

Peroxide-Forming Chemicals Standard Operating Procedure (SOP)

Purpose

Peroxide-forming chemicals (e.g., ethers, THF, dioxanes, isopropanol, styrene) can form unstable organic peroxides when exposed to air, light, or time in storage. The relatively weak oxygen-oxygen bond is the characteristic structure of organic and inorganic peroxide molecules and is the basis for their reactivity and tendency for spontaneous decomposition. These peroxides are highly shock-, friction-, and heat-sensitive and may explode violently, particularly during opening, evaporation, or distillation. All personnel must recognize peroxide hazards and follow this SOP to prevent serious injury or death.

Scope

This SOP applies to all Chemistry Department laboratories using, storing, or disposing of peroxide-forming chemicals. Labs may supplement this SOP with experiment-specific procedures as needed.

Key Hazards

- **Chemical structures:** Certain functional groups contain auto-oxidizable hydrogen atoms and form peroxides readily (Appendix A).
- **Storage conditions:** Peroxidation may be accelerated by exposure to heat, light (especially UV/sunlight), and oxygen or air. Storing chemicals in open, partially empty or transparent containers and at elevated temperatures may promote peroxidation.
- **Concentration by evaporation or distillation:** Peroxides are less volatile than the parent compound, and thus they concentrate as the parent compound evaporates. **Never distill peroxide-formers without testing first.**
- **Inhibitors:** Inhibitors slow but do not eliminate peroxide formation. Inhibitors are depleted as peroxides are formed and degraded.

Peroxide-Former Classification

Peroxide-formers fall into three groups (Appendix B):

- **Group A:** Can form explosive peroxides during normal storage
- **Group B:** Dangerous when concentrated (distillation/evaporation)
- **Group C:** May auto-polymerize due to peroxide initiation

Group determines storage limits and testing frequency (Appendices C–D).

Responsibilities

Principal Investigators/Supervisors must ensure:

- Appropriate training of individuals you supervise
- Proper storage and labeling
- Timely testing and disposal
- Lab-specific SOPs when needed

Individuals Working with Peroxide-Forms must:

- Follow this SOP
- Wear required PPE
- Test as required
- Report concerns immediately

Safety Coordinator:

Provides support, inspection assistance, labels, and coordination with EHS.

EHS

Provides campus-wide training, guidance, and response for high-risk containers.

Before Purchase (Planning Stage)

Before ordering peroxide-formers:

- Review SDS and this SOP
- Check existing inventory first
- Purchase the smallest quantity needed
- Purchase inhibited product when available
- Obtain peroxide test strips (or coordinate with Safety Coordinator)

Receiving & Labeling Requirements

Upon receipt:

- Confirm expiration date and inhibitor status
- Label immediately with:
 - Date received
 - Date opened
 - Assigned expiration date
 - “Peroxide-Forming Compound” warning

Regular check-ins: Assign a lab member to routinely check the receipt, opened, and expiration dates of all peroxide-forming chemicals in your lab.

Storage Requirements

Peroxide-formers must be stored:

- tightly sealed
- away from heat and sunlight
- in amber bottles when possible
- in flammable storage cabinets
- only in flammable-safe refrigerators if cooling is required

Avoid:

- long-term storage past limits (Appendix C)
- partially empty containers kept indefinitely
- returning unused material to stock bottles

Do not store peroxide-formers near freezing conditions (peroxide precipitation hazard).

Safe Use Practices

- Use only in a certified chemical fume hood
- Keep sash low
- Plan experiments carefully for incompatibilities
- Never use metal spatulas with peroxide residues

Do Not Open If Any Warning Signs Are Present:

- crystals around cap
- discoloration
- stratified layers
- solids inside bottle

Treat as potentially explosive and call EHS immediately: (505) 277-2753.

Distillation or Evaporation Controls

Before concentrating peroxide-formers:

- Test for peroxides first
- Never distill if peroxides are present
- Always leave $\geq 10\%$ volume in flask
- Stir with magnetic stirrer or an inert gas bleed
- Do not distill uninhibited Group C chemicals

Special Note: 2-Propanol (Isopropanol / IPA)

IPA is a common but under-recognized Group B peroxide-former.

Key controls:

- Store in flammable cabinet
- Use amber containers when possible
- Test per Appendix D if stored long-term

Testing Requirements

Peroxide levels must remain **below 30 ppm**.

Test:

- Before any distillation/evaporation
- Periodically per Appendix D
- Before use if past safe storage period

Method:

- Use peroxide test strips (see Appendix F)
- Record results on bottle label and in lab records

Action Thresholds:

- **≤30 ppm:** continue storage + testing
- **>30 ppm:** dispose immediately
- **≥100 ppm:** contact EHS immediately for disposal
- **Visible crystals or solids:** do not test — call EHS, 505-277-2753

Disposal Requirements

- Do not mix peroxide waste with other waste streams
- Triple rinse empty containers immediately
- Waste >25% peroxide-former must be tested and documented on waste label
- Containers missing received, opened, or manufacturers' expiration dates must be tested prior to disposal

Emergency Procedures

Plan for possible emergencies involving peroxide-forming chemicals:

- Notify nearby personnel
- For large spills: eliminate ignition sources and evacuate
- Call 911 for emergencies
- Activate fire alarm for fire/explosion
- Consult SDS for cleanup materials before working

If an explosion occurs:

- Activate the fire alarm and leave quickly
- Get under sturdy table if things are falling around you
- Watch for weakened floors and stairways and falling debris
- If you are trapped, signal with phone or tap on pipes or walls. Cover your mouth and nose and try not to shout to avoid inhaling dangerous amounts of dust

Training Requirements

All personnel working with peroxide-formers must complete:

- Peroxide-former training covering:

- hazard recognition
- storage/testing schedules
- emergency response
- location of SOPs/SDSs

Awareness-level training is required for others working nearby.

Inspections & Monitoring

Peroxide storage areas must be reviewed at least twice per year to identify:

- Expired peroxide-formers
- Missing labels/dates
- Overdue testing
- Containers requiring disposal

Recordkeeping

- Labs must maintain testing records for each peroxide-former
- Safety Coordinator and EHS maintain inspection documentation

Appendices

A: Peroxide-Forming Structures

B: Peroxide-Forming Chemicals

C: Safe Storage Periods for Peroxide-Forming Chemicals

D: Quick Guide for Peroxide-Forming Chemicals

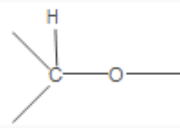
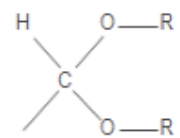
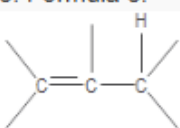
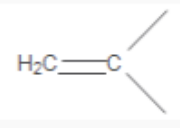
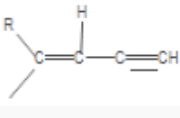
E: Example of Peroxide-Forming Chemicals Label

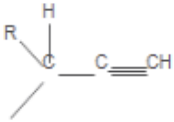
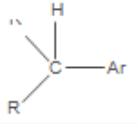
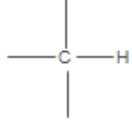

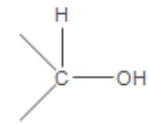
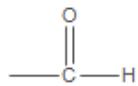
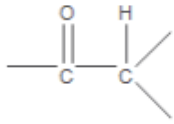
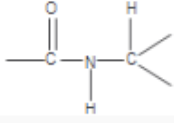
F: Testing Procedure

G: Signature Page

Appendix A: Peroxide-Forming Structures

Organic structures (in approximate order of decreasing hazard)

Formula	Description
1. Formula 1: 	Ethers with alpha hydrogen atoms (Isopropyl ether, ethyl ether, glyme)
2. Formula 2: 	Acetals with alpha hydrogen atoms (acetal, benzylacetal)
3. Formula 3: 	Olefins with allylic hydrogen atoms (butylene, cyclohexene)
4. Formula 4: 	Chloroolefins and fluoroolefins (tetrafluoroethylene)
5. Formula 5: 	Vinyl halides, esters, and ethers (vinylidne chloride, vinyl chloride, vinyl acetate)
6. Formula 6: 	Dienes (butadiene, chloroprene)
7. Formula 7: 	Vinylacetylenes with alpha hydrogen atoms (diacetylene, vinylacetylene)

<p>8. Formula 8:</p> 	Alkylacetylenes with alpha hydrogen atoms (3- methyl-1-butyne)
<p>9. Formula 9:</p> 	Alkylarenes that contain tertiary hydrogen atoms (Isopropyl benzene)
<p>10. Formula 10:</p> 	Alkanes and cycloalkanes that contain tertiary hydrogen atoms (ethylcyclohexane)
<p>11. Formula 11:</p> 	Acrylates and methacrylates, (methyl methacrylate, acrylonitrile)
<p>12. Formula 12:</p> 	Secondary alcohols (sec-butyl alcohol, diphenylmethanol)
<p>13. Formula 13:</p> 	Aldehydes (benzaldehydes)
<p>14. Formula 14:</p> 	Ketones with alpha hydrogen atoms (diisopropyl ketone, MEK)
<p>15. Formula 15:</p> 	Ureas, amides, lactams with hydrogen atom on carbon atom attached to nitrogen (N-ethylacetamide, N- Isopropyl acetamide)

Appendix B: 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.

Group A: Chemicals that form explosive levels of peroxides without concentration

*When stored as a liquid, the peroxide-forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluoroethylene) should then be considered as List A compounds.

Chemical	CAS No.
Divinyl acetylene	821-08-9
Divinyl ether	109-93-3
Isopropyl ether	108-20-3
Potassium amide	17242-52-3
Chemical	CAS No.
Potassium metal	7440-09-7
Sodium amide	7782-92-5
Vinylidene chloride	75-35-4

Group B: Chemicals that form explosive levels of peroxides on concentration

Chemical	CAS No.
1,4-Dioxane	123-91-1
1-Phenylethanol	98-85-1
2-Butanol Dioxanes	
2-Cyclohexen-1-ol	822-67-3
2-Hexanol	626-93-7
2-Pentanol	6032-29-7
2-Phenylethanol	60-12-8
3-Methyl-1-butanol	125-51-3
4-Heptanol	589-55-9

4-Methyl-2-pentanol	108-11-2
4-Penten-1-ol	821-09-0
Acetal	105-57-7
Acetaldehyde	75-07-0
Benzyl alcohol	100-51-6
Chlorofluoroethylene	2317-91-1
Cumene (isopropylbenzene)	98-82-8
Cyclohexene	110-83-8
Cyclopentene	142-29-0
Decahydronaphthalene (decalin)	91-17-8
Diacetylene (butadiyne)	460-12-8
Dicyclopentadiene	77-73-6
Diethylene glycol dimethyl ether (diglyme)	111-96-6
Ethyl ether (Diethyl ether)	60-29-7
Ethylene glycol dimethyl ether (glyme)	110-71-4
Ethylene glycol ether acetates (cellosolves)	
Furan	110-00-9
Methyl acetylene	74-99-7
Methyl isobutyl ketone	108-10-1
Methylcyclopentane	96-37-7
Other secondary alcohols	
t-Butyl alcohol	75-65-0
Tetrahydrofuran	109-99-9
Tetrahydronaphthalene	119-64-2
Vinyl ethers	

Group C: Chemicals that may auto-polymerize as a result of peroxide accumulation

Chemical	CAS No.
9,10-Dihydroanthracene	613-31-0
Acrylic acid	79-10-7
Acrylonitrile	107-13-1
Butadiene*	106-99-0
Chlorobutadiene (chloroprene)*	126-99-8
Chlorotrifluoroethylene	79-38-9
Indene	95-13-6
Methyl methacrylate	80-62-6
Styrene	100-42-5
Tetrafluoroethylene*	116-14-3
Vinyl acetate	108-05-4
Vinyl acetylene	89-97-4
Vinyl chloride	75-01-4
Vinyl pyridine	

Appendix C: Safe Storage Periods for Peroxide-Forming Chemicals

Peroxide-forming chemical	Safe storage period
Unopened chemicals from manufacturer	Up to 12 months or manufacturer's expiration date whichever comes first
Opened containers: Chemicals in Group A	3 months or manufacturer's expiration date whichever comes first
Opened containers: Chemicals in Group B	12 months or manufacturer's expiration date whichever comes first
Opened uninhibited chemicals in Group C	24 hours
Opened inhibited chemicals in Group C	12 months* or manufacturer's expiration date whichever comes first

*Do not store under inert atmosphere, oxygen required for inhibitor to function.

Appendix D: Quick Guide for Peroxide-Forming Chemicals

Quick Rules:

1. Identify the peroxide group (A, B, or C) before use.
2. Purchase only what you need and choose inhibited if available (unless incompatible with your experiment).
3. Label immediately with date received, date opened, and expiration date. Use labels from the Safety Coordinator.
4. Use or dispose of chemical by safe storage deadline.
5. Store properly: tightly closed, away from heat and sunlight, in amber bottles, in flammable cabinets.
6. Test peroxide on schedule (see table below). Always before distillation or evaporation.
7. Record testing results directly on the bottle label.

STOP!
DO NOT OPEN OR MOVE

- Crystals / Particles
- Cap Residue
- Discoloration / Layers

Contact EHS: (505) 277-2753

Disposal Safely

- ✓ Dispose if peroxide levels are >30 ppm
- ✓ If peroxide levels are ≥ 100 ppm, contact EHS
- ✓ Indicate peroxide concentration on the waste label

When in doubt – Stop & Ask!
Safety Coordinator or EHS

Safe Storage Periods & Testing Frequency

Group	A	B	C
Peroxide formation	Can form explosive peroxide levels during normal storage (even unopened)	Typically hazardous only when concentrated (distillation/evaporation)	Can auto-polymerize as a result of peroxide formation
Safe Storage Period			
Open & Uninhibited	3 months	12 months	24 hours
Open & Inhibited	12 months	12 months	12 months
Unopen	12 months	12 months	12 months
Testing Frequency			
Within Safe Storage Period	Every 3 months	Every 6 months	Every 6 months
After Safe Storage Period	Dispose (no extended storage allowed)	Uninhibited – every 3 months + before each use Inhibited – every 6 months + before each use	Uninhibited – Dispose (no extended storage allowed) Inhibited – every 6 months and before each use

*For isopropanol that is stored in dark and closed container, test every 12 months.

Appendix E: Peroxide-Forming Chemicals Label

Peroxide Forming Compound

Date Received: _____ Inhibitor Added: YES NO

Date Opened: _____ Peroxide Group: A B C D

Expiration Date: _____

Testing Frequency (months): 3 6 12 Before use

Test Date: _____	PPM: _____	Tester: _____
Test Date: _____	PPM: _____	Tester: _____
Test Date: _____	PPM: _____	Tester: _____

Dispose when approaching 30ppm.

Contact EHS if >30ppm.

Contact Safety Coordinator for labels.

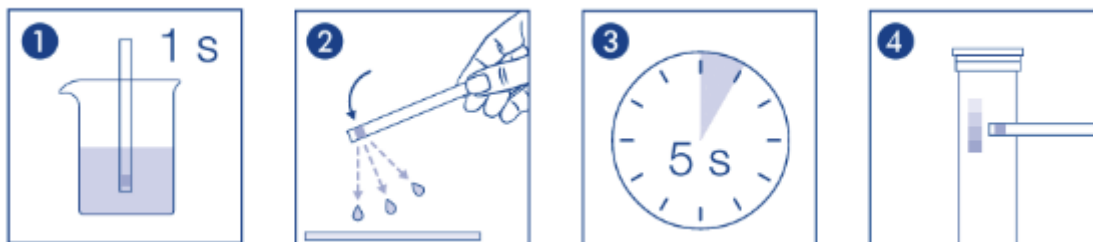
Appendix F: Testing Procedure

QUANTOFIX® Peroxide 100 test strips are used by EHS's hazardous waste vendor. To be as consistent as possible, we use the same brand of test strips in our department.

Instructions for use: Remove only as many test strips as are required. Close the container immediately after removing a strip. Do not touch the test fields.

1. Dip the test strip into the test solution for 1 second.
2. Shake off excess liquid.
3. Wait 5 seconds. (When detecting hydroperoxides in organic solvents, moisten the test field with 1 drop of water after evaporation / drying of the solvent.)
4. Compare test field with the color scale. If hydrogen peroxide is present, the test field turns blue. Take the value which matches closest with the colored test field.

***Color changes after 1 minute do not represent a positive reaction.**



Interferences: If the sample solution has a pH value of 2 – 9, the reaction will take place without interferences. Strong acid solutions must be buffered with sodium acetate, and alkaline solutions with citric acid to a pH of 5 – 7. The presence of other strong oxidants will also lead to false positive results. The following ions interfere with the determination only when the concentrations below are exceeded: 3 mg/L: free chlorine (hypochlorite) 4 mg/L: bromine (Br₂)

Disposal: Used test strips can be placed in the normal household waste.

