Procedure: Hydrofluoric acid handling

Purpose

This procedure is intended to provide a consistent approach to the management of Hydrofluoric acid (HF) across the University. Topics surrounding the management of HF covered by this document include training, purchasing, handling, storing, disposing and managing HF related emergencies.

All personnel who are intending to use HF need to be aware of the information set out in this procedure as well as their responsibilities.

Procedure

Introduction/Background

1. This hazard management procedure has been developed by the University to ensure the safe and reliable management of hydrofluoric acid (HF) within the University. In managing HF, the University advocates a risk management approach to minimise the risks to staff, students, contractors and visitors in relation to the purchase, storage, handling and disposal of HF associated within the range of research, teaching and operational tasks undertaken within the University.

2. Hydrogen fluoride is extremely corrosive. It is a fuming, colourless liquid at normal atmospheric pressure and less than 19 degrees. Above 19 degrees, hydrogen fluoride is a gas. Hydrogen fluoride is industrially available as a liquid under pressure (anhydrous hydrofluoric acid) or more commonly, as an aqueous solution (aqueous hydrofluoric acid (HF), with a concentration in the range of 30 – 70 % HF w/v. The most common concentration for analytical grade HF is 48 % HF w/v.

3. Hydrofluoric acid is commonly used for digesting minerals, etching glass, metal pickling, and as a fluorinating agent.

4. Hydrofluoric acid exposure may be –

Acute (short term)	Contact with HF can cause death
	Spillage on the skin, or splash in the

	eyes. This causes; intense pain, either immediately or after some hours, a tough white coagulation over the burnt area (a slow healing ulcer), and progressive destruction of tissue including decalcification and necrosis of bone. Hydrofluoric acid penetrates rapidly and deeply below fat layers binding and depleting tissue calcium. A 2% (approximately 360 cm2) body burn from 70% hydrofluoric acid can cause death. The eyes are especially sensitive.
	Inhalation of gas or mists, leading to asphyxia from pulmonary oedema (fluid in the lungs) and convulsions.
	Ingestion, burning of mouth and pharynx, nausea, vomiting, abdominal pain.
Chronic (long term)	Skin ulcers
	Bone and teeth damage
	Irritation of nose, throat and bronchi
	Chronic poisoning is not common

General Management

5. HF is only to be handled by laboratory workers who have been adequately trained and assessed as competent in its use. Supervisors and members of research groups who are using HF must:

- Plan work in the knowledge that any exposure may cause permanent

incapacity or death;

- Ensure all personnel working in the laboratory containing HF are familiar with the properties and hazards of HF;
- Ensure all HF users are trained and deemed competent in the handling and using HF;
- Document a risk assessment for its intended use, prior to that use;
- Document and follow the appropriate safe work procedure;
- Undertake workplace inspections and competency assessment at least twice a year.

Training

6. The University is committed to providing appropriate training to ensure workers, students and visitors have the skills and knowledge necessary to fulfil their WHS obligations. Supervisors and those directly responsible for HF use must attend training sessions on the use and properties of corrosive substances. See: Corrosive training course.

Purchasing HF

7. The following considerations are to be made when purchasing HF:

- Before purchasing HF, prospective users must conduct a risk assessment of the chemical(s) and potential uses. Developing appropriate chemical handling procedures should also commence. Work with HF is considered a high risk process. See: A guide to developing a Chemical Handling Protocol.
- Research group leaders are responsible for approving hazardous chemical purchases, including hydrofluoric acid.
- Safety Data Sheets (SDS) are available on the Chemwatch online database system or from the manufacturer/ supplier. See: Chemwatch
- Purchase minimum quantities of HF just prior to required use. Containers holding HF can degrade and should not be stored for long periods of time. The maximum container to be purchased should not exceed 500 mL, to minimise decanting risks.
- Storage considerations need to be accounted for during the purchasing process. Storage requirements can be identified on the product SDS.

Procedures for Using and Handling HF

8. All activities involving HF must have a documented risk assessment and a

chemical handling protocol. Any research project involving HF must have approval from the Head of School.

9. An eyewash station, safety shower and first aid shall be in close proximity to the HF work. Also ensure that the first aid kit has the necessary content, is kept up to date and is complete to adequately respond to potential HF exposure.

10. Eliminating the use of HF should be considered where possible. Alternative methods and procedures which do not require the use of HF, but which may give the same results should be investigated. There should be limited personnel access to HF, with a minimum number of people required to handle this substance.

11. No persons are permitted to work alone with HF or after 5.00pm, before 8.00am or on weekends, when normal emergency assistance services, for example, first aid, building wardens are not available.

12. All HF work involving the release of HF should be conducted in a scrubbed fume cupboard. The integrity of the scrubber, fume-cupboard surfaces and the pH of the tank water should be checked regularly as part of a lab maintenance program. See: Managing fume exhaust system

13. Alert other workers in the laboratory that you are using HF in the fume-cupboard and place signage to that effect either on the fume-cupboard sash or laboratory door. Always lower fume-cupboard sash when access to the cupboard is not required.

14. Never add water to the acid. In dilution, a small amount of HF should be added to plenty of water. If using a dispenser it is preferable to add HF under the surface of the water in order to minimise the generation of HF vapour and splashes. HF is also highly reactive with most metals, glass, ceramics and fibreglass.

Personal Protective Equipment for HF

15. There are specific Personal Protective Equipment (PPE) requirements for handling HF. It is essential that PPE be worn correctly and is regularly checked and in good repair. All glove materials eventually degrade in the presence of HF. Double gloving is recommended and gloves should be regularly inspected and replaced. No areas of skin should be exposed. In addition to standard laboratory PPE (lab coat, safety glasses, enclosed shoes, long pants and sleeves), the following PPE shall be used when handling HF:

- a face shield for handling and transferring and,
- safety goggles with fume-cupboard sash down for pipette dispensing and,
- a PVC apron and,

- neoprene (most desirable) or PVC gloves, sleeve protectors or gauntlet style gloves

Transport and Storage of HF

16. Solutions of HF should not be routinely transported out of or around a laboratory. If transport is required keep volumes to a minimum, ensure caps are secure and always use secondary containment (i.e. enclosed bottle carrier made of compatible material).

17. HF should be stored in a cool, dry well-ventilated area away from heat and within a bunded tray (i.e. secondary container that can withhold the volume if primary container ruptures.). Storage areas should be clearly labelled.

18. HF shall be stored in a secure area that is in a restricted, locked laboratory in a ventilated storage cupboard or a locked storage cupboard.

19. Bottles of HF shall be entered in the Chemical Inventory System. A regulated substance register should be used to record volume of HF stored and used every time. See: Chemical Inventory System. See: Regulated substance register.

20. HF is not compatible with glass or metals. Glass containers shall not be used for storage. Polyethylene is a suitable storage container for HF and the container should be regularly inspected for degradation.

Labelling

21. All containers holding HF solutions and waste residue must be appropriately labelled.

22. A decanted hazardous chemical must be labelled with the following as a minimum:

- the product identifier; and
- hazard pictograms or
- hazard statements.

23. See: Hazardous substances label template for decanted substances.

24. See: Labelling of hazardous substances.

25. See: Labelling Hazardous Waste

26. Labels can also be created by using Chemwatch. See: Chemwatch

HF Spills

27. See: Appendix A

HF First Aid and Emergency Procedures

28. HF is corrosive and can cause severe burns to skin and eyes. Contact with skin may not cause pain immediately and appearance of symptoms can be delayed for up to 24 hours. Hydrofluoric acid is also an irritant and toxic (lethal) to the respiratory system and very toxic if swallowed.

29. All research groups using HF must have:

- Personnel trained in the correct first aid treatment for HF.
- A HF first aid kit easily accessible within the laboratory.
- Calcium gluconate gel available and a program to regularly check that it is within the 'Use by' date. The gel must be discarded and replaced after the expiry date.
- Safety showers and eye wash facilities in the laboratory where HF is used. These should be checked regularly, with checks recorded on a placard hanging from the safety shower.
- **OPTIONAL** a Hexafluorine Autonomous Portable Shower for body exposure or a Hexafluorine portable eye wash for eye exposure can also be obtained in addition to the above criteria. These are available from www.prevor.com.

30. A typical HF first aid kit must contain at least:

- 3 pairs of disposable gloves (e.g. Nitrile)
- Container of 500-1000 mg (available calcium) Caltrate tablets
- Calcium Gluconate Gel (has a limited shelf life ~ 1 yr)
- At least 300mL Saline solution (sodium chloride) e.g. Steri Tube, Eyesaline® solution or equivalent
- Eye pads
- Bandages.

31. First Aid Officers should avoid contact with contaminated skin, clothing and equipment. They should also avoid inhalation of vapours or aerosols in the contaminated area. First aid instructions are supplied in Appendix B and should be placed in the HF first aid kit.

32. First Aid Officers must protect themselves by wearing:

- Nitrile gloves under chemical resist gauntlets
- Eye-protection (face-shield and safety glasses)
- Lab coat, or protective overalls, for protection.

33. An advice sheet (Appendix C) for medical staff dealing with HF exposure should be located in the HF first aid kit and accompanying the affected person to hospital.

34. All incidents involving HF must be reported using the ANU Incident Report. See: Incident notification

HF Waste Disposal

35. If HF is consumed within the reaction then residue solutions can be placed in normal laboratory waste containers. The pH of the waste from such procedures should be regularly checked. Small amounts of HF can be neutralised and diluted.

36. If there is residual HF in the experiment waste, then there should be a dedicated HF residue container. This waste container should be clearly labelled. Residues can be disposed through the normal hazardous waste pickup. The container integrity should be checked. Waste containers should not be overfilled. Ensure that containers are inspected and sturdy before filling.

37. The residue container should be segregated according to compatibility. Similarly any solid waste (e.g. gloves) that may be contaminated with HF, should be segregated and disposed of separately as HF waste. Redundant stock of HF should be disposed. Do not store indefinitely.

Appendix A

HF Spills

38. For spills involving large volumes or concentrated acid, the laboratory should be evacuated immediately. The Laboratory Supervisor, Head of School, Operational Manager and Security shall be contacted. A HAZMAT response team may be required. Special acid gas respirators and protective gas tight suits are required to treat large spills outside a fume cupboard. Do not allow personnel to re-enter the laboratory. Also report the incident immediately. See: Incident notification.

39. Minor HF spills (< 10ml dilute HF) must be cleaned up immediately as spilt material may release vapour. Immediately alert others in the laboratory to the location of the spill. Ensure the correct PPE is worn when cleaning up the spill. Also see HF spill control below for response to larger spills.

40. For minor spills:

- Wear appropriate PPE
- Make sure the spillage is contained. If possible, do not allow HF to enter

drains or confined areas. Contain spills with absorbent boom

- Neutralise HF with calcium hydroxide or lime or HF absorbent – HF Chemizorb*
- Wipe up with paper towel
- Place all material in plastic bag, seal and label " Hazard- Neutralised HF"
- Dispose via Hazardous Waste pickup
- Report the incident. See: Incident notification

41. *Chemizorb Hydrofluoric Acid is a powder mixture consisting of a synthetic copolymer as the absorbent, a calcium salt as the neutraliser and precipitant, and a pH indicator. The neutralisation process releases CO2. When the HF has been neutralised the indicator colour changes from reference orange to yellow. About 150g of Chemizorb HF is required to absorb and neutralise 100ml of HF.

42. Contaminated clothing should be washed with bicarbonate of soda solution. Contaminated equipment or surfaces can be neutralised with calcium hydroxide or slaked lime, before being washed with water.

43. A HF spills kit shall contain at least:-

- The local procedure and/or this procedure. As well as a Safety Data Sheet (Chemwatch) and treatment sheet Appendix C.
- 3 pairs of nitrile gloves
- 1 pair neoprene gauntlet gloves
- Safety Glasses/Goggles
- HF Chemiszorb absorbent and/or neutralising material (calcium hydroxide or lime)
- Plastic bags
- Material for wiping surfaces.

44. The HF spills kits should be visible and located close to where HF work is being undertaken.

HF Spill Control

45. The Plastics and Chemicals Industries Association (PACIA) have developed a Hydrofluoric Acid Code of Practice. This document contains procedures for manufacturers, distributors and uses on the regulation, labelling, first aid and medical treatment for hydrofluoric acid.

46. At ANU, the procedure and equipment required to manage a HF spill

depends primarily on the volume and concentration of HF involved. There are three recommended methods (I, II and III) for cleaning up HF spill. To determine which method to use, refer to the table below.

Method	Volume of HF	Conditions
I	< 5 to 10 mL	Small volumes of any commercially available concentration, unless heated or excessively off-gassing. In which case refer to method II.
II	10 mL to 500 mL	For volumes towards the higher end of the range, or concentrations greater than 40 % HF which are warm or heated, additional precautions may be necessary depending on the spill location (i.e.. outside a fume cupboard).
III	> 500 mL	Where this is a concentrated acid (particularly if spilt outside a fume cupboard) consideration shall be given to allowing the fire brigade to handle the spill. Spills involving winchesters (2.5 L) require the fire brigade HAZMAT unit, as chemical splash suits and SCBA are required.

47. These methods detail extra useful information for your consideration to clean up the spill.

48. **You must avoid contact with the liquid and inhalation of vapour**

Method I – (Small volumes, for up to 10 mL)

Additional Equipment	**Personal** Protective Equipment (minimum)	**Adsorbent** material	**Neutralising agent**
Plastic bucket	Safety glasses Gloves (rubber) Laboratory coat Good footwear	Paper towel	Any readily available calcium salt. e.g. calcium hydroxide, calcium carbonate or HF Chemizorb

49. Make a reasonable amount of a calcium solution in the bucket.

50. Adsorb the HF liquid onto paper towel. Place the paper towel into the bucket containing the calcium solution and leave to soak. Dispose of the paper in normal garbage after rinsing.

51. Wipe the spill area with paper towel soaked in calcium solution. This may need to be repeated several times to ensure complete neutralisation and removal of fluoride.

Method II – (Moderate volume, 10 to 500 mL)

Additional Equipment	**Personal** Protective Equipment (minimum)	**Adsorbent** material	**Neutralising agent**
Plastic bucket Plastic bag	Gloves (rubber) Respirator (full–	Porous plastic, or paper towel mixed	Slaked lime Water or

Plastic dust pan or shovel	face, with acid gas filters or SCBA) Laboratory coat PVC apron Rubber boots	with slaked lime (CaOH, CaO) or gypsum (CaSO4)	HF Chemizorb

52. Make a dam around the spill area with a mixture of slaked lime and plastic beads or fibres.

53. Carefully cover the spill with the plastic/lime mix. Note: If strong effervescence occurs initially use the plain plastic material, then cover the spill with the lime/plastic fibre mix. Allow to react. Mix occasionally. Add more slaked lime until the neutralisation is complete. Scrape up the waste into plastic bags and seal. Dispose of the material in normal garbage.

54. Sprinkle the area with lime. Wipe the spill area with moist paper towel, until the area is clean. Washing the area with water if possible.

Method III – (Large volumes, greater than 500 mL)

55. Consider allowing the Fire Brigade's HAZMAT Unit to clean up the spill, depending on the concentration involved.

Appendix B

First Aid Procedures

56. **PROTECT YOURSELF and call for HELP**. Avoid becoming contaminated or injured yourself. Wear gloves and safety glasses. Also see PPE section Point 15.

- Gloves – any clean chemical resistant gloves will do. Avoid contact with the contaminated skin, clothing and equipment.
- Safety Glasses or goggles to prevent splashes entering the eyes.
- Respirator – avoid the inhalation of Hydrofluoric acid vapours or fumes during rescue in contaminated areas by wearing suitable respiratory protection (an approved air-purifying respirator fitted with acid gas canisters). A respirator should not be required for first aiders treating an injured person away from the accident site after the water washing has commenced.

57. **REMOVE**. Immediately remove the casualty from the contaminated area and remove contaminated clothing with gloved hands.

58. **WASH**. Flush the affected area with lots of water. Use a safety shower/eye wash where possible.

59. **TREAT** as described below

60. **REPORT**, complete an injury/exposure report. See: Incident notification

SKIN – First Aid Treatment

61. **Obtain emergency medical attention immediately.**

62. If a large area is involved – deluge the contaminated areas with water. Otherwise, flush contaminated skin area with gently running water.

63. While washing with water, remove contaminated clothing, footwear and leather goods (e.g. watchbands, belts). Be careful when removing any contaminated eye wear from potential HF exposure.

64. Wearing protective gloves the first aider should gently massage the 2.5% calcium gluconate gel into and around the affected area. If gel is not readily available, continue washing with water.

65. OPTIONAL: If available use Hexafluorine body wash (portable shower) within the first minute of exposure and continue washing until arrival to hospital (more information can be found from www.prevor.com).

66. Remove to hospital by ambulance accompanied by the Safety Data Sheet (Chemwatch) and treatment sheet Appendix C. Continue application of gel during transport.

67. Continue massaging the gel in with fingers to the affected area for 15 minutes after the pain has subsided. Wear clean gloves while applying gel. This may be required for several hours, but continue massaging with the gel so long as there is improvement in the symptoms.

EYES – First Aid Treatment

68. **Obtain emergency medical attention immediately.**

69. NOTE: do not use any of the skin treatment preparations for burns of the eye.

70. Using the eyewash station – Irrigate with copious quantities of isotonic saline or water, holding the eyelid(s) open. Take care not to rinse contaminated water into a non- affected eye and removal of contaminated eye wear.

71. OPTIONAL: If available use Hexafluorine eyewash within the first minute of exposure and continue washing until arrival to hospital (more information can be found from www.prevor.com).

72. Continue irrigation for at least 15 minutes (by the clock).

73. Remove to hospital by ambulance accompanied by the Safety Data Sheet (Chemwatch) and treatment sheet Appendix C.

74. Continue eye irrigation during transport to hospital.

INHALATION - First Aid Treatment

75. **Obtain emergency medical attention immediately.**

76. Remove to fresh air.

77. Apply artificial respiration and oxygen if necessary.

78. Remove to hospital by ambulance accompanied by the Safety Data Sheet (Chemwatch) and treatment sheet Appendix C.

79. Continue observation for 48 hours because of the dangers of pulmonary oedema.

INGESTION - First Aid Treatment

80. **Obtain emergency medical attention immediately.**

81. Do not give anything by mouth if victim is losing consciousness or is unconscious or convulsing.

82. **Do not induce vomiting.**

83. Give copious quantities of milk, water drinks, milk of magnesia, Mylanta® or effervescent calcium gluconate tablets dissolved in water (in spite of vomiting). If vomiting occurs naturally, have victim lean forward to reduce risk of aspiration. Rinse mouth of victim thoroughly with water and spit out rinse water.

84. Remove to hospital by ambulance accompanied by the Safety Data Sheet (Chemwatch) and treatment sheet Appendix C.

Appendix C

85. This sheet should accompany the affected person to hospital

86. Advice to a Doctor for Dealing with Hydrofluoric Acid Burns and Exposure

87. Hydrogen fluoride in aqueous solution is usually referred to as hydrofluoric acid

88. The damage caused by exposure to this product is far more extensive than that caused by hydrochloric acid and other acids. First aid and medical treatment appropriate to simple acids (e.g. Hydrochloric acid) is not beneficial with hydrofluoric acid burns. Hydrofluoric acid penetrates rapidly and deeply below fat

layers binding and depleting tissue calcium. Failure to commence the correct medical treatment promptly may be fatal.

89. There is a **major risk of systemic toxicity** following inhalation, ingestion or skin burns. Calcium depletion and electrolyte disorders **may be fatal**. A skin burn involving more than 1 % of body area with 50 % or more concentration of hydrofluoric acid or more than 5 % of body area with any lesser concentrations may be associated with systemic effects. Treatment with intravenous calcium gluconate should commence immediately.

90. Intensive care unit facilities are likely to be needed. Serum calcium and magnesium determinations should be performed frequently and correction of electrolyte balance may be necessary. EKGs should be monitored routinely for prolonged Q- T interval or bradycardia. Hepatic and renal function should be monitored. IV corticosteroids may be necessary.

91. **Inhalation** may lead to chemical pneumonitis, haemorrhagic pulmonary oedema or laryngeal oedema and may be fatal. Be prepared to intubate or perform a tracheotomy. The use of nebulised calcium gluconate in a 2.5 % solution should be considered.

92. **Skin burns** may become necrotic and gangrenous and damaged area may spread. Where available use Hexafluorine® product for flushing. Infiltration of calcium gluconate into the surrounding tissue may be required for severe burns; this can be performed by the injection of 5 % calcium gluconate solution. Injection should be performed with care on the hands, feet and face.

93. For fingers and toes and less severe burns, continue the application of 2.5 % calcium gluconate gel four to six times daily for up to three to four days. Wear clean gloves while applying gel. If calcium gluconate solution is injected into the fingers or toes great care should be exercised and no more than 0.5 ml should be used. Pain not relieved by use of gel is best managed by intra-arterial infusion of calcium gluconate solution in a unit that is experienced in the technique. Surgical debridement of affected area may be necessary in larger burns to control hypocalcaemia. Delayed pulmonary oedema is likely with burns to the face or neck. Local anaesthesia is contra-indicated, so that the splitting of finger and toe nails should be performed under general anaesthesia.

94. Following contact of this product with **the eyes**, ensure first aid treatment has been carried out. Instil 1 % calcium gluconate solution every two to three hours for as long as considered necessary. Topical anaesthetic and corticosteroid drops may be useful. An ophthalmologist should always be consulted, as severe corneal damage is possible. Long term monitoring may be necessary.

95. Further information about the treatment of hydrofluoric acid burns can be obtained from the National Poisons Information Centre on 13 1126.

96. Reference: Modified extract from Plastics and Chemicals Industries Association, Hydrofluoric acid, Code of Practice, June 1997.

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