a *Chemistry 350* lab, but you should be aware of the special problems that these materials can cause. When using a fire extinguisher, aim at the base of the fire and use a sweeping motion. Note that you should never attempt to extinguish a laboratory fire using water. (A possible exception might be to extinguish a burning paper towel by placing it in a sink and turning on the tap.)

d. if your clothing catches fire, wrap yourself in a fire blanket (or a coat if no fire blanket is available) and roll on the ground.

10. **Report all accidents.** All accidents, however minor, must be reported to your supervisor and the details entered in the accident book. If you are involved in an accident, do not resume work until you have received the appropriate first aid or medical attention. Never work with open cuts on your hands; cover all small cuts and scratches with 'band-aids'.

11. **Always dispose of chemical wastes in the correct manner.** In general, you would never dispose of chemicals, particularly organic solvents, by pouring them down the drain. Throughout the *Chemistry 350* laboratory manual you will find that you are told repeatedly to "pour excess reagents into the waste container provided". Ensure that waste chemicals are placed in the correct container—putting the wrong material into a container is potentially dangerous. Never attempt to return "used" chemicals to their original containers. Note that certain substances, such as dilute acids or solutions of "harmless" compounds (e.g., sodium chloride), etc., *may* be washed down the drain with copious amounts of water. When in doubt, check with your instructor. Be particularly careful to place any chlorinated hydrocarbons in the waste container designated for such substances.

12. **Never pour concentrated inorganic acid (e.g., H_2SO_4) or base into a bottle marked 'Organic Waste only'.** Violent exothermic reactions can occur between potential reagents, causing a splatter of toxic and corrosive material.

13. **Never over fill a waste bottle.** Keep an eye on the volume level in the waste bottle and let the instructor know when it is ¾ full.

Some General Advice About Laboratory Work

1. People with clean and tidy benches are less likely to be involved in accidents. Communal areas, such as balance rooms and fume hoods, should also be kept tidy. Clean up all spills. Any glassware containing chemicals that is left in a communal area should be clearly labelled with the owner's name and details of the contents (e.g., L. Worker, concentrated nitric acid).

2. Do not rummage through a cupboard or communal glassware/supply drawer or box without care and attention. Sharp object may be present. Discard sharp objects (needles, razor blades, broken glass in the appropriate sharps discard receptacle.

3. Wear your lab coat at all times when working in the lab, and wear protective latex gloves whenever handling corrosives and solvent. Do not store sharp objects (e.g., Pasteur pipettes) in your coat pocket.

4. When assembling apparatus or glassware, always check with the instructor before proceeding with the experiment.

5. Handle all organic solvents (e.g., acetone, dichloromethane) with care. Most are flammable, and many have a long-term, cumulative effect on the body.

6. If a fire starts, or the fire alarm sounds, unplug any electrical apparatus and vacate the laboratory in an orderly manner.

7. When diluting a concentrated acid, always **add the acid to the water**. Do so slowly, with stirring.

8. If you get acid on your clothing, neutralize it with **dilute** ammonia solution ($1\ mol \cdot L^{-1}$) and wash well with water.

9. If you get alkali on your clothing, wash it off with large quantities of water.

10. If you get any corrosive chemical on your skin, wash it off immediately with water and consult your instructor. Pay special attention to the safety notes given in bold type in the "Procedure" sections of the lab manual. These notes will inform you of any special precautions that you might need to take, and will also inform you if the "wash well with water" maxim does not apply.

11. If you spill a large quantity of acid on the bench or floor, use crude sodium bicarbonate (available from the instructor) to neutralize the acid and then wash well with water.

12. Mercury from broken thermometers presents a special kind of hazard. The vapour from the spilled mercury represents a long-term hazard and so the liquid mercury should be cleaned up very carefully. If you break the thermometer, ask your instructor for assistance in cleaning up the mercury. Do not touch the mercury globules with your hands.

13. Always check for any possible hazards associated with using a given chemical. The quickest way of doing so is to make certain that you read the label on the container from which the chemical is removed. Some chemical manufacturers use symbols or codes on the labels of their chemical containers to indicate possible hazards. When in doubt, consult your instructor.

14. In the event of a real emergency, it could be important for medical personnel to know certain facts about you, facts that they could not obtain if you were unconscious or in a severe state of shock. On the next page is a copy of a *Medical Information Form* that you should have received either with this laboratory manual, or separately in the mail. We advise you to fill out the form that you received, and paste it inside the front cover of your lab notebook. You might regard some of this information as being rather personal. However, keep in mind that normally we do not expect you to show us your lab notebook (see "Writing Laboratory Reports") so confidentiality of your medical history should be maintained. If you still have doubts, keep in mind that, in the event of an accident, your instructor has been asked to put your lab notebook on your stretcher as they carry you off to the hospital.

15. As mentioned in the safety rules, all accidents that result in injury must be reported and recorded in the accident book. In addition, an "Accident Report Form" must be completed and returned to the course co-ordinator. A sample form is shown on the page after next.

Note: The *Medical Information Form* on the next page is adapted from one suggested by Ben Ruekberg and David W. Ball, *Journal of Chemical Education*, 63, **A247** (1986).

CHEMISTRY LAB SAFETY DO's and DON'TS

Before You Attend a Chemistry Lab	
DO's	**DON'T's**
Read your lab manual 'Safety' section.	Think that ignorance is bliss.
Know the procedures.	Forget your lab manual and rely on your memory.
Know the dangers.	Have a casual attitude.
Bring a lab coat.	Wear your best clothes.
Be well rested and alert.	Sleep-in and arrive late.
Fill out the Medical Information Form in your lab manual or inform the instructor of any personal medical condition.	Hide a medical condition that might jeopardize your safety or the safety of others.
Some people will approach the laboratory component of their AU chemistry course with a certain amount of trepidation. In a sense, this is a good thing because: **NO ONE SHOULD EVER ADOPT A COMPLACENT ATTITUDE TOWARDS LAB SAFETY**	

During a Chemistry Lab	
SAFETY DO's:	**SAFETY DON'T's:**
Keep your workbench neat and organized.	Place full reagent flasks near the edge of the bench.
Label all reagents/containers.	Mix unknown chemicals.
Read the MSDS for a hazardous chemical.	Forget WHMIS stands for Workplace Hazardous Materials Information System.
Ask how to discard used reagents.	Pollute the environment.
Wear your safety glasses at all times.	Take off your safety glasses or touch your face with soiled latex gloves.
Report accidents to the instructor immediately.	Attempt to clean up a spill by yourself or leave the lab to treat an injury by yourself.
Take a rest break now and then.	Be in a rush to finish.
AN EXPERIMENT DONE WELL IS... AN EXPERIMENT DONE SAFELY.	

Sample Medical Information Form: *Chemistry 350*

Name: A. Student

Social Insurance Number: 123 456 789

Address: 4812, 43rd Street, Small Town, Alberta

Phone: 675-6111

Alberta Health Care Number: 987.65.432.123

Age: 35

Sex: M

Height: 173 cm

Weight: 68 kg

Chronic medical problems: Epilepsy

Current medical problems: None

Do you normally wear contact lenses? No

Physical disabilities: Partially deaf

Allergies to medication: Allergic to penicillin

Current medication being used: None

Personal physician: Dr. V. Rich

In case of emergency, please contact: Susan Student (wife) 675-6111

Special information: My religious beliefs prevent me from accepting a blood transfusion.

Chemistry Laboratory Accident Form (Student Labs)

Name of injured student: Alan Student

Date of incident: April 1, 2006

Time of incident: 2:06 p.m.

Course: *Chemistry 350*

Instructor: A. Tutor

Nature of injury: Glass tubing penetrated palm of right hand.

How injury incurred: Student was attempting to insert glass tubing into rubber stopper without using recommended lubricant.

First aid rendered: Wound was washed thoroughly, a piece of glass appeared to be embedded in the hand. Pressure applied around the wound using a ring pad. Covered with built-up dressing.

First aid rendered by: A. Tutor (instructor), G. Help (student)

Further medical treatment sought? (if yes give details). Patient was driven to outpatients at the nearest hospital where the wound was examined and the embedded glass removed.

Instructor's comments: Student returned to lab at 4 p.m. to collect belongings. His wife had been contacted and she came to drive him home.

Was instructor in the room when the incident occured? Yes

Student's signature: A. Student

Follow up (course co-ordinator): Contacted student by phone (April 3), his condition is now being monitored by his family physician.

WHMIS

On October 31, 1988, the Workplace Hazardous Materials Information System (*WHMIS*) went into effect. This is a national system intended to provide laboratory personnel with uniform information on chemicals used in the workplace. There are three main features of WHMIS:

1. Chemical manufacturers are now obliged to label each container of hazardous material, giving details on the product's hazards and what action to take in an emergency.

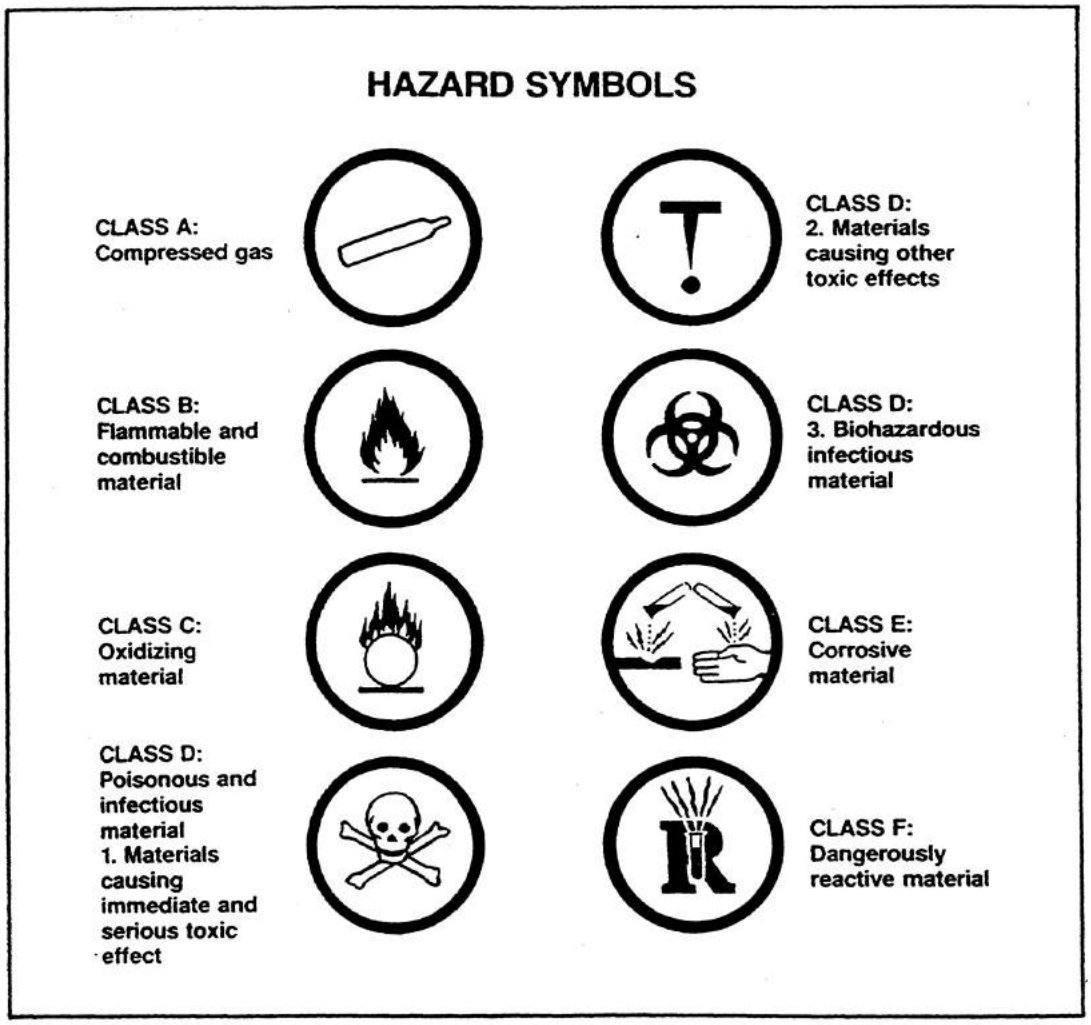
2. The manufacturer must provide the consumer with a Material Safety Data Sheet (*MSDS*) for each hazardous product. These sheets give complete details on the possible health effects that exposure to the product can produce, preventive measures that should be taken, etc.

3. Employers must provide an appropriate education program for all workers whose work may bring them into contact with hazardous products.

The WHMIS regulations do not affect you as a student, although if you are involved in a chemistry-related job you should be familiar with them. Most of the chemicals that you will handle in this course are no longer in their original containers. Under the WHMIS regulations, such chemicals do not require detailed labels. However, you should read all labels carefully, and pay special attention to the hazard warnings that appear throughout the laboratory manual. The hazard symbols that you may observe on certain chemical containers are reproduced on the following page. A file containing up-to-date MSDSs for all the chemicals used in *Chemistry 350* is maintained at each of the locations where laboratory sessions for these courses are held. Additional information on WHMIS may be obtained from Alberta Community and Occupational Health, Occupational Health and Safety Division.

Note: Athabasca University is now requiring all lab students take a certified WHMIS Training course (either with us or show proof that you have take one elsewhere).

Hazard Symbols



Experiment 1
Melting-point Determinations

Observe the sample through the illuminated magnifying lens. You may be able to observe **four stages of melting** may be observed:

1. first signs of change (for example, shrivelling).
2. first signs of liquid formation. Record the lower limit at this point
3. formation of a meniscus.
4. formation of a completely clear liquid. Record the upper limit.

Not all samples will behave in this ideal manner. The range that you should record is that for steps 2-4; i.e., from the first sign of liquid formation to the formation of a completely clear liquid.

If the melting point of the sample is unknown, you will need to employ a slightly different procedure from that described above. Your first step will be to determine the approximate melting point by carrying out a "preliminary run," employing a rapid rate of heating throughout. Once the approximate melting point has been determined, you may proceed as described above.

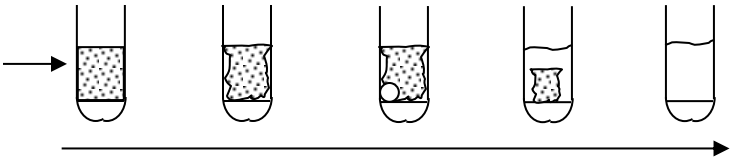
If you have a series of melting points to determine, it is advisable to do the sample with the lowest melting point first, the second lowest melting point next, and so on. This strategy will eliminate the necessity of having to allow the apparatus to cool down between determinations. The approximate times required for the apparatus to cool down between certain temperatures are given in Table 1.2. **Note: cooling times can be lessened by blowing air gently into the heating block area of the mp apparatus, using a piece of rubber tubing and some compressed air.**

Table 1.2: Cooling Times for the Electrothermal Melting Point Apparatus

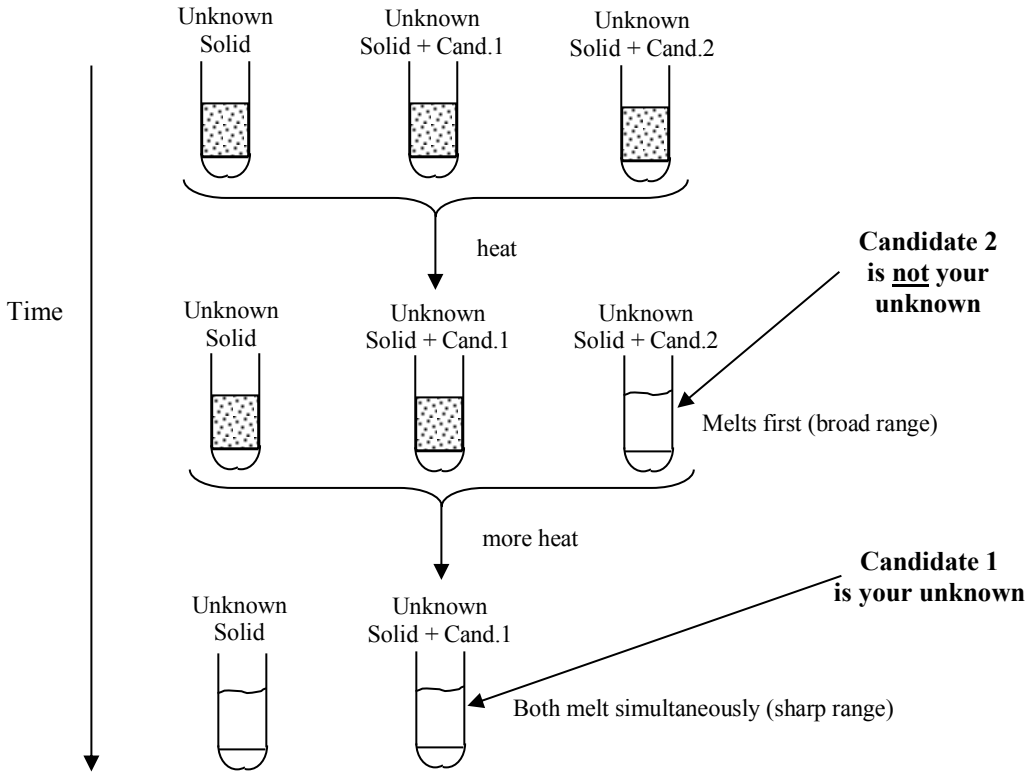
To cool	from	to	requires
	360°C	300°C	1.5 minutes
	300°C	200°C	3.0 minutes
	200°C	100°C	4.5 minutes
	100°C	40°C	7.0 minutes

Experiment 1 Background Information

This experiment contains two parts. In the first part, you will determine the melting point of an unknown, then check with your instructor on the accuracy of your reading. In the process you will learn how to fill a melting point tube, how much sample to place into the tube, how to operate the melting point apparatus. Finally, you will observe the four stages of a melting point.



In the second part, you will determine the identity of an unknown compound using the mixed melting point procedure. Note that you have been provided with two candidate identities for your unknown compound. The quickest way to determine the identity of your unknown is to prepare three melting point tubes, the first containing your unknown, the second your unknown mixed with candidate 1, and the third, your unknown mixed with candidate 2. Read all three tubes simultaneously in the melting point apparatus. Eventually one of the mixed tubes will begin to melt. This is the candidate that your sample is **not**. Finally, two of the tubes will melt simultaneously. This candidate, which you've mixed your sample, is the identity of your unknown.



Chemicals, Equipment, Utilities Required:

All equipment used for melting points must be clean and free of any organic contamination.

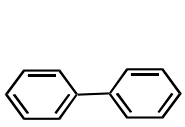
Chemicals	Equipment	Utilities
benzoic acid, biphenyl, 4-nitrobenzoic acid, 4-nitrobenzaldehyde, 2-methylbenzoic acid, urea, trans-cinnamic acid, 3-chlorbenzoic acid, salicylic acid, wash acetone.	-melting-point apparatus (Gallenkamp or Electrothermal), -thermometer, melting point tubes, porous plate, spatula, beaker, buret drop tube, mortar and pestle -hazardous waste disposal containers (in fume hood)	115V electrical

Part A: List of Compound Codes Used as Simple Melting Point Unknowns

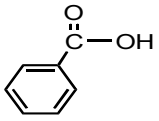
Unknown Code	Melting Point is within the range of:
1-A-1	60-80° C
1-A-2	110-130° C
1-A-3	230-250° C

Part B: List of Compound Used as Mixed Melting Point Unknowns

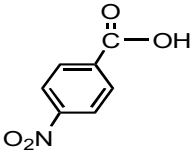
Unknown Code	Candidate 1	Candidate 2
1-B-1	4-nitrobenzaldehyde	2-methylbenzoic acid
1-B-2	4-nitrobenzaldehyde	2-methylbenzoic acid
1-B-3	urea	*trans*-cinnamic acid
1-B-4	urea	*trans*-cinnamic acid
1-B-5	3-chlorobenzoic acid	salicylic acid
1-B-6	3-chlorobenzoic acid	salicylic acid



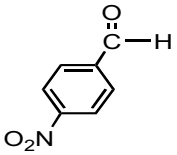
biphenyl



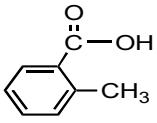
benzoic acid



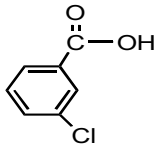
4-nitrobenzoic acid



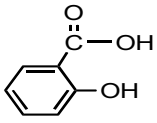
4-nitrobenzaldehyde



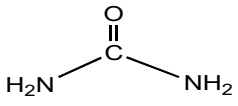
2-methylbenzoic acid



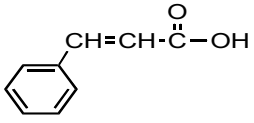
3-chlorobenzoic acid



salicylic acid



urea



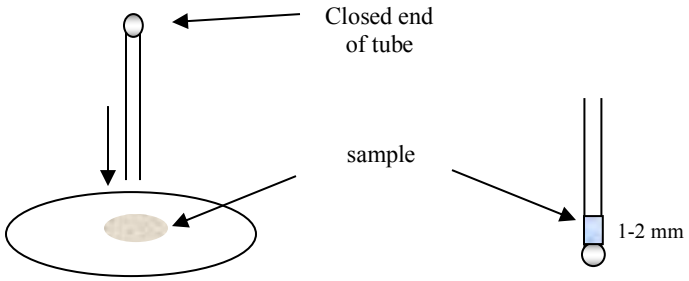
trans-cinnamic acid

Procedure

To Prepare a Melting Point Sample

1. Place about 0.1 g (a small amount) of the compound onto a porous plate, watch glass or in a mortar. Crush the solid to a fine powder by gently rubbing it with the flat end of a spatula or pestle.
2. Transfer a small quantity of the fine powder to the capillary tube by pushing it in the open end.
3. Pack the sample by using a 'drop tube'. The packed sample should be 1-2 mm in height.

Use just enough of the material so you can see it melt.



If you need more information, ask your instructor, or read the sections on "Sample Preparation" and "Loading the Melting Point Tube", page 33 in J.W. Zubrick's *The Organic Chem Lab Survival Manual*.

Part A: Single Melting-point Determination

Determine the melting point of the sample provided. You will be told the approximate melting point of the sample so that you can decide on the most appropriate setting for the melting point apparatus. Note that it may be necessary to crush the sample using a mortar and pestle before loading the melting-point tube. Record your experimentally determined melting point, and the code number of the sample.

Part B: Mixed Melting Point

You will be assigned an unknown sample and will be given a number of suggestions about its possible identity. Look up the melting point of each of these compounds in one of the reference books provided (see Appendix 1 for help if necessary) to get an approximate idea of the melting point of your compound. Determine the melting point of your assigned compound using the "melting-point apparatus". Crush a sample of your compound with each of the compounds that you believe it could be (50:50 mixture), load both into melting point tubes, and then determine the melting point of each of these mixtures. From your results, deduce the identity of the unknown compound.

Write-up

Follow the format for a standard investigative report. Be brief. An outline of what you did, the results obtained, a note of any observations made, and an answer to the assigned question is all that is required. Please make sure that your results are presented clearly. An example of how this could be done is shown below.

Part A

Melting point of sample # _____ = _____

Part B

Possible identity of unknown compound # _____ :

1. _____ ; m.p. (Reference)

2. _____ ; m.p. (Reference)

Melting point of unknown compound # _____ = _____

Melting point obtained when unknown compound # _____ is mixed with

1. _____ = _____

2. _____ = _____

Conclusion: The above results indicate that unknown compound # _____ is

probably _____.

Questions

1. In the introduction to this experiment you were warned that heating the sample too quickly in the region of the melting point will result in the experimentally determined melting point being higher than the true value. Explain why this is so.

2. What is a "eutectic mixture"? How would you decide whether a given sample was a pure compound or an eutectic mixture of two compounds?

3. You are working in the lab, and you find an unlabelled vial with a white crystalline solid inside. To determine the identity of the compound, what would you do?

4. i. Give two reasons why you should calibrate your thermometer before using it for a melting point determination.
   ii. How do you properly 'cool off' a melting point thermometer?

Remember to photocopy you lab report before mailing it to your academic expert for marking.

For additional information

If you have any questions regarding the operation of the melting point apparatus, please talk to your laboratory instructor. The instruction booklet for the apparatus, *A Guide to Melting Point Determination*, 2nd ed., published by Electrothermal Engineering Ltd., 1978, should be available for consultation in the laboratory.

Experiment 2
Recrystallization

Remember the 5 steps of a recrystallization. They are:

1. Select solvent (soluble in hot, insoluble in cold)*.
2. Dissolve the solid in a minimum of hot solvent to give a saturated solution.
3. Decision time? Hot gravity filter if solid impurities (particulates) are present. Add charcoal if coloured impurities are present.
4. Cool slowly to room temperature. Allow crystals to form. Cool crystals on ice.
5. Collect crystalline product by vacuum filtration. Save the filtrate for possible second crop of crystals. Wash crystals with **ice cold** solvent, and allow to air dry to a constant weight.

***More on Selecting a Suitable Solvent:**

A suitable solvent should also meet as many as possible of the following criteria:

1- Have a boiling point in the 60-100° C range, and this temperature should be lower than the melting point of the solid (to avoid 'oiling out').
2- Have a freezing point well below room temperature, preferably below 4° C.
3- The solvent must not react with the solid compound being purified.
4- Impurities should be highly soluble, or totally insoluble in the solvent.
5- The solvent must not be excessively hazardous.
6- 100 mL of the solvent should dissolve about 5 to 25 g of the solid when boiling and less than 2 g when cold, with at least a 5:1 ratio between the two values.

Important: You should consider a two-solvent recrystallization only when a single suitable solvent cannot be found.

Chemicals, Equipment, Utilities Required:

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
acetanilide (impure), sucrose calcium carbonate silica (optional) distilled water ice wash acetone	-Hot plate, drying oven melting-point apparatus (Gallenkamp or Electrothermal), -250 mL Erlenmeyer flask, boiling stones, short stemmed funnel, filter paper -thermometer, melting point tubes, porous plate, spatula, buret drop tube, mortar and pestle -hazardous waste disposal containers (in fume hood)	-115V electrical, -vacuum or water aspirator line

About Handling Hot Glassware and Hotplates

- At all times use hand protection (finger cots, 'hot-hands', or insulated gloves) when holding heated glassware.
- Do not place a dry empty flask on the hot plate. It will crack.
- The surface of the hot plate is like a clothes iron. You cannot see if it is hot!! Hot plates are the most frequent source of burns to the skin in the laboratory.
- Never fill and heat a flask more than 2/3 full (even with boiling stones). The solvent will boil over.

Erlenmeyer Flasks vs. Beakers

Beakers are never used for a recrystallization. Erlenmeyer flasks are used instead. Why?

- Erlenmeyer flasks have a narrow neck that allows some refluxing of the solvent, and thus slows the rate of solvent evaporation.
- The narrow neck of an Erlenmeyer flask also allows you to swirl the liquid, thereby aiding in dissolving the solid.
- A flask can be stoppered to prevent evaporation during the cool down. You cannot easily stopper a beaker.
- It is only slightly more difficult to remove crystals from an Erlenmeyer flask than a beaker.

Procedure — Single Solvent Recrystallization

1. In this experiment, Step 1 of recrystallization, **'selecting the solvent'**, has already been done for you. Water dissolves acetanilide when hot, and acetanilide is highly insoluble in cold water.

2. **Dissolving the acetanilide.**

   a. Obtain about 100 mL of distilled water in a 250-mL Erlenmeyer flask, add one or two boiling stones, and heat the flask on a hot plate until the water boils.

   b. While you are waiting for the water to boil, place a short-stemmed funnel and a second 250-mL Erlenmeyer flask in an oven set at about 120°C, and measure out about 5 g of impure acetanilide into a third 250 mL Erlenmeyer flask. Also fill a melting point tube with a small amount of the impure acetanilide.

   c. Add one or two boiling stones to the flask containing the acetanilide, and then add about 10-15 mL of boiling water from the first flask.

   d. Place the flask containing the suspension of acetanilide on the hot plate, and bring the water to the boil. Continue to add hot water from the first flask to the acetanilide until all the latter appears to have dissolved. (Remember, the sample that you were given contains impurities, so not all of the solid will disappear.) When all the acetanilide appears to have dissolved, add a further 5-10 mL of hot water to the solution to help keep the acetanilide in solution during the hot gravity filtration.

   e. Allow the boiling solution to cool for a moment (to prevent 'bumping' of the liquid), then add a pinch of activated charcoal (see pp. 55-56 in *The Organic Chem Lab Survival Manual* or pp.127-128 in the third edition). Carefully bring the solution back to the boil in preparation for the hot gravity filtration.

3. **Hot gravity filtration.**

   a. Prepare a fluted filter paper as described in *The Organic Chem Lab Survival Manual*, pp. 61-63 (pp.132-133 in third edition).

   b. Remove the **short-stemmed funnel** and 250-mL Erlenmeyer flask from the oven. Place the funnel into an iron ring attached to a ringstand and put the fluted filter paper into the funnel. Place the clean, warm Erlenmeyer flask beneath the funnel. (See Figure 26 on p. 51 of *The Organic Chem Lab Survival Manual* or Fig.59 on p. 122 in third edition).

c. Pour a small quantity (about 5-10 mL) of solvent (hot distilled water) through the filter, and then begin to filter your acetanilide solution. **Try to keep your unfiltered acetanilide solution close to boiling all the time.**

d. When the filtration is complete, pour 5-10 mL of boiling water through the filter paper, particularly if it appears that some of the acetanilide has crystallized onto the paper. If major crystallization has occurred, consult your instructor.

Cautionary note: It is very tempting to turn the hot-plate control to its highest setting during the above steps, but you should try to resist this temptation as it is likely to result in the solution "boiling over". In this experiment we have used water as a solvent, and so there is no risk of fire. In later experiments the solvents that you use to recrystallize your products are likely to be flammable. When a flammable solvent comes into contact with an overheated hot plate, fire can result. Use an appropriate setting on your hot plate at all times, never leave a flask or beaker heating on a hot plate unattended, and do not forget to use a new boiling stone each time you heat or reheat a liquid or solution.

4. **Crystal Formation**

Loosely stopper the mouth of the Erlenmeyer flask that contains the hot filtrate, and allow the solution to cool while you proceed with another experiment. If crystals started to form in this flask during the filtration (step 3d above), redissolve them by warming the flask before you stopper it. In extreme cases, for example, if the entire contents of the flask seems to have solidified, consult your instructor.

5. **Vacuum or Suction filtration.**

a. After the filtrate has been cooling for 25-30 minutes, a good crop of crystals should have formed and the Erlenmeyer flask containing these crystals should be placed in an ice-bath for a further 10-15 minutes. During this time, the apparatus for performing a vacuum filtration should be set up. (See *The Organic Chem Lab Survival Manual*, pp. 53-55 and 56-58 or pp.123-129 in the third edition).

b. Filter off the acetanilide crystals (from the surrounding liquid; called the 'mother liquor'), washing the crystals with a small quantity of cold distilled water, as described in *The Organic Chem Lab Survival Manual*. Allow the crystals to dry overnight, or until your next laboratory session.

Note: Do not discard your filtrate until after your instructor has determined whether you need to obtain a "second crop" of crystals.

Final Analysis: Melting-point determination.

1. Determine the mass of pure, dry acetanilide obtained, and calculate your percentage yield.

2. If you have already completed Experiment 1, determine the melting point of your starting material and product. If you have not yet completed Experiment 1, please do so before you attempt to determine the melting point of your recrystallized acetanilide.

3. Submit your sample to your instructor in a suitably labelled vial. (See Section 22, "On Products," in *The Organic Chem Lab Survival Manual*, Chapter 11 in the third edition).

Optional: The "second crop."

If your yield is particularly low, for example, if you used an excessive amount of solvent, your instructor may advise you to obtain a "second crop" of crystals. Transfer the filtrate obtained from the vacuum filtration to a 250-mL Erlenmeyer flask, add a boiling stone and a pinch of activated charcoal, and then boil this solution until its volume has been reduced to about 25% of its original volume. Carry out a hot gravity filtration as before, allow the filtrate to cool, and separate the crystals from the mother liquor by vacuum filtration. After the crystals are dry, determine the yield and melting point of this second crop, and submit them to the instructor in a suitably labelled vial. Note that second-crop crystals are often not as pure as those obtained in the first crop.

Write-up

Use an investigative style report for this write-up. Be brief, and be sure to record the mass of impure acetanilide used, the mass of pure acetanilide recovered, the percentage recovery yielded, the melting point of starting material and product, and finally, the structure of the product.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to these questions should be submitted with your report.

1. The table below shows the solubility of a certain organic compound in water at five different temperatures.

Temperature (^oC)	Solubility of compound (in 100 mL of water)
0	1.5 g
20	3.0 g
40	6.5 g
60	11.0 g
80	17.0 g

   a. Plot a graph of the solubility of the compound versus temperature. Draw a smooth curve through the data points.
   b. If a student attempts to recrystallize a 0.5 g sample of this compound by heating it to 80^o C with 5.0 mL of water, would all of the sample dissolve? Briefly justify your answer.
   c. Assuming that the answer to part b is "Yes", at what temperature will the crystals begin to appear when the student's solution begins to cool?
   d. If the student cooled the solution to 0^o C and filtered off the crystals, what is the maximum possible percentage recovery? What mass of the sample will remain in the filtrate?

2. Explain why you should slowly cool the filtered saturated solution obtained in step 3 of the recrystallization procedure?

3. During the last step of the recrystallization procedure, you collect the crystals by vacuum filtration. Why do you use ice cold recrystallization solvent to help transfer all the crystals to the Büchner funnel and wash the crystals?

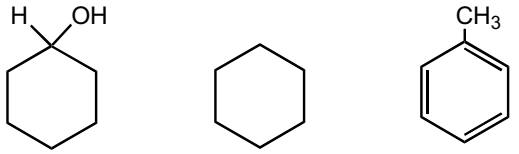
4. Briefly explain the circumstances under which a mixed solvent recrystallization method would be used to recrystallize a given compound.

Experiment 3
Distillation

Distillation Procedure:
Remember there are six steps required to perform a distillation. They are:

1. Select the heat source (heating mantle, Bünsen burner, steam bath, or water bath).
2. Clean, dry and assemble the distillation apparatus. Use joint grease?-No.
   - i) Start assembling the apparatus from the bottom up.
   - ii) Place heat source in position. Use lab jack to adjust height.
   - iii) Clamp distillation flask in position.
   - iv) Place three-way connector into distillation flask.
   - v) Place thermometer adapter into the top of three-way connector.
   - vi) Set approximate height of receiving flask using a utility clamp.
   - vii) Place condenser into position and secure with joint clamps.
   - viii) Attach tubing to water inlet and water outlet to the condenser.
   - ix) Adjust height of thermometer.
   - x) Inspect to ensure no joint is under stress, and that the system can be safely heated. (i.e., it is open to the air via the vacuum take-off adapter and it is not a BOMB.)
3. Turn on the cold water supply to the condenser. Check for water leaks.
4. Add the liquid to be distilled to the distillation pot. Add boiling stones.
5. Heat the liquid and collect the product in the receiving flask.
6. Allow the apparatus to cool and disassemble it. Clean all glassware parts thoroughly with acetone (discard in organic wastes) before washing with soapy water.

In Part A of this experiment, you will be given an impure sample of cyclohexanol (contaminated with toluene (soluble impurity)). You will remove the contaminating toluene first (called the 'forerun'), then collect a second fraction containing 'purified' cyclohexanol.



cyclohexanol cyclohexane toluene

In Part B of this experiment, you will be given a 1:1 mixture of cyclohexane and toluene. You will fractionally distil the mixture, collecting first mainly the cyclohexane (fraction 1), then you will collect an intermediate second fraction containing the both cyclohexane and toluene, and finally a third fraction containing mainly toluene.

Important: The boiling point of a liquid is defined as the temperature at which the atmospheric pressure and the vapour pressure of the liquid are equal. Thus the boiling point of a liquid is pressure dependent. (e.g. the lower the atmospheric pressure the lower the boiling point or the higher the elevation the lower the boiling point**). Approximate correction is 0.5° C per 10 torr difference from 760 torr (1 atm).**

Chemicals, Equipment, Utilities Required:

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (impure), toluene vacuum (glass joint) grease distilled water ice wash acetone	-heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three-way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, fractionation column, boiling stones) -hazardous waste disposal containers (in fume hood)	-115V electrical, -cold water supply

About Assembling Distillation Glassware, and Using Boiling Stones and Heating Mantles

Distillation Glassware

- Remember to inspect all glassware for **star-cracks** (especially the distillation round bottom flask).

Boiling Stones

- Never add a boiling stone to a solution that is already hot! A violent degassing of the liquid might result, which will cause the hot liquid to splatter out of the vessel. Also, when 're-boiling' a liquid, use a fresh boiling stone.

Heating Mantles

- Do not use a heating mantle with a damaged electrical cord.
- Never add reagents to a flask while it is sitting in a heating mantle.

Procedure

In the first part of this experiment you will purify a sample of cyclohexanol (b.p. 161°C) by simple distillation. The reason that we have chosen to use cyclohexanol is because you will use this compound in a later experiment, and the purified sample that you obtain today can be saved for use in the later experiment. The second part of today's experiment involves the separation of a mixture of cyclohexane and toluene by fractional distillation. In Experiment 4 you will determine how successful this separation has been by measuring the refractive index of a number of fractions of the distillate.

Part A: Simple Distillation

Place 20 mL of impure cyclohexanol in a clean 100-mL round-bottom flask* and **add one or two boiling stones** to the liquid. Set up the apparatus for simple distillation as shown in Figure 51 on page 104 of *The Organic Chem Lab Survival Manual* (Fig. 96, p.190 in 3rd ed.) with a 25-mL round-bottom flask as the receiver and supporting the heating mantle (i.e., the 'heat source') using a lab jack. Pay particular attention to the positioning of the thermometer **(range: -10 ° to 260 °C):** the top of the bulb should be level with the bottom of the side arm (see Figure 3.3, below).

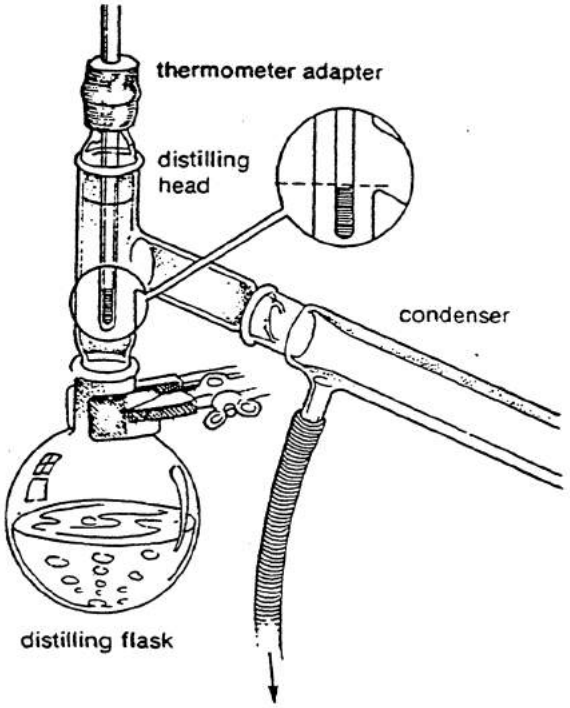


Figure 3.3. Thermometer placement during a simple distillation

Begin to heat the cyclohexanol by turning on the heating mantle to a setting of 6 or 6.5. After 10-15 minutes the liquid will begin to boil and the reading on the thermometer will increase. Allow about 4-6 mL of liquid to distil over and then replace the receiver with a clean 25-mL round-bottom flask*. The cyclohexanol should distil at a rate of about 10-20 drops per minute (monitor chilled water supply to condensor, as cyclohexanol may solidify in the condensor). Record the temperature range over which this fraction distils. This is the boiling range (i.e., the boiling point) of cyclohexanol and it should be in the order of 160°C. Collect about 14-15 mL of cyclohexanol in this way; that is continue until only a few millilitres of liquid remain in the distillation flask, or until the temperature recorded on the thermometer begins to increase. **Remember: Never distil to dryness.** Use a graduated cylinder to measure the volume of distillate collected, transfer the distilled cyclohexanol to a suitable labelled container, and hand it to your instructor for grading. Your sample will be returned to you for use in Experiments 4 and 8. Place the first few millilitres of distillate that you collected, called the **fore-run**, and the cyclohexanol that remained in the distillation flask should be placed in the container provided.

***Note:** If there are no 100-mL heating mantles available, use a 250-mL mantle and flask, and 75 mL of cyclohexanol.

Part B: Fractional Distillation

Place 25 mL of the cyclohexane-toluene mixture in a 100-mL round-bottom flask^ and add one or two boiling stones to the mixture. **Loosely** pack a fractionating column with steel sponge. Assemble the apparatus for fractional distillation as shown in Figure 56 on page 114 of *The Organic Chem Lab Survival Manual* (Fig.104, p.206 in 3rd ed.). Use a heating mantle (supported by a lab jack) as the 'heat source'. Slowly heat the contents of the flask (a setting of 3-4 on the heating mantle is about right to begin with) and watch the vapours rise in the column. When the vapours begin to reach the bulb of the thermometer, reduce the rate of heating so that for several minutes the ring of condensing vapours is kept between the top of the column packing and the sidearm. This procedure allows the vapour composition to stabilize before any distillate is collected. Now, turn up the heat slightly so that the mixture begins to distil. Collect the first few millilitres of fore-run in a small round-bottom flask and discard this material in the container provided. Collect three fractions of distillate in three different clean, dry, round-bottom flasks. The first fraction will consist of material that distils below 85°C, the second fraction will consist of material that distils between 85°C and 100°C, and the third fraction will consist of material that distils between 100° and 105°C. Use a graduate cylinder to measure the volume of each fraction, transfer the three fractions to three suitably labelled containers, and hand them in to the instructor for grading. The samples will be returned to you for use in Experiment 4.

^**Note:** As in Part A, if a 100-mL heating mantle is not available, use a 250-mL flask and mantle. If this is necessary, the volume of cyclohexane-toluene mixture used should be increased to 75 mL.

Safety

Cyclohexanol is flammable, irritating to the skin and eyes, and is harmful if inhaled or ingested.

Cyclohexane is flammable and may irritate the skin, eyes and respiratory tract. Avoid contact with the liquid or its vapour, and keep it away from hot surfaces and open flames.

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in nausea, headaches, vomiting and dermatitis. Avoid contact with the liquid, do not breathe its vapours, and keep it away from hot surfaces and flames.

Additional information about the potential hazards involved in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Write-up

Only a 'brief' standard investigative report of what you did is necessary. However, be sure to record the volume of each of the fractions collected, and ensure that you report the boiling point (or range) of each fraction.

Questions

Answers to these questions should be submitted with your report.

1. A student who was performing a distillation for the first time failed to position the thermometer correctly. The bulb was set too high. What effect would this have on the observed boiling point of the liquid being distilled?

2. Under perfect conditions, the number of theoretical plates required to separate and ideal mixture of two components of boiling points T_A and T_B is given by the relationship:

$$= \frac{120}{T_A - T_B}$$

   On this basis, how many theoretical plates are needed to separate a mixture of cyclohexane and toluene? **Note:** In practice, the actual number of theoretical plates required may be as high as double the number predicted by this equation!

1. You suddenly notice you have forgotten to add boiling stones to your round bottom distillation flask, but the distillation is now in progress. What should you do?

2. What is the purpose of the condenser during a distillation?

Experiment 4
Refractive Index

Summary of Refractive Index Procedure

1. Turn on refractometer, and clean the sample application area.
2. Apply sample carefully using a Pasteur pipette.
3. Adjust side hand wheel to bring the light and dark halves to the center of the X.
4. Adjust thumb wheel for chromatic abberation and sharpen the interface between the light and dark halves.
5. Readjust side hand wheel to recenter the light and dark halves in the X.
6. Read meter by holding down the on/off switch and reading the upper scale.

Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (impure and pure), toluene, cyclohexane Exp. #B fractions 1-3 wash acetone	-Refractometer, Pasteur pipettes -hazardous waste disposal containers (in fume hood)	-115V electrical,

Warning about Using the Abbé Refractometer

Please be careful. Do not scratch the surface of the glass on the refractometer.

Procedure

Part A: Refractive Index of Cyclohexanol

For this part of the experiment, use the impure and purified cyclohexanol that you obtained from the simple distillation in Experiment 3. See the instructor if your sample has not yet been returned to you.

1. Ensure that the refractometer is plugged into a main outlet.

2. Open the hinged prism and use a Pasteur pipette to apply a small drop of sample (i.e., cyclohexanol) to the lower (fixed) prism.

   Caution: Do not touch the prism with your Pasteur pipette. The prism is easily scratched by any hard object, and scratching will wreck the instrument.

3. Close the prisms. A thin film of liquid will form between the surfaces of the two prisms. Turn on the instrument. The switch is on the left-hand side of the instrument as you look at it.

4. Look through the eyepiece and adjust the illuminator so that you obtain the best possible contrast between the light and dark halves of the visible field. The illuminator is adjusted by simply moving it up or down. This process requires patience and practice. Consult your instructor if necessary. Remember that certain organic liquids evaporate very quickly, although this should not be a problem with cyclohexanol.

5. Set the borderline between the light and dark halves on the intersection of the two crosshairs. This is achieved by rotating the hand-wheel located on the right hand side of the instrument as you look at it (see Figure 4.2).

6. If the borderline between the light and dark areas of the visible field appears as a coloured band (see Figure 4.4), **chromatic abberation** (colour dispersion) is said to have occurred, and you must **achromatize** the borderline. Achromatization can be achieved by rotating the compensator dial located just below the eyepiece.

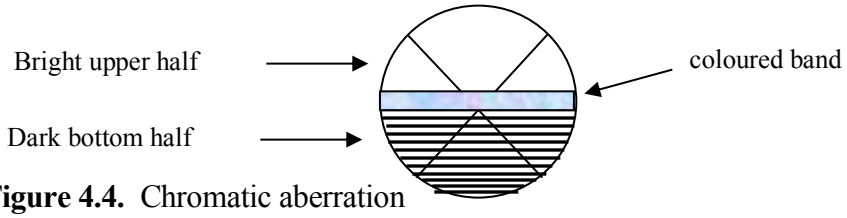


Figure 4.4. Chromatic aberration

7. Depress the contact switch (the same switch that you used to turn on the instrument) and read the refractive index of the sample from the top scale that will become visible through the eyepiece (see Figure 4.5).

   Note: The bottom scale is used for determining "total dissolved solids" and should be ignored.

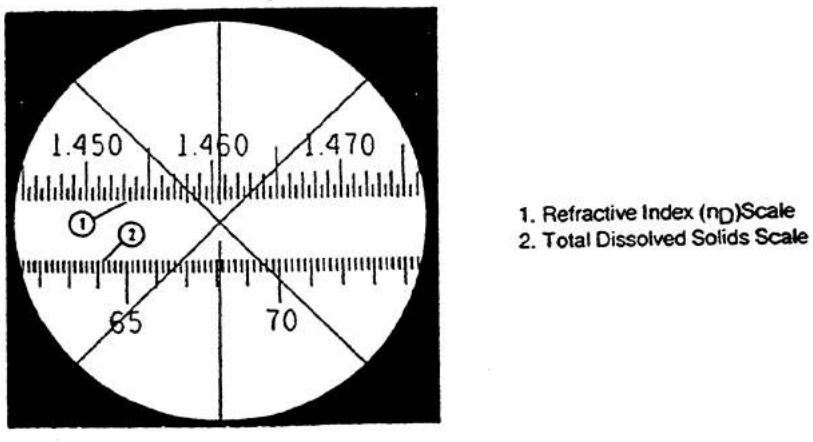


Figure 4.5. Reading the refractive index scale of an Abbé refractometer

8. Open the hinged prism and gently clean the two surfaces with a soft tissue made damp with acetone, ethanol or petroleum ether. When the solvent has evaporated from the prism surfaces, they should be locked together. **Remember:** do not touch the surfaces of the prisms with any hard or abrasive substance.

9. Proceed to Part B, or if you have completed the experiment, turn off the instrument.

Part B: The Composition of a Toluene-Cyclohexane Mixture

1. Using the instructions given in Part A as a guide, determine the refractive index of each of the following mixtures:

    a. the toluene-cyclohexane mixture used in Experiment 3.

    b. the three fractions retained from the fractional distillation carried out in Experiment 3. (**Note:** work quickly as sample will evaporate.)

2. Look up and record the literature values for the refractive indices of toluene and cyclohexane.

Safety

Cyclohexane is flammable and may irritate the skin, eyes and respiratory tract. Avoid contact with the liquid or its vapour, and keep it away from hot surfaces and open flames.

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in nausea, headaches, vomiting and dermatitis. Avoid contact with the liquid, do not breathe its vapours, and keep it away from hot surfaces and flames.

Additional information about the potential hazards involved in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Write-up

Only a brief standard investigative report is required. Provide an outline of what you did, the results you obtained, a note of any pertinent observations, and the literature values of the refractive indices of cyclohexanol, cyclohexane and toluene. Calculate the percentage error in the value of n_D that you observed for cyclohexanol. Determine the (mole) percentage composition of the three mixtures that you examined, and use these results to assess the efficiency of the separation achieved in your fractional distillation.

Questions

Answers are to be included with your report.

1. Look up the boiling points of cyclohexanol, cyclohexane and toluene in a suitable reference book and report your findings. Don't forget that when you quote a boiling point, melting point, or similar physical property you should always cite the source. Example:

   1,3-Butadiene; b.p. = -4.4° C (*Handbook of Chemistry and Physics*, 47th ed. Cleveland, Ohio: The Chemical Rubber Co., 1966)

2. Suggest a reason why the boiling point of cyclohexanol is so much higher than those of cyclohexane and toluene.

3. Suggest a reason why the refractive index of cyclohexanol is higher than that of water.

4. To reduce the percentage error in the n_D reading of your purified cyclohexanol (compared to the literature value), what should you do?

For Additional Information

If you have any questions about the operation of the Abbé refractometer, please talk to your laboratory instructor. The instruction booklet for the refractometer, *The Bausch and Lomb Abbé-3L Refractometer Operator's Manual*, published by Bausch and Lomb, Inc., 1983, should be available for consultation in the laboratory.

Experiment 5
Extraction, separation and the use of drying agents

Summary of Liquid-Liquid Extraction Procedure

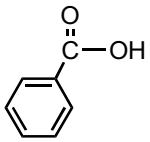
Remember there are essentially five steps to performing a extraction using a separatory funnel.

1. Dissolve the unknown compound in a solvent. Place the mixture in the separatory funnel supported with a ring clamp on a retort stand.
2. Add the extraction solvent to the separatory funnel.
3. Stopper the funnel, invert the funnel, vent, shake gently and vent again. Continue shaking/venting until no further pressure is released and then gently shake the funnel for 30 sec.
4. Return the separatory funnel to the ring clamp and allow the layers to separate.
5. Remove the stopper, drain the lower layer through the stopcock (out the bottom). Remove the upper layer by pouring it out of the top of the separatory funnel.

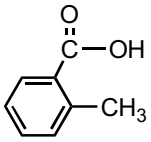
Experiment 5 Background Information

In this experiment, you will be given an unknown solid containing three organic compounds, one acidic, one basic and one neutral. You will separate the mixture using the extraction procedure, isolate the separated compounds, and then identify the individual compounds using mixed melting points. The compounds you will be working with are shown below.

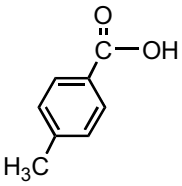
Acidic



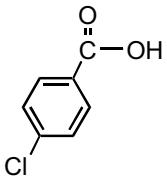
benzoic acid



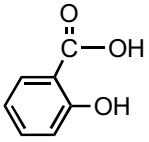
2-methylbenzoic acid



4-methylbenzoic acid

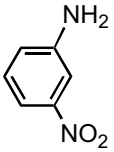


4-chlorobenzoic acid

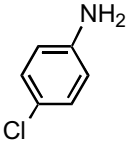


salicylic acid

Basic

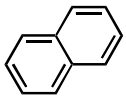


3-nitroaniline



4-chloroaniline

Neutral



naphthalene

Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
unknown organic solid mixture, dichloromethane, 5% NaOH, 1.5 M HCl, 12 M conc. HCl, 6M NaOH, distilled water, ice, methanol, ethanol, ethyl acetate, hexanes, wash acetone.	-separatory funnel and stopper, ring clamp, powder funnel -125 ml Erlenmeyer flasks (3-4) -10 mL graduated cylinder (2), Pasteur pipettes (2), stirring rod, pH indicator paper, water-ice bath -filter flask, Büchner funnel plus adapter, vacuum tubing, Whatman #1 filter paper circle -flat bottomed recrystallization dish, hot plate, Erlenmeyer flasks (2), sample vials plus labels -melting-point apparatus -rotary evaporator apparatus -halogenated and non-halogenated organic waste disposal containers (in fume hood)	-water aspirator , 115V electrical outlet

About Handling Separatory Funnels and Dichloromethane

- Inspect your separatory funnel for 'star-cracks'. Ensure that the stopper is the correct size for the separatory funnel. Pre-test your separatory funnel with acetone to check for leaks from the stopper or stopcock region.
- Very lightly grease the stopper and stopcock to prevent leaking, sticking or freezing of the ground glass joints. If the separatory funnel has Teflon® stoppers and stopcocks, greasing is not necessary, since Telfon® is self-lubricating.
- Also, choose the size of the separatory funnel so that the total volume of liquid in the funnel is less than 75% of the total capacity of the funnel. (Ref: Mayo et al, 1989. Microscale Organic Laboratory, John Wiley & Sons, New York, p.77).
- Latex gloves provide little protection against dichloromethane. Use the **Viton® rubber gloves** provided when handling this solvent. Use the **halogenated** organic waste container to dispose of unused / used dichloromethane.

Your instructor will assist you when you first use the rotary evaporator. However, by the end of the course you should be comfortable using this useful piece of equipment.

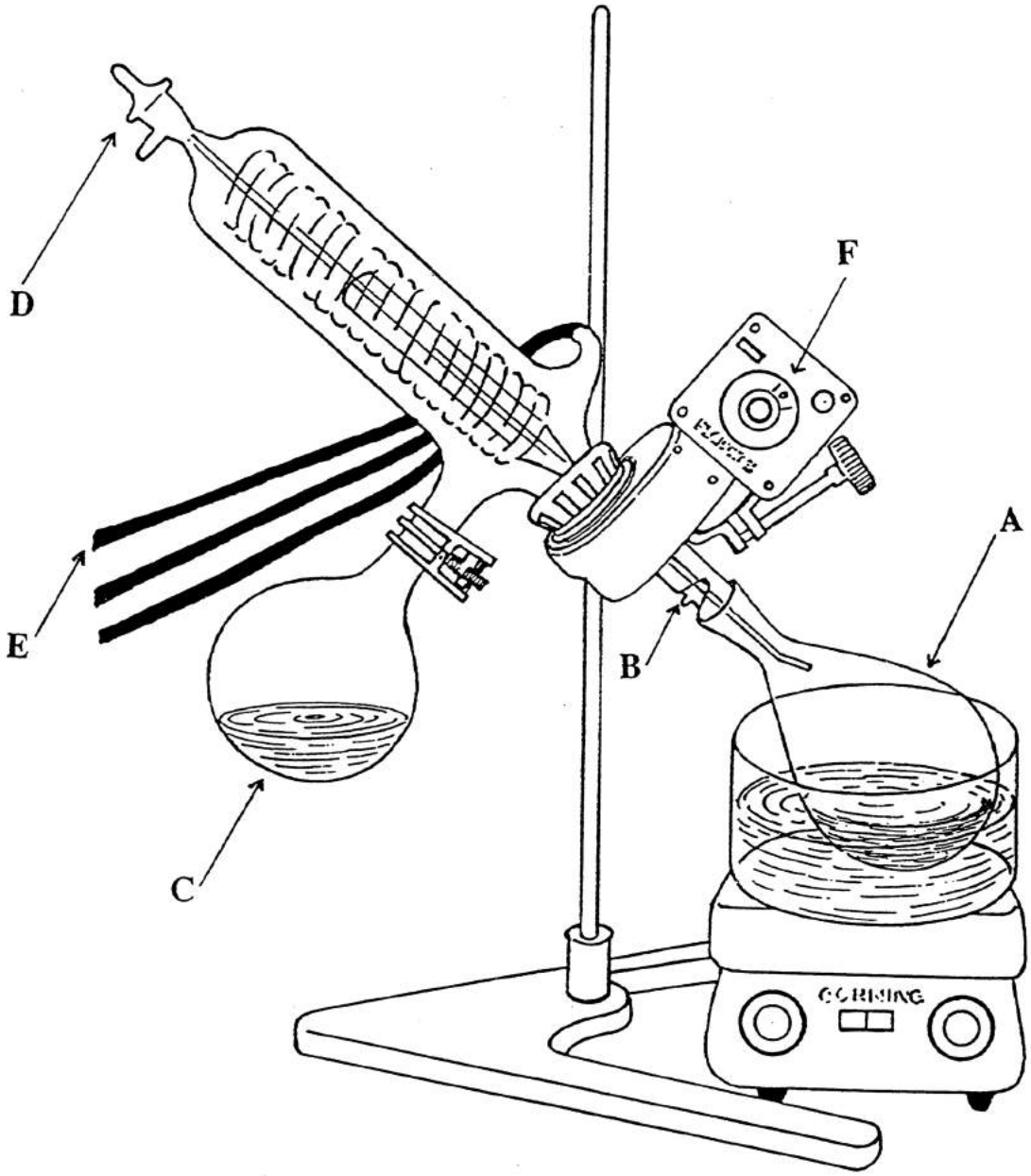


Figure 5.1. A Büchi Rotavapor
(Model used may not be exactly as illustrated.)

Calculation of Amt. of conc. HCl needed to neutralize a given amt. of base.

Given: # of mol of acid to add = # of mol of base used
NaOH conc. = 5%
Tot.Vol. NaOH used = 50 mL
conc. HCl = **12 M**

1. Convert Weight Percentage (%) of Base to Molarity (M)

Need: M = mol/L and Mwt. = g/mol or mol = g/Mwt.
substitute for mol
Therefore: M = g/Mwt/L

Since: 5% NaOH means 5 g/100mL NaOH (or 50 g/1000 mL)

Calculate: M= (5 g)/(40.00 g/mol)/0.1 L or ((50 g)/(40.00 g/mol)/1 L)
M= 1.25 mol/L

2. Determine the Number of moles of Base Used

Using: M= mol/L or mol = M x L

Calculate: mol = 1.25 M x 0.05 L
mol = 0.0625 mol (must use the same # of mol of acid to neutralize)

3. Determine the Number of mL of Acid Required to Neutralize the Base

Using: M= mol/L or L = mol/M

Calculate: L = 0.0625 mol/12 M
L = 0.0052 L
or Vol. = **5.2 mL** of conc.HCl req. to neutralize 50 mL of 5% NaOH.

Summary Equation: mol Acid = mol Base (using M = mol/L)
or M Acid × L Acid = M Base × L Base
Thus: **L Acid = (M base) × (vol Base)/(M Acid)**
L Acid **=** ((5 g)/(40.00 g/mol)/0.1 L) × 0.05 L Base)/12 M Acid
L Acid = 0.0052 L

Procedure

Part A: Extraction of the Organic Acid and Organic Base

You will be provided with about 3 g of a mixture containing an unknown organic acid, an unknown organic base and naphthalene.

1. Determine the mass of your sample and dissolve the mixture in 25 mL of dichloromethane.

2. Transfer the solution to a separatory funnel that is supported by an iron ring attached to a retort stand (see Figure 5.2) and add 20 mL of 5% sodium hydroxide solution. Stopper the funnel and shake it vigorously several times, cautiously releasing the pressure by opening the stopcock (see *The Organic Chem Lab Survival Manual*, Chapter 11 or Chapter 15 in 3rd ed.).

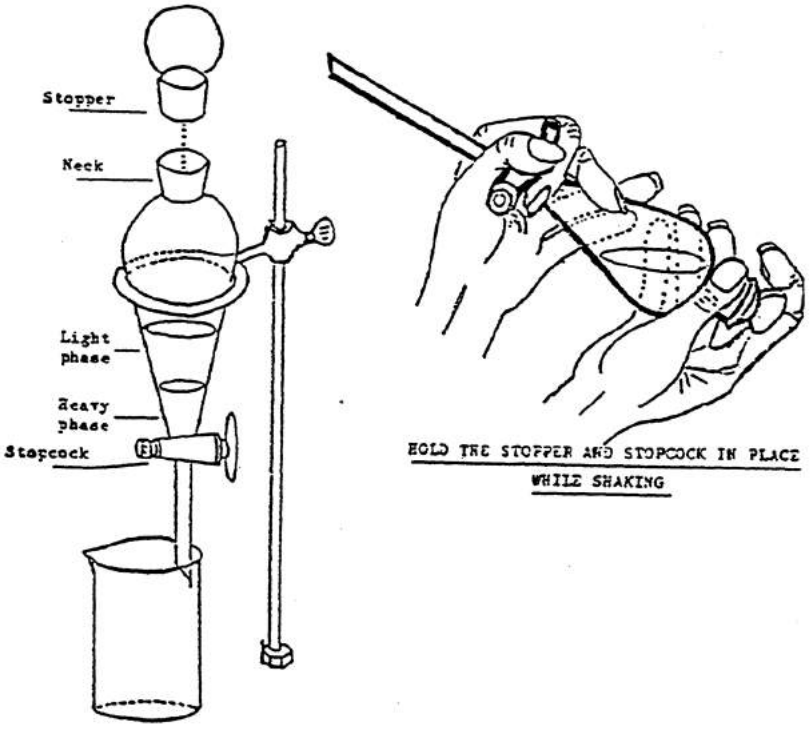


Figure 5.2. Use of a separatory funnel

3. Return the funnel to the iron ring, remove the stopper, and allow the layers to separate. Draw off the bottom layer (dichloromethane) through the stopcock into a 125-mL Erlenmeyer flask. Pour the aqueous layer out through the top of the funnel into another 125-mL flask and set it to one side for the time being.

4. Return the dichloromethane layer to the separatory funnel and add a second 20-mL portion of 5% sodium hydroxide solution. Shake, vent and allow the layers to separate as before. Draw off the lower (dichloromethane) layer into a 125-mL Erlenmeyer flask and pour the aqueous layer out through the top of the funnel into the Erlenmeyer flask containing the aqueous layer from the first separation.

5. Wash the aqueous layer by returning it to the separatory funnel, adding 15 mL of dichloromethane, shaking, venting, allowing the layers to separate, drawing off the organic layer into the 125-mL Erlenmeyer that already contains the dichloromethane from before, and pouring the aqueous layer through the top of the funnel into the 125-mL Erlenmeyer that has previously been used from storing this solution.

Confused? Take a moment to review what you have done so far. You should now have two 125-mL Erlenmeyer flasks. One of these flasks contains approximately 40 mL of dichloromethane in which the naphthalene and organic base are still dissolved. The second flask contains an aqueous solution of the sodium salt of the organic acid, plus any excess sodium hydroxide. Let us now separate the organic base from the naphthalene.

6. Pour the dichloromethane solution of naphthalene and the organic base into the separatory funnel and add 15 mL of 1.5 mol· L^{-1} hydrochloric acid. Shake, vent and separate as described previously.

7. Return the dichloromethane solution to the separatory funnel and extract with a further 15 mL of 1.5 mol· L^{-1} hydrochloric acid.

8. Combine the two hydrochloric acid extracts and wash the combined solution with 15 mL of dichloromethane. Combine the dichloromethane washings with the dichloromethane solution that you should have saved from the acid extraction.

Let us review the situation again. You should now have three 125-mL Erlenmeyer flasks, each containing a solution. The first flask contains an aqueous solution of the sodium salt of the organic acid; the second flask contains an aqueous solution of the hydrochloride salt of the organic base; and the third flask contains a solution of naphthalene in dichloromethane. The next phase of the experiment is to isolate the organic acid, the organic base, and the naphthalene.

Part B: Isolation of the Organic Acid

1. Place the Erlenmeyer flask that contains the sodium hydroxide extract into an ice bath and *carefully* add cold concentrated hydrochloric acid. (**Note:** You should calculate the volume of hydrochloric acid required before you came to the laboratory.) A precipitate of the organic acid should form. Use litmus paper (or universal indicator paper) to test the pH of the mixture and to ensure that a slight excess of hydrochloric acid has been added so that all of the organic acid will be precipitated. Filter off the precipitate by suction filtration, and wash the solid obtained several times with 10-mL aliquots of ice-cold distilled water. Allow the solid to dry (preferably overnight), and then recrystallize from an appropriate solvent. (The latter should be determined in consultation with your instructor.)

2. When the recrystallized product has dried, determine its yield (mass) and melting point. From the given list of possible organic acids, identify the one that was most likely present in your mixture. Confirm your deduction by the mixed melting point technique. If you have not done so already, transfer your product to a suitable sample vial. Hand the vial to your instructor for grading.

Part C: Isolation of the Organic Base

1. Place the Erlenmeyer flask that contains the hydrochloric acid extract into an ice bath and *carefully* add cold sodium hydroxide solution (6 mol· L^{-1}). (**Note:** You should calculate the approximate volume of sodium hydroxide required before you come to the laboratory.) Continue the dropwise addition of the sodium hydroxide solution until the pH of the solution in the Erlenmeyer flask is about 10. (Use universal indicator paper to verify the pH.) A precipitate of the organic base should appear.

   Note: If your organic base appears as an oil rather than as a precipitate, follow the procedure given at the end of this section.

2. Filter off the precipitated organic base by suction filtration, and wash the solid several times with 10-mL aliquots of ice-cold distilled water. Allow the solid to dry (preferably overnight), and then recrystallize from a solvent determined in consultation with your instructor.

3. When the recrystallized product has dried, determine its melting point. From the given list of possible organic bases, identify the one that was most likely present in your mixture. Confirm your deduction by the mixed melting point technique.
   Determine the yield (mass) of product obtained. Transfer your product to a suitable vial, and hand it to your instructor for grading.

   If your organic base appeared as an oil instead of a solid, transfer the contents of the Erlenmeyer flask to a separatory funnel. Wash the Erlenmeyer flask with three 15-

mL aliquots of dichloromethane and transfer these washings to the separatory funnel. Shake and vent the funnel, and allow the layers to separate. Run the (lower) dichloromethane layer into a clean 125-mL Erlenmeyer flask. Wash the aqueous solution remaining in the funnel with an additional 15 mL of dichloromethane and combine the washing with the dichloromethane solution in the Erlenmeyer flask. Dry the dichloromethane solution by adding anhydrous magnesium sulfate to the solution, placing a cork in the mouth of the Erlenmeyer flask, and allowing it to stand for about 10 minutes. (See Section 23 of *The Organic Chem Lab Survival Manual* or Chap.10 in 3rd ed. in order to find out how to determine the quantity of anhydrous magnesium sulfate to use.) Filter off the drying agent (gravity filtration) and evaporate off the dichloromethane using the rotary evaporator (if necessary, see your instructor for assistance). A solid organic base should be obtained. Purify the base by the method described in 3, above.

Part D: Isolation of the Neutral Hydrocarbon (optional)

1. Transfer the dichloromethane solution that contains the neutral hydrocarbon (naphthalene) from its Erlenmeyer flask to a separatory funnel. Wash the dichloromethane layer with two 20-mL aliquots of distilled water.

2. Run the dichloromethane into a 125-mL Erlenmeyer flask and dry this solution by adding anhydrous magnesium sulfate, placing a cork in the mouth of the flask, and allowing it to stand for about 10 minutes. (See Section 23 of *The Organic Chem Lab Survival Manual* in order to find out how to determine the quantity of anhydrous magnesium sulfate to use.)

3. Filter off the drying agent (gravity filtration) and evaporate off the dichloromethane using the rotary evaporator (if necessary, see your instructor for assistance).

4. Naphthalene can be readily purified by the process of sublimation. **Note:** If your instructor has substituted some other hydrocarbon for naphthalene, please consult her or him before you proceed with this stage of the experiment.

5. Transfer the crude naphthalene into a clean, dry 100-mL beaker and stand the beaker on a hot plate. Clamp a 50-mL round-bottomed flask filled with ice-cold water in such a way that the bottom of the flask is in the mouth of the beaker. (**Note:** The outside of the flask *must* be dry.)

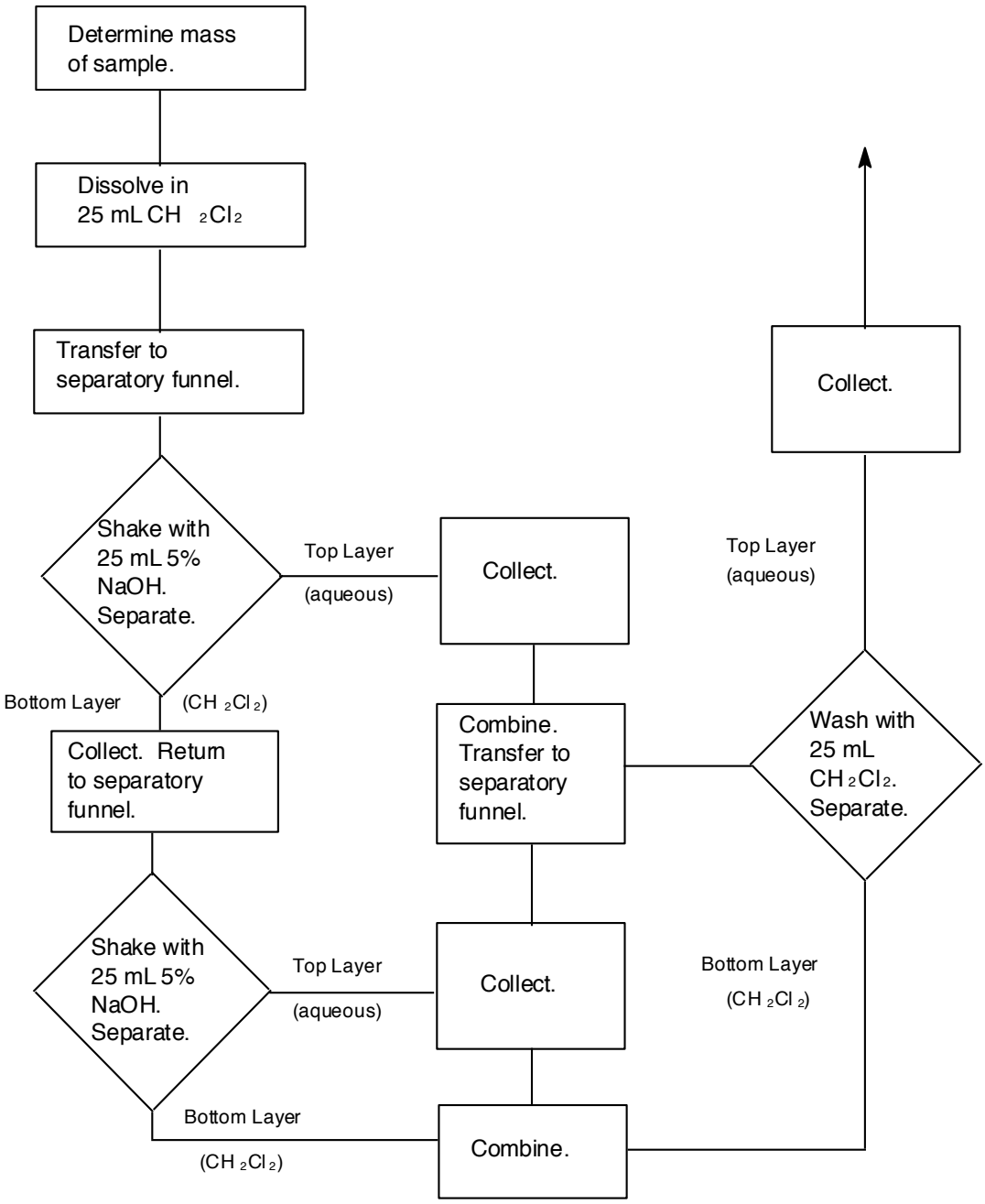
6. **Gently warm** (alternate between low and off) the beaker by turning on the hot plate to a low setting. If the naphthalene melts, you are heating too strongly. After a short while, crystals of naphthalene will appear on the bottom of the flask. When the crystals are large, scrape them off into a vial and collect a second crop. Continue with this procedure until most of the naphthalene has sublimated.

7. Determine the melting point and yield of your product. Hand the vial containing the product to your instructor for grading.

Flow-charts

The procedure described above may seem long and complicated. The student who carries out the experiment with one finger on the instructions is quite likely to make a mistake (e.g., by skipping a line) and rarely understands the significance of each step in the procedure. It is often a good idea to prepare a flow-sheet for any given experiment *before* you come to the laboratory. The flow-sheet can be used during the experiment to guide you through all the necessary steps, *in the correct order*. In addition, the very act of trying to condense several pages of instructions into a **one-page** flow-sheet can assist you in obtaining a better understanding of how each step in the procedure fits into the overall experiment. Before you come to the laboratory you should complete the flow-sheet and hand it in to your instructor. (**Note:** For this experiment, a series of short flow-charts might be more appropriate than one large one.) The flow-chart shown in Figure 5.3 summarizes steps 1-5 in Part A of this experiment.

Figure 5.3. Example of a flow-chart



Safety

Dichloromethane (methylene chloride) is harmful if inhaled, swallowed or absorbed through the skin. Wear gloves and eye protection. Use in well-ventilated area or fume hood. Potential carcinogen.

Sodium hydroxide is corrosive. Skin contact is harmful. Can cause severe burns and is dangerous to the eyes. Wear gloves and eye protection.

Hydrochloric acid is harmful to eyes, lungs and skin. If concentrated, use only in a fume hood. Wear gloves and eye protection.

Benzoic acid, 4-methylbenzoic acid, 2-methylbenzoic acid, 4-chlorobenzoic acid and salicylic acid do not present any specific hazards, but all the usual precautions should be taken, e.g., avoid ingestion, skin contact, etc.

3-Nitroaniline is toxic. It can be absorbed through the skin, so wear gloves. Avoid breathing dust. In case of contact, wash exposed area with water for at least 15 minutes.

4-Chloroaniline does not present any specified hazards, but avoid ingestion and contact with skin.

Naphthalene is harmful by ingestion, inhalation and by skin contact.

Additional information about the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste Disposal

Solutions of sodium hydroxide and hydrochloric acid should be diluted with water and washed down the sink.

Dichloromethane should be placed in the bottle labelled "waste halogenated solvents."

Special containers will be provided for all other waste materials.

Write-up

A standard investigative report is required. In this report, you should list any significant observations, report any problems or difficulties, etc. Do not write out a detailed account of the procedure, as these details will have been included in a flow-chart, which should be re-submitted with your report. Your grade will be largely determined by your having correctly identified the unknown compounds in the given mixture, and by the quality and quantity of the samples that you submit. **Remember** to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with report.

1. When extracting an organic compound from an aqueous solution into an organic solvent (e.g., diethyl ether), a chemist will sometimes add sodium chloride to the aqueous solution. What is the purpose of such an addition? What is the procedure called?

1. Why is the procedure used in this experiment called liquid-liquid extraction?

2. A CHEM350 student was working on her yield determination of her recrystallized *p*-aminobenzoic acid, when some naphthalene was inadvertently spilt into her crystals. You happen along the scene, and offer the following advice to the distraught student:
   a) Redissolve all the solid in dichloromethane, extract with dilute aqueous acid, , re-isolate the organic compound by precipitating the salt of the base with strong base, and recrystallize your *p*-aminobenzoic acid again.
   b) Redissolve all the solid in dichloromethane, extract with dilute aqueous base, re-isolate the organic compound by precipitating the salt of the acid with strong acid and recrystallize *p*-aminobenzoic acid again.
   c) Do either a or b.
   d) Discard everything into the hazardous waste container. Nothing can be done.

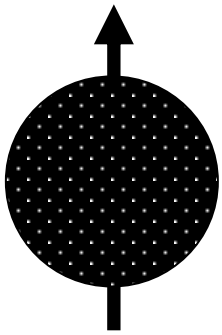
4. When an aqueous solution of an organic compound is shaken with an immiscible organic solvent, such as diethyl ether, the solute distributes itself between the two phases. When the two phases separate into two distinct layers, an equilibrium will have been established such that the ratio of the concentrations of the solute in each solvent defines a constant, K, called the distribution coefficient (or partition coefficient).

   $$K = \frac{\text{concentration of solute in solvent A, e.g., diethyl ether } (g \cdot L^{-1})}{\text{concentration of solute in solvent B, e.g., water } (g \cdot L^{-1})}$$

   The distribution coefficient for compound X in the diethyl ether/water system is 3.0. If you were given a solution containing 8.0 g of X in 500 mL of water and wanted to extract compound X into diethyl ether, show that it would be more effective to extract X using three 50 mL aliquots of diethyl ether rather than a single 150 mL aliquot. (**Hint:** Determine how much of X would remain in the aqueous solution in each case.)

Experiment 6

Reactions of the Common Functional Groups
Part 1: Hydrocarbons
Part 2: Infrared Spectroscopy Tutorial



Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
pentane, cyclohexene, phenylacetylene, biphenyl, toluene, bromine in dichloromethane sol'n, Baeyer Reagent, Ammoniacal Silver Test Reagent, Conc. Sulfuric acid., ice wash acetone, chloroform, carbon tetrachloride, nujol	-test tubes, test tube racks -IR Spectrophotometer -KBr salt blocks/disks -mortar and pestle -Pasteur pipettes, Kim-wipes®, -hazardous waste disposal containers (in fume hood)	-115V electrical

About Using the IR Spectrophotometer

- KBr salt blocks are readily fogged and dissolved by water. Use only anhydrous solvents to clean the disks. Store at all times in the dessicator.

Procedure

Make sure that your test tubes are clean and dry. The presence of acetone in your test tubes may affect your results.

Carry out the tests described below on each of the following substances: pentane, cyclohexene/methylpentenes (use the product you will obtain in Experiment 8), phenylacetylene, biphenyl, toluene, and one of the unknowns if provided.

For each test carried out, record your observations, explain what the observations infer, and write an equation. (See "Write-up" section for suggested format.)

1. Bromine Test

Dissolve three drops (or a few crystals) of the hydrocarbon in 0.5 mL of dichloromethane. Add, dropwise, about 0.5 mL of the bromine in dichloromethane solution. If the brown-red colour persists, stopper the test tube and allow it to stand in light for at least one hour. Test for the evolution of hydrogen bromide using moist litmus paper.

2. Baeyer Test

To three drops (or a few crystals) of the hydrocarbon add, drop by drop, with shaking, about 0.5 mL of a solution made from equal volumes of potassium permanganate (0.03 mol· L^{-1}), and sulfuric acid (3 mol· L^{-1}).

3. Ammoniacal Silver Nitrate Test

In each of four ultra-clean test tubes, use distilled water to dilute 2 mL of (0.3 mol· L^{-1}) silver nitrate solution to 5 mL. Add 2 drops of concentrated ammonia. **(CARE: This solution has a concentration of 14.8 mol· L^{-1}. Use it only in the fume hood. Protect your eyes and hands.)** Shake each test-tube so that the brown precipitate that forms just redissolves. Add 1 drop (or a few crystals) of each of the hydrocarbons to each tube and shake. If a precipitate forms, destroy it with a little concentrated nitric acid before discarding the contents of the tube.

CARE: Concentrated nitric acid has a concentration of 15 mol· L^{-1}. Protect your eyes and hands. Use only in a fume hood.

4. Sulfuric Acid Test

CARE: The sulfuric acid used here has a concentration of 18 mol· L^{-1}. Protect your eyes and hands.

To 1 mL of **cold** concentrated sulfuric acid, *cautiously* add, with shaking, three drops (or a few crystals) of the hydrocarbon. For the test with phenylacetylene, make sure to use a large test tube and perform in the fumehood.

Safety

In addition to the dangers involved when using concentrated sulfuric acid, concentrated nitric acid and concentrated ammonia, you should also be aware of the hazardous nature of the following substances listed below.

Pentane is highly flammable. High concentrations of pentane vapours have a narcotic effect. Liquid pentane is harmful if swallowed or if it gets into the eyes.

Cyclohexene vapour irritates the eyes, skin and respiratory system. The liquid is harmful if swallowed. Highly flammable.

Phenylacetylene is a lachrymator and an irritant! Use only in a fume hood. Wear gloves and eye protection.

Biphenyl is harmful if swallowed, inhaled or absorbed through the skin.

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in headaches, nausea, vomiting and dermatitis. Avoid contact with the liquid and do not breathe its vapours. Flammable.

Bromine solutions—Bromine is extremely irritant to the eyes, lungs and skin. Poisonous if swallowed. Wear gloves and eye protection. Use only in a fume hood.

Permanganate solutions—Potassium permanganate is a skin irritant. Wear gloves and eye protection.

Silver acetylides are explosive when dry. Destroy by adding concentrated nitric acid.

Additional information about the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste Disposal

Separate containers will be available for the disposal of each of the following materials:

halogenated compounds—including products from the bromine test
waste permanganate
waste silver
waste concentrated sulfuric acid

Do *not* dispose of any of the substances used in this experiment in any way other than by placing them in the special containers provided.

Part 1 Write-up

Keep the 'Introduction' brief. Do not rewrite the lab manual theory section (pp.100-104 of the CHEM350 lab manual), simply define the purpose of the various tests. The results of this experiment may be presented in the form of a four-column table, as illustrated below. You should attempt to write a conclusion about the prospects of your being able to differentiate between alkanes, alkenes, alkynes and aromatic hydrocarbons using the tests investigated in this experiment. Finally, do not forget to answer the questions at the end of this experiment.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Test	Observation	Inference	Equation
1.Dissolved 3 drops 1-pentene in 0.5 mL CH_2Cl_2 and added (dropwise) about 0.5 mL Br_2/CH_2Cl_2 solution. 2. Etc.	Red-brown colour of Br_2 disappeared as soon as the two solutions mixed.	Bromine reacts 1-pentene because the latter contains a carbon-carbon double bond.	$CH_3(CH_2)_2CH=CH_2$ $\downarrow Br_2$ $CH_3(CH_2)_2CH\text{-}CH_2Br$ Br

Table 6.1 Correlation Table of Infrared Absorption and Functional Group.

Type of Absorption	Wavenumber (cm^{-1})	Intensity of Absorption	Absorption of:
O-H stretch	3400-3640	strong, broad	alcohol
	2500-3300	strong, very broad	carboxylic acid
N-H stretch	3310-3350	medium ('W' shape)	amine (1°)
C-H stretch	3300	strong	sp C-H of alkyne
	3030	medium	aromatic
	3020-3100	medium	sp^2 C-H of alkene
	2850-2960	medium to strong	sp^3 C-H of alkane
	2750 & 2850	weak-medium ('W' shape)	O=C-H of aldehyde
C≡N stretch	2210-2260	medium, sharp	nitrile
C≡C stretch	2100-2260	medium, sharp	alkyne
C=O stretch	1670-1780	strong, sharp	carbonyl
	1730-1750		ester
	1720-1740		aldehyde
	1705-1725		ketone
	1700-1725		carboxylic acid
	1640-1700		amide
	ca 1800 and 1760		anhydride
C=C stretch	1650-1670	weak-medium, sharp	alkene
	1600, 1500, 1450	strong sharp	aromatic
C=N stretch	1640-1670	medium, sharp	imine
N-H bend	1500-1650	medium to strong, sharp	amine and amide
N=O stretch	1500-1600 (1540) and 1320-1390	strong, sharp	nitro-compound
C-N stretch	1030, 1230	medium	amine
C-O stretch	1050-1150	strong	alcohol
	1250-1310	strong broad	ester-conjugated
	1240	strong, broad	ester-acetates
	1175	strong, broad	ester-unconjugated
C-Cl stretch (terminal)	600-800	strong	alkyl halide
Ar-Cl stretch	1000-1175	medium-strong	aryl halide
C-Br stretch (terminal)	500-760	strong	alkyl halide
C-I (terminal)	500	strong	alkyl halide

Note: when a C=C bond is in conjugation with a carbonyl, the observed carbonyl absorption frequency will be < ~ 30 cm^{-1}.

Calculation of the # Degrees of Unsaturation in a Compound

Number of Degrees of Unsaturation = nC +1 + 1/2N - 1/2 nH - 1/2 nX

e.g., Therefore, for Compound A, C_7H_{12} = (7) +1 + 1/2(0) - 1/2 (12) - 1/2(0)
= 7 + 1 - 6 = **2** degrees of unsaturation in Compound A.

Note: an aromatic ring = 4 degrees of unsaturation, 1 for the ring + 3 for the 3 double bonds = 4

Part 2. How to Interpret an Infrared Spectrum

Step 1 Divide the infrared spectrum into four main areas (use pencil and ruler and take into account any off-shift in the spectrum's wavenumbers).

i) Above 3000 cm^{-1}
ii) Between 3000 and 2000 cm^{-1}
iii) Between 2000 and 1400 cm^{-1}
iv) Below 1400 cm^{-1} (fingerprint region)

Step 2 Starting at the left of the spectrum, examine the area **above 3000 cm^{-1}**, first looking in the region near 3300 cm^{-1} and record in tabular format the presence/absence of:

i) a broad, very strong absorption band of an **'O-H'**. If present, it means you know that your molecule is at least an **alcohol**.
ii) A broad, weak to medium strength, double or single absorption band of **'N-H'**. If present it means you have an **amine** (1° or 2°) or possibly an **amide**.
iii) A sharp, medium to strong, single absorption band of **'≡C-H'** of a **terminal alkyne**. Note: If present, it means you should also see a 'C≡C' absorption near 2250 cm^{-1}.

After examining the region around 3300 cm^{-1}, look for any sharp, weak to medium absorption just above 3000 cm^{-1} (e.g. 3050 cm^{-1}) resulting from the 'C-H' stretch of a sp^2 hybridized carbon. If present, it means you have a **'C=C-H'** of an alkene or aromatic compound.

Step 3 Next examine the area between **3000 and 2000 cm^{-1}** and record the presence/absence of absorption bands or peaks.

i) First look just below 3000 cm^{-1} (e.g. 2850-2950 cm^{-1}) resulting from the 'C-H' stretch of a sp^3 hybridized carbon. If present, it means you are seeing the **'C-H'** stretch of an **-CH_2 or -CH_3** group. Note: This absorption is not very informative as most organic compounds have -CH_2 or -CH_3 groups.
ii) Then look for the extremely broad peak, actually starting at 3300 cm^{-1} and extending all the way to ~2500 cm^{-1}, caused by the **O-H dimer** between two **carboxylic acid** molecules (COOH). This absorption is probably the most difficult to see as other absorption peaks may be overlapping the broad peak.
iii) Finally look for a sharp, weak to medium peak caused by either **'C≡C'** or **'C≡N'**.
iv) If present, then the compound is an alkyne (might also have the 'C-H' of a terminal alkyne, see step 2 above) or a nitrile.

Step 4 Next examine the area between **2000 and 1400 cm^{-1}** and record the presence/absence of absorption bands or peaks.

i) First look near 1700 cm^{-1} (e.g. 1680-1750 cm^{-1}) for a sharp, strong peak resulting from the **'C=O'** stretch of a **carbonyl**. Note: <u>This absorption is very informative</u> and will be present if your compound is an aldehyde, ketone, ester, amide, or carboxylic acid.
ii) Next look near 1650 cm^{-1} (e.g. 1600-1670 cm^{-1}) for a sharp, weak peak resulting from the **'C=C'** stretch of an **alkene**.
iii) Finally look near 1600 cm^{-1} and 1500 cm^{-1} for a sharp, double peak resulting from the **'C=C'** stretch of an **aromatic ring**.

Step 5 If you dare, you may look in the **fingerprint region** (**area below 1400 cm^{-1}**) and record the presence of absorption bands or peaks.

i) First look near 1200 (1160-1310) cm^{-1} for a sharp, strong peak resulting from the **'C-O'** stretch of an **ester**.
Note: This absorption is very difficult to see and may or may not be present, i.e. conclusive if present, inconclusive if not present.

ii) If you suspect you have an aromatic ring (absorption bands at ~3030 and 1600 and 1500 cm^{-1} present), you may try to discern the substitution pattern of the benzene ring by looking at the strong absorption bands of the **ring 'C-H'** out-of-plane bending vibrations in the region 680-900 cm^{-1}.

Benzene Substitution Pattern	Ring 'C-H' Absorption Bands Present (cm^{-1})
monosubstituted	2 sharp peaks, 730-770, 690-710
ortho disubstituted	1 sharp peak, 735-770
meta disubstituted	3 sharp peaks, 860-900, 750-810, 680-725
para disubstituted	1 sharp peak, 800-860
1,2,3 trisubstituted	2 sharp peaks, 760-780, 705-745
1,3,5 trisubstituted	2 sharp peaks, 810-865, 675-730
1,2,4 trisubstituted	2 sharp peaks, 870-885, 805-825

Ref: McMurry, J., 1992. Organic Chemistry, 3rd ed, Brooks/Cole, p.549-550, (4th ed, p.559)
Nakanishi, K., 1964. Infrared Absorption Spectroscopy, Holden Day p.27.

iii) Again, if you have an aromatic, you may also try to discern the ring substitution pattern of the benzene ring by looking at the very weak overtone-combination absorption bands of the **ring 'C-H'** stretch vibrations in the region 1670-2000 cm^{-1}.

Benzene Substitution Pattern	Ring 'C-H' Overtone Bands Present (cm^{-1})
monosubstituted	4 weak equally spaced and shaped sharp peaks
ortho disubstituted	3 weak irregularly spaced/shaped sharp peaks
meta disubstituted	2 weak sharp peaks + one weak broad peak
para disubstituted	2 weak sharp peaks

iv) If you suspect you have a long straight chain (>4 C) alkane, (absorption bands at 2850-2950 cm^{-1} present but not much else), you may try to see the sharp, weak absorption due to the concerted rocking of >4 $-CH_2$ in a chain. It lies in the region 720 ± 10 cm^{-1}.

Step 6 Finally, you will summarize your results by making a statement about what functional groups you suspect to be present in the molecule or perhaps you will be asked to select from a list of suggested structures, which molecule most likely would generate the spectrum just analyzed.

Instructor Led Group Infrared Analysis Problems

Use the tables below to record your results of the 'Infrared Spectral Analyses' for the following compounds (infrared spectra on pages 124-130 of this lab manual). Label the absorption bands.

Cyclohexanol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	3331	broad	strong	O-H stretch alcohol
3000-2000 cm^{-1}	2	2932 & 2855	sharp	strong	C-H sp^3 stretch
2000-1500 cm^{-1}	none				
(Fingerprint)	*3*	*1068*	*sharp*	*strong*	*C-O of alcohol*

Functional Group absent: no ≡C-H, no N-H, no sp^2 H-C=, no C≡C, no C≡N, no C=O, no C=C alkene or aromatic

2-methyl-3-butyn-2-ol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	~3380	broad	strong	O-H stretch alcohol
	2	3303	sharp	strong	
3000-2000 cm^{-1}	3	2876,2938,2987	sharp	med-str.	
	4	2120	sharp	weak	
2000-1500 cm^{-1}	none				

Functional Group absent: no N-H, no sp^2 H-C=, no C≡N, no C=O, no C=C alkene or aromatic

3-buten-2-ol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	~3350	broad		
	2	3083 & 3012		strong	C-H ____ stretch
3000-2000 cm^{-1}	3		sharp		C-H ____ stretch
2000-1500 cm^{-1}	4	1646			

Functional Group absent: no ≡C-H, no N-H, no C≡C, no C≡N, no C=O, no C=C aromatic

benzhydrol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	3392-3359	broad		
	2	3049 & 3027	sharp		C-H ____ stretch
3000-2000 cm^{-1}	3	2900	sharp		C-H ____ stretch
2000-1500 cm^{-1}	4	1598,1495,1458	sharp		

Functional Group absent: no ≡C-H, no N-H, no C≡C, no C≡N, no C=O, no C=C alkene

Instructor Led Group Infrared Analysis Problems (cont.)

benzaldehyde	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent: no O-H, no ≡C-H, no N-H, no sp^3 C-H, no C≡C, no C≡N, no C=C alkene

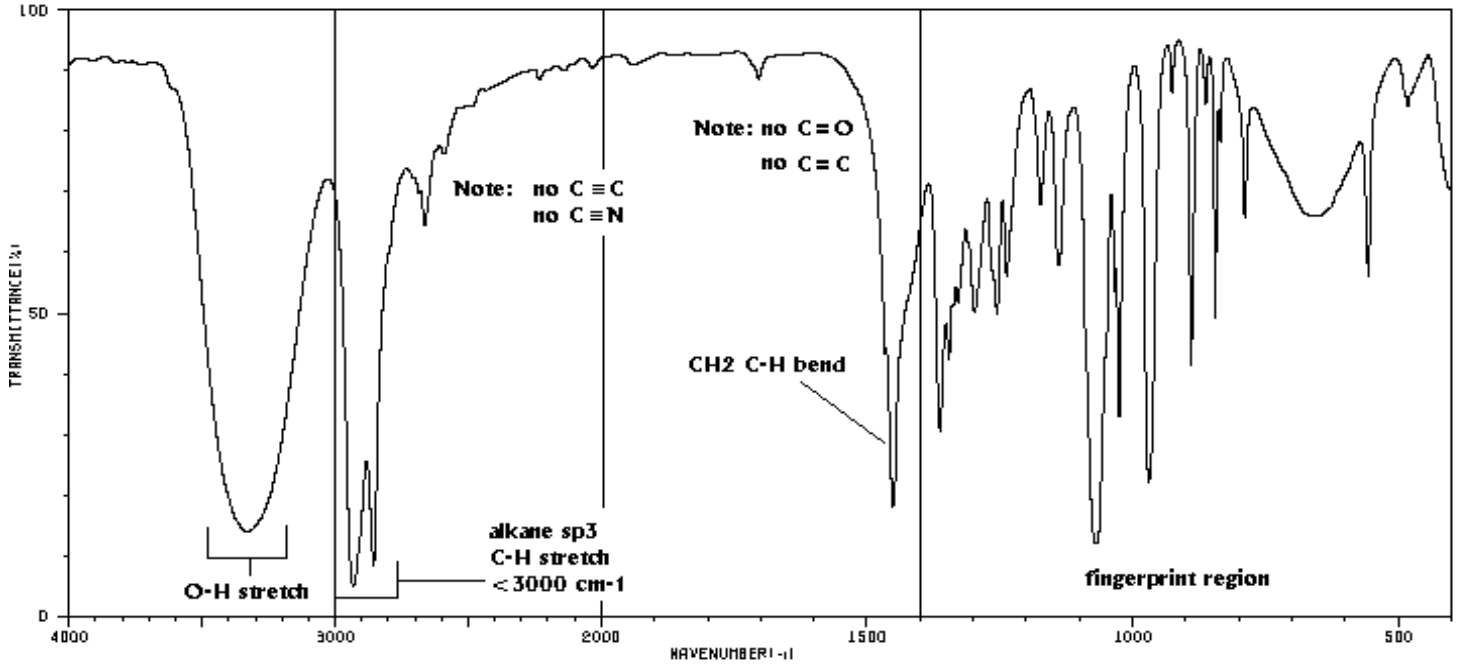
acetic acid	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

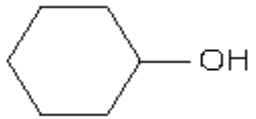
dibutylamine	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

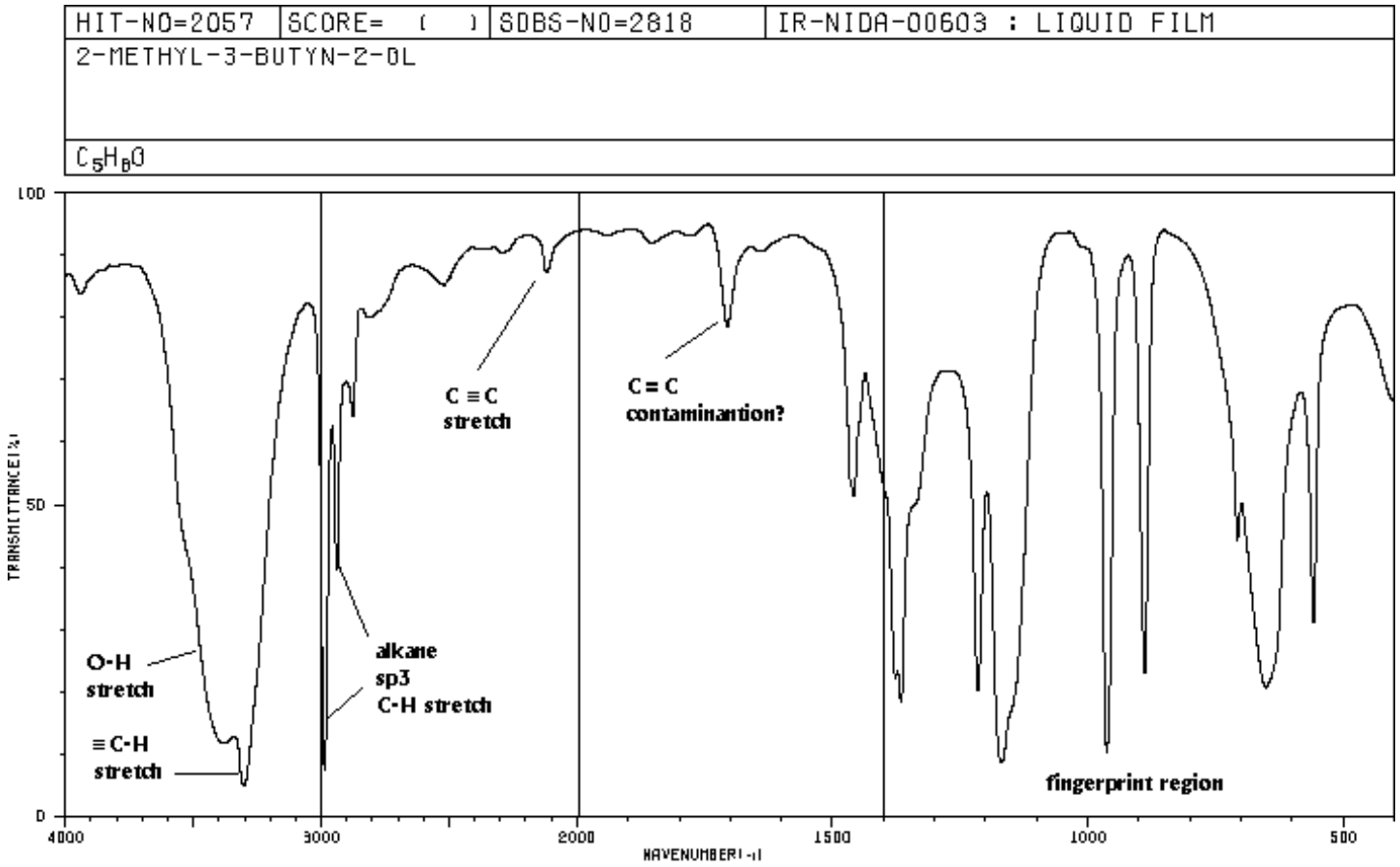
Functional Group absent:

HIT-NO=1077	SCORE= ( )	SDBS-NO=581	IR-NIDA-09018 : LIQUID FILM
CYCLOHEXANOL			
$C_6H_{12}O$			

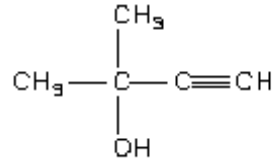


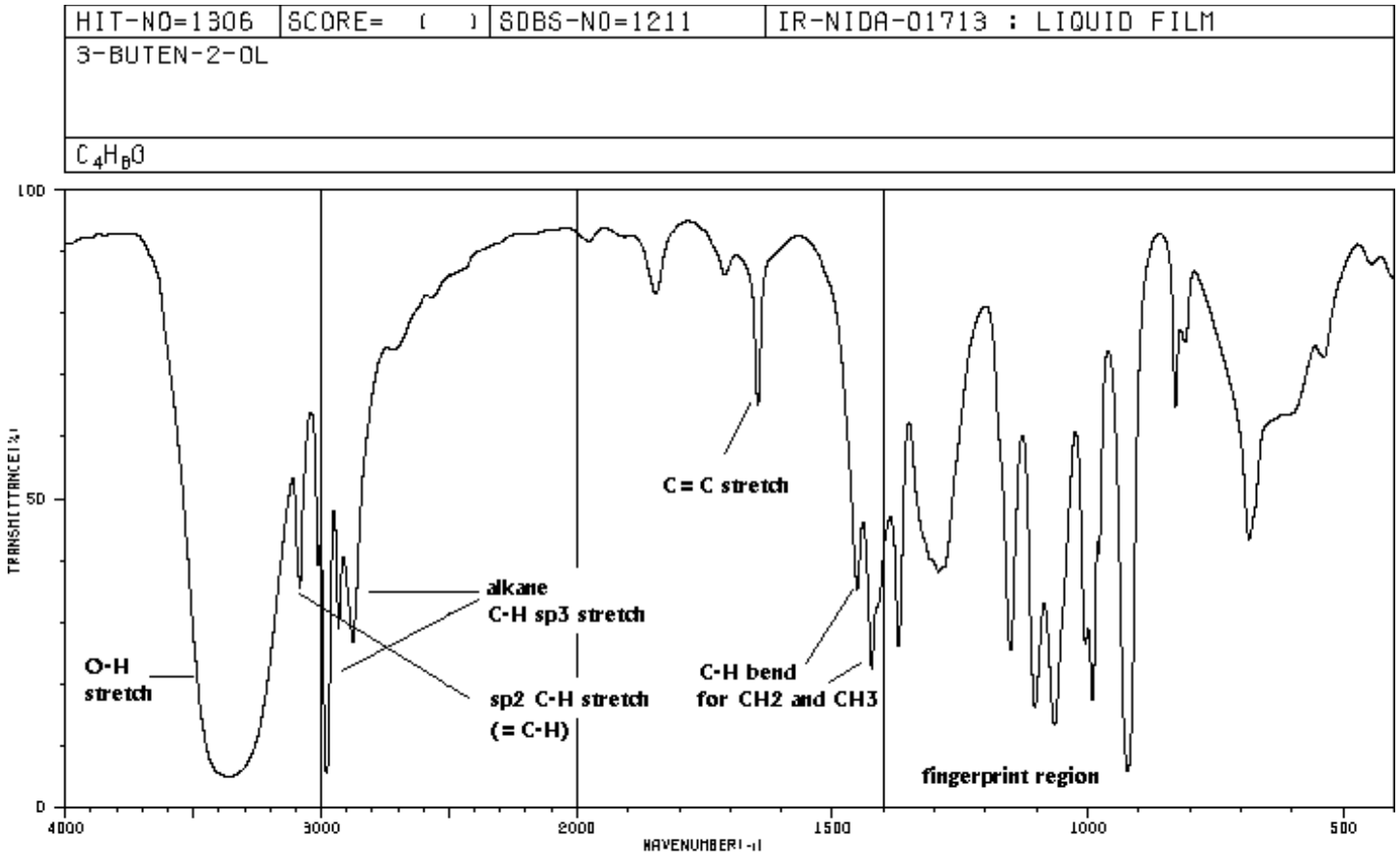
3331	13	1704	86	1256	47	970	21	667	64
2932	4	1467	42	1238	53	926	84	557	53
2855	8	1452	17	1174	86	890	39	462	61
2686	68	1363	29	1140	55	863	81		
2666	82	1346	41	1068	11	845	47		
2588	74	1329	50	1034	52	835	74		
2233	84	1298	49	1025	32	789	64		



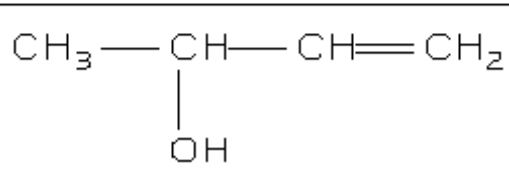


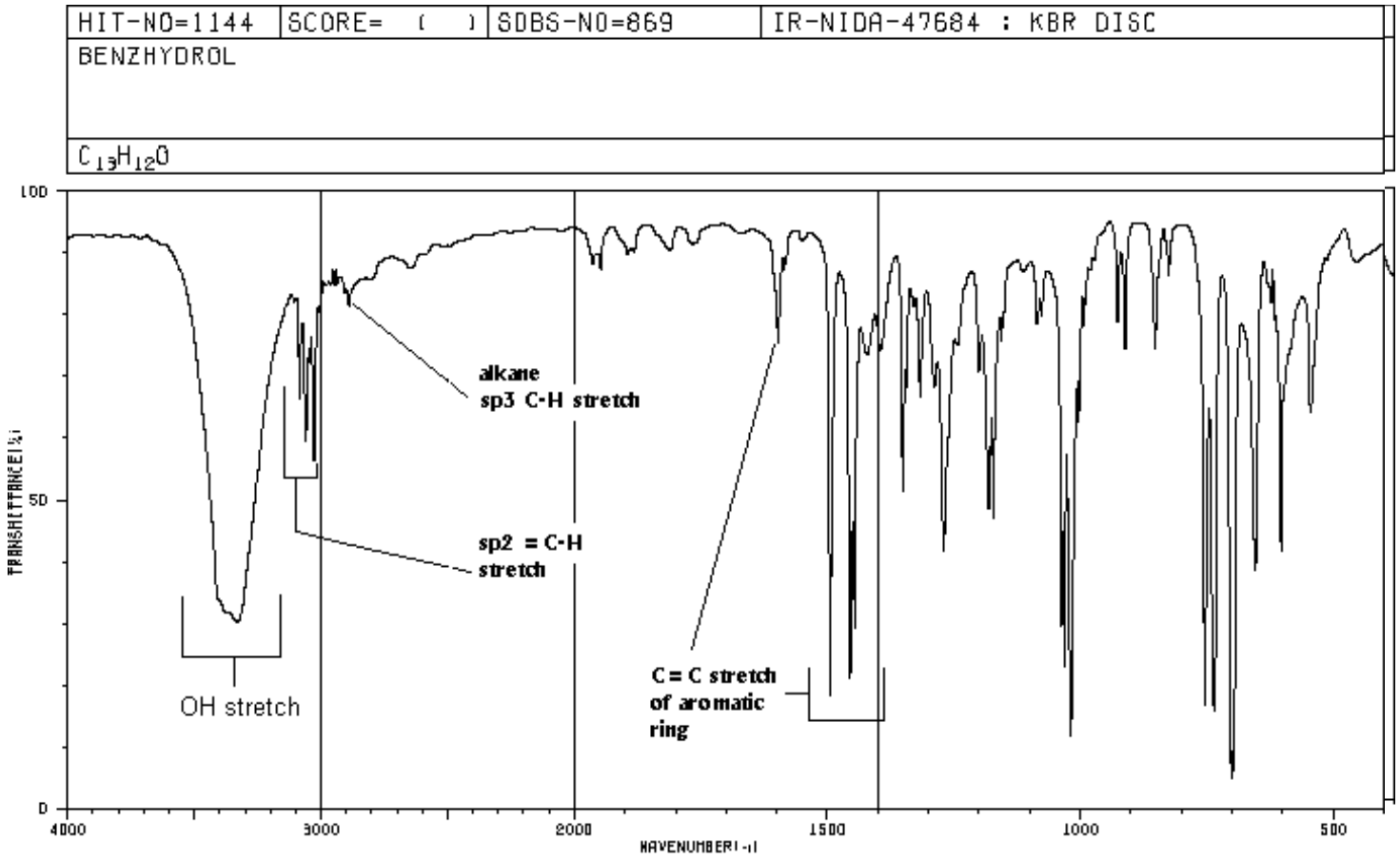
3939	81	2120	84	1170	8
3303	4	1706	74	963	10
2987	7	1465	52	889	22
2938	38	1459	49	708	42
2876	62	1378	21	652	20
2811	77	1368	17	556	30
2619	81	1216	19		



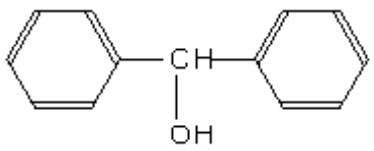


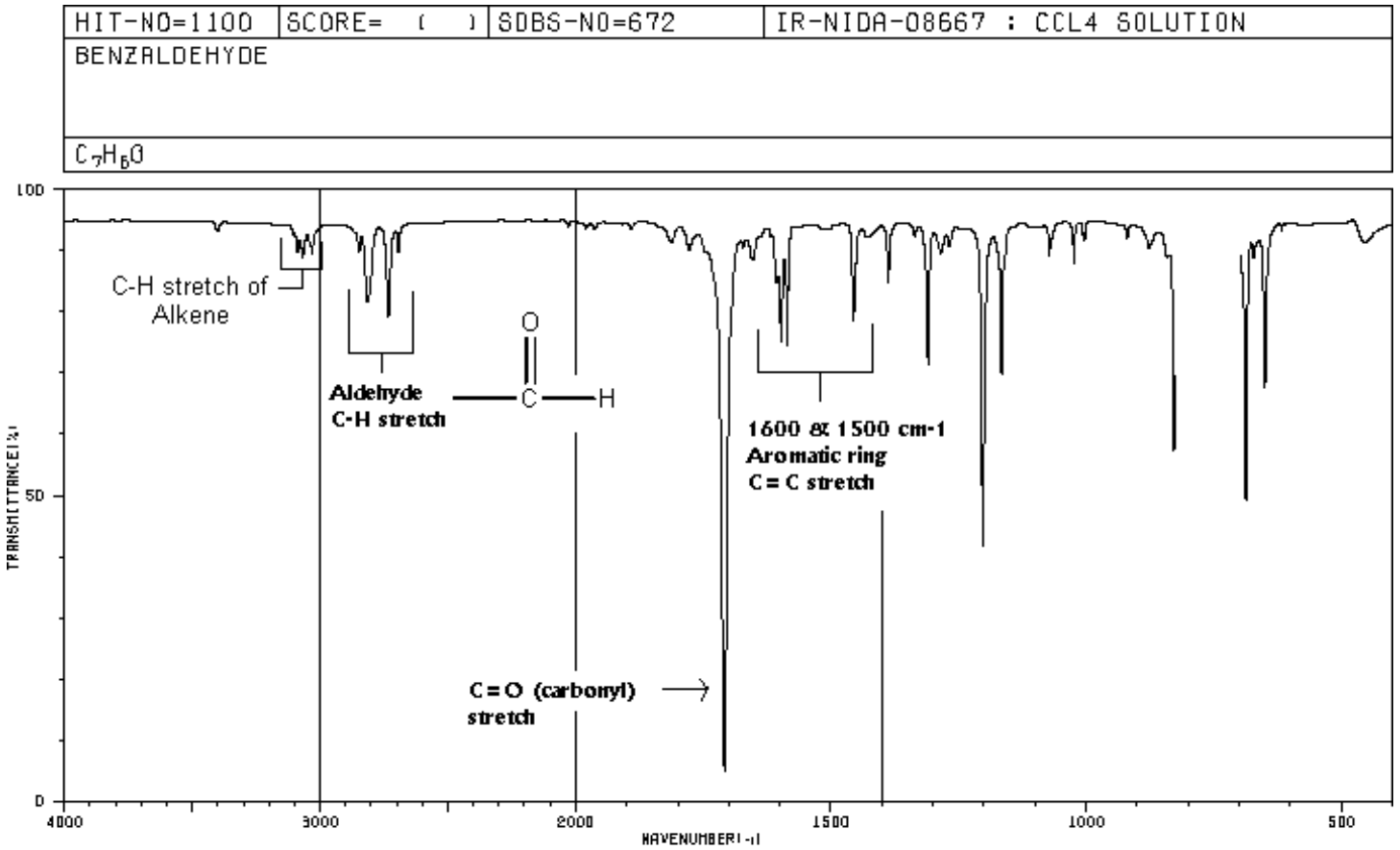
3083	33	1646	62	1066	12	686	41
3012	36	1452	33	1005	24	539	70
2979	4	1424	20	991	15	443	64
2932	26	1371	29	978	30		
2876	24	1292	35	922	5		
1646	79	1152	25	829	60		
1711	81	1103	14	810	72		



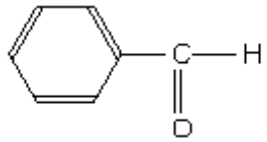


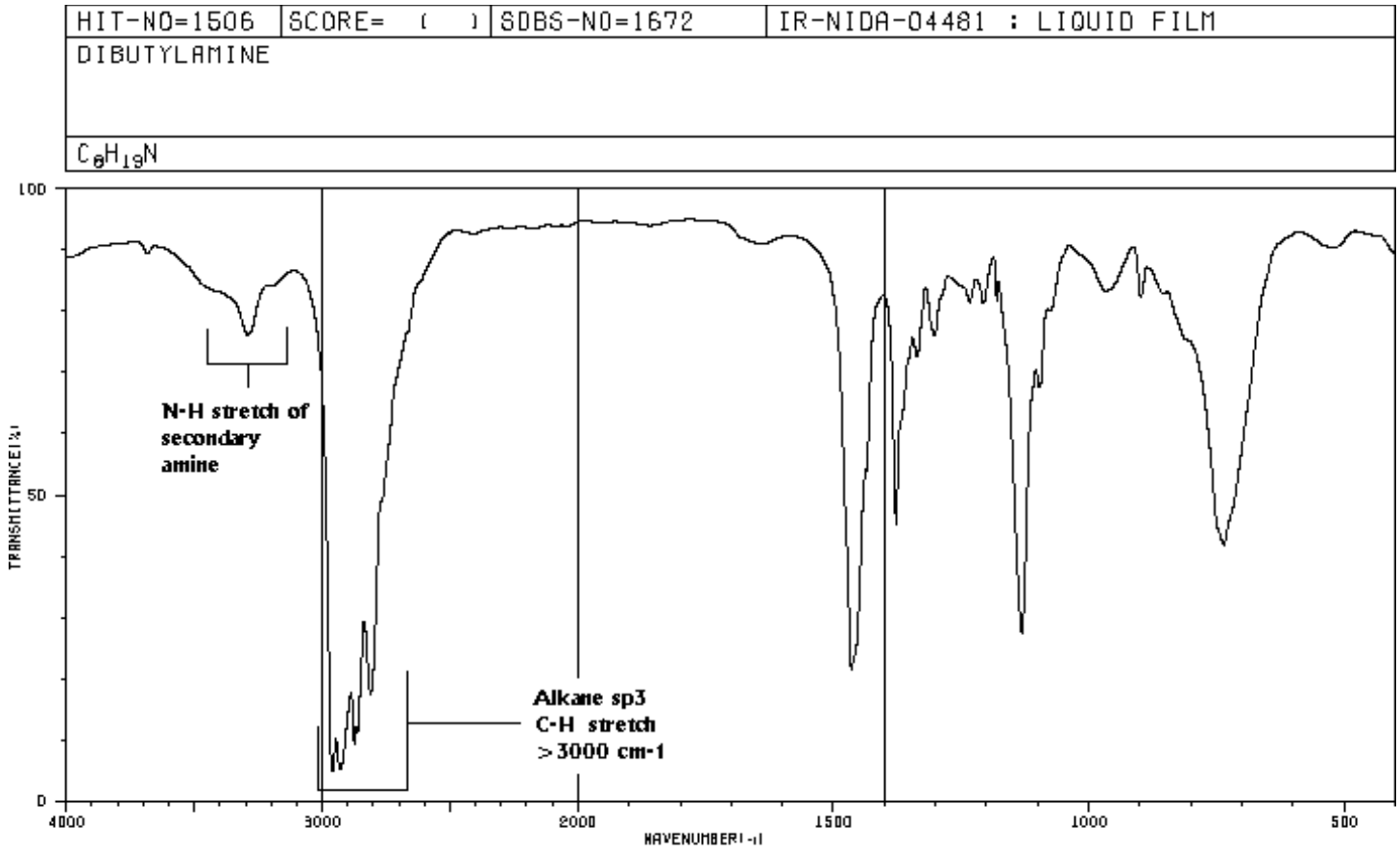
3392	26	1598	72	1345	66	1172	44	863	72
3359	30	1495	17	1317	64	1156	72	754	16
3331	29	1458	21	1289	86	1037	28	735	15
3086	64	1446	27	1271	39	1032	22	702	4
3059	57	1422	70	1244	72	1019	11	654	37
3049	70	1395	72	1201	88	1003	60	604	39
3027	63	1361	49	1182	46	912	72	646	62



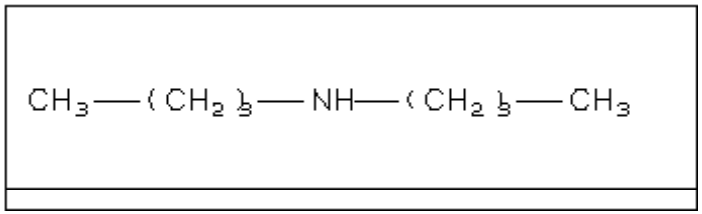


3088	86	1778	86	1388	81	1024	84
3068	86	1709	4	1310	68	828	55
3032	86	1653	84	1285	86	688	47
2847	86	1607	81	1203	39	673	86
2814	79	1598	72	1167	68	650	64
2732	77	1586	72	1160	84		
2693	86	1466	74	1072	86		





3684	86	1466	20	1181	79
3290	72	1378	43	1131	26
2959	4	1338	70	1096	84
2929	6	1302	72	966	79
2874	9	1245	81	961	81
2862	10	1234	79	898	79
2810	16	1206	79	736	41
[illegible]	66	892	41		



Infrared Analysis Practice Problems

Use the tables below to record your results of the 'Infrared Spectral Analyses' of the provided known spectra on pages 133-139 of this lab manual.

cyclohexanone	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

benzaldehyde	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

ethyl benzoate	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

benzoic acid	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

Infrared Analysis Practice Problems (cont.)

Use the tables below to record your results of the Infrared Spectral Analyses of the provided known spectra.

phenylacetylene	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

benzonitrile	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or ,weak)	Functional Group Indicated

Functional Group(s) absent:

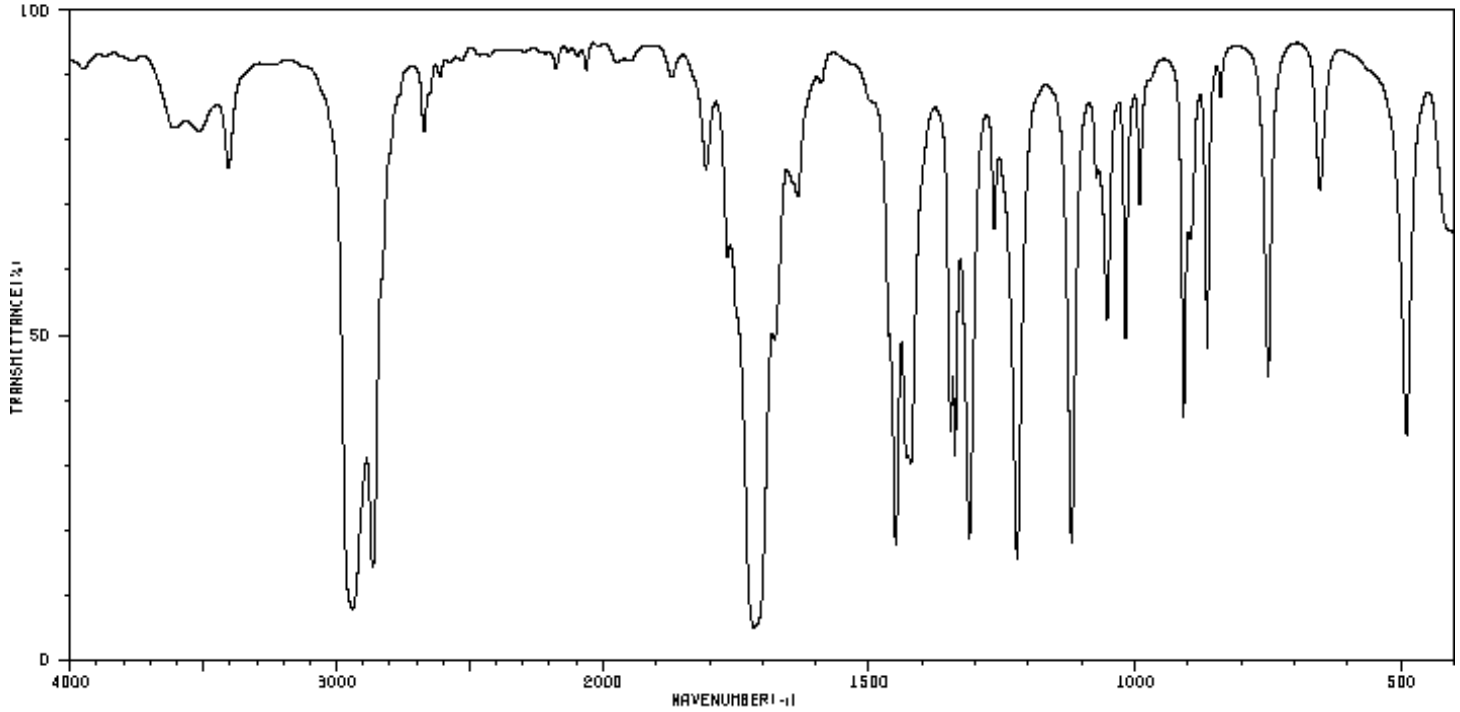
styrene	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

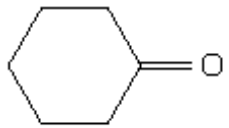
diethyl ether	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

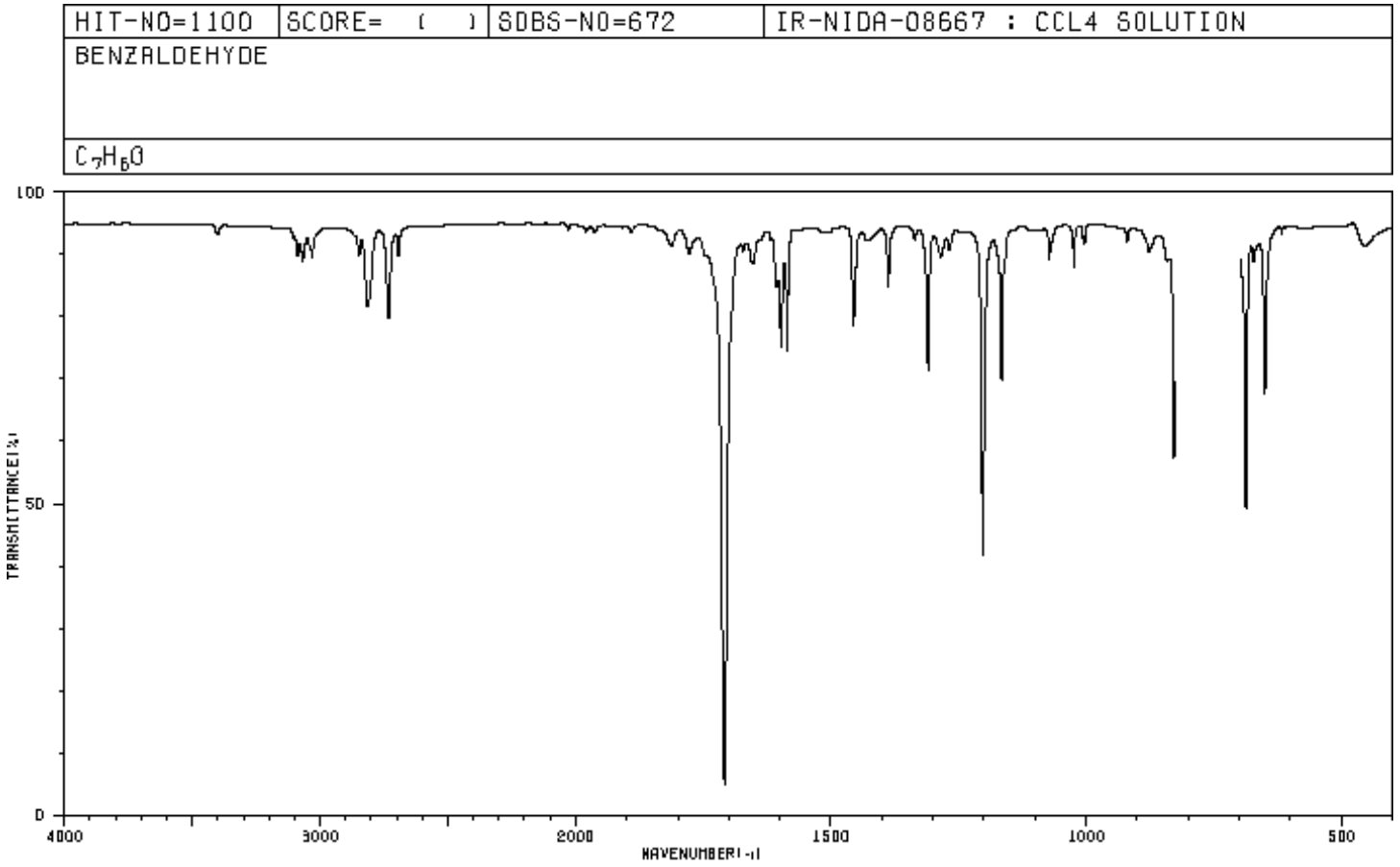
Functional Group(s) absent:

HIT-NO=1070	SCORE= ( )	SDBS-NO=571	IR-NIDA-05262 : LIQUID FILM
CYCLOHEXANONE			
$C_6H_{10}O$			

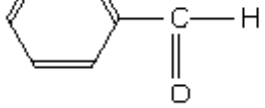


3610	79	2611	86	1460	17	1222	16	896	62
3515	79	1870	86	1429	30	1119	17	864	46
3407	72	1808	72	1422	28	1073	72	839	64
2941	7	1766	60	1347	34	1062	60	760	42
2864	13	1716	4	1338	30	1018	47	652	70
2870	79	1677	47	1311	17	991	68	490	33
2664	84	1634	68	1266	64	909	36		





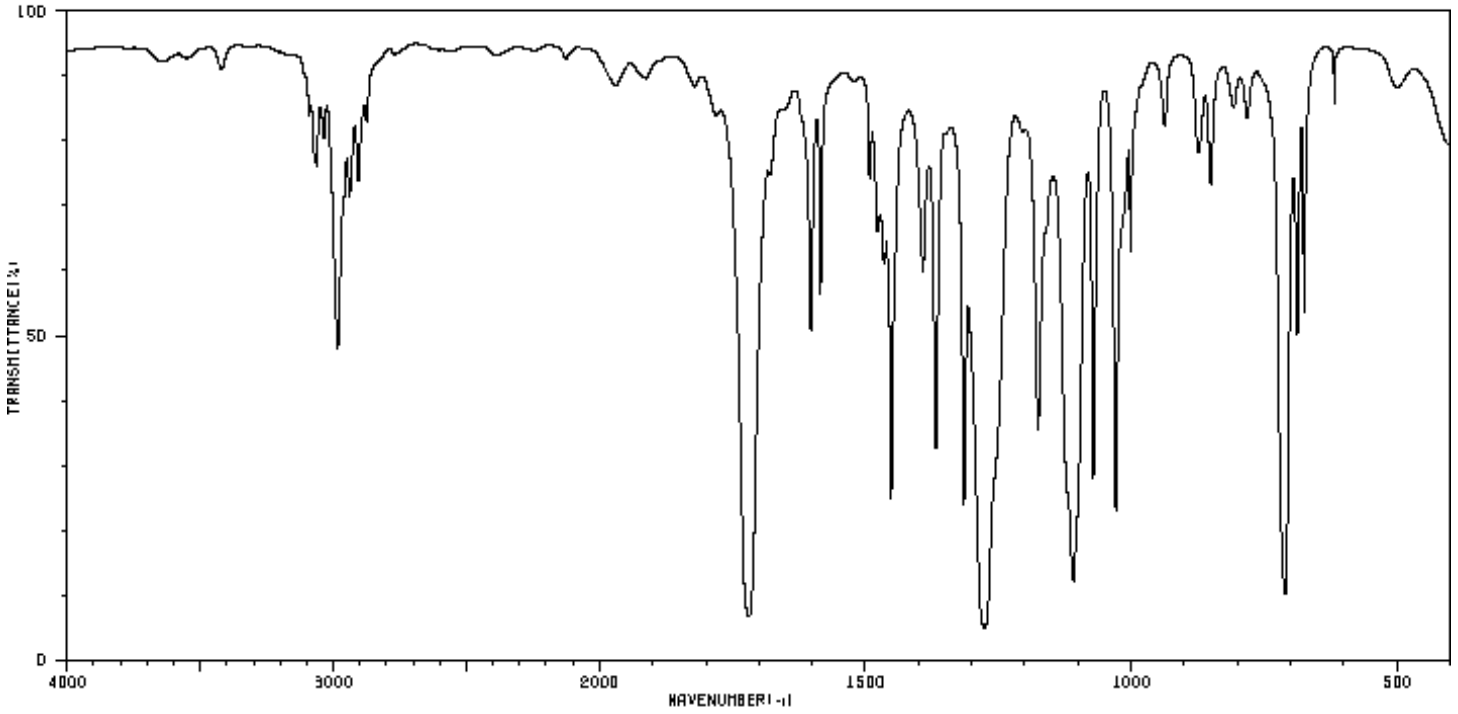
3088	86	1778	86	1388	81	1024	84
3068	86	1709	4	1310	68	828	55
3032	86	1653	84	1285	86	686	47
2847	86	1607	81	1203	39	673	86
2814	79	1598	72	1167	68	650	64
2732	77	1586	72	1160	84		
2693	86	1466	74	1072	86		



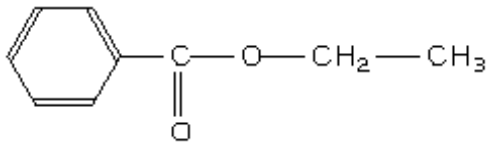
HIT-NO=1451	SCORE= ( )	SDBS-NO=1460	IR-NIDA-04316 : LIQUID FILM

ETHYL BENZOATE

$C_9H_{10}O_2$



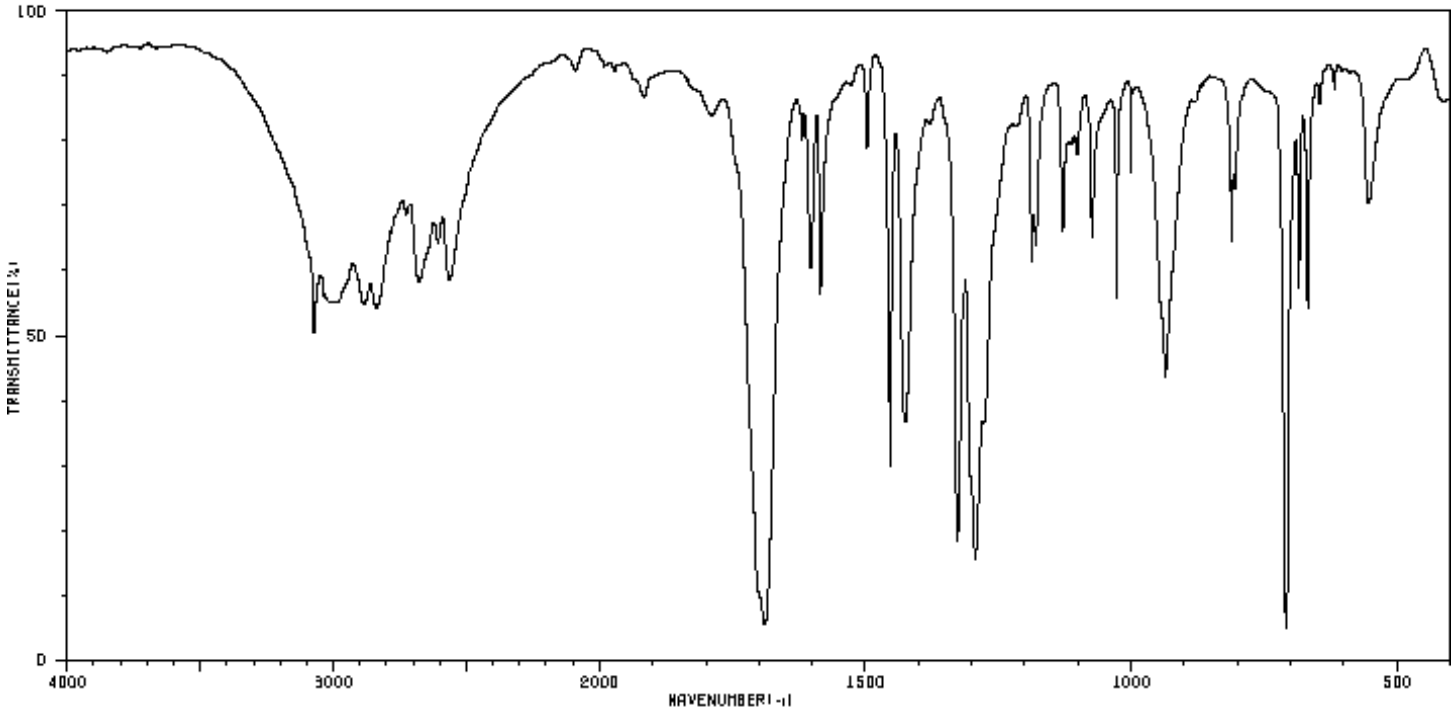
3091	81	1969	84	1466	68	1109	12	807	81
3064	72	1822	84	1452	23	1071	26	782	79
3035	77	1719	6	1392	57	1029	21	711	9
2983	46	1603	49	1368	31	1002	60	688	47
2939	68	1585	53	1315	23	937	79	675	52
2907	70	1492	72	1276	4	873	74	618	61
2874	79	1478	64	1176	34	861	70	606	84



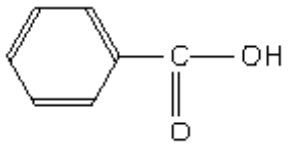
HIT-NO=1081	SCORE= ( )	SDBS-NO=673	IR-NIDA-63340 : KBR DISC

BENZOIC ACID

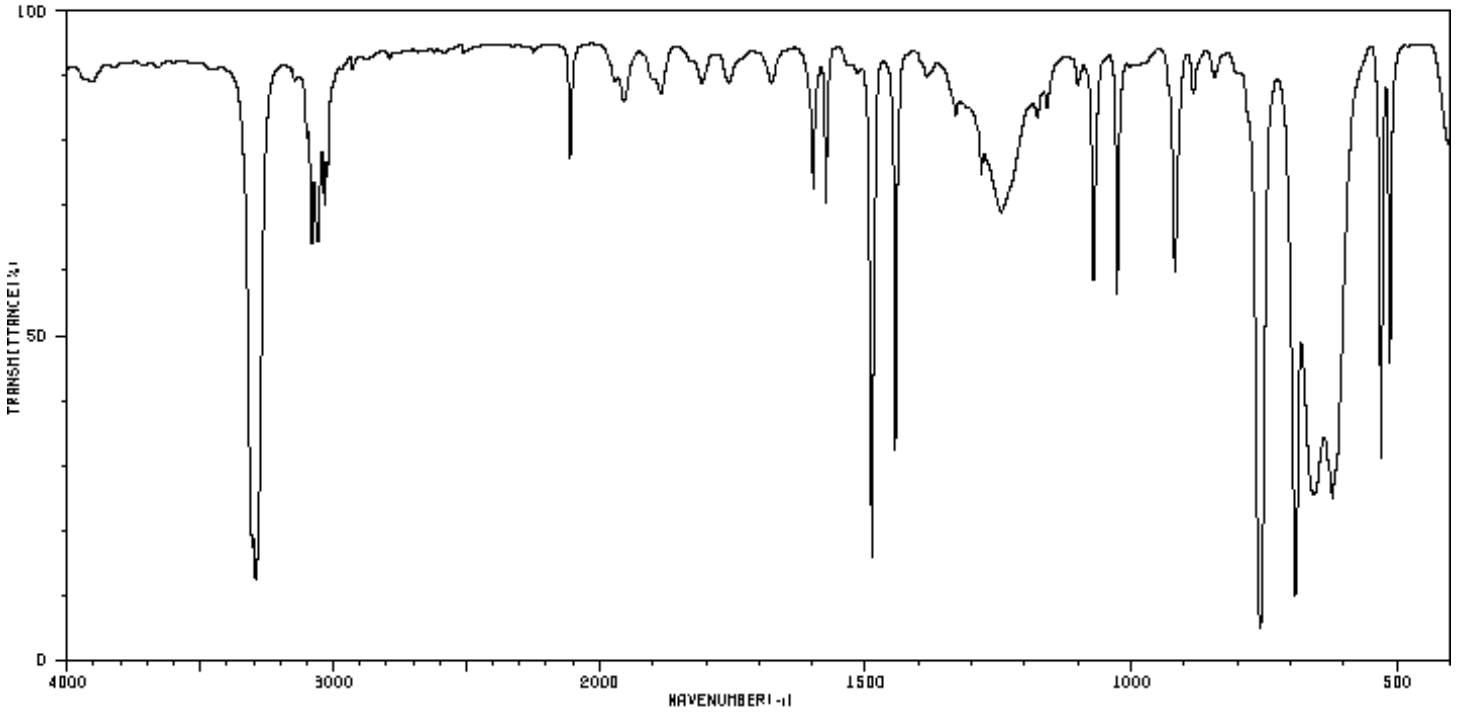
$C_7H_6O_2$



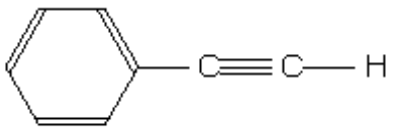
3073	49	2678	67	1426	36	1112	77	936	42
3012	53	2607	62	1327	17	1107	77	812	62
2998	53	2564	57	1294	14	1102	74	805	70
2986	53	1689	6	1187	68	1074	62	708	4
2886	52	1603	58	1180	60	1028	53	685	55
2838	52	1585	59	1129	84	1001	72	667	52
2726	66	1464	28	1118	77	943	60	664	68



HIT-NO=1445	SCORE= ( )	SDBS-NO=1444	IR-NIDA-63379 : LIQUID FILM
PHENYLACETYLENE			
C_8H_6			



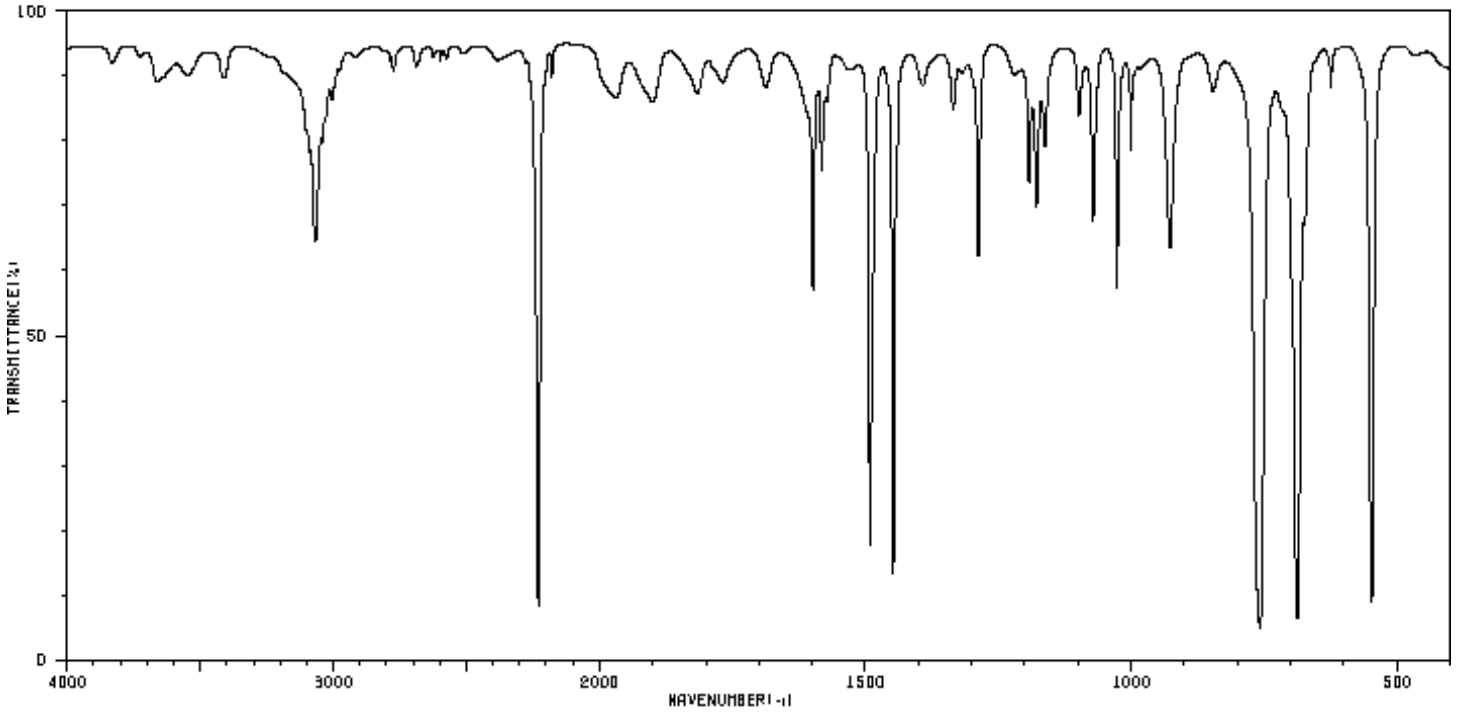
3906	86	2110	74	1674	68	1176	81	843	86
3306	16	1954	84	1488	15	1159	81	757	4
3291	12	1900	86	1444	31	1100	84	692	9
3081	62	1886	84	1386	86	1071	57	666	24
3058	62	1808	86	1331	81	1026	53	621	23
3034	68	1757	86	1282	72	918	57	530	30
3022	72	1698	70	1245	66	883	84	614	43



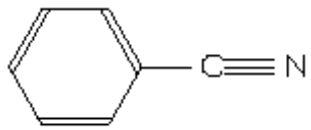
HIT-NO=1114	SCORE= ( )	SDBS-NO=669	IR-NIDA-05064 : LIQUID FILM

BENZONITRILE

C_7H_5N



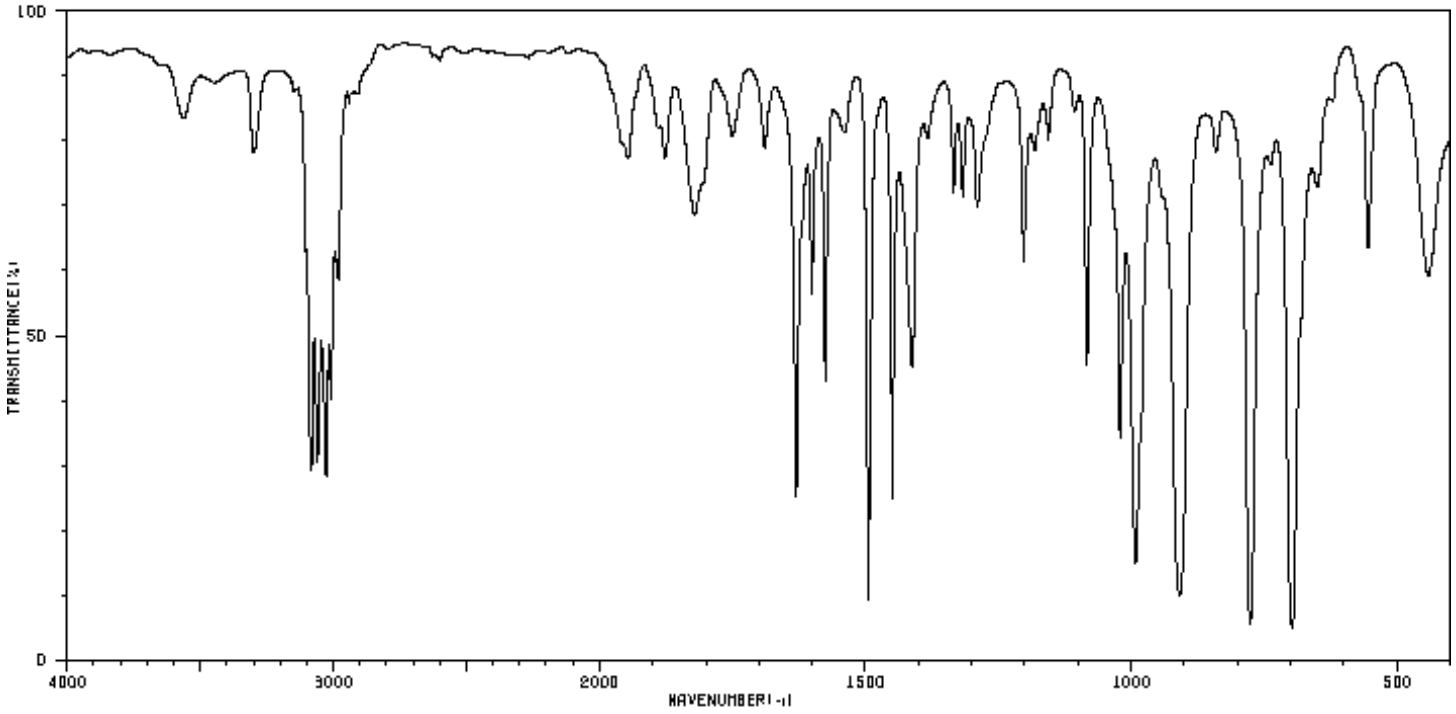
3646	86	2178	86	1582	72	1288	60	1001	74
3412	86	1969	84	1572	81	1193	70	927	60
3088	74	1899	81	1492	17	1178	66	846	64
3066	62	1816	84	1448	12	1163	77	758	4
3004	84	1768	86	1441	72	1098	81	688	6
2256	84	1688	84	1392	84	1072	64	625	64
2230	8	1599	66	1336	81	1027	66	548	8



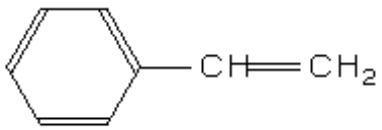
HIT-NO=2170	SCORE= ( )	SDBS-NO=3044	IR-NIDA-10290 : LIQUID FILM

STYRENE

C_8H_8



3299	74	1946	74	1496	9	1202	68	841	74
3082	28	1876	74	1449	23	1182	74	777	5
3060	29	1821	66	1412	43	1156	77	736	72
3027	27	1689	77	1383	77	1083	49	698	4
3009	38	1630	24	1334	70	1021	33	650	70
2980	57	1601	55	1317	66	992	14	555	60
1955	77	1575	41	1290	66	909	9	442	57



Infrared Unknowns Worksheet

Use the tables below to roughly record your results of the 'Infrared Spectral Analyses' for the unknowns (obtained from your instructor or found at the end of this Report Book or online at: http://science.athabascau.ca/Labs/resources/350Unkns/index.php username = auchem350 password = reaction). Please neatly fill out the same table on the unknown spectra and remember to fully label each of the absorption bands identified.

Code: Name:	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Code: Name:	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Code: Name:	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Code: Name:	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Part 2 Write-up

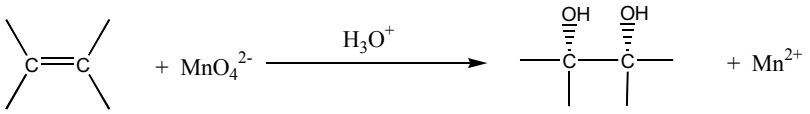
Submit your analyses tables of the 'Instructor Led Group Infrared Analysis Problems' and your analyses tables and spectra for the practice problems. Label your spectra thoroughly.

Also submit your analyses tables and spectra for the 4 unknowns. Label your spectra and clearly indicate the correct structure of the unknowns.

Experiment 6 Questions

Answers are to be submitted with your lab report.

1. The reaction of an alkene with acidic potassium permanganate is an example of a redox reaction. Use the method that you learned in your general chemistry course to write out a balanced equation for the reaction below.



a C_2H_4 + b $KMnO_4$ + c H^+ <------> d $C_2H_6O_2$ + e K^+ + f Mn^{+2}

Half Rxns.

reduction: ___MnO_4^- + ___H^+ + ___e^- ------>___Mn^{2+} + ___H_2O

oxidation: ___C_2H_4 + ___H_2O ----------> ___$C_2H_6O_2$ + ___ e^- + ___H^+

Bal. Equation: _____

2. The reaction of an alkene with potassium permanganate can also occur in a basic medium, in which case the inorganic product is a brown precipitate of manganese (IV) oxide. (The organic product is again the diol.) Write a balanced redox equation for the reaction of an alkene with alkaline potassium permanganate.

3. What are the major differences you would see in the infrared spectra of an alkane, alkene, and alkyne?

Experiment 7
Extraction of Usnic Acid from Lichen

Solid-Liquid Extraction Procedure:

There are only 4 steps involved in performing a solid liquid extraction.

1. Add the unknown mixture and extraction solvent to a vessel.
2. Allow time for the extraction to take place.
3. Gravity filter to remove the unwanted source material
4. Remove the solvent to concentrate the desired extracted solute.

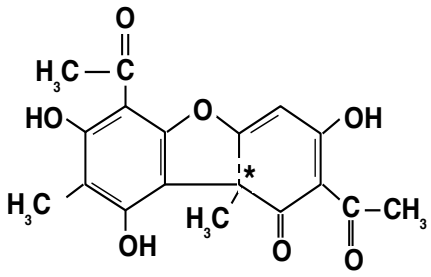


Figure 7.2. Structure of usnic acid (* = chiral or stereogenic C)

Cahn-Ingold-Prelog Sequence Rules

1. Rank atoms attached to stereogenic C in order of atomic #, High 1, Low 4. (e.g., Br>Cl>O>N>C>H)
2. If decision cannot be reached, look at second atom of substituent, etc.
3. Multiple bonded C are equivalent to the same # of single bonded atoms.
4. Mentally orient the molecule so that the lowest priority group (R4) is pointing directly back, away from you.

Note: Usnic acid has only one chiral center, and therefore only 2 enantiomers.

Chemicals, Equipment, Utilities Required

All glassware used for solid-liquid extraction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
lichen (dried and crushed), reagent & HPLC grade acetone, ethanol, L-tartaric acid, distilled water, tetrahydrofuran, ice.	-stirrer-hot Plate, lab jack, retort stands, utility clamps -polarimeter -melting-point apparatus -hazardous waste disposal containers (in fume hood)	-115V electrical, -water aspirator -air-line

About Using the Polarimeter

- The light source for the polarimeter is a very expensive sodium lamp. Do not switch the light source on and off, as this will drastically shorten the life-span of the bulb.

To be able to make meaningful comparisons between results obtained by different groups of workers, instead of reporting observed rotations, chemists usually report the results of polarimetry measurements in the form of **specific rotation**, $[\alpha]_D^{20}$ where

$$[\alpha]_D^{20} = \frac{\alpha}{\mathrm{L} \times \mathrm{d}} \quad \text{for a liquid, and}$$

$$[\alpha]_D^{20} = \frac{\alpha}{\mathrm{L} \times \mathrm{c}} \quad \text{for a solution.}$$

In the above equations, the superscript (20) indicates the temperature at which the measurements were made and the subscript (D) indicates that the measurements were made using the D line obtained from a sodium lamp (i.e., a wavelength of 589.3 nm). The observed rotation is represented by α, and the length of the sample tube (in dm) is presented by L. When the measurement is made on a liquid, it is necessary to know the density of the liquid, d, in $g \cdot mL^{-1}$. When using a solution, the concentration of the solution, c, must be included in the calculation using the units $g \cdot mL^{-1}$. To be complete, the specific rotation must include a sign to indicate the direction of the rotation:

\+ for rotation to the right (dextrorotatory), − for rotation to the left (levorotatory).

Procedure

Part A: Extraction of (+ or -)-Usnic Acid

1. Place 10.0 g of previously oven dried (40° C) crushed or cut up lichen into a clean 500 mL Erlenmeyer flask containing a 1" magnetic stirrer and loosely capped with a cork stopper or Parafilm™. To the flask with lichen add 150 mL of acetone.

2. Mix the lichen/acetone mixture for 0.5 hours at room temperature. Frequently resubmerge any lichen that adheres to the sides of the flask.

Part B: Isolation of Usnic Acid

1. **Gravity** filter the mixture, and collect the filtrate in a clean 250 mL Erlenmeyer flask.

2. Evaporate the acetone under a gentle stream of air in the hood with the flask suspended ~1" above a hot plate set on low or use a rotary evaporator (see Exp. 5) to remove almost all the acetone. Allow the last amount of acetone to evaporate at room temperature.

Part C: Purification and Characterization of Usnic Acid

1. Recrystallize the crude usnic acid from as solution of acetone-95% ethanol (10:1). Dissolve the crystals in the minimum amount of hot acetone, and then add the ethanol.

2. Collect the yellow crystals by vacuum filtration, wash with ice cold acetone and dry the crystals on a sheet of filter paper.

3. Weigh the usnic acid to determine your yield, and calculate the percentage of the acid in the lichen by weight.

4. Determine the melting point of the purified usnic acid, confirm the identity of usnic acid by mixed melting point procedure and compare it to the literature.

5. Optional: The instructor may also obtain an IR spectrum of several samples of the purified material, and these will be compared to an authentic sample.

6. While you wait for a suitable moment to determine the specific rotation of the usnic acid, familiarize yourself with the use of the polarimeter by determining the specific rotation of the unknown sample provided.

Part D: Polarimetry-The Specific Rotation of an Unknown Compound

1. Prepare an aqueous solution of the given unknown by dissolving 5 to 6 g of solid (weighed-out on analytical balance) in a 25-mL volumetric flask.

2. Ensure that the polarimeter is set up correctly. The polarimeter should be connected to the control box, the control box should be connected to the step-up transformer, and the step-up transformer should be plugged into a power outlet. The unit is turned on by means of the on-off switch on the control box, and the sodium lamp is lit by pressing the red button adjacent to the on-off switch. At first, when viewed through the eyepiece, the light from the sodium lamp will appear red, but after approximately two minutes the colour will change to bright yellow. When this happens, the unit is ready.

3. Obtain the 200-mm polarimeter tube from the instructor. (**CARE:** This is an expensive item!) Notice that one end of the tube has a smaller diameter than the other. Make sure that the cap on the end with the larger diameter is secure, but not too tight. Remove the cap from the other end (i.e., the end with the smaller diameter), and rinse the tube with distilled water.

4. Secure the tube using a utility clamp and a ring stand. Fill the tube with distilled water. Carefully avoiding the creation of any air bubbles, slide the glass disc across the end of the tube, and screw the cap (including the rubber gasket) onto the end of the tube. Ensure that the outside of the tube is dry, and then insert it into the measuring chamber of the polarimeter with the broader end closest to the eyepiece.

5. Look through the eyepiece and adjust the Vernier scale so that the two half circles that appear are of equal brightness (see Figure 7.4).

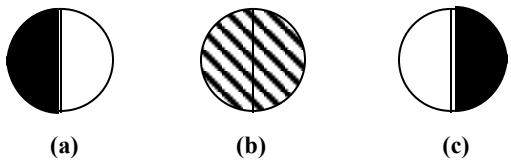


Figure 7.4. Possible views through the eyepiece of the polarimeter

6. Read the Vernier scale. Consult your instructor if you are not sure how to do this, although Figure 7.5 may be of assistance.

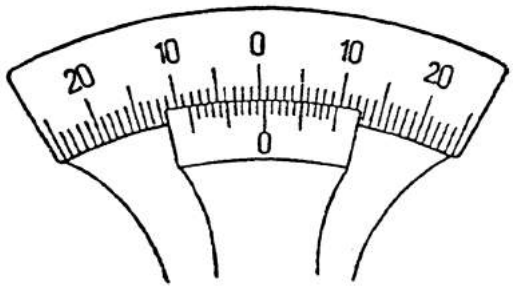


Figure 7.5. Reading the Vernier scale on the polarimeter

In Figure 7.5, the zero of the lower scale is between 0 and 1 on the upper scale. This indicates that the reading is between 0% and 1%. We next look to see which line to the right of the zero on the lower scale coincides with a line on the upper scale. In fact, the seventh line on the lower scale coincides with a line on the upper scale, thus the reading is 0.7%.

Determine the reading several times, approaching the correct adjustment from both possible directions. Your readings will show some variation, record them all and use the mean value in your results. This is a "blank" value and will have to be subtracted from your "test" result. Ideally, the blank value would be 0.0^{o}.

7. Remove the cap from the smaller end of the tube and empty this water into the sink. Rinse the tube with a *small* amount of your test solution. Fill the tube with the test solution as described in step 4 and determine the observed rotation of the sample as described in steps 5 and 6.

Note: when the sample tube is inserted into the polarimeter with the Vernier scale set at the value obtained for the "blank", when you look through the eyepiece, half of the circle will appear dark and the other half light. **If the darker half is to the right, the test substance is dextrorotatory. A darker left half indicates a levorotatory substance.**

8. Place the solution of the unknown in the container provided. Rinse the sample tube with water. Unless you are ready to determine the specific rotation of usnic acid, return the tube to the instructor.

Part E: Polarimetry—The Specific Rotation of Usnic Acid

1. After showing the instructor the usnic acid that you obtained from Part A, weigh-out, on an analytical balance, 80 mg of your sample into a clean 25 mL volumetric flask and add spectral grade tetrahydrofuran (THF) until at the 25.00 mL mark.. If you do not have sufficient usnic acid, combine your product with that of another student or see your instructor.

2. Set up the polarimeter as described in Part D. This time, obtain the "blank" reading using an empty polarimeter tube instead of a tube filled with water. Rinse the tube with a small quantity of (+) or (-) usnic acid, then fill the tube with this substance and determine its observed rotation as described for the unknown compound in Part D. The specific rotation is then calculated using the equation given in the introduction to this experiment.

3. Place the usnic acid in the container provided. Clean the polarimeter tube with acetone and return the polarimeter tube to the instructor.

Safety

Usnic Acid is harmful if swallowed, inhaled or absorbed through the skin. Wear gloves. In case of contact, flush affected area with copious amounts of water. Inv-mus LD50 25 mg/kg.

Acetone (propanone) is an irritant to the eyes, skin and lungs, and harmful to the liver and kidneys if swallowed. Highly flammable. Use in a well ventilated area. TLV (mg/m^3) =1780.

95% Ethanol may contain denaturing substances that enhance its toxicity. Also flammable.

Tetrahydrofuran (THF) or diethylene oxide is harmful if inhaled. Exposure to vapors of THF in excess of 200 ppm in air will result in liver damage. TLV (mg/m^3) =590.

Additional information about the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste Disposal

Solutions containing the usnic acid (i.e., the filtrates from the suction filtrations) should be placed in the container provided.

Write-up and Calculations

This experiment may be written up using the standard preparative format. Keep the "Introduction" and "Procedure" sections brief. Remember to define what is meant by specific rotation. Be sure to include all the numerical data from the polarimetry sections in your report. You should calculate:

1. the specific rotation of the unknown solid.
2. the specific rotation of the usnic acid.
3. the optical purity of the usnic acid.

When calculating the specific rotation, remember to take into account the reading obtained for the blank; for example,

> Observed rotation obtained for the solution of unknown compound = +6.2°
> Observed rotation obtained for water = +0.5°
> Observed rotation, [α], to be used in calculation = 5.7°

To determine the percentage purity of usnic acid you will need to look up the specific rotation of this substance in an appropriate handbook. **Remember** to photocopy you lab report before mailing it to your academic expert for marking.

Questions

1. Define the difference between diastereomers and enantiomers. Choose a specific example (e.g., glucose/fructose) to help explain your answer.

2. Draw a line/wedge diagrams for the two enantiomers of usnic acid (see Figure 7.1).

For Additional Information

If you have any questions about the operation of the polarimeter, please talk to your laboratory instructor. The instruction booklet for the instrument, *Instruction Manual for Model SR-6 Polarimeter*, should be available for consultation in the laboratory.

Experiment 8
Preparation of Cyclohexene from Cyclohexanol

Review of Distillation Procedure

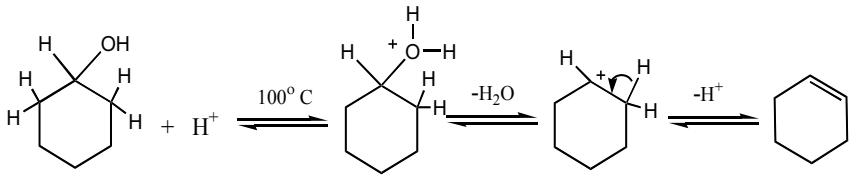
Remember there are 6 steps to performing a distillation.

1. Select the heat source (heating mantle, Bünsen burner, steam bath, water bath).
2. Clean, dry and assemble the distillation apparatus. Use joint grease?
   - i) start assembling the apparatus from the bottom up. Use a lab jack.
   - ii) Place the heat source in position. Use lab jack to adjust height.
   - iii) Clamp the distillation flask in position.
   - iv) Place the three way connector into the neck of the distillation flask.
   - v) Place the thermometer adapter into the top of three way connector.
   - vi) Approximately set the height of receiving flask using an utility clamp.
   - vii) Place the condenser into position and secure it with joint clamps.
   - viii) Attach tubing to the water inlet and water outlet of the condenser.
   - ix) Adjust the height of thermometer
   - x) Inspect to ensure no joint is under stress and that the system can be safely heated (i.e. it is open to the air (via the vacuum take-off adapter) and it is not a BOMB.)
3. Turn on the cold water supply to the condenser. Check for leaks.
4. Add the liquid to be distilled to the distillation pot. Add boiling stones.
5. Heat the liquid and collect the product in the receiving flask.
6. Allow the reaction to cool, then disassemble the apparatus. Clean all parts thoroughly with acetone (discard in organic wastes) before washing with soapy water in the sink.

In this experiment, you will use the sample of cyclohexanol you purified in Experiment 3A. This reaction is a reversible E_1 elimination type reaction (E_1 =

$H^+ = H_3PO_4$ (Mwt = 98.0 g/mol, d=1.7 g/mL, ~14.7 M)
In the first step, protonation of the alcohol, the poor leaving group (-OH) is converted to a better leaving group (-OH_2^+).

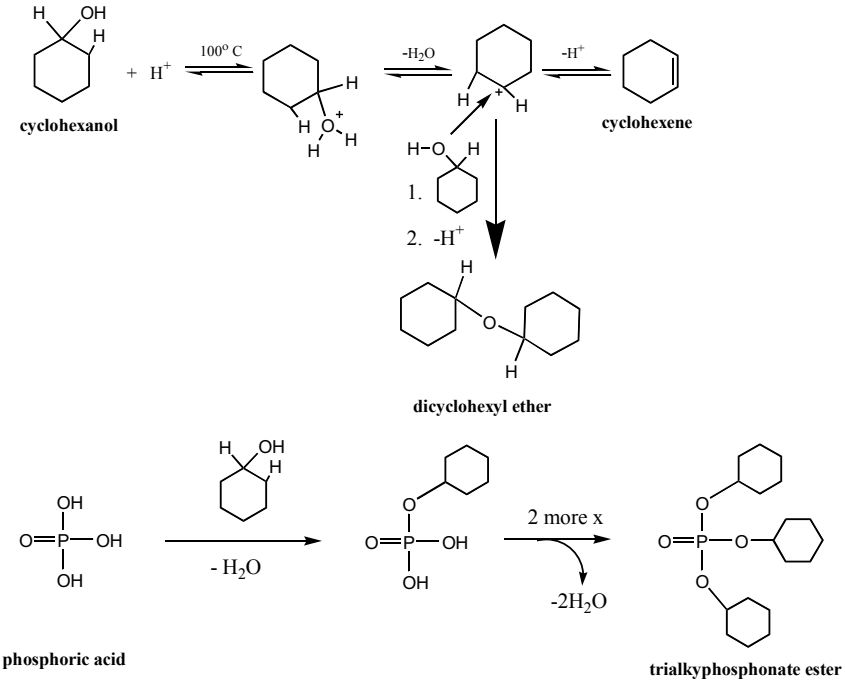
In our experiment, the overall equilibrium is shifted to the right by the removal of cyclohexene and water from the reaction mixture as they are formed.



cyclohexanol
Mwt.= 100.16 g/mol
d = 0.963 g/mL
Vol Used =
mol =

cyclohexene
Mwt. = 82.14 g/mol
d = 0.8102 g/mL
Theor.Yield =
Yield =
% Yield =

Byproducts of acid-catalyzed dehydrations

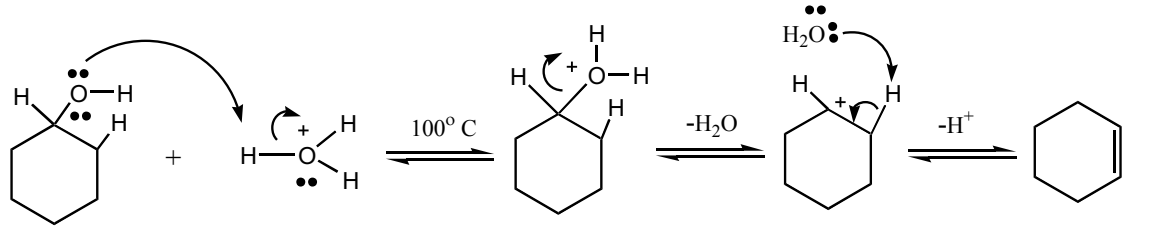


E_1 Reaction Mechanism

The reaction used in the this experiment (cyclohexanol in the presence of 85% phosphoric acid and heat (100°C) occurs via a three step mechanism:

1) protonation of the alcohol oxygen,
2) loss of water to generate a carbocation intermediate, and
3) loss of a proton from the neighbouring carbon atom and formation of a double bond.

Tertiary alcohols will react faster than secondary, which will react faster than primary alcohols (3° > 2° >1°). This is because the tertiary alcohol carbocation is more stable than the secondary or primary carbocations. Please note that fairly harsh conditions were required to form the cyclohexanol carbocation in this experiment. A more sensitive alcohol molecule would not survive such treatment.



Chemicals, Equipment, Utilities Required

All equipment used for the reaction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (purified), 85% phosphoric acid, vacuum (glass joint) grease, sodium chloride, 10% sodium carbonate, brine (sat. sodium chloride, anhydrous calcium chloride, ice, distilled water, wash acetone	-graduated cylinders -heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, boiling stones) -125 mL separatory funnel -hazardous waste disposal containers (in fume hood)	-115V electrical, -cold water supply

Procedure for Cyclohexene Synthesis

You must complete at least steps 1-8 before stopping.

A. Reagent and Equipment Preparation

1. Use graduated cylinders to measure out 21 mL of cyclohexanol (previously distilled in Experiment 3) and 5 mL of 85% phosphoric acid into a 100-mL round bottom flask. **Caution:** 85% phosphoric acid is corrosive and viscous. Wear gloves, protect your eyes and work with it in the fume hood. Pipette carefully.

2. Add a few boiling stones, and then attach the flask to a simple distillation apparatus (see *The Organic Chem Lab Survival Manual*, pp. 103-109; pp.189-194 in 3rd ed.), making sure that the thermometer has been positioned correctly (see Experiment 3). Note that the collecting vessel is a 50-mL round bottom flask, cooled in an ice-water bath.

B. Reaction

3. Start the cooling water circulating through the condenser, and begin to heat the reaction mixture using a heating mantle.

4. As the cyclohexene begins to distil, the control on the heating mantle should be adjusted so that the temperature of this distilling vapour does not exceed 100°C. Record the temperature changes you observe and correct them for barometric pressure.

C. Quenching the Reaction

5. When only a few millilitres of liquid remain in the distilling flask, stop the distillation by lowering the lab jack and removing the heating mantle. The appearance of white fumes in the distillation flask is a good indication that the distillation has proceeded far enough. **Remember:** Never try to distil to dryness! Proceed immediately to the next step.

D. Reaction Workup/Product Recovery

6. Add solid sodium chloride to the distillate until no more salt will dissolve. The sodium chloride should be added little by little using a spatula, and the flask would be shaken after each addition.

7. Add enough 10% sodium carbonate solution to make the solution in the flask basic to litmus. **(Take care: Some gas may be evolved.)** Transfer the neutralized mixture to a separatory funnel and separate the two layers. The aqueous layer should be drained through the stopcock and the upper layer poured through the neck of the separatory funnel into a 125-mL Erlenmeyer flask.

8. Wash the organic layer in the separatory funnel with 10 mL of brine (=saturated sodium chloride). Remove and discard the wash/aqueous layer.

9. Add 2 to 3 g of anhydrous calcium chloride to the cyclohexene in the Erlenmeyer flask. Place a cork in the mouth of the flask, and swirl the contents occasionally as the cyclohexene dries over a period of 10 to 15 minutes. The cyclohexene should be clear when all the water has been removed. While you are waiting, clean your condenser and prepare to carry out another simple distillation.

E. Product Purification and Analysis

10. Gravity filter (or decant) the dry cyclohexene into a clean, dry 50-mL round bottom flask, and add a few boiling stones. Distil the cyclohexene, collecting the fraction that boils over a range of 80-85ºC (corr.). Note: Remember that the boiling point of your product needs to be corrected for barometric pressure.

F. Product Analysis

11. Determine the yield (mass) of cyclohexene obtained, and calculate your percentage yield. Optional: Perform infrared spectroscopy on the sample. Determine the density of your sample by also measuring the volume of product (d=m/v), and determine the refractive index (n_D^{20}).

12. Transfer the sample to a suitably labelled screw cap vial and submit it to your instructor. Save this sample as it is needed for use in Experiment 6.

Safety

Cyclohexanol is flammable, irritating to the skin and eyes, and is harmful if inhaled or ingested.

Cyclohexene vapour irritates the eyes, skin and respiratory system. The liquid is harmful if swallowed. Highly flammable.

Phosphoric acid burns the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

Sodium chloride and **sodium carbonate** do not normally constitute a safety hazard, but you should treat all chemicals with respect.

Saturated sodium chloride (brine) does not normally constitute a safety hazard, but you should treat all chemicals with respect.

Calcium chloride (anhydrous) is an irratant and is hygroscopic. Wash away any dust with lots of water.

Additional information about the potential hazards in handling these chemicals may be obtained from the *Material Safety Data Sheets* that are available in the laboratory.

Waste Disposal

Cyclohexanol/phosphoric acid residues should be placed in the container provided for this purpose.

The **aqueous layer from the separation** may be washed down the sink with plenty of water.

The **cyclohexene residue** from the final distillation should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

Write-up

This experiment should be written-up using the standard format for preparative experiments (see the "Reports" section of this *Laboratory Manual*.)

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with report.

1. What is the purpose of adding 10% sodium carbonate solution to the distillate in step 7 of the procedure?

2. Identify two possible by-products that could be formed from cyclohexanol in this experiment. [**Hint:** You may have to search through your textbook to find what other reactions can occur between an alcohol and a concentrated mineral acid (e.g. phosphoric acid)

Experiment 9
The Nitration of Acetanilide

Chemicals, Equipment, Utilities Required

All glassware used must be clean of any organic contamination (**especially acetone**).

Chemicals	Equipment	Utilities
acetanilide (purified) acetic acid (glacial) nitric acid (conc.) sulfuric acid (conc.) ice distilled water ethanol wash acetone	-stirrer/hotplate, lab jack, retort stands, utility clamps, latex gloves -Büchner funnel & adapter, filter flask, Whatman #1 filter paper circle, sample vial + label -recrystallization (flat bottom) dish -melting-point apparatus -hazardous waste disposal containers (in fume hood)	-115V electrical, -water aspirator

About Concentrated Acids

- **Dilute all conc. acids** to < 3M using cold water before rinsing down the drain.
- **Always add acid to water (AtoW).**

For example, say you have 10 mL of unused conc. sulfuric acid left over after measuring out all you needed for the reaction. To dispose of the unwanted sulfuric acid you must calculate how much to dilute it before rinsing it down the drain.

Given: conc. sulfuric acid is 18 M.
Therefore the number of moles you have to dispose of = 18M × 0.01L = 0.18 moles.
To dilute it to < 3M, you must place it into a minimum of 'x' L of water.
Since M = moles/L, then L = moles/M
L = 0.18 moles/3 M = 0.06 L or **60 mL** of water.

Treat all glassware that has come into contact with concentrated acids with extreme care. Small amounts of the acid are coating the surface and must be diluted and rinsed away. To rinse away the acid

1. in a sink, turn on the water, cold and slow flow.
2. pointing the opening of the vessel *away* from you, place the acid contaminated glassware beneath the stream of water until near overflowing. Dump the contents down the drain and flush the glassware 2 more times with the water.
3. finally, clean the glassware with hot soapy water, rinse with hot water, and >3 times with distilled water. Dry with acetone and air-dry or oven dry to allow the acetone to evaporate before using the glassware for measuring more reagents. This is particularly important in this experiment, as any trace acetone will react with the nitronium ion, producing a coloured impurity.

Procedure

1. Carefully add 3 mL of concentrated nitric acid (15 mol· L^{-1}) to 4 mL of concentrated sulfuric acid (18 mol· L^{-1}) in a **very clean** smaller flask. Cool the resulting nitrating mixture to room temperature. Have the flask clamped into position in the ice bath to keep the flask from tipping over!

   Caution: Nitric acid, sulfuric acid and the nitrating mixture are highly corrosive. Wear gloves, protect your eyes, and work in a fume hood. Excess nitric and sulfuric acid measured out should be properly disposed. See your instructor.

2. Place 10 mL of concentrated (i.e., 18 mol· L^{-1}) sulfuric acid contained in a 125-mL Erlenmeyer flask and cool in an ice-water bath.

   Caution: Sulfuric acid is extremely hazardous. Wear gloves and proper eye protection.

3. Meanwhile, ask your instructor for the acetanilide that you purified in Experiment 2. Dissolve about 7.0 g of the acetanilide in 7 mL of glacial (i.e., 100%) acetic acid by warming the two substances together in a small Erlenmeyer flask in a fume hood (use setting 2 on hot plate).

   Caution: Acetic acid is corrosive and its vapour is extremely irritating. Wear gloves, protect your eyes, and work in a fume hood.

   Cool the solution until crystals just begin to form, then warm slightly to redissolve, and then pour the solution slowly, with stirring, into 10 mL of concentrated (i.e., 18 mol· L^{-1}) sulfuric acid contained in the 125-mL Erlenmeyer flask, which is being kept cool in an ice-water bath (from step 2 above).

   Continue to cool the solution to about 5° C (this can take ~30 min). Use lots of ice, and swirl frequently.

4. Use a Pasteur pipette to **slowly transfer** the nitrating mixture prepared in step 1 to the Erlenmeyer flask containing the acetanilide solution prepared in step 3. Swirl the flask continuously during the addition and keep the temperature of the mixture below 20° C by cooling in an ice-water bath.

5. When all the nitrating mixture has been added, allow the reaction mixture to stand at room temperature for 30 minutes.

6. Add the reaction mixture slowly, with stirring, to a mixture of 100 mL of water and 25 g of ice in a 400-mL beaker. (You should have a frothy, pale-yellow slurry.)

7. Collect the solid by suction filtration (refer to Experiment 2, if necessary). Break up the solid with a spatula, being careful not to tear the filter paper, and wash the solid with cold water.

8. Remove the solid from the Büchner funnel and transfer it to a 400-mL beaker. Add 100 mL of distilled water and stir vigorously. Collect the solid by suction filtration and again wash with cold water.

9. Repeat step 8. Use blue litmus paper to test the wash water collected in the filter flask to see if it is still acidic. If it is, you should repeat step 8 again.

10. When the wash water is no longer acidic, press the solid between two filter papers until it is as dry as possible and then allow it to dry in air.

11. Determine the mass of crude *p*-nitroacetanilide obtained. Recrystallize the product using a 4:1 mixture of ethanol and water. You should expect to use about 100-150 mL of solvent. Remember that using either too much or too little solvent will reduce your final yield.

12. When your product is dry (you may have to leave it drying in air until your next laboratory session), determine its yield and melting point.

13. Ask your instructor to assist you in obtaining an infrared spectrum of both your starting material (acetanilide) and your product (4-nitroacetanilide).

14. Store your sample in a suitably labelled sample vial and hand it to your instructor for grading and possible use in a subsequent experiment.

Safety

Acetanilide was formerly used as a dusting powder, as a mild antiseptic and anesthetic. It can be harmful if taken internally.

***p*-Nitroacetanilide** is not considered to be particularly hazardous; however, you should avoid allowing this compound to come into contact with your skin or eyes. Wash your hands before eating.

Concentrated nitric acid is a corrosive liquid with an irritating vapour. Protect your hands and eyes. Use only in a fume hood.

Concentrated sulfuric acid is very corrosive to eyes, skin and other materials. Wear gloves and protect your eyes.

Glacial acetic acid can cause burns. Its vapour is irritating to the skin and eyes. Wear gloves and use only in a fume hood. Poisonous if swallowed.

Ethanol can be poisonous if swallowed. The denaturing substances present in laboratory ethanol increase its toxicity. Highly flammable.

Waste Disposal

Excess concentrated nitric and sulfuric acid measured out during Step 1 of the procedure must be neutralized before discarding. **See your instructor for the procedure**.

The acidic filtrate and washings from the suction filtrations should be diluted with copious amounts of water and washed down the drain.

The ethanol/water mixture from the recrystallization should be placed in the container provided.

Write-up

This experiment should be written up using the standard format for "preparative type" experiments. Do not forget to report the mass of acetanilide used, the mass of crude *p*-nitroacetanilide obtained, and the mass, percentage yield and melting point of the recrystallized product. Tabulate your data wherever possible.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with your lab report.

1. During the nitration of acetanilide (Step 4 of the procedure), care is taken to keep the reaction mixture cool. What do you think might be the consequences of allowing the reaction mixture to become too warm?

2. What organic compound (other than ethanol) would you reasonably expect to isolate from the ethanol/water mixture that was used o recrystallize your 4-nitroacetanilide.

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
acetanilide	$CH_3CONHC_6H_5$	S	135.17	113-115			Toxic, irritant
acetanilide,4-methyl	$CH_3CONHC_6H_4CH_3$	S	149.19	149-151			Irritant
acetanilide, *p*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	216			Irritant
acetanilide, *o*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	94	1.419		Irritant
acetanilide, *m*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	154-156			Irritant
acetic acid, glacial (17.4 M)	CH_3CO_2H	L	60.05	118.1	1.049		Corrosive, hygroscopic
acetic acid, *p*-ethoxyphenyl	$C_2H_5OC_6H_4CH_2CO_2H$	S	180.2	87-90			Irritant
acetic anhydride	$(CH_3CO)_2O$	L	102.09	140	1.082	1.3900	Corrosive, lachrymator
acetone	CH_3COCH_3	L	58.08	56.5	0.7899	1.3590	Flammable, irritant
acetone, diethylamino	$(C_2H_5)_2NCH_2COCH_3$	L	129.2	64/16mm	0.832	1.4250	Irritant
acetophenone	$C_6H_5COCH_3$	L	120.15	202	1.030	1.5325	Irritant
activated carbon		S					(see charcoal)
allyl alcohol (2-propen-1-ol)	$CH_2=CHCH_2OH$	L	58.08	96-98	0.854	1.4120	Highly Toxic, flammable
ammonia (14.8 M)	NH_3	L	17.03		0.90		Corrosive, lachrymator
ammonium hydroxide (14.8 M)	NH_4OH	L	35.05		0.90		Corrosive, lachrymator
aniline	$C_6H_5NH_2$	L	93.13	184	1.022	1.5860	Highly toxic, irritant
aniline, 4-bromo	$BrC_6H_4NH_2$	S	172.03	62-64			Toxic, irritant
aniline, 4-chloro	$ClC_6H_4NH_2$	S	127.57	72.5			Highly toxic, irritant
aniline, *o*-ethyl	$CH_3CH_2C_6H_4NH_2$	L	121.18	210		1.5590	Toxic, irritant
aniline, 2-ethoxy	$CH_3CH_2OC_6H_4NH_2$	L	137.18	231-233	1.051	1.5550	Irritant, light sens.
aniline, 4-methyl	$CH_3C_6H_4NH_2$	L	107.16	196	0.989	1.5700	Toxic, irritant
aniline, 3-nitro	$NO_2C_6H_4NH_2$	S	138.13	114			Highly toxic, irritant
aspirin (see salicylic acid, acetate)	$CH_3CO_2C_6H_4CO_2H$	S	180.16	138-140			Irritant, toxic
benzaldehyde	C_6H_5CHO	L	106.12	179.5	1.044	1.5450	Hi.toxic, cancer susp.agnt
benzaldehyde, 4-methyl	$CH_3C_6H_4CHO$	L	120.15	204-205	1.019	1.5454	Irritant (*p*-tolualdehyde)
benzaldehyde,4-methoxy	$CH_3OC_6H_4CHO$	L	136.15	248	1.119	1.5730	Irritant, (anisaldehyde)
benzaldehyde, 4-nitro	$NO_2C_6H_4CHO$	S	151.12	106			Irritant
benzene	C_6H_6	L	81.14	80.1	0.908	1.4990	Flamm., cancer susp.agnt
benzene, bromo	C_6H_5Br	L	157.02	155-156	1.491	1.5590	Irritant
benzene, chloro	C_6H_5Cl	L	112.56	132	1.107	1.5240	Flammable, irritant
benzoate, ethyl	$C_6H_5CO_2C_2H_5$	L	150.18	212.6	1.051	1.5050	Irritant
benzoate, methyl	$C_6H_5CO_2CH_3$	L	136.15	198-199	1.094	1.5170	Irritant
benzocaine, or 4-aminobenzoic acid, ethyl ester,	$H_2NC_6H_4CO_2C_2H_5$	S	165.19	88-92			Irritant
benzoic acid	$C_6H_5CO_2H$	S	122.12	122.4			Irritant
benzoic acid, 4-acetamido	$CH_3CONHC_6H_4CO_2H$	S	179.18	256.5			Irritant
benzoic acid, 4-amino	$H_2NC_6H_4CO_2H$	S	137.14	188-189	1.374		Irritant
benzoic acid, 3-chloro	$ClC_6H_4CO_2H$	S	156.57	158			Irritant
benzoic acid, 4-chloro	$ClC_6H_4CO_2H$	S	156.57	243			Irritant
benzoic acid, 3-hydroxy	$HOC_6H_4CO_2H$	S	138.12	210-203			Irritant
benzoic acid, 4-hydroxy	$HOC_6H_4CO_2H$	S	138.12	215-217			Irritant
benzoic acid, 2-methyl	$CH_3C_6H_4CO_2H$	S	136.15	103-105			See also *o*-toluic acid
benzoic acid, 4-methyl	$CH_3C_6H_4CO_2H$	S	136.15	180-182			See also *p*-toluic acid
benzoic acid, 4-nitro	$O_2NC_6H_4CO_2H$	S	167.12	239-241			Irritant
benzonitrile	C_6H_5CN	L	103.12	191	1.010	1.5280	Irritant
benzophenone	$(C_6H_5)_2CO$	S	182.22	49-51			Irritant
benzoyl chloride	C_6H_5COCl	L	140.57	198	1.211	1.5530	Corrosive, toxic
benzyl alcohol	$C_6H_5CH_2OH$	L	108.14	205	1.045	1.5400	Irritant, hygroscopic

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
benzyl amine	$C_6H_5CH_2NH_2$	L	107.16	184-185	0.981	1.5430	Corrosive, lachrymator
benzyl chloride	$C_6H_5CH_2Cl$	L	126.59	179	1.1002		Hi.toxic, cancer susp.agnt
biphenyl	$C_6H_5C_6H_5$	S	154.21	69-71	0.992		Irritant
boric acid	H_3BO_3	S	61.83		1.435		Irritant, hygroscopic
Brady's Reagent	$(NO_2)_2C_6H_3NHNH_2$	L	See hydrazine, 2,4-dinitrophenyl				
bromine	Br_2	L	159.82	58.8	3.102		Highly toxic, oxidizer
butanal	$CH_3CH_2CH_2CHO$	L	72.11	75			Flammable, corrosive
1,3-butadiene, E,E-1,4-diphenyl	$C_6H_5C_4H_4C_6H_5$	S	206.29	153			Irritant
butane, 1-bromo	$CH_3CH_2CH_2CH_2Br$	L	137.03	101.3	1.276	1.4390	Flammable, irritant
butane, 2-bromo	$CH_3CH_2CHBrCH_3$	L	137.03	91.3	1.255	1.4369	Flammable, irritant
butane, 1-chloro	$CH_3CH_2CH_2CH_2Cl$	L	92.57	78.4	0.886	1.4024	Flammable liquid
butane, 2-chloro	$CH_3CH_2CHClCH_3$	L	92.57	68.2	0.873	1.3960	Flammable liquid
1-butanol	$CH_3CH_2CH_2CH_2OH$	L	74.12	117-118	0.810	1.3990	Flammable, irritant
2-butanol	$CH_3CH_2CHOHCH_3$	L	74.12	99.5-100	0.807	1.3970	Flammable, irritant
2-butanone	$CH_3CH_2COCH_3$	L	72.11	80	0.805	1.3790	Flammable, irritant
2-butanone, 3-hydroxy-3-methyl	$(CH_3)_2C(OH)COCH_3$	L	102.13	140-141	0.971	1.4150	Irritant
1-butene, 3-chloro-	$CH_3CH(Cl)CH=CH_2$	L	90.55	62-65	0.900	1.4155	Flammable, lachrymator
3-buten-2-ol	$CH_2=CHCH(OH)CH_3$	L	72.11	96-97	0.832	1.4150	Flammable, irritant
n-butyl butyrate	$C_3H_7CO_2C_4H_9$	L	144.21	164-165	0.871	1.4060	Irritant
3-butyn-2-ol, 2-methyl	$CH{\equiv}CC(CH_3)_2OH$	L	84.12	104	0.868	1.4200	Flammable, toxic
calcium carbonate	$CaCO_3$	S	100.09		2.930		Irritant, hygroscopic
calcium chloride, anhydr.	$CaCl_2$	S	110.99		2.150		Irritant, hygroscopic
camphor (1R, +)	$C_{10}H_{16}O$	S	152.24	179-181	0.990	1.5462	Flamm., irritant
carbon dioxide, solid	CO_2	S	44.01	-78.5(subl.)			Frost bite burns
carbon tetrachloride	CCl_4	L	153.82	76	1.594		Susp. cancer agent
charcoal (Norit)		S	Decolourizing agent, used in recrystallizations				Irritant
chloroform	$CHCl_3$	L	119.38	61.3	1.500		Highly toxic
cinnamaldehyde, *trans*	$C_6H_5CH=CHCHO$	L	132.16	246(decomp)	1.048	1.6220	Irritant
cinnamic acid, trans	$C_6H_5CH=CHCO_2H$	S	148.16	135-136			Irritant
crotonaldehyde	$CH_3CH=CHCHO$	L	70.09	102.4	0.846	1.4365	Highly toxic, flammab.
cyclohexane	C_6H_{12}	L	84.16	80.7	0.779	1.4260	Flammable, irritant
cyclohexane, bromo	$C_6H_{11}Br$	L	163.06	166.2	1.324	1.4950	Flammable, irritant
cyclohexane, methyl	$C_6H_{11}CH_3$	L	98.19	101	0.770	1.4220	Flammable, irritant
cyclohexene	C_6H_{10}	L	82.15	83	0.811	1.4460	Flammable, irritant
cyclohexanol	$C_6H_{11}OH$	L	100.16	161.1	0.963	1.4650	Irritant, hygroscopic
cyclohexanone	$C_6H_{10}(=O)$	L	98.15	155.6	0.947	1.4500	Corrosive, toxic
cyclohexanone, 4-methyl	$CH_3C_6H_9(=O)$	L	112.17	170	0.914	1.4460	Corrosive, toxic
cyclopentane	C_5H_{10}	L	70.14	49.5	0.751	1.4000	Flammable, irritant
cyclopentane, bromo	C_5H_9Br	L	149.04	137-138	1.390	1.4881	Flammable
cyclopentanone	$C_5H_8(=O)$	L	84.12	130.6	0.951	1.4370	Flammable, irritant
dichloromethane	CH_2Cl_2	L	84.93	40.1	1.325	1.4240	Toxic, irritant
diethyl ether (see ethyl ether)	$C_2H_5OC_2H_5$	L	74.12	34.6	0.708	1.3530	Flammable, toxic
1,4-dioxane	$C_4H_8O_2$	L	88.11	100-102	1.034	1.4220	Flamm., cancer susp.agnt
diphenylmethanol	$(C_6H_5)_2CH(OH)$	S	184.24	65-67			Irritant

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
ethyl acetate	$CH_3CO_2C_2H_5$	L	88.11	76-77	0.902	1.3720	Flammable, irritant
ethyl alcohol, anhydrous	CH_3CH_2OH	L	46.07	78.5	0.785	1.3600	Flammable, poison
ethyl ether, absolute	$CH_3CH_2OCH_2CH_3$	L	74.12	34.6	0.708	1.3530	Flammable, irritant
fluorene	$C_{13}H_{10}$	S	166.22	114-116			Irritant
formaldehyde (sol'n)	HCHO	L	30.03	96	1.083	1.3765	suspect. cancer agent
formamide, N,N-dimethyl	$HCON(CH_3)_2$	L	73.10	149-156	0.9487	1.4310	suspect. cancer agent
furfuryl amine	$(C_4H_3O)CH_2NH_2$	L	97.12	145-146	1.099	1.4900	Irritant
gold	Au	S	196.97	1064	19.28		Expensive/valuable
***n*-hexane**	$CH_3(CH_2)_4CH_3$	L	86.18	69	0.659	1.3750	Flammable, irritant
hydrazine, 2,4-dinitrophenyl	$(NO_2)_2C_6H_3NHNH_2$	70% soln	198.14				Flammable, irritant
hexanes	C_6H_{14}	L	86.18	68-70	0.672	1.3790	Flammable, irritant
hydrochloric acid, conc. 12 M	HCl	L	36.46		1.20		Corrosive, highly toxic
iodine	I_2	S	253.81	133	4.930		Corrosive, highly toxic
lichen		S					Allergin
ligroin (high bp petrol. ether)	C_6-C_7 (light naphtha)	L		60-80	0.656	1.3760	Flammable, irritant
Lucas Reagent		Solution	of hydrochloric acid/zinc chloride (from zinc dust)				Toxic, irritant
magnesium (metal)	Mg	S	24.31	651	1.75		Flammable
magnesium oxide	MgO	S	40.31		3.58		Moist. sens., irritant
magnesium sulfate, anhydrous	$MgSO_4$	S	120.37		2.660		Hygroscopic
magnesium sulfate, 7-hydrate	$MgSO_4.7H_2O$	S	246.48		1.670		(epsom salt)
manganese dioxide	MnO_2	S	86.94	535 (dec.)	5.026		Oxidizer, irritant
methanol, anhyd.	CH_3OH	L	32.04	64.5	0.791	1.3290	High. toxic, flammable
methanol, diphenyl	$(C_6H_5)_2CH(OH)$	S	184.24	69			Irritant
methanol, triphenyl	$(C_6H_5)_3C(OH)$	S	260.34	164.3			Irritant
methylene chloride	CH_2Cl_2	L	84.93	40.1	1.325	1.4230	See dichlormethane
mineral spirits (light kerosene)	C_{12}-C_{14}	L		179-210	0.752	1.4240	Flammable, irritant
naphthalene	$C_{10}H_8$	S	128.17	80.5			Flamm., susp.cancer agent
nitric acid (conc. 15.4 M)	HNO_3	L	63.01		1.400		Corrosive, oxidizer
2-octanone	$CH_3(CH_2)_5COCH_3$	L	128.22	173	0.819	1.4150	Irritant
pentane	C_5H_{12}	L	72.15	36.1	0.626	1.3580	Flammable, irritant
2-pentanol, 4-methyl	$C_6H_{14}O$	L	102.18	132	0.802	1.4110	Irritant
3-pentanol	$C_2H_5CH(OH)C_2H_5$	L	88.15	115/749mm	0.815	1.4100	Flammable, irritant
3-penten-2-one, 4-methyl	$(CH_3)_2C{=}CHCOCH_3$	L	98.15	129	0.858	1.4450	Flammable, lachrymator
1-pentene, 2-methyl	C_6H_{12}	L	84.16	62	0.682	1.3920	Flammable, irritant
1-pentene, 4-methyl	C_6H_{12}	L	84.16	53-54	0.665	1.3820	Flammable, irritant
2-pentene, 2-methyl	C_6H_{12}	L	84.16	67	0.690	1.400	Flammable, irritant
2-pentene, 3-methyl	C_6H_{12}	L	84.16	69	0.698	1.4040	Flammable, irritant
2-pentene, 4-methyl	C_6H_{12}	L	84.16	57-58	0.671	1.3880	Flammable, irritant
petroleum ether, (Skelly B)	Mixt. of C_5-C_6	L		35-60	0.640		Flammable, toxic
petroleum ether, hi bp (ligroin)	Mixt. of C_6-C_7	L		60-80	0.656	1.3760	Flammable, toxic
phenethyl alcohol	$C_6H_5CH_2CH_2OH$	L	122.17	221/750mm	1.023	1.5320	Toxic, irritant
phenol	C_6H_5OH	S	94.11	40-42	1.071		Highly toxic, corrosive
phenol, 2,4-dimethyl	$(CH_3)_2C_6H_3OH$	S	122.17	22-23	1.011	1.5380	Corrosive, toxic
phenol, 2,5-dimethyl	$(CH_3)_2C_6H_3OH$	S	122.17	75-77	0.971		Corrosive, toxic
phenylacetylene	$C_6H_5C{\equiv}CH$	L	102.14	142-144	0.930	1.5490	Flamm., cancer susp.agent
phenylmagnesium bromide	C_6H_5MgBr	L	181.33		1.134		Flammable, moist.sensit.
phosphoric acid (85%, 14.7 M)	H_3PO_4	L	98.00		1.685		Corrosive

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
potassium chromate	K_2CrO_4	S	194.20	968	2.732		Canc.susp.agent, oxidizer
potassium dichromate	$K_2Cr_2O_7$	S	294.19	398			Hi.toxic, canc.susp.agent
potassium hydroxide	KOH	S	56.11				Corrosive, toxic
potassium iodide	KI	S	166.01	681	3.130		Moist.sens., irritant
potassium permanganate	$KMnO_4$	S	158.04	d<240	2.703		Oxidizer, corrosive
propane, 2-chloro, 2-methyl	$(CH_3)_3CCl$	L	92.57	50	0.851	1.3848	Flammable
propane, 2-nitro	$(CH_3)_2CHNO_2$	L	89.09	120	0.992	1.3940	Canc.susp.agent, flamm.
2-propanol, 2-methyl-	$(CH_3)_3COH$	L	74.12	82.3	0.7887		Flammable, irritant
propionate, ethyl	$C_2H_5CO_2C_2H_5$	L	102.13	99	0.891	1.3840	Flammable, irritant
propionic acid	C2H5CO2H	L	74.08	141	0.993	1.3860	Corrosive, toxic
rosaniline hydrochloride	$C_{20}H_{14}(NH_2)_3Cl$	Solution	337.86	250 (dec)			Susp. cancer agent
salicylic acid	$HOC_6H_4CO_2H$	S	138.12	158-160			Toxic, irritant
salicylic acid, acetate ester	$CH_3CO_2C_6H_4CO_2H$	S	180.16	138-140			Irritant, toxic
Schiff's Reagent		Solution	of roseaniline hydrochloride & sulfur dioxide				Toxic
silane, tetramethyl	$Si(CH_3)_4$	L	88.23	26-28	0.648	1.3580	Flammable, hygroscopic
silica, sand	SiO_2	S	60.09	NA			abrasive
silver nitrate	$AgNO_3$	S	169.88	212	4.352		Highly toxic, oxidizer
sodium acetate	CH_3CO_2Na	S	82.03				hygroscopic
sodium acetate, trihydrate	$CH_3CO_2Na\ 3H_2O$	S	136.08	58	1.45		Hygroscopic
sodium bisulfite	$NaHSO_3$	S			1.480		Severe irritant
sodium borohydride	$NaBH_4$	S	37.38	400			Flam. solid, corrosive
sodium bicarbonate	$NaHCO_3$	S	84.01		2.159		Moist. sensitive
sodium carbonate	Na_2CO_3	S	105.99	851	2.532		Irritant, hygroscopic
sodium chloride	NaCl	S	58.44	801	2.165		Irritant, hygroscopic
sodium dichromate, dihydrate	$Na_2Cr_2O_7.2H_2O$	S	298.00		2.350		Hi.toxic, cancer susp.agent
sodium hydrogen carbonate	$NaHCO_3$	S	84.01		2.159		See sodium bicarbonate
sodium hydroxide	NaOH	S	40.00				Corrosive, toxic
sodium iodide	NaI	S	149.89	661	3.670		Moist.sens., irritant
sodium metabisulfite	$Na_2S_2O_5$	S	190.10		1.480		Moist.sens., toxic
sodium methoxide	$NaOCH_3$	S	54.02				Flam. solid, corrosive
sodium sulfate	Na_2SO_4	S	142.04	884	2.680		Irritant, hygroscopic
styrene	$C_6H_5CH{=}CH_2$	L	104.15	146	0.909		Flammable
styrene, β-bromo	$C_6H_5CH{=}CHBr$	L	183.05	112/20mm	1.427	1.6070	Irritant
sucrose	$C_{12}H_{22}O_{11}$	S	342.30	185-187	1.5805		Tooth Decay!
sulfur dioxide	SO_2	Gas	64.06	-10 bp			Nonflamm, corrosive
sulfuric acid (conc. 18 M)	H_2SO_4	L	98.08		1.840		Corrosive, oxidizer
sulfurous acid	H_2SO_3	L	82.08		1.030		Corrosive, toxic
L-tartaric acid	$HO_2CC_2H_2(OH)_2CO_2H$	S	150.09	171-174			Irritant
tetrahydrofuran	C_4H_8O	L	72.11	65-67	0.889	1.4070	Flammable, irritant
tetramethylsilane	$Si(CH_3)_4$	L	88.23	26-28	0.648	1.3580	Flammable, hygroscopic
tin	Sn	S	118.69		7.310		Flammable solid, moist.sens.
Tollen's Reagent		L	See ammonia + silver nitrate				
toluene	$C_6H_5CH_3$	L	92.14	110.6	0.867	1.4960	Flammable, toxic
toluene, 4-nitro	$NO_2C_6H_4CH_3$	S	137.14	52-54	1.392		Hi.toxic, irritant
o- or 2-toluic acid	$CH_3C_6H_4CO_2H$	S	136.15	103-105			Probable irritant
p- or 4-toluic acid	$CH_3C_6H_4CO_2H$	S	136.15	180-182			Probable irritant
triethylphosphite	$(C_2H_5O)_3P$	L	166.16	156	0.969	1.4130	Moist. sens., irritant

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
triphenylmethanol	$(C_6H_5)_3C(OH)$	S	260.34	164.3			Probable irritant
urea	NH_2CONH_2	S	60.06	135	1.335		Irritant
(-) usnic acid	$C_{18}H_{16}O_7$	S	344.32	198			Toxic
(+) usnic acid	$C_{18}H_{16}O_7$	S	344.32	201-203			Toxic
water	H_2O	L	18.02	100		1.33	Will burn skin when hot
water, ice	H_2O	S/L	18.02	0	1.00		Frostbite, hypothermia
xylenes	$CH_3C_6H_4CH_3$	L	106.17	137-144	0.860	1.4970	Flammable, irritant
zinc dust	Zn	S	65.37	419.5			Flammable, moist.sens.
zinc chloride	$ZnCl_2$	S	136.28	283	2.91		Corrosive, toxic.

*Be sure to consult the chemical's MSDS for more specific detail on hazardous properties.

Athabasca University

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CHEM350: ORGANIC CHEMISTRY I

PREPARATION, PERFORMANCE, AND PRODUCT EVALUATION FORM*

NT NAME: _____ AU I.D.# _____ Date _____

EXP.#	PRODUCT SUBMITTED	DATE COMPL.**	RESULTS FOR:	YIELD (Amt.Used)	UNKOWN ID	PRODUCT CHARACTERISTICS							PERFORM. & PROD. GRADE	INSTR. INIT.
						DESCRIPT.	M.P./B.P.(°C)^	IR(Y/N)	RI Temp	RI/SpecRot	BaroPress	Other		
1	Unkown Code # _____		Single M.P.	N/A	N/A			N/A	N/A	N/A	N/A			
(5 mks)	Unkown Code # _____		Mixed M.P.	N/A				N/A	N/A	N/A	N/A			
2	**ACETANILIDE**		1° Crop		N/A			N/A	N/A	N/A	N/A			
(5 mks)	Impure acetanilide		Amt Used (g) =		N/A			N/A	N/A	N/A	N/A			
3	A.CYCLOHEXANOL		Simple Distill'n		N/A			N/A	N/A	N/A				
	B. FRACT'L DISTILLAT'N		80-85 C		N/A			N/A	N/A	N/A				
	(Amt.PartA used=)		85-100 C		N/A			N/A	N/A	N/A				
(5 mks)	(Amt. PartB used=)		100-105 C		N/A			N/A	N/A	N/A				
4	CYCLOHEXANOL		Refractive Index	N/A	N/A	N/A	N/A	N/A			N/A			
	FRACT'L DISTILLAT'N		RI 80-85 C	N/A	N/A	N/A	N/A	N/A			N/A			
			RI 85-100 C	N/A	N/A	N/A	N/A	N/A			N/A			
(5 mks)			RI 100-105 C	N/A	N/A	N/A	N/A	N/A			N/A			
5	Unknown Code#_____		Amt.Unkn Used (g)=		N/A	N/A	N/A	N/A	N/A	N/A	N/A			
	ORGANIC ACID		Yield/M.P.					N/A	N/A	N/A	N/A			
	ORGANIC BASE		Yield/M.P.					N/A	N/A	N/A	N/A			
(5 mks)	NEUTRAL		Yield/M.P.					N/A	N/A	N/A	N/A			
6	INFRARED SPECTRA		CH- Tests	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A			
(0 mks)	UNKNOWN# (4 spectra)***		Unknowns	N/A		N/A	N/A		N/A	N/A	N/A			
7	**USNIC ACID**		1° Crop/Sp.Rot.		N/A			N/A	N/A		N/A			
	(Amt.Lichen used=)			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A			
(5 mks)			Unk'n Sp.Rot.	N/A		N/A	N/A	N/A	N/A		N/A			
8	**CYCLOHEXENE**		Yield/B.P./RI/d		N/A									
(10 mks)	cyclohexanol		Amt. Used (mL)=		N/A		N/A		N/A	N/A				
9	**4-NITROACETANILIDE**		1° Crop		N/A				N/A	N/A	N/A			
(10 mks)	acetanilide		Amt. Used (g)=		N/A			N/A	N/A	N/A	N/A			
												Total=		
												(/50)		

^M.P. (°C) must be reported as a range

N/A = not applicable

* This form is the official results form for CHEM350. To get credit for the lab, it must be fully completed and then initialed by the instructor. Keep safe at all times.

** It is very strongly suggested that lab reports are due 1 month after completion of each experiment. Late lab reports may lose 10% per month.

*** CHEM350 Infrared Unknowns are to be downloaded from: http://science.athabascau.ca/Labs/resources/organic_chemistry.php (username= auchem350, password = reaction)