

TEMPORARY CHANGE REQUEST

TCR NO. TCR-ESHD-5008-Ch8,Sect1,R6-002

(e.g., TCR-ENG-021,R0-001)

The Temporary Change Request (TCR) Form is to be used to process urgent or minor changes for PPPL Policies, Organization/Mission Statements and Procedures. The TCR should be used when changes are:
1) urgent, and can not wait the 2-4 week period for Department Head review/comment, or
2) minor, and do not warrant Department Head review.

Person Requesting Change: William Slavin

Phone Ext: 2533

Department Name: ES&H

Document Number: ESHD-5008 Sect.8 Chapter 1

Revision No.: 6

Document Title: Chemicals

Reason for change:

Addition of requirements for crystalline silica

Change description: (Summarize and attach changed pages, with changes clearly indicated)

Added paragraph 1.14 Crystalline Silica with basic requirements and information on handling of this material.

Added 2005 date to first reference in accordance with 10 CFR 851 requirements.

1. Does this TCR significantly alter the intent or scope of the document? YES: NO: X

2. Does this TCR significantly impact ES&H? YES: NO: X

If 1 or 2 is YES, Explain why the changes should not be routed for Department Head review:

Bill Slavin

2/2/16

Department/Division Head Approval

Date

John DeLooper

2/2/16


Head, Best Practices and Outreach/designee

Date

Release/Effective date of this TCR: 2/2/16

Incorporate this TCR into next revision of this document?

YES: X NO:

PPPL	PRINCETON PLASMA PHYSICS LABORATORY ES&H DIRECTIVES		
	ES&HD 5008 SECTION 8, CHAPTER 1 Chemicals		
Approved	Date: 6/5/15	Revision 6	Page 1 of 23

TCR-ESHD-5008-Sec8-Cha1, R6-002

CHAPTER 1 CHEMICALS

1.1 INTRODUCTION

Chemicals are used on a routine basis at the Laboratory. Most chemicals possess some potential hazards which can result in serious consequences if handled improperly. This section covers the safe handling and storage of these substances.

1.2 SCOPE

This section covers the use, handling, and storage of all chemicals and chemical-like substances at PPPL and applies to all Laboratory personnel and contractors.

1.3 DEFINITIONS (Refer to Section 8, Chapter 12, “Hazard Communication,” for a more complete chemical glossary)

Chemical - Any single compound or mixture of compounds. For the purposes of this chapter, a chemical includes:

1. All solids, liquids, and gases not excepted below;
2. All stock materials such as wood, metal and plastic that will be cut or formed into other shapes; and
3. Solder, welding rods, grinding wheels and any other materials that will be used up or worn down as part of their use.

Exceptions include:

1. Articles – items sold in their finished shape where their use is a function of that shape. (NOTE: This does not include liquids or powders; such items are considered chemicals);
2. Wood products that are not treated, and will not be cut;
3. Tobacco, food and beverages, drugs, cosmetics;
4. Hazardous waste (refer to Section 7 of ESHD 5008); and
5. Items having radiological or biological hazards (refer to Section 10 of ESHD 5008 for rules pertaining to radiological hazards, contact Industrial Hygiene for information on biological hazards).

Hazardous Material or Chemical - Any substance that has the capability of producing adverse effects on the health and safety of humans. This may be defined by relative measures of toxicity, corrosiveness, flammability, or reactivity. A material shall be considered hazardous if it is

deemed so by any regulatory or recognized advisory agency (e.g. NFPA, OSHA, NJ Department of Health, ACGIH, NIOSH, EPA, DOT, etc.)

Material Safety Data Sheets (MSDS) - Forms which contain hazard communication information on materials found in the workplace. Refer to Section 8, Chapter 12 of this manual for further information on MSDS and chemical information.

Permissible Exposure Limit (PEL) - The Occupational Safety and Health Administrations' (OSHA) maximum airborne exposure level for a substance to a worker, as stated in 29 CFR 1910.1000 to -.1046.

Threshold Limit Value (TLV) - The American Conference of Governmental Industrial Hygienists' (ACGIH) guidelines which refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.

1.4 RESPONSIBILITIES

1.4.1 Department/Division Heads are responsible for ensuring implementation of this section. Some responsibilities in Section 8, Chapter 1.4.2 may rest directly with these responsible persons.

1.4.2 Line Supervisors are responsible for:

- A. Reviewing the type of work to be performed.
- B. Reviewing the hazards associated with the substances that will be used.
- C. Ensuring that employees are not being exposed to air concentrations of substances over the materials' PEL and TLV (this should be done in cooperation with the Industrial Hygienist).
- D. Establishing safe practices for working with the chemicals.
- E. Providing proper and safe storage for all chemical substances.
- F. Procuring the proper protective equipment needed to work safely with the chemicals in question.
- G. Instructing their workers about:
 1. The possible hazards associated with the chemicals.
 2. The safety precautions that must be observed.
 3. The consequences of an accident.
 4. The proper actions to take if an accident were to occur.

- H. Reviewing the hazards and intended use of chemicals, before purchasing, with Industrial Hygiene (IH) by complying with Chapter 13 of this Section, “ES&H Review of Procurements.”
- I. Properly disposing of chemicals which have been stored longer than the appropriate storage time (refer to Section 8, Chapter 1.8.5).

1.4.3 Industrial Hygiene (IH) is responsible for:

- A. Assisting supervisors and workers with information on the hazardous properties of materials.
- B. Recommending methods for controlling the hazards of specific operations.
- C. Training supervisors and workers regarding the proper way to handle chemicals in order to minimize hazards.
- D. Monitoring the work environment to assess employees’ exposures to hazardous chemicals, using only American Industrial Hygiene Association (AIHA) Accredited Laboratories for sample analysis.
- E. Reviewing and approving/disapproving procedures and facilities used for chemical handling.
- F. Reviewing and approving/disapproving the acquisition of chemicals in accordance with Section 8, Chapter 13.
- G. Assisting in finding suitable replacement chemicals for substitution of hazardous chemicals.

1.4.4 The Maintenance and Operations Division is responsible for designing, installing, and maintaining engineering controls (see Section 8, Chapter 4, “Ventilation”) incorporating the criteria developed by IH and the line supervisor.

1.4.5 Procurement is responsible for checking to see that IH has approved the use of the chemical before a purchase order is drawn up. No purchase order for a chemical will be issued without this approval. (Refer to Chapter 13 of this Section.)

1.4.6 Quality Assurance is responsible for auditing compliance with this section.

1.4.7 All other employees are responsible for:

- A. Wearing and using personal protective and other equipment issued to them in accordance with instructions and training provided by their supervisors and IH.
- B. Cleaning, maintaining and properly storing the protective equipment (see Section 8, Chapter 6, “Personal Protective Equipment”).

- C. Following handling instructions in accordance with procedures set down by their supervisors and IH.
- D. Reporting malfunctioning engineering controls and ventilation systems to their supervisors.
- E. Using only personal protective equipment that has been designated and approved for that particular job.

1.4.8 Human Resources and Training is responsible for maintaining records of all training they provide on topics covered in this Chapter.

1.4.9 Chemical Cabinet Accountable Individuals are responsible for ensuring that all chemicals in the cabinet(s) for which they are responsible are stored properly. (Refer to paragraph 1.8 of this Chapter).

1.5 REQUIREMENTS

1.5.1 All acquisitions of chemical substances by any means (including but not limited to: requisition through Procurement, purchase by open order, credit card purchase, etc.) must have prior approval from IH in accordance with Chapter 13 of this Section.

1.5.2 All airborne chemical exposures to employees shall be maintained below the most recent ACGIH TLV's and the OSHA PEL's (whichever is most restrictive).

1.5.3 All precautions shall be taken to reduce the risk of chemical exposure through oral, cutaneous, and optical routes of exposure to as low as reasonably possible along with the inhalation route.

1.5.4 Carcinogens are covered in Section 8, Chapter 2.

1.6 GENERAL PRACTICES

The following general safety precautions shall always be observed when working with chemicals.

- A. Keep the work area clean and orderly.
- B. Use all specified safety equipment.
- C. Carefully label every container with the identity of its contents and hazard warnings according to Section 8, Chapter 12, of this Manual.
- D. Store incompatible chemicals so that they are separated by structural barriers such as walls. Contact IH for more information.

- E. Limit the volume of volatile, flammable, toxic, or otherwise hazardous material to the minimum needed for short operation periods (1 week supply or 1 gallon (231 cubic inches) whichever is greater).
- F. Provide secondary means of containing the material if equipment or containers should break or spill their contents.
- G. Isolate hazardous operations in separate rooms and limit access and the number of personnel involved.
- H. Substitute a less toxic material whenever possible.
- I. Follow the requirements of Section 9.11 (Pressure Vessels) when systems that can generate pressure or are operated under pressure are involved.
- J. Do not dump chemicals down the sanitary or storm sewer system without prior approval from IH and Environmental Engineer.
- K. Use adequate ventilation. This may include the use of laboratory fume hoods, dust collecting systems, and cooling fans. Never use a chemical in a confined area without proper ventilation and IH approval. If the chemical is flammable, ensure that the ventilation system motor is listed for the appropriate atmosphere. Above all, remember that the purpose of ventilation is to remove the air contaminant from a worker's breathing zone. (See Section 8, Chapter 4 "Ventilation".)
- L. Wear good, impermeable gloves as specified by IH. Many chemicals can enter the body through the skin and improper gloves may provide no protection at all from contact with the chemical. Never wear cloth or leather gloves for handling chemicals.
- M. If there is a potential for the chemical to splash or spill, as in most situations, then chemical splash goggles must be worn. Additional protection, such as boots, gloves and aprons, should be worn as needed.
- N. Never wear contact lenses when working with chemicals. If a chemical splashes into the eyes with contacts in, the lenses must be removed before irrigation begins.
- O. Food and drink should never be stored, prepared, or consumed in a place where chemicals are stored or used.
- P. Chemicals shall not be stored in refrigerators marked "Food Only," and food shall not be kept in "Chemicals Only" refrigerators.
- Q. Never mix chemicals together when you are not sure of the end result. Many chemicals can react violently or may give off heat and toxic vapors.

- R. When leaving a work area where chemicals are used and exposure of the skin to chemicals is possible, cleanse the skin thoroughly with a mild soap and water.
- S. Provide a back-up method of shutting off power to any heat source in case of emergency involving chemical spill or fire.
- T. Never smoke in any area where chemicals are stored or used. In addition to the flammability hazard, many chemical vapors become more hazardous when heated or combined with tobacco smoke.
- U. Know where the nearest eyewash, safety shower, and telephone are in case of emergency.

1.7 CHEMICAL HAZARDS

The number of hazardous chemicals is so large that knowledge of all of them cannot be assumed, even of chemists. Therefore, when the chemical properties of a material and its reactions are not fully known, it should be treated as toxic and otherwise hazardous. Initial testing and research of the material should be carried out with the utmost safety precautions to reduce the magnitude of unexpected events.

1.7.1 Toxicity

Toxicological information discussed in this section includes systemic hazards due to ingestion or inhalation, as well as hazards to external structures such as skin and eyes. The Laboratory is concerned with any adverse effect to an employee's health. This includes simple discomfort due to irritation or odor, as well as a complex physiological change due either to chronic or acute chemical exposure. It must be realized that numbers used as hygienic guidelines (e.g. TLV's or PEL's) are only guidelines and cannot be regarded as the boundary between safe and dangerous conditions or concentrations. Because these guides are not intended as relative indices of toxicity, they must be interpreted by trained personnel. The guides are developed and regularly reviewed by several national groups. With adequate safeguards, any compound can be used safely, but the need for a specific material must justify the hazards presented and the controls necessary to protect employees from injury or illness.

A. Definitions

1. Acute Effects - Physiological changes, usually severe and rapid, following exposure to a substance, and involving either:
 - a. temporary conditions from a single exposure or
 - b. abrupt onset of a condition after repeated exposures; may later change to chronic effects.
2. Acute Exposure - Exposure to high concentrations of toxic substances over a short period of time that may result in Acute Effects.

3. Allergy - A condition of unusual or exaggerated specific susceptibility to a substance which in similar amounts is harmless to the majority of the population.
4. Anesthesia - A partial or entire loss of feeling or sensation; unconsciousness.
5. Central Nervous System (CNS) - The system which coordinates and regulates nerves and nerve centers, and which directly controls behavior and consciousness. Symptoms of damage can include headache, irritability, lassitude, disorientation, and finally stupor and unconsciousness.
6. Chronic Effects - Physiological changes, from exposure to a compound, involving any of the following:
 - a. irreparable damage from repeated exposure
 - b. accumulative damage from repeated exposures
 - c. delayed damage following either single or repeated exposures, even after cessation of the exposure and regardless of the time interval.
7. Chronic Exposure - Exposure to low levels of toxic substances over a long period of time. May result in Chronic Effects.
8. Narcosis - A state of stupor or unconsciousness.
9. Sensitization - A process of rendering a specific system sensitive to an agent or a complement of the agent.
10. Systemic - Pertaining to or affecting the body as a whole. (Systemic changes generally refer to nonspecific physiological changes.)

B. Routes of Exposure

1. Inhalation - The lungs represent the greatest body surface exposure to potentially hazardous compounds, and lung tissue acts as a selective barrier for sorption and desorption of gases. In addition to the sensitive and easily damaged barrier mechanism, the lungs are the main port of entry of contaminants into the body.
 - a. Upper Respiratory Irritants - Irritants and corrosive chemicals, such as acids, alkalis, solvents, and many other substances may cause direct inhalation damage in the nasopharyngeal and upper bronchial regions. The damage is usually reversible except after repeated exposures to high concentrations or exposure to extreme conditions. Many exposure limits, such as those for butyl acetate and some acids, are based on the

irritating properties of the substance even though concentrations higher than the limit may not cause systemic poisoning.

- b. Non-Irritants - Irritation is one of the body's warning mechanisms; gases and vapors which do not irritate the upper respiratory system may be inhaled deeper into the respiratory tract, and into the lungs, where they may be absorbed, or cause local damage to the alveolar walls. This form of damage may be reversible, such as a transient pneumonitis, but is often irreversible, such as in an emphysema or the production of non-functioning scar tissue.
- c. Sensitizers - Some gases, vapors, and fumes are capable of causing an asthma-like reaction at extremely low concentrations. TDI (toluene diisocyanate) vapors, epoxy resins, some insecticides, and many chemicals encountered in pharmaceutical and organic research are known sensitizers. If the lungs become sensitized to a material, succeeding exposures may produce an asthma-like reaction, such as tightness in the chest, wheezing, non-productive cough and, in some cases, vocal disturbances and elevated temperature. It is impossible to predict who may become sensitized, and even the degree of severity is unpredictable. Individuals who are naturally sensitive, or who become sensitized through exposure, to certain compounds must be removed completely from any potential exposure if repeat attacks are to be prevented.
- d. Means of Toxicity – The primary mode of entry for toxic gases and vapors is sorption through the lungs to various organs in the body. Either the inhaled substance or the products formed from its metabolism may damage tissue cells. Compounds such as alcohol and trichloroethylene (TCE) are only moderately toxic to living cells, but the metabolic products are highly toxic.
- e. Toxic Dusts - The upper respiratory system separates inhaled particulate matter selectively, according to size. The size range of unit density particles penetrating into the lower lungs is less than 10 microns. Larger particles are removed in the upper respiratory tract by phagocytosis or by ciliary action at the walls of the bronchi and bronchioles. A limited number of substances cause lung damage without being absorbed. They include silica (silicosis), asbestos (asbestosis), beryllium (berylliosis), and some other substances. Other particulates are more readily dissolved, and may thereby, cause damage to various organs. Lead, mercury, cadmium, and other metals and metal oxides produce first a lung response, then after dissolution and concentration in various organs, they produce reactions through toxic mechanisms.
- f. Exposure Control - The exposure of any worker to environments known to contain toxic substances must be controlled, especially when

exposure to concentrations in excess of the TLV is possible. Adequate engineering control and/or respiratory protection must be provided. The ES&H Division should be contacted before starting a program requiring the use of unfamiliar or toxic substances so that potential hazards can be evaluated and control procedures recommended.

2. Skin - There are four major concerns with skin toxicology: surface absorption, sensitivity and allergic reactions, surface corrosion, and carcinogenesis.
 - a. Absorption - Although the skin is an excellent protective barrier, many chemicals, even in the vapor phase, can be absorbed through it. Skin absorption is more often a surface contact problem. Atmospheric concentrations high enough to cause toxic reactions via skin absorption present an even greater inhalation hazard. The most common and difficult exposure to control are to substances such as cleaning solvents, because the skin is in direct contact with the unit being cleaned, facilitating solvent absorption through the skin unless precautionary measures are taken.

EXAMPLES OF HAZARDOUS CHEMICALS ABSORBED THROUGH INTACT SKIN

Allyl alcohol	Dimethylformamide	Xylene
Carbon disulfide	Dimethyl Sulfoxide	Almost all nitro compounds
Carbon monoxide	Dinitrobenzene	Almost all halogen compounds including carbon tetrachloride, the most hazardous of the common solvents.
Cresols	Ethylene chlorohydrin	
Cyanides	Phenols	
Decaborane	Tetryl	
Dimethylaniline	TNT	

- b. Sensitizers/Allergic Reactions - Allergic or sensitivity reactions may be caused by surface contact as well as by inhalation. Skin sensitivity reactions resemble those of poison ivy and result from repeated contact with the sensitizing material.

EXAMPLES OF SKIN SENSITIZERS

Epoxide monomers & catalysts	Aliphatic mono and polyamines
Aromatic amines	Aromatic hydrazines
Aromatic isocyanates	Aromatic nitro compounds (some)
Chlorinated biphenyls	Toluene diisocyanate (TDI)

1.7.2 Corrosiveness

A. Definitions

1. Corrosive - A substance which possesses the property of severely damaging living tissue and of attacking other materials such as metals, wood, or glass.
2. Acid - A substance which in solution will donate a proton. Typically, an acid will have a pH of less than 7.0.
3. Base - A compound that reacts with an acid to form a salt. It is another term for alkali. Bases will, typically, have a pH of greater than 7.0.
4. Vesicant - A substance which will produce blistering of the skin.

B. Controls and requirements

Whenever corrosive chemicals are used, a safety shower and eye wash fountain must be located in the immediate vicinity. Face shields, safety goggles, waterproof aprons, and rubber or neoprene gloves must be worn at all times when handling corrosive chemicals.

EXAMPLES OF CORROSIVES AND THEIR EFFECTS ON SKIN

Burns, Corrosion, Ulceration	Vesicants		Drying, Scaling, Cracking
Acetic acid	Alkalis (NaOH, Lime)	Nitric Acid	Soaps and detergents
Ammonia	Carbon disulfide	Phenols	Most Solvents
Arsenic trioxide	Hydrofluoric Acid	Phosphorus	
	Hydrogen Peroxide	Sulfuric Acid	
	Iodine		

1.7.3 Flammability

For the safe handling of flammable and combustible chemicals, refer to Section 5, Fire Safety, of the ES&H Manual, ESHD 5008.

1.7.4 Reactivity

The range of reactions possible between chemicals is so wide and varied that no one can predict all of the possible outcomes of a mixture of chemicals, as random factors may produce an odd or unexpected result. Some general guidelines are:

- A. Never mix chemicals together unless the outcome is known with a large degree of confidence.
- B. Never mix or store acids and bases together.

- C. Never mix or store acids and oxidizing compounds together.
- D. Never mix or store acids or oxidizers and flammables together.
- E. Always add acid to water, never water to acid. This could result in a violent reaction.
- F. Never pour chemicals down the sink; you never know what may already be down there.
- G. Never put chemicals into a container that has been used for something else. You could cause a reaction with any chemical residues or water which is left in the container from its previous use.
- H. IH shall be consulted before any chemicals are used or mixed for the first time and for storage compatibility of chemicals.

1.8 CHEMICAL STORAGE

The storage of chemicals plays a major role in how safely they are being handled, and how much exposure is present.

1.8.1 Definitions

- A. Incompatible - A liquid or solid which cannot be mixed with another specified material without the possibility of a dangerous reaction.
- B. Secondary Containment - A storage container other than the one in direct contact with the chemical (which is the primary container). Examples are: flammable storage cabinets, retention basins, etc. A secondary containment must be able to hold, at a minimum, the quantity of liquid kept in the largest primary container within its confines.

1.8.2 Incompatibles

Many chemicals are incompatible with one another and must be kept separate. This can be accomplished by distance (as in one room to another) or by secondary containments, depending on the type of incompatibility, the severity of any possible reactions, and the quantities of the respective chemicals.

1.8.3 Flammable liquids

Liquids which are flammable must be stored in accordance with Section 5, Fire Safety, of the ES&H Manual, ESHG 5008.

1.8.4 Corrosives

Quantities of corrosive chemicals in excess of 5 gallons must be kept in a metal cabinet, and quantities in excess of 25 gallons must be kept in a corrosives storage cabinet. All corrosives shall have a secondary containment. This may include a bin or bucket constructed of plastic or other corrosion-resistant material.

1.8.5 Aging of Chemicals

Some chemicals lose effectiveness with age while others, notably peroxides, become more hazardous and often explosive when aged. Corrosives have been demonstrated to cause fatiguing and leaking if they are kept in plastic or polyethylene containers, including manufacturer's shipping containers, for longer than six months. In general, no chemical should be kept longer than six months for these reasons. Materials with a listed shelf life of greater than six months may be kept for the time period listed. Other materials may be kept for extended periods of time only with approval of IH. Therefore, all chemicals should be ordered in quantities which will be used within this time period.

1.8.6 Quantities of Stored Chemicals

In any single room or laboratory, the maximum allowable quantity of any one chemical is a one week supply or one gallon (231 cubic inches), whichever is greater. Chemicals which must be ordered in larger quantities may be kept in outdoor storage facilities and transferred to smaller containers for inside use. Any exceptions to this rule must be approved by IH.

1.8.7 Chemical Storage Cabinet Accountable Individual

Every flammable liquid cabinet or corrosives cabinet shall be assigned an accountable individual to ensure that all chemicals in that cabinet are stored properly. These cabinets will have the name and contact information of the accountable individual, as well as a unique identifying number, posted on the front of the cabinet. In order to facilitate the proper storage of chemicals, a user aid will also be posted on the cabinet. An example of a user aid may be found in Attachment 1 of this chapter.

1.9 EMERGENCY PROCEDURES

Installation or change of location for any chemical emergency equipment (such as eye washes and safety showers) must have prior approval by IH.

1.9.1 Eye Contact

Most chemicals will damage the eyes if contact occurs. If a chemical contacts the eyes, immediately flush the eyes with copious amounts of water, preferably at the nearest eyewash station. A minimum of 15 minutes rinse time is required. The Emergency Services Unit (ESU) should be called as soon as possible at ext. 3333. Do not stop flushing the eyes until ESU personnel arrive on the scene and inform you to do so.

1.9.2 Skin Contact

If a chemical comes into contact with the skin, immediately rinse the affected area with large amounts of running water. This may be done in a sink if the hands are the only portion of the body contacted, or under a safety shower if the contact is more extensive. ESU should be notified immediately if the chemical is a corrosive or may be absorbed through the skin. Remove contaminated clothing while under the shower and do not put clothing back on until it has been decontaminated. Remain under the shower until ESU personnel inform you to stop.

1.9.3 Spills

A spill is any uncontrolled release, drip, leak, etc. of a chemical which escapes from its primary container. Any spill involving a hazardous material will be handled by ESU and the Materiel and Environmental Services (M&ES) Division. If the chemical spilled is considered to be non-hazardous, then it is the responsibility of the personnel who created the spill, or the person responsible for the area, to clean up the spill immediately. This includes food and beverage spills as well as “chemical” spills. If the substance released is of hazardous or unknown properties, the area should be evacuated immediately, and ESU notified. Untrained personnel should not try to clean or contain spills of hazardous materials because of the possibility of creating a worse scenario, e.g., igniting a flammable liquid.

1.10 RESTRICTED CHEMICALS

Certain chemicals and compounds are restricted or banned from use at PPPL and require special procedures.

1.10.1 The following chemicals are banned from use at the Lab except under extreme conditions where no substitute can be found and with special written approval from IH. Notify IH if any of these chemicals are found in storage or in use. They are extremely toxic, both as individual chemicals and as components of other products. Effective substitutes are available for most uses. The use and handling of these chemicals is extremely hazardous and requires extreme protective measures.

CARBON TETRACHLORIDE
CARBON DISULFIDE

HYDROFLUORIC ACID
BENZENE

1.10.2 The following materials are a selection of the many chemicals which require special handling for safe use. Contact IH if any of these are found in use or in storage.

<u>SOLVENTS</u>	<u>METALS</u>
Ethers Methylene Chloride Hexane Cellosolve Cellosolve Acetate Butyl Cellosolve Butyl Cellosolve Acetate Dimethyl Sulfoxide (DMSO)	Mercury and its compounds Beryllium and its compounds Lead and its compounds Arsenic and its compounds Cadmium and its compounds
<u>CORROSIVES</u>	<u>MISCELLANEOUS</u>
Chromic acid Perchloric acid Picric acid Nitric acid Sulfuric acid Hydrochloric acid	Isocyanates (TDI) Phenol Formaldehyde Cyanide compounds Asbestos Sodium / Potassium hydroxide

1.10.3 Materials which are human, or suspect human, carcinogens must also be handled with care and only with Industrial Hygiene approval. See Chapter 2, "Carcinogens," of this section for more details.

1.11 SPECIFIC CHEMICAL REQUIREMENTS

Certain chemical substances have specific regulations which govern their use. Whenever such regulations exist, all requirements shall be followed as applicable. If conflicts occur between regulations and/or Lab policies, the most stringent requirements shall apply. One such material is Lead, for which an OSHA standard exists (29 CFR 1910.1025). The requirements of that standard are summarized here.

1.11.1 The permissible exposure limit (PEL) for airborne lead shall be $50 \mu\text{g}/\text{m}^3$ averaged over an 8-hour period. When an action level of $30 \mu\text{g}/\text{m}^3$ averaged over an 8-hour period is exceeded, certain actions must be taken (see below).

1.11.2 Exposure monitoring for any lead work shall be conducted at the beginning of the work by IH and shall be repeated at least every 6 months if the action level is exceeded.

1.11.3 The preferred order for implementation of control measures is: engineering controls, administrative controls, and personal protective equipment.

1.11.4 Respiratory protection will be provided by PPPL if required to maintain levels below the PEL. Any personnel required to wear respirators must be trained, medically qualified and fit tested (see Chapter 7 of this Section).

1.11.5 In situations where an employee may be exposed above the PEL, protective work clothing and equipment shall be provided.

1.11.6 Good housekeeping shall be maintained to avoid accumulations of lead dust. Vacuuming using a high efficiency particulate air (HEPA) filter vacuum is the preferred method of cleaning.

1.11.7 In situations where an employee may be exposed above the PEL, showers, change rooms, lunchrooms and lavatories shall be provided. NO FOOD, BEVERAGES, TOBACCO PRODUCTS, OR COSMETICS SHALL BE USED OR STORED IN A LEAD WORK AREA.

1.11.8 Medical surveillance including blood tests shall be provided to all employees exposed above the action level for more than 30 days per year.

1.11.9 Personnel shall be removed from all lead associated work if their blood lead level is found to be greater than 50 $\mu\text{g}/100\text{g}$ blood and can not return to such work until their blood lead level drops below 40 $\mu\text{g}/100\text{g}$ of blood.

1.11.10 All employees shall be informed of the contents of the OSHA standard and shall undergo a training course if they are subject to lead exposure. The OSHA lead standard is available to all affected employees.

1.11.11 Signs stating "WARNING – LEAD WORK AREA – POISON – NO SMOKING OR EATING" shall be posted wherever the PEL is exceeded.

1.11.12 Records of lead monitoring must be kept for at least 40 years or for the duration of employment plus 20 years, whichever is greater. Record shall be made available to employees or designated representatives upon request.

1.11.13 During any monitoring, the employee being monitored has the right to act as or appoint an observer of monitoring. This observer will be informed of the monitoring procedures, may observe all monitoring steps, and record all results.

1.12 NANOPARTICLES

Because of their small size, nanoparticles exhibit properties that may differ significantly from more conventional forms of the material. This may lead to additional hazards not easily recognized, including increased toxicity, unusually high reactivity, and increased risk of fire or explosion. The following guidelines are intended to reduce the risks posed by nanoparticles.

All work associated with nanoparticles must comply with the requirements of the Contractor Requirements Document (CRD) portion of DOE N456.1, "The Safe Handling of Unbound Engineered Nanoparticles".

Each experiment involving nanoparticles must be separately approved by the Manager, Princeton Site Office (PSO) prior to initiation, following review by a combined safety review committee consisting of PPPL and PSO members.

1.12.1 Definitions

“Engineered” nanoparticles – intentionally created particles with one or more dimensions greater than 1 nanometer and less than 100 nanometers (nm).

Unbound engineered nanoparticles (UNP) – engineered nanoparticles that, under reasonably foreseeable conditions encountered in the work, are not contained in a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure.

Nanomaterial worker – a worker that does any of the following: handles UNP and has the potential for inhalation or dermal exposure to UNP; routinely spends time in an area with potential to have engineered UNP dispersed in air; works on equipment that might contain or bear UNP and that could release UNP during servicing or maintenance.

1.12.2 Work Planning

Any use of nanomaterials at PPPL must include a thorough planning review that must include a Job Hazard Analysis (JHA) approved by IH, identifying all potential hazards of the material (refer to Procedure ESH-004).

1.12.3 Control Measures

Controls for the hazards identified in 1.12.2 above must incorporate the standard hierarchy of control measures in order of preference: Engineering Controls, Administrative Controls, Personal Protective Equipment. All controls must be in accordance with the Contractor Requirements Document (CRD) portion of DOE N456.1.

A. Engineering Controls may include using nanomaterials embedded in a solid or liquid form of the material as opposed to dry forms that are more easily dispersed, controlled work areas, and exhaust ventilation that is ducted outside and/or is HEPA filtered.

B. Administrative Controls include good housekeeping practices, utilizing closed and sealed containers, vacuuming with HEPA filtered vacuums (no dry sweeping), and posting areas and containers clearly with terms indicating the presence of nanoscale materials. Posting and labeling must follow the Contractor Requirements Document (CRD) portion of DOE N456.1.

C. Personal Protective Equipment (PPE) may include eye protection, skin protection, and respiratory protection appropriate to the level of the hazard and the nature of the material. The PPE required for safe handling of the nanomaterial must be clearly indicated on the JHA.

1.12.4 Exposure Assessment

IH shall conduct an exposure assessment for all activities involving UNP, and monitor for the presence of nanomaterials to determine effectiveness of controls and potential for exposure to personnel, following the Contractor Requirements Document (CRD) portion of DOE N456.1.

1.12.5 Worker Identification and Competency

All personnel who will work with or around nanomaterials shall be identified and must be familiar, through appropriate and current training per the Contractor Requirements Document (CRD) portion of DOE N456.1, with the potential hazards and necessary controls to reduce exposure.

1.12.6 Medical Surveillance

All nanomaterial workers with potential exposure duration of more than 40 hours per year shall be referred to the Occupational Medicine Office and offered a baseline medical evaluation. The medical surveillance requirements of the Contractor Requirements Document (CRD) portion of DOE N456.1 will be followed.

1.12.7 Transportation

Nanomaterials that qualify, or are suspected to qualify, as Department of Transportation Hazardous Materials (DOT HazMat) shall be packaged and shipped in accordance with DOT regulations, 49 CFR 100 to 185. All other materials must be packaged using the equivalent of a DOT-certified Packing Group I (PG I). All packages inside the PG 1 package must be labeled with "Caution: Nanomaterials sample consisting of (technical description here). Contact (name of point of contact) at (contact number) in case of container breakage." When multiple layers of packaging are used, label the innermost receptacle or container with a label that communicates an appropriate level of caution and description of the contents.

1.12.8 Nanomaterial Wastes

Waste streams from nanomaterial operations must be treated as hazardous waste, packaged and handled according to 40 CFR 261. Packages should be labeled to indicate the presence of nanomaterials. The waste management requirements of the Contractor Requirements Document (CRD) portion of DOE N456.1 must also be followed.

1.12.9 Spills

Utilize appropriate measures to clean up any spill of nanomaterial, treating it as a hazardous material spill. Utilize wet methods and/or HEPA filtered vacuums to clean up materials. All personnel must be adequately protected from possible exposure to the spilled material.

1.12.10 Additional Information

For further information on the safe handling of nanomaterials, refer to the Contractor Requirements Document (CRD) portion of DOE N456.1, "The Safe Handling of Unbound Engineered Nanoparticles" and Department of Energy Nanoscale Science Research Centers "Approach to Nanomaterial ES&H" (5/12/08, Rev. 3a).

1.13 LITHIUM

Lithium is a lightweight alkali metal that is reactive and flammable. Like other alkali metals, it is highly reactive with water and may burn on contact with air, especially if water is present. These properties also make the lithium corrosive to human tissue, and several reaction products

are toxic as well. Due to the nature of these hazards, special handling is required for working with lithium metal. The following requirements apply to all activities involving more than 1 gram of solid lithium or any amount of finely divided lithium (such as powder).

1.13.1 Work Planning

In addition to the PPPL Work Planning process as found in ENG-032, a Safety Assessment Document (SAD) is required as per ESHD 5008, Section 11, Chapter 1. This document must be reviewed by the Lithium Experts Committee (LitEC) in addition to the Safety Review Committee (SRC). If the scope of work for the lithium activity changes, the SAD must be revised. The SAD should include topics such as area access controls, emergency actions, compatibility of materials, fire protection, humidity and water control.

1.13.2 Location

Lithium activities and storage must occur only in areas designated for this type of work. Rooms will be evaluated by the LitEC, which may recommend restrictions to certain activities. A list of designated lithium areas is available on the Lithium Safety website (<http://www-local.ppppl.gov/esh/LithiumSafety.html>). Examples of requirements for a designated lithium area may include: nearby exhaust ventilation such as a fume hood, high level ventilation for exhaust of hydrogen, and appropriate fire extinguishing media, such as Lith-X powder or extinguisher. The location shall be posted with a sign containing appropriate information, for example:

DANGER
Lithium-Water Reactive Metal
Use Class D extinguisher

1.13.3 Control Measures

- A. Due to its reactive nature, all handling of lithium metal should take place under an inert atmosphere (typically argon).
- B. Keep away from all possible contact with water to avoid violent reaction and possible fire.
- C. Wear protective gloves, clothing, eye and face protection as appropriate for the task. Respiratory protection should be considered when handling powder or otherwise dispersed forms of lithium.
- D. In case of fire, use Lith-X (Ansul) for extinguishing. Graphite, or copper powder may be alternatives if approved for the situation. In all cases, fire fighting can only be performed by persons trained specifically on lithium fire fighting.
- E. In case of skin or eye contact, rinse with copious amounts of water to remove product.
- F. Dispose of product by submerging in mineral oil and completing a Hazardous Waste ID tag as per procedure EWM-001
- G. General Lithium Hazard Awareness Training has been developed and is required for all employees working in Lithium areas. This training is available on line on the Training Human Resources e-learning page at: Lithium Safety. This training does not constitute qualification for working with lithium operations. Specific training and/or briefings for lithium evolutions will be given by a subject matter expert as required by procedures

for those evolutions (see 1.13.4.E.5). See Section 7 of the Lithium Safety Program document (http://bp.pppl.gov/plans/Lithium-Safety-Program_R0.pdf) for more details.

TCR-ESHD-5008-Sec8-Cha1, R6-001

1.13.4 Procedures

A written procedure is required for each lithium activity at the Lab. Procedures shall include the following, at a minimum:

- A. General equipment set-up and preparation.
- B. An assessment of fault modes and their mitigation or elimination.
- C. Fall-back, hold points and exit strategies at key steps in the activity to address anomalies that might occur during an evolution. TCR-ESHD-5008-Sec8-Cha1, R6-001
- D. Cleanup process for removal of excess lithium and for closure of the activity, as well as handling and/or final disposition of equipment.
- E. Handling of additional lithium related hazards such as:
 1. Water cooling or other water sources near lithium
 2. Molten lithium, especially above 220 Celsius, since lithium will ignite spontaneously with air at this temperature.
 3. Work with lithium above 320 Celsius as it will form solid nitride on contact with nitrogen, creating hazardous system blockages.
 4. Pressurization of liquid lithium that could result in rupture or release.
 5. Training and qualification requirements for personnel.

A pre-job brief is required prior to conducting any lithium related activity. Consideration should be given to include the Responsible Line Manager, Safety, Environmental Services, Site Protection, and representatives of the LitEC.

1.13.5 Maximum Allowable Quantities of Lithium

The maximum allowable quantities (MAQs) of lithium in control areas are obtained from Table 60.2.2.1(a) of NFPA 1, and Tables 34.1.3.1 and 34.1.3.2(c) of NFPA 5000. A control area is defined by the NFPA Glossary of Terms (2014 Edition) as “a building or portion of a building within which hazardous materials are allowed to be stored, dispensed, used, or handled in quantities not exceeding the maximum allowable quantities (MAQ).” For the purposes of this section, control area means a lithium area designated per 1.13.2 above.

The Safety Data Sheet (SDS) for lithium identifies it as a flammable solid and water reactive, and indicates that the NFPA ratings for this material are 3 for flammability and 2 for reactivity. The lithium MAQs using the NFPA tables for flammable solids and water reactive material are given in the following paragraphs.

The NFPA Glossary of Terms (2014 Edition) defines the following:

- Business Occupancy (as applied to PPPL): An occupancy used for the transaction of business other than research experiments or support for such experiments.

- Storage: The keeping, retention, or leaving of hazardous materials in closed containers, tanks, cylinders, or similar vessels; or vessels supplying operations through closed connections to the vessel.
- Closed System Use: Use of a solid or liquid hazardous material in a closed vessel or system that remains closed during normal operations where vapors emitted by the product are not liberated outside of the vessel or system and the product is not exposed to the atmosphere during normal operations, and all uses of compressed gases.
- Open System Use: Use of a solid or liquid hazardous material in a vessel or system that is continuously open to the atmosphere during normal operations and where vapors are liberated, or the product is exposed to the atmosphere during normal operations.

1.13.5.1 Lithium MAQs for Control Areas Not in Business Occupancies

- Storage + Use: 50 lb (22.67 kg) solid plus liquid
- Use in closed systems: 50 lb (22.67 kg) solid plus liquid
- Use in open systems: 10 lb (4.53 kg) solid plus liquid

These MAQs are based on NFPA 5000 Table 34.1.3.1, and NFPA 1 Table 60.2.2.1(A). According to the footnotes in these tables, these MAQs are permitted to be increased 100 percent where stored in approved cabinets, gas cabinets, exhausted enclosures, explosives magazines, or safety cans, as appropriate for the material stored, in accordance with NFPA 1. The MAQs are permitted to be increased an additional 100 percent (for a total of 3 times the MAQs above) in buildings equipped throughout with an automatic sprinkler system in accordance with NFPA13.

1.13.5.2 Lithium MAQs for Control Areas in Business Occupancies

- 5 lb (2.26 kg) solid plus liquid

This MAQ is based on the NFPA 5000 Table 34.1.3.2(c) value for flammable solid, which is more conservative than the Class 2 water-reactive material MAQ (10 lb) consistent with the NFPA rating for reactivity per the SDS (see 1.13.5 above).

1.14 CRYSTALLINE SILICA

Crystalline silica, also known as quartz, is a natural constituent of the earth's crust and is a basic component of sand and granite. Respirable silica refers to particles small enough to get through the respiratory tract and enter the lungs. Inhalation of respirable silica particles has long been known to cause silicosis, a disabling, non-reversible and sometimes fatal lung disease. More recently, it has been determined that respirable silica may also cause lung cancer.

1.14.1 Sources of exposure

Crystalline silica is most commonly found in construction materials such as brick, mortar, concrete and stone. It may be found in other materials including asphalt. When silica is bound into a substrate, such as a concrete sidewalk, there is no exposure. It becomes a hazard when small particles are generated, as when mixing dry concrete or breaking up the sidewalk with a jackhammer or saw.

1.14.2 Control Measures

Controlling exposure to silica must be done by using engineering controls, administrative actions and personal protective equipment (PPE).

1.14.2.1 Engineering controls are preferred and include: using non-silica materials, using exhaust ventilation, containing the source, and wet cutting methods.

1.14.2.2 Administrative actions include: limiting exposure time, changing clothes to remove dust, and good housekeeping methods to keep dust levels down.

1.14.2.3 Personal protective equipment typically consists of respiratory protection and coveralls.

1.14.3 Requirements

- A. Prior to starting work that could generate airborne respirable crystalline silica, a Job Hazard Analysis (JHA) must be completed as per ESH-004. The Safety Division must be contacted prior to start of work for determination of proper control measures and for any needed airborne sampling. All controls for dust control as specified on the JHA must be implemented before work can begin.

TCR-ESHG-5008-Sec8-Cha1, R6-002

1.15 REFERENCES

American Conference of Governmental Industrial Hygienists (ACGIH), TLV's - Threshold Limit Values and Biological Exposure Indices, 2005 edition (or more recent if more restrictive), Cincinnati, OH. TCR-ESHG-5008-Sec8-Cha1, R6-002

American Industrial Hygiene Association (AIHA), Hygienic Guide Series, Akron, OH.

National Safety Council, Fundamentals of Industrial Hygiene, Chicago, IL, 1988.

Occupational Safety and Health Administration (OSHA), 29 CFR 1910.1000 to - .1046.

Department of Energy Nanoscale Science Research Centers (NSRC), Approach to Nanomaterial ES&H, Revision 3a, 5/12/08.

Department of Energy, Secretarial Policy Statement on Nanoscale Safety, DOE P 456.1, 9/15/05.

Department of Energy, The Safe handling of Unbound Engineered Nanoparticles, DOE N456.1.

National Fire Protection Association, NFPA 1, Fire Code.

National Fire Protection Association, NFPA 5000, Building Construction and Safety Code.

National Fire Protection Association, NFPA Glossary of Terms, 2014 Edition, 9/16/14.

ATTACHMENT 1

CHEMICAL STORAGE REQUIREMENTS USER AID (example)

DO ensure that every container has a label.

Labels **MUST** include:

BRAND NAME of chemical

AND

HAZARD WARNING

Do **NOT** store flammable liquids in squeeze bottles.

Do **NOT** use food containers for chemical storage.

Do **NOT** store other materials in cabinets with flammable liquids.

Do **NOT** overfill cabinets beyond maximum rated capacity.

Do **NOT** stack containers in unstable condition.

Do **NOT** keep more than the minimum quantity of chemicals necessary for short operation periods.

Do **NOT** store inappropriate chemicals in the cabinet (i.e., flammables cabinet for flammable materials, corrosives cabinet for corrosive materials, etc.)

DO ensure that MSDSs are available for all chemicals stored in cabinets.

DO contact M&ES, X3380, for disposal of any unwanted, no longer being used, or old chemicals. These may become unstable over time.

DO contact IH, x2533 or 2531, for information on chemical use, labeling and storage.