

Chapter 4

Hydrogen fluoride

4.1. Background

4.1.1 Basic chemical information

75. Hydrogen fluoride (HF) is primarily a gas under environmental conditions. The gas is colourless with a pungent odour. It is highly toxic and irritating and dissolves in water to produce hydrofluoric acid.

Conversion factors at 25°C and 101 kPa:

$$1 \text{ ppm} = 0.82 \text{ mg/m}^3; 1 \text{ mg/m}^3 = 1.22 \text{ ppm}$$

4.1.2 Sources

76. Estimates of the release of hydrogen fluoride to air are reported by the National Atmospheric Emission Inventory and the Pollution Inventories of the Environment Agency and Scottish Environment Protection Agency. The largest sources of hydrogen fluoride in the atmosphere are coal-fired power stations (the largest emission sector in the United Kingdom) and aluminium smelters. Other smaller sources include phosphate fertiliser plants; glass, brick and tile works; plastics manufacture; copper and nickel production; and adhesive production. Some releases may also come from the chemical and oil industries.
77. In the United Kingdom emissions of hydrogen fluoride fell by 73% between 1970 and 2000 as a result of the decline in coal use and, since 1993, the installation of flue gas desulphurisation at Drax and Ratcliffe power stations.
78. Hydrogen fluoride is produced at three sites in the United Kingdom for organic chemistry uses, namely Runcorn, Avonmouth and Rotherham.

4.1.3 Ambient levels

79. Hydrogen fluoride can be measured using several methods many of which measure the fluoride present in the resulting sample but none of these are able to determine short-term exposures at likely environmental concentrations. There are no ongoing long-term measurements of hydrogen fluoride in United Kingdom ambient air. As such, levels of

exposure and the number of persons potentially exposed to hydrogen fluoride are not known.

80. A modelling study suggested that the natural background concentration of fluoride was 0.61×10^{-6} ppm (0.5×10^{-6} mg/m³). When anthropogenic emissions were included, the background concentration increased to 3.66×10^{-6} ppm (3×10^{-6} mg/m³) (Slooff *et al.*, 1988).
81. In heavily industrialised urban areas within Europe, background concentrations are in the range of 0.61×10^{-3} to 2.44×10^{-3} ppm (0.5×10^{-3} to 2.0×10^{-3} mg/m³) but in some cases are as high as 3.66×10^{-3} ppm (3×10^{-3} mg/m³) (WHO, 2000).
82. Only a very limited number of recent ambient measurements of hydrogen fluoride have been made in the United Kingdom and these have been in the vicinity of three industrial plants. Although many samples were below the limit of detection, measurable values were in the range 4.1×10^{-5} to 2.87×10^{-3} ppm (3.36×10^{-5} to 2.35×10^{-3} mg/m³) as approximate monthly averages. Values at one site in Wales with results reported up to 13.4×10^{-3} ppm (11×10^{-3} mg/m³) have been excluded because of uncertainty in the analysis. Brickworks are a known source of fluoride emissions and measurements made between 1984 and 1986 in the Marston Vale region of Bedfordshire revealed monthly mean concentrations of gaseous fluorides of 4.9×10^{-5} to 10.5×10^{-4} ppm (4×10^{-5} to 8.6×10^{-4} mg/m³), and daily mean fluoride concentrations of up to 2.7×10^{-3} ppm (2.2×10^{-3} mg/m³) (99.8%ile). Monthly mean concentrations were correlated with brick production over the same period (Clark *et al.*, 1990; 1991). If it is assumed that nationally, coal burning is the largest source of hydrogen fluoride and that all the reactive fluorine is emitted as hydrogen fluoride, it is possible to estimate hydrogen fluoride levels from those of SO₂, by using a method directly analogous to that indicated for hydrogen chloride in paragraphs 110-111. On this basis it might reasonably be expected that maximum 1-hour mean hydrogen fluoride concentration would reach about 3.0×10^{-3} ppm (2.46×10^{-3} mg/m³) at a rural site exposed to power station plumes.
83. Estimates of total oral fluoride intake may vary from 0.9-3.0 mg/day, depending on diet and whether the water is fluoridated. The World Health Organisation (WHO) guideline for drinking water is 1.5 mg/l; this is higher than that recommended for fluoridation of water supplies, which stands at 1 mg/l (WHO, 1984). Children appear more sensitive to fluoride intake than adults, as dental fluorosis is closely associated with fluoride intake during the period of tooth development (Fomon *et al.*, 2000).

4.2. Health effects

84. The Panel considered controlled animal and human studies involving acute and subacute exposure to hydrogen fluoride. In addition, data from occupational exposures and industrial accidents were reviewed.
85. Hydrogen fluoride is a highly irritating and corrosive gas with a pungent odour. Skin contact with liquid hydrogen fluoride can cause severe burns. It is a severe irritant to eyes, skin and nasal passages. When inhaled, the absorption of hydrogen fluoride will be virtually complete, due to a strong reaction with mucous membranes (moist body linings) at the site of deposition. On absorption, hydrogen fluoride gives rise to the fluoride ion that is taken up by bone and enamel in teeth (WHO, 1984) and is excreted mainly in the urine. Penetration into the lungs results in pulmonary haemorrhage and oedema (bleeding and build up of fluids in the lungs) and may result in death.
86. The critical effects of chronic exposure to low concentrations of hydrogen fluoride are due to the systemic effects of fluoride (fluorosis), which affects the skeleton. Classical symptoms are osteosclerosis, formation of exostose and ossification of ligaments.
87. Skeletal fluorosis is associated with a systemic uptake of hydrogen fluoride exceeding 5 mg/day in a relatively sensitive section of the general population (WHO, 2000), whereas dental fluorosis occurs at concentrations in drinking water above 1.5-2.0 mg/l (WHO, 1984).

4.2.1 Animal studies

88. Large variations exist in the reported concentrations of hydrogen fluoride causing similar effects among different animal species. Some of this variation may be due to strain and species differences, but the diversity in the results is more likely to be explained by changes in sampling and analytical methodology.
89. For 60-minute inhaled exposures, only mild and occasional signs of eye, nasal or respiratory (breathing) irritation were observed in the dog at 157 ppm (131 mg/m³) and in the rat at 103 and 126 ppm (86 and 105 mg/m³) (Rosenholtz *et al.*, 1963). Gross and microscopic examination revealed concentration-dependent lesions in the kidney, liver, nasal passage, bone marrow and skin.
90. The lowest 60-minute LC₀⁴ values ranged from 263 ppm (219 mg/m³) for the mouse to 1087 ppm (904 mg/m³) for the rat (Wohlslagel *et al.*, 1976).

⁴ LC₀ is the highest concentration resulting in no deaths.

91. Sixty-minute LC₅₀⁵ values ranged from 342 ppm (284 mg/m³) for the mouse (Wohlslagel *et al.*, 1976) to 2300 ppm (1900 mg/m³) for the rat (Haskell Laboratory, 1990). The lowest LC₅₀ for the rat was 996 ppm (803 mg/m³) (Vernot *et al.*, 1997). Pathological examination of rats and mice that died during or after exposure revealed pulmonary oedema (build up of fluid in the lungs). For the rhesus monkey, statistical analysis has led to an LC₅₀ value of 1774 ppm (1476 mg/m³) (MacEwen and Vernot, 1970).
92. One subacute study using rats reported a no observable adverse effect level (NOAEL) of 1 ppm (0.72 mg/m³) (Placke and Griffin, 1991). In other subacute studies, using a variety of species, lung and kidney damage was found at 18.5 ppm (15.4 mg/m³) and 33 ppm (27 mg/m³).

4.2.2 Acute effects in humans

93. The acute effects of hydrogen fluoride have been assessed in 20 healthy, non-smoking male volunteers who were exposed for 1 hour to three concentration ranges known to occur among workers in the aluminium industry: 0.2 to 0.7 ppm (0.17 to 0.58 mg/m³) (*n* = 9); 0.85 to 2.9 ppm (0.71 to 2.4 mg/m³) (*n* = 7); and 3.0 to 6.3 ppm (2.5 to 5.2 mg/m³) (*n* = 7) (Lund *et al.*, 1997). Volunteers rested during the first 45 minutes of exposure and exercised during the last 15 minutes on a stationary bicycle. The two lower ranges resulted in either no or low sensory and lower airway irritation (chest tightness, soreness, coughing, expectoration and wheezing). In the highest exposure group, three subjects reported upper respiratory irritation (itching or soreness of the nose or throat) of greater than three on a scale of 0 (no symptoms) to 5 (the most severe symptoms), and one subject reported a lower airway irritation score of greater than three.
94. Hydrogen fluoride has also been shown to induce an immediate nasal inflammatory and antioxidant response in healthy human volunteers (Lund *et al.*, 2002). Following a 1-hour exposure to hydrogen fluoride at a concentration range 4.0 to 4.8 ppm (3.3-3.9 mg/m³), seven out of ten individuals reported upper airway symptoms. These airways symptoms correlated significantly with changes in indicators of inflammatory response in nasal lavage (washings) fluid, including a statistically significant increase in the number of nasal neutrophils. Like all irritant gases, accidental inhalation exposure to high levels of hydrogen fluoride has the potential to initiate reactive airways dysfunction syndrome (RADS), a form of irritant-induced asthma (see Appendix 2).

4.2.3 Subacute effects in humans

95. Largent (1960, 1961) exposed five male volunteers to variable concentrations of hydrogen fluoride (0.9-8.1 ppm or 0.75-6.70 mg/m³) for six hours per day over a period of 15 to 50 days. Effects in two

⁵ LC₅₀ is that concentration lethal to 50% of those exposed of the stated time

individuals exposed to up to 7.9 and 8.1 ppm (6.6 and 6.7 mg/m³) over a 25- and 50-day period, respectively, were no more severe than in other volunteers exposed to lower concentrations. One individual who tolerated 1.42 ppm (1.18 mg/m³) for 15 days without noticeable effects was, at a later date, exposed to 3.39 ppm (2.82 mg/m³) and experienced redness of the face by day 10 and some flaking of the skin by day 11. At 2 ppm (1.7 mg/m³) subjects experienced slight irritation to the eyes, nose and facial skin and noted a sour taste during the exposure. Any signs of discomfort disappeared after cessation of exposure and systemic effects were not observed (USEPA, 2000).

4.2.4 Occupational exposure

96. Chronic industrial exposure to hydrogen fluoride has been reported to lead to skeletal fluorosis, but airborne concentrations are often estimated or are unknown and exposures are usually to both hydrogen fluoride and fluoride dusts (NIOSH, 1976; ATSDR, 1993). Reports of asthmatic symptoms in pot room workers engaged in the production of aluminum have suggested that respiratory irritants in the working atmosphere (hydrogen fluoride, sulphur dioxide and fluoride particles) may cause asthma or chronic obstructive pulmonary disease (Lund *et al.*, 1997). Despite numerous studies the relation between the irritant agents and the symptoms remains unresolved.

4.2.5 Industrial accidents

97. Approximately 3,000 people were evacuated from a community in Texas, USA when around 24100 kg of caustic hydrogen fluoride and 3000 kg of isobutene were released from a petrochemical plant (Wing *et al.*, 1991). Samples taken down-wind one and two hours after the release contained 10 ppm (8.3 mg/m³) and minimal traces of hydrogen fluoride, respectively. The most frequently reported symptoms in people presenting at emergency rooms were eye irritation, burning throat and soreness, headache, shortness of breath, chest pain, cough and nausea. The USEPA (1993) cited a separate study by Trevino (1991) in which an industrial accident in Mexico resulted in seven workers being exposed to approximately 10000 ppm (8300 mg/m³) of hydrogen fluoride for several minutes. Periodic examinations for up to 11 years after exposure revealed no long-term or delayed effects.
98. Several instances of exposure to hydrogen fluoride have resulted in death but no data have been located on human deaths following inhalation-only exposure.

4.2.6 Carcinogenicity

99. Several studies indicated an increased incidence of respiratory cancers among workers in industries with exposure to hydrogen fluoride and fluoride dusts. However, the confounding effects of exposure to other chemicals, the lack of information on smoking status of these individuals and the absence of data on exposure concentrations make the studies of questionable relevance (ASTDR, 1993). No experimental or epidemiological studies with hydrogen fluoride are available. IARC

(The International Agency for Research on Cancer) concluded that there was no substantive evidence for carcinogenicity of fluoride in drinking water in either humans or animals (group 3 unclassifiable IARC 1987). This view was supported by a report from the UK Medical Research Council (MRC, 2002). IARC (1992) has evaluated the carcinogenicity of mists of strong inorganic acids. However hydrogen fluoride was not included in this evaluation and the overall evaluation is not relevant for the concentrations considered here.

100. Studies of other health consequences of chronic exposure to hydrogen fluoride in humans, including developmental or reproductive effects or genotoxicity, have not been identified, as far as the Panel is aware.

4.2.7 Evaluations and recommendations by other organisations

101. The Health and Safety Commission (HSE 2002) has set an occupational exposure limit of 3 ppm (2.5 mg/m^3) as a 15-minute short-term exposure limit based on human volunteer data from the study of Largent and Columbus (1960). In addition, an 8-hour time-weighted average limit of 1.8 ppm (1.5 mg/m^3), which would not be expected to cause fluorosis in workers exposed day after day, was set based on evidence by Dinman *et al.* (1976). This is in accordance with the European Commission's indicative occupational exposure limit values (IOELVs) listed in the First Consolidated IOELV Directive (2000/39/EC).

4.3. Justification for the air quality guideline value

102. The Panel considered the effects arising from exposure to low levels of hydrogen fluoride on the eyes, skin and respiratory tract owing to its well-known irritant properties. As noted, hydrogen fluoride is a highly irritating and corrosive gas and has a pungent odour that is detectable at about 0.04 ppm (0.03 mg/m^3) (European Union Risk Assessment Report, 2001). It is a severe irritant to eyes, skin and nasal passages.
103. The Panel considered that a concentration of 1 ppm (0.82 mg/m^3) should be regarded as a NOAEL for irritant effects on the face, eye and respiratory airways. This is based on the human healthy volunteer studies of Largent (1960, 1961), which indicate that hydrogen fluoride concentrations of 2 ppm (1.7 mg/m^3) were slightly irritating, and Lund *et al.* (1997), which reported respiratory irritation at concentrations of 3.0-6.3 ppm ($2.5\text{-}5.2 \text{ mg/m}^3$). To take into account the more susceptible individuals in the general population, the Panel considered the application of a safety factor of 5 would be adequate for exposure in the ambient air. Therefore the Panel concluded that 0.2 ppm (0.16 mg/m^3) would be an appropriate guideline value for hydrogen fluoride, allowing for its irritant effects on the skin, eyes and respiratory mucosa (moist lining of the breathing airways). A longer-term guideline value to protect against the chronic effects of hydrogen fluoride exposure will be recommended in an addendum to this report.

104. The Panel considered that there were no grounds for regarding hydrogen fluoride as a human carcinogen, especially at the very low levels considered.

4.4. Recommendation

105. **The Panel recommends that a concentration of hydrogen fluoride gas or mass equivalent aerosol not exceeding 0.2 ppm (0.16 mg/m³) over a 1-hour averaging period should protect against irritant and inflammatory effects on the eyes, skin and breathing airways.**

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