

Chemical Hygiene Plan & Hazard Communication Program

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Chapter 1.0

Chemical Hygiene Plan & Hazard Communication Program

This document serves as:

- The BNL Chemical Hygiene Plan for [OSHA “Occupational Exposures to Hazardous Materials in Laboratories” \(29 CFR 1910.1450\)](#) (i.e., Lab Standard) for laboratories, and
- The written BNL Hazard Communication Program for [Federal Occupational Safety and Health Administration \(OSHA\) “Hazard Communication Standard” \(29 CFR 1910.1200\)](#) (i.e., HazCom) for shops and large experimental apparatus settings.

1.1. Purpose & Scope

1.2. Labeling

1.3 Posting & Signage

1.4. MSDS

1.5. Training

1.1 Purpose and Scope

The purpose of this Chemical Hygiene Plan (CHP) is to provide requirements and guidance to BNL line and operations management to ensure a safe and healthy workplace is provided to all workers, guests, contractors, and visitors of BNL and for the safe handling, use, and storage of hazardous materials in laboratory, shop and office settings. This plan identifies responsibilities for these personnel and establishes procedures for identifying, evaluating, and controlling hazardous materials.

The classification of the areas and operations are:

Hazard Communication Standard (HazCom) 29 CFR 1910.1000	Chemicals used in routine operations in production, maintenance, or custodial operations. <i>HazCom areas</i> include Shops, Workrooms, Janitor lockers, accelerator facilities, custodial activities and similar areas/operations where non-administrative activities are performed.
Occupational exposure to hazardous chemicals in Laboratories (Laboratory Standard) 29 CFR 1910.1450	<i>Laboratory areas</i> are limited to areas where operations meeting the OSHA definition of a “workplace where relatively small quantities of hazardous chemicals are used on a non-production basis. In laboratories, the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person. Laboratories are regulated by the Lab Standard. Examples: Chemistry labs, multi-purpose labs and biology laboratories

The program is designed to ensure that the hazards of all chemicals brought to BNL are evaluated, and that information concerning their hazards is transmitted to employers and employees, including:

- Evaluate the potential hazards of chemicals used;
- Communicate information concerning hazards of the chemicals to the workers at BNL;
- Communicate the appropriate protective measures to workers to eliminate hazardous exposure.

The OSHA Hazard Communication Standard does not apply to:

- Hazardous Waste containers.
- Any hazardous substance when the hazardous substance is the focus of remedial or removal action being conducted under CERCLA in accordance with the Environmental Protection Agency regulations.
- Tobacco or Tobacco Products.
- Wood or wood products, including lumber which will not be processed, where the chemical manufacturer or importer can establish that the only hazard they pose to workers is the potential for flammability or combustibility.
- Food or alcoholic beverages intended for personal consumption by workers while in the workplace.
- Any drug, when it is in solid, final form for direct administration to the patient (e.g., tablets or pills, over-the-counter drugs, first aid supplies) and controlled or pharmaceutical for animal research.
- Cosmetics intended for personal consumption by workers while in the workplace.
- Consumer products in the quantity used by household consumers.
- Etiologic Agents and Biohazard in Research applicable substances.
- Radiological & nuclear materials.
- Beryllium articles (parts, formed objects) which are covered by the [Beryllium](#) Subject Area.

Offices and conference rooms are generally not “HazCom” areas and not “laboratories” and are not covered by the Chemical Hygiene Plan. The only “chemicals” used are small quantities of consumer products such as copier toners and household cleaning products.

Questions or comments may be addressed to the [Chemical Hygiene Officer](#) or at ext. 3066.

1.2. Labeling

A major emphasis of the OSHA standards on chemical safety is for containers of chemicals to be properly labeled to inform workers of the contents and hazards of the chemicals.

Required Procedure

A. Do not remove manufacturer provided labels on incoming containers of hazardous chemicals or deface them so that they cannot be read.



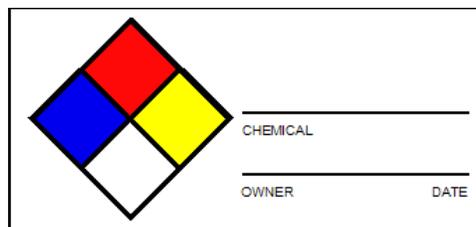
B. If the manufacturer label needs to be removed, or chemicals are transferred into a different container, label containers based on the following area:

B.1. Laboratories: label the container with at a minimum the chemical name (in English).

Methylene Chloride

B.2. HazCom Areas:

- Label portable containers with a minimum of the chemical name, hazards and target organs.
- The NFPA diamond label can be used to indicate hazards. The label will contain all information in English. NFPA diamond ratings are provided at the [Chemical Management Web Site NFPA Rating List](#).
- If the chemical is a carcinogen, add the word “carcinogen” to the NFPA label.



Sample of an adequate HazCom label added by BNL to a new container

- B.3. Label large fixed containers with a minimum of:
- 1.) Chemical name, hazards and target organs or
 - 2.) Chemical name, NFPA diamond label, and if the chemical is a carcinogen, the word “carcinogen”. The size of the label and NFPA diamond must be large enough to be viewed at a safe distance from the tank in the event of an emergency.



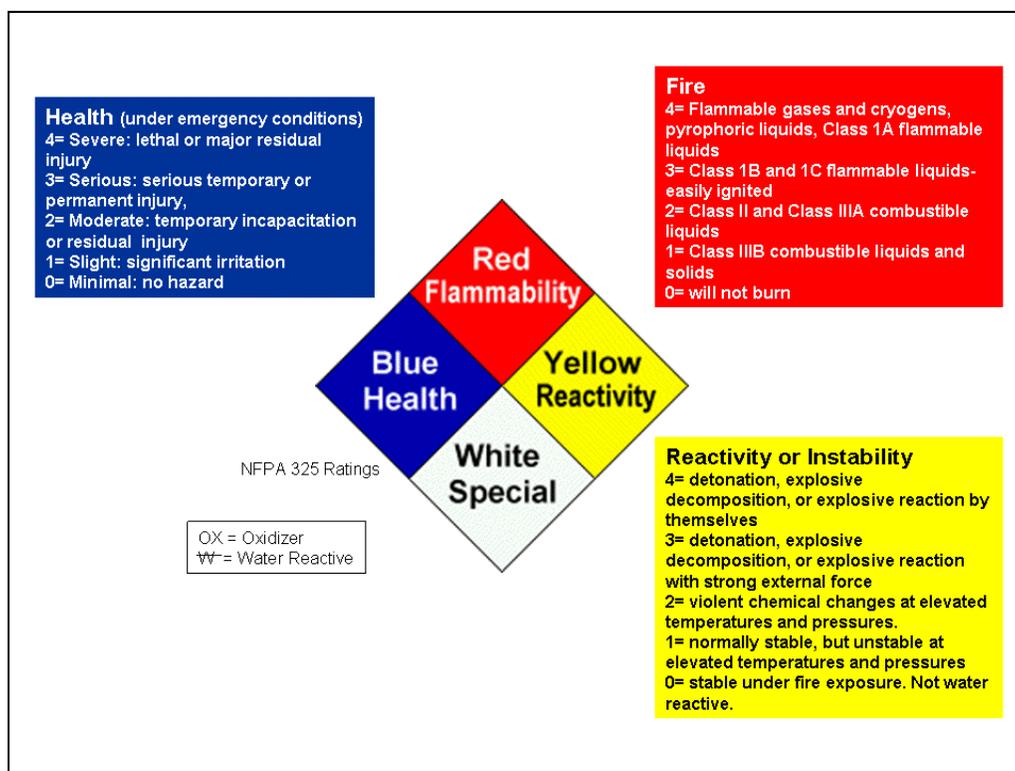
- B.4. Label containers of chemicals created at BNL that are shipped to other workplaces per the B.2 HazCom Area requirements.

Guidance

The following types of containers are NOT subject to labeling under OSHA requirements:

- Pesticides – subject to labeling by the Environmental Protection Agency;
- Chemical substances or mixtures – subject to labeling under the Toxic Substances Control by the Environmental Protection Agency;
- Food, food additives, color additives, drugs, cosmetics, and medical/veterinary devices or products, including materials intended for use as ingredients in such products (e.g., flavors and fragrances) – subject to the labeling requirements by either the Food and Drug Administration or the Department of Agriculture;
- Distilled spirits (beverage alcohols), wine, or malt beverages intended for nonindustrial use – subject to labeling regulations by the Bureau of Alcohol, Tobacco, and Firearms;
- Consumer products or hazardous substances – subject to a consumer product safety standards or labeling requirement of those acts or regulations issued by the Consumer Product Safety Commission;
- Agricultural or vegetable seed treated with pesticides – labeled in accordance with the Department of Agriculture;
- Nuisance particulates where the chemical manufacturer or importer can establish that they do not pose any physical or health hazard covered under this section;
- Ionizing and non-ionizing radiation; and
- Biological hazards.

Figure: HazCom label symbol and ratings.



1.3 Posting and Signage

Required Procedure

- A. The chemical hazards of an area are to be indicated on a *Hazard Information Placard/Emergency Information* sign at the entrance(s) to the areas. Follow the requirements in the [Signs, Placard, and Labeling for ESH Hazards](#) Subject Area.
- B. Use the following Icons to indicate chemical hazards and to designate areas for OSHA Particularly Hazardous Substances (see Chapter 6.2) on the *Hazard Information Placard/Emergency Information*:

 <ul style="list-style-type: none">• FLAMMABLE• SELF REACTIVE• PYROPHORIC• SELF-HEATING• EMITS FLAMMABLE GAS• ORGANIC PEROXIDE	 <p>HIGHLY ACUTE</p>
 <ul style="list-style-type: none">• EXPLOSIVE• SELF REACTIVE• ORGANIC PEROXIDE	 <p>OXIDIZER</p>
 <ul style="list-style-type: none">• CARCINOGEN• RESPIRATORY SENSITIZER• REPRODUCTIVE TOXICITY• TARGET ORGAN TOXICITY• MUTAGENICITY• ASPRITATION TOXICITY	 <p>CORROSIVE</p>
 <ul style="list-style-type: none">• IRRITANT• DERMAL SENSITIZER• ACUTE TOXIN• NARCOTIC EFFECT• RESPIRATORY TRACT	 <p>GAS UNDER PRESSURE</p>

1.4 Material Safety Data Sheets (MSDSs)

A Material Safety Data Sheet (MSDS) is an informational document prepared by the manufacturer or importer of a hazardous chemical that describes its physical and chemical properties, its physical and health hazards, and recommended precautions for handling, storage and disposal. An MSDS provides safety and health related information such as known hazards of the material, its physical and chemical properties, exposure limits, precautionary measures, and emergency and first aid procedures.

Required Procedure

- A. HazCom Areas: A Material Safety Data Sheet (MSDS) must be available to workers for all chemicals in an area.
- The preferred method is by the BNL [MSDS](#) Database.
 - Paper copies maybe kept at work locations but the documents must be controlled per the [Document Control](#) Subject Area by the line organization maintaining the paper copy to ensure it is the current version.
- B. Laboratories: Workers have access to the MSDS for laboratory chemicals maintained in the BNL [MSDS](#) Database. If the chemical will only be used at BNL in a laboratory, an MSDS is not needed unless the chemical introduces a new category of hazard to the laboratory.
- C. For chemicals that are created at BNL:
- If the chemical will only be used within a BNL laboratory, an MSDS is not needed unless the chemical introduces a new category of hazard to the laboratory.
 - If the chemical will be used in BNL HazCom areas and for shipments off-site, BNL must produce an MSDS for the new owner (unless quantity exemptions apply). Consult the Chemical Hygiene Officer [via e-mail](#) or at x-3066 for preparation of the MSDS.

Guidance

- BNL maintains all MSDSs received in the [MSDS](#) Database. This database serves as the official site for MSDS at BNL and ensures that the most current version is available to BNL workers. The BNL system maintains all current and previous copies of MSDSs that BNL has previously been in the database.
- Backup Copies of MSDSs are kept in a central location (CMS/MSDS Team Office) should the online system fail. Contact the CMS/MSDS Team for an MSDS when the online database is not available by calling phone x-6387 or x-2028 or email the [CMS Team](#).
- If an MSDS is not available for a chemical in your workplace, contact the CMS Team by calling phone extension x-6387 or x-2028 or email the [CMS Team](#). They will locate the appropriate MSDS and ensure that the MSDS is put into the system as soon as possible.

The only official copy of this file is the one on-line in SBMS.
Before using a printed copy, verify that it is the most current version by checking the *effective date*.

- If you obtain an MSDS that is not in the MSDS database, email or send a copy via regular mail to the CMS Team in Building 120 so that the database can be updated.

1.5. Training on Chemical Hazards

Training for workers working in areas where hazardous chemicals are present is completed for one of two work settings: Laboratory Areas or HazCom Areas. Work with certain hazardous chemicals in HazCom Areas has additional training related to specific chemicals.

Required Procedure

- Line managers are responsible to identify required training and ensure that workers complete training prior to performing work with chemicals.
- Minimum training to work with chemicals:

B1. HazCom Operations:

- [Hazard Communication](#) (HP-IND-200) (training to conduct work covered by HazCom regulations).

B2. Laboratories (training to enter laboratories):

- [Laboratory Standard](#) (HP-IND-220)
- Personnel without Laboratory Standard Training (HP-IND-220) may enter a laboratory if one of the following applies:
 - Hazard Communication trained worker performs only HazCom work in the laboratory (e.g., plumber installing a drain line).
 - Vendor service technician with Guest Site Orientation or Contractor Vendor Orientation (CVO) who is escorted by a BNL Laboratory Standard-trained person who communicates the hazards in the laboratory.
 - Vendor service technician with Guest Site Orientation or Contractor Vendor Orientation (CVO) who has reviewed the Work Planning documentation and is aware of the hazards present and the restrictions in the lab.
 - Untrained person (e.g., visitor or salesperson) who is escorted by a Laboratory Standard-trained person who deems it safe for the visitors to enter the lab and communicates the hazards to the untrained person.

B3: Specialized training for individuals performing specific roles:

- [Beryllium Use at BNL](#) (TQ-BERYLLIUM1) required for those handling Beryllium (powders and articles) in a laboratory.
- [Beryllium Use at BNL](#) (TQ-BERYLLIUM1) required for conducting HazCom work involving Beryllium, including articles.
- [Chemical Protective Clothing User Training](#) (HP-OSH-157) required for those who establish PPE requirements for areas or operations.
- [Chemical Protective Clothing User Training](#) (HP-OSH-157) required for those required to wear Level A equipment (unless equivalently trained in another courses such as HazWoper).

- [Cadmium Training for HazCom Operations](#) (TQ-CADMIUM) required for those handling cadmium at levels that create a Regulated Area in a HazCom area or laboratory.
- Corrosive Etch Solutions (TQ-Corrosive Etch) required for those handling Corrosive Etch Solutions (see Chapter 6.1.B)
- [Compressed Gas Safety](#) (TQ-COMPGAS1) available for those working with this type material.
- [Cryogen Safety](#) (HP-OSH-025) available for those working with this type material.
- [Ergonomics in Mechanical and Industrial Work](#) (TQ-ERGO-IND) available for those working with this type of equipment.
- [Ergonomics in the Laboratory Setting](#) (TQ-ERGO-LAB) available for those working with this type of equipment.
- [Ergonomics of Office Work Stations](#) (TQ-ERGO-OFFICE-W) available for those working with this type of equipment.
- [Glovebox Worker Awareness](#) (TQ-ERGO-GB) available for those working with this type of equipment.
- [Fire Extinguisher Safety](#) (TQ-FIRE-EXT) available for those working with chemicals with the potential to create a fire.
- [Lead in the Workplace](#) (TQ-LEAD1) available for those handling lead in any setting; required for those exposed above occupational exposure limits.
- [Nanotechnology for Nano Workers](#) (TQ-NC-HS2) required for those handling unbound nanomaterials in a laboratory.
- [Nanotechnology for Support Personnel](#) (TQ-NC-HS1) available for those entering areas with unbound nanomaterials.
- [Methylene Chloride Training for HazCom Operations](#) (TQ-MCAT) required for those handling Methylene chloride at levels that create a Regulated Area in a HazCom area or laboratory.

Guidance

- For more information, contact the Department/Division [Training Coordinator](#) or see the BNL [Training and Qualifications](#) Web site. Develop and implement worker training programs regarding hazards of chemicals and protective measures (HazCom Training).
- All workers needs to know the location of emergency eyewash, safety shower, fire alarm pull-box, telephone, fire extinguisher, and spill control materials before beginning work.
- Operation/procedure-specific training is provided individually or in small groups by the line manager. The purpose of this training is to review the hazards of a worker's assigned work, the uses and limitations of controls, the warning signs of exposure to hazardous materials used in the operations (e.g., odors, irritation, etc.), and the emergency procedures for off-normal events. Line managers are responsible for ensuring workers are trained in the hazards and controls associated with new materials introduced into the work area.
- [Safety & Health Representatives](#) are available to assist line management in providing job specific training on chemical hazards.

Chapter 2.0

Chemical Procurement, Acquisition, and Inventory

Brookhaven National Laboratory accounts for chemicals accounted in the [Chemical Management System \(CMS\)](#). CMS provides a site-wide chemical inventory to chemical owners, ES&H staff and emergency response teams. Chemical inventory reports are also provided for compliance with DOE, EPA, and NY State regulations. Chemicals are to be accounted for in one of the following categories:

- Bar-coded with a CMS label;
- Static Inventory Designation list; or
- Exempt from CMS.

See [What Chemicals Need to Be Inventoried in the CMS](#).

Required Procedure

- A. Order chemicals using a CMS approved method described in Section 1 of the [Chemical Safety](#) Subject Area.
- B. Manufacturer-labeled chemical containers obtained by a CMS approved method are inventoried and bar-coded in the Chemical Management System and containers are added to the inventory during processing for delivery to users.
- C. Manufacturer-labeled chemical containers brought on-site by BNL staff require the container owners to register the chemical using the [Web Transactions and Forms](#) page of the CMS Web site. (Unless a specific CMS exemption applies). Once registered, a barcode is sent from the CMS team to be placed on the chemical container by the container owner.
- D. The container owner is responsible for the CMS record that covers the containers in an area in the following manner:
 - Providing information during the completion of chemical purchase requisition;
 - Providing information via a CMS-approved credit card source;
 - Completing and returning information that is provided with any BNL stock chemical purchase;
 - Completing paper work enclosed with shipping papers when none of the above processes are used; or
 - Notifying the [CMS Team](#) if a chemical has not been properly assigned to a location or user.
 - Informing CMS to remove the chemical from the inventory when moved or consumed (see Requirements E, F, and G).
- E. Update a static posting when the inventory of chemicals changes in the area by one of the following methods:
 - Use the Create/Edit/Delete Static Inventory online on the CMS Web site.

- Use the Create/Edit/Delete Static Inventory on a paper form. This form is available online from on the [CMS Website](#) or contact the [CMS Team](#) for additional assistance.
 - Markup a COPY of an existing static posting and send it to the CMS team at Building 120. Do not remove the original static posting unless all chemicals have been removed and the entire inventory on the list is being deleted.
- F. When bar-coded chemical containers are moved between locations or owners, provide the new information including: date, bar code number, contact person, organization code, building and room number. Do not remove the bar code. Transfer bar-coded chemical containers using one of the following methods:
- [Web Transactions and Forms](#) page of the CMS Web site
 - Paper [Chemical Transfer Sheet](#). Forward the Chemical Transfer Sheet with the new information to the CMS Team, Building 120.
- G. When a container is empty or placed into a hazardous waste accumulation area, delete the barcode from the CMS inventory by one of the methods below:
- Deface or remove the bar code from the container; delete your bar code online using the [Web Transactions and Forms](#) page of the [CMS website](#).
 - Remove the bar code, attach the bar code or write in the number on the Removal Sheet and send it to CMS, Building 120. Bar Code Label Removal Sheets can be obtained from the CMS Team or from the [Chemical Management System Website](#).
-

Guidance

- New chemical containers arriving on-site via the Web Requisition System are automatically inventoried and bar-coded as necessary at the Receiving Building by the Safety and Health Services Division's CMS Team.
- The line organization should periodically coordinate with the CMS Team to ensure that chemicals in their areas are inventoried accurately and up-to-date.
- Non-manufacturer containers (such as bottles, flasks, and test tubes) can be bar-coded on request. However, this is optional. Contact the CMS team.
- The Revolving or Static inventory allows for the tracking of chemicals without the placement of a bar code directly on the container. Static inventory bar-coding is typically used for high turnover (revolving) product that is used more than once a year. An inventory posting is provided with the bar-code numbers at the work location that indicates the maximum number of containers of the items that you use. Examples of items that are typically found on static postings are: compressed gas cylinders, spray paint, glues, janitorial supplies, and home use type products.
- Chemicals are recorded in the CMS database under a specific location (building, room, set of rooms, work area), and optional specific storage location (e.g., flammable cabinet).
- Chemical inventories are recorded in the CMS database under a specific Chemical Owner (Contact Person). The Human Resources Division notifies the CMS Team of upcoming employee terminations. The CMS Team sends the terminating Contact Person, their supervisor and their ES&H Coordinator a report listing their assigned chemical inventory.

The Contact Person is responsible for reconciling their chemical inventory before departing and notifying the CMS Team as to its final disposition. If you change status as an employee of BNL and return as a guest, inform the CMS Team of your new guest number so that your inventory can be updated accordingly. [Chemical Transfer Sheets](#) can be obtained from the CMS Team or from the [Chemical Management System Website](#).

- When transferring to another Department/Division, notify the CMS Team as to your new organization, as well as the disposition of your chemical inventory. Notify the CMS Team when a "Request for Change in Employee Status" Form (BNL F 1081) is prepared for a person on the Contact Person List.

Chapter 3.0

Chemical Hazard Assessment and Planning Requirements

Hazard Assessments identify the hazards and necessary controls for chemicals used in shop, field, and laboratory work environments. These evaluations are part of the Work Planning process. See the [Work Planning and Control for Experiments and Operations](#) Subject Area for further information.

Exposure Assessments evaluate the potential airborne and dermal exposure to workers to ensure that occupational exposure standards are met and that protective measures are implemented.

Required Procedure

- A. In laboratories: Develop Standard Operating Procedures (or equivalent) that addresses the safety and health considerations for laboratory work that involves the use of hazardous chemicals. The requirements and guidance in this Chemical Hygiene Plan Chapters 4.0 to 11.0 along with the controls in the Experimental Safety Review (ESR) provide the equivalent documentation for routine laboratory operations.

When hazardous activities are not covered by the CHP and ESR, complete the [Work Planning and Control for Experiments and Operations](#) (WP&C) documentation and update the documentation when new chemical hazards are introduced. Use a planning tool, such as:

- A formal Standard Operating Procedure,
- Prescribed work document: instructional work documents (e.g., written and approved internal procedures, contractor health and safety plan, contractor procedure, and vendor operating or maintenance manuals), or
- Work Permit Form.

- B. In HazCom area: Complete the [Work Planning and Control for Experiments and Operations](#) (WP&C) documentation when planning chemical operations and update the documentation when new chemical hazards are introduced. WP&C uses one the following processes to plan and control work, depending on the hazards, complexities, and job coordination levels:

- **Project Management**
- **Standard Operating Procedures**
- **Work Planning and Control for Operations**, which uses three methods:
 - (1) **Worker planned work:** recognizes the skill levels and technical capabilities of the workers. Worker planned job activities do not require the level of rigor detailed in permit planned work,
 - (2) **Prescribed work:** relies on instructional work documents (e.g., written and approved internal procedures, contractor health and safety plan, contractor procedure, and vendor operating or maintenance manuals).

- (3) **Permit planned work:** requires use of a site-wide Work Permit Form for all moderate- and high-hazard work that is not covered by prescribed work documents.

For Non-routine Tasks: Any of the processes listed above may be used for non-routine tasks, as long as the organizations performing work uses the method to inform employees of the hazards of non-routine tasks (for example, the cleaning of reactor vessels).

- C. In a laboratory: If working with a hazardous chemical occurs outside of an engineering control in a manner capable of generating airborne levels of chemicals (see Chapter 4.0), contact a [Safety & Health Representative](#) for an evaluation of the need for exposure monitoring. The [Safety & Health Representative](#) will determine if chemical operations have been previously characterized by worker exposure monitoring or if additional monitoring is needed. This requirement should be addressed in the Experimental Safety Review (ESR) review by ESH professional.
- D. In a laboratory: If working with OSHA Particularly Hazardous Substances, contact a [Safety & Health Representative](#) for an evaluation of the need for exposure monitoring. The [Safety & Health Representative](#) will determine if chemical operations have been previously characterized by worker exposure monitoring or if additional monitoring is needed. This requirement should be addressed in the Experimental Safety Review (ESR) review by ESH professional.
- E. In a HazCom area or laboratory: If work with an OSHA Regulated Substance (29CFR 1910.1002 to 1119) generates employee exposures above the occupational exposures above the OSHA Permissible Exposure Limits, create a regulated area for compliance with requirements in the applicable OSHA Standard.

Guidance

- Plan to order the smallest quantity of chemical to meet immediate needs. Avoid purchasing more than needed (i.e., to get a volume discount).
- Plan to perform the task in an area where chemicals can be safely handled and make provisions for compatibility with other operations in the area/building; engineering controls (e.g., ventilation of vapors, fumes, or dust); fire protection concerns; and decontamination concerns.
- An exposure assessment is performed to determine the risk of personnel exposure to hazardous chemical, or physical agents, and the adequacy of hazard controls. Results of exposure assessments are used to validate or improve hazard controls, to extend the same controls to workers with similar exposures, to provide workers with appropriate medical tests and examinations (i.e., medical surveillance) to monitor worker health, and to demonstrate compliance with regulations. Exposure assessments may be either qualitative or quantitative assessments of risk. Qualitative exposure assessments result from observation and the use of

professional judgment, whereas quantitative assessments involve conducting measurements (i.e., exposure monitoring) or by estimating or modeling of exposures.

- Worker exposure monitoring may be needed to verify that exposure levels do not exceed the OSHA action level, OSHA Permissible Exposure Limit [PEL] and ACGIH Threshold Limit Value®). The main type of exposure monitoring is personal (or breathing zone) air sampling. Other techniques that assist in determining worker chemical risk include wipe sampling and bulk sampling.

Chapter 4.0

General Chemical Safety Work and Control Practices for All Chemicals

Work Planning is designed to minimize worker exposure to hazards by utilizing the hierarchy of controls when controlling workplace hazards. Work practice controls include pre-planning work, practicing good housekeeping and personal hygiene to minimize exposure to hazardous materials, and using common sense. Work practice controls must be used regardless of the type of hazardous material handled. See Chapter 6 for special handling instructions for specific chemicals.

Determine controls based on the following hierarchy of controls and implement them accordingly:

- Elimination of hazardous chemicals: elimination of hazard source, such as removing a hazard in the design process; or elimination of exposure by design, such as eliminating exposure to a source in the design.
- Substitution of a chemical to a less hazardous chemical.
- Reduction of a chemical's hazard, such as reducing a source's potential to expose worker by concentration, pressure, or temperature.
- Engineering controls: controlling a hazard with a mechanical device, as in a ventilation system (such as a lab hood or local exhaust).
- Warning Systems: audible and visual signals;
- Administrative controls: procedures, rules, and training.
- Personal protective equipment worn/used by a worker, such as glasses/face shields; respirators; head/body/hand protection (lab coats, hard hats, coveralls, gloves); etc. (See the [Personal Protective Equipment and Respirators](#) Subject Area).

The best controls are those that eliminate the hazard. Next are those that control the source or shield the worker from the source. Next is work planning that limits workers exposure to the source. Finally, the least desirable approach for controlling exposure is the use of protective equipment worn by the worker. Contact the [ES&H Coordinator](#) for assistance.

Required Procedure

- A. The Principal Investigator, responsible person, or Supervisor incorporates the controls, work practices, and emergency measures of this CHP into their work planning and control documents (see the [Work Planning and Control for Experiments and Operations](#) Subject Area).
- B. Conduct operations with hazardous chemicals in a functioning laboratory hood, glove box, or other engineering controlled setting whenever feasible. When engineering controls are not feasible, use administrative controls, work planning, and Personal Protective Equipment (PPE) to minimize risk to any possible exposure. Examples of operations that need controls

are reactions, pouring, evaporation, or other vapor, mist, fume, or dust-generating operations that have the potential for worker exposure. Exhaust ventilation (such as laboratory fume hoods, glove boxes, “snorkels” or industrial ventilation) is required when handling chemicals in a manner that can produce an airborne hazard. Use ventilation for:

- Particularly hazardous substances (i.e., acutely toxic, carcinogenic, or reproductive toxins);
- Sensitizers;
- Volatile toxic liquids;
- Organic liquids or solvents;
- Procedures that generate airborne particulates (e.g., dust) or liquid aerosols of even moderately toxic chemicals;
- Diluting concentrated acids and bases;
- Discharging gases/vapors from vacuum pumps and distillation columns;
- Discharging harmful gases and vapors from drying ovens and muffle furnaces.

C. Observe limitations on food, beverage, and cosmetics in Laboratory Areas or HazCom Areas:

- Do not consume or store food, candy, gum, or beverages.
- Do not apply cosmetics, ointments, skin cream, or similar items.
- Do not store food in refrigerators.
- Do not use lab microwaves and ovens for food.
- Do not use laboratory glassware or utensils to prepare or consume food or beverages.
- Do not smoke within any BNL building.

D. Proper handling of glassware in Laboratory Areas or HazCom Areas:

- Never use mouth suction to pipette chemicals or to start a siphon.
- Tape or shield vacuum-jacketed glass apparatus.
- Visually inspect glassware.

E. When hazardous chemical operations in laboratories are conducted outside of the normal business hours and no one who is cognizant of the hazards of the operation will be present, complete and post the Unattended Chemical Experiment Form. Follow the instructions on the Unattended Chemical Experiment Form and Instructions.

F. Use and store Explosives, Organic Peroxide- Class UD, Oxidizer- Class 4, Pyrophoric, and Unstable (reactive)- Class 4 or Class 3 detonable (based on Fire Code of New York State and NFPA 5000) only in a building 100% equipped with an automatic sprinkler system. Check with the [Fire Protection Engineer](#) if there is any question on the status of a building.

Guidance

Working Alone:

- Working alone (after 5pm and on weekends) is strongly discouraged.

- If unavoidable, obtain Supervisor approval and verify that someone else is in the general area and is aware of your work with chemical activities, including the location and duration of the work; or
- Notify the Safeguards and Security Division at x2238 of location, duration of work, and estimated time of departure.

Work areas:

- Keep work areas clean and free of obstructions. Clean the work area at the completion of an operation or at the end of the day. Reducing clutter reduces the chances for an accident and minimizes the effects if an accident does occur.
- Wipe drips and residues from containers of hazardous materials. Skin contact with residues may cause dermal absorption, chemical burns, skin irritation, and possible accidental ingestion as a result of hand-to-mouth transfer.
- Clean spilled chemicals immediately and dispose of all wastes properly.
- Do not use stairways and hallways as storage areas. Store equipment and chemicals properly and avoid clutter.
- Keep working quantities of all hazardous materials to a minimum. Procure, use, and store the minimum amount of material necessary.

Personal Hygiene:

- After handling chemicals, wash hands with soap and water before leaving the laboratory/shop area.
- Always remove gloves before touching common use items such as phones, doorknobs, and computers to prevent contamination.
- Confine long hair and loose clothing when working in the laboratory/shop.
- Remove jewelry to prevent contact with electrical sources and chemicals and from catching on laboratory or shop equipment.

Workplace Controls:

- Nonhazardous chemical operations may be done on lab benches. These types of operations are those that have negligible risk to eye, skin, or inhalation exposure (no potential to create airborne levels of chemicals above ambient levels).
- Limit work with hazardous chemicals on laboratory benches to operations such as opening packing boxes, preparing labels for containers, handling closed containers of chemicals, and preparing non-hazardous test media or equipment (i.e., operations that do not have the potential to result in worker exposure to hazardous levels of chemicals).
- Use glove boxes or gas cabinet for operations involving alkali metals and pyrophoric materials. The need for ventilation and monitoring of highly toxic and toxic gases are described in the [Compressed Gas Cylinders and Related Systems](#) Subject Area.
- Use plastic or metal connectors should on gas tubing whenever possible.
- Refer to the [Compressed Gas Cylinders and Related Systems](#), [Pressure Safety](#), [Fire Safety](#), [Cryogenics Safety](#) Subject Areas for requirements and guidance for operations with pressurized/evacuated systems, lab equipment, and cylinders of gases.

- Some organizations may require approval for purchase of chemicals. Contact your ES&H Coordinator.
- Substitute a safer chemical when possible. A [Safety & Health Representative](#) can be consulted to provide assistance to identify substitute chemicals.
- Engineering controls include local exhaust ventilation systems, laboratory fume hoods, enclosures and shields. Except for substitution, these provide the most effective means of control because they enclose the hazard or physically separate it from the worker.
- Some chemical fume hoods need to be manually restarted after a power outage. Check to be sure there is flow in the hood before using it.
- Administrative controls (or work practice controls) are changes in work procedures such as written safety policies, rules, supervision, schedules, and training with the goal of reducing the duration, frequency, and severity of exposure to hazardous chemicals or situations. Although administrative controls can (and should) always be used to control worker exposure, they are prone to human error and cannot be relied upon to reduce exposure all the time. Additional control mechanisms such as substitution of less hazardous materials/procedures, engineering controls and personal protective equipment (PPE) may be required to address worker exposure to the hazard(s). Some specific examples of administrative controls include:
 - Perform maintenance operations that involve toxic substances at night when the usual production workers are not present.
 - Rotate workers through various job assignments so that their exposure time is lessened.

Glassware:

- Use adequate hand protection (e.g., proper gloves) when inserting glass tubing into rubber stoppers or corks, or when placing rubber tubing on glass hose connections.
- Protect hands (i.e., use tools or wear tear- and puncture-resistant gloves) when picking up broken glass.
- Glass tubing should be fire-polished or rounded and lubricated, and hands should be held close together to limit movement of glass should fracture occur.
- Dispose of glass in marked cardboard boxes or bags designated for that purpose. Glassware must be free of liquids prior to disposal.

Chapter 5.0 Personal Protective Equipment

Personal protective equipment (PPE) is used to supplement but not substitute for engineering and administrative controls. PPE includes chemically resistant gloves, eye wear, footwear, lab coats, aprons, coveralls and respiratory protection. PPE may be used as a sole means of control if the use of other controls is not feasible. Provide PPE at no personal expense to the individual. To be effective, workers must understand the proper selection, use and limitations of PPE. For additional information on BNL's policies on PPE, see the [Personal Protective Equipment and Respirators](#) Subject Area.

Required Procedure

- A. Follow the Area-based Personal Protective Equipment requirements posted at entrances to areas where chemicals are stored. Follow: SBMS *PPE & Respirators* Section [1. Planning for Area-Based Personal Protective Equipment Requirements](#).
- B. Follow the Operation-based Personal Protective Equipment requirements for work with chemicals that is specified in one of the following:
 - SBMS *PPE & Respirators* Section: [2. Planning for Use of Operation-Based Personal Protective Equipment](#)
 - SBMS *Chemical Safety*: Exhibit [Personal Protective Equipment Requirements for Working with Chemicals](#), or
 - PPE requirements in other sections of this Chemical Hygiene Plan, or
 - Work Planning and Control document (such as an ESR, Job Risk Assessment [JRA], Facility/Area Risk Assessment, Work Permit).If not addressed in any of the above sources of PPE requirements, have a workplace hazard assessment performed by the ESH professional with written certification that evaluates the prevention of injury or impairment of any part of the body through absorption, inhalation or physical contact. Document the workplace evaluation on the [Operation-Based Protective Clothing Selection Form](#), or other appropriate document.
- C. Principal Investigator or supervisor communicates PPE requirements to each affected worker and ensures that each worker is knowledgeable in the PPE they use (what PPE is necessary; its limitation; how to properly don, doff, adjust, and wear it; and the proper care, maintenance, useful life and disposal of the PPE). Training for supervisors and workers is provided in:
 - [Laboratory Standard](#) (HP-IND-220) or [Hazard Communication](#) (HP-IND-200);
 - [Chemical Protective Clothing User Training](#) (HP-OSH-157) and
 - [Respirator - Air Purifying & Powered Air Purifying](#) (HP-IND-301-W) Training.
- D. Workers are responsible to maintain PPE for eyes, face, head, and extremities in a sanitary and reliable condition and report problems with PPE to Principle Investigator or Supervisor

immediately. Keep lab coats free of chemical contamination by laundering or frequent replacement. See the SBMS *PPE & Respirators* Exhibit [Lab Coat Ordering and Laundering](#) in the [Personal Protective Equipment and Respirators](#) Subject Area.

- E. Remove contaminated lab coats, coveralls and gloves prior to going to common areas such as lunch rooms, conference rooms, offices, rest rooms, and the cafeteria, and entering personal vehicles to avoid transferring any potential contamination. Remove gloves before touching common use items such as phones, computers, light switches and door knobs. Follow SBMS *PPE & Respirators* Exhibit [Lab Coat Use and Storage](#)
- F. Ensure that contaminated PPE is properly disposed of. Consult with the Department/Division [Environmental Compliance Representative \(ECR\)](#) for information on disposal of PPE with known chemical contamination.
-

Guidance

- Consult a [Safety & Health Representative](#) to provide guidance on the hazard assessment and proper selection and use of PPE.
- Normally, disposable PPE used in laboratory settings (such as gloves, Tyvek coveralls, and booties) with no known contamination may be disposed of as regular trash. Tyvek PPE may be eligible for recycling - consult with an Environmental Compliance Representative.
- Wear gloves when using hazardous chemicals, when handling materials at temperature extremes or when handling materials with sharp or rough surfaces.
- Store gloves in a clean area outside of fume hoods and away from equipment that could potentially contaminate them.
- Factors to consider in selecting gloves include how and where they will be used. In shop environments, gloves may be subjected to rougher handling and may be totally immersed in chemicals such as cleaners and degreasers. However, in labs, manual dexterity may be an issue, and splashes, as opposed to total immersion in the chemical, are more common. Gloves used in shop settings are thus recommended to be more resistant to tears and abrasion than those used in laboratory environments and are normally thicker (greater than 10-15 mils). In laboratories, thin, lightweight gloves are generally preferred (less than 10 mils). As a point of reference, typical dishwashing gloves are approximately 15 to 20 mils thick, and surgical latex gloves are on the order of 3 to 8 mils thick.
- Consider an individual's sensitivity to the materials and chemicals used in the manufacture of gloves. Some people have allergic reactions to natural rubber proteins in latex, glove powder (used for absorbing perspiration), or other chemical constituents, such as rubber accelerators.
- Chemically resistant gloves are manufactured from a variety of materials, including nitrile, neoprene, polyvinyl chloride, natural rubber (latex), and Viton. No single glove material provides universal protection against all chemical agents. Therefore, select gloves on the basis of their resistance to the material(s) being handled, their suitability for the procedures being conducted, and their resistance to wear, as well as temperature extremes. Consult MSDSs and follow the instructions in the work planning documentation, or consult a

[Safety & Health Representative](#) if you have any questions about a particular chemical compound. See the [Chemical Resistance Chart](#) for guidance in choosing chemical protective material by Chemical Class. The Web sites from glove manufacturers are helpful in determining the best gloves for chemical exposure applications.

- Safety glasses are the minimum protection when handling hazardous chemicals. Supplement safety glasses with chemical splash goggles and/or face shields when there is a greater risk of exposure to chemical splashes or flying particles (e.g., when pouring or mixing chemicals or cryogenics). Chemical splash goggles are recommended for operations where there is a greater risk of exposure to chemicals. Cover goggles are recommended where there is a greater risk of flying particles. They are also recommended for activities producing airborne eye irritants including gases, vapors, fumes, dusts, and mists. Safety glasses provide no protection against eye irritants.
- Contact lenses may be worn in work areas. However, contact lenses do not provide eye protection and sometimes removal of the lenses are recommended depending on the work.
- Face shields protect the entire face and are recommended for operations that present a high likelihood of exposure to flying particles or splashes from liquid chemicals or cryogenic fluids. Use face shields in conjunction with safety glasses or chemical goggles, because face shields can be lifted up during use, exposing the eyes to hazards. Safety shields are used for protection against possible explosions or uncontrolled reactions.

Chapter 6.0 Additional Controls Practices for Specific Hazardous Chemicals

Several chemicals and classes of substances have unique and additional hazards identification, controls, and PPE that are to be followed in addition to the requirements in Chapters 1-5:

6.1 Acids and Bases

Required Procedure

- A. Identify acids and bases used in the work area. Review sources such as [MSDSs](#) for specific compounds.
 - B. Assess the hazards, controls, and Personal Protective Equipment necessary to limit worker exposures to these agents in the Work Planning and Control documents. Consult the exhibit [Personal Protective Equipment Requirements for Working with Chemicals](#). Consult with an ES&H Coordinator or [Safety & Health Representative](#) for operations not listed in that exhibit.
 - C. Post the area entrances to acid/base use and storage areas with information on the hazards (i.e. “corrosive”) and emergency contact information.
 - D. Use a fume hood or other appropriate exhaust ventilation when handling acids and bases in a manner that may produce an airborne hazard (such as fumes, gases, vapors, and mists). This includes procedures such as transfer operations, preparation of mixtures, blending, sonification, spraying, and heating.
 - E. Ensure an emergency eyewash and safety shower is located within 10 seconds travel time with an unobstructed pathway in areas where acids or bases are used. In the event of skin or eye contact, flush the affected area for at least 15 minutes and contact Emergency Services x-2222 for evaluation and treatment.
-

Guidance

- Acids and bases are corrosive and will destroy body tissue. The extent of injury depends on factors such as the type and concentration of the chemical, the route of exposure, the type of tissue contacted, and the speed used in applying emergency measures. Acids, especially in concentrated form, are most likely to cause immediate pain upon contact with tissues.
- The eyes are especially susceptible to acids and bases and must be immediately flushed with water for at least 15 minutes if exposure occurs. Inhaling acid fumes and airborne dust and mist from bases irritate the nose, throat, and lungs. Pulmonary edema, a severe irritation of the lungs resulting in fluid production that prevents the transfer of oxygen to the

bloodstream, can also occur from intense extreme airborne exposures. Secondary toxic effects may occur if the material is absorbed from the lungs into the bloodstream. The extent of these effects depends on the concentration in air and the duration of exposure. Ingestion causes severe burns of the mucous membranes of the mouth, throat, esophagus, and stomach.

- Dilution of acids and bases is exothermic. This is particularly true for sulfuric acid and potassium hydroxide. Concentrated solutions of inorganic acids and bases are not in themselves flammable. Combustion can occur, however, when an oxidizing acid is mixed with other chemicals or with combustible materials. Acids also react with many metals, resulting in the liberation of hydrogen, a highly flammable gas. Bases such as sodium hydroxide will liberate hydrogen gas upon reaction with aluminum, magnesium, tin, and zinc metal. Some acids are strong oxidizing agents and can react destructively and violently when they come in contact with organic or other oxidizable materials.
- Transfer 1+ gallon containers of acid and base solutions between work areas in bottle carriers.
- Do not pour water into acid. Slowly add the acid to the water and stir.
- Open bottles or carboys slowly and carefully, and wear protective equipment to guard hands, face, and body from splashes, vapors, gases, and fumes. Wipe drips from containers and bench tops. Be especially careful to wipe up visible residues of sodium hydroxide and potassium hydroxide from all surfaces.
- Cleanup spills per the Work Planning and Control documentation following the [Spill Response](#) Subject Area. Avoid using combustible or reactive materials (such as paper towels) to clean up or absorb large spills. Do not clean up or neutralize acid spills with strong bases (including soda ash, sodium carbonate) and base spills with strong acids. A potential aggressive and exothermic reaction may ensue. Gaseous carbon dioxide generated from the neutralization reaction can cause splattering.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.1A Hydrofluoric Acid (HF)

Hydrofluoric Acid (HF) causes severe skin burns. Even very dilute solutions can cause burns (often painless). These effects may be delayed by several hours with weaker concentrations. High concentrations of hydrofluoric acid will cause immediate pain and tissue destruction. HF deeply penetrates before disassociating. Burns may involve underlying bone. Systemic fluoride ion poisoning from severe burns is associated with low calcium and magnesium and high potassium in the blood and sudden death. Inhalation can cause fluid in the lungs, and severe respiratory burns. Contact with eyes is extremely damaging and painful.

Required Procedure

- A. Ensure Work Planning and Control Documentation (Work Permit or ESR) specifically addresses
 - Personal Protective Equipment (including degradation rate and breakthrough time),
 - Spill Response,
 - First Aid, HF Burn Kit Location, First Aid Training,
 - Method of disposing of HF waste,
 - Special requirements for work with HF after hours must be approved by the OMC Manager and the BNL Chemical Hygiene Officer).
- B. Using the [Designated Area Posting](#) in the subject area or equivalent, post areas where HF is used as a Designated Area (i.e., Highly Acute Toxin). The Designated Area is recommended to be small as reasonably achievable to prevent contamination.
 - Identify the location of Hydrofluoric acid on the [Fire Rescue Run Card system](#) and Hazard Information Placard at doorways.
 - HF must be used in an engineered controlled environment such as a fume hood or glove box.
- C. Follow the decontamination plan in Chapter 8 for the Designated Area and any equipment. The Designated Area must remain posted until decontaminated.
- D. Ensure personnel working with HF in laboratories or personnel who may be expected to give HF first aid take the Lab Standard Training before using HF.
- E. Use the following Personal Protective Equipment:
 - Chemical Splash Goggles when working with any amount of HF. A Face shield is required when handling solutions greater than 2% (1 molar), or if high splash potential exists.

- Long pants and a long sleeve shirt (or an ankle length skirt/dress with long sleeve shirt); Lab coat; HF resistant Apron (e.g., thick butyl rubber, neoprene, etc.) when handling solutions greater than 2% (1 molar), or if high splash potential exists.
 - Socks and fully enclosing shoes are required.
 - Impervious gloves are required. (See Guidance for recommendations on glove materials).
- F. Do not work alone with HF. Two HF trained people must be able to communicate verbally and be within hearing range of each other at all times while HF is being used.
- G. Do not work outside of normal working hours (unless approved by OMC and the BNL Chemical Hygiene Officer).
- H. Store HF properly as per Chapter 7 Chemical Storage.
- I. Provide Emergency Equipment:
- Ensure an eye wash station and shower is within the immediate area.
 - Provide an HF Burn Kit within the immediate area. Report the location(s) of HF Burn Kits to the BNL Chemical Hygiene Officer (CHO) so it is included in site inventory of HF Burn Kits which helps facilitate the annual inspection program.
 - Inspect HF Burn Kits on an annual basis using the Checklist located in the burn kit. Contact your [Safety & Health Representative](#) for assistance in the inspection. Include the following in the inspection:
 - Examine the outside of the case for chemical contamination, damage, cracks and broken closures. Replace/clean if necessary. If contamination is suspected, don gloves before handling the kit.
 - Examine the Calcium Gluconate tubes for expiration dates. Replace if expired.
 - Observe the conditions of disposal gloves in the kit. Replace if they are degraded, cracked, discolored, or damaged.

Additional Information

Recommended Spill Response Actions for HF

- Large Quantity (>10 ml) or any quantity outside of fume hood: Evacuate area. Call x2222. Do not attempt clean-up of HF and avoid inhalation of Vapors.
- Small Quantity (<10 ml) Inside Fume Hood: Apply powdered calcium carbonate or calcium hydroxide or use a commercial HF Spill kit, such as HF Acid-Eater (NPS Corp) or HF Spill Tamer (JT Baker/Mallinckrodt). HF is a weak acid and does not completely dissociate. Therefore, sufficient time must be allowed for the neutralizing agent to neutralize the acid. Properly dispose of waste.

First Aid for HF Exposure: Because the worker may not feel an HF burn immediately, assume any liquid exposure detected is HF and respond per the first aid instructions in the exhibit [HF Burn First Aid Directions](#).

Guidance

Working with HF

- Do not transfer HF in glass or metal containers as it is reactive with these materials. Always use non-HF reactive tools (e.g., Platinum, Teflon, etc.) for immersion work. Never perform immersion work with hands, even if gloved.
- Some HF containers have a yellow dye indicator around the mouth of the bottle to indicate if the cap on the bottle has failed. Send bottles that indicate failure to Waste Management.

Personal Protective Equipment Recommendations for Work with HF

- Chemical Splash gloves are not approved for spill cleanup. A combination of an inner composite glove with a heavy Neoprene outer glove is recommended.
- Gloves for spill cleanup are required to be Neoprene, Butyl rubber, or composite type gloves, or combinations of these gloves with a manufacturer approved degradation rate and breakthrough time greater than the anticipated length of operation. Glove choice and glove combinations for use with HF are a very important component of protection from HF. Contact the Chemical Safety Subject Matter Expert (Chemical Hygiene Officer) for specific advice regarding your application. Below are recommended glove choices:
 - <2% concentration (1 molar) and no splash potential - Neoprene disposable gloves (e.g., Ansell brand Neotouch). Nitrile disposable gloves are not recommended for HF use. Gloves are to be immediately removed or changed out if there is any HF contact on gloves;
 - >2% concentration or if a splash potential exists - Neoprene, Butyl rubber, or Silver Shield or Barrier composite type gloves with a degradation rate and breakthrough time greater than the anticipated length of operation are required (e.g., Ansell Brand Dermashield offer good dexterity and clean room quality for these type of operations);
 - >20% concentration - Neoprene, Butyl rubber, or Silver Shield type gloves with a manufacturer approved degradation rate and breakthrough time greater than the anticipated length of operation are required.
- A combination of double gloving that meets the degradation and breakthrough criteria is acceptable and often the preferred method of hand protection when working with concentrated HF (e.g., an impermeable glove underneath a close forming glove).
- The dexterity requirements of the operation should be taken into consideration when selecting gloves. Neoprene is the glove of choice for dexterity. Some vinyl gloves may be acceptable for breakthrough but are slippery when wet.
- Always check gloves for breakthrough (leaks) prior to use. Discard any damaged gloves.
- Decontaminate reusable gloves after use per the decontamination plan described in the experimental work planning.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals

6.1B Etching Solutions (e.g., Piranha Etch, Aqua Regia, Nochromix®, etc.)

The hazards of *Etching Solutions*, which are mixtures of strong corrosive and oxidizing chemicals, are:

- **Pressurization**– Pressure will develop in sealed bottles causing potential violent vessel failure/ rupture. For solutions containing a strong oxidizer such as hydrogen peroxide, this can occur weeks to months after use.
- **Violent reaction** – resulting from mixing with organic compounds (e.g., acetone, photoresist, isopropyl alcohol, and nylon),
- **Highly corrosive** – vapors are acidic and destructive to mucous membranes
- **Inhalation hazard** – severe
- **Exothermic** – self heating upon mixing and contact with organic materials, potentially exceeding 100°C.

Common *Etching Solutions* used at BNL include (not inclusive):

<i>Etching Solutions</i>	
Name	Composition (peroxide containing formulations)
<i>Piranha etch</i>	Traditionally 3:1 mixture (range from 2:1 to 7:1): Sulfuric acid (H ₂ SO ₄) 98% and Hydrogen peroxide (H ₂ O ₂) 30%
<i>Base piranha</i>	3:1 mixture of Ammonium hydroxide (NH ₄ OH) and Hydrogen peroxide (H ₂ O ₂) 30%.
<i>Nakagawa Etch</i>	3:2:2 mixture of : Hydrofluoric Acid (HF); Hydrogen Peroxide (H ₂ O ₂); and Water
<i>RCA clean</i>	<i>SC-1 Organic Clean</i> is 1:1:5 mixture of: Ammonium Hydroxide (NH ₄ OH) 28%; Hydrogen Peroxide (H ₂ O ₂) 30%; and Water
	<i>DHF Oxide Strip</i> at 25°C. mixture of: Hydrofluoric Acid (HF) and Water
	<i>SC-2 Ionic Clean</i> 1:1:6 mixture of: Hydrochloric acid (HCl); Hydrogen Peroxide (H ₂ O ₂); and Water
<i>Nano Strip™</i>	Mixture of: Sulfuric Acid (H ₂ SO ₄) (90%); Peroxymonosulfuric Acid (5%); Hydrogen Peroxide (H ₂ O ₂); (<1%); and Water (5%).
<i>Hydrochloric acid/ Hydrogen peroxide</i>	Mixture of: Hydrochloric acid (HCl) and Hydrogen Peroxide (H ₂ O ₂) 3%
Name	Composition (peroxide-free formulations)
<i>Aqua regia</i>	1:3 mixture of: Nitric acid concentrated (HNO ₃) and Hydrochloric acid (HCl)
<i>Bromine/Methanol Solution</i>	Bromine (Br ₂); Methanol (CH ₃ OH)

<i>EAg Solution</i>	Nitric Acid (HNO ₃); Water (H ₂ O) : Potassium Dichromate (K ₂ CrO ₇): Silver Nitrate (AgNO ₃)
<i>Everson Solution</i>	Hydrogen fluoride(HF): Nitric Acid (HNO ₃): Lactic Acid
<i>Nochromix®</i>	Mixed by user: Proprietary powder- Ammonium peroxodisulfate ((NH ₄) ₂ S ₂ O ₈) and Sulfuric Acid (H ₂ SO ₄)
<i>Saucedo Solution</i>	Hydrogen fluoride (HF): Nitric Acid (HNO ₃): Water (H ₂ O): Silver Nitrate (AgNO ₃)

Required Procedure:

- A. Include the hazards and controls of *Etching Solutions* in Experimental Safety Review and/or Standard Operating Procedure (SOP) documentation.
- B. Indicate the location of *Etching Solution* operations in:
- Hazard Validation Tool described in the [Signs, Placards, and Labels for ESH Hazards](#) Subject Area.
 - Chemical Management System (CMS) inventory. Contact the CMS Team to have a room where *Etching Solution* operations take place added to the inventory.
- C. Ensure workers handling the corrosives are knowledgeable in the hazards and risks and how to protect themselves, including:
- Health effects and routes of exposure (e.g., ingestion, inhalation, and skin contact).
 - Personal protective equipment and engineering controls.
 - What to do in case of emergency.

The [Laboratory Standard](#) (HP-IND-220) and Corrosive Etch CBT (TQ-CorrosiveEtch) courses cover the special hazards.

- D. Wear appropriate Personal Protective Equipment (PPE) when mixing, pouring, or using *Etching Solutions*.
- Area-based PPE required for entry into the room/area.
 - Lab coat, long pants (or an ankle length skirt/dress with long sleeve shirt), socks and fully enclosing shoes.
 - Impervious gloves
 - Reusable gloves: (Neoprene, Nitrile, butyl) when mixing solutions and when significant contact possible
 - Disposable nitrile gloves: only when significant contact is not probable.
 - Apron (when high splash potential exists).
 - Eye & face protection:
 - Hydrofluoric acid (HF) containing etchant:
 - Splash Goggles when working with any amount of HF.
 - Face shield when handling solutions greater than 2% (1 molar) or if high splash potential exists.
 - All other non-HF acidic etchant, use one of the following:

- Safety glasses with side shields and lowered lab hood sash or
- Safety glasses & face shield or
- Combo goggle/faceshield unit.

E. Prepare limited amounts of *Etching Solution*:

- Purchase the least amount of material the work requires. Avoid buying large quantities of the components for the savings from bulk quantities. This increases the hazards in the area.
- Do NOT mix *Etch Solutions* with organic compounds, as it will result in a violent reaction. This includes, but isn't limited to, acetone, photoresist, isopropyl alcohol, and nylon. Remove containers of organic compounds from the mixing area.
- Use the *Etching Solutions* on the day they are mixed unless a multiple day policy is specifically addressed in an ESR. Note: Storage of most solutions for future use is not permitted and in most cases impacts the effectiveness of the etching process.

F. Conduct etching operations safely to prevent over-pressurization and splashing of solutions.

- *Etching Solutions* are not meant to clean large amounts of organics coatings from surfaces.
 - Clean surfaces of organic material as much as possible before immersion into *Etching Solutions*.
 - Rinse and dry substrates before placing them in an *Etching Solution*.
- Work within a chemical fume hood with the sash between you and the solution.
- Mix etchant solutions in open top vessels (such as beakers).
- When preparing acidic solutions, add peroxide to the acid very slowly and carefully.



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- Make sure the open top vessel is clearly labeled with the contents, for example:

Acidic Piranha Etch
Sulfuric acid; Hydrogen Peroxide

- At the end of etching, leave the open top vessel in the secondary containment in the fume hood (sash lowered). Leave the vessel un-covered to cool and off-gas for a minimum of 12 hours.

- Post the room with the [Unattended Chemical Experiment Form and Instructions](#) for the period the *Etching Solution* is left unattended, such as overnight. The document may be posted at the lab entrance, or in a noticeable spot near the experiment, such as on the hood sash.
- The *Etching Solution* must stop reacting (no longer generating heat and finished outgassing) before being transferred to a waste container that will be capped. To verify, swirl the vessel and verify no bubbles are formed (i.e. off-gassing has stopped). The temperature should have also cooled to room temperature.

WARNING
Always allow used solution to cool down and stop reacting prior to adding to a closed container. Even a container with pressure relief may over pressurize if the solution is actively outgassing.

- Depending on the etchant strength, composition, and organic compounds present in the mixture, several days to weeks may be necessary until it is safe to transfer to a waste container that will be capped.

G. Use the waste container specified in your ESR, or SOP (See Step H). Solutions collected in inappropriate containers will not be picked up by Waste Management.

- Use a new container. Do not use recycled solvent bottles.
- The containers in the table below are suitable for use with *Etching Solutions*:

Vented cap for 2.5 liter glass containers and plastic containers (screw size 38-430)	BNL Stock Room Item C15972 [Performance Systemix Inc. product #38439C4/RC.] (Cap has an air permeable membrane and small hole in top of the cap.)	
Bottle for basic solutions & acidic solutions (except HF):	BNL Stock Room Item C15970 [Poly-coated glass container Sigma Aldrich Poly-coated acid bottle (2.5 L) product #Z568686; 12/case].	
Bottle & cap for HF acid solutions:	Polyethylene container and polyethylene cap.	

<p>Eco Funnel System (Can be used for acidic and basic solutions, with and without peroxide)</p>	<p>Polyethylene container or poly-coated glass container with sealable funnel (preferred for all peroxide containing etchants)</p>	
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- Waste containers must be managed in a satellite accumulation area (SAA) in accordance with the [Hazardous Waste Management](#) Subject Area requirements.
- While in the SAA, the containers must be labeled with an etch warning label, a hazardous waste label and the contents of the container.

<div style="border: 2px solid orange; padding: 10px; text-align: center;"> <p>WARNING</p> <p>Over-pressurization and Explosion Hazard</p> <p>Etching Solution May Off-gas</p> <p><u>NO ORGANICS</u></p> </div>	<div style="border: 2px solid red; padding: 10px;"> <p style="text-align: center; font-size: 24px; font-weight: bold; color: white;">HAZARDOUS WASTE</p> <hr/> <p>NRWCF No. _____ Generator <u>J. SMITH</u> Building _____ Dept. Code _____ Phone _____ Hazardous Contents (must include chemical name(s)) <u>SULFURIC ACID</u> <u>HYDROGEN PEROXIDE</u></p> <hr/> <table border="0" style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>Hazardous Properties (check all that apply)</p> <p><input type="checkbox"/> Ignitable <input type="checkbox"/> Toxic <input type="checkbox"/> Reactive <input checked="" type="checkbox"/> Corrosive <input checked="" type="checkbox"/> Other <u>OXIDIZER</u></p> <p>Waste Form</p> <p><input type="checkbox"/> Solid <input checked="" type="checkbox"/> Liquid <input type="checkbox"/> Gas</p> </td> <td style="width: 50%; vertical-align: top;"> <p>90-Day Accumulation Area Placement Date _____ Out-of-Service Date _____ (PCBs ONLY) WM Received Date _____</p> </td> </tr> </table> <p style="font-size: 8px;">BNLF 3025B 0408</p> </div>	<p>Hazardous Properties (check all that apply)</p> <p><input type="checkbox"/> Ignitable <input type="checkbox"/> Toxic <input type="checkbox"/> Reactive <input checked="" type="checkbox"/> Corrosive <input checked="" type="checkbox"/> Other <u>OXIDIZER</u></p> <p>Waste Form</p> <p><input type="checkbox"/> Solid <input checked="" type="checkbox"/> Liquid <input type="checkbox"/> Gas</p>	<p>90-Day Accumulation Area Placement Date _____ Out-of-Service Date _____ (PCBs ONLY) WM Received Date _____</p>
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H. Process waste solutions for hazardous waste disposal per the [Hazardous Waste Management](#) Subject Area.

- Solutions containing a strong oxidizer like hydrogen peroxide have the potential to continue to off-gas over time. These solutions require specific waste handling methods, depending on the specific chemistry involved. Piranha etches, specifically; will require deactivation prior to disposal. Develop the waste management methodology for your specific etching activity with the involvement of your WMR, ECR and SHSD Rep during the activity’s work planning process. Document the resulting methodology in the Experimental Safety Review or SOP.
- Ensure the waste labels are legible and mark the date the waste is moved to the 90-day storage area.

I. Inspections

- Etchant operations and waste storage need to be inspected to assure conformance to the requirements in this section. Document how the inspections are to be conducted, by whom and the period in the ESR or related SOP. The recommended period is weekly. However, the period may be monthly for very low frequency (< 1/wk) etching activities. Perform the inspection per the schedule in the ESR or SOP using a formalized Inspection Checklist. The following checklist can be used, but it can be modified to reflect the specific requirements of the activity being inspected.

Inspection Checklist for Etching Operations				
Inspector:			Date of inspection:	
	Yes	No	N/A	Comments
Solution cool to the touch?				
Do you have the right container?				
Container has pressure relief?				
Container filled below the fill line?				
Proper warning labels?				
Unattended operation sign used?				

J. Emergency preparedness:

- Know the locations and how to use the eyewash and safety shower
- Prepare for spills. Predetermine the actions to be taken in the event of a spill.

K. Exposure Response

- Treat any exposure to personnel seriously, no matter how slight it may seem. Call BNL Emergency Response (631) 344-2222 from any phone (or x-911 from a BNL phone) and request assistance.
- Provide immediate first aid:
 - Ingestion: Seek medical attention immediately.
 - Skin exposure: Use Emergency Shower. Flush exposed skin with water for at least 15 minutes while removing any contaminated clothing.
 - Eye exposure: Use Emergency Eyewash. Flush eyes with water for at least 15 minutes. The affected person may need help holding their eyes open under water.
- Do not allow personnel into an area where spill has occurred. Wait for the responders to secure the scene and initiate clean-up.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.2 Particularly Hazardous Substance & OSHA Regulated Substances: Carcinogens, Highly Acute Toxins, and Reproductive Toxins

When handling certain substances (typically carcinogens, they are regulated by OSHA specific standards which requires creation of “regulated areas” or “designated areas where special provisions are required.

Required Procedure

A. Identify areas/operations with high hazard chemicals:

Laboratories: Identify chemicals with concentrations greater than 0.1% of substances defined by OSHA as Particularly Hazardous Substances (PHS) (i.e., Select Carcinogens, Highly Acute Toxins, and Reproductive Toxins). The OSHA PHS are listed in CMS in:

Link: [Chemical Hazards at BNL](#)

Generate Report for the following sub-groups of chemicals:

Carcinogens: CARCINOGENS OSHA SELECT (CAROS)

Highly Acute Toxins: TOXIC HIGHLY (THCH0)

Reproductive Hazards: TOXIN REPRODUCTIVE- ALL (TOXR0)

HazCom & laboratories: Identify chemicals (in concentrations > 0.1%) that are regulated by OSHA in Standards 29 CFR 1910.1003 to 1052, (i.e., OSHA Regulated Substances which are mostly carcinogens). The chemicals Regulated by OSHA Standards are listed in the CMS in:

Link: [Chemical Hazards at BNL](#)

Generate Report for: CARCINOGEN OSHA REGULATED (CAROR)

B. Post Areas when hazardous conditions are present:

Laboratories: Establish a Designated Area where Particularly Hazardous Substances will be used. Post the Designated Area to communicate the hazard of the PHS to workers and limit access to authorized personnel. Use the Hazard Information Placard & follow the exhibit *Designated & Regulated Area Posting*. When PHS are in use, limit access to Authorized

personnel that have completed [Laboratory Standard](#) (HP-IND-220) training or are under escort by Laboratory Standard Trained Personnel and have been informed of the Area Specific Hazards and Controls.

HazCom: Establish a Regulated Area where OSHA Regulated Substances are used and the atmospheric concentration exceeds the OSHA Action Levels listed in the OSHA standard 29 CFR 1910.1003 to 1052. Post the Regulated Area to communicate the hazard to workers and limit access to authorized personnel. Use the Hazard Information Placard or follow the exhibit *Designated & Regulated Area Posting*. When Regulated Substances are in use and the Action Level is exceeded, limit access to Authorized personnel that have completed [Hazard Communication](#) (HP-IND-200) Training.

C. Training and employee information:

Laboratories: Advise personnel working with OSHA Particularly Hazardous Substances of the special hazard of the chemicals in use prior to assignments involving new exposure situations, as appropriate. The [Laboratory Standard](#) (HP-IND-220) course covers the special hazards.

HazCom and laboratories: Advise personnel working with OSHA Regulated Substances of the special hazard of the chemicals in use prior to assignments involving new exposure situations, as appropriate. The [Hazard Communication](#) (HP-IND-200) and the [Laboratory Standard](#) (HP-IND-220) course cover the special hazards.

D. When using Particularly Hazardous Substances or Regulated Substances, include special provisions in the work planning to address these hazards.

Laboratories: Address PHS in the Experimental Safety Review. Contact a [Safety & Health Representative](#) for guidance.

HazCom: When using OSHA regulated substances include special provisions in the work planning to address these hazards. Contact a [Safety & Health Representative](#) for guidance.

E. Laboratories: Use containment devices, such as fume hood or a glove box (e.g., chemical fume hood, glove box, or effective exhaust-capturing equipment), when handling Particularly Hazardous Substances in a manner that may produce an airborne hazard (such as fumes, gases, vapors, and mists). This includes operations such as transfer operations, preparation of mixtures, blending, sonification, spraying, heating, and distilling.

F. Conduct worker exposure monitoring specified in the Work Planning & Control documentation to verify that exposure levels do not exceed the OSHA action level (or in the absence of an action level, the OSHA Permissible Exposure Limit [PEL] or ACGIH Threshold Limit Value®). Contact a [Safety & Health Representative](#) to perform worker exposure monitoring to determine if existing monitoring is representative of the area and operation.

- G. When there is a potential for leakage from equipment containing OSHA Regulated Substances provide for leak testing following the program described in the guidance section on *Leakage Detection* at the end of this Chapter. Contact your [Safety & Health Representative](#) for assistance in setting up this program.
- H. When an occupational workplace evaluation has determined there is unacceptable risk from reproductive hazards posed to their worker(s), Supervisors must reassess job assignments and controls.
-

Guidance

- A designated area may be a lab or room, a section of a lab or room, a bench top or a containment device (such as a lab hood).
 - Minimize the Designated Area to provide as small a possible area for workplace contamination (ALARA). This is necessary to prevent the spread of contamination to other areas. Ideally, designated areas are specific locations within a lab for work involving Particularly Hazardous Substances. Their purpose is to ensure that proper controls are in place and that all activities involving these higher hazard materials are confined within the designated area.
 - Storage areas may be included in Designated Areas, but it is also acceptable to have the Designated Area limited to the location where the PHS chemical is handled and to not include the storage cabinet/shelf where closed containers are stored.
-

Reproductive Hazards

- Reproductive hazard chemicals can adversely affect the reproductive health of both male and female workers. Workers who are pregnant or seeking to bear children (both male and female) are encouraged to seek professional evaluation of their work areas for reproductive hazards.
 - a. Staff and supervisors can request an occupational workplace evaluation by contacting their [ESH Coordinator](#) or [Safety & Health Representative](#) for assistance in evaluating your area.
 - b. Contact the Occupational Medicine Clinic (OMC) to discuss medical concerns that pertain to reproductive hazards.
- The effects of reproductive hazards can occur before or after conception takes place. Reproductive hazard chemicals can cause chromosomal damage (mutations); effects on fetuses (teratogenesis); impaired fertility; altered success of a pregnancy; or impaired or delayed development of an embryo, baby, or child.

- Workers can obtain information on reproductive hazards in BNL training courses, such as Chemical Hygiene Laboratory Standard, Hazard Communications, and Lead courses (see the [Training and Qualifications](#) Web Site).
- Basic chemical hygiene practices (such as wearing protective gloves and washing hands frequently) are always important when working with hazardous materials. These practices are even more important for women who work in laboratories while they are pregnant or attempting to become pregnant.
- Pregnant laboratory workers may discuss the work they perform and the hazardous materials they handle with their personal physicians to determine if any work restrictions are necessary. In some cases, certain chemicals may need to be substituted for other reagents, or certain activities curtailed, for the duration of the pregnancy. Restrictions placed by the attending physician may be discussed with BNL's Occupational Medicine Clinic (OMC) Manager.

Guidelines on Breastfeeding regarding Reproductive Hazards:

- Chemicals found in human milk are generally fat soluble and poorly metabolized. In some instances, women with occupational exposures to certain chemicals may have concentrations of chemical contaminants, which exceed the levels that are permitted by the Food and Drug Administration in cow's milk for human consumption.
- Women who are breast feeding and working with any of the following chemicals in processes with the potential for significant exposure should consult the Industrial Hygiene Group and the Occupational Medicine Clinic for evaluation of risk for transfer to breast milk:

Disclaimer: The following is a partial list of chemicals known to have been found in breast milk. This list is a guideline and may not be inclusive. Other agents may pose a risk. Contact the Industrial Hygiene Group and the Occupational Medicine Clinic for evaluation of potential workplace hazards.

- Polychlorinated compounds
- Persistent organochlorine pesticides
- Polychlorinated biphenyls
- Polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF)
- Polybrominated compounds
- Polycyclic aromatic hydrocarbons (PAH)
- Nitrates, nitrites, and nitrosamines
- Nicotine, caffeine, and ethanol
- Certain drugs

Based on: Somogyi A, Beck H. Nurturing and breast-feeding: exposure to chemicals in breast milk. *Environmental Health Perspectives Supp.* 101(2):45-52 (1993).

Leakage Detection for Particularly Hazardous Substances

The ambient atmosphere should be routinely measure when there is a potential for vapor/gas leaks of OSHA regulated chemicals (including Benzene, 1,3-Butadiene, Methylene Chloride, Ethylene Oxide and Formaldehyde. A storage leak is defined as the continuous loss of minute quantities of chemical (typically by volatilization) from process equipment (such as a piping system or reaction vessel).

Appropriate Leak detection systems:

- *Indicator Tubes*: A detection system using a manually operated piston or bellows pump and glass tubes filled with treated chemical granules specific for the substance.
- *Direct Reading Instrumentation*: An electronic meter with a sensor that detects a particular chemical substance. The meter presents a real-time (instantaneous) display in concentration of the chemical sensed by the detector.



Recommended Procedure for detecting leaks

1. Using the detection system, sample potential leak surfaces of the equipment (e.g. fittings, valves, spigots, sites of damage, etc.).
2. If no concentration above background is detected, the seal “passes” the test.
3. If a concentration above background is detected, tighten, realign, or otherwise attempt to improve the seal of the equipment. Wait about 10 minutes and re-test the seal area. If the concentration is not above background, the seal “passes” the test.
4. If a concentration above background is detected and attempts to improve the seal of the equipment still result in a concentration above background, the seal “fails” the test. Repair or replace the equipment so that a passing test is obtained or the process terminated.

Sampling Frequency: This test should be repeated:

- On a quarterly basis for process equipment when the chemical is present in the system.
- Anytime that the seal or integrity of the equipment is in question
- After any change in process equipment that has the potential to alter the seal of the equipment.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.3 Explosive Chemicals (including Azides and Picric Acid)

An explosive is any chemical compound or mechanical mixture that is designed to undergo a very rapid chemical change with the evolution of large volumes of highly heated gases and will deflagrate or detonate when subjected to heat, impact, friction, shock, or other suitable initiation stimuli.

At BNL most explosives are used in dilute solutions. For explosives in solution concentrations \leq 25% (w/w), the main hazards are those associated with the solvent and the chemical as opposed to explosive properties of the material. However, if the solvent evaporates or if the explosive crystallizes or precipitates, then the primary hazard is associated with solution is the explosion hazard.

- Picric acid (synonym: 2,4,6-trinitrophenol [TNP]) becomes highly shock-sensitive when its normal water content is allowed to evaporate.
- Heavy metal azides, such as lead azide are very unstable primary high explosives detonable when heated or shaken.

Required Procedure

- A. Identify explosive from the Chemical Management System for a list of explosive chemicals:

Link: [Chemical Hazards at BNL](#)

Generate Report for: EXPLOSIVE (EXP00)

- B. BNL workers who use explosives follow the BNL [Explosives Safety](#) Subject Area. This subject area provides procedures for obtaining approval to procure, handle, use, store, and dispose of explosive materials at BNL. Safeguards and Security Division operations involving the procurement, distribution, and usage of munitions in the course of fulfilling their mission are exempt from this subject area.
- C. Use & store Explosives and Unstable (reactive) Class 4 or Class 3 detonable (based on Fire Code of New York State and NFPA 5000) only in a building 100% equipped with an automatic sprinkler system. Check with the [Fire Protection Engineer](#) if there is any question on the status of a building.
- D. Inspect Picric acid monthly to insure it is wet. Rehydrate the material every six months with deionized water to maintain a wet paste.
- E. Dispose of picric acid within two years of receipt.

- F. Do not pour picric acid down a drain; it could react with copper or iron piping to form explosive salts.
- G. Use a fume hood or other appropriate exhaust ventilation when handling azides in a manner that may produce an airborne hazard (such as fumes, gases, vapors, and mists). This includes procedures such as transfer operations, preparation of mixtures, blending, sonification, spraying, and heating. Use of Azide acid (above 100 mg per year) must be done in a specifically designed hood with a “wash down system,” unless permission is given the Work Planning review process with concurrence of the [Chemical Safety SME](#).
- H. Ensure the building where explosive chemicals are used is full sprinkler protection. Consult the [Fire Safety](#) subject area and contact [Fire Protection Engineering](#) for assistance.
-

Guidance

Picric Acid

- When the material appears dry, do not open the container.
- Store picric acid wet (i.e., store in a bottle under a layer of water). When picric acid is dry (to less than 10% water by volume), it is relatively sensitive to shock and friction and poses an explosion hazard.
- Use glass or plastic bottles. Do not use metal containers or containers with metal lids. Picric acid can form metal picrate salts that are even more sensitive and hazardous than the acid.
- Do not use metal spatulas to remove material.
- Clean the bottleneck, caps, and threads with a wet cloth before resealing.
- When possible, purchase premixed solutions of 1% or less.
- Handling Questionable Containers:
 - If an old container is found with a metal cap, shock sensitive metal picrates may have formed on the cap contact area. Explosive experts should be contacted via Environmental Protection Division.
 - If a plastic cap is present but the acids inside have dried, some crystals may be on the threads and the friction of removing the plastic cap might be enough to detonate the container. Place the container in pale of water and allow the water to enter the caps and threads and dissolve the crystals. Leave it for several days until water can be seen inside the bottle.

Azides

- Sodium azide is toxic (LD₅₀ oral (rats) = 27 mg/kg) and can be absorbed through the skin. Sodium azide decomposes explosively upon heating to above 275 °C. Sodium azide reacts vigorously with CS₂, bromine, nitric acid, dimethyl sulfate, and a series of heavy metals, including copper and lead. In reaction with water or Brønsted acids, the highly toxic and explosive hydrogen azide is released. It has been reported that sodium azide and polymer-bound azide reagents react with dichloromethane and chloroform to form di- and

triazidomethane resp., which are both unstable in high concentrations in solution. Various devastating explosions were reported while reaction mixtures were being concentrated on a rotary evaporator.

- Heavy-metal azides that are highly explosive under pressure or shock are formed when solutions of sodium azide or HN_3 vapors come into contact with heavy metals or their salts. Heavy-metal azides can accumulate under certain circumstances, for example, in metal pipelines and on the metal components of diverse equipment (rotary evaporators, freeze drying equipment, cooling traps, water baths, waste pipes), and thus lead to violent explosions. Some organic and other covalent azides are classified as highly explosive and toxic (inorganic azides as neurotoxins; azide ions as cytochrome c oxidase (COX) inhibitors). Solid iodoazide is explosive and should not be prepared in the absence of solvent.
- Transport containers of azide solutions in bottle carriers.
- Open bottles or carboys slowly and carefully, and wear protective equipment to guard hands, face, and body from splashes, vapors, gases, and fumes.
- Wipe drips from containers and bench tops.
- Conduct surface contamination testing of ventilation equipment, unless process knowledge of the entire history of ventilation equipment is known:
 - At demolition or modification of any hood or local exhaust duct,
 - On an annual basis while Azides are in use (above 100 mg per year),
 - At the end of a project that used Azides.

Label contaminated ventilation equipment with the test date and label “Azide contaminated”. Contact the [Safety & Health Representative](#) for testing.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.4 Flammable and Combustible Liquids & Gases

Flammable and combustible chemicals include liquids and gases such as organic solvents, oils, greases, tars, oil base paints, and lacquers, as well as flammable gases.

Flammable and combustible liquids are defined by their flash points. They are defined by National Fire Protection Association and OSHA and are listed in the BNL Chemical Management system in the table:

Link: [Chemical Hazards at BNL](#)

Generate report for: FLAMMABLE – ALL (FLM00)

Flammable gases are discussed in the [Compressed Gas Cylinders and Related Systems](#), [Pressure Safety](#), and [Fire Safety](#) Subject Areas.

Required Procedure

- A. Assess the hazards and necessary controls to limit worker risk from flammable and combustible materials in Work planning & Control documentation.
- B. Train workers via: [Hazard Communication](#) (HP-IND-200) or [Laboratory Standard](#) (HP-IND-220). Ensure that users of flammable liquids are trained in safe handling procedures and safe limits for the environment that they are working in.
- C. Store and transfer flammable and combustible chemicals per Chapter 7 Chemical Storage and the [Fire Safety](#) Subject Area.

Guidance

- Transfer Class I liquids in laboratories from containers of less than 5-gallon capacity in one of the following manners:
 - In a laboratory hood designed for flammable liquids;
 - In a ventilated area to prevent the accumulation of a flammable vapor/air mixture exceeding 25% of the lower flammable limit; or
 - In an inside storage room that complies with the requirements of NFPA 30 Flammable and Combustible Liquids Code and 29 CFR 1910.106.

- Class I B liquids (e.g., ethanol) may be transferred from containers or tanks by gravity through piping, hoses and self- or automatic closing valves that have been reviewed and approved by a [Fire Protection Engineer](#). Conduct transfer operations with spill control and secondary containment. Moreover, the nozzle and containers must be bonded to each other (i.e., electrically interconnected) to prevent static electricity discharges.
- Consider routine inspections of Flammable Storage Cabinets. Contact your [Safety & Health Representative](#) for assistance in setting up a program.

Guidance on Criteria for the Inspection of Flammable Storage Cabinets

References: NFPA 45 Standard on Fire Protection for Laboratories Using Chemicals; NFPA 49: Hazardous Chemical Data; NFPA 325: Fire hazard Properties of Flammable Liquids, Gases, and Volatile Solid.

Safety Precaution

When inspecting a cabinet, do not stand directly in front of the cabinet when opening the door. After opening, allow 30 seconds before placing your head near the cabinet to avoid inhalation of any accumulated vapors. Watch for visible signs and odor that indicate chemical containers are not intact. Stop if spillage is seen or smelled.

Check the location of the cabinet

- Make sure the cabinet is not in a passageway that is used to egress rooms or adjacent to (within 10 feet) the primary exit of a room.

Inspect the design and condition of the cabinet

- Observe if the cabinet is properly certified (label such as FM, UL, or statement of OSHA compliance).
- Examine the outside of the cabinet for any indications of a problem, such as dents, rust, or penetrations.
- Inspect the working of the latch. The unit should have a *3-point locking mechanism*: latches catches on the bottom, top and middle of the door.
- Observe the status of seal & bung holes and venting.

Inspect contents of the cabinet (volume, types of chemicals, storage, and compatibility)

- Examine chemical containers for proper labeling.
- Observe the types of containers in the cabinet. Alert the owner to immediately remove oxidizers in the cabinet.
- Observe if non-flammable chemicals or excess paper/word are stored in the cabinet. These should be minimized to allow for maximum use of the cabinet.
- Observe the condition of containers.
 - If a chemical container is physically compromised (e.g. severely rusted, unlabeled, residues at cap, cap damaged, etc.) have the container owner move it to a secondary containment tray in a fume hood until the situation can be remedied.
 - If there is a chemical spill in the cabinet, close the cabinet and ensure the spill is addressed immediately. Depending on the severity/size of the spill, call x-2222 and report the spill for cleanup.
 - Immediately inform the ESH Coordinator and Facility Project Manager about these issues.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.5 Laser Dyes and Solvents

Dye lasers normally use a lasing medium consisting of a fluorescent organic dye dissolved in an organic solvent. For most dyes, little is known about their toxic properties, except that they are often members of chemical families that contain highly toxic materials. Furthermore, limited testing has indicated that some laser dyes are carcinogenic or mutagenic. Consequently, most dyes should be treated as hazardous chemicals. In many cases, the solvent in which the dye is dissolved plays a major role in the hazards. Most solvents used for dye solutions are flammable and toxic by inhalation and/or skin-absorption.

Required Procedure

- A. Identify laser dyes and solvents used in the work area. Review sources such as MSDSs for specific compounds.
 - B. Conduct an assessment of the hazards and controls to limit worker exposures to these agents. Contact a [Safety & Health Representative](#) to provide assistance.
 - C. Train workers who either handle or who may be exposed to laser dyes and solvents in the specific hazards and controls of the dyes and solvents being handled.
 - D. Label primary and secondary containers with the identity of the substance and its hazards. This includes dye pumps.
 - E. Use a fume hood, glove box or engineering control device when mixing laser dyes or when handling them in a manner that may generate an airborne hazard (such as fumes, gases, vapors, and mists).
 - F. Wear safety glasses with side shields, laboratory coats (coveralls are acceptable in shop settings) and closed-toe shoes when handling these materials. Chemical goggles, face shields, chemical aprons, disposable coveralls, and chemically resistant gloves must be worn if there is a greater chance of chemical exposure. Use of respiratory protection is required if determined by an industrial hygiene hazard evaluation. A [Safety & Health Representative](#) may be contacted for assistance in selecting appropriate gloves and respiratory protection.
-

Guidance

- All dyes and solvents should be stored in sealed, air-impermeable containers. Dark amber glass containers with tight-fitting caps are recommended. This prevents the evaporation of contents. Containers with loose-fitting lids or glass stoppers should not be used.

- Solvents such as dimethyl sulfoxide (DMSO) and methyl alcohol readily penetrate unbroken skin. Hazardous mutagenic or carcinogenic dyes can enter the body through skin-absorption when dissolved in solvents such as these.
- Identify and use safer chemical alternatives (e.g., non-mutagenic/carcinogenic dyes or less concentrated forms) if possible. If a safer chemical can't be used, then limit what you buy or contact the [Chemical Management Surplus Page](#) to assist you in finding a source of the chemical at BNL. Conduct periodic cleanouts to prevent accumulating unneeded chemicals. Procure and use the minimum amount of material required for the operation and keep working quantities of chemicals to a minimum. Don't stockpile chemicals.
- Minimize the quantity of pure dye or solutions containing >0.1% of mutagenic/carcinogenic dyes in storage or in use at any time.
- Install spill pans under pumps and reservoirs.
- Leak-test dye pump loops, as appropriate.
- Do not use combustible or reactive materials (such as paper towels) to clean up or absorb spills of laser dye and solvents. Keep an adequate number of appropriate spill kits to meet anticipated needs. Typically, products containing diatomaceous earth are used for absorbing organic solvents.
- Wash hands after handling laser dyes and solutions.
- Since many chemicals readily pass through the skin, it is important to select gloves that are chemically resistant to the material.
- Select gloves on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted, and their resistance to wear, as well as temperature extremes. Improper selection may result in glove degradation, permeation of the chemical through the glove and ultimately personal exposure to the chemical. This is a potentially serious situation. A [Safety & Health Representative](#) may also be contacted for assistance in selecting appropriate gloves.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.6 Perchlorates and Perchloric Acid

Perchloric acid is a strong mineral acid commonly used as a laboratory reagent. It is a clear, colorless liquid with no odor. Most perchloric acid is sold as 60%-62% or 70%-72% acid in water. Under some circumstances it may act as an oxidizer and/or present explosion hazards.

Use of perchloric acid can create deposits of highly explosive metal perchlorates in hoods, ducts, fan housing, and other system components. Hammering, banging, and parts disassembly can result in very hazardous explosion and subsequent injury of maintenance or construction personnel.

Required Procedure

- A. Operations involving heating or evaporating perchloric acid must be evaluated in the Work Planning Process to determine if special controls (such as using an acid fume hood with wash-down systems to prevent the accumulation of explosive perchlorate crystals) are needed. Unless otherwise determined, perform heated perchloric acid operations only in a specially designed fume hood with a water wash down system. This system prevents the buildup of explosive perchlorates in the duct work.
- B. Evaluate and document operations involving heating or evaporating perchloric acid by Work Planning and Control process.
- C. Before demolition or modification of any hood or local exhaust duct and at the end of a project or work that used perchloric acid: conduct quantitative Surface Wipe analysis of lab hoods and exhaust ventilation equipment, unless process knowledge of the entire history of the equipment can verify that perchlorates/perchloric acid were never used in the system. (Equipment that by process knowledge is known to be non-contaminated does not need to be tested). Contact the [Safety & Health Representative](#) for testing.
- D. Label ventilation equipment testing has found to be contaminated with the date and "*Perchlorate contaminated.*" Develop a plan for future action with the [Safety & Health Representative](#).

Guidance

Perchloric acid may form explosive perchlorate crystals, which are shock-sensitive and can detonate. Acids can form toxic reaction products when combined with cyanide or sulfide salts. The corresponding products are hydrogen cyanide and hydrogen sulfide gas.

- Keep the quantities of perchloric acid in storage to a minimum.
- Substitute with less hazardous chemicals when appropriate.
- Use dilute solutions (<60%) whenever possible.
- Store Perchloric acid in its original container within compatible secondary containment, preferably glass or porcelain. Wipe the trays periodically.
- If a bottle containing perchloric acid has turned dark and has crystals forming around the bottom of the bottle, there is a potential explosion hazard. Do NOT move the bottle. Immediately contact the Environmental Protection Division's Waste Management Group for assistance.
- Transfer perchloric acid over suitable containment in order to catch any spills and afford a ready means of cleanup and disposal. Perform operations on chemically resistant surfaces. Avoid contact with cellulose materials such as wood, paper and cotton, which could result in a fire or explosion.
- In the event of spills, neutralize with soda ash or other appropriate neutralizing agent. Soak up the spill with an inorganic based absorbent. Do NOT use rags, paper towels, or sawdust and then put them aside to dry out, as such materials may spontaneously ignite. Likewise, spills on wood may present a fire hazard after the liquid dries.

- **≥72% Perchloric Acid at Room Temperature:** Concentrated perchloric acid (≥70%) is an oxidizer only at temperatures above 150° C. Do not mix Perchloric acid with organic materials if there is a possibility that temperatures will become elevated beyond ambient levels. Perchloric acid may react violently with many chemicals, including acetic anhydride, alcohol, reducing agents, and many metals.

- **≤72% Perchloric Acid at Room Temperature:** At room temperature, perchloric acid up to concentrations of 72% has properties similar to other strong mineral acids. It is a highly corrosive substance and causes severe burns on contact with the eyes, skin, and mucous membranes. Take these precautions when using perchloric acid at room temperature:
 - Conduct operations involving non-heated perchloric acid in a properly functioning laboratory hood. If operations are conducted frequently or in large quantities contact SHSD to determine if a specially designed hood dedicated to perchloric acid use is needed.
 - When using or storing perchloric acid solutions, avoid contact with strong dehydrating agents (concentrated sulfuric acid, anhydrous phosphorous pentoxide, etc.). These chemicals may concentrate the perchloric acid and make it unstable.

- **≤72% Perchloric Acid Heated:** When heated to temperatures above 150° C perchloric acid becomes a strong oxidizer and eventually becomes unstable. Concentrated solutions are very dangerous and can react violently with many oxidizable substances, such as paper and wood, and can detonate. Vapors may also contaminate work surfaces or ventilation equipment with perchlorate residues, which may form highly unstable compounds, such as metallic perchlorates. These compounds may ignite or detonate under certain conditions.
 - If procedures involving heated perchloric acid are performed only rarely, you may use a method to capture and contain vapors in place of using a perchloric acid hood.

- Contact the [Safety & Health Representative](#) immediately for an evaluation of perchlorate contamination of the hood if operations involving heated perchloric acid work in a laboratory hood not designed for perchloric acid use have occurred.
- Lower the fume hood sash as much as possible so that it can function as a physical barrier or use a safety shield to provide splash/splinter protection. Perchloric acid fume hoods should have shatterproof glass.
- Do not heat perchloric acid in an oil bath or with an open flame. Electric hot plates, electrically or steam-heated sand baths, heating mantles, or steam baths are preferred. Use explosion proof electrical equipment.
- Avoid allowing hot perchloric acid to come into contact with any organic materials, including paper or wood, because a fire or explosion can occur. Avoid storing these materials in perchloric acid work hoods. Avoid using greases or hoses that are incompatible with perchloric acid.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.7 Peroxide Forming Substances

Peroxides can form in solvents, reagents, gases, and solids by the auto-oxidation or peroxidation of a compound with molecular oxygen. The reaction can be initiated by light, heat, introduction of a contaminant, or the loss of an inhibitor. Some chemicals have inhibitors such as BHT (2,6-di-tert-butyl-4-methylphenol) hydroquinone and diphenylamine to slow peroxide formation.

Most organic peroxide crystals formed in peroxide forming chemical liquids are sensitive to heat, shock, or friction, and their accumulation in laboratory reagents has resulted in numerous explosions. Organic peroxide vapors and gases increase the pressure within closed containers and can cause the container to rupture causing a fire or damage from the ruptured containers

Peroxidizable gases pose a potential hazard of rapid polymerization initiated by internally formed peroxides. Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory, and it is difficult to be sure that there is no residual air in the receiving container. Before transferring these chemicals into secondary container, first purge the receiving container with nitrogen. Put an inhibitor into secondary cylinders before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in the secondary container. Peroxidizable gases (even if inhibited) that have been put into a secondary container under conditions that create a liquid phase must be discarded within twelve months.

The peroxide forming compounds recognized by BNL are grouped in the following categories:

BNL Hazard Group
Group A: Severe Peroxide Hazard on Storage with Exposure to Air: May explode even without being concentrated. (Required Testing & Disposal Schedule)
Group B: Peroxide Hazard on Concentration: Require concentration (such as distillation or evaporation) in order to present a hazard. (Required Testing & Disposal Schedule)
Group C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides (Required Testing & Disposal Schedule)
Group D: Chemicals identified in sources such as MSDSs that indicate potential for peroxide formation. (Testing & Disposal Schedule are Guidance)

Required Procedure

- A. Identify peroxide forming chemicals** from the *Chemical Hazards List* Table listed in CMS.
The link to the peroxide forming compounds is:

Link: [Chemical Hazards Lists](#)

Generate report for: PEROXIDE FORMING COMPOUNDS GROUP ALL (PFC00)

B. Label the container when received and as conditions change with a label (or a reference to a written log where this information is kept) that indicates Date received, Date opened, and Expiration date.

Peroxide Forming Compound	
Received:	
Opened:	
Expiration Date:	

C. Segregate peroxide forming compounds into a separate containment tray to facilitate periodic testing for peroxide formation.

D. Testing & Expiration dates: Test and dispose of chemicals following the frequency schedule set in Table D using one of the procedure listed in the section *Peroxide Testing Procedure*, unless one of the following exceptions is met:

- Gases in their original pressurized container
- Solids stored in inert gas or under liquids that eliminates oxygen presence (such as oil or kerosene)
- Liquids that are always kept in inert atmospheres
- Containers with specialized closures (such as a septum or Sure/Seal^[tm] cap) when there is an atmosphere of inert gas maintained at all times within the bottle.
- Liquids or gasses have an inhibitor that prevents peroxide formation and indicates the presence of peroxides (such as XPell® www.xplosafe.com).

Table D: Testing and Expiration Schedule		
Hazard Group	Physical State	Testing and Expiration Frequency
Group A: Hazard on Storage with Exposure to Air	Liquid	Dispose of containers at the earliest of manufacturer's expiration date or 24 months of initial receipt.
		Once opened, test every 3 month. Contact ECR/WMR if containers testing >100 ppm. If not tested for 6 months, do not open for testing.
	Solid	Dispose of containers at manufacturer's expiration date.
		Testing not applicable.
	Gas	Dispose of containers at the earliest of manufacturer's expiration date or 36 months of initial receipt.
		Testing not applicable.
Group B: Hazard on Concentration	Liquid	Dispose of containers at the earliest of manufacturer's expiration date or 24 months of initial receipt.
		Once opened, test every 6 months. Contact ECR/WMR if containers testing >100 ppm. If not tested for 12 months, do not open for testing.
	Solid	Dispose of containers at manufacturer's expiration date.
		Testing not applicable.

Table D: Testing and Expiration Schedule		
Hazard Group	Physical State	Testing and Expiration Frequency
	Gas	Dispose of containers at the earliest of manufacturer's expiration date or 36 months of initial receipt.
		Testing not applicable.
Group C: Hazard of Polymerization by Internally Formed Peroxides	Liquid	Dispose of containers at the earliest of manufacturer's expiration date or 24 months of initial receipt.
		Once opened, test every 6 months. Contact ECR/WMR if containers testing >100 ppm. If not tested for 12 months, do not open for testing.
	Solid	Dispose of containers at Manufacturer's expiration date
		Testing not applicable.
	Gas	Dispose of containers at the earliest of manufacturer's expiration date or 36 months of initial receipt.
		Testing not applicable.
Group D: Advisory Chemicals	Liquid	Dispose of at Manufacturer's expiration date.
		Test at owner's discretion: recommended testing at 6 months. Contact ECR/WMR if containers testing >100 ppm.

E. Dispose of waste containers.

1. Dispose of containers prior to their reaching the expiration date listed in the Table D.
2. Label and process waste containers as per the [Hazardous Waste Management](#) Subject Area.
3. Prior to submitting a Waste Control Form, ensure the container has been properly tested for peroxide forming compounds.
4. In any of the following conditions exist, immediately notify your Waste Management Representative or Environmental Compliance Representative, follow the Emergency Procedures, and do not place containers into a satellite area or 90-day storage area:
 - o Container with an indication of peroxide formation listed in Step D.
 - o Container exceeding the expiration date set by the manufacturer or Table D.
 - o Container with an age that is unknown.
 - o Container exceeding the testing period set in Table D.
 - o Container with test results are >100 ppm.

Additional Information

Emergency Procedures for Peroxide-forming Compounds

WARNING: DO NOT HANDLE CONTAINERS WITH ANY OF THESE SIGNS
<ul style="list-style-type: none"> • Crystallization or precipitate in the liquid in the container, • Crystallization on the lid, cap or exterior of a container, • Signs of stratification of the liquid in the container, • The container is deformed (from pressure), • Other irregularities in the container or contents not consistent with typical handling.

Immediately contact your Waste Management Representative or Environmental Compliance Representative for instructions on further actions.

Consult the Chemical Hygiene Plan Chapter 9 *Emergency Practices and Equipment*, for actions regarding chemical spills and personal exposure to chemicals. In addition, the following applies to peroxide-forming compounds:

- Ensure an emergency eyewash and safety shower is located in areas where peroxide forming compounds are used.
- First Aid: In the event of skin or eye contact, flush the affected area for at least 15 minutes and contact Emergency Response for assistance (x-2222).
- Spill Clean-up: Do not attempt to clean up peroxide forming compound spills if the spill exceeds your ability to safely correct the incident.
 - Call for Emergency Response assistance (x-2222) in any situation you are not competent to handle.
 - Have a product specifically designed for use in clean-up of these materials available where they are used. (Typically, these materials contain diatomaceous earth).
 - Do not attempt to clean up peroxide forming compound spills if there is any indication that these actions could initiate a detonation, fire, or polymerization.
 - Never use combustible or reactive materials (such as paper towels) to clean up or absorb spills of peroxide formers.

Peroxide Test Procedure

Peroxide Test Procedure
WARNING
Do not perform testing on any container with the following:
<ul style="list-style-type: none">• Indications of peroxide formation (see Step D.3).• Exceeding the test frequency in Table D.• Crystals are observed at the cap threads or in the bottle. Crystals of peroxides are EXPLOSIVE when disturbed. Do not touch the container, prevent it from being handled, and contact your Waste Management Representative or Environmental Compliance Representative for instructions on further actions.
<ul style="list-style-type: none">• Use safety glasses, lab coat, and impervious gloves (such as nitrile exam gloves).• Perform test behind a lab hood sash.
Test the following types of containers: <ul style="list-style-type: none">• Opened containers of peroxide forming liquid substances (except those meeting exemptions below).• Unopened containers once they reach the age listed in Table D.• Containers with specialized closures (such as a septum or Sure/Seal^[tm] cap) without provisions to maintain an inert atmosphere within the bottle. Test by removing a small aliquot of peroxide forming compounds using a sampling device such as a syringe, rather than removing the cap.• Ion Exchange column systems.• Secondary containers of peroxide forming compounds that are kept for more than 6 months.

Record the test on a label on the container (or indicate a reference to an equivalent written log where this information is kept). Add/replace the following label after each test:

Peroxide Forming Compound List A: Test every 3 months. Tested: _____
--

or

Peroxide Forming Compound List B, C, or D: Test every 6 months. Tested: _____

Test results criteria:

- Peroxides in solution <100 ppm pass the test. Document the test on the bottle label.
- Peroxides in solution >100 but <10,000 ppm FAIL the test and need to be processed as hazardous waste or treated to remove the peroxides as described in the guidance section.
- Peroxides in solutions >10,000 ppm (1%) FAIL the test. Immediately be processed for waste disposal.

Perform the test using one of the following methods to detect peroxide compounds in liquids on Lists A, B, and C (optional for List D):

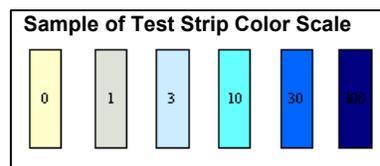
Method 1: Potassium Iodide Solutions:

- Add 1 to 3 milliliters (ml) of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates the presence of peroxides;
- Add 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of an organic liquid in a 25-mL glass cylinder. Produces a yellow color if peroxides are present; or
- Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous potassium iodide solution and 0.5 ml of dilute hydrochloric acid to which a few drops of starch solution has been added just before the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.

Method 2: Peroxide Test Strips: Indicator strips that turn to an indicative color in the presence of peroxides. These strips are available from the [Chemical Management System Team](#). Note that these strips must be air-dried until the solvent evaporates and then exposed to moisture for proper operation. Check the expiration date of the test strips. Do not use if expired. Store test strips in a cool (<85F/30C), dry place or refrigerator. Use a test strip only once.

Aqueous Solutions

1. Remove the test strip from its container/bag and immediately reclose the container.
2. Dip the test strip into the solution for 1-2 seconds. Remove the test strip and shake off excess liquid.
3. After 30 seconds, compare the test strip to the color scale provided with the test strips.



Organic Solutions

1. Remove the test strip from its container/bag and immediately reclose the container.

2. Dip the test strip into the solution for 1-2 seconds.
3. Remove the test strip. Gently wave the strip in the air until the solvent has evaporated (typically 3-30 seconds).
4. Dip the test strip into distilled water for 1 second and shake off excess liquid. (Water is necessary for the color change to occur).
5. After 30 seconds, compare the test strip to the color scale provided with the test strips.

Guidance

- Peroxides in solution at concentrations up to about 1 percent (10,000 ppm) do not normally present thermal or shock hazards. Such solutions may be safely disposed of or treated to remove peroxides.
- Order the smallest quantity of peroxide forming compounds practical for the operations.
- Purchase peroxide forming compounds with specialized closures (such as a septum cap) to minimize introduction of air into the container.
- Store polymerizable monomers with a polymerization inhibitor from which the monomers can be separated by distillation just before use.

Examples of specialized closures for containers are shown below:



Distillation and Evaporation Precautions

"Prudent Practices in the Laboratory," National Research Council, National Academy Press, Washington, DC, 1995.

- Test all List A or B compounds for peroxides before distillation or evaporation (or treated to positively ensure peroxide destruction). If the material tests positive, it must be disposed of or treated to remove the peroxides. Add a suitable polymerization inhibitor before distilling any List C material.
- Most accidents associated with distillation of peroxidizable compounds have occurred when peroxides have become concentrated in the distillation residue. It is therefore essential to never distill a peroxidizable solvent to a dry residue.
- One solution for compounds showing no more than a trace of peroxide on testing is to discontinue the distillation when a 10 percent heel remains.

- Another solution is to add a high molecular weight inerting solvent, which will not distill, such as mineral oil or a phthalate ester. This solvent will act as a desensitizing diluent for residual peroxides when distillation is complete.
- In addition to safety glasses, use a shield when evaporating or distilling mixtures that may contain peroxides.

Removal of Peroxides from Peroxide Forming Liquid Compounds

Only knowledgeable laboratory workers should carry out these procedures. Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principle hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and di-t-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.

- **Removal of Peroxides with Alumina**

A 2 x 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 ml of solvent, whether water-soluble or water-insoluble. After passage through the column, test the solvent for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety, it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is properly discarded.

- **Removal of Peroxides with Molecular Sieves**

Reflux 100 ml of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.

- **Removal of Peroxides with Ferrous Sulfate**

A solution of 6 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ml of concentrated sulfuric acid, and 11 ml of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

Dialkyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfate, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.

- **Removal of Peroxides with Silicon Oxide/Molybdenum Trioxide (XploSafe Xpell):** commercial product that is an antioxidant and indicator. Follow manufacturer's instructions.

- **Destruction of Diacyl Peroxides**

For 0.01 mol of diacyl peroxide, 0.022 mol (10% excess) of sodium or potassium iodide is dissolved in 70 ml of glacial acetic acid and the peroxide is added gradually, stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution may be properly discarded.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.

Destruction of Dialkyl Peroxides

One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90° to 100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours, before being properly discarded.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.8 Water-reactive Chemicals

Water-reactive chemicals react violently with water, releasing heat and, in some cases, explosive by-products. Of chief concern are the alkali metals. Alkali metals react vigorously with water to form the hydroxide and gaseous hydrogen. The alkali metal-water reaction is exothermic. The heat generated can ignite the hydrogen gas. The rate of reaction and the hazard severity increase as atomic weight increases. Lithium reacts slowest and poses the least hazard. Rubidium and cesium react explosively. A DOE document entitled “DOE-HDBK-1081-94, Primer on Spontaneous Heating and Pyrophoricity” provides additional information. Hygroscopic or water-reactive compounds can auto-ignite on exposure to air or moisture.

Required Procedure

A. Identify water reactive compounds. The link to the peroxide forming compounds is:

Link: [Chemical Hazards Lists](#)

Generate report for: WATER REACTIVE –ALL (WAT00)

- B. Contact a [Fire Protection Engineer](#) for assistance in the proper selection of an appropriate extinguishing agent.
- C. Indicate Water Reactive Chemicals are present on emergency plans, placards, and the Facility Use Agreement.
- D. Use & store Unstable (reactive) Class 4 or Class 3 detonable (based on Fire Code of New York State and NFPA 5000) only in a building 100% equipped with an automatic sprinkler system. Check with the [Fire Protection Engineer](#) if there is any question on the status of a building.

Guidance

- Most water reactive materials react violently with common fire suppression agents such as water, foam agents, halogenated agents, and carbon dioxide gas. Some water reactive materials cannot be extinguished with water and require special extinguishing powders (for Class D fires), or special inert gases.
- Water Reactive materials should be handled in a glove-box made of materials that are compatible with the substance with an inert gaseous atmosphere such as dry argon.

Skin or Eye Contact:

- If any alkali metal fragment or drop enters the eye, it will immediately generate considerable heat, which is likely to result in severe eye injury. In such cases, the eyes should be flushed with water from an eyewash/safety shower. Continue to flush the eye with water and call x2222 for emergency help.
- When alkali metal comes in contact with the skin, remove all contaminated clothing. If contact with the metal occurs at only one or two spots on the skin, it is best to wash off those areas with mineral oil. A container with at least one quart of mineral oil should be available in alkali metal work areas labeled for this purpose. If contact with the metal is widely distributed over the body, a decision on the best course of first aid must be made immediately. If the material is already burning, the individual should be drenched continually under a safety shower until emergency help arrives. If the material is not burning, the metal should be removed by wiping the skin with mineral oil. In all cases, dial x2222 for assistance.
- Do not use combustible or reactive materials (such as paper towels) to clean up or absorb spills of pyrophoric substances. Keep an adequate number of appropriate spill kits to meet anticipated needs.
- An emergency eyewash and safety shower should be located in all areas where pyrophorics are used. In the event of skin or eye contact, flush the affected area for at least 15 minutes and report to the Occupational Medicine Clinic for evaluation and treatment.

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.9 Heated Temperature Baths

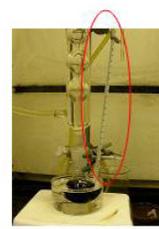
Heated baths containing oils or salts are often used to heat small or irregularly shaped vessels or when a constant temperature is desired. These units pose hazards from overheating of the oil which can result in fires, electrical incidents from the heating sources, and over pressurization or heating of the chemicals being heated.

Required Procedure

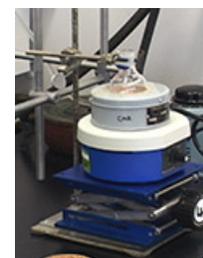
- A. Set-up oil bath on a stable surface, away from flammable and combustible materials including wood and paper.
- B. Ensure heating sources for baths are equipped with properly working electric systems, heat controls and a power source located in such a way that the power can be cut off at any time. Fit unattended oil baths with thermal sensing devices that will turn off the electric power if the bath overheats.
- C. Wear heat-resistant gloves, a fire-proof lab coat and safety glasses when handling a hot bath.
- D. Label oil baths with the type of oil they contain (i.e., mineral oil, silicone oil, etc.).

Guidance

- Locate the oil bath of hazardous substances in a fume hood or operate with vacuum system.
- Do not heat the oil baths to a temperature that generates smoke or overheating. Use a thermometer or other thermal sensing devices to ensure that its temperature does not exceed the flash point of the oil being used. Smoke, caused by the decomposition of the oil or of organic materials in the oil, is a health hazard.
- Use a Pyrex vessel, metal pan or a heavy-walled porcelain dish as the oil vessel. Ensure the heated oil vessel can withstand an accidental strike by a hard object.
- Silicone oil is recommended for higher temperatures and is a safer substitute for other oils. Always refer to an MSDS for information on flashpoints.
- Liquids expand when heated. Avoid overfilling the baths.
- Take care to keep water from leaking into hot oil baths, which can cause hazardous popping and splattering. Such an accident can splatter hot material over a wide area and cause serious injuries.
- Mount baths on a stable horizontal support using a laboratory jack to raise



Thermometer used to monitor temperature of the bath liquid



Jack used to support bath and allow lowering of bath in case of emergency

and lower the bath. Clamp equipment high enough above a hot bath that if the reaction begins to overheat, the bath can be lowered immediately without having to readjust the equipment setup. Mount the reaction flask and baths in such a way that they cannot be overturned.

- Mix oil baths well to ensure that there are no “hot spots” around the elements that take the surrounding oil to unacceptable temperatures.
- Ensure the product to be heated does not touch the sides or bottom of the oil vessel to avoid localized overheating (hot spot).
- Avoid using glass, Pyrex®, Kimax®, or borosilicate glass when oils will be above 100°C.
- Provide secondary containment when glass is used as the oil bath in the event of a spill of hot oil.

Properties of some typical bath fluids

Fluid	Usable Range	Flash Point
Silicone Oil Type 200.05	-40°C to 130°C	133°C
Silicone Oil Type 200.10	-30°C to 160°C	211°C
Silicone Oil Type 200.20	10°C to 230°C	232°C
Silicone Oil Type 200.50	30°C to 278°C	280°C
Silicone Oil Type 710	80°C to 300°C	302°C
Mineral Oil	10°C to 175°C	177°C
Bath Salt, Potassium Nitrate 53% Sodium Nitrite 40% Sodium Nitrate 7%	180°C to 550°C	n/a

Examples of heating devices:

		
<p>Hot plate as the heat source Do not store volatile flammable materials near a hot plate. Check for corrosion of thermostats.</p>	<p>Heating mantle used as the heat source: Heating element enclosed in layers of fiberglass cloth. The flask should fit snugly. A small flask in a large mantle might lead to local overheating.</p>	<p>Immersed coil heater used as the heat source [Best Choice for Maximum safety]</p>

Chapter 6 Additional Controls Practices for Specific Hazardous Chemicals (continued)

6.10 Mercury and Mercury Compounds

Elemental (metallic) mercury and all of its compounds are toxic. Exposure to excessive levels can permanently damage or fatally injure the brain and kidneys.

Elemental mercury can also be absorbed through the skin and cause allergic reactions. Ingestion of inorganic mercury compounds can cause severe renal and gastrointestinal damage.

Organic compounds of mercury such as methyl mercury are considered the most toxic forms of the element. Exposures to very small amounts of these compounds can result in devastating neurological damage and death. For fetuses, infants and children, the primary health effects of mercury are on neurological development. Even low levels of mercury exposure such as result from mother's consumption methylmercury in dietary sources can adversely affect the brain and nervous system. Impacts on memory, attention, language and other skills have been found in children exposed to moderate levels in the womb.

Required Procedure:

- A. When using elemental mercury and mercuric compounds, include special provisions in the work planning to address these hazards.

Laboratories: Address mercury and mercury compounds in the Experimental Safety Review. Contact a [Safety & Health Representative](#) for guidance.

HazCom: When using mercury at level that present a potential for exposure above the occupational exposure limits (OSHA and ACGIH) include special provisions in the work planning to address these hazards. Contact a [Safety & Health Representative](#) for guidance.

- B. Laboratories: Use containment devices, such as fume hood or a glove box (e.g., chemical fume hood, glove box, or effective exhaust-capturing equipment), when handling mercury and mercury compounds in a manner that may produce an airborne hazard (such as fumes, gases, vapors, and mists). This includes operations such as transfer operations, preparation of mixtures, blending, spraying, and heating.
- C. Training and employee information in Laboratories and HazCom: Advise personnel working with mercury of the special hazard of the chemicals in use prior to assignments involving new exposure situations, as appropriate.
- D. Conduct worker exposure monitoring specified in the Work Planning & Control documentation to verify that exposure levels do not exceed the OSHA action level (or in the absence of an action level, the OSHA Permissible Exposure Limit [PEL] or ACGIH Threshold Limit Value®). Contact a [Safety & Health Representative](#) to perform worker

exposure monitoring to determine if existing monitoring is representative of the area and operation.

- E. When handling organic mercury compounds, personal protective equipment to prevent skin contact is required. Contact your [Safety & Health Representative](#) for assistance in determining the correct glove for the work.
- F. When there is a potential for leakage from equipment containing elemental mercury provide secondary containment to capture leaks.
- G. If elemental mercury is spilled, contact your [Safety & Health Representative](#) for assistance in detecting the spill, monitoring the level, and contacting the proper personnel to clean up the spill.
- H. When an occupational workplace evaluation has determined there is unacceptable risk from reproductive hazards posed to their worker(s), Supervisors must reassess job assignments and controls.

Guidance:

Use a *Mercury Vacuum Cleaner* during spill clean-up (a device that pulls air into the apparatus and collects mercury by one of several methods including filtration, adsorption on activated carbon/cartridge, or collection in a jar attachment). Once a vacuum cleaner is used, all interior components of the vacuum are potentially contaminated with mercury.

The appropriate personal protective equipment to protect the person handling the vacuum cleaner and debris are:

- **Hand:** Use disposable gloves. Exam-style, splash gloves are acceptable. Acceptable elastomers are: Nitrile, PVC, and Natural Rubber.
- **Body:** Wear disposable suits with booties and hood. Acceptable CPC materials include: Tyvek®, KleenGuard®, and cotton.
- **Foot:** Disposable shoe coverings, boots or booties should be used. Acceptable CPC material include: Tyvek®, KleenGuard®, and rubber.
- **Respiratory:** Respiratory protection may be not required if real-time monitoring is done. If mercury levels in the area exceed or are likely to exceed the OSHA or ACGIH standards, wear APR with mercury cartridges (need end of service life indicator). A half face or full face APR or PAPR respirator with mercury cartridge or an airline respirator may be used up to the assigned protection factor listed in the SHSD's Respiratory Protection Selection procedure SOP IH72200.
- **Eye:** Safety Glasses with side shields. If exposure is above the Occupational Exposure Limit (PEL/TLV), vapor-proof goggles or full-face respirator must be used.

Chapter 7.0 Chemical Storage

Proper chemical storage is required to minimize the hazards associated with leaks, spills and accidental mixing of incompatible chemicals.

Required Procedure

- A. Label refrigerators used for storing chemicals, samples or media with words to the effect as follows: “Caution—Do Not Store Food or Beverages in This Refrigerator.”
- B. Refrigerators and freezers for storing flammable liquids must be designed, constructed, approved, and labeled for that purpose. Ordinary refrigerator/freezers that have been modified to remove spark sources are not acceptable.
- C. Store flammable liquids in metal or polyethylene safety cans approved for such storage (UL listed or FM approved):
 - Self-closing cap, automatic vent, and flame arrester;
 - Current carrying insert embedded into the can for proper grounding and a funnel;
 - Do not exceed Building code limits for the "Control Area" (as determined by a [Fire Protection Engineer](#));
 - Seal cabinet vent openings with properly fitted metal bungs; or when the cabinets are required to be vented to remove hazardous vapors, ensure they are vented to the outside and sealed using non-combustible ductwork and a non-sparking fan assembled with the motor out of the air stream.

Table 7G: Maximum Size of Containers for Combustible and Flammable Fluids

Class	Flammable liquids			Combustible liquids	
	1A	1B	1C	II	III
Glass	1pt ^a	1qt ^a	1gal	1gal	5gal
Metal (other than Department of Transportation (DOT) drums)	1gal	5gal	5gal	5gal	5gal
Safety cans ^b	2gal	5gal	5gal	5gal	5gal
Metal drums (DOT specifications)	60gal	60gal	60gal	60gal	60gal
Approved portable tanks	660gal	660gal	660gal	660gal	660gal

- D. Store pyrophoric, flammable and combustible chemicals in compliance with Fire Safety Regulations:
 - Keep away from any source of ignition: heat, sparks, or open flames.
 - Use an approved flammable storage cabinet for storing 10 or more gallons of flammable liquids.
 - Do not exceed maximum quantity storage listed on Flammable Storage Cabinets.

- Do not store flammable or combustible liquids in exit egress routes (e.g., stairwells, common hallways, emergency egress routes).
- Do not place flammable storage cabinets or other storage cabinets against interior walls in a way that obstructs interior passageways to corridors, aisles, or exit doors (see fig. 1).
- Interior passageways must be clear of obstruction and remain as wide as the exit doors.
- Do not store flammable or combustible liquids in exit enclosures (e.g., stairwells, common hallways), or in a way that obstructs corridors, aisles, or exit doors.
- Do not store Class I flammable liquids in basements.
- If the laboratory space has one exit, do not place hoods and flammable liquid cabinets adjacent to the exit. A physical separation of at least 10 feet is required.
- Store Explosives, Organic Peroxide- Class UD, Oxidizer- Class 4, Pyrophoric, and Unstable (reactive)- Class 4 or Class 3 detonable (based on Fire Code of New York State and NFPA 5000) only in a building 100% equipped with an automatic sprinkler system. Check with the [Fire Protection Engineer](#) if there is any question on the status of a building.

Fig. 1 shows a laboratory suite with interior passageway. Cabinets may be placed against the inside of Fire-Rated walls in the Lab Suite or in the lab passage against the interior walls if they do not restrict the width of the internal passageway to be less than the width of the exit door.

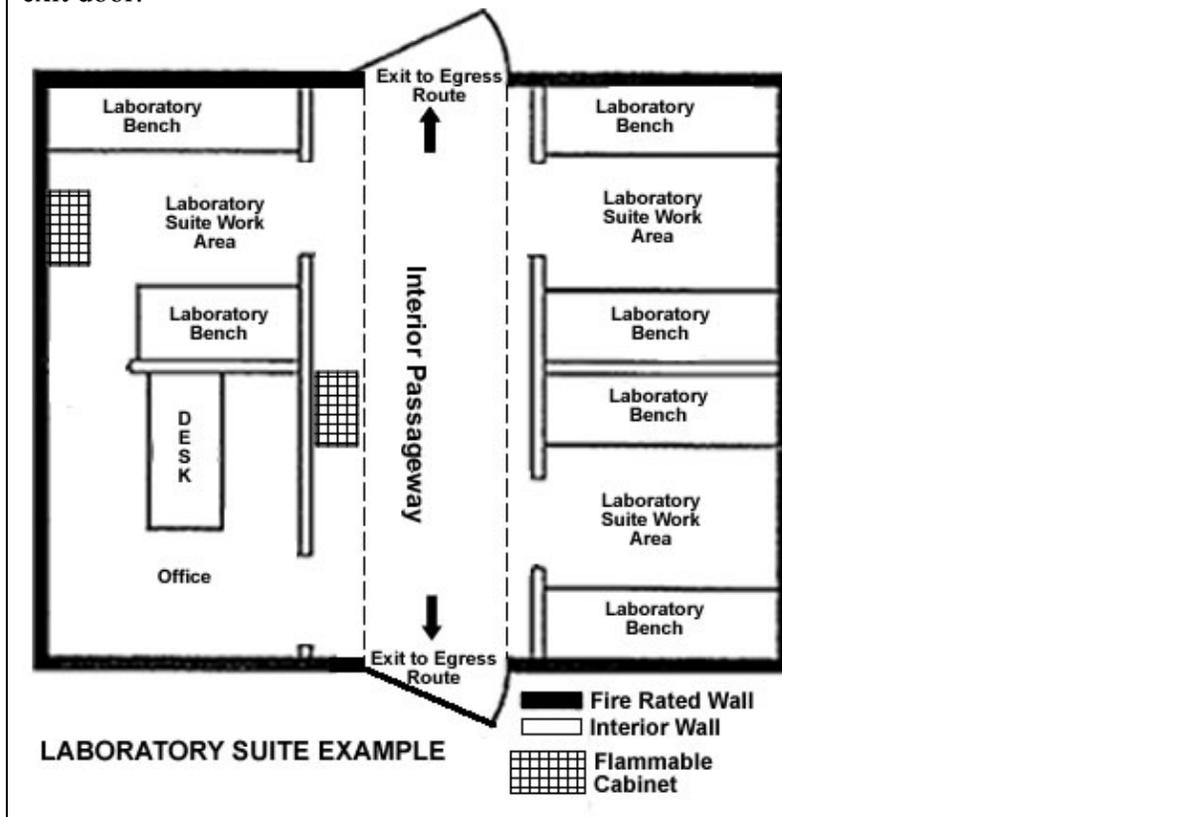
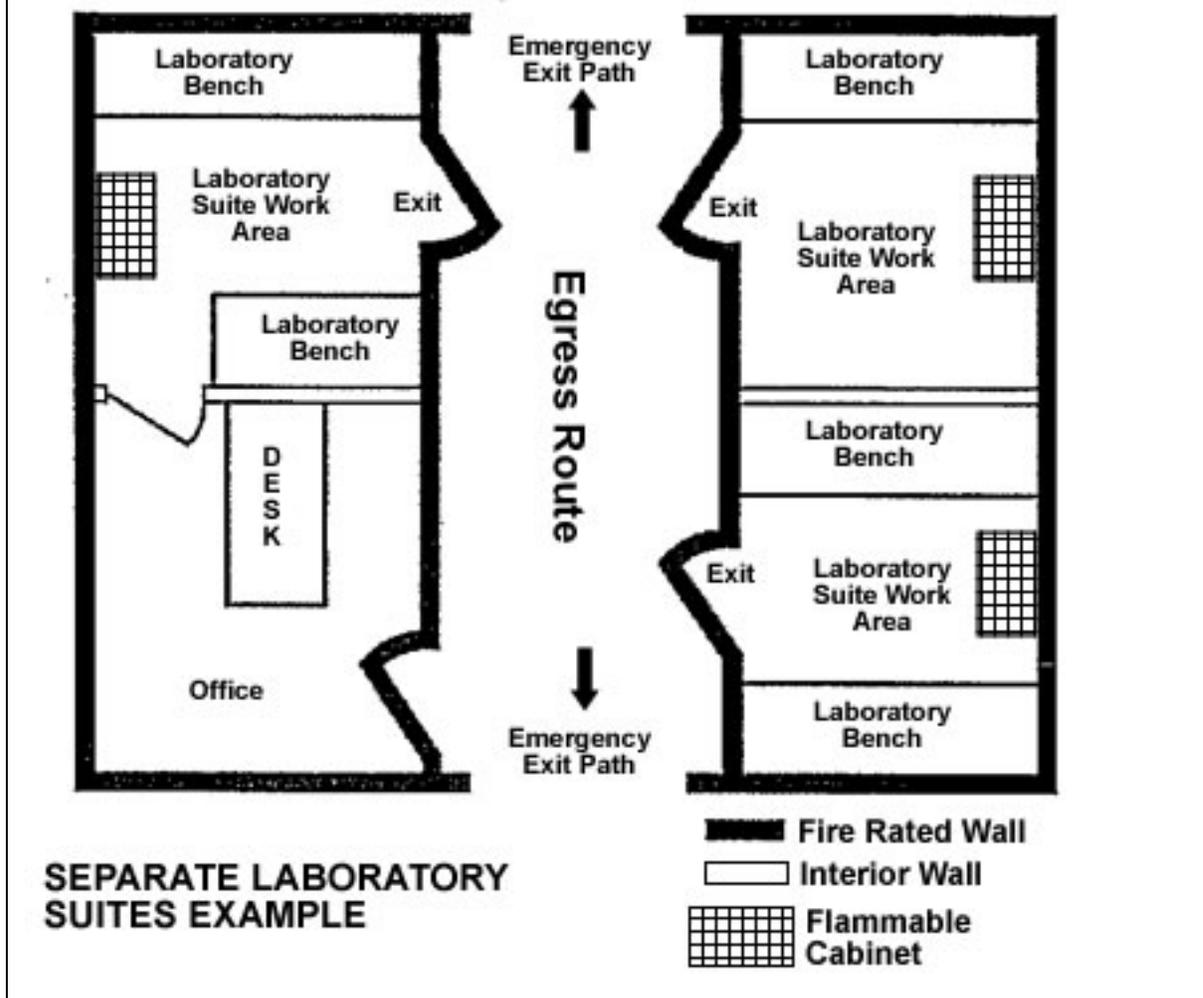


Fig. 2 shows an interior passageway that is a required egress route for exiting the area. It may not have any flammable cabinets. No other storage against the walls in the Egress Route is allowed if it restricts egress in any manner.



Guidance

- Store toxic chemicals according to the nature of the chemical, using appropriate security where necessary. Do not store chemicals alphabetically unless they have first been separated into hazard class. Use sources such as MSDSs for guidance on storage, incompatibility, reactivity, and stability of chemicals. Follow these chemical storage guidelines in the exhibit [BNL Chemical Storage Recommendations](#).

- Do not store chemicals (except cleaners) under sinks.
- Do not store chemicals over sinks or drains where breakage could cause entry into the sanitary system.
- Avoid storing chemicals in heat or direct sunlight.
- Store chemicals in cabinets or on shelves when not in use. Avoid storing chemicals on countertops or in fume hoods except for those currently used.
- Toe boards (0.5 inch high lips on the front of the shelf) on shelves lessen the chance of accidentally dislodging bottles from the shelf.
- Ensure that caps and lids on all chemical containers are tightly closed to prevent evaporation of contents. A Teflon or PVC cap liner may be used to provide a better seal. These are available through several commercial sources. Check containers regularly for leaks.
- Minimize the quantities stored.
- Store acids and bases separately from each other and from other incompatible chemicals. For example, store oxidizing acids (such as nitric, perchloric, and sulfuric acids) separately from combustible and flammable liquids/materials. Nitric acid and hydrochloric acid may be stored in the same corrosive storage cabinet, but they must be kept in separate drip trays. Do not store liquid acids and caustic liquids above eye level. Store large quantities of acids and bases in cabinets specifically designed for corrosives. Label squeeze bottles, wash bottles and Nalgene bottles with the identity of the substance and its hazards. Be aware that squeeze bottles have varying resistances to different chemicals. (They are usually made from plastics, such as polyethylene or polypropylene). They may deteriorate over time, especially when exposed to direct sunlight or UV sources.
- Store flammable and combustible liquids in a cool, dry environment free from extremes of temperature and humidity.
- Segregate liquid chemicals that are incompatible within a flammable cabinet in separate secondary storage containers (e.g., polypropylene, “Nalgene” tubs) to avoid accidental contact from leaking containers.
- Store large quantities of flammable and combustible liquids in the following preferred order:
 - Separate building detached from the main building;
 - Exterior attached building;
 - Dedicated interior flammable liquids room at or above the first floor;
 - Interior flammable liquids storage cabinet located out of the exit;
 - Safety containers in the workplace; and
 - Original containers in the workplace.

Secondary Containment for Liquids: Drip Trays

- Store all hazardous liquid chemicals in drip trays to minimize the impact and spread of a spill resulting from broken/leaking containers.
 - Size the tray capacity to 110% of the largest container or 10% of the aggregate volume of all containers, whichever is larger.
 - Use chemical resistance data to select the proper material when using plastic drip trays. (Avoid using aluminum roasting pans. They do not offer good resistance to corrosive chemicals such as acids and alkali bases).



- Photo trays provide good resistance for aqueous solutions and some organic solvents, but may not be a good choice for halogenated solvents.
- Polypropylene and Hi Density Polyethylene Trays are subject to attack by some aromatic and halogenated hydrocarbons.
- Stainless Steel and Pyrex Trays are resistant to a broader spectrum of chemicals. However they are more costly than plastic trays and aren't available in as many different sizes and configurations.

Temporary Storage of Waste

- Some wastes are very difficult to dispose of due to chemical contents or mixtures of chemicals. The Environmental Protection Division (EPD) recommends keeping the following chemicals segregated from other hazardous constituents:
 - Mercury;
 - Polychlorinated biphenyls (PCB);
 - Asbestos.
- Due to nationwide restrictions, the WMD recommends as much advanced notice as possible when disposing of the following chemicals:
- Arsenic trioxide, unused;
 - Mercurous fluoride;
 - Pentachlorophenol and its mixtures.
- Store combustible metal waste in separate non-combustible containers and empty the containers from the work place daily. Ensure proper disposal through Environmental Protection Division.
 - Transfer un-needed chemicals to hazardous waste for disposal according to the [Hazardous Waste Management](#) Subject Area.

Chapter 8.0 Decontamination of Equipment, Building, Laboratories, and Shops

All surfaces and equipment should be cleaned and put into a safe condition prior to vacating, transferring or relocating laboratory and shop spaces. Clearing laboratory and shop spaces of debris and contamination prior to transfer of ownership safeguards the personnel who work in these areas during space or building demolition, renovation, and construction activities. It also prevents delays in renovation and demolition schedules.

Required Procedure

- A. Line managers, PIs, and Supervisors of laboratory and shop spaces are responsible for removing visible residues, standing liquids, loose particulate material (whether known or unknown material) on floors, bench tops, shelves, inside drawers, cabinets, refrigerators, surfaces of local exhaust enclosures (e.g., chemical fume hoods and glove boxes) and any other potentially contaminated surfaces and any equipment that is to be moved.
- B. Remove equipment, supplies, products, and materials such as apparatuses, thermometers, gas cylinders, medical waste containers, sharps containers, sharps (needles and razor blades), trash, absorbent material, and other miscellaneous lab or shop material prior to vacating the space.
- C. If Particularly Hazardous Chemicals (either solid or liquid) have been used in a laboratory, have surface wipe samples taken before removing designated area postings. Contact a Safety & Health Representative for assistance in sampling.
- D. If perchloric acid has been used in a laboratory, have surface wipe samples taken before removing area postings. Contact a Safety & Health Representative for assistance in sampling.
- E. For construction, renovation or building demolition projects, the Project Manager is responsible for ensuring that chemical hazards have been removed by line managers, PIs, and Supervisors of laboratory and shop spaces prior to turning the building or space over to the demolition/construction subcontractor.

Guidance

- Line Managers, PIs, and Supervisors of laboratory and shop spaces are the most familiar with the hazards, historical spills, contamination, etc., in their space and are therefore responsible for ensuring that chemical, physical, biological, and radiological hazards have been removed prior to releasing these spaces to new occupants.
- Contact a Safety & Health Representative if assistance is needed with identifying hazards. In some cases, a separate hazard evaluation may be necessary.

The only official copy of this file is the one on-line in SBMS.
Before using a printed copy, verify that it is the most current version by checking the *effective date*.

- It is recommended that surfaces be wiped down with mild detergents such as soap and water.
- Contact a Safety & Health Representative if mercury droplets from historical spills are found to determine the appropriate spill-response actions.

Chapter 9.0 Emergency Procedures and Equipment

Required Procedure

- A. Ensure emergency procedures are in place per the [Emergency Preparedness](#) and [Spill Response](#) Subject Areas.
- B. Ensure workers know the location of emergency eyewash, safety shower, fire alarm pull-box, telephone, fire extinguisher, and spill control materials before beginning work.
- C. In the event of a major spill, evacuate the area and from a safe location call x2222 for Emergency Services Division.
- D. Ensure that all personnel receive a medical evaluation by the OMC when they exhibit signs or symptoms associated with chemical exposure or receive significant exposure from a chemical spill or leak.
- E. Provide plumbed emergency eyewashes and safety showers in areas where a splash hazard to corrosives, formaldehyde, eye irritants, or chemicals that are toxic via skin and/or eye contact exist. Install shower/eyewashes in the immediate work area at a location that can be reached by a blinded worker in an unimpeded path within 10 seconds (approximately 50 feet).
 - For laboratories where safety showers are not located in the work area, and where possible use the Chemical Safety Subject Area exhibit [Permanent Procedure for Interim Administrative Controls in Case of Eyewash or Safety Showers Pathway Deficiencies](#).
 - In HazCom operations where eyewash and shower are not immediately available (such as in remote locations), provide alternative means of eye and skin protection.
 - New Emergency eyewashes and safety showers need to comply with ANSI Z358.1 “American National Standard for Emergency Eyewash and Shower Equipment.”
 - Have emergency eyewashes and safety showers inspected annually by F&O to ensure they continue to meet ANSI Z358.1 “American National Standard for Emergency Eyewash and Shower Equipment.” Ensure an inspection tag is completed by F&O to document this activity. Notify your ES&H Coordinator if a tag is found that shows a past due date.

Guidance

Activate Eyewashes: routine activation and testing of eyewash stations and safety showers help ensure proper operation when needed in an emergency.

- “Activation” means a brief test to verify water flows. All users are permitted and encouraged to activate their equipment regularly. When chemical use is very intermittent, an acceptable practice can be activating the eye wash prior to use of chemicals.

- “Testing” means measurement of flow, temperature, and spray pattern. This is a task performed by F&O.
- The recommended “activation” and “testing frequency” is established based on regulatory drivers and best management practice documents.

BNL Eyewash & Safety Shower Recommendations for Activation

Work Area/ Operation Classification	Hazard	Frequency of Activation	
		Eyewash	Shower
HazCom	Only Chemicals that are <u>not</u> corrosive to eye or skin	Annual	Annual
HazCom	Chemicals that are <u>corrosive</u> to eye or skin	Weekly	Weekly
HazCom	Formaldehyde (>1%)	Weekly	Weekly
Laboratory Standard	Only Chemicals that are <u>not</u> corrosive to eye or skin	Quarterly	Annual
Laboratory Standard	Chemicals that are <u>corrosive</u> to eye or skin	Quarterly	Quarterly
Laboratory Standard	Formaldehyde (>1%)	Weekly	Weekly
References			
<ul style="list-style-type: none"> • ANSI Z358.1- 2009 • 29CFR1910.1450 <i>Occupational exposure to hazardous chemicals in laboratories.</i> • 29CFR1910.151 <i>Medical services and first aid.</i> • 29CFR1910.1030 <i>Bloodborne pathogens.</i> • 29CFR1910.1048-- <i>Formaldehyde.</i> • OSHA Instruction CPL 2-2.52 Office of Health Compliance Assistance <i>Subject: Enforcement Procedures for Occupational Exposure to Formaldehyde 11/20/1990</i> • OSHA Instruction CPL 2-2.52 for 1910.1048 Appendix C (Non-mandatory) Evaluation Criteria for Emergency Showers and Eyewashes (FORMALDEHDE) • 29CFR1910.1052-- <i>Methylene Chloride.</i> • 29CFR1910.1045-- <i>Acrylonitrile.</i> • 29CFR1910.1018-- <i>Inorganic arsenic.</i> • 29CFR1910.1044-- <i>1,2-dibromo-3-chloropropane.</i> • 29CFR1910.133-- <i>Eye and face protection for General Industry</i> • 29CFR1926.102-- <i>Eye and face protection for Construction</i> 			

Use the [Spill Response Subject Area Flowchart](#) in the [Spill Response](#) Subject Area as a guide to determine how you should handle a spill. For more guidance, see the [Emergency Preparedness](#) and [Spill Response](#) Subject Areas.

As described in your work planning, limit small spills using Spill Kits and procedures (e.g., seal drains).

You can consider cleaning up a small chemical spill when the following conditions are present:

- The spill is less than a gallon.

- You have been approved to do spill cleanup by your supervisor.
- There is no potential for release to the environment. **Note:** Care must be taken to avoid spreading or tracking chemical contamination to other areas.
- There are no personal injuries resulting from the spill.
- You know the chemical, its hazards, and the correct cleanup procedures.
- You have the proper spill cleanup materials and PPE to protect yourself during the cleanup. This may be different PPE than what you wear to work with the chemical.

When a spill exceeds your ability to safely and effectively clean up the spill:

- Leave the immediate area.
- Close the door.
- Stay close by and control access. Post the entrance with a warning such as “Spill—Do Not Enter”.
- Call (or have someone call) ext. 2222 for assistance.

- Keep spill cleanup kits in your work area. There are different types for acids, bases and solvents. These are commercially available. Absorbents and other materials need to be “inert” to the spilled material. Combustible materials such as sawdust and paper towels are generally inappropriate substitutes for the materials contained in spill kits.
- For mixed (i.e., radiological and chemical) spills, call x2222 and contact your Supervisor, your ES&H Coordinator, and the assigned [Facility Support Representative](#).
- Ensure waste materials are properly contained and labeled and are placed in an approved Satellite Accumulation Area.

Personal Injury from or Exposure to Chemicals

In general, adhere to the following First Aid Measures for accidental exposures:

- Inhalation:
 - Leave the area immediately or remove affected co-workers if it is safe for you to do so.
 - Make others nearby aware of the emergency.
 - Close the door.
 - Call x222 for assistance.

- Skin or eye contact:
 - Flush exposed or irritated eyes with copious amounts of water or saline for at least 15 minutes. While flushing, or as soon as possible, call x2222 or have someone drive you to the Occupational Medicine Clinic once sufficient flushing has taken place.
 - For small areas of skin contamination: Remove contaminated clothing; wash the skin thoroughly with water.
 - For large areas of skin contamination: Remove contaminated clothing; wash the area thoroughly in a safety shower; and call (or have someone else call) x2222 for assistance.
 - Flush the affected area for at least 15 minutes (see exceptions for phenol and hydrofluoric acid).

- Ingestion:

- Call x2222 as soon as possible.
- If spontaneous vomiting appears imminent or occurs, help the person keep a clear airway.
- If victims are unconscious or cannot sit up, turn them on their side to help avoid possible aspiration of vomitus.
- Never give liquid to a person showing signs of sleepiness or who may become unconscious.

- Injection:
 - Injections can occur from lacerations and punctures when handling sharps (needles, phlebotomy supplies) that are contaminated with chemicals.
 - All sharps injuries MUST be reported to the Occupational Medicine Clinic.
 - First stop the bleeding. Minor cuts and scrapes usually stop bleeding on their own. If they don't, apply gentle pressure with a clean cloth or bandage.
 - Rinse out the wound with clear water. Soap can irritate the wound.
 - Report to the Occupational Medicine Clinic or call x2222.
 - In all cases, it is important for personnel to identify the chemical involved in order to provide treatment. Provide the chemical name to emergency response personnel and health care professionals.

Fire Extinguishers: Follow the [Fire Safety](#) Subject Area

- If additional extinguishers are needed for an area or if special extinguishers are needed for materials such as combustible metals, contact the [BNL Fire Safety Subject Matter Expert](#) for information concerning recommendations and requirements.
- Fire extinguishers are to be used by BNL personnel who have taken General Employee Training and are confident that they can fight the fire safely. [Fire Extinguisher Safety](#) (TQ-FIRE-EXT) may be required by your Work Planning.
- If the fire is too large or too dangerous, leave the building and pull the fire alarm on your way out. Once at a safe location, call x2222 and inform the dispatcher of the fire location (building and room number) and what is burning, if known.

Chapter 10.0 Medical Consultation and Medical Surveillance

Required Procedure

- A. Medical surveillance is required for workers exposed to OSHA Regulated Chemicals & OSHA Particularly Hazardous Substance at airborne concentrations requiring the creation of Regulated Areas. Consult a [Safety & Health Representative](#) for an assessment regarding chemical exposures and regulatory exposure levels.
 - B. Supervisors inform the Occupational Medicine Clinic (OMC) of employee(s) who require medical surveillance using the Job Assessment Form.
-

Guidance

- Medical consultations and examinations related to employee exposure are provided by the Occupational Medicine Clinic (x3670) to any employee exposed at or above an Action Level (or in the absence of an established AL, one-half the lower of the OSHA PEL or the ACGIH TLV); when an employee develops a sign or symptom of exposure to a hazardous material; or when an uncontrolled event such as a spill, leak, or explosion takes place in which there is a likelihood of employee exposure. Anyone with a concern or question may request a medical consultation.
- The Occupational Medicine Clinic may also be consulted by women who are pregnant or anyone (male or female) with concerns regarding reproduction.
- Medical surveillance may be requested when there is a possibility of exposure above the OSHA regulatory limits.
- Complete the Job Assessment Form (JAF) before an examination at the OMC. A second form, Additional Medical Surveillance (AMS) Form, is used to request surveillance for those items not on the JAF. These evaluations can be done at the time of the scheduled examination, on request, or at any time.

Chapter 11.0 Transporting Hazardous Materials

Required Procedure

- A. Follow the [Movement by Vehicle of Hazardous and Radiological Materials On-site](#) Subject Area
 - B. Follow the [Transportation of Hazardous and Radioactive Materials Off-Site](#) Subject Area
-

Guidance

None

Appendices to the BNL Chemical Hygiene Plan

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Appendix A3: Chemical Toxicology Overview	93

Appendix A1: Glossary of Terms

<i>Action Level</i>	A chemical concentration designated in an OSHA standard for a specific substance. The action level initiates certain required activities such as exposure monitoring and medical surveillance.
<i>Acute effect</i>	Symptom of exposure to a hazardous material that appears soon after a short-term exposure, coming quickly to a crisis.
<i>Acute toxicity</i>	Adverse biological effects of a single dose of a toxic agent.
<i>American Conference of Governmental Industrial Hygienists (ACGIH)</i>	The American Conference of Governmental Industrial Hygienists is a voluntary membership organization of professional industrial hygiene personnel in governmental or educational institutions. The ACGIH develops and publishes recommended occupational exposure limits each year called Threshold Limit Values (TLVs) for hundreds of chemicals, physical agents, and Biological Exposure Indices (BEIs), to assess worker exposure. (As per 10 CFR 851, the value published in the ACGIH 2005 Threshold Limits Values for Chemical Substances and Physical Agents & Biological Exposure Indices is observed at BNL.)
<i>Administrative controls</i>	Methods of minimizing inhalation and physical contact exposures through measures such as: <ul style="list-style-type: none"> • Periods away from contaminant or physical stressor through job rotation, limitation of exposure time, or work/rest regimens; • Laboratory safety and health procedures; • Signs and postings.
<i>American National Standards Institute (ANSI)</i>	This privately funded, voluntary organization develops standards for the safe design and operation of equipment and safe practices or procedures for industry.
<i>Anesthetic</i>	A chemical that causes drowsiness. Large doses of anesthetic chemicals can cause unconsciousness, coma, and death.
<i>Asphyxiant</i>	A chemical vapor or gas that replaces air and can, thereby, cause death by suffocation. Asphyxiants are especially hazardous in confined spaces.
<i>Boiling point</i>	The temperature at which the vapor pressure of a liquid equals atmospheric pressure or at which the liquid changes to a vapor. The boiling point is usually expressed in degrees Fahrenheit. If a flammable material has a low boiling point, it indicates a special fire hazard.
<i>Carcinogen</i>	<ul style="list-style-type: none"> • Carcinogens are agents that cause neoplasms (tumors) in humans and/or animals. Some carcinogens react directly with a cell's genetic information (the DNA), causing changes (mutations) that are incorporated into subsequent generations of that cell. • Select Carcinogens are chemicals that are designated as carcinogens by specific agencies per OSHA under the Laboratory Standard in the Particularly Hazardous Substances Requirements of the Chemical Hygiene Plan. • Regulated Carcinogens which require need special accommodations such as change out rooms, showers, etc., similar to an asbestos job. <p>A chemical substance used in the workplace that has been designated as a carcinogen or potential carcinogen in the following sources:</p> <ul style="list-style-type: none"> • National Toxicology Program (NTP), Annual Report on Carcinogens (Known or Reasonably Anticipated); • International Agency for Research on Cancer (IARC), Monographs

	<p>(Group 1A, 2A, & 2B);</p> <ul style="list-style-type: none"> • OSHA Standard 29 CFR 1910, Subpart Z, Toxic and Hazardous Substances cited as carcinogens; and • American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Chemical Substances and Physical Agents (Appendix A, Categories A1 and A2).
<i>CAS number</i>	Identifies a particular chemical by a number assigned by the Chemical Abstracts Service, a service of the American Chemical Society that indexes and compiles abstracts of worldwide chemical literature called <u>Chemical Abstracts</u> .
<i>Central nervous system</i>	The part of the body made up of the brain, spinal cord, and nerves.
<i>Chemical</i>	Any element, chemical compound, or mixture of elements and/or compounds. As broadly applied to the chemical industry, an element or a compound produced by chemical reactions on a large scale for either direct industrial, consumer use, or for reaction with other chemicals.
<i>Chemical Hygiene Officer (CHO)</i>	An employee who is designated by BNL to provide technical guidance in the development and implementation of the <u>Chemical Hygiene Plan</u> and the Hazard Communication Program. BNL Chemical Hygiene Officer is the Chemical Safety Subject Matter Expert (SME).
<i>Chemical Hygiene Plan (CHP)</i>	A written program developed and implemented by BNL to set forth procedure, equipment, and work practices that protect employees from the health hazards presented by hazardous chemicals in laboratory settings and meet the requirements of 29CFR 1910.1450 ii (e).
<i>Chemical Hygiene Plan (CHP)</i>	The written Web-based program developed by BNL to comply with the federal OSHA “Lab Standard.” The CHP addresses all elements of the OSHA-mandated <u>Chemical Hygiene Plan</u> and provides further information specific to BNL.
<i>Chemical Laboratory Operation</i>	Laboratory use of chemicals that meets the following conditions: <ul style="list-style-type: none"> • Chemical manipulations are easily carried out by one person; • Multiple chemical procedures or chemicals are used; • The procedures involved are not part of a production process, nor in any way simulate a production process; • Protective laboratory practices and equipment are available and in common use to minimize the potential for employee exposure to hazardous chemicals.
<i>Chemical reaction</i>	A change in the arrangement of atoms or molecules to yield substances of different composition and properties.
<i>Chemical Management System (CMS)</i>	BNL's chemical management system that enables retrieval of MSDS, chemical forms, location of chemicals and chemical contact persons, communication with the CMS team, and other information on chemicals and chemical resources.
<i>Chronic effect</i>	Symptom of exposure to a hazardous material that develops slowly after many exposures or that recurs often.
<i>Chronic exposure</i>	Repeated exposure or contact with a toxic substance over a long period. Adverse biological effects from chronic exposure develop slowly, last a long time, and frequently recur.
<i>Chronic toxicity</i>	Adverse biological effect of repeated doses or long-term exposure to a toxic agent.

<i>Closed Container</i>	A container sealed by means of a lid or other device such that liquid, vapor or dusts will not escape from it under ordinary conditions of use or handling.
<i>Combustible</i>	Able to catch on fire and burn. According to the DOT and NFPA, combustible liquids are those having a flash point at or above 100°F (37.8°C), or liquids that will burn. They do not ignite as easily as flammable liquids. Non-liquid substances that will burn, such as wood and paper, are called “ordinary combustibles” (see flammables).
<i>Combustible gas</i>	A combustible gas is: <ul style="list-style-type: none"> • A gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70°F (21.1°C); or • A gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 130°F (54.4°C) regardless of the pressure at 70°F (21.1°C); or • A liquid having a vapor pressure exceeding 40 psi at 100°F (37.8°C) as determined by ASTM D-323-72.
<i>Combustible liquid</i>	A liquid having a flash point at or above 100°F (37.8°C). Combustible chemical liquids are subdivided as follows: <ul style="list-style-type: none"> • Class II liquids include those having flash points at or above 37.8°C (100°F) and below 60°C (140°F). • Class IIIA liquids include those having flashpoints at or above 60°C (140°F) and below 93°C (200°F). • Class IIIB liquids include those having flash points at or above 93°C (200°F).
<i>Control Area</i>	Spaces within a building that are enclosed and bounded by exterior walls, fire walls, fire barriers and roofs, or a combination thereof, where quantities of hazardous materials that do not exceed the maximum allowable quantities per control area are stored, dispensed, used or handled.
<i>Corrosive</i>	A chemical that causes visible destruction of, or irreversible changes in, living tissue by chemical action at the site of contact, or that has a severe corrosion rate on structural materials.
<i>Cryogenic liquid</i>	A refrigerated liquefied gas having a boiling point colder than -90°C (-130°F) at 1.1.3 pKa (14.7 psi) absolute.
<i>decomposition</i>	The breakdown of a material into simpler compounds by chemical reaction, decay, heat, or other process.
<i>Department of Transportation (DOT)</i>	The United States Department of Transportation is the federal agency that regulates the labeling and transportation of hazardous materials.
<i>Dermal</i>	Refers to the skin.
<i>Dermatitis</i>	An inflammation of the skin that can be caused by irritation (chemical, physical, or mechanical) or allergic reaction.
<i>Designated area</i>	An area that may be used for work with Particularly Hazardous Substances including OSHA “Select Carcinogens,” reproductive toxins or substances that have a high degree of acute toxicity (Highly Acute Toxins). A designated area may be the entire laboratory, an area within a laboratory, or a device such as a fume hood.
<i>Engineering controls</i>	Methods of controlling exposures by eliminating or reducing the presence of the chemical. It includes measures such as: <ul style="list-style-type: none"> • Substituting a less hazardous chemical; • Isolating or enclosing a process or work operation (e.g., use of a closed system, glove box, or toxic gas cabinet);

	<ul style="list-style-type: none"> Using wet methods to reduce aerosol generation; Using local exhaust ventilation at the point of generation or laboratory fume hood.
<i>Evaporation rate</i>	The rate at which a material is converted to vapor (evaporates) at a given temperature and pressure when compared to the evaporation rate of a reference material (e.g., butyl acetate). Health and fire hazard evaluations of materials involve consideration of evaporation rates as one aspect of the evaluation.
<i>Explosive</i>	Chemicals that cause a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.
<i>Flammable Gas</i>	Any gas that forms a flammable mixture (explosive mixture) with air at atmospheric pressures.
<i>Flammable liquid</i>	A liquid having a flash point below 100°F (37.8°C) and having a vapor pressure not exceeding 40 lb. per sq. in. (absolute) (2068 mm Hg) at 100°F (37.8°C). Class I liquids are subdivided as follows <ul style="list-style-type: none"> Class IA includes those having flash below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). Class IB includes those having flash points below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). Class IC includes those having flash points below 73°F (22.8°C) and below 100°F (37.8°C).
<i>Flammable Liquids Cabinet</i>	A cabinet meeting the requirements of OSHA. OSHA does not approve cabinets. Vendors certify compliance with 10CFR1910.106 requirements.
<i>Flammable solid</i>	A substance that is solid, other than a blasting agent or explosive as defined in 1910.109(a); that is liable to cause fire through friction, absorption of moisture, spontaneous chemical change, or retained heat from manufacturing or processing; or that can be ignited readily and when ignited burns so vigorously and persistently as to create a serious hazard. A chemical is considered to be a flammable solid if, when tested by the method described in 16 CFR 1500.44, it ignites and burns with a self-sustained flame at a rate greater than one-tenth of an inch per second along its major axis.
<i>Flashpoint</i>	"Flashpoint" means the minimum temperature at which a liquid gives off a vapor in sufficient concentration to ignite when tested as follows: <ul style="list-style-type: none"> Tagliabue Closed Tester (See American National Standard Method of Test for Flash Point by Tag Closed Tester, Z11.24-1979 [ASTM D 56-79]) for liquids with a viscosity of less than 45 Saybolt Universal Seconds (SUS) at 100 deg. F (37.8 deg. C), that do not contain suspended solids and do not have a tendency to form a surface film under test; or Pensky-Martens Closed Tester (see American National Standard Method of Test for Flash Point by Pensky-Martens Closed Tester, Z11.7-1979 [ASTM D 93-79]) for liquids with a viscosity equal to or greater than 45 SUS at 100 deg. F (37.8 deg. C), or that contain suspended solids, or that have a tendency to form a surface film under test; or Seta flash Closed Tester (see American National Standard Method of Test for Flash Point by Seta flash Closed Tester [ASTM D 3278-78]). Organic peroxides, which undergo auto accelerating thermal decomposition, are excluded from any of the flashpoint determination methods specified above.
<i>Formula</i>	The molecular composition of a chemical compound written in scientific symbols. Water is H ₂ O; hydrochloric acid is HCl.

<i>Fume hood</i> <i>(Laboratory Hood)</i>	A ventilation device comprised of an enclosure on five sides with a movable sash on the remaining side. Fume hoods are constructed and maintained to draw air from the open side in order to prevent or minimize the escape of air contaminants into the work area. This device allows chemical manipulations to be conducted in the enclosure without insertion of any portion of the employee's body other than hands and arms.
<i>Gas Cabinet</i>	A fully enclosed, noncombustible enclosure, rated or listed for gas storage, used to provide an isolated environment for compressed gas cylinders in storage or use. Doors and access ports for exchanging cylinders and accessing pressure-regulating controls are allowed to be included.
<i>Gas Room</i>	A separately ventilated, fully enclosed room in which only compressed gases and associated equipment and supplies are stored or used.
<i>Hazard Communication (HAZCOM) Program</i>	A written document that describes BNL's implementation of the OSHA Hazard Communication Standard 29CFR 1910.1200. The purpose of the program is to ensure that chemical hazards are communicated to employees in a consistent manner across BNL. BNL's plan includes using the Chemical Hygiene Plan in the Chemical Safety Subject Area and Hazard Communication Training.
<i>Hazardous material</i>	Any substance or compound that has the capability of producing adverse effects on the health and safety of humans as a hazardous waste, as well as reaction or change.
<i>Health Hazard</i>	Any substance that may cause acute or chronic health effects in exposed individuals. Such substances include the following: <ul style="list-style-type: none"> • Carcinogens; • Toxic or acutely toxic agents; • Reproductive or developmental toxins; • Irritants; • Corrosives; • Sensitizers; • Liver, kidney, and nervous system toxins; • Agents that act on the blood-forming systems; • Agents that damage the lungs, skin, eyes, or mucous membranes; • Biologically produced chemical agents.
<i>Hematopoietic system</i>	The blood-forming organs of the body, including bone marrow and the spleen.
<i>Hepatotoxin</i>	A chemical that can cause liver damage (e.g., carbon tetrachloride).
<i>Highly Acute Toxin</i>	A chemical that is classified under 29CFR 1910.1200 as Toxic or Highly Toxic. Substances of high acute toxicity include materials that may be fatal or cause damage to target organs from a single exposure or from exposures of short duration. They also include materials capable of causing intense irritation that can result in pulmonary edema (fluid and swelling in the lungs), chemical asphyxia, and systemic (body wide) poisoning. BNL maintains a list of Highly Acute Toxins that you can search for by various criteria such as work area. The MSDS provides information on the toxicity of substances that you may be working with. A Safety & Health Services Representative may also be consulted for additional guidance.
<i>Highly Toxic Chemical</i>	A chemical falling within any of the following categories: <p>(a) A chemical that has a median lethal dose (LD50) of 50 milligrams or less per kilogram of body weight when administered orally to albino rats weighing</p>

	<p>between 200 and 300 grams each.</p> <p>(b) A chemical that has a median lethal dose (LD50) of 200 milligrams or less per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each.</p> <p>(c) A chemical that has a median lethal concentration (LC50) in air of 200 parts per million by volume or less of gas or vapor, or 2 milligrams per liter or less of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.</p>
<i>Ignitable</i>	A solid, liquid, or compressed gas that has a flash point of less than 140°F.
<i>Ignition temperature</i>	The lowest temperature at which a substance will ignite and continue to burn. The lower the ignition temperature, the more likely the substance is to be a fire hazard.
<i>Incompatible Materials</i>	Materials that, when mixed, have the potential to react in a manner that generates heat, fumes, gases or by products which are hazardous to life or property.
<i>Ingestion</i>	Taking a material into the body through the mouth and swallowing it.
<i>Inhalation</i>	Breathing in of airborne substances that may be in the form of gases, fumes, mists, vapors, dusts, or aerosols.
<i>Inhibitor</i>	A substance that is added to another to prevent the occurrence of an undesirable chemical reaction.
<i>Irritant</i>	A chemical, which is not corrosive, but which causes a reversible inflammatory effect on living tissue by chemical action at the site of contact.
<i>Laboratory Area</i>	A facility where the "laboratory use of hazardous chemicals" occurs. It is a workplace where relatively small quantities of hazardous chemicals are used on a non-production basis. An area that meets the definition under the Laboratory Standard as performing laboratory scale work.
<i>Laboratory Area (Fire Safety Definition)</i>	A facility where the "laboratory use of hazardous chemicals" occurs. It is a workplace where relatively small quantities of chemicals are used to synthesize new compounds on a non-production basis. The mere use of chemicals or combining of chemicals does not define laboratory use (e.g., mixing a two part epoxy for repairs)
<i>Laboratory hood</i>	A device located in a laboratory that is made up of an enclosure on five sides with a movable sash or fixed partial enclosure on the remaining side; constructed and maintained to draw air from the laboratory and to prevent or minimize the escape of air contaminants into the laboratory; and allows chemical manipulations to be conducted in the enclosure without insertion of any portion of the employee's body other than hands and arms.
<i>Laboratory scale</i>	Work with substances in which the containers used for reactions, transfers, and other handling of substances 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.
<i>Laboratory use of Hazardous chemicals</i>	<p>Handling or use of such chemicals in which all of the following conditions are met:</p> <ul style="list-style-type: none"> • Chemical manipulations are carried out on a laboratory scale; • Multiple chemical procedures or chemicals are used;

	<ul style="list-style-type: none"> The procedures involved are not part of a production process, nor in any way simulate a production process; and Protective laboratory practices and equipment are available and in common use to minimize the potential for employee exposure to hazardous chemicals.
<i>Lower Explosive Limit (LEL)/Lower Flammable Limit (LFL)</i>	The minimum concentration of vapor in air at which propagation of flame will occur in the presence of an ignition source. The LFL is sometimes referred to as LEL of lower explosive limit.
<i>Material Safety Data Sheet (MSDS)</i>	Written or printed materials, supplied by the manufacturer or BNL, containing information on chemical identity, physical and chemical properties, physical hazards, health hazards, protective safety methods, and emergency procedures.
<i>Organic peroxide</i>	An organic compound that contains the bivalent -O-O-structure and that may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms have been replaced by an organic radical. (i.e., compounds that release oxygen readily and are capable of violent or explosive decomposition when exposed to air).
<i>Organic Peroxide (Fire Safety Definition)</i>	<p>An organic compound that contains the bivalent -O-O-structure and that may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical. Organic peroxides can pose an explosion hazard (detonation or deflagration) or they can be shock sensitive. They can also decompose into various unstable compounds over an extended period of time.</p> <ul style="list-style-type: none"> Unclassified detonable: Organic peroxides that are capable of detonation. These peroxides pose an extremely high-explosion hazard through rapid explosive decomposition. Class I: formulations that are capable of deflagration but not detonation. Class II: formulations that burn very rapidly and that pose a moderate reactivity hazard. Class III: formulations that burn rapidly and that pose a moderate reactivity hazard. Class IV: formulations that burn in the same manner as ordinary combustibles and that pose a minimal reactivity hazard. Class V: formulations that burn with less intensity than ordinary combustibles or do not sustain combustion and that pose no reactivity hazard.
<i>OSHA Laboratory Standard</i>	The OSHA requirements for safe handling of chemical hazards in a laboratory setting, as defined in 29 CFR 1910.1450 - Occupational exposure to hazardous chemicals in laboratories .
<i>OSHA Regulated Chemicals</i>	Chemicals for which OSHA has promulgated specific regulations in 29 CFR 1910 or 29 CFR 1926.
<i>Oxidizer</i>	A chemical other than a blasting agent or explosive as defined in 1910.109(a), that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases.
<i>Oxidizer (Fire Safety BCNYS Definition)</i>	<p>A material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion or combustible materials. Examples of other oxidizing gases include bromine, chlorine, and fluorine.</p> <ul style="list-style-type: none"> Class 4 can undergo an explosive reaction due to contamination or exposure to thermal or physical shock. In addition, the oxidizer will enhance the burning rate and can cause spontaneous ignition of

	<p>combustibles.</p> <ul style="list-style-type: none"> • Class 3 will cause a severe increase in the burning rate of combustible materials with which it comes in contact or that will undergo vigorous self-sustained decomposition due to contamination or exposure to heat • Class 2 will cause a moderate increase in the burning rate or that causes spontaneous ignition of combustible materials with which it comes in contact. • Class 1 slightly increases the burning rate, which is its primary hazard, but does not cause spontaneous ignition when it comes in contact with combustible materials.
<i>Oxidizing Gas</i>	A gas that can support and accelerate combustion of other materials.
<i>Particularly Hazardous Substance (PHS)</i>	<p>OSHA established a category of chemicals for laboratory work known as Particularly Hazardous Substances (PHSs) for which additional precautions are required. Particularly Hazardous Substances include select carcinogens, reproductive toxins, and substances with a high degree of acute toxicity. Specific lists of these Particularly Hazardous Substances are found here:</p> <ul style="list-style-type: none"> • Carcinogen (see the BNL Carcinogen List); • Reproductive Toxin (see the CMS Reproductive Toxins Table); • Highly Acute Toxin (see the CMS Highly Acute Toxin Table).
<i>Permissible Exposure Limits (PELs)</i>	Airborne concentrations of substances that represent conditions under which it is believed nearly all workers may be repeatedly exposed, daily, without adverse effects. PELs represent time-weighted average concentrations, usually expressed in units of mg/m ³ or parts per million (ppm) for an 8-hour workday within a 40-hour work week and two days off. The permissible exposure limits for air contaminants can be found in 29 CFR 1910.1000, Table Z-1 Limits for Air Contaminants .
<i>Personal Protective Equipment (PPE)</i>	A control measure that places a barrier between the worker and the hazards, which is used when engineering and administrative controls are not sufficient to control exposure; while engineering controls are being installed; and when engineering and administrative controls are not possible. Examples of PPE are gloves, respirators, lab coats, coveralls, and protective suits.
<i>Physical Hazard</i>	A chemical for which there is scientifically valid evidence that it is a combustible liquid, compressed gas, explosive, flammable, organic peroxide, oxidizer, pyrophoric, unstable (reactive), or water-reactive.
<i>Physical Hazard (BCNYS)</i>	A chemical for which there is evidence that it is a combustible liquid, compressed gas, cryogenic, explosive, flammable gas, flammable liquid, flammable solid, organic peroxide, oxidizer, pyrophoric or unstable (reactive) or water-reactive material.
<i>Pyrophoric</i>	A chemical that will ignite spontaneously in the ambient atmosphere at or below 130°F (54.4°C).
<i>Pyrophoric (BCNYS)</i>	A chemical with an auto-ignition temperature in air, at or below a temperature of 13°F (-11°C)
<i>Reproductive Toxin</i>	Agents that affect the chromosomal structure of a cell or will adversely affect the developing fetus. Reproductive toxins affect reproductive capabilities including chromosomal damage (mutations) and produce effects on developing fetuses (teratogenesis). Reproductive toxins can affect both men and women. Examples of adverse reproductive health effects include birth defects, spontaneous abortion, fetal developmental damage, and infertility.

<i>Safety Can</i>	An approved container of not more than 5-gallon (19L) capacity having a spring-closing lid and spout cover so designed that it will relieve internal pressure when subjected to fire exposure.
<i>Secondary Container</i>	Any container into which chemicals are transferred (e.g., beaker, jar, vial).
<i>Secondary Containment</i>	Trays or outer jacketing surrounding a container used to minimize or contain a spill if the container breaks or leaks. It is able to accommodate the contents of the largest container in the secondary containment, given the area that any other containers in the secondary containment take up.
<i>Short-Term Exposure Limit® (STEL®)</i>	Amount of a chemical you can safely be exposed to over a 15-minute period. (As per 10 CFR 851, the value published in the ACGIH 2005 Threshold Limits Values for Chemical Substances and Physical Agents & Biological Exposure Indices is observed at BNL.)
<i>Target organ toxin</i>	Chemical that adversely affects a particular organ in the body.
<i>Threshold Limit Value® (TLV®)</i>	A time-weighted average airborne concentration for a normal 8-hour work day and 40-hour work week to which nearly all workers may be repeatedly exposed without adverse effect. The Conference of Governmental Industrial Hygienists (ACGIH) adopts threshold limit values. (As per 10 CFR 851, the value published in the ACGIH 2005 Threshold Limits Values for Chemical Substances and Physical Agents & Biological Exposure Indices is observed at BNL.)
<i>Toxic chemical</i>	A chemical falling within any of the following categories: <ul style="list-style-type: none"> • A chemical that has a median lethal dose (LD50) of more than 50 milligrams per kilogram but not more than 500 milligrams per kilogram of body weight when administered orally to albino rats weighing between 200 and 300 grams each. • (b) A chemical that has a median lethal dose (LD50) of more than 200 milligrams per kilogram but not more than 1,000 milligrams per kilogram of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each. • (c) A chemical that has a median lethal concentration (LC50) in air of more than 200 parts per million but not more than 2,000 parts per million by volume of gas or vapor, or more than two milligrams per liter but not more than 20 milligrams per liter of mist, fume, or dust, when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.
<i>Unstable (reactive)</i>	Chemical that decomposes, condenses, or becomes self-reactive under conditions of shock, pressure, or temperature.
<i>Water reactive</i>	Chemical that reacts with water to release a gas that is flammable, explosive, or a health hazard.
<i>Work area</i>	A room or defined space in a workplace where hazardous chemicals are produced or used, and where employees are present
<i>Workplace</i>	The BNL site, off-site job site, or project at one geographical location containing one or more work areas.

Appendix A2: Primer on OSHA Chemical Regulations

The purpose of BNL's Chemical Hygiene Plan is to establish procedures to protect employees from the hazards of the chemicals in their work area. This is also a legal requirement mandated by several Federal Occupational Safety and Health Administration standards, including the Hazard Communication Standard, the Exposure to Hazardous Materials in Laboratories Standard, and the OSHA PPE Standard.

[Hazard Communication Standard \(29 CFR 1910.1200\)](#)

The OSHA Hazard Communication Standard (HCS) is intended to reduce the incidence of chemically related occupational illnesses and injuries. The Standard establishes the minimum requirements that employers are to adhere to for communicating hazards to workers. This standard is often referred to as the "worker right-to-know" standard.

[Exposure to Hazardous Materials in Laboratories Standard \(Lab Standard\) \(29 CFR 1910.1450\)](#)

Laboratory workers are protected by a related but different OSHA regulation, "Occupational Exposures to Hazardous Chemicals in Laboratories."

The "Lab Standard" relies on the technical judgment of line management to inform all people who work in their laboratories of the steps to protect themselves from hazardous exposures to chemicals in the laboratory and what to do if an exposure should occur.

The Chemical Hygiene Plan is a description of the facilities, rules, procedures and policies of the laboratory that are aimed at minimizing employee exposures to hazardous chemicals during normal operations and during unplanned events such as chemical spills. Additional information on chemical hygiene and prudent laboratory practices may be found in [29 CFR 1910.1450 Appendix A](#).

Material Safety Data Sheets (MSDSs) Guidance

An MSDS is a technical bulletin detailing information about a hazardous chemical. Every chemical manufacturer or importer is to develop or obtain an MSDS for each hazardous chemical it supplies (29 CFR 1910.1200[g]). Distributors also are to provide MSDSs for their hazardous chemicals to other distributors and commercial purchasers. As an employer, BNL is to maintain an MSDS for each hazardous chemical in the workplace. An MSDS for hazardous chemicals is received with incoming shipments and is to be maintained and made readily accessible to employees. BNL has developed an electronic MSDS database for employees to access.

No standard format for the MSDS is specified but all required information is to be included. The MSDS is to be written in English and at a minimum, contain the following:

- the identity (any chemical or common name) that is used on the container label;
- the chemical and common name of all ingredients having known health hazards if present in concentrations greater than 1% and for carcinogens, if present at 0.1% or more;
- the physical and chemical characteristics of the hazardous components;
- the physical and health hazards, including signs and symptoms of exposure and prior and/or existing contra-indicating medical conditions;
- the primary routes of entry;
- any known exposure limits (OSHA PELs or ACGIH TLVs);
- whether the hazardous chemical is listed in the NTP Annual Report on Carcinogens or is a potential carcinogen according to IARC or OSHA;
- precautions for safe handling/use and procedures for spill/leak cleanup;
- control measures;
- emergency first aid procedures;
- date of preparation; and

- the name, address, and telephone number of the company or the responsible employee distributing the MSDS.

When an MSDS is prepared, the chemical has to be evaluated based on the mandatory hazard determination requirements. When uncertainty exists concerning a chemical's hazards, the preparer should be conservative in the evaluation to ensure employee protection.

How to Read an MSDS

The MSDS outlines precautions for safe handling of the chemical in the sections on fire and explosion hazards, spill or leak procedures, special protection information, and special precautions. In many cases, the emergency first aid procedures and handling precautions are written to deal with a worst-case scenario, such as extensive exposure. For a minor incident, that immediate medical attention may not be needed even though it is called for by the MSDS. However, in the absence of an informed opinion by a designated health professional, a prudent response is the best policy.

It is important to check the date when the MSDS was prepared. Out-of-date MSDSs may not be reliable. The MSDS provides information on health and physical hazards. The MSDS includes at least eight sections. The style and layout may vary. However, every section is to be filled in, even if the item is not applicable (indicated by "N/A"). There should be no blank spaces. The information on the MSDS is prepared by the manufacturer of the product; some MSDSs contain excellent information, some are adequate, and others are poor. Other sources of data on toxic and health effects should be consulted for more complete information.

Product Identity

- Identity: The name of the product as it appears on the label. A product may be a mixture of two or more chemicals.
- Manufacturer's name, address, and phone number: Self-explanatory. If the data comes from a source other than the manufacturer, the actual source is to be indicated. The date of preparation or revision is to be indicated.
- Emergency telephone number(s): 24-hour number(s) that the manufacturer provides, so that emergency information can be obtained (e.g., medical emergencies).
- Chemical family: The general class of compounds to which the hazardous substance or mixture belongs (e.g., ethers, acids, ketones). This term does not give you the exact content of the product.
- Formula: The chemical formula may be given for single elements and compounds (e.g., sulfur dioxide [SO₂], formaldehyde [HCHO]). This is not the formulation for mixtures.

Manufacturers may withhold certain information on a Material Safety Data Sheet (such as specific chemical identities and/or amount of its components) if the information is considered a trade secret. The Chemical Hygiene Officer and OMC have the right to obtain this information from the manufacturer to evaluate the potential health risk if potential overexposure or adverse health effects are suspected.

Hazardous Ingredients

- If the product is a mixture, all hazardous ingredients are to be listed. However, ingredients that are not hazardous, or make up less than 1% of the product (less than 0.1% for carcinogens), do not have to be reported. The % column is intended to show the approximate percentage by weight or volume of each hazardous ingredient compared to the total weight or volume of the product. Normally, percentages will be listed to the nearest 5%. When the substance constitutes less than 5% of the product, this is indicated.

- Exposure standards: Threshold Limit Value (TLV) and Permissible Exposure Limit (PEL) are included in this section, or under Health Hazards. Note that the higher the number for a TLV or PEL, the less hazardous the substance.
- CAS number: The Chemical Abstract Service registry number identifies specific chemicals only, not mixtures; it is optional.

Physical Data

This section contains very important data to help predict the behavior of the material in experimental situations. The information provided is for the material as a whole, rather than for each hazardous ingredient. Vapor pressure, vapor density, % volatiles, and evaporation rate all basically tell you the same thing: whether breathing the vapors will be a problem, thus indicating the need for proper ventilation.

- Boiling point: The temperature at which a liquid changes to a vapor at a given pressure; usually in degrees Fahrenheit (°F) at the sea-level pressure of 760 millimeters of mercury (mm of Hg). For mixtures, the initial boiling point or the boiling range may be given. A low boiling point may be a special fire hazard.
- Vapor pressure: Refers to the pressure exerted by a saturated vapor above its own liquid, usually stated in mm of Hg at 25°C (77°F). The lower the boiling point, the higher the vapor pressure. A high vapor pressure indicates easy evaporation.
- Vapor density: Tells whether the material is heavier or lighter than air. This is useful information to indicate a confined-space hazard. If heavier than air, the material will concentrate in low places, such as floors, elevator shafts, sewers, or the bottom of tanks.
- Percentage volatility by volume: How much of the material evaporates at room temperature. A substance that is 100% volatile will evaporate completely, leaving no residues.
- Evaporation rate: The rate at which the material will evaporate when compared to the rate of evaporation of a known material, usually butyl acetate. If another material is used for comparison, it should be indicated. If the number is greater than 1, the product evaporates more easily than the comparison material.
- Solubility in water: The percentage of a material (by weight) that will dissolve in distilled water, at room temperature.
- Specific gravity: The ratio of the weight of a volume of material to the weight of an equal volume of water. For insoluble materials, a specific gravity of less than one means the material is lighter than water and will float. Greater than one means that it sinks in water.
- Melting point: The temperature at which a solid becomes a liquid under normal room conditions.
- Appearance and odor: A brief description of the material at normal room temperature and atmospheric conditions. Do not rely on odor to alert you to a dangerous exposure. Some substances can reach hazardous levels and have no noticeable odor.

Fire and Explosion Hazard Data

This section should clearly indicate whether the material is flammable. If it is flammable, make sure there are no ignition sources nearby and that you have the correct fire extinguisher on hand. If you work with solvents, peroxides, explosives, metal dusts, or other unstable substances, this section is very important.

- Flash point: The lowest temperature at which the material gives off enough vapor to ignite; this will help determine storage and handling procedures. The method used to obtain this information should be stated (e.g., closed cup).
- Flammable or explosive limits: The range over which a flammable vapor, when mixed with the proper proportions of air, will flash or explode if ignited. The range is designated by lower explosive limit (LEL) and upper explosive limit (UEL), and is expressed in percentage of volume of vapor in the air.
- Extinguishing media: Indicates what type of fire extinguisher to use, such as water, fog, foam, alcohol foam, carbon dioxide, or dry chemical.

- Special firefighting procedures: Special handling procedures, personal protective equipment, and unsuitable firefighting substances should be listed. For example, water should not be used on fires involving reactive metals. General firefighting methods are not described.
- Unusual fire and explosive hazards: Hazards that might occur as a result of overheating or burning of the material, including any chemical reactions or change in chemical form or composition.

Reactivity Data

This section indicates how unstable the substance is and lists conditions to avoid in order to prevent dangerous reactions. This information will help you handle and store the material properly.

- Stability: indicates whether the material is stable or unstable and under what conditions instability occurs.
- Incompatibility: materials and conditions to avoid. Such conditions may include extreme temperatures, jarring, or inappropriate storage. This is important to determining what other chemicals the material can be stored or used with.
- Hazardous decomposition products: hazardous materials that may be produced if the material is exposed to burning, oxidation, heating, or certain chemical reactions. The product shelf life should be included, when applicable.
- Hazardous polymerization: Polymerization is a chemical reaction in which two or more molecules of a substance combine to form repeating structural units of the original molecule. A hazardous polymerization causes an uncontrolled release of energy (heat). If this reaction can occur, it is to be indicated.

Health Hazard Data

This section lists routes of entry (inhalation, skin absorption, ingestion), and gives signs and symptoms of overexposure, such as skin rash, tremors or dizziness. Short-term (acute) and long-term (chronic) health hazards, such as the ability to cause cancer (carcinogenicity), birth defects (teratogenicity), or “target organ” damage, should be listed. Some products cause both types of effects. This section may lack adequate information, especially on the health effects of long-term exposure.

Instructions for first aid and emergency procedures for victims of acute inhalation, ingestion, or skin or eye contact are to be included. Medical conditions that can be aggravated by exposure are to also be detailed.

Information on exposure standards, such as TLV, PEL, or STEL, and toxicity data (indicated by an LD50 number), may be included here. Toxicity data is an estimate of the degree of toxicity, based on experiments with test animals.

Precautions for Handling

This information will help you prepare for emergencies by having the proper materials and equipment on hand. This section lists methods, special equipment, and precautions necessary to control and clean up spills, leaks, and other releases. For example, if respirators are required to clean up a spill, that fact should be shown.

Acceptable waste-disposal methods, as well as prohibited methods, are described. The user will also be alerted to any potential environmental danger to the general population, crops, water supplies, etc.

Instructions for safe handling and storage, such as the warning not to store acids and bases together, may be given. Any additional special precautions not addressed elsewhere in the MSDS should also be listed here. These may include instructions for storage life or transportation, such as special packaging or temperature control.

Control Measures

This section lists personal protective equipment, such as proper gloves, safety glasses, respirators, ventilation necessary to work safely with the material, and work/hygienic practices. Types and descriptions of necessary equipment should be specified (e.g., organic vapor cartridge, neoprene gloves). If the material has a low TLV, indicating a dangerous health hazard, local ventilation is recommended, not general or dilution ventilation. Engineering controls, such as exhaust ventilation, are always preferable to relying on respirators.

Appendix A3: Chemical Toxicology Overview

Toxicology is the study of the nature and action of poisons. Toxicity is the ability of a chemical substance to produce injury at a susceptible site or on the body.

Dose-Response Relationships

The potential toxicity (harmful action) inherent in a substance is exhibited only when that substance comes in contact with a living biological system. The potential toxic effect increases as the exposure increases. All chemicals will exhibit a toxic effect given a large enough dose. The toxic potency of a chemical is defined by the dose (the amount) of the chemical that will produce a specific response in a specific biological system.

Routes of Entry into the Body

There are four main routes by which hazardous chemicals enter the body through:

- Respiratory tract via inhalation.
- Skin via dermal contact. There are 170 known “skin-absorbing” chemicals. Please consult the following Web site to identify chemicals that have this property:
www.osha.gov/web/dep/chemicaldata/#target.
- Digestive tract via ingestion. (Ingestion can occur through eating or smoking with contaminated hands or in contaminated work areas.)
- Percutaneous (injection, e.g., syringe needle or broken glass). This is possible but not a common route of exposure in chemical laboratories. However, needle sticks are significant routes of exposure in biomedical, health care and radiological work.

Most exposure standards, such as the Threshold Limit Values (TLVs) and Permissible Exposure Limits (PELs), are based on the inhalation route of exposure. These limits are normally expressed in terms of either parts per million (ppm) or milligrams per cubic meter (mg/m³) concentration in air. If a significant route of exposure for a substance is through skin contact, the MSDS, PEL and/or TLV will have a “skin” notation. Examples of substances where skin-absorption may be a significant factor include: pesticides, carbon disulfide, carbon tetrachloride, dioxane, methanol, acetonitrile, mercury, thallium compounds, xylene, and hydrogen cyanide.

Types of Effects

An acute effect is characterized by sudden and severe exposure and rapid absorption of the substance. Normally, a single large exposure is involved. Adverse health effects are often reversible. *Examples: carbon monoxide or cyanide poisoning.*

A chronic effect is characterized by prolonged or repeated exposures of a duration measured in days, months or years. Symptoms may not be immediately apparent. Health effects are often irreversible. *Examples: lead or mercury poisoning.*

A local effect refers to an adverse health effect that takes place at the point or area of contact (skin, the respiratory tract, eyes, etc.). Absorption does not necessarily occur. *Examples: strong acids or alkalis.*

A systemic effect refers to an adverse health effect that takes place at a location distant from the body’s initial point of contact and presupposes absorption has taken place. *Examples: arsenic affects the blood, nervous system, liver, kidneys and skin; benzene affects bone marrow.*

Cumulative poisons build up in the body as a result of numerous chronic exposures. The effects are not apparent until a critical point is reached. *Example: heavy metals.*

A synergistic effect is when two or more hazardous materials are present at the same time, the resulting effect of which can be greater than the effect anticipated based on the cumulative effect of the individual substances. This is also called “potentiating effect.” *Example: exposure to alcohol and chlorinated solvents; or smoking and asbestos.*

Other Factors Affecting Toxicity

- Rate of entry and route of exposure; that is, how fast the toxic dose is delivered and by what means.
- Age can affect the capacity to repair tissue damage.
- Previous exposure can lead to tolerance, increased sensitivity or make no difference.
- State of health, physical condition and life style can affect the toxic response.
- Pre-existing disease can result in increased sensitivity.
- Environmental factors such as temperature and pressure.
- Host factors including genetic predisposition and the sex of the exposed individual.

Physical Classifications:

A gas is a substance that is in the gaseous state at room temperature and pressure. A vapor is the gaseous phase of a material that is ordinarily a solid or a liquid at room temperature and pressure.

When considering the toxicity of gases and vapors, the solubility of the substance is a key factor. Highly soluble materials, like ammonia, irritate the upper respiratory tract. On the other hand, relatively insoluble materials, like nitrogen dioxide, penetrate deep into the lung. Fat-soluble materials, like pesticides, tend to be retained longer in the body and have a cumulative effect.

An aerosol is composed of solid or liquid particles of microscopic size dispersed in a gaseous medium. The toxic potential of an aerosol is only partially described by its airborne concentration. For a proper assessment of the toxic hazard, the size of the aerosol’s particles must be determined. A particle's size will determine whether a particle is deposited within the respiratory system and the location of deposition. Particles above 10 micrometers tend to be deposited in the nose and other areas of the upper respiratory tract. Below 10 micrometers, particles enter and are deposited in the lung. Very small particles (<0.2 micrometers) are generally not deposited but exhaled.

Physiological Classifications of Chemicals: Chemicals and hazardous materials can be classified according to the effect they have on individuals.

Irritants: Irritants are materials that cause inflammation of the mucous membranes with which they come in contact. Inflammation of tissue results from exposure to concentrations far below those needed to cause corrosion. *Examples include:*

<i>Ammonia</i> <i>Alkaline dusts and mists</i> <i>Arsenic trichloride</i> <i>Diethyl/dimethyl sulfate</i>	<i>Halogens</i> <i>Hydrogen chloride</i> <i>Hydrogen fluoride</i> <i>Nitrogen dioxide</i>	<i>Ozone</i> <i>Phosgene</i> <i>Phosphorus chlorides</i>
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Irritants can also cause changes in the mechanics of respiration and lung function. *Examples include:*

<i>Acetic acid</i> <i>Acrolein</i> <i>Formaldehyde</i>	<i>Formic acid</i> <i>Iodine</i>	<i>Sulfur dioxide</i> <i>Sulfuric acid</i>
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Long-term exposure to irritants can result in increased mucous secretions and chronic bronchitis.

A **primary irritant** exerts no systemic toxic action, either because the products formed on the tissue of the respiratory tract are nontoxic or because the irritant action is far in excess of any systemic toxic action.

Example: hydrogen chloride.

A **secondary irritant's** effect on mucous membranes is overshadowed by a systemic effect resulting from absorption. *Examples include:*

<i>Alcohols Aromatic hydrocarbons</i>	<i>Asphyxiants have the ability to deprive tissue of oxygen.</i>	<i>Halogenated hydrocarbons Hydrogen sulfide</i>
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Simple Asphyxiants are gases that displace oxygen. *Examples include:*

<i>Argon</i>	<i>Helium</i>	<i>Nitrogen</i>
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Chemical Asphyxiants reduce the body's ability to absorb, transport, or utilize inhaled oxygen. They are often active at very low concentrations (a few ppm). *Examples include:*

<i>Carbon monoxide</i>	<i>Cyanides</i>	<i>Hydrogen sulfide</i>
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Primary Anesthetics have a depressant effect upon the central nervous system, particularly the brain. *Examples include:*

<i>Chloroform</i>	<i>Diethyl ether</i>	
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Hepatotoxic Agents cause damage to the liver. *Examples include:*

<i>Carbon tetrachloride</i>	<i>Nitrosamines</i>	<i>Tetrachloroethane</i>
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Nephrotoxic Agents damage the kidneys. *Examples include:*

<i>Halogenated hydrocarbons</i>	<i>Uranium compounds</i>	
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Neurotoxic Agents damage the nervous system. The nervous system is especially sensitive to organometallic compounds and certain sulfide compounds. *Examples include:*

<i>Carbon disulfide Methyl mercury Manganese</i>	<i>Organic phosphorus insecticides Tetraethyl lead</i>	<i>Thallium Tri-alkyl tin compounds</i>
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Hematopoietic System Toxins act on the blood or hematopoietic system. The blood cells can be affected directly or the bone marrow (which produces the blood cells) can be damaged. *Examples include:*

<i>Aniline Benzene</i>	<i>Nitrites Nitrobenzene</i>	<i>Toluidine</i>
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Pulmonary Toxins produce damage to the pulmonary tissue (lungs) but not by immediate irritant action. Fibrotic changes can be caused by free silica and asbestos. Other dusts can cause a restrictive disease called pneumoconiosis. *Examples include:*

<i>Coal dust</i>	<i>Cotton dust</i>	<i>Wood dust</i>
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Carcinogens initiate or increase the proliferation of malignant neoplastic cells or the development of malignant or potentially malignant tumors. *Known human carcinogens include:*

<i>Asbestos</i> <i>Alpha-naphthylamine</i> <i>Bis-chloromethyl ether</i> <i>3,3'-Dichlorobenzidine</i> <i>Ethylene oxide</i>	<i>N-nitrosodimethylamine</i> <i>4-nitrobiphenyl</i> <i>Methyl chloromethyl ether</i> <i>Inorganic arsenic</i>	<i>1,2-Dibromo-3-chloropropane (DBCP)</i> <i>Coal tar pitch volatiles</i> <i>Vinyl chloride</i>
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Reproductive Toxins (Mutagens and Teratogens) A mutagen interferes with the proper replication of genetic material (chromosome strands) in exposed cells. If germ cells are involved, the effect may be inherited and become part of the genetic pool passed onto succeeding generations. A teratogen (embryotoxic or fetotoxic agent) is an agent that interferes with normal embryonic development without causing a lethal effect to the fetus or damage to the mother. Effects are not inherited. *Examples include:*

<i>Lead</i>	<i>Thalidomide</i>	
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Sensitizers cause an allergic reaction in normal tissue after repeated exposure to the chemical. The reaction may be as mild as a rash (allergic dermatitis) or as serious as anaphylactic shock. *Examples include:*

<i>Chromium compounds</i> <i>Chlorinated hydrocarbons</i>	<i>Epoxies</i> <i>Nickel compounds</i>	<i>Poison ivy</i> <i>Toluene diisocyanate</i>
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