ENVIRO

Technical

Information for

Problem

Spills

PROPYLENE

October 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

EnviroTIPS manuals are available from

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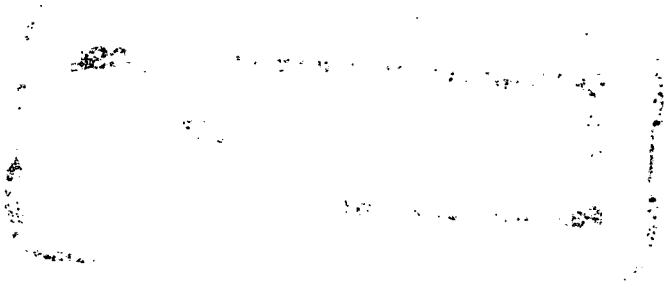Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

PROPYLENE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

October 1984

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

iii

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1   SUMMARY

PROPYLENE (CH_2CHCH_3)

Colourless gas with a mild odour

SYNONYMS

Methylethene, Methylethylene, 1-Propene, Propene, 1-Propylene

IDENTIFICATION NUMBERS

UN. No. 1077; CAS No. 115-07-1; OHM-TADS No. 7216875; STCC No. 4905782

GRADES & PURITIES

Refinery grade: < 92 percent
Chemical grade: 92-95 percent
Polymer grade: 99.5 percent

IMMEDIATE CONCERNS

Fire: Flammable. Flashback may occur along vapour trail

Human Health: Low toxicity by all routes

Environment: Not harmful to aquatic life

PHYSICAL PROPERTY DATA

Shipping State: liquid (liquefied gas)
State (15°C, 1 atm): gas
Boiling Point: -47.7°C
Flammability: flammable
Vapour Pressure: 1047.3 kPa (21°C)
Density: 0.6007 g/mL (liquid at -50°C),
  1.9149 g/L (gas at 25°C)

Solubility (in water): 0.04-0.08 g/100 mL
  (20°C)
Behaviour (in water): floats and boils;
  no reaction
Behaviour (in air): vapour is heavier
  than air; forms explosive mixtures
Odour Threshold: 20-70 ppm

HUMAN HEALTH

No TLV or IDLH established

Exposure Effects

Inhalation: In high concentrations (5 percent or higher) and for long exposure periods, causes dizziness, drowsiness, and unconsciousness. At low concentrations, is relatively harmless

Contact: Vapour is practically harmless to skin. Contact with liquefied propylene will cause frostbite.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify distributor. Eliminate sources of ignition. Stop the flow if safe to do so. Avoid contact with liquid and vapour; stay upwind of release.

Fire Control

Do not extinguish fire unless release can be stopped. Use foam, dry chemical, carbon dioxide, water spray or fog to extinguish. Cool fire-exposed containers with water. Stay clear of tank ends. Containers may explode in heat of fire.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Treat as vapour release only

Water: Treat as vapour release only

Air: Use water spray to disperse flammable vapour

NAS HAZARD RATING

Category	Rating
Fire	4
Health	
Vapour Irritant	0
Liquid or Solid Irritant	0
Poison	1
Water Pollution	
Human Toxicity	0
Aquatic Toxicity	0
Aesthetic Effect	0
Reactivity	
Other Chemicals	1
Water	0
Self-reaction	1

NFPA
HAZARD
CLASSIFICATION

Flammability

Health   4   Reactivity
          1   1
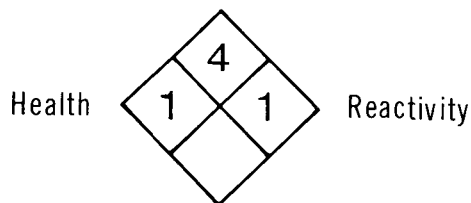
2   PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas; when liquefied, is a colourless liquid (Air Products SGMSDS 1978)
Usual shipping state(s)	Liquid (liquefied gas) (Dow ERIS 1979)
Physical state at 15°C, 1 atm	Gas
Freezing point	-185.25°C (HCG 1981; PPCC 1959)
Boiling point	-47.7°C (HCG 1981; Kirk-Othmer 1982)
Vapour pressure	1047.3 kPa (21°C) (Air Products SGMSDS 1978)

Densities

Density	Gas: 1.9149 g/L (25°C) (Ullmann 1975) Liquid: 0.6007 g/mL (-50°C) (Kirk-Othmer 1982) (at boiling point) (Air Products SGMSDS 1978)
Specific gravity (liquid; water = 1)	0.512 (20°C) (MCA 1956) 0.609 (-47/4°C) (Verschueren 1984)
Vapour specific gravity (air =1)	1.4529 (HCG 1981) 1.48 (Ullmann 1975; Matheson 1980)

Fire Properties

Flammability	Flammable gas (NFPA 1978)
Autoignition temperature	455°C (NFPA 1978; Ullmann 1975) 480°C (Matheson 1980)
Burning rate	8 mm/min (CHRIS 1978)
Upper flammability limit	11.1 percent (v/v) (NFPA 1978)
Lower flammability limit	2.0 percent (v/v) (NFPA 1978)
Burning characteristics	Burns with a yellow, sooty flame (Merck 1976)
Flash point	-108.0°C (Matheson 1980)
Heat of combustion	2058 kJ/mole (Gross, to H_2O (liquid) + CO_2) (Matheson 1980) 1926 kJ/mole (Net, to H_2O (gas) + CO_2) (Matheson 1980)
Combustion products	Carbon dioxide and water (CRC 1980)
Flashback potential	May travel considerable distance to a source of ignition and flash back (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge

Other Properties

Molecular weight of pure substance	42.081 (CRC 1980; Kirk-Othmer 1982)
Constituent components of typical chemical grade:	Propylene, 92-95 percent Propane, < 8 percent Ethane, < 0.4 percent C_4 and greater, < 0.2 percent Others, < 0.1 percent
Constituent components of typical polymer grade:	Propylene, 99.5 percent Ethane, < 1000 ppm Others, < 500 ppm (Kirk-Othmer 1982)
Refractive Index	1.3567 (-70°C) (CRC 1980)
Viscosity	0.0084 mPa·s (vapour at 25°C) (Ullmann 1975) 0.18 mPa·s (liquid at -50°C) (Ullmann 1975)
Liquid interfacial tension with air	15.8 mN/m (liquid at -40°C) (Matheson 1980)
Latent heat of fusion	3.0 kJ/mole (-185°C) (HCG 1981)
Latent heat of vaporization	18.4 kJ/mole (at boiling point) (HCG 1981)
Heat of formation	20.2 kJ/mole (25°C) (Sussex 1977)
Gibb's energy of formation	62.7 kJ/mole (101 kPa, 25°C) (Kirk-Othmer 1982)
Heat capacity	
constant pressure (C_p)	91.555 J/(mole·°C) (liquid at -49.8°C) (Matheson 1980) 62.345 kJ/(mole·°C) (gas at 15.6°C) (Matheson 1980)
constant volume (C_v)	54.035 kJ/(mole·°C) (gas at 15.6°C) (Matheson 1980)
specific heat ratio (γ) (C_p/C_v)	1.154 (Matheson 1980)
Critical pressure	4619.5 kPa (HCG 1981)
Critical temperature	91.77°C (HCG 1981)
Coefficient of thermal expansion	0.00339/°C (liquid expansion between -21°C and 21°C) (MCA 1956)
Saturation concentration	18 000 g/m^3 (21°C) (calc.)
Log_{10} octanol/water partition coefficient	1.77 (Hansch and Leo 1979)
Entropy	227 J/(mole·K) (Ullmann 1975)
Dipole moment	0.366 D (Matheson 1980)
Dielectric constant	1.875 (liquid at 20°C) (Matheson 1980)
Molar volume	21.976 L (25°C) (Ullmann 1975)

| Thermal conductivity | 0.156 Wm^{-1} K^{-1} (liquid at -50°C) (Ullmann 1975) |
| | 0.0184 Wm^{-1} K^{-1} (gas at 25°C) (Ullmann 1975) |

Solubility

In water	0.039 g/100 mL (22.05 cm^3/100 mL) (20°C) (Matheson 1980)
	0.079 g/100 mL (44.6 cm^3/100 mL) (20°C) (Kirk-Othmer 1982)
In other common materials	Soluble in ethanol (1250 mL/100 g) and in acetic acid (524.5 mL/100 g) (20°C) (Kirk-Othmer 1982)

Vapour Weight to Volume Conversion Factor

1 ppm = 1.746 mg/m^3 (20°C) (Verschueren 1984)

Chemical/Physical Properties and Behaviour

Vapour Explosions. Explosions have been reported when liquefied propylene contacts water at temperatures of 42 to 75°C. These explosions are in fact the result of rapid evaporation in contact with the warm water. The behaviour of liquefied propylene on water is summarized in the following table (Kirk-Othmer 1982):

Initial Water Temperature (°C)	Result of Liquid Propylene Contact
38 to 41	ice formation
42 to 75	explosion
76 to 85	rapid pops

Variation of Chemical Properties. Propylene has been studied thoroughly. Full data on the variation of its properties are thus available. The Van der Waals equation of state is (Kirk-Othmer 1982):

$$\left(P + \frac{a}{V^2} \right) (V-b) = RT$$

where: P = pressure, in kPa

V = volume, in L

a = 6.373

b = -0.08272

R = 8.314 J/(mole·K)

T = temperature, in K (= °C + 273.15)

A number of Virial equations of state have been developed and the following is recommended (Dymond 1969):

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V}$$

where P, V, R, T are the same as the above. B is given at different temperatures as follows:

T (K)	T (°C)	B
280	7	-392
300	27	-342
320	47	-297
340	67	-260
380	107	-204
420	127	-162
460	187	-132
500	227	-105

Two Antoine equations for predicting vapour pressures are also given for a temperature range of 160 to 240 K (-113 to -33°C) (Kirk-Othmer 1982):

$$Log_{10} P_V = A + \frac{B}{T + C}$$

where: P_V = vapour pressure, in kPa

T = temperature, in K (°C = K - 273.15)

A = 5.94327

B = 784.86

C = -26.15

and for a temperature range of 123 to 356 K (-150 to 83°C):

$$Log_{10} P_V = A + \frac{B}{T} + C \, Log \, T + DT$$

where: P_V = vapour pressure, in kPa

T = temperature, in K (°C = K - 273.15)

A = 34.752

B = -1725.5

C = -12.057

D = 8.9943 x 10^{-3}

The liquid density can be calculated as follows (Kirk-Othmer 1982):

$$e = AB^{-(1-\frac{T}{Tc})\ 2/7}$$

where:　　e = density, in g/cm^3

T = temperature, in K (K = C + 273.15)

A = 0.2252

B = 0.2686

Tc = critical temperature = 365.05 K

PROPYLENE

CONVERSION NOMOGRAMS

Temperature

| °C | -40 | -30 | -20 | -10 | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| °F | -40 | | 0 | | 50 | | 100 | | 150 | | 200 | |

Pressure   1 kPa = 1 000 Pa

| kPa | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| Atmospheres | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |

| kPa | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| psi | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

| kPa | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| mmHg(torr) | 0 | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 |
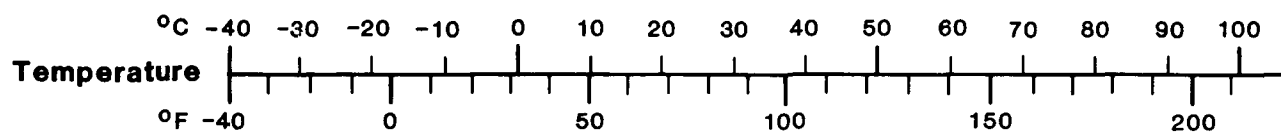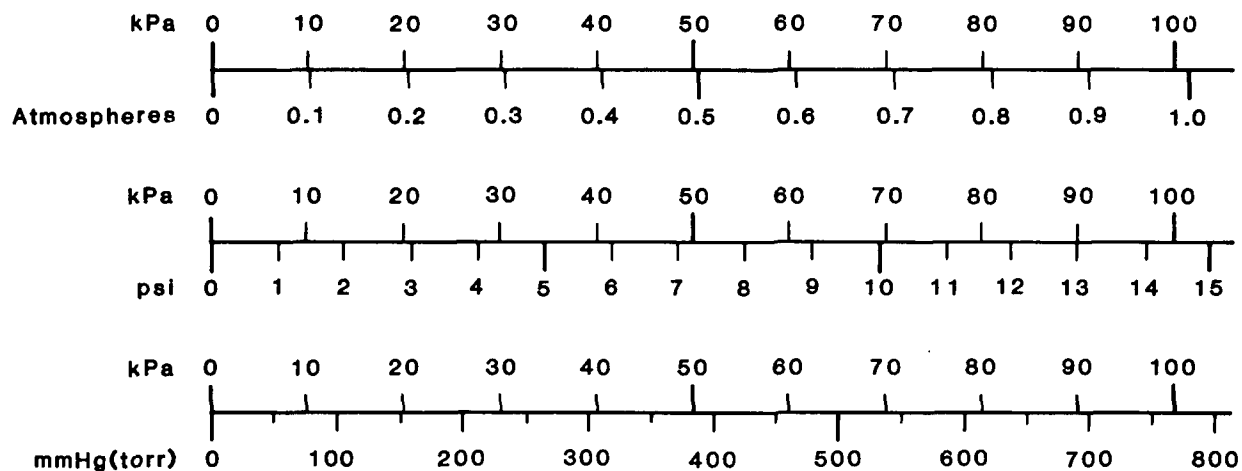
Viscosity

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

| kJ | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| kcal | 0 | | 5 | | 10 | | 15 | | 20 | | 25 |

| kJ | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| BTU | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

| kg/m^3 | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

Density

| lb/ft^3 | 0 | | 1 | | 2 | | 3 | | 4 | | 5 | | 6 |
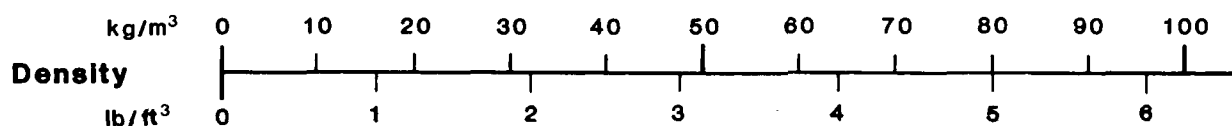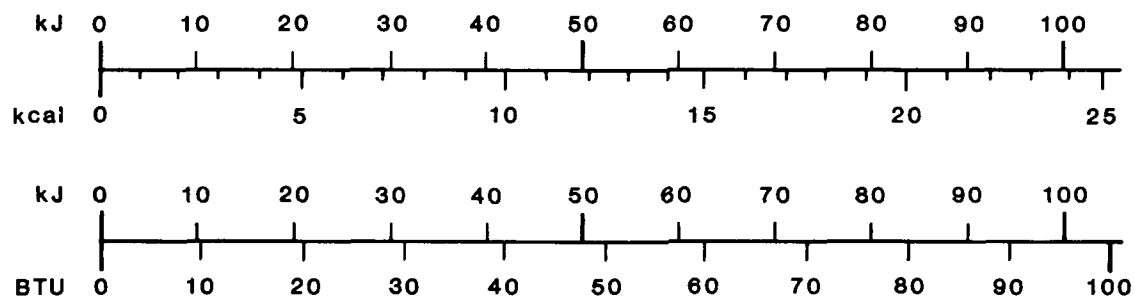
FIGURE 1

PROPYLENE

VAPOUR PRESSURE vs TEMPERATURE
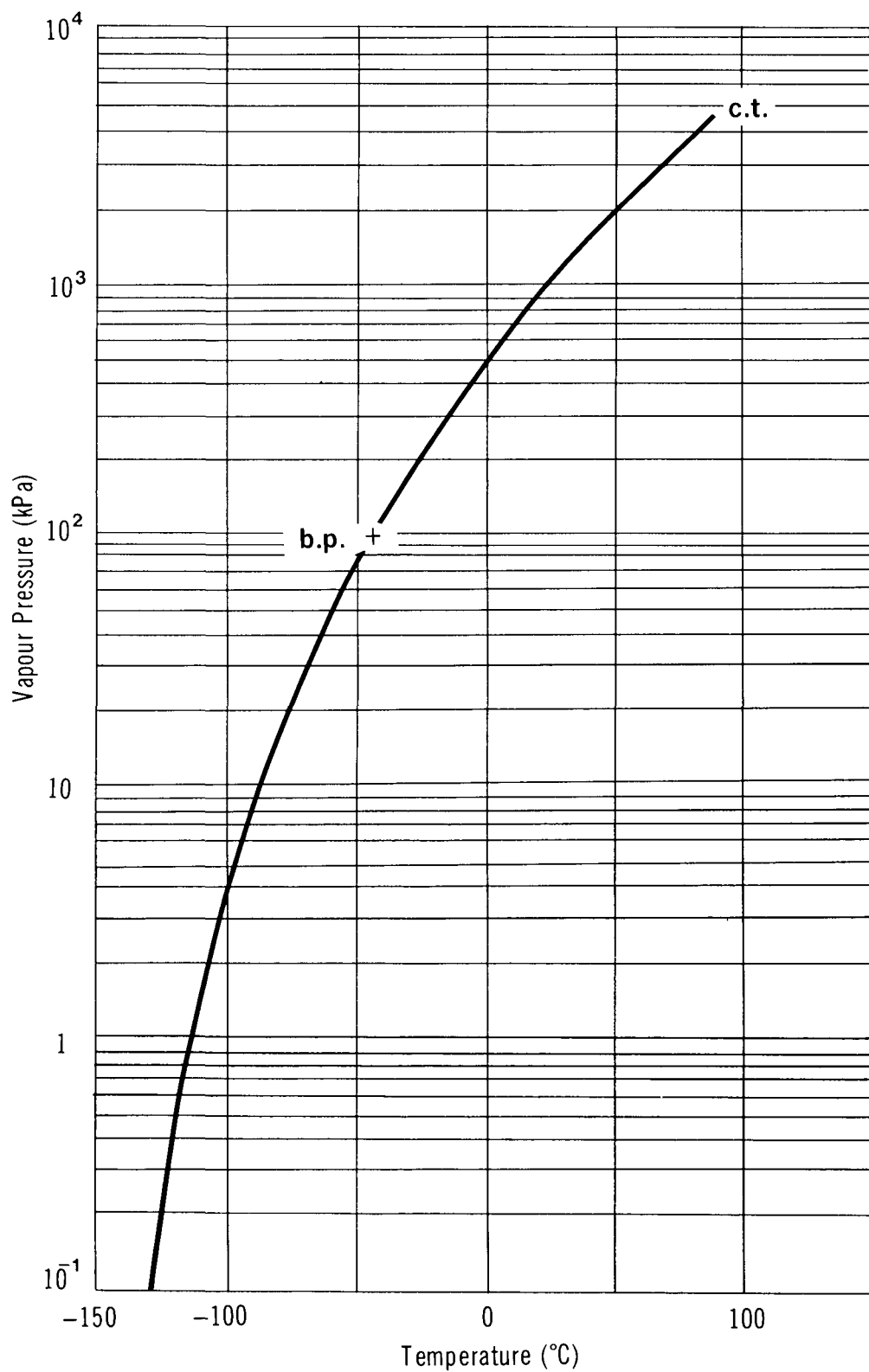
FIGURE 2

PROPYLENE

LIQUID DENSITY vs TEMPERATURE
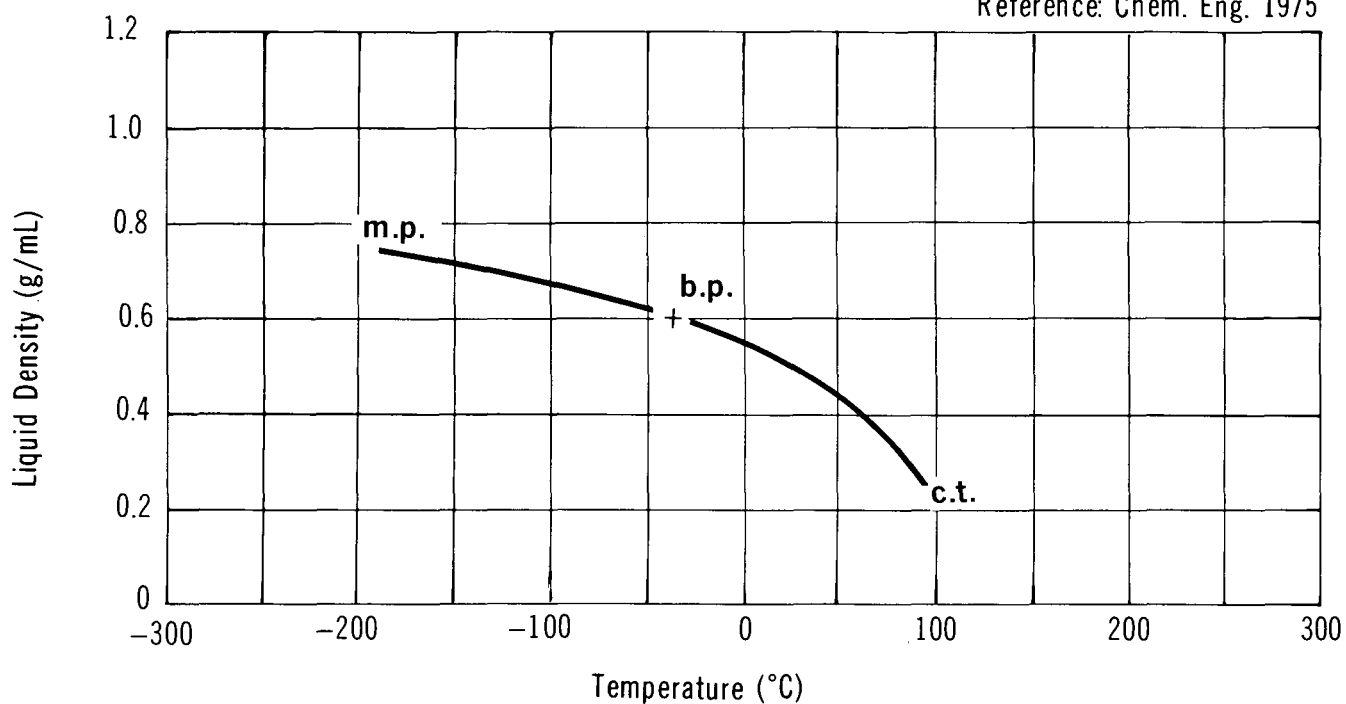
FIGURE 3

PROPYLENE

LIQUID INTERFACIAL TENSION WITH AIR
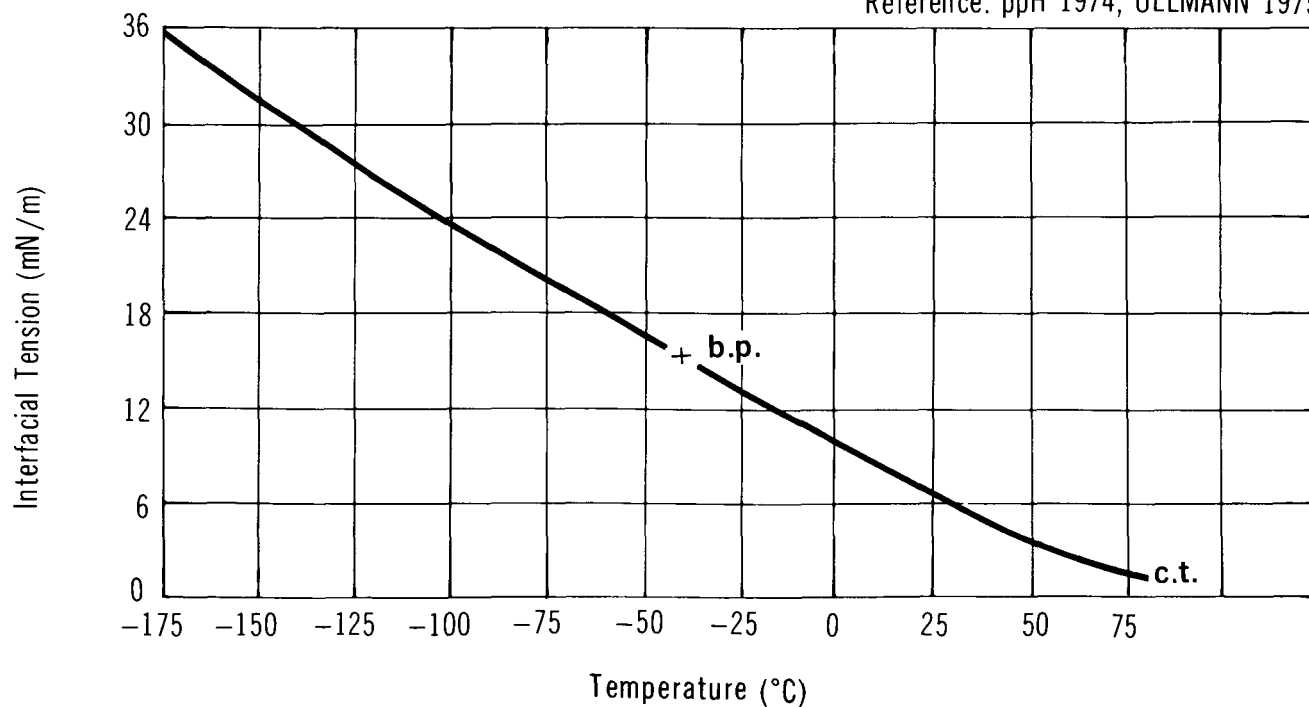
FIGURE 4

PROPYLENE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1975
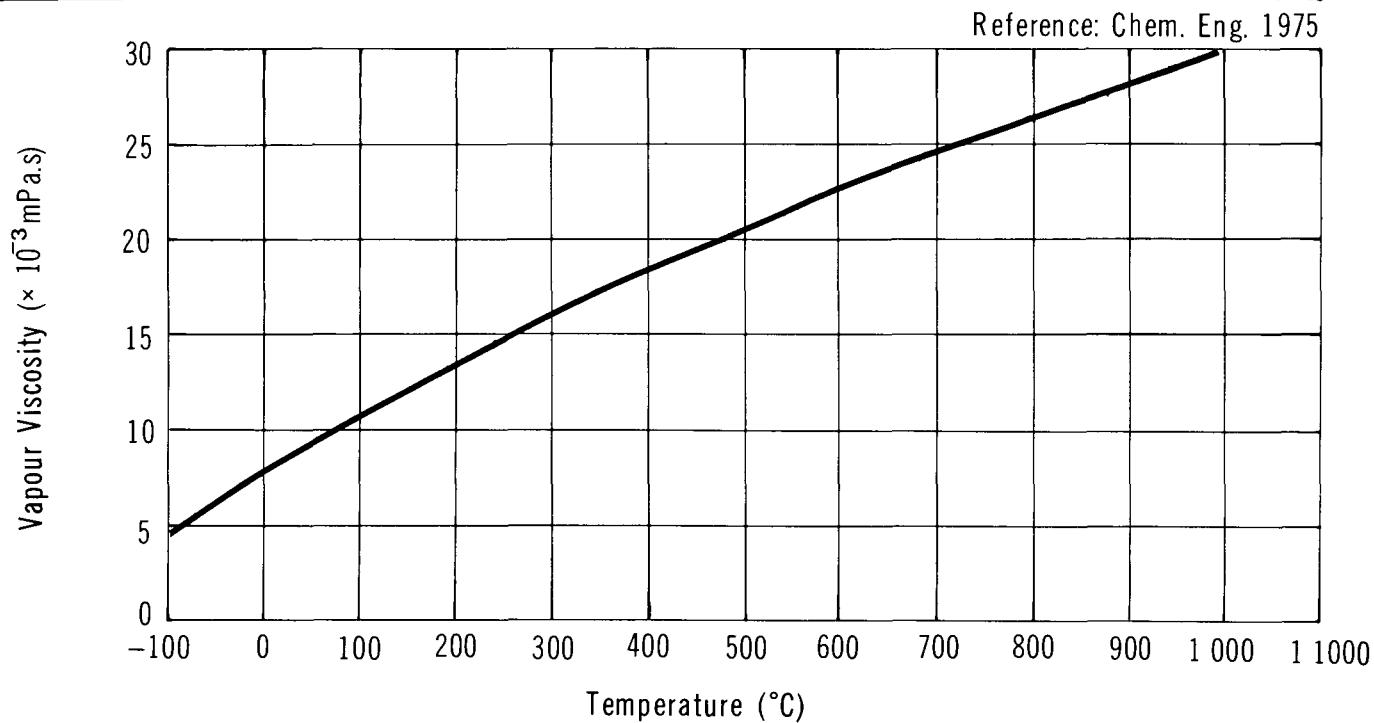
FIGURE 5

PROPYLENE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1975
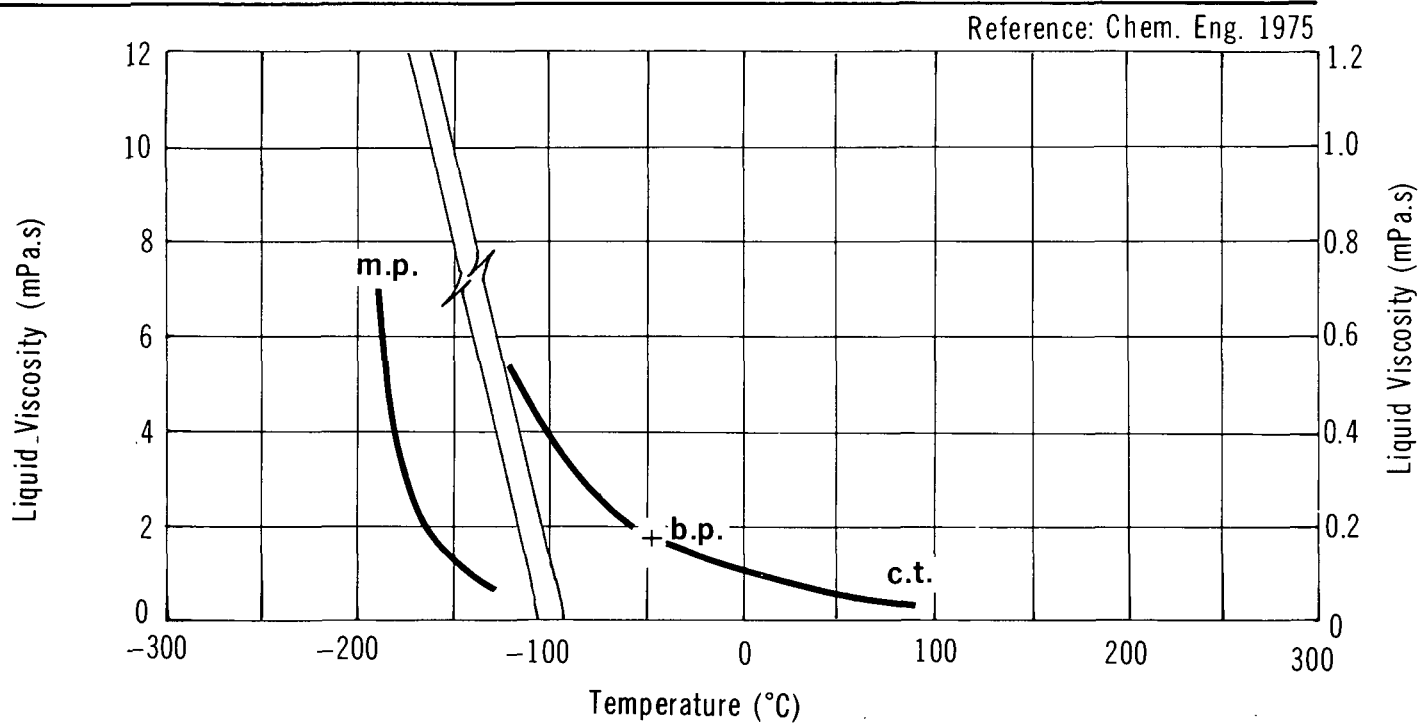
PHASE DIAGRAM
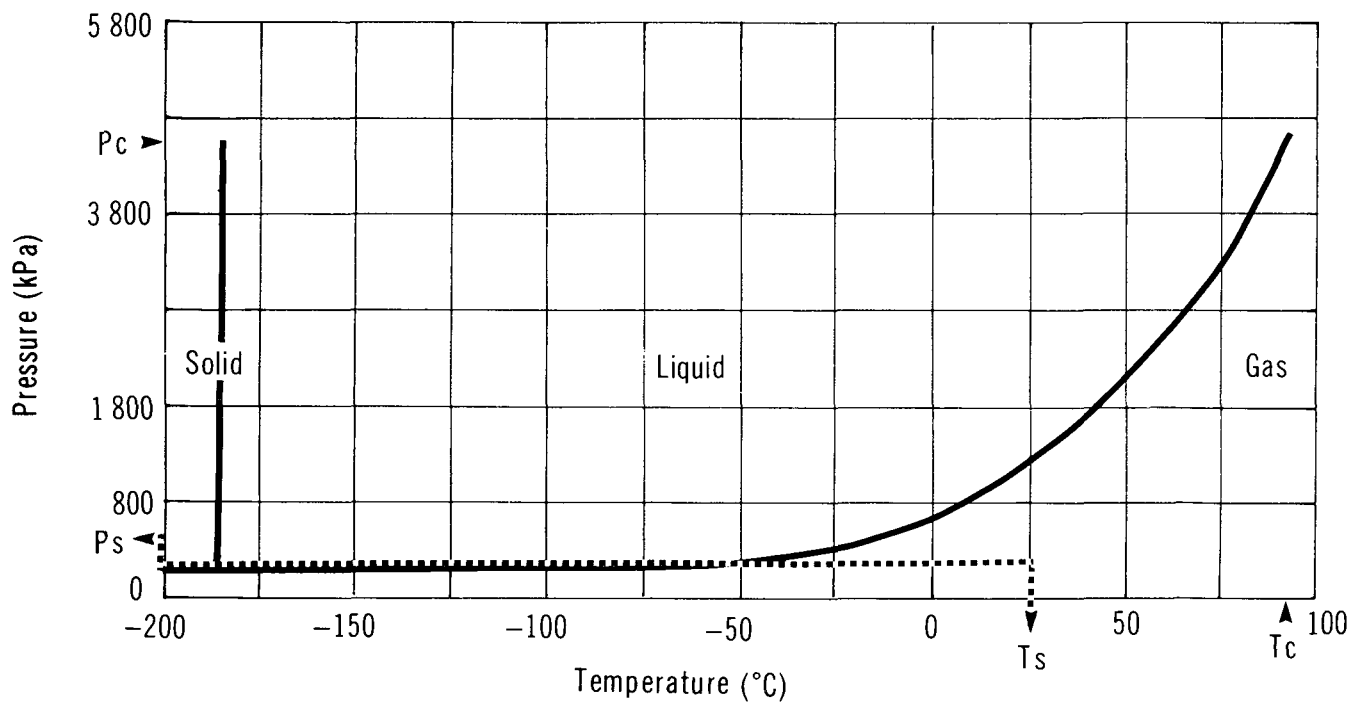
3   COMMERCE AND PRODUCTION

3.1   Grades, Purities (Kirk-Othmer 1982; Ullmann 1975; Corpus 1983)

Propylene is most commonly sold as a liquefied gas in three grades: chemical (92-95 percent propylene), polymer (99.5 percent propylene), and refinery grade material (usually less than 92 percent propylene). Research grade (99.7 percent) for laboratory use is another grade encountered. Refinery grade is variable in terms of content and is used in the manufacture of products such as isopropanol and higher alkenes.

The specification for chemical-grade propylene is as follows:

	Content	
Component	North America	Europe
Propylene	92-94 percent	92-95 percent
Ethane and methane	< 0.4 percent	< 2000 ppm
Propane	< 8.0 percent	variable
Ethylene	< 0.02 percent	< 20 ppm
C_4 and heavier	< 0.2 percent	< 1000 ppm
C_5 and heavier	< 0.005 percent	included in above
Acetylenes, dienes	< 100 ppm	< 30 ppm
Total H_2, O_2, CO, CO_2, N_2	< 100 ppm	see below
Sulphur	< 10 ppm	< 5 ppm
Water	< 50 ppm	< 10 ppm
Halides	< 10 ppm	< 5 ppm
Alcohols	< 50 ppm	< 50 ppm
Amines	< 5 ppm	not specified
Butadiene	< 20 ppm	not specified
Butenes	< 125 ppm	< 40 ppm
Dimethyl formamide	< 0.3 ppm	not specified

The product specification for polymer-grade propylene is as follows:

	Content	
Component	North America	Europe
Propylene	99.5 percent	99.5-99.8 percent

| Component | Content | |
	North America	Europe
Ethane	< 1000 ppm	< 100 ppm
Total acetylenes and dienes	< 10 ppm	< 2 ppm
Ethylene	included in above	< 20 ppm
Hydrogen	< 2 ppm	< 1 ppm
Oxygen	< 8 ppm	not specified
Carbon monoxide	< 4 ppm	< 5 ppm
Water	< 10 ppm	< 10 ppm
Sulphur	< 5 ppm	< 5 ppm
Total nitrogen, aldehydes, ketones and alcohols	< 10 ppm	< 50 ppm

3.2 Domestic Manufacturers (Corpus 1983; CBG 1980; Scott 1979).

BP Canada Ltd.
1245 Sherbrooke St. West
Montreal, Quebec
H3G 1G7
(514) 849-4789

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Finachem Canada Inc.
1 Place Ville-Marie
Montreal, Quebec
H3B 4A9
(514) 866-3911
(514) 866-2094

Gulf Canada Ltd.
800 Bay Street
Toronto, Ontario
M5S 1Y8
(416) 924-4141

Petromont Inc.
Suite 2000
2020 University Street
Montreal, Quebec
H3A 2A5
(514) 282-9091

Petrosar
785 Hill Street
P.O. Box 5000
Corunna, Ontario
N0N 1G0
(519) 862-2911

Shell Canada Ltd.
505 University Avenue
Toronto, Ontario
M5G 1X4
(416) 579-7111

3.3 Other Supplier (CBG 1980)

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

3.4 Major Transportation Routes

Current Canadian production of propylene is located primarily in Ontario, in Corunna, Sarnia and Trafalgar (70 percent of total production). Other production facilities are in Quebec, in Montreal and Varennes (26 percent of total production) and in Dartmouth, Nova Scotia. The market area for propylene is in Ontario and Quebec. The product is shipped by tank cars, tank trucks or cylinders. Distribution is fairly universal throughout eastern Canada.

3.5 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Chemical Grade:	
Esso Chemical Canada, Sarnia, Ont.	85
PetroCanada, Trafalgar, Ont.	18
Petromont, Montreal, Que.	55
Petromont, Varennes, Que.	95
Petrosar, Corunna, Ont.	315
Refinery Grade:	
Esso Chemical Canada, Dartmouth, N.S.	29
Esso Chemical Canada, Montreal, Que.	27
Esso Chemical Canada, Sarnia, Ont.	120
Finachem Canada, Montreal, Que.	24
Gulf Canada, Montreal, Que.	26
Petrocan Chemicals, Montreal, Que.	24
Shell Canada, Corunna, Ont.	18
TOTAL	836
Domestic Production (1982)	608
Imports (1982)	1.7
TOTAL SUPPLY	609.7

3.6 **Manufacture of Propylene** (Shreve 1977; CCPA 1983; Kirk-Othmer 1982)

3.6.1 **General.** Propylene is manufactured in Canada by the cracking of a liquid petroleum gas, gas oil, or naphtha.

3.6.2 **Raw Materials.** Liquefied petroleum gas (LPG) (usually propane or a similar light hydrocarbon) is produced as a by-product of the refining of natural gas, gas oil or naphtha.

3.6.3 **Manufacturing Process.** Propylene is derived from the feedstock by thermal or catalytic decomposition ("cracking" or "pyrolysis") followed by compression, purification and fractionation (required in order to isolate the products of the pyrolysis). A common catalyst used in this process is zeolite.

3.7 **Major Uses in Canada** (Corpus 1983)

Chemical-grade propylene is used in production of the polymer-grade material, which in turn is used to make polypropylene, for the production of ethylene oxide and butyraldehydes. Refinery-grade material is used in the production of isopropanol, cumene, nonene, tetramer, neptane and motor gasoline. In 1982, 36 percent of domestic production was exported, 18 percent was used for polypropylene production, 12 percent for isopropanol production, 10 percent for butyraldehyde production, 7 percent in ethylene oxide manufacture, and 6 percent in tetramer production.

3.8 **Major Buyers in Canada** (Corpus 1983)

BASF Canada, Laval, Que.
Dow Chemical of Canada, Sarnia, Ont.
Hercules Canada, Varennes, Que.
Shell Canada, Corunna, Ont.

4   MATERIAL HANDLING AND COMPATIBILITY

4.1   Containers and Transportation Vessels

4.1.1   General. Liquid propylene is transported under pressure in steel cylinders and railway tankers equipped with safety devices and pressure tested at regular intervals. Some bulk users receive it by pipeline (PC 1981).

4.1.2   The Cylinder. Propylene cylinders are typically of steel construction and must comply with CTC/DOT specifications 3A300, 3AA300, 3B300, 4A300, 4B300 and 4BA300 (HCG 1981; RTDCR 1974). Class 3A and 3AA cylinders having higher service pressures also may be used. Each specification is described in Table 2. Laboratory cylinders are equipped with a CGA No. 510 valve with an outlet with 0.885 in., 14 threads per inch, left hand threads accepting a bullet-shaped internal nipple. Lecture bottles have a special 5/16 in., 32 thread per inch, female outlet and a 9/16 in., 18 threads per inch, male dual outlet.

TABLE 2   CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3A300	Seamless steel cylinder. Maximum service pressure 2070 kPa (300 psi).
3AA300	Seamless steel cylinder. Maximum service pressure 2070 kPa (300 psi). Steels definitely prescribed. Maximum carbon content 0.28%.
3B300	Seamless nickel cylinder. Maximum service pressure 2070 kPa (300 psi).
4A300	Forge welded steel cylinder. Maximum service pressure 2070 kPa (300 psi).
4B300	Welded and brazed steel cylinder. Maximum service pressure 2070 kPa (300 psi).
4BA300	Welded and brazed steel cylinder. Definitely prescribed steels. Maximum service pressure 2070 kPa (300 psi).

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

4.1.3   Railway Tank Cars. Railway tank cars transporting propylene must comply with CTC/DOT specifications 105A400W or 112A400W, or greater specifications e.g., 105A500W or 105A600W, described in Table 3 (TCM 1979; RTDCR 1974). A 105A500W car is illustrated in Figure 7; technical details are given in Table 4. The details for the 105A400W tank car are nearly identical.

TABLE 3   RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A400W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Safety valve (2760 kPa) (400 psi). Bottom outlet or washout prohibited.
112A400W	Steel fusion-welded tank with manway nozzle. Uninsulated. Upper 2/3 of tank must be painted. Maximum one opening per head for purging. Top unloading arrangement required. Safety valve (2760 kPa) (400 psi). Bottom outlet or washout prohibited.
105A500W	As 105A400W except safety valve at 3450 kPa (500 psi).

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

Two angle valves on the longitudinal centre line of the car are for unloading liquid propylene. The angle valve on the transverse centre line is connected to the vapour space. Opposite this gas valve is a gauging device. A 6 mm (1/4 in.) test tube with angle valve and a 19 mm (3/4 in.) thermometer well complete the dome cover fittings (TCM 1979).

Under each liquid valve is an eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a rising-ball, excess-flow valve designed to close when the rate of flow of liquid exceeds about 3180 kg/h (7000 lb./h). This is a protective device designed to close automatically against the flow of liquid if the angle valve is broken off or, under certain conditions, if the unloading line is severed. The safety relief valve is of the spring-loaded type and is usually combined with a breaking pin assembly.

GAUGING DEVICE

AIRLINE CONNECTION

THERMOMETER WELL

SAFETY VALVE

DISCHARGE OUTLET
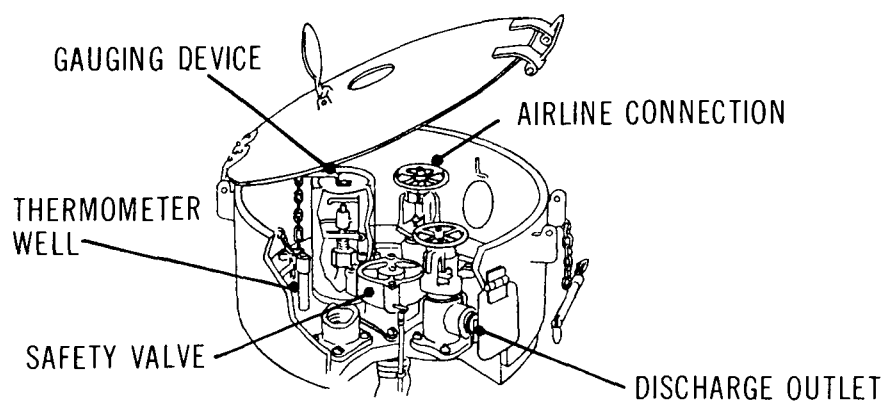
Detail of top unloading arrangement

UNLOADING ARRANGEMENT
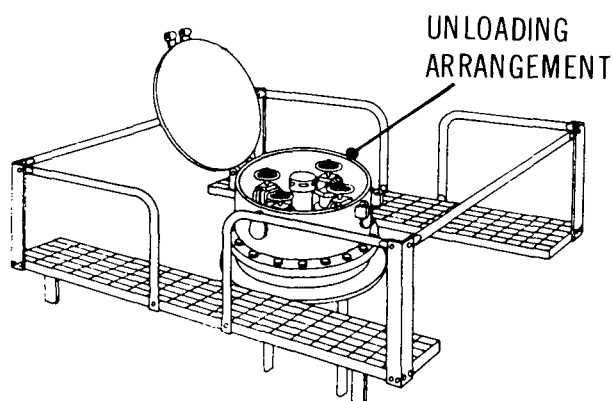
Detail of loading platform

INSULATION

LOADING PLATFORM
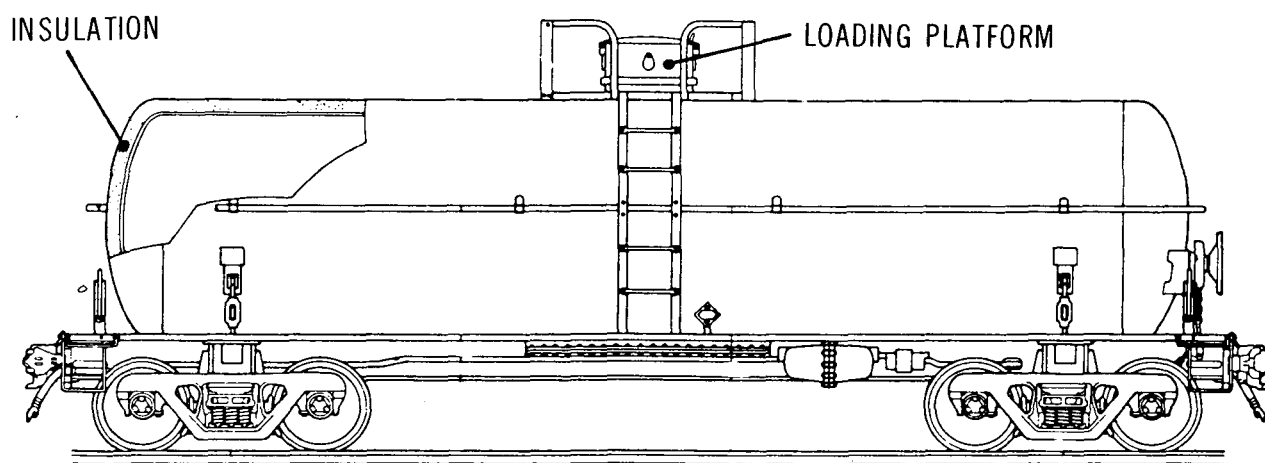
Illustration of tank car layout

TABLE 4   TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A500W

Description	Tank Car Size (Imp. Gal.)			
	8800 (55 ton)		15 000 (90 ton)	
Overall				
Nominal capacity	40 000 L	(8 800 gal.)	68 000 L	(15 000 gal.)
Car weight - empty	33 800 kg	(74 600 lb.)	37 400 kg	(82 500 lb.)
Car weight - (max.)	99 800 kg	(220 000 lb.)	106 400 kg	(263 000 lb.)
Tank				
Material	Steel		Steel	
Thickness	17-24 mm	(11/16-15/16 in.)	17-24 mm	(11/16-15/16 in.)
Inside diameter	2.2 mm	(88 in.)	2.6 m	(102 in.)
Test pressure	3450 kPa	(500 psi)	3450 kPa	(500 psi)
Burst pressure	8620 kPa	(1250 psi)	8620 kPa	(1250 psi)
Approximate Dimensions				
Coupled length	13 m	(41 ft.)	15 m	(48 ft.)
Length over strikers	12 m	(39 ft.)	14 m	(46 ft.)
Length of truck centres	9 m	(28 ft.)	11 m	(35 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)
Overall width	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(7-10 ft.)	2-3 m	(7-10 ft.)
Width of grating	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)
Loading/Unloading Fixtures				
Unloading connection	51 mm (2 in.) via valve and 76 mm (3 in.) check valve; 6 mm (1/4 in.) outlet			
Valving	51 mm (2 in.) valve to vapour space			
Gauging Device	Float-type gauging device and thermometer well			
Safety Devices	Safety relief valve set at 2590 kPa (375 psi)			
Insulation	51-152 mm (2-6 in.) fibreglass insulation			

4.2   Off-loading

4.2.1   Off-loading Equipment and Procedures for Cylinders. The following points should be observed when handling and storing cylinders:

- Valve protection hoods should be in place.
- Containers should not be stored near ventilation systems.
- Store to minimize external corrosion.
- Store cylinders upright and secured by chain.
- Store full and empty containers separately.

4.2.2   Off-loading Equipment and Procedures for Railway Tank Cars. The following precautionary steps should be undertaken (MCA 1956):

- Unloading operations to be performed only by properly instructed personnel.
- Non-sparking tools are recommended.
- Personal safety equipment should be used when working on top of railway cars.
- Dead-end siding used only for propylene rail cars to be provided.
- Lighting must be rated explosion-proof.
- Brakes must be set, wheels chocked and a proper derail employed.
- Cars should be grounded.
- Suitable operating platform to be provided at unloading point.

Railway tank cars are preferentially unloaded by compressor (CCPA 1983). In this method, vapours are withdrawn from the storage tank and compressed for discharge into the tank car vapour space. This increases the tank car pressure, thereby causing flow of liquid from the tank car to the storage tank. When the tank car is unloaded of all liquid, the direction of vapour flow can be reversed, allowing much of the vapour to be recovered. The compressor is turned off when the tank pressure is about 35 kPa (5 psi) (MCA 1956).

4.2.3   Specifications and Materials for Off-loading Equipment. The components of a typical off-loading system handling propylene at commonly employed temperatures and pressures will be discussed. These include pipes and fittings, flexible connections, valves, gaskets, gauges, pumps and storage tanks.

Pipes and fittings should be of steel and designed for working pressure of at least 2070 kPa (300 psi) in accordance with the ASME Pressure Piping Code (MCA 1956).

Pipelines 63 mm (2 1/2 in.) and over should be flanged or welded. When threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints (MCA 1956). Threaded joints should be back-welded (CCPA 1983).

Flexible connectors, consisting of a loop of copper or copper alloy construction, should be installed between cylinders and rigid piping systems. Seamless copper water tube per ASTM B88 in the annealed state with Type K wall thickness, or heavier, is recommended. Rubber hose rated for at least 2070 kPa (300 psi) pressure may also be used. Connectors for railway tank cars should be of similar high pressure hose. Currently, a number of firms have replaced flexible unloading equipment with unloading arms (CCPA 1983).

Shut-off valves and control valves should be of steel construction and designed for working pressures of at least 2070 kPa (300 psi). Relief devices may be of steel or brass construction (MCA 1956). Gaskets may be synthetic rubber, Buna N or Viton. Pumps should be designed for propylene service and should be piston-type (MCA 1956).

Storage tanks above ground should be of all-steel welded construction in accordance with API Code (MCA 1956). Underground caverns offer safe and economical storage where a suitable geological formation exists (HCG 1981).

4.3 Compatibility with Materials of Construction

The compatibility of propylene 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

| Application | Condition | | Material of Construction | | |
	State	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Dry Gas	20	Schedule 80 Seamless Steel (MCA 1956)		
	Gas	24-100	CS With Glass Lining (CDS 1967)		

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

| Application | Condition | | Material of Construction | | |
	State	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)				Copper SS Brass (MCA 1956)	
2. Valves	Gas	20		All Steel 2070 kPa Rating (MCA 1956)	
3. Storage	Liquid	20		CS ASTM A-283 (MCA 1956)	

TABLE 6   MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Brass
CS	Carbon Steel
	Copper
	Fluorine Rubber (Viton)
	Glass
	Natural Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
	Nickel
	Nickel-Copper Alloy (Monel)
SS (followed by grade)	Stainless Steel

5   CONTAMINANT TRANSPORT

5.1   General Summary

Propylene is commonly transported in tanks as a liquid under pressure. When spilled in the environment, it will form a boiling liquid pool, spreading on the surface of a water body or on the ground as well as forming a flammable vapour cloud. Vapour is released rapidly from the pool to the atmosphere by evaporation.

When spilled on water, propylene will tend to float and will evaporate rapidly. Propylene has a low solubility in water. The vapour cloud tends to hug the water and spread rather than lift off and disperse.

Propylene spills on soil surfaces will mostly evaporate; soil and groundwater contamination are thus not a serious problem.

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

```
                 Leak from                        ┌─ Rate of discharge
               ┌─ tank ─────────────────────      └─ Percent remaining

Contaminant    │                                  ┌─ Vapour emission rate
Transport  ────┼─ Air ─────────────────────────   └─ Hazard zone
               │
               └─ Water ──────────────────────────── Spread on water
```
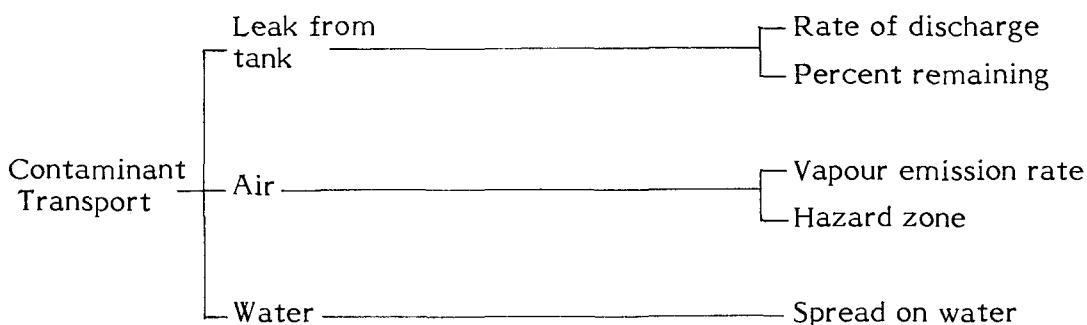
5.2   Leak Nomograms

5.2.1   Introduction. Propylene is commonly transported as a liquid under pressure at ambient temperature. While the capacities of the railway tank cars vary widely, one size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. This size has been chosen throughout the EnviroTIPS series to allow for comparison among the various substances.

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

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 1600 kPa. In real life, a puncture in the top would cause a "flash" of propylene vapour to exit and thus a large initial release. It is estimated that the continuous flow could be 1 to 3 orders of magnitude slower, depending on the amount of insulation present, the ambient temperature and the position of the tank car (i.e., in water, above ground, etc.). These situations are difficult to model.

The assumption of isothermal conditions made here will maximize the continuous gas release rate from the tank and will be conservative for most cases.
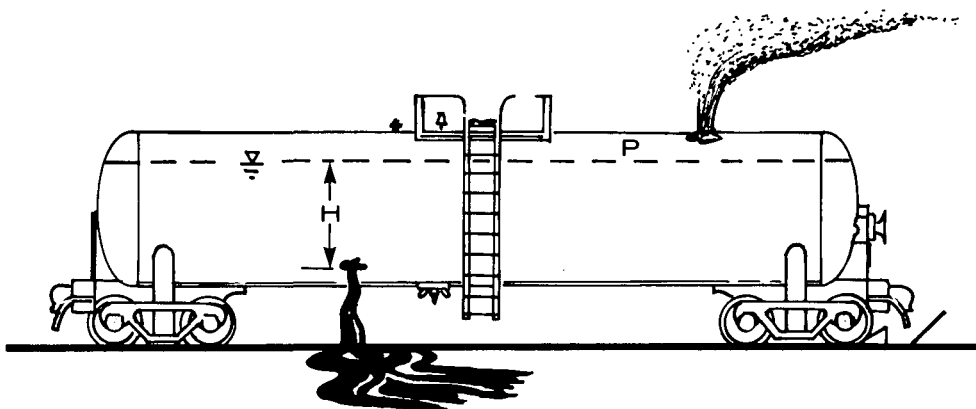
FIGURE 8   TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

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

5.2.2   Nomograms.

5.2.2.1   Bottom puncture - liquid venting.

Figure 9:   Percent remaining versus time.   Figure 9 provides a means of estimating the percent of propylene remaining in the standard tank car after the time of puncture for a number of different hole diameters.   The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

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

Figure 10:   Discharge rate versus puncture size.   Figure 10 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2   Top puncture - gas venting.

Figure 11:   Percent remaining versus time.   Figure 11 provides a means of estimating the percent of propylene 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.   As isothermal conditions have been assumed, the internal pressure and venting rate are constant.

Figure 12:   Discharge rate versus puncture size.   Figure 12 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car.   For any one hole size, the venting rate will be constant until all the liquid is vaporized.   This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 12 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 1600 kPa.

FIGURE 9

PROPYLENE

PERCENT REMAINING vs TIME

Puncture in Bottom of Tank car (Liquid release)

Time from Puncture, t (min)
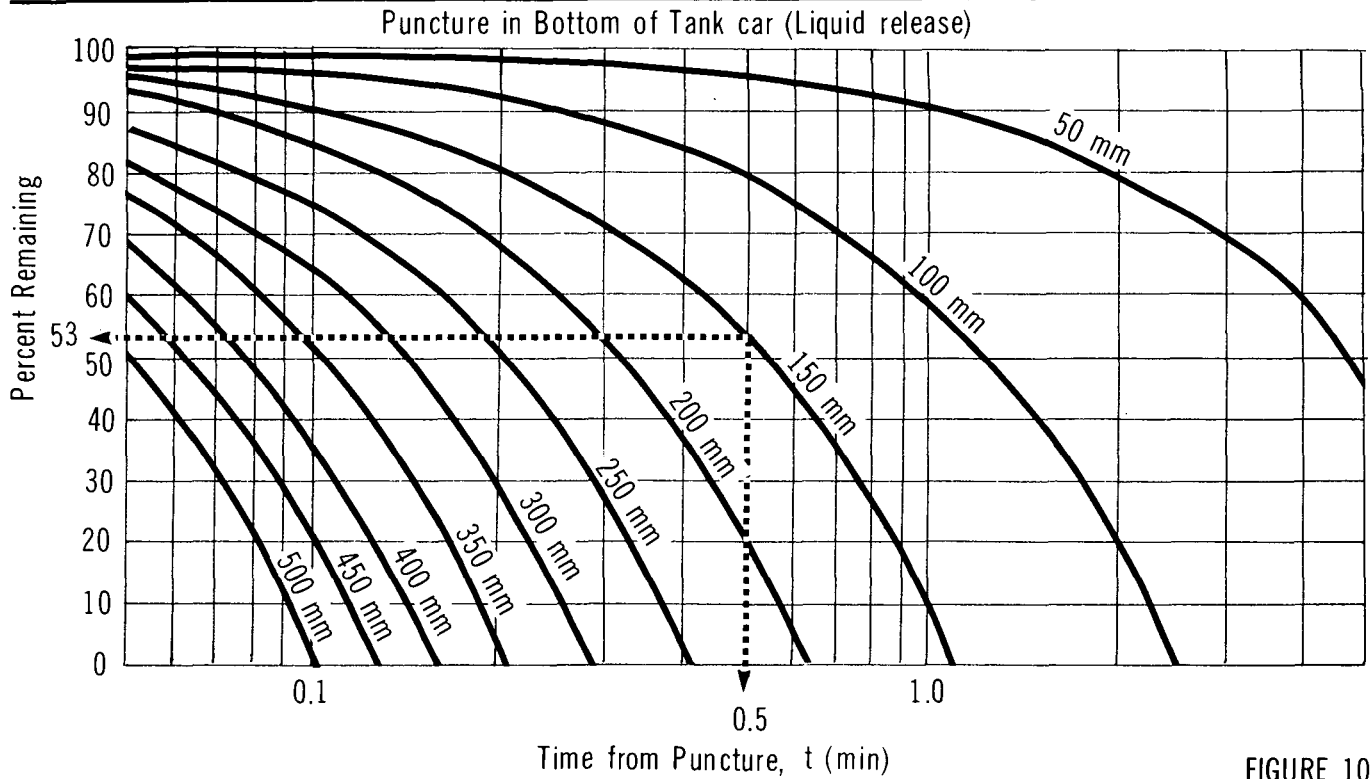
FIGURE 10

PROPYLENE

DISCHARGE RATE vs PUNCTURE SIZE

Puncture in Bottom of Tank car (Liquid release)

Equivalent Diameter of Puncture, d (mm)

FIGURE 11

PROPYLENE   **PERCENT REMAINING vs TIME**

Puncture in Top of Tank car (Vapour release)

Percent Remaining

Time from Puncture, t (min)
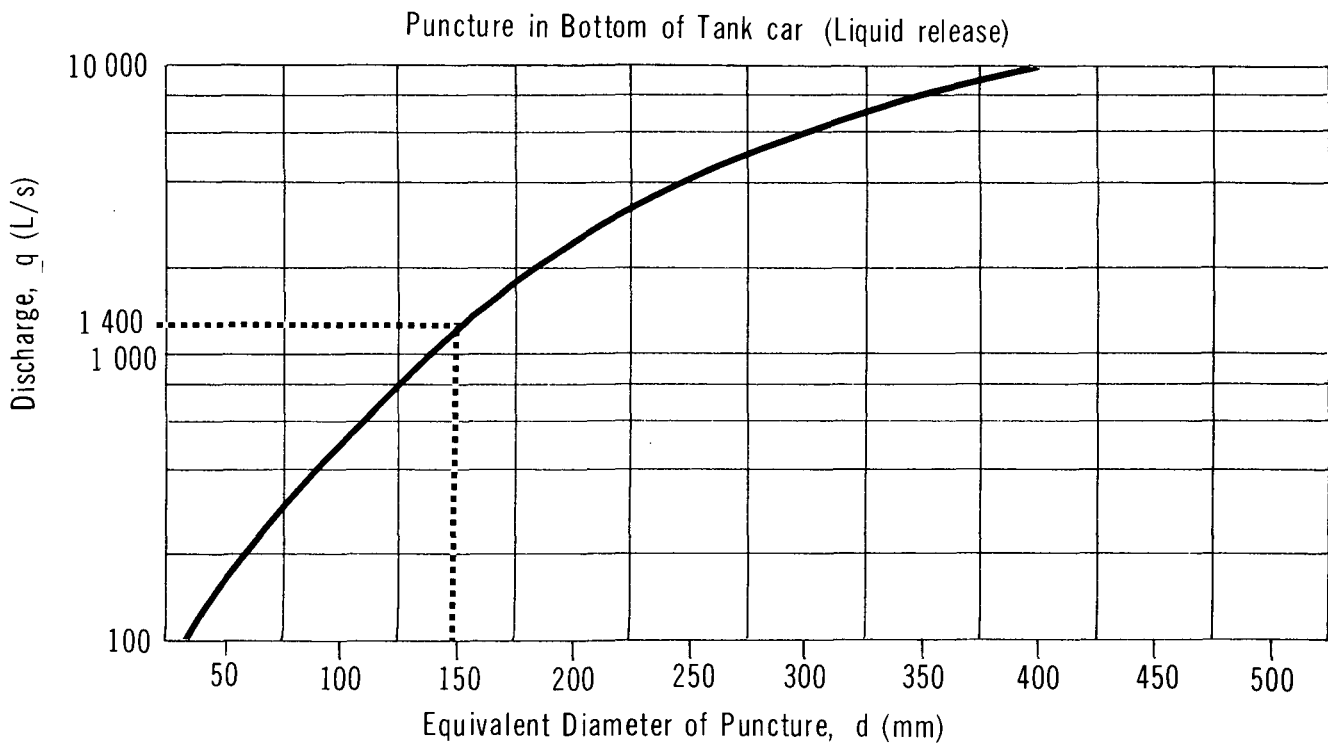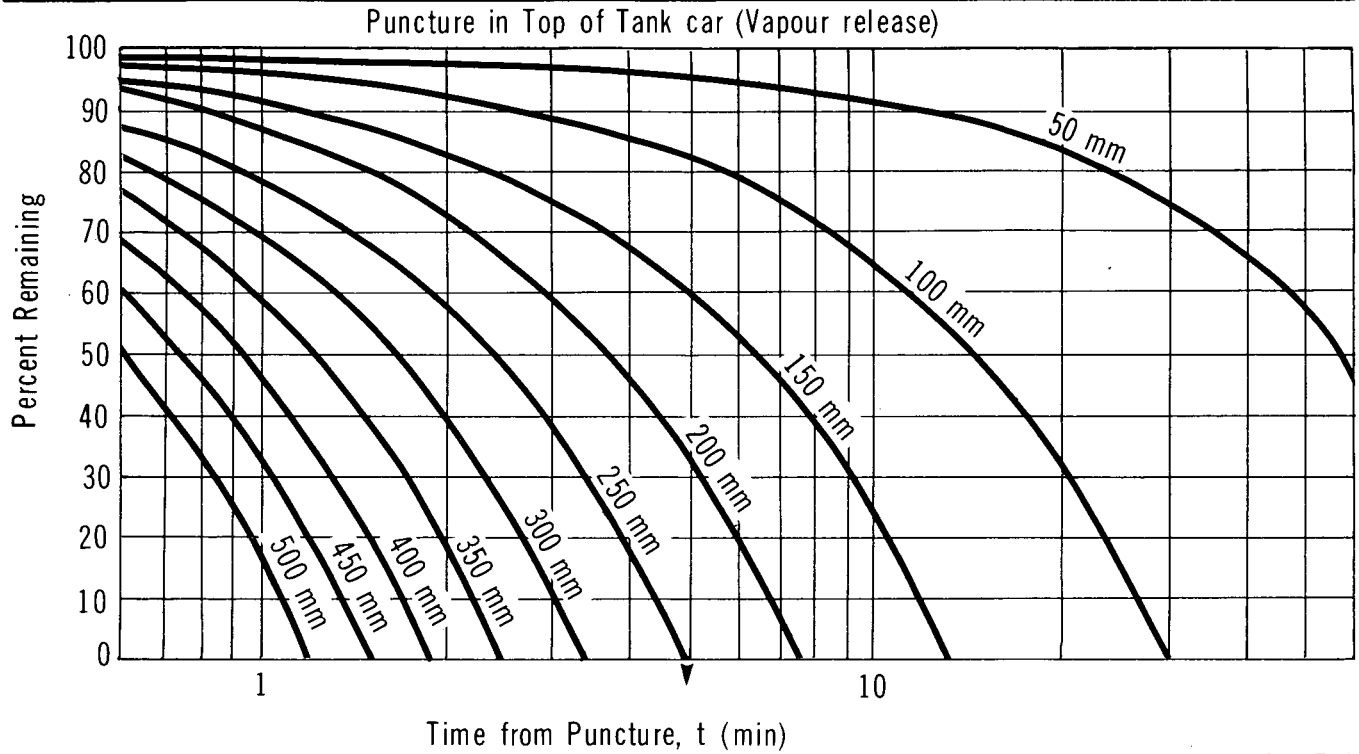
FIGURE 12

PROPYLENE   **DISCHARGE RATE vs PUNCTURE SIZE**

Puncture in Top of Tank car (Vapour release)

Discharge, q (kg/s)

Equivalent Diameter of Puncture, d (mm)
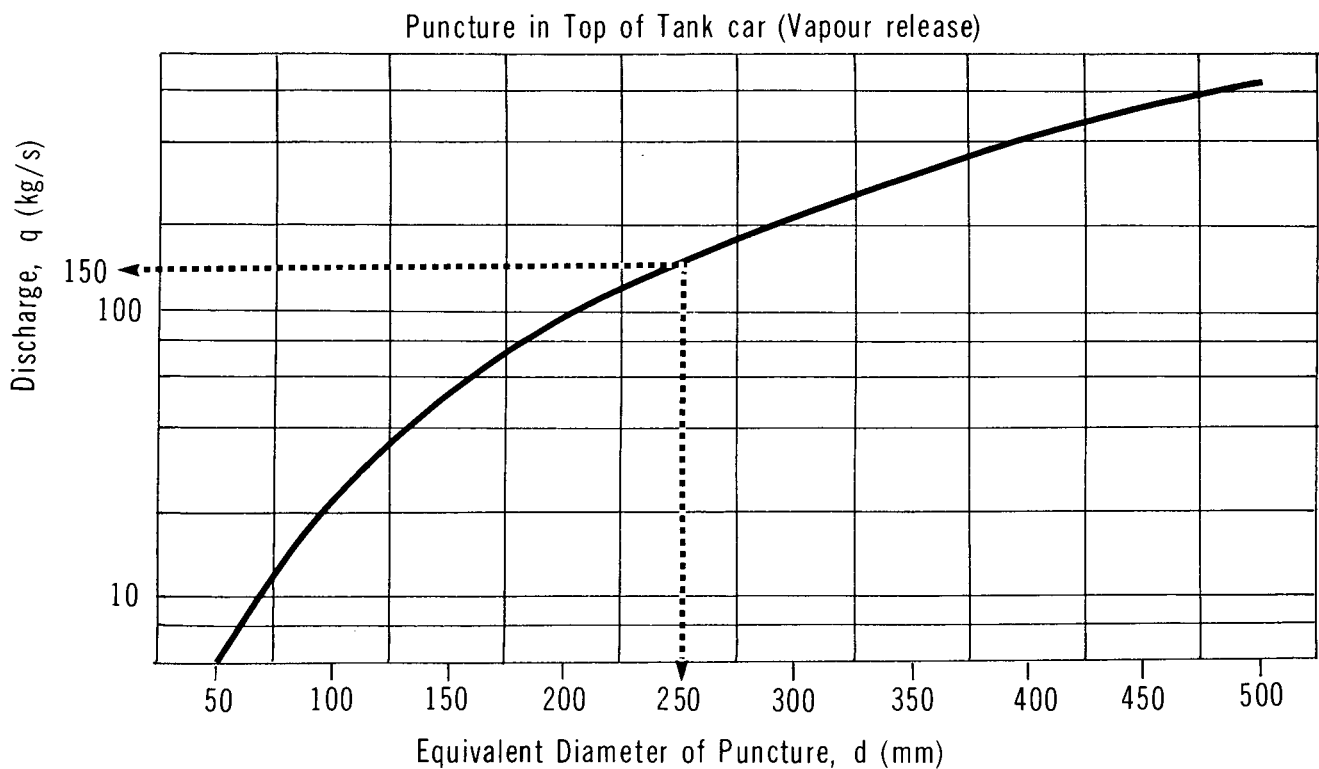
5.2.3   Sample Calculations.

i)   <u>Problem A</u>

The standard tank car filled with propylene at 40°C 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 0.5 minute and what is the instantaneous discharge rate from the tank?

<u>Solution to Problem A</u>

Step 1:   Calculate amount remaining at t=0.5 min

   .   Use Figure 9

   .   With t=0.5 min and d=150 mm, the amount remaining is about 53 percent or 42 000 L

Step 2:   Calculate the discharge rate

   .   Use Figure 10

   .   With d=150 mm, the instantaneous discharge rate (q) = 1100 L/s

ii)   <u>Problem B</u>

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

<u>Solution to Problem B</u>

Step 1:   Calculate the time to empty

   .   Use Figure 11

   .   With d=250 mm, the tank empties (0 percent remaining) in approximately 5 min

Step 2:   Calculate the discharge rate

   .   Use Figure 12

   .   With d=250 mm, the venting rate is constant at 150 kg/s. Note: this rate is based on isothermal assumptions and as such represents the maximum discharge rate. The actual rates could be the 1 to 3 orders of magnitude slower depending on amount of insulation lost, ambient temperature and other conditions.

5.3   Dispersion in the Air

5.3.1   Introduction. Since propylene under pressure is an extremely volatile liquid, vapour released from a liquid pool spilled on a ground or water surface vaporizes rapidly

enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release 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 13 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

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

Figure 7: weather conditions

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

Table 8: maximum puff hazard half-widths

Figure 16: vapour puff travel distance as a function of travel time elapsed since the spill and wind speed

The flowchart given in Figure 14 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 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 (C/Q_T) at the centreline of the contaminant puff. 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.

SCHEMATIC OF CONTAMINANT PUFF

Wind Speed (U)

Liquid Spill Site $\otimes$

Initial Vapour Puff

Concentration at Ground Level

Puff Width (W)

Downwind Distance (X)

FIGURE 14
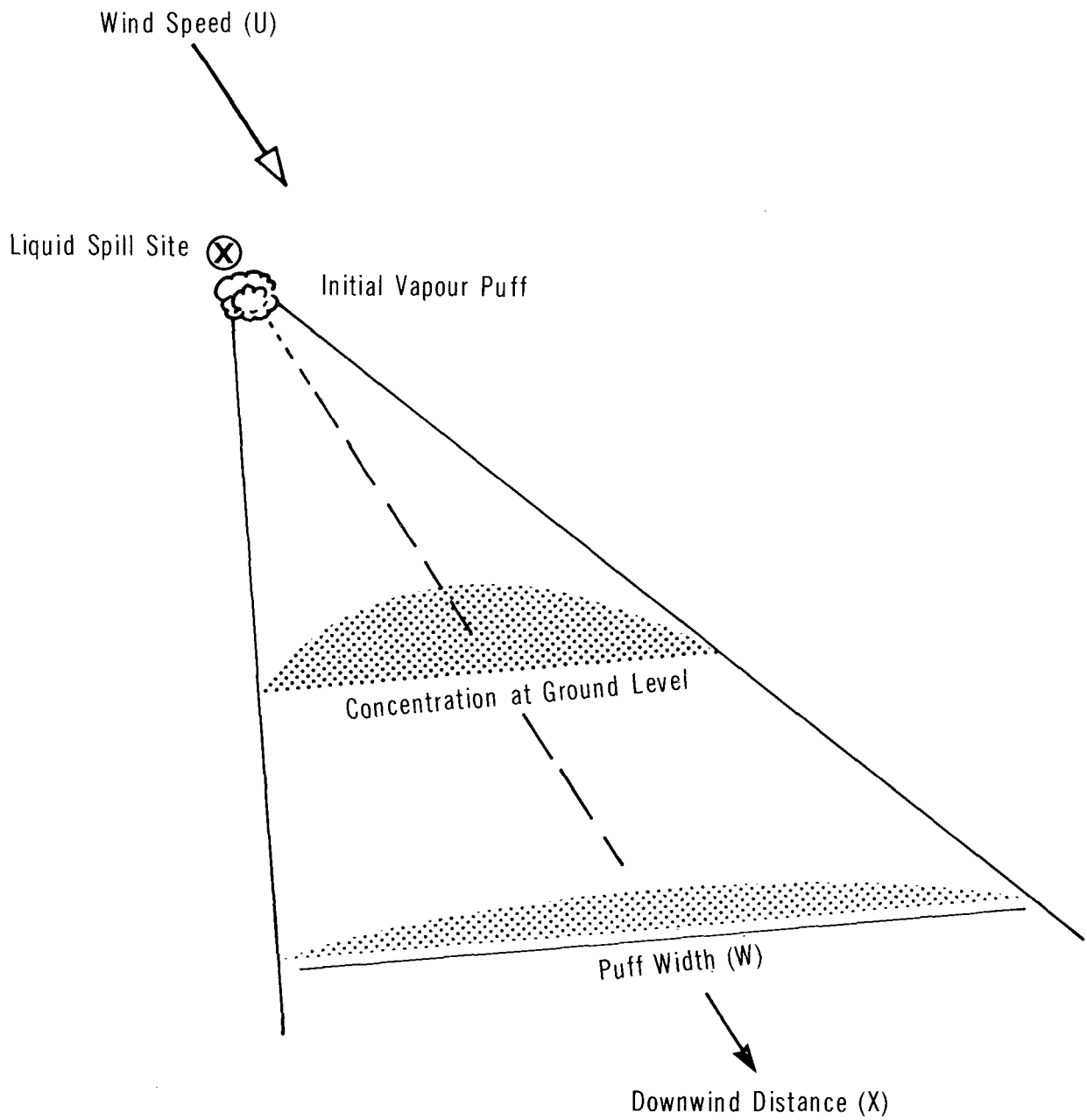
PROPYLENE

**FLOW CHART TO DETERMINE
VAPOUR HAZARD ZONE**

```
┌─────────────────────┐
│      ACCIDENT:      │
│   LIQUID SPILLED    │
└─────────────────────┘
          │
┌─────────────────────┐
│ DETERMINE TOTAL AMOUNT │
│      DISCHARGED     │
└─────────────────────┘
          │
┌─────────────────────────────┐
│ DETERMINE WIND SPEED (U)    │
│      AND DIRECTION (D)      │
└─────────────────────────────┘
          │
┌─────────────────────────────┐
│ DETERMINE WEATHER CONDITION │
└─────────────────────────────┘
          │
┌──────────────────────────────────┐
│ DETERMINE HAZARD CONCENTRATION   │
│ (C) - LOWER OF LFL or TLV® × 10  │
└──────────────────────────────────┘
          │
┌─────────────────────┐
│   COMPUTE C ÷ Q_T   │
└─────────────────────┘
          │
┌──────────────────────────────────┐
│ CALCULATE HAZARD DISTANCE FROM   │
│   INSTANTANEOUS POINT SOURCE     │
└──────────────────────────────────┘
          │
┌─────────────────────┐
│  CALCULATE HAZARD   │
│ HALF-WIDTH (W/2)max.│
└─────────────────────┘
          │
┌─────────────────────────────┐
│ DETERMINE TIME (t) SINCE SPILL │
└─────────────────────────────┘
          │
┌────────────────────────────────────┐
│ CALCULATE DISTANCE (X_t) TRAVELLED │
│ BY PUFF SINCE TIME (t) OF ACCIDENT │
└────────────────────────────────────┘
          │
┌─────────────────────┐
│ HAZARD ZONE AND PUFF │
│  LOCATION DEFINED   │
└─────────────────────┘
```

Step 1: Use Figure 9 Section 5.2

Time since rupture .... minutes

Equivalent diameter of rupture .... mm

Percent of chemical remaining .... %

Amount discharged:

q = 80 000 L – % × 80 000 L = ... L

Q_T= .... L × density (kg/L) ÷ 1000 = ... tonnes

= .... tonnes × 10^6 grams/tonne = ... grams

Step 2: Observed or estimated

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

Step 3: Use Table 7

Condition = ...

Step 4: C = 40 g/m^3 for propylene LFL

Step 5: Computation required

C/Q_T = ... m^{-3}

Step 6: Use Figure 15

X = ... km

Step 7: Use Table 8

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

Step 8:

t = ... s

Step 9: Use Figure 16

with U from Step 2

X_t = ... km

Maximum Downwind Hazard Distance, X (km)

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	All other weather conditions

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

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)

- U, the wind speed (m/s)

- the weather condition

- 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). For a simple asphyxiant, no TLV® value is pertinent. The concentration of contaminant that will lower the oxygen level to less than 18 percent v/v (asphyxiation level) is 14 percent v/v. Therefore, the lower of 14 percent v/v or the LFL is used. Note, to convert the LFL (in percent by volume) or the asphyxiation level (in percent by volume) to concentrations in g/m^3, use Figure 17.

5.3.2.2   Table 8: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T 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 the propylene Lower Flammability Limit (LFL) of 40 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the propylene vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of the LFL. Table 8 is therefore only applicable for a propylene ha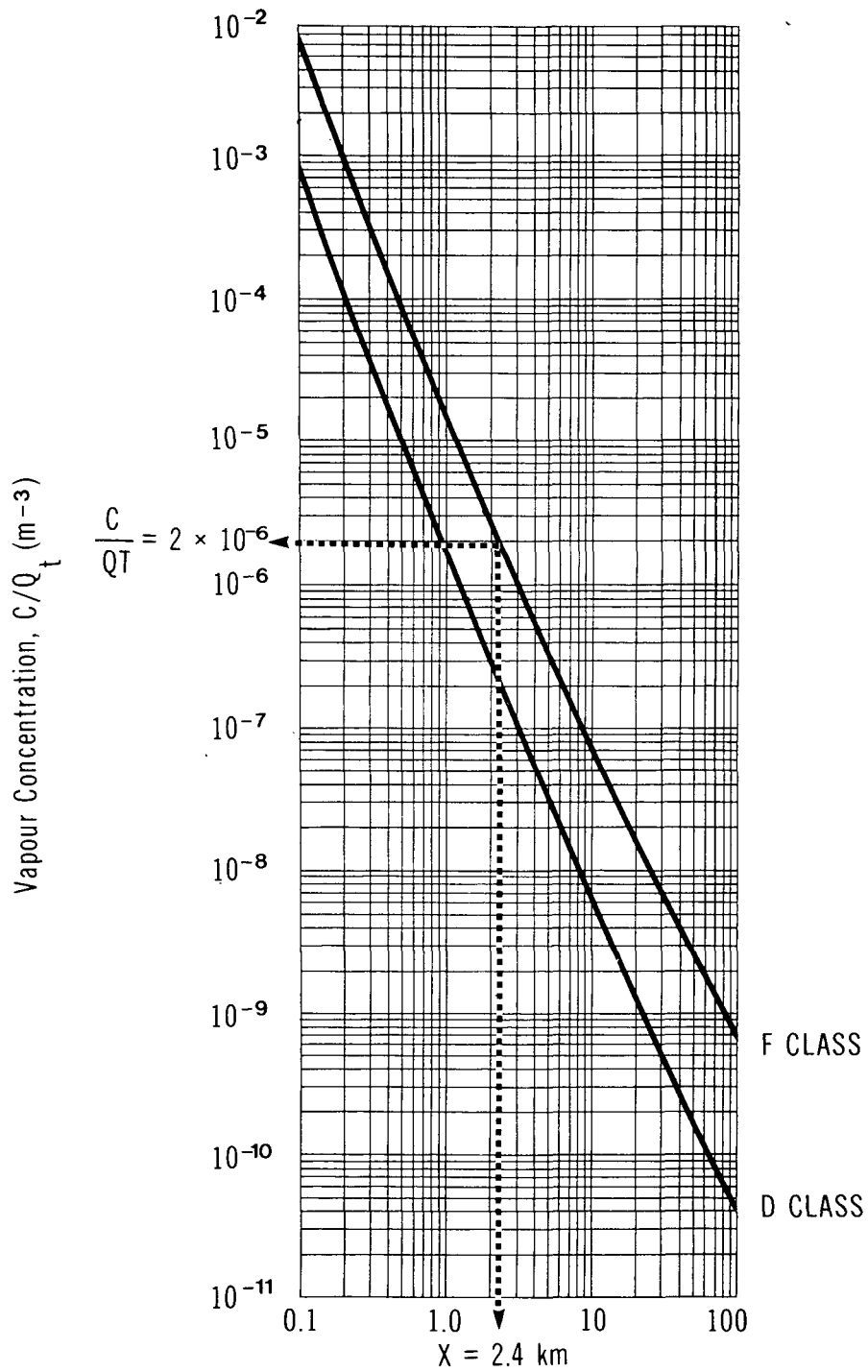zard concentration limit of the LFL or 40 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.5 to 1 300 000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 gal.) tank car spill, the mass

TABLE 8   MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR PROPYLENE)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
1 300 000	4 045	(99.9 km)*	60 000	1 860	(99.5 km)*
1 200 000	3 920		50 000	1 720	
1 000 000	3 660		25 000	1 280	
750 000	3 275		10 000	865	
500 000	2 805		5 000	645	
250 000	2 150		2 500	480	
200 00	1 980		1 000	335	
150 000	1 770		750	300	
100 000	1 520		500	255	
75 000	1 360		250	195	
50 000	1 160		100	135	
25 000	890		50	105	
10 000	640		25	80	
5 000	495	Q_T = 20 tonnes →	20	75	→ $(W/2)_{max}$ = 75 m
2 500	380		10	55	
1 000	270		5	45	
500	210		2.5	35	
250	165		1	25	
100	115		0.5	20	
50	90				
25	70				
20	65				
10	50				
5	40				
1	25				
0.5	10	* Data are provided up to a maximum downwind hazard distance of 100 km			

Example: Under weather condition F and Q_T = 20 tonnes, then puff hazard half-width $(W/2)_{max}$ = 75 m

Note: Above table is valid only for a propylene concentration of the LFL value, or 40 g/m^3.

spilled would be 48 700 kg or approximately 49 tonnes. Therefore, under class D of Table 8, data are provided for up to 26 500 times this amount. Clearly, this is a very unlikely amount to be spilled. This high value results from maintaining a consistent maximum downwind hazard distance (100 km) for the calculations.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.5 to 60 000 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 1200 times a standard rail car load (see note as per class D above).

Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values). Also refer to the example at the bottom of Table 8.

5.3.2.3 Figure 16: Puff travel time versus travel distance.

Figure 16 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

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

5.3.3 Sample Calculation.

The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid propylene. 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 quantity) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of liquid propylene 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_T = 20 tonnes

- Q_T = 20 tonnes or 20 x 10^6 g
- Q_T = 2 x 10^7 g

PROPYLENE

**PUFF TRAVEL TIME
VS TRAVEL DISTANCE**

Wind Speed, U (km/h)

Puff Travel Time (s)

Puff Travel Distance, X $_t$ (km)
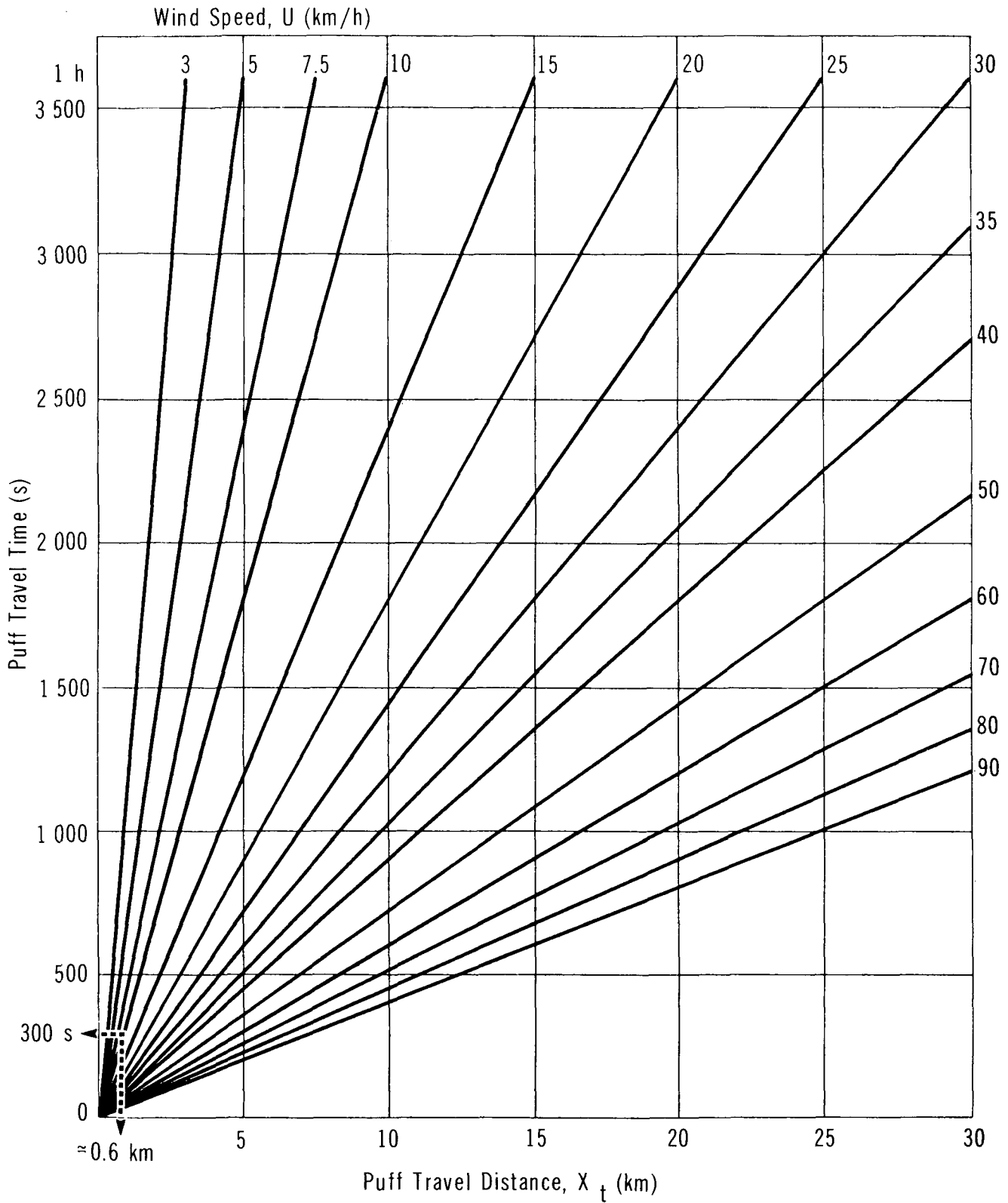
PROPYLENE

**CONVERSION OF LOWER FLAMMABILITY
LIMIT (LFL) UNITS (volume % to g/m³)**
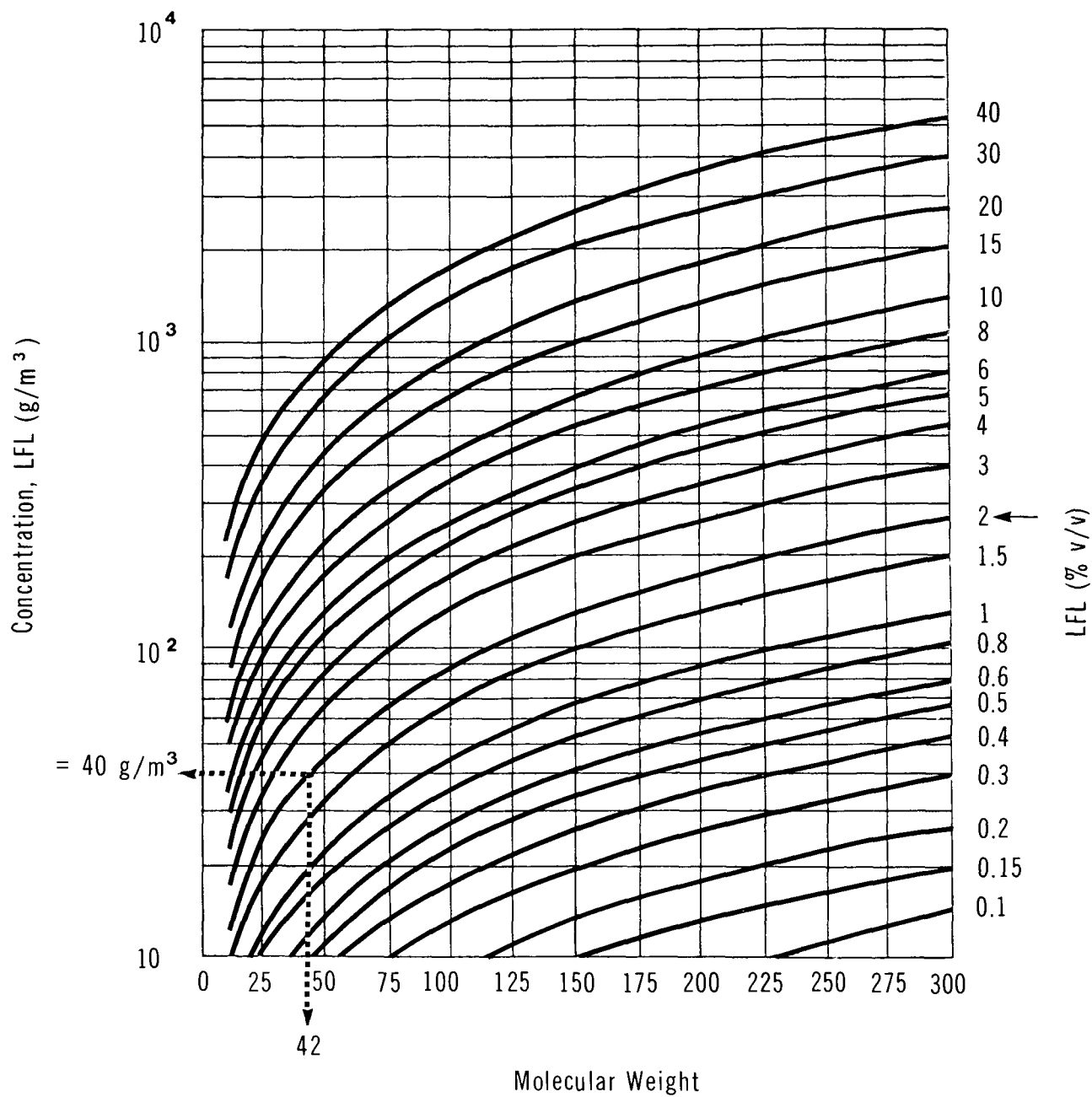
Example: Propylene, MW = 42, LFL = 2%, then LFL in g/m³ = 40

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

Step 2: Determine wind speed (U) and direction (D)

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

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

Step 3: Determine weather condition

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

Step 4: Determine hazard concentration limit (C)

- This is the lower of the asphyxiation level, or the LFL, so for propylene C = 40 g/m^3 (LFL = 40 g/m^3; asphyxiation level ≃ 280 g/m^3)

Step 5: Compute C/Q_T

- $$C/Q_T = \frac{40}{2 \times 10^7} = 2.0 \times 10^{-6} \ m^{-3}$$

Step 6: Calculate hazard distance (X) from the instantaneous point source

- From Figure 15, with $C/Q_T = 2.0 \times 10^{-6} \ m^{-3}$ and weather condition F, X ≃ 2.4 km

Step 7: Calculate puff hazard half-width, $(W/2)_{max}$

- Use Table 8
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 75 m

Step 8: Determine the time since spill

- t = 5 min x 60 = 300 s

Step 9: Calculate distance travelled (X_t) by vapour puff since time of accident

- Using Figure 16 with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10:
- Map the hazard zone
- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (75 m) by the maximum hazard distance downwind of the instantaneous point source (2.4 km) along the direction of the wind, as shown in Figure 18
- If the wind is reported to be fluctuating by 20° around 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 19

FIGURE 18

PROPYLENE

**HAZARD AREA FOR STEADY
WINDS, EXAMPLE PROBLEM**

Wind U = 7.5 km/h from 315° (NW)

Spill Site

Hazard Area

X = 2.4 km

Puff Hazard Half-width

$(W/2)_{max.} \cong 75$ m
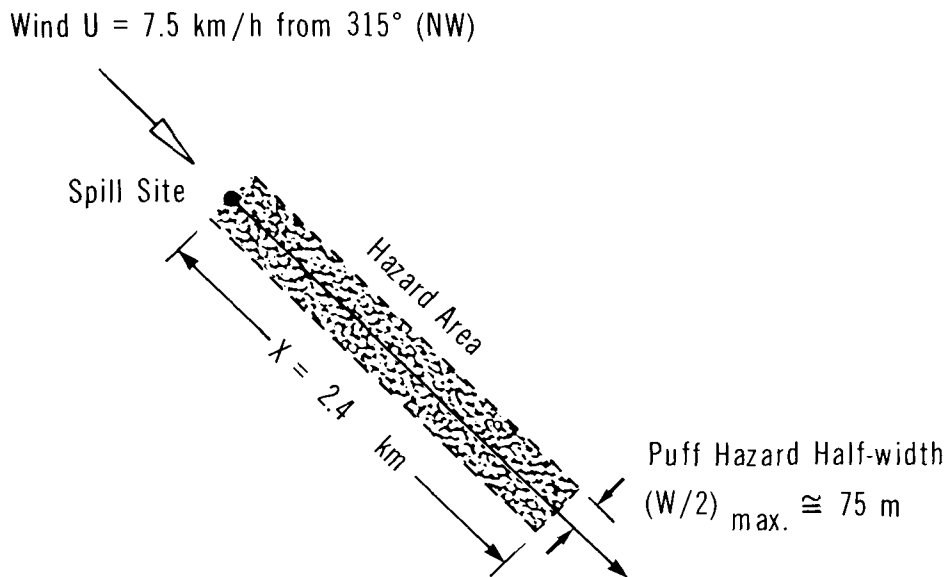
FIGURE 19

PROPYLENE

**HAZARD AREA FOR UNSTEADY
WINDS , EXAMPLE PROBLEM**

Wind U = 7.5 km/h from 315° ± 10°

Spill Site

Hazard Area

X = 2.4 km

10°

Puff Hazard Half-width

$(W/2)_{max.} \cong 75$ m

Effective Puff Hazard
Half-width

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

$= \underline{\quad 2.4 \times \quad} 1000 \times \tan 10° + \underline{\quad 75 \text{ m} \quad}$

$= \underline{\quad 500 \quad}$ m
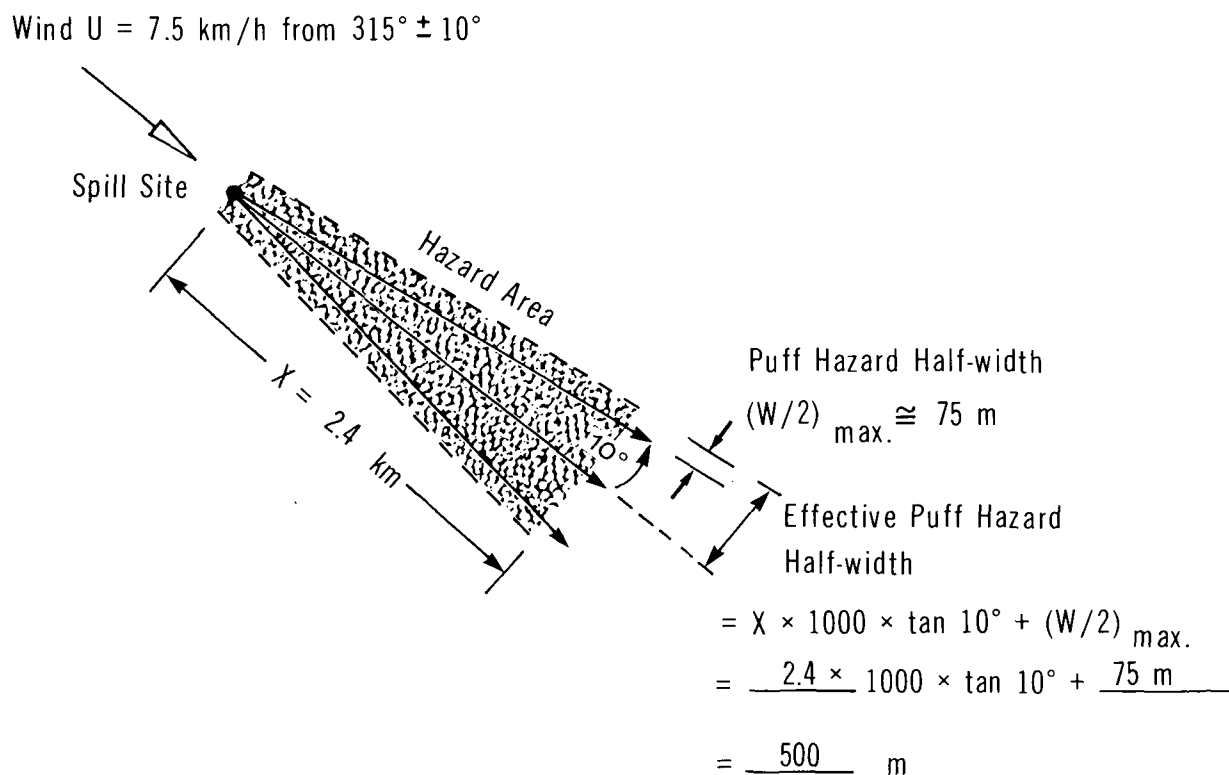
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 14 minutes before the puff reaches the maximum downwind hazard distance of 2.4 km

5.4 Behaviour in Water

5.4.1 Introduction.

When spilled on water, propylene will evaporate and at the same time will spread on the surface. Because it has a low solubility, little propylene will be lost from the pool by dissolution. For the purpose of nomogram preparation, the extent of spread on the surface of the water has been estimated, accounting for the loss due to vaporization.

The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since cryogenic liquids, such as propylene, are evaporated quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size.

5.4.2 Nomogram for Spreading on Still Water.

Figure 20 is presented to simplify the calculation of spreading on still water (without dissolution) and to estimate the time for complete evaporation for a range of spill sizes. Assuming no dissolution in water, Figure 20 provides a simple means of estimating the maximum spill radius for propylene, if the spill size is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The bracketed figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not considered.

5.4.3 Sample Calculation.

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

FIGURE 20

PROPYLENE
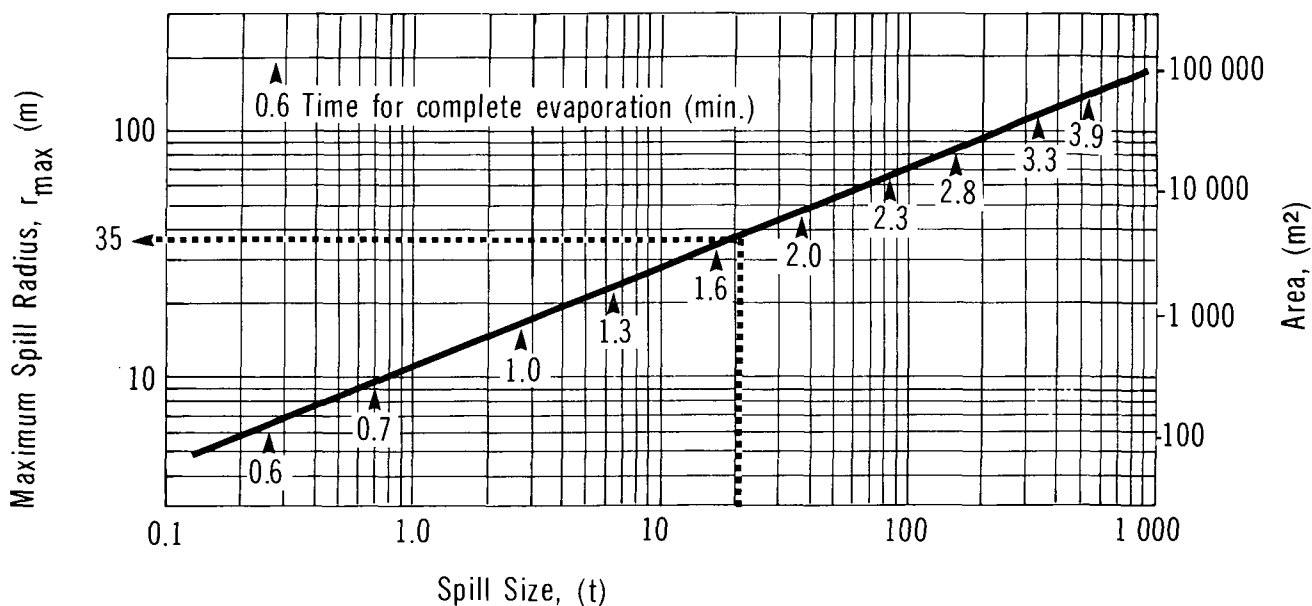
Solution

- Use Figure 20
- With mass = 20 tonnes, r_{max} = 35 m
- Time for complete evaporation is about 1.7 min

5.5 Subsurface Behaviour: Penetration into Soil

Because propylene boils at -48°C and is insoluble in water, infiltration of either liquid or gaseous propylene into soil, and from it into ground water, is not likely to present a problem in foreseeable spill circumstances. Because of this, no models to estimate propylene movement in soil have been prepared.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. No limits have been set in Canada for propylene in drinking water; 0.5 mg/L is recommended as a maximum in drinking water in the USA (WQCDB-1 1970; Verschueren 1984). The USSR also has a limit of 0.5 mg/L based on organoleptic qualities.

6.1.2 Air. No specific limits have been promulgated or recommended in Canada or the United States.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Propylene has been assigned a TL_m 96 of greater than 1000 mg/L (RTECS 1979).

6.2.2 Measured Toxicities. None available.

6.3 Toxicity to Other Biota

6.3.1 Plants. Seed plants have shown some effects from propylene exposure; examples cited are epinasty in tomato petiole at 50 ppm for 2 days, and declination in sweet pea seedlings at 1000 ppm for 3 days (Verschueren 1984).

6.4 Degradation

Propylene volatilizes and disperses quickly; on-site degradation is therefore not a factor (OHM-TADS 1981).

6.5 Long-term Fate and Effects

There is no potential for food chain contamination (CHRIS 1978).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the toxicological effects of test animal and human exposures to propylene. Propylene has been classified as a simple asphyxiant by the USA-ACGIH. It has anesthetic properties. The gas is a nonirritant to the skin; however, burns may result from direct contact with the liquid form.

Propylene has been reported in TOX TIPS (a summary of current research activity) as having been selected for testing by the NCI for carcinogenesis bioassay. No data were encountered in the literature regarding the effect of propylene exposure on reproduction. Propylene was not found to be mutagenic when tested with *E. coli*. This chemical has been reported in the EPA TSCA Inventory.

The toxicological data summarized here have been extracted from reliable standard reference sources and are representative of information in the literature. 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 propylene are based upon its asphyxiant properties. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
Simple Asphyxiant	USA-ACGIH	Minimal oxygen content of breathing air should be 18 percent by volume	TLV 1981
Maximum Permissible Level		4000 ppm	Braker 1977
Threshold Limit Value		4000 ppm	CHRIS 1978
Asphyxiant Simple	Québec	Minimum oxygen content should be 19.5 percent by volume under normal atmospheric conditions	Québec 1979
Short-term Exposure Limits (STEL)		No data	
Other Human Toxicities		No data	

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Gas	Not irritating to the skin even in high concentrations	MCA 1956
Liquid	Contact will cause frostbite	CHRIS 1978

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Gas	Not noticeably irritating to eyes even at high concentrations	MCA 1956
Liquid	Contact will cause frost burns	MCA 1956

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Aromatic, neutral to unpleasant (Verschueren 1984). Odour Index: 14 792 (Verschueren 1984).

Parameter	Concentration	Reference
Odour Threshold	17.3 mg/m^3 (10 ppm)	Patty 1981
TOC (recogn.)	67.6 ppm	Verschueren 1984
TOC (Absolute Perception Limit)	22.5 ppm	Verschueren 1984

7.3.2 Taste. No data.

7.4   Long-term Studies

7.4.1   Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
75, 50 and 40 percent (by volume) (Few min)	Reddening of eyelids, flushed face, lacrimation, coughing. No variation in respiratory or pulse rates or electro-cardiograms noted	Patty 1981
50 percent (2 min)	Anesthesia in 2 minutes, followed by complete recovery without any physiologic indications	Patty 1981
40 and 35 percent (Unspecified duration)	Two subjects vomited during or after experiments. One complained of vertigo	Patty 1981
33 and 24 percent (3 min)	Mild intoxication, paresthesia, inability to concentrate. Unconsciousness	Patty 1981
24 percent propylene and 33 percent oxygen (3 min)	Intoxication, unconsciousness	MCA 1956
12.8 percent (1 min)	Mild intoxication, paresthesia, inability to concentrate	Patty 1981
6.4 percent propylene and 26 percent oxygen (2.25 min)	Mild intoxication, drowsiness, tingling of the skin and inability to concentrate	MCA 1956
6.4 percent (2.25 min)	Mild intoxication, paresthesia, inability to concentrate	Patty 1981
SPECIES: Dog		
Unspecified	Cardiac sensitizer	Patty 1981
SPECIES: Cat		
Concentration of 70 percent	Blood pressure decrease and rapid pulse	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
Concentration of 70 percent (1 to 3 min)	Deep anesthesia with no CNS signs or symptoms	Patty 1981
Concentration of 65 percent (2 to 5 min)	Deep anesthesia with no CNS signs or symptoms	Patty 1981
Concentration of 40 percent	Light anesthesia, no toxic symptoms within 6 hours	Patty 1981

7.4.2   Ingestion. Ingestion is unlikely as propylene is a gas under normal atmospheric conditions.

7.4.3   Mutagenicity.   Propylene was not mutagenic when tested with *E. coli.* (Patty 1981).

7.5   Symptoms of Exposure

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

7.5.1   Inhalation.

1. Need for fresh air.
2. Rapid, occasionally irregular breathing.
3. Headache.
4. Fatigue.
5. Giddiness
6. Nausea and vomiting.
7. Mental confusion.
8. Exhaustion.
9. Narcosis, irregular heartbeat.
10. Loss of consciousness.
11. Convulsions.
12. Death.

7.5.2   Ingestion. Ingestion is unlikely as propylene is a gas under normal atmospheric conditions.

7.5.3 **Skin Contact.** Gaseous propylene is not irritating to skin (Patty 1981). Liquid may cause frostbite (CHRIS 1978).

1. Feeling of intense cold (Lefèvre 1980).
2. Insensitivity to pain.
3. Congestion of blood vessels, rapidly becoming painful (freezing) (Lefèvre 1980).

7.5.4 **Eye Contact.** The vapours have no serious irritating effect on the eyes (MCA 1956). Contact with the liquid may cause frostbite (Lefèvre 1980).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Propylene 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	●													NFPA 1978
Heat	●													NFPA 1978
High Pressure		●			●								Explosive decomposition under 486 000 kPa pressure	Bretherick 1979
Water (42 to 75°C)		●											Vapour-expansion explosion of liquefied propylene on contact with warm water	Bretherick 1979; Kirk-Othmer 1982
SPECIFIC CHEMICALS														
Lithium Nitrate and Sulphur Dioxide		●			●								Mixture of three explodes (polymerizes)	Bretherick 1979
Nitrogen Tetroxide		●											Mixture explodes	NFPA 1978
Trifluoromethyl Hypofluorite		●											Explodes on mixing with several hydrocarbons	Bretherick 1979

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 some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1   Fire Concerns. Propylene is an extremely flammable gas. Its vapours may travel along surfaces to ignition sources and flash back. The gas forms explosive mixtures with air (NFPA 1978). Flame impingement on the outer shell (vapour area) of a propylene tank can weather the metal and lead to a boiling liquid expanding-vapour explosion (Bleve) (CCPA 1983).

9.1.2   Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent puncture (ERG 1980).

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

Move containers from fire area if this can be done without risk. Stay away from tank ends. For massive fire in cargo area, use unmanned hose holder or monitor nozzles (ERG 1980).

9.1.3   Spill Actions, Cleanup and Treatment

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 (Air Products SGMSDS 1978). Water spray may be used to reduce vapours and to protect men effecting the shut-off (ERG 1980; MCA 1956).

Leaking containers should be removed to an isolated, well-ventilated area and, if possible, the contents transferred to other suitable containers. If the leak cannot be stopped, let the gas disperse in air (MCA 1956).

9.1.3.2   Spills on land. As propylene will evaporate rapidly, treat as vapour spill.

9.1.3.3   Spills in water. As propylene will evaporate rapidly, treat as vapour spill.

9.1.4   Disposal. Return all unused quantities to manufacturing company for disposal (Air Products SGMSDS 1978). Propylene may be burned but do not allow the flame to go out since the release of a cloud of propylene to the environment poses a major fire/explosion hazard (OHM-TADS 1981; MCA 1956).

9.1.5   Protective Measures. For <u>entry</u> into a situation where the spilled material and its characteristics are <u>unknown</u>, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be propylene:

- Safety goggles, impervious clothing and positive pressure self-contained breathing apparatus should be worn (OHM-TADS 1981; Air Products SGMSDS 1978).
- Rubber gloves and face protecting shield (HTHC 1981).
- Chemical safety goggles for eye protection and faceshields for face protection should also be considered (MCA 1956).
- Plastic or neoprene-coated canvas gloves should be worn where liquid propylene is handled (MCA 1956).

9.1.6   Special Precautions. Protect cylinder against physical damage. Store cylinders in a cool, dry, well-ventilated area of noncombustible construction. Protect cylinders from excessive temperature rise by storing away from sources of heat. No part of a cylinder should be subjected to a temperature above 52°C. Store cylinders in an upright position and secure firmly. Segregate full and empty cylinders. Isolate from oxygen and other oxidizers. Avoid exposure to areas where salt or other corrosive chemicals are present. Ground and bond all lines and equipment used with propylene. Do not use near sparking motors or other equipment which is not explosion-proof (Air Products SGMSDS 1978).

10 PREVIOUS SPILL EXPERIENCE

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

Although spills of this material have been recorded, no significant information regarding cleanup methods or response has been documented.

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 Propylene in Air

11.1.1   Gas Chromatography (ASTM 1981). A range of 0.1 percent and above of propylene in air may be determined by gas chromatography. A direct injection of the sample is suggested.

A known volume of air is drawn into a gas sampling bag. A sample size of 5 L is recommended. A suitable sample bag connection which allows injection of the sample into the detector is used. The concentration is determined using retention times and peak height as well as a standard curve.

Typical gas chromatograph conditions are: a 30 ft. x 1/4 in. column of 17 percent hexamethylphosphoramide on 35 to 80 mesh chromosorb, helium carrier gas flow rate of 60 to 70 mL/min, column temperature at 30°C, and thermal conductivity detection.

11.2   Qualitative Method for the Detection of Propylene in Air

The sample is collected using a vacuum pump and a 7 cm charcoal adsorbent tube. It is then desorbed with 0.5 mL of carbon disulphide. Two drops of sample are placed in a clean test tube and a 1 percent solution of bromine in carbon tetrachloride is

added drop-wise. De-colouration of the bromine solution indicates the presence of an alkene (Owen 1969; Supelco 1977).

11.3   Quantitative Method for the Detection of Propylene in Water

11.3.1   Partition Infrared (AWWA 1981). A range of 17.01 to 170.12 ppm propylene may be determined in water using a partition infrared method which is suitable for a variety of organic compounds.

A minimum of 1 L of representative sample is collected in an appropriate container and acidified to pH 2 or lower with dilute hydrochloric acid. A 5 mL volume of acid should be sufficient. The sample is transferred to a separatory funnel. A 30 mL volume of Freon 113® (1,1,2-trichloro-1,2,2-trifluoroethane) is used to rinse and is then added to the separatory funnel. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon 113® extractions are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon 113® and the sample scanned on a suitable infrared spectrophotometer from 3000 to 900 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.4   Qualitative Method for the Detection of Propylene in Water

The sample is collected as in Section 11.3.1. Two drops of sample are placed in a dry test tube and a 1 percent solution of bromine in carbon tetrachloride is added drop-wise. De-colouration of the bromine solution indicates the presence of an alkene (Owen 1969).

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EnviroTIPS

Common Abbreviations

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