



Peroxide Forming Chemicals (PFCs)



Examples: Tetrahydrofuran, Diethyl ether, Isopropyl ether, Acetaldehyde, Styrene
 For more PFCs, see Appendix

Areas with blue text indicate that information must be provided or modified by researcher prior to the SOP approval.

This SOP is not a substitute for hands-on training.

Print a copy and insert into your laboratory SOP binder.

Department:	Chemistry
Date SOP was written:	Monday, October 24, 2016
Date SOP was approved by PI/lab supervisor:	
Principal Investigator:	Name: R. Sarpong Signature: _____
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Location(s) covered by this SOP:	Latimer Hall 831,832,834,836,837,838,839,842,844,847,849

1. Purpose

This SOP covers the precautions and safe handling procedures for the use of Peroxide Forming Chemicals (PFCs).

For a list PFCs covered by this SOP and their use(s), see the "List of Chemicals". Procedures described in Section 12 apply to all materials covered in this SOP.

If you have questions concerning the applicability of any recommendation or requirement listed in this procedure, contact the Principal Investigator/Laboratory Supervisor or the campus Chemical Hygiene Officer at ucbcho@berkeley.edu

2. Physical & Chemical Properties / Definition of Chemical Group

Peroxide forming chemicals are usually flammable, and all may form explosive peroxides.



A wide variety of organic compounds spontaneously form peroxides by a free radical reaction of the hydrocarbon with molecular oxygen. Under normal storage conditions, formed peroxides can accumulate in the chemical container and may explode when subjected to heat, light, friction or mechanical shock.

Organic functional groups likely to form peroxides include:

- Ethers and acetals
- Alkenes and allylic hydrogen
- Chloroalkenes and fluoroalkenes
- Vinyl halides, esters, ethers
- Dienes
- Vinylalkynes with α hydrogen
- Alkylalkynes with α hydrogen
- Alkylarenes with tertiary α hydrogen
- Alkanes and cycloalkanes with tertiary hydrogen
- Acrylates and methacrylates
- Secondary alcohols
- Ketones with α hydrogen
- Aldehydes
- Ureas, amides, and lactams with α hydrogen on a carbon attached to nitrogen

3. Potential Hazards/Toxicity

PFCs are chemicals that when exposed to air may produce unstable and dangerous hydroperoxide and peroxides products over time.

PFCs may also have other hazardous properties including toxicity. Safe use requires assessing all potential hazards.

It is the Principal Investigator's responsibility to ensure activity-specific laboratory procedures and/or processes are taken into account when using this Chemical Class SOP.

Please, review the SDS of any chemical before use (see Section 11 – SDS Location).

4. Engineering Controls

Lab-specific information on engineering controls may be included in the Protocol/Procedure section.

The following is the set of engineering controls required when handling PFCs:

- Work with PFC – the work must be conducted in a fume hood unless other controls are designated in the lab-specific Protocol/Procedure section. Sash height must be kept as low as possible to avoid escaping fumes and provide a physical barrier.
- Laboratories and rooms where PFCs are used must have general room ventilation that is negative pressure with respect to the corridors and external environment. The laboratory/room door must be kept closed at all times.

5 Personal Protective Equipment

At a minimum, the following PPE must be worn at all times.



Eye and Face Protection

- A. ANSI Z87.1-compliant safety glasses with side shields, or chemical splash goggles.
 - Ordinary prescription glasses will NOT provide adequate protection unless they also meet ANSI standard and have compliant side shields.
- B. If the potential for explosion/splashing exists, and adequate coverage is not provided by the hood sash, a face shield must be worn.

Skin and Body Protection

1. Gloves are required when handling hazardous chemicals.
 - Refer to specific chemical SDS for information on glove selection.
 - For additional information on glove selection, go to:
<http://ehs.berkeley.edu/hs/63-laboratory-safety/94-glove-selection-and-usage.html>
2. Lab coats are required when handling hazardous chemicals in the lab. Select the type of lab coat according to the hazards at the specific workplace.
3. Long pants, closed-toe/closed-heel shoes, covered legs, and ankles.

Respiratory Protection

Respiratory protection is normally not required for UC Berkeley laboratory activities. Any lab personnel considering the use of a respirator (e.g. N-95 respirator, dust mask) must contact EH&S for a workplace assessment.

6. First Aid Procedures and Medical Emergencies

In the event of an injury, notify your supervisor immediately and EH&S within 8 hours.



Go to the Occupational Health Facility (Tang Health Center, on campus); if after hours, go to the nearest emergency room (Alta Bates, 2450 Ashby Ave in Berkeley); or



Call 911 (from a cell phone: 510-642-3333) if:

- ***it is a life threatening emergency; or***
- ***you are not confident in your ability to fully assess the conditions of the environment and/or the condition of the contaminated/injured person, or you cannot be assured of your own safety; or***
- ***the contaminated/injured person is not breathing or is unconscious.***

Please remember to provide a copy of the appropriate manufacturer SDS (if available) to the emergency responders or physician. At a minimum, be ready to provide the identity/name of any hazardous materials involved.

In case of skin contact

If skin contact occurs, and/or skin or clothing are on fire, immediately drench in the safety shower with copious amounts of water for no less than 15 minutes to remove any remaining contaminants. If possible to do so without further injury, remove any remaining jewelry or clothing.

In case of eye contact

Rinse thoroughly with plenty of water using an eyewash station for at least 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible.

If swallowed



Do NOT induce vomiting unless directed otherwise by the SDS. Never give anything by mouth to an unconscious person. Rinse mouth with water.

If inhaled

Move into fresh air.

Needle stick/puncture exposure

Wash the affected area with antiseptic soap and warm water for 15 minutes.

7. Special Handling, Storage, Testing and Disposal Requirements

Lab-specific information on handling and storage may be included in Section 12-Protocol/Procedure.

Precautions for Safe Handling:

- **Label each container with the Date Received, Date Opened and Date Last Tested.**
- Test chemicals for peroxide before any distillation or purification of PFCs.
- Do not allow to evaporate to near dryness unless absence of peroxides has been shown. When possible, add a non-volatile organic compound (such as mineral oil) to dilute any peroxides remaining after distillation.
- Use extreme caution before concentrating or purifying PFCs as most explosions occur during these processes.
- PFCs must be stored in their original manufacturer’s container whenever possible. This is very important in the case of diethyl ether because the iron in the steel shipping containers acts as a peroxide inhibitor. PFCs must be stored in sealed, air-impermeable containers and must be kept away from light (light can initiate peroxide formation). Dark amber glass with a tight fitting cap is appropriate.
- Keep away from sources of ignition – Open flames (e.g., Bunsen burner). In particular, take measures to prevent the build-up of heat or electrostatic charge.
- Eliminate or substitute for a less hazardous material when possible.
- Design your experiment to use the least amount of material possible to achieve the desired result.
- Do not exceed the scale of procedures specified in Protocol/Procedure section without approval of the PI.
- Verify your experimental set-up and procedure prior to use.
- Know the location of the nearest eyewash, safety shower and fire extinguisher before beginning work.
- Upon leaving the work area, remove any personal protective equipment worn and wash hands.
- At the end of each project, thoroughly decontaminate the work area according to the material being handled.

Conditions for Safe Storage and Shelf Life

- Peroxides tend to form in materials slowly over several months to years. Therefore, it is imperative that researchers are aware of the age of their PFCs.
- PFCs must be stored in their original manufacturer’s container whenever possible. Minimize peroxide formation in ethers and other PFC by storing in tightly sealed containers in a cool place in the absence of light.



- Some PFCs must be kept under inert atmosphere, but others that contain inhibitors require oxygen to function. Refer to manufacturer’s recommendation for proper storage of those materials.
- Each container of a PFC, upon **arrival** in the laboratory, must be dated. It must also be dated when **opened** for the first time. Special labels, provided by EH&S and attached to the container, are used to record these dates, as shown below. Additionally, dates of **testing** must be added to the label.

Warning: May Form Explosive Peroxides Store in tightly closed original container. Avoid exposure to light, air and heat. If crystals, discoloration or layering is visible, do not move or open; contact EHS&S immediately. Check for peroxides each time before distilling or concentrating.		
Date Received	Date Opened	
Test or Dispose _____ months after receipt, or _____ months after opening		
Test date	Peroxides	ppm
Test date	Peroxides	ppm
Do not use chemical if >100 PPM peroxides are detected.		

Visual Inspection

Visually inspect all PFCs before any operation.

For liquids: Evidence of possible peroxide formation in liquids includes:

- Solids or crystals are observed in either the liquid
- Solids or crystals are observed around the cap of PFCs
- Visible discoloration
- Liquid stratification

Diethyl ether is commonly sold in steel containers which prevents visual inspection of the liquid. Therefore, diethyl ether containers whose age and use history are unknown must be assumed to contain dangerous levels of peroxides and must not be disturbed.

For solids: Evidence of possible peroxide formation in solids (potassium metal, potassium amide, and sodium amide) includes:

- Formation of a surface crust (for example, potassium metal forms a yellow or orange superoxide at the surface)
- Discoloration of the solid

Evaluation of alkali metals and their amides is based on visual criteria only. These substances react strongly with water, and the SOP for handling water reactive materials (WR) must be followed for these chemicals, as well as the precautions described in this SOP.

Only chemicals that pass visual inspection must be tested.

Testing for Peroxides



- Researchers must never test containers of unknown age or origin. Older containers are far more likely to have concentrated peroxides or peroxide crystallization in the cap threads and therefore can present a serious hazard when opened for testing.
- Never try to force open a rusted or stuck cap on a container of a PFC.
- All PFCs which are to be distilled must be tested prior to distillation regardless of age.

The most convenient test method is the use of peroxide test strips manufactured by Aldrich and several other suppliers; they may be obtained from EH&S. Strips that offer a 1-100 ppm peroxide range are useful for determining if the material is below the control point of 100 PPM. Other testing methods are available. Contact EH&S at 642-3073 for more information.

Disposal

- A PFC must be disposed of by the end of the expiration date, or tested for peroxide content.
- Assume that containers that exhibit any unusual visual characteristics contain dangerous levels of peroxides and do not disturb the container. Notify EH&S, who will assist in the further evaluation. If there is any doubt about the safety of handling a chemical container, notify EH&S immediately.
- Any container found to have a peroxide concentration greater than or equal to 100 ppm must be disposed of. Contact EH&S at 642-3073 for assistance.
- Materials which are older than the suggested shelf life but have been tested and have peroxide concentrations less than 100 ppm may be retained but must be tested at regular intervals (see manufacturer's recommendation for proper testing and disposal).
- Waste materials generated must be treated as a hazardous waste.
- The empty container must be rinsed three times with a COMPATIBLE solvent; leave it open in the back of the hood overnight. Solvent rinses and water rinse must be disposed of as hazardous waste.
- As an alternative, unrinsed empty containers can be disposed of through EH&S as hazardous waste. The unrinsed empty containers must be capped.
- Do not mix with incompatible waste streams.
- Decontamination of containers in order to use them for other purposes is not permitted.

8. Spill and Accident Procedure

Spill – Assess the extent of danger; if necessary request help by calling **911** (from a cell phone: **510-642-3333**) for emergency assistance or 510-642-3073 for non-life threatening situations. If you cannot assess the conditions of the environment well enough to be sure of your own safety, do not enter the area. If possible help contaminated or injured persons. Evacuate the spill area. Avoid breathing vapors from spill. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

- **Minor Spill** – In the event of a minor spill, if there is no potential for hazardous chemical exposure, report the spill to 510-642-3073 and proceed to clean it, if you are trained. Use appropriate personal protective equipment and clean-up material for chemical spilled. Double bag spill waste in clear plastic bags, label and request pick-up.
- **Major Spill** – Any hazardous chemical spill that involves chemical exposure, any chemical spill that due to size and/or hazard requires capabilities beyond your training, or any chemical spill



that gives the perception (because of odor, for example) that there has been a hazardous release. Call **911** or 510-642-3073 for assistance.

9. Cleaning and Decontamination

Lab-specific information on decontamination may be included in Section 12 - Protocol/Procedure.

- Wearing proper PPE, laboratory work surfaces must be cleaned at the conclusion of each procedure and at the end of each work day.
- Decontaminate all equipment before removing from a designated area.

10. Hazardous Waste Disposal

Label Waste

- Label all waste containers. See the EH&S Fact Sheet, "Hazardous Waste Management" for general instructions on procedures for disposing of hazardous waste.

Dispose of Waste

- Dispose of regularly generated chemical waste within 6 months.
- Contact EH&S at 642-3073 if you need assistance.

11. Safety Data Sheet (SDS) Location

SDS can be accessed online at <http://ucsd.com>



-Take Ownership of Your Safety-



Before starting any work, ask yourself:

- 1- **What will I be doing?**
- 2- **Do I know what the hazards are?**
- 3- **Do I have everything I need to do the job safely?**
- 4- **Am I doing the job safely?**
- 5- **What can we do better?**



12. Protocol/Procedure – Peroxide Forming Chemicals (PFC)

Section 12 must be customized to your specific needs. Delete any procedure that does not apply to your laboratory.

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
1. PFC used as a solvent in reactions and extractions.	Up to 2 L as supplied in the reagent bottle per reaction or extraction. Remember to obtain PI approval if higher scale is necessary.	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox. Open flames and possible sparking and static electricity must be avoided. Blast shield is required if a PFC may be distilled to dryness or evaporated to dryness.	<p>Eye protection: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields.</p> <p>Face Protection: Face shields are to be used when there is no protection from the hood sash.</p> <p>Hand Protection: Confirm compatibility of glove material with chemical being used. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use.</p> <p>Clothing: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.</p>	<p>Distillation/evaporation of PFCs efficiently removes all stabilizers. Collected fractions (rotavap) must be treated as unstabilized. And must be disposed of soon after generation.</p> <p>Peroxide forming chemicals must never be used with a strong oxidizing agent.</p> <p>Dispense solvents from the solvent purification system as instructed. Using syringe or cannula, transfer to reaction flask. If using bulk solvent (greater than 30 mL) dispense directly into reaction flask using a slow and controlled flow to avoid static build-up.</p> <p>All stored PFC containers must contain a date for which they were last filled.</p> <p>Solvents must be checked prior to use if evaporation to dryness is required. Solvents can be checked with peroxide strips or by adding 1 mL of the solvent to 1 mL of acetic acid containing 0.1 g of KI. A yellow color indicates low peroxide concentration while a brown color suggests high peroxide concentration.</p> <p>If peroxide concentration is high, the solvent should be submitted directly as waste</p>



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				<p>containing an oxidizer.</p> <p>If a PFC is concentrated on the rotary evaporator, use two dry ice traps to collect solvent vapors.</p> <p>Pressure can be built up if a PFC is used in reactions. Adequate ventilation (pressure bubbler on Schlenk manifold, or an equilibrating balloon) has to be used to prevent dangerous over pressurization.</p> <p>Pressure is built up if a PFC is used in extractions. Adequate ventilation (open the valve frequently during the extraction) has to be used to prevent dangerous over pressurization.</p> <p>If heated, the reaction apparatus has to be fitted with an adequately sized condenser and an adequate flow of cooling water has to be provided to prevent evaporation. Cooling hoses have to be secured with metal hose clamps to the condenser and the outler.</p> <p>If distillation or evaporation of a PFC to dryness is possible, a second worker must be present outside the potential explosion zone.</p>
Notes	Any deviation from this SOP requires approval from PI.			



Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
<p>2. PFC used as a reagent.]</p>	<p>Up to 5g or 100 mL as supplied in the reagent bottle.</p> <p>Remember to obtain PI approval if higher scale is necessary.</p>	<p>All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox</p> <p>Open flames and possible sparking and static electricity must be avoided.</p> <p>Blast shield is required if a PFC may be distilled to dryness or evaporated to dryness.</p>	<p>Eye protection: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields.</p> <p>Face Protection: Face shields are to be used when there is no protection from the hood sash.</p> <p>Hand Protection: Confirm compatibility of glove material with chemical being used. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use.</p> <p>Clothing: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.</p>	<p>Distillation/evaporation of PFCs efficiently removes all stabilizers. Collected fractions (rotavap) must be treated as unstabilized.</p> <p>See section above for detailed instructions using PFC's.</p>
Notes	Any deviation from this SOP requires approval from PI.			



Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
<p>3. PFC used as solvent in column chromatography.</p>	<p>Up to 1 L total eluent volume as supplied in the reagent bottle.</p> <p>Remember to obtain PI approval if higher scale is necessary.</p>	<p>All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible. Or in an inert atmosphere glovebox.</p> <p>Open flames and possible sparking and static electricity must be avoided.</p> <p>Blast shield is required if a PFC may be distilled to dryness or evaporated to dryness.</p>	<p>Eye protection: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields.</p> <p>Face Protection: Face shields are to be used when there is no protection from the hood sash.</p> <p>Hand Protection: Confirm compatibility of glove material with chemical being used. General guidance (unless otherwise specified in the specific SDS): Nitrile gloves must be used to prevent incidental contact. For spill handling or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Wash and dry hands after use.</p> <p>Clothing: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.</p>	<p>Distillation/evaporation of PFCs efficiently removes all stabilizers. Collected fractions (rotavap) must be treated as unstabilized.</p> <p>See the first section for detailed instructions on the handling of PFC's.</p>
Notes	Any deviation from this SOP requires approval from PI.			



Appendix: List of Peroxide Forming Chemicals (non-exhaustive list)

List A:

Chemicals that form explosive levels of peroxides without concentration. These are the most hazardous and can form explosive peroxide levels even if not opened. Test for peroxide formation or discard after 3 months of receiving the chemicals.

Isopropyl ether	Divinyl acetylene	Potassium metal
Potassium amide	Sodium amide	Vinylidene chloride
Divinyl ether		

List B:

Chemicals that form explosive levels of peroxides on concentration through distillation, evaporation, or exposure to air after opening. Test for peroxide formation or discard after 12 months.

Acetal	Acetaldehyde	Benzyl alcohol
2-Butanol	Chlorofluoroethylene	Cumene (isopropylbenzene)
Cyclohexene	2-Cyclohexen-1-ol	Cyclopentene
Decahydronaphthalene (decalin)	Diacetylene (butadiyne) (gas)	Dicyclopentadiene
Diglyme	Diethyl ether (ether)	Ethylene glycol ether acetates
Furan	4-Heptanol	2-Hexanol
Methyl acetylene (gas)	3-Methyl-1-butanol	Methyl isobutyl ketone
4-Methyl-2-pentanol	2-Pentanol	4-Penten-1-ol
1-Phenylethanol	Tetrahydrofuran (THF)	Tetrahydronaphthalene (tetralin)
Vinyl ethers	Secondary alcohols	Dioxanes
Ethylene glycol dimethyl ether (glyme)		Methyl cyclopentane

List C:

Chemicals that may autopolymerize as result of peroxide formation. Test for peroxide formation or discard after 12 months

Acrylic acid	Styrene	Acrylonitrile
Tetrafluoroethylene (gas)	Butadiene	Vinyl acetylene (gas)
Chloroprene	Vinyl acetate	Chlorotrifluoroethylene (gas)
Vinyl chloride (gas)	Methyl methacrylate	Vinyl pyridine
Chlorobutadiene	Vinylidene chloride	



List of Chemicals

Chemical(s)	Chemical(s)	Chemical(s) – Use(s) :
1,2-dimethoxyethane	1,3-butadiene, gas	2,3-dihydro-4h-pyran
2-acetylfuran	2-chloro-1,3-butadiene	2-methoxyethanol
2-propenenitrile	2-propenoic acid	allyl ether
anisole	bicyclo[4.4.0]decane	cumene
cyclohexene	cyclopentene	dicyclopentadiene
Diglyme	diisopropyl ether	dimethoxymethane
ethyl vinyl ether	furan	isopropyl alcohol
methyl isobutyl ketone	p-anisaldehyde	propyne
sodium amide	styrene	tetralin
vinyl acetate		