



Safety in Academic Chemistry Laboratories

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ACCIDENT PREVENTION
FOR FACULTY AND ADMINISTRATORS
7TH EDITION

A Publication of the American Chemical Society Joint Board–Council
Committee on Chemical Safety

Safety in Academic Chemistry Laboratories

VOLUME 2

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AND ADMINISTRATORS
7TH EDITION**

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Joint Board–Council Committee on Chemical Safety

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Foreword from the Chair

When the Committee on Chemical Safety of the American Chemical Society (ACS) published the first edition of *Safety in Academic Chemistry Laboratories (SACL)* almost 30 years ago, there was very little emphasis on teaching laboratory safety. During the intervening years, the distribution of the six prior editions approached a million copies. *SACL* is one of the most widely used laboratory safety guidance documents in print today. Although written as a guideline for safe practices in academic chemistry laboratories, its application is not limited to educational facilities. The information presented in this manual is adaptable to all laboratories and workplaces using chemicals, including research, analytical, quality control, clinical, and process development laboratories.

As we learn more about the hazards and risk of the chemicals in our laboratories, we must share this knowledge with our colleagues and our students. The ACS Division of Chemical Health and Safety disseminates current research and developments in its national meeting technical programs and through its journal, *Chemical Health and Safety*. Precollege science teachers have begun to include chemical safety in their classroom instruction. The Committee on Chemical Safety has prepared two companion publications to assist those involved in elementary and secondary school science education. Copies of *Safety in the Elementary (K–6) Science Classroom* and *Chemical Safety for Teachers and Their Supervisors: Grades 7–12* are available through the ACS Office of Society Services.

I am pleased to introduce the seventh edition of the committee's flagship publication and wish to thank the many individuals who generously contributed their time and wisdom to this and the previous editions. Their efforts have helped to make academic chemistry laboratories much safer places with fewer accidents and injuries. Jay Young has contributed to several editions of *SACL*; he was the major contributor and served as Editor of this edition. The comprehensiveness and lucidity of this volume are the direct result of his dedication and commitment. The Editor's Preface acknowledges those who contributed to the revisions and development of the seventh edition. The final draft was reviewed by Dan McDonald, Russ Phifer, and Rubye Torrey. Larry Funke coordinated the efforts of those ACS staff members involved in the production and distribution activities.

All comments are welcome. Please direct them to the Committee on Chemical Safety, American Chemical Society, 1155 16th St., NW, Washington, DC 20036.

Kenneth P. Fivizzani
Chair, ACS Committee on Chemical Safety
October 2002

Preface from the Editor

The first edition of this book was written in 1972 by members of the ACS Committee on Chemical Safety under the direction and urging of its chair, Howard H. Fawcett (now deceased). It was published as an 11-page, double-spaced, typed and mimeographed document. Since then, almost a million copies of the original and its five subsequent editions have been distributed. The objective has remained unchanged; however, the details have become more complex.

Our knowledge of chemical hazards has advanced; chemical safety has become an important part of both the precollege and the college and university undergraduate teaching curriculum. *Safety in Academic Chemistry Laboratories* is now published in three parts—*Safety in the Elementary (K–6) Science Classroom*, *Chemical Safety for Teachers and Their Supervisors: Grades 7–12*, and *Safety in Academic Chemistry Laboratories* (now in two volumes—this volume for chemistry faculty, graduate student teaching assistants, and institution administrators, with a companion volume for undergraduate students who learn from their work with chemicals in college and university laboratories).

As students mature, their instruction is presented less passively, and they take a more active role in learning. By the time they reach the college or university level, students' active participation should be an essential part of the learning process. To reflect the active participation of the maturing student, we have added a subtitle, *Accident Prevention*, to this edition.

I wish to acknowledge the helpful suggestions and contributions of the members of the Joint Board–Council Committee on Chemical Safety, with particular thanks to Robert Alaimo, Charles Greenlief, Rubye Torrey, and George Wahl, members of the Revision Subcommittee, and to Eileen Segal, Russell Phifer, Stephen Sichak, Dan McDonald, and Bernard Blais.

Jay A. Young
Editor
October 2002

Disclaimer

The materials contained in this manual have been compiled by recognized authorities from sources believed to be reliable and to represent the best opinions on the subject. This manual is intended to serve only as a starting point for good practices and does not purport to specify minimal legal standards or to represent the policy of the American Chemical Society. No warranty, guarantee, or representation is made by the American Chemical Society as to the accuracy or sufficiency of the information contained herein, and the Society assumes no responsibility in connection therewith. This manual is intended to provide basic guidelines for accident prevention. Therefore, it cannot be assumed that all necessary warning and precautionary measures are contained in this document and that other or additional information or measures may not be required. Users of this manual should consult pertinent local, state, and federal laws and legal counsel prior to initiating any accident-prevention program.

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Introduction

The ACS Joint Board–Council Committee on Chemical Safety has prepared this volume for the prevention of accidents in college and university educational chemistry laboratories. Individuals directly responsible for accident prevention can use the general recommendations in this volume as a basis for a chemical hygiene plan or other detailed safety instructions. The information here can be adapted to practices in all research, clinical, quality control, and development laboratories that use chemicals, as well as in other workplaces that use chemicals.

This volume is addressed to institution administrators and chemistry department faculty and staff, including graduate students and other teaching assistants. The companion work, Volume 1, is intended for the instruction of and use by undergraduate college and university students enrolled in chemistry laboratory courses.

Performing work with chemicals in a safe manner can reduce the probability of accidents, including toxic exposures, to a negligible level. To reduce the probability of accidents,

- acquire and practice the habit of accident prevention,
- use appropriate engineering controls for chemical containment,
- use personal protective equipment properly and consistently,
- use the smallest quantity of material necessary to accomplish the goal of the experiment,
- when possible, substitute a less hazardous chemical or laboratory procedure for a more hazardous one; and
- anticipate consequences.

Before you begin an operation or perform an experiment, ask yourself, “What would happen if...?” Answering this question requires you to understand the hazards associated with the chemicals and equipment involved. The reactivity, flammability, corrosivity, and toxicity of the chemicals you use will dictate the precautions you take. Such precautionary information might well form an introductory section in all written routine procedures.

Accident prevention requires an effective safety program, which must have direct and enthusiastic support from the top administrative officer, who, after all, is ultimately responsible for safety in a facility. Without direct and strong support from him or her and the active involvement of all faculty and staff members, few accidents will be prevented.

A safety officer, appropriately trained, qualified, and with the authority to act, is also essential. However, even the best safety officer cannot relieve top administration, the head of the laboratory, the faculty, the staff, and the students of their responsibility for the safety of operations under their jurisdiction. A good accident-prevention program includes constant training and reminders of the common hazards to which laboratory workers may be exposed and attention to the materials, equipment, and facilities with which they work. The rapid pace of new information and changing regulations demands ongoing training, even for experienced laboratory workers.

To achieve safe conditions for students and other laboratory workers, an accident-prevention program must include

- regular safety inspections at intervals of no more than three months (and at shorter

- intervals for certain types of equipment, such as safety showers and eyewash fountains),
- regular monitoring of the performance of equipment and ventilation systems,
 - formal and regular procedures to ensure that sufficient full-time personnel are trained in the proper use of emergency equipment and procedures, and
 - procedures that ensure proper disposal of waste chemicals.

This volume summarizes many of the aspects of laboratory safety from a teaching and administrative viewpoint, including consideration of the regulations developed under the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and the Occupational Safety and Health Act. However, accident prevention, not the regulations, is the essential component of all laboratory operations:

**Doing things safely is not merely the right way to work
—it is the *only* way.**

This manual provides a basis from which both institutional and individual safety policies and procedures can be developed. It is not intended to replace existing rules or regulations. It is a starting point for understanding accident prevention; further and more detailed information can be found in the references in Appendix 1. Most of the material presented here is the result of the many years of practical knowledge of the members of the Joint Board–Council Committee on Chemical Safety with additional information derived from regulatory sources.

1. Organizing for Accident Prevention

An academic institution's chief executive officer is responsible for the safety of the students and employees in its laboratories. The chief executive officer must

- establish and maintain an effective accident-prevention program;
- arrange for its documentation;
- initiate the establishment of a chemical hygiene plan (see 29 CFR [Code of Federal Regulations] 1910.1450, the Laboratory Standard); and
- appoint a chemical hygiene officer, as is required by the Laboratory Standard.

The faculty and staff of the chemistry (or science) department are responsible for administering the accident-prevention program. All must perform their jobs safely and participate in appropriate training programs. In addition to a general review of the hazardous properties of chemicals and what precautions to take, this training should include instruction on Material Safety Data Sheets (MSDSs) and labels; all emergency equipment within the academic facility and its location, proper use, and maintenance¹; and compliance with the OSHA Laboratory Standard, 29 CFR 1910.1450.

Laboratory instructors are responsible for the safety of their laboratory students; no more than 25 students should be assigned at the same time to work in a laboratory under the supervision of an instructor. The laboratory instructor should be in the laboratory during the entire laboratory period for undergraduate-level courses, including so-called "undergraduate research" laboratory work. The laboratory instructor allows neither untrained students nor visitors to work with chemicals.

Each faculty and staff member of the chemistry department has the following responsibilities:

- Set a good example by
 - observing the rules and recommendations outlined in the chemical hygiene plan (CHP),
 - wearing appropriate protective equipment, and
 - practicing accident prevention.
- Review the procedures with the students for potential health, safety, and environmental problems for each laboratory session.
- Review the relevant MSDSs and labels before allowing students to perform any laboratory procedures.
- Be alert for unsafe conditions.
- Maintain good housekeeping in laboratory spaces.
- Provide discipline and enforce rules.
- Conduct frequent and thorough inspections.
- Promptly take effective corrective action when necessary.
- Conduct appropriate safety and evacuation drills on a regular basis.
- Be familiar and keep up to date with publications on accident prevention in the chemical laboratory.

¹The emergency equipment should include, at a minimum, telephones or other means of emergency notification, safety showers, eyewash fountains, fire extinguishers, building alarms, and first aid necessities.

Safety Officers and Safety Committees

Experience shows that effective accident-prevention programs require a firm commitment at the highest administrative level. A safety officer should be appointed whose primary responsibility is advising and assisting administrators, faculty, and staff on safety and health issues. The safety officer also may be the chemical hygiene officer (a chemical hygiene officer is required by the Laboratory Standard, OSHA 29 CFR 1910.1450). Otherwise, the safety officer's position should be considered a substantial part of the regular workload—not as a secondary responsibility.

An accident-prevention committee should be formed to assist and report to the safety officer. Members should include faculty and staff from the major divisions of the chemistry or science department. The committee also should include members from the administration. The accident-prevention committee should be organized to advise and assist administrators, lab supervisors, students, and workers, but it should not be responsible for working conditions and practices related to safety. That responsibility rests on the safety officer jointly with the faculty, the laboratory supervisors, and the students in the laboratory.

The committee should set up and supervise regularly scheduled safety inspections of the laboratory facilities, including unoccupied areas and storerooms. Records of the findings of the inspections should be kept for at least 5 years and reviewed at intervals to ensure that accident-prevention practices show a general improvement over time, as noted below.

Hazardous conditions should be reported and corrected. Including the serial number and date for every hazardous condition reported helps keep track of the conditions until they are corrected. In practice, a revolving inspection team is preferable because it brings the judgment and participation of more individuals into the system. The person responsible for an area in which a hazard is identified should be formally advised of the hazard and be given suggestions for correction, including a target date for completion of the corrective action. After corrective measures have been completed, the person responsible should report to the accident-prevention committee chair. Periodically, the chair should review past reports for recurrent hazards and institute recommendations and actions to eliminate them, consulting with the safety officer, the faculty, and others for suggestions. See Appendix 3 for further information.

2. Personal Protective Equipment

Eye and Face Protection

It is universally agreed that the use of proper eye protection is required of everyone who enters a chemical work area. There is always a need for protection from splashes of toxic and/or corrosive chemicals and flying particles. Safety goggles that protect the top, bottom, front, and sides of the eyes are mandatory. Neither spectacles with side shields nor safety glasses with side shields provide adequate protection from chemical splashes, because they do not fit firmly against the skin. Suitable safety goggles that do fit firmly are described in the current edition of the American National Standards Institute (ANSI) Z87.1-1989 (R1998) as Protector Type G, H, or K. Other eye-protection devices described in this standard are not suitable for use in a chemical laboratory.

In some workplaces where hazardous chemicals are used or handled, wearing contact lenses is prohibited or discouraged. These prohibitions are based on rumors and perceived risks. Studies of the literature have refuted these risks. The ACS Joint Board–Council Committee on Chemical Safety studied and reviewed the issue. The consensus is that contact lenses can be worn in most chemical laboratories, as long as safety goggles are also worn (Protector Type G, H, or K).

Face shields alone are not considered adequate eye protection. In addition to safety goggles, face shields conforming to Protector Type N of ANSI Z87.1-1989 (R1998) are necessary when working with severely corrosive liquids, glassware under reduced or elevated pressure, glass apparatus used in combustion or other high-temperature operations, cryogenic liquids, and whenever there is any other possibility of an explosion or implosion. The face shields should be wide enough and long enough to protect the face, neck, and ears of the wearer.

Considerable discomfort and damage to the eye can result from exposure to UV light. Absorption of this radiation by the outer layers of the eye (cornea and conjunctiva) produces keratitis and conjunctivitis. UV-absorbing protective glasses should be worn whenever exposure to erythemically effective radiation is likely. The use of lasers requires special eye protection as specified in the current edition of ANSI Z136.1.

Protective Clothing

Aprons, lab coats, gloves, and other protective clothing, preferably made of chemically inert material, should be readily available and used. Note that most lab coats and aprons are made of substances that will burn. Gloves must provide sufficient arm protection to minimize the chance of spilled chemicals making contact with the skin of the arm. Gloves are made from a variety of materials, no one of which is impervious to every chemical. Examine the manufacturers' claims and test data carefully; use the gloves only under the conditions for which they are intended as protection against the penetration of the chemical(s) for which they have been designed. Remember that given enough time, any glove will be permeated by the chemical to which it is "impermeable."

Protection for legs and feet should be provided by a lab coat or apron and shoes or, in some cases, boots. Shoes that have high heels or open toes, uppers made of cloth, woven leather strips, or other woven material should not be worn, because they do not provide suitable protection.

Respirators and Self-Contained Breathing Apparatus

Rather than relying on respirators, most academic laboratories should instead rely on administrative controls, engineering controls, and work practices to limit exposures to hazardous vapors, dusts, and mists.

However, at least two 30-minute self-contained breathing apparatus (SCBA) devices (not air-line-supplied or canister or filter gas masks) should be available for emergency evacuation in the event of high concentrations of toxic vapors, dusts, mists, or oxygen-deficient atmospheres. Personnel should be trained to use them ahead of time. These respirators should be kept in permanent wall-mounted cabinets located outside the potential danger area. OSHA regulations require that before someone can use such a respirator, a physician must certify that he or she is physically able to operate it. See the current edition of ANSI Z88.2, Practices for Respiratory Protection, and OSHA regulation 29 CFR 1910.134. Individuals who are untrained or out of practice should *not* use them, even during an emergency.

Cleanup of a medium to large toxic spill may require using canister, filter gas masks, or air-line-supplied respirators. The requirements of 29 CFR 1910.134 apply. Depending on your situation, you may want to call off-campus contractors when the degree of complex service mandated by 29 CFR 1910.134 is required.

Hearing Conservation

Hearing conservation should be practiced through proper design of equipment, modifications of existing sources of noise, and the use of ear protection. See the box for the OSHA allowable occupational noise exposure limits taken from 29 CFR 1910.95.

Exposure to impact noise should not exceed 140 dB peak sound pressure level. Ear protection includes earmuffs and earplugs. Generally, earmuffs have a greater attenuation factor than earplugs. Some people experience discomfort at sound levels below 90 dBA.

Responsibility for Training

Academic institutions have a moral and professional responsibility to train students in safe laboratory practices.

Students are expected to comply with the local accident-prevention rules (see Appendix 2 for suggestions) and to participate conscientiously in any training exercises. Also, inform students that they have the responsibility to obtain advice and guidance whenever they are in doubt about accident-prevention procedures or potential hazards in their laboratory work.

The institution is responsible for training students working in the laboratory, teaching assistants provided by the department, faculty members, custodial staff, and any

| OSHA Occupational Noise Exposure Limits from 29 CFR 1910.95 | |
|---|---------------------------------|
| Duration per day, hours | Sound level, dBA slow response* |
| 8 | 90 |
| 6 | 92 |
| 4 | 95 |
| 3 | 97 |
| 2 | 100 |
| 1.5 | 102 |
| 1 | 105 |
| 0.5 | 110 |
| 0.25 or less | 115 |

*Decibels when measured on the A-scale of a standard sound-level meter at slow response.

other employees working with or exposed to chemicals. The OSHA Laboratory Standard requires that all such employees be trained to safely handle and use the hazardous chemicals with which they work and that training records be maintained. Administrators should be aware that sometimes faculty members, even with advanced degrees, may not be well instructed in the safe handling of hazardous chemicals. Useful references in instruction are included in Appendix 1.

Undergraduate and beginning graduate students in laboratory research studies should be closely supervised. Most of the older literature and some recent literature references that beginning students are likely to consult often do not discuss the hazards involved in the work they describe. Some references do not even mention hazards that have been fatal at the hands of a beginner.

The research director is responsible for understanding that beginning research students probably will not recognize potential dangers in the laboratory work they plan to conduct. The research director must ensure that appropriate precautions are followed.

Evacuation and Fire Drills

Evacuation routes should be prominently and permanently posted in every laboratory and at other appropriate locations throughout the building.

Students should know the location of and how to operate the fire exits, telephones, and alarms in use during regular school hours as well as after-hours. Instruction in fire drills should be scheduled on a regular basis (at least annually or as otherwise specified by local regulations).

Consult local fire officials about the frequency of fire drills and whether they should be announced or unannounced. Identify specific locations for gathering after exiting the building. For each group exiting, designate one person and a deputy to be responsible for counting those present after exiting and reporting that information to the person in charge. No one can return to the building until he or she is authorized to by the individual in charge.

Conduct a critique after each drill; remember that the purpose of every drill is to “do it better” than the last time.

3. Labeling

Consult the current edition of the ANSI Standard, Z129.1, Hazardous Chemicals—Precautionary Labeling. Also see the OSHA booklet 3084, *Chemical Hazard Communication*, which summarizes the federal regulatory requirements for labeling containers in the workplace. Also consult your local and state regulations because they may differ.

Label all chemicals with the date of receipt, the date of initial opening, and the decision date (see the discussion on storage protocol, page 37). Repackaged chemicals should have secure, waterproof labels in waterproof ink. The labels should include the chemical's name, concentration, purity, date it was packaged, information on its hazards, and what precautions to take. Many institutions also label chemicals with the identity (such as the legibly written initials or name) of the person, section, or division responsible for the chemical. This practice is recommended.

4. Material Safety Data Sheets (MSDSs)

MSDSs are references intended primarily to train workers on the hazards and precautions for chemicals that they will use in an industrial workplace.² OSHA defines hazardous substances as any chemical that presents a hazard under normal-use conditions or in a foreseeable emergency. OSHA requires that all hazardous chemical suppliers furnish MSDSs to their customers and that employers³ make them readily available to their employees for every hazardous chemical on the premises.⁴ The MSDSs can be stored in databases, provided that workers can readily access them.

OSHA requires that known and suspected carcinogens recognized by relevant authorities must be identified in MSDSs. No recognized authority exists yet for the identification of human reproductive toxins. Therefore, although a substance is or might be mutagenic or teratogenic, OSHA does not require its identification in an MSDS. In practice, only a few MSDSs include statements that identify a substance as a reproductive toxin. At present, the absence of a statement that a substance is a reproductive toxin can only be taken to mean that such information is absent from the MSDS. For information on whether a substance is or might be a reproductive toxin, see “Reproductive Hazards” on page 19.

OSHA has prepared a suggested format for MSDSs, but any format that supplies the information required by 29 CFR 1910.1200 is acceptable. Few chemical suppliers have adopted the specific, detailed, multipage format described in the current edition of the voluntary ANSI standard for MSDSs, Z400.1. Although this format provides information in an understandable style that seems to satisfy both the OSHA specifications and those of several other countries, most suppliers use either OSHA's reconcile format or a variation.

Regardless of format, the principal topics required in an MSDS include physical data, fire and explosion hazards, toxicity hazards, other health hazards, propensity to react vigorously (often called an incompatible chemicals list or reactivity description), spill and leak clean-up procedures, and, above all, precautionary measures that (if followed) will materially reduce the probability of harm. Even if it isn't written in an easily comprehensible style, a properly prepared MSDS is a useful tool for students. Although OSHA has no authority to require student training on hazardous chemicals, faculty can take advantage of valid MSDSs to train students in descriptive and theoretical chemistry as well as accident prevention.

However, it is important to recognize that an MSDS is a *tertiary source* of information and that not all MSDSs are prepared from reliable secondary sources. Therefore, some MSDSs are less than accurately informative. Not all fully describe the known hazardous properties of the substance, and some even attribute hazards that are not attributable to the subject chemical. It is often useful to compare MSDSs from differ-

²Consequently, some of the information included in an MSDS may not apply to that chemical when used, handled, or stored as a laboratory chemical. Conversely, some of the information that is omitted from an MSDS might be hazard and precautionary information that applies to the use, handling, and storage of the chemical in a laboratory.

³Some states require that for every hazardous chemical on the premises, one of its MSDSs must come from the supplier.

⁴OSHA regulations, including those pertaining to MSDSs, are applicable to employers and employees but not to students. However, it is generally considered that good practice includes considering the OSHA requirements, e.g., the limits such as PELs and TLVs, as though they did apply to students. In any event, faculty and staff are employees and their protection is subject to OSHA regulations.

Common MSDS Errors

Before relying on MSDSs as an educational resource, instructors should examine them carefully for omissions, inaccurate statements, and internal inconsistencies. The following are errors commonly found in current MSDSs.

No identification, or incorrect identification, of the “target organs.” For example, liver, kidney, lungs, central nervous system, or other organ(s) or organ system(s) that are threatened by the chemical when it is improperly handled.

Incomplete PEL statement. For example, the MSDS may state that the permissible exposure limit (PEL) is 100 ppm, but a quick look at the current 29 CFR 1910.1000 may (in this imaginary example) clearly indicate that the PEL includes a short-term exposure limit (STEL) of 300 ppm. The correct MSDS information would include both limits, the time-weighted average of 100 ppm and the excursion limit of 300 ppm.

A statement that the percent volatile is “nil” or “not available.” But in a different location in the same MSDS, there is a statement that the vapor pressure is, say, 40 mm at 70 °F.

A statement that the chemical is not flammable. But the MSDS states elsewhere that to fight fires, one should use carbon dioxide or another fire-extinguishing agent when that chemical is burning.

For a chemical that is altered in the heat of a fire and forms toxic products. The MSDS states that such products “may be toxic” when the correct wording is “will be toxic,” “are toxic,” or “is toxic.”

A description of certain consequences following overexposure. But no explanation in the MSDS of the criteria by which an exposure is to be identified as an overexposure.

A statement in one section that overexposure *might* cause a certain adverse effect. But the MSDS states in another section that overexposure *will* cause those results.

A recommendation to wear impervious gloves or other clothing. But the MSDS fails to identify the material (e.g., butyl rubber, neoprene, polyethylene) of which the glove or clothing should be made in order to be impervious. Or, if the material is identified, the MSDS does not further state that even though it may be considered impervious, it will resist penetration for only a few hours, at most.

First aid procedures that instruct you not to administer any liquids to an unconscious person. But the MSDS fails to instruct what to do instead if the victim is unconscious.

Statements to keep a chemical away from ignition sources. But the MSDS does not explain that the vapors can travel hundreds of feet away from their source or otherwise describe how to determine how many feet constitute a safe distance “away from ignition sources.”

Statements recommending that a chemical be used only with adequate ventilation. But the MSDS does not define what is meant by adequate ventilation. (Adequate ventilation is properly defined as ventilation sufficient to maintain the concentration of vapors in the user’s breathing air below the PEL or threshold limit value (TLV), provided that the vapor concentration is determined by quantitative measurements.)

Peculiar disclaimer statements. In effect, these say, “The information contained herein is based upon information believed to be reliable. However, we cannot guarantee that any of it is, in fact, correct.”

ent suppliers for the same chemical. Try to find the primary literature; however, it is often difficult to obtain. Refer to reliable sources such as the National Institute for Occupational Safety and Health (NIOSH)/OSHA *Occupational Health Guidelines for Chemical Hazards*, *Patty's Toxicology*, *Gosselin's Clinical Toxicology of Commercial Products*, *Bretherick's Handbook of Reactive Chemical Hazards*, the American Conference of Governmental Industrial Hygienists (ACGIH) Documentation Volumes, and the NIOSH *Criteria Documents* (all listed in Appendix 1).

MSDSs can provide unique opportunities for students to gain insight into how practical decisions are made when the use of a chemical is being considered. The information on toxicity and precautions in a reliable MSDS can help faculty select a suitable less toxic chemical to use, rather than a more toxic one. For example, substitute for the more toxic barium chloride with the less toxic strontium chloride in a study of insoluble sulfates. Similarly, an MSDS section on the incompatibility (reactivity) of acetic acid with potassium permanganate or some other oxidizer reminds faculty to limit the amounts to be used by students in an experimental investigation.

MSDSs should be available to students, faculty, and staff. OSHA requires that employers provide an MSDS for a hazardous chemical on the premises to any employee who requests it. Although students are usually not employees, most educational institutions provide them with MSDSs; an MSDS can be educational, even though some of them may be difficult to fully understand. Hazard and precautionary information from reliable MSDSs should be incorporated as part of all laboratory procedures. As gleaned from MSDSs, student laboratory reports could include accident-prevention and health concerns, the management of hazardous chemicals in their laboratory work, and, where appropriate, the proper disposal of both products and leftover reagents. Students might be taught that the practical information found in the reactivity section of an MSDS is useful in designing safe experimental procedures. The value of focusing on MSDSs is long-term; students who go on to work and supervise others in a lab will be more likely to handle chemicals safely.

5. Preparing for Medical Emergencies

The ACS Joint Board–Council Committee on Chemical Safety strongly recommends that MSDSs and competent medical authorities be consulted in advance regarding first aid treatment for all chemicals used in the laboratory. First aid supplies approved by a consulting physician should be readily available. For specific guidelines on providing appropriate first aid training, see the OSHA Guidelines on First Aid Training, OSHA Directive CPL 2–2.53, January 7, 1991, available at www.osha-slc.gov/SLTC/medicalfirstaid/index.html.

When you plan for potential emergencies, consult with local emergency personnel (the institution's physician, hospital emergency room, ambulance services, fire chief, police chief, etc.) in advance and establish plans for handling chemical and other emergencies before you start any activity. Medical personnel involved in recommending first aid procedures should understand exactly what chemicals are involved and have access to pertinent and reliable MSDSs on their own premises.⁵

At a minimum, make the following preparations:

- See that first aid equipment is readily available.
- Prominently post the location and phone numbers of the local physicians who are qualified and have agreed to handle chemical emergency cases and of local medical facilities that are similarly qualified and have agreed. Also, post the location of the MSDS file.
- Ensure that sufficient staff is trained in basic first aid and cardiopulmonary resuscitation (CPR).⁶ Red Cross certification or its equivalent should be encouraged for all personnel. Contact the local Red Cross chapter for information about appropriate training modules.
- Before an accident occurs, arrange for someone knowledgeable to accompany the victim to get medical help in the event of an accident. The individual should bring along a copy of the MSDS(s) for the chemical(s) involved in the accident. Maintain a file of extra copies of all MSDSs for this purpose, or arrange in advance for the local physicians and medical facilities that have agreed to be available to have access on their terminals to the MSDS files in your institution's computer database.
- If it appears that first aid treatment is sufficient, ensure that a nurse or physician qualified to handle chemical emergencies agrees that no further treatment is necessary.

Other preparations must be made before handling emergencies involving laboratory chemicals. For example, if first aid treatment is not described in the MSDS, add this information to the MSDS without delay.

⁵The institution or chemistry department can supply them; however, they should be reviewed from time to time and kept current. Also, see the fourth bullet below.

⁶If automatic external defibrillators (AEDs) are part of the emergency equipment, the training should of course include instruction for using them.

Examples of Emergencies To Expect

- thermal, cryogenic, and chemical burns;
- cuts and puncture wounds from glass or metal that is contaminated with chemicals;
- glass in the eye (the glass may be contaminated with chemical residue);
- chemicals (liquid splashes, mist, dust) in the eye;
- skin irritation by chemicals;
- poisoning by ingestion, inhalation, skin absorption, or injection;
- asphyxiation; and
- lachrymatory vapor irritation.

6. Reporting Accidents

Report all accidents and near-misses. Keep records of all accidents, including those requiring only first aid or involving only minor medical treatment or observation. Prepare a formal written report, stating the causes and consequences of each accident or near-miss. File a copy with the department safety officer and discuss recommendations for the prevention of recurrences with him or her.

When a student causes an accident or a near-miss, it is educationally useful to require a written report from the student. The report should address how he or she thinks it could have been prevented, rather than discuss the cause. When the students know about this requirement from the first day of class, this technique has proved especially useful in preventing laboratory accidents.

A periodic review of accident and near-miss reports will often reveal problem areas that need special attention. Also, certain OSHA reporting requirements may apply, depending on the institution and the nature of the accident. To alert others, report unusual or inexplicable chemical accidents in the Letters to the Editor column of *Chemical & Engineering News*.

7. Reducing Hazards

One of the best ways to lessen the intensity of any hazardous condition is to reduce the quantity. Work with a few grams, or better yet, a fraction of a gram, of a toxin or a corrosive. Instead of equipment requiring 120 volts AC, use equipment that will run on 24 volts AC. Reduce the buildup of static charge by grounding the containers or apparatus involved. When possible, use lower temperatures instead of higher temperatures; work with dilute solutions in preference to concentrated solutions.

Plan ahead, read and heed the information in the MSDSs and on the labels, and be aware in advance of the harmful propensities of the chemicals to be used. Before you begin the work, put on the correct personal protective equipment and take other necessary precautions.

Inform your co-workers of your planned work, and be aware of theirs. It is part of your responsibilities to protect your co-workers from harm—and their responsibility to protect you.

Risk Assessment

It may be useful to assign categories of risk to some or all chemicals, apparatus, and equipment. For example, classify chemicals that have known reproductive hazards, are carcinogens or environmental pollutants, or are explosively unstable or highly toxic as “High Risk”; label others as “Medium Risk” or “Low Risk.”

Similarly, apparatus under high vacuum, heated oil baths, ultra-centrifuges, NMR equipment, and high-temperature ovens might be classified as presenting a greater risk compared with other apparatus and equipment that would be classified as presenting moderate or low risk.

Also, certain laboratory procedures could be considered for classification. Examples include vacuum distillations, work with Class III and IV lasers, work with radioactive materials, work with unstable or explosive chemicals, handling highly toxic chemicals, and handling chemicals that present carcinogenic or reproductive hazards. Assign appropriate accident-prevention and safety protocols for each risk category.

Also consider applying other risk-analysis techniques, such as safety inspections, checklists, failure mode and effects analyses, “what if” evaluations, fault-tree assessments, or hazard and operability studies. For further information, see *Understanding Risk Analysis*, American Chemical Society, 1998.

Flammable Liquids

Flammable liquids are hazardous. They can be ignited at concentrations less than their lower flammable limits.⁷ They can also be ignited at temperatures below their flash point.⁸ With very few exceptions (e.g., methanol) the molecular weight of a flammable liquid is significantly greater than the averaged molecular weight of air (approximately 29); therefore, the vapors of that flammable liquid can travel long distances, even more than 100 feet, along the floor or ground, from the liquid itself to an

⁷Flammable limit values are measured in a laboratory under controlled conditions. The actual conditions often differ from the controlled conditions, making the numerical value of the flammable limit only approximate. For example, the flammable range widens sharply as the temperature of the surroundings increases; a lower flammable limit of, say, 15% can drop to 5%, or less, at temperatures only slightly higher than ambient.

⁸Flash point temperatures are also measured in a laboratory under controlled conditions. These conditions rarely correspond to the actual conditions under which a flammable liquid is being used and handled. Consequently, a flash point temperature is at best only an approximate temperature—not in any sense an accurate, limiting parameter.

ignition source. The vapors flowing from the source are invisible; they go undetected until they “flash back” from the distant ignition source.

Another error that sometimes causes accidents: thinking that if vapors of the flammable liquid are maintained at a concentration above the upper flammable limit then they cannot be ignited. This would be a valid and safe protocol for handling flammable liquid vapors—except for the fact that the usual way to reduce the concentration of such a vapor in the air–vapor mixture is by diluting the mixture with more air to bring it well below the lower flammable limit; in doing so, however, the mixture passes through the flammable range. A safer procedure in this case is flooding with an inert gas.

Most flammable liquids are toxic, and some can penetrate intact skin. All are skin irritants on contact and can cause dryness and cracking. The vapors also are toxic, some more so than others. Typical symptoms from overexposure to vapors include dizziness, slurred speech, unconsciousness, and, rarely, death. Typical target organs include the central nervous system, liver, and kidneys. Avoid skin contact with these liquids. Avoid breathing their vapors.

All flammable liquids and solids are reducing agents. Some (e.g., acetone) are strong reducing agents. Keep flammable liquids and solids away from oxidizers. A few flammable liquids and solids are also strong oxidizing agents (e.g., methyl ethyl ketone peroxide, benzoyl peroxide) and therefore require special precautions in their use and storage; see their MSDSs.

Inadvertent contact of a flammable liquid or solid with an ignition source generally results in a fire or explosion. Some ignition sources are well known: flames, frayed or damaged electrical wiring, sparks from motors equipped with brushes and commutators, and static electrical sparks.

Other non-sparking ignition sources whose surface temperatures can exceed the autoignition temperatures of many flammable liquids and solids may not be as well known: examples include hot plates, the hot glass envelope of an incandescent light bulb, the even hotter glass envelope of a halogen light tube, and the hot shaft of an operating induction (brushless) motor with a defective bearing. Electric heating mantles can be a source of ignition if the mantle is torn or damaged, allowing the vapors into the hot nichrome heating coil wire within the mantle.

Some hot plates present a triple hazard: the hot surface, sparks from the temperature-control device hidden under the skirt, and sparks from the brush/commutator of the magnetic stirrer motor, also under the skirt.

Only limited quantities of flammable liquids and solids should be permitted on open shelves in the laboratory, and the containers should always be stored overnight in a storage cabinet approved for flammables. Except when concerns about purity are involved, flammable liquids used in the laboratory should be stored in safety cans. Some safety cans are poorly designed, clumsy to use, and tend to spill when poured. Do not use such safety cans in the laboratory; efficiently designed safety cans are available from suppliers.

A few flammable liquids can form unstable, potentially explosive peroxides. See the discussion on peroxides on page 22.

Follow the storage and handling recommendations for flammable liquids described in NFPA (National Fire Protection Association) 30, Flammable and Combustible Liquids Code, and NFPA 45, Fire Protection for Laboratories Using Chemicals.

Follow the electrical bonding and grounding procedures described in NFPA 77, Static Electricity, when you transfer flammable liquids from one metallic container to another, and when you transfer between a metallic container and a non-metallic container. Also see 29 CFR 1910.106.

Explosion Hazards

Students in a typical academic chemistry laboratory do not ordinarily work with very many substances that are explosive. Picric acid is rarely used; other nitrated organic compounds are used only occasionally. Perchloric acid is rarely used for oxidations involved in analytical work or other oxidative procedures. Organic peroxides (e.g., benzoyl peroxide) might be used now and then as polymerization initiators. Occasionally, unstable compounds (e.g., diazo derivatives) are used in some undergraduate research projects, but this is rare.

These functional groups pose an explosion hazard: azide, ozonide, nitro, nitroso, diazo, halogen-substituted amine, and peroxide (see below).

Some unstable compounds explode in the presence of a catalyst; others tend to explode at high temperatures. Some mixtures are shock-sensitive and will explode if impacted. Examples include carbon disulfide and potassium perchlorate, powdered aluminum or magnesium and sodium nitrate, many diazo compounds, and some organic nitrates.

Suspensions of oxidizable dust (e.g., magnesium, sulfur, aluminum) in the air explode when ignited by a static electrical spark, flame, or other ignition source.

Keep explosive substances and mixtures well away from other laboratory workers. Both in the laboratory and in storage, keep such substances well separated from other unstable compounds, flammables, and toxins. For explosion hazard information, refer to the MSDS (which might not be reliable) and to *Bretherick's Handbook of Reactive Chemical Hazards* (which is reliable).

Distillation of peroxide formers presents an explosion hazard, even if tests indicate that no peroxide is present.⁹ When you conduct these distillations, always make sure you are protected by shielding on all sides, and wear both a Type N face shield and Type G, H, or I safety goggles. Have a fire extinguisher at the ready; if the person distilling is not qualified to use it, someone else who is qualified should be immediately available. Even if the tests for the presence of peroxides is negative, do not distill these liquids to dryness (see “Storing and Handling Peroxide Formers” on page 23). Stop the distillation while there is still a considerable amount of liquid remaining in the distillation flask.

If an ignition source is present, any flammable gas or vapor can explode when mixed in suitable proportion with air, oxygen, chlorine, or other gaseous oxidizer. Acetylene and hydrogen are particularly hazardous in this respect because of their very wide flammability limits. Liquid oxygen is particularly dangerous. Liquid nitrogen that has been standing open to the air for some time becomes a mixture of liquid nitrogen and oxygen, which is also particularly dangerous; see “Cryogenic Hazards” on page 27.

When an explosion is a possibility, use less than 1 gram total of all chemicals

⁹Although a test procedure can produce a false negative, the point here is twofold: (1) As the distillation proceeds, the concentration of peroxide that was below the detection limit in the original liquid can increase to dangerous levels as the volume of residue in the distillation flask decreases. (2) In the presence of air, some peroxide formers that are initially free of peroxide can form peroxides at distillation temperatures.

involved. Wear both a Type N face shield and Type G, H, or K safety goggles and a buttoned-up, thick, quilted, lab coat; cover any glass apparatus with a fabric—not plastic—tape (e.g., use duct tape); and surround the work with shatter-proof shielding. Do not rely on an ordinary hood to provide protection. If it is considered necessary to work with or to produce more than 1 gram of an explosive compound or mixture, the work should be performed in a laboratory setting that is designed for such dangerous activities. The details involved are beyond the scope of this volume.

Electrical Hazards

OSHA regulations require that all electrical outlets have a grounding connection for use only with three-pronged plugs. If laboratory equipment is not equipped with a three-pronged plug, follow the requirements of the National Electrical Code (NEC), replace the plug and cord with a three-prong plug and three-wire cord, and connect them so that the equipment will be grounded when in use. Protect all electrical outlets with ground-fault interrupters; note that the NEC requires that all outlets within 6 feet of any source of water be so protected.

Check the polarity of outlet wiring and the continuity of grounding connections, including leads to the building ground itself. Follow the NEC in all installations.

The condition of wiring, plugs, cords, and related equipment should be frequently inspected. Replace wiring that is frayed or worn; do not allow wires to be stretched across the floor where they would present a tripping hazard. Eliminate obstructions near wall-mounted switch boxes and panel boards. Label unlabeled panel boards. Repair electrical outlets that have open (or missing) cover plates. Prohibit excessive use of extension cords.

All faculty and staff should know the location of circuit breakers and how to cut off all electrical service in case of fire or accident. All circuit breakers should be labeled properly.

Sparks

Some protection from static electricity and sparks when handling flammable liquids can be obtained by properly grounding and bonding containers and equipment. The risk of static charge buildup is increased under conditions of low humidity (e.g., cold weather). For details, refer to NFPA 77, Static Electricity.

Common potential sources of electrical sparks and electrostatic discharges include

- ungrounded metal tanks and containers;
- clothing or containers made of plastic or synthetic materials;
- making or breaking an electric circuit while the circuit or part of it is energized;
- exposed hot nichrome wires (e.g., in hot air dryers, damaged heating mantles);
- temperature-control systems and brush/commutator motors in some hot plates;
- discharge of gas from high-pressure gas cylinders; and
- brush/commutator motors, often used in hot air dryers, stirrer motors, and air-moving fans.

Toxic Substances

The harm caused by a toxic substance depends on the quantity, frequency, and duration to which the victim is exposed, which combined is called the dose. Any chemical can become toxic if the dose is high enough.

The Four Common Routes of Exposure

- absorption through intact skin or via a body orifice (e.g., eyeball sockets, ears, but not the nose)
- injection (e.g., from a contaminated needle or broken glass fragment)
- ingestion
- inhalation

The most likely exposure route in a laboratory is by inhalation. Ingestion is unlikely, as long as everyone practices good personal hygiene; otherwise, ingestion is considered to be in second place (behind inhalation) or even in first place. Injection is possible, but if you wear cut-resistant gloves when you clean up fragments of broken glass, it isn't probable. Needles and knives are not often used in chemistry laboratories; when their use is necessary, use the appropriate precautions (see "Sharp Objects" on page 20.) If you always wear safety goggles, and face shields when necessary, exposure via eyeball sockets and ears is almost impossible. The habit of promptly flushing off spills on skin or clothing prevents significant absorption via cuts in the skin or even intact skin.

To minimize or avoid inhaling toxic substances, maintain the breathing air in all laboratories well below the limits prescribed by OSHA in 29 CFR 1910.1450, the Laboratory Standard. For further information, refer to Volume 1 (Part 3, Equipment Use, Laboratory Hoods, page 27) and the sections in this volume on Laboratory Ventilation (page 32), Laboratory Hoods (page 33), and Ductless Hoods (page 34).

Reproductive Hazards

Reproductive toxins adversely affect the reproductive process. Examples are mutagens, which can cause damage to chromosomes in males and females, and teratogens, which can affect fetal development and/or cause birth defects, including fetal death. Currently, although there have been a few well-controlled studies, the evidence that a given chemical can or cannot produce an adverse reproductive effect is limited.

For the best readily available and up-to-date information, refer to DART/ETIC (Developmental and Reproductive Toxicology/Environmental Teratology Information Center), a bibliographic database on TOXNET (National Library of Medicine Toxicology Data Network). Go to www.sis.nlm.nih.gov and click on TOXNET under "Toxicology and Environmental Health." Keep in mind that only some of the data reported in DART/ETIC have been peer-reviewed. Two useful and recommended books are *Reproductive Hazards of the Workplace* (L. M. Frazier and M. L. Hage; Wiley, 1998) and *Catalog of Teratogenic Agents* (T. H. Shepard; 9th ed.; Johns Hopkins University Press, 1998; consult subsequent editions if available).

One reasonable response is to simply ban the laboratory use of any substance identified as a reproductive hazard in DART/ETIC, the above books, or other reliable sources. This policy is not as draconian as it might appear. Except for a few organic compounds (e.g., ethanol) and some inorganic compounds (e.g., compounds of lead and lead itself), there are few candidates. And for those that are candidates, it is generally not difficult to conjure a suitable alternative.

Establishing a Policy on Reproductive Toxins

Clearly, a policy addressing reproductive toxins is necessary. The policy should be discussed with the institution's attorney and be well publicized. Consider the following factors.

Define *reproductive hazard* and how the institution will determine whether a substance is a reproductive hazard or not. State that

- (a) no such substances will be used in any undergraduate laboratory work;
- (b) no such substances will be used in freshman and sophomore laboratories, for example, but are allowed in upper class laboratory work; or
- (c) identify which laboratory courses will be allowed to use which substances (e.g., all, or only those that meet specified criteria).

If option b or c is adopted, male and female students enrolled in laboratory courses using a reproductive toxin are advised to consult their parents or guardians and their physicians, and then be given the opportunity to withdraw from the laboratory course either without penalty, or with specific other arrangements (e.g., allow pregnant students to take the laboratory portion of the course at a later time).

If they opt to continue their laboratory work, they must sign a declaration of their assumption of the risks involved.

Keep copies of all documents associated with the institution's policy determinations. For example, list the courses in which the use of reproductive toxins will be allowed, the reasons for doing so, and signed copies of students' declarations of their assumption of the risks involved.

Sharp Objects

Require the use of Kevlar or similar cut-resistant gloves when using cutting tools and handling sharp objects (e.g., pieces of broken glass). Use Kevlar or similar gloves for protection when handling glassware under stress, such as inserting tubing through a rubber stopper or freeing a "frozen" glass joint. In general, if the equipment being handled could easily produce sharp edges from mishandling or breaking, require Kevlar or similar protection.

Note that the open-mesh weave of Kevlar and similar gloves does not protect against penetrating objects such as needles and knife points.

Wear Kevlar or similarly lined gloves when washing glassware.

Compressed Gases

Gases used in laboratories are typically supplied in cylinders at high pressure. The high-pressure compounds are potential chemical hazards. The safe use of compressed gases includes these precautions:

- Handle cylinders of compressed gases as high-energy sources and therefore as potential explosives.
- Restrain cylinders of all sizes, whether empty or full. Use straps, chains, or a suitable stand to prevent them from falling.
- When storing or moving cylinders, secure the protective caps in place over the valves in order to protect the valve stems.
- When moving cylinders, use only properly designed wheeled carts, and before moving, strap the cylinders securely in place on the cart.
- Do not expose cylinders to temperatures higher than about 50 °C. The rupture devices on some cylinders will release the contents at about 65 °C. Some small cylinders, such as lecture bottles, are not often fitted with rupture devices and may

explode if exposed to high temperatures.

- Never use cylinders if their contents cannot be identified positively.
- Never lubricate, modify, force, or tamper with cylinder valves.
- Use toxic, flammable, or reactive gases only in laboratory hoods that are known to be operating properly.
- Cylinders awaiting use should be stored outdoors, not indoors, in a sheltered but open structure such that they are protected from the weather.
- Never direct compressed air or high-pressure gases at a person.
- Do not use compressed gas or compressed air to blow away dust or dirt; the resultant flying particles are dangerous.
- Be aware that rapid release of a compressed gas will cause an unsecured gas hose to whip dangerously.
- Rapid release of a compressed gas builds up a static charge that could ignite the gas if it is flammable or combustible.
- Do not extinguish a flame involving a combustible or flammable gas until the source of gas has been shut off; otherwise, it can reignite and burn or even explode.
- Close main cylinder valves tightly when not in use.
- Promptly remove the regulators from empty cylinders and replace the protective caps at once. Label the cylinder to show that it is empty.
- Never bleed cylinders completely. Leave a slight pressure to keep out contaminants.
- Use the appropriate regulator on each gas cylinder. The threads on the regulators are designed to avoid improper use. Adaptors and homemade modifications can be dangerous—don't use them.
- Do not put oil or grease on the high-pressure side of a cylinder of oxygen, chlorine, or of any other gaseous oxidizing agent. A fire or explosion can result. Never put oil or grease in, on, or near a regulator for the same reason.
- Always wear Type G, H, or K safety goggles when handling and using compressed gases.
- Observe the following special rules when working with acetylene cylinders.
 - Always store acetylene cylinders upright. They are partially filled with liquid acetone, which can be discharged instead of or along with acetylene if the cylinder is not upright.
 - Do not use an acetylene cylinder that has been stored or handled in a nonupright position until it has remained in an upright position for at least 30 minutes.
 - Ensure that the outlet line of an acetylene cylinder is protected with a flash arrester.
 - Never exceed the pressure limit indicated by the warning red band of an acetylene pressure gauge.¹⁰
- Use the correct kind of noncuprous tubing to transport gaseous acetylene. Tubing made of copper or high-copper brass will form copper acetylides, which are explosively unstable and shock- and impact-sensitive.

For more information, see Alaimo's *Handbook of Chemical Health and Safety* and the Compressed Gas Association's *Safe Handling of Cryogenic Liquids*.

¹⁰Acetylene polymerizes rapidly and spontaneously when under "red line pressures." The polymerization reaction is rapid, violent, and exothermic.

Oil and Sand Baths

Although they are useful, heated oil baths and sand baths pose unique hazards. They do not appear hot; can spatter if a low-boiling liquid is spilled into the bath; can generate toxic and/or irritating smoke from decomposing oil or foreign organic contaminants; and, if overheated or left unattended, can catch fire (the oil of an oil bath and typical contaminants in the sand of a sand bath are combustible).

Consider these factors when assigning students to use heated oil or sand baths:

- size of the bath;
- location—preferably away from possible sources of spilled water or chemicals;
- desired operating temperature—use a thermometer or thermocouple or bimetallic temperature indicator, a temperature-control device, and a high-temperature shut-off device;
- type of oil used (silicone oil or Dow Corning 550 is suggested for most heating needs) and its maximum operating temperature;
- use of signs, e.g., “Hot Oil” or “Do not allow the temperature to exceed ____ °C”;
- students have been cautioned to inspect glassware closely for absence of cracks and other imperfections;
- students have been cautioned regarding the hazard of splattering if a low-boiling liquid is spilled into the hot oil or sand;
- available ventilation;
- method for cooling the hot oil or sand; and
- storage of the oil or sand for reuse.

Peroxides

Peroxy compounds are examples of chemicals that present special problems in the laboratory because they can be violently reactive and/or explosive. Their handling, storage, and disposal deserve careful attention.

Inorganic Peroxides and Superoxides

Inorganic peroxy compounds are generally stable, but their contact with any oxidizable or combustible material may lead to a fire or explosion. When in contact with organic compounds, they may generate organic peroxides and hydroperoxides. Inorganic peroxy compounds must be stored, handled, and used with caution. Peroxides of alkali metals are not sensitive to shock but are decomposed slowly by moisture and violently by bulk water. The most common inorganic peroxy compounds are sodium peroxide, hydrogen peroxide, sodium perborate, and sodium persulfate.

The higher-atomic-weight alkali metals readily form superoxides (which are not peroxides), some of which are reactive. For example, when metallic potassium is being cut with a knife, the KO_2 (potassium superoxide) on its surface, if any, can react violently with the hydrocarbon film remaining from its (partial) immersion in that hydrocarbon. KO_2 , which is *not* a peroxide, forms spontaneously on the surface of potassium when exposed to air, for example, on the exposed surface of potassium after some of the kerosene, in which the potassium had been immersed, has evaporated while in unattended storage. Then, when cut with a knife or spatula, the movement of the cutting edge of the knife can put particles of KO_2 in contact with the film of kerosene on the surface of the potassium, and the violent reaction ensues.

Small spills of inorganic peroxy compounds can be treated cautiously with aqueous sodium bisulfite solution; larger spills should be taken up with inert solids such as vermiculite, sand, or salt and treated with sodium bisulfite in a safe area. Skin that has been burned by these chemicals should be washed gently but thoroughly and receive prompt medical attention.

Organic Peroxides and Hydroperoxides

The molecules of organic peroxy compounds contain a reducing agent and an oxidizing agent in an intimate relationship, each with the other in the same molecule. When you use, handle, or store these compounds, keep in mind that they are always unstable under all conditions.

Most organic peroxy compounds fall into one of four classes: dialkyl or diarylalkyl peroxides, peracids, diacyl peroxides, and alkyl or arylalkyl hydroperoxides. As noted above, all are unstable to some degree and therefore generally are not offered in high purity, because their instability increases with concentration. The hazard decreases, however, with increasing molecular weight. Those of lower molecular weight can deflagrate or detonate. Examples include *tert*-butyl peroxide, *tert*-butyl hydroperoxide, peracetic acid, benzoyl peroxide, and isopropylbenzene (cumene) hydroperoxide.

Because peroxy compounds are unstable and in fact decompose continuously at a lesser or greater rate, bulk quantities may generate enough heat to autoaccelerate up to ignition or explosion. They are sensitive to heat, mechanical shock, friction, impact, light, and strong oxidizing and reducing agents. All organic peroxides are quite flammable, and fires involving bulk quantities should be approached with extreme caution. Because they generate free radicals, their presence as a contaminant or as a catalyst in a reaction mixture can change the course of a planned reaction.

Organic peroxy compounds are generally more stable when water is present. For example, benzoyl peroxide is a solid (m.p. 104–106 °C) that can ignite or explode from heat, impact, or friction; it *must* be kept moist and stored in its original, as-received fiber carton or paper sack. Do not use a metallic implement (e.g., knife or scissors) to open the carton or sack. Do not repackage benzoyl peroxide. Never repackage benzoyl peroxide into any metal or glass container with a screw cap. Unscrewing a container that has dry benzoyl peroxide or other peroxide crystals caught in the lid threads can cause the entire contents of the container to explode. Keep on hand no more than a short-term supply of any peroxide, and check the containers at regular intervals. If in doubt, it is best to call an expert for disposal of these dangerous chemicals.

Storing and Handling Peroxide Formers

Peroxide formers react with oxygen, even at low concentrations and ordinary temperatures, to form peroxy compounds that are usually hydroperoxides. In addition to any other hazards that they have, they pose a “peroxide threat,” especially if the oxygenated product crystallizes out when the material is cooled or becomes concentrated by evaporation or distillation of the unoxidized portion. Peroxide crystals may form on the ground glass or other surfaces of a sealing plug or within the threads of a cap. Removing the plug, unscrewing, or otherwise removing the cap has caused detonations with serious, and in some cases fatal, consequences.

Peroxidation seems to be no problem with gases and vapors; generally peroxidation is a problem that involves liquid peroxide formers. Solid peroxide formers present

only a small problem unless they are finely divided, in which case, because the peroxidation reaction occurs only on surfaces exposed to air, the hazard increases substantially.

Peroxide formers cannot form peroxy compounds without exposure to oxygen or other oxidizers. Typically, peroxidation

occurs when containers are not well sealed or, if sealed, not blanketed with an inert gas. Blanketed or not, poorly sealed containers permit “breathing,” which occurs with changes in temperature and/or barometric pressure. The rate of ensuing peroxide buildup is usually slow, because the atmospheric exchange is usually slow. Containers should always be inert-blanketed and tightly sealed. Flush out the air from the free space with nitrogen or some other inert gas. Use plastic caps or stoppers; do not use glass or metal caps or stoppers.

Typically, if sufficient oxygen is supplied to a fast peroxide former, there is an induction period, followed by a relatively fast accumulation of peroxide or hydroperoxide, which tapers off at a maximum level, usually 5–15%. Then, the concentration stabilizes or even decreases because the peroxide or hydroperoxide itself undergoes decomposition, forming byproducts such as alcohols and water that tend to interfere with the free-radical chain reaction of peroxidation. The byproduct content may continue to grow, but the peroxide content does not. Of course, if conditions are such that the peroxide product precipitates out of solution as it continues to be produced, the concentration of the product remaining in solution may indeed stabilize or even decrease slightly, but the formation of additional peroxide product does not cease.

Follow these precautions for storing and handling peroxide formers¹¹:

- Label the chemicals as known peroxide formers or (in some cases) as possible peroxide formers.
- Store peroxide formers blanketed with an inert gas (e.g., nitrogen or argon), well sealed and away from sources of light, in the containers as received from the supplier or in amber-colored glass bottles equipped with plastic caps. Maintain the inert atmosphere in the free space of each container.
- To minimize the rate of peroxide formation, maintain storage conditions at cool temperatures. However, *do not refrigerate* peroxide formers. Peroxide formers, liquid peroxides, or solutions of peroxides that are cooled to refrigerator or freezer temperatures can freeze out or precipitate the peroxide.¹²

¹¹For the storage of peroxides, not peroxide formers, see “Inventory Management, Storage, and Disposal” on page 37.

¹²When present as a solid, peroxides are extra sensitive to shock and heat. For example, do not store diethyl ether in a refrigerator or freezer. At ordinary refrigerator temperatures, diethyl ether peroxide is insoluble in diethyl ether and forms the solid shock-sensitive diethyl ether peroxide. If a container has solid peroxidized diethyl ether present and is removed from the refrigerator, it can explode violently merely by being jostled during the removal. Further, considering the requirement for frequent testing for peroxides and the requirement for disposal within three months maximum after receipt, peroxides and peroxide formers should not be stored in a refrigerator or freezer where their presence can be overlooked for periods much longer than three months.

The Four Main Compound Groups of Known Peroxide Formers or Precursors

- ethers with primary and/or secondary alkyl groups attached to the oxygen, including open chain and cyclic ethers, acetals, and ketals
- hydrocarbons with allylic, benzylic, or propargylic hydrogens
- conjugated dienes, enynes, and diynes
- saturated hydrocarbons with exposed tertiary hydrogens

Examples

| | |
|----------------------------------|---------------------------|
| diethyl ether | diisopropyl ether |
| tetrahydrofuran (THF) | <i>p</i> -dioxane |
| cyclohexane | isopropylbenzene (cumene) |
| tetrahydronaphthalene (tetralin) | divinylacetylene |
| decahydronaphthalene | 2,5-dimethylhexane |

- Limit the stock of any item to a three-month supply or less. Dispose of any stock remaining after three months, unless it has been tested (see “Detecting Peroxides,” below) at the end of the three-month period and found to be peroxide-free.
- Unless it would compromise the material’s usefulness, add an oxidation inhibitor to it. The recommended amount is from 0.001 to 0.01% of inhibitors such as hydroquinone, 4-*tert*-butylcatechol, or 2,6-di-*tert*-butyl *p*-methylphenol (BHT).
- Avoid friction, grinding, and all forms of impact, especially with solid organic peroxides. Do not use glass containers with metal screw lids or glass stoppers.
- Never use a metal spatula with organic peroxides. Contamination by metals can cause explosive decomposition. Use ceramic or plastic spatulas instead.
- Before distilling any known or suspected peroxide former, check it carefully for peroxide (see below). If any is present, eliminate it by chemical treatment or percolation through a suitable adsorbent, or add a high-boiling aliphatic hydrocarbon (such as mineral oil) to prevent the peroxide from concentrating to a dangerous level. Never distill a peroxide former to dryness.
- Because peroxy compounds are generally strong irritants, avoid ingestion, inhalation, and skin contact. Treat any skin contact as a burn, and get medical attention.

A variety of chemicals used as solvents or in synthesis, even alcohols, have been found to contain significant amounts of peroxides (as high as 0.1%). Such small amounts could arise from impurities that are peroxide formers.

Detecting Peroxides

The presence of most peroxy compounds, including all hydroperoxides, can be detected by this test: mix 1–3 mL of the liquid to be tested with an equal volume of glacial acetic acid in a test tube, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates presence of a peroxide. If the color is faint, run a blank to make sure the test is really positive. A testing kit that includes treated paper strips is available from chemical suppliers.

However, to test for the presence of peroxide in a peroxide former, of course it is necessary to open the container. If peroxide has already formed in the container, opening it can cause a detonation. (A positive test!) Therefore, test peroxide formers for peroxide immediately on receipt from the supplier, and repeat the testing at frequent intervals. If the test for peroxide is positive, take the appropriate steps; if negative, record the date and the result (e.g., on a tag or label affixed to the container) and return the container to its proper place in storage.

Disposing of Peroxides

Consider calling a bomb squad to dispose of peroxides. Peroxides normally must be diluted before disposal. Small quantities (25 g or less) of peroxides are generally disposed of by diluting with water to a concentration of 2% or less and then transferring to a polyethylene disposal bottle. The bottle must contain enough aqueous solution of a reducing agent (e.g., ferrous sulfate or sodium bisulfite) to reduce some of the peroxide. After a suitable interval, test (as described above) for the absence of peroxide. If peroxide is still present, add more reducing agent. When peroxide is no longer detectable, the resulting mixture may be handled like any other waste chemical, but do not add it to a container holding other wastes for disposal.

Spilled peroxides should be absorbed on vermiculite as quickly as possible. Under the supervision of an experienced chemist, and while wearing an appropriately padded garment and other personal protective equipment, stir the vermiculite–peroxide mixture with a high-molecular-weight aliphatic hydrocarbon liquid to form a slurry, which is then treated as above. Never flush organic peroxides down the drain.

Disposing of large quantities (more than 25 g) of peroxide requires special handling. Each case should be considered separately, and a handling, storage, and disposal procedure must be established as determined by the physical and chemical properties of the particular peroxide and applicable regulations.

Consider including your institution's use, handling, storage, and disposal procedures in the chemical hygiene plan for your laboratory or institution.

Further Information

For further information on the use, formation, handling, storage, and disposal of peroxides and peroxide formers, see *Bretherick's Handbook of Reactive Chemical Hazards* and *Alaimo's Handbook of Chemical Health and Safety*.

Hazards from Radioactive Materials

Before you start any work, your institution must have a radioactive materials license from a state or federal agency. Coordinate all work requiring the use of radioactive materials with the person responsible for the laboratory and under the direction of the institution's radiation safety officer. Clearly label all radioactive materials, the vessels in which they are used, and the work area itself as a radioactive material use area.

Anyone considering the use of radioactive materials should consult the institution's radiation safety officer for advice on the regulations concerning procurement, handling, and disposal. All materials that may have become contaminated must be thoroughly cleaned or properly disposed of. These materials ordinarily would include glassware, wipes, gloves, spill pads, TLC plates, pipets, and so forth. Anyone planning to work with radioactive materials must first be trained in their safe handling. Worker protection requires good practices, adequate supervision, and exposure monitoring. The ALARA (as low as reasonably achievable) exposure premise must be the guiding principle behind all radioactive work. This requires that the amount of radiation or radioactive material used is kept to a minimum and that exposures are minimized by providing shielding when possible. Personal exposure monitoring may be required for users of radioactive materials. Such monitoring includes personal film badges, bioassay testing, and other scanning methods. The institution's radiation safety officer is responsible for providing appropriate guidance on personal monitoring.

Lasers

Where lasers are used, the institution must have a laser safety officer who is knowledgeable in evaluating and controlling laser hazards and is authorized and responsible for supervising their safe operation. Lasers and laser systems as received from manufacturers must be classified (I–IV) and appropriately labeled in accordance with the current edition of ANSI Z136.1. Class I lasers are of low intensity and pose little or

no risk for physiological harm. Under certain conditions, Class II lasers can cause eye injury in people who lack a normal eye-aversion response to bright light. Class III and IV lasers are high powered and can do considerable physiological damage, especially to the eyes; a medical professional should review the use and operation of Class III and IV lasers. Even reflected beams from a Class III or IV laser can cause eye injury.

Higher-power lasers present additional hazards. The power density of the beam can be sufficient to ignite chemicals and other combustibles. The high voltages involved present shock hazards. Some of the dyes used in dye-lasers are reproductive toxins or are carcinogenic.

Only authorized individuals with specific training should use lasers. Everyone should obey all warning signs posted at the entrance to laser areas.

Cryogenic Hazards

Cryogenic conditions are generally agreed to include the temperature range from the temperature of dry ice downward to temperatures approaching absolute zero. All cryogenic liquids are liquefied gases. The liquefied gases embrace the hazards of flammability, reactivity, corrosivity, toxicity, asphyxiation, and the vigorous support of combustion. Even liquid nitrogen, ordinarily considered to be inert chemically, will condense oxygen from the air when allowed to stand exposed in an open container. The resulting liquid mixture should be handled as though it is as hazardous as pure liquid oxygen.

For example, when either liquid oxygen or oxygen-contaminated liquid nitrogen is spilled on a flammable or combustible solid (e.g., clothing, asphalt, wood), the oxygen, now a gas, tends to remain on and around the surface of the solid for several hours. If a source of energy (e.g., an ignition source) is brought near, a violent explosion can occur. Thus, asphalt on which liquid oxygen has recently been spilled can explode violently when struck with a hammer.

Follow these necessary precautions:

- Know the first aid procedures for frostbite before using, handling, or storing a cryogenic liquid.
- Keep flammables and combustibles well away from liquefied oxidizing gases. For example, under suitable conditions, steel burns when in liquid oxygen.
- Avoid pouring a cryogenic liquid on or over the edge of a glass Dewar flask when filling or emptying the flask; the flask may break and implode.
- Do not put a cryogenic liquid into a household Thermos bottle or other insulated container ordinarily used to keep food or drinks cold.
- When using, handling, or storing cryogenic liquids, wear a laboratory coat without pockets (or at least without outside pockets) or wear a laboratory apron. Wear cuffless pants and high-topped leather shoes; to deflect any spills, the bottoms of the pants should cover the tops of the shoes. Remove watches, rings, and other jewelry.
- The eyes are particularly vulnerable to harm from exposure to cryogenic liquids. Wear both Type G, H, or K safety goggles and a Type N face shield when using, handling, or storing cryogenic liquids.
- If it is necessary to handle chilled parts of the apparatus, consider wearing insulating gloves. If the gloves become contaminated with an oxidizing cryogenic liquid, handle the gloves as though they are flammable for at least 24 hours.
- Avoid skin contact with cryogenic liquids. Even a very brief contact can result in severe frostbite and/or torn flesh.

- Laboratory workers who use, handle, or store toxic cryogenic liquids and all others in the area should wear appropriate respiratory equipment.
- Avoid inhaling air that has been cooled to near-cryogenic temperatures.
- The chilled vapors from evaporated cryogenic liquids tend to accumulate in pits and low-lying areas. These gases are of course invisible and have partially or completely displaced oxygen from the areas they occupy. Do not enter such areas without wearing an oxygen-supplying respirator.
- Never transport cryogenic liquids in an elevator. In the event of elevator malfunction, the resulting collection of evaporated gas in the elevator shaft from the cryogenic liquid could be disastrous.¹³ Even a so-called closed Dewar has a pressure-relief valve that can release evaporating vapors.
- Many solids become brittle and fragile at cryogenic temperatures. Before allowing an unfamiliar solid to be chilled to cryogenic temperatures, learn its properties at such temperatures.
- Immediately evacuate any area in which there is an uncontrolled release of a cryogenic liquid or vapor.

For more information, see Alaimo's *Handbook of Chemical Health and Safety* and the Compressed Gas Association's *Safe Handling of Cryogenic Liquids*.

X-Ray Generators and Particle Accelerators

These instruments can be dangerous because of the radiation they generate and the high voltages produced by their power supplies. Follow all the regulations of the Nuclear Regulatory Commission (NRC), your state department of public health, and your local radiological health service. Post warning signs in the area and on or near the main power switch of the instrument.

Visitors to the Laboratory

Visitors should be escorted during their visits. While in the laboratory, visitors should wear Type G, H, or K safety goggles. Small children should not be allowed to enter a laboratory where chemicals are being used or are available on open shelves.

¹³If accumulated in an elevator shaft, nitrogen and other inert gases are asphyxiants; accumulations of oxygen and other oxidizing gases can cause spontaneous ignition and explosion; and accumulations of flammable gas are explosive.

8. Facilities and Equipment

General

Provide all chemical laboratories and other chemical work areas with safety showers, eyewash fountains, and appropriate fire extinguishers. Adequate ventilation, wash sinks, and approved waste disposal facilities are also necessary. All of these should be conveniently located, properly maintained, and frequently tested. Every lab should have two or more well-marked and unobstructed exits for evacuating. Keep aisles, exits, and the areas around safety showers, eyewash fountains, and fire extinguishers clear at all times.

The safety showers, eyewash fountains, fire extinguishers, and telephones should be readily available, located strategically, in working order, and identified by distinctive signage on the adjacent wall. Post emergency telephone numbers in clear sight near the telephone. If an outside line is necessary, post this information also. Some suggested numbers are identified on the inside front cover of this volume and Volume 1.

Highly visible signs, temporary or permanent as appropriate, should be posted in designated areas where toxic, reactive, radioactive, or highly flammable chemicals are used or stored and at other locations where hazardous operations are performed. Emphasize to all laboratory workers that before using flame, spark-producing, or hot surface equipment such as motors, hot plates, and open heaters, it is crucial to verify that no flammable vapors are in the area. The sparks from turning a light on or off as well as the ringing of a telephone have ignited flammable vapors.

Minimize storage of chemicals in laboratories. Instead, use stockroom or chemical storage room spaces for storage longer than a few days. The NFPA publication *Fire Protection for Laboratories Using Chemicals* (NFPA 45) mandates maximum quantities and maximum container sizes for flammable and combustible liquids to be used or stored in laboratories.

Provide a general alarm system to alert facility emergency and security services. Automatic smoke and fire alarms are recommended and, in some cases, required by local building codes, especially in the absence of automatic water sprinklers. Such systems must be properly maintained and monitored, and a record must be kept of the results. All persons using the building should be familiar with and recognize the different meanings of the sounds of the different alarms used in the building.

Ensure that individuals with physical disabilities can easily access the safety equipment and be readily evacuated. Arrange in advance for individuals to assist students, faculty, or staff who are disabled to evacuate in an emergency.

Emergency drills are essential. As part of the drill, students, faculty, and staff should be required to go to a designated safe area outside the building and remain there until accounted for. Review your plans for fire containment and handling and for emergency drills with local fire officials. If applicable, be sure that your facility is in compliance with the requirements of Title III of the Superfund Amendments and Reauthorization Act (SARA).

Safety Showers and Eyewash Fountains

Safety showers and eyewash fountains should be located at least 5 feet apart. Often, a victim who needs either of these facilities also will need help from one or two co-workers. If an accident has two victims, one who needs the safety shower and the other the eyewash fountain (a not improbable event), it would be impossible to properly use both facilities if they were closer than 5 feet.

The water supply lines to eyewash fountains and safety showers should be valve-free in order to supply an uninterrupted flow of water. If it is necessary to install a shut-off valve, a lock should be attached to keep the valve in the open condition—with a tag affixed stating that the valve must be kept open during normal operation of the facility.

Safety Showers

All students should know the locations of the safety showers and how to operate them. When possible, encourage students to practice the procedure.

Each laboratory area must be equipped with at least one safety shower. ANSI Z358.1 requires that safety showers be located no more than 10 seconds or 100 feet (walking distance, not a straight line) from any location in the room. The shower area must be kept clear of obstructions and be clearly labeled by signage on the wall. Chain pulls to activate the shower should be provided with a large ring. The valve should open readily when the chain is pulled and remain open until intentionally closed. Water flow must be sufficient to drench the subject rapidly. ANSI Z358.1 requires a 30-gallon-per-minute minimum flow of potable water. Provide temperate water for all safety showers; it is impossible to remain under a drenching shower for 15 minutes if the water is cold. Although a nearby floor drain is desirable, its absence should not prohibit installation of a safety shower.

The ANSI standard requires that safety showers be activated weekly to ensure that they are working properly. Keep a record of such tests, for example, on a tag affixed to the shower plumbing.

ANSI Z358.1 mandates a minimum 3-gallon-per-minute water flow for hand-held drench hoses and states that, although they are well-adapted for flushing when a safety shower or eyewash fountain cannot be used to flush a hazardous chemical from eyes or skin, drench hoses are not a substitute for safety showers or eyewash fountains.

When drench hoses are installed in a laboratory, every student should know their limitations, their location, and how to operate them. When feasible, encourage students to practice the procedure.

Eyewash Fountains

Every student should know the locations of the eyewash fountains and how to operate them. When possible, encourage students to practice the procedure.

Eyewash fountains should provide a copious and gentle flow of temperate aerated potable water at 0.4 gallon per minute for a period of at least 15 minutes (15 minutes of cold water is intolerable). Plumbed installations are the best and are strongly recommended. Use of the hands should not be required to maintain the water flow.

Small, hand-held portable eyewash units cannot provide a supply of water sufficient to copiously flush two eyes for at least 15 minutes. Also, the small units, the multigallon portable units, and the nonplumbed wall-mounted units provide an environment for the growth of microorganisms. All require strict attention in order to maintain sterility of the contained water. The small bottle-sized units should not be used. The use of multigallon portable units and of multigallon nonplumbed wall-mounted units is strongly discouraged unless the sterility of the contents can be ensured and testing shows that they will flush both eyes simultaneously and will deliver at least 0.4 gallon per minute of temperate water for at least 15 minutes.

As with safety showers, ANSI Z358.1 requires that eyewash fountains be activated weekly by flushing them. Such flushing reduces the threat of eye infections from contaminated standing water. Keep a record of these test flushes (e.g., on a tag affixed to the eyewash fountain plumbing). ANSI Z358.1 requires that eyewash units be located no more than 10 seconds or 100 feet (walking distance, not a straight line) from the working stations of potential victims.

Always follow up every first aid treatment for the eyes with prompt treatment by a member of the institution's medical staff or an ophthalmologist qualified to treat chemical injuries.

Fighting Fires

Post the emergency telephone number of the fire department prominently at every telephone. If it is necessary to use an access number to get an outside line, include that information on the posting. If a different phone number must be used after hours or on weekends, state that clearly on the posting. Provide prominent and distinctive wall signage at the location of each fire extinguisher and safety shower.

If the shower is not readily available, douse the individual with water. Get him or her to stop, drop, and roll; that is, to lie down and roll to put out the fire. Then, try to extinguish any small, still-burning flames by patting them out. Beat out the flames around the head and shoulders, then work downward toward the feet. Next, cover the victim with a coat, blanket, or whatever is available but leave the head uncovered. Do not use fire blankets until the fire is extinguished. While wearing gloves if necessary, remove any clothing contaminated with chemicals. To prevent contamination of the eyes, use scissors when removing pullover shirts or sweaters. Place clean, wet, cold cloths on burned areas. Wrap the victim to avoid shock and exposure. Get medical attention promptly. Properly dispose of any blankets containing asbestos.

Fire extinguishers in the laboratory should be the appropriate type for the expected fire emergency. Dry chemical fire extinguishers may be preferred for certain areas, but carbon dioxide is satisfactory for most small fires (with the notable exception of fires of alkali, alkaline earth, and certain other metals) and is cleaner to use around most equipment. Conventional dry chemical extinguishers expel a stream of sodium or potassium bicarbonate or other powder and are not recommended for Class A fires (wood, paper); if used, be prepared to sweep up a lot of powder. Multipurpose dry chemical extinguishers are often preferred, but they release a stream of monoammonium phosphate, and that requires a laborious cleanup of powder.

Freon fire extinguishers are exceptionally useful where computers and similar equipment are located, but the products of the chemical reactions that help extinguish the fire include phosgene and other severely toxic compounds. Consequently, never use Freon fire extinguishers in any circumstance with the possibility of human exposure.

Do not let anyone without hands-on training operate a fire extinguisher. Without training, the user can become trapped by the fire and unable to reach an exit (to say nothing of precious wasted seconds and the wasted fire extinguisher). Use a fire extinguisher only if you have been trained hands-on by a qualified firefighter and the extinguisher you plan to use is a type you have been trained to use.

Fight fires only if you are able to escape, for example, you're between the fire and an exit. If the fire starts to move between you and the exit, leave *immediately*.

Severely toxic gases and smoke develop during a fire—individuals who use a fire

extinguisher to contain a fire must avoid breathing these gases and smoke. Portable fire extinguishers exhaust their contents within a few seconds and are likely to be used only when a fire is just starting, so a significant buildup of toxic gases and smoke probably would not yet occur. However, if the fire extinguisher has been exhausted and the fire is not extinguished, it is possible by that time that hazardous concentrations of toxic gases and smoke are present. For these reasons, do not use a second extinguisher—leave the area after your first fire extinguisher has been exhausted.

Smother fires involving reactive metals with powdered graphite or with a fire extinguisher designed for metal fires. Carbon dioxide fire extinguishers will intensify fires of alkali, alkaline earth, and certain other metals, including aluminum, magnesium, and zirconium.

Immediately after a fire, all extinguishers that were used should be recharged or replaced with full ones.

When chemicals are involved in a fire, there is always the chance of an explosion. In advance, take special care to keep the potential for fire or excessive heat as far as possible from flammable solvents, compressed gas cylinders, reactive metals, and explosive compounds.

Maintain a detailed and current inventory of chemicals. Ensure that a copy is readily available if an emergency arises, and, if requested, regularly provide copies to the fire chief.

Laboratory Ventilation

Some airborne toxic substances (dusts, mists, and fumes) are chronic toxins. In many academic institutions, most laboratory work is conducted on laboratory benches instead of in laboratory hoods. Exposure to airborne toxins should be minimized. Laboratory ventilation and good practice in the use of hoods are both essential. Where appropriate, consider microscale experimentation in place of multigram quantities.

Both the OSHA Laboratory Standard, 29 CFR 1910.1450, which for employees mandates PEL concentration limits for several chemicals, and the ACGIH TLV voluntary limiting concentration levels for an even greater number of chemicals are based on the responses of adult physiological systems to toxic substances. As stated elsewhere, both the OSHA and ACGIH systems of concentration limits assume an average 8 hours per day, 40 hours per week potential exposure for the working lifetime of an average person. Typically, undergraduate college and university students are not yet fully grown physiologically; consequently, they are more susceptible to toxins than older adults.

Therefore, if concentration limits were established for these young individuals, the concentrations would generally be less than those established in the PELs and TLVs. Because no such concentration limits have been established and young students will not be exposed to breathing laboratory air containing toxic substances for 8 hours per day, 40 hours per week, it is probably acceptable to use the established PEL and TLV requirements. However, it is both reasonable and prudent to ensure that the maximum concentrations of hazardous vapors, dusts, and mists are kept well below those limiting concentrations.

Laboratory managers should ensure that laboratory ventilation is consistently sufficient to maintain air concentrations of toxic substances at values less than the limits

established by OSHA and/or the ACGIH. Laboratory managers also should ensure that laboratory ventilation is consistent with the current edition of the ANSI Z9.5, Laboratory Ventilation.

Laboratory Hoods

Safely handling chemicals in laboratories requires a properly installed and operating laboratory hood system and individuals who are instructed in its correct use. Many users of hoods are not familiar with the details of the various procedures required in their proper use. A handy reference is Saunders' *Laboratory Fume Hoods: A User's Manual*. The current edition of the ANSI Z9.5, Laboratory Ventilation, provides additional useful information.

The supply air for hoods comes from the laboratory room and must be adequate to meet the exhaust air-rate requirements. Failure to meet this need is probably the most common reason a hood system is unsatisfactory.

Users should ensure that both the rear ducts and front airfoils of the laboratory hood they are using are free and clear of all obstructions. All work should be conducted within the hood enclosure, at least 15 cm (6 in.) from the front edge of the hood. Do not rely on a laboratory hood for protection in case of an explosion inside the hood. Typical laboratory hoods cannot offer protection against any but the mildest of explosions.

The hood face exhaust rate is not a reliable measure of laboratory hood performance because air supply to the room and drafts across the hood face alter its effectiveness. Face velocity data has only one useful application: Recent hood face velocity measurements could be used to indicate whether there has been a significant change in hood performance since the last ANSI/ASHRAE 110 test.

A greater hood face exhaust rate than is needed for protection is uneconomical, and such rates can cause turbulence that further degrades hood performance. A uniform face velocity as low as 80 feet per minute (fpm) in ideal systems with good work practices is often adequate. Systems less well designed may benefit from higher exhaust rates, but not greater than 120 fpm. These greater rates can worsen the protection by causing turbulence and "spill-out" of contaminated air from within the hood into the laboratory room.

Instead of hood face exhaust velocities, rely on applicable performance tests such as the ANSI/ASHRAE 110 test; see the current edition of ANSI Z9.5, Laboratory Ventilation, and Saunders' *Laboratory Fume Hoods: A User's Manual* for detailed information. A permanently mounted air-vane or similar continuous semiquantitative indicating device is useful, but only to show that the hood exhaust fan is working approximately as well as it was when the last ANSI/ASHRAE 110 test was performed. A strip of tissue paper taped to the edge of the hood frame and waving in the breeze is not reliable as an indicator.

At regular intervals, inspect the condition of the laboratory hoods, and check the functioning of the ducts and associated exhaust system. Hood duct fans should be located outside the building so that all ductwork within the building is under negative pressure. Ensure that exhaust air from the laboratory hood duct exits outside the building and does not recirculate back into the building.

Do not use laboratory hoods for storing chemicals or apparatus. If well-ventilated long-term storage facilities are desired, modify what was a laboratory hood to meet

that need and label it to prominently indicate that it is for storage only and not to be used as a hood.

Prepare an emergency plan to follow in case of hood failure.

Because of the difficulty of attaining airflow balance and appropriate exhaust rates, canopy-style hoods on a bench top normally do not provide acceptable protection. Under unique conditions, canopy hoods can fit special needs, for example, to handle instrument exhaust. In other applications, the use of flexible ductwork (elephant trunks) may be more suitable. But in general, standard bench-mounted laboratory hoods best meet the needs for laboratory work that requires hood use.

The design of an effective laboratory hood system is beyond the scope of this manual. Architects and engineers use references such as the current edition of *Industrial Ventilation* by the ACGIH when designing laboratory hood installations.

Ductless Hoods

At one time, using ductless hoods seemed appropriate. However, their use is now acceptable only in very specific instances. Arguments favoring their use include lower cost of installation, convenience of placement, and simplicity of operation.

Opponents make the following arguments against using ductless hoods: escape of toxic vapors through the filter and into the room in the event of a large spill under the hood; failure of the sensors to monitor filter performance and the resulting spillover of toxic vapors into the laboratory breathing air; the difficulty of matching the various filter adsorption specifics and the different toxic vapors that can potentially be released during expected use; and the inevitable release into the breathing air of toxic substance Z, caused by vapor X, which, when it is generated under the ductless hood, reacts with Y, which was previously adsorbed on the filter, to produce Z.

Given the above information, ductless hoods can be used in exceptional instances only when

- the need is clearly justified;
- use is restricted to individuals who thoroughly understand the potential hazards of an inadvertent release of toxic vapors into the laboratory atmosphere;
- all the users can assume full responsibility in the event of a toxic release;
- an adequate inspection and maintenance program is established; and
- a record is kept showing the time, date, and manner of use; the chemicals involved; the type of filter installed; and user names.

Glassware and Plasticware

Ordinarily, the only soft glass provided in the laboratory should be reagent bottles, measuring equipment, stirring rods, and tubing. Borosilicate glassware is recommended for all other laboratory glassware except for special experiments that use UV or other light sources. Glassware should be routinely inspected to ensure that it is free from cracks, chips, and other obvious defects. Use polarized light to examine glassware for strains.

Any glass equipment to be evacuated, such as suction flasks, should be heavy-walled. Dewar flasks and large vacuum vessels made of borosilicate glass should either be taped with duct tape or other fabric-backed tape or contained in a perforated/screen metal jacket to prevent flying glass in the case of an implosion. Do not use plastic tape as a substitute for fabric-backed tape. Thermos bottles are usually con-

structed of soft glass and have thin walls; they are not acceptable substitutes for laboratory Dewar flasks.

All glass tubing and rods, including stirring rods, should be fire-polished before use. Unpolished freshly cut glass has a razor-like edge, which can lacerate the skin and cut into cork and rubber stoppers and tubing. After fire-polishing and bending glass, allow ample time for it to cool before you grasp it.

Microwave Ovens

Operations performed in microwave ovens by using open vessels can boil over and splatter. Remove splattered substances promptly; if a subsequent use of the oven involves the splattering of a substance that is incompatible with the previous splattered substance, the ensuing chemical reaction could be violent. Some liquids, including aqueous solutions and even water itself, can be superheated in a microwave oven and erupt violently when removed.

Do not use microwave ovens to heat liquids to temperatures near their boiling points. Keep the inside surfaces of the microwave oven compartment clean. Before using an oven, inspect the interior to ensure the absence of residues from a prior use.

When using closed vessels in microwave ovens, ensure that the closed vessel will be able to withstand any internal pressures that might develop. Many reactions for which microwave ovens can be used require the use of closed vessels. If the liquid fills the vessel completely, thermal expansion of the liquid as its temperature rises can burst the vessel. If the liquid does not fill the vessel, and the liquid in the closed vessel is heated to temperatures higher than its normal boiling point, the closed vessel could burst. Similarly, if the heating promotes a decomposition reaction, the pressure inside the closed vessel could exceed the bursting strength of the vessel material. Use only closed vessels that permit monitoring of the temperature and pressure within the vessel while they are being heated in a microwave oven. Alternatively, use an open-vessel microwave system that is designed for the purpose (see Cresswell, S. L.; Haswell, S. J. *J. Chem. Educ.* **2001**, 78, 900–904).

Computer Terminals

There is no evidence that viewing computer terminals harms your eyes. However, improper use or awkward operation of a terminal can cause muscular discomfort and pain of sufficient magnitude to distract your attention from accident prevention.

Maintain good posture while viewing a screen. Adjust your eyeglasses (if worn), adjust the tilt of the screen, and change the location of the terminal or the height of your chair or stool so that your body, hands, arms, neck, and eyes are comfortable.

Eliminate glare. Minimize brightly illuminated or deeply darkened areas in the room; adjust the lighting in the room so that objects and surfaces in your field of view have nearly equal brightness. To match the luminance on the screen with your surroundings, use a screen that can display high screen luminance.

Increase the screen resolution, if possible. Adjust the size of the characters on the screen. Black characters on a white or light-colored background are less stressful to most individuals than white characters on a dark background.

For additional information, see B. R. Blais, Visual Ergonomics of the Office Workplace, *Chemical Health and Safety*, **1999**, 6 (4), 31–38.

Sinks

To prevent contamination of the potable water supply, the supplies for laboratory sinks and for drinking water and safety showers or eyewashes must be separate. Otherwise, back siphonage or back pressure can suck sink water into the potable water system through hoses or other apparatus. Building codes require that check valve systems be periodically tested. As frequently required by the local building code, conduct and keep records of such tests. Where it is appropriate, it is advantageous to separate laboratory sink drainage from the sanitary drainage to facilitate independent treatment of wastes.

9. Inventory Management, Storage, and Disposal

Inventory Management

Managing chemical inventory requires

- a realistic appraisal and selection of chemicals that are necessary versus those that are desirable but not required to conduct a viable chemistry program,
- an understanding of the incompatibility of chemicals,
- a qualitative risk assessment of the available space and the location of the chemical containers therein,
- a reasonable method of identifying chemicals for disposal, and
- a proper disposal strategy, which includes labeling and monitoring.

Storage

The first step is to reduce the number and quantity of chemicals that need to be stored to a reasonable minimum. This will require special coordination with faculty and staff, so that, for example, chemical inventories might be shared.

The next step is to classify the chemicals into hazards—in-storage groups with the help of color-coded labeling systems such as those used by many laboratory chemical suppliers.¹⁴ Also see Pipitone's *Safe Storage of Laboratory Chemicals*. As readers know, incompatible chemicals that are not separated into different groups can react and explode or generate heat, fire, or toxic or flammable gases. Some unstable compounds (nitrated organic compounds, picric acid, benzoyl peroxide, etc.) must be kept moist while in storage to reduce the possibility of an explosion. The storage area must be adequate to separate the different groups from each other. If only a very few chemicals in a particular hazard class are used, it may be expedient to purchase those chemicals in limited quantity as they are needed. Ideally, each group should be placed in well-separated areas, but this is not always possible. Many publications offer help in describing the groups and the reactions between and among them. Especially recommended is *Bretherick's Handbook of Reactive Chemical Hazards*.

Ensure that security procedures are adequate to prevent unauthorized access to stored chemicals. Ensure that the housekeeping practices for storage areas will keep them neat and orderly. Storage shelves and other equipment must be firm and secured against sliding and collapse and not be subject to flooding. Make sure that shelf units are stable, well supported, and in no danger of tilting. In regions subject to earthquakes, restraints should be installed on every shelf. Provide storage for large containers of reagents on low shelves. Containers of liquids should be placed in trays that have rims high enough to furnish secondary containment in case of spills or leaks. Store corrosives below eye level as an additional precaution to prevent injury to the eyes. Never store anything on the floor, even temporarily; containers of chemicals belong on shelves and benches, and (temporarily) on delivery carts; empty boxes and other empty containers belong in trash receptacles.

Chemical storage rooms and buildings must be adequately ventilated, with a rated air change of at least six turnovers per hour; they must have vents and intakes at both ceiling and floor levels and be located to eliminate pockets of undisturbed air. Every

¹⁴Note that different suppliers use different colors to signify the same type of storage hazard. Do NOT store Supplier X's color-coded purple-stripe chemicals with Supplier Y's color-coded purple-stripe chemicals. Use only the color-code storage system from either Supplier X or Supplier Y—or design your own color-code and apply it to each container label.

storage room should have at least two exits. The floor should be diked to contain liquid spills and equipped with a drain leading to a controlled spill collection area. Automatic water sprinklers are necessary, except of course for spaces where water reactives are stored. Lights, switches, fans, motors, phones, and so forth should be spark-proof. Each storage area should be equipped with at least one fire extinguisher and one self-contained escape respirator such as a Scott “air pack” or an equivalent.¹⁵

When poured, pumped, or otherwise caused to flow, the movement of a flammable, non-conducting liquid generates a static electrical potential difference between the liquid and the surfaces it touches as it moves. The charge that develops is often large enough to generate a spark of more than sufficient energy to ignite the flammable vapor-air mixture that is always present when a flammable liquid is poured, pumped, or otherwise caused to flow. Therefore, when a flammable liquid is withdrawn from a drum, or when a drum is filled from another source, both the drum and the other equipment must be electrically wired to each other and to the ground to avoid developing static charge. Only small quantities should be transferred to glass, plastic, or other nonelectrically conductive containers. When a flammable liquid is transferred from a metal container to a nonelectrically conductive container, and vice versa, the metal container should be grounded.

As mandated by OSHA regulation 29 CFR 1910.106 and as described in NFPA 45, keep only minimum quantities of flammable liquids in the laboratory for current work. Some authorities recommend that in most laboratories, the maximum quantity and container sizes allowed by NFPA 45 should be reduced to half or even one-third. In the laboratory, keep small quantities of flammable liquids in small safety cans, not glass bottles, except when the use of a safety can would impugn the purity of the liquid or would be clumsy and therefore possibly cause spillage.

Store larger quantities in safety cans and away from ignition sources in fire-resistant, properly ventilated flammable liquid storage cabinets. The ventilation of such cabinets is described in local fire codes. Bulk quantities of flammable liquids larger than 4 liters should be stored in a separate storage building dedicated for this purpose and be equipped with an automatic fire-extinguishing system.

Storage of chemicals in household (domestic) refrigerators constitutes a unique hazard because the various control switches and defroster heaters can spark and ignite flammable materials. Explosions and fires can result. Never use household refrigerators for chemical storage of any kind. Although most household refrigerators can be modified by a trained technician to remove internal sources of spark, such modification is not recommended. The motor and other electrical parts on the exterior of a modified domestic refrigerator can still ignite flammable vapors leaking out of the refrigerator or already in the room. In so-called explosion-proof refrigerators, the internal wiring has been modified to eliminate ignition sources, and the external motor and switches are sealed. These refrigerators should be clearly labeled “No Food or Drink.” Refrigerators used for food and beverages must be labeled “Food Only, No Laboratory Chemicals” and be located outside of and well away from all chemical work areas.

If the quantity of a hazardous chemical in a container exceeds 1 liter or 1 kilogram, transport the chemical by using the container-in-a-carrier concept. Use a chemically resistant bucket or other carrier designed for the purpose. This will shield a carried

¹⁵Not to be confused with a self-contained breathing apparatus (SCBA), the use of which requires training and medical clearance.

glass container from breaking if there is a sudden change of movement. The bucket or other carrier should be large enough to contain spills and leaks from the carried container.

When transporting chemicals, negotiate stairs with care or use an elevator that has been designated as suitable for carrying chemicals. No one should ride in that elevator when it is being used to move chemicals from one floor to another; use the stairs or wait until the chemicals have been removed. Place a prominent sign in the elevator, along with the chemicals, warning others to not board the elevator. Smoking is never allowed around chemicals and apparatus in transit. Cryogenic liquids are never allowed in an elevator (see “Cryogenic Hazards,” page 27).

Many chemicals deteriorate while they are stored. It is recommended that the date of receipt and the date of initial opening of every chemical container be recorded on the container label. Chemical manufacturers list expiration dates for some chemicals (e.g., isopropyl ether, a peroxide former) by stamping a date on the label. However, manufacturer-supplied expiration dates are the exception and not the rule. Keep stored chemicals cool and dry and away from heat and direct sunlight. Chemicals cannot be stored indefinitely; establish guidelines for determining the length of time in storage for various chemicals. Thus, although the deterioration of a specific compound cannot be predicted in detail, one can often generalize about the reaction characteristics of groups of compounds. Then some general conclusions about the stability of classes of chemicals can be reached, and reasonable storage time limits can be established.

The principal criteria for assigning storage time periods to chemicals are the conditions in the storage space, the rates at which the compounds oxidize or react with moisture, and in some cases, the different ways and rates that they may polymerize or otherwise deteriorate. The reaction of compounds with air or moisture over time can produce products that are hazardous (e.g., explosive or toxic). The lifetime of the container should also be considered.

The end of the storage time period is, of course, a calendar date, called the decision date for that chemical in that container. When the decision date of a chemical in storage has been reached, the container is removed from the shelf and a chemist to whom this task has been explained and assigned either overrides the decision date and sends the compound back to the storage shelf with a new decision date or schedules the chemical for disposal. To simplify the administration of this protocol, decision dates might be limited to the first day of each month or quarter and coded by bar code labels, color marking, or some other way, on each container label. Chemicals that have been stored for a long period of time (perhaps 5 years) should be scheduled for disposal with no further extension of the decision date.

To facilitate administration of time-in-storage protocols, the use of bar code labeling and appropriate computer programming is recommended. However, be sure that the ease of administration of such a procedure does not replace visual observation. There is no substitute for “eyeball” inspection of stored chemicals.

Peroxide-forming chemicals deserve special attention while in storage. Peroxide formation is accelerated by the presence of UV light and elevated temperature. Careful records of the storage history of compounds that form peroxides on standing should be maintained and periodically reviewed. Do not store peroxide formers in a refrigerator or other chilled space at or below the temperature at which the formed peroxide

would freeze or precipitate. While in solution, peroxides are less likely to detonate, whereas in the form of a solid, precipitated out of solution by lowering the temperature of the liquid in which they have been dissolved, they are more likely to do so. Storing peroxides and peroxide formers is discussed on page 23.

Waste Disposal

A material is usually defined as a waste when it is determined that the material should no longer be used and it is time to discard it. In the past, the laboratory worker has often been the one who determined when an unwanted material is to be declared a waste; more recently, federal and state regulations have expanded our understanding of what constitutes a waste. Thus, according to federal regulations (discussed below), a material is also a waste, for example, if it has been abandoned or if it is considered to be “inherently waste-like.” This means that a material that has been spilled, degraded, or obviously contaminated is often considered to be a waste according to the regulations.

In the United States, disposal of certain chemical wastes is governed by the requirements of the Resource Conservation and Recovery Act (RCRA) of 1976 and the Hazardous and Solid Waste Amendments of 1984. RCRA is administered by the U.S. Environmental Protection Agency (EPA) and authorized state environmental agencies. Note that regulations promulgated by states and local jurisdictions take precedence over federal regulations and may be different or more restrictive. Make it your practice to obtain detailed, up-to-date information from state environmental agency offices. For details on the federal RCRA regulations, consult parts 260–268 of Title 40 of CFR.

Under federal regulations, any material that is discarded or intended to be discarded is considered a *solid* waste (regardless of its physical state). A subset of solid waste is hazardous waste, which must meet certain criteria defined in RCRA in two categories: characteristic wastes and listed wastes.

There are four kinds of characteristic wastes: characteristics of ignitability, corrosivity, reactivity and toxicity.¹⁶ Listed wastes are named in lists found in 40 CFR 261.31–261.33. These wastes are materials generated through either specific or nonspecific processes and include materials such as spent solvents, which are frequently generated by laboratory facilities. The lists also include numerous commercial products that are regulated as hazardous when they are discarded, such as many common laboratory reagents.

The status of a material as a hazardous or non-hazardous waste depends on its identification as possessing one or more of the four characteristics and/or on its identification as a material named in one or another of the lists of listed wastes. The “Waste

Indications for Disposal of Chemicals Include

- slightly cloudy liquids,
- chemicals that are changing color,
- spotting on solids,
- caking of anhydrous materials,
- existence of solids in liquids or of liquids in solids,
- pressure buildup in bottles,
- evidence of reaction with water, or
- damage to the container.

¹⁶See “Waste Classification” at right.

Classification” Section below will help you determine the status of various wastes based on their characteristics or listing.

Before shipping hazardous wastes off-site for disposal, the institution will need a generator identification number from the EPA or your state environmental agency. There is no cost to acquire an identification number; call the RCRA hotline (800-424-9346) or your state environmental agency to obtain the proper form. It can also be obtained online from EPA at www.epa.gov/epaoswer/hazwaste/data/form8700/forms.htm.

Most institutions that generate hazardous wastes work with a disposal contractor or consultant to arrange for off-site disposal. Competent contractors can provide a number of valuable services, but it is important to understand that the waste generator retains virtually all liability for the proper packaging, transportation, and disposal of wastes.

A Competent Contractor Must Be Able To

- properly package wastes according to U.S. Department of Transportation (DOT) requirements;
- label wastes according to the U.S. Environmental Protection Agency (EPA) and DOT requirements;
- prepare necessary forms, including disposal facility approval documents and the waste manifest used for transportation; and
- transport waste to a permitted treatment, storage, or disposal facility (TSDF).

Great care should be taken in the process of selecting a contractor, including a review of references, qualifications, capabilities, and permits, as applicable.

Although contractors may assert that they “take title to” hazardous waste or otherwise claim responsibility for its proper disposal, it is important to know that the generator, not the contractor, always maintains responsibility for the waste, from “cradle to grave”—from the time the waste is first generated until its ultimate destruction.

Under another federal law, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, frequently referred to as Superfund, generators may be held liable for clean-up costs if their hazardous waste or other waste from other generators, all located in the same disposal location unit, poses a threat to human health or the environment. This concept, referred to as joint and several liability, emphasizes the importance of choosing good contractors and facilities for waste disposal.

Waste Classification

EPA waste classification terminology is quite specific and cannot necessarily be inferred from a general knowledge of chemistry. The four characteristics are defined as follows:

Ignitability. A waste material is classified as Ignitable (EPA Waste Number D001) if it is

- a liquid (other than an aqueous solution containing less than 24% alcohol by volume) and has a flash point of less than 60 °C (140 °F);
- not a liquid and is capable under standard temperature and pressure of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, it burns so vigorously and persistently that it creates a hazard;
- an ignitable compressed gas (as defined in 49 CFR 173.300); or
- an oxidizer (as defined in 49 CFR 173.151).

Waste Is Classified into Four Categories:

| | |
|-----------|-----------|
| Ignitable | Corrosive |
| Reactive | Toxic |

Corrosivity. A waste material is classified as Corrosive (EPA Waste Number D002) if it has either of the following properties:

- it is aqueous and has a pH equal to or less than 2 or greater than or equal to 12.5 by using EPA test methods, or
- it is liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.25 in.) per year at a test temperature of 55 °C (130 °F).

Reactivity. A waste material is classified as Reactive (EPA Waste Number D003) if it has any of the following properties:

- it is normally unstable and readily undergoes violent change without detonation;
- it reacts violently with water;
- it generates toxic gases, vapors, or fumes when mixed with water;
- it is a cyanide- or sulfide-bearing waste that generates toxic gases, vapors, or fumes at a pH between 2 and 12.5;
- it is capable of detonating or exploding when it is subjected to a strong initiating course or if it is heated under confinement; or
- it is a forbidden Class A or Class B explosive as defined by DOT.

Toxicity. A waste is classified as Toxic by RCRA (EPA Waste Numbers D004–D043) if an extract from the Toxicity Characteristic Leaching Procedure (TCLP) test results in a waste leachate above certain concentration levels. Included on the list are 8 common metals (As, Ba, Cd, Cr, Hg, Pb, Se, Ag), 20 solvents, and 12 pesticides. The list and the levels are provided in 40 CFR 261.24.

Other Waste Generator Requirements

In addition to properly classifying chemical wastes, laboratories are obligated to meet requirements within designated generator categories based on the quantity of hazardous waste on the premises. For example, large universities are typically required to remove accumulated wastes every 90 days, whereas smaller colleges and high schools that generate smaller quantities may be able to store for longer periods. Facilities designated as “small-quantity generators”—those who generate 100–1000 kg of hazardous waste in any given month—may store their wastes for 180 or 270 days depending on the location of their designated disposal facility. Still smaller generators (those who generate less than 100 kg in any given month) may store their wastes indefinitely under some conditions.

All generators must ship wastes off-site by using a hazardous waste manifest that tracks wastes from “cradle to grave.” Appropriate labeling, marking, and placarding requirements also apply.

Mixed Waste

Some wastes generated by laboratories may present a combination of chemical, radioactive, and/or biological hazards, which are generally referred to as mixed wastes. Although much of the above discussion for chemical hazardous wastes may apply, these wastes may require special management considerations because the treatment method for one of the hazards may be inappropriate for the treatment of one or more of the others.

The management of mixed wastes is further complicated by legal requirements that

may not be consistent with the risks of each of the different hazards present. Thus, chemical wastes are regulated by RCRA, and radioactive wastes are regulated by the NRC. Various states also regulate medical/infectious wastes. There are currently few options for disposal of mixed RCRA and radioactive wastes; most wastes are stored on-site pending the permitting of facilities designed to treat multiple hazards.

10. The OSHA Laboratory Standard

In January 1990, OSHA published the final rule, Occupational Exposures to Hazardous Chemicals in Laboratories, better known as the “Laboratory Standard.” This rule recognizes that the exposure potential for laboratory-scale work with hazardous materials may be different from exposures in the industrial sector.

The main component of the laboratory standard is the requirement for a written chemical hygiene plan (CHP) that describes the procedures for training employees and handling hazardous chemicals in laboratory work. The laboratory administrator has considerable flexibility in developing appropriate means, consistent with the OSHA intent, to minimize the hazards of laboratory work. The CHP must include all the components listed below. However, the description and the manner of implementation are at the laboratory administrator’s discretion, provided that all of the following are explained in his or her written CHP:

- standard operating procedures;
- criteria for implementing specific control measures;
- a requirement that laboratory hoods function properly;
- employee information and training requirements;
- circumstances under which a particular laboratory operation shall require prior approval from the employer;
- provisions for medical consultation and exams;
- designation of a chemical hygiene officer and, if appropriate, establishment of a chemical hygiene committee; and
- provisions for additional protection for work with substances that are particularly hazardous, such as certain carcinogens, reproductive toxins, and substances that have a high degree of acute toxicity.

Also see Young, Kingsley, and Wahl’s *Developing a Chemical Hygiene Plan*.

Other OSHA and EPA Requirements

Generally, the OSHA regulations, Title 29 of CFR, apply to academic institutions. Some of the lesser-known regulations are identified here.

- The employer’s safety and health protection policy must be posted. See section 1903.2(a)(1) and (2). Whether the state or federal posting is required depends on the existence of a state plan. The requirements for posting in multiple work locations should be carefully reviewed.
- A written emergency action plan and a written fire protection plan must be prepared. See sections 1910.38(a) and (b).
- Portable fire extinguishers must be inspected monthly. See section 1910.156(d). Hands-on training in the use of fire extinguishers must be provided annually for certain employees. See section 1910.157(g).
- Safety shower and eyewash facilities must meet the requirements of section 1910.151(c) and be tested monthly. Also see the current edition of ANSI Z358.1.
- Respirators must be inspected and records maintained. See section 1910.134.

EPA requires that a contingency plan be prepared that includes spill prevention, control and countermeasures for fires, explosions or accidental releases, and hazardous waste management. Details are given in 40 CFR parts 265.50 to 265.56, and 265.112.

It is recommended that copies of 29 CFR and 40 CFR be obtained and thoroughly studied. These publications are updated irregularly in the *Federal Register* and are revised annually. Purchase copies from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402-9328 or download them from www.osha.gov and www.epa.gov. Further information can be obtained from regional EPA and OSHA offices. Several states have regulations that require written plans or other reports. Check with the appropriate state authorities or agencies for information.

Appendix 1. Sources of Additional Information

The references cited below have been topically organized for the readers' convenience. In many instances, a reference could just as well have been listed under a different category. If available, consult subsequent editions to those listed.

Facilities and Equipment

Blais, B. R. Visual ergonomics of the office workplace. *Chemical Health and Safety*, 1999, 6 (4) 31–38.

DiBerardinis, L. J., et al. *Guidelines for Laboratory Design: Health and Safety Considerations*, 3rd ed.; Wiley/Interscience: New York, 2001.

Emergency Eyewash and Shower Equipment, ANSI Z358.1.

Industrial Ventilation, 24th edition; ACGIH: Cincinnati.

Laboratory Design, Construction and Renovation: Participants, Process, and Product; National Academy Press: Washington, DC, 2000.

Laboratory Ventilation, ANSI Z9.5 (current edition).

Method of Testing Performance of Laboratory Fume Hoods; ANSI/ASHRAE Standard 110-1995, American Society of Heating, Refrigerating, and Air Conditioning Engineers: Atlanta, 1995.

Pipitone, D. A., Ed. *Safe Storage of Laboratory Chemicals*, 2nd ed.; Wiley/Interscience: New York, 1991.

Saunders, G. T. *Laboratory Fume Hoods: A User's Manual*; Wiley/Interscience: New York, 1993.

Inventory Management, Storage, and Disposal

The ACS Guide for Chemical Spill Response Planning in Laboratories; ACS: Washington, DC, 1995.

Environmental Management Guide for Small Laboratories, 2nd ed.; Office of the Administrator, EPA: Washington, DC, 2000.

Little Known but Allowable Ways to Deal with Hazardous Waste; Small Business Division, EPA: Washington, DC, 2000.

Labeling and Material Safety Data Sheets

Chemical Laboratory Information Profiles (CLIPs) in issues of the *Journal of Chemical Education*, published by the ACS Division of Chemical Education.

Organizing for Accident Prevention

Safety Audit/Inspection Manual, American Chemical Society (ACS): Washington, DC, 2000; see chemistry.org/committees/ccs (click on Publications).

The OSHA Laboratory Standard

The Laboratory Standard is directly related to the Hazard Communication Standard (29 CFR 1910.1200); www.osha.gov/SLTC/hazardcommunications/index.html.

Young, J. A.; Kingsley, W. K.; Wahl, G. H. *Developing a Chemical Hygiene Plan*; Oxford University Press: New York, 1990.

Reducing Hazards

- Bingham, E., Cohrssen, B., Powell, C. H., Eds. *Patty's Toxicology*, Vols. 1–9, 5th ed.; Wiley/Interscience: New York, 2001.
- Criteria Documents*; NIOSH: Cincinnati (various years).
- Documentation of TLVs and BEIs*; ACGIH: Cincinnati.
- Fire Protection Guide on Hazardous Materials*, contains NFPA 325M, NFPA 49, NFPA 491M, and NFPA 704; NFPA: Quincy, MA, 2001.
- Fire Protection for Laboratories Using Chemicals*, NFPA 45; NFPA: Quincy, MA, 2002.
- Flammable and Combustible Liquids Code*, NFPA 30; NFPA: Quincy, MA, 2000.
- Frazier, L. M.; Hage, M. L. *Reproductive Hazards of the Workplace*; Wiley: New York, 1998. Also, refer to DART/ETIC within www.sis.nlm.nih.gov (click on "Toxicology and Environmental Health").
- Gosselin, R., et al. *Clinical Toxicology of Commercial Products*, 5th ed.; Lippincott, Williams, and Wilkins: Philadelphia, 1984.
- Handbook of Compressed Gases*; CGA: Arlington, VA, 1999.
- IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans*; IARC: Lyon, France.
- Ninth Report on Carcinogens*; National Toxicology Program; Public Information Office: Research Triangle Park, NC, 2000; <http://ehis.niehs.nih.gov/roc/toc9.html>.
- Occupational Health Guidelines for Chemical Hazards* (and supplements); NIOSH/OSHA/DOE Health Guidelines: Cincinnati, January 1981.
- Safe Handling of Cryogenic Liquids*; CGA: Arlington, VA, 1993.
- Shepard, T. H. *Catalog of Teratogenic Agents*, 9th ed.; Johns Hopkins University Press: Baltimore, 1998.
- Static Electricity*, NFPA 77; NFPA: Quincy, MA.
- Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*; ACGIH: Cincinnati (revised annually).
- Understanding Risk Analysis*; ACS: Washington, DC, 1998.

Other Useful Sources

- Alaimo, R. J., Ed. *Handbook of Chemical Health and Safety*; Oxford University Press: New York, 2001.
- Copies of ANSI standards can be obtained from the American National Standards Institute, 11 West 42nd St., New York, NY 10036.
- Copies of NFPA publications can be obtained from the National Fire Protection Association, 1 Batterymarch Park, Quincy, MA 02269-9101. Also see www.nfpcatalog.org.
- OSHA Guidelines on First Aid Training*; OSHA Directive CPL 2-2.53 (January 7, 1991); also available at www.osha.gov (click on Directives, search for First Aid Training).
- Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*; National Academy Press: Washington, DC, 1995.
- See articles in *Chemical Health & Safety* published by the ACS Division of Chemical Health and Safety.
- Urban, P. G., *Bretherick's Handbook of Reactive Chemical Hazards*, 6th ed.; (book and CD-ROM) Butterworth-Heinemann: London, 2000.

Useful Websites

American Chemical Society

chemistry.org

ACS Committee on Chemical Safety

chemistry.org/committees/ccs

American Conference of Governmental Industrial Hygienists

www.acgih.org

American Society of Heating, Refrigerating & Air Conditioning Engineers

www.ashrae.org

Compressed Gas Association

www.cganet.com

International Agency for Research on Cancer

www.iarc.fr

National Fire Protection Association

www.nfpa.org

National Institute for Occupational Safety and Health

www.cdc.gov/niosh

National Library of Medicine

www.sis.nlm.nih.gov

Nuclear Regulatory Commission

www.nrc.gov

Occupational Safety & Health Administration

www.osha.gov

U.S. Department of Energy

www.energy.gov

U.S. Environmental Protection Agency

www.epa.gov

Appendix 2. Suggested Rules for Accident Prevention

The following list is an example set of accident-prevention rules for the chemical laboratory:

- Always wear Type G, H, or K¹⁷ safety goggles for eye protection in the laboratory.
- In addition to goggles, wear a face shield large enough to protect your ears, neck, and face in severe exposure conditions.
- Be aware of the hazards of the chemicals you will work with. Always take the precautions appropriate for those hazards.
- Always wear a chemically resistant lab coat or apron. Do not wear shorts, cutoffs, or miniskirts. Do not wear high-heeled shoes, open-toed shoes, sandals, or shoes with tops made of fabric, leather strips, or other woven material.
- Confine long hair and loose clothing.
- Always wash your hands and arms with soap and water before leaving the laboratory, even if you wore gloves.
- Never work alone in the laboratory.¹⁸
- Never eat, drink, chew gum or tobacco, smoke, or apply cosmetics in areas where chemicals are used or stored.
- Never perform unauthorized work, preparations, or experiments in the laboratory.
- Never engage in horseplay, pranks, or other acts of mischief.
- Never remove chemicals from the laboratory without proper authorization.

All students should attest by signature that they have received, read, understood, and pledged to follow the rules stated in their copies of the accident-prevention rules. Advise students that willful and/or repeated inadvertent noncompliance could result in suspension or dismissal from the laboratory.

¹⁷Type G is a cover goggle without ventilation. Type H is a cover goggle with indirect ventilation. Type K is a cup goggle with indirect ventilation that fits tightly against the eye sockets and is generally considered to be uncomfortable if worn for long periods.

¹⁸Undergraduate students in the laboratory should be supervised by an instructor at all times.

Appendix 3. Inspections and Audits Prevent Accidents

Accidents are caused by mistakes. Clearly, regular inspections and audits cannot prevent every accident-causing mistake. Equally clearly, it is worth the expenditure of some time and effort to conduct more than an occasional inspection and an infrequent audit. The following discussion is introductory; for a detailed treatment of this topic, including a suggested checklist of specific items, see the *Safety Audit/Inspection Manual*, American Chemical Society, Washington, DC, 2000. This publication is also available at <http://membership.acs.org/c/ccs/pubs/safety.pdf>.

The term *audit* reminds most of us of the sometimes-awesome initials “IRS” or perhaps the less-threatening “CPA.” A properly conducted safety audit is certainly intensive, but instead of involving columns of figures, a safety audit is a systematic review of operations intended to ensure that what should be done is, in fact, being done, both in spirit and to the letter.

A safety audit has two parts: acquiring information and then evaluating it. Several guides known as *regulations* identify the details of the information to be acquired: Occupational Safety and Health Administration regulations, particularly 29 CFR 1910, but elsewhere in 29 CFR as well; Environmental Protection Agency regulations in 40 CFR; Department of Transportation regulations in 49 CFR; corresponding state and local regulations; and institutional policies and rules.

Of course, a safety audit should reveal current defects and weaknesses in the operation of an institution; however, perhaps more important, it should also identify its strengths. Audit data are acquired by reviewing records and procedures, identifying records that should be available but are not, and conducting interviews. Data are collected from management and operations. Too often, in these latter collections, maintenance and janitorial operations are overlooked. Remember to review the mail room, the shipping department, and the personnel in other service operations.

The term *inspection* often brings to mind an image of a white-gloved inspector scrutinizing minute details, making people wish they were elsewhere. Of course, a proper safety inspection is a monitoring function with a positive purpose: to identify existing and potential accident-causing hazards, actions, and failures to act, which, once identified, can be corrected.

Safety inspections are conducted by teams, not by the safety committee. The safety committee is appointed by top management. Intermediate management appoints a team, which is guided by and reports to the safety officer.¹⁹ The team gives copies of its reports to the safety committee. The committee is responsible to top management. Through the safety officer, the team is responsible for the safety of students, lab supervisors, faculty, and other staff members. At least one member of the committee should have a sophisticated knowledge of safety. It may be necessary to bring in an outside consultant to meet this need, although it is better to have such competence come from within the institution. Equally important is the presence on the team or committee of a person with practical knowledge that has been gleaned from personal work experience; a janitor, a maintenance person, or a security guard could fulfill this role.

Proper safety inspections are time-consuming; it is often practical to inspect only a limited area for safety this week, for example, electrical safety, and to cover another area, perhaps the frequency of toxic exposures, or hazards of a physical nature, on a following occasion. Guided by the decisions of an active committee, over the course of time, the entire institution will be thoroughly safety-inspected by one team or another—and then it will be time to begin all over again.

¹⁹The safety officer primarily, but jointly with the faculty and with the cooperation of laboratory supervisory personnel and the students, is responsible for safe practices and the conditions in which laboratory work is conducted.

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