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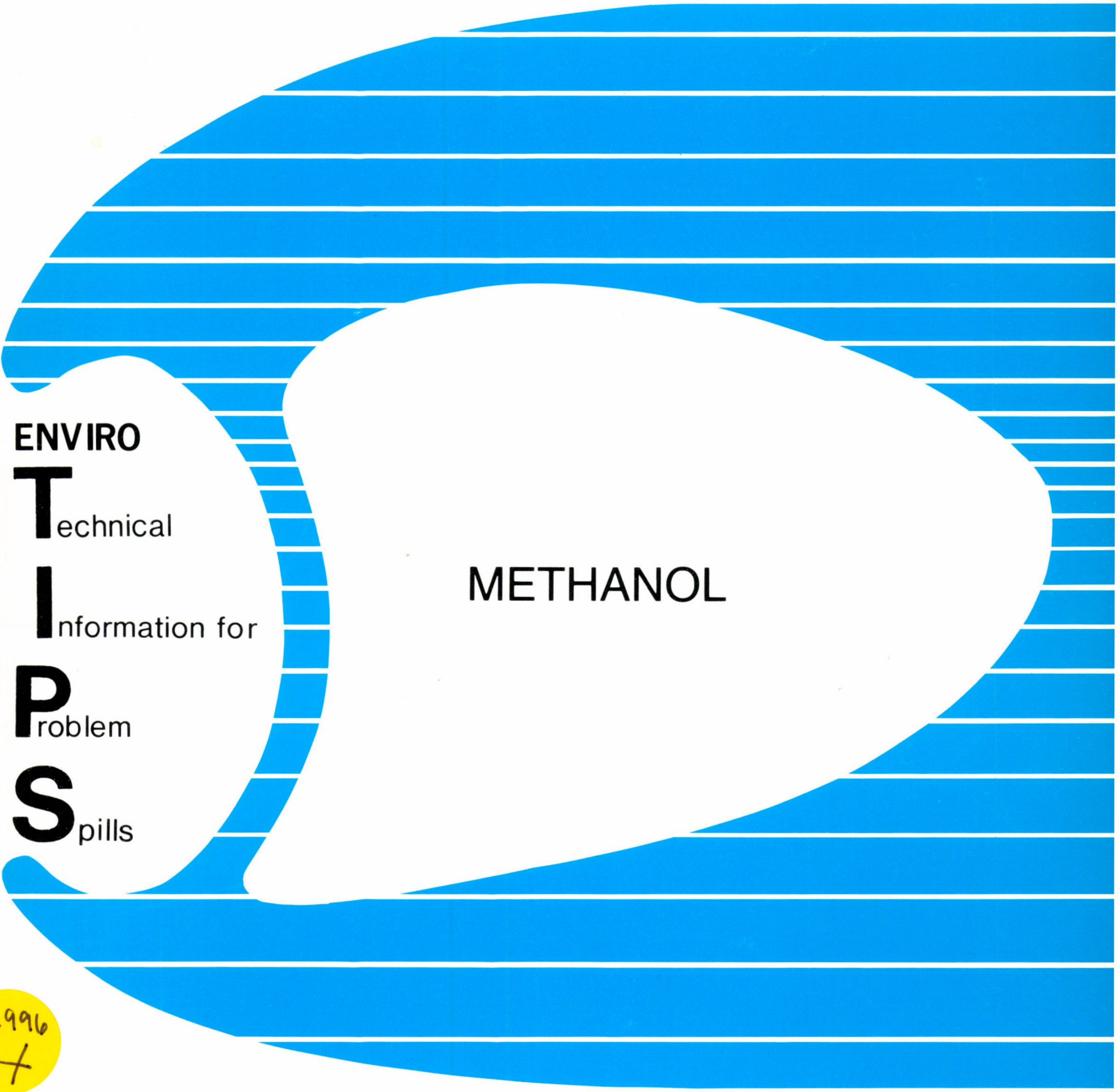

ENVIRO
Technical
Information for
Problem
Spills

METHANOL

January 1985

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.

EnviroTIPS manuals are available from

Publications Section
Environmental Protection Service
Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

METHANOL

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

January 1985

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 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

METHANOL (CH_3OH)

Clear, colourless liquid with an alcohol-like odour

SYNONYMS

Wood Alcohol, Wood Naphtha, Wood Spirit, Carbinol, Colonial Spirit, Columbian Spirit, Methyl Alcohol, Methyl Hydroxide, Monohydroxymethane, Pyroxylic Spirit, Alcool Méthylique (Fr.)

IDENTIFICATION NUMBERS

UN. No. 1230; CAS No. 67-56-1; OHM-TADS No. 7216784; STCC No. 4909230

GRADES & PURITIES

Pure grades: A or AA, 99.85 percent minimum

Solvent grades: 90 to 99 percent

IMMEDIATE CONCERNS

Fire: Flammable. Flashback along vapour trail may occur

Human Health: Low toxicity by contact; moderate toxicity by inhalation

Environment: Harmful to aquatic life.

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): liquid
Boiling Point: 64.7°C
Melting Point: -97.7°C
Flammability: flammable
Flash Point: 12-16°C
Vapour Pressure: 17 kPa (25°C)
Density: 0.787 g/mL (25°C)

Solubility (in water): completely soluble
Behaviour (in water): floats and mixes
Behaviour (in air): vapours are heavier than air
Odour Threshold Range: 5 to 7000 ppm

ENVIRONMENTAL CONCERNS

Methanol is toxic to aquatic life and microorganisms at concentrations above about 1000 ppm. Methanol biodegrades rapidly.

HUMAN HEALTH

TLV®: 200 ppm (260 mg/m^3) (skin)
IDLH: 25 000 ppm

Exposure Effects

Inhalation: Irritation to respiratory tract. Will cause headache, conjunctivitis, fatigue, nausea, convulsions, central nervous system depression, loss of consciousness and possibly death.

Contact: Contact with the skin results in irritation; if absorbed, produces symptoms similar to those of inhalation. Contact with the eyes results in irritation, blurred vision and conjunctivitis.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning "FLAMMABLE & POISON". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Do not extinguish fire unless release can be stopped. Use alcohol foam, dry chemical, carbon dioxide, water spray or fog to extinguish. Direct water stream should not be used. Cool fire-exposed containers with water. Containers may explode in heat of fire.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb residual liquid with natural or synthetic sorbents.

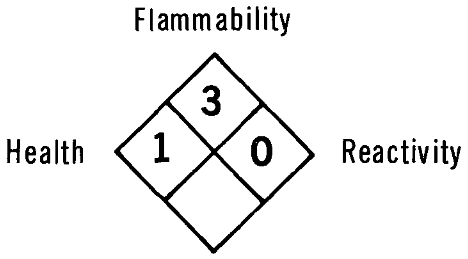
Water: Contain by damming, water diversions or natural barriers. Remove highly contaminated water for treatment if possible.

Air: Use water spray to knock down vapour. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

Category	Rating
Fire	3
Health	
Vapour Irritant	1
Liquid or Solid Irritant	1
Poison	2
Water Pollution	
Human Toxicity	1
Aquatic Toxicity	1
Aesthetic Effect	1
Reactivity	
Other Chemicals	2
Water	0
Self-reaction	0

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Clear, colourless, mobile liquid (Celanese PB)
Usual shipping state	Liquid (Celanese PB)
Physical state at 15°C, 1 atm	Liquid
Freezing point	-97.68°C (Kirk-Othmer 1981)
Boiling point	64.70°C (Kirk-Othmer 1981)
Vapour pressure	12.8 kPa (20°C) (Celanese PB) 16.96 kPa (25°C) (Liley 1982)

Densities

Density	0.78663 g/mL (25°C) (Kirk-Othmer 1981)
Specific gravity, liquid (water = 1)	0.7923 (20°/20°C) (Celanese PB)
Specific gravity, vapour (air = 1)	1.11 (Celanese PB)

Fire Properties

Flammability	Flammable liquid (NFPA 1978)
Flash point	
CC	11°C (NFPA 1978) 12°C (Kirk-Othmer 1981)
OC	15.6 (Tag open cup) (ISH 1977)
Autoignition temperature	385°C (NFPA 1978) 470°C (Kirk-Othmer 1981; Ullmann 1975)
Burning rate	1.7 mm/min (CHRIS 1978)
Upper flammability limit	36 percent (v/v) (NFPA 1978) 36.5 percent (v/v) (Ullmann 1975)
Lower flammability limit	6.0 percent (v/v) (NFPA 1978)
Burning characteristics	Burns with a nonluminous bluish flame (Merck 1976)
Heat of combustion	723 kJ/mole (25°C) (CRC 1980)
Combustion products	Carbon dioxide and water (CRC 1980)

Other Properties

Molecular weight of pure substance	32.04 (CRC 1980)

Constituent components of typical commercial grade	Pure grades: >99.85 percent CH_3OH (Celanese PB) Solvent grades: 90-99 percent CH_3OH
Refractive index	1.3288 (20°C) (CRC 1980)
Viscosity	0.614 mPa•s (20°C) (Celanese PB)
Liquid interfacial tension with air	22.55 mN/m (20°C) (Celanese PB)
Latent heat of fusion	3.3 kJ/mole (at melting point) (Kirk-Othmer 1981)
Latent heat of sublimation	37.4 kJ/mole (25°C) (Lange's Handbook 1979)
Latent heat of vaporization	36.17 kJ/mole (at boiling point) (Kirk-Othmer 1981)
Free energy of formation	-161.8 kJ/mole (25°C) (Kirk-Othmer 1981)
Heat of formation	Liquid: -239.1 kJ/ mole (25°C) (Sussex 1977) Gas: -201.4 kJ/mole (Ullmann 1975)
Ionization potential	10.85 eV (Rosenstock 1977)
Heat of solution	-672 kJ/mole (CHRIS 1978)
Heat capacity	
constant pressure (C_p)	Liquid: 81.16 J/(mole•°C) (25°C) (Kirk-Othmer 1981) Gas: 43.89 J/(mole•°C) (25°C) (Kirk-Othmer 1981)
constant volume (C_v)	65 J/(mole•°C) (25°C) (CRC 1980; CHRIS 1978)
Critical pressure	8096 kPa (Kirk-Othmer 1981)
Critical temperature	239.4°C (Kirk-Othmer 1981)
Coefficient of thermal expansion	1.24×10^{-3}/°C (55°C) (Celanese PB)
Thermal conductivity	0.202 W/(m•K) (25°C) (Kirk-Othmer 1981)
Saturation concentration	166 g/m^3 (20°C), 270 g/m^3 (30°C) (Verschueren 1984)
Dielectric constant	32.7 (25°C) (Kirk-Othmer 1981)
Entropy	Liquid: 126.9 J/(mole•K) (Ullmann 1975) Gas: 241.5 J/(mole•K) (25°C) (Ullmann 1975)
Vapour pressure equation	$\ln P = 15.76 - \frac{2846}{T} - \frac{3.743 \times 10^5}{T^2} + \frac{2.189 \times 10^7}{T^3}$ (P is pressure in kPa, T is temperature in K) (Kirk-Othmer 1981)
Diffusivity	0.132 cm^2/s (0°C) (Perry 1973) 1.6×10^{-5} cm^2/s (in water 25°C) (Perry 1973)
Log $_{10}$ octanol/water partition coefficient	-0.77 (Hansch and Leo 1979)

Evaporation rate	1.2 g/($m^2 \cdot s$) (20°C, wind 4.5 m/s) (this work)

Solubility

In water	Soluble in all proportions (Celanese PB)
In other common materials	Miscible with alcohols and ether (Celanese PB). Miscible with acetone and very soluble in benzene (CRC 1980)
Azeotropes	Methanol forms a number of azeotropes; the following are most useful (Ullmann 1975):

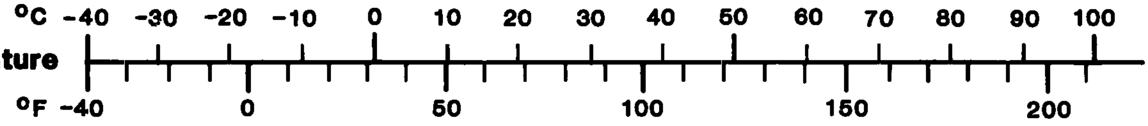
Material	Percent Methanol	B.P.
Acetone	12	55.7
n-Pentane	15.5	30.4
Benzene	39.1	57.5
Toluene	69	63.8
Carbon Tetrachloride	20.7	55.7
Trichloroethylene	38.0	59.4
Methylene Chloride	7.3	37.8

Vapour Weight to Volume Conversion Factor

1 ppm = 1.330 mg/m^3 (20°C) (Verschueren 1984)

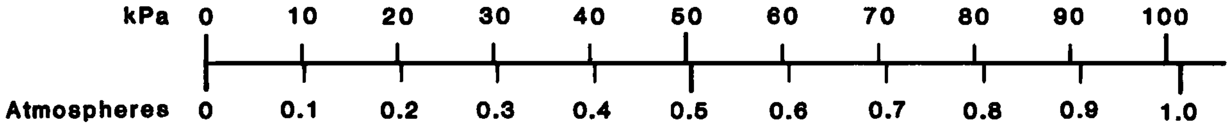
CONVERSION NOMOGRAMS

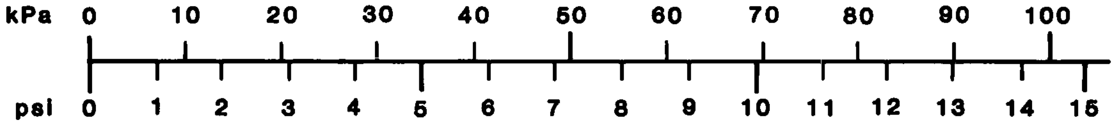
Temperature

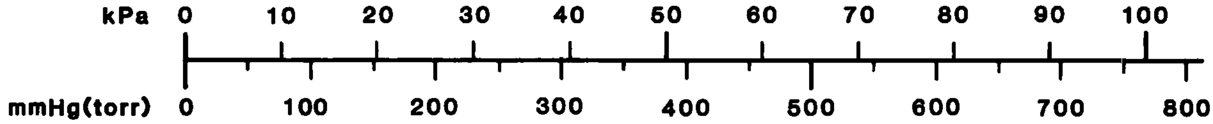


Pressure

1 kPa = 1 000 Pa







Viscosity

Dynamic 1 Pa·s = 1 000 centipoise (cP)

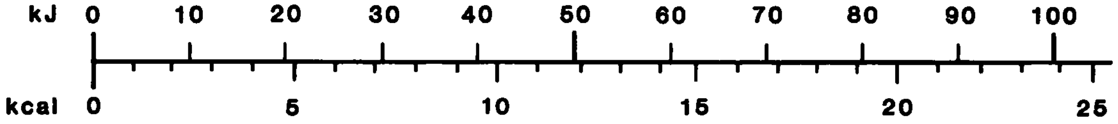
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

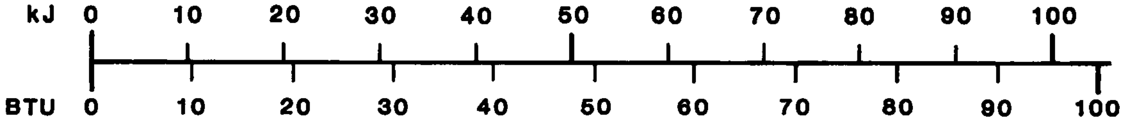
Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat)

1 kJ = 1 000 J





Density

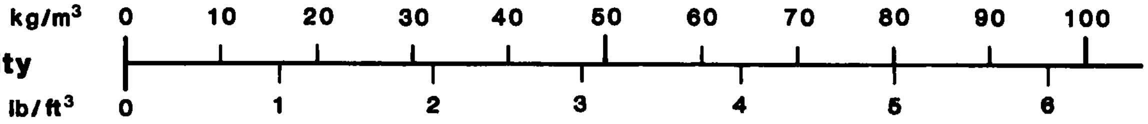
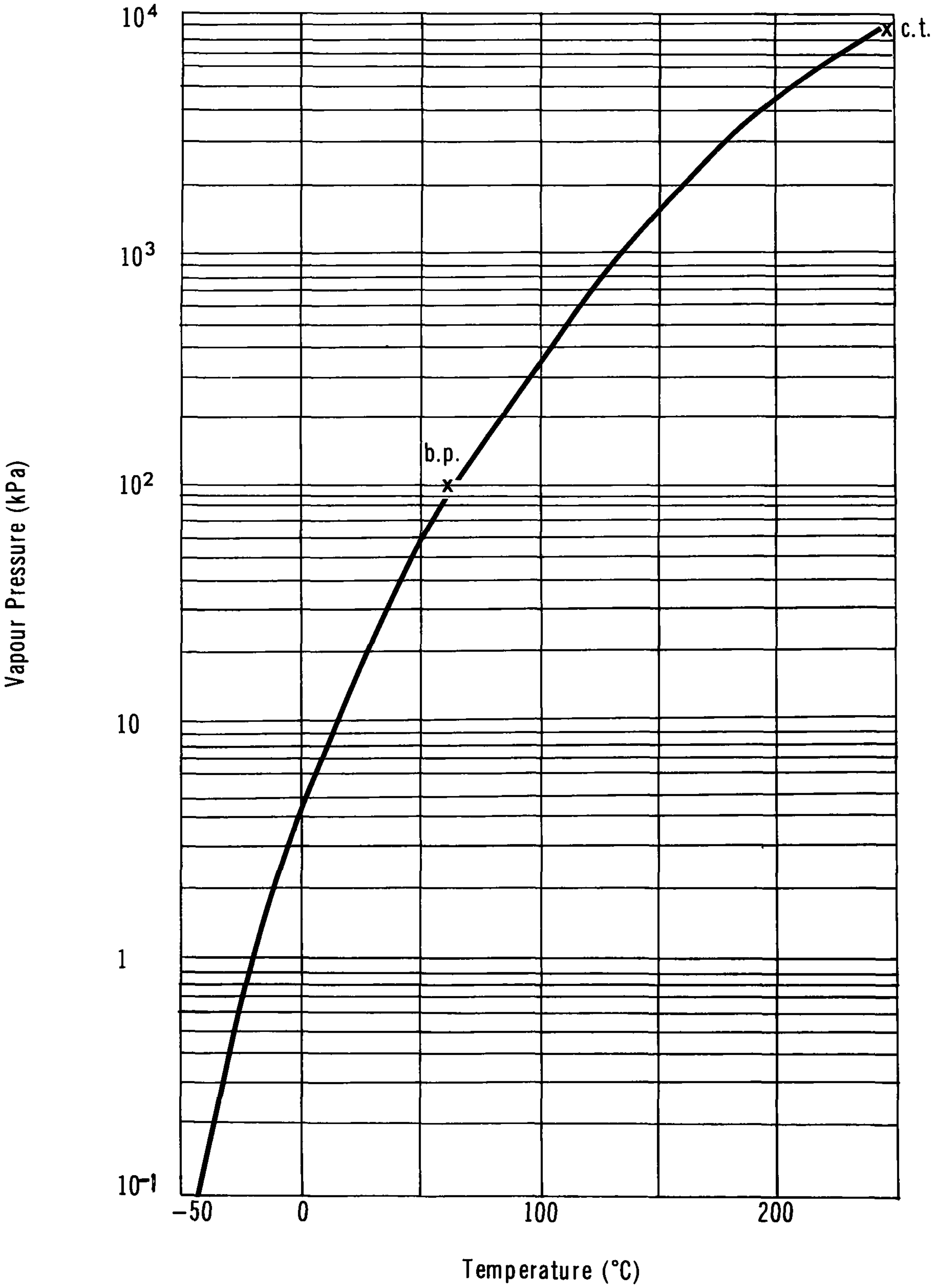


FIGURE 1

METHANOL

VAPOUR PRESSURE VS TEMPERATURE

Reference: Chem.Eng. 1976



PHASE DIAGRAM OF THE $CH_3OH \cdot H_2O$ SYSTEM

Reference: ISH 1977; ULLMANN 1975

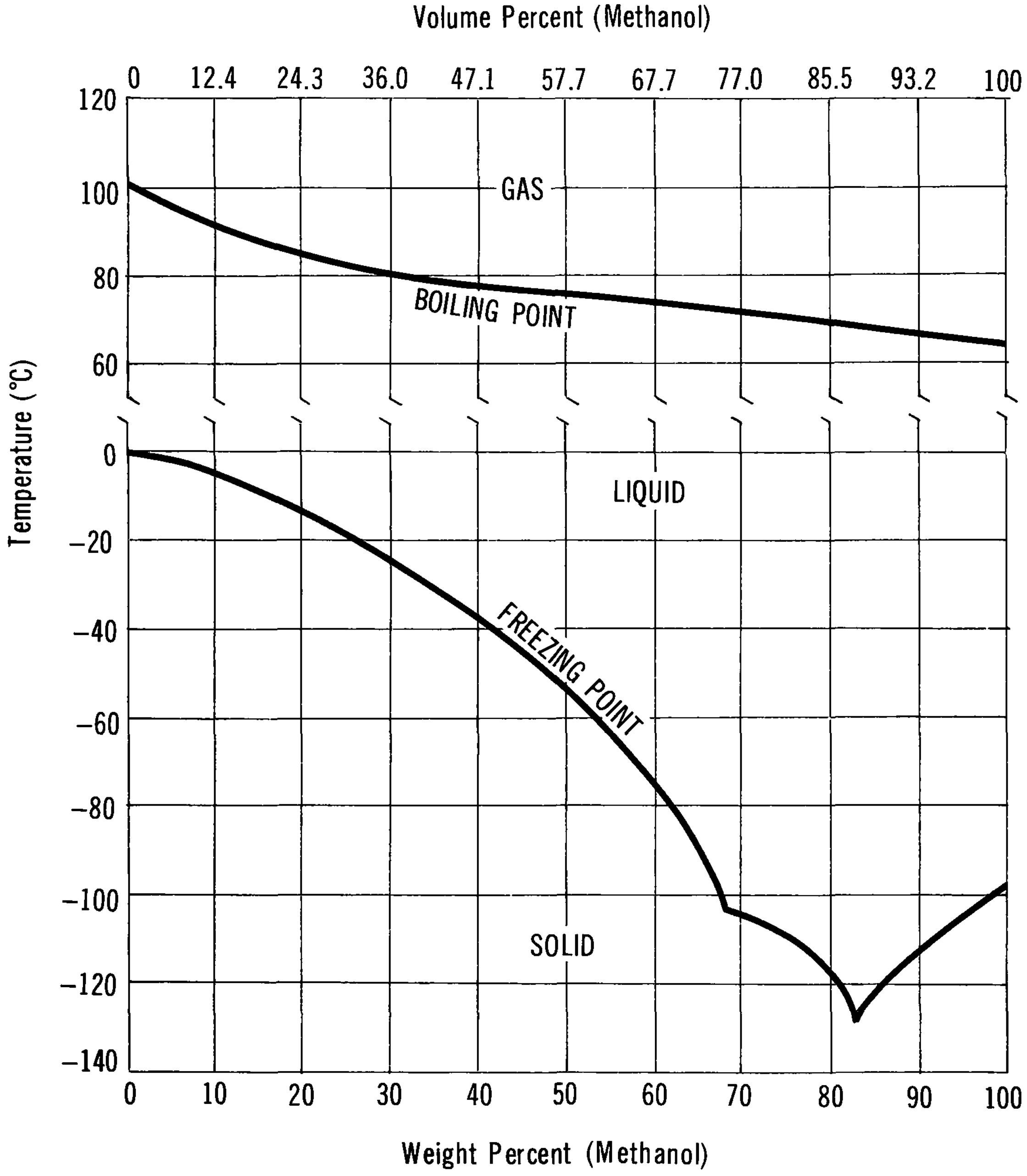


FIGURE 3

METHANOL

DENSITY OF SOLUTIONS

Reference: ISH 1977

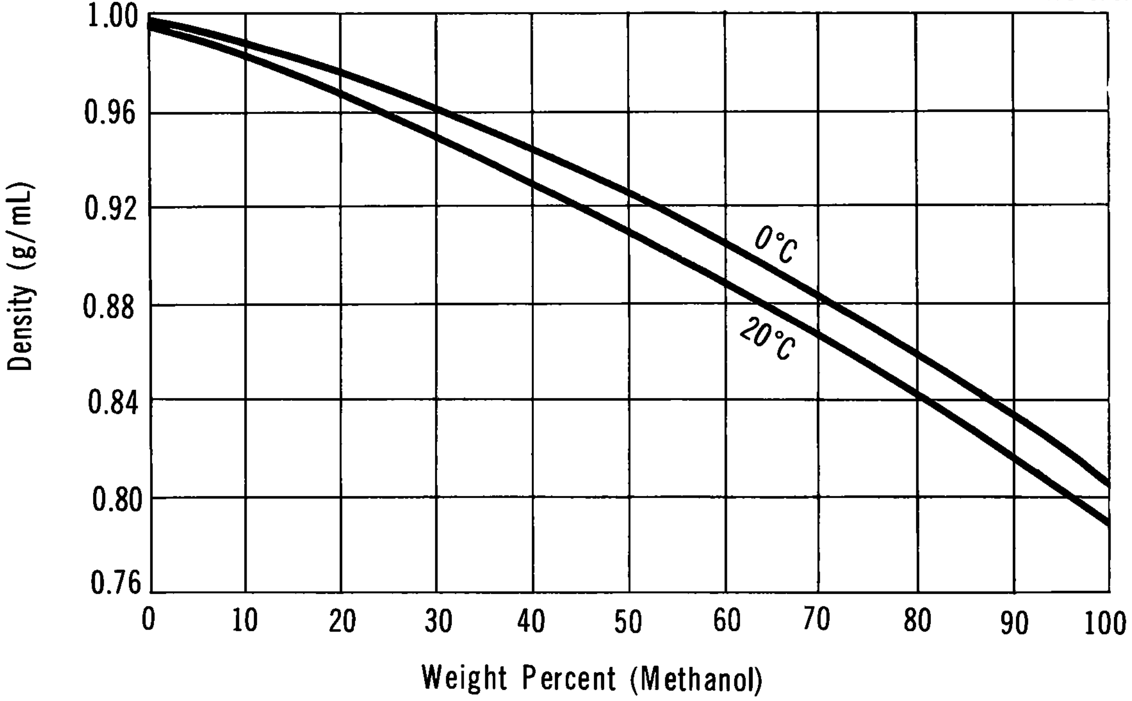


FIGURE 4

METHANOL

VAPOUR VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

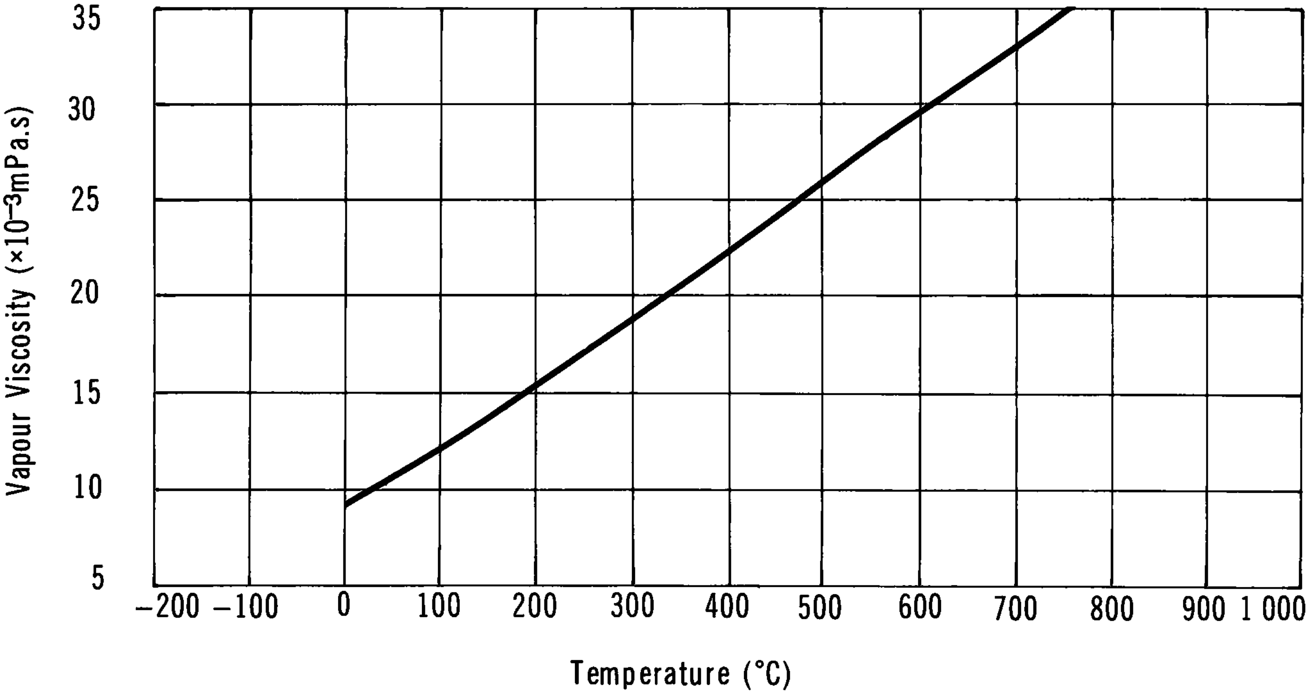


FIGURE 5

METHANOL

LIQUID VISCOSITY VS TEMPERATURE

Reference: Chem.Eng. 1976

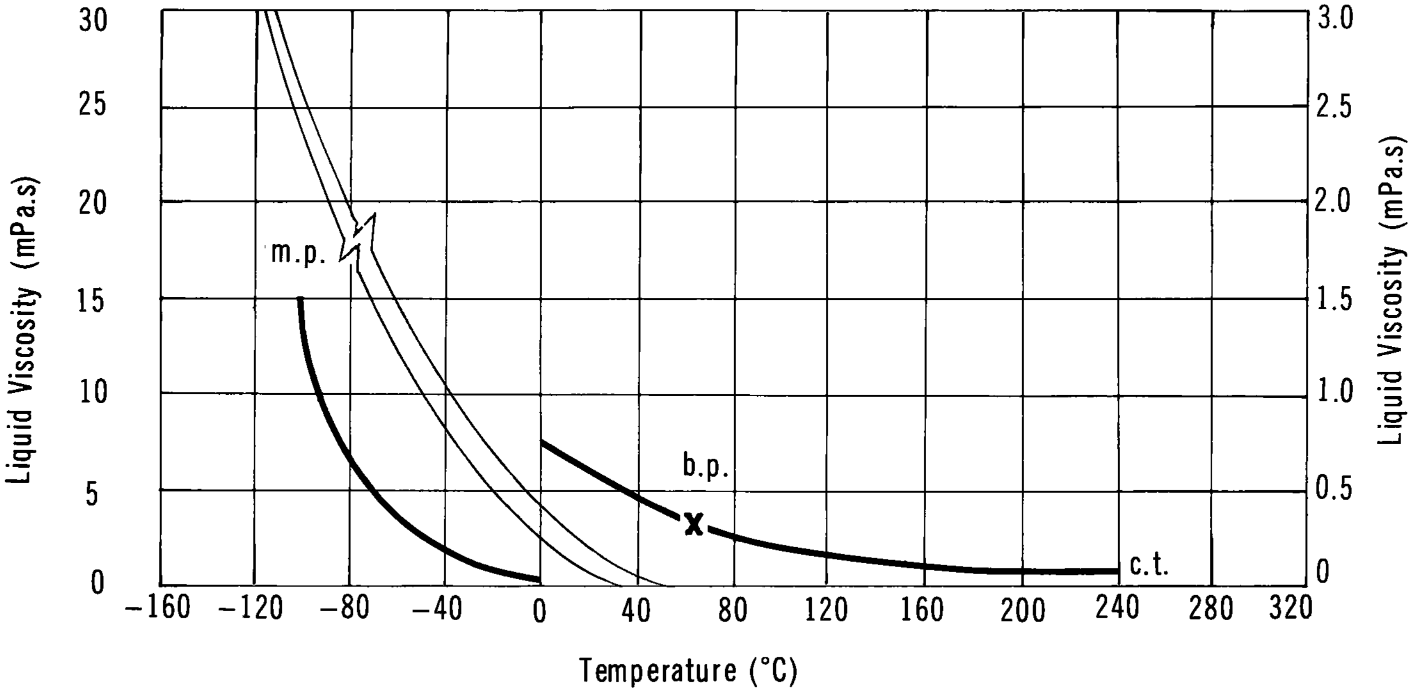
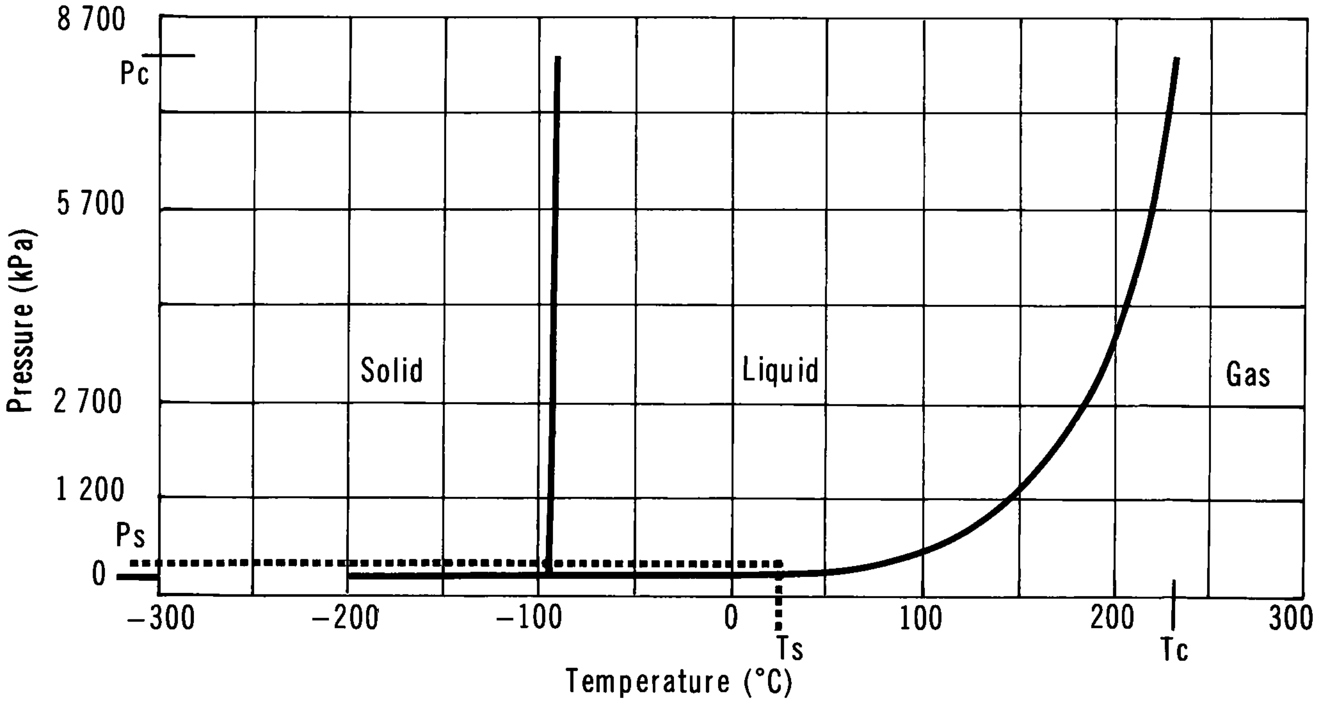


FIGURE 6

METHANOL

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 **Grades, Purities** (Kirk-Othmer 1981; Ullmann 1975; Celanese PB)

Methanol is sold in pure or solvent grades. Solvent grades are not tightly specified and may vary from 90 to 99 percent methanol. Pure methanol is sold in either Grade A or AA (sometimes referred to as regular and premium grades, respectively). The specifications for these grades are as follows:

	Grade A	Grade AA
Minimal Methanol Content	99.85 percent	99.85 percent
Maximum Acetone and Aldehydes	30 ppm	30 ppm
Maximum Acetone	-	20 ppm
Maximum Ethanol	-	10 ppm
Maximum Acid (as acetic acid)	30 ppm	30 ppm
Maximum Water	1500 ppm	1000 ppm
Specific Gravity (20/20°C)	0.7928	0.7928

3.2 **Domestic Manufacturers** (Corpus 1984; CBG 1980; Chemfacts 1982)

These are corporate headquarters' addresses and are not intended as spill response contacts:

Alberta Gas Chemicals Ltd.
11456 Jasper Avenue, Suite 400
Edmonton, Alberta
T5K 0M1
(403) 482-6361

Celanese Canada Inc.
800 Dorchester Blvd. West
Montreal, Quebec
H3C 3K8
(514) 878-1581

Ocelot Industries Ltd.
BP House
333 Fifth Avenue SW
Calgary, Alberta
T2P 0S2
(403) 261-2000

3.3 **Other Suppliers** (CBG 1980; Corpus 1984)

A & K Petro-Chem Industries Ltd.
710 Arrow Road
Weston, Ontario
M9M 2M1
(416) 746-2991

Anachemia Ltd.
P.O. Box 147
Lachine, Quebec
H8S 4A7
(514) 489-5711

Arliss Chemical Co. Inc.
325 Hymus Blvd.
Pointe Claire, Quebec
H9R 1G8
(514) 694-2170

Ashland Chemical/Solvents Division
Valvoline Oil & Chemical
150 Bronoco Avenue
Toronto, Ontario
M6E 4Y1
(416) 651-2822

Bates Chemical Co. Ltd.
160 Lesmill Road
Don Mills, Ontario
M3B 2T7
(416) 445-7050

Bayer (Canada) Inc.
7600 TransCanada Highway
Pointe Claire, Quebec
H9R 1C8
(514) 697-5550

Borden Chemical Canada
Division of Borden Products Ltd.
595 Coronation Drive West
West Hill, Ontario
M1E 2K4
(416) 286-1000

Canada Colours & Chemicals Ltd.
80 Scarsdale Road
Don Mills, Ontario
M3B 2R7
(416) 924-6831

Ceda Research Ltd.
Division Ceda Manufacturers and Sales
626-58 Avenue SE
Calgary, Alberta
T2H 0P8
(403) 253-4333

Degussa (Canada) Ltd.
3370 South Service Road
Burlington, Ontario
L7N 3M6
(416) 639-5710

DuPont Canada Inc.
555 Dorchester Blvd. West
Montreal, Quebec
H3C 2V1
(514) 861-3861

Esso Chemical Canada
Division of Imperial Oil Ltd.
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Harrisons & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

International Chemical Canada Ltd.
P.O. Box 385
Brampton, Ontario
L6V 2L3
(416) 453-4234

Mallinckrodt Canada Inc.
600 Delmar Avenue
Pointe Claire, Quebec
H9W 1E6
(514) 695-1220

Recochem Inc.
850 Montee De Liesse
Montreal, Quebec
H4T 1P4
(514) 341-3550

Shefford Chemicals Ltd.
1028 Principale
Granby, Quebec
J2G 8C8
(514) 378-0125

Shell Canada Ltd.
505 University Avenue
Toronto, Ontario
M5G 1X4
(416) 866-7111

Stanchem Division
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9
(514) 933-6721

Stormont Chemicals Ltd.
5845 Fourth Line East
Mississauga, Ontario
L4W 2K5
(416) 677-1335

Syndel Laboratories Ltd.
8879 Selkirk Street
Vancouver, British Columbia
V6P 4J6
(604) 266-7131

Travis Chemicals
715 5th Avenue SW, E 1710
Calgary, Alberta
T2C 2X6
(403) 263-8660

Van Waters & Rogers Ltd.
9800 Van Horne Way
Richmond, British Columbia
V6X 1W5
(604) 273-1441

3.4 Major Transportation Routes

Current Canadian production of methanol is located in Alberta, Ontario, and British Columbia. Methanol is primarily shipped by tank cars. Significant quantities are exported via Vancouver and Montreal. A large portion is exported via rail to the United States.

3.5 Production Levels (Corpus 1984)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1983)
Alberta Gas Chemical, Medicine Hat, Alta.		760
Celanese Canada, Edmonton, Alta.		700
Celanese Canada, Millhaven, Ont.		4.5
Ocelot Industries, Kitimat, B.C.		360
	TOTAL	1824.5
Domestic Production (1983)		1652
Imports (1983)		7
	TOTAL SUPPLY	1659

3.6 Manufacture of Methanol (FKC 1975; Kirk-Othmer 1981)

3.6.1 General. Methanol is produced by the catalytic reaction of synthesis gas (a mixture primarily composed of carbon monoxide and hydrogen) with hydrogen. One producer makes synthesis gas from naphtha; all others use natural gas feedstock.

3.6.2 Raw Materials Occurrence and Extraction. Since the catalysts used in making synthesis gas are sensitive to sulphur poisoning, natural gas feedstock is hydrotreated to convert organosulphur compounds to hydrogen sulphide. The process stream is then passed through an amine solution which absorbs the hydrogen sulphide.

3.6.3 Raw Materials Processing. Desulphurized natural gas feedstock is catalytically reacted with steam to form a product containing hydrogen and carbon monoxide, with some unreacted methane and some carbon dioxide. The catalyst is quite often nickel-impregnated ceramic. The entrance temperature is 425-550°C and the exit temperature is 840-880°C at 700-1700 kPa:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The reaction produces more hydrogen than is necessary for methanol formation. The excess may be used in hydrotreating feedstock (above), or for fuel for process heat; or carbon dioxide may be added to the synthesis gas to provide a more favorable carbon-hydrogen ratio.

3.6.4 Manufacturing Process. Synthesis gas is cooled, compressed and reacted, commonly at 5000-10 000 kPa and 200-300°C, in the presence of a copper-based catalyst:

$$CO + 2H_2 \rightarrow CH_3OH \text{ (+ by-products)}$$

Typically, about 2.5 percent of the reaction mixture is converted to methanol. This is condensed from the reaction mixture, which is then recirculated over the catalyst beds. The condensed reaction product is purified by distillation, generally in several columns which remove gases, water, dimethyl ether, fusel oils and higher alcohols.

3.7 Major Uses in Canada (Corpus 1984)

Methanol is used as a chemical intermediate in the manufacture of formaldehyde, acetic acid and glycol methyl ether; in dehydrating pipelines; as a solvent and de-icing agent; in the production of methylamines and chlorine dioxide; and as an automotive fuel. In 1983, 86 percent of domestic production was exported, 9 percent was used for formaldehyde production, and 2 percent was used for dehydrating pipelines.

3.8 **Major Buyers in Canada** (Corpus 1984)

Abitibi-Price, Smooth Rock Falls, Ont.
Alberta Natural Gas, Calgary, Alta.
Alberta & Southern, Calgary, Alta.
Ashland Chemical, Mississauga, Ont.
Bakelite Thermosets, Belleville, Ont.
Bate Chemical, Toronto, Ont.
Borden Chemical, Toronto, North Bay, Ont.
CP Rail, Montreal, Que.
Canadian National, Montreal, Que.
Canada Colors & Chemicals, Toronto, Ont.
Celanese Canada, Edmonton, Alta.
Chinook Chemical, Sarnia, Ont.
Cisco, Toronto, Ont.
Domtar, Cornwall, Ont.
Esso Chemical Canada, Toronto, Ont.
Fraser, Edmunston, N.B.
Gulf Canada, Toronto, Ont.
Hall Chemical, Montreal, Que.
Harrisons & Crosfield, Toronto, Ont.
Kert Chemical, Toronto, Ont.
Laurentide Chemicals, Shawinigan, Que.
Linwo Industries, Toronto, Ont.; Edmonton, Alta.
Nova, Calgary, Alta.
Quality Oils, Montreal, Que.
Recochem, St. Remi de Napierville, Que.
Reichhold, North Bay, Thunder Bay, Ont.
Shefford Chemicals, Granby, Que.
Shell Canada, Toronto, Ont.
Stanchem, Montreal, Que.
Stormont Chemicals, Mississauga, Ont.
TransCanada Pipelines, Toronto, Ont.
Van Waters & Rogers, Vancouver, B.C.
Westcoast Transmission, Vancouver, B.C.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 **Bulk Shipment.** Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars and highway tank vehicles. A significant portion of Canadian production is shipped in railway tank cars.

4.1.1.1 **Railway tank cars.** Railway tank cars permitted for methanol service are described in Table 2 (RTDCR 1974). Figure 7 shows a typical 111A60W1 railway car used to transport methanol; Table 3 indicates railway tank car details associated with this drawing. Cars are equipped for unloading by pump or gravity flow through a bottom outlet. In addition to bottom unloading, the cars may be unloaded from the top by pump. In this case, the liquid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is never used for unloading these tanks (MCA 1970).

A safety relief valve set at 414 kPa (60 psi) is required on top of the rail car (TCM 1979). A gauging device, either the rod type or the tape type, is required. The top unloading connection must be protected by a housing cover.

4.1.1.2 **Tank motor vehicles.** Methanol is transported by tank motor vehicles with tanks classed as nonpressure vessels (TDGC 1980). Design pressure for such tanks does not exceed 14 kPa (2 psi). Motor vehicle tanks carrying methanol are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve. Air pressure is never used (MCA 1970). The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars, to be discussed later.

4.1.2 **Packaging.** Methanol, in addition to railway bulk shipments, is also transported in drums. Drums fabricated from a variety of construction materials are permitted (TDGC 1980). Table 4 describes these drums.

4.2 Off-loading

4.2.1 **Off-loading Equipment and Procedures for Railway Tank Cars.** Prior to off-loading, certain precautions must be taken (MCA 1970):

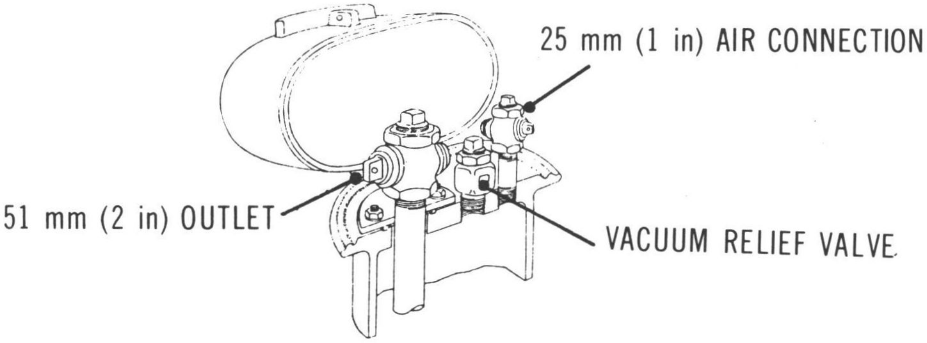
- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

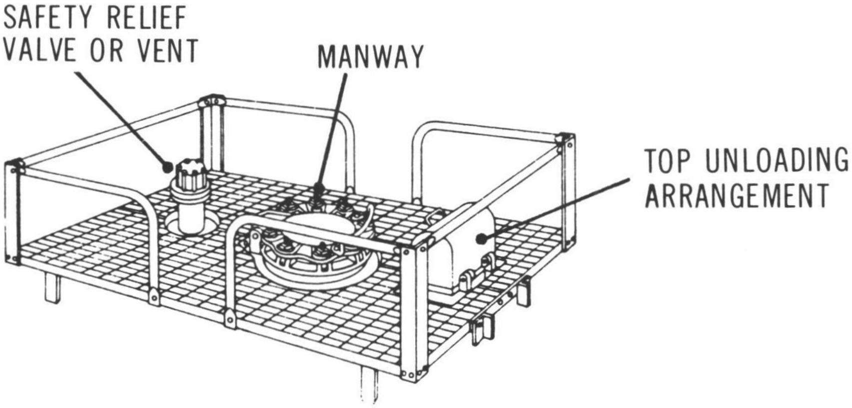
CTC/DOT Specification	Tank Material	Insulation	Test Pressure kPa (psi)	Dome	Bottom Outlet	Bottom Washout	Gauging Device
103W	steel	optional	414 (60)	required	optional	optional	optional
103ALW	aluminum alloy	optional	414 (60)	required	optional	optional	optional
104W	steel	optional	414 (60)	required	optional	optional	optional
105A100W	steel	required	690 (100)	none	prohibited	prohibited	standard
105A100ALW	aluminum alloy	required	690 (100)	none	prohibited	prohibited	standard
109A100ALW	aluminum alloy	optional	690 (100)	none	prohibited	optional	standard
111A60W1	steel	optional	414 (60)	none	optional	optional	required
111A60ALW1	aluminum alloy	optional	414 (60)	none	optional	optional	required
111A60F1	steel	optional	414 (60)	none	optional	optional	required
111A100W3	steel	required	690 (100)	none	optional	optional	required
111A100W4	steel	required	690 (100)	none	prohibited	prohibited	required
111A100W6	alloy steel	optional	690 (100)	none	optional	optional	required
112A200W	steel	none	1380 (200)	none	prohibited	prohibited	standard
112A400F	steel	none	2760 (400)	none	prohibited	prohibited	standard
114A340W	steel	none	2340 (340)	none	optional	optional	standard

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

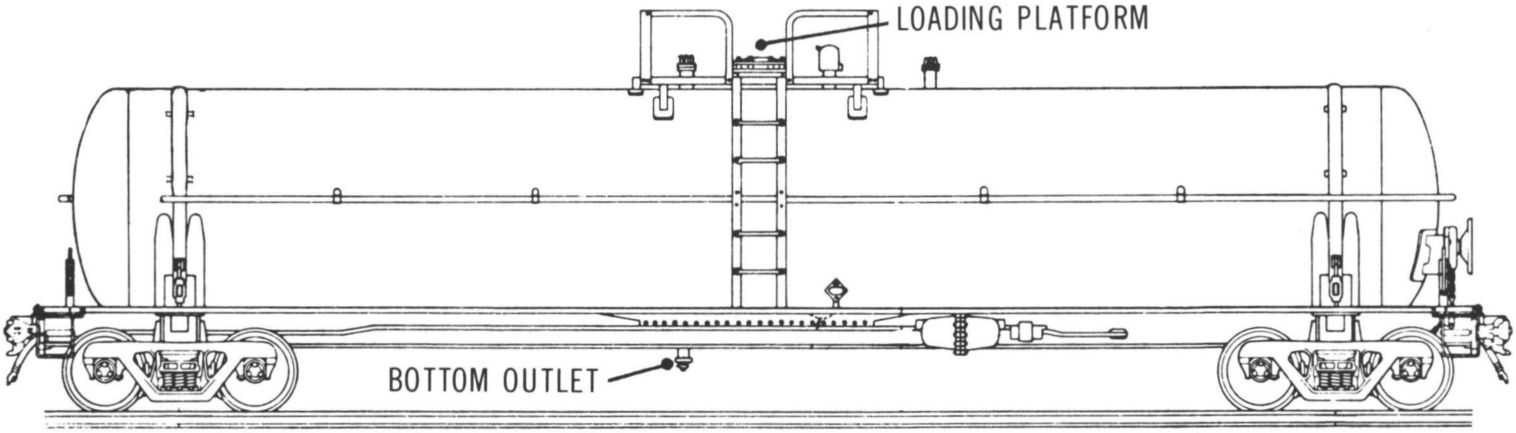


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. Gal.)		
Description	**16 700**	**17 200**	**20 000**
Overall			
Nominal capacity	75 700 L (16 700 gal.)	78 000 L (17 200 gal.)	90 900 L (20 000 gal.)
Car weight - empty	33 900 kg (74 700 lb.)	33 900 kg (74 700 lb.)	38 900 kg (85 800 lb.)
Car weight - max.	119 000 kg (263 000 lb.)	83 500 kg (184 000 lb.)	119 000 kg (263 000 lb.)
Tank			
Material	Steel	Steel	Steel
Thickness	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)	11.1 mm (7/16 in.)
Inside diameter	2.60 m (102 in.)	2.62 m (103 in.)	2.74 (108 in.)
Test pressure	414 kPa (60 psi)	414 kPa (60 psi)	414 kPa (60 psi)
Burst pressure	1640 kPa (240 psi)	1640 kPa (240 psi)	1640 kPa (240 psi)
Approximate Dimensions			
Coupled length	17 m (57 ft.)	17 m (57 ft.)	18 m (60 ft.)
Length over strikers	16 m (53 ft.)	16 m (53 ft.)	17 m (57 ft.)
Length of truck centres	13 m (42 ft.)	13 m (42 ft.)	14 m (45 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)	4 m (13 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)	5 m (15 ft.)
Overall width (over grabs)	3.2 m (127 in.)	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (8-10 ft.)	2-3 m (8-10 ft.)	2-3 m (8-10 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			
Top Unloading			
Unloading connection	51 mm (2 in.)	51 mm (2 in.)	51 mm (2 in.)
Manway/fill hole	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)	203-356 mm (8-14 in.)
Air connection	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)	25-51 mm (1-2 in.)
Bottom Unloading			
Bottom outlet	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)	102-152 mm (4-6 in.)
Safety Devices	Safety vent or valve		
Dome	None		
Insulation	Optional		

TABLE 4 DRUMS

Type of Drum	Designation	Description	Figure No. (If Any)
Steel	1A1	Nonremovable head, reusable	8
	1A1A	1A1 with reinforced chime	8
	1A1B	1A1 with welded closure flange	8
	1A1D	1A1 with coating (other than lead)	8
	1A2	Removable head, reusable	8
	1A3	Nonremovable head, single use only	8
Monel*	TC5M		8
Aluminum	1B1	Nonremovable head	8
	1B2	Removable head	8
Steel Drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)	
Fibreboard Drums with inner plastic receptacles	6HG1	Outer containers of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity of 225 L (49 gal.)	

*See Section 4.3 of this report.

- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Two means of off-loading are used for rail cars, top off-loading and bottom off-loading.

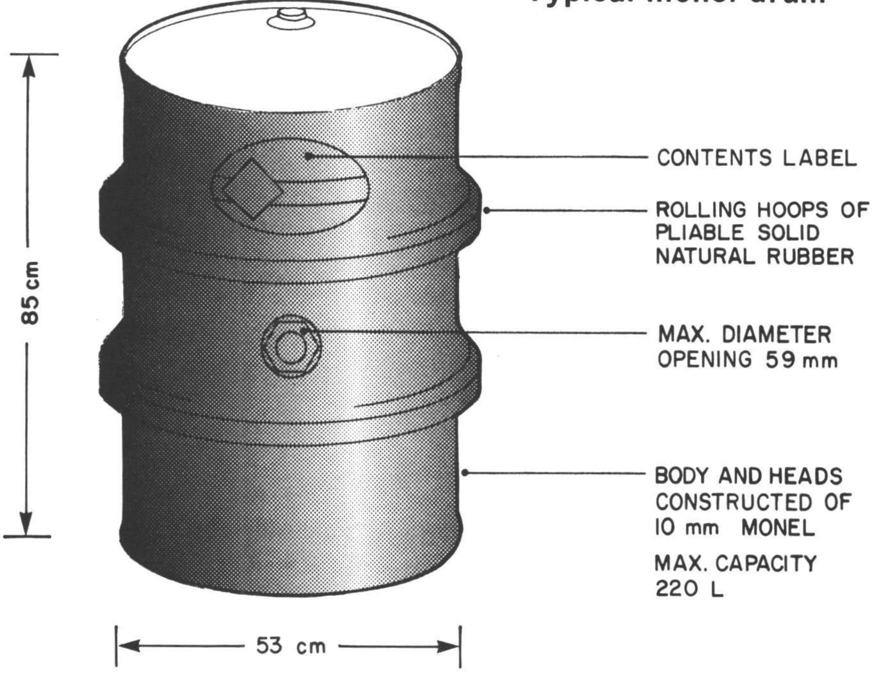
Proceed with top off-loading as follows (MCA 1970):

- Relieve the tank of internal vapour pressure by cooling the tank with water or venting it at short intervals.

FIGURE 8

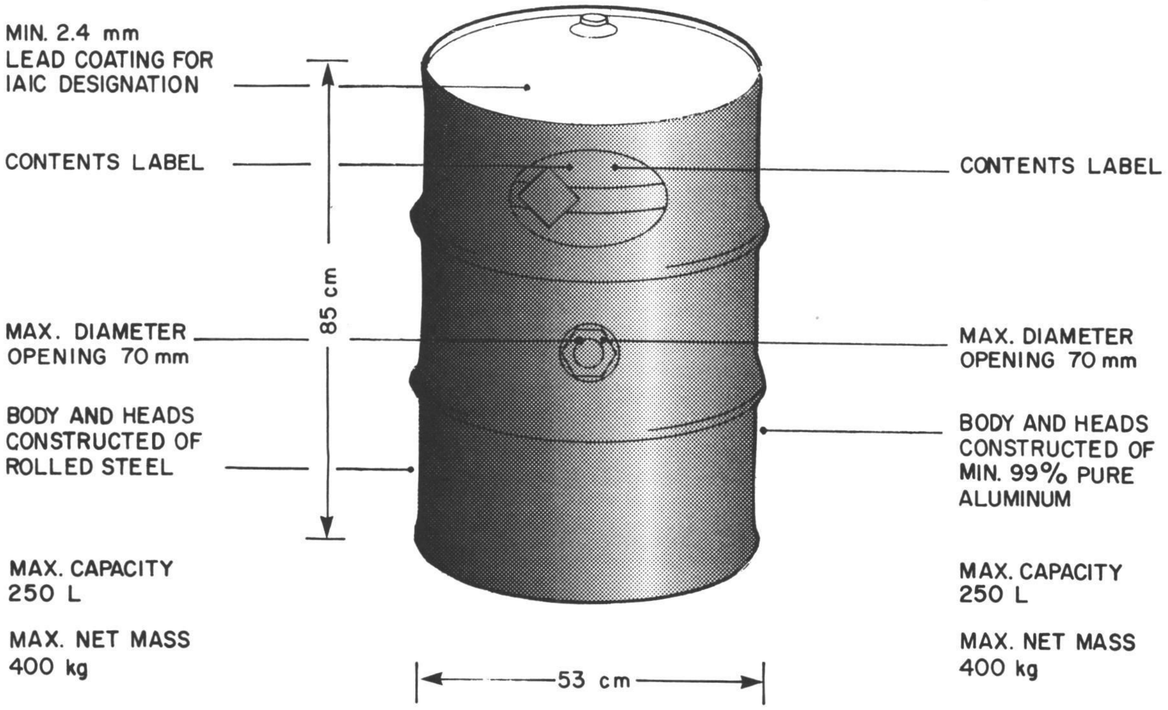
TYPICAL DRUM CONTAINERS

Typical monel drum



Typical steel drum

Typical aluminum drum



- After removing the protective housing from the discharge line at the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only.

Proceed with bottom off-loading in the following manner using gravity flow or pump:

- Relieve internal pressure as previously mentioned.
- After connecting the unloading line to a 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity or pump.

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. It is recognized that other materials may be used for particular applications, as indicated in Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with chlorinated polyether resins are recommended for methanol lines (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. The pipeline should be tested with air at pressures from 345 to 518 kPa (50-75 psi) and all leaks carefully stopped.

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on tank cars; process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Some installations use natural rubber or Viton hose (GF).

Cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (Dow PPS 1972). Viton may be used as a gasket material at normal temperature ranges (DCRG 1978).

A single-suction positive displacement pump with "wet end" material of 316 stainless steel gives good results (ASS). Provision must be made for draining the pump so that repairs can be made safely. The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

4.3 Compatibility with Materials of Construction

The compatibility of methanol with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. 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 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	All	23		ABS (DPPED 1967)	
		60	PVC I PVC II (DPPED 1967)		
		66	PVDC (DCRG 1978)		
		93	PP (DCRG 1978)		
		107	Chlorinated Polyether (DCRG 1978)		
		135	PVDF (DCRG 1978) Brass Copper (Celanese MSDS 1978)		
2. Valves	All	66	Alloy 20 SS 316 (JSSV 1979)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Storage	All	Most	CS CS lined SS 304 (Celanese MSDS 1978)	Aluminum	
4. Others	All	20	SS 302 SS 304 SS 316 SS 430 (ASS)		
		60	PVC (TPS 1978)		
	Technically Pure	40	uPVC, PE PP, POM NR, NBR IIR, EPDM CR, FPM CSM (GF)		
		65	POM, NBR IIR, EPDM CSM (GF)	PE, PP CR (GF)	uPVC, NR FPM (GF)
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978) SBR (GPP)		
	Up to 100%	24 to 100	Glass (CDS 1967)		
	20, 40, 60, 80, 100%	24	Concrete (CDS 1967)		
	100%	24	Wood (CDS 1967)		

TABLE 6 MATERIALS OF CONSTRUCTION

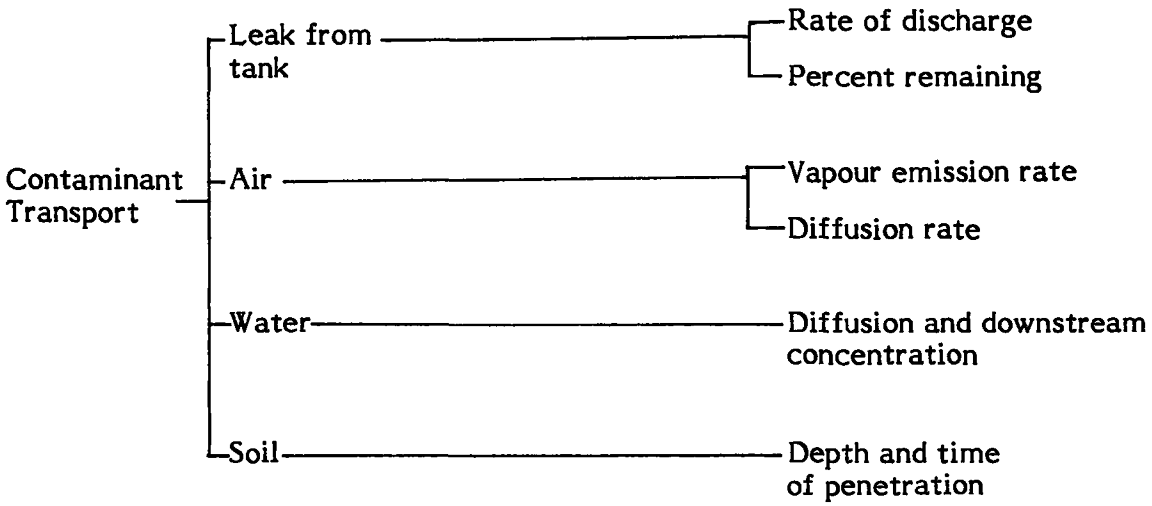
Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Alloy 20
	Aluminum
	Brass
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Copper
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

5.1 General Summary

Methanol is normally transported as a liquid in railway tank cars. When spilled on water, methanol will mix and dissolve on contact. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater may be an environmental concern. Vapour from a spill will be released continuously to the atmosphere.

The following factors are considered for the transport of a spill of methanol in water and on soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Methanol acid is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series 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.

If a tank car loaded with methanol is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the moderate volatility of methanol and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

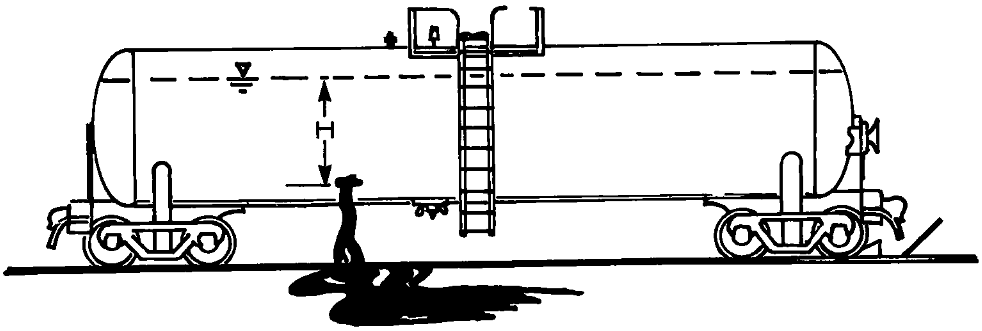


FIGURE 9 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 10: Percent remaining versus time. Figure 10 provides a means of estimating the percent of liquid 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 is assumed to be initially full (at t=0) with a volume of about 80 000 L of methanol. 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.

5.2.2.2 Figure 11: Discharge rate versus time. Figure 11 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

FIGURE 10

METHANOL

PERCENT REMAINING vs TIME

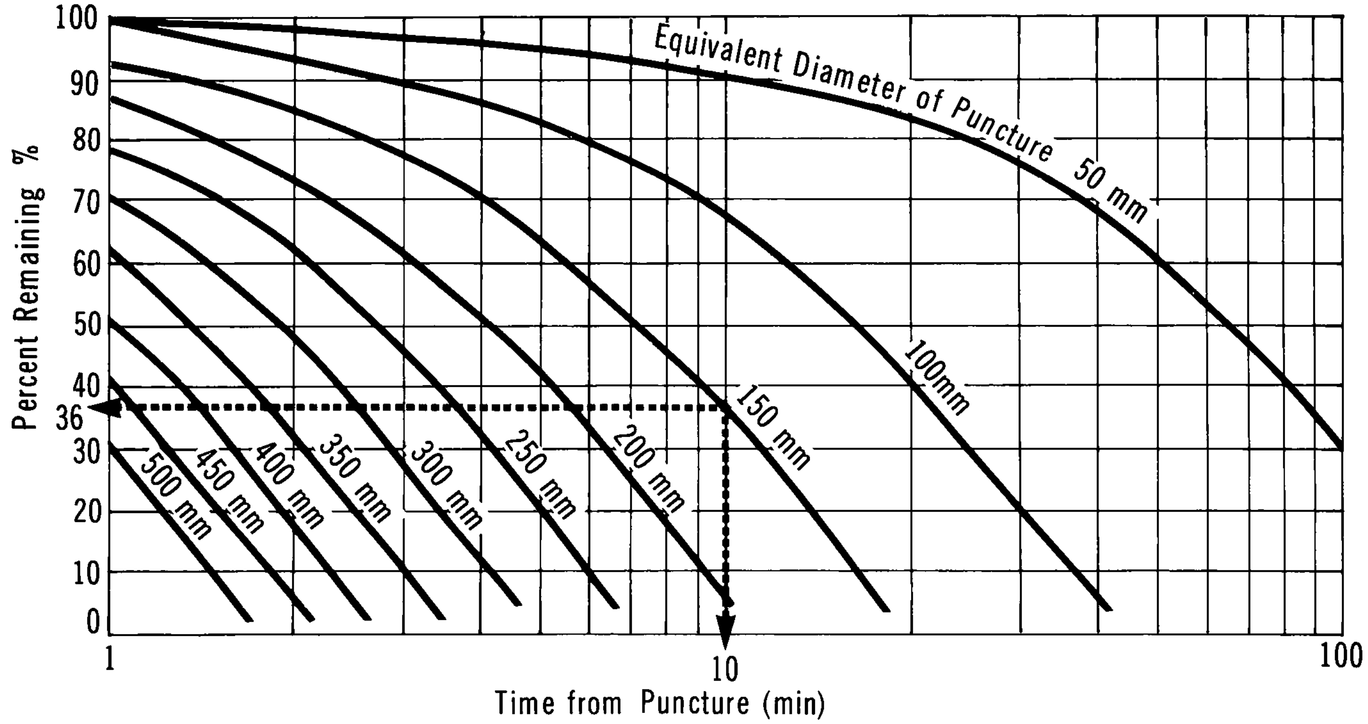
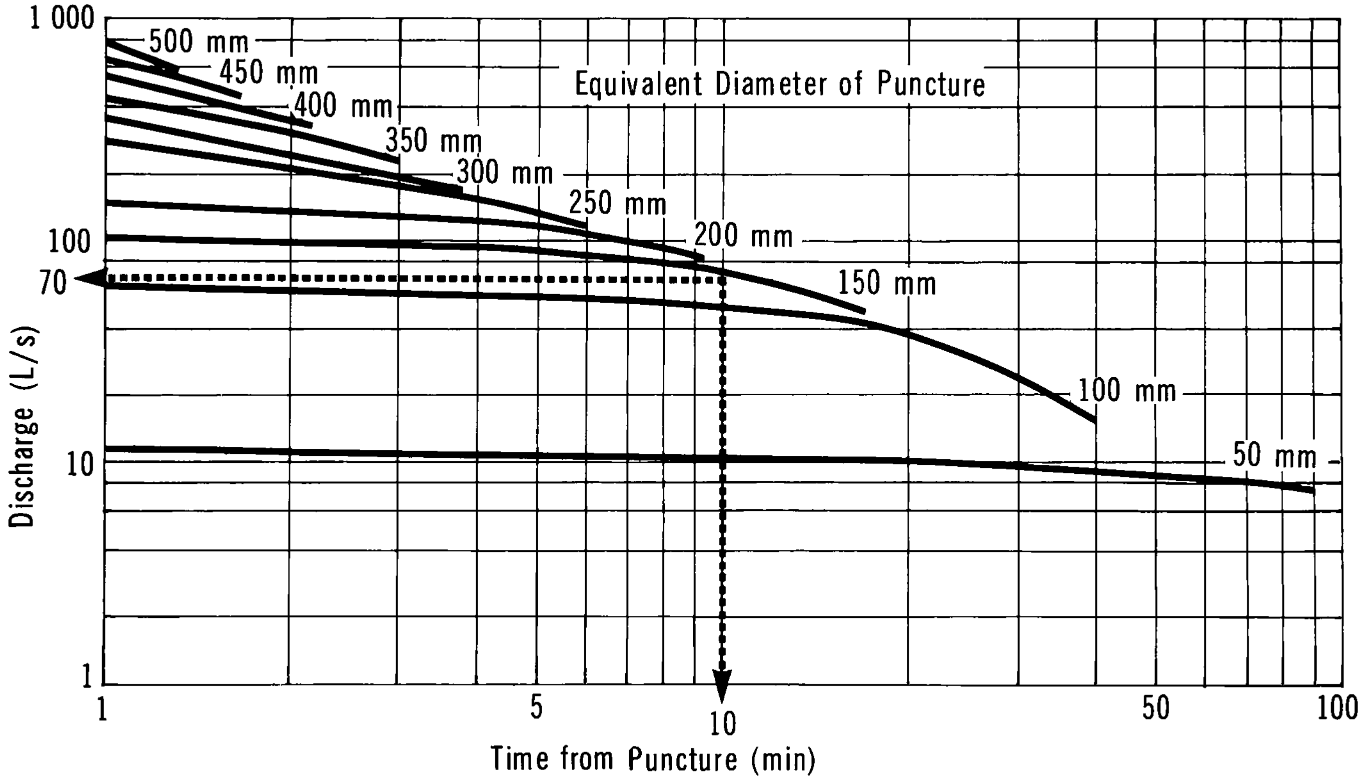


FIGURE 11

METHANOL

DISCHARGE RATE vs TIME



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with methanol solution has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 10
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 11
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since methanol is a moderately volatile liquid, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

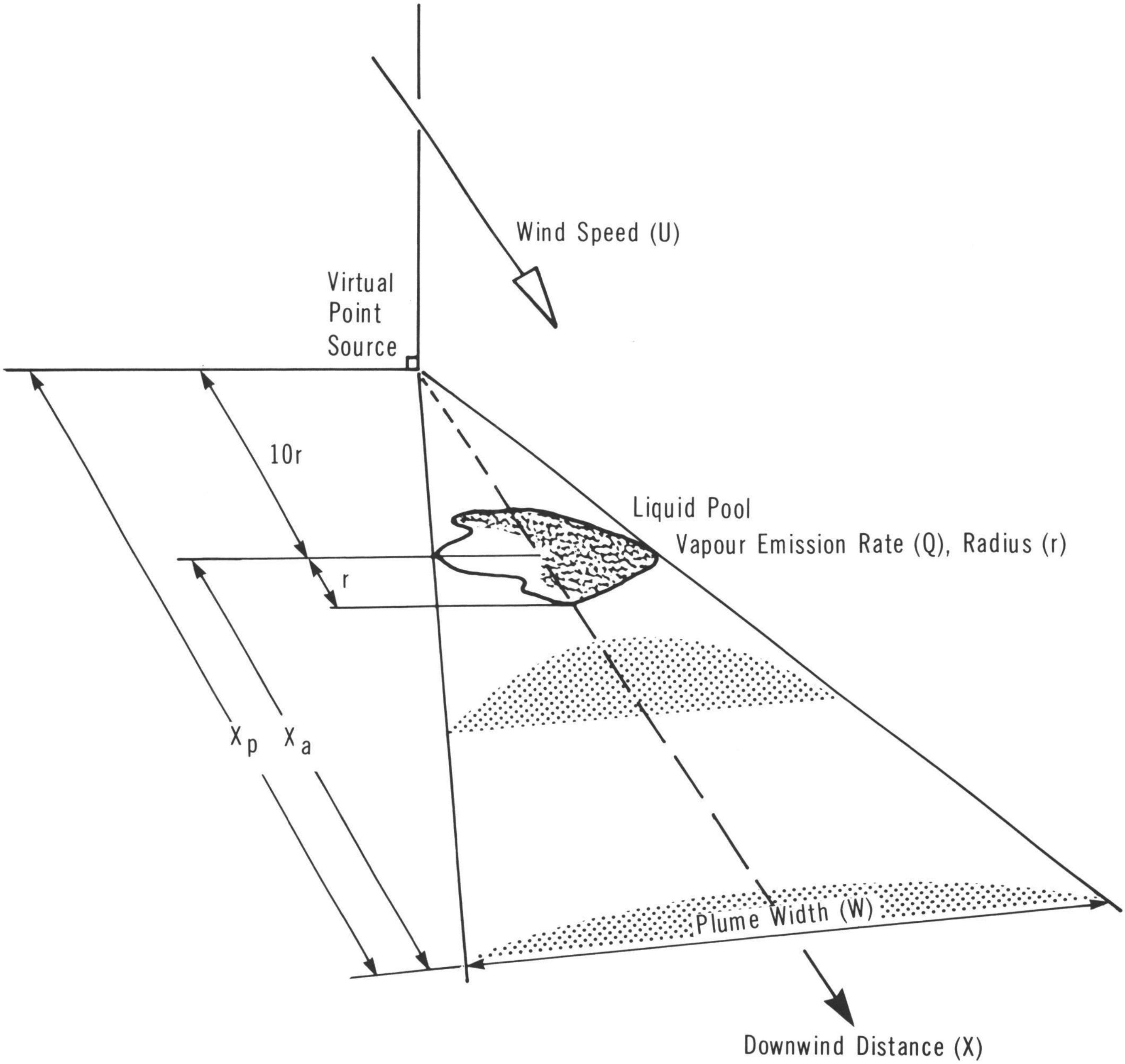
To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely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

Figure 12 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source 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 the toxicity or flammability of a vapour

FIGURE 12

SCHEMATIC OF CONTAMINANT PLUME



cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Figure 14: vapour emission rate from a liquid pool as a function of maximum pool radius

Table 7: weather conditions

Figure 15: normalized vapour concentration as a function of downwind distance and weather conditions

Table 8: maximum plume hazard half-widths

Figure 18: vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 13 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" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 14: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for methanol has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for methanol at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 1.2 g/(m^2s). 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 (Chem. Eng. 1976) of methanol at that temperature. For example, evaporation rates of 0.42 g/(m^2s) at 0°C and 2.1 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s.

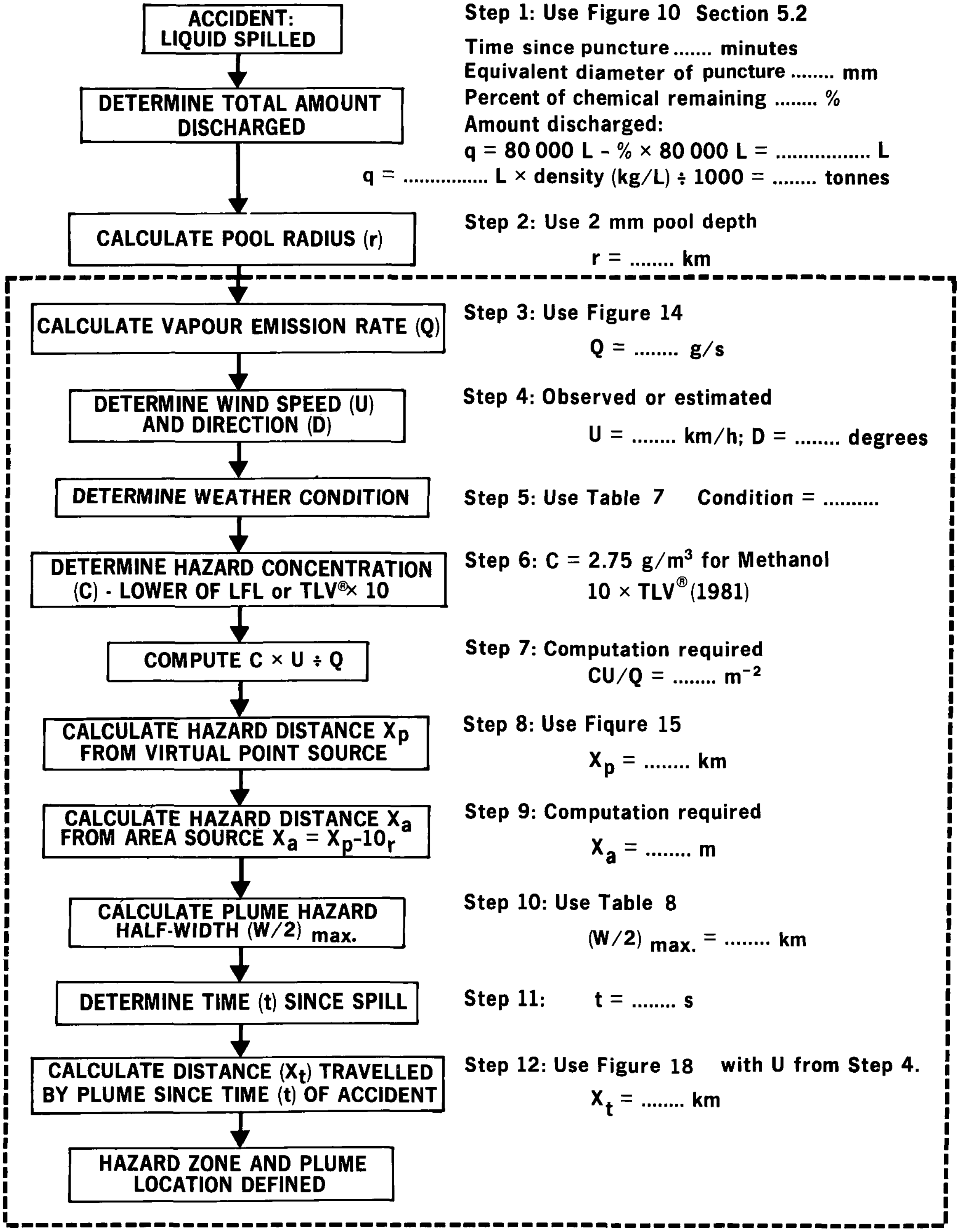
Use: For a pool of methanol of known radius, the rate (Q) at which methanol vapour is released to the atmosphere at a given temperature can then be estimated from Figure 14. The solid portions of the curves represent spills of 0.05 to 63 tonnes, the latter representing about one standard 80 000 L rail car load of methanol. It should be noted that Figure 14 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 methanol 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 the determination of the emission rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was arbitrarily chosen as an intermediate value between that of benzene (a moderately

FIGURF 13

METHANOL

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 10 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) ÷ 1000 = ... tonnes

Step 2: Use 2 mm pool depth

r = ... km

Step 3: Use Figure 14

Q = ... g/s

Step 4: Observed or estimated

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

Step 5: Use Table 7 Condition = ...

Step 6: $C = 2.75\ g/m^3$ for Methanol
10 × TLV® (1981)

Step 7: Computation required

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

Step 8: Use Fiqure 15

X_p = ... km

Step 9: Computation required

X_a = ... m

Step 10: Use Table 8

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

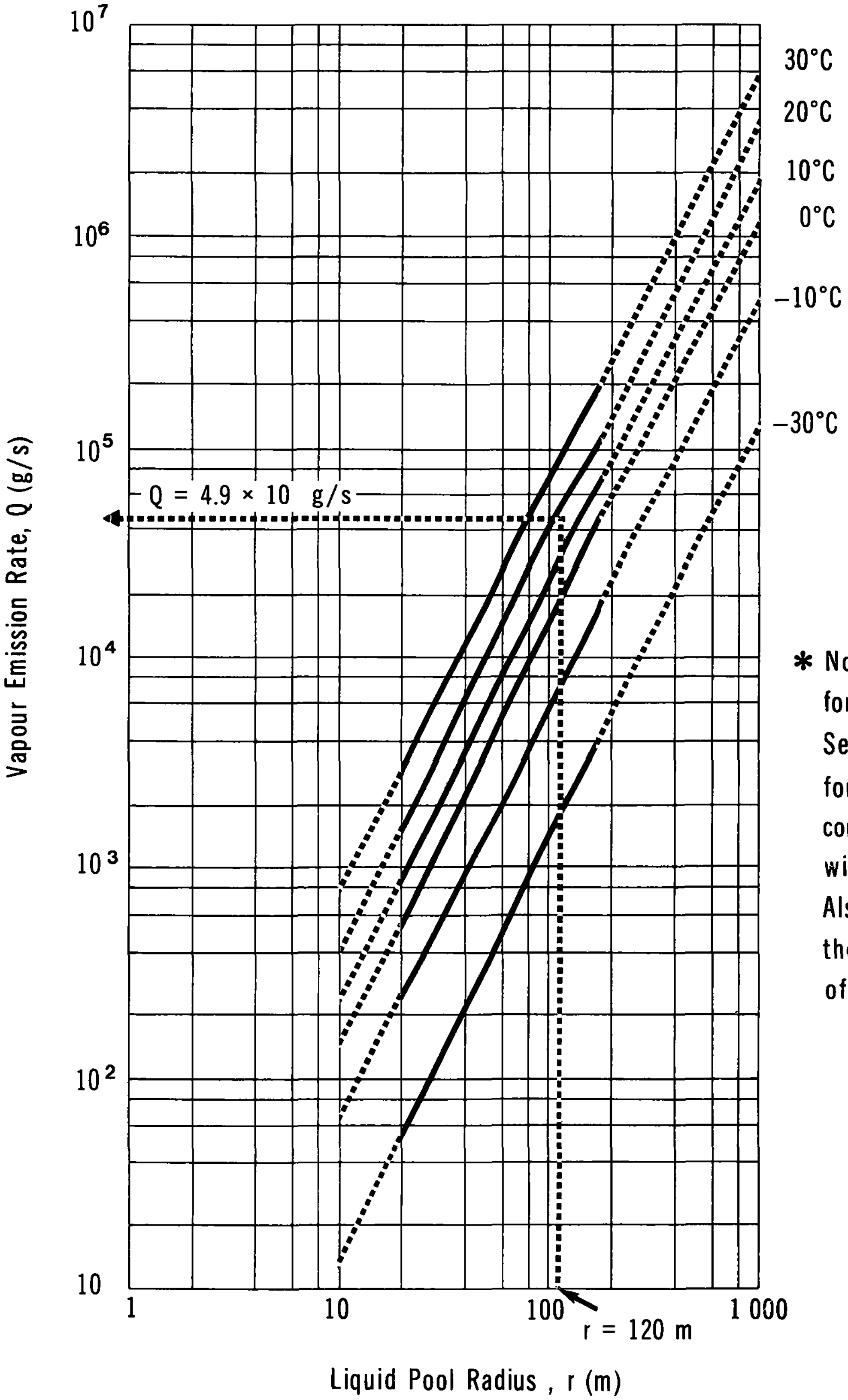
Step 11: t = ... s

Step 12: Use Figure 18 with U from Step 4.

X_t = ... km

FIGURE 14

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 63 tonnes.

volatile liquid) and that of iso-amyl nitrite (a nonvolatile liquid). This model situation was chosen to apply for water-soluble liquids with boiling points above ambient temperature, and to a limited number of water-soluble and water-insoluble organic liquids that are not treated by CHRIS (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 15: Vapour concentration versus downwind distance.** Figure 15 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 15, the weather condition must be determined from Table 7.

TABLE 7 WEATHER CONDITIONS

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

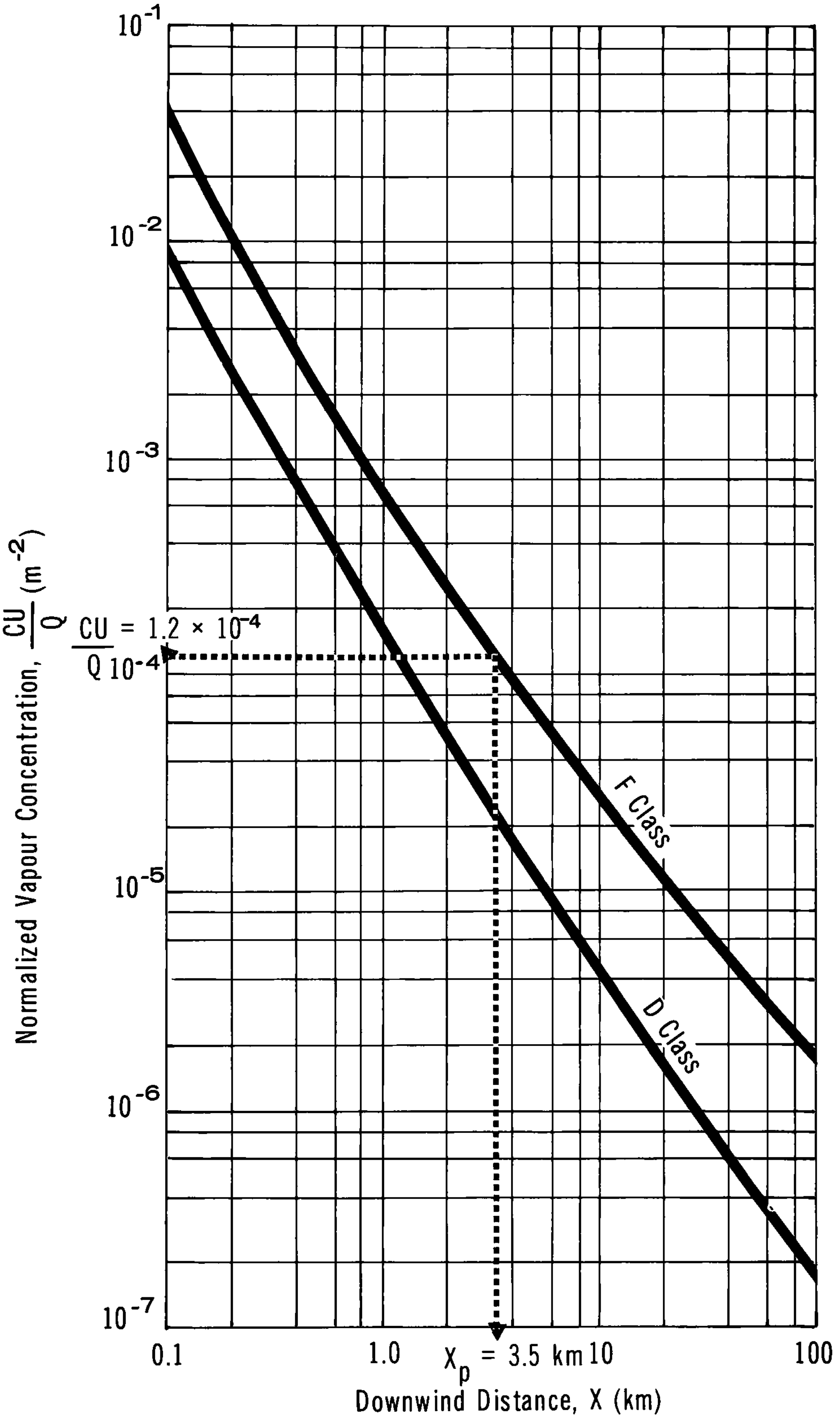
Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 15 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition

FIGURE 15

METHANOL

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV® (in ppm) and the LFL (in percent by volume) to concentrations in g/m^3, use Figures 16 and 17

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health in 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.

5.3.2.3 **Table 8: 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 a value of 10 times the methanol Threshold Limit Value (TLV®) of 0.275 g/m^3, or 2.75 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the methanol vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 8 is therefore only applicable for a methanol hazard concentration limit of 10 x TLV®, or 2.75 g/m^3. 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 75 000 to 17 500 000 g/s, corresponding to methanol spills in the range of about 35 to greater than 8000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 63 400 kg, or approximately 63 tonnes. Therefore, under class D of Table 8, data are provided for up to about 125 times this amount.

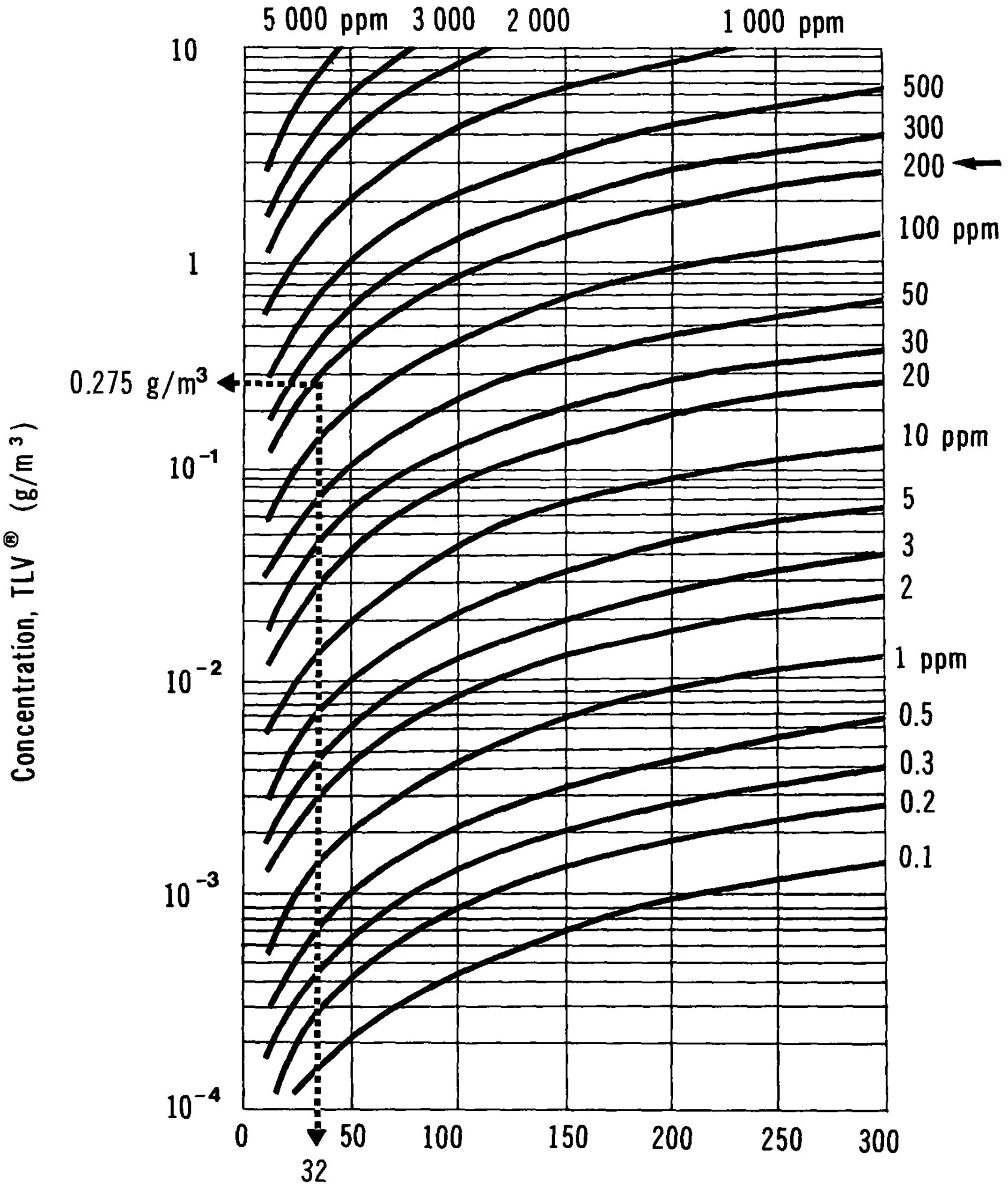
Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 7500 to 1 750 000 g/s, corresponding to methanol spills in the range of about 1 to 5000 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 79 times a standard rail car load.

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 8.

5.3.2.4 **Figure 18: Plume travel time versus travel distance.** Figure 18 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind

FIGURE 16

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



Molecular Weight

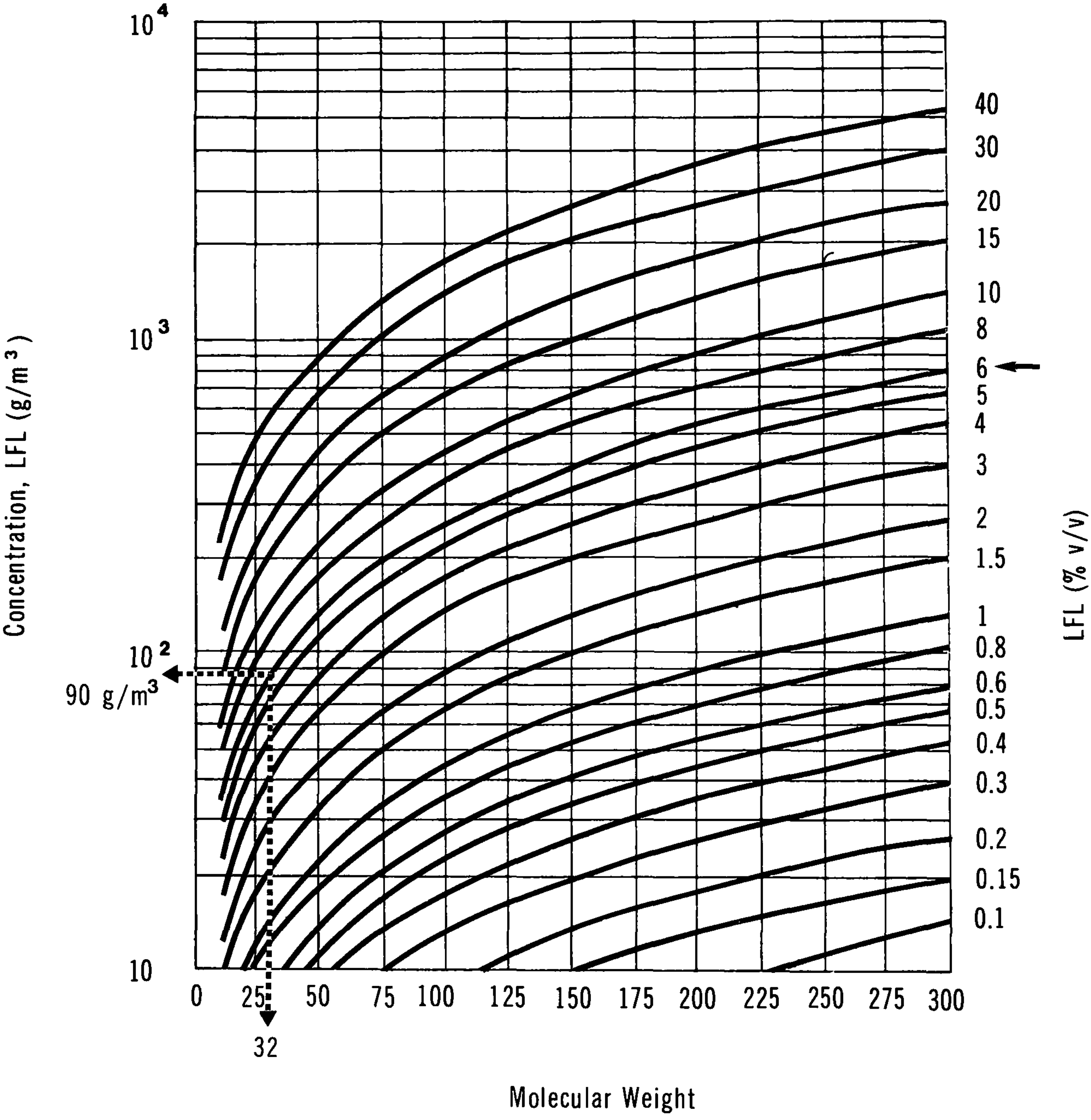
Example: Methanol, MW = 32, TLV® = 200 ppm,
then TLV® in g/m³ = 0.275

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

FIGURE 17

METHANOL

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Methanol, MW = 32, LFL = 6%, then LFL in g/m³ = 90

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

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR METHANOL 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)	
17 500 000	3230	(99.5 km)*	1 750 000	1495	(99.5 km)*
15 000 000	2940		1 500 000	1335	
12 500 000	2625		1 250 000	1165	
10 000 000	2285		1 000 000	985	
7 500 000	1915		750 000	795	
5 000 000	1490		500 000	590	
3 750 000	1245		250 000	350	
2 500 000	970		200 000	305	
2 000 000	845		150 000	255	
1 500 000	710		100 000	195	
1 000 000	560		75 000	165	
750 000	470		50 000	125	
500 000	370	Q/U = 23 330 →	25 000	80	→ $(W/2)_{max}$ = 80 m
250 000	250		10 000	45	
200 000	220		5 000	30	
150 000	185		2 500	20	
100 000	145				
75 000	120				
50 000	95				
25 000	65				
10 000	40				
5 000	30				
2 500	20				

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

Example: A spill releasing methanol vapour at the rate of Q = 4.9×10^4 g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 23 330 g/m, which results in a maximum plume hazard half-width $(W/2)_{max}$ = 80 m.

Note: Above table is valid only for a methanol concentration of 10 x TLV®, or 2.75 g/m^3.

speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

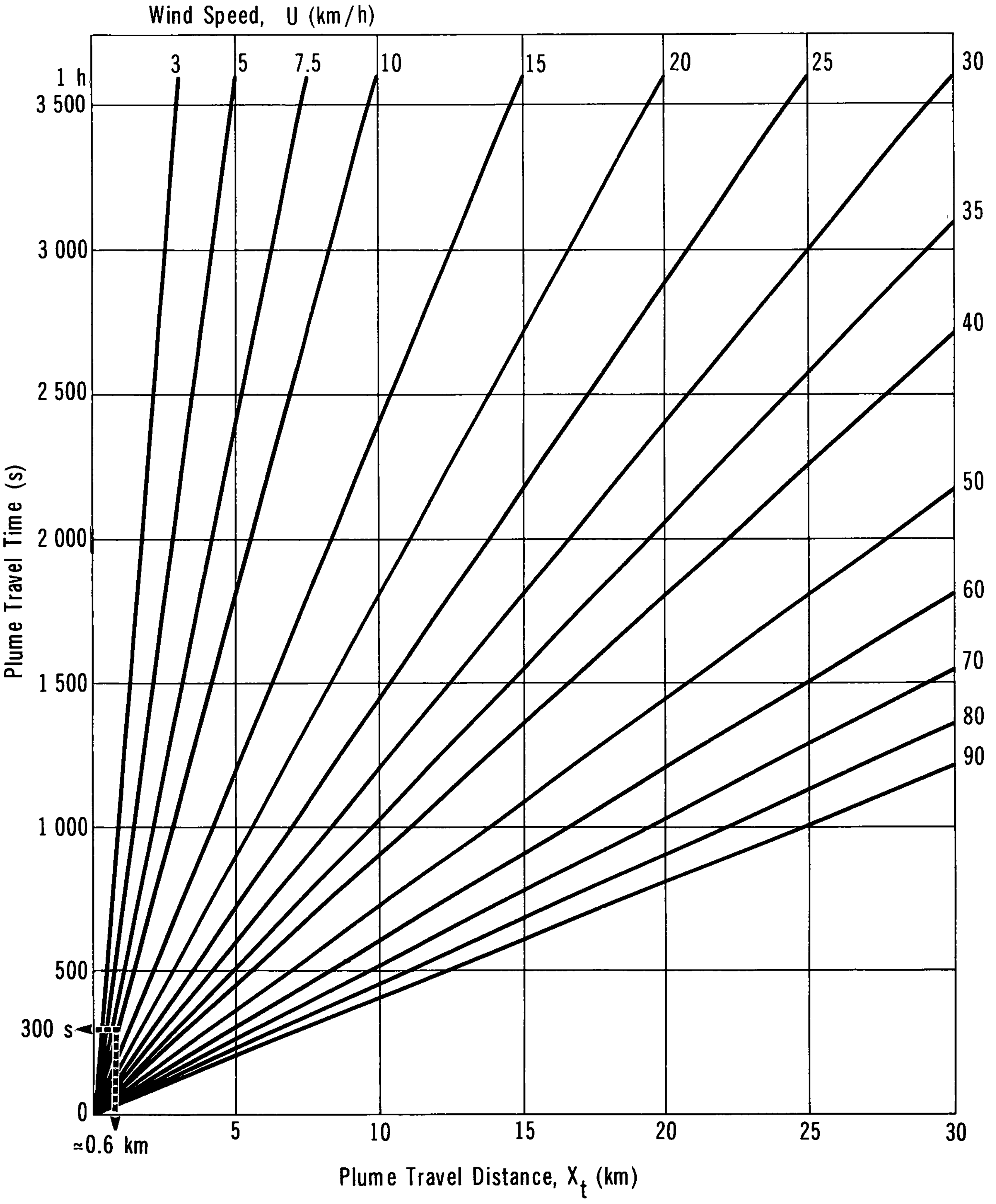
Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the plume has travelled.

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

FIGURE 18

METHANOL

PLUME TRAVEL TIME VS TRAVEL DISTANCE



of liquid methanol. 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 methanol were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind 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 the pool radius (r) for a spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use the maximum radius calculated using a 2 mm spill thickness
- Radius $(r) = 120 \text{ m} \div 1000 = 0.12 \text{ km}$

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

- From Figure 14, for $r = 120$ m and $T = 20°C$, $Q = 4.9 \times 10^4$ g/s

Step 4: Determine the 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 the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL, so for methanol $C = 2.75 \text{ g/m}^3$ (TLV® $= 0.0275 \text{ g/m}^3$; LFL $= 90 \text{ g/m}^3$)

Step 7: Compute CU/Q

- $$CU/Q = \frac{2.75 \times 2.1}{4.9 \times 10^4} = 1.18 \times 10^{-4} \text{ m}^{-2}$$

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

- From Figure 15, with CU/Q = 1.2×10^{-4} m^{-2} and weather condition F, $X_p \approx 3.5$ km

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

- With $X_p = 3.5$ km and r = 0.12 km, then
  $X_a = X_p - 10\ r = 3.5\ km - 10\ (0.12\ km) = 2.3\ km$

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

- Use Table 8
- With Q = 4.9×10^4 g/s and U = 2.1 m/s

  $$\text{then } Q/U = \frac{4.9 \times 10^4}{2.1} = 23\ 330\ g/m$$

- Then for weather condition F, the closest Q/U value is 25 000 g/m, which gives $(W/2)_{max} \approx 80$ m

Step 11: Determine the time since the spill

- t = 5 min x 60 = 300 s

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

- Using Figure 18, with t = 300 s and U = 7.5 km/h, then $X_t = 0.6$ km (more accurately from Ut = 2.1 m/s x 300 s = 630 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 (80 m) by the maximum hazard distance downwind of the area source (2.3 km) along the direction of the wind, as shown in Figure 19
- If the wind is reported to be fluctuating by 20°C about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 20
- 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 13 minutes before the plume reaches the maximum downwind hazard distance of 2.3 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, methanol will dissolve on contact, allowing the spill to be diluted. This mixing can generally be described by

FIGURE 19

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

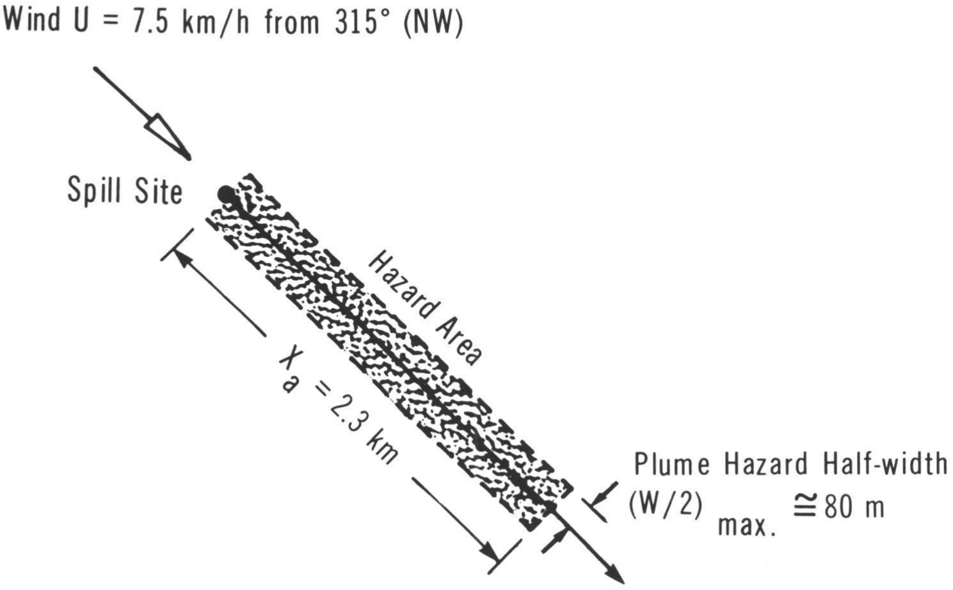
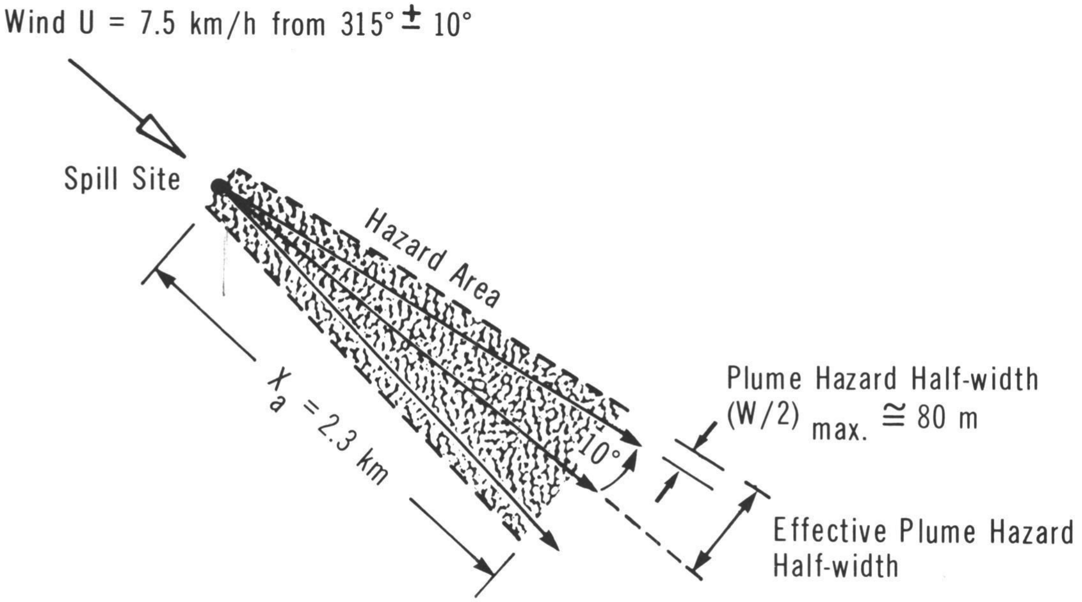


FIGURE 20

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



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

$= 2.3 \times 1\,000 \times \tan 10° + 80$ m

= 485 m

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. 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 assumes a Manning's roughness coefficient of 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.

5.4.2 **Nomograms.** The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water):

Non-tidal Rivers

Figure 22: time versus distance for a range of average stream velocities

Figure 23: hydraulic radius versus channel width for a range of stream depths

Figure 24: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 25: alpha* versus diffusion coefficient for various time intervals

Figure 26: alpha versus delta* for a range of spill sizes

Figure 27: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 28: volume versus radius for the hazard zone for a range of lake depths

Figure 29: average concentrations versus volume for the hazard zone for a range of spill sizes

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

The flowchart in Figure 21 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figure 22 through 29) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 22: Time versus distance. Figure 22 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 22.

Figure 23: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration 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 the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 23 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 24: Diffusion coefficient versus hydraulic radius. Figure 24 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 23 and the average stream velocity (U).

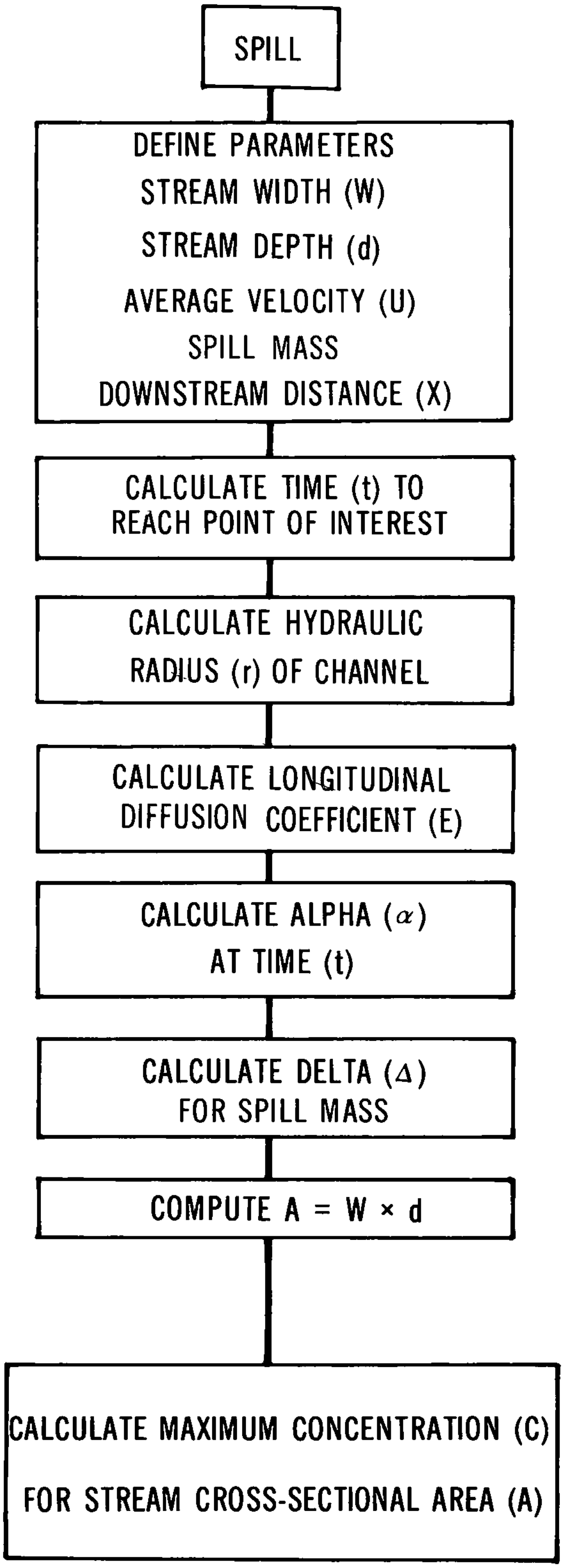
Figure 25: Alpha versus diffusion coefficient. Figure 25 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 26: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 26 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 27: Maximum concentration versus delta. Figure 27 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 from Figure 27 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

FIGURE 21

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 22

t = ________ minutes

Step 3: Use Figure 23

r = ________ m

Step 4: Use Figure 24

E = ________ m^2/s

Step 5: Use Figure 25

α = ________

Step 6: Use Figure 26

Δ = ________

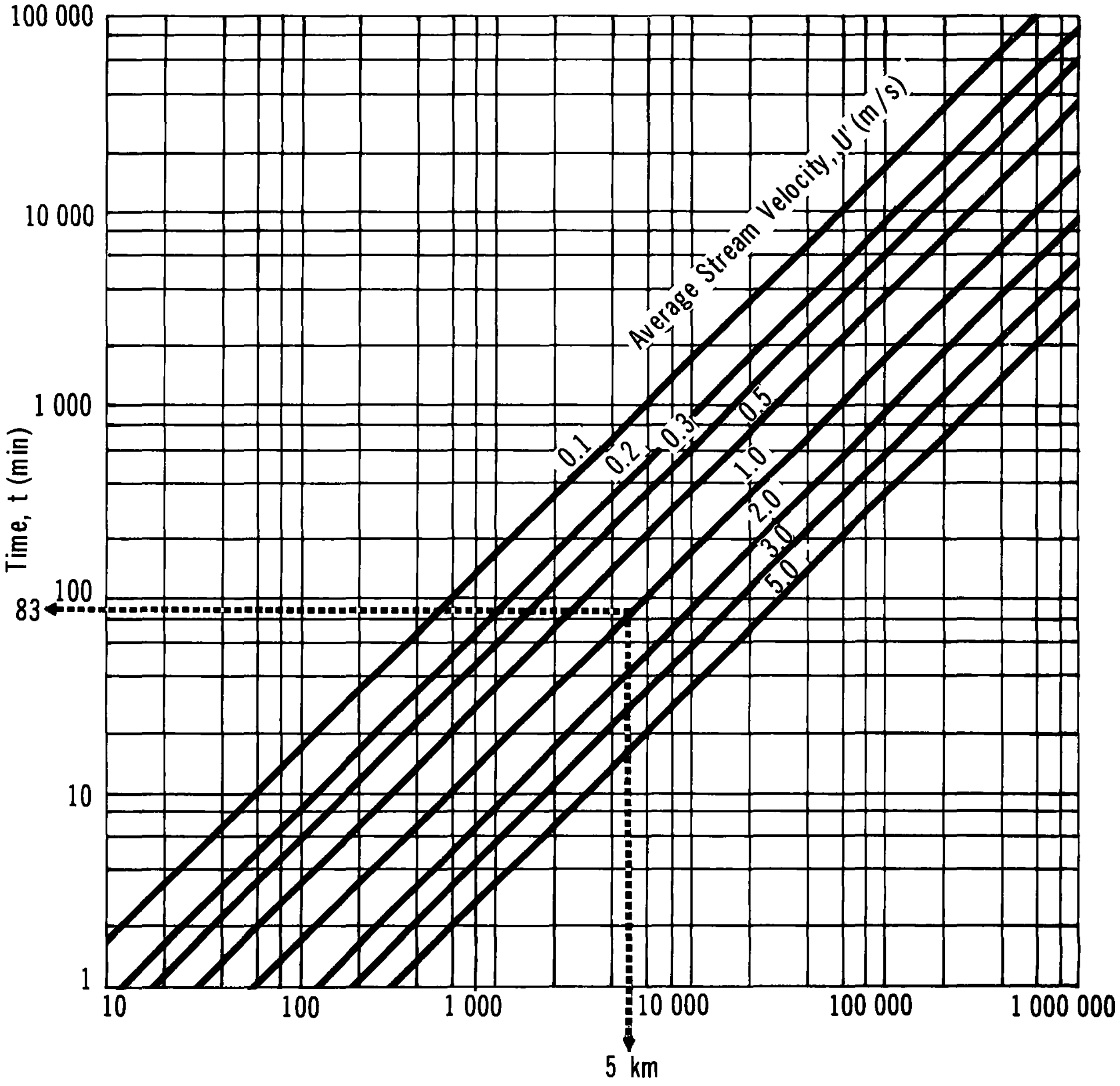
Step 7: Compute stream cross-sectional Area (A)

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

Step 8: Use Figure 27

C = ________ ppm

TIME vs DISTANCE



Distance, X (m)

FIGURE 23

HYDRAULIC RADIUS VS CHANNEL WIDTH

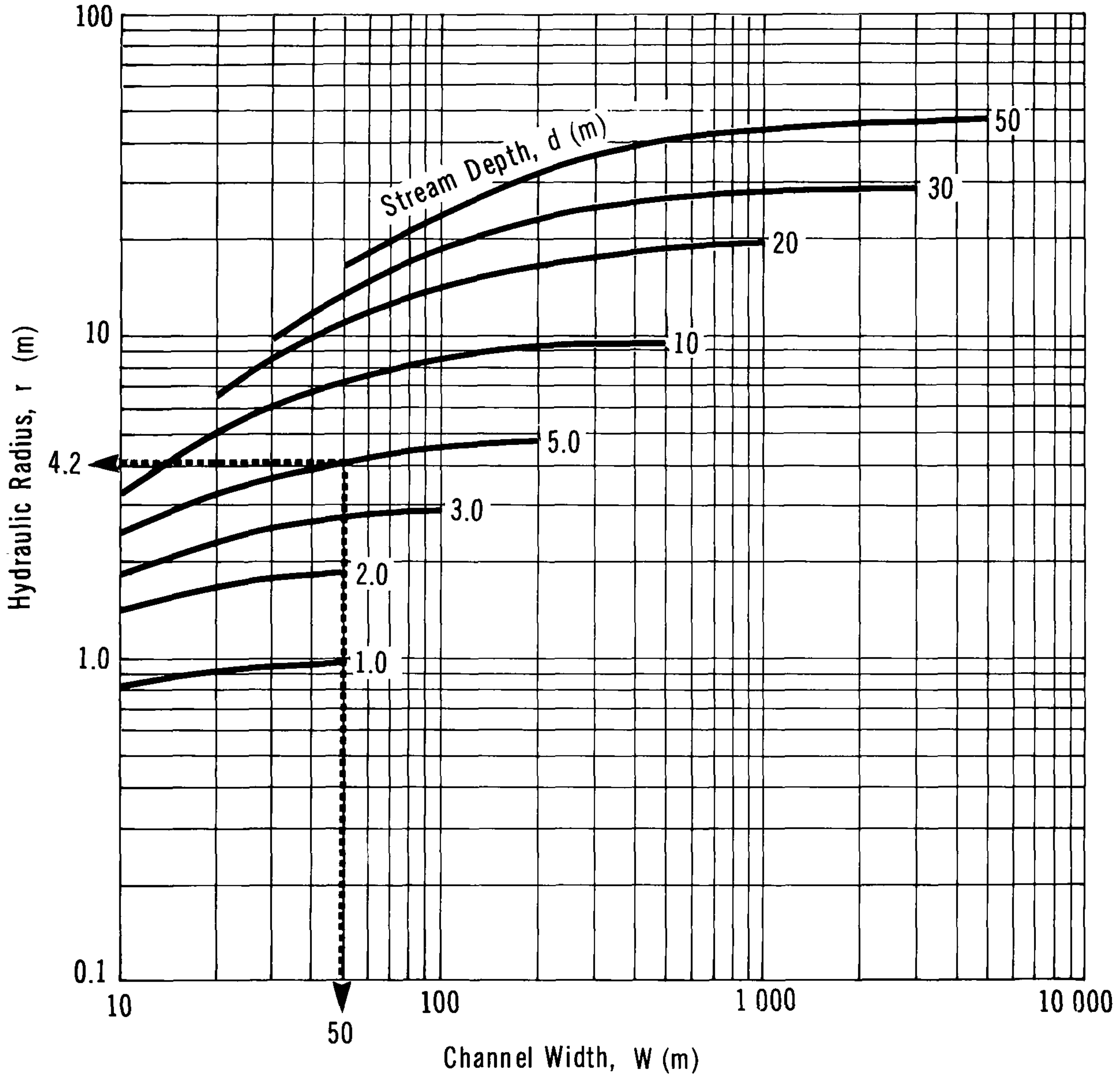


FIGURE 24

METHANOL

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

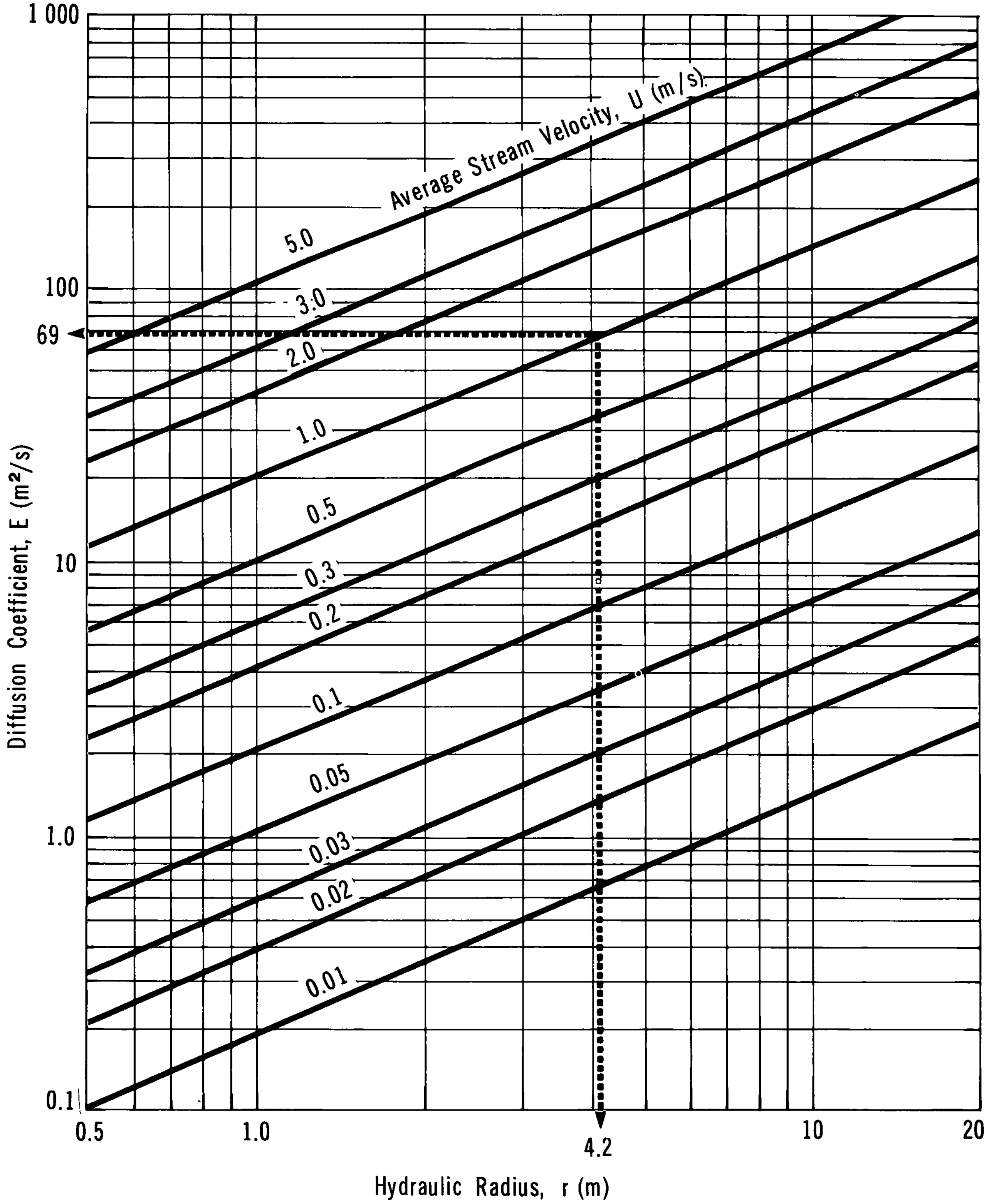
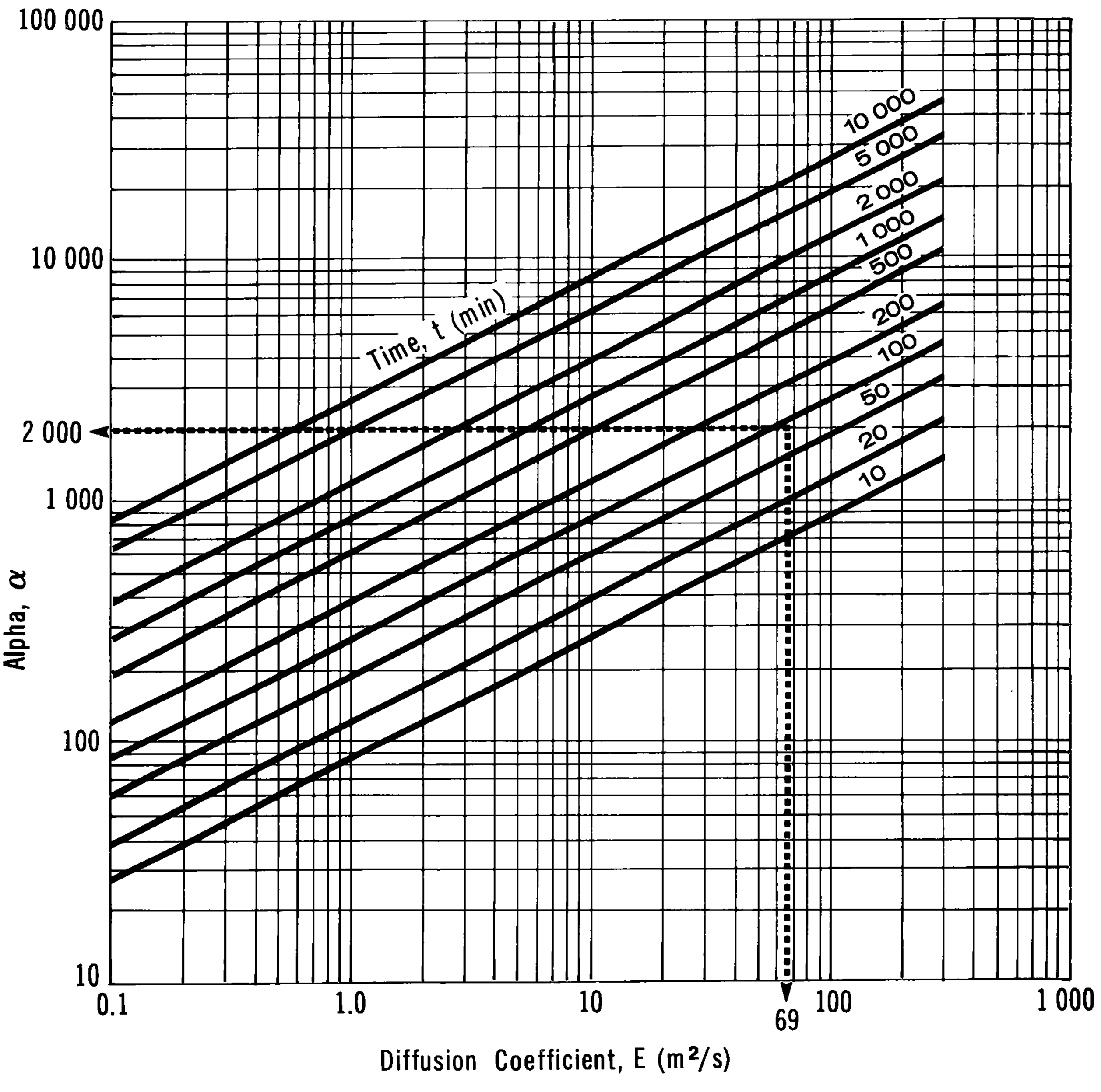


FIGURE 25

METHANOL

ALPHA vs DIFFUSION COEFFICIENT



ALPHA vs DELTA

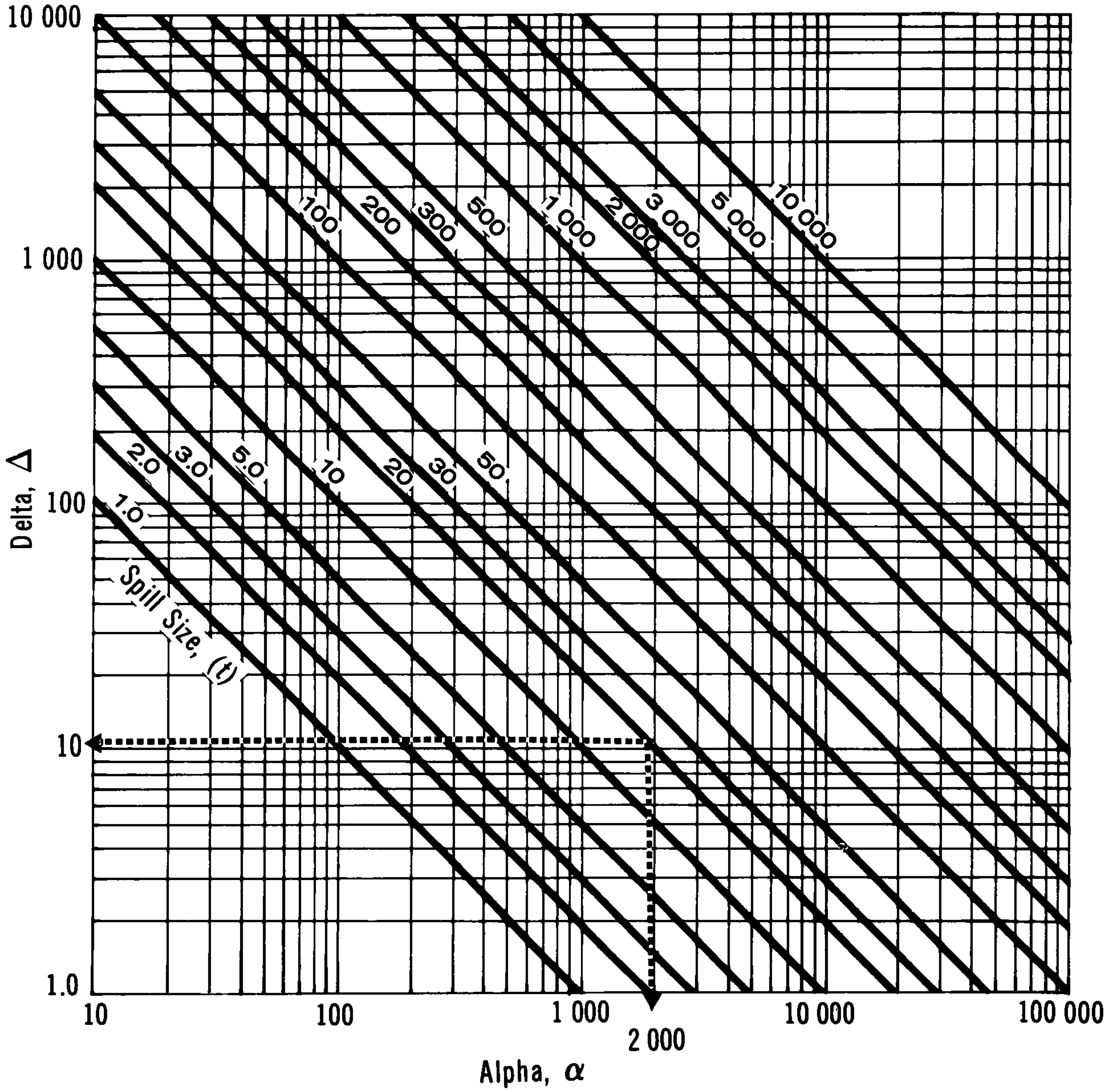
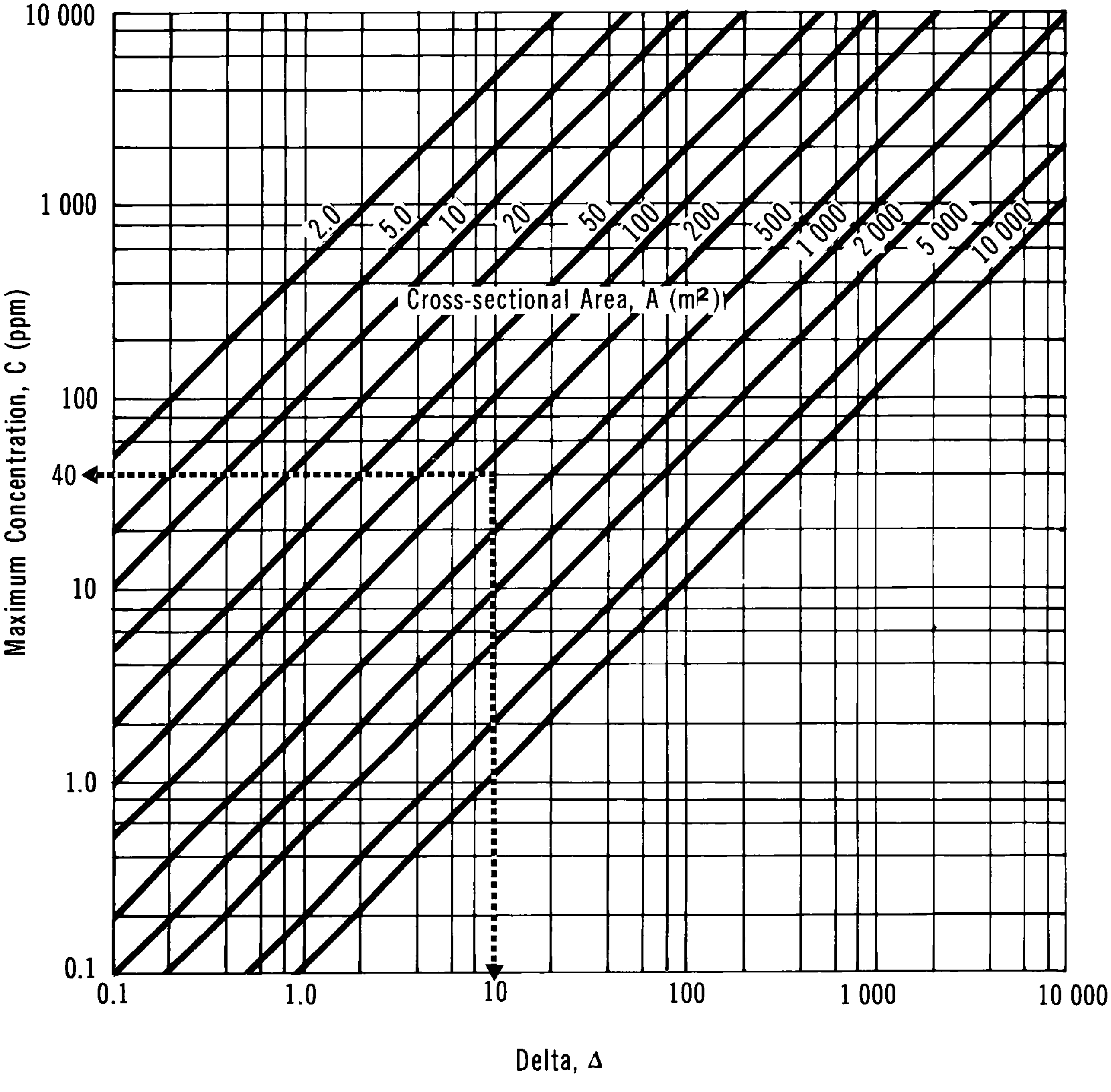


FIGURE 27

METHANOL

MAXIMUM CONCENTRATION vs DELTA



5.4.2.2 Nomograms for lakes or still water bodies.

Figure 28: 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 28. The radius (r) represents the distance from the spill to the point of interest.

Figure 29: 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 29 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.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of methanol 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
- spill mass = 20 tonnes of methanol

Step 2: Calculate the time to reach the point of interest

- Use Figure 22
- With $X = 5000$ m and $U = 1$ m/s, $t = 83$ min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 23
- With $W = 50$ m and $d = 5$ m, $r = 4.2$ m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 24
- With $r = 4.2$ m and $U = 1$ m/s, $E = 69$ m^2/s

FIGURE 28

METHANOL

VOLUME vs RADIUS

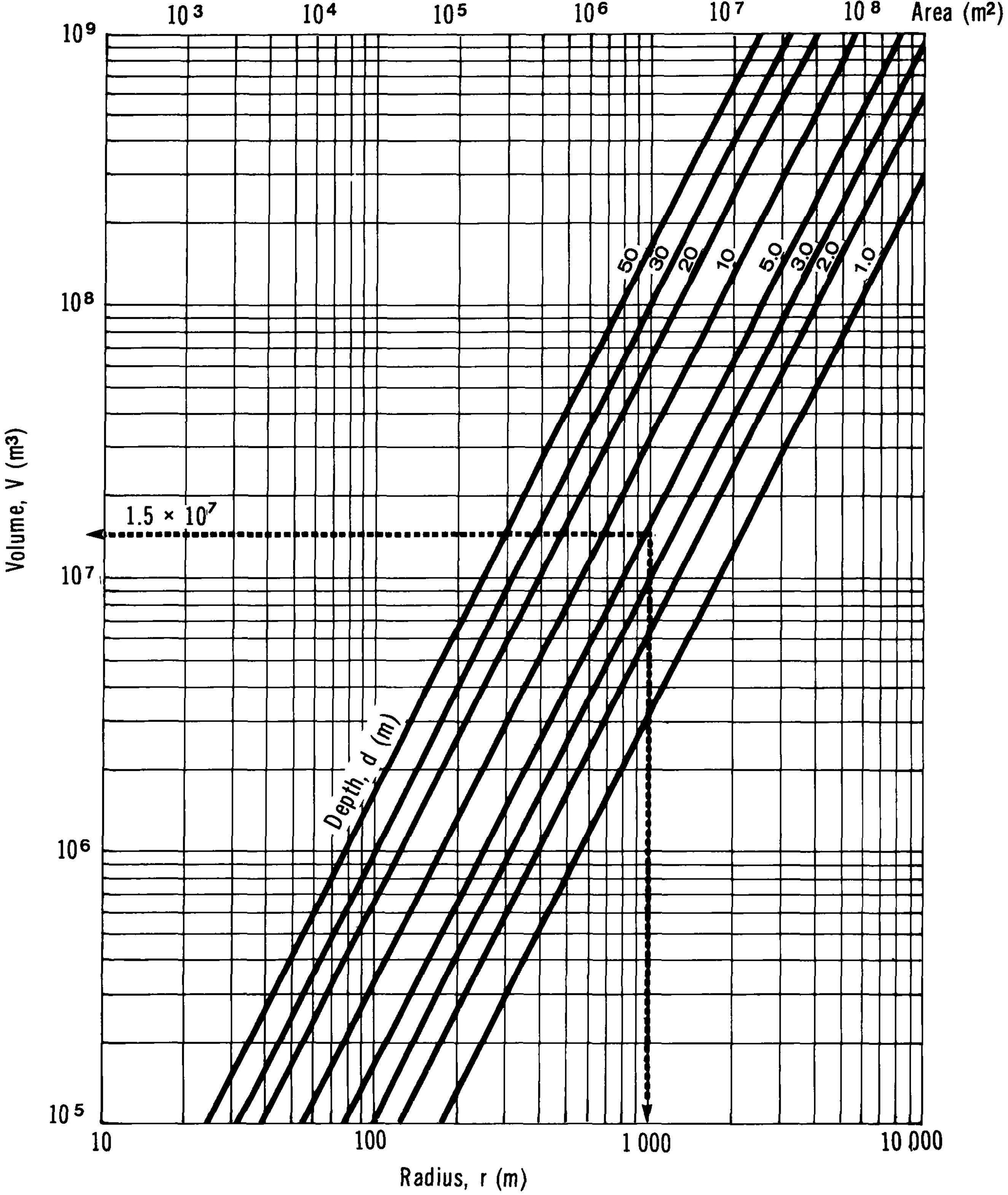
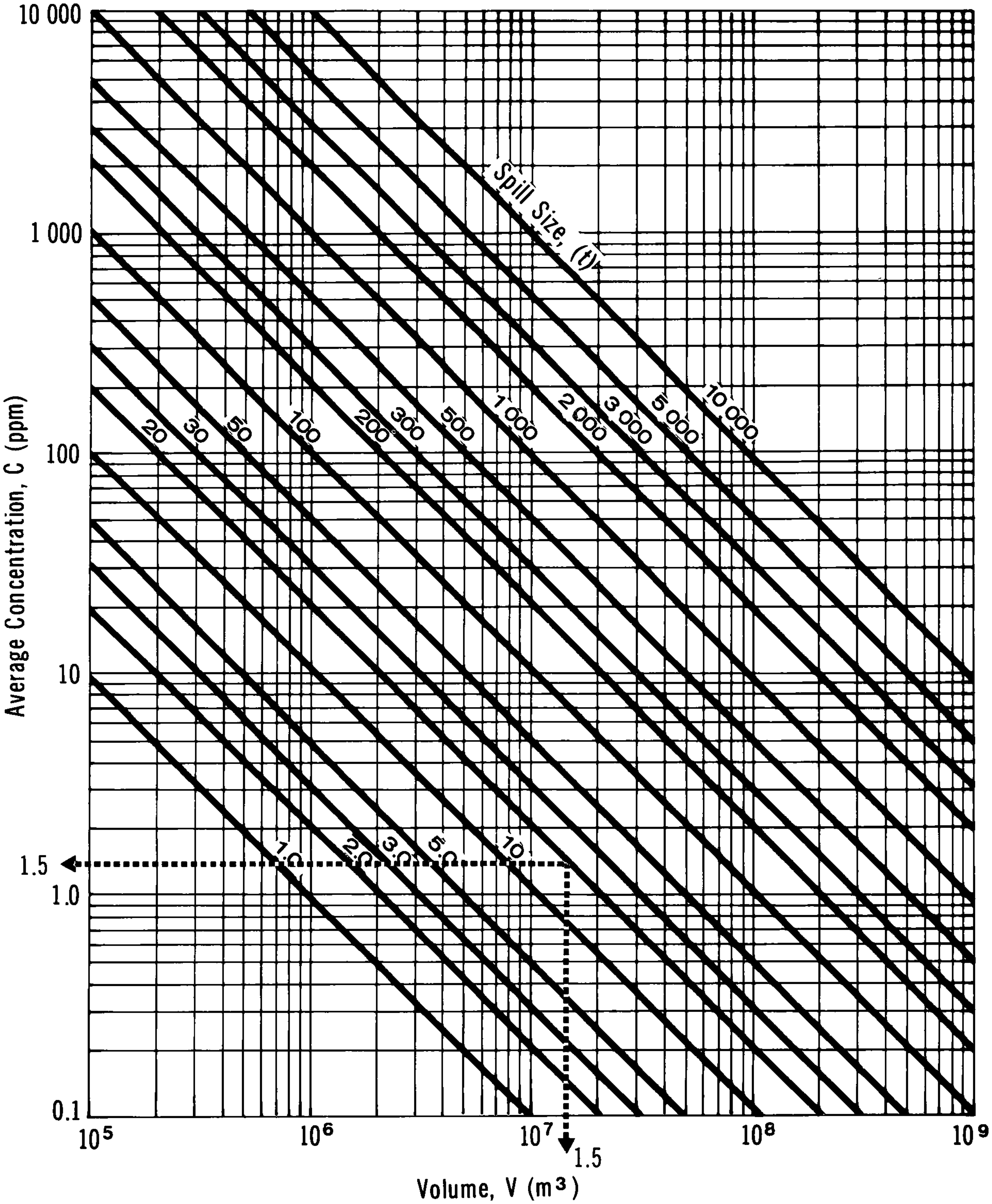


FIGURE 29

METHANOL

AVERAGE CONCENTRATION vs VOLUME



Step 5: Calculate alpha (α)

- Use Figure 25
- With E = 69 m^2/s and t = 83 min, α = 2000

Step 6: Calculate delta (Δ)

- Use Figure 26
- With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10

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

- A = W x d = 50 x 5 = 250 m^2

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

- Use Figure 27
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.3.2 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of methanol 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 mass = 20 tonnes

Step 2: Determine the volume of water available for dilution

- Use Figure 28
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 29
- With V = 1.5 x 107 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 **Mechanisms.** The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of methanol onto soil and its transport downward through the soil are presented here.

Methanol mixes readily with water and, if spilled onto soil, will infiltrate rapidly. Precipitation falling at the time of a spill or water used to flush the site will dilute the infiltrating fluid. Significant evaporation will occur from spills of high-purity methanol.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled methanol will run off and/or evaporate. For this work, the soils have been assumed to be at field capacity. 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 methanol will continue to evaporate. However, significant amounts are expected to remain for transport down toward the groundwater table. The analysis used here neglects evaporation. Upon reaching the groundwater table, the methanol will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and diffusion serving to reduce the concentrations. This is shown schematically in Figure 30.

5.5.2 Equations Describing Methanol 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 Methanol in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

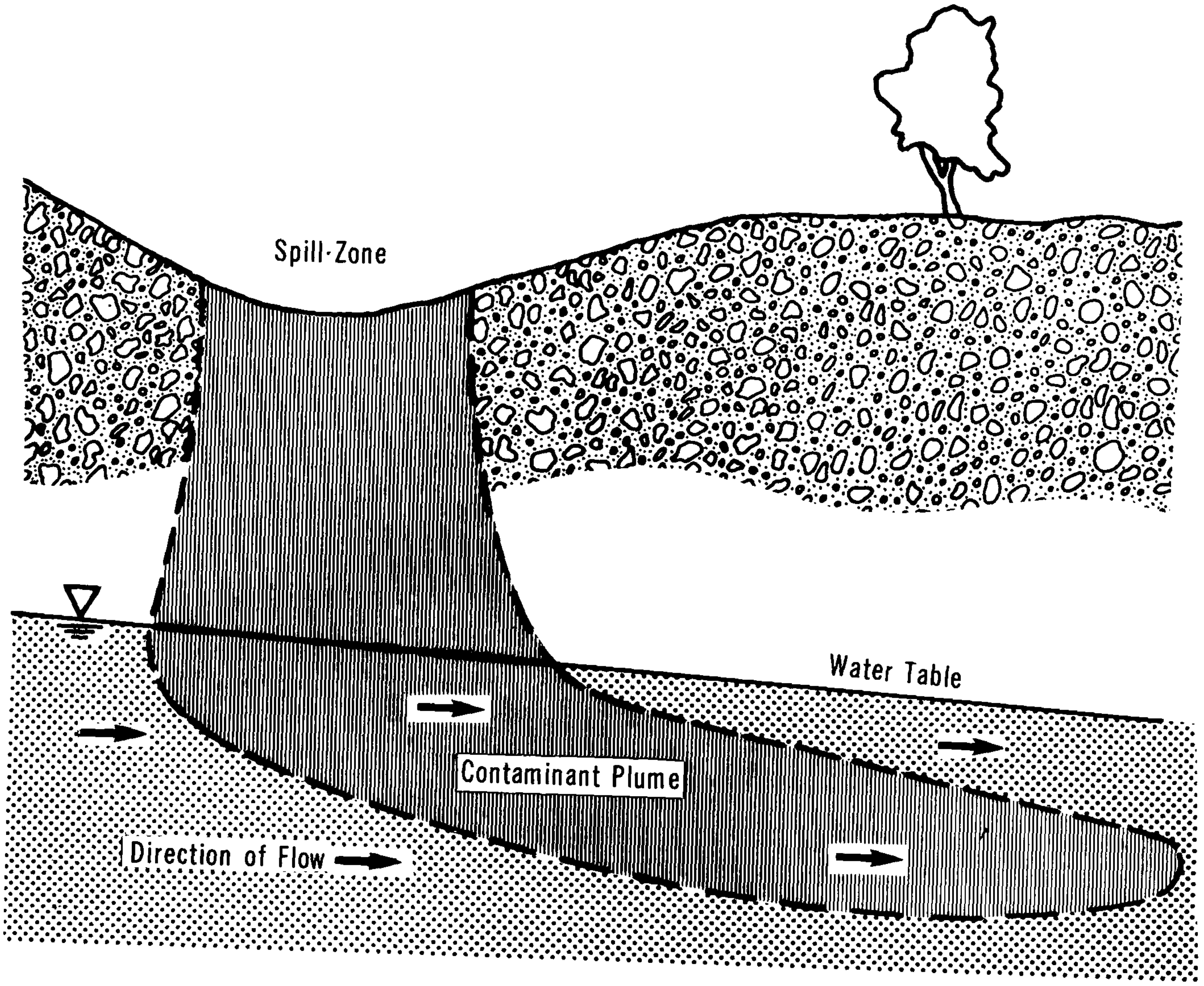
$$K_o = \frac{(\rho g)k}{\mu}$$

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 pure and 30 percent by weight methanol, and water. The water calculations represent the extreme as methanol is diluted. The appropriate properties of methanol are in the following chart.

FIGURE 30

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

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

–Field Capacity (θ_{fc}) = 0.075

Property	Pure Methanol		30% Methanol	Water
	20°C	4°C	(20°C)	(20°C)
Mass density (ρ), kg/m^3	791	795	951	998
Absolute viscosity (μ), Pa•s	0.65 x 10^3	0.75 x 10^{-3}	1.8 x 10^{-3}	1.0 x 10^{-3}
Saturated hydraulic conductivity (K_o), m/s	(1.19x10^7)k	(1.04x10^7)k	(0.52x10^7)k	(0.98x10^7)k

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

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 methanol 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 31. The nomograms are presented as Figures 32, 33, and 34. 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 methanol becomes diluted with water.

5.5.6 **Sample Calculation.** A 20 tonne spill of methanol has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 10 minutes after the spill.

FIGURE 31

FLOWCHART FOR NOMOGRAM USE

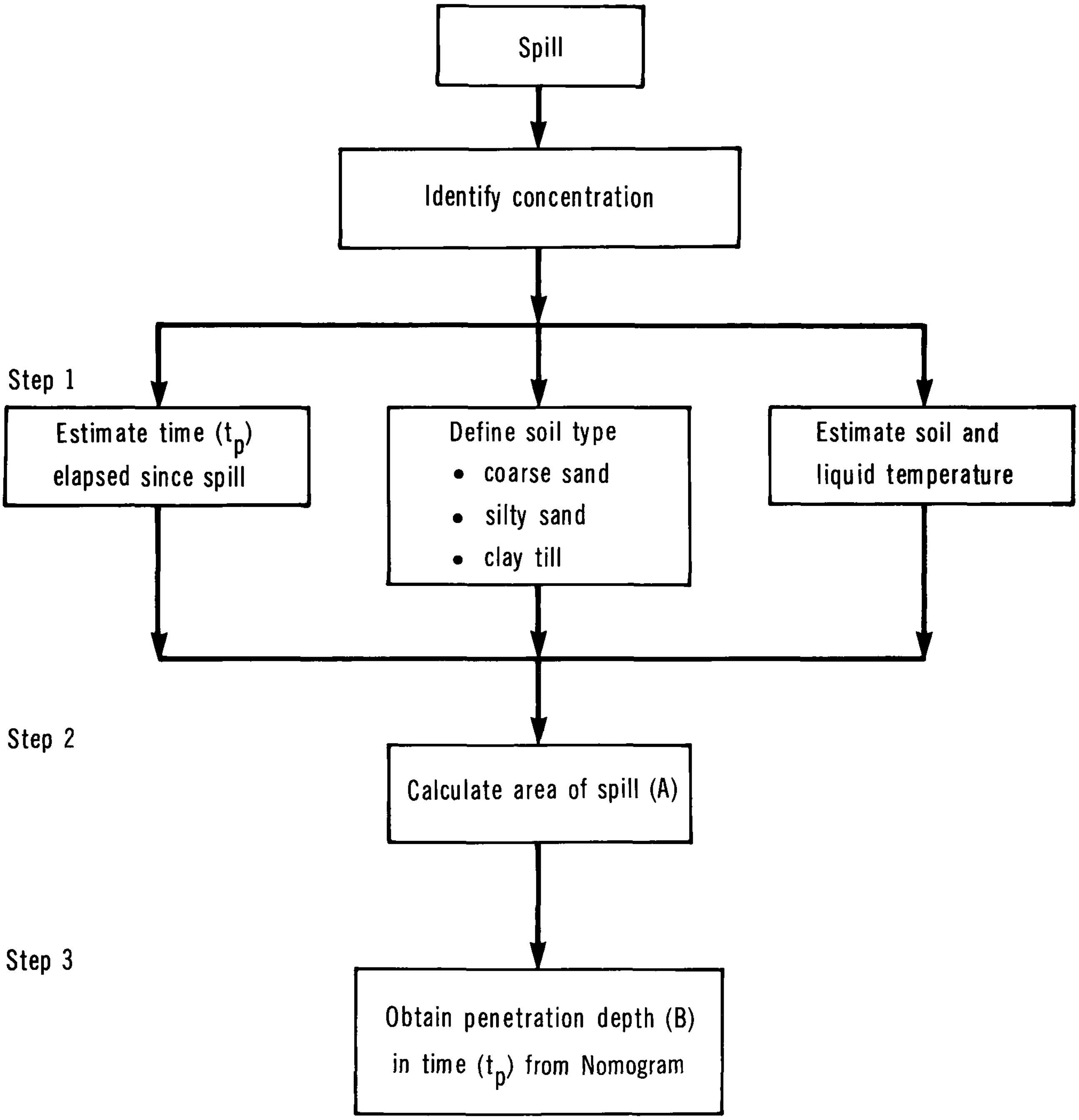
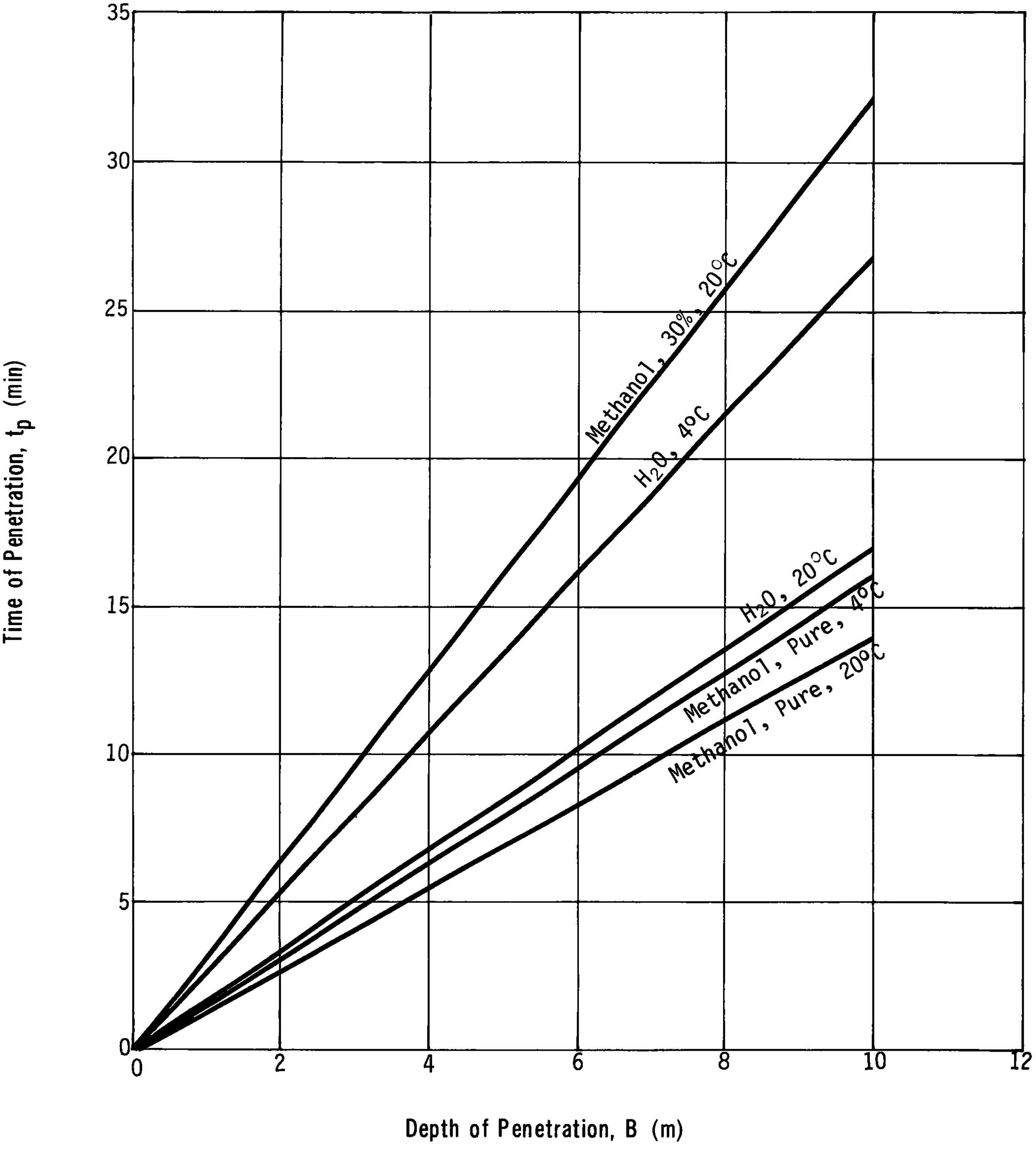


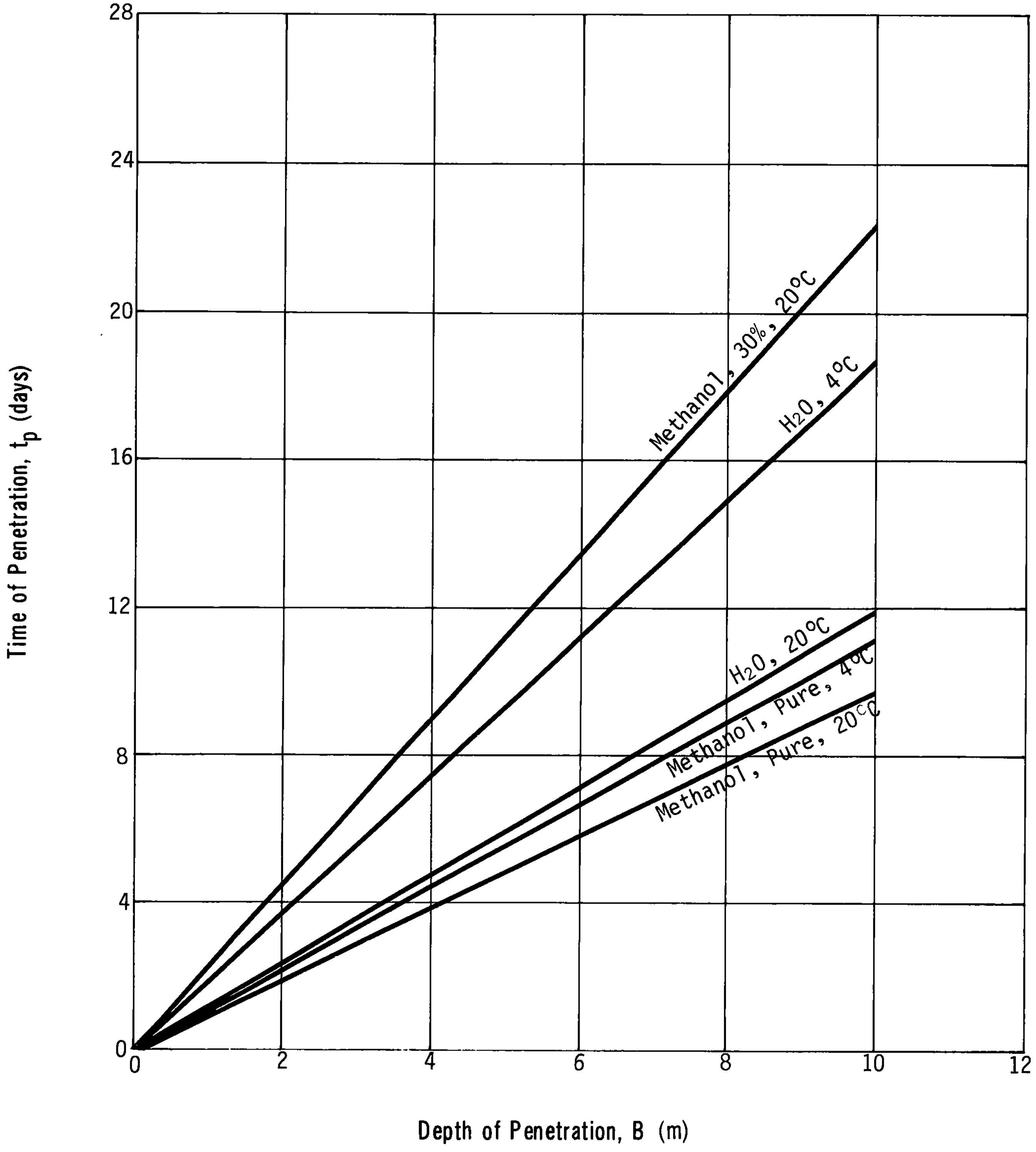
FIGURE 32

METHANOL

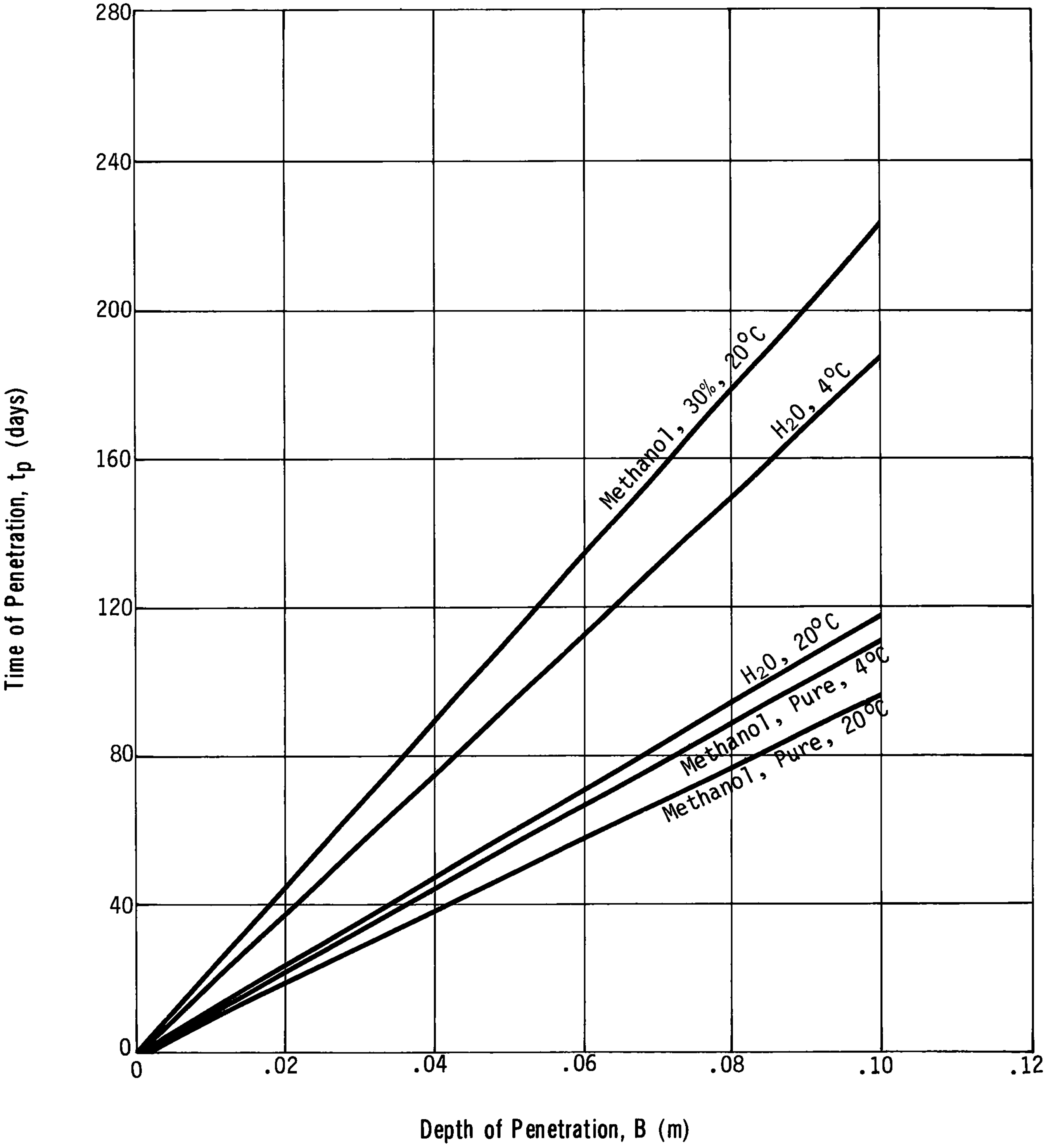
PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND



PENETRATION IN CLAY TILL



Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- $r = 8.6$ m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 10 min

Step 2: Calculate area of spill

- $A = \pi r^2 = 232\ m^2$

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

- For coarse sand, B = 7.1 m at t_p = 10 min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. In the United States, a recommended drinking water limit for methanol is 0.001 mg/L (OHM-TADS 1981).

6.1.2 Air. Ontario's environmental limit for airborne methanol is 8400 µg/m^3 air (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Methanol has been assigned a TL_m96 of greater than 1000 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
17 000	24	"Fish"	lethal		Ryerman 1966
250	11	Goldfish	died	distilled	WQC 1963
Fish Toxicity Tests					
19 000	96	Rainbow trout	LC_{50}	12°C	Johnson 1980
8100	24	Fingerling trout	no harmful effects	natural	WQC 1963
8000	24	Creek chub	LC_0	Detroit River water	Gillette 1952
17 000	24	Creek chub	LC_{100}	Detroit River water	Gillette 1952
8000	48	Trout	TL_m	-	Verschueren 1984
10 900	336	Guppy	LC_{50}	-	JWPCF 1983
Microorganisms					
31 000		Algae (*Chlorella pyrenoidosa*)	toxic		Verschueren 1984

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
10 000		Algae (*Scenedesmus*)	LD		Verschueren 1984
6000	-	Bacteria (*Pseudomonas*)	LD_0		Verschueren 1984
1250	-	Protozoa (*Colpoda*)	LD_0		Verschueren 1984
6600	-	Bacteria (*Pseudomonas*)	inhibition of cell multiplication		Verschueren 1984
530	-	Algae (*Microcystis aeruginosa*)	inhibition of cell multiplication		Verschueren 1984
8000	-	Green algae (*Scenedesmus quadricauda*)	inhibition of cell multiplication		Verschueren 1984
710 000	-	Protozoa (*Entosiphon sulcatum* and *Uronema parduczi*)	inhibition of cell multiplication		Verschueren 1984
Invertebrates - Freshwater					
32 000	-	Daphnia	immobilization threshold		WQC 1963
10 000	48	Daphnia	no effect		Verschueren 1984
Invertebrates - Saltwater					
10 000	24	Brine shrimp	TL_m		Price 1974
1700	96	Brown shrimp	LC_{50}		Portman 1970
10 000	96	Cockle	LC_{50}		Portman 1970

6.3 Other Land and Air Toxicity

The effects of methanol have not been extensively studied. Recent Russian work suggests concentrations above 0.2 mg/m^3 may reduce photosynthesis in some tree species (CHIPS 1980).

6.4 Degradation

B.O.D. kg/kg	B.O.D. % Theor.	Days	Seed	Method	Reference
-	48-53.5	5	-	-	Verschueren 1984
>1	76	5	Sewage seed		Price 1974
>1	95	20	Sewage seed		Price 1974
>1	69	5	Sewage seed	saltwater	Price 1974
>1	97	20	Sewage seed	saltwater	Price 1974
>1	90	5	Activated sludge	quiescent	Ryerman 1966
<1	3	5	Activated sludge	treatment plant	Ryerman 1966
>1	55	1	Activated sludge	treatment plant	Ryerman 1966
>1	54	6	Pure bacterial culture		Ryerman 1966
>1	67	20	Sewage seed		Gloyna 1963
0.76 to 1.12	-	5	Various	various	Verschueren 1984
-	62.7	10	Sewage seed	mineralized dilution water	Verschueren 1984

Concentrations of methanol in excess of 5000 mg/L reduce purification efficiency in treatment plants (Breszkiewicz 1979). The C.O.D. of methanol has been measured at 1.05 to 1.50 (w/w) for 95 to 99 percent of Th.O.D. (Verschueren 1984).

6.5 Long-term Fate and Effects

Methanol biodegrades very rapidly (OHM-TADS 1981).

7 HUMAN HEALTH

The toxic effects of methanol have been widely documented. Absorption of methanol can occur through the oral, inhalation and dermal routes. Absorption through any of these routes may lead to marked central nervous system effects, including narcosis and, most prominently, irreversible damage to the optic nerve, potentially causing blindness. Because the compound and its harmful metabolites are eliminated slowly, methanol is regarded as a cumulative poison (Sax 1981).

Much of the toxicological work done on methanol pre-dates 1970. NIOSH prepared a review document on the health effects due to methanol exposure in 1976 (NIOSH 1976). No reference to mutagenic, teratogenic or carcinogenic properties of methanol was found in the literature. The compound is listed in the EPA TSCA Inventory.

The toxicological data summarized here have been extracted from reliable standard reference sources. 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. Only acute (short-term) exposure data are given for nonhuman mammalian species to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for methanol are based upon prevention of its adverse effects on the eye and the central nervous system, and on prevention of metabolic acidosis and the occurrence of exposure-induced headaches (Doc. TLV 1981). Canadian provincial guidelines generally are similar to those of the USA-ACGIH unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV* - Skin (8 h)	USA-ACGIH	200 ppm (260 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	200 ppm (260 mg/m^3)	NIOSH/OSHA 1981
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	250 ppm (310 mg/m^3)	TLV 1983
Ceiling (15 min)	USA-NIOSH	800 ppm (1048 mg/m^3)	NIOSH/OSHA 1981

Guideline (Time)	Origin	Recommended Level	Reference
Other Human Toxicities			
IDLH	USA-NIOSH	25 000 ppm	NIOSH Guide 1978
TC_{LO} (inhalation)	-	86 000 mg/m^3	RTECS 1979
LD_{LO} (oral)	-	340 mg/kg	RTECS 1979
Probable oral lethal dose	-	5.0 to 0.5 g/kg (1 pint to 1 ounce for 150 lb. man)	TDB (on-line) 1981

Inhalation Toxicity Index

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

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

At 20°C, ITI = 1315.12 (96 mm Hg/200 ppm)

At 20°C, ITI = 6.3×10^2

7.2 Irritation Data

7.2.1 **Skin Contact.** Methanol may be absorbed through the intact skin, leading to systemic toxic effects. Only irritation effects of skin contact will be reported in this section. See Section 7.4.3 for data pertaining to systemic effects resulting from skin contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Contact with liquid can produce defatting and mild dermatitis	USDHEW 1977
Unspecified	Skin lesion of both the erythematous and scaling type on infants and children whose clothing was soaked in methanol	Gimenez 1968. IN NIOSH 1976
Unspecified	Dermatitis	Albany 1917. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
500 mg/kg (24 h)	Moderate irritation	RTECS 1979

7.2.2 **Eye Contact.** Methanol can cause severe eye damage by a variety of routes of exposure. Only eye irritation by direct topical exposure to the liquid or vapour are reported in this section.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
F 2000 ppm	Virtually nonirritating to the eyes	USDHEW 1977
5 ppm (24 h)	Moderate irritation	RTECS 1979
Unspecified	Conjunctivitis	ITII 1981
SPECIES: Rabbit		
40 mg	Moderate irritation	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Faint alcohol-like odour (CHRIS 1978)

Odour Index: 2393 (Verschueren 1984)

Parameter	Media	Concentration	Reference
Odour Threshold	In air	5900 ppm	May 1966. IN NIOSH 1976
Odour Threshold for unadapted panelists	In air	2000 ppm	May 1966. IN NIOSH 1976
Odour Threshold	In air	8.5 to 3.3 ppm	Chao Chin-Tsi 1959. IN NIOSH 1976.

Parameter	Media	Concentration	Reference
Recognition Threshold	In air	100 ppm	ASTM 1980
Recognition Threshold	In air	59 ppm	ASTM 1980
Detection Range	In air	5 - 7000 ppm	Verschueren 1984
Recognition Range	In air	500 - 11 000 ppm	Verschueren 1984
Distinct Odour Threshold	In air	8800 ppm	Verschueren 1984
100% Recognition Threshold	In air	2313 ppm	Verschueren 1984

7.3.2 **Taste.** No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
65 000 ppm	TC_{LO}, Irritation	RTECS 1979
2000 ppm (1 h)	Severe toxic effects begin	Verschueren 1984
500 to 6000 ppm	Exposure in confined spaces produced headaches and blurred vision	Doc. TLV 1981
1000 ppm (1 h)	Tolerance level	Kirk-Othmer 1981
800 to 1000 ppm (8 h)	Exposure to about 8 grams believed to seriously affect eyes	Doc. TLV 1981
500 ppm (8 h)	Tolerance level	Kirk-Othmer 1981
300 ppm	TC_{LO}, CNS effects	ITII 1981
200 ppm (24 h)	Tolerance level	Kirk-Othmer 1981
3.1 ppm	Sharp change in subjects' eye sensitivity. No response was seen at 2.4 ppm	Ubaydullayer 1968. IN NIOSH 1976
3 ppm (60 d)	Tolerance level	Kirk-Othmer 1981
2.5 ppm	Subjects began to show diminution of light sensitivity	Chao Chen-Tsi 1959. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
Unspecified	Death and blindness	Doc. TLV 1981
Unspecified	Acute methanol intoxication in 24 men: 9 had no ocular effect, 7 had transient effects including peripapillary edema, optic disc hypermia, diminished papillary light reaction, central scotoma	TDB (on-line) 1981
Unspecified	In 24 men with acute intoxication, 8 had permanent optic disc pallor, arteriole attenuation and sheathing, diminished pupillary light reaction, diminished visual acuity, central scotoma, and other nerve fibre bundle effects. Complete blindness in 2, severe visual deficit in 4	TDB (on-line) 1981
SPECIES: Monkey		
1000 ppm	LC_{LO}	RTECS 1979
SPECIES: Dog		
Unspecified	In the eyes, hyperemia of choroid, and edema of the ocular tissue with early signs of degeneration of ganglionic cells of the retina, and nerve fibres, were found after exposure by inhalation	TDB (on-line) 1981
Unspecified	Petechial hemorrhages in lungs and pulmonary edema	TDB (on-line) 1981
SPECIES: Cat		
65 700 ppm (4.5 h)	LC_{50}	Verschueren 1984
33 600 ppm (6 h)	Incoordination, 50 died	TDB (on-line) 1981
18 300 ppm (6 h)	Cats survived, initial salivation	TDB (on-line) 1981
SPECIES: Rabbit		
61 100 ppm (134 min)	LC_{50}	Verschueren 1984
Unspecified	Patchy bronchopneumonia, edema, congestion and desquamation of alveolar epithelium	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
49 700 ppm (1 h)	Drowsy	TDB (on-line) 1981
<u>Chronic Exposures</u>		
SPECIES: Human		
4000 to 13 000 ppm (up to 12 h)	Conjunctivitis, headache, giddiness, insomnia, gastric disturbances and failure of vision. One woman died	Doc. TLV 1981
160 to 780 ppm	No evidence of injury among exposed workers	Doc. TLV 1981
200 to 375 ppm	Exposure to mixed volatiles including 5 to 98 percent methanol. Headaches were reported	Kingsley and Hirsh 1955. <u>IN</u> NIOSH 1976
300 ppm	During the operation of duplicating machines, headaches were reported	Doc. TLV 1981
40 to 45 ppm	Employment exposures were from 9 months to 2 years. Visual disturbances reported	Greenburg et al. 1938. <u>IN</u> NIOSH 1976

7.4.2 **Ingestion.**

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
0.5 to 5 g/kg	Probable oral lethal dose: 1 pint to 1 ounce for a 70 kg man	TDB (on-line) 1981
15 to 500 mL (40 percent)	Of 323 individuals, 41 died, 115 were acidotic. Latent period between ingestion and onset of symptoms was 6 to 72 hours, with an average at about 24 hours. All acidotic victims showed signs of visual impairment and complained of blurred vision; 62 percent with	Bennett et al. 1953. <u>IN</u> NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
	headache, 30 percent with dizziness, weakness, general malaise. Several were stuporous and comatose. Some degree of amnesia was reported. Nausea and vomiting in 52 percent, diarrhea in 10 percent; 67 percent complained of excruciating upper abdominal pain and 25 percent of acidotic patients showed some degree of respiratory distress	
70 to 100 mL	Usually is fatal	TDB (on-line) 1981
25 to 100 mL	Fatal dose	Kirk-Othmer 1981
15 mL	Caused blindness	TDB (on-line) 1981
SPECIES: Monkey		
7000 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Dog		
7500 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Rabbit		
7500 mg/kg	LD_{LO}	RTECS 1979
SPECIES: Rat		
13 g/kg	LD_{50}	RTECS 1979
SPECIES: Mouse		
420 mg/kg	LD_{LO}	RTECS 1979

7.4.3 Percutaneous. Methanol can be absorbed through the intact skin to produce systemic toxic effects.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Unspecified	Nineteen children were exposed by wearing methanol-soaked clothes applied to their stomachs. Duration between exposure and onset of symptoms was 1 to 13 hours, 7-1/4 hours being the average. Symptoms included central nervous system depression, respiratory depression and convulsions. Twelve children died of cardiac or respiratory arrest. Papilledema and ocular fundus bleeding were observed in 2 cases. Five showed abdominal skin lesions	Gimenez 1968. IN NIOSH 1976
SPECIES: Monkey		
500 mg/kg	LD_{LO} (skin)	RTECS 1979
SPECIES: Rabbit		
20 g/kg	LD_{50} (skin)	RTECS 1979
Chronic Exposures		
SPECIES: Human		
Unspecified	One painter, employed intermittently (3 to 4 days at a time) for 3 years, used methanol regularly to clean his hands and arms. Suddenly became blind after a brief illness. Complained of dizziness and misty vision while on the job. Prior to loss of sight, experienced chills and numbness and shooting pains in his lower extremities	De Schwernitz 1901. IN NIOSH 1976

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity.

No data.

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. Irritation.
2. Headaches.
3. Giddiness, vertigo.
4. Insomnia (TDB (on-line) 1981).
5. Conjunctivitis.
6. Gastric disturbances.
7. Diminution of pupillary light reaction (NIOSH 1976).
8. Respiratory depression.
9. Blurred vision.
10. Peripapillary edema.
11. Optic disc hyperemia.
12. Scotoma (TDB (on-line) 1981).
13. Permanent optic disc pallor.
14. Degeneration of ganglionic cells of retina and nerve fibres.
15. CNS depression.
16. Acidosis.
17. Petechial hemorrhage in lungs.
18. Blindness.
19. Pulmonary edema.
20. Death (Doull 1980).

7.5.2 Ingestion.

1. Headache.
2. Vertigo.
3. Nausea.
4. Vomiting.
5. Severe upper abdominal pain.
6. Back pain (TDB (on-line) 1981).

7. Blurred vision.
8. Cold clammy extremities.
9. Diarrhea.
10. Dyspnea.
11. Motor restlessness (TDB (on-line) 1981).
12. Hypermia of the optic disc.
13. Slow pulse (TDB (on-line) 1981).
14. Pupils unreactive to light.
15. Delirium.
16. Coma.
17. Convulsions.
18. Acidosis.
19. Blindness.
20. Neurological damage.
21. Death.

7.5.3 Skin Contact.

1. Irritation.
2. Dermatitis.
3. Skin lesions.
4. CNS depression.
5. Blindness (NIOSH 1976).
6. Respiratory depression.
7. Convulsions.
8. Papilledema.
9. Ocular fundus bleeding (TDB (on-line) 1981).
10. Cardiac arrest (TDB (on-line) 1981).
11. Respiratory arrest (TDB (on-line) 1981).
12. Death.

7.5.4 Eye Contact.

1. Irritation.
2. Conjunctivitis (ITII 1981).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Methanol 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														
Fire		●	●										Moderate explosion hazard when exposed to flame	Sax 1979
Heat		●											Flammable liquid	Sax 1979
SPECIFIC CHEMICALS														
Acetyl Bromide							●				●		Evolution of hydrogen bromide gas	Bretherick 1979
Alkylaluminum Solution			●								●			Bretherick 1979
Barium Perchlorate			●											Bretherick 1979
Beryllium Dihydride											●		Reactions are violent even at -196°C	Bretherick 1979
Bromine			●								●			Bretherick 1979
Chlorine		●	●											Bretherick 1979
Chromic Anhydride (Chromium Trioxide)		●	●											NFPA 1978

8.1 Compatibility of Methanol 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
Cyanuric Chloride	●										●		Exothermic reaction	Bretherick 1979
Dichloromethane		●											Dichloromethane becomes flammable in air at 27°C/100 kPa in the presence of less than 0.5 volume percent of methanol	Bretherick 1979
Diethylzinc		●	●								●			Bretherick 1979
Hydrogen Peroxide			●										Capable of detonation by shock or heat	Bretherick 1979
Iodine and Mercuric Oxide			●										Mixture of three explodes	NFPA 1978
Lead Perchlorate			●											NFPA 1978
Magnesium											●		Capable of detonation	Bretherick 1979
Nitric Acid			●								●		Explosive ester is formed	Bretherick 1979
Perchloric Acid			●										Formation of methyl perchlorate which is very explosive	NFPA 1978
Phosphorus Trioxide					●								Charring may occur	Bretherick 1979; NFPA 1978

8.1 Compatibility of Methanol 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
Potassium		●									●		When mixed with chloroform	Bretherick 1979
Potassium Hydroxide	●													NFPA 1978
Potassium tert-Butoxide		●												Bretherick 1979
Sodium Hydroxide	●												When mixed with chloroform	NFPA 1978
Sodium Hypochlorite			●											Bretherick 1979
CHEMICAL GROUPS														
Alkali and Alkaline Earth Metals	●	●		●							●		Flammable hydrogen gas is produced	EPA 600/2-80-076
Azo Compounds												●	Nitrogen gas is formed	Bretherick 1979
Isocyanates	●												Carbamates are formed	EPA 600/2-80-076
Nitrides			●	●									Flammable ammonia gas is produced. Detonation of nitrides may cause explosion	EPA 600/2-80-076
Organic Peroxides	●	●												EPA 600/2-80-076

8.1 Compatibility of Methanol 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
Oxidizing Agents	●	●	●											EPA 600/2-80-076
Reducing Agents		●	●	●									Flammable hydrogen gas is produced	EPA 600/2-80-076
Water Reactive Compounds	●			●			●						Explosion may occur or highly unstable mixtures may result - reaction with methanol may be same as with water	EPA 600/2-80-076

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 source has been presented essentially unchanged - in so doing, it is recognized that there may be 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. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Methanol is a flammable liquid. Its vapours may spread away from the spill area and ignite. Container may explode in heat of fire (ERG 1980; GE 1977).

9.1.2 Fire Extinguishing Agents. Use water spray at a safe distance to cool containers involved in a fire to prevent rupture (ERG 1980; NFPA 1978). Water in a straight hose stream should not be used, due to scattering of the liquid and spreading of the fire (MCA 1970).

Small fires: Dry chemical, CO_2, water spray, or foam (alcohol)

Large fires: Water spray, fog or foam

Move containers from fire area if this can be done without risk. Stay away from tank ends (ERG 1980).

9.1.3 Spill Actions.

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

A fluorocarbon water foam can be applied to the spill to diminish vapour and fire hazard (EPA 670/2-75-042). Hycar and carbopol, which are absorbent materials, have shown possible applicability for vapour suppression and/or containment of methanol in spill situations (ICI 1982).

Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area and the contents transferred to other suitable containers (MCA 1970).

The following materials are recommended for plugging leaks of methanol: polyester (Glad bag), imid polyester (brown-in-bag) (EPA 600/2-76-300); stafoam urethane foam, sea-going epoxy putty and MSA urethane (EPA 68-01-0106).

9.1.3.2 **Spills on land.** Contain if possible by forming mechanical or chemical barriers to prevent spreading (EPA 670/2-75-042). Remove material with pumps or vacuum equipment. Treat the land with sorbent materials such as vermiculite or activated carbon to remove the remaining methanol. Remove sorbents after use.

9.1.3.3 **Spills in water.** Contain if possible by using natural barriers. Then remove trapped material with suction hoses (EPA 670/2-75-042). Sorbents such as zeolite F (K form), clinoptilolite and activated carbon should also be considered for in situ cleanup (CG-D-38-76). Contaminated water may be removed if possible for treatment. Activated carbon can be applied at 10 percent the spill amount over region occupied by 10 mg/L or greater concentrations. Then use mechanical dredges or lifts to remove sorbents (EPA 670/2-75-042).

9.1.4 Cleanup and Treatment.

9.1.4.1 **General.** The following treatment processes have shown possible applicability for spill countermeasures.

Process	Percent Removal (TSA 1980)
Biological	30 to 85
Reverse Osmosis	0 to 40
Carbon Adsorption	4 to 33

Reverse osmosis was used to remove methanol. One membrane (NS-200) was found to remove about 40 percent; aromatic polyamide (B9) and cross-linked polyethyleneimine (NS-100) membranes removed about 30 percent (Fang 1976).

9.1.5 **Disposal.** Waste methanol must never be discharged directly into sewers or surface waters. Large quantities of waste methanol can either be disposed of at a licensed waste solvent disposal company or reclaimed by filtration and distillation. It can also be incinerated (GE 1977).

9.1.6 **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.

If the spilled material is known to be methanol:

- 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 repeated or prolonged skin contact with liquid methyl alcohol (NIOSH/OSHA 1981).
- Splash-proof and chemical safety goggles are recommended for eye protection (NIOSH/OSHA 1981; MCA 1970).
- Polyvinyl plastic, neoprene or rubber is recommended for protective clothing and gloves (OHM-TADS 1981).
- The following chemical suit materials are recommended for protection against methanol (EE-20): butyl, neoprene and PVC (excellent resistance).
- The following clothing materials showed penetration times of greater than 1 hour: butyl rubber, nitrile and Viton. The following showed penetration times of about 1 hour: polyethylene, natural rubber, neoprene, chlorinated polyethylene, polyurethane, and styrene-butadiene rubber. The following showed penetration times less than 1 hour: polyvinyl alcohol and polyvinylchloride (Little 1983).
- Any clothing which becomes wet with liquid methyl alcohol should be removed immediately and not reworn until the methyl alcohol is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1977).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where methanol is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 200 ppm
Vapour Concentration	
2000 ppm or less	Any supplied-air respirator.
	Any self-contained breathing apparatus.
10 000 ppm or less	Any supplied-air respirator with a full facepiece, helmet or hood.
	Any self-contained breathing apparatus with a full facepiece.
25 000 ppm or less	A Type C supplied-air respirator with a full

	facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 25 000 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 escape self-contained breathing apparatus.

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

9.1.7 Storage Precautions. Store in a well-ventilated, fire-proof area. Ground and electrically interconnect containers for transfer. Use spark-proof tools. Keep away from heat and ignition sources. No smoking in areas of storage or use. Keep containers away from oxidizing agents (GE 1977).

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® Rockwell External Leak Plugging System
Land Containment	"MSAR" Dike Pak System Portafoam System
Temporary Storage	Portable Collection Bag System
Treating Agents	Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

10.1 General

A number of spill accidents for this chemical have been documented. The incident discussed here has been selected primarily because significant information, potentially useful in future spill circumstances, has been learned from it.

10.2 Train Derailment (PC BCMOE 1982; HMIR 1982)

A rockslide in a remote area caused a train derailment involving 16 tank cars containing approximately 134 000 L of methanol each. Two cars fell off an 8 m cliff into a river, where one tank car lost all of its contents and the second car lost a substantial amount. Two other cars were punctured by rocks and by coupling devices during the collision and came to rest with their ruptured ends up, spilling smaller amounts of methanol.

Response crews arrived at the spill site with cranes mounted on rail cars and heavy equipment to clear the tracks. Minor leaks from the domes of overturned tank cars were contained with lead wire and rubber and wooden plugs. Earthen dikes were constructed to contain any methanol being spilled; however, this proved unsuccessful since the methanol seeped through the dike. Methanol vapours were found to be minimal due to low temperature conditions decreasing the vaporization rate.

On the next day, the transfer of methanol from the overturned tank cars to new tank cars proceeded. It took approximately 5 days to open the tracks to traffic and complete the cleanup.

Approximately 466 000 L of methanol spilled into the river from the mishap. Water monitoring in the river indicated that the methanol concentration posed no immediate threat to water supplies and that the methanol would be diluted to undetectable levels in the near future. It was fortunate that there was sufficient water for dilution to low levels. No fish kill was observed to result from the spill, although no specific environmental studies were conducted.

11 ANALYTICAL METHODS

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

Methods have been documented here for the 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 Methanol in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 140 to 540 mg/m^3 (107 to 412 ppm) of methanol in air may be determined by gas chromatography. A known volume of air is drawn through a 7 cm x 6 mm O.D. silica gel tube containing 2 sections of 20/40 mesh silica gel separated by a 2 mm portion of urethane foam. The first section contains 100 mg whereas the second section contains 50 mg. A silylated glass wool plug is placed before the front absorbing section. A sample size of 5 L of air sampled at 200 mL/min is recommended.

The silica gel tube sample is scored before the first section of silica gel and broken. The larger section of silica gel is transferred to a 2 mL stoppered sample container containing 1.0 mL of distilled water. The same operation is performed with the back-up section. The sample should be allowed to desorb for 4 hours. A 5 μL aliquot of sample is injected into a gas chromatograph equipped with a flame ionization detector.

The methanol is determined using an electronic integrator which measures peak area in conjunction with a calibration curve. Typical gas chromatograph conditions are: a 10 ft. x 1/8 in. stainless steel column packed with 10 percent FFAP on 80/100

Chromosorb W-AW, nitrogen carrier gas flow at 30 mL/min, hydrogen gas flow at 30 mL/min, air flow at 300 mL/min, injector temperature at 200°C, detector temperature at 300°C, and a column temperature of 80°C.

11.2 Quantitative Method for the Detection of Methanol in Water

11.2.1 Gas Chromatography (ASTM 1979). A range of 140 to 540 mg/m^3 (107 to 412 ppm) of methanol in water may be determined by direct aqueous injection into a gas chromatograph equipped with a flame ionization detector. A minimum volume of 2 L of representative sample is collected in a clean glass bottle having a screw cap of TFE-fluorocarbon lined with aluminum foil. A 2 to 5 µL sample is injected into a gas chromatograph equipped with a flame ionization detector. Kovats index or retention time is used to identify the compound, and the area of the peak may be used to quantitate the compound by direct comparison with standard responses.

Typical gas chromatograph operating conditions are: a flame ionization detector, helium carrier gas flow at 45 mL/min, injector temperature at 200°C, detector temperature at 250°C, column temperature 50 to 250°C at 8°C/min. The column is 20 ft. x 1/8 in. O.D. stainless steel packed with Carbowax 20M (5 percent) 80/100 AW, Chromosorb W.

11.3 Quantitative Method for the Detection of Methanol in Soil

11.3.1 Gas Chromatography (ASTM 1979; NIOSH 1977). A range of 140 to 540 mg/m^3 (107 to 412 ppm) of methanol in the extracting solution may be detected using a flame ionization detector. Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. A suitable amount of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the methanol from the soil. The Freon® is distilled from the soil on a water bath at 70°C. Air is drawn through the containing flask for the final minute to remove all traces of Freon®. The residue is dissolved in a suitable amount of carbon disulphide and an aliquot is injected directly into a gas chromatograph equipped with a flame ionization detector. The methanol is determined using an electronic integrator which measures area under the peak and retention times in conjunction with a calibration graph.

Typical gas chromatograph conditions are: a 10 ft. x 1/8 in. stainless steel column packed with 10 percent FFAP on 80/100 mesh acid-washed DMCS Chromosorb W, injector temperature at 195°C, column temperature at 85°C, detector temperature at 250°C, nitrogen carrier gas flow at 50 mL/min, hydrogen gas flow at 65 mL/min, air flow at 500 mL/min.

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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 immission 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
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	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