

University College Dublin



***Guide To The Safe Use Of
Hydrofluoric Acid***

Rev 1. Issued December 2014

University SIRC Office

University College Dublin Guide To The Safe Use Of HF

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Revision History

Rev 0. Issued August 2007.

Rev 1. Issued December 2014. Minor changes made.

1. Introduction

Hydrofluoric acid (HF) is a colourless solution of hydrogen fluoride dissolved in water. Above approximately 60% solution HF fumes. HF is of particular concern because whilst it can cause severe burns like many concentrated acids, its fluoride ions readily penetrate the skin and can cause systemic poisoning. These fluoride ions bind to primarily the body's calcium and magnesium ions leading to electrolyte imbalance, decalcification of bone, cardiac arrhythmia and death. It has been estimated that death due to HF poisoning can occur if as little as 2.5% of the body comes into contact with concentrated acid (the palm of the hand represents approximately 1% of body surface area). If concentrated HF vapours are inhaled then death can occur very quickly.

At concentrations above 50% HF exposure causes immediate destruction of living tissue and severe burns and pain. Systemic fluoride poisoning may also result. Death may be caused by the burns or the systemic poisoning.

At concentration between 20% and 50% contact with HF may not cause immediate pain and exposure may go unnoticed but there is still the potential for severe burns and systemic poisoning. Such signs of the exposure may not become readily identifiable for up to eight hours.

At less than 20% concentration burns may not become apparent for 24 hours.

The inhalation of HF vapours may cause almost immediate death at high concentrations, and severe lung damage and pulmonary oedema at lower concentrations. As with skin exposure symptoms of exposure to low concentrations may not become apparent for a number of hours.

As with all acids even minor eye exposure may cause permanent damage and loss of the eye or its sight.

Long-term or chronic exposure to HF may result in fluorosis, a condition characterized by weight loss, bone embrittlement, anaemia and general ill health.

It is therefore essential that HF of any concentration is not used or handled in any University facility unless absolutely necessary. Every effort must be made to identify a less hazardous agent for use.

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In the event that HF must be used then appropriate management systems and safe systems of work must be put in place for its purchase, storage, use and disposal. The only effective way to prevent HF injuries is through the implementation of a proper safety management system.

2. HF Fatalities

Between 1984 and 1994 Hydrofluoric Acid (HF) accounted for at least nine deaths in the United States. Four of these deaths were the result of skin contact with concentrated HF whilst the remaining five cases involved both skin contact and inhalation. Of these nine fatalities three occurred within 30 minutes of exposure; five occurred within six hours of exposure; and the final person died 15 hours after exposure. In five of these fatalities calcium gluconate was administered to the victims but failed to prevent death, although from the information available it did appear to delay it somewhat.

Blodgett DW, Suruda AJ and Crouch BI (2001). Fatal unintentional occupational poisonings by hydrofluoric acid in the U.S. Am. J. Ind. Med., 40(2); 215 - 20.

In the mid 1990's a laboratory technician in Australia died following exposure to HF. He was using HF to perform an acid digestion on rock samples in a fume hood when he spilled approximately 230mls of 70% HF onto both of his thighs. He died 15 days after the incident but not before the amputation of his right leg in an effort to treat his injuries.

Muriale. L., Lee, E., Genovese, J. and Trend, S. (1996). Fatality due to acute fluoride poisoning following dermal contact with hydrofluoric acid in a palynology laboratory. Annals Occ. Hygiene 40(6); 705 - 710.

Again it should be borne in mind that death due to HF poisoning can occur if as little as 2.5% of the body comes into contact with the concentrated acid.

3. Storage Considerations

1. Always store HF in a clearly labelled container.
2. Always ensure that there is secondary containment of the primary container, i.e. a container within a container.
3. Never store HF in glass or metal containers. Always store HF in polyethylene, polypropylene or Teflon containers. Be aware that prolonged storage of HF can cause plastic materials to become brittle.
4. Ensure that concentrated (>50%) HF is always stored in a secure chemicals cabinet or laboratory.
5. Storage of HF in fume hoods should be avoided where possible. Otherwise store small amounts of weak solutions in sealed containers wherever possible.
6. Store HF containers as close to the ground as possible away from pedestrian routes.
7. Store HF away from incompatible chemicals, e.g. metals, organic compounds. If in doubt as to the compatibility of chemicals refer to the *Chemical Reactivity Worksheet* (free download – Google for link).
8. Store HF only in HF designated laboratories. Do not store HF in a central chemical stores for longer than it takes for the delivery to be processed.
9. Ensure that a HF spill kit; first aid kit, an SDS and this document are readily available where HF is being stored and in a conveniently located secondary location where no HF is being stored.

4. Personal Protective Equipment (PPE)

When working with any concentration of HF suitable personal protective equipment (PPE) must be worn. In so far as is possible there should be no exposed / uncovered skin on a HF user. The use of PPE is to provide a last line of defence against HF exposure. PPE is not a substitute for safe systems of work.

Gloves

1. Gloves should always be considered as offering only a limited simple barrier protection and no protection against long term contact with HF. Assume a very short breakthrough time for all gloves.
2. Once contaminated gloves should be removed immediately and the hands washed with running water.
3. Before use all gloves should be inspected for damage. Damaged gloves should be discarded.
4. Two pairs of gloves should always be worn when working with HF. An inner disposable pair made from a suitable material such as nitrile (but not latex) should be worn under an outer heavy duty pair. The nature of the outer pair will depend on the concentration of the acid being used and the nature of work process. The outer glove pair should always be constructed of a heavy duty material which reaches to at least the mid forearms and where possible the elbows. Materials such as PVC, Neoprene and Natural Rubber are suitable for outer gloves.
5. When the outer gloves become contaminated they should be immediately removed and soaked in a caustic solution before being worn again.
6. The outer gloves should be washed down with clean water before removing them.
7. The answering of telephones, the using the computers, etc. should be avoided when working with HF.
8. Contaminated gloves should be washed in a caustic solution before disposal in an appropriate manner.

Protective Clothing

1. Protective clothing is designed to offer a simple physical barrier to HF contamination. Assume a very limited breakthrough time for all protective clothing.
2. Always wear a closed full length laboratory coat.
3. When handling concentrated acid also wear a chemical apron over the laboratory coat made from a suitable HF resistant material, e.g. PVV, Natural Rubber, etc.

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4. Do not wear shorts, skirts or open toed shoes when working with any concentrations of HF.
5. If desired a full body acid suit may be worn in lieu of a lab coat.

Footwear

1. Do not wear open toed sandals when HF of any concentration is being handled.
2. When concentrated HF is being used then rubber boots or similar should be worn.

Face / Eye Protection

1. Always wear safety glasses or goggles when working with any concentration of HF.
2. When working with concentrated HF wear a full face shield over the safety glasses / goggles.

Respiratory Protection

1. The use of respiratory protection when working with HF under normal circumstances is prohibited. The use of HF should never generate the need to wear respiratory protection. The need to wear respiratory protection under normal circumstances of use indicates a failure of safety management.
2. When dealing with HF spillages outside of a fume hood a full face mask with inorganic / acid gas filters should be worn – see Section 6 below.

Contaminated PPE and all normal clothing should be removed immediately and washed in a caustic solution before being examined for damage. Damaged PPE must be disposed of immediately. Face masks must be disposed of after dealing with a spillage.

5. Hydrofluoric Acid First Aid

It takes two people to effect a first aid response to a HF exposure. Never work with HF alone, always have a 'buddy' in the lab with you.

Skin Exposure

Symptoms Of Skin Exposure

- Skin whitening
- Severe pain
- For concentration of acid less than 50% it can take up to 24 hours for the symptoms to manifest.

Treatment Of Skin Exposure

1. Raise the alarm by calling 7999 on an internal telephone and requesting an ambulance for a HF burn victim; or by breaking a red wall mounted fire alarm break glass unit if you cannot get to a telephone.
2. Immediately remove the victim away from the source of contamination – do not place yourself at risk when doing this. Ensure that you are wearing all appropriate PPE. Do not attempt to render any assistance if you are not wearing the appropriate personal protective equipment or if there is a risk that HF vapours are present.
3. Run clean water over the wound for at least 5 minutes. With a gloved hand wash the affected area with the running water. For large body exposures or significant exposure to clothing place the person under an emergency shower.
4. If HF has gotten under the fingers nails scrub with a small nail brush.
5. Help the victim to remove all contaminated clothing, jewellery and protective equipment. Remove eye / face protection last if necessary. Place all contaminated material into a safe area for future treatment e.g. a bag or a fume hood.
6. After the wound has been washed for at least five minutes quickly dry the affected area and apply calcium gluconate gel liberally using a clean gloved hand. Continuously massage the gel into the wound. If a callus develops over the site of exposure remove the callus and continue to massage the gel in. Reapply new gel every 10 minutes.
7. If HF has gotten under the fingernails then scrub with gel.
8. If victim is conscious administer a source of calcium carbonate e.g. milk of magnesia
9. If calcium gluconate gel is not available then continue to wash the wound with clean running water until the emergency services arrive.

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10. If possible note the time of the incident, the treatment administered and the number of times the gel was applied. Provide all this information to the emergency services.
11. Ensure that the person is accompanied to hospital by an SDS for HF, this document and a HF first aid kit.

Eye Exposure

Symptoms Of Eye Exposure

- Severe eye pain
- Eye spasms
- Reddening of eye

Treatment Of Eye Exposure

1. Raise the alarm by calling 7999 on an internal telephone and requesting an ambulance for a HF burn victim; or by breaking a red wall mounted fire alarm break glass unit if you cannot get to a telephone.
2. Immediately remove the victim away from the source of contamination – do not place yourself at risk when doing this. Ensure that you are wearing all appropriate PPE. Do not attempt to render any assistance if you are not wearing the appropriate personal protective equipment or if there is a risk that HF vapours are present.
3. Flush the eye with clean running water for at least five minutes.
4. For large body exposures or significant exposure to clothing place the person under an emergency shower.
5. Do not use calcium gluconate gel in the eyes.
6. Help the victim to remove all contaminated clothing, jewellery and protective equipment. Place all contaminated material into a safe area for future treatment e.g. a closed bag or a fume hood.
7. If available a sterile calcium gluconate solution may be used to flush out the eye after washing with water.
8. If victim is conscious administer a source of calcium carbonate e.g. milk of magnesia
9. Continue to wash the eye with water until the emergency services arrive.
10. If possible note the time of the incident and the treatment administered. Provide all this information to the emergency services.
11. Ensure that the person is accompanied to hospital by an SDS for HF, this document and a HF first aid kit.

Inhalation

Symptoms Of Inhalation

- Breathing difficulties
- Muscle spasms
- Convulsions
- Coughing
- Choking
- For mild exposure symptoms may not appear for 24 hours.

Treatment Of Inhalation

1. Raise the alarm by calling 7999 on an internal telephone and requesting an ambulance for a HF burn victim; or by breaking a red wall mounted fire alarm break glass unit if you cannot get to a telephone.
2. Immediately remove the victim away from the source of contamination to a clean air area – do not place yourself at risk when doing this. Ensure that you are wearing all appropriate PPE. Do not attempt to render any assistance if you are not wearing the appropriate personal protective equipment or if there is a risk that HF vapours are present. Remember, if the victim has been exposed to HF vapours there is a good chance that you may be as well.
3. If possible place the victim in an emergency shower.
4. Help the victim to remove all contaminated clothing, jewellery and protective equipment. Remove eye / face protection last if necessary. Place all contaminated material into a safe area for future treatment e.g. a closed bag or a fume hood.
5. If available administer oxygen.
6. If victim is conscious administer a source of calcium carbonate e.g. milk of magnesia
7. If the victim falls unconscious give mouth to mouth resuscitation only after washing the mouth and nose area with clean water and using a resuscitation mask.
8. If possible note the time of the incident and the treatment administered. Provide all this information to the emergency services.
9. Ensure that the person is accompanied to hospital by an SDS for HF, this document and a HF first aid kit.

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Ingestion

Symptoms Of Ingestion

- Convulsions
- Nausea
- Vomiting
- Diarrhoea
- Abdominal pain

Treatment Of Ingestion

1. Raise the alarm by calling 7999 on an internal telephone and requesting an ambulance for a HF burn victim; or by breaking a red wall mounted fire alarm break glass unit if you cannot get to a telephone.
2. Immediately remove the victim away from the source of contamination – do not place yourself at risk when doing this. Ensure that you are wearing all appropriate PPE. Do not attempt to render any assistance if you are not wearing the appropriate personal protective equipment or if there is a risk that HF vapours are present.
3. Flush the mouth with clean running water and encourage the victim to drink water in order to dilute the acid.
4. For large body exposures or significant exposure to clothing place the person under an emergency shower.
5. Help the victim to remove all contaminated clothing, jewellery and protective equipment. Remove eye / face protection last if necessary. Place all contaminated material into a safe area for future treatment e.g. a closed bag or a fume hood.
6. Continue to rinse the mouth and give water to drink until the emergency services arrive.
7. If victim is conscious administer a source of calcium carbonate e.g. milk of magnesia
8. Do not induce vomiting.
9. Ensure that the person is accompanied to hospital by an SDS for HF, this document and a HF first aid kit.

Immediate medical attention must be sought for all known or suspected HF exposures, no matter how small. All persons working with HF must be aware of the symptoms of exposure and if they experience any of these symptoms they must seek immediate medical attention. All HF exposures no matter how small must be reported to the University SIRC Office.

6. Hydrofluoric Acid Spill Response

It takes two people to effect a response to a HF spillage. Never work with HF alone, always have a 'buddy' in the lab with you.

Spillage Inside A Fume Hood

1. Immediately close the fume hood sash
2. Inform all other lab users
3. Evacuate all unnecessary personnel from the lab
4. Open fume hood sash as little as possible and slowly add a caustic solution to the spill, e.g. calcium carbonate solution.
5. Ensure that the caustic solution is added slowly so that the neutralising reaction does not proceed too quickly.
6. Use litmus paper or similar to test spillage. When the pH is greater than 7 then all acid has been neutralised.
7. Dry up spillage using paper towels or absorbent pads and dispose of waste appropriately **or** wash neutralised spillage down the sink if it is a small amount.
8. Wipe / wash down the fume hood working area with a caustic solution and use litmus paper or similar to ensure that all surfaces are at least pH 7.

Spillage Outside A Fume Hood (<50% concentration)

1. Immediately evacuate the lab.
2. Raise the alarm by calling 7999 on an internal telephone and reporting a HF spillage.
3. Place a warning sign on the outside of the lab door restricting access.
4. If the amount spilled is considered to be small enough to deal with and the concentration is less than 50% then the spillage may be treated by suitably trained lab personnel.
5. At least two persons must treat the spillage.
6. Persons treating spillage should don an acid resistant suit with hood, rubber / pvc gloves, rubber / pvc boots and a full face mask rated for inorganic / acid gases whilst outside of the contaminated lab. Before entering the lab co-workers should check to ensure that there is no exposed skin on the person treating the spillage.
7. Ensure that the lab door is closed at all times but that persons inside the lab are visible during the treatment of the spillage.
8. Do not touch or walk in spillage.
9. The spillage should be contained using booms or absorbent pads if necessary.
10. A caustic solution should be added to the spillage slowly.

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11. Ensure that the caustic solution is added slowly so that the neutralising reaction does not proceed too quickly.
12. Use litmus paper or similar to test spillage. When the pH is greater than 7 then all acid has been neutralised.
13. Dry up spillage using paper towels or absorbent pads.
14. All resultant waste should be disposed of appropriately.
15. All visible surfaces in the lab should be washed down with a caustic solution and tested with litmus paper or similar to ensure that the pH is at least 7 in all areas.
16. The persons treating the spillage should wipe themselves down using a caustic solution before removing their PPE or they should stand under an emergency shower for a full wash down.

Spillage Outside A Fume Hood (>50% concentration)

1. Immediately evacuate the lab.
2. Raise the alarm by calling 7999 on an internal telephone and reporting a HF spillage or by breaking a red wall mounted fire alarm break glass unit if you cannot get to a telephone.
3. Place a warning sign on the outside of the lab door restricting access.
4. All spillages of >50% HF will be dealt with by the emergency services or specialist contractors.

All spillages of HF no matter how small must be reported to the University SIRC Office.

7. Waste Disposal

For liquid wastes:

1. Treat liquid wastes with a caustic agent in a suitable container i.e. not glass or metal.
2. Ensure pH is at least seven.
3. Dispose of using a specialist contractor.

For solid wastes:

1. Soak material in a caustic solution or wash down material with a caustic solution.
2. Ensure pH of solution is at least 7.
3. Dispose of wastes using a specialist contractor.

8. HF Lab Safety Equipment

First Aid

To be located in every HF lab and in at least one other readily accessible area known to chemical users but where HF is not used

- Standard first aid box
- HF first aid kit to include calcium gluconate gel (check use by date regularly) and solutions
- HF resistant gloves
- Milk of magnesia or similar
- Eye wash bottles
- Nail brush
- This document

HF Spill Kit

To be located in every HF lab and in at least one other readily accessible area where HF is not used

- Chemical spill kit
- Source of caustic agent
- Two full sets of PPE to include gloves, boots, acid suit and face masks
- This document
- Signage warning of HF spillage

Paperwork Folder

To be located in every HF lab and in at least one other readily accessible area where HF is not used

- This document
- HF SDS
- All relevant procedures and risk assessments

Emergency Shower

To be located in lab where concentrated HF is in use or immediately adjacent.

Clean Running Water

All labs where HF is in use must have a guaranteed supply of clean running water.

9. Hydrofluoric Acid Fume Hoods

- All work with HF must be carried out in a fume hood.
- Where concentrated HF is in use this fume hood should be restricted for HF use only.
- If fume hoods are shared between users then the hood must be wiped down with a caustic solution after use and the pH checked with litmus paper or similar before being used again.
- Fume hoods in which HF at a concentration of more than 50% is used must be designed for use with HF and have a washdown facility; a non glass sash and no exposed metal components.
- Fume hoods must be washed with a caustic solution before any maintenance is carried out and maintenance staff must be informed that HF is in use in the fume hood.
- Fume hoods must have a lip or raised edge to prevent spilled liquids running out of the hood.
- Ensure secondary containment in the fume hood if possible.
- Do not sit at the fume hood when working with concentrated HF.
- Persons using HF in a fume hood must ensure good fume hood practices:
 - Every fume hood must be checked on an annual basis to ensure that it is functioning correctly.
 - Material held in a hood should be located towards the rear of the working surface. Materials held at the front of the working surface can reduce the efficiency of the hood.
 - The sash should be kept as low as possible when the hood is in use and should be completely closed when the hood is unattended.
 - Arm movements in the hood should be kept to a minimum.
 - Air extracts should not be blocked or covered.
 - Minimise air flow across the front of the hood by ensuring any adjacent doors and windows are kept closed when the hood is in use and that persons do not walk in front of the hood when it is being used.
 - Clean all chemical residues and spillages from the hood immediately.

10. Working Safely With HF

- Replace HF with a less hazardous chemical whenever possible.
- Use the lowest concentration possible.
- Assume all concentrations above 50% will fume.
- Do not heat HF as this increases the amount of fumes being given off.
- Have a written procedure in place for every process that HF is used in.
- Have a written risk assessment for every process HF is used in (refer to *UCD Chemical Safety Manual* (www.ucd.ie/sirc) for information on chemical risk assessment).
- Ensure that all lab users are fully trained in the safe use of HF and the response to be taken in an emergency.
- Every HF user should be aware of the signs of exposure and the response to take.
- HF must always be used in a suitable fume hood.
- Do not sit at the fume hood when working with concentrated HF.
- Ensure secondary containment in the fume hood if possible e.g. by placing containers in trays.
- Always wear the appropriate PPE.
- Remove contaminated PPE immediately.
- Ensure safe storage of HF.
- In so far as possible dedicate specific labs for HF use only.
- Ensure adequate warning signage is displayed outside of the lab.
- Ensure that all the necessary first aid and emergency response equipment is held in the area that HF is used and in a readily accessible second area.
- Ensure that calcium gluconate gel is in date and has not expired.
- In very hot weather calcium gluconate gel may require storage in a fridge or a cool environment.
- Hold as little HF in the lab as possible. Do not bulk buy.
- Treat all HF wastes immediately to render them less hazardous.
- Hold no more than one day's supply of HF in the fume hood.
- Wash your hands after every HF use.
- In so far as practicable cover all exposed skin when using HF.
- Cover all cuts and abrasions with a waterproof dressing when using HF.
- Users of HF should hold a tube of calcium gluconate gel in their homes to treat burns.

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- There should be no unauthorised access to HF labs – cleaning and maintenance staff should only access the lab with the prior approval of the lab manager and should be accompanied where necessary.
- Persons using HF should if possible be visible from outside of the lab.
- Lone working with HF is prohibited. Always work with a ‘buddy’. It takes at least two people to respond to a HF spillage or exposure.
- Medical attention must be sought for all known and suspected exposures. Persons seeking medical attention should bring this document, an SDS and if possible a HF first aid kit.

Appendix 1. Advice To Medical Practitioners

Skin Exposure

For dilute solutions of hydrofluoric acid, calcium gluconate gel applied topically will often relieve the pain and reduce the injury. Exposure of subungual tissue may require the removal of the nail in order to treat adequately. Continued pain and destruction may be treated by subcutaneous administration of calcium gluconate. Arterial calcium perfusions have been used. Systemic fluoride poisoning can result from dermal exposure, particularly with concentrated and extensive exposures. The treatment described above needs to be considered. Early removal of skin may need to be considered in cases of extensive skin damage and refractory hypocalcaemia. Continue application of the calcium gluconate gel to the skin for 15 minutes after the pain has completely subsided. This may require several hours but, providing improvement in the lesions and symptoms continues, massaging with the gel should be continued. In cases where a thick necrotic coagulum has formed, it may act as a barrier and prevent the penetration of the gel. This will be indicated by lack of improvement. In these cases, the necrotic tissue should be excised and the gel massaged into the base of the burn, taking usual aseptic precautions. If the burn fails to respond to the calcium gluconate gel, injection of a sterile 10 per cent solution of calcium gluconate into and under the burn should be considered. Relief of pain is an indication that sufficient solution has been injected. Because of this, an anaesthetic should not be given except in situations where the skin is tightly adherent to the underlying tissues. In these cases, a general anaesthetic should be given as local anaesthesia is contra-indicated. Once symptoms have subsided, the burn should be covered with a sterile dressing. If the pain recurs, for example, after burn from dilute acid, the patient should return for further symptomatic treatment. In cases of large areas of skin contamination, for example, greater than 65 sq cm, six effervescent tablets, each containing 400 mg calcium and 20 mg ascorbic acid, should be given in water by mouth every two hours until the patient is admitted to hospital. Serum calcium and/or magnesium may have to be replaced intravenously if indicated by clinical signs or by electrolyte monitoring. Systemic administration is by the slow intravenous route.

Eyes

Irrigation with water and isotonic saline and obtain an ophthalmologic consultation.

Inhalation

Acute respiratory failure may develop requiring airway support, 100 per cent oxygen and positive end expiratory pressure treatment for pulmonary oedema. In addition, treatments and monitoring for systemic fluoride poisoning described above may be required.

Ingestion

Nasogastric suction with calcium gluconate solution may reduce systemic fluoride toxicity. The possibility of chemical burns to the gastrointestinal tract needs to be kept in mind. Acute systemic fluoride poisoning may cause profound hypocalcaemia (hypomagnesemia) requiring intravenous calcium (magnesium) therapy. Electrocardiogram results and blood calcium/magnesium need to be monitored in acute systemic fluoride poisoning.

Contact:

Poisons Information Centre,
Beaumont Hospital,
Dublin 9.
Telephone 01-837 9964 / 809 2566

Additional Resource

<http://www.chem.purdue.edu/chemsafety/Equip/HFfacts11.pdf>