The Dangers of Using Perchloric Acid

Introduction:

Perchloric acid is extremely hazardous, and every effort must be made to find safer alternatives, its use should be avoided when possible. Perchloric acid is bought as a 70-72% solution (the dihydrate) and in this form it is simply an extremely corrosive liquid. Its major hazard, however, is the variety of ways it can be involved in explosions and fires. When the water concentration falls (due to distillation or addition of a dehydrating agent), the acid becomes an extremely strong oxidising agent and can react explosively with organic materials. The acid itself can explode: organic perchlorates can explode: some inorganic perchlorates can explode. The materials can be sensitive to heat, friction or shock, and even the most trivial of mishandling can have catastrophic results.

The following is an extract from the C.R.C. Handbook of Chemical Safety *

"Considerable interest has been taken in the explosive hazards to be encountered in the use of perchloric acid since a mixture of perchloric acid and acetic acid exploded in a Los Angeles factory in 1947, killing 15, injuring 400, and causing $2 million damage. On a smaller scale, Robinson reported a detonation of 3g of a perchlorate salt of a rhodium-polyamine complex undergoing an evaporation step in a rotary evaporator. A violent explosion destroyed the evaporator, smashed a lab jack, cracked the bench top and chipped walls over 15 feet away. Fortunately, this happened in an empty laboratory."

Using Perchloric Acid:

The use of perchloric acid or perchlorates will only be countenanced after all reasonable alternatives have been considered and discarded as not being reasonably practicable. It is therefore recommended that perchloric acid and its compounds should not be used without first having informed the Safety and Environmental Protection Services (SEPS). Some tried and tested analytical procedures are probably quite safe but equally some processes from research papers, especially from older publications, may be suspect. It is essential that any process involving perchloric acid and associated compounds reacting with organic material is viewed as high risk.

If Schools/Units decide it is essential to use these substances in certain activities and that the Head of the Management Unit has given written permission for this activity then they must take the following steps:-
1. Carry out a COSHH Risk Assessment and record what procedures and control measures will be put in place to minimise the risks involved in the activity being undertaken. This should include storage, use of transportation (if required), disposal procedures of any excess or waste perchloric acid or associated substances and emergency arrangements. The COSHH Risk Assessment should also include:

   - A copy of the written permission given by the Head of the Management Unit for the activity to be undertaken.
   - Detailed emergency plans for dealing with an explosion or spillage during use.
   - The maximum amount of material that should be used for the activity to be undertaken.
   - Where the substance is stored. It is recommended that the container of perchloric acid be placed in an enamel tray containing a significant layer of sand and stored away from organic materials or dehydrating agents such as sulphuric acid.
   - The allocated fume cupboard facility where the activity is to take place. Any process using perchloric acid or perchlorates involving heat or dehydrating agents must be carried out behind blast shields and undertaken in a fume cupboard fitted with a scrubber facility.
   - If required, the method by which the perchloric acid or perchlorate is to be heated. It is recommended that heating should be by use of a sand bath, a water bath or heating mantle, never an oil bath.
   - That the use of perchloric acid on wooden benches or in wooden fume cupboards is prohibited.
   - That any glassware or other suitable vessels used must not be sealed with corks or rubber bungs, or with greased glass stoppers.

2. A copy of the recorded COSHH Risk Assessment should be discussed with SEPS to have the assessment findings and procedure validated.

3. When the COSHH Risk Assessment has been validated, the procedure and control measures recorded should be carried out as agreed and without modification.

**Perchloric Acid Digestions:**

There have been several incidents where perchloric acid fumes and organic materials such as dust have interacted in fume cupboard ducts causing explosions. There have also been several reports of old wooden fume cupboards exploding after the use of perchloric acid. During a digestion it is strongly recommended that the sample is treated first with concentrated nitric acid to remove any easily oxidised material before adding the perchloric acid. The fume cupboard used must be kept clear of any other materials.

**Magnesium Perchlorate:**

The use of "Anhydrone" (magnesium perchlorate) for drying organic solvents should be considered as a high risk operation. A suitable alternative drying agent should be sought.
**Spillages of Perchloric Acid:**

When dealing with a spillage of perchloric acid appropriate personal protective equipment must be worn. After perchloric acid has been spilled on the floor or bench it should not be mopped up nor soaked up with dry combustible materials such as sawdust or paper towels. It should first be neutralised with sodium bicarbonate and then mopped up. The spill area should then be thoroughly washed down. The mop should then be thoroughly rinsed out and while still wet, sealed in a plastic bag and disposed of as flammable waste.

**Fume Cupboard Removal:**

The dismantling of fume cupboards used for perchloric acid and the dismantling of fume cupboard extract ducting systems whether for disposal or relocation is extremely hazardous. Suitable procedures should be set up after discussion with the Safety and Environmental Protection Services and the Estates and Buildings Services Unit before dismantling of the fume cupboard takes place.