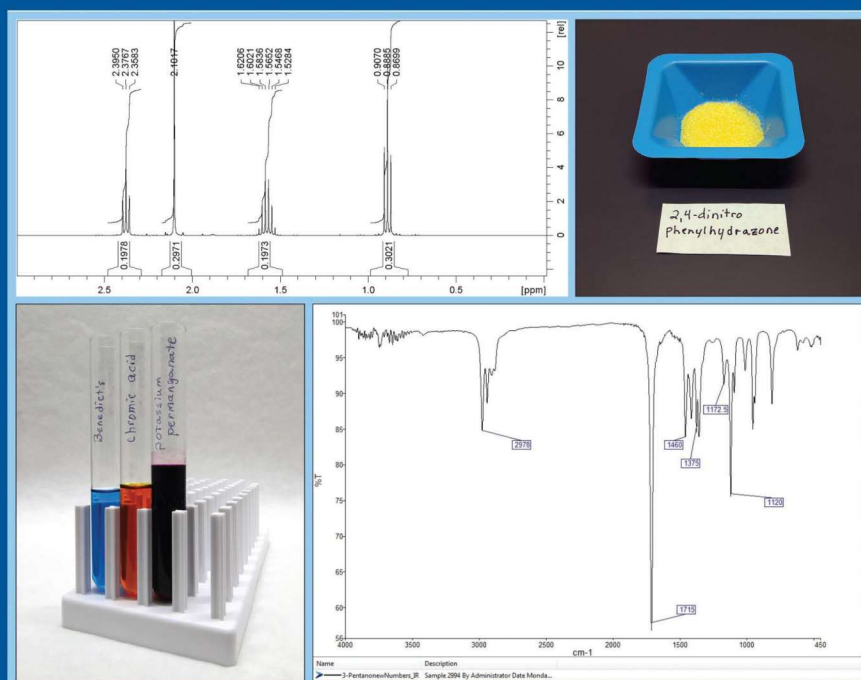


Ninth Edition

The Systematic Identification of Organic Compounds



Christine K. F. Hermann • Terence C. Morrill
Ralph L. Shriner • Reynold C. Fuson



WILEY

THE
**SYSTEMATIC
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OF ORGANIC COMPOUNDS

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CHRISTINE K. F. HERMANN

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Preface

Ralph Shriners and Reynold Fuson wrote the first edition of "The Identification of Organic Compounds" in 1935. In those days, students had to identify organic compounds by solubility tests, physical properties, elemental tests, classification tests, and by preparing a derivative. The classification tests, the derivative experiments, and the derivative tables were expanded in the second edition in 1940 and in the third edition in 1948. The solubility tables were also redrawn in the third edition. David Curtin was added as author in the fourth edition in 1956. The title of the book was changed, in the fourth edition, to "The Systematic Identification of Organic Compounds." Infrared spectroscopy was added, with correlation tables. A discussion of ultraviolet spectroscopy was added. Raman spectroscopy and nuclear magnetic resonance spectroscopy were mentioned as "show promise of becoming increasingly important."

In the fifth edition, in 1964, 712 new entries were added to the original 2000 entries in the derivative tables. In the preface to this edition, proton magnetic resonance was considered second in importance to infrared spectroscopy. Proton nuclear magnetic resonance, including chemical shifts, peak areas, and spin-spin coupling, was described. Terence Morrill wrote the majority of the sixth edition, in 1980. Ralph Shriners provided the well-tryed and chemical tests, in addition to providing advice from years of teaching organic chemistry and qualitative organic analysis. The chemical tests, the preparation of derivatives, and spectroscopy were combined into one large chapter. More infrared spectra and proton nuclear magnetic resonance spectra were included. The discussion of carbon-13 nuclear magnetic resonance spectroscopy, including spectra, was in a later chapter.

The seventh edition, in 1998, was written by Terence Morrill and Christine Hermann. Spectroscopy, the classification tests, and the preparation of derivatives were separated into three chapters. An introduction section was added to each set of functional groups in the classification tests and preparation of derivatives chapters. Cleaning up instructions were added at the end of each experiment. Many new drawings of apparatus were included. Almost all of these drawings were done by Christine Hermann's husband, Richard Hermann. The derivative tables were greatly expanded. A solutions manual was written to accompany this book.

The eighth edition was written by Christine Hermann. The photographs were new for this edition. Chromatography, which had been previously in several chapters, was combined into Chapter 4. Chapter 4 also contains the separation of mixtures, based upon extractions and distillation techniques. Spectroscopy is now divided into three chapters. Chapter 6 describes NMR spectrometry, including DEPT, COSY, and HETCOR. IR spectrometry is discussed in Chapter 7. Chapter 8 discusses mass spectrometry and ultraviolet spectrometry. Chapters 6, 7, 8, and 11 contain all new spectra for this edition. More problems have been added throughout the book. Thomas Glass (Virginia Tech) and Geno Iannoccone (Virginia Tech) contributed several NMR spectra for this edition. Vernon Miller (Roanoke College) contributed mass spectra. Terra Hosp (Radford University) contributed IR spectra and tested the new classification tests in the laboratory. A solutions manual was written with the answers to all of the problems.

The ninth edition was written by Christine Hermann. A new chapter on laboratory safety was added. The separations of mixtures chapter were moved later after the solubility chapter. Discussions on instrumentation have been updated. All spectra are new for this edition. The HETCOR discussion has been replaced with HSQC. A discussion of ATR was added for this edition. Any experiments including picric acid were removed since picric acid is dangerous. Many new problems have been added throughout the chapters.

I am grateful to several chemists for contributing their time and ideas to this edition.

Sydney Fisher (Radford University) contributed all of the spectra that appear in this edition of the textbook. She is acknowledged under each spectrum in the textbook. I thank Laura Angell for creating cover for this textbook. I owe a special debt of gratitude to Steve Pond, for his patience during the preparation of this manuscript.

In summary, I hope that I have provided a book that is useful in the identification of organic compounds. I would appreciate input from faculty, students, and professional chemists on the value of the book and any comments about the book.

Christine K. F. Hermann
Radford University

About the Companion Website

This book is accompanied by a companion website.

www.wiley.com/go/hermann/identorganiccomp9e



This website includes:

- Chapter 13 with structural problems from experimental data for students to practice how to reason and solve.

Chapter 1

Introduction

1.1 SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS: THE NEED FOR ORGANIC QUALITATIVE ANALYSIS

Qualitative organic chemistry has been in use since long before the advent of modern spectroscopy. Modern spectroscopic techniques have assisted the chemist by providing spectra that can be interpreted to give more detail about the interaction between atoms and functional groups. Some students have difficulty identifying structures using exclusively nuclear magnetic resonance (NMR) spectra, infrared (IR) spectra, and mass spectra. The information obtained through chemical tests allows the student to narrow down the possible functional groups. Additionally, by taking a course in qualitative organic chemistry, a student is given the freedom of selecting, for himself or herself, the functional group classification tests that are needed to identify a compound.

In roughly two dozen chapters or more of a standard organic text, the student encounters many chemical reactions. Literally, millions of different organic compounds have been synthesized. Chemical companies sell thousands of compounds, and industrial-scale production generates thousands of different compounds on various scales. Characterization of organic compounds can be done by a handful of physical and chemical observations if it is done in a systematic manner. The list of more common and readily available chemicals is much smaller than the millions that are possible.

In this text, we have focused our attention on an even smaller list of compounds that can be used as “unknowns.” The melting point-boiling point tables give a very accurate idea of the focus

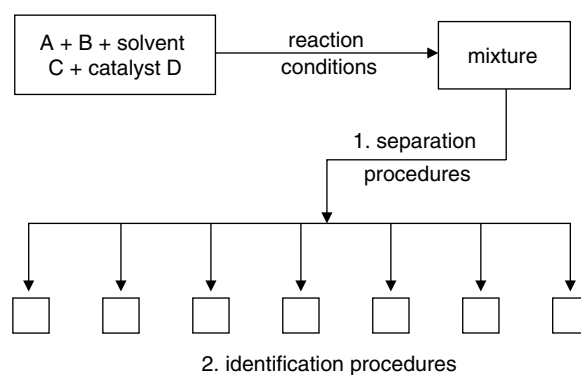
of this book. Instructors using this book may very well use other references, such as the CRC reference volumes,¹ the Millipore Sigma website, the Fisher Scientific website, and others, for a more extensive list of possibilities for “unknown” compounds.

Organic chemists are often confronted with either of the following extreme situations:

1. Determination of the identity of a compound that has no prior history. This is often the case for a natural-products chemist who must study a very small amount of sample isolated from a plant or an animal. A similar situation applies to the forensic chemist who analyzes very small samples related to a lawsuit or crime.
2. The industrial chemist or college laboratory chemist who must analyze a sample that contains a major *expected* product and minor products, all of which could be expected from a given set of reagents and conditions. It is entirely possible that such a sample with a well-documented history will allow one to have a properly preconceived notion as to how the analysis should be conducted.

The theory and technique for identifying organic compounds constitute an essential introduction to research in organic chemistry. This study organizes the accumulated knowledge concerning physical properties, structures, and reactions of thousands of carbon compounds into a systematic, logical identification scheme. Although its initial aim is the characterization of previously known compounds, the scheme of attack constitutes the first stage in the elucidation of structure of newly prepared organic compounds.

If, for example, two known compounds A and B are dissolved in a solvent C, a catalyst D is added, and the whole subjected to proper reaction conditions of temperature and pressure, a mixture of new products plus unchanged starting materials results.



Immediately two questions arise:

1. What procedure should be chosen to separate the mixture into its components?
2. How are the individual compounds (E through K) to be positively characterized? Which ones are unchanged reactants? Which compounds have been described previously by other chemists? Finally, which products are new?

These two problems are intimately related. Separations of organic mixtures use both chemical and physical processes and are dependent on the structures of the constituents.

The present course of study focuses on the systematic identification of individual compounds first. The specific steps are given in Chapter 3. Physical properties are described in Chapter 4.

¹ For example, Z. Rappaport (editor), *Handbook of Tables for Organic Compound Identification*, 3rd ed. (CRC Press, Boca Raton, 1996).

The use of these principles for devising efficient procedures for the separation of mixtures is outlined in Chapter 5. Solubility techniques are described in Chapter 6. Spectroscopy methods are discussed in Chapters 7–9. The classification tests for functional groups are given in Chapter 10, and the preparation of derivatives is given in Chapter 11.

In recent years, the question of scale has become an issue. Scale has always been a focal point for qualitative analysis. The issue has been recognized at an even earlier point in the chemistry curriculum, and a very large number of colleges now incorporate some sort of microscale or miniscale approach into their sophomore organic courses. Organic qualitative analysis has always been a test tube subject and thus should philosophically be in tune with the microscale revolution. Most of our experiments are at the scale of the past editions of this text and thus many chemistry instructors may wish to scale down. Scaling down to 1/2, 1/5, or 1/10 of the cited amount should be very straightforward in most cases, and thus scale is the option of the course coordinator. The only warning is that certain reactions (for example, conversion of a carboxylic acid to an amide or of an alcohol to a 3,5-dinitrobenzoate) are notoriously sensitive to the purity of the reagents. Thus, a larger-scale reaction is likely desirable here.

Cleanup and Waste Disposal

A related, and in some ways bigger, issue is that of waste disposal. The trend at most colleges in recent years is to have waste disposal done by a licensed company under contract with the college. Most instructors are not qualified to dispose of waste and thus they can only provide cleanup guidelines. We have attempted to prepare this edition with that in mind. It is usually the job of the instructor to provide containers for waste disposal. Waste disposal vessels are usually labeled as to their use, such as solids vs. liquids and inorganic vs. organic compounds. Special containers are used for especially toxic wastes such as halogenated organic compounds or heavy metal solutions. Additionally, there are usually special containers for broken glass equipment. There may be places to recycle paper, and finally, there are simple trash cans for garbage. There is usually a classification decision for every act of discarding material. Most importantly, the students should receive instructions from their lab instructors that are in accordance with local regulations.

1.2 SUGGESTIONS TO STUDENTS AND INSTRUCTORS

Schedule

An exact time schedule applicable to all schools cannot be set because of the varied use of semester, quarter, trimester, and summer session terms of instructions. However, for a semester of 15 weeks, two 3-hr laboratory periods per week plus one “lab lecture” per week work well. Modifications can be made to adapt the course to individual schools.

Lecture Material

The first lecture should emphasize safety and all safety protocols as described in Chapter 2. Next, the course overview is described as outlined in Chapter 3. Next, a review of spectroscopic techniques, including operating instructions, should be discussed (Chapters 7–9). Physical properties (Chapter 4), including melting point and boiling point, should be described next. Solubility of the unknown should be reviewed (Chapter 5). Recrystallization (Section 4.4) and separation of mixtures (Chapter 6) could be explained. It is not necessary to lecture on all the experiments and procedures (Chapters 10 and 11), but an introduction to the most common tests should be discussed.

After the first one or two unknowns have been completed, it will be valuable to work on some of the problems of Chapter 13 (available on book companion website) in class and discuss the structure correlation with chemical reactions and spectral data. It is the instructor's choice whether or not to make the *Solutions Manual* available to the students.

Laboratory Work—Unknowns

By use of spectroscopic data and chemical reactions, it is possible for students to work out six to eight single compounds and two mixtures (containing two or three components each) in a 15-week semester.

To get a rapid start and illustrate the systematic scheme, it may be useful to give a titratable acid to each student for a first unknown. The student is told that the substance is titratable and that he or she is to get the elemental analysis, melting or boiling point, and neutralization equivalent and to calculate the possible molecular weights. Then, if the unknown contains halogen or nitrogen, the student is to select and try three or four (but no more) classification tests. Next, a list of possible compounds with derivatives is prepared by consulting the table of acids (Appendix II). One derivative is made and turned in with the report (Sections 3.1 and 3.11). This first unknown should be completed in two 3-hr laboratory periods.

Since many schools run organic qualitative analysis in a lab course connected to the second semester (or last term) of the traditional sophomore course, the decision about how to order the functional groups possible for the unknown may very well depend upon the order of coverage of these groups in the lecture course.

The other unknowns should be selected to provide experience with compounds containing a wide variety of functional groups.

It is recommended to check the student's progress after the preliminary tests, solubility classification, and elemental analyses have been completed. This checking procedure is highly recommended for the first one or two unknowns for each student. It is best to give deadlines throughout the semester for the submission of lab reports. It is not in the best interest of the student to have everything due at the end of the semester.

Purity of Unknowns Although every effort is made to provide samples of compounds with a high degree of purity, students and instructors should recognize that many organic compounds decompose or react with oxygen, moisture, or carbon dioxide when stored for a considerable time. Such samples will have wide melting or boiling point ranges, frequently lower than the literature values. Hence, for each unknown, the student should make a preliminary report of the observed value for melting or boiling point. The instructor should verify these data and if necessary tell the student to purify the sample by recrystallization or distillation and to repeat the determination of the physical constant in question. This avoids the waste of time and frustration from conflicting data.

Amounts of Unknowns As a general guide, the following amounts are suggested:

Unknown No. 1, a titratable acid, 4 g of a solid or 10 mL of a liquid

Unknown No. 2, 3 g of a solid or 8 mL of a liquid

Unknown No. 3, 2 g of a solid or 5 mL of a liquid

Unknown No. 4, 1 g of a solid or 3 mL of a liquid

Mixtures should contain 4–5 g of each component. *Note:* If purification of a sample is required, an additional amount should be furnished to the student.

The amounts listed above are essentially macroscale unknowns; the use of analytical techniques and instrumentation such as thin-layer chromatography and gas chromatography may very well allow sample sizes of unknowns to be ca. 20% of that listed above. *In such cases—that is, for microscale samples—it is imperative that chemical test and derivatization procedures described in Chapters 10 and 11 be scaled down correspondingly.*

Toward the end of the term, when the student's laboratory technique has been perfected and the facility in interpreting reactions has been obtained, it is possible to work with still smaller samples of compounds by using smaller amounts of reagents in the classification tests and by using a smaller scale in the derivatization procedure.

Timesaving Hints

It is important to plan laboratory work in advance. This can be done by getting the elemental analyses, physical constants, solubility behavior, and IR and NMR spectra on several unknowns during one laboratory period. This information should be carefully recorded in the notebook and then reviewed, along with the discussion in each of these steps, the evening before the next laboratory period. A list of a few selected classification tests to be tried is made and carried out in the laboratory the next day. In some cases, a preliminary list of possible compounds and desirable derivatives can be made. It is important to note that a few of the 47 classification tests should be run on a given compound. It should not be necessary to make more than two derivatives; usually, one derivative will prove to be unique. The object is to utilize the sequence of systematic steps outlined in Chapter 3 in the most efficient manner possible.

The instructor should guide the students so that the correct identification results from a process of logical deductive reasoning. Once the structure of the unknown is established, an understanding of the test reactions and spectra becomes clear. Practice in this phase of reasoning from laboratory observations to structure is facilitated by early guidelines in Chapter 13 (available on book companion website). One method for developing this ability is for the instructor to write a structural formula on the chalkboard and ask the students to predict the solubility behavior and select the appropriate classification tests.

To tie together the identification work in this course with actual research, the instructor can select a few typical examples of naturally occurring compounds, such as nicotine, D-ribose, quinine, penicillin G, and vitamin B₁, and review the identifying reactions used to deduce these structures. The recent literature also furnishes examples of the value of IR and NMR spectra in establishing structures. Knowledge of the mechanisms of the reactions used for classification tests and for preparing derivatives requires an understanding of the functional groups and their electronic structures.

Throughout this book, references to original articles, monographs, and reference works are given. Many of these will not be used during a one-semester course. However, the citations have been selected to furnish valuable starting sources for future work and are of great use in senior and graduate research.

The use of this manual will be greatly facilitated by the preparation of a set of index tabs for each chapter and parts of chapters. The time spent in preparing the index tabs is more than recovered in speeding up the location of experiments for functional groups, derivatization procedures, and tables of derivatives.

Chapter 2

Laboratory Safety

2.1 WORKING SAFELY IN THE LABORATORY

At all times, the instructor and students should observe safety rules. They should always wear safety glasses in the laboratory and should become familiar with emergency treatment.

Laboratories are places of great responsibility. Careful practice and mature behavior can prevent most mishaps. The following are all very important. Treating the lab with respect makes it far less dangerous. The following list is a set of rules that must be followed in a laboratory.

Eye Protection Chemical splash goggles must be worn at all times. Eyeglasses, with shatter-proof glass, are inadequate without goggles or safety glasses. Side shields are required for all protective eyewear.

Shoes Closed-toe and closed-heel shoes that completely cover the feet are required in the laboratory.

Protective Clothing A protective apron or lab coat is recommended in the laboratory. If any chemical is spilled on your skin or clothing, it must be washed off immediately.

Food and Drink Food and beverage are strictly prohibited in the laboratory. Do not taste or smell any chemicals.

No Unauthorized Experiments Unauthorized experiments are forbidden in the laboratory. Do not work alone in the laboratory. Chemicals, supplies, or equipment must not be removed from the laboratory. All experiments must be approved by the instructor.

Smoking Smoking is prohibited in the laboratory.

Personal Items No bookbags, coats, or books, except the lab book, should be brought into the laboratory. Ask your instructor where these items can be stored while you are in the laboratory. Laptop computers may be used in a designated area that is free from chemicals and equipment. Bring in only the items that are needed during the laboratory period. These items can be damaged by the chemicals in the laboratory.

Use of Equipment Do not use any equipment until the instructor has shown you how to use it.

Glassware Do not use any broken, chipped, or cracked glassware. Get replacement glassware from your instructor. Ask your instructor where to place broken glassware.

Bench Cleanup At the end of the laboratory period, put away all equipment, clean the laboratory bench, and wash your hands.

Use of Chemicals Take only the amount that is needed. Leave all bottles in their proper places. Place the lids on the bottles after use. Clean up all spilled chemicals immediately.

Careful Reading of Labels A Safety Data Sheet is available for each chemical in the laboratory. Ask your instructor where the paper copies are located. Safety Data Sheets are also available on the web. Many chemical companies have posted this information. Use web search engines to locate this information. Students are encouraged to obtain this information prior to using the chemical in the laboratory. Safety, health, and fire precautions are the most important information to locate. Special instructions for the handling of certain reagents may be posted by the instructor.

Waste Disposal In recent years, the rules regarding waste disposal have become more rigidly defined. Reagents are never poured down the sink. Containers for chemical wastes are provided in the laboratory. Different containers are needed for different types of waste chemicals, such as chlorinated hydrocarbons, hazardous materials, and metals. All reagents in the waste container are listed on the container.

Fume Hoods Most laboratories provide fume hood areas or benchtop fume hoods. Always use these. If you think the hoods are not turned on, bring this to the attention of your instructor. Often students are provided with simple methods of testing hood efficiency, and these should be used periodically. Safety regulations usually prohibit storage of toxic substances in hoods, and fume cupboards for such compounds are normally available.

Gloves Most laboratories provide boxes of disposable gloves. Gloves have their place and can certainly protect your hands from obnoxious odors or chemicals that can cause allergic responses. But they are not a license for sloppy technique. Moreover, they often are easily penetrated by some compounds. Due care is still required.

Compressed Gas Cylinders Compressed gas cylinders, especially those that are nearly as tall as an adult, can be dangerous if not clamped to the bench top. Gas cylinders containing inert gases such as nitrogen or helium may well be around the lab. Cylinders containing chlorine or more toxic reagents should be stored in a fume cupboard.

Safety Equipment Know the location of all safety equipment. Moreover, you should know when you should use these.

Most of the following items should be readily available in the chemistry laboratory; items on this list or their description may vary due to local safety regulations:

- Fire blanket
- Fire extinguisher
- Eyewash fountain
- Shower
- First aid kit
- Washes for acid or base (alkali) burns

Accident Reporting All accidents should be reported to the instructor. It is also important that someone accompany an injured person who is sent out of the laboratory for special care; if the injured person should faint, the injury could easily become compounded.

Medical treatment, except in the simplest of cases, is usually not the responsibility of the instructor. Very simple, superficial wounds can be cleaned and bandaged by the instructor. More serious injuries must be evaluated by a medical professional. The student should be sent to the college health center accompanied by someone from the chemistry department.

All chemicals in the laboratory may not be inhaled, ingested, absorbed, or injected. This rule also applies to chemicals purchased at the grocery store for laboratory use. Food purchased for laboratory use must have the sign “Not for Human Consumption” attached to the bottle.

In all labs, the instructor should provide the students with instructions that are consistent with local regulations.

Explosion Hazards of Common Ethers

A number of violent explosions due to accidental detonation of peroxides, which can build up in common ether solvents, have been reported. These ethers include diethyl ether, diisopropyl ether, dioxane, and tetrahydrofuran. The greatest hazard exists when ethers have been exposed to air, especially for extended periods of time. Each ether container should be labeled with the date that it is opened. Check with your instructor if this date is several months old. The danger is enhanced when the ethers are concentrated—for example, by distillation. *Any ether solvent that displays a precipitate or that seems to be more viscous than usual may well contain peroxides; do not handle such samples and report their condition to your instructor IMMEDIATELY.* The situation described here involves ether samples that are not acceptable for laboratory use.

Several qualitative tests exist to test for the presence of peroxides in ethers; two are described here. **Do not carry out these procedures without permission from your instructor.** Your instructor may decide that ether peroxide tests are not necessary if fresh ether is used.

Procedure A: Ferrous Thiocyanate Test for Peroxide

Use only a freshly prepared solution. Combine 5 mL of 1% ferrous ammonium sulfate, 0.5 mL of 0.5 M sulfuric acid solution, and 0.5 mL of 0.1 M ammonium thiocyanate solution. Add a trace of zinc dust, if necessary, to decolorize the solution. Shake this solution with an equal quantity of the solvent to be tested. If peroxides are present, a red color will develop.

Procedure B: Potassium Iodide Test for Peroxides

Add 1 mL of a freshly prepared 10% potassium iodide solution to 10 mL of diethyl ether in a 25-mL glass-stoppered cylinder of colorless glass protected from light. View the glass cylinder transversely against a white background. Observe the color. The appearance of a yellow color indicates

the presence of peroxides. Shake 9 mL of diethyl ether with 1 mL of a saturated potassium iodide solution. A yellow color indicates the presence of more than 0.005% peroxide. Purify or discard the ether if a yellow color is present.

Removal of Peroxides from Ethers

Ferrous sulfate can be used to remove peroxides from ethers. In the hood, treat each liter of ether with 40 g of 30% ferrous sulfate solution. *The reaction may be vigorous and produce heat if the ethers contain appreciable amounts of peroxide.* The ether can be dried with magnesium sulfate and distilled.

A simple method for removing peroxides from high-quality ether samples, without the need for the distillation or appreciable loss of ether, consists of percolating the solvent through a column of Dowex-1 ion-exchange resin. Use a column of alumina to remove peroxides and traces of water from ethyl ether, butyl ether, dioxane, and hydrocarbons. Use this method also to remove peroxides from tetrahydrofuran, decahydronaphthalene (decalin), 1,2,3,4-tetrahydronaphthalene (tetralin), cumene, and isopropyl ether.

2.2 TRAINING

It is the responsibility of the administration, the faculty, the students, and the staff to create and maintain a safe environment for everyone to work in and to prevent accidents. All faculty and students must receive training before working in a laboratory. The faculty should receive yearly training from the college or university environmental health and safety department. The students must receive training at the beginning of each lab course in each semester and pass a safety quiz.

The common causes of accidents in the laboratory are not following directions, not using common sense, making a mistake, weighing the wrong chemical or wrong amount, or a not-caring attitude.

Many topics are covered in this training including topics such as personal protection equipment, storing of chemicals, using chemicals, disposal of chemicals, and housekeeping. Chemicals must be safely transported in designated containers or carts with sides.

It is important to use chemicals safely and clean up spills in the laboratory. Additionally, glassware must be cleaned and put away at the end of the lab period. Signs must be posted on all laboratory doors and chemical storage rooms to indicate the hazardous nature of the chemicals located within the room. Additionally, emergency contact information needs to be posted on the doors.

2.3 PERSONAL PROTECTION EQUIPMENT

Personal protection equipment is a requirement for faculty, staff, and students working in the laboratory. Chemical splash goggles are a requirement for working in the laboratory. Do not share eye protection. Closed-toe and closed-heel leather shoes offer maximum protection for the feet. Sandals, high-heeled shoes, or woven shoes are not allowed in the laboratory. Shorts, miniskirts, and cutoffs are not allowed in the laboratory. Long pants are the best protection. Lab coats are worn to protect skin and clothing. Rings, bracelets, and watches are not recommended in the laboratory. Gloves may be worn when appropriate. Long hair must be tied back.

The best location to perform lab experiments is a laboratory hood. If laboratory hoods are not available, then experiments may be performed on bench tops, if adequate ventilation is available.

Always wash your hands before leaving the laboratory.

2.4 SAFETY DATA SHEETS

Safety Data Sheets, formerly known as Material Data Safety Sheets, contain all information about a chemical. The following categories are on a Safety Data Sheet. As of June 1, 2015, the Hazard Communication Standard requires all chemical manufacturers or distributors to provide Safety Data Sheets with each chemical to list the hazards of the chemical. These must be reviewed prior to working with the chemical in the laboratory.

1. *Identification*: The manufacturer's name, address, phone number, and emergency phone number are listed here. Recommended use and restrictions on use are also listed.
2. *Hazard(s) identification*: Hazards regarding the chemical are listed here, including the hazard pictograms. Hazard pictograms were developed by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (Figure 2.1).

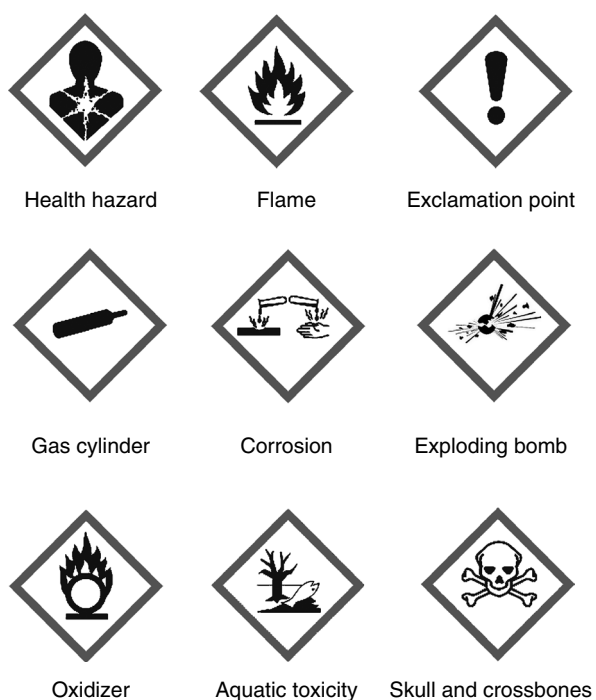


Figure 2.1 The GHS pictograms for chemicals.

The health hazard pictogram indicates that the chemical has the following health hazards of carcinogen, mutagenicity, respiratory sensitizer, reproductive toxicity, aspiration toxicity, or target organ toxicity. The flame pictogram shows that the chemical is flammable, pyrophoric, self-reactive, organic peroxide, an emitter of flammable gas, or self-heating. The exclamation mark lists that the chemical is a skin and eye irritant, is a skin sensitizer, has narcotic effects, can cause acute toxicity, or is a respiratory irritant. The gas cylinder means a gas under pressure. The corrosion pictogram indicates a chemical that causes skin corrosion, causes burns, can cause eye damage, or is also corrosive to metals. The exploding bomb shows that a chemical is self-reactive, an organic peroxide, or an explosive. The oxidizer can cause a fire in the presence of oxygen. The chemical with an aquatic toxicity pictogram is hazardous to aquatic species. The skull and crossbone shows that a chemical has acute toxicity, and may be toxic if inhaled, swallowed, or has contact with skin.

Signal words are also listed here.

3. *Composition/information on ingredients:* A list of chemical ingredients is given here.
4. *First aid measures:* A description of first aid measures is listed, such as general advice, and what to do if the chemical is inhaled, or is in contact with eyes or skin. Also, acute and delayed symptoms and effects are listed.
5. *Fire-fighting measures:* Advice such as extinguishing media, special hazards, advice to fire-fighters, and other information are given.
6. *Accidental release measures:* Protective equipment, emergency procedures, environmental precautions, and cleanup information are given.
7. *Handling and storage:* Safe handling and storage of the chemical are described, along with chemical incompatibilities.
8. *Exposure controls/personal protection:* Occupational exposure limits, appropriate engineering controls, eye protection, face protection, skin protection, body protection, and respiratory protection are described.
9. *Physical and chemical properties:* Physical properties such as appearance, melting point, boiling point, and density are listed. Other physical properties are vapor pressure, viscosity, and others.
10. *Stability and reactivity:* Characteristics such as chemical stability, hazardous reactions, reactivity, conditions to avoid, incompatible materials, and hazardous decomposition products are listed.
11. *Toxicological information:* Toxicological effects may include acute toxicity, skin irritation, eye irritation, respiratory irritation, cell mutagenicity, carcinogenicity, reproductive toxicity, or organ toxicity.
12. *Ecological information:* Toxicity to wildlife, algae, and bacteria is given. Bioaccumulative potential and other adverse effects are listed.
13. *Disposal considerations:* Water treatment methods are described.
14. *Transport information:* Department of Transportation (DOT), International Maritime Dangerous Goods (IMDG) Code, and International Air Transport Association (IATA) transport information for the chemical is given.
15. *Regulatory information:* Some states have a right-to-know component.
16. *Other information:* This may include copyright information.

2.5 STORAGE OF CHEMICALS

A database of chemicals should be maintained. Chemicals should be stored on chemically resistant shelves with a side rail and a lip. Storage rooms must have continuous ventilation. The Safety Data Sheets must be available for all chemicals stored in that room. Chemicals should not be stored in the hoods or on laboratory benches. Chemicals must be stored according to compatibility: inorganic acids, organic acids, organic bases, caustics, inorganics, oxidizers, water reactive, carcinogens, flammable materials, and peroxides. These categories may have subcategories so that the chemicals are stored by functional groups in addition to chemical compatibility. Flammable chemicals are stored in flammable cabinets. Acids must be stored in acid cabinets. Chemicals that must be refrigerated are stored in explosive-proof refrigerators. No food may be stored in these refrigerators.

Secondary containers must be labeled with the name of the chemical and the hazards associated with the chemical.

Gas cylinders must be secured above the midpoint but below the shoulder of the tank.

2.6 DISPOSAL OF CHEMICALS

The containers that are used as waste containers must be in good condition and no larger than 4 L. The container must have a screw-top lid, not a stopper or a cork. The waste container is labeled with a hazardous waste label before any waste is put into it. This label will list the chemicals that will be put into the bottle. Only add compatible chemicals to a waste container. These containers must remain closed unless waste is being added to them. The waste containers should only be filled 80% with the waste. The outside of the container must remain clean. When the container is ready to be picked up, notify your Safety Office. The Safety Office at each school, college, and university will provide information on how the waste bottle should be labeled and how the waste is picked up.

2.7 SAFELY USING EQUIPMENT IN THE LABORATORY

Before using any equipment, students or faculty must be trained on that equipment. Training will include proper preparation of the sample, introducing the sample into the instrument, programming the instrument, and cleanup afterward.

Report any nonworking electrical equipment to your instructor. Do not use equipment with frayed or melted electrical cords. A centrifuge needs to be secure on a tabletop. The vials should be put into the centrifuge so it is balanced. Do not look into the ultraviolet light to see if it is on. Ultraviolet rays can damage the eyes. Vacuum desiccators should have the atmospheric pressure restored before opening them. Water aspirators are used for filtration or rotary evaporators. A vacuum pump must have a trap between the pump and the apparatus so that solvents do not contaminate the pump oil. Do not use a Bunsen burner until you have been shown how to use it. Always light a Bunsen burner away from any apparatus. Caution must be used with sand and oil baths. Both heat up and cool down slowly. Splattering can occur if solvents fall into a hot oil or sand bath. Dry ice and cryogenics must be used with caution and with gloves.

Chapter 3

Identification of Unknowns

There are two scenarios in which the information outlined in this chapter can be applied. In the first scenario, a student is asked to identify a compound already described in the literature. The second scenario is the characterization of a new compound.

The following directions are intended as a guide in the process of identifying an unknown. Good laboratory technique dictates that students keep their own careful and systematic records of observations. The suggested sequence of operations will simplify the process of identifying the unknown compound.

First, the assumption is made that the student has a sample that is one pure compound. This compound has probably been characterized in the literature. If the sample is made of more than one major component, Chapter 5 on separation techniques should be consulted.

3.1 DISCUSSION OF REPORT FORM

By following the sequence of steps in the report form, a student can successfully identify the unknown compound.

BLANK REPORT FORM

Compound _____ Name _____

Unknown Number _____ Date _____

1. Physical Examination:

- (a) Physical state _____
(b) Color _____
(c) Odor _____
(d) Ignition test _____
(e) TLC _____
(f) GC _____

2. Physical Constants:

- (a) mp: observed _____; corrected _____
(b) bp: observed _____; corrected _____

3. Elemental Analysis:

F _____, Cl _____, Br _____, I _____, N _____, S _____
Metals _____

4. Solubility Tests:

H ₂ O	Ether	NaOH	NaHCO ₃	HCl	H ₂ SO ₄

Reaction to litmus: _____

Reaction to phenolphthalein: _____

Solubility class: _____

Possible compounds: _____

5. Molecular Weight Determination: _____

6. IR Spectrum (attach to the end of report):

Solvent: _____ (if used)

Frequency (cm ⁻¹)	Bond	Compound Type

7. NMR Spectrum (attach to the end of report):

Solvent: _____

¹H NMR spectrum.