Hydrofluoric acid

IDENTIFICATION

Hydrofluoric acid
Fluoric acid
Hydrogen fluoride
Fluoride of hydrogen

ZVG number: 520038
CAS number: 7664-39-3 Hydrogen fluoride, anhydrous
INDEX number: 009-003-00-1
EC number: 231-634-8

CHARACTERISATION

SUBSTANCE GROUP CODE

120510 Acids, inorganic
133100 Fluorine compounds, inorganic

STATE OF AGGREGATION

At 1013 mbar/20 °C: liquid

PROPERTIES

Colour: colourless

CHEMICAL CHARACTERISATION

Non-combustible liquid.
Mixable with water.
Hygroscopic.
Fumes in contact with air.
(in concentrations > 70 %)
Acute or chronic health hazards result from the substance.
(see: CLASSIFICATION/LABELLING).
FORMULA

HF
H—F

Molar mass: 20,01 g/mol

Conversion factor: 1 ml/m³ = 0,832 mg/m³ at 1013 mbar/20 degrees C

PHYSICAL AND CHEMICAL PROPERTIES

SOLUBILITY IN WATER

entirely mixable

HAZARDOUS REACTIONS

Hazardous chemical reactions:

Risk of explosion in contact with:
potassium
sodium
cyanogen fluoride; metals; potassium permanganate; nitric acid + glycerin;

The substance can react dangerously with:
ammonia
organic substances
sulfuric acid
acetic anhydride; 2-aminoethanol; ammonium hydroxide;
metal oxides; glass; metal silicides; sodium hydroxid;
oleum; phosphorus pentoxide; quartz; silicon compounds;
v vinyl acetate; bismuthic acid;

OCCUPATIONAL HEALTH AND FIRST AID

ROUTES OF EXPOSURE

Main Routes of exposure:
The main intake pathways for hydrofluoric acid (H. / aqueous HF aerosols) proceed via the respiratory tract and through the skin. [99996]

Respiratory tract:
Because of the azeotropic mixing ratio in aqueous HF-systems of 38% HF: 62% H₂O, concentrated H.
fumes in moist air. On the other hand, from mixtures of less than 38% H. a great deal more water than HF is transferred in the vapor phase in open systems. Therefore, a high inhalative risk was reported to exist only if >60% H. is carelessly handled. [99997]

However, this does not apply when more diluted H. is heated to at least 60 degrees C (for instance 10% H. would exert a partial pressure of approximately 2 hPa in this case) or when aerosols are formed during technical processes. [61]

From kinetic inhalative experiments on volunteers (concentration up to 6 ppm) complete absorbability was found to have taken place and already mainly in the upper airways. [99997]

Skin:
Absorption through the skin is confirmed by accidents in which skin contact resulted in increased concentrations of fluoride in the blood and the onset of systemic effects. [99997]
Absorption (to an unknown degree) must even be expected if the skin initially seems to still be intact following impact of slightly concentrated H. [99996]

In experiments with up to 2% H. on rabbits, strong increase of the fluoride concentration in the serum was already found 1 hour after occlusive application. [2050]

More highly concentrated H. rapidly leads to destruction of the tissue, so that nearly unlimited absorption during the exposure time is assumed. [99999]

Gastrointestinal tract:
H. is expected to be rapidly and almost completely absorbed in the gastrointestinal tract. [99996]

On the other hand, the presence of high concentrations of fluoride-binding ions (in particular of calcium and aluminium) can limit absorption. [2050]

TOXIC EFFECTS

Main toxic effects:
Acute:
Severely irritating up to corrosive action to the mucous membranes and skin, depending on the concentration; [2050]
disturbances to the metabolism, cardiovascular and nervous systems

Chronic:
Irritation to the mucous membranes and skin,
damage to the bones (skeletal fluorosis) [7619]

Acute toxicity:

Even low concentrations of H. cause deep damage on all directly contacted tissues. [2050]
Following contamination of the eyes, distinct damage is expected at concentrations from approximately 1% H. upwards. [99999]

100 ul of 1.06% H. instilled into rabbits’ eyes caused reddening and swelling of the conjunctiva, corneal damage and impaired perfusion (ischemia). In another test on rabbits’ eyes, 0.5% H. produced temporary ischemia and 8% H. ischemia lasting for several weeks. [2050]

More concentrated H. damaged human eyes in accidents resulting in the following symptom complex: serious pain, lacrimation, severe damage to the conjunctiva and cornea (with complications such as glaucoma, uveitis, scarring/deformation, perforation of the bulb, xerotic keratitis) through to irreversible eye damage. [99996]

Skim damage following contact with H. frequently appears only after a latency period which is depends on the concentration and duration of the contact. Onset of depth pain mostly proceeds earlier. [2050]
Concentrated H. (>50%) rapidly causes deep destruction of the tissue with intense depth pain; following contact with 20 – 25% H., the extent of corrosion mostly becomes noticeable only within 1 – 8 h; if the H. content is below 20%, the contact area can initially remain relatively inconspicuous and show distinct damage possibly only after 24 hours. [99997]

2% H. applied to rabbits’ skin for 1 h initially only caused paleness or reddening initially but after 96 h necrosis, ulceration and subcutaneous edema. [220]
Vapors of H. can also produce serious chemical burns. [7637]
Besides the local effects, skin contact can also produce serious, life-threatening poisoning. H. containing 70% or more HF triggered serious, often lethal poisoning when 2.5 – 8% of the skin surface had been contaminated. Moistening of 46% of the skin surface with 30% H. resulted in serious poisoning symptoms: nausea, vomiting, severe metabolic disturbances (hypocalcemia), functional disturbances of the heart, dyspnea and pain in the chest. [99996]
Vapors of H. irritate and damage the airways in particular. Volunteers exposed to an atmosphere containing 2.5 – 5.2 mg HF/m3 (3 – 6.2 ppm) felt irritation in the upper airways (nose, throat) but the eyes and lower airways were less affected. Concentrations of 25 mg HF/m3 could only be tolerated for a (very) short period because of distinct impairment, and 50 mg HF/m3 triggered immediate irritation to the conjunctiva and mucous membranes in the nose and throat. [7619]
Accidental exposure to non-quantified concentrations of vapors and aerosols led to serious lung damage (hemorrhagic pulmonary edema, atelectasis and bleeding in the airways). Death mostly occurred very rapidly (30 – 150 minutes after exposure). On the other hand, damage to the lungs may also become manifest only after hours or days. Survivors sometimes suffered from difficulties in breathing for months. [99997]
Exposure to 42 mg/m3 (50 ppm HF) for 30 – 60 minutes was assumed to be capable of causing death of humans. The IDLH (immediately dangerous to life or health) value was set to 25 mg/m3 (30 ppm). [7930]
Following oral intake of H., serious and very painful chemical burns in the mouth, throat, esophagus and gastrointestinal tract are expected, which are life threatening. Systemic fluoride-specific effects can be caused in addition. [419]
These can consist in serious metabolic disturbances and functional impairment of the cardiovascular, muscular and nervous systems. [7978]
Fatal cases were described, e.g. following intake of approximately 100 ml of a product containing 6 – 8% HF. Findings (besides gastrointestinal effects) were: tachycardia, ventricular fibrillation, CNS depression, tetaniform cramps, disturbances in the electrolyte balance (hypocalcemia, hyperkaliemia), pulmonary edema and respiratory depression/paralysis. [99996]

**Chronic toxicity:**
Because the corrosive action of H., even in low concentrations, is widely known, frequent contact of the skin with the liquid is not expected. Corresponding scenarios have not been studied, not even in animal experiments. [99999]
Following long-term inhalative exposure, irritation to the mucous membranes and skin are assessed to be the critical effects.
Volunteers exposed to concentrations above 1.2 mg HF/m3 (1.4 ppm) suffered from slight complaints. Test persons exposed to 1.5 – 4.3 mg HF/m3 (1.8 – 5.2 ppm) for 25 days (6 h/d) felt a slight burning sensation in the eyes and on the face as well as slight irritation to the nasal mucous membranes. In several studies on large groups of persons exposed occupationally (in particular those employed in the manufacture of aluminium) who were exposed to gaseous HF mixed with respirable dust of fluorides, adverse effects in the respiratory tract were reported, e.g. irritation to the airways, reduced lung capacity, bronchitis, shortness of breath or emphysema. [7619]
These studies also repeatedly indicated increased incidences of bronchial hypersensitivity or asthma. For instance, in a group of aluminium workers (“potroom” workers) exposed to 0.56 mg HF/m3 and 0.15 mg particle-bound fluoride/m3, asthmatic symptoms (such as wheezing, dyspnea) were registered with 3.4 – 5.2 fold incidence compared with the control group. Because there was mixed exposure, also to further irritant gases (e.g. SO2) and metal dust, concentration-effect relationships for HF cannot be derived. [99996]
An allergic action of HF is not assumed.
No impairment of the lung function was registered in 2 studies on workers exposed to HF concentrations of 0.85 mg/m3 and lower than 2.5 mg/m3, respectively. [2050]
As for the fluorides, the critical systemic effect following long-term exposure to H./HF is considered to be the risk of skeletal fluorosis which increases with increasing accumulation of fluoride in the bones. After a increase of the bone density and hardness follows a decrease of the mechanical strength of the bone (increased risk of fracture) and skeletal stiffening. Subjective complaints are similar to a rheumatic disease with pain and stiffness of the joints.
Persons occupationally exposed provided indications of a developing skeletal fluorosis following exposure to 3.4 mg/m3 for 14 years. Another study demonstrated pronounced fluorosis if 2.4 – 6 mg fluoride/m3 (in
part gaseous) was inhaled for at least 10 years. [7619]
According to knowledge from epidemiological studies on persons who were exposed to fluoride mainly via
drinking water, the total intake of 14 mg fluoride/d leads to skeletal fluorosis. The threshold for fluoride
intake which can lead to adverse effects in the bones has been found to be still lower but it could not be
verified definitely. [83]
Persons occupational exposed are assumed to be able to tolerate 10 mg fluoride/day. This value was
taken into account for the derivation of the workplace threshold value for HF, together with data for the
local irritative action. [7619]

Reproductive Toxicity, Mutagenicity, Carcinogenicity:
For classifying the reproductive toxicity and mutagenic and carcinogenic potential see list in Annex VI of
the CLP regulation or TRGS 905 or List of MAK values.
(see section REGULATIONS).
[99983]
Reproductive toxicity:
There is no reason to fear a risk of damage to the
developing embryo or foetus when MAK and BAT values are
observed.
Mutagenicity:
HF/H. did not show any genotoxic potential in Ames tests.
Isolated in-vivo tests are not suitable as a basis of an assessment because of methodical shortcomings.
Also the numerous tests carried out with sodium fluoride do not permit a definite assessment of the
genotoxic potential of bioavailable fluoride. [7619]
Carcinogenicity:
No substance-specific data is available for H/HF. [99983]
Results from epidemiologic studies on persons with increased exposure to fluoride and animal
experimental studies with sodium fluoride to examine whose carcinogenic potential did not indicate any
cause for a suspicion of carcinogenicity. However, further investigations are required to enable the final
assessment of the carcinogenic potential of systemically available fluoride. There are no studies available
on possible local actions by H. in particular. [7619]

Biotransformation and Excretion:
Exposure to H. leads to the uptake of fluoride into the blood. Once absorbed it is rapidly distributed
throughout the organs. Adult persons rapidly eliminate approximately 50% of the amount taken in. The
excretion proceeds mainly within 24 hours with the urine and to a minor part via other pathways (with the
feces, sweat, saliva and minor amounts with mother’s milk).
The proportion which remains long-term in the body is almost exclusively (by approximately 99%)
deposited in the bones and teeth. During this, hydroxyl groups in the carbonate-apatite structure are
replaced by fluoride ions. The accumulated fluoride can at least partially be remobilized and excreted. The
half life for elimination out of the bones was reported to be 8 – 20 years. [83]
Under prolonged steady exposure to fluoride, the fluoride contents in urine and plasma directly reflect the
intensity of actual exposure. After occupational exposure ceases, the amount remaining in the body could
be higher than what would be expected from the current level of exposure because of the slow
mobilization of the part in the bones. [7620]

Annotation:
This occupational health information was compiled on 18.01.08.
It will be updated if necessary.

FIRST AID

Eyes:
Immediate and intensive rinsing of the contaminated eye with plenty of water (whilst protecting the
unimpaired eye) is the most important measure. [99997]
Turn the mild water jet directly towards the eye: residues of the acid must be rapidly diluted and completely removed. [160]
Then immediately transport the casualty to an eye doctor. [80105]

Skin:
Remove contaminated clothing while protecting yourself. Thoroughly rinse contaminated skin with plenty of water. Then immediately apply calcium gluconate gel (2.5%) generously and rub it in as gently as possible. If the gel is not available, apply compresses soaked with 10% calcium gluconate solution to the affected area. Arrange medical treatment. Following contamination of large areas immediately put the casualty under a shower (if a deluge shower is available, remove clothing in the shower, otherwise before showering). First aid operators must take care to protect themselves! Once rinsed, the skin should be covered with calcium gluconate compresses. Always immediately call a physician to the site of the accident. [80105]
If the body has been moistened with acid of >40%, in particular if the upper part of the body has been contaminated, concurrent massive inhalation is likely (for first aid measures see “Respiratory tract”). [99997]

Respiratory tract:
Whilst protecting yourself remove the casualty from the hazardous area and take him to the fresh air. Even if there are no complaints, the casualty should be (if possible) carried or driven. Have him take a half-upright position. As soon as possible repeatedly have the casualty deeply breath a glucocorticoid inhalation spray in. In the case of breathing difficulties have the casualty inhale oxygen. Lay the casualty down in a quiet place and protect him against hypothermia. For respiratory arrest, carry out artificial ventilation, if possible with breathing apparatus; the first aider must pay attention to protect himself. Always call a physician to the site of the accident. [80105]

Swallowing:
Rinse the mouth and spit the fluids out. Immediately: have the casualty drink 1 – 4 drinking ampules “frubiase calcium T” [80105] or 1% calcium gluconate solution in small sips (if this is not available: milk or a suspension of powdered chalk as alternatives or otherwise water). Always call a physician to the site of the accident as soon as possible. [7978] During spontaneous vomiting hold the head of the casualty low with the body in a prone position in order to avoid aspiration. Lay the casualty down in a quiet place, protect him against hypothermia and have him assume a head down position to treat him for shock. [99999]

Information for physicians:
Hydrofluoric acid (H.) triggers serious local and systemic effects. These sometimes only become noticeable after a latency period which can lead to an underestimation of the risk. Every contact with H. requires careful decontamination and treatment. [99997]

- Symptoms of acute poisoning:
  Eyes: serious pain, lacrimation -> ischemia, corneal opacity, stromal edema, vascularization, epithelial separation from the stroma, bulb perforation -> danger of irreversible eye damage [7979]
  Skin: progressive chemical burns (even due to slightly concentrated H. or also to vapors), affected areas may initially show no symptoms (erythema/paleness), even while H. is still penetrating deep into the tissue (-> damage of vessels, muscles, bones); depth pain is typical (rapid onset means that prognosis is serious); following extensive contact particularly with concentrated H., danger of severe absorptive-toxic effects
  Inhalation: due to vapors irritation/chemical burns to the mucous membranes, pain in the airways,
dyspnea, obstruction of the airways, hemorrhage, pulmonary edema (mostly starting relatively rapidly but still possible even after days); absorptive-toxic effects possible

Ingestion: severe irritation up to corrosion of the mucous membranes in contact with H., serious abdominal pain, nausea, vomiting, diarrhea, rapid onset of systemic effects

Absorption: metabolic disturbances (hypocalcemia, hypomagnesiemia, hyperkaliemia), disturbance to the heart function (tachycardia, ventricular fibrillations, hypotension) and to the muscular and nervous system (unconsciousness/coma, tremor, tetaniform cramps; respiratory paralysis), functional disturbances to the kidneys. [99997]

- Medical advice:
  Following contact with the eyes, rinse thoroughly and repeatedly with a lot of water or physiological saline. [99996] Then, rinsing with 1% calcium gluconate solution is recommended (see "Recommendations"). [80105] Arrange further treatment by an ophthalmologist as soon as possible (who should apply corticosteroids and antibiotics). [99996]
  Cover affected skin extensively with calcium gluconate gel and if possible rub it in gently. Intermittently wash it off with water and replace it by new gel. After the pain has ceased, still continue this treatment for a further 15 minutes.

For chemical burns of 2nd/3rd degree (expected for concentrations of >20% H.), calcium gluconate should be injected into the tissue concerned: local injections of 10% calcium gluconate solution [80105] or a mixture of 5 ml of 10% calcium gluconate with 5 ml of 2% lidocain is recommended. Inject 0,5 ml/cm² skin into the border region of the damaged area (up to 3 times/d or dependent on the intensity of pain; see also "Recommendations").

On the hands and feet (especially the fingers/toes), the injection seems to be problematic; so an intraarterial application of calcium gluconate may become necessary (see below).

Any blisters should be opened and treated with compresses soaked with 10% calcium gluconate solution. [7978]

For chemical burns of 3rd degree on an area equal or larger than the palm of a hand, substitution of calcium and magnesium via infusions is indicated (serum levels and the ECG must be monitored). [80105] Always further intensive care observation and treatment (therapy for shock, application of analgetics, treatment of the systemic-toxic effects; soon prophylaxis for tetanus) are indicated. [7978]

Following inhalative exposure to vapors/aerosols, immediately apply oxygen. [99997]. In addition inhalation of 2,5 – 3% calcium gluconate solution in physiological saline using a nebulizer is recommended. Carry out thorough monitoring of the respiratory function and all further prophylactic measures for pulmonary edema (including application of glucocorticoids). Following massive inhalation substitute calcium and magnesium systemically via infusions (serum levels and the ECG must be monitored). Soon also prophylaxis for pneumonia. Always carry out intensive care observation and treatment in hospital. [80105] If diluted H. has been swallowed, the initial measures recommended are dependent on the situation: careful endoscopic examination and emptying of the stomach as soon as possible; gastrolavage with 1% calcium gluconate solution. Then instill 40 g Ca gluconate. Once vital functions have been secured, always hospitalize the casualty immediately. [80105]

Some specific recommendations were provided to treat chemical burns in hospital:

Damage of subungual tissue requires extraction of the nail. Excision of chemically burned tissue (except necrotic areas) is not recommended. [7978]

Intraarterial infusion of Ca gluconate (following burns on fingers or toes) should be carried out extremely cautiously and only in hospital by a physician with experience with intraarterial infusion techniques: puncture of the centric arteria in the damaged area, catheterization, intraarterial infusion of a solution containing 20 ml of 10% calcium gluconate and 30 ml of physiological saline solution (0,9%) during 4 hours and additional prophylaxis for thrombosis. [80105]

Recommendations:

Provide the physician information about the substance/product and treatment already administered. In order to be able to give first aid, the following materials should be kept available in workplaces: the calcium gluconate formulations mentioned above, a glucocorticoid inhalation spray and drinking ampules "frubiase calcium T". [80105]

The application of calcium gluconate to the eyes is controversial because of possible calcification in the corneal stroma. On the other hand, there is the advantage that calcium gluconate can bind hydrogen
fluoride which is extremely reactive both locally and systemically. [99996]
For alleviation of H.-related depth pain or pain resulting from the injection of calcium, analgetics should be
used. [7978] On the other hand, other authors are of the opinion that pain is accepted as a safe indicator
for pathologic processes in the tissue and/or for the necessity of further injections of calcium and therefore
should not be inhibited. This decision taken by the physician responsible. [99997]
To date, the inhalation of nebulized 2.5 – 3% calcium gluconate solution following inhalation of HF has
only been used in isolated cases, so comprehensive clinical experience is not available.
The effectiveness of hemodialysis following poisoning with H. (apparently successful in isolated cases) has
not definitely been demonstrated. [99996]

Annotation:
This first aid information was compiled on 13.04.10.
It will be updated if necessary.

HANDLING AND USAGE

USAGE

The substance is used for the production of:
- fluorides
- fluorocarbons
- fluoroplastics
- cleaning and etching agents for polishing crystal glass
  or single crystal silicon plates for microelectronics
The substance is used for:
- etching/frosting of glass

TECHNICAL MEASURES - HANDLING

Workplace:
Provision of very good ventilation in the working area.
The floor must be acid resistant.
The floor has to be fluoride resistant.
The floor should not have a floor drain.
Washing facility at the workplace required.
Eye bath required. These locations must be signposted
clearly.
When handling excessive amounts of the substance an emergency shower is required.

Equipment:
Use only closed apparatus.
If dangerous pressure can arise from contact with heat, suitable safety measures and equipment should
be provided.
If release of the substance cannot be prevented, then it should be suctioned off at the point of exit.
Consider emission limit values, a purification of waste gases if necessary.
Label containers and pipelines clearly.
The equipment has to be designed so that any skin contact
with hydrofluoric acid can be safely ruled out.

Suitable materials:
Steel
Copper
Nickel
Monel
Inconel
Polyethylene PE
Polyvinyl chloride
Polystyrene
Polypropylene

Attention! Metal materials as iron, copper and nickel are stable only against concentrated hydrofluoric acid, due to formation of a fluoride protective layer. Nevertheless, corrosion liberating hydrogen increases with increasing water content. Steel is stable only against hydrofluoric acid exceeding 60 %. It should only be used if hydrofluoric acid concentration exceeds 70 %.

Unsuitable materials:
Glass
Ceramic

Advice on safer handling:
Take care to maintain clean working place.
The substance must not be present at workplaces in quantities above that required for work to be progressed.
Hydrofluoric acid containers may be under pressure.
Open and handle container carefully.
Do not leave container open.
Use leak-proof equipment with exhaust for refilling or transfer.
Avoid splashing.
Fill only into labelled container.
Use equipment that is resistant to hydrofluoric acid.
Avoid any contact when handling the substance.
Prevent seepage into flooring (use of a steel tub).
Do not transport together with incompatible substances.
Use an appropriate exterior vessel when transporting in fragile containers.
Provide lockable containers with slacklime powder.

Cleaning and maintenance:
Use protective equipment while cleaning if necessary.
Only conduct maintenance and other work on or in the vessel or closed spaces after obtaining written permission.
Only work with vessels and lines after they have been thoroughly rinsed.

TECHNICAL MEASURES - STORAGE

Storage:
Keep in locked storage or only make accessible to specialists or their authorised assistants.
Do not use any food containers - risk of mistake.
Containers have to be labelled clearly and permanently.
Store in the original container as much as possible.
Preferably use unbreakable containers rather than glass containers.
Place fragile vessels in break-proof outer vessels.
Keep container tightly closed.
Store in a cool place.
Store in a dry place.
Keep container in a well-ventilated place.
Below containers has to be a liquid-tight impounding basin.
that is impervious to hydrofluoric acid. It must be possible to remove escaping acid without danger. Containers have to be equipped with a shut-off valve. Equipment for storage or transportation has to be tested for leaks before starting up or after significant repairs or modifications.

**Conditions of collocated storage:**
Storage class 6.1 B (Non-combustible acutely toxic Cat. 1 and 2 substances)
Only substances of the same storage class should be stored together.
Collocated storage with the following substances is prohibited:
- Pharmaceuticals, foods, and animal feeds including additives.
- Infectious, radioactive and explosive substances.
- Gases.
- Flammable liquids of storage class 3.
- Other explosive substances of storage class 4.1A.
- Flammable solid substances or desensitized substances of storage class 4.1B.
- Spontaneously flammable substances.
- Substances liberating flammable gases in contact with water.
- Strongly oxidizing substances of storage class 5.1A.
- Ammonium nitrate and preparations containing ammonium nitrate.
- Organic peroxides and self reactive substances.
Under certain conditions the collocated storage with the following substances is permitted (For more details see [TRGS 510](#)):
- Oxidizing substances of storage class 5.1B.
- Combustible solids of storage class 11.
The substance should not be stored with substances with which hazardous chemical reactions are possible.

**TECHNICAL MEASURES - FIRE AND EXPLOSION PROTECTION**

**Technical, constructive measures:**
Substance is non-combustible. Select fire and explosion prevention measures according to the other used substances.

**ORGANISATIONAL MEASURES**

Instruction on the hazards and the protective measures using instruction manual ([TRGS 555](#)) are required with signature if just more than one minor hazard was detected.
Instruction must be provided before employment and then at a minimum of once per annum thereafter.
An escape and rescue plan must be prepared when the location, scale, and use of the work-site so demand.
It must be assured that the workplace limit values are being maintained. If the limit values are exceeded, additional protection measures are necessary.
The measurements must be recorded and kept on file.
The number of employees who work with the hazardous substance must be kept to a minimum. Observe the restrictions on juvenile employment as defined in the "Jugendarbeitsschutzgesetz". Observe the restrictions on the employment of expectant and nursing mothers as defined in the "Mutterschutzverordnung".
Only employees are permitted to enter the work areas. Signposting to this effect must be displayed.

**PERSONAL PROTECTION**
Body protection:
Depending on the risk, wear a tight, long apron and boots or suitable chemical protection clothing.
The protection clothing should be acid resistant.

Respiratory protection:
In an emergency (e.g.: unintentional release of the substance, exceeding the occupational exposure limit
value) respiratory protection must be worn. Consider the maximum period for wear.
Respiratory protection: Gas filter E, colour code yellow.
For details on the requirements and the maximum concentrations for use, consult the "Regeln für den
Einsatz von Atemschutzgeräten" (BGR 190).
Perhaps also necessary for improved protection:
Respiratory protection: Combination filter E - P2 or E - P3, colour code yellow-white.
For details on the requirements and the maximum concentrations for use, consult the "Regeln für den
Einsatz von Atemschutzgeräten" (BGR 190).
Respiratory protection: insulating device.
Use for concentrations above the usage limits for filter devices, for oxygen concentrations below 17%
volume, or in circumstances which are unclear.

Eye protection:
Sufficient eye protection must be worn.
Wear chemical safety goggles.
If the face is at risk as well as the eyes, a protective shield must also be worn.
If vapours or aerosols that may injure the eyes arise, then safety of the eyes can best be guaranteed by
wearing a full mask.

Hand protection:
Use protective gloves. The glove material must be sufficiently impermeable and resistant to the substance.
Check the tightness before wear. Gloves should be well cleaned before being removed, then stored in a
well ventilated location. Pay attention to skin care.
Textile or leather gloves are completely unsuitable.
For concentrations < 10% :
The following materials are suitable for protective gloves (Permeation time >= 8 hours):
Natural rubber/Natural latex - NR (0,5 mm) (use non-powdered and allergen free products)
Polychloroprene - CR (0,5 mm)
Nitrile rubber/Nitrile latex - NBR (0,35 mm)
Butyl rubber - Butyl (0,5 mm)
Fluoro carbon rubber - FKM (0,4 mm)
Polyvinyl chloride - PVC (0,5 mm)

For concentrations < 40% :
The following materials are suitable for protective gloves (Permeation time >= 8 hours):
Polychloroprene - CR (0,5 mm)
Butyl rubber - Butyl (0,5 mm)
Fluoro carbon rubber - FKM (0,4 mm)
Polyvinyl chloride - PVC (0,5 mm)

Protective gloves of the following materials should not be worn longer than 4 hours continually
(Permeation time >= 4 hours):
Natural rubber/Natural latex - NR (0,5 mm) (use non-powdered and allergen free products)

Protective gloves of the following materials should not be worn longer than 1 hour continually (Permeation
time >= 1 hour):
Nitrile rubber/Nitrile latex - NBR (0,35 mm)
For concentrations < 73%:

The following materials are suitable for protective gloves (Permeation time >= 8 hours):
Fluoro carbon rubber - FKM (0,4 mm)

Protective gloves of the following materials should not be worn longer than 4 hours continually (Permeation time >= 4 hours):
Butyl rubber - Butyl (0,5 mm)

Protective gloves of the following materials should not be worn longer than 2 hours continually (Permeation time >= 2 hours):
Polychloroprene - CR (0,5 mm)

Following materials are unsuitable for protective gloves because of degradation, severe swelling or low permeation time:
Natural rubber/Natural latex - NR
Nitrile rubber/Nitrile latex - NBR
Polyvinyl chloride - PVC

The times listed are suggested by measurements taken at 22 °C and constant contact. Temperatures raised by warmed substances, body heat, etc. and a weakening of the effective layer thickness caused by expansion can lead to a significantly shorter breakthrough time. In case of doubt contact the gloves’ manufacturer. A 1.5-times increase / decrease in the layer thickness doubles / halves the breakthrough time. This data only applies to the pure substance. Transferred to mixtures of substances, these figures should only be taken as an aid to orientation.

**Skin protection:**
Skin protection preparations do not protect sufficiently against the substance. Wear protective gloves. The skin must be washed with soap and water before breaks and at the end of work. Clean area around the fingernails carefully. Apply fatty skin-care products after washing.

**Industrial hygiene:**
Foods, beverages and other articles of consumption must not be consumed at the work areas. Suitable areas are to be designated for these purposes. Avoid contact with skin. Do not allow the substance or its solution to dry on the skin. In case of contact wash skin. Avoid contact with eyes. In case of contact rinse the affected eye(s). Avoid inhalation of vapour or mist. Avoid contact with clothing. Contaminated clothes must be exchanged and cleaned carefully. Before cleaning clothes rinse thoroughly first in water. Provide washrooms with showers and if possible rooms with separate storage for street clothing and work clothing.

**DISPOSAL CONSIDERATIONS**
Hazardous waste according to Waste Catalogue Ordinance (AVV). If there is no way of recycling it must be disposed of in compliance with the respective national and local regulations.

Collection of small amounts of substance:
Do not put/place waste into sink or dust bin. Inorganic fluoride solutions must be handled with great care. Avoid any contact and only work with it in a powerful hood with a closed front panel. Residuals dissolved in water can precipitate as calcium fluoride.
Place precipitate in collecting container for inorganic solids. Place filtrates in collecting containers for salt solutions (pH 6-8) or in collecting containers for toxic inorganic residuals and heavy-metal salts and their solutions.
Collection vessels must be clearly labelled with a systematic description of their contents and with the hazard symbol and the R and S phrases. Store the vessels in a well-ventilated location. Entrust them to the appropriate authorities for disposal.

ACCIDENTAL RELEASE MEASURES

Evacuate area. Warn affected surroundings.
The hazardous area may only be entered once suitable protective measures are implemented. Only then can the hazardous situation be removed.
Wear respiratory protection, eye protection, hand protection and body protection (see chapter Personal Protection).
Take up with an absorbent (absorbent and neutralizer for spilled acids) and dispose of according to regulations.
Pump off larger quantities.
Afterwards ventilate area and wash spill site.

Endangerment of drinking water and environment:
Avoid escape into water, drainage, sewer, or the ground. A hazard for drinking water sources when larger quantities get into groundwater. Inform the responsible authorities.

FIRE FIGHTING MEASURES

Instructions:
Substance is incombustible. Select fire fighting measures according to the surrounding conditions.
In case of ambient fire:
Cool surrounding containers with water spray.
If possible, take container out of dangerous zone.
Contain vapours with water spray.
Stay on upwind side.
Do not allow runoff to get into the sewage system.

Special protective equipment:
Ambient fire may liberate hazardous vapours or decomposition products.
Hydrogen fluoride
Wear self-contained breathing apparatus and special tightly sealed suit.

REGULATIONS

GHS-CLASSIFICATION AND LABELLING

Classification:
Acute toxicity, Category 2, inhalation; H330
Acute toxicity, Category 1, dermal; H310
Acute toxicity, Category 2, oral; H300
Skin corrosion, Category 1A; H314
Signal Word: "Danger"

Hazard Statement - H-phrases:
H330: Fatal if inhaled.
H310: Fatal in contact with skin.
H300: Fatal if swallowed.
H314: Causes severe skin burns and eye damage.

Precautionary Statement - P-phrases:
P260: Do not breathe dust/fume/gas/mist/vapours/spray.
P264: Wash ... thoroughly after handling.
P280: Wear protective gloves/protective clothing/eye protection/face protection.
P284: Wear respiratory protection.
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.

Manufacturer's specification by Sigma-Aldrich Group

Source: 01221

The substance is listed in appendix VI, table 3.1 of CLP regulation.

Source: 99999

GHS-CLASSIFICATION OF MIXTURES
Skin Corr. 1A; H314: C >= 7 %
Skin Corr. 1B; H314: 1 % <= C < 7 %
Eye Irrit. 2; H319: 0,1 % <= C < 1 %

The general concentration limits from Annex 1 of the Regulation (EU) 1272/2008 are to be used for possible further available substance classifications.

Source: 07500

EUROPEAN CLASSIFICATION

T++; R26/27/28
C; R35

T+ Very toxic
C Corrosive
Risk phrases (R-phrases):
R 26/27/28  Very toxic by inhalation, in contact with skin and if swallowed
R 35      Causes severe burns

Safety advices (S-phrases):
S (1/2)  Keep locked up and out of the reach of children (if sold to the general public)
S 7/9    Keep container tightly closed and in a well-ventilated place
S 26    In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S 36/37 Wear suitable protective clothing and gloves
S 45    In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

EU classification according to GHS regulation, appendix VI, table 3.2
(formerly according to 26th adaption directive 2000/32/EEC).

Source: 07500

CLASSIFICATION OF MIXTURES

Specific Concentration Limits:
C; R35: C >= 7 %
C; R34: 1 % <= C < 7 %
Xi; R36: 0,1 % <= C < 1 %

The general concentration limits from Preparation Directive 1999/45/EU are to be used for possible further available substance classifications.

Hydrofluoric acid
Source: 07500

WORKPLACE LABELLING ACCORDING TO GERMAN ASR A1.3

Prohibition label:

No Smoking
No admittance for unauthorized persons
No eating and drinking

Warning label:
Caution - toxic material

Caution - corrosive material

Precept label:

Use safety goggles

Wear safety gloves

GERMAN WATER HAZARD CLASS

Substance No: 254
WGK 2 - hazard to waters
Classification according to Annex 3 of the Administrative Regulation of Substances Hazardous to Water (VwVwS)

TRANSPORT REGULATIONS

UN Number: 1790
Shipping name: Hydrofluoric acid, aqueous solution, with more than 60 % hydrogen fluoride
Hazard Identification Number: 886
Class: 8 (Corrosive Substances)
Packing Group: I (high danger)

Shipping name: Hydrogen fluorides, aqueous solution, with not more than 60 % hydrogen fluoride
Hazard Identification Number: 86
Class: 8 (Corrosive Substances)
Packing Group: II (medium danger)

Danger Label: 8/6.1
Tunnel restrictions:
Depending on the packing group.

**TRGS 900 - GERMAN OCCUPATIONAL EXPOSURE LIMIT VALUES**

1 ml/m³
0,83 mg/m³

Peak limitation: Excursion factor 2
Duration 15 min, mean; 4 times per shift; interval 1 hour
Category I - Substances for which local irritant effects determine the exposure limit value, also respiratory allergens

Risk of percutaneous absorption
There is no reason to fear a risk of damage to the developing embryo or foetus when AGW and BGW are adhered to.

Source: DFG
Source: 05350

**EC OCCUPATIONAL EXPOSURE LIMIT VALUES**

RL 2000/39/EG
Recommended indicative occupational exposure limit value for the European Community
A national occupational exposure limit value has to be set.
8 hours limit value: 1,5 mg/m³ (1,8 ppm)
Short term limit value: 2,5 mg/m³ (3 ppm)

**RECOMMENDATIONS OF MAK-COMMISSION**

This data is recommended by scientific experience and is not established law.

1 ml/m³
0,83 mg/m³

Limitation of exposure peaks: Excursion factor 2
Duration 15 min, mean; 4 times per shift; interval 1 hour

Pregnancy: Group C
There is no reason to fear a risk of damage to the developing embryo or foetus when MAK and BAT values are adhered to.

Source: 08096

**GERMAN BIOLOGICAL EXPOSURE INDECES**

Measured parameter:
Fluoride
Value: 7 mg/g
creatinine
Sampling time: end of exposure/end of shift
Assay material: Urine
HF and inorganic Fluorine compounds
Source: 05347

Measured parameter:
Fluoride
Value: 4 mg/g creatinine
Sampling time: at the beginning of the next shift
Assay material: Urine
HF and inorganic Fluorine compounds
Source: 05347

GERMAN ORDINANCE OF FAILURE

Annex I - No: 1
Threshold for operating range to §1 sec. 1
- Record 1: 5000 kg
- Record 2: 20000 kg
Scope: very toxic substances

Please note: In the GESTIS database only the lowest amount threshold of a substance is given. If a substance has several classifications, use must be made of the amount threshold from appendix I which corresponds to the respective classification.

RESTRICTIONS OF USE / BANS OF USE

Annex XVII, Point 3
1. The putting into circulation and the utilisation of the substance is not allowed in decorative objects, games and joke articles.
2. Substances labelled with R 65 which can be utilised as fuels in decorative lamps and are put in circulation in amounts of 15 l or less must not contain a dye and/or a perfume.
Further information on prohibitions can be taken from the regulation.

Prohibitions of Chemicals Ordinance; status - November 2010
Annex to §1, Section 5

Directives on Safety in School (GUV-SI 8070); status - March 2003
Part I -3.9 Restrictions of contact for pupils
Pupils must not conduct experiments with this substance.
The substance must not be provided for home experiments.

Consumer Goods Ordinance; status - February 2011
Attachment 1 to § 3, Point 5
The substance must not be utilised for the production or treatment of joke articles.
FURTHER REGULATIONS

TRGS 200
Einstufung und Kennzeichnung von Stoffen, Zubereitungen und Erzeugnissen; Ausgabe Februar 2007, berichtet Februar 2010, mit Änderungen und Ergänzungen August 2010

TRGS 201
Einstufung und Kennzeichnung von Abfällen zur Beseitigung beim Umgang; Ausgabe Juli 2002

TRGS 400
Gefährdungsbeurteilung für Tätigkeiten mit Gefahrstoffen; Ausgabe Januar 2008

TRGS 555
Betriebsanweisung und Information der Beschäftigten; Ausgabe Februar 2008; geändert und ergänzt Juli 2009

TRGS 600
Substitution; Ausgabe August 2008

TRGS 402
Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition; Ausgabe Januar 2010

TRGS 420
Verfahrens- und stoffspezifische Kriterien (VSK) für die Gefährdungsbeurteilung; Ausgabe Januar 2006; zuletzt geändert und ergänzt Februar 2010

TRGS 401
Gefährdung durch Hautkontakt, Ermittlung - Beurteilung - Maßnahmen; Ausgabe Juni 2008; berichtet Februar 2010

TRGS 500
Schutzmaßnahmen; Ausgabe Januar 2008, ergänzt Mai 2008

TRGS 510
Lagerung von Gefahrstoffen in ortsbeweglichen Behältern; Ausgabe Oktober 2010

BG-Grundsätze für arbeitsmedizinische Vorsorgeuntersuchungen
G 34 : Fluor oder seine anorganischen Verbindungen

PREVENTIVE MEDICAL CHECK-UPS

Preventive medical check-ups have to be offered if during activities involving the substance the worker is exposed to it.

The employer shall request regular preventive medical check-ups if for activities with the substance the occupational exposure limit value is exceeded or if the substance is subject to dermal absorption and such absorption could endanger health and safety of the worker.