Chemical Safety Guidance

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Safe Storage of Hazardous Chemicals in Stockrooms, Workshops and Laboratories

Occupational Health and Safety Service
HSD051C (rev3)

UNIVERSITY OF CAMBRIDGE

Contents

1. Introduction

Poor or incorrect chemical storage practices can lead to inadvertent reactions between incompatible materials with the potential to cause harm, fire or even explosions.

All chemicals should be stored in such a manner as to prevent incompatible materials from being accidentally mixed together in the event of the breakage of one or more containers in the storage area, or to prevent the formation and build up of reactive vapours. The correct storage of chemicals within storage areas / stock rooms, workshops and laboratories is an on-going problem which can sometimes be complex and potentially confusing. The overall purpose of correct storage is to maintain control over the chemicals so that they can be both stored and retrieved safely.

Risk assessments must consider the storage of substances as well as their use

Many chemicals, including waste chemicals awaiting safe disposal, have special storage requirements with temperature, time, or security restrictions and practical problems can arise because of the number of separations that could be desirable. Correct storage must address the compatibility issues of flammable substances, unstable materials, highly reactive chemicals and vapours of highly toxic materials.

Safe storage of chemicals can be achieved by arranging the materials to provide separation based on their chemical properties. This requires planning and will involve, an inventory list, accurate labelling, an appreciation of chemical incompatibilities and a range of suitable containers and storage facilities.

In essence, the most important reasons for proper chemical storage are:

1. to provide for effective management of chemicals
2. to lessen the risk of fire
3. to prevent accidental mixing in emergencies
4. to minimise exposure to corrosive and toxic chemicals
5. to comply with relevant statutory security obligations

Accidents resulting from poor chemical storage techniques are preventable and appendix 1 lists some common examples of improper storage practices to avoid.

2. Chemical Storage Facilities

2.1 General Considerations

Safe storage of chemicals must begin with identification of the chemicals to be stored and their intrinsic hazardous properties. Since many chemicals have several hazards, which may vary in degree of severity, depending on quantity and concentration, it is not always straight forward to determine what protection is needed for safe storage and where best to store a particular chemical. However, typical storage considerations may include temperature, ignition control, ventilation, segregation and identification.

Separation (i.e. use of distance), segregation (i.e. use of a physical boundary) or isolation is recommended depending upon the severity of hazard, total quantities stored, and the size, break resistance and durability of individual containers (i.e. fragility of glass bottles, perforation or degradation of plastic containers, and corrosion or puncture of metal containers). Hence, the physical composition and even the size of storage containers may also affect the need for special storage practices and safety procedures.

It should be noted that ventilation is needed for chemicals and their containers which may release dangerous or damaging quantities of vapours or gases that are flammable, corrosive, irritating or toxic. Ventilated storage is particularly important for those substances classed as fuming or highly volatile.

Ventilation should be by air extraction from the storage area to an external exhaust at a safe distance, at least 3 m, from openings into the building. This can sometimes be achieved via appropriate connection to an adjacent fume cupboard extraction system (consult an extraction engineer). Highly odorous chemicals should also be stored in a well-ventilated area; a ventilated cabinet is preferable.

In general the storage of chemicals within fume cupboards is strongly discouraged, unless it is for the reaction at hand, as materials stored in the fume cupboard can adversely affect the containment provided and increase the risk of accidental spillage and /or contact with incompatible substances.

Highly toxic chemicals (such as cyanide, cacodylic acid), shock-sensitive chemicals (such as solid sodium azide or picric acid), and habit-forming chemicals (amyl nitrite) must be stored in locked cabinets to prevent theft.

Peroxide-forming chemicals and those that may become shock-sensitive with long-term storage should be stored separately and labelled with date of receipt, date of opening and disposal date. Peroxide-forming chemicals should be stored in a cool, dark, dry place.

Flammable liquids should be stored in clearly labelled, flammable-liquid cabinets (flame-resistant metal cabinets) which are at least:

- of 30 minutes fire resisting construction
- robust enough to withstand foreseeable accidental damage
- able to retain spillage equivalent to 110% of the contents of the largest container (bunded)
- appropriately labelled to indicate contents and signed to indicate the nature of the hazard
- sited so as to ensure adequate separation of incompatibles, and away from sources of heat or ignition, as necessary, and away from hazardous areas and emergency escape routes

The maximum volume of flammable liquid that should be stored in such a flame resistant cabinet(s) in a workroom or laboratory is 50 litres, regardless of the capacity of the storage cabinet(s). Storage in excess of 50 litres per room should be avoided where ever practicable and would only be permitted in very exceptional circumstances and only if a cabinet fully meeting BS EN 14470-1:2004, with at least 90 minutes fire resisting construction and self closing doors were used for **all** the solvents in the workroom or laboratory, to an absolute maximum of 200 litres (although this is NOT recommended).

Empty flammable substance containers, unless completely free of liquid or vapour must also be kept in the highly flammable liquids store and must be securely closed until appropriate disposal is arranged or the containers have been washed out and aired to dry.

Hazardous substances cabinets should be designated for, and restricted to, a particular class of substance. In particular, other substances should not be stored with highly flammable substances. No other combustible material, including packaging, should be kept in, or within 1 metre of, a hazardous substances cabinet.

Every storage area should have emergency, and where necessary, evacuation procedures in case of a leak, spill or fire within the room. It may be necessary to consider incidents in adjacent parts of the premises, which may affect the storage. Fire-fighting equipment should be provided at readily accessible locations at the storage area, if necessary, consult the Fire Safety Unit for further guidance.

Where necessary, adequate drainage should be provided to deal with water used for fire protection, fire fighting or post fire cooling (acetylene cylinders), to minimise environmental damage. Interceptors or special drainage systems may be necessary to minimise the risk of contamination of watercourses.

Storage areas and buildings, rooms, cupboards and bins should be adequately maintained.

The location of frequently used chemical storage areas should be based on consideration of safety in travel to the storage area and transport of chemicals to and from storage.

Chemicals stored at the bench or other work areas should be those that are used frequently and quantities should be limited to the minimum that is convenient.

2.2 Open Air Stores

These must have the means of controlling a spillage. This may be an impervious sill or low bund, typically 150 mm high and big enough to hold 110% of the contents of the largest container. The alternative is to drain the area to a safe place, such as a remote sump or separator. Absorbent granules or another means of clearing up small spills must be provided but it should be noted that some granules such as clay are not suitable for certain chemicals e.g. hydrofluoric acid. Care must be taken to ensure that any absorbent materials used are compatible with the chemicals being stored.

The surface of the storage area should be sloped so that any spillage does not accumulate around the containers but can drain to a safe area or to a sump / interceptor. There should be no combustible materials (including vegetation) in the storage area or within 1m of the sill or bund wall.

2.3 Stores in Buildings

Where there are centralised storage areas / stock rooms the following requirements exist:

- Store rooms / buildings should be adequately ventilated to disperse vapour from any leakage or spillage and should have at least five air changes per hour
- Means of containing spillage should be provided for example a sloping floor or a 150 mm sill across door openings
- Ramps may need to be provided for ease of access for wheeled trolleys etc
- The floor should be impermeable and inert with respect to the liquids stored
- Any heating and lighting provided in the store should not be able to act as a source of ignition. There should be no possibility of flammable vapour being ignited by hot surfaces and adequate ventilation of the store must be maintained
- External storage buildings, whether or not they are fire-resisting structures, should have a lightweight roof to act as explosion relief. For internal stores, relief panels may be provided in one or more walls, providing the relief can vent to a safe place
- All stores should be operated so that the risk of spillage is minimised. They should not normally be used for dispensing operations, nor should other materials be kept in them.
- Any area where an explosive atmosphere could exist or be generated (ie: as a result of a spillage) must be assessed with respect to the Dangerous Substances and Explosive Atmosphere Regulations (DSEAR) and zoned where appropriate.

2.4 Refrigerator Storage (Fridges and Freezers)

Refrigerator temperatures are often higher than the flash points of extremely / highly flammable liquids and ignition sources are readily available inside the storage compartment of an unmodified domestic type refrigerator. Also the compressor and its circuits are typically located at the bottom of the units, where vapours from flammable liquid spills or leaks of liquid (or vapour) may easily accumulate. Furthermore should a refrigerator malfunction the internal temperature can rise above the flash point of most if not all flammable liquids aka flammable solvents, therefore…..

Flammable liquids must not be stored in ordinary domestic refrigerators.

Flammable liquids must only be stored in fridges and freezers expressly designed or modified for the purpose, i.e. those which have all ignition sources removed.

Some domestic type refrigerators can be modified to become **internally** ‘explosion-safe’ aka ‘spark-free’ aka ‘spark-proof’ permitting storage of flammable liquids. To avoid confusion these refrigerators will be hereafter referred to as internally **‘spark-free’**. The modifications needed include relocation of manual temperature controls to the exterior of the storage compartment, removal of light switches and assemblies, replacing mechanical door latches with magnetic door gaskets and sealing any holes left. The purpose of these modifications is to eliminate ignition of vapours inside the storage compartment by removing ignition sources within the compartment. Ideally, labs requiring refrigerator storage for flammable liquids should purchase commercial ‘spark –free’ models that require no modification.

Modifications may only be conducted by qualified electricians who will certify the safety of the work.

Under no circumstances should lab workers attempt to perform modifications themselves.

Note: 'explosion-proof' refers to refrigeration equipment that has been designed to protect against ignition of flammable vapours both inside and outside the storage compartment (i.e. it is ATEX rated).

Internally **'spark-free'** refrigerators are **NOT** 'explosion-proof' and thereby **NOT** ATEX rated

If refrigerators are **not internally 'spark free'** (or 'explosion-proof'), they must be labelled 'Caution: Not approved for flammable liquid storage' or similar. Flammable liquids must not be stored in cold rooms that do not have explosion-proof wiring and fixtures. Such storage facilities pose explosion hazards because the various control switches and defroster heaters can spark and ignite flammable vapours.

Chemicals stored in refrigerators or cold rooms should be sealed and appropriately labelled, including the name of the person who stored the material.

Food and drink must not be stored in a refrigerator used for chemical storage. The refrigerator should be labelled 'Food and Drink Must NOT Be Stored in this Refrigerator' or equivalent. Refrigerators used for food should be marked 'Food and Drink Only' or equivalent and must not be in the work area.

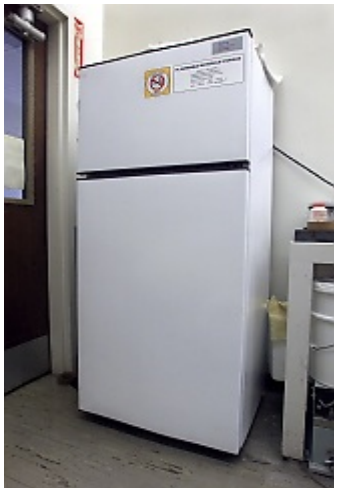

Figure 1 – Modified domestic-type refrigerator used to store chemicals

2.5 Workshop Storage

Most workshops will usually not have large quantities of chemicals, indeed a workshop is not the appropriate location for the bulk storage of hazardous chemicals.

Typically a workshop might contain:

- Solvents such as:
  - degreasing agents
  - paraffin (kerosene)
  - methylated spirits
  - paint thinners
- Aerosol cans, often pressurised by butane
- Petrol, diesel or other fuels in small quantities.
- Solvent based paints
- Acids for cleaning, de-scaling or de-rusting etc

- Gas cylinders (see: University Guidance for the Use of Compressed Gases; HSD032C on the safety Office website).

Many workshops will only contain small quantities of hazardous chemicals and can maintain adequate segregation and safe storage by following the guidance in this document and through the application of good practice and common sense:

- Minimise the amount of chemicals stored in the workshop
- Keep all toxic chemicals in cupboards and secure where appropriate
- Do not store or use acids with bleach i.e. solutions containing hypochlorite
- Avoid using any agents containing hydrofluoric acid which is particularly toxic and will require specialised storage
- The total quantity of flammable solvent on the open bench should not exceed one litre
- Store all other bulk flammable solvents in a metal solvent cabinet, the grand total stored in a workshop must not exceed 50 litres.
- Do not store any flammable solvents in close proximity to any source of ignition including:
    - Open (naked) flames such as burners, heaters, glass blowing / cutting / welding torches or forge benches.
    - Grinding wheels, hand held or fixed
    - Electric heaters or heat guns
    - Electric arc welders
    - Electrical tools and equipment
    - Sources of static electricity

It should be noted that cylinders of acetylene represent a significant risk of explosion in a fire and it is standard emergency services practice to hose them down with water for 24 hours following a fire, before they can be moved. Therefore it may be worth giving some consideration when locating acetylene cylinders as to drainage available and what the consequences would be to the surrounding areas.

Note: It would be expected that most workshops can comply with this guidance without the need for a plethora of specialised storage cabinets, by minimising the quantities held and by spatial separation of incompatible substances.

3. Storage According to Hazard Class and Incompatibility

The risk associated with incompatible chemicals coming into contact must be avoided wherever chemicals are handled or stored as when incompatible chemicals react, the generation of energy may be extremely violent resulting in catastrophic explosions. Gaseous products may be formed which are dangerously flammable, giving off vapours which can rapidly travel outward to an ignition source, thus creating a dangerous fire situation. Reaction products may also release toxic vapours capable of overcoming nearby personnel. Finally, even non-hazardous vapours may be harmful if given off in a great enough volume to displace the oxygen in an enclosed area thus creating an oxygen deficient environment (see the Health and Safety Office website for guidance on oxygen depletion)

The most common chemical storage practice is that of simply storing chemicals in alphabetical order on shelves. This often results in incompatible chemicals being stored together e.g. alphabetical arrangement could result in hydrogen peroxide (a strong oxidizer) being stored next to hydrazine (a very strong reducer). Chemicals should not be stored alphabetically unless they have first been separated into their hazard classes.

There are no absolute rules on how many classes of chemicals should be segregated. The degree of segregation will depend upon the risk. However, isolation of chemicals into the basic hazard classes will eliminate most accidental adverse reactions that may occur due to breakages or leakages in storage areas (see Figure 2 below).

In general chemicals should only be stored with compatible substances according to the following categories (note: always consult the SDS):

		1	2a	2b	3	4	5a	5b	5c	6
		Flammable Liquids	Acids, Inorganic	Acids, Organic	Alkalis (Bases)	Oxidizers	Poisons, Inorganic	Poisons, Organic	Schedule 1 Poisons	Air / Water Reactives
1	Flammable Liquids	✓	X	✓	X	X	X	✓	X	X
2a	Acids, Inorganic	X	✓	X	X	✓	X	X	X	X
2b	Acids, Organic	✓	X	✓	X	X	X	X	X	X
3	Alkalis (Bases)	X	X	X	✓	✓	✓	X	X	X
4	Oxidizers	X	✓	X	✓	✓	✓	X	X	X
5a	Poisons, Inorganic	X	X	X	✓	✓	✓	X	X	X
5b	Poisons, Organic	✓	X	X	X	X	X	✓	X	X
5c	Schedule 1 Poisons	X	X	X	X	X	X	X	✓	X
6	Air / Water Reactives	X	X	X	X	X	X	X	X	✓

KEY - X = NOT compatible – do NOT store together ✓ = Maybe compatible – consult SDS

Figure 2 - Chemical Incompatibility Matrix

3.1 Storage Categories and Guidance

Common storage problems can lead to mixing incompatible chemicals. The most serious of these is the storage of inorganic acids (especially oxidizing acids) with flammable substances. However, organic acids tend to be flammable and if so, should be stored as such i.e. glacial acetic acid.

See Appendix 2 for examples of chemicals stored by hazard class; Appendix 3 for examples of common chemical incompatibilities and; Appendix 4 for a suggested best practice storage scheme.

1. Flammable liquids / solvents and halogenated solvents:

Many organic and inorganic materials are combustible, that is they can be ignited and will then burn in air. Some have such a high degree of combustibility that they are designated flammable and must be stored in approved fire resisting safety cans or cabinets.

Under the **old** Chemical (Hazard Information and Packaging for Supply) Regulations 2002 (CHIP), substances **were** classified into 3 categories of danger according to their flashpoint.

Extremely Flammable	– Flashpoint less than 0°C and a boiling point lower or equal to 35°C
Highly Flammable	– Flashpoint less than 21°C
Flammable	– Flashpoint equal to or greater than 21°C and less than or equal to 55°C

Since December 2010 the introduction of the United Nations Globally Harmonised System (GHS) of classification and labelling has raised the upper threshold and redefined these 3 categories of danger according to both their flashpoints and boiling points: Appendix 5

Extremely Flammable	– Flashpoint less than 23°C and a boiling point lower or equal to 35°C
Highly Flammable	– Flashpoint less than 23°C and a boiling point greater than 35°C
Flammable	– Flashpoint equal to or greater than 23°C and less than or equal to 60°C

The old CHIP labelling can clearly be distinguished by its characteristic square orange pictograms (left) whilst the new GHS uses white diamonds with a red border (right);

Common flammable solvents include:

- **Alcohols** - methanol, ethanol, propanol, butanol, amyl alcohol, hexanol
- **Aldehydes & Ketones** - acetaldehyde, acetone, methyl ethyl ketone, MIBK
- **Alkanes** (hydrocarbons) - butane, hexane, heptane, octane, nonane, ligroin, naphtha, petroleum naphtha, petroleum ether, petroleum distillates, pentane, petrol
- **Aromatics** - benzene, bromobenzene, cumene, pyridine, toluene, xylene
- **Ethers** - ether, ethyl ether, methyl ether, isopropyl ether, ethylene glycol monomethyl ether, cellosolve
- **Highly Toxic** - acrolein, carbon disulfide, ethyleneimine, ethylene oxide, silane
- **Miscellaneous** - acetic acid, acetyl chloride, acetonitrile, cyclohexane, dichloroethane, dioxane, ethyl acetate, ethylenediamine, furan, methyl methacrylate, propylene oxide, tetrahydrofuran, triethyl amine, (some scintillation liquids)
- **Halogenated Hydrocarbons** – □□,□,□-trifluorotoluene, bromobenzene, Chlorobenzene, 1,1-dichloroethylene, vinyl chloride, bromoethylene, chloroethane, ethyl bromide

Non-flammable halogenated solvents (chloroform, methylene chloride, etc.) may be stored with flammable liquids if you have adequate storage space ie: does not displace flammables.

Do NOT store flammables with the following:

- **Oxidizing agents** such as chlorates, nitrates, perchlorates, permanganates, and peroxides. They usually do not combust on their own but provide the oxygen to accelerate the combustion rate of other chemicals
- **Corrosive chemicals** (acids or bases that destructively attack organic and non-organic material). Common acids include sulfuric acid, acetic acid, and nitric acid. Common alkalis (bases) include ammonium hydroxide, calcium oxide (slaked lime), and sodium hydroxide (lye)
- **Materials susceptible to spontaneous heating and/or explosions**. Hydrogen peroxide contacting combustible material can result in spontaneous combustion. Picric acid can be explosive if dry (sensitive to shock and friction when dry)
- **Substances that react with air or moisture** to create heat (water-reactive materials react with water to release hydrogen gas that is flammable or presents a health hazard). Concentrated sulfuric acid is a corrosive that can react violently with water, giving off heat and an irritating toxic fume.

Avoid storing flammables in direct sunlight or near other heat sources; eliminate all sources of ignition (heat, sparks, or open flames). Keep the area dry and cool. Use internally **'spark-free'** refrigerators designed for chemical storage when chemicals require cold storage (see SDS). Most flammable vapours are heavier than air and will settle low to the ground where they are free to do so. Provide adequate ventilation to prevent the accumulation of large amounts of vapour.

Flammable liquids with a flashpoint in the range 23°C to 60°C will not normally produce a flammable atmosphere when stored at an ambient temperature below 23°C. However room temperatures could easily exceed 23°C. Flammable liquids can produce flammable atmospheres if heated above their flash point **or if released as a mist, spray or foam** and will ignite and burn readily if exposed to fire from another source. It is preferable for these higher flashpoint liquids to be stored either in the open air or in a store, which is in a safe place or is fire resisting.

Note: The flashpoint of a multi-component system will vary depending upon the composition and solubility's of the individual components. For instance the flashpoint of pure ethanol is 13°C, but making a 10% solution of ethanol in water could raise this to 48°C. However, adding water to an immiscible solvent will not change its flashpoint. It should be remembered that flash points can be determined by different methods and quoted values may vary by a few degrees (see Appendix 5).

2. Acids:

Contact of a concentrated oxidizing acid with a flammable substance can result in a fire or an explosion. Organic acids are combustible materials and many of them are combustible liquids.

a. **Inorganic mineral acids** (e.g. nitric, sulfuric, phosphoric, chromic, hydrochloric and perchloric acids)
   - Store in a labelled ventilated corrosive storage cabinet if possible separated from flammable and combustible materials
   - Corrosive to metal surfaces
   - Store in chemically resistant secondary container where possible e.g. BDH / VWR Safepak (available in a range of sizes from 100 ml to 2500 ml)
   - Segregate acids from reactive metals such as sodium, potassium, magnesium, etc
   - Segregate acids from chemicals which could generate toxic or flammable gases upon contact, such as sodium cyanide, iron sulphide, calcium carbide, etc
   - Segregate acids from bases
   - Perchloric acid presents special hazards - carefully isolate it from acetic anhydride, bismuth and its alloys, alcohol, paper, wood, oil, ether, grease, and sulfuric acid
   - Take special precautions to keep perchloric acid away from acetic acid i.e., oxidisable materials and dehydrating agents

Hydrofluoric acid (HF) is uniquely hazardous and must be stored with extreme care and only handled by competent trained persons.

It should be isolated i.e. stored in a separate acid resistant cabinet away from all other substances. See University Guidance for HF Users.

b. **Organic acids** (e.g. acetic, butyric, formic, trifluoroacetic and mercaptoproprionic acids)

Organic acids can safely be stored with flammable and combustible liquids, but they should generally not be stored with oxidizing mineral acids, which could react more or less violently with organic acids.

- Store separately from oxidizing mineral acids
- Corrosive to metal surfaces
- Store in a ventilated corrosive storage cabinet if possible
- Can be stored with organic solvents unless otherwise noted on the Material Safety Data Sheet
- Take special precautions to keep acetic acid away from perchloric acid

Remember: All acids must be segregated from any chemicals which could generate toxic or flammable gases upon contact (e.g. cyanide salts, metal sulfides, calcium carbide) and reactive metals (e.g. sodium, potassium, magnesium).

3. Alkalis / Bases (e.g. sodium hydroxide, ammonium hydroxide, glutaraldehyde):

Alkalis / bases are corrosive or irritating. Those that are liquid in large glass containers, such as ammonium hydroxide, should be stored in a separate cabinet or area.

- Segregate bases from acids, metals, explosives, organic peroxides and easily ignitable materials
- Store in tubs or trays in a labelled cabinet / cupboard where possible

4. Oxidizers including organic peroxides (e.g. hydrogen peroxide, ammonium persulfate):

Oxidisers are corrosive and irritating and must be stored to avoid contact with incompatible materials such as flammable and combustible liquids, greases and other materials that could react with the oxidiser or catalyse its decomposition. **Liquid oxidizers, such as ammonium persulfate and hydrogen peroxide, react with nearly everything.** They may potentially cause explosions, and must be double contained (i.e., the primary container must be kept inside a canister, tray, or tub) since fires may be initiated by the action of oxidizing agents on organic materials. This includes organic packaging material e.g. paper and cardboard which should be excluded from the area where oxidisers are stored or used.

- Store in a cool, dry place (some may require refrigeration – consult the SDS)
- Keep away from combustible and flammable materials
- Keep away from reducing agents such as zinc, alkali metals, and formic acid
- Store in a labelled ventilated corrosive storage cabinet / cupboard where possible

5. Poisons and toxic chemicals (including habit formers):

a. Inorganic poisons (e.g. mercury, heavy metals and their salts)
b. Organic poisons (e.g. phenol, sodium azide, pharmacological drugs*)
c. Regulated and Reportable Poisons must be managed in such a way as to be able to comply with current legislation. Regulated Poisons should be kept under lock and key, see the Safety Office website for more information.

Toxic chemicals that are acid-sensitive, such as cyanides and sulphides, should be stored in a separate location from acids or protected from contact with acids. Store poisons and toxic substances according to the nature of the chemical using appropriate security where necessary e.g. locked cabinets with strict key controls.

Volatile poisons e.g. poisons, toxics, and carcinogens, such as carbon tetrachloride, chloroform, dimethylformamide, dimethyl sulfate, formamide, formaldehyde, halothane, mercaptoethanol, methylene chloride, and phenol

- Store in a ventilated cabinet
- May be stored with flammable liquids **if** bases are not present

Non-volatile liquid poisons e.g. acrylamide solutions, coomassie blue stain, diethylpyrocarbonate, diisopropyl fluorophosphate, uncured epoxy resins, ethidium bromide, triethanolamine. This group contains carcinogens and highly toxic chemicals.

- Store in a normal cabinet, preventing contact with other materials
- May be stored with non-hazardous liquids, such as buffer or salt solutions
- Double contain quantities greater than one litre

* the storage of certain substances are subject to control under The Misuse of Drugs Regulations and the Drug Precursor Regulations and may be required to be kept secure under lock and key

6. Air / Water reactive chemicals and combustible solids (e.g. sodium and potassium metals, lithium aluminium hydride, metal hydrides, butyl lithium):

Water Reactive Chemicals react violently with water releasing heat and in some cases explosive by-products. Of chief concern are the alkali metals e.g. sodium and potassium. **All alkali metals react vigorously (i.e. exothermically) with water to form the hydroxide, liberating hydrogen gas.** The heat generated from the reaction can ignite the hydrogen resulting in an explosion. The rate of reaction increases as the atomic weight increases. Alkali metals can also react with oxygen, acids, halogenated hydrocarbons and carbon dioxide.

- Store all metals in the container provided by the manufacturer
- Store in a cool, dry environment, away from light and free from extremes of temperature and humidity and away from any water source
- Store alkali metals under mineral oil or in an inert atmosphere. Note: Lithium reacts with nitrogen
- Make certain that a L2 D-metal fire extinguisher is available (for use on flammable metal fires only)
- Use secondary containment
- May be stored with dry solids
- Certain compounds require the container headspace to be purged with inert gas after use
- Consider the use of drying agents and desiccators where appropriate

Pyrophoric Substances are substances / materials which will react with the air to ignite when exposed, e.g., white phosphorus

- Store in a cool, dry place making provisions for an airtight seal

7. Dry solids e.g. all hazardous and non-hazardous powders, should be stored separately from the above categories on open shelves or in either a normal or ventilated cabinet as appropriate. Where space is limited, dry solids may be stored above compatible liquids / solutions. If properly double contained, dry solids can be stored with metal hydrides

Solid picric acid or picric sulfonic acid may be stored with dry solids, but should be checked regularly for dryness. When completely dry, picric acid is explosive and may detonate upon shock or friction.

8. **Compressed gases** (e.g. oxygen, nitrogen, hydrogen, arsine, and acetylene) – see University Guidance http://www.admin.cam.ac.uk/cam-only/offices/safety/publications/hsd032c/hsd032c.pdf

    - Store securely mounted
    - Segregate oxygen from flammable gases, particularly propane.
    - Store acutely toxic and toxic gases securely outside, or in gas cabinets or fume hoods

9. **Peroxide forming chemicals** including:

    - **Ethers and acetals**. Especially dangerous are cyclic ethers (e.g. Tetrahydrofuran and dioxane) and ethers derived from primary and secondary alcohols, particularly diisopropyl ether. Ethers having an aromatic group bonded to the oxygen generally do not peroxidize under normal conditions.
    - **Benzylic hydrogen** containing compounds, especially tertiary hydrogens, (e.g. cumene, tetralin).
    - **Allylic hydrogen** containing compounds (CH_2=$CHCH_2R$), including most alkenes (e.g. cyclohexene, cyclooctene).
    - **Ketones**, especially cyclic ketones.
    - **Dienes and vinylacetylenes** (e.g. divinylacetylene, butadiene).
    - **Paraffinic and alkylaromatic** hydrocarbons with tertiary hydrogens (e.g. decalin, methylcyclopentane).
    - **Vinyl and vinylidene** compounds (e.g., vinyl acetate, vinylidene chloride).
    - **Aldehydes** (particularly anhydrous acetaldehyde); ketones with an alpha- hydrogen (methyl isobutyl ketone); ureas, amides, lactams.
    - **Potassium metal** (actually forms the yellow superoxide KO_2) and alkali metal amides such as sodium amide.

    Peroxide forming compounds should be:

    - Stored in airtight containers in a dark, cool, and dry place
    - Containers must be labelled with receiving, opening, and disposal dates
    - Periodically tested for the presence of peroxides
    - Where possible, container headspace should be purged with an inert gas

The chemical incompatibilities discussed above are by no means exhaustive. As a result, it is important for laboratory personnel to thoroughly research the properties of the chemicals they are using. Safety Data Sheets (SDSs) have sections on chemical incompatibility. The container's label should also provide storage guidelines.

4. General Storage Guidelines

1. Limit the amount of chemicals stored to the minimum required
2. Storerooms, cupboards and bins should be marked to indicate their contents e.g. Highly Flammable, Acids, Oxidisers
3. Avoid exposure of chemicals to heat or direct sunlight. This may lead to the deterioration of storage containers as well as the degradation of the chemicals
4. Individual containers should be clearly marked to indicate their contents and the degree of flammability, toxicity
5. Store all hazardous liquid chemicals in drip trays or secondary containers that are chemically resistant. 'Photographic trays' can provide good containment for some chemicals (see Figures 3 and 4 below), others may require different plastics (solvent resistant), metal (stainless steel) or even glass

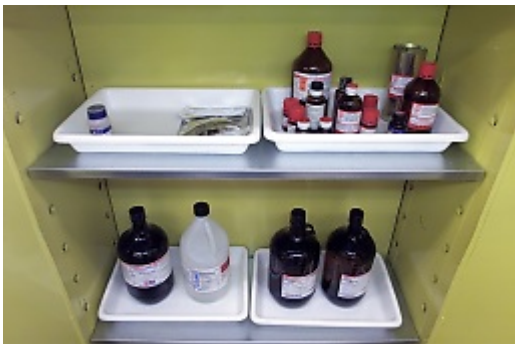

Figure 3 – Bottles stored in drip trays within flammables cabinet

Figure 4 – Bottles stored in drip trays within ventilated acids cabinet including example of chemically resistant secondary containment (BDH / VWR Safepak bottom right)

6. Ensure that caps and lids on all chemical containers are tightly closed to prevent evaporation of contents
7. The storage of chemicals above head height must be minimised to reduce the risk of spillage when being removed or replaced, particularly important with large or glass containers
8. Ensure all shelving is suitable and secure – consider the implications of a shelf failing
9. A system of stock rotation should be employed so that the oldest containers are removed from store first
10. If date-marked, substances must be used or disposed of by the 'use by' or 'disposal date', as guidelines for storage as appropriate
11. Avoid storing chemicals on bench tops or in fume cupboards except for those being currently used
12. Label all containers (including squeeze bottles and Nalgene bottles) to which hazardous materials are transferred with the identity of the substance and its hazards. NB. Be aware that squeeze bottles and Nalgene bottles have varying resistances to different chemicals
13. Evaluate/test stored chemicals that can form peroxides for crystal formation, deterioration, and integrity (see http://www.admin.cam.ac.uk/cam-only/offices/safety/chemical/peroxides.html for further information on peroxides and peroxide formers)
14. Use approved corrosive storage cabinets (constructed of chemically resistant components) for storing acids and bases. These should ideally be connected to exhaust ventilation
15. All corrosives should be stored where ever possible in sealed, air-impermeable containers. Therefore, containers with tight-fitting caps are necessary and containers with loose fitting lids or glass stoppers should not be used
16. Use flammable storage cabinets, containers or bins to store flammable liquids (see Figure 5)
17. All stored containers should be periodically inspected to ensure the packaging is in good condition and there are no leaks. If a leak is found, the container should be removed to a safe place and its contents transferred to another container
18. Refrigerators used for storing chemicals must be appropriately labelled
19. Drip trays or fridge boxes should be used to prevent chemicals stored in refrigerators from being accidentally broken and to contain any spills (cardboard boxes are not suitable)
20. Refrigerators and freezers must be regularly defrosted to prevent the build-up of ice (see Figure 6)

Figure 5 – Flammable substance storage – bins, cans and cabinets

Figure 6 – Poor refrigerator storage practices

NB. The materials stored in the boxes in the top of the refrigerator are actually frozen within the ice.

5. Inspection of Stored Chemicals

Chemical storage areas should be inspected at least annually and any unwanted or expired chemicals must be removed and safely disposed of via the University's Hazardous Waste Disposal Service. During this inspection, the list of chemicals present in the laboratory should be updated or verified and the date and name of the inspector recorded.

Although the deterioration in storage of a specific compound cannot be predicted in detail, generalizations can often be made about the reaction characteristics of groups of compounds. Some general conclusions about the stability of classes of chemicals can be reached, and corresponding storage time spans can be identified. Visual inspection of stored chemicals is important in the disposal decision.

Chemicals showing any of the indications listed below should be sent for disposal:

- Slightly cloudy liquids which were once clear
- Darkening or change in colour
- Spotting on solids
- Caking of anhydrous materials indicating uptake of water
- Existence of solids in liquids or liquids in solids
- Pressure build-up in containers
- Evidence of reaction with water
- Corrosion or damage to the container
- Missing or damaged (i.e., illegible) labels
- Old chemicals of unknown origin e.g. research materials

A suggested chemical storage checklist can be found in Appendix 6.

References and Further Reading

1. Prudent Practices in the Laboratory: Handling and Disposal of Chemicals, National Research Council, 1995
2. Hazards in the Chemistry Laboratory, Bretherick,
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6. Improving Safety in the Chemical Laboratory: A Practical Guide, Jay A. Young, 1991
7. CRC Handbook of Laboratory Safety, 5th Edition, 2000
8. Chemical Warehousing – the Storage of Packaged Dangerous Substances, HSG71, HSE Books
9. The Storage of Flammable Liquids in Containers, HSG51, HSE Books
10. Environmental Protection Act 1990, HMSO
11. Environmental Protection (Duty of Care) Regulations 1992, HMSO
12. Storing Packaged Dangerous Substances: Segregation Table, C30, HSE Publications
13. Disposal of Chemical Waste – University Policy and Guidance, Health and Safety Office

Appendix 1 - Common Examples of Improper Storage Practices

More than one of the following examples of improper storage practices can be found in many laboratories and workshops or their associated stockrooms and storerooms:

- Chemicals are stored in alphabetical order by name without consideration of incompatibilities
- Chemicals are stored according to poorly chosen categories e.g. all acids are stored together, all organics are stored together
- Chemicals are stored in the fume cupboard
- Chemicals are stored on shelves above average eye-level / head height
- Shelves are overcrowded and containers and bottles of liquid are stood on top of other containers
- Chemicals are left out on benches rather than returned to their appropriate storage area after use
- Chemicals are stored in direct sunlight causing degradation of both the chemicals and the plastic packaging
- Inventory control is poor or non-existent: many containers are not identified with the date of receipt, date of opening or the person responsible for the chemical (in shared facilities)
- Containers have no label or the label is illegible
- Containers are reused but not relabelled
- Flammable solvents incorrectly stored in domestic fridges which have not had all ignition sources removed
- Unused and unwanted chemicals are stored away in cabinets rather than disposed of

Appendix 2 – Examples of Chemicals Stored by Hazard

Poisons, Toxic Chemicals and Habit Formers	Inorganic Bases and Inorganic Reducers/Salts	Organic Bases and Organic Compounds	Inorganic Acids and Oxidizers	Flammable Organics and Organic Acids
Poisons: • Arsenic trioxide (carcinogen) • Sodium azide (solid may be shock-sensitive) • Sodium cacodylate (solid) • Sodium nitroprusside • Strychnine • Tetrodotoxin **Carcinogens:** • Acrylamide • Aflatoxins • Aniline • Benzene • Benzidine • Carbon tetrachloride • Chloroform • 3,3'-Diamino-benzidine • Ethidium bromide (mutagen) • Hydrazine • Nitrosodiethyl-amine • Urethane **Habit Formers:** • Amyl nitrite • Sodium pentobarbital	**Inorganic Bases:** • Ammonium hydroxide • Potassium hydroxide • Sodium hydroxide **Inorganic Reducers:** • Sodium sulfite **Inorganic Salts:** • Calcium chloride • Lithium carbonate • Sodium silicate	**Organic Bases:** • Diaminopentane • Diethylamine • Hexamethyleneimine **Organic Compounds:** • Dextrose • Ethylenediamine-tetraacetic acid (EDTA) • Formaldehyde (carcinogen) • Formamide • Isoleucine • Naphthol	**Inorganic Acids:** • Chromic acid (separate from nitric) • Hydrochloric acid • Hydrofluoric acid • Nitric acid (separate from chromic) • Perchloric acid **Inorganic Oxidizers:** • Ammonium persulfate (separate from sodium nitrite) • Chromium trioxide • Hydrogen peroxide • Silver nitrate • Sodium nitrate	**Flammable Organics:** • Acetone • Benzene (carcinogen) • Diethyl ether (peroxide-former) • Ethanol • Pyridine • Tetrahydrofuran (peroxide-former) • Xylene(s) **Organic Acids:** • Acetic acid • Formic acid

Appendix 3 – Chemical Incompatibilities

This Table is adapted from one presented in Bretherick 'Hazards in the Chemistry Laboratory' and in the American Chemical Society 'Safety in Academic Chemistry Laboratories'. Chemicals here may react vigorously, uncontrollably or otherwise unpleasantly with their 'incompatibles'.

Chemical	Incompatibles
Acetic acid	Chromic acid, nitric acid, sulfuric acid, hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Acetone	Concentrated nitric and sulfuric acid mixtures
Alkali and alkaline earth metals (such as powdered aluminium or magnesium, calcium, lithium, sodium, potassium)	Water, carbon tetrachloride or other chlorinated hydrocarbons, carbon dioxide, halogens
Ammonia (anhydrous)	Mercury (in manometers, for example), chlorine, calcium hypochlorite, iodine, bromine, hydrofluoric acid (anhydrous)
Ammonium nitrate	Acids, powdered metals, flammable liquids, chlorates, nitrites, sulfur, 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
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, powdered metals, sulfur, finely divided organic or combustible materials
Chromic acid and chromium	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 or inorganic)
Cyanides	Acids
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	All other chemicals
Hydrocarbons (such as butane, propane, benzene)	Fluorine, chlorine, bromine, chromic acid, sodium peroxide
Hydrocyanic acid	Nitric acid, alkalis

Hydrofluoric acid (anhydrous); Hydrogen fluoride	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, any flammable liquid, combustible materials, aniline, nitromethane
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous)
Mercury	Acetylene, fulminic acid (produced in nitric acid-ethanol mixtures), ammonia
Nitrates	Acids, reducing agents
Nitric acid (concentrated)	Acetic acid, acetone, alcohol, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, nitratable substances
Nitrites	Acids, oxidizing agents
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury, and their salts
Oxygen	Oils, grease, hydrogen, flammable materials (liquids, solids, or gases)
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils (all organics)
Peroxides, organic	Acids (organic or mineral); avoid friction, store cold
Phosphorus (white)	Air, oxygen, alkalis, reducing agents
Phosphorus pentoxide	Alcohol, strong bases, water
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium chlorate (see also chlorates)	Acids
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver and silver salts	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid (produced in nitric acid-ethanol mixtures)
Sodium (see also alkali metals)	Carbon tetrachloride, carbon dioxide, water
Sodium hypochlorite (bleach)	Acids
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium peroxide	Any oxidizable substance, such as ethanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerol, ethylene glycol, ethyl acetate, furfural
Sulfides	Acids
Sulfuric acid	Acetic acid, chlorates, perchlorates, permanganates
Tellurides	Reducing agents

Appendix 4 – Suggested Best Practice Storage Scheme for some chemicals

	**Flammable liquids:** H224, 225, 226	Do not store anything else in the cupboard except substances that are non-hazardous AND have been packaged in non-combustible containers, e.g. glass.
	**Combustible solids:** H250, 260, 261	Keep segregated from everything else – INCLUDING flammable liquids.
	**Toxic substances:** H300, 301, 310, 311, 331, 340, 341, 350, 351, 360, 361, 370, 371, 372, 373	Do not routinely store anything alongside these except non-hazardous substances.
	**Corrosive substances:** H314, 318 and EUH071	Avoid keeping incompatible substances such as acids & alkalis together.
	**Oxidizing substances:** H270, 271, 272	Keep entirely segregated from all other classes.
	**Organic peroxides:** H240, 241, 242 (May also have other warning symbols)	Keep segregated from everything else.

Appendix 5 – Examples of Flash Points, Boiling Points and Auto-ignition temps

Chemical	Flash Point (°C)	Boiling Point (°C)	Auto-ignition temp (°C)
Acetaldehyde	-38	21	175
Acetic Acid	43	118	426
Acetone	-19	57	465
Acetonitrile	6	82	524
Acrylonitrile	0	77	481
Benzene	-11	80	561
1-Butanol	35	118	343
2-Butanol	24	99	406
Carbon disulfide	-30	46	**90**
Cyclohexane	-18	82	245
1,2-Dichloroethane	13	83	413
Diesel fuels (several grades)	52 to 96	246 to 388	177 to 285
Diethylamine	-26	55	312
Diethyl ether	-45	34.6	160
Diisopropyl ether (DIPE)	-28	69	443
1,4 Dioxane	12	101	180
Ethanol	13	79	363
70% Ethanol	17	79	363
Ethyl acetate	-4	77	427
Ethyl formate	-20	53	440
Hexane	-23	68	234
Kerosene/Paraffin oil (several grades)	35 to 72	150 to 300	220
Methanol	11	65	464
Piperidine	16	106	320
Petrol/Gasoline (several grades)	< -45	38 to 205	246 to 280
Propan-2-ol (iso-propyl alcohol)	12	83	465
Pyridine	20	115	482
Tetrahydrofuran	-14	66	321
Toluene	4	111	535
1,1,1-Trichloroethane	'none'	74	536
Trichloroethylene (Trike)	'none'	87	410
Triethylamine	-17	89	230
Vinyl acetate	-8	72	402
White Spirit (several grades)	21 to > 55	130 to 220	230 to 240

These figures should be regarded as guidance only, they can NOT be taken as being absolute.

The *flash point* of a flammable liquid is the lowest temperature at which a flame will propagate through the vapour above it in a given test, i.e. it is the minimum temperature at which a flammable liquid produces a sufficient concentration of vapour above it to form an ignitable mixture with air in that test.

Note: **Different test methods can give different results.**

The *boiling point*s of substances having a potentially variable composition are shown as a range.

The *autoignition temperature* of a substance is the lowest temperature at which it will spontaneously ignite in normal air at atmospheric pressure without an external source of ignition, i.e. flame or spark.

Appendix 6 – Chemical Storage Checklist

Taking stock of current storage conditions and procedures is the first step in managing a safe chemical storeroom. The following example checklist was developed to help assess safety in the storeroom. The checklist format not only facilitates a systematic assessment of storage and housekeeping conditions, but also identifies general and specific areas of concern. The completed checklist serves as a record of needed improvements. An affirmative answer to each item indicates a satisfactory storage condition.

YES	NO	N/A	STORAGE AREAS
			Storage rooms are properly marked or identified.
			Storage rooms are secured whenever not in use and are available only to authorised personnel.
			Storage areas are well illuminated.
			Storage areas are well ventilated.
			Aisles in the storage area are free from obstruction.
			Ladders with handrails are available where needed.
			SHELF STORAGE
			Large bottles and containers are stored on shelves near the floor.
			Containers of chemicals are stored below eye level.
			Where possible shelves have raised edges or rim guards to prevent the accidental dislodging of containers.
			Reagent bottles or containers do not protrude over the shelf edges.
			Enough space is available so that chemicals are not overcrowded.
			Empty bottles are removed from shelves.
			Shelves are level and stable. Shelving units are securely fastened to wall or floor.
			Shelves are clean-free of dust and chemical contamination.
			STORAGE CONTAINERS
			Storage containers are inspected periodically for rust, corrosion, or leakage.
			Damaged containers are removed or repaired immediately.
			Chemicals are kept in airtight bottles, not in beakers or open vessels.
			Stoppers form an airtight seal with containers.
			Stoppers are easily removed from bottles or containers.
			LABELING OF CHEMICAL CONTAINERS
			All containers are clearly labelled as to contents.
			Labels are readable and free of encrustation or contamination.
			Labels are firmly attached to containers.
			Chemical containers are labelled with the appropriate hazard warning (e.g. poison, corrosive, etc).
			All container labels include both date of receipt and group name.

YES	NO	N/A	STORAGE AREAS
			HOUSEKEEPING
			Cleanliness and order are maintained in the storage areas at all times.
			Unlabeled, contaminated, or undesirable chemicals are discarded properly.
			Chemicals in storage cabinets and on shelves are inspected for decomposition on a regular basis.
			Unused chemicals are never returned to stock bottles.
			Packing materials and empty cartons are removed at once from the area.
			Waste receptacles are properly marked and easily located.
			Separate disposal containers are available for broken glass.
			EMERGENCY PREPAREDNESS
			Equipment and supplies for cleaning up spills are readily available.
			Fire extinguishers are immediately accessible.
			Fire extinguishers are periodically inspected and maintained.
			CHEMICAL STORAGE
			Chemicals are not exposed to direct sunlight or localised heat.
			Containers of corrosive chemicals are stored in trays large enough to contain spillage or leakage.
			Chemicals are stored by, reactive class (e.g. flammables with flammables, oxidizers with oxidizers).
			Incompatible chemicals are physically segregated from each other during storage.
			1. **Acids**
			Large bottles of acids are stored in acid cabinets.
			Oxidizing acids are segregated from organic acids and flammable and combustible materials.
			Acids are separated fro caustics and from active metals such as sodium, magnesium, and potassium.
			Acids are segregated from chemicals that can generate toxic gases on contact, such as sodium cyanide and iron sulfide.
			Bottle carriers are used for transporting acid bottles.
			Absorbents or acid neutralizers are available for acid spills.
			2. **Caustics**
			Caustics are stored away from acids.
			Solutions of inorganic hydroxides are stored in polyethylene containers.
			Absorbents or caustic neutralizers are available for spills.

YES	NO	N/A	STORAGE AREAS
			3. **Flammables**
			Flammables are kept away from any source of ignition: flames, heat or sparks.
			Where refrigerators are used for flammable liquid storage they are internally **'spark-free'.**
			Bonding and grounding wires are used where flammables are stored and dispensed.
			Absorbents are available for leaks or spills.
			4. **Peroxide-Forming Chemicals**
			Peroxide-forming chemicals are stored in airtight containers in a dark, cool, and dry place.
			Peroxide-forming chemicals are properly disposed of before the date of expected peroxide formation.
			Suspicion of peroxide contamination is immediately evaluated by use of safe procedures.
			Chemicals are labelled with date received, date opened, and disposal date.
			5. **Water-Reactive Chemicals**
			Chemicals are kept in a cool and dry place.
			In case of fire, a Class D fire extinguisher is used.
			6. **Oxidizers**
			Oxidizers are stored away from flammable, combustible, and reducing agents (e.g. zinc, alkaline metals).
			7. **Toxic Compounds**
			Toxic compounds are stored according to the nature of the chemical, with appropriate security employed where necessary.

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This document was republished as (rev3) in February 2017 to clarify small sections of phraseology with respect to storing flammable solvents. These changes bring the phraseology into line with HSD19C but do NOT change the tenor of the guidance.

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