Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

UN Class 3 Flammable Liquids

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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 UN Class 3 flammable liquids at the University of Auckland.

2 Disclaimer

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

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

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

3 Classification

This SMOU covers the use of UN Class 3 flammable liquids gases. In the other chemical classification systems of NZ, this includes:

HSNO class 3.1A Flammable Liquids with a flashpoint below 23 °C and an Initial Boiling Point below or equal to 35 °C

HSNO Category 3.1B: Flammable Liquids with a flashpoint below 23 °C and an Initial Boiling Point above 35 °C

HSNO Category 3.1C: Flammable Liquids with a flashpoint between 23 and 65 °C

Note that these correspond to the GHS7 categories of **flammable liquids category 1-3** respectively.

See Appendix 1 for a list of flash points of some common laboratory solvents.

Note: Halogenated organic solvents generally have much higher flashpoints than unsubstituted solvent. Chlorinated solvents such as chloroform do not pose a fire safety hazard although they are still toxic.

4 Incompatibilities

HSNO Class 3.1 Flammable Liquids shall NOT be stored with HSNO Class 2 flammable gases or aerosols, HSNO Class 4 Reactive solids, HSNO Class 5.1 Oxidising agents, or HSNO Class 5.2 Organic Peroxides.

HSNO Class 3.1 Flammable Liquids shall NOT be stored or used near any sources of ignition.

5 Storage

HSNO Class 3.1 flammable liquids shall be stored in a flame-proof cabinet, with some exceptions:

- Fume hoods shall not be used for long term storage of HSNO Class 3.1 Flammable liquids. However working containers of solvent waste may be stored in a fume hood while in use at a ratio of one 5L waste container per three fume hoods maximum.
- Up to 10 litres of flammable liquid may be kept in the open laboratory outside a flame-proof cabinet. Acceptable examples include capped diluted acetone wash residues being collected for recycling, and solvent wash bottles typically found on a sink bench.
- All storage shall be within a cabinet/cupboard fitted with secondary containment capable of retaining at least half the volume of flammable goods stored.

Additional controls

- NO MORE THAN 100 litres of solvent may be stored within a flame-proof cabinet
- Bulk solvents shall be kept inside a licensed Dangerous Goods store

- Minimal quantities of solvent shall be kept in the laboratory at any one time.
- Ensure that these solvents are returned to flame-proof storage cabinets after use.
- Flammable liquids shall NOT be stored in refrigerators unless the refrigerator has been extensively modified by installation of spark-proof thermostatic switch and other components to make it intrinsically safe.

6 Storage of Ethers - Special Precautions

Ethers that have been exposed to the atmosphere for any length of time almost invariably contain peroxides. Di-isopropyl ether, diethyl ether and tetrahydrofuran are especially prone to generate peroxides.

- Peroxides are hazardous because they are unstable and decompose violently at elevated temperatures.
- Ethers should not be stored for longer than 12 months if there are no peroxide inhibitors and the presence of peroxides has not been tested.
- Ethers shall NEVER be distilled to dryness.

Please refer to the **SMOU "Peroxide-forming chemicals"** for further information.

7 Decanting Class 3.1 Flammable Liquids

Sources of ignition shall be kept well away from the area in which these solvents are being used.

Ventilation

HSNO 3.1 flammable liquids shall only be opened and poured in a suitable fume cupboard, or at a location where flammable vapours will not accumulate, and local ventilation will ensure that the concentration of flammable vapour does not exceed 10% of the Lower Explosive Limit (LEL) at any actual or potential ignition source.

Where opening and pouring operations cannot be carried out in a fume cupboard and the laboratory is well ventilated, the following will apply:

- Containers should be opened for as short a time as possible and never near any source of ignition.
- In any one place, the duration that any container of flammable liquid is opened shall not exceed 10 minutes and the volume should not exceed:
  - 1500 ml decanted volume of any flammable liquid with a flashpoint less than or equal to 10 °C above ambient temperature; or
  - 5000 ml decanted volume of any flammable liquid with a flashpoint greater than 10 °C above ambient temperature.

Static

When pouring, decanting, or pumping any flammable liquid from one metal container to other precautions to prevent the build-up of static should be taken.

Static can be generated by swirling, splashing, high flow rates, venturi effects, turbulence, cavitation, or microfiltration. Minimising these effects will reduce the static generated. Before pouring, decanting, pumping or micro-filtering from a metal container into another metal container the containers shall be efficiently bonded together and connected to a common earth. The resistance between earth and any container shall not exceed 10 ohms.

Refilling containers

Note: Less than 0.5 ml of residual ethanol in a 2.5 litre Winchester can produce a saturated air/ethanol vapour mixture. Refilling a 2.5 litre Winchester which has held ethanol at 19°C will release 2.5 litres of a saturated ethanol vapour/air mixture. This can result in over 42 litres of flammable vapour.

Liquids with a higher vapour pressure and/or lower explosive limit will produce a larger flammable zone.

(see Appendix 1 for flashpoints of common laboratory solvents)

8 Personal Protective Equipment for Handling Flammable Liquids

Nitrile gloves should be used when handling many of these compounds to reduce skin absorption.

The primary barrier will be the use of a tested and certified fume hood to extract solvent vapours away from laboratory worker - reducing the chance of fire and explosion and reducing the possibility of exposure to toxic solvents.

9 Toxicity of Common Flammable Liquids

The SDS should always be consulted for more specific information about toxicity.

The high vapour pressure of commonly used solvents means that the most likely pathway of absorption is inhalation, but dermal absorption can also occur. Compounds dissolved in these solvents will often be absorbed by the skin much more freely, bypassing the body's first line of defence - the skin.

9.1 Aliphatic hydrocarbons

C6 to C8 aliphatic hydrocarbons (hexanes to octanes) can cause contact dermatitis as well as damage the central nervous systems.

n-Alkanes are neurotoxic because their oxidised metabolites are potent neurotoxins.

9.2 Aromatic solvents

Benzene attacks the haemopoietic system and at higher exposures has been linked to aplastic anaemia and leukaemia. The metabolites of benzene are thought to have a major role in suspected genetic damage. Safe exposure levels have been revised downward in the last 20 years to 0.05 ppm.

Alkylbenzenes (toluene and xylene) are not as toxic as benzene, but at higher concentrations can result in headaches and nausea.

9.3 Alcohols

Alcohols are metabolised into aldehydes which are considerably more toxic than their parent alcohol, reacting with proteins and amine neurotransmitters.

10 Disposal

Except for small quantities of ethanol or acetone flushed with water, all HSNO 3.1 flammable liquids shall be disposed by a licensed chemical waste contractor.

Class 3 Flammable liquids waste shall be stored in flame-proof cabinets or in Dangerous Goods stores. Class 3 Flammable waste liquids SHALL NOT be stored in the open laboratory.

Contact the Chemical Safety Advisor for advice on disposal.

All HSNO Class 3 waste shall be packed separately, and the package labelled clearly as: "HSNO Class 3 - Flammable Liquids"

11 Spills

Refer to the Chemical Risk Management Protocol Guideline "2. Using Chemicals" section 11 for full spill response instructions.

Small spills

- Extinguish all sources of ignition
- Use correct gloves
- Use absorbent material in spill kits to wipe up solvent – wiping from outside of spill toward centre
- Place used absorbent material in impermeable/airtight container
- Inform Laboratory Manager and arrange for immediate disposal

Large spills

- Extinguish all sources of ignition immediately
- Evacuate laboratory immediately
- Close all doors to laboratory and prevent re-entry until ‘all-clear’ given
- Call fire brigade immediately
- Inform Laboratory Manager and/or arrange for SDS to be made available.
- Prepare to evacuate building

Appendix 1: Representative List of HSNO 3.1 Flammable Liquids with Flashpoints

Note these are not exhaustive lists. You can use a Container Search in SciTrack to search for chemicals in your lab that are on the lists for HSNO 3.1A, 3.1B and 3.1C.

HSNO 3.1A Flammable Liquids: Liquids with a flashpoint below 23 °C and an Initial Boiling Point below or equal to 35 °C

Chemical	**Flashpoint (°C)**
Acetaldehyde	-40
Carbon disulfide	-33
Diethyl ether	-10
Isopentane	-51
Isopropylamine	-37
n-Pentane	-49
propylene oxide	-37
Trimethylamine solution	-20
Vinyl ethyl ether	-30

HSNO 3.1B Flammable Liquids: Liquids with a flashpoint below 23 °C and an Initial Boiling Point above 35 °C

Chemical	**Flashpoint (°C)**
Acetone	-17
Acetonitrile	5
n-Amyl acetate	23
Benzene	-11
2-Butanone	-3
n-Butyl acetate	22
sec-Butyl acetate	16
tert-Butyl acetate	15
tert-Butyl alcohol	11
Cyclohexane	-1
Cyclohexene	-12
Di-isopropyl ether	-12
Di-isopropylamine	-6
Di-n-propyl ether	4
Diethyl ketone	12
Diethylamine	-28
Dimethylamine	15
Dimethyldichlorosilane	-20
Dioxane	15
Ethanol	12
Ethyl acetate	-3
Ethyl acrylate	15
Ethyl isobutyl ketone	13
Ethylene dichloride	6
Ethylene glycol diethyl ether	20
Ethylene glycol dimethyl ether	0
n-heptane	-1
heptene	-8
n-hexane	-23
Isopropanol	22
Isopropyl acetate	16

Methanol	11
Methyl acetate	20
Methyl acrylate	6
Methyl ethyl ketone	-3
Methyl formate	-32
Methyl isobutyl ketone	13
Methyl methacrylate	10
1-Methyl piperidine	3
Methyl propionate	6
Methyl propyl ketone	7
Methyltetrahydofuran	6

Piperidine	4
n-Propanol	15
2-Propanol	23
n-Propyl acetate	12
Propionaldehyde	-26
Pyridine	20
Tetrahydrofuran	-17
Toluene	4
Triethylamine	-6
Vinyl acetate	-6

HSNO 3.1C Flammable Liquids: Liquids with a flashpoint between 23 and 65 °C

Chemical	**Flashpoint (°C)**
Acetic Acid	40
Anisole	51
Butanol	35
2-Butanol	26
Butyl acrylate	39
Butyl alcohol (2-butanol)	26
Cyclohexanone	46
p-Cymene	47
n-Decane	46
Di-n-butyl ether	25
Diethylene glycol mono-n-butyl ether	47
Dimethyl Formamide	57
Ethoxyethanol	42

Formaldehyde	56
2-heptanone (n-Amyl methyl ketone)	47
n-heptanal (n-heptaldehyde)	35
1-hexanol (n-hexanol)	60
2-hexanol	41
Isoamyl acetate	25
Isoamyl alcohol	45
Isobutyric acid	55
Isopropyl benzene	46
Morpholine	35
Petroleum spirits	57
m-Xylene	25
o-Xylene	32
p-Xylene	27