Utilisation de l'acide fluorhydrique dans les laboratories de chemie: Prévention des risques

[Utilization of hydrofluoric acid in chemical laboratories: Prevention of risks]

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ABSTRACT

The use of strong acids is widespread in laboratories and their corrosive properties are well documented. Hydrofluoric acid is a special case because the burns it causes, made more critical by its affinity for blood calcium, require immediate medical care in order to prevent possibly drastic consequences. This account of its effects is aimed at all laboratory users of hydrofluoric acid.

Key Words: hydrofluoric acid; laboratory toxicity; occupational risk; first aid

The recent article "Manipulations dans les laboratories de chemie: Risque et prevention" [Manipulations in chemical laboratories -- Risks and prevention] published by the INRS [1], presents the entirety of the preventive measures that are applicable in the framework of the activities of chemical laboratories where, notably, the corrosive properties of acids and bases are well known.

Among the acids, two can give rise to serious accidents due to their affinity for serum calcium: these are hydrofluoric acid and oxalic acid (concentrated or dilute). The latter is less frequently used in laboratories, while there are multiple known applications of hydrofluoric acid solutions in analytical chemistry and industry.

It seems opportune to propose a review of risk prevention for contact with this acid and first aid measures to be undertaken in case of accidents.

1. Physico-chemical properties

1.1. Physical properties [2]

Hydrogen fluoride is a liquid at less than 200˚ C, volatile with an irritating odor, and fumes in air. It is highly soluble in water.

1.2. Chemical properties [2]

Physical Characteristics

Molecular weight:	20.01
Melting point:	-83.40˚ C
Boiling point (at atmospheric pressure):	+19.50˚ C
Density at 0˚ C	1.002
Vapor density/air:	0.7

Hydrogen fluoride is a stable compound with highly reactive properties and polymerizes easily. It is one of the strongest mineral acids.

It reacts vigorously with water. In the presence of humidity, its vapor produces abundant white fumes. It attacks silica and silicates (and therefore, glass): in the course of this reaction it forms very volatile and corrosive hydrogen hexafluorosilicate.

In the absence of water, it does not attack steel, nickel, aluminum, or copper. In contrast, aqueous solutions attack the majority of metals with evolution of hydrogen (very violent reactions with alkalines and the alkaline earths): only platinum, gold, silver, and mercury are not attacked. Fluoride polymers (teflons) are resistant to the action of hydrogen fluoride. Polyethylene and polystyrene are only resistant to dilute aqueous solutions. The acid reacts violently with strong bases, anhydrous or in concentrated solutions.

1.3. Storage containers [2,3]

Because of its physico-chemical properties, hydrofluoric acid should not be stored in glass containers. Stainless steel is suitable for the anhydrous acid or solutions greater than 70% hydrogen fluoride; for strengths less than 70% containers of bronzed aluminum, lead, materials based on synthetic resins, or polyethylene (in the latter case, the National Safety Council specifies strengths less than 52% [3]).

2. Toxic risks

2.1. General risks due to corrosive acids

At high concentrations, they all cause penetrating lesions.

Table I displays the list of acids and similar compounds with their corrosive and pulmonary effects at 1N concentration [4].

In this series, oxalic acid and hydrofluoric acid are considered separately because of their ability to bind serum calcium when in contact with the body.

Local effects of corrosive acids

All cause severe cutaneous burns, then necrotic eschars with slow healing.

In the eye, all can cause corneal ulcerations which scar over and leave a film. Blindness is possible following large splashes (sulfuric acid).

Inhalation of corrosive acids

For all, the profile of severe injury is the same: respiratory distress with pulmonary edema, cyanosis, and anoxia. Hemoptysis and dyspnea can last for several days (notably in the case of exposure to nitric acid vapors).

Ingestion of corrosive acids

Pain in the mouth, pharynx and the digestive tract can be immediate. Diarrhea and bloody vomiting and a state of shock can follow. If the subject survives, some severe complications are to be feared in the days which follow the ingestion.

2.2. The specific case of hydrofluoric acid

In the tissues of the organism, hydrofluoric acid forms numerous salts of which only calcium fluoride and magnesium fluoride are relatively insoluble and stable; the others are soluble and dissociable, liberating fluoride ion which remains available to pursue its chemical action on the tissues. The very diffusible fluoride ion penetrates the skin and the adjacent soft tissues, and then the deep layers and causes liquefaction necrosis and even corrosion of the bones.

From the metabolic viewpoint, its avidity for calcium causes sometimes severe hypocalcemia (shock states leading to death). The rapidity of intervention, during contact with the acid, is often contrary due to the fact of the character of the burns which only become apparent after a certain time period (from 30 minutes to sometimes several hours, depending on the dilution of the solution).

The penetration of the acid is rapid when it is not neutralized and especially when it penetrates the epidermis and the dermis: necrosis is then inevitable and necessitates resection of the tissues. This is why urgent first aid in cases of skin contact with the acid is paramount.

The risk of accidental ingestion by mouth is particularly serious, with localized gastrointestinal tract burns complicated by a generalized risk of binding of serum calcium.

3. First aid
[5 to 11]

3.1. In case of eye splashes [7,10]

In 1986, the *Documents pour le médecin du Travail* [Documents for the Occupational Physician] distributed a worksheet concerning the risks of hydrofluoric acid [7].

The treatment described by P. McCulley et al in 1983 (United States [10]) following animal studies with HF ocular burns was reviewed in this worksheet, comprising:

- Immediate lavage of the effected eye with the eyelids opened for 15 minutes with copious amounts of water;
- No colloid, but eventually an isotonic artificial tears solution;
- Transporting the burned patient immediately to the nearest hospital (emergency department or ophthalmology) and communicating the nature of the chemical agent responsible for the burn.

3.2. In case of skin splashes [5,7 to 9,11]

A 1985 paper from the United States (W.M. Bracken et al [11]) described an animal experiment evaluating the evolution of 70% HF burns after different treatments which included quarternary ammonium salts, magnesium oxide, and magnesium sulfate among others, especially calcium gluconate.

According to these authors, only calcium gluconate had an undeniable protective action against progression of the lesions in a lasting manner.

The conclusions of this experiment are found in treatment protocols described in the literature [5,7,9]:

- In case of skin contact with HF, it is a priority to remove contaminated clothing and wash with a copious amount of water for at least 15 minutes. This step is essential;
- In case of exposure of a large body surface area (greater than 20 cm^2), lavage should be performed during transport to the nearest hospital (paramedics or fire/EMS in rural areas);
- Then apply 2.5% calcium gluconate gel until the pain is relieved;
- If the total body surface area of the burn exceeds 20 cm^2, administer calcium gluconate tablets or drinkable ampoules;
- The worker should be transported to the nearest hospital for a consultation, even for a burn which has been relieved (a healthcare provider should accompany the patient and ambulance transportation is necessary). Transmit to the receiving facility the nature of the acid and the etiology of the burn.

3.3. In case of vapor inhalation

After having removed the worker from the contaminated atmosphere, transport the patient to a hospital (transport by an ambulance with respiratory assistance capabilities or paramedics). Eventually, contact a poison center.

3.4. In case of accidental ingestion by mouth

- Do not induce vomiting.
- Call paramedics or EMTs for rapid transport to a hospital.
- Give nothing by mouth except in cases of delay (long transport time); consider administering 5% calcium in water (ampoules, tablets).
- If the poisoned patient is unconscious, place in the left lateral decubitus position and assess the pulse and respirations.

4. Experience in chemical laboratories

In several laboratories of the INRS and the Caisses Régionales d'Assurance Maladie (CRAM) [Regional Health Insurance Offices], some solutions of hydrofluoric acid are currently utilized for mineralizing atmospheric samples on quartz fiber filters (ultra-pure silica). In anticipation of potential skin burns, frequent washing of the hands and forearms was specified (latex gloves were permeable to the acid after prolonged contact). For treatment purposes, pots of 2.5% calcium gluconate gel were kept in the refrigerator and others were placed in the analytical area (see Appendix 1). The stock was renewed annually, which is the shelf life of this product.

In addition, each technician at risk was provided a pot of calcium gluconate gel to keep at home in order to treat any painful skin manifestations that occurred after work hours.

These measures, of modest cost to the laboratory, have been practiced for 15 years without any burns that did not rapidly resolve. Since 1998, special eyewash devices containing Hexafluorine have been placed in the INRS laboratories. This equipment was completed at the end of 1999 by Hexafluorine portable stand-alone showers that can be taken to the work area (Appendix I).

These emergent first aid measures were evident among the measures of preventive techniques presented in this note and which are in permanent application in the laboratories

5. Prevention

This information should be given to users: hydrofluoric acid is a corrosive acid, its utilization carries the same risks as all acids enumerated in Table I, moreover, it has an affinity for serum calcium. However, pain which occurs in a nearly immediate fashion with other concentrated or dilute corrosive agents, can appear late during an exposure.

5.1. Prevention techniques

- Stocking of small quantities (several liters of solution at most), in an area with adequate local ventilation, in an inert container (not glass) [2,3].
- High-volume shower and eyewashes, eyewashes close to work areas.
- Mandatory personal protection: water-tight goggles, HF resistant cuffed gloves, PVC boots and apron.
- Handling under a well-ventilated hood behind a screen. The hood should be made of materials compatible with HF (no glass windows), utilize small quantities at a time.
- No smoking during manipulation.
- No work should be done with bare hands, even with very dilute solutions.

5.2. Medical prevention

This is defined by the occupational physician.

Insist on having safety personnel available in all activities where hydrofluoric acid is in current use.

A placard should clearly display the indispensable telephone numbers: paramedics, fire department, poison center.

The pharmacy chest should be provided with:

- Calcium gluconate in injectable and oral solutions (replace according to the expiration dates);
- Calcium tablets;
- Pots of 2.5% calcium gluconate gel. Anticipatory stocking at potential accident sites (see Appendix I);
- Hexafluorine individual eyewashes placed in laboratories at risk and replaced according to the expiration date (see Appendix I).

6. Regulation -- labeling

The INRS fiche toxicologique No. 6 [toxicology memo No. 6] summarizes all the texts which have dealt with hygiene and workplace safety in the presence of hydrofluoric acid [2].

In the category of prevention of accidents from skin or mucous membrane contact with this acid are above all found in texts dealing with labeling and protection of the environment and the general public.

6.1. Labeling

- For anhydrous hydrogen fluoride.
  The order of April 20, 1994 (Journal Officiel [Official Journal] of May 8, 1994) which specifies labels which state **Very Toxic** and **Corrosive** as well as risk statements R 26/27/28-35 and cautionary recommendations [2].

- For aqueous solutions of hydrogen fluoride of 0.1% and greater.
  The order of April 20, 1994 (Journal Officiel [Official Journal] of May 8, 1994) as follows:
  - for concentrations >/= 7%: **Very Toxic, Corrosive,** risk phrases: R 23/24/25-34;
  - for concentrations between 1 and 7%: **Toxic, Corrosive**, risk phrases: R 23/24/25-34
  - for concentrations between 0.1 and 1%: **Noxious**; risk phrases: R 20/21/22-36

- For preparations other than aqueous solutions listed above and containing hydrogen fluoride.
  Order of February 21, 1990 modified (Journal Officiel [Official Journal] of March 24, 1990); the concentration limits are set in Annex I of the order of April 24, 1994.

6.2. Protection of the environment

Installations classées pour la protection de l'environment [Installations classified for protection of the environment], Paris, Imprimerie des Journaux Officiels [Official Journals Printing Office], brochures No. 1001:

- No. 1110, manufacturing;
- No. 1111, use or storage;
- Order of September 26, 1985 modified relative to workplaces for surface treatments;
- Order of March 31, 1980 concerning the electrical installations of establishments that may present a risk of explosions;
- Orders of July 10, 1990 and March 1, 1983 modified relative to wastes.

6.3 Protection of the general public

Decree of December 29, 1988 relative to poisonous substances and preparations (articles R. 5149 to R. 5170 of the Code de la Santé Publique [Code of Public Health]) and circulated September 2, 1990 (Journal Officiel [Official Journal] of October 13, 1990).

Conclusion

The utilization of strong acids is widespread in laboratories and their corrosive properties are well known. The case of hydrofluoric acid is particular because the burn which it causes, aggravated by its strong affinity for serum calcium, imposes immediate therapeutic measures in order to prevent sequelae which can be dramatic.

The present review is designed to be used by all laboratory technicians who utilize this acid.

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References

[Refer to the French original]

TABLE I
CORROSIVE AND PULMONARY EFFECTS OF ACIDS

Acids and Related Compounds; 1N Concentration	Corrosive effects	Pulmonary effects
Acetic acid	2	2
Acetic anhydride	2	2
Hydrobromic acid	4	4
Hydrochloric acid	4	4
Chlorosulfonic acid	4	4
Formic acid	2	1
Hydroiodic acid	4	4
Lactic acid	2	1
Nitric acid	4	4
Osmic acid	4	4
Peracetic acid	4	1
Perchloric acid	4	2
Phosphoric acid	4	1
Sulfurous acid	4	4
Sulfuric acid	4	4
Tartric acid	2	1
Trichloroacetic acid	4	4
Acetic anhydride	3	3
Chloric anhydride	4	4
Maleic anhydride	2	1
Sulfurous anhydride	4	4
Sulfuric anhydride	4	4

APPENDIX 1
Suppliers of 2.5% Calcium Gluconate Gel

Pharmacie centrale des hôpitaux de Paris
[Paris hospitals central pharmacy]
7, rue du Fer-à-Moulin
75005 Paris
(20 g tube -- shelf-life 30 months)

Pharmacie Bérnard "Sécurimed"
[Bérnard "Sécurimed" Pharmacy]
28, rue Blanqui
BP 49
59411 Coudekerque Branche cedex
Tel: 03 28 64 75 45
(45 g pots -- shelf-life 12 months)

Suppliers of Hexafluorine® for Eyewashes and Stand-Alone Portable Showers

Sécurimed
28, rue Blanqui
BP 49
59411 Coudekerque Branche cedex
Tel: 03 28 64 75 45

Prevor
Moulin de Verville
95760 Valmondois
Tel: 01 34 08 96 96