STANDARD OPERATING PROCEDURE FOR HANDLING STORAGE AND DISPOSAL FOR TIME SENSITIVE CHEMICALS

1. PURPOSE & SCOPE
   1.1. This procedure describes methods for safely using, storing, and disposing of time sensitive chemicals. This procedure applies to all University of Notre Dame personnel whose work involves time sensitive chemicals.
2. RESPONSIBILITIES
   2.1. Principal Investigators shall ensure this procedure is implemented in their work areas and labs.
   2.2. Once notified, RMS shall ensure proper disposal of time sensitive chemicals, which are expired or no longer needed are properly disposed. RMS or designee shall manage the stabilization of time sensitive chemicals that are suspect and could create an explosion or fire hazard.
3. SPECIAL PRECAUTIONS:
   3.1. Time-sensitive materials should be monitored in the laboratory and properly disposed at regular intervals. If these materials are left in storage long enough to form hazardous by-products, their management and disposal becomes increasingly hazardous and costly.
   3.2. If you discover time-sensitive materials that have expired or are undated:
      3.2.1. DO NOT TOUCH THE BOTTLE.
         3.2.1.1. Never, under any circumstances, touch or attempt to open a container of peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of unscrewing the cap could detonate the bottle.
      3.2.2. Visually inspect the bottle for product identification and expiration date.
      3.2.3. Visually inspect for water content.
      3.2.4. If you determine that the container may have crystals - immediately secure the area and notify RMS (631-5037)
4. HAZARD DESCRIPTION:
   4.1. Time Sensitive Chemicals are any chemical or chemical product that develops additional hazards upon prolonged storage. Examples of these chemicals include peroxidizables, polynitrated aromatics, chloroform and anhydrous HF. (Appendix A presents additional examples of time sensitive chemicals.)
   4.2. Peroxidizables are oxygenated organic compounds that will react with atmospheric oxygen to form explosive peroxides.
   4.3. Polynitrated aromatics have reactive nitrate groups that can form explosive picrate salts when exposed to certain metals.
   4.4. Chloroform will react with air over time to form phosgene.

4.5. Anhydrous HF easily liquefies and can react with a carbon steel cylinder to create hydrogen and can cause an increase in pressure inside the cylinder.

5. CONTROLS:
   5.1. Time sensitive chemicals should not be stored in ground glass stoppered bottles or in bottles with metal foil lined caps. Instead, they should be stored in dark colored glass to avoid reactions with light.
   5.2. Purchase the smallest quantity that is practical for all time-sensitive materials. Substitution with less hazardous materials is preferable.
6. SPECIAL DETECTION METHODS:
   6.1. With any time sensitive material, the date the material was purchased and the date it was opened or transferred to a secondary container shall be clearly marked on the container by the user/owner of the chemical.
   6.2. The following methods may be used to identify hazardous conditions:
      6.2.1. Peroxidizables may be characterized by having a "mossy" look around the cap. There may be a white film or residue around the neck, threads or cap of container or there may be crystals in the liquid.
      6.2.2. Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially (VWR # EMD 10081-1). These strips must be air-dried until the solvent evaporates and then exposed to moisture for proper operation. To use most of these, simply dunk the strip in the suspect material and then compare the color on the strip to the calibration chart that comes with the test kit. This gives a quantitative peroxide concentration, usually in parts per million (ppm). Caution:
         6.2.2.1. These strips have finite ranges. You may need to buy several different test kits to cover all possible ranges - read the product information or call the manufacturer for more information.
      6.2.3. Polynitrated Aromatics (Picric Acid) which have dehydrated will be pale in color and there will be crystals formed.
      6.2.4. Chloroform will have a normal appearance. The only way to determine stability is by determining the age of the material by the lot number or date marked on the container.
      6.2.5. Anhydrous HF cylinders may show a build up of pressure in the regulator of the cylinder.
7. PEROXIDIZABLES:
   7.1. Materials from Table 1, Appendix A should be dated, tested before use and disposed of within three months of opening or receipt.
   7.2. Materials from Table 2, Appendix A should be dated, tested before use and disposed of within twelve months of opening or receipt.
   7.3. Materials from Table 3, Appendix A should be dated, tested and disposed of within twelve months of opening or receipt.

7.4. Materials should be marked with the date they were tested for peroxides. Note: Based on the chemical manufacturer's recommendations, these expiration and disposal dates may be modified, as appropriate.
  7.4.1. Appendix B contains an example of a label.
7.5. Make sure the purchase of materials that contains an appropriate peroxide inhibitor, such as butylated hydroxytoluene (BHT). If non-inhibited material must be stored, be sure to store the material under an inert atmosphere of nitrogen or argon and test it for peroxides at least once a month.
7.6. Do not distill, evaporate or concentrate the material until you have first tested the material for the presence of peroxides. Peroxides are usually less volatile than their parent material and tend to concentrate in the (hot) distillation pot.
7.7. NOTE: Never, under any circumstances, touch or attempt to open a container of peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of unscrewing the cap could detonate the bottle with disastrous results.

8. POLYNITRATED AROMATICS (Picric Acid, 2,4-dinitrophenol):
8.1. Picric acid and its derivatives should be stored in small quantities, within the original container and in a cool, dry, well-ventilated area that is away from sources of heat.
8.2. Picric acid is considered a flammable solid and is incompatible with oxidizers, reducing agents, inorganic salts, metals, alkaloids and albumin.
8.3. Improperly managed or stored picric acid may become sensitive to shock, friction, and heat.
8.4. Picric acid allowed to dry out to less than 10% water by volume, becomes unstable and may pose an explosion hazard. If the material appears dry, do not open or handle the container – immediately contact the RMS Office: 631-5037.
8.5. Picric Acid should be monitored for water content every three months and disposed of as hazardous waste within two years of receipt.

9. CHLOROFORM:
9.1. Chloroform should be stored in a cool, dry, well-ventilated area [less than 30 degrees C (86 degrees F)] and in tightly sealed containers.
9.2. Chloroform decomposes at normal temperatures in sunlight in the absence of air, and in the dark in the presence of air.
9.3. Phosgene is a decomposition product of chloroform. Phosgene exposure can cause damage to the central nervous system in concentrations at only a small fraction of the permissible exposure limit of chloroform.
9.4. If possible, chloroform that is stabilized with alcohol should be purchased. If non-stabilized chloroform is necessary for the work, it needs to be treated like peroxide forming compounds and be used up in a short amount of time. Amylene is also used as a stabilizer, but there is evidence that it may not prevent phosgene generation.

9.5. If an unstabilized chloroform older than one year is discovered it should be disposed as hazardous waste.
9.6. Stabilized chloroform should be disposed of after it has been open for longer than one year.

10. ANHYDROUS HF (GAS):
    10.1. Hydrogen Fluoride may react with the iron in carbon steel cylinders to form iron fluoride and hydrogen. The gaseous hydrogen collects in the vapor space and builds pressure over an extended period of time.
    10.2. In order to minimize the possibility that the pressure would build to unsafe levels, cylinders should be pressure checked with a suitable pressure gauge during the recommended maximum two-year shelf life period. Cylinders should be returned to the supplier after two years, if they are not being used.
    10.3. A First In First Out (FIFO) inventory rotation should be applied to any cylinders that you may be using in your laboratory. The potential exists for pressure excursions of several hundred pounds to occur during the recommended storage time frame of Anhydrous HF. Pressures may continue to rise over longer storage periods. If you discover any HF cylinders that have been in storage longer than two years, immediately contact RMS: 631-5037.
11. PERSONAL PROTECTIVE EQUIPMENT (PPE):
    11.1. Review the Material Safety Data Sheet (MSDS) for the specific compound that is being used for the appropriate PPE requirements. At a minimum, wear goggles, lab coat or apron, and appropriate gloves.
12. WASTE DISPOSAL:
    12.1. Request a Hazardous Waste Pickup two months before the expiration date.
    12.2. If there are time-sensitive materials that are expired or compromised, please contact RMS Waste Personnel prior to pick-up. Contact information is available on the RMS web site at http://riskmanagement.nd.edu/laboratory-safety/hazardous-waste-pickup-schedule/
13. RECORD KEEPING:
    13.1. All chemicals shall be listed on the lab's chemical inventory. Time sensitive chemicals shall also be dated on the inventory.
    13.2. The chemical inventory shall be reviewed annually.
    13.3. Remove time sensitive chemicals from the inventory when they have been disposed.
14. FREQUENCY OF REVIEW:
    14.1. RMS will review SOP on an annual basis.
    14.2. Review date will be added to SOP upon review.

APPENDIX A

List of Common Peroxide-Forming Chemicals

1. Chemicals that may auropolymerize as a result of peroxide accumulation. Uninhibited chemicals must be disposed of within 24 hours of being opened. RMS must be notified by the lab personnel before their purchase and use. Inhibited chemicals must be disposed of within 12 months of being opened:

Acrylic acid [b]	Tetrafluoroethylene [c]
Acrylonitrile [b]	Vinyl acetate
Butadiene [c]	Vinyl acetylene
Chloroprene [c]	Vinyl chloride
Chlorotrifluoroethylene	Vinyl pyridine
Methyl Methacrylate [b]	Vinyladiene chloride
Styrene	

2. Chemicals that form explosive levels of peroxides without concentration by evaporation or distillation. Some of these may form explosive concentrations of peroxide even if never opened. These chemicals must be disposed of within 3 months of being opened:

Butadiene [a]	Isopropryl ether [a]
Chloroprene [a]	Tetrafiuoroethylene
Divinylacetylene	Vinylidene chloride

3. Chemicals that form explosive levels of peroxides on concentration by evaporation or distillation or otherwise treated to concentrate the peroxides. These peroxide formers that must be disposed of within 12 months of being opened:

(2-Ethoxythyl)-o-benzoyl benzoate	Buten-3-yne
> 80% Hydrogen Peroxide	Chloroacetadehydediethyl acetal
§ - Bromophenetole	Chloromethyl methyl ether [e]
§ - Chlorophenetole	Chloromethylene
1 - Pentene	Cumene
1–(2-Chlororethoxy)–2-Phenoxyethane	Cyclohexanol
1-(2-Ethoxyethoxyethyl)ethyl acetate	Cyclohexene
1, 1-Dimethoxymethane	Cyclooctane
1, 2-Bis(2-chloroethoxy) ethane	Cyclopropyl methyl ether
1, 2-Dibenzyloxyethane	Decahydronaphtalene

1, 2-Dichloroethyl ethyl ether	Di(1-propynyl) ether [f]
1, 2-Diethoxyethane	Di(2-propynyl) ether
1, 2-Epoxy-3-isopropoxypropane	Diacetylene
1, 2-Epoxy-3-phenoxypropane	Diallyl ether
1, 3-Dioxepne	Dicyclopentadiene
1, 5-p-Methadiene	Diethoxymethane
1, 3 Butadiyne	Diethyl acetal isoamyl benzyl ether
1, 3, 3-Trimethoxypropene	Diethyl ether
1-Ethoxynaphthalene	Diethyl ethoxymethylene malonate
1-Ethyoxy-2-propyne	Diethyl fumarated
1-Phenylethanol	Diethylene glycoldimethyl ether
2, 2-Diethoxypropane	Diethylketene [f]
2, 4-Dichlorophenetole	Dimethoxymethane
2, 4 Dinitrophenetole	Dimethylketene [f]
2, 5 Hexadiyn-1-ol	Di-n-propoxymethane
2-Bromomethyl ethyl ether	Dioxanes
2-Butane	Ethoxyacetophenone
2-Chlorobutadiene	Ethyl §-ethoxypropionate
2-Cyclohexen-1-ol	Ethyl Vinyl Ether
2-Ethoxyethyl acetate	Ethylene glycol dimethyl ether (glyme)
2-Ethylacrylaldehyde oxime	Furan p-Phenylphenetone
2-Ethylbutanol	Isoamyl benzyl ether
2-Ethylhexanal	Isoamyl ether
2-Hexanol	Isobutyl vinyl ether
2-Methoxy ethanol	Isopropy 1, 2, 4, 5 trichlorophenoxyacetate
2-Methoxyethyl vinyl ether	1, 1, 2, 3 –Tetrachloro-1, 3-butadiene
2-Methyltetrahydrofuran	Limonene
2-Penten-1-ol	Isophorone
2-Phenylethanol	m, o, p-Diethoxybenzene
2-Propanol	Methoxy-1, 3, 5, 7-cyclooctateraene
3-Ethoxy-o-propionitrile	Methyl isobutyl ketone
3, 3-Dimethyoxypropene	Methyl p-(n-amyloxy) benzoate
3-Bromopropyl phenyl ether	Methyl-1-butanol
3-Isoproposypropiontrile d	Methylacetylene
3-Methoxy ethyl acetate	Methylcyclopentane
3-Methoxy-1-butyl acetate	m-Nitrophenetole 1-Octene
4-Heptanol	n-Amyl ether
4, 5-Hexadien-2-yn-1-ol	n-Butyl phenyl ether

4-Methyl-2-pentanol	n-Butyl vinyl ether
4-Methyl-2-pentanone	n-Hexyl ether
4-Penten-1-ol	n-Methylphenetole
4-Vinyl Cyclohexene	n-Propylisopropyl ether
Acetal	o, p-Ethoxyphenyl isocyanate
Acetaldehyde	o,p-Iodophenetole
Acrolein	o-Bromophenetole
Allyl ether	o-Chlorophenetole
Allyl ethyl ether	Other Secondary Alcohols
Allyl phenyl ether	Oxy bis (2 ethyl acetate)
a-Phenoxypropionitrile chloride	Oxy bis (2-ethyl benzoate)
B,B Oxdipropionitrile	p-(n-Amyloxy)benzoyl chloride
Benzyl 1-naphthyl ether	p-Bromophenetole
Benzyl alcohol	p-Chlorophenetole
Benzyl ether	p-Dibenzyloxybenzene
Benzyl ethyl ether	p-Di-n-butoxybenzene
Benzyl methyl ether	Perchloric Acid
Benzyl n-butyl ether	Phenoxy acetyl chloride
Bis(2-chloroethyl) ether	Phenyl o-propyl ether
Bis(2-ethoxyethyl) ether	p-Phenylphenetone
Bis(2-ethoxyethyl) phthalate	Sodium 8, 11, 14 elcosate traenoate
Bis(2-methoxyethyl) adipate	Sodium ethoxyacetylide
Bis(2-methoxyehtyl) carbonate	Tert-Butyl ethyl ether
Bis(2-methoxyethyl) ether	Tert-Butyl methyl ether
Bis(2-methoxyethyl phthalate	Tetrahydrofuran (THF)
Bis(2-methoxymethyl) adipate	Tetrahydronaphthalene
Bis(2-n-butoxyethyl) phthalate	Tetrahydropyran
Bis(2-phenoxyethyl) ether	Triethylene glycol diacetate
Bis(4-chlorobutyl) ether	Trithylene glycol dipropionate
Bis(chloromethyl) ether [c]	Vinyl ethers
Bis[2-(methoxyethoxy)ethyl] ether	Vinylene carbonate
B-methoxypropionitrile	Vinylidene chloride

Key:

a. When stored as a liquid monomer
b. Although these chemicals form peroxides, no explosion involving these monomers have been reported.
c. When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.
e. OSHA regulated carcinogen.
f. Extremely reactive and unstable compounds.

APPENDIX B

CAUTION

PEROXIDE FORMING CHEMICAL

Date Received: _____ Date Opened: _____ Date Expired: _____	INHIBITOR ADDED Y___ N___ Type _____

Limited shelf life. Store tightly closed away from light and heat.

Test Date_____ Peroxide _____ Tester Initials _____
Test Date_____ Peroxide _____ Tester Initials _____
Test Date_____ Peroxide _____ Tester Initials _____