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Environmental Protection Service

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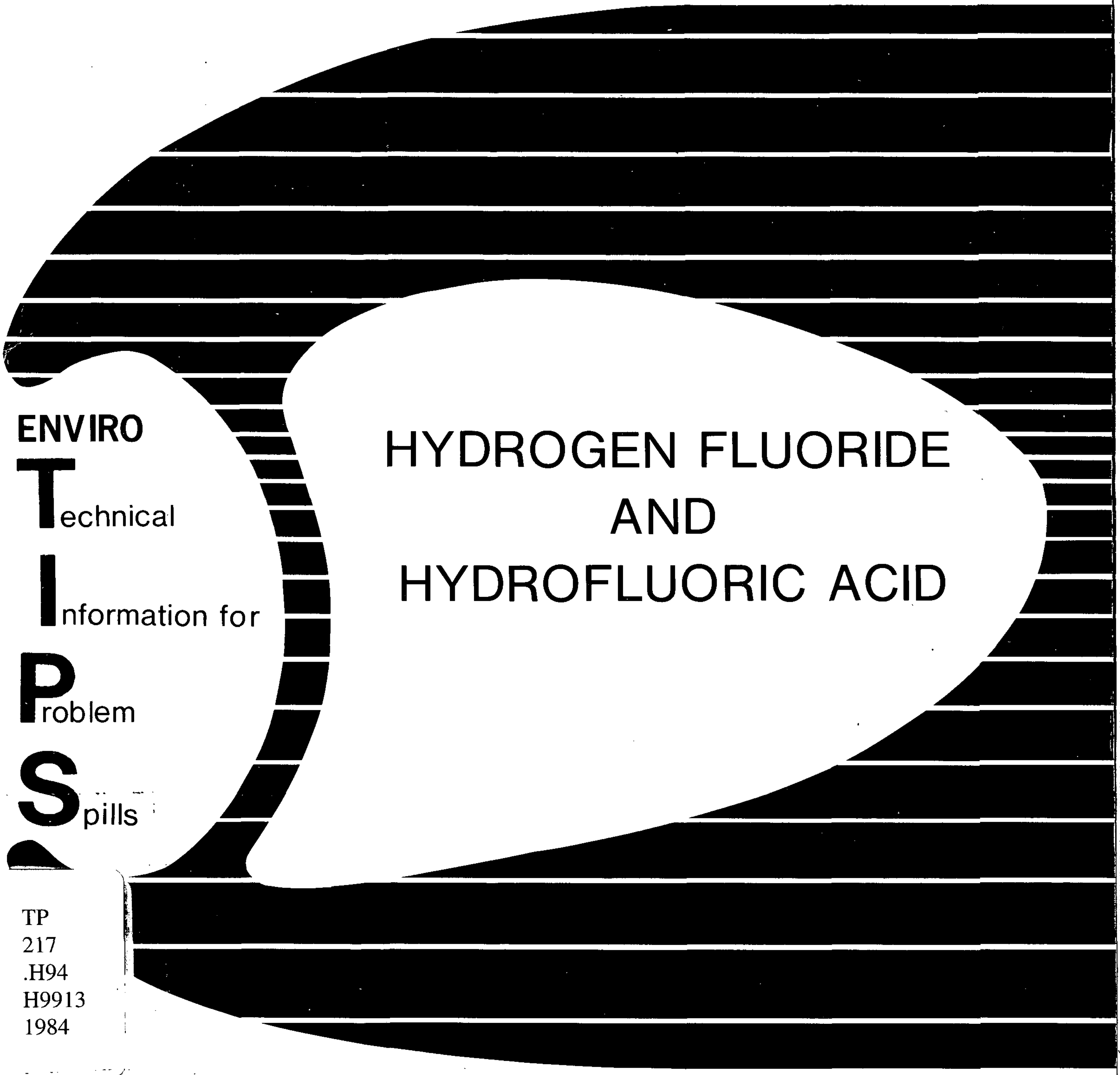

ENVIRO

Technical
Information for
Problem
Spills

HYDROGEN FLUORIDE AND HYDROFLUORIC ACID

JULY 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

HYDROGEN FLUORIDE AND HYDROFLUORIC ACID

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

July 1984

Cat. No. En 48-10/15-1984E
ISBN 0-662-13423-0
BEAUREGARD PRESS LIMITED

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations, and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

HYDROGEN FLUORIDE/HYDROFLUORIC ACID (HF)

Colourless to water-white liquid or colourless gas with a pungent, suffocating odour

SYNONYMS

Anhydrous: Hydrogen Fluoride, AHF; Hydrofluoric Acid, anhydrous

Aqueous: Etching Acid, Acide Fluorhydrique (Fr.), Hydrogen Fluoride (aqueous), Fluorhydric Acid, Fluohydric Acid

IDENTIFICATION NUMBERS

UN No. 1052 (hydrogen fluoride, anhydrous), 1790 (hydrofluoric acid, solution); CAS No. 7664-39-3; OHM-TADS No. 7216750; STCC No. 4930022 (aqueous), 4930024 (anhydrous)

GRADES & PURITIES

Anhydrous: 99 to 99.9 percent purity

Aqueous: 70 percent HF (most common); 5 to 52 percent HF

IMMEDIATE CONCERNS

Fire: Not combustible

Human Health: Highly toxic by inhalation, ingestion and skin absorption

Environment: Harmful to aquatic life in very low concentrations

PHYSICAL PROPERTY DATA

	Anhydrous	70% Aqueous
Shipping State:	liquid (liquefied gas)	liquid
State (25°C, 1 atm):	gas	liquid
Boiling Point:	19.54°C	66.4°C
Melting Point:	-83.55°C	-70°C
Flammability:	noncombustible	noncombustible
Vapour Pressure:	103.42 kPa (20°C)	20 kPa (25°C)
Density:	0.96 g/mL (25°C)	1.26 g/mL (0°C)
Behaviour (in water):	dissolves, floats and boils, evolving heat and HF vapour	sinks and mixes, producing HF fumes
Behaviour (in air):	disperses as a heavy gas, hugs the ground	
Odour Threshold Range:	0.03 to 0.11 mg/m^3	

ENVIRONMENTAL CONCERNS

Hydrogen fluoride in water is harmful to many species of fish at concentrations of 40 mg/L and is toxic to other aquatic life at levels as low as 10 mg/L. Hydrogen fluoride vapour dissolves in water and is harmful to various plant species.

HUMAN HEALTH

TLV®: 3 ppm (2.5 mg/m^3) (as F)
IDLH: 20 ppm (anhydrous)

Exposure Effects

Inhalation: Anhydrous: Causes irritation of mucous membranes, pain in throat, difficult breathing, headache, fatigue, shock, coma, death

Aqueous: May severely burn respiratory tract, cause rapid lung inflammation and congestion

Contact: Anhydrous: Readily absorbed; severe burns and damage to tissue. Burns eyes and may cause irreparable damage. Absorption of even a small amount may be fatal

Aqueous: Causes severe burns to skin and eyes. Absorption of even a small amount can cause absorption of calcium in the body and can be fatal. Symptoms, especially for the dilute solutions (20-52%), may be delayed for 1 to 8 hours. In both cases, speed of treatment for contact exposure is vital

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE!; POISON!" Notify manufacturer or supplier. Approach spill only with SCBA and full protective clothing. Evacuate from downwind. Stop or reduce discharge and contain spill, if safe to do so. Avoid skin contact and inhalation; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible. Wear SCBA and full protective clothing. Use water to knock down vapours. Water should not be sprayed directly on large pools. Cool fire-exposed containers with water spray. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on:

Soil: Construct barriers to contain spill. Neutralize the material with lime or other suitable alkaline material. Remove neutralized material with pumps or vacuum equipment. Neutralize contaminated soil with alkaline materials

Water: Contain by damming or water diversion. Neutralize with lime or other suitable alkaline material

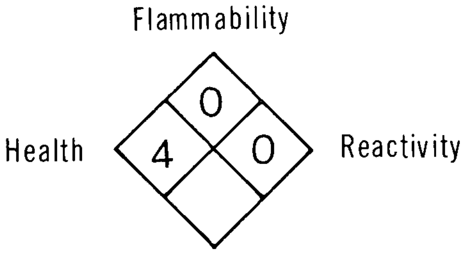
Air: Use water spray to knock down vapours. Control runoff, by dyking, for later treatment

NAS HAZARD RATING

Category	Rating
Fire	0
Health	
Vapour Irritant	4
Liquid or Solid Irritant	4
Poison	4
Water Pollution	
Human Toxicity	4
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	4
Water	2
Self-reaction	0

NFPA

HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

	Anhydrous	Aqueous, 70% HF
Appearance	Liquid: Colourless, fuming (MCA 1970) Vapour: Colourless, forms white mist in contact with air (MCA 1970)	Colourless to water-white, fuming liquid (MCA 1970)
Usual shipping state(s)	Liquid (liquefied gas)	Liquid
Physical state at 15°C, 1 atm	Gas	Liquid
Melting point	-83.55°C (Kirk-Othmer 1980)	
Freezing point		-69°C (Kirk-Othmer 1980) -70.1°C (MCA 1970)
Boiling point	19.54°C (Kirk-Othmer 1980)	66.4°C (Kirk-Othmer 1980)
Vapour pressure	103.42 kPa (20°C) (Kirk-Othmer 1980)	20 kPa (25°C) (Kirk-Othmer 1980)
Decomposition temperature	~4,000°C (Kirk-Othmer 1980)	

Densities

Density	1.002 g/mL (liquid at 0°C) (Kirk-Othmer 1980; Matheson 1980) 0.9576 g/mL (25°C) 2.201 g/L (vapour at 25°C) (Kirk-Othmer 1980; Matheson 1980)	1.22 g/mL (25°C) (Kirk-Othmer 1980)
Specific gravity	1.858 (vapour at 25°C) (air = 1) (Matheson 1980)	1.258 (0°C) (water = 1) (MCA 1970)

Fire Properties

	Anhydrous	Aqueous, 70% HF
Flammability	Noncombustible (NFPA 1978)	Noncombustible (NFPA 1978)
Behaviour in a fire	Toxic and irritating hydrogen fluoride vapours are generated in the presence of heat. There is a latent fire and explosion hazard due to possible generation of hydrogen in containers or piping (Air Products MSDS 1978)	

Other Properties

	Anhydrous	Aqueous, 70% HF
Molecular weight of pure substance	20.006 (Kirk-Othmer 1980) (HF vapour shows a molecular weight of 78.24 at boiling point and 49.08 at 100°C, because of polymerization. Only above 200°C will the monomer with a molecular weight of 20 be apparent (Kirk-Othmer 1980; Ullmann 1975))	
Constituent components (%) (of typical commercial grade)	99.99 percent HF 0.001 percent H_2SiF_6 0.003 percent SO_2 0.005 percent H_2SO_4 0.0004 percent H_2O (Kirk-Othmer 1980)	
	99.96-99.98 percent HF 0.02-0.002 percent H_2O 0.001-0.007 percent nonvolatile acidity 0.003-0.004 percent SO_2 (Allied 1978; du Pont DS 1982)	70.3 percent HF 0.10 percent SO_2 0.1 percent nonvolatile acidity 0.03 percent iron (Fe) (Allied 1978)
Refractive index	1.2675 (10°C) (CRC 1980)	1.1574 (liquid at 25°C) (Kirk-Othmer 1980)
Viscosity	0.256 mPa•s (0°C) (Kirk-Othmer 1980)	
Liquid surface tension	10.1×10^{-4} mN/m (10°C) (Kirk-Othmer 1980)	
Hygroscopicity	Very hygroscopic (Ullmann 1975)	Very hygroscopic (Ullmann 1975)

	Anhydrous	Aqueous, 70% HF
Latent heat of fusion	3.931 kJ/mole (-83.55°C) (Kirk-Othmer 1980)	
Latent heat of sublimation	7.6 kJ/mole (Perry 1973)	
Latent heat of vaporization	7.493 kJ/mole (19.54°C) (Kirk-Othmer 1980)	
Heat of formation	-272.54 kJ/mole (25°C) (JANAF 1971)	-321.9 kJ/mole (25°C) (Sussex 1977)
Entropy	173.7 J/(mole•°C) (ideal gas at 25°C) (Ullmann 1975)	
Ionization potential (eV)	16.01 eV (Rosenstock 1977)	
Heat of solution	-61.5 kJ/mole (25°C) (CRC 1980)	
Heat of hydration	48.39 kJ/mole (Ullmann 1975)	
Heat capacity constant pressure (Cp)	Liquid: 51.21 J/(mole•°C) (20°C) (Kirk-Othmer 1980) Vapour: 456 J/(mole•°C) (22°) (Kirk-Othmer 1980)	
constant volume (Cv)	Vapour: 46.27 J/(mole•°C) (20°C) (Kirk-Othmer 1980)	
Critical temperature	188°C (Kirk-Othmer 1980)	
Critical pressure	6480 kPa (Kirk-Othmer 1980)	
Thermal conductivity	2.547 x 10^{-2} W/(m•K) (100.6°C) (Matheson 1980)	
Diffusivity	0.225 cm^2/s (15°C) (Perry 1973)	
Electrical conductivity	<1.6 x 10^{-1} ohm^{-1} cm^{-1} (du Pont DS 1982)	0.79 ohm^{-1} cm^{-1} (Kirk-Othmer 1980)
Saturation concentration	979 g/m^3 (25°C) (CRC 1980)	

	Anhydrous	Aqueous, 70% HF
Evaporation rate	5.69 g/(m^2•s) (20°C, wind 4.5 m/s) (this work) 0.86 g/(m^2•s) (20°C) (CHRIS 1974)	
Dielectric constant	83.6 (0°C) (Kirk-Othmer 1980)	
Dipole moment	1.829 D (Kirk-Othmer 1980)	
Solubility (g/100 mL)		
In water	Completely soluble in water, with evolution of heat (CRC 1980; MCA 1970)	Completely soluble in water, with evolution of heat (CRC 1980; MCA 1970)
In other common materials	Very soluble in alcohol (CRC 1980) Very soluble in alcohols, ethers, ketones and nitriles (Ullmann 1975)	
Azeotropes	With water, forms an azeotrope at a point from 37.7 to 38.2 percent HF which boils at 111.4 to 112.2°C (du Pont 1982; Ullmann 1975)	

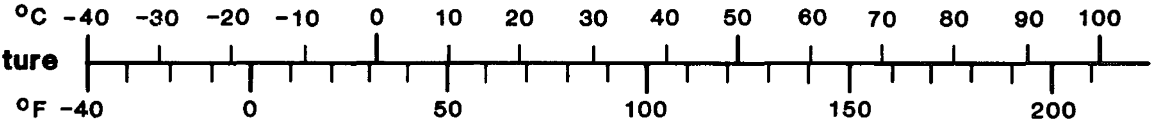
Structure/Properties

In air, hydrogen fluoride shows a high degree of association, that is, it polymerizes. Polymers up to H_6F_6 have been identified. Molecular weights of 78.24 and 49.08 are shown at 20°C and 100°C, respectively; the true molecular weight of 20.006 only appears at temperatures greater than 200°C. The result of this association is that hydrogen fluoride behaves much more like a heavy gas than would be predicted without knowledge of this polymerization (Bailar 1973; Kirk-Othmer 1980; Ullmann 1975).

In water, association is also evidenced by the freezing and boiling point behaviour. Association between water and hydrogen fluoride molecules is thought to result in relatively stable forms of $H_2O \cdot HF$, $H_2O \cdot 2HF$ and $H_2O \cdot 4HF$. This results in higher boiling and freezing points at concentrations where these are most stable (Bailar 1973; Ullmann 1975).

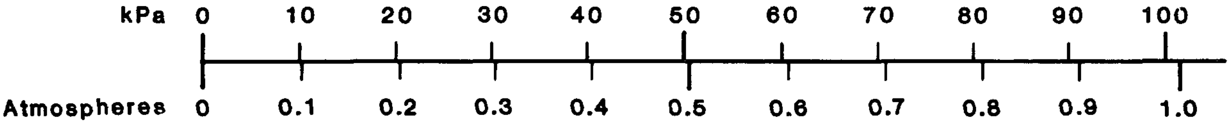
CONVERSION NOMOGRAMS

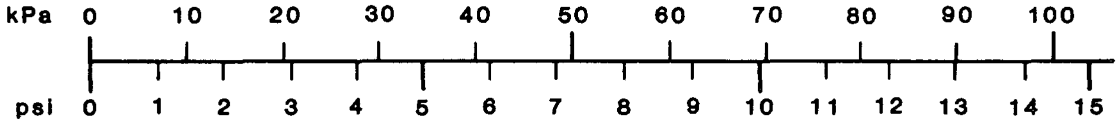
Temperature

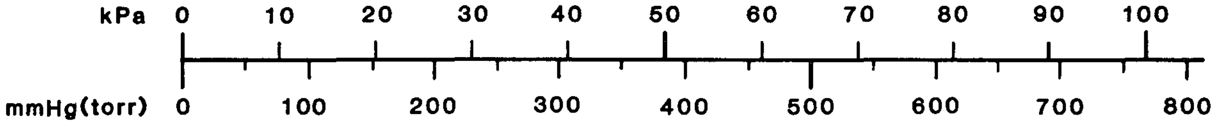


Pressure

1 kPa = 1,000 Pa







Viscosity

Dynamic 1 Pa-s = 1,000 centipoise (cP)

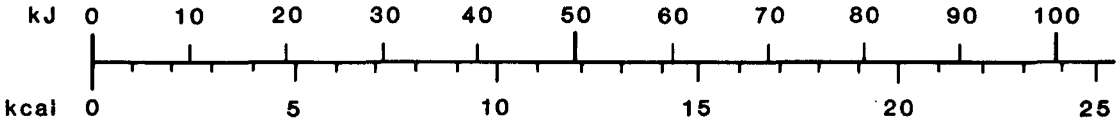
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

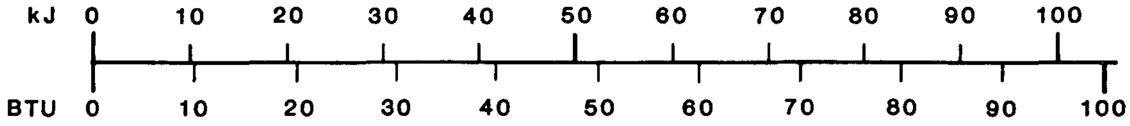
Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat)

1 kJ = 1,000 J





Density

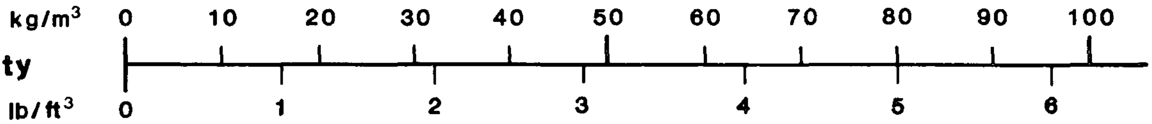


FIGURE 1

HYDROGEN FLUORIDE (Gas)

APPARENT MOLECULAR WEIGHT vs TEMPERATURE

Reference: ULLMANN 1975; BAILAR 1973

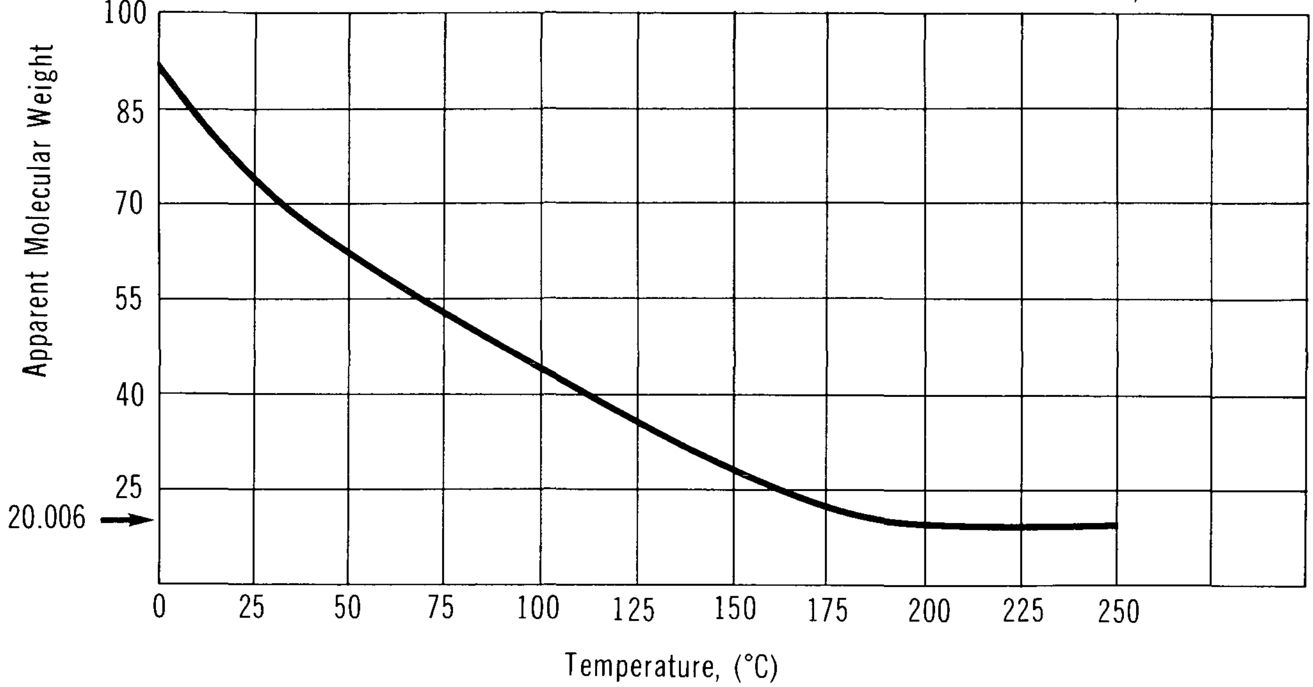


FIGURE 2

HYDROFLUORIC ACID

FREEZING POINT

Reference: DU PONT 1982; ULLMANN 1975

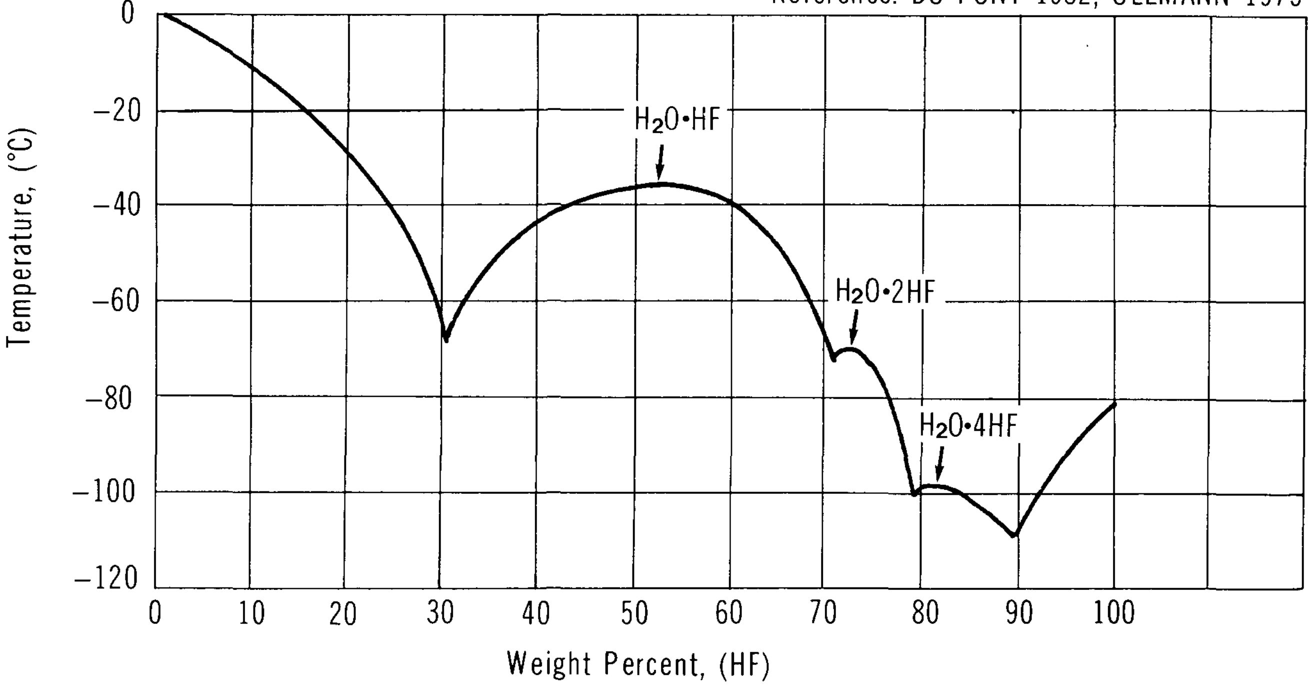


FIGURE 3

HYDROGEN FLUORIDE and HYDROFLUORIC ACID

LIQUID DENSITY vs TEMPERATURE

Reference: KIRK-OTHMER 1980

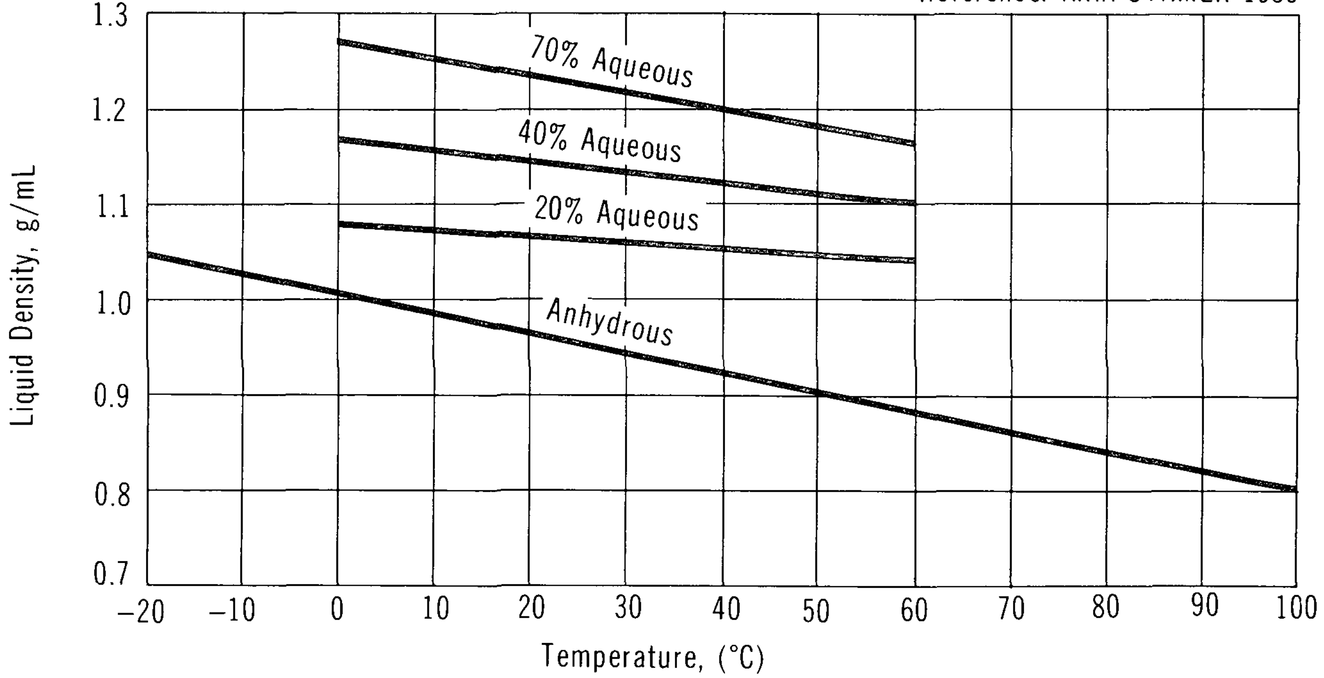


FIGURE 4

HYDROGEN FLUORIDE

SATURATED VAPOUR DENSITY vs TEMPERATURE

Reference: KIRK-OTHMER 1980

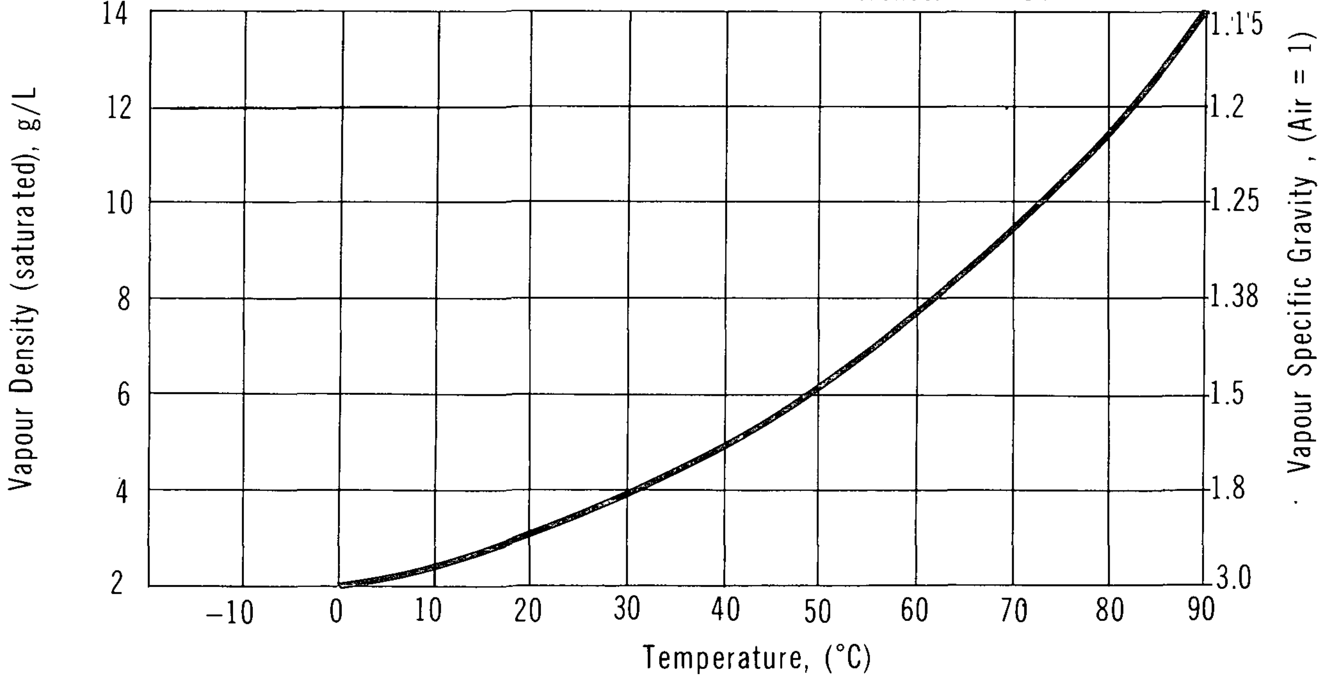


FIGURE 5

HYDROGEN FLUORIDE

VAPOUR PRESSURE VS TEMPERATURE

Reference: Chem. Eng. 1974; DU PONT 1982

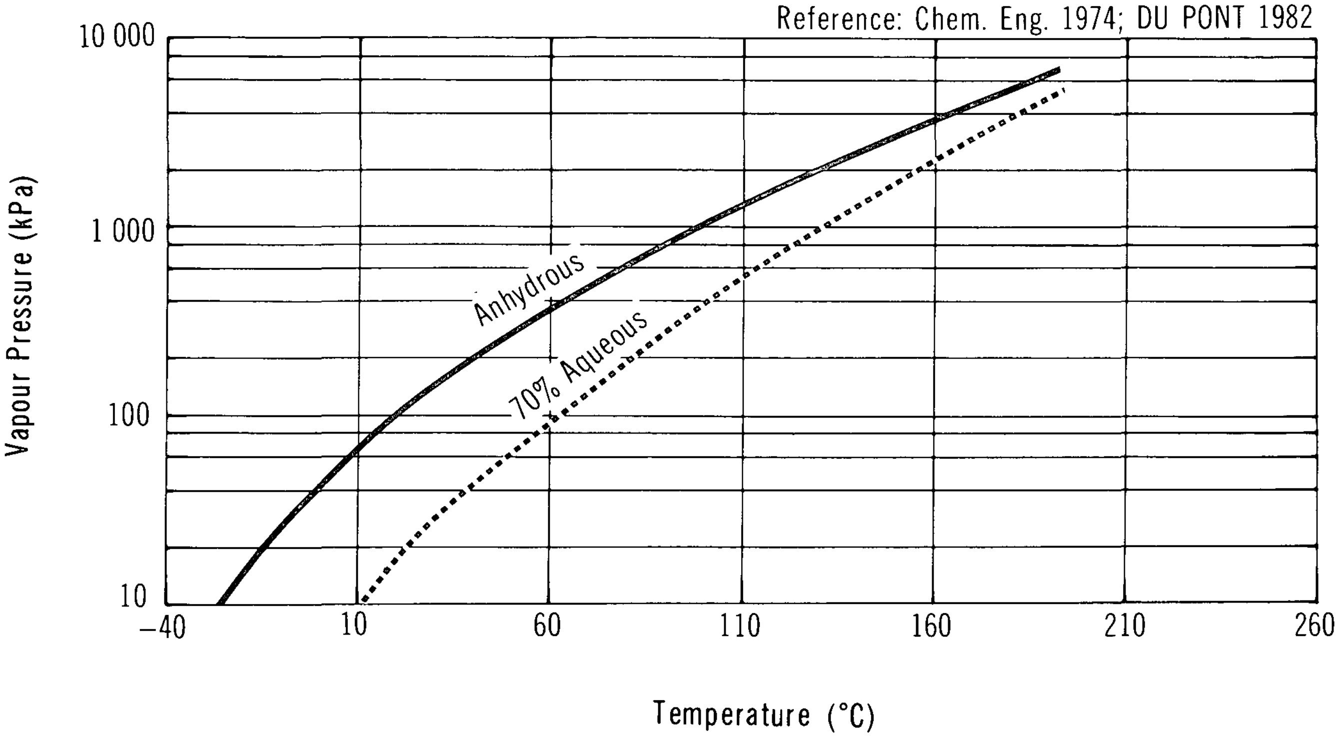


FIGURE 6

HYDROGEN FLUORIDE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

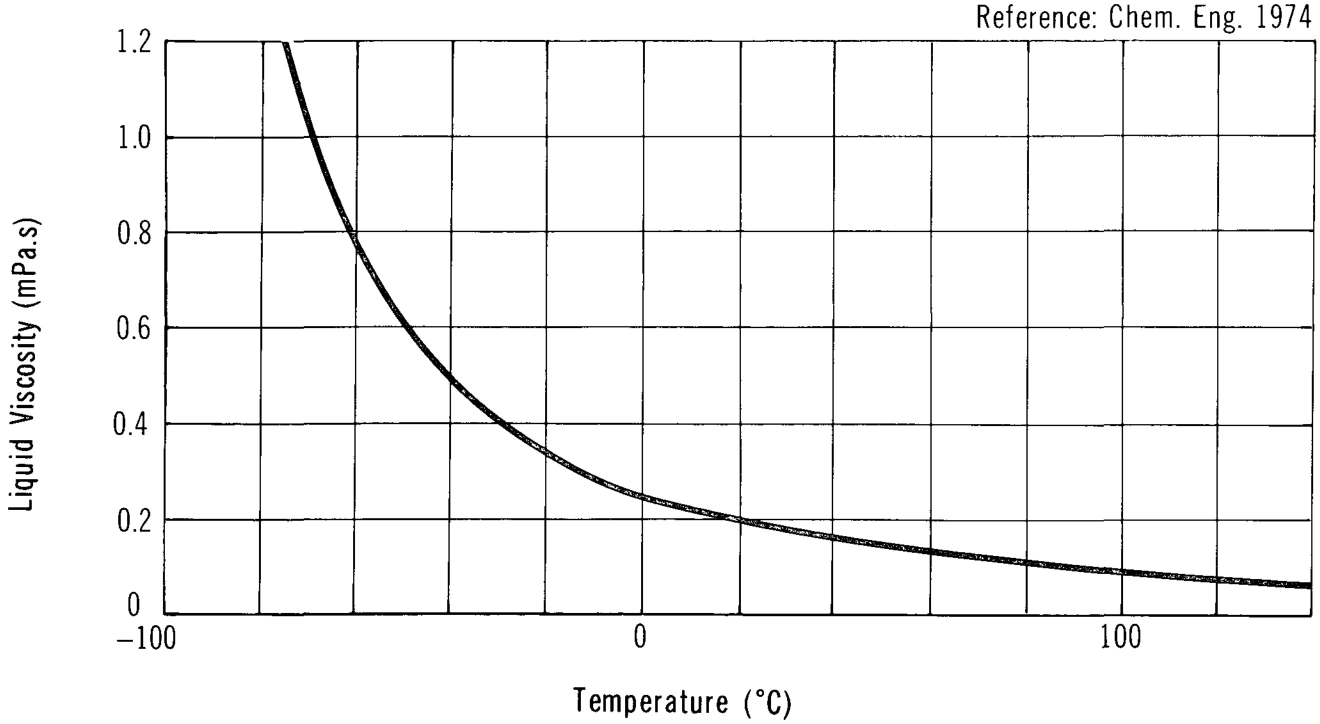


FIGURE 7

HYDROGEN FLUORIDE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

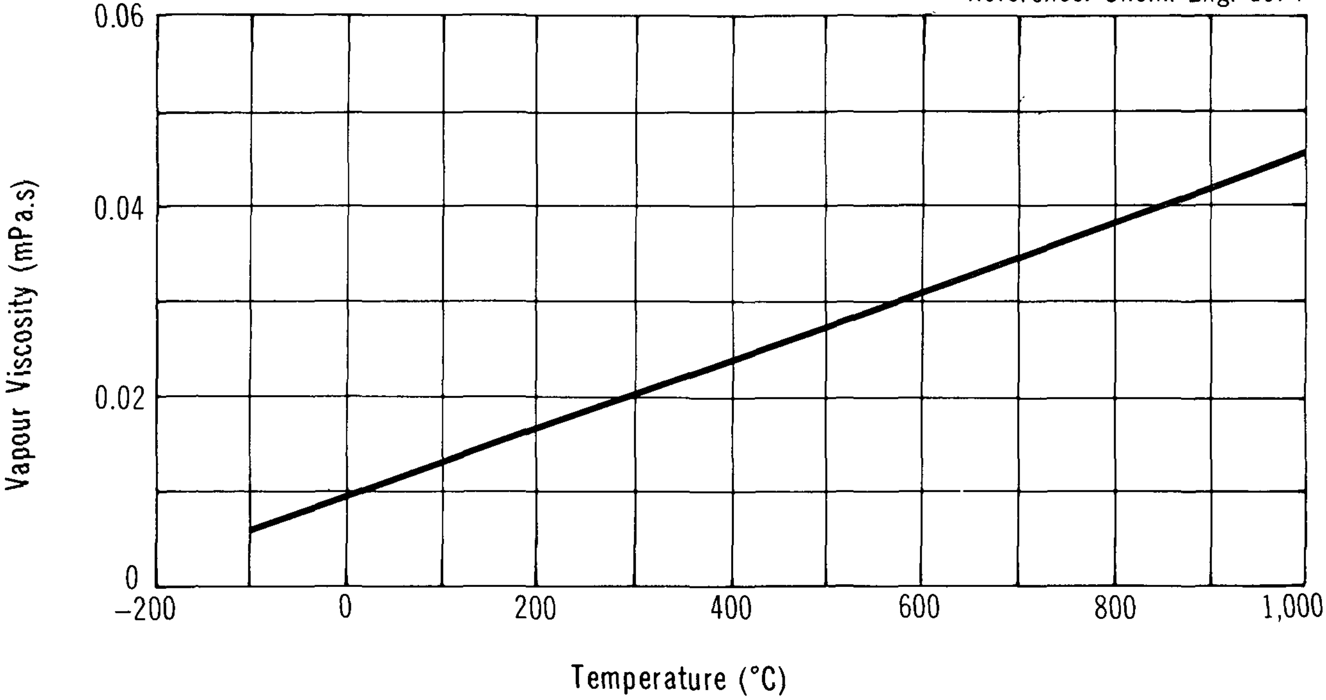
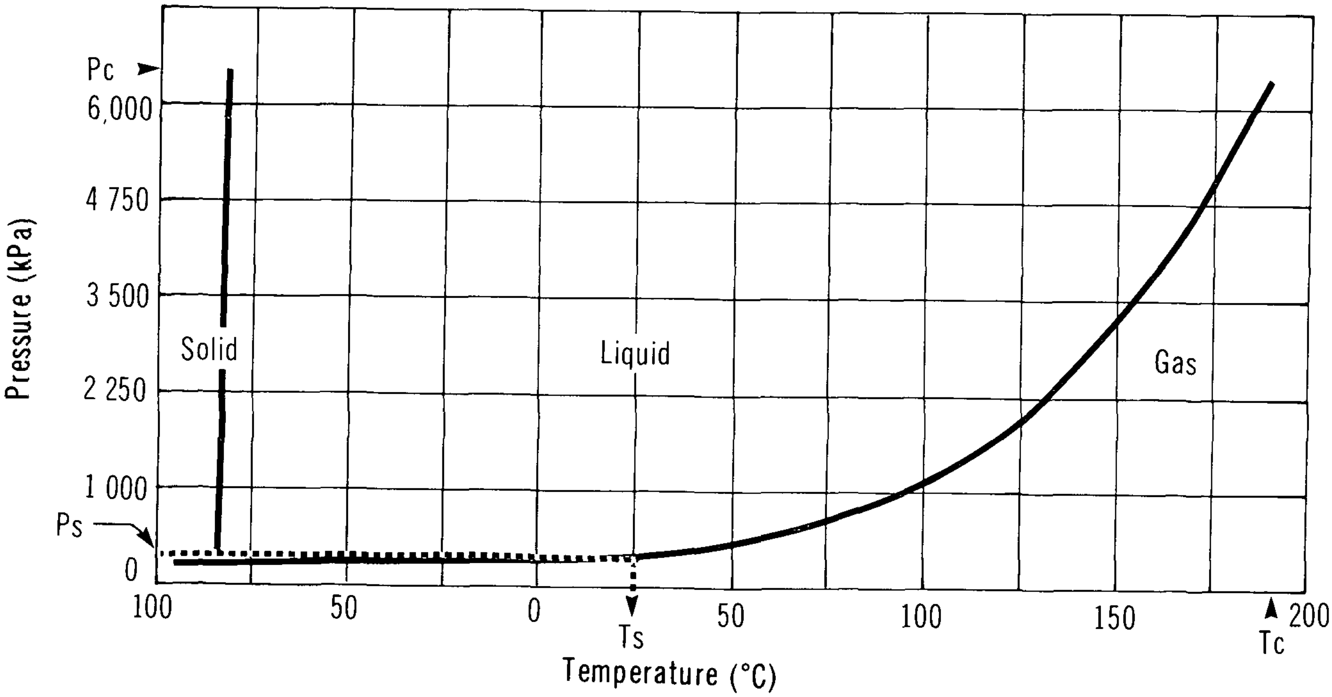


FIGURE 8

HYDROGEN FLUORIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

3.1.1 **Hydrofluoric Acid** (CCPA 1982). Hydrofluoric acid is primarily produced as a 70 percent hydrogen fluoride solution. Electronic and reagent grades of 5 to 52 percent HF are also produced.

3.1.2 **Hydrogen Fluoride** (CCPA 1982). Hydrogen fluoride (anhydrous) is produced with a purity of 99 to 99.99 percent.

3.2 Domestic Manufacturers (Corpus 1982; CBG 1980)

Alcan Smelters & Chemicals Ltd.
P.O. Box 6090,
1 Place Ville Marie
Montreal, Quebec
H3C 3H2
(514) 877-2340

Allied Chemical, A Division of Allied
Canada, Inc.
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 276-9211
Emergency: (416) 276-9211

3.3 Other Suppliers (Corpus 1982; CBG 1980; CCPA 1981)

Du Pont of Canada Ltd.
555 Dorchester Blvd. West
Montreal, Quebec
H3C 2V1
(514) 861-3861

Minerals and Chemicals Ltd.
1117 Catherine St. West
Montreal, Quebec
H3B 1H9
(514) 849-6366

Pennwalt of Canada Ltd.
700 Third Line
Oakville, Ontario
L6J 5A3
(416) 827-9841

3.4 Major Transportation Routes

Current Canadian production of hydrogen fluoride and hydrofluoric acid is located only in Quebec and Ontario. Major plants are in Jonquière, Quebec and Amherstburg, Ontario (Southern Ontario).

The market area is mainly in Ontario and Quebec, with a small amount transported to B.C. and Alberta. Transportation is primarily by rail.

3.5 **Production Levels** (Corpus 1982)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1981)
Alcan Smelters and Chemicals, Jonquière, Que.*		35
Allied Chemical Canada, Amherstburg, Ont.		50
	TOTAL	85
Domestic Production (1981)		78.5
Imports (1981)		0.5
	TOTAL SUPPLY	79

* Captive use only.

3.6 **Manufacture of Hydrogen Fluoride** (Shreve 1977)

3.6.1 General. Hydrogen fluoride is produced in Canada by the reaction of sulphuric acid and fluorspar (calcium fluoride).

3.6.2 Raw Materials. Raw materials used are 93 to 99 percent sulphuric acid and pulverized "acid grade" (>97 percent CaF_2) fluorspar.

3.6.3 Manufacturing Process (Kirk-Othmer 1980; Shreve 1977; PB 294276). Sulphuric acid and fluorspar are charged continuously to one end of a rotary kiln with an internal screw conveyor. Because the reaction is endothermic, the kiln is heated; reaction occurs at 200 to 250°C. The residence time in the kiln is of the order of 30 to 60 minutes, from when the fluorspar-acid mixture is charged to when the screw conveyor discharges it through an air lock at the opposite end as waste calcium sulphate. Hydrogen fluoride gas is withdrawn at the top:

$$CaF_2 + H_2SO_4 \longrightarrow 2HF(gas) + CaSO_4$$

The reaction rate and yield of hydrogen fluoride are largely determined by the fluorspar particle size and purity, and by reactor mixing.

The hydrogen fluoride gas produced is passed through a condenser to remove sulphuric acid, fluorosulphonic acid, and particulate matter; through a coke box to remove organics; and scrubbed with oleum or concentrated sulphuric acid to remove moisture. It is refrigerated and liquefied to produce anhydrous hydrogen fluoride, then distilled to remove impurities and piped to storage tanks. The gas may also be absorbed in water to produce aqueous solutions. The overall hydrogen fluoride yield in the process is 85 to 95 percent, based on fluorspar.

3.6.4 By-products. By-products are calcium sulphate and silicon tetrafluoride (from SiO_2 in starting material, typically less than 1 percent of final product) which is hydrolyzed to form fluorosilicic acid.

3.7 Major Uses in Canada (Corpus 1982; Eco/Log 1981)

Hydrofluoric acid and anhydrous hydrogen fluoride are used in the production of aluminum fluoride, synthetic cryolite, fluorochloromethanes, uranium hexafluoride and motor gasoline alkylate. They are also used as pickling agents in stainless steel manufacturing. In 1981, 40 percent of the product manufactured in Canada was used for aluminum fluoride production, 46 percent was exported, 8 percent was used in the production of fluorochloromethanes, and 2 percent was used to produce uranium hexafluoride.

3.8 Major Buyers in Canada (CBG 1980; Corpus 1982)

A & K Petro-Chem, Weston, Ont.
Anachemia, Lachine, Que.
Bayer (Canada), Montreal, Que.
Canada Colors & Chemicals, Toronto, Ont.
Canadian Hanson, Toronto, Ont.
Ciscochem, Brampton, Ont.
Du Pont Canada, Maitland, Ont.
Eldorado Nuclear, Port Hope, Ont.
Gulf Canada, Edmonton, Alta.; Clarkson, Ont.
Imperial Oil, Edmonton, Alta.; Sarnia, Ont.
Mackenzie & Feinmann, Vancouver, B.C.
Minerals & Chemicals, Montreal, Que.
Petro Canada, Taylor, B.C.
Shell Canada, Montreal East, Que.
Suncor, Sarnia, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 **Bulk Shipment.** Hydrofluoric acid is shipped in specially designed railway tank cars, tank motor vehicles, and polyethylene carboys.

Hydrogen fluoride is shipped under pressure as a liquid in railway tank cars and highway tankers; small amounts for laboratory usage may be shipped in cylinders.

4.1.1.1 **Railway tank cars.** Railway tank cars used in the transportation of hydrofluoric acid are described in Table 2.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (RTDCR 1974)

Commodity Type	CTC/DOT* Specification Number	Description
Anhydrous	105A300W	Steel tank with dome. Insulation required. Safety valve set at 1550 kPa (225 psi). Bottom outlet and washout prohibited.
	112A400W	Steel tank with dome. Insulation not used. Safety valve set at 2070 kPa (300 psi). Bottom outlet and washout prohibited.
	112S400W	Special permit tank car. Same as 112A400W above, except no insulation used and equipped with head shield.
	114A400W	Steel tank with dome. Insulation not used. Safety valve set at 2070 kPa (300 psi). Bottom outlet and washout optional.
Acid Solutions, 60 to 80 percent	103AW	Steel tank with dome. Insulation optional. Safety valve set at 241 kPa (35 psi). Bottom outlet prohibited. Bottom washout optional.
	105A100W	Steel tank with dome. Insulation required. Safety valve set at 517 kPa (75 psi). Bottom outlet and washout prohibited.
	111A100W2	Steel tank without dome. Insulation optional. Safety valve set at 517 kPa (75 psi). Bottom outlet prohibited. Bottom washout optional.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (RTDCR 1974) (Cont'd)

Commodity Type	CTC/DOT* Specification Number	Description
	111A100W4	Steel tank without dome. Insulation required. Safety valve set at 517 kPa (75 psi). Bottom outlet and washout prohibited.
Acid Solutions, less than 40 percent	103BW	Rubber-lined steel tank with dome. Insulation optional. Safety vent, burst at 413 kPa (60 psi). Bottom outlet and washout prohibited.
	111A100W5	Rubber-lined steel tank without dome. Insulation optional. Safety valve set at 517 kPa (75 psi). Bottom outlet and washout prohibited.

* Canadian Transport Commission and Department of Transportation (U.S.)

Anhydrous hydrogen fluoride is commonly shipped in class 105A300W (or 105A400W or 105A500W) tank cars, with approximate capacities of 18 000 L (4000 gal.), 36 000 L (8000 gal.), 41 000 L (9000 gal.), 45 500 L (10 000 gal.), or 73 000 L (16 000 gal.); tank cars of class 112S400W with approximate capacities of 20 500 L (4500 gal.), 36 000 L (8000 gal.), 73 000 L (16 000 gal.) and 82 000 L (18 000 gal.) may also be used. The latter size is a preferred shipping size for economical reasons (CCPA 1982; Allied 1978; du Pont 1982). Figure 9 shows a typical class 105A300W car. The other classes used for anhydrous hydrogen fluoride are similar in appearance and design. Specifications associated with the class 105A300W tank car are given in Table 3.

The only opening permitted in the tank is a single manway located in the centre at the top. Five valves are mounted inside the dome cover. Four of these are 25 mm (1 in.) angle valves; the fifth, mounted in the centre, is the safety relief valve (MCA 1970).

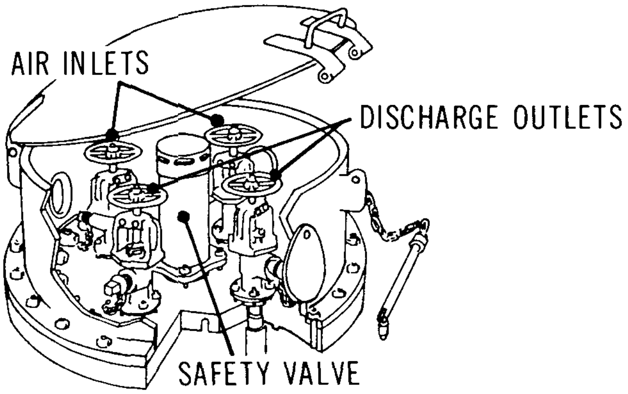
Under each liquid valve is a 32 mm (1 1/4 in.) eduction pipe fastened to the manway cover and extending to the bottom of the tank. The safety relief valve is of the spring-loaded type and is usually combined with a frangible disc.

Railway tankers may be rubber-lined for solutions of up to 40 percent aqueous hydrofluoric acid. Safety valves of approved design must be used complete with frangible disc. As indicated in Table 2, a domeless manway or dome option is available, depending on the class of the car (TCM 1979).

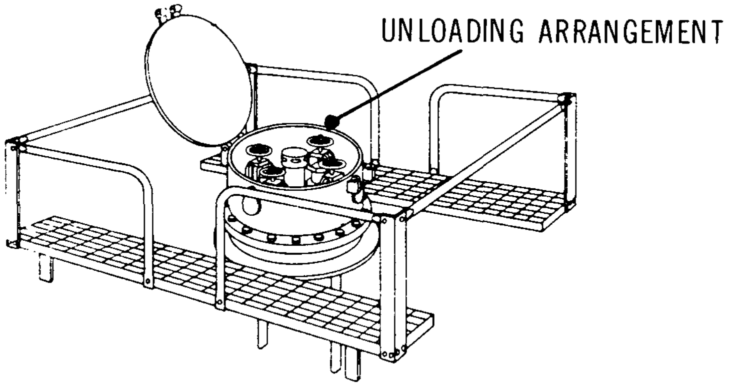
FIGURE 9

RAILWAY TANK CAR - CLASS 105A300W

(Reference: TCM 1979; RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

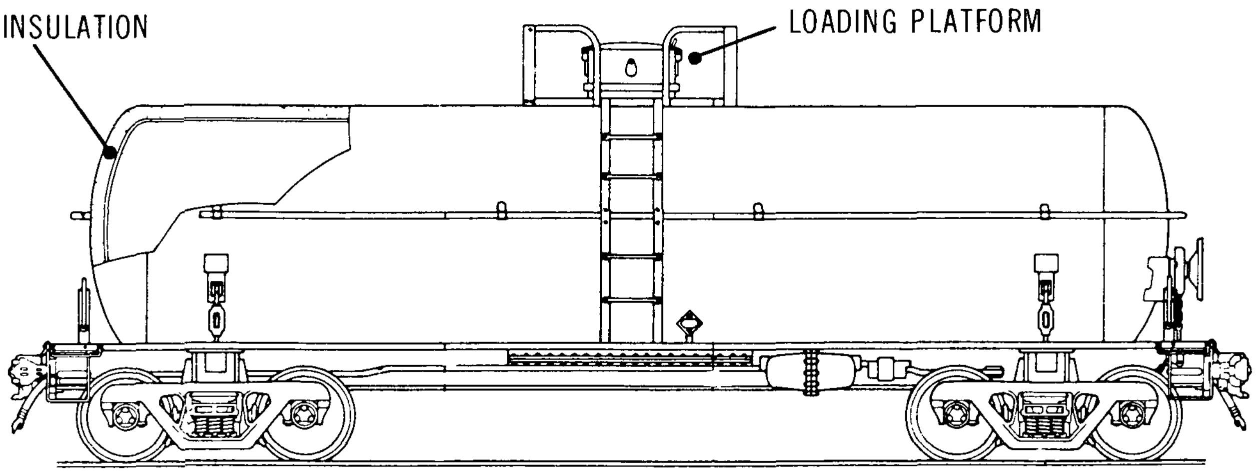


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A300W (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. gal.)					
Description	9000		21 000		28 000	
Overall						
Nominal capacity	41 000 L	(9000 gal.)	95 000 L	(21 000 gal.)	127 000 L	(28 000 gal.)
Car weight - empty	30 300 kg	(66 800 lb.)	40 800 kg	(90 000 lb.)	50 800 kg	(112 000 lb.)
Car weight - (max.)	80 300 kg	(177 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	Steel		Steel		Steel	
Thickness	17.5 mm	(11/16 in.)	17.5 mm	(11/16 in.)	17.5 mm	(11/16 in.)
Inside diameter	2.2 m	(88 in.)	2.4 m	(95 in.)	3.0 m	(120 in.)
Test pressure	2070 kPa	(300 psi)	2070 kPa	(300 psi)	2070 kPa	(300 psi)
Burst pressure	51 700 kPa	(750 psi)	51 700 kPa	(750 psi)	51 700 kPa	(750 psi)
Approximate Dimensions						
Coupled length	13 m	(42 ft.)	20 m	(65 ft.)	20 m	(67 ft.)
Length over strikers	12 m	(40 ft.)	19 m	(63 ft.)	20 m	(64 ft.)
Length of truck centers	9 m	(29 ft.)	16 m	(52 ft.)	16 m	(53 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(12 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(7-10 ft.)	2-3 m	(7-10 ft.)	2-3 m	(7-10 ft.)
Width of grating	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)
Loading/Unloading Fixtures						
Unloading connection	25 mm (1 in.) via valve and 32 mm (1 1/4 in.) check valve					
Valving	2 unloading connections and 2 valves to vapour space					
Safety Devices	Safety relief valve set at 1550 kPa (225 psi)					
Insulation	102 mm (4 in.) foam or cork insulation					

4.1.1.2 Tank motor vehicles. Aqueous hydrofluoric acid is shipped by tank motor vehicles with steel tanks with capacities up to 18 900 L (4200 gal.) (Allied 1978). Similar to railway tank cars, these highway tankers are unloaded from the top; the stand pipe is usually extended down over the back of the tank. Compressed air is used for unloading. The air inlet is usually a 25 mm (1 in.) diameter male threaded connection located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied.

Tank motor vehicles must conform to Transport Canada Specification TC312, as outlined in Table 4. Hydrofluoric acid solutions are not transported under pressure. Highway tankers must be pressure-tested at 311 kPa (55 psi) minimum to allow for the compressed air pressure of 207 kPa (30 psi) used during top unloading. The maximum working pressure of the tanker is in effect 207 kPa (30 psi).

TABLE 4 TANK MOTOR VEHICLE SPECIFICATIONS

TC/DOT* Specification Number	Description
TC312 (MC312)	Steel butt-welded tank. Design and construct in accordance with ASME Code when unloading by pressure in excess of 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment as required by ASME Code. One minimum 380 mm (15 in.) diameter manhole per compartment. Bottom washout optional.

* Transport Canada and Department of Transportation (U.S.)

Anhydrous hydrogen fluoride is occasionally transported in highway tankers similar to those used for aqueous hydrofluoric acid.

4.1.1.3 Cylinders. Cylinders may be used to transport small volumes of anhydrous hydrofluoric acid. DOT Specifications 4B and 4BA are the types most commonly used (MCA 1970). Table 5 describes these cylinders. Brazed cylinders and safety relief devices are not authorized (MCA 1970). Cylinders are most commonly used for laboratory service, with the industry designations of LB (0.4 kg or 0.8 lb.) and G (5.4 kg or 12 lb. HF) being the most common (Linde 1982).

TABLE 5 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
4B	Welded and brazed steel cylinders. Service pressure 1035 to 3450 kPa (150 to 500 psi). Capacity must not exceed 450 kg (1000 lb.) water.
4BA	Welded or brazed steel cylinders made of definitely prescribed steels. Service pressure 1550 to 3450 kPa (150 to 500 psi). Capacity must not exceed 450 kg (1000 lb.) water.

* Canadian Transport Commission and Department of Transportation (U.S.)

4.1.2 **Other Packaging.** Glass carboys are not frequently used; they are used for acid solutions of 52 percent or less (CCPA 1982). A polyethylene container (Specification 2SL) with a steel overpack (Specification 6D) is frequently employed. The container has a 118 kg (260 lb.) capacity and is designed for one-way service, but is returned for disposal (Allied 1978).

4.2 Off-loading

4.2.1 **Off-loading Equipment and Procedures for Railway Tank Cars.** Prior to off-loading hydrofluoric acid, certain precautions must be taken:

- The unloading crew should have available full protective gear and emergency showers (CCPA 1982).
- The use of nonsparking tools is recommended (MCA 1970).
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed (MCA 1970).
- A safe operating platform must be provided at the unloading point.

Proceed with off-loading using pressurized gas as follows (MCA 1970; Allied 1978; du Pont 1982):

- Connect the 51 mm (2 in.) unloading line to the discharge outlet (or both outlets may be used) and connect the 25 mm (1 in.) air line. Gas pressure must be reduced to 193 kPa (28 psi) for unloading. A safety relief valve must be installed in the air line to release at 207 kPa (30 psi) (MCA 1970). Compressed dry nitrogen or hydrocarbon gases may be used in addition to air. The use of air for padding or unloading results in dissolved oxygen and thus leads to corrosion. Thus some users prefer other gases.

- After opening the air supply valve, the unloading connection valve can then be opened to unload the car into the storage tank.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line to be vented to the hydrofluoric acid absorption system.
- Reverse the above procedure to close up the car.

The principles involved in unloading aqueous hydrofluoric acid or anhydrous hydrogen fluoride highway tankers are similar to those of railway tankers. Prior to off-loading anhydrous hydrogen fluoride, measures similar to those for aqueous hydrofluoric acid must be taken.

The railway tank car may be unloaded by compressed air or inert gas (nitrogen or hydrocarbon gases). Liquid anhydrous hydrogen fluoride is discharged from one of the two liquid angle valves. Opening and closing procedures must be followed precisely and in the order recommended by the supplier. Valving must allow for venting of hydrogen fluoride to an absorption system. Gauges are required to ensure that pressures do not drop below vapour pressure.

Pump unloading may be preferred over compressed gas unloading for safety reasons. It may be necessary to pressurize the tank somewhat for priming the pump and to maintain a pressure in the tank. In this case, the pressure should be the minimum needed for effective pumping and large enough to prevent a vacuum from being created in the tank (du Pont 1982).

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in hydrogen fluoride service. It is recognized that other materials may be used for particular applications, as indicated in the following section.

Schedule 80 seamless steel pipes (ASTM A53) and welding fittings are recommended for hydrofluoric acid. Grade ARB or butt-welded steel pipes are recommended for anhydrous hydrogen fluoride. Flanged joints should be used and these should be welded. Screwed connections are not recommended (Allied 1978; du Pont 1982). To minimize corrosion, piping systems should be designed so that they are full of acid at all times (Allied 1978).

Hoses for unloading should be of reinforced construction, with a Teflon inner liner (Allied 1978).

Plug valves in "20" alloy or Monel will serve adequately for all room temperature concentrations of acid. Refer to Table 6 for other material possibilities. Sleeves of tetrafluoroethylene are recommended (Allied 1978). Diaphragms should be made of KEL-F or a laminate of neoprene and Teflon (du Pont 1982).

Polyvinylidene fluoride can be used as gasket material in all acid strengths (DCRG 1978; CCPA 1982).

Centrifugal transfer pumps with wetted parts of "20" alloy stainless steel, Hastelloy G or Monel are recommended for service at ambient temperature. Seals are mechanical and usually water-cooled; they should be specifically designed for hydrofluoric acid service (Allied 1978; du Pont 1982). Steel is not suitable for close-fitting moving parts as iron fluoride build-up can cause seizure (du Pont 1982).

Welded flange-quality A-285 Grade C steel (fully-killed mild steel) storage tanks are commonly used for hydrogen fluoride. This material has a limit of about 65°C; tank materials of Monel and Hastelloy are recommended for higher temperatures (du Pont DS 1982). Normal capacity should be approximately 57 000 L (12 500 U.S. gal.) (Allied 1978). Monometer gauges, strain-gauge load cells, electronic sensors, or tetrafluoroethylene shielded sight gauges may be used for measuring the amount of hydrofluoric acid in a storage tank (Allied 1978). Tanks are subject to indiscriminate hydrogen blistering and must be routinely inspected (CCPA 1982). Desulphurized grades of steel (<0.01 percent S) are less likely to blister (du Pont DS 1982).

4.3 Compatibility with Materials of Construction

The compatibility of hydrofluoric acid with materials of construction is indicated in Table 6. The unbracketed abbreviations are described in Table 7. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	10%	23	PE ABS* PVC I (DPPED 1967)	PVC II (DPPED 1967)	
	10%	49	PE (DPPED 1967)		
	10%	60		PVC I (DPPED 1967)	PVC II (DPPED 1967)
	10%	71			ABS (DPPED 1967)
	<30%				ABS (MWPP 1978)
	<30%	24	PVC I (MWPP 1978)		
	<30%	To operating limit of material	PE (MWPP 1978)		
	37%	79	PVDC (DCRG 1978)		
	37%	93	PP (DCRG 1978)		
	37%	121	PVDF Chlorinated Polyether (DCRG 1978)		
	48%	23	PVC I (DPPED 1967)	PVC II (DPPED 1967)	
	48%	60		PVC I (DPPED 1967)	PVC II (DPPED 1967)
	48%	66	PVDC (DCRG 1978)		
	48%	93	PP (DCRG 1978)		
	48%	107	PVDF (DCRG 1978)		

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (cont'd)	48%	121	Chlorinated Polyether (DCRG 1978)		
	60%	93	PP (DCRG 1978)		
	60%	107	PVDF (DCRG 1978)		
	60%	121	Chlorinated Polyether (DCRG 1978)		
	70%	<120	PVDC (MCA 1970)		
	100% (anhydrous)	93	PP, PVDF (DCRG 1978)		
	100% (anhydrous)	Not specified	Teflon (du Pont DS 1982)		Chlorinated Polyether (DCRG 1978)
	100% (anhydrous)	24	PVC I (MWPP 1978)		PE (MWPP 1978)
2. Valves	<10% or <60%	21	SS J-20 (JSSV 1979)		SS 316 (JSSV 1979)
3. Pumps	See Section 4.2.2				
4. Storage	See Section 4.2.2				

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others	All	20			SS 302, SS 304 SS 316, SS 410 SS 430 (ASS) Leather, Rubber, Glass, Concrete (Allied PSDS 1981) Cast Iron, SS 400, Hardened Steels (du Pont 1982)
	Dilute	22	PVC CPVC (TPS 1978)		
	Dilute	23	PP (TPS 1978)		
	Dilute	100	PP (TPS 1978)		
	30%	22	PVC, CPVC (TPS 1978)		
	30%	49	PP (TPS 1978)		
	30%	66	PVDF (TPS 1978)	PP (TPS 1978)	
	40%	22	PVC, CPVC (TPS 1978)		
	40%	49	PP (TPS 1978)		
	40%	66		PP (TPS 1978)	
	Up to 40%	20	uPVC, PE, PP, CSM (GF)	NR, IIR, EPDM, CR, FPM (GF)	POM NBR (GF)
	40%	60	PE PP (GF)	uPVC FPM CSM (GF)	POM, NR, NBR, IIR, EPDM, CR (GF)

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (cont'd)	50%	22	PVC CPVC (TPS 1978)		
	50%	23	PP		
	50%	60			PVC (TPS 1978)
	60%	20	PE PP (GF)	IIR, EPDM, FPM, CSM (GF)	uPVC, POM, NR, NRB, CR (GF)
	70%	20		PE, PP, IIR*, EPDM*, CSM* (GF)	uPVC, POM, NR, NBR, CR, FMP (GF) SBR, IIR, CSM, EPDM (GPP)
	>70%	various	Low CS (MCA 1970)		Copper, Copper Alloys, Cast Iron, Type 400 Stainless Steels, Hardened Steels (du Pont 1982)
	>70%	various	Nickel (over 10% <100°C), Lead (chemical grade, <60%, <100°C), Silver, Carpenter 20, 70-30 Copper-Nickel Alloy, Magnesium (<85°C), Hastelloy Alloys B, C, D, Karbate, Neoprene (<50%, <60°C) uPVC		Steel, Stainless Steels, Ni-resist Cast Iron, High Silicon Iron, Glass, Ceramics, Aluminum, Inconel (<10%, <77°C), Wood Tantalum Titanium Zirconium Asbestos

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)			Rubber-lined Steel (<60%, <60°C), Butyl-rubber Lined Steel (<60%, <60°C), Carbon-filled Sulphur Cement, Saran-lined Pipe, Polypropylene, Vinylidene Fluorides, Fluorocarbons, Platinum		Hardened steels (du Pont 1982)
	70%	various	Magnesium (MCA 1970) Inconel, Hastelloy B, C & D, Nickel, Ni-resist Carpenter 20, Durimet - 20, Magnesium, Chlorimet 2 & 3, PE, uPVC, Fluorocarbons, Platinum, Molybdenum	Low-carbon Steels (to 150°C), Karbate (70%), Saran-lined Pipe (70%, <49°C)	Yellow Brass, Lead, Cast Iron, High-silicon Iron, Aluminum, Stainless Steels, Tantalum, Titanium, Zirconium, Rubber, Glass, Ceramics, Epoxies, Asbestos
	>10%	<100	Nickel (MCA 1970)		
	<10%	<77			Inconel (MCA 1970)

* This material has been given a lower rating in a similar application by another reference.

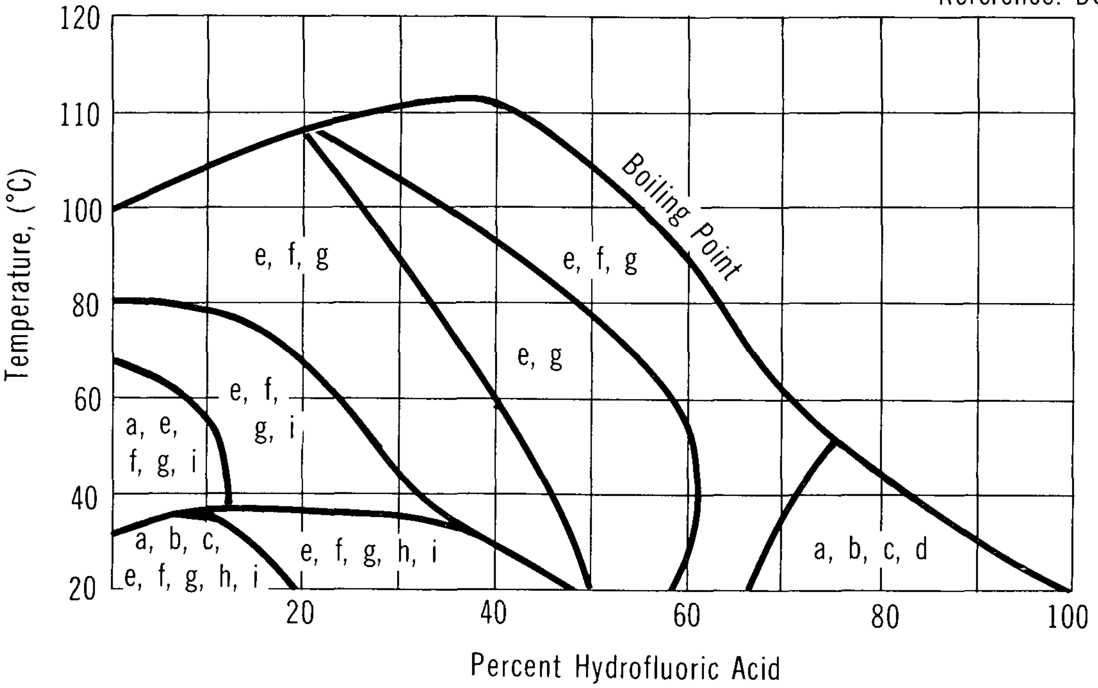
TABLE 7 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
	Chlorinated Polyether
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FEP	Fluorinated Ethylene/Propylene (Teflon)
FPM	Fluorine Rubber (Viton)
IIR	Isobutylene/Isoprene Rubber (Butyl)
	Magnesium
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Nickel
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S)
SS (Followed by grade)	Stainless Steel
TFE	Tetrafluoroethylene (Teflon)
uPVC	Unplasticized Polyvinyl Chloride

FIGURE 10

MATERIALS YIELDING CORROSION RATES LESS THAN 0.5 mm (0.02 in.) PER YEAR

Reference: DU PONT 1982



a	carpenter 20 C6-3
b	worthite
c	durimet 20
d	carbon steel
e	Cu-Ni CA 715
f	copper (no air, low velocity)
g	lead (no air, low velocity)
h	nickel (no air)
i	NORDEL

All areas:

Chlorimet 3

Hastelloy C

Monel 400

Gold

Silver

Platinum

Teflon

5 CONTAMINANT TRANSPORT

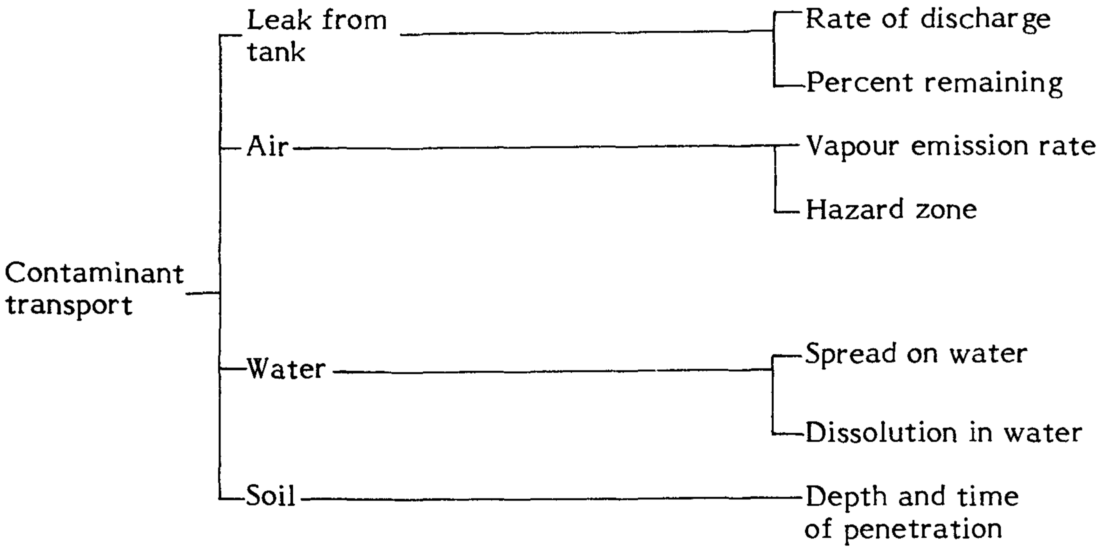
5.1 General Summary

Hydrogen fluoride is commonly transported in tanks as a liquefied gas. When spilled in the environment, it will form both a liquid pool, spreading on the surface of a water body or on the ground, and a vapour cloud. Vapour is released rapidly from the pool to the atmosphere by evaporation.

When spilled on water, some will dissolve and the rest will evaporate to the atmosphere. The vapour cloud tends to hug the ground and spread, rather than lift off the ground and disperse.

Hydrogen fluoride spills on soil surfaces will partly evaporate and partly adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport of the liquid toward the groundwater table may be an environmental problem. Hydrofluoric acid will behave similarly when spilled, although much less hydrogen fluoride will be emitted.

The following factors are considered for the transport of a spill in the air, water and soil media:



5.2 Leak Nomograms

5.2.1 Introduction. Nomograms for leaks of anhydrous hydrogen fluoride from railway tank cars are given in this section. While the capacities of the railway tank cars vary widely, one size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. This size has been used throughout the EnviroTIPS series to allow for comparisons among the different chemicals.

If a tank car loaded with hydrogen fluoride is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole size (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, the discharge coefficient has been assumed to be constant at 0.8.

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal), equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 200 kPa.

The assumption of isothermal conditions, which maximize the gas release rate from the tank, will generally provide worst case values. Because the boiling point of anhydrous hydrogen fluoride is 19.54°C, evaporation will rapidly cool the liquid past its boiling point. This will in many cases result in significantly less evaporative loss than predicted by the isothermal model. It is estimated that the time for gas venting as predicted below would be correct in situations where the tank car has no insulation or has lost a significant portion of its insulation and is involved in a fire which compensates for the evaporative cooling. It is also estimated that the venting times predicted would be 1 order of magnitude slower (10 times longer) if the tank car had lost most of its insulation and the ambient temperature was warm; 2 to 4 orders slower if the tank car had lost less of its insulation and the temperature was cooler; and 4 to 7 orders slower if little insulation was lost and the ambient temperature was low.

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

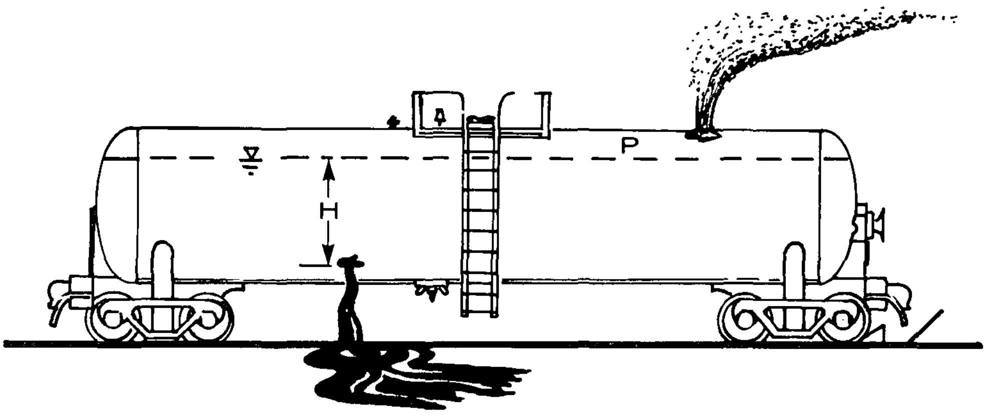


FIGURE 11 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 12: Percent remaining versus time. Figure 12 provides a means of estimating the percent of hydrogen fluoride remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m ∅ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80 000 L of hydrogen fluoride at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 13: Discharge rate versus puncture size. Figure 13 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate only changes slowly as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 14: Percent remaining versus time. Figure 14 provides a means of estimating the percent of hydrogen fluoride remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

FIGURE 12

HYDROGEN FLUORIDE

PERCENT REMAINING vs TIME

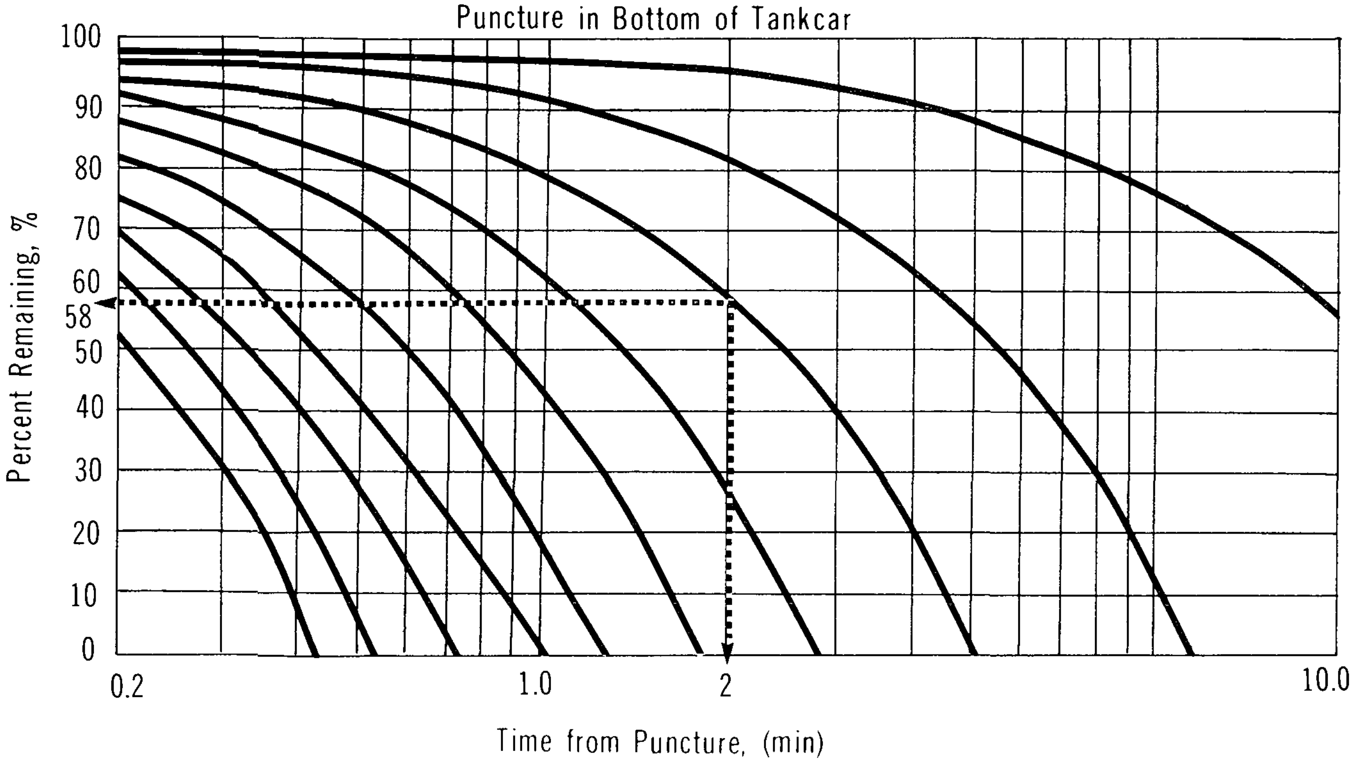
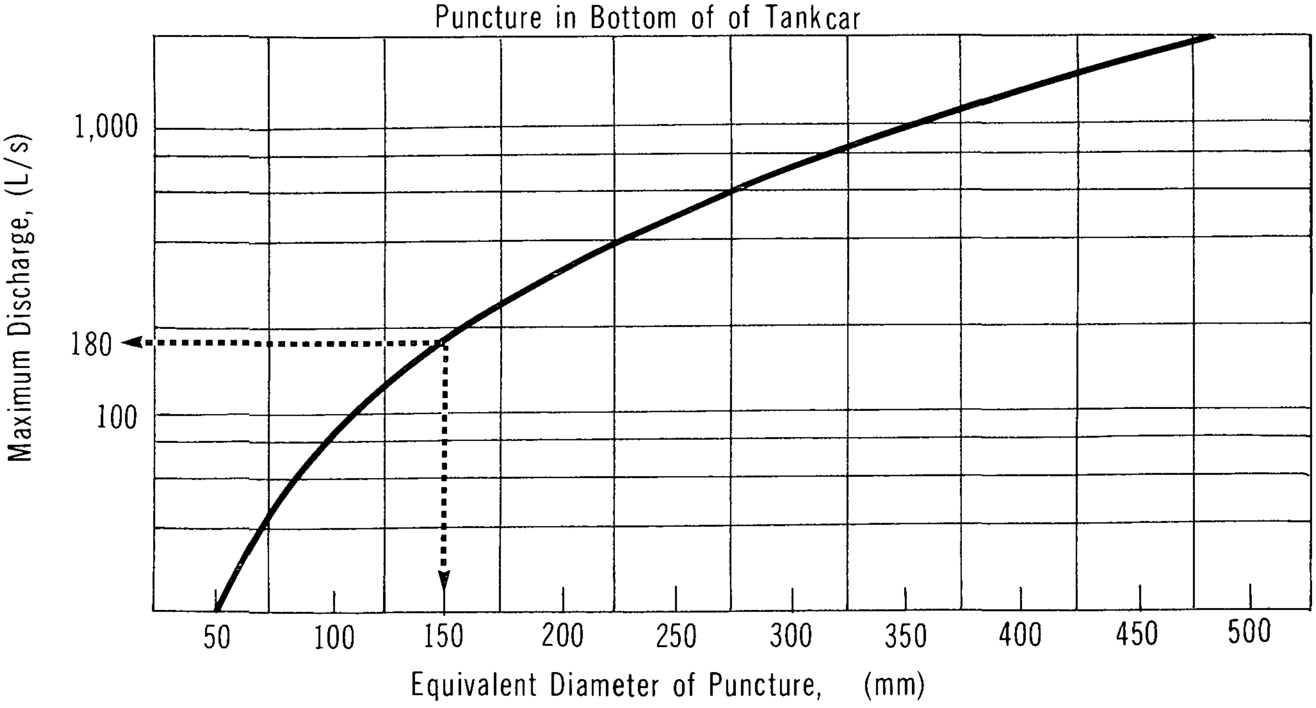


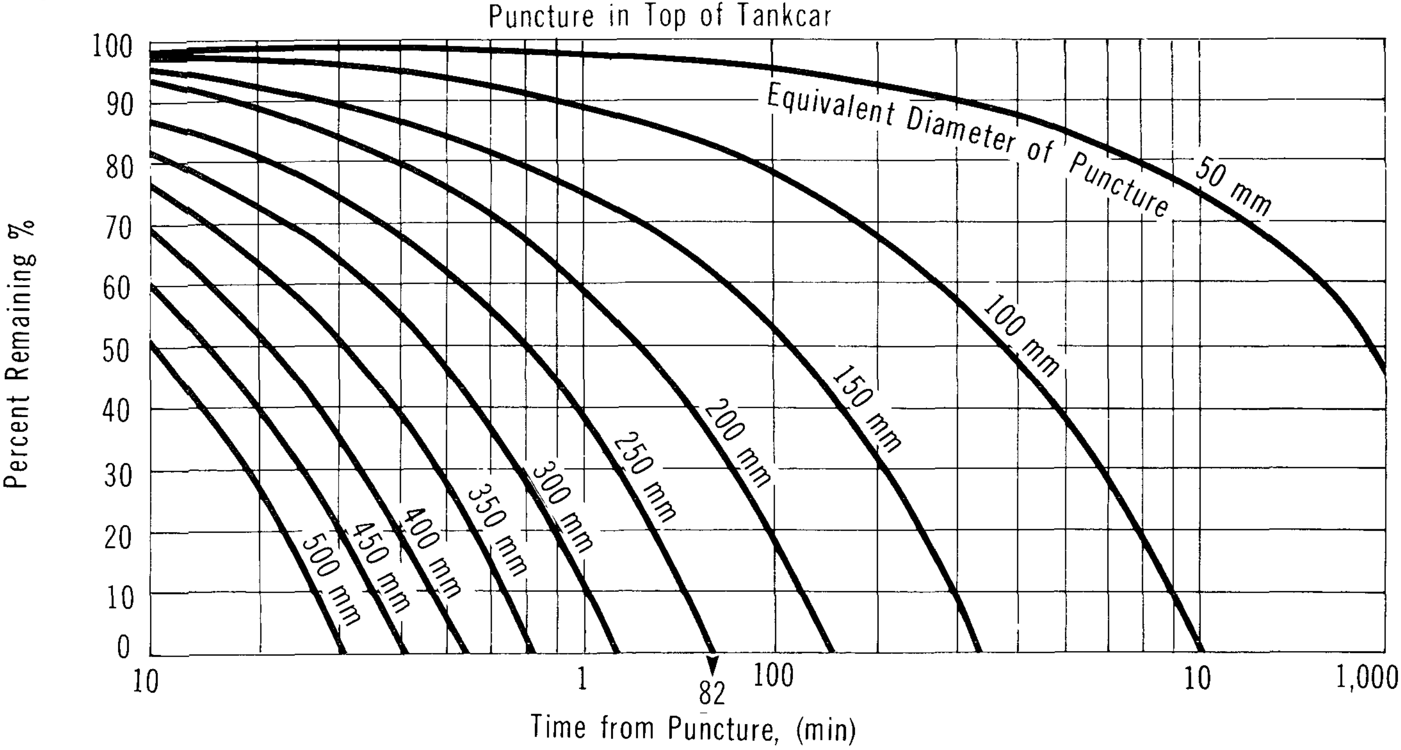
FIGURE 13

HYDROGEN FLUORIDE

DISCHARGE RATE vs PUNCTURE SIZE



PERCENT REMAINING vs TIME



As isothermal conditions have been assumed, the internal pressure and venting rate are constant. Users should note that the rate predicted by this figure can be much slower than predicted above.

Figure 15: Discharge rate versus puncture size. Figure 15 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

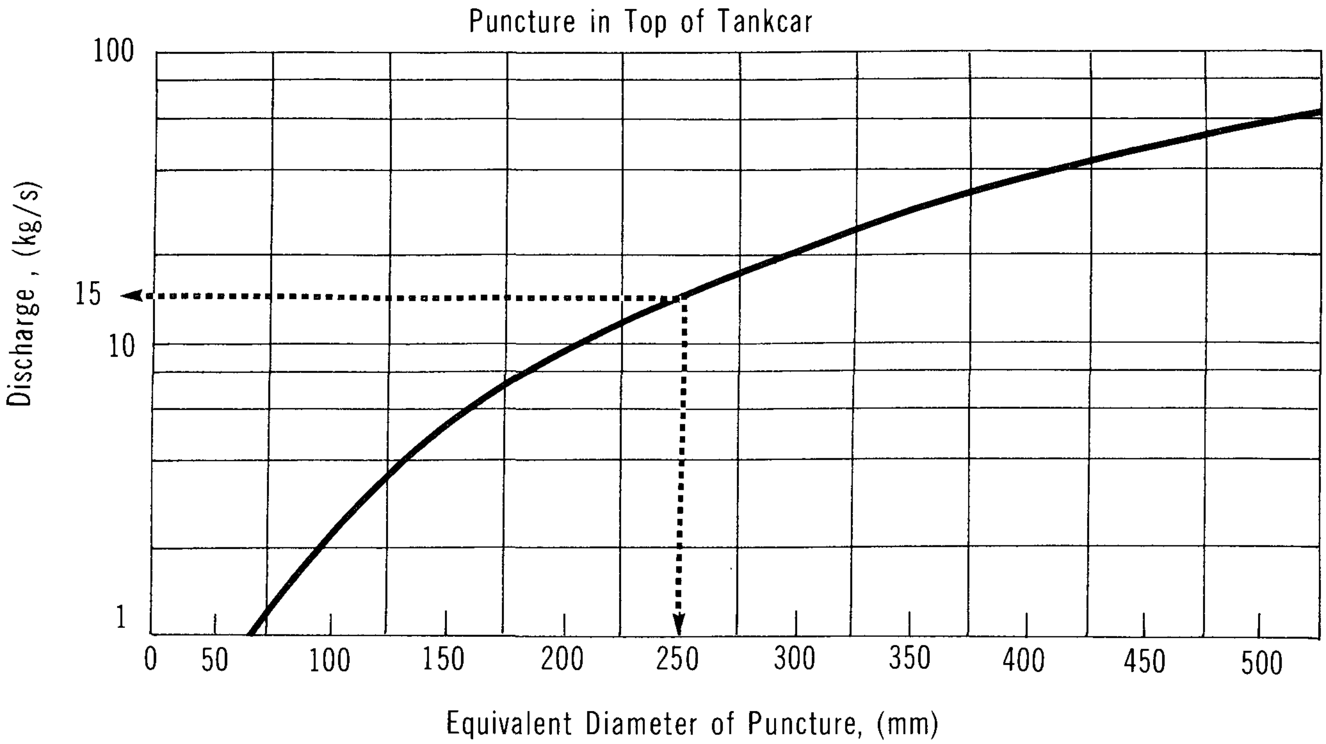
The values presented in Figure 15 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 200 kPa. Again, users should note that the discharge rate could be much shorter, as indicated above.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with hydrogen fluoride at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the

DISCHARGE RATE vs PUNCTURE SIZE



initial 80 000 L remains after 2 minutes and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate amount remaining at t=2 min

- Use Figure 12
- With t=2 min and d=150 mm, the amount remaining is about 58 percent or 46 000 L

Step 2: Calculate the discharge rate

- Use Figure 13
- With d=150 mm, the instantaneous discharge rate (q) =180 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 14

- With d=250 mm, the tank empties (0 percent remaining) in approximately 82 min

Step 2: Calculate the discharge rate

- Use Figure 15
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 15 kg/s. As noted, depending on ambient temperature and tank car insulation, the time for complete venting could be much longer and the rate much smaller

5.3 Dispersion in the Air

5.3.1 Introduction. Although anhydrous hydrogen fluoride is a relatively volatile liquid (boiling point 19.5°C), direct venting of the vapour to the atmosphere from a hole in a punctured vessel is not considered here. Only vapour released from a liquid pool spilled on a ground or water surface is treated here. Direct venting may be calculated by using the instantaneous discharge rates given in Figure 15 and using the methodology described later.

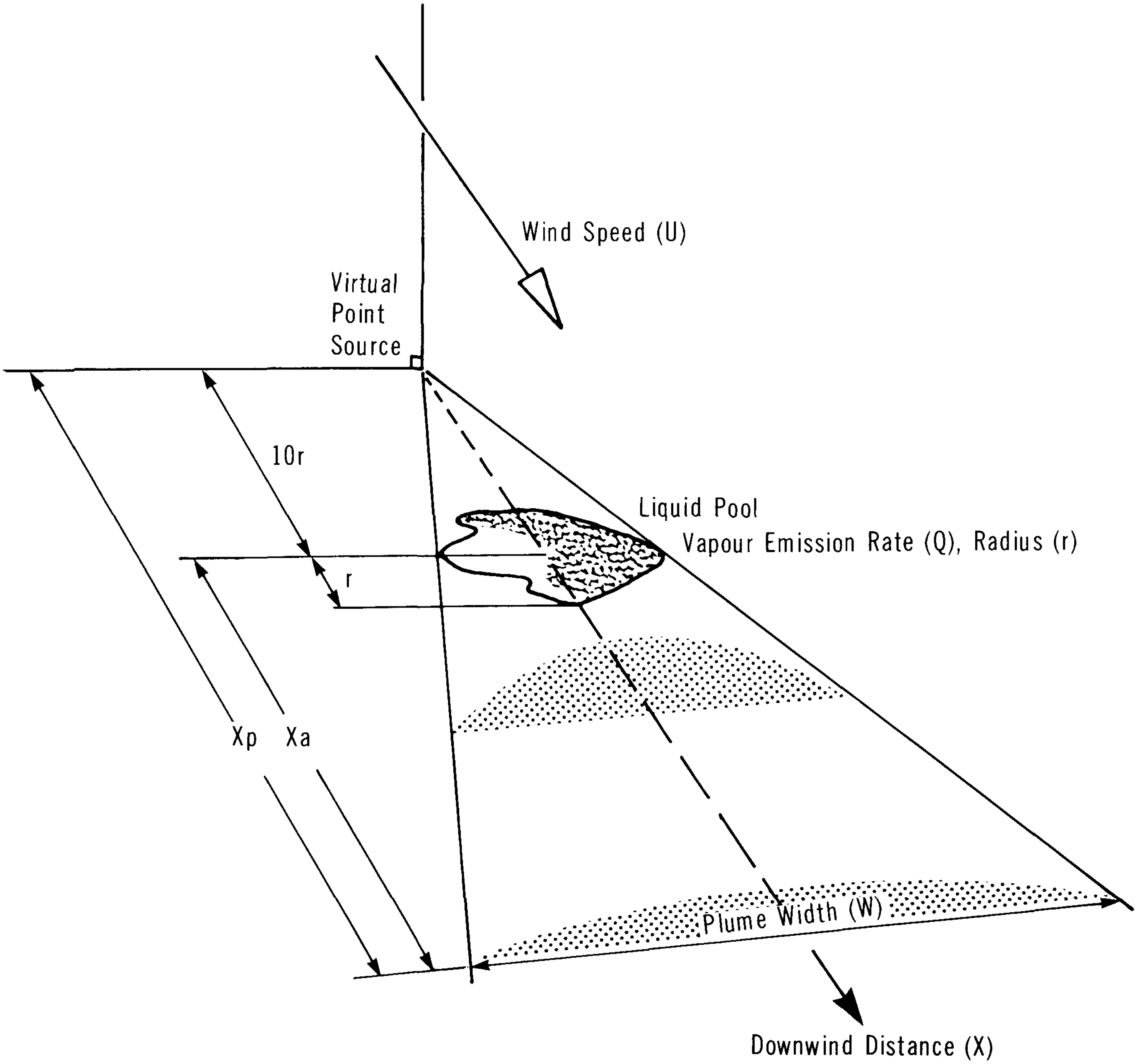
Spills of hydrofluoric acid may be treated in the same manner as anhydrous hydrogen fluoride. Since hydrofluoric acid is less volatile than anhydrous hydrogen fluoride, the use of the vapour dispersion nomograms and tables presented for anhydrous hydrogen fluoride will overestimate the hazard as a result of hydrofluoric acid spills.

It has been reported (Beattie 1978) that the observed properties of hydrogen fluoride vapour can best be explained on the basis of an equilibrium between a hexameric species $(HF)_6$ and the monomer (HF). High temperatures and low partial pressures tend to favour the monomer. At ambient temperatures, hydrogen fluoride shows an apparent molecular weight of 70 to 80 (Kirk-Othmer 1980). Initially, then, the vapour would behave similarly to chlorine, since the respective molecular weights are similar, i.e., 71 for chlorine and 70 to 80 for hydrogen fluoride (at 101.3 kPa and 20°C).

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 16 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source

SCHEMATIC OF CONTAMINANT PLUME



as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

Figure 18:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 8:	weather conditions
Figure 19:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 9:	maximum plume hazard half-widths
Figure 21:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 17 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

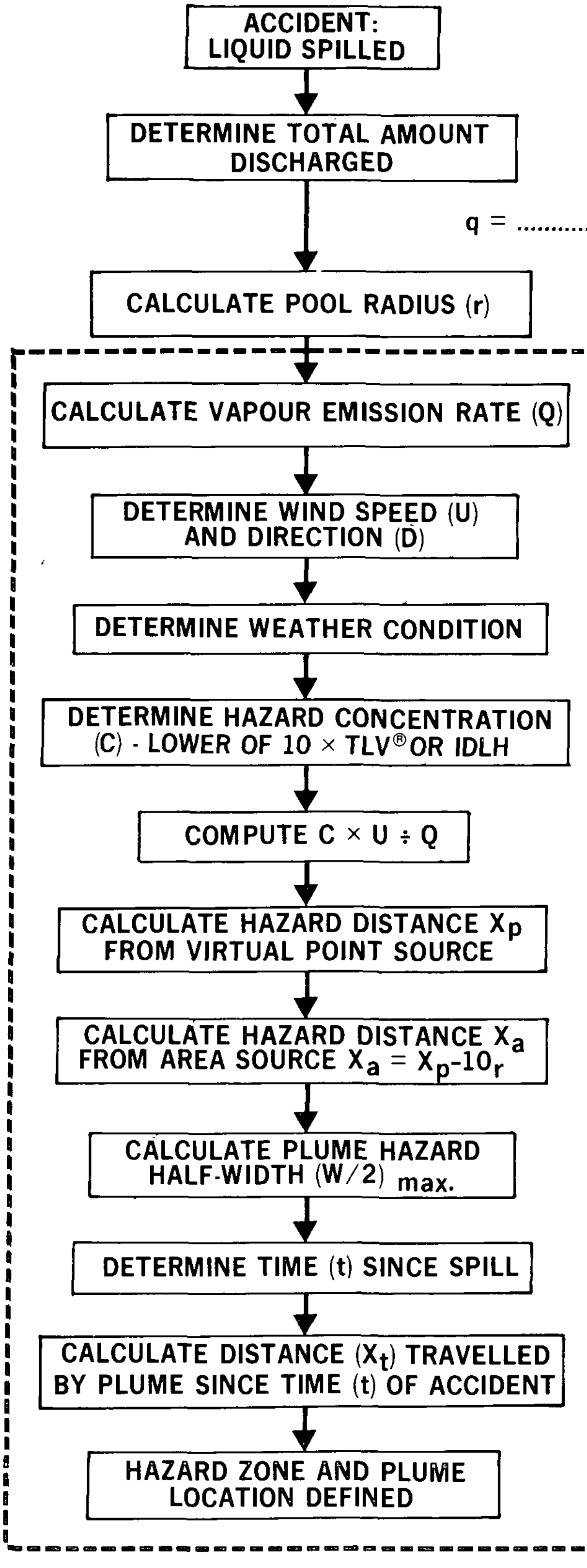
5.3.2.1 Figure 18: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for anhydrous hydrogen fluoride has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for hydrogen fluoride at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 5.69 g/(m^2•s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which, at a given wind speed, is dependent on ambient temperature and the vapour pressure (CRC 1980; Perry 1973) of hydrogen fluoride at that temperature. For example, evaporation rates of 2.89 g/(m^2•s) at 0°C and 7.74 g/(m^2•s) at 30°C were calculated for a wind speed of 4.5 m/s.

Using Figure 24, Section 5.4, the maximum spill radius corresponding to various spill amounts of hydrogen fluoride may be determined. The resultant spill areas and the hydrogen fluoride evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 18.

Use: For a pool of hydrogen fluoride of known radius, the rate (Q) at which hydrogen fluoride vapour is released to the atmosphere at a given temperature can then

FIGURE 17

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 12 Section 5.2

Time since puncture....... minutes
Equivalent diameter of puncture........ mm
Percent of chemical remaining .... %
Amount discharged:
q = 80,000 L - % × 80,000 L = ... L
q = ... L × density (kg/L)× 1,000 = ... tonnes

Step 2: Use Figure 24 Section 5.4

r = ... km

Step 3: Use Figure 18

Q = ... g/s

Step 4: Observed or estimated

U = ... km/h; D = ... degrees

Step 5: Use Table 8 Condition = ...

Step 6: C = 0.017 g/m^3 for Hydrogen Fluoride IDLH

Step 7: Computation required

CU/Q = ... m^{-2}

Step 8: Use Fiqure 19

X_p = ... km

Step 9: Computation required

X_a = ... m

Step 10: Use Table 9

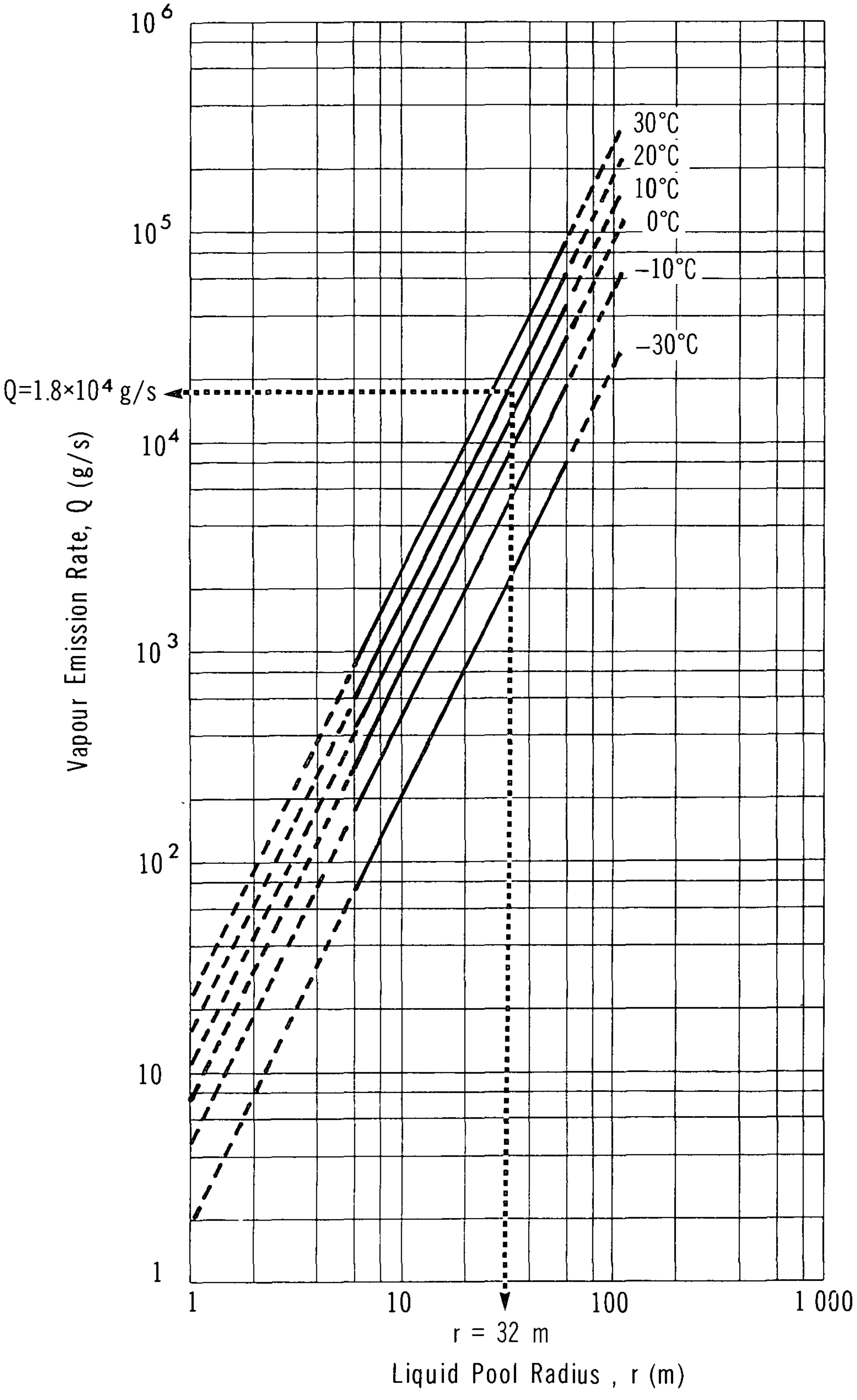
$(W/2)_{max.}$ = ... m

Step 11: t = ... s

Step 12: Use Figure 21 with U from Step 4.

X_t = ... km

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.05 to 70 tonnes

be estimated from Figure 18. The solid portions of the curves represent spills of 0.05 to 70 tonnes, the latter representing about one standard 80 000 L rail car load of hydrogen fluoride. It should be noted that Figure 18 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of hydrogen fluoride vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that determination of the evaporation rate is based on the spill radius on calm water (Table K1, CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

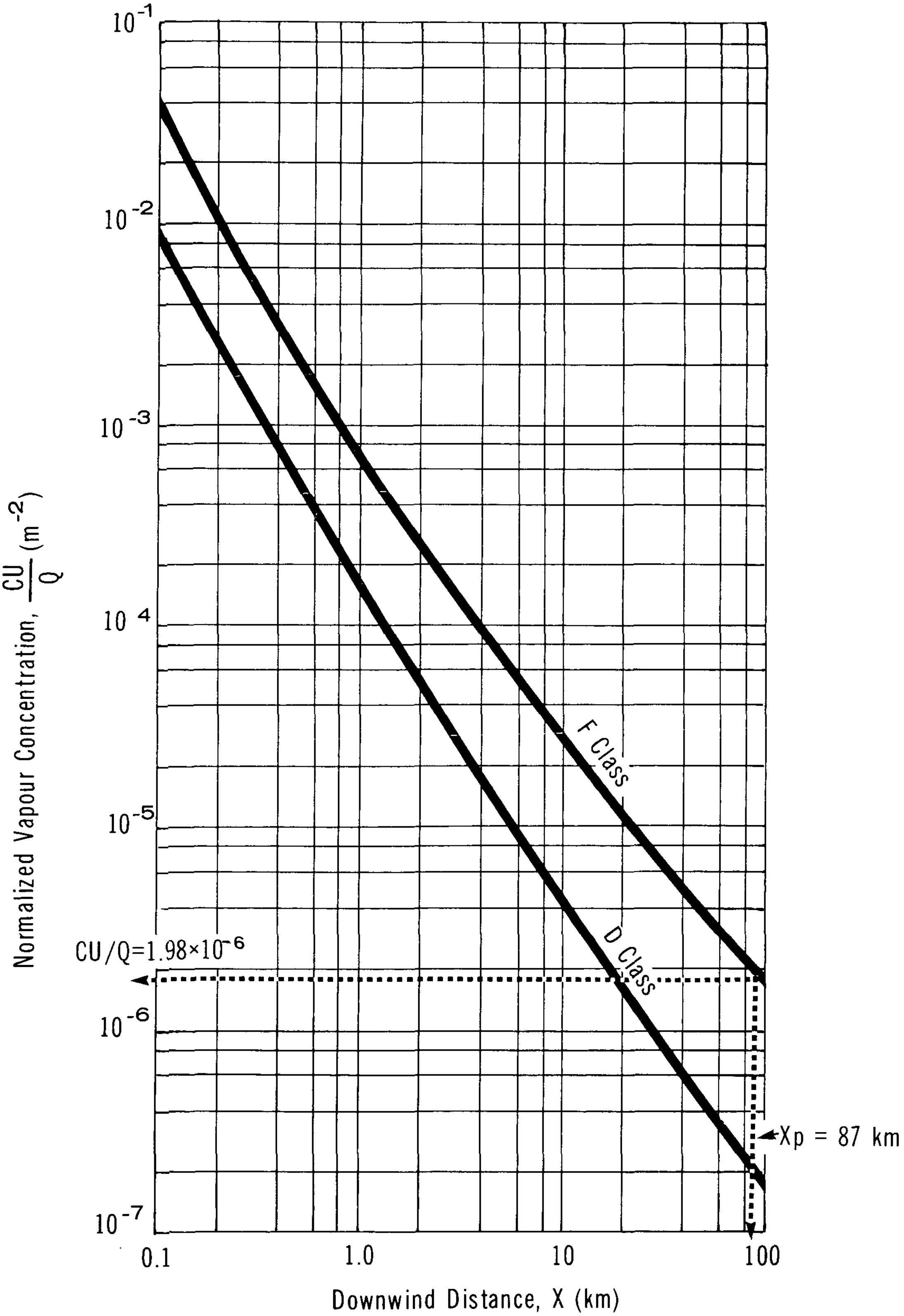
5.3.2.2 **Figure 19: Vapour concentration versus downwind distance.** Figure 19 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 17, the weather condition must be determined from Table 8.

TABLE 8 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed less than 11 km/h (~3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	All other weather conditions

Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 17 knowing:

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of times the Threshold Limit Value® (TLV, in g/m^3), or the Immediate Danger to Life and Health value (IDLH, in g/m^3). Note: To convert the TLV®, in ppm, or the IDLH, in ppm, to concentrations in g/m^3, use Figure 20.

A hazard concentration limit of 10 times the TLV® (or, in some instances, the IDLH) has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones. It should be noted that the IDLH of 20 ppm may be a case where the example chosen represents a high value. A public exposure limit of 10 ppm for 10 minutes and 5 ppm for 60 minutes has been suggested for emergencies (PB 203465).

5.3.2.3 **Table 9: Maximum plume hazard half-widths.** This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$ for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for the hydrogen fluoride IDLH value of 0.017 g/m^3 (the maximum plume vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of the IDLH value). Table 9 is therefore only applicable for a hydrogen fluoride hazard concentration limit of 0.017 g/m^3 (IDLH). Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 750 to 110 000 g/s, corresponding to hydrogen fluoride spills in the range of about 0.05 to 200 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 79 400 kg, or approximately 79 tonnes. Therefore, under Class D of Table 9, data are provided for up to 2.5 times this amount to allow for the modelling of incidents involving more than one tank car, e.g., multiple tank cars or storage tanks.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 75 to 10 000 g/s, corresponding to hydrogen fluoride spills in the range of about 1 to 1000 tonnes, respectively. Therefore, under class F of Table 10, data are provided for up to about 10 percent of a standard rail car load.

TABLE 9 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR HYDROGEN FLUORIDE AT 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
110 000	3 265	(99.5 km)*	10 000	1 410	(99.5 km)*
100 000	3 080	Q/U = 8 570→	9 000	1 300	→$(W/2)_{max}$ = 1 300 m
80 000	2 680		7 500	1 140	
60 000	2 245		5 000	840	
50 000	2 005		4 000	710	
40 000	1 750		3 000	575	
30 000	1 460		2 000	425	
25 000	1 305		1 500	345	
20 000	1 140		1 000	265	
15 000	950		750	220	
10 000	740		500	170	
7 500	620		200	95	
5 000	490		100	60	
1 500	245		50	40	
1 000	190		25	30	
750	160				
500	130				
200	75				
100	50				
50	35				
25	25				

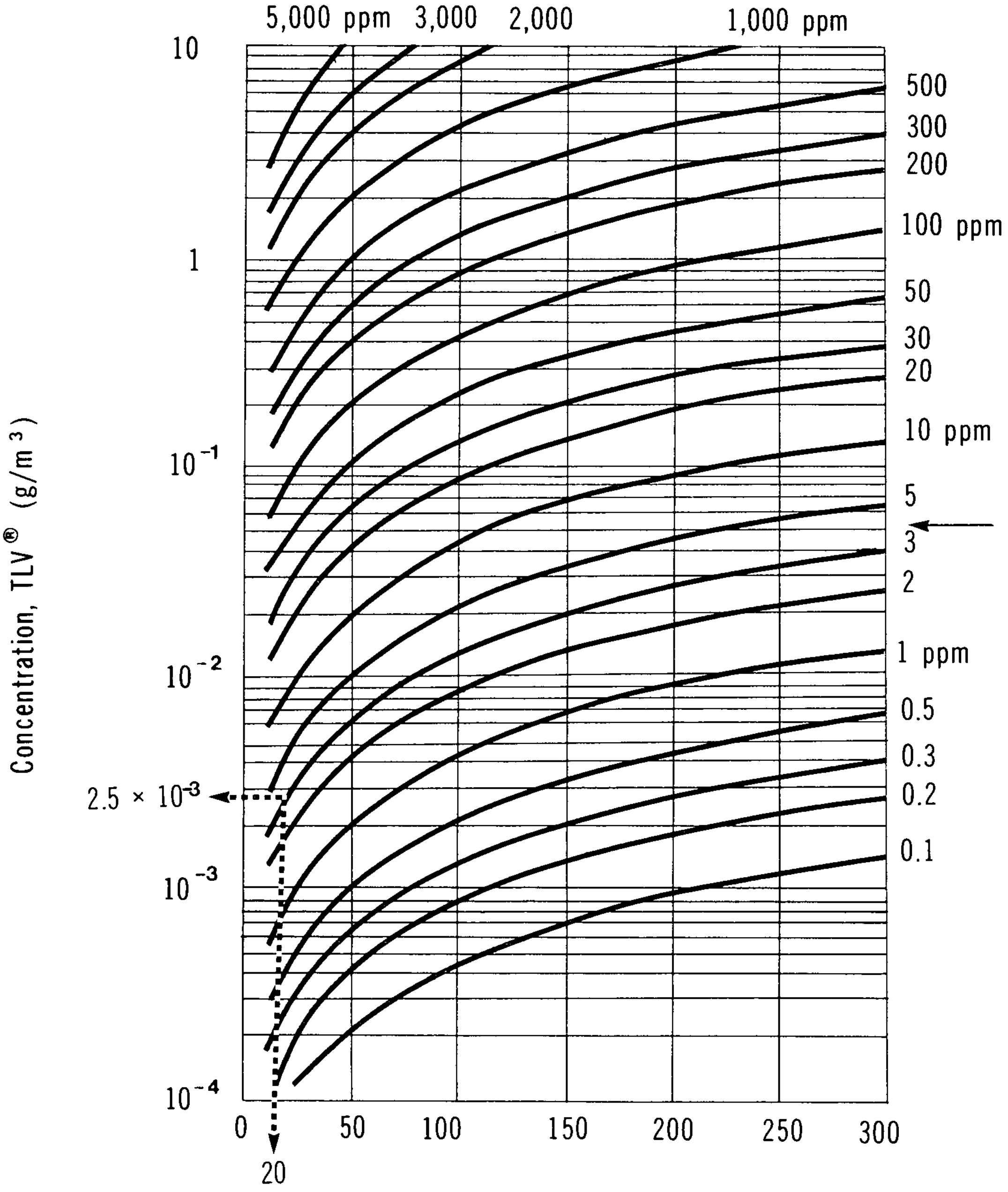
* Data are provided up to a maximum downwind hazard distance of 100 km.

Example: A spill releasing hydrogen fluoride vapour at the rate of $Q = 1.8 \times 10^4$ g/s under weather conditon F and a wind speed U = 2.1 m/s means Q/U = 8570 g/m, which results in a maximum plume hazard half-width $(W/2)_{max}$ = 1300 m.

Note: Above table is valid only for a hydrogen fluoride concentration of 0.017 g/m^3 (the IDLH).

FIGURE 20

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Molecular Weight

Example: Hydrogen Fluoride, MW=20, TLV®=3 ppm
then TLV® in g/m³ =2.5×10⁻³

Note: data applicable at 25° and 760 mm Hg pressure

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 9.

5.3.2.4 **Figure 21: Plume travel time versus travel distance.** Figure 21 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the plume has travelled.

5.3.3 **Sample Calculation.** The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquefied hydrogen fluoride. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e. of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of anhydrous hydrogen fluoride were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind speed is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given, q = 20 tonnes

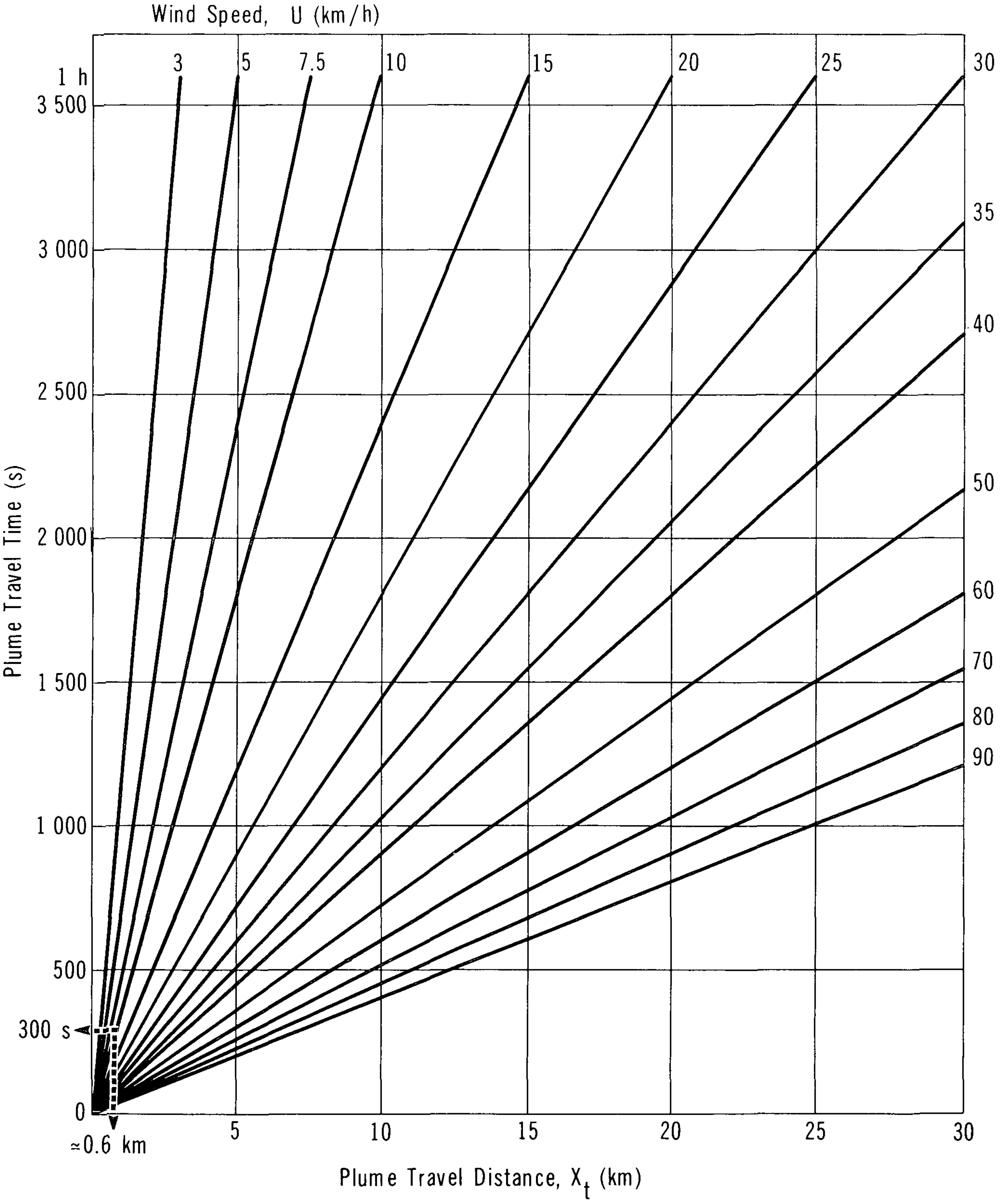
Step 2: Determine pool radius (r) for spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius from Figure 24, Section 5.4. Note that use of these data, which apply specifically to spills on water, will result in an exaggerated pool radius on land
- Radius (r) = 32 m ÷ 1000 = 0.032 km

Step 3: Calculate vapour emission rate (Q) at T = 20°C

- From Figure 18, for r = 32 m and T = 20°C, $Q = 1.8 \times 10^4$ g/s

PLUME TRAVEL TIME VS TRAVEL DISTANCE



Step 4: Determine wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: $U = 7.5$ km/h, then $U = 7.5 \div 3.6 = 2.1$ m/s

  D = NW or 315° (D = Direction from which wind is blowing)

Step 5: Determine weather condition

- From Table 8, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the IDLH, so for hydrogen fluoride

  $C = 0.017$ g/m^3 (TLV® = 0.0025 g/m^3; IDLH = 0.017 g/m^3)

Step 7: Compute CU/Q

- $$Cu/Q = \frac{0.017 \times 2.1}{1.8 \times 10^4} = 1.98 \times 10^{-6} \text{ m}^{-2}$$

Step 8: Calculate downwind distance (X_p) from the virtual point source

- From Figure 19 with CU/Q = 1.98×10^{-6} m^{-2} and weather condition F, $X_p \simeq 87$ km (± 2 km)

Step 9: Calculate hazard distance (X_a) downwind of the area source

- With $X_p = 87$ km and $r = 0.032$ km, then

  $X_a = X_p - 10\,r = 87 \text{ km} - 10\,(0.032 \text{ km}) = 87$ km

Step 10: Calculate plume hazard half-width, $(W/2)_{max}$

- Use Table 9
- With $Q = 1.8 \times 10^4$ g/s and $U = 2.1$ m/s

  $$\text{then } Q/U = \frac{1.8 \times 10^4}{2.1} = 8\,570 \text{ g/m}$$
- Then for weather condition F, the closest Q/U value is 9 000 g/m which gives $(W/2)_{max} \simeq 1{,}300$ m

Step 11: Determine the time since spill

- $t = 5 \text{ min} \times 60 = 300$ s

Step 12: Calculate distance travelled (X_t) by vapour plume since time of accident

- Using Figure 21 with $t = 300$ s and $U = 7.5$ km/h, then $X_t = 0.6$ km (more accurately from $Ut = 2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63$ km)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (1300 m) by the hazard distance downwind of the area source (87 km) along the direction of the wind, as shown in Figure 22
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 23.
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 690 minutes before the hydrogen fluoride vapour plume reaches the maximum downwind hazard distance of 87 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, hydrogen fluoride will boil, vaporize and at the same time will spread on the surface and mix with the water to form hydrofluoric acid. Concentrated hydrofluoric acid will boil (react violently), release some hydrogen fluoride, sink, and mix.

For the purpose of nomogram preparation, two worst case situations have been assumed. First, the extent of spread on the surface of the water has been estimated, assuming that none of the hydrogen fluoride is dissolved in the water. However, the loss due to vaporization has been taken into account. Secondly, the water pollution hazard has been evaluated by assuming all of the hydrogen fluoride is dissolved with water and no vaporization occurs. These two cases represent the worst case situations for the extent of spread of hydrogen fluoride on the surface of water and for the water pollution hazard associated with hydrogen fluoride dissolved in water.

5.4.2 Spreading on Water. The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since liquids such as hydrogen fluoride are evaporated quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization. The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size. No dissolution is assumed for this case to allow for a worst-case prediction. The spreading is primarily used to predict the

FIGURE 22

HYDROGEN FLUORIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

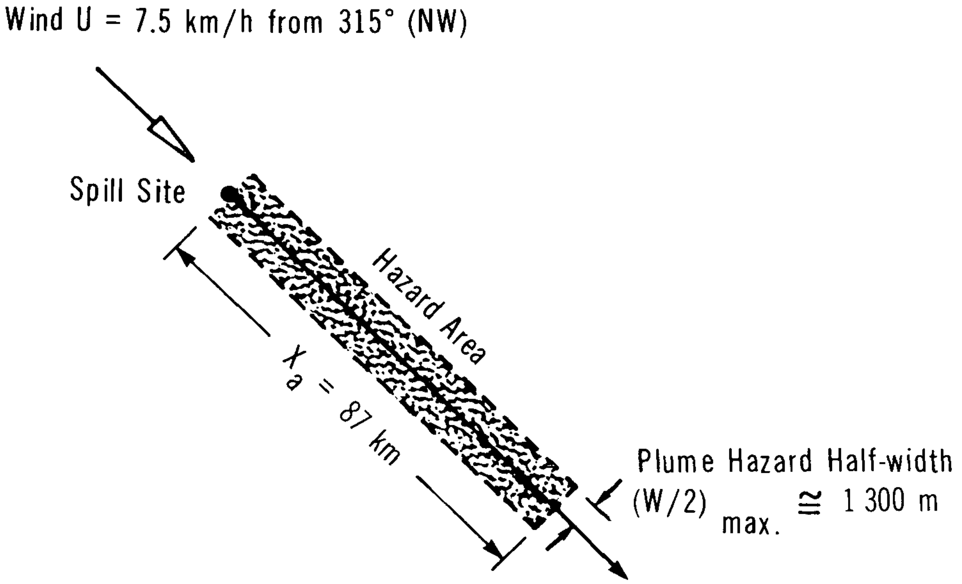
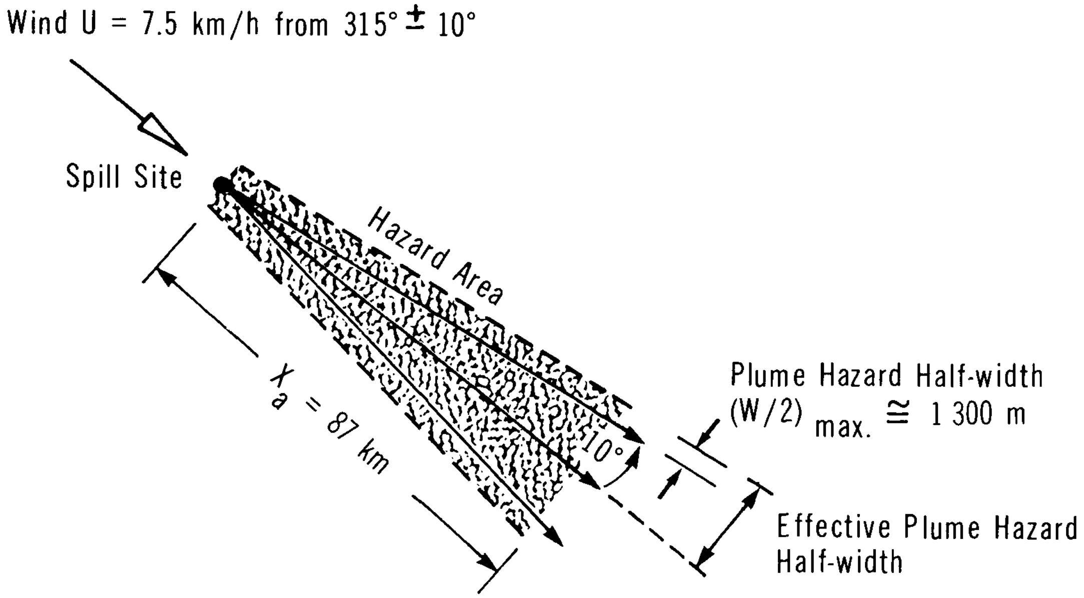


FIGURE 23

HYDROGEN FLUORIDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



$= X_a \times 1000 \times \tan 10° + (W/2)_{max}$

$= 87 \times 1\,000 \times \tan 10° + 1\,300$ m

$= 16\,640$ m or 16.6 km

worst case for a land spill since on water the evaporation and dissolution will make the radius very much smaller than predicted here.

5.4.3 Dissolution in Water. For this condition, all of the spilled hydrogen fluoride is assumed to dissolve rapidly without any vaporization. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water and therefore is applicable to hydrogen fluoride.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and the Manning's roughness coefficient is 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.4 Nomograms. The following nomograms are presented to calculate spreading on still water (without dissolution) and to estimate pollutant concentrations in non-tidal rivers and in lakes (without vaporization).

Spreading on Still Water

Figure 24: maximum spill radius versus spill size with estimated times for complete evaporation

Dissolution in Water - Non-tidal Rivers

Figure 26: time versus distance for a range of average stream velocities

Figure 27: hydraulic radius versus channel width for a range of stream depths

Figure 28: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 29:	alpha* versus diffusion coefficient for various time intervals
Figure 30:	alpha versus delta* for a range of spill sizes
Figure 31:	maximum concentration versus delta for a range of river cross-sectional areas

Dissolution in Lakes or Still Water Bodies

Figure 32:	volume versus radius for the hazard zone for a range of lake depths
Figure 33:	average concentration versus volume for the hazard zone for a range of spill sizes

5.4.4.1 Nomograms for spreading on still water.

Figure 24: Maximum spill radius versus spill size. Assuming no dissolution in water, Figure 24 provides a simple means of estimating the maximum spill radius for hydrogen fluoride, if the spill size is known. This nomogram is used primarily for predicting worst case situations on land. In water, evaporation and dissolution will make the radius very much smaller. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The bracketed figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not considered.

5.4.4.2 Nomograms for dissolution in water - non-tidal rivers. The flowchart in Figure 25 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 26 through 31) are described in the following subsections.

Figure 26: Time versus distance. Figure 26 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 26.

Figure 27: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate

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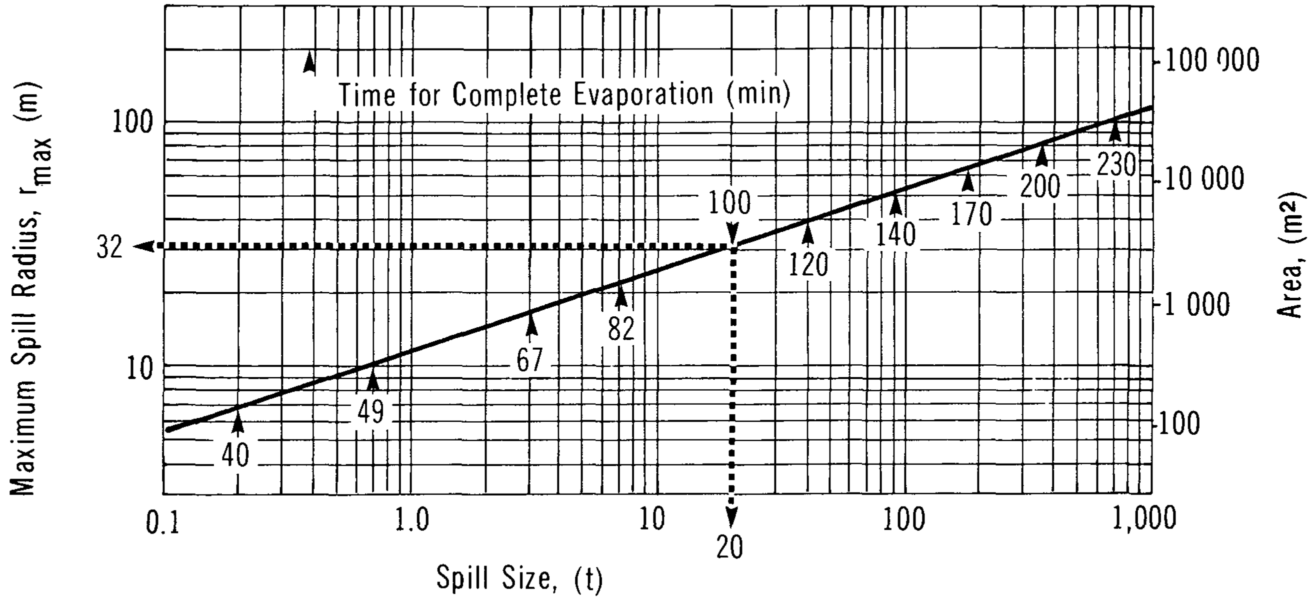
* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 24

HYDROGEN FLUORIDE

MAXIMUM SPILL RADIUS VS SPILL SIZE



the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 27 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

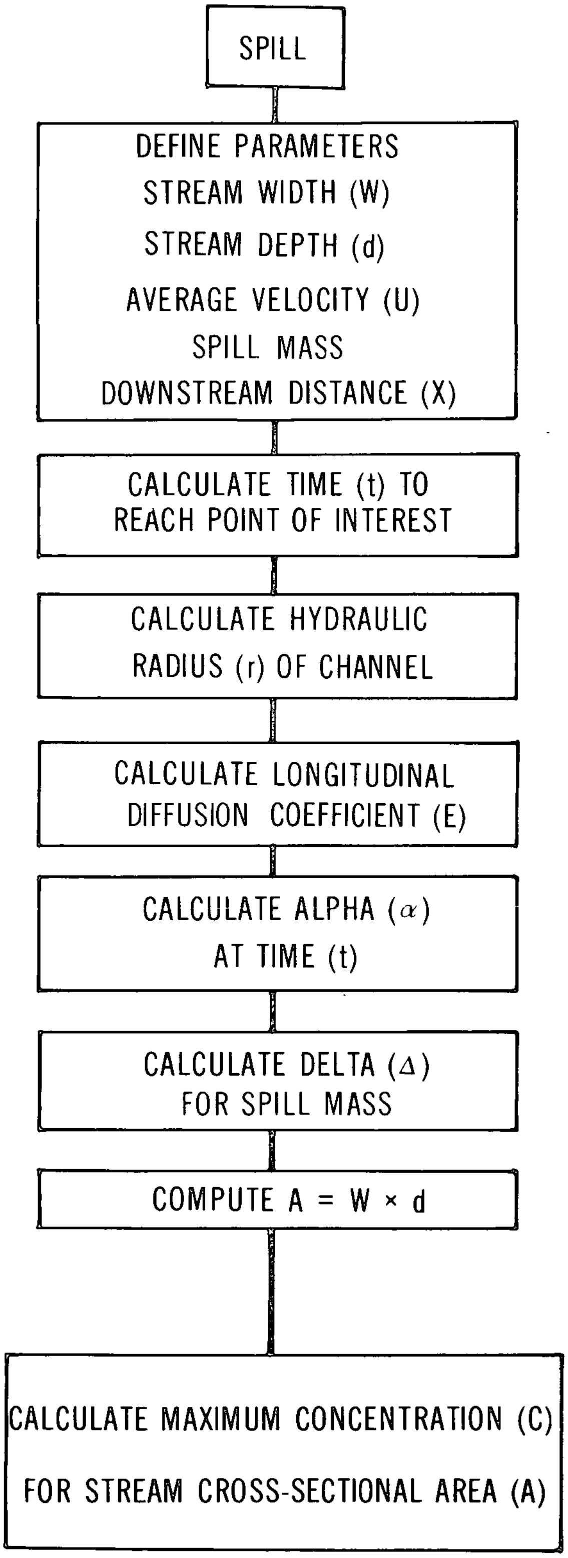
Figure 28: Diffusion coefficient versus hydraulic radius. Figure 28 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 27 and the average stream velocity (U).

Figure 29: Alpha versus diffusion coefficient. Figure 29 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 30: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 30 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 31: Maximum concentration versus delta. Figure 31 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS



Step 1: Observed or Estimated

W = __________ m

d = __________ m

U = __________ m/s

MASS = __________ tonnes

X = __________ m

Step 2: Use Figure 26

t = __________ minutes

Step 3: Use Figure 27

r = __________ m

Step 4: Use Figure 28

E = __________ m^2/s

Step 5: Use Figure 29

α = __________

Step 6: Use Figure 30

Δ = __________

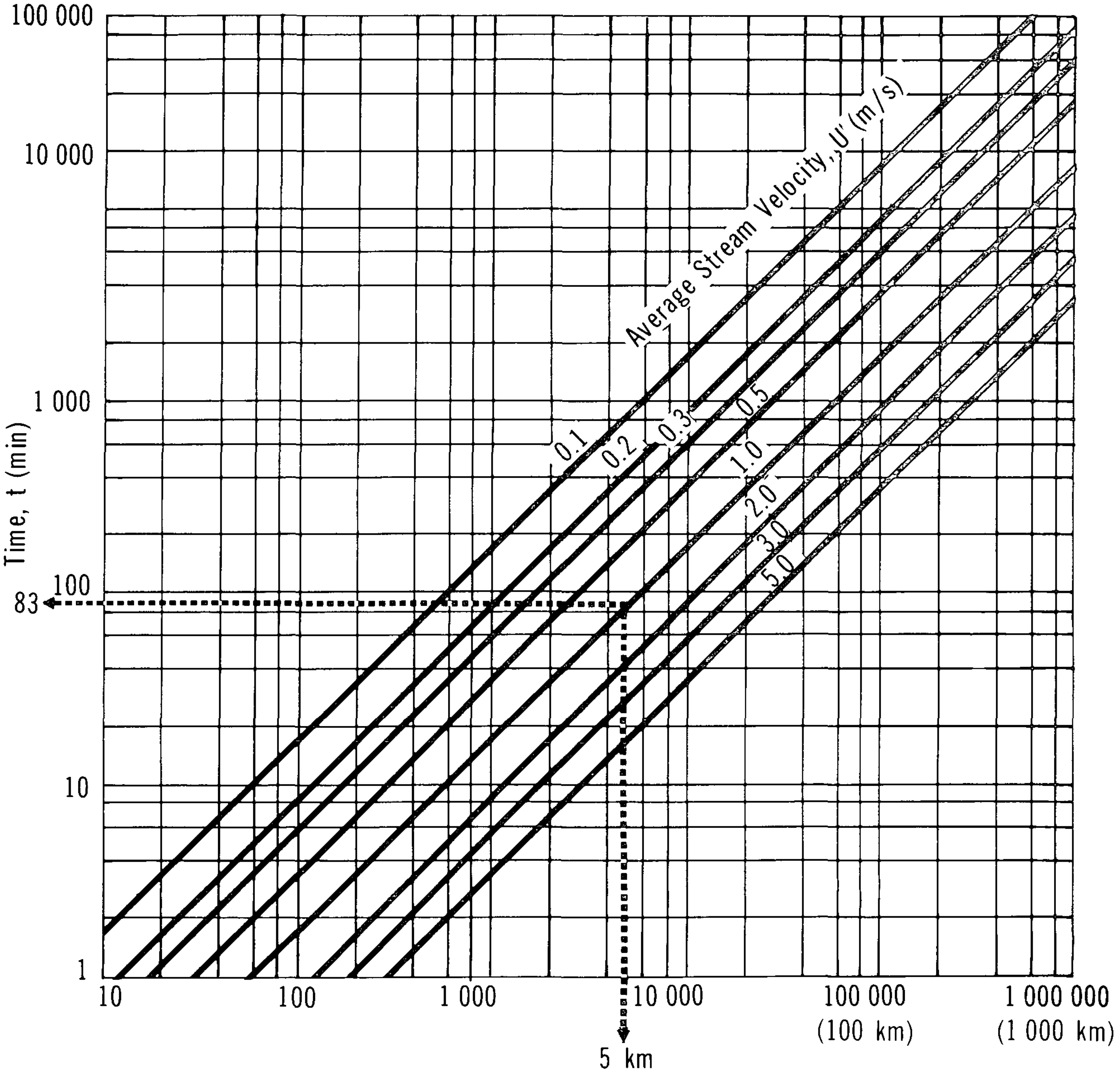
Step 7: Compute stream cross-sectional Area (A)

$A = W \times d$ ______ m^2

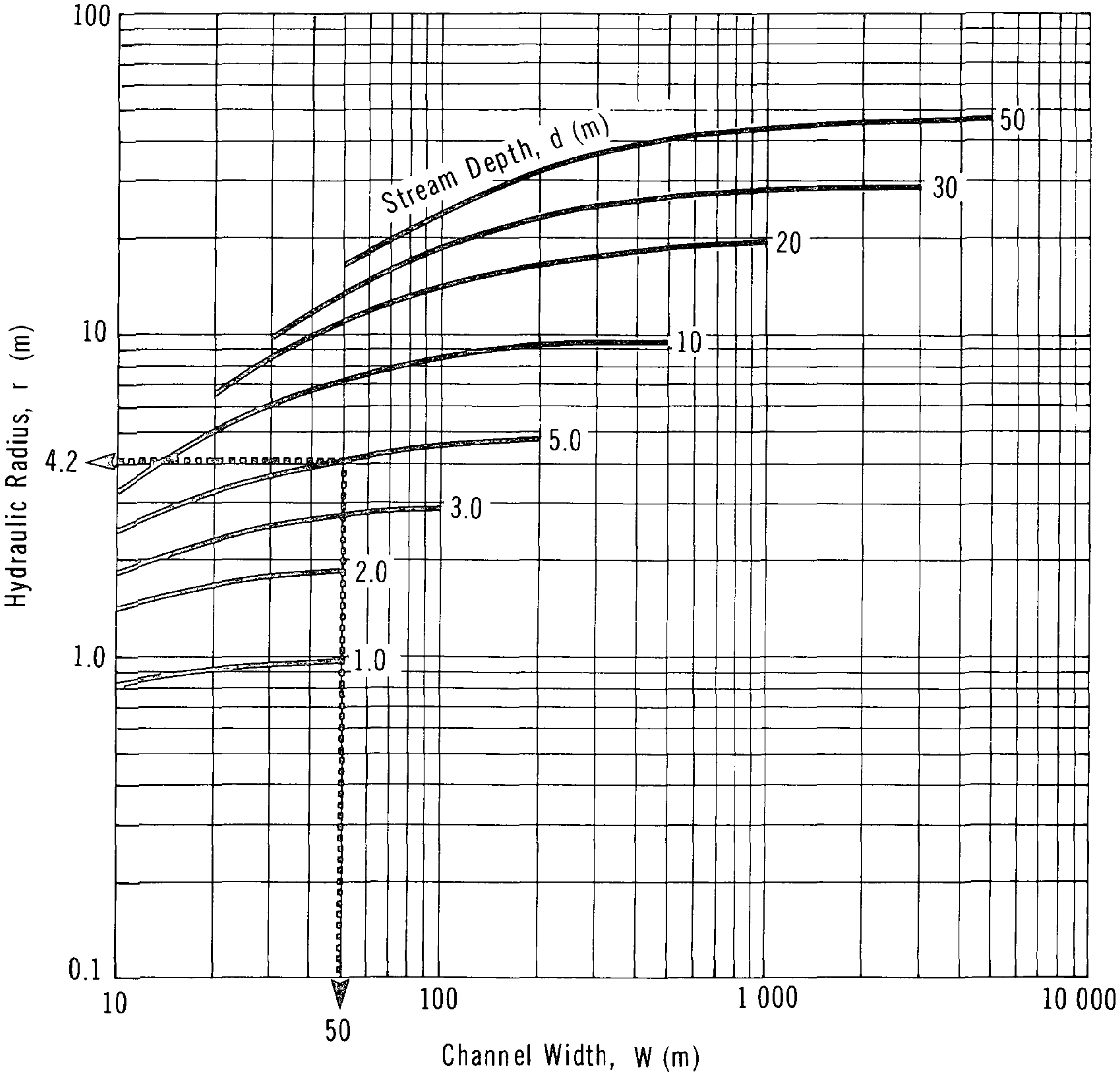
Step 8: Use Figure 31

C = __________ ppm

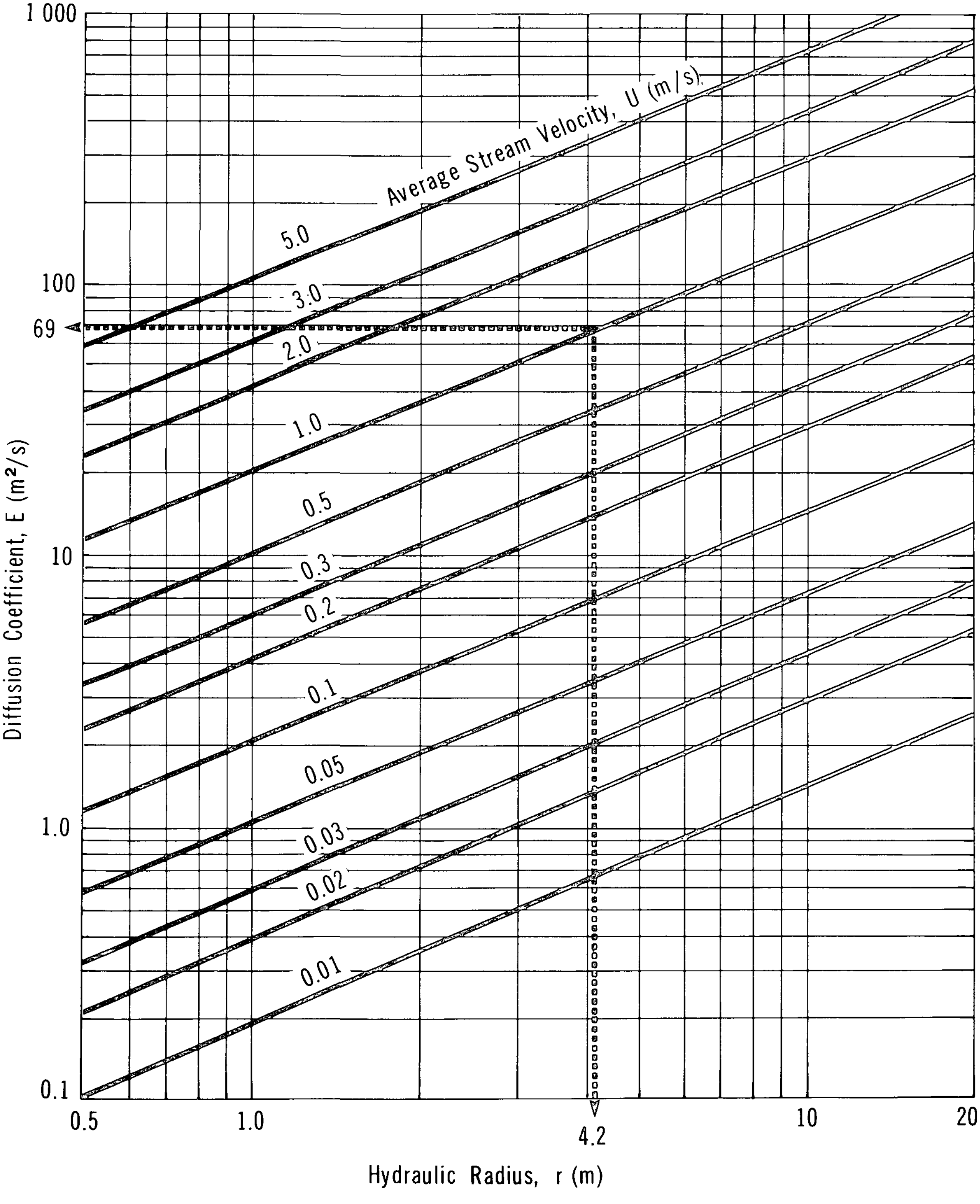
TIME vs DISTANCE



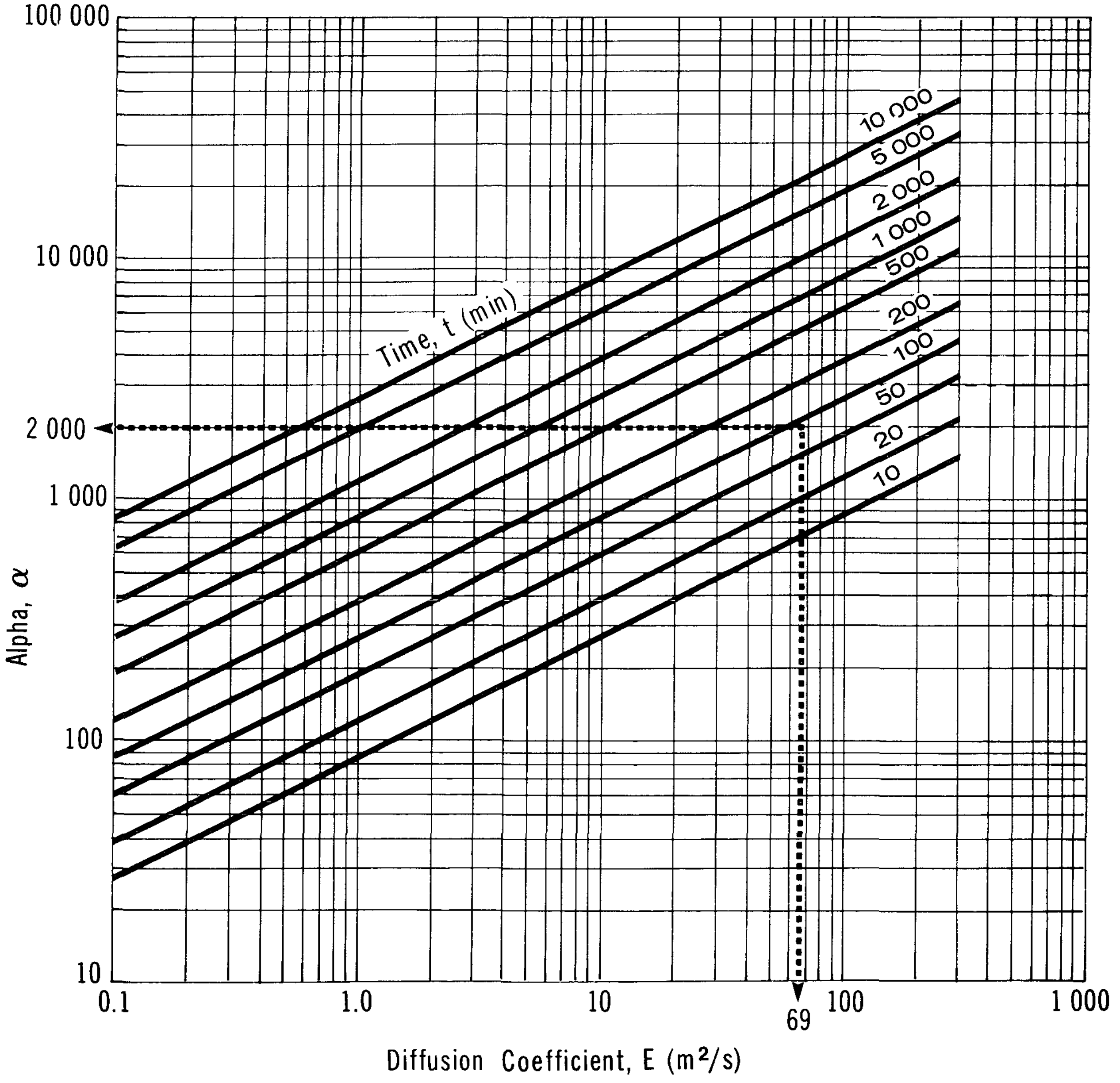
HYDRAULIC RADIUS VS CHANNEL WIDTH



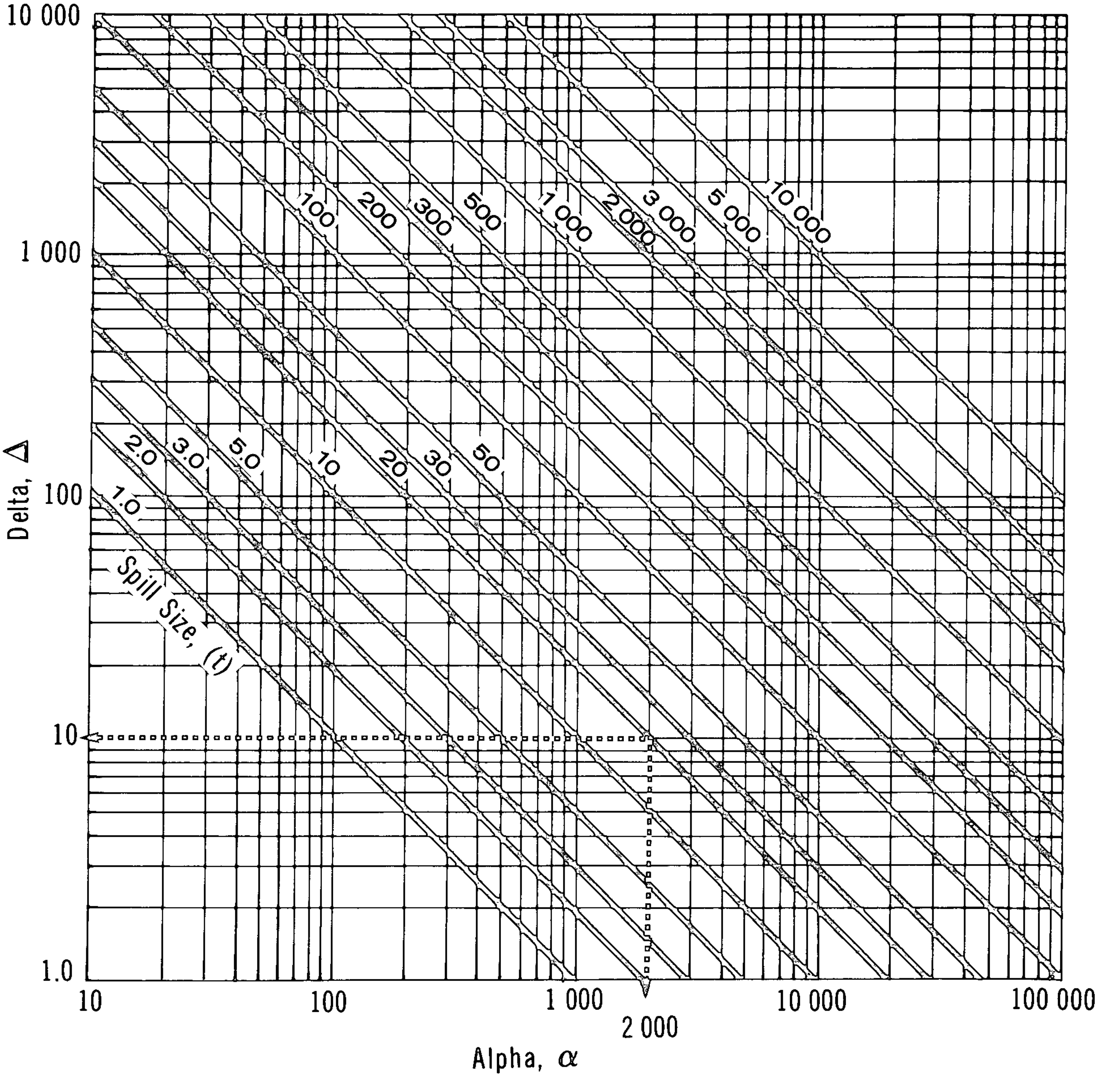
DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT

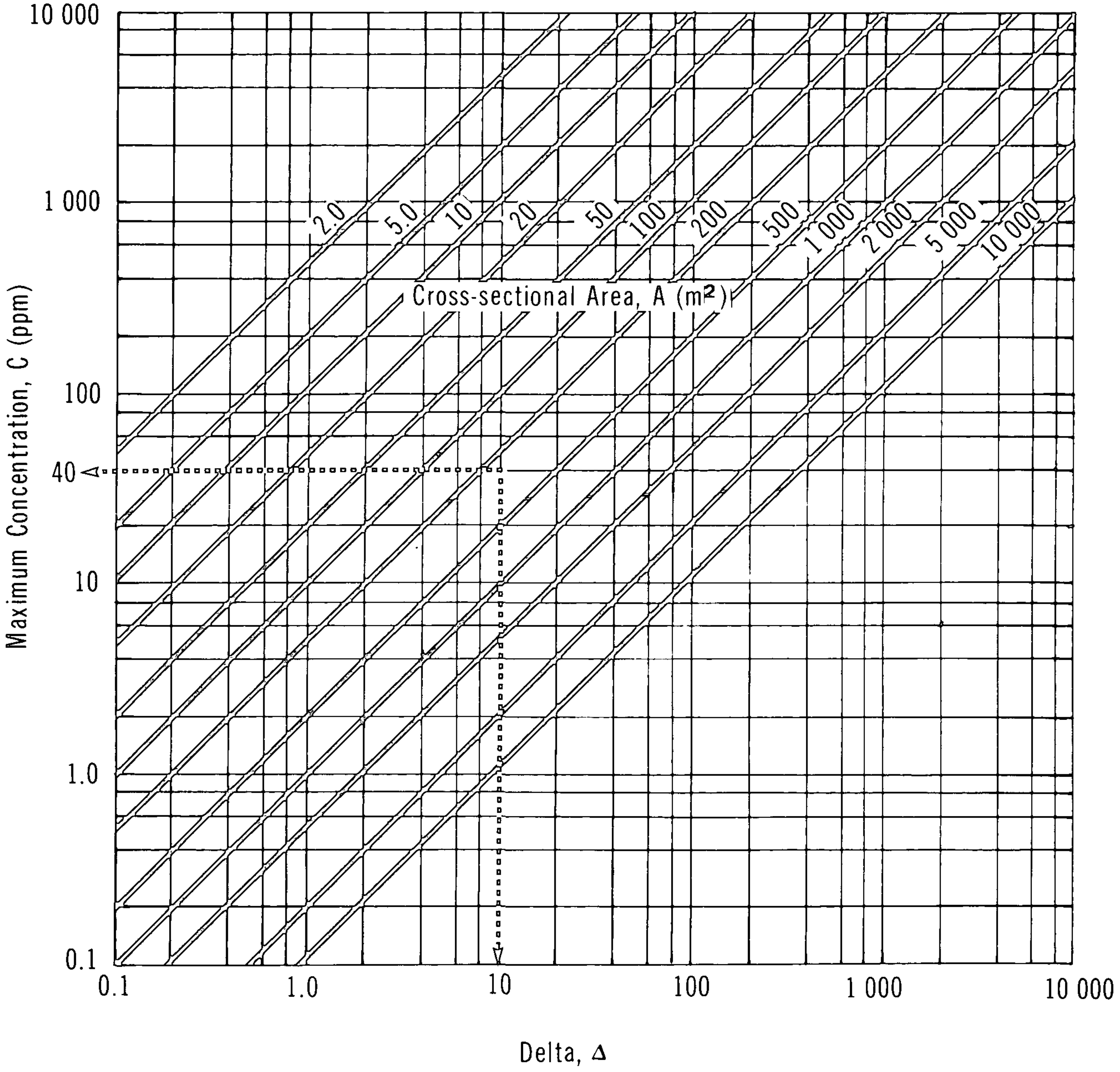


ALPHA vs DELTA



HYDROGEN FLUORIDE

MAXIMUM CONCENTRATION vs DELTA



from Figure 31 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.4.3 Nomograms for lakes or still water bodies.

Figure 32: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 31. The radius (r) represents the distance from the spill to the point of interest.

Figure 33: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 33 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.5 Sample Calculations.

5.4.5.1 Spreading on still water. A 20 tonne spill of hydrogen fluoride has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 24
- With spill size = 20 tonnes, r_{max} = 32 m
- Time for complete evaporation is 100 min (1.7 h)

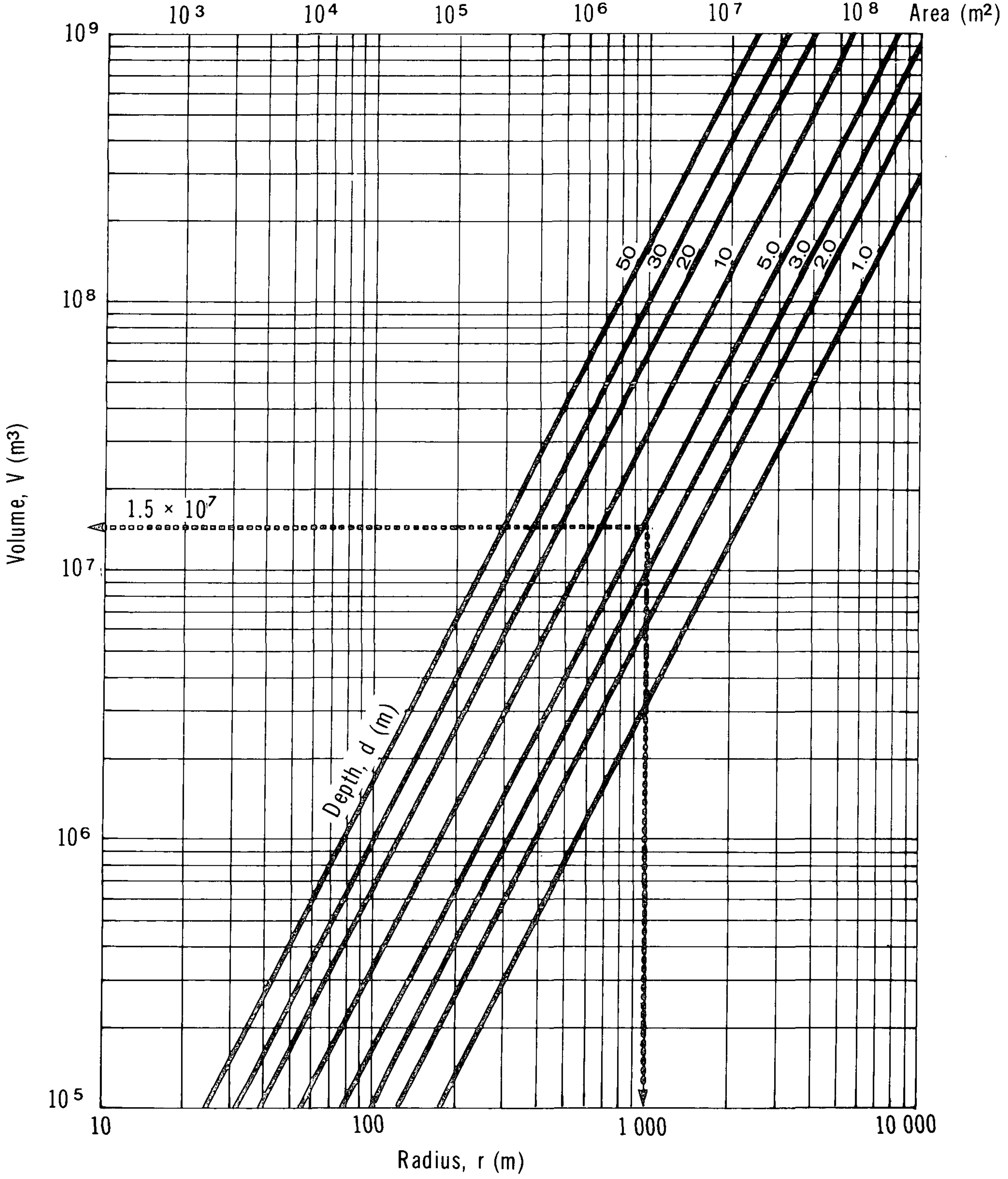
5.4.5.2 Pollutant concentration in non-tidal rivers. A 20 tonne spill of hydrogen fluoride has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

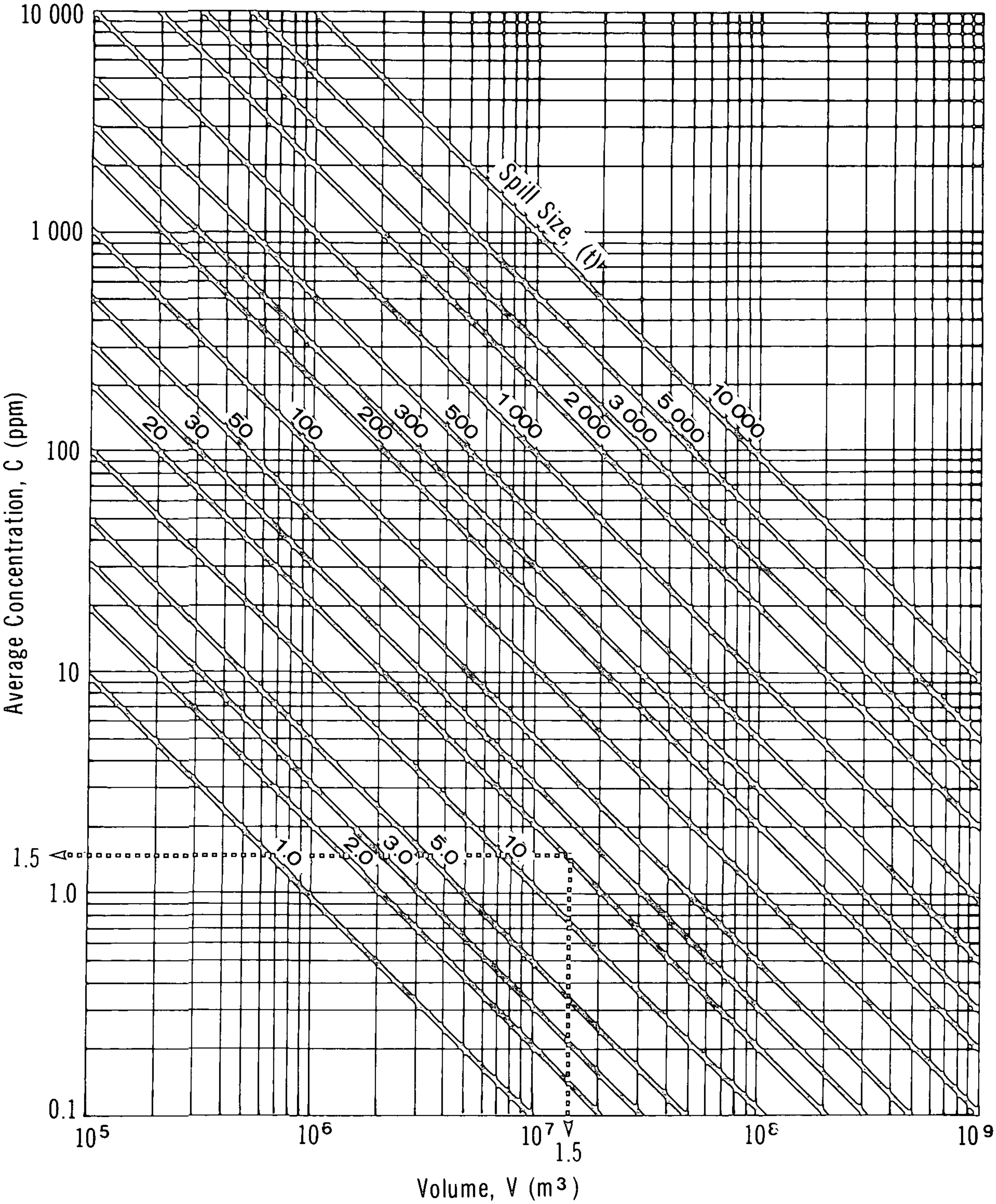
Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s

VOLUME vs RADIUS



AVERAGE CONCENTRATION vs VOLUME



- spill size = 20 tonnes

Step 2: Calculate time to reach point of interest

- Use Figure 26
- With $X = 5000$ m and $U = 1$ m/s, $t = 83$ min

Step 3: Calculate hydraulic radius (r)

- Use Figure 27
- With $W = 50$ m and $d = 5$ m, $r = 4.2$ m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 28
- With $r = 4.2$ m and $U = 1$ m/s, $E = 69\ m^2/s$

Step 5: Calculate alpha (α)

- Use Figure 29
- With $E = 69\ m^2/s$ and $t = 83$ min, $\alpha = 2000$

Step 6: Calculate delta (Δ)

- Use Figure 30
- With alpha (α) = 2000 and spill size = 20 tonnes, delta (Δ) = 10

Step 7: Compute stream cross-sectional area (A)

- $A = W \times d = 50 \times 5 = 250\ m^2$

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 31
- With $\Delta = 10$ and $A = 250\ m^2$, $C = 40$ ppm

5.4.6 **Average Pollutant Concentration in Lakes or Still Water Bodies.** A 20 tonne spill of hydrogen fluoride has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- $d = 5$ m
- $r = 1000$ m
- spill size = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 32
- With $r = 1000$ m, $d = 5$ m, the volume is approximately $1.5 \times 10^7\ m^3$

Step 3: Determine the average concentration

- Use Figure 33
- With $V = 1.5 \times 10^7\ m^3$ and spill size = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant behaviour in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of hydrogen fluoride/hydrofluoric acid onto soil and the transport downward through the soil are presented here.

Anhydrous hydrogen fluoride has a boiling point of 19.54°C. Consequently, when it is spilled onto soil, significant evaporation will occur. The rate of evaporation from a pool at 20°C is estimated to be $5.69\ g/(m^2 \cdot s)$. When the chemical is spilled onto soil, while some is lost to evaporation, the balance will infiltrate the soil. Evaporation will continue within the soil but at a reduced rate.

Since hydrogen fluoride is miscible with water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of chemical movement in the soil. Dilution through mixture with water will increase the viscosity more than the mass density. This will have the net effect of reducing the velocity of downward movement in the soil. This will also result in a decrease in the hydrogen fluoride vapour pressure and reduce the rate of evaporation.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off and/or evaporate.

For this work, the soils have been assumed to be at field capacity (the maximum water the soil can hold after the excess has been drained off). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport through the soil, the hydrogen fluoride will dissolve some of the soil material, in particular quartz and carbonate-based materials. The acid will be neutralized to some degree, with adsorption of fluoride ion also occurring on clay minerals. However, significant amounts of acid are expected to remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors.

Upon reaching the groundwater table, the acid will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 34.

5.5.2 Equations Describing Hydrogen Fluoride/Hydrofluoric Acid Movement into Soil.

The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Hydrogen Fluoride/Hydrofluoric Acid in Soil.

The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)\, k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)
ρ = mass density of the fluid (kg/m^3)
μ = absolute viscosity of the fluid (Pa•s)
g = acceleration due to gravity = 9.81 m/s^2

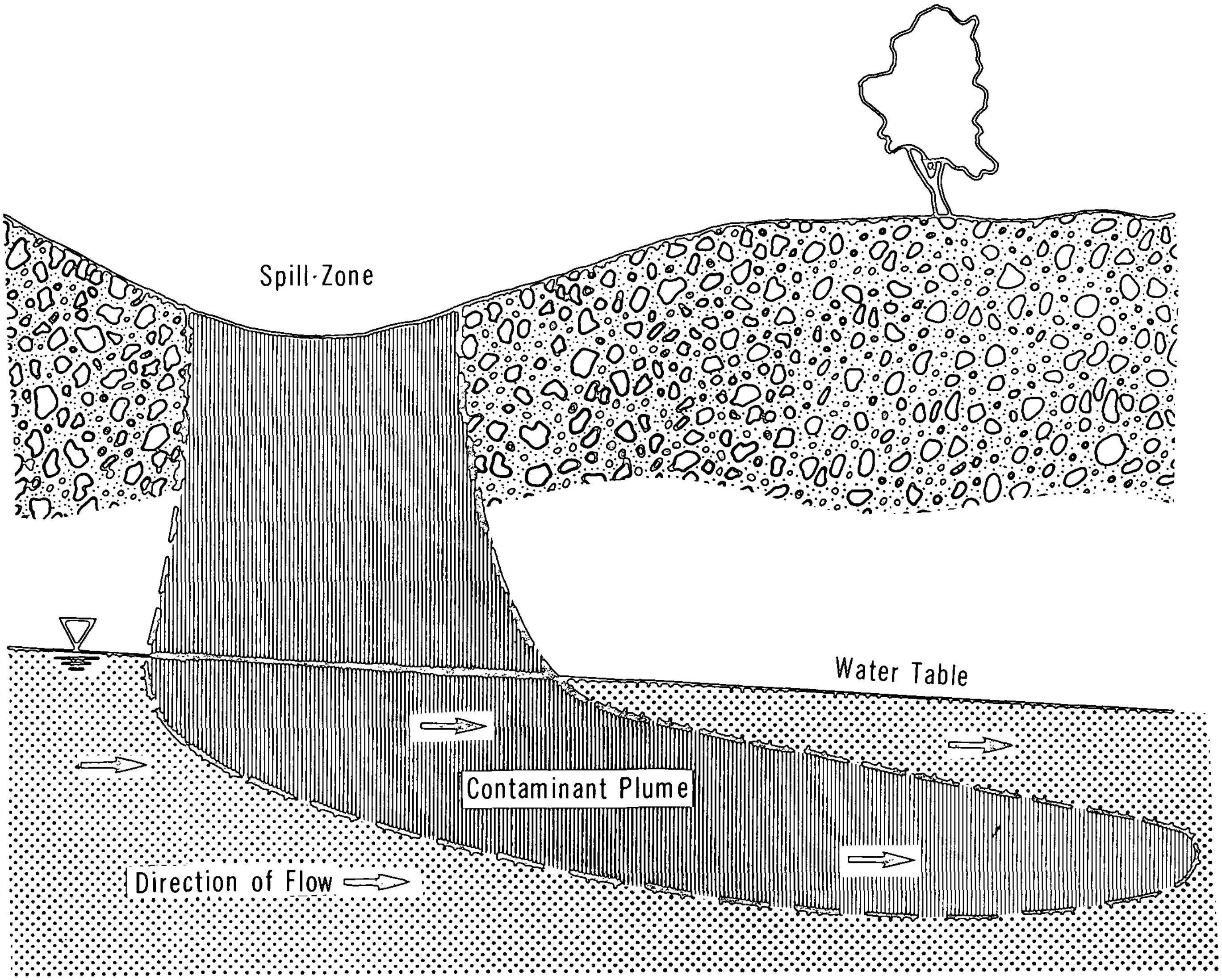
The fluids involved are hydrogen fluoride (anhydrous), hydrofluoric acid, and water. The water calculations represent the extreme as hydrofluoric acid is diluted.

Property	Hydrogen Fluoride (Anhydrous)		70% Hydrofluoric Acid, 20°C	Water, 20°C
	20°C	4°C		
Mass density (ρ), kg/m^3	950	1000	1200	998
Absolute viscosity (μ), Pa•s	0.2×10^{-3}	0.25×10^{-3}	0.44×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(4.66 \times 10^7)k$	$(3.92 \times 10^7)k$	$(2.68 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils.

The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

Property	Soil Type Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (Θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of hydrogen fluoride/hydrofluoric acid into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 35. The nomograms are presented as Figures 36, 37, and 38. The water line on the nomograms represents the maximum penetration of water at 20°C, in time t_p. It is a limiting condition as hydrofluoric acid becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of anhydrous hydrogen fluoride has occurred on silty sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 95 minutes after the spill and check the corresponding evaporation loss.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 95 min

Step 2: Calculate area of spill

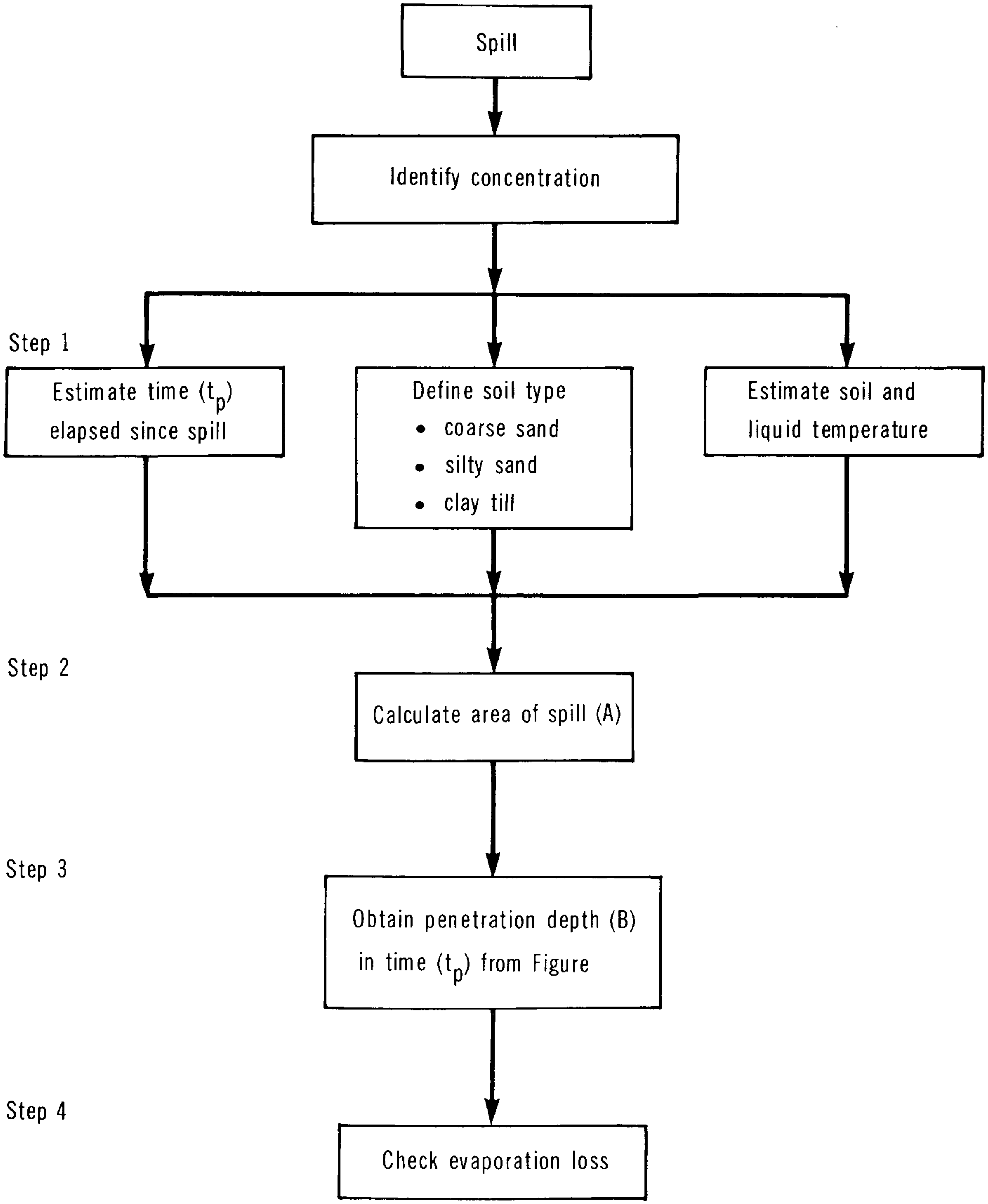
- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Estimate depth of penetration (B) at time (t_p)

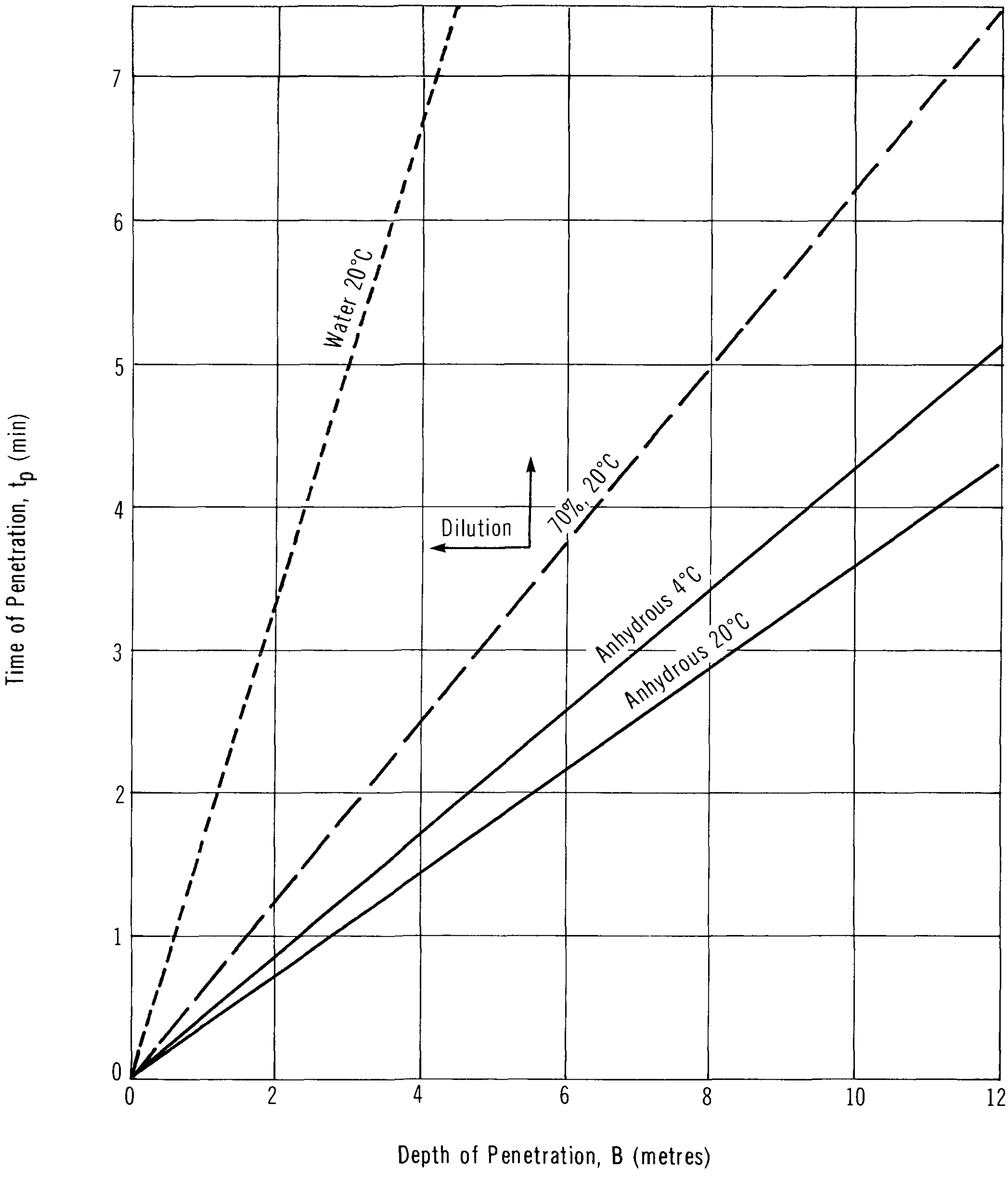
- For silty sand, B = 9.2 m at t_p = 95 min

FIGURE 35

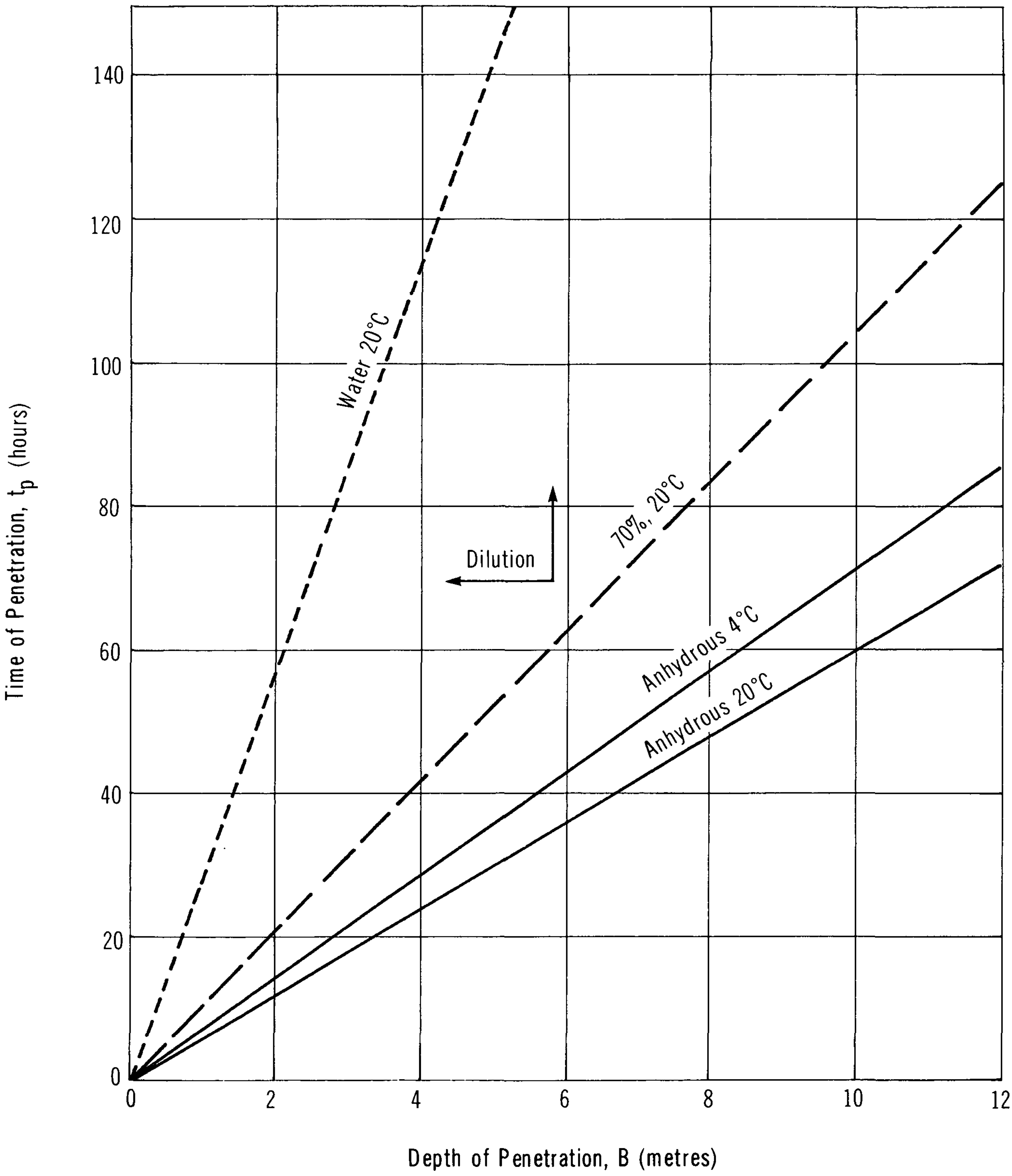
FLOWCHART FOR NOMOGRAM USE



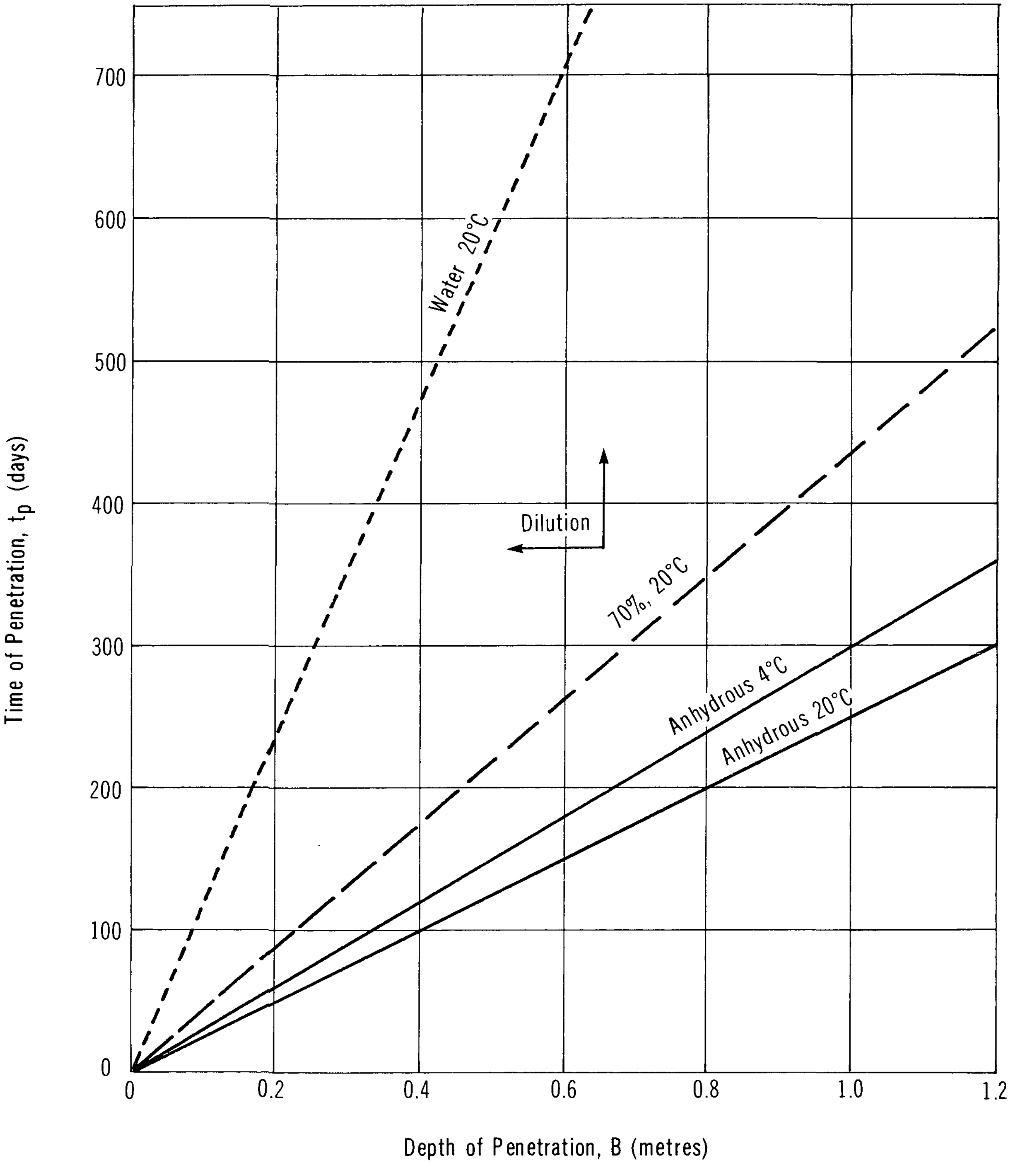
PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND



PENETRATION IN CLAY TILL



- Groundwater table has not been reached in this time

Step 4: Check evaporation loss

- Pool evaporation rate at 20°C (from Section 5.3)

  $Q = 5.69\ g/(m^2 \cdot s)$
- Evaporative loss (E) = $Q \times t_p$

  $E = 5.69\ g/(m^2 \cdot s) \times 232\ m^2 \times 95\ min \times 60\ s/min \times 10^{-3}\ kg/g$

  E = 7.520 kg

  E = 38 percent of the total mass spilled. Note, dissolution with water would reduce this evaporation rate

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Drinking Water.

6.1.1.1 Canada. The maximum acceptable concentration for fluoride in drinking water is 1.5 mg/L (WQS 1979). The objective is 1.0 mg/L of fluoride in all regions of Canada except the Arctic and Sub-Arctic zones, where concentrations of 1.2 mg/L have been allowed (Guidelines/Canadian/Water 1978; Water Management Goals 1978).

6.1.1.2 Other countries. The recommended fluoride limit in the United States is 1.2 mg/L (DWS 1973). The International World Health Organization (WHO) 1961 recommendation for fluoride is 1.5 mg/L maximum (WQCDB-2 1971). The European WHO recommendation is 0.7 mg/L; Sweden's is 1.5 mg/L; Bulgaria's is 0.7 to 1.0 mg/L; and Tanzania's is 8.0 mg/L (Jorgensen 1979).

6.1.2 Air.

Contaminant	Period of Time	Average Amount of Concentration or Total Amount of Contaminant at 10°C and 101.3 kPa	Reference
Fluorides (Gaseous) April 15 to October 15	1/2 hour average 24 hours 30 days	4.3 $\mu g/m^3$ 0.86 $\mu g/m^3$ 0.34 $\mu g/m^3$ (expressed as HF)	Ontario E.P. Act 1971
Total Fluorides (Gaseous and Particulate) April 15 to October 15	1/2 hour average 24 hours 30 days	8.6 $\mu g/m^3$ 1.72 $\mu g/m^3$ 0.69 $\mu g/m^3$ (expressed as HF)	Ontario E.P. Act 1971
Total Fluorides (Gaseous and Particulate) October 16 to April 14	1/2 hour average 24 hours 30 days	17.2 $\mu g/m^3$ 3.44 $\mu g/m^3$ 1.38 $\mu g/m^3$ (expressed as HF)	Ontario E.P. Act 1971

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. No aquatic toxicity rating has been assigned (RTECS 1979). Marine waters should not exceed 1/10 of 96-hour LC_{50} data for organisms most sensitive to fluoride. It is suggested that concentrations of fluoride equal to or exceeding 1.5 mg/L constitute a hazard in the marine environment, and levels less than 0.5 mg/L present minimal risk of deleterious effects (WQC 1972; WQS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc.* (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
1.5	not stated	Fish eggs	affect hatching		WQC 1972
2.3 to 7.3	not stated	Rainbow trout	TL_m	18°C, soft	WQC 1963
5.9 to 7.5	not stated	Trout	TL_m	7.5°C, soft	WQC 1963
64	240	Trout	TL_m		WQC 1963
419	96	Mosquito fish	TL_m	turbid	WQC 1963
358	not stated	Rainbow trout	toxic	soft	Klein 1957
Fish Kill Data					
60 (HF)	not stated	Fish	lethal		WQC 1963
40 (HF)	not stated	Fish	harmful		WQC 1963
120 (F^-)	96	Goldfish	killed		WQC 1963
1 000 (F^-)	12	Goldfish	killed	soft	WQC 1963
1 000 (F^-)	60	Goldfish	killed	hard	WQC 1963

Conc.* (mg/kg)	Time (hours)	Species	Result	Reference
Vertebrates				
112		Frog	LD_{LO}, subcutaneous mode of entry	RTECS 1979

Conc.* (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Microorganisms					
270	not stated	*Daphnia*	threshold	23°C	WQC 1963
95	96	*Scenedesmus*	threshold	24°C	WQC 1963
180	96	*E. coli*	threshold	27°C	WQC 1963
1 700	not stated	Protozoa; Rotifers	lethal		WQC 1963

* Values given are for fluoride ion.

6.2.2.2 Saltwater toxicity.

Conc*. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
100	96	Mullet	no effect		Hemens 1972
52	72 days	Mullet	physical deterioration	salinity	Hemens 1972
Invertebrates					
100	96	Penaeid prawns	no effect		Hemens 1972
7.2	108	Brown mussels	toxic		Hemens 1972
52	72 days	Crab	physical deterioration	saline	Hemens 1972

* Values given are for fluoride ion.

Conc.* (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
52	72 days	Shrimp	affects reproduction	20% saline	Hemens 1972
0.9 to 4.5	not stated	Lobster	not toxic		WQC 1963

* Values given are for fluoride ion.

6.2.3 Aquatic Studies. Lower temperatures appear to reduce toxic reactions. Hardness lengthens resistance time. Reduction of the pH can cause massive kills of aquatic organisms (EPA 440/4-75-009).

6.3 Toxicity to Other Biota

6.3.1 Livestock. Maximum levels of the fluoride ion in water that are tolerated by livestock are difficult to define from the available experimental work. The species, volume, and continuity of water consumption, other dietary fluoride, and age of the animals, all have an effect. It has been recommended that the upper limit for fluorides in livestock drinking water be 2.0 mg/L. Although this level may result in some tooth mottling, it should not be excessive for animal health or deposition of the element in meat, eggs or milk (WQC 1972). In Ontario, the maximum recommended total fluorides in forage for consumption by livestock is 35 mg/kg (dry weight) (Ontario E.P. Act 1971).

The fluoride ingested by animals is largely deposited in their bones. Adult animals normally have concentrations of about 500 ppm in their bones; concentrations of 5000 ppm must be reached before visible signs of fluoride contamination appear. Studies have revealed the following sequence in which the effects of fluoride contamination appear: dental lesions, primarily in the incisors; hyperostosis or bone overgrowth; lameness; loss of appetite; decrease in milk production; and reduced reproduction. The last two effects are believed to occur from the decreased food intake due to the loss of appetite. In one study, cattle were fed forage containing 600 to 1200 ppm of fluoride resulting in a 50 percent decrease in their food consumption. A continual intake of 40 to 50 ppm of fluoride eventually results in the destruction of incisors, limiting grazing. The safe levels of fluoride for livestock are shown below (PB 294276):

Animal	Source of Fluoride Soluble Fluoride (ppm)	Rock Phosphate (ppm)
Dairy cattle	30 - 50	60 - 100
Beef cattle	40 - 50	65 - 100
Sheep	70 - 100	100 - 200
Swine	70 - 100	100 - 200
Chickens	150 - 300	300 - 400
Turkeys	300 - 400	-

6.3.2 Plants.

6.3.2.1 Measured toxicities.

Conc. (mg/m^3)	Time (hours)	Species	Effect	Reference
Crops				
0.083 (HF acid)	3 to 4	Plants	minimal effect	DPIMR 1981
403 kg/ha (NaF)	not stated	Buckwheat	reduced yields at pH 4.5 (soil); no injury at pH >5.5	WQC 1972
0.9 ng F/m^3 (HF gas)	96	Wheat *(Triticum aestivum)*	reduced yield (due to smaller spikes); no foliar injury	MacLean 1981
0.5 ng F/m^3	32 days	Corn (Macross sweet)	elliptical chlorotic lesions on leaves; accumulation of foliar F	Mandl 1980
up to 3 µg/m^3 (gaseous HF)	not stated	Gladiolus	reduced chlorophyll content, dry matter accumulation and productivity, severe damage at 3 µg/m^3	Pandey 1979; PB 203465
10 (HF gas)	24	Rice (Milyang 23; Jinheung)	destroyed leaf area, reduced sugar content in leaves	Kim 1979

Conc. (mg/m^3)	Time (hours)	Species	Effect	Reference
36% (HF acid) (on soil)	not stated	Garden cress *(Lepidium sativum)* Bush bean *(Phaseolus vulgaris)*	germination and growth diminished considerably	Tauchnitz 1979
3.87 to 46.4 (F^-)	not stated	Grapes (vineyards)	variety of phyto-pathological effects; diffuse lesions to almost complete necrosis; leaves absorbed most F	Quaroni 1979

Conc. ($mg\ HF/m^3$)	Time (hours)	Species	Result	Reference
Trees				
0.25 to 0.3	not stated	Scotch pine, Larch (13 to 14-yr old)	visual changes occurred rapidly, increased hydration and N content, decrease in reducing sugar	Rozhkov 1980
0.25	1/2 (daily)	Scotch pine, Larch (3 to 5-yr old)	injurious effects by 7 to 8 days	Rozhkov 1980
0.021	6 h/d (2 d)	Scotch pine (seedlings)	CO_2 exchange rate changed: drop in photosynthesis, stimulation of respiration	Lorenc-Plucinska 1980

Gaseous hydrogen fluoride will directly attack foliage, especially in high concentrations. In low concentrations, hydrogen fluoride is absorbed by the leaves; the effects on the plant are dependent on the level and time of exposure. The degree of sensitivity can vary even in the same species. This is shown in the following table for different commercial crops (PB 29427):

MAXIMUM EXPOSURE TO HYDROGEN FLUORIDE (before economic and visual damage is evident)

	Sensitive Varieties		Resistant Varieties	
Crop	Concentration (ppb)	Exposure	Concentration (ppb)	Exposure
Corn	2	10 days	800	4 hours
Tomato	10	100 days	700	6 days
Alfalfa	100	120 days	700	10 days
Sorghum	7	15 days	15	3 days

Most forage crops, as well as several species of vegetables and deciduous trees, are fairly tolerant. Some species more sensitive to fluoride are conifers, fruits, berries and grasses. These sensitive species generally exhibit damage at concentrations between 0.5 ppb and 1.2 ppb for several days exposure. In comparison, 5 to 10 ppm (fluoride) are normally accumulated by most plants in the absence of an atmospheric source. The most apparent effect of fluoride on vegetation is necrosis or tip burn. The injury is characterized by discolouration around the edges of the leaves where the accumulation of fluoride occurs. Exposure to fluoride may also result in abnormalities or a decrease in reproductivity (PB 294276).

6.4 Degradation

Hydrogen fluoride does not biodegrade. Dilution and natural buffering will reduce the acidity; if calcium ions are present in water, insoluble calcium fluoride will precipitate (OHM-TADS 1981; DPIMR 1981).

6.5 Soil

6.5.1 Effects on Soil Chemistry. Soil can bind fluorides if the pH is greater than 6.5. High calcium content will also immobilize fluorides (DPIMR 1981).

Due to the capacity of neutral and alkaline soils to inactivate fluoride, relatively high maximum concentrations for continuous use on these soils may be permitted. Recommended maximum concentrations are 1.0 mg/L for continuous use on all soils and 15 mg/L for use for a 20-year period on neutral and alkaline fine textured soils (WQC 1972; WQS 1979).

7 HUMAN HEALTH

Data concerning the health effects of hydrogen fluoride exposure relate primarily to acute exposures from inhalation or from accidental spills of both anhydrous and aqueous forms of hydrogen fluoride. Chronic exposure data are reported from occupational hydrogen fluoride exposure studies.

Since 1977, only one research project on the toxicology of hydrogen fluoride has been reported in TOX TIPS (a summary of current research activity). That project exposed guinea pigs to fluoride-containing dusts.

Published work on hydrogen fluoride toxicology has been reviewed recently by the National Institute for Occupational Safety and Health (NIOSH).

The toxicological data summarized here have been extracted from reliable standard reference sources and are representative of information in the literature. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for hydrogen fluoride are based upon prevention of fluorosis. Data obtained from the studies of human exposures to hydrogen fluoride alone are limited in number, and insufficient to derive a standard to prevent fluorosis. From comparative absorption and excretion studies, it is clearly indicated that the metabolism of fluoride in humans is the same, independent of whether the fluoride ion is absorbed as a gaseous or particulate inorganic fluoride. Consequently, data used in the derivation of the standard include inorganic fluoride exposure studies.

Only studies pertaining specifically to hydrogen fluoride exposure have been referenced in this document.

Canadian provincial guidelines are generally similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	2.5 mg/m^3 (3.0 ppm) (as F)	TLV 1983
PEL (8 h)	USA-OSHA	2.5 mg/m^3 (3.0 ppm)	NIOSH/OSHA 1981

Guideline (Time)	Origin	Recommended Level	Reference
TWA (8 h)	USA-NIOSH	2.5 mg/m^3 (3.0 ppm) (as F)	NIOSH 1976
Not Stated	ANSI	2.5 mg/m^3 (3.0 ppm)	Doc. TLV 1980
MAC	USSR	(0.5 mg/m^3) 0.6 ppm	Doc. TLV 1980
MAC	Czech.	(1 mg/m^3) 1.2 ppm	Doc. TLV 1980
MAC	Sweden	(2.1 mg/m^3) 2.5 ppm	Doc. TLV 1980
Permissible Concentration (8 h)	British Columbia	2 mg/m^3 3 ppm	B.C. 1980
Time-weighted Average Exposure Criteria (8 h)	Ontario	2 mg/m^3 (as F) (proposed)	Ont. 1981
Concentrations Admissibles (moyennes) (8 h)	Quebec	2.5 mg/m^3 (Fluorures, exprimés en F)	Quebec 1979
Contamination (8 h average)	Saskatchewan	2 mg/m^3 as F (2.4 ppm)	Sask. 1981
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	5.0 mg/m^3 (6 ppm) (as F)	TLV 1983
STEL (15 min)	USA-OSHA	5.0 mg/m^3	Doc. TLV 1980
15 min. average contamination limit	Saskatchewan	4.0 mg/m^3 (as F)	Sask. 1981
Not stated	Sweden	2.0 mg/m^3	ILO 1980
Max.	Romania	2.0 mg/m^3	ILO 1980
Short-term Public Limits (STPL)			
STPL	suggested	3 mg/m^3 (4 ppm) for up to 60 min (frequency limit 1 h daily)	PB 203465
STPL	suggested	1 mg/m^3 (1 ppm) for up to 5 h per day (frequency limit 3-4 days/month)	PB 203465

Guideline (Time)	Origin	Recommended Level	Reference
Public Emergency Limits (PEL)			
PEL	suggested	8 mg/m^3 (10 ppm) for up to 10 min	PB 203465
PEL	suggested	4 mg/m^3 (5 ppm) for up to 60 min	PB 203465
Other Human Toxicities			
IDLH	USA-NIOSH	20 ppm	NIOSH Guide 1978
LC_{LO} (30 min)		50 ppm	RTECS 1979
TC_{LO} (1 min)		110 ppm	RTECS 1979

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg)/(TLV®, in ppm)

Hydrogen Fluoride:

Vapour pressure at 20°C = 103.42 kPa = 775.7 mm Hg

Hydrofluoric Acid: (70%) (most common form):

Vapour pressure at 25°C = 20 kPa = 150.0 mm Hg

TLV® = 3 ppm

Therefore: ITI: Hydrogen fluoride = 3.4×10^5

Hydrofluoric acid = 6.6×10^4 (70% HF)

7.2 Irritation Data

7.2.1 Skin Contact. Hydrogen fluoride may enter the body through the skin and cause systemic poisoning. A number of instances of accidental systemic poisonings resulting in severe symptoms and death have been reported (NIOSH 1976).

Skin contact causes severe burns and deep scarring. Some cases of skin effects have been reported as a result of exposure to the vapour and are reported with the inhalation studies data. There is no information on the effects of specific exposure levels on the skin.

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Accidental fine spray of hydrofluoric acid	Considerable loss of corneal epithelium, despite immediate copious flushing with water and irrigation for 3 hours with 0.5% solution of benzethonium chloride. Recovery of normal vision occurred within 19 days	NIOSH 1981
2.6 to 4.7 ppm (in air)	Mild irritation	Largent 1961. IN NIOSH 1976
0.9 to 2.1 ppm (in air)	No eye effects noted	Largent 1961. IN NIOSH 1976

Based on the destructive action from skin contamination, one would expect that eye contact with hydrofluoric acid solutions and anhydrous hydrogen fluoride would cause severe and probably permanent damage to the eye; however, specific accounts of such injury were not found in the literature (NIOSH 1976).

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristic:	Pungent, irritating
Odour Index:	28 351 835 (at 20°C) (AAR 1981)

Parameter	Media	Concentration	Reference
Overall range of odour threshold	In air	0.03 to 0.11 mg/m^3	Sadilova 1968. IN NIOSH 1976
Threshold odour concentration	In air	0.03 mg/m^3 (0.04 ppm)	Sadilova 1968. IN NIOSH 1976
Threshold odour concentration	In air	0.04 mg/m^3	Lindberg 1972. IN NIOSH 1976
Upper recognition threshold	In air	0.036 ppm (0.03 mg/m^3)	AAR 1981

7.3.2 Taste.

Taste Characteristic: Sour, flat

7.4 Toxicity Studies

7.4.1 Inhalation and Contact with Vapour.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
120 ppm (1 min)	Smarting of skin, conjunctival and respiratory irritation, recognition of flat, sour taste. Reported to be highest concentration tolerable to man	Patty 1981
110 ppm (1 min)	Irritation of respiratory tract	DPIMR 1981
60 ppm	Irritation of mucous membranes	Patty 1981
50 ppm (30 min)	LC_{LO}	DPIMR 1981
32 ppm	Mild smarting of nose and eyes. Ability to taste HF delayed. Atmosphere uncomfortable	Patty 1981
12 ppm	Burning sensation in nose	PB 203465
10 ppm	Burning of eyes and lacrimation	PB 203465
SPECIES: Monkey		
1774 ppm (1 h)	LC_{50}	AAR 1981; DPIMR 1981
SPECIES: Rabbit		
1800 ppm (5 min)	Death	Patty 1981
1200 ppm (30 min)	Death	PB 203465
312 ppm (7 h)	LC_{LO}	DPIMR 1981
260 ppm (2 h)	LC_{LO}	DPIMR 1981
SPECIES: Guinea Pig		
4347 ppm (15 min)	LC_{50}	DPIMR 1981
4250 ppm (15 min)	LC_{50}	Patty 1981
1800 ppm (5 min)	Death	Patty 1981

Exposure Level (and Duration)	Effects	Reference
1200 ppm	LC_{LO}	AAR 1981
300 ppm (2 h)	Death	Doc. TLV 1980
40 ppm (41 h)	Animals survived	Doc. TLV 1980
SPECIES: Rat		
4870 ppm (5 min)	LC_{50}	Patty 1981
2640 ppm (15 min)	LC_{50}	Patty 1981
2000 ppm (30 min)	LC_{50}	Patty 1981
1310 ppm	LC_{50}	AAR 1981
1290 ppm (60 min)	LC_{50}	Patty 1981
1276 ppm (60 min)	LC_{50}	DPIMR 1981
300 ppm (15 min)	Irritation of eyes and nose	PB 203465
96 ppm (30 min)	Irritation of eyes and nose	PB 203465
4980 $\mu g/m^3$ (4 h) (6 ppm)	TC_{LO}: Reproductive effects with animals 1 to 22 days pregnant	RTECS 1981
470 $\mu g/m^3$ (4 h) (0.6 ppm)	TC_{LO}: Reproductive effects with animals 1 to 22 days pregnant	RTECS 1981
SPECIES: Mouse		
456 ppm (1 h)	LC_{50}	DPIMR 1981
SPECIES: Mammals (unspecified)		
1500 ppm (15 min)	Rapidly fatal to most animals	DPIMR 1981
1200 ppm (30 min)	Tissue damage but no deaths	Patty 1981
600 ppm (45 min)	Signs of weakness and ill health, but no deaths	Patty 1981
<120 ppm (5 h)	No deaths	Patty 1981
>60 ppm	Severe irritation. Eyes were kept closed; paroxysms of coughing and sneezing more frequent, respiration was slowed, copious discharge from noses and eyes	Patty 1981
<60 ppm	Mild irritation, such as coughing and sneezing	Patty 1981

Exposure Level (and Duration)	Effects	Reference
29 ppm	No fatalities	Patty 1981
Chronic Exposures		
SPECIES: Human		
13 to 25 ppm (5 yr intermittent)	Skeletal fluorosis in pelvis and and spine of ten men. Hemoglobin, chest X-ray normal	Machle and Evans 1940. IN NIOSH 1976
4.7 ppm (6 h/d for 10 to 50 d)	Tolerated without severe effects. Redness of skin, burning and irritation of nose, skin and eyes at concentrations above 3 ppm	Doc. TLV 1980
<4.3 ppm (Occupational)	Threshold for minimal increase in bone density fluorosis	Doc. TLV 1980
<3 ppm (HF and SiF_4) (Occupational)	No increase in respiratory complaints	Doc. TLV 1980
1.03 ppm (Occupational)	No significant changes in pulmonary function	Doc. TLV 1980
Unspecified (2 to 33 yr)	Of 40 workers, 24 showed changes in trabecular pattern of jaws. Fewer dental cavities. Some transitory hyperemia of exposed skin	Dale and McCauley 1948. IN NIOSH 1976
(Unspecified) (Up to 32 yr)	of 47 men, 72% showed osteosclerotic changes corresponding to length of employment. Some HF burn scars. Otherwise, physical findings normal. Complaints of back pain, stiffness, shortness of breath	Peperkorn and Kahling 1944. IN NIOSH 1976
Unspecified (10 to 17 yr)	One of three workers showed fluorosis of lower thoracic spine	Largent 1951. IN NIOSH 1976
Unspecified (2.7 yr average)	No differences in chest X-rays. Upper respiratory tract irritation	Evans 1940. IN NIOSH 1976
SPECIES: Dogs, Rabbits, Guinea Pigs, Mice, Rats		
7 and 25 mg/m^3 (6 h/d, 30 d)	Higher concentrations were lethal to all rats and mice, not to others. Rabbits showed slight weight loss. Guinea pigs began to lose weight after third week of exposure. Dogs suffered minor effects	Patty 1981; PB 203465

Exposure Level (and Duration)	Effects	Reference
25 mg/m^3 (6 h/d, 30 d)	Moderate hemorrhage and edema of lungs in dog, rabbit, rat. Renal cortical degeneration and necrosis in rat. Ulceration of scrotum in dog	Patty 1981
7 mg/m^3 (6 h/d, 30 d)	Localized hemorrhages in the lung of one dog. No changes in rat or rabbit	Patty 1981
SPECIES: Rabbits, Guinea Pigs, Pigeons		
10 ppm (2 x 3 h periods/d for 31 d)	Lethal to 2 rabbits, 7 guinea pigs, 1 pigeon. At autopsy, emphasymatous lungs, broncho-pneumonitis, lesions of nasal mucous membranes. Survivors lost up to 23% weight, had anemia, and were less resistant to the effects of typhus innoculation	NIOSH 1976
SPECIES: Rhesus Monkey, Rabbit, Guinea Pigs		
183 ppm (6 to 8 h day, total 309 h)	Lung, liver, kidney cellular changes in 2 guinea pigs which died within 8 months after exposure	Machle and Kitzmiller 1935. IN NIOSH 1976

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
80 mg/kg	LD_{LO}	AAR 1981

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Guinea Pig		
100 mg/kg	LD_{LO}	AAR 1981

7.4.4 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
25 mg/kg	LD_{LO}	RTECS 1981

7.4.5 Teratogenicity, Mutagenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Unspecified		
Inhalation 470 μg/m^3 or 0.56 ppm (4 h)	TC_{LO}. Reproductive effects with animals 1 to 22 days pregnant	RTECS 1981
Inhalation 4,980 μg/m^3 or 5.98 ppm (4 h)	TC_{LO}. Reproductive effects with animals 1 to 22 days pregnant	RTECS 1981
Inhalation 1.3 ppm (6 wk)	DNA damage (strand breaks, cross-links)	RTECS 1981
Inhalation 2.9 ppm	Sex chromosome loss and non-disjunction	RTECS 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Burning in nose, may cause nosebleed (NIOSH 1976).
2. Burning in throat, upper respiratory tract, eyes.
3. Muscle spasms.
4. Coughing, spitting blood, dyspnea.
5. May cause ulcers of the upper respiratory tract.
6. Inflammation and congestion of the lungs (GE 1977).
7. Bronchial pneumonia and pulmonary edema.
8. Cyanosis and jaundice.
9. Hematuria and albuminuria.
10. Shock.
11. Convulsions and parasthesias.
12. Kidney damage has been observed in acute overexposures.
13. Prolonged low-level exposures may cause skeletal abnormalities and bone changes.
14. Hypocalcemia (MacKinnon 1983).
15. Can be fatal.

7.5.2 Ingestion.

1. Swallowing causes burns, corrosion of mouth, esophagus, stomach, and small bowel.
2. Nausea, vomiting, abdominal pain.
3. Diarrhea.
4. Shock.
5. Cyanosis, jaundice.
6. Convulsions, parasthesias.
7. Hypocalcemia (MacKinnon 1983).
8. Can be fatal.

7.5.3 Skin Contact.

1. Highly irritating to skin and mucous membranes.
2. Pain is immediate and severe (with 50 percent or greater concentration of HF).
3. If the solution is not promptly removed, the skin may be penetrated by fluoride ion, leading to the later development of painful ulcers which heal slowly (Patty 1981).
4. Fluoride ion readily penetrates the skin and travels to deep tissue layers causing liquefaction necrosis of the soft tissue and decalcification and corrosion of the bone (NIOSH 1976). The appearance of this area is white and necrotic (MacKinnon 1983).

For acid concentrations of 20 to 50%, symptoms may not appear for 1 to 8 h after the exposure (Allied MM 1979).

5. Burn effects can be delayed especially with dilute solutions (MacKinnon 1983; Trevino 1980).
6. The subcutaneous tissue may be affected by becoming blanched and bloodless.
7. May enter the body through the skin and cause systemic poisoning.
8. Hypocalcemia (MacKinnon 1983).
9. Burn areas over 30 to 100 cm^2 are of great concern and can lead to death (Trevino 1980; MacKinnon 1983).
10. All contact exposures are serious, treatment is required immediately (MacKinnon 1983; Trevino 1980).

7.5.4 Eye Contact.

1. Conjunctivitis.
2. Corneal burns and scarring.
3. Corneal clouding (Trevino 1980).
4. Permanent visual defects.
5. Blindness.

7.6 Human Toxicity to Decay or Combustion Products

Hydrogen fluoride/hydrofluoric acid may generate flammable and explosive hydrogen in contact with some metals and moisture (AAR 1981).

7.6.1 Hydrogen. Hydrogen is a colourless, tasteless, odourless gas which, when mixed with air, forms explosive mixtures. With an ignition source, the air-gas mixture burns readily or explodes if concentrations are sufficient.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Hydrogen Fluoride with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Heat							x							Sax 1979
Water							x						Forms toxic and corrosive fumes	Sax 1979
CHEMICALS GROUPS														
Alkalis	x												Reacts exothermically	Allied PSDS 1981
Carbonates							x						Forms CO_2	Allied PSDS 1981
Cyanides								x					Forms HCN	Allied PSDS 1981
Metals				x									Forms H_2 gas with many metals	Allied PSDS 1981
Sulphides								x					Forms H_2S	Allied PSDS 1981
SPECIFIC CHEMICALS														
Acetic Anhydride									x				Mixture with 48.7% hydrofluoric acid	NFPA 1978

8.1 Compatibility of Hydrogen Fluoride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
2-Aminoethanol									x				Mixture with 48.7% hydrofluoric acid	NFPA 1978
Ammonium Hydroxide									x				Mixture with 48.7% hydrofluoric acid	
Arsenic Trioxide		x											Incandesces with hydrogen fluoride	Bretherick 1979
Bismuthic Acid										x			With 40% hydrofluoric acid	Bretherick 1979
Calcium Oxide											x		With HF acid	NFPA 1978
Chlorosulfonic Acid									x				Mixture with 48.7% HF acid	NFPA 1978
Concrete								x					May form silicon tetrafluoride	Allied PSDS 1979
Cyanogen Fluoride			x		x								Causes violent polymerization	Bretherick 1979
Ethylene Diamine									x				Mixture with dilute HF acid	NFPA 1978
Ethyleneimine									x				Mixture with 48.7% HF acid	NFPA 1978

8.1 Compatibility of Hydrogen Fluoride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Fluorine		x									x		Fluorine passed into 50% HF acid caused violent reaction with flame	NFPA 1978
Mercury (II) Oxide									x		x		Reaction can get out of control and explode	Bretherick 1979
Nitric Acid and Lactic Acid			x										Closed container of 2 materials plus HF acid exploded	NFPA 1978
Oleum									x				With 48.7% HF acid	NFPA 1978
N-Phenylazo-piperidine										x			In large quantities	Bretherick 1979
Phosphorus Pentoxide										x			Below 20°C	Bretherick 1979
Potassium permanganate											x		With 60 to 90% HF acid	Bretherick 1979
Potassium Tetra-fluorosilicate											x		With liquefied hydrogen fluoride	Bretherick 1979
Propiolactone (Beta)									x				With 48.7% HF acid	NFPA 1978

8.1 Compatibility of Hydrogen Fluoride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Propylene Oxide									x				With 48.7% HF acid	NFPA 1978
Silica and Silicic Acid								x					Forms silicon tetrafluoride and fluosilicic acid	du Pont 1982
Sodium										x			With HF acid	Bretherick 1979
Sodium Hydroxide	x								x				With 48.7% HF acid	NFPA 1978
Sulphuric Acid	x								x				With 48.7% HF acid	NFPA 1978
Vinyl Acetate									x				With 48.7% HF acid	NFPA 1978

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original sources has been presented essentially unchanged - in doing so, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Hydrogen fluoride is nonflammable and noncombustible (NFPA 1978; GE 1977, 1978). In the presence of heat, toxic and irritant vapours are liberated (Air Products MSDS 1978). In the concentrated form, hydrofluoric acid can attack metals and release explosive hydrogen gas. Anhydrous hydrogen fluoride is hygroscopic, forming an acidic solution with a high release of heat. Water contamination of pressurized containers or piping systems containing hydrogen fluoride could allow hydrogen generation by acid attack on metal (GE 1977, 1978).

9.1.2 Fire Extinguishing Agents. Use water on fires in which hydrogen fluoride or hydrofluoric acid is involved (NFPA 1978). Use water spray to cool containers involved in a fire to help prevent rupture (ERG 1980). Avoid spraying leaks directly as the resulting corrosion may increase the hole size (Allied PSDS 1981). Large volumes of water should be employed to effect a dilute solution (du Pont 1982). Water should be impounded for later treatment.

Small fires:	Dry chemical or CO_2.
Large fires:	Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from ends of tanks (ERG 1980). Do not get water inside containers (EAG 1978).

9.1.3 Evacuation. The following information consists of evacuation distances which appear in the literature. Important parameters such as spill quantity, concentration level to which evacuation is suggested, and environmental conditions may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zone in Section 5.3 of this manual which use the above data.

The following are recommended evacuation distances from the immediate danger area of a spill based on prevailing winds of 10 to 19 km/h (EAG 1978):

Approximate Size of Spill	Distance to Evacuate From Immediate Danger Area	For Maximum Safety, Downwind Evacuation Should be
20 m^2	145 m (192 paces)	1.6 km long, 0.8 km wide
35 m^2	205 m (270 paces)	2.4 km long, 1.6 km wide
55 m^2	255 m (336 paces)	2.4 km long, 1.6 km wide
75 m^2	295 m (390 paces)	3.2 km long, 1.6 km wide

Caution: Although hydrogen fluoride does not form an explosive mixture with air, the container in which it is shipped may explode under heat from a fire. For maximum safety, evacuate 600 m in all directions.

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact or inhalation (GE 1977, 1978).

If a leak in a container cannot be stopped, the container should be removed to the outdoors or to an isolated, well ventilated area. The container should be placed in such a position that the leak is up and thus releasing vapour, not liquid. Let the vapour or gas dissipate. The gas should be exhausted into an absorption system (possibly containing soda ash or slaked lime) (A 1970; Allied PSDS 1981).

The following absorbent materials have been tested and recommended for vapour suppression and/or containment of anhydrous hydrogen fluoride (Braley 1980): polyacrylamide and polymethyl methacrylate; 40 percent hydrogen fluoride solution could also be contained by using a mixture of anionic and nonionic polyacrylamide. Regular scrubber types (spray, venturi, wet cyclone, impingement and packed beds) are effective on hydrogen fluoride (Braley 1980). The effluent scrubber liquid is neutralized, usually with lime, to remove the fluoride ion as insoluble calcium fluoride (Allied PSDS 1981).

9.1.4.2 Spills on land. Spills on porous surfaces should be cleaned and neutralized immediately with alkaline materials (GE 1977, 1978). Contain if possible and cover with lime to form a neutral slurry. The slurry can be shoveled into steel containers for disposal (GE 1977, 1978).

Other recommended neutralizing agents are sodium bicarbonate or a mixture of equal parts of soda ash and slaked lime (Air Products MSDS 1978) and calcium carbonate (CG-D-38-76). Powdered ferro-chromium slag may also be used (Wilder 1972). Small spills can be diluted with water or water spray and neutralized with sodium bicarbonate or a soda ash-slated lime mixture (du Pont 1982). Care must be taken in all neutralization to ensure adequate ventilation and that heat produced by neutralization is controlled.

9.1.4.3 Spills in water. Contain if possible and neutralize with lime (OHM-TADS 1981). Other recommended neutralizing agents are: sodium bicarbonate or a mixture of equal parts of soda ash and slaked lime (Air Products MSDS 1978) and calcium carbonate (CG-D-38-76). The following sorbents should also be considered: activated carbon, carbonized sulphonated sawdust, Dowex 1 and 1x10, Amberlite IRA 402 or IRA 93 and DeSal process resin (CG-D-38-76).

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills on land. Liquid wastes may be neutralized in a trench with lime at a remote location away from buildings and people. The trench should then be filled with earth and covered with lumber or sheets or metal until the earth settles (GE 1977, 1978). The neutralized slurry and contaminated soil could also be removed and disposed of to a secure landfill.

9.1.5.2 General. For treatment of contaminated water, the following procedure is recommended (EPA 600/2-77-227): gravity separation of solids followed by precipitation (pH 11.0) with a mixture (50/50) of soda ash and lime. The solids are removed after the reaction is complete (usually overnight). The treated water is then passed through dual media filtration and finally neutralized with hydrochloric acid. Any waste water from backwashing of the filtration unit is returned to the gravity separator.

9.1.6 Disposal. Waste hydrofluoric acid must never be discharged directly into sewers or surface waters. Treat small amounts by adding to an excess of water and neutralizing with lime slurry, lime, soda ash or other alkali. Add the alkali to the acid slowly as HF vapour may be released as well as significant heat (Allied PSDS 1981). Large quantities are best disposed of by neutralization with lime which precipitates the fluoride ion as insoluble calcium fluoride. Other neutralizing agents such as waste alkali streams, dolomite, ammonia, caustic potash, caustic soda, and soda ash have been successfully used. Limestone is not normally used because the calcium fluoride precipitate coats the limestone thus reducing its effectiveness (Allied PSDS 1981).

9.1.7 **Protective Measures.** For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn. It should be noted that in most spills of hydrogen fluoride or the acid, this requirement would stand. The "lower" requirements are included only for application to minor spills of dilute solutions or where the concentrations are known and would not change during the operation.

If the spilled material is known to be hydrogen fluoride (in the anhydrous or aqueous form):

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of repeated or prolonged skin contact with liquid hydrogen fluoride. Splash-proof safety goggles are also recommended for eye protection (NIOSH/OSHA 1981).
- Gloves should be of gauntlet-type construction. Neoprene or PVC are recommended (GE 1977, 1978). Safety shoes with PVC, neoprene or composition soles should be used (du Pont 1982). Soft-brimmed hats or caps may be worn to give protection against liquid leaks and splashes (MCA 1970).
- The following chemical suit materials are recommended for protection against hydrofluoric acid (EE-20): cloropel, neoprene and PVC (excellent resistance) and butyl (good resistance).
- Non-impervious clothing which becomes contaminated with hydrogen fluoride should be removed immediately and not reworn until the hydrogen fluoride is removed from the clothing (NIOSH/OSHA 1981).
- Chemical showers and eye wash stations should be readily available to areas of use and spill situations (GE 1977, 1978).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where hydrogen fluoride is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 3 ppm
Gas or Vapour Concentration 20 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against hydrogen fluoride. A gas mask with a chin-style or a front- or back-mounted canister and filter providing protection against hydrogen fluoride. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 20 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen fluoride. Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen fluoride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 20 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 Special Precautions for Storage. Protect cylinders against physical damage. Store cylinders in a cool, dry, well-ventilated area of noncombustible construction. Protect cylinders from excessive temperature rise by storing away from sources of heat.

No part of a cylinder should be subjected to a temperature above 52°C. Store cylinders in an upright position and firmly secured. Segregate full and empty cylinders (Air Products MSDS 1978).

Cylinders may be stored in the open but must be protected against extremes of weather and screened from the direct rays of the sun. Do not allow cylinders to contact the ground in order to prevent rusting. Store away from solvents, gasoline and sources of ignition. Do not store near heavily trafficked areas (Air Products MSDS 1978).

Keep 50 percent hydrofluoric acid in tightly closed containers coated with polyethylene, Teflon, lead, wax or paraffin. Concentrations greater than 60 percent hydrofluoric acid can be handled in passivated steel containers and piping of appropriate design. In its concentrated form, it will attack yellow brass, lead, stainless steel, aluminum, cast iron and other metals and release explosive hydrogen gas from the chemical reaction (GE 1977, 1978). Steel used for the storage or transfer of hydrogen fluoride or concentrated acids should be regularly inspected for blistering and for thickness (corrosion loss) (du Pont 1982). Tanks should be diked to confine accidental spills. Diversion-type dykes can be used for the concentrated acids to divert any spills away from the tank to where they can be diluted and disposed of, but still allow access to the tank during emergencies (du Pont 1982).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study:

Leak Plugging	Plug N' Dike™
Temporary Storage	Portable Collection Bag System

du Pont has developed a special leak-plugging system for railway tank cars similar to the Chlorine Institute "C" Kit, but for fluorine (CCPA 1982).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in planning spill response. Only those which meet these criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 **Truck Leak** (Personal Communication with CDEP 1982; HMIR 1980)

A truck containing approximately 18 000 L of hydrofluoric acid developed a small leak in its front section while in transit. The driver noticed the smell of hydrofluoric acid vapour and brought the tank car to the nearest truck terminal for inspection. The truck was parked on an upslope to reduce the amount of hydrofluoric acid leaking from the front of the tank.

Response crews arrived on scene and were uncertain that although the manifest papers indicated a cargo of 70 percent hydrofluoric acid, the truck might have actually contained 40 percent hydrofluoric acid. The high water content in the latter would increase the reactivity of the hydrofluoric acid solution with metal. As a precaution, in case the acid corroded the wall of the tank, response personnel constructed two 1.2 m high dirt dykes around the tank car and poured about 150 kg of lime and sodium bicarbonate onto the ground to neutralize any spilled material.

The hydrofluoric acid, previously leaking from a pinhole, started to corrode the slag inclusion from the weld. The response crew, wearing Scott Air-packs and Acid-King acid suits applied a neoprene patch to the widening hole and secured it with stainless steel straps. A total of less than 180 L of hydrofluoric acid was released by the time the patch was made secure. Most of the hydrofluoric acid vaporized while approximately 10 L spilled on the ground and was neutralized by the available lime. The neutralized material was recovered and incorporated with soil in a nearby parking lot. Later that day, the remaining hydrofluoric acid was transferred into a replacement tank car with vacuum pumps.

The authors feel that this spill experience illustrates the need and benefit for rapid containment and leak plugging methodology, as well as the usefulness of the neoprene patch/stainless steel strap method of leak plugging.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Hydrogen Fluoride in Air

11.1.1 Specific Ion Electrode (NIOSH 1977). A range of 1.33 to 4.50 mg/m^3 (0.002 to 0.005 ppm) hydrogen fluoride in air may be analyzed by specific ion electrode. The gaseous hydrogen fluoride is determined with the use of a fluoride ion specific electrode and reference electrode.

A known volume of air is drawn through a midget bubbler containing 10 mL of 0.1 N sodium hydroxide. A 45 L air sample is recommended. The sample is made up to 25 mL with 0.1 N sodium hydroxide. Total ionic strength buffer is prepared by adding 57 mL of glacial acetic acid, 58 g sodium chloride, and 0.30 g of sodium citrate to approximately 500 mL of double distilled water with stirring. The buffer is then adjusted to pH 5.0 to 5.5 by the slow addition of 5 N sodium hydroxide, cooled to room temperature and diluted to 1000 mL with double distilled water. A 25 mL aliquot of this buffer is added to the sample. The fluoride specific ion electrode is lowered into the stirred sample solution and the gaseous hydrogen fluoride is determined from the direct millivolt reading using a calibration curve. The method is quick and the bubbler collection efficiency is 99 percent.

11.2 Qualitative Method for the Detection of Hydrogen Fluoride in Air

A known volume of air is drawn through a midget bubbler as in Section 11.1.1. The sample is acidified and added to a zirconyl chloride-alizarin dye mixture. The dye mixture is prepared by dissolving 0.5 g of alizarin in 200 mL of 95 percent alcohol with heating. Then 1.5 g zirconyl chloride is dissolved in 100 mL of water and added to the alcohol solution. The resulting solution is mixed and diluted to 1 L with water. A colour change from red to yellow indicates the presence of fluoride ion (Welcher 1955).

11.3 Quantitative Methods for the Detection of Hydrofluoric Acid in Water

11.3.1 **Ion Selective Electrode** (ASTM 1979). A range from 0.1 to 1000 mg/L (ppm) of fluoride ion in water can be determined using an ion selective electrode. The fluoride ion is determined using an ion selective fluoride electrode in conjunction with a reference electrode and direct reading off a millivolt scale, using a calibration curve.

A representative sample, approximately 50 mL, is collected. A 50 mL aliquot of total ionic strength buffer, having a pH between 5.0 to 5.5, is added to the sample in a beaker. The buffer is prepared as in Section 11.1.1. The solution is then magnetically stirred and the fluoride is determined by direct reading off the millivolt scale and a standard curve. This method is applicable to a variety of water types.

11.3.2 **Photometric** (ASTM 1979). Concentrations up to 1.4 mg/L (ppm) of fluoride ion in water can be determined using this method. The fluoride is isolated by distillation and measured photometrically.

A representative sample, approximately 300 mL, is collected in an appropriate container. Approximately 400 mL of water is placed in a distillation flask and to this, 200 mL of concentrated sulphuric acid is added with continuous swirling. Boiling stones are added and the solution is heated to 180°C. The distillate is discarded and the remaining solution in the distillation flask is cooled below 100°C. A 300 mL aliquot of sample is then added to the flask and the solution is heated to 180°C. The distillate is collected in a calibrated vessel until 300 mL in total have been collected. If free chlorine is present, it must be removed using sodium arsenite solution, which is prepared by dissolving 2.0 g of sodium arsenite in 1 L of water. Zirconyl-SPADNS (sodium 2-(parasulphophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulphonate) acid reagent is prepared by mixing equal volumes of zirconyl acid solution and SPADNS solution. The SPADNS (sodium2-(parasulphophenylazo)-1,8-dihydroxy-3,6-napthalenedisulphonate) solution is prepared by dissolving 0.958 g of reagent in 500 mL of water, dissolving 0.133 g of zirconyl chloride octahydrate in 25 mL of water and then by adding 350 mL of concentrated hydrochloric acid and diluting to 500 mL. A 10 mL aliquot of zirconyl-SPADNS is added to a 50 mL aliquot of the distillate. Using a suitable spectrophotometer, the absorbance is read at 570 nm. Absorbance may also be read on a suitable filter photometer equipped with a green-yellow filter having maximum transmittance between 550 to 580 nm and a light path of at least 1.0 cm.

11.4 Qualitative Method for the Detection of Hydrofluoric Acid in Water. A representative water sample is collected, acidified and added to a zirconyl chloride-alizarin dye mixture. The zirconyl chloride dye mixture is prepared as in Section 11.2. A colour change from red to yellow indicates the presence of fluoride ion (Welcher 1955).

11.5 Quantitative Method for the Detection of Hydrogen Fluoride in Soil

11.5.1 Distillation - Colourimetric (Hesse 1972). Hydrogen fluoride can be determined as total fluorine by steam distillation to decompose fluorine compounds and then quantitated colourimetrically using thorium nitrate. The method measures the total fluoride content in the soil. Free hydrogen fluoride is gassed off and is not measured.

One gram of 0.15 mm oven dried soil is placed in an appropriately sized distillation flask. Sulphuric acid (50 mL in 25 mL water) is added to the flask. The mixture is heated to 150°C, steam admitted, and then heated to 165°C; the distillate is collected in a 500 mL flask at a rate of 6 to 8 mL per minute until approximately 500 mL of distillate have been collected. To the distillate, 10 mL of 10 percent sodium hydroxide are added and the solution evaporated to near dryness. Sufficient water is then added to the residue to bring the total volume to 30 mL. The solution is then placed in a clean distilling flask with a mixture of 50 mL perchloric acid and 25 mL of water. After precipitation of any chloride present has occurred, a slight excess of 15 percent w/v silver perchlorate is added, followed by one drop each of 50 percent sodium hydroxide and 0.5 percent p-nitrophenol. The mixture is heated to 128°C, steam admitted, and then heated to 135°C. A distillation rate of 4 mL per minute is used until 400 mL of distillate have been collected. The receiver is changed and a total of 100 mL more distillate is collected. Both distillates may be analyzed. The second portion acts as a check of total recovery.

A 50 mL aliquot is taken and 1.0 M perchloric acid is added dropwise until the yellow colouration contributed by p-nitrophenol is discharged. The solution pH is adjusted to 3.3 using 0.1 M perchloric acid. A 1 mL volume of chrome azural-S indicator solution is then added and the solution titrated with 0.0005 M thorium nitrate until the colour matches the colour blank. The colour blank is prepared by combining 1 mL of indicator solution, 0.1 mL of 0.0005 M thorium nitrate, and the pH adjusted to 3.3 with 1.0 M perchloric acid. The total volume is made up to 50 mL with water. Duplicate 2 mL volumes of standard fluorine (10 μg/mL F^-) are diluted to 50 mL. A 1 mL volume of indicator solution (chrome azural-S) is added and the solution titrated with 0.0005 M thorium nitrate to match the colour blank. A reagent blank is also titrated in the same manner. Titre A is given by deducting the reagent blank from the test solution. Titre B is given by deducting 0.1 mL from the titre of standard fluorine solution and multiplying by 20. The fluoride content in the 50 mL of solution titrated is then found by multiplying A by B.

11.6 Qualitative Method for the Detection of Hydrogen Fluoride in Soil

The sample is collected as in Section 11.5.1. It is acidified and a suitable amount is added to a zirconyl chloride-alizarin dye mixture. The zirconyl chloride-alizarin dye mixture is prepared as in Section 11.2. A colour change from red to yellow indicates the presence of fluoride ion (Welcher 1955).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc.	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immision concentration
min	minute or minimum
mm	millimetre
μg	microgram
μm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
T_d	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
T_s	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight