TABLE OF CONTENTS

Microscale Approach to Organic Laboratory Techniques (Fifth Edition)

Chemicals and Supplies for Each Experiment
Answers to Questions

Answers to Problems in the Techniques Section

PREFACE

Introduction to Organic Laboratory Techniques: A Microscale Approach (Fifth Edition) continues our dedication to the microscale approach to the teaching of the organic laboratory. In this edition we have devoted considerable effort toward improving the safety of all of the experiments. Technique Chapter 1, "Laboratory Safety," places strong emphasis on the safe use and disposal of hazardous chemicals. We have included information on Material Safety Data Sheets (MSDS) and Right-to-Know laws. We have continued to update and improve instructions for the handling of waste products that are produced in the experiments. We recommend that virtually all waste, including aqueous solutions, be placed into appropriate waste containers.

We are keenly aware of the legal aspects of the safety issue. Students take a organic chemistry safety quiz each quarter for every chemistry lab course at Western Washington University. This test is taken online so that it reduces the paperwork associated with grading the test. The program grades the quiz and one of our faculty members relays the information to us. Students gain the appreciation that we, as instructors, take safety very seriously! Students can review or study safety related issues associated with organic chemistry online before taking the quiz: http://atom.chem.wwu.edu/dept/osafety/index.htm

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This edition of the Microscale book continues the tradition of including stand-alone technique experiments: Solubility, Crystallization, Extraction, Separation and Purification Scheme, Chromatography, Simple and Fractional Distillation, and Infrared Spectroscopy and Boiling Point Determination (Experiments 2-8). These seven experiments emphasize understanding of and proficiency in performing the techniques.

The new experiments are listed in the Preface of the Textbook. These include several new "green" chemistry experiments and some project-based experiments. In the latter experiments, students must either solve a significant problem or they must generate all of part of the experimental procedure. The Green Chemistry essay has been updated and some of the experiments have been modified to make them more "green." We also offer an alternative way of solving unknowns using mainly spectroscopy.

At the request of some of you, we have included Chemical Abstract Services (CAS) registry numbers for each of the chemicals. In this way, you should find it easier to locate chemicals when alternative names may be used in catalogs. We hope that this instructor's manual will assist you in preparing
solutions, chemical reagents, supplies, and equipment necessary for each experiment that you choose to do. The lists of chemicals and equipment required for each experiment are based on the amount required for ten students. For chemicals, the amounts indicated include some excess. At the end of the manual we have included a section that correlates the experiments with topics presented in standard organic lecture courses.

The time required for each experiment is given in laboratory periods. It is assumed that a laboratory period is about three hours in length. For laboratory periods that are either shorter or longer, appropriate adjustments must be made.

The technique chapters of the textbook are designed to stand independently from the experiments. You may have a favorite experiment that you like to do in your course. If this is the case, you can freely add your experiment and still take advantage of the technique chapters in the textbook. Since both standard-scale and microscale techniques are described in the technique chapters, you may even add some small-scale experiments and still be able to refer your students to the appropriate sections in these chapters for information on each technique.

A new feature of the Instructor's Manual is the inclusion of some laboratory practical exams that test students on two basic organic laboratory techniques: crystallization and extraction. You may find these exams to be a useful way of evaluating student technique. The idea is to have students perform techniques without the textbook and without looking over another student's shoulder for help!

If you encounter problems with any of the experiments in the Textbook or if you need help in setting up your laboratory, please contact us. We would also like to hear from you if you have any suggestions for improvements in techniques or in any of the experiments.

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EQUIPPING THE ORGANIC CHEMISTRY LABORATORY

SETTING UP A MICROSCALE LABORATORY

This section will be most useful for laboratory instructors who have not yet taught the organic laboratory using microscale techniques. For instructors already experienced in teaching microscale, there may be some new ideas presented here. In addition, this section will provide information for all instructors on some of the laboratory requirements for doing the experiments found in the textbook.

Dispensing and Measuring Liquids

Where possible, liquid reagents and solvents should be stored in a hood in small glass or plastic bottles. To avoid waste, the exact amount of liquid should be transferred to the student's container by one of the methods described below. Students should not pour an approximate amount of liquid into one container and then measure the required volume, leaving some excess liquid behind which must be discarded.

When accuracy is not important, one-piece polyethylene transfer pipettes or calibrated Pasteur pipettes shown in Technique 5, Figures 5.5B and 5.5C provide an efficient method for delivering liquids, especially solvents to be used for extractions or crystallizations. We tape a test tube to the bottle containing the liquid in order to hold the pipette.

Dispensing pumps (Technique 5, Figure 5.2) may be used to deliver liquids accurately. *Care must be taken to ensure that the tip is filled with liquid and that no air bubbles are observed in the tubing.* These units easily lose their "prime" especially with more volatile solvents. We have observed that some solvents swell the plastic plunger such that it can not be pulled up easily. If this happens to you, remove the solvent from the unit. After drying out thoroughly, the unit can be used again (with another solvent!).

For a class of 20 students, one 10-100 μL automatic pipette for smaller volumes and two 100-1000 μL pipettes for larger volumes are adequate. The tips should be reused as much as possible. The automatic pipette should be placed near the appropriate reagent and supported in a vertical holding device. When the maximum volume of the pipette is required, students may occasionally draw liquid past the disposable tip into the barrel of the pipette. The automatic pipette is very accurate with aqueous solutions, but it is not as accurate with organic liquids. With all limiting reagents, it will be necessary to obtain the weight in order to determine accurately the amount of substance used. Automatic pipets should not be used with corrosive or caustic liquids, such as sulfuric acid, hydrochloric acid, or sodium hydroxide. Since most of the errors that occur in the laboratory may be attributed to "sloppy" transfers, you should give a thorough demonstration of how to use the automatic pipet. Students should be alerted to looking carefully to see that liquid is being drawn up into the automatic pipet. If the unit sticks or drips when withdrawing a liquid, you will need to correct the problem.

The instructor should place the appropriate measuring device with each reagent and solvent. In most cases, the device will be an automatic pipet, a dispensing pump, or a one-piece

polyethylene pipet. **The person who prepares the laboratory for an experiment should read the procedure in order to determine which device is appropriate.**

Dispensing Solids and Weighing Reagents

Four top-loading balances that read to 0.01 or 0.001 gram are required for a class of 20 students. The balances should be used with draft shields to improve accuracy. It is convenient to store solids in containers near the balances. To avoid the possibility of contamination, we provide a community spatula with the reagent.

Evaporation of Solvents

Ideally, the laboratory should be equipment with rotary evaporators. However, students can remove solvent by directing a stream of nitrogen or air through a Pasteur pipet into a flask or conical flask in order to evaporate a solvent. This procedure gives a student complete control of the evaporation process, but only works well in a laboratory with many individual hoods. In laboratories where there are only a few hoods it becomes necessary to have a permanent community evaporation station assembled in the hood. One method is to provide a community sand bath heated by a hot plate with a source of nitrogen gas or dry air. By using a series of Y-tube connectors and screw clamps with flexible tubing, it is possible to provide a gas source for several students from one tank of gas. Pasteur pipets or blunt-end syringe needles are connected to each open end of the flexible tubing. Using three-finger clamps, the Pasteur pipets or needles can be directed into containers placed in the warm sand bath. Generally a temperature of 50-60 ^{o}C will be sufficient. The disadvantages of this system are that pressure changes will occur as screw clamps are loosened or tightened and occasionally sand may be blown around, possibly resulting in contamination of samples.

This second problem may be solved by replacing the sand bath with a large aluminum block or several small aluminum heating blocks [see Lodwig, S.N. "The Use of Solid Aluminum Heat Transfer Devices in Organic Chemistry Laboratory Instruction and Research." *Journal of Chemical Education, 66* (1989): 77]. A system which solves both problems is the N-EVAP evaporator. Several models are available from Organomation Associates, Inc., 266 River Road West, Berlin, MA 01503; phone: 888-838-7300. These units consist of an electrically heated water-bath container and a gas manifold equipped with blunt-end, stainless-steel needles. The holders are made with 12, 24, or 36 positions and will accept a variety of containers including conical vials, test tubes, and Erlenmeyer flasks. The smallest model with 12 positions provides an exceptionally efficient means of evaporating solvents in a lab with 20 students. This model costs about $1600.

Rotary Evaporators

It is becoming more common to equip the laboratory with rotary evaporators to avoid some environmental problems with evaporating solvents in the hood. We suggest systems that have coolers attached to the evaporators to improve solvent recovery thereby making the laboratory a greener environment for students and instructors. You may want to continue evaporating small amounts of solvents, approximate 10 mL or less, as indicated in the above section. Use a rotary

evaporator for larger amounts, about 25 mL or more. The use of a rotary evaporator can create a large student backup unless reserved for evaporating large volumes of solvent.

A "rotacool" model rotary evaporator is available from Heidolph-Brinkmann for about $10,000. It is equipped with vacuum pump, condensation cooler and rotacool circulating chiller. This is a very efficient system that does a great job of collecting even the most volatile solvents. If you can afford to buy a rotary evaporator with a cooler, you won't regret it!

Stirrer/Hot Plates

For most reactions or distillations requiring heating or stirring, we use a small stirrer/hot plate with an aluminum top and an aluminum block as our heating source. **You should not use hot plates with ceramic tops unless you are certain that the tops will withstand high temperatures without cracking.** Instead of an aluminum block, you may use a sand bath consisting of a crystallizing dish (80 x 40 mm) filled with about 1 cm of sand. A Petri dish can be used instead of the crystallizing dish, but sand spills are more likely. We prefer to use the aluminum heating block rather than a sand bath. The holes that have been drilled in the aluminum block easily support and accommodate conical vials and Craig tubes. We also provide a second aluminum block that holds small round-bottom flasks. The aluminum block is especially useful when temperatures above 200 ^{o}C are required. The stirrer/hot plate units should provide a temperature range of about 60 to above 250 ^{o}C.

We recommend that you replace all of your mercury thermometers, with non-mercury thermometers. We do not recommend that either type of thermometer be inserted in an aluminum block, especially mercury ones. Glass thermometers break too easily especially when inserted in the aluminum blocks. We have switched over to metal dial thermometer for use in our aluminum blocks and hot plates. See Technique 6, Fig 6.3 of the Textbook for suggestions. **Unfortunately, we have found that the non-mercury thermometers do not work as well when determining boiling points. We keep a few of the mercury thermometers in the laboratory, but we do not issue them to each student unless needed for determining boiling points. You may want to consider purchase of a Vernier LabQuest unit is a stand-alone hand held unit for determining boiling points (see below). This device uses a metal probe.**

Students often worry more about what the temperature is on the hot plate or aluminum block rather that what is happening in the boiling flask! Because of this, we have removed much of the emphasis on the temperature of the hot plate and have students pay close attention to what is happening in the flask or conical vial. Obviously, if a student is refluxing the contents of a flask, the temperature of the hot plate isn't all that important!

Melting Point Apparatus

Four electrically-heated melting point apparatus should be provided for a class of 20 students (Mel-Temp or Electrothermal). A Thomas-Hoover Uni-Melt apparatus may be considered if the class is determining micro boiling points. This device has a rapid temperature response (see below for an alternative boiling point procedure). The Mel-Temp or Electrothermal units are less

expensive and more serviceable alternative, but the temperature response is not as rapid and micro boiling point determinations may be more difficult to perform. You should try several different melting point units before buying them to see which one is the best for you.

Boiling Point Determination

Obtaining a boiling point is often a frustrating experience! It is recommended that you consider purchasing digital thermometers for boiling point determinations. See Technique 13, Section 13.4 and Figure 13.7 for suggestions. These alternatives to thermometers utilize a stainless steel probe. The Vernier LabQuest unit is a stand-alone hand held unit while the Vernier LabPro unit employs a computer.

Gas Chromatographs

At least two gas chromatographs should be provided for every 20 students, if students are expected to perform their own injections. Conditions for running samples on the Gow-Mac 69-350 or Hewlett Packard 5890 gas chromatographs are given in this textbook. If students are expected to collect samples from a chromatograph, Gow-Mac models 69-350 or 580 can be equipped with a convenient sample collection device. Gow-Mac instruments should be equipped with an 8-foot column packed with Carbowax 20M and an 8-foot column containing 20% DC-710. Columns required for the Hewlett Packard chromatographs are given in the textbook or in this manual.

Spectrometers/Polarimeters

The laboratory should have at least one FT-infrared spectrometer for every 20 students. The FT-infrared instruments increase the through-put of students in the laboratory. If you can afford it, an FT instrument with ATR (attenuated total reflectance) accessory is highly recommended. Use of this accessory makes analysis of solids totally trivial! Otherwise, you will need to make do with determining a spectrum using the dry film method or with a KBr pellet. For conventional IR spectroscopy we have available two of the hand press units for solids. NMR spectroscopy is important in the modern organic chemistry laboratory and you should make this available to your students. The availability of both proton and carbon NMR increases student interest especially when solving unknowns. The laboratory should be equipped with one polarimeter for use by the class (see Technique 23 for types of instruments).

Centrifuges

Several microscale techniques require the use of a centrifuge. One or two "clinical" centrifuges are adequate for 20 students. They should hold 15 mL centrifuge tubes. A number of other centrifuges are also available, but check to see if the Craig tube assembly will fit into the unit with the top down. Some centrifuges will need to be modified in order for the Craig tubes to fit properly into the unit.

Vortex Mixer

Extractions can be carried out conveniently in a 15-mL centrifuge tube. Although the tube can be stoppered and shaken to mix the layers, mixing can be accomplished efficiently with a vortex mixer. This method eliminates the problems of pressure buildup and leakage. One mixer easily serves 20 students.

Syringes and Rubber Septa

In several experiments a syringe is used to add reagents to a reaction mixture. A 1-mL glass or plastic syringe should be provided to allow use with organic solvents without contamination occurring. The plastic syringes are readily available and are much cheaper and durable than glass syringes. Disposable hypodermic needles may be used for most applications. The "disposable" syringe needles should be dispensed from the stockroom or by the instructor. We recommend 1 1/2- or 2-inch needles (21 or 22 gauge). When the experiment is completed, they should be saved for reuse. In general, needles should not be included with individual student glassware and equipment.

Although the Teflon inserts provided with conical vials can be punctured with a needle when a reagent must be added without opening the system to air, the punctured insert may cause problems in future experiments. Specifically, it may leak when the insert is used with a cap and conical vial in extraction procedures. One alternative is to replace the cap and Teflon insert with a standard rubber septum (serum bottle stopper) when it is necessary to add a reagent with a syringe. It should be noted, however, that some septa will partially degrade when exposed to organic vapors. Another alternative, which may prevent this problem, is to use a disc cut with a cork borer from a sheet of silicone rubber. This material is normally used to make septa for the injection ports in a gas chromatograph. A disc cut the same size as the Teflon insert can be used with the plastic cups provided in the microscale glassware kits.

Washing Glassware and Equipment

A plastic dishpan provides a convenient container in which to soak and wash dirty glassware. You may want to consider buying an ultrasound cleaner (sonicator) cleaner for the laboratory. Especially dirty glassware can often be effectively cleaned with one of these devices. There are some disadvantages: they are noisy and students often forget to retrieve their glassware.

Monometers

Several monometers should be available in the laboratory for use in vacuum distillations. A simple U-tube manometer is shown on page 775 of the Textbook.

Sublimation Equipment

It is suggested that the drawer stock in the laboratory be supplied with sublimation equipment such as that shown in Technique 17, Figure 17.2 A. This apparatus is equipped with 14/10 joints and can be used to perform all sublimation procedures. If not included in the drawer stock, we suggest 5 complete units as part of the community equipment.

WASTE MANAGEMENT GUIDELINES

These guidelines are intended for schools where the chemistry department is responsible for its own waste management. Although most of this information should apply to your situation, specific waste management practices will depend on the size of your program, other hazardous wastes generated on your campus, and state and local regulations. This information may not cover everything you need to know; however, it can help you get started or may provide some new ideas that will improve your existing waste management program.

To get started, you need to determine who regulates hazardous waste in your state. The U.S. Environmental Protection Agency (EPA) has ultimate responsibility for regulating hazardous waste in all 50 states plus the District of Columbia, Puerto Rico, and the Virgin Islands. Many states have been delegated the authority to regulate their own hazardous waste by the EPA. States which have the authority to regulate their own hazardous waste must have regulations that are as strict as the federal laws. If you operate in a state that has a hazardous waste regulating agency, then you must follow the regulations for your state rather than the federal regulations. The EPA has a home page (http://www.epa.gov) and ten regional offices that can help you find out if there is a state program in your area.

Region	States in the Region	Telephone Number
1	ME, NH, VT, MA, RI, CT	617-565-3423
2	NY,NJ,PR,VI	212-637-5000
3	PA,DE,DC,MD,VA,WV	800-438-2474
4	KY,TN,NC,SC,MS,AL,GA,FL	800-241-1754
5	MN,WI,IL,MI,IN,OH	800-621-8431
6	NM,TX,OK,AR,LA	214-665-2200
7	NE,KS,IA,MO	913-551-7000
8	MT,ND,WY,SD,UT,CO	800-227-8917
9	CA,NV,AZ,HI	415-744-1500
10	WA,OR,ID,AK	800-424-4372

You must obtain a Resource Conservation and Recovery Act (RCRA) site identification number if your campus does not already have one. This number identifies your site and all the waste generated there. This identification number is obtained through the agency that regulates hazardous waste in your state. You must supply this number to waste disposal firms when you ship waste off site, and it identifies your site on your annual hazardous waste report.

We collect all chemical waste generated in student laboratories, and we make a serious attempt to teach students that waste management is important. Therefore, students do not dispose of any chemical materials down the drain or in the trash. We find that labeling waste containers with the experiment name and a list of the chemicals that should be placed in the container greatly increases the chances that students will put wastes into the correct containers. We will use our "Isolation of Caffeine from Tea" experiment to give an example. The students generate an aqueous

layer contaminated with methylene chloride. Unfortunately, the small amount of methylene chloride that dissolves in water renders the entire aqueous solution hazardous waste. The waste bottle would be labeled as follows:

Isolation of Caffeine from Tea
Hazardous Waste
Aqueous layer contaminated w/ methylene chloride
Suspect Human Carcinogen

Note that "Hazardous Waste" must be included on the label, as required by law. Also, the primary hazard of the waste, the last entry on this label, is required by law. Refer to the material safety data sheet (MSDS) for the primary or most hazardous constituent of the waste to determine an appropriate warning.

Wastes collected from student labs are consolidated by waste type or treated, if it is safe and legal to do so. We find that all wastes we generate fit into one of the following categories:

Nonhazardous Solids such as paper, tea bags, and corks are disposed of with the ordinary trash.

Broken Glassware is disposed of in a container designated for this purpose. When the container is full, it is packaged securely and disposed of with the ordinary trash.

Organic Solids with halogens are consolidated with our halogenated organic solvents, and those without halogens are consolidated with our non-halogenated organic solvents.

Inorganic Solids such as alumina and drying agents are accumulated together and disposed of as hazardous waste.

Non-Halogenated Organic Solvents such as alcohols, toluene, hexane, and diethyl ether are disposed of as hazardous waste. Intentional evaporation or drain disposal of these materials is illegal. However, evaporation of these solvents as part of the workup in an experiment *is legal*, since the material is not yet waste and the evaporation is a legitimate part of the procedure.

Halogenated Organic Solvents such as dichloromethane (methylene chloride), chloroform, and carbon tetrachloride are disposed of as hazardous waste. Intentional evaporation or drain disposal of these materials is illegal. However, evaporation of these solvents as part of the workup in an experiment is legal, since the material is not yet waste and the evaporation is a legitimate part of the procedure.

Inorganic Acids without heavy metals or halogenated solvent contamination are neutralized and discharged to the sewer. A log of these treatment activities is maintained.

Inorganic Bases without heavy metals or halogenated solvent contamination are neutralized

and discharged to the sewer. A log of these treatment activities is maintained.

Aqueous Solutions Contaminated with Halogenated Solvents are disposed of as hazardous waste. Intentional evaporation or drain disposal of these materials is illegal.

Aqueous Solutions with Heavy Metals may either be treated to remove the heavy metal or disposed of as hazardous waste. If you treat these wastes, you must test the pH and metal levels before discharge of the treated waste to the sewer to confirm successful treatment. In most states, the water may be legally evaporated to reduce the waste volume, and the remaining metal sludge treated as hazardous waste. The original amount of waste including water must be reported on your annual hazardous waste report.

Most states allow some forms of treatment by the waste generator without the need for special permits. Before you treat a waste you must make sure that your regulators allow the treatment practice. Prior to waste treatment, all of the constituents of the waste, such as heavy metal, solvent content, and low or high pH must be determined. You also need to contact your local sewer district to find out if they have limits on what may be discharged to their system. In many cases a material may not be considered hazardous waste by the EPA or a State Environmental Regulatory Agency, but is restricted from disposal to the sanitary sewer. Treatment and discharge of waste is not recommended if you are on a septic system.

If you elect to treat waste, you are required to test the treated waste for each constituent that made the untreated waste hazardous before you discharge it to the sewer. For example, if you treated an aqueous waste that contained silver, barium, and chromium by precipitating the metals, you would have to check the barium, silver, and chromium levels of the treated waste before discharge to the sewer. Because of this burden, we limit our treatment to neutralization of non-heavy-metal-bearing aqueous wastes that have a low or high pH. Also, remember that intentional evaporation of solvents, and dilution and drain disposal of hazardous wastes not only violates EPA regulations but is also harmful to the environment.

Maintain a log of all wastes treated on site. At a minimum this log should include: a description of the waste, the amount of waste treated, the name of the person treating the waste, the treatment method, and the treatment date. Hazardous wastes that are treated on site must be "counted" and reported on your annual hazardous waste report.

Maintain a waste generation log, which includes the total amount of waste treated and generated. At a minimum this log should include: date, description of the waste, amount, and identity of generator. This log must be included in the annual hazardous waste report that is described below.

We recommend that you limit the amount of waste you accumulate not only to simplify your regulatory requirements, but also to minimize the risk of leaks and spills. In most states, by accumulating less than 55 gallons of each type of waste you simplify the storage and record keeping requirements associated with waste storage. Larger waste accumulation areas must be inspected weekly and equipped with emergency response supplies. Waste must be stored in a secure (locked) area, segregated by type, capped when not in use, and provided with secondary containment

(several bottles of the same type of waste can be placed in a tray or individual bottles may be stored in pails). We recommend hazardous waste shipments at intervals as dictated by your operation to limit the amount of waste stored.

At smaller schools you may find that annual waste shipments are a good management practice. At larger schools shipments each semester, quarterly, or even monthly may be required. At Western Washington University, the motor pool and the physical plant operations generate far more waste than the chemistry department. You may find it worthwhile to coordinate your waste disposal with other departments or operations within your school.

If you elect to ship your own waste, you must learn and follow all of the mandated procedures. As a simpler alternative, there are private contractors who will consolidate, treat, package, and ship your waste for you. However, this alternative does not keep you from having to keep good records.

Contact your local fire department to find out about requirements concerning hazardous material storage. Often these agencies require chemical inventory and storage information about your site so that they can respond appropriately in the event of an emergency.

Establish written hazardous waste management procedures for your campus and communicate these procedures to those involved with waste handling. Also, assure that the person on your campus who signs manifests has received Department of Transportation training on hazardous material shipping.

Retain copies of all manifests and land disposal restriction certifications, sometimes known as "land bans", of waste sent off site for disposal. Manifests can be thought of as the shipping papers for hazardous waste shipments. Land disposal restriction certifications accompany manifests and document disposal and treatment restrictions based on the characteristics of the waste being sent for disposal.

Complete an annual hazardous waste report for all hazardous waste activities on your campus. This report is required by law and must be submitted to the agency that regulates hazardous waste in your area. The report summarizes your hazardous waste activities for the previous calendar year. To complete this report you will need: your RCRA site identification number, copies of all manifests for the past year and your treatment and generation logs.

LABORATORY EQUIPMENT AND SUPPLIES

A. Individual student glassware and equipment contained in the locker

1. Organic Chemistry Kit (14/10 joints), including caps, liners and rubber O-rings

   5 mL Conical reaction vials (2)
   3 mL Conical reaction vial
   5 mL Thin-walled reaction vial for sublimation

Sublimation tube
10 mL Round-bottom flask
20 or 25 mL Round-bottom flask
Teflon stoppers (optional, 2)
Air reflux condenser
Water-cooled reflux condenser
Claisen head adapter
Hickman distillation head, side ported preferred
Drying tube
Multipurpose adapter
Thermometer adapter
Teflon spin vane
Magnetic spin bar
2 mL Craig tube and inner plug
1 mL Plastic syringe and needle
Microchromatographic column (optional)
Equipment for preparative gas chromatography (optional)
    0.1 mL Conical reaction vials, 5/5 joint (2)
    Collection tubes, 5/5 joint (2)
Equipment for conventional distillation (optional)
    Distillation head
    Vacuum take-off adapter

2. Other glassware

Beakers; 10 mL (2), 20 mL (2), 50 mL (2), 100 mL (1),
    150 mL (1) and 250 mL (1)
Erlenmeyer flasks; 10 mL (2), 25 mL (2), 50 mL (2) and
    125 mL (1)
Graduated cylinder; 10 mL
Filter flask; 50 mL
Aspirator trap bottle
Conical funnel; 50 mm
Hirsch funnel, plastic preferred
Test tubes or culture tubes; 10 x 75 mm (6);
    16 x 100 mm (5); 15 x 125 mm (3),
Side arm test tube, 20 x 150 mm
Thermometer, 360^{o} (non-mercury preferred)
Thermometer, metal dial, to insert in aluminum blocks
Thermometer, microscale; 300^{o}
Watch glasses; 25 mm (2) and 50 mm (2)
Pasteur pipets; 5 3/4-inch (6) and 9-inch (2)
Graduated pipet; 1.0 mL (0.01-mL divisions) (optional)
Centrifuge tube, screw cap with liner; 15 mL (2)
    Kimble #73785 -15 tube and Kimble #73802-15415 cap
Centrifuge tubes, plastic (no screw cap), 15 mL (2)

Separatory funnel, 60 mL (optional)
Crystallizing dish (80 x 40 mm) for use as a sand bath (optional)

3. Equipment

Aluminum block to fit conical vials and Craig tube
Aluminum block to fit 10 and 25 mL round-bottom flasks
Aluminum collars (pair)
Metal thermometer to fit aluminum blocks or hot plate (optional)
Clamps, microscale-3-prong with clamp holders (2)
Clamp, utility (optional)
Dropper bulbs, latex, 2 mL (4)
Rubber policeman (optional)
Stirring rod
Neoprene adapters, numbers 1 and 2
Rubber septum (serum bottle stopper), to fit over 14/10 Joint
Brushes, small and large
Microburner and chimney (optional)
Test tube holder
Forceps
Microspatulas, large and small
Test tube block
Rubber tubing
Pressure tubing
Scorer or file
Safety glasses
Copper wire for Craig tube
Desiccator (optional)

B. Community Equipment

The following equipment should be available in the laboratory or nearby.

(Numbers in parentheses indicate requirements for 20 students)

Hot plate/stirrer (20)
Automatic pipets; 10 - 100 μL (1) and 100 - 1000 μL (2)
Dispensing pumps; 1, 2 and 5 mL sizes (2 each)
Pipet pump (or available from stockroom, 10)
Ring stands (20)
Iron rings (20)
Small container for washing dishes (1/2 gallon, 20)
Sponges (10)
Glass surface for performing work, 14 inch square (optional, 20)
Screw cap bottle for chromatography (20)
Steam baths (optional, 20)

Ice buckets (5)
Melting point apparatus (2 or 3 units)
Top-loading balances with draft shields, 0.001 g (2)
Refractometer (1)
Polarimeter (1)
Centrifuges (2)
Gas Chromatograph, GOW-MAC, model 69-350, with metal adapter for collection of samples (2)
Vortex mixer (optional, 1)
Infrared Spectrometer (1 or 2)
Potassium bromide hand press (2)
Salt plates (2 pairs)
Solution cells (optional)
NMR spectrometer, 60 MHz or higher field
Ovens (2)
Glass working bench (1)
Cork borers (1 set)
Scissors (2)
Handbook of Chemistry and Physics (mounted on board)
Handbook of Tables for Organic Compound Identification
Merck Index (mounted on board)
Aldrich catalogs

C. Community Supplies

1. Chemicals and supplies
The following materials should be available at all times on the side shelves or desks.

Boiling stones, inert such as corundum, must be small enough to fit in conical vials
Decolorizing carbon, pelletized
Corks, assorted
Sample vials for submitting products
Glass tubing
Filter paper for vacuum and gravity filtrations
Stopcock grease (macroscale experiments)
pH paper
Red and blue litmus paper
Glycerol in dropper bottle
Copper wire
Capillary tubes, sealed on one end
Glass wool
Cotton
Labeling tape

Matches or gas lighters
Soap
Celite (Filter Aid)
Rock salt
Anhydrous magnesium sulfate (powdered)
Anhydrous calcium chloride (4-20 mesh)
Anhydrous sodium sulfate (granular)

2. Acids and bases
The solutions and reagents should be placed in one area of the laboratory on a chemically resistant surface.

Sodium hydroxide solutions; 5%
Sodium bicarbonate solution, 5%
Hydrochloric acid solutions; concentrated and 5%
Sodium chloride solution, saturated
Nitric acid, concentrated
Ammonium hydroxide, concentrated
Sulfuric acid, concentrated

3. Common solvents
These solvents should be placed in a hood during use and stored in a metal fireproof cabinet at other times (see below).

Hexane
Petroleum ether (various boiling ranges)
Acetone
Methanol
Toluene
Methylene chloride (dichloromethane)
95% Ethanol
Diethyl ether
Carbon tetrachloride (1 pt), kept in a hood near the infrared spectrometer, with an Pasteur pipet attached.

4. Test reagent shelves
We usually keep the reagents and known compounds for Experiment 52 (qualitative analysis) in a designated area of the laboratory at all times. The noxious chemicals are kept in a hood.

D. Safety

Storage cabinet for flammable organic solvents
Fire extinguishers
Eye wash fountains
Showers and Fire blankets
Solvent waste containers (see individual experiment)

E. Safety References (see page 590 and 591 of the Textbook)

F. Gloves

There are a number of different types of gloves that are available for use with chemicals (see the Fisher Catalog). Care should be taken to try to match the type of glove to the actual application. *The wrong type of glove may provide little or no protection.* Six types of gloves are in common use. This is a very general discussion; see a catalog for complete descriptions.

Nitrile gloves. These gloves tend to be used, routinely, in the organic chemistry laboratory. They come in several styles varying from bulky ones that use thicker material (11- 22 mil) to form-fitting ones that use thinner material (6 mil). The latter style fit tightly and provides more protection. It is not recommended that you use latex gloves in the organic chemistry laboratory. Although nitrile gloves do provide some protection when used for routine transfer, they often will not protect the student totally! Students should be informed of this. The thicker nitrile gloves work reasonably well with many organic solids and with strong inorganic acids and bases. They can be used with acetic acid, chromic acid and alcohols. Nitrile gloves provide some, but limited protection, with organic solvents. *Unfortunately, methylene chloride and many other solvents will easily penetrate them.* When wearing nitrile gloves, you do not want to splash large quantities of organic solvents on them. If so, the gloves should be removed immediately, and the hands washed. The bulky versions of nitrile gloves provide more protection than the form-fitting ones.

Butyl gloves. These gloves are often loose fitting and so are bulky to use in general applications. Because of their bulk, you are not likely to wear them all the time. They work reasonably well with some acids, acetone, dimethyl sulfoxide, acetonitrile and dimethylformamide. Butyl gloves are not recommended for diethyl ether or for hydrocarbon solvents.

Viton gloves. These gloves are the best choice when working with some chlorinated hydrocarbon solvents, mainly polychlorinated ones. They are also used with hydrocarbon solvents. Since they are usually bulky to wear, Viton gloves are usually not worn all the time. Some chlorinated hydrocarbon solvents such as methylene chloride will penetrate Viton gloves.

Silver Shield Laminate gloves. These gloves are made of Norfoil, a lightweight and flexible laminate. Gloves made of this material are impervious to most all solvents, including methylene chloride. They can be used as an inner glove with other types of gloves for protection against tears or punctures.

Neoprene gloves. These gloves are often used when someone is handling petroleum products such as greases and oils. They are also used with nitric acid and other strong acids and bases. Because of their bulk, they are only worn when transferring solvents when spills are likely.

Latex gloves. Latex Examination gloves are often used in the medical field. Although

they provide some protection when working with solids and aqueous solutions, they provide little or no protection against organic solvents. **Because of this problem*, latex gloves are not recommended for use in the organic chemistry laboratory.***

ORGANIC LABORATORY TECHNIQUES PRACTICAL EXAMS

Some instructors may desire to test students on two very basic organic laboratory techniques: crystallization and extraction. We call this a laboratory practical exam. With the technique exam, you can determine who really has the best technique and who the leaders and followers are in your laboratory course. Students do their work without a textbook in front of them. They are prohibited from looking at what other students are doing.

Organic lab practical exam advice for instructors

You may desire to give this test to students at the end of the first organic laboratory course. Each student will be required to purify a compound either by acid-base extraction or crystallization. These students have completed Experiment 3 (Crystallization) and Experiment 4 (Extraction). They have also completed Experiment 5 (A Separation and Purification Scheme).

Several days before the exam they are given the handout titled "Organic Lab Practical Exam Instructions for Students". At this point they don't know if they will be doing an extraction or crystallization. Therefore, they must prepare for both possibilities. On the test day, they are given either the sheet titled "Extraction" or "Crystallization" and a sample of an impure compound. They have three hour to complete this assignment, but most students are done after two hours.

We make up the samples for crystallization by mixing thoroughly 12 g of urea and 0.53 g of *trans*-cinnamic acid. Each student is given 1.0 g of the mixture. We don't tell them the actual weight and they are told not to weigh it. For the extraction, dissolve 3.0 g of fluorene and 0.75 g of benzoic acid in 60 mL of methylene chloride. Each student is given 4.0 mL of this solution. Students should use a centrifuge tube to perform the extraction procedure.

Because of the way this test is designed, students do not know how much of the compound they start with or the melting point. Therefore, it is impossible for them to change their data to get a better grade.

Organic lab practical exam instructions for students

For this lab practical exam you will be given an impure sample of a compound to be purified either by acid/base extraction or crystallization. You are to carry out this task without the aid of other students or any written or electronic resources.

When you arrive in lab, you will be given an impure sample and an instruction sheet that

will inform you whether the compound is to be purified by acid/base extraction or crystallization. You will be told the structure of the compound, but not the melting point.

Extraction. On the instruction sheet for the acid/base extraction purification you will be told the structure of the neutral compound, the approximate weight of the compound, and what organic solvent it is dissolved in (the compound and impurity will already be dissolved in an appropriate solvent to do the extraction). The volume of this solution will be 4.0 mL. Therefore, you should use a centrifuge tube to perform the extraction. You will also be told whether the impurity is an organic acid or base (amine) and how much 1*M* NaOH or 1 *M* HCl you should use for the extraction step. You do not have to isolate the acid or base impurity. You must decide whether to use NaOH or HCl to extract the impurity.

Your goal will be to separate the neutral compound from the acid or base impurity, isolate it in a pure form, and determine the weight recovered and the melting point. You will **not** know exactly how much of the neutral compound is in the original sample or the melting point.

Crystallization. For the crystallization purification, you will be told the structure of the impure compound and the approximate weight of the sample. You will also be given three suggestions as to which solvent could be used for crystallization. One of these solvents will be suitable for crystallizing this compound. The compound will be too soluble in one of them and not soluble enough in the third solvent. Your goal will be to determine the best solvent, purify your sample by crystallization, and determine the weight recovered and melting point. You will **not** know the exact amount of the compound that you start with or the literature melting point of the compound

General comments and grading procedures. You may **not** use your textbook, handbooks, or any other resources (written or electronic) while completing this exercise. You may not talk to other students and you should refrain from looking at the set-ups used by other students. This exam will be worth 20 points and will be based on the weight recovered of the purified material and the purity based on melting point. You will also be graded on how your sample looks and whether or not the sample is dry. You may have a second sample, but it will cost you 2 points. If you take a third sample, this will cost you an additional 3 points.

Organic lab practical exam instructions and report sheet for crystallization

_____ Name

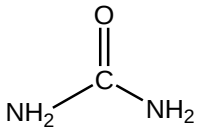
_____ Tube Number

You may **not** use your textbook, handbooks, or any other written material while completing this exercise. You may not use any electronic resources. However, you may take down notes on this sheet of paper. You may not talk to other students during this exercise and you should refrain from looking at the set-ups used by other students. If you have questions during the lab, **ask your instructor.**

There will be a 2-point subjective grade. The subjective grade will be determined by the instructor's assessment of such things as whether or not you talk to other students or if you

obviously look at what other students are doing. You may have a second sample, but it will cost you 2 points.

Instructions. You will be given a sample of impure urea that has a weight between 0.8 – 1.2 g. **Do not weigh the sample**. You should crystallize the entire sample**. Write down the number of the tube and your name in the space above.**

The structure of urea is: 

Urea can be crystallized from one of the three following solvents: 95% ethyl alcohol, water, or hexane. You may determine which solvent to use either by experimentation or by making an educated guess.

After crystallizing the sample of impure urea, determine the weight and melting point of the dry crystals. The melting point should be between 120 - 140° C. Turn in this sheet and your sample in a vial labeled as follows: your name, the name of the compound, weight of sample, and melting point. You will be graded on the recovery and purity, as determined by appearance and melting point. Record the recovery and melting point below:

Recovered weight of sample_____

Melting point of sample _____

Organic lab practical exam instructions and report sheet for extraction

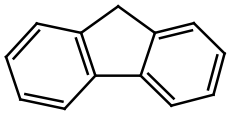
_____ Name

You may **not** use your textbook, handbooks, or any other written material while completing this exercise. You may not use any electronic resources. However, you may take down notes on this sheet of paper. You may not talk to other students during this exercise and you should refrain from looking at the set-ups used by other students. If you have questions during the lab, **ask your instructor.**

There will be a 2-point subjective grade. The subjective grade will be determined by the instructor's assessment of such things as whether or not you talk to other students or if you obviously look at what other students are doing. You may have a second sample, but it will cost you 2 points.

Instructions. You will be given 4.0 mL of a methylene chloride solution containing fluorene (a neutral compound) and an **acid** impurity. The weight of fluorene will be between 0.15 - 0.25 g. Your goal is to isolate the neutral compound and determine its weight and melting point. To remove the impurity, you should extract the methylene chloride solution with two 2-mL portions of either 1.0*M* NaOH or 1.0*M* HCl. After drying the organic layer, evaporate off the methylene chloride. Weigh the solid and determine the melting point. The melting point should be between

105-125 °C.

Fluorene: 

Turn in this sheet and your sample in a vial labeled as follows: your name, the name of the compound, weight of sample, and mp. You will be graded on the recovery and purity, as determined by appearance and melting point. Record the recovery and melting point below

Recovered weight of sample _____

Melting point of sample _____

Experiment 1

INTRODUCTION TO MICROSCALE LABORATORY

TIME ESTIMATE: 1 hour

CHEMICALS AND SUPPLIES PER 10 STUDENTS:

Laboratory Exercise 1

Hexane	6 mL
Automatic pipet (100 to 1000 μL range) (Option A)	
Dispensing pump, 1-mL size, adjusted to deliver 0.500 mL (Option B)	
Graduated pipets, 1.0 mL (Option C)	10
Pipet pumps (Option C)	10
Waste disposal container for hexane	

Laboratory Exercise 2

Pasteur (disposable pipettes)	10
Rubber bulbs	10

CAS Registry number:
Hexanes 110-54-3

Experiment 2

SOLUBILITY

TIME ESTIMATE: Parts A-D (3 hours); Part E (1 hour)

CHEMICALS AND SUPPLIES PER 10 STUDENTS:

Part A

Benzophenone (Grind up the flakes into a powder)	0.5 g
Malonic acid	0.5 g
Biphenyl	0.5 g
Methyl alcohol	40 mL
Hexane	40 mL

Part B

Methyl alcohol	13 mL
1-Butanol	13 mL
1-Octanol	13 mL
Hexane	40 mL

Part C

95 % Ethyl alcohol (denatured alcohol is OK)	13 mL
Diethyl ether	13 mL
Methylene chloride	25 mL
Hexane	13 mL

Part D

Benzoic acid	1.2 g
Ethyl 4-aminobenzoate	1.2 g
1M NaOH	25 mL
1M HCl	25 mL
6M NaOH	6 mL
6M HCl	6 mL
Litmus paper	

Part E

1. Acetone 25 mL

   Hexane 13 mL

2. We give each pair of students two mixtures. Each mixture contains 2 mL of each liquid and about 0.1 g of the dissolved solid. There are many possible combinations of substances to use. The mixtures we have used contain one of the following combinations of solid and liquids (the solid is listed first): fluorene, methylene chloride, water; triphenylmethanol, diethyl ether, water; salicylic acid, methylene chloride, 1M NaOH; ethyl 4-aminobenzoate, diethyl ether, 1M HCl; naphthalene, hexane, water; benzoic acid, diethyl ether, 1M NaOH; *p*-aminoacetophenone, methylene chloride, 1M HCl. The mixtures containing ethyl 4-aminobenzoate and
   p- aminoacetophenone should be made up fresh on the same day as the lab, otherwise the solutions become colored.

3. Tetraphenylcyclopentadienone 0.3 g

   Methyl alcohol 13mL

CAS Registry numbers:

Benzophenone	119-61-9
Malonic acid	141-82-2
Biphenyl	92-52-4
Hexanes	73513-42-5
Methyl alcohol	67-56-1
1-Butanol	71-36-3
1-Octanol	111-87-5
Ethyl alcohol (ethanol), 95%	64-17-5
Diethyl ether	60-29-7
Methylene chloride	75-09-2
Benzoic acid	65-85-0
Ethyl 4-aminobenzoate	94-09-7
Acetone	67-64-1
Fluorene	86-73-7
Triphenylmethanol	76-84-6
Salicylic acid	69-72-7
Naphthalene	91-20-3
p-Aminoacetophenone	99-92-3
Tetraphenylcyclopentadienone	479-33-4

SPECIAL NOTES

In Part A, it is very important that students follow the instructions carefully for stirring the mixtures. The spatula shown on page 606 of the Textbook is very effective in achieving consistent stirring from one mixture to another.

We have found that some students have difficulty performing Critical Thinking Application #2 (p. 17 of the Text) on the same day that they complete the rest of this experiment. Many students need time to assimilate the material in this experiment before they can complete this exercise successfully. One approach is to assign Critical Thinking Applications from several technique experiments (for example, Experiments 2 - 4) on a laboratory period following the completion of the individual technique experiments. This provides an effective way of reviewing some of the basic techniques.

Part A (expected results)

Compound	Water	Methyl alcohol	Hexane
Benzophenone	Insoluble	Soluble in about 25 sec	Soluble in about 60 sec
Malonic acid	Soluble in about 10 sec	Soluble in about 10 sec	Insoluble
Biphenyl	Insoluble	Partially soluble	Soluble in about 40 sec

Part B (expected results)

Compound	Water	Hexane
1-Octanol	Insoluble	Soluble
1-Butanol	Partially soluble	Soluble
Methanol	Soluble	Insoluble

ANSWERS TO QUESTIONS

1. a) yes f) yes
   b) no g) no
   c) yes
   d) no
   e) no

2. a) miscible
   b) miscible
   c) miscible
   d) immiscible
   e) miscible

3. Ibuprofen is a carboxylic acid which is converted to a water-soluble salt in 1.0M NaOH.

4. Thymol has a phenolic OH group which is acidic. In 1.0M NaOH, thymol is converted into a water-soluble salt.

5. Cannibinol is only slightly soluble in methyl alcohol because the large hydrocarbon component of cannibinol negates the fact that they belong to the same family.

Experiment 3

CRYSTALLIZATION

TIME ESTIMATE: Parts A and C (3 hours) or Parts B and C (3 hours)
Note: most students cannot do Parts A, B, and C in 3 hours

CHEMICALS AND SUPPLIES PER 10 STUDENTS:

****Alert students to change fluorenone to fluorene on page 29 of the Textbook, 3rd line from end of upper paragraph.**

Part A

Impure sulfanilamide (5% Fluorenone as the impurity) Grind thoroughly to make homogeneous.	4.0 g
95% Ethyl alcohol	100 mL
Filter paper for Hirsch funnel	
Melting point capillary tubes	
Waste container for non-halogenated organic wastes.	

Part B

Impure sulfanilamide (5% Fluorenone as the impurity) Grind thoroughly to make homogeneous.	1.3 g
95% Ethyl alcohol	35 mL
Copper wire for Craig tube assembly	
Melting point capillary tubes	
Waste container for non-halogenated organic wastes.	

Part C

The appropriate solvent for crystallizing the impure fluorene is methyl alcohol. Fluorene is too soluble in toluene and insoluble in water at all temperatures.

Impure fluorene (5% fluorenone as the impurity)	
Grind thoroughly to make homogeneous.	
If doing semi-microscale crystallization	4.7 g
If doing microscale crystallization	2.0 g
Methyl alcohol	
If doing semi-microscale crystallization	125 mL
If doing microscale crystallization	65 mL
Toluene	25 mL

Waste container for non-halogenated organic wastes.

Part D Mixture melting points

Acetylsalicylic acid	2 g
Benzoic acid	2 g
Benzoin	2 g
Dibenzoyl ethylene	2 g
Succinimide	2 g
o-toluic acid	2 g

CAS Registry numbers:

Sulfanilamide	63-74-1
Acetanilide	103-84-4
95% Ethyl alcohol (Ethanol)	64-17-5
Fluorene	86-73-7
Fluorenone	486-25-9
Methyl alcohol (methanol)	67-56-1
Toluene	108-88-3
Acetylsalicylic acid	50-78-2
Benzoic acid	65-85-0
Benzoin	119-53-9
Dibenzoyl ethylene	4070-75-1
Succinimide	123-56-8
o-toluic acid	118-90-1

Part E (Answers)

1. Phenanthrene
   95% ethyl alcohol - best solvent
   water - not soluble
   toluene - too soluble

2. Cholesterol
   ether - too soluble
   95% ethyl alcohol - best solvent
   water - not soluble

3. Acetaminophen
   95% ethyl alcohol - too soluble
   water - best solvent
   toluene - not very soluble

4. Urea
   water – too soluble
   95% ethyl alcohol – best solvent
   hexane - not very soluble

SPECIAL NOTES

In the Pre-lab Calculations for Parts A and B, students calculate the amount of sulfanilamide which will remain in the mother liquor. If they perform the Optional Exercise in Parts A and B, they determine the weight of solid in the mother liquor. However, the actual weight of solid in the mother liquor is usually much greater than the amount calculated in the Pre-lab Calculations. This is because the calculation does not take into account the impurity, which ends up in the mother liquor. Also, the calculation assumes that a minimum amount of solvent is used to dissolve the impure sulfanilamide at 78 ^{o}C. It is likely that most students use more than the minimum amount.

ANSWERS TO QUESTIONS

1. Too much solvent was added. Since 10 mL of 95% ethyl alcohol will dissolve 0.14 g of sulfanilamide at 0 ^{o}C, none of the 0.1 g of sulfanilamide will crystallize when the solution is cooled. To make the crystallization work, the excess solvent must be evaporated.

2. The boiling point of the solvent is higher than the melting point of fluorenol. While performing this crystallization, it is possible that the fluorenol would melt rather than dissolve, thus forming an oil which could be difficult to crystallize.

3. Biphenyl is highly soluble in both hot and cold benzene. The solubility curve would like **C** in Figure 11.1 on page 679 of the Textbook.