Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Peroxide-forming chemicals

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1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory person (DLPs), and all staff and students who direct or participate in the use of chemicals that are prone to forming explosive peroxides over time, particularly after frequent or prolonged exposure to air and light.

2 Disclaimer

Please read this SMOU in conjunction with the Chemical Risk Management Guidelines.

The Safety Data Sheet (SDS) should be consulted for specific information about the chemical you will be using. The Gold FFX SDS Database is available on the Library database. Instructions on how to source this information can be found on the Health, Safety and Wellbeing Databases website:

https://www.auckland.ac.nz/en/health-safety-wellbeing/health-safety-topics/laboratory-safety/chemical-safety/databases.html

Note: 'Shall' denotes a mandatory requirement and 'should' denotes a recommendation.

For more detailed information, please see the references at the end of this document.[1-5]

3 Risks of peroxide-forming chemicals

Peroxide-forming chemicals may react with oxygen to form unstable peroxides, which may detonate with extreme violence when they become concentrated by evaporation or distillation. These may also form a detonable mixture when combined with other chemicals, that may explode when disturbed by heat, shock, or friction.

Peroxides formed in chemicals by auto–oxidation have caused many accidents and injuries. These include the unexpected explosions of the residue of solvents after distillation, and explosions when removing the rotary evaporator solvent trap after concentrating peroxide-containing material. Common solvents such as diethyl ether,

tetrahydrofuran and isopropanol have exploded upon distillation due to peroxide concentration.

Factors that increase the risk of peroxide formation/explosion are:

- Exposure to light/air/heat
- Containers in frequent use
- Prolonged storage
- Extensive evaporation, containers not properly sealed
- Distillation
- No inhibitors present

WARNING: Do not open containers of unknown age or origin. Old bottles may contain concentrated peroxides, or peroxides may have crystallised in the cap threads, presenting a serious hazard when opening the bottle for testing.

Do not open any containers with precipitate around the lid, crystals inside, visible discoloration, or liquid stratification. Contact the Chemical Safety Advisor.

4 Responsibilities of Chemical Owners

Chemical Owners of peroxide-forming chemicals shall ensure peroxidisable chemicals are appropriately handled and monitored. This includes:

- Ensuring lab users are aware of storage and handling best practice.
- Peroxide testing is performed and recorded annually as required. Peroxide testing dip sticks can be purchased for easy testing.
- Decanted containers are kept track of, well labelled, and disposed when no longer needed.
- Old, expired, and/or unneeded peroxidisable chemicals are disposed of before they become a liability.
- Anyone using the chemicals in a high-risk process such as distillation, is aware of safe handling (see section 6.1 below).

5 Management of classes of peroxide-forming chemicals

Peroxide-forming chemicals are categorised based on their hazards, and each group needs to be treated slightly differently. [1-3] See the Appendix for more details on the types of chemicals likely to be peroxide-formers.

Group A: Chemicals that form explosive levels of peroxides without concentration by evaporation or distilling.

These present a serious shock-sensitive peroxide hazard after prolonged storage, especially after exposure to air.

- ➔ Do not open old containers that have not been regularly tested for peroxides. Get these disposed of.
- ➔ Test for peroxide formation before use, always before distilling. Recommended to discard 3 months after opening or by manufacturer expiry date.
- ➔ Do not store these chemicals long-term, even if unopened

Butadiene (liquid monomer)	**Diisopropyl ether – notorious for causing explosions***
Vinylidene Chloride (1,1-dichloroethylene)	Chloroprene (liquid monomer)
Tetrafluoroethylene (liquid monomer)	Divinylacetylene

* **Diisopropyl ether** forms peroxides that may not be detected by peroxide tests, therefore it is recommended to dispose of this within 3 months of opening.

Inorganic peroxides also pose an explosive hazard when concentrated. The following Group A peroxide-forming chemicals are solids, therefore are not practical to test for peroxides. Care must be taken with their use and storage.[2]

Potassium metal	Potassium amide	Sodium amide

Group B: Chemicals that form explosive levels of peroxides on concentration.

These typically only present a hazard when evaporated, distilled or otherwise treated to concentrate peroxides present in the solvent.

- ➔ These should be tested for peroxides every 12 months after opening, or every 18 months where inhibitors are present.
- ➔ THF or diethyl ether that has had inhibitors removed can form significant levels of peroxides within a few days.
- ➔ Do not distil, significantly concentrate, or evaporate large amounts without being sure these are free of peroxides.

The list below includes the peroxide-forming Group B chemicals that are most common at the University. For a more complete list, use SciTrack to interrogate your inventory (see Section 7).

Benzylic secondary alcohols e.g. alpha-methylbenzyl alcohol (1-phenylethanol)	2-Butanol	Dimethoxyethane
Glycol ether solvents e.g. Diethylene glycol dimethyl ether	Cumene	1,4- and 1,3-Dioxane
Secondary alcohols e.g. cyclohexanol, 2-butanol, 2-pentanol	Cyclohexene	Isopropanol*
Vinyl ethers e.g. ethyl vinyl ether	Decahydronaphthalene (Decalin)	2-Methoxyethanol
Acetal	Dicyclopentadiene	3-Methyl-1-butanol
Acetaldehyde	Diethyl ether	4-Methyl-2-pentanone
Benzyl alcohol	Diethoxymethane	Tetrahydrofuran
Benzyl ethers	Dimethoxymethane	Tetrahydronaphthalene

* **Isopropanol** has caused explosions when distilled due to accumulated peroxides.[6] However if isopropanol is used only for cleaning or other purposes that do not involve heating, reacting, distillation or significant evaporation, and is stored in the dark in a well-sealed container, it should not need testing. Please contact the Chemical Safety Advisor if you have any questions.

Group C: Chemicals that may exothermically polymerise, if peroxides are accumulated and decompose.

- ➔ **These can explode during storage.**
- ➔ Where these contain inhibitors, do not store under inert gas.
- ➔ If treated to remove inhibitors, these chemicals should be used immediately and not stored, except in very small quantities (<10 g or 10 mL) for up to 24 hours.
- ➔ These should be disposed of by the manufacturer's expiry date, or within 12 months of purchase if no expiry date.
- ➔ Some guidance recommends testing liquids every 12 months, however note that peroxide testing is often unreliable for these chemicals as it does not detect all the types of peroxides that may form. Therefore do not open or distil old bottles of these chemicals!

Acrylates including ethyl, methyl acrylate	Chlorotrifluoroethylene	Vinyl acetate
Acrylic acid	Divinylacetylene	Vinyl chloride
Acrylonitrile	Methyl methacrylate	Vinylacetylene
Butadiene (gas)	Styrene	Vinylidiene chloride
Chloroprene (gas)	Tetrafluoroethylene (gas)	Vinylpyridine

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

- ➔ The following list of chemicals is not exhaustive. Safety data sheets state which chemicals are likely to form peroxides.
- ➔ Any liquid should be tested every 12 months for peroxides.

(2-Bromoethyl)benzene	4'-Methoxyacetophenone	Diethylene glycol monoethyl ether acetate
1,2-Bis(2-chloroethoxy)ethane	4-Methyl-2-pentanone	Dihexyl ether
1,2-Epoxy-3-phenoxypropane	Acetal	Dipentene
1-Octene	Acrolein	Dipentyl ether
2-Chloroethyl ether	Allyl ethyl ether	Ethyl 3-ethoxypropionate
2-Ethoxyethyl acetate	Benzyl isoamyl ether	Glycidyl isopropyl ether
2-Ethyl-1-butanol	Bis(2-butoxyethyl) phthalate	Isophorone

2-Ethylhexanal	Bis(2-ethylhexyl) adipate	Limonene
2-Methoxyethyl acetate	Bromomethyl methyl ether	Phenoxyacetyl chloride
3-Ethoxypropionitrile	Chloroacetaldehyde solution	tert-Butyl methyl ether
3-Methoxybutyl acetate	Chloromethyl methyl ether	Tetraethylene glycol dimethyl ether
3-Methoxypropionitrile	Diethyl ethoxymethylenemalonate	Tetrahydropyran
3-Pentanone	Diethyl fumarate	Vinylene carbonate

6 Storage and Use

1) Store peroxide-forming chemicals away from light. Amber bottles or other opaque containers are ideal.
2) Store uninhibited peroxide-forming chemicals under nitrogen or argon gas.
3) Decant into small containers that can be completely emptied, rather than taking small amounts from a large container over time. This is to reduce evaporation and exposure to oxygen.
4) If unopened, general guidance is to dispose of peroxide-forming chemicals by manufacturer's expiry date, or if no expiry then within 2 years of purchase.
5) Containers should be marked with the date they are opened and with the date of required disposal and/or testing. Mark these dates on the container using an indelible marker or attach a warning label such as the one below:

Warning: May Form Explosive Peroxides

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

Check for peroxides before distilling or concentrating.

This Chemical Has a Limited Shelf Life!

Date Received _____Date Opened_____

Dates Tested for Peroxides _____

_____

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

6.1 Testing for peroxide formation

Implement a regular testing plan for all peroxide-forming chemicals, based on the type of peroxide-formers you have (refer to section 5). Peroxide test strips can be purchased from SciTrack suppliers.

- If in doubt, do not open to test (see boxed warning on Page 4).
- Follow the manufacturer's instructions when performing peroxide testing using dip sticks. Different techniques may be required for volatile vs non-volatile liquids.
- Dispose of any liquids that show >100 ppm peroxides when tested.
- Note that the generally-accepted 100 ppm peroxide limit has no real scientific backing, therefore it may be overly cautious in some cases. Conversely it does not mean there is no risk from solvents with peroxides tested to be less than 100 ppm.

6.2 Distillation

Distillation of peroxide-forming solvents has the potential to cause an explosion.

- Before distilling any Group A-C chemicals, perform a peroxide test. Do not distil any with > 100ppm peroxides, or any that appear to have crystals inside, visible discoloration, or liquid stratification.
- Distil behind a blast shield.
- Keep air out of distillation operations.
- Do not distil to dryness. Leave at least 10% behind and dispose of this.
- Do not distil isopropanol that has been stored in the light.

6.3 Peroxide inhibitors

Inhibitors (e.g. BHT, butylated hydroxytoluene) are often added to peroxide-forming solvents. These scavenge adventitious peroxides, increasing the safe shelf-life of peroxide-forming chemicals.

Note:

- Do not refrigerate inhibited chemicals unless recommended by the manufacturer.
- Phenolic inhibitors (e.g. BHT) require some oxygen to work, therefore do not store chemicals inhibited with these under inert gas.
- Inhibitors are expended over time. If inhibited chemicals are kept for a long time, unless the amount of inhibitor is able to be tested, the chemical needs to be treated as uninhibited.

7 Identifying and Reporting on Peroxide-Forming Chemicals in SciTrack

SciTrack can help you identify peroxide-forming chemicals in your lab.

7.1 SciTrack Container Search for Chemicals on a List

Refer to SciTrack Quick Guide 10. Container Search and Operations for detailed instructions on how to use Container Search.

1) In SciTrack go to Container Search, then select the Advanced Search tab.
2) Select the location of the lab(s) of interest
3) Open up the Materials section and click the List Names box. Either type a name to filter or scroll to choose from the drop-down. Click on one or more of the following lists to select them:
- **Peroxide-forming chemicals (Groups A-D)**
4) Click Search

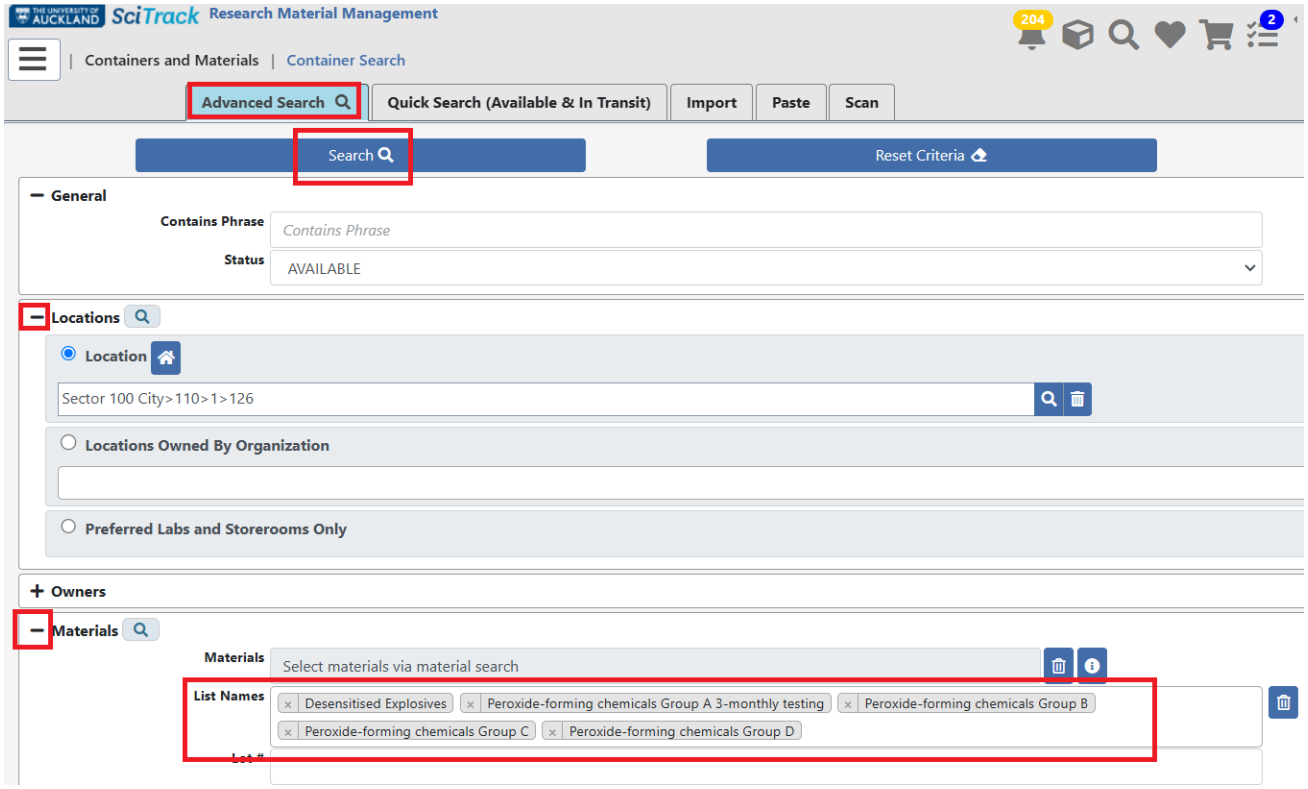

FIGURE 1: ADVANCED CONTAINER SEARCH SCREENSHOT FROM SCITRACK

7.2 Set Up a Report to be Emailed Periodically

You can set up a Container Inventory Report to be emailed to you periodically, with a list of peroxide-forming chemical containers in your lab. See SciTrack Quick Guide 12. Advanced features for further instructions.

1) From the SciTrack menu, choose Reports > Schedule Report
2) From the Activity Reports section, select Container inventory Report
3) In the Emails section, type the email address you want the report to be sent to
4) Directly below the Emails section, click "Day of Week", "Day of Month" or "Day of Quarter" to choose when and how often you want to receive these emailed reports.
5) Select one or more locations of interest and/or a container owner
6) Select Container Status: Available
7) Under Regulations (Multi), select the hazardous chemical lists you want to search on. Hold Ctrl button while clicking to select multiple lists

For assistance with this, please contact scitrack@auckland.ac.nz

References

1. Kelly, R. J., Review of Safety Guidelines for Peroxidizable Organic Chemicals. *Chemical Health & Safety* **1996,** *3* (5), 28-36.
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4. Carolina, U. o. S. USC EH&S Peroxide Formers Guidance, Public Spreadsheet. http://tiny.cc/usc-peroxide-spreadsheet (accessed 9 Feb 2024).
5. Environmental Health & Safety, U. o. W. EH&S GUIDELINES FOR PEROXIDE FORMING CHEMICALS 2022. https://www.ehs.washington.edu/system/files/resources/Peroxide_Forming_Chemicals.pdf (accessed 09/02/2024).
6. Cismesia, M. A.; Vásquez Céspedes, S., Reconsidering the Safety Hazards Associated with Peroxide Formation in 2-Propanol. *Organic Process Research & Development* **2022,** *26* (6), 1558-1561.

8 Appendix

Common classes of compounds that form peroxides include:

1. Ethers, acetals, and ketals (ketones), especially cyclic ethers and those with primary and secondary alkyl groups
2. Aldehydes, including acetaldehyde and benzaldehyde
3. Compounds containing benzylic hydrogens
4. Ureas, amides and lactams with an α-hydrogen on a carbon attached to nitrogen ($RCONHCHR_2$).
5. Compounds containing allylic hydrogens (C=C-CH), including most alkenes, vinyl and vinylidene compounds.
6. Compounds containing a 3° C-H group (decalin and 2,5-dimethylhexane)