

HAZARDS ASSOCIATED WITH THE USE OF PERCHLORIC ACID

Reactions of perchloric acid with organic or combustible material usually occur when perchloric acid is added to a sample which has not been sufficiently treated with nitric acid to remove easily oxidized material. Provided that nitric acid is present in sufficient quantity to prevent blackening, the triple mix $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HClO}_4$ is a safe oxidizing mixture.

Combustible materials, such as sawdust, wood, paper, natural fibre bags, cotton waste, rags, grease, oil and most organic compounds contaminated with perchloric acid solution are highly flammable. Such materials may ignite spontaneously or explode on heating, by flame, impact or friction. Rinsing the material in cold water will remove perchloric acid and reduce the hazard.

Possible sources of unstable perchlorates are:

- (a) Perchlorate crystals around the tops of reagent bottles stored for lengthy periods after opening.
- (b) Metallic or organic perchlorates deposited in improperly designed fume hood systems.
- (c) Reaction of perchloric acid fumes with grouting material used to seal stoneware hoods.
- (d) Reaction of perchloric acid fumes with lubricants used in blower system of the fume cupboard.
- (e) Reaction of perchloric acid fumes with metals used in ductwork systems of a fume cupboard.
- (f) Reaction of perchloric acid fumes with flammable material deposited in bends or porous construction materials in horizontal runs in ductwork.
- (g) Deposition of perchlorate salts in the burner slot from aspirating aqueous solutions of perchloric acid into an atomic absorption spectrometer.

SAFE WORKING CONDITIONS

The following conditions are recommended for the use of perchloric acid in the laboratory:

- (a) Work involving the use of perchloric acid should be carried out in a suitable water scrubbing fume cupboard manufactured in accordance with AS/NZS 2243.8, reserved for this purpose.
- (b) Perchloric acid should not be allowed to contact organic matter of any kind including wooden benches, wooden floorboards or vinyl tiles. The floor material in the vicinity of the fume cupboard should be inert to perchloric acid, non-absorbent and free from cracks. Wax floor polish or other organic finishes should not be used.
- (c) Where perchloric acid is to be used regularly, consideration should be given to setting aside an area of the laboratory solely for the work.
- (d) Perchloric acid should only be stored in designated locations. Bottles of perchloric acid should be stored in watertight trays or containers (and caps) made from inert material and of sufficient size to hold the contents of a bottle. Bottles should be carried in suitable carriers.
- (e) Only minimum quantities of perchloric acid should be retained in the laboratory area.
- (f) Spillages should be neutralized with soda ash and flushed with water.

LABORATORY PRACTICE

The following practices should be observed when using perchloric acid in the laboratory:

- (a) The supervisor should ensure that any person intending to use perchloric acid is fully conversant with the possible hazards and is aware of the appropriate safety requirements.
- (b) Stocks of perchloric acid should be maintained at the practicable minimum.
- (c) Where perchloric acid is to be used as a mixed reagent, e.g. with nitric acid, premixing of these reagents for stock should not be performed. Only the immediately required quantity should be mixed.
- (d) Stocks should be examined periodically, and any suspect material diluted with water and disposed of immediately by careful neutralization.
- (e) Organic chemicals should not be placed or used in fume cupboards employed for perchloric acid digestions.

- (f) The nature of materials and containers stored beneath fume cupboards set aside for perchloric acid should be reviewed critically.
- (g) Safety screens or shields should be used by operators carrying out perchloric acid digestions.
- (h) Oil baths should not be used for heating perchloric acid solutions. Glass-to-glass unions, corks, rubber tubes or stoppers, or mineral-based grease should not be used in apparatus for perchloric acid digestions. The following apparatus should be used:
 - (i) Heat-resistant reaction beakers, flasks or test tubes.
 - (ii) Electric hotplates, cast aluminium heating blocks or sand baths.
 - (i) In wet digestions with perchloric acid, the minimum sample quantity consistent with the requirements for analytical precision should be used and the sample should be pre-treated with nitric acid to destroy easily-oxidizable matter. Nitric acid should always be used to pre-treat organic matter, or any material of unknown composition or behaviour prior to treatment with perchloric acid.
- (j) For digestions involving matter which may form an immiscible phase, especially fat, very careful preliminary treatment with nitric acid (or nitric acid and sulfuric acid if permissible) should be carried out.
- (k) Evaporation to dryness should be avoided where possible. Perchloric acid should not be allowed to concentrate above 72% aqueous solution. However, if complete digestion is required (where all trace of perchloric acid is to be boiled off), a sulphuric acid/perchloric acid/nitric acid digestion mixture should be used.