SAFE WORK PROCEDURE	Insert Reference Code: **UBC-RMS-OHS-SWP-17-003**
Department of Risk Management Services www.rms.ubc.ca	Effective date: November 27, 2017 Review date: NA Supersedes: NA

Working Safely with Peroxide Forming Compounds

1. SCOPE

All UBC employees working with and/or handling peroxide forming compounds should follow this safe work procedure. It describes methods to detect peroxides and to safely handle, use, and store peroxidizable compounds. It also describes how to remove peroxide contamination from chemicals.

2. PURPOSE

Peroxides are chemical substances that contain the reactive peroxo unit (O22-, or R-O-O-R). Several different organic chemicals are capable of forming peroxides. Peroxide formation in solvents and reagents has caused many laboratory accidents.

WorkSafe BC regulates peroxide-forming compounds. Section 30.23 of WorkSafe BC Regulations requires the testing of peroxide-forming compounds regularly after the container was first opened. The record of the tests must be kept for as long the compound is stored. Compounds contaminated with peroxide materials must be disposed of using safe work procedures or must be treated chemically to eliminate the peroxides.

3. RESPONSIBILITY

Supervisors and workers must:

- Keep an inventory of all peroxidizable compounds
- Label all compounds known to form peroxides (see Appendix B for example of label)
- Test peroxidizable compounds periodically
- Purchase, store, and use the minimum quantity of peroxidizable substances necessary
- Document and follow the appropriate safe work procedure.

4. TRAINING REQUIRED

All employees working with peroxide forming compounds should have completed the Chemical Safety Course offered by Risk Management Services.

5. HAZARD

Ethers are ubiquitous peroxide formers but many other types of compounds also produce dangerous levels of peroxides. Peroxide inhibitors are sometimes added to such compounds, but these may not be sufficient to control peroxide formation once the container has been opened.

The more volatile the peroxidizable compound, the easier it is to concentrate the peroxides. Pure compounds are more subject to peroxide accumulation because impurities can inhibit peroxide formation or catalyze their slow decomposition.

There are four classes of peroxide forming chemicals based upon the peroxide formation hazard:

- Class A – severe peroxide hazard
- Class B – concentration hazard
- Class C – shock and heat sensitive
- Class D – potential peroxide-forming chemicals

Appendix A lists common chemicals belonging to each of the four classes.

The following are general guidelines concerning the degree of hazard associated with peroxide contamination (of ether solvents) at the levels indicated.

Peroxide concentration in ether	Guidelines for use of ether
< 3 ppm	Reasonably safe for most laboratory procedures involving moderate quantities.
3 - 30 ppm	Moderate hazard depending on type of use. Avoid concentration of peroxides. Disposal recommended if ether is not used immediately.
> 30 ppm	Unacceptable; may pose a serious hazard. Dispose of ether or remove peroxides using a suitable procedure.

If the containers show any evidence of crystal formation in solution or around the cap, or of oil formation, treat as extremely hazardous and do not handle. Treat the container as a bomb!

6. TESTING FOR PEROXIDES

Do not test peroxidizable chemicals in old containers!
Contact Risk Management Services at 604 822 2029

The testing schedule depends on the peroxide class according to the schedule below:

	Class A	Class B	Class C	Class D
Date opened	3 months	6 months	6 months	1 year

All peroxide forming chemicals, which are to be distilled, must be tested prior to distillation regardless of age.

Peroxide test strips

Peroxide test strips detect inorganic and organic compounds that contain peroxides or hyperperoxides. Test strips are suitable for the routine testing of peroxides formed from simple ethers such as diethyl ether, tetrahydrofuran, and *p*-dioxane.

Test strips are available from several suppliers. Before purchasing, consider their sensitivity and shelf life. Follow the manufacturer's instructions when using these strips.

Iodide test

To 1 mL of the ether to be tested, add a solution of 100 mg of potassium iodide in 1 mL of glacial acetic acid. A pale yellow colour indicates a low concentration (0.001 to 0.0005 %) of peroxides, and a bright yellow or brown colour indicates a high (> 0.1%) and hazardous concentration of peroxides. This chemical test is more sensitive than the test strips, as it will detect di-alkyl peroxides as well as hydroperoxides.

Remember that these tests are valid only for relatively simple chemicals. Complicated organic structures may also act as oxidizing agents and therefore appear to give positive tests for peroxides. There are no testing methods for peroxides of potassium metal.

7. GUIDELINES FOR SAFE WORK PRACTICES

7.1. Storage

- Peroxides tend to form in materials as a function of age and exposure to oxygen; each container of peroxidizable chemical must have the following dates written on label:
  - Date received
  - Date first opened
  - Date to be discarded
- Testing dates should be noted on the label; an example of a label is shown in Appendix B
- Peroxide forming chemicals should be stored in the original manufacturer container whenever possible
- Peroxidizable chemicals should be stored in sealed, air-impermeable containers and should be kept away from light; a dark amber glass bottle with a tight fitting cap is generally appropriate
- If refrigeration is needed, use only refrigerators designated "explosion-proof"

7.2. Management and Disposal of Containers

- Older containers of peroxidizable chemicals, or containers of unknown age of history, must be handled very carefully and should never be opened by researchers
- Any peroxidizable chemical with visible discoloration, cloudiness, crystallization, wisp-like structures, or oily layer should be treated as potentially explosive

- If any of these conditions are observed on a peroxidizable chemical, or if the origin and age of the container are unknown, do not attempt to move or open the container – contact Risk Management Services (604 822 2029)
- Empty containers of ethers and other peroxide-formers must be triple-rinsed with water before discarding

7.3. Removal of Peroxides – *Test the peroxide content after the procedure.*

Activated Alumina Method

Peroxides can be conveniently removed by passing the solvent through a short column of activated alumina. This method is effective for both water-insoluble and water-soluble solvents (except low molecular weight alcohols). Since this method does not destroy peroxides, the alumina should be flushed with a dilute acid solution of potassium iodide or ferrous sulfate following treatment to remove peroxides.

The amount of alumina required depends on the quantity of peroxide. As a start, a column containing 100 g of alumina should be used for 100 mL of solvent. More alumina or passage through a second column may be required to eliminate peroxides.

Ferrous Salt Method

Peroxide impurities in water-soluble solvents are easily removed by shaking with a concentrated solution of ferrous salt. A frequently used ferrous salt solution can be prepared either from 60 gm of ferrous sulfate + 6 mL concentrated sulfuric acid + 100 mL of water, or from 100 gm of ferrous sulfate + 42 mL concentrated hydrochloric acid + 85 mL of water. The peroxide former is washed two to three times with an equal volume of the reagent. Drying over sodium or magnesium sulfate can be used to remove dissolved water. Shaking should be very gentle for the first extraction.

7.4. Distillation & Evaporation of Peroxide Forming Chemicals

- Peroxide forming materials must be tested prior to use in a distillation, and must be peroxide free
- In addition to wearing the standard personal protective equipment (lab coat, loose fitted pants, liquid resistant fully enclosed shoes) safety glasses should be worn at all times
- Distillations will always be done inside a fume hood; the sash of the fume hood should be lowered completely when access inside the fume hood is not necessary
- Evaporation (e.g. in a rotary evaporator) concentrates the peroxides therefore posing an additional hazard
- When the volume is small and the evaporation is carried out near room temperature, ethers that were found safe for use at last testing, can be safely evaporated

- When high volumes and/or high temperatures are used, the ether must be tested and found peroxide free prior to evaporation

7.5. Chromatography

- Peroxides formers with moderate levels of peroxides are suitable for a variety of forms of chromatography, provided that the ether is not going to be subsequently evaporated
- Peroxides bind to alumina and to some other adsorbents; this may concentrate peroxides at the top of a column, resulting in a hazard if the column is not washed with a suitable solvent and is then allowed to dry out

8. REVIEW AND RETENTION

This SWP is reviewed annually or whenever deemed necessary by the responsible Risk Management Services representative.

9. DOCUMENT INFORMATION

Written / Reviewed by:	RMS Advisor, Chemical Safety
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APPENDIX A

Class A – Severe Peroxide Hazard: spontaneously decompose and become explosive with exposure to air without concentration.

Butadiene (liquid monomer)	Isopropyl ether	Sodium amide (sodamide)
Chloroprene (liquid monomer)	Potassium amide	Tetrafluoroethylene (liquid monomer)
Divinyl acetylene	Potassium metal	Vinylidene chloride

Class B – Concentration Hazard: require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

Acetal	Diethylene glycol dimethyl ether (diglyme)	4-Methyl-2-pentanol
Acetaldehyde	Diethyl ether	2-Pentanol (isopropyl alcohol)
Benzyl alcohol	Dioxanes	4-Penten-1-ol
2-Butanol	Ethylene glycol dimethyl ether (glyme)	1-Phenylethanol
Cumene	uran	2-Phenylethanol
Cyclohexanol	Heptanol	2-Propanol
Cyclohexene	2-Hexanol	Tetrahydrofuran
2-Cyclohexen-1-ol	Methylacetylene	Tetrahydronaphthalene
Decahydronaphthalene	3-Methyl-1-butanol	Vinyl ethers
Diacetylene	Methylcyclopentane	Other secondary alcohols
Dicyclopentadiene	Methyl isobutyl ketone	

Class C – Shock and Heat Sensitive: highly reactive and can auto-polymerize as a result of internal peroxide accumulation. The peroxides formed in these reactions are extremely shock and heat sensitive.

Acrylic acid	Chlorotrifluoroethylene	Vinyl acetate
Acrylonitrile	Methyl methacrylate	Vinylacetylene (gas)
Butadiene (gas)	Styrene Vinylpyridine	Vinyladiene chloride
Chloroprene	Tetrafluoroethylene (gas)	Vinyl chloride (gas)

Class D – Potential Peroxide Forming Chemicals: may form peroxides but cannot be clearly categorized in Class A, B, or C.

Acrolein	p-Chlorophenetole	4,5-Hexadien-2-yn-1-ol
Allyl ether	Cyclooctene	n-Hexyl ether
Allyl ethyl ether	Cyclopropyl methyl ether	o.p-Iodophenetole
Allyl phenyl ether	Diallyl ether	Isoamyl benzyl ether
p-(n-Amyloxy)benzoyl chloride	p-Di-n-butoxybenzene	Isoamyl ether
n-Amyl ether	1,2-Dibenzyloxyethane	Isobutyl vinyl ether
Benzyl n-butyl ether	p-Dibenzyloxybenzene	Isophorone

Benzyl ether	1,2-Dichloroethyl ethyl ether	b-Isopropoxypropionitrile
Benzyl ethyl ether	2,4-Dichlorophenetole	Isopropyl-2,4,5-trichlorophenoxy acetate
Benzyl methyl ether	Diethoxymethane	n-Methylphenetole
Benzyl-1-napthyl ether	2,2-Diethoxypropane	2-Methyltetrahydrofuran
1,2-Bis(2-chloroethoxyl)ethane	Diethyl ethoxymethylenemalonate	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl)ether	Diethyl fumarate	2-Methoxyethanol
Bis(2-(methoxyethoxy)ethyl) ether	Diethyl acetal	3-Methoxyethyl acetate
Bis(2-chloroethyl) ether	Diethylketene	2-Methoxyethyl vinyl ether
Bis(2-ethoxyethyl) adipate	Diethoxybenzene (m-,o-,p-)	Methoxy-1,3,5,7-cyclooctatetraene
Bis(2-methoxyethyl) carbonate	1,2-Diethoxyethane	b-Methoxypropionitrile
Bis(2-methoxyethyl) ether	Dimethoxymethane	m-Nitrophenetole
Bis(2-methoxyethyl) phthalate	1,1-Dimethoxyethane	1-Octene
Bis(2-methoxymethyl) adipate	Di(1-propynl) ether	Oxybis(2-ethyl acetate)
Bis(2-n-butoxyethyl) phthalate	Di(2-propynl) ether	Oxybis(2-ethyl benzoate)
Bis(2-phenoxyethyl) ether	Di-n-propoxymethane	b,b-Oxydipropionitrile
Bis(4-chlorobutyl) ether	1,2-Epoxy-3-isopropoxypropane	1-Pentene
Bis(chloromethyl) ether	1,2-Epoxy-3-phenoxypropane	Phenoxyacetyl chloride
2-Bromomethyl ethyl ether	p-Ethoxyacetophenone	a-Phenoxypropionyl chloride
beta-Bromophenetole	1-(2-Ethoxyethoxy)ethyl acetate	Phenyl-o-propyl ether
o-Bromophenetole	2-Ethoxyethyl acetate	p-Phenylphenetone
p-Bromophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	n-Propyl ether
3-Bromopropyl phenyl ether	1-Ethoxynaphthalene	n-Propyl isopropyl ether
tert-Butyl methyl ether	o,p-Ethoxyphenyl isocyanate	Sodium 8-11-14-eicosatetraenoate
n-Butyl phenyl ether	1-Ethoxy-2-propyne	Sodium ethoxyacetylide
n-Butyl vinyl ether	3-Ethoxypropionitrile	Tetrahydropyran
Chloroacetaldehyde diethylacetal	2-Ethylacrylaldehyde oxime	Triethylene glycol diacetate
2-Chlorobutadiene	2-Ethylbutanol	Triethylene glycol dipropionate
1-(2-Chloroethoxy)-2-phenoxyethane	Ethyl-b-ethoxypropionate	1,3,3-Trimethoxypropene
Chloroethylene	Ethylene glycol monomethyl ether	1,1,2,3-Tetrachloro-1,3-butadiene
Chloromethyl methyl ether	2-Ethylhexanal	4-Vinyl cyclohexene
beta-Chlorophenetole	Ethyl vinyl ether	Vinylene carbonate
o-Chorophenol	2,5-Hexadiyn-1-ol	

References:

National Safety Council: Data Sheet I-655 Rev. 87
NFPA: NFPA 432, Code for the Storage of Organic Peroxide Formulations
Reactive Hazards Reduction, Inc. http://www.rhr-inc.com/
FDNY: 3 RCNY Chapter §10-01 – Chemical Laboratories

APPENDIX B

PEROXIDIZABLE

Purchase date:______________________

Expiry date:_________________________

Open date:_________________________

Test dates: ____________ PPM________

____________ PPM________

____________ PPM________