Cross reference to University Policy Statements: Storage of flammable liquids S1/05

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Document Control

Date document last changed	31 March 2020
Date document reviewed	31 March 2021
Version number	1.01
Number of pages	8

1. Introduction:

The purpose of this document is to explain the principles of safe chemical storage in laboratories and to provide guidance on best practice. It is not a definitive guide and in all cases the material safety data sheet [MSDS] for the substance must be referred to in order to determine safe storage conditions and any incompatibilities.

There is a range of storage facilities suitable for chemicals in the laboratory environment. Several of these are specially designed for the safe storage of different types of hazardous substances. It is important to understand what substances can be safely stored in which storage container.

2. Principles of Safe Storage:

- **Labelling**: All chemical containers must be appropriately and clearly labelled with the following information:
 - Name of substance
 - Hazard category (e.g. corrosive, flammable, oxidising, and toxic). In situations where there may be very small vessels or sample vials containing hazardous substances, such that individual labelling is not practicable, these should be secured within a secondary container such as a rack or tray which should then be labelled as above.
- **Compatibility**: It is essential to segregate incompatible substances. The improper storage or mixing of chemicals can result in serious incidents and injuries. See Appendix 1, Incompatibility table for common laboratory chemicals.
- **Minimise quantities:** Store the minimum stock levels of hazardous materials that is reasonable for the level of usage in the lab. Large quantities of hazardous materials should be stored in purpose built external chemical stores.
- **Maintain good housekeeping**: As in all work areas, clutter should be kept to a minimum on general shelving as well as in storage cabinets/cupboards.
- **Maintain good stock control** and be aware of time-sensitive compounds such as ethers which once opened and exposed to the air can produce peroxides which are highly explosive. This means a regular review of what is being stored and disposal of surplus or unwanted chemicals. Pay particular attention to expiry dates and the date when a bottle is first opened should be clearly shown on the label.
- **Do not store chemicals under sinks** as they may leak and some chemicals react when wet?
- Store large breakable containers, particularly of liquids, below shoulder height: Storage of other materials e.g. plastic containers, above this height is acceptable provided that there is a safe means of access to the storage location.
- Sensible shelf storage ensure shelves are not so high that workers need to access them via the benches or lab chairs. Keep light and/or infrequently used containers on the higher shelves. Lips on shelves are helpful as is ensuring that chemicals stored on shelves over the centre of the bench, cannot be pushed back and fall off the far side.
- **Items in cabinets should be stored on trays**, whether the trays be integral to the storage cabinet or are additional.

3. Storage Facilities:

- Shelving provided for storing hazardous substances should be fit for purpose and fitted to an appropriate standard by a competent person. The advice of the Estates Office should be sought where new or additional shelving is required. The following principles should be followed in relation to storage on shelves:
 - Do not overload shelves if they are bowed they are overloaded.
 - Store breakable containers, particularly of liquid and hazardous chemicals below shoulder height.
 - Store large heavy containers at low level.

- Where items are stored above this level ensure they are light weight/infrequently used and that there is a safe means of access (e.g. step stool or ladders).
- Central shelving on benches should have raised edges/lips to prevent items being pushed off the other side.
- Acid cabinets: Modern versions are made of acid resistant materials (such as
 polypropylene or HDPE) and contain a tray to catch any leakage or spillage. Wooden
 cabinets should not be used for storage of oxidising acids such as nitric or perchloric.
 Some acid storage cabinets currently in use may be made of metal and after
 prolonged use will show signs of corrosion. Where acid storage cabinets are acquired
 for the first time, or old ones replaced these should be acid resistant. Acid cabinets
 should have the following sign on the exterior.



• Flammable liquid cabinets: The materials used to build sides, top, bottom, door(s) and lid are capable of providing the required fire resistant (i.e. 30 minutes integrity (minimum) or 60 or 90 minutes) and reaction to fire (i.e. minimal risk) and safety storage cabinets are according to European standard EN 14470-1. They should contain a spillage tray made of suitable material that is compatible with solvents. They should have one of the following sign on the exterior:



- Ventilated cabinets: These are cabinets which are fitted with forced ventilation. They may be free-standing with their own extract system, or may be situated beneath a fume cupboard and attached to its duct. They are designed to safely store chemicals that give off noxious fumes and smells. These fumes are sucked away by the forced ventilation.
- Fridges & freezers may be used for storage of certain hazardous substances however where the substances are flammable the unit must not contain any internal light source or thermostat that could provide a source of ignition for any flammable vapour. Proprietary laboratory fridges and freezers that meet these requirements are available from major lab supply companies, domestic appliances should be avoided.
- **Fume cupboards** are not designed or intended to be used as storage areas and they should be kept clear of materials and containers when these are not needed for the ongoing operational work. Materials stored in fume cupboards may disrupt the air-flow making the fume cupboard less efficient and compromising the safety of the user.

4. Storage of Different Materials:

- Acids Concentrated acids must be safely stored inside a suitable cabinet as detailed above. Small quantities of dilute acids, such as used with pH meters, may be stored on the bench providing they are appropriately labelled. Fuming acids, acids chlorides should be stored in ventilated enclosures. Incompatibles: Alkalis & Flammable liquids are incompatible with acids and must be stored separately.
- **Alkalis** Even although these materials are marked with a corrosive label, as are acids, they must be stored separately from acids since any accidental mixing of the concentrated materials will generate large quantities of heat and fumes.
- Flammable solvents (e.g. alcohols, toluene, hexane etc.) should only be stored in specialised flammable solvent cabinets as detailed above. Such cabinets must be clearly labelled and positioned away from doors or other means of escape from the laboratory.
- **Fridges** used for flammable substances should be **spark-proof**. This is to avoid the possibility of an internal light or thermostat control unit providing a source of ignition should a container containing flammable substances leak or break.
- Maximum quantity of flammable solvent, including waste flammable solvent, stored in a lab area should not exceed **50 litres** in total for extremely, highly flammable or those flammable liquids below with a flash point below the maximum ambient temperature of the WORKING area and no more than **250 litres** for flammable liquids with a higher flashpoint of up to 60°C (compliance with DSEAR 2002 and HSE). For working volumes, i.e. those kept on the bench, **500ml** in a suitable closed container should be adequate for most purposes, though these should be kept to a minimum and be appropriately labelled as to content and hazard.
- **Peroxide formation:** A significant number of laboratory solvents can undergo autooxidation under normal storage conditions to form unstable and potentially dangerous peroxide by-products. This process is catalyzed by light and heat and

occurs when susceptible materials are exposed to atmospheric oxygen. The following commonly used laboratory solvents can produce organic peroxides that are significantly less volatile than the solvent in which they are formed, as a result, evaporative concentration or distillation can produce dangerous levels of peroxides.

- i. diethyl ether,
- ii. tetrahydrofuran,
- iii. cyclohexene,
- iv. glycol ethers,
- v. decalin,
- vi. 2-propanol
- These solvents are sufficiently volatile that multiple openings of a single container can result in significant and dangerous peroxide concentration. The following precautions should be taken in relation to these materials:
 - All peroxide-forming solvents should be checked for the presence of any peroxides prior to distillation or evaporation.
 - Solvents containing low levels of free radical scavengers such as the antioxidant Butylated hydroxytoluene (BHT) should be used whenever the presence of the stabilizing species does not interfere with intended application.
 - Uninhibited materials should be stored with care and frequently checked for peroxide formation.
 - Peroxide-forming solvents should be purchased in limited quantities and older material in inventory should be preferentially selected for use.
 - Materials should be stored away from light and heat with tightly secured caps and labelled with dates of receipt and opening.

- Periodic testing to detect peroxides should be performed and recorded on previously opened material.
- Further information on peroxide formation can be found in the following Sigma article: <u>http://www.sigmaaldrich.com/chemistry/solvents/learningcenter/peroxide-formation.html</u>.
- **Compatibility** Do not store flammable liquids with any of the following:
 - o Concentrated acids, e.g. nitric acid, sulphuric acid, hydrochloric acid
 - Chlorinated solvents
 - oxidising agents, e.g. halogenated substances, peroxides, perchlorates, nitrates)
 - o reducing agents, e.g. sodium borohydride, lithium aluminium hydride
 - must never be stored with flammable solvents since fires and explosions can result after any spillage, even without a naked flame or heat. The cabinet or bin must be kept securely closed at all times to prevent spread of fire.

Chlorinated solvents - (e.g. chloroform, dichloromethane (DCM), trichloroethylene) are best stored in ventilated cabinets separately from flammable solvents, because there are violent reactions when certain flammable solvents and chlorinated solvents are allowed to mix. Also, when chlorinated solvents are involved in a fire they can generate toxic gases such as phosgene. They should not be stored with alkali metals such as lithium, potassium or sodium, since any mixing may cause an explosion. They can be stored in metal bins if ventilated storage is not available.

Solvent waste - It is very important to keep chlorinated/halogenated solvents in separate containers from other solvents. Solvent waste containers must be clearly labelled as to their contents and must be of appropriate material which are available from most lab supply companies. The quantity of flammable waste solvent stored in BioEscalator fume cupboards or ventilated cabinets

should be the minimum necessary, being limited to the container in use, and the container should be removed when full. This minimises the fire load arising.

Noxious chemicals - Ventilated cabinets are designed to safely hold chemicals which give off noxious fumes and smells. These fumes are sucked away by forced ventilation. Often these are located under fume cupboards and use the same extract system as the fume cupboard. However, free-standing units are also available with their own ventilation system. These should be used to store materials such as mercaptans and amines which have a strong smell. They can also be used to store lachrymators. If you do not have ventilated cabinet, containers of these noxious materials can be stored in sealed secondary containers which should only be opened in a fume cupboard.

Oxidisers - (e.g. peroxides, perchlorates and nitrates) are best stored separately from other materials. Ideally, they should be stored in a bin or cabinet made from metal or other non-organic material. Oxidising agents must never be stored with flammable solvents or reducing agents since fires and explosion can result after any spillage, even without a naked flame or heat. They should not be stored where they can come in contact with wooden shelves or paper. Perchloric acid is especially hazardous and is best stored standing in a tray filled with sand within a cabinet or bin, away from organic materials or dehydrating agents such as sulphuric acid.

Carcinogens and Mutagens (class 1 and 2) and Substances Toxic to Reproduction - These must be stored in a locked and secure cupboard and a list of the contents maintained. Only authorised persons should be permitted access. The compatibility of substances should be checked.

Substances subject to special security & licensing requirements: These include

- Poisons Section 7 of the Poisons Act (1972) lists toxic substances known as Schedule 1 Poisons. This has been amended by various Orders of Parliament. This list includes most of the well-known poisons such as arsenic, cyanide, strychnine: <u>http://www.rpharms.com/meppdfs/mep34s1-5.pdf</u>.
- Drugs Precursor Chemicals. Details of these can be found in the Safety Office document: <u>https://www.admin.ox.ac.uk/safety/memoranda/m9-10/</u>

Access to these substances should be restricted to authorised persons and a requirement of licence from the home office and appropriate measures should be in place to ensure secure storage and records of use.

Appendix 1:

Incompatibility Table of Commonly used lab chemicals

Please note this is not an exhaustive list.

Chemical	Incompatible with
Acetic acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol,
	perchloric acid, peroxides, permanganates
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentrated nitric acid and sulphuric acid mixtures
Alkali and	
alkaline earth metals	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (e.g., in manometers), chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid (anhydrous)
Ammonium nitrate	Acids, powered metals, flammable liquids, chlorates, nitrites, sulphur, finely divided organic combustible materials
Aniline	Nitric acid, hydrogen peroxide
Arsenical materials	Any reducing agent
Azides	Acids
Bromine	See Chlorine
Calcium oxide	Water
Carbon (activated)	Calcium hypochlorite, all oxidizing agents
Chlorates	Ammonium salts, acids, powered metals, sulphur, finely divided organic or combustible materials
Chromic acid	
and chromium trioxide	Acetic acid, naphthalene, camphor, glycerol. Alcohol, flammable liquids in general
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided
	metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulphide
Copper	Acetylene, hydrogen peroxide
Cumene hydroperoxide	Acids (organic and inorganic)
Cyanides	acids
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	All other chemicals
Hydrocarbons	(such as Fluorine, chlorine, bromine, chromic acid, sodium peroxide
2	butane, propane, benzene)
Hydrocyanic acid	Nitric acid, alkali
Hydrofluoric acid (anhydrous)	Ammonia (aqueous or anhydrous)
Hydrogen sulphide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
lodine	Acetylene, ammonia (aqueous or anhydrous), hydrogen
Mercury	Acetylene, fulminic acid, ammonia
Nitrates	Acids
Nitric acid (concentrated)	Acetic acid, aniline, chromic acid, hydrocyanic acid, hydrogen sulphide, flammable liquids and gases, copper, brass, any heavy metals
Nitrites	Acids
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury
Oxygen	Oils, grease, hydrogen, flammable liquids, solids, and gases

Perchloric acid	Acetic acid, anhydride, bismuth and its alloys, alcohols, paper, wood, grease, oils
Peroxides, organic	Acids (organic or mineral), avoid friction, store cold
Phosphorus (white)	Air, oxygen, alkalis, reducing agents
Potassium chlorate	Sulphuric and other acids
Potassium perchlorate (see also	chlorates) Sulphuric and other acids
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulphuric acid
Selenides	Reducing agents
Silver	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid
Sodium	Carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium peroxide	Ethyl and methyl alcohol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerin, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulphides	Acids
Sulphuric acid	Potassium chlorate, potassium perchlorate, potassium
	permanganate (similar compounds of light metal, such as sodium, lithium)
Tellurides	Reducing agents