

Chemical Safety Guidance Series

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Hydrofluoric Acid: User Guidance

Occupational Health and Safety Service
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UNIVERSITY OF
CAMBRIDGE

Hydrofluoric Acid (HF): User Guidance



1 What is HF?

In the chemical context the abbreviation 'HF' could stand for two things, 'hydrogen fluoride gas' and/or 'hydrofluoric acid', where hydrofluoric acid is a solution of hydrogen fluoride gas in water. Hydrofluoric acid is available in a range of concentrations (typically 40 to 70%) dependent upon how much gas is dissolved in a given volume of water.

Most commonly in the laboratory environment, 'HF' is taken to refer to hydrofluoric acid.

2 The Properties of 'HF'

Hydrogen fluoride gas is a colourless fuming gas which liquefies at 19°C and readily dissolves in water. It is very toxic by inhalation, ingestion or absorption. The liquefied gas causes severe painful burns on any tissue it touches. The vapour severely irritates the eyes and respiratory system, and can also burn the skin.

Hydrofluoric acid is a colourless liquid, both in dilute and in concentrated forms. In concentrations above 40 to 50% (dependent upon room temperature) the acid gives off significant quantities of corrosive fumes (HF gas) which have a pungent odour similar to chlorine. Unless heated, solutions of less than 40% concentration do not give off significant vapour concentrations. 'Concentrated HF' acid may be between 40 and 70%. The liquid is corrosive, can dissolve glass, corrode most metals, and destroy clothing and human tissue.

It should be remembered that it is the **systemic fluoride ion toxicity that represents the greatest hazard**, rather than its classical acid properties!

Containers of HF now carry the following GHS hazard warning symbols (black pictogram in a red diamond) and safety statements.



Toxic



Corrosive

Signal word: '**Danger**'

Hazard statement(s):

H300 Fatal if swallowed.

H310 Fatal in contact with skin.

H314 Causes severe skin burns and eye damage*.

H330 Fatal if inhaled.

Precautionary statement(s):

P260 Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.

P264 Wash hands thoroughly after handling.

P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.

P284 Wear respiratory protection (RPE).

P301 + P310 IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

P302 + P350 IF ON SKIN: Gently wash with plenty of soap and water.

3 Effects of Exposure

3.1 Absorption:

HF is easily and rapidly absorbed through the skin.

Absorption of HF through the skin or eyes causes severe burns and damage to tissue, bones and potentially internal organs. HF is unique among the inorganic acids in its ability to easily penetrate intact skin.

Burns from concentrated solutions (40 to 70%) are severe and extremely painful.

The initial signs are redness, oedema and blistering, as well as internal systemic damage.

Burns from more dilute solutions do not necessarily cause pain immediately. However dilute solutions can still penetrate deeply into the body causing delayed injury and symptoms due **the systemic toxicity of the fluoride ion** and the resultant cellular destruction.

A burn from a 20 – 40% HF may take up to eight hours to become apparent.

A burn from HF below 20% may take up to twenty four hours to become apparent.

There could be a significant delay in realising that you have an HF burn !

The severity and rapidity of onset of symptoms depends on the, concentration, quantity, area of the body covered, duration of exposure, and the penetrability of the exposed tissue.

HF can cause extensive damage to the eyes*.

***The University strongly recommends that DipHex Hexafluorine® is readily available for immediate use in the event of an HF splash to the eye**

A hydrofluoric acid splash in the eye may make the cornea opaque and blindness can result from untreated or severe exposure.

Burns to the fingers and nail beds may leave the overlying nail intact whilst destroying the underlying tissue and bones.

HF diffuses through the tissues and disassociates into the hydrogen ion and the fluoride ion. The fluoride ion affects tissue integrity and metabolism by, liquefaction necrosis, bone decalcification and destruction (i.e. it removes calcium from bones). HF binds calcium and magnesium to form insoluble salts, which interfere with cellular metabolism, causing cell necrosis and death. The loss of calcium from the blood results in loss of calcium from the bones to try to equilibrate the decreased serum calcium. This may cause a delayed fatal event as calcium is important for muscles, including the cardiac muscle. **Without calcium many metabolic pathways break down.**

HF is a systemic poison and if the HF is not rapidly neutralised and the fluoride ion bound, tissue destruction may continue for several days and result in limb loss or death. If burns are left untreated potentially life-threatening metabolic imbalances can develop. This can be true both for burns from concentrated solutions and from burns caused by dilute solutions.

3.2 Inhalation:

Inhalation of small quantities of HF vapour (gas) can cause irreversible damage, having a serious effect on the mucous membranes. Symptoms may include coughing, choking, chest tightness, chills, fever and cyanosis. Pulmonary oedema may occur 24 hours or so later.

3.3 Ingestion:

Ingestion of HF causes severe burns to the mouth, oesophagus and stomach and gives rise to severe systemic effects. Ingestion of small quantities of HF has resulted in death.

Users must be aware of these exposure effects before work commences, and must seek advice and treatment if they suspect that they could have had HF on their skin.

4 Case Studies and Examples:

A worker who was dealing with a solution containing 5% HF had gloves that contained a pinhole. When she consulted her doctor later for pain in her finger a non-specific burn ointment was applied. After several days the damage had developed to the extent that when, still in pain, she finally presented at hospital it was necessary to amputate her finger, due to the serious and irreversible damage that the acid had done to the bone.

In 1996 a New York City sanitation worker died after inhaling HF fumes; a second worker was hospitalised after coming to his aid. A plastic container with 70% HF was disposed of improperly. The container had burst when the waste was being compacted in the lorry.

A laboratory technician died after an incident in which he accidentally spilt between 100 and 230 ml of 70% HF onto his legs. He sustained burns to 9% of his body area, despite attempting to wash the acid off. He took refuge in a swimming pool from which he was rescued by an ambulance approximately 40 minutes later. He was hypothermic and hypocalcaemic on admission to hospital and died after 15 days, of multiple organ failure.

An earlier fatality in 1980 resulted from burns to only 2.5% of the body.

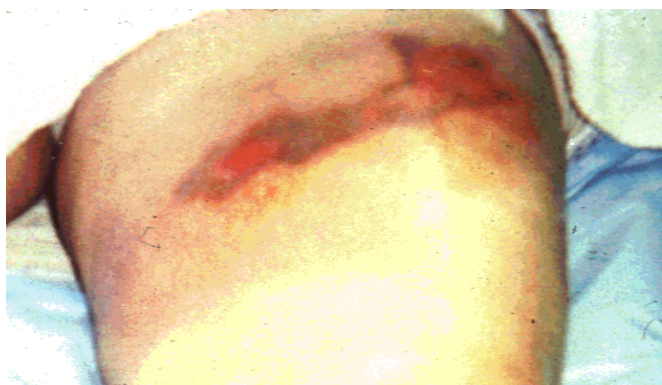
Grade 1 Hydrofluoric acid burns of the fingertips from leaking gloves. The patient has severe pain (maximum middle digit) with only minimal redness of the nail beds:



Grade 3 Hydrofluoric acid burns of the fingertips from leaking gloves. Note how the nail-bed and tip of the fingers have been severely injured, but the nails show no damage:



Hydrofluoric acid burn to thigh from a spill on a bench.



5 Statutory Inhalation Exposure Limits for HF

The UK Workplace Exposure Limits (WELs) are for inhalation of HF vapour/gas. The short term exposure limit (15 minutes) for hydrofluoric acid fumes is 2.5 mg m⁻³, (3 ppm), and the long term limit exposure limit (8hrs) is 1.5 mg m⁻³ (1.8 ppm).

In view of the serious health effects that have already been described, every effort must be made to avoid ALL exposure to HF by all users, workers, visitors, cleaners, first aiders or waste contractors etc.

The odour threshold at which many, but not all, people can smell HF gas is quoted as a very broad range from 0.042ppm up to 3ppm. Therefore in an emergency the absence of an 'HF smell' alone must not be taken to be indicative of a complete lack of HF gas, **an HF gas monitor would be required to make this assessment.** (note: HF gas is lighter than air)

6 User Responsibilities

Users have legal and moral obligations for the safety of themselves and others affected by their actions.

All users must have done, or read and understood, a Risk Assessment.

The risk assessment must take account of the substances being used, their intrinsic potential for causing harm, the quantities, the concentrations and what they are doing with them i.e. the process being undertaken. **It should also include a clear procedure to deal with spillages.**

The risk assessment should identify the relevant control measures to minimise the probability of anyone being harmed by the work. **Users are also responsible for ensuring that control measures are in place and are used.** For hydrofluoric acid these will be principally measures to reduce the possibility of exposure by **inhalation and/or eye or skin contact.**

7 Control Measures

Control measures are likely to include:

- **Buy the smallest amount of the most dilute hydrofluoric acid that the work will permit.** Any money 'saved' on bulk quantities is insignificant should a spillage occur.
- **Use the smallest amount of the lowest concentration possible**
- **Work at room temperature wherever possible**
- **DO NOT WORK ALONE; always have a 'buddy' within sight and sound**
- **Do NOT work with HF out of 'normal hours' without carrying out a 'Working Out-of-Hours' risk assessment (see Safety Office website) and explicit permission from your department in writing**
- **Work in a dedicated labelled fume cupboard and STAND, do not sit. Note:**
 - o If handling anything other than very small amounts of hydrofluoric acid the fume cupboard could require
 - A specialised glass free sash to avoid etching
 - A scrubber to remove HF from the exhaust air
 - A wash down facility to clean the inside of the fume cupboard
- **Use Personal Protective Equipment (see Appendix A)**
 - o Safety glasses, visors or goggles to minimise the possibility of eye contact
 - o Gloves that are 'impervious' to HF (see note below)
 - o Protective clothing
 - Laboratory coats
 - Aprons where concentrated solutions are used or decanted
- **Use appropriate plastic spill trays to contain liquid spills**
- **Have washing facilities: shower hose AND eye wash bottles**
- **Have 'in date' calcium gluconate gel, BOTH inside and outside the room, for treatment of HF burns. (It may be needed outside if the room is contaminated.)**
 - o **And /or DipHex Hexafluorine® solution** if required (see Appendix B).

- **Have a specialist HF absorbing / neutralising agent for spillage response i.e.**
 - o MERCK's Chemisorb® HF; an absorbent / neutralizer with a colour indicator
- **Don't Forget Good housekeeping**
 - o Do not work in a restricted or cluttered area
 - o Do not leave solutions in unmarked containers,
 - o Clean, wash and dry after work, so as not to leave HF on surfaces

Note: Hydrofluoric acid can permeate through some glove materials over time; the thinner the glove, the shorter the 'breakthrough time'. Disposable gloves in particular have short breakthrough times and are not suitable for work with HF. Always consult the manufacturer's catalogues and websites for hydrofluoric acid breakthrough times before choosing your gloves.

HF users must have a contingency plan for use in the event of an emergency, this should include the summoning of a First Aider. **First aiders MUST NOT enter an area where HF gas is present.** Users should consider the need for an HF gas monitor in their risk assessment. The plan should include details of the initial treatment e.g. washing and the application of calcium gluconate gel, (see Appendix B which includes an example first aid emergency poster). HF users should consult an HF trained first aider prior to commencing work to agree the emergency plan and discuss potential emergency scenarios.

7.1 Standard Clean-up After Using HF

As a minimum, the work area should always be wet wiped and dried to ensure it is clean.

A solution of sodium bicarbonate can be used to ensure small residual traces of HF are neutralised before the final wet wipe and drying.

Hydrofluoric acid can only be present if there is a 'liquid' - by definition a completely dry surface has no residual hydrofluoric acid.

Where fitted, wash down facilities in fume cupboards should be used as directed by the manufacturer's instructions

7.2 Equipment clean-up

- Goggles/safety spectacles should be washed in warm water and dried.
- Reusable gloves should be washed, checked for pinholes ^b and dried
- Reusable aprons should be washed and dried
- The user should thoroughly clean and dry any apparatus or equipment used with HF

^b Ensure that the outer gloves are tested for pinholes by filling with water, twisting the cuff to seal and squeezing, any pinholes should be easy to spot as jets of water, usually from the vulnerable finger tips. After testing, ensure the gloves are thoroughly dried before reuse.

The inner 'disposable' gloves should always be discarded.

8 Emergency Actions Following an Incident

8.1 Initial Approach - The first rule is to avoid becoming a casualty yourself.

Summon a first aider and an ambulance if it is obvious one will be needed.

Do not enter a room where a casualty is without first checking whether there has been a release of HF vapour/gas, from concentrated HF or any other source. If so, there could be significant quantities of HF vapour/gas in the room, and that being the case anyone entering the room to perform a rescue operation will need specialist respiratory protective equipment to perform this task (i.e. call the Fire and Rescue Service on 1-999 or 9-999).

If the casualty is conscious they should remove themselves from any area where there is vapour, so that they can be treated in a safe place nearby.

Not: There is also a risk of inhalation if you are close to a casualty who has spilled concentrated HF on themselves and it has not yet been diluted with water.

Start washing off the HF immediately to prevent further absorption and once dilution has taken place, the inhalation hazard is insignificant at normal room temperatures.

If the HF in use was below 40%, there should be little risk of vapour release at normal room temperatures unless the HF has reacted with other materials. You need to be aware of the potential hazards of any liquids spilt in the room; particularly those spilt on the injured party or the floor around them and never touch any liquid without wearing gloves or kneel directly in any liquid on the floor.

Note: A fume cupboard is a 'partial containment device' designed to contain gases and vapours, but not liquids. A large liquid spill inside of a fume cupboard, but outside of a spillage tray, has the potential to run out of the cupboard under the front aerofoil and onto the floor ! In addition the standard air flow rate in many fume cupboards means that a spill in excess of 25 ml of concentrated HF could result in a small amount of vapour escaping containment.

8.2 Immediate Decision-Making Process

Summon urgent professional medical help in the form of an ambulance if:

- The casualty is collapsed or has been unconscious due to inhalation of HF fumes
- The casualty has or is suspected of having HF in the eyes
- The casualty has or is suspected of having ingested HF

The Fire and Rescue Service will be required if a person has collapsed in an HF atmosphere, and you have been unable to ventilate the atmosphere and make it safe without putting yourself at risk.

If any of these is the case, send someone to make a 1-999 or 9-999 call immediately, before deciding on your next action. Make sure that the following information is passed on:

- The direct dial number of a telephone close to you, so that the emergency services can call you back if necessary
- The exact location of the incident, including the department name and the room number
- An indication of the seriousness of the incident, and that it is HF exposure.
- The number of casualties involved.

Ensure, so far as you can, that someone is sent to meet the emergency services (ambulance / fire brigade) and guide them to the casualty.

8.3 Assisting a Casualty

If you are assisting a casualty arising from a spillage of hydrofluoric acid (or any other hazardous/ toxic chemical) always wear appropriate personal protective equipment, **to a minimum of safety glasses, gloves** and a laboratory coat or apron. (see Appendix A)

8.4 Making the Area Safe

It is the responsibility of the users/the department to ensure that the area is made safe – e.g. the room ventilated, spills absorbed/neutralised, the area washed clean and dried. All materials contaminated with HF must be suitably contained i.e. at least double bagged in labelled sealed robust plastic bags

However, if the incident has been serious, requiring the transport of the casualty to hospital in an ambulance, only the minimum clearing up should be done – confined to making the area safe, because a formal investigation may be required.

8.5 The Immediate Aftermath and Reporting the Incident

A normal accident report form should be completed. In addition, the DSO and the person who has supervisory responsibility for the area concerned must be informed as soon as possible,

Note: This document is published in association with the companion guidance for first aiders: HSD023E 'First Aid – Special Hazards 1 – Hydrofluoric Acid'

Appendix A.

Specifications for the Protective Equipment needed by First Aiders

Gloves

Reusable 'thick' Nitrile, Neoprene (or rubber*) gloves are suitable for the outer gloves, see

Marigold / comasec at http://www.comasec.com/UserFiles/Gloves_chemical_chart_EN.pdf
and

Kimberly Clark at <http://www.kcprofessional.co.uk/resources/chemical-protection-guide>
and

Ansell at http://www.ansellpro.com/download/Ansell_7thEditionChemicalResistanceGuide.pdf
Etc.....

Purely as an example, Ansell's Nitrile SOL-VEX gloves have a break through time of 334 minutes with 48% Hydrofluoric acid, (more concentrated HF acid will breakthrough in a shorter time).

Good quality Nitrile disposable gloves are adequate for the inner pair.

Thicker gloves, of a given material, give longer breakthrough times, but reduce dexterity.

* Rubber gloves should only be used when you are certain that no one who might use them is allergic to latex.

Aprons

Aprons may be made from polyethylene or rubber and are required when handling, using or decanting concentrated HF and recommended for all work with HF.

Safety Glasses, Face Shields (visors) or Goggles

Chemically resistance goggles are often the preferred choice as they give greater protection against splashes and if fitted properly are capable of preventing liquids running down the face into the eyes. For further general information on eye protection see the University guidance document; HSD071C '*Eye Protection for Handling Chemicals*' available on the Safety Office website. **It is very strongly recommended that where prescription safety glasses are used, then 'close fitting' prescription safety glasses should be provided and worn.**

Suggested PPE Procedures

The dressing sequence:

- Lab coat
- Apron
- Eye protection
- Inner gloves
- Outer gloves

And the removal sequence:

- Apron
- Outer gloves
- Eye protection
- Lab coat
- Inner gloves

If at any point the inner gloves are contaminated with HF they should be discarded as hazardous waste and new ones put on immediately.

Appendix B. Summary of First Aid Treatments

First assess the situation to decide on the protective measures necessary for yourself. These will include gloves, eye protection and an apron. Summon a trained first aider and where safe to do so commence primary first aid immediately i.e.

SKIN	EYES	INHALATION	INGESTION
Remove or cut off contaminated clothing using scissors. Wear gloves and protective clothing. Flush the burn with water for 1 to 5 minutes, then whilst wearing clean gloves apply calcium gluconate gel, gently massaging it into the burn, (or use DipHex Hexafluorine® following the manufacturer's instructions). Continue applying gel for at least 15 minutes AFTER pain is relieved. The person applying the gel should always wear gloves. Transport to hospital (this can be started as soon as washing is finished). Take the SDS to the hospital	Immediately flush the eye with DipHex Hexafluorine® (following the manufacturer's instructions). Or flush with water saline eye wash for at least 15 minutes, this will need to be continued while the casualty is being transported to hospital, using eye wash bottles. (NB: Do not put calcium gluconate gel in the eye) Transport to hospital should be arranged immediately. Take the SDS to the hospital	(Unlikely unless exposed to HF at 40-50% or greater) Remove the casualty from the contaminated area immediately and place in fresh air. If necessary, the first aider may need to resuscitate the casualty and administer oxygen. Call an ambulance. Send the casualty to Hospital. Take the SDS to the hospital	Never attempt to induce vomiting. If the casualty is conscious, rinse out the mouth with water or milk. Call an ambulance and send the casualty to Hospital. If necessary, the first aider may need to resuscitate the casualty. Be prepared to resuscitate the casualty. Take the SDS to the hospital

DipHex Hexafluorine® is a commercial wash solution that is claimed by the manufacturer to have a number of beneficial effects when used to treat HF burns to the skin and eyes. **It is recommended that HF users seriously consider the potential need for DipHex Hexafluorine® as an emergency treatment in the work they are doing.** For further information see the manufacturer's website at <http://www.diphex.com/>.



EMERGENCY PROCEDURES FOR HYDROFLUORIC ACID EXPOSURE



SEEK IMMEDIATE MEDICAL ATTENTION
CALL 1-999 OR 9-999
HYDROFLUORIC ACID CAN CAUSE SERIOUS TISSUE
DAMAGE AND EVEN DEATH !

BEGIN FIRST AID IMMEDIATELY AND SUMMON FIRST AIDER

SKIN CONTACT:

1. Remove or cut off all contaminated clothing. Wear neoprene/nitrile gloves and eye protection (and protective clothing, including apron if doing this for someone else).
2. Flush the burn with copious amounts of water for at least 5 minutes, ie: shower.
3. Using gloves apply Calcium Gluconate gel as soon as possible after washing and keep reapplying fresh gel for at least 15 minutes AFTER pain is relieved.
4. Transport to hospital with SDS etc, this can occur as soon as washing is finished! ie: you can apply gluconate gel during transport to hospital and whilst at hospital.

EYE CONTACT:

1. IMMEDIATELY wash the eyes with copious quantities of water for at least 15 minutes whilst holding eyelids open (do NOT apply calcium gluconate gel to eyes).
2. Transport to hospital as soon as possible and continue to irrigate the eyes en route.

INGESTION:

1. NEVER attempt to induce vomiting.
2. If casualty conscious, rinse out mouth with water or milk, give water or milk orally to dilute, followed by antacid or several glasses of milk to bind the fluoride ions.
3. Burns may cause severe swelling of the wind pipe, refer to Hospital immediately.

INHALATION:

1. If the casualty has collapsed; do NOT enter a toxic HF atmosphere unless trained and equipped to do so. Summon the Fire and Rescue Service (1-999 or 9-999).
2. If safe to do so (non fuming HF / no toxic vapour release into room likely) remove the casualty to fresh air and treat any burns appropriately as above.
3. HF trained first aider to administer oxygen as soon as possible.

Review History: Reviewed wrt use of DipHex Hexafluorine® in 2016 and 2020



**UNIVERSITY OF
CAMBRIDGE**

Safety Office
Greenwich House
Maddingley Road
Cambridge CB3 0TX

Tel: 01223 333301
Fax: 01223 330256
safety@admin.cam.ac.uk
www.safety.admin.cam.ac.uk/

HSD178C
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