Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Management of Time-Sensitive Chemicals

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1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory persons (DLPs), and all staff and students who direct or participate in the use of time-sensitive chemicals at the University of Auckland.

2 Disclaimer

Safety Data Sheet (SDS) Databases should be consulted for specific information about the compound you will be using. 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

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

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

3 Time-Sensitive Chemicals

Over time, some laboratory chemicals degrade and/or become unstable. These time-sensitive chemicals have caused incidents in many laboratories, such as:

- Bottles exploding while in storage, or when being opened.
- Chemicals bursting and spraying out of containers.
- Explosions during use in lab processes

To reduce these risks, perform regular clear-outs of old chemicals that are unlikely to be used. Dispose through the University's chemical waste contractor.

Examples of time-sensitive chemicals and specific measures to be taken are shown in the following sections.

3.1 Chemicals known to be unstable after prolonged storage

These chemicals may degrade over time, producing gas (sometimes toxic) that creates internal pressure. This may lead to rupture of the container.

3.1.1 Identification

There is not an exhaustive list of these. They may be identified by:

- Safety Data Sheet, section 7 for Handling and Storage specifies that the material decomposes to produce gas.
- A sticker or warning label on the container stating that internal pressure may be generated.

See Appendix I for a representative list of these chemicals, or refer to section 3.5 for how to search SciTrack for chemicals on the list "Unstable on prolonged storage".

Some common examples include:

Formic acid when highly concentrated (>90%) can decompose upon prolonged storage to form carbon monoxide gas. The formation of gas can cause explosion of the container. Containers should have self-venting caps; dispose of any that are old and do not have these.

Chloroform degrades if exposed to sunlight, producing phosgene gas which is a nerve gas. If stabilised with ethanol, it is safer for longer. Otherwise it should be disposed 1 year after purchase.

Hydrogen peroxide degrades when exposed to light or organic compounds, forming oxygen gas. It should be stored in an opaque plastic container with a vented lid in the fridge.

3.1.2 Important management steps

- Check all chemical containers annually to ensure they appear in good condition with no bulging or crusting around the lid.
- Dispose of old containers, especially if past a marked expiry date.

- If opening old chemicals of this class, only open in a fume hood behind a blast shield, pointing the lid away from you.
- If there is a marked expiry date on the container, enter this in SciTrack. Search for the barcode in Container Search, and click the edit icon, to add the date.

3.2 Desensitised explosives

Please refer to SMOU Picric Acid for more detail about managing picric acid.

Desensitised explosives are sold with a certain percentage of water or other desensitising agent included to inhibit explosivity. Alternatively, these are supplied as a dilute solution. The required storage condition must be maintained through regular checking. Please check the SDS for specific advice for each chemical.

3.2.1 Identification

Desensitised explosives will contain a warning in their Safety Data Sheet that they are explosive when dry. They may also have a UN Transport shipping label called "Desensitized explosive". See Appendix II for a representative list of these chemicals, or refer to section 3.5 for how to search SciTrack for chemicals belonging to the list "Desensitised explosives". Always check the SDS for specific instructions.

Some common examples include:

Substance	**Required storage condition**
Cellulose nitrate or Collodion	Keep in solution
2,4-Dinitrophenylhydrazine	33% water
HOAt (1-Hydroxy-7-azabenzotriazole)	Keep in solution
4-Nitrophenylhydrazine	10% water
Picric acid (2,4,6 Trinitrophenol)	30% water
Picrylsulfonic acid	Check supplier SDS
Tetrazole	Keep in solution

3.2.2 Important Management Steps

- **Do not open any containers that appear to have dried out.** Check for dry powder around the lid before opening.
- Implement a monitoring system to check water/moisture levels (or other required storage condition as per the SDS) every 3 months.
- For those desensitised with water it is advisable to store containers inside a larger container that has water in it, to maintain a moist environment.
- Contact the Chemical Safety Advisor if you find containers that may be dried up.

3.3 Peroxide-forming chemicals

Please refer to SMOU Peroxide-forming Chemicals for more details.

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.

3.3.1 Identification

See **SMOU Peroxide-forming Chemicals** for lists of these chemicals. The Safety Data Sheet for these chemicals will state that peroxides may form.

Common examples of peroxide-forming chemicals include:

- Diisopropyl ether
- Diethyl ether
- Tetrahydrofuran

3.3.2 Important management steps

- Label bottles with date of receipt and date opened.
- Test annually for peroxide formation, or dispose. Always test for peroxides before distilling, concentrating, or evaporating these solvents.
- Store away from light

- If there is a marked expiry date on the container, enter this in SciTrack. Search for the barcode in Container Search, and click the edit icon, to add the date.

3.4 Chemicals that may undergo hazardous polymerisation in storage

Please refer to SMOU Peroxide-forming Chemicals, section "Group C" for more details.

These chemicals may polymerise, generating heat and pressure that may cause containers to explode. Polymerisation may be initiated by peroxide formation during prolonged storage.

3.4.1 Identification

See **SMOU Peroxide-forming Chemicals Group C** for a list of these chemicals.

Examples of these include:

- Vinyl acetate
- Methyl and ethyl acrylate

3.4.2 Important management steps

- Check containers annually for any damage/bulging/formation of crystals.
- Dispose of old containers, especially if past a marked expiry date.
- If there is a marked expiry date on the container, enter this in SciTrack. Search for the barcode in Container Search, and click the edit icon, to add the date.

3.5 Identifying and Reporting on Time-Sensitive Chemicals in SciTrack

SciTrack can help you identify time-sensitive chemicals in your lab. Note that while we have included all the chemicals we are aware of that fit these categories, it is not an exhaustive list. Consult the Safety Data Sheet for specific storage conditions for all chemicals in prolonged storage.

3.5.1 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).** Group C includes those that may undergo hazardous polymerisation
- **Unstable on prolonged storage**
- **Desensitised explosives**

4) Click Search

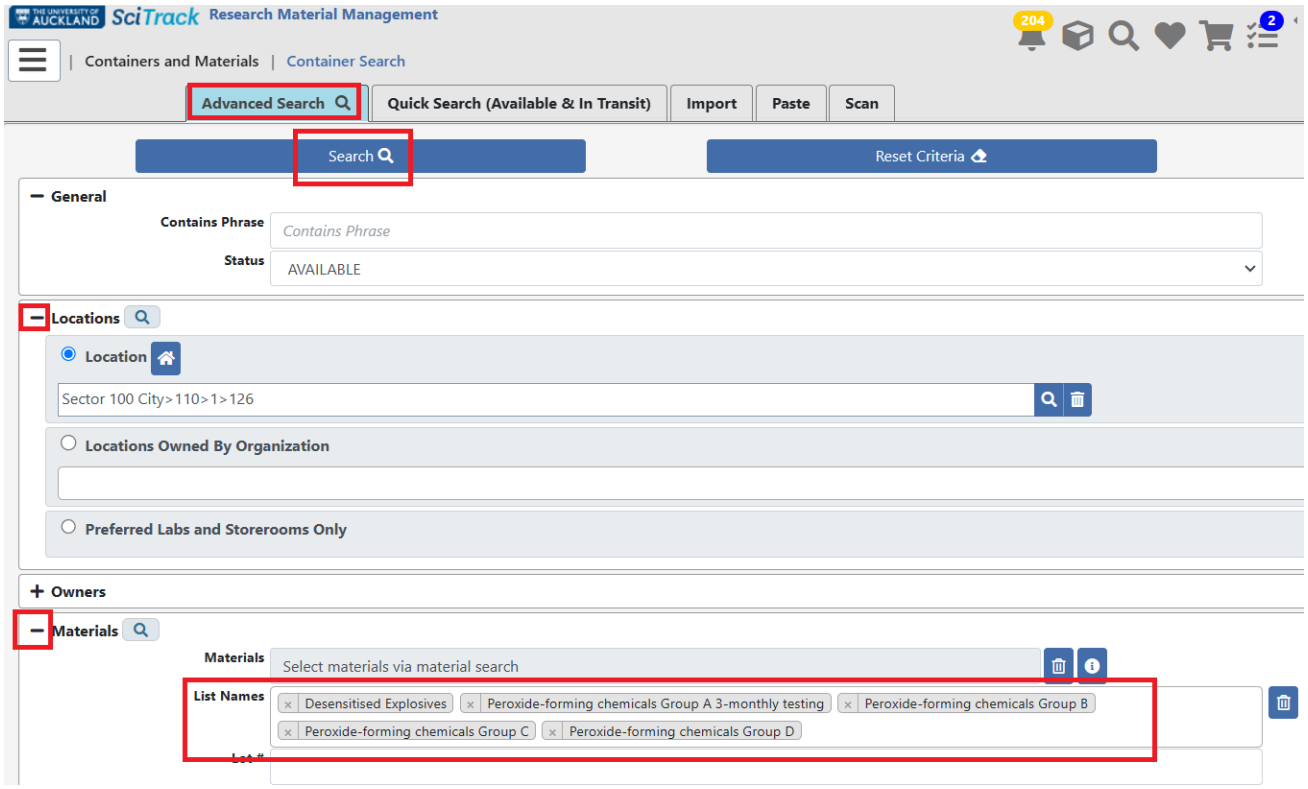

FIGURE 1: ADVANCED CONTAINER SEARCH SCREENSHOT FROM SCITRACK

3.5.2 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 time-sensitive chemical containers in your lab. See SciTrack Quick Guide 12. Advanced features for 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. To find a container owner, type their last name only in the search bar and click Search.
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

Appendix I Chemicals Unstable on Prolonged Storage

Note this is not an exhaustive list, please consult the SDS to identify chemicals that can decompose to produce gas

Allyl chloroformate	Aluminum chloride	Aluminum lithium hydride
Ammonia solution	Ammonium hydroxide	Ammonium persulfate
Anisyl chloride	Aqua regia	Benzenesulfonyl chloride
Benzyl chloroformate	Bleach	Bleaching powder
Calcium carbide	Calcium hydride	Calcium hypochlorite
Chloroform	Chromic acid	Cumene hydroperoxide
Cyclohexene	Diethyl pyrocarbonate	Dimethylamine
Formic Acid	Hydrogen peroxide	Isopropyl chloroformate
Lauroyl peroxide	Lithium aluminum hydride	Lithium hydride
Nitric acid	Nitrosoguanidine	Peracetic acid
Phenol	Phosphorus trichloride	Potassium Persulfate
Silicon tetrachloride	Sodium borohydride	Sodium dithionite
Sodium hydride	Sodium hydrosulfite	Sodium hypochlorite
Sodium peroxide	Sodium persulfate	Thionyl chloride
Urea peroxide	Zinc	

Appendix II Desensitised explosives

Note this is not an exhaustive list.

Desensitised explosives that require addition of water

Substance	**Minimum percentage water to be added**
2-amino 4,6 dinitrophenol	20%
Ammonium picrate	10%
Barium azide	50%
2,4-Dinitrophenol	15%
2,4-Dinitrophenylhydrazine	33%
2,5-Dinitrophenol	15%
2,6-Dinitrophenol	15%
Dinitroresorcinol	15%
Dipicryl sulfide	10%
Nitroguanidine	20%
4-Nitrophenylhydrazine	10 %
Pentaerythrate tetranitrate	25 % or added phlegmatizer
Picric acid (2,4,6 Trinitrophenol)	30%
Picramide (Trinitroaniline)	30%
Picramic acid (2 amino-4,6 dinitrophenol)	30%
Silver picrate	30%
Sodium dinitro-o-cresolate	15%
Sodium picramate	20%
2,4,6 Trinitrobenzene	30%
2,4,6 Trinitrotoluene	30%
Urea nitrate	20%
Zirconium picramate	20%

Desensitised explosives with other storage requirements

Substance	Storage condition
Cellulose nitrate/nitrocellulose or Collodion	Keep in solution: >25% water or ethanol
Isosorbide dinitrate	>60% lactose, mannose, starch or calcium hydrogen phosphate
Tetrazole	Keep in solution
HOAt (1-Hydroxy-7-azabenzotriazole)	Keep in solution
HOBT (1-Hydroxybenzotriazole)	Anhydrous: 20% water. As hydrate: check supplier SDS. Merck sells with 12% water.
Picrylsulfonic acid (2,4,6-Trinitrobenzenesulfonic acid)	Check supplier SDS