Safe Storage of Chemicals

Proper storage of chemicals within a laboratory is a difficult and continuing problem. Some experts have stated that the majority of laboratory accidents are related to improper storage of chemicals. The overall purpose is to maintain control over the chemicals so that they can be safely stored and retrieved. Since it is almost inevitable that a bottle will fall and hit other bottles, chemicals should be arranged so that no adverse reaction occurs between the chemicals. Many chemicals have special storage requirements with temperature, time, or security restrictions. Many practical problems arise because of the number of separations that would be desirable.

Chemicals should not be stored alphabetically. Acetic acid and acetlehyde could be adjacent members on a shelf and are an incompatible pair. It is also a good idea to separate liquids from solids because chemicals must come into contact to react and this is avoided by having liquids and solids separated. The general approach is to separate all the chemicals into compatible groups. Then separate each group from the other groups by a barrier. While this is a good idea, most facilities do not have the space for such a system. However, the use of secondary containment, such as plastic bins, can maximize the space allowed for chemical storage.

In summary, proper storage must address flammables, unstable materials (including those that can form explosive peroxides), reactives and vapors from highly toxic materials. This can be achieved by arranging the materials to provide separation based on their chemical properties. See the various literature resources and the MSDSs for determining the characteristics of a compound.

The following groups should be separated:

1. Acids and bases - Acids should be further separated into inorganic acids and organic acids.
2. Oxidizing agents from reducing agents
3. Potentially explosive materials
4. Water reactive materials
5. Pyrophoric chemicals
6. Peroxide forming materials - these must be properly managed and disposed of within recommended time periods
7. Materials which can react with themselves (Polymerization for example)
8. Incompatible chemicals
9. Chemicals showing hazards such as flammability, reproductive toxicity, or suspect and confirmed carcinogens

A specific storage arrangement, based on hazard and compatibility, is shown below:

1. General procedures:
    a) Perchloric acid is separated from all other substances
    b) Concentrated nitric acid is separated from all other substances
    c) Highly toxic and carcinogenic chemicals are stored in ventilated safety storage cabinets
    d) Inorganic and organic acids are stored separately
    e) Bases are stored separately
    f) Explosives or potential explosives are separated

g) Inorganic and organic flammables are separated. In addition, organic flammables are further separated into two classes based on compatibility
h) Oxidizing and reducing agents are separated
i) Other chemicals can generally be grouped together (but compatibility must be considered).

2. The separations, either by distance or physcial barriers, should be enough to prevent the mixing of two incompatibles if a container is dropped and breaks a second container. Ideally the separation would also reduce the amount of materials that could become involved in a fire. Some laboratories have found fiber glass trays useful for limited separation and containment.

3. Extremely toxic (and/or carcinogenic) or dangerous materials should be double containerized and carried back and forth from the storage cabinet to the hood in an unbreakable outer container.

4. Cabinets for flammables and corrosives make ideal storage cabinets. However, depending on the quantity and variety of chemicals, the cost may be high. These cabinets can be conveniently vented to the outside so that toxic vapors do not enter the laboratory. A ventilation rate of approximately 8 -15 cfm is usually adequate. Several cabinet manufacturers make smaller stackable units. Each cabinet should have a spill containment reservoir in the bottom.

The Flinn Chemical Catalog Reference Manual suggests organic and inorganic groupings which are further sorted into compatible families. The compatible families suggested are:

	Inorganic	**Organic**
1.	Metals, hydrides	Acids, anhydrides, peracids
2.	Halides, sulfates, sulfites, thiosulfates, phosphates, halogens	Alcohols, glycols, amines, amides, imines, imides
3.	Amides, nitrates (except ammonium nitrate), nitrites, azides, nitric acid	Hydrocarbons, esters, aldehydes
4.	Hydroxides, oxides, silicates, carbonates, carbon	Ethers, ketones, ketenes, halogenated hydrocarbons, ethylene oxide
5.	Sulfides, selenides, phosphides, carbides, nitrides	Epoxy compounds, isocyanates
6.	Chlorates, perchlorates, perchloric acid, chlorites, hypochlorites, peroxides, hydrogen peroxide	Peroxides, hydroperoxides, azides
7.	Arsenates, cyanides, cyanates	Sulfides, polysulfides, sulfoxides, nitriles
8.	Borates, chromates, manganates, permanganates	Phenols, cresols
9.	Acids (except nitric)	
10.	Sulfur, phosphorus, arsenic, phosphorus pentoxide	

Suggested Shelf Storage Patterns*

A. Inorganic (*Bottom shelf is #1 & top shelf is #5)

1. Acids, except nitric, should be stored in an acid cabinet, separate from other inorganic chemicals. Store nitric acid away from other acids unless the acid cabinet provides a separate compartment for nitric.
2. Cabinet No. 1 - bottom shelf, No. 1, has hydroxides, oxides, silicates, carbonates and carbon. Shelf No. 2 - metals and hydrides (store away from water); store flammable solids in separate cabinet. Shelf No. 3 - amides, nitrates (not ammonium nitrate), nitrites, azides; store ammonium nitrate away from <u>all</u> other substances (isolate it). Shelf No. 4 - halides, sulfates, sulfites, thiosulfates, phosphates, halogens and acetates. Shelf No. 5 - top shelf, has sulfur, arsenic, phosphorus, and phosphorus pentoxide.
3. Cabinet No. 2 - bottom shelf, No.1 - miscellaneous. Shelf No. 2 - chlorates, perchlorates, chlorites, perchloric acid, peroxides, hypochlorites, and hydrogen peroxide. Shelf No. 3 - borates, chromates, manganates, and permanganates. Shelf No. 4. - sulfides, phosphides, carbides, and nitrides. Shelf No. 5 - top shelf - has arsenates, cyanides, and cyanates - store away from water).

B. Organic (*Bottom shelf is #1 & top shelf is #5)

- Store severe poisons in poisons cabinet.
- Store flammables in a dedicated cabinet: bottom shelf No. 1 - ethers and ketones; shelf No. 2 - hydrocarbons, esters, etc.; top shelf - has alcohols and glycols.

1. Cabinet No. 1 - bottom shelf - No. 1 - sulfides and polysulfides. Shelf No. 2 has epoxy compounds and isocyanates. Shelf No. 3 - ethers, ketones, ketenes, halogenated hydrocarbons, and ethylene oxide (store flammables in a dedicated cabinet). Shelf No. 4 - hydrocarbons, esters, aldehydes (store flammables in a dedicated cabinet). Top shelf - No. 5 - has alcohols, glycols, amines, amides, and imines (store flammables in a dedicated cabinet).
2. Cabinet No. 2 - bottom shelf - No. 1, and shelf 2 - miscellaneous. Shelf No. 3 - acids, anhydrides, and peracids (store certain organic acids in acid cabinet). Shelf No. 4 - has peroxides, azides, and hydroperoxides). Top shelf - no. 5 - phenol and cresols.

Avoid using the floor for storage if possible.

Hazards Due to Chemical Reactions (Incompatibles)

Generation of Heat - e.g. acid and water
Fire - e.g. hydrogen sulfide and calcium hypochlorite
Explosion - e.g. picric acid and sodium hydroxide
Toxic gas or vapor production - e.g. sulfuric acid and plastic
Flammable gas or vapor production - e.g. acid and metal
Formation of a substance with greater toxicity than reactants - e.g. chlorine and ammonia
Formation of shock or friction-sensitive compounds
Pressurization of closed vessels - fire extinguisher
Solubilization of toxic substances - e.g. hydrochloric acid and chromium
Dispersal of toxic dusts and mists
Violent polymerization - e.g. ammonia and acrylonitrile

Flammables

Many organics are flammable and should be treated accordingly. When flammable materials are used, care should be taken to avoid a flammable or explosive mixture with air.

A general rule is that controls should be in place (or quantities limited) so that the concentration of a flammable will not exceed 25% of the lower explosive limit (please refer to NFPA 45, "Fire Protection for Laboratories Using Chemicals", for the quantities of flammables allowed in the laboratory and storage requirements). A list of selected flammable limits is shown below. If it is necessary to have the concentration of a flammable in the explosive range, all sources of ignition must be excluded.

Explosive Limits of Hazardous Materials

Compound	LEL%	UEL%	Flashpoint (ºF)	Vapor Density
Acetone	2.15	13	-4	2.0
Acetylene	2.50	100	Gas	0.9
Ammonia, anhydrous	16	25	Gas	0.6
Benzene	1.30	7.1	12	7.8
Carbon Monoxide	12.4	74	Gas	1.0
Gasoline	1.4	7.6	-45	3-4
Cyclohexane	1.3	8.4	-4	3.0
Toluene	1.2	7.1	40	3.1
Vinyl chloride	3.6	33	Gas	2.2
p-xylene	1.0	6.0	90	3.7

Selection and Use of Refrigerators

A. Ordinary Refrigerators

Not designed for chemical storage. Hot surfaces (light bulb), possibly sparking switches, heating tapes, drains used for the water to run out, and potential ignition sources from the motor.

1. Not for storage of flammable materials
2. Motor produces sparks outside storage area
3. Not for use in hazarous environment

B. Refrigerators for Flammable Materials

Designed for storing flammables. magnetic door seals (to avoid pressure buildup). No sparks or hot surfaces inside. The motor and motor controls may generate sparks.

1. For use in ordinary laboratory
2. No sparks or hot surfaces, but motor produces sparks outside storage area
3. Not for use in hazardous environments

C. Explosion-Proof Refrigerators

This provides a safe spark free interior and can be used in a hazardous envirnment (Class I, Division I & II Group C and D applications).

1. For storage of flammables
2. Uses magnetic door latches and produces no sparks, has no hot surfaces
3. For use in hazardous environments

Control of Vapors Within a Refrigerator

In spite of the lower temperatures, the odors tend to accumulate in a refrigerator of freezer and are then released into the laboratory and become another source of exposure.

It is possible to ventilate a refrigerator by installing a slot hood along the edges of the door. The door is opened only a couple of inches and held there a few minutes. The slot ventilation causes the air to sweep through the refrigerator and out the ventilation system. This system has some disadvantages:

- Moisture condenses on the cold surfaces of the contents of the refrigerator
- There is always that annoying 5 minute wait

Another method which is very satisfactory for reducing the vapors of pesticides and many solvents is to place a tray of activated charcoal in the refrigerator. The charcoal should be handled in the hood because of the dust but it effectively controls many vapors.

Vented Fire Cabinets

Fire safety cabinets are required by regulation to be vented in many localities. The ventilation rate specified in the manual is 5-20 CFM provided by a roof mounted motor. The inlet should have a spark arrestor. However the NFTA has not taken a position on the venting of the fire safety cabinets. The cabinets were designed to protect the contents of the cabinet from fire and were not designed as storage cabinets. The concern is whether forced venting affects the fire rating.

A Second Suggested Shelf Pattern for Chemical Storage

I have used the following chart to label shelves in my stockroons. The system is pretty straightforward, and after everyone gets used to it I find it works very well. Within each category, chemicals ARE stored alphabetically (and this tends to please the old-timers). But the categories are arranged by compatibility and reactivity. What I have always done is create a pretty chart (I no longer have the original from Flinn) and then make multiple copies. I post a few in convenient locations around the stockroom so that folks can refer to it to find things. I also cut out the labels and place the appropriate one on each shelf so that folks can find the correct category easily. It has worked well for me. I hope you find the same true for you.

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The following shelf pattern segregates chemicals first into organic and inorganic. Chemical organization then follows compatibility groupings within the major organic/inorganic headings. Finally, those chemicals appearing at the top of the chart are less reactive and therefore can be stored higher off the ground, while those nearest the bottom of the chart are more reactive and should be stored closer to the floor to reduce the chance of breakage if dropped from the shelf.

Organic #2: Alcohols, Glycols	Inorganic #10: Sulfur, Phosphorus, Arsenic, Phosphorus pentoxide
Organic #3: Hydrocarbons, Esters	Inorganic #2: Halides, Sulfates, Sulfites, Thiosulfates, Phosphates
Organic #4: Ethers, Ketones	Inorganic #3: Amides, Nitrates, Nitrites
Organic #5: Epoxy compounds, Isocyanates	Inorganic #1: Metals and Hydrides (No Water!)
Organic #7: Sulfides, Polysulfides	Inorganic #4: Hydroxides, Oxides, Silicates
Organic #8: Phenol, Cresols	Inorganic #7: Arsenates, Cyanide (above acids)
Organic #6: Peroxides, Azides	Inorganic #5: Sulfides, Selenides, Phosphides, Carbides, Nitrides
Organic #1: Acids, Anhydrides, Peracids	Inorganic #8: Borates, Chromates, Manganates, Permanganates
2nd shelf: Miscellaneous	Inorganic #6: Chlorates, Perchlorates, Chlorites, Perchloric acid, Peroxides
Bottom shelf: Miscellaneous (Nitric Acid)	Inorganic #9: Acids (not nitric)

http://people.ccmr.cornell.edu/~baker/group/safety/Chemical%20Storage%20Guide.pdf