A Guideline for the Use of Perchloric Acid and Perchloric Acid Fume Hoods

April 2016

Office of the Chief Inspector of Mines

Publication Information

This is the first edition of “A Guideline for the Use of Perchloric Acid and Perchloric Acid Fume Hoods”.

Table of Contents

Introduction

Purpose

The purpose of this document is to provide guidance on recommended laboratory standards for the use, handling, and storage of perchloric acid and perchloric acid fume hoods. This document is to be used in conjunction with the Health, Safety and Reclamation Code for Mines in British Columbia (HSR Code) and other Ministry of Energy and Mines guidance materials.

Perchloric Acid

The use, storage and handling of perchloric acid requires special consideration due to the potential for the substance to be violently reactive. Laboratories where perchloric acid is used must have written procedures that detail the appropriate practices, precautions and personal protective equipment required for its use, storage and handling. Written procedures must also be created for spill scenarios, and for the use, cleaning and maintenance of the perchloric acid fume hood. Whenever possible, perchloric acid should be substituted with a less hazardous substance.

Perchloric acid is classified under the Workplace Hazardous Materials Information System (WHMIS) as a powerful oxidizer (Class C) and highly corrosive (Class E). As per the Globally Harmonized System for Classification and Labelling of Chemicals (GHS), perchloric acid is generally classified as an oxidizing liquid (Category 1), corrosive to metals (Category 1), having acute toxicity (oral - Category 4), and causing skin corrosion/irritation (Sub-category 1A), serious eye damage/eye irritation (Category 1) and specific organ toxicity (category dependent on supplier). Classifications may differ between perchloric acid products and manufacturers; always check the classifications specific to the product used on site. The stability of a solution of perchloric acid depends on a number of factors, including temperature, concentration and storage conditions. Perchloric acid is more stable when stored at room temperature in a concentration of 70% or less, than at higher temperatures or concentrations. Anhydrous perchloric acid is extremely reactive with water and capable of explosive reactions when improperly handled. If required for a task, anhydrous perchloric acid must be generated and used within one work shift. Any work requiring the use of perchloric acid must be completed in a designated perchloric acid fume hood.

When heated, the oxidizing strength of perchloric acid increases, making it more reactive when exposed to metals and organic and combustible materials. When a task requires heating perchloric acid, do not use direct flame, oil baths, or electric hot plates with electric motor-driven stirrers. Perchloric acid should only be heated using hot plates with pneumatically driven stirrers; electric or steam-heated sand baths or steam baths.

Perchlorate Salts

The formation of perchlorate salts is a major concern when using and storing perchloric acid. Perchlorate salts, also known as perchloric acid crystals, are extremely shock-sensitive and unstable, having a high risk of explosion when exposed to shocks and vibrations. Perchlorate salts can form during long-term storage if the solution becomes contaminated and anytime perchloric acid is allowed to dry out. For example, perchlorate salts can form when perchloric acid is heated and the resulting vapours are allowed to condense onto a surface and dry. Perchlorate salt formation is a significant concern in fume hood exhaust systems and is one of the reasons a designated fume hood is required. Spills of perchloric acid and spill clean-up materials must be immediately cleaned-up and prevented from drying out to avoid formation of perchlorate salts. The formation of perchlorate salts can be avoided through the use of proper equipment and efficient management of perchloric acid storage.

Figure 1: *An accumulation of unknown crystals can be seen through the window of this perchloric acid fume hood scrubber system. Deposits such as this must be avoided and carefully removed.*

Storage

Perchloric acid must be stored in designated areas as per Part 2.3.3 of the Health, Safety and Reclamation Code for Mines in British Columbia.

To be acceptable to an inspector, a designated storage area for hazardous materials must be:

- Dedicated to the specific purpose of storing hazardous materials (i.e. no work other than storage and transfer of hazardous materials should take place in the area);
- Kept clean, dry and organized so that stored materials are not placed, stacked or stored in a way that could constitute a hazard to persons;
- Adequately ventilated to prevent accumulation of harmful gases and vapors;
- Designed to ensure that stored containers are stable, will not suffer damage, or be exposed to temperatures outside of recommended storage conditions for the product;
- Equipped with storage structures (shelving, cabinets, etc.) and secondary containment systems that are compatible with the stored materials;

- Constructed with impermeable floors to prevent absorption and accumulation of spilled or leaked hazardous materials;
- Organized to ensure incompatible materials cannot combine in the event of a leak or spill;
- Supplied with the appropriate, accessible emergency equipment such as emergency wash facilities and firefighting and spill clean-up equipment;
- Identified by signs that clearly indicate the hazards in the area and required precautionary actions (e.g. advising against smoking in a flammable storage area);
- Located away from emergency exits, elevators and frequented passageways;
- Capable of being secured to prevent unauthorized access (e.g. untrained persons); and
- Arranged so that stored hazardous materials can be regularly inspected to ensure leaking containers do not go unnoticed.

In addition to these requirements, perchloric acid should always be stored in its original container. If an alternative container is required, it must be made from compatible materials that are transparent to allow monitoring for any discolouration or deposits of perchlorate salts. The container must remain sealed when not in use. Perchloric acid must never be stored on wooden pallets or floors. Containers of perchloric acid should be stored in a non-combustible structure that is designed for acid/corrosives storage and is accessible for regular inspections for the formation of perchlorate salts. It is best practice for perchloric acid to be stored separately from other hazardous materials. Solid and liquid Class 5 oxidizing substances (e.g. perchloric acid) must be stored separated from the rest of the building by a fire compartment having a fire-resistance rating of not less than 2 hours.

Storage Quantities

The amount of perchloric acid stored outside of a designated storage area should be limited to what is required to conduct the tasks for that shift. A worker should only ever handle the smallest amount of perchloric acid necessary to complete a required task.

To limit the potential amount of structural damage and worker harm incurred by a perchloric acid explosion, it is recommended that the maximum amount of perchloric acid stored in any one area of a building be limited to 6.4 kg (14 lbs). A 2.5 L bottle of 70% Perchloric Acid is 4.2 kg; always check the product's Material Safety Data Sheet (MSDS). If more than this amount requires storage in the same building, it is recommended that each storage area containing 6.4 kg (14 lbs) be in a separate fire compartment.

Storage Inspections

Due to the potential for precipitation of perchlorate salts during long-term storage and contamination of open bottles, all containers of perchloric acid should be labelled with the date the shipment was received and date that the bottle was opened.

It is recommended that all containers of perchloric acid be inspected at least once a month and that a record of inspections be kept. If a perchloric acid container is found to have discoloration or crystallization, it should be considered an explosion hazard and must be immediately disposed of by trained personnel wearing appropriate personal protective equipment (PPE).

Incompatible Materials

Adequate separation from incompatibles is often achieved by secondary containment. Containers used for secondary containment of perchloric acid must be acid/corrosion resistant, made of compatible materials, and be capable of containing 110% of the volume of the largest container in storage or 10% of the total volume of all containers in storage, whichever is greater. Ensure that secondary containment used for perchloric acid is regularly cleaned and inspected for perchlorate salt deposits.

Perchloric acid is incompatible, and will react vigorously, with a number of organic, flammable and combustible materials, such as wood, some rubber, and greases. Concentrations of 70% perchloric acid are classified under the Transportation of Dangerous Goods Regulations as a Class 5.1 and Class 8 dangerous good; always check the product's MSDS. Perchloric acid must not be stored in the same fire compartment as flammable and combustible solids, gases, and liquids, other corrosives and organic peroxides (for example see BC Fire Code Table 3.2.7.6).

A more comprehensive list of incompatibles is available in Appendix A of this document. The MSDS for the product should always be consulted for identifying incompatible materials.

Personal Protective Equipment (PPE)

The appropriate PPE must always be worn when handling perchloric acid. Written procedures for handling perchloric acid, maintenance and use of perchloric acid fume hoods, and containing and cleaning up perchloric acid spills should contain specific details on the type of PPE required to perform the various tasks.

When working with any concentration of perchloric acid, the following PPE should be worn as a minimum requirement:

- Impact-resistant chemical goggles and/or a face shield*
- Protective gloves compatible with perchloric acid (usually thick rubber)**
- Full-length heavy rubber or plastic lab coat
- Close-toed shoes

*A face shield is a minimum recommended requirement when performing reactions with perchloric acid and when handling perchloric acid at concentrations higher than 70%. In accordance with CAN/CSA Z94.3, as updated from time to time, Class 6 protection (face shields) must be worn in conjunction with either Class 1(spectacles) or Class 2 (goggles) protection.

**Not all types of rubber are compatible with perchloric acid. A gauntlet-style glove should be used when handling anhydrous perchloric acid.

Perchloric acid can contaminate PPE over time with repeated use. It is recommended that PPE which may become contaminated during repeated use (i.e. lab coat, gloves) be designated specifically for handling perchloric acid. Contaminated PPE should be treated as hazardous waste and collected and disposed of by trained personnel.

Spill Clean-up

Spilled perchloric acid must be contained, neutralized, and cleaned up as soon as possible by trained personnel wearing appropriate PPE, as per Part 2.3.7 of the HSR Code.

Once it has been determined safe to do so, the spill should be contained using non-combustible materials and neutralized with a neutralizing agent such as sodium carbonate. Absorb the neutralized spill with inorganic based sorbents. Organic materials such as bench paper, paper towels, rags and sawdust should not be used to absorb perchloric acid spills, especially if the acid is still warm from a reaction. A second neutralization and rinsing of the spill area is recommended.

Perchlorate salts or any form of crystallization found in an area where perchloric acid is used or stored should be treated as if it were a perchloric acid spill and if determined safe by trained personnel, immediately cleaned up by wetting with water and continuing with an appropriate perchloric acid spill response procedure.

Sufficient materials to contain a spill must be readily available where perchloric acid is used and stored. The use of a spill kit is recommended as a way to store these materials together so they

can be quickly identified and accessed in an emergency. At a minimum, a spill kit should contain the following:

- non-combustible, inorganic-based absorbents;
- a neutralizing agent;
- enough PPE for trained spill response personnel including appropriate acid-gas cartridges for respirators;
- containers for intermediate containment of hazardous waste; and
- hazardous waste storage labels.

Waste materials generated from perchloric acid clean-up must remain thoroughly wetted and sealed in an appropriate container. If allowed to dry, perchlorate salts can form on the waste materials as the liquid evaporates, creating a significant ignition/explosion risk. Waste materials must be disposed of as soon as possible and treated as hazardous flammable waste. While awaiting disposal, waste materials must be stored in a container constructed of non-combustible materials with a close-fitting lid and kept in a well-ventilated area. The waste container must be appropriately labelled to indicate:

- it holds hazardous waste;
- the contents of the container and its associated hazards (risk phrases);
- precautionary statements (required PPE, etc.); and
- an MSDS is available for reference.

Perchloric Acid Fume Hoods

A fume hood designated for the use of perchloric acid must be used when handling or performing a reaction with perchloric acid. There are risks of fire and/or explosion should perchloric acid contact incompatible materials or perchloric acid vapors, released by the heating of perchloric acid, condense and crystallize on laboratory surfaces. Using a proper perchloric acid fume hood with a wash-down system is imperative in preventing inadvertent contact with incompatibles and the formation of perchlorate salts. Perchlorate salts are highly explosive and sensitive to shocks and vibrations, including the normal working vibrations of a fume hood.

Written procedures regarding the safe use, operation, maintenance and cleaning of the perchloric acid fume hood must be developed and made available to the appropriate personnel. A visual check of the fume hood should be performed every time the hood is used to ensure that the wash-down system is functioning correctly and that air is being pulled into the hood. This check can be facilitated by installing an airflow alarm and water pressure gauge. The wash-down components of the hood should be inspected monthly to confirm that all spray nozzles are functioning effectively (for example see PWGSC, 2006). The mechanical components of the fume hood ventilation should be performance tested at least once a year or more frequently as determined by manufacturer recommendations. The standards set out in ACGIH "Industrial Ventilation: A Manual of Recommended Practice" and the ASHRAE Standard 110-1995 "Method of Testing Performance of Laboratory Fume Hoods" are recommended for conducting fume hood testing. A log book must be kept for each hood to record the performance of the hood, malfunctions or problems that have occurred, and dates on which it was tested and maintained. The fume hood must be clearly labelled to indicate its purpose as a hood designated for the use of perchloric acid and that combustible and organic materials are not permitted in the hood, for example: "perchloric acid fume hood: combustibles and organics prohibited".

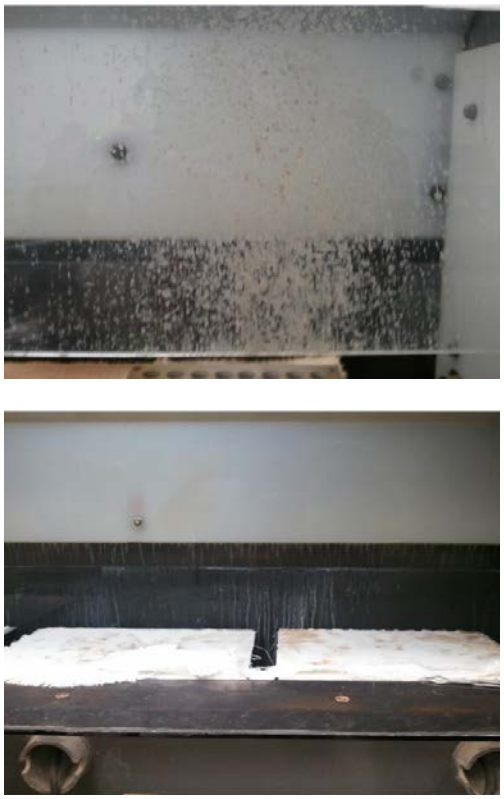

Figure 2. *(Top) Build-up of unknown material on fume hood sash. (Bottom) Build-up of material on wash-down screen. Build-ups of material such as these should be avoided by implementing a regular cleaning schedule.*

Wash-down Procedures

Written laboratory procedures for the wash-down process of the perchloric acid fume hood must be developed and made available to appropriate personnel. These procedures should include the length of time the system must remain running after hood use is completed and how often a complete cleaning of all hood surfaces is required. Depending on hood use, a complete cleaning may be required daily. Regular cleaning of the perchloric acid fume hood is important to ensure that build-ups of dust or material that may contain perchlorate salts do not occur.

A sufficient amount of time should be provided for the wash-down system to thoroughly wet the ventilation system before conducting work with perchloric acid. The system should remain on while working in the hood and for a suitable amount of time once work is completed to clear

the system. The length of time needed to complete the wash-down procedure depends on the type of reaction and the length of time required to conduct the reaction. The rinsate should be tested after procedures have been conducted in the hood to determine how long the wash-down system must remain on after completing work in the hood. This time should be included in written procedures.

Fume Hood Design

Fume hoods for the use of perchloric acid should be constructed of shatterproof materials and have surfaces and duct work with smooth, cleanable joints. NFPA 91, "Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Noncombustible Particulate Solids," section 7.12 of the NFPA 45 "Standard on Fire Protection for Laboratories Using Chemicals (2015)," and MD15129-2006 "Perchloric Acid Fume Hoods and their Exhaust Systems" are valuable resources for perchloric acid fume hood design.

The design of a perchloric acid hood must include the following specifications:

- Perchloric acid hoods and exhaust ductwork must be constructed of materials that are impervious to and non-reactive with perchloric acid and/or its by-products;
- The hood must be equipped with a wash-down system to prevent the formation of perchlorate salts. There should be a way to quantitatively identify that the system is continuously functional. This can be accomplished by installing a water pressure gauge and/or flow meter. The water spray system must be installed so as to allow complete flushing of all duct and hood surfaces. Piping for the wash-down system must be protected from freezing;
- The hood baffles must be removable for inspection and cleaning. The baffles should not interfere with the ability to visually check the flow of the wash-down system.
- Ductwork for perchloric acid hoods and exhaust systems should take the shortest path to the outside of the building and should not be in the same manifold as other exhaust systems. Horizontal ductwork should be avoided as it creates difficulties for drainage and spray coverage. If unavoidable, horizontal runs should be as short as possible, with no sharp turns or bends, and sloped to ensure drainage.

The required face velocity for a perchloric acid fume hood to effectively capture contaminants will vary depending on the design of the laboratory and interfering cross-drafts. As a general guideline, perchloric acid fume hoods should have a target face velocity of 125 fpm (PWGSC, 2006).

References

ANSI/AIHA (American National Standards Institute and American Industrial Hygiene Association). ANSI/AIHA Z9.5 - Laboratory Ventilation. http://webstore.ansi.org/RecordDetail.aspx?sku=ANSI%2fAIHA%2fASSE+Z9.5-2012

British Columbia Fire Code. http://www.bccodes.ca/

Health, Safety and Reclamation Code for Mines in British Columbia (HSR Code). http://www2.gov.bc.ca/gov/DownloadAsset?assetId=318C27C47FE14F228E47B9E5C836A173&filename=health_safety_and_reclamation_code_2008.pdf

National Research Council of the National Academies. Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards. http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654

NFPA (National Fire Protection Association). NFPA 91: Standard for Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Particulate Solids. http://www.nfpa.org/codes-and-standards/document-information-pages?mode=code&code=91

NFPA (National Fire Protection Association). NFPA 45: Standard on Fire Protection for Laboratories Using Chemicals. http://www.nfpa.org/codes-and-standards/document-information-pages?mode=code&code=45

PWGSC (Public Works and Government Services Canada). MD15129 – 2006: Perchloric Acid Fume Hoods and their Exhaust Systems. http://www.tpsgc-pwgsc.gc.ca/biens-property/sngp-npms/bi-rp/tech/entretien-engineering-eng.html

WorkSafeBC. Laboratory Health and Safety Handbook. http://www.worksafebc.com/publications/health_and_safety/by_topic/assets/pdf/laboratory_handbook.pdf

Appendix A

Chemicals Incompatible with Perchloric Acid*

The following chemicals are incompatible with perchloric acid and must not be stored with perchloric acid due to the risk of causing an explosion or fire (always reference the MSDS for the product):

- Acetic acid
- Acetic anhydride
- Alcohols
- Aniline and formaldehyde mixtures
- Antimony compounds (trivalent)
- Bismuth
- Dehydrating agents
- Diethyl ether
- Fluorine
- Glycerine and lead oxide mixtures
- Glycols
- Glycol ethers
- Hydriodic acid
- Hydrochloric acid
- Hypophosphites
- Ketones
- Nitrogen triiodide
- Nitrosophenol
- Organic matter (paper, wood, charcoal, rags, cotton, etc.)
- Sodium iodide
- Sulfoxides
- Sulfur trioxide

*Source: WorkSafeBC's Laboratory Health and Safety Handbook (http://www.worksafebc.com/publications/health_and_safety/by_topic/assets/pdf/laboratory_handbook.pdf)