

PERCHLORIC ACID SAFETY GUIDELINES

Perchloric acid is a strong mineral acid commonly used as a laboratory reagent. It is a clear, colorless liquid with no odor. Most perchloric acid is sold as solutions of 60% to 72% (w/w) acid in water. Perchloric acid is considered one of the strongest superacids. It is highly reactive with metals, dangerously corrosive and readily forms explosive mixtures. Anyone who works in laboratories containing perchloric acid should familiarize themselves with its SDS and a clear Standard Operating Procedure (SOP) should be established. Therefore, careful precautions should always be taken when handling this chemical. This document discusses the properties, health and safety hazards, how to properly handle and store perchloric acid. Also included are emergency procedures for dealing with accidental perchloric acid contact, including first aid treatment information.

▲ WARNING A:: In addition to being a corrosive liquid, while not combustible, under some circumstances perchloric acid may act as an oxidizer and present an explosion hazards. Organic materials are especially susceptible to spontaneous combustion if mixed or contacted with perchloric acid. Under some circumstances, perchloric acid vapors form perchlorates in ductwork, which are shock sensitive.

1. **Properties**

Names: perchloric acid; hydronium perchlorate; dioxonium perchlorate usually sold in solutions of 60-72% (w/w) in water; anhydrous perchloric acid (>85% w/w)

Chemical Formula: HClO₄

CAS #: 7601-90-3

Physical aspect (solution 72% w/w):

Colorless liquid, oily Odorless to slight chlorine smell Very hygroscopic and water soluble



Table 1. Physical and Toxicological Properties of Perchloric Acid (60-72% w/w)

Molar Mass	100.46 g mol ⁻¹
Boiling point	203°C
Melting point	-20°C
Vapor pressure	6.8 mm Hg at 25°C
Density	1.67g·cm ⁻³
pKa (water)	≈-8
PEL (TWA)	N/A
IDHL	N/A

2. Hazard Classification

WHMIS 1988

Perchloric acid at concentration of 60-72% (w/w) in water is classified as:



C: Oxidizing materials E: Corrosive material D1B: Toxic materials D2B: Toxic materials B6: Reactive flammable material

WHMIS 2015



Oxidizing liquids (Category 1) Corrosive to metals (Category 1) Acute oral toxicity (Category 4) Skin Corrosion/irritation (Category 1A) Serious Eye Damage/Eye Irritation (Category 1) Specific target organ toxicity - single exposure (Category 3): Respiratory system Specific target organ toxicity - repeated exposure (Category 2): Thyroid



NFPA



Flammability: Non-flammable Health hazard: Potential acute and chronic health effects (severe) Instability/Reactivity: Highly reactive and concentrated form and/or salts may be explosive in the presence of heat, flame, spark, organic materials, and alkalis.

Concentrated solutions (>72%) are strong oxidizers

3. Reactivity, Fire and Explosion Hazards:

Perchloric acid is non-combustible but may ignite other combustible materials and increase the intensity of a fire. Solutions of <72% (w/w) of perchloric acid are normally stable. The anhydrous (dehydrated) acid or solutions of >85% (w/w) present a serious explosion hazard. They are unstable and can decompose explosively or spontaneously combust at ordinary temperatures if mixed with organic compounds. Heating produces toxic fumes of chlorine compounds. Under some circumstances, perchloric acid vapors form perchlorates in ductwork, which are shock sensitive. Many heavy metal perchlorates and organic perchlorate salts are extremely sensitive explosives; the ammonium, alkali metal, and alkali earth perchlorates are somewhat less hazardous.

Solutions of <72% (w/w) of perchloric acid are strong acids but are not considered to be strong oxidizing agents; however, more concentrated solutions (>72% w/w) are good oxidizers. Temperature increases the oxidizing power of perchloric acid, and hot concentrated solutions are very dangerous. Evaporation of a spill of the <72% (w/w) solution may lead to the formation of more dangerous concentrations.

Drying agents and acetic anhydride cause the concentration of aqueous solutions to increase; the now more concentrated acid reacts, often explosively. Mixtures of perchlorates with many oxidizable substances are explosive. Here are some examples of perchloric acid incompatible mixtures:

- Nitric acid and cellulose material explosive
- Hydroxyl compounds explosive
- Dimethyl sulphoxide explosive
- Ketones and glycols violent reactions
- Ferrous sulphate explosive
- Reducing agents explosive

4. Health Hazards

At room temperature, perchloric acid up to concentrations of 72% has properties similar to other strong mineral acids. The acute toxicity of perchloric acid is moderate to high. It is a highly corrosive substance and causes severe burns on contact with the eyes, skin, and mucous membranes. Liquid or spray mist



may produce tissue damage on mucous membranes of the eyes. Inflammation of the eye is characterized by redness, watering, itching and blurred vision. It can also lead to loss of vision or blindness. Skin contact may produce inflammation characterized by itching, reddening and blistering. Inhalation of spray or mist may produce severe respiratory tract irritation, causing sore throat, coughing, labored breathing and even lung edema. Ingestion of perchloric acid will cause mouth, throat, stomach and intestinal tract burns, along with abdominal pain and diarrhea.

Epidemiological data available for occupational exposure to perchloric acid is limited and exposure limits have not been defined (National Institute of Occupational Safety and Health, 2000). Prolonged or repeated inhalation may cause nosebleeds, nasal congestion, erosion of the teeth, and perforation of the nasal septum, chest pains, and bronchitis. Prolonged or repeated eye contact may cause conjunctivitis. Repeated dermal exposure may cause sensitization dermatitis and destruction or ulceration of the skin.

Perchloric acid has not been shown to be carcinogenic or to show reproductive or developmental toxicity in humans.

5. Safety Precautions for Perchloric Acid Use

a) Training

Students and employees who handle perchloric acid must have read the Safety Data Sheet (SDS) and receive training on the hazards of perchloric acid from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS must always be kept within the immediate vicinity of the working area along with the Standard Operating Procedure (SOP) developed by the student / employee's department.

b) Ventilation / Fume Hood

Perchloric acid should always be handled in a working fume hood to keep the level of exposure as low as possible. Perchloric acid digestions and other procedures performed above ambient temperatures should be done in a specially designed perchloric acid fume hoods equipped with a wash down system. Solutions of 72% (w/w) perchloric acid at room temperature have no vapor pressure and therefore no vapor should get into the hood. However, work involving anhydrous perchloric acid (>85% w/w) should always be done in a dedicated perchloric acid fume hood. Dedicated perchloric acid fume hood and ducts are made of stainless steel. An exhaust air scrubber system is present in the ductwork and behind the baffle to emit a fine water spray to dilute and wash down the acid fumes and vapours when the fume hood is in use. Solvents must never be used or stored in a designated perchloric acid fume hood. A dedicated perchloric acid hood can be found on the Loyola Campus at SP-601.13. This fume hood belongs to the Chemistry Department and necessary request for use and/or training should be done with the Department prior performing any work with perchloric acid inside this fume hood.

c) Eye Protection

Splash goggles and a face shield MUST be worn when handling perchloric acid solutions.



d) Gloves

Natural rubber, neoprene, PVC, nitrile and Viton gloves are suggested when working with <72% (w/w) perchloric acid solutions. Thicker and longer gloves (gauntlets) should be worn when using anhydrous perchloric acid (>85% w/w).

e) Protection Clothing

A chemical apron over a lab coat with long sleeves MUST be worn when handling perchloric acid solutions. **No exposed skin is allowed**; long pants, sleeves, and closed toe shoes must be worn.

f) Safe Work Practice

For < 72% Perchloric Acid at Room Temperature

At room temperature, perchloric acid up to concentrations of 72% has properties similar to other strong mineral acids. 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 laboratory (chemical) hood with current certification sticker.
- Always transfer perchloric acid over 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, which could result in a fire or explosion.

For < 72% Perchloric Acid Heated

When heated to temperatures above 150°C, perchloric acid becomes a strong oxidizer and eventually becomes unstable and can react violently with many oxidizable substances and detonate. Vapors may also contaminate work surfaces or ventilation equipment with perchlorate residues, which may form highly unstable compounds, such as metallic perchlorates.

- Perchloric acid digestions and other procedures performed at elevated temperatures should be done in a specially designed perchloric acid fume hoods.
- 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.
- 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.
- Wash down perchloric acid hood after each use, following operating instructions provided by the manufacturer of the perchloric acid hood.
- All apparatus should have glass-to-glass joints. Use silicon based lubricants for glass-to-glass joints. Do not use rubber stoppers, tubes or stopcocks.
- 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.

For Anhydrous Perchloric Acid (> 85% concentration)

Anhydrous perchloric acid is very unstable and will usually explode when it encounters organic materials.

Only experienced research workers should handle anhydrous perchloric acid and follow these additional precautions:

- Never work alone when handling anhydrous perchloric acid. A second worker has to be informed of the work and 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.
- The work has to be done in a designated perchloric acid fume equipped with a wash down system.
- No extraneous chemicals should be present in the fume hood while performing the work.
- Longer and thicker gloves (in addition to the recommended PPE) should be worn.
- Use only freshly prepared acid. Do not make any more anhydrous perchloric acid than is required for a day/shift.

6. Storage, Spill and Waste Issues

a) 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.

Perchloric acid should be separated from other chemicals, but may be stored with other inorganic acids, preferably in a metal cabinet designed for acid/corrosive storage. 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. Perchloric acid is incompatible with the following chemicals and must not be stored with them because of the danger of explosion or fire:

- Acetic acid
- Acetic anhydride
- Alcohols

- Aniline
- Antimony compounds (trivalent)
- Bismuth



- Dehydrating agents
- Diethyl ether
- Formaldehyde mixtures
- Fluorine
- Glycerine
- Glycols
- Glycol ethers
- Hydriodic acid
- Hydrochloric acid

- Hypophosphites
- Ketones
- Lead oxide mixtures
- Nitrogen triiodide
- Nitrosophenol
- Organic matter (e.g. paper, wood, charcoal, rags, cotton, etc.)
- Sodium iodide
- Sulfoxides and Sulfur trioxide

b) Spills

In the case of a small spill, the spill can be cleaned by laboratory staff assuming that the correct equipment is present and that the staffs understands the hazards associated with perchloric acid.

- 1. Neutralize it with soda ash (sodium carbonate) or other appropriate neutralizing agent.
- 2. Soak up the neutralized spill with an inorganic based absorbent (if possible).
- 3. Do not use organic materials, such as kimwipes or toweling as they **may spontaneously ignite** upon contact with perchloric acid.
- 4. If rags or paper towels are in advertently used, **wet them with water** and place them in a tightly sealed plastic bag.
- 5. Do NOT use rags, paper towels, or sawdust and then put them aside to dry out, as such materials may spontaneously ignite.
- 6. A second neutralization and rinsing of the wetted area is recommended.
- 7. Perchloric acid waste must not be mixed with other wastes. It should be placed into acid resistant containers that are clearly labeled "Perchloric Acid Wastes" on them.
- 8. Contact EHS (<u>hazardouswaste@concordia.ca</u>) to request an immediate pick-up of the containers of spilled product and contaminated absorbent material.

Surfaces can also be tested to check for perchlorate contaminations:

- *Diphenylamine Test*: Dissolve one gram of diphenylamine in 10 mL of "1 to 1" (18N) 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.

In the event of a large spill located outside a chemical fume hood, the spill must be cleaned by only personnel trained to handle explosives

- 1. Advise and warn co-workers.
- 2. Evacuate the area immediately.



- 3. Restrict the access to the area.
- 4. Notify Security at ext. **3717** or **514 848-3717**, providing them with the following information:
 - a. Name of hazardous material
 - b. Quantity involved
 - c. Related health risks and precautions to be taken
- 5. Provide Safety Data Sheet (SDS) or appropriate documentation.

c) Waste Handling

Perchloric acid waste should never be mixed with other organic wastes. It should be kept in clearly identified containers labelled "Perchloric Acid Waste". 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 touch the container,** as it might be highly unstable and shock sensitive. Any attempts to move or open the container might result into an explosion. Visually inspect the container in order to identify the content and to look for an expiration date.

- 1. Evacuate the laboratory and secure the area by restricting access
- 2. Call Security at ext. **3717** indicating the possibility of dry perchloric acid being present in the laboratory

7. Emergency Procedures

a) Skin Contact

- 1. Remove contaminated clothing and immediately wash the affected area with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
- 2. Apply a magnesia/glycerol paste (or anti-bacterial cream) to the affected area. A magnesia/glycerol paste should be in your first aid kit if perchloric acid is handled in your laboratory.
- 3. Call Security at ext. **3717** for emergency medical assistance.

b) Eye Contact

- 1. Immediately wash the affected eye with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
- 2. Do not allow the victim to rub or keep eyes closed.
- 3. Call Security at ext. **3717** for emergency medical assistance.

c) Inhalation

- 1. Immediately move the victim to fresh air.
- 2. If breathing is difficult, administer oxygen.
- 3. Call Security at ext. **3717** and ask for medical assistance.



d) Ingestion

- 1. Wash out the mouth thoroughly with water and give water to drink (about 8 oz.) followed by Milk of Magnesia. Milk of Magnesia should be part of your laboratory first aid kit if perchloric acid is handled in your laboratory.
- While the victim is rinsing his/her month, someone should someone should call Security at ext.
 3717 and ask for medical assistance.
- 3. Do not induce vomiting.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) must be brought to the emergency room, as the treating physician might be unaware of the treatment measures for perchloric acid. All perchloric acid incidents must be reported to your Supervisor and to Environmental Health & Safety (EHS). An injury/near-miss report must be filled for any incident involving perchloric acid spill or exposure.

If you have any concerns about the use of perchloric acid at Concordia University, please contact EHS at <u>ehs@concordia.ca</u>.

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References:

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