UNIVERSITY OF DURHAM - DEPARTMENT OF CHEMISTRY

NOTES OF GUIDANCE FOR USERS OF PERCHLORIC ACID

1. These notes, adapted from the Government Health & Safety Executive's information document HSE 294/29 issued in October 1987, form **Special Code of Practice D** of the Chemistry Safety Policy. They give advice on the hazards associated with perchloric acid and precautions that should be taken when it is handled or stored.

2. Perchloric acid forms a constant-boiling mixture with water containing 72.4% acid by weight (w/w). It is typically sold commercially in 2 grades, 60-62% and 70-72% acid w/w. At room temperature the solutions are hygroscopic and are very strong acids but are virtually non-oxidising. The oxidising power of perchloric acid solutions increases with temperature and at 160°C the 70% w/w solution has very powerful oxidising properties. The constant-boiling mixture boils at 203°C and decomposes above 315°C to give chlorine, water and oxygen.

3. Anhydrous perchloric acid is an extremely powerful oxidising agent at room temperature and contamination with small traces of organic material such as dust can cause violent explosions. The anhydrous acid may explode spontaneously after storage for extended periods. There have been occasions when the pure anhydrous acid has exploded spontaneously after 30 days of storage. Any slight impurity will reduce that time significantly. Therefore, anhydrous perchloric acid should be made, only if absolutely necessary, freshly as required and used IMMEDIATELY. Any unused acid should be disposed of without delay and not stored.

HAZARDS

4. Solutions of perchloric acid are hazardous in contact with the following: heavy metals and their salts; ketones and aldehydes; many chlorinated hydrocarbons; alkyl sulphoxides; ethers; esters; alcohols; amines and their salts; diazonium salts; azo compounds; fluorine; organic cyanides (nitriles); periodic acid; iodides; organo-phosphorus compounds. Contact with potential dehydrating agents (e.g. acetic anhydride, with which it forms solutions of the anhydrous acid that can be sensitive to heat or mechanical shock and give off a flammable vapour on heating) can also be hazardous.

5. Solutions containing perchloric acid should not normally be distilled under reduced pressure as this can result in concentrations of the acid of over 75% w/w.

6. Most hazards arising from the use of solutions of perchloric acid are due to contamination, by spillage, of fume cupboards and their surrounding areas, or from fumes resulting from digestion experiments that require heating to dryness. Wood containing 0.8% w/w perchloric acid can ignite when exposed to mild radiant heat and spontaneous ignition can occur at concentrations of 2.9% w/w.

7. Incidents have occurred while sodium perchlorate has been heated and while re-activating magnesium perchlorate; the latter, in anhydrous form, is a commonly used desiccant (trade names: An-hydrone, Dehydrite). Explosions have resulted when the desiccant has been used to dry ethylene oxide, unsaturated hydrocarbons, dimethyl sulphide and trimethyl phosphite, possibly due to the presence of traces of the anhydrous acid arising from manufacture.

8. Perchloric acid solutions are highly corrosive to most metals and cause acute irritation and corrosion to skin, eyes and mucous membranes.

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STORAGE AND USE

9. Perchloric acid solutions should be stored in a suitable fire-resistant structure (advice as to the standard of construction is available). The store should be wood-free, as perchloric acid can ignite when soaked into wood, and should have internal surfaces that are impervious. Perchloric acid should be isolated from incompatible materials (see section 4). The anhydrous acid should never be stored (see Section 3). Should fire occur in a perchloric-acid storage area, an explosion should be assumed to be imminent. The store's location should be notified to the local fire authority by the occupier of the premises.

10. Spillages are often caused by solutions running down the side of a bottle; all pouring operations should, therefore, be carried out over a sink or a plastic tray. Bottles should then be returned to their plastic containers after cleaning the outside of the bottles with water over a tray and then wiping dry. Care should be taken, as pressure-sensitive mixtures can be formed with such materials as paper and cotton. The materials used for wiping should be washed thoroughly. Amounts in working areas should be limited to the smallest quantity practicable.

11. Fume cupboards where perchloric acid solutions are used frequently should be constructed from polyvinyl chloride (PVC) and fitted with a water scrubber to allow the washing down of the extractor hood after exposure of the cupboard to perchloric-acid solutions.

12. If contamination of wooden surfaces is suspected, specialised assistance should be obtained.

13. Soda ash (sodium carbonate) should be spread liberally over spillages, which may then be mopped up or flushed to a drain using copious quantities of water.

J M Sanderson
13 September 2019 (Review Date, 13 September 2020)

This section is to be completed electronically, and then the PDF sent by email to Dr John Sanderson, CG112.

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I have read the notes of guidance for users of perchloric acid and retain a copy for reference. I agree to follow their recommendations.

Signed: Date:

Name:

Email address: