

NIOSH Skin Notation Profiles

Hydrogen Flouride/Hydrofluoric Acid (HF)

SKK

ID^{SK}

[SK]

SYS

SYS (FATAL)

DIR

DIR (IRR)

DIR (COR)

SEN

NIOSH Skin Notation (SK) Profiles

Hydrogen Fluoride/Hydrofluoric acid (HF)

[CAS No. 7664–39–3]

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Foreword

As the largest organ of the body, the skin performs multiple critical functions, such as serving as the primary barrier to the external environment. For this reason, the skin is often exposed to potentially hazardous agents, including chemicals, which may contribute to the onset of a spectrum of adverse health effects ranging from localized damage (e.g., irritant contact dermatitis and corrosion) to induction of immune-mediated responses (e.g., allergic contact dermatitis and pulmonary responses), or systemic toxicity (e.g., neurotoxicity and hepatotoxicity). Understanding the hazards related to skin contact with chemicals is a critical component of modern occupational safety and health programs.

In 2009, the National Institute for Occupational Safety and Health (NIOSH) published *Current Intelligence Bulletin (CIB) 61: A Strategy for Assigning New NIOSH Skin Notations* [NIOSH 2009–147]. This document provides the scientific rationale and framework for the assignment of multiple hazard-specific skin notations (SK) that clearly distinguish between the systemic effects, direct (localized) effects, and immune-mediated responses caused by skin contact with chemicals. The key step within assignment of the hazard-specific SK is the determination of a substance's hazard potential, or its potential for causing adverse health effects as a result of skin exposure. This determination entails a health hazard identification process that involves use of the following:

- Scientific data on the physicochemical properties of a chemical
- Data on human exposures and health effects
- Empirical data from in vivo and in vitro laboratory testing
- Computational techniques, including predictive algorithms and mathematical models that describe a selected process (e.g., skin permeation) by means of analytical or numerical methods.

This *Skin Notation Profile* provides the SK assignment and supportive data for hydrogen fluoride/hydrofluoric acid (HF, CAS No. 7664–39–3). In particular, this document evaluates and summarizes the literature describing the substance's hazard potential and its assessment according to the scientific rationale and framework outlined in CIB 61. In meeting this objective, this *Skin Notation Profile* intends to inform the audience—mostly occupational health practitioners, researchers, policy- and decision-makers, employers, and workers in potentially hazardous workplaces—so that improved risk-management practices may be developed to better protect workers from the risks of skin contact with the chemical of interest.

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Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ATSDR	Agency for Toxic Substances and Disease Registry
CIB	Current Intelligence Bulletin
cm ²	square centimeter(s)
cm/hr	centimeter(s) per hour
(COR)	subnotation of SK: DIR indicating the potential for a chemical to be corrosive following exposure of the skin
DIR	skin notation indicating the potential for direct effects to the skin following contact with a chemical
EC	European Commission
(FATAL)	subnotation of SK: SYS indicating chemicals are highly or extremely toxic and may be potentially lethal or life-threatening following exposure of the skin
GHS	Globally Harmonized System of Classification and Labeling of Chemicals
HF	hydrogen fluoride/hydrofluoric acid
IARC	International Agency for Research on Cancer
LD ₅₀	dose resulting in 50% mortality in the exposed population
LD _{Lo}	dermal lethal dose
LOAEL	lowest-observed-adverse-effect level
mg	milligram(s)
mg/cm ² /hr	milligram(s) per square centimeter per hour
mg/kg	milligram(s) per kilogram body weight
mg/m ³	milligram(s) per cubic meter
mL	milliliter(s)
MW	molecular weight
NIOSH	National Institute for Occupational Safety and Health
NOAEL	no-observed-adverse-effect level
NTP	National Toxicology Program
OSHA	Occupational Safety and Health Administration
SK	skin notation
SYS	skin notation indicating the potential for systemic toxicity following exposure of the skin
USEPA	United States Environmental Protection Agency

Glossary

Absorption—The transport of a chemical from the outer surface of the skin into both the skin and systemic circulation (including penetration, permeation, and resorption).

Acute exposure—Contact with a chemical that occurs once or for only a short period of time.

Cancer—Any one of a group of diseases that occurs when cells in the body become abnormal and grow or multiply out of control.

Contaminant—A chemical that is (1) unintentionally present within a neat substance or mixture at a concentration less than 1.0% or (2) recognized as a potential carcinogen and present within a neat substance or mixture at a concentration less than 0.1%.

Cutaneous (or percutaneous)—Referring to the skin (or through the skin).

Dermal—Referring to the skin.

Dermal contact—Contact with (touching) the skin.

Direct effects—Localized, non-immune-mediated adverse health effects on the skin, including corrosion, primary irritation, changes in skin pigmentation, and reduction/disruption of the skin barrier integrity, occurring at or near the point of contact with chemicals.

Immune-mediated responses—Responses mediated by the immune system, including allergic responses.

Sensitization—A specific immune-mediated response that develops following exposure to a chemical, which, upon re-exposure, can lead to allergic contact dermatitis (ACD) or other immune-mediated diseases such as asthma, depending on the site and route of re-exposure.

Substance—A chemical.

Systemic effects—Systemic toxicity associated with skin absorption of chemicals after exposure of the skin.

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1 Introduction

1.1 General Substance Information

Chemical: Hydrogen fluoride/
Hydro fluoric acid (HF)*

CAS No: 7664–39–3

Molecular weight (MW): 20

Formula: HF

Synonyms:

HF; Anhydrous hydrogen fluoride;
Aqueous hydrogen fluoride; Hydrofluoric acid; HF-A; Antisal 2B;
Etching acid; Fluorohydric acid;
Fluoric acid

Use:

HF is primarily used as an industrial raw material, in separating uranium isotopes, as a cracking catalyst in oil refineries, etching processes, and as a solvent in the manufacturing of silicon semiconductor chips and in analytical chemistry laboratories; an estimated 770 million pounds (~350 million kilograms) of HF was used in 2001 [ATSDR 2003].

1.2 Purpose

This *Skin Notation Profile* presents (1) a brief summary of technical data associated with skin contact with HF and (2) the rationale behind the hazard-specific skin notation (SK) assignment for HF. The SK assignment is based on the scientific rationale and logic outlined in the *Current Intelligence Bulletin (CIB) 61: A Strategy for Assigning New NIOSH Skin Notations* [NIOSH 2009]. The summarized information and health hazard assessment are limited to an evaluation of the potential health effects of dermal exposure to HF. A literature search was conducted through July 2010 to identify information on HF,

including but not limited to data relating to its toxicokinetics, acute toxicity, repeated-dose systemic toxicity, carcinogenicity, biological system/function-specific effects (including reproductive and developmental effects and immunotoxicity), irritation, and sensitization. Information was considered from studies of humans, animals, or appropriate modeling systems that are relevant to assessing the effects of dermal exposure to HF.

1.3 Overview of SK Assignment for HF

HF is potentially capable of causing both systemic toxicity and direct adverse effects on the skin following dermal exposure. A critical review of available data provides evidence that skin contact with HF may be extremely hazardous and life-threatening, causing severe skin corrosion and acute systemic toxicity. NIOSH has designated HF with the following SK assignment:

*The exposure guidelines and SK assignment stated in this document apply to hydrogen fluoride and hydrofluoric acid. Unless otherwise specified, the term hydrogen fluoride or the abbreviation “HF” refers to all evaluated substances.

Table 1. Summary of the SK assignment for HF

Skin notation	Critical effect(s)	Available data
SK: SYS (FATAL)	Cardiac arrhythmia; systemic fluorosis; hypocalcemia, hyperkalemia; hypomagnesemia	Sufficient human data; sufficient animal data
SK: DIR (COR)	Skin corrosivity	Sufficient human data; sufficient animal data

SK: SYS (FATAL)-DIR (COR). Table 1 provides an overview of the critical effects and data used to develop the SK assignment for HF. The following section provides additional detail about the potential health hazards of skin contact with HF and the rationale behind the SK assignment.

2 Systemic Toxicity from Skin Exposure (SK: SYS)

No *in vivo* or *in vitro* toxicokinetic data were identified that would enable estimating the absorption of HF following dermal exposure. However, several fatalities have been reported in the literature following accidental occupational dermal exposure to anhydrous (approximately 100%) HF covering as little as 2.5% of total body surface area [Tepperman 1980] or dilute HF solutions (up to 70% concentration) covering as little as 9% of the body surface area [Mayer and Gross 1985; Chan et al. 1987; Blodgett et al. 2001]. Bjornhagen et al. [2003] reported that an individual who had 7% of the body surface exposed to 71% HF suffered from severe burns, pronounced fluoride intoxication, and recurrent ventricular fibrillation. Accidental exposures to household consumer products containing dilute HF [Mullett et al. 1987; Blodgett et al. 2001] have also resulted in fatalities. In all these cases, death from HF skin burns was due to severe systemic fluorosis resulting in electrolyte imbalances,

such as hypocalcemia, hyperkalemia, and hypomagnesemia. These imbalances lead to cardiac arrhythmias, the primary cause of death in HF injuries [Greco et al. 1988; Bertolini 1992; Wedler et al. 2005]. Evidence of dermal absorption of HF has also been provided by studies in animals. For example, topical application of 2% HF to rabbits for 1 hour or 4 hours under occluded conditions resulted in significant systemic absorption of fluoride [Derelanko et al. 1985]. In that study, the amount of fluoride absorbed correlated with the duration of exposure. In another study, dermal application of 0.25 milliliter (mL) or 0.5 mL of 48% HF to 6 square centimeters (cm²) (2% of body surface area) to the abdomen of rats for 5 minutes or application of the same volumes to the back for 10 minutes resulted in toxic plasma fluoride concentrations [Boink et al. 1995]. Several other studies in animals have also indicated that HF caused death from dermal exposure [Bracken et al. 1985; Dunn et al. 1992; Kim et al. 2004].

The human dermal lethal dose (LD_{Lo}) of HF has not been estimated. Although fatalities from severe skin burns have been reported in the literature following single occupational and nonoccupational accidental exposures to anhydrous or dilute HF solutions [Tepperman 1980; Mayer and Gross 1985; Chan et al. 1987; Mullett et al. 1987; Blodgett et al. 2001], the dermal doses were not reported in these case reports. A single study reporting dermal

Table 2. Summary of the carcinogenic designations* for HF by numerous governmental and nongovernmental organizations

Organization	Carcinogenic designation
NIOSH [2005]	No designation
NTP [2009]	No designation
USEPA [1988]	Data inadequate for an assessment of human carcinogenic potential
IARC [2007]	No designation
EC [2010]	No designation
ACGIH [2005]	Insufficient data to designate a classification

Abbreviations: ACGIH = American Conference of Governmental Industrial Hygienists; Joint Research, Institute for Health and Consumer Protection; IARC = International Agency for Research on Cancer; NIOSH = National Institute for Occupational Safety and Health; NTP = National Toxicology Program; USEPA = United States Environmental Protection Agency.

*Note: The listed cancer designations were based on data from nondermal (such as oral or inhalation) exposure rather than dermal exposure.

LD₅₀ (lethal dose in 50% of the exposed population) values was identified. Boink et al. [1995] reported dermal LD₅₀ values associated with application of 48% HF (0.25 mL applied to the abdomen and 0.5 mL applied to the back) in rats. The HF was applied directly within a plastic ring pasted onto shaved areas. The approximate LD₅₀ values were 401 milligrams per kilogram (mg/kg) and 802 mg/kg, depending on the volume applied, the concentration of the material, and the body weight of the animals. The calculated acute dermal LD₅₀ value for HF in rats is lower than the critical dermal LD₅₀ value of 2000 mg/kg body weight that identifies chemical substances with the potential for acute dermal toxicity [NIOSH 2009], indicating that HF is systemically available and can be acutely toxic following dermal exposure. The data from animals support those from humans indicating that dermal exposure to HF can result in systemic effect, including fatality.

No repeat-dose studies following dermal exposure of humans or animals to HF were identified in the literature, most likely because of the corrosive nature of the substance. No standard toxicity or specialty studies were identified that evaluated the biological system/function-specific effects

(including reproductive and developmental effects and immunotoxicity) following dermal exposure to HF. An acute dermal toxicity study [Derelanko 1985] revealed significantly reduced weight of the testes after occluded application of a 2% HF solution to the skin of rabbits for 4 hours. However, microscopic examination of the testes in control and treated animals revealed no apparent adverse effects associated with HF exposure.

No studies were identified that evaluated the potential of HF to be a carcinogen following dermal exposure. Table 2 provides a summary of carcinogenic designations from multiple governmental and nongovernmental organizations for HF.

No studies were identified that estimated the degree of HF absorption through the skin. The potential for systemic effects is supported by evidence from several case reports [Tepperman 1980; Mayer and Gross 1985; Chan et al. 1987; Mullett et al. 1987; Blodgett et al. 2001][†] indicating that skin burns following acute dermal exposure to anhydrous (approximately

[†]References in bold text indicate studies that served as the basis of the SK assignments.

100%) or dilute solutions of HF can cause systemic fluorosis, leading to hypocalcemia, hypomagnesemia, hyperkalemia, cardiac arrhythmia, and ultimately death. Studies in animals have also shown that dermal exposure to varying concentrations of HF can cause significant systemic absorption of fluoride [Bracken et al. 1985; Derelanko et al. 1985; Dunn et al. 1992; Kim et al. 2004]. Although the lack of repeat-dose dermal studies, apparently due to the corrosiveness of HF, precludes estimation of a safe dose for HF, evidence from case reports and from studies in animals is sufficient to indicate that HF is absorbed through the skin, is systemically available, and can cause systemic effects (such as cardiac arrhythmia, systemic fluorosis, hypocalcemia, hyperkalemia, and hypomagnesemia), including death. Therefore, on the basis of the data for this assessment, the SK: SYS (FATAL) notation is assigned to HF.

3 Direct Effects on Skin (SK: DIR)

Several literature surveys and studies of animals were identified that provide sufficient evidence that anhydrous HF or dilute HF solutions are corrosive to the skin; depending on the concentration, serious burns can become apparent several hours after exposure without an immediate pain warning. Kim et al. [2004] studied two surveys of occupational dermatitis and reported increased incidence of HF burns. Of the 2,736 patients observed over a 3-year period in one survey, 2% suffered injury from chemical burns, and 76.9% of these were classified as HF burns. In a later survey, spanning 6 years, 1.2% of patients (number not reported) suffered chemical burns, of which 74.2% were HF burns. Hatzifotis et al. [2004]

also conducted a survey, in which individuals were exposed to 1% to 98% HF (38.5% of cases involved solutions with a concentration of less than 1%). The solution covered 0.5% to 10% total body surface area and caused varying degrees of skin burns. Individuals exposed topically to concentrations up to 71% covering varying areas of the skin have developed severe burns [Bjornhagen et al. 2003; Buckingham 1988; Dunser and Rieder 2007; Edinburg and Swift 1989]. Improper use of household products containing dilute HF solutions also caused skin burns. For example, dermal exposure to consumer products containing dilute (5% to 11%) HF, such as rust removers, caused some degree of dermal injury to human skin [El Saadi et al. 1989; Mangion et al. 2001; Fujimoto et al. 2002; Hatzifotis et al. 2004]. It has been reported that the severity of HF skin burns and the degree of pain and systemic effect depend on the concentration of the HF solution, its quick penetration, the area involved, and the duration of exposure [Bertolini 1992; Wedler et al. 2005]. According to Wedler et al. [2005], concentrations of HF of 15% or more caused immediate symptoms, whereas it may take up to 1 hour for concentrations less than 15% to produce symptoms.

Several animal studies (including those using standard testing methods) have shown that HF is corrosive to the skin. For example, Derelanko et al. [1985] investigated the effects of occluded topical application of a 2% HF solution to rabbit skin for exposure times of 1 hour or 4 hours or of aqueous solutions (0.01% to 2%) for exposure times of 1 to 60 minutes. Results of this study indicated that a 2% solution was not corrosive when applied for 1 minute, but it was corrosive when applied for 5 minutes or more, with severity of injury increasing with contact time. In addition, visible lesions were observed

following topical application of solutions of HF with concentrations as low as 0.01% for exposure periods as short as 5 minutes. On the basis of their results, Derelanko et al. [1985] suggested that exposure to aqueous HF solutions as low as 0.01% for as short as 5 minutes could possibly cause injury to the more sensitive areas of human skin. Rats exposed to 50% HF for 3 minutes experienced severe burns [Höjer et al. 2002]. Topical application of 2 drops of a 70% HF solution (approximately 0.05 mL) for 60 seconds resulted in instantaneous burns to the treated area [Bracken et al. 1985]. Skin burns were also reported to occur in guinea pigs following topical application of varying concentrations of HF (5%, 25%, and 50%) [Kim et al. 2004]. In that study, severity of dermal damage and penetrability of exposed tissue depended on the HF concentration and the duration of exposure. Epidermal necrosis, with continuous tissue destruction, was also noted in pigs following application of patches of 0.4 mL of 38% HF for 9, 12, or 15 minutes [Dunn et al. 1992].

Sufficient data were identified from case reports or literature surveys [Edinburg and Swift 1989; El Saadi et al. 1989; Fujimoto et al. 2002; Hatzifotis et al. 2004; Kim et al. 2004], as well as dermal exposure studies involving animals [Derelanko et al. 1985; Höjer et al. 2002; Kim et al. 2004], to demonstrate the corrosivity of undiluted HF or diluted HF solutions. Therefore, on the basis of the data for this assessment, the skin notation SK: DIR (COR) is assigned to HF.

4 Immune-mediated Responses (SK: SEN)

No occupational exposure studies that investigated the skin sensitization potential of HF were identified. No diagnostic

(human patch) tests or predictive tests in animals (such as guinea pig maximization tests, Buehler tests, murine local lymph node assays, or mouse ear swelling tests) or any other studies that evaluated the potential of the substance to cause skin sensitization were identified. In the absence of such studies, an SK: SEN notation is not assigned to HF.

5 Summary

No studies were identified that estimated the degree to which HF can be absorbed through the skin. However, several case reports [Tepperman 1980; Mayer and Gross 1985; Chan et al. 1987; Mullett et al. 1987; Blodgett et al. 2001], and acute dermal studies in animals [Bracken et al. 1985; Derelanko et al. 1985; Dunn et al. 1992; Kim et al. 2004] indicate that HF is absorbed through the skin. Although no repeat-dose dermal studies involving humans or animals were identified, the acute dermal studies indicated that HF can cause systemic toxicity, including fluorosis, leading to cardiac arrhythmia and eventually death. There is sufficient evidence from several case reports [Edinburg and Swift 1989; El Saadi et al. 1989; Fujimoto et al. 2002; Hatzifotis et al. 2004; Kim et al. 2004] and from dermal exposure studies involving animals [Derelanko et al. 1985; Höjer et al. 2002; Kim et al. 2004] to show that undiluted HF or diluted HF solution is corrosive to the skin. Available data suggest that concentrations of HF as low as 0.01% applied for as short as 5 minutes could possibly cause injury to the more sensitive areas of human skin. No diagnostic or predictive tests were identified that evaluated the potential of HF to cause skin sensitization. On the basis of the information available for this assessment, the composite skin notation of

Table 3. Summary of the previously issued skin hazard designations for HF

Organization	Dermal classification
NIOSH [2006]	None
OSHA [2009]	None
ACGIH [2005]	[skin]: Based on concern for corrosivity and skin penetration
EC [2010]	R27: Very toxic in contact with skin R34: Causes burns; solutions containing 1 to 7% HF R35: Causes severe burns; solutions containing >7% HF C: Corrosive

Abbreviations: ACGIH = American Conference of Governmental Industrial Hygienists; EC = European Commission, Joint Research, Institute for Health and Consumer Protection; NIOSH = National Institute for Occupational Safety and Health; OSHA = Occupational Safety and Health Administration.

SK: SYS (FATAL)—DIR (COR) is assigned to HF.

Table 3 summarizes the skin hazard designations for HF previously issued by NIOSH and other organizations. The equivalent Globally Harmonized System (GHS) of Classification and Labeling of Chemicals dermal designation for HF is Acute Toxicity Category 1 (Hazard statement: Fatal in contact with skin), Skin Corrosion Category 1A (Hazard statement: Causes severe skin burns and eye damage) for solution containing more than 7% HF and Skin Corrosion Category 1B (Hazard statement: Causes severe skin burns and eye damage) for solutions containing between 1 to 7% HF [European Parliament 2008].

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Note: Asterisks (*) denote sources cited in text; daggers (†) denote additional resources.

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