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Document 14.1

LLNL Chemical Safety Management Program

Recommended for approval by the ES&H Working Group

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New document or new requirements

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- New document
 Major requirement change

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14.1

LLNL Chemical Safety Management Program*

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14.1

LLNL Chemical Safety Management Program

1.0 Introduction

This document describes the Lawrence Livermore National Laboratory (LLNL) Chemical Safety Management Program and identifies other *Environment, Safety and Health (ES&H) Manual* documents that address related topics (see Table 1). This document provides general requirements and an overview for planning the acquisition, safe use, handling, storage, inventory management, and disposal of hazardous chemicals used in laboratory and nonlaboratory areas (shop, maintenance, and production workplaces) at LLNL. See Appendix A for the definitions of “hazardous chemical,” “chemical,” and other terms used in this document.

This document is written for first-line supervisors, work planners, management, staff, and others to integrate ES&H requirements into LLNL work activities. It also serves as a reference to ES&H professionals in providing consistent ES&H guidance for LLNL work. The first-line supervisor plays a key role in chemical safety by developing and communicating safe-work practices to be implemented by workers. The area ES&H Teams, particularly the industrial hygienists, assist the supervisor, workers, and management chain.

The requirements in this document do not apply to LLNL activities conducted at the Nevada Test Site (NTS). LLNL workers at NTS shall contact their ES&H Team for NTS-specific chemical safety requirements.

1.1 Exemption from Requirements for Offices and Similar Workplaces

Places where hazardous chemicals are used and stored in the manner and quantities associated with typical offices are exempt from the requirements in this document, except those listed in Section 3.10. This includes most offices and computer work areas and excludes industrial workplaces, shops, and most laboratories. Examples of hazardous chemicals used in typical office workplaces include 4-fluid-ounce bottles of rubber cement or 19-ounce cans of aerosol glass cleaner. If you have a question as to whether a workplace is exempt, contact the area ES&H Team for determination.

Table 1. ES&H Manual documents related to the LLNL Chemical Safety Management Program*

No.	Title
2.1	Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management
2.2	Managing ES&H for LLNL Work
2.5	Procured Services Subcontractor ES&H Program
3.1	Nonnuclear Safety Analysis Program
3.2	Safety Basis Thresholds
10.1	Occupational Medical Program
10.2	LLNL Health Hazard Communication Program
11.1	Personal Protective Equipment
12.1	Access Control, Safety Signs, Safety Interlocks, and Alarm Systems
12.2	Ventilation
12.3	Evaluation and Control of Facility Airborne Effluents
12.4	Work Enclosures and Local Exhaust Systems for Toxic and Radioactive Materials
12.5	High-Efficiency Particulate Air (HEPA) Filter System Design for LLNL Applications
12.7	Shutdown or Transfer of Facilities, Operations, or Associated Equipment
12.8	Decontamination and Disposition of Process-Contaminated Facilities and Associated Equipment
14.2	LLNL Chemical Hygiene Plan for Laboratories
14.3	Toxic, Corrosive, or Reactive Gases
14.4	Implementation of the Chronic Beryllium Disease Prevention Program Requirements
14.5	Safe Handling of Mercury and Mercury Compounds
14.6	Safe Handling of Fluorine
14.7	Safe Handling of Alkali Metals and Their Reactive Compounds
14.8	Working Safely with Corrosive Chemicals
14.9	Safe Handling of Asbestos-Containing Material During Construction Work
14.10	Safe Handling of Lead and Lead Compounds in General Industry and Construction Operations
14.11	Laser Dyes
14.12	Safe Handling of Carcinogenic Materials
14.13	Pesticide Management
14.14	Management of Polychlorinated Biphenyls
17.1	Explosives
17.2	LLNL Energetic Materials Stability Review Program
18.1	Pressure
18.4	Hydrogen
18.5	Cryogens
21.1	Acquisition, Receipt, Transportation, and Tracking of Hazardous Materials
21.2	Onsite Hazardous Materials Packaging and Transportation Safety Manual
22.1	Emergency Management
22.2	Environmental Emergency Response
22.4	Earthquakes
22.5	Fire
30.1	Waste Minimization and Pollution Prevention
36.1	Hazardous, Radioactive, and Biological Waste Management Requirements
40.1	LLNL Training Program Manual
40.2	Environment, Safety & Health Training and Education

*Other *ES&H Manual* documents will apply, as appropriate.

1.2 Health Hazard Communication and the Chemical Hygiene Plan

The proper use of chemicals is facilitated when workers are informed of possible hazards. Two Work Smart Standards (WSSs) [29 CFR 1910, Subpart Z, "Toxic & Hazardous Substances" (29 CFR 1910.1200 for nonlaboratories and 29 CFR 1910.1450 for laboratories)] require workers to be informed about chemical hazards and are reflected in *ES&H Manual* documents. These standards define "laboratory" in a specific manner and create different training requirements for "laboratory" and "nonlaboratory" work places. "Laboratory" and related terms are defined in Appendix A.

Health hazard communication and other specific chemical safety requirements for laboratories are provided in Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual*. The LLNL program for communicating information on occupational health hazards, including those arising from the use of hazardous chemicals in places other than laboratories, is found in Document 10.2, "LLNL Health Hazard Communication Program," in the *ES&H Manual*.

Other laboratories (e.g., physics, materials processing, or laser laboratories) as well as shops that do not meet all of the requirements of this definition are not considered laboratories in the context of this document and are not expected to comply with the Chemical Hygiene Plan in Document 14.2. However, they shall comply with Document 10.2.

2.0 Hazards

Many chemicals are hazardous because they are toxic, irritating, corrosive, carcinogenic, flammable, pyrophoric, and/or explosive. Chemicals that may be relatively safe when used alone can become very dangerous when mixed with other substances, either in a planned experiment or unintentionally. Therefore, workers who use, store, dispose of, or transport chemicals need to consider the hazards and use appropriate controls and procedures.

3.0 Controls

3.1 Applying the Hierarchy of Controls to Chemical Safety

An important part of chemical safety is controlling worker exposure to hazardous chemicals in the air and exposure through contact with the skin. By doing so, worker-exposure levels will be kept below occupational exposure limits established in relevant standards, and adverse environmental impacts will be prevented by applying the "hierarchy of controls" described in this section.

Hazardous chemicals are controlled using the hierarchy of controls (see Document 2.2, "Managing ES&H for LLNL Work," and Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual*) as a guide. The hierarchy of controls is, in order of preference: (1) elimination of hazards through materials and process design selections; (2) engineering controls to confine, shield, or remove hazards; (3) administrative or procedural controls; and (4) using personal protective equipment (PPE).

3.1.1 Material and Process Design Controls

Material and process design controls include:

- Selecting the safest chemical for a given job [e.g., using a noncarcinogen instead of a carcinogen or using a noncombustible or combustible chemical instead of a flammable chemical (see Appendix A for definitions of "combustible" and "flammable")].
- Using and storing the smallest useful quantities.
- Generating the smallest amount of hazardous waste.

3.1.2 Engineering- and Facility-Related Controls

Engineering- and facility-related controls include:

- Providing engineering controls and suitable facilities to minimize hazards (e.g., enclosure of equipment and transfer lines, using exhaust ventilation, or selecting materials compatible with the chemicals), including exposures to airborne forms of the chemical.
- Using the smallest vessels, apparatus, or equipment practical and safe for a given job.

See Section 3.4 for more information.

3.1.3 Administrative Controls

Some administrative controls [e.g., preparing Integration Work Sheet/Safety Plans (IWSs/SPs)] are required to meet Integrated Safety Management (ISM) requirements during planning phases. Acquisition control, inventory management, safe work practices, label reading, training, maintaining access to Material Safety Data Sheets (MSDSs), and segregating incompatible chemicals are other administrative controls.

Sections 3.2 through 3.3 and 3.5 through 3.9 provide information on procedural controls applicable to chemicals. Training and medical surveillance are considered to be

administrative controls. Section 4.0 provides information on training, and Section 5.0 addresses medical surveillance. Information on labels is found in Document 10.2.

Special first-aid preparations may be beneficial in certain cases (e.g., working with hydrogen fluoride or cyanides). Health Services Department representatives assigned to the ES&H Teams shall provide advice to the Responsible Individual (RI) and other ES&H Team members as to when special first-aid preparations are warranted and provide guidance as to how special first-aid supplies are stored, maintained, and, when necessary, used.

3.1.4 Personal Protective Equipment

Personal Protective Equipment (PPE) controls include using appropriate PPE such as gloves appropriate for the chemicals of interest, coveralls, aprons, indirectly vented goggles, and respirators, per Document 11.1, "Personal Protective Equipment," in the *ES&H Manual*.

3.2 Planning

This section addresses planning required for the safe use of hazardous chemicals. The Hazards Control Department is responsible for supporting RIs, facility management, chemical custodians, and authorizing organizations in project planning and subsequent phases of an activity by:

- Assisting supervisors and workers in maintaining safe-work areas by providing information, through the ES&H Teams, on the hazardous properties of chemicals and relevant regulations.
- Helping RIs identify hazardous chemicals while preparing IWSs, IWS/SPs, or FSPs.
- Recommending methods for controlling and monitoring chemical hazards in the work environment.

3.2.1 Hazard Analysis

The Responsible Individual/work supervisor (both referred to as RI in this document), and workers shall, in conjunction with ES&H personnel, analyze the hazards associated with each chemical work activity. This involves:

- Considering chemical properties that make the chemical hazardous, physical hazards (e.g., flammability or pressure), toxicity, reactivities, and incompatibilities of the chemicals used or created.

- Ensuring that tasks or operations and the chemicals involved are reviewed by an RI, principal investigator, or supervisor in advance of the operation. As needed, the hazards and controls shall be documented in an IWS or IWS/SP.
- Selecting the least hazardous waste disposal and waste minimization options.

Document 2.2 describes how to perform the hazard analysis and document the results following ISM. Documentation for chemical and other work depends upon its Work Authorization Level (WAL). The hazard analysis for work operations that require PPE, particularly respiratory protection, shall be documented using a Hazards Assessment and Control Form (HAC) prepared by the ES&H Team, except where alternatives are permitted in Document 11.1. The HAC can be appended to the IWS or IWS/SP arising from the hazard evaluation/risk assessment described in the preceding text of this section.

3.2.2 Safety Basis Envelope

When a chemical activity is scheduled to take place in a facility under the provisions of Document 2.2, the RI shall consult with facility management to determine the requirements imposed by the facility, including facility specific Safety Basis Envelope (SBE) requirements. The facility management, working with RIs, shall control chemical inventories in accordance with SBE requirements. Safety Basis Envelope requirements are specified in Documents 3.1, "Nonnuclear Safety Basis Program," and 3.2, "Safety Basis Thresholds," in the ES&H Manual. Categorized nuclear facilities are specified in Document 51.1, "Documented Safety Analysis Program Plan," in the *ES&H Manual*.

3.2.3 Waste Minimization and Pollution Prevention for Chemical Management

In practice, many concepts of the pollution prevention hierarchy and the source reduction reuse/recycle treatment methods (See Document 30.1, "Waste Minimization and Pollution Prevention," in the *ES&H Manual* for more detail) parallel the hierarchy of controls for reducing the hazards of chemical use as addressed in Section 3.1. Prior to purchasing chemicals, workers shall ensure that the chemicals can be disposed of.

Using the Least Hazardous Chemical. The first step in using chemicals safely and minimizing chemical waste is to use the least hazardous chemical appropriate for the job whenever possible. Select the least environmentally damaging chemical according to environmental regulations; see Document 30.1. The ES&H Team supporting the relevant organization can provide assistance in selecting alternatives and concur with substitutions made after multiple concerns such as flammability, environmental impact, and toxicity have been considered. Exercise care when balancing environmental and worker protection issues (e.g., a carcinogen should not replace a noncarcinogen to meet pollution prevention objectives), noting that worker safety takes precedence over environmental concerns.

Pollution Prevention Planning. Waste minimization and pollution prevention efforts are most effective when considered during the planning stages of any experiment or job. Choose equipment, chemicals, procedures, and techniques that meet the criteria of the first bullet of Section 3.1.1, to reduce toxicity, improve efficiency of material usage, and minimize the generation of “surplus waste.” Develop, improve, and implement new procedures and techniques that meet the criteria of the second bullet of Section 3.1.1 to improve safety and reduce probability of unexpected contamination.

These measures concurrently reduce pollution and improve safety wherever hazardous chemicals are stored and used, and limit the amount of hazardous chemicals that can become involved in a fire, spill, environmental release, or other contingency. Waste minimization and pollution prevention practices are both environmentally and economically beneficial, because they promote prudent use of materials and reduce costs and administrative difficulties associated with hazardous waste disposal.

Waste Minimization and Pollution Prevention Practices. In addition to planning experiments and jobs to minimize the inventories of hazardous chemicals, other pollution prevention practices can be applied. Experimenters and workers should:

- Share inventories of hazardous chemicals with other workers in the area. This reduces both the duplication of hazardous chemicals and the generation of hazardous waste. Sharing inventories also reduces the amounts of materials that could be involved in a disaster or fire, avoids potential authorization basis concerns, and helps prevent containers from reaching the end of their shelf lives or being discarded as waste.
- Reuse hazardous chemicals whenever possible. Select procedures and equipment that allow hazardous chemicals to be reused whenever practical and safe. For example, mineral acids used to clean new glassware can be reused several times before disposal.
- Transfer surplus hazardous chemicals, if possible, to others at LLNL who can use them before you dispose of them. The Chemical Exchange Warehouse (CHEW) is operated by the Environmental Protection Department's (EPD) Radioactive and Hazardous Waste Management Division (RHWM) to reduce hazardous waste generated at LLNL. The CHEW collects, sorts, and temporarily stores unused and surplus chemicals and advertises their availability to other users (both onsite and offsite), and supplies surplus chemicals free of charge to LLNL requestors.

The benefits of transferring surplus chemicals are two-fold: (1) the chemical recipients can reuse the surplus chemicals from another organization; and (2) the chemical donors do not have to pay for the waste disposal.

Contact the program or facility waste minimization coordinator or, if a waste minimization coordinator has not been appointed for your area, the ES&H Team environmental analyst regarding any questions you may have on implementing waste minimization ideas.

3.2.4 Considerations for Chemical Waste Disposal

Waste chemicals and used chemical solutions produced by LLNL operations can pose a threat to the environment if they are not properly managed. Such wastes are disposed of by RHWM. Before disposing of any chemicals, contact your area ES&H Team environmental analyst or hazardous waste technician for guidance on proper packaging, labeling, and storage requirements. See Document 36.1, "Hazardous, Radioactive, and Biological Waste Management Requirements," in the *ES&H Manual* for an overview of waste types and waste management practices that ensure work is performed safely and according to all applicable regulations and LLNL policies.

Waste generators identify the hazardous chemicals to be disposed of, as required by LLNL's Waste Acceptance Criteria (WAC), in consultation with the area ES&H Team environmental analyst. It is usually expensive and time consuming to analyze an unknown chemical to determine its chemical and radiological composition. The WAC's Internet Address is:

http://www.llnl.gov/es_and_h/wac_rev1/wac_contents.html

3.3 Chemical Acquisition

This section provides requirements and guidelines regarding chemical acquisitions.

3.3.1 Overall LLNL Policy Guidance on Acquisition and Onsite and Offsite Transportation of Chemicals

See Document 21.1, "Acquisition, Receipt, Transportation, and Tracking of Hazardous Materials," in the *ES&H Manual* for LLNL policy on the acquisition of hazardous chemicals and the onsite and offsite transportation of chemicals from LLNL. The steps of the acquisition process are summarized in Figure 1 in Document 21.1, which provides specific requirements and available resources for chemical procurement and for alternatives to purchasing new chemicals.

3.3.2 Chemicals that Require Special Reviews or Approvals

The Hazards Control Department automatically reviews chemical purchases and procurements, including transfers of hazardous or potentially hazardous chemicals within the DOE complex whenever a Technical Release Representative (TRR) places an

order for a chemical. It has one workday in which to review a proposed chemical procurement; otherwise, the procurement proceeds automatically. In addition, there are other special approvals required for certain types or groups of chemicals, as described in the current Controlled Items/Services List (CISL). Contact any TRR, the area ES&H Team, or refer to the following intranet address to obtain the current CISL:

<http://www-r.llnl.gov/pm/trr/html/controlitem.html>

The following chemicals require procurement approval, either by the Hazards Control Department or other organizations. The approval requirements are as follows:

- Alkali metals and their alloys: Hazards Control Department.
- Asbestos: Hazards Control Department and Plant Engineering.
- Beryllium: Hazards Control Department.
- Certain carcinogens and OSHA-regulated chemicals: Hazards Control Department.
- Ethyl alcohol: purchases are processed by the Materials Distribution Division (MDD) Customer Service. Hazards Control Department shall review the purchase but its approval is not required.
- Toxic, corrosive, or reactive gases: Hazards Control Department.
- Narcotics (“Controlled Substances”): Hazards Control Department.
- Precious metals: Precious Metals Control Officer approval is required; Hazards Control Department shall review the purchase.

3.4 Engineering- and Facility-Related Controls

This section addresses the facilities and equipment necessary to adequately control chemical hazards. The RI, working with facility management and the ES&H Team, shall ensure that the following controls are in place before beginning work, when applicable.

3.4.1 Control Ventilation and Facility Effluent Considerations

When required, exhaust ventilation and systems that control facility effluents shall be planned, designed, constructed, installed, and used in accordance with Documents 12.2, “Ventilation”; 12.3, “Evaluation and Control of Facility Airborne Effluents”; 12.4, “Work Enclosures and Local Exhaust Systems for Toxic and Radioactive Materials”; and 12.5, “High-Efficiency Particulate Air (HEPA) Filter System Design for LLNL Applications” in the *ES&H Manual*.

3.4.2 Seismic Bracing

Shelving and cabinets over 5-feet-high located in chemical use and storage areas shall be installed using the Plant Engineering Department's tie-down standard ("Seismic Tiedown for Shelving and Cabinets," PEL-S-13082). Restraining devices (e.g., shelf bars, rods) shall also be used to prevent chemical containers from falling during an earthquake. (See Document 22.4, "Earthquakes," in the *ES&H Manual* for details.)

3.4.3 Safety Showers/Eyewashes

A safety shower/eyewash station shall be installed in locations where any person may be exposed to corrosive or injurious chemicals, and be situated so that they are immediately available in emergencies. All safety shower/eyewash plans and specifications shall be reviewed and approved by the area ES&H Team industrial hygienist before equipment is procured or installed. Appendix B ("Safety Showers/Eyewashes") provides criteria for when safety showers/eyewashes are required, where they shall be placed, and the testing and engineering specifications. To determine if equipment not previously used at LLNL is suitable, purchase and install only one unit of the model before procuring others of that model. The Chemical and Biological Safety Section (CBS) of the Hazards Control Department shall maintain a list of safety shower/eyewash models that have been successfully used at LLNL. Further assistance can also be obtained through your ES&H team.

3.4.4 Chemical Storage Requirements

General engineering and administrative controls for hazardous-chemical storage areas are as follows:

- Provide fresh-air ventilation.
- Clearly label the storage area and each container.
- Store incompatible chemicals separately to prevent accidental mixing (e.g., spills during an earthquake). For example, acids and bases are incompatible, as are flammables and oxidizers. Contact your area ES&H Team for information on segregating and safely storing specific chemicals. Copies of signs that list compatible chemicals by groups and give precautions for storing them are in Appendix C ("Storage Groups for Hazardous Chemicals"). These signs can be posted on the doors of storage cabinets, bulletin boards and so forth.
- If possible, store corrosive liquids such as acids and bases below eye level or on a low shelf.
- Provide compatible secondary containment to hold spills (e.g., trays), particularly for liquids in glass containers.

- Limit, to the minimum necessary, hazard chemical quantities needed for storage and use (See Section 3.2.3 for details.).
- Provide adequate storage space and use appropriate containers.
- Store hazardous chemicals requiring refrigeration in refrigerators or freezers approved for chemical storage, and clearly label them to prevent the storage of food and drinks.
- Observe the safety-based shelf-life limits for chemicals, particularly peroxides and peroxidizable chemicals. (See Section 3.7.3.)
- See Document 22.5, "Fire," in the *ES&H Manual* for storage requirements for flammable liquids. This document covers significant topics such as safe handling of combustible and flammable chemicals, appropriate containers for storage, different storage limits for different classes of flammable or combustible chemicals, and controlling ignition sources.

Responsible Individuals shall ensure that their names are posted on the Hazard Notice Door Sign in any chemical storage area for which they are responsible.

Contact your ES&H Team for more information on the appropriate storage equipment, facilities, and requirements for your area.

3.5 Managing Hazardous Chemical Inventories

Hazardous chemical inventories are managed by following these steps:

- Identify and track hazardous chemicals. ChemTrack is the primary chemical tracking tool. See Section 3.5.1.
- Control quantities of hazardous chemicals. An important part of inventory control is determining when to dispose of hazardous chemicals, which can be done based on predetermined age, testing procedures, or upon observation of an unsatisfactory condition. See Section 3.5.2.
- Conduct reviews of hazardous chemicals in use and in storage areas periodically to ensure age and testing procedures are being fulfilled, and to identify cases where containers or their contents show evidence of deterioration. See Sections 3.5.3 and 3.5.4.

The authorizing organization is responsible for implementing these steps, except where specified in the text of this section. In addition, some chemicals can become hazardous with the passage of time, most notably chemicals that form peroxides. These are addressed in Sections 3.5.5 and 3.7.3. Legacy chemical concerns associated with the departure of workers or the decommissioning of a facility are addressed in Sections 3.5.6.

3.5.1 Chemical Tracking and Inventory Management Functions

ChemTrack is the primary tool for tracking hazardous chemicals, although local inventory systems may be needed to address hazardous chemical use not captured by ChemTrack. To this end, chemical custodians shall:

- Ensure that ChemTrack bar code labels are on all primary and certain secondary containers (see Appendix A for the definition of a “secondary container”) when required. Contact your ES&H Team for guidance on when to bar code label secondary containers.
- Update or notify ChemTrack (Ext. 4-4404) when obtaining either new chemicals or items to be entered into ChemTrack.
- Update or notify ChemTrack when disposing of bar coded chemical containers or transferring them to a non-LLNL location. This can be done by:
 - Accessing the ChemTrack Home Page at:
<http://chemtrack.llnl.gov/>
and clicking on Update Inventory.
 - Alternatively, remove the lower half of the bar code, affix it to a ChemTrack Disposal/Transfer Form, and mail the form to the ChemTrack Group (L-621).
- Comply with the facility’s chemical inventory procedures.
- Working with facility management and RIs, ensure that hazardous chemical inventories are compiled and annually updated for both laboratory and nonlaboratory areas as part of the annual ChemTrack inventory and reconciliation process.
- Ensure that current, accurate information is entered into ChemTrack to facilitate informed decision making by the authorizing organization decisions concerning retaining, testing/treating, or disposing of stored chemicals per Section 3.5.5.

The ChemTrack Operations Group shall provide assistance with chemical inventories, and also maintains the Laboratory’s MSDS database, the Chemical Safety databases, and ChemTrack/MSDS Hotline (extension 4-4404). ChemTrack responsibilities are defined in Document 21.1.

3.5.2 Controlling Quantities of Hazardous Chemicals

Authorizing organizations shall:

- Establish controls for hazardous chemical inventories based on quality control and program considerations.

- Manage chemical inventories and ensure that hazardous chemical inventories are limited to amounts needed to meet operational requirements. This shall be done by evaluating the:
 - Amount of a hazardous chemical in inventory,
 - Use,
 - Age (e.g., if older materials are in use or reasonably could be used, if the containers are deteriorating, or if other changes listed in section 3.5.4 are evident), and
 - Safety or suitability of the chemicals for use.
- Ensure that hazardous chemicals are procured and stored consistent with program, safety, and waste minimization objectives (the LLNL Waste Minimization Program and how to minimize the quantities of chemicals in storage or use are described in Section 3.2.3).

Chemical custodians shall ensure that inventories of chemicals that are not being used (“stockpiles”) are reviewed annually to assess ongoing need (based on safety and/or quality control considerations). The chemical custodian or designee shall also evaluate the status of hazardous chemicals being stored (e.g., use, age, condition of storage container) on an ongoing basis to guide decisions about retaining or removing chemicals in an inventory.

3.5.3 Inspections

A visual periodic examination of stored hazardous chemicals is important for safety and decision making on continuing to store or dispose of chemicals. General requirements for evaluating hazardous chemical storage follow in this section.

Chemical Custodian Reviews. Chemical custodians shall ensure that their hazardous chemicals, including those on or in shelves and cabinets used to store chemicals, are periodically reviewed. A review frequency may be determined by the authorizing organization as appropriate. These reviews can be informal evaluations used to identify:

- Incompatible chemicals.
- Out-of-date chemicals.
- Chemicals no longer in use.
- Problem indicators listed in Section 3.5.4.

Hazards Control Department Inspections. The area ES&H Teams shall periodically check hazardous chemicals in accordance with Chemical/Biological Safety Discipline Action Plan Item 30, “Chemical Storage.”

The chemical custodian and Hazards Control Department inspection activities can be coordinated.

3.5.4 Visible Changes Indicating a Chemical is Dangerous or Ready for Disposal

Some visible changes may indicate a chemical presents an imminent danger.

Contact the RI or, if the RI or other knowledgeable person is not available, call the Fire Department (dial 911, or, if using a cell phone or calling from offsite, dial 1 (925) 447-6880) if any of the following are found:

- Evidence of material peroxidization, such as
 - Exterior crystal growth.
 - Layering of liquids.
 - Discoloration.
- Bulging or overpressurization.
- Any other reaction that could potentially cause container handling to be extremely hazardous. This condition may have been observed, or an individual may have reason to believe it might have occurred.

These visible changes may indicate a chemical is ready for disposal:

- Slightly cloudy liquids.
- Change in chemical color.
- Spotting on solid chemicals.
- Caking of anhydrous chemicals (evidence of reaction with moisture).
- Presence of precipitates or particulates in liquids, or of liquid in solids.
- Container damage and age-related effects, such as
 - Signs of corrosion.
 - Cracking.
 - Changing shape or color.
 - Fading or deteriorating labels, labels falling off, or missing labels.
- Missing, deteriorating, or broken caps.

3.5.5 Stability of Hazardous Chemicals in Storage

Chemicals can become hazardous with the passage of time. At this time, the only groups of chemicals assessed for age-related hazards are the organic peroxides, peroxidizable compounds, explosives, and certain alkali metal compounds, although other chemicals

exist that can become hazardous with the passage of time. Age limits have been set to minimize these hazards associated with peroxidizable chemicals (see Section 3.7.3). Age limits have also been set for toxic, corrosive, and reactive gases for a mixture of safety- and quality-related reasons.

Information on specific groups of materials that pose age-related hazards can be found in the *ES&H Manual* as follows:

- Storage and age limits of explosives: Documents 17.1, "Explosives," and 17.2, "LLNL Energetic Materials Stability Review Program."
- Age limits for toxic and reactive gases: Document 14.3, "Toxic, Corrosive, or Reactive Gases."
- Age-related hazards of peroxide and superoxide compounds of alkali metals: Document 14.7, "Safe Handling of Alkali Metals and Their Reactive Compounds."

A list of specific peroxidizable chemicals can be obtained by going to the ChemTrack home page, clicking on the "Reports" button to the left, then clicking on the ES&H button, logging in and then entering the type of report sought (e.g., "LLNL peroxidizables").

For the chemicals described in this section, the chemical custodian shall ensure that:

- Those nearing the ends of their safety- or quality-based age limits are evaluated to determine if they are still useful and test them, if practical.
- Those at the end of their shelf lives, as evident by visible signs described in Section 3.5.4 or other means, are promptly sent off for disposal.

Chemical custodians, working with RIs, shall also ensure that chemicals are periodically, but not less than annually, evaluated to determine if they are to be retained or sent for disposal.

3.5.6 Chemicals Used by Departing Workers

Responsible Individuals shall ensure that workers moving out of a lab or shop either dispose of hazardous chemicals for which they are responsible as hazardous waste, or transfer unused or partially used hazardous chemicals to others before leaving. Chemicals that are still usable but no longer needed should be recycled through the CHEW, if it is safe to do so. See Documents 12.7, "Shutdown or Transfer of Facilities, Operations or Associated Equipment," and 12.8, "Decontamination and Disposition of Process-Contaminated Facilities and Associated Equipment," in the *ES&H Manual* for requirements relating to chemicals in an activity that is being discontinued and for facilities being demolished or entering inactive status, respectively.

3.6 Labeling and Signage

This section addresses labeling and signage requirements.

3.6.1 Labeling

Proper labeling of hazardous chemicals warns users of hazards and helps ensure that eventual disposal is carried out properly. Workers shall read the label of any chemical they are using for the first time to determine if it is hazardous, what the hazards are, and to identify appropriate controls.

Responsible Individuals shall ensure that the labeling requirements of Documents 10.2 regarding labeling chemical containers, and requirements of Document 14.2 regarding labeling chemicals in laboratories are met.

3.6.2 Signage

Responsible Individuals shall ensure that areas where chemicals are used and stored are posted with the appropriate signs, and that Documents 10.2 and 14.2 requirements for signs are met. Signs for specific chemicals or chemical classes are noted in the chemical-specific documents in Part 14 of the *ES&H Manual*.

For both laboratory and nonlaboratory areas, the RI shall indicate, or arrange to indicate, the hazards present by generic categories (e.g., corrosive, flammable, oxidizer, reducing agent, explosive, highly toxic, and reactive) on the Hazard Notice Door Signs, as specified in Document 10.2 (provide link to Document 10.2, Figure B-1).

3.7 Chemical Handling

This section discusses the requirements for handling solid and liquid chemicals, gases, peroxides, and peroxidizable materials.

3.7.1 Precautions for Handling Hazardous Solid and Liquid Chemicals

Workers shall:

- Keep the work area as clean and orderly as the operation will allow.
- Use exhaust ventilation (e.g., laboratory hoods, flexible duct exhausts, lateral exhaust hoods) to minimize personnel exposures to air contaminants when performing operations that can generate air contaminants (e.g., aerosols and gases/vapors), unless the ES&H Team has evaluated the work and approved performing the work without these controls. See Documents 12.2, 12.3, 12.4, and 12.5 for planning and using exhaust ventilation.

- Use protective equipment such as safety shields and enclosures, and lower the sashes of laboratory hoods so the face is protected from spatter and splinters. Enclosures also maximize protection provided by exhaust ventilation.
- Do not eat, drink, smoke, or apply cosmetics, or store these items in an area where hazardous chemicals are handled.
- Wash hands immediately after handling all chemicals, regardless of whether gloves have been worn.
- Use mechanical aids for all pipetting procedures (never mouth pipette).
- Evaluate hazards and identify proper containers and controls before transferring or dispensing chemicals from manufacturer-supplied chemical containers.
- Provide secondary containment for retaining spills.
- Limit the volume of volatile or flammable chemicals, preferably to the amount required for daily operations.
- Follow the requirements in Document 18.1, "Pressure," in the *ES&H Manual* if the operating system is used under pressure or if it can generate pressure.
- Keep hazardous chemicals out of offices.
- Use the required PPE as specified in Document 11.1, "Personal Protective Equipment" in the *ES&H Manual*.

To the extent feasible, workers should observe the following guidelines:

- Isolate hazardous operations by performing them in separate rooms and limit the number of workers involved.
- Assure that safe and convenient lavatory facilities are available.
- Do not use solvents for personal cleanup.

Facility management shall ensure that break areas are not located where hazardous chemicals are handled or stored.

Newly synthesized chemicals, of which the toxicity, chemical, and physical properties have not been fully characterized or studied, shall be considered hazardous by all workers. Therefore, use only a small quantity of these chemicals to minimize both the effects of unexpected reactions and the potential for toxicity resulting from exposure.

The Hazards Control Department is responsible for conducting the workplace chemical hazard monitoring. This monitoring measures or otherwise evaluates the extent of an employee's exposure to hazardous chemicals and assesses compliance with regulations

and documenting the monitoring results. This activity is described in more detail in Document 10.2.

3.7.2 Handling Chemically-Hazardous Gases

Workers who handle gases shall be familiar with their properties and health effects, and exercise care in handling them. Gases may be corrosive, flammable, toxic, radioactive (e.g., tritium), or explosively reactive when they come into contact with other chemicals (including air, water, or nonhazardous chemicals).

Responsible Individuals shall be familiar with Document 18.1, "Pressure"; Document 18.5, "Cryogen"; and 14.3, "Toxic, Corrosive, or Reactive Gases" in the *ES&H Manual*. For detailed information on specific gases, especially those that are toxic, see:

- *Matheson Gas Data Book*.
- *Fire Protection Guide on Hazardous Materials* (National Fire Protection Association).
- The area ES&H Team.

3.7.3 Peroxidizable Chemicals

Workers shall implement the requirements specified in LLNL's *Standard for Storing and Using Peroxidizable Organic Chemicals* (UCRL-AR-133218, Rev. 1), when working with peroxides or peroxidizable chemicals. This standard contains requirements for special labeling and periodic testing of contents and can be found at the following intranet address:

<http://www-r.llnl.gov/ibis/lof/documents/pdf/235534.pdf>

Peroxidizable chemicals form unstable peroxides when they are in the presence of oxygen, stored for long periods of time, or exposed to light. Peroxides may also be formed even if preservatives or inhibitors are added to slow down the peroxidization process. These chemicals may explode when disturbed, when the caps are removed from their containers, or when they are used. Thus, these chemicals shall be protected from exposure to light, heat, and air. The chemicals indicated as High Hazard in Table 2 shall be stored under inert gas, while the remaining chemicals listed in Table 2 are stored in sealed containers.

In addition, workers shall store peroxidizable chemicals in accordance with the time limitations specified in Table 2. Old containers of peroxide-forming chemicals improperly stored are most likely to be dangerous, especially if discoloration, crystallization, or layering is observed. If you believe that dangerous levels of peroxides may be present in a container (e.g., observing visible signs of deterioration as listed in

Section 3.5.3), immediately contact the Fire Department [dial 911 or, if using a cellular phone or dialing from offsite, 1 (925) 447-6880]. The Fire Department manages the response until it is determined that the container does not pose an imminent hazard.

Peroxidizable chemicals are the best understood of the chemicals with age-related hazards. However, age has played a role in incidents involving other types of chemicals. Chemical/Biological Safety (CBS) shall set hazardous chemical age-related limits based on known safety considerations using available information, including consultation with knowledgeable people (e.g., chemists performing research using such chemicals). Most chemicals will not be affected by safety-related age limits.

3.8 Hazardous Chemical Spills and Emergency Response

This section discusses steps to take in the event of a hazardous chemical spill or exposure. Spill control kits and equipment are commercially available for use in a broad range of situations. Appropriate equipment should be staged near where spills are possible and shall be staged by RIs working with the ES&H Teams and facility managements when required by *ES&H Manual* documents. Workplace-specific procedures should be developed for spill response and shall be developed when specified in *ES&H Manual* documents. RIs shall record spill cleanup procedures in FSPs, IWSs/SPs, or other appropriate safety documentation. Section 4.4 addresses spill cleanup and spill response training.

Table 2. Common chemicals that form explosive levels of peroxides and their storage limits.^a

Peroxidizable chemicals		
High hazard: autopolymerizes (24 hr-12 month storage under inert gas) ^{b,c}	Medium hazard: may become heat or shock sensitive on the shelf (3-month storage)	Potentially hazardous: may form heat or shock sensitive residue on evaporation or distillation ^{d,b} (12-month storage)
Acrylic acid Acrylonitrile ^{e,f} Butadiene ^{e,g} Chloroprene Chlorotrifluoroethylene Methyl methacrylate Styrene Tetrafluoroethylene Vinyl acetate Vinyl acetylene Vinyl chloride ^e Vinyl pyridine	Butadiene ^{c,e} Chloroprene ^f Divinyl acetylene Isopropyl ether Potassium metal Sodium amide Tetrafluoroethylene ^f Vinylidene chloride	Acetal Acetaldehyde Benzyl alcohol 2-Butanol Cyclohexanol 2-Cyclohexene-1-ol Cumene Decahydronaphthalene Diacetylene Dicyclopentadiene Diethyl ether Diethylene glycol dimethyl ether Dioxanes Ethylene glycol dimethyl ether 4-Heptanol Methyl acetylene Methyl isobutyl ketone 3-Methyl-1-butanol Methylcyclopentane 2-Pentanol 4-Pentene-1-ol 1-Phenylethanol 2-Phenylethanol 2-Propanol Tetrahydrofuran Tetrahydronaphthalene Vinyl ethers Other secondary alcohols

a As listed in UCRL-AR-133218, Rev.1. Other chemicals than those listed may form peroxides. Contact your ES&H Team for further information.

b Uninhibited chemicals are to be stored for no more than 24 hours. Inhibited chemicals can be stored for up to 12 months.

c When stored as an inhibited liquid monomer.

d May become unstable if concentrated.

e OSHA-regulated carcinogen.

f When stored as a liquid monomer.

g When stored as a gas.

3.8.1 Emergency Response

In the event of a hazardous chemical exposure to the eyes, proceed to the nearest eyewash and flush eyes for at least fifteen minutes. In the event of a serious exposure to the skin, proceed to the nearest shower and flush skin for at least five minutes. Call the Fire Department [911, or if using a cellular phone or dialing from offsite, 1 (925) 447-6880 for cellular phones] for assistance with any significant chemical exposure. When in doubt, call the emergency numbers listed above.

The Health Services Department shall evaluate all employees who have had a chemical exposure that exceeds or may have exceeded applicable occupational exposure limits.

3.8.2 Hazardous Chemical Spill Response

Workers shall not clean up spills unless they are familiar with the material involved and the associated hazards. Small hazardous chemical spills can usually be cleaned up safely by trained workers. A small spill has all of these characteristics:

- The nature and potential hazard of material/waste are known.
- The incident results in no injury, or just minor injury requiring simple first aid.
- The release presents no actual or potential threat to human health, the environment, or property.

Call the Fire Department immediately following large incidents [911 or, if using a cellular phone or dialing from offsite, 1 (925) 447-6880]. An incident is considered "large" when any of the following apply:

- Area personnel are unfamiliar with the hazards of the spilled material.
- An accident or spill involving hazardous material results in personnel injury.
- Hazardous material is released to the sewer system.
- The spilled material exceeds the amount two workers can handle in one hour or if additional assistance or supplies are needed to contain and clean up the material.
- The released material or waste cannot be identified.
- Material or waste is released and migrates into a storm drain or sewer.
- A fire or explosion occurs.
- A building or facility is evacuated.

When in doubt, call the emergency numbers listed above. The LLNL Fire Department operates a HAZMAT (hazardous material) truck to respond to larger spills.

General information on hazardous waste spills can be found in Document 22.2, "Environmental Emergency Response," in the *ES&H Manual*.

Environmental regulations and DOE orders have reporting requirements for hazardous chemical spills above certain amounts, or when there is a potential for harm to individuals, property, or the environment. After the initial cleanup or response, the RI shall report all hazardous chemical spills to the area ES&H Team and facility management, to determine if there is a need for follow-up actions such as medical follow up, swipe sampling, and so forth. During off-hours, contact the Environmental Duty Officer through the Fire Department dispatcher at 911 or 1 (925) 447-6880.

3.9 The Material Safety Data Sheet

This section describes MSDSs and how they shall be prepared for LLNL-developed chemicals.

3.9.1 Availability

By law, chemical manufacturers and importers must prepare MSDSs for their products. Each MSDS provides information on the physical, chemical, and toxicological properties of a particular chemical, and on the recommended handling procedures.

Responsible Individuals shall ensure that MSDSs are readily available to the workers in the work area throughout each work shift. This should be done electronically using the ChemTrack MSDS collection. Paper MSDS collections should not be maintained unless there is a specific reason to do so (e.g., historical information or for use in places where ready access to electronic MSDSs can not be provided). See Document 10.2 for information on how MSDSs are obtained and used at LLNL and Document 21.1 for a description of the ChemTrack MSDS system.

When RIs or ChemTrack custodians receive MSDSs directly from vendors, they shall send a copy to the ChemTrack MSDS coordinator, including the name of the chemical custodian, ChemTrack bar code number, and the building and room number where the material is located. A copy of the MSDS should also be faxed to ChemTrack to ensure they received the MSDS.

3.9.2 MSDSs for LLNL-Developed Chemicals

When LLNL Must Develop MSDSs. Whenever a new chemical is synthesized or formulated, the RI shall ensure that an MSDS is prepared before the chemical is used for non-research applications (e.g., the chemical is to be used as an adhesive, paint, explosive).

MSDSs do not need to be prepared if small quantities are to be used for research purposes. MSDSs are not required in the following circumstances:

- Onsite in laboratories covered by Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual*. (See Section 3.2.3.)
- Offsite in the United States if the chemical is sent to a laboratory covered by a Chemical Hygiene Plan (CHP) prepared in accordance with 29 CFR 1910.1450 or state OSHA equivalent. The chemical shall not be sent to another organization without an MSDS, unless that organization advises the RI that it will use the LLNL chemical under its CHP.
- Outside of the United States. Situations involving chemicals sent outside of the United States shall be addressed on a case-by-case basis by the RI, the ES&H Team industrial hygienist supporting the RI, and the Chemical/Biological Safety Section of the Hazards Control Department (CBS). However, the review may determine that an MSDS or modified MSDS is the best tool for informing a foreign user of the hazards associated with the chemical.

Hazardous wastes are exempted from the requirement to prepare an MSDS.

An LLNL-generated MSDS shall be updated at the request of the RI when a worker becomes aware of significant information regarding the hazards of a chemical or of ways to protect against a chemical's hazards. In these cases, the worker shall notify the MSDS generator, who are responsible for updating the MSDS within 3 months.

Process for Developing MSDSs at LLNL. If an MSDS is required for a LLNL-developed chemical, the RI shall ensure that an MSDS is prepared before the new chemical is sent to the user. When a chemical or a mixture of existing chemicals is put into routine commercial, military, or public use, toxicological screening shall be performed based on the judgment of the RI, the ES&H Team industrial hygienist, and CBS. Instructions for preparing MSDSs for these chemicals are given in Appendix D. The ES&H Team industrial hygienist shall coordinate the preparation and updates of these MSDSs while working with the RI or his/her designee, and serve as the contact point for outside organizations as requested. The CBS Section shall review new or updated MSDSs. The RI shall forward a copy of LLNL-prepared MSDSs to the MSDS coordinator at L-621.

3.10 Requirements for Offices and Similar Workplaces

Places where hazardous chemicals are used and stored only in the manner and quantities associated with typical offices shall follow the requirements of this section. The chemical safety briefing given during Hazards Control Department Course HS0001, "New Staff Safety Orientation," is sufficient to meet the chemical safety training requirements for workers and supervisors in these areas. Any use of hazardous

chemicals in these areas not covered under this exemption (e.g., setting up a graphic arts activity in an office area) shall be brought to the attention of the area ES&H Team by the area's RI prior to beginning work.

Chemical safety requirements for offices and similar workplaces are:

- Workers shall read the labels of all products prior to using for the first time, to determine if the products are hazardous and to identify appropriate precautions.
- Workers shall store and use chemicals in accordance with manufacturers' instructions or in a manner approved by both the area ES&H Team and facility management.
- The RI shall ensure that flammable or combustible chemicals are handled in accordance with Document 22.5. If flammable materials or combustible liquids are being used more intensively than in the incidental manner associated with office use, contact the area ES&H Team.
- The RI shall ensure that ChemTrack requirements of Document 21.1 are met. The area ES&H Team shall provide advice to RIs as needed.

4.0 Training

Authorizing organizations shall ensure that workers receive the training that enables them to safely handle and use hazardous chemicals. This includes providing them with information and training on hazardous substances in their work area at the time of their initial assignment, and whenever a new hazard is introduced into their work area.

4.1 Chemical Hazard Training

All workers who handle hazardous chemicals are informed of their hazards and are trained in safe handling techniques. The training addresses physical safety and chemical and toxicity hazards. Chemical-safety training requirements depend upon whether or not the activity is conducted in a laboratory, as defined in Appendix A of this document and are defined by the WSSs addressed in Document 10.2 (for non-laboratories) and Document 14.2 (for laboratories).

The formal LTRAIN courses that provide the core of this training are

- HS4240-W, "Chemical Safety."
- HS4246-W, "Laboratory Safety."

- HS4050-W, "Health Hazards Communication for Supervisors."
- HS4052-W, "Health Hazards Communication for Supervisors of Chemical Labs."

The RI shall take the appropriate supervisor training (i.e., either HS4050-W or HS4052-W) and identify the appropriate training for the workers, considering their work activities and the authorizing organization's Organizational Training Requirements (OTRs). Other formal HS courses are listed in Document 10.2. Workers are responsible for taking the chemical safety training identified by the RI.

This training is conducted and documented in accordance with Documents 40.1, "LLNL Training Program Manual," and 40.2, "Environment, Safety, & Health Training and Education," in the *ES&H Manual* and the training plan for each authorizing organization. The RI is responsible for ensuring that appropriate training is provided for identified hazards and their associated controls for activities covered by IWS/SPs and FSPs.

4.2 Training in the Use of Safety Showers and Eyewashes.

Requirements for training safety showers/eyewash users are found in Document 10.2 for nonlaboratory situations, and Document 14.2 for laboratory situations. The RI shall provide or arrange with the area ES&H Team to provide training on the proper use of emergency safety shower/eyewash equipment located in their areas.

4.3 Training for Waste Generators

Hazardous waste generators and waste handlers attend hazardous waste generator training as required by Document 36.1, "Hazardous, Radioactive, and Biological Waste Management Requirements," in the *ES&H Manual*.

4.4 Training in Spill Cleanup

The RI shall determine what constitutes appropriate worker training for cleaning up small spills and responding to larger spills and arrange to deliver that training. The ES&H Team shall provide assistance. Workers who enter an area in response to a chemical spill, but are not assigned to the responding organization (e.g., Health & Safety Technicians, Hazardous Waste Technicians) shall receive emergency-responder training. The organization providing spill-response workers shall determine the training they need and ensure the training is provided.

5.0 Medical Surveillance

The Health Services Department conducts medical surveillance as necessary for specific chemical exposures, as well as providing medical services for chemical exposure incidents when needed. Consult the ES&H Team to obtain guidance concerning appropriate medical surveillance. Specific details on the Occupational Medical Program are available in Document 10.1, "Occupational Medical Program," in the *ES&H Manual*.

6.0 Responsibilities

This section lists the responsibilities of individuals who work with hazardous chemicals. All workers and organizations shall refer to Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual* for a list of general responsibilities.

6.1 Workers

Workers shall:

- Ensure that chemicals can be disposed of prior to purchasing them, per Section 3.2.3.
- Read the labels of chemicals they are using for the first time, per Section 3.6.1. This applies to workers in all work locations, including offices.
- Keep the work area as clean and orderly as the operation will allow, per Section 3.7.1.
- Use exhaust ventilation (e.g., laboratory hoods, flexible duct exhausts, lateral exhaust hoods) to minimize personnel exposures to air contaminants when performing operations in which they can be generated, unless the ES&H Team has evaluated the work and approved performing the work without these controls, per Section 3.7.1.
- Use protective equipment such as safety shields and enclosures, and lower the sashes of laboratory hoods so the face is protected from spatter and splinters, per Section 3.7.1.
- Not eat, drink, smoke, or apply cosmetics, or store these items in an area where hazardous chemicals are handled, per Section 3.7.1.
- Wash hands immediately after handling all chemicals, regardless of whether gloves have been worn, per Section 3.7.1.

- Use mechanical aids for all pipetting procedures (never mouth pipette), per Section 3.7.1.
- Evaluate hazards and identify proper containers and controls before transferring or dispensing chemicals from manufacturer-supplied chemical containers, per Section 3.7.1.
- Provide secondary containment for retaining spills, per Section 3.7.1.
- Limit the volume of volatile or flammable chemicals, preferably to the amount required for daily operations, per Section 3.7.1.
- Follow the requirements in Document 18.1, "Pressure," in the *ES&H Manual*, if the operating system is used under pressure, or if it can generate pressure, per Section 3.7.1.
- Keep hazardous chemicals out of offices, per Section 3.7.1.
- Use the required PPE as specified in Document 11.1, per Section 3.7.1.
- Consider newly synthesized materials as hazardous until the toxicity, chemical, and physical properties have been fully characterized, per Section 3.7.1.
- Be familiar with chemically-hazardous gas properties and their health effects, and exercise care in handling them, per Section 3.7.2.
- Implement the requirements specified in LLNL's *Standard for Storing and Using Peroxidizable Organic Chemicals* (UCRL-AR-133218, Rev. 1) when working with peroxides or peroxidizable chemicals, and store them in accordance with the time limitations specified in Table 2, per Section 3.7.3.
- Protect peroxidizable chemicals from exposure to light, heat, and air. Store the chemicals indicated as High Hazards in Table 2 under inert gas, and the remaining chemicals shown in Table 2 in sealed containers, per Section 3.7.3.
- Store peroxidizable chemicals in accordance with the time limitations specified in Table 2, per Section 3.7.3.
- Avoid cleaning up spills, unless familiar with the material involved and the associated hazards, and call the Fire Department immediately following large incidents, per Section 3.8.2.
- Notify the generator of an LLNL-developed MSDS when becoming aware of significant safety-related information on a chemical hazard, per Section 3.9.1.
- Store and use office-area chemicals in accordance with manufacturers' instructions or in a manner approved by both the area ES&H Team and facility management, per Section 3.10.

- Take the chemical safety training identified by the RI, per Section 4.1.

6.2 Responsible Individual/Work Supervisor

The Responsible Individual/work supervisor (RI) shall:

- Analyze, in conjunction with ES&H personnel, the hazards associated with each chemical work activity, per Section 3.2.1.
- Consult with facility management to determine the requirements imposed by the facility, including facility-specific SBE requirements, per Section 3.2.2.
- Ensure that, when applicable, engineering and administrative controls and PPE needed for handling chemicals are in place as specified in the text of Section 3.4.
- Ensure that their names are posted on the Hazard Notice Door Sign in any chemical storage area for which they are responsible, per Section 3.4.4.
- Ensure that workers moving out of a lab or shop either dispose of hazardous chemicals for which they are responsible as hazardous waste, or transfer unused or partially used hazardous chemicals to others before leaving, per Section 3.5.6.
- Ensure that the labeling requirements are met, per Section 3.6.2.
- Indicate or arrange to indicate the hazards present in an area by generic categories on the Hazard Notice Door Sign, per Section 3.6.2.
- Be familiar with Documents 18.1, "Pressure"; 18.5, "Cryogenics"; and 14.3, "Toxic, Corrosive, and Reactive Gases" in the *ES&H Manual* when appropriate, per Section 3.7.2.
- Working with the ES&H Teams and facility managements, stage spill-response equipment when required by *ES&H Manual* documents, per Section 3.8.
- Record spill-cleanup procedures in FSPs, IWSs/SPs, or other appropriate safety documentation, per Section 3.8.
- Report all hazardous chemical spills, after the initial cleanup or response, to the area ES&H Team and facility management, per Section 3.8.2.
- Ensure that MSDSs are readily available to the workers in the work area throughout each work shift, and send copies of MSDSs received directly from vendors to ChemTrack, per Section 3.9.1.
- Ensure that, under circumstances described in Section 3.9.2, an MSDS is prepared for an LLNL-developed chemical before it is sent to the user.

- Working with the ES&H Team, determine when a chemical or mixture of existing chemicals needs toxicological screening if the chemical will be put into routine commercial, military, or public use, per Section 3.9.2.
- Forward a copy of an LLNL-prepared MSDSs to the ChemTrack MSDS coordinator, per Section 3.9.2.
- Bring to the ES&H Team's attention any use of hazardous chemicals in office areas not covered under the office-area exemption (Section 1.1) of this document (e.g., setting up a graphic arts activity in an office area) prior to beginning work, per Section 3.10.
- Ensure that flammable or combustible chemicals in office areas are handled in accordance with Document 22.5 and that ChemTrack requirements of Document 21.1 are met for chemicals in office areas, with ES&H Team assistance as needed, per Section 3.10.
- Take the appropriate supervisor training and identify the appropriate training for the workers, per Section 4.1.
- Ensure appropriate training is provided for identified hazards and their associated controls for activities covered by IWS/SPs and FSPs, per Section 4.1.
- Provide, or arrange with the area ES&H Team to provide, training on the proper use of emergency safety shower/eyewash equipment located in their areas, per Section 4.2.
- Determine what constitutes appropriate worker training for cleaning up small spills and responding to larger spills and arrange to deliver that training, per Section 4.3.

6.3 Chemical Custodian

The chemical custodian shall:

- Ensure that ChemTrack bar code labels are on all primary and certain secondary containers, per Section 3.5.1.
- Update or notify ChemTrack when obtaining either new chemicals, or items to be entered in ChemTrack, per Section 3.5.1.
- Update or notify ChemTrack when disposing of bar coded chemical containers or transferring them to a non-LLNL location, per Section 3.5.1.
- Ensure that hazardous-chemical inventories are compiled and annually updated for both laboratory and nonlaboratory areas as part of the annual ChemTrack inventory and reconciliation process, per Section 3.5.1.

- Comply with the facility's chemical inventory procedures, per Section 3.5.1.
- Working with facility management and the RIs, ensure that hazardous chemical inventories are compiled and annually updated for both laboratory and nonlaboratory areas as part of the annual ChemTrack inventory and reconciliation process, per Section 3.5.1.
- Ensure that accurate information is entered into ChemTrack, per Sections 3.5.1 and 3.5.5.
- Ensure that inventories of chemicals not being used ("stockpiles") are reviewed annually to assess ongoing need (based on safety and/or quality control considerations), per Section 3.5.2.
- Evaluate the status of hazardous chemicals being stored (e.g., use, age, condition of storage container) on an ongoing basis, to guide decisions about retaining or removing chemicals in an inventory, per Section 3.5.2.
- Ensure that hazardous chemicals are periodically, but not less than annually, reviewed to identify incompatible chemicals, out-of-date chemicals, chemicals no longer in use, and problem indicators listed in Section 3.5.4, per Section 3.5.3.
- Ensure that chemicals nearing the ends of their safety- or quality-based age limits are evaluated to determine if they are still useful and test them, if practical, per Section 3.5.5.
- Ensuring that chemicals at the end of their shelf lives, as evident by visible signs described in Section 3.5.4 or other means, are promptly sent off for disposal, per Section 3.5.5.
- Ensure that chemicals are periodically, but not less than annually, evaluated to determine if they are to be retained or sent for disposal, per Section 3.5.5.

6.4 Facility Management

The facility management shall:

- Working with RIs, control chemical inventories in accordance with SBE requirements, per Section 3.2.2.
- Ensure that break areas are not located where hazardous chemicals are handled or stored, per Section 3.7.1.
- Working with RIs and the ES&H Teams, identify where safety showers/eyewashes are needed and ensure that they are installed in a manner and location as specified in Appendix B.

- Do the following when a safety shower/eyewash is no longer needed at a specific location, per Section B.1.3:
 - Post it with an “Out of Service/Untested” sign.
 - Evaluate it before it can be reactivated for operations requiring the use of safety shower/eyewash equipment. The normal testing cycle shall resume thereafter.
- Ensure that safety-plumbed safety showers/eyewashes are tested when installed, and periodically thereafter, and that records of the tests are kept as specified in Section B.3 of Appendix B.

6.5 Hazards Control Department

The Hazards Control Department shall:

- Assist supervisors and workers in maintaining safe work areas by providing information, through the ES&H Teams, on the hazardous properties of chemicals and relevant regulations, per Section 3.2.
- Help RIs identify hazardous chemicals while preparing IWSs, IWS/SPs, or FSPs, per Section 3.2.
- Recommend methods for controlling and monitoring chemical hazards in the work environment, per Section 3.2.
- Document or ensure that PPE requirements are documented using a HAC or otherwise, in accordance with Document 11.1, per Section 3.2.1.
- Review chemical purchases and procurements and approve purchases and procurements of specific groups of chemicals, per Section 3.3.2.
- Set hazardous chemical age-related limits based on known safety considerations using available information, including consultation with knowledgeable people (e.g., chemists performing research using such chemicals), per Section 3.5.2.
- Check hazardous chemicals periodically, but not less than annually, per Section 3.5.3.
- Conduct workplace monitoring of chemical hazards and document the monitoring results in accordance with the CBS Discipline Action Plan (CBSDAP), per Section 3.7.1.
- Coordinate the preparation and updates of MSDSs for LLNL-developed chemicals, working with the RI or his/her designee, and serve as the contact point for outside organizations as requested, per Section 3.9.2.

- Support the preparation of MSDSs for LLNL-developed chemicals and review new updated MSDSs in accordance with Appendix D, per Section 3.9.2.
- Assist RIs in providing spill cleanup training, per Section 4.4.
- Review plans for safety shower/eyewash installations and maintain a list of safety shower/eyewash models that have been successfully used at LLNL, per Appendix B.
- Document exemptions from safety shower/eyewash requirements, per Section B.1.2.
- Document situations where modifications to the testing frequencies specified in Section B.3 of Appendix B are warranted.
- Track the status of infrequently-used safety shower/eyewash equipment before the start of work in an area where a unit is to be returned to work, per Section B.3 of Appendix B.
- Post an infrequently-used safety shower/eyewash, per Section B.3 of Appendix B.

6.6 Environmental Protection Department

The Environmental Protection Department shall:

- Provide assistance with chemical inventories, per Section 3.5.1.
- Maintain the Laboratory's MSDS database, the Chemical Safety pages, and ChemTrack/MSDS Hotline, per Section 3.5.1.

6.7 Health Services Department

The Health Services Department provides services covered in Document 10.1. With respect to chemicals, the Health Services Department shall:

- Provide advice to the RI and ES&H Teams as to when special first-aid preparations are warranted and provide guidance about how special first-aid supplies are stored, maintained, and used, per Section 3.1.3.
- Evaluate all employees who have had a chemical exposure that exceeds or may have exceeded applicable occupational exposure limits, per Section 3.8.1.
- Support the preparation of MSDSs for LLNL-developed chemicals, when applicable, per Section 3.9.2.

6.8 Authorizing Organizations

Authorizing organizations shall:

- Ensure that hazardous chemicals are procured and stored consistent with program, safety, and waste minimization objectives, per Section 3.
- Identify and track hazardous chemicals, per Section 3.5.
- Manage chemical inventories to control quantities of hazardous chemicals and limit hazardous chemical inventories to amounts needed to meet operational requirements, per Section 3.5.
- Determine when to dispose of hazardous chemicals, per Section 3.5.
- Conduct reviews periodically of hazardous chemicals in use and in storage areas to ensure age and testing procedures are being fulfilled and to identify cases where containers or their contents show evidence of deterioration, per Section 3.5.
- Make decisions about retaining, testing/treating, or disposing of stored chemicals, per Sections 3.5.1 and 3.5.5.
- Establish controls for hazardous chemical inventories based on quality control and program considerations, per Section 3.5.2.
- Manage chemical inventories and ensure that hazardous chemical inventories are limited to amounts needed to meet operational requirements, per Section 3.5.2.
- Ensure that hazardous chemicals are procured and stored consistent with program, safety, and waste minimization objectives, per Section 3.5.2.
- Ensure that workers receive training that enables them to safely handle and use hazardous chemicals and that RIs have received appropriate training for their duties, per Section 4.0.
- Organizations providing spill-response workers from throughout the Laboratory shall determine the emergency-responder training these workers need, and ensure that it is provided.
- Ensure that non-plumbed safety showers/eyewashes are tested on installation and periodically thereafter and that records of the tests are kept as specified in Section B.3 of Appendix B.

6.9 Generator of an MSDS for an LLNL-Developed Chemical

The generator, or successor, of an MSDS for an LLNL-developed chemical shall update the MSDS after being advised of significant information regarding the hazards of the chemical or ways to protect against those hazards, per Section 3.9.2.

7.0 Work Smart Standards

10 CFR 850, "Chronic Beryllium Disease Prevention Program."

29 CFR 1910.94, "Ventilation."

29 CFR 1910.107, "Spray Finishing using Flammable and Combustible Materials."

29 CFR 1910.108, "Dip Tanks Containing Flammable or Combustible Liquids."

29 CFR 1910.120, "Hazardous Waste Operations and Emergency Response."

29 CFR 1910, Subpart I, "Personal Protective Equipment" as of July 1, 2000 (1910.132–1910.138, except 29 CFR 1910.139).

29 CFR 1910, Subpart K, "Medical and First Aid."

29 CFR 1910, Subpart Z, "Toxic & Hazardous Substances."

– For nonlaboratories, 29 CFR 1910.1200.

– For laboratories, 29 CFR 1910.1450.

29 CFR 1926.50, "Medical Services and First Aid."

29 CFR 1926.62, "Lead."

29 CFR 1926, Subpart Z, "Toxic & Hazardous Substances."

40 CFR 68.150–68.190, "Chemical Accident Prevention Provisions, Risk Management Plan."

40 CFR 170, "Worker Protection Standard."

40 CFR 171, "Certification of Pesticide Applicators."

40 CFR 260, "Hazardous Waste Management System: General."

40 CFR 261, "Identification and Listing of Hazardous Waste."

40 CFR 262, "Standards Applicable to Generators of Hazardous Waste."

40 CFR 763, Subpart E, Appendix C, "Asbestos Model Accreditation Plan."

ACGIH, *Industrial Ventilation Manual* (23rd Edition).

ACGIH TLVs and BEIs: *Threshold Limit Values for Chemical Substances and Physical Agents*, 2002 (excluding TLVs for Ergonomics, Ionizing Radiation, and Lasers).

ANSI Z358.1-1990, *American National Standard for Emergency Eyewash and Shower Equipment*. This standard was accepted with the exception that testing frequency for emergency showers is to be monthly rather than weekly as required by the standards.

ANSI Z9.5-1992, *American National Standard for Laboratory Ventilation* (see Sections 5.7 and 5.8).

ANSI Z49.1-1994, *Safety in Welding, Cutting, and Allied Processes*.

ANSI Z88.2-1992, *American National Standard for Respiratory Protection*.

Book of SEMI Standards.

Standard F4-1990, "Guide for Remotely Actuated Cylinder Valves."

Standard F6-1992, "Guide for Secondary Containment of Hazardous Gas Piping Systems."

Standard F13-1993, "Guide for Gas Source Control Equipment."

Standard F14-1993, "Guide for Gas Source Equipment Enclosures."

Standard S2-1993, "Safety Guidelines for Semiconductor Manufacturing Equipment."

Standard S5-1993, "Safety Guidelines for Flow Limiting Devices."

Compressed Gas Association (CGA).

Pamphlet P-1-1991, *Safe Handling of Compressed Gases in Containers*.

Pamphlet P-12-1993, *Safe Handling of Cryogenic Liquids*.

Pamphlet S-1.1-1995, *Pressure Relief Device Standards, Part 1, "Cylinders for Compressed Gases."*

Pamphlet S-1.2-1995, *Pressure Relief Device Standards, Part 2, "Cargo and Portable Tanks for Compressed Gases."*

Pamphlet S-1.3-1995, *Pressure Relief Device Standards, Part 3, "Compressed Gas Storage Containers."*

Department of the Army Pamphlet 40-8, *Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Nerve Agents GA, GB, GD, and VX* (12/4/90).

Department of the Army Pamphlet 40-173, *Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Mustard Agents H, HD and HT* (8/30/91).

DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees," Attachment 2, "Contractor Requirement Document," Sections 1–11, 13-18 (delete item 18.a), 19 (delete item 19.d.3), and 22.

Kelley, R.J., Fulton, G.P., and Davis, H.P., *Asbestos Management*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-146618, November, 2001.

Miller, G., Fulton, G., and Bergman, W., *HEPA Filter and In-place Leak Testing Standard*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-133354, April, 2003.

NFPA 45, *Standard on Fire Protection for Laboratories using Chemicals* (1996 Edition).

8.0 Resources for More Information

8.1 Contacts

See the ES&H Contact list.

8.2 Lessons Learned

Lessons Learned concerning chemicals are available at the LLNL Lessons Learned Web Site at:

http://www-r.llnl.gov/es_and_h/lessons/lessons.shtml

When the page opens, click on the "Chemical" button, which will connect you to a large number of Lessons Learned concerning chemicals.

8.3 Other Sources

American Chemical Society Committee on Chemical Safety, *Safety in Academic Chemistry Laboratories*, American Chemical Society, 5th Edition, 1990.

American Society of Heating, Refrigerating, and Air-Conditioning Engineers, *ASHRAE Handbook of Fundamentals*, Chapter 15, "Airflow Around Buildings," (1997).

Book of SEMI Standards, Standard F3-1994, "Guide for Welding Stainless Steel Tubing for Semiconductor Manufacturing Operations."

Kelly, R. and Miller, G., *Standard for Storing and Using Peroxidizable Organic Chemicals*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-133218, Rev.1, May 1999.

Lawrence Livermore National Laboratory Plant Engineering Standards and Documentation Group Facilities Standard, "Emergency Eyewash & Shower Units," PEL-M-11610 (replaced PEL-M-6.02). November 2001.

National Fire Protection Association, *Fire Protection Guide on Hazardous Materials* (NFPA, 2001).

Yaws, Carl, *Matheson Gas Data Book*, McGraw-Hill, 2001, 7th Edition.

Appendix A

Definitions

Activation (of safety eyewash or shower)	Operation of the unit for a brief interval, lasting from a few seconds to a few minutes, to verify the unit is working properly. It is <i>not</i> a 15-minute flow test.
Approve (procurement of a chemical)	Concur with a proposed purchase in writing or by e-mail.
Chemical	Any chemical or chemical product (often called "material"). This includes generic chemicals, elements, and hazardous chemical products that contain one or more chemicals, such as cleaning products, solvents, and lubricants.
Chemical custodian	The person identified in the ChemTrack database or other local inventory system who is administratively responsible for chemicals in a given location. These responsibilities include those identified in Section 8.2 of <i>ES&H Manual</i> Document 21.1.
Combustible	Ordinary solids (e.g., wood, paper, rags, and plastics) and liquids or gases with a flash point of $\geq 100^{\circ}\text{F}$.
Flammable	Liquids or gases with a flash point of $< 100^{\circ}\text{F}$.
Flow pattern (of a safety shower or eyewash device)	The shape, dimension and location of the flow of delivered water measured at a plane parallel to the ground at a specified location, as well as the uniformity of the water flow as determined at that location.
Hazardous chemical	Any chemical, as defined above, that is a physical or health hazard. This includes flammable and combustible substances, toxic substances, carcinogens, mutagens, teratogens, those that are corrosive or injurious on contact with the skin or eyes, and substances that can be harmful by other ways.

Incompatible chemicals	Chemicals that will create strong releases of energy or hazardous reaction products if mixed in an unanticipated or uncontrolled manner. Examples include either acids and caustics that will create intense heat when mixed with each other or water and acids and cyanide salts that produce deadly hydrogen cyanide gas when mixed.
Laboratory	A facility where the laboratory-scale use of hazardous chemicals occurs, or a workplace where relatively small quantities of hazardous chemicals are used on a nonproduction basis.
Laboratory scale	Work with substances in which the containers used for chemical reactions, transfers, and other handling are designed to be easily and safely manipulated by one person. Laboratory scale excludes those workplaces whose function is to produce commercial quantities of materials.
Laboratory use of hazardous chemicals	The handling or use of such chemicals where all of the following conditions are met: <ol style="list-style-type: none">1. Chemical manipulations are carried on a laboratory scale.2. Multiple procedures or chemicals are used.3. The procedures involved are neither part of a production process nor in any way simulate one.4. Protective laboratory practices and equipment are available and are commonly used to minimize the potential for worker exposure to hazardous chemicals.
Occupational exposure limit (OEL)	The maximum concentration of an air contaminant to which working people can be exposed for a specified time interval, usually the maximum average exposure allowed throughout an entire eight-hour shift.
Personal eye irrigation device	A device, such as a squeeze bottle filled with saline solution, used to irrigate the eyes after a splash incident. Not to be confused with a safety eyewash.

Physical hazard	A chemical for which there is scientifically valid evidence that it is combustible liquid, compressed gas, explosive, flammable, organic peroxide, oxidizer, pyrophoric, unstable (reactive), or water reactive.
Plumbed (safety eyewash or shower)	Connected to a plumbing system so the location is fixed. A non-plumbed unit can be located where plumbing is not provided or it can be "portable."
Portable (safety eyewash or shower)	A non-plumbed safety shower or eyewash that can be moved about.
Primary chemical container	Container shipped by the chemical manufacturer and the basic unit tracked in the ChemTrack inventory system.
Review (procurement of a chemical)	The evaluation of a proposed procurement by a Hazards Control Department representative. The reviewer is allowed one workday to act on the procurement or it proceeds automatically with implied approval.
Secondary chemical container	Any container, vessel, or other chemical storage device that is not a primary container.
Teratogen	A chemical that can produce adverse effects on fetuses.

Appendix B

Safety Showers/Eyewashes

Safety showers/eyewashes are important safety equipment because they can be used to prevent serious injury or permanent disability. For this reason, facility management, using inputs from RIs and the ES&H Teams, shall identify where safety showers/eyewashes are needed and ensure that safety showers/eyewashes meet specifications, plumbed units are connected to potable water supplies, and the units are installed where and as specified in this appendix. This appendix provides the following information:

- When safety showers/eyewashes are required.
- Where they shall be placed.
- Frequency of testing.
- Engineering specifications.

B.1 Situations Requiring Safety Showers/Eyewashes

This section discusses situations that require safety showers/eyewashes.

B.1.1 When Safety Showers/Eyewashes Are Needed

Situations for which safety showers/eyewashes are required include, but are not limited to:

- Work areas where corrosive or injurious chemicals (including trade-name products identified through the MSDS process) are used, such as:
 - Solutions of inorganic or organic acids or bases with a pH of 2.0 or less, or 12 or more.
 - Other organic or inorganic chemicals that are corrosive or irritating to eyes or skin (e.g., methylene chloride, phenol).
 - Organic or inorganic chemicals that are significantly toxic by skin absorption (e.g., phenol).
- Work areas where corrosive/injurious chemicals are used in a closed system that can catastrophically fail and cause the chemicals to leak (i.e., liquid lead-acid battery charging areas, or areas where pressurized systems with corrosive liquids are used).
- Storage areas where breakable containers of corrosive/injurious chemicals (1 gallon or more) are handled outside their original shipping cartons.

- Waste accumulation and all chemical handling and storage areas that could contain corrosive/injurious chemicals.
- Work areas where formaldehyde solutions in concentrations greater than or equal to 0.1% are handled.
- Work areas where operations involve the use of air or water reactive liquids or solids.

B.1.2 Exemption from Safety Showers/Eyewashes Requirements

Safety showers/eyewashes are not needed if the ES&H Team industrial hygienist reviews the operation and documents why, in writing, a safety shower/eyewash is not needed, based on all of the following considerations:

- The aggregate quantity of injurious/corrosive substances stored is less than 8 ounces,
- The chemicals are used at room temperature, and
- The chemicals are used at an aggregate rate of less than 2 ounces per day.

This exemption does not apply to chemicals such as perchloric acid, hydrofluoric acid, cyanide compounds, and the alkali metals. This exemption can be modified for other substances and conditions, only with the joint concurrence of the ES&H Team industrial hygienist and the CBS Section Leader. Exemptions shall be documented in accordance with CBS procedures.

B.1.3 Discontinuing Use of Safety Shower/Eyewash

When a specific safety shower/eyewash is no longer needed, facility management shall:

- Post it with an "Out of Service/Untested" sign.
- Evaluate it, before it can be reactivated, for operations requiring the use of safety shower/eyewash equipment. The normal testing cycle shall resume thereafter.

B.2 Locations of Safety Showers/Eyewashes

Safety showers/eyewashes shall be located within ten seconds travel time of where splash exposure could occur. When determining the location of a safety eyewash, personal eye-irrigation devices shall not be counted as safety eyewashes. The shower/eyewash should be located as close as possible, but at a sufficient distance so the splashed person could use the equipment safely in the event of a major spill or fire. The path shall be free of tripping hazards, eye hazards, and other objects that could impede

travel of a person impaired by the splash incident to the shower/eyewash, such as doors opening against the direction of travel, stairs, and hot surfaces. There should be no more than two doors in the path of travel.

B.3 Testing and Inspection

Facility management shall ensure that tests and inspections of plumbed safety showers/eyewashes are performed when the units are installed and periodically thereafter and that records are kept of the tests and inspections. The testing and inspection of non-plumbed units are the responsibility of the organization authorizing the work that required them.

Safety eyewashes and showers shall be inspected and tested when they are installed to determine:

- They are in good condition and meet specifications.
- The valves function properly.
- Shower spray patterns comply with specifications, and eyewashes will wash both eyes simultaneously at a velocity low enough not be injurious to the user.

The following tests and inspections shall subsequently be performed for all plumbed safety shower/eyewashes by an appropriate individual and/or organization assigned by the facility management. The authorizing organization responsible for non-plumbed units shall test and inspect the units or arrange to have the units tested and inspected. Each safety shower/eyewash shall be checked or tested as follows:

- Weekly activation of eyewashes.
 - For plumbed eyewashes: activate, for only the time needed, to verify that the nozzle covers pop off, the water flows into the discharge area, the valve remains open, and a flow of clear odorless water occurs.
 - For gravity-fed portable units: activate just long enough to verify flow is established and *promptly* shut off flow. A bucket may be necessary to catch runoff. Replace lost liquid with clean tap water and be sure to replace the fill port cap. (Activate weekly or before use of units to support work in infrequently occupied splash-hazardous locations, whichever comes later. Units located in infrequently occupied spaces shall be tagged per Section B.1.3 while they are not in use.)
 - For air-pressurized portable units: activate the eyewash for only long enough to verify flow is established and that the valve remains open. If applicable, activate the drench hose long enough to verify same. A bucket may be necessary to catch runoff. Replace lost liquid with clean

tap water and repressurize according to manufacturer's instructions. (Activate weekly or before use of units to support work in infrequently occupied splash-hazardous locations, whichever comes later. Units located in infrequently occupied spaces shall be tagged per Section B.1.3 while they are not in use.)

- Monthly activation of safety showers for only that time needed to verify the valve remains open and a flow of clear odorless water is obtained.
- Annual activation of plumbed eyewash units during hot weather periods for eyewashes/showers located outdoors, to ensure the lines are sufficiently insulated so the water delivered by the shower/eyewash is not so hot that it will aggravate the chemical injury, or cause additional injury.
- Weekly checking of heated thermal jackets of outdoor equipment during periods of potentially freezing weather to ensure that they are working properly.
- Monthly inspection of condition and accessibility. The requirements are:
 - There shall be 36 inches of free floor area, unimpeded by equipment or articles stored on the sides of the safety shower/eyewash or on walkways and paths needed to gain access to the safety shower/eyewash.
 - No objects shall be stored or placed by an eyewash and/or under a shower that a person would need to remove to use the safety eyewash or shower. This includes carts.
- Quarterly or semiannually flushing out the water supply, adding fresh water, and adding fresh bacteriostatic solution to non-plumbed eyewashes in accordance with the eyewash unit and the bacteriostatic solution instructions.
- Checking the flow pattern created by the unit, fixed or portable, upon installation, to ensure the flow pattern (see Appendix A for definition) meets the manufacturer's specifications.

The results of all tests shall be recorded and maintained in a easily accessible location. The test log shall:

- Identify the shower being tested.
- List the date and type of the test.
- List the initials of the person making the test.
- Identify the type of test (e.g., weekly activation, monthly activation.)

- Record the annual check of temperature for outdoor unit, weekly check of thermal jacket during cold season, or monthly inspection of condition/accessibility.

If the potential for exposure is infrequent (e.g., less than quarterly), then a modification in the testing frequency may be justified. The concurrence of the ES&H Team industrial hygienist shall be documented in accordance with Industrial Hygiene Policy and Information Manual Procedure No. 12, "Application of Standards," prior to start of a modified testing cycle. The area ES&H Team shall begin tracking the status of this equipment before the start of work. The ES&H Team shall do one of the following:

- The safety shower/eyewash shall be posted with a WARNING sign, as defined in Document 12.1, "Access Control, Safety Signs, Safety Interlocks, and Alarm Systems," in the *ES&H Manual*, advising that the equipment may not provide protection and that the safety shower/eyewash shall be tested before splash hazardous work begins.
- The safety shower/eyewash shall be posted "Out of Service/Untested," as described in the preceding bullet of this section, tested before splash-hazardous work begins, and reposted "Out of Service/Untested" when the splash-hazardous work is finished.

A record shall be kept of these less frequent tests, in a visible or easily accessible place near the shower as specified earlier in this section, noting when the tests were performed prior to the start of work.

B.4 Engineering Specifications

Safety showers shall meet the engineering-related requirements of LLNL Facility Standard PEL-M-11610. This standard requires that safety showers/eyewashes meet the requirements of ANSI Z358.1 "American National Standard for Emergency Eyewash and Shower Equipment." Only potable water shall be used to supply safety showers/eyewashes. An eyewash discharge shall be connected or plumbed to a bucket, carboy, sanitary sewer drain, or retention tank to collect water runoff and avoid creating a significant nuisance and slipping hazard. Environmental protection requirements and health and safety concerns related to safety shower drainage shall be addressed during facility design.

Non-plumbed units shall not be installed or used at LLNL, unless there is no other practical way to provide eyewash/shower equipment. Non-plumbed units, when it is necessary to use them, shall meet the requirements of the Work Smart Standards. Portable units weighing more than fifty pounds when loaded with water shall be mounted on wheels (a portable eyewash that provides flushing for 15-minutes contains ≥45 lbs. of water).

Appendix C

Storage Groups for Hazardous Chemicals

This appendix provides information on groups of chemicals that can be safely stored together. The specific arrangements for segregating chemicals will depend on the chemicals and conditions of use. Separate chemical storage groups may be needed. This information is provided in the form of signs that can be posted in appropriate places (e.g., on the doors of chemical or flammable liquid storage cabinets). Copies of the storage group signs can be obtained at the intranet addresses indicated. These signs should be posted in areas where hazardous chemicals are used. The storage groups listed, in order of appearance, are:

- Water reactive chemicals.
- Oxidizers.
- Pyrophoric, light-sensitive, and peroxide-forming substances.
- Flammables.
- Toxic compounds.
- Acids and bases.

Water Reactive Chemicals

(This is a representative, not a complete, listing)



W A R N I N G

These chemicals will react with water to form flammable or toxic gases or other hazardous conditions.

Storage Precautions:

- Store them in a cool, dry place.
- In case of fire, keep water away.

SOLIDS:

Aluminum chloride, anhydrous	Maleic anhydride
Calcium carbide	Phosphorous pentachloride
Calcium oxide	Phosphorous pentasulfide
Cesium	Potassium*
Ferrous sulfide	Sodium*
Lithium*	Sodium-potassium alloy ("NaK")
Magnesium	

NOTE:

*Cesium, lithium, potassium, and sodium should be stored under mineral oil.

LIQUIDS:

Acetyl chloride	Stannic chloride
Chlorosulfonic acid	Sulfur chloride
Phosphorous trichloride	Sulfuryl chloride
Silicon tetrachloride	Thionyl chloride



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Oxidizers

(This is a representative, not a complete, listing)



Storage Precautions:

- Store them in a cool, dry place.
- Keep away from flammable and combustible materials (such as paper, wood, solvents, etc.).
- Keep away from reducing agents (such as metals, hydrazine, formic acid, or concentrated/glacial acetic acid).

SOLIDS:

Ammonium dichromate	Perchlorate compounds ⁶
Ammonium perchlorate	Periodic acid Permanganic acid
Ammonium persulfate	Peroxides ⁷
Benzoyl peroxide ¹	Potassium dichloroisocyanurate
Bromate salts ²	Potassium dichromate
Calcium hypochlorite	Potassium periodate
Ceric sulfate	Potassium permanganate
Chlorate salts ³	Potassium persulfate
Chromium trioxide	Sodium chlorite
Iodate salts ⁴	Sodium dichromate
Iodine	Sodium nitrate
Magnesium perchlorate	Sodium perborate
Manganese dioxide	Trichloroisocyanuric acid
Nitrate salts ⁵	

LIQUIDS:

Bromine	Nitric acid
Chromic acid	Perchloric acid ⁶
Hydrogen peroxide	Sulfuric acid

GASES

Chlorine	Nitrogen dioxide
Chlorine dioxide	Nitrogen oxide
Chlorine fluorides	Oxygen
Fluorine	Ozone

NOTES:

- 1 — Benzoyl peroxide is an organic peroxide. It can decompose explosively with minimum external catalyzation.
- 2 — Potassium bromate, sodium bromate, etc.
- 3 — Potassium chlorate, etc.
- 4 — Sodium iodate, etc.
- 5 — Ammonium nitrate, ferric nitrate, etc.
- 6 — See *ES&H Manual* Document 14.8 "Working Safely with Corrosive Chemicals", for information about perchloric acid and perchlorates
- 7 — Lithium peroxide, sodium peroxide, etc. See *ES&H Manual* Documents 14.7, "Safe Handling of Alkali Metals and Their Reactive Compounds" and 14.1, "Chemicals", for information about alkali metal peroxides and organic peroxides, respectively.



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Pyrophoric Chemicals

(This is a representative, not a complete, listing)



W A R N I N G

Ignite spontaneously on contact with air.

Storage Precaution:

- Store them in a cool, dry place.

Boron ¹	Nickel ¹
Cadmium ¹	Organometallics, NOS ²
Calcium ¹	Phosphorous, yellow ³
Carbonyl compounds ²	Silane ⁴
Cobalt ¹	Titanium ¹
Diborane	Triethyl aluminum
Iron ¹	Triethyl boron
Lead ¹	Zinc ¹
Manganese ¹	Uranium ¹

NOTES:

- 1 — Finely divided materials in powder form are a pyrophoric hazard.
- 2 — Check the MSDS to determine if a specific carbonyl or organometallic compound is pyrophoric (by explicit warning or flash point <130 °F).
- 3 — Yellow phosphorous should be stored and cut under water.
- 4 — Silane can accumulate before spontaneously igniting. When this happens, the result is an explosion-like deflagration.

Light-Sensitive Chemicals

(This is a representative, not a complete, listing)

Storage Precautions:

- Avoid exposure to light
- Store in amber bottles in a cool, dry place

Bromine	Mercurous nitrate
Ethyl ether (peroxidizable)	Oleic acid
Ferric ammonium citrate	Potassium ferricyanide
Hydrobromic acid	Silver salts
Mercuric salts	Sodium iodide

NOTES:

- 1 — Mercuric chloride, mercuric iodide, etc.
- 2 — Silver acetate, silver chloride, etc.

Peroxide Forming Chemicals

QuickTime™ and a
PDF (Acrobat) Reader
are needed to see this picture.

See Section 3.7 and Table 2 of *ES&H Manual* Document 14.1, "LLNL Chemical Safety Management Program", for precautions and a list, respectively.



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Flammable Chemicals

(This is a representative, not a complete, listing)



Storage Precautions:

- Store in approved safety cans or cabinets.
- Segregate from oxidizing acids and oxidizers
- Keep away from ignition sources: flames, hot objects, sparks.
- Ground/bond drums and safety cans when transferring materials.
- Keep firefighting equipment readily available.
- have spill cleanup materials handy.
- Store highly volatile flammable liquids in a specially equipped, labeled refrigerator.

SOLIDS:

Aluminum powder
Cobalt resinate
Magnesium powder

Naphthalene
Paraformaldehyde
Silicon powder

Titanium powder
Uranium powder
Zirconium powder

LIQUIDS:

Acetaldehyde
Acetone
Acetyl chloride
Allyl alcohol (also acutely toxic)
Allyl chloride
n-Amyl acetate
n-Amyl alcohol
Benzene
n-Butyl acetate
n-Butyl alcohol
n-Butylamine
Carbon disulfide
Chlorobenzene
Cyclohexane
Diethylamine
Diethyl carbonate
p-Dioxane
Ethanol
Ethyl acetate
Ethyl acrylate

Ethylamine
Ethyl benzene
Ethylene chloride
Ethyl ether
Ethyl formate
Furan
Gasoline
Heptane
Hexane
Hydrazine
Isobutyl alcohol
Isopropyl acetate
Isopropyl alcohol
Isopropyl ether
Mesityl oxide
Methanol
Methyl acetate
Methyl acrylate
Methylal
Methyl butyl ketone
Methyl ethyl ketone

Methyl formate
Methyl isobutyl ketone
Methyl methacrylate
Methyl propyl ketone
Morpholine
Naphtha
Nitromethane and most nitrohydrocarbons
Octane
Piperidine
Propanol
Propyl acetate
Propylene oxide
Pyridine
Styrene
Tetrahydrofuran
Toluene
Turpentine
Vinyl acetate
Xylene

GASES:

Acetylene
Ammonia
Arsine
Butane
Carbon monoxide
Diborane
Ethane
Ethyl chloride

Ethylene
Ethylene oxide
Formaldehyde
Hydrogen
Hydrogen cyanide
Hydrogen sulfide
Methane
Phosphine

Propane
Propylene
Silane



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Toxic Chemicals

(This is a representative, not a complete, listing)



W A R N I N G

The chemicals are dangerous or extremely dangerous to health and life when inhaled, swallowed, or absorbed by skin contact.

Take proper precautionary measures to avoid exposure.

Storage Precautions:

- Store according to hazard group of chemical, using appropriate security when necessary.

SOLIDS:

Antimony compounds
 Arsenic compounds
 Barium compounds
 Beryllium
 Brucine
 Cadmium compounds
 Calcium oxide
 Chromates, salts of (also corrosive)
 Cyanides, salts of
 Fluorides, salts of
 Hydroquinone
 Iodine
 Lead compounds
 Mercuric compounds
 Nickel carbonyl and other compounds
 Nitroaniline
 Osmium tetroxide

Oxalic acid
 Phenol
 Phenylenediamine
 Phosphorous, yellow
 Phosphorous pentachloride (corrosive, water reactive)
 Picric acid (also explosive)
 Potassium (also water reactive)
 Resorcinol
 Selenium compounds
 Silver compounds
 Sodium (also water reactive)
 Sodium hydroxide (also corrosive)
 Sodium hypochlorite (also corrosive)
 Thallium and compounds
 Vanadium pentoxide

LIQUID CHEMICALS:

Acrolein (also flammable)
 Acrylonitrile (also flammable)
 Allyl Alcohol (also flammable)
 Aniline
 Benzene (also flammable)
 Benzonitrile
 Bromine (also corrosive)
 Bromoacetone
 Bromoform
 Carbon disulfide (also flammable)
 Carbon tetrachloride
 Chloroform
 Chromic acid (also corrosive)
 Dimethyl mercury
 Ethylene glycol
 Formaldehyde & solutions such as "formalin"
 Formic acid (also corrosive)
 Furfuryl alcohol
 Hydrazine (flammable, reactive)
 Hydrobromic acid (also corrosive)

Hydrochloric acid (also corrosive)
 Hydrofluoric acid (also corrosive)
 Hydrogen peroxide (also an oxidizer)
 Hydrogen sulfide (also flammable)
 Isocyanate and diisocyanate compounds (can be water-reactive)
 Mercury
 Methylene chloride
 Methyl iodide
 Nitric acid (also corrosive & an oxidizer)
 Perchloric acid (also an oxidizer, reactive)
 Phosphorous trichloride (also corrosive & water reactive)
 Sulfuric acid (also corrosive)
 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (also known as dioxin)
 Tetrachloroethane
 Tetrachloroethylene
 Toluidine

Toxic Chemicals (continued)**GASES:**

Arsine (also flammable)	Hydrogen bromide (also corrosive)
Boron trichloride (also corrosive)	Hydrogen chloride (also corrosive)
Boron trifluoride (also corrosive)	Hydrogen cyanide (also flammable)
Carbon monoxide (also flammable)	Hydrogen sulfide (also flammable)
Chlorine (also corrosive)	Nitrogen dioxide
Cyanogen	Phosgene
Diborane (also pyrophoric)	Phosphine (also pyrophoric)
Fluorine (also corrosive, strong oxidizer)	Sulfur dioxide

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Acids and Bases

(This is a representative, not a complete, listing)



ACIDS

Storage Precautions:

- Store large bottles of acids on low shelves or acid storage cabinets
- Segregate oxidizing acids from organic acids and flammable or combustible chemicals.
- Segregate acids from bases and reactive metals, such as sodium, potassium, magnesium, etc.
- Segregate acids from chemicals that could generate toxic gases upon contact, such as cyanide or sulfide compounds.
- Keep spill control and cleanup materials or kits on hand.

Acetic acid ¹

Benzoyl Chloride ^{1,2}

Chloroacetic acid ¹

Chromic acid ³

Formic acid ¹

2-Furaldehyde ⁴

Hydrobromic acid ³

Hydrobromous acid

Hydrochloric acid

Hydrofluoric acid ⁵

Hydriodic acid

Iodic acid ³

Muriatic acid

Nitric acid ³

Nitrous acid

Perchloric acid ³

Phosphoric acid

Phosphorous acid

Propionic acid ¹

Sulfamic acid ¹

Sulfanilic acid ¹

Sulfuric acid ³

Sulfurous acid

Trichloroacetic acid ¹

NOTES:

1 — Organic acid.

2 — Reacts with water

3 — Strong oxidizing acid.

4 — Reacts with *both* acids and bases

5 — Special spill cleanup materials needed.

5 — Reacts with water

BASES:

Storage Precautions:

- Segregate bases from acids.
- Store solutions of inorganic hydroxides in polyethylene containers..
- Keep spill control and cleanup materials or kits on hand.

Ammonium hydroxide

Bicarbonate salts ⁴

Carbonate salts ⁵

Calcium hydroxide

Potassium hydroxide

Sodium hydroxide

Sodium metasilicate

Triethylenetetramine

Trisodium phosphate

NOTES:

4 — Sodium bicarbonate, potassium bicarbonate, etc.

5 — Calcium carbonate, sodium carbonate, etc.



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Appendix D

Instructions for Preparing Material Safety Data Sheets

D.1 Coordination of Effort

Completion of the MSDS requires technical information from some or all of the following:

- Chemical producer.
- Health Services Department.
- Hazards Control Department.
- Environmental Protection Department.

The latter three shall be provided by the area ES&H Team. In addition, technical experts from other LLNL organizations may be consulted for their particular expertise and to review the assembled material. The LLNL chemical producer and the area industrial hygienist serving the producer shall prepare the draft MSDS using a nationally recognized format such as OSHA Form 174, "Material Safety Data Sheet." The draft shall be reviewed and approved by the Chemical/Biological Safety Section of the Hazards Control Department prior to release.

D.2 Material Safety Data Sheets Content

Each MSDS shall contain the following whenever they are known:

- Identity of the material, including hazardous ingredients comprising 1% or more of mixtures, or 0.1% or more of carcinogens. Refer to the LLNL Controlled Carcinogen List for Laboratories in Document 14.12, "Safe Handling of Carcinogenic Materials," in the *ES&H Manual*. The complete IARC and NTP lists of carcinogens are available at the following Internet address.

<http://chemtrack.llnl.gov>

- Physical and chemical characteristics.
- Physical hazards, including the potential for fire, explosion, and reactivity.

- Health hazards, including signs and symptoms of exposure, and any medical conditions generally recognized as being aggravated by exposure to the chemical.
- Primary routes of entry into the body.
- Occupational exposure limit.
- Whether the hazardous chemical is listed as a carcinogen.
- Any generally applicable precautions for safe handling.
- Any generally applicable control measures such as engineering controls, work practices, or PPE.
- Emergency and first-aid procedures.
- Date the MSDS was prepared or last changed.
- Name, address, and telephone number of the responsible party who prepared and distributed the MSDS and can provide additional information on the hazards and appropriate emergency procedures.

D.3 Data Sources

The Laboratory is not required to conduct new or additional health and safety testing of a product. If test results from scientific literature are available, they should be included. Besides this literature, contacts and reports available through the DOE complex should be identified and considered for inclusion. If no relevant information is found for a given category, the MSDS shall be marked to indicate that finding.