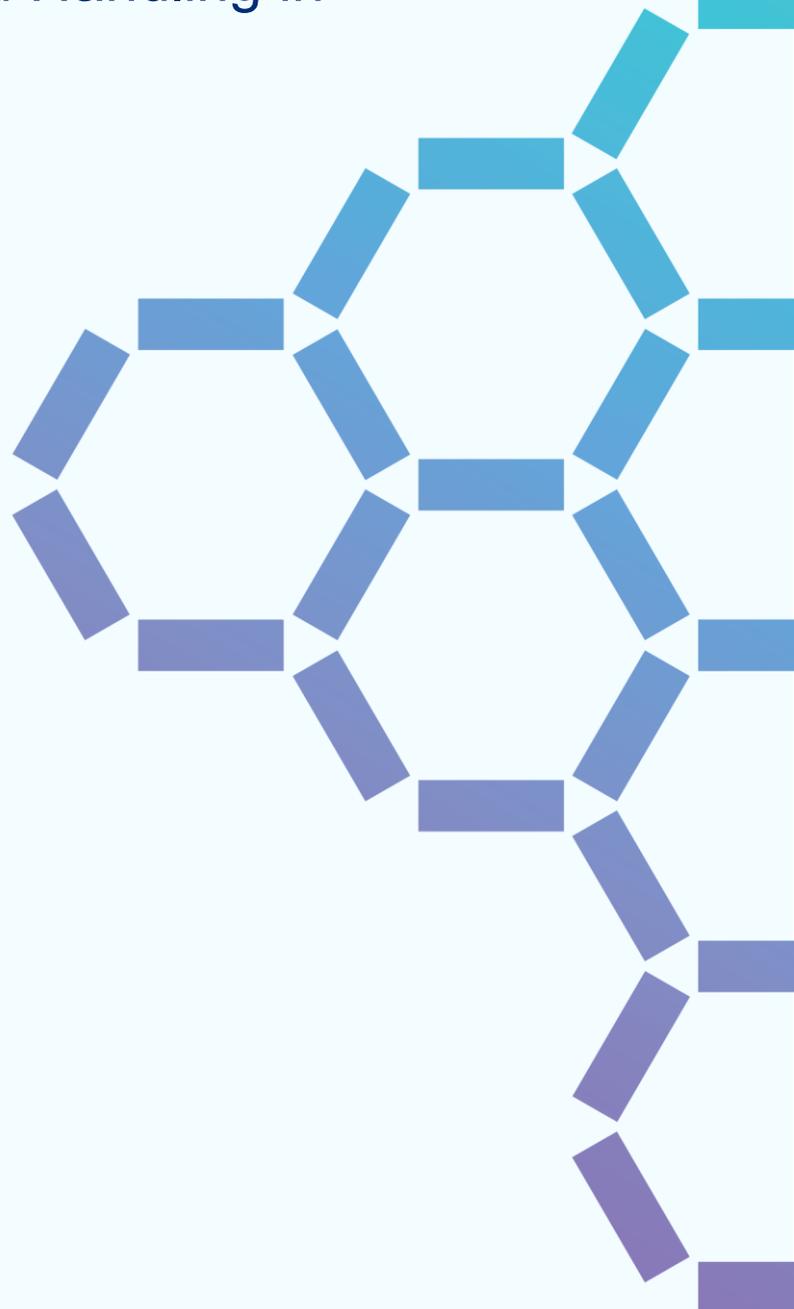


Hydrofluoric Acid Guidance – Section J

Hydrofluoric Acid Handling in Laboratories



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Introduction

The Hydrofluoric Acid Sector Network of the Chemical Industries Association (CIA) has developed this Guidance. It is intended to provide a standard to cover the safe practices necessary when using HF within laboratory environments. The Guidance is based upon many years of practical experience.

This Guidance reflects the best current practice (at the time of publication) and is recommended for use in conjunction with information from the supplier(s) of HF. It is intended as a recommendation and not as a mandatory standard to which all manufacturers and users of HF must adhere. As the title suggests, it provides Guidance on best practice for HF handling in laboratories only.

The Guidance is not to be used as a substitute for any applicable legislation. Whilst all reasonable efforts have been made to ensure the accuracy of the contents and legislative requirements at the time of publication, readers must refer to these themselves to ensure their compliance with current legislation or regulation.

Several other relevant HF Network Guidance documents are noted in J1 – however, if a laboratory is engaged in analysis of HF samples, the **HF Network Guidance Section E 'Sampling of Hydrofluoric Acid and Mixtures'** should be particularly noted in relation to the arrangements for safe transfer and storage of samples for testing.

Acronyms

COSHH The Control of Substances Hazardous to Health Regulations

HF Hydrogen Fluoride, Hydrofluoric Acid

FEP Fluorinated Ethylene Propylene

HAZOP Hazard and Operability Study

HCl Hydrogen Chloride / Hydrochloric Acid

HDPE High Density Polyethylene

PFA Perfluoroalkoxy

PPE Personal Protective Equipment

PTFE Polytetrafluoroethylene

PTW Permit To Work

PVDF Polyvinylidene Difluoride

SDS Safety Data Sheet (also MSDS)

J1 Relevant Documentation for Laboratory Risk Assessments

The following documents and also sections from other parts of CIA HF Network Guidance are relevant when considering the risk assessments necessary when handling HF in laboratories:

- Supplier's chemical safety data sheet (SDS) for anhydrous HF
- Supplier's SDS for aqueous HF
- Physical properties of anhydrous HF and hydrofluoric acid solutions
- HF Network Guidance Section A – Training requirements for Facilities Handling HF
- HF Network Guidance Section B – Personal Protective Equipment
- HF Network Guidance Section E – Sampling of Hydrofluoric Acid & Mixtures
- HF Network Guidance Section I – Emergency First Aid for HF Exposure.

J2 Safe Systems of Work

J2.1 Planning

The handling of HF is a hazardous operation and should be completed only in dedicated locations within laboratories which should be clearly labelled as HF Handling Areas. This document is intended only for laboratories handling HF and, where referred to, a 'Laboratory' means an HF Handling Laboratory.

J2.2 Alternatives to HF

Before working with HF in a laboratory, thought should be given to either eliminating the use of HF where possible or substituting HF for a less hazardous alternative.

J2.3 Unforeseen HF Formation

It is important to consider the reaction products and the possibility of HF formation during the reaction, when fluorine containing compounds are in use, e.g. by hydrogenation of halocarbons, reaction of fluorides with acid or thermal breakdown of compounds. The same HF hazards from such a reaction are present and therefore the same precautions should be observed.

J2.4 Scale of Experiments

For safety reasons experiments should be performed on as small a scale as possible. Be aware, however, that for continuous experiments, equipment such as pumps and rotameters have lower limits on flow rates.

J2.5 Materials of Construction

HF must only be stored and handled in equipment that is known to be compatible with HF. Care must be taken to ensure that all components coming into contact with HF are HF-compatible. Materials which are incompatible with HF, and which are common in laboratories, include glass and silica-containing materials. HF containers must also be impact resistant to avoid loss of containment in the event of, for example, being accidentally dropped.

J2.6 Containment

In process safety, the phrase *Keep it in the Pipe* is commonly used, this is *primary containment*. However, in abnormal cases, there may be fugitive emissions, in which case we rely upon *secondary containment*. The HSE define secondary containment on chemical plant as a second line of defence for preventing, controlling or mitigating major hazards events, e.g. bunds, drip trays, off-gas treatment systems, interceptors/sumps, expansion vessels, double skinned tanks/vessels, concentric pipes, building structures/ventilation. See: HSE reference: <https://www.hse.gov.uk/comah/sragtech/techmeascontain.htm>

J3 Risk Assessment

Each laboratory handling HF should prepare a suitable and sufficient risk assessment as required under The Control of Substances Hazardous to Health Regulations (COSHH) prior to starting each new experiment or task. The risk assessment process should be completed by the laboratory team and with input from an independent representative to provide an alternative viewpoint. The risk assessment may include the following details:

- Clear identification of the task and the individuals involved
- Clear identification of the equipment required
- A review of the competence and understanding of the individuals involved
- An evaluation of the risks associated with each step of the task
- Clear identification of the possibility of exposure to all hazards
- Elimination or mitigation of as many hazards as possible
- A review of the appropriate level of personal protective equipment (PPE) required for each step of the task and at what point the PPE should be worn, and consideration given to additional hazards introduced as a result of specified PPE- for example loss of dexterity or trip hazards
- Clear identification of any health implications associated with the task, the individuals involved in the task and the PPE to be used
- Clear identification of the expected duration of the task and any hygiene implications
- Clear identification of the decontamination procedures required
- Clear identification of any back up emergency plan, if appropriate.

One stipulation of the risk assessment should be that all individuals involved will have undergone specific training in the handling of HF in a laboratory and that lone working rules are to be considered. For example, a site may decide that lone working in a laboratory with HF is not permitted, as part of a suitable and sufficient risk assessment.

J4 First Aid

Prior to starting work involving HF within a laboratory environment, it is important to have a plan in place to deal with potential exposure to HF. Refer to **HF Network Guidance Section I – Emergency First Aid for HF Exposure**, with which all staff handling HF should be fully familiar.

Specifically in regard to laboratory handling, a HF Emergency Kit containing calcium gluconate gel must be located close to the dedicated area within the laboratory where HF is used. Each member of the laboratory team should be issued with up to two tubes of calcium gluconate gel with the recommendation that one tube to be stored in a safe location at home. The out-of-hours medical emergency procedure including telephone number should be issued to all laboratory personnel.

Note: It is important to begin treatment with gel as soon as possible if HF contamination is suspected. The retention of a tube of gel in the home is intended for individuals to begin treatment at the earliest opportunity, where delayed symptoms are suspected. However, it is important to report any incident, whether actual HF contamination or not, and to receive follow up advice from a medical professional.

Calcium gluconate gel is available from several suppliers and the employer should ensure an uninterrupted supply is available on site. The gel typically has a shelf life of 3 years from manufacture. For additional information on first aid treatment refer to **HF Network Guidance Section I**.

J5 Signs & Labelling

It is important that others should be aware of people working with HF in the immediate vicinity. To this end the following signs should be exhibited where HF is in use.

Position	Sign
On the laboratory door	“HF IN USE” “CORROSIVE” “TOXIC”
On the office door	List of out of hours telephone numbers of HF users in the lab
Strategic position in the laboratory	“HF IN USE” “CORROSIVE” “TOXIC” Telephone number of emergency services
Individual fume cupboards	“HF IN USE”
HF pipework	Should be clearly labelled and colour coded.

J6 Personal Protective Equipment

The correct PPE should be available within the laboratory. The level of PPE worn at any time is dependent upon the nature of the task being performed. For further information refer to **HF Network Guidance Section B – Personal Protective Equipment**.

Note: In all cases under normal conditions PPE should NOT be relied upon as the primary or only defence mechanism. The hierarchy of control should be such that laboratory equipment design should eliminate or minimise the risk of exposure of personnel involved in HF handling duties or activities, so that the wearing of PPE becomes a necessary precautionary measure as opposed to the only exposure prevention one.

It is highly recommended that an emergency locker containing a full set of the equipment required in case an emergency is situated away from the laboratory handling HF. This will allow easy access to the correct equipment (PPE, tools, etc.) needed to mitigate an emergency.

Gloves should be tested daily for pin holes by inflating with air, immersing in water and observing any bubbles produced. A glove test chart should be displayed.

Note: It is important to note that ‘normal’ laboratory type gloves may be completely unsuitable for any work with HF; ALL gloves in use within a laboratory where HF is used should have been shown to be resistant to HF. For further information refer to **HF Network Guidance Section B – Personal Protective Equipment**.

J7 Materials of Construction

The selection of materials of construction is an important subject and consultation with a competent design engineer is strongly recommended. **CIA HF Network Guidance Section G - Establishing an Inspection Regime for Processes Handling HF** discusses how in carbon steel, the combination of the carbon (C) content and the residual element content such as chromium (Cr), nickel (Ni), copper (Cu) can significantly affect corrosion. Section G considers alloys such as Hastelloy (C276, C22, C2000), Monel (400 - 70Ni/30Cu). Further reading on metal alloys and their resistances with grades of HF can also be found in National Association of Corrosion Engineers *NACE TR5A171-2022, Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*. Therefore, the information below is intended to provide an overview rather than detailed guidance, see *Table 1: Examples of common materials compatible with varying strengths of HF at room temperature, below:*

Material	Grade of HF		
	Anhydrous	Greater than or equal to 70%	Less than 70%
Mild steel*	*	X	X
Stainless steel	*	X	X
PTFE ^	*	*	*
FEP	*	*	*
PFA	*	*	*
Monel	*	*	*
Inconel	*	*	*
Hastelloy	*	*	*
HDPE	X	X	• At Ambient
Polypropylene (PP)	X	X	*
PVDF	X	X at ambient	X
Glass or glass fibre	X	X	X
Silica containing ceramics	X	X	X
Natural rubber	X	X	X
Silicone rubber	X	X	X
Polyamides, e.g. Nylon	X	X	X

Key: * – Acceptable X – Not acceptable

Table 1: Examples of common materials compatible with varying strengths of HF at room temperature

*‘Mild steel’ has a lower carbon content than ‘carbon steel’.

^Note: PTFE, if filled, must be filled with a suitable material (e.g. CaF₂ but not glass).

J7.1 Further Notes and Comments

Note: Material suitability depends greatly upon the temperature and pressure they will be subjected to and the nature of other components present, e.g. HCl or organic compounds.

Note: When considering materials of construction consideration should also be given other components which may be present, or which may be formed during the experiment. For example, some of the materials above, though compatible with HF would not be suitable for use with organic components and this loss of containment of HF may not have been considered during the risk assessment. This may be of particular importance when considering the purchase of standard equipment, e.g. peristaltic pumps.

- Lead washers can be used with the fittings on HF cylinders. It is safe to use in this manner but should not be considered for rig building.
- Mechanical properties must also be considered when choosing materials, e.g. copper would not be selected for building a rig due to its lack of mechanical strength.
- Care should be taken when handling HF around wooden surfaces as the HF can absorb into the surfaces leaving it unsafe to touch and difficult to decontaminate. If HF is thought to have come into contact with a wooden surface, then it should be scrubbed with a potassium carbonate solution, with routine checks on pH of the wooden surface must be taken (wet a piece of pH paper and apply to the surface) as HF will continue to desorb from the wood over time.
- It is important to segregate HF compatible materials (e.g. PTFE, FEP) from materials which are not HF compatible (e.g. polyamides such as Nylon). It is recommended that only HF compatible tubing is used and stored in laboratories using HF.
- It is also important to keep HF compatible lubricating agents away from lubricants which are incompatible with HF. It is recommended that only HF compatible lubricating agents are used and stored in laboratories using HF. This is particularly important where valves are to be used under severely corroding conditions. They must be supplied lubricated with PTFE / perfluoroether greases instead of the standard silicone grease.
- Labelling of METAL tubing is essential to avoid confusion where differing materials of similar appearance are used in one rig (e.g. Monel and stainless steel). In cases where confusion arises, an alloy detector should be used to determine the composition of the material of construction.

J8 Working Practices

- (i) All personnel who work with HF must be trained in the use of HF. Refer to **HF Network Guidance Section A – ‘Training requirements’**
- (ii) Lone working with HF is not recommended. Experiments involving HF should not be left unattended unless the equipment has been designed to be fail-safe and has been subject to a hazard and operability (HAZOP) study. Comment: Not every experiment handling HF needs to undergo HAZOP. **Note: based upon the risk assessment by a competent person, previous experience, scale and control measures in place alternative formal process safety assessment may be appropriate.**
- (iii) All staff starting to work with HF for the first time should undergo a medical examination for lung function capability and base fluoride concentration in urine. The suitability of staff with medical conditions such as asthma or epilepsy to work with HF should be considered and documented as part of the risk assessment
- (iv) Other workers in the laboratory or visitors, even if not directly concerned with the HF experiments, shall be informed of its hazards and the precautions necessary to avoid contact with HF. The adequate and correct labelling of equipment, pipework, reactants and products is an important part of this process
- (v) It is recommended that personnel who are not working directly with HF but are working in a laboratory in which HF is used should also have received HF training
- (vi) Care should be taken to prevent HF contamination spreading outside the fume cupboard or outside the laboratory, e.g. via equipment and protective equipment. Special care should be taken not to touch equipment whilst wearing HF-contaminated gloves, e.g. taps, door handles, etc.
- (vii) Before starting any experimentation potassium carbonate (or similar) solution and solid should be on hand so HF contamination can be dealt with speedily
- (viii) Gloves and equipment should be rinsed in potassium carbonate (or similar) solution immediately after use, followed by rinsing in clean water to avoid the risk of powdery fluoride contamination
- (ix) No entry is permitted to offices or control rooms whilst wearing protective equipment, nor are any HF samples allowed within these areas.
- (x) Workers involved in maintaining equipment which could be contaminated with HF should adequately trained. The maintenance work should be risk assessed and if deemed necessary the work should be authorised under a permit to work system
- (xi) Local screening of high-risk joints / restrictors should be considered when designing experimental rigs

- (xii) HF shall never be discharged into the environment e.g. to atmosphere, water course or foul sewer. HF should only be discharged into a laboratory drain provided that all materials of construction are HF compatible and the HF is either recycled or neutralized
- (xiii) Experiments involving complex high-pressure rigs using HF shall always undergo a hazard study, the results of which shall be retained. Such hazard studies shall always involve a member of the appropriate laboratory team and will have methods of containment built into them (e.g. dump tanks/scrubbers) to cope with a major release resulting from equipment failure
- (xiv) When planning an experiment or a series of experiments involving the use of HF cylinders, the inventory of HF in the lab should be governed by the frequency that the HF cylinder may need to be changed. It is recommended that cylinders should be sized to last no more than six months.

J9 Fume Cupboard Practices

- (i) Polycarbonate screens should be fitted to all fume cupboard doors where there is HF in use
- (ii) Fume cupboards close to laboratory doors should be HF-free zones
- (iii) Laboratories should operate their fume cupboards on an 'all on' or 'all off' policy, i.e. if one fume cupboard is faulty in the lab then none of the others can be used until it is fixed. Fume cupboard vents should be designed to ensure that 'suck back' from vents into other fume cupboard in-takes is not feasible
- (iv) Proper use should be made of sashes or doors to minimize openings when HF is in use within the fume cupboard
- (v) All fume cupboards should be designed and operated to meet the necessary release calculations.

J10 HF Rig Building

- (i) Any rig that is to operate at higher than atmospheric pressure should be referred to a design engineer and the rig should undergo a full HAZOP study
- (ii) The correct materials of construction should be used to prevent corrosion. For anhydrous HF, at relatively low temperature, stainless steel can be used. However, if there is any possibility of more corrosive HF mixtures coming into contact with the material Inconel, Monel or Hastelloy shall be used. Such corrosive mixtures could be HF/water, HF/HCl, etc. The wall thickness of pipework should also be considered as well as the design flow velocities
- (iii) Pipework should be firmly supported. This is particularly relevant to valves, where there is mechanical stress when opening and closing and to HF manifold lines used to feed more than one rig in a laboratory
- (iv) Where there is a HF manifold, a clear line diagram of the apparatus connected to the cylinder and instructions for purging the lines should be readily available. The laminated diagram and instructions should be clearly visible close to the manifold
- (v) HF pipework should be characteristically labelled or colour-coded
- (vi) Care should be taken in the siting of sample points for streams containing HF. A minimum of two isolation valves is preferred and the sample point should point away from the operator in the event of the sample valves failing
- (vii) The sampling procedure for any experimentation should be prepared and included in the Risk Assessment
- (viii) Care must be taken to avoid liquid HF being trapped in a closed length of pipe, e.g. between two valves. Under no circumstances should lines suspected to contain trapped HF be heated
- (ix) To protect vulnerable parts of rigs, e.g. mass flow controllers or rotameters, from HF vapour that may diffuse back along lines the use of sodium fluoride traps should be considered. These consist of a tube packed with sodium fluoride pellets, in the case of HF diffusion the sodium fluoride absorbs the HF and forms sodium bifluoride. Care must be taken when dismantling these traps as the sodium bifluoride has similar toxicity and corrosion properties to HF, they should be immersed in carbonate solution wearing the appropriate personal protective equipment.

J11 Anhydrous HF In Use

Anhydrous HF is a liquid with a low boiling point of 19.5°C, which fumes on contact with air and reacts violently with water and bases, evolving a considerable amount of heat. Due to its low boiling point, its use is limited for liquid phase work at atmospheric pressure (see Appendix 1 for the main physical properties of HF).

Experiments using HF under reflux can be carried out by using PTFE equipment which includes a condenser.

Experiments at reasonably low temperatures (0 to 15°C) can be carried out using PTFE, PFA or FEP. FEP is particularly suitable due to its translucence, although it is expensive and equipment constructed in this material is not as widely available as PTFE.

J11.1 Cylinders

J11.1.1 Inventory & Use Control

- (i) Incidents have been reported where cylinders of HF have ‘exploded’ due to over-pressurisation because of hydrogen build-up caused by the reaction of HF / water impurity with the metal of the cylinder. This increase in pressure generally takes many years (15 to 20 years) to reach a dangerous level. To prevent such occurrences, the inventory of HF cylinders stocked in the workplace should be carefully managed. Cylinders over two years old should be checked for excessive pressure build up before use.
- (ii) Store cylinders in a DRY, COOL, VENTILATED place away from direct sunlight or where there is a risk of fire.
- (iii) If excessive pressure is found in a cylinder it should be vented through an appropriate scrubbing system with a nitrogen bleed to prevent suck back. For cylinders with dip-pipes it may be necessary to invert the cylinder to ensure that the gaseous head space is vented.

J11.1.2 How to Tell if a Cylinder Is Empty

A check should be made that lack of flow is not due to the cylinder being too cold or that there is a blockage in any line. HF cylinders should be weighed and compared with tare weights. The empty weight is always stamped on the cylinder, so that it can be weighed to check on the cylinder contents.

Note: HF is invariably trapped in pipework, so never take chances when changing even apparently empty cylinders. When breaking into any line that may have contained liquid HF the correct level of PPE should be worn.

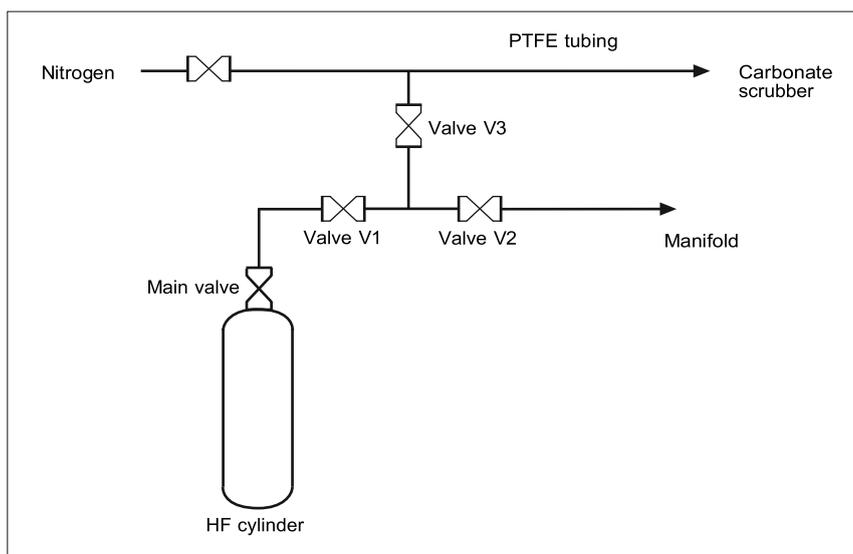


Figure 1. Typical valve arrangement for HF cylinder on a manifold.

During normal running the PTFE tubing attached to valve V3 (Figure 1, above) is replaced with a blanking nut.

To change the cylinder:

- (i) Ensure that the main valve is closed and valves V1, V2 and V3 are also closed
- (ii) Remove the blanking nut and replace with PTFE tubing with a T piece and nitrogen purge to a carbonate scrubber. Note: The installation of a vacuum trap in the line to the scrubber is recommended (in case any abnormal situation arises where N₂ pressure is lost or cooling results in vacuum) to prevent suck back of scrubber contents to cylinder or pipework.
- (iii) Carefully open valve V3 and allow any HF into the scrubber
- (iv) Gently heat the pipework between valves V1, V2 and V3 with a hair dryer
- (v) When the HF has all been released carefully open valve V1 and again allow any HF to the scrubber
- (vi) Repeat the gentle heating with the hair dryer for all the pipework between the main cylinder valve and the valve V2 to the manifold.
- (vii) When the HF has all been released break the line on the Swagelock fitting before valve V1, this causes less stress to the system than trying to release the tailpipe on the cylinder
- (viii) Ensure that the main cylinder valve is shut on the new cylinder before removing the blanking nut
- (ix) Release the tailpipe on the old cylinder and replace the blanking nut
- (x) Replace the gasket in the nut before reconnecting the tailpipe to the new cylinder
- (xi) Reconnect the pipework, ensure that all valves are closed and carefully open the new cylinder main valve
- (xii) Test for any leaks using an ammonia wash bottle
- (xiii) Remove the PTFE tubing and replace with a Swagelock blanking nut.

Note: Always keep the main valve on HF cylinders closed when not in use. Remember to decontaminate all tools and gloves when finished.

J11.1.3 Connecting a New Cylinder

Where a HF cylinder is connected to a permanent rig or manifold thought should be given at the design stage to facilitate the changing of the cylinder, see *Figure 1* above which shows a typical system.

J11.1.4 Cylinders with Seized Valves

Do not attempt to open seized valves on HF cylinders. Replace the blanking nut and dome, fix a label and arrange for the cylinder to be returned to the supplier.

J11.2 Feed Systems

J11.2.1 Atmospheric Pressure HF Feed

This has many advantages over rotameters, low flows 10-20 ml/min can be obtained which are both reproducible and constant.

Note: The specification of a “carrier gas” should be considered, especially water content.

When a gas is sparged through a liquid, the off – gas contains a volume of the liquid dependent on the vapour pressure of the liquid at the temperature and pressure of the liquid. This principle can be used to feed low levels of HF into an experiment where a low volume of diluent, such as nitrogen, will not affect the experiment. Depending upon the pressure and the rate required, the HF is heated or cooled and the sparge rate varied.

HF at a temperature of 0°C has a vapour pressure of 0.48 bara. Thus 0.52ml of nitrogen should pick up 0.48ml HF. However, HF boils in the form of an oligomer and therefore 1ml of nitrogen will give approximately 2ml HF.

The feed system (figure 2) can be filled from a weighed HF reservoir at a pressure of ~2 barg by closing valves V1, V2 and V3 and opening valves V4 and V6. This would allow the available volume of the sample bomb to be filled before the pressures equalised and the flow ceased. Ensure that there is a nitrogen flow through the buffer vessel and to the scrubber. Close valves V4 and V6, then carefully crack open valve V3 to release the excess pressure to the scrubber. This can then be fully opened whilst the temperatures and pressures equilibrate. The metered nitrogen feed can be added by opening valve V1 and continuing to feed the off gas to the scrubber. When steady conditions are obtained, the feed can be diverted to the experiment by opening valve V2 and closing valve V3. The nitrogen purge to the scrubber prevents any suck-back of the scrubber liquor.

The actual rate of HF can be adjusted by altering the nitrogen feed, or the temperature of the water bath and determined by titrating the HF against caustic soda using phenolphthalein. *Figure 2* below shows an example of an atmospheric HF feed system.

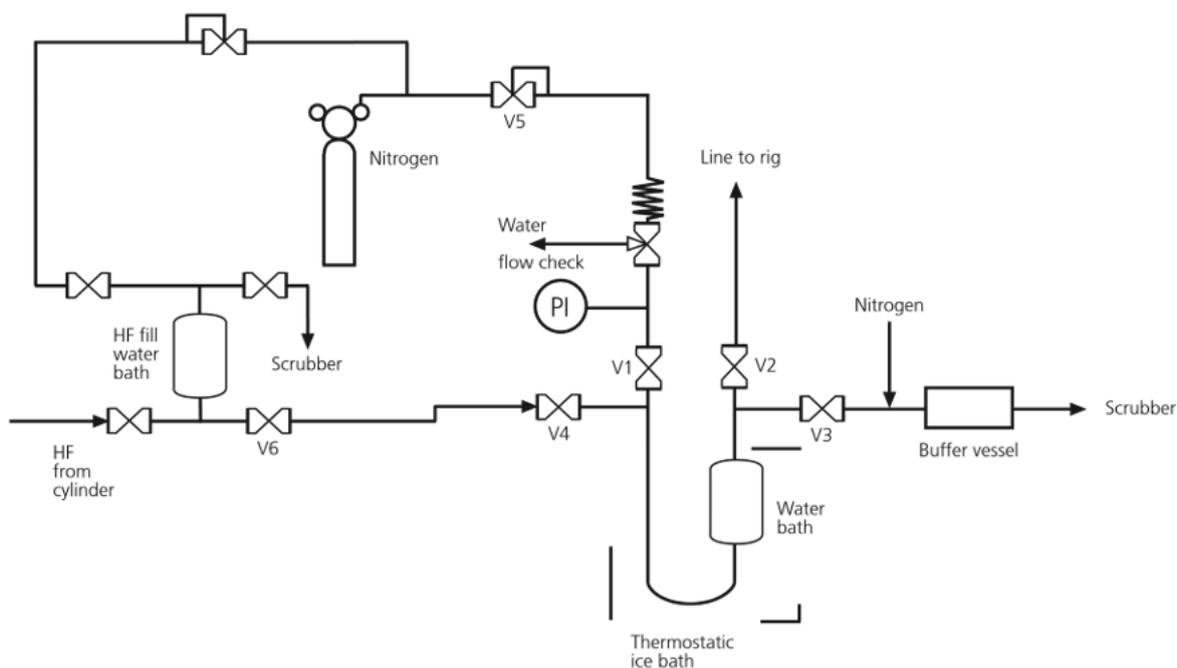


Figure 2. Example of an atmospheric HF feed system.

J11.2.2 High Pressure HF Feed

High HF flows (up to 7g/min)

For pressure systems, liquid HF can be fed from a reservoir via an appropriate pump and vaporised by trace heating or an electrically heated block on route to the reactor. Rate of flow is typically measured by weight change in the reservoir versus time. A double diaphragm pump should be used with a fluorinated fluid inserted between the diaphragms.

Low flows (0.5-2g/min)

Nitrogen Sparge System

A similar arrangement as the atmospheric sparge system can also be used at pressure. The thermostatic ice bath is substituted by a hot oil bath and the nitrogen is controlled by a mass flow controller protected from HF vapour by a sodium fluoride trap. The temperature of the oil is dependent on the working pressure of the rig. For a pressure of 10 barg a temperature of 80°C will give a flow of HF equivalent to 0.5ml for every ml of nitrogen.

Care should be taken on materials of construction and in the operating instructions to prevent hot HF at pressure from being ejected inadvertently to atmosphere.

Flow Restrictor

A more recent development has been to use flow restrictors (see Figure 3 below) and pass liquid HF through a crimped tube packed with silicone carbide powder. Standard practice is to pack an 1/8" outer diameter (OD) tube which is itself contained in a 1/4" tee. The other arm of the tee is linked to a potassium carbonate scrubber in case there is any leak from the crimped tube. The HF is fed from a sample bomb pressurised with nitrogen controlled by a valve. A manifold system of restrictors can be used since the performance of the restrictors does vary with time. The HF can be vaporised downstream from the restrictors using trace heating tape or a heating block. This method has the advantage of no moving parts, is easy to maintain and can, when the restrictors have settled in, give steady HF flows for long periods of time.

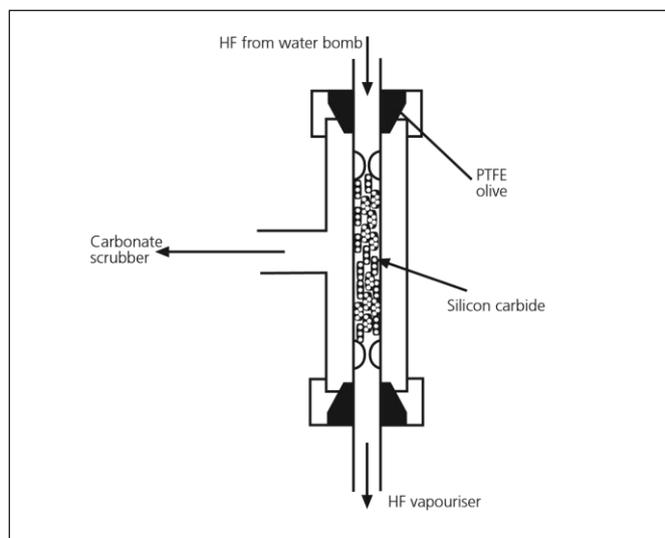


Figure 3. Example of a Flow Restrictor

J12 Aqueous HF in Laboratory or Operational Use

Aqueous HF can be more hazardous than its anhydrous form because of its lower volatility and therefore higher persistence; it does not fume at lower concentrations below about 50% HF making it hard to distinguish from other chemicals or water. The burns caused by aqueous solutions can be life threatening and may have delayed symptoms which causes late treatment and therefore the effect of a burn may be more pronounced.

It is important to carry out a suitable and sufficient risk assessment for the proposed work prior to ordering aqueous HF. The greatest care must be taken in handling this material, with the appropriate personal protective equipment being worn, as described earlier. The smallest volume required should be ordered to prevent unnecessary disposal problems at the end of an experiment.

Several concentrations are readily available. For HF concentrations below 40% or between 40% and 60%, dilute the next highest strength HF to the required strength with water, adding the acid to the water. Always carefully add acid to water, possibly as ice in a suitable vessel with stirring and cooling, wearing the appropriate PPE.

For concentrations between 60% and 100%, dilution of anhydrous HF with aqueous HF is required. Wear the appropriate personal protective equipment. In a fume cupboard weigh, or measure by volume, HF into an ice-cooled polypropylene measuring cylinder by slowly passing liquid via 1/4" PTFE or stainless-steel tubing connected to a dip-pipe HF cylinder. HF should never be removed from the fume cupboard in a measuring cylinder or any open vessel.

Calculate the amount of 40% aqueous HF needed to achieve the required strength of HF, e.g. 100ml of 85% HF would require 75g of anhydrous HF plus 25g of 40% aqueous HF. Cool the aqueous acid in a plastic container held in ice, then add the anhydrous HF with stirring, at a very slow rate. Reweigh the vessel.

WARNING: A violent reaction occurs with evolution of heat with a loud crackling sound and spitting if the addition is uncontrolled or the temperature is too high. Not only is this potentially hazardous, but the required concentration will not be achieved as HF will be lost as vapour.

The prepared solution should be stored in a properly labelled chemically resistant (see earlier table), FEP bottle – or Monel, Inconel or Hastelloy sample bomb (depending upon the vapour pressure of the prepared solution) in a safe place, e.g. in a bunded container enclosed in a ventilated area.

J13 Disposal

The correct level of PPE should be worn during this procedure. Refer to **HF Network Guidance Section A – Training Requirements for HF Handling Facilities**, and **HF Network Guidance Section B - Personal Protective Equipment**

Solutions containing HF should be neutralised by pouring slowly, with stirring, into an excess solution of sodium or potassium carbonate (20% w/w with ice) contained in a plastic vessel.

Carbonate is preferable to hydroxide since the evolution of carbon dioxide (CO₂) has the advantage of removing heat, although the resultant frothing must be controlled by the rate of addition and constant stirring.

After neutralisation (checked by pH paper / indicator), any organic phase should be separated and disposed of by suitable methods. The aqueous phase, if in the pH range 6-9, may be discarded by pouring slowly down a sink simultaneously with copious amount of cold water.

Anhydrous liquid HF can be disposed of by pouring into a solution of ~69% w/w calcium chloride hexahydrate CaCl₂ and ice contained in a plastic vessel and sending the product for approved landfill. Approximately 20% excess of the chloride is used, 5.5kg of CaCl₂.6H₂O with 2.5kg of ice being used to dispose of every kilogram of anhydrous HF.

Liquid HF must be fed via a pipe into the bottom of the vessel.

If possible, CaCl₂.6H₂O should be utilised as soon as possible after mixing so that full use is made of the cooling that has been generated.

HF containing vapour should be neutralised by passing the vapour, diluted with an air or nitrogen stream to prevent suck back, into a static potassium carbonate scrubber using phenolphthalein as indicator. Thought should be given as to the need for an anti-suck-back device in case there is an interruption in the air or nitrogen supply. Visible traps should be used wherever possible so that any 'suck-back' can be traced visibly. If the carbonate is totally neutralised additional carbonate should be added to the scrubber and then flushed down the drain with copious amounts of water.

J14 Decontamination

Further Guidance on Decontamination of equipment in HF service is given in **HF Network Guidance Section H**. It is important that everything that has possibly been in contact with HF should be thoroughly decontaminated after use. HF has a tendency to form a layer on metallic surfaces; it is readily absorbed into wood and will dissolve and form an aqueous layer on moist surfaces. Tools, gloves, etc. should be immersed into a sodium or potassium carbonate bath before washing with water.

All PPE used during an experiment should be assumed to have been contaminated with HF and should be thoroughly decontaminated, e.g. by use of a safety shower. Practical Note: Use of a safety shower in the laboratory for assumed contamination could result in localised flooding which introduces slip hazards. In this case, a check may first take place for contamination and then if PPE is known to have been contaminated the safety shower is used. An indicator spray may be used to check for such areas of potential contamination and then if small contamination is found, bicarbonate wipes may be used to clean the PPE before doffing.

Particular care should be taken with removing PPE to ensure that secondary contamination does not occur. Where PPE is known to have been contaminated it should be decontaminated and safely and properly disposed of.

Wooden surfaces should be wiped with carbonate solution. Known spillages of HF onto wooden surfaces should be treated with carbonate solid followed by washing with carbonate solution and finally water.

Appendix 1 Physical Properties of Anhydrous HF

Parameter	Value
Molecular weight	20.01 (monomeric)
Boiling point	19.5°C at 760mm Hg
Melting point	-84.0°C
Specific gravity	0.98 at 10°C
Vapour density (Air = 1)	2.4 at 20°C
Critical temperature	187.9°C
Critical pressure	64.9 bar
Critical density	290.0kg/m ³
Heat of vaporisation at boiling point	374.5kJ/kg
Heat of fusion at freezing point	196.9kJ/kg
Specific heat at constant pressure Liquid at boiling point, Vapour at 25°C, 760 mm Hg (*Heat evolved when 1kg of anhydrous liquid HF at 25°C is diluted to the given concentration)	2.32 kJ/kg°C 1.46 kJ/ kg°C*
Viscosity of liquid at 0°C	0.25cP
Surface tension at 0°C	10.27mN/m
Flash point	Non flammable
Explosive range	Non explosive
Solubility in water	Soluble in all ratios
Odour threshold	<1 ppm

Table 1. Physical Properties of Anhydrous HF

Temperature °C	Vapour pressure Bar Abs	Density saturated vapour kg/ m ³	Density liquid kg/ m ³
-10	0.31	-	1025
0	0.49	2.15	1002
10	0.71	2.52	980
20	1.03	3.17	968
30	1.46	3.98	945
40	2.02	4.98	928
50	2.76	6.19	908
60	3.7	7.65	888
70	4.9	9.39	867
80	6.4	11.44	844
90	8.25	13.85	820
100	10.52	16.64	796

Table 2. Variation of vapour pressure, vapour density and liquid density with temperature

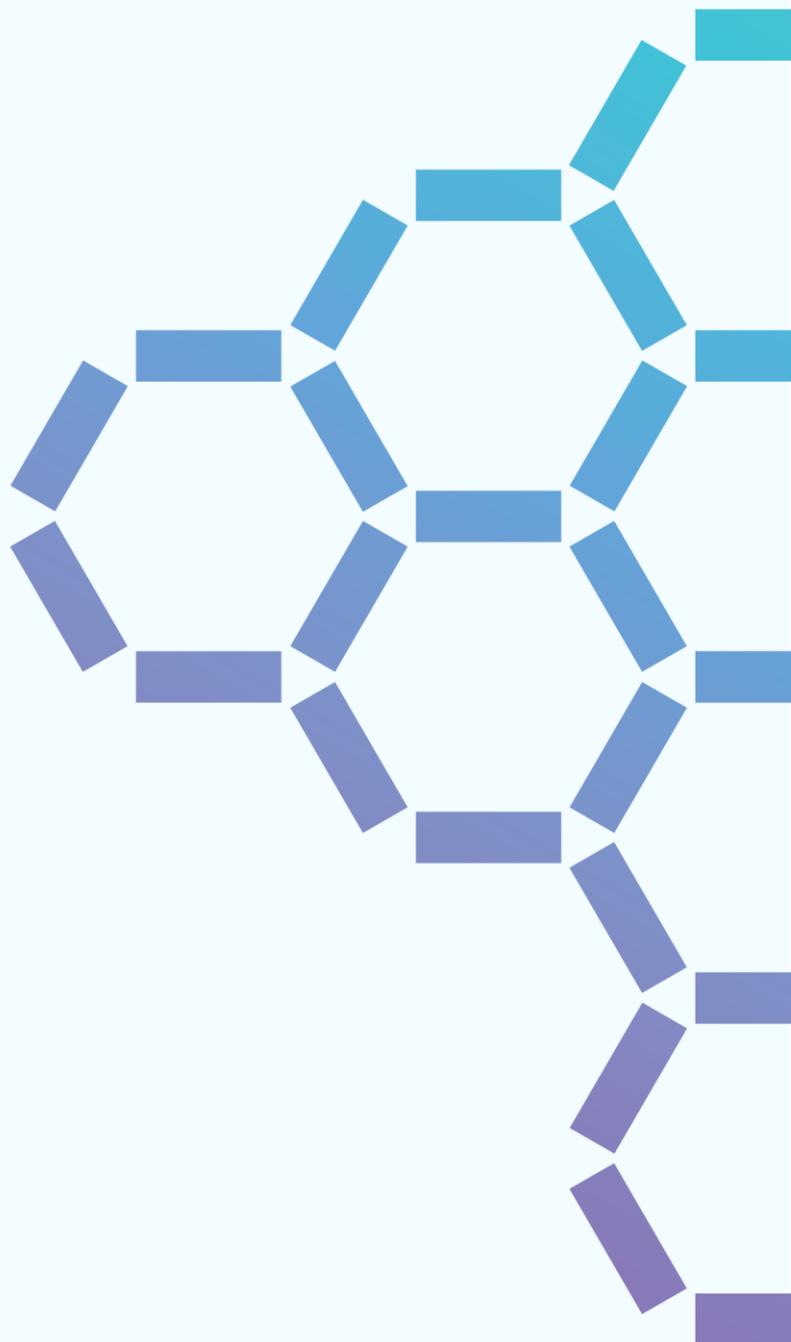
Temperature °C	Vapour density kg/m ³
19.5	2.93
30	1.79
40	1.13
50	0.85
60	0.77
70	0.74
80	0.71
90	0.68

Table 3. Variation of density of superheated vapour at 1013 mbar with temperature

Concentration of HF % w/w	Heat of dilution* kJ/kg
100	0
90	217
80	380
70	502
60	623
50	736
40	820
30	874
20	912
10	937
0	970

Table 4. Heat of Dilution of HF

* Heat evolved when 1kg of anhydrous liquid HF at 25°C is diluted to the given concentration.



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