

Rubin's group laboratory operating procedure series

# 4. Reactive and Explosive Materials

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**REVISION RECORD**

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## 1. SCOPE

The purpose of this standard operating procedure is to provide *guidelines* for the safe handling of reactive and explosive materials. **SPECIFIC SOPs ARE REQUIRED FOR INDIVIDUAL EXPLOSIVE OR REACTIVE MATERIALS.** Consult the MSDS for specific information about a particular reactive or explosive material. Check the appendices at the end of this guide to identify potentially explosive compounds.

## 2. DEFINITIONS

### 2.1. Explosive

Explosive materials are chemical compounds or mechanical mixtures that, when subjected to heat, impact, friction, detonation, or other suitable initiation, undergoes rapid chemical change. Large volumes of highly heated gases are evolved that exert pressure on the surrounding medium. The term applies to materials that either detonate or deflagrate. Heat, light, mechanical shock, and certain catalysts initiate explosive reactions. For a comprehensive list of potentially explosive compounds, visit the website:

<http://www.ehs.berkeley.edu/pubs/guidelines/pecguidelines.html>

The list is included in the Appendices. View this list **VERY CAREFULLY**.

The following are some commonly used chemicals that can become an explosion hazard under certain conditions:

- Organic chemicals that form **PEROXIDES** through exposure to air or light (see Appendix 2 - Peroxide Forming Chemicals)
- Organic azides and the azide salts of heavy metals.
- Hydrated picric acid that becomes dry or becomes contaminated with metals that form metal picrate salts
- Sodium amide that reacts with air or moisture to form **superoxides**, as evidenced by yellow or brown discoloration
- Certain alkyl nitrates (e.g., butyl nitrate or propyl nitrate) that become contaminated with nitrogen oxides
- Certain normally-stable perchlorates (e.g., pyridium perchlorate or tetraethylammonium perchlorate) that become unstable at elevated temperatures

**Note: Most explosions occur while purifying or distilling mixtures. Therefore, use extreme caution before concentrating or purifying any mixture that may contain an explosive chemical (e.g., a peroxide forming chemical or perchlorate).**

There is an additional group of chemicals that should be considered although they are not necessarily heat-, light-, friction-, or shock-sensitive. These chemicals give off gaseous degradation by-products that may cause over-pressurization of the container and explode. They can degrade over time and should be incorporated into a safety and handling system that will prevent them from becoming explosive hazards (see Appendix 3).

## **2.2. Pyrophoric**

Pyrophoric materials ignite spontaneously when exposed to air at a temperature of 54.4 °C (130 °F) or below. Reaction by-products are toxic fumes or gases and liberation of heat. Many pyrophoric materials are water reactive as well. Examples include white phosphorus, many finely divided metals, some metal hydrides, certain silanes and certain alkyl lithiums, for example, *t*-butyl lithium. The reader is directed to the specific SOP for using pyrophoric materials.

## **2.3. Reactive (unstable)**

Reactive (unstable) materials are chemicals that will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shocks, pressure or temperature.

## **2.4. Water reactive**

Water reactive materials react violently with water to produce toxic, corrosive, or flammable gases and the liberation of heat. Some examples are listed.

Alkali metals

Alkali metal hydrides

Alkali metal nitrides

Calcium carbide

Phosphorus pentoxide

Non-metal Halides (*e.g.* BCl<sub>3</sub>, BF<sub>3</sub>, PCl<sub>3</sub>, SiCl<sub>4</sub>, S<sub>2</sub>Cl<sub>2</sub>)

Inorganic acid halides (*e.g.* POCl<sub>3</sub>, SOCl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>)

Anhydrous metal halides (*e.g.* AlCl<sub>3</sub>, TiCl<sub>4</sub>, ZrCl<sub>4</sub>, SnCl<sub>4</sub>)

Organic acid halides and anhydrides of low molecular weight

Metal and non-metal hydrides (boranes,  $\text{LiAlH}_4$ )

### **3. PERSONAL PROTECTIVE EQUIPMENT (PPE)**

Chemical splash GOGGLES for eye protection in combination with a FULL-LENGTH FACE SHIELD to fully protect the face and throat.

Heavy, non-reactive GLOVES should be worn when handling reactive compounds or in the event it is necessary to reach behind a shielded area while a hazardous experiment is in progress. Check glove manufacturer for recommendations on a suitable glove for the specific chemical.

LAB COAT, flame resistant.

Close-toed shoes (non-fabric) with non-slip soles.

If a respirator is needed, then user must use their personal respirator fitted to their face.

### **4. ENGINEERING AND VENTILATION CONTROLS**

All procedures involving reactive materials must be conducted in a fume hood to protect against runaway reactions and hazardous exposure.

### **5. SPECIAL HANDLING PROCEDURES**

These procedures are general. For *specific* compounds and procedures, consult the specific SOP.

- 1) If you are using reactive reagents, inform your lab mates. They need to be aware of what you are doing, what chemicals you are using, and they will need to know how to deal with an emergency.
- 2) Conduct procedures in a fume hood.
- 3) Use a BLAST SHIELD in combination with the hood sash to protect personnel and equipment from injury or damage from a possible explosion or fire. Consider using the sliding screen also.
- 4) Minimize the quantity of reactive (unstable) materials used and stored in the work area.
- 5) Label incoming containers with the date of receipt. Do not use reactive materials past their expiration date.

6) Exercise due care when handling peroxide formers. Visually inspect bottle cap and threads of container (without handling) for presence of organic peroxide crystals. If present, evacuate area and deny entry. Contact EH&S. If container appears free of encrustation, test for peroxides using the methods below. If peroxides are detected, contact EH&S for disposal. NOTE: Test should be conducted semi-annually.

- Add 1 to 3 mL of the liquid to be tested to an equal amount of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides. Alternatively, addition of 1 mL of a freshly prepared 10% solution of potassium iodide to 10 mL of an organic liquid in a 25-mL glass cylinder should produce a yellow color if peroxides are present.
- Add 0.5 mL of the liquid to be tested to a mixture of 1 mL of 10% aqueous potassium iodide solution and 0.5 mL of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.
- Use commercially available peroxide test strips.

## 6. LABELLING REQUIREMENTS

Label storage cabinets or areas with appropriate descriptor: **WATER REACTIVE, PYROPHORIC, OR EXPLOSIVE.**

Label all incoming containers with the date of receipt.

## 7. STORAGE REQUIREMENTS

Minimize the amount of reactive materials used and stored.

Store peroxide formers in tightly sealed metal containers in areas away from oxidizers.

Do not return unused material to the original container.

## 8. SPILL AND ACCIDENT PROCEDURES

See chemical spill clean-up SOP and UCLA laboratory safety manual (Chapter 10).

## 9. WASTE DISPOSAL

Handle all waste following UCLA guidelines (laboratory safety manual Chapter 11).

## 10. APPENDIX 1: Explosive and Potentially Explosive Chemical Families

### *Acetylene or acetylide compounds:*

N-Chloro-3-aminopropyne  
Propiolic acid  
Propynethiol

### *Acyl azides*

Acetyl azide  
Cyanodiazooacetyl azide  
Phenylphosphonic azide chloride

### *Acyl hypohalites*

Acetyl hypobromite  
Hexafluoroglutaryl dihypochlorite

### *Alkyl nitrates*

Ethylidene dinitrate  
Glyceryl trinitrate  
Propyl nitrate

### *Alkyl perchlorates*

Hexyl perchlorate  
Ethyl perchlorate  
1-Chloro-2-propyl perchlorate

### *Allyl trifluoromethanesulfonates*

2-Chloro-2-propenyl trifluoromethanesulfonate

### *Amminemetal oxosalts*

Ammonium hexanitrocobaltate  
Bis(1,2-diaminoethane) diaquacobalt (III) perchlorate  
Trihydrazine nickel (II) nitrate

### *Aromatic nitrates*

Picric acid  
Trinitrobenzene  
Picryl sulfonic acid

### *Azides*

Sodium azide  
Lead azide  
Hydrogen azide

### *Aziridines*

### *Diazo compounds*

2-Buten-1-yl diazoacetate  
Diethyl diazomalonate  
Dinitrodiazomethane

### *Diazonium carboxylates, perchlorates, salts, sulfates, tetrahaloborates, and, triiodides*

Benzenediazonium-2-carboxylate  
4-Aminobenzenediazonium perchlorate  
6-chloro-2,4-dinitrobenzenediazonium sulfate  
2-Nitrobenzenediazonium tetrachloroborate  
4-Toluenediazonium triiodide

### *Difluoroaminoalkanols*

1,1-Difluorourea  
Perfluoro-N-cyanodiaminomethane

### *Fluoro-nitro compounds*

1-Fluoro-1,1-dinitrobutane  
Fluorodinitromethyl azide

### *Fulminating metals*

Lead fulminate  
Gold fulminate  
Silver fulminate

### *Furazan N-oxides*

Dicyanofurazan N-oxide  
4-Oximino-4,5,6,7-tetrahydrobenzofurazan N-oxide

### *Hydroxooxidiperoxochromate salts*

1-Ammonium hydroxooxidiperoxochromate  
Potassium hydroxooxidiperoxochromate

### *Iodine Compounds*

Calcium 2-iodylbenzoate  
Iodobenzene  
2-Iodylvinyl chloride

### *Isoxazoles*

3-Aminoisoxazole  
3,5-Dimethylisoxazole

### *Metal Azide Halides*

1-Bromoaziridine

***Azocarbaboranes***

1,1-'Azo-1,2-dicarbadeborane

***N-Azolium nitroimidates***

Benzimidazolium 1-nitroimidate

4-Nitroamino-1,2,4-triazole

2-(N-Nitroamino)pyridine N-oxide

***N-Metal Derivatives***

Cadmium nitride

Dibutylthallium isocyanate

Sodium amide

***Metal Fulminates***

Mercury (II) fulminate

Sodium fulminate

Tripropyllead fulminate

***Metal Halogenates***

Lead bromate

***Metal Hydrides***

Stibine (Antimony hydride)

***Metal Nitrophenoxides***

Lithium 4-nitrothiophenoxide

Potassium 4-nitrophenoxide

***Metal Oxides***

Bis (1-chloroethylthallium chloride) oxide

Magnesium chloride trioxide

***Metal Oxohalogenates***

Ammonium iodate

Lead acetate—lead bromate

***Metal Oxometallates***

Bis (benzene) chromium dichromate

***Metal Perchlorates***

Chromyl perchlorate

Chromyl azide chloride

Molybdenum diazide tetrachloride

Tungsten azide pentachloride

***Metal Azides***

Aluminum azide

Bis(cyclopentadienyl)tungsten diazide oxide

Mercury (I&II) azide

Sodium azide

***Nitroso Compounds***

Dinitrosylnickel

Ethyl N-methyl-N-nitrosocarbamate

Potassium nitrosodisulfate

***N—S Compounds***

Disulfur dinitride

Potassium sulfurdiimide

Tetrasulfur tetranitride

Thiotriethiazyl nitrate

***Organic Acids***

Picric acid

Trinitroresorcinol

***Organic Azides***

Diazidomethyleneazine

Picryl azide

Vinyl azide

***Organolithium Reagents***

o-Trifluoromethyl phenyllithium

m-Bromo phenyllithium

***Organomineral Peroxides***

Bis(triethyltin) peroxide

Diethylhydroxotin hydroperoxide

***Oximes***

Bromoacetone oxime

Hydroxycopper glyoximate

Potassium cyclohexanehexone 1,3,5-trioximate

***Oxosalts of Nitrogenous Bases***

***Metal Peroxides***

Many transition metal peroxides are dangerously explosive.

***Metal Peroxomolybdates***

2-Potassium tetraperoxomolybdate

2-Sodium tetraperoxomolybdate

***Metal Picramates***

Palladium picramate

Uranyl picramate

***Nitroaryl Compounds***

N-Chloro-4-nitroaniline

***Nitrogenous Base Nitrite Salts***

Methylammonium nitrite

***aci-Nitroquinonoid Compounds***

Sodium 1,4-bis(aci-nitro)-2,5-cyclohexadienide

***aci-Nitro Salts***

Ammonium aci-nitromethanide

Dipotassium aci-dinitromethanide

Thallium aci-phenylnitromethanide

***Peroxyacid salts***

Calcium peroxodisulfate

Potassium tetraperoxomolybdate

Tetramethylammonium pentaperoxodichromate

***Peroxyacids***

Benzenperoxyseleonic acid

Peroxyacetic acid

Peroxyformic acid

***Peroxycarbonate esters***

O-O-tert-Butyl isopropyl monoperoxy carbonate

Diallyl peroxydicarbonate

Dimethyl peroxydicarbonate

***Phosphorus esters***

Diethyl phosphite

Dibenzyl phosphorchloridate

Ammonium tetranitroplatinate (II)

Diamminepalladium (II) nitrate

1,2-Diammonioethane nitrate

***Ozonides***

trans-2-Butene ozonide

Ethylene ozonide (1,2,4-trioxolane)

Trifluoroethylene ozonide

***Perchlorate Salts of Nitrogenous Bases***

Pyridinium perchlorate

Tetraethylammonium perchlorate

***Perchloramide Salts***

Barium perchloramide

Mercury (II) N-perchloryl benzylamide

Silver perchlorylamide

***Perchloryl Compounds***

2,6-Dinitro-4-perchlorylphenol

Perchloryl fluoride

N-Perchloryl piperidine

***Strained-Ring Compounds***

2-Azatricyclo[2.2.1.0<sup>2,6</sup>]hept-7-yl perchlorate

Dicyclopropyldiazomethane

Prismane

***Tetrazoles***

5-Aminotetrazole

Silver and mercury salts of 5-nitrotetrazole

Tetrazole

***Triazoles***

3-Diazo-5-phenyl-3H-1,2,4-triazole

4-Hydroxy-3,5-dimethyl-1,2,4-triazole

1,2,3-Triazole

***Polymerization (violent)***

Acrylic acid

Ethylene oxide

Vinyl acetate

***Picrates***

Nickel picrate (anhydrous)  
 S-7-Methylnonylthiuronium picrate  
 Sodium picrate

***Platinum Compounds***

Ammine-decahydroxydiplatinum  
 cis-Diammineplatinum (II) nitrate  
 Trimethylplatinum hydroxide

***Poly(dimercuryimmonium) Compounds***

Poly(dimercuryimmonium picrate)  
 Poly(dimercuryimmonium permanganate)  
 Poly(dimercuryimmonium trinitrobenzoate)

***Polynitroalkyl Compounds***

Dinitroacetonitrile  
 Hexanitroethane  
 Potassium trinitromethanide

***Polynitroaryl Compounds***

5,6-Dinitro-2-dimethyl aminopyrimidinone  
 4-Nitro-1-picryl-1,2,3-triazole  
 2,4,6-Trinitrotoluene

***Silver Compounds***

Silver nitride (fulminating silver)  
 Disilver ketenide  
 Phenylsilver  
 Silver azide  
 Silver Osmate

**APPENDIX 2: COMMON PEROXIDE-FORMING COMPOUNDS**

List A—**Chemicals that may form explosive levels of peroxides without concentration by evaporation or distillation.** These materials are particularly dangerous because they can be hazardous even if never opened.

Butadiene  
 Chloroprene  
 Divinylacetylene  
 Isopropyl ether  
 Tetrafluoroethylene  
 Vinylidene Chloride

List B—**Chemicals that form explosive levels of peroxides on concentration.** They typically accumulate hazardous levels of peroxides only when evaporated, distilled or otherwise treated to concentrate the peroxides (e.g. deactivation or removal of peroxide inhibitors). Therefore, they have the potential of becoming far more hazardous after they are opened.

Acetal	Diacetylene	3-Methyl-1-butanol	Tetrahydrofuran
Acetaldehyde	Dicyclopentadiene	Methylcyclopentane	Tetrahydronaphthalene
Benzyl alcohol	Diethyl ether	Methyl isobutyl ketone	Vinyl ethers
2-Butanol	Diglyme	4-Methyl-2-pentanol	Other secondary alcohols
Cumene	Dioxanes	2-Pentanol	
Cyclohexanol	Glyme	4-Penten-1-ol	
2-Cyclohexen-1-ol	4-Hepitanol	1-Phenylethanol	
Cyclohexene	2-Hexanol	2-Phenylethanol	
Decahydronaphthalene	Methylacetylene	2-Propanol	

List C—**Chemicals that may autopolymerize as a result of peroxide accumulation.** These chemicals have been associated with hazardous polymerization reactions that are initiated by peroxides which have accumulated in solution. These materials are typically stored with polymerization inhibitors to prevent these dangerous reactions.

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

List D: **Other peroxidizable chemicals which cannot be placed into the other categories but nevertheless require handling with precautions.**

Acrolein	tert-Butyl methyl ether	Di(1-propynyl) ether	n-Methylphenetole
Allyl ether	n-Butyl phenyl ether	Di(2-propynyl) ether	2-Methyltetrahydrofuran
Allyl ethyl ether	n-Butyl vinyl ether	Di-n-propoxymethane	3-Methoxy-1-butyl acetate
Allyl phenyl ether	Chloroacetaldehyde diethylacetal	1,2-Epoxy-3-isopropoxypropane	2-Methoxyethanol
p-(n-Amyloxy)benzoyl chloride	2-Chlorobutadiene	1,2-Epoxy-3-phenoxypropane	3-Methoxyethyl acetate
n-Amyl ether	1-(2-Chloroethoxy)-2-phenoxyethane	p-Ethoxyacetophenone	2-Methoxyethyl vinyl ether
Benzyl n-butyl ether	Chloroethylene	1-(2-Ethoxyethoxy)ethyl acetate	Methoxy-1,3,5,7-cyclooctatetraene
Benzyl ether	Chloromethyl methyl ether	2-Ethoxyethyl acetate	b-Methoxypropionitrile
Benzyl ethyl ether	b-Chlorophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	m-Nitrophenetole
Benzyl methyl ether	o-Chlorophenetole	1-Ethoxynaphthalene	1-Octene
Benzyl-1-naphthyl ether	p-Chlorophenetole	o,p-Ethoxyphenyl isocyanate	Oxybis(2-ethyl acetate)
1,2-Bis(2-chloroethoxy)ethane	Cyclooctene	1-Ethoxy-2-propyne	Oxybis(2-ethyl benzoate)
Bis(2-ethoxyethyl)ether	Cyclopropyl methyl ether	3-Ethoxypropionitrile	b,b-Oxydipropionitrile
Bis(2-(methoxyethoxy)ethyl) ether	Diallyl ether	2-Ethylacrylaldehyde oxime	1-Pentene
Bis(2-chloroethyl) ether	p-Di-n-butoxybenzene	2-Ethylbutanol	Phenoxyacetyl chloride
Bis(2-ethoxyethyl) adipate	1,2-Dibenzoyloxyethane	Ethyl-b-ethoxypropionate	a-Phenoxypropionyl chloride
Bis(2-methoxyethyl) carbonate	p-Dibenzoyloxybenzene	2-Ethylhexanal	Phenyl-o-propyl ether
Bis(2-methoxyethyl) ether	1,2-Dichloroethyl ethyl ether	Ethyl vinyl ether	p-Phenylphenetone
Bis(2-methoxyethyl) phthalate	2,4-Dichlorophenetole	Furan	n-Propyl ether
Bis(2-methoxymethyl) adipate	Diethoxymethane	2,5-Hexadiyn-1-ol	n-Propyl isopropyl ether

Bis(2-n-butoxyethyl) phthalate	2,2-Diethoxypropane	4,5-Hexadien-2-yn-1-ol	Sodium 8-11-14-eicosatetraenoate
Bis(2-phenoxyethyl) ether	Diethyl ethoxymethylenemalonate	n-Hexyl ether	Sodium ethoxyacetylde
Bis(4-chlorobutyl) ether	Diethyl fumarate	o,p-Iodophenetole	Tetrahydropyran
Bis(chloromethyl) ether	Diethyl acetal	Isoamyl benzyl ether	Triethylene glycol diacetate
2-Bromomethyl ethyl ether	Diethylketene	Isoamyl ether	Triethylene glycol dipropionate
beta-Bromophenetole	m,o,p-Diethoxybenzene	Isobutyl vinyl ether	1,3,3-Trimethoxypropene
o-Bromophenetole	1,2-Diethoxyethane	Isophorone	1,1,2,3-Tetrachloro-1,3-butadiene
p-Bromophenetole	Dimethoxymethane	b-Isopropoxypropionitrile	4-Vinyl cyclohexene
3-Bromopropyl phenyl ether	1,1-Dimethoxyethane	Isopropyl-2,4,5-trichlorophenoxy acetate	Vinylene carbonate
1,3-Butadiyne	Dimethylketene	Limonene	Vinylidene chloride
Buten-3-yne	3,3-Dimethoxypropene	1,5-p-Methadiene	
tert-Butyl ethyl ether	2,4-Dinitrophenetole	Methyl-p-(n-amyloxy)benzoate	
	1,3-Dioxepane	4-Methyl-2-pentanone	

### **APPENDIX 3. CHEMICALS THAT MAY EXPLODE DUE TO OVER-PRESSURIZED CONTAINER**

Aluminum chloride  
 Aluminum lithium hydride  
 Ammonia solution  
 Ammonium hydroxide  
 Ammonium persulfate  
 Anisyl chloride  
 Aqua regia  
 Benzenesulphonyl chloride  
 Bleach  
 Bleaching powder  
 Calcium carbide  
 Calcium hydride  
 Calcium hypochlorite  
 Chloroform  
 Chromic acid  
 Cumene hydroperoxide  
 Cyclohexne  
 Diethyl pyrocarbonate  
 Dimethylamine  
 Formic Acid  
 Hydrogen peroxide  
 Lauroyl peroxide  
 Lithium aluminum hydride  
 Lithium hydride  
 Nitric acid  
 Nitrosoguanidine  
 Peracetic acid  
 Phenol  
 Phosphorus trichloride  
 Potassium Persulphate

Silicon tetrachloride  
Sodium borohydride  
Sodium dithionite  
Sodium hydride  
Sodium hydrosulphite  
Sodium hypochlorite  
Sodium peroxide  
Sodium persulphate  
Thionyl chloride  
Urea peroxide  
Zinc