Chemical Laboratory Safety and Security

A Guide to Prudent Chemical Management

Lisa Moran and Tina Masciangioli, *Editors*

Committee on Promoting Safe and Secure
Chemical Management in Developing Countries

Board on Chemical Sciences and Technology
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Foreword

As developing countries become more economically competitive and strive to increase capacity in chemical sciences, they face many challenges in improving laboratory safety and security. Safety and security practices are intended to help laboratories carry out their primary functions in efficient, safe, and secure ways. Improving safety and security is mistakenly seen as inhibitory, but lack of understanding of safety and security procedures, cultural barriers, lack of skills, and financial constraints can easily be overcome. Promotion of good safety and security procedures can eventually lead to greater productivity, efficiency, savings, and most importantly, greater sophistication and cooperation. It is for this reason that the U.S. National Research Council set out to provide guidance for laboratories in the developing world on safe and secure practices in the handling and storage of hazardous chemicals.

A select committee composed of experts in synthetic organic and pharmaceutical chemistry and processing; chemical safety, security, and management; and chemical education and behavioral change examined the barriers to and needs for improving laboratory safety practices in developing countries. An emphasis throughout the study was on understanding socioeconomic and cultural conditions of developing nations. The committee's findings are reflected in this book, which is based on the study *Promoting Chemical Laboratory Safety and Security in Developing Countries,* as well as the seminal reference book on chemical laboratory safety in the United States, *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards.*

Every day, chemists throughout the world work in laboratories with hazardous chemicals. They also generally follow the necessary procedures for safe handling and disposal of these chemicals. It is our hope that this book and the accompanying materials will assist chemists in developing countries to increase the level of safety and security in their labs through improved chemicals management and following the best laboratory practices possible.

This book and accompanying materials are based on two reports of the National Research Council:

1. *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards,* which serves as a seminal reference book on chemical laboratory safety in the United States and was prepared by the Committee on Prudent Practices in the Laboratory: An Update; and

2. *Promoting Chemical Laboratory Safety and Security in Developing Countries,* prepared by the Committee on Promoting Safe and Secure Chemical Management in Developing Countries.

Both books are available on the Internet through the National Academies Press at *www.nap.edu*

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Chemical Laboratory Safety and Security

A Guide to Prudent Chemical Management

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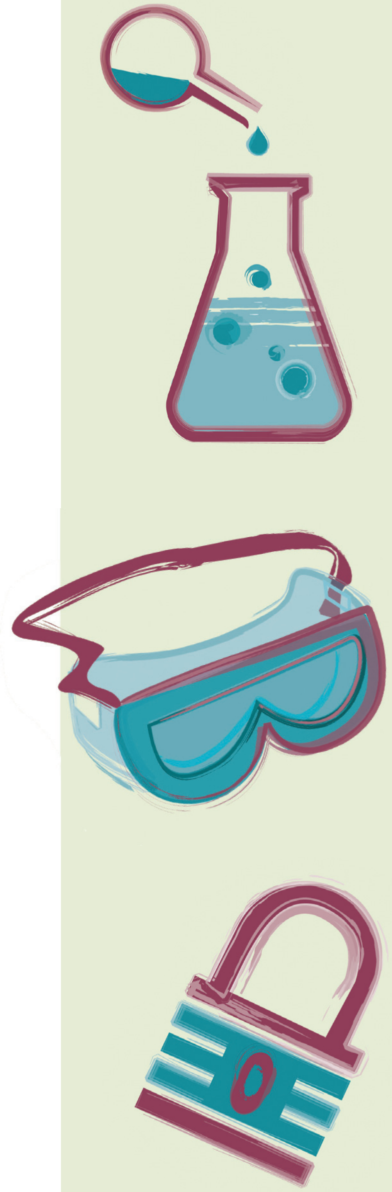
Executive Summary



Why Are Chemical Safety and Security Important for Your Institution?

Over the past century, chemistry has increased our understanding of the physical and biological world as well as our ability to manipulate it. The work carried out in chemistry laboratories around the globe continues to enable important advances in science and engineering. The chemical laboratory has become the center for acquiring knowledge and developing new materials for future use, as well as for monitoring and controlling those chemicals currently used routinely in thousands of commercial processes.

Institutions must be aware of the potential for the accidental misuse of chemicals, as well as their intentional misuse for activities such as terrorism or illicit drug trafficking.

Most of the chemicals produced and used today are beneficial, but some also have the potential to damage human health, the environment, and public attitudes toward chemical enterprises. Institutions must be aware of the potential for the accidental misuse of chemicals, as well as their intentional misuse for activities such as terrorism or illicit drug trafficking. Laboratories face a number of threats, including the theft of sensitive information, high-value equipment, or dual-use chemicals that may be employed for weapons. Chemical safety and security can mitigate these risks.

A new culture of safety and security consciousness, accountability, organization, and education has developed around the world in the laboratories of the chemical industry, government, and academe. Chemical laboratories have developed special procedures and equipment for handling and managing chemicals safely and securely. The development of a "culture of safety and security" results in laboratories that are safe and healthy environments in which to teach, learn, and work.

Fostering a Culture of Chemical Safety and Security

Establishing a culture of safety and security rests on the recognition that the welfare and safety of each person depends on both teamwork and individual responsibility. A safety and security culture must be something that each person owns and not just an external expectation driven by institutional rules.

A successful safety and security program requires a daily commitment from everyone in the institution.

Academic and teaching laboratories have a unique responsibility to instill in their students a lifelong attitude of safety and security consciousness and prudent laboratory practice. Teaching safe practices should be a top priority in the academic laboratory. Nurturing basic habits of prudent behavior is a crucial component of chemical education at every level and remains critical throughout a chemist's career. By promoting safety during the undergraduate and graduate years, faculty members have an impact not just on their students, but on everyone who will share their future work environments.

A successful safety and security program requires a daily commitment from everyone in the institution. People at all levels must understand the importance of eliminating risks in the laboratory and work together toward this end. Institutional leaders have the greatest power and authority, and therefore the greatest responsibility for cultivating a culture of safety and security.

Responsibility and Accountability for Laboratory Safety and Security

Laboratory safety and security require mandatory rules and programs, a commitment to them, and consequences when those rules and expectations are not met. Institutions need well-developed administrative structures and supports that extend beyond the laboratory's walls to the institution itself. Responsibility for safety and security rests ultimately with the head of the institution and its operating units. Other personnel with responsibility for maintaining a safe and secure laboratory environment include the following:

- **Environmental Health and Safety Office:** This office should be staffed by experts in chemical safety, engineering, occupational medicine, fire safety, toxicology, or other fields. The environmental health and safety office is most effective when it shares in a genuine partnership with all department chairpersons or directors, principal investigators or managers, and laboratory personnel. The office should help design safety and security programs that provide technical guidance and training support that are relevant to the operations of the laboratory, are practical to carry out, and comply with the law and basic standards of safety and security.

Responsibility for safety and security rests ultimately with the head of the institution and its operating units.

- **Chemical Safety and Security Officer (CSSO):** The CSSO establishes a unified effort for safety and security management and provides guidance to people at all levels of the institution. The CSSO should be equipped with the knowledge, responsibility, and authority to develop and enforce an effective safety and security management system.
- **Laboratory Managers, Supervisors, and Instructors:** Besides the CSSO, direct responsibility for management of the laboratory safety program typically rests with the laboratory manager. In coursework, laboratory instructors carry direct responsibility for actions taken by students. Instructors must promote a culture of safety and security and teach the skills that students and other personnel need if they are to handle chemicals safely.
- **Laboratory Students and Staff:** Although they are guided by institutional leaders, students and other laboratory personnel are directly responsible for working safely and safeguarding the chemicals they use. Anyone working in a laboratory, student or employee, should follow all of the safety and security protocols for the protection of themselves and others.

Types of Hazards and Risks in the Chemical Laboratory

The new culture of laboratory safety and security emphasizes experiment planning that includes regular attention to risk assessment and consideration of hazards for oneself and others. Every worker in a laboratory should be informed about potential hazards and reduce them to a minimum as much as possible. An institution can approach an accident-free workplace by setting a goal of zero incidents and zero excuses.

Laboratories face a variety of risks, from both inside and outside the facility. Some risks may affect mainly the laboratory itself, but others could affect the larger institution and even the public if handled improperly.

Large-Scale Emergencies and Sensitive Situations

Many types of large-scale events can affect an institution and severely disrupt laboratory operations. Some of the most common large-scale emergencies and sensitive situations include the following:

- fire, flooding, and earthquakes;
- pandemic alert;
- power outages;
- travel restrictions;
- extensive absences due to illness;
- hazardous material spill or release;
- high-profile visitors;
- political or controversial researchers or research;
- intentional acts of violence or theft;
- loss of laboratory materials or equipment;
- loss of data or computer systems;
- loss of mission-critical equipment; and
- loss of high-value or difficult-to-replace equipment.

Security Breach

An institution must be aware of the potential for security breaches in the laboratory, either by personnel or by outside agents. Even unintentional security breaches pose a serious risk. Possible breaches include

- theft or diversion of mission-critical or high-value equipment;
- theft or diversion of dual-use chemicals or materials that may be utilized for weapons of mass destruction;

- threats from activist groups;
- accidental or intentional release of or exposure to hazardous materials;
- sabotage of chemicals or high-value equipment;
- release of sensitive information;
- rogue work or unauthorized laboratory experimentation; and
- other external threats.

Toxic Chemical Exposure

One of the least predictable, most dangerous risks that personnel face inside a laboratory is the toxicity of various chemicals. In the chemistry laboratory, **no substance is entirely safe** and **all chemicals result in some toxic effects if a large enough amount of the substance comes in contact with a living system**. Many chemicals display more than one type of toxicity. Table ES.1 lists the most common classes of toxic substances.

Table ES.1 Common Classes of Toxic Substances

Toxic Substance	Examples	Effects
Acute toxicants	Hydrogen cyanide, nitrogen dioxide	Cause a harmful effect after a single exposure
Irritants	Silyl halides and hydrogen selenide	Cause reversible inflammatory effects
Corrosive substances	Chlorine, nitric acid	Destroy living tissue by chemical action at the site of contact
Allergens and sensitizers	Diazomethane	Produce an adverse reaction by the immune system; affect people differently depending on their sensitivities
Asphyxiants	Carbon dioxide, methane	Interfere with the transport of an adequate supply of oxygen to vital organs of the body
Neurotoxins	Mercury, carbon disulfide	Induce an adverse effect on the structure or function of the central or peripheral nervous system; can be permanent or reversible
Reproductive toxins	Arsenic	Cause chromosomal damage or teratogenic effects in fetuses and have adverse effects on various aspects of reproduction, including fertility, gestation, lactation, and general reproductive performance
Developmental toxins	Organic solvents (toluene)	Act during pregnancy and have adverse effects on the fetus
Toxic substances	Chlorinated hydrocarbons	Affect organs other than those in the neurological and reproductive systems
Carcinogens	Benzene, chloromethyl methyl ether	Cause cancer after repeated or long-duration exposure; effects may become evident only after a long latency period

Flammable, Explosive, and Reactive Chemicals

Hazards from flammable, explosive, and reactive chemicals pose great risks for laboratory personnel. All laboratory personnel need to be aware of the likelihood of a fire or an explosion when in the presence of these chemicals.

- **Flammable chemicals** are those that readily catch fire and burn in air, and they may be solid, liquid, or gaseous. Proper use of flammable substances requires knowledge of their tendencies to vaporize, ignite, or burn under the variety of conditions in the laboratory. Preventing the coexistence of flammable vapors and an ignition source is the best way to deal with the hazard.

- **Reactive chemicals** are substances that react violently in combination with another substance. They include water-reactive substances, such as alkali metals; pyrophoric materials, such as finely divided metals; and incompatible chemicals, such as pure liquid or gaseous hydrocyanic acid and bases.

- **Explosive chemicals** include a variety of substances that can explode under certain conditions. They include explosives, organic azo compounds and peroxides, oxidizing agents, and certain powders and dusts.

Other explosion risks come from laboratory activities, not just the chemicals themselves. Explosive boiling, scaling up reactions, running new and exothermic reactions, and running reactions that require an induction period can also lead to explosions.

Biohazards

Biohazards are a concern in laboratories that handle microorganisms or materials contaminated with them. These hazards are usually present in clinical and infectious disease research laboratories but may also be present in other laboratories. Risk assessment for biohazardous materials requires the consideration of a number of factors, including the organism being manipulated, any alterations made to the organism, and the activities that will be performed with the organism.

Physical Dangers from Laboratory Equipment

Some laboratory operations pose physical hazards to personnel because of the substances or equipment used. The physical hazards in the laboratory include the following:

- compressed gases;
- nonflammable cryogens;

- high-pressure reactions;
- vacuum work;
- radio-frequency and microwave hazards; and
- electrical hazards.

Personnel also face general workplace hazards that result from conditions or activities in the laboratory. Potential physical hazards include cuts, slips, trips, falls, and repetitive motion injuries.

Hazardous Waste

Virtually every laboratory experiment generates some waste. Waste is material that is discarded or intended to be discarded, or is no longer useful for its intended purpose. A material may also be declared a waste if it is abandoned or if it is considered "inherently waste-like," as in the case of spilled materials. Wastes are classified as either hazardous or nonhazardous and may include items such as used disposable laboratory supplies, filter media, aqueous solutions, and hazardous chemicals. Wastes that pose potential hazards have one or more of the following properties: ignitability, corrosivity, reactivity, or toxicity.

Enforcing Laboratory Safety and Security

Safe practice by laboratory personnel requires continuing attention and education; it must be mandatory. A program of periodic laboratory inspections will help keep laboratory facilities, equipment, and personnel safe and secure. The institution's management should help design the inspection program and decide on the types of inspections, their frequency, and the personnel who will conduct them.

A comprehensive inspection program may include some or all of the following types of inspections:

- routine inspections of equipment and facilities, conducted frequently by all laboratory personnel;
- program audits conducted by a team that may include the laboratory supervisor and other management;
- peer inspections by laboratory coworkers from different departments;
- environmental health and safety inspections conducted on a regular basis;
- self-audits of practices and equipment; and
- inspections by external entities, such as emergency responders or regulatory bodies.

Barriers to Compliance with Safety and Security Procedures

There may be occasions when personnel do not comply with laboratory safety and security procedures, either intentionally or unintentionally. Some possible barriers to compliance include

- rapid turnover of students and staff who must be trained in safety and security procedures;
- variable levels of laboratory experience among students, staff, and even supervisors;
- a shortage of instructors or others who can train new students and staff;
- the time burden of adequate training and recordkeeping;
- the cost or limited availability of safety and security equipment;
- environmental conditions that make compliance difficult, such as climates that make personnel uncomfortable when wearing personal protective equipment;
- cultural beliefs that minimize the importance of individual health and safety; and
- the lack of private companies to discard dangerous wastes from laboratories.

Institutions must be aware of and address the possible barriers to compliance when designing safety and security policies and procedures.

Finding and Allocating Resources

Organizations to contact for information, training, and funding include the following:

- **The U.S. Chemical Security Engagement Program**
  www.csp-state.net
- **International Union of Pure and Applied Chemistry—Safety Training Program**
  www.iupac.org/standing/coci/safety-program.html
- **Federation of Asian Chemical Societies**
  www.facs-as.org
- **Organization for the Prohibition of Chemical Weapons**
  www.opcw.org
- **American Chemical Society—Division of Chemical Health and Safety**
  www.dchas.org
- **Arab Union of Chemists**
  www.arabchem.org (Arabic language)

- **Federation of African Societies of Chemistry**
  www.faschem.org
- **The American Chemistry Council**
  www.responsiblecare-us.com
- **The International Program on Chemical Safety INCHEM program**
  www.inchem.org
- **Strategic Approach to International Chemicals Management**
  www.saicm.org
- **Stockholm Convention on Persistent Organic Pollutants**
  http://chm.pops.int

What Can You Do to Improve Chemical Safety and Security?

Each institution shares the ethical, legal, and financial burden of ensuring that work conducted in its laboratories is carried out safely and responsibly. The institution must establish general guidelines for what constitutes safe and secure practices in laboratory work. It is responsible for setting standards and keeping records of any necessary training of laboratory personnel. Finally, the institution is responsible for developing and implementing laboratory policies and standards for emergency response procedures and training.

Each institution should develop its own safety and security management system based on the guidelines listed below. The manner and extent to which the individual elements of this framework are applied depend on the conditions of each institution.

Ten Steps to Establish a Safety and Security Management System

1. **Develop a safety and security policy statement.** Implement a formal policy to define, document, and endorse a chemical safety and security management system. A formal policy statement establishes expectations and communicates the institution's intent.
2. **Designate a Chemical Safety and Security Officer.** Designate a CSSO to oversee the safety and security management program. Give the CSSO dedicated time, resources, and the necessary authority to carry out his or her responsibilities. The CSSO should have direct access, when necessary, to the senior authorities accountable to the public.
3. **Identify and address particularly hazardous situations.** Conduct a risk-based evaluation to determine the impact and adequacy of existing control measures, prioritize needs, and incorporate corrective actions based on level of importance and available resources. The information

collected will provide the foundation for a robust safety management system, as well as help prioritize efforts to improve safety and security.

4. **Implement administrative controls.** Administrative controls define an institution's rules and procedures for safe and secure practices and establish the responsibilities of individuals involved. Administrative controls should also provide mechanisms for managing and responding to change, such as new procedures, technologies, legal requirements, staffing, and institution changes. These controls should include general safety rules, laboratory housekeeping procedures, manuals for use of materials and equipment, and other documents to communicate rules and expectations to all laboratory personnel.
5. **Establish procedures for chemical management.** Chemical management is a critical component of a laboratory safety program and includes defined procedures for
   - buying chemicals;
   - handling chemicals, including adequate ventilation, appropriate use of personal protective equipment (PPE), and institutional rules and procedures, especially for spills and emergencies;
   - storing chemicals;
   - inventory tracking of chemicals;
   - transporting and shipping chemicals; and
   - disposing of chemical waste.
6. **Employ Personal Protective Equipment and Engineering Controls.** Every institution must provide appropriate facilities and equipment for laboratory personnel. Engineering measures, such as a laboratory hood, local exhaust ventilation, or a glove box, are the primary methods for controlling hazards in the chemical laboratory. Personal protective equipment, such as safety glasses, goggles, and face shields, should supplement engineering controls.
7. **Train, communicate, and mentor.** The best way to create a culture of safety in the workplace is to set a good example every day by following and enforcing safety and security rules and procedures. It is vitally important to establish a system for training and mentoring all people working in the laboratory. Every institution should also establish effective channels for communicating about chemical safety with personnel at all levels of the institution. The materials in the toolkit accompanying this

book include case studies and other resources that are helpful for training laboratory managers and staff.

8. **Evaluate facilities and address weaknesses.** Design all laboratories to facilitate experimental work as well as reduce accidents. Safety and security must be considered when designing and maintaining a laboratory and its workspaces.
9. **Plan for emergencies.** Every institution, department, and individual laboratory should have an emergency preparedness plan. The steps in developing an emergency plan include the following:
   - assessing what types of incidents are most likely to occur;
   - identifying the decision makers and stakeholders, as well as laboratory priorities;
   - creating a plan for the types of emergencies identified in the first step; and
   - training staff in the procedures outlined in the plan.
10. **Identify and address barriers to safety and security compliance.** As discussed earlier, there are many barriers to compliance with safety and security systems, including changes in personnel and the conditions unique to a laboratory. The institution must identify these barriers and establish incentives for all laboratory personnel to comply with safety and security measures.

The culture of laboratory safety depends ultimately on the working habits of individual chemists and their sense of teamwork.

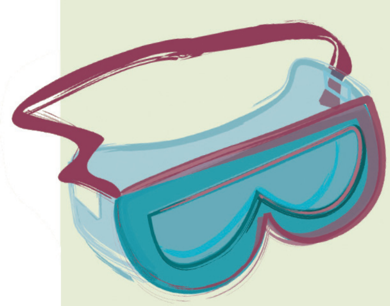
Chemical Safety and Security at the Laboratory Level

The culture of laboratory safety depends ultimately on the working habits of individual chemists and their sense of teamwork for protection of themselves, their neighbors, and the wider community and environment. Institutional leaders should require laboratory personnel to take the following steps to improve the culture of safety and security in the facility:

1. Preplan all experiments and follow institutional procedures on safety and security during planning.
2. Whenever possible, miniaturize chemical laboratory operations to reduce hazards and waste.
3. Assume that all chemicals encountered in the laboratory are potentially toxic to some degree.
4. Consider the flammability, corrosivity, and explosivity of chemicals and their combinations when performing laboratory operations.
5. Learn and follow all institutional procedures regarding safety and security.

1

The Culture of Laboratory Safety and Security



Over the past century, chemistry has increased our understanding of the physical and biological world, as well as our ability to manipulate it. Most of the items we take for granted in modern life involve synthetic or natural chemical processing, and the work carried out in chemistry laboratories around the globe continues to enable important advances in science and engineering.

Since the age of alchemy, laboratory chemicals have demonstrated dramatic and dangerous properties. In the past, martyrdom for the sake of science was acceptable. In an 1890 address, the great chemist August Kekulé said: "If you want to become a chemist, so Liebig told me, when I worked in his laboratory, you have to ruin your health. Who does not ruin his health by his studies, nowadays will not get anywhere in Chemistry."

Today, that attitude seems as ancient as alchemy. Over the years we have developed special techniques, procedures, environmental controls, and equipment for handling and managing chemicals safely. The development of a "culture of safety" has resulted in laboratories that are safe and healthy environments in which to teach, learn, and work.

Unfortunately, there is now growing concern about the possible use of hazardous laboratory chemicals by those seeking to perpetrate acts of terrorism. This security threat presents a new challenge to working with chemicals in the laboratory.

Creating a culture of safety and security rests on the recognition that the welfare of each individual depends on both teamwork and personal responsibility. This culture must become an internalized attitude, not just an external expectation driven by institutional rules.

Learning to participate in habitual risk assessment, planning, and consideration of worst-case possibilities—for oneself and one's fellow workers—is as much part of a scientific education as learning the

Editor's Note: Two icons appear frequently throughout this book:

Content available in Appendixes

Content available in the Toolkit

theoretical background or the step-by-step protocols for doing experiments. Nurturing basic attitudes and habits of prudent behavior is a crucial part of chemical education at every level and remains critical throughout a chemist's career.

Academic research and teaching laboratories have a unique responsibility to instill in their students a lifelong attitude of safety and security consciousness and prudent laboratory practice. Teaching such practices should be a top priority in the laboratory, as faculty prepare students for careers in industrial, governmental, academic, and health sciences laboratories. By promoting safety and security during the undergraduate and graduate years, faculty impact not just their students, but everyone who will share their future work environments.

A successful safety and security program requires a daily commitment from everyone in the institution.

A culture of safety and security within an institution forms a solid foundation on which a successful laboratory chemical management program can be built. A successful safety and security program requires a daily commitment from everyone in the institution. Individuals at all levels should understand the importance of eliminating the risk of exposure to hazardous materials in the laboratory and must work together toward this end.

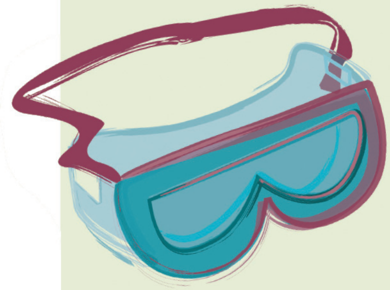
This book is written particularly for laboratory managers, who need guidance on developing a system for managing the day-to-day safety and security operations of a chemical laboratory. It provides specific information on acquiring, using, and disposing of laboratory chemicals, and guidance on fostering a culture of safety among laboratory staff and students.

Guide to This Book

This book consists of 11 chapters. Some readers may have an interest only in a particular chapter at any given time. However, the book is most effective if the reader moves through the chapters in order. A CD with a copy of this book and Appendix material can be found in the back of this book. It contains more detailed information and reference material that laboratory managers may find useful. In addition, the accompanying Toolkit contains educational resources to be used in conjunction with this book and for training activities involving laboratory staff and students.

2

Establishing an Effective Chemical Safety and Security Management System



2.1 Introduction

Establishing a culture of safety and security requires sustained commitment to high standards at all levels—from the top institutional leadership to the day-to-day laboratory worker. This chapter recommends a framework for integrating safety and security into small-scale chemical laboratories. Creating a safety and security management system will improve laboratory operations and anticipate and prevent circumstances that might result in injury, illness, or adverse environmental impact. How the individual elements of this framework are applied will depend on the size of the institution, the nature of its activities, and the hazards and conditions specific to its operations.

2.2 Whose Job Is It? Responsibility for Laboratory Safety and Security

Individuals within an institution have varying roles and responsibilities for establishing and maintaining safe and secure practices. Setting a good example is the best method for people at all levels to demonstrate their commitment.

2.2.1 Leaders

Responsibility for safety and security rests ultimately with the head of the institution and its operating units. In some cases, institutional leaders may be under legal obligations to provide a secure and safe working environment. Leaders can also make a difference in convincing workers to embrace a safety and security program. Workers will ignore even a well-conceived program if top management neglects it.

2.2.2 Chemical Safety and Security Officers (CSSOs)

Each institution should designate a chemical safety and security officer (CSSO). The CSSO establishes and supports a unified effort for safety management and provides guidance to people at all levels. The CSSO should be equipped with the knowledge, responsibility, and authority to develop and enforce an effective safety and security management system. More than one person may hold the position and share the responsibilities as necessary.

RESPONSIBILITIES OF THE CSSO

1. **Developing and following an integrated safety and security program over the life cycle of all laboratory chemicals**
   - Following the policies on laboratory chemicals and ensuring compliance with applicable regulations as required
   - Assisting in purchasing, storage, use, and waste disposal at the laboratory level
   - If required, operating a waste management program for offsite waste disposal; The program includes receipt of wastes, transportation, and final disposal of the material through commercial vendors
   - Logging orders of laboratory chemicals
   - Receiving chemicals and keeping an accurate inventory
2. **Auditing and inspecting for compliance**
   - Auditing inventory logs and cabinet security at least annually
   - In cases of noncompliance, suspending authorizations to use laboratory chemicals
   - Maintaining complete records of program standard operating procedures (SOPs) that can easily be retrieved, distributed, and inspected
3. **Managing and investigating incidents involving chemicals (spills, missing chemicals, injuries, etc.)**
4. **Training managers, supervisors, and workers to develop appropriate SOPs and comply with the safety program**

2.2.3 Environmental Health and Safety Office

Some larger institutions also have an environmental health and safety office staffed by one or more CSSOs and additional experts in chemical safety, engineering, occupational medicine, fire safety, toxicology, or other fields. Such an office assists in making policies and promoting laboratory safety standards. It often handles hazardous waste issues, accident reviews, inspections and audits, compliance monitoring, training, recordkeeping, and emergency response.

2.2.4 Laboratory Managers, Supervisors, and Instructors

Direct responsibility for the safety and security management program typically rests with the CSSO and the laboratory manager. In coursework, laboratory instructors carry direct responsibility for actions taken by students. Instructors are responsible for promoting a culture of safety and for teaching the skills that students and other workers need to handle chemicals safely.

RESPONSIBILITIES OF THE LABORATORY MANAGER OR SUPERVISOR

1. **Making sure laboratory workers receive training on general chemical safety and security.**
2. **Making sure laboratory workers understand how to work with chemicals safely. Provide chemical- and procedure-specific training, including how to develop and review SOPs.**
3. **Giving laboratory workers appropriate engineering controls and personal protective equipment (PPE) needed to work safely with chemicals.**
4. **Making sure that the laboratory has the appropriate level of security for chemicals.**
5. **Setting expectations for safety and security. Including safety and security in performance appraisals.**
6. **Reviewing and approving work with laboratory chemicals.**

2.2.5 Students and Workers

Although they depend on the guidance of their managers and teachers, students and other laboratory workers actually do the work. They must work safely and securely with the chemicals they use. Anyone working in a laboratory—student or employee—is responsible for following all of the safety and security protocols to protect themselves and others.

RESPONSIBILITIES OF STUDENTS AND WORKERS

1. **Attending laboratory safety training.**
2. **Reviewing written procedures and following these procedures.**
3. **Making sure to understand all of the hazards and safety and security protocols before working with a chemical or procedure for the first time. Reviewing or developing and approving SOPs.**
4. **Asking the laboratory supervisor or the CSSO if unsure about the hazards.**
5. **Using engineering controls and PPE as appropriate.**
6. **Reporting all incidents, security issues, and potential chemical exposures to the laboratory manager.**
7. **Documenting specific operating procedures for work with particularly hazardous chemicals or equipment. Amending procedures as needed.**

2.3 Ten Steps to Creating an Effective Laboratory Chemical Safety and Security Management System

One of the most important pieces of a successful safety and security management system is the commitment of institutional leaders. Leadership must take the first steps in creating a plan and assigning people to put the plan in place.

2.3.1 Create an Institutional Safety and Security Oversight Committee and Appoint a CSSO

The top institutional leader should create a committee to provide oversight for chemical safety and security in the institution. The committee should have representatives from all affected sections and at all levels. The committee should report directly to the top leaders and receive the necessary financial and administrative support.

The institution should also appoint at least one CSSO to oversee the safety and security management program. The responsibilities and accountability of the CSSO must be clearly defined and communicated to the CSSO and the institution's leadership, laboratory managers, workers, and students. (See Section 2.2.2. for more on the responsibilities of the CSSO.)

An effective CSSO must have dedicated time, resources, and the necessary authority to carry out his or her responsibilities. The CSSO should have direct access to the senior authorities who are ultimately accountable to the public. If the CSSO does not have direct access to senior level authorities, the institution should provide some other means of reporting to the leadership.

2.3.2 Develop a Chemical Safety and Security Policy

Institutional leaders should create a formal policy to define and document a chemical safety and security management system. A formal policy statement sets expectations and communicates the institution's support. The policy should state the intent to

- prevent or mitigate human and economic losses arising from accidents, adverse occupational exposures, and environmental events;
- build safety and security considerations into all phases of operations;
- achieve and maintain compliance with laws and regulations; and
- continually improve performance.

The institution should communicate and post the policy statement for employees and review and revise it as often as necessary.

2.3.3 Create Administrative Controls and Processes for Performance Measurement

Administrative controls define the specific safety and security rules and procedures and list the responsibilities of individuals involved. Administrative controls should also provide ways to manage and respond to change, such as new procedures, technologies, legal requirements, staff, and organizational changes.

The CSSO should develop general safety rules, laboratory housekeeping procedures, manuals for use of materials and equipment, and other documents to communicate expectations to all laboratory workers. These documents should also clearly define the individual responsibilities of laboratory students, workers, managers, institutional leaders, contractors, emergency service providers, and visitors.

Evaluating the safety and security of laboratory operations should be part of everyday activities. For example, begin all department or group meetings with a safety moment—discuss a daily activity, the safety or security concerns it presents, and what can be done to avoid potential incidents.

Begin all department or group meetings with a safety moment—discuss a daily activity, the safety or security concerns it presents, and what can be done to avoid potential incidents.

2.3.4 Identify and Address Particularly Hazardous Situations

Managers, principal investigators, lead researchers, team leaders, and supervisors should take active roles in managing the safety and security of their laboratories. Conduct an initial status review to assess the scope, adequacy, and use of safety procedures. Use the status review as a foundation to build a safety and security program and help set priorities for improvement. Perform a risk-based evaluation to determine the adequacy of existing control measures, to set priorities among needs, and to incorporate corrective actions according to importance and available resources.

SAMPLE POLICY STATEMENT

This university is committed to providing a safe and healthful environment for its employees, students, and visitors and to managing the university in an environmentally sensitive and responsible manner. We further recognize an obligation to demonstrate safety and environmental leadership by maintaining the highest standards and by serving as an example to our students and to the community at large.

The university will strive to improve our safety and environmental performance continuously by adhering to the following policy objectives:

- Developing and improving programs and procedures to ensure compliance with all applicable laws and regulations
- Making sure that personnel are properly trained and provided with appropriate safety and emergency equipment
- Taking appropriate action to correct hazards or conditions that endanger health, safety, or the environment
- Considering safety and environmental factors in all operating decisions, including those related to planning and acquisition
- Engaging in sound reuse and recycling practices and exploring feasible opportunities to minimize the amount and toxicity of waste generated
- Using energy efficiently throughout our operations
- Encouraging personal accountability and emphasizing compliance with standards, university policies, and best practices during employee training and in performance reviews
- Communicating our desire to improve our performance continuously
- Fostering the expectation that every employee, student, and contractor on university premises will follow this policy and report any environmental, health, or safety concern to university management
- Monitoring our progress through periodic evaluations

Adopted [date] by the Safety, Health, and Environment Committee

STEPS IN SECURING CHEMICALS OF CONCERN (COCs)

All laboratory security measures should suit the potential risks, avoid hampering research, and utilize local resources.

Laboratory security planning includes the following:

1. **Determine physical security needs: security guards, door locks (electronic or key), locked cabinets, alarm systems, et cetera.**
2. **Establish access permissions: who is authorized to use the materials.**
3. **Oversee access issues: key distribution and collection, et cetera.**
4. **Set expectations.**
5. **Question the presence of unfamiliar people in laboratories.**
6. **Report all suspicious activity.**
7. **Lock laboratory doors when the laboratory is not in use.**
8. **Follow security procedures, including replacing materials and securing them when not in use.**
9. **Prohibit unauthorized use of laboratory materials and facilities.**
10. **Train laboratory workers on security issues and expectations.**
11. **Include security issues in regular laboratory inspections.**
12. **Establish a protocol for reporting security concerns.**

For more information on general laboratory security, see Chapter 6.

To begin the process of creating an effective chemical management system, laboratory management should establish a list of all chemicals that are in the laboratory, especially *chemicals of concern* (COCs).

CHEMICALS OF CONCERN (COCs)

COCs are highly hazardous chemicals or chemicals that are potential precursors of highly hazardous materials. Typically, the list would include chemicals listed by the Chemical Weapons Convention, chemicals that have potential for mass destruction, explosives and precursors of improvised explosive devices, and chemicals of high acute toxicity (rated as Category 1 in the Globally Harmonized System of Classification and Labeling of Chemicals). See Chapters 6 and 8 for more information on setting up a chemical inventory.

See *Appendix A.1. Example List of Chemicals of Concern.*

2.3.5 Evaluate Facilities and Address Weaknesses

It is especially important to address the role of physical access control in improving the security of buildings in which chemicals are stored and used. This may require a security vulnerability assessment and policy setting. See Chapters 5, 6, and 7, respectively, for more information on laboratory facilities, laboratory security, and assessing hazards and risks in the laboratory.

2.3.6 Set Procedures for Chemical Handling and Management

Chemical management is a critical component of a laboratory program. Safety and security should be part of the entire life cycle of a chemical, including purchase, storage, inventory, handling, transport, and disposal. The overall process is described in more detail in Chapters 8 (managing chemicals), 9 (working with chemicals), and 11 (managing chemical waste).

Chemical management should include procedures for screening for COCs as part of the normal purchasing process. There should be an inventory process to track the use of a chemical until it is completely consumed or disposed of. The inventory and record keeping system are important to

1. Make sure that chemicals are secure by accounting for their use;
2. Provide a resource to consult for possible sharing of chemicals;
3. Provide information that allows managers to know when to reorder chemicals;
4. Provide the location of hazards in the laboratories for emergency responders;
5. Determine future needs and uses of chemicals; and
6. Minimize excess inventory and chemical waste quantities (which reduces costs).

All laboratory workers should be held accountable for following chemical use procedures. Managers should consider ways to recognize and reward those who exhibit the best practices for handling and working with chemicals. Managers may also need to consider enforcement tools when workers bypass the system.

2.3.7 Use Engineering Controls and Personal Protective Equipment

Engineering controls, such as a laboratory hood, local exhaust ventilation, or a glove box, are the primary ways to control hazards in the chemical laboratory.

Personal protective equipment, such as safety glasses, goggles, and face shields, should supplement engineering controls. Laboratory management should not allow an experiment to proceed if inadequate engineering controls or PPE are unavailable. More detailed guidance on chemical handling is provided in Chapters 9 and 10.

2.3.8 Plan for Emergencies

Laboratories should make plans to handle emergencies and unplanned incidents. Keep on hand emergency equipment and supplies, such as fire extinguishers, eye washes, safety showers, and spill kits. COCs may need special plans, such as antidotes for unintentional exposures (for example, atropine for organophosphorus agents). Some COCs may ignite spontaneously and require special fire-extinguishing methods. Emergency preparedness should involve local emergency responders, such as fire departments, to make sure they have the appropriate equipment and information. See Chapter 3 for more details on emergency planning.

2.3.9 Identify and Address Barriers to Following Safety and Security Best Practices

Good safety and security practices involve having people consistently follow policies and procedures. However, it is often challenging to change behaviors and foster a culture of best practices. Local social and cultural barriers may keep a laboratory manager, laboratory personnel, and others from following the best safety and security practices. Institutions must make an effort to address and overcome the barriers, as discussed in detail in Chapter 4.

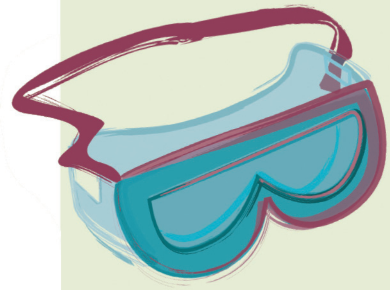
2.3.10 Train, Communicate, and Mentor

The CSSO is responsible for setting safety and security procedures and making sure that everyone knows about them and follows them. However, it takes a strong commitment by top leaders in the institution to create the best safety and security systems. Top leaders are ultimately accountable for chemical safety and security. They must create a culture that protects workers and the public.

See the accompanying *Toolkit* for educational tools that have been developed for training.

3

Emergency Planning



3.1 Introduction

Although most laboratory personnel are prepared to handle incidental spills or minor chemical exposures, many other types of large-scale emergencies can affect a laboratory. Emergencies may range from power outages to floods or intentional malicious acts.

There are four major phases to managing a large-scale emergency: mitigation, preparedness, response, and recovery:

1. The **mitigation phase** includes efforts to minimize the likelihood that an incident will occur and limit the effects of an incident that does occur. Mitigation efforts may be procedural, such as safe storage of materials, or physical, such as a sprinkler system.
2. The **preparedness phase** is the process of developing plans for managing an emergency and taking action to ensure that the laboratory is ready to handle an emergency. This phase might include storing adequate supplies, training personnel, and preparing a communications plan.
3. The **response phase** involves efforts to manage the emergency as it occurs and may include outside responders as well as laboratory staff. The effectiveness and efficiency of a response depends on everyone understanding their roles and having the supplies they need on hand. Training and planning ahead of time are therefore critical.
4. The **recovery phase** encompasses the actions taken to restore the laboratory and affected areas to their previous conditions so they may function safely again. This stage also provides an opportunity for a review of the other phases.

The four phases are interconnected. Each phase affects the other. The most important step in managing an emergency, however, is planning for one.

3.2 Developing an Emergency Preparedness Plan

Every laboratory should have an *emergency preparedness plan*. The level of detail of the plan will vary depending on the department and plans already in place. Planning follows several steps:

1. **Assess** what types of incidents are most likely to occur to determine the type and scope of planning required.
2. **Identify** the decision makers and stakeholders as well as laboratory priorities.
3. **Create** a plan for the types of emergencies identified in the first step, including a plan for how to handle communications.
4. **Train** staff in the procedures outlined in the plan.

Emergency planning is a dynamic process. Personnel, operations, and events change, and every possibility cannot be accounted for. Use the emergency preparedness plan as a guide that allows for some flexibility during an actual emergency. The steps for creating a plan are outlined in more detail in the following sections.

3.3 Assessing Laboratory Vulnerabilities

The first step in developing an emergency preparedness plan is to assess laboratory vulnerabilities. What kinds of emergencies are most likely? What is the possible impact of a major emergency on laboratory operations?

For each possible type of emergency, the laboratory manager and personnel should consider the history of occurrence in their laboratory and at laboratories with similar circumstances. The types of emergencies to consider vary depending on the type of laboratory, geographical location, and other factors unique to a facility. Focus more attention on events that have a higher likelihood and greater impact. The most common emergencies include the following:

- fire;
- natural disasters, such as floods or earthquakes;
- extensive absences of staff due to travel restrictions or illness;
- hazardous material spill or release;
- high-profile visitors;
- political or controversial researchers or research;
- intentional acts of violence or theft;
- loss of laboratory materials or of mission-critical, high-value, or difficult-to-replace equipment;
- loss of data or computer systems;
- loss of power for extended periods of time.

3.4 Identifying Leadership and Priorities

Put in place ahead of time a clear succession of leadership and priorities to help provide clarity in an emergency situation. Leaders need to be able to make decisions, set priorities, and put plans in motion.

3.4.1 Decision Makers

Determine who will provide leadership for the laboratory in case of an emergency. Designate an emergency coordinator to oversee emergency preparedness for the laboratory. The emergency coordinator will typically be the laboratory manager but could also be a senior-level researcher in the laboratory or other individual. Make a list of individuals authorized to make decisions, including financial commitments. Assume that there will be absences and include a succession. Keep in mind that in an emergency situation, the most practical leadership succession does not always follow the organizational chart. Make sure that the people on the list know and understand their responsibilities.

3.4.2 Essential Personnel

In an emergency, there may be a facility closure or travel bans that would prevent people from reporting to work. If the laboratory must remain at least partially operational and certain people must report to work, these staff members must be recognized as "essential personnel." Make sure that essential personnel understand and accept their responsibilities in an emergency, which may be different from their usual responsibilities. Make sure that essential personnel keep with them documentation from the institution stating their positions, which they may have to provide to a law enforcement officer.

3.4.3 Laboratory Priorities

Consider laboratory priorities ahead of time, to reduce the decision-making burden during an emergency. Think about what will happen to experiments and lab equipment if there were circumstances that placed limitations on lab operations. Review the operations and materials in the laboratory and make a list of items in order of most important to least important.

3.5 Creating a Plan

A thorough emergency preparedness plan includes details about the following:

- a laboratory survival kit;
- communications;
- evacuations;
- sheltering in place;
- loss of power;
- an institutional or building closure;
- community emergencies; and
- fire or loss of the laboratory.

Information for creating each of these parts of a plan is presented in the following sections.

3.5.1 Survival Kit

In the event that an emergency causes laboratory personnel to stay at work, keep a survival kit in the laboratory with the following items:

- a flashlight;
- a first aid kit.
- a radio and batteries; and

SAMPLE LABORATORY PRIORITY LIST

Priority 1: **Protect human life.** This includes both research and support staff.

Priority 2: **Protect research animals.** These include grant-funded research animals, thesis-related research animals, and other research animals.

Priority 3: **Protect property and the environment.** These include mission-critical property, high-value equipment, difficult-to-replace materials, and chemicals of concern.

Priority 4: **Maintain integrity of research.** This includes grant-funded research, thesis-related research, and other research.

EMERGENCY PREPAREDNESS PLAN CHECKLIST

- List of high-priority operations
- List of personnel who can perform these operations
- Communications plan
- Data backup plan
- Leadership succession
- Key dependencies within the organization (e.g., essential goods and services that other departments or groups provide) and alternatives
- Key dependencies outside the organization, with alternate vendors
- List of essential equipment, purchase records, and information on how to replace it permanently or temporarily
- Restoration plan and priorities

Laboratory personnel should have personal survival kits that contain the following items:

- a change of clothing and shoes;
- medications;
- contact lens solution;
- nonperishable snacks;
- drinking water; and
- a blanket or jacket.

3.5.2 Communications

One of the most important elements of emergency preparedness is the communications plan. Laboratory personnel should know how to find information, how to contact people, and what to expect in terms of communications, especially if regular means of communication are disrupted.

Check the web pages of organizations such as the International Red Cross for lists of materials to have on hand in case of an emergency that requires personnel to shelter in place.

3.5.2.1 *Contact List*

Institutions should have extensive contact information for key laboratory personnel who are familiar with the operations of the lab and can discuss them clearly with outside responders. Laboratory managers and others with emergency leadership roles should have up-to-date contact lists for all laboratory personnel that are accessible from both the laboratory and home.

Contact information should include whether or not each person can get to the laboratory easily during an emergency and his or her mode of transportation. Also include the name and contact information for at least one friend or family member for each individual.

See *Forms: Laboratory Emergency Information Sheet* in the accompanying Toolkit.

3.5.2.2 *Communications Methods*

There are many ways to communicate during an emergency. Each institution, department, and laboratory group should have a communications plan that explains which means of communication may be used. Laboratory personnel should be aware of the plan and know what to expect and what is expected of them.

- **Telephone:** The telephone is often the most direct way to contact people. Consider a mass notification system that sends voice messages to several phone numbers at the same time or a simple telephone chain for sharing information. Hotlines with recorded messages from a person in charge are also helpful. However, during large-scale emergencies, telephone systems may quickly become overloaded or unusable. Instruct laboratory personnel to limit their use of phones during such times and use other forms of communication. Do not rely only on telephones for communication of important instructions or information.
- **Text messages:** Text messaging can be more reliable than cellular phone service during a large-scale emergency. Text messages can be sent via cell phone or e-mail. Collect the text message information for all laboratory personnel in the contact list.
- **E-mail:** Collect a non-work e-mail address for each person in the lab, in the event the institution's computer system is affected by an emergency. Prepare a Listserv or e-mail list for use during an emergency.
- **Internet and blogs:** Posting updates on the institution or laboratory web site or blog is an easy way to reach multiple people. Instruct individuals to visit the site in the event of an emergency.

WAYS TO ESTABLISH GOOD COMMUNICATION WITH OUTSIDE RESPONDERS

- Invite responders to the facility for a tour of the areas of most concern.
- Provide information about areas of greater risk of fire, spill, or other emergency.
- Provide maps and other tools to help them navigate the facility and familiarize themselves with the locations of laboratory buildings or special facilities.
- Inform responders and local hospitals of the presence of hazardous chemicals.

3.5.2.3 *Assembly Point*

Establish an assembly point for laboratory personnel. In an emergency, essential personnel would be expected to report to that assembly point whether or not they received specific instructions.

3.5.2.4 *Media and Community Relations*

Some emergencies, regardless of their extent, may attract attention from the media. Make sure that the institution or laboratory has a spokesperson to handle any conversations with reporters. In the event of a serious chemical incident that affects the community, public communications may be handled by the department chair.

3.5.2.5 *Outside Responders*

Some emergencies require police, fire, or ambulance crews or other outside responders. Establish good communication with these responders in advance of emergencies.

3.5.3 Evacuations

Fires, spills, and other emergencies may require evacuation of the laboratory. All laboratory staff should be aware of the facility's evacuation procedures.

3.5.3.1 *Shutdown Procedures*

Some operations, materials, or equipment could pose a risk if left unattended for an extended period. Set procedures for shutting down processes, experiments, or equipment during an evacuation.

1. Make a list of processes that need to be shut down prior to evacuation. Post the procedures in a conspicuous place, such as exits, and make sure that all laboratory personnel are aware of them.
2. Note the risks of experiments left unattended for an extended period. For routine procedures that fit into this category, create protocols for safely terminating the procedure prior to evacuation.
3. In the event a proper shutdown is not conducted prior to an evacuation and may pose a risk to health, property, or the environment, inform

emergency responders. Emergency responders may escort a person into the laboratory to shut down the process, or they may ask for advice on how to do so themselves.

3.5.3.2 *Evacuation Routes and Assembly Points*

Post main and alternate evacuation routes, as well as assembly points for each section of a building or laboratory group. At the assembly point, the designated emergency coordinator should account for all staff and should advise emergency responders. Laboratory managers should make sure that all personnel are familiar with the evacuation routes and assembly points.

3.5.4 Sheltering in Place

For certain emergency situations, emergency responders may advise people to shelter in place, or remain inside the building. Inside the laboratory, post the following actions to take when directed to shelter in place:

1. Go or stay inside the building.
2. Do not use elevators.
3. Close and lock doors and windows.
4. If possible, go to a location within the building that has no exterior doors or windows.
5. If possible, monitor the situation by radio, Internet, or telephone.

3.5.5 Loss of Power

Consider the effects of short-term and long-term power loss and make plans to minimize negative outcomes.

3.5.5.1 *Short-Term Power Loss*

Sometimes the outcome of a short-term power loss may be more than just an inconvenience. For example, some equipment must be restarted manually after a shutdown, resulting in long-term power loss. During a short-term power loss when laboratory personnel are present, take the following actions to reduce the impact of the emergency:

1. **Turn off equipment,** particularly if leaving before power is restored. Some equipment can be damaged if turned on abruptly once power comes back online. If no one is in the laboratory when the power is restored, equipment that turns on will be running unattended.
2. **Discontinue operations requiring local ventilation,** such as chemical fume hoods. The building ventilation system may not be on emergency power.
3. **Close chemical fume hood sashes.**

3.5.5.2 *Long-Term Power Loss*

Develop plans to minimize the effects of a long-term power loss on the following laboratory systems:

- **Security systems:** For specialized security systems, such as card readers or electronic locks, determine whether locks are locked or unlocked in the event of power failure. Make a backup plan for laboratory security in the absence of these systems.
- **Environmental and storage conditions:** The most common problem during a power outage is storage of materials that require specialized environmental conditions, such as refrigeration and humidity controls. Make a backup plan to avoid either destruction of the materials or harm to others through exposure to the materials.
- **Running experiments:** Experiments that rely on power may have to be discontinued and disassembled. Assign a person the responsibility for walking through the laboratory to identify problems and ensure that materials are safely stored.

3.5.5.3 *Planning for Power Loss*

Consider these options to plan for a power loss and minimize its effects:

- **Generator power:** If the laboratory is connected to a generator, find out what will continue to run during a power loss, such as emergency lighting, security systems, ventilation systems, or all systems. Ask about the possibility of connecting certain equipment to the generator. Find out how long the laboratory can rely on the operating generator. Be aware that with a generator, there is usually a slight delay, up to several seconds, from the time the power is lost to the time that the power load is taken up by the generator. A generator may not be the right solution for equipment that is sensitive to a minor power disruption.
- **Uninterruptible power supply:** When generator power is not available or if equipment is sensitive to the slight power delay, uninterruptible power supply (UPS) systems may be the right choice for continued power. UPS systems are composed of large rechargeable batteries that immediately provide emergency power when the main supply is interrupted. UPS systems come in a variety of types and sizes. When purchasing a UPS for equipment other than a computer, talk with the equipment manufacturer to help choose the right solution.
- **Dry ice:** Dry ice may be helpful in maintaining temperatures in refrigerators or freezers. Because demand for dry ice increases significantly during

a power loss, have a list of multiple vendors. To conserve resources, prioritize experimental materials needing refrigeration and combine them as much as possible.

3.5.6 Institutional or Building Closure

Some emergencies may require closure of the laboratory. Ensure that certain laboratory personnel have been designated and trained as essential personnel (see Section 3.4.2). Take the following steps to prepare for short- and long-term closures:

- **Short-term closure:** For laboratory closures lasting a day or less, the main concerns include security and unattended experiments. If the closure is unexpected, experiments may be left running. Plan for problems that may occur with running processes.
- **Long-term closure:** Consider the impact of a long-term closure on research and services provided to outside groups. Inform such groups about service disruptions.

  During a long-term closure, it may be possible to share another laboratory or set up a temporary laboratory elsewhere. Make a list of essential items for an alternative facility:

  - equipment and materials needed to perform priority tasks;
  - space;
  - environmental controls for temperature, humidity, et cetera;
  - security requirements; and
  - ventilation requirements.

3.5.7 Emergencies Affecting the Community

When an emergency affects the local community or a larger area, resuming normal laboratory operations may take a long time. The laboratory may be indirectly affected by a community emergency when goods and services are unavailable. Take these steps to plan for community emergencies.

- **Disruption of deliveries of goods and services:** As part of the planning process, consider the following:
  - Prepare a list of alternate vendors and service providers in the event that the primary vendors are unavailable.
  - Ensure that primary vendors have up-to-date business continuity plans.
  - Ensure that the institution or laboratory is a priority for your primary vendors and service providers.

- **Laboratory staff shortage:** Staff may not be able to report to the laboratory. For continuity of laboratory operations, make sure that workers are cross-trained to be able to fill in for a person who is absent. Have a succession plan that clarifies who is responsible when supervisors are not available.

3.5.8 Fire or Loss of the Laboratory

Even when fire does not damage the laboratory directly, it may result in service disruptions, limited access to the laboratory, or damage caused by smoke, water, or fire-extinguishing materials. Take these steps to plan for fire loss:

1. Assess the vulnerabilities within the laboratory. Take action to prevent fire (see Chapters 8 and 10 for more information on fire prevention).
2. Make sure that there is an adequate level of detection and, where possible, that there are extinguishing systems. Take additional steps to limit the impact of a fire.
3. Think about how the laboratory would manage after a fire and make plans for continuing operations. Keep records for both the existing equipment and replacement equipment. Know what alternatives are available and where to get them to speed up the resumption of laboratory activities.

Laboratory staff may have to suspend work because of emergencies in structures nearby.

3.6 Emergency Training

All laboratory personnel should be trained in what to do in an emergency. Topics may include the following:

- evacuation procedures;
- emergency shutdown procedures;
- communications during an emergency;
- the location of fire extinguishers and spill control equipment, and how and when to use them;
- how to report a fire, injury, chemical spill, or other emergency and how to summon emergency response;
- the location of emergency equipment such as safety showers and eyewash units;
- the locations of all available exits for evacuation from the laboratory;
- how police, fire, and other emergency responders handle laboratory emergencies and the role of laboratory personnel in emergency response;

- security issues;
- protocol for absences due to travel restrictions or illness;
- safe practices for power outages;
- shelter-in-place procedures;
- protocols for handling suspicious mail or phone calls; and
- laboratory-specific protocols relating to emergency planning and response.

Include as part of the training program periodic drills to assist in training and evaluation of the emergency plan. Conduct fire drills and test the alarm systems regularly. Conduct other drills or exercises that allow laboratory personnel to simulate their responses to an emergency. These drills and exercises may be full-scale, where people are expected to carry out their responsibilities and procedures; tabletop exercises, where individuals discuss their response but do not physically take action; or a combination of both.

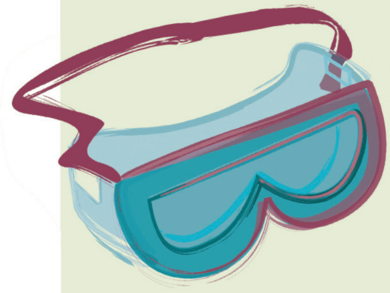
Laboratory personnel should know their levels of expertise when using fire extinguishers and emergency equipment, dealing with chemical spills, and handling injuries. They should not take actions outside the limits of their expertise but instead should rely on trained emergency responders.

The above information should be available in descriptions of laboratory emergency procedures and in the institution's chemical hygiene plan. Laboratory supervisors should make sure that all laboratory personnel are familiar with this information.

See *Appendix B.1. Sources of Chemical Information.*

4

Implementing Safety and Security Rules, Programs, and Policies



4.1 Introduction

Setting rules, programs, and policies for laboratory safety and security works best when institutional leaders enforce them and when laboratory managers and workers follow them. Incentives are needed to make sure that people understand and follow rules, programs, and policies. Institutions also need to identify the barriers to chemical laboratory safety and security and find ways to overcome them.

4.2 Essential Administrative Controls

Essential administrative controls include the following:

- **clearly defined and communicated rules, programs, and policies,** including
  - general safety and security rules;
  - housekeeping procedures;
  - manuals for the use of materials and equipment;
  - documents that clearly define the individual responsibilities of laboratory students, workers, managers, institutional leaders, contractors, emergency service providers, and visitors;
  - performance measurements for all staff; and
  - enforcement and incentive policies for all staff.
- **a program of performance measurements,** which should include
  - regular inspections;
  - incident reporting;
  - incident investigation; and
  - incident follow-up.
- **a policy of enforcement and incentives,** including
  - rule, program, and policy enforcement; and
  - recognition and reward.

The performance measurement program should emphasize fact finding, not fault finding.

The performance measurement program should emphasize fact finding, not fault finding. This principle applies to all the safety and security programs and policies described in other chapters of this book. Starting and maintaining a good performance measurement system will help to do the following:

- give organization leaders useful information about the effectiveness of safety and security systems and about needs for improvements;
- give designated safety and security personnel the authority to collect incident reports and to report incidents to higher authorities for action;

- detect patterns of unsafe behavior and facilities, find methods to improve safety and security, and initiate new rules and regulations to protect workers and students;
- increase awareness of safety issues to encourage a culture of improved safety and security;
- give current information to safety officers so that training of all laboratory workers can be improved and specific guidance can be given to individual workers; and
- give information to laboratory leaders so that they can learn how to use, test, and purchase appropriate personal protective equipment (PPE) and other types of equipment to improve safety.

The elements of a performance measurement system and an enforcement and incentive policy are discussed in more detail in the following sections.

4.3 Inspections

A crucial part of a performance measurement system is a program for regular inspections of all safety and security practices and facilities. However, conducting an inspection is just the first step. An institution must resolve issues to achieve a safer and more secure status. It is essential to document and share with staff the results of inspections and the resolutions of problems.

See *Appendix C.1. Types of Inspection Programs, C.2. Elements of an Inspection,* **and** *C.3. Items to Include in an Inspection* **for more information about inspections.**

See *Forms: Inspection Checklist* **in the accompanying Toolkit.**

Conducting inspections also gives chemical safety and security officers (CSSOs) opportunities to notice and reward best practices and to communicate them to the larger scientific community. Leaders of the institution may want to authorize CSSOs to recommend individuals or groups for special recognition and even material reward. See Chapter 2 on management systems for more information about the responsibilities of CSSOs.

4.4 Incident Reporting and Investigation

As part of a performance measurement system, every institution should set up a process for incident reporting and investigation. This process should emphasize the free exchange of information, without penalty to the people who report an incident. The objectives of an incident reporting process are to help people feel comfortable sharing information about problems they have noticed and to promote the idea that laboratory workers' personal safety is paramount.

The hardest part of starting a good reporting process is to convince personnel to report problems. Personnel must have confidence in the fairness and objectivity of their organization's leaders. An institution's leaders should see the reporting system as a method of educating and training valuable, safe, and skilled workers and students, not as a means of justifying punishments. The institution may have to make a fundamental cultural change to conduct bold and open discussions among employees, students, and leaders. Credibility is established by actions. If an organization's leaders use accident or incident reports as the basis of punishments against particular people, personnel will never trust and use the reporting system.

4.5 Enforcement and Incentive Policies

Both positive and critical feedback are necessary to make sure that safety and security rules are properly enforced. An enforcement and incentive policy should list the consequences of not reporting incidents and of not complying with safety and security rules. It should also outline the rewards for reporting and following rules and procedures. Giving rewards to individuals and groups that display consistent safe behavior reinforces the desired behavior. An institution should encourage workers and students to speak up when they witness incidents, lapses in following safety rules, or outright violations. Laboratory incidents such as sink fires, chemical hood fires, chemical spills, waste disposal accidents, and safety shower activations need to be reported to a CSSO and the laboratory supervisor. These types of incidents should not be considered trivial even if there is no serious consequence, such as a fire or a serious injury.

There are three general categories of incidents that should be reported and addressed immediately: safety violations, security violations, and suspicious activity.

4.5.1 Safety Violations

Laboratory supervisors are responsible for reporting safety violations in their laboratories. Supervisors should fill out a form that indicates clearly the names of the people involved, the name of the department, the date and time of the incident or violation, and details of the factors that contributed to the violation. Penalties for not reporting should be severe enough to discourage hiding safety incidents and violations.

4.5.2 Security Violations

All security violations, small or large, need to be reported in writing to the appropriate authorities. Reporting security incidents helps to improve security systems, which has immense value. People who report security violations immediately should be rewarded.

4.5.3 Suspicious Activity

All personnel should be trained to look out for suspicious activities or people. They should learn to report such activities in a timely manner. People who report suspicious activity should receive special recognition from institutional leaders.

See *Forms: Incident Report* in the accompanying Toolkit.

4.6 Best Practices of a Performance Measurement Program

4.6.1 Reporting Inspection Outcomes

The institution should encourage the laboratory community to report outcomes of inspections. Positive recognition of good practices during an inspection will help encourage a culture of safety and security.

4.6.2 Protecting Those Who Report Incidents

An institution should create clearly written rules to protect those who witness and report a safety or security incident or suspicious activity. Most of the time, when witnesses do not come forward to make a report, it is to avoid conflict with others. Reporting rules should provide complete protection from punishment and anonymity to witnesses, if required.

4.6.3 Maintaining Accessible Reporting Methods

Reporting forms should be clear, easy, and quick to complete. Long, tedious forms may discourage workers and students from using the reporting system. As part of their basic and continuing safety training, all workers and students need instruction on when and how to fill out the form. The safety committee for the institution should create procedures to receive reports and take appropriate and timely action. Institutions should also consider allowing anonymous incident reports. There should be a secure place, web site, or designated third party where people can confidentially file reports of incidents or questionable safety actions.

The purpose of filing incident forms is not to lay blame, but to make it possible for the CSSO and other leaders to address basic safety and security problems and to evaluate and modify the rules for laboratory safety and security.

4.6.4 Conducting Investigations

Institutions should use investigations to establish the facts of an incident, determine the cause of a problem, and recommend improvements. Investigations should follow a process established by the safety committee. All incidents should be investigated, but the seriousness of an incident determines the depth of each investigation. For example, a minor incident may require only a phone call or a short interview with an individual or group. The findings of all investigations should be put in writing.

4.7 Twelve Approaches to Following Best Practices

It is challenging to change behaviors and foster a culture of best practices. Local social and cultural barriers may keep a laboratory manager, laboratory personnel, students, and others from following the best safety and security practices. This section discusses approaches that can be used to change poor behaviors and improve laboratory safety and security.

4.7.1 Setting Organizational Safety Rules, Policies, and Implementation Strategies

Following best practices requires clear rules, policies, and processes that institutional leaders, safety and security officers, and laboratory managers have all agreed to. It is also critical that key stakeholders in the organization agree to a clear, direct strategy for implementing rules. Rules need to be approved by the highest authorities, such as a board of governors or trustees, if they are to be legitimate and legally binding. Rules should be printed and circulated as official institutional documents from the office of the chancellor or president.

4.7.2 Coping with Limited Financial Resources

Creating and improving a best practices system requires sustained financial support. However, increasing safety does not have to be expensive. Strong leadership can lead to changes in personal behavior that result in improved chemical safety and security. Changing personal behavior can be an effective and inexpensive way to improve chemical safety and security.

4.7.3 Adjusting for Climate

Many best practices for chemical safety and security were developed with temperate climates in mind. In some developing countries, heat and humidity are excessive during most of the year, and mechanical ventilation and air conditioning are not always available. Recommended safety practices and rules need to be adjusted to keep people comfortable while they work. For example, one university in the Philippines made it possible for laboratory staff to work in humid conditions by purchasing anti-fog chemical splash goggles.

4.7.4 Providing Training and Education

People require training to become aware of potential hazards. No one should be allowed to work in a chemical laboratory without adequate training in laboratory standard operating procedures. A laboratory manager should use educational tools to foster best practices. For example, case studies can be developed and used to train laboratory personnel.

Laboratory personnel should be comfortable asking safety and security officers for expert advice on what to do, before they proceed with risky actions. Safety and security officers should have updated and adequate knowledge to guide others. These officers may be sent to civil defense organizations or other public agencies for training.

Scientific leaders, safety and security officers, and others in authority also need to be careful when writing directions and instructions that they distribute. Material that is distributed should be checked for accuracy and thoroughness. Sloppy, offhand, or ill-informed instructions can be harmful.

See *Instructor's Guide* in the accompanying Toolkit for various classroom lessons on laboratory safety and security.

4.7.5 Encouraging Rest and Well-Being

Working while physically or mentally tired is one of the main causes of laboratory accidents and lapses in security. Workers and students need to look out for each other and encourage ill or exhausted coworkers to leave the laboratory and get rest or sleep so that they will be able to meet the stress and effort of work. The institution should support workers and students in participating in interesting, extracurricular activities on a regular basis to reduce mental stress and achieve a better-balanced life. Happy, rested workers are productive and safe.

4.7.6 Enforcing Consequences for Risky Behavior

The institution should widely publicize, in advance, all rules for safe behavior and the penalties for their violation. If people know that negligent or deliberate risky behavior or violations in security will have no consequences, they will have little incentive to change their habits. Consequences of safety or security violations might include publication of the violations, restrictions on use of laboratory facilities and equipment, monetary fines, withdrawal of financial support, or job termination. Consequences should fit the severity of the violations. To promote adherence to rules, leaders also need to reward people who have consistently taken safe actions and behaved responsibly. A reward might be money or favorable recognition.

4.7.7 Relieving Time Pressures and Avoiding Shortcuts

Trying to do laboratory processes too fast can lead to mistakes and accidents or incidents. Shortcuts in standard operating procedures can compromise safety. Supervisors and laboratory leaders need to be aware of the time required to complete assigned work. They should avoid increasing demands for productivity or speed. In designing experiments, supervisors should consult with workers to allow the proper amount of time required for every step of an experiment. Adequate time is needed to do things the right way. Additional education and training may be required to give people incentives to avoid dangerous shortcuts. Every person in a laboratory should learn about the consequences of shortcuts and the penalties for taking them. Coworkers should learn to encourage each other to work safely.

4.7.8 Taking Special Safety Precautions for Women

Women require additional safety measures to protect their reproductive health. For example, certain chemicals are reproductive toxins that women should not handle. Institutional leaders must make sure that female laboratory personnel have the appropriate guidelines, training, and equipment needed for their safety and security.

In addition, cultural traditions might keep men from giving women physical assistance that they need in emergencies. In case of such situations, laboratory safety and security offices should hire a mix of women and men.

4.7.9 Protecting People in All Job Categories

It is important that the laboratory provide adequate PPE and training to all people exposed to or handling hazardous chemicals, so staff may avoid harm to their health in the line of duty. This includes everyone from the trained chemists working in the laboratory to people in lower job categories who might be cleaning glassware, classrooms, or laboratories. Institutional leaders need to become role models for fair, objective, and humane treatment of all workers and students.

In some cases, leaders may be legally obligated to take such measures. Large personal fines or even prison sentences may be put in place if leaders do not provide a safe and secure working environment for students and staff.

4.7.10 Accommodating Propriety in Dress and Behavior

All laboratory staff and visitors should be educated about the need to wear proper clothing and protective shoes. They should have ready access to proper clothing for the laboratory, such as lab coats and gloves, even if they prefer to wear traditional clothing outside. Emotions and modesty may discourage people, particularly women, from taking safety precautions if they have been splashed with hazardous materials. Some people may not want to remove contaminated clothing immediately or use safety showers properly. To accommodate proprieties in dress and behavior, modesty curtains should be added to safety showers, and a supply of replacement clothing should be kept nearby. It may also be necessary for institutions to provide separate laboratory times or locations for male and female students. An institution may need to specially design personal protective clothing and equipment that can fit under or over traditional attire.

4.7.11 Confronting Coworkers or Superiors

Laboratory workers may witness safety or security violations, but be fearful about confronting coworkers and authorities. These are normal feelings and reactions that should be countered by providing anonymity for informants whenever possible, protecting informants, and preventing reprisals.

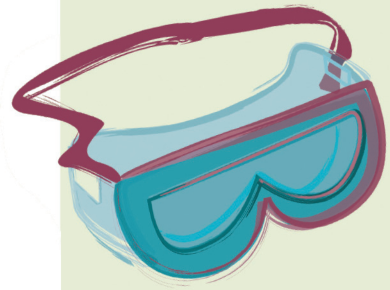
Proper handling of such a situation depends heavily on having clear, published rules and an objective, fair, well-publicized and understood strategy for investigating incidents and administering the consequences. The messenger should not be blamed, but rather thanked for a valuable service.

4.7.12 Looking Out for Coworkers

Institutions should establish specific rules or strong guidance in when and how to help others and oneself in emergencies. Most importantly, personnel and students should be encouraged to cooperate with others to prevent accidents and emergencies. All laboratory workers and students should also receive education on the importance of both wearing PPE and using it properly, which are critical laboratory safety rules.

5

Laboratory Facilities



5.1 Introduction

All laboratories should be designed to facilitate experimental work as well as reduce accidents. Laboratory workers must understand how the facilities operate. All trained personnel need to understand the capabilities and limitations of the ventilation systems, environmental controls, laboratory hoods, and other exhaust devices and know how to use them properly. Experimental work should be viewed as part of the entire laboratory and its facilities, for both safety and efficiency.

5.2 General Laboratory Design Considerations

5.2.1 Relationship Between Wet Laboratory Spaces and Other Spaces

Modern laboratories often include wet laboratories and other spaces with varying degrees of chemical use and hazards.

- Wherever possible, separate wet chemical areas or those with a higher degree of hazard from other, low-hazard areas by means of a physical barrier, such as a wall, divider, or control device.
- When such areas cannot be physically separated, or where the risk cannot be eliminated completely, the chemical safety and security officer (CSSO) will have to evaluate the level of protection required to control the risk of exposure in the low-hazard areas. For example, personnel in a computer lab may need to wear eye protection if they are located too close to an area in which hazardous chemicals are being handled.

5.2.2 Relationship Between Laboratory and Office Spaces

Almost all laboratory workers need office support space located near the lab. Whenever possible, locate all offices outside of the laboratory to allow a safer and quieter workspace. Place the office zone very close to or adjacent to the laboratory for easy access and communication.

If the laboratory must have office spaces within the research areas, create an obvious separation between the laboratory area and the office area using partitions or, at a minimum, aisle space. Provide an office exit that does not pass through laboratory space.

5.2.3 Shared Spaces

Some equipment may be shared by researchers and research groups. Locate shared equipment in a space that is not part of an individual's work zone. If the equipment is located near a lab, it can be walled off to reduce noise. Specific pieces of equipment, such as freezers and incubators that contain very valuable samples, should be equipped with alarms. Determine which pieces of equipment must be dedicated to specific users and not shared.

Equipment that may be shared includes

- HPLCs;
- Ice machines;
- Weigh enclosures;
- NMRs;
- Balances;
- Incubators;
- Gas chromatographs;
- Centrifuges;
- Refrigerators, freezers;
- Mass spectrometers;
- pH meters; and
- Ovens.

Note: HPLC = high-performance liquid chromatography;
NMR = nuclear magnetic resonance.

5.2.4 Noise and Vibration Issues

During the early planning stages of a laboratory, choose the best location for any piece of equipment that makes a lot of noise or is sensitive to vibrations. Large equipment, such as centrifuges, shakers, and water baths, often works best in separate equipment rooms where the equipment may be seen but not heard.

Another consideration is the allowable vibration tolerance. Most analytical equipment, such as nuclear magnetic resonance (NMR) spectrometers, sensitive microscopes, mass spectrometers, and equipment using lasers will require vibration isolation tables and/or an area that is structurally designed to minimize vibration. Clarify the requirements for these tolerances with the equipment manufacturer.

5.2.5 Safety Equipment and Utilities

1. Each laboratory should have one or more each of safety showers, eyewash units, and fire extinguishers easily accessible to laboratory personnel. See *Appendix I.1. Precautions for Working with Specific Equipment* for more information.
2. Sprinkler systems may be required and are recommended. For areas with water-sensitive equipment or materials, consider pre-action systems as opposed to dry or alternative systems that do not function with laboratory hoods and other ventilation.
3. Locate utility shutoff switches outside or at the exit of the laboratory. Room purge buttons should be located at exits in laboratories with hoods.

Safety shower and eyewash may be installed as one unit.

Fire extinguishers and fire alarms are standard safety equipment for laboratories.

4. Install abundant electrical supply outlets to eliminate the need for extension cords and multiplug adapters. Place electrical panels in an accessible area. Install ground fault circuit interrupters (GFCIs) near sinks and wet areas.
5. Provide appropriate emergency power in case of outages.
6. Where possible, install chilled water loops for equipment that requires cooling to save energy, water, and sewer costs.

See *Appendix D.1. Design Considerations for Casework, Furnishings, and Fixtures* **for more information on laboratory fixtures and furnishings.**

5.3 Laboratory Inspection Programs

Every institution should conduct a program of periodic laboratory inspections to maintain the safety of laboratory facilities, equipment, and personnel. For more information on inspection programs, see Chapter 4.

See *Appendix C.1. Types of Inspection Programs, Appendix C.2. Elements of an Inspection,* **and** *Appendix C.3. Items to Include in an Inspection* **for more information about inspections.**

See *Forms: Inspection Checklist* **in the accompanying Toolkit.**

5.4 Laboratory Ventilation

The laboratory ventilation system is critical to controlling airborne chemicals in the laboratory. A well-designed laboratory ventilation system should include, at a minimum,

- adequate heating and cooling for personnel comfort and equipment operation, and
- a differential between the amount of air exhausted from the laboratory and the amount supplied to the laboratory to maintain a “negative” pressure between the laboratory and adjacent non-laboratory spaces. This pressure differential prevents chemical vapors from leaving the laboratory in an uncontrolled way.

5.4.1 Ventilation Risk Assessment

There are many devices that may be used to control exposure or atmospheric buildup of laboratory materials. A risk assessment helps to determine the best choice for a particular operation or material.

For all materials, the objective is to keep airborne concentrations below established exposure limits (see Chapter 7). Where there is no established exposure limit, where mixtures are present, or where reactions may result in products that are not completely characterized, it is best to keep exposures as low as reasonably achievable. This is the ALARA (as low as reasonably achievable) principle.

A flexible exhaust vent carries fumes outside.

- For **chemicals,** find out whether the material is flammable or reactive or if it poses a health hazard from inhalation. If any chemical poses a risk, look at the physical properties of the chemical, specifically its *vapor pressure* and *vapor density.*
  - Check the vapor pressure of a chemical. A low vapor pressure (less than 10 mm Hg) indicates that the chemical does not readily form vapors at room temperature and general lab ventilation or an alternative such as the elephant trunk or snorkel may be appropriate. A high vapor pressure indicates that the material easily forms vapors and may require the use of a ventilated enclosure, such as a laboratory hood.
  - Check the vapor density compared to air, which is 1. A chemical having a vapor density greater than 1 can be controlled with a laboratory hood or a ventilation device that draws air from below, such as a downdraft table, slot hood, or elephant trunk with the exhaust aimed low. A chemical with a vapor density less than 1 will need a ventilation device that draws air from above, such as an elephant trunk or snorkel with the exhaust aimed above.
- For **radioactive or biological materials,** think about whether operations could cause the materials to aerosolize or become airborne and whether this poses a risk to health or to the environment. Determine whether filtration or trapping is required or recommended.
- For **particulates,** a laboratory hood or similar equipment with higher air flow may be too turbulent. Weighing boxes or ventilated balance enclosures are a better fit.

- For **nanomaterials,** consider whether a laboratory hood might be too turbulent. Also decide whether to filter the exhaust containing these tiny particles. Studies have shown that HEPA (high-efficiency particulate air) filters are very effective for nano-sized particles. Also consider that laboratory hoods allow for a very minor amount of leakage outside of the hood, which may be a large volume when considering nanoparticles. Other ventilation, such as biosafety cabinets, may be more appropriate. See Section 5.5.3.

5.4.2 General Laboratory Ventilation and Environmental Control Systems

General ventilation systems control the quantity and quality of the air supplied to and exhausted from the laboratory. The general ventilation system should replace the laboratory air continuously so that concentrations of odoriferous or toxic substances do not increase during the workday and are not recirculated from laboratory to laboratory.

Exhaust systems fall into two main categories: general and specific. General systems serve the laboratory as a whole and include devices such as laboratory hoods and snorkels. Specific systems serve isotope hoods, perchloric acid hoods, or other high-hazard sources that require isolation from the general laboratory exhaust systems.

See *Appendix D.2. Laboratory Engineering Controls for Personal Protection* for an overview of types of ventilation systems and their uses.

5.4.3 Laboratory Hoods

Laboratory hoods (also known as chemical fume hoods) are the most important components used to protect laboratory workers from exposure to hazardous chemicals and agents used in the laboratory. A standard laboratory hood is a fire- and chemical-resistant enclosure having one opening (face) in the front with a movable window (sash) to allow user access into the interior. Large volumes of air are drawn through the face and out the top to contain and remove contaminants from the laboratory.

Laboratory hoods should be regarded as backup safety devices that can contain and exhaust toxic, offensive, or flammable materials when the containment of an experiment or procedure fails and vapors or dusts escape from the apparatus being used. Laboratory hoods are the best choice particularly when mixtures or uncharacterized products are present and any time there is a need to manage chemicals using the ALARA principle.

5.4.3.1 *Guide to Maximizing Hood Efficiency*

Many factors can compromise the efficiency of a hood operation. Follow these practices to maximize hood efficiency:

1. Keep laboratory hood exhaust fans on at all times.
2. If possible, position the laboratory hood sash so that work is performed by extending the arms under or around the sash, placing the head in front of the sash, and keeping the sash between the worker and the chemical source. The sash will act as a primary barrier if a spill, splash, or explosion should occur.
3. Avoid opening and closing the laboratory hood sash rapidly, and avoid swift arm and body movements in front of or inside the hood.
4. Place chemical sources and apparatus at least 6 inches (15 cm) behind the face of the hood. Consider painting a colored stripe or applying tape to the hood work surface 6 inches (15 cm) back from the face to serve as a reminder. Concentration of contaminant in the breathing zone can be 300 times higher from a source located at the front of the hood face than from a source placed at least 6 inches back.
5. Place equipment as far to the back of the hood as practical without blocking the bottom baffle.
6. Separate and elevate each instrument by using blocks or racks so that air can flow easily around all apparatus.
7. Do not use large pieces of equipment in a hood, because they tend to cause dead spaces in the airflow and reduce the efficiency of the hood.
8. If a large piece of equipment emits fumes or heat outside a laboratory hood, have a special-purpose hood designed and installed to ventilate that particular device.
9. Do not modify laboratory hoods in any way that adversely affects hood performance. This includes adding, removing, or changing any of the laboratory hood components, such as baffles, sashes, airfoils, liners, and exhaust connections.
10. Make sure that all highly toxic or offensive vapors are scrubbed or adsorbed before the exit gases are released into the hood exhaust system.

Work with significant hazards in a separate hood from general purpose work.

11. Keep the sash closed whenever the hood is not actively in use or is unattended.
12. Keep laboratory hoods and adjacent work areas clean and free of debris at all times.
13. Keep solid objects and materials (such as paper) from entering the exhaust ducts of hoods, because they can lodge in the ducts or fans and harm their operation.
14. Keep unnecessary equipment and glassware outside of the hood at all times and store all chemicals in approved storage cans, containers, or cabinets (not in the laboratory hood).
15. Keep the work space neat and clean in operations involving the use of hoods to avoid disturbing, or even destroying, what is being done.

See *Appendix D.3. Laboratory Hoods* for more information.

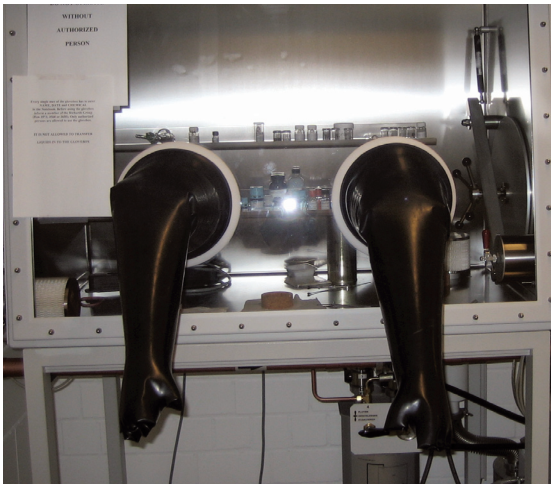
5.5 Special Systems

5.5.1 Glove Boxes

Unlike a laboratory hood, gloves boxes are fully enclosed and under negative or positive pressure. Glove boxes are usually small units with multiple mounted arm-length rubber gloves, which the operator uses to work inside.

A glove box is used when personnel or experiments need special protection.

A glove box operating under negative pressure is generally used for highly toxic materials, when a laboratory hood might not offer adequate protection. A rule of thumb is that a laboratory hood will offer protection for up to 10,000 times the immediately dangerous concentration of a chemical. Glove box exhaust must be filtered or scrubbed before being released into the exhaust system. Since glove boxes are designed with very low airflow rates, the rate of contaminant dilution is minimal. Therefore, these devices must routinely be leak tested. If leakage is found, identify and repair the source of contaminant release before resuming any work.



A glove box operating under positive pressure may be used for experiments that require protection from moisture or oxygen or a high-purity inert atmosphere. In most cases, the chamber is pressurized with argon or nitrogen. If this type of glove box is to be used with hazardous chemicals, test the glove box for leaks before each use. Install a method to monitor the integrity of the system, such as a shutoff valve or a pressure gauge.

5.5.2 Clean Rooms

Clean rooms are special laboratories or work spaces in which large volumes of air are supplied through HEPA filters to reduce the particulates present in the room. Special construction materials and techniques, air handling equipment, filters, garments, and procedures are required, depending on the cleanliness level of the facility. Consult a laboratory consultant or expert in clean room operation before a clean room is built or used.

5.5.3 Biological Safety Cabinets

Biological safety cabinets (BSCs) are common containment and protection devices used in laboratories working with biological agents. BSCs are specially designed and constructed to offer protection to the worker and clean, filtered air to the materials within the workspace. They may also be effective for controlling nanoparticles. BSCs and other facilities in which viable organisms are handled require special construction and operating procedures to protect workers and the environment. Conventional laboratory hoods should never be used for work with most biological agents or to contain biological hazards.

BSCs are *not* suited for work with hazardous chemicals. Most BSCs exhaust the contaminated air back into the lab through HEPA filters that will not contain most hazardous materials, particularly gases, fumes, or vapors.

5.6 Ventilation System Management Program

The laboratory ventilation system is one of the most important aspects of laboratory safety and is also likely the highest consumer of energy in the laboratory building. Managing all facets of the ventilation system is crucial to maximize safety and energy conservation. Overall, there are three main aspects of a ventilation system management program: design criteria, training for laboratory personnel, and system maintenance.

5.6.1 Design Criteria

The institution should determine the criteria it will use for all laboratory hoods and other ventilation systems. These criteria might include

- laboratory hood design check (e.g., face velocity criteria at specific sash height, sash design);

STAKEHOLDER CONSIDERATIONS

Laboratory Designers:

What ventilation systems do we install?

Trained Laboratory Personnel:

What systems do I use?

How and when do I use them?

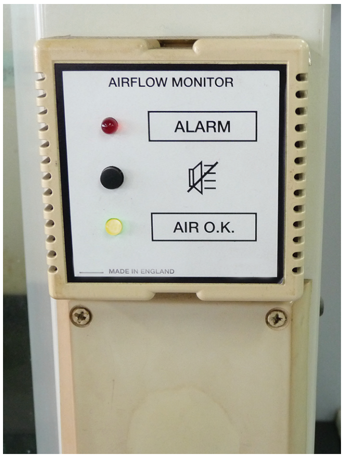
Facility Managers:

How often and how do we maintain the systems?

Laboratory Managers and Safety Managers:

How often and how do we inspect the systems?

What training is needed and how should it be provided?



An airflow monitor sounds an alarm when exhaust air flow falls below a set level.

- types of continuous monitoring systems preferred or required (e.g., face velocity reading, magnehelic gauge);
- number of fume hoods available per person or per total building area (i.e., diversity factors);
- energy conservation strategies;
- alarm systems;
- type of duct work;
- noise criteria;
- preference for variable air volume (VAV) systems (e.g., designing one extra fan into each system); and
- backup power source.

5.6.2 Training Program

Training of laboratory personnel is *essential* in ventilation management. All managers, workers, and students should receive training that includes

- how to use the ventilation equipment;
- the consequences of improper use;
- what to do in the event of system failure;
- what to do in the event of a power outage;
- special considerations or rules for the equipment; and
- the significance of signage, postings, et cetera.

Conduct training in whatever format suits the institution, including one-on-one, in classroom, or remote.

Good signage and postings complement training and act as constant reminders. Consider the following types of signs and postings:

- sash position for laboratory hoods;
- ribbons or similar materials on laboratory hood sashes as an indicator of adequate air flow;
- meanings of any audible or visual alarms;
- functions of occupancy sensors (e.g., setback mode tied to light switch);
- down times if the system has a setback mode that is on a timer; or
- reminder to lower the sash when not in active use.

See *Signs* in the accompanying Toolkit for examples.

5.6.3 Inspection and Maintenance

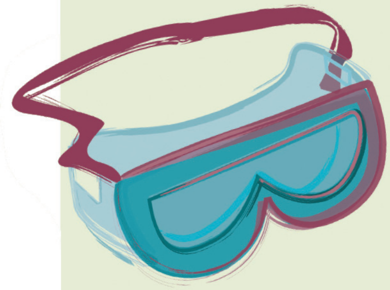
Maintenance is key to a ventilation system management program. The program should describe the elements of the inspection and maintenance program, including

- who conducts inspections and how often;
- how inspections are recorded;
- inspection criteria for laboratory hoods, such as
  - face velocity testing, including equipment used and its history;
  - method of recording velocity;
  - type of information to post on the hood; and
  - whether the maximum sash height will be marked and how;
- criteria for working on roofs and around stacks;
- fan maintenance schedule;
- VAV system maintenance schedule;
- alarms and controls maintenance schedule; and
- recommissioning schedule for the ventilation system.

See *Appendix D.4. Maintenance of Ventilation Systems* for more information on conducting ventilation system maintenance.

6

Laboratory Security



6.1 Introduction

Security has become an important component of laboratory operations. A good laboratory security system can lessen a number of risks, such as

- theft or diversion of critical or high-value equipment;
- theft or diversion of dual-use chemicals or materials that may be used for illegal activities;
- threats from activist groups;
- accidental or intentional release of or exposure to hazardous materials;
- sabotage of chemicals or high-value equipment;
- release of sensitive information; and
- rogue work or unauthorized laboratory experimentation.

The type and extent of the security system depend on several factors, including

- the types of perceived threats and quantities of materials and equipment;
- the knowledge of groups or individuals posing a threat;
- the history of theft, sabotage, and violence directed at or near the laboratory;
- regulatory requirements or guidance;
- the presence of an attractive nuisance; or
- concerns regarding dual use or information security.

6.2 Security Basics

A laboratory security program will employ a combination of human, physical, electronic, and operational components for an integrated system.

- **Trained human resources:** adequately trained, able, and well-aware security guards
- **Physical or architectural security:** doors, walls, fences, locks, barriers, and roof access
- **Electronic security:** access control systems, alarm systems, and closed-circuit television systems
- **Operational security:** sign-in sheets or logs, security guard patrols, control of keys and access cards, and authorization procedures

Depending on the level of security needed, design a security system to provide a deterrent from unauthorized access, a monitoring system to detect violations, and backups to prevent system failure in the event of power loss or other environmental changes.

Use the concept of *concentric circles of protection,* as shown in Figure 6.1, when planning a laboratory security system. Security begins at the perimeter of the building and becomes increasingly strict in the sensitive interior areas. Security measures need to be implemented in the intervention zones.

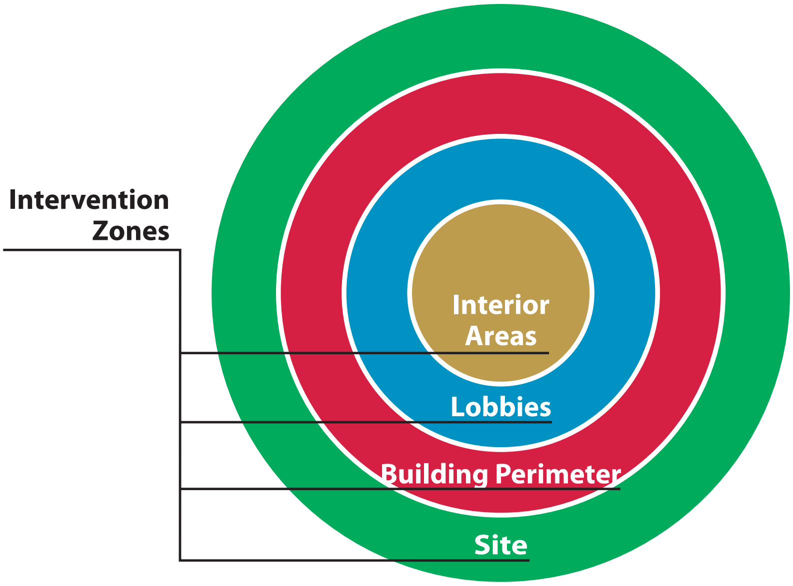


Figure 6.1 Concentric circles of protection.

Security systems should help

- **detect a potential problem,** including intrusion or theft;
- **delay criminal activity** by putting up barriers in the form of personnel and access controls; and
- **respond to problems.**

Facilities should have a security plan that identifies responsible people, procedures, and policies and gives a clear understanding of the roles of internal and external responders, including police.

6.3 Establishing Levels of Security

The institution should establish the level of security needed for a laboratory or portion of a laboratory. Establishing security levels eases the review of security needs for a laboratory and ensures consistency in the application of security principles.

The following is one example of a laboratory security management system, setting three security levels based on operations and materials.

6.3.1 Normal or Security Level 1

A laboratory or area characterized as Security Level 1 poses low risk for extraordinary chemical, biological, or radioactive hazards. Loss to theft, malicious pranks, or sabotage would have minimal impact to operations.

Table 6.1 Security Features for Security Level 1

Physical	• Lockable doors and windows
Operational	• Lock doors when not occupied • Make sure all laboratory personnel receive security awareness training • Control access to keys and use judgment in providing keys to visitors

6.3.2 Elevated or Security Level 2

A laboratory or area characterized as Security Level 2 poses moderate risk for potential chemical, biological, or radioactive hazards. The laboratory may contain equipment or material that is attractive for theft, could threaten the public, or might be misused. Loss to theft, malicious pranks, or sabotage would have moderately serious impact on the research programs and the reputation of the institution.

Table 6.2 Security Features for Security Level 2

Physical	• Lockable doors, windows, and other passageways • Door locks with high-security cores • Separation from public areas • Hardened doors, frames, and locks • Perimeter walls extending from the floor to the ceiling to prevent access from one area to the other over a drop ceiling
Operational	• Secure doors, windows, and passageways when not occupied • Make sure all laboratory personnel receive security awareness training • Employ security guards to detect security breaches • Escort visitors and contractors and register them in an entry log
Electronic	• Access control system recommended • Intrusion alarm recommended where sabotage, theft, or diversion is a concern

6.3.3 High or Security Level 3

A laboratory or area characterized as Security Level 3 poses serious or potentially lethal biological, chemical, or radioactive hazards to people and the environment. The laboratory may contain equipment or material that could be misused, could threaten the public, or is of high value. Equipment or material loss to theft, malicious pranks, or sabotage would have serious impact and consequences on the research programs, the facilities, and the reputation of the institution.

Table 6.3 Security Features for Security Level 3: Same as Security Level 2 plus these additional items

Physical	• High-security locks • Double door vestibule entry
Operational	• Lock doors, windows, and passageways *at all times* • Escort and log in visitors and contractors • Inspect items carried into or removed from the laboratory • Establish an inventory system for materials of concern • Conduct background checks on individuals with direct access to materials of concern or the control zone
Electronic	• Access control system that records the transaction history of all authorized individuals • Biometric personal verification technology recommended • Intrusion alarm system • Closed-circuit television cameras for exits, exit points, materials storage, and special equipment

6.4 Reducing the Dual-Use Hazard of Laboratory Materials

A wide range of hazardous laboratory reagents present an extra safety threat because of the risk of terrorism and illicit drug production. It is important to be aware of the potential for intentional misuse of such dual-use or multiple-use laboratory chemicals.

Laboratory security should focus on a range of dual-use materials, including biological agents such as live pathogens and biological toxins, synthetic reagents, and chemical toxins. Security should also consider the possibility that the laboratory itself could be used for the illicit synthesis of terror substances.

See *Appendix A.1. Example List of Chemicals of Concern* for other possible dual-use chemicals and chemicals of concern (COCs).

Take these steps to reduce the risk of theft or the use of dual-use chemicals for terrorist activity.

1. Periodically and carefully review laboratory access controls to areas where dual-use agents are used or stored.

POSSIBLE DUAL-USE CHEMICALS

- acetone
- ammonia
- chlorinated hydrocarbons
- chlorine
- cyanogen chloride
- ethanol
- hydrogen peroxide
- osmium tetroxide
- phosgene
- sodium azide
- sodium cyanide
- nitric acid

The chemicals listed are intended to provide a sample of a wide range of dual-use chemicals. This is *not* an exhaustive list.

2. Limit the number of laboratory personnel who have access to dual-use agents.
3. Provide training to all laboratory personnel who have access to these substances, including a discussion of the risks of dual use.
4. Remain alert and aware of the possibility of removal of any chemicals for illicit purposes and know how to report such activity to a responsible person.
5. Maintain inventory records of these materials (see Chapter 8).
6. If electronic access controls are in place, maintain a log of who has gained access to areas where dual-use materials are used or stored.

Include these materials in the Security Vulnerability Assessment (see Section 6.6) and make sure that the security plans adequately protect these materials.

6.5 Establishing Information Security

Information security is as critical as the security of equipment and materials. The issue of dual use applies to data as well as laboratory materials. Cybersecurity violations may lead to sensitive information getting into the hands of terrorists, enemy groups, or criminals. Develop information security policies and procedures such as those detailed in the next sections.

6.5.1 Making Data Backups

Develop a plan for backing up data on a regular basis. Consider the benefits of keeping backup media offsite, either in fire-safe storage or at a central facility (e.g., the institution's information technology facility).

6.5.2 Protecting Confidential or Sensitive Information

Assess the types of data produced by the laboratory. Data may fit into the following categories:

- public, shared freely with anyone;
- internal, shared freely within the institution;
- departmental, shared only within the department;
- laboratory, shared only in the laboratory; or
- confidential, shared only with those directly involved with the data or on a need-to-know basis.

If the laboratory produces private, sensitive, or proprietary data, take the following steps with the guidance of the institution's information technology group or an outside consultant:

1. Provide training to those with access to this information, stressing the importance of confidentiality. Review any procedures for releasing such information outside the laboratory.
2. Obtain a written and signed confidentiality agreement for those with access to such information.
3. Change passwords routinely. Do not store or write them in an obvious place. Keep passwords confidential.
4. Safeguard keys, access cards, or other physical security tools.
5. Before discarding materials that contain sensitive information, render them unusable by shredding them or by erasing magnetic tape.
6. Report any known or suspected violations in security immediately to the institutional security office and the chemical safety and security officer.

6.6 Conducting Security Vulnerability Assessments

The purpose of a Security Vulnerability Assessment (SVA) is to find out the potential security risks to the laboratory, the magnitude of the threats, and the adequacy of the systems already in place. The SVA helps determine the security planning needs for the laboratory.

See *Appendix E.1: Developing a Comprehensive Security Vulnerability Assessment.*

To conduct an SVA, start with a walkthrough of the laboratory perimeter. Focus the assessment by discussing with laboratory personnel the chemicals, equipment, procedures, and data that they produce.

The following is a partial list of issues to review as part of an SVA:

- Existing threats, based on the history of the institution (e.g., theft of laboratory materials, sabotage, data security violations, protests)
- Chemicals, biological agents, radioactive materials, or other laboratory equipment or materials with dual-use potential (see Section 4.4)
- Sensitive data or computerized systems
- Animal care facilities
- Infrastructure vulnerabilities (e.g., accessible power lines, poor lighting)
- Security systems in place (e.g., access control, cameras, intrusion detection)
- Laboratory personnel identification (e.g., badges, escorted access)
- Institutional culture (e.g., open laboratories, no questioning of visitors)
- Security plans in place
- Training and awareness of laboratory personnel

Conduct an SVA with a committee of two or three motivated faculty members and researchers with the required knowledge and awareness of chemical safety and security. Where resources are available, consider hiring a laboratory security consultant to conduct the SVA with the security, safety, and laboratory staff.

6.7 Creating a Security Plan

The results of the SVA provide a list of needed security measures beyond a lock and key. There is no single approach to a laboratory security plan. However, the following elements should be considered for any laboratory security plan.

1. Restrict perimeter access to the facility where there is a high risk of theft, diversion, sabotage, or intentional release of particularly hazardous chemicals.
2. Secure the assets identified in the SVA in a manner that prevents access by unauthorized individuals.
3. Monitor the security of those assets, so that a security violation would be noticed and, for high-risk materials, laboratory or security personnel can respond immediately.

4. Screen and control access to the facility using electronic access controls and security guards. Check individuals and, in some cases, vehicles to make sure people do not bring harmful materials into the laboratory.
5. Delay a security violation through the use of security measures already discussed, to give responders more time to prevent a successful attack.
6. Secure shipping, receiving, and storage of target materials.
7. Deter theft or diversion of target materials through inventory controls, visitor control, identification badges, and electronic controls.
8. Conduct background checks on anyone working with laboratory materials, especially dual-use or high-security materials. Verify employment and education background information and note gaps in a person's history.
9. Deter cyber sabotage, including unauthorized onsite or remote access to critical process controls.
10. Develop and implement emergency response plans and practice those plans.
11. Identify the leadership structure for security issues.
12. Maintain monitoring, communication, and warning systems.
13. Keep records of the security plan and its use.
14. Provide training to laboratory personnel on the security measures and the importance of following those measures.
15. When a threat is issued, raise the level of security.
16. Report significant incidents involving chemical security to local law enforcement.
17. Investigate reports of security-related incidents and document the findings and resolution.

6.8 Managing Security

The institution's chemical safety and security oversight committee is responsible for creating an overall security plan. The person responsible for managing security in the laboratory should have at least basic security knowledge, understand the risks and vulnerabilities, and have the appropriate level of responsibility and authority.

Security should be an integral part of the laboratory safety training program. Train all personnel to understand and use the laboratory's security measures, in addition to safety measures. Many measures that increase safety also increase security, including

- minimizing the use of hazardous chemicals to reduce risks;
- minimizing the supply of materials on hand;
- minimizing the time for which such materials need to be stored;
- restricting access to those who need to use hazardous materials and understand their safety and security risks; and
- knowing what to do in an emergency and recognizing threats.

6.9 Regulatory Compliance

For most laboratories there are no regulatory requirements for security. Security measures are based on the needs of the laboratory. However, for some materials or operations, there are guidance documents.

- **Biological materials and infectious agents:** Certain biological organisms, including viruses, bacteria, fungi, prions, and their genetic elements, may pose a risk to individuals or a community. Biological materials pose a unique problem because these materials are able to replicate; thus, theft of even small amounts is significant. See the World Health Organization *Laboratory Biosafety Manual* (Third edition) at *www.who.int/csr/resources/publications/biosafety/WHO_CDS_CSR_LYO_2004_11/en* for guidance.
- **Research animals:** Animal research is the focus of numerous animal rights activists. Vivarium security is critical for the safety of the animals and the researchers. The Association for Assessment and Accreditation of Laboratory Animal Care International (AAALAC) provides guidance for security of laboratory animals and research facilities. AAALAC has a link on international resources and regulations: *www.aaalac.org/resources/internationalregs.cfm.*
- **Radioactive materials and radiation-producing equipment:** In most laboratories, the quantity, isotope, and intensity of the radioactive materials used for research or teaching do not pose a serious risk to individuals or the community. However, some materials and equipment pose a higher risk, and even low-risk materials may cause concern. See the International Atomic Energy Agency web site (*www.iaea.org*) for guidance.
- **Chemicals:** Chemical security is attracting increasing attention from regulators. As mentioned earlier, some common laboratory chemicals have the potential to be used in the production of illicit drugs or chemical

weapons. See the Organization for the Prohibition of Chemical Weapons web site (*www.opcw.org*) for more information.

The Organization for the Prohibition of Chemical Weapons offers classes in using gas chromatography to analyze chemicals with weapons potential (and various other types of chemicals) in different types of environmental samples.

6.10 Physical and Operational Security

There are many systems available for laboratory security. The choice and implementation depend on the level of security needed and the resources available.

6.10.1 Security Guards and Procedures

Security guards are often the most commonly available laboratory security measure. They control access to buildings and laboratories by checking badges or other forms of identification of staff and visitors. They can also oversee locking doors and windows, patrolling inside and outside buildings, and reviewing closed-circuit television (CCTV) monitors.

If using security guards, set clear policies for checking badges, keeping a sign-in log, and defining areas of access, patrol routes, and schedules. This includes procedures for reporting suspicious people or activities and reviewing CCTV information. Never ask or allow security guards to check on the status of unattended experiments involving highly toxic materials.

6.10.2 Door Locks

Many types of door locks are available. Every door lock system requires management and maintenance. For keys, make sure that there is a program in place to collect them before a person leaves the workplace.

6.10.3 Closed-Circuit Television

In addition to guards and locks, closed-circuit television is another tool often used for laboratory security. CCTV may be monitored continuously by security guards or may be reviewed after an incident. CCTV may be used to recognize unusual activity and validate personnel identities and entry authorization. CCTV cameras should be located at entryways or exits, not necessarily in the work area itself.

Formulate a policy and procedure for using the system and for reviewing recordings. Store CCTV data for at least a month. Make a policy stating the circumstances under which the information may be viewed and by whom.

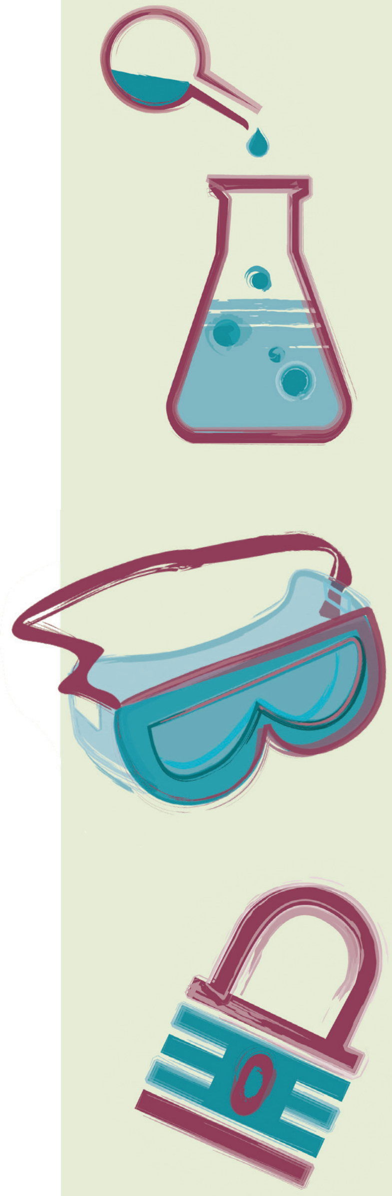
6.10.4 Other Measures

Other security measures available include

- hiring additional security guards;
- glass break alarms for windows and doors;
- intrusion alarms;
- hardware to prevent tampering with window and/or door locks;
- lighting for places where people may enter a secure area;
- locks on roof access;
- boundary walls, fences, and shrubbery;
- internal walls that extend from the floor to the structural ceiling;
- tamper-resistant door jambs;
- blinds on windows;
- badges or other forms of identification; and
- sign-in logs.

7

Assessing Hazards and Risks in the Laboratory



7.1 Introduction

A key element of experiment planning involves assessing the hazards and risks associated with the chemicals and operations proposed in the experiment. This chapter provides a practical guide to assessing hazards and risks. Although the responsibility for carrying out these assessments lies primarily with the people who will be conducting the experiment, risk assessments should involve consultation with the immediate laboratory supervisor and, in many instances, the laboratory chemical safety and security officer (CSSO).

This chapter provides guidelines for assessing the risks of using hazardous chemicals in the laboratory, including information on how to

- consult sources of information on the hazardous chemicals to be used;
- evaluate the toxic risks of chemicals using basic principles of toxicology;
- assess the toxic risks associated with specific classes of hazardous chemicals;
- select appropriate procedures to minimize exposure to toxic chemicals; and
- assess other risks associated with hazardous chemicals, such as flammability.

See *Forms: Laboratory Hazard Assessment Checklist* for a sample form that can be used in assessing the hazards associated with laboratory work.

7.2 Consulting Sources of Information

As the first step in a risk assessment, laboratory personnel should examine their plan for a proposed experiment and identify the chemicals with unfamiliar hazards. Many resources are available to assist with assessing the hazards and risks of chemicals in the laboratory. The most well known and universally used include

- chemical hygiene plans;
- Material Safety Data Sheets (MSDSs);
- Laboratory Chemical Safety Summaries (LCSSs);
- International Chemical Safety Cards (ICSCs);
- labels; and
- the Globally Harmonized System for Hazard Communication (GHS).

See *Appendix B.1. Sources of Chemical Information* for more information on each of these resources.

7.3 Evaluating the Toxic Risks of Laboratory Chemicals

Toxicology is the study of the adverse effects of chemicals on living systems. All laboratory personnel should understand certain basic principles of toxicology and learn to recognize the major classes of toxic and corrosive chemicals. The next sections summarize the key concepts involved in assessing the risks of using toxic chemicals in the laboratory. (Also see Chapter 9, Section 4.)

7.3.1 Dose-Response Relationships

The basic tenets of toxicology are that *no substance is entirely safe* and that *all chemicals result in some toxic effects if a high enough amount of the substance comes in contact with a living system*. The single most important factor that determines whether a substance is harmful or safe is the relationship between the concentration of the chemical and the toxic effect it produces.

The basic tenets of toxicology are that no substance is entirely safe and that all chemicals result in some toxic effects if a high enough amount of the substance comes in contact with a living system.

For all chemicals, there is a range of concentrations that result in a graded effect between the extremes of no effect and death. In toxicology, this range is referred to as *the dose-response relationship* for the chemical. The dose is the amount of the chemical absorbed (through inhalation, ingestion, or skin absorption) and the response is the effect the chemical\ produces. This relationship is unique for each chemical, although for similar types of chemicals the dose-response relationships are often similar. For most common chemicals, a threshold dose has been established below which a chemical is not considered to be harmful to most individuals.

One way to evaluate the acute toxicity of chemicals, or their toxicity after a single exposure, is to examine their lethal dose (LD) or lethal concentration (LC) value.

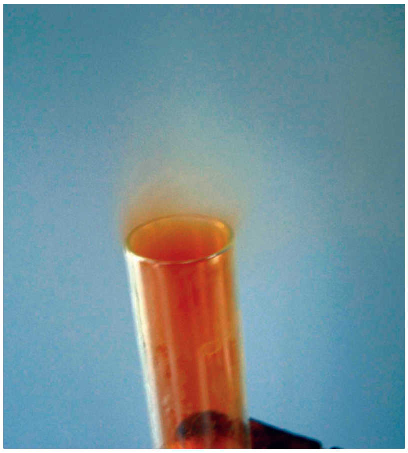
- **LD_{50}** is the amount of a chemical that when ingested, injected, or applied to the skin of a test animal under controlled laboratory conditions kills one-half (50%) of the animals. The LD_{50} is usually expressed in milligrams or grams per kilogram of body weight.
- **LC_{50}** is the concentration of the chemical in air that will kill 50% of the test animals exposed to it. The LC_{50} is given in parts per million, milligrams per liter, or milligrams per cubic meter. LC_{50} is used more often for volatile chemicals or chemicals with sufficient vapor pressure that inhalation is an important route of chemical entry into the body.
- Also useful are **LC_{100}** and **LD_{100}** values, which are defined as the lowest concentrations or doses that cause the death of test animals.

In general, the higher the LD_{50} or LC_{50}, the lower is the toxicity of the chemical.

7.3.2 Duration and Frequency of Exposure

Toxic effects of chemicals occur after single (acute), intermittent (repeated), or long-term repeated (chronic) exposure. An acutely toxic substance causes damage as the result of a single short-duration exposure. Hydrogen cyanide, hydrogen sulfide, and nitrogen dioxide are examples of acute toxins. In contrast, a chronically toxic substance causes damage after repeated or long-duration exposure or causes damage that becomes evident only after a long latency period. Chronic toxins include all carcinogens, reproductive toxins, and certain heavy metals and their compounds. Many chronic toxins are extremely dangerous because of their long latency periods. The cumulative effect of low exposures to such substances may not become apparent for many years. Many chemicals may be hazardous both acutely and chronically depending on exposure level and duration.

Nitrogen dioxide, a yellow-brown gas, is acutely toxic by inhalation.



7.3.3 Routes of Exposure

Exposure to chemicals in the laboratory occurs through inhalation, contact with skin or eyes, ingestion, and injection. Consider each of these different pathways when evaluating the toxic hazards of a chemical.

See *Appendix F.1. Assessing Routes of Exposure for Toxic Chemicals* for more information on assessing the risks of exposure associated with toxic chemicals.

7.4 Assessing the Toxic Risks of Specific Laboratory Chemicals

The first step in assessing the risks of a planned experiment involves identifying which of the chemicals to be used are potentially hazardous substances. This section explains how to assess the risks associated with specific classes of toxic chemicals.

The chemicals used in the laboratory can be grouped into several different classes of toxic substances. Many chemicals display more than one type of toxicity. Following are the most common classes of toxic substances encountered in laboratories.

7.4.1 Acute Toxicants

Acute toxicity is the ability of a chemical to cause a harmful effect after a single exposure. Acutely toxic agents can cause local toxic effects, systemic toxic effects, or both. This class of toxicants includes corrosive chemicals, irritants, and allergens (sensitizers). The most common chemicals with a high level of acute toxicity that are encountered in the laboratory are

- acrolein;
- arsine;
- chlorine;
- diazomethane;
- diborane (gas);
- dimethyl mercury;
- hydrogen cyanide;
- hydrogen fluoride;
- methyl fluorosulfonate;
- nickel carbonyl;
- nitrogen dioxide;
- osmium tetroxide;
- ozone;
- phosgene;
- sodium azide; and
- sodium cyanide (and other cyanide salts).

Handle these compounds using the additional procedures outlined in Chapter 9, Section 4. When planning an experiment, find out whether an acute toxicant should be treated as a particularly hazardous compound by considering

- the total amount of the substance to be used;
- the physical properties of the substance (e.g., *Is it volatile? Does it tend to form dusts?*);
- its potential routes of exposure (e.g., *Is it readily absorbed through the skin?*); and
- the circumstances of its use in the proposed experiment (e.g., *Will the substance be heated? Is it likely to generate aerosols?*).

It may be helpful to decide how to treat an acute toxicant in consultation with a laboratory manager or CSSO.

See *Appendix F.2. Assessing Risks Associated with Acute Toxicants* for more information on how to determine acute toxicity hazard levels and probable lethal doses for humans.

7.4.2 Irritants, Corrosives, Allergens, and Sensitizers

LD_{50}, LC_{50}, and other toxicity values generally provide little guidance in assessing the risks of corrosives, irritants, allergens, and sensitizers because these toxic substances exert their harmful effects locally. Use the following guidelines to assess the risks of these chemicals.

7.4.2.1 *Irritants*

Irritants are noncorrosive chemicals that have reversible inflammatory effects (swelling and redness) on living tissue by chemical action at the site of contact.

Pay special attention to the LCSSs, MSDSs, and other sources of information on irritant chemicals. A wide variety of organic and inorganic chemicals are irritants, such as silyl halides and hydrogen selenide. Take steps to minimize skin and eye contact with all reagent chemicals in the laboratory.

Corrosives such as nitric acid require protective wear, including corrosion-resistant gloves. Nitric acid is also an oxidant.

7.4.2.2 *Corrosive Substances*

Corrosive substances are solids, liquids, or gases that destroy living tissue by chemical action at the site of contact. Corrosive effects occur not only on the skin and eyes but also in the respiratory tract and, when ingested, in the gastrointestinal tract. Common corrosive substances found in many labs include

- ammonia;
- bromine;
- calcium oxide;
- chlorine;
- chloramine;
- hydrochloric acid;
- hydrofluoric acid;
- hydrogen peroxide;
- metal hydroxides;
- nitric acid;
- nitrogen dioxide;
- phenol;
- phosphorus; and
- phosphorus pentoxide.

When planning an experiment that involves corrosive substances, review basic careful handling practices to make sure that the skin, face, and eyes are protected adequately. Choose the proper corrosion-resistant gloves and protective clothing and eyewear, including, in some cases, face shields.

7.4.2.3 *Allergens and Sensitizers*

A chemical allergy is an adverse reaction of the immune system to a chemical. Such allergic reactions result from previous sensitization to that chemical or a structurally similar chemical. Some allergic reactions are immediate, occurring within a few minutes after exposure. Anaphylactic shock is a severe immediate allergic reaction that results in death if not treated quickly. Delayed allergic reactions take hours or even days to develop. The skin is the usual site of such delayed reactions, becoming red, swollen, and itchy even after the chemical has been removed.

People exhibit wide differences in their sensitivity to laboratory chemicals. When working with known allergens, follow laboratory policy on their handling and containment.

Because an allergic response is triggered in a sensitized individual by an extremely small quantity of the allergen, laboratory personnel should be alert for signs of allergic responses to chemicals.

7.4.3 Asphyxiants

Asphyxiants are substances that interfere with the transport of an adequate supply of oxygen to vital organs of the body. The brain is the organ most easily affected by oxygen starvation, and exposure to asphyxiants leads to rapid collapse and death. Acetylene, carbon dioxide, argon, helium, ethane, nitrogen, methane, and butane gas are common asphyxiants. Certain other chemicals have the ability to combine with hemoglobin, thus reducing the capacity of the blood to transport oxygen. Carbon monoxide, hydrogen cyanide, and certain organic and inorganic cyanides are examples of such substances.

7.4.4 Neurotoxins

Neurotoxins have an adverse effect on the structure or function of the central or peripheral nervous system, which can be permanent or reversible. The detection of neurotoxic effects may require specialized laboratory techniques, but often the effects are seen in behavior such as slurred speech and staggered gait. Many neurotoxins are chronically toxic substances with adverse effects that are not immediately apparent. Some chemical neurotoxins are mercury (inorganic and organic), organophosphate pesticides, carbon disulfide, xylene, tricholoroethylene, and *n*-hexane.

7.4.5 Reproductive and Developmental Toxins

Reproductive toxins are substances that cause chromosomal damage (mutagens) and substances with lethal or teratogenic (malformation) effects on fetuses. These substances cause problems in various aspects of reproduction, including fertility, gestation, lactation, and general reproductive performance and can affect both men and women. Male reproductive toxins in some cases lead to sterility. Many reproductive toxins are chronic toxins that cause damage after repeated or long-duration exposures, with effects that become evident only after long latency periods.

Developmental toxins act during pregnancy and have adverse effects on the fetus. When a woman is exposed to a chemical, generally the fetus is exposed as well because the placenta is an extremely poor barrier to chemicals. Developmental toxins have the greatest impact during the first trimester of pregnancy. Because a woman often does not know that she is pregnant during this period of high susceptibility, women of childbearing potential are advised to be especially cautious when working with chemicals, especially those that are absorbed rapidly through the skin (e.g., formamide). Pregnant women and women intending to become pregnant should seek advice from knowledgeable sources before working with substances that are suspected to be reproductive toxins. As minimal precautions, people should follow the general procedures outlined in Chapter 9, Section 4, although in some cases it will be appropriate to handle the compounds as particularly hazardous substances.

Information on reproductive toxins can be obtained from LCSSs, MSDSs, and ICSCs and by consulting safety professionals in the environmental safety department, industrial hygiene office, or medical department.

7.4.6 Toxins Affecting Other Organs

Toxic substances also affect organs outside the reproductive and neurological systems. Most of the chlorinated hydrocarbons, benzene, other aromatic hydrocarbons, some metals, carbon monoxide, and cyanides, among others, produce one or more effects in target organs. Many LCSSs mention the effects of toxins on organs such as the liver, kidneys, lungs, or blood.

7.4.7 Carcinogens

A carcinogen is a substance capable of causing cancer. Carcinogens are chronically toxic substances; that is, they cause damage after repeated or long-duration exposure, and their effects may become evident only after a long latency period. Carcinogens are particularly insidious toxins because they may have no immediately apparent harmful effects.

Because a woman often does not know that she is pregnant during the first trimester of pregnancy, which is a period of high susceptibility, women of childbearing potential are advised to be especially cautious when working with chemicals, especially those rapidly absorbed through the skin.

A vast majority of substances encountered in research, especially in laboratories involved with the synthesis of new compounds, have not been tested for carcinogenicity. Handle chemicals that are known carcinogens as particularly hazardous substances using the basic practices in Chapter 9, Sections 3 and 4. Consultation with the CSSO may be necessary to decide whether a chemical should be classified as a particularly hazardous substance. Lists of known human carcinogens and compounds can be found on the World Health Organization International Agency for Research on Cancer web site, *www.iarc.fr.*

For chemical substances for which there are no data on carcinogenicity, trained laboratory personnel must evaluate the potential risk that the chemical in question is a carcinogenic substance. This determination is sometimes made on the basis of knowledge of the specific classes of compounds and functional group types that are correlated with carcinogenic activity.

Whether a suspected carcinogenic chemical is treated as a particularly hazardous substance is affected by the scale and circumstances associated with the intended experiment. Laboratory personnel must decide whether the amount and frequency of use, as well as other circumstances, require additional precautions beyond the basic prudent practices of Chapter 9, Section 3. For example, the large-scale or recurring use of a suspected carcinogen might suggest that the special precautions of Chapter 9, Section 4, be followed to control exposure. In other cases, following the basic procedures in Chapter 9, Section 3, may provide adequate protection from a single use of a small amount of such a substance.

When evaluating the carcinogenic potential of chemicals, note that exposure to certain combinations of compounds (not necessarily simultaneously) causes cancer even at exposure levels where neither of the individual compounds would have been carcinogenic. Understand that the response of an organism to a toxicant typically increases with the dose given, but the relationship is not always a linear one. At lower doses, natural protective systems prevent genetic damage, but when the capacity of these systems is overwhelmed, the organism becomes much more sensitive to the toxicant. However, people have differences in their levels of protection against genetic damage as well as in other defense systems. These differences are determined in part by genetic factors and in part by the total exposure of the individual to all chemicals within and outside of the laboratory.

7.4.8 Using Control Banding to Assess Risk

Control banding is a qualitative risk assessment and management approach that minimizes the exposure of personnel to hazardous material. It helps determine the appropriate handling of materials without occupational exposure limits (OELs). Control banding is not intended to be a replacement for OELs but an additional tool. The system uses a range of exposure and hazard “bands” that, when mapped for a given material and application, help the user determine the appropriate safety controls that should be in place. Control banding applies a graduated scale of controls by considering the hazards posed by the material (e.g., toxicity), the quantity used, the intended use or application, and the mode of exposure (e.g., inhalation). The controls may include general ventilation requirements, containment of the material, or recommendations to seek expert advice.

Control banding is useful because the approach provides simplified guidance for assessing hazards and applying controls that can be applied in a variety of settings. It is also useful for prioritizing chemical hazards and hazard communication.

More information about control banding can be found at these web sites:

- U.K. Health and Safety Executive (HSE) Control of Substances Hazardous to Health Regulations (COSHH)
  www.coshh-essentials.org.uk
- International Labour Organization (ILO) Programme on Safety and Health at Work and the Environment (SafeWork)
  www.ilo.org/safework/lang--en/index.htm

7.5 Assessing Flammable, Reactive, and Explosive Hazards

In addition to the hazards due to the toxic effects of chemicals, a risk assessment must consider the chemical hazards due to flammability, reactivity, and explosivity.

7.5.1 Flammable Hazards

7.5.1.1 *Flammable Substances*

Flammable substances, those that readily catch fire and burn in air, may be solid, liquid, or gaseous. Proper use of substances that cause fire requires knowledge of their tendencies to vaporize, ignite, or burn under various conditions in the laboratory.

For a fire to occur, three conditions must exist together:

1. an oxidizing atmosphere, usually air;
2. a concentration of flammable gas or vapor that is within the flammable limits of the substance; and
3. a source of ignition.

Preventing the coexistence of flammable vapors and an ignition source is the best way to deal with the hazard. When the vapors of a flammable liquid cannot always be controlled, strict control of ignition sources is the best approach to reduce the risk of flammability.

There are certain characteristics of substances that make them more flammable.

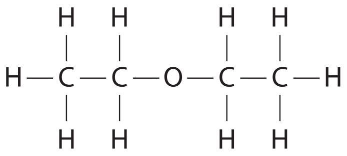
7.5.1.2 *Flammability Characteristics*

- **Flash point:** The flash point is the lowest temperature at which a liquid has a sufficient vapor pressure to form an ignitable mixture with air near the surface of the liquid. Note that many common organic liquids have a flash point below room temperature. The degree of hazard associated with a flammable liquid also depends on other properties, such as its ignition point and boiling point. Commercially obtained chemicals are generally labeled with regard to flammability and flash point.
- **Ignition temperature:** The ignition temperature of a substance, whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion independent of the heat source. The lower the ignition temperature, the greater is the potential for a fire to be started by typical laboratory equipment. A spark is not necessary for ignition when the flammable vapor reaches its ignition temperature. Heat can also cause ignition.
- **Limits of flammability:** Each flammable gas and liquid (as a vapor) has two fairly definite limits of flammability defining the range of concentrations in mixtures with air that will produce a flame and cause an explosion.
    - The *lower explosive limit (LEL)* is the minimum concentration (percent by volume) of the fuel (vapor) in air at which a flame is produced when an ignition source is present.

   - The *upper explosive limit (UEL)* is the maximum concentration (percent by volume) of the vapor in air above which a flame is not produced.

The flammable or explosive range consists of all concentrations between the LEL and the UEL. This range becomes wider with increasing temperature and in oxygen-rich atmospheres. It also changes depending on the presence of other components. However, the limitations of the flammability range provide little margin of safety from the practical point of view because when a solvent is spilled in the presence of an energy source, the LEL is reached very quickly, and a fire or explosion follows before the UEL is reached.

Flammability characteristics of substances may not pertain during typical laboratory use, so apply large safety factors. In a real situation, for example, local concentrations may be much higher than the average. Thus, it is good practice to set the maximum allowable concentration for safe working conditions at some fraction of the tabulated LEL; 20% is a commonly accepted value. Among the most hazardous liquids are those that have flash points near or below 38°C and below 60.5°C. These materials can be hazardous in the common laboratory environment. There is particular risk if their range of flammability is broad. Some commonly used substances are potentially very hazardous, even under relatively cool conditions. Because of its extreme flammability and tendency for peroxide formation, diethyl ether is available for laboratory use only in metal containers. Carbon disulfide is almost as hazardous.



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Diethyl ether is extremely flammable and can form the highly explosive diethyl ether peroxide if not properly stored and tested regularly.

See *Appendix F.3. Flash Points, Boiling Points, Ignition Temperatures, and Flammable Limits of Some Common Laboratory Chemicals* **for more information.**

7.5.1.3 *Causes of Ignition*

- **Spontaneous combustion:** Spontaneous combustion or autoignition takes place when a substance reaches its ignition temperature without the application of external heat. Always consider the possibility of spontaneous combustion, especially when storing or disposing of materials. Examples of materials susceptible to spontaneous combustion include oily rags, dust accumulations, organic materials mixed with strong oxidizing agents (e.g., nitric acid, chlorates, permanganates, peroxides, persulfates), alkali metals (e.g., sodium, potassium), finely divided pyrophoric metals, and phosphorus.

- **Ignition sources:** Potential ignition sources in the laboratory include the obvious torch and Bunsen burner, as well as a number of less obvious electrically powered sources, including refrigerators, stirring motors, and microwave ovens (see Chapter 10, Section 2). Whenever possible, replace open flames with electrical heating. Situate ignition sources at a level lower than the flammable substance being used. For metal lines and vessels discharging flammable substances, properly bond and ground them to discharge static electricity.

Hydrogen peroxide is an oxidant and is also corrosive, and potentially explosive.

- **Oxidants other than oxygen:** The most familiar fire involves a combustible material burning in air. However, the oxidant driving a fire or explosion need not be oxygen itself, depending on the nature of the reducing agent. Examples of non-oxygen oxidants are shown in Table 7.1.

Table 7.1 Examples of Non-Oxygen Oxidants

Substances	Examples
Gases	Chlorine, fluorine, nitrous oxide, oxygen, ozone, steam
Liquids	Bromide, hydrogen peroxide, nitric acid, perchloric acid, sulfuric acid
Solids	Bromates, chlorates, chlorites, chromates, dichromates, hypochlorites, iodates, nitrates, nitrites, perchlorates, peroxides, permanganates, picrates

7.5.1.4 *Special Flammable Hazards*

Compressed or liquefied gases present fire hazards because heat causes the pressure to increase and the container may rupture. Flammability, toxicity, and pressure buildup become more serious on exposure of gases to heat. Leakage or escape of flammable gases produces an explosive atmosphere in the laboratory. Acetylene, hydrogen, ammonia, hydrogen sulfide, propane, and carbon monoxide are especially hazardous.

Even if not under pressure, a liquefied gas is more concentrated than the vapor phase and evaporates rapidly. Oxygen is an extreme hazard, and liquefied air is almost as dangerous because nitrogen boils away first, leaving an increasing concentration of oxygen. Liquid nitrogen standing for a period of time may have condensed enough oxygen to require careful handling. When a liquefied gas is used in a closed system, pressure may build up and require adequate venting. If the liquid is flammable (e.g., hydrogen, methane), explosive concentrations may develop without warning unless an odorant has been added.

7.5.2 Reactive Hazards

7.5.2.1 *Water Reactives*

Water-reactive materials are those that react violently with water. Alkali metals (e.g., lithium, sodium, potassium), many organometallic compounds, and some hydrides react with water to produce heat and flammable hydrogen gas, which ignites or combines explosively with atmospheric oxygen. Some anhydrous metal halides (e.g., aluminum bromide), oxides (e.g., calcium oxide), and nonmetal oxides (e.g., sulfur trioxide) and halides (e.g., phosphorus pentachloride) react exothermically with water. This results in a violent reaction if there is insufficient coolant water to dissipate the heat produced.

7.5.2.2 *Pyrophorics*

For pyrophoric materials, oxidation of the compound by oxygen or moisture in air proceeds so rapidly that ignition occurs. Many finely divided metals are pyrophoric, and their degree of reactivity depends on particle size, the presence of moisture, and the thermodynamics of metal oxide or metal nitride formation. Other reducing agents, such as metal hydrides, alloys of reactive metals, low-valent metal salts, and iron sulfides are also pyrophoric.

7.5.2.3 *Incompatible Chemicals*

Accidental contact of incompatible substances results in a serious explosion or the formation of substances that are highly toxic or flammable or both. Laboratory personnel need to follow storage compatibility guidelines, particularly in seismically active zones. Other natural disasters and chemical explosions themselves can also set off shock waves that empty chemical shelves and result in the mixing of chemicals.

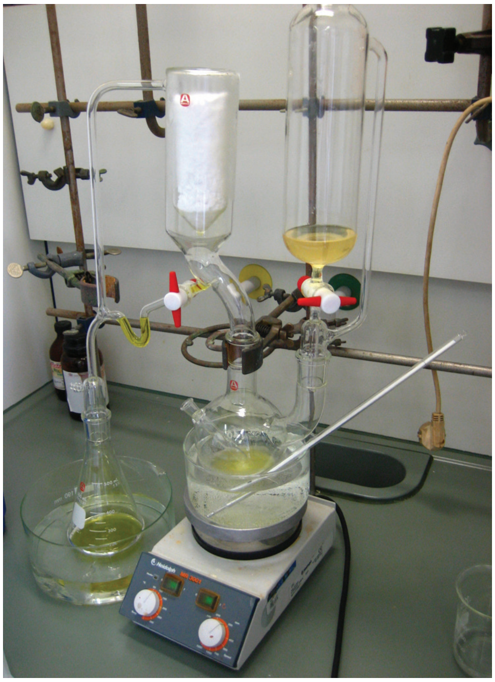
Some compounds pose either a reactive or a toxic hazard, depending on the conditions. For example, hydrocyanic acid (HCN), when used as a pure liquid or gas in industrial applications, is incompatible with bases because it is stabilized against violent polymerization by the addition of acid inhibitor. HCN can also form when cyanide salt is mixed with an acid. In this case, the toxicity of HCN gas, rather than the instability of the liquid, is the characteristic of concern.

Some general guidelines lessen the risks involved with these substances. Concentrated oxidizing agents are incompatible with concentrated reducing agents. Either may pose a reactive hazard even with chemicals that are not strongly oxidizing or reducing. For example, sodium and potassium are strong reducing agents frequently used to dry organic solvents. However, they are extremely reactive toward halocarbon solvents, which are not strong oxidizing agents. Strong oxidizing agents are frequently used to clean glassware, but they should be used only on the last traces of contaminating material.

7.5.3 Explosive Hazards

7.5.3.1 *Explosives*

An explosive is any chemical compound or mechanical mixture that, when subjected to heat, impact, friction, detonation, or other suitable initiation, undergoes rapid chemical change and creates large volumes of highly heated gases that exert pressure on the surrounding medium. The term applies to materials that either detonate or deflagrate. Heat, light, mechanical shock, and certain catalysts initiate explosive reactions. Hydrogen and chlorine react explosively in the presence of light. Acids, bases, and other substances catalyze the explosive polymerization of acrolein, and many metal ions can catalyze the violent decomposition of hydrogen peroxide. Shock-sensitive materials include acetylides, azides, nitrogen triiodide, organic nitrates, nitro compounds, perchlorate salts (especially those of heavy metals such as ruthenium and osmium), many organic peroxides, and compounds containing diazo, nitroso, and ozonide functional groups. Some compounds are set off by the action of a metal spatula on the solid. Some are so sensitive that they are set off by the action of their own crystal formation. Diazomethane (CH_2N_2) and organic azides, for example, may decompose explosively when exposed to a ground glass joint.



This appartus for diazomethane preparation uses smooth-surface (not ground glass) joints to minimze the risk of explosion.

7.5.3.2 *Azo Compounds, Peroxides, and Peroxidizables*

Organic azo compounds and peroxides are among the most hazardous substances handled in the laboratory. However, they are also common reagents used as free radical sources and oxidants. They are generally low-power explosives that are sensitive to shock, sparks, or other accidental ignition. Limit the stocks of these chemicals and subject them to routine inspection. Many require refrigerated storage. Do not cool liquids or solutions of these compounds to the point at which the material freezes or crystallizes from solution; this significantly increases the risk of explosion.

Refrigerators and freezers storing such compounds should have a backup power supply in the event of loss of electricity.

Certain common laboratory chemicals form peroxides on exposure to oxygen in air. Over time, some chemicals continue to build peroxides to potentially dangerous levels. Others accumulate a relatively low equilibrium concentration of peroxide, which becomes dangerous only after being concentrated by evaporation or distillation. The peroxide becomes concentrated because it is less volatile than the parent chemical. A related class of compounds includes inhibitor-free monomers prone to free radical polymerization that on exposure to air can form peroxides or other free radical sources capable of initiating violent polymerization. Take care when storing and using these monomers. Most of the inhibitors used to stabilize these compounds require the presence of oxygen to function properly (as described below). Always refer to the MSDS and supplier instructions for proper use and storage of polymerizable monomers.

Essentially all compounds containing C-H bonds pose the risk of peroxide formation if contaminated with various radical initiators, photosensitizers, or catalysts. For example, secondary alcohols, such as isopropanol, form peroxides when exposed to normal fluorescent lighting and contaminated with photosensitizers. Acetaldehyde, under normal conditions, auto-oxidizes to form acetic acid. Although this auto-oxidation proceeds through a peroxy acid intermediate, the steady-state concentrations of that intermediate are extremely low and pose no hazard. However, in the presence of catalysts (Co^{2+}) and under the proper conditions of ultraviolet (UV) light, temperature, and oxygen concentration, high concentrations of an explosive peroxide may form.

As a laboratory precaution, discard old samples of organic compounds of unknown origin or history. Also discard those prone to peroxidation if contaminated, such as secondary alcohols.

See *Appendix F.4. Chemicals That Can Form Peroxides* for representative lists of chemicals that can form peroxides and pose explosive hazards.

7.5.3.3 *Other Oxidizers*

Oxidizing agents may react violently when they come in contact with reducing materials and sometimes with ordinary combustibles. Such oxidizing agents include halogens, oxyhalogens and organic peroxyhalogens, chromates, and persulfates as well as peroxides. Inorganic peroxides are generally stable. However, they may generate organic peroxides and hydroperoxides in contact with organic compounds, react violently with water (alkali metal peroxides), and form superoxides and ozonides (alkali metal peroxides). Perchloric acid is a powerful oxidizing agent with organic compounds and other reducing agents. Perchlorate salts are explosive and should be treated as potentially hazardous compounds.

For many years, sulfuric acid-dichromate mixtures were used to clean glassware. A sulfuric acid-peroxydisulfate solution is now recommended because disposal of chromate is a problem. Confusion about cleaning baths has led to explosions when people mixed potassium permanganate with sulfuric acid and when they mixed nitric acid with alcohols.

7.5.3.4 *Powders and Dusts*

Suspensions of oxidizable particles (e.g., flour, coal dust, magnesium powder, zinc dust, carbon powder, flowers of sulfur) in the air constitute a powerful explosive mixture. Use these materials with adequate ventilation and do not expose them to ignition sources. Some solid materials, when finely divided, spontaneously combust if allowed to dry while exposed to air. These materials include zirconium, titanium, Raney nickel, finely divided lead (e.g., as prepared by pyrolysis of lead tartrate), and catalysts such as activated carbon containing active metals and hydrogen.

7.5.3.5 *Explosive Boiling*

Not all explosions result from chemical reactions. Some explosions have physical causes. A dangerous explosion can occur if a hot liquid or a collection of very hot particles comes into sudden contact with a lower boiling-point material. Sudden-boiling eruptions occur when a nucleating agent (e.g., charcoal, boiling chips) is added to a liquid heated above its boiling point. Even if the material does not explode directly, the sudden formation of a mass of explosive or flammable vapor can be very dangerous.

7.5.3.6 *Other Considerations*

- **Running a new reaction** can cause hazards. Consider these hazards carefully if the chemical species involved
  - contain functional groups associated with explosions;
  - are unstable near the reaction or work-up temperature;
  - are subject to an induction period during the reaction; or
  - create gases as by-products.

  Use modern analytical techniques to determine reaction exothermicity under suitable conditions. Use minimum amounts of these hazardous materials with adequate shielding and personal protective equipment. Even a small sample may be dangerous, because the hazard is associated not with the total energy released but with the remarkably high rate of a detonation reaction. A high-order explosion of even milligram quantities can drive small fragments of glass or other matter deep into the body.

A compound is apt to be explosive if its heat of formation is more than 100 cal/g less than the sum of the heats of formation of its products. In making this calculation, use a reasonable reaction to yield the most exothermic products.

- **Scaling up reactions** introduces several hazards. These problems include heat buildup and the serious hazard of explosion from incompatible materials. The rate of heat input and production must be weighed against that of heat removal. Bumping the solution or a runaway reaction can result when heat builds up too rapidly.
- **Exothermic reactions** can run out of control if the heat evolved is not dissipated. When scaling up experiments, provide enough cooling and surface for heat exchange, and consider mixing and stirring rates. Detailed guidelines for circumstances that require a systematic hazard evaluation and thermal analysis are given in Chapter 9, Section 7.
- **Reactions susceptible to an induction period** can also lead to problems. Give particular care to the rate of reagent addition versus its rate of consumption. Finally, the hazards of exothermic reactions or unstable or reactive chemicals are exacerbated under extreme conditions, such as the high temperature or high pressure used for hydrogenations, oxygenations, or work with supercritical fluids.

7.6 Assessing Physical Hazards

7.6.1 Compressed Gases

Compressed gases can expose people to both mechanical and chemical hazards, depending on the gas. Hazards can result from the flammability, reactivity, or toxicity of the gas; from the possibility of asphyxiation; and from the gas compression itself, which could lead to a rupture of the tank or valve.

See *Appendix F.5. Specific Chemical Hazards of Select Gases.*

7.6.2 Nonflammable Cryogens

Nonflammable cryogens (chiefly liquid nitrogen) can cause tissue damage from extreme cold because of contact with either liquid or boil-off gases. In poorly ventilated areas, inhalation of gas due to boil off or spills can result in asphyxiation. Other hazards include explosions from liquid oxygen condensation in vacuum traps, ice plug formation, or lack of functioning vent valves in storage Dewars. Because one volume of liquid nitrogen at atmospheric pressure vaporizes to 694 volumes of nitrogen gas at 20°C, the warming of such a cryogenic liquid in a sealed container produces enormous pressure, which can rupture the vessel.

7.6.3 High-Pressure Reactions

Experiments carried out at pressures above one atmosphere can lead to explosion from equipment failure. Hydrogenation reactions are frequently carried out at elevated pressures. A potential hazard is the formation of explosive O_2-H_2 mixtures and the reactivity or pyrophoricity of the catalyst. The use of supercritical fluids may also cause high pressures.

7.6.4 Vacuum Work

Vacuum lines and other glassware used at subambient pressure pose substantial danger of injury in the event of glass breakage. However, injury due to flying glass is not the only hazard in vacuum work. Additional dangers can result from the possible toxicity of the chemicals contained in the vacuum system, as well as from fire following breakage of a flask (e.g., of a solvent stored over sodium or potassium).

Because vacuum lines typically require cold traps (generally liquid nitrogen) between the pumps and the vacuum line, observe precautions regarding the use of cryogens as well. Health hazards associated with vacuum gauges include the toxicity of mercury used in manometers and McLeod gauges; overpressure and underpressure situations arising with thermal conductivity gauges; electric shock with hot cathode ionization systems; and the radioactivity of the thorium dioxide used in some cathodes.

7.6.5 Radio-Frequency and Microwave Hazards

Radio-frequency (RF) and microwaves used in RF ovens and furnaces, induction heaters, and microwave ovens occur within the range 10 kHz to 300,000 MHz. Extreme overexposure to microwaves can result in the development of cataracts, sterility, or both. Laboratories should use only microwave ovens designed for laboratory or industrial use. Use of metal in microwave ovens can result in arcing and, if a flammable solvent is present, in fire or explosion. Superheating of liquids can occur. Capping of vials and other containers used in the oven can result in explosion from pressure buildup within the vial. Inappropriately selected plastic containers may melt.

7.6.6 Electrical Hazards

Laboratories can almost eliminate the electrocution hazards of electrically powered instruments, tools, and other equipment by taking reasonable precautions. However, the possibility of serious injury or death by electrocution is very real if careful attention is not paid to engineering, maintenance, and personal work practices. All laboratory personnel should know how to turn off power to burning equipment by using electrical shutoff switches and/or circuit breaker switches.

Some special electrical concerns arise in a laboratory. The insulation on wires can be eroded by corrosive chemicals, organic solvent vapors, or ozone (from ultraviolet lights, copying machines, and so forth). Immediately repair eroded insulation on electrical equipment in wet locations such as cold rooms or cooling baths. In addition, sparks from electrical equipment can serve as an ignition source in the presence of flammable vapor. Operation of certain equipment (e.g., lasers, electrophoresis equipment) may involve high voltages and stored electrical energy. The large capacitors used in many flash lamps and other systems are capable of storing lethal amounts of electrical energy and should be regarded as live even if the power source has been disconnected.

Loss of electrical power can produce extremely hazardous situations. Flammable or toxic vapors may be released from freezers and refrigerators as chemicals stored there warm up. Certain reactive materials may decompose energetically on warming. Laboratory chemical hoods may cease to function. Stirring (motor or magnetic) required for safe reagent mixing may cease. Return of power to an area containing flammable vapors may ignite them.

7.6.7 Other Hazards

Among the most common injuries in laboratories are those arising from broken glass and from slipping, tripping, or improper lifting. General workplace hazards also apply in the laboratory. For example, laboratory personnel can sustain repetitive motion injuries or back strain. It is important to be aware of and to control such issues to reduce occupational injuries.

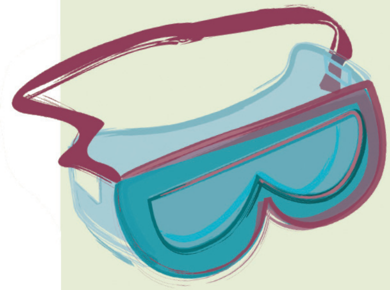
7.7 Assessing Biohazards

Biohazards are a concern in laboratories in which microorganisms, or materials contaminated with them, are handled. These hazards are usually present in clinical and infectious disease research laboratories but may also be present in other laboratories.

Risk assessment for biohazardous materials requires the consideration of a number of factors, including the organism being manipulated, any alterations made to the organism, and the activities that will be performed with the organism. Risk assessment for biological toxins is similar to that for chemical agents. It is based primarily on the potency of the toxin, the amount used, and the procedures in which the toxin is used. For more information see the U.S. Centers for Disease Control and Prevention *Biosafety in Microbiological and Biomedical Laboratories* (4th Edition) at *www.cdc.gov/od/ohs/biosfty/bmbl4/bmbl4toc.htm.*

8

Managing Chemicals



8.1 Introduction

When managing laboratory chemicals, not all risk can be eliminated. However, laboratory safety and security are greatly improved through informed risk assessment and careful risk management. The careful management of a chemical's life cycle not only minimizes risks to humans and to the environment, but also decreases costs.

8.2 Green Chemistry for Every Laboratory

Green chemistry is the philosophy of designing products and processes that reduce or eliminate the use and generation of hazardous substances. The 12 principles of green chemistry listed below can be applied to every laboratory and used as guidelines for prudent experimental design and execution.

Some of these strategies are discussed in greater detail in the following sections.

8.2.2 Preventing Waste

Minimization of the material used at each step of an experiment is essential to waste prevention, as well as to laboratory safety and security. To prevent waste, follow these strategies:

1. Think about how a reaction product will be used and make only the amount needed for that use.

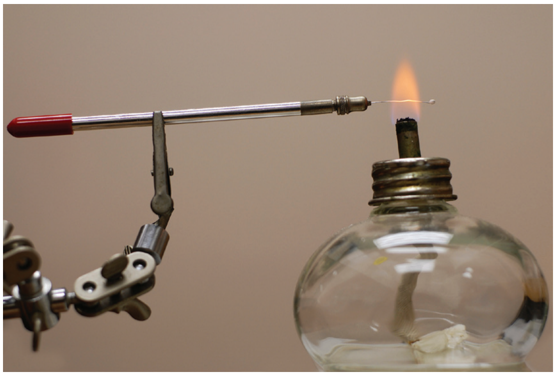
Reagents in storage.

TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. **Prevent waste.** Design chemical syntheses that leave no waste to treat or clean up.
2. **Design safer chemicals and products.** Design chemical products that are fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses.** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks.** Avoid depleting raw materials and feedstocks. Renewable feedstocks are made from agricultural products or the wastes of other processes. Nonrenewable feedstocks are mined or made from fossil fuels (i.e., petroleum, natural gas, coal).
5. **Use catalysts, not stoichiometric reagents.** Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. **Avoid chemical derivatives.** Derivatives use additional reagents and generate waste. Avoid using blocking or protecting groups or any temporary modifications.
7. **Maximize atom economy.** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions.** Avoid using solvents, separation agents, or other auxiliary chemicals. If these are necessary, use harmless chemicals.
9. **Increase energy efficiency.** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use.** Chemical products that break down to harmless substances after use do not accumulate in the environment.
11. **Analyze in real time to prevent pollution.** Include in-process real-time monitoring and control during syntheses to limit or eliminate the formation of by-products.
12. **Limit the potential for accidents.** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents, including explosions, fires, and releases to the environment.

—Based on those originally published by Paul Anastas and John Warner in Green Chemistry: Theory and Practice *(Oxford University Press: New York, 1998).*

2. Think about the cost of making and storing unneeded material.
3. Search for ways to reduce the number of steps in an experiment.
4. Improve yields.
5. Recycle and reuse materials whenever possible.
6. Coordinate work with coworkers who may be using some of the same chemicals.
7. Use the most sensitive analytical methods available when performing analyses.
8. Consider the amount of reagents, solvents, and hazardous materials used by automated laboratory equipment when purchasing a new system.
9. Isolate nonhazardous waste from hazardous waste.
10. Consider using a column purification system for recycling of used solvent (see Chapter 11, Section 3.3).



Microscale equipment, useful in teaching chemistry, reduces both risk and costs.

8.2.3 Using Microscale Work

One successful method of reducing hazards is to carry out chemical reactions and other laboratory procedures on a smaller scale, or *microscale*. In microscale chemistry, the amounts of materials used are reduced to 25 to 100 mg for solids and 100 to 200 µL for liquids, compared to the usual 10 to 50 g for solids or 100 to 500 mL for liquids.

Going to the microscale level saves many tons of waste and millions of dollars. In addition, microscale work reduces fire hazards and the likelihood and severity of accidents that expose people to hazardous chemicals.

8.2.4 Using Safer Solvents and Other Materials

Laboratories are safer and more secure when they substitute nonhazardous, or less hazardous, chemicals whenever possible. Consider alternate synthetic routes and alternate procedures for working up reaction mixtures. Ask the following questions when choosing a reagent or solvent material for an experimental procedure:

- Could we replace this material with one that poses less potential hazard to the experimenter and others?
- Could we replace this material with one that will reduce or eliminate the hazardous waste and the cost of its disposal?

When choosing an organic solvent, consider some key factors:

1. Avoid solvents listed as reproductive toxins, hazardous air pollutants, or select carcinogens (for a definition of select carcinogens, see Chapter 7, Section 4.7 on carcinogens).
2. Choose solvents with relatively high threshold limit values (TLVs).

The best substitute solvent meets these conditions. It also has physiochemical properties (e.g., boiling point, flash point, dielectric constant) that are similar to the original solvent. Consider the benefits to safety, health, and the environment as well as cost.

8.3 Purchasing Chemicals

Part of purchasing a chemical is an analysis of its life cycle and cost. The purchase cost is only the beginning. The handling costs, both human and financial, and disposal costs must be taken into account. Without this analysis, orders may be duplicated and unused chemicals may become a significant portion of the laboratory's hazardous waste.

There are several reasons for ordering chemicals as needed and in smaller containers.

- Small package sizes substantially reduce the risk of breakage.
- Smaller containers reduce the risk of accident and exposure to hazardous material.
- Inventories of single sizes reduce storeroom space needs.
- Smaller containers are emptied faster, resulting in less chance for decomposition of reactive compounds.
- Large containers often must be subdivided. This requires other equipment, such as smaller transfer containers, funnels, pumps, and labels, as well as additional labor and personal protective equipment (PPE), for the hazards involved.
- Smaller containers of unused hazardous material cost less to discard.

An institution should also minimize the amount of chemical accepted as a gift or as part of a research contract to limit the cost of maintaining or disposing of unnecessary chemicals.

8.3.1 Ordering Chemicals

The institution may centralize authority to place chemicals orders in one purchasing office or disperse the authority throughout the institution. A central purchasing system should control the ordering of certain types of materials, such as flammables in containers over a certain size.

Before purchasing a chemical, personnel should ask several questions:

- Is the material already available from another laboratory within the institution or from a surplus chemical stockroom?
- What is the minimum quantity needed for the experiment?
- What is the most appropriate-size container in areas where the material will be used and stored? Establish a maximum allowable quantity for laboratory storage chemicals, such as flammables and combustibles.
- Can the chemical be managed safely when it arrives? Does it require special storage, such as a dry box, refrigerator, or freezer? Do receiving personnel need to be notified of the order and given special instructions for receipt? Will any necessary special equipment be ready when the order arrives?
- Is there a risk of potential intentional misuse of the chemical? See discussion of the dual-use hazards of materials in Chapter 6, Section 4.
- Is the chemical unstable? Inherently unstable materials may have very short storage times. They should be purchased just before use to avoid losing a reagent and creating an unnecessary waste of material and time.
- Can the waste be managed satisfactorily? An appropriate waste characterization and method for proper disposal should be identified before the chemical is ordered.

If possible, use a computerized system of ordering to track information about deliveries, purchasing history, and distribution of chemicals across buildings. For example, centralized ordering may assist in tracking flammables, locations of drug precursors, and chemicals of concern (COCs). Think about keeping a central storage of Material Safety Data Sheets (MSDSs) on a computer network. MSDS data for each chemical should be available to all employees at all times.

8.3.2 Receiving Chemicals

Confine deliveries of chemicals to areas that are equipped to handle them, such as a loading dock, receiving room, or laboratory. Do not make chemical deliveries to departmental offices that are not equipped to receive these packages. However, if delivery to such an office is the only option, identify a separate, undisturbed location, such as a table or shelf, for chemical deliveries. Upon the arrival of a chemical, immediately notify the person who ordered it.

The following are steps to ensure the proper receipt of chemicals:

1. Train receiving room, loading dock, and clerical personnel to recognize hazards that may be associated with chemicals coming into the

facility. They need to know what to do about problems, such as a leaking package or a spill.

2. Equip the receiving room with proper equipment for receiving chemicals. This includes chains for temporarily holding cylinders and carts designed to move various types of chemical containers safely (for more on storing and moving compressed gas cylinders, see Chapter 10, Section 3). Set up shelves, tables, or caged areas for packages to avoid damage by receiving room vehicles.
3. Open incoming packages promptly and inspect them to confirm what was ordered and make sure that containers are sealed in good condition. Laboratory personnel should verify that arriving containers are labeled with an accurate name and the date of receipt on a well-adhered label. Leave labels placed by the manufacturer. Immediately enter new chemicals into the laboratory's inventory.
4. Store unpacked chemicals safely. In particular, promptly unpack and store reactive chemicals shipped in sealed metal containers (e.g., lithium aluminum hydride, sodium peroxide, phosphorus). Proper storage prevents degradation and corrosion and makes chemicals available for periodic inspection.
5. Safely transport chemicals within the facility. Personnel may carry single boxes of chemicals in their original packaging. Move groups of packages or heavy packages by a cart that is stable, has straps or sides to secure packages, and has wheels large enough to handle uneven surfaces easily.
6. If outside delivery people do not handle materials according to the receiving facility's standards, seek immediate correction or other carriers or suppliers.

8.4 Inventory and Tracking of Chemicals

All laboratories should keep an accurate inventory of the chemicals on hand. An inventory is a record, usually a database, of the chemicals in the laboratory and essential information on their proper management. A well-managed inventory includes chemicals obtained from commercial sources and those synthesized in the laboratory, as well as the storage location for each container of each chemical. Inventories help in ordering, storing, handling, and disposing of chemicals, as well as emergency planning.

See *Appendix G.1. Setting Up an Inventory* for more information on setting up and maintaining an inventory.

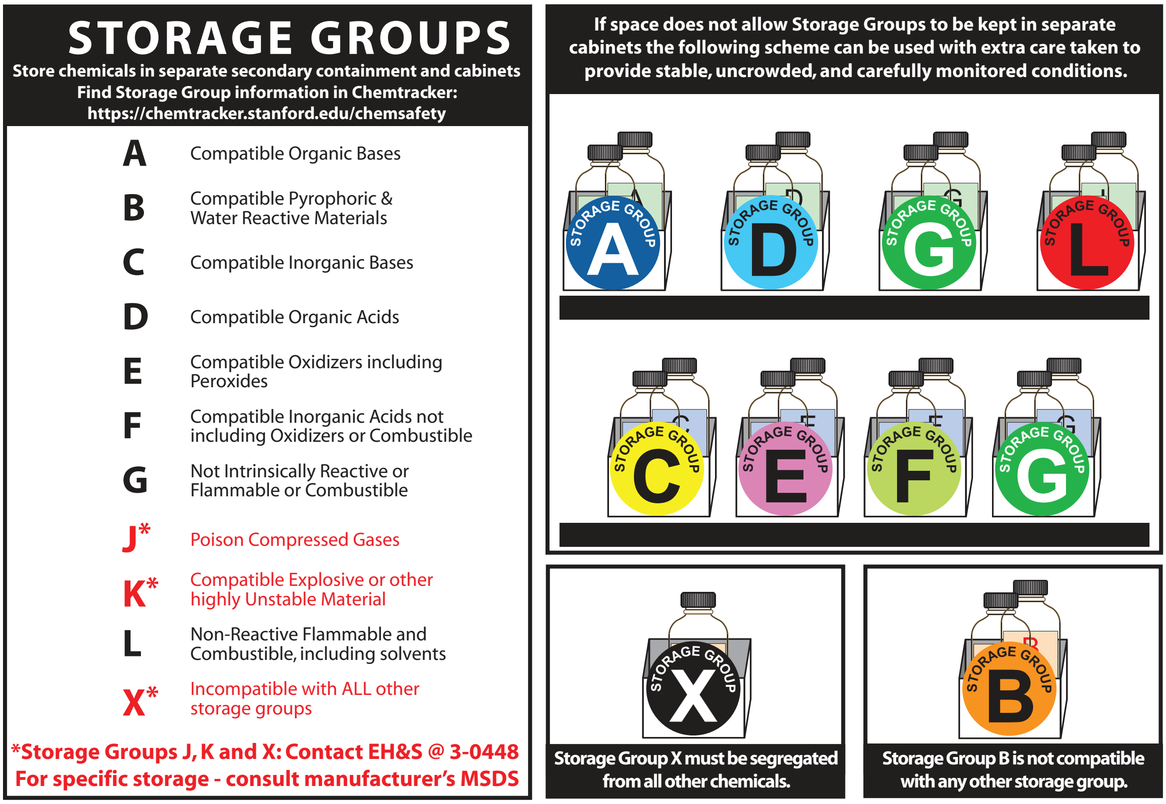
See *Forms: Inventory Log* in the accompanying Toolkit.

8.5 Storage of Chemicals

Follow these general guidelines when storing chemicals and chemical equipment:

1. Provide a definite storage place for each chemical and return the chemical to that location after each use.
2. Store materials and equipment in cabinets and on shelving designated for such storage.
3. Secure shelving and other storage units. Make sure they contain front-edge lips to prevent containers from falling. Ideally, place containers of liquids on metal or plastic trays that could hold the liquid if the container broke. These precautions are especially important in regions where there are earthquakes or other extreme weather conditions.
4. Avoid storing chemicals on bench tops, except for those chemicals in use. Also avoid storing materials and equipment on top of cabinets. If sprinklers are present, maintain a clearance of *at least 18 inches from the sprinkler heads.*
5. Do not store materials on shelves higher than 5 feet (~1.5 m).
6. Avoid storing heavy materials up high.
7. Keep exits, passageways, areas under tables or benches, and emergency equipment areas free of stored equipment and materials.
8. Label all chemical containers appropriately. Place the user's name and the date received on all purchased materials to help inventory control.

Closed containers and proper labeling contribute to good management practices.



STORAGE GROUPS

Store chemicals in separate secondary containment and cabinets
Find Storage Group information in Chemtracker:
https://chemtracker.stanford.edu/chemsafety

A	Compatible Organic Bases
B	Compatible Pyrophoric & Water Reactive Materials
C	Compatible Inorganic Bases
D	Compatible Organic Acids
E	Compatible Oxidizers including Peroxides
F	Compatible Inorganic Acids not including Oxidizers or Combustible
G	Not Intrinsically Reactive or Flammable or Combustible
J*	Poison Compressed Gases
K*	Compatible Explosive or other highly Unstable Material
L	Non-Reactive Flammable and Combustible, including solvents
X*	Incompatible with ALL other storage groups

***Storage Groups J, K and X: Contact EH&S @ 3-0448**
For specific storage - consult manufacturer's MSDS

If space does not allow Storage Groups to be kept in separate cabinets the following scheme can be used with extra care taken to provide stable, uncrowded, and carefully monitored conditions.

Storage Group X must be segregated from all other chemicals.

Storage Group B is not compatible with any other storage group.

Figure 8.1
Compatible storage group classification system. Use this system in conjunction with specific storage conditions taken from the manufacturer's label and MSDS.
SOURCE: Adapted from Stanford University's *ChemTracker Storage System*. Used with permission from Stanford University.

9. Avoid storing chemicals in chemical fume hoods, except for those chemicals in current use.
10. Store volatile toxic or odoriferous chemicals in a ventilated cabinet. If a chemical does not require a ventilated cabinet, store it inside a closable cabinet or on a shelf that has a front-edge lip.
11. Store flammable liquids in approved flammable liquid storage cabinets.
12. Do not expose stored chemicals to heat or direct sunlight.
13. Store chemicals in separate compatible groups sorted alphabetically. See Figure 8.1. for one color-coded method of arranging chemicals.
14. Observe all precautions regarding the storage of incompatible chemicals.
15. Assign responsibility for the storage facility and above responsibilities to one primary person and a backup person. Review this responsibility at least yearly.

See *Appendix G.2. Examples of Compatible Storage Groups* for a list of compatible chemicals.

8.5.1 Containers and Equipment

Follow the specific guidelines below on containers and equipment used to store chemicals.

1. Use secondary containment, such as an overpack, to retain materials if the primary container breaks or leaks.
2. Use corrosion-resistant storage trays as a secondary containment for spills, leaks, drips, or weeping. Polypropylene trays are suitable for most purposes.
3. Provide ventilated cabinets beneath chemical fume hoods for storing hazardous materials.
4. Seal containers to minimize escape of corrosive, flammable, or toxic vapors.

8.5.2 Cold Storage

Safe storage of chemical, biological, and radioactive materials in refrigerators, cold rooms, or freezers requires good labeling and organization. The laboratory manager assigns responsibility for keeping these units safe, clean, and organized and monitors their proper operation. Follow these cold storage guidelines:

1. Use chemical storage refrigerators *only* for storing chemicals. Use waterproof tape and markers to label laboratory refrigerators and freezers.

See *Signs* in the accompanying Toolkit for examples of cold storage labels.

2. Do not store flammable liquids in a refrigerator unless it is approved for such storage. If refrigerated storage is needed inside a flammable storage room, choose an explosion-proof refrigerator. Do not store oxidizers or highly reactive materials in the same unit as flammables.
3. All containers must be closed and stable. Secondary containment, such as plastic trays, is necessary for round bottom flasks and recommended for all containers.
4. Label all materials in the refrigerator with contents, owner, date of acquisition or preparation, and nature of any potential hazard.
5. Organize contents by owner, but keep incompatibles separate. Organize contents by labeling shelves and posting the organization scheme on the outside of the unit.

6. Every year, review the entire contents of each cold storage unit. Dispose of all unlabeled, unknown, or unwanted materials, including those belonging to personnel who have left the laboratory.

8.5.3 Storage of Flammable and Combustible Liquids

There should be a limited amount of flammable and combustible liquids in laboratories. The quantity allowed depends on a number of factors, including

- the construction of the laboratory;
- the number of fire zones in the building;
- the floor level where the laboratory is located;
- fire protection systems built into the laboratory;
- the presence of flammable liquid storage cabinets or safety cans; and
- the type of laboratory (i.e., instructional or research and development).

Follow these guidelines for storing flammable and combustible liquids:

1. When space allows, store combustible liquids in flammable storage cabinets.
2. Store combustible liquids either in their original (or other approved) containers or in safety cans. When possible, store quantities of flammable liquids greater than 1 L in safety cans.
3. Store 55-gallon (~208-L) drums of flammable and combustible liquids in special storage rooms for flammable liquids.
4. Keep flammable and combustible liquids away from strong oxidizing agents, such as nitric or chromic acid, permanganates, chlorates, perchlorates, and peroxides.
5. Keep flammable and combustible liquids away from any ignition sources. Remember that many flammable vapors are heavier than air and can travel to ignition sources.

8.5.4 Storage of Gas Cylinders

Check international, regional, or local building and fire codes to determine the maximum amount of gas to be stored in a laboratory. With toxic and reactive gases, or large quantities of asphyxiating gases, a special gas cabinet may be required. Gas cabinets are designed for leak detection, safe change-outs, ventilation, and emergency release.

For commonly used laboratory gases, consider the installation of in-house gas systems. Such systems remove the need for transport and in-laboratory handling of compressed gas cylinders. Chapter 10, Section 3, provides additional information on managing compressed gases in the laboratory.

8.5.5 Storage of Highly Reactive Substances

Check international, regional, or local building and fire codes to determine the maximum amount of highly reactive chemicals that can be stored in a laboratory. Follow the general guidelines below when storing highly reactive substances.

1. Consider the storage requirements of each highly reactive chemical before bringing it into the laboratory.
2. Consult the MSDSs or other literature in making decisions about storing highly reactive chemicals.
3. Bring into the laboratory only the quantities of material needed for immediate purposes (up to a 6-month supply, depending on the materials).
4. Be sure to label, date, and inventory all highly reactive materials as soon as received.

See *Signs* in the accompanying Toolkit for examples of labels for highly reactive substances.

5. Do not open a container of highly reactive material that is past its expiration date. Call your institution's hazardous waste coordinator for special instructions.
6. Do not open a liquid organic peroxide or peroxide former if crystals or a precipitate are present. Consult with your CSSO for special instructions.
7. For each highly reactive chemical, determine a review date to reevaluate its need and condition and to dispose of (or recycle) material that degrades over time.
8. Separate the following materials:
   - oxidizing agents from reducing agents and combustibles;
   - powerful reducing agents from readily reducible substrates;
   - pyrophoric compounds from flammables; and
   - perchloric acid from reducing agents.

Acids should be stored in glass bottles set in individual containers and kept on trays. These measures will keep the materials segregated and catch any spills.

9. Store highly reactive liquids in trays large enough to hold the contents of the bottles.
10. Store perchloric acid bottles in glass or ceramic trays.
11. Store peroxidizable materials away from heat and light.
12. Store materials that react vigorously with water away from possible contact with water.
13. Store thermally unstable materials in a refrigerator. Use a refrigerator with these safety features:
    - all spark-producing controls on the outside;
    - a magnetic locked door;
    - an alarm to warn when the temperature is too high; and
    - a backup power supply.
14. Store liquid organic peroxides at the lowest possible temperature consistent with the solubility or freezing point. Liquid peroxides are particularly sensitive during phase changes. Follow the manufacturer's guidelines for storage of these highly hazardous materials.
15. Inspect and test peroxide-forming chemicals periodically and label them with an acquisition or expiration date. Dispose of expired chemicals.
16. Store particularly sensitive materials or larger amounts of explosive materials in explosion relief boxes.
17. Restrict access to the storage facility.

8.5.6 Storage of Highly Toxic Substances

Take the following precautions when storing carcinogens, reproductive toxins, and chemicals with a high degree of acute toxicity.

1. Store chemicals known to be highly toxic in ventilated storage in unbreakable, chemically resistant secondary containment.
2. Keep quantities at a minimum working level.
3. Label storage areas with appropriate warning signs.
4. Limit access to storage areas.
5. Maintain an inventory of all highly toxic chemicals.

8.6 Transfer, Transport, and Shipment of Chemicals

When moving chemical materials onsite, use secondary containment, such as a rubber bucket, for carrying bottled chemicals. Institutions with a large campus may want to designate a special courier or vehicles to transport regulated materials.

International regulations apply to the movement of chemicals, samples, and other research materials on public roads, by airplane, or by mail or other carrier. National and international laws strictly regulate domestic and international transport of samples, specimens, drugs, and genetic elements, as well as research equipment, technologies, and supplies—even if the material is not hazardous, valuable, or uncommon.

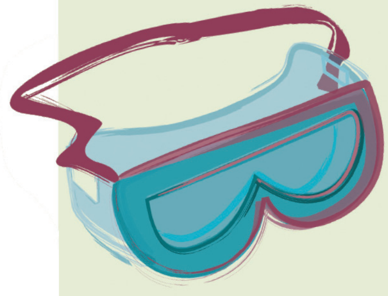
For most chemicals, biological agents, and radioactive materials, shipping domestically or internationally is regulated by the International Air Transport Association (IATA; see *www.iata.org*). An individual who holds IATA certification must inspect the packaging, review the paperwork, and sign the shipping papers.

Label as completely as possible any samples of experimental materials that are to be moved. When available, provide the following information with transported experimental materials:

- **Originator:** the name of the owner or individual who first obtained the material. If sending the material to another facility, add contact information for the person who can provide safe handling information.
- **Identification:** the laboratory notebook reference.
- **Hazardous components:** the known primary hazardous components.
- **Potential hazards:** the possible hazards.
- **Date:** the date that the material was placed in the container and labeled.
- **Ship to:** the name, location, and telephone number of the person to whom the material is being transferred.
- **MSDS:** include this with hazardous samples sent to another institution.

Transport hazardous materials in specially designated vehicles that follow international regulations. Do not use personal, company, or institutional vehicles (including airplanes), for transporting hazardous chemicals.

9



Working with Chemicals

9.1 Introduction

Safe and secure execution of experiments requires work practices that reduce risk and protect the health and safety of laboratory personnel as well as the public and the environment. This chapter presents general guidelines for laboratory work with hazardous chemicals rather than specific standard operating procedures for individual substances. Laboratory personnel should conduct their work under conditions that reduce risks due to both known and unknown hazardous substances. The general work practices in this chapter show how to achieve that goal.

Four fundamental principles underlie all the work practices discussed in this chapter:

1. **Plan ahead.** Determine the potential hazards associated with an experiment before beginning (see Chapter 7 for more details on assessing hazards). Have a plan in place for handling waste generated in the laboratory before any work is begun (see Chapter 11 for more on managing waste).
2. **Limit exposure to chemicals.** Do not allow laboratory chemicals to come in contact with the body. Use laboratory chemical hoods and other ventilation devices to prevent exposure to airborne substances whenever possible (see Chapter 10 for more on laboratory equipment).
3. **Do not underestimate risks.** Assume that any mixture of chemicals will be more toxic than its most toxic component. Treat all new compounds and substances of unknown toxicity as toxic substances.
4. **Be prepared for accidents.** Before beginning an experiment, know what specific action to take in the event of accidental release of any hazardous substance. Know the location of all safety equipment and the nearest fire alarm and telephone, and know what telephone numbers to call and whom to notify in the event of an emergency. Be prepared to provide basic emergency treatment. Keep your coworkers informed of your activities so they can respond appropriately.

Many elements of a good emergency plan can be easily implemented. Post emergency phone numbers where they can be found and used immediately.

9.2 Careful Planning

Before beginning any laboratory work, determine the hazards and risks associated with the experiment or activity, and take the necessary safety precautions.

1. Ask this hypothetical question prior to starting work: *What would happen if ...?* For example, what would happen if the laboratory lost electrical power or water pressure? Consider the possible backup plans and prepare to take appropriate emergency actions.

2. Be familiar with the laboratory's emergency preparedness plan (see Chapter 3 for more details on emergency planning).
3. Determine the physical and health hazards associated with chemicals before working with them, as outlined in Chapter 7.
4. Pay attention to the potential safety implications of subtle changes in experimental procedures. Slight changes to operations—solvents, suppliers, reagent concentration, reaction scale, and materials of construction—may cause unintended hazards.
5. Check every step of the waste minimization and removal processes against applicable regulations if they exist.

9.3 General Procedures for Working with Hazardous Chemicals

9.3.1 Personal Behavior

All personnel should follow the following professional standards:

1. Avoid distracting or startling other personnel.
2. Do not allow practical jokes, boisterous conduct, or excessive noise at any time.
3. Use laboratory equipment only for its designated purpose.
4. Review basic safety procedures with all visitors to laboratories where hazardous substances are stored or in use or where hazardous activities are in progress.
5. If minors are permitted in laboratories, ensure that they are under the direct supervision of qualified adults at all times. Develop a policy regarding minors in the laboratory, and review and approve all activities of minors prior to their arrival. Make sure other laboratory personnel in the area are aware of the presence of minors.

9.3.2 Reducing Exposure to Chemicals

Take care to avoid exposure by the principal routes: skin and eye contact, inhalation, and ingestion. The preferred methods for reducing chemical exposure, in order of preference, are as follows:

1. Substitution of less hazardous materials or processes
2. Engineering controls
3. Administrative controls
4. Personal protective equipment (PPE; Also, see section 10.5)

9.3.2.1 *Engineering Controls*

Engineering controls are measures that eliminate, isolate, or reduce exposure to chemical or physical hazards through the use of various devices. Examples include laboratory chemical hoods and other ventilation systems, shields, barricades, and interlocks. *Engineering controls must always be the first and primary line of defense to protect personnel and property. PPE should not be used as a first line of protection.* For instance, a personal respirator should not be used to prevent inhalation of vapors when a laboratory chemical hood (formerly called fume hood) is available.

9.3.2.2 *Avoiding Eye Injury*

Eye protection is required for all personnel and visitors in all locations where laboratory chemicals are stored or used, whether or not a person is actually performing a chemical operation. Make eye protection available to all visitors at the entrances to all laboratories. Researchers should assess the risks associated with an experiment and use the appropriate level of eye protection. Operations that are at risk of explosion or that present the possibility of projectiles must have engineering controls as a first line of protection.

Contact lenses offer no protection against eye injury and are no substitute for safety glasses or chemical splash goggles. Contact lenses should not be worn where there is the possibility of exposure to chemical vapors, chemical splashes, or chemical dust. Contact lenses can be damaged under these conditions.

Goggles and gloves are essential to protect eyes and hands from accidental chemical exposure in the laboratory.

9.3.2.3 *Avoiding Ingestion of Hazardous Chemicals*

In the laboratory, **do not allow**

- eating, drinking, smoking, gum chewing, applying cosmetics, and taking medicine where hazardous chemicals are used;
- storing food, beverages, cups, and other drinking and eating utensils where hazardous chemicals are handled or stored;
- preparation or consumption of food or beverages in glassware used for laboratory operations;
- food storage or preparation in laboratory refrigerators, ice chests, cold rooms, and ovens;
- the use of laboratory water sources and deionized laboratory water as drinking water;

- tasting of laboratory chemicals; and
- pipetting done by mouth (a pipette bulb, aspirator, or mechanical device should be used to pipette chemicals or start a siphon).

Wash hands with soap and water immediately after working with any laboratory chemicals, even if gloves have been worn.

9.3.2.4 *Avoiding Inhalation of Hazardous Chemicals*

Sniff laboratory chemicals only in certain controlled situations. Never deliberately sniff toxic chemicals or compounds of unknown toxicity. Conduct under a chemical hood all procedures involving volatile toxic substances and all operations involving solid or liquid toxic substances that may result in the generation of aerosols (see Chapter 5 for more information on laboratory chemical hoods). Air-purifying respirators are required for use with some chemicals if engineering controls cannot prevent exposure. Significant training is necessary for the use of respirators.

In a controlled setting, instructors may tell students to sniff the contents of a container. In such cases, screen in advance the chemical being sniffed to make sure that it is safe. If instructed to sniff a chemical, gently waft the vapors toward your nose using a folded sheet of paper. Do not directly inhale the vapors.

Do not use laboratory chemical hoods for disposal of hazardous volatile materials by evaporation. Such materials should be treated as chemical waste and disposed of in appropriate containers according to institutional procedures and government regulations (see Chapter 11 for more on managing waste).

9.3.2.5 *Minimizing Skin Contact*

Wear gloves whenever handling hazardous chemicals, sharp-edged objects, very hot or very cold materials, toxic chemicals, and substances of unknown toxicity. No single glove material provides effective protection for all uses.

The following general guidelines apply to the selection and use of protective gloves:

1. Select gloves carefully to make sure that they are impervious to the chemicals being used and are of correct thickness to allow reasonable dexterity while also providing adequate barrier protection.
   - In general, nitrile gloves are suitable for incidental contact with chemicals.
   - Both nitrile and latex gloves provide minimal protection from chlorinated solvents and should not be used with oxidizing or corrosive acids.
   - Latex gloves protect against biological hazards but offer poor protection against acids, bases, and most organic solvents. In addition,

No single glove material provides effective protection for all uses.

latex is considered a sensitizer and triggers allergic reactions in some individuals.

   - Neoprene and rubber gloves with increased thickness are suggested for use with most caustic and acidic materials.
   - Leather gloves are appropriate for handling broken glassware and inserting tubing into stoppers, where protection from chemicals is not needed.
   - Insulated gloves should be used when working with very hot or very cold materials.

2. Do not use a glove beyond its expiration date. Gloves degrade over time, even in an unopened box.
3. Inspect gloves for small holes, tears, and signs of degradation before use.
4. Wash gloves appropriately before removing them. (*Note:* Some gloves, such as leather and polyvinyl alcohol, are water permeable. Unless coated with a protective layer, polyvinyl alcohol gloves will degrade in the presence of water.)
5. Wash and inspect reusable gloves before and after each use. Replace them periodically because they degrade with use, depending on the frequency of use and their permeation and degradation characteristics relative to the substances handled.
6. Gloves that might be contaminated with toxic materials should not be removed from the immediate area (usually a laboratory chemical hood) in which the chemicals are located. They should never be worn outside the laboratory or when handling common items, such as doorknobs, telephones, switches, pens, and computer keyboards.
7. Wear a double set of gloves when a single glove material does not provide adequate protection for all the hazards encountered in a given operation. For instance, operations involving a chemical hazard and sharp objects may require the combined use of a chemical-resistant glove (butyl, viton, neoprene) and a cut-resistant glove (leather, Kevlar, etc.).

Heavy lab gloves have been chosen to provide adequate protection for the task.

Gloves are needed even when handling chemicals in bottles—which may break.

8. When not in use, store gloves in the laboratory but not close to volatile materials. To prevent contamination, do not store gloves in offices, breakrooms, or lunchrooms.
9. Personnel with known latex allergies should not wear latex gloves and should avoid working in areas where latex gloves are used.

9.3.3 Housekeeping

An orderly laboratory is a safe laboratory. By contrast, a disorderly laboratory can hinder or endanger emergency responders. Follow these housekeeping rules:

1. Never obstruct access to exits and emergency equipment such as fire extinguishers and safety showers. Follow local fire codes for emergency exits, electrical panels, and minimum aisle width.
2. Regularly clean work areas, including floors, to reduce respiratory hazards.
3. Properly label and neatly store all chemicals in order. Face labels outward for easy viewing. Containers themselves should be clean and free of dust. For containers and labels that have begun to degrade, replace, repackage, or dispose of them in the proper location.
4. Return all equipment and laboratory chemicals to their designated storage locations at the end of the day.
5. Secure all compressed gas cylinders to walls or benches.
6. Do not store chemical containers on the floor.
7. Do not use floors, stairways, and hallways as storage areas.

9.3.4 Handling Flammable Substances

Flammable and combustible materials are a common laboratory hazard. Always consider the risk of fire when planning laboratory operations.

1. To reduce the risk of fire, first learn the flammability and explosive characteristics of the materials being used. Read solvent labels, material safety

data sheets (MSDSs), or other sources of information to learn the flash point, vapor pressure, and explosive limit in air of each chemical handled.

2. Whenever possible, remove ignition sources and avoid the combined presence of a fuel and an oxidizer. Control, contain, and reduce the amount of fuels and oxidizers. Do not use containers that have large openings (e.g., beakers, baths, vats) with highly flammable liquids or with liquids above their flash point. Consider using inert gases to blanket or purge vessels containing flammable liquids.
3. Plan to both prevent and respond to a flammable liquid spill. Place distillation and reaction flasks in secondary containment to prevent the spread of flammable liquid in the event of breakage.
4. Learn the institution's and laboratory's emergency preparedness plans and procedures for responding to fires. Use fire extinguishers in the immediate vicinity of an experiment that are appropriate to the particular fire hazards. Post in a prominent location the telephone numbers to call in an emergency or accident. For more on emergency planning, see Chapter 3.

Any ignition source, such as this flame test for lithium salt, represents a potential source of fire.

9.3.5 Working with Scaled-up Reactions

Special care and planning are necessary to keep scaled-up work safe. Scaled-up reactions include those producing a few milligrams or grams to those producing more than 100 g of a product, and they may increase risks significantly. Although the procedures and controls for large-scale reactions may be the same as those for smaller ones, great differences may exist in heat transfer, stirring effects, times for dissolution, and the effects of concentration. Evaluate the hazards of a scaled-up reaction if any of the following conditions exist:

- The starting material and intermediates contain functional groups that have a history of being explosive bonds or that could explode to give a large increase in pressure.
- A reactant or product is unstable near the reaction or work-up temperature (a preliminary test consists of heating a small sample in a melting point tube).
- A reactant is capable of self-polymerization.
- A reaction is delayed, meaning that an induction period is required.
- Gaseous by-products are formed.
- A reaction is exothermic, and plans must be made to provide or regain control of the reaction if it begins to run away.

- A reaction requires a long reflux period and solvent may be lost due to poor condenser cooling.
- A reaction requires temperatures less than 0°C and may pose a hazard if it warms to room temperature.
- A reaction involves stirring a mixture of solid and liquid reagents. (Ask questions such as, Will magnetic stirring be sufficient at large scale or will overhead mechanical stirring be required? What will happen if stirring efficiency is not maintained at large scale?)

In addition, thermal phenomena that produce significant effects on a larger scale may not have been detected in smaller-scale reactions and therefore could be less obvious than toxic or environmental hazards. Use thermal analytical techniques to determine whether any process modifications are necessary.

Consider scaling up the process in multiple small steps, evaluating the above issues at each step. Be sure to review the literature and other sources to fully understand the reactive properties of the reactants and solvents, which may not have been present at a smaller scale.

9.3.6 Leaving Experiments Unattended and Working Alone

It is inadvisable to work alone at the bench in a laboratory building. Personnel working alone should make arrangements to check on each other periodically or ask security guards to check on them. Do not undertake hazardous experiments alone in a laboratory.

Avoid unattended operations whenever possible. However, sometimes laboratory operations involving hazardous substances must be carried out continuously or overnight with no one present. In those cases, personnel should design experiments to prevent the release of hazardous substances in the event that utility services such as electricity, cooling water, and flow of inert gas are interrupted.

For unattended operations, leave on laboratory lights and post signs identifying the nature of the experiment and the hazardous substances in use. If appropriate, make arrangements for other workers to periodically inspect the operation. Post information indicating how to contact the responsible person in the event of an emergency.

9.3.7 Responding to Accidents and Emergencies

All laboratory personnel should know what to do in an emergency. Every laboratory should have a written emergency response plan that addresses injuries, spills, fires, accidents, and other possible emergencies and includes procedures for communication and response. Laboratory work should not be undertaken without knowledge of the emergency response plan. See Chapter 3 for more information on responding to emergencies.

9.3.7.1 *Handling the Accidental Release of Hazardous Substances*

Always design experiments to reduce the possibility of an accidental release of hazardous substances. Laboratory staff should use the minimum amount of hazardous material possible and perform the experiment so that, as much as possible, any spill is contained.

In the event of an incidental, laboratory-scale spill, follow these general guidelines, in order:

1. **Notify other laboratory personnel of the accident.** In some cases, such as incidents involving the release of highly toxic substances or spills occurring in non-laboratory areas, it may be appropriate to activate a fire alarm to alert people to evacuate the entire building. Call the proper emergency responders. Follow your institution's policies for such situations.
2. **If necessary, evacuate the area.** If a highly toxic gas or volatile material is released, evacuate the laboratory and post personnel at entrances to prevent others from inadvertently entering the contaminated area.
3. **Tend to any injured or contaminated personnel and, if necessary, request help.** If a person is injured or contaminated with a hazardous substance, tending to him or her generally takes priority over implementing the spill control measures. Obtain medical attention for the person as soon as possible by calling emergency responders. Provide a copy of the appropriate MSDS to the attending physician, as needed. *If you cannot assess the conditions of the environment well enough to be sure of your own safety, do not enter the area.* Call emergency responders and describe the situation as best you can.
4. **Take steps to confine and limit the spill if this can be done without risk of injury or contamination** (see below for more information).
5. **Clean up the spill using appropriate procedures** (see below for more information).
6. **Dispose of contaminated materials properly** (see Chapter 11 for more details).

9.3.7.2 *Spill Containment*

All people who work in a laboratory where hazardous substances are used should know their institution's spill control policy. For nonemergency spills, spill control kits may be available that are tailored to the potential risk of the materials being used. These kits are used to confine and limit the spill if it can be done without risk of injury or contamination. Assign a person to maintain the kits. Store spill kits near laboratory exits for ready access. Typical spill control kits might include the following items:

Absorbent materials for chemical spills are best stored near exits, where they can readily be found when needed.

- Spill control pillows. In general, use these commercially available pillows for absorbing solvents, acids, and caustic alkalis, but not hydrofluoric acid.
- Inert absorbents, such as vermiculite, clay, and sand. Paper is not an inert material and should not be used to clean up oxidizing agents such as nitric acid.
- Neutralizing agents for acid spills such as sodium carbonate and sodium bicarbonate.
- Neutralizing agents for alkali spills such as sodium bisulfate and citric acid.
- Large plastic scoops and other equipment such as brooms, pails, bags, and dustpans.
- Appropriate PPE, warnings, barricade tapes, and protection against slips or falls on the wet floor during and after cleanup.

In an emergency, follow institutional guidelines regarding spill containment.

A nonemergency response is appropriate in the case of an incidental release of hazardous substances where the substance can be absorbed, neutralized, or otherwise controlled by nearby personnel or maintenance personnel. An emergency is a situation that poses an immediate threat to personal safety and health, the environment, or property that cannot be controlled and corrected safely and easily by people at the scene.

9.3.7.3 *Spills with Substances of High Toxicity*

Be sure that emergency response procedures, spill kits, and emergency response kits cover highly toxic substances. Train all laboratory personnel in their proper use. Spill kits for toxic substances should be marked, contained, and sealed to avoid contamination and make them accessible in an emergency. Essential contents include spill control absorbents, impermeable surface covers (to prevent the spread of contamination while conducting emergency response), warning signs, emergency barriers, first aid supplies, and antidotes.

Carry out experiments conducted with highly toxic chemicals in work areas designed to contain accidental releases. Use trays and other types of secondary containment to contain inadvertent spills. Observe careful techniques to reduce the risk of spills and releases.

Post all toxicity and emergency response information *outside* the immediate area so it is accessible in emergencies. Train all laboratory personnel who could be exposed how to respond in such an emergency. Conduct occasional emergency response drills. Such dry runs may involve medical personnel as well as emergency cleanup crews.

9.3.7.4 *Spill Cleanup*

Specific procedures for cleaning up spills vary depending on the location of the accident, the amount and hazards of the spilled material, and the training of the people involved. Perform any cleanup while wearing appropriate PPE and in line with institutional procedures. Below are general guidelines for cleaning up several common incidental, nonemergency spills.

- **Materials of low flammability that are not volatile or that have low toxicity.** This category of hazardous substances includes inorganic acids (e.g., sulfuric and nitric acid) and caustic bases (e.g., sodium and potassium hydroxide). For cleanup, wear appropriate PPE, including gloves, chemical splash goggles, and shoe coverings if necessary. Neutralize the spilled chemicals with materials such as sodium bisulfate (for alkalis) and sodium carbonate or bicarbonate (for acids), then absorb them onto an inert material such as vermiculite, scoop them up, and dispose of them appropriately.
- **Flammable solvents.** Fast action is crucial when a flammable solvent of relatively low toxicity is spilled. This category includes petroleum ether, pentane, diethyl ether, dimethoxyethane, and tetrahydrofuran. Alert other personnel in the laboratory, extinguish all flames, and turn off any spark-producing equipment. In some cases, shut off power to the laboratory with the circuit breaker, but keep the ventilation system running. Soak up the spilled solvent with spill absorbent or spill pillows as quickly as possible. If this cannot be done quickly, consider evacuating the laboratory. Seal used absorbent and pillows in containers and dispose of them properly. Use non-sparking tools in cleanup.

Apply an inert absorbent to clean up spilled chemicals but be sure to neutralize them first and wear appropriate PPE.

- **Highly toxic substances.** Do not attempt to clean up highly toxic substances alone. Notify emergency responders, and contact the laboratory chemical safety and security officer (CSSO) or laboratory manager for help in evaluating the hazards involved. These professionals will know how to clean up the material.
- **Debris management.** Handle debris from the cleanup as hazardous waste if the spilled material falls into that category.

9.3.7.5 *Handling Spills of Elemental Mercury*

When spilled in a laboratory, mercury can become trapped beneath floor tiles, under cabinets, and even between walls. Even at very low levels, chronic mercury exposure can be a serious risk, especially in older laboratory facilities where multiple spills may have occurred. Use a portable atomic absorption spectrophotometer with a sensitivity of at least 2 ng/m^3 to find mercury residues and reservoirs from laboratory spills and for the final clearance survey. Follow these general guidelines for handling incidental, nonemergency elemental mercury spills:

1. First, isolate the spill area. Keep people from walking through and spreading the contamination.
2. Wear protective gloves while performing cleanup activities.
3. Collect the droplets on wet toweling, which consolidates the small droplets to larger pieces, or with a piece of adhesive tape. Do not use sulfur. This practice is ineffective, and the waste creates a disposal problem.
4. Consolidate large droplets by using a scraper or a piece of cardboard.
5. Use commercial mercury spill cleanup sponges and spill control kits.
6. Use specially designed mercury vacuum cleaners that have special collection traps and filters to prevent the release of mercury vapors. Never use a standard vacuum cleaner to pick up mercury.
7. Place waste mercury in a thick-wall high-density polyethylene bottle and transfer it to a central depository for reclamation.
8. Decontaminate the exposed work surfaces and floors by using an appropriate decontamination kit.
9. Verify decontamination to the current standards by using the portable atomic absorption spectrophotometer described above.

Prevent mercury spills by using supplies and equipment that do not contain mercury.

9.3.7.6 *Responding to Fires*

Fires are among the most common types of laboratory accidents. All personnel should be familiar with the general guidelines below to prevent and reduce injury and damage from fires.

1. Make sure all laboratory personnel know the locations of all fire extinguishers in the laboratory, what types of fires they can be used for, and how to operate them correctly. Also make sure they know

Clothing and long hair left unsecured could catch fire or become contaminated. Keep loose material away from equipment and processses.

the location of the nearest fire alarm pull station, safety showers, and emergency blankets.

2. In case of fire, immediately notify emergency responders by activating the nearest fire alarm.
3. Attempt to put out a fire only if you are trained to use the appropriate type of extinguisher, can do it successfully and quickly, and are between the fire and an exit to avoid being trapped. Do not underestimate the danger. When in doubt, evacuate immediately instead of attempting to extinguish the fire.
4. Put out fires in small vessels by covering the vessel loosely. Never pick up a flask or container of burning material.
5. Extinguish small fires involving reactive metals and organometallic compounds (e.g., magnesium, sodium, potassium, metal hydrides) using specialized extinguishers or by covering with dry sand. Apply additional fire suppression methods if solvents or combustibles become involved. Because these fires are very difficult to extinguish, sound the fire alarm before attempting to put out the fire.
6. In the event of a more serious fire, evacuate the laboratory and activate the nearest fire alarm. Tell emergency responders what hazardous substances are in the laboratory.
7. If a person's clothing catches fire, douse him or her immediately in a safety shower. The drop-and-roll technique is also effective. Use fire blankets only as a last resort because they tend to hold in heat and to increase the severity of burns by creating a chimney-like effect. Remove contaminated clothing quickly. Wrap the injured person in a blanket to avoid shock, and get medical attention promptly.

9.4 Working with Substances of High Toxicity

People who work with highly toxic chemicals should know the general guidelines for the safe handling of chemicals in laboratories. However, these guidelines alone are not sufficient when handling such substances. Additional precautions are needed to set up *multiple lines of defense to reduce the risks* posed by highly toxic substances.

Careful planning should come before any experiment involving a highly toxic substance, whenever the substance is to be used for the first time, or whenever an experienced user carries out a new protocol that increases the risk of exposure substantially. Planning should include consultations with colleagues and experts in the institution's laboratory safety program. Thoroughly review the wealth of information available in the MSDS, the literature, and toxicological and safety references. Always consider substituting less toxic substances for highly toxic ones, and be sure to use the smallest amount of material possible. Refer to Chapter 7, Section 4, for more information on planning experiments with highly toxic substances.

9.4.1 Planning for Experiments Involving Highly Toxic Chemicals

Before the experiment begins, prepare a plan that describes the additional safeguards that will be used for all phases of the experiment, from acquiring to disposing of the chemical. Record the amounts of materials used and the names of the people involved in the written summary and the laboratory notebook.

Find out whether monitoring is necessary to keep experimenters safe, if there is reason to believe that exposure levels of the substances in the experiment could exceed established safety levels.

People who conduct the work should know the signs and symptoms of acute and chronic exposure, including delayed effects. Consult a physician or other medical experts to determine if health screening or medical surveillance is appropriate.

9.4.2 Assigning Designated Areas

Confine experimental procedures involving highly toxic chemicals to a designated work area in the laboratory that is recognized by all personnel. This includes their transfer from storage containers to reaction vessels. Post signs conspicuously to indicate the designated areas. The area may be used for other purposes, as long as all laboratory personnel comply with training, safety, and security requirements, and they are familiar with the emergency response protocols of the institution.

In consultation with the CSSO, the laboratory supervisor should determine which procedures and highly toxic chemicals need to be confined to designated areas.

9.4.3 Controlling Access

For laboratories where highly toxic chemicals are in use, restrict access to people who are authorized for this laboratory work and trained in the special precautions that apply. See Chapter 6 for procedures used to control access to highly toxic substances.

When long-term experiments involving highly toxic compounds require unattended operations, include fail-safe backup options, such as shutoff devices, in case a reaction overheats or pressure builds up. In addition, include equipment interlocks that shut down experiments by turning off devices such as heating baths, reagent pumps, solenoid valves, or laboratory chemical hoods. An interlock should place the experiment in a safer mode if a problem occurs and should not reset even if the hazardous condition is reversed.

Protective devices should include alarms that indicate their activation. Never ask or allow security guards and untrained personnel to check on the status of unattended experiments involving highly toxic materials. Post warning signs on locked doors that list the trained laboratory personnel to contact in case an alarm sounds within the laboratory.

Keep a detailed inventory of highly toxic chemicals. See Chapter 8 for more details on keeping inventories.

9.4.4 Minimizing Exposure to Highly Toxic Chemicals

Listed below are necessary precautions that promote safety in laboratory work with highly toxic chemicals.

1. Conduct procedures involving highly toxic chemicals that can generate dust, vapors, or aerosols in a laboratory chemical hood, glove box, or other suitable containment device.
2. Wear gloves when working with toxic liquids or solids to protect the hands and forearms.
3. Wear face and eye protection to prevent ingestion, inhalation, and skin absorption of toxic chemicals.
4. Isolate from the general laboratory the equipment used in handling highly toxic chemicals. Consider venting laboratory vacuum pumps used with these substances through high-efficiency scrubbers or an exhaust hood. Motor-driven vacuum pumps are recommended because they are easy to decontaminate (conduct decontamination in a designated hood).
5. Always practice good laboratory hygiene where highly toxic chemicals are handled. After using toxic materials, wash the face, hands, neck, and arms. Never remove from the environment the equipment reserved for

handling toxic materials, including PPE such as gloves, without complete decontamination. Choose laboratory equipment and glassware that is easy to clean and decontaminate. Never smell or taste mixtures that contain toxic chemicals or substances of unknown toxicity.

6. Carefully plan the transportation of very toxic chemicals. For more information on transporting these substances, refer to Chapter 8.

Consult Chapter 10 for more information on PPE. See Chapter 5 for more information on laboratory hoods, glove boxes, and vacuum pumps.

9.4.5 Storage and Waste Disposal

Follow safe and secure practices for the storage and disposal of highly toxic chemicals. Label all containers of highly toxic chemicals with chemical composition, known hazards, and warnings for handling. Properly store these chemicals in specially designated areas.

Follow the institution's procedures for waste disposal. Otherwise, consider the possibility of pretreatment of waste either before or during accumulation. In-laboratory destruction may be the safest and most effective way of dealing with waste, but regulatory requirements may affect this decision.

See Chapter 8, Section 5.6., for more information on storage of these substances. Refer to Chapter 11, Sections 3 and 5, for more on the disposal of highly toxic chemical waste.

9.5 Working with Biohazardous Materials

Use biological materials with the same general precautions as hazardous chemicals. Take the following additional measures to reduce risks when handling infectious agents.

1. Eliminate or work very carefully with sharp objects (such as needles, scalpels, Pasteur pipettes, and capillary tubes).
2. Work carefully to reduce the potential for aerosol formation. Confine aerosols as closely as possible to their sources with a biosafety cabinet.
3. Disinfect work surfaces and equipment after use.
4. Wash hands after removing protective clothing, after contact with contaminated materials, and before leaving the laboratory.

Other practices that are most helpful for preventing laboratory-acquired infections or intoxications are as follows:

1. Keep laboratory doors closed when experiments are in progress.
2. Use leak-proof secondary containment to move or transfer cultures.
3. Decontaminate infectious waste before disposal.

9.6 Working with Flammable Chemicals

All laboratory personnel should know the properties of the chemicals they are handling and have a basic understanding of how laboratory conditions might affect these properties. MSDSs or other sources of information should be consulted for information such as vapor pressure, flash point, and explosive limit in air. See Chapter 7 for more guidance on assessing the flammability of chemicals.

Follow these general practices for working with flammable chemicals:

1. Use the smallest amounts possible.
2. As much as possible, reduce or eliminate the combined presence of flammable material and an oxidizer, such as air. Cap bottles and vessels not in use. Use inert gas blankets when possible.
3. Store chemicals properly, physically separating flammable materials from other operations and sources of ignition.
4. Store flammable substances that require low-temperature storage only in refrigerators designed for that purpose. Never use ordinary refrigerators for storing chemicals.
5. Eliminate ignition sources from areas where flammable substances are handled. These sources include Bunsen burners; matches; smoking tobacco; gas burners; gas-fired space heating or water-heating equipment; electrical equipment such as stirring devices, motors, relays, and switches; and low-level ignition sources, such as hot plates, static discharge from clothing, steam lines, or other hot surfaces.
6. Never heat flammable substances with an open flame. Preferred heat sources include steam baths, water baths, oil and wax baths, salt and sand baths, heating mantles, and hot air or nitrogen baths.
7. Before igniting a flame, check for the presence of a flammable substance.
8. Properly ground static sources of ignition, and use the least hazardous alternative available.
9. Ground accumulated static charge when transferring flammable liquids in metal containers to avoid sparks.
10. Always attend to equipment such as hot plates, oil baths, heating mantles, stills, ovens, dryers, and other heating devices when in operation. When

In a heating mantle, the heating element is insulated from the glass container, reducing the risk of igniting flammable substances.

purchasing these devices, choose those models with automatic high-temperature shutoffs.

11. Keep appropriate fire extinguishing equipment readily available.

9.6.1 Working with Flammable Liquids

Follow these procedures for working with flammable liquids:

1. Avoid creating flammable vapor concentrations.
2. Keep containers of flammable liquids closed except during content transfer.
3. Dilute flammable vapors by ventilation to avoid flammable concentrations. Use appropriate and safe exhaust whenever appreciable quantities of flammable substances are transferred from one container to another, allowed to stand in open containers, heated in open containers, or handled in any other way.
4. Conduct transfers only in laboratory chemical hoods or in other areas where ventilation is sufficient to avoid a buildup of flammable vapor concentrations.
5. When using dilution techniques, make certain that equipment such as fans are explosion proof and that sparking items are located outside the air stream.
6. Properly ground or earth metal lines and vessels discharging flammable liquids to disperse static electricity. For example, when transferring flammable liquids in metal equipment, avoid static-generated sparks by grounding or earthing and the use of ground straps. Development of static electricity is related closely to the level of humidity and may become a problem on cold, dry, winter days. When nonmetallic containers (especially plastic) are used, contact with the grounding or earthing device should be made directly to the liquid rather than to the container. In the rare circumstance that static electricity cannot be avoided, carry out all processes as slowly as possible or handle them in an inert atmosphere to give the accumulated charge time to disperse.

9.6.2 Working with Flammable Gases

Leakage or escape of flammable gases can produce an explosive atmosphere in the laboratory. Acetylene, hydrogen, ammonia, hydrogen sulfide, propane, and carbon monoxide are especially hazardous. Acetylene, methane, and hydrogen have a wide range of concentrations at which they are flammable (flammability limits), which adds greatly to their potential fire and explosion hazard. Install flash arresters on hydrogen cylinders. Prior to introduction of a flammable gas into a reaction vessel, purge the equipment by evacuation or with an inert gas. Repeat the flush cycle three times to reduce residual oxygen to approximately 1%.

9.7 Working with Highly Reactive or Explosive Chemicals

Highly reactive and explosive materials used in the laboratory require appropriate procedures. More information on assessing the risks of highly reactive or explosive chemicals may be found in Chapter 7.

Follow these steps to avoid serious accidents when highly reactive materials are in use:

1. Use the minimum amounts of hazardous materials with adequate shielding and personal protection.
2. Keep emergency equipment at hand.
3. Assemble all apparatus so that if a reaction begins to run away, it is possible to immediately remove any heat source, cool the reaction vessel, cease adding the reagent, and close the laboratory chemical hood sashes. A heavy transparent plastic explosion shield should be in place to provide extra protection in addition to the chemical hood window.
4. If a reaction runs away, restrict access to the area until the reaction is under control. Consider remote operating controls.
5. Provide enough cooling and surface for heat exchange to allow control of reactions. Highly reactive chemicals lead to reactions with rates that increase rapidly as the temperature increases. If the heat produced is not dissipated, the reaction rate increases until an explosion results. This is particularly a problem when scaling up experiments.
6. Avoid excessive concentrations of solutions, especially when a reaction is being attempted or scaled up the first time. Give special care to the rate of reagent addition versus its rate of consumption, especially if the reaction is subject to an induction period.
7. Follow special storage, handling, and disposal procedures for large-scale reactions with organometallic reagents and reactions that produce flammable materials or are carried out in flammable solvents. Where active metals are present, use fire extinguishers with special extinguishing materials such as a plasticized graphite-based powder or a sodium chloride-based powder.

8. Avoid slow decomposition on a large scale if there is inadequate heat transfer or if the evolved heat and gases are confined. The heat-initiated decomposition of some substances, such as certain peroxides, is almost instantaneous. In particular, reactions that are subject to an induction period can be dangerous because there is no initial indication of a risk. After induction, however, a violent process can result.
9. Conduct large-scale calorimetry determination of exothermic onset temperatures and drop weight testing for scale-up reactions that are exothermic at a low temperature or evolve a large amount of heat that might present a hazard. In situations where formal operational hazard evaluation or reliable data from any other source suggest a hazard, have an experienced group review or modify the scale-up conditions to avoid the possibility that a person might overlook a hazard or the most appropriate procedural changes.
10. Avoid causing physical explosions from actions such as bringing a hot liquid into sudden contact with a lower boiling-point liquid or adding water to the hot fluid of a heating bath. Explosions can also occur when warming a cryogenic material in a closed container or overpressurizing glassware with nitrogen (N_2) or argon when the regulator is incorrectly set. Violent physical explosions have also occurred when a collection of very hot particles is suddenly dumped into water.

9.7.1 Working with Reactive or Explosive Compounds

Occasionally, it is necessary to handle materials that are known to be explosive or that may contain explosive impurities such as peroxides. Explosive chemicals must be treated with special care. Work with explosive (or potentially explosive) materials generally requires the use of special protective apparel, such as face shields, gloves, and laboratory coats. Also use protective devices such as explosion shields, barriers, or even enclosed barricades or an isolated room with a blowout roof or window.

Before beginning work with a potentially explosive material, discuss the experiment with a laboratory supervisor or an experienced coworker. Read the relevant literature and carry out a risk assessment.

Check local and international regulations governing the transportation and use of explosive materials. Bring explosive materials into the laboratory only as required and in the smallest quantities adequate for the experiment. Reduce direct handling and separate the explosives from other materials that could create a serious risk to life or property should an accident occur.

9.7.1.1 *Using Protective Devices*

Use barriers such as shields, barricades, and guards to protect personnel and equipment from injury or damage from an explosion or fire.

A barrier should completely surround any hazardous area. On benches and laboratory chemical hoods, install a 0.25-inch-thick (0.6 cm) acrylic sliding shield, which is screwed together in addition to being glued. This shield can effectively protect trained laboratory personnel from glass fragments in a laboratory-scale explosion. The shield should be in place whenever hazardous reactions are in progress or whenever hazardous materials are being stored temporarily. However, such shielding is not effective against metal shrapnel.

Hood sashes provide safety shields only against chemical splashes or sprays, fires, and minor explosions. If more than one hazardous reaction is carried out, the reactions should be shielded from each other and separated as far as possible.

When handling potentially explosive materials capable of detonation in an inert atmosphere, fit dry boxes with safety glass windows overlaid with 0.25-inch-thick (0.6 cm) acrylic. This protection is adequate against most internal 5-g explosions. Wear protective gloves over the rubber dry box gloves to provide additional protection. Use other safety devices with the gloves that allow remote manipulation. Adequate grounding or earthing is essential to prevent detonation of explosives from static sparks in dry boxes. Also use an antistatic gun or antistatic ionizer.

To protect against detonations less than the acceptable 20-g limit, use reinforced or armored laboratory chemical hoods or barricades made with thick (1.0 inch, or 2.54 cm) polyvinylbutyral resin shielding and heavy metal walls. These barriers are typically designed to contain a 100-g explosion, but a maximum of 20 g is usually followed because of the noise that would be generated in the event of an explosion. Such chemical hoods should be equipped with mechanical hands that let personnel remotely operate the equipment and handle containers inside the hood.

Use miscellaneous protective devices, such as both long- and short-handled tongs, for holding or manipulating hazardous items at a safe distance. Also use remote control equipment, such as mechanical arms, stopcock turners, labjack turners, remote cable controllers, and closed-circuit television monitors.

9.7.1.2 *Using Personal Protective Equipment*

Use the following PPE when handling explosive materials:

- safety glasses that have solid side shields or chemical splash goggles;
- full-length shields that fully protect the face and throat (use special care when operating or manipulating synthesis systems that may contain explosives, such as diazomethane, when bench shields are moved aside, and when handling or transporting such systems);

- heavy leather gloves for reaching behind a shielded area while a hazardous experiment is in progress or when handling reactive compounds or gaseous reactants; and
- laboratory coats made of flame-resistant material that are easily removed.

9.7.1.3 *Evaluating Potentially Reactive Materials*

Always evaluate potentially reactive materials for their possible explosive characteristics by reading the literature and considering their molecular structures. There are three methods for determining the sensitivity of very explosive compounds:

1. a drop-test using recorded sound, which is not always entirely satisfactory;
2. an electrostatic test; and
3. the use of friction generated by grinding two porcelain surfaces together under load.

Highly reactive chemicals should be separated from materials that might interact with them and create a risk of explosion. They should not be used past their expiration date.

9.7.1.4 *Determining Reaction Quantities*

When handling highly reactive chemicals, use the smallest quantities needed for the experiment. In conventional explosives laboratories, no more than 0.1 g of product should be prepared in a single run. During the actual reaction period, no more than 0.5 g of reactants should be present in the reaction vessel. Consider the diluent, the substrate, and the energetic reactant when determining the total explosive power of the reaction mixture. Establish special formal risk assessments to examine operational and safety problems involved in scaling up a reaction in which an explosive substance is used or could be generated.

9.7.1.5 *Conducting Reaction Operations*

When potentially explosive materials are being handled, post warning signs in the area:

WARNING: Vacate the area at the first indication of [*the indicator for the specific case*] and stay out.

CALL: [*responsible person*] at [phone number].

CAUTION: Do not enter — risk of explosion.

See *Signs* in the accompanying Toolkit for an example of a caution sign.

Use heating devices in such a way that if an explosion were to occur, the heating medium would be contained. Heating baths should consist of nonflammable materials. All controls for heating and stirring equipment should be operable from outside the shielded area.

Vacuum pumps should carry tags indicating the date of the most recent oil change. Change oil once a month or sooner if it is known that the oil has been exposed to reactive gases. Trap all pumps or vent them into a hood. Vent lines may be Tygon, rubber, or copper. If Tygon or rubber lines are used, support them so they do not sag and act as a trap for condensed liquids.

When condensing explosive gases, determine the temperature of the bath and the effect on the reactant gas of the condensing material selected. Use very small quantities because explosions may occur. Always use a taped and shielded Dewar flask when condensing reactants. Observe maximum quantity limits. Use liquid nitrogen for reactive gases, rather than a dry ice solvent bath.

9.7.2 Working with Organic Peroxides

Organic peroxides are a special class of compounds with unusually low stability that makes them among the most hazardous substances commonly handled in laboratories, especially as initiators for free radical reactions. Although they are low-power explosives, they are hazardous because of their extreme sensitivity to shock, sparks, and other forms of accidental detonation. Many peroxides that are used routinely in laboratories are far more sensitive to shock than most primary explosives (e.g., TNT), although many have been stabilized by the addition of compounds that inhibit reaction. Nevertheless, even low rates of decomposition may automatically accelerate and cause a violent explosion, especially in bulk quantities of peroxides (e.g., benzoyl peroxide). These compounds are sensitive to heat, friction, impact, and light, as well as to strong oxidizing and reducing agents. All organic peroxides are highly flammable, and fires involving bulk quantities of peroxides should be approached with extreme caution.

Precautions for handling peroxides include the following:

1. Limit the quantity of peroxide to the minimum amount required. Do not return unused peroxide to the container.
2. Clean up all spills immediately. Absorb solutions of peroxides on vermiculite or other absorbing material and dispose of them according to organizational procedures.
3. Reduce the sensitivity of most peroxides to shock and heat by diluting them with inert solvents, such as aliphatic hydrocarbons. However, do not use aromatics (such as toluene), which are known to cause the decomposition of diacyl peroxides.

4. Do not use solutions of peroxides in volatile solvents under conditions in which the solvent might vaporize, because this will increase the peroxide concentration in the solution.
5. Do not use metal spatulas to handle peroxides because contamination by metals can lead to explosive decomposition. Magnetic stirring bars can unintentionally introduce iron, which can initiate an explosive reaction of peroxides. Ceramic, Teflon, or wooden spatulas and stirring blades may be used if it is known that the material is not shock sensitive.
6. Do not permit smoking, open flames, and other sources of heat near peroxides. It is important to label areas that contain peroxides so that this hazard is evident.
7. Avoid friction, grinding, and all forms of impact near peroxides, especially solid peroxides. Do not use glass containers that have screw-cap lids or glass stoppers. Use polyethylene bottles that have screw-cap lids.
8. To minimize the rate of decomposition, store peroxides at the lowest possible temperature consistent with their solubility or freezing point. Do not store liquid peroxides or solutions at or lower than the temperature at which the peroxide freezes or precipitates. Peroxides in these forms are extremely sensitive to shock and heat.

9.7.3 Working with Peroxidizable Compounds

Certain common laboratory chemicals form peroxides on exposure to oxygen in air. Over time, some chemicals continue to build peroxides to potentially dangerous levels. Others accumulate a relatively low equilibrium concentration of peroxide, which becomes dangerous only after being concentrated by evaporation or distillation. The peroxide becomes concentrated because it is less volatile than the parent chemical.

Exclude oxygen by storing potential peroxide formers under an inert atmosphere (N_2 or argon) to greatly increase their safe storage lifetime. Purchasing the chemical stored under nitrogen in septum-capped bottles is also possible. In some cases, stabilizers or inhibitors (free radical scavengers that terminate the chain reaction) are added to the liquid to extend its storage lifetime. Because distillation of the stabilized liquid removes the stabilizer, the distillate must be stored with care and monitored for peroxide formation. Furthermore, high-performance liquid chromatography (HPLC)-grade solvents generally contain no stabilizer, and the same considerations apply to their handling.

Follow these steps when handling peroxidizable compounds:

1. If a container of a Class A peroxidizable is past its expiration date or if the presence of peroxides is suspected or proven, do not attempt to open the container. These compounds can be deadly when peroxidized, and the act of unscrewing a cap or dropping a bottle can be enough to detonate them. Only experts should handle such containers. Contact your CSSO for assistance.
2. If a container of Class B or C peroxidizables is past its expiration date and there is a risk that peroxides may be present, open it with caution and dispose of it according to institutional procedures.
3. Test for the presence of peroxides if there is a reasonable likelihood of their presence and the expiration date has not passed. The following tests detect most (but not all) peroxy compounds, including all hydroperoxides.
   - Add 1 to 3 mL of the liquid to be tested to an equal volume of acetic acid. Add a few drops of 5% aqueous potassium iodide solution and shake. The appearance of a yellow to brown color indicates the presence of peroxides. Otherwise, the addition of 1 mL of a freshly prepared 10% solution of potassium iodide to 10 mL of an organic liquid in a 25-mL glass cylinder produces a yellow color if peroxides are present.
   - Add 0.5 mL of the liquid to be tested to a mixture of 1 mL of 10% aqueous potassium iodide solution and 0.5 mL of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within one minute indicates the presence of peroxides.
   - Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially. Note that these strips must be air dried, until the solvent evaporates, and then exposed to moisture for proper operation.

Because they seldom contain stabilizers (i.e., free radical scavengers), solvents used in HPLC require the same cautions as peroxidizable compounds.

None of these tests should be applied to materials that may be contaminated with inorganic peroxides, such as metallic potassium.

9.7.4 Working with Hydrogenation Reactions

Hydrogenation reactions pose additional risks because they are often carried out under pressure with a reactive catalyst. Take the following precautions for the gas cylinders and flammable gases, plus the additional precautions for reactions at pressures greater than 1 atmosphere.

1. Choose a pressure vessel appropriate for the experiment, such as an autoclave or pressure bottle. For example, most preparative hydrogenations of substances such as alkenes are carried out safely in a commercial hydrogenation apparatus using a heterogeneous catalyst (e.g., platinum and palladium) under moderate (<80 psi H_2) pressure.
2. Review the operating procedures for the apparatus, and inspect the container before each experiment. Glass reaction vessels with scratches or chips are at risk of breaking under pressure. Damaged vessels should not be used.
3. Never fill the vessel to capacity with the solution. Filling it half full or less is much safer.
4. Remove as much oxygen from the solution as possible before adding hydrogen. This is one of the most important precautions to be taken with any reaction involving hydrogen. Failure to do this could result in an explosive oxygen-hydrogen (O_2-H_2) mixture. Normally, the oxygen in the vessel is removed by pressurizing the vessel with inert gas (N_2 or argon), followed by venting the gas. If available, a vacuum can be applied to the solution. Repeat this procedure of filling with inert gas and venting several times before hydrogen or another high-pressure gas is introduced.
5. Stay well below the rated safe pressure limit of the bottle or autoclave; a margin of safety is needed if heat or gas is generated. A limit of 75% of the rating in a high-pressure autoclave is advisable. If this limit is exceeded accidentally, replace the rupture disk on completion of the experiment.
6. Monitor the high-pressure device periodically as the heating proceeds to avoid excessive pressure.
7. Carefully filter palladium or platinum on carbon, platinum oxide, Raney nickel, and other hydrogenation catalysts from hydrogenation reaction mixtures. The recovered catalyst is usually saturated with hydrogen, is highly reactive, and inflames spontaneously on exposure to air.

8. Especially for large-scale reactions, do not allow the filter cake to become dry. Put the funnel containing the still-moist catalyst filter cake into a water bath immediately after completion of the filtration.
9. Use nitrogen or argon as a purge gas for hydrogenation procedures so that the catalyst can be filtered and handled under an inert atmosphere.

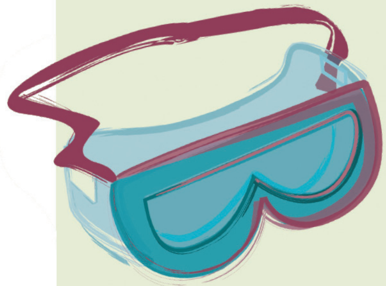
See ***Appendix H.2. Materials Requiring Special Attention Due to Reactivity, Explosivity, or Chemical Incompatibility*** **for more information on handling highly reactive or explosive materials.**

9.7.5 Working with Incompatible Chemicals

For each chemical, follow specific storage recommendations in MSDSs and other references with respect to containment and compatibility. Keep incompatible materials separate during transport, storage, use, and disposal. Contact could result in a serious explosion or the formation of substances that are highly toxic or flammable. Store oxidizers, reducing agents, and fuels separately to prevent contact in the event of an accident. Some reagents pose a risk on contact with the atmosphere.

10

Working with Laboratory Equipment



10.1 Introduction

Many of the accidents that occur in the laboratory happen because of improper use or maintenance of laboratory equipment. The most common equipment-related hazards in laboratories come from electrically powered equipment and devices for work with compressed gases, high or low pressures, and high or low temperatures. This chapter discusses safe practices for handling laboratory equipment.

10.2 Working with Electrically Powered Equipment

Electrically powered equipment found in the laboratory includes fluid and vacuum pumps, lasers, power supplies, electrochemical apparatus, X-ray equipment, stirrers, hot plates, heating mantles, microwave ovens, and ultrasonicators. These devices present both mechanical and electrical hazards. Regular, proper maintenance and correct use of these devices can reduce most risks.

Only a properly trained and qualified technician should repair and calibrate electrical equipment, so that equipment meets acceptable standards for electrical safety. Each person using electrical equipment in experiments *must* know all the applicable safety issues and potential dangers.

10.2.1 General Precautions for Working with Electrical Equipment

1. Properly insulate and visually inspect all electrical equipment monthly. Have qualified personnel replace frayed or damaged cords.
2. Make sure that electrical equipment and power supplies are completely isolated electrically. In every experimental setup, enclose all power supplies so that accidental contact with power circuits is impossible.
3. Install explosion-proof lighting and electrical fixtures where large amounts of flammable solvents are used.

Electrical equipment in laboratories—from hot plates to the ultraviolet-visible spectroscopy equipment used to analyze chemical structure—should be used properly and inspected regularly.

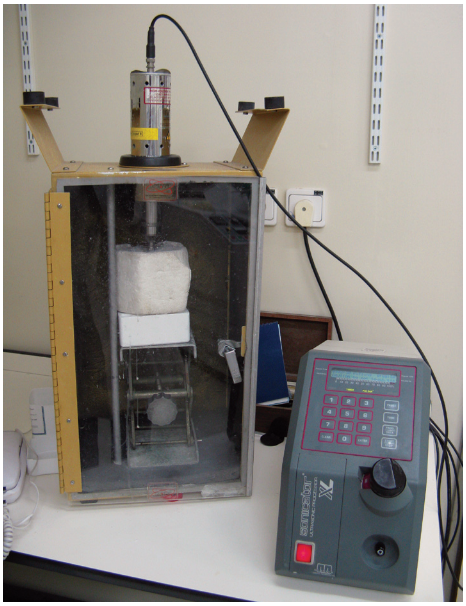
4. Where volatile flammable materials may be present, modify motor-driven electrical equipment with either non-sparking induction motors or air motors. Avoid series-wound motors that use carbon brushes. Do not use appliances with series-wound motors that cannot be modified (e.g., kitchen refrigerators, mixers, blenders) near flammable materials.
5. Remove flammable vapors before bringing in electrical equipment with series-wound motors, such as vacuum cleaners and portable electric drills.
6. Do not use variable autotransformers to control the speed of an induction motor. The motor will overheat, which could start a fire.
7. Locate electrical equipment to reduce contact with spills or flammable vapors. If water or a chemical spills on electrical equipment, shut off the power immediately at a main switch or circuit breaker and unplug the apparatus using insulated rubber gloves.
8. Reduce condensation that can cause electrical equipment to overheat, smoke, or catch fire. In such a case, shut off the power immediately at a main switch or circuit breaker and unplug the apparatus using insulated rubber gloves.
9. To reduce the possibility of electrical shock, carefully ground or earth the equipment using a suitable flooring material. Install ground fault circuit interrupters (GFCIs).
10. Unplug equipment before making any adjustments, modifications, or repairs. When it is necessary to handle equipment that is plugged in, be certain hands are dry. If possible, wear nonconductive gloves and shoes with insulated soles.
11. Make sure that all workers know the location and operation of main switches and circuit breaker boxes. High-voltage breaker boxes with an arc or flash hazard should be labeled and used only by qualified personnel familiar with alternative power shutoffs and wearing proper personal protective equipment (PPE).
12. Make sure that trained laboratory workers know how to safely shut down equipment with rotating or moving parts. Train personnel how to enclose or shield hazardous parts.

10.2.2 Precautions for Working with Specific Equipment

There are also specific safety measures for electrical devices such as those listed below:

- Water cooling equipment
- Vacuum pumps

- Refrigerators and freezers
- Stirring and mixing devices
- Heating devices, including ovens, hot plates, heating mantles and tapes, oil baths, salt baths, sand baths, air baths, hot-tube furnaces, hot-air guns, and microwave ovens
- Ultrasonicators and centrifuges
- Electromagnetic radiation sources, such as ultraviolet lamps, arc lamps, heat lamps, lasers, microwave and radio-frequency sources, and X-rays and electron beams
- Nuclear magnetic resonance (NMR) spectrometer systems



Specific types of lab equipment, such as this sonicator, often require their own safety measures.

See *Appendix I.1. Precautions for Working with Specific Equipment* for safety measures for specific electrical devices.

10.3 Working with Compressed Gases

Precautions are necessary for handling the various types of compressed gases and the cylinders, piping, and vessels in which they are stored and used. *Make regular inventories of cylinders and check their integrity. Promptly dispose of those no longer in use.* (See Chapter 7 for a discussion of the chemical hazards of compressed gases.)

10.3.1 General Guidelines for Working with Compressed Gases

1. Allow only trained personnel to conduct high-pressure operations and only with equipment specifically designed for this use.
2. Use only appropriate components during the assembly of pressure equipment and piping.
3. Avoid strains and concealed fractures resulting from the use of improper tools or excessive force.
4. Do not force threads that do not fit smoothly.
5. Use Teflon tape or a suitable thread lubricant, but never use oil or lubricant on any equipment that will be used with oxygen.
6. Inspect all tubing and replace it when necessary.

7. Shield all reactions under pressure.
8. Do not fill autoclaves and other pressure reaction vessels more than half full so that space remains for expansion of the liquid when it is heated.
9. Post warning signs prominently when a pressure reaction is in progress.
10. Follow the special safety measures for compressed gas devices such as those listed below:
    - Pressure-relief devices
    - Pressure gauges
    - Piping, tubing, and fittings
    - Glass equipment
    - Plastic equipment
    - Valves
    - Gas monitors
    - Teflon tape applications

See *Appendix I.2. Guidelines for Working with Specific Compressed Gas Equipment* for more on the safe handling of compressed gas devices.

10.3.2 Handling Compressed Gas Cylinders

10.3.2.1 *Purchasing*

The laboratory should select the smallest cylinder that meets its need. Mark and return empty cylinders. Avoid purchasing nonreturnable lecture bottles. Lease the cylinders and purchase only the contents.

10.3.2.2 *Storing*

1. Do not accept compressed gas cylinders that are not labeled. If the contents of a cylinder cannot be identified, mark it as "contents unknown" and contact the manufacturer.
2. Clearly label compressed gas cylinders with a durable label that cannot be removed from the cylinder, such as a stencil or stamp on the cylinder itself. If possible, provide tags for entering the names of users and dates. Color-code the labels to distinguish hazardous gases. Do not depend on the manufacturer's color codes. These may vary across companies.
3. Clearly label all gas lines leading from a compressed gas supply to identify the gas, the laboratory served, and relevant emergency telephone numbers.
4. Securely strap or chain gas cylinders to a wall or bench top. In seismically active areas, use more than one strap or chain.

Securely cap gas cylinders when they are no longer in use.

5. Separate gas cylinder storage from other chemical storage. Ideally, store gas cylinders in a lockable cage and secure them to the walls. Locate cages outside of buildings.
6. Keep incompatible classes of gases stored separately. Do not store corrosives near gas cylinders or lecture bottles. Corrosive vapors from mineral acids can deface markings and damage valves. Keep flammables away from reactives, which include oxidizers and corrosives. For more information on the storage of flammable gases, see Chapter 8.
7. Post signs where flammable compressed gases are stored.
8. Separate empty cylinders from full cylinders.
9. When cylinders are no longer in use, shut the valves, relieve the pressure in the gas regulators, remove the regulators, and cap the cylinders.
10. Do not abandon cylinders in the dock storage areas.
11. Return cylinders to the supplier when you are finished with them.

10.3.2.3 *Handling and Use*

1. Handle gas cylinders carefully. Leave the valve protection cap in place until the cylinder is ready for use. Transport cylinders on approved, wheeled cylinder carts with retaining straps or chains.
2. Secure compressed gas cylinders firmly and individually at all times using a clamp and belt or chain between the “waist” and “shoulder.” Put cylinders in well-ventilated areas.
3. Make sure that the rotary cylinder valve handle at the top is accessible at all times. Close the cylinder valve when the equipment is not in use.
4. Only use tools provided by the cylinder supplier to remove a cap or open a valve.
5. When possible, open the valve on a cylinder containing an irritating or toxic gas outside. Train personnel to stand upwind with valves pointed away from themselves. Open a valve inside only in a laboratory chemical hood or specially designed cylinder cabinet.

10.3.2.4 *Preventing Leaks*

1. Regularly check cylinders and hoses for leaks. Use a flammable gas leak detector or look for bubbles after application of soapy water or a 50% glycerin-water solution. Do not use soap or other solutions to test for oxygen leaks, because of the potential for ignition.
2. Use pressure regulators to maintain a satisfactory delivery pressure and flow level. Only trained personnel should attempt to repair or modify regulators. Never use oil or grease on regulator valves or cylinder valves because these substances may react with some gases, such as oxygen. Check regulators before use to be sure they are free of foreign objects and correct for the particular gas. All pressure regulators should be equipped only with spring-loaded pressure-relief valves. When used on cylinders with hazardous gases, vent the relief valve to a laboratory chemical hood or other safe location.
3. Keep cylinders of flammable gas away from all sources of ignition in case they leak. Use flash arrestors for flammable gases. Do not exchange flammable gas equipment for similar equipment used with other gases. Ground or earth cylinders to prevent static electricity buildup. Separate flammable gas cylinders from cylinders of oxidizing gases (i.e., oxygen, fluorine, chlorine) by at least 20 feet (~6 m) or by a fire-resistant partition. Store all flammable gas cylinders in a well-ventilated place.

10.3.2.5 *Handling Leaks*

Leaking gas cylinders are serious hazards that may require an immediate evacuation of the area and a call to emergency responders. Only trained personnel should attempt to handle leaks. If a leak occurs, do not apply extreme tension to close a stuck valve. Wear appropriate PPE, which usually includes a self-contained breathing apparatus or an air-line respirator, when entering the area with the leak. Below are guidelines for handling leaks of various types of gases. Contact the gas supplier for specific information and guidance.

- **Flammable, inert, or oxidizing gases.** If it is safe, move the leaking cylinder to an isolated area, away from combustible material if the gas is flammable or an oxidizing agent. Post signs that state the hazards and warnings. Take care when moving leaking cylinders of flammable gases so that accidental ignition does not occur. If possible, move the leaking cylinder into a chemical hood until it is exhausted.
- **Corrosive gases.** Corrosive gases may increase the size of the leak as they are released, and some corrosives are also oxidants, flammable, or toxic.

Move the cylinder to an isolated, well-ventilated area, and direct the gas into an appropriate chemical neutralizer. If there is apt to be a reaction with the neutralizer that could lead to a suck-back into the valve (e.g., aqueous acid into an ammonia tank), place a trap in the line before starting neutralization. Post signs that state the hazards and warnings.

- **Toxic gases.** The same procedure should be followed for toxic gases as for corrosive gases. Warn others of the exposure risks.

10.4 Working with High and Low Pressures and Temperatures

Work with hazardous chemicals at high and low pressures and/or high and low temperatures requires planning and special precautions. For many experiments, extremes of both pressure and temperature must be managed at the same time. Appropriate equipment must be used to prevent accidents.

10.4.1 Working with Pressure Vessels

High-pressure operations should be performed only in special chambers designed for this purpose. Trained laboratory personnel should make sure that the equipment for operations using pressure vessels is properly selected, labeled, installed, and protected by pressure-relief and necessary control devices.

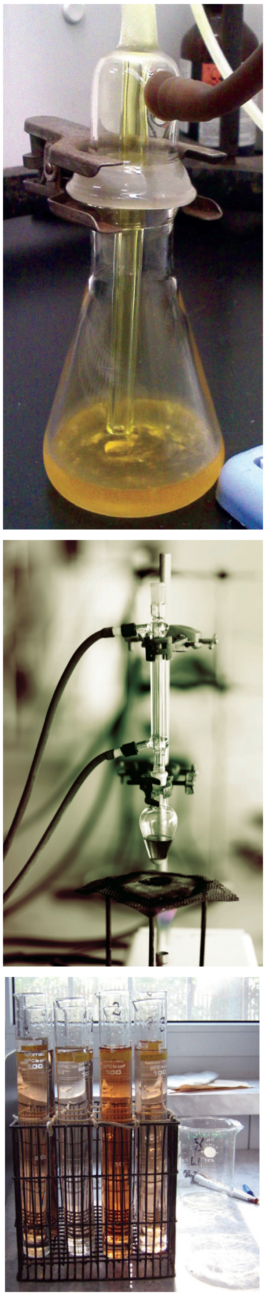
1. Label each pressure vessel with a unique stamped number or fixed label plate that identifies it. Also keep the following information: the maximum allowable working pressure; allowable temperature at this pressure; material of construction; a burst diagram; and the vessel's history of temperature extremes, modifications, repairs, and inspections or tests.
2. Stamp the relieving pressure and setting data on a metal tag attached to installed pressure-relief devices. Seal the setting mechanisms.
3. Inspect or test all pressure equipment periodically. Test and inspect vessels used with corrosives or otherwise hazardous service more frequently. Hydrostatic proof tests should be as infrequent as possible but performed before the vessel is placed in initial service and every 10 years after that. Also test after a significant repair or modification, and if the vessel experiences overpressure or overtemperature. To detect leaks at threaded joints, packings, and valves, test the entire apparatus with soap solution and air or nitrogen pressure to the maximum allowable working pressure of the weakest section of the assembled apparatus.
4. Pressure-test and leak-test final assemblies to ensure their integrity. Consult an expert on high-pressure work as the high-pressure process is designed, built, and operated. Take extreme care when disassembling pressure equipment.

10.4.2 Working with Glass Equipment

Whenever possible, run reactions under pressure in metal equipment, not glass. For any reaction run on a large scale (more than 10 g total weight of reactants) or at a maximum pressure in excess of 690 kPa (100 psi), use only a suitable high-pressure autoclave or shaker vessel.

Assume that glass used under pressure will fail. If glass is required due to concerns about materials of construction, then use a metal reactor with a glass or Teflon liner instead of a glass vessel under pressure. Take these precautions when using glass containers:

1. Carefully handle and store glassware to avoid damage. Discard or repair chipped or cracked items.
2. Vent gases properly.
3. Use suitable shielding, such as mesh, around the glassware to prevent injury from flying glass or from corrosive or toxic reactants.
4. Protect the hands and body when performing forceful operations involving glassware. For example, use leather or Kevlar gloves when placing rubber tubing on glass hose connections.
5. Seal centrifuge bottles with rubber stoppers clamped in place, wrapped with friction tape, and shielded with a metal screen or surrounded by multiple layers of loose cloth toweling. Clamp the bottles behind a good safety shield. If a pressure gauge is available, estimate the maximum allowable pressure by calculation.
6. Use a Teflon pressure-relief valve when working with corrosive materials. Steam is the preferred source of heat for such vessels.
7. Carry out reactions with Teflon pressure-relief valves in a chemical hood, and label the area with signs indicating the risk of explosion.
8. Fill glass tubes used under pressure no more than three-quarters full.
9. Handle vacuum-jacketed glassware with extreme care to prevent implosions. Tape, shield, or coat evacuated equipment such as Dewar flasks or vacuum desiccators. For vacuum work, only use glassware designed for that purpose.
10. Use proper shielding for condensing materials and sealing tubes.
11. Use fabricated, commercial adaptors made from plastic, metal, or other materials instead of constructing adaptors from glass tubing and rubber or cork stoppers.



All laboratory glassware can break. Exercise appropriate care.

12. Carry out vacuum work on a Schlenck line as long as the proper technique is used.
13. Use PPE, including shields, masks, coats, and gloves, during tube-opening operations.
14. Examine under polarized light any newly fabricated or repaired glass pressure or vacuum equipment. Check for flaws and strains. Use only a liquid seal, Bunsen tube, or equivalent positive relief device as relief devices for protection of glassware against excess pressure. Use only proper metal fittings with glass pipe.
15. Use tongs, a tweezer, or puncture-proof hand protection when picking up broken glass. Small pieces should be swept up with a brush into a dustpan.
16. Do not attempt glassblowing operations unless proper annealing facilities are available.

10.4.3 Working with Liquefied Gases and Cryogenic Liquids

The primary hazards of cryogenic liquids are frostbite, asphyxiation, fire or explosion, pressure buildup, and weakening of structural materials. The extreme cold of cryogenic liquids and the vapors that boil off require special care in their use. Gases such as oxygen, hydrogen, methane, and acetylene are explosion hazards. Take the precautions outlined in the following sections when working with liquefied gases and cryogenic liquids.

10.4.3.1 *Precautions When Using Liquefied Gases and Cryogenic Liquids*

1. Furnish all cylinders and equipment containing flammable or toxic liquefied gases with a spring-loaded pressure-relief device. Protect pressurized containers that contain cryogenic material with multiple pressure-relief devices.
2. Store, ship, and handle cryogenic liquids in containers designed for the pressures and temperatures to which they may be subjected. Dewar flasks used for small amounts of cryogenic material should have a dust cap over the outlet to prevent atmospheric moisture from condensing and plugging the tube neck.
3. Wear eye protection, preferably chemical splash goggles and a face shield, when handling liquefied gases and other cryogenic fluids. Transfer liquefied gases very slowly and while supervised when done for the first time. Do not let unprotected parts of the body come in contact with uninsulated vessels or pipes that contain cryogenic liquids, because

PPE for handling cyrogens includes loose fitting thermal insulated or leather gloves, which can be easily removed.

extremely cold material may bond firmly to the skin. Wear gloves that are impervious to the fluid being handled and loose enough to be tossed off easily. If possible, wear long sleeves.

4. Use tongs or potholders to handle objects that are in contact with cryogenic liquids.
5. Make sure the work area is well ventilated to prevent poisoning, explosion, or asphyxiation.
6. Do not transfer liquid hydrogen in an air atmosphere to avoid a possible risk of explosion.
7. Keep liquid oxygen from organic materials, and clean spills on surfaces that oxidize.
8. Install oxygen meters and alarms in rooms that contain appreciable quantities of liquid nitrogen (N2). Do not store liquid nitrogen in a closed room because the oxygen content of the room can drop to unsafe levels.
9. Store cylinders and other pressure vessels used for liquefied gases at no more than 80% of capacity to avoid bursting from hydrostatic pressure. If the possibility exists that the temperature of a cylinder may increase to above 30°C, a lower percentage (e.g., 60%) of capacity should be the limit.

10.4.3.2 *Precautions When Using Cold Traps and Cold Baths*

1. Choose cold traps that are large enough and cold enough to collect the condensable vapors.
2. Check cold traps frequently to make sure they do not become plugged with frozen material.
3. After completing an operation using a cold trap, remove and vent the trap in a safe and environmentally acceptable way. Cold traps under continuous use should be cooled electrically and monitored by low-temperature probes.
4. Wear appropriate gloves and a face shield when using cold baths. Use dry gloves when handling dry ice.
5. Avoid lowering of the head into a dry ice chest to prevent asphyxiation.
6. Use isopropyl alcohol or glycols, not acetone-dry ice, for dry ice cooling baths. Add the dry ice slowly to the liquid portion of the bath. Keep dry ice and liquefied gases used in refrigerant baths open to the atmosphere.
7. Take extreme caution when using liquid nitrogen as a coolant for a cold trap. Do not open a system that is connected to a liquid nitrogen trap

until the liquid nitrogen Dewar or container has been removed. This precaution prevents oxygen from condensing in the atmosphere and creating a highly explosive mixture. Even if the system is closed after a brief exposure to the atmosphere, some oxygen may have already condensed, producing the same potential for explosion.

8. Apply caution when using argon, because it condenses as a colorless solid at liquid nitrogen temperature and presents an explosion hazard if allowed to warm without venting.

In addition to hazards from extreme cold, a cold trap may condense liquid oxygen or other gases that are potentially explosive. After completing an operation using a cold trap, remove and vent safely.

10.4.3.3 *Precautions When Using Low-Temperature Equipment*

Select low-temperature equipment carefully. When combinations of materials are required, consider the temperature dependence of their volumes so that leaks, ruptures, and glass fractures can be avoided. The stainless steels containing 18% chromium and 8% nickel retain their impact resistance down to approximately –240°C. The impact resistance of aluminum, copper, nickel, and many other nonferrous metals and alloys increases with decreasing temperatures. Use special alloy steels for liquids or gases containing hydrogen at temperatures greater than 200°C or at pressures greater than 34.5 MPa (500 psi).

10.4.3.4 *Precautions When Using Cryogenic Lines and Supercritical Fluids*

Design liquid cryogen transfer lines so that liquid cannot be trapped in any non-vented part of the system. Experiments in supercritical fluids include high pressure. Conduct them with appropriate safety systems.

10.4.4 Working with Vacuums and Vacuum Apparatus

Vacuum work can result in an implosion and the possible hazards of flying glass, spattering chemicals, and fire. Equipment at reduced pressure is especially prone to rapid pressure changes, which can create large pressure differences within the apparatus. Such conditions can push liquids into unwanted locations and cause accidents.

10.4.4.1 *Assembly of Vacuum Apparatus*

Assemble vacuum apparatus so as to avoid strain when moved or used. Protect vacuum and Schlenk lines from overpressurization with a bubbler, not gas regulators and metal pressure-relief devices. If a slight positive pressure of gas on these lines is desired, this pressure should not exceed 1-2 psi and can easily be obtained by proper bubbler design.

Place vacuum apparatus well back onto the bench or into the hood where it will not be inadvertently hit. If the back of the vacuum setup faces the open laboratory, protect it with panels of suitably heavy transparent plastic to prevent injury to nearby workers from flying glass in case of explosion.

10.4.4.2 *Precautions When Using Vacuums*

1. Use an explosion shield, a face mask, and a laboratory chemical hood.
2. Do not allow water, solvents, and corrosive gases to be drawn into a building vacuum system. When the potential for such a problem exists, use a cold trap, not water aspirators.
3. Protect mechanical vacuum pumps by cold traps. Vent exhausts to an exhaust hood or outside of the building. If solvents or corrosive substances are inadvertently drawn into the pump, change the oil before any further use.
4. Cover the belts and pulleys on vacuum pumps with guards.

10.4.4.3 *Precautions When Using Other Vacuum Apparatus*

Special precautions should be taken when working with other vacuum apparatus, such as

- glass vessels
- desiccators
- Dewar flasks
- rotary evaporators

See *Appendix I.3. Precautions When Using Other Vacuum Apparatus* for more detailed safety measures.

10.5 Using Personal Protective, Safety, and Emergency Equipment

It is essential for each person to make sure that the laboratory is a safe working environment. It is the responsibility of the institution to provide appropriate safety and emergency equipment for trained laboratory personnel and for emergency responders. Everyone must take responsibility for dressing appropriately to avoid accidents and injury.

See *Appendix H.1. Personal Protective, Safety, and Emergency Equipment* for more detailed information on all of the following safety and emergency equipment.

10.5.1 Protective Equipment and Apparel for Laboratory Personnel

- **Personal Clothing:** Personal clothing should fully cover the body. Wear appropriate, fire-resistant laboratory coats buttoned and with the sleeves rolled down. Always wear protective apparel if there is a possibility that personal clothing could become contaminated or damaged with chemically hazardous material. Avoid unrestrained long hair, loose clothing, and jewelry.
- **Foot Protection:** Wear substantial shoes in areas where hazardous chemicals are in use or mechanical work is being done. In many cases, wear safety shoes.
- **Eye and Face Protection:** Wear safety glasses with side shields for work in laboratories and, in particular, with hazardous chemicals. A laboratory should also provide impact goggles that include splash protection (chemical splash goggles), full-face shields that also protect the throat, and specialized eye protection (i.e., protection against ultraviolet light or laser light).
- **Hand Protection:** At all times, use gloves that are appropriate to the degree of hazard. Barrier creams and lotions can provide some skin protection but should never replace gloves, protective clothing, or other protective equipment.

10.5.2 Safety and Emergency Equipment

10.5.2.1 *Contents and Storage*

An institution must provide the following *safety equipment:*

- spill control kits;
- safety shields;
- fire safety equipment, such as fire extinguishers, heat and smoke detectors, fire hoses, and automatic fire-extinguishing systems;
- respirators;
- safety showers; and
- eyewash units.

The laboratory should provide the following *emergency equipment:*

- self-contained breathing apparatus (for use by trained personnel only);
- blankets for covering the injured;
- stretchers (although it is generally best to wait for qualified medical help); and

For new personnel, prominent signage helps locate the safety shower and eyewash. Portable water and CO_2 fire extinguishers are available to address different types of fire.

- First aid equipment for unusual situations where immediate first aid is required.

Keep all safety and emergency equipment in well-marked, highly visible locations in all laboratories. Make fire alarm pull stations and telephones with emergency contact numbers readily accessible. It is the responsibility of the laboratory supervisor to ensure proper training and provide supplementary equipment as needed.

10.5.2.2 *Equipment Inspections*

It is the responsibility of the laboratory supervisor or chemical safety and security officer (CSSO) to establish a routine inspection system and verify that inspection records are maintained. Inspections of emergency equipment should include the following steps.

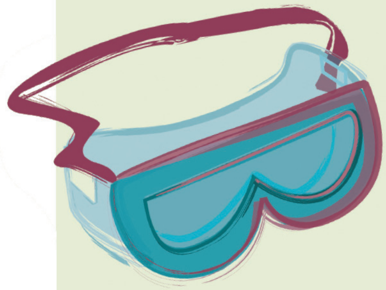
1. Inspect fire extinguishers for broken seals, damage, and low gauge pressure. Check for proper mounting. Some types of extinguishers must be weighed annually and may require periodic hydrostatic testing.
2. Check self-contained breathing apparatus at least once a month and after each use to determine whether it is maintaining proper air pressure. Look for signs of deterioration or wear of rubber parts, harness, and hardware. Make certain that the apparatus is clean and free of visible contamination. Trained personnel should perform fit tests periodically to make sure the masks form a good seal to the face.
3. Visually examine safety showers and eyewash units and test their mechanical function. Purge units as needed to remove particulate matter from the water line.

10.5.3 Establishing Emergency Procedures

The laboratory manager should establish general emergency procedures for responding to fires, explosions, spills, or medical or other laboratory accidents. Clearly post telephone numbers to call in emergencies near all telephones in hazard areas. Train and inform all laboratory personnel of the protocols for their particular institution. See Chapter 3 for more information.

11

Managing Chemical Waste



11.1 Introduction

Virtually every laboratory experiment generates some waste, which may include such items as used disposable labware, filter media, aqueous solutions, and hazardous chemicals. The overriding principle governing the safe and secure handling of laboratory waste is that no activity should begin unless a plan for the disposal of nonhazardous and hazardous waste has been made.

No activity should begin unless a plan for the disposal of nonhazardous and hazardous waste has been formulated.

The decisions that are made when dealing with chemical waste affect the person who generated the waste, that person's institution, and society as a whole. Laboratory personnel who generate waste have an obligation to consider the ultimate fate of the materials resulting from their work. This includes consideration of the cost of disposal, the potential hazards to people outside the laboratory, and the potential impacts on the environment. There also may be regulatory considerations to take into account.

11.1.1 What Is Waste?

Waste is material that is discarded, intended to be discarded, or no longer useful for its intended purpose. A material may also be declared a waste if it is abandoned or if it is considered "inherently waste-like," as in the case of spilled materials. Wastes are classified as either hazardous or nonhazardous.

11.1.2 Who Is Responsible for Waste?

Once material becomes a waste, the initial responsibility for its proper disposal rests with the trained laboratory personnel who used or synthesized the material. These individuals are in the best position to know the characteristics of the material. It is their responsibility to evaluate the hazards and provide information necessary to determine its proper disposal. Their decisions must be consistent with the institution's framework for handling hazardous materials and with applicable regulations.

11.1.3 What Are the Steps for Managing Waste?

The main steps for managing chemical waste are as follows.

1. Identify the waste and its hazards.
2. Methodically collect and store wastes.
3. Consider hazard reduction where appropriate.
4. Dispose of wastes properly.

The application of these steps will vary depending on the resources and setup of each laboratory. This chapter discusses each step in detail.

11.2 Identifying Waste and Its Hazards

Because proper disposal requires information about the properties of the waste, identify all chemicals that are used or generated in the laboratory. In general, this means keeping chemical wastes in clearly marked containers. If wastes have been generated within the laboratory, define their source clearly on the container and in a readily available notebook record. It is particularly important to identify clearly all materials in academic laboratories where student turnover is frequent. Appropriately identifying wastes and their hazardous characteristics is just as important for small quantities as it is for large quantities of material.

11.2.1 Properties of Hazardous Waste

- **Ignitability:** Ignitable materials include most common organic solvents, gases such as hydrogen and hydrocarbons, and certain nitrate salts. Ignitable materials are defined as having one or more of the following characteristics:
  - liquids that have a flash point of less than 60°C or some other characteristic that has the potential to cause fire;
  - materials other than liquids that are capable, under standard temperature and pressure, of causing fire by friction, absorption of moisture, or spontaneous chemical changes *and,* when ignited, burn so vigorously and persistently as to create a hazard;
  - flammable compressed gases, including those that form flammable mixtures; and
  - oxidizers that stimulate combustion of organic materials.
- **Corrosivity:** Corrosive liquids have a pH ≤ 2 or ≥ 12.5 or corrode certain grades of steel. Most common laboratory acids and bases are corrosive.
- **Reactivity:** Reactivity includes substances that are unstable, react violently with water, are capable of detonation if exposed to some initiating source, or produce toxic gases. Alkali metals, peroxides and compounds that have peroxidized, and cyanide or sulfide compounds are classed as reactive.
- **Toxicity:** Toxicity involves substances that tend to be leached (extracted) from the waste material under certain circumstances, such as a landfill.

It is also important to know whether or not a waste is *regulated* as hazardous, because regulated hazardous waste must be handled and disposed of in specific ways.


Explosive


Flammable


Oxidizer


Corrosive


Acute Toxicity (Severe)


Irritant

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) sets hazard classifications and labels.

This determination has important implications that can lead to significant differences in disposal cost. More information on evaluating hazardous waste can be found in Chapter 7.

11.2.2 Assessing Unknown Materials

The identity of all waste materials should be readily available. However, in cases of unidentified chemical wastes, simple tests can be used to determine the hazards. Generally, it is not necessary to determine the molecular structure of the unknown material precisely. However, it is important to know what analytical data will be required by the facility that will ultimately dispose of the waste.

See *Appendix J.1. How to Assess Unknown Materials* for instructions.

11.3 Collecting and Storing Waste

Chemical waste first accumulates and is temporarily stored in or near the laboratory. It is often then moved to a central accumulation area within the institution before ultimate disposal elsewhere.

11.3.1 Waste Collection and Storage in the Laboratory

Safety considerations must be a priority when establishing a system for temporary waste collection in the laboratory. Follow these general guidelines:

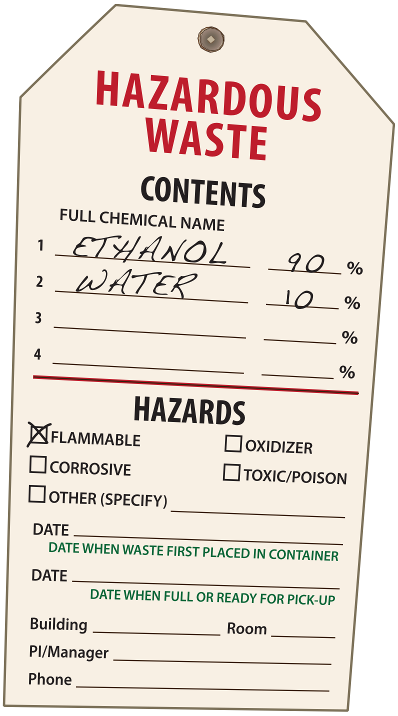
- **Use of Waste Collection Containers:** Store waste in clearly labeled containers in a designated location that does not interfere with normal laboratory operations. In some cases, ventilated storage may be appropriate. Use secondary containment, such as trays, in case of spills or leakage from the primary containers. Securely cap waste containers at all times except when adding or removing waste.
- **Mixing of Different Chemical Wastes:** Different kinds of waste can be collected within a common container. Commingled waste must be

STOP AND THINK: IS IT REALLY WASTE?

Shortly after the waste is generated is an appropriate time to decide whether to recycle or reuse surplus materials rather than send them for disposal. All of the costs and benefits of either decision should be evaluated at this time. Once wastes have been combined, recycling or reuse may be more difficult.

chemically compatible to make sure that heat generation, gas evolution, or another reaction does not occur. For example, waste solvents can usually be mixed for disposal, with due regard for the compatibility of the components. However, halogenated and nonhalogenated wastes must be handled separately. Physically separate containers of incompatible materials or store them in another protective manner.

- **Labeling of Waste Containers:** Label every container of hazardous waste with the material's identity, its hazard (e.g., flammable, corrosive), and the words "Hazardous Waste." When compatible wastes are collected in a common container, keep a list of the components to aid in later disposal decisions. Make labeling clear and permanent.
- **Choosing Appropriate Containers:** Collect waste in dependable containers that are compatible with their contents.



HAZARDOUS WASTE

CONTENTS

FULL CHEMICAL NAME

1 ETHANOL 90 %

2 WATER 10 %

3 %

4 %

HAZARDS

☒ FLAMMABLE ☐ OXIDIZER

☐ CORROSIVE ☐ TOXIC/POISON

☐ OTHER (SPECIFY)

DATE

DATE WHEN WASTE FIRST PLACED IN CONTAINER

DATE

DATE WHEN FULL OR READY FOR PICK-UP

Building Room

PI/Manager

Phone

Clearly label hazardous waste for storage.

  - **Containers for Liquid Waste:** Use plastic (e.g., polyethylene) or metal (e.g., galvanized or stainless steel) safety containers for collecting liquid waste, especially for flammable liquids. Glass bottles are impervious to most chemicals but present a breakage hazard. Narrow necks can cause difficulty in emptying the bottles. Do not store amines or corrosive materials in metal containers. Also, do not use galvanized steel safety cans for halogenated waste solvents because they tend to corrode and leak.
  - **Containers for Aqueous Waste:** Collect aqueous waste separately from organic solvent waste. Some laboratories may be served by a wastewater treatment facility that allows the disposal of certain types of aqueous waste to the sanitary sewer (see Section 11.5.2). Collect aqueous waste for non-sewer disposal in a container that is resistant to corrosion. Do not use glass if there is danger of freezing.
  - **Containers for Solid Waste:** Place solid chemical waste, such as reaction by-products or contaminated filter or chromatography media, in an appropriately labeled container to await disposal. Separate
  - unwanted reagents for disposal in their original containers, if possible. If using original containers, make sure labels are intact and legible.

- **Considerations of Quantity and Length of Time:** In general, do not hold waste in the laboratory in large quantities or for longer than one year. A central accumulation area may be appropriate for managing larger volumes of waste. Some institutions (and, in some places, regulations) require recording the date that collection begins.
- **Decontaminating Empty Containers:** Rinse empty waste containers (glass, metal) contaminated with organic material with a water-miscible solvent (acetone, methanol). Then triple-rinse them with water. Add the rinses to a chemical waste container. Discard the decontaminated container as scrap.

11.3.2 Waste Collection at a Central Accumulation Area

A central accumulation area is an important component in a chemical management plan. The principles for waste collection in the laboratory provided in the section above also apply to managing chemicals at a central accumulation area. Follow these guidelines specific to central accumulation areas.

1. **Mixing of Different Chemicals:** Considerable cost savings may be gained by commingling compatible waste materials in a central accumulation area before disposal. Commingling is particularly suitable for waste solvents. Disposal of liquid in a large container (e.g., 200 L or 55-gallon drum) is generally much less expensive than disposal of the same volume of liquid in small containers.
2. **Transportation of Waste:** Transportation of waste between laboratories and the central accumulation area requires specific attention to safety. Transported materials must be held in appropriate and clearly labeled containers. There must also be a plan for spill control in case of an accident during transportation. Larger institutions should have an internal tracking system to follow the movement of waste.
3. **Preparations for Disposal:** Decisions on disposal and final preparations for disposal usually occur at the central accumulation area. Unknown materials must be identified at this point because unidentified waste cannot be shipped to a disposal site.
   - Vendors may be involved with this phase of waste management. The decision of whether, how, and when to involve vendors is based largely on logistics and economics.
4. **Maintenance of Records:** Records are needed to monitor the success of the hazardous waste management program. The central accumulation

area is often the most suitable place for creating and keeping all appropriate and required records. The facility should keep records for onsite activities that include the following:

- the quantities and identification of waste generated and shipped;
- documentation of analyses of unknown materials;
- documentation of waste shipping as well as verification of disposal; and
- any other information that is required by regulations and that prevents long-term liability.

11.3.3 Recycling of Chemicals and Laboratory Materials

11.3.3.1 *General Considerations*

Before making a decision on recycling, calculate the costs of recycling versus waste disposal. Identify users for a recycled product before wasting time and energy on making a product that must still be disposed of as a waste. Recycling some of the chemicals used in large undergraduate courses is especially cost effective because the users are known well in advance.

Unclean materials must be brought to a higher level of purity or changed to a different physical state before they can be recycled. Recycling occurs onsite or offsite.

- **Offsite Recycling:** Commercial firms recycle, reclaim, purify, and stabilize vacuum pump oil, solvents, mercury, rare materials, and metals. Offsite recycling is preferable to disposal and sometimes is less expensive. Another offsite option is to work with suppliers of laboratory chemicals who accept return of unopened containers, including of highly reactive chemicals. Gas suppliers sometimes accept returns of partially used cylinders.
- **Onsite Recycling:** Recycling also occurs at the laboratory or at a central location that collects recyclables from several laboratories. Onsite recycling may not be economical. Even a small amount of waste may require very expensive disposal by a commercial vendor. Because of the difficulty of maintaining the needed level of cleanliness and safety, avoid onsite recycling of mercury and other toxic metals.

Whether recycling on- or offsite, the recyclable waste stream needs to be kept as clean as possible. If a laboratory produces a large quantity of waste xylene, for example, small quantities of other organic solvents should be collected in a separate container, because the distillation process gives a better product with fewer materials to separate. Also take steps to avoid getting mercury into oil baths and oils used in vacuum systems. Similarly, certain ions in a solution of waste metal salts have a serious negative impact on the recrystallization process.

Many recycling processes result in some residue that is not reusable and will probably have to be handled as a hazardous waste. See Chapter 7 and below for additional information.

11.3.3.2 *Solvent Recycling*

Before purchasing solvent recycling equipment, know the intended use of the redistilled solvent. The choice of a distillation unit for solvent recycling depends largely on the level of purity desired in the solvent. A simple flask, column, and condenser setup may be adequate for a solvent that will be used for crude separations or for initial glassware cleaning. For a much higher level of purity, use a spinning band column. Stills with automatic controls that shut down the system under certain conditions are best because they enhance the safety of the distillation operation. Overall, distillation is likely to be most effective when the laboratory accumulates fairly large quantities (roughly 5 L) of relatively clean, single-solvent waste before beginning the distillation process.

11.3.3.3 *Recycling Containers, Packaging, and Labware*

Laboratory materials other than chemicals may also be recycled. These may include

- Clean glass and plastic containers
- Drums and pails
- Plastic and film scrap
- Cardboard
- Office paper
- Light bulbs
- Circuit boards
- Other electronics
- Metals such as steel and aluminum
- Computer equipment

11.4 Treatment and Hazard Reduction

It is possible to reduce the volume or the hazardous characteristics of many chemicals through reactions carried out within the laboratory. In fact, it is becoming common practice to include such reactions as the final steps in an experiment. Chemical deactivation as part of the experimental procedure can have considerable economic advantage by eliminating the need to treat small amounts of surplus materials as hazardous waste.

See *Appendix J.2. Procedures for Laboratory-Scale Treatment of Surplus and Waste Chemicals* for instructions on the treatment of specific types of hazardous wastes.

11.4.1 Treatment of Laboratory Chemicals

Waste treatment involves changing the physical, chemical, or biological character or composition of the waste. The purpose of treatment is to neutralize the waste, recover energy or material resources, or make the waste nonhazardous or less hazardous.

Before carrying out any processes that could be considered treatment, the responsible trained laboratory personnel or the institution's environmental health and safety office should check with local and national agencies to clarify the applicable rules. Small-scale treatment of waste in the laboratory is not allowed in all places. Specific circumstances in which treatment may be performed without a permit typically include the following:

- Treatment in an accumulation container.
- Elementary neutralization, or the mixing of acidic and alkaline waste to form a salt solution. Address safety considerations, especially the use of dilute solutions to avoid rapid heat generation.
- Treatment of a by-product of an experiment before it becomes a waste. Treatment of experimental by-products assumes the material has not been declared a waste or handled in a waste-like manner. Do not perform such treatment anywhere other than the location where the by-product was generated.

11.4.2 Reduction of Multihazardous Waste

Multihazardous waste is waste that presents any combination of chemical, radioactive, or biological hazards. Management of multihazardous wastes is difficult and complex. For example, disposal of multihazardous waste that includes both hazardous chemicals and materials contaminated with microorganisms requires special procedures to prevent the release of infectious agents to the environment.

Safe and secure waste management methods include a commitment by senior management to develop and support a waste reduction program. Some simple operational improvements can help reduce mixed waste. For example, laboratory managers can

- purchase chemicals and radioactive materials in the quantities necessary for a planned experiment to avoid creating surplus materials that may end up as waste;
- establish procedures that will prevent commingling radioactive waste with noncontaminated materials and trash; and
- consider substituting less hazardous constituents for either the chemical or the radioactive source of the mixed waste.

11.5 Disposal Options

Laboratories often use several disposal options because each has its own advantages for specific wastes.

11.5.1 Incineration

Incineration is a common disposal method for laboratory wastes. Incineration is normally performed in rotary kilns at high temperatures (649-760°C). This technology completely destroys most organic materials and significantly reduces the volume of residual material that must be put in landfills. However, it is an expensive option that requires the use of high volumes of fuel to reach the required temperatures. Also, some materials, such as mercury and mercury salts, may not be incinerated due to regulations and limitations of the destruction capability.

11.5.2 Disposal in the Sanitary Sewer

Disposal in the sewer system (down the drain) used to be common, but this practice has changed markedly. Many industrial and academic laboratory facilities have completely eliminated sewer disposal. Most sewer disposal is controlled locally, and it is best to consult with the local sewer facility to find out what is allowed. Consider disposal of some chemical waste materials in the sanitary sewer if the sewer facility permits it.

Chemicals that may be permissible for sewer disposal include aqueous solutions that readily biodegrade and low-toxicity solutions of inorganic substances. Water-miscible flammable liquids are frequently prohibited from disposal in the sewer system. Water-immiscible chemicals should never go down the drain.

Dispose of appropriate waste only in drains that flow to a sewer facility, never into a storm drain or septic system. Flush waste with at least a hundredfold excess of water. Periodically check that the laboratory's wastewater effluent is not exceeding concentration limits.

11.5.3 Release to the Atmosphere

The release of vapors to the atmosphere, such as through open evaporation or fume hood effluent, is not an acceptable disposal method. Install appropriate trapping devices on all apparatus for operations expected to release vapors.

Fume hoods are designed as safety devices to transport vapors away from the laboratory in case of an emergency, not as a routine means for disposal of volatile waste. Some laboratories have units containing absorbent filters, but these have limited absorbing capacity. Redirection of fume hood vapors to a common trapping device can completely eliminate discharge into the atmosphere.

11.5.4 Disposal of Nonhazardous Waste

When safe and allowed by local regulation, disposal of nonhazardous waste via the normal trash or sewer can substantially reduce disposal costs. However, there are risks associated with materials that may be improperly labeled or described. In addition, local regulations may restrict the disposal of waste in municipal systems.

The laboratory retains the final responsibility for the long-term fate of the waste.

Check the rules and requirements of the local solid waste management authority. Develop a list of waste materials that may be disposed of safely and legally in the normal trash. The common wastes usually not regulated as hazardous include certain salts (e.g., potassium chloride, sodium carbonate), many natural products (e.g., sugars, amino acids), and inert materials used in a laboratory (e.g., noncontaminated chromatography resins and gels). In some places, the hazardous waste vendor may assist with disposal of inert materials.

11.5.5 Offsite Waste Disposal

The ultimate destination of waste may be a treatment, storage, and disposal facility. Here waste is held, treated (typically via chemical action or incineration), or actually disposed of. Although the waste has left the laboratory, the laboratory retains the final responsibility for the long-term fate of the waste. The laboratory must have complete trust and confidence in the disposal facility, as well as in the transporter who carries the waste to the facility.

11.5.6 Disposal of COC Waste

The end of the life cycle of a chemical of concern (COC) is either its consumption in a laboratory process or its disposal. Develop and implement a chemical disposal program that includes the following steps.

1. Ensure that disposal facilities or processes are available for the COC.
2. Develop procedures that detail
   - how to safely collect and store the waste;
   - how waste will be removed from the laboratory; and
   - how laboratory workers should notify the chemical safety and security officer (CSSO) that they have unwanted materials for disposal.
3. Maintain records to comply with regulatory requirements that include, at a minimum, date of disposal, quantities disposed, and method of disposal.
4. Secure disposal records indefinitely or per regulatory requirements.

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Page 16: Wikimedia Commons; **49 and 50** *(bottom)*: Safety and Security Department, University of Karachi, Pakistan **51, 53, and 56:** Chemical Security Engagement Program team; **54:** Rune Welsh; **75:** Fabexplosive; **83:** U.S. Geological Survey; **85:** Zergonian; **92:** André Luis Carvalho, Leandro Maranghetti Lourenço; **98 and 101:** Chemical Security Engagement Program team; **107:** Patrick John Y. Lim; **109, 112 and 119** (*left and right*): Safety and Security Department, University of Karachi, Pakistan; **111:** Chemical Residue Laboratory, South Carolina Department of Agriculture; **116:** Chemical Security Engagement Program team; **137 and 150** (*bottom*): Wikimedia Commons; **139:** Eyal Bairey, Weizmann Institute for Science; **141:** Ildar Sagdejev; **144** (*top*): Workingclass91; **144** (*bottom*): Panek; **146:** USDA, Scott Bauer; **147:** Firsthuman; **150** (*top*): Patrick John Y. Lim

Appendixes

A

A.1. Example List of Chemicals of Concern

The following tables (A.1 to A.5) are examples of the types of chemicals that a laboratory should include in an inventory of chemicals of concern (COCs).

TABLE A.1 Chemical Weapons and Chemical Weapons Precursors[a]

Chemical of Concern	Synonym	CAS Registry Number[b]
1,4-Bis(2-chloroethylthio)-*n*-butane		142868-93-7
Bis(2-chloroethylthio)methane		63869-13-6
Bis(2-chloroethylthiomethyl) ether		63918-90-1
1,5-Bis(2-chloroethylthio)-*n*-pentane		142868-94-8
1,3-Bis(2-chloroethylthio)-*n*-propane		63905-10-2
2-Chloroethyl chloromethyl sulfide		2625-76-5
Chlorosarin	*O*-Isopropyl methylphosphonochloridate	1445-76-7
Chlorosoman	*O*-Pinacolyl methylphosphonochloridate	7040-57-5
DF	Methyl phosphonyl difluoride	676-99-3
Ethyl phosphonyl difluoride		753-98-0
HN1 (nitrogen mustard-1)	Bis(2-chloroethyl)ethylamine	538-07-8
HN2 (nitrogen mustard-2)	Bis(2-chloroethyl)methylamine	51-75-2
HN3 (nitrogen mustard-3)	Tris(2-chloroethyl)amine	555-77-1
Isopropylphosphonyl difluoride		677-42-9
Lewisite 1	2-Chlorovinyldichloroarsine	541-25-3
Lewisite 2	Bis(2-chlorovinyl)chloroarsine	40334-69-8
Lewisite 3	Tris(2-chlorovinyl)arsine	40334-70-1
Sulfur mustard (mustard gas (H))	Bis(2-chloroethyl) sulfide	505-60-2
O-Mustard (T)	Bis(2-chloroethylthioethyl) ether	63918-89-8
Propylphosphonyl difluoride		690-14-2
QL	*O*-Ethyl-*O*-2-diisopropylaminoethyl methylphosphonite	57856-11-8
Sarin	*O*-Isopropyl methylphosphonofluoridate	107-44-8
Sesquimustard	1,2-Bis(2-chloroethylthio)ethane	3563-36-8
Soman	*O*-Pinacolyl methylphosphonofluoridate	96-64-0
Tabun	*O*-Ethyl *N,N*-dimethylphosphoramido-cyanidate	77-81-6
VX	*O*-Ethyl-S-2-diisopropylaminoethyl methyl phosphonothiolate	50782-69-9

NOTE: Toxic chemicals with few or no legitimate uses, developed or used primarily for military purposes. [a]U.S. Chemical Weapons Convention Schedule 1; see *http://www.cwc.gov/* (accessed October 28, 2009). [b]See Chemical Abstract Service web site *www.cas.org* (accessed October 28, 2009). SOURCE: U.S. Department of Homeland Security list of Chemicals of Interest (6 CFR Part 27 Appendix to Chemical Facility Anti-Terrorism Standards; Final Rule; November 20, 2007).

TABLE A.2 Explosives and Improvised Explosive Device Precursors

Chemical of Concern	Synonym	CAS Registry Number
Aluminum (powder)		7429-90-5
Ammonium nitrate		6484-52-2
Ammonium perchlorate		7790-98-9
Ammonium picrate		131-74-8
Barium azide		18810-58-7
Diazodinitrophenol		87-31-0
Diethyleneglycol dinitrate		693-21-0
Dingu	Dinitroglycoluril	55510-04-8
Dinitrophenol		25550-58-7
Dinitroresorcinol		519-44-8
Dipicryl sulfide		2217-06-3
Dipicrylamine [or] Hexyl	Hexanitrodiphenylamine	131-73-7
Guanyl nitrosaminoguanylidene hydrazine		–
Hexanitrostilbene		20062-22-0
Hexolite	Hexotol	121-82-4
HMX	Cyclotetramethylene-tetranitramine	2691-41-0
Hydrogen peroxide (concentration of at least 35%)		7722-84-1
Lead azide		13424-46-9
Lead styphnate	Lead trinitroresorcinate	15245-44-0
Magnesium (powder)		7439-95-4
Mercury fulminate		628-86-4
Nitrobenzene		98-95-3
5-Nitrobenzotriazol		2338-12-7
Nitrocellulose (not filters)		9004-70-0
Nitroglycerine		55-63-0
Nitromannite	Mannitol hexanitrate, wetted	15825-70-4
Nitromethane		75-52-5
Nitrostarch		9056-38-6
Nitrotriazolone		932-64-9
Octolite		57607-37-1
Octonal		78413-87-3
Pentolite		8066-33-9
PETN	Pentaerythritol tetranitrate	78-11-5
Phosphorus		7723-14-0
Potassium chlorate		3811-04-9
Potassium nitrate		7757-79-1
Potassium perchlorate		7778-74-7
Potassium permanganate		7722-64-7
RDX	Cyclotrimethylenetri-nitramine	121-82-4
RDX and HMX mixtures		121-82-4
Sodium azide		26628-22-8

TABLE A.2 Continued

Chemical of Concern	Synonym	CAS Registry Number
Sodium chlorate		7775-09-9
Sodium nitrate		7631-99-4
Tetranitroaniline		53014-37-2
Tetrazene	Guanyl nitrosaminoguanyl-tetrazene	109-27-3
1*H*-Tetrazole		288-94-8
TNT	Trinitrotoluene	118-96-7
Torpex	Hexotonal	67713-16-0
Trinitroaniline		26952-42-1
Trinitroanisole		606-35-9
Trinitrobenzene		99-35-4
Trinitrobenzenesulfonic acid		2508-19-2
Trinitrobenzoic acid		129-66-8
Trinitrochlorobenzene		88-88-0
Trinitrofluorenone		129-79-3
Trinitro-*m*-cresol		602-99-3
Trinitronaphthalene		55810-17-8
Trinitrophenetole		4732-14-3
Trinitrophenol	Picric acid	88-89-1
Trinitroresorcinol		82-71-3
Tritonal		54413-15-9

SOURCE: U.S. Department of Homeland Security list of Chemicals of Interest (6 CFR Part 27 Appendix to Chemical Facility Anti-Terrorism Standards; Final Rule; November 20, 2007).

TABLE A.3 Weapons of Mass Effect

Chemical of Concern	Synonym	CAS Registry Number
Arsine		7784-42-1
Boron tribromide		10294-33-4
Boron trichloride	Borane, trichloro	10294-34-5
Boron trifluoride	Borane, trifluoro	7637-07-2
Bromine chloride		13863-41-7
Bromine trifluoride		7787-71-5
Dinitrophenol		25550-58-7
Dinitroresorcinol		519-44-8
Carbonyl fluoride		353-50-4
Chlorine pentafluoride		13637-63-3
Chlorine trifluoride		7790-91-2
Cyanogen	Ethanedinitrile	460-19-5
Cyanogen chloride		506-77-4
Diborane		19287-45-7
Dichlorosilane	Silane, dichloro-	4109-96-0
Dinitrogen tetroxide		10544-72-6
Fluorine		7782-41-4
Germane		7782-65-2
Germanium tetrafluoride		7783-58-6
Hexafluoroacetone		684-16-2
Hydrogen bromide (anhydrous)		10035-10-6
Hydrogen chloride (anhydrous)		7647-01-0
Hydrogen cyanide	Hydrocyanic acid	74-90-8
Hydrogen fluoride (anhydrous)		7664-39-3
Hydrogen iodide, anhydrous		10034-85-2
Hydrogen selenide		7783-07-5
Hydrogen sulfide		7783-06-4
Methyl mercaptan	Methanethiol	74-93-1
Methylchlorosilane		993-00-0
Nitric oxide	Nitrogen oxide (NO)	10102-43-9
Nitrogen trioxide		10544-73-7
Nitrosyl chloride		2696-92-6
Oxygen difluoride		7783-41-7
Perchloryl fluoride		7616-94-6
Phosgene	Carbonic dichloride or carbonyldichloride	75-44-5
Phosphine		7803-51-2
Phosphorus trichloride		7719-12-2
Selenium hexafluoride		7783-79-1
Silicon tetrafluoride		7783-61-1
Stibine		7803-52-3
Sulfur dioxide (anhydrous)		7446-09-5
Sulfur tetrafluoride	Sulfur fluoride (SF_4), (T-4)-	7783-60-0
Tellurium hexafluoride		7783-80-4

TABLE A.3 Continued

Chemical of Concern	Synonym	CAS Registry Number
Titanium tetrachloride	Titanium chloride ($TiCl_4$), (T-4)-	7550-45-0
Trifluoroacetyl chloride		354-32-5
Tungsten hexafluoride		7783-82-6

SOURCE: U.S. Department of Homeland Security list of Chemicals of Interest (6 CFR Part 27 Appendix to Chemical Facility Anti-Terrorism Standards; Final Rule; November 20, 2007).

TABLE A.4 Examples of Acutely Toxic Chemicals (based on the United Nations Globally Harmonized System, Hazard Category 1)[a]

Chemical of Concern	Synonym	CAS Registry Number
Acrolein	2-Propenal or acrylaldehyde	107-02-8
2-Aminopyridine		462-08-8
Arsenic pentafluoride gas		784-36-3
Arsine gas		7784-42-1
Benzyl chloride		100-44-7
Boron trifluoride	Borane, trifluoro	7637-07-2
Bromine		7726-95-6
Chlorine		7782-50-5
Chorine dioxide	Chlorine oxide (ClO_2)	10049-04-4
Chlorine trifluoride		7790-91-2
Cyanogen chloride		506-77-4
Decaborane		17702-41-9
Diazomethane		334-88-3
Diborane		19287-45-7
Dichloroacetylene		79-36-7
Dimethylmercury		593-74-8
Dimethyl sulfate		77-78-1
Dimethyl sulfide		75-18-3
Ethylene chlorohydrin		107-07-3
Ethylene fluorohydrin		371-62-0
Fluorine		7681-49-4
2-Fluoroethanol		371-62-0
Hexamethylene diisocyanate		822-06-0
Hydrogen cyanide	Hydrocyanic acid	74-90-8
Hydrogen fluoride		7664-39-3
Iron pentacarbonyl	Iron carbonyl ($Fe (CO)_5$), (Tb5-11)-	13463-40-6
Isopropyl formate		625-55-8
Methacryloyl chloride		920-46-7
Methyacrylonitrile	2-Propenenitrile, 2-methyl-	126-98-7
Methyl chloroformate	Carbonochloridic acid, methyl ester	79-22-1
Methylene biphenyl isocyanate		101-68-9
Methyl fluoroacetate		453-18-9
Methyl fluorosulfate		421-20-5
Methyl hydrazine	Hydrazine, methyl-	60-34-4
Methyl mercury and other organic forms		—
Methyl trichlorosilane		75-79-6
Methyl vinyl ketone		78-94-4
Nickel carbonyl		13463-39-3
Nitrogen dioxide		10102-44-0
Nitrogen tetroxide		10544-72-6
Nitrogen trioxide		10544-73-7
Osmium tetroxide		20816-12-0
Oxygen difluoride		7783-41-7
Pentaborane		19624-22-7
Perchloromethlyl mercaptan	Methanesulfenyl chloride, trichloro-	594-42-3

TABLE A.4 Continued

Chemical of Concern	Synonym	CAS Registry Number
Phosgene	Carbonic dichloride or carbonyl dichloride	75-44-5
Phosphine		7803-51-2
Phosphorus oxychloride	Phosphoryl chloride	10025-87-3
Phosphorus pentafluoride		7641-19-0
Phosphorus trichloride		7719-12-2
Sarin	*o*-Isopropyl methylphosphonofluoridate	107-44-8
Selenium hexafluoride		7783-79-1
Silicon tetrafluoride		7783-61-1
Sodium azide		26628-22-8
Sodium cyanide (and other cyanide salts)		143-33-9
Stibine		7803-52-3
Sulfur monochloride		10025-67-9
Sulfur pentafluoride		10546-01-7
Sulfur tetrafluoride	Sulfur fluoride (SF_4), (T-4)-	7783-60-0
Sulfuryl chloride		7791-25-5
Tellurium hexafluoride		7783-80-4
Tetramethyl succinonitrile		3333-52-6
Tetranitromethane	Methane, tetranitro-	509-14-8
Thionyl chloride		7719-09-7
Toluene-2,4-diisocyanate		584-84-9
Trichloro(chlormethyl)silane		1558-25-4
Trimethyltin chloride		1066-45-1

[a] For more information refer to the *Globally Harmonized System of Classification and Labelling of Chemicals* Third revised edition. United Nations, 2009. Available on the Internet at http://www.unece.org/trans/danger/publi/ghs/ghs_rev03/03files_e.html (accessed June 11, 2010).

TABLE A.5 Chemicals Used in Clandestine Production of Illicit Drugs

Chemical of Concern	Target Product
Acetic acid	Phenyl-2-propanone (P-2-P)/cocaine
Acetic anhydride	Heroin/P-2-P/methaqualone
Acetone	Cocaine/heroin/others
Acetyl chloride	Heroin
N-Acetylanthranilic acid	Methaqualone
Ammonium formate	Amphetamines
Ammonium hydroxide	Cocaine/others
Anthranilic acid	Methaqualone
Benzaldehyde	Amphetamines
Benzene	Cocaine
Benzyl chloride	Methamphetamine
Benzyl cyanide	Methamphetamine
2-Butanone (MEK)*	Cocaine
Butyl acetate	Cocaine
N-Butyl alcohol	Cocaine
Calcium carbonate	Cocaine/others
Calcium oxide/hydroxide	Cocaine/others
Chloroform	Cocaine/others
Cyclohexanone	Phencyclidine (PCP)
Diacetone alcohol	Cocaine
Diethylamine	Lysergic acid diethylamide (LSD)
Ephedrine	Methamphetamine
Ergometrine (ergonovine)	LSD
Ergotamine	LSD
Ethyl acetate	Cocaine
Ethyl alcohol	Cocaine/others
Ethyl amine	Ethylamphetamine/3,4-methylenedioxy- *N*-ethylamphetamine (MDE)
Ethyl ether	Cocaine/heroin/others
N-Ethylephedrine	Ethylamphetamine/MDE
N-Ethylpseudoephedrine	Ethylamphetamine/MDE
Formamide	Amphetamines
Hexane	Cocaine
Hydriodic (hydriotic) acid	Methamphetamine
Hydrochloric acid	Cocaine/heroin/others
Isopropyl alcohol	Cocaine
Isosafrole	Cocaine
Kerosene	Cocaine
Lysergic acid	LSD
Methyl alcohol	Cocaine
Methylamine	Methamphetamine/3,4-methylenedioxymethamphetamine (MDMA)
Methylene chloride	Cocaine/heroin/others
3,4-Methylenedioxyphenyl-2-propanone	3,4-Methylenedioxyamphetamine (MDA)/MDMA/MDE
N-Methylephedrine	Amphetamines
N-Methylpseudoephedrine	Amphetamines
Nitroethane	Amphetamines
Norpseudoephedrine	4-Methylaminorex

TABLE A.5 Continued

Chemical of Concern	Target Product
Petroleum ether	Cocaine/others
Phenylacetic acid	Phenyl-2-propanone
Phenylpropanolamine	Amphetamines/4-methylaminorex
1-Phenyl-2-propanone	Amphetamines/methamphetamine
Piperidine	PCP
Piperonal	MDA/MDMA/MDE
Potassium carbonate	Cocaine
Potassium permanganate	Cocaine
Propionic anhydride	Fentanyl analogues
Pseudoephedrine	Methamphetamine
Pyridine	Heroin
Safrole	MDA/MDMA/MDE
Sodium acetate	P-2-P
Sodium bicarbonate	Cocaine/others
Sodium carbonate	Cocaine/others
Sodium cyanide	PCP
Sodium hydroxide	Cocaine/others
Sodium suifate	Cocaine/others
Sulfuric acid	Cocaine/others
Toluene	Cocaine
o-Toluidine	Methaqualone
Xylenes	Cocaine

NOTES: Organizations may opt not to treat the commonly used chemicals on this list as COCs (e.g., acetone).

*2-Butanone and methyl ethyl ketone (MEK) are two names for the same substance.

SOURCE: Sevick, J. R. 1993. *Precursor and Essential Chemicals in Illicit Drug Production: Approaches to Enforcement*. National Institute of Justice. *http://www.popcenter.org/problems/meth_labs/PDFs/Sevick_1993.pdf* (accessed July 2009).

B

B.1. Sources of Chemical Information

Chemical Hygiene Plans

Chemical hygiene plans include standard operating procedures for work with specific chemical substances. These plans may be sufficient as the primary source of information used for risk assessment and experiment planning. However, most chemical hygiene plans provide only general procedures for handling chemicals. Safe and secure experiment planning requires that laboratory personnel check additional sources for information on the properties of the substances involved in the proposed experiment.

Material Safety Data Sheets

Material safety data sheets (MSDSs) provide information on the potential hazards of commercial substances and safety measures that users need to follow. Institutions should retain and make readily available to workers, emergency responders, and others the MSDSs provided by chemical suppliers.

Personnel should examine the MSDS for each unfamiliar chemical before beginning work. MSDS files may be present in each laboratory or maintained only in a central location. Many laboratories now access MSDSs electronically. Laboratory personnel can always contact the chemical supplier directly and request that an MSDS be sent by mail.

MSDSs are good sources of information for assessing the hazards and risks of chemical substances. However, MSDSs have the following limitations:

- The quality of MSDSs produced by different chemical suppliers varies widely.
- The unique morphology of solid hazardous chemicals may not be addressed in MSDSs.
- MSDSs must describe control measures and precautions for work on a variety of scales, ranging from microscale laboratory experiments to large manufacturing operations. Some procedures outlined in an MSDS may therefore be unnecessary or inappropriate for laboratory-scale work.
- Many MSDSs comprehensively list all conceivable health hazards associated with a substance without differentiating which are most significant and which are most likely to be encountered.

Laboratory Chemical Safety Summaries

The National Research Council's *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (National Academy Press: Washington, DC) contains a set of 99 laboratory chemical safety summaries (LCSSs) that provide information on chemicals in the context of laboratory use. These documents are summaries and are not intended to be comprehensive or useful to all conceivable users of a chemical.

International Chemical Safety Cards

International Chemical Safety Cards (ICSCs) provide essential health and safety information on chemicals. ICSCs include information on the hazards of specific chemicals, first aid and fire-fighting measures, and information about precautions for spillage, disposal, storage, packaging, labeling, and transport. ICSCs are peer reviewed by a group of scientists. This makes them more reliable than some other sources of information on chemicals, such as MSDSs that are generated by companies and not peer reviewed.

ICSCs are currently available on the Internet in a variety of languages at the following address: http://www.ilo.org/public/english/protection/safework/cis/products/icsc/.

Labels

Commercial suppliers typically provide precautionary labels on their chemical containers. Labels usually indicate the principal hazards associated with their contents. Note that precautionary labels do not replace MSDSs, LCSSs, and ICSCs as a primary source of information for risk assessment. However, labels serve as valuable reminders of the key hazards associated with the substance. As with the MSDS, the label quality can be inconsistent. If a container is received without the commercial label, appropriate hazard markings should be put on the container before it is made available for use within the laboratory.

Globally Harmonized System for Hazard Communication

The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) is an internationally recognized system for hazard classification and communication. GHS classifies substances by the physical, health, and environmental hazards they pose and provides standard pictogram-based labels to represent those hazards.

Container labels should include a product identifier with hazardous ingredient disclosure, supplier information, a hazard pictogram (Figure B.1), a signal word, a hazard statement, first aid information, and supplemental information. Three of these elements—the pictograms, signal word, and hazard statements—are standardized under GHS. The signal words “Danger” or “Warning” reflect the severity of the hazard posed. Hazard statements are standard phrases that describe the nature of the hazard posed by the material (e.g., heating may cause explosion).

GHS recognizes 16 types of physical hazards, 9 types of health hazards, and an environmental hazard.

Physical Hazards

- Explosives
- Flammable gases
- Flammable aerosols
- Oxidizing gases
- Gases under pressure
- Flammable liquids
- Flammable solids
- Self-reactive substances
- Pyrophoric liquids
- Pyrophoric solids
- Self-heating substances

- Substances that, in contact with water, emit flammable gases
- Oxidizing liquids
- Oxidizing solids
- Organic peroxides
- Substances that are corrosive to metals

Health Hazards

- Acute toxicity
- Skin corrosion or irritation
- Serious eye damage or eye irritation
- Respiratory or skin sensitization
- Germ cell mutagenicity
- Carcinogenicity
- Reproductive toxicology
- Target organ systemic toxicity—single exposure
- Target organ systemic toxicity——repeated exposure
- Aspiration hazard

Environmental Hazards

- Hazardous to the aquatic environment
  - Acute aquatic toxicity
  - Chronic aquatic toxicity
    - Bioaccumulation potential
    - Rapid degradability

In addition to the labeling requirements, GHS requires a standard format for Safety Data Sheets (SDSs) that accompany hazardous chemicals. SDSs must contain a minimum of 16 elements:

- Substance identification
- Hazard(s) identification
- Composition, information on ingredients
- First aid measures
- Fire-fighting measures
- Accidental release measures
- Handling and storage
- Exposure controls, personal protection
- Physical and chemical properties
- Stability and reactivity

- Toxicological information
- Ecological information
- Disposal considerations
- Transport information
- Regulatory information
- Other information

Laboratory personnel should use the information on SDSs and container labels to develop safety and emergency response policies tailored to the lab.

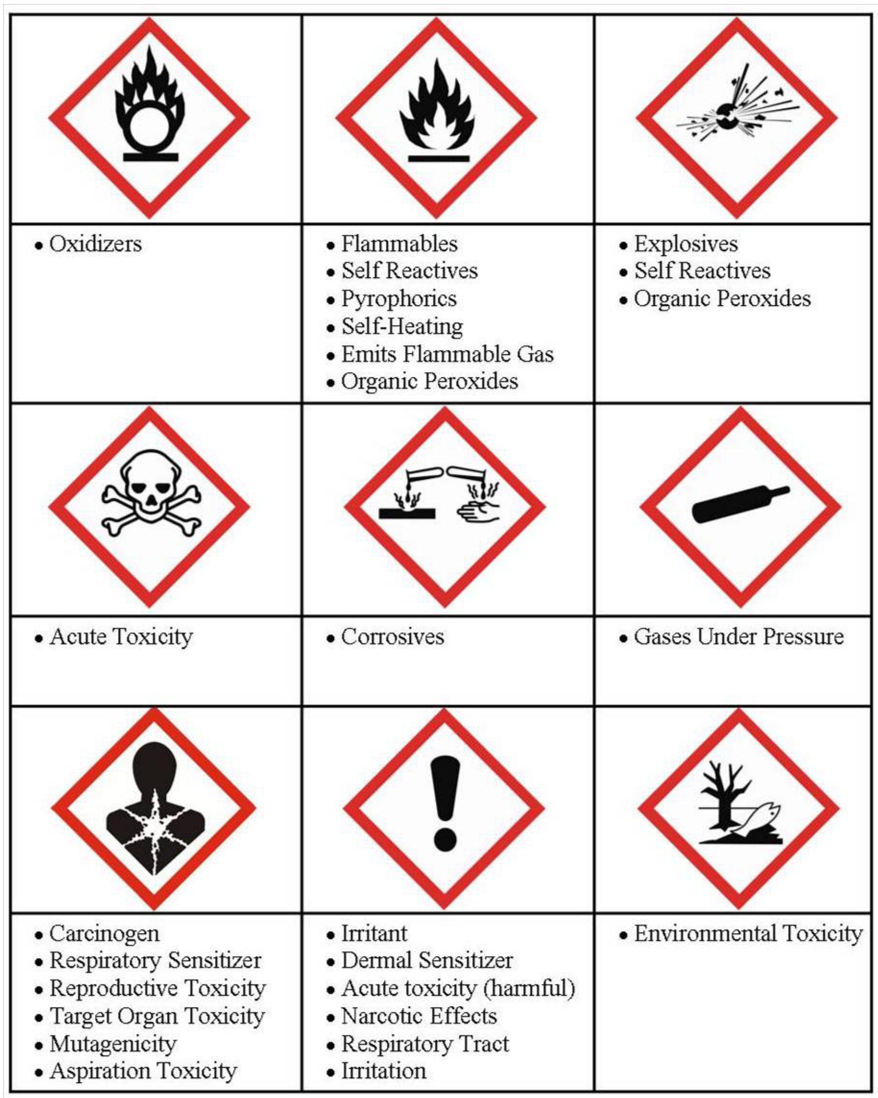

FIGURE B.1 GHS pictograms for labeling of containers of hazardous chemicals.

SOURCE: See "Globally Harmonized System of Classification and Labelling of Chemicals" *http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html*

C

C.1. Types of Inspection Programs

There are several types of inspection programs, each providing a different perspective and function. A comprehensive inspection program includes some or all of these types.

Routine Inspections

All laboratory personnel should conduct frequent, routine general equipment and facility inspections. Daily inspections may be appropriate for equipment in constant use, such as gas chromatographs. Other less frequently used equipment may need only weekly or monthly inspection or inspection prior to use. Keep a record of inspection attached to the equipment or visible nearby. Encourage all personnel to develop the habit of inspection.

Program Audits

A program audit includes both a physical inspection and a review of the operations and the facilities. This type of audit is generally conducted by a team, which may include the laboratory supervisor, senior management, and laboratory safety representatives.

The audit may begin by discussing the safety program and culture, reviewing operations, reviewing written programs and training records, and reviewing pertinent policies and procedures and how they are used in the laboratory. This is followed by a laboratory inspection and interviews with trained laboratory personnel to determine the level of safety awareness. Audits also include an open discussion of how workers, supervisors, managers, and safety officers can better support each other. This type of audit provides a much more comprehensive view of the laboratory than a simple routine inspection.

Peer Inspections

One of the most effective safety tools is periodic peer-level inspections. The people who fulfill this role work in the institution but not in the area being surveyed. People may volunteer or be selected and can function on an ad hoc basis or as part of a formal working group, such as a "safety committee." Peer inspections depend heavily on the knowledge and commitment of the inspectors. Peer inspectors should serve for a length of time that gives them enough knowledge about operations to observe and comment constructively but not so long as to lose the desired level of diligence.

A peer inspection program has the advantage of being perceived as less threatening than other forms of surveys or audits. A high-quality peer inspection program may reduce the need for frequent inspections by supervisors, but should not replace other inspections completely.

Environmental Health and Safety Inspections

The institution's environmental health and safety staff, the safety committee, or an equivalent group may also conduct laboratory inspections on a routine basis. These inspections may be comprehensive; targeted to certain operations or experiments; focused on a particular type of inspection, such as safety equipment and systems; or "audits" to check the work of other inspectors. Facility engineers or maintenance personnel may also participate in safety inspection programs.

Self-Audits

Some institutions have trained laboratory personnel conduct self-audits for their own benefit. An institution may also ask personnel to conduct their own inspections, write reports, and use routine inspections as a check on the self-audits. This approach benefits everyone by raising awareness, promoting the institutional safety culture, and easing the burden on management.

Inspections by External Entities

Many different types of elective inspections or audits can be conducted by outside experts, regulatory agencies, emergency responders, or other organizations. They may inspect a particular facility, equipment, or procedure either during the pre-experiment design phase or during operations. Inspections by regulatory or municipal groups, such as the fire department, offer the opportunity to build relationships with government agencies and the public. Open houses or invitations targeted to specific people or groups may help build relations with the public. Inspections and audits by outside consultants or peer institutions may be especially helpful in identifying best practices and vulnerabilities. They may also be economically beneficial.

C.2. Elements of an Inspection

Preparing for an Inspection

Whether an inspection is announced or unannounced depends on the objective. Announced inspections help the inspectors interact with trained personnel and feel more like a value-added service than a “safety police” action. However, if the objective is to observe “real-time” conditions in preparation for a regulatory inspection, an unannounced targeted inspection might be appropriate.

Before the inspection, have a checklist of inspection items, along with the criteria and the basis for each issue. It may be helpful to share the checklist with trained personnel prior to the inspection, so they may perform self-audits before and after the inspection. Take pictures to help show personnel the matters that need attention.

Inspection Checklists

Inspection checklists may take a variety of formats and will vary in length depending on the type and focus of the inspection. Each inspection item should be in the form of a YES or NO question. Pose questions in which a positive outcome results in a YES, making it easy to spot problems. Always leave room for comments. Search commercial products for applications that work on computers, personal digital assistants (PDAs), and other hand-held devices. These products can help streamline the reporting process.

Conducting the Inspection

Inspectors should perform the following tasks.

- Interact with laboratory personnel. Trained personnel can provide a great deal of information, as well as provide feedback on training and safety programs.
- Take notes and make comments on the inspection form in order to provide details on problems in the report. Take photos of issues that need particular attention.
- Point out problems and show laboratory workers how to fix them. If a problem is corrected during the inspection, it should be noted in the report.

Inspection Reports

Inspectors should prepare a report as soon as possible after an inspection and provide it to the laboratory manager and others, such as the chemical safety and security officer (CSSO) or the department chair or manager. Key individuals may want to meet to review the findings.

The report should include

- all of the problems noted during the inspection, along with the criteria for correcting them;
- any photographs taken;
- notes of any best practices or improvements made since the last inspection; and
- a reasonable time line for corrective actions.

Inspectors should follow up with the laboratory and offer support in helping to find reasonable solutions to any problems.

Corrective Actions

In most cases the laboratory will take appropriate corrective actions. If the laboratory does not make the necessary changes, the institution will have to decide what steps to take for those individuals who are employing unsafe work practices or are not following institutional policies or external regulations.

C.3. Items to Include in an Inspection

The following list is representative, not exhaustive. Depending on the laboratory and the type of work it conducts, other items may also be targeted for inspection.

- Required personal protective equipment is available and is used consistently and correctly (e.g., laboratory coats, gloves, safety glasses, goggles, face shields).
- Compressed gas cylinders are secured correctly. Cylinders are capped if not connected for use. Proper regulators are used.
- Requirements have been established on where eating and drinking are allowed.
- Requirements have been established limiting around-the-clock access to laboratories.
- Electrical cords not placed on surfaces where spills of flammable materials are likely to occur. Cords are in good condition and not displaying signs of excessive wear (fraying, not pinched).
- Laboratory hoods have been tested and are operating. Inspection information is visible. Hoods are used properly, and work is conducted 6 inches (15 cm) inside the hood face. Large pieces of equipment do not significantly impact airflow.
- Vacuum glassware is inspected and maintained in good condition. Pressure reaction vessels with pressure relief and temperature or pressure measuring capability are used for high-pressure reactions.
- Health classification of materials is conducted (particularly for unknown molecular entities). Associated work practices and containment based on the hazard or risk classification of the material is followed (e.g., low hazard, hazardous, particularly hazardous materials and associated requirements for use of ventilated enclosures, disposal of waste, labeling of areas where work with high-hazard materials is conducted, decontamination of work surfaces).
- Access to emergency equipment (e.g., safety showers, eye wash units, fire extinguishers) is unobstructed and equipment is maintained in good working order. Minimum clearance to sprinkler heads, as required by local building and fire codes, is maintained.
- Chemicals are properly stored and separated (e.g., flammables, strong acids, strong bases, peroxides).

- Personnel can demonstrate the ability to access Material Safety Data Sheets and knowledge of handling requirements for various classifications of materials.
- Guards on rotating machinery and high-temperature devices are in place and working properly. Safety switches and emergency stops are working properly.
- Associated egress corridors are unobstructed and minimum egress as required by building and fire code is maintained. Combustible and surplus materials and equipment are removed from exit passageways.

D

D.1. Design Considerations for Casework, Furnishings, and Fixtures

Casework, Furnishings, and Fixtures

Use metal casework rather than plastic laminate or wood. The material should be easy to clean and not prone to rust. For clean rooms, polypropylene or stainless steel may be preferable. Make sure work surfaces are chemically resistant, smooth, and easy to clean.

Work areas, including computers, should incorporate ergonomic features, such as adjustability, task lighting, and convenient equipment layout. Make sure that there is adequate space for ventilation and cooling of computers and other electronics.

Hand-washing sinks for particularly hazardous materials may require elbow or electronic controls. Do not install more cupsinks than necessary to avoid odorous dry traps.

Flooring

Wet labs should have chemically resistant covered flooring. Sheet goods are usually preferable to floor tiles because floor tiles may loosen or degrade over time, particularly near laboratory hoods and sinks.

Doors, Windows, and Walls

Finish walls in a manner that is easy to clean and maintain. Fire code may require doors, frames, and walls to be fire-rated.

Doors should have view panels. These windows prevent opening the door into a person on the other side, and they allow people to see into the laboratory in case of an accident or injury.

Windows in laboratories should be closed if there are laboratory hoods or other local ventilation systems operating in the facility. Windows can be open if there is no ventilation system in place and hazardous chemicals are not being used, such as in a teaching laboratory.

D.2. Laboratory Engineering Controls for Personal Protection

General laboratory ventilation is typically set to provide 6 to 12 room air changes per hour (Table D.1). More airflow may be required to cool laboratories with high internal heat loads, such as those with analytical equipment; to service laboratories with large specific exhaust system requirements; or to service those with high densities of laboratory hoods or other local exhaust ventilation devices. In all cases, air should flow from the offices, corridors, and support spaces into the laboratories. All air from laboratories should be exhausted outdoors and not recirculated. Thus, the air pressure in the laboratories should be negative with respect to the rest of the building. Put outside air intakes for a laboratory building in a location that reduces the possibility of re-entrainment of laboratory exhaust or contaminants from other sources, such as waste disposal areas and loading docks.

Although the supply system itself provides dilution of toxic gases, vapors, aerosols, and dust, it gives only modest protection, especially if these impurities are released into the laboratory in any significant quantity. Operations that can release these toxins, such as running reactions, heating or evaporating solvents, and transferring chemicals from one container to another, should normally be performed in a laboratory hood. Laboratory apparatus that may discharge toxic vapors, such as vacuum pump exhausts, gas chromatograph exit ports, liquid chromatographs, and distillation columns, should vent to an exhaust device such as an elephant trunk.

TABLE D.1 Laboratory Engineering Controls for Personal Protection

Type of Ventilation	Typical Number of Air Changes	Examples of Use
General lab ventilation	6 to 12 air changes per hour, depending on lab design and system operation	Nonvolatile chemicals, nonhazardous materials, trace amounts of hazardous materials
Environmental rooms	Zero air changes	Materials needing special environmental controls, nonhazardous amounts of flammable, toxic, or reactive chemicals
Laboratory chemical hoods	10 to 15 air changes per minute	Flammable, toxic, or reactive materials, up to 10,000 times the concentration known to be immediately dangerous; products or mixtures with unknown hazards
Unventilated storage cabinets	Zero air changes	Flammable liquids (if equipped with flame arrestors), corrosives, moderately toxic chemicals
Ventilated storage cabinets	1 to 2 air changes per hour	Highly toxic or hazardous chemicals
Recirculating biosafety cabinets	Zero air changes for chemicals, many for particles	Biological materials used in processes that may form aerosols, nanoparticles
Glove box	Varies from very low to very high, depending on the glove box and the application	Positive-pressure specialty environments, negative-pressure highly toxic materials

D.3. Laboratory Hoods

Laboratory Hood Face Velocity

The average velocity of the air drawn through the face of the hood is called the *face velocity*. The face velocity of a hood greatly influences its containment efficiency, or the ability of the hood to contain hazardous substances. Face velocities that are too low or too high will reduce the containment efficiency of a hood. For traditional hoods, the recommended face velocity is between 0.41 and 0.51 meters per second (m/s). Face velocities between 0.51 and 0.61 m/s may be used for substances of very high toxicity or where outside influences adversely affect hood performance. Do not use face velocities approaching or exceeding 0.76 m/s, because they may cause turbulence around the periphery of the sash opening and actually reduce the capture efficiency of the laboratory hood.

Determine the average face velocity in one of two ways. One way is to measure the individual points across the plane of the sash opening and calculate their average. The other is to measure the hood volume flow rate with a pitot tube in the exhaust duct and divide this rate by the open face area. (Note the latter method does not identify high or low spots of face velocity across the face, which can allow contaminant release due to low airflow or turbulence respectively.)

Verify containment using one of the flow visualization techniques on laboratory hood testing (see below). Each hood, laboratory, facility, or site must define the acceptable average face velocity, minimum acceptable point velocity, maximum standard deviation of velocities, and whether to require visualization testing. These requirements should then be incorporated into the laboratory's chemical hygiene plan and/or ventilation system management plans.

Laboratory Hood Design and Construction

When specifying a laboratory hood for use in a particular activity, trained laboratory personnel should be aware of all the design features of the hood. Get assistance from an industrial hygienist, ventilation engineer, or laboratory consultant when deciding to purchase a laboratory hood.

Choose laboratory hoods and associated exhaust ducts made of nonflammable materials. They should be equipped with vertical, horizontal, or combination vertical-horizontal sashes that can be closed. The glass within the sash should be either laminated safety glass that is at least 0.55 cm (7/32 inch) thick or other equally safe material that will not shatter if there is an explosion within the hood. Place the utility control valves, electrical receptacles, and other fixtures outside the hood to minimize the need to reach within the hood proper. Other specifications regarding the construction materials, plumbing requirements, and interior design will vary, depending on the intended use of the hood.

Although hoods are most commonly used to control concentrations of toxic vapors, they can also serve to dilute and exhaust flammable vapors. Although theoretically possible, it is extremely unlikely (even under most worst-case scenarios) that the concentration of flammable vapors will reach the lower explosive limit (LEL) in the exhaust duct. However, somewhere between the source and the exhaust outlet of the hood, the concentration will pass through the upper explosive limit (UEL) and the LEL before being fully diluted at the outlet. Both the hood designer and the user should recognize this hazard and eliminate possible sources of ignition within the hood and its ductwork if there is a potential for explosion. The use of duct sprinklers or other suppression methods in laboratory fume ductwork is not necessary, or desirable, in the majority of situations. However, in limited situations, this may be required by International Mechanical Codes, such as IMC 510.

Fume Hood Airflow Types

- Constant air volume (CAV)
- Variable air volume (VAV)
- Non-bypass
- Bypass
- Auxiliary air
- Ductless

Factors That Affect Laboratory Hood Performance

- Proximity to traffic
- Proximity to supply air diffusers
- Proximity to windows and doors
- Proximity to ceiling fans

Laboratory Hood Performance Checks

Check whether hoods are performing properly using the following guidelines.

- Evaluate each hood before use and on a regular basis (at least once a year) to verify that the face velocity meets the criteria specified for it in the laboratory's chemical hygiene plan (see "Laboratory Hood Face Velocity" above).
- Verify the absence of excessive turbulence.
- Make sure that a continuous monitoring device for adequate hood performance is present, and check it every time the hood is used.

Testing and Verification

Annually conduct periodic performance testing consisting of a face velocity analysis and flow visualization using smoke tubes, bombs, or fog generators. Trained laboratory personnel should request a laboratory hood performance evaluation any time there is a change in any aspect of the ventilation system. Changes in the total volume of supply air or in the locations of supply air diffusers, or the addition of other auxiliary local ventilation devices (e.g., more hoods, vented cabinets, snorkels), all call for reevaluation of the performance of all hoods in the laboratory.

Evaluate performance against the design specifications for uniform airflow across the hood face as well as for the total exhaust air volume. Equally important is the evaluation of operator exposure. The steps in the evaluation of hood performance are as follows.

1. Use a smoke tube or similar device to determine that the hood is on and exhausting air.
2. Measure the velocity of the airflow at the face of the hood.
3. Determine the uniformity of air delivery to the hood face by making a series of face velocity measurements taken in a grid pattern.

D.4. Maintenance of Ventilation Systems

Even the best-made and most carefully installed ventilation system requires routine maintenance. Some laboratory ventilation systems have become so complex that it may be a good idea to have a special team of facility staff dedicated to the maintenance of the system.

- Inspect and maintain on a regular basis any facility-related environmental controls and safety systems, including laboratory hoods and room pressure controls, fire and smoke alarms, and special alarms and monitors for gases,
- Evaluate each laboratory periodically for the quality and quantity of its general ventilation and any time a change is made, either to the general ventilation system for the building or to some aspect of local ventilation within the laboratory. Airflow paths into and within a room can be determined by observing smoke patterns. There should be no areas in which air remains static or there are unusually high airflow velocities. If stagnant areas are found, consult a ventilation engineer, and make appropriate changes to supply or exhaust sources to correct the deficiencies.
- The rate at which air is exhausted from the laboratory facility should equal the rate at which supply air is introduced to the building. The number of air changes per hour within a laboratory can be estimated by dividing the total volume of the laboratory (in cubic meters) by the rate at which exhaust air is removed (in cubic meters per second). For each exhaust port (e.g., hoods), the product of the face area (in square meters) and the average face velocity (in linear meters per second) will give the exhaust rate for that source (in cubic meters per second). The sum of these rates for all exhaust sources in the laboratory yields the total rate at which air is being exhausted from the laboratory. Decreasing the flow rate of supply air (perhaps to conserve energy) decreases the number of air changes per hour in the laboratory, the face velocities of the hoods, and the capture velocities of all other local ventilation systems.
- Airflows are usually measured with thermal anemometers or velometers. These instruments are available from safety supply companies or laboratory supply houses. The proper calibration and use of these instruments and the evaluation of the data are separate disciplines. Consult an industrial hygienist or a ventilation engineer whenever

serious ventilation problems are suspected or when decisions on appropriate changes to a ventilation system are needed to achieve a proper balance of supply and exhaust air.

- All ventilation systems should have a device that readily permits the user to monitor whether the total system and its essential components are functioning properly. Manometer, pressure gauges, and other devices that measure the static pressure in the air ducts are sometimes used to reduce the need to manually measure airflow. "Telltales" and other similar simple devices can also serve as indicators of airflow. Determine the need for and the type of monitoring device on a case-by-case basis. If a chemical substance has excellent warning properties and the consequence of overexposure is minimal, the system will need less stringent control than if the substance is highly toxic or has poor warning properties.

E

E.1. Developing a Comprehensive Security Vulnerability Assessment

A Security Vulnerability Assessment (SVA) may include an entire institution or specific facilities in an institution. It involves a series of comprehensive investigations and an integrated analysis. The purpose of an SVA is to catalog potential security risks to a laboratory to determine the magnitude of the risks and assess the adequacy of systems that are in place. An SVA helps determine the security planning needs of a facility and should include the following items:

- Asset evaluation
- Threat assessment
- Site survey and analysis
- Physical vulnerability survey

Asset Evaluation

This investigation identifies and quantifies valuable assets—such as equipment, instruments, libraries, and documents—that should be protected from loss or damage through accidents, natural disasters, or theft or destruction by people who intend to do harm. The evaluation should include information about sources of replacement and alternative resources at the institution or elsewhere that could permit continuity of operations.

Threat Assessment

This identifies possible types of threats to the institution and specific facilities. Threats could be generic or site specific, from natural disasters or terrorist attacks. To the extent possible, a threat assessment should describe the adversary groups or individuals and their ideological and economic motivations; their members and supporters; leadership and organizational characteristics; their record of illegal or disruptive activities; their preferred mode of action and potential capabilities to attack a target; and what they typically want to communicate to the public and how they prefer to do it. However, institutions must be careful to adhere to laws within their country that protect personal privacy. Describe in detail the possibilities of attack or action against the institution and its facilities.

Also estimate the consequences of natural disasters, including wind, water, fire, earthquake, and multifocal events, such as those that occur during cyclones, hurricanes, tornadoes, earthquakes, tsunamis, and volcanic eruptions. Generate best- and worst-case scenarios to predict a measure of the potential severity of either a natural or a malicious event.

Site Survey and Analysis

This part of an SVA is specific to the physical facilities covered by the security and facility access policy. Up-to-date drawings of institutional features, vehicular and pedestrian traffic, site and terrain, and buildings are critical resources for this investigation. Conduct walking tours of specific buildings that use or store chemicals, as well as the entire institution. Document these inspections with photographs or videos of specific conditions.

It is important to investigate all areas and all sides of a building enclosure's integrity with regard to weather and physical intrusion. Include in the inspection the roof and subsurface extensions, tunnels, utility routes, and entry points into buildings. Also analyze the locations of air intakes for mechanical and natural ventilation and the locations and conditions of storage elements for chemicals and other hazardous materials.

The site survey and analysis should include a vehicular traffic plan that highlights areas for material deliveries, truck routes, parking, and building entries and exits. The site analysis should address traffic patterns of vehicles and pedestrians over 24-hour periods on normal workdays and weekends; physical protection and security features; building uses; and people that are allowed access. Such a comprehensive review is necessary to permit an accurate survey of physical vulnerability. A site survey helps put into place the procedures for detection, delay, and assessment systems to protect physical assets and operations that could be interrupted or sabotaged.

Physical Vulnerability Survey

A physical vulnerability survey includes several kinds of investigation, within the limits of local legal frameworks. A survey includes the following components:

- Identifying potential targets and the access to those targets.
- Identifying and rating potential threat(s) based on historical context. For example, threats that have been carried out have more significance than threats without precedent. This pertains to both natural threats, such as the likelihood of flood, and malicious action.
- Identifying employees, students, contractors, vendors, and visitors who may have personal problems or conflicts with the institution and who may also be able to identify internal physical facility vulnerabilities and obtain access to facilities.

Consider various questions in a vulnerability survey.

- What potential targets are clearly recognizable with little or no knowledge?
- What potential facility targets store chemicals?
- What are the quantities, concentrations, and hazards of the chemicals that could be involved in each potential target?
- What is the potential for offsite release or illegal use of the chemicals?
- What physical protection measures are in place to reduce the harm that might result from a chemical release or spill?

Devise a matrix or other analytical tool to estimate the severity of the effects of each scenario in the threat analysis. The severity level will contribute to the overall risk analysis. For worst-case scenarios, estimate

- how many people would be affected;
- what the monetary loss of property would be;
- how much money and time would be needed to acquire replacement facilities;

- what the loss of productivity and the period of shutdown and recovery would be; and
- what value in public trust, support, and image would be lost.

Developing a Site Security Plan

A comprehensive site security plan integrates all the information gained in the analyses, surveys, and investigations mentioned above. It addresses workplace security guidelines and emergency response. A site security plan provides a physical protection strategy to detect, delay, and respond quickly and effectively to interrupt, prevent, or mitigate both threats of malicious intent and natural disasters. Methods in the public domain (such as Responsible Care, Cefic—European Chemical Industry Council, International Union of Pure and Applied Chemistry, and International Organization of Standardization) outline many approaches to developing a plan that meets the goals of the institution's security policy.

Institutions may consider applying concepts of crime prevention through environmental designs that are cost-effective, such as barrier shrubs and other plantings. Also consider systemic improvements that do not depend solely on technology, such as using additional security guards. The security and access control policy should be the basis of the site security plan.

F

F.1. Assessing Routes of Exposure for Toxic Chemicals

Inhalation

Toxic materials that enter the body through inhalation include gases, the vapors of volatile liquids, mists and sprays of both volatile and nonvolatile liquid substances, and solid chemicals in the form of particles, fibers, and dusts. Inhalation of toxic gases and vapors produces poisoning by absorption through the mucous membranes of the mouth, throat, and lungs and also seriously damages these tissues by local action. The lungs are the main organ for absorption of many toxic materials. Inhaled gases and vapors pass into the capillaries of the lungs and are carried into the circulatory system, where absorption is extremely rapid.

Listed below are factors that affect how an inhaled material is absorbed by the body.

- **Solubility:** Water-soluble gases or vapors dissolve predominantly in the lining of the nose, windpipe (trachea), and smaller tubes of the airways. Gases and vapors that are more fat soluble penetrate the airways down into the deep lung, where they can enter the blood and be carried to other organs.
- **Size:** The smallest particles of inhaled substances (nanometer to micrometer scale) are absorbed by the lungs and could be retained for long periods of time depending on their solubility.
- **Vapor pressure:** The higher the vapor pressure, the greater is the potential concentration of the chemical in the air. Even very low vapor

pressure chemicals are dangerous if the material is highly toxic (e.g., elemental mercury).

- **Temperature:** Heating solvents or reaction mixtures increases the potential for high airborne concentrations.
- **Evaporation rates:** Volatile chemicals evaporate very quickly because of their high vapor pressure, creating a significant exposure potential.
- **Density:** If a material has a very low density or a very small particle size, it tends to remain airborne for a considerable time.
- **Aerosol generation (suspensions of microscopic droplets in air):** Operations such as vigorous boiling, high-speed blending, or bubbling gas through a liquid increase the potential for exposure through inhalation.

Contact with Skin or Eyes

Chemical contact with the skin is a frequent mode of injury in the laboratory. Many chemicals can cause skin irritation, allergic skin reactions, severe burns, local toxic effects, or even systemic toxicity. Absorption of chemicals through the skin depends on

- chemical concentration;
- chemical reactivity;
- solubility of the chemical in fat and water;
- the thickness of the skin (toxicants cross membranes and thin skin more easily than thick skin);
- damage to the skin (burns, skin diseases, and dehydration increase penetration);
- the part of the body exposed;
- the duration of contact; and
- contact with other chemicals that increase skin permeability.

Chemical contact with the eyes is of particular concern because the eyes are sensitive to irritants. Because the eyes contain many blood vessels, they also are a route for the rapid absorption of many chemicals. Alkaline materials, phenols, and acids are particularly corrosive and can cause permanent loss of vision.

Ingestion

Many of the chemicals used in the laboratory are extremely hazardous if they enter the mouth or are swallowed. Absorption of toxicants in the gastrointestinal tract depends on many factors, including the physical properties of the chemical, the speed at which it dissolves, the size of the body surface area, permeability, and residence time in various segments of the tract. More chemical will be absorbed if the chemical remains in the intestine for a long time. If a chemical is in a relatively insoluble solid form, its rate of absorption will be low. If it is an organic acid or base, it will be absorbed in that part of the gastrointestinal tract where it is most fat soluble. Fat-soluble chemicals are absorbed more rapidly and extensively than water-soluble chemicals.

Injection

Exposure to toxic chemicals by injection occurs inadvertently through mechanical injury from sharp objects such as glass or metal contaminated with chemicals or syringes used for handling chemicals. The intravenous route of administration is especially dangerous because it introduces the toxicant directly into the bloodstream, bypassing the process of absorption. Sharp objects should be placed in special trash containers and not ordinary scrap baskets. If possible, have syringe needles with blunt ends for laboratory use. Protective gloves may also need to be worn when handling sharp or breakable objects.

F.2. Assessing Risks Associated with Acute Toxicants

In assessing the risks associated with acute toxicants, classify a substance according to the acute toxicity hazard level as shown in Table F.1. Table F.2. lists the probable lethal doses for humans as related to animal LD_{50} values. The doses in Table F.2. are expressed as milligrams or grams per kilogram of body weight for a 70-kg person. Give special attention to any substance classified according to these criteria as having a high level of acute toxicity hazard.

TABLE F.1 Acute Toxicity Hazard Level

Hazard Level	Toxicity Rating	Oral LD_{50} (rats, per kg)	Skin Contact LD_{50} (rabbits, per kg)	Inhalation LC_{50} (rats, ppm for 1 h)	Inhalation LC_{50} (rats, mg/m^3 for 1 h)
High	Highly toxic	<50 mg	<200 mg	<200	<2,000
Medium	Moderately toxic	50 to 500 mg	200 mg to 1 g	200 to 2,000	2,000 to 20,000
Low	Slightly toxic	500 mg to 5 g	1 to 5 g	2,000 to 20,000	20,000 to 200,000

TABLE F.2 Probable Lethal Dose for Humans

Toxicity Rating	Animal LD_{50} (per kg)	Lethal Dose When Ingested by 70-kg (150-pound) Human
Extremely toxic	<5 mg	A taste (<7 drops)
Highly toxic	5 to 50 mg	Between 7 drops and 1 tsp
Moderately toxic	50 to 500 mg	Between 1 tsp and 1 oz
Slightly toxic	500 mg to 5 g	Between 1 oz and 1 pint
Practically nontoxic	>5 g	>1 pint

SOURCE: Modified, by permission, from Gosselin, R.E, R. P. Smith, and H. C. Hodge., *Clinical Toxicology of Commercial Products,* Reprinted by permission from Williams and Wilkins, Baltimore, Maryland. Copyright 1984.

Because the greatest risk of exposure to many laboratory chemicals is by inhalation, trained laboratory personnel must understand the use of exposure limits listed on Material Safety Data sheets (MSDSs) and International Chemical Safety Cards (ICSCs).

The threshold limit value (TLV), assigned by the American Conference of Governmental Industrial Hygienists (ACGIH), defines the concentration of a chemical in air to which nearly all people can be exposed without adverse effects. These limits are recommended by the scientific community and are not legal standards. They are designed to be an aid to industrial hygienists. The TLV time-weighted average (TWA) refers to the concentration that is safe for exposure during an entire 8-hour workday. The TLV short-term exposure limit (TLV-STEL) is a higher concentration to which workers may be exposed safely for a 15-minute period up to four times during an 8-hour shift, with at least 60 minutes between these periods.

TLV values allow the trained laboratory personnel to quickly determine the relative inhalation hazards of chemicals. In general, substances with TLVs of less than 50 ppm should be handled in a fume hood. Comparison of these values to the odor threshold for a given substance will often indicate whether the odor of the chemical provides sufficient warning of possible hazard. However, individual differences in ability to detect some odors, as well as anosmia ("olfactory fatigue") for ethylene oxide or hydrogen sulfide, can limit the usefulness of odors as warning signs of overexposure. Laboratory Chemical Safety Summaries (LCSSs) are a good source of information on odor threshold ranges and whether a substance is known to cause olfactory fatigue.

F.3. Flash Points, Boiling Points, Ignition Temperatures, and Flammable Limits of Some Common Laboratory Chemicals

	Flash Point (°C)	Boiling Point (°C)	Ignition Temperature (°C)	Flammable Limits (percent by volume)	
				Lower	Upper
Acetaldehyde	–39	21	175	4	60
Acetic acid (glacial)	39	118	463	4	19.9
Acetone	–20	56	465	2.5	12.8
Acetonitrile	6	82	524	3	16
Carbon disulfide	–30	46	90	1.3	50
Cyclohexane	–20	82	245	1.3	8
Diethylamine	–23	57	312	1.8	10.1
Diethyl ether	–45	35	180	1.9	36
Dimethyl sulfoxide	95	189	215	2.6	42
Ethyl alcohol	13	78	363	3.3	19
Heptane	–4	98	204	1.05	6.7
Hexane	–22	69	225	1.1	7.5
Hydrogen		–252	500	4	75
Isopropyl alcohol	12	83	399	2	12.7 @ 200 (93)
Methyl alcohol	11	64	464	6	36
Methyl ethyl ketone	–9	80	404	1.4 @ 200 (93)	11.4 @ 200 (93)
Pentane	<–49	36	260	1.5	7.8
Styrene	31	146	490	0.9	6.8
Tetrahydrofuran	–14	66	321	2	11.8
Toluene	4	111	480	1.1	7.1
p-Xylene	25	138	528	1.1	7

SOURCE: Adapted from U.S. National Fire Protection Association. 2002. *Fire Protection Guide to Hazardous Materials,* 13th edition, pp. 325-9 to 325-117. Also see International Chemical Safety Cards at *http://www.inchem.org/pages/icsc.html*.

F.4. Chemicals That Can Form Peroxides

Class A: Chemicals that form explosive levels of peroxides without concentration

Isopropyl ether
Butadiene
Chlorobutadiene (chloroprene)
Potassium amide
Potassium metal
Sodium amide (sodamide)
Tetrafluoroethylene
Divinyl acetylene
Vinylidene chloride

Class B: Chemicals that are a peroxide hazard on concentration through distillation or evaporation (perform a test for peroxide if concentration is intended or suspected[a])

Acetal
Cumene
Cyclohexene
Cyclooctene
Cyclopentene
Diacetylene
Dicyclopentadiene
Diethylene glycol dimethyl ether (diglyme)
Diethyl ether
Dioxane (*p*-dioxane)
Ethylene glycol dimethyl ether (glyme)
Furan
Methyl acetylene
Methyl cyclopentane
Methyl isobutyl ketone
Tetrahydrofuran
Tetrahydronaphthalene
Vinyl ethers

Class C: Unsaturated monomers that may autopolymerize as a result of peroxide accumulation if inhibitors have been removed or are depleted[a]

Acrylic acid
Butadiene
Chlorotrifluoroethylene
Ethyl acrylate
Methyl methacrylate
Styrene
Vinyl acetate
Vinyl chloride
Vinyl pyridine

[a] These lists are illustrative, not comprehensive.

SOURCE: Jackson, H. L. et al. *1970. Journal of Chemical Education* , 47: A175; Kelly, R. J. 1996*. Chemical Health and Safety*, 3: 28.

Class A compounds are especially dangerous when peroxidized and should not be stored for long periods in the laboratory. Discard them within three months of receipt. Keep inventories of Class B and C materials to a minimum and manage them on a first in, first out basis. Store Class B and C materials in dark locations. If they are stored in glass bottles, use amber glass. Mark containers with their opening date and inspect them every six months thereafter.

Class B materials are often sold with auto-oxidation inhibitors. If the inhibitor is removed from a chemical or there is no inhibitor, take particular care in the chemical's long-term storage due to the greater likelihood of peroxide formation. Purge the container headspace with nitrogen. Several procedures, including test strips, are available to check Class B materials for peroxide contamination. No special disposal precautions are required for peroxide-contaminated Class B materials.

In most cases, commercial samples of Class C materials come with polymerization inhibitors that **require** the presence of oxygen to function and, therefore, should not be stored in an inert atmosphere. Keep inhibitor-free samples of Class C compounds (i.e., the compound has been synthesized in the laboratory or the inhibitor has been removed from the commercial sample) in the smallest quantities required and in an inert atmosphere. Dispose of unused material immediately, or if long-term storage is necessary, add an appropriate inhibitor.

Types of Compounds Known to Auto-oxidize to Form Peroxides

The chemicals described above represent only those materials that form peroxides in the absence of such contaminants or otherwise atypical circumstances.

- Ethers containing primary and secondary alkyl groups (never distill an ether before it has been shown to be free of peroxide)
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=C-CH)
- Compounds containing a tertiary C-H group (e.g., decalin and 2,5-dimethylhexane)
- Compounds containing conjugated, polyunsaturated alkenes and alkynes (e.g., 1,3-butadiene, vinyl acetylene)
- Compounds containing secondary or tertiary C-H groups adjacent to an amide (e.g., 1-methyl-2-pyrrolidinone)

F.5. Specific Chemical Hazards of Select Gases

Laboratory personnel should consult LCSSs and MSDSs for specific gases. Below is a list of certain hazardous substances that may come as compressed gases.

- ***Boron trifluoride and boron trichloride*** (BF_3 and BCl_3, respectively) react with water to give hydrofluoric acid (HF) and hydrochloric acid (HCl), respectively. Their fumes are corrosive, toxic, and irritating to the eyes and mucous membranes.
- ***Chlorine trifluoride*** (ClF_3) in liquid form is corrosive and very toxic. It is a potential source of explosion and causes deep, penetrating burns on contact with the body. The effect may be delayed and progressive, as in the case of burns caused by hydrogen fluoride. Chlorine trifluoride reacts vigorously with water and most oxidizable substances at room temperature, frequently with immediate ignition. It reacts with most metals and metal oxides at elevated temperatures. In addition, it reacts with silicon-containing compounds and thus can support the continued combustion of glass, asbestos, and other such materials. Chlorine trifluoride forms explosive mixtures with water vapor, ammonia, hydrogen, and most organic vapors. The substance resembles elemental fluorine in many of its chemical properties and handling procedures, which include precautionary steps to prevent accidents.
- ***Hydrogen selenide*** (H_2Se) is a colorless gas with an offensive odor. It is a dangerous fire and explosion risk and reacts violently with oxidizing materials. It may flow to ignition sources. Hydrogen selenide is an irritant to eyes, mucous membranes, and the pulmonary system. Acute exposures can cause symptoms such as pulmonary edema, severe bronchitis, and bronchial pneumonia. Symptoms also include gastrointestinal distress, dizziness, increased fatigue, and a metallic taste in the mouth.
- **Hydrogen sulfide** (H_2S) is a highly toxic and flammable gas. Although it has a characteristic odor of rotten eggs, it fatigues the sense of smell. This could result in failure to notice the seriousness of the situation before health becomes at risk and is problematic for rescuers who think danger has passed when the odor disappears.
- ***Methyl chloride*** (CH_3Cl) has a slight, not unpleasant, odor that is not irritating and may pass unnoticed unless a warning agent has been added. Exposure to excessive concentrations is indicated by symptoms similar to those of alcohol intoxication: drowsiness, mental confusion,

nausea, and possibly vomiting. Methyl chloride may, under certain conditions, react with aluminum or magnesium to form materials that ignite or fume spontaneously with air. Avoid contact with these metals.

- ***Phosphine*** (PH_3) is a spontaneously flammable and explosive, poisonous, colorless gas with the foul odor of decaying fish. The liquid can cause frostbite. Phosphine is a dangerous fire hazard and ignites in the presence of air and oxidizers. It reacts with water, acids, and halogens. If heated, it forms hydrogen phosphides, which are explosive and toxic. There may be a delay between exposure and the appearance of symptoms.
- ***Silane*** (SiH_4) is a pyrophoric colorless gas that ignites spontaneously in air. It is incompatible with water, bases, oxidizers, and halogens. The gas has a choking, repulsive odor.
- ***Silyl halides*** are toxic colorless gases with a pungent odor. They are corrosive irritants to the skin, eyes, and mucous membranes. When silyl halides are heated, they may emit toxic fumes.

G

G.1. Setting Up an Inventory

Each record in a chemical inventory database generally corresponds to a single container of a chemical rather than merely to the chemical itself. The inventory should contain the following data fields for each item:

- Name as printed on the container
- Molecular formula
- Chemical Abstracts Service (CAS) registry number, for unambiguous identification
- Source
- Size of the container or original quantity of the chemical

In addition, the following information may be useful:

- Hazard classification, as a guide to safe storage, handling, and disposal
- Date of acquisition, to avoid storage beyond useful life
- Storage location
- Onsite owner or staff member responsible for the sample

If possible, use a computer-based inventory system, especially for more than a few hundred chemicals. A simple and low-cost alternative to a computerized system is an inventory on index cards kept in an accessible location.

Barcode labeling of chemical containers as they are received provides a means of rapid error-free entry of information for a chemical tracking system.

Proprietary software packages for tracking chemicals are available. Institutions may even want to track the quantity of material in each container. The investment in hardware, software, and personnel to set up and maintain a chemical inventory system is costly but pays greatly in terms of economical, safe, and secure management of chemicals.

Maintaining an Inventory

Inventories are valuable to laboratory operations if everyone supports and contributes to them. To make sure that an inventory is well managed and useful, take these actions.

- Enter every laboratory chemical into the inventory.
- Keep the inventory current. Designate one or more people who maintain the inventory and enter new materials into the system. These people are the only personnel who should have write or edit access to the inventory.
- Audit inventories and tracking systems periodically to remove any inaccurate data. Every year, make a physical inventory of chemicals stored, verify the data on each item, and reconcile any differences. At the same time, identify unneeded, outdated, or deteriorated chemicals and arrange for their disposal.
- Make sure that empty containers are removed from the active inventory.

Removing Unwanted Inventory

- Consider disposing of materials that are not expected to be used within a reasonable period, such as two years. For stable, relatively nonhazardous substances with indefinite shelf lives, a decision to retain them in storage should take into account their economic value, availability, and storage costs.
- Make sure to look for deteriorating containers or containers in which evidence of a chemical change in the contents is apparent. These containers should be inspected and handled by someone experienced in the possible hazards of such situations.
- Dispose of or recycle chemicals before the expiration date on the container.

- Replace deteriorating labels before information is obscured or lost.
- Aggressively remove odoriferous substances from storage and inventory.
- Aggressively reduce the inventory of chemicals that require storage at reduced temperature in environmental rooms or refrigerators. Because these chemicals may include air- and moisture-sensitive materials, they are especially prone to problems from condensation.
- Dispose of all hazardous chemicals associated with laboratory personnel who have ended tenure or transferred to another laboratory. The institution should set up a cleanup policy for departing laboratory researchers and students and should enforce the policy strictly to avoid abandoned unknown chemicals that may pose hazards to others.
- Develop and enforce procedures for transfer or disposal of chemicals and other materials when decommissioning laboratories because of renovation or relocation.
- Try to avoid receiving entire chemical inventories from decommissioned laboratories and do not donate entire chemical inventories to schools or small businesses.

G.2. Examples of Compatible Storage Groups

A : COMPATIBLE ORGANIC BASES

Diethylamine
Piperidine
Triethanolamine
Benzylamine
Benzyltrimethylammonium hydroxide

B: COMPATIBLE PYROPHORIC AND WATER-REACTIVE MATERIALS

Sodium borohydride
Benzoyl chloride
Zinc dust
Alkyllithium solutions such as methyllithium in tetrahyfrofuran
Methanesulfonyl chloride
Lithium aluminum hydride

C: COMPATIBLE INORGANIC BASES

Sodium hydroxide
Ammonium hydroxide
Lithium hydroxide
Cesium hydroxide

D: COMPATIBLE ORGANIC ACIDS

Acetic acid
Citric acid
Maleic acid
Propionic acid
Benzoic acid

E: COMPATIBLE OXIDIZERS INCLUDING PEROXIDES

Nitric acid
Perchloric acid
Sodium hypochlorite
Hydrogen peroxide
3-Chloroperoxybenzoic acid

F: COMPATIBLE INORGANIC ACIDS NOT INCLUDING OXIDIZERS OR COMBUSTIBLES

Hydrochloric acid
Sulfuric acid
Phosphoric acid
Hydrogen fluoride solution

J: POISON COMPRESSED GASES

Sulfur dioxide
Hexafluoropropylene

K: COMPATIBLE EXPLOSIVES OR OTHER HIGHLY UNSTABLE MATERIALS

Picric acid, dry (<10% H_2O)
Nitroguanidine
Tetrazole
Urea nitrate

L: NONREACTIVE FLAMMABLES AND COMBUSTIBLES, INCLUDING SOLVENTS

Benzene
Methanol
Toluene
Tetrahydrofuran

X: INCOMPATIBLE WITH ALL OTHER STORAGE GROUPS

Picric acid, moist (10-40% H_2O)
Phosphorus
Benzyl azide
Sodium hydrogen sulfide

H

H.1. Personal Protective, Safety, and Emergency Equipment

Protective Equipment and Apparel for Laboratory Personnel

Personal Clothing

- Clothing that leaves large areas of skin exposed is inappropriate in laboratories where hazardous chemicals are in use. Personal clothing should fully cover the body.
- Wear appropriate laboratory coats buttoned with the sleeves rolled down. Always wear protective apparel if there is a possibility that personal clothing could become contaminated or damaged with chemically hazardous material. Washable or disposable clothing worn for laboratory work with especially hazardous chemicals includes special laboratory coats and aprons, jumpsuits, special boots, shoe covers, and gauntlets, as well as splash suits. Protection from heat, moisture, cold, and/or radiation may be required in special situations. Disposable garments provide only limited protection from vapor or gas penetration.
- Laboratory coats should be fire-resistant. Cotton coats are inexpensive and do not burn readily, but they react rapidly with acids. Polyester coats are not appropriate for glassblowing or work with flammable materials. Plastic or rubber aprons can provide good protection from corrosive liquids but can be inappropriate in the event of a fire. Plastic aprons can also accumulate static electricity, so they should not be used around flammable solvents, explosives sensitive to electrostatic

discharge, or materials that can be ignited by static discharge. Laboratory coats or laboratory aprons made of special materials are available for high-risk activities.

- Leave laboratory coats in the laboratory to minimize the possibility of spreading chemicals to public, eating, or office areas. Clean coats regularly.
- Choose protective apparel that is resistant to physical, chemical, and thermal hazards and is easy to move in, clean, or discard.
- Disposable garments that have been used when handling carcinogenic or other highly hazardous material should be removed without exposing anyone to toxic materials. They should be disposed of as hazardous waste.
- Unrestrained long hair and loose clothing, such as neckties, baggy pants, and coats, are inappropriate in a laboratory where hazardous chemicals are in use. Such items can catch fire, dip in chemicals, and get caught in equipment.
- Do not wear rings, bracelets, watches, or other jewelry that could be damaged, trap chemicals close to the skin, come in contact with electrical sources, or get caught in machinery.
- Do not wear leather clothing or accessories in situations where chemicals could be absorbed into the leather and held close to the skin.

Foot Protection

Not all types of footwear are appropriate in a laboratory where both chemical and mechanical hazards may exist. Wear substantial shoes in areas where hazardous chemicals are in use or mechanical work is being done. Clogs, perforated shoes, sandals, and cloth shoes do not provide protection against spilled chemicals. In many cases, safety shoes are best. Wear steel toes when working with heavy objects such as gas cylinders. Shoe covers may be required for work with especially hazardous materials. Shoes with conductive soles are useful to prevent buildup of static charge, and insulated soles can protect against electrical shock.

Eye and Face Protection

- Always wear safety glasses with side shields for work in laboratories and in particular with hazardous chemicals. Ordinary prescription glasses with hardened lenses do not serve as safety glasses. Contact lenses may be worn safely with appropriate eye and face protection (see, however, Chapter 9, Section 3.2.2.).

- Wear chemical splash goggles, which have splash-proof sides to fully protect the eyes, if there is a splash hazard in any operation involving hazardous chemicals.
- Wear impact protection goggles if there is a danger of flying particles.
- Wear full-face shields with safety glasses and side shields for complete face and throat protection. When there is a possibility of liquid splashes, wear both a face shield and chemical splash goggles. This is especially important for work with highly corrosive liquids. Use full-face shields with throat protection and safety glasses with side shields when handling explosive or highly hazardous chemicals.
- If work in the laboratory could involve exposure to lasers, ultraviolet light, infrared light, or intense visible light, wear specialized eye protection.
- Provide requisite eye protection for visitors. Post a sign in the laboratory that indicates that eye protection is required in laboratories where hazardous chemicals are in use.

Safety and Emergency Equipment

Safety equipment—including spill control kits, safety shields, fire safety equipment, respirators, safety showers and eyewash units, and emergency equipment—should be available in well-marked, highly visible locations in all chemical laboratories. Fire alarm pull stations and telephones with emergency contact numbers must be readily accessible. There may be a need for other safety devices in addition to the standard items. The laboratory supervisor is responsible for making sure that everyone is properly trained and provided with the necessary safety equipment.

Safety Shields

Use safety shields for protection against possible explosions or splash hazards. Shield laboratory equipment on all sides so that there is no line-of-sight exposure of personnel. The front sashes of chemical hoods can provide shielding. However, use a portable shield when performing manipulations, particularly with hoods that have sashes that open vertically rather than horizontally.

Portable shields can protect against hazards of limited severity, such as small splashes, heat, and fires. A portable shield, however, provides no protection at the sides or back of the equipment. In addition, many portable shields are not sufficiently weighted for forward protection and may topple toward the worker when there is a blast. A fixed shield that completely surrounds the experimental apparatus can afford protection against minor blast damage. Polymethyl methacrylate, polycarbonate, polyvinyl chloride, and laminated safety plate glass are all satisfactory transparent shielding materials. Where combustion is possible, the shielding material should be nonflammable or slow burning. Laminated safety plate glass may be the best material for such circumstances, if it can withstand the working blast pressure. Polymethyl methacrylate offers an excellent overall combination of shielding characteristics when considering cost, transparency, high tensile strength, resistance to bending loads, impact strength, shatter resistance, and burning rate.

Polycarbonate is much stronger and self-extinguishing after ignition but is readily attacked by organic solvents.

Fire Safety Equipment

Fire Extinguishers

All chemical laboratories should have carbon dioxide and dry chemical fire extinguishers. Provide other types of extinguishers depending on the work performed in the laboratory. Listed below are the four most common types of extinguishers and the type of fire for which they are suitable. Multipurpose extinguishers may also be available.

1. ***Water extinguishers*** are effective against burning paper and trash. Do not use these for extinguishing electrical, liquid, or metal fires.
2. ***Carbon dioxide extinguishers*** are effective against burning liquids, such as hydrocarbons or paint, and electrical fires. They are recommended for fires involving computer equipment, delicate instruments, and optical systems because they do not damage such equipment. They are less effective against paper and trash fires and *must not be used* against metal hydride or metal fires. Care must be taken in using these extinguishers, because the force of the compressed gas can spread burning combustibles, such as papers, and can tip over containers of flammable liquids.
3. ***Dry powder extinguishers***, which contain ammonium phosphate or sodium bicarbonate, are effective against burning liquids and electrical fires. They are less effective against paper and trash or metal fires. They are not recommended for fires involving delicate instruments or optical systems because of the cleanup problem. Computer equipment may need to be replaced if exposed to sufficient amounts of the dry powders. These extinguishers are generally used where large quantities of solvent may be present.

4. ***Met-L-X extinguishers*** and others that have special granular formulations are effective against burning metal. Included in this category are fires involving magnesium, lithium, sodium, and potassium; alloys of reactive metals; and metal hydrides, metal alkyls, and other organometallics. These extinguishers are less effective against paper and trash, liquid, or electrical fires.

Every extinguisher should carry a label showing the types of fires it fights and its last inspection date. There are a number of other, more specialized types of extinguishers that are available for unusual fire hazard situations. Each trained laboratory person should be responsible for knowing the location, operation, and limitations of the fire extinguishers in the work area. It is the responsibility of the laboratory supervisor to make sure that all personnel are aware of the locations of fire extinguishers and are trained in their use. Designated personnel should promptly recharge or replace an extinguisher that has been used.

Heat and Smoke Detectors

Heat sensors and/or smoke detectors may be part of the building safety equipment. They may automatically sound an alarm and call the fire department; they may trigger an automatic extinguishing system; or they may only serve as a local alarm. Because laboratory operations may generate heat or vapors, carefully evaluate the type and location of the detectors in order to avoid frequent false alarms.

Respirators

Each respirator in the laboratory should have written information available that shows the equipment's limitations, fitting methods, and inspection and cleaning procedures. People who use respirators in their work must be thoroughly trained in the fit testing, use, limitations, and care of such equipment. Training should take place before initial use and annually thereafter and should include demonstrations and practice in wearing, adjusting, and properly fitting the equipment.

Users should inspect respirators before each use, and the laboratory supervisor should inspect them periodically. Self-contained breathing apparatus should be inspected at least once a month and cleaned after each use.

Safety Showers and Eyewash Units

Safety Showers

Make safety showers available in areas where chemicals are handled. They should be used for immediate first aid treatment of chemical splashes and for extinguishing clothing fires. Every person working in the laboratory should know where the safety showers are located and should learn how to use them. Test safety showers routinely to make sure their valves are operable and remove any debris in the system.

Make sure each shower is capable of drenching subjects immediately and is large enough to accommodate more than one person if necessary. Each shower should have a quick-opening valve requiring manual closing. A downward-pull delta bar is satisfactory if it is long enough, but chain pulls are not advisable because they can hit the user and be difficult to grasp in an emergency. Install drains under safety showers to reduce the slip and fall risks and facility damage that is associated with flooding in a laboratory.

Eyewash Units

Install eyewash units if laboratory substances present an eye hazard or if workers may encounter unknown eye hazards. An eyewash unit should provide a soft stream or spray of aerated water for an extended period (15 minutes). Locate these units close to the safety showers so that, if necessary, the eyes can be washed while the body is showered.

H.2. Materials Requiring Special Attention Due to Reactivity, Explosivity, or Chemical Incompatibility

The following list is not all-inclusive. Seek further guidance on reactive and explosive materials from pertinent sections of this book and other sources of information.

- **Acetylenic compounds** can be explosive in mixtures of 2.5 to 80% with air. At pressures of 2 or more atmospheres, acetylene (C_2H_2) subjected to an electrical discharge or high temperature decomposes with explosive violence. Dry acetylides detonate on receiving the slightest shock. Acetylene must be handled in acetone solution and never stored alone in a cylinder.
- **Alkyllithium compounds** are highly reactive. Violent reactions may occur on exposure to water, carbon dioxide, and other materials. Alkyllithium compounds are highly corrosive to the skin and eyes. *tert*-Butyllithium solutions are the most pyrophoric and may ignite spontaneously on exposure to air. Concentrated solutions of *n*-butyllithium (50-80%) are the most dangerous and immediately ignite on exposure to air. Contact with water or moist materials can lead to fires and explosions. Store these compounds and handle them in an inert atmosphere in areas that are free from ignition sources. For more detailed information about handling of organolithium compounds, see Schwindeman, J.A., C.J. Wolterman, and R.J. Letchford. 2002. *Chem. Health & Safety*, May/June issue, 6-11.
- **Aluminum chloride ($AlCl_3$)** is a potentially dangerous material. If moisture is present, sufficient decomposition may form hydrogen chloride (HCl) and build up considerable pressure. When opening a bottle after long storage, completely enclose it first in a heavy towel.
- **Ammonia (NH_3)** reacts with iodine to give nitrogen triiodide, which detonates on touch. Ammonia reacts with hypochlorites to give chlorine. Mixtures of ammonia and organic halides sometimes react violently when heated under pressure. Ammonia is combustible. Inhalation of concentrated fumes can be fatal.
- **Azides**, both organic and inorganic, and some azo compounds can be heat and shock sensitive. Azides such as sodium azide can displace halide from chlorinated hydrocarbons such as dichloromethane to form highly explosive organic polyazides. This substitution reaction is facilitated in solvents such as dimethyl sulfoxide (DMSO).

- **Boron halides** are powerful Lewis acids and hydrolyze to strong protonic acids.
- *tert*-**Butyllithium**: See alkyllithium compounds.
- **Carbon disulfide (CS_2)** is both very toxic and very flammable. Mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or a light bulb.
- **Chlorine (Cl_2)** is toxic and may react violently with hydrogen (H_2) or with hydrocarbons when exposed to sunlight.
- **Chromium trioxide-pyridine complex ($CrO_3 \cdot C_5H_5N$)** may explode if the CrO_3 concentration is too high. The complex should be prepared by addition of CrO_3 to excess C_5H_5N.
- **Diazomethane (CH_2N_2)** and related diazo compounds should be treated with extreme caution. They are very toxic, and the pure gases and liquids explode readily even from contact with sharp edges of glass. Solutions in ether are safer from this standpoint. An ether solution of diazomethane is rendered harmless by drop-wise addition of acetic acid.
- **Diethyl and other ethers**, including tetrahydrofuran, 1,4-dioxane, and particularly the branched-chain type of ethers, sometimes explode during distillation due to the concentration of peroxides that have developed from air oxidation. Use ferrous salts or sodium bisulfite to decompose these peroxides. Passage over basic active alumina can remove most of the peroxidic material. In general, however, dispose of old samples of ethers if they give a positive test for peroxide.
- **Diisopropyl ether** is a notoriously dangerous peroxide former. The peroxide crystallizes as it is being formed. There are numerous reports of old bottles of diisopropyl ether being found with large masses of crystals settled at the bottom of the bottle. These crystals are extremely shock sensitive, even while wetted with the diisopropyl ether supernatant. Mild shock (e.g., bottle breakage, removing the bottle cap) is sufficient to result in detonation. Do not store this ether in the laboratory. Purchase only the amount required for a particular experiment or process. Dispose of any leftover material immediately.
- **Dimethyl sulfoxide (DMSO), $(CH_3)_2SO$,** decomposes violently on contact with a wide variety of active halogen compounds, such as acyl chlorides. Explosions from contact with active metal hydrides have been reported. Dimethyl sulfoxide does penetrate and carry dissolved substances through the skin membrane.

- **Dry benzoyl peroxide ($(C_6H_5CO_2)_2$)** ignites easily and is sensitive to shock. It decomposes spontaneously at temperatures greater than 50°C. It is reported to be desensitized by addition of 20% water.
- **Dry ice** should not be kept in a container that is not designed to withstand pressure. Containers of other substances stored over dry ice for extended periods generally absorb carbon dioxide (CO_2) unless they have been carefully sealed. When such containers are removed from storage and allowed to come rapidly to room temperature, the CO_2 may develop sufficient pressure to burst the container with explosive violence. On removal of such containers from storage, loosen the stopper or wrap the container itself in towels and keep it behind a shield. Dry ice can produce serious burns, as is also true for all types of dry ice cooling baths.
- **Drying agents**, such as Ascarite® (sodium hydroxide-coated silica), should not be mixed with phosphorus pentoxide (P_2O_5) because the mixture may explode if it is warmed with a trace of water. Because the cobalt salts used as moisture indicators in some drying agents may be extracted by some organic solvents, restrict the use of these drying agents to drying gases.
- **Dusts** that are suspensions of oxidizable particles (e.g., magnesium powder, zinc dust, carbon powder, flowers of sulfur) in the air can constitute powerful explosive mixtures. Use these materials with adequate ventilation and do not expose them to ignition sources. When finely divided, some solids, including zirconium, titanium, Raney nickel, lead (such as prepared by pyrolysis of lead tartrate), and catalysts (such as activated carbon containing active metals and hydrogen), can combust spontaneously if allowed to dry while exposed to air. They should be handled wet.
- **Ethylene oxide (C_2H_4O)** has been known to explode when heated in a closed vessel. Use suitable barricades when carrying out experiments using ethylene oxide under pressure.
- **Fluorine (F_2)** is an extremely toxic, reactive, oxidizing gas with extremely low permissible exposure levels. Authorize only trained personnel to work with fluorine. Anyone planning to work with fluorine must be knowledgeable of proper first aid treatment and have the necessary supplies on hand before beginning.
- **Halogenated compounds**, such as chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and other halogenated solvents, should not be dried with sodium, potassium, or other active metals. Violent explosions

usually result. Many halogenated compounds are toxic. Oxidized halogen compounds—chlorates, chlorites, bromates, and iodates—and the corresponding peroxy compounds may be explosive at high temperatures.

- **Hydrogen fluoride** and hydrogen fluoride generators are very dangerous. Anhydrous hydrofluoric acid (HF) or hydrogen fluoride is a colorless liquid that boils at 19.5°C. It has a pungent, irritating odor and a time-weighted average exposure of 3 ppm for routine work. Aqueous HF is a colorless, very corrosive liquid that fumes at concentrations greater than 48%. It attacks glass, concrete, and some metals, especially cast iron and alloys containing silica, as well as organic materials such as leather, natural rubber, wood, and human tissue. Although HF is nonflammable, its corrosive action on metals can result in the formation of hydrogen in containers and piping, creating a fire and explosion hazard. Store HF in tightly closed polyethylene containers. HF attacks glass and therefore should never be stored in a glass container. Containers of HF may be hazardous when empty since they retain product residues. HF and related materials (e.g., NaF, SF_4, acyl fluorides) capable of generating HF upon exposure to acids, water, or moisture are of major concern because of their potential for causing serious burns.

  HF causes severe injury via skin and eye contact, inhalation, and ingestion. It is very aggressive physiologically because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers and decalcification of bone. Unlike other acids, which are rapidly neutralized, this process may continue for days if left untreated. When exposed to air, concentrated solutions and anhydrous HF produce pungent fumes, which are especially dangerous. Skin contact with HF can cause serious, penetrating burns of the skin that may not be painful or visible for several hours. HF exposures require immediate and specialized first aid and medical treatment.

There are a number of ways to prevent HF exposure:

- ➢ Use HF only when necessary. Consider substitution of a less hazardous substance whenever possible.
- ➢ Draw up standard operating procedures for work with HF.
- ➢ Make sure all workers in a laboratory where HF is used are informed about the hazards and the first aid procedures involved.

  - ➢ Only use HF in a chemical hood.
  - ➢ Depending on the concentration used, workers should wear butyl rubber, neoprene, 4H, or Silvershield gloves. Also wear protective laboratory coats or aprons.
  - ➢ At a minimum, wear chemical splash goggles when working with HF. Also wear a face shield when there is a significant splash hazard.

  Train laboratory personnel in first aid procedures for HF exposure before they begin work. Keep calcium gluconate gel (2.5% w/w) readily accessible in work areas where any potential HF exposure exists. Check the expiration date of your supply of commercially obtained calcium gluconate gel, and reorder as needed to make sure there is a supply of fresh stock. Homemade calcium gluconate gel has a shelf life of approximately four months.

- **Hydrogen peroxide (H_2O_2)** stronger than 3% can be dangerous; in contact with skin, it causes severe burns. Thirty percent H_2O_2 may decompose violently if contaminated with iron, copper, chromium, or other metals or their salts. Stirring bars may inadvertently bring metal into a reaction and should be used with caution.
- **Liquid nitrogen-cooled traps** open to the atmosphere condense liquid air rapidly. When the coolant is removed, an explosive pressure buildup occurs, usually with enough force to shatter glass equipment if the system has been closed. Only sealed or evacuated equipment should be cooled in this way. Do not leave vacuum traps under a static vacuum. Remove liquid nitrogen in Dewar flasks from these traps when the vacuum pumps are turned off.
- **Lithium aluminum hydride ($LiAlH_4$)** should not be used to dry methyl ethers or tetrahydrofuran. Fires from reactions with damp ethers are often observed. The reaction of $LiAlH_4$ with carbon dioxide has reportedly generated explosive products. Do not use carbon dioxide or bicarbonate extinguishers for $LiAlH_4$ fires. Instead, smother such fires with sand or some other inert substance.
- **Nitrates, nitro, and nitroso compounds** may be explosive, especially if more than one nitro group is present. Alcohols and polyols form highly explosive nitrate esters (e.g., nitroglycerine) from reaction with nitric acid.
- **Organometallics** may be hazardous because some organometallic compounds burn vigorously on contact with air or moisture. For

example, solutions of *t*-butyllithium ignite some organic solvents on exposure to air. Get the pertinent information for a specific compound.

- **Oxygen tanks** should be handled with care because serious explosions have resulted from contact between oil and high-pressure oxygen. Do not use oil or grease on connections to an O_2 cylinder or a gas line carrying O_2.
- **Ozone (O_3)** is a highly reactive toxic gas. It is formed by the action of ultraviolet light on oxygen (air). Therefore, certain ultraviolet sources may require venting to the exhaust hood. Ozonides can be explosive.
- **Palladium (Pd) or platinum (Pt)** on carbon, platinum oxide, Raney nickel, and other catalysts presents the danger of explosion if additional catalyst is added to a flask in which an air-flammable vapor mixture or hydrogen is present. Avoid the use of flammable filter paper.
- **Perchlorates** should be avoided whenever possible. Perchlorate salts of organic, organometallic, and inorganic cations are potentially explosive and have been set off either by heating or by shock. Whenever possible, replace perchlorate with safer anions, such as fluoroborate, fluorophosphates, and triflate.

  Do not use perchlorates as drying agents if there is a possibility of contact with organic compounds or of proximity to a dehydrating acid strong enough to concentrate the perchloric acid ($HClO_4$) (e.g., in a drying train that has a bubble counter containing sulfuric acid). Use safer drying agents.

  Seventy percent $HClO_4$ boils safely at approximately 200°C, but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter, leads to serious explosions. Never allow oxidizable substances to contact $HClO_4$. This includes wooden bench tops or chemical hood enclosures, which may become highly flammable after absorbing $HClO_4$ liquid or vapors. Use beaker tongs, rather than rubber gloves, when handling fuming $HClO_4$.

  Carry out perchloric acid evaporations in a chemical hood that has a good draft. Wash the hood and ventilator ducts with water frequently to avoid the danger of spontaneous combustion or explosion if this acid is in common use. Special $HClO_4$ hoods are available from many manufacturers. Begin the disassembly of such chemical hoods by washing the ventilation system to remove deposited perchlorates.
- **Permanganates** are explosive when treated with sulfuric acid. If both compounds are used in an absorption train, place an empty trap between them and monitor for entrapment.

- **Peroxides (inorganic)** should be handled carefully. When mixed with combustible materials, barium, sodium, and potassium peroxides form explosives that ignite easily.
- **Phenol** is a corrosive and moderately toxic substance that affects the central nervous system and can cause damage to the liver and kidneys. It is readily absorbed through the skin and can cause severe burns to the skin and eyes. Phenol is irritating to the skin, but has a local anesthetic effect, so that no pain may be felt on initial contact. A whitening of the area of contact generally occurs, and severe burns may develop hours after exposure. Exposure to phenol vapor can cause severe irritation of the eyes, nose, throat, and respiratory tract. In the event of skin exposure to phenol, do not immediately rinse the site with water. Instead, treat the site with low molecular weight polyethylene glycol (PEG), such as PEG 300 or PEG 400. This will safely deactivate phenol. Irrigate the site with PEG for at least 15 minutes or until there is no detectable odor of phenol.
- **Phosphorus (P) (red and white)** forms explosive mixtures with oxidizing agents. Store white phosphorus under water because it ignites spontaneously in air. The reaction of phosphorus with aqueous hydroxides gives phosphine, which may either ignite spontaneously or explode in air.
- **Phosphorus trichloride (PCl_3)** reacts with water to form phosphorous acid with HCl evolution. The phosphorous acid decomposes on heating to form phosphine, which may either ignite spontaneously or explode. Take care in opening containers of PCl_3. Do not heat samples that have been exposed to moisture without adequate shielding to protect the operator.
- **Potassium (K)** is much more reactive than sodium. It ignites quickly on exposure to humid air. Therefore, handle it under the surface of a hydrocarbon solvent, such as mineral oil or toluene (see Sodium). Potassium can form a crust of the superoxide (KO_2) or the hydrated hydroxide ($KOH \cdot H_2O$) on contact with air. If this happens, the act of cutting a surface crust off the metal or of melting the encrusted metal can cause a severe explosion. This is due to oxidation of the organic oil or solvent by superoxide or the reaction of the potassium with water liberated from the hydrated hydroxide.
- **Residues from vacuum distillations** have been known to explode when the still was vented suddenly to the air before the residue was cool. To avoid such explosions, vent the still pot with nitrogen, cool it

before venting, or restore pressure slowly. Sudden venting may produce a shockwave that detonates sensitive materials.

- **Sodium (Na)** should be stored in a closed container under kerosene, toluene, or mineral oil. Destroy scraps of sodium or potassium by reaction with *n*-butyl alcohol. Avoid contact with water, because sodium reacts violently with water to form hydrogen (H_2) with evolution of sufficient heat to cause ignition. Do not use carbon dioxide, bicarbonate, and carbon tetrachloride fire extinguishers on alkali metal fires. Metals such as sodium become more reactive as the surface area of the particles increases. Use the largest particle size consistent with the task at hand. For example, use of sodium balls or cubes is preferable to use of sodium sand for drying solvents.
- **Sodium amide ($NaNH_2$)** can undergo oxidation on exposure to air to give sodium nitrite in a mixture that is unstable and may explode.
- **Sulfuric acid (H_2SO_4)** should be avoided, if possible, as a drying agent in desiccators. If it must be used, place glass beads in it to help prevent splashing when the desiccator is moved. To dilute H_2SO_4, add the acid slowly to cold water. Addition of water to the denser H_2SO_4 can cause localized surface boiling and spattering on the operator.
- **Trichloroethylene (Cl_2CCHCl)** reacts under a variety of conditions with potassium or sodium hydroxide to form dichloroacetylene. This substance ignites spontaneously in air and detonates readily even at dry ice temperatures. The compound itself is highly toxic; take suitable precautions when it is used.

I

I.1. Precautions for Working with Specific Equipment

Each piece of electrical equipment in a laboratory has its own safety considerations.

Water-Cooled Equipment

Use refrigerated recirculators for cooling laboratory equipment, because they conserve water and reduce the likelihood and impact of floods.

Vacuum Pumps

Avoid using water aspirators. Distillation or similar operations requiring a vacuum must employ a trapping device to protect the vacuum source, personnel, and the environment. Vent the output of each pump to a proper air exhaust system. Scrub or absorb the gases exiting the pump. Drain, replace, and properly dispose of the pump oil as it becomes contaminated. General-purpose laboratory vacuum pumps should have a record of use in order to prevent cross-contamination or reactive chemical incompatibility problems. Belt-driven mechanical pumps must have protective guards.

Refrigerators and Freezers

- ***Never use laboratory refrigerators and freezers to store food or beverages for human consumption.*** Laboratory refrigerators and freezers should have permanent labels warning against the storage of food and beverages.

- As a general precaution, place laboratory refrigerators against fire-resistant walls. Refrigerators should have heavy-duty power cords and be protected by their own circuit breakers.
- Enclose contents of a laboratory refrigerator in unbreakable secondary containment. At a minimum, use catch pans for secondary containment.
- Do not place potentially explosive or highly toxic substances in a laboratory refrigerator.
- Use explosion-proof refrigerators for the storage of flammable materials, rather than a modified, spark-proof refrigerator.
- Never place uncapped containers of chemicals in a refrigerator. Caps should provide a vapor-tight seal to prevent a spill if the container is tipped over. Do not use aluminum foil, corks, corks wrapped with aluminum foil, and glass stoppers to cap containers of chemicals in a refrigerator. The most satisfactory temporary seals are screw-caps lined with either a conical polyethylene insert or a Teflon insert. The best containers for samples that are to be stored for longer periods of time are sealed, nitrogen-filled glass ampoules.
- Carefully label all samples placed in refrigerators and freezers with both the contents and the owner's name. Do not use water-soluble ink. Labels should be waterproof or covered with transparent tape. Storing samples with due consideration of chemical compatibility is important in these often small, crowded spaces.

Stirring and Mixing Devices

The stirring and mixing devices commonly found in laboratories include stirring motors, magnetic stirrers, shakers, small pumps for fluids, and rotary evaporators for solvent removal. These devices are typically used in chemical hoods. It is important that they be operated in a way that reduces the generation of electrical sparks. Use only spark-free induction motors in power stirring and mixing devices or any other rotating equipment used for laboratory operations.

Make sure that in the event of an emergency, stirring and mixing devices can be turned on or off from a location outside the hood. Heating baths associated with these devices (e.g., baths for rotary evaporators) should also be spark-free and controllable from outside the hood.

Heating Devices

Perhaps the most common types of electrical equipment found in a laboratory are the devices used to supply heat to effect a reaction or separation. These include ovens, hot plates, heating mantles and tapes, oil baths, salt baths, sand baths, air baths, hot-tube furnaces, hot-air guns, and microwave ovens. Use steam-heated devices rather than electrically heated devices whenever temperatures of 100°C or less are required. Steam-heated devices can be left unattended with assurance that their temperature will never exceed 100°C, because they do not present shock or spark risks.

A number of general precautions need to be taken when working with heating devices in the laboratory. The heating element in any heating device should be enclosed in a glass, ceramic, or insulated metal case that prevents workers or any metallic conductor from accidentally touching the wire carrying the electric current. Do not use most household appliances (e.g., hot plates, space heaters) in a laboratory because they do not meet this criterion. If any heating device becomes so worn or damaged that its heating element is exposed, discard or repair the device to correct the damage before it is used again. Resistance devices used to heat oil baths should not contain bare wires.

The external cases of all variable autotransformers have perforations for cooling and ventilation, and some sparking may occur whenever the voltage adjustment knob is turned. Therefore, locate these devices where water and other chemicals cannot be spilled onto them and where their movable contacts will not be exposed to flammable liquids or vapors. Mount variable autotransformers on walls or vertical panels and outside of hoods. Do not place them simply on laboratory bench tops.

When using an electrical heating device, use either a temperature controller or a temperature-sensing device that will turn off the electric power if the temperature of the heating device exceeds some preset limit. It is absolutely essential that temperature-sensing devices be securely clamped or firmly fixed in place so that the device maintains contact with the object or medium being heated at all times. If the temperature sensor for the controller is not properly located or has fallen out of place, the controller will continue to supply power until the sensor reaches the temperature setting. This can create extremely hazardous situations.

Hot plates, oil baths and heating mantles that can melt and combust plastic materials (e.g., vials, containers, tubing) can cause laboratory fires. Remove hazards from the area around the equipment prior to use. Be aware that dry and concentrated residues can ignite when overheated in stills, ovens, dryers, and other heating devices.

Ovens

Electrically heated ovens are commonly used in the laboratory to remove water or other solvents from chemical samples and to dry laboratory glassware. *Never use laboratory ovens to prepare food for human consumption.*

Laboratory ovens should have their heating elements and temperature controls physically separated from their interior atmospheres. Do not use ovens to dry any chemical sample that has even moderate volatility and might pose a hazard because of acute or chronic toxicity. If it is necessary to use ovens for this purpose, take special precautions to make sure there is continuous venting of the atmosphere inside the oven.

To avoid explosion, do not use an oven to dry glassware that has been rinsed with an organic solvent. First rinse the glassware again with distilled water. Potentially explosive mixtures may form from volatile substances and the air inside an oven.

Use bimetallic strip thermometers to monitor oven temperatures.

Hot Plates

Many workers use laboratory hot plates to heat solutions to 100°C or above or when safer steam baths cannot be used as the source of heat. Only use hot plates that have completely enclosed heating elements. Take care to distinguish the controls for the stirrer and the temperature on combined stirrer-hot plates. A fire or explosion may occur if the temperature rather than the stirrer speed is increased inadvertently.

Heating Mantles

Heating mantles are commonly used to heat round-bottomed flasks, reaction kettles, and related reaction vessels. These mantles enclose a heating element in layers of fiberglass cloth. As long as the fiberglass coating is not worn or broken, and as long as no water or other chemicals are spilled into the mantle, heating mantles pose minimal shock hazard. Always use heating mantles with a variable autotransformer to control the input voltage. Never plug them directly into an electrical outlet.

Oil, Salt, and Sand Baths

Electrically heated oil baths are often used to heat small or irregularly shaped vessels or to maintain a constant temperature with a stable heat source. Use a saturated paraffin oil for temperatures below 200°C. Use a silicone oil for temperatures up to

300°C. Take care with hot oil baths not to generate smoke or have the oil burst into flames from overheating. Always monitor an oil bath by using a thermometer or other thermal-sensing device to make sure that its temperature does not exceed the flash point of the oil being used.

Mix oil baths well to make sure there are no “hot spots” around the elements that result in unacceptable temperatures of the surrounding oil. Contain heated oil in either a metal pan or a heavy-walled porcelain dish. A Pyrex dish or beaker can break and spill hot oil if struck accidentally with a hard object.

Mount the oil bath carefully on a stable horizontal support, such as a laboratory jack that can be raised or lowered easily without danger of the bath tipping over. Always clamp equipment high enough above a hot plate or oil bath so that if the reaction begins to overheat, the heater can be lowered immediately and replaced with a cooling bath without having to readjust the clamps holding the equipment setup. Never support a bath on an iron ring because of the greater likelihood of accidentally tipping the bath over. Provide secondary containment in case of a spill of hot oil. Wear proper protective gloves when handling a hot bath.

Molten salt baths, like hot oil baths, offer the possible advantages of good heat transfer, a higher operating range (e.g., 200 to 425°C), and a high thermal stability (e.g., 540°C). The reaction container used in a molten salt bath must be able to withstand a very rapid heat-up to a temperature above the melting point of the salt. Take care to keep salt baths dry, because they are hygroscopic, a property that can cause hazardous popping and splattering if the absorbed water vaporizes during heat-up.

Heat Guns

Laboratory heat guns are constructed with a motor-driven fan that blows air over an electrically heated filament. They are frequently used to dry glassware or to heat the upper parts of a distillation apparatus during distillation of high-boiling materials. The heating element in a heat gun typically becomes red-hot during use and, necessarily, cannot be enclosed. Also, the on-off switches and fan motors are not usually spark-free. For these reasons, heat guns almost always pose a serious spark hazard. Never use them near open containers of flammable liquids, in environments where appreciable concentrations of flammable vapors may be present, or in chemical hoods used to remove flammable vapors.

Microwave Ovens

Microwave heating presents several potential hazards not commonly encountered with other heating methods. Extremely rapid temperature and pressure rise, liquid superheating, arcing, and microwave leakage are major concerns. Microwave ovens designed for the laboratory have built-in safety features and operation procedures to reduce or eliminate these hazards. Users of such equipment must be thoroughly knowledgeable of operation procedures and safety devices and protocols before beginning experiments, especially when there is a possibility of fire (with flammable solvents), overpressurization, or arcing (for more information see Foster, B. L.; Cournoyer, M. E. 2005. *Chemical Health & Safety* 12: 27). Below are some general precautions for using microwave ovens.

- Domestic microwave ovens are not appropriate for laboratory use. Use microwave ovens specifically designed for laboratory use that have industrial-grade instruments, explosion-proof chambers, exhaust lines, and temperature and pressure monitors.
- To avoid exposure to microwaves, never operate ovens with the doors open.
- Closely watch reactions conducted in a microwave oven, especially when combustible materials are in it. Conduct reactions on the smallest scale possible to determine the potential for explosions and fires. Take precautions for proper ventilation and potential explosion.
- Do not use metal containers or metal-containing objects (e.g., stir bars) in the microwave, because they can cause arcing.
- In general, do not heat sealed containers in a microwave oven, because of the danger of explosion.

Ultrasonicators

Human exposure to ultrasound with frequencies of between 16 and 100 kHz can be divided into three distinct categories: (1) airborne conduction, (2) direct contact through a liquid coupling medium, and (3) direct contact with a vibrating solid.

Exposure to ultrasound through airborne conduction does not appear to pose a significant health hazard to humans. However, exposure to the associated high volumes of audible sound can produce a variety of effects, including fatigue, headaches, nausea, and tinnitus. Ultrasonic equipment must be enclosed in a 2-cm-thick wooden box or in a box lined with acoustically absorbing foam or tiles to substantially reduce acoustic emissions (most of which are inaudible).

Avoid direct contact of the body with liquids or solids subjected to high-intensity ultrasound that promote chemical reactions. Under some chemical conditions, cavitation is created in liquids, and it can induce high-energy chemistry in liquids and tissues. Cell death from membrane disruption can occur even at relatively low acoustic intensities. Exposure to ultrasonically vibrating solids, such as an acoustic horn, can lead to rapid frictional heating and potentially severe burns.

Centrifuges

Properly install centrifuges, and allow only trained personnel to operate them. Centrifuges are designed for use with a certain rotor. Rotors are rated for a maximum speed and a load of specific weight. Avoid the risk of rotor failure. It is important to balance the load each time the centrifuge is used and to ensure that the lid is closed before starting the centrifuge. Do not overload a rotor beyond the rotor's maximum mass without reducing the rated rotor speed. The disconnect switch should automatically shut off the equipment when the top is opened. Follow the manufacturer's instructions for safe operating speeds. Do not run a rotor beyond its maximum rated speed. Inspect rotors routinely for signs of corrosion. Metal fatigue will eventually cause any rotor to fail. Be sure to follow the manufacturer's guidelines about when to retire a rotor. For flammable and/or hazardous materials, the centrifuge should be under negative pressure to a suitable exhaust system.

Visible, Ultraviolet, and Infrared Laser Light Sources

Seal or enclose direct or reflected ultraviolet light, arc lamps, and infrared sources to reduce overexposure whenever possible. Wear appropriately rated safety glasses, chemical splash goggles, and/or face shields for eye protection. Wear long-sleeved clothing and gloves to protect arms and hands from exposure.

Operate high-energy lasers only in posted laser-controlled areas. No one but the authorized operator of a laser system should ever enter a posted laser-controlled laboratory when the laser is in use.

Radio-frequency and Microwave Sources

Other devices used in the laboratory besides microwave ovens can also emit harmful microwave or radio-frequency emissions. Train the people working with these devices in their proper operation and in measures to prevent exposure to harmful emissions. Shields and protective covers should be in proper position when the equipment is operating. Post warning signs on or near these devices to protect people wearing heart pacemakers.

Nuclear Magnetic Resonance (NMR) Systems

Because of the large attractive force of NMR systems, many ferromagnetic objects, such as keys, scissors, knives, wrenches, other tools, oxygen cylinders, buffing machines, and wheelchairs should be excluded from the immediate vicinity of the magnet. This is to protect laboratory personnel and equipment, as well as data quality.

Even relatively small peripheral magnetic fields can adversely affect credit cards, computer disks, and other magnetic objects. Post warnings and rope off areas with more than 10 to 20 gauss (G) at the 5-G line. Limit access to knowledgeable staff. People wearing heart pacemakers and other electronic or electromagnetic prosthetic devices should be kept away from strong electromagnetic sources.

Superconducting magnets use liquid nitrogen and liquid helium coolants. Follow the precautions associated with the use of cryogenic liquids. (Also see Chapter 10, Section 4.3.)

I.2. Guidelines for Working with Specific Compressed Gas Equipment

Pressure-Relief Devices

Protect all pressure or vacuum systems and all vessels that may be subjected to pressure or vacuum by properly installing them and testing their pressure-relief devices. Experiments involving highly reactive materials that might explode may also require the use of special pressure-relief devices and may have to be operated at a fraction of the permissible working pressure of the system.

Pressure Gauges

The proper choice and use of a pressure gauge involves several factors, including the flammability, compressibility, corrosivity, toxicity, temperature, and pressure range of the fluid with which it is to be used. In general, select a gauge with a range that is double the working pressure of the system.

A pressure gauge is normally a weak point in any pressure system because its measuring element must operate in the elastic zone of the metal involved. Use a diaphragm gauge with corrosive gases or liquids or with viscous fluids that would destroy a steel or bronze Bourdon tube.

Consider alternative methods of pressure measurement that may provide greater safety than the direct use of pressure gauges. Such methods include the use of seals or other isolating devices in pressure tap lines, indirect observation devices, and remote measurement by strain-gauge transducers with digital readouts.

Mount pressure gauges so that they can be read easily during operation. Pressure gauges often have built-in pressure-relief devices. Make sure that in the event of failure, this relief device is set up so that it is directed away from people.

Piping, Tubing, and Fittings

The proper selection and assembly of components in a pressure system are critical safety factors. Consider the materials used in manufacturing the components, their compatibility with the materials to be under pressure, the tools used for assembly, and the reliability of the finished connections. Do not use oil or lubricant of any kind in a tubing system with oxygen because the combination produces an explosion hazard. All-brass and stainless steel fittings should be used with copper or brass and steel or stainless steel tubings, respectively. It is important to install fittings of this type correctly. Do not mix different brands of tube fittings in the same apparatus assembly because construction parts often are not interchangeable.

Glass Equipment

Whenever possible, avoid the use of glassware for work at high pressure. Glass is a brittle material. It can fail unexpectedly because of mechanical impact and assembly or tightening stresses. Poor annealing after glassblowing can leave severe strains. Glass equipment that is incorporated in metallic pressure systems, such as rotameters and liquid-level gauges, must have shutoff valves at both ends to control the discharge of liquid or gaseous materials in the event of breakage. Mass flowmeters are available that can replace rotameters in desired applications.

Plastic Equipment

In general, do not use plastic equipment for pressure or vacuum work. Tygon and similar plastic tubing have quite limited applications in pressure work. These materials can be used for hydrocarbons and most aqueous solutions at room temperature and moderate pressure. Reinforced plastic tubing that can withstand higher pressures is also available. However, loose tubing under pressure can cause physical damage by its own whipping action.

Valves

Valves come in a wide range of types, materials of construction, and pressure and temperature ratings. The materials of construction (metal, elastomer, and plastic components) must be compatible with the gases and solvents being used. The valves must be rated for the intended pressure and temperature. Ball valves are preferred over needle valves because their status (on-off) can be determined by quick visual inspection. Only use metering or needle valves when careful flow control is important to the operation. Sometimes micrometers can be used with needle valves to allow quick determination of the status.

Gas Monitors

Electronic monitors and alarms are available to prevent hazards due to asphyxiant, flammable, and many toxic gases. Consider using them in operations employing these gases, especially with large quantities or large cylinders. Make sure that the monitor is properly rated for the intended purpose because some detectors are subject to interference by other gases.

Teflon Tape Applications

Use Teflon tape on tapered pipe thread where the seal is formed in the thread area. Tapered pipe thread is commonly found in applications where fittings are not routinely taken apart (e.g., general building piping applications).

Do not use Teflon tape on straight thread (e.g., Swagelok) where the seal is formed through gaskets or by other metal-to-metal contacts that are forced together when the fitting is tightened (e.g., compression fittings). Metal-to-metal seals work without the need for Teflon tape or other gasketing materials. If Teflon tape is used where it is not needed, as on CGA (Compressed Gas Association) fittings, the tape spreads and weakens the threaded connections and can plug up lines that it enters accidentally.

I.3. Precautions When Using Other Vacuum Apparatus

Glass Vessels

Although glass vessels are frequently used in low-vacuum operations, evacuated glass vessels may collapse violently. This can happen either spontaneously from strain or from an accidental blow. Conduct pressure and vacuum operations in glass vessels behind adequate shielding. It is advisable to check for flaws such as star cracks, scratches, and etching marks each time a vacuum apparatus is used. These flaws can often be noticed by holding the vessel up to a light. Use only round-bottomed or thick-walled (e.g., Pyrex) evacuated reaction vessels specifically designed for operations at reduced pressure. Do not use glass vessels with angled or squared edges in vacuum applications unless specifically designed for the purpose (e.g., extra-thick glass). Repaired glassware must be properly annealed and inspected with a cross-polarizer before vacuum or thermal stress is applied. Never evacuate thin-walled, Erlenmeyer, or round-bottomed flasks larger than 1 L.

Dewar Flasks

Dewar flasks are under high vacuum and can collapse as a result of thermal shock or a very slight mechanical shock. They should be shielded, either by a layer of fiber-reinforced friction tape or by enclosure in a wooden or metal container. Shielding reduces the risk of flying glass in case of collapse. Use metal Dewar flasks whenever there is a possibility of breakage.

Styrofoam buckets with lids can be a safer form of short-term storage and conveyance of cryogenic liquids than glass vacuum Dewars. Although they do not insulate as well as Dewar flasks, they eliminate the danger of implosion.

Desiccators

If a glass vacuum desiccator is used, it should be made of Pyrex or similar glass. Make sure it is completely enclosed in a shield or wrapped with friction tape in a grid pattern that leaves the contents visible and at the same time guards against flying glass should the vessel implode. Plastic (e.g., polycarbonate) desiccators reduce the risk of implosion and may be preferable, but they should also be shielded while evacuated. Solid desiccants are preferable. *Never carry or move an evacuated desiccator.* Take care in opening the valve to avoid the spraying of the desiccator contents from the sudden inrush of gas.

Rotary Evaporators

Glass components of the rotary evaporator should be made of Pyrex or similar glass. Completely enclose them in a shield to guard against flying glass in case the components implode. Increase gradually the rotation speed and application of vacuum to the flask whose solvent is to be evaporated.

J

J.1. How to Assess Unknown Materials

The first concern in identification of an unknown waste is safety. Make sure that trained laboratory personnel who carry out the procedures know the characteristics of the waste and any necessary precautions that must be taken. Because the hazards of the materials being tested are unknown, the use of proper personal protection and safety devices, such as chemical hoods and shields, is imperative. Older samples are particularly dangerous because they may have changed in composition, for example, through the formation of peroxides. (See Chapter 9 for more information about peroxides.)

The following information is commonly required by treatment disposal facilities before they agree to handle unknown materials:

- physical description
- water reactivity
- water solubility
- pH and possibly also neutralization information
- ignitability (flammability)
- presence of oxidizer
- presence of sulfides or cyanides
- presence of halogens
- presence of radioactive materials
- presence of biohazardous materials
- presence of toxic constituents
- presence of polychlorinated biphenyls (PCBs)
- presence of high-odor compounds

Procedures to Test Unknown Materials

- ***Physical description:*** Include the state of the material (solid, liquid), the color, and the consistency (for solids) or viscosity (for liquids). For liquid materials, describe the clarity of the solution (transparent, translucent, or opaque). If an unknown material is a bi- or tri-layered liquid, describe each layer separately, giving an approximate percentage of the total for each layer. After taking appropriate safety precautions for handling the unknown, including the use of personal protection devices, remove a small sample for use in the following tests.
- ***Water reactivity:*** Carefully add a small quantity of the unknown to a few milliliters of water. Observe any changes, including heat evolution, gas evolution, and flame generation.
- ***Water solubility:*** Observe the solubility of the unknown in water. If it is an insoluble liquid, note whether it is less or more dense than water (i.e., does it float or sink?). Most nonhalogenated organic liquids are less dense than water.
- ***pH:*** Test the material with multirange pH paper. If the sample is water soluble, test the pH of a 10% aqueous solution. It may also be desirable or even required to carry out a neutralization titration.
- ***Ignitability (flammability):*** Place a small sample of the material (<5 mL) in an aluminum test tray. Apply an ignition source, typically a propane torch, to the test sample for 0.5 second. If the material supports its own combustion, it is a flammable liquid with a flash point of less than 60°C. If the sample does not ignite, apply the ignition source again for 1 second. If the material burns, it is combustible. Combustible materials have a flash point between 60 and 93°C.
- ***Presence of oxidizer:*** Wet commercially available starch-iodide paper with 1 N hydrochloric acid, and place a small portion of the unknown on the wetted paper. A change in color of the paper to dark purple is a positive test for an oxidizer. The test can also be carried out by adding 0.1 to 0.2 g of sodium or potassium iodide to 1 mL of an acidic 10% solution of the unknown. Development of a yellow-brown color indicates an oxidizer. To test for hydroperoxides in water-insoluble organic solvents, dip the starch-iodine test paper into the solvent, and let it dry. Add a drop of water to the same section of the paper. Development of a dark color indicates the presence of hydroperoxides.
- ***Presence of peroxides***: The following tests detect most (but not all) peroxy compounds, including all hydroperoxides:

  - Add 1 to 3 mL of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides. Alternatively, addition of 1 mL of a freshly prepared 10% solution of potassium iodide to 10 mL of an organic liquid in a 25-mL glass cylinder produces a yellow color if peroxides are present.
  - AAdd 0.5 mL of the liquid to be tested to a mixture of 1 mL of 10% aqueous potassium iodide solution and 0.5 mL of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within one minute indicates the presence of peroxides.
  - APeroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially. Note that these strips must be air dried until the solvent evaporates and then exposed to moisture for proper operation.

  None of these tests should be applied to materials (such as metallic potassium) that may be contaminated with inorganic peroxides.
- ***Presence of sulfide:*** Use commercial test strips to detect the presence of sulfide. If the test strips are not available in the laboratory, the following test can be performed. **Warning: This test produces hazardous and odiferous vapors. Use only small quantities of solution for the test and use appropriate ventilation.** The test for inorganic sulfides is carried out only when the pH of an aqueous solution of the unknown is greater than 10. Add a few drops of concentrated hydrochloric acid to a sample of the unknown while holding a piece of commercial lead acetate paper, wet with distilled water, over the sample. Development of a brown-black color on the paper indicates the generation of hydrogen sulfide.
- ***Presence of cyanide:*** Use only commercial test strips to test for the presence of cyanide.
- ***Presence of halogen:*** Heat a piece of copper wire in a flame until it is red. Cool the wire in distilled or deionized water, and dip it into the unknown. Heat the wire again in the flame. The presence of halogen is indicated by a green color around the wire in the flame.

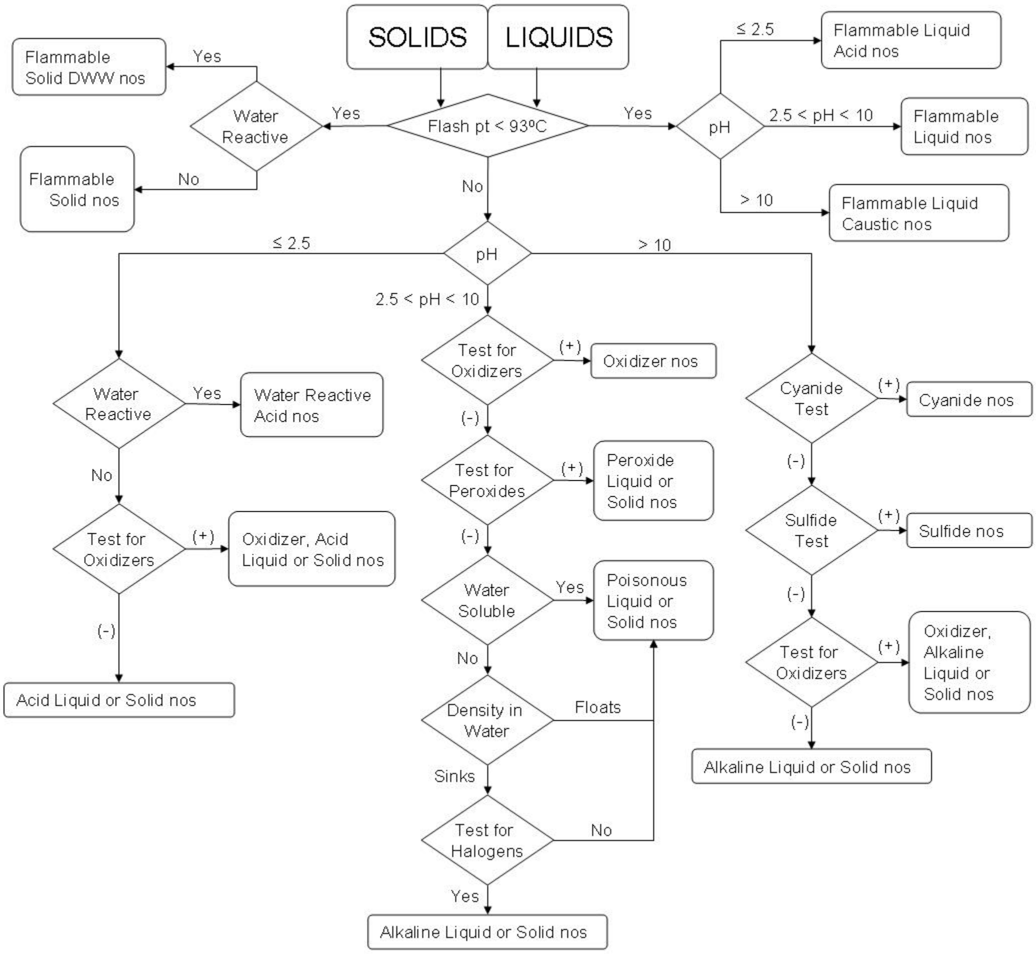

FIGURE J.1 Flow chart for categorizing unknown chemicals for waste disposal.
This decision tree shows the sequence of tests to be performed to determine the appropriate hazard category of an unknown chemical. NOTE: DWW = dangerous when wet; nos = not otherwise specified.

J.2. Procedures for Laboratory-Scale Treatment of Surplus and Waste Chemicals

Concerns about environmental protection, bans on landfill disposal of waste, and limited access to sewer disposal have encouraged the development of strategies to reduce hazardous waste from laboratories. The small-scale treatment and deactivation of products and by-products as part of the experiment plan is one approach that can be used to address the problem at the level of the laboratory worker. However, unless there is a significant reduction in risk by such action, there may be little benefit in carrying out a procedure that will simply produce another kind of waste with similar risks and challenges for disposal. Furthermore, there is the question of what constitutes "legal" treatment within the laboratory.

Nevertheless, such in-laboratory treatment often has merit. Below are some procedures of general use at the laboratory scale. Additional procedures can be found in other books listed at the end of this appendix. More specific procedures for laboratory treatment may be found in the experimental sections of chemical journals and in series publications such as *Organic Syntheses* (*www.orgsyn.org/*) and *Inorganic Syntheses* (*www.inorgsynth.com/*).

Safety must be the first consideration before undertaking any of the procedures that follow. Only a trained scientist or technologist who understands the chemistry and hazards involved should carry out or directly supervise these procedures. Use appropriate personal protection. With the exception of neutralization, the procedures are intended for application to small quantities, or not more than a few hundred grams. Because risks tend to increase exponentially with scale, larger quantities should be treated only in small batches unless a qualified chemist has demonstrated that the procedure can be scaled up safely. The person treating the waste must make sure that the procedure eliminates the regulated hazard before the products are disposed of as nonhazardous waste. In addition, if the procedure suggests disposal of the product into the sanitary sewer, this strategy must comply with local regulations. (See Chapter 9 and Appendix H for further information on protective clothing.)

Acids and Bases

Most laboratories generate waste acids and bases, so it is most economical to collect them separately and then neutralize one with the other. However, because the products of the reaction are often disposed of in a sanitary sewer, it is important to make sure that hazardous wastes such as toxic metal ions are not part of the effluent. If additional acid or base is required, sulfuric or hydrochloric acid and sodium or magnesium hydroxide, respectively, can be used.

If the acid or base is highly concentrated, it is best to first dilute it with cold water (adding the acid or base to the water) to a concentration below 10%. Then mix the acid and base, and slowly add water when necessary to cool and dilute the neutralized product. The concentration of neutral salts disposed of in the sanitary sewer generally should be less than 1%.

Organic Chemicals

Thiols and Sulfides

Small quantities of thiols (mercaptans) and sulfides can be destroyed by oxidation to a sulfonic acid with sodium hypochlorite. If other groups that can be oxidized by hypochlorite are also present, the quantity of this reagent used must be increased accordingly.

Procedure for oxidizing 0.1 mol of a liquid thiol:

$RSH + 3OCl^- \rightarrow RSO_3H + 3Cl^-$

Five hundred milliliters (0.4 mol, 25% excess) of commercial hypochlorite laundry bleach (5.25% sodium hypochlorite) is poured into a 5-L three-necked flask located in a fume hood. Equip the flask with a stirrer, thermometer, and dropping funnel. Add the thiol (0.1 mol) dropwise to the stirred hypochlorite solution, initially at room temperature. Gradually add a solid thiol through a neck of the flask or dissolve it in tetrahydrofuran or other appropriate nonoxidizable solvent. Add the solution to the hypochlorite. (The use of tetrahydrofuran introduces a flammable liquid that could alter the final disposal method.) Rinse traces of thiol from the reagent bottle and dropping funnel with additional hypochlorite solution. Oxidation, accompanied by a rise in temperature and dissolution of the thiol, usually starts after a small amount of the thiol has been added. If the reaction has not started spontaneously after about 10% of the thiol has been added, stop the addition and warm the mixture to about 50°C to initiate this reaction. Resume the addition only after it is clear that oxidation is occurring. Maintain the temperature at 45 to 50°C by adjusting the rate of addition and using an ice bath for cooling if necessary. Addition requires about 15 minutes. If the pH drops below 6 because of generation of sulfonic acid, it may be necessary to add some sodium hydroxide or additional bleach because hypochlorite is destroyed under acidic conditions. Continue stirring for 2 hours while the temperature gradually falls to room temperature. The mixture should be a clear solution, perhaps containing traces of oily by-products. The reaction mixture can usually be flushed down the drain with excess water. The unreacted laundry bleach need not be decomposed.

(Because sodium hypochlorite solutions deteriorate on storage, it is advisable to have relatively fresh material available. A 5.25% solution of sodium hypochlorite has 25 g of active chlorine per liter. If determination of the active hypochlorite content is justified, it can be accomplished as follows: Dilute 10 mL of the sodium hypochlorite solution to 100.0 mL. Then add 10.0 mL of this diluted reagent to a solution of 1 g of potassium iodide and 12.5 mL of 2 M acetic acid in 50 mL of distilled water. Using a starch solution as indicator, titrate the solution with 0.1 N sodium thiosulfate. One milliliter of titrant corresponds to 3.5 mg of active chlorine. A 5.25% solution of sodium hypochlorite requires approximately 7 mL of titrant.)

Calcium hypochlorite may be used as an alternative to sodium hypochlorite and requires a smaller volume of liquid. For 0.1 mol of thiol, stir 42 g (25% excess) of 65% calcium hypochlorite (technical grade) into 200 mL of water at room temperature. The hypochlorite soon dissolves. Then add the thiol as in the above procedure.

Deodorize laboratory glassware, hands, and clothing contaminated with thiols using a solution of Diaperene, a tetraalkylammonium salt used to deodorize containers in which soiled diapers have been washed. Small amounts of sulfides, RSR', can be oxidized to sulfones (RSO_2R') to eliminate their disagreeable odors. The hypochlorite procedure used for thiols can be employed for this purpose, although the resulting sulfones are often water insoluble and may have to be separated from the reaction mixture by filtration.

Destroy small amounts of the inorganic sulfides, sodium sulfide, or potassium sulfide in aqueous solution with sodium or calcium hypochlorite using the procedure described for oxidizing thiols.

$$Na_2S + 4OCl^- \rightarrow Na_2SO_4 + 4Cl^-$$

Acyl Halides and Anhydrides

Acyl halides, sulfonyl halides, and anhydrides react readily with water, alcohols, and amines. They should never be allowed to come into contact with waste that contains such substances. Most compounds in this class can be hydrolyzed to water-soluble products of low toxicity.

Procedure for hydrolyzing 0.5 mol of RCOX, RSO_2X, or $(RCO)_2O$:

$$RCOX + 2NaOH \rightarrow RCO_2Na + NaX + H_2O$$

Place a 1-L three-necked flask equipped with a stirrer, dropping funnel, and thermometer on a steam bath in a hood. Pour 600 mL of 2.5 M aqueous sodium hydroxide (1.5 mol, 50% excess) into the flask. Add a few milliliters of the acid derivative dropwise while stirring. If the derivative is a solid, it can be added in small portions through a neck of the flask. If reaction occurs, as indicated by a rise in temperature and dissolution of the acid derivative, continue the addition at such a rate that the temperature does not rise above 45°C. If the reaction is sluggish, which may be the case with less soluble compounds such as *p*-toluenesulfonyl chloride, heat the mixture before adding any more acid derivative. When the initial material added has dissolved, add the remainder dropwise. As soon as a clear solution is obtained, cool the mixture to room temperature, neutralize it to about pH 7 with dilute hydrochloric or sulfuric acid, and wash it down the drain with excess water.

Aldehydes

Many aldehydes are respiratory irritants, and some, such as formaldehyde and acrolein, are quite toxic. There is sometimes merit in the oxidation of aldehydes to the corresponding carboxylic acids, which are usually less toxic and less volatile.

Procedure for permanganate oxidation of 0.1 mol of aldehyde:

$$3RCHO + 2KMnO_4 \rightarrow 2RCO_2K + RCO_2H + 2MnO_2 + H_2O$$

Stir a mixture of 100 mL of water and 0.1 mol of aldehyde in a 1-L round-bottomed flask equipped with a thermometer, dropping funnel, stirrer, steam bath, and if the aldehyde boils below 100°C, a condenser. Add approximately 30 mL of a solution of 12.6 g (0.08 mol, 20% excess) of potassium permanganate in 250 mL of water over a period of 10 minutes. If the temperature rises above 45°C, cool the solution. If this addition is not accompanied by a rise in temperature and loss of the purple permanganate color, heat the mixture on the steam bath until a temperature is reached at which the color is discharged. Slowly add the rest of the permanganate solution at within 10°C of this temperature. Then raise the temperature to 70 to 80°C, and continue stirring for 1 hour or until the purple color has disappeared, whichever occurs first. Cool the mixture to room temperature until it is acidified with 6 N sulfuric acid. **(CAUTION: Do not add concentrated sulfuric acid to permanganate solution because explosive manganese oxide (Mn_2O_7) may precipitate.)** Add enough solid sodium hydrogen sulfite (at least 8.3 g, 0.08 mol) with stirring at 20 to 40°C to reduce all the manganese. This is indicated by loss of purple color and dissolution of the solid manganese dioxide. Wash the mixture down the drain with a large volume of water.

If the aldehyde contains a carbon-carbon double bond, as in the case of the highly toxic acrolein, use 4 mol (20% excess) of permanganate per mol of aldehyde to oxidize the alkene bond and the aldehyde group. Formaldehyde is oxidized conveniently to formic acid and carbon dioxide by sodium hypochlorite. Thus, stir 10 mL of formalin (37% formaldehyde) in 100 mL of water into 250 mL of hypochlorite laundry bleach (5.25% NaOCl) at room temperature. Allow the mixture to stand for 20 minutes before flushing it down the drain. This procedure is not recommended for other aliphatic aldehydes because it leads to chloro acids, which are more toxic and less biodegradable than corresponding unchlorinated acids.

Amines

Acidified potassium permanganate efficiently degrades aromatic amines. Diazotization followed by hypophosphorous acid protonation is a method for deaminating aromatic amines, but the procedure is more complex than oxidation.

Procedure for permanganate oxidation of 0.01 mol of aromatic amine:

Prepare a solution of 0.01 mol of aromatic amine in 3 L of 1.7 N sulfuric acid in a 5-L flask. Add 1 L of 0.2 M potassium permanganate. Allow the solution to stand at room temperature for 8 hours. Reduce the excess permanganate by slow addition of solid sodium hydrogen sulfite until the purple color disappears. Flush the mixture down the drain.

Organic Peroxides and Hydroperoxides

Generally dispose of small quantities (≤25 g) of peroxides by dilution with water to a concentration of 2% or less. Then transfer the solution to a polyethylene bottle containing an aqueous solution of a reducing agent, such as ferrous sulfate or sodium bisulfite. At this point, the material can be handled as a waste chemical; however, it must not be mixed with other chemicals for disposal. Absorb spilled peroxides on vermiculite or other absorbent as quickly as possible. Burn the vermiculite-peroxide mixture directly or stir it with a suitable solvent to form a slurry that can be handled according to institutional procedures.

Large quantities (>25 g) of peroxides require special handling and should be disposed of ***only*** by an expert or a bomb squad. Consider each case separately. Determine the handling, storage, and disposal procedures by using the physical and chemical properties of the particular peroxide (see also Hamstead, A.C. 1964. *Industrial and Engineering Chemistry*, 56(6): 37–42). Dispose of peroxidized solvents such as tetrahydrofuran (THF), diethyl ether, and 1,4-dioxane in the same manner as the non-auto-oxidized solvent. Take care to make sure that the peroxidized solvent is not allowed to evaporate and thus concentrate the peroxide during handling and transport. **(CAUTION: Peroxides are particularly dangerous. Allow only knowledgeable laboratory personnel to carry out these procedures.)** Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principal hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which also may be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide, *t*-butyl hydroperoxide, and di-*t*-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.

Removal of peroxides with alumina:

A 2 × 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 mL of solvent, whether water soluble or water insoluble. After passing the solvent through the column, test it for peroxide content. The alumina usually decomposes the peroxides formed by air; it does not merely absorb them. However, for safety it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before discarding it.

Removal of peroxides with Molecular Sieves:

Reflux 100 mL of the solvent with 5 g of 4- to 8-mesh-indicating activated 4A Molecular Sieves for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.

Removal of peroxides with ferrous sulfate:

$ROOH + 2Fe^{2+} + 2H^{+} \rightarrow ROH + 2Fe^{3+} + H_2O$

Stir a solution of 6 g of $FeSO_4 \cdot 7H_2O$, 6 mL of concentrated sulfuric acid, and 11 mL of water with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

Diacyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfite, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.

Procedure for destruction of diacyl peroxides:

$(RCO_2)_2 + 2NaI \rightarrow 2RCO_2Na + I_2$

For 0.01 mol of diacyl peroxide, dissolve 0.022 mol (10% excess) of sodium or potassium iodide in 70 mL of glacial acetic acid. Gradually add the peroxide with stirring at room temperature. The solution darkens rapidly by the formation of iodine. After a minimum of 30 minutes, wash the solution down the drain with a large excess of water.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.

Procedure for destruction of dialkyl peroxides:

Add 1 mL of 36% (w/v) hydrochloric acid to the above acetic acid-potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. Heat the solution to 90 to 100°C on a steam bath over the course of 30 minutes and hold at that temperature for 5 hours.

Inorganic Chemicals

Metal Hydrides

Most metal hydrides react violently with water with the evolution of hydrogen, which can form an explosive mixture with air. Some, such as lithium aluminum hydride, potassium hydride, and sodium hydride, are pyrophoric. Most can be decomposed by gradual addition of (in order of decreasing reactivity) methyl alcohol, ethyl alcohol, *n*-butyl alcohol, or *t*-butyl alcohol to a stirred, ice-cooled solution or suspension of the hydride in an inert liquid, such as diethyl ether, tetrahydrofuran, or toluene, under nitrogen in a three-necked flask. Although these procedures reduce the hazard and should be a part of any experiment that uses reactive metal hydrides, the products from such deactivation may be hazardous waste that must be treated as such on disposal.

Hydrides commonly used in laboratories are lithium aluminum hydride, potassium hydride, sodium hydride, sodium borohydride, and calcium hydride. The following methods for their disposal demonstrate that the reactivity of metal hydrides varies considerably. Most hydrides can be decomposed safely by one of the four methods, but the properties of a given hydride must be well understood to select the most appropriate method. **(CAUTION: Most of the methods described below produce hydrogen gas, which can present an explosion hazard. Carry out the reaction in a hood, behind a shield, and with proper safeguards to avoid exposure of the effluent gas to spark or flame. Any stirring device must be spark-proof.)**

Decomposition of lithium aluminum hydride:

Lithium aluminum hydride ($LiAlH_4$) can be purchased as a solid or as a solution in toluene, diethyl ether, tetrahydrofuran, or other ethers. Although dropwise addition of water to its solutions under nitrogen in a three-necked flask has frequently been used to decompose it, vigorous frothing often occurs. An alternative is to use 95% ethanol, which reacts less vigorously than water. A safer procedure is to decompose the hydride with ethyl acetate, because no hydrogen is formed.

$$2CH_3CO_2C_2H_5 + LiAlH_4 \rightarrow LiOC_2H_5 + Al(OC_2H_5)_3$$

Slowly add ethyl acetate to the hydride solution in a flask equipped with a stirrer. The mixture sometimes becomes so viscous after the addition that stirring is difficult and additional solvent may be required. When the reaction with ethyl acetate has ceased, add and stir a saturated aqueous solution of ammonium chloride. The mixture separates into an organic layer and an aqueous layer containing inert inorganic solids. Separate the upper, organic layer and dispose of it as a flammable liquid. Generally dispose of the lower, aqueous layer in the sanitary sewer.

Decomposition of potassium or sodium hydride:

Potassium and sodium hydride (KH, NaH) in the dry state are pyrophoric, but they can be purchased as a relatively safe dispersion in mineral oil. Either form can be decomposed by adding enough dry hydrocarbon solvent (e.g., heptane) to reduce the hydride concentration below 5% and then adding excess *t*-butyl alcohol dropwise under nitrogen with stirring. Then add cold water dropwise, and separate the two resulting layers. The organic layer can be disposed of as a flammable liquid. Usually the aqueous layer can be neutralized and disposed of in the sanitary sewer.

Decomposition of sodium borohydride:

Sodium borohydride ($NaBH_4$) is so stable in water that a 12% aqueous solution stabilized with sodium hydroxide is sold commercially. To effect decomposition, add the solid or aqueous solution to enough water to make the borohydride concentration less than 3%, and then add excess equivalents of dilute aqueous acetic acid dropwise with stirring under nitrogen.

Decomposition of calcium hydride:

Calcium hydride (CaH_2), the least reactive of the materials discussed here, is purchased as a powder. It is decomposed by adding 25 mL of methyl alcohol per gram of hydride under nitrogen with stirring. When reaction has ceased, gradually add an equal volume of water to the stirred slurry of calcium methoxide. Neutralize the mixture with acid and dispose of it in the sanitary sewer.

Inorganic Cyanides

Inorganic cyanides can be oxidized to cyanate using aqueous hypochlorite following a procedure similar to the oxidation of thiols. Hydrogen cyanide can be converted to sodium cyanide by neutralization with aqueous sodium hydroxide, and then oxidized.

Procedure for oxidation of cyanide:

$NaCN + NaOCl \rightarrow NaOCN + NaCl$

Cool an aqueous solution of the cyanide salt in an ice-cooled, three-necked flask equipped with a stirrer, thermometer, and dropping funnel until it reaches 4 to 10°C. Slowly add a 50% excess of commercial hypochlorite laundry bleach containing 5.25% (0.75 M) sodium hypochlorite with stirring while maintaining the low temperature. When the addition is complete and heat is no longer being evolved, allow the solution to warm to room temperature and stand for several hours. Then wash the mixture down the drain with excess water. The same procedure can be applied to insoluble cyanides such as cuprous cyanide (although copper salts should not be disposed of in the sanitary sewer). In calculating the quantity of hypochlorite required, the experimenter should remember that additional equivalents may be needed if the metal ion can be oxidized to a higher valence state, as in the reaction

$$2CuCN + 3OCl^- + H_2O \rightarrow 2Cu^{2+} + 2OCN^- + 2OH^- + 3Cl^-$$

Use a similar procedure to destroy hydrogen cyanide, but take precautions to avoid exposure to this very toxic gas. Dissolve hydrogen cyanide in several volumes of ice water. Add approximately 1 molar equivalent of aqueous sodium hydroxide at 4 to 10°C to convert the hydrogen cyanide into its sodium salt. Then follow the procedure described above for sodium cyanide. **(CAUTION: Sodium hydroxide or other bases, including sodium cyanide, must not be allowed to come into contact with liquid hydrogen cyanide because they may initiate a violent polymerization of the hydrogen cyanide.)**

This procedure also destroys soluble ferrocyanides and ferricyanides. Alternatively, these can be precipitated as the ferric or ferrous salt, respectively, for possible landfill disposal.

(See Chapter 9 for more information on working with hazardous gases.)

Metal Azides

Heavy metal azides are notoriously explosive. Only trained personnel should handle them. Silver azide (and also fulminate) can be generated from Tollens reagent, which is often found in undergraduate laboratories. Sodium azide is explosive only when heated to near its decomposition temperature (300°C), but avoid heating it. Never flush sodium azide down the drain. This practice has caused serious accidents because the azide can react with lead or copper in the drain lines to produce an azide that may explode. It can be destroyed by reaction with nitrous acid:

$$2NaN_3 + 2HNO_2 \rightarrow 2N_2 + 2NO + 2NaOH.$$

Procedure for destruction of sodium azide:

The operation must be carried out in a hood because of the formation of toxic nitric oxide. Put an aqueous solution containing no more than 5% sodium azide into a three-necked flask equipped with a stirrer and a dropping funnel. Add and stir approximately 7 mL of 20% aqueous solution of sodium nitrite (40% excess) per gram of sodium azide. Then gradually add a 20% aqueous solution of sulfuric acid until the reaction mixture is acidic to litmus paper. **(CAUTION: The order of addition is essential. Poisonous, volatile hydrazoic acid (HN_3) will evolve if the acid is added before the nitrite.)** When the evolution of nitrogen oxides ceases, test the acidic solution with starch iodide paper. If it turns blue, excess nitrite is present, and the decomposition is complete. Wash the reaction mixture down the drain.

Alkali Metals

Alkali metals react violently with water, with common hydroxylic solvents, and with halogenated hydrocarbons. Always handle alkali metals in the absence of these materials. The metals are usually destroyed by controlled reaction with an alcohol. The final aqueous alcoholic material can usually be disposed of in the sanitary sewer.

Procedure for destruction of alkali metals:

Waste sodium is readily destroyed with 95% ethanol. Carry out the procedure in a three-necked, round-bottomed flask equipped with a stirrer, dropping funnel, condenser, and heating mantle. Cut the solid sodium into small pieces with a sharp knife while wet with a hydrocarbon, preferably mineral oil, so that the unoxidized surface is exposed. Directly treat a dispersion of sodium in mineral oil. Place the pieces of sodium in the flask and flush it with nitrogen. Then add 13 mL of 95% ethanol per gram of sodium at a rate that causes rapid refluxing. **(CAUTION: Hydrogen gas is evolved and can present an explosion hazard. Carry out the reaction in a hood, behind a shield, and with proper safeguards (such as in Chapter 9, Section 7) to avoid exposing the effluent gas to spark or flame. Any stirring device must be spark-proof.)** Begin stirring as soon as enough ethanol has been added to make this possible. Stir and heat the mixture under reflux until the sodium is dissolved. Remove the heat source, and add an equal volume of water at a rate that causes no more than mild refluxing. Cool the solution, neutralize it with 6 M sulfuric or hydrochloric acid, and wash it down the drain.

To destroy metallic potassium, use the same procedure and precautions as for sodium, except use the less reactive *t*-butyl alcohol in the proportion of 21 mL per gram of metal. **(CAUTION: Potassium metal can form explosive peroxides. Do not use a knife to cut metal that has formed a yellow oxide coating from exposure to air, even when wet with a hydrocarbon, because an explosion can be promoted.)**

If the potassium is dissolving too slowly, gradually add a few percent of methanol to the refluxing *t*-butyl alcohol. Put oxide-coated potassium sticks directly into the flask and decompose them with *t*-butyl alcohol. The decomposition will require considerable time because of the low surface-to-volume ratio of the metal sticks.

Lithium metal can be treated by the same procedure, using 30 mL of 95% ethanol per gram of lithium. The rate of dissolution is slower than that of sodium.

Metal Catalysts

Slurry metal catalysts such as Raney nickel and other fine metal powders into water. Then add dilute hydrochloric acid carefully until the solid dissolves. Depending on the metal and on local regulations, discard the solution in the sanitary sewer or with other hazardous or nonhazardous solid waste. Precious metals should be recovered from this process.

Water-Reactive Metal Halides

Liquid halides, such as $TiCl_4$ and $SnCl_4$, can be added to well-stirred water in a round-bottomed flask cooled by an ice bath as necessary to keep the exothermic reaction under control. It is usually more convenient to add solid halides, such as $AlCl_3$ and $ZrCl_4$, to stirring water and crushed ice in a flask or beaker. The acidic solution can be neutralized and, depending on the metal and local regulations, discarded in the sanitary sewer or with other hazardous or nonhazardous solid waste.

Halides and Acid Halides of Nonmetals

Halides and acid halides such as PCl_3, PCl_5, $SiCl_4$, $SOCl_2$, SO_2Cl_2, and $POCl_3$ are water reactive. The liquids can be hydrolyzed conveniently using 2.5 M sodium hydroxide by the procedure described earlier for acyl halides and anhydrides. These compounds are irritating to the skin and respiratory passages and, even more than most chemicals, require a good hood and skin protection when handling them. Moreover, PCl_3 may give off small amounts of highly toxic phosphine (PH_3) during hydrolysis.

Sulfur monochloride (S_2Cl_2) is a special case. It is hydrolyzed to a mixture of sodium sulfide and sodium sulfite, so the hydrolyzate must be treated with hypochlorite, as described earlier for sulfides, before it can be flushed down the drain.

The solids of this class (e.g., PCl_5) tend to cake and fume in moist air and therefore are not conveniently hydrolyzed in a three-necked flask. It is preferable to add them to a 50% excess of 2.5 M sodium hydroxide solution in a beaker or wide-mouth flask equipped with a stirrer and half-filled with crushed ice. If the solid has not all dissolved by the time the ice has melted and the stirred mixture has reached room temperature, complete the reaction by heating on a steam bath; then neutralize the acidic solution and dispose of it in the sanitary sewer.

Inorganic Ions

Many inorganic wastes consist of a cation (metal or metalloid atom) and an anion (which may or may not contain a metalloid component). It is often helpful to examine the cationic and anionic parts of the substance separately to determine whether either constitutes a hazard.

If a substance contains a "heavy metal," it is often assumed to be highly toxic. Although salts of some heavy metals, such as lead, thallium, and mercury, are highly toxic, those of others, such as gold and tantalum, are not. On the other hand, compounds of beryllium, a "light metal," are highly toxic. In Table J.1, cations of metals and metalloids are listed alphabetically in two groups: those whose toxic properties as described in the toxicological literature present a significant hazard and those whose properties do not. The basis for separation is relative, and the separation does not imply that those in the second list are "nontoxic." Similarly, Table J.2 lists anions according to their level of toxicity and other dangerous properties, such as strong oxidizing power (e.g., perchlorate), flammability (e.g., amide), water reactivity (e.g., hydride), and explosivity (e.g., azide).

Materials that pose a hazard because of significant radioactivity are outside the scope of this volume, although they may be treated chemically in a manner similar to the nonradioactive materials discussed in this appendix. Their handling and disposal are highly regulated in most countries.

Chemicals in Which Neither the Cation nor the Anion Presents a Significant Hazard

Chemicals in which neither the cation nor the anion presents a significant hazard consist of those chemicals composed of ions from the right-hand columns of Tables J.1 and J.2. Those that are soluble in water to the extent of a few percent can usually be disposed of in the sanitary sewer. Dispose only of laboratory quantities in this manner, and use at least 100 parts of water per part of chemical. Check local regulations for possible restrictions. Also handle dilute slurries of insoluble materials, such as calcium sulfate or aluminum oxide, in this way, provided the material is finely divided and not contaminated with tar that might clog the piping. Some incinerators can handle these chemicals. If time and space permit, boil down dilute aqueous solutions or allow them to evaporate and leave only a sludge of the inorganic solid for landfill disposal. However, consider appropriate precautions, including the use of traps, to make sure that toxic or other prohibited materials are not released to the atmosphere.

An alternative procedure is to precipitate the metal ion with the agent recommended in Table J.1. The precipitate can often be disposed of in a secure landfill. The most generally applicable procedure is to precipitate the cation as the hydroxide by adjusting the pH to the range shown in Table J.3.

Precipitation of Cations as Their Hydroxides

Because the pH range for precipitation varies greatly among metal ions, it is important to control it carefully. Adjust the aqueous solution of the metal ion to the recommended pH (Table J.3) by addition of a solution of 1 M sulfuric acid, or 1 M sodium hydroxide or carbonate. The pH can be determined over the range 1 through 10 by use of pH test paper.

TABLE J.1 High- and Low-Toxicity Cations and Preferred Precipitants

High Toxic Hazard		**Low Toxic Hazard**	
Cation	**Precipitant**[a]	**Cation**	**Precipitant**[a]
Antimony	OH^-, S^{2-}	Aluminum	OH^-
Arsenic	S^{2-}	Bismuth	OH^-, S^{2-}
Barium	SO_4^{2-}, CO_3^{2-}	Calcium	SO_4^{2-}, CO_3^{2-}
Beryllium	OH^-	Cerium	OH^-
Cadmium	OH^-, S^{2-}	Cesium	–
Chromium(III)[b]	OH^-	Copper[c]	OH^-, S^{2-}
Cobalt(II)[b]	OH^-, S^{2-}	Gold	OH^-, S^{2-}
Gallium	OH^-	Iron[c]	OH^-, S^{2-}
Germanium	OH^-, S^{2-}	Lanthanides	OH^-
Hafnium	OH^-	Lithium	–
Indium	OH^-, S^{2-}	Magnesium	OH^-
Iridium[d]	OH^-, S^{2-}	Molybdenum(VI)[b,e]	–
Lead	OH^-, S^{2-}	Niobium(V)	OH^-
Manganese(II)[b]	OH^-, S^{2-}	Palladium	OH^-, S^{2-}
Mercury	OH^-, S^{2-}	Potassium	–
Nickel	OH^-, S^{2-}	Rubidium	–
Osmium(IV)[b,f]	OH^-, S^{2-}	Scandium	OH^-
Platinum(II)[b]	OH^-, S^{2-}	Sodium	–
Rhenium(VII)[b]	S^{2-}	Strontium	SO_4^{2-}, CO_3^{2-}
Rhodium(III)[b]	OH^-, S^{2-}	Tantalum	OH^-
Ruthenium(III)[b]	OH^-, S^{2-}	Tin	OH^-, S^{2-}
Selenium	S^{2-}	Titanium	OH^-
Silver[d]	Cl^-, OH^-, S^{2-}	Yttrium	OH^-
Tellurium	S^{2-}	Zinc[c]	OH^-, S^{2-}
Thallium	OH^-, S^{2-}	Zirconium	OH^-
Tungsten(VI)[b,e]			
Vanadium	OH^-, S^{2-}		

[a] Precipitants are listed in order of preference: OH^-, CO_3^{2-} = base (sodium hydroxide or sodium carbonate), S^{2-} = sulfide, SO_4^{2-} = sulfate, and Cl^- = chloride.

[b] The precipitant is for the indicated valence state.

[c] Very low maximum tolerance levels have been set for these low-toxicity ions in some countries, and large amounts should not be put into public sewer systems. The small amounts typically used in laboratories will not normally affect water supplies, although they may be prohibited by the local publicly owned treatment works (POTW).

[d] Recovery of these rare and expensive metals may be economically favorable.

[e] These ions are best precipitated as calcium molybdate(VI) or calcium tungstate(VI).

[f] **CAUTION: Osmium tetroxide, OSO_4, a volatile, extremely poisonous substance, is formed from almost any osmium compound under acid conditions in the presence of air. Reaction with corn oil or powdered milk will destroy it.**

Separate the precipitate by filtration, or as a heavy sludge by decantation, and pack it for disposal. Some gelatinous hydroxides are difficult to filter. In such cases, heating the mixture close to 100°C or stirring with diatomaceous earth, approximately one to two times the weight of the precipitate, often facilitates filtration. As shown in Table J.1, precipitants other than a base may be superior for some metal ions, such as sulfuric acid for calcium ion. For some ions, the hydroxide precipitate will redissolve at a high pH (Table J.3). For a number of metal ions the use of sodium carbonate will result in precipitation of the metal carbonate or a mixture of hydroxide and carbonate.

Chemicals in Which the Cation Presents a Relatively High Hazard from Toxicity

In general, waste chemicals containing any of the cations listed as highly hazardous in Table J.1 can be precipitated as their hydroxides or oxides. Alternatively, many can be precipitated as insoluble sulfides by treatment with sodium sulfide in neutral solution (Table J.4). Several sulfides will redissolve in excess sulfide ion, so it is important that sulfide ion concentration be controlled by the adjustment of pH. Achieve the precipitation of the hydroxide as described above. Accomplish the precipitation as the sulfide by adding a 1 M solution of sodium sulfide to the metal ion solution and then adjusting the pH to neutral with 1 M sulfuric acid. **(CAUTION: Avoid acidifying the mixture because hydrogen sulfide could be formed.)** Separate the precipitate by filtration or decantation and pack it for disposal. Excess sulfide ion can be destroyed by the addition of hypochlorite to the clear aqueous solution.

TABLE J.2 High- and Low-Hazard Anions and Preferred Precipitants

	High–Hazard Anions		**Low–Hazard Anions**
Ion	**Hazard Type**[e]	**Precipitant**	
Aluminum hydride, AlH_4^-	F,W	–	Bisulfite, HSO^{3-}
Amide, NH_2^-	F,E[b]	–	Borate, BO_3^{3-}, $B_4O_7^{-2}$
Arsenate, AsO_3^-, AsO_4^{3-}	T	Cu^{3+}, Fe^{2+}	Bromide, Br^-
Arsenite, AsO_2^-, AsO_3^{3-}	T	Pb^{2+}	Carbonate, CO_3^{2-}
Azide, N_3^-	E, T	–	Chloride, Cl^-
Borohydride, BH_4^-	F	–	Cyanate, OCN^-
Bromate, BrO_3^-	O, F, E	–	Hydroxide, OH^-
Chlorate, ClO_3^-	O, E	–	Iodide, I^-
Chromate, CrO_4^{2-}, $Cr_2O_7^{2-}$	T, O	[c]	Oxide, O^-
Cyanide, CN^-	T	–	Phosphate, PO_4^{3-}
Ferricyanide, $\{Fe(CN)_6\}^{-3}$	T	Fe^{2+}	Sulfate, SO_4^{2-}
Ferrocyanide, $\{Fe(CN)_6\}^{-4}$	T	Fe^{3+}	Sulfite, SO_3^{2-}
Fluoride, F^-	T	Ca^{2+}	Thiocyanate, SCN^-
Hydride, H^-	F, W	–	
Hydroperoxide, O_2H^-	O, E	–	
Hydrosulfide, SH^-	T	–	
Hypochlorite, OCH^-	O	–	
Iodate, IO_3^-	O, E	–	
Nitrate, NO_3^-	O	–	
Nitrite, NO_2^-	T, O	–	
Perchlorate, ClO_4^-	O, E	–	
Permanganate, MnO_4^-	T. O	–	
Peroxide, O_2^{2-}	O, E	[d]	
Persulfate, $S_2O_8^{2-}$	O	–	
Selenate, SeO_4^{2-}	T	Pb^{2+}	
Selenide, Se^{2-}	T	Cu^{2+}	
Sulfide, S^{2-}	T	[e]	

[a] T = toxic; O = oxidant; F = flammable; E = explosive; W = water reactive.

[b] Metal amides readily form explosive peroxides on exposure to air.

[c] Reduce and precipitate as Cr(III).

[d] Reduce and precipitate as Mn(II); see Table J.1.

[e] See Table J.4.

The following ions are most commonly found as oxyanions and are not precipitated by base: As^{3+}, As^{5+}, Re^{7+}, Se^{4+}, Se^{6+}, Te^{4+}, and Te^{6+}. Precipitate these elements from their oxyanions as the sulfides by the above procedure. Precipitate the oxyanions of Mo^{6+} and W^{6+} as their calcium salts by the addition of calcium chloride. Absorb some ions by passing their solutions over ion-exchange resins. Landfill the resins, and pour the effluent solutions down the drain.

Another class of compounds whose cations may not be precipitated by the addition of hydroxide ions involves the most stable complexes of metal cations with Lewis bases, such as ammonia, amines, and tertiary phosphines. Because of the large number of these compounds and their wide range of properties, it is not possible to give a general procedure for separating the cations. In many cases, metal sulfides can be precipitated directly from aqueous solutions of the complexes by the addition of aqueous sodium sulfide. If a test-tube experiment shows that other measures are needed, the addition of hydrochloric acid to produce a slightly acidic solution will often decompose the complex by protonation of the basic ligand. Metal ions that form insoluble sulfides under acid conditions can then be precipitated by dropwise addition of aqueous sodium sulfide.

TABLE J.3 pH Ranges for Precipitation of Metal Hydroxides and Oxides

	pH: 1 2 3 4 5 6 7 8 9 10
Ag^{1+}	9 ⟶ 1N
Al^{3+}	7 — 8
As^{3+}	Not precipitated (precipitate as sulfide)
As^{5+}	Not precipitated (precipitate as sulfide)
Au^{3+}	7 — 8
Be^{2+}	7 — 8
Bi^{3+}	7 ⟶ 1N
Cd^{2+}	7 ⟶ 1N
Co^{2+}	8 ⟶ 1N
Cr^{3+}	7 ⟶ 1N
Cu^{1+}	9 ⟶ 1N
Cu^{2+}	7 ⟶ 1N
Fe^{2+}	7 ⟶ 1N
Fe^{3+}	7 ⟶ 1N
Ga^{3+}	7 — 8
Ge^{4+}	6 — 8
Hf^{4+}	6 — 7
Hg^{1+}	8 ⟶ 1N
Hg^{2+}	8 1N
In^{3+}	6 ⟶ pH13
Ir^{4+}	6 — 8
Mg^{2+}	9 ⟶ 1N
Mn^{2+}	8 ⟶ 1N
Mn^{4+}	7 ⟶ 1N
Mo^{6+}	Not precipitated (precipitate as Ca salt)
Nb^{5+}	1 — 10
Ni^{2+}	8 ⟶ 1N
Os^{4+}	7 — 8
Pb^{2+}	7 — 8
Pd^{2+}	7 — 8
Pd^{4+}	7 — 8
Pt^{2+}	7 — 8
Re^{3+}	6 ⟶ 1N
Re^{7+}	Not precipitated (precipitate as sulfide)
Rh^{3+}	7 — 8
Ru^{3+}	7 ⟶ 1N
Sb^{3+}	7 — 8
Sb^{5+}	7 — 8
Sc^{3+}	8 ⟶ 1N
Se^{4+}	Not precipitated (precipitate as sulfide)
Se^{6+}	Not precipitated (precipitate as sulfide)
Sn^{2+}	7 — 8
Sn^{4+}	7 — 8
Ta^{5+}	1 — 10
Te^{4+}	Not precipitated (precipitate as sulfide)
Te^{6+}	Not precipitated (precipitate as sulfide)
Th^{4+}	6 ⟶ 1N
Ti^{3+}	8 ⟶ 1N
Ti^{4+}	8 ⟶ 1N
Tl^{3+}	9 ⟶ 1N
V^{4+}	7 — 8
V^{5+}	7 — 8
W^{6+}	Not precipitated (precipitate as Ca salt)
Zn^{2+}	7 — 8
Zn^{4+}	6 — 7

A third option for this waste is incineration, provided that the incinerator ash will be sent to a secure landfill. Incineration to ash reduces the volume of waste going to a landfill. Waste that contains mercury, thallium, gallium, osmium, selenium, or arsenic should not be incinerated because volatile, toxic combustion products may be emitted.

TABLE J.4 Precipitation of Sulfides

Precipitated at pH 7	Not Precipitated at Low pH	Soluble Complex at High pH
Ag^{+}	–	–
As^{3+a}	–	–
Au^{+a}	–	X
Bi^{3+}	–	X
Cd^{2+}	–	–
Co^{2+}	X	–
Cr^{3+a}	–	–
Cu^{2+}	–	–
Fe^{2+a}	X	–
Ge^{2+}	–	X
Hg^{2+}	–	X
In^{3+}	X	–
Ir^{4+}	–	X
Mn^{2+a}	X	–
Mo^{3+}	–	X
Ni^{2+}	X	–
Os^{4+}	–	–
Pb^{2+}	–	–
Pd^{2+a}	–	–
Pt^{2+a}	–	X
Re^{4+}	–	–
Rh^{2+}	–	–
Ru^{4+}	–	–
Sb^{3+a}	–	X
Se^{2+}	–	X
Sn^{2+}	–	X
Te^{4+}	–	X
Tl^{+a}	X	–
V^{4+}	–	–
Zn^{2+}	X	–

NOTE: Precipitation of ions listed without an X is usually not pH dependent.

[a] Higher oxidation states of this ion are reduced by sulfide ion and precipitated as this sulfide.

SOURCE: Swift, E. H., and Schaefer, W. P. 1961. *Journal of Chemical Education*, 38:607.

Chemicals in Which an Anion Presents a Relatively High Hazard

The more common dangerous anions are listed in Table J.2. Many of the comments made above about the disposal of dangerous cations apply to these anions. The hazard associated with some of these anions is their reactivity or potential to explode, which makes them unsuitable for landfill disposal. Most chemicals containing these anions can be incinerated, but introduce strong oxidizing agents and hydrides into the incinerator only in containers of not more than a few hundred grams. Transfer incinerator ash from anions of chromium or manganese to a secure landfill.

Precipitate some of these anions as insoluble salts for landfill disposal, as indicated in Table J.2. Convert small amounts of strong oxidizing agents, hydrides, cyanides, azides, metal amides, and soluble sulfides or fluorides into less hazardous substances in the laboratory before disposing of them. Suggested procedures are presented in the following paragraphs.

Procedure for Reduction of Oxidizing Salts

Reduce hypochlorites, chlorates, bromates, iodates, periodates, inorganic peroxides and hydroperoxides, persulfates, chromates, molybdates, and permanganates with sodium hydrogen sulfite. A dilute solution or suspension of a salt containing one of these anions has its pH reduced to less than 3 with sulfuric acid. Gradually add a 50% excess of aqueous sodium hydrogen sulfite with stirring at room temperature. An increase in temperature indicates that the reaction is taking place. If the reaction does not start on addition of about 10% of the sodium hydrogen sulfite, a further reduction in pH may initiate it. Colored anions (e.g., permanganate, chromate) serve as their own indicators of completion of the reduction. Wash the reduced mixtures down the drain. However, if large amounts of permanganate have been reduced, it may be necessary to transfer the manganese dioxide to a secure landfill, possibly after a reduction in volume by concentration or precipitation. Do not dispose of chromium salts in the sanitary sewer.

Reduce hydrogen peroxide by the sodium hydrogen sulfite procedure or by ferrous sulfate as described earlier for organic hydroperoxides. However, it is usually acceptable to dilute it to a concentration of less than 3% and dispose of it in the sanitary sewer. Handle with great care any solutions with a hydrogen peroxide concentration greater than 30%, to avoid contact with reducing agents, including all organic materials, or with transition metal compounds, which can catalyze a violent reaction.

Keep concentrated perchloric acid (particularly when stronger than 60%) away from reducing agents, including weak ones such as ammonia, wood, paper, plastics, and all other organic substances, because it can react violently with them. Dilute perchloric acid is not reduced by common laboratory reducing agents such as sodium hydrogen sulfite, hydrogen sulfide, hydriodic acid, iron, or zinc. Perchloric acid is most easily disposed of by stirring it gradually into enough cold water to make its concentration less than 5%, neutralizing it with aqueous sodium hydroxide, and washing the solution down the drain with a large excess of water.

Nitrate is most dangerous in the form of concentrated nitric acid (70% or higher), which is a potent oxidizing agent for organic materials and all other reducing agents. It can also cause serious skin burns. Dilute aqueous nitric acid is not a dangerous oxidizing agent and is not easily reduced by common laboratory reducing agents. Neutralize dilute nitric acid with aqueous sodium hydroxide before disposal down the drain. Dilute concentrated nitric acid carefully by adding it to about 10 volumes of water before neutralization. Metal nitrates are generally quite soluble in water. The metals listed in Table J.1 as having a low toxic hazard, as well as ammonium nitrate, should be kept separate from oil or other organic materials because, on heating such a combination, fire or explosion can occur. Otherwise, these can be treated as chemicals that present no significant hazard.

Destroy nitrites in aqueous solution by adding about 50% excess aqueous ammonia and acidifying with hydrochloric acid to pH 1:

$$HNO_2 + NH_3 \rightarrow N_2 + 2H_2O.$$

More Information

Armour, M.A. 2003. *Hazardous Laboratory Chemicals Disposal Guide, Third Edition*. Boca Raton, Fla.: CRC Press.

Lunn, G., and E. B. Sansone. 1990. *Destruction of Hazardous Chemicals in the Laboratory*. New York: John Wiley & Sons.

National Research Council, 1983. *Prudent Practices for Disposal of Chemicals from Laboratories*, National Academy Press, Washington D.C.

Pitt, M. J., and E. Pitt. 1985. *Handbook of Laboratory Waste Disposal: A Practical Manual*. New York: Halsted.

In addition, the International Agency for Research on Cancer (IARC) has issued a number of monographs on the destruction of hazardous waste. These may be consulted for guidance beyond that provided here. See the IARC web site for more information: *http://monographs.iarc.fr/.*