THE UNIVERSITY OF QUEENSLAND
AUSTRALIA
CREATE CHANGE

Time-Sensitive Chemicals Management Safe Operating Procedure (SOP)

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Section 1 - Purpose and Scope

(1) The University of Queensland (UQ) is committed to managing risks associated with the storage, use, handling and disposal of time-sensitive chemicals (TSCs).

(2) Even under normal storage conditions, TSCs can develop additional hazards that were not present in their original formulation.

(3) TSCs can undergo unwanted reactions or physical changes that can result in potentially explosive materials which present a significant hazard to chemical users, infrastructure and the environment. For this reason, TSCs have a limited shelf life.

(4) If TSCs are managed appropriately, they pose no additional risk beyond those identified in their safety data sheet (SDS).

(5) This SOP provides advice on risk management of TSCs and should be read in conjunction with any UQ PPL procedures.

Section 2 - Key Requirements

Identifying TSCs

(6) The SDS of a chemical should be consulted for its specific hazards.

a. Specific statements in *Section 2 Hazards Identification* of the SDS which may relate to time-sensitive properties are:

i. AUH001 Explosive when dry.

ii. AUH019 May form explosive peroxides.

iii. H206 Fire, blast projection hazard; increased risk of explosion if desensitised agent is reduced.

iv. P230 Keep wetted with phlegmatiser.

b. Examples of general statements in *Section 7 Handling and Storage* of the SDS that may indicate hazards associated with TSCs include:

i. may form explosive peroxides on standing or following concentration by distillation.

ii. slowly decomposes releasing gas and may pressurise containers.

iii. may develop pressure in containers; open carefully. Vent periodically.

iv. dry crystals may be present in the threads of screw top containers and present a detonation hazard when opening the container.

v. when dry is a highly unstable and heat, friction-, and impact- sensitive explosive.

vi. decomposes at ordinary temperatures in sunlight, in the absence of air, and in the dark in the presence of air.

vii. protect from light.

viii. ensure proper stock-control measures are maintained to prevent prolonged storage.

ix. rotate all stock to prevent ageing.

x. should not be stored in steel cylinders for more than 2 years due to potential over-pressurization from hydrogen gas formation.

xi. explosive sensitivity increases when trace metals are present.

xii. the consequences of accidental contamination from returning withdrawn material to the storage container can be disastrous.

(7) There are four general categories of TSCs:

a. peroxide formers;

b. peroxide formers that can undergo hazardous polymerisation;

c. materials that become shock or friction sensitive upon the evaporation of a stabiliser (including chemicals which become explosive when dry);

d. materials that generate significant additional hazards by undergoing slow chemical reactions.

Organic peroxide formulations

(8) While not generally incorporated into lists of TSCs, organic peroxides that have been purchased or synthesised (whether purposefully or as a by-product) share many of the hazards associated with peroxides that form due to auto-oxidisation during storage.

Solids which become hazardous upon oxidation

(9) Some solids form hazardous oxidation products on storage, for example, potassium metal, sodium amide.

(10) Look for discolouration or formation of a brown, yellow or orange coating. The coating can catch fire or explode when handled.

(11) Even when these materials are stored under mineral oil, oxygen can dissolve in the oil and cause oxidation.

(12) Evaluation of hazardous oxidation of alkali metals and their amides is based on visual inspection only (no testing). These solids should be disposed of after 3 months or as per their manufacturer expiry date, whichever is sooner.

Picric acid and other polynitrated aromatic compounds

(13) Picric acid and other tri- and di-nitrated aromatic compounds, when dry, are an extremely high-risk explosion hazard and are sensitive to shock, friction, and heat.

(14) Picric acid and other polynitrated aromatics should be purchased in small quantities and stored in the original container in a cool area away from heat sources.

(15) Polynitrated aromatic compounds should be monitored every three months to check the integrity of the container and lid and for any sign that the water content is decreasing, e.g. consistency of solids changing from free flowing to clumping or vice versa.

(16) Polynitrated aromatic compounds should be disposed of as hazardous waste within a year of receipt.

(17) If the material is suspected to be dry, treat as potentially explosive material. Do not handle. Notify the local Safety Team IMMEDIATELY.

Other TSCs

(18) List D in the Appendix “Lists of TSCs”, gives examples of other substances which may form hazards on storage. This list is not exhaustive. The chemical SDS should always be checked for its specific hazards.

(19) Anhydrous hydrogen fluoride (HF) (and other hydrogen halide gases) react with steel cylinders over time to generate hydrogen gas which can over-pressurise the cylinder, eventually leading to cylinder failure. The supplier’s recommendations regarding expiry of cylinders should be followed. These cylinders should not be purchased unless an agreement is in place with the supplier that they will accept the return of cylinders, both empty and partially used. Return cylinders to the supplier before the expiry date, even if they are not empty

(20) Chloroform ($CHCl_3$) reacts with air to form phosgene gas ($COCl_2$) which is extremely toxic. Wherever possible, chloroform that is stabilised with alcohol should be purchased and stored in a cool, dark place. Always open chloroform in a fume hood. Bottles of ethanol stabilised chloroform should be disposed of after 2 years and chloroform that does not contain ethanol as a stabiliser, after 1 year.

(21) Some chemicals decompose over time liberating gaseous by-products which can over-pressurise the container causing them to rupture. For example, formic acid decomposes to form carbon monoxide and water. Ensure a procedure for venting is in place and documented for each individual chemical and vent or discard containers frequently.

(22) Plastic containers should not be used as they can become brittle over time causing them to disintegrate when handled which can expose users to hazardous chemicals.

Purchasing

(23) TSCs should only be purchased in amounts that will be used in a 3-to-6-month time period

(24) When possible, purchase TSCs that have inhibitors added by the manufacturer (e.g. peroxide inhibitors for peroxide forming chemicals).

(25) Label all TSCs containers, including containers holding TSCs decanted from their original container, with the date received, the date opened, and the expiry date (plus test/inspection date and results if applicable). See the Appendix “TSC Labels”, for an example of label content. Using a bright colour for the label will assist with easy identification of the presence of TSCs within the chemical storage cabinet/area.

(26) A chemical inventory is essential in ensuring that TSCs do not pass their expiry date which can lead to the formation of potentially highly hazardous by-products. Inventories are used to track individual packages and record the location, date acquired, date opened, expiry date and inspection or re-testing date. ChemInventory should be used for inventorying purposes.

Storage

(27) All TSCs should be identified in the inventory, including date of opening and date the chemicals should be discarded, inspected or tested. See the Appendix “TSC types and disposal / testing / inspection schedules”, for further information on discard and test dates.

(28) TSCs should be stored in their original containers where possible. Containers should be sealed, airtight with tight-fitting caps. Storage of peroxide forming chemicals in partially empty containers promotes peroxide formation. For TSCs that have the potential for bottle over-pressurisation, choose products that are supplied with vented caps if available. Do not use vented caps unless approved for the specific product by the manufacturer.

(29) TSC containers should be opaque if not being stored in the dark or if exposed to light for extended periods of time. Ensure glass bottles are amber and returned to a dark storage location immediately after use. Exposure of peroxide forming chemicals to light promotes peroxide formation.

(30) Store peroxide forming chemicals under nitrogen, other inert gas or in an inert atmosphere chamber. Note: Some inhibitors used to prevent free radical accumulation in monomers, for example phenolic compounds such as hydroquinone methyl ether (MEHQ) and butylated hydroxytoluene (BHT), need small amounts of oxygen to function and it may be appropriate that chemicals containing these types of inhibitors are not stored under an inert atmosphere. Follow the manufacturer’s recommendations.

(31) Containers should be inspected at least every 6 months, to verify their condition and check for signs of hazard formation (loss of water or other phlegmatiser, deformation of containers, formation of solids in liquids or solutions, contamination etc.).

(32) The SDS for the chemical will state whether it is unstable under certain conditions or after a period of time in storage, this information should be highlighted in the risk assessment.

Handling and use

(33) For peroxide forming liquids:

a. Signs of peroxide formation include crystal formation in the container or around the lid, a “mossy” appearance around the lid, discoloration, or formation of multiple layers.

b. If signs of peroxide formation or chemical container deterioration are identified, the container should not be handled, in particular, DO NOT attempt to remove the lid. If explosive crystals have formed around the lid, the friction created by the unscrewing of the cap may be enough to detonate the compounds. Treat as potentially explosive material. Notify the local Safety Team IMMEDIATELY.

c. Test for the presence of peroxides using test strips before distilling (see Testing for peroxides). Do not distil or concentrate a liquid containing >25 ppm peroxides.

d. Most explosions of peroxide forming chemicals occur when a material is distilled to dryness (always leave a residual volume of at least 20%). Stir distillations with a mechanical stirrer or a bubbling inert gas. Never use air or an oxygen-containing mixture for bubbling or stirring a peroxide forming chemical.

e. After distillation, chemicals will no longer contain inhibitors present before the distillation.

(34) Safe handling and use of List D TSCs (see Appendix “Lists of TSCs”) is dependent on the potential hazard, and should be guided by the risk assessment and any controls that are identified, for example:

a. Chemicals that may form toxic gases should be opened in a fume cupboard before use. If these chemicals are to be used outside of a fume cupboard, then they may need to be purged with an inert gas before removing from the fume cupboard.

b. Chemicals that may form gases which pressurise the container should be inspected before use to check for signs of deformation.

i. If signs of container deformation are noted, opening of the container (including handling before the pressure can be released) should be performed with appropriate controls, including, use of a fume cupboard, weighted safety shield, impact resistant face shield, lab coat and cut resistant gloves and sleeves.

ii. If the container does not show evidence of deformation, it may still be pressurised causing the contents to spray when opened. Consideration should be given to having controls in place when opening the container to prevent injury, e.g. chemical safety googles or face shield, long-cuff gloves, lab coat, apron and splash shield.

c. Substances that are explosive when dry, through loss of water or other type of volatile phlegmatising agent, should:

i. be checked before use to confirm the integrity of the container and lid such that the water or other phlegmatiser has not had a chance to evaporate.

ii. be checked before returning to storage to ensure the thread of the container and lid are clean and the integrity of the container and lid are intact.

iii. have an associated risk assessment to determine which controls should be in place when opening the container if friction sensitive solids have accumulated in the tread of the container (e.g. fume cupboard, weighted safety shield, impact-resistant face shield, fire-retardant lab coat, cut resistant gloves and sleeves).

iv. be monitored for physical changes (e.g. from a free-flowing power to clumps or vice versa) which may indicate that it is dry or no longer contains the phlegmatiser.

v. be stored in closed containers and in a cool location when not being used.

vi. be handled with plastic spatulas to reduce friction and eliminate the chance of metal contamination from metal spatulas.

vii. not subjected to unnecessary friction such as scraping sintered glass frits with spatulas or use of ground glass jointed glassware.

viii. have solutions of these substances inspected to confirm that solids have not precipitated as these may be shock or friction sensitive explosives.

d. Inspect containers for signs of contamination before use as contamination may accelerate the formation of hazards. When using chemicals care should be taken to prevent contamination of the stock container (e.g. the use of dirty or used spatulas). Do not return decanted chemicals to the stock container due to the risk of contamination. If decanted chemicals are to be stored, this should be done in a new, compatible container with compliant labelling, otherwise they should be disposed of.

(35) See the Appendix “Handling of specific TSCs” for advice on handling of specific chemicals.

Testing for peroxides

(36) Liquid peroxide forming chemicals should be regularly tested for peroxides (where safe to do so) in line their SDS or TSC list type (see Appendix “TSC types and disposal / testing / inspection schedules” and Appendix “Lists of TSCs”).

(37) The Appendix, “Procedure for scheduled peroxide testing” has information on the testing procedure. The person testing a particular chemical should:

a. be trained in the safe use and handling of the chemical,

b. have at least one year of experience in the use and handling of the class of chemical to be tested,

c. have read and understood this SOP and a risk assessment for the testing procedure should be in place and has been read and understood by the person conducting the procedure.

(38) All List A peroxide forming chemicals are disposed of according to their recommended shelf life or expiry date (as per the SDS or manufacturer’s instructions) regardless of testing results.

(39) The date scheduled for peroxide testing should be recorded on the container and in ChemInventory or other inventory software. TSCs which have an inhibitor should still be tested for peroxide-levels as the inhibitor can be depleted.

(40) If a peroxide test indicates peroxide levels over 100 ppm, treat as potentially explosive material. Notify the local Safety Team IMMEDIATELY. Do not send to UQ Science Store for disposal.

(41) Moderate levels of peroxides (30-100 ppm) show that the peroxidation process has been initiated and the conditions may exist for the level of peroxides to rapidly increase to hazardous levels. The chemical should immediately be sent for disposal via UQ’s Chemical Waste stream.

(42) The results of peroxide testing should be recorded on the TSC label of the prior to collection for disposal, UQ Chemical Store will check the label.

(43) Do not test contents of containers of unknown age or origin. Old bottles may contain concentrated peroxides, or peroxides may have crystallised in the cap threads, which would present a serious hazard when opening the bottle for testing. Contact the local Safety Team for managing old containers. Do not send to UQ Science Store for disposal.

Distillation of peroxide forming TSCs

(44) Distillation of peroxide forming chemicals can concentrate peroxides already in the chemical and remove the inhibitor (which is placed in these chemicals to inhibit peroxide formation). Therefore, prior to distillation of peroxide forming TSCs your distillation procedure should be reviewed that either:

a. the chemical to be distilled has been tested for peroxides within 24 hours of performing the distillation and shown to contain less than 20 ppm peroxides; or

b. if a chemical contains low to moderate levels of peroxides (up to 100ppm), in some cases it may be possible to remove the peroxides from the chemical. See Appendix – “Removal of peroxides”.

(45) When undertaking distillation, the process should be designed to minimise the risk posed by peroxide concentration and should be risk assessed in UQSafe.

(46) Distilled peroxide forming chemicals should be used in a subsequent chemical process, or made safe for continued storage (e.g. addition of an appropriate inhibitor) within:

a. 24 hours for List A and List C substances.

b. 1 week for List B substances.

(47) Distilled chemicals which have been made safe for continued storage are managed as described in this SOP.

Disposal

(48) Before disposal consult the SDS to ensure any foreseeable risks to personnel required to handle the substance after being sent for disposal (including outside contractors) have been mitigated.

(49) Dispose of TSCs within the timeframe indicated in the Appendix “TSC types and disposal / testing / inspection schedules”, as stated in the SDS, or as per the manufacturer’s recommendations (whichever is sooner).

(50) Prior to sending TSCs for disposal their container should be inspected to confirm it is in good condition and intact. Old containers that have been used to store a substance may have degraded to the point that they cannot withstand the forces experienced during transport. If there is any doubt regarding the integrity of the container a compatible waste container should be ordered from the Science Store and the substance transferred to, or the old container securely packed within, the new container.

Disposal of peroxide forming chemicals

(51) All List A peroxide forming chemicals in the Appendix “Lists of TSCs”, are disposed of according to their recommended shelf life or expiry date (as per the SDS or manufacturer’s instructions) regardless of peroxide levels.

(52) List B and C and related peroxide forming chemicals are disposed of according to their expiry date (as per the SDS or manufacturer’s instructions). Where an expiry date is not documented, these chemicals are disposed or peroxide tested according to the schedule stated in Appendix “TSC types and disposal / testing / inspection schedules” and Appendix

"Lists of TSCs". If these chemicals are to be retained past the recommended disposal schedule, a risk assessment should be completed.

(53) If any of the following criteria are met, liquid waste containing peroxide forming chemicals should be peroxide tested prior to sending to the UQ Science Store, with the date of testing, peroxide concentration and tester's initials recorded on the container:

a. List A liquid peroxide formers are present in any concentration;

b. List B substances that have been treated with an oxidising agent or subjected to an active aeration process are present in any concentration;

c. List B substances that remain after a process involving evaporation are present in any concentration;

d. List B substances that have been poorly stored (e.g. poorly sealed, stored in warm environments, exposed to sunlight) are present in any concentration;

e. List B substances that would commonly contain peroxide inhibitors that have been purchased inhibitor-free or have been distilled and no longer contains an inhibitor are present in any concentration.

f. List B substances decanted from the original container are present in a combined total of greater than 10%;

g. List B substances in the original container which was first opened over 12 months ago;

h. List B substances in an unopened bottle greater than 18 months old;

i. List A or List B liquid peroxide formers are present in any concentration in waste older than 3 months, or a peroxide test has not been performed within the previous 3 months.

(54) Peroxide forming chemicals which have had regular, documented testing as per their required testing schedule, show no evidence of crystal formation and have a peroxide level of <100ppm can be disposed through the University's chemical waste system. Information regarding chemical waste disposal can be found on the UQ Science Store webpage.

(55) If the peroxide forming chemical is of unknown age or history, or peroxide formation is evident (e.g. appearance of crystals), or if a peroxide test indicates peroxide levels over 100 ppm, treat as potentially explosive material. Notify the local Safety Team IMMEDIATELY. Do not send to UQ Science Store for disposal.

Disposal of List D chemicals

(56) List D type TSCs should be disposed of 12 months after opening or after 18 months if unopened, or as per the manufacturer's instructions.

(57) Due to the lack of safe, general, and easily performed purity tests for these TSCs, testing is either not applicable or not recommended. Instead, they should be visually checked for hazards, or vented if appropriate, and this recorded on the container along with the date.

(58) If any List D type TSC is suspected of being a risk to personnel required to handle it (including Science Store staff and external waste contractors), do not send to UQ Science Store for disposal. Treat as potentially explosive / harmful material. Notify the local Safety Team IMMEDIATELY. For example, an explosive when dry substance is suspected of having insufficient water content or contamination is suspected, the container is pressurised etc.

(59) Gas forming List D type TSCs should be safely vented before sending for disposal and the date vented recorded on the container.

(60) Aqueous solutions of explosive when dry TSCs are to be disposed of 6 months after preparing. Before sending for disposal, ensure they are checked to confirm they are free of solids, and should be further diluted to eliminate the chance of solids forming during transport and handling.

(61) Solutions of explosive when dry TSCs in volatile solvents (e.g. ethanol) are not be stored in this state. Instead, they should be used immediately, or water should be added before disposal. Care should be taken when adding water that it does not cause the substance to precipitate. If precipitation is a possibility, the solution should be further diluted with solvent before the addition of water.

(62) Solutions of materials that require other volatile phlegmatisers should be disposed of a week after preparing, and diluted or otherwise treated to render safe for transport and handling before being sent for disposal.

Section 3 - Appendix

TSC types and disposal / testing / inspection schedules

(63) Expiry and testing schedules are to be followed as below, as stated in the SDS, or as per the manufacturer's recommendations (whichever is sooner).

(64) Peroxide forming chemicals should be tested prior to distillation. Distillation of peroxide forming chemicals can concentrate peroxides already in the chemical and remove the inhibitor (which is placed in these chemicals to inhibit peroxide formation).

(65) Prior to distillation of peroxide forming TSCs review the distillation procedure to ensure that:

a. The chemical to be distilled has been tested for peroxides within 24 hours of performing the distillation and shown to contain less than 20 ppm peroxides; and

b. The process to be used considers the risk of peroxide formation and concentration, is designed to minimise this risk, and the process is risk assessed on UQSafe.

(66) List A – Chemicals that form a peroxide hazard on storage:

a. They are not kept past their expiration date, regardless of testing results.

b. Unopened containers are disposed of at 12 months, regardless of testing results.

c. Open containers are disposed of after 3 months, regardless of testing results.

d. Solid list A TSCs cannot be peroxide tested.

(67) List B – Chemicals that form a peroxide hazard on concentration (distillation or evaporation):

a. Unopened containers are disposed of or peroxide tested after 18 months. If a peroxide concentration of 30-100 ppm is detected dispose of the chemical immediately (if >100 ppm is detected treat as potentially explosive and contact the local Safety Team.

b. Opened containers are disposed of after 12 months or peroxide tested every 3 months, or as specified in the SDS. If a peroxide concentration of 30-100 ppm is detected dispose of the chemical immediately (if >100 ppm is detected treat as potentially explosive and contact the local Safety Team.

(68) List C – Chemicals that form a peroxide-initiated polymerisation hazard:

a. If uninhibited dispose of after 24 hours once opened or distilled.

b. If inhibited, for those chemicals that also appear in List A follow List A management and disposal schedule, otherwise, dispose of 12 months after opening (18 months if unopened).

c. When some List C chemicals (acrylic acid, methyl methacrylate, styrene) are inhibited with phenolic-type compounds (e.g. MEHQ, BHT etc.), oxygen is required for the inhibitor to function, so they should not be stored under an inert atmosphere. Refer to the SDS and manufacturers' instructions.

(69) List D – Other TSCs and explosive when dry polynitrated aromatic compounds:

a. Shelf life varies.

b. Visually inspect every 6 months to check the integrity of the container, evidence of contamination, changes in physical appearance of the chemical, presence or evaporation of a phlegmatiser, or other properties as determined by the associated hazard.

Lists of TSCs

(70) These lists are not exhaustive. Always check the SDS of the chemical for its specific hazards.

List A: Chemicals that form a peroxide hazard on storage	
Butadiene [106-99-0]	Isopropyl ether [108-20-3]
Chlorobutadiene (chloroprene) [126-99-8]	Perfluoroethylene (tetrafluoroethylene) [116-14-3]
1,1-Dichloroethylene (vinylidene chloride) [75-35-4]	Potassium metal [7440-09-7] and alloys
Divinyl acetylene [821-08-9]	Potassium amide [17242-52-3]
Divinyl ether [109-93-3]	Sodium amide [7782-92-5]

List B: Chemicals that form a peroxide hazard on concentration (distillation or evaporation)	
Acetal [105-57-7]	Di-*n*-propoxymethane [505-84-0]
Acetaldehyde [75-07-0]	1,2-Epoxy-3-isopropoxy propane [4016-14-2]
Allyl ethyl ether [557-31-3]	1,2-Epoxy-3-phenoxypropane [122-60-1]
Allyl phenyl ether [1746-13-0]	*p*-Ethoxyacetophenone [1676-63-7]
4-(*n*-Amyloxy)benzoyl chloride [36823-84-4]	(2-Ethoxyethyl)-*o*-benzoyl benzoate [604-63-7]
Benzyl alcohol [100-51-6]	1-Ethoxynaphthalene [5328-01-8]
Benzyl *n*-butyl ether [588-67-0]	*o*-Ethoxyphenyl isocyanate [5395-71-1]
Benzyl ether [103-50-4]	*p*-Ethoxyphenyl isocyanate [32459-62-4]
Benzyl ethyl ether [539-30-0]	1-Ethoxy-2-propyne [628-33-1]
Benzyl isopentyl ether [122-73-6]	3-Ethoxypropionitrile [2141-62-0]
Benzyl methyl ether [538-86-3]	2-Ethylacrylaldehyde oxime [99705-27-8]
Benzyl 1-naphthyl ether [607-58-9]	Ethylene glycol dimethyl ether (glyme) [110-71-4]
1,2-Bis(2-chloroethoxy)ethane [112-26-5]	2-Ethylhexanal [123-05-7]

Bis(2-ethoxyethyl) adipate [109-44-4]	Furan [110-00-9]
Bis(2-ethoxyethyl) phthalate [605-54-9]	2,5-Hexadiyn-1-ol [28255-99-4]
Bis(2-methoxyethyl) carbonate [626-84-6]	4,5-Hexadien-2-yn-1-ol [2749-79-3]
Bis(2-methoxyethyl) phthalate [117-82-8]	4-Heptanol [589-55-9]
Bis(2-methoxymethyl) adipate [142013-82-9]	2-Hexanol [626-93-7]
Bis(2-*n*-butoxyethyl) phthalate [117-83-9]	*n*-Hexyl ether [112-58-3]
Bis(2-phenoxyethyl) ether [622-87-7]	Isoamyl Ether [544-01-4]
Bis(4-chlorobutyl) ether [6334-96-9]	*o*-Iodophenetole [614-73-3]
Bis(chloromethyl) ether [542-88-1]	*p*-Iodophenetole [699-08-1]
2-Bromoethyl ethyl ether [592-55-2]	Isophorone [78-59-1]
β-Bromophenetole [589-10-6]	3-Isopropoxypropionitrile [110-47-4]
o-Bromophenetole [583-19-7]	Isopropyl 2,4,5-trichlorophenoxyacetate [93-78-7]
p-Bromophenetole [588-96-5]	Isobutyl vinyl ether [109-53-5]
2-Butanol [78-92-2]	3-Methoxy-1-butyl acetate [4435-53-4]
tert-Butyl methyl ether [1634-04-4]	Methoxy-1,3,5,7-cyclooctatetraene [7176-89-8]
Chloromethyl methyl ether [107-30-2]	2-Methoxyethyl vinyl ether [1663-35-0]
β-Chlorophenetole [622-86-6]	Methyl acetylene [74-99-7]
o-Chlorophenetole [614-72-2]	Methyl *p*-(*n*-amyloxy)benzoate [5416-97-7]
p-Chlorophenetole [622-61-7]	2-Methyl-1-butanol [137-32-6]
Cumene [98-82-8]	Methylcyclopentane [96-37-7]
Cyclohexene [110-83-8]	Methyl isobutyl ketone [108-10-1]
Cyclooctene [931-88-4]	4-Methyl-2-pentanol [108-11-2]
Cyclopentene [142-29-0]	*o*-Methylphenetole [614-71-1]
Cyclopropyl methyl ether [540-47-6]	*p*-Methylphenetole [622-60-6]
Decahydronapthalene (decalin) [91-17-8]	2-Methyltetrahydrofuran [96-47-9]
cis-Decalin [493-01-6]	*m*-Nitrophenetole [621-52-3]
trans-Decalin [493-02-7]	Oxybis(2-ethyl acetate) [628-68-2]
Diacetylene [460-12-8]	Oxybis(2-ethyl benzoate) [120-55-8]
Diallyl ether [557-40-4]	β,β-Oxydipropionitrile [16852-14-5]
Dibenzyloxybenzene [621-91-0]	2-Penten-1-ol [1576-95-0]
1,2-Dibenzyloxyethane [622-22-0]	4-Penten-1-ol [821-09-0]
p-Di-*n*-butoxybenzene [104-36-9]	Phenoxyacetyl chloride [701-99-5]
1,2-Dichloroethyl ethyl ether [623-46-1]	α-Phenoxypropionyl chloride [122-35-0]
2,4-Dichlorophenetole [5392-86-9]	1-Phenylethanol [98-85-1]
2,2-Diethoxypropane [126-84-1]	2-Phenylethanol [60-12-8]

Diethyl ethoxymethylenemalonate [87-13-8]	Phenyl *n*-propyl ether [622-85-5]
Diethyl fumarate [623-91-6]	*p*-Phenylphenetole [613-40-1]
m-Diethoxybenzene [2049-73-2]	2-Propanol [67-63-0]
o-Diethoxybenzene [2050-46-6]	*n*-Propyl ether [111-43-3]
p-Diethoxybenzene [122-95-2]	*n*-Propyl isopropyl ether [627-08-7]
1,2-Diethoxyethane [629-14-1]	Tetrahydronaphthalene [119-64-2]
3,3-Dimethoxypropene [6044-68-4]	Triethylene glycol diacetate [111-21-7]
2,4-Dinitrophenetole [610-54-8]	Triethylene glycol dipropionate [141-34-4]
1,3-Dioxepane [505-65-7]	1,3,3-Trimethoxypropene [17576-35-1]
Dicyclopentadiene [77-73-6]	1,1,2,3-Tetrachloro-1,3-butadiene [921-09-5]
Diethylene glycol dimethyl ether (diglyme) [111-96-6]	4-Vinylcyclohexene [100-40-3]
Diethoxymethane [462-95-3]	Vinylene carbonate [872-36-6]
Diethyl ether [60-29-7]	Other ethers [various]
1,1-Dimethoxymethane [109-87-5]	Other secondary alcohols [various]
Dioxane [123-91-1]	Other vinyl ethers [various]
Tetrahydrofuran [109-99-9]	Must be peroxide tested every 3 months after opening and disposed of after 12 months.

List C: Chemicals that form a peroxide initiated polymerisation hazard	
Acrylic acid [79-10-7]	Styrene [100-42-5]
Acrylonitrile [107-13-1]	*Tetrafluoroethylene [116-14-3]
*Butadiene [106-99-0]	Vinyl acetate [108-05-4]
*Chlorobutadiene (chloroprene) [126-99-8]	Vinyl acetylene [689-97-4]
Chlorotrifluoroethylene [79-38-9]	Vinyl chloride [75-01-4]
*1,1-Dichloroethylene (vinylidene chloride) [75-35-4]	2-Vinyl pyridine [100-69-6]
Methyl methacrylate [80-62-6]	4-Vinyl pyridine [100-43-6]
If uninhibited dispose of after 24 hours once opened or distilled. If inhibited dispose of 12 months after opening (18 months if unopened). *Inhibited shelf life as per List A (opened 3 months / unopened 12 months).	

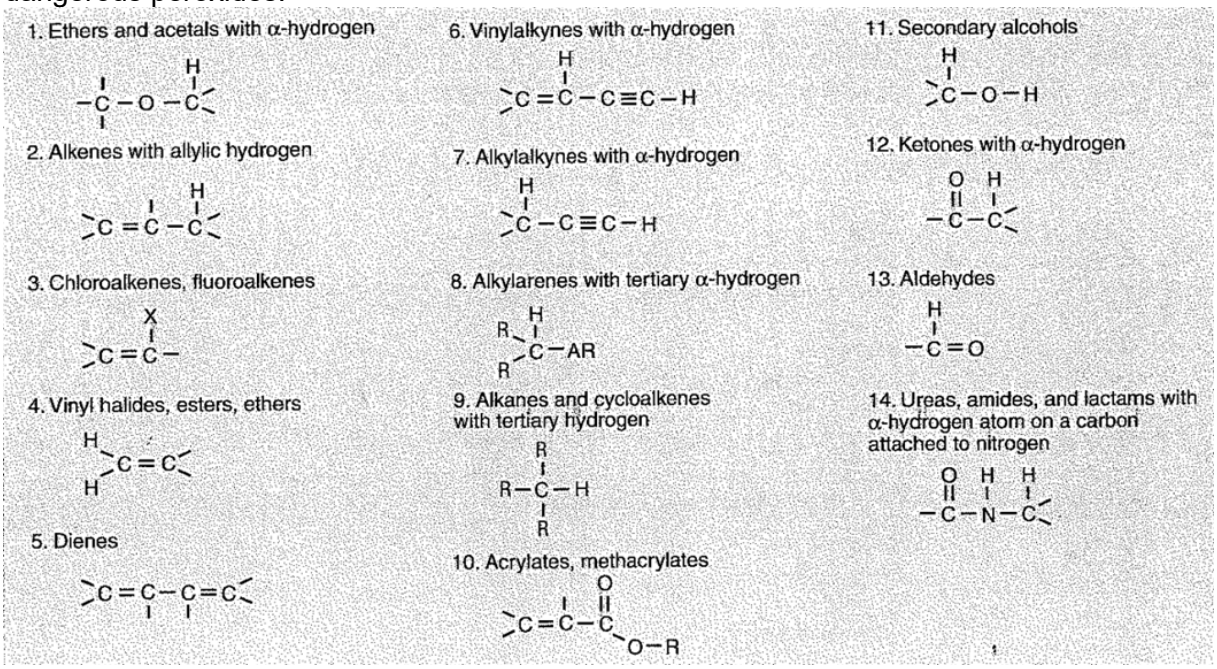
List D: Other time-sensitive chemicals (shelf life varies)	
Acetylene [74-86-2]	Formic acid [64-18-6]
Ammonium nitrate [6484-52-2]	Hydrazine [302-01-2]
Ammonium perchlorate [7790-98-9]	Hydrogen chloride (anhydrous) [7647-01-0]
Calcium carbide [75-20-7]	Hydrogen bromide (anhydrous) [10035-10-6]

Calcium nitrate [10124-37-5]	Hydrogen fluoride (anhydrous) [7664-39-3]
Chloroform [67-66-3]	Perchloric acid [7601-90-3]
Ethylene oxide [75-21-8]	Sodium azide [26628-22-8]

Polynitrated aromatic compounds (explosive when dry)	
2,4-Dinitrophenylhydrazine [119-26-6]	Picric acid [88-89-1]
2,4-Dinitrophenol [51-28-5]	Picrylsulfonic acid [2508-19-2]
Aqueous solutions of explosive when dry compounds are to be disposed of after 6 months. Volatile solvent (e.g. ethanol) solutions of explosive when dry compounds must not be stored.	

Peroxidizable organic moieties

(71) Some peroxidizable organic moieties ranked from most [1] to least [14] likely to form dangerous peroxides.



(72) Peroxide-forming chemicals commonly contain an auto oxidizable hydrogen atom that is activated by adjacent structural components. For example, activated hydrogen atoms are often on a:

a. carbon atom adjacent to an ethereal oxygen atom (-O-CH<, e.g. ethers and acetals);

b. carbon atom adjacent to a vinyl group or benzene ring (C=C-CH< or Ph-CH<, e.g. allyl or benzyl compounds);

c. tertiary carbon atom (-CH<, e.g. secondary alcohols, tertiary alkanes);

d. vinyl group (-CH=CH_2, e.g. vinyl compounds, dienes, styrenes or other monomers).

(73) Not all compounds containing these groups form peroxides, however, the presence of any of these groups in a compound (especially those with low molecular weight) provide a warning that hazardous concentrations of unstable peroxides might be present. Chemical structures that include more than one of these groups are at particular risk of peroxidation.

Handling of specific TSCs

Formic acid

(74) Formic acid will slowly decompose to give carbon monoxide gas at room temperature, resulting in increased pressure if containers are sealed or unvented.

(75) If bottles of formic acid of unknown age are discovered, in addition to standard PPE, don a face shield and cut-resistant gloves and transfer to a fume cupboard behind a safety shield and vent.

(76) Vent formic acid bottles every 6 months or 6 months from the recorded date that it was last opened. Use a face shield in addition to standard PPE as a precaution should liquid be sprayed from a bottle that is under pressure.

Tetrahydrofuran

(77) Tetrahydrofuran (THF) has the potential for rapid peroxide crystal formation. It is especially important for THF that risk assessment for storage of peroxide formers should be developed prior to purchase and include consideration of shelf life, peroxide testing frequency, and chemical storage conditions.

(78) Stabilised THF should be purchased wherever possible. Non-stabilised THF should only be purchased if absolutely necessary, used within a week and stored under inert conditions. Bottles with a Sure/Seal™ should have parafilm wrapped around the base of the lid to assist with sealing the bottle from air ingress. Large quantities stored in Winchesters should be completely used once the bottle is opened. Glass Winchesters do not have a Sure/Seal™ and should not contain unused portions.

(79) THF stored in solvent purification kegs in a well-maintained sealed system can be stored for longer periods to be determined via risk assessment.

(80) The SDS for stabilised THF states that THF should be stored for no longer than 12 months and peroxide tested every 3 months. The point at which the peroxide inhibitor has been consumed is not immediately obvious and along with the possibility of damaged or ill-fitting lids can lead to the rapid formation of hazardous peroxide crystals.

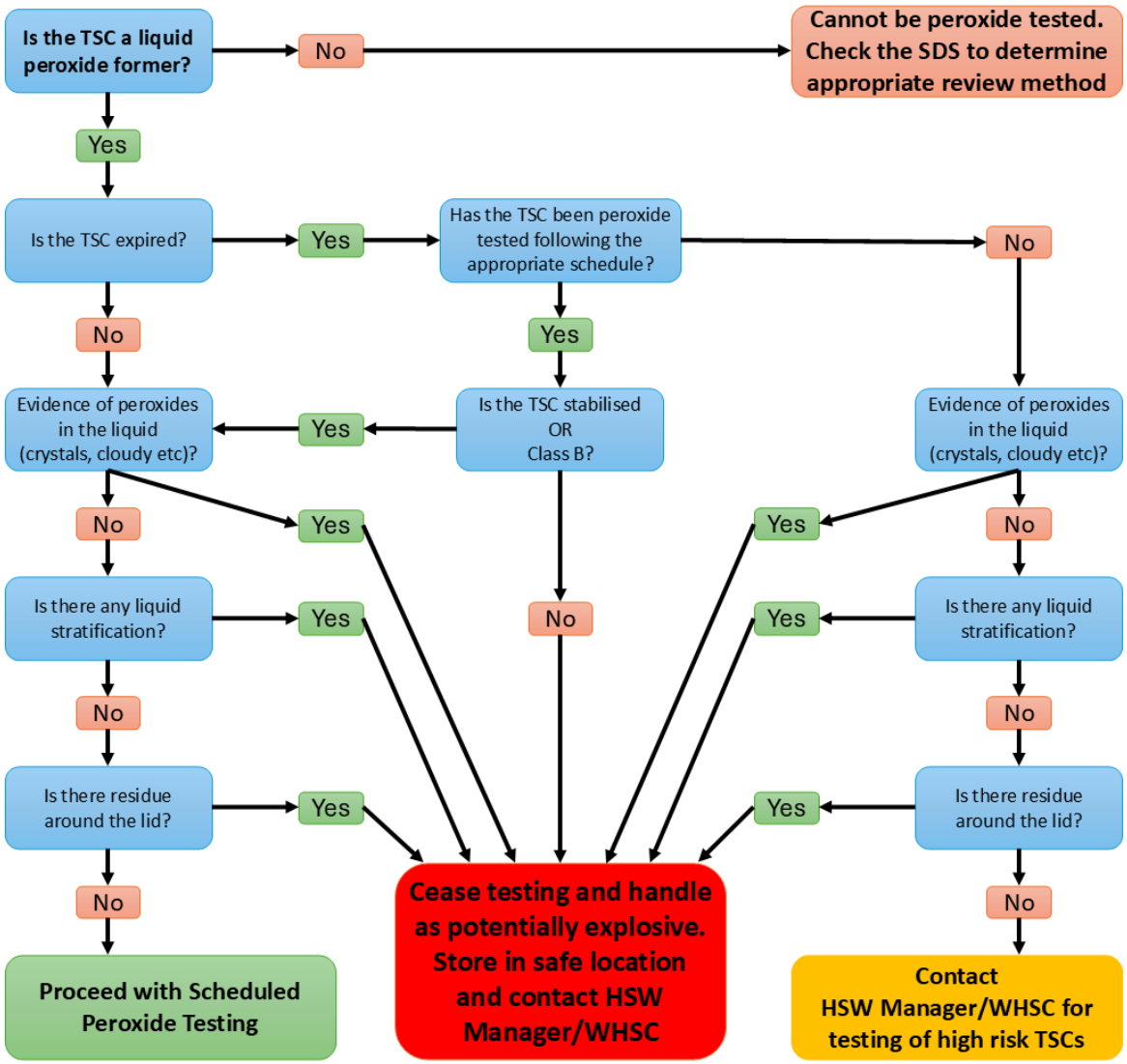
(81) Ensure that THF is peroxide tested prior to disposal.

(82) Never handle THF with crystals, contact HSW personnel.

2-Propanol (Isopropanol)

(83) 2-Propanol should not be stored in wash bottles as this results in exposure to both oxygen and light. If 2-propanol is required to be used in a wash bottle, after use it should be transferred to an air-tight container which is stored in the dark. When using 2-propanol as a mobile phase, ensure the solvent reservoir bottle is opaque and an air-tight lid is in place when not in use.

Decision flow chart for peroxide testing



Procedure for scheduled peroxide testing

(84) This procedure is generally applicable for liquid peroxide forming chemicals only and cannot be used with semi-solids (e.g. *tert*-butanol) or gases (e.g., butadiene) or TSCs whose risk is not due to peroxide formation. Refer to the SDS of the individual chemical to be tested prior to undertaking any testing and confirm:

a. the method is appropriate for the chemical;

b. any further controls required;

c. first aid and spills response;

(85) If there is any evidence that the chemical to be tested may have peroxide formation (either in the solution or around the cap), or if the history of the chemical is undocumented, or all appropriate scheduled testing has not previously occurred, contact the local Safety Team for further advice.

(86) A risk assessment should be in place before testing is conducted.

Safety notes

(87) Alkali metals and their amides should not be peroxide tested due to their inherent hazards.

(88) Old containers of peroxidisable chemicals, or containers of unknown age or history should be handled very carefully, and only if there are no visible signs of peroxidation. Avoid agitation.

(89) Never attempt to force open a rusted or stuck cap on a container of a peroxide-forming chemical.

(90) Never attempt to clean by scraping or rubbing glassware or other containers that may contain peroxides or peroxide-forming materials.

(91) If crystals are discovered around the thread of the lid or bottle do not re-cap.

(92) Do not move chemicals with visible signs of peroxidation (e.g. crystals). Notify the local Safety Team IMMEDIATELY.

Equipment required

(93) General equipment for testing:

a. peroxide test strips;
b. glass Pasteur pipette – long (230 mm);
c. Pasteur pipette bulb;
d. microfuge tube;
e. paper towel;
f. 10 mL Falcon tubes (x2);
g. microfuge tube rack.

(94) Minimum personal protective equipment:

a. lab coat;
b. disposable gloves;
c. safety glasses;
d. enclosed footwear.

Determine if it is safe to peroxide test the TSC

(95) Check the management of the chemical:

a. Is the bottle past its expiry date?
b. Has it previously been peroxide tested, and if so, what were the peroxide levels?
c. If previously tested, was testing within the appropriate time schedule for the TSC?

(96) If confirmed the chemical has been appropriately managed visually inspect the bottle working to answer the following questions:

a. Are any crystals present?
b. Is there any liquid stratification (layers)?
c. Is there any residue around the lid?
d. Is it stabilised?
e. What volume of liquid in the bottle?

(97) If there are any crystals present or there is residue around the lid cease testing and handle as potentially explosive. Notify the local Safety Team IMMEDIATELY.

(98) If advised by the local Safety Team, very carefully place the bottle in a safe location (behind a weighted safety shield or in a strong cabinet).

Confirm that peroxide test strips are functioning correctly

(99) Peroxide test strips are available through UQ eMarket. Always follow manufacturer's instructions for storage and use. Each peroxide test should use as a minimum low-level peroxide (0-100 ppm) test strips.

(100) Prior to using peroxide test strips for testing of chemicals with unknown peroxide levels, the batch of strips to be used should be pre-tested to ensure they are still acting effectively.

(101) Dilute a small amount (1 drop) of aqueous 30% hydrogen peroxide solution into a sample of water (10 mL) to obtain a solution of approximately 100 ppm hydrogen peroxide. Dilute 1 drop of this solution into water (10 mL) to obtain a solution of approximately 10 ppm hydrogen peroxide.

(102) To confirm the strips are effective, follow the manufacturer's instructions and test each of the prepared hydrogen peroxide solutions and compare to the test pad colour scale.

(103) If the tests provide evidence that the strips are working, move on to peroxide testing of the desired chemicals. If the test fails, or is not clear, dispose of the test strips and replace with a new batch (again, test the new batch prior to use).

Peroxide testing of TSCs

(104) If all management processes have been followed, and there is no evidence of peroxide crystal formation the chemical can be tested for peroxides.

(105) Testing should only be done in normal working hours and never in isolation, by appropriately qualified/trained personnel.

(106) All required PPE is worn.

(107) Testing to be conducted in a fume cupboard which is:

a. clear of hazardous material/chemicals;

b. near a safety shower and eyewash station.

(108) Wearing appropriate PPE, move the chemical for testing to the fume hood.

(109) Review chemical for any potential crystals or residue – this includes visualisation of the liquid, as well as review of the cap to rule out any visible peroxide formation.

(110) If determined by visual inspection to be free of crystals or residue, carefully open the bottle and use a pipette to transfer a small sample from the bottle into a microfuge tube.

(111) Follow manufacturer's instructions to test for peroxides using the test strip. A general procedure is as follows;

a. use the Pasteur pipette to draw up a small amount (~0.5mL) of the liquid and transfer to a microfuge tube, ensuring that all liquid is expelled from the Pasteur pipette. If the bottle has a Sure-seal, inert atmosphere transfer techniques should be used to sample the contents of bottle;

b. carefully remove the pipette bulb and dispose of the Pasteur pipette in a waste container suitable for glass. Replace the lid on the bottle;

c. pre-wet the strip only if required by the manufacturer's instructions;

d. dip the test strip into the liquid for the time specified by the manufacturer. After removing the test strip dab it gently onto a piece of paper towel or tissue to remove excess liquid.

(112) After the recommended time, compare the test strip with the colour scale on the test strip packaging. Colour development may continue after the time period specified by the manufacturer but can be disregarded.

(113) Dispose of the test strip, tubes and residual chemicals as appropriate.

What to do following testing

(114) Management of TSCs should be based of the specific hazards of the chemical and informed by the SDS. Management recommendations based on peroxide concentrations are a guide only.

(115) Low levels of peroxides (≤ 10 ppm):

a. the chemical may continue to be stored and used in the laboratory but should be tested every 3 or 6 months (dependent on the class of chemical);

b. if the chemical is no longer required, it should be sent for disposal via UQ's Chemical Waste stream;

c. prior to sending the chemical for disposal, place a label on the container that states, "Tested for Peroxides (Date) – X ppm", indicating the concentration of peroxide found.

(116) Moderate levels of peroxide present (10 – 100 ppm):

a. moderate levels of peroxides show that the conditions may exist for the level of peroxides to rapidly increase to hazardous levels and it is recommended that the chemical be sent for disposal via UQ's Chemical Waste stream. Once peroxide concentrations above 30 ppm are detected, the chemical should be disposed of immediately;

b. tetrahydrofuran should be sent for disposal as soon as moderate levels of peroxides (> 10 ppm) are discovered due to the potential for rapid peroxide crystal formation;

c. prior to sending the chemical for disposal, place a label on the container that states, "Tested for Peroxides (Date) – Safe to dispose – X ppm", indicating the concentration of peroxide found.

(117) High levels of peroxides present (over 100 ppm):

a. if crystals are discovered around the lid or thread do not recap;

b. close the chemical (if safe to do so) and notify the local Safety Team immediately. DO NOT send to UQ Science Store for disposal;

c. pending advice from the local Safety Team, these chemicals should be placed behind shielding (weighted safety shield or in a cabinet) and signage posted warning people of potentially explosive peroxides in the area.

Removal of peroxides

(118) If a chemical contains low to moderate levels of peroxides (up to 100ppm), in some cases it may be possible to remove the peroxides from the chemical.

(119) A risk assessment should be undertaken for each chemical individually to determine if peroxides can be safely removed via chemical treatment. The risk assessment should be peer reviewed by someone with sufficient chemical knowledge and experience with

peroxides prior to approval. Should crystalline peroxide material be present then chemical treatment should not be attempted.

(120) Consider that after treatment inhibitors may no longer be present and testing and disposal timeframes for uninhibited material should be adhered to. If fresh inhibitor is added at appropriate concentrations, then the relevant testing and disposal timeframes may be reinitiated.

(121) The risk assessment and selection of appropriate peroxide removal process should consider at a minimum:

a. the chemical properties of the original chemical;

b. the types of peroxides which may have formed (are dialkyl or higher peroxides likely to be present);

c. will the method generate undesirable waste products for example sieves or alumina with non-reduced reactive peroxides;

d. the environment and surrounding hazards where the procedure will be performed;

e. required competency to undertake the proposed process;

f. complete PPE requirements;

g. emergency procedures.

TSC labels

Refer to the SDS or this SOP for testing schedules.

Peroxide forming Chemicals

TIME SENSITIVE CHEMICAL (TSC) PEROXIDE FORMER This chemical has a limited shelf life. Store tightly closed away from light and heat.		
Date Received: **Date Opened**: **Date Expires**:	**Select TSC Type**: Ensure peroxide testing is undertaken at the frequency required for the TSC list type. A | B | C **Inhibitor added?** Yes | No	
Date:	Peroxide ppm:	Tester:
Date:	Peroxide ppm:	Tester:
Date:	Peroxide ppm:	Tester:
Date:	Peroxide ppm:	Tester:
Date:	Peroxide ppm:	Tester:

Other TSCs (The label may be modified to identify a specific List D TSC)

TIME SENSITIVE CHEMICAL (TSC) – List D **This chemical has a limited shelf life.** **Store tightly closed away from light and heat.**		
Date Received:	Specific Hazard:	
Date Opened:	Inspection / treatment required:	
Date Expires:		
Date:	Results:	Reviewer:
Date:	Results:	Reviewer:
Date:	Results:	Reviewer:
Date:	Results:	Reviewer:
Date:	Results:	Reviewer:

Small label for use when larger labels do not fit.

TSC Type _____	
Received:_____ Opened: _____ Expires: _____	
Date:	Results:
Date:	Results:
Date:	Results:
Date:	Results:
Date:	Results:

Literature

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