

Recommendation from Scientific Committee

on Occupational Exposure Limits

*for Fluorine, Hydrogen Fluoride and Inorganic Fluorides
(not uranium hexafluoride)*

Biological limit value for fluorine, : 8 mg F⁻/l in urine
hydrogen fluoride and inorganic fluorides (end of shift value)

	8-hour TWA	STEL (15 mins)
Mixtures of inorganic fluorides and hydrogen fluoride	2.5 mg/m ³	-
Pure hydrogen fluoride	1.5 mg/m ³ as F ⁻	3 ppm (2.5 mg/m ³)
Fluorine	1 ppm (1.58 mg/m ³)	2 ppm (3.16 mg/m ³)
Additional classification	:	-

Substances:

	FLUORINE F₂	HYDROGEN FLUORIDE HF
Synonyms	: Bifluoride	Hydrofluoric acid, fluorohydric acid
EINECS N°	: 231-954-8	231-634-8
EEC N°	: 009-001-00-0	003-003-00-1; 003-002-00-6
Classification	: R7 T+; R26 C; R35	T+; R26/27/28 C; R35
CAS N°	: 7782-41-4	7664-39-3; 32057-09-3
MWt	: 38.0	20.01
M.Pt	: -220 °C	-83.37 °C
B.Pt	: -188 °C	19.51 °C
Vapour density	: 1.7	0.7 (air = 1)

Conversion factor (20°C, 101 kPa)
: 1.58 mg/m³ = 1 ppm 0.83 mg/m³ = 1 ppm

INORGANIC FLUORIDES

The most common inorganic fluorides are:

<u>Compound</u>	<u>CAS No.</u>	<u>EEC No</u>	<u>EINECS NO.</u>	<u>FORMULA</u>	<u>M. Wt.</u>
ammonium fluoborate	13826-83-0		237-531-4	NH ₄ BF ₄	104.8
ammonium fluoride	12125-01-8	009-006-00-8	235-185-9	NH ₄ F	37.0
ammonium hydrogen fluoride	1314-49-7		215-676-4	NH ₄ HF ₂	57.0
calcium fluoride (fluorite)	7789-75-5		232-188-7	CaF ₂	78.1
calcium fluosilicate	16925-39-6	009-013-00-6	240-991-9	CaSiF ₆	182.2
cesium fluoride	13400-13-0		236-487-3	CsF	151.9

<u>Compound</u>	<u>CAS No.</u>	<u>EEC No</u>	<u>EINECS NO.</u>	<u>FORMULA</u>	<u>M. Wt.</u>
fluorapatite (phosphate rock)	1306-05-4		215-144-1	Ca ₁₀ (PO ₄) ₆ F ₂	1015
lithium fluoride	7789-24-4		232-152-0	LiF	25.9
magnesium fluoride	7783-40-6		231-995-1	MgF ₂	62.3
potassium fluoborate	14075-53-7		237-928-2	KBF ₄	125.9
potassium fluoride	7789-23-3	009-005-00-2	232-151-5	KF	58.1
potassium fluosilicate	16871-90-2	009-012-00-0	240-896-2	K ₂ SiF ₆	220.3
potassium fluotantalate	16924-00-8		240-989-1	K ₂ TaF ₇	392.1
potassium fluotitanate (hydr)	23969-67-7			K ₂ TiF ₆ .H ₂ O	258.10
potassium fluozirconate	169-23-95-8		240-985-6	K ₂ ZrF ₆	283.4
potassium hydrogen fluoride	7789-29-9		232-156-2	KHF ₂	78.1
rubidium fluoride	13446-74-7		236-603-2	RbF	104.5
sodium aluminium fluoride	15096-52-3		239-148-8	3NAF.AIF ₃	209.9
sodium fluoride	7681-49-4	009-004-00-7	231-667-8	NaF	42.0
sodium fluosilicate	16893-85-9	009-012-00-0	240-934-8	Na ₂ SiF ₆	188.1
sodium hydrogen fluoride	1333-83-1		215-608-3	NaHF ₂	62.0
strontium fluoride	7783-48-4		232-000-3	SrF ₂	125.6
zinc fluoride	7783-49-5		232-001-9	ZnF	193.4

<u>Compound</u>	<u>CLASSIFICATION</u>	<u>M.Pt (°C)</u>	<u>B.Pt. (°C)</u>
ammonium fluoborate		S	-
ammonium fluoride	T; R 23/24/25	S	-
ammonium hydrogen fluoride		125.6	-
calcium fluoride (fluorite)		1360	2500
calcium fluosilicate	Xn; R 22	-	-
cesium fluoride		682	1251
fluorapatite (phosphate rock)		-	-
lithium fluoride		842	1676
magnesium fluoride		1261	2239
potassium fluoborate		D	D
potassium fluoride	T; R 23/24/25	846	1505
potassium fluosilicate	T; R 23/24/25	D	-
potassium fluotantalate		-	-
potassium fluotitanate (hydr)		780	D
potassium fluozirconate		-	-
potassium hydrogen fluoride		D	D
rubidium fluoride		775	1410
sodium aluminium fluoride		1000	-
sodium fluoride	T; R 23/24/25	988	1695
sodium fluosilicate	T; R23/24/25	D	-
sodium hydrogen fluoride		-	-
strontium fluoride		1450	2489
zinc fluoride		872	1500

S : sublimes; D : decomposes

Occurrence/use:

Fluorine is a pale yellow gas at normal temperature with an odour similar to that of ozone, which is detectable at 0.1 - 0.2 ppm (16 - 32 mg/m³). It is extremely reactive and organic and hydrogen-containing compounds may burn or explode when exposed to it. Fluorine ranks as the thirteenth element in order of abundance. Due to its extreme reactivity it rarely occurs in nature in the form of F₂, but as fluorides, particularly phosphate rock deposits and fluorspar. Fluorine is used mainly in the nuclear power industry, as UF₆, and in production of various inorganic fluorides, and is commonly generated and used captively. Exposures in gaseous

diffusion plants have been recorded as averaging 1 ppm (1.58 mg/m³) or less (Lyon, 1962), but these values may be inaccurate due to difficulties in analysing this reactive gas. This evaluation does not apply to uranium hexafluoride, because of the specific toxicity of uranium oxide which is formed on contact with water.

Hydrogen fluoride is a colourless liquid or vapour, with a pungent, irritating odour, which is detectable at about 0.04 ppm (0.03 mg/m³). In contact with metals, hydrogen may be released, giving rise to fires and explosions. Hydrogen fluoride is used in many industries, such as production of aluminium, inorganic fluorides, oil alkylation, etching of glass and ceramics and particularly, production of fluorocarbons. Production in the EC is in the region of 300,000 tonnes per annum, mostly used at the site of production. Typical levels of exposure are not known.

Inorganic fluorides are used in a wide range of activities and industries, including metallurgy, building construction, textiles, chemical production and treatment of drinking water.

Health Significance:

Acute topical exposure to fluorine or hydrogen fluoride results in irritation or corrosion.

Five human volunteers were exposed to controlled concentrations of fluorine in the air (Keplinger and Suissa, 1968). A concentration of 10 ppm (15.8 mg/m³) was not found particularly irritating for as long as 15 minutes, but 25 ppm (39.5 mg/m³) was slightly irritating to the eyes. At 50 ppm (79 mg/m³) respiratory irritation was also reported. Several repeated exposures at 10 ppm (15.8 mg/m³) resulted in skin irritation.

Hydrogen fluoride acts primarily as a corrosive, but secondary tissue necrosis may result from the toxicity of the free fluoride ion in the tissues (Harris and Rumack, 1981). Exposure of five volunteers to hydrogen fluoride at concentrations in the region 2.6 - 4.7 ppm (2.1 - 3.9 mg/m³) for 6h per day over 10 - 50 days, gave rise to slight irritation of the facial skin, eyes and nose (Largent and Columbus, 1960). Exposures to an average concentration of 1.42 ppm (1.2 mg/m³) were considered to have no effects, although an unpleasant taste in the mouth was experienced.

When inhaled, absorption of fluorine gas or hydrogen fluoride can be expected to be virtually complete. Fluorine is converted to fluoride, and then distribution and retention will follow the normal patterns for inorganic fluoride (WHO, 1984). The critical effects of chronic exposure to low concentrations of fluorine and hydrogen fluoride are due to the systemic effects of fluoride. The remainder of this evaluation will therefore consider the effects of the fluoride ion.

About 50% of absorbed fluoride is retained by the bone and 99% of body fluoride is taken up by the bones (Dinman *et al.*, 1976a). Renal excretion is the main elimination route and accounts for 40 to 60% of absorbed fluoride. When workers are exposed to particulate fluoride and hydrogen fluoride there is a correlation between the fluoride excreted in eight hours and the plasma fluoride level (Ehrnebo and Ekstrand, 1986). In the aluminium industry it is generally accepted that pre-shift and post-shift levels of fluoride in the urine constitute a good index of fluoride exposure (Dinman *et al.*, 1976b).

The critical effect of chronic exposure to fluoride ion is fluorosis, particularly affecting the skeleton. Classical symptoms are osteosclerosis, exostosis and calcification of ligaments. Skeletal fluorosis was not found in aluminium workers whose urine was monitored, average concentrations being 2.78 mg F⁻/l in pre-shift samples and 7.7 mg F⁻/l in post-shift samples for the high-exposure group (Dinman *et al.*, 1976b).

If a worker is exposed to fluorine at 1 ppm (1.58 mg/m³), then the normal respiration rate at 1 m³ per hour will result in inhalation of about 1.5 mg of fluorine, which is assumed to be fully absorbed. About half of this amount will eventually be excreted in the urine. By the end of the workday, steady-state conditions will be approximated, with about 0.75 mg being excreted per hour. Assuming urinary flow of about 1.5 ml/min, the fluoride concentration in the urine at the end of the shift will then be approximately 8 mg/l, i.e. equivalent to the level found not to result in fluorosis by Dinman *et al.*, (1976b).

Studies of genotoxicity have given variable results, but a recent bioassay has shown a small number of osteosarcomas in rats exposed to high levels of sodium fluoride (NTP, 1991). These findings were judged to be equivocal evidence of carcinogenicity. No data are available on teratogenicity.

Recommendation:

The SCOEL recommended that a biological limit value should be considered to protect against the systemic effects of fluoride resulting from exposure to inorganic fluorides, hydrogen fluoride or fluorine. The study of Dinman *et al.* (1976b), indicating a urinary NOAEL of 8 mg/l, was considered to be the best available basis for setting exposure limits. The recommended end-of-shift urinary limit value is 8 mg F⁻/l. Taking into account the differences of absorption and kinetics of fluoride compounds (Pierre *et al.*, 1995), this limit value is not exceeded by the application of the following 8-hour TWA air limit values:

- An 8-hour TWA of 2.5 mg/m³ of F⁻ for mixtures of hydrogen fluoride and inorganic fluorides (gas and particulate), commonly occurring at the workplace (Kaltreider *et al.*, 1972);
- An 8-hour TWA of 1.5 mg/m³ of F⁻ for pure hydrogen fluoride (Hogstedt, 1984);
- An 8-hour TWA of 1 ppm (1.58 mg/m³) for fluorine (Grandjean, 1992);
- For less soluble fluorides such as calcium fluoride, a higher limit could be acceptable.

Based upon the study of Largent and Columbus (1960), conducted in volunteers exposed for 6 h/d for 10-50d, a STEL (15 mins) of 3 ppm (2.5 mg/m³) was proposed for hydrogen fluoride to limit peaks in exposure which could result in irritation. A STEL (15 mins) of 2 ppm (3.16 mg/m³) is required for fluorine to protect against a significant increase in the critical body burden, which could result in fluorosis.

A “skin” notation was not considered to be necessary, as dermal absorption would only significantly contribute to the total body burden in circumstances where exposure to corrosive concentrations of fluorine or hydrogen fluoride occurred.

At the levels recommended, no measurement difficulties are foreseen but appropriate techniques should be carefully selected.

This recommendation may be re-examined after the risk assessment report produced in the framework of the Council Regulation on the evaluation and control of the risks of existing substances 793/93 has become available.

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