

**Perchloric Acid Safety**

**Introduction**

Perchloric acid (HClO4) is a mineral acid used as a synthetic reagent, eluent in ion exchange chromatography and for carrying out digestions and etching processes. Perchloric acid is one of the strongest mineral acids known to science and therefore can be very damaging to the skin, eyes and mucus membranes on contact. Inhalation of the vapours can also lead to severe damage to the respiratory system.

At concentrations of up to 72% perchloric acid can be treated largely as a strong mineral acid so long as it remains at low temperature. If heated to 150°C or above it can also act as a strong oxidiser and can react violently with organic materials resulting in a potential explosion. Once the concentration reaches 85% (perchloric acid monohydrate) it can also act as a strong oxidiser at room temperature further increasing the risk of an explosion in the event of contamination / contact with organic materials.

Where possible perchloric acid should be substituted for another less hazardous material or used in lower concentrations (<60%). Where this is not possible it should only be used under controlled conditions following a robust CoSHH assessment.

**Note: Anhydrous perchloric acid is extremely unstable and will explode on contact with organic material (or spontaneously on storage). Care should be taken to ensure perchloric acid is not mixed with dehydrating agents to avoid producing it.**

**Note: Like all strong mineral acids, when diluting perchloric acid the acid should always be added to water and never the other way around to avoid a violent, exothermic reaction.**

**Storage and Stock Management**

Perchloric acid should be stored in a suitable cabinet in a cool, dry location away from incompatible materials such as organic materials and dehydrating agents (e.g. sulphuric acid). Subject to these conditions it can generally be stored with mineral acids other than sulphuric acid but should never be stored with solvents, acetic acid or acetic anhydride. Further recommendations for storage are listed below:

* Wooden cabinets should **never** be used for the storage of perchloric acid to avoid the possibility of an adverse reaction or contamination of the acid. Shelves or trays should not be lined with paper (including BenchKote or equivalent).
* Perchloric acid should always be stored in its original container and where possible secondary containment should be used to contain spillages. Secondary containers should be made of compatible materials such as glass or ceramic and never plastic or metal.
* Only the minimum amount of perchloric acid should be purchased and containers should be clearly marked with the date of receipt.
* Over time perchloric acid can degrade to form explosive perchlorate compounds if any contamination is present in the bottle. It is recommended that containers of perchloric acid are disposed of no more than one year after opening.
* Perchloric acid bottles should be inspected on a monthly basis for signs of degradation (e.g. darkening or crystallisation) and any found to have degraded should be disposed of via the University’s approved chemical waste contractor.

**Using Perchloric Acid**

The use of perchloric acid (or perchlorate compounds) should only be undertaken after all possible alternatives have been considered and discarded as not being suitable for the process. In the event that no alternative is available it is recommended that before beginning work the process is discussed with a local competent person and/or the Safety and Environmental Protection Service (SEPS). There are many tried and tested analytical procedures that use perchloric acid and in general these can be performed safely assuming that the necessary precautions are taken. However, many procedures taken from older publications have been found to be very hazardous and explosions have occurred when following an unsuitable procedure. To ensure that a safe system of work is undertaken it is essential that any process involving perchloric acid is treated as potentially high risk.

Prior to beginning any work with perchloric acid a comprehensive CoSHH assessment should be undertaken recording the details of the process and the control measures that will be taken to reduce the risks to staff and students. This assessment should include requirements for storage, use, waste disposal and emergency procedures to be followed in the event of a leak, spillage, fire, explosion or other foreseeable accident.

We strongly recommend that the process (including the CoSHH assessment) should be reviewed by a competent person and countersigned before permission is given to begin the process. In some areas, permission is required from the Head of Management Unit, Principal Investigator or another senior individual before work with perchloric acid / perchlorates can begin and this is seen as a sensible precaution. It is worth ensuring that the process of authorisation is clearly communicated to users to avoid any misunderstandings. Some additional safety precautions are outlined below:

* Perchloric acid should only be handled in a properly functioning ducted fume hood fitted with a chemically resistant surface, wooden and metal fume cupboards should be avoided to reduce the risk of an explosion. Fume hoods should be washed down after every use to prevent any residue from being left behind.
* When perchloric acid is in use no combustible (or otherwise incompatible materials) should be present within the fume cupboard, this should include paper towels and other cellulosic materials.
* Where perchloric acid is regularly used at elevated temperatures (or high concentrations) a dedicated fume hood fitted with a wash down system should be operated. This is to prevent perchloric acid vapours interacting with the metal ducting leading to a build-up of explosive perchlorate compounds. Such fume hoods should be fitted with shatter resistant glass, clearly marked and not used for any other purpose (especially storage of solvents).
* Glassware used should be clean and undamaged and **must not** be sealed using corks or rubber bungs / septa nor should rubber or plastic hoses be used. Glass stoppers may be used but neither these nor any glass joints should be greased.
* If heating is required the use of oil baths and open flames should be forbidden. Heating mantles, water baths or sand baths should be used to heat the reaction vessel taking care to ensure that precautions are taken to manage the increased oxidising ability of perchloric acid at elevated temperatures.
* Where there is a requirement to use either heat or dehydrating agents in the process the risk of an explosion is significantly increased and this should only be undertaken where no alternative exists. Blast shields should be used and the area around the fume hood should be kept as clear as possible.
* Perchloric acid **must not** be distilled under vacuum to avoid formation of the unstable anhydride.
* It is strongly recommended that perchloric acid monohydrate and anhydrous perchloric acid are not used or generated due to their extremely hazardous nature.
* Perchloric acid waste should never be allowed to enter the drainage system, all perchloric acid waste should be retained for disposal via the university’s appointed chemical waste contractor.

**Note: Lone working and out of hours working with perchloric acid and perchlorates should not be permitted, overnight experiments using this material should be strongly discouraged.**

**Note: Once the CoSHH assessment / procedure has been agreed, the procedure should be carried out entirely as recorded and the agreed safety precautions implemented in full without modification.**

**Perchloric Acid Digestions**

Perchloric acid digestions are usually carried out using concentrated perchloric acid at high temperatures significantly increasing the risk of an explosion. This has led to fires and explosions occurring when perchloric acid fumes have reacted with organic materials (including dust) in the ducting of local exhaust ventilation systems or with the metal of the ducting itself to form highly unstable perchlorates.

During a digestion process, it is strongly recommended that samples are treated first with concentrated nitric acid to remove any easily oxidised material before perchloric acid is added. The fume cupboard being used must be kept free of other materials during the procedure. As noted previously where perchloric acid is regularly used at elevated temperatures (or high concentrations) a dedicated fume hood fitted with a wash down system should be operated.

**Perchlorate Compounds**

Perchloric acid will react with metals to form perchlorate salts and certain organic compounds such as alcohols to form perchlorate esters. Perchlorate compounds may also form in stored perchloric acid due to the presence of contaminants in the solution. Perchlorate compounds are highly unstable and prone to explosion and therefore their formation should always be avoided, consider the following:

* Avoid contact with incompatible materials such as metals or organic compounds.
* Remember that metal perchlorates can be formed when perchloric acid vapour reacts with fume hood ducting. For regular or prolonged processes dedicated “wash down” fume cupboards should be used.
* Avoid contamination of perchloric acid containers with organic material
* Regularly inspect perchloric acid containers and dispose of any that exhibit discolouration or crystallisation.

Magnesium perchlorate (aka Anhydrone) is a very effective dehydrating agent that has been used in the past to dry organic solvents. However, it presents a very serious risk of explosion and use of this material is considered a “high-risk” procedure. When there is a requirement to dry solvents, an alternative method should be sought. **Anhydrone must not be used.**

**Spillages of Perchloric Acid**

When a small leak or spillage of perchloric acid has occurred in a fume cupboard, it should be contained and cleaned up as soon as possible by a competent person using the appropriate PPE (to include as a minimum nitrile gloves, face shield and lab coat). Spillages of perchloric acid should be treated cautiously, they **must not** be absorbed or mopped up with combustible materials such as sawdust, paper towels, cloths etc. as this could lead to spontaneous ignition as the material dries out.

The spillage should first be neutralised with sodium bicarbonate / sodium carbonate. The neutralised spill may then be swept up or absorbed with an inorganic absorbent medium, any materials or equipment used should be soaked in water and retained for disposal as contaminated waste). Residue and contaminated materials should be clearly labelled and securely stored for disposal. To minimise the risk of any residue remaining on the floor / surface it is recommended that a second wash with a sodium bicarbonate / sodium carbonate solution is undertaken.

**Note: In the event of a large spillage or a spillage outside the fume cupboard the area should be evacuated and expert advice / assistance sought.**

**Note: Should anyone come into contact with perchloric acid, normal skin and eye washing procedures should be followed i.e. remove contaminated clothing and irrigate for 15min. Due to the severity of the burns caused this should be done as quickly as possible.**

**Fume Cupboard Decommissioning and Removal**

The dismantling / removal of fume cupboards (and associated extract ducting) that have been used for processes involving perchloric acid either for the purposes of disposal or relocation can be extremely hazardous. Procedures and safety precautions should be set up after discussion with the Safety and Environmental Protection Service and Estates and Commercial Services before the commencement of any works.

**Further Guidance and Support**

Perchloric acid is an extremely unstable and dangerous substance. It should only be used when no other viable alternative exists and even then only following a robust risk assessment which should be approved by a competent person within the management unit. For further information and guidance please use the contact details below:

**General Office:** 0141 330 5532

**Chemical Safety Adviser:**  0141 330 2799

**E-mail:** safety@glasgow.ac.uk