Time-sensitive Chemicals

UTK Environmental Health & Safety Guide LS-021

Document Contact: Laboratory Safety Services
Date effective: July 1, 2022
Revision Date: July 1, 2022

Purpose

Some laboratory chemicals can become dangerous over time. The danger can be due to chemical reactions, over-pressurization of containers, increased toxicity, or other hazardous properties. For this reason, the proper handling and storage of time-sensitive chemicals are of particular importance. This document will provide guidance on proper storage, handling, and disposal of time-sensitive chemicals. The list of time-sensitive chemicals includes:

- Peroxide-forming chemicals (diethyl ether, tetrahydrofuran, sodium amide, etc.)
- Picric acid and other multi-nitrated aromatics
- Chloroform
- Time-sensitive compressed gas cylinders (e.g., hydrogen fluoride, anhydrous; hydrogen bromide, anhydrous; hydrogen sulfide, anhydrous; hydrogen cyanide, anhydrous; hydrogen chloride, anhydrous)
- Formic acid
- Alkali metals (e.g., potassium, sodium, and lithium)

Scope and Applicability

This guidance shall apply to all research and teaching laboratories and academic shops and maker spaces on the Knoxville campus of the University of Tennessee.

This shall apply to all students, staff and faculty on the Knoxville campus of the University of Tennessee.

Definitions and Abbreviations

Definitions

Butylated hyroxytoluene (dibutylhydroxytoluene) – chemical used to prevent radical-mediated oxidation. Chemical used to slow peroxide formation in organic ether, solvents, and laboratory chemicals.

Multi-nitrated aromatics – aromatic compounds containing at least two nitro (-NO2) functional groups attached directly to a benzene ring (e.g., dinitrotoluene, picric acid, dinitrophenol). Chemicals are sensitive to shock and friction and may explode.

Peroxide-forming chemicals – organic solvents that can react with atmospheric oxygen to undergo autoxidation or peroxidation, producing unstable and dangerous organic peroxides and hydroperoxides (e.g., diethyl ether, tetrahydrofuran, 1,4-dioxane). Substances which have undergone peroxidation are sensitive to thermal or mechanical shock and may explode violently.

Abbreviations

BHT: Butylated Hydroxytoluene (dibutylhydroxytoluene)

EHS: Environmental Health and Safety

HBr: Hydrogen Bromide (hydrobromic acid)

HF: Hydrogen Fluoride (hydrofluoric acid)

IDLH: Immediately Dangerous to Life or Health

PPM: Parts per Million

PSI: Pounds per Square Inch

Peroxide-forming Chemicals

Peroxide-forming chemicals can react with atmospheric oxygen to undergo autoxidation or peroxidation, producing unstable and dangerous organic peroxides and hydroperoxides. Peroxide-forming chemicals include aldehydes, ethers (especially cyclic ether), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl, and vinylidine compounds. A list of these chemicals can be found in **Appendix A** – Lists A, B, and C.

Formation of peroxides is accelerated by light and heat. Substances which have undergone peroxidation are sensitive to thermal or mechanical shock and may explode violently. All laboratory workers must learn to recognize and safely handle peroxidizable compounds. Contact EHS if any of the following visual cues for possible peroxide formation exist: mossy look around the cap; white film or residue around the neck, threads or cap; crystals in liquid; discoloration; or surface crust for solid peroxide formers.

Safe Handling and Usage

- Purchase peroxide forming chemicals in limited quantities. Whenever possible, purchase material that contains an appropriate peroxide inhibitor or stabilizer, such as butylated hydroxytoluene (BHT) or ethanol.
- Label peroxide-forming substances appropriately with the date the container was received, the date it was first opened, and the date and concentration of any peroxide testing. Include a notice such as **Warning Peroxide-Former** on the container.
- Store peroxide-forming chemicals appropriately:
    - Store peroxides and peroxide-forming compounds according to the manufacturer's recommendations, away from light and heat.
    - If storing peroxide formers in a refrigerator, the refrigerators must be designed for the storage of flammable substances. Do not use domestic refrigerators to store flammable liquids.
    - Peroxide formers containing inhibitors (e.g., BHT or ethanol) should not be stored under an inert atmosphere as the inhibitor requires oxygen to function properly.
    - Store non-inhibited peroxide formers under an inert atmosphere of nitrogen or argon and test it for peroxides at least once a month (see below).
- Check for the presence of peroxides while in storage based on the suggested shelf-life using peroxide test strips.
    - If peroxides are found at a concentration <100 parts per million (ppm), the material must be treated (to remove peroxides) or stabilized (to prevent further peroxide formation) and turned in to UTK EHS for your respective campus for disposal. The date of treatment or stabilization must be written on the label. If >100 ppm peroxides are found contact UTK EHS for assistance. See disposal instructions below.

  - The date and results of any testing must be placed on the container label.
- Never use a metal spatula with peroxides. Contamination by metals or disturbance of the crystals can lead to explosive decompositions.
- Do not distill, evaporate or concentrate the material until you have first tested the material for the presence of peroxides. Peroxides are usually less volatile than their parent material and tend to concentrate in the (hot) distillation pot.
- **Do not open or test the contents of the container** if 1) crystals are visibly present on or in the container or lid, 2) if a precipitate has formed or an oily viscous layer is present, or 3) if the container has been opened but not tested and is more than two years old. The friction of unscrewing the cap could detonate the bottle and cause severe injury. Contact UTK EHS (865-974-5084 or ehs_labsafety@utk.edu) for assistance.

High-Hazard Work Practices with Peroxide-forming Chemicals

Certain high-hazard procedures may increase the likelihood of peroxide detonation (e.g. concentration, distillation, etc.). Before these procedures, always check peroxide-forming chemicals for peroxides or impurities that could increase the risk. Also determine whether the procedure will remove the inhibitor and determine how you will stabilize the solvent after the procedure is finished.

- Obtain documented prior approval from the principal investigator.
- Perform a hazard assessment to include age of material, inhibitor status, peroxide level of the solvent or chemical in question. List the process in Appendix A, Section 7 (Prior Approvals) form of the laboratory-specific chemical hygiene plan.
- High-hazard procedures with peroxide forming chemicals (e.g. distillation) must never be performed alone.
- Test for peroxides before distilling; do not distill if the test shows > 20 ppm peroxides.
- Distill under an inert atmosphere and set up your distillation apparatus with Teflon sleeves between glassware joints to reduce friction as peroxides may accumulate in glassware joint during distillation.
- Never distill to dryness. Stop distillations of a peroxide forming chemical when 20% of starting volume remains or add a nonvolatile oil such as mineral oil, which ensures going to dryness is not possible and also can help dilute any peroxides formed in the distillation pot.
- Be cautious agitating or shaking the distillation pot. Do not refrigerate/freeze the remaining solvent.
- Distillation removes inhibitors so it is important to add an inhibitor post-distillation or sparge and store the distillate with inert gas.

Disposal of Peroxide Forming Chemicals

- Dispose of List A peroxidizable solvents (see Appendix A) within one year of purchase if unopened or within 3 months of the opening.
- List B or C peroxide-forming substances greater than 1 year old and less than 2 years old are to be tested for peroxide formation using peroxide test strips at least quarterly. The peroxide concentration and date tested should be recorded on the bottle. If the peroxide concentration is less than 100 ppm add 1 teaspoon of hydroquinone per pint of solvent to prevent further peroxide formation and contact UTK EHS for disposal. If the concentration is greater than 100 ppm contact UTK EHS for assistance. If the peroxide former is expired and over 2 years old, it must be properly disposed of through UTK EHS.
- If the peroxide-forming substance is greater than 2 years old and less than 5 years old **do not open the container** to check for peroxide concentration. Contact UTK EHS for assistance.

- **If the container is greater than 5 years old, do not move the container at all**. Contact UTK EHS for assistance.

Picric Acid and Multi-nitrated Aromatics

Picric acid and its derivatives should be stored in small quantities, within the original container, and in a cool, dry, well-ventilated area away from heat sources. Picric acid is considered a flammable solid and is incompatible with oxidizers, reducing agents, inorganic salts, metals, alkaloids and albumin. Improperly managed or stored picric acid may become sensitive to shock, friction, and heat.

Picric acid must be monitored for water content every three months. The material should look like a wet paste. Picric acid allowed to dry out to less than 10% water by volume may be unstable and explode if agitated. **If the material appears dry, pale in color, or crystalline, do not open or handle the container. Immediately contact the UTK EHS Office: 865-974-5084.**

Do not use a metal spatula when working with any polynitrated aromatics.

Dispose of unused picric acid as hazardous waste within two years of receipt.

Chloroform

Chloroform ($CHCl_3$) reacts with air to form phosgene gas (CCl_2O), a decomposition product which has a very low IDLH (immediately dangerous to life or health) value of 2 ppm. Phosgene exposure can cause damage to the central nervous system, and can be fatal. Decomposed chloroform will have a normal appearance. To reduce risks:

- Always open/work with chloroform in a fume hood!
- If possible, purchase chloroform stabilized with ethanol (shelf-life is approximately 5 years).
- If non-stabilized chloroform, or chloroform stabilized with amylene (shelf-life < 12 months), is necessary for the procedure(s), purchase in limited volumes.
- Immediately dispose expired chloroform as hazardous waste. Unless otherwise indicated by the manufacturer's expiration date, dispose of non-stabilized chloroform within 6 months of opening.

Time-sensitive Compressed Gas Cylinders

Compressed gases such as hydrogen fluoride (HF), hydrogen bromide (HBr), hydrogen sulfide, hydrogen cyanide, and hydrogen chloride (all anhydrous forms) have a short shelf-life provided, typically defined by the manufacturer, which must be strictly adhered to. Over time, moisture can slowly enter the cylinder, which initiates corrosion. As the corrosion continues, HF and/or HBr slowly react with the internal metal walls of the cylinder to produce hydrogen. The walls of the cylinder weaken due to the corrosion, while at the same time the internal pressure increases due to the hydrogen generation. The potential exists for pressure increases of several hundred pounds to occur during the recommended storage time frame. Ultimately, these cylinders fail and create extremely dangerous projectiles and toxic gas release.

All time-sensitive compresses gases must be disposed in accordance with the expiration date indicated by the manufacturer. Lecture bottles have a typical working pressure of 1800 psi and these chemicals have a 2 year shelf life.

Formic Acid

Formic acid (90-100% CH_2O_2) decomposes to form carbon monoxide and water ($CO + H_2O$). Pressure greater than 100 psi can develop with prolonged storage of 1 year or greater which is sufficient to break a sealed glass container. Vent containers frequently and read the product literature. Some have pressure relief caps and some Safety Data Sheets may recommend refrigeration.

Alkali Metals

The alkali metals (such as potassium, sodium, lithium and sodium-potassium alloys) can react with dissolved oxygen when stored under mineral oil to form oxides and superoxides that can catch fire upon cutting. The oxidation forms a yellow or orange crust or coating. Lithium stored under nitrogen can form nitrides, which are autocatalytic and can eventually autoignite. Lithium nitride often appears as a dark-colored tarnish. Alkali metals should be checked every 6 months for signs of oxidation (or nitride formation). Dispose of alkali metals that exhibit signs of oxidation (or nitride formation) immediately.

Please contact the EHS office at ehs_labsafety@utk.edu or (865) 974-5084 if you need clarification on this or any other chemical safety or hazardous waste procedures.

References and Related Documents

29 CFR 1910.1450, OSHA Standard, Occupational Exposure to Hazardous Chemicals in Laboratories

LS-001 Laboratory Health & Safety Program

LS-020 Chemical Hygiene Plans

If you do not have access to one of these resources, contact UTK EHS Lab Safety Services (ehs_labsafety@utk.edu or 865-974-5084) for more information.

- NRC Prudent Practices – Chapter 6.G.3 Organic Peroxides
- Bailey, J., D. Blair, L. Boada-Clista, D. Marsick, D. Quigley, F. Simmons, and H. Whyte, Management of time-sensitive chemicals (I): Misconceptions leading to incidents. *Chemical Health & Safety* **2004** *11* (5), 14-17. DOI: 10.1016/j.chs.2004.05.014
- Bailey, J., D. Blair, L. Boada-Clista, D. Marsick, D. Quigley, F. Simmons, and H. Whyte, Management of time-sensitive chemicals (II): Their identification, chemistry and management. *Chemical Health & Safety* **2004** *11* (6), 17-24. DOI: 10.1016/j.chs.2004.05.017

Disclaimer

Appendix A: Time-Sensitive Chemical Lists

List A: Chemicals that form explosive levels of peroxides without concentration (3 months)[1]		
Butadiene[2] (106-99-0)	Isopropyl Ether (108-20-3)	Tetrafluoroethylene[2] (116-14-3)
Chloroprene[2] (126-99-8)	Potassium Metal (7440-09-7)	Vinylidene Chloride (75-35-4)
Divinyl Acetylene (821-08-9)	Sodium Amide (7782-92-5)	
List B: Chemicals that form explosive levels of peroxides on concentration (12 months)[1]		
1,1-Dimethoxymethane (109-87-5)	Benzyl alcohol (100-51-6)	Di-n-propoxymethane (505-84-0)
1,2-Epoxy-3-isopropoxy propane (4016-14-2)	Benzyl n-butyl Ether (588-67-0)	1,4-Dioxane (123-91-1)
1,2-Dibenzyloxyethane (622-22-0)	Benzyl Ether (103-50-4)	Diethyl Ether (60-29-7)
1-Phenylethanol (98-85-1)	Benzyl Ethyl Ether (539-30-0)	Ethylene Glycol Dimethyl Ether (110-71-4)
2-Butanol (78-92-2)	Benzyl 1-naphthyl Ether (607-58-9)	Isoamyl Ether (544-01-4)
2-Hexanol (626-93-7)	Cumene (98-82-8)	Isophorone (78-59-1)
2-Methyl-1-butanol (137-32-6)	Cyclohexene (110-83-8)	Methyl Isobutyl Ketone (108-10-1)
2-Penten-1-ol (1576-95-0)	Cyclooctane (292-64-8)	Methyl Acetylene (74-99-7)
2-Phenylethanol (60-12-8)	Decahydronapthalene (91-17-8)	Methylcyclopentane (96-37-7)
2-Propanol (67-63-0)	Diacetylene (460-12-8)	Other secondary alcohols (N/A)
4-Heptanol (589-55-9)	Diallyl Ether (557-40-4)	p-Dibenzyloxybenzene (621-91-0)
4-Methyl-2-pentanol (108-11-2)	Dicyclopentadiene (77-73-6)	p-Isopropoxypropionitrile (110-47-4)
4-Penten-1-ol (821-09-0)	Diethoxymethane (462-95-3)	Tetrahydrofuran (109-99-9)
Acetal (105-57-7)	Diethyl acetal isoamyl benzyl ether (N/A)	Tetrahydronaphthalene (119-64-2)
Acetaldehyde (75-07-0)	Diethylene Glycoldimethyl Ether (diglyme) (111-96-6)	Vinyl Ethers (N/A)
Allyl Ether (557-40-4)	Dimethoxymethane (109-87-5)	
List C: Chemicals that may autopolymerize as a result of peroxide accumulation (12 months)[1,3,4]		
Acrylic Acid (79-10-7)	Methyl Methacrylate (80-62-6)	Vinyl Chloride (75-01-4)
Acrylonitrile (107-13-1)	Styrene (100-42-5)	Vinylidene chloride (75-35-4)
Butadiene[2] (106-99-0)	Tetrafluoroethylene[2] (116-14-3)	2-Vinyl Pyridine (100-69-6)
Chloroprene[2] (126-99-8)	Vinyl Acetate (108-05-4)	4-Vinyl Pyridine (100-43-6)
Chlorotrifluoroethylene (79-38-9)	Vinyl Acetylene (689-97-4)	
List D: Other Time-sensitive Chemicals (varies)[5]		
Acetylene (74-86-2)	Ethylene oxide (75-21-8)	Nitrogen triiodide (13444-85-4)
Ammonium Nitrate (6484-52-2)	Germanium (7440-56-4)	Nitrogen trichloride (10025-85-1)
Ammonium Perchlorate (7790-98-9)	Hexanitrodiphenylamine (131-73-7)	Nitroglycerin (55-63-0)
Ammonium Picrate (131-74-8)	Hexanitrostilbene (20062-22-0)	Nitrogylcol (628-96-6)
Calcium Nitrate (10124-37-5)	Hydrazine (302-01-2)	Nitroguanidine (556-88-7)
Chloroform (67-66-3)	Hydrazoic acid (7782-79-8)	Nitrourea (556-89-8)
Dinitrotoluene (121-14-2)	Hydrogen Compound Gases (NA)	Perchloric acid (7601-90-3)
Dinitrophenol (51-28-5)	Lead styphnate (15245-44-0)	Picric acid (88-89-1)

1. Safe storage periods are given for an open container of each class of peroxidizable material. Unopened containers from the manufacturer have a safe storage period of 12 months.
2. When stored in liquid form these chemicals may form explosive levels of peroxides without concentration. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.
3. If chemical from List C is inhibited, do not store under an inert atmosphere. Oxygen is required for inhibitor to function.
4. Uninhibited chemicals from List C have a safe storage period of 24 hours.
5. Please refer to the Time-sensitive Chemicals guide for more details on safe storage and shelf life.