Safe Method of Use 4
Storage of Chemicals in the Laboratory

General Guidelines

- The Safe Method of Use for particular classes of chemicals and MSDS for specific chemicals must be consulted for specific requirements for storage, use and disposal.
- The requirements of the Safe Method of Use for particular classes of chemicals ***must*** be followed.
- Quantities of hazardous substances in the laboratory ***should*** be kept to a minimum, commensurate with needs and shelf life. Substances unstable at room temperature ***shall*** be stored in controlled temperature storage. Incompatible chemicals ***shall*** be segregated.
- The quantity of hazardous substances stored on bench tops or shelves ***should*** be kept to a minimum.
- Storage cabinets ***should*** be used where practical.
- Flammable, reactive, highly toxic or corrosive substances not in regular use ***shall*** be stored in storage cabinets.
- Bottles and jars of ready-to-use reagents stored on benches or on shelves between benches ***should*** not exceed:
  (a) 1 litre capacity for Category A Hazardous Substances
  (b) 2.5 litres capacity for all other hazardous substance categories

- Liquids that are flammable, corrosive or toxic ***should*** *b*e provided with secondary containment.

- Secondary containment ***may*** be provided by:

  (i) Sumps within Flammable or Corrosive liquids cabinets
  (ii) Plastic trays underneath corrosive substances
  (iii) Metal trays for organic solvents

Segregation

- The purpose of segregation is to prevent inadvertent mixing of incompatible substances that would lead to a dangerous reaction.
- Segregation can be achieved by the use of distance or secondary containment.

- The distance required for segregation will depend on the quantity of the incompatible substances and their mobility. Containers of less than 100 ml or 100 g require very small distances to achieve segregation.
- Segregation can also be achieved through the use of secondary containment which allows even smaller segregation distances.
- The Safe Method of Use for particular classes of chemicals and MSDS for specific chemicals must be consulted for specific requirements for storage, use and disposal.
- For guidance and rules regarding segregation of classes of chemicals see Appendix 1.

Reactive Chemicals

- Care must be taken to ensure correct storage of many reactive chemicals. Some of these are listed in Appendix 2.
- Classes of potentially explosive chemicals are listed in Appendix 3. particular care must be taken with trinitroaromatics such as picric acid to ensure they have adequate desensitizing agent at all times- see Safe Method of Use for Hazardous Substances of Higher Risk 2 – Picric acid.
- If ethers or dienes are being used see Safe Method of Use for Hazardous Substances of Higher Risk 4 – Storage and Testing for Peroxide Forming Chemicals.

Storage cabinets and refrigerators

- Storage cabinets ***should*** have secondary containment if they are used to store liquids.
- No more than 100 litres ***should*** be stored in any one cabinet and secondary containment ***shall*** be able to retain at least 50% of contents of the cabinet.
- Storage cabinets containing incompatible substances ***shall*** be separated by at least 1.0m horizontally. Cabinets with secondary containment in each cabinet ***shall*** be separated by not less than 0.5m.
- Refrigerators used to store open containers of Class 3.1A and Class 3.1B flammable substances, with a flash point less than 15 ^{0}C, ***shall*** be spark proofed. (ie thermostats have been externally mounted and light fittings removed). The refrigerator ***shall*** be labelled as suitable for use with these substances.

Storage of Waste

Containers for collecting and storing hazardous substances wastes in laboratories:

(a) ***Shall*** not exceed 5 litres for category A substances or 20 litres for all other categories.

(b) ***Shall*** not be placed on the floor under or between benches, in walkways or corridors unless containers are attached to analytical equipment.

(c) ***Shall*** be kept in a storage cabinet, unless:
  - the room where flammable liquids are being collected is ventilated to ensure that flammable vapour will not exceed 10% of the LEL, or
  - safety containers are used that are self closing and have a flash arrester.

(d) Containers not stored in storage cabinets ***should*** be provided with secondary containment.

Inspection of Containers

Laboratory Managers ***shall*** ensure an annual review and inspection of all containers (and closures) used for long-term storage of hazardous substances to ensure adequate containment. Any leaking containers or closures ***will*** be disposed of immediately.

Appendix 1: Segregation of Chemicals

General Rules

COMPOUND	INCOMPATIBLE WITH
Class 3 Flammable Liquids	Class 4 Reactives; Class 5.1 Oxidisers and 5.2 organic peroxides Sources of ignition
Class 4.1 reactives	With no other class; Sources of ignition
Class 4.2	Class 3 Flammable Liquids; Class 5.1 Oxidisers and 5.2 organic peroxides
Class 4.3	Class 3 Flammable Liquids; Class 5.1 Oxidisers and 5.2 organic peroxides water
Class 5.1	Class 3 Flammable Liquids; Class 4 reactives Any Organic combustible
Class 5.2	With no other class; Sources of ignition and heat

Class 6

Cyanides will be kept away from acids

Class 8 – Corrosives

Stored to prevent reactions between:
Acids and alkalis
Acids and hypochlorites
Acids and cyanides
Acids and Class 4.3 compounds
Oxidising acids (e.g. conc nitric and perchloric) and combustibles

NB: The distance required for segregation will depend on the quantity of the incompatible substances and their mobility.

Partial List of Incompatible Chemicals (Toxic Hazards)

Substances in the left hand column should be stored and handled so that they cannot possibly accidentally contact corresponding substances in the center column, because toxic materials (right hand column) would be produced.

COMPOUND	INCOMPATIBLE WITH	COMPOUND PRODUCED
Arsenates	Reducing agent	Arsine
Azides	Acids	Hydrogen Azide
Cyanides	Acids	Hydrogen Cyanide
Hypochlorites	Acids	Chlorine or Hypochlorous Acid
Formaldehyde	HCl or hypochlorite solutions	bis-chloromethyl ether
Nitrates	Sulfuric Acid	Nitrogen Dioxide
Nitric acid	Copper, Brass, Heavy Metals	Nitrogen Dioxide
Nitrites	Acids	Nitrous Fumes
Phosphorus	Caustic Alkalies/ Reducers	Phosphine
Selenides	Reducers	Hydrogen Selenide
Sulfides	Acids	Hydrogen Sulfide
Tellurides	Reducers	Hydrogen Telluride

Incompatible Chemicals

The following is a partial listing of incompatible chemicals.

CHEMICAL	IS INCOMPATIBLE WITH
ACETIC ACID	Chromic acid, nitric acid, hydroxyl-containing compounds, ethylene glycol, perchloric acid, peroxides, and permanganates
ACETONE	Concentrated sulfuric and nitric acid mixtures or chloroform and bases
ACETYLENE	Copper tubing, halides, silver, mercury and their compounds
ALKALI METALS	Aluminum, calcium, lithium, magnesium, potassium and sodium with water or chlorinated hydrocarbon, carbon dioxide, halogens
AMMONIA, ANHYDROUS	Mercury, halogens, calcium hypochlorite, hydrogen fluoride
ANILINE	Nitric acid and hydrogen peroxide
AZIDES	Acids
BROMINE	Ammonia, acetylene, butadiene, butane, hydrogen, sodium carbide, turpentine
CHLORATES	Ammonium salts, acids, metal powders, sulfur, finely divided organic and combustible materials
CHROMIC ACID	Acetic acid, alcohol, camphor, flammable liquids, glycerol, naphthalene

CHEMICAL	**IS INCOMPATIBLE WITH**
CHLORINE	Ammonia, acetylene, butadiene, benzene and other petroleum fractions, hydrogen, sodium carbides, powdered metals
COPPER SALTS	Acetylene, hydrogen peroxide
CYANIDES	Acids
ETHYLENEDIAMINE	Greater than 3 percent with methylene chloride (explosive)
FLAMMABLE LIQUIDS	Ammonium nitrate, chromic acid, hydrogen peroxide, halogens, nitric acid, sodium peroxide
HYDROCARBONS	(Butane, Halogens, chromic acid, peroxides Propane, Benzene)
HYDROGEN PEROXIDE	Copper, chromium, iron, most metals and their salts, flammable fluids, aniline, and nitromethane
HYDROGEN SULFIDE	Nitric acid and oxidizing gases
IODINE	Acetylene, ammonia
MERCURY	Acetylene, hydrogen
METHYLENE CHLORIDE	Greater than 3 percent ethylenediamine (explosive)
NITRIC ACID	Acetic, chromic and hydrochloric acids, aniline, carbon, hydrogen sulfide, flammable fluids, or gases which are readily nitrated
OXYGEN	Oils, grease, hydrogen, flammable liquids, solids, and gases
OXALIC ACID	Mercury, silver
PERCHLORIC ACID	Acetic anhydride, alcohol, organic materials, e.g., wood, paper, grease, and oils
PHOSPHORUS	Air, alkalis, oxygen, reducing agents
PHOSPHORUS PENTOXIDE	Water
SODIUM	Carbon dioxide, carbon tetrachloride, water
SODIUM PEROXIDE	Any oxidizable substances; acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerol, ethylene glycol, ethyl acetate, methanol
SULFURIC ACID	Potassium chlorate, potassium perchlorate, potassium permanganate

Appendix 2: Reactive Chemicals

Reactive chemicals are substances which, under certain ambient or induced conditions, enter into violent reactions with spontaneous generation of large quantities of heat, light, gases (flammable and non-flammable), or toxicants that can be destructive to lives and property. Types of reactive chemicals have been loosely categorized:

Explosives

In general, protect explosive substances from shock, elevated temperatures, rapid temperature changes, and other reactive chemicals, Some examples: nitroglycerin, nitrocellulose, and organic peroxides. Many substances, when mixed, are potentially explosive (such as hydrazines and nitric acid).

Oxidizing and Reducing Substances

In many oxidizing and reducing reactions, both agents must be present. In some cases, one or the other substance may create a hazard by coming into contact with a normally innocuous substance. These reactions tend to generate heat and are often explosive, e.g., glycerol and potassium permanganate blended at room temperature for a few minutes react violently producing fire.

The following examples of typical oxidizers may:

Increase Rate of Combustion

Aluminum nitrate
Ammonium persulfate
Barium chlorate
Barium peroxide
Calcium chlorate
Calcium nitrate
Calcium peroxide
Cupric nitrate
Hydrogen peroxide
Lead nitrate
Lithium hypochlorite
Lithium peroxide
Magnesium nitrate
Magnesium perchlorate
Magnesium peroxide
Nickel nitrate
Nitric acid 70% or less
Perchloric acid 60% or less
Potassium chlorate
Potassium dichromate
Potassium nitrate
Potassium persulfate
Silver nitrate
Silver nitrite
Sodium perborate
Sodium perchlorate
Sodium persulfate
Strontium chlorate
Strontium nitrate
Strontium nitrite
Thorium nitrite
Uranium nitrate
Zinc chlorate
Zinc peroxide

Cause Spontaneous Ignition with Reactant

Calcium hypochlorite
Chromic acid
Hydrogen peroxide (27.5-52%)
Sodium chlorite (>40%)
Sodium peroxide
Sodium permanganate

Nitric acid
Potassium bromate
Potassium permanganate
Trichloroisocyanuric acid
Sodium dichloroisocyanurate

Decompose with Catalyst or Heat

Ammonium dichromate
Hydrogen peroxide (52-91%)
Calcium hypochlorite (>50%)
Perchloric acid (60-72.5%)
Potassium dichloroisocyanurate
Sodium dichloroisocyanurate

Cause Explosive Reaction when exposed to Catalyst or Heat

Ammonium perchlorate
Ammonium permanganate
Perchloric acid
Potassium superoxide

Water Sensitive Substances

These chemicals react with water, steam, and moisture in the air to evolve heat and/or flammable or explosive gases. Isolate water-sensitive substances from other reactive compounds, and store in a cool, waterproof area.

Some substances that liberate flammable gases when exposed to water are: hydrides, nitrites, carbides, and anhydrous metallic salts.

In some cases, water sensitive substances react extremely violently with water and are stored under oil or in inert atmospheres to prevent such reactions eg: pure alkali metals.

Air Reactive Substances

These materials are capable of rapid release of energy by themselves, as by self-reaction or polymerization, for example white phosphorous. Also included in this category are substances that can be easily ignited by common sources of heat when mixed with air, for example: alkali metals, ammonium nitrate, ammonium perchlorate, ammonium permanganate, benzoyl peroxide, boron hydrides, lithium hydride.

Acid Reactive Substances

These chemicals react with acid to evolve heat, flammable and/or explosive gases, and toxicants. Some examples are: alkali metals, hydroxides, carbides, nitrites, arsenic and related elements, cyanides, sulfides, and structural alloys (most metals).

Special Organic Compounds

These compounds are unstable and may decompose spontaneously or through contact with the immediate environment (air, water, and other reactants). Some examples: butyl lithium, diazonium compounds, diazomethane, chlorination intermediates, butadiene, nitration intermediates, organic sulfates, polymerization reactions, and highly nitrated compounds.

Pyrophoric Agents

Pyrophoric agents burn when exposed to air. In general, they require absolute protection against air. Examples: phosphorus and activated zinc.

Appendix 3 – Explosive and Potentially Explosive Chemicals

Explosive chemicals can release tremendous amounts of destructive energy rapidly. If not handled properly, these chemicals can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies. For example, an explosion of old isopropyl ether killed a laboratory worker when he attempted to remove a glass stopper from the container. In another instance, tetrazole exploded inside a hazardous waste incinerator, causing major damage and costly repairs.

Potentially explosive chemicals (PECs), which include peroxidizable organic chemicals. Most chemicals that are used in research and teaching laboratories
are stable and non-explosive at the time of purchase. Over time, some chemicals can oxidize, become contaminated, dry out, or otherwise destabilize to become PECs (e.g., isopropyl ether, sodium amide, and picric acid). See Appendix I—Explosive and Potentially Explosive Families— for examples.
Unlike known explosives, which are designed to be stable under normal conditions, PECs are particularly dangerous because they may explode if they are subjected to heat, light, friction, or mechanical shock.

Common Laboratory PECs

There are many PECs used in academic research laboratories.

The following are some commonly used chemicals that can become an explosion hazard under certain conditions:

- Organic chemicals that form peroxides through exposure to air or light (see Appendix II — Peroxide Forming Chemicals)
- Hydrated picric acid that becomes dry or becomes contaminated with metals that form metal picrate salts
- Sodium amide that reacts with air or moisture to form superoxides, as evidenced by yellow or brown discoloration
- Certain alkyl nitrates (e.g., butyl nitrate or propyl nitrate) that become contaminated with nitrogen oxides
- Certain normally stable perchlorates (e.g., pyridium perchlorate or tetraethylammonium perchlorate) that become unstable at elevated temperatures

Note: Most explosions occur while purifying or distilling mixtures. Therefore, use extreme caution before concentrating or purifying any mixture that may contain an explosive chemical (e.g., a peroxide forming chemical or perchlorate).

There is an additional group of chemicals that should be considered although they are not necessarily heat-, light-, friction-, or shock-sensitive. These chemicals give off gaseous degradation by-products that may cause overpressurization of the container and explode. They can degrade over time and should be incorporated into a safety and handling system that will prevent them from becoming explosive hazards.

Explosive and Potentially Explosive Chemical Families

Acetylene or acetylide compounds: N-Chloro-3-aminopropyne Propiolic acid Propynethiol	*Diazo compounds* 2-Buten-1-yl diazoacetate Diethyl diazomalonate Dinitrodiazomethane
Organic Azides Diazidomethyleneazine Picryl azide Vinyl azide Acetyl azide Cyanodiazoacetyl azide Phenylphosphonic azide chloride	*Diazonium carboxylates, perchlorates, salts, sulfates, tetrahaloborates, and, triiodides* Benzenediazonium-2-carboxylate 4-Aminobenzenediazonium perchlorate 6-chloro-2,4-dinitrobenzenediazonium sulfate 2-Nitrobenzenediazonium tetrachloroborate 4-Toluenediazonium triiodide
Acyl hypohalites Acetyl hypobromite Hexafluoroglutaryl dihypochlorite	*Difluoroaminoalkanols* 1,1-Difluorourea Perfluoro-N-cyanodiaminomethane
Alkyl nitrates Ethylidene dinitrate Glyceryl trinitrate Propyl nitrate	*Fluoro—nitro compounds* 1-Fluoro-1,1-dinitrobutane Fluorodinitromethyl azide
Alkyl perchlorates Hexyl perchlorate Ethyl perchlorate 1-Chloro-2-propyl perchlorate	*Fulminating metals* Lead fulminate Gold fulminate Silver fulminate
Allyl trifluoromethanesulfonates 2-Chloro-2-propenyl trifluoromethanesulfonate	*Furazan N-oxides* Dicyanofurazan N-oxide 4-Oximino4,5,6,7-tetrahydrobenzofurazn N-oxide
Amminemetal oxosalts Ammonium hexanitrocobaltate Bis(1,2-diaminoethane) diaquacobalt (III) perchlorate Trihydrazine nickel (II) nitrate	*Hydroxooxodiperoxochromate salts* 1-Ammonium hydroxooxodiperoxochromate Potassium hyroxooxodiperoxochromate
Aromatic nitrates Picric acid Trinitrobenzene Picryl sulfonic acid Trinitroresorcinol	*Iodine Compounds* Calcium 2-iodylbenzoate Iodobenzene 2-Iodylvinyl chloride
Azides Hydrogen azide	*Isoxazoles* 3-Aminoisoxazole 3,5-Dimethylisoxazole
Aziridines 1-Bromoaziridine	*Metal Azide Halides* Chromyl azide chloride Molybdenum diazide tetrachloride Tungsten azide pentachloride
Azocarbaboranes 1,1-‘Azo-1,2-dicarbadecaborane	*Metal Azides* Aluminum azide Bis(cyclopentadienyl)tungsten diazide oxide

	Mercury (I&II) azide Lead azide
N-Azolium nitroimidates Benzimidazolium 1-nitroimidate 4-Nitroamino-1,2,4-triazole 2-(N-Nitroamino)pyridine N-oxide	*N-Metal Derivatives* Cadmium nitride Dibutylthallium isocyanate Sodium amide
Perchloramide Salts Barium perchloramide Mercury (II) N-perchloryl benzylamide Silver perchlorylamide	*Metal Fulminates* Mercury (II) fulminate Sodium fulminate Tripropyllead fulminate
Metal Halogentates Lead bromate	*Perchloryl Compounds* 2,6-Dinitro-4-perchlorylphenol Perchloryl fluoride N-Perchloryl piperidine
Metal Hydrides Stibine (Antimony hydride)	*Peroxyacid salts* Calcium peroxodisulfate Potassium tetraperoxomolybdate Tetramethylammonium pentaperoxodichromate
Metal Nitrophenoxides Lithium 4-nitrothiophenoxide Potassium 4-nitrophenoxide	*Peroxyacids* Benzenperoxyselennic acid Peroxyacetic acid Peroxyformic acid
Metal Oxides Bis (1-chloroethylthallium chloride) oxide Magnesium chloride trioxide	*Peroxycarbonate esters* O-O-tert-Butyl isopropyl monoperoxycarbonate Diallyl peroxydicarbonate Dimethyl peroxydicarbonate
Metal Oxohalogenates Ammonium iodate Lead acetate–lead bromate	*Phosphorus esters* Diethyl phosphite Dibenzyl phosphorchloridate
Metal Oxometallates Bis (benzene) chromium dichromate	*Nitroso Compounds* Dinitrosylnickel Ethyl N-methyl-N-nitrosocarbamate Potassium nitrosodisulfate
Metal Perchlorates Chromyl perchlorate	*N–S Compounds* Disulfur dinitride Potassium sulfurdiimidate Tetrasulfur tetranitride Thiotrithiazyl nitrate
Metal Peroxides Many transition metal peroxides are dangerously explosive.	*Organolithium Reagents* o-Trifluoromethyl phenyllithium m-Bromo phenyllithium
Metal Peroxomolybdates 2-Potassium tetraperoxomolybdate 2-Sodium tetraperoxomolybdate	*Organomineral Peroxides* Bis(triethyltin) peroxide Diethylhydroxotin hydroperoxide
Metal Picramates Palladium picramate Uranyl picramate	*Oximes* Bromoacetone oxime Hydroxycopper glyoximate Potassium cyclohexanehexone 1,3,5-trioximate
Nitroaryl Compounds N-Chloro-4-nitroaniline	*Oxosalts of Nitrogenous Bases* Ammonium tetranitroplatinate (II) Diamminepalladium (II) nitrate 1,2-Diammonioethane nitrate
Nitrogenous Base Nitrite Salts Methylammonium nitrite	*Ozonides* trans-2-Butene ozonide

	Ethylene ozonide (1,2,4-trioxolane) Trifluoroethylene ozonide
aci-Nitroquinonoid Compounds Sodium 1,4-bis(aci-nitro)-2,5-cyclohexadienide	*Perchlorate Salts of Nitrogenous Bases* Pyridinium perchlorate Teteraethylammonium perchlorate
aci-Nitro Salts Ammonium aci-nitromethanide Dipotassium aci-dinitromethanide Thallium aci-phenylnitromethanide	*Triazoles* 3-Diazo-5-phenyl-3*H*-1,2,4-triazole 4-Hydroxy-3,5-dimethyl-1,2,4-triazole 1,2,3-Triazole
Picrates Nickel picrate (anhydrous) S-7-Methylnonylthiouronium picrate Sodium picrate	*Poly(dimercuryimmonium) Compounds* Poly(dimercuryimmonium picrate) Poly(dimercuryimmonium permanganate) Poly(dimercuryimmonium trinitrobenzoate)
Polymerization (violent) Acrylic acid Ethylene oxide Vinyl acetate	*Polynitroalkyl Coumpounds* Dinitroacetonitrile Hexanitroethane Potassium trinitromethanide
Polynitroaryl Compounds 5,6-Dinitro-2-dimethyl aminopyrimidinone 4-Nitro-1-picryl-1,2,3-triazole 2,4,6-Trinitrotolune	*Silver Compounds* Silver nitride (fulminating silver) Disilver ketenide Phenylsilver Silver azide Silver Osmate
Strained-Ring Compounds 2-Azatricyclo[2.2.102,6]hept-7-yl perchlorate Dicyclopropyldiazomethane Prismane	*Tetrazoles* 5-Aminotetrazole Silver and mercury salts of 5-nitrotetrazole Tetrazole