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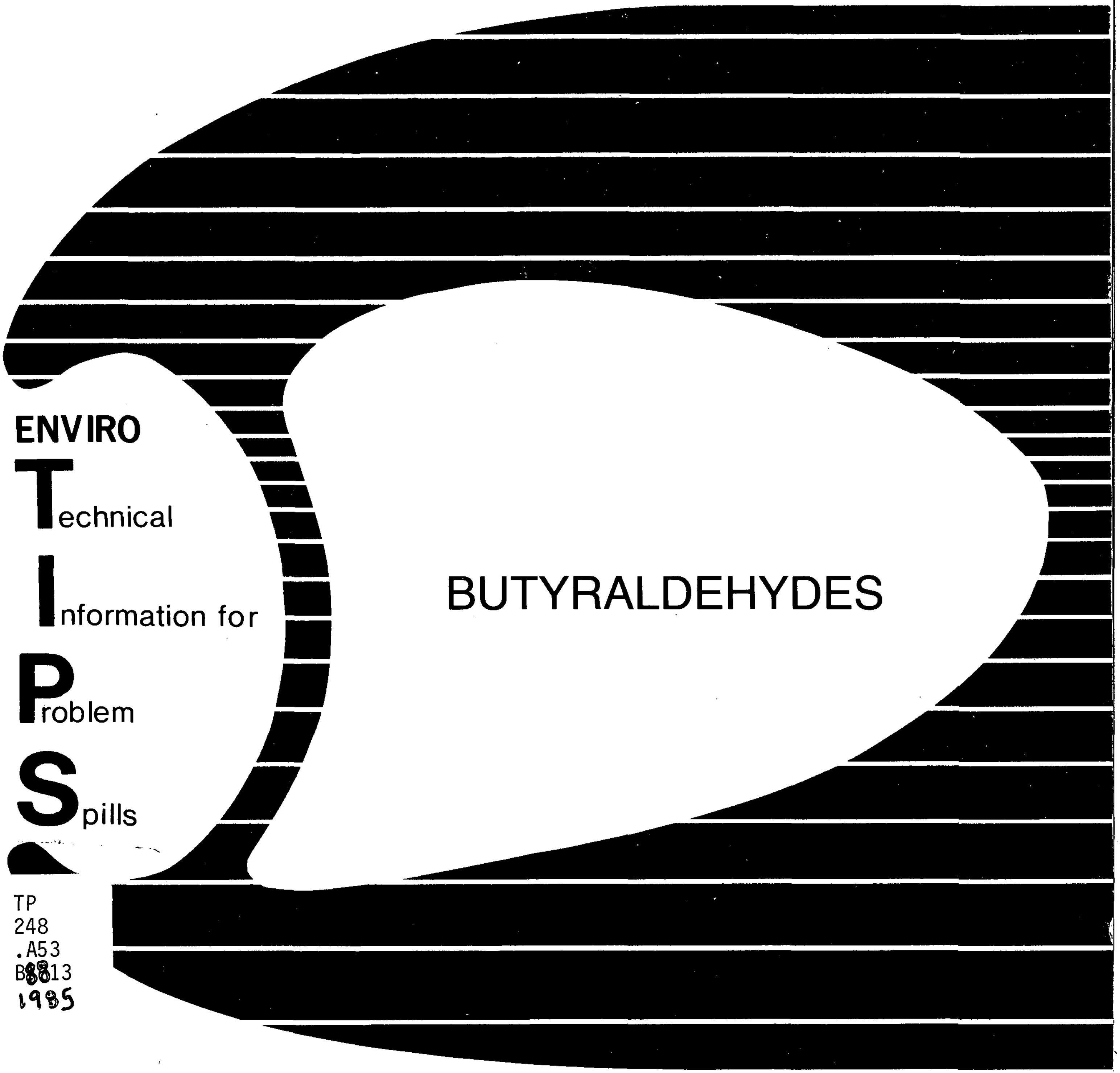

ENVIRO
Technical
Information for
Problem
Spills

BUTYRALDEHYDES

June 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.

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BUTYRALDEHYDES

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

June 1985

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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 TIPS 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 of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation and Waterloo Engineering Limited.

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1 SUMMARY

BUTYRALDEHYDES ($CH_3(CH_2)_2CHO$) or ($(CH_3)_2CH_2CHO$)(iso)

Colourless liquid with a pungent odour.

SYNONYMS

n-Butyraldehyde: n-Butanal, Butyl Aldehydes, Butyrals, Butyric Aldehydes, Butals, Butaldehydes, Butalydes, Aldéhyde Butyrique (Fr.); iso-Butyraldehyde: iso-Butanal, 2-Methyl Propanol, Isobutyric Aldehyde, Isobutyl Aldehyde

IDENTIFICATION NUMBERS

UN No. 1129; CAS No. 123-72-8; OHM-TADS No. 7216620; STCC No. 4908119

GRADES & PURITIES

Commercial: water-saturated, 97 percent; dry, 99.5 percent

IMMEDIATE CONCERNS

Fire: Flammable. Flashback along vapour trail may occur.

Human Health: Moderately toxic by dermal route.

Environment: Harmful to aquatic life in low concentrations.

PHYSICAL PROPERTY DATA

	n-Butyraldehyde	iso-Butyraldehyde
State (15°C, 1 atm):	liquid	liquid
Boiling Point:	75.7°C	64.5°C
Melting Point:	-99.0°C	-65.9°C
Flammability:	flammable	flammable
Flash Point:	-22°C (CC)	-18°C (CC)
Vapour Pressure:	12.2 kPa (20°C)	18.4°C kPa (20°C)
Specific Gravity:	0.817 (20°/4°C)	0.794 (20°/4°C)
Solubility (in water):	7.9 percent (w/w) (20°C)	6.7 percent (w/w) (20°C)
Behaviour (in water):	floats and mixes with no reaction	floats and mixes with no re-
Behaviour (in air):	vapour is heavier than air	action vapour is heavier than air
Odour Threshold Range:	4 to 25 ppb	25 to 300 ppb

ENVIRONMENTAL CONCERNS

n-Butyraldehyde is harmful to aquatic life in low concentrations, generally below 10 ppm. Waterfowl are threatened by spills of butyraldehyde on water. n-Butyraldehyde degrades at a moderate rate and shows no potential for bioconcentration.

HUMAN HEALTH

No TLV® or IDLH established

Exposure Effects

Inhalation:	Irritation to mucous membranes causing difficult breathing, headache, vomiting, nausea and muscular weakness, possible loss of consciousness.
Contact:	Irritation to skin and eyes.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". 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 skin contact or inhalation; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use alcohol foam, dry chemical or carbon dioxide to extinguish. Water may be ineffective as it may spread burning liquid. Cool fire-exposed containers with water. Containers may explode in fires.

COUNTERMEASURES

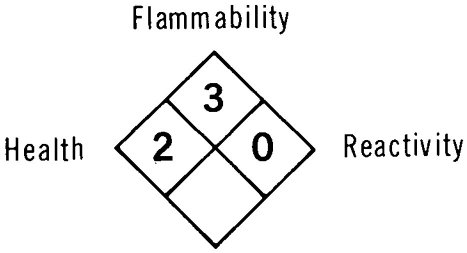
Emergency Control Procedures in/on

Soil:	Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb small amounts of spill with natural or other noncombustible sorbents and shovel into containers with covers.
Water:	Contain with booms, weirs, water diversion or natural barriers.
Air:	Use water spray to disperse flammable vapours. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

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

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties	Normal	Iso
Appearance	Colourless, watery liquid (CHRIS 1978)	
Usual shipping state	Liquid (CCD 1977)	
Physical state at 15°C, 1 atm	Liquid	Liquid
Melting point	-99°C (CRC 1980)	-65.9°C (Verschueren 1984)
Boiling point	75.7°C (CRC 1980)	64.5°C (Ullmann 1975)
Vapour Pressure	12.2 kPa (20°C) (Kirk-Othmer 1978)	18.4 kPa (20°C) (Kirk-Othmer 1978)
Densities		
Density	0.8048 g/L (20°C) (Kirk-Othmer 1978)	0.7938 g/L (20°C) (Kirk-Othmer 1978)
Specific gravity	0.8170 (20°/4°C) (CRC 1980)	0.7938 (20°/4°C) (CRC 1980)
Vapour density	2.48 (Verschueren 1984)	2.48 (Verschueren (1984)
Fire Properties		
Flammability	Flammable liquid (NFPA 1978)	
Flash point CC OC	-22°C (NFPA 1978) -9.4°C (Kirk-Othmer 1978)	-18°C (NFPA 1978) -10.6°C (Kirk-Othmer 1978)
Autoignition temperature	218°C (NFPA 1978)	210°C (NFPA 1978)
Burning rate	4.4 mm/min (CHRIS 1978)	4.8 mm/min (CHRIS 1978)
Upper flammability limit	12.5 percent (v/v) (NFPA 1978)	10.6 percent (v/v) (NFPA 1978)
Lower flammability limit	1.9 percent (v/v) (NFPA 1978) 1.4 percent (v/v) (Ullmann 1975)	1.7 percent (v/v) (NFPA 1978) 1.6 percent (v/v) (Ullmann 1975)

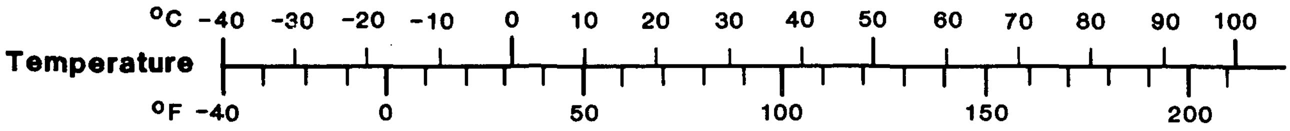
	Normal	Iso
Heat of combustion (25°C)	2477.1 kJ/mole (Sussex 1977)	2467.2 kJ/mole (Sussex 1977)
Combustion products	Water and carbon dioxide (CRC 1980)	
Flashback potential	Vapours may travel considerable distance to a source of ignition and flash back (NFPA 1978)	
Explosiveness	Vapours form explosive mixtures with air (NFPA 1978)	
Behaviour in a fire	Butyraldehydes are easily ignited and fires are difficult to control due to ease of re-ignition (NFPA 1978)	
Other Properties		
Molecular weight of pure substance	72.12 (CRC 1980)	72.12 (CRC 1980)
Constituent components of typical commercial grade	97 to 99.5 percent n-butyraldehyde (MCA 1960)	97 percent iso-butyraldehyde (MCA 1960)
Refractive index	1.3843 (20°C) (CRC 1980)	1.3730 (20°C) (CRC 1980)
Viscosity	0.433 mPa•s (20°C) (Kirk-Othmer 1978) 0.087 mPa•s (vapour at 100°C) (PPH 1984)	0.445 (20°C) (Ullmann 1975)
Liquid interfacial tension with air	24.6 mN/m (20°C) (CHRIS 1978) 29.9 mN/m (24°C) (Ullmann 1975)	23.2 mN/m (20°C) (Ullmann 1975)
Liquid interfacial tension with water	5.7 mN/m (22°C) (CHRIS 1978)	7.2 mN/m (23°C) (CHRIS 1978)
Latent heat of fusion (at melting point)	11.1 kJ/mole (Lange's Handbook 1979)	

	Normal	Iso
Latent heat of vaporization (25°C)	33.7 kJ/mole (Sussex 1977)	31.5 kJ/mole (Sussex 1977)
Heat of formation	-241.2 kJ/mole (25°C) (Sussex 1977)	-248.9 kJ/mole (25°C) (Sussex 1977)
Dipole moment	2.72 D (vapour at 20°C) (Kirk-Othmer 1978)	-
Dielectric constant	14.9 (20°C) (Ullmann 1975)	13.6 (20°C) (Ullmann 1975)
Ionization potential	9.83 eV (Hernandez 1977)	9.82 eV (Hernandez 1977)
Heat capacity		
constant pressure (Cp)	153 J/(mole•°C) (Kirk-Othmer 1978)	183 J/(mole•°C) (Kirk-Othmer 1978)
constant volume (Cv)	141 J/(mole•°C) (Kirk-Othmer 1978; CHRIS 1978)	167 J/(mole•°C) (Kirk-Othmer 1978; CHRIS 1978)
Critical pressure	4053 kPa (CHRIS 1978)	4154 kPa (CHRIS 1978)
Critical temperature	248°C (Ullmann 1975)	267°C (Ullmann 1975)
Coefficient of thermal expansion	1.14 x 10^{-3}/°C (20°C) (CCD 1977)	
Thermal conductivity	1.42 x 10^{-3} W/(cm•K) (20°C), 1.67 x 10^{-4} W/(cm•K) (gas at 100°C) (PPH 1984)	
Saturation concentration (calc.)	436.5 g/m^3 (15°C) (CRC 1980)	670.3 g/m^3 (20°C) (Verschueren 1984)
Diffusivity (15°C)	0.086 cm^2/s (Perry 1973)	
Log$_{10}$ octanol/water coefficient (20°C)	1.20 (Hansch and Leo 1979) 0.87 (NRC 1981)	1.20 (Hansch and Leo 1979)

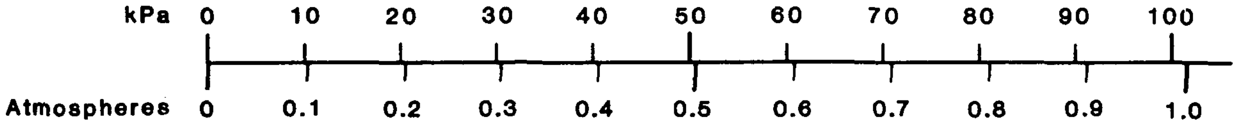
	Normal	Iso
Evaporation rate	1.9 g/(m^2s) (20°C, 4.5 m/s wind speed) (this work)	
Solubility		
In water	7.9 percent by wt. (20°C) (Kirk-Othmer 1978)	6.7 percent by wt. (20°C) (Ullmann 1975)
In other common materials	Miscible in ethanol and diethyl ether. Very soluble in acetone and benzene (CRC 1980)	Soluble in ethanol, acetone and chloroform (CRC 1980)
Azeotropes	with ethanol, 60.6 percent, BP = 70.7°C; with hexane, 74.0 percent, BP = 60°C; with water, 8.8 percent, BP = 68°C (Ullmann 1975)	with water, 6.0 percent, BP = 60.5°C (Ullmann 1975)
Vapour Weight to Volume Conversion Factor	1 ppm = 2.993 mg/m^3 (20°C) (Verschueren 1984)	

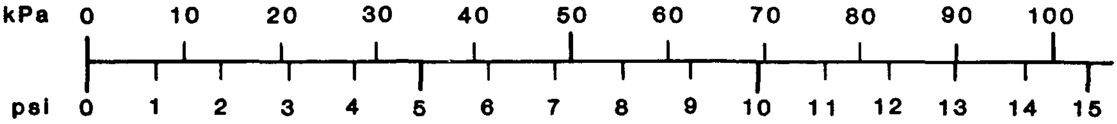
TABLE 1

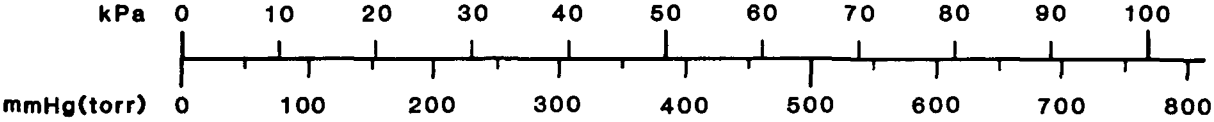
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

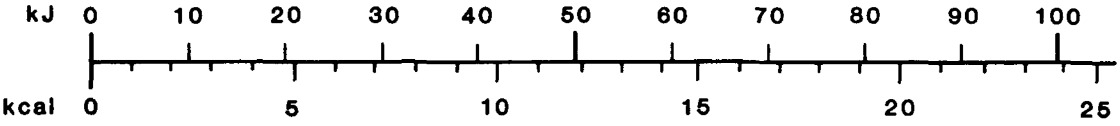
Dynamic 1 Pa·s = 1 000 centipoise (cP)

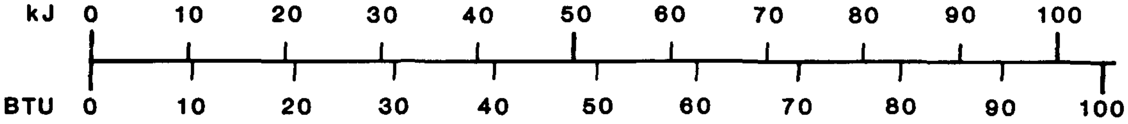
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





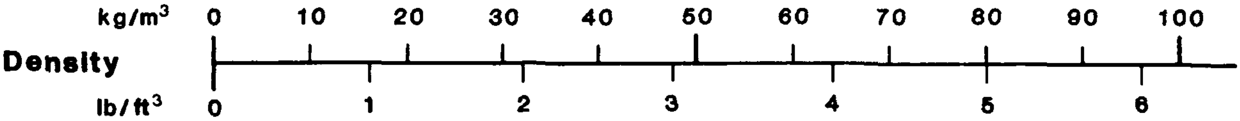


FIGURE 1

BUTYRALDEHYDES

VAPOUR PRESSURE vs TEMPERATURE

Reference: ISH 1977; KIRK-OTHMER 1978

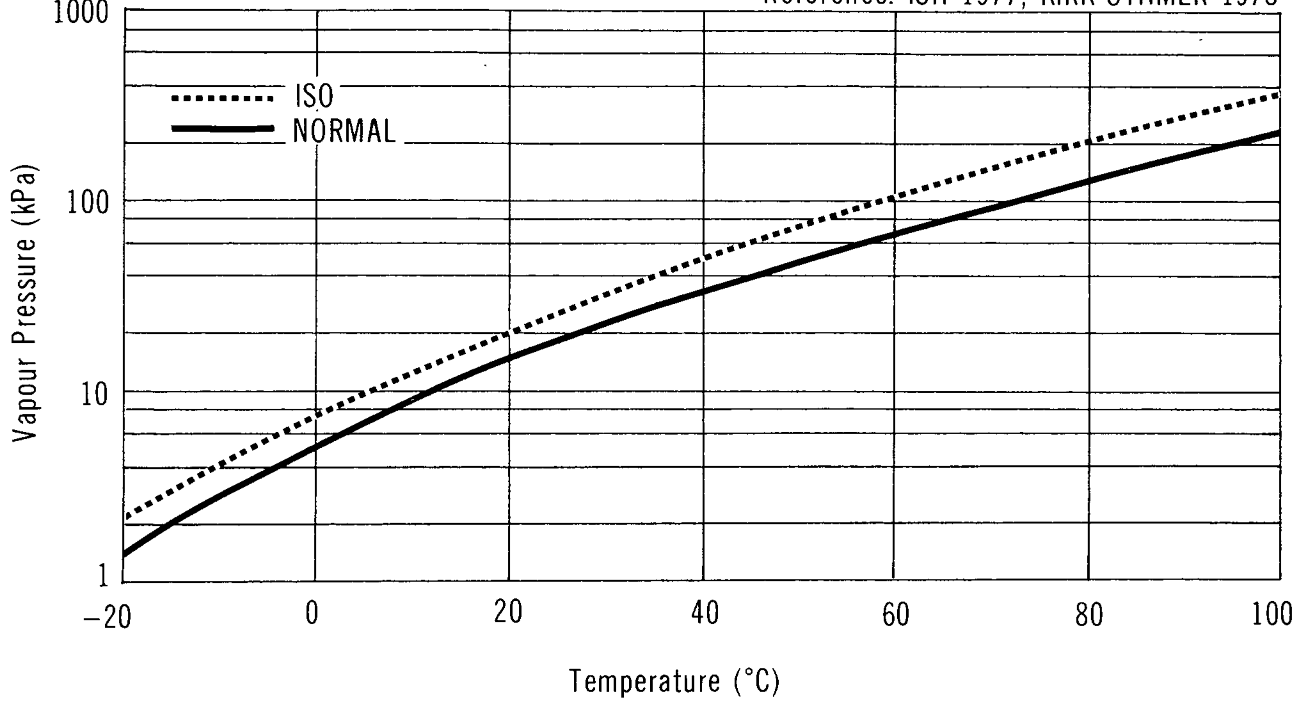


FIGURE 2

BUTYRALDEHYDES

LIQUID DENSITY

Reference: PPH 1984

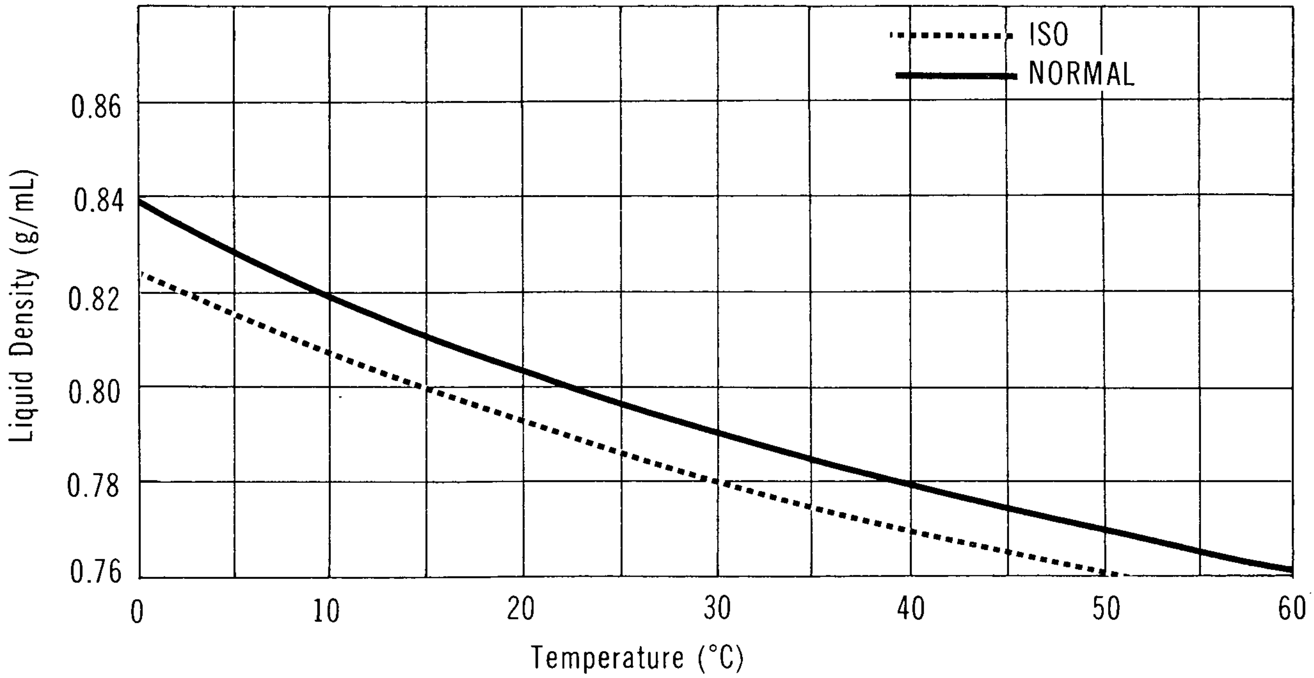


FIGURE 3

BUTYRALDEHYDES

WATER SOLUBILITY

Reference: ULLMANN 1975

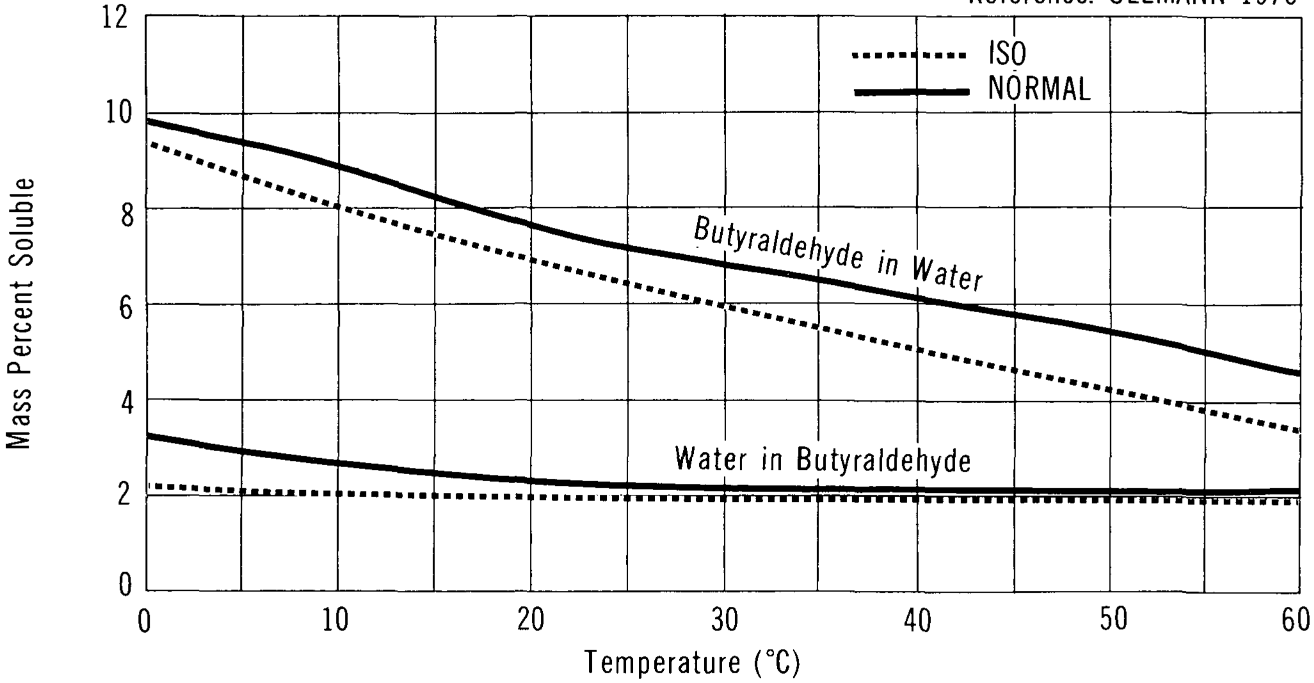


FIGURE 4

BUTYRALDEHYDES

LIQUID VISCOSITY

Reference: PPH 1984

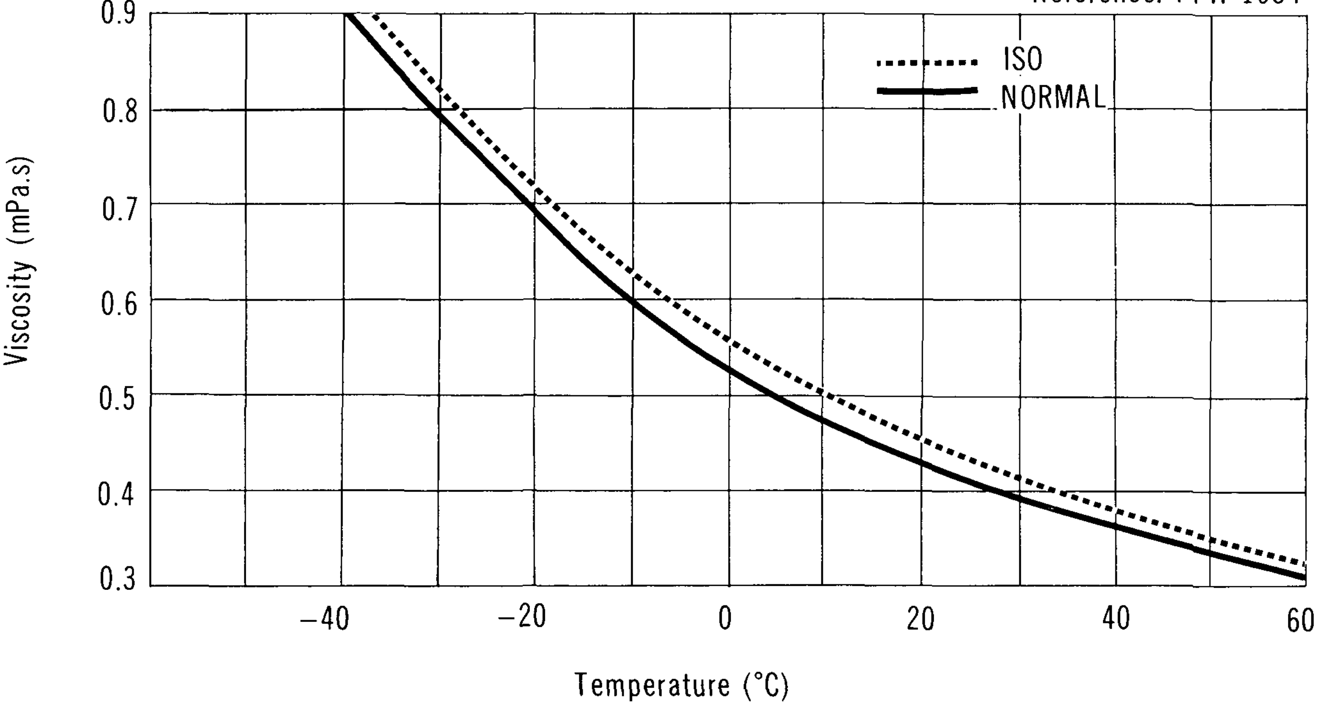
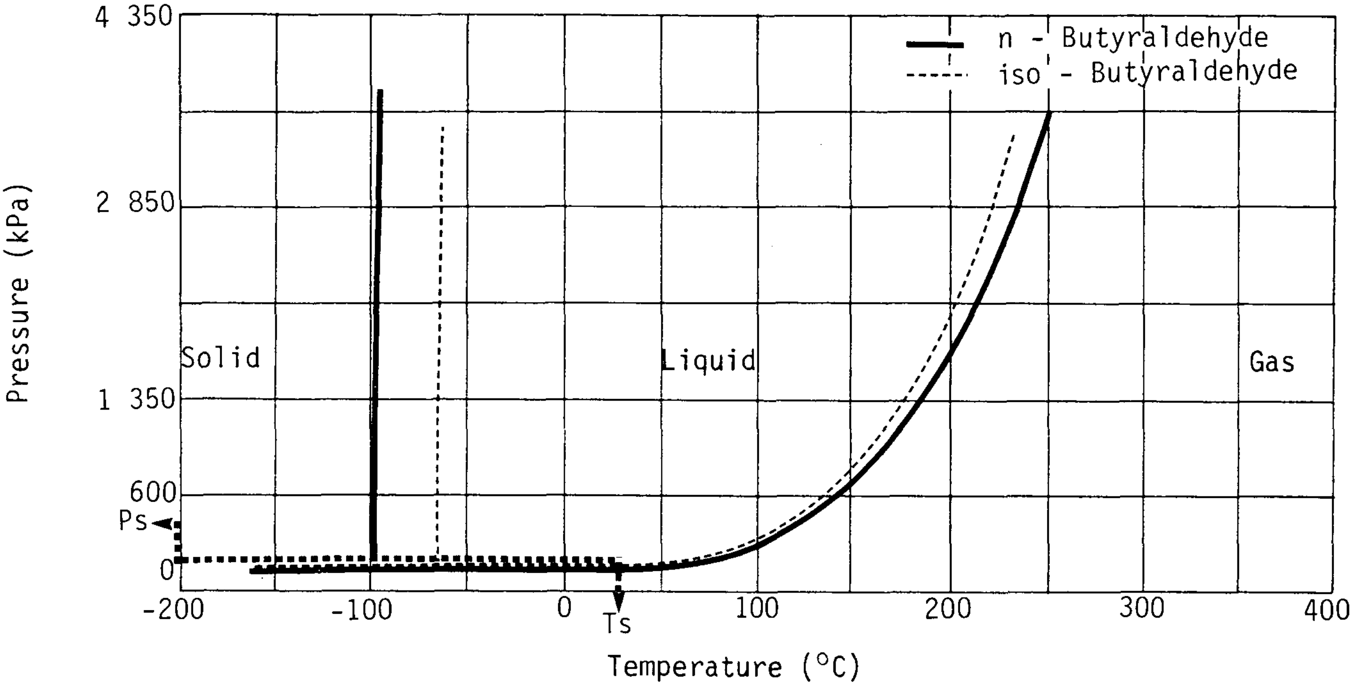


FIGURE 5

BUTYRALDEHYDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

Iso- and n-butyraldehydes are produced in a commercial grade, either in a water-saturated or a dry form, with 97 and 99.5 percent purities, respectively (MCA 1960). The contents of the typical commercial grades are given below (Ullmann 1975):

	n-Butyraldehyde	iso-Butyraldehyde
Content as n-butyraldehyde (percent)	96.0 (min.)	0.1 (max.)
Content as iso-butyraldehyde (percent)	0.3 (max.)	95.0 (min.)
Specific gravity (20/4°C)	0.807 to 0.812	0.790 to 0.794
Refractive index	1.381 to 1.382	1.373 to 1.376
Water content (percent)	3.0 (max.)	2.0 (max.)

3.2 **Domestic Manufacturer** (Corpus 1983; CBG 1980)

This is a corporate headquarter's address and is not intended as a spill response contact:

BASF Canada Ltd.
5850 Cote de Liesse
Montreal, Quebec
H4T 1C1
(514) 341-5411

3.3 **Other Supplier** (CBG 1980)

Eastman Chemical International Ltd.
40 Wynford Drive
Don Mills, Ontario
M3A 2L3
(416) 449-0160

3.4 Major Transportation Routes

Current Canadian production of butyraldehydes is in Laval, Quebec. Little transportation takes place outside of Eastern Canada.

3.5 **Production Levels** (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
BASF Canada, Laval, Quebec*		100
Domestic Production (1982)		67
Imports (1982)		0.03
	TOTAL SUPPLY	167.03

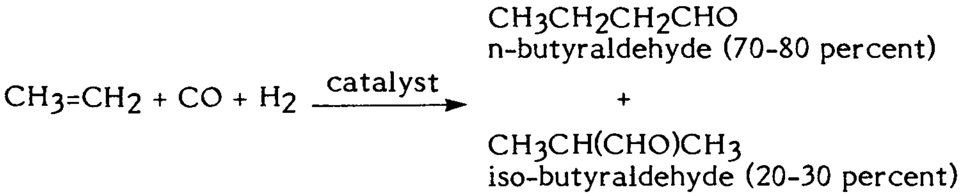
* Captive for use in manufacture 2-ethylhexanol and butanols.

3.6 **Manufacture of Butyraldehydes** (FKC 1975; Kirk-Othmer 1978)

3.6.1 General. Butyraldehydes may be produced by the oxo process, from propylene and producer gas (CO + H_2), or from acetaldehyde via aldol condensation. The former process is used in the Canadian plant.

3.6.2 Processes.

3.6.2.1 Oxo process. In this process, 90 to 95 percent propylene is fed with producer gas to an "oxo reactor". The reaction, which takes place in the liquid phase at 10 to 30 mPa and 120 to 160°C, is usually catalyzed by cobalt compounds:



$$CH_3{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} \begin{array}{l} CH_3CH_2CH_2CHO \\ \text{n-butyraldehyde (70-80 percent)} \\ \qquad + \\ CH_3CH(CHO)CH_3 \\ \text{iso-butyraldehyde (20-30 percent)} \end{array}$$

The reaction mixture is fractionated to remove unreacted gases and catalyst and to separate the isomers.

3.6.2.2 Aldol condensation. Aldol condensation of acetaldehyde proceeds according to this reaction:

$$2CH_3CHO \rightarrow CH_3CH_2CH_2CHO$$

The reaction mixture is purified by fractionation.

3.7 Major Uses in Canada (Corpus 1983)

Butyraldehydes are used for the production of 2-ethylhexanol, n-butanol, i-butanol, and rubber chemicals. In 1982, 63 percent of domestic production was used for 2-ethylhexanol production; 27 percent was used for butanol production.

3.8 Major Buyer in Canada (Corpus 1983)

Uniroyal Chemical, Elmira, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Transportation vessels and containers in this category have been grouped under the classification of railway tank cars and highway tank vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used to transport butyraldehydes are classified under a number of CTC/DOT specifications described in Table 2 (RTDCR 1974).

Figure 6 shows a 111A60W1 railway car commonly used to transport butyraldehyde; Table 3 indicates railway tank car details associated with this drawing. The cars are unloaded from the top by pump. The butyraldehyde 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 butyraldehyde tanks (MCA 1960). During unloading, a gas connection, also on top of the car, is connected to a supply of inert gas, usually nitrogen, so that the vapour space will be filled (MCA 1960). A safety relief valve or a safety vent is required on top of the rail car (RTDCR 1974). A gauging device, either the rod type or the tape type, is required. The top unloading connection must be protected by a housing.

4.1.1.2 Tank motor vehicles. Butyraldehydes are transported by tank motor vehicles with tanks classed as nonpressure vessels (MCA 1960). Design pressure for such tanks does not exceed 21 kPa (3 psi). Motor vehicle tanks carrying butyraldehydes are similar to the railway tanks previously described. These highway tankers are unloaded by pump from the top unloading connection valve. Air or gas pressure is not recommended (MCA 1960).

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. Butyraldehydes, in addition to railway bulk shipments, are also transported in drums (Table 4). Drums fabricated from a variety of construction materials are permitted (TDGC 1980). Fibreboard boxes with inner containers of glass, earthenware or metal may also be used (MCA 1960).

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 1960).

- The vented storage tank must be checked to make sure that it will hold the contents of the car.

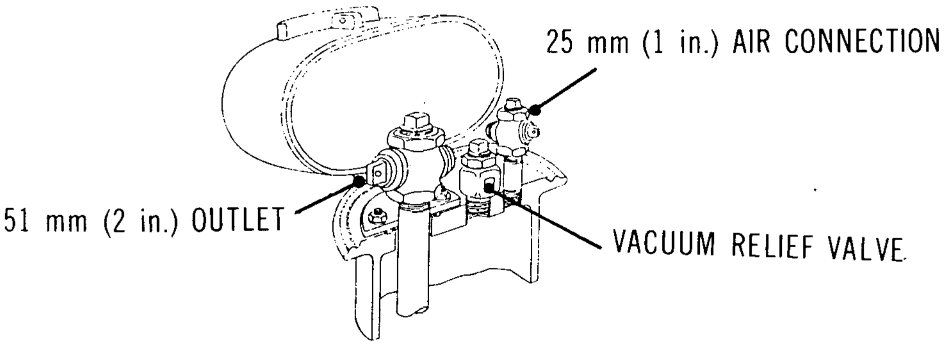
TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (RTDCR 1974)

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

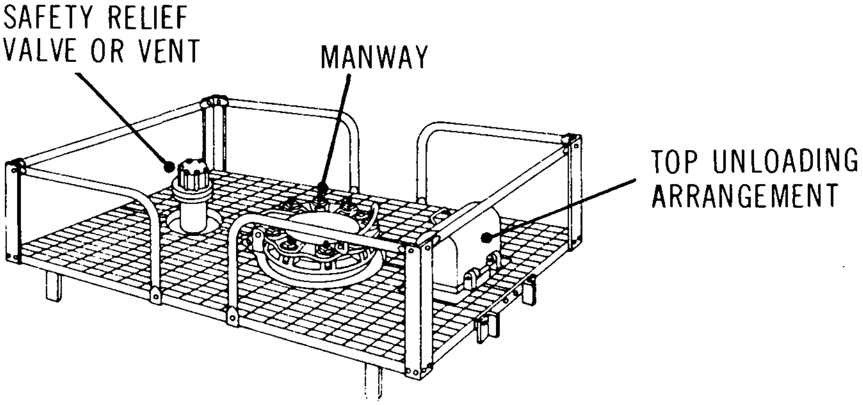
FIGURE 6

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979; RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

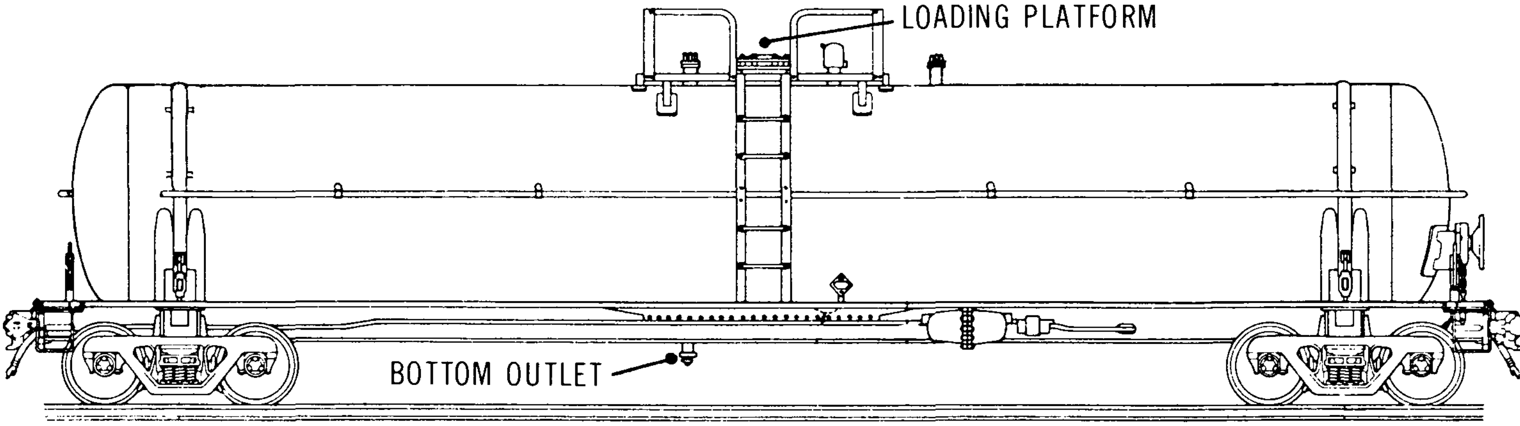


Illustration of tank car layout

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 m (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 (12 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 to 3 m (8 to 10 ft.)	2 to 3 m (8 to 10 ft.)	2 to 3 m (8 to 10 ft.)
Width of grating	1.5 to 2 m (5 to 6 ft.)	1.5 to 2 m (5 to 6 ft.)	1.5 to 2 m (5 to 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 to 356 mm (8 to 14 in.)	203 to 356 mm (8 to 14 in.)	203 to 356 mm (8 to 14 in.)
Air connection	25 to 51 mm (1 to 2 in.)	25 to 51 mm (1 to 2 in.)	25 to 51 mm (1 to 2 in.)
Bottom Unloading			
Bottom outlet	102 to 152 mm (4-6 in.)	102 to 152 mm (4-6 in.)	102 to 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	1A3	Nonremovable head, single use only.	7
Monel*	TC5M		7
Steel drums with inner plastic receptacles	6HA1	Outer steel sheet in shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)	
Fibreboard	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

- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed, and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Electrically ground the tank car.
- Do not unload during an electrical storm.

Proceed with top off-loading as follows (MCA 1960):

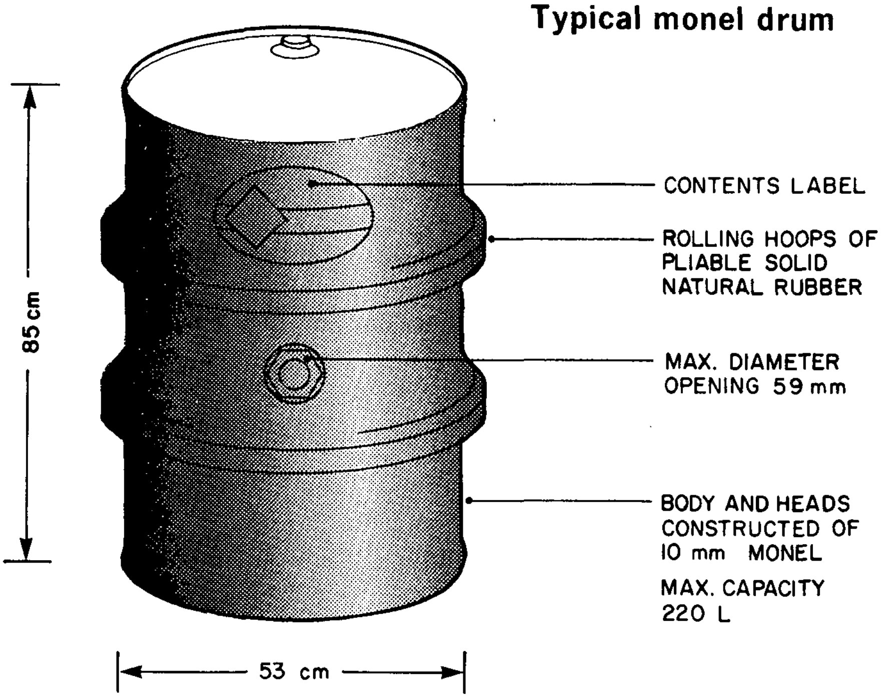
- Relieve the tank of internal vapour pressure by cooling the tank with water or venting the tank at short intervals.
- After removing the protective housing from the discharge line at top of car, connect the 51 mm (2 in.) unloading line.
- Connect the gas valve to the nitrogen supply.
- Off-load the tanker by pump only.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in butyraldehyde applications as indicated in

FIGURE 7

TYPICAL DRUM CONTAINERS

Typical monel drum



Typical steel drum

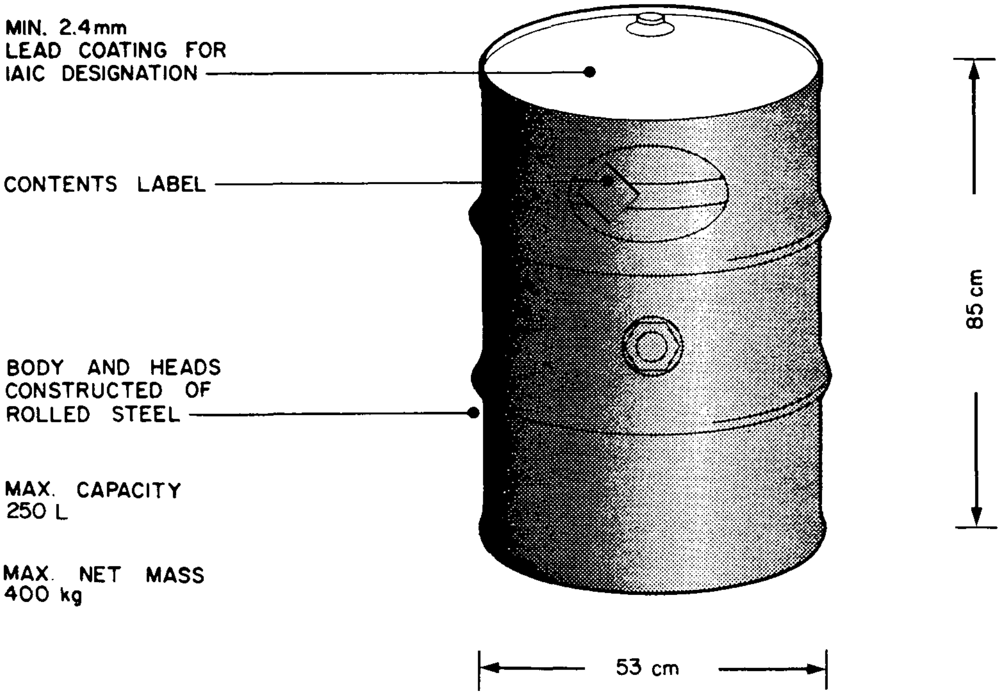


Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves and pumps.

Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with polyvinylidene fluoride resins are recommended for butyraldehyde 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. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air at pressures from 345 to 518 kPa (50 to 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 should 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 hoses with an interior lining of Teflon.

Cast iron or cast steel diaphragm valves lined with polyvinylidene fluoride resin will serve adequately (Dow PPS 1972).

A single-suction centrifugal pump with "wet end" material of 316 stainless steel gives good results (MCA 1960). 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 butyraldehyde 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	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Butyric Acid	22	PVC I (DPPED 1967)	PVC II (DPPED 1967)	PE, ABS (DPPED 1967)
	100%	66	SS (MCA 1960)		
		66	PVDF (DCRG 1978)		Chlorinated Polyether
		24	PVDC (DCRG 1978)		
2. Valves	Butyric Acid (All concentrations)	66	SS 316 (JSSV 1979)		
3. Pumps	100%	66	SS (MCA 1960)		
4. Storage	100%	66	SS Aluminum Glass-lined CS (MCA 1960) Baked phenolic-lined steel (Kirk-Othmer 1978)		
5. Others	Butyric Acid	66	PVC I (MWPP 1978)	ABS (MWPP 1978)	PE (MWPP 1978)
	Most	Most	Stainless steel Aluminum (Kirk-Othmer 1978)		

TABLE 6 MATERIALS OF CONSTRUCTION

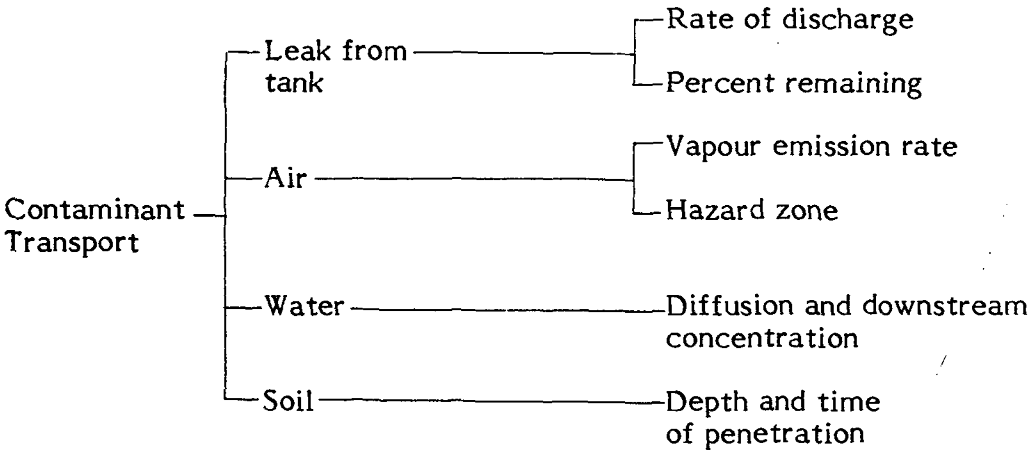
Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Aluminum
CS	Carbon Steel
	Fluorine Rubber (Viton)
	Glass
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
PVC (followed by grade)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS (followed by grade)	Stainless Steel

5 CONTAMINANT TRANSPORT

5.1 General Summary

Butyraldehyde will initially float when spilled in water. Because of its moderate solubility, the slick will dissolve after some time. Its vapour is flammable and irritating. The vapour cloud tends to hug the ground and spread rather than lift off the ground and disperse. 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 table may cause environmental problems.

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

5.2 Leak Nomograms

5.2.1 Introduction. Butyraldehyde is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size (with a capacity of 80 000 L) has been chosen throughout the EnviroTIPS series for development of the leak nomograms.

If a tank car loaded with butyraldehyde 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 relatively low volatility of butyraldehyde 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.

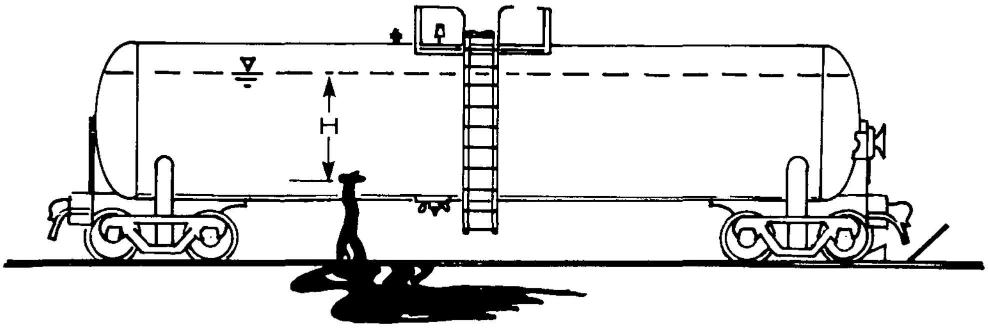


FIGURE 8 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the liquid above the puncture hole (H), and a coefficient of discharge (Cd).

As the gravitational force predominates over viscous and other forces for a wide range of fluid conditions, the rate of discharge is relatively independent of fluid temperature and viscosity (Rouse 1961). Consequently, it is reasonable to assume a constant discharge coefficient for butyraldehyde for a wide range of temperature and viscosity. For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2 Nomograms.

5.2.2.1 Figure 9: Percent remaining versus time. Figure 9 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.

FIGURE 9

BUTYRALDEHYDE

PERCENT REMAINING VS TIME

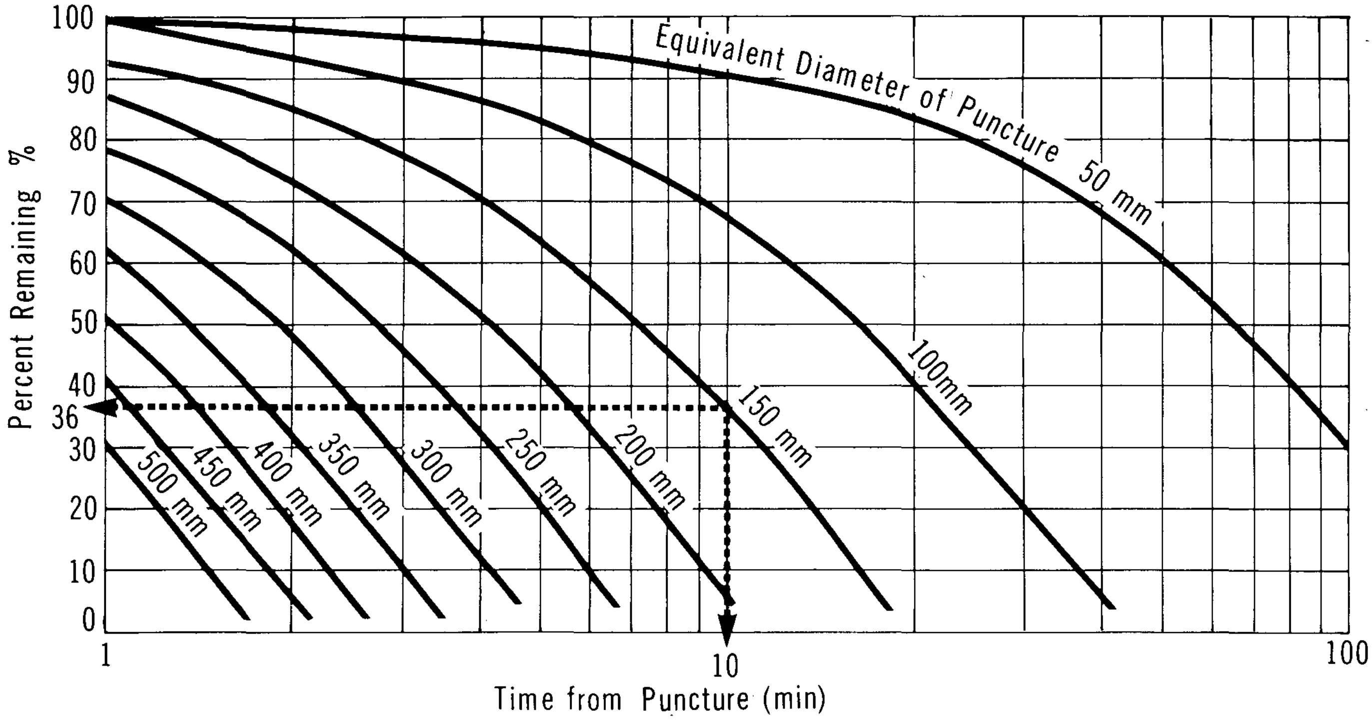
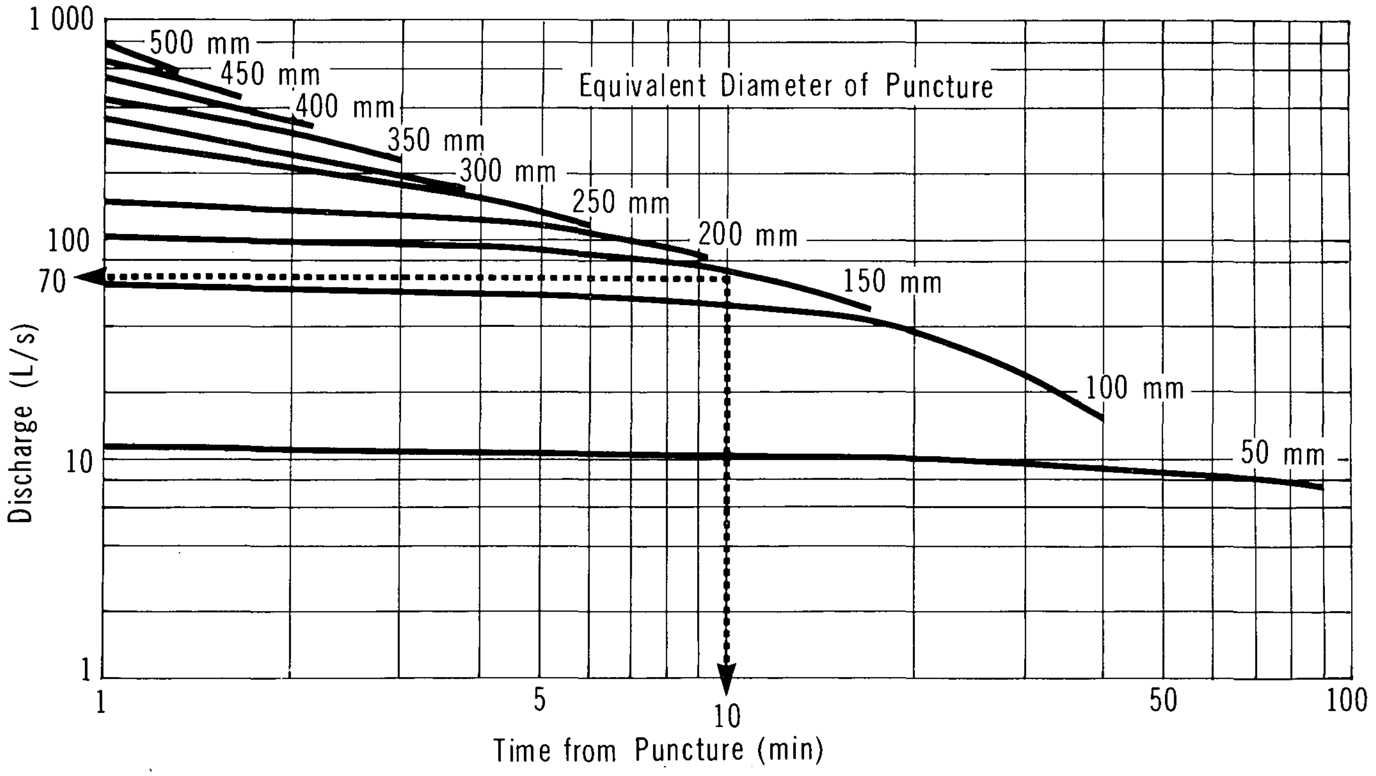


FIGURE 10

BUTYRALDEHYDE

DISCHARGE RATE VS TIME



The standard tank car is assumed to be initially full (at t = 0) with a volume of about 80 000 L of butyraldehyde. 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 10: Discharge rate versus time. Figure 10 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.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with butyraldehyde 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 9
- 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 10
- 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 butyraldehydes are moderately volatile liquids, 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 11 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 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 13:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 7:	weather conditions
Figure 14:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum plume hazard half-widths
Figure 17:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 12 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" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 13: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for butyraldehydes (as n-butyraldehyde) has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for butyraldehyde at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 1.9 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 of butyraldehyde at that temperature (Verschueren 1984). For example, evaporation rates of 0.80 g/(m^2s) at 0°C and 2.95 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s.

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

FIGURE 11

BUTYRALDEHYDE

SCHEMATIC OF CONTAMINANT PLUME

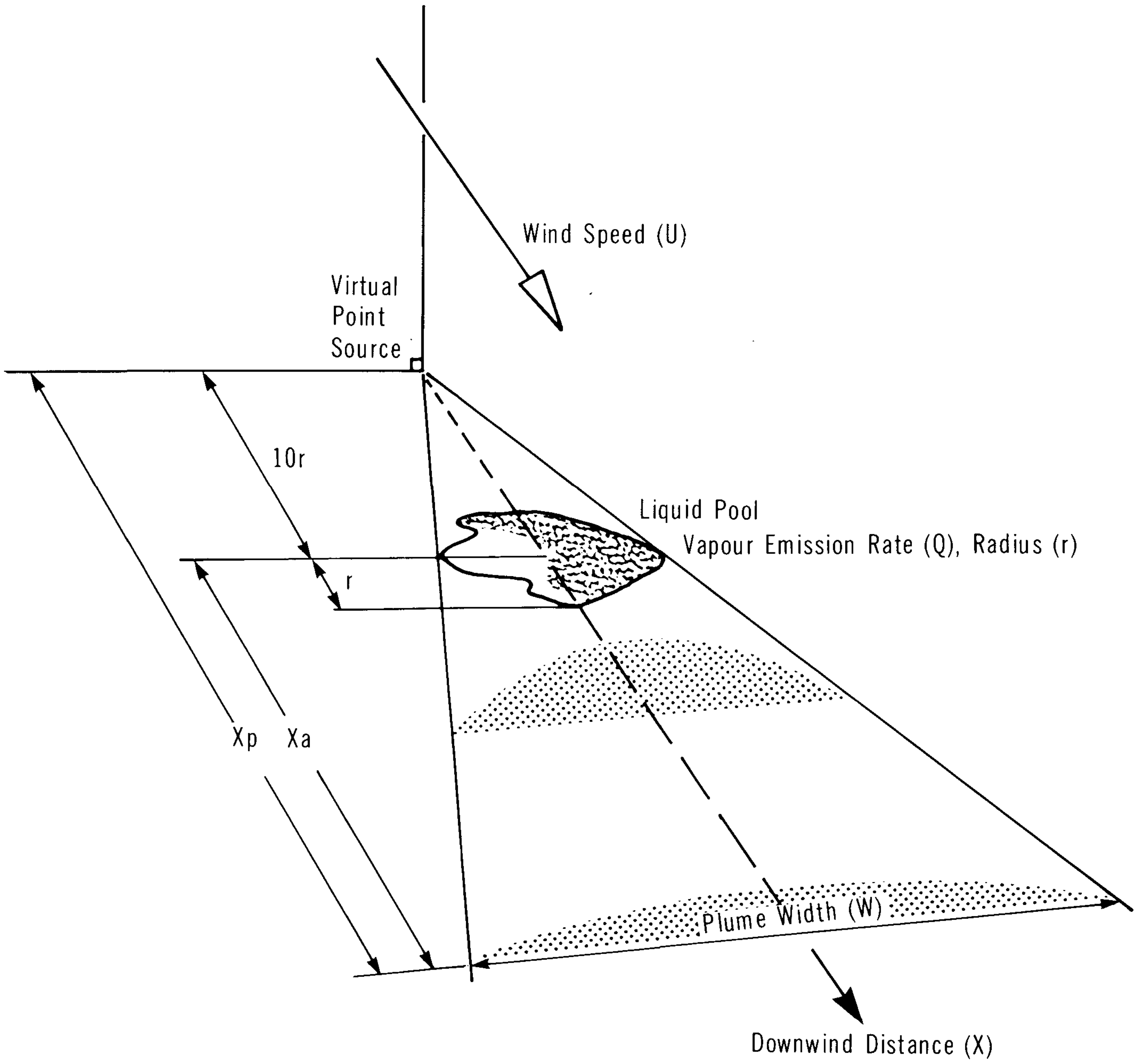
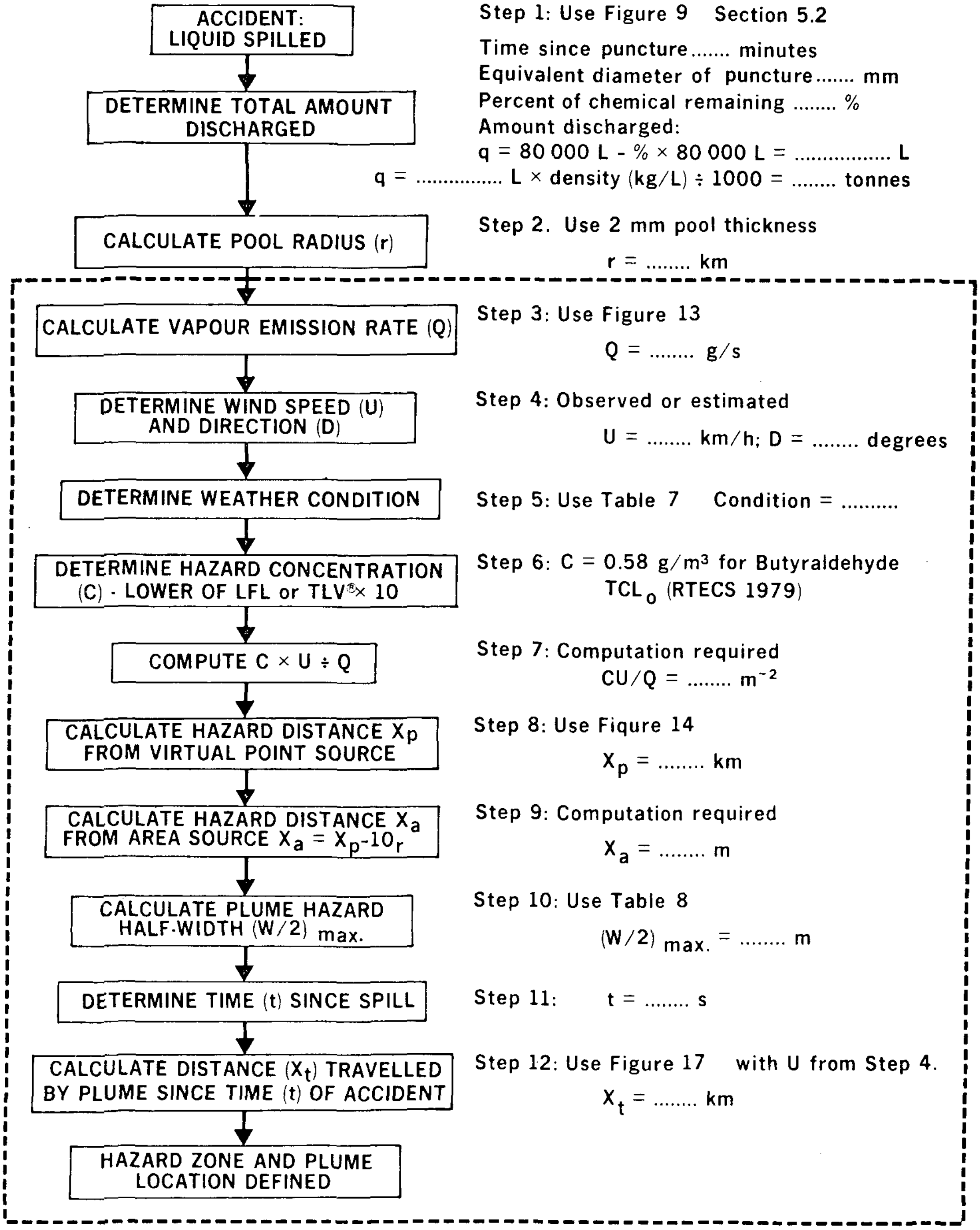


FIGURE 12

BUTYRALDEHYDE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE



Step 1: Use Figure 9 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 thickness

$r =$ .... km

Step 3: Use Figure 13

$Q =$ .... g/s

Step 4: Observed or estimated

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

Step 5: Use Table 7 Condition = ...

Step 6: $C = 0.58$ g/m³ for Butyraldehyde
TCL_0 (RTECS 1979)

Step 7: Computation required
$CU/Q =$ .... m^{-2}

Step 8: Use Fiqure 14

$X_p =$ .... km

Step 9: Computation required

$X_a =$ .... m

Step 10: Use Table 8

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

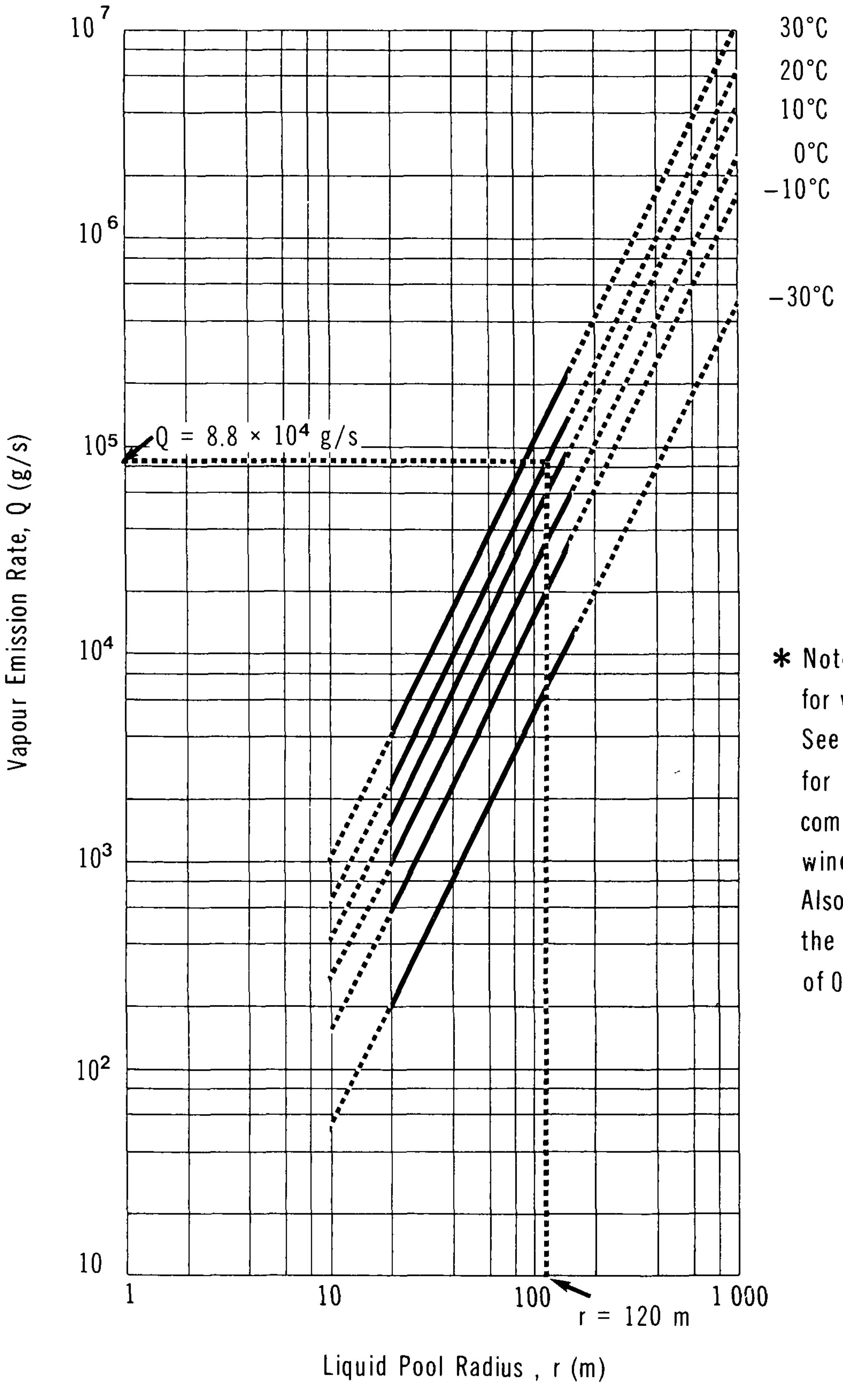
Step 11: $t =$ .... s

Step 12: Use Figure 17 with U from Step 4.
$X_t =$ .... km

FIGURE 13

BUTYRALDEHYDE

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applie
for wind speed of 4.5 m
See Introduction Manua
for relationships to
compute values for othe
wind speeds, if necessa
Also, the solid portions
the curves represent sp
of 0.05 to 64 tonnes.

estimated from Figure 13. The solid portions of the curves represent spills of 0.05 to 64 tonnes, the latter representing about one standard 80 000 L rail car load of butyraldehyde. It should be noted that Figure 13 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 butyraldehyde 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 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 14: Normalized vapour concentration versus downwind distance. Figure 14 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 centerline 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 14, the weather condition must be determined from Table 7.

Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 14 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower of the TCL_O (inhalable Toxic Concentration Low, in g/m^3); the TCL_O is used in the absence of a TLV® value for

FIGURE 14

BUTYRALDEHYDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

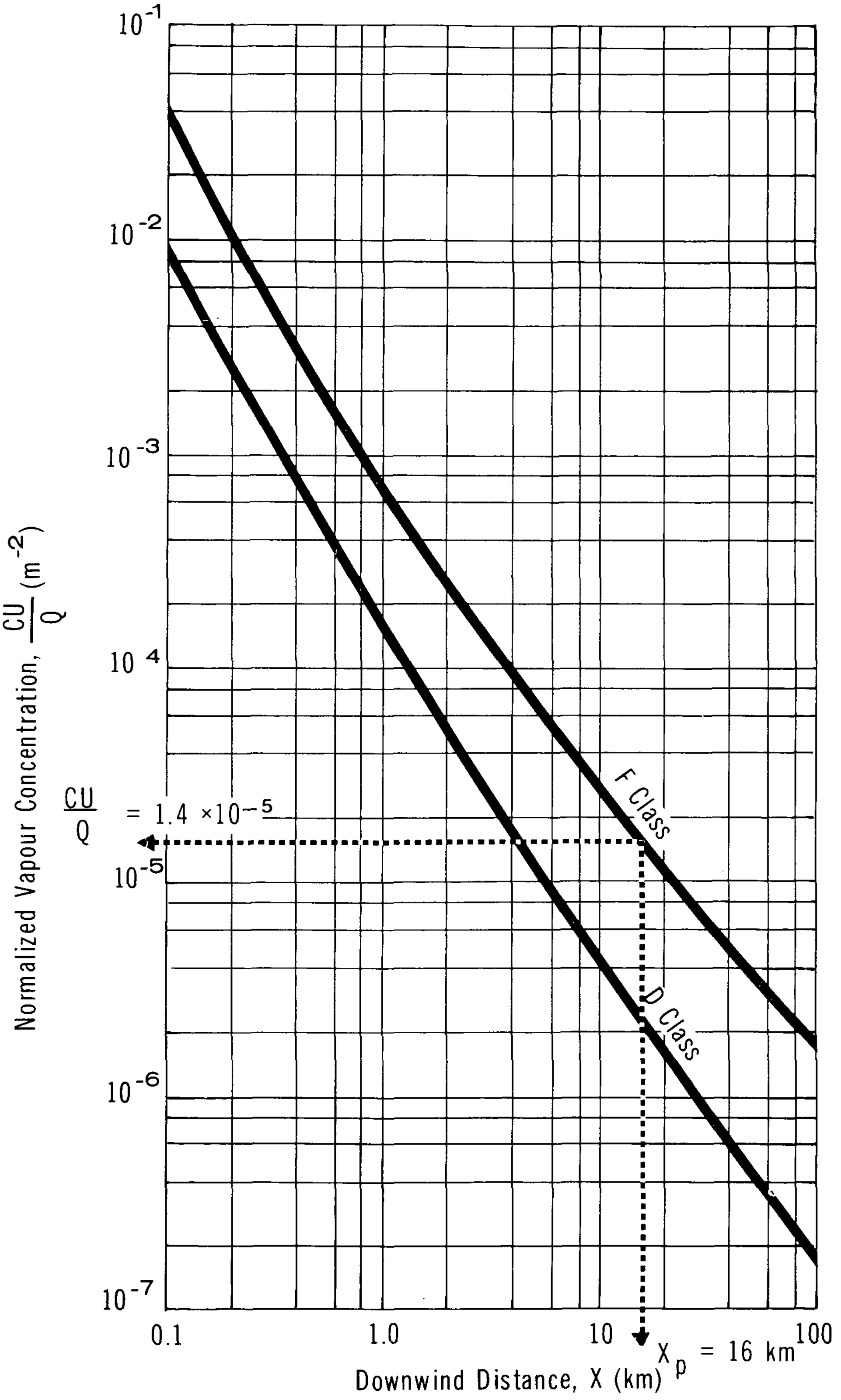


TABLE 7 WEATHER CONDITIONS

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

n-butyraldehyde), or the Lower Flammability Limit (LFL in g/m^3). Note: To convert the LFL, in percent by volume, to a concentration in g/m^3, use Figure 15. Since the TCL_O is given in units of g/m^3, the conversion nomogram (from ppm to g/m^3), Figure 16, may be used if a hazard concentration limit value other than the TCL_O is used and the value is in units of ppm.

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 the butyraldehyde TCL_O value of 0.58 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the butyraldehyde cloud, downwind of the spill site, corresponding to a hazard concentration limit of the TCL_O. Table 8 is therefore only applicable for a butyraldehyde hazard concentration limit of the TCL_O or 0.58 g/m^3. Also, data are provided up to a maximum hazard distance of 100 km.

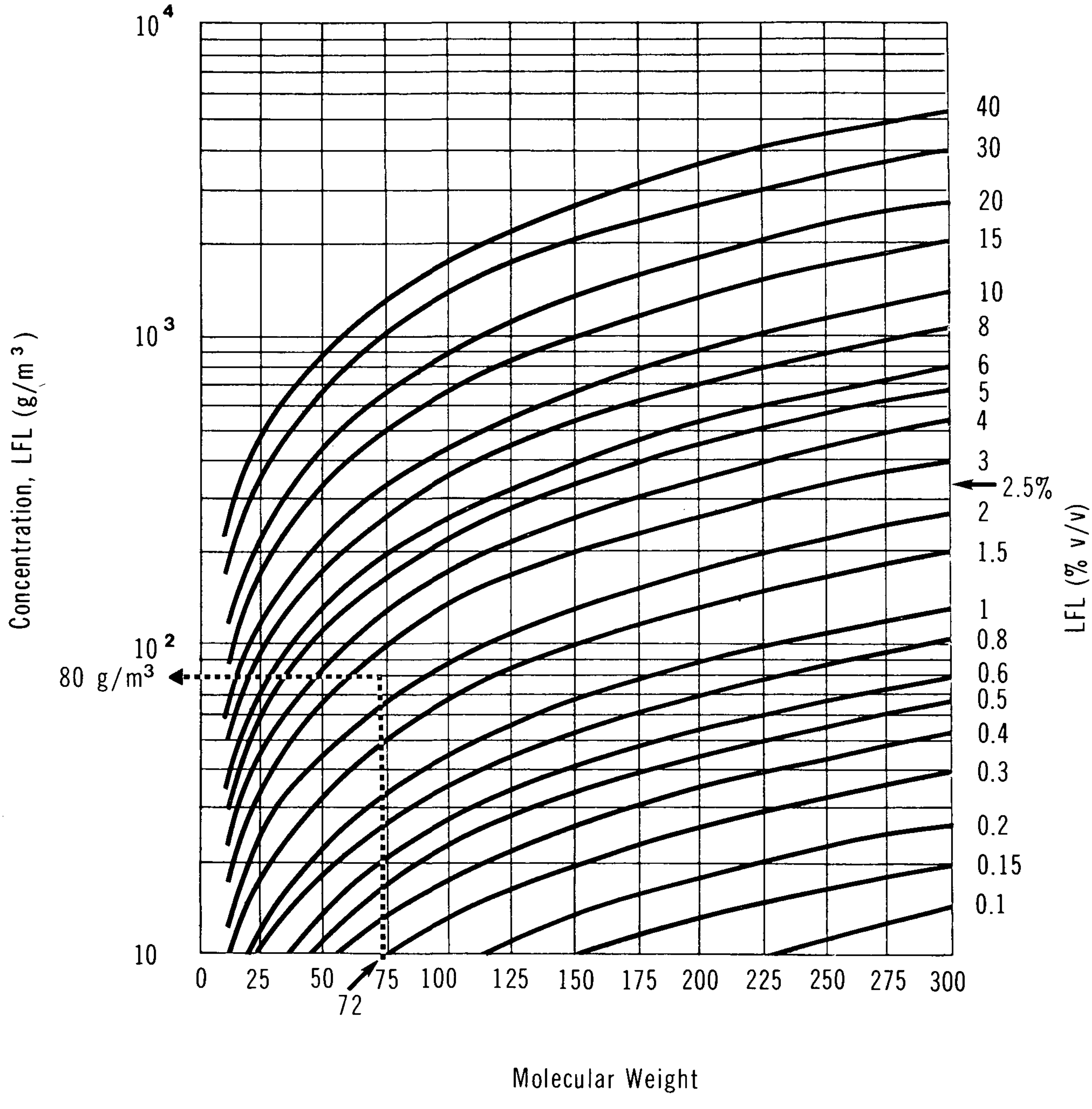
Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 7500 to 4 000 000 g/s, corresponding to butyraldehyde spills in the range of about 0.5 to 6000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spills, the mass spilled would be 64 200 kg, or approximately 64 tonnes. Therefore, under class D of Table 8, data are provided for up to about 93 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 750 to 350 000 g/s, corresponding to butyraldehyde spills in the range of about 0.05 to 170 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 2.5 times a standard rail car load.

FIGURE 15

BUTYRALDEHYDE

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



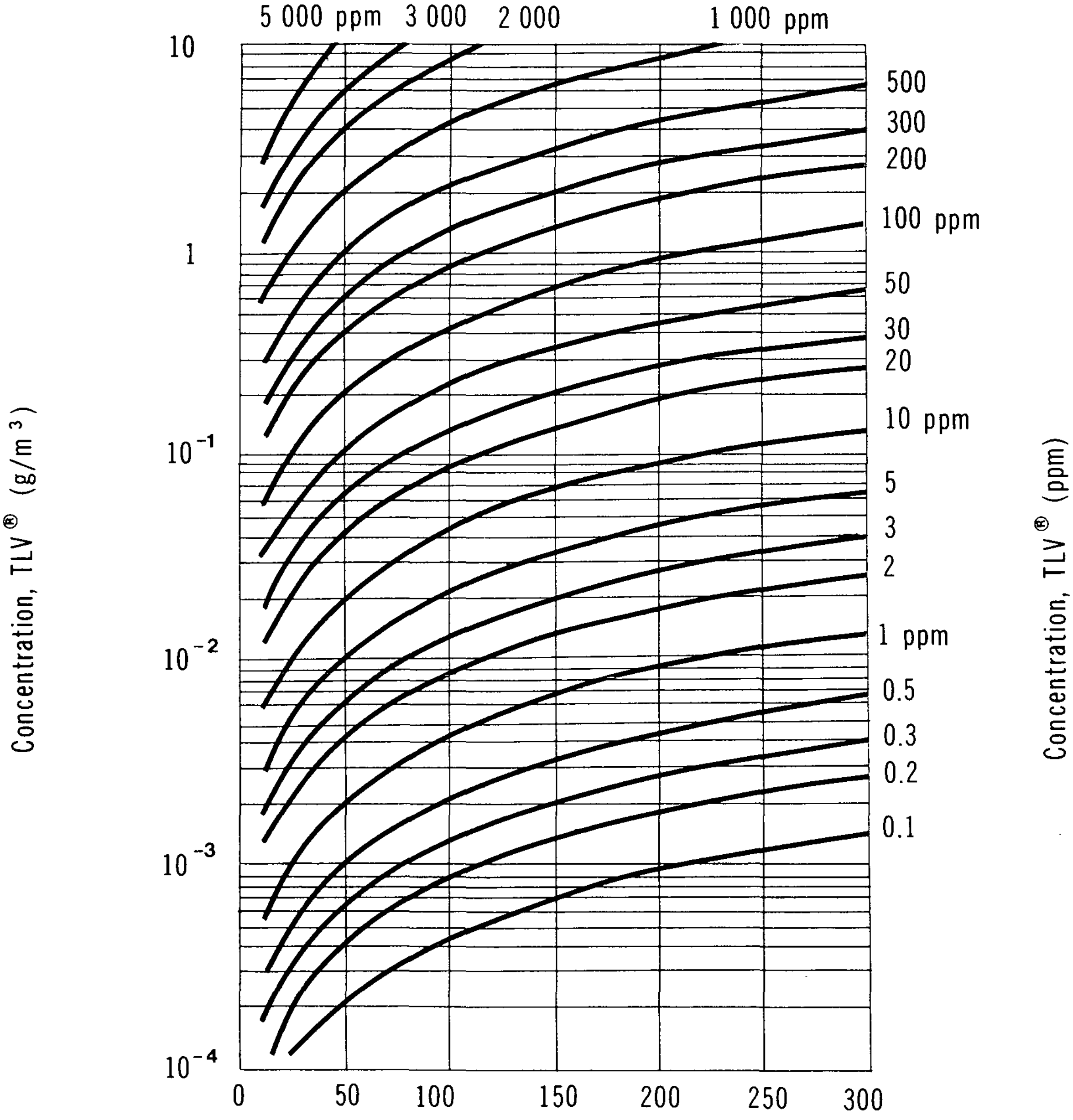
Example: Butyraldehyde, MW = 72, LFL = 2.5%, then LFL in g/m³ = 80

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

FIGURE 16

BUTYRALDEHYDE

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



Molecular Weight

Since the TCL $_0$ value for butyraldehyde is given in g/m³, a worked sample is not shown. Nomogram may be applicable if other data (in ppm) are used.

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

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR BUTYRALDEHYDE 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)	
4 000 000	3 400	(99.5 km)*	350 000	1 435	(99.5 km)*
3 500 000	3 130		300 000	1 280	
3 000 000	2 845		250 000	1 120	
2 500 000	2 540		200 000	950	
2 000 000	2 210		150 000	765	
1 500 000	1 850		100 000	565	
1 000 000	1 440		75 000	455	
750 000	1 205	Q/U = 41 900 →	50 000	340	→ $(W/2)_{max}$=340 m
500 000	940		25 000	220	
350 000	750		10 000	120	
250 000	610		7 500	100	
200 000	540		5 000	80	
150 000	460		2 500	50	
100 000	360		1 000	30	
75 000	305		500	20	
50 000	240		250	15	
25 000	160				
10 000	90				
5 000	65				
2 500	45				
1 000	30				
500	20				
250	15				

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

Example: A spill releasing butyraldehyde vapour at the rate of Q = 8.8 x 10^4 g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 41 900 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 340 m.

Note: Above table is valid only for a butyraldehyde concentration at the TCL_O, or 0.58 g/m^3.

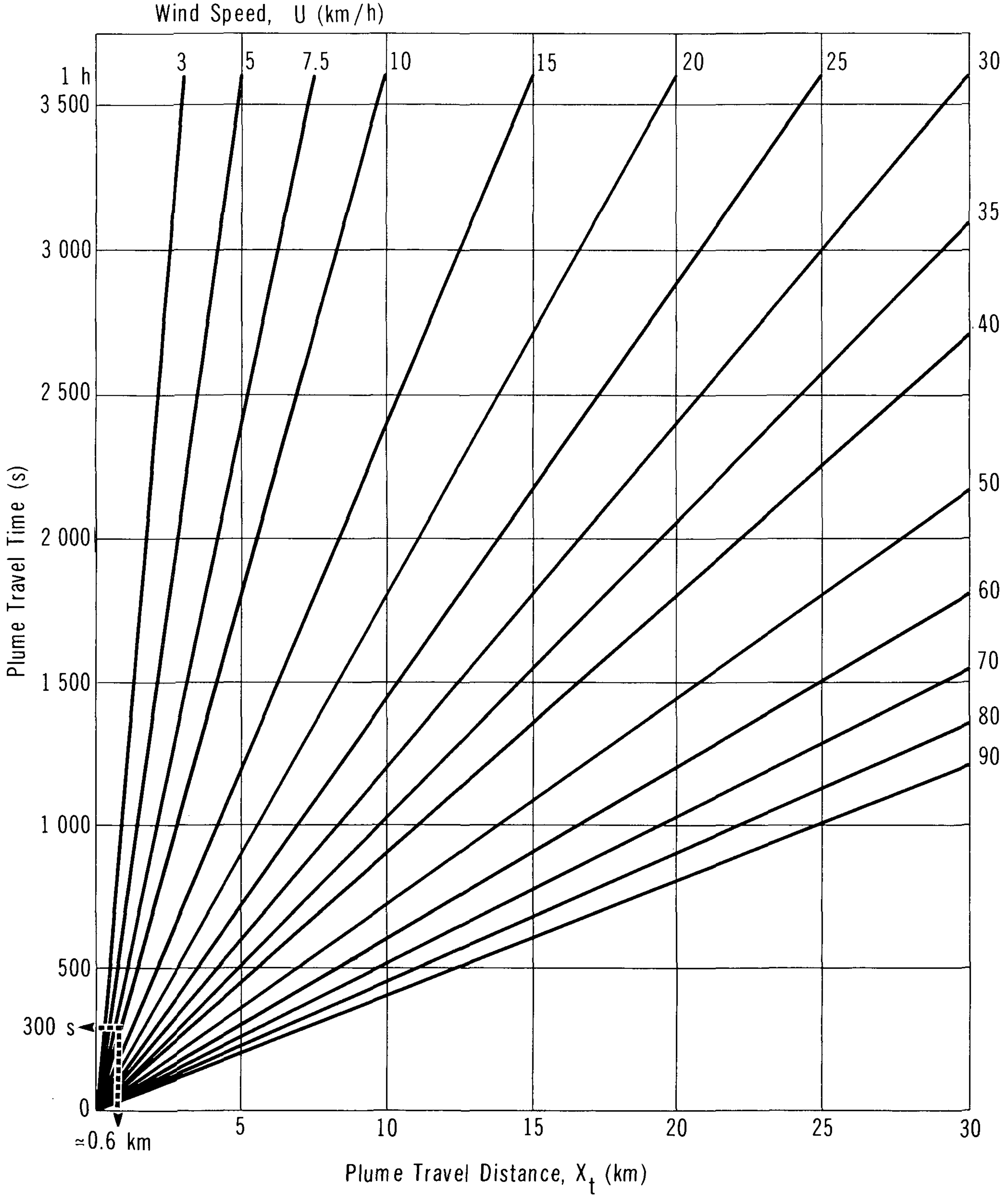
Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table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

5.3.2.4 **Figure 17: Plume travel time versus travel distance.** Figure 17 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship X_t = Ut for a range of typical wind speeds.

FIGURE 17

BUTYRALDEHYDE

PLUME TRAVEL TIME VS TRAVEL DISTANCE



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

5.3.3 Sample Calculation.

The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid butyraldehyde. The user is cautioned to take note of the limitations in the calculation procedure 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 spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of butyraldehyde 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 assuming a 4 mm spill thickness
- Radius (r) = 120 m ÷ 1000 = 0.12 km

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

- From Figure 13, for r = 120 m and T = 20°C, Q = 8.8×10^4 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 ÷ 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 the TCL_O or the LFL, so for butyraldehyde $C = 0.58$ g/m^3 ($TCL_O = 0.58$ g/m^3; LFL = 80 g/m^3)

Step 7: Compute CU/Q

- $$CU/Q = \frac{0.58 \times 2.1}{8.8 \times 10^4} = 1.38 \times 10^{-5} \text{ m}^{-2}$$

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

- From Figure 14, with $CU/Q = 1.4 \times 10^{-5}$ m^{-2} and weather condition F, $X_p \simeq 16$ km

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

- With $X_p = 16$ km and $r = 0.12$ km, then
  $X_a = X_p - 10\ r = 16$ km $- 10$ (0.12 km) $= 14.8$ km

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

- Use Table 8
- With $Q = 8.8 \times 10^4$ g/s and $U = 2.1$ m/s
  $$\text{then } Q/U = \frac{8.8 \times 10^4}{2.1} = 41\ 900 \text{ g/m}$$
- Then for weather condition F, the closest Q/U value is 50 000 g/m, which gives $(W/2)_{max} \simeq 340$ m

Step 11: Determine the time since the spill

- $t = 5$ min x 60 s/min = 300 s

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

- Using Figure 17, 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 (340 m) by the maximum hazard distance downwind of the area source (14.8 km) along the direction of the wind, as shown in Figure 18

FIGURE 18

BUTYRALDEHYDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

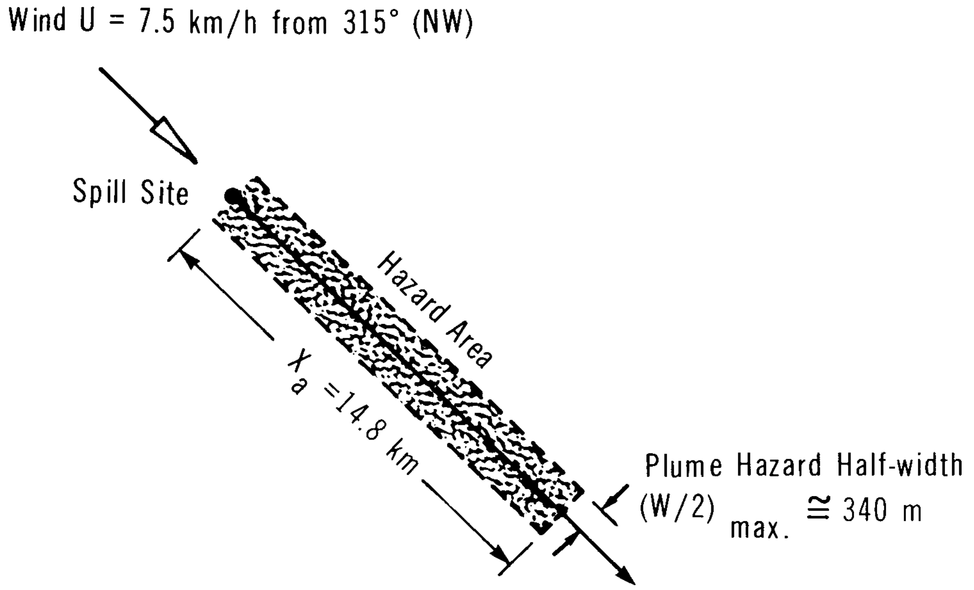
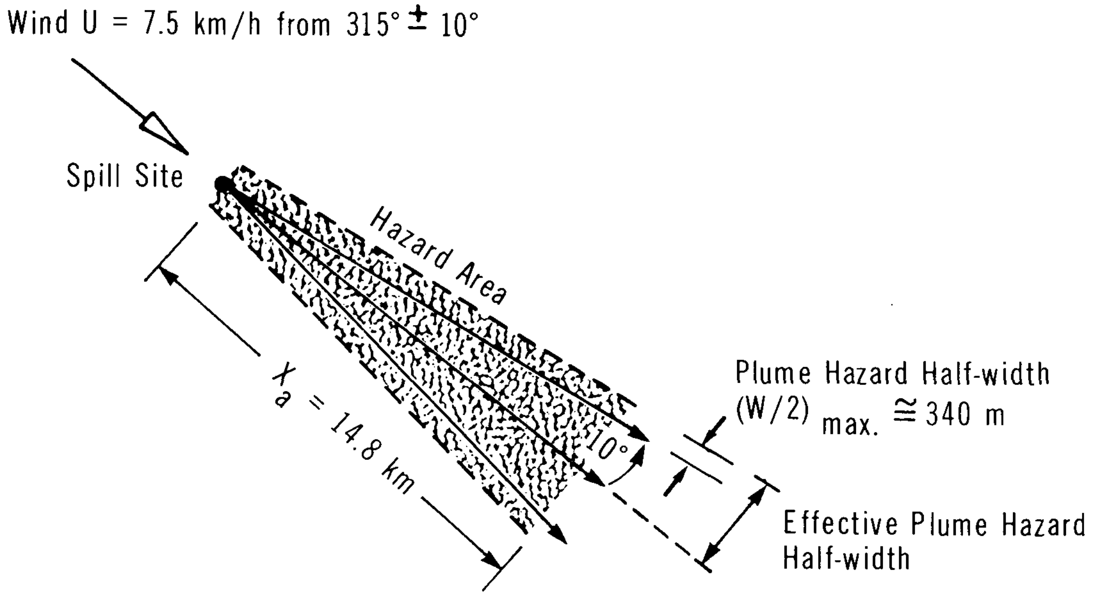


FIGURE 19

BUTYRALDEHYDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM



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

$$= 14.8 \times 1000 \times \tan 10^\circ + 340 \text{ m}$$

$$= 2950 \text{ m or } 3.0 \text{ km}$$

- 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 19
- 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 113 minutes before the plume reaches the maximum downwind hazard distance of 14.8 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, butyraldehyde will float and mix with water, allowing the spill to be diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. 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 21:	time versus distance for a range of average stream velocities
Figure 22:	hydraulic radius versus channel width for a range of stream depths
Figure 23:	diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 24:	alpha* versus diffusion coefficient for various time intervals
Figure 25:	alpha versus delta* for a range of spill sizes

---

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

Figure 26: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 27: volume versus radius for the hazard zone for a range of lake depths

Figure 28: average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 20 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 21 through 28) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 21: Time versus distance. Figure 21 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 21.

Figure 22: 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 22 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

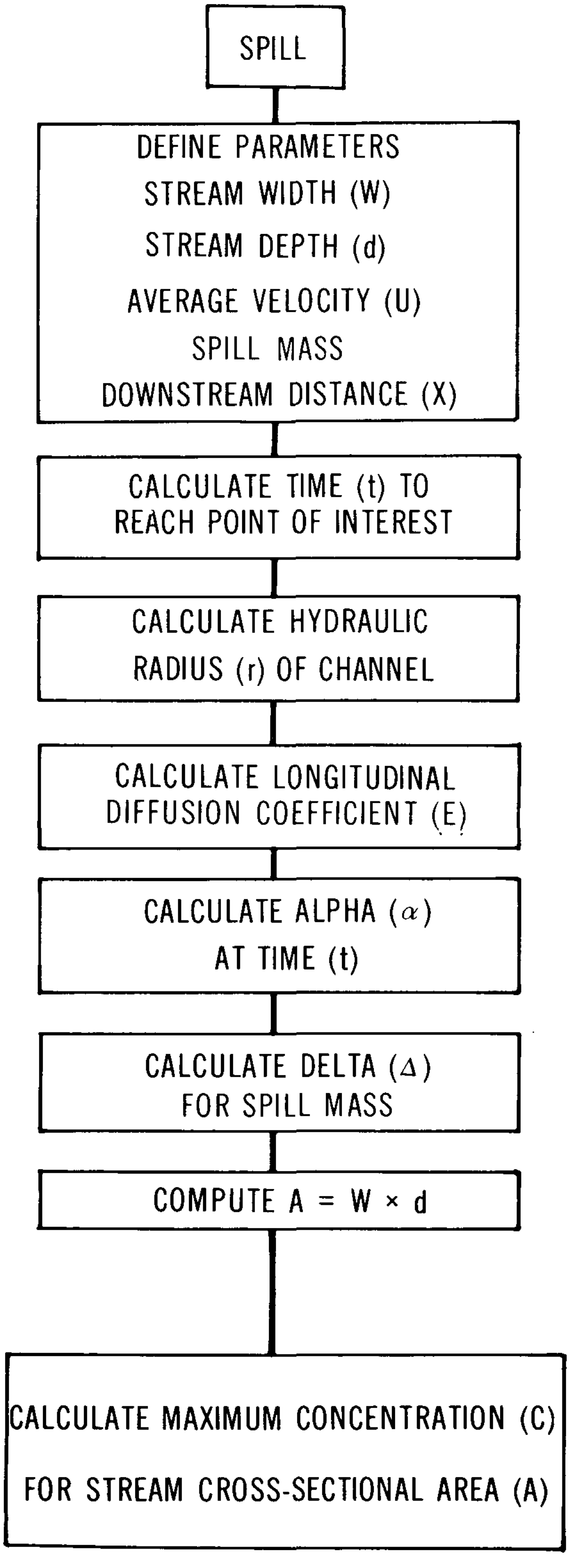
Figure 23: Diffusion coefficient versus hydraulic radius. Figure 23 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 22 and the average stream velocity (U).

Figure 24: Alpha versus diffusion coefficient. Figure 24 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 25: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 25 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 20

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 21
t = __________ minutes

Step 3: Use Figure 22
r = __________ m

Step 4: Use Figure 23
E = __________ m^2/s

Step 5: Use Figure 24
α = __________

Step 6: Use Figure 25
Δ = __________

Step 7: Compute stream cross-sectional Area (A)
A = W × d _____ m^2

Step 8: Use Figure 26
C = __________ ppm

BUTYRALDEHYDE

TIME vs DISTANCE

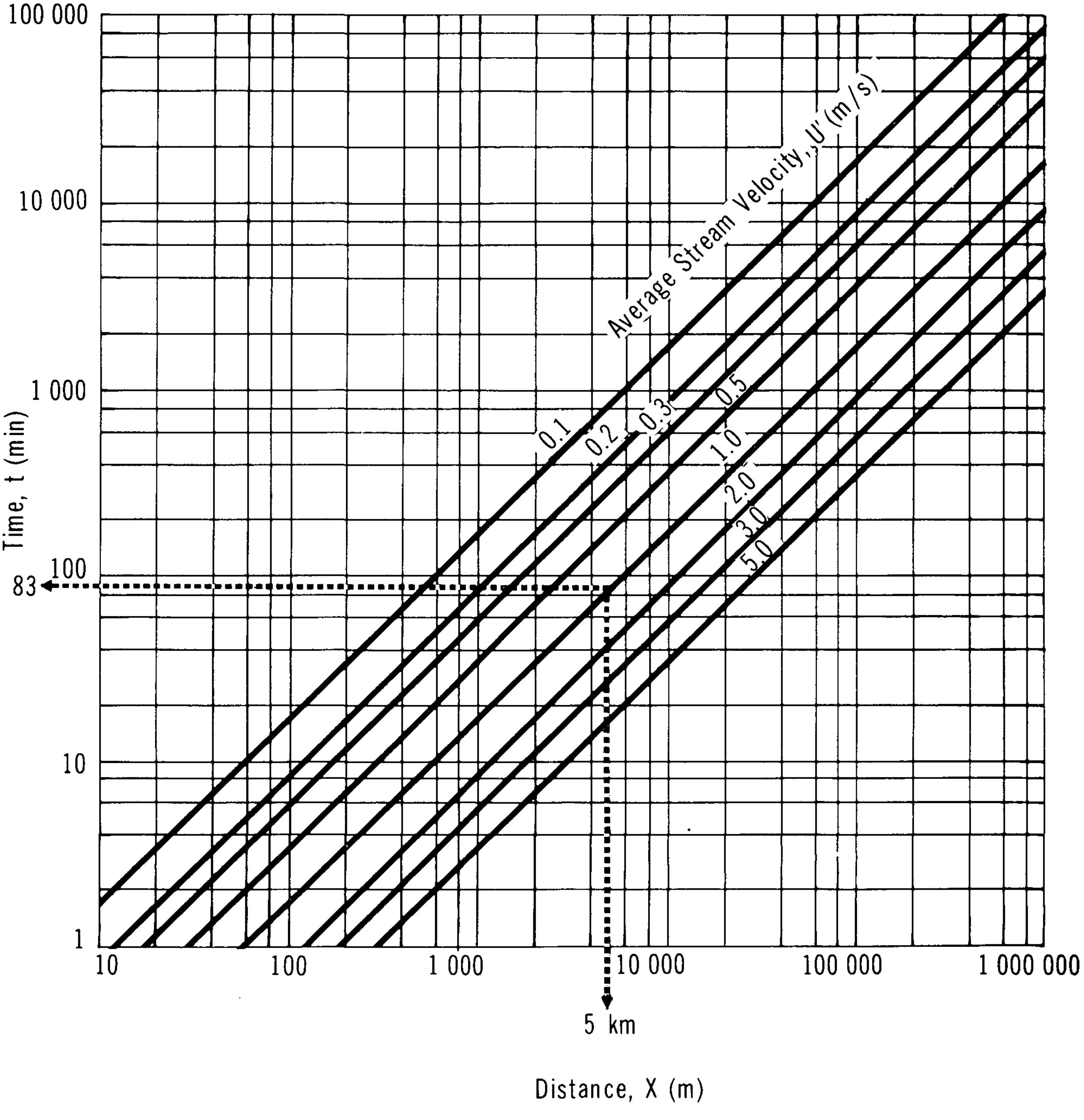


FIGURE 22

HYDRAULIC RADIUS VS CHANNEL WIDTH

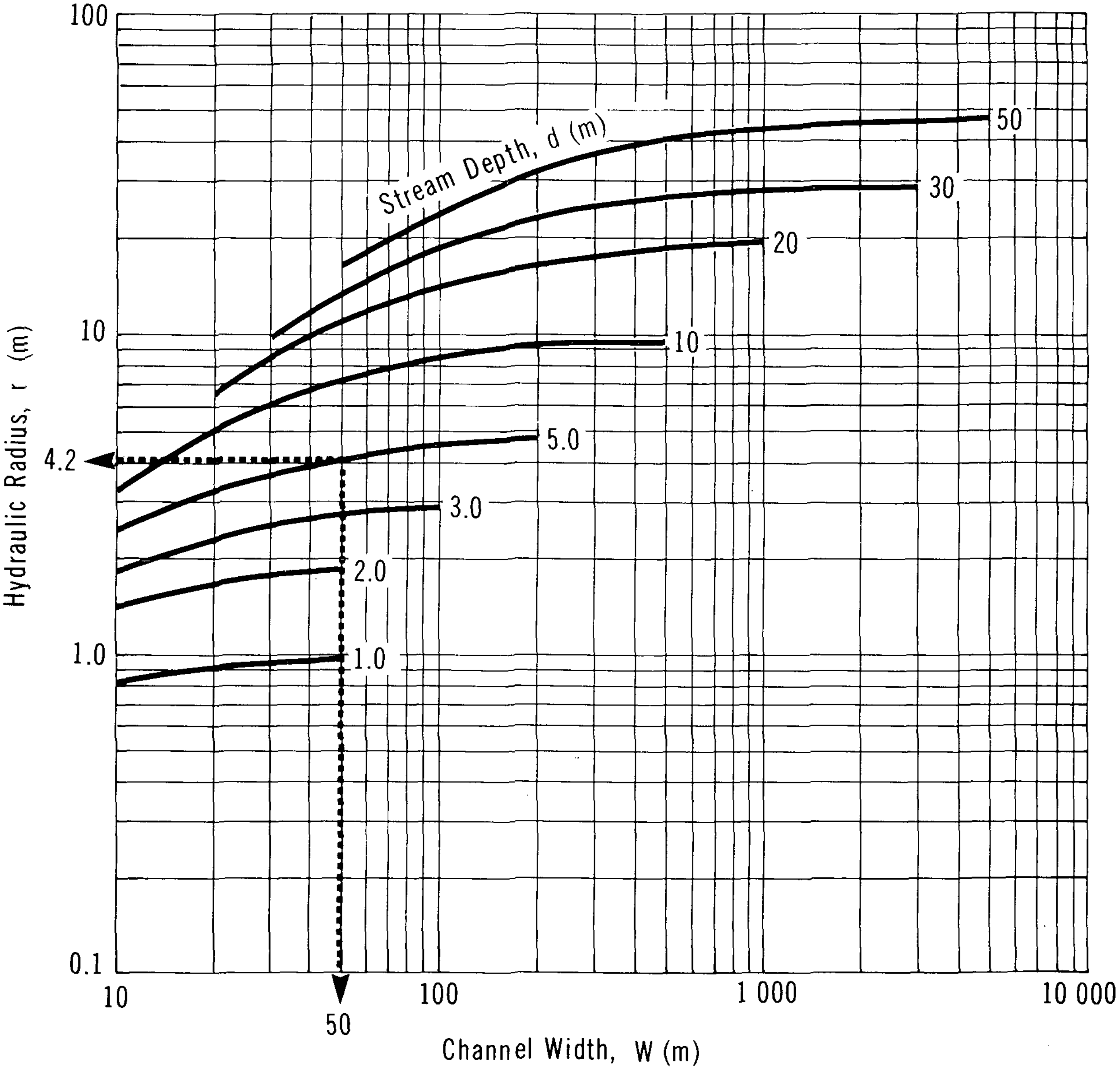
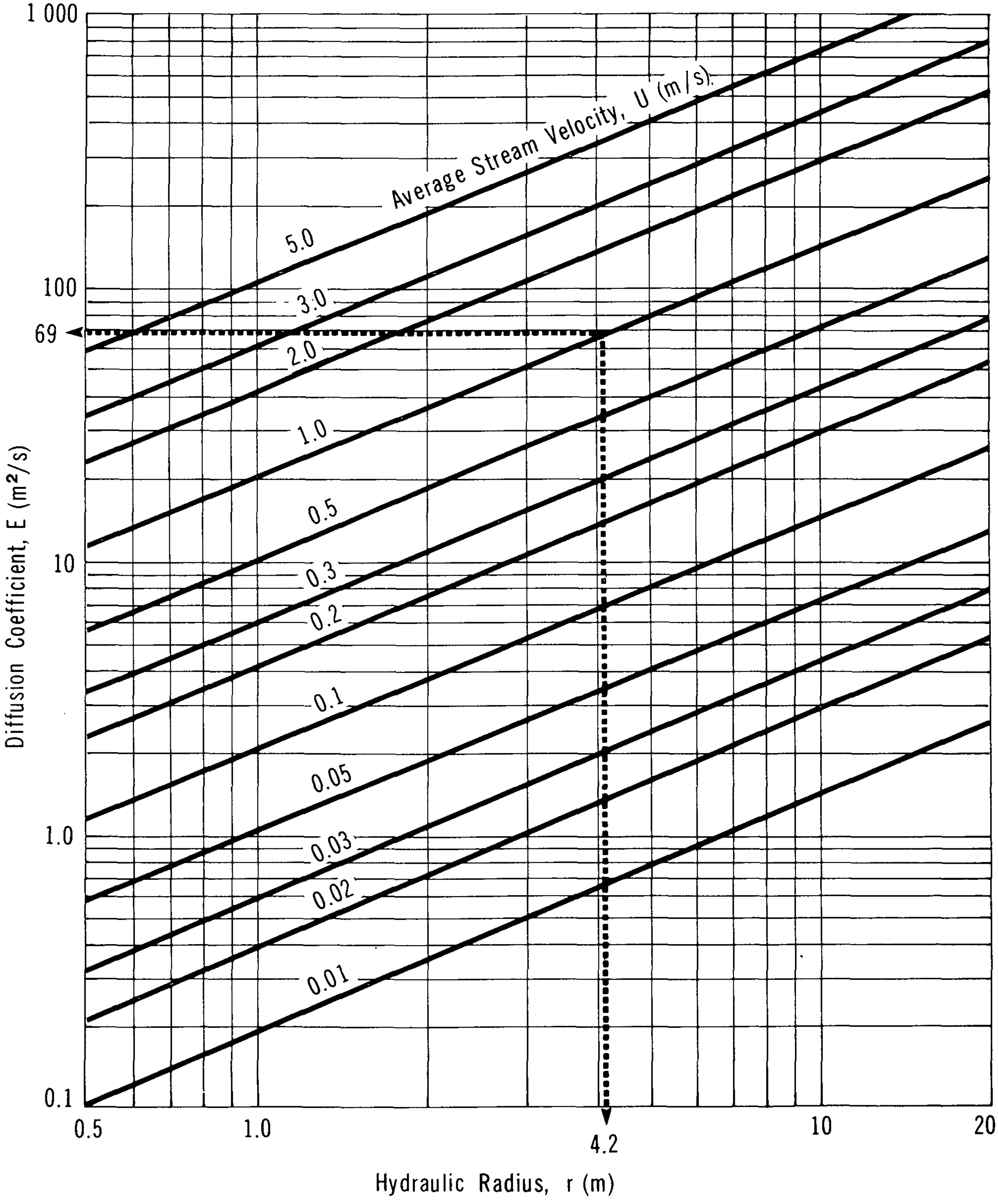


FIGURE 23

BUTYRALDEHYDE

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



BUTYRALDEHYDE

ALPHA vs DIFFUSION COEFFICIENT

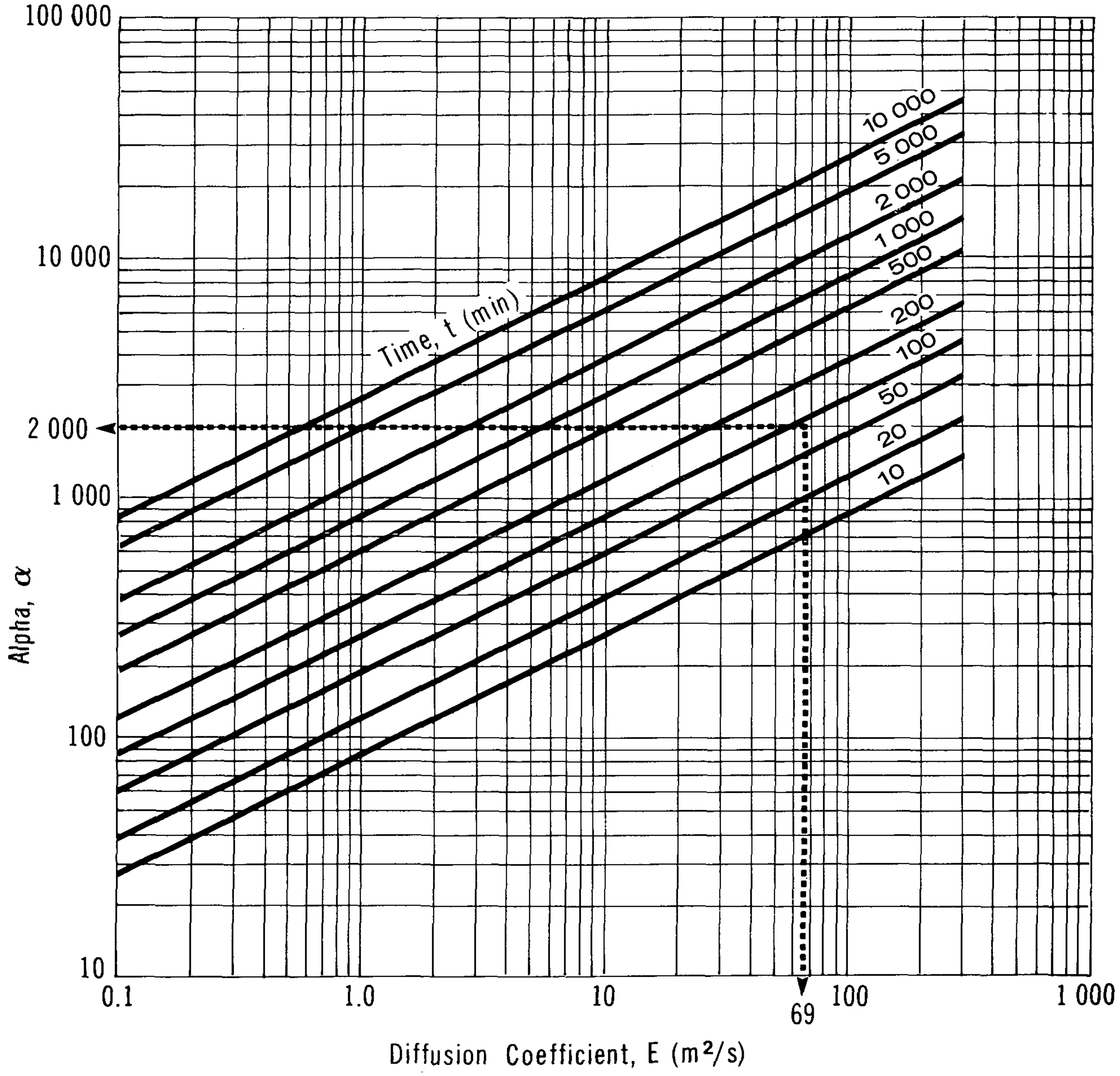


FIGURE 25

BUTYRALDEHYDE

ALPHA vs DELTA

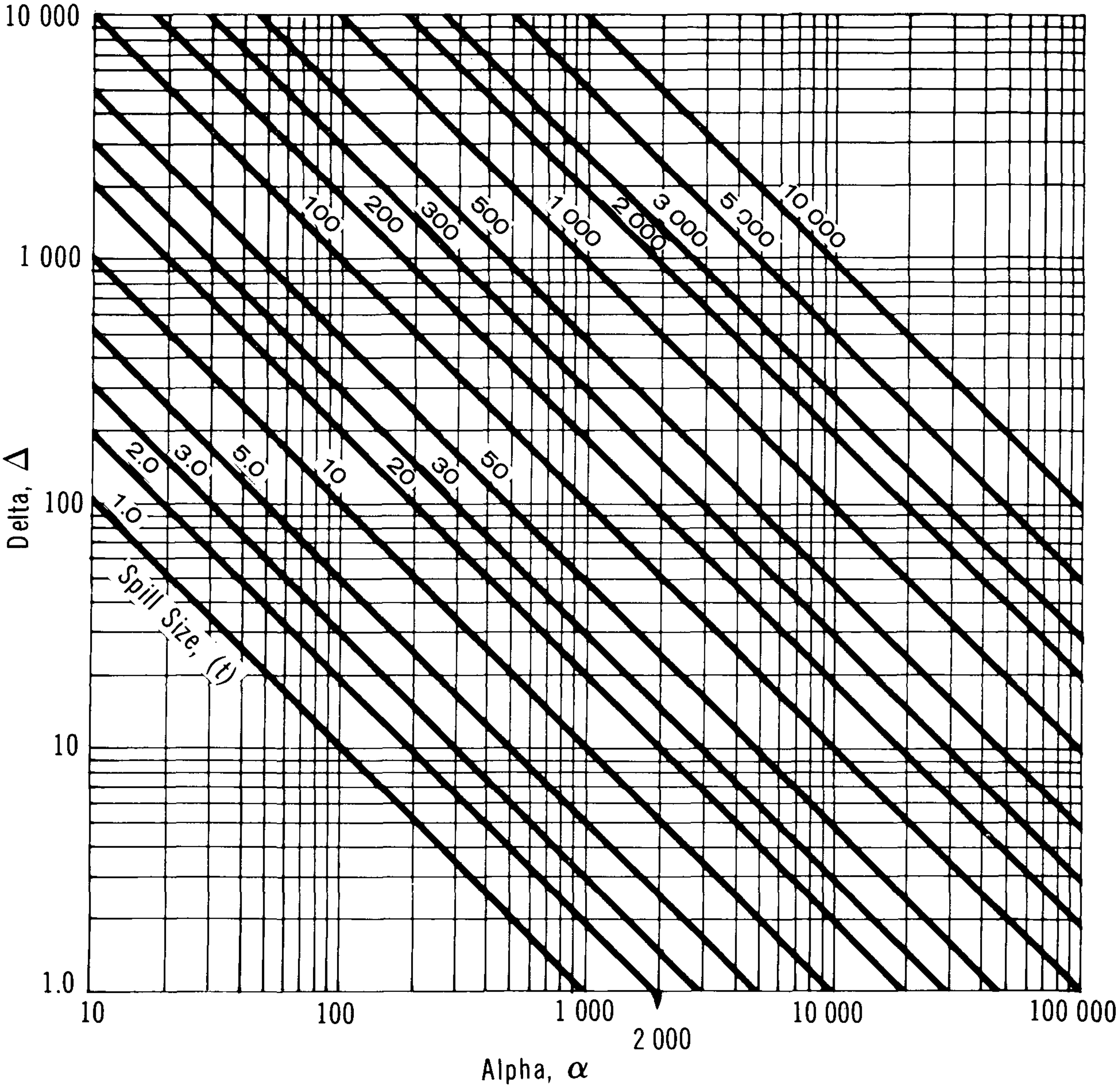


Figure 26: Maximum concentration versus delta. Figure 26 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 26 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 27: 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 27. The radius (r) represents the distance from the spill to the point of interest.

Figure 28: 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 28 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 butyraldehyde 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?

<u>Solution</u>

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes of butyraldehyde

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

- Use Figure 21
- With X = 5000 m and U = 1 m/s, t = 83 min

FIGURE 26

BUTYRALDEHYDE

MAXIMUM CONCENTRATION vs DELTA

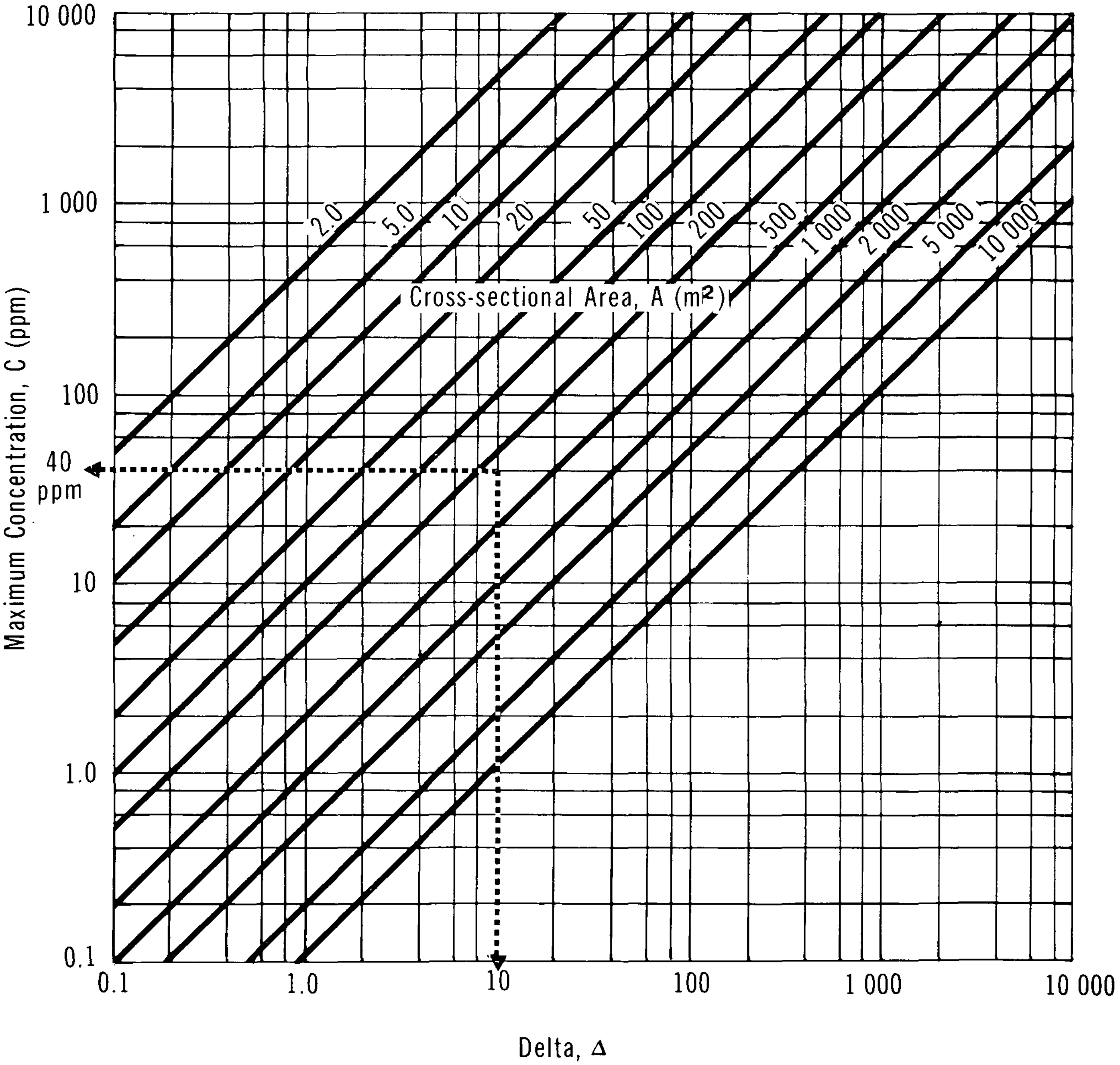


FIGURE 27

BUTYRALDEHYDE

VOLUME vs RADIUS

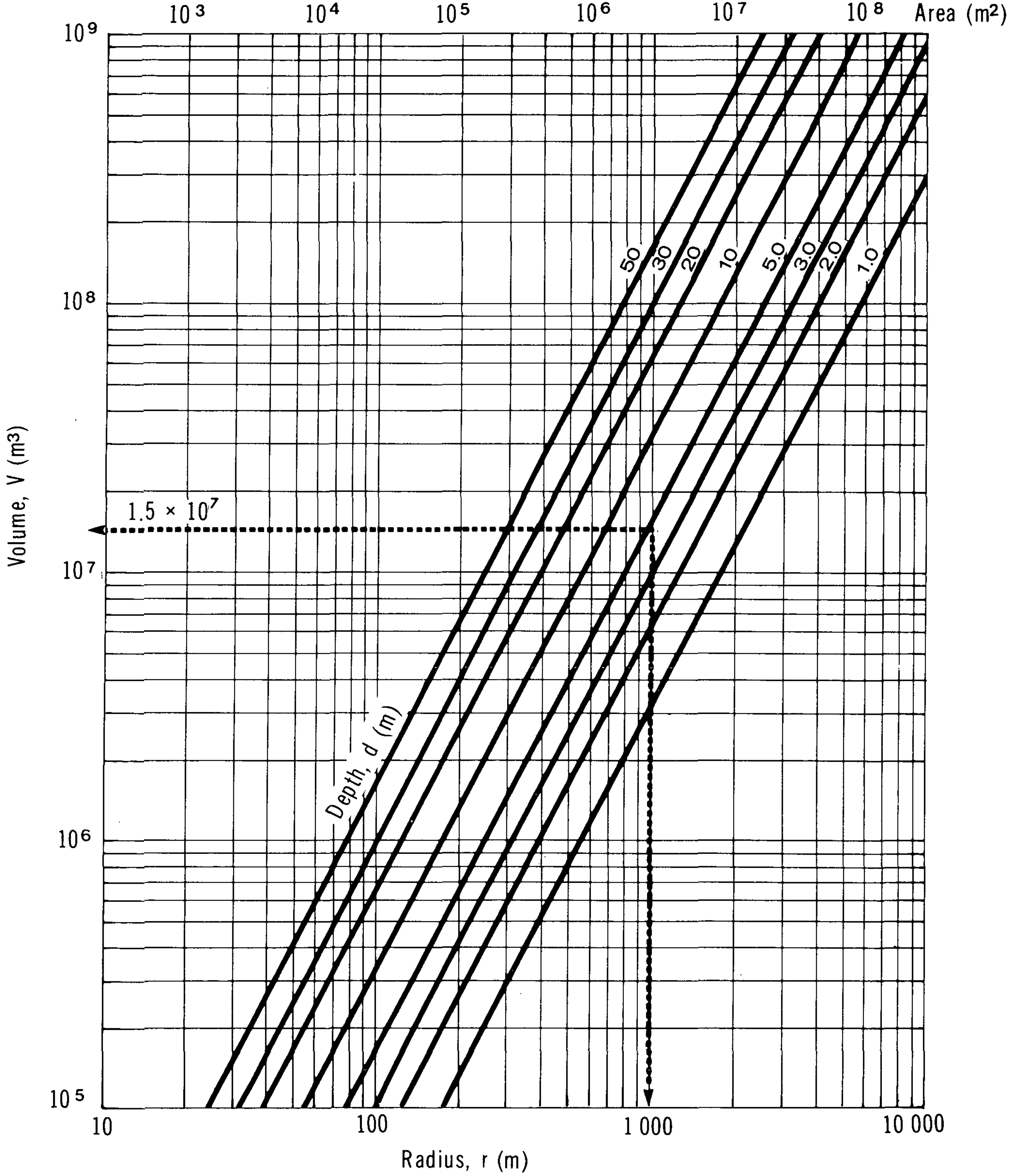
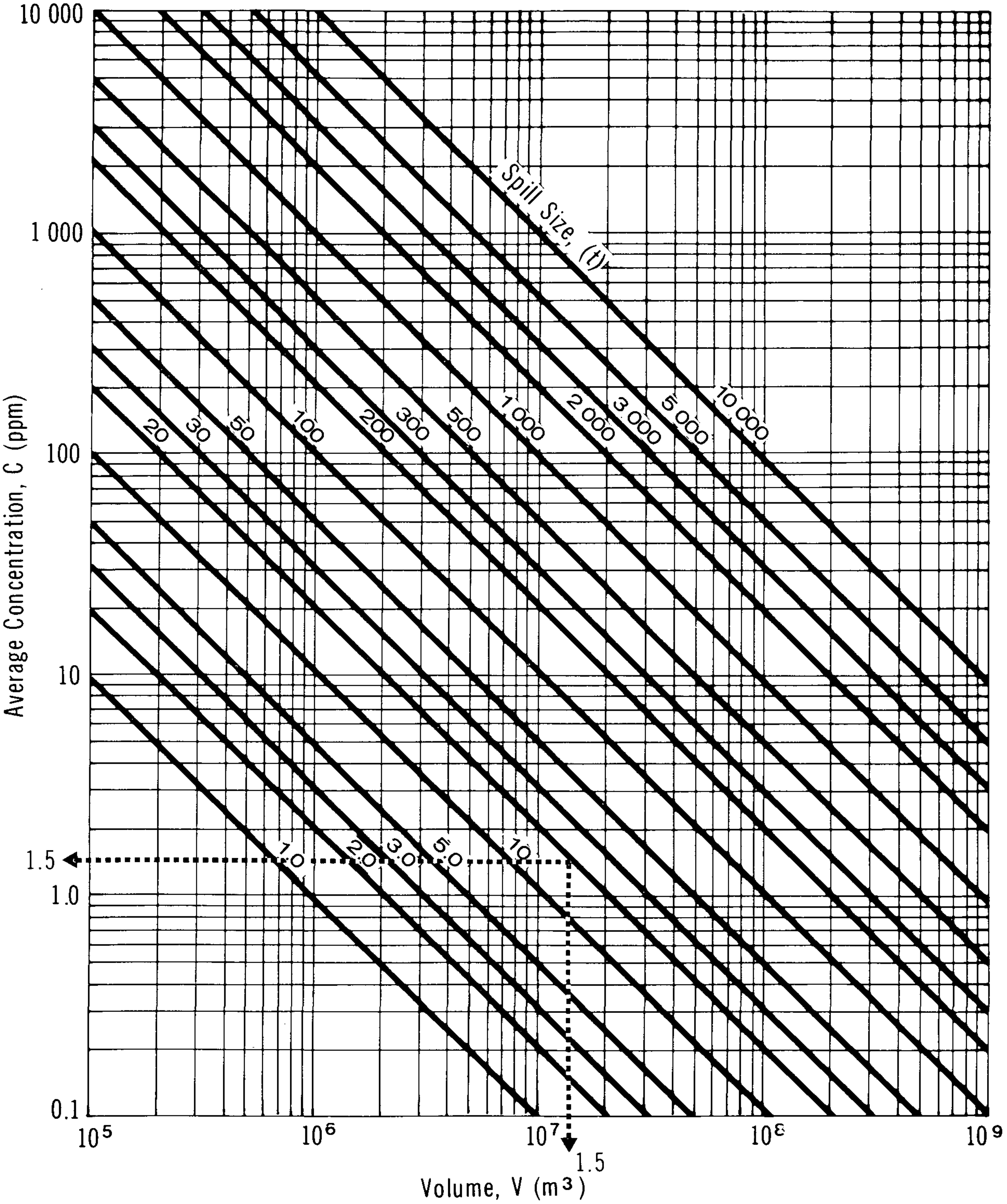


FIGURE 28

BUTYRALDEHYDE

AVERAGE CONCENTRATION vs VOLUME



Step 3: Calculate the hydraulic radius (r)

- Use Figure 22
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 23
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 24
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calculate delta (Δ)

- Use Figure 25
- 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 26
- 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 butyraldehyde 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 (butyraldehyde)

Step 2: Determine the volume of water available for dilution

- Use Figure 27
- With r = 1000 m, d = 5 m, the volume is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 28

- With V = 1.5×10^7 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

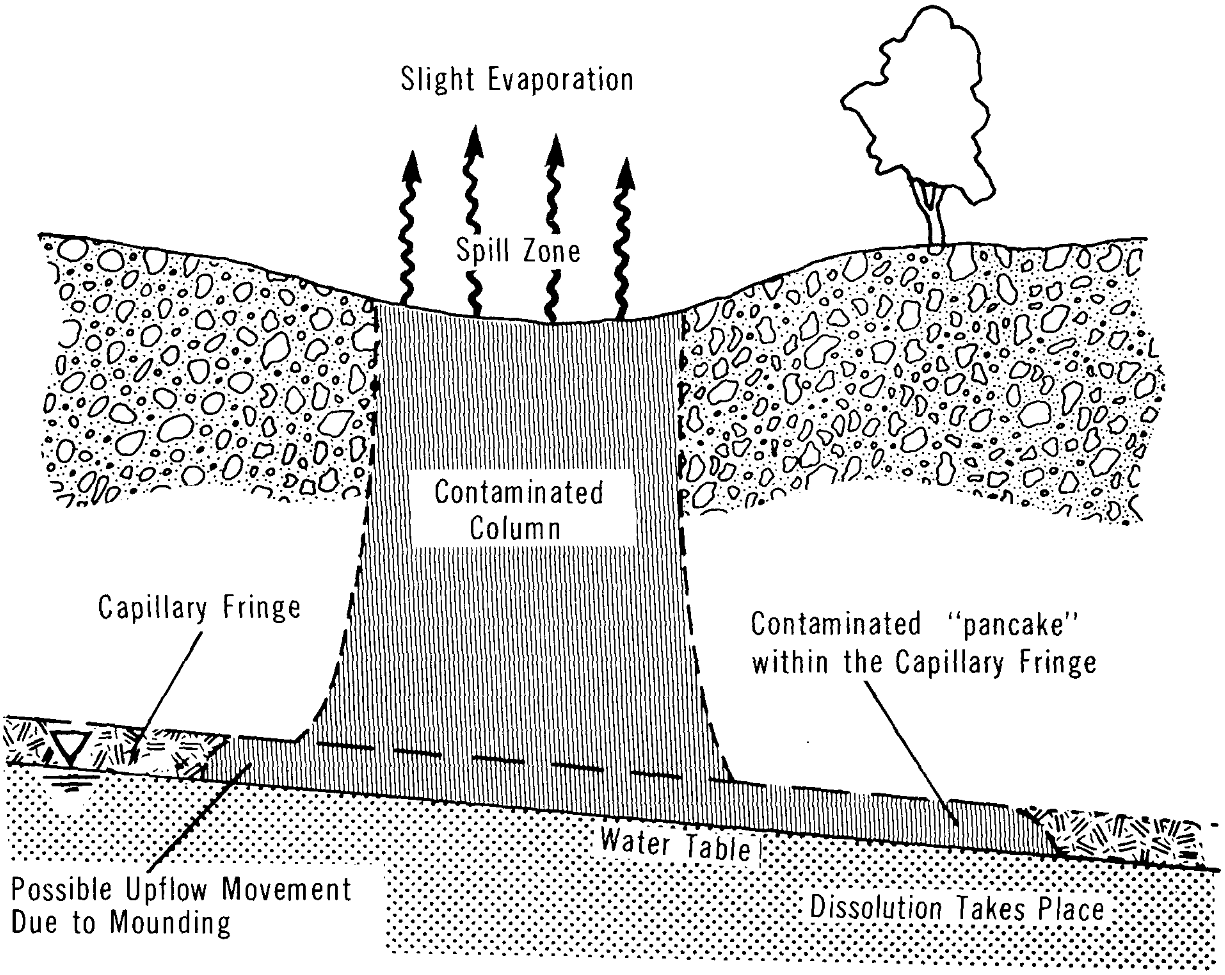
5.5.1 Introduction. Butyraldehydes are slightly soluble in water. Consequently, when spilled onto soil, infiltration and transport downward through the soil involve multiphase phenomena. The phases of concern are liquid butyraldehyde, water, soil and gas or vapours.

Unfortunately, sufficient data do not exist to permit a detailed assessment of contaminant transport in a specific circumstance. A few extensive field investigations have been carried out, especially involving spills of oil, gasoline and PCBs. For butyraldehyde, very limited information exists. Consequently, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to other more extensively studied materials. A pattern for the downward movement of immiscible fluids in soil has been prepared by comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979). It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled butyraldehyde fills the pores at the soil surface and begins to penetrate downward. It is assumed that the liquid moves downward through the soil as a saturated slug, but leaving behind a constant residual amount (S_o) within the soil pores. Downward transport will continue until the volume of butyraldehyde spilled per area (B_o) equals the amount retained in the soil as S_o. Some lateral spreading may occur due to capillary action. If B_o is greater than the volume that can be retained as S_o above the groundwater table, the excess butyraldehyde will spread as a "pancake" within the saturated groundwater capillary fringe. The resultant contaminated zone consists of a "vertical" column and "horizontal" pancakes of soil containing the residual amount of butyraldehyde, S_o. This is shown schematically in Figure 29.

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

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

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

–Field Capacity (θ_{fc}) = 0.075

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

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 appropriate properties of butyraldehyde (taken as an average of the n- and iso- isomers) are given in the chart below:

Property	Butyraldehyde 4°C	Butyraldehyde 20°C
Mass density (ρ), kg/m^3	822	798
Absolute viscosity (μ), Pa•s	0.50×10^{-3}	0.43×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(1.61 \times 10^7)k$	$(1.82 \times 10^7)k$

5.5.4 **Soils.** Three soils were selected for this work. Their relevant properties are:

Property	Soil Type Coarse Sand	Soil Type Silty Sand	Soil Type 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
Residual fraction (S_o), m^3/m^3	0.05	0.1	0.2

5.5.5 **Penetration Nomograms.** Nomograms for the penetration of butyraldehyde into the unsaturated zone above the groundwater table were prepared for each soil. The nomograms show the total depth of butyraldehyde penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_o). Temperatures of 4°C and 20°C were used. Calculations were based on equations developed in the Introduction Manual.

A flowchart for use of the nomograms is shown in Figure 30. The nomograms are presented as Figures 31, 32 and 33.

5.5.6 Sample Calculation. A 20 tonne spill of butyraldehyde has occurred on coarse sandy soil. The temperature is 20°C; the spill radius is approximately 8.6 m. Calculate the depth of penetration after 5 minutes.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- Mass density $\rho = 798$ kg/m^3
- $r = 8.6$ m
- $t_p = 5$ min

Step 2: Calculate the volume and area of spill

- $V = \dfrac{M}{\rho} = \dfrac{2 \times 10^4 \text{ kg}}{798 \text{ kg/m}^3} = 25.1 \text{ m}^3$
- $A = \pi r^2 = 232 \text{ m}^2$

Step 3: Estimate the depth of penetration (B) from Figure 31

- For coarse sand, B = 5.7 m

FIGURE 30

FLOWCHART FOR NOMOGRAM USE

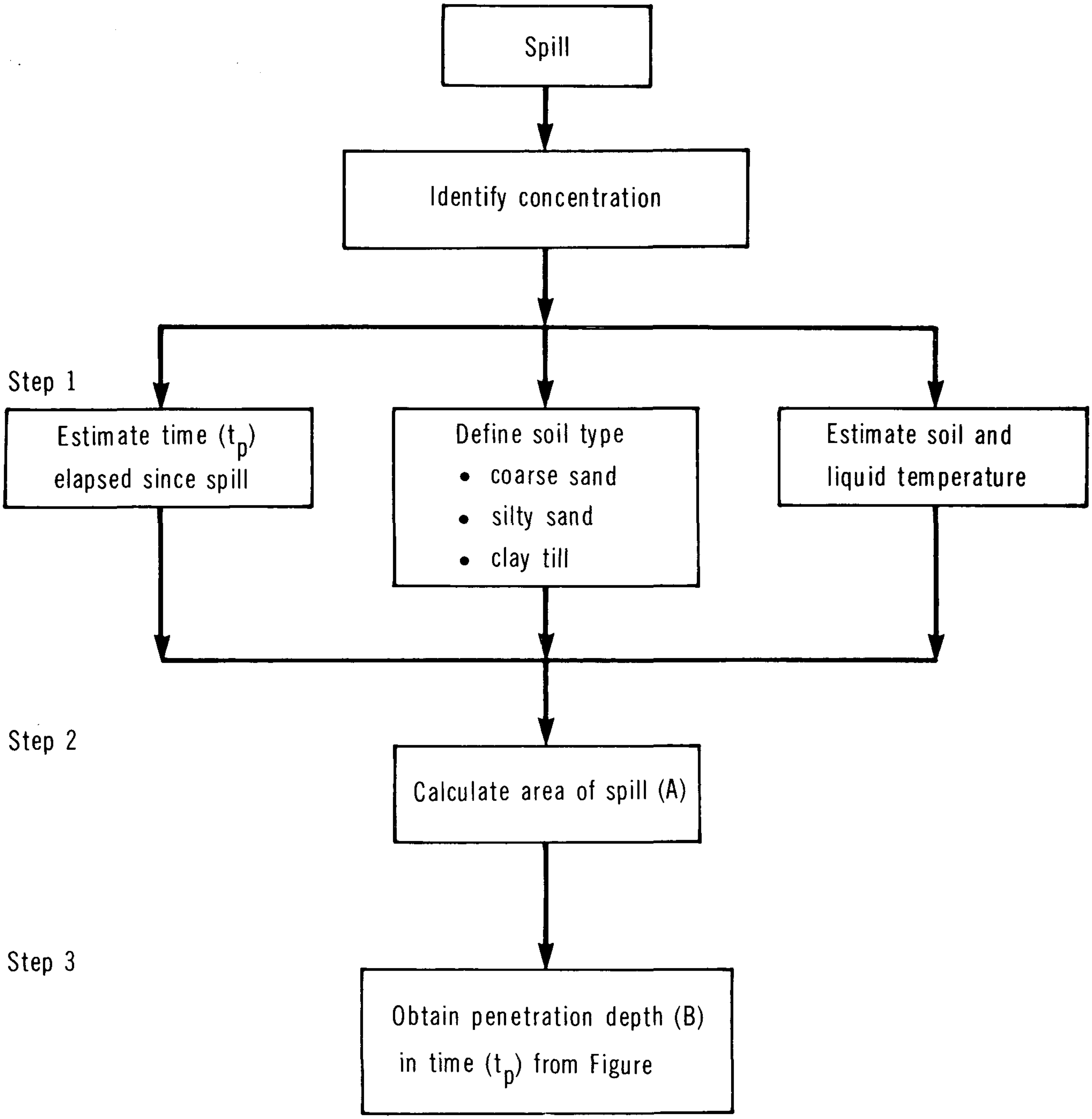


FIGURE 31

BUTYRALDEHYDES

PENETRATION IN COARSE SAND

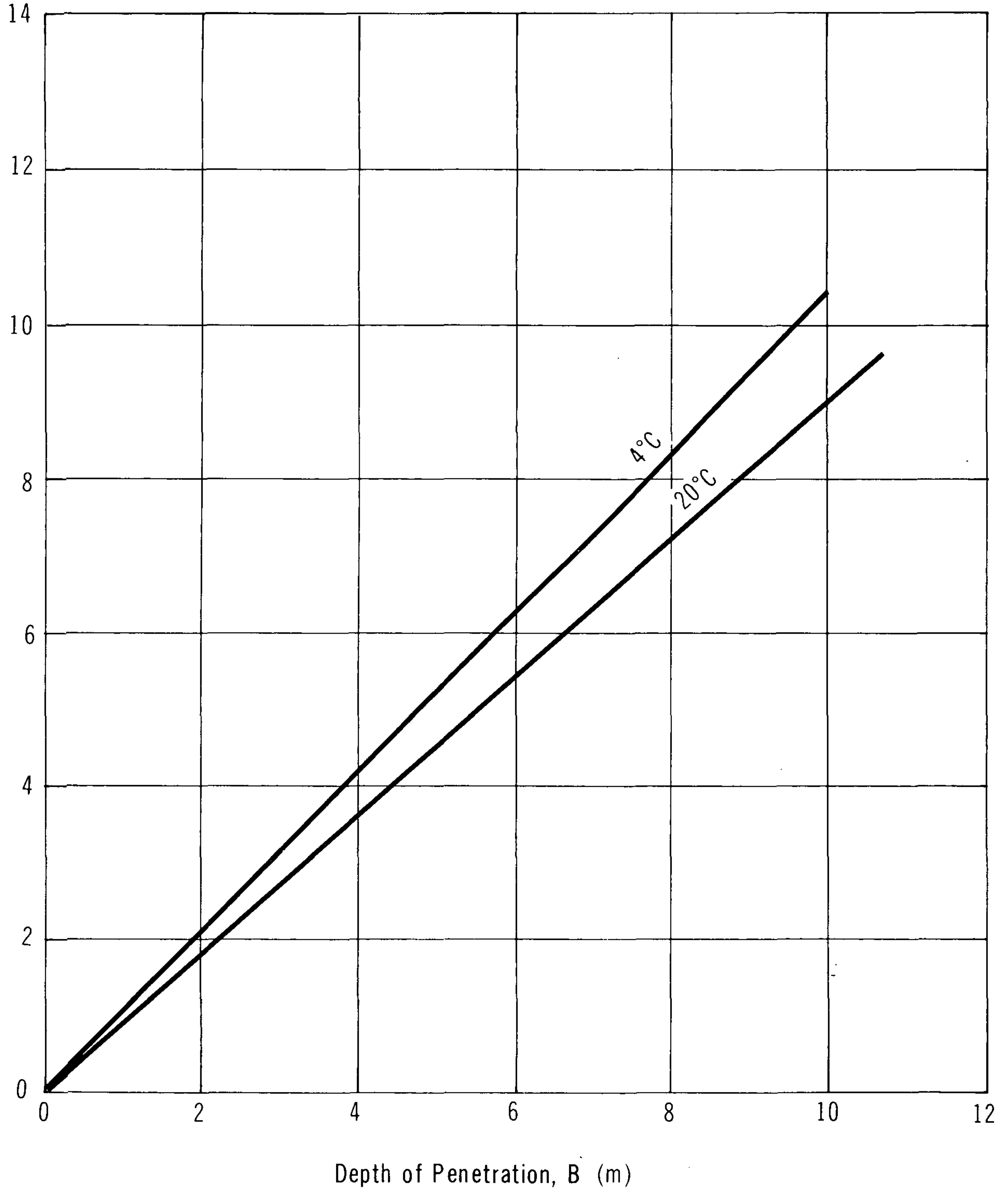


FIGURE 32

BUTYRALDEHYDES

PENETRATION IN SILTY SAND

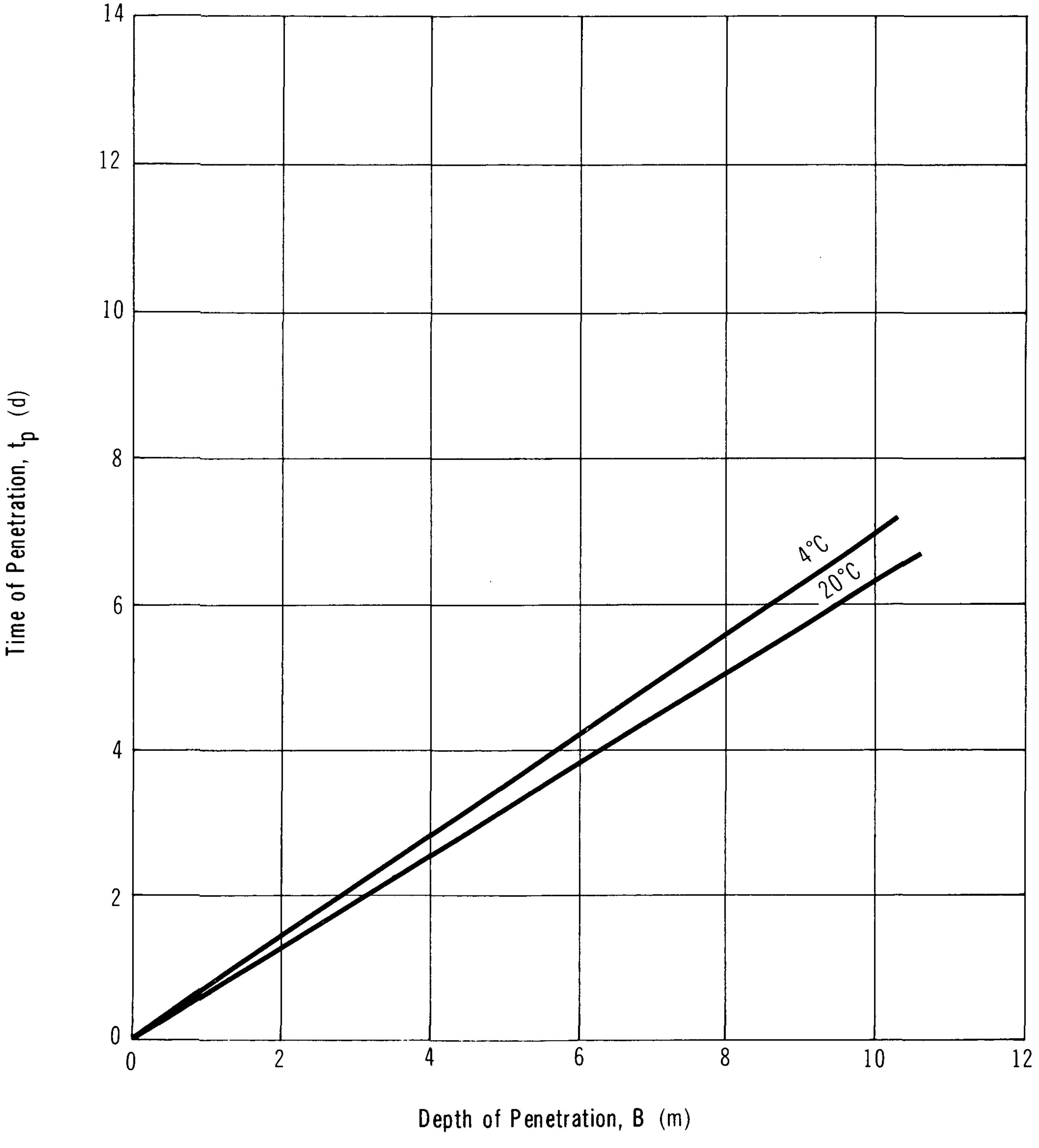
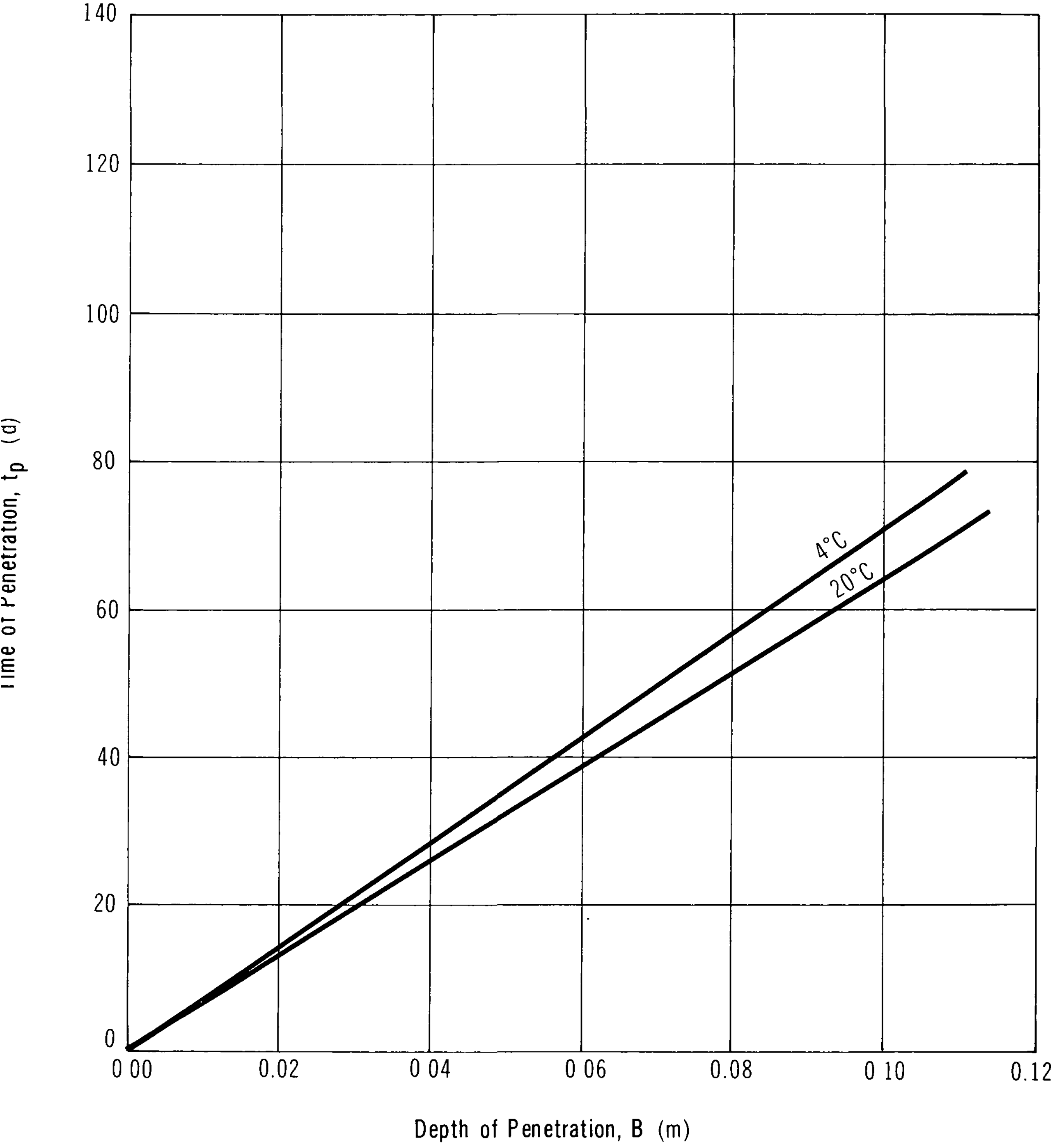


FIGURE 33

BUTYRALDEHYDES

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. A recommended maximum allowable concentration in class I waters for drinking purposes is 0.01 mg/L (Verschueren 1984).

6.1.2 Air. Environmental limits for butyraldehydes have not been specifically addressed.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. n-Butyraldehyde has been assigned a TL_m96 of 1 to 10 ppm; iso-butyraldehyde has been assigned a value of 100 to 1000 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
Fish Toxicity Data					
25.8	96	Fathead Minnow (*Pimephales promelas*)	LC_{50}	static, 22°C, HD = 40-48	JWPCF 1982
1	tns	toxic to chinook salmon, but not to squaw fish, steelhead trout or coho salmon		-	NRC 1981
5	24	not toxic to rainbow trout or bluegill		-	NRC 1981

Conc. (mg/L)	Species	Result	Reference
Microorganisms			
100	Bacteria (*Pseudomonas putida*)	inhibition of cell multiplication	Verschueren 1984
19	Algae (*Microcystis aeruginosa*)	inhibition of cell multiplication	Verschueren 1984
83	Green algae (*Scenedesmus quadricauda*)	inhibition of cell multiplication	Verschueren 1984

Conc. (mg/L)	Species	Result	Reference
4.2	Protozoa (*Entosiphon sulcatum*)	inhibition of cell multiplication	Verschueren 1984
98	Protozoa (*Uronema parduczi*)	inhibition of cell multiplication	Verschueren 1984
2500	Algae (*Chlorella pyranoidosa*)	toxicity threshold	Jones 1971

6.3 Mammalian Toxicity

The mean lethal dose in air (as aerosol) for mice is 4.8 mg/m^3 (Salem 1960). The no-effect level in rats is 1000 ppm (12 6-hour exposures) (Verschueren 1984).

6.4 Other Land and Air Toxicity

Irradiated butyraldehyde was applied to 8-day-old pinto beans and petunias at levels of 8.5 to 17.7 ppm; severe damage occurred to both plant types (NRC 1971).

6.5 **Degradation** (n-butyraldehyde)

B.O.D.	% Theo.	Days	Seed	Method	Reference
1.06 to 1.6	28 to 43	5	standard dilute sewage	-	Verschueren 1984
-	59.8	10			Verschueren 1984
-	66.4	20			Verschueren 1984
-	68.9	50			Verschueren 1984
<1	35	0.95	butanol-acclimated activated sludge	treatment plant	Ryerman 1966
<1	38	5	pure bacterial culture		Ryerman 1966
<1	22.8	1	activated sludge		Gerhold 1966
1.62	-	5	sewage seed		Henkelekian 1955

n-Butyraldehyde degrades at a moderate rate. Exposed material will oxidize to butyric acid (OHM-TADS 1981). The theoretical oxygen demand (TOD) is 2.44 kg/kg and the COD is 99 percent of the TOD (Verschueren 1984).

6.6 Long-term Fate and Effects

Limited testing indicated that butyraldehydes did not bioconcentrate in aquatic organisms (NRC 1981). In air, butyraldehydes ultimately break down to hydrocarbons and simple gases. n-Butyraldehyde undergoes the following reactions:

$$C_2H_5CHO \xrightarrow{\text{sunlight}} C_2H_5 + HCO$$

(rate is 2-4 x 10^{-5} s^{-1})

and

$$\xrightarrow{\text{sunlight}} C_2H_6 + CO$$

(rate is 1 x 10^{-6} s^{-1})

These reactions as well as the interaction with other species would imply that the half-life of butyraldehyde in air is less than 1 month (NRC 1981).

7 HUMAN HEALTH

Very little information on the toxicity of butyraldehydes was found in the published literature. No systemic effects in humans due to industrial exposures were encountered in the published literature, although animal experiments indicate that large doses may produce depression of the central nervous system and anesthesia. Contact of the liquid with the eye or skin will produce irritation, injury and possibly burns. Toxicity is considered to be low in general and moderate via the dermal route. There is no published TLV® for the compound.

Butyraldehyde was selected for carcinogenesis bioassay by the NCI. It has also been reported in the EPA TSCA Inventory. The toxicology 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

No exposure limits for butyraldehyde were found in the literature.

Effect	Origin	Level	Reference
Other Human Toxicities			
TC_{LO} (irritation)	-	n-butyraldehyde 580 mg/m^3	RTECS 1979

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Cause	Reference
SPECIES: Human		
Unspecified	Moderate irritation.	NRC 1981
SPECIES: Rabbit		
n-Butyraldehyde 500 mg (24 h)	Severe irritation.	RTECS 1979

Exposure Level (and Duration)	Cause	Reference
n-Butyraldehyde 410 mg	On open skin caused mild irritation.	RTECS 1979

7.2.2 Eye Contact.

Exposure Level (and Duration)	Cause	Reference
SPECIES: Human		
Unspecified	Will cause irritation and burns.	CHRIS 1978; NRC 1981
SPECIES: Rabbit		
n-Butyraldehyde 20 mg (24 h)	Severe irritation.	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: (iso-butyraldehyde) Pungent (CHRIS 1978).
(n-butyraldehyde) Pungent aldehyde; pungent and intense (CHRIS, 1978). Sweet and rancid, unpleasant (Verschueren 1984)

Odour Index for: n-butyraldehyde: 2 984 615 (Verschueren 1984).
iso-butyraldehyde: 948 000 (Verschueren 1984).

Note: All odour thresholds given are for n-butyraldehyde.

	Concentration		
Parameter	n-Butyraldehyde	iso-Butyraldehyde	Reference
Threshold Odour Concentration	4 to 25 ppb	25 to 300 ppb	Verschueren 1984
100% Recognition	39 ppb	300 ppb	Verschueren 1984

Parameter	Concentration n-Butyraldehyde	 iso-Butyraldehyde	Reference
50% Recognition	9.2 ppb	141 ppb	Verschueren 1984
Absolute Perception Limit	4.6 ppb	47 ppb	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		
n-Butyraldehyde 580 mg/m^3	LC_{LO} (Irritation)	RTECS 1979
230 ppm (10 min)	No irritation.	NRC 1981
SPECIES: Rat		
59 160 ppm (30 min)	LC_{50}	NRC 1981
8000 ppm (4 h)	LC_{50}	NRC 1981
SPECIES: Mouse		
n-Butyraldehyde 4.8 mg/m^3	Mean lethal dose.	OHM-TADS 1981
Chronic Exposures		
SPECIES: Rat		
n-Butyraldehyde 1000 ppm (6 h/d, 12 d)	No serious effect.	NRC 1981
iso-Butyraldehyde 1000 ppm (6 h/d, 12 d)	Slight nasal irritation.	NRC 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
n-Butyraldehyde (Unspecified concentration)	Ingestion unlikely due to irritating properties; however, severe damage to mucous membranes may occur.	AAR 1981
SPECIES: Rat		
n-Butyraldehyde 5890 mg/kg	LD_{50}	NRC 1981
n-Butyraldehyde 2490 mg/kg	LD_{50}	RTECS 1979
iso-Butyraldehyde 2810-3730 mg/kg	LD_{50}	NRC 1981

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
n-Butyraldehyde 10 g/kg	LD_{LO}	RTECS 1979
SPECIES: Mouse		
n-Butyraldehyde 2700 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutagenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: *Pseudomonas putida*		
n-Butyraldehyde 100 mg/kg	Inhibitory or toxic action noted; test was negative for mutagenicity.	NRC 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. Irritation of mucous membranes.
2. Headache (AAR 1981).
3. Nausea.
4. Vomiting.
5. Change in conditioned reflex (OHM-TADS 1981).
6. Change in blood serum composition (OHM-TADS 1981).
7. Loss of consciousness (AAR 1981).

7.5.2 Ingestion. Ingestion unlikely due to irritating properties; however, severe damage to mucous membranes may occur (AAR 1981).

7.5.3 Skin Contact.

1. Irritation.

7.5.4 Eye Contact.

1. Irritation.
2. Burns.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Butyraldehydes with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Heat, Fire		●	●										Flammable liquid; vapours form explosive mixtures with air.	Sax 1979; NFPA 1978
SPECIFIC CHEMICALS														
Chlorosulphonic Acid	●								●				In a closed container.	NFPA 1978
Nitric Acid	●								●				With 70 percent nitric acid.	NFPA 1978
Oleum	●								●				In a closed container.	NFPA 1978
Sulphuric Acid	●								●				With 96 percent sulphuric acid.	NFPA 1978
CHEMICAL GROUPS														
Alkali and Alkaline Earth Metals	●			●									Hydrogen gas may evolve.	EPA 600/2-80-076
Amines	●													EPA 600/2-80-076
Azo Compounds	●												Generation of nitrogen gas occurs.	EPA 600/2-80-076

8.1 Compatibility of Butyraldehydes 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
Caustics	●				●									EPA 600/2-80-076
Dithiocarbamates					●		●						Toxic flammable carbon disulphide may evolve.	EPA 600/2-80-076
Nitrides	●			●									Ammonia gas may be formed.	EPA 600/2-80-076
Nitro Compounds	●												Condensation may occur.	EPA 600/2-80-076
Organic Peroxides	●		●			●					●		Hydrogen gas may be evolved.	EPA 600/2-80-076
Unsaturated Aliphatics	●													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. Butyraldehydes are flammable liquids. Vapours form explosive mixtures with air and may travel to distant sources of ignition and flash back. Easily ignited, butyraldehyde fires are difficult to control due to ease of reignition (NFPA 1978). Containers may explode in heat of fire (ERG 1980).

9.1.2 Fire Extingishing Agents. Water may be ineffective (due to spreading) but should be used to keep fire-exposed containers cool. If a leak or spill has not ignited, use water spray to disperse the vapours (NFPA 1978).

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

Move containers from fire area if this can be done without risk. Stay away from tank ends. For massive fires, 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.

Hycar, an absorbent material, has shown possible applicability for vapour suppression and/or containment of butyraldehyde spills (ICI 1982).

9.1.3.2 Spills on land. Contain if possible by dyking. Adsorb spilled material on sand or other noncombustible absorbent material and shovel into containers for disposal (ERG 1980).

9.1.3.3 Spills on water. Contain if possible. Application of the following materials to sorb butyraldehydes should be considered (CG-D-38-76): activated carbon, polyurethane foam, polypropylene fibres, cellulose fibres, Amberlite XAD-1-8 and polyolefin fibres.

Carbon adsorption was found to be possibly applicable in spill situations by removing 53 percent of butyraldehyde in contaminated water (TSA 1980).

Butyraldehydes can also be removed by treating the contaminated water with activated sludge (Metry 1980). An anaerobic lagoon was shown to remove 70 to 90 percent in 1 day. In another test, activated sludge showed 14 percent removal of TOD (theoretical oxygen demand) in 6 hours, 21.7 percent in 12 hours, and 22.8 percent in 24 hours. Air stripping removed 85 percent in 8 hours. Reverse osmosis rejected 72.1 percent from a 0.01 m solution. Absorbability on activated carbon is 0.106 g/g carbon. A reduction of 52.8 percent was shown with an input of 1000 mg/L (Verschueren 1984).

9.1.4 **Disposal.** Waste butyraldehydes must never be discharged directly into sewers or surface waters. Following treatment, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill.

9.1.5 **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 butyraldehyde:

- Chemical safety goggles, spectacle-type safety goggles or face shields (20 cm minimum) should be worn to provide eye protection (MCA 1960).
- Self-contained breathing apparatus or positive pressure hose masks or air-line masks or chemical cartridge respirators should be worn to prevent inhalation of butyraldehyde vapours (MCA 1960).
- Butyl rubber has been recommended as a chemical suit material (excellent resistance) for protection against butyraldehyde (EE-20).

9.1.6 **Storage Precautions.** Protect containers against physical damage. Outside or detached storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Bulk storage tanks should be aluminum, stainless steel, or glass-lined, and blanketed with inert gas. Separate from oxidizing materials (NFPA 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.

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 Butyraldehyde in Air

11.1.1 High Pressure Liquid Chromatography (NIOSH, 1979). Butyraldehyde may be determined in air using a method for acetaldehyde. A range of 170 to 670 $\mu g/m^3$ (57.6 to 227.2 ppm) of butyraldehyde in air may be determined by high performance liquid chromatography.

A known volume of air is drawn through a midget bubbler containing 15 mL of Girard T reagent. A sample of 60 L at a flow of 500 mL/min is recommended. The Girard T reagent is prepared by dissolving 5.39 g of citric acid, 6.63 g of disodium hydrogen phosphate, and 16.77 g of Girard T reagent in approximately 400 mL of distilled water. The solution is transferred to a 500 mL volumetric flask and diluted to volume. This solution should be stored in the dark.

A 5 mL aliquot of sample is transferred to a 100 mL flask and diluted to volume with a standard eluent of 0.022 M disodium hydrogen phosphate and 0.019 M sodium dihydrogen phosphate. The eluent is prepared by combining 100 mL of stock eluent, 200 mL of 95 percent ethanol, and diluting to 1 L with distilled water. The stock eluent is prepared by dissolving 31.2 g of disodium hydrogen phosphate and 26.2 g of sodium dihydrogen phosphate in 1 L of distilled water. A 0.5 mL volume of sample is injected into a suitable high pressure liquid chromatograph.

The sample concentration is determined using a suitable electronic integrator which measures peak area. This, in conjunction with a calibration curve, is used to determine the concentration.

Typical high pressure liquid chromatograph conditions are: a 50 µL sample loop, ambient column temperature, flow rate at 0.75 mL/min, a mobile phase of 0.022 M disodium hydrogen phosphate and 0.019 M sodium dihydrogen phosphate in 20 percent ethanol, a UV detector, an analytical wavelength of 245 nm, and a 50 cm by 2 mm I.D. stainless steel column packed with Zipax SCX.

11.2 Qualitative Method for the Detection of Butyraldehyde in Air

Concentrations greater than 100 ppm of butyraldehyde in air may be determined with the use of a Drager detector tube for acetaldehyde. A known volume of air is drawn through a Drager detector tube for acetaldehyde using a Drager multi-gas detector pump. A colour change of the orange indicating layer to brownish-green indicated butyraldehydes with a lower sensitivity. The colour change is based on the reaction between an aldehyde and chromosulphuric acid (Drager 1979).

11.3 Quantitative Method for the Detection of Butyraldehyde in Water

11.3.1 Partition Infrared (AWWA 1981). Concentrations greater than 40 ppm of butyraldehyde (or less if concentrations are techniques used) in water may be determined using partition infrared spectrophotometry.

A minimum of 1 L of representative sample is collected in an appropriate container. The sample is acidified to pH 2 or lower with dilute hydrochloric acid. A 5 mL volume should be sufficient. The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is added after it is used to rinse the sample container. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® extractions are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®. Less than 40 ppm can be determined if the procedure is adjusted to achieve a greater concentration.

The sample is scanned on a suitable infrared spectrophotometer from 2800 to 1000 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.4 Qualitative Method for the Detection of Butyraldehyde in Water

The sample is collected and extracted as in Section 11.3.1. A 0.5 mL volume of 5 percent silver nitrate solution is transferred to a clean test tube. A small amount of dilute ammonia is added drop-wise until the brown precipitate initially formed just redissolves. The smallest possible amount of sample is added, and the mixture shaken and heated on a water bath to 50-60°C. A silver mirror formed on the test tube wall indicates an aldehyde (Owen 1969).

11.5 Quantitative Method for the Detection of Butyraldehyde in Soil

11.5.1 Partition Infrared (AWWA 1981). Concentrations greater than 40 ppm of butyraldehyde in soil may be determined by partition infrared spectrophotometry.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the butyraldehyde.

The extracts are combined in a 100 mL volumetric flask and the volume taken to 100 mL with Freon®. The sample is scanned on a suitable spectrophotometer from 2800 to 1000 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Butyraldehyde in Soil

The sample is collected and extracted as in Section 11.5.1. The sample is scanned on a suitable spectrophotometer from 2800 to 1000 cm^{-1} using matched 1 cm cells. The presence of characteristic absorption bands indicates the presence of butyraldehyde (AWWA 1981).

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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