C4. Handling Perchloric Acid

BACKGROUND

Certain laboratory procedures may require the use of perchloric acid. Formation of explosive perchlorate crystals may be a by-product of the experiment. Special fume hoods, commonly known as perchloric acid fume hoods, **MUST** be used when conducting experiments that require perchloric acid. The fume hoods have self-contained wash-down units to inhibit crystal formation within the fume hood and the exhaust ductwork.

Anyone planning to use perchloric acid must read and understand the applicable Safety Data Sheet (SDS). If any portion of the SDS cannot be understood, please contact Health, Safety & Environment.

NOTE: use perchloric acid fume hood for any work with perchloric acid, no matter the concentration

Standard fume hoods used for normal chemical operations **must not be used for perchloric acid work**. Fires and explosions have occurred where organic residues present in the fume hood system were rendered explosive after contact with the perchloric acid fumes and vapours. The acid fumes are usually formed during heating or digestion of materials. The digestion of organic materials may be a highly exothermic reaction and may create acid fumes.

Perchloric acid (60-72 percent) reacts with alcohols and certain other organic compounds to form very unstable perchlorate esters at room temperature.

Perchloric acid (68-72 percent) acts as a strong acid at room temperatures. Perchloric acid is an exceedingly strong and active oxidizing agent as well as a strong dehydrating agent at elevated temperatures (approximately 160 °C, or 320 °F).

Anhydrous perchloric acid (highly unstable) is usually formed when perchloric acid is mixed with concentrated sulphuric acid or phosphorus pentoxide.

Perchloric acid must be used in laboratories with perchloric acid fume hood facilities. Special fume hoods and ducts for perchloric acid work have been constructed of stainless steel. An exhaust air scrubber system has been installed in the ductwork and behind the baffle to emit a fine water spray to dilute and wash down the acid fumes and vapors when the fume hood is in use.

Substitute with less hazardous chemicals when appropriate. Use dilute solutions (< 60%) whenever possible.

REGULATIONS

Use of perchloric acid in the laboratory is regulated by WorkSafe BC Occupation Health and Safety Regulations:

1. OSH Regulation 30.8 Laboratory fume hoods (5) (b) A laboratory fume hood that will be or is being used for working with perchloric acid must be clearly labeled with applicable restrictions on its use
2. OSH Regulation 30.10 Ducting (b) perchloric acid must not be connected to a manifold system.
3. OSH Regulation 30.21 Specific Substances Procedure -Perchloric acid

PERSONAL PROTECTIVE EQUIPMENT (PPE)

- Consult the SDS for appropriate Personal Protective Equipment.

- Protective rubber gloves, aprons, and eye protection devices should be worn when handling perchloric acid. The use of a full-face shield is recommended for carrying out reactions. Also, a sturdy bench type laboratory shield should be placed between the operator and the reaction.

- Workers are to be familiar with the location of the nearest emergency shower and eyewash station.

USING PERCHLORIC ACID

General Precautions

Perchloric acid must be used in a fume hood designed exclusively for its use and posted with a notice which:

A. Identifies the hood as being for perchloric acid use, and
B. Prohibits the use or storage of combustibles in the hood.

Exhaust ducts must be as short as possible, routed directly outdoors with no interconnections to other exhaust ducts, and provided with wash down facilities. The LSC perchloric acid fume hood meets these criteria.

Direct flames, oil baths and electrical stirring equipment must not be used to heat perchloric acid.

Experimental apparatus should utilize glass-to-glass joints. Cork or rubber stoppers and equipment with rubber components must not be used with perchloric acid. Teflon stopcocks have been used safely. In addition, Viton (fluoro elastomer) has satisfactory computability and Ethylene-Propylene fair compatibility

Greases, including silicone types, are not be used. Fluorocarbon lubricants are recommended.

FOR PERCHLORIC ACID CONCENTRATIONS UP TO 72.5%

In concentrations up to 72.5% and when used at room temperature, perchloric acid is normally stable. Precautions for using perchloric acid under these conditions are similar to those for other mineral acids, including:

1. Wear suitable Neoprene gloves, chemical splash and impact goggles, a face shield, a rubber apron, and other protective clothing to protect in the event of splashes and spills.
2. Dilute only by adding perchloric acid slowly to water while stirring, not the other way around.
3. Limit quantities in storage to what is needed for the next 6-12 months.
4. Perform all work involving evaporation of perchloric acid inside a perchloric acid fume hood with the sash down. This is a specially designed fume hood that has a wash down system that will prevent the build-up of explosive perchlorates in the ductwork.
5. Do not store organic materials near perchloric acid.
6. Do not allow perchloric acid to come into contact with strong dehydrating agents (e.g., concentrated sulphuric acid, anhydrous phosphorous pentoxide, etc.).
7. Handle the smallest quantities of perchloric acid possible for the task.
8. Be sure you understand the reaction(s) that can occur when using perchloric acid

When heated to temperatures above 150° C perchloric acid becomes a strong oxidizer and eventually becomes unstable:

1. Lower the fume hood sash as much as possible so that it can function as a physical barrier and use a safety shield to provide splash protection. Perchloric acid fume hoods should have shatterproof glass.
2. Never heat perchloric acid in an oil bath or with an open flame. Electric hot plates, electrically or steam-heated sand baths, heating mantles, or steam baths are preferred. Use explosion proof electrical equipment.
3. Do not allow hot perchloric acid to come into contact with any organic materials, including paper or wood, because a fire or explosion can occur. Avoid storing these materials in perchloric acid work hoods. Avoid using greases or hoses that are incompatible with perchloric acid.
4. Do not distill perchloric acid in a vacuum, because unstable anhydride may be formed and cause a spontaneous explosion.
5. To prevent apparatus cracks or breaks due to thermal or mechanical shock consider using quartz apparatus when it is necessary to chill perchloric acid rapidly from the boiling point

COMPATIBLE AND INCOMPATIBLE MATERIALS

The following materials are not recommended for use with 72% perchloric acid:

- Nylon/polyamides
- Dacron/polyester
- Bakelite
- Lucite
- cellulose-based lacquers
- copper/brass/bronze (which form shock sensitive salts)
- aluminum (dissolves)

- high nickel
- alloys (dissolve)

The following are suitable for use with 72% perchloric acid:

- Viton
- Tantalum
- chemically pure titanium
- PVC
- Teflon
- Polyethylene
- Polypropylene
- vinylidene fluoride
- Saran
- epoxy resins
- glass
- glass- lined steel

FOR PERCHLORIC ACID CONCENTRATIONS AT OR ABOVE 72.5%

At concentrations equal to or above 72.5%, perchloric acid is often referred to as anhydrous perchloric acid. Anhydrous perchloric acid is a powerful oxidizing agent. It is unstable and dangerously reactive, capable of decomposing explosively while standing or when subjected to shock. It will also react vigorously with water, evolving heat very rapidly. Because of these properties, anhydrous perchloric acid should not be used without proper authorization from RMS. Note that perchloric acid does not become anhydrous in storage because of the azeotrope formed with water at a concentration of 72.5%.

Perchloric acid should not be mixed or used with organic materials if there is a possibility that temperatures will become elevated beyond ambient levels.

Perchloric acid digestions and other uses at elevated temperatures require that the procedures be conducted in a perchloric acid fume hood (as defined earlier).

If work with anhydrous perchloric acid is necessary and has been authorized, as noted above, the following precautions MUST be observed:

1. Only experienced researchers may work with anhydrous perchloric acid and must be thoroughly familiar with the literature on this acid.
2. Work with anhydrous perchloric acid must never be done alone. A second person must always be in view at all times and must be trained to perform rescue should the need arise.
3. A safety shield must be used to protect against a possible explosion and the work must be done in a specifically designed fume hood, as noted above.
4. Do not handle near open flame heat or other sources of ignition
5. Keep the minimum necessary equipment and remove unnecessary chemicals from the fume hood.
6. Chemical splash and impact goggles, a face shield, protective gloves, and a rubber apron MUST be worn at all times while handling this acid. Contact the chemical supplier for further information. Note that drying of perchloric acid on clothing or combustible material may cause fire.
7. Use thick gauntlets in addition to PPE previously recommended.

8. Only freshly prepared acid should be used and only the absolute minimum quantity required for the work should be prepared.
9. Dispose of any unused anhydrous perchloric acid at the end of the work via dilution and neutralization (see procedure for a small spill, below).
10. Prevent all contact of this acid with organic materials, as an explosion will occur.
11. If the anhydrous perchloric acid appears discolored, it must be disposed of immediately, via the method indicated below.

AFTER COMPLETE WORK WITH PERCHLORIC ACID

1. The bottle and tray must be rinsed with water when procedures are complete. Note: persons who have picked up bottles that were externally contaminated with perchloric acid have received severe acid burns.
2. Thoroughly rinse all surfaces and lab-ware used in the experiment after each use to remove residues.

Remember:

- Combustible materials that have been previously wetted with perchloric acid solution and allowed to dry will burn.
- Dilute perchloric acid that was spilled on combustible material such as wood benches or shelving can be ignited by friction, heat, or impact after the perchloric acid dries. Greases, oil, burlap, sawdust, etc. may ignite spontaneously on contact with the acid
- Clothing that has become contaminated with perchloric acid can be highly flammable and should be removed and rinsed thoroughly with water.
- Store perchloric acid and dispose of waste according to established protocols.

STORAGE OF PERCHLORIC ACID

1. No more than 6.4 kg (14 lbs) of perchloric acid may be stored in a laboratory
2. Containers of perchloric acid must be stored in such a manner that, in the event of breakage, the spilled acid will not contact flammable materials, wood or similar combustible materials.
3. Store the perchloric acid either in a glass-stopper glass bottle, or in the original bottle. The containers should be kept in a heavy glass, Pyrex, porcelain, or ceramic tray. The tray and perchloric acid should be stored in a metal cabinet (designed for acid/corrosive storage) separate away from organic chemicals or other combustibles, and away from sources of heat.
4. Anhydrous perchloric acid may only be used if freshly made, and any unused perchloric acid must be disposed of safely at the end of the experiment or procedure but must not be kept for more than one day.
5. If experiments are to continue the next morning, it is permissible to store the materials and apparatus within the approved perchloric acid fume hood.
6. Do not allow the perchloric acid to freeze.
7. Stored perchloric acid must be inspected at least monthly and if any discoloration is noted it must be disposed of immediately according to established disposal procedures (See: Disposal Procedures)

8. Perchloric acid at concentrations less than 85% should be stored separately room other chemicals if possible. If it is not feasible to do this, store the solution with other inorganic acids and away from organic chemicals and materials. The containers should have secondary containment, such as a glass or porcelain tray, in the event of spills. Refrigeration provides no additional safety benefits.
9. Perchloric acid at concentrations above 85% should not be stored in any quantity. Dispose of any unused solutions at the end of the day via dilution and neutralization.
10. Discoloration: Discard the material if a bottle containing perchloric acid has turned dark.
11. Crystal Formation: If crystals have formed around the bottom of the bottle, there is a potential explosion hazard. **Do NOT move the bottle**, contact HSE through Campus Security at 250-807-8111 for immediate assistance.

PERCHLORIC ACID SPILLS

General Steps:

1. *Notification/Evacuation.*
    a. Notify other people in the vicinity of the spill.
    b. Inform the supervisor.
    c. Evacuate and post warnings in the area if necessary.

2. *Reportable Spill?*
    a. Determine if the spill is a reportable spill by contacting Health, Safety & Environment

3. *Hazards of Spilled Material.* Before responding to the spill, obtain:
    a. Name of the chemical(s)
    b. Quantity spilled, and
    c. Hazards of the chemical (review Safety Data Sheets (SDS)).

4. *Clean-Up Procedures.* Perform clean-up procedures only if:
    a) All hazards have been identified and assessed;
    b) the appropriate spill control material, equipment and protective clothing are available
    c) personnel are familiar with equipment and clean-up procedures;
    d) more than one person is in the lab and available to participate; and
    e) no ignition sources are present

Specific Steps

1. ***Slowly*** apply acid neutralizer (Spill X-A, Neutrasorb or equivalent product) from the perimeter of the spill, inward. **Note**: *The quantity of neutralizer will vary with the concentration of the acid*.
2. Mop up with wet rags or paper towels. Contaminated paper or rags (combustibles) must be kept wet to prevent combustion upon drying.
3. Wipe up spill site with wet rags.

4. Place wet rags or towels in a plastic bag, seal and put into a flammable waste disposal can (non-metal).
5. Contact Health, Safety & Environment (www.hse.ok.ubc.ca)
6. Complete UBC Incident/Accident forms and send to Risk Management Services

DISPOSAL PROCEDURE

1. Liquid perchloric acid wastes must be kept separate from other acids.
2. Perchloric acid wastes must be placed in a glass bottle.
3. Transport all materials and wastes back to your main laboratory. Do not leave any materials in the perchloric acid fume hood.
4. Do not accumulate large volumes of waste.
5. Contact Health, Safety & Environment (www.hse.ok.ubc.ca) if you have any questions.

FUME HOODS CONTAMINATED WITH PERCHLORIC ACID

If you know that a regular fume hood (i.e., one that is not designed specifically for work with perchloric acid) has been used when heating perchloric acid, contact Health, Safety & Environment (HSE).

For other questions and consultative assistance with respect to perchloric acid, contact RMS.

This information is provided as a supplement to the information available on the MSDS for Perchloric Acid.

Follow the posted instructions for using a perchloric fume hood.

WASH DOWN THE FUMEHOOD AFTER EVERY USE