4.03 CHEMICAL STORAGE PROGRAM

This program contains requirements for practices designed and implemented to protect University employees, students, visitors and the environment from the risks of hazardous chemicals that are used and stored on University property.

A. SCOPE

This program is applicable to all University students, faculty and staff that are required by the nature of their job to use and store hazardous chemicals.

B. DEFINITIONS

Material Safety Data Sheet (MSDS) - Written or printed material prepared by the manufacturer of a hazardous chemical that contains information about the hazards of the chemical and the appropriate work practices required for use.

NFPA-approved - Approved by the National Fire Protection Association

Pyrophoric chemicals - Any liquid or solid chemicals that will ignite spontaneously in air below 130^{o}F (54.4^{o}C)

U.S. Department of Transportation hazard classes and divisions – see 49 CFR Part 173.

2.1 Flammable gas –

- Is a gas at 68^{o} and burns readily in air
- Is ignitable at 101.3 KPa (14.7 psia) when in a mixture of 13 percent or less by volume with air.
- Has a flammable range at 101.3 KPa (14.7 psia) with air of at least 12 percent regardless of the lower limit

2.2 Non-flammable compressed gas - Gas shipped at a pressure >= 41 psi absolute, which is neither flammable nor poisonous. $PSI_{absolute} = PSI_{gauge} + PSI_{atmospheric}$

2.3 Poisonous gas - Is a gas at 68^{o}F and has an LC_{50} <5,000 ml/m^{3} (i.e., one half of one percent concentration in air will kill half of the animals in a laboratory test)

3 Flammable liquid - Liquid with a flash point <=141^{o}F Note: Flash point is the temperature at which a liquid gives off enough vapor to ignite and "flash" back to the liquid surface.

3 Combustible liquid - Liquid with a flash point above 141^{o}F but below 200^{o}F.

4.1 Flammable solid - Strongly exothermic decomposition at normal temperatures or ignites through friction (e.g., matches) or burns very fast or persistently when ignited

4.2 Spontaneously combustible material - Spontaneously ignites within 5 minutes on exposure to air or can undergo strongly exothermic decomposition even in the absence of oxygen

4.3 Dangerous when wet material - Spontaneously ignites or emits flammable or toxic gasses when contacted with water

5.1 Oxidizer - Any solid, liquid or gaseous chemical that causes or enhances combustion of other materials or readily react to oxidize combustible materials, generally by yielding oxygen (e.g., sodium nitrite, oxygen gas, hydrogen peroxide, etc.)

5.2 Organic peroxide - A specific chemical group that is generally reactive, which contains oxygen in the bivalent –O-O- structure and which may be considered a derivative of hydrogen peroxide

6.1 Poisonous materials - Solids or liquids that are poisonous as defined by:

- Oral Toxicity – A material with an acute LD_{50} of not more than 300 mg//kg
- Dermal Toxicity – A material with an acute LD_{50} of not more than 1000 mg/kg
- Inhalation Toxicity – A dust, or mist with an acute LC_{50} of not more than 4 mg/L

8 Corrosive material - Any solid, liquid or gaseous chemicals that dissolve steel or aluminum, or that burn, irritate, destructively attack organic tissues, and destroy skin tissue

C. GENERAL STORAGE REQUIREMENTS FOR ALL CHEMICALS

1. Label all chemical containers appropriately. If transferring chemicals out of their original container to another container or if the original container label is illegible, follow the chemical labeling guidelines as detailed in UNM's Hazard Communication Program.

2. Be knowledgeable of the procedures contained in SRS's Chemical Spill Response Program to prepare yourself and others in the event that any chemical container leaks or is spilled.

3. Follow all precautions regarding the storage of incompatible chemicals. Consult the label and Material Safety Data Sheet (MSDS) for each chemical to ensure that you are familiar with the chemical and how it should be handled, stored and disposed. **Separate all chemicals into compatible groups.**

4. Provide a definite storage place for each chemical and return the chemical to that same location after each use.

5. Avoid storing chemicals in laboratory fume hoods or on bench tops, except for those chemicals intended to be used by the end of the day.

6. Store volatile toxic chemicals and odorous chemicals in a ventilated cabinet, if possible. The cabinet's associated electrical components must be explosion-proof if flammable materials are being ventilated. If located in a laboratory, locate the cabinet near the fume hood. Store other chemicals inside a closable cabinet or on a shelf that has a lip to prevent containers from sliding off in the event of a fire or other serious accident.

7. Do not expose stored chemicals to heat, direct sunlight or freezing conditions.

8. Store all containers of liquids on compatible plastic trays that are capable of holding the contents of the container if it leaks. Store liquids on lower shelves, if at all possible.

9. Close all chemical containers well to minimize the escape of flammable, corrosive, irritating or toxic vapors or gases.

10. Ventilation is required for chemicals that may release dangerous or damaging quantities of vapors or gases which may be flammable, corrosive, irritating or toxic (see item 6 above).

11. For every chemical storage area, there should be evacuation and emergency procedures to be followed and fire extinguishers available in the case of personal exposure or a leak, spill or fire within the room. Ventilation rates should exceed at least six air changes per hour.

D. STORAGE REQUIREMENTS FOR FLAMMABLE AND COMBUSTIBLE CHEMICALS

1. The storage area should be separated and protected so that a fire or spill in the storage area is not likely to spread beyond the storage area.

2. If containers of flammable and combustible liquids are larger than five (5) gallons in size, special provisions are necessary to prevent liquid from flowing out of the storage area in the event of a spill or leak. Contact SRS at 277-2753 for further details.

3. When possible, store quantities of flammable liquids greater than four (4) liters in NFPA-approved safety cans. Store all flammable liquids and solids in NFPA-approved storage cabinets.

4. Do not store flammable chemicals in any refrigerator unless it has been designed for that purpose. Ordinary refrigerators contain spark sources that can ignite flammable vapors. If refrigerated storage is needed inside of a flammable storage room, an explosion-proof refrigerator must be used. Use chemical storage refrigerators only for storing chemicals, never food or drink. Label these refrigerators with the following signage:

   NO FOOD OR DRINK TO BE STORED IN THIS REFRIGERATOR

5. **Safety Equipment for Storage of Flammable Liquids**

Safety Cans: Safety cans are containers that have built-in safety features for protecting flammable liquids from exposure to a fire situation. In a fire situation, a safety can is exposed to extremely high temperatures. This heat is transmitted to the contents, which in turn boil and

produce a large vapor pressure. Every safety can is fitted with a spring-loaded cap that vents these vapors safely without bursting the can. The other safety feature of a safety can is the flame arrestor that consists of a cylindrical wire screen. Vapors emitted from a safety can will ignite when exposed to the flames of a fire. Since flames usually flash back to the source of liquid, the flame arrestor serves as a heat dissipator. The temperature in the space above the liquid in a safety can is lowered below the ignition temperature and ignition of the contents is eliminated.

Flammable Liquid Storage Cabinets: Flammable liquid storage cabinets are designed to maintain the temperature at the top of the cabinet interior below 325ºF when subjected to a 10-minute fire test. Cabinets built to withstand the temperature rating during the 10-minute fire test are acceptable by OSHA standards if: (a) the maximum capacity of Flammable liquids is not more than 60 gallons; and (b) the cabinet is labeled with conspicuous lettering, such as FLAMMABLE-KEEP FIRE AWAY. All storage cabinets should have self-closing doors that will close the latch automatically when released. These doors must not be blocked open.

Special Refrigerators: Special refrigerators that can safely store flammable liquids have a spark-free interior such that all wiring and thermostat controls have been removed from the interior. Two types of these refrigerators are commercially available: a "flammable liquid storage" model and an "explosion-proof" model. A "flammable liquid storage" model is normally used in a non-explosive area where no flammable vapors are present. Such a refrigerator is normally powered through a standard three-wire cord plugged into an electrical outlet. An "explosion-proof" refrigerator is required when the area in which the refrigerator will be located has the potential for ignition of flammable vapors. An explosion-proof refrigerator is supplied with a "pigtail" cord that must be wired directly to a power source using metal conduit as specified by local electrical codes. Choosing the appropriate refrigerator will depend on the area in which it will be located.

E. STORAGE REQUIREMENTS FOR REACTIVE CHEMICALS

1. Consider the storage requirements of each reactive chemical prior to purchasing.

2. Consult the label and MSDS in making decisions about storage of reactive chemicals.

3. Use and store only the quantities of material you will need for immediate use.

4. Cyanides and sulfides should be stored in a location separate from acids or protected from contact with acids.

5. All acids should be stored separately from all alkaline materials (bases).

6. Date all highly reactive materials as soon as received and make sure the label states:

DANGER! HIGHLY REACTIVE MATERIAL

7. Do not open a container of highly reactive material that is past its expiration date. Call SRS at 277-2753 for assistance.

8. Dispose of highly reactive material through SRS prior to the expiration date.

9. Segregate the following materials:

   - oxidizing agents (**5.1**) from reducing agents, flammables (**3**) and combustibles (**3**)
   - powerful reducing agents from readily reducible substrates
   - pyrophoric compounds from flammables (**3**)
   - perchloric acid from reducing agents and combustibles (**3**)

10. Store reactive liquids in trays constructed of compatible materials which are large enough to contain the contents of the bottles. Store perchloric acid bottles in glass or ceramic trays.

11. Store materials that react vigorously with water away from any possible contact with water. If chemicals are to be stored that are reactive if exposed to the air or water, they can safely be stored in sprinklered areas where sprinkler discharge would serve to prevent rupture of the outer container.

12. Temperature control or refrigeration must be provided, as needed, for chemicals that deteriorate or react if their temperatures exceed safe limits recommended by the manufacturer or person synthesizing the chemical. Store thermally unstable materials in a refrigerator with the following safety features: all spark-producing controls are on the outside, a magnetic locked door, an alarm to warn when the temperature is too high.

13. Assign responsibility for the storage areas utilized for highly reactive materials to one (1) primary person and a backup person. Review this responsibility at least twice yearly.

14. Some highly reactive shock/heat sensitive materials are:

Ammonium perchlorate	Dibenzoyl peroxide
Ammonium permanganate	Diisopropyl peroxydicarbonate
Anhydrous perchloric acid	Dinitrobenzene (ortho)
Butyl hydroperoxide	Ethyl methyl ketone peroxide
Butyl perbenzoate	Ethyl nitrate
t-Butyl peroxyacetate	Hydroxylamine
t-Butyl peroxypivalate	Peroxyacetic acid
1-Chloro-2,4-dinitrobenzene	Picric acid (<10% water content)
Cumene hydroperoxide	Trinitrobenzene
Diacetyl peroxide	Trinitrotoluene

F. STORAGE REQUIREMENTS FOR OXIDIZERS

Oxidizing agents such as chlorates, perchlorates, peroxides, nitric acid, nitrates, nitrites and permanganates represent a significant hazard because of their propensity under certain conditions to undergo vigorous reactions when they come into contact with easily oxidized material such as metal powders and organic materials like wood, paper and other combustible material. Mineral acids such as perchloric acid, sulfuric acid and nitric acid, as well as other oxidizers, should be stored separate from flammables and combustibles, by separate rooms, cabinets or break resistant containers. If large bottles must be stored in proximity of flammable materials, acid resistant trays must be used to prevent the oxidation of wood or corrosion of metal shelves.

1. Class I Oxidizer

Class I oxidizers will cause an increase of the burning rate of combustible material with which it comes in contact. Some examples are:

Hydrogen peroxide (8-28%)	Magnesium perchlorate
Nitric acid (70% or less)	Silver nitrate
Perchloric acid solutions (less than 60% wt/wt)	

2. Class II Oxidizer

Class II oxidizers will cause an increase of the burning rate or may cause spontaneous ignition of combustible material with which it comes in contact. Some examples are:

Calcium hypochlorite (50% or less wt/wt)	Chromic acid
Hydrogen peroxide (28-52% wt/wt)	Sodium peroxide
Liquid oxygen	

Contact SRS if quantities are stored in excess of 1,000 lbs.

3. Class III Oxidizers

Class III oxidizers will cause a severe increase in the burning rate of combustible material with which they come in contact, or will undergo vigorous self-sustained decomposition when catalyzed or exposed to heat. Regulated quantities are permitted to be stored only on the ground floor of a building with no basement. Some examples are:

Ammonium dichromate	Perchloric acid solutions (60-73%)
Hydrogen peroxide (52-91% wt/wt)	Sodium chlorate

Contact SRS if quantities are stored in excess of 200 lbs.

4. Class IV Oxidizer

Class IV oxidizers can undergo an explosive reaction when catalyzed or exposed to heat, shock, or friction. Regulated quantities are permitted to be stored only in detached storage. Storage areas for Class IV oxidizers must be provided with a means to vent fumes in any type of emergency. Some examples are:

Ammonium perchlorate	Perchloric acid solutions
Ammonium permanganate	(greater than 72.5%)
Hydrogen peroxide (greater than 91% wt/wt)	Potassium superoxide

Contact SRS if quantities are stored in excess of 10 lbs.

G. STORAGE REQUIREMENTS FOR TOXIC CHEMICALS

1. Store chemicals known to be highly toxic, including carcinogens, in ventilated storage in unbreakable, chemically resistant secondary containers.

2. Keep quantities on hand at an absolute minimum.

3. Limit access to these areas, and label storage areas with appropriate warning signs, e.g.:

CAUTION! REPRODUCTIVE TOXIN STORAGE

-or-

CAUTION! CANCER-SUSPECT AGENT STORAGE

4. Storage areas for pesticides and other toxic chemicals should be secured when the storage areas are not supervised by a responsible person so that unauthorized personnel are kept out.

H. STORAGE REQUIREMENTS FOR PEROXIDIZABLE CHEMICALS

Some chemicals can spontaneously form unstable peroxides during storage or after prolonged exposure to air and light. Certain peroxides may detonate with extreme violence when they become concentrated by evaporation or distillation, when combined with other compounds to yield a detonable mixture, or when simply disturbed by unusual heat, shock or friction.

1. The following compounds, which form peroxides, must be properly labeled with compound identity, the date received, date opened, testing frequency for the chemical, and dates tested with peroxide strips:

Peroxidizable Chemical Classifications

List I (Three Months)*	**List II** (Six Months)*	**List III** (Twelve Months)*
Peroxide Hazard on Storage	**Peroxide Hazard On Concentration**	**Hazard Due to Peroxide Initiation of Polymerization**
Diethyl Ketene	Acetal	1,3-Butadiene
Divinyl Ether	Acetaldehyde	Chlorobutadiene
Isopropyl Ether	Cyclohexene	Chlorotrifluoroethylene
Potassium Metal	Cyclopentene	Styrene
Potassium Amide	Cumene	Tetrafluoroethylene
Sodium Amide	Diacetylene	Vinyl Acetate
Sodium Ethoxyacetylide	Dicyclopentadiene	Vinyl Acetylene
Vinylidene Chloride	Diethylene Glycol Dimethyl Ether	Vinyl Chloride
	p-Dioxane	Vinyl Pyridine
	Ethyl Ether	
If stored as a liquid:	Ethylene Glycol Dimethy Ether	
Butadiene	Furan	
Chloroprene	Methyl Acetylene	
Tetrafluoroethylene	Methylcyclopentane	
	Tetrahydrofuran	
	Tetrahydronaphthalene	
	Vinyl Ethers	

***Note:** Peroxide testing frequency after opening. Write on label (below) upon receipt.

Label:

Peroxidizable Compound_____
Warning: May Form Explosive Peroxides!
Date received _____ Date opened _____
Dispose of or test within _____ months after opening!
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Test Date_____Peroxides_____ppm
Contact SRS at 277-2753 for disposal or questions.

2. SRS disposal guidelines and administrative procedures:

SRS waste disposal personnel **will not pick up or take for disposal** any peroxidizable compounds **that have not been timely tested** for peroxides by researchers, in accordance with the following time periods and instructions:

List I: Must have been tested for peroxides within the previous three months;
List II: Must have been tested for peroxides within the previous six months;
List III: Must have been tested for peroxides within the previous twelve months;

Unopened containers must not exceed 18 months in storage, untested; and , all compounds must contain less than 10 ppm when offered to SRS as waste for disposal.

For those peroxidizable compound containers not meeting these timelines or criteria, SRS will tape a red warning label on the container, and arrange for a high hazard contractor to handle the compound and neutralize/stabilize/prepare it for disposal at the Principal Investigator's department's cost.

3. Storage and handling procedures:

Each person responsible for a laboratory must develop and maintain an inventory of the peroxidizable materials in the laboratory. The inventory should be reviewed every three (3) months, at which time containers/samples from List I (three (3) months or older), List II (six (6) months or older), and List III (twelve (12) months or older) would either be tested for peroxides or disposed of through SRS. Quantities of peroxidizable compounds should be purchased in smaller container sizes to minimize exposure to air from multiple openings of the container and minimize potential for formation of peroxides.

Store all peroxidizable compounds in tightly closed original container, and away from heat and light. Sunlight is an especially good promoter of peroxidation. Protection from physical damage and ignition sources during storage is also essential. Particular care should be given to ensure tight closure on storage containers. Loose or leaky closures may permit evaporation of storage material, leaving a hazardous concentration of peroxides in the container, and peroxide crystallization in the cap threads. Most common container materials, such as steel, stainless steel, copper, nickel, aluminum, baked phenolic linings and ceramics, are suitable for containers; however, they must be clean and free of metal oxides because iron or copper oxides may actually promote peroxide formation. The use of oxidation inhibitors is especially important in the safe handling of peroxidizable materials. Hydroquinone, alkyl phenols, aromatic amines or similar materials are recommended by the manufacturers as being effective in slowing peroxide formation during storage. Peroxidization in a chemical process may not only be a serious hazard because of the explosion potential, but may also affect lower yield and produce unwanted impurities.

These chemicals should be tested for peroxide formation before use. Commercially available peroxide test strips are simple to use, but require different test protocols depending upon the

nature of the sample and the manufacturer. Although views differ in the USA about unsafe/dangerous peroxide levels, it is recommended by SRS that researchers do not use the compound, if the peroxide test is above 100 ppm. For disposal, these compounds must be neutralized below 10 ppm peroxide.

4. Management and disposal of **old/outdated** containers:

Older containers of peroxidizable chemicals, or containers of unknown age, vintage or history, must be handled very carefully and should never be opened by researchers. Compounds that are suspected of having very high peroxide levels because of visual observation of unusual viscosity, visible discoloration, liquid stratification, crystal formation, or because of age should be considered extremely dangerous. The precautions taken for disposal of these materials should be the same as for any material that can be detonated by friction or shock. **IT IS OF THE UTMOST IMPORTANCE THAT THE CONTAINER NOT BE OPENED.** The act of opening the container **COULD DETONATE PEROXIDE CRYSTALS** under the container cap or other closure. Researchers must/shall call SRS at 277-2753 for assistance with any potential peroxide **waste** issue. SRS will arrange to have the container(s) inspected, and if necessary, will arrange for a high hazard contractor to handle the container and neutralize/stabilize/prepare it for disposal.

I. CHEMICAL INCOMPATIBILITY CHART

Do not store these US DOT hazard classes together:

2.3	**with**	**2.1, 3, 4.1, 4.2, 4.3, 5.1, 5.2 or 8**
5.1	**with**	**2.3, 3, 6.1 or 8**
6.1	**with**	**2.1, 3, 4.1, 4.2, 4.3, 5.1, 5.2 or 8**
8	**with**	**4.1, 4.2, 4.2, 5.1 or 5.2**

J. CHEMICAL COMPATIBILITY CHART

RELATED AND COMPATIBLE STORAGE GROUPS

In general, chemicals should be separated and stored together according to the following compatible storage groups or categories:

- Inorganic (Solid/Liquid)
  Including but not limited to sulfates, chlorides, metals, etc.

- Inorganic (Acids)
  Including but not limited to nitric, sulfuric, hydrochloric, etc.,
  Note: Concentrations of 4N or greater requires compatible secondary containment.

- Inorganic (Bases)
  Including but not limited to ammonium hydroxide, sodium hydroxide, etc.,
  Note: Concentrations of 4N or greater requires compatible secondary containment.

- Organic (Solids)
  Including but not limited to citric, oxalate, etc.

- Organic (Liquids)
  Such as flammable solvents, acids, bases, etc.
  Storage in a NFPA 30 approved flammable storage cabinet with acids and bases separated and placed in compatible secondary containment.

- Poisons (Solids/Liquids)
  Including but not limited to cyanides, arsenic, thallium, etc.

- Oxidizers (Solids/Liquids)
  Including but not limited to nitrates, permanganates, bromates, etc.

- Explosives or Unstable Reactives
  When designated as waste, these compounds should be promptly and properly disposed of.
  Examples include but are not limited to nitroglycerine, picrates, etc.
  UNM does not currently possess authorized explosive storage facilities.