

## Working Safely with Peroxide Forming Compounds

### 1. OVERVIEW

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.

Peroxides are chemical substances that contain the reactive peroxy unit ( $O_{22^-}$ , 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 ([WSBC:30.23](#)) 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.

### 2. HAZARD

Most Peroxide Forming Chemicals are flammable. However, some of these chemicals might also be characterized by additional hazards (consult the SDS of each specific chemical). Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. Under normal storage conditions the materials listed in this document have the potential to generate and accumulate peroxide crystal formations, which may violently detonate when subjected to thermal or mechanical shock. 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. 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!

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.

### 3. RESPONSIBILITY

Employer - All work must be pre-approved by the Principal Investigator (PI) prior to initial use. PIs are required to provide all PPE and safety training specific to each hazard and method of use.

Employee - Must be aware of the hazards, know the details of this SWP and be fully trained and signed off in the proper use, disposal, and emergency procedures before starting work. All workers must:

- Maintain an inventory of all peroxidizable compounds
- Label all compounds known to form peroxides (see Appendix B for example of label)
- Test peroxidizable compounds as required based on the class (see appendix A)
- Purchase, store, and use only those quantities of peroxide-forming chemicals that you expect to use within expiration and disposal timeframes.

#### 4. TRAINING REQUIRED

Training must include:

- Chemical Safety Course (offered by SRS)
- Documented specific training and demonstrated competence on the techniques and processes to be used.
- Reading and understanding the relevant Safety Data Sheets.

A review of this SWP and re-approval is required when there are any changes to procedures, personnel, equipment, or when an incident or near miss occurs.

#### 5. GUIDELINES FOR SAFE WORK PRACTICES

##### A. 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 formers 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”

##### B. Testing for Peroxides

**Do not test peroxidizable chemicals in old containers!  
Contact UBC Safety and Risk 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, 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 hyper-peroxides. 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. Here are some examples:

[sigmaaldrich.com/peroxide-strips](https://sigmaaldrich.com/peroxide-strips)

[www.mpbio.com/peroxide-test-kit](https://www.mpbio.com/peroxide-test-kit)

[fishersci.ca/peroxide-test-strips](https://fishersci.ca/peroxide-test-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.

**C. 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.

**D. Management and Disposal of Containers**

- Older containers of peroxidizable chemicals, or containers of unknown age or 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 UBC SRS (604 822 2029)
- Empty peroxide-former containers must be triple-rinsed with water before discarding

**6. SAFE WORK PROCEDURE****A. 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, 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

## B. 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 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 then allowed to dry.

## C. Waste Disposal

- 1) All UBC researchers (faculty, staff and students), as users and generators of hazardous waste are personally responsible to ensure that regulatory compliance is met and must follow the general waste disposal guidelines ([Hazardous Waste Management | UBC Safety & Risk Services](#))
- 2) Peroxide forming materials that have been tested, dated and are due for disposal, file a hazardous waste pickup request via the Hazardous Waste Inventory System (HWIS). ([HWIS access portal](#)).
- 3) Management and Disposal of Containers:
  - Older containers of peroxidizable chemicals, or containers of unknown age or 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 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 UBC SRS (604 822 2029)
  - Empty peroxide-former containers must be triple-rinsed with water before discarding

## D. Emergency Procedures

Spill Response – In case of a chemical spill, alert others in the immediate vicinity and follow the SWP ([Flammable Liquid Spill Clean Up](#)). Determine the severity of the spill and proceed as appropriate. Small spills may be cleaned up by trained laboratory personnel. Spills outside of containment, fires, or explosion call 911. If possible to do so safely (without risk of over-exposure), act to stop the release. Ensure that extraneous personnel remain at a safe distance until the spill is completely cleaned-up. For spills >1L evacuate the area and call for assistance.

Personal exposure – In case of contact with skin or eyes, wash the affected area with water for at least 15 minutes. Call UBC first aid (at 604-822-4444) and/or 911. In case of exposure by inhalation, remove the person to fresh air and seek medical attention. Provide the SDS for the material if possible.

Always report spills and/or exposures in UBC Centralized Accident/Incident Reporting System [UBC CAIRS](#).

## 7. DOCUMENT INFORMATION

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## APPENDIX A - Peroxide Forming Chemicals

The following lists of chemicals are not exhaustive. Researchers must consult the SDS and other information sources for the chemicals used in their work areas to determine the potential for peroxide-formation.

**Class A – Severe Peroxide Hazard:** spontaneously decompose and become explosive with exposure to air without concentration. Test for peroxide formation before using; discard within 3 months.

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. Test for peroxide formation before using; discard within 1 year.

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 (diglyme)	1-Phenylethanol
Cumene	Furan	2-Phenylethanol
Cyclohexanol	4-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. Test for peroxide formation before using; discard within 1 year.

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. Test for peroxide formation before using; discard within 2 years.

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-Dibenzoyloxyethane	Isobutyl vinyl ether

Benzyl n-butyl ether	p-Dibenzoyloxybenzene	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-naphthyl ether	2,2-Diethoxypropane	2-Methyltetrahydrofuran
1,2-Bis(2-chloroethoxy)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-propynyl) ether	Oxybis(2-ethyl acetate)
Bis(2-n-butoxyethyl) phthalate	Di(2-propynyl) 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 ethoxyacetylde
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:

1. WorkSafeBC OHS Regulations Part 30.23 Peroxide-forming compounds. Retrieved from: <https://www.worksafebc.com/en/law-policy/occupational-health-safety/searchable-ohsregulation/ohs-regulation/part-30-laboratories>
2. WorkSafeBC Laboratory health and safety handbook. 2008
3. National Safety Council: Data Sheet I-655 Rev. 87
4. NFPA: NFPA 432, Code for the Storage of Organic Peroxide Formulations
5. Reactive Hazards Reduction, Inc. <http://www.rhr-inc.com/>

## APPENDIX B

PEROXIDIZABLE	
Purchase date:	_____
Expiry date:	_____
Open date:	_____
Test dates:	_____ PPM _____
	_____ PPM _____
	_____ PPM _____