

Safe Method of Use: Hazardous Substances of Higher Risk 4 Specific Storage and Testing Guidelines for Peroxide Forming Chemicals

Purpose: This Safe Method of Use applies to **principal investigators (PIs), sector managers, designated laboratory person (DLPs)**, technical staff and students who use Peroxide Forming Chemicals within the University of Auckland.

A. About Peroxide Forming Chemicals

Many oxygenated organic compounds become more and more dangerous upon prolonged storage because they tend to form explosive peroxides with age. Organic peroxides are carbon-based chemicals that contain the characteristic peroxide O-O bond.

Peroxides may form in freshly distilled, undistilled, and unstabilized ethers within less than two weeks.

Ethers with peroxide inhibitors, such as BHT (butylated hydroxytoluene) will have a longer shelf-life.

Exposure to light and air enhances the formation of the peroxides. Many ethers tend to absorb and react with oxygen from the air to form unstable peroxides which may detonate with extreme violence when they become concentrated by evaporation or distillation. These ethers may also explode when combined with other compounds that produce a detonable mixture or when disturbed by heat, shock, or friction.

Peroxides formed in compounds by auto-oxidation have caused many accidents, including the unexpected explosions of the residue of solvents after distillation. While ethers present one of the most commonly known peroxidizable compound risks, other common solvents such as isopropanol have exploded upon distillation due to peroxide concentration.

While the peroxide formation potential in ethers is the primary hazard, ethers also pose inhalation hazards. Lower molecular weight ethers are powerful narcotics that can cause death in large doses.

With all peroxide forming chemicals it is preferable to use small containers that can be completely emptied, rather than take small amounts from a large container over time. Ethers should be stored in amber bottles or other opaque containers and under a blanket of inert gas, such as nitrogen or argon, or over

a reducing agent to inhibit formation of peroxides. Containers of unstabilised or distilled ether and other peroxide forming chemicals should be marked with the date they are opened and with the date of required disposal. Mark these dates on the container using an indelible marker or attach a PEC warning label (such as the below)

Ethers (note the exception for di-isopropyl ether) with no peroxide inhibitor should be tested or disposed within 12 months after opening, distillation or synthesis.

Ethers with peroxide inhibitor should be tested or disposed within 18 months after opening.

Other peroxide forming compounds should be tested at frequencies given in Appendix One for category A and B

Sample Label for Solutions with no Peroxide Inhibitor

Warning: May Form Explosive Peroxides

Store in tightly closed original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, do not move or open the container, contact Lab Manager immediately.

Check for peroxides before distilling or concentrating.

This Chemical Has a Limited Shelf Life!

Date Received _____ Date Opened _____

Test and or dispose of this chemical 18 months after receipt or 12 months after opening.

B. Testing Schedule for Peroxide Forming Chemicals

Peroxide forming compounds should be tested at frequencies given in Appendix One for category A and B

A peroxide forming chemical should either be disposed or tested for peroxide content by its expiry date. Dispose of any chemicals found to have a peroxide concentration greater than or equal to 100 parts per million. Chemicals that have lasted beyond the recommended shelf life but have been tested and show no detectable peroxides, or whose peroxide concentrations are less than 100 ppm, may be retained but should be tested 6 months later. Testing results should be recorded on the container.

Test all peroxide formers prior to distillation, regardless of age.

Never test containers of unknown age or origin. Old bottles may contain concentrated peroxides, or peroxides may have crystallized in the cap threads, which would present a serious hazard when opening the bottle for testing.

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C. An Analysis of Common Detection Procedures

The following pages are a reprint of part of R. J. Kelly's article, "Review of Safety Guidelines for Peroxidizable Organic Chemicals," originally published in *Chemical Health & Safety*. Kelly's references and a few passages have been omitted. (See References below.)

Peroxide Detection Methods

Although there are numerous quantitative, semiquantitative, and qualitative methods to detect peroxides in organic and aqueous solutions, four are commonly used. They include two qualitative variations on the iodine detection method, the qualitative ferrous thiocyanate method, and the use of semiquantitative redox dip strips. Recently, the use of titanium sulfate has been suggested as a means to detect peroxides, but it is not widely used. The dip strip method has the advantage of being the most gentle test, an important consideration if the chemical is shock sensitive. It also has another substantial advantage: It can detect, to some extent, dialkyl peroxide, polyperoxides, and cyclic peroxides, compounds that are not efficiently detected by the other methods (except, perhaps, the titanium sulfate method). Some solvents, notably isopropyl ether and dioxane, may form significant and hazardous levels of these higher reaction products. Furthermore, the standard peroxide removal procedures may remove all of the hydroperoxides but leave behind dangerous levels of alkyl peroxides, polyperoxides, and cyclic peroxides. The routine ferrous thiocyanate and iodine methods may yield a false negative in this case, but the dip strip test would likely detect the remaining peroxides, although perhaps not quantitatively.

The dip strip method, however is difficult to use with water-immiscible, low volatility chemicals.

Ferrous Thiocyanate Method

This qualitative method relies on the oxidation by peroxide of colorless ferrothiocyanate (Fe^{2+}) to the red ferrithiocyanate (Fe^{3+}). One drop of reagent is added to one drop of the chemical to be tested. A barely discernible pink color indicates that peroxides are present at a concentration of about 10 ppm. A clear pink to cherry color suggests a concentration of about 20 ppm. A red color indicates a concentration of about 80 ppm, and a deep red indicates a concentration as high as 400 ppm. The reagent is prepared by dissolving 9 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml 18% HCl. A little granulated zinc is added, followed by 5 g NaSCN. When the transient red color fades, an additional 12 g NaSCN is added, and the liquid is decanted from the unused zinc into a clean, stoppered bottle. The shelf life of this reagent is very limited. This method is sensitive only to hydroperoxides; it will not detect most other peroxides.

Note: Use only when you suspect hydroperoxides are present.

Iodide Tests

This is the most common qualitative test for adventitious peroxides. The two primary variations on this procedure involve the oxidation of iodide to iodine by the peroxide, with the resulting formation of a yellow to brown color.

Method A

In this method, 1 mL of the material to be tested is added to an equal volume of glacial acetic acid, to which approximately 0.1 g NaI or KI (10% wt/vol) has been added. A yellow color indicates a low concentration of peroxides (40—100 ppm as hydrogen peroxide). A brown color indicates a higher concentration of peroxide. Blanks must always be prepared. The test solution has a very short shelf life and will naturally result in high blank values if stored for any length of time. Variations on this method include the use of a 20% wt/vol reagent and hydrochloric acid instead of glacial acetic acid and the use of sulfuric acid. Heating is recommended to enhance detection of higher peroxides that may not be detected by the routine process. In quantitative variations on this method, the liberated iodine is titrated with 0.1 M NaSCN. This degree of precision is usually unnecessary for routine testing, and these methods do not increase the sensitivity of the method to higher peroxides.

Method B

In this method, 1 mL of a freshly prepared 10% KI solution is added to 10 mL of the organic liquid in a 25-mL glass stoppered vial. A barely visible yellow color suggests a peroxide content of 10—50 ppm. A clear and definite yellow color indicates a concentration of about 100 ppm, and brown color indicates a higher concentration. Variations on this method include using a 20% KI solution and using a 1:1 solvent/reagent ratio. Some authors recommend vigorous shaking or mixing.

Comparison of Methods A and B

Method A is often faster than Method B. Up to 15 minutes may be required for formation of color using Method B, whereas the color usually forms in < 1 minute for Method A. For both procedures, the color formed is a function of the peroxide content and the chemical tested.

Some scientists disagree about the sensitivity of these methods to peroxides other than hydroperoxides. Burfield states that the method is sensitive only to hydroperoxides. Noller and Bolton indicate that the acidified Method A is sensitive to hydroperoxides, peroxyacids, diacyl peroxides, and some peroxide esters, but not to dialkyl and alkyldiene peroxides.

Davies makes a similar statement. Noller and Bolton suggest that heating, perhaps with the addition of hydroiodic acid, may be necessary to detect these compounds. Mair and Graupner use a combination of glacial acetic acid and hydrochloric acid plus heat to detect all peroxides. These latter two

procedures are complex reflux processes that require extensive experience in chemistry and substantial laboratory facilities.

Dip Strips

E. Merck and Aldrich Chemical companies make dip strips for the semi-quantitative detection of peroxides in organic and inorganic solutions, and they are available from many suppliers. The strip incorporates the enzyme peroxidase, which transfers oxygen from peroxide to an incorporated organic redox indicator. The indicator turns blue in the presence of peroxides. Comparison color scales are provided for organic and aqueous tests.

The range for organic chemicals varies, depending on the manufacturer: 0—25 ppm for the Merck product and 1—100 ppm for Aldrich. Higher ranges can be accommodated by dilution of the suspect chemical with a miscible, non-peroxidized chemical.

For volatile organic chemicals, the test strip is immersed in the chemical for 1 second; then the tester breathes slowly on the test strip for 15—30 seconds, or until the color stabilizes.

Vapor in the breath provides water for the reaction to proceed. The color is then compared with the scale provided on the bottle.

Modifications of this procedure are needed to test non-volatile organic compounds. The Aldrich strips have been successfully used as follows. For water-miscible compounds, add three drops of water to one drop of chemical to be tested. Wet the dip strip in the mixture, wait 2—3 minutes or until the color stabilizes, and multiply the result by 4. For water-immiscible compounds, mix three drops of a volatile ether with one drop of the low-volatility compound to be tested. Wet the dip strip and breathe on the reaction zone for 30—60 seconds, or until the color stabilizes, and multiply the measured value by 4.

These strips have a limited shelf life, but refrigeration is not recommended once the container has been opened, because repeated cooling and heating cause condensation that will ruin the strips. Storage under dry, inert atmosphere will prolong the shelf life.

Literature from E. Merck indicates that their test strips will detect hydroperoxides and most higher peroxides, but some polyperoxides may be poorly detected.

Titanium Sulfate

To detect organic peroxides, a solution of titanium sulfate in 50% sulfuric acid is used. When this reagent is added to a peroxidized solvent, a yellow-orange complex is formed. It has been stated that this method will detect higher peroxides, especially polyperoxides.

The higher peroxides are hydrolyzed by the strong acid and are thereby made detectable. The test reagent is prepared by dissolving a small amount of

TiO₂ in hot concentrated sulfuric acid and adding this to an equal volume of water.

This method can only be recommended if it is compared by the user with other methods of known sensitivity and used accordingly.

Summary of Detection Methods

Dip strips provide the highest sensitivity and the most accurate quantification of peroxide concentration for routine testing. Furthermore, they are easier, faster, and safer to use than other methods, and they detect a wider range of peroxides than do other simple methods.

They are, however, somewhat inconvenient to use for testing nonvolatile solvents, and they have a limited shelf life after the container is opened. . . .

Removal of Peroxides

In some cases, it might be desirable to remove peroxides from chemicals rather than dispose of the entire chemical. This can be done safely for relatively low levels of peroxides (less than 500 to 1000 ppm). Scrubbing of concentrations greater than 1000 ppm may pose an unacceptable hazard, depending on the chemical involved. Scrubbing of discolored, crystallized, or layered peroxide formers is almost certainly too hazardous and should not be attempted. These severely peroxidized compounds should be treated as potential bombs.

Method 1

Hydroperoxides can be removed by passing the solvent through a column of activated alumina. This method works for water-soluble and water-insoluble chemicals. The washed solvent should be retested to ensure that it has been cleaned adequately. The alumina apparently catalyzes the degradation of some peroxides, but in some cases the peroxide may remain intact on the alumina, making it potentially shock sensitive. The alumina can be deactivated by flushing with a dilute acid solution of potassium iodide or ferrous sulfate.

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. This method is relatively slow and expensive, but it avoids shaking the solvent and does not add water. It will not reliably remove dialkyl peroxides, although there is some controversy about this.

Method 2

Peroxides in water-insoluble chemicals can be removed by shaking with a concentrated solution of ferrous salt; 60 g FeSO₄, 6 mL concentrated H₂SO₄, and 110 mL water are a standard solution. Another formulation is 100 g FeSO₄, 42 mL concentrated HCl, and 85 mL water. The peroxide former is

extracted 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. This method has been shown repeatedly to be quite effective for most peroxides, but it is not reliable for removing alkyl peroxides.

Method 3

Blue-indicating molecular sieve (4–8 mesh, type 4A) is added to containers of peroxidized chemicals and allowed to sit for 1–30 days. An amount equivalent to about 5%–10% (wt/vol) of the peroxidized liquid is used. Alternatively, the mixture can be refluxed, and the reaction occurs within 4 hours. The peroxide is broken down, and the indicator in the sieve is consumed. When run at room temperature, this process is apparently safe, slow, and controlled. Dialkyl peroxides are not efficiently removed, especially from dioxane.

This method may be particularly suited to treatment of THF, diisopropyl ethers, and diethyl ethers, which may be decontaminated at room temperature in a couple of days.

Other methods for removing higher peroxides including dialkyl peroxides

In one suggested procedure, a 10% molar excess of sodium or potassium iodide is dissolved in 70 mL glacial acetic acid. A small quantity of 36% (wt/vol) HCl is added, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90°C–100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours. Zinc dissolved in acetic or hydrochloric acid has been recommended. Prolonged treatment with ferrous sulfate in 50% sulfuric acid has also been recommended.⁴

REFERENCES

- 1 *Journ. of Chem. Education* 1964, 41:(8) A 575-A579.
- 2 Illinois. Env. Protection Agency, *News*, Feb. 22, 1991, 91-117.
- 3 *Prudent Practices for Disposal of Chemicals from Laboratories*, Appendix I, National Academy Press, Washington, DC, 1983, pp. 245-246.
- 4 Kelly, R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals," American Chemical Society—*Chemical Health & Safety*, 1996, 4(5), pp. 33-36.

Appendix I - Common Peroxide-Forming Compounds

The following table lists some common peroxide-forming chemicals.

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. It is particularly important that they contain peroxide inhibitors.

Butadiene (liquid monomer)	Chloroprene (liquid monomer)
Divinylacetylene	Isopropyl ether
Tetrafluoroethylene (liquid monomer)	Vinylidene Chloride

Sodium amide may form dangerous oxidation products if exposed to air. Explosives peroxides may also form in containers with potassium metal.

These compounds should be tested every 6 months for peroxides.

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	Tetrahydrofuran	Acetaldehyde
Dicyclopentadiene	Methylcyclopentane	Benzyl alcohol
Diethyl ether	Vinyl ethers	Diglyme
Cumene	Dioxanes	Cyclohexene
Glyme	Decahydronaphthalene	Methylacetylene
Tetrahydronaphthalene	Cyclopentene	Decahydronaphthalene
Methyl acetylene	2-Chlorobutadiene	Chloroethylene
Diallyl ether	n-Propyl ether	Furan
Tetrahydropyran		

These compounds should be tested every 12 months for peroxides or every 18 months where inhibitors are present.

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.

Any liquid should be tested every 24 months for peroxides.

Acrylic acid	Vinyl acetate
Acrylonitrile	Vinylacetylene

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Butadiene (gas)
 Chloroprene (gas)
 Chlorotrifluoroethylene
 Tetrafluoroethylene (gas)
 Styrene

Vinyl chloride
 Vinylpyridine
 Vinylidene chloride
 Methyl methacrylate

D. Other peroxidizable chemicals which can not be placed into the other categories but nevertheless require handling with precautions.

Any liquid should be tested every 24 months for peroxides.

Acrolein	tert-Butyl methyl ether	Di-n-propoxymethane	n-Methylphenetole
Allyl ether	n-Butyl phenyl ether	1,2-Epoxy-3-isopropoxypropane	2-Methyltetrahydrofuran
Allyl ethyl ether	n-Butyl vinyl ether	1,2-Epoxy-3-phenoxypropane	3-Methoxy-1-butyl acetate
Allyl phenyl ether	Chloroacetaldehyde diethylacetal	p-Ethoxyacetophenone	2-Methoxyethanol
p-(n-Amyloxy)benzoyl chloride	1-(2-Chloroethoxy)-2-phenoxyethane	1-(2-Ethoxyethoxy)ethyl acetate	3-Methoxyethyl acetate
n-Amyl ether		2-Ethoxyethyl acetate	2-Methoxyethyl vinyl ether
Benzyl n-butyl ether	Chloromethyl methyl ether	(2-Ethoxyethyl)-a-benzoyl benzoate	Methoxy-1,3,5,7-Cyclooctatetraene
Benzyl ether	b-Chlorophenetole	1-Ethoxynaphthalene	b-Methoxypropionitrile
Benzyl ethyl ether	o-Chlorophenetole	o,p-Ethoxyphenyl isocyanate	m-Nitrophenetole
Benzyl methyl ether	p-Chlorophenetole	1-Ethoxy-2-propyne	1-Octene
Benzyl-1-naphthyl ether	Cyclooctene	3-Ethoxypropionitrile	Oxybis(2-ethyl acetate)
1,2-Bis(2-chloroethoxy)ethane	Cyclopropyl methyl ether	2-Ethylacrylaldehyde oxime	Oxybis(2-ethyl benzoate)
Bis(2-ethoxyethyl)ether	p-Di-n-butoxybenzene	2-Ethylbutanol	b,b-Oxydipropionitrile
Bis(2-(methoxyethoxy)ethyl) ether	1,2-Dibenzoyloxyethane	Ethyl-b-ethoxypropionate	1-Pentene
Bis(2-chloroethyl) ether	Bis(2-methoxyethyl) carbonate	p-Dibenzoyloxybenzene	Phenoxyacetyl chloride
Bis(2-ethoxyethyl) adipate Chloride	Bis(2-methoxyethyl) ether	1,2-Dichloroethyl ethyl ether	a-Phenoxypropionyl
Phenyl-o-propyl ether	Bis(2-methoxyethyl) phthalate	2,4-Dichlorophenetole	2-Ethylhexanal
p-Phenylphenetone	Bis(2-methoxymethyl) adipate	Diethoxymethane	Furan
n-Propyl isopropyl ether	Bis(2-n-butoxyethyl) phthalate	2,2-Diethoxypropane	2,5-Hexadien-1-ol
Sodium 8-11-14-Eicosatetraenoate	Bis(2-phenoxyethyl) ether	Diethyl ethoxymethylenemalonate	4,5-Hexadien-2-yn-1-ol
Sodium ethoxyacetylde	Bis(4-chlorobutyl) ether	Diethyl fumarate	n-Hexyl ether
Bis(chloromethyl) ether	Diethyl acetal	Isoamyl benzyl ether	o,p-Iodophenetole
2-Bromomethyl ethyl ether	Diethylketene	Isoamyl ether	Triethylene glycol diacetate
dipropionate	beta-Bromophenetole	m,o,p-Diethoxybenzene	Triethylene glycol
1,3,3-Trimethoxypropene	o-Bromophenetole	1,1,2,3-Tetrachloro-1,3-butadiene	Isobutyl vinyl ether
Dimethoxymethane	Isophorone	4-Vinyl cyclohexene	1,2-Diethoxyethane
3-Bromopropyl phenyl ether	b-Isopropoxypropionitrile	Isopropyl-2,4,5-trichlorophenoxy acetate	p-Bromophenetole
1,3-Butadiyne	1,1-Dimethoxyethane	Limonene	Vinylene carbonate
Buten-3-yne	Dimethylketene	1,5-p-Methadiene	Vinylidene chloride
2,4-Dinitrophenetole	3,3-Dimethoxypropene	1,3-Dioxepane	tert-Butyl ethyl ether
4-Methyl-2-pentanone	Methyl-p-(n-amyloxy)benzoate		

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