

Potentially Explosive Chemicals (PECs)

Guidelines for Safe Storage and Handling

Iowa State University

TABLE OF CONTENTS

1. Introduction
 2. Common Laboratory PECs
 3. General Storage Precautions
 4. Specific Storage and Testing Guidelines for Peroxide Forming Chemicals
 - 4.1 About Peroxide Forming Chemicals
 - 4.2 Testing Schedule for Peroxide Forming Chemicals
 - 4.3 Dip Strips
 5. Picric Acid & other di- and tri-nitro compounds
 - APPENDIX 1 – Representative Peroxide Forming Compounds
 - APPENDIX 2 – Additional PEC Detection Methods
 - APPENDIX 3 – PEC Treatment Methods
 - REFERENCES
 - DISCLAIMER
-

1. Introduction

Explosive chemicals can rapidly release tremendous amounts of destructive energy. If not handled properly, these chemicals can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies.

There are two classes of explosive chemicals. The first is **known explosive chemicals** that are designed and produced for use as an explosive (e.g., TNT, explosive bolts, bullets, blasting caps, and fireworks). The other class is **potentially explosive chemicals (PECs)**. PECs are materials that may oxidize, decompose, polymerize, become contaminated, dry out or destabilize and subsequently become explosive when subjected to heat, light, friction or mechanical shock.

The class of PECs that require the most attention at ISU and is the major focus of this document are the **peroxidizable compounds** (other PECs such as picric acid are addressed in section 5). In addition to personnel injury and property damage from explosions, the cost of disposing of unknown and/or out-dated PECs is exorbitant. ISU uses a contractor to remotely open and

stabilize each PEC making it safe for disposal. Costs for this service can range from \$2000 to \$6000 per chemical event for this special handling service.

NOTE: There is a great deal of uncertainty regarding the hazards and safe handling of PECs. For example, with peroxide forming chemicals, there are no definite data available about the concentration and specific conditions at which these peroxides will detonate. Several common test methods may not detect all types of unstable peroxides. Deperoxidation procedures may not remove all types of unstable peroxides. Also, there are no specific federal or state OSHA regulations on this subject. It is paramount that researchers be aware of the hazards associated with PECs.

2. Common Laboratory PECs

There are many PECs used in academic research and teaching laboratories. 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
- Hydrated picric acid or other tri-nitro and di-nitro compounds that become dry or become contaminated with metals that form explosive metal 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).

Contact ISU Environmental Health & Safety (EH&S) at 294-5359 or Ames Laboratory Environment, Safety, Health & Assurance (ESH&A) at 294-2153 immediately if you suspect a material is an outdated PEC. Post warning signs so others do not handle or disturb the material. Safety office personnel will inspect the chemical and devise an appropriate action plan that ensures safe disposal.

3. General Storage Precautions

It is important that chemical users track and dispose of chemicals before they become a problem. Proper inventory management systems can help mitigate risk to personnel and avert higher than normal disposal costs.

- Identify all explosive and potentially explosive chemicals in your inventory. Never store unlabeled chemicals. Before they can be shipped to a disposal site, unknown chemicals require special testing to determine which hazardous properties they possess. In some cases, an unknown chemical that is not a PEC could be classified as a PEC because its

outward appearance resembles other known explosives. The handling and disposal of these chemicals costs significantly more than known chemicals.

- Record the opening date and the date that the chemical should be discarded on the label of chemicals that may degrade to become potentially explosive. Labels are available from ISU EH&S, ISU Chemistry Stores or Ames Laboratory ESH&A.
- Keep explosive chemicals away from all ignition sources such as open flames, hot surfaces, spark sources, and direct sunlight.
- Consider designating a special area for explosive chemical use. Store explosive chemicals in an explosive magazine or approved flammable safety cabinet and inspect areas weekly to comply with the Fire Code.
- Periodically check containers of chemicals that could become over-pressurized, like highly concentrated formic acid. Note: DO NOT release the pressure. Contact ISU EH&S or Ames Laboratory ESH&A immediately for assistance.
- As part of your group-specific safety training, make sure everyone who uses chemicals that are explosive or could become potentially explosive read the Material Safety Data Sheet (MSDS) and are thoroughly trained in safe storage methods, conditions to avoid (e.g., contamination), the hazards of the chemical, and disposal procedures.

4. Specific Storage and Testing Guidelines for Peroxide Forming Chemicals

4.1 About Peroxide Forming Chemicals

Many oxygenated organic compounds become increasingly 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. 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 autooxidation 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.

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 ether and other peroxide forming chemicals should be marked with date received and date opened. Mark these dates on the container using an indelible marker or attach a PEC warning label. Labels are available from Chemistry Stores (1351 Gilman) or ISU EH&S or Ames Laboratory ESH&A.

4.2 Testing Schedule for Peroxide Forming Chemicals

Persons using a peroxide forming chemical should either dispose of it or test it for peroxide content based on Table 1.

IMPORTANT! 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 peroxide concentrations less than 100 ppm, may be retained but should be tested every 6 months at a minimum. Testing results shall be recorded on the container. Test all peroxide formers prior to distillation, regardless of age. If peroxides are detected, at any concentration, the solvent shall be treated (see Appendix 3) prior to distilling.

IMPORTANT! Never test containers of unknown age or origin. Undated bottles may contain concentrated peroxides, or peroxides may have crystallized in the cap threads, which may explode when opening the bottle for testing. Call ISU EH&S or Ames Laboratory ESH&A for managing undated containers.

Table 1

Testing and Disposal Requirements for Peroxidizable Chemicals

(See Appendix 1 for Chemical List)

Status of Container	Testing & Disposal Requirement
Opened	Test every 6 months; dispose of any chemicals with > or equal to 100 ppm peroxides.
Unopened	Test at or before expiration date and every 6 months thereafter; dispose of any chemicals with > or equal to 100 ppm peroxides.

NOTES:

- 1) Exceptions are chemicals under an inert atmosphere, compressed gases in cylinders, and solvents such as ether and THF used as carriers for reducing agents.
- 2) It is recommended that a regular semi-annual testing schedule be set for peroxidizable chemicals (e.g. test all peroxidizable chemicals on January 1st and July 1st).

4.3 Dip Strips

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. Repeated cooling and heating cause condensation that will ruin the strips. Storage under dry, inert atmosphere will prolong the shelf life

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 other methods (except, perhaps, the titanium sulfate method)(NOTE: Literature from E. Merck indicates that their test strips will detect hydroperoxides and most higher peroxides, but some polyperoxides may be poorly detected

E. Merck and Aldrich Chemical companies make dip strips for the semi-quantitative detection of peroxides in aqueous solutions and organic solvents. 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. The Quantofix Peroxide 100, which has a range of 1-100 mg/l is recommended. Procedures for use are as follows:

For volatile organic chemicals:

- 1) Dip the test strip in the chemical for 1 second, so that the reaction zone is completely wetted.
- 2) Move the test strip to and fro until solvent has evaporated from the reaction zone.
 - a) dip into distilled water for 1 second, shake off excess water.OR
 - b) breathe on it 4 times each for 3-4 seconds

For aqueous solutions:

- 1) Dip the test strip in the chemical for 1 second, such that the reaction zone is completely wetted.
- 2) Remove the test strip, shake off excess liquid and compare the reaction zone with the color scale after 15 seconds.

NOTE: For aqueous solutions outside the pH range of 2-12, consult manufacturer's instructions. If peroxide level is >100 ppm, do not dilute. Call ISU EH&S or Ames Laboratory ESH&A to arrange for disposal.

NOTE: If test results are positive, for any concentration of peroxides **DO NOT DISTILL** before treating the peroxides (see Appendix 3 for treatment methods).

Vendor information:

Sigma-Aldrich Catalog No. Z10, 168-0 (package of 100)
Fischer Scientific Catalog No. 91312 (package of 100)
Chemistry Stores

WARNING! MAY FORM EXPLOSIVE PEROXIDES

For handling information consult: Potentially Explosive Chemicals *Guidelines for Safe Storage and Handling*.
Keep in tightly closed original container. Avoid exposure to light, air and heat.
If any crystals, discoloration, or layering are visible, do not open.
Contact ISU EH&S (294-5359) or AL ESH&A (294-2153) for assistance.

THIS CHEMICAL HAS A SHELF LIFE

Date received _____ Date opened _____

PEROXIDE TEST RESULTS

(If peroxides are present **DO NOT DISTILL** before treating)

Mandatory Testing Interval - 6 months

Date _____ Result _____ Initials _____ Date _____ Result _____ Initials _____

Date _____ Result _____ Initials _____ Date _____ Result _____ Initials _____

Date _____ Result _____ Initials _____ Date _____ Result _____ Initials _____

Section 5. Picric Acid & other di- and tri-nitro compounds

Di- and tri-nitro compounds are potentially explosive in certain situations. Picric Acid is probably the most common example of a tri-nitro compound found on the ISU campus. Picric acid is distributed by the manufacturers wet with greater than 10% water and is classified as a flammable solid. As the water evaporates over time, the substance becomes dry picric acid crystals. Dry picric acid is highly explosive especially when it is combined with metals such as copper, lead, zinc, and iron. It will also react with alkaline materials including plaster and concrete to form explosive materials. This material is shock sensitive and corrosive to metal containers. The following are guidelines for the use of picric acid at ISU:

- Make sure picric acid is kept wet! Check the hydration of your picric acid at least every six months.
- If a container of Picric Acid of unknown vintage is found, DO NOT attempt to open the container. The container could explode from friction on the crystals between the grooves of the cap and the threads. Contact ISU EH&S (294-5359) or AL ESH&S (294-2153) immediately for assistance.
- Be sure to clean the bottle neck, cap and threads with a wet cloth before resealing.
- Dispose of old bottles with metal caps.
- Do not store large amounts of picric acid.
- Dispose of bottles that have exceeded the expiration date.

Appendix 1

Representative Peroxide Forming Compounds

The compounds subject to peroxide testing and/or disposal are ethers and olefins/alkynes. Ethers are generally more important sources of peroxides themselves. However, alkenes (olefins) and alkynes are subject to polymerization reactions that can be very exothermic and thus occasionally be explosive. Representative compounds are listed below, but THIS LIST IS NOT AND SHOULD NOT BE CONSIDERED EXHAUSTIVE.

NOTE: *It is the researcher's responsibility to know whether a compound contains an ether or alkene functional group.*

Exceptions:

Despite its name "petroleum ether" is not an ether. Instead, it is a particular fraction of hydrocarbon distillate. It is thus NOT especially susceptible to peroxide formation.

Ethers

diethyl ether = ethyl ether

diisopropyl ether = isopropyl ether

tetrahydrofuran = THF

methyl *tert*-butyl ether = MTBE

allyl ether

Any other compound with the word "ether" in the name

phenetol or derivatives

anisole or derivatives

dioxane

Any compound with these word/prefixes:

methoxy

ethoxy

propoxy

butoxy

Olefins/Alkenes and Alkynes

Compounds containing the following words/segments:

ethylene

ethane

acetylene

propylene

butene

pentene

hexane

heptene

octene

nonene

decene

ethyne

propyne

butyne

pentyne

hexyne

heptyne

octyne

nonyne

decyne

acrolein

acrylate

allyl

diene

enyne

diyne

propargyl

vinyl

Appendix 2

Additional PEC Detection Methods

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.

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 and should only be conducted by an experienced chemist.

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 TiO_2 in hot concentrated sulfuric acid and adding this to an equal volume of water.

Appendix 3

PEC Treatment Information

As stated previously, prudent chemical management practices include the purchase of a minimum amount of a chemical and consumption or disposal prior to the expiration date or other time-sensitive information. 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.

The following is a discussion of several treatment methods:

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 FeSO_4 , 6 mL concentrated H_2SO_4 , and 110 mL water are a standard solution. Another formulation is 100 g FeSO_4 , 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.

REFERENCES

1. *Guidelines for Explosive & Potentially Explosive Chemicals – Safe Storage & Handling*, Office of Environment, Health & Safety, UC Berkeley (used with permission)
2. *Prudent Practices for Disposal of Chemicals from Laboratories*, Appendix I, National Academy Press, Washington, DC, 1983, pp. 245-246.
3. Kelly, R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals," *American Chemical Society–Chemical Health & Safety*, 1996, 4(5), pp. 33-36. Used with permission.
4. Cameron, Mark. "Picric Acid Hazards", found as PDF document on the Web.

DISCLAIMER

Iowa State University, Department of Environmental Health and Safety (EH&S), Ames Laboratory Environment, Safety, Health and Assurance (ESH&A) and their employees assume no legal liability for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed in this document.