Guidelines for Using Perchloric Acid

Perchloric acid ($HClO_4$) is a strong mineral acid. Under some circumstances it may act as an oxidizer and/or present an explosion hazards. These guidelines present information on how to handle and store perchloric acid safely. Please notify EH&S if you are using perchloric acid in your laboratory by contacting one of the following:

Chemical Safety Office – 644-7682
Laboratory Safety Office – 644-8916
Research Support – 644-8800

Using Perchloric Acid (< 72%) at Room Temperature

At room temperature, perchloric acid up to concentrations of 72% has properties similar to other strong mineral acids. It is a highly corrosive substance and causes severe burns on contact with the eyes, skin, and mucous membranes. When used under these conditions, perchloric acid reacts as a strong non-oxidizing acid. The following precautions should be taken when using perchloric acid under these conditions:

· Substitute with less hazardous chemicals when appropriate. Use dilute solutions (< 60%) whenever possible.
· Conduct operations involving cold perchloric acid in a properly functioning chemical fume hood with current EH&S certification. If operations are conducted frequently or in large quantities contact EH&S to determine if a specially designed fume hood dedicated to perchloric acid use is required.
· Always use impact-resistant chemical goggles, a face shield, neoprene gloves, and a rubber apron when handling perchloric acid.
· When using or storing even dilute perchloric acid solutions avoid contact with strong dehydrating agents (concentrated sulfuric acid, anhydrous phosphorous pentoxide, etc.). These chemicals may concentrate the perchloric acid and make it unstable.
· Always transfer perchloric acid over a sink or other suitable containment in order to catch any spills and afford a ready means of cleanup and disposal.
· Perform all operations on chemically resistant surfaces. Avoid contact with cellulose materials such as wood, paper and cotton. Perchloric acid may become concentrated and cause a fire or explosion.

Using Heated Perchloric Acid (>72%)

When heated to temperatures above 150° C perchloric acid becomes a strong oxidizer and eventually becomes unstable. Concentrated solutions are very dangerous and can react violently with many oxidizable substances, such as paper and wood, and can detonate. Vapors may also contaminate work surfaces or ventilation equipment with perchlorate residues, which may form highly unstable compounds, such as metallic perchlorates. These compounds may ignite or detonate under certain conditions. The

following additional precautions should be followed when heating perchloric acid:
· Perchloric acid digestions and other procedures performed at elevated temperatures should be done in a specially designed perchloric acid fume hoods. Contact EH&S for information regarding design specifications. If procedures involving heated perchloric acid are performed only rarely other accepted methods to capture and contain vapors may be used in place of a perchloric acid hood. If you have been performing perchloric acid digestions in a fume hood not designed for perchloric acid, contact EH&S immediately for an evaluation of perchlorate contamination of the hood.
· Lower the fume hood sash as much as possible so that it can function as a physical barrier or use a safety shield to provide splash/splinter protection. Perchloric acid fume hoods should have shatterproof glass.
· 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.
· Avoid allowing 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.
· Be sure you understand the reaction(s) that can occur when using perchloric acid. Perchloric acid may react violently with many chemicals, including acetic anhydride, alcohol, reducing agents, and many metals.
· In wet digestions with perchloric acid, treat the sample first with nitric acid to destroy easily oxidizable matter.
· Do not distill perchloric acid in a vacuum, because the unstable anhydride may be formed and cause a spontaneous explosion. Protect vacuum sources from perchloric acid/perchlorate contamination. Vacuum pumps should be thoroughly flushed and refilled with Kel-F or Fluorolube.
· Wash down perchloric acid hoods after each use, following operating instructions provided by the manufacturer of the perchloric acid hood.
· If an apparatus cracks or breaks due to thermal or mechanical shock, the hazards are sufficient to make it desirable to consider using quartz apparatus since it is necessary in many experiments to chill perchloric acid rapidly from the boiling point. Glass-to-glass unions, lubricated with 72% perchloric acid, seal well and prevent joint freezing arising from the use of silicon lubricants. Rubber stoppers, tubes, or stopcocks are incompatible with perchloric acid.
· When handling beakers of hot acid use properly designed tongs or other remote-handling devices.

Using Anhydrous Perchloric Acid

Anhydrous perchloric acid (> 85% concentration) is very unstable and will usually explode when it comes in contact with organic materials. Follow these additional precautions when working with anhydrous perchloric acid.
· Allow only experienced research workers to handle anhydrous perchloric acid. These workers shall be thoroughly familiar with the literature on the acid. Assure that a second

worker is informed of the intended use of the anhydrous perchloric acid. This second worker should be in sound or sight contact with the worker using anhydrous perchloric acid.
· Use a safety shield to protect oneself against the effects of a possible explosion.
· Use the acid in a designated, properly designed perchloric acid hood with a minimum of equipment present. No extraneous chemicals should be present in the hood.
· Use thick gauntlets in addition to PPE previously recommended.
· Use only freshly prepared acid. Do not make any more anhydrous perchloric acid than is required for a day/shift.

Perchloric Acid Spills

CLEAN UP SPILLS OF PERCHLORIC ACID ONLY IF YOU HAVE BEEN TRAINED TO DO SO AND THE APPROPRIATE EQUIPMENT IS AVAILABLE! If you need assistance, call EH&S at 644-7682 or 644-6895. To clean a spill, neutralize it with soda ash (sodium carbonate) or other appropriate neutralizing agent. Soak up the neutralized spill with an inorganic based absorbent, if possible. If rags, paper towels are used, wet them and place them in a plastic bag and seal it. Do NOT use rags, paper towels, or sawdust and then put them aside to dry out, as such materials may spontaneously ignite. A second neutralization and rinsing of the wetted area is recommended. Label waste as flammable hazardous waste, and contact EH&S at 644-0971 for pickup.

Storage

The quantities of perchloric acid kept in storage should be kept to a minimum. Perchloric acid should be stored in its original container within compatible secondary containment, preferably glass or porcelain. Glass trays should be wiped periodically. It should be separate from other chemicals, but may be stored with other inorganic acids, preferably in a metal cabinet designed for acid/corrosive storage. It may also be stored in a perchloric acid fume hood. Perchloric acid must be stored away from organic chemicals, flammable or combustible materials and strong dehydrating agents such as sulfuric acid and anhydrous phosphorus pentoxide.
If a bottle containing perchloric acid has turned dark and has crystals forming around the bottom of the bottle, there is a potential explosion hazard. Do NOT move the bottle, but contact EH&S at 644-7682 or 644-0971 for immediate assistance.

Inappropriate and Appropriate Materials

· The following materials are not recommended for use with 72% perchloric acid: Nylon/polyamides, Dynel/modacrylic ester, Dacron/polyester, Bakelite, Lucite, vegetable-based Micarta, cellulose-based lacquers, copper/brass/bronze (which form

shock sensitive salts), aluminum (dissolves), high nickel alloys (dissolve), cotton, wool, wood, and letharge (glycerin and lead oxide).

· The following are suitable for use with 72% perchloric acid: Viton, tantalum, chemically pure titanium, zirconium, niobium, Hastelloy C (slight corrosion rate), PVC, Teflon, polyethylene, polypropylene, Kel-F, vinylidene fluoride, Saran, epoxy resins, glass, glass-lined steel, alumina, and Fluorolube.

Design and Maintenance of Perchloric Acid Fume Hoods

The following procedural and design guidelines apply to chemical fume hoods where perchloric acid is heated regularly. They are intended to minimize the build-up of potentially explosive perchlorates on the inside of the hood, its ductwork, or fan. If you need more information on perchloric acid fume hoods, call EH&S.· Construct hood interiors using materials that will not corrode or react with perchloric acid such as type 316 stainless steel and ceramic. Polyvinyl chloride may be used for light-duty systems or as a liner for a stainless steel hood.
· Provide 1/2 inch "dished" liquid-tight hood. An integral trough should be placed at the back to collect wash water runoff and shall be provided for new perchloric acid hoods. Minimize joints wherever possible. Use non-reactive sealants or gasket materials if joints are present (Teflon and fluorocarbon greases and caulking are usually acceptable.) The collected water runoff shall be processed and handled in a manner specified by EH&S.
· Construct the exhaust ducting using non-reactive and perchloric acid resistant materials. Type 316 stainless steel or PVC is acceptable. Never manifold the ductwork to any other ventilation system. Use the steepest, straightest, and shortest route for ductwork. Avoid sharp turns. Slope horizontal runs of ductwork at least 1 inch per foot back toward the hood. Where possible, avoid horizontal runs where condensed perchloric acid can accumulate. Never use flexible connections. Seal ductwork to prevent liquid from escaping. Preferred methods are welded stainless steel or welded PVC. Use screws of 316 stainless steel or equivalent corrosion-resistant and non-reactive material to connect sections of ductwork. Use only gaskets or sealants that are non-reactive and resistant to perchloric acid.
· Install fan blades that are non-reactive, spark-and corrosion-resistant. Teflon or PVC coated blades can be used. The exhaust fan motor shall not be installed in the ductwork and the pulley shall be conductive as specified by NFPA 45.
· Equip the ventilation system with a built-in water wash-down system. Ensure that the system will adequately spray all interior surfaces of the ducting, tack, fan, plenum, baffles, and hood. The hood shall be washed down at least each day after use or more frequently if specified in a safety plan. The water shall be drained to an appropriate holding tank pending removal for treatment and disposal.
· Inspect new systems for the presence of inappropriate gaskets, caulking, or other materials that may be potentially explosive as part of acceptance procedure. Require vendors and contractors to furnish blueprints and specifications describing the materials of construction.
· The baffles of new hoods shall be easily removable to allow for inspecting and cleaning

of accumulations of explosive perchlorate residues.
· Design and construct perchloric acid ventilation systems to allow for the easiest possible visual inspection. Include easily removed hood baffles for routine inspection of perchlorate buildup.
· Specify shatterproof hood sashes.
· Assure that hoods in which perchloric acid is heated are designated as perchloric acid hoods, dedicated to perchloric acid work, and are labeled:
"WARNING: Perchloric acid work is done in this hood."
· Thoroughly flush the interior of a perchloric acid hood just prior to maintenance or removal of the hood. Wash duct joints, the fan motor, and its housing. Check the various surfaces and joints using the methylene blue or diphenylamine tests. If perchlorates are detected, further washing is required. Collect the rinse water. Call EH&S at 644-7682 for an evaluation to determine if the rinsate must be disposed of as hazardous waste.
· Test hoods and exhaust systems for perchlorate residues before doing any inspection, maintenance, or cleaning if the perchloric acid was heated above ambient temperature. Also test perchloric acid hoods being put into use for any other purpose after water washing them to remove perchlorate residues.

Surface Contamination Tests for Perchlorates

· Diphenylamine Test: Dissolve one gram of diphenylamine in 10 ml of "1 to 1" (18 normal) sulfuric acid to form a diphenylamine sulfate solution. Using a medicine dropper apply this solution to the test surface. The liquid turns black upon contact with perchlorate. The solution also reacts with nitrates, but turns blue.
· Methylene Blue Test: Use 0.4% solution of methylene blue in water. Add a few drops of indicator solution to about 25 ml of trial solution, such as water used to test rinse from a length of potentially contaminated duct. Perchlorates will produce a violet precipitate.

1. This Guideline was taken from Harvard University and relies on information taken from Lawrence Livermore National Laboratory's ES&H Manual, Chapter 14.8 Working Safely with Corrosive Chemicals. Additional information is included from; CRC Handbook of Laboratory Safety, NFPA 45 Fire Protection for Laboratories Using Chemicals, and fact sheets from the University of Ottawa, University of Illinois at Urbana Champaign, University of California at San Francisco and the Oklahoma Medical Research Foundation. “