DURHAM UNIVERSITY

Board of Studies in Chemistry

SAFE USE OF ELEMENTAL FLUORINE

These notes form codes of practice **S-COP E** of the current Chemistry Safety Policy

Elemental fluorine is to be handled in room CG004 only. The specially designed fume cupboards in that room should be used for all manipulations. Anyone wishing to use either substance must consult PROFESSOR GRAHAM SANDFORD who is responsible for instructing persons in the use of fluorine. Anhydrous Hydrogen Fluoride (aHF) is not to be used in the Department without a separate risk assessment. Reactions carried out using fluorine gas do produce solvated hydrogen fluoride as a by-product and so first aid treatment for solvated HF (in a solvent or as a solution in water) is included in this Code of Practice.

A. SUPPLIES OF FLUORINE

Cylinders of Fluorine gas, supplied as a mixture of F_2 in N_2 (20% *v/v*) are purchased from Air Liquide (France). The fluorine/nitrogen mixture is shipped in high-pressure gas cylinders (size K) and the pressure inside a full cylinder is approx. 120 bar.

B. CODE OF PRACTICE FOR STORAGE OF FLUORINE

It is required that:

1. No more than one primary cylinder of fluorine (Size K) be kept within the laboratory (CG004) at any time.

2. Spare full cylinders be stored safely in the departmental store outside the building. Cylinders must not be removed from the store without first consulting PROFESSOR G SANDFORD.

C. CODE OF PRACTICE FOR USE OF FLUORINE

1. Installation and replacement of Fluorine Cylinders

(i) Fluorine supply cylinders may only be removed from and fitted to the equipment by PROFESSOR G SANDFORD and an assistant.

(ii) The Fluorine cylinder is equipped with a valve outlet connection CGA 679. The valve outlet has a thread size of 254 mm (1.0 inch) diameter (see Figure 1).

CGA 679
1 inch l.h. external using flat seat with washer

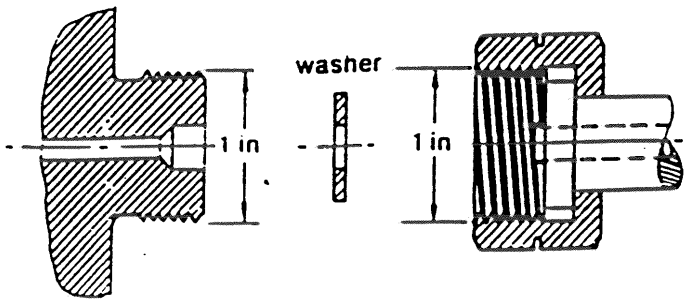


Figure 1

The fluorine cylinder is situated inside a vented gas cabinet in CG004 and is attached to a manifold equipped with a pneumatic shut-off valve, a pressure regulator system designed and supplied by the Spectron (Figure. 2) and operated following the manufacturer's instructions.

Figure 2

When installing and replacing Fluorine supply cylinders in the main vented cabinet the following procedure must be followed and it is strictly required that:-

a) Two persons, who have knowledge of the hazards of fluorine and are acquainted with normal manipulative techniques for fluorine, must be in attendance when changing the main Fluorine cylinder.

b) Face-shields and appropriate gloves must be worn when changing the Fluorine cylinder

(iii) Removal of Empty Fluorine cylinders

Before disconnecting the empty fluorine cylinder from the manifold the operator must ensure that the cylinder valve is securely closed, all of the pipe work within the cabinet has been thoroughly purged with dry nitrogen and the pipe work connecting the cylinder to the manifold is at atmospheric pressure. Once the cylinder has been disconnected from the manifold the cylinder must be capped immediately.

(iv) Installation of Full Fluorine Cylinders

Before removing the cap from the new cylinder ***the operator must be certain that the cylinder is securely closed at its valve.*** After fitting the cylinder the cabinet pipe work must be pressurised with nitrogen and tested for leaks with a suitable liquid leak detector. After thorough purging of the pipework with dry nitrogen all the valving should be closed, the cylinder opened momentarily, then reclosed. All of the pipe work and fittings should then be rechecked for leaks with moist starch iodide paper (it will be necessary to reopen the pneumatic and external manual shut off valves). The full normal routine checking procedure should then be undertaken.

During the cylinder change procedure, care should be taken to keep any open pipe work clean and dry. If there is anything that gives any cause for concern, ensure that the system is in a safe condition and consult PROFESSOR G SANDFORD.

2) Use of Fluorine Cylinder, Manifolds and the Filling of Secondary Cylinders with Fluorine

It is strictly required that:-

a) The main valve of the primary Fluorine cylinder must **not** be opened unless two persons, who have knowledge of the hazards of fluorine and are acquainted with normal manipulative techniques for fluorine, are in attendance.

b) Face-shields and appropriate gloves must be worn when opening the Fluorine cylinder

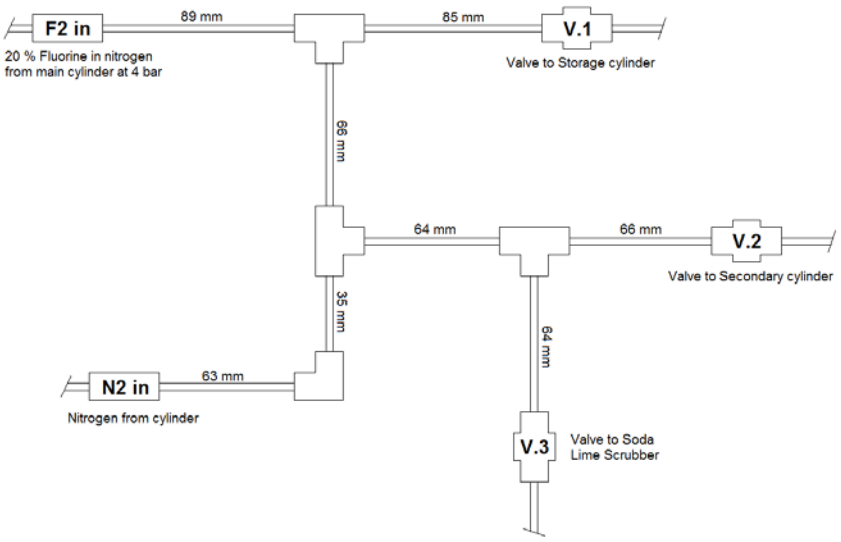
(i) Filling of Secondary Cylinders with Fluorine/Nitrogen mixtures

In order to minimise the number of times the valves on the main cylinder are manipulated, secondary cylinders of suitable capacity may be charged to low pressure (approx 4 bar) from the main cylinder. In each of the two adjacent fumes cupboards (to the right and left side of the cabinet) are located fixed secondary cylinders which are connected via permanent manifolds and valving to the fluorine cabinet.

Anyone wishing to use either the Right Hand (Figures 3) or the Left Hand Rig (Figure 4) for charging a secondary cylinder with fluorine must have obtained prior instruction on their operation and use from PROFESSOR G SANDFORD. Each rig is constructed from stainless steel pipework (all 1/4 inch external diameter BSP standard tubing) and fitted with either stainless steel or Monel Swagelok valves and connections supplied by Teesside Fluid System Technologies Ltd.

Figure 3 - RIGHT HAND RIG

FC 5 Panel 1



FC 5 Panel 2

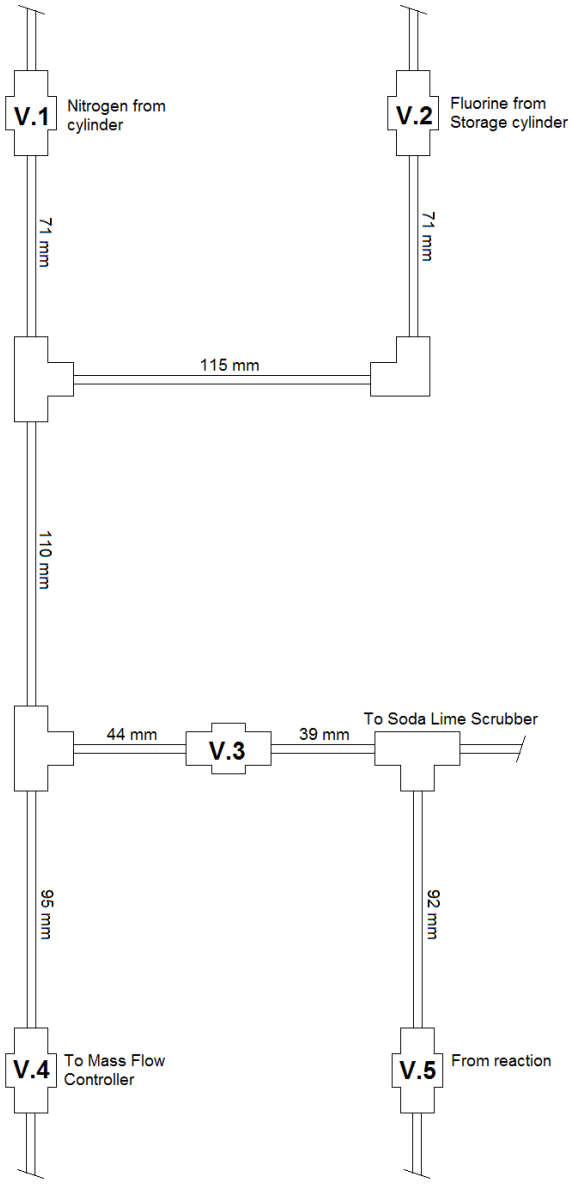
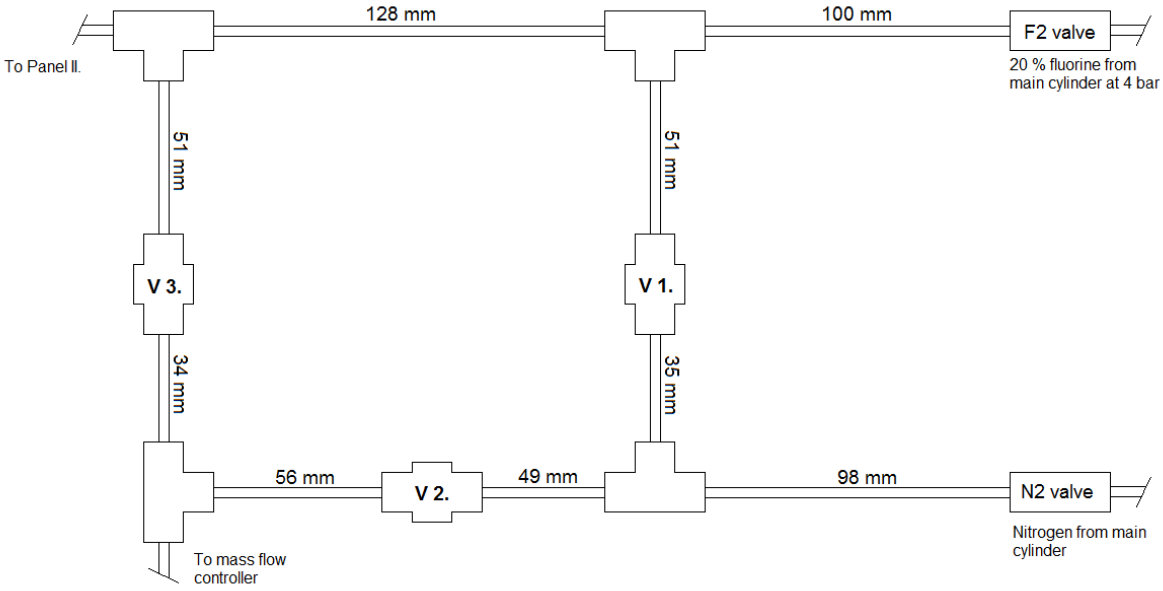
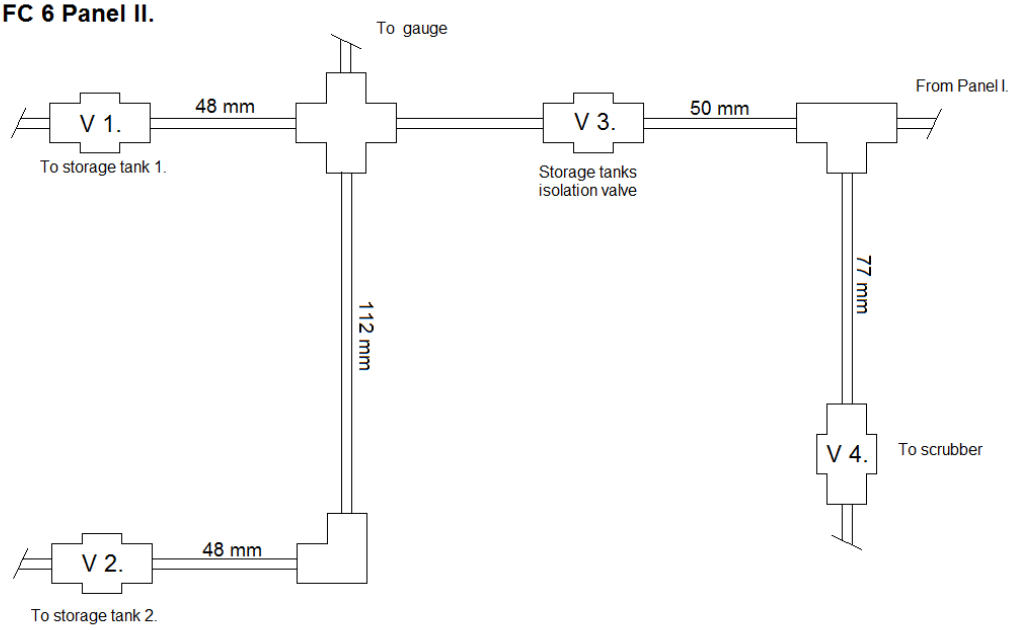


Figure 4 - LEFT HAND RIG

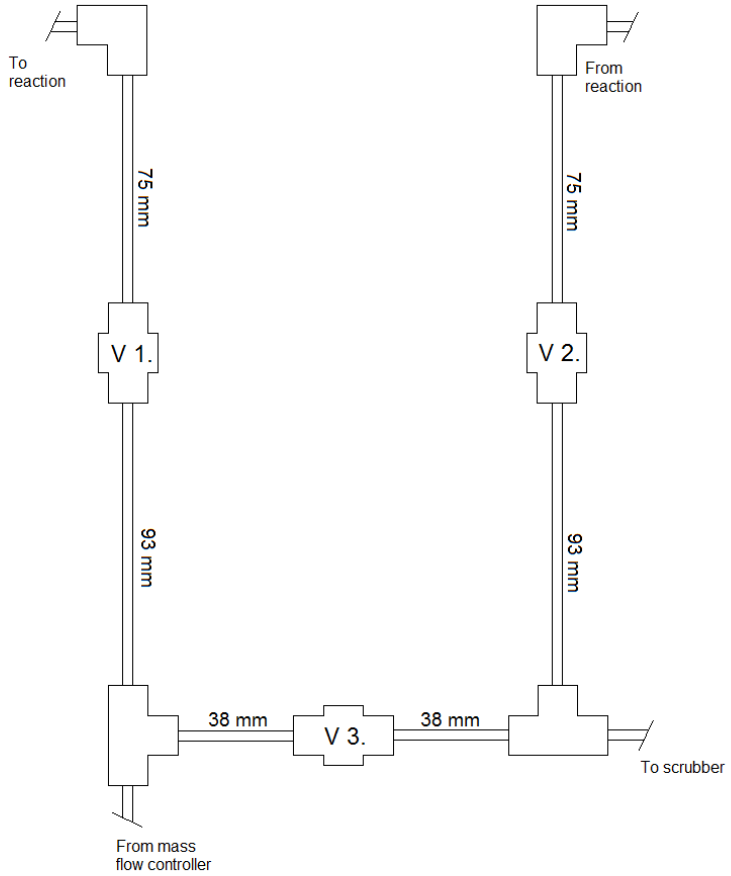
FC 6 Panel I.



FC 6 Panel II.



FC 6 Panel III.



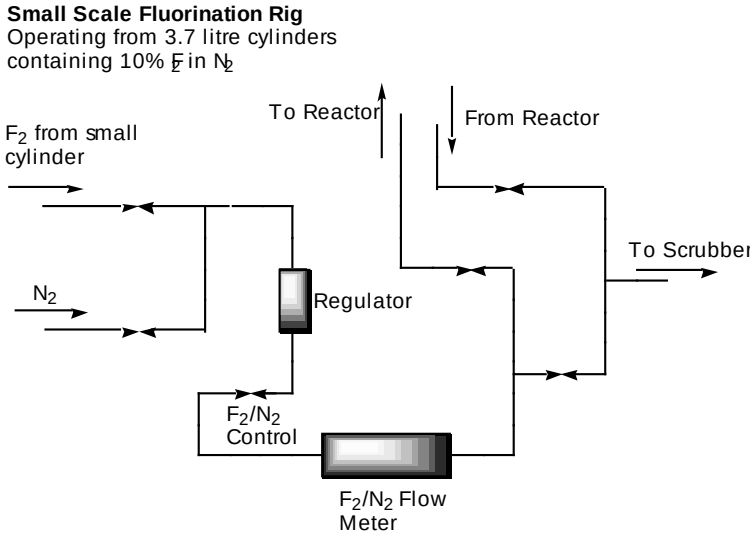
Once a secondary cylinder is charged with fluorine, the main cylinder is isolated and the contents of the secondary cylinder may be diluted with nitrogen if required. The use of a secondary cylinder reduces the risk of exposure of operators to larger quantities of fluorine in the event of an equipment failure.

The manifold located in the fumes cupboard to the right of the vented fluorine cabinet has the facility to charge smaller portable secondary cylinders which are used to carry out fluorination reactions in conjunction

with a small scale fluorination rigs (Figure 5) which are located in fumes cupboards in CY004. Each small rig is constructed from stainless steel pipework and fitted with either stainless steel or Monel Swagelok valves supplied by Swagelok Teesside.

When fluorine is charged to, or discharged from, the storage cylinders on the small gas handling rig, any experimental apparatus should be physically disconnected. This is to prevent the uncontrolled admission of higher pressure/concentration fluorine to an environment where flammable materials may be present in the event of a valve failure.

Figure 5 - SMALL SCALE FLUORINATION RIGS



Anyone wishing to use the Right-Hand Rig (Figures 3) for charging a portable secondary cylinder with fluorine and the small fluorination rigs must have obtained prior instruction on their operation and use from PROF. G SANDFORD.

(ii) The following additional precautions must be taken.

(a) All manipulations of fluorine and volatile fluorides should be carried out on as small a scale as is practicable.

(b) All containers in which fluorine gas are stored must be correctly labelled.

(iii) Maintenance of Fluorine Rigs

(i) Replacement of pipework or valves

Replacement of valves and pipework is necessary when, for example, either a gas leak or a blockage occurs. If a gas leak or blockage is observed on any of the Fluorine rigs, report the problem IMMEDIATELY to PROF. G SANDFORD, who will advise on the repair of the fault.

Prior to the placing of any equipment, lines, valves or fittings into service, they must be thoroughly cleansed of all foreign matter, flushed with a non-aqueous degreasing solvent such as dichloromethane and thoroughly purged with a stream of nitrogen. In particular, new valves are supplied with hydrocarbon based lubricant on their surfaces. This must be removed by thorough cleaning and replaced by a fluorocarbon lubricant. The equipment should then be passivated with increasing concentrations of fluorine in nitrogen (1% - 10%) before it is exposed to fluorine at high pressures.

(ii) General Maintenance of All Fluorine Rigs

The following procedure should be followed on a regular basis and recorded:

(a) The pressures of the two nitrogen cylinders (pneumatic operating supply and process);

(b) The pressure of the fluorine supply cylinder;

(c) With the system pressurised, but with the cylinder valve closed, starting from the cylinder all valve heads and pipe joints within the cabinet should be inspected for leaks using moist starch iodide paper. Particular attention should be paid to the inspection of all the pipe and fittings that lie between the cylinder and the regulator (high pressure region).

(iii) Gas Leaks

In the event of observing a gas leak in any of the fluorine rigs the FOLLOWING PROCEDURE MUST BE ADOPTED TO REPAIR THE LEAK:-

(a) The fluorine supply from either the main or secondary fluorine cylinder to the leak should be stopped immediately

(b) The system must be thoroughly purged with dry nitrogen. NO ATTEMPT SHOULD BE MADE TO REPAIR ANY LEAKS UNTIL THE SYSTEM HAS BEEN THOROUGHLY PURGED OF FLUORINE AND DEPRESSURISED TO ATMOSPHERIC PRESSURE.

(c) Repair the leak by replacing the valve or pipework as necessary, purge the system thoroughly with dry nitrogen and check for leaks using a suitable liquid leak detector. Before exposing the repaired system to fluorine consult PROFESSOR G SANDFORD.

D. SAFETY PRECAUTIONS

Fluorine is corrosive and when in contact with the skin can cause painful burns; in addition, the vapours are irritant and toxic. Care must be always be exercised to avoid breathing these gases or allowing them to come into contact with the skin.

1. Safety Equipment

Users of fluorine must satisfy themselves in advance that the following are readily accessible and in satisfactory condition:

(a) face shields, rubber or polyvinyl-chloride gauntlets;
(b) an adequate supply of clean water on tap and an emergency shower;
(c) eye-wash provision in the laboratory;
(d) HF antidote gel (calcium gluconate 5%; PL No. 1021-0001);
(e) a copy of section F of this document to accompany any injured person to hospital or to a medical practitioner;
(f) a gas bottle containing medical-quality oxygen with inhalation mask, and an Ambu resuscitator.

All personnel using fluorine should be trained in the use of the breathing apparatus and re-trained on an annual basis (organised by Mr Paul White).

2. Precautions

(a) Wear face shield and suitable hand protection in addition to the usual laboratory coat whenever using the fluorine equipment (Full-body protection is available from Mr D Hunter.)
(b) Do not breathe vapours.
(c) Do not expose skin to vapour contamination.
(d) Ensure that assistance is available and can be summoned quickly in case of an accident.
(e) Know the location of compressed-air breathing apparatus.

NOTE: If there is any possibility that gauntlets, face shields, etc. have been contaminated, they should be dipped in a 5% aqueous solution of sodium carbonate, then rinsed and allowed to dry. Only the outside of gloves should be dipped and gloves should be examined for defects before use.

3. Gas Leaks

In the event of gas escaping:

(a) warn people in the vicinity;
(b) put on compressed-air breathing apparatus and protective clothing (if not already worn);
(c) switch off the electrical supply (low voltage D.C.) to the generator and shut off hydrogen fluoride if it is being added;
(d) open all doors and windows, and leave the room until it is clear of gas;
(e) discard any clothing that has been contaminated and treat any affected areas of the skin as described overleaf. The University Hospital of North Durham does not have facilities for decontamination. You must ensure that all contaminated clothing is dealt with in the Department. Alternative clothing is available from the Stores.

(f) Small leaks of fluorine will trigger the alarms (Alarm 1 0,5 ppm F2; Alarm 2 1.0 ppm F2) installed in CG004 in July 2017.

If any of the audible and/or visual alarms are triggered:

· Everyone should immediately leave the lab. closing the door and pull barrier across door.

· Do not re-enter or allow anyone to enter the lab.

· Leave the building by the nearest exit.

· Prof. Graham Sandford (CG118; Tel. 42039), inform Security (Tel. 43333) and Chemistry Safety Chair, Dr John Sanderson (CG112; Tel. 42107) or the Chemistry Safety Coordinator Dr Connor Sibbald (CG004 Tel. 42046).

· Do not press any buttons on the control panel.

· Identify on panel gas channel causing alarm (Alarm 1 or 2 red LEDs lit – inform Security).
· NB. Gases 1, 5, 6, 7 may be isolated by closing bottles located in Chemistry Courtyard.

· Audible warning and flashing beacon will remain activated until gas drops below Alarm 1.

· Do not enter lab until told it is safe by the Chemistry Safety Coordinator or his deputy.

4. First Aid

The following persons have attended a course in the treatment HF injuries:

Miss Kerry Strong, CG193	43662
Mr Malcolm Richardson, CG015	42017

(The user should complete this section, should detach it then should give it to Prof. Graham Sandford)

DURHAM UNIVERSITY - BOARD OF STUDIES IN CHEMISTRY

Safe use of elemental fluorine

I have read and understood the Board's guidance and agree to follow it.

SIGNATURE: _____ Date: _____
NAME IN CAPITALS
(SURNAME UNDERLINED): _____

FIRST AID ARRANGEMENTS

Fluorides are potent poisons whether by swallowing, inhaling or skin absorption.

EMERGENCY NUMBERS	INTERNAL	43333
	OUTSIDE LINE	(9) 999
UNIVERSITY HOSPITAL OF NORTH DURHAM		(9) 333 2135
Health and Safety Office		42660; 42662; 42663

Take these notes to the hospital with you.

SKIN - Hydrofluoric acid is highly corrosive to the skin and can cause anything from irritation and sores to deep third degree burns depending upon the concentration of the acid, length of exposure and the promptness of treatment.

FIRST AID

Remove contaminated clothing immediately wearing protective gloves.

Flood the skin with clean cool water for 20 minutes.

No immediate pain may be felt on skin contact unless the acid is very strong.

Rub calcium gluconate gel into the affected areas and massage until 15 minutes after the pain has subsided.

Transfer the patient to hospital accompanied by a First Aider or colleague.

Report the accident to the Health and Safety Office.

EYES - Both the liquid and vapour are severely irritating to the eyes and eyelids and may cause burns, prolonged or permanent visual defects.

FIRST AID

Wash the eye with flowing water for 10 minutes, then irrigate with normal saline for at least 30 minutes.

Do not use calcium gluconate gel.

Refer to Sunderland Eye Infirmary (9) 528 3616

MOUTH - Hydrofluoric acid causes necrosis of the oesophagus and stomach, nausea, vomiting, diarrhoea and may be fatal if swallowed.

FIRST AID

Do not make the casualty vomit.

If conscious give milk or water to drink.

If unconscious treat as for inhalation.

Refer to the hospital.

LUNGS - Inhalation of fumes may cause tracheitis, bronchitis and pulmonary oedema.

FIRST AID

Remove casualty from area of exposure.

Loosen clothing at neck and waist.

If conscious, keep the patient at rest - encourage him/her to suppress the desire to cough.

Give oxygen if available.

If unconscious give artificial ventilation and chest compressions or place in the recovery position as necessary.

Phone for an ambulance and refer to hospital.

To be taken to the Hospital

HYDROFLUORIC ACID

For the guidance of Medical Officers

Name of works .....

Name of patient ..... Age .....

The patient* (a) received skin burns from hydrofluoric acid

(b) had hydrofluoric acid in eye/eyes

(c) inhaled fumes of hydrofluoric acid

at ..... am/pm on .....*(date)*

** Delete where necessary.*

This is a dangerous acid for which the specific treatment detailed below is required and the acid has the following characteristics.

(a) Skin burns cause intense pain, onset of which may be delayed for several hours and in the absence of treatment persist for several days. They are more serious than is first apparent because of deep penetration by the acid, the action of which is progressive, causing destruction of subcutaneous tissue over a period of several days.

(b) Because of the penetrating characteristics of the acid, eye damage is likely to be more extensive than is first apparent.

(c) Inhalation of fumes may cause tracheitis, bronchitis and pulmonary oedema.

/continued .....

INITIAL TREATMENT

(a) Skin: Immediate immersion in water. Removal of contaminated clothing. Massage into the burn the calcium gluconate gel until 15 minutes after the pain has subsided.

(b) Eyes: Irrigation with copious amounts of isotonic saline or water. Instil sterile calcium gluconate (10%) drops. Treat symptomatically.

(c) Inhalation: Rest and Oxygen therapy.

(d) Ingestion: Large quantities of liquid - lime water, milk or water.

Further Treatment

(a) Skin: If pain present or recurs continue to massage calcium gluconate gel into the base of the burn. Where there is a thick necrotic coagulum this should be excised and where fingers or toes are burnt - the nails may require to be split or removed. Local anaesthesia is contra-indicated; use general anaesthesia. Continue dressing with calcium gluconate gel.

(b) Eyes: Corneal burns may be very severe - consult ophthalmologist.

(c) Inhalation: Expect onset of pulmonary oedema up to 48 hours after exposure - ensure that all facilities are available for treatment.

(d) Ingestion: Stomach pump may be required. Treat symptomatically.

(e) Electrolyte Imbalance: Large burns of over 160 sq cm (25 sq in). After inhalation or ingestion there may be an electrolyte imbalance due to removal of calcium and/or magnesium from the serum.

Under electrolytic monitoring control give 6 effervescent tablets of calcium (400 mg. calcium+ 20 mg. ascorbic acid) in water by mouth every 2 hours until the balance is restored.

Signature .....

Date ..... Time .....