CHEMICAL HYGIENE DLAN



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Office of Environmental Health and Safety



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	Minor text corrections and edits		
Section !	5.0		
	Minor text corrections and edits		
Pg 5.6	Link to Table 9.3 added		
Pg 5.9	Chemical inventory: RSS reference and link added		
Section	6.0		
	Minor text corrections and edits		
Pg. 6.10	Simple Asphyxiants and Carbon Dioxide SOP and Short Program links added		
Section [•]	7.0		
	Minor text corrections and edits		
Pg. 7.2	Bruno database removed under "Requirements"		
Pg. 7.4	Vermiculite information updated with new link in footnote		
Pg. 7.6	Reference to Bruno removed; RSS added		
Pg. 7.24	New link for "8 CCR §4845"		
Pg. 7.27	 • New link for Materials of Trade • CCR Title 49 changed to CFR Title 49 with new link added 		
Pg. 7.28	FedEx link for shipping hazardous materials updated		
Section	8.0		

	Minor text corrections and edits
Pgs. 8.1	• Bullet point added: "Personnel shall print and store SDSs for all Category 1 acute toxicants and phenol-containing materials at or near the work area where they are used."
Pg. 8.2	• "8 CCR §5191 (e) (H)" link added

Pg. 8.4	 Email contact labsafety@usc.edu changed to injuryprevention@usc.edu
Pg. 8.24, 8.28	• Bretherick's Handbook of Reactive Chemical Hazards link updated
Pg. 8.30	New link for "granulatomas" added

Section 9.0

Pg. 9.2	 New Waste Pickup link: https://ehs.usc.edu/hazmat-mgmt/request-a-hazardous- waste-pickup/
Pg. 9.3	• Updated "22 CCR § 66265.173 (a)" link

Section 10.0

	Minor text corrections and edits
Pg. 10.4	 "How to Use the Emergency Eyewash & Safety Shower in a Laboratory at USC" video link added to Table 10.1 at row Eye/Skin Contact

Appendix B

•	Minor text	corrections	and edits
		confections	and carts

Appendix C

Pg. C.1 • "19 CCR §572" link added

Appendix D

• Minor text corrections and edits

Appendix E

• Winter Recess memo updated

Appendix F

• Links repaired/updated

Appendix G

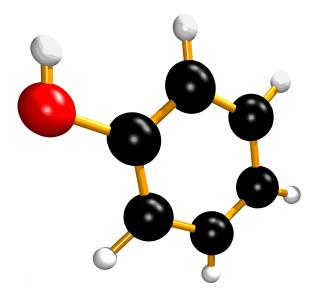
• Minor text corrections and edits

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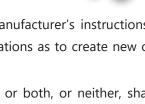
Purpose and Scope

The University of Southern California (USC) Chemical Hygiene Plan (CHP) is a broadly applicable manual covering chemical safety and many areas of general laboratory safety. The CHP is intended to be a useful resource for USC laboratory personnel and principal investigators (PI), providing accessible and relevant information to enable safe operations. The CHP is also designed to aid laboratory personnel and PIs in complying with government safety regulations, university policies, and with USC Office of Environmental Health and Safety (EH&S) recommendations and requirements.



The USC Chemical Hygiene Plan:

- Covers general laboratory safety and chemical safety.
- Applies to all research laboratories and other research facilities which • contain any amount of hazardous materials.¹
 - Facilities in which hazardous materials are present may fall under the EH&S Shop Safety Program rather than the Laboratory Safety Program, provided the following conditions are met:
 - The hazardous materials are commercially sourced domestic, industrial, or engineering products with clearly defined applications (e.g., cements, paints, adhesives, cleaning agents, lubricants, fuels, art materials, film processing chemicals), and:
 - The hazardous materials are being used broadly in line with manufacturer's instructions/ recommendations, or at least not so far outside the recommendations as to create new or unexpected hazards, or to constitute chemical research.
 - Final determination of whether a facility is a laboratory, workshop, or both, or neither, shall be made by the Chemical Hygiene Officer (CHO) and/or Shop Safety Program Manager as appropriate.



¹ For the purposes of this CHP, "hazardous material" is used as the generic descriptor for any substance or mixture of substances which poses risk to personnel on account of its chemical hazards (e.g. toxicity, flammability), and/or physical hazards (e.g. low temperature cryogen, high pressure compressed gas).

- Applies to all USC personnel who work with hazardous materials or who supervise others who work with hazardous materials. This includes but is not limited to staff, faculty, employees, students, volunteers, visiting scholars, teaching lab managers, and teaching assistants.
- Shall be implemented by the USC Chemical Hygiene Officer (CHO) and the Office of Environmental Health and Safety (EH&S), with assistance, where appropriate, from safety committees, School- or Departmental-level safety officers, and other stakeholders.
- Shall be reviewed and evaluated for effectiveness by EH&S, at least annually, and updated as necessary (<u>8 CCR §5191 (e) (4)</u>).

In addition to EH&S safety resources (CHP, fact sheets, website, training), laboratory-specific Standard Operating procedures (SOPs), lab-specific training materials, and lab-specific safety rules are also required for safe laboratory operation. Lab-specific safety is ultimately the responsibility of the Principal Investigator (PI). Procedures posing unusually high potential hazards may also require approval or guidance from the Chemical Hygiene Officer (CHO). The CHO can be reached at <u>labsafety@usc.edu</u>.

Research groups that use biological materials, radioactive materials, lasers, and/or workshop equipment can seek additional guidance from the USC <u>Biosafety Manual</u>, <u>Radiation Safety Manual</u>, <u>Laser Safety Manual</u>, or <u>Shop Safety Manual</u>, as well as the USC <u>EH&S website</u>.

Sources of Safety Information

There is a definite hierarchy of information sources to consider when making decisions about safety, including decisions about what to include in this CHP. The hierarchy is based first on whether an information source has force of law, and second, how authoritative and well-reviewed the information source is, and thus how accurate, reliable, and conforming to best practice it may be presumed to be. The hierarchy may vary somewhat in specific cases, but is usually as illustrated in Figure 1.1 and as explained in the following paragraphs.



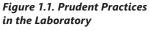
Figure 1.1. Basic hierarchy of sources of safety information.

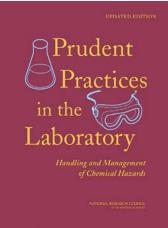
Hierarchy of Sources, With Notable Examples

The following list gives more information about the hierarchy of sources of safety information, from most to least authoritative, with specific important examples:

- 1. Codes (regulations), promulgated by regulatory bodies. Codes have the force of law and adherence to codes is non-optional. For general and chemical laboratory safety at USC, the following are some of the key codes:
 - a. Cal-OSHA Title 8 regulations (<u>https://www.dir.ca.gov/samples/Search/query.htm</u>)
 - i. §5191. Occupational Exposure to Hazardous Chemicals in Laboratories (https://www.dir.ca.gov/title8/5191.html)
 - ii. §3382. Eye and Face Protection (http://www.dir.ca.gov/title8/3382.html)
 - iii. §5162. Emergency Eyewash and Shower Equipment (https://www.dir.ca.gov/title8/5162.html)
 - iv. §5194. Hazard Communication (https://www.dir.ca.gov/title8/5194.html)
 - v. Article 110. Regulated Carcinogens (http://www.dir.ca.gov/title8/sb7g16a110.html)
 - b. California Proposition 65 carcinogens and reproductive toxicants (<u>https://oehha.ca.gov/</u> proposition-65/proposition-65-list)
 - c. Los Angeles City Fire Code (<u>http://www.lafd.org/fire-prevention/fire-code</u>)
- 2. Formal standards and official guidelines from generally recognized professional associations, industry bodies, non-profit standards organizations, and government agencies. Standards do not intrinsically have force of law, but some are given force of law by being specifically referenced in codes; however, all standards, whether mandatory or not, represent an accepted source of best practice which should be followed. Some organizations publish safety guidelines, which are also a valuable source of best practice. Relevant standard/guideline-promulgating bodies include:
 - a. Cal/OSHA guidelines (Note: Distinct from regulations)
 - Available publications, guidelines, and fact sheets (<u>http://www.dir.ca.gov/dosh/puborder.asp</u>).
 - *ii. Guide to the California Hazard Communication Regulation* (<u>www.dir.ca.gov/dosh/dosh_publications/hazcom.pdf</u>)
 - b. OSHA publications, guidelines, and fact sheets (<u>https://www.osha.gov/pls/publications/</u> publication.AthruZ?pType=AthruZ)
 - c. National Fire Protection Association (NFPA; http://www.nfpa.org/codes-and-standards)
 - i. NFPA 45 *Standard on Fire Protection for Laboratories Using Chemicals* (very useful key reference)
 - d. American National Standards Institute (ANSI; <u>http://webstore.ansi.org/</u>). Information is not free, but can often be obtained via the USC libraries subscription to the Techstreet[™] Store standards database. (Safety Eyewear, ANSI/ISEA Z87.1-2015; safety eyewash/showers ANSI/ISEA Z358.1-2014; workplace first aid kits ANSI/ISEA Z308.1-2015.).

- e. National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards (https://www.cdc.gov/niosh/npg/). Provides highly authoritative information on exposure hazards and appropriate respirators. Although the NIOSH exposure limits are not legally binding, they should be followed for all materials, except in cases where there is lower Cal/OSHA PEL, which should be followed instead.
- f. American Chemical Society (ACS; official ACS publications, not simply journal articles)
 - i. Laboratory hazard identification and evaluation (http://tiny.cc/acs-labHaz-ID-eval)
 - ii. Creating Safety Cultures in Academic Institutions (http://tiny.cc/acs-acad-safT-cult)
 - iii. Classroom chemical safety (<u>https://www.acs.org/content/acs/en/education/policies/safety.</u> <u>html</u>)
 - iv. Various resources (<u>https://www.acs.org/content/acs/en/about/governance/committees/chemicalsafety.html</u>)
- g. National Research Council (NSF; publishes the useful, authoritative, comprehensive, and free pdf book *Prudent Practices in the Laboratory* (See Figure 1.1) <u>https://www.ncbi.nlm.nih.gov/books/NBK55878/pdf/Bookshelf NBK55878.pdf</u>).
- h. Official safety information from other states
 - New Jersey Right to Know Hazardous Substance Fact Sheets (http://web.doh.state.nj.us/rtkhsfs/indexfs.aspx)
- If a safety question is not resolved or covered by the authoritative information sources mentioned above, or the question is too specific to be covered by those sources, then recourse can be had to:





Source: NRC/NSF

- a. Standard practice, as determined from:
 - i. Peer-reviewed journal articles
 - 1. Journal of Chemical Education (http://pubs.acs.org/journal/jceda8)
 - 2. Current Protocols series of journals (https://currentprotocols.onlinelibrary.wiley.com/)
 - a. Article on chemical safety, and safety and disposal of some highly hazardous chemicals used in biochemistry and related disciplines (<u>http://onlinelibrary.wiley.</u> <u>com/doi/10.1002/0471142956.cy0304s36/pdf</u>)
 - b. Series of articles on essential laboratory techniques and safety in biochemistry and related disciplines http://onlinelibrary.wiley.com/book/10.1002/9780470089941/toc
 - 3. Newer experimental procedures, which incorporate safety warnings.
 - ii. Other universities' safety information.

- iii. Safety information from US government labs
 - National Institutes of Health, Division of Occupational Health and Safety, chemical safety website (<u>https://www.ors.od.nih.gov/sr/dohs/safety/laboratory/chemicalsafety/</u> <u>Pages/default.aspx</u>)
- iv. General information from professional societies
 - American Chemical Society (ACS) internal resources and links to external resources (USEFUL) <u>https://www.acs.org/content/acs/en/education/policies/safety/chemicalhealth-and-safety.html</u>
 - 2. C&EN Safety (https://cen.acs.org/topics/safety.html)
- v. General safety information from a reputable company, e.g., HF safety and first aid information from Honeywell (<u>https://www.honeywell-hfacid.com/wp-content/uploads/2014/06/2734-Medical-Treatment-for-HF-Acid-Exposure_v7-WEB.pdf</u>) and Calgonate ® (<u>http://www.calgonate.com/safety_info.php</u>).
- vi. Manufacturers operating manual, for potentially hazardous equipment.
- b. Information about specific materials:
 - i. Safety information from the manufacturer or supplier (e.g., Safety Data Sheet (SDS)). NOTE: Not all SDS information is consistent or high quality across vendors. Source SDSs from reputable vendors rather than from random websites that turn up in internet searches. The following reputable sources provide high quality SDSs that are free to the public:

<u>Alfa Aesar</u>	Millipore Sigma*	TCI America
<u>Airgas</u> (gases)	<u>Linde</u> (gases)	<u>Matheson</u> (gases)

* High-quality SDSs available online for a myriad of chemicals, including all common and almost all uncommon laboratory reagents. Millipore Sigma also has SDSs for a select number of gases.

- ii. Links to other sources for more obscure SDSs may be found at <u>http://www.ilpi.com/msds/</u> index.html and <u>https://blink.ucsd.edu/safety/resources/SDS/sources/index.html</u>.
- c. Reliable foreign information sources:
 - i. UK Health and Safety Executive (HSC; http://www.hse.gov.uk/)
 - Royal Society of Chemistry (RSC; <u>http://www.rsc.org/learn-chemistry/collections/health-and-safety</u>)
- d. Books on lab and chemical safety:
 - *i. CRC Handbook of Laboratory Safety* (5th edition; available from the USC Science and Engineering Library, call number QD51 .C73 2000).
- 4. In the absence of authoritative safety information, laboratory personnel may call upon the professional judgment of themselves, their colleagues, their PIs, departmental safety staff, and the staff of EH&S.

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Regulatory Requirements

In the US, employee safety is regulated at the Federal level by the Occupational Safety and Health Administration (OSHA); however, states are permitted to regulate employee safety themselves, provided state regulation is at least as strict as the Federal standards. In California, employee safety is regulated by the Division of Occupational Safety and Health (DOSH), which is more commonly called Cal-OSHA or Cal/OSHA. The regulations which Cal-OSHA enforces are to be found in Title 8 of the California Code of Regulations (CCR).

Chemical usage in research laboratories is very different from industry. For example, dozens of different chemicals in small quantities may be used in a lab in a single day, whereas an industrial process may use multi-ton quantities of a small number of chemicals and use the same chemicals for the life of the process, which may be years. To be able to regulate chemical safety in research labs, but without making it impractical for labs to operate, Cal-OSHA clearly distinguishes laboratory from production chemical usage, and principally regulates the former through a key standard, *"Occupational Exposure to Hazardous Chemicals in Laboratories"* (<u>8 CCR §5191</u>).

A key requirement of 8 CCR §5191 is that employers produce and implement a Chemical Hygiene Plan (CHP). The regulations define a CHP as follows: "A written program developed and implemented by the employer which sets forth procedures, equipment, personal protective equipment and work practices that: 1) are capable of protecting employees from the health hazards presented by hazardous chemicals used in that particular work place and; 2) meets the requirements of subsection 5191(e)." The stated subsection then specifies the required minimum contents of the CHP, which are as follows:

- (A) Standard operating procedures relevant to safety and health considerations to be followed when laboratory work involves the use of hazardous chemicals;
- (B) Criteria that the employer will use to determine and implement control measures to reduce employee exposure to hazardous chemicals including engineering controls, the use of personal protective equipment and hygiene practices; particular attention shall be given to the selection of control measures for chemicals that are known to be extremely hazardous;
- (C) A requirement that fume hoods comply with Section 5154.1, that all protective equipment shall function properly and that specific measures shall be taken to ensure proper and adequate performance of such equipment;
- (D) Provisions for employee information and training as prescribed in subsection 5191(f);
- (E) The circumstances under which a particular laboratory operation, procedure or activity shall require prior approval from the employer or the employer's designee before implementation;
- (F) Provisions for medical consultation and medical examinations in accordance with subsection 5191(q);

- (G) Designation of personnel responsible for implementation of the Chemical Hygiene Plan including the assignment of a Chemical Hygiene officer and, if appropriate, establishment of a Chemical Hygiene Committee; and
- (H) Provisions for additional employee protection for work with particularly hazardous substances. These include "select carcinogens," reproductive toxins and substances which have a high degree of acute toxicity. Specific consideration shall be given to the following provisions which shall be included where appropriate;
 - 1. Establishment of a designated area;
 - 2. Use of containment devices such as fume hoods or glove boxes;
 - 3. Procedures for safe removal of contaminated waste; and
 - 4. Decontamination procedures.

3.0

Roles and Responsibilities

USC has an official Injury and Illness Prevention Policy which explicitly lays out the health and safety roles and responsibilities of the various members of the USC community (<u>https://policy.usc.edu/injury-and-illness-</u> <u>prevention/</u>). **It is recommended that all USC persons (especially PIs and other supervisory personnel) read and understand this policy.**

Research Safety Oversight Committee (RSOC)

The RSOC:

- Has the following members:
 - Vice-President for Research Chair
 - EH&S Director
 - Director of Research Compliance
 - Chairpersons of other USC-wide safety committees
 - USC senior managers
- Provides high-level oversight of all aspects of health and safety at USC.
- Facilitates communication between the specialized safety committees:
 - Institutional Biosafety Committee (IBC)
 - Radiation Safety Committee (RSC)
 - Campus-Wide Chemical Safety Committee (CCSC)
- Reports administratively to the USC Provost and President.

Campus-Wide Chemical Safety Committee (CCSC)

The CCSC:

- Reviews, approves, and suggests improvements to EH&S policies, programs, guidelines, and activities related to general and chemical laboratory safety.
- Reviews laboratory incidents or accidents that occur at USC (except incidents falling under the purview of other safety committees such as the IBC or RSC).
- Reviews the adequacy of response of EH&S, PIs, Departments, or Schools to laboratory incidents or accidents.
- Reviews safety controls and management of high-hazard facilities, or proposed potentially highly hazardous research.
- Provides high-level enforcement of laboratory safety standards in the event of egregious non-compliance or refusal to cooperate with EH&S.
- Refers important items to the RSOC via the CCSC Chairperson, who is also an *ex officio* RSOC member.

Other Safety Committees

Departments and Schools are encouraged to set up their own internal safety committees. Typically, such a committee might meet three or four times during each academic year and be concerned with subjects such as:

- Overseeing instructional laboratory (and workshop) incident recordkeeping, including reviewing specific incidents and recommending appropriate action (e.g. modifying experiments by substituting less hazardous chemicals, improving the safety information in lab manuals). [Note: Minor incidents in instructional labs may not rise to the level where EH&S investigates; however, all incidents should be investigated and recorded by the PI and/or manager who oversees the lab.]
- Initiating and overseeing student-led safety initiatives.
- Reviewing Pls' compliance with EH&S recommendations/requirements, especially after an incident which EH&S has investigated, or after a laboratory safety inspection uncovers serious findings.
- Encouraging emergency planning at the research group level.

Office of Environmental Health & Safety

The Office of Environmental Health and Safety is responsible for managing and implementing the Laboratory Safety Program, which covers general lab safety and chemical safety. The EH&S Chemical Hygiene Officer and laboratory safety staff are responsible for day-to-day oversight of the lab safety program. The organizational structure of EH&S is shown in Figure 1.2.



Figure 1.2. Organization structure of USC EH&S.

Laboratory Safety Subdivision

The USC Laboratory Safety Program is implemented and managed by the EH&S laboratory safety subdivision, consisting of the Chemical Hygiene Officer (CHO) and chemical/laboratory safety specialists and technicians.

The CHO is the primary subject matter expert on laboratory, hazardous materials, and chemical safety related items and may be consulted during risk assessments of new or existing projects.

The laboratory safety subdivision:

- Assists in the development of general policies for laboratory safety.
- Develops and distributes information related to laboratory safety.
- Evaluates equipment and physical facilities.
- Evaluates operational techniques and procedures for hazardous materials and physical hazards.
- Conducts risk assessments when required.
- Conducts training programs in lab safety.
- Implements an inspection program to ensure that laboratory facilities and procedures are in place, in accordance with USC policies and all applicable laboratory safety regulations, and that safe work practices are being followed by laboratory personnel.
- Responds to emergencies, or assists Hazmat Division in emergency response, as appropriate.
- Investigates laboratory safety incidents and provides recommendations.

EH&S Inspections

Laboratory safety specialists schedule and conduct annual safety inspections of USC laboratories using the <u>General Lab Inspection Checklist</u> and <u>PPE Inspection Checklist</u>. EH&S works with PIs, Lab Managers, and lab staff to:

- Identify and remedy potential hazards. A report of all findings, resolutions, and recommendations will be made available within 1 business day. Research labs will have five (5) to twenty (20) business days to remediate the findings depending on their severity.
- Remediation of hazards outside the PI's direct responsibility (e.g. provision of safety showers, repair of building infrastructure) will be referred to FPM or other appropriate personnel.
- EH&S will schedule a follow up inspection to confirm laboratory compliance and report finding as corrected (see <u>Laboratory</u> <u>Inspection Process Flow Chart</u>).
- Labs designated by EH&S as high hazard will be subject to safety inspections twice a year. A definition of high hazard labs is given in <u>Appendix A</u>.

EH&S also conducts inspections focusing on appropriate lab attire and PPE. All laboratory buildings on the HSC and UPC campuses are subject to unannounced PPE compliance inspections.

Principal Investigator (PI)

The PI has primary authority and responsibility for the safety and management of his/her laboratory, including primary authority and responsibility for hazardous materials storage and use. The PI is obligated to comply with <u>university safety policies</u> and all applicable regulations.

The CHO and EH&S laboratory safety staff will assist the PI to meet safety and regulatory requirements. For satisfactory laboratory safety, EH&S **strongly** recommends that PIs institute a safety management structure within the research group. This is further discussed under <u>Group Safety Management and</u> <u>Safety Culture</u> in Section 4.0.

The PI's additional responsibilities include:

- Providing instruction and training on safe and proper safety practices to all persons working within the Pl's area.
- Determining and documenting appropriate personal protective equipment (PPE) needed for each procedure.
- Maintaining control of the hazardous materials.
- Providing necessary equipment for safe work with hazardous materials.
- Properly labeling all areas where hazardous materials are stored or handled.
- Notifying EH&S of:
 - Accidents/incidents involving or suspected of involving hazardous materials.
 - Any significant changes in lab design or procedures.
 - Plans to relocate the lab or leave the university.
- Keeping online chemical inventory and online personnel records up to date (see <u>EHSA</u> or <u>RSS</u>).
- Conducting and documenting lab-specific safety training.
- Providing <u>annual laboratory safety refresher</u> <u>training</u> to all staff working with hazardous

materials.

- Providing easy access to Safety Data Sheets (SDSs).
- Preparing Standard Operating Procedures (SOPs), including safe work practices for all routine processes involving hazardous materials, hazardous procedures, or hazardous equipment.¹
- Holding safety meetings regularly.
- Providing emergency procedures for laboratory personnel. These procedures must include the names and telephone numbers of key lab personnel (e.g., Lab Manager, Safety Officer) to be contacted in case of emergency. These procedures shall be prominently posted in work areas where hazardous materials are used.

Research Staff

Research staff work under the supervision of a PI. Although PIs have overall management responsibility for staff under them, the staff also have their own responsibilities, which include:

- Following safety instructions from the PI, PI's designee (e.g., Lab Manager, Group Safety Officer), EH&S, and from School/ Departmental safety staff.
- Reading, understanding, and following the USC Chemical Hygiene Plan.
- Attending General Laboratory Safety training provided by EH&S, which must be successfully completed before starting work in the laboratory.

1 EH&S has a variety of model SOPs available on its <u>Standard Operating Procedures</u> web page including templates for creating labspecific SOPs.

- Attending lab-specific safety training provided by the PI or PI's designee (e.g., Lab Manager).
- Reading, comprehending, and following appropriate SOPs and SDSs when working with hazardous materials.
- Researching safety information, including downloading and reading SDSs, and performing a risk assessment as an integral part of the process of planning new experimental work.
- Knowing where SOPs and SDSs are located or how to access them.
- Knowing the locations of eye wash and safety shower stations, first aid kits, fire extinguishers, fire alarm pull stations, circuit breaker boxes, gas shut-off valves, emergency stop buttons, and other safety related items throughout all labs and offices in which they work.
- Knowing egress routes and assembly locations.
- Following proper emergency procedures if an accident or incident happens when handling hazardous materials.
- Reporting any unsafe practices or concerns to the PI, and if necessary, also to School/ Departmental safety staff, and/or EH&S.
- Notifying EH&S if any accident or incident happens that includes hazardous materials, physical hazards, or chemical hazards.

Training Requirements

General Laboratory Safety (GLS) Training

Prior to beginning any laboratory work, all personnel who work in research laboratories are required to take the <u>General Laboratory Safety Training (GLS)</u> offered by EH&S. This includes undergraduates or volunteers placed in research labs.

GLS is offered as a live, online session or a selfdirected course in Trojan Learn. Extra live online sessions may be scheduled at busy periods of the year, or by special request from Schools or Departments. The GLS training covers various topics including but not limited to:

- Injury and Illness Prevention Program (IIPP)
- Hazard Communication and "Employee Right to Know"
- Classes of hazardous materials
- How to work with different classes of hazardous materials safely

- Safety Data Sheets
- Labeling and signage
- Personal protective equipment (PPE)
- General fire safety and emergency procedures.

GLS attendees who complete the initial General Lab Safety Training (live online session or Trojan Learn) must attend a GLS Meet & Greet session. This is a one-time requirement.

The GLS Meet & Greet is a workshop that:

- Introduces new USC researchers to EH&S
 Research Safety staff.
- Promotes the exchange of safety information, anecdotes, and/or experiences between colleagues.
- Connects researchers with EH&S staff to assist in addressing questions or concerns.

Lab-Specific Training

The materials, equipment, and procedures utilized in every laboratory are different; therefore, safety training specific to the conditions of a particular laboratory must be given to incoming personnel.

The level of lab-specific training must be appropriate to the prior experience incoming personnel bring with them. For example, an undergraduate joining a lab for summer research will likely require much more lab-specific training than an incoming postdoc. Lab-specific training can be given by the PI or by experienced laboratory personnel designated by the PI.

The PI should keep internal training records, which may take two forms, as appropriate for the specific training given. One type of training record is a signature sheet appended to an SOP, whereby the trainer and trainee sign and date to affirm that the trainee has read, understood, been trained upon, and agrees to follow, the contents of the SOP.

The second, more general type of training record, more suited for training on basic, lower-hazard operations, is a list summarizing topics trained upon (e.g. *"The trainee was trained upon the following basic laboratory procedures..."*), signed and dated by the trainer and trainee. For this type of training record, if the incoming person is trained over a definite period of time, that should be reflected on the training record (e.g. *"Trainee [name] was trained in the following basic laboratory procedures by trainer [name] [position] in the laboratory of [PI name] between the dates of [start date] and [end date]...").* Lab-specific training records should be kept by the PI and not sent to EH&S; however, EH&S may request records during a safety inspection or incident investigation. SOPs and training record templates will be made available on the EH&S website.

NOTE: Research staff may not conduct experimentation with high hazard materials (e.g. pyrophoric, explosive, highly reactive, highly acutely toxic, etc.) unless thoroughly trained on specific procedures by the PI, or by designated senior laboratory staff, to the satisfaction of the PI.

Annual Refresher Training

USC requires all PIs with labs to provide their staff with annual refresher safety training. Under the current system, all PIs are emailed an official memo in January providing details of subjects to be covered in the refresher, together with a training record form. Unlike for routine lab-specific training, EH&S requires a copy of the refresher training record to enter in the central database. Instructions for how to submit the information is included on the training record form.

For more information, refer to the <u>Annual Safety</u> <u>Refresher Training Memo</u>.

Undergraduate Teaching Labs

Undergraduates attending instructional laboratories as part of their academic program are not required to attend GLS training, although they may attend on a voluntary basis. This is due to instructional labs being closely supervised and only containing low level and well controlled hazards. It is recommended for managers of undergraduate labs which use hazardous materials, and for teaching assistants (TAs) in such labs, to attend GLS training. It is the responsibility of Departments running teaching labs to provide appropriate safety information and training to undergraduates attending the labs. This training may be provided via the responsible PIs and teaching lab managers, and should be broadly overseen by the Department or School Safety Committee. Typically, this type of training may be done through a combination of written safety instructions, in-person safety training given at the beginning of the lab course, refresher safety talks, and safety exercises (e.g. having to look up and compare safety data sheets (SDSs)).

The department should retain records (e.g. through signature sheets) of trainings attended in person, and to confirm that written safety instructions distributed to students have been read and agreed to.

Other Training

GLS training is a fundamental requirement which must be met by any individual wishing to perform any research laboratory activity; however, it is not necessarily the only training requirement.

Certain types of laboratory or research also mandate specific trainings offered by EH&S in the areas of radiation safety, laser safety, blood-borne pathogens, biosafety, workshop safety, controlled substances, and shipping of biological materials. Work with animals may require DAR (Department of Animal Resources) training in animal care and use.

Consult the <u>Safety Training Matrix for Research</u> <u>Personnel Guide Sheet</u> (see Figure 3.1) and/or the <u>Training Catalog</u> for further information. All persons using a respirator are **required** to enroll in the EH&S respirator program which includes a training component. Consult the <u>Respiratory</u> <u>Protection Program Fact Sheet</u> (see Figure 3.2) for further information.

Contact <u>safetytraining@usc.edu</u> for more information on training courses and schedules. Contact <u>firesafety@usc.edu</u> (Fire Safety and Emergency Planning) for information on fire extinguisher training.

Injury and Illness Prevention Plan (IIPP)

Under California Law, organizations of ten or more persons are required to have an effective written IIPP. To increase manageability of the IIPP program, USC is subdivided into smaller units, each of which customizes and implements an IIPP based on a template provided by EH&S.

Contact your department or school for a copy of your local IIPP and the identity of your IIPP Administrator. For further information, refer to the EH&S IIPP webpage (https://ehs.usc.edu/occhealth/injury-prevention/iipp/), and the fact sheet (http://tiny.cc/usc-iipp-fs).

Figure 3.1. Safety Training Matrix for Research Personnel



Figure 3.2. Respiratory Protection Program Fact Sheet





Hazard, Risk, and Safety Management

In the context of safety, the terms *hazard* and *risk* are not interchangeable. The authoritative safety source *Prudent Practices in the Laboratory* (2011, page 2) contains a clear exposition of the meaning of *hazard* and *risk*, and it is worth quoting in full:

"With regard to safe use of chemicals, the committee distinguishes between hazard, which is an inherent danger in a material or system, and the risk that is assumed by using it in various ways. Hazards are dangers intrinsic to a substance or operation; risk refers to the probability of injury associated with working with a substance or carrying out a particular laboratory operation. For a given chemical, risk can be reduced; hazard cannot."

The object of safety management is to eliminate all hazards which can be eliminated, and for the remaining hazards which cannot be eliminated, to adequately reduce, control, and monitor the risk they pose.

Hierarchy of Safety Controls

Background and Application of the Hierarchy

The hierarchy of safety controls is a fundamental set of simple rules which lay out the relative reliability and effectiveness of possible methods of managing hazards. It is important to understand the hierarchy of safety controls and use them as the basic framework for planning safe laboratory work.

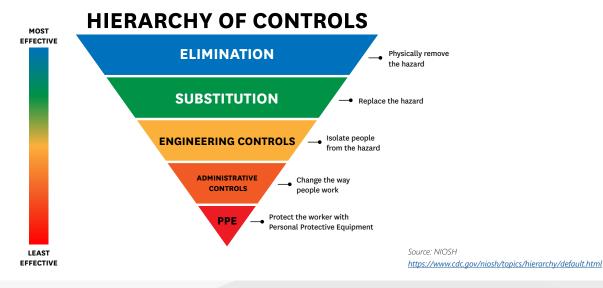


Figure 4.1. Hierarchy of Safety Controls

There is a universally applicable hierarchy of generalized safety controls, which are, ranked from most to least effective (see Figure 4.1):

- **Elimination** of the hazardous substance, process, activity, or equipment.
 - Example: Deciding not to do a specific experiment due to the hazards being too great.
- Substitution i.e. a hazardous substance, process, activity, or piece of equipment is replaced by something less hazardous.
 - Example: Modifying a procedure to use molecular sieves for drying instead of an alkali metal.
- Engineering Controls. Engineering controls are physical safety systems designed to operate substantially or completely independently of worker behavior. Examples include:
 - Belt guards on vacuum pumps.
 - Fume hoods to reduce exposure to toxic materials (see Figure 4.2).
 - A fume hood is the single most important item of safety equipment in most labs which use hazardous chemicals!
 - Glove boxes to prevent air exposure of pyrophoric materials.
 - Biosafety cabinets to reduce exposure to biohazardous materials.
 - Safety interlocks (e.g., to prevent a centrifuge from being opened until the rotor has stopped)





Source: ESCO

- Administrative Controls (including work controls). The distinguishing practice characteristic of administrative controls is that they operate by means of influencing worker behavior. This level of controls includes lab safety rules, training, supervision inexperienced personnel, standard of operating procedures (SOPs), and any work practice which must be followed to avoid a known or predicted hazard. Administrative controls are regarded as less reliable than engineering controls because, unlike the latter, administrative controls are entirely dependent on human behavior for their effectiveness. Furthermore, their effectiveness is a function of the extent to which compliance by workers is monitored and enforced by Pls, lab managers, and other supervisors. Examples of administrative controls include:
 - SOP specifying safer work practices, e.g., diluting sulfuric acid by adding acid to water, never the other way around.

- Written laboratory safety rules, which must be agreed to and signed by new group members.
- Group rule to require individual researchers to download and read SDSs and conduct a risk assessment as part of planning new experiments.
- Proper labeling of hazardous materials (this is also part of *Hazard Communication*).
- Personal Protective Equipment (PPE). PPE is used as the last line of defense in the hierarchy of controls (see Section 8 Personal Protective Equipment for more details). PPE acts to increase personal safety in the event an incident occurs and the other controls prove insufficient (see Figure 4.3).

Examples include:

- Safety glasses
- Goggles
- Face shield (not permitted to be worn alone; goggles/safety glasses must be worn underneath)
- Lab coat (e.g., Nomex, Flame Resistant Treated Cotton)
- Ear plugs / ear muffs.
- Gloves (e.g., chemical resistant / hightemperature / low temperature / cut resistant)
- Respirators (see <u>Respiratory Protection</u> <u>Program Fact Sheet</u>; special rules apply)

Note that in some schemes, elimination and substitution are included in the category of engineering controls, giving only three categories instead of five.



is most appropriate.

Enforcement and Documentation of Safety Controls

Administrative controls should always be documented for quality control and accountability purposes. Reliance on human memory and human nature for effectiveness is ineffective as administrative controls tend to lapse unless the responsible manager (e.g., PI) ensures regular reiteration of rules, refresher safety training, and safety meetings, and takes active measures to monitor and enforce compliance.

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Figure 4.3. Articles of PPE

Note that although engineering controls and PPE are not administrative controls *per se*, ensuring that lab personnel consistently, appropriately, and correctly use engineering controls and PPE falls under administrative controls. Therefore, engineering control and PPE policy, procedures, training, instances of non-compliance, and enforcement measures should be documented.

Group Safety Management and Safety Culture

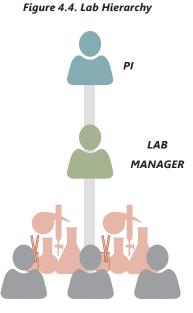
A robust and cooperative safety management and culture involves safety consciousness, accountability, organization, and education. All staff must recognize that personal safety is dependent on responsibility, accountability, and teamwork. Internal SOPs, safety plans, group safety meetings, and annual lab safety refreshers are used to reinforce the laboratory's safety culture.

Safety Management Structure

To achieve and maintain satisfactory standards of laboratory safety, it is strongly recommended that PIs institute a formal management structure within their groups, to facilitate the two-way flow of safety-related information, to enable personnel to be held accountable, and to explicitly delineate responsibilities (see Figure 4.4).

There are two basic models for group safety management:

- 1. Permanent Lab Manager who spends most of his/her time in the lab and who:
 - a. Is appointed Safety Officer by the PI.
 - b. Keeps an eye on the safety behavior of other personnel and holds them accountable when deviation from safety rules is observed.
 - c. Keeps the PI informed of all safety matters.
 - d. Delegates and manages all routine safety-related lab activities.
- 2. When there is no permanent Lab Manager, the PI should appoint lab personnel to positions of defined responsibility for safety. The positions, which may be rotated on an annual basis (or twice yearly for the more time-consuming jobs) may include:
 - a. Safety Officer, who keeps an eye on the safety and labhousekeeping behavior of all other personnel and reports all safety matters to the PI.
 - b. Waste Lead, who holds personnel accountable for the proper segregation, storage, and labeling of hazardous waste, and who submits waste pickup requests.



RESEARCH PERSONNEL

- c. Inventory Lead, who ensures the chemical inventory is maintained, that all hazardous materials are appropriately stored, that time-sensitive materials are not over-aged, and oversees all group members for a collaborative annual reinventory.
- d. Other delegated roles as appropriate for the lab, e.g., maintainer of a specific item of equipment, person who defrosts the freezer, etc.

Models one and two are not mutually exclusive. Even in the presence of a permanent lab manager, other safety related formal roles can be created.

Group Safety Rules

PIs should institute written group safety rules and expectations. It is suggested that new group members be required to sign the rules as one of the conditions of lab access. Safety rules appropriate to the lab can be developed from the contents of this CHP and from EH&S online resources, including guide sheets. It is also suggested that rules incorporate a lab security policy, which should include a prohibition on leaving labs unlocked when not occupied.

Personnel exiting research groups without first taking responsibility for their hazardous materials and equipment is a considerable safety hazard and a chronic contributor to poor laboratory housekeeping. Implementing strong group rules against this practice is a valuable aid in preventing hazardous conditions from developing in labs. The following is an example of the form such rules may take: Before leaving the research group, a member is required to take responsibility for their accumulated impact on the laboratory by doing the following, to the satisfaction of the PI, or PI's designee:

- 1. The member shall determine which of their samples and chemicals the PI wishes to keep and shall inventory said samples and chemicals and place in safe storage. The member shall arrange safe disposal for all their other samples and chemicals.
- 2. The member shall clean, decontaminate, and put away all their equipment and apparatus, clean and decontaminate all their work areas, and leave all their storage areas in good order.

Group Emergency Plan

It is strongly recommended that labs maintain an emergency action plan in the event of a disaster (earthquake, fire, flood, etc.). Include:

- Evacuation routes and assembly points outside.
- Emergency generators for critical equipment.
- Designated personnel to shut down equipment, compressed gas supplies, etc.
- Locations of the gas shut off valves and circuit breakers and record on the lab floor plan.
- Designated personnel to closely examine all glass apparatus, fridges, freezers, and chemical storage areas after a small to moderate earthquake, to ensure no breakages are missed. (After a significant earthquake, lab buildings would be closed to re-entry pending inspection by Hazmat personnel.)
- Phone tree, to gather information to account for all personnel, and to distribute information, e.g., that the building is closed.

It is highly advisable for research groups to plan for the possibility of an earthquake; this is covered in <u>Appendix D</u>, which should be read by all laboratory personnel.

Pls should ensure the recommendations of Appendix <u>D</u> are effectively implemented in their research groups, and earthquake awareness and safety should be made a part of regular group safety meetings and safety training.

When the PI is Away

If a PI knows they are going to be unavailable due to vacation, travelling, or any other reason, they should plan in advance to ensure their research group is adequately supervised.

The PI who is to be absent should gain formal agreement from a second PI to act as the responsible supervisor during the absence of the first PI. The group members should be notified in advance of the dates during which their PI will be absent and should be notified of the supervisory arrangements which have been made to cover the absence.

A PI who has agreed to cover group supervision during the absence of a colleague need not be expected to be involved in day-to-day lab management, which the group members should be able to handle, especially if they are in communication with the absent PI. However, the PI who is acting as temporary cover would be expected to act in place of the absent PI in the event of an incident, emergency, or other unforeseen circumstance which requires immediate action.

Safety Meetings

Pls should regularly incorporate safety topics into group meetings. For the purposes of maintaining internal training records, the safety topics covered should be recorded, and there should be a sign-in sheet to record meeting participants and date of the training.

Working Alone and/or Outside Normal Working Hours

Due to the hazards inherent in many laboratory activities, it is very important for PIs to institute and enforce effective rules governing when it is or is not appropriate for researchers to work in labs alone and/or outside normal working hours. USC circulates an official memorandum each December before the winter recess begins, to remind personnel of safe work practices. Although special emphasis is placed on this issue during the winter recess, the basic message of the memo is applicable year-round:

- "For research that continues beyond normal business hours and after regularly scheduled closure times, research staff and/or students should not work alone under any circumstance on experimental procedures involving hazardous chemicals, biohazardous materials, or high physical hazards."
- "...it is especially critical that researchers take extra precautions during off-hours or periods of campus closure when the number of individuals present in laboratories is greatly diminished."

• "While it is always preferable for research staff and/or students to work with a colleague, exceptions may be made for low-risk research activities if the PI or Supervisor: (a) verifies that each research staff member or student fully understands emergency and standard operating procedures, (b) has access to and utilizes all required PPE, and (c) has ready access to an effective communication system that consists of a two-way radio, telephone, or cellular phone with adequate reception."

It is advised to read the full memo (see <u>Appendix E</u>). <u>Prudent Practices</u>, (section 2.C.2, page 17-18) also reinforces the message that personnel should not perform hazardous laboratory work alone. PIs and research personnel should:

 Plan ahead to maximize work during regular business hours and minimize working at irregular hours.



- Coordinate to ensure active surveillance of personnel (through regular visual or verbal communication) working alone in laboratories:

 (a) after business hours and/or (b) at remote locations during and after business hours.
- Suspend use of hazardous substances and operations when alone.
- NEVER work with hazards while fatigued.

Internal Safety Audits

It is recommended for research groups to carry out regular internal safety audits e.g., use EH&S' <u>Laboratory Inspection Checklist</u> and the <u>Lab Self-</u><u>Inspection Guide</u>. These can be performed by the PI, laboratory manager, and/or research staff. This is an effective way of keeping on top of various issues including equipment maintenance, chemical inventory, housekeeping, hazardous materials labelling, hazardous waste storage and disposal practices, and review of training records and SOPs.

Working in Other PIs' Labs

It is common for research groups to share resources. Many PIs have group rules governing non-group members borrowing or using equipment or materials, and it is advisable for PIs who have not already done so to develop such rules. It is the responsibility of PIs to communicate rules to lab personnel, and it is the responsibility of lab personnel to abide by those rules, and to ask for clarification when in doubt.

From the perspective of safety, the following is essential:

- No researcher should perform any experimental procedure or use any valuable or potentially hazardous instrumentation or equipment in the lab of another PI without knowledge and approval of their own PI and the other PI, and without receiving lab-specific training to the satisfaction of the other PI.
- Potentially hazardous material or equipment should not be physically transferred from the lab of one PI to the lab of another PI unless both PIs are satisfied that appropriate training and safety controls are in place.

It is recommended that access rules be documented and signed by all parties, and that signed logs be kept of all hazardous substances or items that are lent or borrowed.

Basics of Lab Facilities and Equipment

New Lab Builds / Lab Remodeling: Design for Safety

During the planning and construction phases of laboratory buildings, or lab renovations/remodels, project managers are responsible for ensuring that all infrastructure conforms to all applicable building codes, plumbing/mechanical/electrical codes, fire codes, Cal-OSHA codes, environmental codes, and all standards (e.g., ANSI, NFPA) incorporated into the codes by reference.



Project managers should ensure that they fully understand the intended end-use of the space to be constructed/renovated and should ensure they engage the requisite laboratory safety design and engineering expertise early in the design process.

EH&S strongly recommends that in addition to being code-compliant, new infrastructure is also fully compliant with best practice as summarized in the *Laboratory Safety Design Manual* (University of California). It is also recommended that lab design conforms to recognized standards (e.g., NFPA 45 (2015)) even when not incorporated into codes by reference. EH&S is available to consult on specific safety-related questions on proposed research infrastructure. Email <u>labsafety@usc.edu</u> with questions or concerns.

Ingress, Egress, Doors, and Lab Security

Ensure that pathways leading to exit doors are clutter-free and have a minimum of 36" clearance.

If it is proposed to block access to any door, for example by the placement of large equipment, taking the door out of use will need to be approved by Fire Safety and Emergency Planning to ensure that blockage of the specific door is permitted by fire code.



Note that in most cases, blocking of doors is strictly prohibited; it is only in the rare case of very small rooms with more than one exit that it may be allowed on a case-by-case basis. Non-functional doors should be clearly signed "not an entrance" on a corridor side and "not an exit" on any side adjoining a room. (If the non-functional door is between two rooms, both sides should be signed "not an exit".)

To allow safe egress in an emergency, the following should be adhered to:

- There must be no items in the vicinity of doors which may fall in an earthquake and block the door or prevent the door from opening.
- Doorways, corridors, and stairwells should at all times be free of flammables, combustibles, trip hazards, obstructions, and items which may fall.
- Egress pathways within labs must be free of obstructions and trip hazards. Configure labs so that storage of combustibles, flammables, and other hazardous materials is not in the vicinity of egress pathways.

The doors of laboratories should be kept closed whether the laboratory is in use or not. This is especially important for laboratories which handle hazardous materials and utilize fume hoods. The reasons for keeping doors closed are as follows:

- Building HVAC systems and fume hoods are adjusted for correct airflow balance with laboratory doors closed. When doors are open, airflow may be affected so as to cause:
 - a. Impaired fume hood operation.
 - b. Loss of laboratory negative pressure. In a correctly air-balanced laboratory building, labs are maintained at a slightly negative pressure relative to corridors, public areas, and offices. Thus, with the door closed, any air leakage flows into the lab and not in the other direction, confining airborne contamination or odor to the laboratory. Building airhandling systems do not develop anywhere near the airflow required to maintain a pressure differential across an open doorway, so as soon as a lab door is opened, all control on the direction of airflow is lost.
- Fire safety. Closed doors are an important barrier to prevent the spread of fire and smoke.
- 3. Security. Opportunistic thieves have been active in USC research buildings and lab personnel have lost computers and personal items as a result. Keeping doors closed will impede the activity of potential thieves. Personnel should develop the habit of closing doors behind them and preferably also locking doors to labs which are to be unoccupied for any length of time.

 a. There is more to security than just closing doors. Lab personnel should also read and understand the Laboratory Security Fact Sheet, <u>http://tiny.cc/usclab-security-fs</u>.

NOTE: It is not acceptable for laboratories to produce nuisance or noxious airborne contamination and then open doors or windows as a way of venting it out of the lab. The solution is to change work practices in order to prevent airborne contamination in the first place.

In cases of accidental release of fumes into the laboratory atmosphere, the lab may need to be vacated (with the door kept closed) until the lab air system has cleared the contamination.

Communications

It is strongly recommended that the following have a hard-wired (landline) phone, preferably mounted on the wall in a conspicuous position near the entrance:

- Laboratories in basements or other areas without cell phone reception.
- Cleanrooms and other facilities where cellphones are either prohibited or not readily accessible.

Other laboratories are recommended to have a hard-wired phone. This is important to enable lab personnel to summon assistance in an emergency without being reliant on personal cell phones which may be unavailable, not charged, or may exhibit poor reception. Communication requirements for laboratory suites, in which a number of small subsidiary rooms branch off from a main lab, may be satisfied by having a hard-wired phone in the main lab.

The telephone number shall be displayed on lab phones. Pls and lab personnel should be aware of the location and phone number of all their lab phones. Lab and office phone numbers should be included in the group emergency plan, and preferably also programmed into group member's cellphones.

Storage and Ceiling Clearance

General Storage

Items shall not be stored in any manner which impedes access to firefighters, or which results in areas which cannot be reached by a stream of water or other extinguishant from a hose or fire extinguisher, or which impedes egress of water from a sprinkler head, or which is hazardously close to a heat or ignition source.

- 315.3 "...Storage of combustible materials shall be separated from heaters or heating elements by distances or shielding so that ignition cannot occur."
- 315.3.8.1 "...A clearance of at least 18 inches (457 mm) shall be maintained between stored materials and lighting fixtures."
- Broad piles of items stacked too close to the ceiling are an unacceptable fire hazard as extinguishant cannot reach the center of the pile in the event of fire. Therefore, broad piles of items (which covers essentially anything not stored in a linear manner along shelves or the top of reasonably narrow cabinets):
 - Shall have a ceiling clearance of at least 2 feet in non-sprinklered areas.

- Shall have a ceiling clearance of at least 18 inches in sprinklered areas.
- Items stored in a linear manner on shelves or along the top of reasonably narrow cabinets may be stored to the ceiling, PROVIDED:
 - A vertical and horizontal clearance of 18 inches is provided around any sprinkler head which lies above the shelf or cabinet, AND
 - Items do not extend more than three feet horizontally from the wall, or two feet horizontally from the centerline of a freestanding shelving unit or cabinet.

Note: Items stacked in large piles in labs may be deemed an "excessive accumulation of combustibles" by EH&S or FSEP and disallowed, on a case-by-case basis, depending on the combustibility, quantity, size of the room, and whether the items are essential or of low importance (e.g. a pile of empty cardboard boxes is usually deemed an "excessive accumulation of combustibles").

Note: Side-wall sprinklers designed to throw a water spray a significant horizontal distance into a room may require additional horizontal and vertical clearance to avoid blocking the spray. Fire Safety and Emergency Planning (FSEP; <u>firesafety@usc.edu</u>) will advise on a case-by-case basis.

Hazardous Materials Storage

As best practice, hazardous materials should not be stored above eye level. However, in labs with limited storage space, it may be necessary to store some hazardous substances above eye level. If this has to be done, the following rules shall apply (in addition to the "General Storage" rules above):

- Flammable liquids, combustible metals, and other substances of high flammability, or which pose an ignition risk, shall have a minimum two foot vertical clearance to the ceiling (whether or not sprinklers are present).
- Seismic safety rules (see 4.12 4.13) also apply, which in summary PROHIBITS the following materials from being stored above eye level:
 - Liquids which are pyrophoric, toxic, corrosive, sensitizers, carcinogens, or reproductive toxicants
 - Solids which are highly acutely or chronically toxic, significantly carcinogenic, highly reactive, or pyrophoric
- Liquids stored above eye level shall be in containers of one liter or less in capacity (see 4.12).

Responsibilities and Adjudication

Either EH&S or FSEP may, in the first instance, use professional judgment to assess the fire risks posed by lab storage practices. If EH&S conducts the initial assessment and the case is complicated, the judgment is not clear-cut, the hazards appear unusually large, or if there is any disagreement between the lab and EH&S, then EH&S will pass the case to FSEP. In all instances, FSEP shall have final jurisdiction.

Equipment Which May Act as an Ignition Source

Equipment which may pose an ignition risk (e.g. heatproducing devices such as hotplates, ovens, furnaces, gas burners) shall have a minimum clearance of four feet between the top of the equipment and the ceiling when the equipment is in operation. (If the equipment is merely being stored in an unpowered state, disconnected from electricity and gas supplies, then the "General Storage" rules, above, are applicable.)

- Exceptions may be granted if the setup is designed to cope with heat in a safe manner.
 - Example: A clearance of less than four feet is permitted between the top of a furnace and a ceiling-mounted exhausted furnace hood constructed of non-combustible materials.
- If fire hazard or heat output is exceptional (e.g. large burners, large high temperature furnaces), EH&S or FSEP (Fire Safety and Emergency Planning) may require a larger ceiling clearance and/or other safety controls such as a fireproof ceiling covering or additional airflow through the room.
 - Before installing extreme heat-output equipment, it may be necessary to utilize the services of a qualified lab design engineer to ensure the proposed setup meets applicable codes and recognized safety standards.
 - Email <u>firesafety@usc.edu</u> for consultation and to determine if a hot work permit is required.

Either EH&S or FSEP may, in the first instance, use professional judgment to assess the fire risks provided by equipment which may pose an ignition risk, and may decide whether an exception be granted, or additional safety controls be required. If EH&S conducts the initial assessment and the case is complicated, the judgment is not clear-cut, the hazards appear unusually large, a hot-work permit may be required, or if there is any disagreement between the lab and EH&S, then EH&S will pass the case to FSEP. In all instances, FSEP shall have final jurisdiction.

Flammable Cabinets and Approved Refrigerators

Laboratories shall have appropriate facilities for storing flammable and combustible liquids (see Figure 4.5). Since the specifications and requirements of flammable cabinets and approved refrigerators are closely tied to their operational use, they are covered in <u>Section 7.0 Chemical Inventory, Storage,</u> <u>and Transport</u>.

Figure 4.5. Flammable Cabinet



Ceilings

Ceiling tiles are part of the fire protection infrastructure of rooms. Laboratory personnel shall NOT:

- Remove ceiling tiles.
- Pierce ceiling tiles with holes or cut them in any way.
- Run tubes or cables in the space above ceiling tiles.

NOTE: Earthquake restraints for objects of any appreciable mass need to be anchored into wall studs and not just drywall.

Seismic Safety

Los Angeles is in a high-risk earthquake zone and lab personnel must be aware of the possibility of earthquake at any time and must plan accordingly. This section provides some basic information on appropriate precautions to ensure items in labs are stored with earthquakes in mind. For important information on earthquake emergency planning and response for laboratory personnel, see <u>Appendix D</u>.

It is important to:

- Store heavy items (e.g., equipment, boxes, supplies, etc.) as low as possible.
- Securely fasten equipment and furniture over 48" tall to the wall or to the floor.
 - Immobile objects can be directly and securely bolted to the wall, or bolted via spacers or brackets if a gap needs to be left between the object and the wall.
 - Items which need to be movable, e.g., equipment carts, should be tethered using chains securely attached to the wall.
 Some system should be provided so that the chains can be attached and detached from the item, for example, by using pairs of chains which go around the item and clasp together using a spring-loaded hook. The chains must not fit the item too loosely or they will be ineffective at preventing falling.

- Items which are extremely wide and deep relative to their height, and which are therefore essentially immune from falling over, are not required to be restrained, although it is always advisable if possible.
- Some modern designs of lab benches are designed to avoid floor penetrations and make it easy to reconfigure the lab. They have central shelving which reaches near the ceiling and electrical connections that are fed from the ceiling. These types of units should be seismically restrained by chains to the ceiling.
- Items less than 48" tall should also be secured against earthquake if fragile, valuable, hazardous, or if there is a possibility that the item may obstruct egress or block a door if it fell.
- Fit all shelves with earthquake lips to prevent object from falling off.
 - Lips of approximately 1.5" height are most satisfactory. Lips less than 1" height are likely to be ineffective, whereas lips that are too tall are not recommended as they may increase the risk of dropping things by making it awkward to remove items from the shelf.

See above section on Ingress, Egress, Doors, and Lab Security for further seismic safety information.

Seismic Safety and Hazardous Materials Storage

The following shall be adhered to in order to minimize risk in an earthquake:

• Liquids which are pyrophoric, toxic, corrosive, sensitizers, carcinogens, or reproductive toxicants shall not be stored above eye level.

- Other liquids which do not possess significant hazards to skin, eyes, or health may be stored above eye level, but only if there is no other storage location available, and only if they are in bottles of one liter or less in capacity.
- Solid chemicals which are highly acutely or chronically toxic, significantly carcinogenic, highly reactive, or pyrophoric shall not be stored above eve level.
 - Lower hazard solid chemicals may be stored above eye level ONLY if no other storage location is available AND container size is one kilogram (1 kg) or less.
- Gas cylinders require careful storage to minimize risk during earthquake (Figure 4.6).

The following should be adhered to:

- Medium and large size gas cylinders (>18" high) shall be restrained using two chains, placed at the approximate positions one third of the way up from the base, and two thirds of the way up from the base.
 - Chains shall either be bolted securely to a wall, attached to a steel cylinder rack, itself bolted to the wall or the floor, or shall be bolted to a steel cabinet which is itself bolted to the wall or to the floor.
 - It is not permitted to chain cylinders to movable furniture (e.g., tables), to wooden cabinets, or to any other combustible item.
 - Welded chain is strongly preferred.
 - Cylinders are to be individually chained, i.e., it is not permitted to use one chain to simultaneously secure multiple cylinders.
 - Combustible straps shall NOT be used in lieu of chains.

 Double chaining may not be practical for extremely small cylinders (< approx. 18" high). Figure 4.7. Recommended small gas cylinder restraint

Figure 4.6. Recommended Large and Medium Cylinder Restraint



Source: Certified Medical Sales

In such cases, alternate restraining systems may be employed (e.g., see Figure 4.7), provided the restraints are:

- Non-combustible (steel or aluminum).
- Affixed to the wall or floor, or to a steel cabinet which is itself affixed to the wall or floor.
- Clearly more than sufficient to prevent the cylinder from falling or escaping in the event of being knocked or shaken.
- Lecture bottles and similar extremely small cylinders shall be firmly clamped when in use. They must be stored such that they cannot fall or escape, but they do not require individual restraint in storage.



Source: USA Safety

Cryogenic liquid storage devices are an immediate asphyxiation hazard if there is a large spill or breach of containment.

Therefore:

- "Large" (multi-liter) liquid nitrogen Dewars must be secured against tipping.
 - Dewars come in all shapes and sizes; therefore, a precise definition of "large" is not practical to define. In general, any Dewar too large to be carried should be restrained, unless extremely short and wide-based.
 - Possible restraining methods include securely chaining to the wall, bolting to the floor, or using a purpose-built steel rack. In the case of chains, a tall Dewar can be restrained by two chains passed around the body in a manner similar to how gas cylinders are restrained. For shorter Dewars, a more practical method may be to use a very short chain to affix the handle to the wall.
- Pressurized Dewars must be secured regardless of size.
- Liquid nitrogen freezers should be restrained.

Consult the Compressed Gas Storage Fact Sheet (<u>http://tiny.cc/usc-cmpGas-fs</u>; see Figure 4.8) for more information.

Electrical Safety

Working with electricity can be dangerous. Laboratory workers may be directly or indirectly exposed to electrical hazards. Review the Electrical Safety Fact Sheet (<u>http://tiny.cc/usc-electSaft-gs</u>; see Figure 4.9) for more information.

Figure 4.8. Compressed Gas Storage Fact Sheet



Figure 4.9. Electrical Safety Fact Sheet



Preparedness:

- Have an emergency plan on what to do in the event of a power outage.
- Learn where the electric circuit breaker panels and emergency shutoffs are so power can be shut off in an emergency.
 - If circuit breakers are not clearly marked as to what rooms/circuits they service, request assistance from FPM Customer Resource Center (213) 740-6833 UPC, (323) 442-8005 HSC.

Electrical equipment and wiring shall be kept in a good state of repair. Defective equipment or wiring which displays damaged insulation or other defects shall not be used.

Power outlets and circuits shall not be overloaded. Be aware of the current requirements of equipment with high power usage (e.g., furnaces, ovens, heaters, heavy machinery). Do not plug too many high current devices into sockets on the same circuit or overloading may occur, with possible risk of overheating and fire.

 Personnel intending to install multiple high-current devices must check with FPM electricians to ensure their circuits are able to withstand the load. If not, FPM may advise running one or more of the devices from sockets on a different circuit or may require a new circuit and sockets to be installed.

Electrical panels house circuit breakers which protect against overcurrent. Electrical panels:

- Shall be easily accessible in case of emergency.
- Shall not be covered or hidden.

- Shall have a free working area in front, of minimum size 36 inches deep and 30 inches wide (or the width of the electrical panel, if greater than 30 inches) (<u>8 CCR §2340.16 (b)</u>, L.A. Fire Code 605.3).
 - "No storage of any materials shall be located within the designated working space." (L.A. Fire Code 605.3)

Electrical wiring and equipment in flammable vapor areas shall be of an explosion proof type approved for use in such hazardous locations.

For further information on electrical safety, consult the *Cal-OSHA Guide to Electrical Safety*, available online at <u>https://www.dir.ca.gov/dosh/dosh_</u> <u>publications/Electrical_Safety.pdf</u>.

Flexible Cables, Multi-plug Adapters, Extension Cords and Power Strips

Extension cords are not intended as a permanent solution to electrical distribution (L.A. Fire Code 605.5). If there is an apparent need for a permanent extension cord, relocation of equipment or having FPM install more sockets should be done so the cord can be eliminated. Extension cords may be used on a temporary basis to provide power to one appliance, provided they are of sufficient current rating for the equipment they supply, and provided they meet all the conditions in the bulleted list under *power strips*, below. Note that extension cords may overheat below their rated current if excessively long and the excess length is wound into a coil.

Power strips ("relocatable power taps", RTPs) are short (typically 6 ft or less) extension cords with multiple outlets. Power strips are acceptable for long-term usage provided only devices of low current consumption are plugged in, for example computer equipment, or instrumentation, provided they incorporate overcurrent protection (L.A Fire Code 605.4.1), and provided all the following conditions are met:

- They are plugged directly into a permanent outlet (<u>L.A Fire Code 605.4.2</u>)
 - They may not be series connected (daisy chained; see Figure 4.10).

Figure 4.10. Power strip daisy chain

- They are not close to water sources, hazardous materials, or inside fume hoods.
- They are not in a position where heavy items may pinch them, fall on them, or roll over them, and where they are not liable to physical damage, e.g., from sharp objects. (Cal Electrical Code 400.8 (7),¹ L.A. Fire Code 605.5)
- They are not a trip hazard.
 - If a cord must be run across a floor, it is not acceptable to tape it to the floor as it will be pinched and gradually worn every time it is stepped on. A proper anti-trip cable protector should be purchased.
 - Even with a cable protector, running a cable across a trafficked area shall not be used as a permanent solution.

¹ Register at the National Fire Protection Association web site to access the document.

- They do not pass through doorways, windows, or holes in walls, ceilings or floors (<u>Cal</u> <u>Electrical Code 400.8 (2), (3)</u>,¹ <u>8 CCR §2500.8</u>)
- They do not run inside walls, above ceilings, or below floors (<u>Cal Electrical Code 400.8 (5</u>), <u>8 CCR §2500.8</u>).¹
- They do not run under carpets, rugs, or in other positions which may obstruct visual inspection or promote heat buildup.

The above bulleted list, except the requirement to plug directly into an outlet, also applies to the placement of flexible power cables attached to appliances. Additionally, over-long cables attached to high current devices should not be rolled into a coil as this may result in heat buildup.

Multi-plug adapters should not be used. Use overcurrent-protected power strips instead, in accordance with the conditions previously stated.

For more information on extension cord safety, see <u>Fast Facts - Temporary Extension Cords</u> and <u>Fast Facts</u> <u>- Power Strips and Daisy Chains</u>.

Emergency Equipment and Supplies

Safety Shower and Eyewash

Safety showers and eyewash provision is governed by Cal-OSHA under <u>8 CCR §5162</u>, which also incorporates ANSI Z358.1 by reference. The 1981 version of the ANSI standard is the one incorporated, but it is advisable to follow the most recent revision which was in 2014. Very useful guidance may be obtained from the International Safety Equipment Association (ISEA; <u>https://safetyequipment.org/wp-content/uploads/2022/10/EWS-Guide-Feb_2015.pdf</u>) and Guardian Equipment (<u>http://www.gesafety.com/ansi/index.shtml</u>).

Summarizing 8 CCR §5162, the basic safety shower/ eyewash (see Figure 4.11) requirements are as follows:

- 1. When required:
 - a. "...eyewash... shall be provided at all work areas where, during routine operations or foreseeable emergencies, the eyes of an employee may come into contact with a substance which can cause corrosion, severe irritation or permanent tissue damage or which is toxic by absorption."
- b. "...emergency shower... shall be provided at all work areas where, during routine operations or foreseeable emergencies, area of the body may come into contact with a substance which is corrosive or severely irritating to the skin or which is toxic by skin absorption."

Figure 4.11. Eyewash/ shower station



Source: Bradley

- 2. Location:
 - a. "...shall be in accessible locations that require no more than 10 seconds for the injured person to reach."
 - b. "If both an eyewash and shower are needed, they shall be located so that both can be used at the same time by one person."
 - c. "...area... shall be maintained free of items which obstruct their use."
- 3. Maintenance:
 - a. "Plumbed eyewash and shower equipment shall be activated at least monthly to flush the line and to verify proper operation."
- 4. Status of drench hoses, etc:
 - a. "Water hoses, sink faucets, or showers are not acceptable eyewash facilities. Personal eyewash units or drench hoses... may support plumbed or self-contained units but shall not be used in lieu of them." NOTE: A drench hose with: (a) a stay-open valve, (b) two (2) eyewash heads, and (c) compliant with ANSI Z358.1 Sections 5 and 6, can be used as an eyewash e.g., when an eyewash is required immediately adjacent to the hazard.

Summarizing key points from ANSI Z385.1-2009:

- For a safety shower, there shall be no obstruction within sixteen (16) inches of the center of the spray pattern.
- Safety showers and eyewashes shall be clearly signed, and the sign shall be visible throughout the area served.

- 3. Location:
 - a. Safety showers and eyewashes shall be in accessible locations which require not more than 10 seconds travel time to reach.
 - b. The shower / eyewash shall be on the same level as the hazard, i.e. no steps.
 - c. The route to the shower / eyewash shall not be obstructed.
 - When the hazard is a "strong acid or strong caustic", the eyewash shall be immediately adjacent to the hazard.
- Eyewash nozzles should be capped to prevent contamination; the caps should automatically open on activating the eyewash.
- Personnel who may be exposed to hazardous materials shall be instructed on the location and proper use of safety showers/eyewashes.

The appendix of ANSI Z385.1-2009 is not formally part of the standard, but provides useful guidelines for implementation. From said appendix:

- 1. A distance of not more than 55 feet is reckoned as meeting the 10 second rule.
- 2. "A door is considered an obstruction. When the hazard is not corrosive, one intervening door can be present so long as it opens in the same direction of travel as the person attempting to reach the emergency shower and eyewash equipment and the door is equipped with a closing mechanism which cannot be locked to impede access to the equipment."

 Highly hazardous materials might warrant closer placement of emergency eyewash / shower equipment.

EH&S can advise on appropriate placement of safety showers and eyewashes.

Contact <u>labsafety@usc.edu</u> for further information. Correct usage of safety showers / eyewashes is covered in the later section on emergency response. Monthly testing of safety showers and eyewashes is the responsibility of Facilities Planning and Management (FPM).

Fire Extinguishers

Fire extinguishers are provided by the University (via FPM) in corridors, public areas, laboratories, and other locations as required by the LA Fire Code (<u>Ch. 9 §906</u>) and other applicable standards and regulations (e.g., <u>8 CCR §6151</u>).

The standard type of extinguisher provided is the dry powder ABC-type (see Figure 4.12) which is applicable as follows:

- Class A fire ordinary solid combustibles such as paper, cardboard, wood, plastics
- Class B fire flammable or combustible liquids such as mineral oil, organic solvents, gasoline
- Class C fire a Class A or B fire which also involves electrical equipment

Missing extinguishers should be reported to FPM. FPM will inspect and maintain all fire extinguishers, both inside and outside laboratories.

Fire extinguisher training may be available from USC Fire Safety and Emergency Planning; see website for more information (<u>https://fsep.usc.edu</u>).

Fire Extinguishers and Special Hazards

Dry powder ABC extinguishers are NOT suitable for extinguishing reactive metals² and may not be fully effective for reactive metal hydrides³ or pyrophoric solids. Regulations (see <u>Appendix C</u>) require Class D extinguishing agents to be provided where combustible metals are present in physical form (powder, flakes, etc.) which pose a fire hazard. EH&S strongly recommends Class D extinguishing agents (see Figure 4.13) also be provided in labs where reactive metal hydrides, pyrophoric solids, and like materials are stored or used.

Class D extinguishing agents may be provided in the form of a Class D fire extinguisher (yellow in color), and/or other suitable form (e.g., powdered extinguishing agent in a long tube or in a bucket with shovel) to be poured over a fire.



Figure 4.12. ABC fire

² Class D fires: alkali metals, alkaline earth metals, lanthanides, actinides, aluminum, titanium, zirconium, hafnium, scandium, and yttrium

³ Sodium hydride, lithium aluminum hydride, and calcium hydride

Contact labsafety@usc.edu to discuss the most appropriate Class D extinguishing agent provision Figure 4.13. Class D fire for specific laboratories.

Note that for pyrophoric reagents dissolved in organic solvents (e.g., n-butyllithium or t-butyllithium in hexane, heptane, etc.), a Class ABC extinguisher is recommended. (See https:// research.columbia.edu/sites/default/files/content/EHS/Homepage/pyrophorics.pdf and http:// onlinelibrary.wiley.com/doi/10.1002/047084289X.rb395.pub2/pdf).

Fires involving 100% concentration pyrophoric liquids such as trialkylaluminums pose special problems for extinguishment. Users of these materials should contact labsafety@usc.edu for guidance.

First Aid Kit

Pls are responsible for supplying at least one first aid kit (see Figure 4.14) for their research personnel. The kit should be stored in the main lab and be easily accessible to any other lab locations that belong to the group. If the same group occupies labs that are not in immediate proximity (i.e., labs in different buildings or on different floors), a first aid kit shall be available for each set of labs. Each lab member shall know where the kit is located.

First aid kits shall conform to ANSI/ISEA Z308.1-2015 Class A, which specifies minimum items in Table 4.1. If the first aid kit is not conspicuously located (e.g., a storage cabinet), then post signage marking its location. Laboratory personnel must regularly inspect first aid kits to ensure that no items are missing and that none of the items (e.g., ointment) in the kit have expired.

Table 4.1.	First Aid	Kit	contents
10010 4.1.	I USL ALU	nu	contents

Labs containing phenol or hydrofluoric acid are required to provide special first aid materials (e.g., calcium
gluconate gel) to treat exposure to these dangerous corrosive toxic materials.

4.20





extinguisher for metal

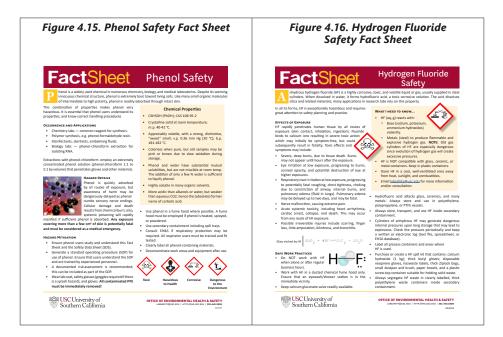
fires

Figure 4.14. First Aid



Consult the <u>Phenol Safety Fact Sheet</u> (see Figure 4.15) and/or the <u>Hydrogen Fluoride Safety Fact Sheet</u> (see Figure 4.16) for exact requirements.

First aid kits and first aid training may be required for research activities away from the campus especially in remote areas where medical care is not readily available; check your Department's or School's field trip policy for more information.



Spill Kit

All University laboratories in which hazardous materials are stored or used must have ready access to a chemical spill kit. A spill kit can be assembled by the laboratory, or a commercial kit can be purchased from a laboratory supply company; see <u>Chemical Spill Kit Guide Sheet</u> for more information. All laboratory personnel must be familiar with the spill kit storage location and use of the spill kit, including limitations, and when it is more appropriate to evacuate the lab and call DPS. If the spill kit is not conspicuously located (e.g., a storage cabinet), then post signage marking its location. Appropriate use of spill kits is covered in <u>Section 10.0 Emergency Response/Injury & Incident Reporting</u>.

Laboratories storing or using hydrofluoric acid must have ready access to a dedicated HF spill kit, see <u>Hydrogen Fluoride Safety Fact Sheet</u> (see Figure 4.16) for details.

Open Flames

Use of open flames at USC is to be avoided whenever possible and is prohibited in certain cases. Any proposed work involving open flames (Bunsen burner, spirit lamp, etc.) should be carefully reconsidered to see if there is an alternative (NFPA 45 (2019), 11.2.7.1)⁴. Refer to the EH&S Laboratory Burner Safety guidelines for additional information.

Open flames should never be used as a heat source for chemical experiments, distillation, or boiling; electric hotplates and heating mantles should always be used for such purposes. Flame sterilization can frequently be replaced by autoclaving, purchasing pre-sterilized items (e.g., disposable inoculation loops), or by using electric heat sources specifically sold for this purpose. If a flame is deemed indispensable for a sterilization role, a self-contained gas burner with push-button ignition, specifically manufactured for the role, should be employed. Such burners extinguish immediately when the button is released and do not present nearly as high of a fire hazard as Bunsen burners and spirit lamps. If substituting safer heat sources for an open flame is not possible, then lab open flame operation shall follow <u>NFPA 45 (2019)</u>, section 11.2.6, which states:

- Bunsen tubing must be in good condition, rated well in excess of working pressure, and shall be clamped at either end. (Note: Labs using gas burners should regularly inspect the tubes as part of their internal safety procedures.)
- Burners must be safe against falling over (use weights or clamp if necessary).
- Outside of a fume hood, do not use a flame under shelves, cabinets, or overhanging equipment.
- Biological use of flames in conjunction with flammable liquids shall additionally conform to the following:
 - Not more than 50 mL flammable liquid in an open container, which must be glass or metal, and must have a tight sliding (i.e. non-screw) lid which can be used to extinguish the liquid if it ignites.
 - Open container of flammable liquid must be capped when not in use.
 - Container of flammable liquid shall be as remote as possible from the flame, and never closer than one foot (31 cm).
 - Extraneous hazardous materials shall be removed and placed in storage.
 - Combustibles shall not be within 2 ft (61 cm) of the flame.
 - Absorbent combustible material (e.g., paper) is not permitted under the flame source.

Use of open flames is strictly forbidden in tissue culture hoods and biosafety cabinets

at USC. This is due to 1) an increased fire hazard in a biosafety cabinet due to recirculating air, 2) the fact that heat from the flame causes turbulence in the protective laminar flow of air, and 3) partly because hot gases may damage the HEPA filter which is intended to prevent infectious particles from entering the lab.

Figure 4.17. Safe Alternatives to Open Flames in a BSC Fact Sheet



4 Register at the National Fire Protection Association web site to access the document.

Consult the Safe Alternatives to Open Flames in a BSC Fact Sheet (<u>http://tiny.cc/usc-alt-flame-fs</u>; see Figure 4.17) for more information.

Open-Circuit Water Usage for Cooling Condensers

Use of Open-Circuit Water for Cooling

Water damage is consistently the most expensive type of property loss incident which occurs at USC. These incidents are also excessively common, despite many of the occurrences being easily avoidable. Individual water damage incidents not uncommonly result in costs in the hundreds of thousands of dollars range and can seriously disrupt research in affected rooms and buildings.

The most common avoidable cause of flooding in labs arises from open-circuit use of water to cool condensers, such as the glass Liebig condensers commonly used for distillation and refluxing. Lab personnel are too often careless in failing to properly secure the ends of the tubes to the faucet and condenser, which can result in a tube detaching and water spraying onto the floor. This usually happens at night when water pressure increases due to low demand, resulting in a gap of several hours before the flooding is discovered. Individual occurrences of this type at USC have caused water damage extending through multiple rooms and floors in lab buildings.

Typical condensers only require a flow of a few drops per second to keep them cool, but researchers commonly greatly overestimate the flow required, which both raises the flooding risk and wastes a lot of water as condensers are typically run for periods of hours to days. Also, typical lab faucets have poor control of flow rate at low flows, and the flow can gradually choke off as the rubber washer in the faucet slowly expands after the faucet is opened; thus, there is a temptation to use an excessive water flow to ensure it does not cut off unexpectedly. Aside from the flood risk, unnecessary open-circuit use of water is somewhat egregious in Southern California due to it being an arid area.

Alternatives to Open-Circuit Water

There are three alternatives to using open-circuit water for cooling condensers:

Closed-Circuit Chiller - This is a relatively expensive solution and is only needed in rare cases where cooling water is required to be below room temperature for prolonged periods of time. In virtually all cases where open-circuit water from a faucet can be used for cooling, a chiller unit is not needed as a replacement, but one of the other two solutions below will suffice.

Air Cooling - Air-cooled condensers utilizing aluminum fins are available (e.g., the <u>Heidolph™ "Findenser</u>™"). These not only completely eliminate the use of water, which can have additional safety benefits when highly water reactive materials are being worked with, but also provide extra convenience through eliminating water tubes.

These devices work best in a fume hood due to the continual air movement. They are a particularly convenient solution for refluxing.

Aside from the initial high cost, air-cooled condensers have two slight disadvantages: (a) they are not transparent and (b) they have to be cleaned manually rather than placing in a base bath or acid bath (both of which will severely attack the aluminum fins).

Water Bucket and Pump - A bucket of water and an inexpensive, low-power submersible aquarium water pump will suffice to keep a condenser cool. Since a small flow is all that is needed, a tiny pump can be used.

Even if the water circuit completely fails, only one bucket of water (approx. two to four gallons) can be spilled. Note that small aquarium pumps produce very little pressure and, therefore, it is not necessary to use hose clamps on the condenser.

The bucket can be placed on a bench, inside a fume hood (if there is space), or outside the fume hood on the floor, or more commonly on a stool. Placing the bucket on the floor is less reliable, since small aquarium pumps have trouble pumping to high head, and if there is too much of a vertical rise and fall there is a possibility of bubble-lock.

Though a little inconvenient to have buckets in the lab, the tradeoff for water-saving and lack of flooding is worthwhile. NOTE: A USC research group completely eliminated the use of open-circuit cooling water, opting for buckets and aquarium pumps in tandem with reflux condensers instead.

It has successfully employed this system in almost all of its experiments (that run from hours to days) for many years. The effectiveness and practicality of using recirculating water for cooling condensers has thus been well tested at USC.

If the condenser is in use for a prolonged period (e.g., overnight), the water temperature will equilibrate somewhat above room temperature due to heat from the condenser and from the 3.5 - 5 W pump (any higher power rating is excessive for this application). The warming is not a problem unless a solvent of exceptionally low boiling point (e.g., < 50 °C) is being refluxed for a prolonged period (e.g., overnight). If extremely low-boiling materials are to be condensed (e.g., diethyl ether), or it is desired to slow the temperature rise, the bucket can be filled with ice water. This is a distinct advantage over open-circuit water use.

Open-Circuit Water for Cooling Condensers: New Requirements

The overarching Chemical Safety Committee has approved the following safety measures. Any requests for exemption should be initially discussed with EH&S (<u>labsafety@usc.edu</u>) who will take the case to the Committee for decision, if required.

- 1. The use of open-circuit water for cooling condensers in research laboratories at USC shall be phased out and ultimately prohibited.
- 2. The Chemical Safety Committee has established a deadline for the elimination of open-circuit water use for cooling condensers in research laboratories.

a. The deadline is currently set at 1st January 2024.

3. After the deadline, any observed open-circuit use of water for cooling condensers shall be considered a finding during EH&S lab inspections. If found, twenty (20) business days shall be given for correction.

Rollout of New Requirements

- 1. EH&S will assist with communication of the new policy to PIs and will develop useful guidance on how labs can implement the policy (e.g. via webpages and guide sheets).
- 2. During the 2023 lab inspection cycle, further reminders will be provided to those labs which have not yet implemented changes.
 - a. Open-circuit use of water for cooling condensers which is discovered during 2023 lab inspections will be cited as an advisory finding, but will not be a formal finding subject to 20 business day follow-up.
- 3. Starting with the 2024 lab inspection cycle, open-circuit water for cooling condensers will be cited as a twenty (20) day finding.

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Hazard Communication (Hazcom) is the generic term for labelling, signage, safety data sheets, and other means used to communicate hazards posed by hazardous materials in the workplace. This section is concerned with materials which are hazardous due to chemical properties, or because they are liquefied or compressed gases. For information on hazard communication requirements for biohazardous or radioactive materials, or lasers, refer to the <u>Biosafety Manual</u>, <u>Radiation Safety Manual</u>, or <u>Laser Safety Manual</u>, as appropriate.

It is essential that all laboratory personnel understand the hazard communication labelling and safety data sheets (SDSs) provided with the chemicals they purchase. It is also important to understand when and how to label chemical storage areas, particularly hazardous substances (PHS), newly synthesized chemicals, etc.

This section covers the regulatory basis of labelling, the basic elements found in modern regulatory-compliant labels and guide sheets, how to label in labs, and the "fire diamond" signage system used on lab door signs. The way in which chemical health hazards and chemical-physical hazards are classified is an important aspect of hazard communication; this is covered in <u>Section 6</u>.

Cal-OSHA, Globally Harmonized System (GHS), and Proposition 65

Cal-OSHA regulates hazard communication (<u>8 CCR §5194</u>), and lays down requirements for importers and suppliers of hazardous materials, and for employers who have hazardous materials in the workplace.

The Cal-OSHA hazard communication regulation references California Proposition 65 (<u>https://oehha.ca.gov/proposition-65</u> - *Safe Drinking Water and Toxic Enforcement Act of 1986*), a statewide ballot initiative which requires employers to warn personnel of hazardous materials which are listed in *Chemicals Known to the State to Cause Cancer or Reproductive Toxicity* (<u>27 CCR § 27001</u>). If Cal-OHSA hazard communication regulations (<u>8 CCR §5194</u>) are followed for hazardous materials on the Prop. 65 list then *"Such compliance shall be deemed compliance with the* [Safe Drinking Water and Toxic Enforcement] *Act."*

• In research labs, compliance with Cal-OSHA hazard communication requirements automatically ensures compliance with Prop. 65.

Cal-OSHA has published a guide to the <u>hazard communication regulations</u>. Further valuable information may be found at the federal OSHA hazard communication portal (<u>https://www.osha.gov/dsg/hazcom/</u>), <u>OSHA GHS guide</u>, and the EH&S <u>Hazard Communication Program</u>.

Cal-OSHA (and the Federal OSHA regulations it incorporates by reference) define a hazard communication language of standardized signal words, phrases, and pictograms, to be used in labels and safety data sheets (SDSs), and also defines how the various hazards of chemicals are to be categorized.

OSHA closely follows the Globally Harmonized System (GHS) developed by the United Nations (UN). Harmonization of OSHA and Cal-OSHA communication regulations with the GHS system took place several years ago (http://www.dir.ca.gov/ dosh/dosh_publications/ghs_fs.pdf); however, pre-GHS labels may still occasionally be found on old chemical containers. For clarity, the current hazard communication regulations are generally referred to throughout this CHP as "OSHA/GHS".

The most basic requirements of Cal-OSHA hazard communication regulations are summed up as follows:

1. Manufacturers, suppliers, and importers of hazardous materials are required to label

them in a regulatory-compliant manner and provide safety data sheets.

- 2. Employers are required to:
 - a. Have a written hazard communication program.
 - b. Train personnel to understand hazard labelling and safety data sheets.
 - c. Have safety data sheets available for hazardous materials present in the workplace.

Non-OSHA/GHS Hazard Communication Systems

On labelling intended for end users of chemicals, non-GHS hazard communication systems may be used alongside GHS labelling, but may not replace the required GHS labelling elements.

OSHA/GHS labelling and safety data sheets are designed to provide information to workers using hazardous materials under normal working conditions. Another signage system - designed primarily for emergency responders rather than chemical end users - is the NFPA 704 "fire diamond", covered in detail on pages 5.3 to 5.5.

Labeling and Signage Systems

OSHA/GHS Labels

Manufacturers and suppliers of chemicals are required to label their products using the OSHA/GHS system specified by OSHA and Cal-OSHA. All commercially-sourced hazardous materials coming into labs will have this labelling, so it is important for lab personnel to understand the information on the labels.

Label elements are standardized and the most important are:

- Product name or identifier
- Hazard pictogram (symbol). The appropriate pictograms are displayed based on the GHS hazard class and category (see Table 5.1).

- OSHA/GHS divides hazardous materials into named hazard classes (e.g., acute toxicants) which may then be further subdivided into categories, types, or divisions denoted alphanumerically.¹
- The OSHA/GHS hazard classification system is covered in detail in <u>Section 6</u>.
- Signal word. One signal word may appear based on the most severe hazard manifested by the substance.
 - "Danger" indicates a more severe hazard
 - "Warning" indicates a less severe hazard
 - If hazards are low, a signal word may not be required.
 - Old pre-GHS labels may say "Caution", but this word is not used in the GHS system.)
- Hazard statements. If the substance is classified as being hazardous in any way then one or more hazard statements will be present to describe the hazard in more detail than is conveyed by the pictograms.
- Precautionary statements. These inform users of basic precautions to minimize risk, based on the hazards present.

Figure 5.1 shows an example of how label elements come together to produce a complete label. Consult the <u>Globally Harmonized System (GHS) Fact Sheet</u> for more information.

NFPA 704 "Fire Diamond"

The "fire diamond" is a symbol defined by a National Fire Protection Association standard (NFPA 704).

Figure 5.1. OSHA GHS label



Source: Seton

It provides a quick visual summary of the most significant hazards of materials in the area signed. Although the fire diamond was principally designed for an intended audience of emergency responders, lab personnel should become familiar with the system. At USC, the fire diamond will be found on laboratory door signs, on signs on the outside of some buildings, and in hazardous materials storage areas.²

The fire diamond is a simple summary based on numeric codes (0-4) in four color-coded categories of *health* (blue), *flammability* (red), *instability* (yellow) and *special hazards* (white); refer to Figure 5.2 for a key to interpretation.

Note that the numerical convention for NFPA fire diamond hazard categorization is the opposite of the OSHA/GHS convention, i.e.:

- Fire diamond larger number indicates more severe hazard.
- OSHA/GHS lower alphanumeric category indicates more severe hazard.

¹ Per the OSHA/GHS convention for hazard class subdivisions, the lower the alphanumeric designation, the more severe the hazard. 2 California Health and Safety Code — HSC § 13143.4: *"The State Fire Marshal shall adopt regulations to authorize National Fire Protection Association 704 Standard System Diamonds...be displayed at entrances to buildings and other locations where hazardous materials are stored."* (http://leginfo.legislature.ca.gov/faces/codes_displaySection.xhtml?lawCode=HSC§ionNum=13143.4.)

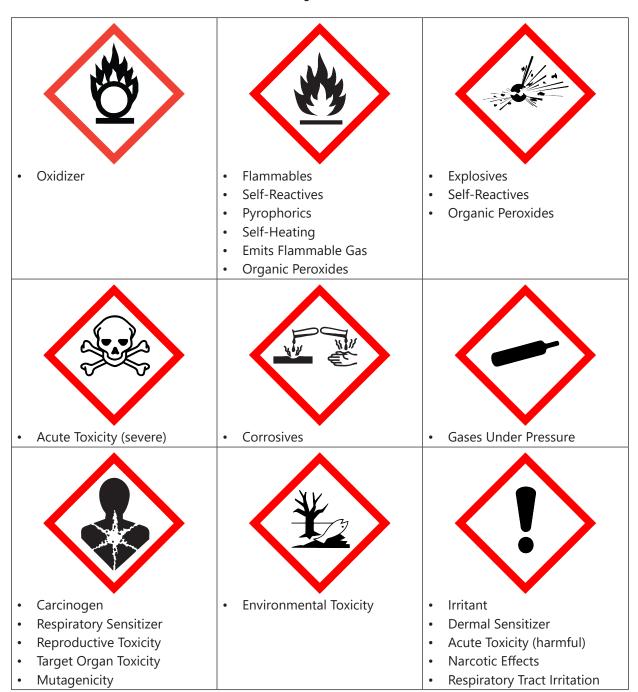


Table 5.1. GHS Pictograms and Hazard Classes

Figure 5.2. NFPA 704 "Fire Diamond" Guide

NFPA RATING EXPLANATION GUIDE

Rating	Health Hazard	Flammability Hazard	Instability Hazard	Special Hazard	Symbol
4	Can be lethal	Gaseous, volatile, or easily dispersed flammable material, or any pyrophoric material	Susceptible to explosion or explosive decomposition under ambient conditions	Oxidizer	ОХ
3	Can cause serious or permanent injury	Liquids and solids that can be ignited under ambient temperate conditions	Susceptible to explosion or explosive decomposition when strongly initiated or heated under confinement	Violent reaction with water	₩
2	Can cause temporary incapacitation or residual injury	Liquids and solids which have to be moderately pre-heated before they become ignitable	Material which undergoes violent reaction at elevated temperature/pressure	Simple asphyxiant gas	SA
1	Can cause significant irritation	Liquids and solids which have to be significantly pre-heated before they become ignitable	Normally stable, but may become unstable at elevated temperature/pressure	2	
0	No appreciable health hazard	Essentially unignitable	Stable material, even under fire conditions	SA	

Labeling and Signage in the Lab: What You Need to Do

In order to satisfy regulatory requirements (<u>8 CCR §5194 (f)</u> and <u>8 CCR §5191 (h)</u>), and maintain high standards of safety, personnel shall pay due care and attention to the labelling of substances within their laboratories. In general, EVERYTHING except substances actively in use shall be labelled. Even vessels of minimal hazard materials require labelling with the identity of the contents, as this minimizes the difficulty of clean-up in case of spillage.

Figure 5.3. Container label

A beneficial side effect of appropriate labelling in labs (see Figure 5.3) is to improve housekeeping and lab efficiency by preventing an accumulation of unlabeled "orphan" containers of substances which no one will claim responsibility for.

Laboratory personnel should adhere to the following rules ("shall" indicates a mandatory rule) and guidelines:



Source: DirectIndustry

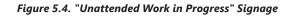
- 1. Labels on hazardous substances purchased by the lab shall not be removed or defaced.
 - a. Exception 1: Empty bottles of substances of low health or environmental hazard (e.g., ethanol, acetone, isopropanol), are considered non-hazardous after decontamination and triple-rinsing. After decontamination and triple-rinsing, the hazard warning label shall be defaced, "rinsed, non-hazardous", or like wording written on, and the bottles can then be re-purposed or disposed of as nonhazardous waste - see <u>Table 9.3</u>.
 - Exception 2: Empty bottles repurposed as waste bottles shall have the original hazard warning label defaced and a hazardous waste sticker placed over the top. NOTE: It is not necessary to clean the bottle if residual contents are chemically compatible with the waste to be added.
- Internal labelling done within a research lab, e.g. labelling of newly synthesized chemicals, need not be done according to the GHS specifications, but it shall provide:
 - a. Sufficient information for lab personnel to be able to identify the general hazards known or predicted to be posed by the substance, AND;
 - b. Either the chemical name or an identifier which can be correlated with a list of abbreviations or a lab book³, to enable personnel to be able to exactly identify the material and look up specific known or predicted hazardous properties, AND;
 - c. The date when the sample was prepared.

- 3. Labels on extremely tiny items (e.g. NMR tubes and GC vials) may omit the date.
- 4. Labels on extremely tiny items (e.g. NMR tubes and GC vials) may omit hazard information, provided appropriate general hazard labelling is present on the secondary container or rack which holds the items.
- 5. If a substance is to be sent outside the lab for any commercial purpose then the lab must supply a safety data sheet and labelling to OSHA/GHS specifications. Contact labsafety@usc.edu for labelling and SDS guidance if your lab is planning to supply any chemically hazardous substances on a commercial basis.
- Lab personnel shall conservatively estimate potential chemical hazards for substances produced within the lab, based on chemical structure, chemical reactivity, known hazards of ingredients, known hazards of chemical analogues, presence of atoms of elements generally associated with toxicity (e.g. selenium, tellurium, lead, arsenic, fluorine), and any other factors deemed relevant.
 - Potential hazards should be reflected by labelling and noted in lab books and on SOPs.
 - Keep copies of specific references used in predicting hazards or keep notes of the citations.
 - c. Contact <u>labsafety@usc.edu</u> for further guidance.

³ An identifier referring to a lab book is acceptable for small samples made and used by an individual researcher. Large quantities of material or materials used by multiple personnel shall be labelled with chemical name and/or abbreviation which can be correlated with the lab abbreviations list.

- Working vessels and experimental setups do not need to be labelled while under control of the user. They shall be labelled if left unattended or overnight or longer.
- Particularly hazardous substance⁴ (PHS) storage areas, secondary containers, and use areas shall be labelled appropriately.
 - a. PHS include carcinogens and reproductive toxicants, so clear hazard labelling of PHS will also satisfy Prop. 65 requirements.
- Unattended experiments shall be labelled with clear signage (see Figure 5.4; refer to <u>Unattended Hazardous Operations</u> <u>Fact Sheet</u> for more information) in the immediate vicinity, concisely giving:
 - a. Simple description of the experiment.
 - b. The hazards.
 - c. In- and out-of-hours contact details for the responsible researcher and either the lab manager or the PI (the PIs name should be provided in either case).

d. Simple instructions for shutting the experiment down in an emergency, if that is practical and safe, e.g. "unplug and turn water off".



START DATE	END DATE
START TIME	END TIME
BLDG/RM	PI
CONTACT	PHONE
EXPLOSIVE OTHER (Describe)	EXTREME TEMPERATUR
EMERGENCY SHUTDOWN	PROCEDURES (Describe)

Safety Data Sheets (SDSs): What Are They?

Under OSHA/GHS rules, safety data sheets (see Figure 5.5) are required to be provided by any commercial vendor of hazardous substances. They expand upon the information present on labels. The content is standardized, and the following sixteen sections are required:

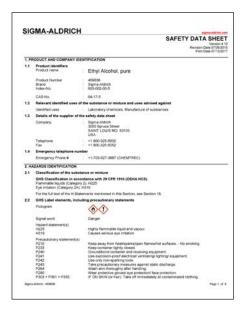
- 1. Product and supplier identification
 - a. Chemical name and/or trade name
 - b. Supplier contact details, including emergency phone number
 - c. Recommended use, including any restrictions

⁴ Refer to Section 6 for details on how PHS are identified and classified.

- 2. Hazards Identification
 - a. OSHA/GHS hazard classification, signal word, pictograms, hazard statements, precautionary statements
 - b. Other hazard information not covered by GHS, e.g., dust explosion hazard
- 3. Composition / Information on Ingredients
 - a. If the product is a mixture or sold under a trade name, this section will give details on the composition.
 - b. Under limited circumstances, some information may be withheld as a trade secret.
- 4. First Aid Measures
- 5. Firefighting Measures
- 6. Accidental Release Measures
- 7. Handling and Storage
- 8. Exposure Controls / Personal Protection
- 9. Physical and Chemical Properties

- 10. Stability and Reactivity
- 11. Toxicological Information
- Sections 12-16 cover ecological information, disposal, transport, regulatory info, and other info. These sections are generally not directly relevant to usage in a research lab.

Figure 5.5. Ethanol SDS



SDSs in The Lab: What You Need to Do

Laboratory personnel should familiarize themselves with sources of SDSs. Note that the thoroughness of the information provided by an SDS varies substantially between different chemical suppliers.

It is recommended to use safety data sheets from major laboratory chemical suppliers (e.g., Alfa Aesar, Sigma Aldrich, Strem, TCI America), or major gas suppliers (e.g. Airgas, Praxair, Matheson Gas, Linde) wherever possible. SDSs for more obscure materials can be sourced from the manufacturer or supplier.

In order to satisfy regulatory requirements and maintain high standards of safety, laboratory personnel should adhere to the following rules ("shall" indicates a mandatory rule) and guidelines:

1. All personnel planning work with hazardous materials shall review safety data sheets during the planning stage before work starts.

- 2. Research groups shall maintain a chemical inventory, to be updated at least annually, or more often as inventory changes.
 - a. Enter chemical inventory in <u>RSS</u> (only if EH&S has created an account for your laboratory and assisted you in the transition to RSS) or <u>EHSA</u>.
- 3. Research groups shall hold safety data sheets for materials they store or use.
 - a. Safety data sheets may be held in paper or electronic form.
 - b. Whatever form the SDSs are held in, research groups shall "ensure that they are readily accessible to laboratory employees during each work shift when they are in their work area(s)" [8 CCR §5191 (h) (1) (B)], and there shall be "no barriers to immediate employee access" [8 CCR §5194 (g) (8)].
- 4. Chemicals sold under an abbreviation or trade names shall be referenced by an SDS containing that abbreviation or trade name.
- 5. Due to the length of many chemical names, lab personnel frequently use abbreviations on labproduced labels.⁵
 - a. Abbreviation listing should be posted in each room which uses the chemicals.
 - b. PI should designate a lab member to maintain the current status of the list.
 - c. All lab personnel must be familiar with how to use the abbreviation list to find the correct safety data sheet.
- 6. A printed copy of a current SDS shall be physically available in the vicinity of any work with materials of very high acute health hazard (e.g. phenol, hydrofluoric acid, cyanides).
 - a. Persons in the lab shall all be aware of the location, existence, and contents of the printed SDS.
 - b. Personnel shall print and store SDSs for all Category 1 acute toxicants and phenol-containing materials at or near the work area where they are used.
 - c. The printed SDS should be provided to medical responders in the event of an incident.
- 7. Lab personnel are not required to author safety data sheets for hazardous substances produced within the lab.
 - a. Exception: If the substance is to be sent outside the lab for any commercial purpose then the lab must supply a safety data sheet and labelling to OSHA/GHS specifications.
 - b. Contact <u>labsafety@usc.edu</u> for labelling and SDS guidance if your lab is planning to supply any chemically hazardous substances on a commercial basis.

Regulations

<u>8 CCR §5191</u> subsections (h) (1) (B), (h) (2) (C), and (e) (1) (a).

8 CCR §5194 (g) subsections (1), (8), (9), and (10).

⁵ Vessels into which a commercially sourced substance is decanted shall only be labelled with an abbreviation if the lab maintains a current abbreviation table allowing for lab-specific abbreviations to be correlated with chemical name (and/or trade name, if appropriate).

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Introduction

This section covers:

- Hazardous chemicals and the nature of the hazards they display.
- Routes of entry of health-hazardous chemicals into the body.
- The OSHA/GHS system of hazard classification, as used in GHS labels and safety data sheets (SDSs).
- The Cal-OSHA definition of Particularly Hazardous Substances (PHS).
- How to identify and classify substances as PHS, including how to recognize potential toxicants or carcinogens for materials whose safety characteristics have not been studied and where adequate safety data is not available.

Note that for brevity and readability, some hazard classification tables were omitted from this section and placed in Appendix G. References to the tables in Appendix G appear in the attendant subsections.

Background

In the context of laboratory safety, Cal-OSHA defines a hazardous chemical as "any chemical which is classified as health hazard or simple asphyxiant in accordance with the [OSHA/GHS hazard classification system]" (8 CCR §5191). Cal-OSHA and hazard communication regulations (8 CCR §5191 and 8 CCR §5194) then proceed to define "health hazard" as any chemical which is either a simple asphyxiant or is in one or more OSHA/GHS health hazard classes (as defined in 29 CFR 1910.1200 Appendix A; see Figure 6.1).

Chemicals may pose physical hazards as a result of the ability to engage in energetic reactions (combustion, explosion, etc), or because they are compressed gases and therefore store mechanical energy. Cryogenic (i.e. extremely cold) liquefied or frozen gases are physically dangerous as they may develop high pressures on evaporation if not properly vented, and they may cause frostbite. The OSHA/GHS hazard classification system defines various chemical-physical hazard classes in <u>29 CFR 1910.1200 Appendix B</u>.

Figure 6.1. NO₂ evolution, a health hazard



A regulatory definition for Particularly Hazardous Substances (PHS) is provided by Cal-OSHA, which states: "Provisions for additional employee protection for work with particularly hazardous substances. These include "select carcinogens," reproductive toxicants and substances which have a high degree of acute toxicity." (8 CCR §5191 (e) (H))

OSHA/GHS Hazard Classes and Subdivisions

The OSHA/GHS system specifies hazard classes (e.g. *irritant, corrosive*, and *explosive*). Certain classes are then subdivided into either *Categories, Types*, or *Divisions* denoted alphanumerically. (The hazard class gases under pressure is an exception as it is subdivided into named *Groups*.) **The GHS system follows the convention that, within each hazard class, the lower alphanumeric designator indicates the more severe hazard**.

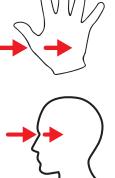
Thus, for example, a Category 1A Corrosive is more hazardous than a Category 1C Corrosive, and a Division 1.1 Explosive is more hazardous than a Division 1.5 Explosive.

The subdivision of health hazard classes and some physical hazard classes is based entirely on the intrinsic properties of the substance. For other physical hazard classes, such as self-reactive chemicals, the degree of hazard is substantially influenced by how the material is packaged, the quantities in each package, and whether the material is desensitized in some way. Note that the detailed definitions of the subdivisions take this into account. The essentials of all the GHS hazard classes and subdivisions are covered in the rest of this section.

Health-Hazardous Chemicals: Routes of Exposure

Health-hazardous chemicals may enter and affect the human body through:

- Skin contact. Many chemicals are absorbed through the skin at a significant rate. Although this effect is usually most pronounced with liquids, there are also lots of solid chemicals which are hazardous by skin contact. Even certain toxic gases may be dangerously absorbed through the skin, but exposure to concentrations of gas able to do this should never be encountered in a research lab.
 - Do not apply hand moisturizers in the lab as it may hold contamination on skin and facilitate absorption.
 - This prohibition also applies at writing desks in the lab.
- Eye contact. The eyes are not only very sensitive to damage by hazardous materials, but they also absorb solid, liquid, and gaseous chemicals much faster than skin.
- Inhalation. Inhalation of aerosols of solid particles (dust, fume) or liquid droplets, or inhalation of gases or vapors is a rapid and highly efficient manner of absorbing hazardous materials.
- Ingestion. Taking in hazardous materials by mouth is obviously an efficient method of introducing contamination into the body.





- Mouth pipetting, eating, drinking, smoking, vaping, and applying cosmetics is forbidden in labs to reduce the possibility of ingesting hazardous materials.
 - This prohibition also applies at writing desks in the lab.
- Hands must be well washed after laboratory work to prevent hazardous materials being transferred to food, etc, outside the lab.
- Injection. Piercing the skin with contaminated

Health-Hazardous Chemicals: OSHA/GHS Hazard Classification

Irritants

Irritants cause non-permanent inflammatory effects on living tissue, which may manifest as redness, itching, sneezing, tickly throat leading to coughing, and various other forms of discomfort. Almost all materials are irritant on sufficient exposure, including substances commonly found at home. Many chemicals found in the laboratory produce substantial or severe irritant effects even on small exposure.

 As a general rule, assume all chemicals are at least irritant, and minimize exposure accordingly.

Insoluble, unreactive materials may be strongly irritant if in the form of dust, or especially when in the form of fibers. For example, glass wool and carbon fiber can be extremely irritant by all routes of exposure, therefore, good industrial hygiene practices are necessary when working with these materials.

Further details of the OSHA/GHS classification with examples may be found in <u>Appendix G: Irritants</u>.

Corrosives

Corrosive chemicals cause local injury at the point where they contact the human body. The injury may arise from a combination of the following mechanisms:



needles or other sharp objects may introduce

Extreme care must be taken when handling

hazardous materials into the body.

needles and cannulae.

causing corrosion and dissolution of tissue. This is the principal mechanism of reactive corrosive chemicals, such as sulfuric acid, nitric acid, and sodium hydroxide. These substances literally eat away at human tissues.

B. Penetration followed by a toxic effect which damages or kills cells. This is the principal mechanism of a number of exceptionally dangerous corrosive substances, including hydrogen fluoride (hydrofluoric acid; see Figure 6.2), phenol (see Figure 6.3), dimethyl sulfate, and 2-chloroethylamine. These substances may not initially produce any visible effect on skin, as they do not cause external burning and corrosion.



Corrosives penetrate the skin (or other part of the body), then cause cellular death and damage in the underlying tissues, which can result in an extremely serious burn appearing, often after a misleading symptomless delay. Burns by these substances may be accompanied by systemic (i.e. non-localized) poisoning, which may be fatal if sufficient material is absorbed.

It should be noted that all corrosives have moreor-less toxic effect when in direct contact with living cells, so the two mechanisms always have some overlap. The chemical burn injury arising from corrosive exposure may manifest on skin as a color change (redness or blanching) in a minor case, all the way to complete death and destruction of tissues necessitating surgical repair, or even amputation. Chemical burns may be extremely painful, and burns caused by tissue damage and death from penetrating corrosives may be extremely slow to heal. Injection or inhalation of corrosive substances causes internal burns in sensitive tissue, which can easily be very serious.

Corrosive agents are very hazardous to eyes, and may cause extreme irritation, pain, and many serious irreversible effects, e.g. corneal opacity.

Many corrosive materials also display reactive hazards, for example nitric acid and perchloric acid are strong oxidizers. Many are also corrosive to non-living matter, for example hydrochloric acid is highly corrosive to steel, aqueous sodium/potassium hydroxide vigorously dissolves aluminum, and hydrofluoric acid dissolves glass.

Figure 6.2. Hydrogen Fluoride Safety Fact Sheet



Figure 6.3. Phenol Safety Fact Sheet



The interaction of acids with many metals and the interaction of bases with aluminum or zinc may also produce hydrogen, which is a highly flammable gas.

Further details of the OSHA/GHS classification with examples may be found in <u>Appendix G: Corrosives</u>.

Acute Toxicants

An acutely toxic material is one which may produce an adverse health effect on the body, or a target organ within the body, after administering the material within a short time frame.



The OSHA regulatory definition is clear and is as follows: "Acute toxicity refers to those adverse effects occurring following oral or dermal administration of a single dose of a substance, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours." (29 CFR 1910.1200 Appendix A).

As noted in the Corrosives section, some toxic materials also have a corrosive effect through damage or death to cells at the point of application. However, being irritant or corrosive is not a general characteristic of toxic substances, many of which redistribute in the body and affect target organs, or produce body-wide effects, without any irritation, corrosion, or other symptoms at the point of entry.

Measurement and Classification of Acute Toxicity

Acute toxicity is usually measured by animal testing, and quoted as an LD_{50} with usual units of mg/kg (also written mg kg⁻¹). The LD_{50} refers to a dose which kills 50% of test animals (usually rats or mice) under the specific testing conditions, and the units refer to the number of milligrams required to do this, per kilogram mass of animal. Mode of administration is also frequently quoted, e.g. LD_{50} (oral) for ingestion or LD_{50} (dermal) for skin application. Toxicity of airborne materials is measured by LC_{50} , which is the concentration in air which kills 50% of test animals. The units of LC_{50} are usually parts per million (ppm) by volume for gases, and mg m⁻³ or mg l⁻¹ for solid particles or liquid droplets (i.e. aerosols, fumes, or mists). Vapors may be quoted using either unit. The lethal concentration is lower the longer the contaminated atmosphere is breathed, so the time of exposure should always accompany an LC_{50} value.

 LD_{50} and LC_{50} values are often found in safety data sheets, and even if specific values are not quoted, OSHA/GHS hazard categories for acutely toxic materials should be given. Categories of acute toxicity as defined by OSHA are shown in Table 6.1. The GHS pictogram, signal word, and hazard statement specified for different acute oral toxicity hazard categories is shown in Table 6.2.

Specific Organ Toxicity – Single Exposure (STOT-SE)

Some toxic materials have a propensity to adversely affect specific organs. According to OSHA, "Specific target organ toxicity - single exposure, (STOT-SE) means specific, non-lethal target organ toxicity arising from a single exposure to a chemical. All significant health effects that can impair function, both reversible and irreversible, immediate and/or delayed and not specifically addressed...[elsewhere in the GHS]...are included."

A common example of a chemical which can cause specific organ toxicity on a single exposure is methanol (STOT-SE Category 1), which targets the brain and eyes (retinas). Severe over-exposure to methanol (e.g., drinking contaminated illicit beverages) may cause blindness.

Subdivision of OSHA/GHS Hazard Class "Acute Toxicity" Based on Toxicological Test Results				
Exposure Route	Category 1	Category 2	Category 3	Category 4
Oral LD ₅₀ (mg/kg body weight)	≤ 5	> 5 and ≤ 50	> 50 and ≤ 300	> 300 and ≤ 2000
Dermal LD ₅₀ (mg/kg body weight)	≤ 50	> 50 and ≤ 200	> 200 and ≤ 2000	> 1000 and ≤ 2000
Inhalation LC ₅₀ - Gases (ppm by volume; 4-hour exposure)	≤ 100	> 100 and ≤ 500	> 500 and ≤ 2500	> 2500 and ≤ 20000
Inhalation LC ₅₀ - Vapors (mg/l; 4-hour exposure)	≤ 0.5	> 0.5 and ≤ 2.0	> 2.0 and ≤ 10.0	> 10.0 and \leq 20.0
Inhalation LC ₅₀ - Dusts and Mists (mg/l; 4-hour exposure)	≤ 0.05	> 0.05 and ≤ 0.5	> 0.5 and ≤ 1.0	> 1.0 and ≤ 5.0

Table 6.1. Table (simplified) from OSHA specifying the acute toxicity categories used for hazard communication purposes.Note that Category 4 is the lowest hazard group.

Table 6.2. Relationship between acute toxicity hazard class and the OSHA/GHS mandatory label elements with examples.

Acute Toxicity Category	Category 1	Category 2	Category 3	Category 4
Pictogram				
Signal Word	Danger	Danger	Danger	Warning
Hazard Statement, Oral	Fatal if swallowed	Fatal if swallowed	Toxic if swallowed	Harmful if swallowed
Hazard Statement, Dermal	Fatal in contact with skin	Fatal in contact with skin	Toxic in contact with skin	Harmful in contact with skin
Hazard Statement, Inhalation	Fatal if inhaled	Fatal if inhaled	Toxic if inhaled	Harmful if inhaled
	Sodium azide (dermal),			
	sodium cyanide (oral,	Sodium azide (oral),	Methanol (oral, dermal,	
	dermal, inhalation),	anhydrous hydrogen	inhalation), sodium	Potassium carbonate,
Examples	sulfur tetrafluoride	fluoride (oral and	fluoride (oral), carbon	Triton® X100, ethylene
	(inhalation),	inhalation), hydrogen	monoxide (inhalation),	glycol, copper (II) sulfate
	anhydrous hydrogen	sulfide (inhalation)	chlorine (inhalation)	
	fluoride (dermal)			

Reference: 29 CFR 1910.1200 Appendix C. Note: Category 4 is the lowest hazard group.

A table illustrating the three categories of Class <u>STOT-</u> <u>SE</u> is available in Appendix G.

Chronic Toxicants: Specific Target Organ Toxicity – Repeated Exposure (STOT-RE)

If multiple small exposures to a substance over an extended period of time cause adverse health effects, the material is said to be chronically toxic. Usually the severity of the adverse health effects increase with the accumulated exposure.

Notable chronic toxicants include many chlorinated solvents which are noted as damaging the liver (hepatotoxicants), and some also damage the kidney (nephrotoxicant); all should be treated with caution. Materials containing mercury, cadmium, thallium, and a number of other toxic metals ("heavy metals") are also noted chronic toxicants.

Acrylamide is a common reagent in biochemical and medical laboratories, used for preparing polyacrylamide gels for separating biomolecules. Acrylamide is a potent neurotoxicant, able to cause persistent nerve damage which may manifest as tingling sensations and poor coordination in arms and legs (<u>http://www.nj.gov/health/eoh/rtkweb/</u> <u>documents/fs/0022.pdf</u>). Polyacrylamide is safe only if no free acrylamide is present.

The OSHA/GHS classification system for this hazard class (<u>STOT-RE</u>), together with some examples, is available in Appendix G.

Reproductive Toxicants

Reproductive toxicants are substances which may affect one or more of the following: The fertility or sexual function of males or females; the development of a fetus; the lactation of a mother; the health of a child by ingesting the substance or harmful metabolites via breast milk.

The OSHA/GHS classification system for this hazard class, together with examples is available in <u>Appendix</u> <u>G: Reproductive Toxicants</u>. Note that substances which may damage DNA and produce inheritable effects in the offspring are classified as *germ cell mutagens*, see the next subsection.

Reproductive Toxicants Focus: Ethylene Glycol Methyl Ethers

The class of ethylene glycol methyl ethers contains some useful solvents, including ethylene glycol monomethyl ether (2-methoxyethanol), ethylene glycol dimethyl ether (1,2-dimethoxyethane; glyme), and diethylene glycol dimethyl ether (diglyme). Unfortunately, all these substances are reproductive toxicants (Category 1B for the three solvents mentioned), possibly because they are metabolized to methoxyacetic acid (a reproductive toxicant, Category 1B).

It is recommended that alternate solvents be substituted wherever possible. Alternatives may include tetrahydrofuran, solvents from the propylene glycol ether group, ethylene glycol ethers with longer alkyl chains (e.g., diethylene glycol monoethyl ether), solketal (isopropylidene glycerol), or 3-methoxy-3methyl-1-butanol (MMB).

Germ Cell Mutagens

Mutagens damage DNA, and if the damaged DNA resides in germ cells, the mutations could be passed to offspring. For this reason, mutagens are regarded as a type of reproductive toxicant.

The OSHA/GHS classification system for germ cell mutagens, together with some examples, is available in <u>Appendix G: Germ Cell Mutagens</u>.

All mutagens should be handled with the utmost care. Besides potential adverse reproductive effects, a great many mutagens are also classified as carcinogens, acute toxicants, or acute or chronic target organ toxicants.

Carcinogens

Hazard communication regulations (29 CFR §1910.1200 Appendix A) provide the following definition: "Carcinogen means a substance or a mixture of substances which induce cancer or increase its incidence.

Substances and mixtures which have induced benign and malignant tumors in well-performed experimental studies on animals are considered also to be presumed or suspected human carcinogens unless there is strong evidence that the mechanism of tumor formation is not relevant for humans."

Acute toxicants tend to give a definite intensity of health effects for a specific dosage, i.e. the doseeffect relationship is deterministic. This is not true for carcinogens, as a given carcinogen dosage may or may not induce cancer, but in the event cancer is induced, the resulting "intensity" of the cancer has no relation to the dosage of carcinogen which induced it. Thus, for carcinogens, the dose-effect relationship is between dosage of carcinogen and probability of developing cancer, i.e. the relationship is stochastic.

Different chemical carcinogens act on the body in different ways, and certain carcinogens are

particularly associated with increasing the risk of particular types of cancer.

For example, breathing tobacco smoke increases the risk of many cancers, but the increased risk of lung cancer is especially pronounced. Inhalation of asbestos markedly increases the risk of mesothelioma. Benzidine and 2-naphthylamine used to be used in the synthetic dye industry, until a high proportion of exposed workers (up to 100% in some groups exposed to 2-naphthylamine) developed bladder cancer.

The risk of developing cancer from carcinogen exposure increases with the time of the exposure and with the concentration to which exposed. The precancerous cellular or genetic damage carcinogens induce may be irreversible, meaning that effects of exposure may accumulate over long time periods, or if the exposures are widely spaced. Furthermore, a notable feature of carcinogens is the long induction period between exposure and cancer appearing, which is typically years to decades, rarely months. For example, even though 2-naphthylamine is an extremely potent carcinogen for bladder cancer, the typical induction period is 16 years.

The OSHA/GHS classification system for carcinogens, together with some examples, is given in Table 6.3. Carcinogens are an important class of Particularly Hazardous Substance (PHS). The PHS definition includes substances which may not fall into the GHS carcinogen hazard class; refer to the PHS information towards the end of Section 6.

Regulatory Definition ¹	Subdivisions ²	Description	Examples
	Category 1	"Known or presumed human carcinogens."	(Used when insufficient data to differentiate 1A over 1B)
"Carcinogen means a substance or a mixture of substances which	Category 1A	"Known to have carcinogenic potential for humans. Classification in this category is largely based on human evidence."	Arsenic(III) oxide, benzene
induce cancer or increase its incidence."	Category 1B	"Presumed to have carcinogenic potential for humans. Classification in this category is largely based on animal evidence."	Ethylene oxide (toxic gas used as a chemical reagent for organic synthesis and for sterilizing medical devices and equipment)
	Category 2	"Suspected human carcinogens."	Chloroform

Table 6.3.	The OSHA/GHS	Hazard Class	Carcinogens.
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1 29 CFR §1910.1200 Appendix A

2 From most severe to least severe hazard

Sensitizers

Sensitizers are materials which susceptible persons may develop an allergy to after initial exposure(s). Typically, the initial exposure(s) are symptomless, but subsequent exposures, often to minute quantities, set off an allergic reaction which may manifest as eye irritation, skin inflammation, hives, dermatitis, occupationally-induced asthma, or any of the symptoms associated with common allergic reactions like hay fever.

According to OSHA: "...sensitization includes two phases: the first phase is induction of specialized immunological memory in an individual by exposure to an allergen. The second phase is elicitation, i.e., production of a cell-mediated or antibody-mediated allergic response by exposure of a sensitized individual to an allergen." Sensitization reactions can be extremely severe; therefore, known potent sensitizers should be handled with the utmost care to minimize exposure.

The OSHA/GHS system for categorizing sensitizers, together with some examples, is given in <u>Appendix</u> <u>G: Sensitizers</u>.

Sensitizers Focus: Acrylate and Methacrylate Esters in Dentistry

Acrylate and methacrylate esters are encountered at USC as components in adhesives and casting resins, especially in Dentistry. These esters are associated with skin sensitization, for example, methyl acrylate and methyl methacrylate are both Category 1 skin sensitizers. Repetitive use over a long period of time is a recognized risk factor for development of allergic contact dermatitis and other inflammatory skin reactions, and acrylate/methacrylate esters are a known occupational hazard for dentistry workers. Refer to <u>Allergic Reactions to Dental Materials-A</u> <u>Systematic Review</u> for an overview of sensitization reactions to methacrylate monomers and other dentistry materials. The incidence of contact allergy to methyl methacrylate was stated as 1%.

Simple Asphyxiants

Simple asphyxiants are not included in the OSHA/ GHS hazard classification system, but are covered in the Cal-OSHA code.

<u>8 CCR §5194</u>: "Simple asphyxiant: A substance or mixture that displaces oxygen in the ambient atmosphere, and can thus cause oxygen deprivation in those who are exposed, leading to unconsciousness and death."

Simple asphyxiants are gases which have minimal or no toxicity, but which cannot sustain human life; therefore, they are hazardous on account of their ability to dilute the oxygen content of air (normally 21 % by volume). Common simple asphyxiants include nitrogen, argon, helium, methane, and sulfur hexafluoride. A distinctive feature of the hazard of simple asphyxiants is that breathing a sufficient concentration may cause rapid (seconds) unconsciousness and collapse, with zero warning symptoms. Permanent disability (brain damage) or death may ensue.

Carbon dioxide is not strictly a simple asphyxiant as it has definite toxic action; however, the concentrations at which the toxic effects become noticeable are much higher than for most other toxic gases, and overlap with asphyxiant concentrations (<u>https://</u><u>www.ivhhn.org/information/information-different-</u><u>volcanic-gases/carbon-dioxide</u>).

Consult the <u>Simple Asphyxiants and Carbon Dioxide</u> <u>SOP</u> and the <u>Simple Asphyxiants and Carbon Dioxide</u>: <u>Hazards</u>, <u>Risk Assessment</u>, <u>and Mitigation Short</u> <u>Program</u> for more information.

Cal-OSHA defines an oxygen deficient atmosphere as being one which contains less than 19.5% oxygen by volume (<u>8 CCR §5149</u>); entry into such an atmosphere is forbidden except by trained personnel with approved breathing equipment. Despite this regulatory definition, it should not be assumed that a 19.5 vol. % atmosphere is either safe or acceptable. To dilute the oxygen concentration to 19.5 vol. % requires an enormous concentration of 71,400 ppm (7.14 vol. %) of inert gas, which is a figure that should not be remotely approached in a safe laboratory environment. Furthermore, asphyxiant gases may create a severe localized hazard even though the mean concentration in the room is not excessive.

This most commonly happens when a gas settles towards the floor on account of it being it being intrinsically denser than air (e.g. carbon dioxide), or cold (e.g. liquid nitrogen boil-off), and is particularly problematic in low-lying areas of poor ventilation, for example basements, or sumps extending below floor level.

Cryogenic liquids (nitrogen, argon, helium, neon) and dry ice (frozen carbon dioxide) produce large volumes of cold gas on evaporation and are the major asphyxiation hazard encountered in research labs. Refer to <u>Cryogens & Dry Ice Fact Sheet</u> for more information.

Low oxygen alarms may be recommended in certain areas where large quantities of asphyxiant gases or cryogens are stored or used, or where the room is small, or ventilation may not be sufficient. Consult the <u>Simple Asphyxiants and Carbon Dioxide</u>: <u>Hazards</u>, <u>Risk Assessment</u>, and <u>Mitigation Short</u> <u>Program</u> for more information.

Contact labsafety@usc.edu for more information.

Chemical-Physical Hazards: OSHA/GHS Hazard Classes

Explosives

Explosives are substances capable of undergoing extremely rapid combustion/decomposition, which may propagate thermally below the speed of sound ("deflagration"), or via a supersonic shock wave ("detonation"). Many explosives produce large volumes of gas and high temperatures on explosion. Explosive hazards may include great physical damage directly from the shock wave or extreme peak pressures, and indirectly from projectiles, together with fire and burn hazards.



The OSHA/GHS hazard class *Explosives* covers explosives and also related pyrotechnic materials, including pyrotechnic materials which do not actually explode. The hazard class and its subdivisions are summarized in <u>Appendix G: Explosives</u>, which also gives examples of commercially available potentially explosive chemicals.

It is important to note that some explosive materials become less sensitive to accidental detonation and move to a lower hazard division when diluted, usually with water. When storing potentially explosive chemicals which are sold in a lower-sensitivity wetted condition, it is very important to regularly monitor them in storage to ensure they are not drying out and becoming more hazardous.

Similarly, solutions of potentially explosive chemicals should not be allowed to evaporate and deposit crystals. Note that the information about thermal runaway, given in the subsection *Self-Reactive Chemicals*, below, also applies strongly to explosives.

Flammables and Combustibles

OSHA hazard communication regulations (29 CFR 1910.1200 Appendix B) define *Flammable Gases*, *Flammable Aerosols*, *Flammable Liquids*, and *Flammable Solids*. ("Aerosols" in the regulations specifically refers to the contents of aerosol spray cans, rather than the scientific meaning of a suspension of finely-divided solid or liquid in a gaseous medium.) Each of these classifications is further subdivided into hazard categories.

Flammable gases, flammable aerosols, and flammable solids are each divided into Category 1 and Category 2, following the usual OSHA/GHS convention of the smaller number indicating the more severe hazard.

Detailed definitions of these hazard categories for solids and aerosols are not required for lab safety purposes; refer to <u>29 CFR 1910.1200</u> Appendix B if needed. For flammable gases, it is sufficient to note that almost all flammable gases are Category 1; see <u>Appendix G: Flammable Gases</u> for more information.

Note that pyrophoric gases (i.e. gases which may spontaneously ignite) do not have a separate hazard classification under OSHA/GHS regulations¹; instead, they are categorized as any other flammable gas. Because pyrophoric gases are generally flammable across wide concentrations in air, it is expected that all pyrophoric gases would fall under the classification Flammable Gas Category 1.

Flammable and Combustible Liquids

Flammable liquids are a widespread laboratory hazard. According to OSHA, *"Flammable liquid means a liquid having a flash point of not more than 93°C (199.4°F)."* Furthermore, *"Flash point means the minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid..."* Flammable liquid subdivisions are important and are given in Table 6.4.



To illustrate the concept of flash point, consider a liquid at room temperature. If the liquid has a flash point below room temperature, a lit match held above the liquid will ignite the vapor and a fire will ensue. If the liquid has a flash point above room temperature, the vapor will (probably) not ignite. However, if the vapor concentration is increased by warming the liquid, or if the liquid is locally heated, for example by soaking it into a porous material (e.g. paper, or a candle wick) and applying a flame, it will take fire.

Flash point must not be confused with ignition temperature, which is the temperature a material must be heated to (under specified testing conditions) in order for it to ignite and start to burn. Typically ignition temperatures are in the low hundreds of °C. Carbon disulfide is unusual in having an unusually low ignition temperature not much above 100 °C, meaning the vapor can potentially be ignited by such things as hotplates, hot glassware, and light bulbs.

¹ No classification in 29 CFR 1910.1200 Appendix B, although 8 CCR §5194 does offer the following definition: "Pyrophoric gas. A chemical in a gaseous state that will ignite spontaneously in air at a temperature of 130 degrees F (54.4 degrees C) or below."

GHS Hazard Class	Category	Criteria	Examples
Flammable Liquid	1	Flash point < 23°C (73.4°F) and initial boiling point \leq 35°C (95°F)	Diethyl ether, propylene oxide
	2	Flash point < 23°C (73.4°F) and initial boiling point > 35°C (95°F)	Tetrahydrofuran, acetone, methanol, ethanol, isopropanol, toluene, cyclohexane, <i>n</i> -octane
	3	Flash point $\ge 23^{\circ}$ C (73.4°F) and $\le 60^{\circ}$ C (140°F)	Butanol, dimethylformamide (DMF), acetic acid, acetic anhydride, decane
	4	Flash point > 60°C (140°F) and \leq 93°C (199.4°F)	Undecane, dodecane
Combustible Liquid	N/A	Flash point > 199.4°F (93°C)	Hydrocarbon oils (e.g. lubricating oil, vacuum pump oil), hexadecane, dimethyl sulfoxide

Table 6.4. The OSHA/GHS Classification of Flammable Liquids and Combustible Liquids.

References: 29 CFR §1910.1200 Appendix B and 8 CCR §5194

Oxidants

From a chemical safety perspective, oxidants (oxidizing agents) are materials which have a propensity to donate electronegative atoms,



most commonly oxygen, but sometimes fluorine or chlorine. The donated atoms are able to react with combustible (reducing) materials in an energetic manner. Oxidants intensify combustion, and oxidantcombustible mixtures may be violently reactive, spontaneously flammable, or explosive.

Commonly encountered oxidants in labs include oxygen, liquid air, hydrogen peroxide, nitric acid, perchloric acid, potassium permanganate, and all metal nitrates, nitrites, perchlorates, chlorates, and chlorites. The subdivisions of the OSHA/GHS hazard class *Oxidants* are given in <u>Appendix G: Oxidants</u> with examples.

Gases Under Pressure and Cryogens

Pressurized gases store mechanical energy, which is very considerable when the volume and pressure are high, as is the case for most gas cylinders. Cryogenic (i.e. extremely cold) liquefied gases are physically hazardous as they may develop high pressures on evaporation if not properly vented, and they may cause frostbite. The OSHA/GHS system categorizes both pressurized gases and cryogens into the hazard class *Gases Under Pressure*, which is further subdivided into four named groups; see <u>Appendix</u> <u>G: Gases Under Pressure</u> for details.

Self-Reactive Chemicals

Self-reactive chemicals are unstable substances which are capable of exothermic (i.e. heat producing) decomposition reactions. Decomposition reactions



accelerate with increasing temperature, so if the decomposition produces heat faster than it can escape, the material may become hotter and hotter and the reaction more and more violent; this effect is known as thermal runaway. In extreme cases, thermal runaway can result in detonation (explosion), deflagration (burning), or thermal explosion (sudden large increase in temperature).

The following all increase the possibility of thermal runaway:

- Low decomposition temperature (i.e. low thermal stability)
 - Stability of some self-reactive chemicals may be reduced when impurities or decomposition catalysts are added.
- High heat output of the decomposition reaction (i.e. high exothermicity)
- Large quantity
 - Heat loss rates roughly scale as the surface area, whereas heat output scales as the volume
 - Doubling the mass doubles the heat output, but area for heat loss is only increased by about 1.6 times
- High ambient temperature or external heating
- Confinement (i.e. sealed container)
- Thermal insulation or other impediment to heat loss

Severe thermal runaway may result in violent fire or even detonation. If self-reactive chemicals are heated under confinement then even a moderate thermal runaway can over-pressurize the container and cause it to explode. OSHA/GHS subdivides selfreactive chemicals into seven *Types*, denoted *A-G*; see <u>Appendix G: Self-Reactive Chemicals</u> for details. Note that although explosives and organic peroxides are capable of exothermic decomposition, under OSHA/GHS regulations, if a substance falls under the Explosive or Organic Peroxide hazard classifications, then those classifications shall be used instead of Self-Reactive Chemical.

Reactive With Air: Self-Heating Chemicals and Pyrophorics

Self-heating chemicals are capable of reacting spontaneously with air, with the production of heat. Self-heating chemicals are distinguished from self-reactive chemicals, covered in the previous subsection, as follows:

- Self-Heating Chemicals Heat-producing reaction is dependent on air. No reaction or heat production can occur in the absence of air.
- Self-Reactive Chemicals Heat-producing decomposition reaction does not require air.

Self-heating chemicals do not normally ignite spontaneously in air; however, extreme conditions may result in thermal runaway leading to ignition, typically after hours to days. Extreme conditions include large amounts (kilograms) of material, external heat sources, and thermal insulation.

Pyrophorics spontaneously react with air more quickly and energetically than self-reactive chemicals, leading to high risk of ignition, which may occur from a fraction of a second to several minutes after air contact. Pyrophorics are very hazardous and working with pyrophorics is covered in <u>Section 8 Working</u> with Pyrophorics. The OSHA/GHS categorization of self-heating chemicals and pyrophorics, together with some examples, is given in <u>Appendix G: Self-Heating</u> <u>Chemicals and Pyrophorics</u>.

The self-heating or pyrophoric tendency of solid chemicals is usually strongly dependent on the surface area of the solid. Thus, a material which is quite unreactive in massive form may be self-heating or even pyrophoric if in a porous form or finely powdered. This is notable for a number of metals, metal hydrides, and similar materials, where very fine powders are classified as self-heating or pyrophoric, but bulk material is not.

Many organometallic compounds used as precursors for chemical film deposition (CVD) are highly pyrophoric liquids, including: Trimethylaluminum, triethylaluminum, trimethylgallium, trimethylindium, and various organo-boranes, and organo-phosphines.

Chemicals Which, in Contact With Water, Emit Flammable Gases

OSHA hazard communication regulations (<u>29 CFR</u> <u>1910.1200</u> Appendix B) state: "Chemicals which, in contact with water, emit flammable gases are solid or liquid chemicals which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities."

Chemicals which, in contact with water, emit flammable gases are classified into three categories. Category 1 materials react vigorously with water at ambient temperature to produce a rapid stream of flammable gases. Additionally, if the gases have any tendency to spontaneously ignite, either because the reaction produces a lot of heat or because the gas is pyrophoric, then the material is classified as Category 1 regardless of the rate of gas evolution. Category 2 and Category 3 materials show decreasingly rapid evolution of flammable gases when in contact with water.

Most commonly, chemicals which, in contact with water, emit flammable gases fall into the following groups, with the gas evolved being indicated in parenthesis:

- Reactive metals and metal hydrides (hydrogen)
- Metal carbides and dicarbides (methane, acetylene, other hydrocarbons, sometimes also hydrogen)
 - Note: This is not a general feature. Many carbides, e.g. silicon carbide, tungsten carbide, and zirconium carbide, are very unreactive and used as ceramics and abrasives.
- Silicides (silane) and phosphides (phosphine, diphosphine) of reactive metals
- Organo-lithium and organo-magnesium compounds (methane, other hydrocarbons)

The subdivisions of this hazard class together with examples is given in <u>Appendix G: Chemicals Which</u>, in <u>Contact With Water</u>, <u>Emit Flammable Gases</u>.

Organic Peroxides

Organic peroxides are unstable molecules which contain a very weak O-O single bond. This is easily broken, making organic peroxides generally



thermally unstable, oxidizing, liable to exothermic self-reaction, and often explosive. The explosive ones may be sensitive to mechanical shock as well as to heat. Because a number of organic peroxides are commercial materials with important uses, mostly as bleaching agents, medicinals, or polymerization initiators, and because of the distinct hazards they pose, OSHA/GHS classifies them into a distinct hazard class *Organic Peroxide*. The subdivision of this class, together with examples, is given in <u>Appendix G:</u> <u>Organic Peroxides</u>.

Note that the information about thermal runaway, given in the subsection Self-Reactive Chemicals, above, also applies strongly to organic peroxides. Additionally, note that a number of organic peroxides are also sensitizers.

Corrosive to Metals

OSHA hazard communication regulations (<u>29 CFR 1910.1200</u> Appendix B) classify all substances which corrode either steel or aluminum (>6.25



mm corrosion per year at 55 °C) as being *corrosive* to metals. There is only one category (*Category 1*).

Substances which are corrosive to metals should evidently not be stored in metal containers. Substances corrosive to metals include many acids and bases.

For information on the categorization of substances corrosive to living tissue, see the previous subsection, *Corrosives*, above.

Particularly Hazardous Substances (PHS)

Definition and Importance

A regulatory definition for *Particularly Hazardous Substances* (PHS) is provided by Cal-OSHA, which states: *"Provisions for additional employee protection for work with particularly hazardous substances. These include "select carcinogens,"* reproductive toxicants and substances which have a high degree of acute toxicity." (<u>8 CCR §5191</u> (e) (H))

Extra caution must be taken when working with PHS. The practicalities of safely working with them are presented in <u>Section 8 Particularly Hazardous Substances</u>; this section concentrates on how to classify substances as PHS.

Acutely Toxic Substances

Highly acutely toxic materials fall under the Cal-OSHA (<u>8 CCR §5191</u>) definition of Particularly Hazardous Substances (PHS), which require additional precautions in use. The following shall be treated as PHS in laboratories at USC:

- All acutely toxic substances in GHS categories 1-3
 - Reminder: Acute Toxicity Category 1, 2, and 3 all correspond to the skull and crossbones pictogram and the "Danger" signal word (Table 6.4).

- All substances of untested toxicity (e.g. newly synthesized chemicals) where there is any degree of suspicion that they might be toxic, based on:
 - Chemical reactivity (e.g. strong electrophiles such as an alkylating or acylating agents).
 - Chemical analogies to known toxic substances.
 - Example: Phosphate, phosphonate, and carbamate esters which potentially have anti-cholinesterase activity.
 - Presence of atoms of elements generally associated with toxicity (e.g. fluorine, selenium, tellurium, lead, arsenic, antimony, cadmium, mercury, thallium, chromium(VI), beryllium).
 - Note: Any organofluorine compounds which can be potentially metabolized into monofluoroacetate in the body should be considered extremely toxic.
 - Presence of anions generally associated with toxicity (e.g. azide, cyanide, chromate, dichromate, fluoride)

Acutely Toxic Substances: Examples

A few notable examples of acutely toxic materials are:

Cyanides (e.g. sodium cyanide, potassium cyanide, cyanogen iodide, hydrogen cyanide).
 Very highly toxic, extremely rapid acting poison (seconds to minutes). Cyanide anion (CN-) inactivates the enzyme systems which enable cells to utilize oxygen to produce energy. Exposure may result in effects all the way from headache to sudden collapse, unconsciousness, convulsions, and death.

 Sodium cyanide: Acute toxicity, oral, category
 1; acute toxicity,
 inhalation, category 1;
 acute toxicity, dermal,
 category 1



- Hydrogen cyanide is a highly toxic gas produced by adding acids to cyanides.
 Take extreme care to not inadvertently produce hydrogen cyanide!
- Ionic azides, e.g. sodium azide. Azides have some similarities to cyanides in effect. Although somewhat less toxic than cyanides, they are still very hazardous acute toxicants.
 - Sodium azide: Acute toxicity, oral, category
 2; acute toxicity, dermal, category 1.
 - Hydrogen azide is a highly toxic and explosive gas produced by adding acids to ionic azides. Take extreme care to not inadvertently produce hydrogen azide!
- Soluble fluorides, e.g., sodium fluoride is classified as: Acute toxicity, oral, category 3.



- Compounds of a number of metals and metalloids ("heavy metals") are acutely toxic, for example, compounds of thallium, cadmium, mercury, and arsenic.
- Hydrogen sulfide. Toxic gas produced by bacterial action in sewers, and also made by adding acids to metal sulfides.

- Carbon monoxide (CO). Colorless odorless gas which may result from incomplete combustion in faulty heating appliances, or in internal combustion engines. It is also encountered in cylinders in some research labs. Carbon monoxide binds to hemoglobin in blood and prevents oxygen transport.
- Many plant alkaloids, such as nicotine (tobacco), coniine (hemlock), aconitine (monkshood), atropine (deadly nightshade), and strychnine and brucine (both from nux vomica).
 - Strychnine and brucine are sometimes used in organic chemistry for separating enantiomers.

Reproductive Toxicants

Reproductive toxicants fall under the Cal-OSHA (<u>8 CCR §5191</u>) definition of Particularly Hazardous Substances (PHS), which require additional precautions in use. As a type of reproductive toxicants, germ cell mutagens are also PHS.

Substances shall be treated as PHS if they are:

- Classified into any of the following GHS hazard classes:
 - Reproductive toxicant
 - Effects via lactation
 - Germ cell mutagen
- OR
 - Listed as a reproductive toxicant on the <u>California Proposition 65 list</u>

Newly synthesized substances for which adequate safety data is not available shall be considered as PHS if there is any suspicion they might be reproductive toxicants based on chemical reactivity or chemical structural analogies to known reproductive toxicants.

Select Carcinogens

Within the regulations applying to hazardous chemical usage in laboratories (<u>8 CCR §5191</u>), Cal-OSHA defines select carcinogens as follows:

"Select carcinogen. Any substance which meets one of the following criteria:

- (1) It is regulated by Cal/OSHA as a carcinogen; or
- (2) It is listed under the category, "known to be carcinogens," in the Annual Report on Carcinogens published by the National Toxicology Program (NTP) (1985 edition); or
- (3) It is listed under Group 1 ("carcinogenic to humans") by the International Agency for Research on Cancer Monographs (IARC) (Volumes 1-48* and Supplements 1-8); or
- (4) It is listed in either Group 2A or 2B by IARC or under the category, "reasonably anticipated to be carcinogens" by NTP, and causes statistically significant tumor incidence in experimental animals in accordance with any of the following criteria:
 - (A) After inhalation exposure of 6-7 hours per day, 5 days per week, for a significant portion of a lifetime to dosages of less than 10 mg/m 3;
 - (B) After repeated skin application of less than 300 mg/kg of body weight per week; or
 - (C) After oral dosages of less than 50 mg/kg of body weight per day."

*Note: There are 118 IARC Monographs now. The listing of classifications is online and easily searchable, <u>http://monographs.iarc.fr/ENG/Classification/</u>.

All IARC group 2A and 2B carcinogens and all substances classified as *"reasonably anticipated to be carcinogens"* by NTP should be regarded and handled as select carcinogens, regardless of whether or not they strictly need to be classified as such based on the OSHA animal testing criteria.

Carcinogen Information Sources

- 1. Safety Data Sheets (SDS)
 - Section 2 (Hazard Identification) will contain the hazard communication (GHS) classification
 - Example: Potassium dichromate

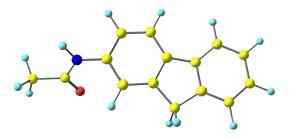
 carcinogenicity category 1B
 - Section 11 (Toxicological Information) in reputable safety data sheets (e.g. from Sigma Aldrich) should contain information on the IARC, NTP, and OSHA classification of carcinogens.
 - Example: Potassium dichromate

 IARC Group 1 (carcinogenic to humans); not listed by
 NTP; is an OSHA specially regulated carcinogen.

2. <u>Cal-OSHA specially regulated carcinogens</u>

 4,4'-methylenedianiline; 1,3-butadiene; dichloromethane (methylene chloride); respirable crystalline silica; chromium (VI) (i.e. chromates, dichromates, chromium trioxide); cadmium; asbestos; non Asbestiform tremolite, anthophyllite, and actinolite; vinyl chloride; coke oven emissions; 1,2-dibromo-3-chloropropane; acrylonitrile; inorganic arsenic; 4,4'-methylenebis(2-chloroaniline); lead; formaldehyde; benzene; ethylene dibromide; ethylene oxide. Thirteen (13) particularly severe carcinogens regulated under
 <u>8 CCR §5209</u> [CAS number]:
 2-acetylaminofluorene [53-96-3] see Figure 6.4);

Figure 6.4. 2-Acetylaminofluorene



4-aminodiphenyl² (4-aminobiphenyl) [92-67-1]; benzidine (and its salts) [92-87-5]; 3,3'-dichlorobenzidine (and its salts) [91-94-1]; 4-dimethylaminoazobenzene² [60-11-7]; alpha-naphthylamine² [134-32-7]; beta-naphthylamine² [91-59-8]; 4-nitrobiphenyl [92-93-3]; *N*-nitrosodimethylamine [62-75-9]; beta-propiolactone [57-57-8]; bischloromethyl ether [542-88-1]; methyl chloromethyl ether [107-30-2]; aziridine² (ethyleneimine) [151-56-4].

- Special regulatory conditions apply to these 13 severe carcinogens. Contact labsafety@usc.edu well in advance of purchasing or using these materials (or their salts, in the case of those that are amines).
- 3. NTP Report on Carcinogens
- 4. <u>Proposition 65 listing</u> of carcinogens and reproductive toxicants known to the State of California.

² Salts of these amines are not specifically mentioned in 8 CCR §5209, but salts should be considered equally hazardous and regulated as the free amines.

5. IARC Monographs, <u>http://monographs.iarc.fr/ENG/Classification/</u>. The classification system is shown in Table 6.5.

Group	IARC Descriptor		
Group 1	Carcinogenic to humans		
Group 2A	Probably carcinogenic to humans		
Group 2B	Possibly carcinogenic to humans		
Group 3	Not classifiable as to its carcinogenicity to humans		
Group 4	Probably not carcinogenic to humans (only one chemical (caprolactam) is currently in		
	Group 4)		

Table 6.5. The carcinogen classification system used by IARC.

Identifying More Obscure Potential or Suspected Carcinogens

Safety data sheets from a reputable source (e.g. Sigma-Aldrich, Alfa Aesar) should generally be sufficient to determine if a substance is carcinogenic, however, some of the more obscure chemicals, or newly synthesized chemicals may not have enough testing data for them to classifiable as carcinogens. In such cases, take a precautionary approach and assume that chemicals in certain classes are potential carcinogens. Some of these classes include polycyclic aromatic hydrocarbons, aromatic amines, aromatic nitro compounds, N-nitroso compounds, strong electrophilic alkylating agents (e.g. benzylic halides, chloromethoxy ethers, alkyl triflates, episulfides, aziridines, epoxides; especially if low molecular mass), strong Michael acceptors (e.g. vinyl ketones and vinyl sulfones), mustards (2-chloroethyl amine and sulfide compounds, and analogs), α -effect compounds reactive with carbonyl groups (hydrazines, hydroxylamines), and reactive aldehydes. All compounds of arsenic and cadmium should also be considered potentially carcinogenic.



Importance and Scope

Hazardous substances may pose a wide range of health and physical hazards. This section provides guidance on appropriately and safely managing these hazards during storage and transport of hazardous materials. This section covers:

- Chemical inventory
- Appropriate storage of hazardous materials.
- Transportation of hazardous materials.

Inventory Records

Importance

Keeping of accurate chemical inventory records is required for the following reasons:

- <u>8 CCR §5194 (e) (1) (A)</u>:"[Employers shall develop, implement, and maintain at the workplace a written hazard communication program... which also includes the following:] A list of the hazardous¹ chemicals known to be present using a product identifier that is referenced on the appropriate safety data sheet (the list may be compiled for the workplace as a whole or for individual work areas)"
- USC (via EH&S, Fire Safety and Emergency Planning, and other offices) must access inventories in order to:
 - Assess building compliance with <u>LA Fire Code, Chapter 50 Hazardous</u> <u>Materials- General Provisions</u> maximum allowable quantities (MAQs)².
 - Prepare disclosures to the City of Los Angeles Department of Building and Safety (LADBS) for plan check and construction/renovation permitting.
 - Prepare Hazardous Materials Inventory Statements (HMIS) and other disclosures required under California Law.
 - Assess compliance with US Department of Homeland Security Chemical Facility chemicals reporting and security requirements (<u>https://www.dhs.gov/appendix-a-chemicals-interest-list</u>)
 - Provide appropriate signage for laboratory entrances.
- Chemical inventory is required for advance emergency planning, and may be required by personnel responding to an incident.

¹ In the context of laboratory safety, Cal-OSHA defines a hazardous chemical as "any chemical which is classified as health hazard or simple asphyxiant in accordance with the [OSHA/GHS hazard classification system]" (8 CCR §5191). Cal-OSHA and hazard communication regulations (8 CCR §5191 and 8 CCR §5194) then proceed to define "health hazard" as any chemical which is either a simple asphyxiant or is in one or more OSHA/GHS health hazard classes (as defined in 29 CFR 1910.1200 Appendix A). 2 This and the following reasons require both health and physically hazardous chemicals to be inventoried.

- Accurate chemical inventory records minimize duplicate purchasing within research groups and across groups if PIs share inventory (which is recommended where possible).
 - Saves money.
 - Promotes safety by reducing total inventory and reducing over-storage of time sensitive chemicals.

Requirements

At USC, research groups shall:

- Maintain a chemical inventory, which should be regularly updated as inventory changes.
- Enter inventory records into a centralized system approved by EH&S; currently the systems are:
 - <u>RSS</u>
 - <u>EHSA</u>

All hazardous chemicals shall be entered in the inventory, including:

- Any chemical which falls into one or more OSHA/GHS health or physical hazard classes according to its labeling and safety data sheet. (Refer back to Sections <u>5</u> and <u>6</u> for details of hazard communication and OSHA/GHS classification of chemical and chemical-physical hazards, respectively).
- Any compressed, liquefied, or frozen gas (including inert gases).

Pls are ultimately responsible for compliance with chemical inventory record requirements. Inventory accuracy will be assessed during laboratory safety inspections. Inventory omissions and inaccuracies will be cited as a finding.

Exceptions

For labs which are not using a barcode inventory system, the following practices are acceptable to make inventory keeping more practical:

- In the case of labs which have a rapid turnover of cylinders of the same type of gas, or of liquid nitrogen Dewars or dry ice, it is acceptable for the inventory to list the maximum quantity which is ever stored at one time - this should be noted in the inventory. It must not be forgotten to update the inventory if the type of gas changes, or if gas or liquid nitrogen usage permanently increases or decreases.
- In the case of labs which have a rapid turnover of non-peroxide-forming solvents, it is acceptable for the inventory to list the maximum quantity which is ever stored at one time (this should be explicitly noted in the inventory). This is acceptable for pentane, hexane(s), cyclohexane, toluene, xylenes, methanol, ethanol, propanol, isopropanol³, butanol, acetone, petroleum ether, naphtha, other petroleum distillates, dichloromethane, ethyl acetate. Individual containers should still be dated when received and when opened.

Recommendations

It is recommended for PIs to institute group rules whereby personnel are required to search the inventory before ordering new chemicals, to avoid duplicate orders, ensure timely usage of timesensitive chemicals, and avoid excessive inventory. It is recommended for research groups to do a comprehensive re-inventory annually.

Personnel should not be tempted to purchase chemicals in bulk to obtain discounts.

³ Isopropanol is reported to be peroxide-forming, but only to a minimal extent, and only under extremely long storage (years). <u>http://cen.acs.org/articles/94/i31/Chemical-safety-peroxide-formation-isopropanol.html</u> and <u>http://pubs.acs.org/doi/abs/10.1021/ed065pA226</u>

Unnecessarily large chemical inventory represents a very significant and avoidable hazard. The following are considered best practices:

- Purchase the minimum quantity of the chemical needed for research.
- Purchase hazardous chemicals in amounts that can be used within 6 months, or the recommended shelf life or storage period if shorter.

PIs are strongly encouraged to share chemical inventories and chemicals with their peers within a building, department, or school. Sharing of chemicals will not only eliminate unnecessary expenses and improve overall safety, but will also encourage collaborations between research personnel.

It is recommended that chemicals which are no longer required, but are still in good condition, be offered to other research groups before contacting Hazmat for disposal.

Physical Inventory: Storage and Segregation of Chemicals

Fundamentals

Training

EH&S outlines some basics of safe chemical storage in General Laboratory Safety Training (GLST). When personnel enter research laboratories, PIs should provide appropriate laboratory-specific training on how to safely store and properly segregate hazardous chemicals. As for other types of safety training provided within research groups, internal training records should be kept.

Secondary Containment

Secondary containment basically means any container which holds one or more smaller containers. Secondary containment is an important factor in safe storage of hazardous materials to:

- 1. Localize and contain spillage from defective or broken chemical containers.
- 2. Prevent incompatible materials from mixing.
- 3. Minimize spread of contamination from highly health hazardous materials.

Secondary containment is particularly important in earthquake zones such as Southern California. In a substantial earthquake, a significant proportion of chemical bottles within storage cabinets could break. Appropriate provision of secondary containment would markedly reduce the quantity of spilled chemical which would escape from cabinets. This would make the subsequent cleanup by Hazmat teams much safer and faster, and would, therefore, potentially allow buildings to reopen sooner.

Secondary containment (See Figure 7.1) should be sufficiently voluminous so that it can hold the contents of the inner containers should they break. Secondary containment is frequently open topped, for example a polypropylene tub with bottles standing in it. This is satisfactory for most hazardous materials.

Closed secondary containment should be used to isolate materials exhibiting potent health hazards. The secondary containment shall be clearly labelled with the potential hazards. It shall also be clearly labeled with the identity of the chemical or group of chemicals being segregated e.g., cyanides or mercury compounds.

When storage space is restricted, it may be necessary to use separate secondary containment to segregate limited quantities of moderately incompatible chemicals within the same chemical storage cabinet. In such cases, the secondary containment shall be clearly labelled with the contents (e.g. inorganic oxidizers), and preferably also with hazard warning pictograms. The labelling must be sufficient that laboratory personnel can readily match up hazardous materials with the appropriate secondary containment, avoiding mix-ups, and enabling appropriate segregation to be maintained over time.

Secondary containment shall not be used as a substitute for separate chemical cabinets for the segregation of severely incompatible materials, for example acids and alkali metals, pyrophorics and flammable liquids, or flammable liquids and oxidizers.

Secondary containment need not be individually labelled when used for general storage, and NOT for isolating highly health-hazardous materials, or for segregating incompatibles within the same cabinet.





Secondary Containment and Pyrophorics

Non-combustible secondary containment is required for storage of pyrophoric materials. It is recommended that steel cans, which chemical suppliers often use as secondary packaging on their products, be retained for this purpose. If the pyrophoric is in a breakable vessel, it is recommended to pack the space between the vessel and the can with vermiculite to provide padding⁴. Vermiculite may also reduce the intensity of a fire if the layer is thick enough to completely contain and cover the liquid in the event of breakage (http://www.sciencedirect.com/science/article/pii/ S0022024806010189).

Individual containers of pyrophoric materials should have their own secondary containment. The secondary containment shall be clearly labelled with the contents and the hazard(s).

Seismic Safety

Store hazardous materials in accordance with <u>Section</u> <u>4 Seismic Safety and Hazardous Materials Storage</u>.

⁴ Vermiculite is a type of expanded mica (<u>https://www.dupreminerals.com/products/loose-vermiculite/</u>) which most labs have easy access to as chemical suppliers frequently use it as a packaging material inside boxes and cans. It is non-combustible.

Basic Considerations

Priorities for storage areas organization are:

- Flammability. When establishing a storage scheme, a major consideration should be the flammability characteristics of the material. If the material is flammable, it should be stored in a flammable cabinet (with narrow exceptions), or refrigerator approved for flammable storage by the manufacturer. Materials which burn very hot and cannot be extinguished with usual extinguishants (e.g. flammable metals) should be segregated into a separate cabinet from flammable liquids.
- Reactivity. If the material may start a fire (pyrophorics, self-heating chemicals, water reactive), or contribute significantly to a fire (oxidizer, organic peroxide, explosive, selfreactive material), it should not be stored with flammables. Materials which are water reactive should be isolated from possible water sources and leaks. Acids and bases are reactive with each other, and with many other materials, and should be segregated.
- Corrosiveness. Next look at the corrosiveness of the material, and store in secondary containers that are resistant to corrosion. Note that a number of corrosives are also oxidizers (e.g. nitric acid, perchloric acid) or flammable/combustible (e.g., acetic acid, acetic anhydride) and need to be segregated from each other.
- Toxicity. Finally, consider the toxicity of the material, with particular attention paid to regulated materials. In some cases, this may mean that certain chemicals will be isolated within a storage area. For example, a material that is highly acutely toxic but is also flammable may be stored inside sealed secondary containment in the flammable storage cabinet to protect it against accidental release.

Segregation of very toxic materials in secondary containment within a dedicated poisons cabinet may also be appropriate.

 Physical Security. Extra physical security such as locked cabinets or restricted room access should be considered for highly potent health-hazardous materials (e.g. cyanides, potent carcinogens), and materials of extreme monetary or scientific value. Approved physical security is required for storage of controlled substances (CS; i.e. DEA controlled drugs); this is covered under the USC CS program.

There are a number of schemes for safely segregating chemicals in storage; one such scheme is shown in Figure 7.2. PIs shall ensure their hazardous materials are segregated in a manner which appropriately reduces the possibility of hazardous interaction between incompatible materials.

Acceptable chemical storage locations may include corrosive cabinets, code-compliant flammable cabinets, laboratory shelves with earthquake lip, or refrigerators or freezers. Note that flammables shall not be stored in refrigerators or freezers unless approved for flammable storage by the manufacturer. Fume hoods should not be used as general storage areas for chemicals, as overcrowding may seriously impair the ventilating capacity of the hood. Chemicals should not be routinely stored on bench tops or stored on the floor.

Additionally, bulk quantities of chemicals (i.e., larger than one-gallon) should be stored in a separate storage area such as a stockroom or supply room, whenever possible. Laboratory shelves should have a raised lip along the outer edge to prevent containers from falling. Hazardous liquids or corrosive chemicals should not be stored on shelves above eye level.

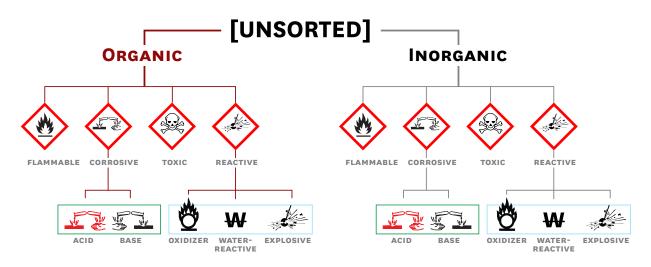


Figure 7.2. A simple scheme for safe segregation of hazardous chemicals in storage.

Chemicals which are highly toxic or corrosive should be in unbreakable secondary containers. Refer to <u>Section 4 Seismic Safety and Hazardous Materials</u> <u>Storage</u> for more information on shelf storage of hazardous materials.

Incompatible materials should be stored in separate cabinets, whenever possible. If these chemicals must be stored in one cabinet due to space limitations, adequate segregation and secondary containment must be ensured to prevent adverse reactions. All stored containers and research samples must be appropriately labeled and tightly capped to prevent vapor interactions and to alleviate nuisance odors. Flasks with cork, rubber or glass stoppers should be avoided because of the potential for leaking. Laboratory refrigerators and freezers must be labeled appropriately with "No Food/Drink" (see Figure 7.4) and shall not be used for the storage of consumables. Freezers should be defrosted periodically so that chemicals do not become trapped in ice formations. Chemicals or materials in glass containers inside freezers shall be placed in secondary containers.

Maximum Allowable Quantities (MAQs)

Maximum allowable quantities (MAQs) are the maximum amount of a hazardous material allowed to be stored or used within a defined area⁵ inside or outside a building. The Los Angeles Fire Code has determined different MAQs for flammable solids/ liquids/gases, oxidizers, toxic substances, pyrophoric materials, and other hazardous materials based on the hazard, the occupancy classification given to the specific building, the number of the floor, and other factors. MAQ compliance is assessed by USC EH&S and Fire Safety based on chemical inventory records. The following are considered best practices to stay in compliance with MAQs:

- Chemicals should be stored in approved cabinets (e.g. flammable/gas cabinets).
- Purchase appropriate quantities and limit accumulation.
- Properly dispose of unused or out-of-date chemicals.
- Contact EH&S and Fire Safety before ordering containers with volumes greater than 5 gallons.
- Maintain chemical inventory in <u>RSS</u> or <u>EHSA</u>.

⁵ In buildings, MAQs are defined per control area. A building floor may be one control area, or it may be split into more than one control area by walls of specified fire resistance.

Flammable Cabinets

The flammable cabinet is designed to store flammable materials while minimizing the risk of spread of fire (see Figure 7.3). Flammable cabinets are also required to fulfill Cal-OSHA and Los Angeles Fire Code requirements. It must be self-closing.⁶

- Store flammable and combustible liquids in flammable cabinets.
- The maximum combined quantity of flammables and combustible liquids that can be stored in an individual flammable cabinet is 60 gallons.
- The maximum amount allowed stored outside a flammable storage cabinet, safety can, or approved refrigerator or freezer is 10 gallons of combined flammables, with no individual container being larger than 1 gallon (8CCR §5538).
- Flammables that are not being used should be stored in a flammable storage cabinet, or approved refrigerator or freezer.
- Flammable cabinets have a catch tray built into the base which acts as secondary containment. Given the high earthquake risk and hazard in the Los Angeles area, it is strongly recommended to provide additional secondary containment for all glass bottles stored above the base.
- Flammable cabinets need to be labelled "FLAMMABLE - KEEP FIRE AWAY" in red letters on a contrasting background (Los Angeles Fire Code §5704.3.2).
- Cabinets shall be placed so that they do not block or impede egress.
- For the purpose of increasing MAQ allowance, flammable cabinets need to comply with construction specifications of the Los Angeles Fire Code (§5704.3.2) in addition to Cal-OSHA regulations (§5533).

- Flammable cabinets need to have self-closing doors.
- Flammable cabinets need to have doors with a three point latch per the LA Fire Code.
- The bottom of the cabinet shall be liquid tight to a height of 2 inches.
- Wooden cabinets must be painted with intumescent-type paint.



Figure 7.3. Flammable Cabinet

Refrigerators and Freezers

All chemicals should be stored with consideration to incompatibilities so that if a container breaks, reactive materials do not mix and react violently. Within refrigerators and freezers, appropriately labelled secondary containment should be used to separate incompatible chemicals. It is required that all glass containers in refrigerators and freezers be placed in secondary containment.

⁶ Older flammable cabinets may not have a self-closing door. This is acceptable for Cal-OSHA, but not for the LA Fire Code. Storage in fire code compliant flammable cabinets allows for doubling of MAQ. If storage quantities are such that MAQ doubling is not required, older cabinets with non-self-closing doors may continue to be used. This will be assessed by EH&S and Fire Safety on a case-by-case basis. All newly purchased flammable cabinets should have self-closing doors.

Laboratory refrigerators and freezers shall **NEVER** be used to store food or beverages for human consumption. They shall have permanent labels warning against the storage of food and beverages for human consumption (see Figure 7.4).

Flammable materials are a hazard in ordinary refrigerators due to the presence of potential ignition sources, such as switches, relays, and, possibly, sparking fan motors; therefore, ordinary refrigerators shall **NEVER** be used for storing flammable chemicals.

Flammable Storage and Explosion-Proof Refrigerators and Freezers

Flammable Storage Refrigerators / Freezers

Laboratory flammable-proof refrigerators and freezers are available which are designed to provide safe storage of flammables and other volatile materials. These superficially resemble ordinary units but differ in having a spark-free interior. Flammable liquids may be stored in these units.

These units are designed to reduce the risk of ignition/explosion INTERNALLY and are appropriate for storage of small amounts of flammable materials, flammable liquids (flash points < 100°F), and combustible liquids (flash points > 100°F). They are NOT appropriate for storage of large quantities of flammables. NOTE: These units are not rated for an external flammable atmosphere (i.e. are not "explosion-proof") and CANNOT be placed in areas where flammable atmospheres may be present.

Any vapors that escape from the stored contents accumulate over time and may get absorbed into the plastic interior and surrounding insulation.

Figure 7.4. No Food or Drink Label



For this reason, it is possible that flammable storage refrigerators may build up an atmosphere that is potentially explosive, flammable, or health hazardous. Precautions to consider:

- Keep head out of refrigerators when searching for a particular sample.
- Never place uncapped containers of chemicals in a refrigerator.
- A tray of activated carbon can be very effective at combatting buildup of vapors in refrigerators. For further information, email <u>labsafety@usc.edu</u>.

Avoid storing opened peroxide formers (e.g., ether) in a refrigerator or freezer, as low temperatures may not slow peroxide formation, and may actually increase hazard by promoting crystallization of explosive solid peroxides.

Explosion-Proof Refrigerators / Freezers

Explosion proof refrigerators (see Figure 7.5) and freezers are designed to be spark-free on both the interior and the exterior⁷. When installed according to electrical code standards, they may be used in areas where a flammable atmosphere may be present.

Note that "explosion-proof" strictly refers to the refrigerators/freezers being designed to not ignite flammable gases/vapors. "Explosion-proof" does NOT indicate that a unit has any resistance to an explosion, or is suitable for storing explosive materials.

⁷ Equipment for use in potentially flammable atmospheres is regulated by the <u>National Electrical Code</u> (NFPA 70, Chapter 5), <u>ANSI</u> standards, and other codes.

General Considerations

Laboratory refrigerators and freezers designed for safe storage of flammables must be externally labelled as such by the manufacturer. They must meet NFPA and OSHA requirements for flammable materials storage. Laboratory refrigerators and freezers should always be operated in accordance with manufacturers' instructions and recommendations. Instruction manuals should be kept for future reference.

If manufacturers labelling is absent or missing, there is no way for EH&S to determine whether a refrigerator/freezer is suitable for flammables storage. All refrigerators or freezers not positively identifiable as approved units shall be considered non-approved and shall be clearly labelled "Not approved for the storage of flammables", or word to that effect.

Flammables stored in refrigerators and freezers are considered to be stored outside a flammable cabinet. Flammables inappropriately stored in a nonapproved refrigerator or freezer will be cited as a finding during safety inspections.

Non-Flammable-Approved Refrigerators and Freezers in Laboratories

Storage of flammable or combustible materials in refrigerators or freezers not flammable-approved is PROHIBITED in all cases which do not meet the criteria for limited exceptions given below. Even in cases which meet the criteria, use of flammableapproved refrigerators or freezers is the preferred storage method.

Flammable materials may be stored in a nonflammable-approved (e.g., household-style) refrigerator or freezer ONLY under Exception A or Exception B, below:

Figure 7.5. Explosion-proof refrigerator.



Source: VWR

Exception A

This exception is applicable to reagent kits of small volume such as are commonly found in biological and biomedical-type labs. Often, one or more of the reagents in these kits contains an organic solvent such as ethanol or acetonitrile in a concentration which is often a trade secret. Many of these kits need to be stored cold. This exception also applies to small sepharose columns wetted with a mixture containing ethanol or other flammable solvent.

- 1. In order to comply with this exception, conditions 2 through 4, shall ALL be met.
- Flammable solvent(s) present in the reagent shall have a boiling point equal to or higher than methanol (boiling point 64.7 °C, 148.5 °F)
 - a. Methanol, ethanol, acetonitrile,
 1-propanol, and isopropanol are
 examples of acceptable solvents.

- b. In the case of a solvent containing a mixture of chemical species and, therefore, boiling over a range of temperatures, the initial boiling point shall be taken.
- Individual bottles shall NOT contain more than 15 mL of flammable reagent.
- 4. Reagent kits shall be stored in secondary containment with air-tight lids.
 - a. Secondary containment shall be of adequate quality and construction to give reasonable assurance of an air-tight seal.
 - Decent quality food storage containers designed to be air-tight should be generally suitable. Other possibilities include polyethylene screw-top containers with good seal (e.g. Nalgene[™] brand).
 - ii. Lids shall be secured by clasps, threaded, or a tight press-fit.
 - b. Secondary containment with warped lids, cracking, damaged sealing surfaces, or where rubber gaskets or other seals are missing shall NOT be used.

Exception B

This exception applies to cases which do not fall under exception A.

- 1. In order to comply with this exception, conditions 2 through 4 shall ALL be met.
- 2. The flash point shall be:
 - a. At least 120 °F (48.9 °C); OR
 - b. At least 100°F (38 °C) **AND** the flammable material is an aqueous solution containing more water than solute.

- The total quantity of flammable material in the fridge or freezer shall not exceed 1 L (liquid) or 1 kg (solid).
 - a. If flammable solids and liquids are both present, then the sum of the mass of solid in kilograms and the volume of liquid in liters shall not exceed 1 (one).
- All vessels containing >1 mL of flammable material shall be stored in an appropriate plastic or metal secondary container with a sealable lid. The secondary container shall be:
 - a. Durable (not readily breakable); AND
 - b. Fitted with a secure air-tight lid; AND
 - c. Not be susceptible to degradation by materials stored in the refrigerator/ freezer.

Flash points may be found in Section 9.1 of SDSs from a reputable vendor (e.g., Sigma Aldrich). Closed cup flash points are preferable as they best represent the temperature at which a flammable material in an enclosed space is able to produce a sufficient concentration of vapor to form a flammable or explosive mixture in air. Note that for mixtures, flash points do not scale linearly with concentration, but are skewed in the direction of the lowest flash point component. Table 7.1 lists selected chemicals in ascending flashpoints.

Table 7.1 Selected Chemical Flashpoints

Chemical	Flashpoint (F)
Isopentane	-60 °F (-51 °C)
Ethyl Ether	-49 °F (-45 °C)
Acetone	1 °F (-17 °C)
Isopropanol	53 °F (12 °C)
Methanol	54 °F (12 °C)
Ethanol	55 °F (13 °C)
tert-Butanol (solid)	59 °F (15 °C)
20% Ethanol	97 °F (36 °C)
Acetic acid	104 °F (40 °C)
Formaldehyde solution, 37% in water, 10-15% MeOH stabilizer	133 °F (56 °C)
Camphor (solid)	148 °F (64 °C)
Paraformaldehyde (solid)	160 °F (70 °C)
Formalin solution, neutral buffered 10%	185 °F (85 °C)
Menthol (solid)	200 °F (93 °C)

Secondary containers may be plastic or metal. For plastic secondary containers, polypropylene or polyethylene are generally to be preferred. Polystyrene, polycarbonate, and acrylic polymers are all susceptible to softening or dissolution by various organic solvents.

Additionally, trace quantities of solvents may cause polystyrene, polycarbonate, and acrylic polymers to become weak and brittle due to environmental stress cracking. If metal cans are used as secondary containment, care shall be taken to avoid the presence of incompatible corrosives.

Secondary containment lids are required to be held closed by a reliable system such as a screw thread or clasps (for plastic containers), or be a tight press fit (for metal cans).

Cold Rooms

Cold rooms are not ventilated, therefore:

- Flammable materials shall not be stored or used in cold rooms.
- Toxic or other health hazardous materials of sufficient volatility to pose an exposure hazard via the vapor phase shall not be stored or used in cold rooms.
- Gas cylinders shall not be stored or used in cold rooms.
- Materials releasing corrosive vapors (e.g. hydrochloric acid, nitric acid) shall not be stored or used in cold rooms.
- Dry ice, liquid nitrogen, other cryogenic liquids, and other materials which may displace oxygen and present an asphyxiation hazard shall not be used or stored in cold rooms.
 - Dry ice in a cold room has produced fatal asphyxiation (<u>Asphyxiation Due</u> to Dry Ice in a Walk-in Freezer)
- Materials which react with water to produce gases may not be used or stored in cold rooms.

Storage of Different Hazard Classes Potentially Explosive Materials and Organic Peroxides

Many commercially available explosive chemicals are sold as a solid wetted with water to make them less sensitive to accidental detonation and to move them to a lower hazard classification. When storing potentially explosive chemicals which are sold in a lower-sensitivity wetted condition, it is very important to regularly monitor them in storage to ensure they are not drying out and becoming more hazardous. Similarly, solutions of potentially explosive chemicals should not be allowed to evaporate and deposit crystals. Potentially explosive materials should be stored in minimal quantities. Consult supplier for recommended storage temperature and other special conditions (quite a few potentially explosive materials and organic peroxides need to be stored at reduced temperature). Keep track of storage time and dispose before the expiration date, or when no longer required. Many potentially explosive materials are rendered more sensitive by impurities — take care not to introduce contamination.

Storing potentially explosive materials as a dilute solution is a safer option whenever possible, for example, this is the preferred storage option for picric acid when used as a dye or stain.

Examples:

- 2,4-Dinitrophenylhydrazine (Brady's reagent) Not classified as an explosive when sold wetted with ≥33% water (classified as *Category 1 Flammable Solid* instead). However, is hazardously explosive when dry.
- Picric acid (trinitrophenol; see Figure 7.6)

 Not classified as an explosive when sold wetted with ≥35% water (classified as Category 1 Flammable Solid instead).

Figure 7.6. Picric Acid



However, is hazardously explosive when dry.

- Picric acid salts may be very dangerously sensitive explosives and may be formed inadvertently if picric acid is allowed to come into contact with metal surfaces e.g., metal spatulas.
- Glyoxime Flammable Solid Category 1 when moistened with ≥ 20% water; hazardously explosive when dry.
 - Metal complexes may be very sensitive explosives.
 - Do not use metal spatulas.
- Ammonium perchlorate Explosive Division 1.1 when in bulk, but may not be labeled as an explosive when sold in research quantities.
 - Quite insensitive and safe under normal lab conditions, but may be an explosion hazard in fire, if heated, or when mixed with other substances.
 - Store as an oxidizer. (Category 1 Oxidizing Solid)

Flammable Chemicals

Flammable liquids must not be kept on the floor or in non-approved refrigerators or freezers. All storage areas containing flammables should be labeled with appropriate labels containing the word "flammable". At all times flammables must be segregated from oxidizing, pyrophoric and water reactive chemicals.

A maximum of ten (10) gallons of flammable liquids may be stored outside of approved flammable storage cabinets (<u>https://www.dir.ca.gov/Title8/5538.</u> <u>html</u>).

In order to qualify for increased MAQs, flammable cabinets need to have self-closing doors with a three point latch per LA Fire Code, Section 5704.3.2.

OSHA compliant flammable storage cabinets (without self-closing doors) may be used when a laboratory doesn't need MAQ doubling. This will be assessed by Fire Safety and EH&S on a case-by-case basis.

Oxidizing Chemicals

Oxidizers should be segregated from flammable, combustible, pyrophoric, water reactive, and reducing materials. Small quantities of inorganic solid oxidizers may be in the same cabinet as general inorganic storage, but should be segregated in separate secondary containment, which should be clearly marked "oxidizer". If large quantities of oxidant are required to be stored, a dedicated noncombustible steel cabinet is strongly recommended.

Perchloric acid and fuming nitric acid shall NOT be kept in wooden cabinets due to the possibility of spontaneous ignition or explosion.

Time-Sensitive Chemicals

Time-sensitive chemicals include organic peroxide formers, potassium and potassium alloys, alkali metal amides, HBr and anhydrous HF in steel cylinders, chloroform, hydrogen peroxide and concentrated formic acid. These materials may become hazardous on prolonged or incorrect storage for a variety of reasons — potassium, alkali metal amides, and organic peroxide formers may become explosive; chloroform may produce highly toxic phosgene gas; HBr and HF in steel cylinders may generate hydrogen overpressure to the extent the cylinder explodes; hydrogen peroxide and concentrated formic acid may generate gas pressure in the bottle. Pls and researchers should understand these hazards and follow appropriate storage and work practices to manage the risk, per EH&S requirements, the CHP, and EH&S Time-Sensitive Chemicals web pages.

Inorganic "Peroxide-Forming" Materials

Potassium, potassium alloys, and alkali metal amides may become dangerously explosive through absorption of oxygen or oxygen and water.

The mechanisms are completely different than organic peroxide formers, and peroxides may not even be involved, but despite the deficiency in the nomenclature, these materials are commonly included in the general class of "peroxide formers".

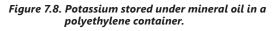
Potassium and Potassium-Sodium Alloy (NaK)

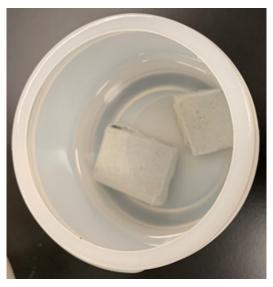
Potassium and potassium alloys react with atmospheric moisture, oxygen, and carbon dioxide to form an external crust containing a variable mixture of potassium oxide, peroxide (K2O2), superoxide (KO2), hydroxide, carbonate, and solid hydrates of KOH. Potassium peroxide and superoxide are powerful and highly reactive oxidants which can react violently with potassium metal and with organic materials, including the hydrocarbon oil in which potassium is commonly stored. Hydrates of potassium hydroxide have potential to react violently with potassium, analogous to the well-known energetic interaction between potassium and water.

Visibly crusted potassium is metastable. At the surface of the potassium, between the reducing metal and the oxidizing portions of the crust, there is presumably a thin layer containing potassium oxide (K2O) separating them. If the crust is soaked in oil (or other hydrocarbon liquid), then any K2O2 or KO2 in the crust will not react with the oil unless initiated by heat, or possibly by friction.

Crusted potassium may sit almost indefinitely without hazardous occurrence only for it to spontaneously explode on squashing (e.g. with tweezers), cutting, or heating. Potassium is commonly stored under oil or in inert atmosphere.

Oil is slightly permeable to oxygen and water vapor so potassium stored under oil in air slowly reacts at the surface. Potassium stored in pure nitrogen or argon (e.g., sealed in a glass ampoule) is indefinitely stable, but if the atmosphere contains even traces of oxygen and water vapor (not uncommon in glove boxes) then slow surface reaction is inevitable. A thin grey coating which does not obscure features of the metal surface (like scratches or imperfections) is generally not hazardous but if there is a coating which completely obscures the metal, is visibly thick, shows surface "fur" or excrescences, or is white, yellow, or very pale grey then the potassium may be dangerous (see Figure 7.8 below).





Storage time is thought to be about two years. There is a thin but significant pale grey crust which is getting close to the limit of what is acceptable.

Before purchasing potassium, consider substituting safer alternatives (e.g. sodium, which does not form a hazardous crust in storage). If potassium or potassium alloys must be used, minimize the inventory.

Laboratories which store or use potassium or potassium alloys shall follow the safety rules specified on the <u>Other Time-Sensitive Chemicals</u> web page.

NOTE: If crusted potassium metal is discovered, DO NOT attempt to move or disturb the material. Immediately notify the PI and other lab personnel and restrict access to the area. Notify EH&S Hazmat (213) 740-7215 or <u>hazmat@usc.edu</u> to have the material assessed and removed.

If a non-dated metal can or other non-transparent container of potassium metal is found which is old or of uncertain age, DO NOT attempt to open to make a visual inspection of the potassium. Notify EH&S Hazmat (213) 740-7215 or hazmat@usc.edu to have the material assessed and removed.

Additional information and case studies:

https://pubs.acs.org/doi/abs/10.1021/ed085p634.2 A chemistry teacher at a Swiss secondary school used a knife to remove a small piece of potassium from a bottle in which the potassium was stored under petroleum.

During the procedure, the small piece of potassium spontaneously exploded causing severe burns to the teacher. The bottle and remaining potassium within were not affected.

https://pubs.acs.org/doi/pdf/10.1021/cen-v080n037. p002 Potassium vacuum-packed in high-density polyethylene bags (0.2 mm thickness) caused a fatal explosion after it was removed, placed in petroleum ether under argon, and warmed to melt the potassium. Chemical analysis of the thick crust which had formed during storage showed a composition of 80-90% potassium hydroxide monohydrate and 10-15% potassium superoxide. This case illustrates the dangers of crusted potassium and also highlights that polyethylene is distinctly permeable to oxygen and water vapor. Only small traces of water and oxygen can be sufficient to cause dangerous crusting if the reaction proceeds for a sufficiently prolonged time.

https://pubs.acs.org/doi/10.1016/j.jchas.2006.09.010

Discussion of potassium safety, including photographs of slightly oxidized potassium and heavily crusted potassium.

Potassium Amide (Potassamide), Sodium Amide (Sodamide), and Other Alkali-Metal Amides

Note that rubidium and cesium amides display the same hazards of sodium and potassium amide, but are extremely uncommon materials.

Potassium and sodium amides (KNH2 and NaNH2, respectively) are combustible solids which pose a number of serious reactive hazards, including with air and water.

In the case of exposure to air, these substances rapidly absorb oxygen with the formation of nitrite and traces of hyponitrite, which are reactive oxidizers.

Exposing sodium/potassium amides to air for even a short period of time results in an intimate oxidizer-combustible mixture which has been known to spontaneously explode without prior warning, sometimes long after the exposure to air occurred. Even a trace exposure to air can result in the material becoming dangerous, since even if it does not become explosive, it may become spontaneously flammable or evolve heat or sparks. Furthermore, the high reactivity of KNH2 and NaNH2 give them potential to absorb oxygen even when the latter is present in extremely small concentrations; thus, storage in a glove box may cause the materials to become hazardous if storage is sufficiently prolonged. There may be no visual sign to indicate that potassium/ sodium amide has become dangerous.

Laboratories which store or use alkali metal amides shall follow the safety rules specified on the <u>Other Time-Sensitive Chemicals</u> web page.

NOTE: Immediately notify EH&S Hazmat (213) 740-7215 or <u>hazmat@usc.edu</u> if alkali metal amide has been inadvertently exposed to air and may have become hazardous.

References

- <u>https://pubs.acs.org/doi/10.1021/</u> <u>cr60041a002</u>
- Sodium amide see reference no. 4459 in Bretherick's Handbook of Reactive Chemical Hazards online <u>https://www.sciencedirect.com/science/</u> <u>article/pii/B9780123725639500161#cesec43</u>

Organic Peroxide Formers

A substantial range of organic compounds are capable of slow reaction with oxygen (typically from air) with the production of peroxides, these being compounds distinguished by the presence of an oxygen-oxygen single bond. Organic peroxides are unstable materials which readily undergo exothermic decomposition. Some organic peroxides slowly decompose at room temperature, but many are stable enough to persist, but will generate heat, flame, or explosion on moderate heating, or for sensitive peroxides, on mechanical disturbance. As a general rule, the larger the proportion of peroxidic oxygen in the molecule (e.g., measured as a weight percentage) the more hazardous and explosive the material is.

The initial products of peroxidation are generally hydroperoxides, containing an R–O–O–H, where R is the organic part of the molecule. Hydroperoxides can be unstable, explosive, and also easily detected by common tests (e.g., commercial peroxide test strips). For certain materials, the initial hydroperoxides may react further to form dialkyl peroxides, R–O– O–R, which may be cyclic or polymeric. These substances are usually more thermally stable than hydroperoxides, but may still be extremely dangerous explosives. Dialkyl peroxides may be unreactive in peroxide tests. However, if significant dialkyl peroxide has formed, then there will be enough precursor hydroperoxide present to give a positive test.

Peroxide formers are classified into Classes A, B, and C; see EH&S Peroxide Formers Guidance Spreadsheet for details. Class A substances can form peroxides in such high concentration that the material becomes a mass explosion hazard. A particularly notorious example of a Class A peroxide former is diisopropyl ether, for which the initially formed hydroperoxide fairly rapidly converts to dimeric and trimeric acetone peroxides, which have a pronounced tendency to crystallize out of the solution in a pure state. Class B peroxide formers, which include diethyl ether, tetrahydrofuran (THF), and 1,4-dioxane may form considerable concentrations of peroxides, but not enough for the material to directly become explosive.

Instead, a serious explosion hazard may arise if the peroxidized material is evaporated, e.g., during distillation, since peroxides are invariably less volatile than the precursor compound and therefore, become concentrated in the unevaporated residue. This is a "classic" cause of laboratory explosions, which are unfortunately still too common - see https:// ehs.berkeley.edu/news/peroxide-explosion-injures-campus-researcher as a representative example. In this incident, THF (stabilizer-free) and diethyl ether were being removed from a reaction product using a rotary evaporator when the glass flask violently exploded, injuring a student via flying shards of glass.

Class C materials are materials where peroxide formation may result in uncontrolled polymerization, which evolves heat. If the temperature reaches the boiling point of the unpolymerized liquid, which may happen fast as the reaction rate increases with temperature in a positive feedback loop, the containment vessel is likely to explode.

The above account is only a brief introduction to organic peroxide formers. Refer to the <u>EH&S Time-Sensitive Chemicals</u> web page and the following references on identification and classification of peroxide formers:

- Review of Safety Guidelines for Peroxidizable Organic Chemicals, Richard J. Kelly, Chemical Health & Safety 1996, 3, 5, 28-36, <u>https://pubs.acs.org/doi/pdf/10.1021/acs.</u> <u>chas.8b03515</u>
- Those pesky peroxides..., Dawn Mason, Journal of Chemical Health & Safety 2014, 21, 3, 13-15, <u>https://pubs.acs.org/doi/ pdf/10.1016/j.jchas.2013.12.011</u>

A list of further references may be found in the "Useful refs" tab of the EH&S Peroxide Formers Guidance Spreadsheet.

Figure 7.9 illustrates polyethylene bottles showing the characteristic "squashed" appearance which commonly occurs on prolonged storage of organic peroxide formers due to adsorption of oxygen within the container. The smaller bottle on the left contains polyethylene glycol monomethyl ether (MW 350) and the larger vessel contains diethylene glycol monoethyl ether.⁸

Figure 7.9. Polyethylene containers on prolonged storage of organic peroxide formers



Organic Peroxide Former Rules

Laboratories which store or use organic peroxide formers shall familiarize themselves with the following webpages and spreadsheet and shall adhere to follow the safety rules specified therein:

 Organic Peroxide Formers: Identification, Hazards, Precautions, Safe Storage [link to page 01]

- 2. Organic Peroxide Former Testing and Labeling [link to page 02]
- 3. The <u>EH&S Peroxide Formers Guidance</u> <u>Spreadsheet</u> - explains classification system, lists specific compounds, and is the definitive reference for maximum storage times.
- Diisopropyl ether shall not be purchased, stored, or used unless there is a compelling technical reason why no other material can be substituted.
 - a. Diisopropyl ether shall NOT be used as a solvent. Diisopropyl ether does not have unique or unusual solvent properties and a safer solvent can always be substituted.
 - Diisopropyl ether purchases shall be subject to approval by EH&S. In the event of any disagreement about the necessity of using diisopropyl ether, the matter shall be adjudicated by the Chemical Safety Committee.
- Laboratories which store or use organic peroxide formers shall familiarize themselves with the following webpages and spreadsheet and shall adhere to follow the safety rules specified therein:
 - a. <u>Organic Peroxide Formers: Identification</u>, <u>Hazards, Precautions, and Safe Storage</u>
 - b. Organic Peroxide Formers: Testing and Labeling
 - c. <u>EH&S</u> <u>Peroxide</u> Formers <u>Guidance</u> <u>Spreadsheet</u> - explains classification system, lists specific compounds, and is the definitive reference for maximum storage times

⁸ As oxygen within the container is adsorbed and the internal nitrogen concentration increases above atmospheric, presumably the direction of overall nitrogen diffusion becomes outwards, otherwise the airspace in the container would not be able to almost completely disappear, as has occurred to the container on the left in the above photograph. For the more thermodynamically-minded, the endpoint of zero net nitrogen diffusion is reached when the fugacity of nitrogen inside the container is equal to that in the surrounding atmosphere.

 If a bottle of peroxide-former is discovered which is old and/or contains solid deposits (e.g. crystals) or oily or viscous liquid material, DO NOT MOVE THE BOTTLE. Immediately warn other lab personnel and notify EH&S Hazmat (213) 740-7215 or hazmat@usc.edu.

Additional Safety Tips

Organic peroxide formers should be stored in a dark, dry, and cool location.⁹ Do not return unused excess back to the original bottle, or introduce impurities, since doing so may increase the rate of peroxide formation.

Purchasers and users of organic peroxide-formers, especially solvents, should familiarize themselves with SDSs and labels. Safety data sheets from reputable sources should contain information on peroxideforming tendencies.¹⁰

Manufacturer's labeling should indicate whether peroxide formers are stabilized or not and give an expiration date.

Purchase peroxide-forming solvents in grades containing a stabilizer (inhibitor) whenever possible. Check vendors' websites for information on the presence of stabilizers when ordering solvents including (but not limited to) diethyl ether, tetrahydrofuran, and 1,4-dioxane. Refer to the <u>EH&S Time-Sensitive Chemicals</u> web page for more information.

Organic Peroxide Formers: Some Interesting Information for the Chemically-Curious

The slow free-radical reaction of oxygen with organic compounds under non-combustion conditions is known as "autoxidation", an old but useful piece of nomenclature. The oxygen molecule is a diradical in its ground state, but in general is insufficiently reactive to instigate free-radical chain reactions with common organic materials at room temperature.

However, there are many environmental factors which can initiate free radical chains, including reactive trace gases (e.g. ozone, nitrogen dioxide), light (especially ultraviolet photons), and reactive oxygen species (e.g., singlet oxygen, hydroxyl radicals, hydrogen peroxide) which themselves may be photochemical in origin. Traces of certain redox-active metal ions may strongly catalyze chain initiation or propagation.¹¹ Traces of light- or UV-absorbing contaminants may greatly increase the ability of illumination to initiate radical chains.

The susceptibility of organic compounds to autoxidation is largely a function of the stability of the organic radical which remains after abstraction of a hydrogen atom.

⁹ Peroxide formation is often catalyzed by light. Storage away from heat sources is highly advisable. However, avoid storing opened peroxide formers (e.g., ether) in a refrigerator or freezer as the low temperatures may not slow peroxide formation, and may actually increase hazard by promoting crystallization of explosive solid peroxides.

¹⁰ Information on peroxide formation is not a mandatory requirement for SDSs, and peroxide-forming tendency is not a part of GHS hazard classification. However, conscientious vendors will often include "May form explosive peroxides" in Section 2.3 Hazards not otherwise classified (HNOC) or not covered by GHS, though absence of this warning is not always a good indicator that peroxides will not form.

¹¹ Autoxidation of highly unsaturated plant-derived "drying oils" such as linseed oil results in cross-linking, which is the reason they slowly gel and eventually harden when exposed to the air. This property is what makes these oils so useful as a treatment for wood or as a base for artist's oil paints; however, the pure oils harden at a very low rate, taking days to weeks. Addition of a small percentage of a "drying agent" as a catalyst, typically an oil-soluble cobalt(II) carboxylate, massively accelerates autoxidation, and can result in a level of hardening in a few hours which would take a week in the absence of the catalyst.

Use of strong chelating agent can preferentially stabilize one oxidation state of a metal ion and eliminate its catalytic activity on autoxidation. This is one reason why chelating agents (e.g. EDTA) are often included in addition to free radial inhibitors (e.g. BHT) to prevent or delay oxidative degradation in things like personal care products (e.g. cosmetics). (The other reason is that chelating agents reduce the availability of trace metals ions to microorganisms, which aids the effectiveness of preservatives.)

Thus, for example, toluene does not peroxidize under normal conditions, but isopropylbenzene (cumene) can form peroxides relatively easily because the PhMe₂C• radical is highly stabilized through being both tertiary and delocalized.

Ethers peroxidize at the alpha position because the oxygen substantially stabilizes the $R^1O(R^2)(R^3)C^{\bullet}$ radical, where R^2 = alkyl/aryl and R^3 = H or alkyl/ aryl. If both R^2 and R^3 are hydrogen then the radical is sufficiently stable that peroxidation at that position is not a concern. Thus, <u>dimethyl ether</u> and methyl tert-butyl ether are unusual amongst ethers in not forming significant quantities of peroxides under normal conditions.

Furthermore, ethers with no alpha-H do not peroxidize, for example <u>2,2,5,5-tetramethyltetrahydrofuran</u>, which is under consideration as a new solvent.

Taking ethers (cyclic and acyclic) as an example, the rate at which autoxidation proceeds has been found to be a function of the following rates: Chain initiation, chain propagation, and chain termination. Chain lengths are substantial (e.g. ~700 found for 2,5-dimethyltetrahydrofuran), which means low rates of chain initiation are all that is needed to produce significant amounts of peroxide. The initial products are hydroperoxides (ROOH), which have similar oxidative reactivity as hydrogen peroxide and are thus easily detected by starch-iodide paper.

Relatively small amounts of effective chainterminating stabilizers (commonly BHT ("butylated hydroxytoluene", or more correctly, 2,6-di-*tert*-butyl-4-methylphenol)) can prevent significant peroxidation for long periods of time, up to years depending on the rate of radical formation but eventually the stabilizer is completely consumed at which point peroxidation will massively accelerate.

Due to the radical chain mechanism of peroxide formation, a definite rate for peroxidation cannot easily be given for a solvent such as THF sitting in a lab in air at room temperature since it is not a thermally driven reaction following Arrhenius kinetics.

Instead, the peroxidation rate is critically dependent on variable and hard-to-measure factors which determine chain initiation and termination rates, including illumination, trace contaminants, and concentration of pollutants in the air.

However, experiments have been done to empirically compare the peroxidation rate of different solvents under "typical" conditions, often in the context of investigating "greener" solvents.¹² For example, in one study, THF under 254 nm light for three hours at room temperature, with air bubbling, was found to have the peroxide concentration (measured using commercial test strips, and presumably reported ppm H2O2 equivalent) increase from "10-30 ppm" to ">100 ppm". In another study using similar methodology, THF was found to generate 14 mg peroxide per liter of solvent per hour (14 mg likely refers to equivalent mass of H2O2, rather than the considerably higher actual mass of THF hydroperoxide present).

In a <u>study</u> investigating a peroxide-forming impurity in γ -valerolactone, initially peroxide-free samples of THF, 2-methyltetrahydrofuran, methyl tert-butyl ether (MTBE), furan, and 2,5-dimethylfuran were

¹² Note that there are sometimes ambiguities in papers as to whether the degree of peroxidation is being reported in terms of oxidizing equivalence to H₂O₂ (which is the direct reading given by commercial (semi-)quantitative test strips) or whether the actual mass or mass proportion of organic hydroperoxide or peroxide is being given.

"kept at room temperature for weeks". A "peroxide number" was determined at intervals by reaction with iodide¹³ and titration of the liberated iodine using thiosulfate. At the termination of the experiments, THF was found to contain 376 mg/kg "peroxide" after 546 h storage (= 22.75 days). 2-MeTHF contained 716 mg/kg peroxide after only 288 h.

In contrast, MTBE produced only 9 ppm peroxide after 663 h storage. 2,5-dimethylfuran produced very large concentrations of peroxide (1583 mg/ kg after 674 h); furan produced much less (9 mg/ kg after 338 h), but since furan tends to "go bad" and produce resins when stored, it may be that the initially-produced hydroperoxides tend to further react and transform into other materials.

It is not generally recommended that labs attempt to remove or destroy peroxides in solvents. However, a <u>paper</u> on the use of self-indicating molecular sieves (presumably containing cobalt(II) as indicator) to remove peroxides from common solvents is interesting on account of the background information and many literature references it contains.

Other Time-Sensitive Chemicals

Refer to the <u>Other Time-Sensitive Chemicals</u> web page for safety guidance on the following timesensitive materials:

- 1. Hydrogen bromide gas and anhydrous hydrogen fluoride in steel cylinders
- 2. Chloroform
- 3. Hydrogen peroxide
- 4. Concentrated formic acid (approx. > 90%).

Pyrophoric Chemicals

Due to the highly reactive nature of pyrophoric chemicals (see Figure 7.10), special precautions must be taken to exclude air and moisture during storage and handling. Pls should personally approve all purchasing of and work with pyrophoric chemicals. More information on using pyrophoric materials safety is to be found in Section 8.0 Working With Hazardous Chemicals. Inventories of pyrophorics should be kept to the minimum practical amount.

Figure 7.10. Pyrophoric Chemicals



Source: Adobe Stock Photos

Follow manufacturer's/supplier's storage instructions determine if inert gas-filled desiccators, gloves boxes, cold-storage, or other special storage conditions are required. Pyrophoric chemicals should never be stored next to flammable or combustible materials or oxidizers. Pyrophorics should be segregated from highly health hazardous materials, compressed gases, and any other materials or items which may increase the hazard in the event of a pyrophoric materials incident.

All storage areas should be below eye level and be conspicuously identified as to the hazard class by the word "**pyrophoric**". Pyrophoric materials should be kept in non-combustible secondary containment, as explained in detail under <u>Secondary Containment</u>

¹³ Reacts readily with hydroperoxides, not with dialkyl peroxides.

and Pyrophorics, page 7.4. Pyrophorics should be stored to minimize the possibility of falling, tipping, or breakage. Pyrophorics should be protected from the possibility of objects stored above from falling on them. Pyrophoric materials should not be removed from the secondary containment except at the point of use.

Note that many pyrophoric materials (e.g. alkyl lithium compounds, especially *tert*-butyl lithium) degrade on storage and may produce inferior experimental results when shelf life is exceeded. Pyrophoric materials should be dated when received, dated when first opened, and not stored for longer than recommended by the manufacturer/supplier.

Pyrophoric gases have stringent storage requirements. There are already some purpose-built facilities at USC which store and use pyrophoric gases. Personnel who wish to initiate new work with pyrophoric gases outside of the existing facilities should contact EH&S to determine safety and infrastructure requirements.

Chemicals Which, In Contact With Water, Emit Flammable Gases

Water reactive chemicals must be stored in appropriate containers away from water, aqueous solutions, and acids. All storage areas should be below eye level and be conspicuously identified as to the hazard class by the word "**water reactive**".

Extremely water reactive materials which may ignite on contact with water (e.g. alkali metals) should be handled and stored with the same precautions as for pyrophorics.

Corrosive Chemicals

The corrosive class of compounds includes a wide range of organic and inorganic acids/bases, as well

as many compounds which can hydrolyze to form acids (e.g. aluminum chloride), and many organic compounds which corrode living tissue through local toxicity mechanisms (e.g. phenol, iodomethane, dimethyl sulfate). All corrosives should be stored below eye level.

Very weak organic acids which do not pose a significant corrosion hazard may be stored with general organic storage (e.g. citric acid, tartaric acid, lauric acid (dodecanoic acid), myristic acid (tetradecanoic acid), stearic acid (octadecanoic acid), oleic acid, benzoic acid).

Toxic organic corrosives which are not acids or bases should be stored in accordance with the health hazards (which may be very severe).

Acids and Bases

Acids and bases should be stored in dedicated cabinets conspicuously identified as to the hazard class by the word "corrosive" (see Figure 7.10) and either "acid" or "base", as appropriate. Separate secondary containment or separate cabinets should be used to segregate organic from inorganic acids, segregate oxidizing acids from other acids, and segregate organic from inorganic bases. The cabinets and/or secondary containment shall be clearly labelled to identify the contents and ensure continued correct segregation.

Figure 7.10. Corrosives Cabinet



Further storage requirements for acids and bases:

- Store in cool, dry well-ventilated areas, away from sunlight. The storage area should not be subject to rapid temperature change.
- Store corrosive liquid containers in secondary containment such as a high density polyethylene tub. The secondary containment volume must exceed the combined volume of stored containers by at least 10 %.
- Consider the potential impact of corrosive vapors. Acid vapors, especially from hydrohalic acids (e.g., hydrochloric, hydrobromic, and hydroiodic) and nitric acid, will corrode many metals. Ammonia and amine vapors may corrode copper and copper-based alloys.
 - Volatile strong acids will corrode most metal cabinets and metal hinges on wooden cabinets. Corrosion resistant acid cabinets are available which will provide a better service life.
 - Do NOT store acids, amines, or ammonia with electrical equipment.
 - Do NOT store hazardous materials in steel cans or drums in the same cupboard as acids.
 - Do NOT store acids, amines, or ammonia under sinks due to risk of corroding the plumbing.
 - Non-volatile, non-water-reactive inorganic bases (i.e. sodium/ potassium hydroxide) may be stored under a sink only if no other location is available.
- Solid inorganic bases (sodium/potassium hydroxide) may be stored in labelled secondary containment on open shelving if:
 - Material is in non-breakable plastic containers.

 Material is not stored above eye level, or stored in a location where it may be knocked by feet.

Acid Storage: Details

Organic acids (e.g. acetic, formic) are flammable or combustible.¹⁴ Certain inorganic acids are oxidizing (nitric, perchloric) or highly reactive (sulfuric). Hypophosphorus acid and hydroiodic acid are inorganic acids which are (unusually) strongly reducing. Oxidizing or highly reactive inorganic acids must be segregated from acids which are flammable, combustible, or reducing:

- Segregate inorganic oxidizing acids from inorganic reducing acids and place them into separately labeled secondary containment.
- Segregate flammable/combustible acids from oxidizing/reactive acids and store in separate cabinets.
 - Where limited quantities are stored, and space constraints are severe, separate labeled secondary containment in the same cabinet may suffice. Contact labsafety@usc.edu for guidance.

Perchloric and fuming nitric acids are extreme oxidants. Fuming nitric acid can cause spontaneous ignition in contact with organic matter. Perchloric acid can react with wood to produce cellulose perchlorate which may explode or spontaneously combust. **Perchloric and fuming nitric acids shall NOT be stored in a wooden cabinet.**

Materials which readily hydrolyze to form acids should be kept in an acid cabinet.

¹⁴ Note that trifluoroacetic acid and trifluoromethansulfonic acid are not combustible or flammable. They are strong acids and should be stored with the inorganic acids.

Common examples include acetyl chloride, acetic anhydride, aluminum chloride, tin tetrachloride, titanium tetrachloride, phosphorus halides, phosphoryl chloride, thionyl chloride, and sulfur chlorides. Bromine is not an acid, but is highly corrosive to living tissue and to metals. Bromine is compatible with non-reducing inorganic acids and should be kept in an acid cabinet.

Health Hazardous Materials

Particularly hazardous substances (PHS) storage areas and work locations are required to be conspicuously identified as to the hazard class by the words "<u>acute</u> <u>toxicant</u>", "<u>carcinogen</u>" and/or "<u>reproductive toxicant</u>" (see Figure 7.11), as appropriate.



PHS shall not be stored under sinks. PHS is preferably stored in labeled secondary containment, except for the following for which labeled secondary containment is required:

Liquid PHS in glass bottles.

- Very highly health hazardous PHS (e.g., potent acute toxicants such as cyanides, mercury compounds, thallium compounds)
 - Secondary containment should preferably be closed by a tight fitting lid for very highly health hazardous PHS.

Highly toxic chemicals (e.g., cyanides) shall be stored under conditions of satisfactory physical security, preferably in a locked cabinet in a restricted access room. Unauthorized personnel should not have ready access to highly toxic chemicals. An access and usage log for highly toxic chemicals is advisable.

Inventories of very highly health hazardous chemicals should be kept to a minimum. Unused inventory should be disposed of as hazardous waste at the end of research projects, unless there is reasonable probability that the material will be required again within the next 6-12 months. Submit a hazardous waste pick-up request via <u>EHSA</u> or <u>RSS</u>.

Compressed Gases

Compressed gas cylinders shall be stored in accordance with the seismic restraint requirements detailed in <u>Section 4, Seismic Safety and Hazardous</u> <u>Materials Storage</u>. In addition:

- Cylinders in use shall be fitted with a regulator compatible with the cylinder fitting, the type of gas, and the pressure of the full cylinder. Gas pipework and valves shall be chemically compatible with the gas and shall be appropriate for the hazards.
 - Always follow manufacturer's/ supplier's compatibility information.
 - NEVER use oil, grease, or PTFE tape on cylinder fittings.

- "All cylinders which are designed to accept valve protection devices [protective cap] shall be equipped with such devices when the cylinders are not in use or connected for use." - <u>8CCR §4650</u>. Certain cylinders are not designed to be fitted with a protective cap, which is the case for some small cylinders or relatively low pressure cylinders.
- Cylinders shall be legibly labeled with the contents chemical name and hazard symbols.
- Compressed gas cylinders shall be tagged as full, in use, or empty, as appropriate.
 - Use removable tags provided by vendor, or labs may write their own tags.
- Cylinders are to be protected from extremes of temperature.
- Cylinders shall not be stored where they are liable to rusting or corrosion.

In general, cylinders shall NOT be stored on mobile carts. If there is an overriding technical reason why a cylinder must be stored on a mobile cart (e.g., the cylinder is part of a welding set), the cylinder shall be restrained to the cart by noncombustible restraints, and when not in active use, the cart shall be restrained to a non-movable non-combustible fixture such that it cannot fall over in an earthquake. For example, the cart can be chained to the wall using steel chain and spring-loaded hooks.

Furthermore:

 "Oxygen cylinders in storage shall be separated from fuel gas cylinders or combustible materials (especially oil or grease) a minimum distance of 20 feet or by a non-combustible barrier at least 5 feet high, or a minimum of 18 inches (46 centimeters) above the tallest cylinder and having a fire-resistance rating of at least one hour." (<u>8 CCR §4650</u>)

- All gas cylinders should be stored in well ventilated areas.
- Toxic or corrosive gases may have special safety requirements, including crosspurging facilities. Contact <u>labsafety@usc.</u> <u>edu</u> for guidance.
- Pyrophoric (phosphine, arsine, diborane, silane, germane etc.) and highly toxic gases (e.g. phosphine, arsine) must be stored and used in enclosed, exhausted cabinets equipped with alarms. Contact <u>labsafety@</u> <u>usc.edu</u> for more information.
- Gas cylinders are to be transported by freight elevators, preferably. If a freight elevator is not available, a regular elevator may be used. Restrain cylinders to prevent falling, or preferably have cylinders secured to a stable cart. Prevent people from entering the elevator while transporting the cylinder (e.g. by using signage of the type "Hazardous Materials: No Entry").
- Gas feeds to oxy-fuel combustion apparatus shall have adequate provision against backflow (<u>8 CCR §4845</u>).
 - Use flashback arrestors designed for the particular oxy-fuel combinations (see Figure 7.12).

Figure 7.12. Flashback Arrestors



Source: Harris

- Laboratory personnel shall NOT refill gas cylinders, or attempt to prepare gas mixtures within cylinders.
 - Cylinders are ONLY to be refilled by a professional gas vendor.

- Care must be taken to avoid internal contamination or corrosion of cylinders.
 - Take steps to prevent backflow of liquid into cylinders.
 - Cylinders are preferably to be considered empty when their internal pressure is still slightly above atmospheric.
 - Do NOT empty cylinders to below atmospheric pressure.
 - Keep cylinder valve closed on empty cylinders.

Cryogenic Liquids

Cryogenic liquids (liquid nitrogen, liquid helium) shall be stored in accordance with the seismic restraint requirements given in <u>Section 4, subsection Seismic</u> <u>Safety and Hazardous Materials Storage</u>. Cryogenic liquids shall be stored in areas of adequate ventilation.

Low oxygen alarms (oxygen deficiency monitors; see Figure 7.13) might be advisable or required in cases where the cryogen quantity is significant in relation to the size of the room and/or available ventilation. EH&S will advise on a case-by-case basis.

Figure 7.13. Oxygen Deficiency Monitor



Controlled Substances

Pls or DEA Registrants, in possession of a valid DEA license, who purchase, store, and use controlled substances for research purposes on USC-controlled property must enroll in the Controlled Substances Use Authorization (CSUA) Program.

For additional information on the controlled substances program, contact <u>ehs-cs@usc.edu</u> or refer to the <u>Controlled Substances and Precursor</u> <u>Chemicals Program</u>.

Transportation of Hazardous Materials

Hand Transportation

Hand transportation (i.e. walking while carrying chemicals, or pushing them on a hand cart) is appropriate within buildings, and between USC buildings within the boundaries of USC controlled property or a USC campus. Laboratory personnel may cross public roads at the Health Science Campus while walking hazardous materials between buildings. Laboratory personnel shall NOT leave the boundary of USC campuses while transporting hazardous materials by hand.

Packaging/Secondary Containment

Hazardous chemicals still in the unopened DOTapproved packaging in which they were originally delivered to USC may be carried by hand or transported on a hand cart. Hazardous chemicals not in DOT-approved packaging shall be placed in robust secondary containment and carried by hand or pushed on a hand cart.

Secondary containment should have a lid and be large enough to hold the contents of the chemical container in the event of breakage. The exterior of the secondary containment should be decontaminated and safe to the touch so no PPE is required for safe transport. Items which are not safe to handle without PPE are NOT permitted to exit a laboratory and may NOT be transported outside of a laboratory.

 NMR tubes are easily broken. Outside of the lab, always transport NMR tubes in secondary containment.

Bottle Carriers

Glass bottles of any significant size (\geq approx. 500 mL) shall be transported in a purpose built bottle carrier with a firmly attached handle.

Bottle carriers with a secure lid designed to prevent spillage in the event of dropping the carrier are preferred (see Figure 7.14).



Figure 7.14. Bottle Carrier with Lid

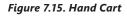
All newly purchased bottle carriers should be of the lidded type. Open-topped bottle carriers should be retired as they become old, or be relegated to the transport of minimal-hazard materials such as distilled water.

Source: Nalgene

Hand Carts

Hand carts should have lips (preferably >2 inches deep) to prevent items from falling (see Figure 7.15). Hand carts should not be overloaded.

Highly-hazardous, easily breakable, or large items should be transported on the lower shelf.





Source: Rubbermaid

Chemicals transported on hand carts should be in secondary containment the same as for hazardous materials carried by hand. A hand cart with deep lips to prevent items from falling and constructed from non-corrodible non-porous polymer is very suitable for laboratory use.

Transportation and PPE

When transporting materials between labs on the same corridor, PPE may be left on, excepting that to prevent possibility of contamination spreading, either no gloves are to be worn, or only one glove, leaving one clean hand exposed. PPE shall NOT be worn for transportation which passes through office areas, between floors, or outside a building. *Reminder*: Items which are not safe to handle without PPE are NOT permitted to exit a laboratory and may NOT be transported outside of a laboratory.

Transportation of Gas Cylinders

Compressed gas cylinders may not be "milk churned" on their ends more than a short distance within rooms, and only then by personnel with sufficient physical strength and balance to be able to keep good control of the cylinder, and ONLY when the safety cap is in place.

All longer hand transportation of gas cylinders (with the exception of very small cylinders light enough to be easily carried) is to be by wheeled cylinder cart (see Figure 7.16), not carrying more cylinders than designed for, and with the cylinder(s) securely fastened to the cart and the safety caps on. Note that cylinders are not normally permitted to be stored on carts (see previous subsection on compressed gas storage).







Vehicular Transport

Transport of hazardous materials in motor vehicles is strictly regulated by the US Department of Transport (DOT; <u>CFR Title 49 Subtitle B Chapter I Subchapter C</u>). Transport of hazardous materials by USC laboratory personnel using motor vehicles is NOT allowed, except under the limited conditions specified in <u>49</u> <u>CCR § 173.6</u> "Materials of trade exceptions" (MOTs).

Consult the "<u>What Are Materials of Trade</u>" brochure and the <u>Federal Motor Carrier Safety Administration</u> web page for more information. For additional guidance, contact EH&S at <u>labsafety@usc.edu</u>.

Laboratory Relocation

Laboratory personnel shall not undertake to transport large quantities of hazardous materials during laboratory relocation. EH&S Hazmat may be able to move hazardous materials within the boundaries of a campus, or will recommend a licensed professional vendor if transportation over public roads is required, or if quantities are large.

If a relocation is planned, please contact <u>hazmat@</u> <u>usc.edu</u> well before the date of the intended move, giving as much information as possible.

Mailing of Hazardous Materials

Hazardous materials may NOT be sent using USC internal mail service. Sending of hazardous materials by parcel carriers (UPS, FedEx, etc) is heavily regulated (49 CFR and other codes), including stringent documentation, packing, and labelling requirements. There may also be registration and training requirements in order to be approved by your shipping company as an originator of hazardous shipments. There may be less onerous "limited quantity" and *de minimis* shipping options available for small size shipments such as samples for analysis. Contact your shipping company for more information, and exactly follow all of their hazmat requirements. Links

- <u>https://www.ups.com/us/en/help-center/packaging-and-supplies/special-care-shipments/</u> hazardous-materials/online-process.page,
- <u>https://www.fedex.com/en-us/service-guide/hazardous-materials/how-to-ship.html</u>
- <u>https://pe.usps.com/cpim/ftp/pubs/Pub52/pub52.pdf</u>

For additional guidance, contact EH&S at <u>labsafety@usc.edu</u>.



Planning Safe Research

All personnel who consider conducting work with hazardous substances must consider beforehand:

- The hazards posed by substances, processes, and equipment, AND;
- The adequacy of available facilities for managing the risks.

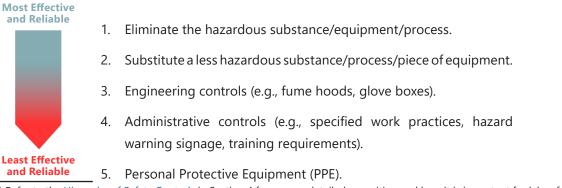
Work shall not take place if the available facilities are inadequate for managing the risks. Pls should consider the adequacy of their facilities before committing to new research projects. EH&S is available for consultation if there are any questions; email <u>labsafety@usc.edu</u>.

Personnel should incorporate consideration of hazards into the early stages of planning laboratory work. Sources of information on hazards include:

- <u>Safety data sheets (SDSs)</u>
 - Personnel shall read the SDSs for all the hazardous materials they intend to use.
 - Personnel shall print and store SDSs for all Category 1 acute toxicants and phenol-containing materials at or near the work area where they are used.
 - Personnel should ensure the SDSs for all materials they use or purchase are included in the lab's paper or electronic repository of SDSs.
- Experimental protocols (note that safety information is often sparse in earlier literature).
- Other sources of safety information as covered in <u>Section 1</u>.

Standard (Safe) Operating Procedures (SOPs)

Personnel should incorporate their assessment of the hazards into a written standard operating procedure (SOP), which should also specify how the risks arising from the hazards are to be managed. Personnel should base their planning for safe work on the hierarchy of safety controls.¹ Briefly, the hierarchy is as follows:



1 Refer to the <u>Hierarchy of Safety Controls</u> in Section 4 for a more detailed exposition and how it is important for lab safety.

<u>SOP templates</u> covering various classes of hazardous substances are available on the EH&S website. Personnel shall customize SOP templates by including information specific to the work they are planning and to the lab in which they intend to work.

SOPs shall specify all the various safety controls to be used, any special training requirements, details of the experimental procedure, and actions to be taken in the event of an emergency. When the safety considerations are similar for a range of related procedures, it is appropriate and most practical to write a generic procedure in the SOP; for example, vacuum distillation safety procedures are similar for many different materials which could be distilled, thus, a generic SOP with suitable safety controls, plus the appropriate safety data sheets, would suffice.

SOPs for hazardous equipment shall be based on manufacturers' operating instructions, when applicable. Completed SOPs shall be reviewed and approved by the responsible PI. SOPs shall be signed by lab personnel confirming that they have been read, understood, and agreed to prior to beginning any laboratory work. These documents must be reviewed by all lab personnel on an annual basis.

SOPs and Internal Training Records

Personnel, if inexperienced, shall be trained on the procedures outlined in the SOP. The trainer (PI or PIs designee, e.g. postdoc), trainee, and PI shall sign to that effect: "(NAME) was trained on the contents of this SOP between (DATE 1) and (DATE 2) by (TRAINER-NAME) to the satisfaction of (PI-NAME)" followed by dated signatures. SOP templates available on the EH&S website contain a training record sheet which may be employed; a Site Specific Training Record (http://tiny.cc/ehs-SSTR) may be used as an alternate form to document annual review of SOPs.

It is always advisable that all lab personnel be aware of the contents of SOPs even if they are not directly involved in the work.

Particularly Hazardous Substances (PHS)

Regulators have identified carcinogens, reproductive toxicants, and highly acutely toxic substances as being of particular concern; these materials are denoted *Particularly Hazardous Substances* (PHS; <u>8</u> <u>CCR §5191 (e) (H)</u>).

At USC, PIs and supervisors are required to ensure their research personnel take appropriate safety measures when using PHS, in accordance with this CHP and best safety practice (e.g., see <u>Prudent</u> <u>Practices in the Laboratory</u>). EH&S can provide further guidance as needed; email <u>labsafety@usc.edu</u>.

Regulation

Cal-OSHA requires: "Provisions for additional employee protection for work with particularly hazardous substances. These include select carcinogens, reproductive toxicants, and substances which have a high degree of acute toxicity." (8 CCR §5191 (e) (H)) Furthermore: "Specific consideration shall be given to the following provisions which shall be included where appropriate;

- (1) Establishment of a designated area;
- (2) Use of containment devices such as fume hoods or glove boxes;
- (3) Procedures for safe removal of contaminated waste; and
- (4) Decontamination procedures."

Identification of PHS

During the planning stages of experimental work, information shall be gathered about the substance(s) to be used to see if they are PHS. The criteria for the identification of PHS are covered in Section 6, Hazardous Chemicals and Hazard Classification, subsection <u>Particularly Hazardous Substances (PHS)</u>.

Working With PHS

Personnel and laboratories working with PHS shall:

- Identify chemical hazards using safety data sheets and other recognized information sources.
 - Safety data sheets must be kept by the lab in electronic or paper format, with no barrier to access for any lab member.
- Have on file a written standard operating procedure (SOP) covering activities with the PHS.
 - See EH&S website for <u>SOP templates</u>. Note that the templates need to be modified by the end user(s) to incorporate information specific to the lab and to the planned work.

- The completed SOP must be approved by the PI, then read, understood, and signed by lab members initially and annually.
- Ensure adequate, documented internal labspecific training.
 - Persons using the PHS must be trained on safe practice to the satisfaction of the PI, or PI's designee, and training records must be maintained by the PI.
- Minimize exposure by using fume hoods and other engineering controls, appropriate PPE, and by paying the utmost attention to good

chemical hygiene practice, avoidance of the spread of contamination, and by decontaminating work areas and equipment after use.



- PHS which are volatile, powdery, or extremely potent shall NOT be weighed in the open lab. Instead:
 - Use a balance in a fume hood, or:
 - Weigh a glass vial with a tight-fitting screw cap using a balance outside a fume hood, add the PHS in a fume hood, seal the vial with a tight screw cap, make sure the exterior is not contaminated, then remove from the fume hood and re-weigh.
- Label areas in which PHS are used.
 - Labels with appropriate symbols and verbiage for select carcinogens, reproductive toxicants, and acute toxicants are available at the EH&S web page (<u>Chemical Labeling and Signage</u>).
- Label PHS storage containers, PHS storage secondary containment, and cupboards and shelves used to store PHS.

- Labels with appropriate symbols and verbiage for select carcinogens, reproductive toxicants, and acute toxicants are available at the EH&S web page (<u>Chemical Labeling and Signage</u>).
- Strictly follow EH&S <u>hazardous waste disposal</u> <u>guidelines</u>.
 - Do not attempt to decontaminate empty containers of PHS. Label the empty containers as hazardous waste, or if suspected to be contaminated on the outside, place in a thick polyethylene bag before labeling, and have it disposed of by Hazmat.

Female researchers who are pregnant or who may become pregnant, should consult their PI if they work with or are planning to work with reproductively toxic substances.

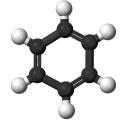
Contact injuryprevention@usc.edu if work with highly potent carcinogens is planned.

PHS Focus: Benzene

Benzene (see Figure 8.1) is often specified as a solvent in older chemical procedures, often for historical rather than technical reasons.

Figure 8.1. Benzene

Benzene is a Category 1A carcinogen particularly associated with increased risk of leukemia in humans, as well as having acute and chronic adverse health effects. Benzene should never be used as a solvent except in rare cases where overriding technical reasons mean no



other solvent will work (e.g. deuterobenzene still has valid application as an NMR solvent). Substitute toluene, cyclohexane, or other less health hazardous alternatives whenever possible. Consult EH&S at <u>labsafety@usc.edu</u> if you have any questions.

PHS Focus: Extreme Carcinogens

Special working conditions may be required to use any of the thirteen (13) particularly severe carcinogens (list and CAS numbers available at link) regulated under <u>8 CCR §5209</u>. Contact <u>injuryprevention@usc.</u> <u>edu</u> well in advance of purchasing or using these materials.

Personal Protective Equipment (PPE)

In the Hierarchy of Safety Controls, as previously covered in Section 4, PPE is placed at the bottom as providing the least reliable assurance of safety. In a laboratory environment, PPE should not normally be relied upon as the primary protection from hazards, but should rather be used as the last line of defense, giving protection to personnel in the event other safety controls fail and an incident occurs.

USC PPE Standard

USC has a mandatory written standard which lays out minimum requirements for personal attire and PPE usage in areas where hazardous materials are present (i.e. labs). All research personnel should become familiar with the standard, which may be viewed at https://ehs.usc.edu/research/lab/manage/ppe/. PIs have ultimate responsibility for ensuring the PPE Standard (see Figure 8.2) is followed within their research groups.

USC Chemical Hygiene Plan

The PPE standard specifies a minimal level of personal attire required to enter an area in which hazardous materials are stored and/or used. If any work is taking place within the area, the PPE standard mandates that appropriate PPE, selected in accordance with a risk assessment, be worn in addition to the minimum standard of personal attire.

EH&S provides a basic risk assessment in the form of the <u>Laboratory Hazard Assessment Tool (LHAT)</u> (see Figure 8.3) which is reviewed at the time of lab inspection. PIs shall update their LHAT annually or whenever significant changes take place in the nature of the work within their labs. The PI shall share the LHAT with members of their research group.

The LHAT provides only a broad overview of hazards, and may need to be supplemented by more specific risk assessments carried out within the research group. Laboratory personnel shall conservatively assess the potential hazards of their work during the planning stages, and shall identify appropriate PPE requirements. This information shall be incorporated into the SOP, and shall be reviewed and approved by the PI. EH&S is available to answer questions on appropriateness of PPE; email <u>labsafety@usc.edu</u>.

Note that PPE may need to be worn by personnel in the vicinity of work being done, and not just by those actually doing the work. This includes personnel sitting at writing desks within the lab, see <u>PPE at</u> <u>Desk in the Laboratory Guide</u> sheet (see Figure 8.4) for details.

EH&S routinely conducts PPE inspections to ensure that hazardous materials users: (a) are adequately protected and (b) comply with local and state regulations.

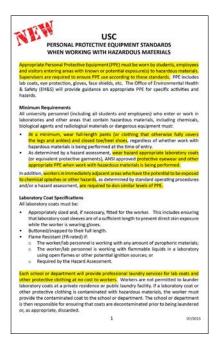
Personal Attire and Foot and Leg PPE

The PPE standard specifies the following minimum level of personal attire required for any person entering a laboratory:

• "At a minimum, wear full-length pants (or clothing that otherwise fully covers the legs and ankles) and closed toe/heel shoes..."

The essential feature of the minimum personal attire standard is that there shall be no exposed skin below the torso.

Figure 8.2. USC PPE Standard





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Natural fiber trousers (cotton, linen, wool) give the most satisfactory leg protection from chemical splashes or fire. Common synthetic fibers (nylon, polyester) melt to skin in a fire and may exacerbate injury. The splash protection even thick trousers offer from chemicals is limited and short-term, so in an emergency it may be necessary to remove them while under a safety shower. For this reason, loose fitting trousers are preferable. A long skirt is permitted in lieu of trousers.

Leggings and other leg attire which are figurehugging or made from very thin fabric are not prohibited by the USC PPE standard; however, they do not provide good protection from chemical splashes or fire, and are difficult to remove in an emergency situation. It is strongly recommended to avoid leg coverings of this type, especially in labs which use pyrophorics, corrosives, or materials toxic by skin absorption, or in labs where there is a raised fire risk. Pls managing labs with these hazards may wish to consider prohibiting leggings and similar leg attire as part of their group safety rules.

Shoes with a non-slip non-absorbent sole are preferred (see Figure 8.5 <u>PPE: Shoes Fact Sheet</u>). Leather soles can become extremely slippery on spillages, and may absorb spilled liquid which may pose a health hazard. Shoes shall have closed toes and closed heels. Preferably, shoe uppers should not be canvas or other absorbent material, and should not have excessive holes. If there is a gap between shoes and leg wear, the skin shall be covered by socks to prevent it from being exposed.

Special hazards to feet and legs include risk of crushing toes (e.g. from lifting of heavy objects), sparks and molten metal splashes (e.g. from welding).

These hazards are unusual in labs, as they are more usually associated with workshops. When present, these hazards may require additional leg and foot PPE, including steel-toed boots, foundry boots, or aramid (e.g. Nomex®) flame resistant trousers. Contact <u>labsafety@usc.edu</u> or <u>injuryprevention@usc.</u> edu for more information.

Figure 8.4. PPE at Desk Guide Sheet



Figure 8.5. PPE: Shoes Fact Sheet



Lab Coats

The majority of laboratory work requires a lab coat to protect against splashing, or splashing and fire. Lab coats are to be selected from 100% cotton, flame retardant (FR) treated cotton, Nomex[®], or fluidresistant barrier coats according to the hazards as assessed in the LHAT; refer to the <u>PPE: Lab Coats Fact</u> <u>Sheet</u> (see Figure 8.6) for details.

USC contracts with an outside vendor to provide a professional service to launder dirty lab coats; visit EH&S' <u>Lab Coat Services</u> web page for details. Note that lab coats which are significantly contaminated by appreciably health-hazardous materials (e.g. PHS) may need to be disposed of as hazardous waste rather than being submitted for laundering. If in doubt, contact <u>labsafety@usc.edu</u>.

Lab coats should be appropriately sized for personnel and shall be fastened all the way up. Snap fastenings allow lab coats to be rapidly removed in the event of an emergency; therefore, snap fastenings are strongly preferred to buttons.

Polyester and polyester-cotton lab coats are liable to melt in flame and are not permitted at USC. The one exception is for specialist fluid resistant barrier coats, which are made from tightly woven 100% polyester, and which prevent penetration of aqueous fluids. Fluid resistant barrier coats are appropriate for use when working with biological materials, bodily fluids, blood, blood-borne pathogens, tissue, cell lines, microbial cultures, and other potentially infectious materials. Fluid resistant (barrier) coats may **NOT** be used with flammable liquids or around open flames (e.g., Bunsen burner). 100% Cotton lab coats are appropriate for use when working with chemicals, radioactive materials, or physical hazards, but only where risk of fire is low. 100% cotton lab coats are not suitable for work with flammable liquids, except where volumes are very low and handling is done under tightly controlled lowrisk conditions (e.g., undergraduate teaching labs).

Flame retardant (FR) (see Figure 8.7) treated cotton lab coats are suitable for work with flammable liquids and well-controlled open flames (e.g., Bunsen burner), but are NOT to be used around pyrophorics. The FR properties may reduce after a certain (substantial) number of laundering cycles; replace according to manufacturers' recommendations.

Figure 8.6. PPE: Lab Coats Fact Sheet

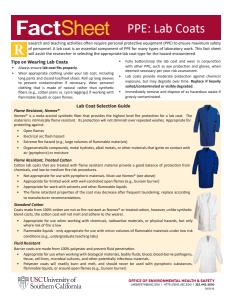


Figure 8.7. FR Lab Coat



Nomex[®], an aromatic polyamide, is hardwearing and highly resistant to fire. It does not melt, but merely chars at high temperature, and these fire resistant properties are unaffected by laundering (see Figure 8.8). Nomex[®] lab coats are the only type suitable for use with pyrophorics, open flames, large volumes of flammable solvents, flammable metals, and other high fire risk materials and equipment.

Eye and Face Protection

Cal-OSHA regulations state that personnel are required to use suitable eye and face protection against hazards including projectiles, hazardous substances, and injurious light rays (including IR and UV; http://www.dir.ca.gov/title8/3382.html).

Standards of construction, testing, and performance for eye and face protection is specified by ANSI/ ISEA Z87.1-2015. All safety eyewear and face shields should be marked as conforming to this standard (at a minimum, marked "ANSI Z87.1").

Regular glasses are NOT safety eyewear! Prescription corrective lenses will not provide adequate protection against most occupational eye and face hazards. Laboratory personnel with corrective lenses are required to either wear ANSI-approved eye protection that incorporates the prescription into the design or wear additional eye protection over their prescription lenses (see Figure 8.9).

Wearing safety eyewear over regular prescription spectacles is the usual option for personnel requiring vision correction. Providing ANSI-approved prescription safety eyewear is at the PI's discretion (see <u>Prescription Safety Glasses</u> web page).

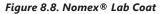




Figure 8.9. Prescription Glasses with Safety Glasses



Note that provision of prescription safety glasses will not obviate the requirement to use goggles for splash hazards.

Contact lenses are prohibited in laboratories. Cal-OSHA regulations (8 CCR §3382) state: "wearing of contact lens is prohibited in working environments having harmful exposure to materials or light flashes, except when special precautionary procedures, which are medically approved, have been established..." Personnel who require vision correction should wear spectacles under ANSI-approved safety eyewear, plus face protection when required.

Selection of Eye and Face Protection

The International Safety Equipment Association (ISEA) provides an authoritative free downloadable guide to the selection and use of eye / face protection (https://



safetyequipment.org/wp-content/uploads/2022/10/ ISEA-EF-2016-Selection-and-Use-1-1.pdf). Selection of appropriate eye / face protection should be in accordance with the ISEA guidelines, EH&S fact sheets (see Figures 8.10 to 8.12), and best practice (e.g., Prudent Practices). Selection shall be commensurate with written hazard assessments (e.g., the LHAT).

The four most common types of eye and face protection are:

- Safety glasses. These protective eyeglasses
 - have safety frames constructed of metal or plastic and impact-resistant



lenses. Safety glasses either fit closely to the curve of the face or have side-shields. Safety glasses are appropriate for projectile hazards. Safety glasses are NOT suitable for splash hazards, i.e. they may not be used with eyehazardous liquids.

• **Goggles**. These are tight-fitting eye protection

that completely cover the eyes, eye sockets and the facial area immediately



surrounding the eyes. Some goggles will fit over corrective lenses.

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Figure 8.10. Eye Protection Fact Sheet

Figure 8.11. Goggle/Face Shield for Splash Hazards Fact Sheet



 Indirectly vented and non-vented goggles protect from projectiles and harmful liquids (splash hazard) and particulates.
 Indirectly vented goggles are usually preferred as they do not fog as easily as non-vented.

- Directly vented goggles should not be purchased for lab use as they do not provide splash protection.
- Face shields. These transparent sheets of plastic extend from the eyebrows to below the chin and across the entire width of the individual's head. As per ANSI/

ISEA recommendations, face shields shall not be worn alone, but shall be worn over safety spectacles (projectile hazards only), or over indirectly vented goggles (projectile hazards or splash hazards). Face shields are appropriate for:

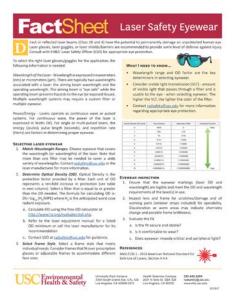
- Severe projectile hazards (e.g. when working with potentially explosive materials).
- Skin-hazardous liquids in large quantity, or used under conditions of substantially raised splash hazard.
- Highly skin-hazardous liquids (e.g. hydrofluoric acid).
- Appropriate for liquid nitrogen operations involving liquid nitrogen under pressure, e.g. filling Dewars from a pressurized tank.
 - Face shield is not required for liquid nitrogen operations in which there is no possibility of being sprayed forcibly in the face, e.g. decanting from a handheld, open-neck (i.e. non-pressurized) Dewar.

Laser safety eyewear. This



specialty eyewear protects against intense concentrations of light produced by lasers. Laser safety eyewear must be matched to the power and wavelength of the laser. Refer to the Laser Safety Manual for more information.

Figure 8.12. Laser Safety Eyewear Fact Sheet



Eye Safety Focus: Glassware

Glass pipettes are easy to break and have resulted in glass fragments being projected into the eye of a USC researcher; therefore, **glass pipettes are considered a projectile hazard**. Glassware under vacuum or pressure (including glass Dewars) is also considered a projectile hazard.

All usage of eye-hazardous materials mandates eye protection, even if handled behind a fume hood or biosafety cabinet sash.

Intense light sources, infrared radiation (e.g., furnaces, molten metal), and ultraviolet radiation all require appropriate safety eyewear to absorb the harmful rays. Refer to the ISEA guide for more information (https://safetyequipment.org/wp-content/uploads/2022/10/ISEA-EF-2016-Selection-and-Use-1-1.pdf). Email radsafety@usc.edu with any questions.

Schools, Departments, and/or individual PIs may choose to implement a stricter eye protection policy whereby a minimum level of eye protection (e.g., safety glasses) are required to be worn upon entering their labs, even if no work is taking place within.

Laboratory Work Which May Not Require Eye Protection

Eyes are extremely easy to damage, so the general presumption should be that laboratory work should require eye protection. However, there are situations in which eye protection is not strictly required, a typical example being a microscope room in which no splash, dust, or projectile hazards are present. A PI may give personnel the option of not wearing eye protection in laboratories/workshops PROVIDED that personnel are:

- Only manipulating non-hazardous liquids (e.g., water, saline solution) and/or nonhazardous solids (e.g., coarse plastic granules) that are strictly non-injurious to the eye; AND
- Not in the vicinity of any equipment, projectile hazards, hazardous materials, or other work (e.g., use of glass pipettes) that mandates eye protection; AND
- Aware and vigilant of the conditions, operations, and materials that do require eye protection and have eye protection available to use as needed.

Gloves

Glove selection can be more complex than selection of lab coats or eye protection, making it essential to consult manufacturers' information on the applicability and limitations of specific gloves.

High Temperature Gloves

Gloves composed of aramid fibers (Nomex[®], Kevlar[®] - see Figure 8.13, Technora[®]), thick leather (e.g. welding gauntlets), or carbonized fiber (e.g. CarbonX[®]) are used to protect hands from inadvertent burns when handling hot objects, opening furnaces, or loading / unloading ovens. Thicker gloves provide appreciable thermal insulation,

allowing hot items to be held for a short time. Thin gloves made from high temperature resistant materials are not designed for directly handling hot objects, but will provide important protection against accidental burns.



Figure 8.13.



- Most high-temperature gloves are porous, do not provide protection from chemicals, and may permanently retain hazardous contamination.
- Thinner high-temperature gloves may be worn under chemical resistant gloves when handling pyrophorics, alkali metals, and other materials of extreme fire hazard.
 - Highly recommended for all pyrophoric work except where reduced dexterity makes work impossible or results in increased hazard.
 - CarbonX® knitted gloves designed for use as a glove liner are available. Long gloves (Figure 8.14) are preferred to give additional forearm protection (see <u>https://www.magidglove.</u> <u>com/carbonxr-cx10020-carbon-fiber-knit-fr-glove-and-sleevecx-100-20</u>).

Figure 8.14. CarbonX FR Liner Gloves



- Thin Nomex flight/aviator/aviation gloves are widely available and have been used as a glove liner for pyrophoric usage.
- Tip for searching online: Heavy duty high temperature gloves suitable for ovens and furnaces may be found by searching for "welding gauntlet" or "foundry gloves".

Low Temperature Gloves

Thick, insulated gloves are manufactured for providing protection from extreme cold, e.g. when handling liquid nitrogen hoses, or handling items removed from -80° C freezers or liquid nitrogen freezers. Note that most low temperature gloves (see Figure 8.15) are porous and not liquid tight. They are suitable for handling solid items at approximately dry ice temperature, or briefly handling colder items.

- Low temperature gloves do NOT provide any protection from insertion in liquid nitrogen!
 - Severe injury has been known to occur from liquid nitrogen soaked low temperature gloves.
- Low temperature gloves shall not be allowed to become soaked in the liquid air which drips from the exterior of liquid nitrogen hoses as this may cause a fire hazard, as well as being a low temperature hazard.
 - Do NOT hold a non-insulated (single skin) liquid nitrogen hose during nitrogen transfer operations.

Certain operations using liquid nitrogen do not present a hazard of touching cold objects, but only present a hazard of minor liquid nitrogen splashes. An example of such an operation is filling a cold trap. Risk assessment of specific operations may reveal that wearing simple chemical resistant gloves might be safer, due to increased dexterity, and because liquid nitrogen droplets bounce off unless trapped.

The <u>Cryogens and Dry Ice SOP</u> shall be customized based upon risk assessments, which need not be lengthy.





Source: Grainger

Cut Resistant Gloves/Puncture Resistant Gloves

Gloves containing hard-to-cut fibers (Kevlar®, Technora®, Vectran®, Spectra®, or high modulus polyethylene, e.g. Dyneema®- see Figure 8.16), metal wires, or hard inserts are available to resist cutting

or puncturing. Gloves of this type may be advisable for lab work which involves handling sharp materials, or where cutting tools have to be used under conditions where normal care and attention cannot assure a minimal risk of accident, and where engineering controls are insufficient or impractical.

Figure 8.16. Dyneema Cut Resistant Gloves



It is important to note that gloves are rated separately for cut resistance and puncture resistance, and many cut resistant gloves have minimal resistance to puncture by thin sharp objects such as hypodermic needles. Furthermore, cut and puncture resistant gloves may offer varied protection at different positions on the hand. Manufacturers' information should be consulted for glove applicability and limitations.

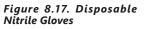
Chemical Resistant Gloves

Chemical resistant gloves should be chosen with care. There are no glove materials which provide an absolute barrier to all types of chemical.

Disposable Chemical Resistant Gloves

Disposable nitrile gloves (see Figure 8.17) are satisfactory for general lab use, and provide generally reasonable protection from aqueous solutions (except highly reactive or corrosive solutions, and except for solutions of HF or non-dilute aqueous solutions of toxic organic materials such as phenol).

Disposable nitrile gloves also provide reasonable protection from oil and grease. However, for most other liquid materials, the protection offered is short-term protection





against splashes at best, and gloves should be changed as soon as possible after being splashed or contaminated with liquid. In the case of liquids likely to penetrate disposable nitrile gloves very rapidly, if other glove options cannot be used due to loss of dexterity, disposable gloves may be an acceptable option if the health hazards of the liquid are not extreme, double gloves are worn, and if the gloves are changed immediately after being splashed. Disposable polychloroprene (neoprene) gloves are available and may offer better protection than nitrile gloves for some chemicals (although worse for others); see links to glove guides in the pages below.

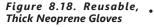
Disposable latex gloves and vinyl gloves are not recommended for general lab use due to inferior protective properties. Latex also elicits allergic reactions in some people.

Dispose of chemically contaminated gloves as hazardous solid chemical waste. Disposable gloves shall not be reused. Reuse of contaminated gloves runs the risk of transferring contamination to the inside of the glove. Personnel who get into the habit of reusing gloves are at risk of inadvertently reusing contaminated gloves. For these reasons, evidence of reuse of disposable gloves will normally be cited as a finding during lab safety inspections and PPE inspections.

Reusable Chemical Resistant Gloves

Reusable gloves (see Figure 8.18) are thicker and available in a wider range of materials than disposable gloves, which enables better protection against a wider range of chemicals, but at the cost of reduced dexterity. Normally, reusable gloves should have longer cuffs than disposable gloves, extending over the wrist and a few inches of the forearm. Lab coat sleeves should be worn under the glove cuffs.

Longer cuffs provide increased protection, but importantly, also allow the gloves to be thoroughly decontaminated, and well washed with soap and water before removal from the hands (it is difficult to adequately wash short cuff gloves without getting water inside them). Reusable gloves should be stored in a clean, dark place. They shall be carefully inspected for degradation, damage, and pinholes before each use. Natural rubber reusable gloves have relatively good grip and





ergonomics, but they are not recommended on account of poor storage qualities (they tend to crack).

Correctly chosen reusable gloves may provide protection from continuous contact, rather than short term splash protection. However, reusable gloves incorrectly matched to the hazardous material may absorb substantial quantities of hazardous material, which may be evidenced by swelling, or which may happen without visible change. Absorbed substances will not be removed by washing, and their permeation through the polymer material of the glove may cause them to slowly desorb from the inside and outside surfaces of the glove, representing an ongoing hazard.

To ease decontamination of reusable gloves and prolong their life, disposable gloves can be worn over them. This also provides an extra layer of protection for extreme hazard materials such as hydrofluoric acid. Note that wearing of disposable gloves under reusable gloves may NOT reliably provide extra protection for the following reasons:

 If there is a pinhole in the outer reusable gloves, liquid may be sucked in by capillary action and wet a substantial area of the inner disposable glove, which may then be slowly penetrated by permeation.

- If there is a pinhole in the outer reusable gloves, and the inner disposable gloves are shorter than the reusable gloves (which is usually the case), liquid may make its way around to the inside of the inner gloves.
- It is much easier to visually see if the outer gloves are admitting liquid if the outer gloves are thin disposable gloves.

Chemical Resistant Glove Selection Guides

Correct glove selection for phenol and hydrofluoric acid (HF) is extremely important; refer to EH&S <u>Phenol</u> <u>Safety</u> (see Figure 8.19) and <u>Hydrogen Fluoride Safety</u> (see Figure 8.20) Fact Sheets.

Figure 8.19. Phenol Safety Fact Sheet



Manufacturer's glove selection guides:

- <u>AnsellGuardian® Chemical Protection glove</u> selector
 - Example: <u>Microflex 93-850</u> extra-lowpinhole reduced-permeation nitrile disposable gloves

- Chemical resistance chart gives time in minutes to the point at which the test liquid is permeating through the glove at a rate of 0.1 µg/cm2/min. The table highlights how quickly many organic solvents can break through even highquality disposable nitrile gloves
- Resistance to many aqueous solutions is good, for example, 37% hydrochloric acid has a breakthrough time of 204 minutes; HOWEVER: (a) 40% hydrofluoric acid breaks through in only two minutes and 49% hydrofluoric acid in zero minutes (likely due to un-ionized HF molecules diffusing through the glove material) and (b) concentrated nitric acid (70%) and concentrated sulfuric acid (96%) degrade the glove material, leading to breakthrough times of 5 minutes and 11 minutes, respectively
- <u>Kimberley-Clark Nitrile Gloves Chemical</u> <u>Resistance Guide</u>
- <u>Microflex® Chemical Resistance Guide</u>
- <u>The Glove Company Chloronite</u> lightweight chemical resistant gloves
 - Double layer gloves polychloroprene outer layer, nitrile inner layer
 - At the thinner end of reusable gloves, practical for lab use
 - Chemical Resistance Guide
- <u>The Glove Company disposable nitrile gloves</u>
 - Chemical resistance charts for <u>TGC Orange</u> <u>Nitrile</u> and <u>TGC Grey Nitrile</u>.

If in doubt, or if chemical protection is required under unusual conditions (e.g., for prolonged periods of time), contact glove manufacturers for guidance. Figure 8.20. Hydrogen Fluoride Safety Fact Sheet



Respirators

Respiratory protection is complex, and is subject to stringent regulatory requirements. The most fundamental requirement is that practical engineering control options to eliminate the respiratory hazard must be exhausted before resorting to respiratory protection. In the overwhelming proportion of USC laboratories, appropriate provision and use of safety controls such as fume hoods removes the respiratory hazard and obviates the need for respiratory protection.

Figure 8.21. 3M Full Face Respirator

For safety and regulatory reasons, personnel at USC are not permitted to use respirators (see Figure 8.21) unless enrolled in the EH&S respiratory protection program.



This program involves assessment of respiratory protection need by an Industrial Hygienist, in consultation with laboratory safety specialists. The assessment may involve exposure monitoring. If engineering and other safety controls are insufficient or impractical and respiratory protection is judged necessary, the program covers selection of appropriate respirators, medical clearance, fit testing, and training of authorized users. Refer to the Respiratory Protection Program Fact Sheet (http://tiny.cc/usc-ehs-RPP-fs; see Figure 8.22) for more information.

Unauthorized respirators in labs will be cited as a safety finding during safety inspections.

Figure 8.22. Respiratory Protection Program Fact Sheet



Engineering Safety Controls

Referring back to <u>Hierarchy of Safety Controls</u> (Section 4), elimination and substitution are the preferred means to eliminate or reduce hazards. If this cannot be done and a hazardous chemical must be employed, engineering safety controls are the next most efficacious means of managing the hazard and reducing the risk, and they must be employed whenever possible.

Please note that engineering controls always need to be backed-up by appropriate administrative controls, to ensure that people are trained to correctly use the engineering controls and to monitor and enforce correct use. Engineering safety controls also need to be backed up by PPE.

Chemical Fume Hoods and Related Equipment

In most laboratories, the fume hood (see Figure 8.23) is the single most important item of safety equipment. Fume hoods are by far the most reliable and efficacious method of reducing airborne exposure of laboratory personnel to hazardous materials, and by following the basic rules of correct fume hood use, exposure should be reduced to negligible levels.

Figure 8.23. Typical Chemical Fume Hood



Source: Labconco

In its barest essentials, a fume hood is a box with a sliding sash allowing access to the interior working space, and which is connected to an exhaust system so air flows unidirectionally from the laboratory, through the fume hood working space, and finally out of an exhaust stack outside the building.

In practice, fume hoods are rather more complicated, incorporating internal baffles to prevent turbulence or internal recirculating flow, a system to keep the face velocity from depending too much on sash position, and usually an aerofoil at the point where the sash closes to prevent turbulence. EH&S' safety video "How To Properly Use and Operate a Fume Hood" illustrates these points: https://www.youtube.com/watch?v=d6l-6rPtWMk.

More information about fume hoods and other airextraction safety systems can be found in Prudent Practices (2011, <u>Section 9.C.1</u> onwards (p 219)). For a presentation on fume hoods and other laboratory exhaust devices and systems, see <u>http://labs21.lbl.</u> <u>gov/workshop/AdvCourse-HPLabExhDev-5.pdf</u>.

Fume Hood Face Velocity and Testing

The velocity of incoming air, measured in the vertical plane of the sash at a specified sash opening, must be within a defined limit. If the velocity is too low then containment is unreliable and may be ineffective, as containment is easily breached by external air currents, e.g. from a person walking past.

If the flow is excessive then turbulence may form in the airflow and cause localized dead zones or reverse flow, impairing containment.

EH&S quantitatively measures face velocity of all fume hoods once per year. General use fume hoods are deemed to pass testing if the mean face velocity is in the range 100 - 150 feet per minute. In accordance with Cal-OSHA (<u>Title 8, §5154.1 (e)(1)</u>), the maximum sash opening at which the fume hood meets the minimum velocity will be marked on the hood, up to a maximum of sixteen (16) inches. Sixteen (16) inches is the highest sash opening at which EH&S will routinely test fume hoods, even if a hood is suspected of being capable of sustaining the required airflow at a sash opening of greater than sixteen (16) inches. Note: Fume hoods at USC have a ruler attached at the side of the sash, for the purposes of measuring the opening.

Fume hoods and 8 CCR §5209 Carcinogens

Special fume hood requirements may apply to use of the <u>thirteen (13) particularly severe carcinogens</u> (list and CAS numbers available at link) regulated under <u>CCR Title 8 §5209</u>. Requirements may include higher average face velocities, and filtering of air before discharge. Please contact <u>labsafety@usc.edu</u> well in advance of purchasing or using these materials.

Safe Use of Fume Hoods

Before using the fume hood:

- Verify that the air gauge indicates that the air flow is within the required range and that the hood has been certified by EH&S within the last year.
- Avoid placing large equipment inside fume hoods.
 - If it is essential to have large equipment inside the fume hood, the equipment must be lifted at least two inches off the base of the hood's interior so air can flow underneath. The equipment should also not be too close to the rear or sides of the hood; leave a gap of at least four inches if possible. The equipment should also preferably be more than six inches from the front of the hood. All of these gaps help avoid turbulence or "dead spots" in the airflow.

- EH&S offers smoke testing to verify operation of fume hoods containing large equipment. Contact <u>labsafety@usc.edu</u> for more information.
- Make certain that no obstructions impede the airflow. It is especially important to not have items too close to the exhaust openings around the baffles at the rear of the hood.
- Never position fans or air conditioners to direct air flow towards or across the face of the fume hood. Doing so interferes with the air flow of the fume hood and may cause turbulence and escape of contaminants.
- Never remove side panels from the fume hood because it disrupts air flow inside the fume hood.
- Close laboratory doors so that the air flow inside the fume hood is not disrupted.
- On the bottom of the sash, it is advisable to affix a strip of tissue paper, or a small card tag on a string. The tissue paper or tag will be sucked inwards by the airflow during normal operation of the hood. Lab personnel should be in the habit of observing the indicator to detect any sign of fault.
- Ensure the hood is suitable for the work planned (e.g., DO NOT heat perchloric acid in a regular fume hood).
- Design experiments to capture or scrub highly toxic or odorous vapors or gases (e.g. fluorine, hydrogen sulfide, methanethiol) rather than simply releasing them into the fume hood.
- In rooms containing multiple fume hoods, ensure they are not all wide open. If too many fume hoods have sashes raised too high, the ventilation system may not be able to supply sufficient make-up air into the room.

This can unacceptably reduce the airflow and face velocity in all fume hoods in the room, including those which do not have their sashes raised.

While using the fume hood:

- Never allow your head to enter the plane of the hood opening. For vertical rising sashes keep the sash below your face. For horizontal sliding sashes, keep the sash positioned in front of you and work around the side of the sash.
- Keep the sash opening as small as can be managed without interfering with the ability to work within the hood. Generally, try to work with sash openings between twelve (12) and sixteen (16) inches.
- Close the sash immediately when the hood is not in use.
- Always wear appropriate PPE working inside of a fume hood does NOT eliminate the need for appropriate PPE.
 - A fume hood sash is not a replacement for appropriate eye protection.
- All materials inside the fume hood need to be kept at least six inches from the sash opening.
- The fume hood should NOT be used for permanent storage of chemicals (see Figure 8.24).
 - Exceptions may be made on a case-bycase basis for high-hazard materials stored in small quantities in secondary containment, provided the storage arrangements do not impede the airflow, and if this is the safest storage option available.
- Violent air movement close to a fume hood disrupts the airflow.

- Do not walk rapidly when close to fume hood openings.
- A fume hood sash is not a blast shield and should not be used in lieu of one.
- Tissue paper and other light materials must not be placed in a hood without restraining them in some way. Unrestrained light items may be sucked into the ductwork and may cause partial blockage.

Fume Hood Signage

Fume hoods used for highly hazardous work or materials shall be signed appropriately. Signage should be displayed when a hood is used for particularly hazardous substances (PHS), highly chronically toxic materials, potentially explosive materials, lasers, or other high-hazard equipment or experiments.

A sign should be displayed if unattended experiments are running in a fume hood, clearly displaying the hazards of the experiment, the experimenter, the responsible PI, and emergency contact information (see Figure 5.4).

Fume Hood Malfunction and Repair

During regular lab safety inspections or fume hood inspections, if EH&S determines a fume hood to be malfunctioning, it will be signed as out of use and a repair request will be submitted to FPM.

Figure 8.24. Chemical Storage in Fume Hood



When FPM have completed repair, they transmit the finished work order back to EH&S, who will revisit the lab to retest the fume hood, certify as safe to use, and remove the out-of-use sign.

If lab personnel are concerned that a specific fume hood seems to have insufficient or excessive face velocity, they shall sign the hood as out-of-service and send a request to have the hood tested to <u>labsafety@usc.edu</u>. If lab personnel find a fume hood to be malfunctioning, they shall immediately contact FPM @ (213) 740-6833 UPC or (323) 442-8005 HSC to place a work order for repair. Lab personnel shall clearly sign the affected hood as out of use (e.g., see Figure 8.25). After repair, FPM will contact EH&S, who will test the fume hood, certify as safe to use, and remove the out-of-use sign.

In all cases, lab personnel shall ensure no uncovered hazardous materials remain in malfunctioning fume hoods. If it is not safe for lab personnel to remove or cap hazardous materials in malfunctioning fume hood(s), they shall prevent access to the affected lab and call EH&S at (323) 442-2200 or DPS (after business hours) at (213) 740-4321.

NOTE: Widespread failure of fume hood exhaust in a building, due to power failure or other cause, may

result in the atmosphere of the building becoming contaminated and hazardous. Occupants of lab buildings should vacate the building for the duration of any event which causes widespread fume hood failure, and should not re-occupy until fume hoods and HVAC are operating normally and have had time to clear all potentially contaminated air from the building.

Low-Flow Fume Hoods, Ductless Fume Hoods

Low-flow fume hoods and ductless fume hoods are NOT permitted by EH&S at USC for regulatory and best practice reasons. Please email <u>labsafety@usc.</u> edu if more information is required.

Specialist Fume Hoods: Perchloric acid fume hoods

Hot and/or \geq 72% perchloric acid may ONLY be used in a specially engineered perchloric acid fume hood, of which there are a number at USC. These fume hoods incorporate an internal wash-down system. They should be operated in accordance with an SOP based on the manufacturer's operating manual.

Perchloric acid shall NOT be used in a regular fume hood if the acid is heated or if it is more concentrated than 72%. Please email <u>labsafety@usc.edu</u> if more information is required.

Specialist Fume Hoods: Acid Fume Hoods (Non-Perchloric)

Some chemical fume hoods at USC are designed to be used for corrosive mineral acids, although they are equally suitable for use with corrosive inorganic bases.

Figure 8.25. Fume Hood Disabled Sign



The main distinguishing feature of acid hoods is that they are lined with non-corrodible materials such as unplasticised PVC (polyvinyl chloride), or the expensive but more temperature resistant PVDF (polyvinylidine fluoride).

Additionally, the sash may be polycarbonate rather than glass, allowing hydrofluoric acid to be used without danger of irreversibly damaging the surface of the sash. **Due to the polymer construction of acid fume hoods, they may be much more easily damaged by heat, fire, or organic solvents than regular chemical fume hoods.** Consult manufacturer's instruction manual for details of the solvent compatibility of acid fume hoods.

Devices which are Somewhat like Fume Hoods: Ducted Laminar Flow Clean Hoods and Ducted Total Exhaust (Class II Type B2) Biosafety Cabinets (BSC)

Some specialist research facilities (e.g. cleanrooms) contain ducted laminar flow clean hoods, which may also be known under other names, such as vertical fully exhausted workstations ("vertical" refers to the direction of the airflow and "fully exhausted" indicates that air is not recirculated into the lab).

Unlike regular hoods, ducted laminar flow clean hoods (see Figure 8.26) protect the internal work area from particulate contamination through a laminar flow of filtered air which is fed into the interior of the hood from above. Similar to regular hoods, there is a flow of air inwards through the sash opening. Thus, they both protect the worker from the sample, but also protect the sample from the worker and from ambient particulates.

Ducted laminar flow hoods provide more limited protection than regular chemical fume hoods, and they are more sensitive to incorrect usage. **Ducted laminar flow hoods are not suited for** work with open flames, pyrophoric materials, extremely toxic or highly carcinogenic materials, radioisotopes, or experiments which use large quantities of flammable solvents, or where there is an appreciable ignition hazard (e.g. distillation, most organic synthesis). Email <u>labsafety@usc.edu</u> if more information is required.

Biosafety cabinets have a number of technical similarities to laminar flow hoods. **Total exhaust** (Class II Type B2) biosafety cabinets are not to be mistaken for chemical fume hoods. They may be used for protection from chemical vapors, but only within limitations specified by the manufacturer. Their suitability for use in lieu of a chemical fume hood should be determined by a qualified person (NFPA 45 2015 7.4.10). Other types of biosafety cabinets recirculate air into the lab through a HEPA (High Efficiency Particulate) filter which allows hazardous gases and vapors to pass straight through. Biosafety cabinets are required to be tested and certified annually. EH&S does not have the technical capability to test biosafety cabinets; this must be done by external contractors, and responsibility for arranging this lies with the PI.

Figure 8.26. Cross Section of Laminar Flow Clean Hood

EXHAUST

LAMINAR FLOW CLEAN HOOD

Refer to the <u>BSC</u> web page for further details and NSF 49 certified vendors.

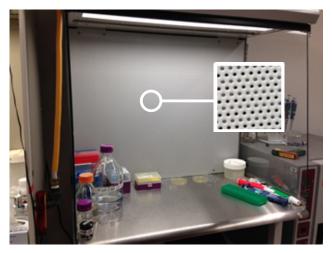
IMPORTANT: Things which are NOT Fume Hoods!

Non-ducted laminar flow hoods, laminar flow benches, and non-ducted (non-exhausted, or recirculating) biosafety cabinets are all designed to keep the work area clean of particulate materials by passing non-turbulent filtered air over the work areas. **These devices provide zero protection from** harmful gases or vapors, as they are recirculated straight into the breathing zone. Non-ducted laminar flow hoods and laminar flow benches also provide zero user protection from harmful particulates.

Figure 8.27 depicts a horizontal laminar flow clean bench. The back wall of the bench is pierced with an array of holes (see inset), out of which flows filtered particle-free air, which keeps the work area clean. There is zero user protection from hazardous materials, as air is simply blown towards the user and into the open lab (acknowledgement to Prof. El Naggar (USC Dornsife) for permission to use this photograph).

Non-ducted biosafety cabinets provide some protection from particulates as the air is HEPA filtered before leaving the cabinet; for example, Prudent Practices (2011, <u>Table 9.3 p 220</u>, and <u>Table 9.6 p 247</u>) states that non-ducted biosafety cabinets (Class I, and Class II types A1, A2, and B1) may be used for protection from nonvolatile toxic chemicals, including nanoparticles; however,

Figure 8.27. Horizontal Laminar Flow Clean Bench



Source: Prof. El-Naggar (USC Dornsife). Used with permission

EH&S recommends that non-ducted biosafety cabinets (i.e. all except Class II Type B2) NOT be used in lieu of a fume hood for protection from chemically hazardous particulate materials, unless there is an overriding technical or biosafety reason mandating use of a biosafety cabinet rather than a chemical fume hood.

Local Exhaust Ventilation: Snorkels

A fairly common form of local exhaust system is the snorkel, sometimes referred to as an elephant trunk. Snorkels have severe limitations, so it is very important for users to understand how they operate, and to use them only when appropriate. Figure 8.28 illustrates the operation and limitations of snorkels. **Snorkels are largely or completely ineffective unless extremely close (<4-6 inches) to the source of airborne contamination.**

This is particularly true if the hazardous material is a dust, gas, or vapor which is denser than air, or a similar density to air. For example, a snorkel positioned in the general vicinity of a source of organic solvent vapors is unlikely to significantly reduce personnel exposure (Figure 8.28 (B)).

Snorkels are more effective at capturing contaminated air when it is directed towards the snorkel. Hot air tends to rise, so a snorkel is quite effective when positioned above a point source of hot fumes such as a furnace vent, soldering iron, or flame (Figure 8.28 (C)).

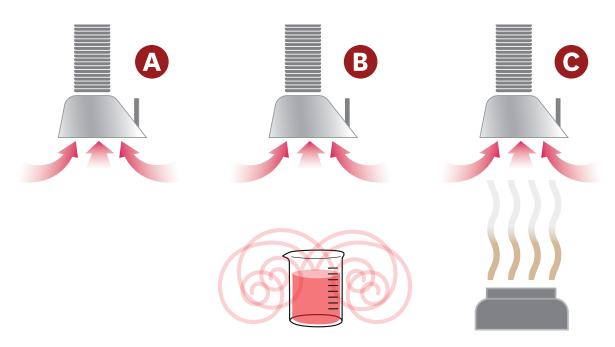


Figure 8.28. Operation and Limitations of Snorkels

(A) Local exhaust snorkel, with arrows showing how the airflow rapidly diverges and weakens at increasing distance from the nozzle. (B) Illustration showing how a snorkel is largely ineffective at abating an omnidirectional source of noxious vapors (e.g., a beaker of organic solvent) if the source is more than a short distance from the suction zone. (C) Illustration showing hot fumes from a furnace vent rising into the suction zone of a snorkel.

Snorkels do not provide the assurance of a fume hood and are not suitable for use with high hazard materials. Contact <u>labsafety@usc.edu</u> to answer any questions about appropriate snorkel use. Snorkels are not quantitatively tested by EH&S. Snorkel performance and capture effectiveness will be qualitatively assessed by EH&S using smoke and other methods, as and when required.

Local Exhaust Ventilation: Other Systems, and Further Information

There are a number of other local exhaust options available, including downdraft tables and backdraft tables (<u>http://www.uvm.edu/riskmanagement/</u> <u>local-exhaust-containment-devices</u> and <u>https://</u> <u>flowsciences.com/the-galaxy-of-containment-</u> <u>devices</u>), and exhausted balance enclosures. However, these are uncommon at USC. Contact <u>labsafety@usc.edu</u> if you have questions about other local exhaust options and their applicability and safe use.

Glove Boxes

A glove box (see Figure 8.29) consists of a working enclosure containing a controlled atmosphere, an airlock to enable items to be taken in and out of the box, a transparent front to allow the worker to observe the interior of the box, and gloves (usually butyl rubber) sealed into the front, to allow working access into the interior. Positive pressure glove boxes (the more common type at USC) are good for protecting the items in the box from the external atmosphere because any leak results in gas flowing out of the box rather than air flowing in. However, protection of the user from hazardous materials within the box is less certain and has limitations. See <u>Appendix B Glove Boxes</u> for more information.



Figure 8.29. Inert Gas Glove box

Source: GS Glovebox

Potentially Explosive Substances

Explosives: Guidelines on Identification

There are only a limited number of explosive chemicals commercially available. They are easily identified by their GHS labelling and SDSs; refer to Section 6 for information on the GHS hazard classification of <u>explosives</u>. There are many more explosive chemicals and mixtures which may be produced advertently or inadvertently within laboratories, and it is important that personnel are able to distinguish these materials, preferably during the planning stage of proposed work.

As a general guideline, any combination of oxidant with flammable, combustible, or reducing substance is to be viewed as a potential explosive. Chemicals containing oxidant and reducing groups within the same molecule or the same crystal structure may be explosive. Substances containing bonds which may break and rearrange to give lower energy products (e.g. O-O, N-N, C=C) may be explosive. Finally, as a general rule, the lower the proportion of "inert" moieties in the molecule or mixture, the more likely the material is to be explosive, e.g., hydrogen azide is a vastly more sensitive and powerful explosive than a long-chain organic azide.

Contact <u>labsafety@usc.edu</u> if you have any questions on identifying potentially explosive materials.

Bretherick's Handbook of Reactive Chemical Hazards (available online at USC Libraries) is a collection of reported violent decompositions and interactions of chemicals; it is a valuable resource which should be referred to by all persons engaged in higher-risk activities like synthetic chemistry.

Examples of oxidants and reductants which, if mixed, may produce violently reactive or explosive materials are given in Table 8.1. Note: Reactions in dilute aqueous solution are usually non-explosive, but mixing pure or concentrated materials may be extremely dangerous.

Table 8.1. Examples of oxidants and reductants which, if mixed, may produce violently reactive or explosive	materials.
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Oxidants	Reductants
 Anions: Nitrite, nitrate, hypochlorite, chlorite, chlorate, perchlorate, iodate, periodate, bromate, perbromate (rare), chromate, dichromate, permanganate, peroxide, superoxide, peroxydisulfate (persulfate) Oxides: Chromium trioxide (chromium (VI) oxide), lead dioxide, silver oxide, platinum dioxide, osmium tetroxide, ruthenium tetroxide, iodine pentoxide Liquids and gases: Tetranitromethane, nitrogen dioxide (dinitrogen tetroxide), nitrous oxide, nitric acid, perchloric acid, chromyl chloride, oxygen, fluorine, chlorine, bromine, ozone Others: Trichloroisocyanuric acid ("solid chlorine") 	 Alkali and alkaline earth metals. Other metals (especially if powdered), particularly: Titanium, zirconium, hafnium, aluminum, zinc, yttrium, lanthanides, and actinides Other elements: Phosphorus, sulfur, carbon, silicon*, boron* Anions: Cyanide, thiocyanate, hexacyanoferrate, sulfide, hypophosphite, thiosulfate, acetate and other organic anions, azide Others: Metal hydrides, boranes, silanes, hydrocarbons, almost any organic material, hydrazine, hydrazinium salts

* When porous or powdered. Unreactive in dense, massive form.

The UN *Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria* (document ST/SG/AC.10/11/Rev.6), on which OSHA and DOT explosives classifications are based, and parts of which are incorporated into the US regulations by reference, gives a table ("Table A6.1") listing some structural features which may indicate explosive properties in organic molecules. An extended version of the table is shown below (Table 8.2):

Table 8.2. Chemical groupings which, if present in organic molecules, may indicate explosive properties.*

Structural Feature	Examples		
C-C unsaturation	 Acetylenes, acetylides, 1,2-dienes Note 1: Acetylides, cumulated acetylenes, and haloacetylenes (X-C≡C-) are notoriously explosive. Note 2: Non-cumulated C=C units do not on their own impart explosive properties, and if incorporated into aromatic units may actually increase the thermal stability of the molecule. 		
C-metal, N-metal	 Grignard reagents, organo-lithium compounds Note 1: Especially hazardous are organometallic compounds containing C-F groups, which have caused serious explosions. Most commonly C-Li or C-Al compounds containing C-F, but analogous compounds of other metals may also be explosive. Metal alkoxides containing C-F bonds have also been known to explode. Refer to <i>Bretherick's Handbook of Reactive Chemical Hazards</i> for more details. Note 2: Some organometallic compounds are susceptible to O₂ insertion into the C-M bond, to give potentially explosive peroxides. 		
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulfonylhydrazides		
Contiguous oxygen atoms	Peroxides, ozonides		
N-0	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles		
N-halogen	Chloramines, fluoramines		
O-halogen	Chlorates, perchlorates, iodosyl compounds		
Chromate or chlorochromate ester	Étard complexes from chromyl chloride oxidation of aromatic methyl compounds.		

* Entries in black are taken verbatim from "Table A6.1 Examples of Chemical Groups Indicating Explosive Properties in Organic Materials" (ST/SG/AC.10/11/Rev.6.); entries in blue have been added for the purposes of this CHP.

Working With Potentially Explosive Substances

Two fundamental rules must be kept in mind when planning safe work with potentially explosive materials:

 A potentially explosive material cannot be assumed as safe simply on the basis that it has been worked with one or more times previously without exploding. Either safety has to be demonstrated by solid empirical data obtained from recognized tests of explosive power, sensitivity, and stability, showing that the material is impossible to detonate under all realizable conditions, or the material must be handled on such a small scale (typically ≤10 mg for highly explosive materials) that explosion will not result in significant hazard, provided appropriate PPE and engineering controls are utilized (e.g., blast shield) as specified in an SOP. It is unsafe to significantly scale-up any work with potentially explosive materials, unless the safety of the planned work can be assured through solid empirical evidence obtained from recognized tests of explosive power, sensitivity, and stability of the material in question; and scaling factors such as exothermicity and heat flow are demonstrated not to result in increased risk; and appropriate facilities and engineering-, administrative-, and PPE-safety-controls are instituted.

All persons who plan to mix oxidants and reductants (except in dilute solution or under conditions recognized to be safe), or who plan to synthesize known or suspected explosive molecules, complexes, salts, or mixtures shall:

- Be thoroughly familiar with the relevant chemistry, to the satisfaction of their Pl.
- Follow a written SOP, approved by the PI and signed by both parties.
 - SOP shall specify satisfactory engineering,
 PPE, and administrative safety controls
 - Engineering controls may include a heavy blast shield designed for the purpose, and constructed from thick, tough polymer which will not shatter (e.g. polycarbonate).

Note: A fume hood sash is NOT a blast shield.

- PPE may include face shield, goggles, flame retardant Nomex lab coat, and depending on the operation, may also include heavy leather gloves and leather apron.
- Hearing protection may be required for all personnel in the vicinity in case of a loud explosion.

- EH&S can provide an SOP template; however, this must be expanded by the end users with lab- and experimentspecific information. For questions or further guidance, email <u>labsafety@usc.</u> <u>edu</u>.
- Be trained in safe working practice to the satisfaction of the Pl.
 - Training may be done by the PI's designee; however, as a supervisor, the PI is ultimately responsible for the quality and appropriateness of lab- and experimentspecific safety training. EH&S can advise; email labsafety@usc.edu.
 - Internal training records shall be kept.
- Ensure all other laboratory personnel are aware of the nature of the work taking place.
 - Other personnel must be protected if in the vicinity of the work, and must be trained on emergency procedures.

Email <u>labsafety@usc.edu</u> if more information is required on working with potentially explosive substances.

Potential Explosives Focus: Azides

Sodium azide is a common reagent in laboratories, and the following must be noted:

- Sodium azide (see Figure 8.30) is stable and non-explosive under ambient conditions, but it may explode when heated.
- Azides of almost all other metals are sensitive explosives.
 - Do not use metal spatulas with sodium azide.
 - Do not mix azide solutions with salts of any metal except sodium and potassium.

- Do not pour sodium azide solutions down the sink. Quite apart from the general prohibition of sink disposal of hazardous materials at USC, azide disposal may cause build-up of explosive metal azide precipitates in waste pipes.
- Hydrogen azide (see Figure 8.30) is a very volatile, highly toxic, extremely sensitive explosive. Hydrogen azide:
 - Is produced by action of acid on ionic azide. Never mix sodium azide with acids.
 - Is explosive as a gas or as an aqueous solution.
 - May condense to a pure liquid, especially if cooled. This is an incredibly unstable explosive.
 - Is one of the most explosive materials known.

For examples of hazardous interactions involving azides, please refer to <u>Bretherick's Handbook of</u> <u>Reactive Chemical Hazards</u>.

Potential Explosives Focus: Nitromethane

Nitromethane (see Figure 8.31) is a moderately common specialist polar solvent and synthetic reagent. It is not classified as an explosive under the OSHA/GHS system because it is extremely insensitive to detonation. However, if detonated, the explosive power is very high, and the sensitivity to detonation may be much increased by additives. Nitromethane can readily form extremely powerful and sensitive explosives with bases, amines, metal salts, and a number of other substances. Nitromethane derivatives may spontaneously detonate, for example, from mixing nitromethane with alkali metal hydroxide. This will result in a spontaneous explosion after a short delay.

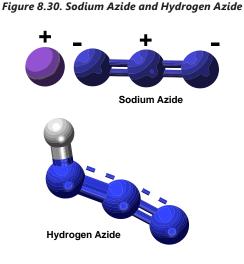
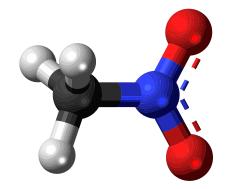


Figure 8.31. Nitromethane



For further information on hazardous interactions involving nitromethane, please refer to <u>Bretherick's</u> <u>Handbook of Reactive Chemical Hazards</u>.

- Avoid using nitromethane whenever possible.
- Always segregate and very clearly label nitromethane waste.
- Never mix nitromethane with bases, amines, or transition metal or heavy metal compounds.
- Never heat nitromethane under confinement.

Working With Pyrophorics

Pyrophorics are one of the most hazardous types of chemical for laboratory use, especially pyrophoric liquids, and pyrophoric solids mixed with flammable liquid. The hazard is especially notable in synthetic chemistry where they are common reagents, and where they are manipulated using cannulae, syringes, and fragile glassware.

It is essential for all pyrophoric users to be adequately trained to the satisfaction of their Pl, for a satisfactory SOP to be written and followed, and for adequate PPE and safety controls to be used. Self-heating chemicals and pyrophorics shall be stored in a cool place away from flammables and oxidizers, and in the minimum possible quantities.

The reactivity of solids with air is strongly dependent on the surface area of the solid. Thus, a material which is quite unreactive in massive form may be self-heating or even pyrophoric if in a porous form or finely powdered. The reactivity with air may also depend on the humidity; for example, coarselycrystalline lithium aluminum hydride may be stable on short exposure to low-humidity air, but ignite in damp air. (Finely powdered lithium aluminum hydride may be pyrophoric regardless of humidity, so it is recommended this reagent always be weighed in a glove box.)

Safe Practice

All persons who plan to work with pyrophoric materials shall:

- Download and study the pyrophoric safety references given below.
- Be thoroughly familiar with the relevant chemistry, to the satisfaction of their Pl.

- Follow a written SOP, approved by the PI and signed by both parties.
 - SOP shall specify satisfactory engineering, PPE, and administrative safety controls.
 - EH&S can provide an SOP template; however, this must be expanded by the end users with lab- and experimentspecific information. For questions/further guidance, email <u>labsafety@usc.edu</u>.
- Be trained in safe working practice to the satisfaction of the PI.
 - Training may be done by the PI's designee; however, as supervisor, the PI is ultimately responsible for the quality and appropriateness of lab- and experimentspecific safety training. EH&S can advise; email labsafety@usc.edu.
 - Internal training records shall be kept.
- Ensure all other laboratory personnel are aware of the nature of the work taking place.
 - Other personnel must be protected if in the vicinity of the work, and must be trained on emergency procedures.

Nomex lab coats are mandatory when using pyrophoric materials. Whenever possible, gloves of aramid, Nomex[®], carbonized fiber, or other recognized heat resistant material should be employed, preferably under chemical resistant gloves; however, it is recognized that many manipulations require high dexterity, which may make the addition of heat-resistant gloves impracticable or even likely to increase the risk of accident.

Email <u>labsafety@usc.edu</u> if more information is required on working with pyrophoric substances.

References: Pyrophorics Safety

It is important that prospective users of pyrophoric substances read and understand safety literature on the hazards and safe handling practices, including the following references:

- DOE Handbook: Primer on Spontaneous Heating and Pyrophoricity (DOE-HDBK-1081-2014), <u>https://www.standards.</u> <u>doe.gov/standards-documents/1000/1081-</u> <u>BHdbk-2014/@@images/file</u>.
- Handling Pyrophoric Reagents, DOE (PNNL-18668), <u>http://www.pnl.gov/main/ publications/external/technical_reports/</u> <u>PNNL-18668.pdf</u>. An important resource for dealing with some of the practical aspects of safe handling of pyrophorics in a research lab. It should be read by all pyrophorics users.
- On the pyrophoricity, safety, and handling of metalorganic chemicals, <u>http://www.</u> <u>sciencedirect.com/science/article/pii/</u> <u>S0022024806010189</u>. This reference is concerned with organometallic compounds used in CVD, such as trimethylaluminum. It contains useful experimental results on the resistance of PPE to pyrophoric materials, and on this account should be read by all users of pyrophorics. Additionally, Figures 1-3 in the

paper graphically show the effect of pouring a pyrophoric liquid into air, and show the burns which pyrophoric liquids can produce on PPE.

- Methods for the safe storage; handling; and disposal of pyrophoric liquids and solids in the laboratory, <u>http://www.sciencedirect.com/</u> <u>science/article/pii/S1871553210000289</u>. An important resource for dealing with some of the practical aspects of safe handling of pyrophoric in a research lab. It should be read by all pyrophoric users.
- Lab safety, PPE, and pyrophoric liquids, <u>http://</u> www.sciencedirect.com/science/article/pii/ <u>S1871553209000838</u>. Short, but informative article.
- Safe handling of organolithium compounds in the laboratory, http://www.sciencedirect.com/ science/article/pii/S1074909802002952. This reference is not as up-to-date as some of the other resources, but much of the information on hazards, properties, and stability and decomposition of organolithium compounds is useful. Note that the recommendation for safety glasses and for using nitrile gloves is no longer considered sufficient when handling pyrophorics.

Beryllium Containing Materials – An Extreme Hazard

Beryllium and beryllium compounds are uniquely dangerous sensitizers, able to cause permanent, incurable, progressive, disabling, and potentially fatal lung disease (*chronic beryllium disease*, also known as berylliosis) in susceptible individuals. Beryllium and its compounds may also cause skin reactions including non-healing granulatomas. Beryllium exposure limits are extraordinarily low and USC does not have the requisite facilities for safely working with beryllium-containing materials. Therefore:

 Beryllium metal, and beryllium-containing alloys, compounds, and ceramics may not be purchased, stored, or used at USC, UNLESS:

- The beryllium-containing material is in mechanically robust, insoluble, prefabricated massive-form (e.g. berylliumcontaining metal, alloy, ceramic, beryl, or chrysoberyl items) AND the berylliumcontaining material is not abraded, machined, etched, chemically attacked, dissolved, or corroded in any way, AND the beryllium-containing material is labelled as beryllium containing, and is appropriately disposed of as hazardous waste at the end of its life., OR:
- The acquisition and use is pre-approved by EH&S and the CCSC and takes place in adequate facilities under the auspices of an approved written beryllium safety program, which may include training, exposure monitoring, surface wipe tests, health monitoring (beryllium lymphocyte proliferation tests), respiratory protection, emergency procedures, and other requirements as dictated by regulation, best practice, and expert opinion.
 - It may take a year or more of planning, preparation, and training before a lab is ready to handle beryllium.
 - Developing a satisfactory beryllium safety program will likely require hiring specialist industrial hygiene expertise from outside USC.

Beryllium metal is used as a window in some X-ray tubes, for making certain TEM sample holders, and in some aerospace components such as gyroscopes. Beryllium oxide (beryllia) ceramic has a high thermal conductivity and is used in a few special applications including ion laser discharge tubes, high power semiconductor devices, and rarely in crucibles and high temperature components. Beryllium-containing devices are generally labelled as such by the manufacturer. They must not be disassembled, machined, abraded, modified, chemically attacked, or allowed to corrode in any way, and all usage must be strictly in accordance with manufacturers' instructions. Dispose of as hazardous waste at the end of life, or return to the manufacturer for recycling when possible.

Beryllium copper alloys have high strength and high electrical and thermal conductivity. Although sometimes incorrectly touted as being safe, machining of beryllium copper has resulted in numerous cases of chronic beryllium disease. **Beryllium copper alloys shall not be worked with at USC**. Projects should be redesigned to make use of non-beryllium alloys.

There are alternatives available for beryllium metal/ alloys, and beryllium oxide ceramics. For example, carbon fiber reinforced resins may substitute when a low density stiff material is needed. Aluminium nitride is a high thermal conductivity ceramic which can often replace beryllium oxide. Stabilized zirconia, boron nitride, and vitreous carbon are some examples of potential replacements for beryllium oxide (beryllia) as a crucible material.

Exposure Monitoring

Safety and regulatory considerations mandate that personnel exposures to hazardous substances be kept below defined levels. The mandated regulatory exposure limits are found in <u>8 CCR §5155 Table AC-1</u>, and are defined as follows:

- "Permissible Exposure Limit (PEL). The maximum permitted 8-hour time-weighted average concentration of an airborne contaminant."
- "Short Term Exposure Limit (STEL). A 15-minute time-weighted average exposure which is not to be exceeded at any time during a workday even if the 8-hour time-weighted average is below the PEL. (A time other than 15 in may be specified for some substances.)"
- "*Ceiling Limit*. The maximum concentration of an airborne contaminant to which an employee may be exposed at any time."

Non-mandatory, but strongly recommended exposure limits are defined for a wider range of substances by NIOSH (https://www.cdc.gov/niosh/ npg/) and ACGIH Threshold Limit Values (TLVs). If there is more than one exposure limit specified for a particular substance, the lowest should normally be followed as best practice. Regulated carcinogens have action levels specified lower than the PEL, which may trigger special monitoring requirements (http:// www.dir.ca.gov/title8/sb7g16a110.html). See <u>Section 6. Carcinogen Information Sources</u> for the list of regulated carcinogens.

In a laboratory environment, all volatile or fine particulate substances of significant health hazard should normally be handled inside a chemical fume hood, or inside a closed system. If the hood or containment system is operating correctly and safe working practices are followed, personnel exposure would normally be expected to be far below levels of concern. Under such circumstances, routine exposure monitoring is not required; however, it may be warranted in the event of suspected sensitivity reaction, suspected adverse health effect, or other unusual circumstance. View the EH&S Industrial Hygiene web page or contact labsafety@usc.edu for more information.

Proposed operations which cannot be confined to a fume hood or closed system, and which have potential to generate airborne hazardous materials should be reconsidered. If the potential airborne hazard cannot be eliminated by substituting a nonhazardous substance, by redesigning the system, or by a local exhaust ventilation system of proven effectiveness, please contact injuryprevention@usc. edu. Exposure monitoring may be required in such cases.

Medical Assessment and Surveillance

Persons who may be exposed to hazardous substances at USC may be entitled to a medical consultation/ examination if there is concern that they may be experiencing any adverse health effects. Generally, personnel exposure to hazardous substances in laboratories is extremely low. The most common health effect in laboratory personnel, but still very rare, is an allergy-like sensitization reaction, which may arise from unmeasurably small exposures in sensitized individuals. Any researcher concerned that they may be having a laboratory-related health reaction should notify their PI; they may also contact <u>injuryprevention@usc.edu</u> for further guidance.

It is strongly recommended that any personnel who may have been exposed to hazardous materials during an incident or emergency seek immediate medical evaluation. A safety data sheet should preferably be taken to show the medical personnel. More information on emergency procedures is available in <u>Section</u> <u>10</u>. The regulatory basis behind offering medical assessments is <u>8 CCR 5191 (g)</u>, which states the following: *"Medical consultation and medical examinations.*

- (1) The employer shall provide all employees who work with hazardous chemicals an opportunity to receive medical attention, including any follow-up examinations which the examining physician determines to be necessary, under the following circumstances;
 - (A) Whenever an employee develops signs or symptoms associated with a hazardous chemical to which the employee may have been exposed in the laboratory, the employee shall be provided an opportunity to receive an appropriate medical examination.
 - (B) Where exposure monitoring reveals an exposure level above the action level (or in the absence of an action level, the exposure limit) for a Cal/OSHA regulated substance for which there are exposure monitoring and medical surveillance requirements, medical surveillance shall be established for the affected employee as prescribed by the particular standard.
 - (C) Whenever an event takes place in the work area such as a spill, leak, explosion or other occurrence resulting in the likelihood of a hazardous exposure, the affected employee shall be provided an opportunity for a medical consultation. Such consultation shall be for the purpose of determining the need for a medical examination."

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9.0 Chemical Waste Disposal

Virtually every laboratory at USC produces hazardous waste. The storage, handling, and disposal of this waste is tightly regulated to protect workers and the environment. It is highly important for laboratory personnel to understand and follow directions on correct waste disposal practices, as communicated by the EH&S Hazardous Materials group (Hazmat; responsible for picking up waste), lab safety personnel, this CHP, the EH&S <u>Hazmat</u> web page, and <u>fact sheets</u>.

Scope

The CHP gives the basics of segregation, labelling, and storage of chemically hazardous waste. For information on management of waste which is biologically or radiologically hazardous, refer to <u>https://ehs.usc.edu/hazmat/</u>.

Useful note: Hazmat will also dispose of "universal waste", which includes batteries, fluorescent lamps and other mercury containing lamps and devices, electronic equipment, cathode ray tubes, and aerosol cans (full or empty). Refer to <u>https://ehs.usc.edu/hazmat/waste/universal/</u> for more information.

Please refer to the website and fact sheets, or email <u>labsafety@usc.edu</u> for more information.

General Considerations

Hazardous Waste Labelling

Correct labelling of hazardous waste is extremely important! Label all chemically hazardous waste with an official hazardous waste tag or sticky label provided by Hazmat (see Figure 9.1). Please keep a stock of labels in the lab and request more from Hazmat before you run out (it is most efficient for Hazmat to drop off labels during their regular waste pickups). Mark hazardous waste labels with the date when waste accumulation started. Alternatively, create waste tags in RSS; follow instructions in the <u>RSS Waste User Tutorial</u>.

Waste labels should be filled in accurately and LEGIBLY, and should be replaced if the writing fades or runs. Chemical formulae should NOT be used and abbreviations should be avoided.

Figure 9.1. Hazmat waste label and tag



Include the essential constituents of the waste, and note any special hazards. Examples of satisfactory waste descriptions to write on hazardous waste labels include:

- Aqueous acid: Dilute sulfuric and hydrochloric acid
- Non-Halogenated solvents: Ethanol, toluene, ethyl acetate
- Halogenated solvents: Dichloromethane, chloroform, trichloroethylene
- HYDROFLUORIC ACID. Extremely corrosive and toxic!!!!

When labelling waste which contains highly toxic elements (Cr(VI), Cd, Hg, As, Sb, Pb, Tl, Se, Te), ensure the elements are clearly marked on the hazardous waste label. The specific chemical state of the element can be specified if known, otherwise the name of the toxic element will suffice. Examples of satisfactory verbiage include:

- Organic waste + toxic heavy metal compounds: Toluene, hydrocarbons, amines, thiols, cadmium, lead, selenium, tellurium, arsenic
- Aqueous chromate / dichromate solution. Carcinogenic!
- Aqueous sodium selenate. Toxic!

For mercury waste, the label should state whether mercury compounds or liquid metallic mercury is present. Example:

- Mercury contaminated solid waste (mercury metal)
- Aqueous mercury(II) chloride
- Non-halogenated solvents + mercury compounds

Segregation

Different types of waste shall be segregated according to Hazmat requirements, as outlined below and on the EH&S website. If in doubt, please email <u>hazmat@usc.edu</u> for guidance.

External Decontamination

Clean all hazardous waste bags or containers on the outside and leave in a safe condition to be handled.

Timeline

It is strongly recommended labs dispose of hazardous waste containers not more than six (6) months from the date of first waste accumulation.

Do NOT store hazardous waste vessels in a lab for more than nine (9) months from the date of first waste accumulation. Give Hazmat ample notice so waste can be picked up before the nine-month limit expires.

Waste Pickup

Please refer to <u>https://ehs.usc.edu/hazmat-mgmt/</u> request-a-hazardous-waste-pickup/ for full information on waste pickup schedules, and how to request pickups.

Management

It is recommended that PIs designate a group member as Waste Officer, with responsibility for ensuring timely disposal of waste.

Liquid Chemical Waste

Liquid Waste Bottles, Secondary Containment, and Caps

Store all liquid waste bottles in secondary containment (See Figure 9.2). All liquid waste bottles shall be capped when not in use, to minimize evaporation. Uncapped waste bottles will be cited as a finding during lab inspections.

 <u>22 CCR § 66265.173 (a)</u>: "A container holding hazardous waste shall always be closed during transfer and storage, except when it is necessary to add or remove waste."

Bottles containing liquid waste may be stored in a cabinet or fume hood. If the waste contains health hazardous volatile components, a fume hood must be used. Ensure fume hoods are not overcrowded, and that waste and secondary containers are positioned where they cannot adversely affect airflow.

Certain wastes have potential for generating gas. Bottles containing such wastes should be plastic, wherever permissible on chemical compatibility grounds. Vented caps should be fitted to all bottles containing waste which may outgas; these caps may be requested from hazmat by emailing <u>hazmat@</u> <u>usc.edu</u>. As an additional precaution, caps may be left unscrewed one half turn until the waste is to be collected. More information is to be found under specific gas generating wastes covered in the subsection Liquid Chemical Waste Requiring Special Caution, below.

Large (4 L or over) glass bottles are particularly fragile. Do not use large glass bottles for disposal of extremely hazardous waste, or waste which has a high density. For example, large glass bottles are not suitable for holding concentrated acid waste.



Figure 9.2. Secondary containment

Bottles of liquid waste shall not be overfilled. As a guide, bottles should not be more than 80% full.

Hazardous Liquid Chemical Waste Segregation

Liquid chemical waste should be segregated into separate waste bottles according to the following basic scheme:

- Non-halogenated organic solvent
- Halogenated organic solvent
- Sulfur-containing organic solvent (dimethyl sulfoxide (DMSO), sulfolane)
- Aqueous acid
- Aqueous base
- Aqueous oxidizer (may also be an acid or base)
- General aqueous

Segregate less hazardous waste (e.g., solvent waste) from more hazardous waste (e.g., waste containing toxic elements such as arsenic or mercury). This is to minimize the volume of the more hazardous waste and hence enable safer and more cost-effective disposal. Unusual waste streams may require further segregation. For example, phenol-chloroform waste, waste containing highly toxic elements (Cr(VI), Cd, Hg, As, Sb, Pb, Tl, Se, Te), cyanide waste, azide waste. Please contact <u>hazmat@usc.edu</u> for more guidance. Mercury-containing waste should be segregated by itself.

Liquid waste should be labelled, capped, stored, and picked up in accordance with the guidelines in the subsections above.

Some additional waste types are discussed in the subsection Liquid Chemical Waste Requiring Special Caution, below.

Sink Disposal

Disposal of hazardous waste by pouring down the sink is prohibited. This includes any waste which contains chemicals potentially hazardous to health or to the environment, and any waste containing biohazardous agents or radioisotopes. Furthermore, **absolutely no agar or other gelatinous, lumpy, or solid materials to be put down sinks.**

The range of materials which are permitted to be sink-disposed at USC is extremely limited, and is **strictly restricted to materials listed in Table 9.1 below**:

Material	Mandatory Restrictions	Prohibited	
Dilute bleach solutions			
Dilute hydrogen peroxide solution	≤6% concentration (20 volume)		
Biodegradable detergents and cleaning agents			
Aqueous washings from the cleaning of glassware and equipment	Hazardous contaminants must be at least double-rinsed into a waste bottle before sink washing of glassware. If the contaminants are particularly hazardous substances, triple rinsing in to a waste bottle should be employed before sink washing.		
Limited quantities (<50 mL) of acetone, ethanol, or isopropanol arising from small-scale rinsing of glassware and equipment	 Hazardous contaminants must be at least double-rinsed into a waste bottle before sink washing of glassware. If the contaminants are particularly hazardous substances, triple rinsing in to a waste bottle should be employed before sink washing. Tips for washing: Give glassware a final rinse with deionized / distilled water whenever possible. Organic rinses do not result in a cleaner or dryer final surface, and they are more hazardous and use more natural resources. Do not leave organic washings in the sink – wash away with water. 	If larger scale use of organic solvent is required for cleaning, DO NOT dispose down the sink. Instead, collect the washings and dispose as organic waste.	
Certain aqueous solutions	 ONLY the following solutes are allowed: Cations: Sodium, potassium, calcium, magnesium Anions: Chloride, sulfate, phosphate, acetate, carbonate, bicarbonate, tartrate, citrate Glycerol, sugars, soluble starch, sugar alcohols (e.g. erythritol, sorbitol, xylitol) Organic nutrients such as vitamins and amino acids Trace quantities of nutrient elements Minimally health hazard buffers (i.e., NOT cacodylate, which contains arsenic!!) 	 SHALL NOT: Contain materials hazardous to health or the environment, including toxicants, carcinogens, reproductive toxicants, heavy metals (e.g. mercury), antibiotics or other antimicrobials, fungicides, drugs, dyes, radioactive isotopes, or biohazardous materials (e.g. organisms, recombinant DNA, prions, toxins). Be strongly acid or basic; pH range 5-9 is acceptable Contain gels or suspended solids. 	

Table 9.1. Materials appropriate for sink disposal.

Before considering sink disposal of any material which is approved according to the above criteria, researchers must be absolutely certain that no chemically-, biologically-, or radiologically-hazardous materials are present in any quantity. This is especially important if brand-name materials are present, as mercury-containing preservatives or other hazardous materials may be hidden in the ingredients.

If in doubt, researchers should always err on the side of disposing materials as hazardous waste rather than by sink-disposal. Contact <u>labsafety@usc.edu</u> for more information. Examples of materials which may or may not be sink-disposed are given in Table 9.2 below.

Substance	Sink Disposal Acceptable?	Comments	
Synthetic seawater	YES		
Sterilized seawater	YES	Provided not sterilized with harmful chemicals not approved for sink disposal.	
Sea or lake water containing live organisms	NO	Potentially biohazardous and/ or environmentally hazardous.	
Phosphate-buffered nutrient solution NOT containing	YES, if liquid.		
drugs, antibiotics, fungicides, organisms, radioisotopes, or hazardous chemicals.	NO, if gel is present or if gel may form on cooling or standing.		
Cacodylate-based buffer	NO	Cacodylate contains arsenic, a health and environmental hazard.	
Aqueous medium containing sodium azide as a preservative	NO	Azide is hazardous to health and the environment, and may produce explosive deposits in waste pipes.	
Abrasive slurry or sand suspension	NO	Insoluble grains like abrasives and sand build up in pipes and cause blockage. If there is no chemical hazard, allow the slurry to stand until the solids settle out, and sink dispose the aqueous layer. The residue can be disposed via Hazmat.	

Table 9.2. Examples of substances which may or may not be sink-disposed.

Liquid Chemical Waste Requiring Special Caution

Chloroform and Acetone

Chloroform and acetone react with each other in the presence of catalytic quantities of base. The reaction evolves heat and may result in boiling, which may lead to severe pressure increase in a closed bottle, with consequent bursting. Chloroform-acetone reactions have been implicated in waste bottle explosions and other lab incidents (see <u>Bretherick's Handbook of Reactive Chemical Hazards</u>). Adhere to the following:

- Chloroform is health hazardous and environmentally noxious and should be replaced by safer alternatives whenever technically possible.
- Do NOT add chloroform to non-halogenated solvent waste bottles.
- Do NOT add acetone to halogenated solvent waste bottles.
- CLEARLY label waste bottles to distinguish between halogenated and non-halogenated solvent waste.
- Do NOT use solvent mixtures containing chloroform and acetone (or chloroform with other ketones or aldehydes).

Nitric Acid

Nitric acid is strongly oxidizing, and the hazard is exacerbated by the production of huge volumes of highly toxic gases (mostly nitric oxide and nitrogen dioxide) during most of its oxidation reactions. Strictly segregate oxidizing waste from flammable, combustible, and organic waste.

Adding nitric acid to the wrong waste bottle may result in explosion after an unpredictable delay.

This is a classic cause of laboratory safety incidents. Nitric acid waste should be collected separately from other waste. Use a sturdy glass bottle - an empty acid bottle is ideal. Ensure that nitric acid waste bottles are very clearly labeled and that laboratory personnel are appropriately trained in waste segregation. Keep the cap unscrewed one half turn until the bottle is ready to be picked up. Store the bottle in a fume hood to extract any toxic nitrogen oxides which outgas.

Hydrogen Peroxide (except Piranha solution)

Waste containing hydrogen peroxide has a particularly high propensity to outgas, and depending

on the composition, gas evolution may continue for hours to months. Explosive bursting of hydrogen peroxide containing waste bottles is a "classic" laboratory incident which carries risk of serious injury — every care must be taken to avoid this hazardous possibility.

- Do NOT mix hydrogen peroxide waste with any other waste stream.
- Use a plastic (polyethylene) waste bottle.
- Use a vented cap on the bottle.
 - Vented caps do not work unless the bottle is upright and not more than 80% filled.
 - Keep the cap unscrewed one half turn until the bottle is ready to be picked up.
- Clearly label the bottle using the hazardous materials waste label (see Figure 9.1).
- Additionally, clearly sign the bottle "Hydrogen Peroxide Waste – Oxidizer – Add No Organics"

Hydrogen peroxide usage should be accompanied by an SOP which covers safe disposal procedures. In labs which use hydrogen peroxide, all personnel must be trained on and understand the importance of proper segregation and disposal of hydrogen peroxide waste, rather than just the personnel who themselves use hydrogen peroxide. This is to minimize the possibility of unaware individuals adding incompatible waste into hydrogen peroxide waste bottles. Hydrogen peroxide waste safety should be covered in internal refresher training.

Piranha Solution

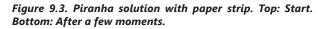
Piranha solution waste (a concentrated mixture of hydrogen peroxide and sulfuric acid) is highly oxidizing, corrosive, and extremely dangerous. It severely outgases and is a known cause of explosive bursting of waste bottles. Due to the corrosive properties, the risk of damage or severe injury from such an incident is substantial. The extreme oxidizing properties may result in violent reaction if mixed with organics or many other substances (see Figure 9.3). Adhere to the following:

- Avoid the use of Piranha solution whenever possible. Other aqueous cleaning agents include ammonium peroxydisulfate, sodium hydroxide, sodium hydroxide + bleach, or potassium permanganate soak followed by dilute oxalic acid / hydrochloric acid mixture to remove any manganese dioxide deposits.
- When Piranha solution must be used, mix only the absolute minimum quantity.

Use a sturdy glass bottle, as the extreme corrosiveness of the solution may affect plastic. An empty sulfuric acid bottle is ideal. **Do NOT use a bottle over 2.5 L size as the solution is dense and larger glass bottles are too fragile.** Use a vented cap on the bottle and keep the cap unscrewed one half turn until the bottle is ready to be picked up. **Allow solution to outgas for at least 24 hours in a fume hood before pouring into the bottle.** Segregate piranha solution waste from all other hydrogen peroxide waste. Label the bottle.

Hydrofluoric Acid

Waste containing hydrofluoric acid, ammonium fluoride, ammonium/sodium/potassium bifluoride, or which may produce hydrofluoric acid on standing (e.g. because it contains soluble fluorides plus materials which could hydrolyze to form acid), must NOT be stored in glass bottles due to the corrosive effect on glass. Thick-walled polyethylene bottles are suitable. Due to the toxic and extremely dangerous corrosive properties of hydrofluoric acid, labeling of waste bottles must be exceptionally bold and clear. Extra warning labels are advisable.







Note that "buffered oxide etch" and some other etching mixtures especially used in cleanrooms contain hydrofluoric acid and must be disposed appropriately.

Aqua Regia

Aqua regia is a yellow-orange liquid mixture of concentrated hydrochloric acid and concentrated nitric acid. This mixture is unstable and cannot be stored as it continually evolves corrosive and toxic gases including chlorine, nitric oxide, nitrosyl chloride, and nitrogen dioxide.

To safely dispose of aqua regia, dilute with water in the ratio 4 volumes water to 1 volume aqua regia. On dilution, it will be observed that the yellow color disappears and the bubbling ceases. The diluted mixture may be safely segregated into a waste bottle labeled "dilute aqueous hydrochloric acid / nitric acid mixture" or words to that effect. Even though outgassing should be greatly reduced from the diluted mixture, it advisable to use a plastic (polyethylene) waste bottle, and either use a vented cap, or leave the cap loose half a turn until the bottle is picked up by Hazmat. Additionally, the bottle should be not be filled more than 70% full.

All labs using Aqua Regia should incorporate the above safe disposal procedure into their SOP.

Solid Chemical Waste

Empty Reagent Containers

Empty chemical containers and bottles should NOT have the original labeling defaced if there is any residue of the original contents remaining. Containers and bottles which are decontaminated and no longer hazardous shall have the original labeling (chemical name, hazard pictograms, and hazard warning statements) defaced, and "clean", "decontaminated", or "washed" should be written on the container.

Empty bottles (e.g., solvent bottles) can be repurposed as waste bottles. If the residual contents are compatible with the waste to be added, then the bottles do not need to be washed. Unwashed bottles should retain the original label until immediately before the first waste is to be added, at which point the original label should be replaced with a hazardous waste sticker.

Do NOT decontaminate bottles by allowing the residue to evaporate in a fume hood or elsewhere. Solvent vapors contribute to photochemical smog. Disposal by evaporation will be cited by EH&S as a

If it is desired to wash and decontaminate empty chemical containers, please follow the instructions in Table 9.3. If in doubt, either label empty containers as hazardous chemical waste and have them collected by hazmat, or email <u>hazmat@usc.edu</u> for guidance.

General Solid Chemical Waste

Solid chemical waste takes many forms, including solid chemicals as well as contaminated items such as gloves, tissues, plastic syringes, centrifuge tubes, and non-broken glass sample vials. Note that glass Pasteur pipettes should be disposed of as broken glass due to their sharp points; see next subsection.

Solid chemical waste may be collected in thick polyethylene bags (e.g., Ziplock® bags) or any leakproof lidded container. If bags are used and the waste has significant health hazard, the filled bag should be taped shut and encased in one or two outer bags. Solid chemical waste may contain tissues or solids which are wetted by liquid, but there shall not be any free-flowing liquid.

Gloves, tissues, etc. contaminated with thiols may emit a foul odor which permeates through polyethylene bags. A useful tip to eliminate the odor problem is to wrap the waste tightly in aluminum foil (somewhat in the manner of an over-wrapper burrito) before bagging. Aluminum is impervious to organic vapors and acts as an effective barrier to odor escape.

finding.

Original Contents (Not more than a few drops remaining)	Procedure	Final Destination	
Relatively low health hazard, biodegradable, water soluble solvents (i.e., methanol, ethanol, propanol, isopropanol, acetone). Non-toxic inorganic salts (e.g., sodium chloride, magnesium sulfate).	 Rinse three times at the sink, then deface label on account of no longer being hazardous. Write "washed" on container. 	Reuse, donate to another lab to reuse, or dispose as non-hazardous regular trash.	
Higher-health-hazard or non-water- soluble solvents (e.g., toluene, hexanes, dichloromethane, THF, DMF, formamide)	 Double-rinse into appropriate waste bottle in fume hood, using ethanol, isopropanol, or acetone as washing solvent. (Triple rinse for PHS such as formamide.) Follow with triple rinse with water at sink, then deface label on account of no longer being hazardous. Write "washed" on container. 	Reuse, donate to another lab to reuse, or dispose as non-hazardous regular trash. Note: Bottle caps which may have PHS remaining under the sealing disc should NOT be disposed in regular trash, but should be disposed as hazardous solid waste.	
Acids: Perchloric acid, acetic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, phosphoric acid Bases: Ammonia solution	 Double rinse with water into a waste bottle in the fume hood. Then triple rinse at sink and wash outside of bottle. Deface label. Write "washed" on container. Bottle caps can be extremely difficult to fully decontaminate as acid/ base may be trapped behind the sealing disc. It may be necessary to pry out the disc and wash behind. 	Reuse, donate to another lab to reuse, or dispose as non-hazardous regular trash. Note: Bottle caps which may have corrosive material remaining under the sealing disc should NOT be disposed in regular trash, but should be disposed as hazardous solid waste.	
Concentrated sulfuric acid	Treat as for other acid bottles, but use extr drops create heat when they are diluted.	ra water for the first rinsing as residual acid	
Nitric acid		e in the fume hood, then leave uncapped ogen oxides . After this, rinse at sink, etc. as	
Low-to-medium health-hazard materials, (e.g., general inorganic salts, alcohols, ketones, esters, hydrocarbons)	Triple-rinse container and cap, using appropriate solvent (water, ethanol, isopropanol, or acetone). Collect washings in appropriate waste bottle in fume hood. Then triple rinse at sink (use detergent for first washing if original contents was water-insoluble organic) and wash exterior of bottle (with detergent, if required). Deface label. Write "washed" on container.	Reuse, donate to another lab to reuse, or dispose as non-hazardous regular trash.	
High health-hazard materials, e.g. cyanides, compounds of toxic elements (mercury, cadmium, thallium, lead, arsenic, antimony, chromium (VI), selenium, tellurium)	Do not attempt to decontaminate empty container. Do NOT deface label. Double-bag, secure with tape, label as hazardous chemical waste.	Pick up by Hazmat.	
Do not attempt to decontaminate empty container. Do NOT deface label. Double-bag, secure with tape, label as hazardous chemical waste.		Pick up by Hazmat.	

 Table 9.3. Acceptable procedures for washing and decontaminating empty chemical containers.

Solid chemical waste shall not contain any amount of liquid sufficient to flow. Vials of liquid shall be emptied into a liquid waste container before the vials are disposed of as solid chemical waste.

Broken Glass and Sharps

Note: Long pointed glass items such as Pasteur pipettes, NMR tubes, or thin capillary tubes should always be disposed of as broken glass, even if unbroken.

Clean broken glass may be disposed of in a cardboard broken glass box (see Figure 9.4) available from VWR. It does not require a hazardous waste label, but must be bagged and clearly labeled as clean glass. Clean broken glass can be picked up by custodial vendors for recycling.

Chemically-contaminated broken glass may be disposed of in a cardboard broken glass box appropriately labelled with a hazardous waste label. However, more satisfactory, or essential if the contamination is highly health hazardous, is to place the broken glass in a puncture resistant plastic container. If a sizable container is required, Hazmat (hazmat@usc.edu) may be able to supply a plastic barrel or green sharps container. The container must be labelled with a hazardous waste label.

Sharps (e.g., needles, razor blades, and scalpel blades) shall be disposed of in a sharps container.¹ A standard sharps container is red and marked with a biohazard symbol; this is appropriate if the sharps are clean or biohazardous. If the sharps are chemically contaminated, a green sharps container should be used (see Figure 9.4), and it shall be labelled with a hazardous waste sticker.

Figure 9.4. Top: Non-infectious sharps container. Bottom: Broken glass box.





Do NOT recap needles before disposal. Syringes may be left attached to needles and disposed of in a sharps container. To reduce contamination, they may be rinsed with a suitable solvent (water, isopropanol, ethanol, acetone) before disposal.

REMEMBER:

- Contaminated broken glass may be disposed of in sharps containers, however, sharps shall NOT be disposed in broken glass containers.
- Sharps containers shall NOT be filled above the fill line (approximately 80% full).
- Broken glass and sharps containers shall NOT contain any amount of liquid sufficient to flow.
- Miscellaneous trash and waste debris (e.g., paper, gloves) shall NOT be disposed of in broken glass or sharps containers.

¹ Stiff or pointed metal wires should also be disposed of as sharps.

Consult the Sharps & Broken Glass Disposal Guide Sheet for information on glass and sharps disposal.

Consult the <u>Chemical Waste Disposal Guide Sheet</u> for information on collecting solid and liquid chemical waste streams for safe disposal.

Gas Cylinders

Gas cylinders are extremely expensive to dispose of; therefore, every effort should be made to have the original manufacturer or supplier pick up empty or unneeded cylinders. If this is not possible, then place request a hazardous waste pick-up via <u>EHSA</u> or <u>RSS</u> giving full information on the cylinder(s), including contents, size, capacity (mass or volume of gas contained), and whether they are known to be empty or full.

Butadiene may undergo hazardous autocatalytic polymerization in cylinders. Butadiene should not be stored past its manufacturer's recommended expiration date. **If an old butadiene cylinder is discovered, do not attempt to move. Restrict access and call Hazmat at (323) 442-2200.**

Steel cylinders of anhydrous hydrogen fluoride may develop a dangerous internal pressure of hydrogen. If a hydrogen fluoride cylinder of uncertain history is discovered, do not attempt to move. Restrict access and call Hazmat at (323) 442-2200.



Incident Reporting

Serious Injury or Illness Reporting

Employers in the State of California are required to notify Cal-OSHA within 8 hours of all serious occupational injuries and illnesses, or any workplace injury or medical event which results in an employee staying in hospital overnight or longer. EH&S investigates and records incidents at USC and determines if Cal-OSHA notification is required, or if other actions are needed. Employers who fail to report serious occupational injury or illness within eight hours are subject to a \$5,000 penalty.

It is essential for PIs, Lab Managers, other laboratory personnel, and HR Partners to notify DPS as soon as possible in the event of the following:

- Exposure to harmful material (chemical, biological, or radiological)
- Eye injury or exposure, regardless of how minor it may appear.
- Needlestick injury
- Chemical or thermal burn
- Cuts or lacerations, if there is significant bleeding, stitches are required, or there are complications such as hazardous materials contamination or embedded broken glass.
- Concussion (actual or suspected)
- Fracture
- Dismemberment
- Death
- Any event requiring transport to hospital, e.g. sudden illness

For a work-related injury or illness that requires emergency response, follow the procedures on the <u>Emergency</u> <u>Notification Protocol</u> web page. Post the <u>1-2-3 Serious Injury Reporting</u> flier in a conspicuous area of the laboratory to help the research group become familiar with the process. It is recommended to post the 1-2-3 flyer in offices and common areas. Contact <u>EHS@usc.edu</u> for printed copies of the poster. NOTE: Work-related injuries and illnesses may be treated at USC-Approved Medical Facilities. Consult the <u>Workers'</u> <u>Compensation</u> web page for a list of approved facilities.



Non-Serious Injury or Illness Reporting

Even if an injury or illness does not meet the requirements for Cal-OSHA reporting, it is important that the affected employee receives proper care. Review the <u>Workers' Compensation web page</u> for more information.

Minor Incidents/Near Misses

Non-emergency laboratory safety incidents/near misses which do not result in injury or harmful materials exposure should still be reported to EH&S. If the incident occurs after hours, reporting may be left until the next business day. EH&S will assess the incident and determine if an investigation is warranted.

How to Report

The USC Department of Public Safety (DPS) has continuous access to EH&S via rotating 24-hour EH&S oncall personnel. DPS is also the contact between USC and emergency services (fire, ambulance, etc.).

Therefore, **DPS should be the first contact in an emergency situation, or when a significant incident needs to be reported**. DPS may be reached as follows:

- DPS Emergency Numbers: 213.740.4321 (UPC) and 323.442.1000 (HSC)
- DPS Non-Emergency Numbers: 213-740-6000 (UPC) and 323-442-1200 (HSC)

It is strongly recommended that all PIs and laboratory personnel have DPS emergency and non-emergency numbers pre-programmed into their mobile phones. It is also recommended for the numbers to be displayed adjacent to fixed-line phones in labs and offices.

Within normal working hours, and in the absence of an emergency, EH&S should be contacted directly on (323) 442-2200 to report safety incidents. Further information on emergency notification and incident reporting may be found on the EH&S website (<u>https://ehs.usc.edu/occhealth/injury-prevention/incident-reporting/</u>).

Incident Investigation

Upon being notified of a laboratory safety incident, EH&S will assess whether further investigation is required. In general, all except the most minor and straightforward incidents will be investigated by EH&S safety specialists, who will gather information by interviewing laboratory personnel and PIs, and by viewing physical evidence. An incident report will be generated which will, at a minimum, be sent to the PI and laboratory personnel who were directly involved in the incident, and to key EH&S personnel.

If an incident results in significant injury, is a "near miss" (i.e. could easily have been much more severe), or reveals systemic problems in safety management and culture within a research group, then the report may be circulated more widely, with appropriate recipients potentially including:

- Department/School
 - Safety Officer/Coordinator (when position exists)
 - Senior management (Head of Department, Dean, Vice Deans)
 - Safety committee chairperson
- USC Senior Management (Associate Senior Vice President for Administrative Operations, Senior Vice President for Administration, Vice President of Research)
- USC-wide safety committee chairpersons and members (CCSC, RSOC, others as appropriate)

The purpose of EH&S investigations is to clarify what happened and to identify contributing factors, in order to learn lessons and thereby improve future safety. Incident reports will normally contain specific recommendations for addressing any safety deficiencies or contributing factors identified during the investigation. It is important for PIs and laboratory personnel to understand that EH&S incident investigations are not intended to be punitive or to apportion blame.

Personnel are expected to cooperate fully with EH&S incident investigations by providing full and accurate information, in accordance with USC policy (<u>https://policy.usc.edu/cooperation-with-compliance-investigations/</u>).

Teaching Labs

Minor safety incidents in undergraduate teaching labs are not uncommon, for example, small cuts, scratches, and thermal burns. Academic departments should have a policy and mechanism in place for investigating such incidents and keeping records. The primary responsibility for investigation may be delegated to teaching lab managers, faculty responsible for teaching labs, or School/Department Safety Officers, as appropriate. Incident reports should be reviewed by the Department or School Safety Committee, preferably at least once per semester, to determine if there are lessons to be learned, and to ensure undergraduate safety training and safety information in lab handbooks are adequately updated. Significant undergraduate teaching lab incidents should immediately be reported to EH&S.

Emergency Response: Chemical Exposure

Immediate expert guidance on first aid treatment for hazardous chemical exposures may be obtained free from the California Poison Control System (CPCS), 1-800-222-1222, at any time (<u>http://www.calpoison.org/</u>).

Chemical Exposure	Response
	Special first aid items and response required; see fact sheet for details (<u>http://tiny.cc/usc-</u>
Phenol	phenol). All laboratories using phenol should have the fact sheet and decontamination
	supplies available in advance of starting work.
	Special first aid items and response required; see fact sheet for details (http://tiny.cc/
Hydrofluoric acid	usc-ehs-fs-HF). All labs using hydrofluoric acid should have the fact sheet and first aid
	supplies available in advance of starting work.
	 Immediately go to the emergency shower/eye wash station and flush affected body area with water for at least fifteen (15) minutes while removing all contaminated clothing and jewelry. If the eyes have been contaminated, forcibly hold them open and flush for at least fifteen (15) minutes. Roll eyeballs around to ensure they are completely washed - see the "How to Use the Emergency Eyewash & Safety Shower in a Laboratory at USC" video. a. If goggles are worn and face is splashed with hazardous material, close eyes, put face under shower, then remove goggles. This prevents accidental transference of contamination to eyes. 2. Hand soap may be used to aid removal of difficultly-soluble organic materials from
Eye/Skin Contact	skin. If soap is used, rub gently; vigorous rubbing may damage skin.
	3. Do not use neutralizing chemicals, creams, lotions or salves unless specifically called for (e.g. see phenol and HF fact sheets).
	4. Notify DPS and request emergency medical assistance if needed (e.g., exposure to high concentration, victim is showing symptoms, or substance is highly health hazardous e.g., phenol, hydrofluoric acid).
	 a. Err on the side of caution – request emergency medical assistance if not sure. b. If not transported by ambulance, affected individual should still seek medical evaluation as soon as possible.
	5. Resume flushing area with water if pain continues.
	6. Provide copy of SDS to emergency responders.
	1. Unless fully trained and equipped with appropriate respiratory protection, do NOT enter a potentially toxic or oxygen-deficient atmosphere in order to attempt a rescue!
	2. Move exposed person to fresh air if safe to do so.
	3. If victim is breathing, loosen victim's clothing and maintain the airway.
Inhalation	a. Contact DPS and request medical assistance if needed.
	b. If not transported by ambulance, affected individual should still seek medical evaluation as soon as possible.
	4. If the victim is not breathing, contact DPS and perform CPR (if certified) until medical assistance arrives. Be careful to avoid secondary exposure to chemical contamination via mouth-to-mouth resuscitation.
	a. Provide copy of SDS to emergency responders.
	1. Contact DPS and request urgent medical assistance. Provide copy of SDS to emergency responders.
	 If possible, determine what material was ingested by victim.
Ingestion	 If victim begins to vomit, turn head or entire body to avoid choking.
	4. Do not induce the victim to vomit or drink any beverage unless instructed by qualified medical personnel.
	 If victim stops breathing, see inhalation, step 4.
	Contact DPS and request urgent medical assistance
Injection	Provide copy of SDS to emergency responders.
	rovide copy of 505 to entergency responders.

Table 10.1. Types of chemical exposure and appropriate responses

Major Chemical Spill

A major chemical spill may result in contamination of large surface areas, internal or external contamination of personnel, and/or serious delay in work procedures.

- Large volume spill
- High hazard substance (in any volume)
- Potential safety or health hazard to the responder
- Chemicals in public areas or adjacent to drains
- Substance which emits harmful or toxic vapor, gas, or dust
- Substance which is highly health hazardous (e.g., highly acutely toxic) by skin contact

Major Spill Response

Lab personnel should NOT attempt to clean up a major chemical spill. Lab personnel should: (1) quickly throw absorbent on the spill **only if safe to do so**, (2) evacuate the lab, closing the door on the way out, and (3) contact DPS. Prevent lab access until the Hazmat Division has cleaned the spill and declared the lab safe to re-enter.

Minor Chemical Spill

A minor chemical spill is generally considered less than one liter and contaminates small areas or equipment, but DOES NOT result in external or internal contamination of personnel or serious delay in work procedures.

- Small volume
- Accessible location
- No inhalation hazard (i.e., no toxic vapor or toxic dust)
- Not highly health hazardous by skin contact
- Does NOT require respiratory protection

Minor Spill Clean-up

- Notify all personnel that a spill has occurred and evacuate non-essential personnel from spill area.
- Clean the spill ONLY if you have suitable training, PPE, spill cleanup supplies, and feel comfortable.
 - a. Do NOT attempt to clean up any spill that requires respiratory protection.
- 3. Wear PPE appropriate for the chemical.
- Follow spill cleanup instructions as directed by the Safety Data Sheet (SDS) of the chemical or by the manufacturer of a professional spill kit.
- 5. Notify DPS of any spill even if it was cleaned by lab personnel.

Mercury Spill

Mercury rapidly emits highly toxic vapor at room temperature. Breathing the vapor for a prolonged time may result in cumulative chronic poisoning with severe health effects.

If spilled mercury is not thoroughly removed, the remaining material tends to become dispersed as invisibly small microdroplets (e.g. by the action of foot traffic), which may emit vapor for years.

Mercury vapor may be strikingly visualized through its resonant absorption of 254 nm ultraviolet light; see <u>https://www.youtube.com/watch?v=lpZF88fqrl8</u>.

1. The number one rule is: **Prevent mercury** contamination from spreading.

- Restrict access to the spill area. Note that mercury droplets are very mobile and may travel further than expected from the immediate location of the spill.
- b. If spilled on the floor, check shoes very carefully for contamination. If tiny metallic droplets are seen, bag the shoes and label as hazardous mercury waste.
- Mercury-contaminated PPE and clothing should be bagged and labelled as hazardous mercury waste.
- 2. Contact DPS.
- 3. Hazmat personnel will visit to clear the spill.
 - a. Hazmat is equipped with a special mercury vacuum cleaner to capture mercury droplets.
 - b. Do NOT attempt to clean the mercury spill yourself – you may just break the mercury into smaller droplets and spread it around.

Mercury spills are a chronic rather than an acute hazard. If the spill happens out-of-hours, it is safe for the spill to be cleared the next day, provided the affected room is closed and very clearly signed to prevent entry. **It is essential to prevent personnel from spreading mercury contamination.**

Mercury contamination cannot be removed from carpet, which tenaciously holds microdroplets and gives severe vapor evolution (https://www.youtube. com/watch?v=lpZF88fqrl8). Contaminated carpets will likely need to be removed by Hazmat.

Spill Kits

It is required for labs that house hazardous materials to possess an appropriate spill kit. Detailed information on how to construct or purchase a spill kit may be found on the <u>Chemical Spill Kit</u> <u>Guide Sheet</u> (see Figure 10.1).

Labs which use hydrofluoric acid are required to have an HF-compatible spill kit, see fact sheet (<u>http://tiny.</u> <u>cc/usc-ehs-fs-HF</u>) for details (see Figure 10.2).











High-Hazard Labs and Labs of Special Interest

Purpose and Designation

For the purposes of general and chemical safety oversight of laboratories, a subset of labs may be designated high-hazard. High-hazard labs will be given a safety inspection biannually, not annually as for other labs. A lab may be designated high-hazard at the discretion of the CHO.

Note that biosafety and radiation safety programs may have alternative definitions of high-hazard for the labs where they have safety oversight.

Definition of High-Hazard Labs

For the purposes of general and chemical laboratory safety, a lab will be deemed to be high-hazard if it falls into one or more of the following categories:

- 1. Any lab using pyrophoric materials
 - a. Exception: A lab in which the only pyrophoric material is a small quantity in a metal vessel semipermanently fixed inside an atomic layer deposition (ALD) machine may be exempted from high-hazard classification at the discretion of the CHO.
- 2. Any lab using hydrofluoric acid or solutions containing hydrofluoric acid (e.g. buffered oxide etch).
- 3. Any lab using toxic gases.
 - a. Exception: Labs using lower-toxicity gases (e.g. ammonia, carbon monoxide, sulfur dioxide) under well-controlled conditions may be exempted from high-hazard classification on a case-by-case basis.
- 4. Any lab using very highly health hazardous materials (e.g. cyanides, potent carcinogens, thallium compounds, volatile potent alkylating agents) in significant quantity.
 - a. Due to the wide range of chemicals which are present at USC, and the large number of uses to which they are put, the CHO, or CHO's designee with suitable chemistry expertise, shall assess, on a case-by-case basis:
 - i. Whether chemicals in the lab are "very highly health hazardous".
 - ii. Whether the very highly health hazardous chemicals are used in significant quantities (e.g. for chemical synthesis), or are only used diluted in minute amounts (e.g. for biological toxicity studies).

- iii. Whether the very highly health hazardous chemicals are used under extremely well controlled conditions (e.g. very dilute solution in a closed system) or less controlled conditions (e.g. chemical synthesis or distillation in glass apparatus).
- 5. Any lab using flammable gases under conditions of significantly increased risk e.g., using hydrogenatmosphere furnaces.
 - a. Note: Flammable gas used under well-controlled conditions e.g., for Bunsen burners or smallscale hydrogen use as a microbial growth atmosphere, generally do not warrant classification of the lab as high-hazard.
- 6. Any lab using potentially explosive materials
 - a. Solid sodium azide and sodium azide used in dilute solution as a preservative/antimicrobial shall not be considered potentially explosive for the purposes of high-hazard lab definition.
 - b. Organic peroxide compositions manufactured for and used as a curing agent for polyesterstyrene resins, adhesives, etc, shall not be considered potentially explosive for the purposes of high-hazard lab definition (unless if stored or used in grossly excessive quantities).
- 7. Any lab using extreme oxidants (fluorine, halogen fluorides, oxygen difluoride, and comparable substances).
- 8. Any lab using highly reactive chemicals in significant quantity.
 - a. Due to the wide range of chemicals which are present at USC, and the large number of uses to which they are put, the CHO, or CHO's designee with suitable chemistry expertise, shall assess, on a case-by-case basis:
 - i. Whether chemicals in the lab are "highly reactive". Typical chemicals which are to be considered highly reactive are violently water-reactive chemicals (e.g. calcium hydride, sulfur trioxide, phosphorus pentoxide), potent oxidants (e.g. chromyl chloride), and other substances which may react with hazardous vigor.
 - ii. Whether the highly reactive chemicals are used in significant quantities (e.g. for chemical synthesis), or are only used diluted in minute amounts (e.g. for biological toxicity studies).
- 9. Any lab using flammable/combustible liquids under conditions of significantly increased risk and hazard, e.g. conducting chemical synthesis or distillation using glass apparatus.
- 10. Any lab not falling into one or more of the above categories, but which, by virtue of the particular hazards present in the lab, is assessed by the CHO or CHO's designee as warranting biannual safety inspections. This may occur if low-to-moderate hazard materials are used in exceptional quantities, or used in equipment or apparatus where the hazard is not well controlled, or requires exceptional expertise to control. This may also occur in a lab which contains unusually hazardous equipment.

The CHO reserves the right to designate any lab as a high-hazard lab based on the CHO's judgment of the specific hazards present in the lab (category 10); however, in the overwhelming number of cases, high-hazard labs will fall under categories 1 through 9, above.

Labs of Special Interest

A laboratory which appears to have systemic safety failings, as revealed by incidents, near-misses, persistently poor state of the lab, persistently unsatisfactory internal training of lab personnel, or other evidence, may be designated a lab of special interest by the CHO or CHO's designee. A lab so designated will be subject to extra scrutiny by EH&S laboratory safety. Extra scrutiny may take the form of additional inspections, unannounced inspections, requirements to provide SOPs or extra internal training, or other measures deemed appropriate by EH&S.¹ Labs will be taken off the special interest list when they are seen to achieve and maintain an appropriate level of safe lab management.

EH&S will work with PIs of *Labs of Special Interest* in order to:

- Help PIs understand the safety concerns.
- Provide information and advice on options for addressing the safety concerns.

¹ EH&S will bring labs of special interest to the attention of the appropriate Department / School and safety committee(s). Where appropriate to aid resolution of safety concerns, labs of special interest may also be referred to the Campus-Wide Chemical Safety Committee (CCSC).

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Appendix B Glove Boxes

Glove Boxes

A glove box (see Figure B.1) consists of a working enclosure containing a controlled atmosphere, an airlock to enable items to be taken in and out of the box, a transparent front to allow the worker to observe the interior of the box, and gloves (usually butyl rubber) sealed into the front, to allow working access into the interior. Positive pressure glove boxes (the more common type at USC) are good for protecting the items in the box from the external atmosphere, as any leak is out of the box, preventing air from entering. Figure B.1. Inert Atmosphere Glove box



Source: Meera Laser Solutions

Many types of glove boxes are available to cover a wide range of applications. Atmospheres inside glove boxes may include filtered air, dried air, once-through inert gas flow, or inert gas circulated through purification columns (sometimes referred to as "catalyst") to remove oxygen and moisture. The choice of inert gas is usually nitrogen (cheap and of wide applicability), or argon (completely inert but more expensive; only needed when materials of unusual reactivity with nitrogen are handled). Helium should generally not be used as it is a dwindling non-renewable resource which offers no chemical advantages over argon as an inert atmosphere.

Positive Pressure Recirculating Inert Atmosphere Glove Boxes

These are the types most commonly used for chemistry and related disciplines. The following points should be noted:

- Provides excellent user protection from pyrophoric materials.
 - Note: Sodium/potassium amide which has been inadvertently exposed to air before entering the box can still be very hazardous, as it can subsequently ignite/explode even in an inert atmosphere.
- Provides less certain protection from health-hazardous materials, because:
 - In the event of a leak, contamination is blown out of the box.
 - Unless the airlock opens into a fume hood (which is unusual), personnel are directly exposed to contamination when they open the airlock in the open lab.
 - It is extremely difficult to effectively clean and decontaminate items before removal, not least because static electricity can rapidly spread contamination over everything in the glove box.

- Typical glove box operation does not involve purging the airlock when items are taken out; thus, contaminated gas exits the airlock when opened.
- Certain toxic liquids (especially small molecule liquids of low to moderate polarity, e.g., nickel tetracarbonyl, dimethylmercury, carbon disulfide, chlorobenzene, iodomethane, chloroform, benzene) can diffuse into common glove materials (butyl rubber), and breakthrough time can be short (minutes). Furthermore, solvents which penetrate gloves (e.g. hexane, heptane) can potentially carry toxic solutes through.
 - https://cdn.mscdirect.com/global/media/pdf/search/ansell/ansell-chemical-gloveresistance-guide.pdf
 - <u>ChemRest® online glove selector</u>
- Non-volatile moderate-to-high health hazard materials should be safe to use in a typical positive pressure glove box, provided good working practices are adhered to. However, use of the following in a typical positive pressure glove box is likely unsafe, and should be discussed with EH&S prior to attempting:
 - Volatile or liquid highly acutely or chronically toxic materials (e.g. dimethyl sulfate, methyl iodide)
 - Extremely highly health hazardous materials in any physical form (e.g. beryllium compounds)
 - Potent carcinogens or potent reproductive toxicants (e.g. benzo[a]pyrene, propanesultone, N-nitrosoamines)
- The deoxygenation column material (often erroneously referred to as "catalyst") can react with a range
 of volatile materials, which will irreversibly and cumulatively reduce its capacity for absorbing oxygen.
 Amines, thiols, organic selenium and tellurium compounds, alkyl halides, and many other materials
 may do this. If it is needed to use such materials in the box, follow manufacturers' instructions for
 turning off and isolating the gas circulator and column, and purge the box with sufficient fresh gas
 before bringing the column back online. This should all be included in the SOP.

All groups using glove boxes should:

- Have an SOP for box use which can be largely based on manufacturer's instructions, but should also include safety and housekeeping requirements, such as the following:
 - Keep the box clean, remove own trash, do not clutter the box, and replace tissue wipes and other communal box supplies before they run out.
 - Do not wear anything which may spike or snag the gloves, including rings, bracelets and watches.
 - Use the glove box with clean hands, or wear fresh nitrile gloves under the glove box gloves (depending on user's or PI's preference). DO NOT wear potentially contaminated lab gloves under the glove box gloves.

- Clean the gloves internally and externally after use.
 - Internally Wipe with dry tissue. If powders are hard to remove, try wiping with a tissue smeared with a trace of silicone grease, followed by wiping with a dry tissue. Bag tissues for safe removal.
 - Externally Wipe with isopropanol (Caution Flammable).
- Wear disposable gloves (nitrile or polychloroprene) over the glove box gloves inside the glove box if handling materials likely to damage or degrade the glove box gloves.
- Restrict taking inappropriate chemicals into the box, including those posing unacceptable contamination hazards due to toxicity, chemicals which may react with sensitive materials stored in the box, and chemicals which may degrade deoxygenation columns.
- Restrict box use to trained and approved users who have signed the SOP.
- Keep a log of glove box usage, including materials taken into the box, and pressure on supply cylinders and readouts from oxygen and moisture sensors, to help troubleshoot malfunctions, discover leakage, etc.
- Have a management system in place (e.g. through an assigned super-user) to ensure timely change out of gas cylinders, regeneration of gas purification columns, glove replacement, pump oil change, checking of gaskets, and other maintenance as recommended by the manufacturer.

Whether or not to wear a lab coat and safety eyewear when using a glove box has been a source of debate in some labs. Glove box SOPs should include PPE rules, and it is suggested they conform to the following:

- In the absence of surrounding hazards which mandate a lab coat, lab coat use at the glove box is
 not strictly required on safety grounds. In such cases, the PI may rule on either using or not using lab
 coats at the box, as the PI sees fit; however, it is better to be consistent one way or the other rather
 than allowing users to individually pick whether or not to use a lab coat.
 - Exception: If pyrophoric materials are used in the glove box, a nomex[®] lab coat is required, to protect arms in the event of an (unlikely but not impossible) incident.
- In the absence of surrounding hazards which mandate eye protection, use of eye protection at the glove box is not strictly required on safety grounds.
 - Exception If the glove box is being used to handle potentially explosive materials in any quantity of more than a few milligrams, wear eye protection appropriate to explosives handling.

The above lab coat and eye protection rules apply when manipulating materials inside the box. When loading or unloading the airlock, PPE appropriate to the hazards shall be employed.

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LA Fire Code - Class D Fire Extinguisher

Regulations covering Class D extinguishers are as follows:

LA Fire Code Chapter 9 §906.3.4: "Class D fire hazards. Portable fire extinguishers for occupancies involving combustible metals shall be selected and placed in accordance with California Code of Regulations, Title 19, Division 1, Chapter 3."

<u>19 CCR §572</u>:

"Size and Placement for Class D Hazards.

- (a) Fire extinguishers or extinguishing agents with Class D ratings shall be provided for fires involving combustible metals.
- (b) Fire extinguishers or extinguishing agents (media) shall be located not more than 75 ft (22.5 m) travel distance from the Class D hazard.
- (c) Portable fire extinguishers or extinguishing agents (media) for Class D hazards shall be provided in those work areas where combustible metal powders, flakes, shavings, chips, or similarly sized products are generated.
- (d) Size determination shall be in the basis of the specific combustible metal, its physical particle size, area to be covered and recommendations by the extinguisher manufacturer on data from control tests conducted.
- (e) The material safety data sheet for the Class D hazard involved should be consulted to assist in selecting the most effective extinguishing agent."

<u>8 CCR §6151 (d) (6)</u>: "The employer shall distribute portable fire extinguishers or other containers of Class D extinguishing agent for use by employees so that the travel distance from the combustible metal working area to any extinguishing agent is 75 feet (22.9m) or less. Portable fire extinguishers for Class D hazards are required in those combustible metal working areas where combustible metal powders, flakes, shavings, or similarly sized products are generated at least once every two weeks." THIS PAGE INTENTIONALLY LEFT BLANK



USC Laboratory Earthquake Preparedness Guide

The following guide is designed to help Department Chairs, Principal Investigators, Lab Supervisors, and Lab Personnel perform an earthquake preparedness self-assessment for their labs and provides recommendations for what to do during and after an earthquake.

Preparation

- While in your lab, if an earthquake occurred, where would you go for protection?
 - Locate safe and dangerous spots in your area. Decide if you would go under a desk or table, in a safe corner, or out of the lab against a corridor wall.
 - Consider flying glass hazards from windows and glass and falling hazards from light fixtures, books, pictures, and equipment when selecting safe spots.
 - Take careful note of potential chemical/biological/radiological hazards from broken containers and spills, asphyxiation hazards from spilled cryogens or damaged superconducting magnets, and physical hazards from failed high-pressure systems, furnaces, etc.
- Do you know the evacuation routes from your building?
 - Be familiar with the location of all stairwells and routes.
 - Be familiar with your building outdoor evacuation assembly area (see the <u>Building Emergency</u> <u>Fact Sheets</u> web page).
 - Do not use elevators.
- Are gas cylinders well secured in an upright position?
 - Are pressure regulators removed and cylinder caps in place on cylinders that are not in use?
 - Two cylinder chains fastened to the lab wall are required for each cylinder.
 - Nylon/polyester/polypropylene straps are not acceptable for cylinder restraint; incombustible steel chains or steel cable must be used.
- Are liquid nitrogen vessels well secured in an upright position?
 - "Large" (multi-liter) liquid nitrogen dewars must be secured. (A precise definition of "large" is not yet decided upon, but in general, any dewar too large to be carried should be restrained, unless extremely short and wide-based.)
 - Pressurized dewars must be secured regardless of size.
 - Liquid nitrogen freezers should be restrained.

- Are chemicals stored properly?
 - Are chemicals recapped and returned to their storage cabinets immediately after use?
 - Are chemical storage cabinets closed and latched?
 - Are chemical storage cabinets secured to prevent tipping or movement?
 - Are chemical storage shelves equipped with lips or restraints to keep chemicals and glassware in place?
 - Are waste chemicals removed regularly?
 - Are chemicals stored in secondary containment trays or tubs?
 - Are non-compatible chemicals stored separately?
- Are fume hood sashes closed as far as possible to contain spills?
- Is heavy equipment and furniture that might block exit routes secured? When large items fall into the
 path of egress, your ability to exit may become compromised. In addition, large items could cause
 significant injury. Work with Facilities Management Services to secure equipment, furniture, shelves,
 and other items.
- Are exits and aisle ways maintained free and clear of obstructions including boxes, equipment, bottles, etc. on floors?
- Do you have equipment and/or processes that could be damaged or pose a fire or health hazard if power was suddenly lost?
- What contingencies have been made to provide backup or emergency power to maintain critical systems?
- Are safety systems (i.e., fire extinguishers, safety showers, eye washes) accessible and in proper operating condition? Does everyone in the lab know how to operate them?
- Do you have extra spill containment equipment available?
- Do you have emergency supplies such as drinking water, flashlight, radio, and batteries available? (USC Emergency Supply Vendor: <u>https://www.sosproducts.com</u>)
- Does your research group have an internal emergency plan which all members are trained on?

During an Earthquake

If you are in an office:

- **DROP** down onto your hands and knees (before the earthquake knocks you down). This position protects you from falling but allows you to still move if necessary.
- **COVER** your head and neck (and your entire body if possible) under a sturdy table or desk. If there is no shelter nearby, only then should you get down near an interior wall (or next to low-lying furniture that won't fall on you) and cover your head and neck with your arms and hands.
- **HOLD ON** to your shelter (or to your head and neck) until the shaking stops. Be prepared to move with your shelter if the shaking shifts it around.



If you are in a lab:

Every lab has different hazards. Therefore, it is very important to have considered your options on where to go in advance, based on the particular lab. Hazards could be chemicals, biohazards, radiation hazards, glassware, open flame, or other unique hazards. In most labs, dropping to the floor may be dangerous when hazards are present.

- Unless the lab is known to contain only minimally hazardous materials and equipment, the best plan
 is almost certainly to move to the corridor and take cover next to an interior wall. Although there is
 some possibility of being injured in the corridor from items falling from the ceiling, remaining in the
 lab may give a much greater potential for injury.
- If the corridor is far away, but the lab has an adjoining office or other room not containing hazardous materials (e.g. a microscope room) and close by, then drop, cover, and hold in the space.
- It cannot be stressed enough that as a matter of routine safety planning, all lab personnel and all research groups shall carefully consider the hazards and physical layout of the labs, and based on this, they shall work out the best place to shelter. Review the plan every time new personnel join the lab. Please ensure a lab-specific plan for sheltering is established before an earthquake strikes!

If you are in a building which contains labs, whether your room is a lab or an office, as soon as the shaking stops:

- After a moderate-to-severe earthquake, lab buildings may rapidly become hazardous as spilled harmful materials, non-functioning fume hoods, and failed ventilation systems combine to create a toxic atmosphere. After the shaking stops:
 - Quickly grab important belongings, shut doors, and vacate building.
 - Hazmat personnel with appropriate protective equipment will assess the internal conditions in lab buildings before you will be permitted to reoccupy the building.

Operations after an Earthquake

Depending on the time and circumstances of the earthquake, you may be asked to stay out of the building for a few minutes to a few weeks, or indefinitely.

- Following a "minor" earthquake, when there are no obvious signs of smoke/fire alarms, structural damage or other hazards, lab personnel should methodically check that:
 - All fridges, freezers, fume hoods, glove boxes, incubators, and other safety-critical or otherwise important equipment is functioning properly.
 - There are no containers fallen over, leaking, spilled, damaged, or broken in any fridge, freezer, chemical cabinet, flammable cabinet, or any other place where hazardous materials are stored. Search everywhere!!

- There are no broken mercury-containing items, including bottles, thermometers, manometers, barometers, or bubblers.
- The joints are not dislodged or leaking on glass apparatus.
- Is your short-term evacuation checklist posted near the exit of your lab? This is a check list of essential steps to take before leaving the building. These include, but are not limited to:
 - Turn off gas burners
 - Check quickly for fires, fire hazards, or spilled chemicals
 - Check for injured or physically limited people who might have trouble evacuating the building
 - Bring emergency supplies (first aid kit, flashlights, etc.) to the emergency assembly area
 - Close the lab door as you leave
 - Report crucial items or hazards to the appropriate official at the emergency assembly area and to DPS at 213-740-4321 (UPC) / 323-442-1000 (HSC)
- Do you have a long-term plan in case you could not get back into your lab for at least a week?
 - Which cell lines/experiments/data are your first priorities?
 - Are provisions made for taking care of lab animals and maintaining freezers? (Remember that normal distribution systems will not work, so you should have your own supply.)
 - Do you have backup copies of important data stored off campus?

Summary

Each of these issues and items could be critical for the health and safety of laboratory occupants. While this guide is directed toward earthquakes, please remember that building fires and other natural or man-made disasters could have a similar impact on your laboratory space and staff. We encourage you to discuss these plans among your staff and take the actions necessary to see that all issues are addressed. It is a good idea to practice your disaster plans periodically to ensure:

- The plans meet the requirements of current laboratory operations,
- All staff are familiar with both the overall plan and their specific role, and
- The plan is successful in accounting for staff and in reporting staff and laboratory conditions to key department administrators.

Your cooperation and preparation will be appreciated by all. For more information about emergency preparedness at USC, contact the Office of Fire Safety & Emergency Planning at <u>firesafety@usc.edu</u> or visit <u>https://fsep.usc.edu/personal-preparedness/</u>. For laboratory safety information, please contact the USC Office of Environmental Health and Safety (EH&S) at <u>labsafety@usc.edu</u> or visit <u>http://ehs.usc.edu/research/lab/</u>.



Appendix E Laboratory Safety Winter Recess Memo

USC Universion Southern	ersity of California	Office of the Vice-President of Research Office of Environmental Health and Safety
MEMORANDUM	I	
Date: December	4, 2023	
To: Principal In	vestigators, Lab Managers, Superv	isors, and Research Staff
	uri, PhD, Vice President of Researd es, MPH, CLS, Executive Director	h De k. T.: Ilinn Willis
Subject: Laboratory	Safety during Winter Recess	
	ark the beginning of the Winter Reces Ve take this time to remind our resea	s where the campus and most of its rch community of the following important
normal response capabi incidents, regardless of s	ity. Immediately report all accidents, size to DPS at (213) 740-4321. Serious 42-2200. EH&S will continue to mon	es Fire Department (LAFD) will maintain fires, hazardous materials spills, or other injuries must also be reported within 8 tor serious injury reports 24 hours a day,
research staff and/or st experimental procedure hazards. Researchers/st	udents are highly advised <u>not to wor</u> s involving hazardous chemicals, bio	hazardous materials, or high physical rs or periods of campus closure are at risk
be made for <i>low-risk</i> res member or student fully and utilizes all required equipment (PPE) must b	earch activities if the PI or Supervisor understands emergency and standar PPE – Remember : Appropriate lab co e utilized in accordance with the <u>USC</u>	d operating procedures, (b) has access to
extinguishers) must be c work only under condition	hecked to confirm their proper opera ons where the availability of emerger	kit, emergency showers/eyewash, and fire tion. Ensure that your staff and students icy aid is compatible with the risk. Please ency aid or request guidance from EH&S.
	r your efforts to fully prepare for the re the health and safety of all laborate	upcoming Winter Recess and to take the bry personnel.
University Park Ca 3434 S. Grand Ave., Los Angeles, CA 900	CAL 120 2001 N. Soto Street, S	BA 329 EHS@usc.edu

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Appendix F Forms, Templates, and **Contact Information**

Assessment

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Lab Self-Inspection Guide	http://tiny.cc/usc-lab-self-insp-ff
Lab Safety Inspection Process Flow Chart	http://tiny.cc/usc-lab-inspection-flow
General Lab Inspection Checklist	http://tiny.cc/usc-ehs-lab-insp-chklst
Online Ergonomic Self-Evaluation	http://tiny.cc/usc-ergo-self-eval
High Hazard Operations Analysis Form	http://tiny.cc/usc-ehs-hazops
PPE Inspection Checklist	http://tiny.cc/usc-ppe-inspect-checklist

Reporting

Workers' Compensation Form	WC form
Manager's Incident Report	Report of Incident
Volunteer Injury or Illness Report	Report of Incident
Report a Safety Concern Online Form	Report a Safety Concern

Other

Site-Specific Training Record Form	Site-Specific Training Record	
Employee Training Record Form	Employee Training Record	

Contact Information

OFFICE OF ENVIRONMENTAL HEALTH & SAFETY



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Introduction

OSHA/GHS Hazard Classification Tables referenced in Section 6 are provided here.

Irritants

GHS Hazard Class	Regulatory Definition ¹	Subdivisions ²	Comments	Examples
Skin Irritant	"Skin irritation is the production of reversible damage to the skin following the application of a test substance for up to 4 hours"	Category 2	Substances which display more severe skin effects are classified as corrosives (see subsection below)	n-octanol, toluene, cyclohexane (most organic solvents irritate the skin, often through removing the natural fats and oils)
Eye Irritant	"Eye irritation is the production of changes in the eye following the application of test substance to the anterior surface of the eye, which are fully reversible within	Category 2A ("irritating to eyes") Category 2B ("mildly irritating	Substances which display more severe eye effects are classified as corrosives (see Corrosives below)	n-octanol, potassium carbonate, Triton® X100 (non-ionic surfactant) (Not many substances are Cat. 2B)
	21 days of application"	to eyes")		are Cat. 2B)

1 29 CFR §1910.1200 Appendix A

2 From most severe to least severe hazard

Corrosives

GHS Hazard Class	Regulatory Definition ¹	Subdivisions ²	Comments	Examples
Eye Damage	"Serious eye damage is the production of tissue damage in the eye, or serious physical decay of vision, following application of a test substance, which is not fully reversible within 21 days of application."	Category 1	The full phrase is "Eye Damage Category 1 (irreversible effects on the eye)"	Butanol, iodomethane, phenol, sulfuric acid, aqueous ammonia, bromine Note how even "mild" substances like butanol can cause severe eye damage.
Corrosive (aka "Skin Corrosive")	"Skin corrosion is the production of irreversible damage to the skin following the application of a test substance for up to 4 hours."	Category 1A Category 1B	Category 1A materials are the most dangerous, and produce severe corrosive effects with a contact time of three minutes or less	lodomethane, bromine, sulfuric acid (conc) Phenol, aqueous ammonia (28% NH3)
		Category 1C		(Not many substances are Cat. 1C)

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2 From most severe to least severe hazard

Acute Toxicants

See <u>Section 6 Acute Toxicants</u> for more details on the OSHA/GHS classification.

Regulatory Definition ¹	Subdivisions ²	Description	Examples	
		"have produced significant		
		toxicity in humans, orhave	Many nitrosamines (acute	
	Category 1	the potential to produce	and chronic potent liver	
		significant toxicity in humans	toxicants), methanol	
		following single exposure."		
" specific, non-lethal	Category 2	"presumed to have the		
		potential to be harmful to	(Uncommon category)	
target organ toxicity		human health following		
arising from a single		single exposure."		
exposure to a chemical."		"Transient target organ		
		effects This category only	Sodium dodecyl sulfate	
	Catagory	includes narcotic effects	(surfactant; dust causes	
	Category 3	[i.e. reversible inhalation-	respiratory irritation), diethyl	
		type anesthetic effects] and	ether (reversible narcotic effect)	
		respiratory tract irritation"		

Specific Target Organ Toxicity - Single Exposure, (STOT-SE)

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2 From most severe to least severe hazard

Specific Target Organ Toxicity - Repeated Exposure (STOT-RE)

Regulatory Definition ¹	Subdivisions ²	Description	Examples (target organs)
"specific target organ toxicity arising from repeated [or prolonged] <i>exposure</i> " Includes chronic toxicants with a more general pattern	Category 1	"have produced significant toxicity in humans, orhave the potential to produce significant toxicity in humans following repeated or prolonged exposure."	Many nitrosamines (acute and chronic potent liver toxicants), carbon disulfide, chloroform (liver, kidney), acrylamide (peripheral nervous system)
of activity: "Assessment shall take into consideration not only significant changes in a single organ or biological system but also generalized changes of a less severe nature involving several organs."	Category 2	"presumed to have the potential to be harmful to human health following repeated or prolonged exposure."	Sodium azide (brain), n-hexane (peripheral nervous system, lung, kidneys, liver, reproductive system, brain; may cause numbness, weakness in the extremities, tingling sensations, and vision disturbance)

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Reproductive Toxicants and Effects via Lactation

GHS Hazard Class	Regulatory Definition ¹	Subdivisions ²	Description	Examples
	"adverse effects on sexual function and fertility[or]	Category 1	<i>"Known or presumed human reproductive toxicant"</i>	(Used when insufficient data to differentiate 1A over 1B)
Reproductive	development of the offspring." NOTE: "For classification	Category 1A	"Known human reproductive toxicant"	Thalidomide
Toxicant	oxicant purposes, the known induction of genetically based inheritable	Category 1B	"Presumed human reproductive toxicant"	Potassium dichromate, formamide, cobalt(II) chloride
effects in the offspring is addressed in Germ cell mutagenicity."	Category 2	"Suspected human reproductive toxicant"	(Uncommon category)	
Effects on or Via Lactation	[chemicals which may interfere with lactation or may pose a risk to the health of the child via breast milk]	None	N/A	(Uncommon category; may be due to a lack of test data for many chemicals)

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2 From most severe to least severe hazard

Note that substances which may damage DNA and produce inheritable effects in the offspring are classified as *germ cell mutagens*.

Germ Cell Mutagens

Regulatory Definition ¹	Subdivisions ²	Description	Examples
"permanent change in the amount or structure of the genetic material in a cell." The regulation is written with precautions in	Category 1	"Substances known to induce heritable mutations or to be regarded as if they induce heritable mutations in the germ cells of humans." "Substances known to	(Used when insufficient data to differentiate 1A over 1B)
mind. A substance which shows mutagenic	Category 1A	induce heritable mutations in germ cells of humans."	(Uncommon category)
action in somatic cells (i.e., any cell from which offspring do not arise), but for which there is no direct evidence	Category 1B	"Substances which should be regarded as if they induce heritable mutations in the germ cells of humans."	Potassium dichromate, colchicine (inhibits microtubule formation and miosis in cells; used as a drug and in genetics studies)
of heritable germ cell mutagenicity, will still be classified as a germ cell mutagen if certain conditions are met.	Category 2	"Substances which cause concern for humans owing to the possibility that they may induce heritable mutations in the germ cells of humans."	Cobalt(II) chloride, ethidium bromide, dimethyl sulfate (also carcinogenic, corrosive, a sensitizer, and very dangerously acutely toxic!)

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2 From most severe to least severe hazard

Carcinogens

See <u>Section 6 Carcinogens</u> for more details on the OSHA/GHS classification.

Sensitizers

GHS Hazard Class	Regulatory Definition ¹	Subdivisions ²	Description	Examples
Respiratory Sensitizer	"a chemical that will lead to hypersensitivity of the airways following inhalation of the chemical."	Category 1, further subdivided into 1A and 1B	Sub-category 1A indicates a more severe sensitization	Formaldehyde, glutaraldehyde, organic isocyanates and diisocyanates, epoxy resins
Skin Sensitizer	"a chemical that will lead to an allergic response following skin contact."	Category 1, further subdivided into 1A and 1B	hazard than 1B. The sub-categories are not always specified on labels and safety data sheets.	(before hardening), nickel and nickel compounds, organic hydrazine derivatives, diazomethane, ethylenediamine, peroxydisulfate (persulfate) salts

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Regulatory Definition ¹	Subdivisions ²	Details of Hazard
"explosive chemical	Division 1.1	"mass explosion hazard (a mass explosion is one which affects
is capable by chemical		almost the entire quantity present virtually instantaneously)."
	Division 1.2	"projection [projectile] hazard but not a mass explosion
reaction of producing gas	DIVISION 1.2	hazard."
at such a temperature		
and pressure and	5	"fire hazard and either a minor blast hazard or a minor
at such a speed as	Division 1.3	projection hazard or both, but not a mass explosion hazard."
to cause damage to		
the surroundings."		"no significant hazardonly a small hazard in the event
"pyrotechnic chemical	Division 1.4	of ignition or initiation. The effects are largely confined
is a chemical designed		to the package An external fire shall not cause virtually
to produce an effect by		instantaneous explosion of almost the entire contents of the
heat, light, sound, gas or		package."
smoke or a combination		"Very insensitivechemicals which have a mass explosion
of these as the result of	Division 1 F	hazard but are so insensitive that there is very little probability
non-detonative self-	Division 1.5	of initiation or of transition from burning to detonation"
sustaining exothermic		[Note: Substantial hazard, but negligible risk.]
chemical reactions."	Division 1.6	"Extremely insensitive items which do not have a mass explosion hazard"

Explosives (Part 1) - which covers both explosive substances and pyrotechnic materials and devices

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2 From most severe to least severe hazard

Examples of commercially available explosive chemicals are exhibited in the Explosives (Part 2) table.

Explosives (Part 2) - examples of commercially available potentially explosive chemicals

Chemical	Explosive Division	Comments
Ammonium perchlorate	1.1	Quite insensitive and safe under normal lab conditions, but may be an explosion hazard in fire, if heated, or when mixed with other substances.
2,4-Dinitrophenyl- hydrazine (Brady's reagent)	1.1 (when dry)	Not classified as an explosive when sold wetted with \geq 33 % water (classified as Category 1 flammable solid instead). However, is hazardously explosive when dry.
Picric acid (trinitrophenol)	1.1 (when dry)	Not classified as an explosive when sold wetted with ≥35 % water (classified as Category 1 flammable solid instead). However, is hazardously explosive when dry. Picric acid salts may be very dangerously sensitive explosives, and may be formed inadvertently if picric acid is allowed to come into contact with metal surfaces.
Glyoxime	1.1 (when dry)	Flammable solid Category 1 when moistened with $\geq 20 \%$ water; hazardously explosive when dry. Metal complexes may be very sensitive explosives.

Flammable Gases

Category	Expamples	Comments
1	Hydrogen, methane, propane, butane, acetylene, other hydrocarbon gases, hydrogen sulfide	The most common category for flammable gases. Almost all flammable gases are Category 1.
1	Diborane, phosphine, silane, germane	These are all pyrophoric gases, but still classified as Category 1. There is no GHS pyrophoric classification for gases, and safety data sheets for these gases do not say "pyrophoric" in Section 2: <i>Hazard Identification</i> .
2	Ammonia	This is a very uncommon category; most flammable gases fall into Category 1. Ammonia is unusual in only being flammable in a very limited range of concentrations in air (provided the air is not oxygen-enriched). It displays minimal fire risk under most laboratory conditions.

Flammable and Combustible Liquids

See Section 6 Flammable and Combustible Liquids for more details on the OSHA/GHS classification.

Oxidants

GHS Hazard Class	Definition ¹	Category ²	Comments	Examples
Oxidizing Gas	"Any gas which maycause or contribute to the combustion of other material more than air does."	1 (only)		Oxygen, fluorine, chlorine*, nitrous oxide, nitrogen dioxide
Oxidizing	A liquid or solid which may or may not be combustible	1	Category is determined by how rapidly a mixture of oxidant and cellulose combusts under standardized	Perchloric acid (commercial 60-70%), 50% hydrogen peroxide, chromyl chloride, potassium chlorate, chromium trioxide 90% Nitric acid, 29-35%
Liquid Oxidizing Solid	itself, but which may "generally by yielding oxygen, cause, or contribute to, the combustion	2	testing conditions. Note: Liquids which spontaneously ignite cellulose on contact are always	hydrogen peroxide, potassium nitrate, potassium dichromate, potassium permanganate, trichloroisocyanuric acid ³
	of other material."		classified as Category 1, regardless of the rapidity of burning.	70% Nitric acid, lead dioxide

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2 From most severe to least severe hazard

3 Example of an oxidant that is unusually a chlorine donor rather than an oxygen donor

Gases Under Pressure (includes cryogens)

Hazard Class Definition	Groups	Group Description (simplified)	Examples
"gases which are contained in	Compressed Gas	A gas under pressure	Oxygen, nitrogen, argon, helium, carbon monoxide, nitric oxide
a receptacle at a pressure of 200 kPa (29 psi) (gauge*) or more, or which are liquefied or liquefied and	Liquefied Gas	A gas under pressure which, depending on the ambient temperature, may be partially condensed into a liquid within the pressure vessel	Propane, butane, ethylene oxide, sulfur hexafluoride, nitrous oxide, carbon dioxide (in cylinders, not when frozen into dry ice)
	Refrigerated Liquefied Gas	A gas which is condensed into liquid on account of its low temperature	Liquid nitrogen, liquid helium, liquid air
* Gauge pressure means pressure referenced to atmospheric pressure as zero.	Dissolved Gas	A gas which is dissolved into a liquid medium on account of raised pressure	Acetylene (ethyne) (Acetylene cannot be stored in regular cylinders as compressed acetylene is explosive. Acetylene cylinders contain a porous material soaked with acetone into which the acetylene dissolves under pressure)

References: 29 CFR §1910.1200 Appendix B

Self-Reactive Chemicals

Regulatory Definition ¹	Subdivisions ²	Description	Examples
	Туре А	"can detonate or deflagrate rapidly, as packaged"	(Uncommon in labs)
"thermally unstable	Туре В	"as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion"	(Uncommon in labs)
liquid or solid chemicals liable to undergo a strongly exothermic decomposition even without participation	Туре С	"chemical possessing explosive properties[but]as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion"	AIBN (azobisisobutyronitrile, 2,2'-azobis(2- methylpropionitrile), used as an initiator for free- radical polymerization)
of oxygen (air)."	Туре D	[Complex definition. In summary, material shows a "medium" effect when heated under confinement]	(Uncommon in labs)
	Types E-F	[Decreasingly smaller effects on heating under confinement]	(Uncommon in labs)

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2 From most severe to least severe hazard

OSHA/GHS subdivides self-reactive chemicals into seven *Types*, denoted *A*-*G*, as summarized in the table above. Note that although explosives and organic peroxides are capable of exothermic decomposition, under OSHA/GHS regulations, if a substance falls under the Explosive or Organic Peroxide hazard classifications, then those classifications shall be used instead of Self-Reactive Chemical.

Self-Heating Chemicals and Pyrophorics

GHS Hazard Class	Definition ¹	Subdivision ²	Comments	Examples
Self-Heating	"by reaction with air and without energy supply, is liable to self- heat; this chemical differs from a pyrophoric liquid	Category 1	Category determined by standardized test in which a cube of sample is heated	Sodium sulfide (anhydrous) Sodium dithionite (sodium hydrosulfite)
Chemical	or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days)."	Category 2	in air, and by spontaneous ignition temperature in large volumes.	Azodicarboamide
Pyrophoric Liquid	"even in small quantities, is liable to ignite within five minutes after coming into contact with air."	Category 1	Extremely hazardous	n-Butyllithium and t-butyllithium solutions (e.g. in hexane), diethyl zinc
Pyrophoric Solid	"even in small quantities, is liable to ignite within five minutes after coming into contact with air."	Category 1	Extremely hazardous	White phosphorus (also called yellow phosphorus), Raney® Nickel

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2 From most severe to least severe hazard NOTE: There is no hazard class for pyrophoric gases; instead, they are categorized as any other flammable gas. Because pyrophoric gases are generally flammable across wide concentrations in air, it is probable that all pyrophoric gases fall under the classification *Flammable Gas Category 1*. Example: Diborane, phosphine, silane, and germane are all pyrophoric gases, classified as Flammable Gas, Category 1.

Regulatory Definition ¹	Subdivisions ²	Description (simplified)	Examples (evolved gas)
"solid or liquid chemicals which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities."	Category 1	React vigorously with water at ambient temperature to produce a rapid stream of flammable gases (≥10 L gas per kg of chemical per minute) OR Gases have any tendency to spontaneously ignite, either because the reaction produces a lot of heat or because the gas is pyrophoric.	Lithium, sodium, potassium, magnesium ribbon/turnings/ powder, calcium hydride, sodium hydride, lithium aluminum hydride, sodium borohydride (all hydrogen) Calcium carbide (acetylene)
	Category 2	Gas evolution per kg chemicals ≥20 L per hour AND <10 L per minute. No tendency to spontaneous ignition.	Aluminum carbide (methane), calcium silicide (hydrogen, silane), magnesium silicide (hydrogen, silane)
	Category 3	Gas evolution per kg chemicals ≥1 L per hour AND <20 L per hour. No tendency to spontaneous ignition.	(Uncommon)

Chemicals Which, in Contact With Water, Emit Flammable Gases

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Organic Peroxides

Regulatory Definition ¹	Subdivisions ²	Description	Examples (commercially available)
"organic chemical which contains the bivalent -0-0- structure" Also, "Organic peroxides are thermally unstable chemicals, which may undergo exothermic self-accelerating decomposition."	Туре А	"Any organic peroxide which,	(Too unstable to
		as packaged, can detonate	be a normal item
		or deflagrate rapidly"	of commerce.)
	Туре В	"Any organic peroxide possessing explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package"	Benzoyl peroxide (not wetted or diluted)
			(Few Type B peroxides are commercially available)
	Туре С	"Any organic peroxide possessing explosive properties when the chemical as packaged cannot detonate or deflagrate rapidly or undergo a thermal explosion"	Benzoyl peroxide (75%, balance water)
	Type D	Types D - G show progressively less hazardous effects on attempted detonation or heating under confinement.	Lauroyl peroxide, MEK peroxide (2-butanone peroxide; 35% solution in high-boiling organic diluent), 3-chloroperbenzoic acid (MCPBA; ≤77%)
	Туре Е		Di- <i>tert</i> -butyl peroxide
	Туре F		<i>tert</i> -Butyl hydroperoxide, 70% in water
	Туре G		(Uncommon)

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