Standard Operating Procedure for Handling Storage and Disposal for Time Sensitive Chemicals

1.0 PURPOSE & SCOPE

1.1. This procedure describes methods for safely using, storing, and disposingof time sensitive chemicals (TSMs). This procedure applies to all University of Notre Dame personnel whose work involves TSMs.

2.0 RESPONSIBILITIES

2.1. Principal Investigator (PI)

2.1.1. PIs shall ensure this procedure is implemented in their work areas and labs.

2.1.2. PIs shall ensure lab personnel are adhering to the requirements of this procedure.

2.1.3. PIs shall immediately notify Risk Management and Safety (RMS) when a TSM container is expired, has crystallization, or suspected to be shock sensitive, potentially explosive, or potentially self-igniting.

2.2. Lab Personnel

2.2.1. Lab personnel shall adhere to the requirements of this procedure.

2.3. Department

2.3.1. Departments shall ensure PIs are adhering to this procedure.

2.3.2. Departments shall take action according to the Laboratory Integrated Safety Plan procedure when PIs are not adhering to the requirements of this procedure.

2.4. Risk Management & Safety (RMS)

2.4.1. RMS shall ensure proper disposal of the expired or no longer needed time sensitive chemicals.

2.4.2. RMS or designee shall manage the stabilization of suspect time sensitive chemicals which are considered high hazard due to an increased risk to create an explosion or fire hazard.

3.0 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!!
    - 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 (574-631-5037).

4.0 HAZARD DESCRIPTION

4.1. Time Sensitive Chemicals are any chemical or chemical product that develops additional hazards upon prolonged storage.
  4.1.1. Examples of these chemicals include peroxidizables, polynitrated aromatics, chloroform and anhydrous hydrofluoric acid (HF).
  4.1.2. 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.

5.0 CONTROLS

5.1. TSMs 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.

5.3. All time sensitive material containers (including stills) shall be labeled with
  5.3.1. the date the time sensitive material was received,
  5.3.2. the date the container was opened,
  5.3.3. the date the material was transferred to a secondary container, and
  5.3.4. if peroxide strip tested, the date(s) the material was strip tested.

5.4. Peroxides Detection Levels and Guidance

5.4.1. The following peroxide levels should be used to determine activities that are deemed safe.

- 0 – 25 ppm: material is safe to use or distill.
- 25 – 50 ppm: material is safe to use, but cannot be distilled or concentrated.
- Above 50 ppm: Material must be disposed immediately through RMS.

6.0 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.

6.1.1. This includes visible dates on stills with time sensitive materials.

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:

- 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 buildup of pressure in the regulator of the cylinder.

7.0 PEROXIDIZABLES

7.1. Materials listed in Appendix A, Section 1 table should be dated, tested before use and disposed of within 24 hours of opening if uninhibited or within 12 months of opening or receipt if inhibited.

7.2. Materials listed in Appendix A, Section 2 should be dated, tested before use and disposed of within three months of opening or receipt.

7.3. Materials listed in Appendix A, Section 3 should be dated, tested and disposed of within twelve months of opening or receipt, unless regular peroxide testing (every 6 months before expiration and every month after expiration) shows peroxide formation under 50 ppm. This testing must be documented and dated on the bottle.

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 to purchase material 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 that has expired. Do not touch or move the chemical 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.

8.0 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 RMS at 574-631-5037.

8.5. Picric Acid should be monitored for water content every three months and disposed of as hazardous waste within two years of receipt.

9.0 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. If possible, chloroform that is stabilized with alcohol should be purchased.

9.4. 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.

10.0 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 shelflife 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 at 574-631-5037.

11.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

11.1. Refer to the Chemical Hygiene Plan Section 8 for PPE requirements.

12.0 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. Do not move the affected bottle or any chemicals surrounding the bottle. Refer to the RMS Hazardous Waste website.

13.0 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.

13.4. TSMs shall be dated on the label with the date tested as well as the test results for each test. These can also be recorded on the RMS form and attached to the bottle (see Appendix B).

14.0 FREQUENCY OF REVIEW

14.1. RMS shall review SOP on a biennial basis.

14.2. Review date shall be added to SOP upon review.

15.0 REVISION HISTORY TABLE

History	Effective Date
Reviewed Formatting changes (spacing, added bullet point, section 6.2.2)	8/26/16
• Add section 6.1.1 to include visible dating of stills; • Reference to CHP for PPE • Typo corrections	8/30/17
• Reorganized information to improve finding information. • Reformatted the appendix tables to better fit the procedure.	3/13/20

• Added PI and Department responsibilities sections.	
• Added labeling requirements and peroxide level detection guidance information in the controls section (5.0)	8/15/2022
• Updated peroxide disposal to allow for testing for Appendix A section 3 chemicals. • Fixed typos. • Added more information on the frequency of peroxide testing and the documentation of said testing.	3/25/2024

APPENDIX A: List of Common Peroxide-Forming Chemicals

1. Chemicals that may autopolymerize as a result of peroxide accumulation. Uninhibited chemicals must be disposed of within 24 hours of being opened. Inhibited chemicals must be disposed of within 12 months of being opened:

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

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, unless regular peroxide testing (every 6 months before expiration and every 1 month after expiration) show peroxide formation below 50 ppm. This testing must be documented on the bottle:

(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, 5trichlorophenoxyacetate
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 to superscripts in the above tables:

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.
d. When stored as a gas, these chemicals may auto- polymerize because of peroxide accumulation.
e. OSHA regulated carcinogen.
f. Extremely reactive and unstable compounds.

APPENDIX B: Peroxide Forming Chemical Label

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 _____	