

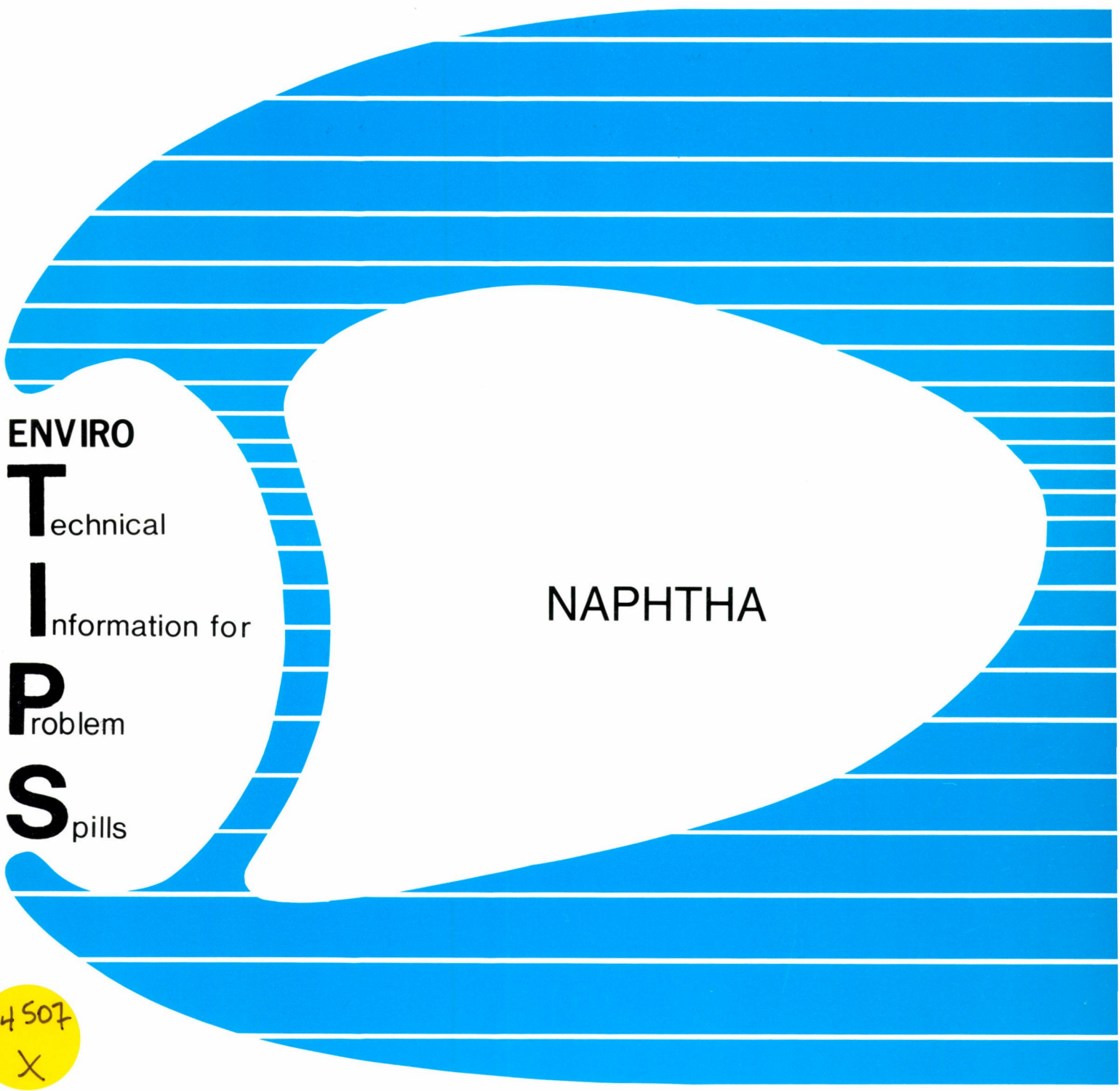
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ENVIRO

Technical

Information for

Problem

Spills

NAPHTHA

14507
X

April 1985

Canada

NAPHTHA

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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

April 1985

FOREWORD

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

ACKNOWLEDGEMENTS

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

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review 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

NAPHTHA

Colourless to yellow, watery liquid with a gasoline-like odour.

SYNONYMS

Aromatic Solvent, Naphtha Solvent or Distillate, Petroleum Benzin, Benzin Petroleum Distillates, Petroleum Ether, Petroleum Naphtha, Hi-Flash Naphthyethylene

COMMON TRADE NAMES

Varsol, Isopar, Iosol, Shell Sol, Sol B, Cyclo Sol, Circosol

IDENTIFICATION NUMBERS

UN No. 1255 (Petroleum), 1256 (Solvent); CAS No. 8030-30-6; STCC No. 4910241, 4910239, 4915239, 4910240 or 4914240.

GRADES

Various, generally based on boiling range, solvency, flash point, and other properties including (listed from the most volatile): petroleum ether, rubber solvent, light spirits, VM & P, coal tar, light mineral spirits, Stoddard solvent and odourless mineral spirits.

IMMEDIATE CONCERNS

Fire: Flammable. Flashback along vapour trail may occur.

Human Health: Moderately toxic by inhalation.

Environmental: Harmful to aquatic life in low concentrations.

PHYSICAL PROPERTY DATA

	<u>Mineral Spirits</u>	<u>VM & P</u>
State (15°C, 1 atm):	liquid	liquid
Boiling Point:	130-155°C	93-149°C
Flammability:	flammable	flammable
Flash Point:	>38°C (CC)	20-55°C (CC)
Specific Gravity (water=1):	0.85-0.87 (20°C)	0.75 (20°C)
Solubility (in water):	insoluble	insoluble
Behaviour (in water):	floats with no reaction	
Behaviour (in air):	vapour heavier than air	
Odour Threshold Range:	1-160 ppm	1-15 ppm

ENVIRONMENTAL CONCERNS

Constituents of naphthas are toxic to aquatic life, generally at concentrations below 100 mg/L. Naphtha constituents biodegrade and volatilize readily.

HUMAN HEALTH

TLV^o: Ranging from 100 to 400 ppm (525-1600 mg/m³)
IDLH: 5000 ppm (Stoddard solvent)

Exposure Effects

Inhalation: Irritation of respiratory tract, headache, vomiting, intoxication, fatigue, pallor, CNS depression, purplish discoloration of skin, possible hemorrhage of vital organs, coma and possibly death.

Contact: Irritation to skin and eyes. May cause erythema, blisters, drying and cracking of skin, and dermatitis.

Ingestion: Burning sensation, vomiting, diarrhea, drowsiness and possibly pulmonary edema.

IMMEDIATE ACTION**Spill Control**

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

Fire Control

Use alcohol foam, dry chemical or carbon dioxide to extinguish. Water may be ineffective due to the spreading it causes. Do not direct stream of water into burning liquid, for it will scatter the fire. 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: 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 synthetic sorbents and shovel into containers with covers.

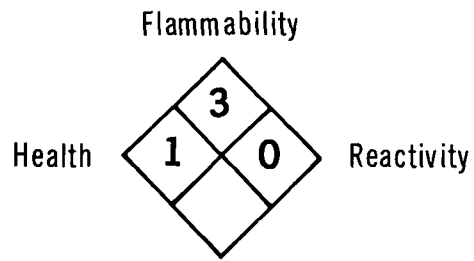
Water: Contain with booms, weirs or natural barriers. Use (oil) skimming equipment to remove slick, followed by the application of sorbents.

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

NAS HAZARD RATING

**NFPA
HAZARD
CLASSIFICATION**

VM&P NAPHTHA



2 PHYSICAL AND CHEMICAL DATA

"Naphtha" generally refers to a wide variety of petroleum or coal tar distillates. Broad standards for these exist; naphthas are usually taken as being one of eight general classes or categories described below (PPH 1960; MPT 1975; ASTM 1962):

Class	Approximate Boiling Point Range (°C)
Petroleum Ether	30-60
Rubber Solvent	45-115
Light Spirits	95-110
VM & P (Varnish makers and painters naphtha)	100-140
Coal Tar Naphtha	100-180
(Light) Mineral Spirits	150-170
Stoddard Solvent (also called Mineral Spirits)	150-200
(Odourless) Mineral Spirits	175-210

These classes overlap; manufacturers may therefore classify the same product in two or more classes. The composition and properties also vary widely within a class.

The properties of some naphthas are listed in the following tables by category:

	Reference	
	CCD 1977	NFPA 1978
Petroleum Ether		
Boiling Point/Distillation Range (°C)	30-60	35-60
Freezing Point (°C)	-73	-
Flash Point (°C)	-49	<-18
Autoignition Temperature (°C)	288	288
Specific Gravity	0.6	0.6
Upper Flammability Limit (volume percent)		5.9
Lower Flammability Limit (volume percent)		1.1
Vapour Density		2.5

VM & P (Naphtha)

	Reference				
	NFPA 1978 (VM & P Naphtha Regular)	NFPA 1978 (VM & P High Flash)	NFPA 1978 (VM & P 50°F Flash)	Alliance 1980	CHRIS 1978
Boiling Point/Distillation Range (°C)	100-160	138-177	116-143	100-160	93-149
Specific Gravity (20°C)	<1	<1	<1	0.75	0.75
Flash Point (°C)	-2	29	10	-7-8	-7-13
Autoignition Temperature (°C)	232	232	232		232
Lower Flammability Limit (volume percent)	0.9	1.0	0.9	0.9	0.9
Upper Flammability Limit (volume percent)	6.0	6.0	6.7	6.0	6.7
Solubility in Water	Insoluble	Insoluble	Insoluble		
Vapour Density		4.3	4.1		
Burning Rate					4.4 mm/min
Behaviour in Fire					Vapour may flash back
Liquid Surface Tension (20°C)					19-23 mN/m
Surface Tension with Water					39-51 mN/m
Heat of Vaporization					3-3.4 x 10 ⁵ J/kg
Heat of Combustion					-424 x 10 ⁵ J/kg

5

Coal Tar Naphtha

	Reference			
	Sax 1984	NFPA 1978	CHRIS 1978	Alliance 1980
Colour	Colourless to straw-coloured		Colourless to pale yellow	
Specific Gravity	0.862-0.892	<1	0.86-0.88 (20°C)	0.85
Boiling Point (°C)	149-216		93-260	138-215
Flash Point (°C)	42	<27	41	38-43
Solubility in Water		Insoluble		
Autoignition Temperature (°C)	277		482-510	
Burning Rate			4 mm/min	
Heat of Vaporization			2.35×10^5 J/kg	
Heat of Combustion			-424×10^5 J/kg	

The following is a generalized description of the composition of some naphthas (NIOSH 1977):

Name	Boiling Range (°C)	Typical Composition
Petroleum ether	30-60	primarily pentane and i-hexane; no aromatics
Rubber solvent	45-125	pentanes to octanes; 70-90 percent paraffins 11-22 percent naphthenes 9-22 percent aromatics
VM & P Naphtha	95-160	C ₇ to C ₁₁ hydrocarbons 45-60 percent paraffins 30-45 percent naphthenes 5-13 percent aromatics
Mineral spirits	150-200	C ₉ to C ₁₂ hydrocarbons 30-65 percent paraffins 15-55 percent naphthenes 10-30 percent aromatics
Stoddard solvent	160-210	C ₉ to C ₁₁ hydrocarbons 30-50 percent paraffins 30-40 percent naphthenes 10-20 percent aromatics

The composition of a light naphtha (e.g., like a rubber solvent) with a boiling point range of 70-95°C is given in the following table (MPT 1975):

Hydrocarbon Constituent	Approximate Boiling Point, (°C)	Percent by Weight Present
Isopentane	28	Trace
n-Pentane	36	0.1
Cyclopentane	49	Trace
2,3-Dimethylbutane	58	0.1
2-Methylpentane	60	0.8
3-Methylpentane	63	3.1
n-Hexane	68.5	36.1
2,2-Dimethylpentane	79	0.6
Methylcyclopentane	72	12.1
2,4-Dimethylpentane	80.5	1.8

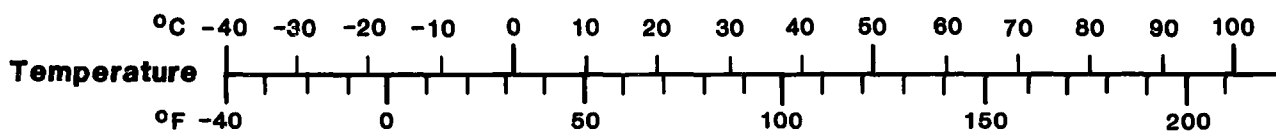
Hydrocarbon Constituent	Approximate Boiling Point, (°C)	Percent by Weight Present
2,2,3-Trimethylbutane	81	0.1
Benzene	80	Trace
3,3-Dimethylpentane	86	0.3
Cyclohexane	81	7.8
2-Methylhexane	90	7.6
2,3-Dimethylpentane	90	3.1
1,1-Dimethylcyclopentane	87.5	0.9
3-Methylhexane	92	8.2
1- <i>cis</i> -3-Dimethylcyclopentane	92	1.6
1- <i>trans</i> -3-Dimethylcyclopentane	91	1.4
3-Ethylpentane	93.5	0.6
1- <i>trans</i> -2-Dimethylcyclopentane	92	2.8
n-Heptane	98.5	7.4
1- <i>cis</i> -2-Dimethylcyclopentane	99	
Methylcyclohexane	101	2.5
2,2,3,3-Tetramethylbutane	106.5	
1,1,3-Trimethylcyclopentane	105	0.1
Ethylcyclopentane	103.5	0.2
2,5-Dimethylhexane	109	0.1
2,4-Dimethylhexane	109.5	Trace
1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane	109	0.1
1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane	110	0.1
2,3,4-Trimethylpentane	113.5	Trace
Toluene	110.5	0.3
2-Methylheptane	118	0.1

A system naming the product by the first two digits of its boiling range (Fahrenheit) is sometimes used to classify naphthas. In this system, "3139" boils between 310 and 390°F. Some commercially supplied solvents are shown in the following table, with fire hazard properties and composition.

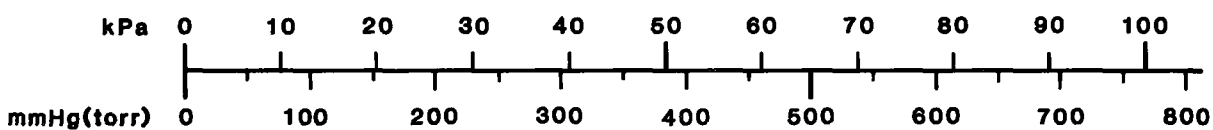
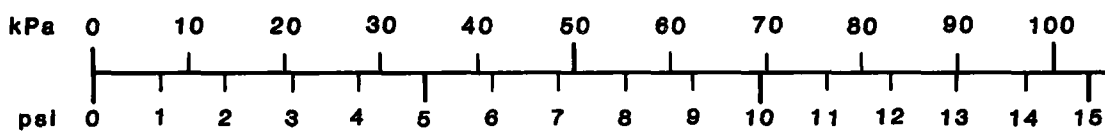
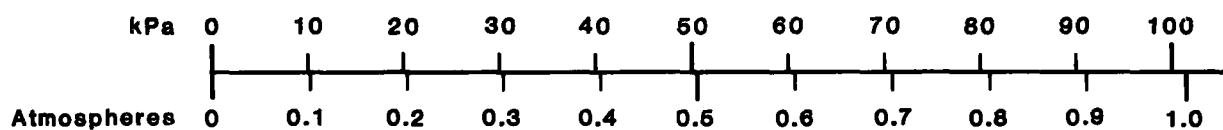
Class	Trade Name	Number	Density (g/mL)	Flash Point (TCC, °C)	Distillation Range (°C)	Percentage Composition					Reference
						Paraffins	Naphthenes	Olefins	Aromatics	Benzene	
Light Spirits	Iosol	(1125)	0.7125	-23	43 to 121	56	40	-	4	-	Esso 1973
Light Spirits	-	1420	0.7038	<20	60 to 95	66	30	0.1	4	2.1	Gulf TS 1983
Light Spirits	-	1426	0.7080	<20	64 to 127	74	22	0.2	5	0.2	Gulf TS 1983
Light Spirits	Iosol	1520	0.7111	-21	66 to 94	63	34	-	3	-	Esso 1973
Light Spirits	-	1521	0.6900	<20	63 to 106	87	5	1	7	0.1	Gulf TS 1983
Light Spirits	Iosol	1921	0.7366	-9	88 to 99	42	54	-	4	-	Esso 1973
Light Spirits	Tolu-Sol 25	(2023)	0.74	-4	92 to 107	67	8	-	24	-	ISH 1977
Light Spirits	Tolu-Sol 45	(2023)	0.771	-5	94 to 112	51	6	-	42	-	ISH 1977
Light Spirits	-	2024	0.7398	<20	89 to 124	46	45	0.1	9	<0.1	Gulf TS 1983
Light Spirits	Iosol	2024	0.7440	-4	93 to 117	39	55	-	6	-	Esso 1973
VM & P	-	2137	0.7572	25	98 to 154	45	41	0.1	14	0.2	Gulf TS 1983
VM & P	-	2329	0.7588	<20	109 to 138	43	41	0.1	16	<0.1	Gulf TS 1983
VM & P	-	2429	0.7599	12	116 to 143	43	45	-	12	-	Esso 1973
VM & P	-	2430	0.7866	<20	116 to 146	44	52	0.1	4	<0.1	Gulf TS 1983
Mineral Spirits	Cyclo-Sol 38	(2831)	0.863	29	136 to 153	4	3	-	94	-	ISH 1977
Mineral Spirits	Varsol	3134	0.7892	42	158 to 200	46	41	-	13	-	Esso 1973
Mineral Spirits	Varsol DX	3135	0.7770	42	156 to 177	44	51	-	5	-	Esso 1973
Mineral Spirits	Varsol	3135	0.7848	41	156 to 177	44	44	-	12	-	Esso 1973
Mineral Spirits	-	3135	0.7858	41	154 to 171	45	38	0.4	17	0	Gulf TS 1983
Mineral Spirits	-	3139	0.788	43.5	155 to 191	45	40	0.1	15	0	Gulf TS 1983
Mineral Spirits	Shell Mineral Spirits	(3238)	0.797	41	159 to 194	37	38	-	26	-	ISH 1977
Stoddard Solvent	Varsol DX	3641	0.7977	57	183 to 211	45	49	-	6	-	Esso 1973
Mineral Spirits	Shell Sol 140	(3740)	0.786	61	187 to 203	48	48	-	4	-	ISH 1977
Mineral Spirits	-	5261	0.8773	138	271 to 325	50	37	0.1	13	0	Gulf TS 1983

NAPHTHA

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa

**Viscosity**

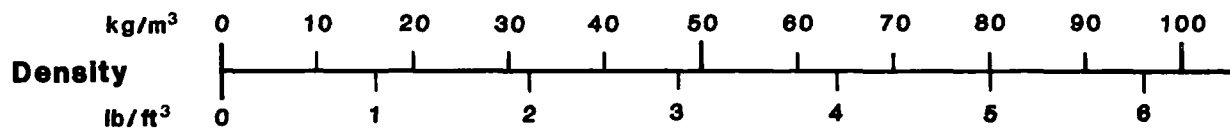
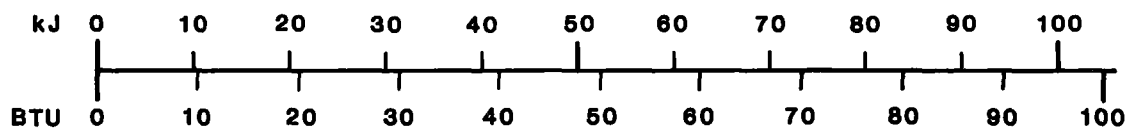
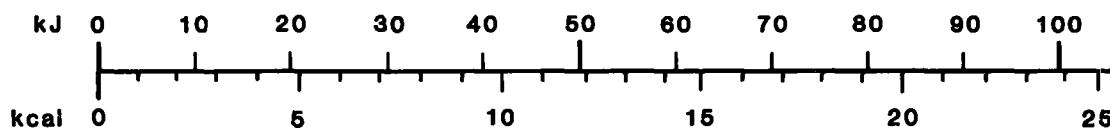
Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m²/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm \cong 1 mg/L

Energy (heat) 1 kJ = 1 000 J



3 COMMERCE AND PRODUCTION

3.1 Grades

A number of grades of "naphtha" are available, differing in boiling point, boiling range, flash point, solvency and other properties depending on the end use. The most commonly used naphthas correspond to VM & P (varnish makers and painters) naphtha, boiling typically in the 100-160°C range, and mineral spirits, boiling in the 160-200°C range. Stoddard solvent, originally developed for dry cleaning, has a boiling range similar to that of mineral spirits but has different solvency and odour requirements.

Many grades have been marketed for other purposes. Manufacturers specifications for such grades have some variability, depending on manufacturing and feedstock differences, and on market demand. Many of these grades are provided in Chapter 2.

3.2 Domestic Manufacturers (CBG 1980)

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

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

Shell Canada
505 Universtiy Avenue
Toronto, Ontario
M5W 1K3
(416) 597-7111

Petrosar Limited
P.O. Box 3060
Sarnia, Ontario
N7T 7M1
(519) 862-2911

3.3 Other Suppliers (CBG 1980)

Apco Industries Co. Ltd.
10 Industrial Street
Toronto, Ontario
M4G 1Z1
(416) 421-6161

Ashland Chemical/Solvents Div.
150 Bronoco Avenue
Toronto, Ontario
M6E 4Y1
(416) 823-7680

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

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

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

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

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

Van Waters and Rogers Ltd.
9800 Van Horne Way
Richmond, B.C.
V6X 1W5
(604) 273-1441

Paisley Products
40 Upton Road
Scarborough, Ontario
M1L 2B8
(416) 755-2216

Petrocan Chemicals
1 Place Ville-Marie
Montreal, Quebec
H3B 4A9
(514) 866-3911
(514) 866-2094

3.4 Production Levels (CPMA 1980)

Production statistics for naphthas are not readily available from manufacturing sources, and estimates are complicated by the multiplicity of naphtha types. The coatings industry (e.g., paints, etc.) uses about 26 kt/yr of "mineral spirits" and 12 kt/yr of "VM & P". This suggests a total use as solvent of about 140 kt/yr, based on consumption of other solvents.

3.5 Manufacturing Process (Shreve 1977)

Naphthas are produced in the refining of petroleum feedstocks, as part of the light distillate fraction. Petroleum feedstock is fed to a catalytic cracker or reformer, where heat and catalytic action cause it to reform to a mixture of hydrocarbon products. These are separated by distillation, the less desirable being reprocessed into more desirable products by polymerization, alkylation, isomerization, hydrogenation or reformation reactions. The light distillable fraction includes naphthas, gasoline, petroleum solvents, kerosene, etc. These are separated by further narrow-cut distillation.

3.6 Major Uses in Canada

Solvent: paint, surface coatings, inks, adhesives, etc.

Feed stock: as feedstock for the petrochemical industry and also for the production of automotive fuels.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars and highway tank vehicles. Naphtha is also transported in bulk by pipeline and ship; however, these will not be covered here.

4.1.1.1 Railway tank cars. Railway tank cars used to transport naphtha are classified under the CTC/DOT Specifications described in Table 2 below (TCM 1979; RTDCR 1974).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test Pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi).

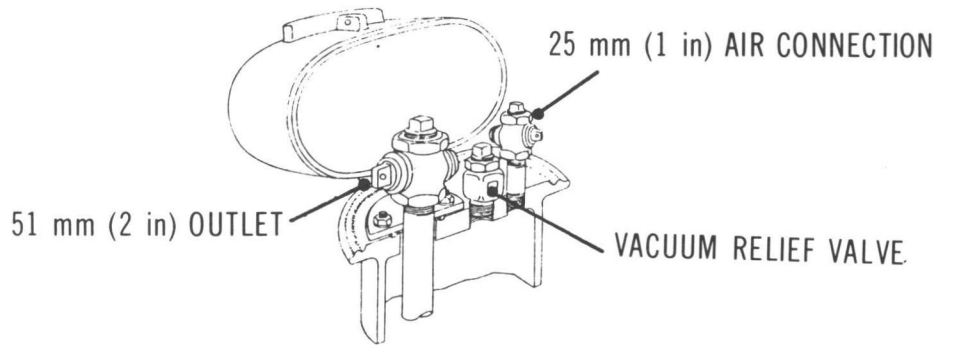
* Canadian Transport Commission and Department of Transportation (U.S.)

Figure 1 shows a 111A60W1 railway car used to transport naphtha; Table 3 indicates railway tank car details associated with this drawing (TCM 1979). Cars are equipped for unloading by pump or gravity flow through a 152 mm (6 in.) diameter bottom outlet provided with an inner plug valve (TDGC 1980). In addition to bottom unloading, the cars may be unloaded from the top by pump. In this case, the naphtha 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.

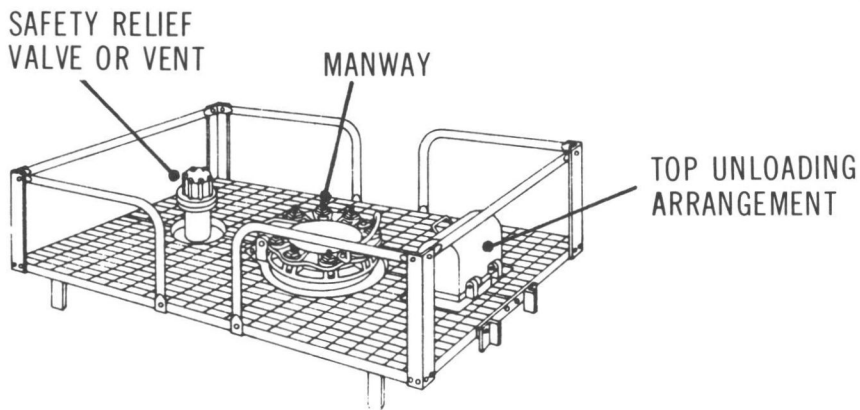
NAPHTHA

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

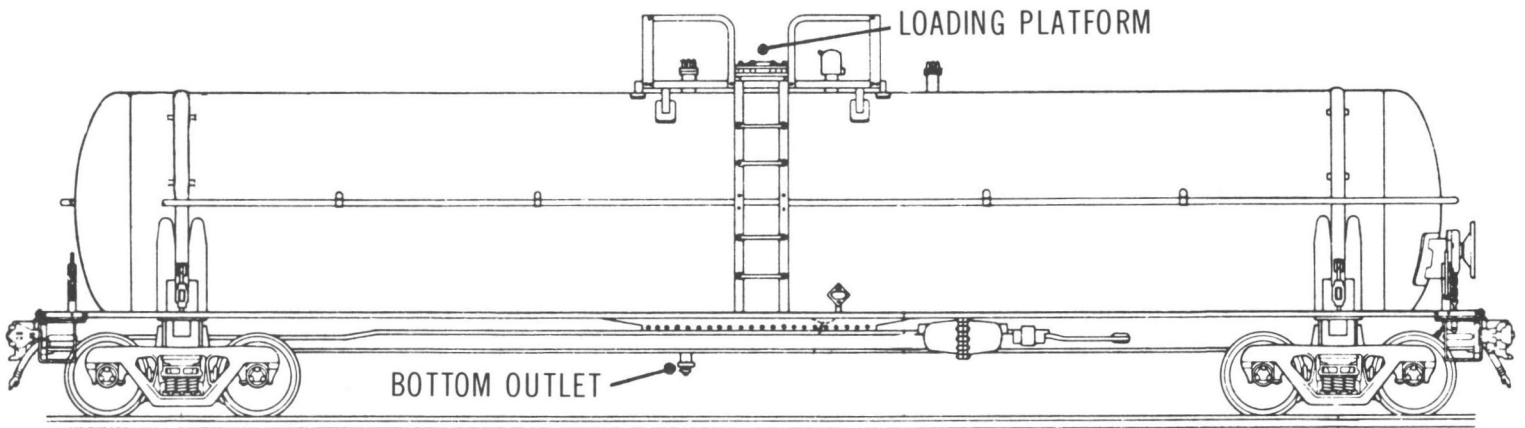


Illustration of tank car layout

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

Description	Tank Car Size (Imp. Gal.)					
	16 700		17 200		20 000	
<u>Overall</u>						
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.)
<u>Tank</u>						
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)
<u>Approximate Dimensions</u>						
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 centers	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.)
<u>Loading/Unloading Fixtures</u>						
<u>Top Unloading</u>						
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.)
<u>Bottom Unloading</u>						
Bottom outlet	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)
<u>Safety Devices</u>						
	Safety vent or valve					
<u>Dome</u>						
	None					
<u>Insulation</u>						
	Optional					

A safety vent set at 414 kPa (60 psi) is required on top of the rail car (TCM 1979). A gauging device, either the rod type or the tape type, is required. The top unloading connection must be protected by a housing. The maximum pressure allowable for the DOT 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi) (TCM 1979).

4.1.1.2 Tank motor vehicles. Naphtha is transported by tank motor vehicles with tanks classed as nonpressure vessels (HMR 1978). Design pressure for such tanks does not exceed 14 kPa (2 psi). Motor vehicle tanks carrying naphtha are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve. 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. Naphtha, in addition to railway bulk shipments, is also transported in drums. Drums fabricated from a variety of construction materials are permitted (Table 4) (TDGC 1980).

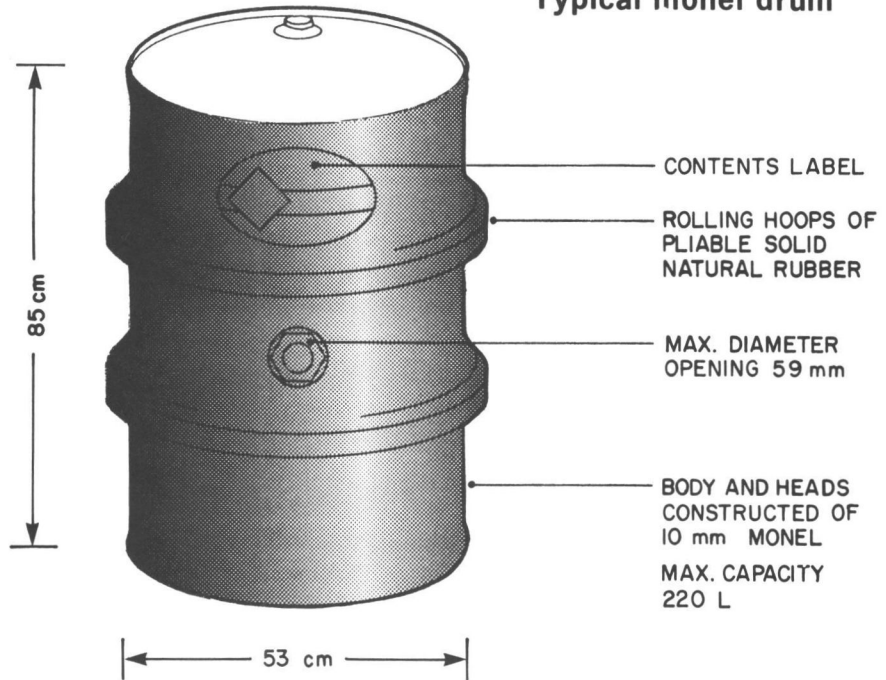
TABLE 4 DRUM SPECIFICATIONS

Type of Drum	Designation	Description	Figure No. (if any)
Steel	1A1	Nonremovable head, reusable	2
	1A1A	1A1 with reinforced chime	2
	1A1B	1A1 with welded closure flange	2
	1A1D	1A1 with coating (other than lead)	2
	1A2	Removable head, reusable	2
	1A3	Nonremovable head, single use only.	2
Monel*	TC5M		2
Aluminum*	1B1	Nonremovable head	2
	1B2	Removable head	2
Steel drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)	
Fibreboard drums with inner plastic receptacles	6HG1	Outer containers of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity of 225 L (49 gal.)	

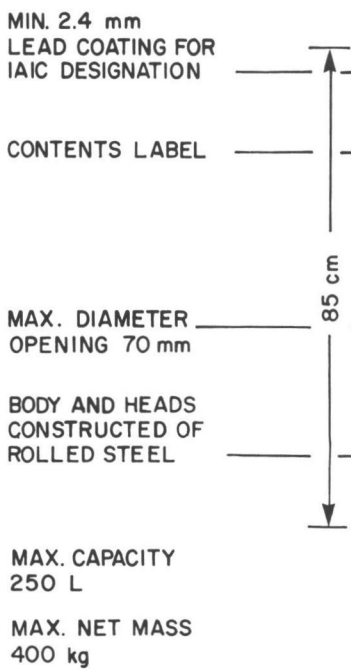
* Monel and aluminum are generally not used for naphtha, although no specific corrosion data relating to these materials were found.

TYPICAL DRUM CONTAINERS

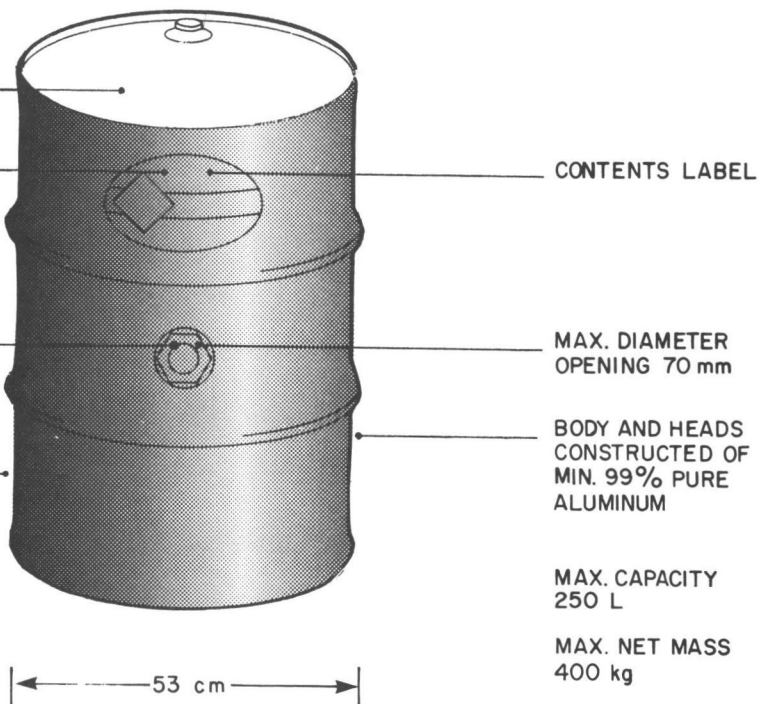
Typical monel drum



Typical steel drum



Typical aluminum drum



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:

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Two means of off-loading are used for naphtha rail cars, top off-loading and bottom off-loading. Proceed with top off-loading as follows (TCM 1979):

- 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 the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only.

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

- In cold weather, apply steam to the bottom unloading connection and to the steam coil connection valves shown in Figure 1.
- Relieve internal pressure as previously mentioned.
- After connecting the unloading line to a 15 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity or pump.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used. It is recognized that other materials may be used for particular applications as indicated in Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless ASTM A106 carbon steel pipes and fittings lined with chlorinated polyether resins are recommended for naphtha 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 (50-75 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, but process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Some installations of flexible line are made with standard lined fittings using a number of screwed elbows.

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

A centrifugal pump with "wet end" material of 316 stainless steel gives good results. 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 naphtha 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:

<u>Recommended:</u>	This material will perform satisfactorily in the given application.
<u>Conditional:</u>	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
<u>Not Recommended:</u>	Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Temp. (°C)	Material of Construction		
		Recommended	Conditional	Not Recommended
1. Pipes and Fittings	To operating limit of material	PVC I (MWPP 1978)	PE (MWPP 1978)	ABS (MWPP 1978)
		Steel Carbon Steel Stainless Steel	Monel Aluminum	
	135	PVDF (DCRG 1978)		
	121	Chlorinated Polyether (DCRG 1978)		
	66	PVDC (DCRG 1978)		
	52	PP (DCRG 1978)		

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene Aluminum Carbon Steel Chlorinated Polyether Fluorine Rubber (Viton) Monel Nickel-Copper Alloy (Monel)
PE	Polyethylene
PP	Polypropylene
PVC (followed by grade if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride Stainless Steel Steel

5 CONTAMINANT TRANSPORT

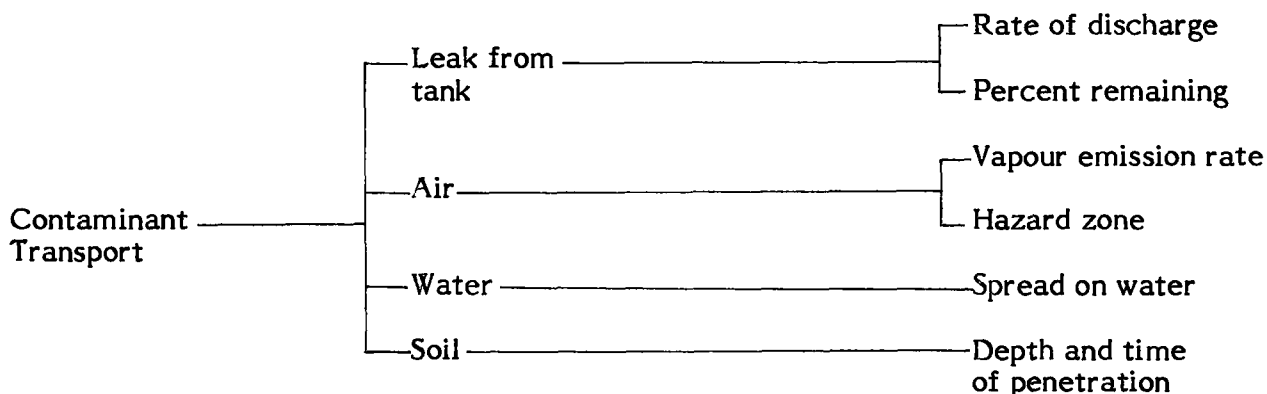
5.1 General Summary

Naphtha is a colourless, watery, volatile liquid that is commonly transported in railway tank cars. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground, being absorbed by the soil. A flammable vapour is released continuously to the atmosphere by evaporation. The vapour cloud tends to hug the ground and spread rather than lift off the ground and disperse.

When spilled on water, the slick has a natural tendency to spread. Since it is insoluble and less dense than water, none will be dissolved; however, the material will evaporate to the atmosphere until it is removed.

Naphtha when spilled on the ground is gradually absorbed into the soil, at a rate dependent on the soil type and its degree of saturation with water. At the same time, the downward transport of the liquid toward the groundwater table may cause environmental problems.

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



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.

5.2 Leak Nomograms

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

It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with naphtha 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 tank cars carrying naphtha are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

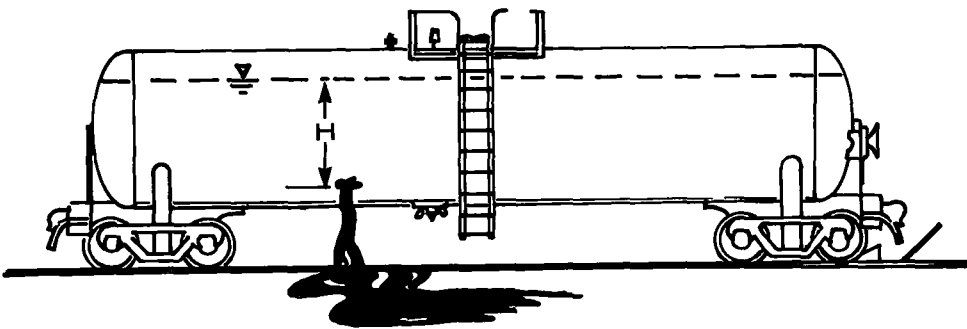


FIGURE 3 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

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). The venting rate (q) is a function of hole size (A) and shape, the height of the fluid above the puncture hole (H), and a coefficient of discharge (C_d). 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 4: Percent remaining versus time. Figure 4 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at $t=0$) with a volume of about 80 000 L of VM & P naphtha. 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 5: Discharge rate versus time. Figure 5 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 VM & P naphtha 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 4
- 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 5
- With $t=10$ min and $d=150$ mm, the instantaneous discharge rate (q) = 70 L/s

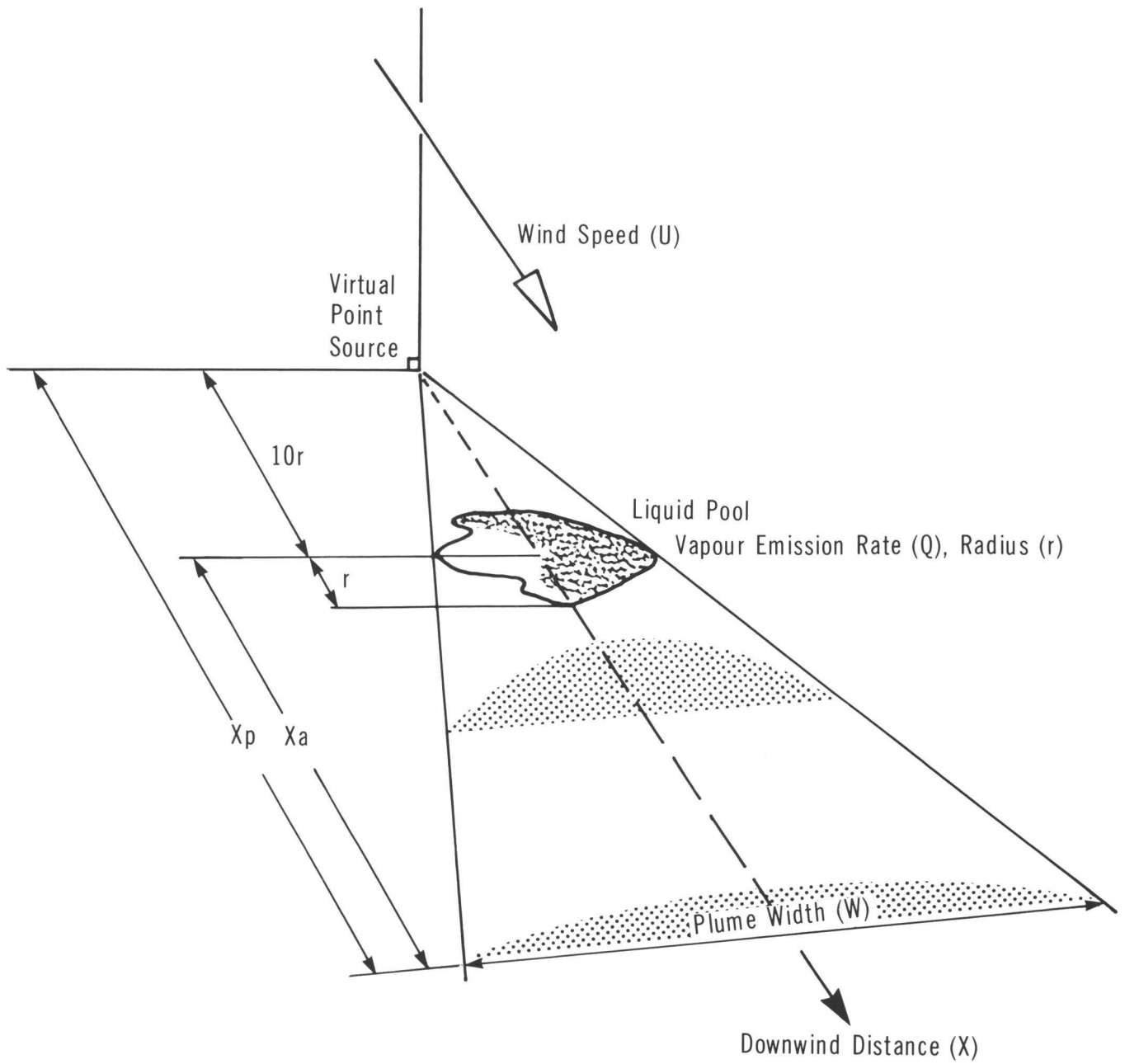
5.3 Dispersion in the Air

5.3.1 Introduction. Since naphtha is a moderately volatile liquid, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute as significant a hazard downwind as vapour released from a liquid pool spilled on a ground or water surface. 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 6 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.

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SCHEMATIC OF CONTAMINANT PLUME



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 8: vapour emission rate from a liquid pool as a function of maximum pool radius
- Table 7: weather conditions
- Figure 9: normalized vapour concentration as a function of downwind distance and weather conditions
- Table 8: maximum plume hazard half-widths
- Figure 12: vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 7 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" and "equivalent pool radius" are contained in Sections 5.2 and 5.4, respectively. A description of each vapour dispersion nomogram and its use follows.

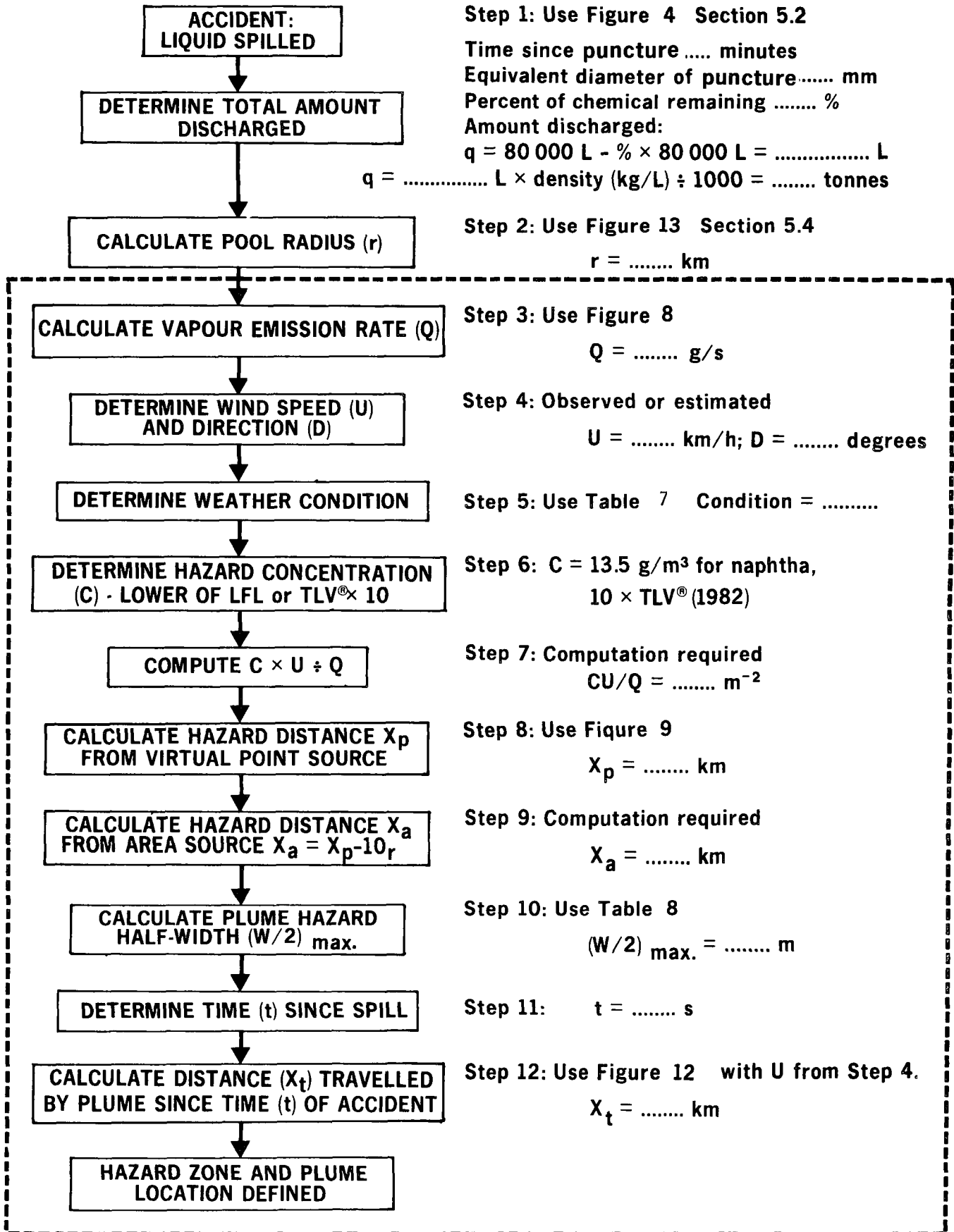
5.3.2.1 Figure 8: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for naphtha (VM & P) has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for naphtha at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.78 g/(m²s). 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 (calculated from the boiling point using the Clapeyron equation) of naphtha at that temperature. For example, evaporation rates of 0.30 g/(m²s) at 0°C and 1.22 g/(m²s) at 30°C were calculated for a wind speed of 4.5 m/s.

Using Figure 13, Section 5.4, the maximum spill radius corresponding to various spill amounts of naphtha may be determined. The resultant spill areas and the naphtha evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 8.

Use: For a pool of naphtha of known radius, the rate (Q) at which naphtha vapour is released to the atmosphere at a given temperature can then be estimated from Figure 8. The solid portions of the curves represent spills of 0.05 to 60 tonnes, the latter

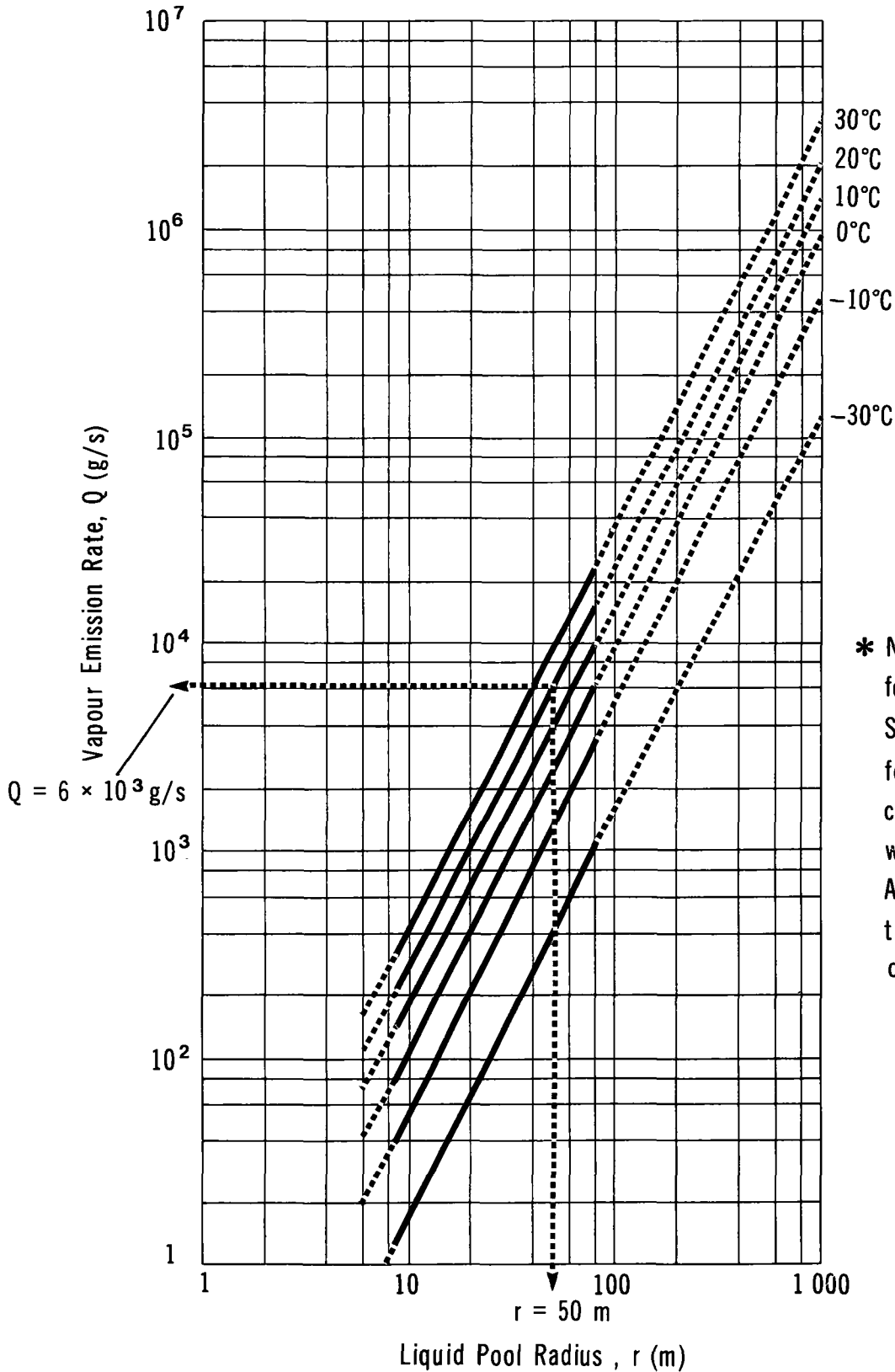
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**FLOW CHART TO DETERMINE
VAPOUR HAZARD ZONE**



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VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.05 to 60 tonnes.

representing about one standard 80 000 L rail car load of naphtha. It should be noted that Figure 8 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 naphtha 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). 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 9: Normalized vapour concentration versus downwind distance.

Figure 9 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 9, the weather condition must be determined from Table 7.

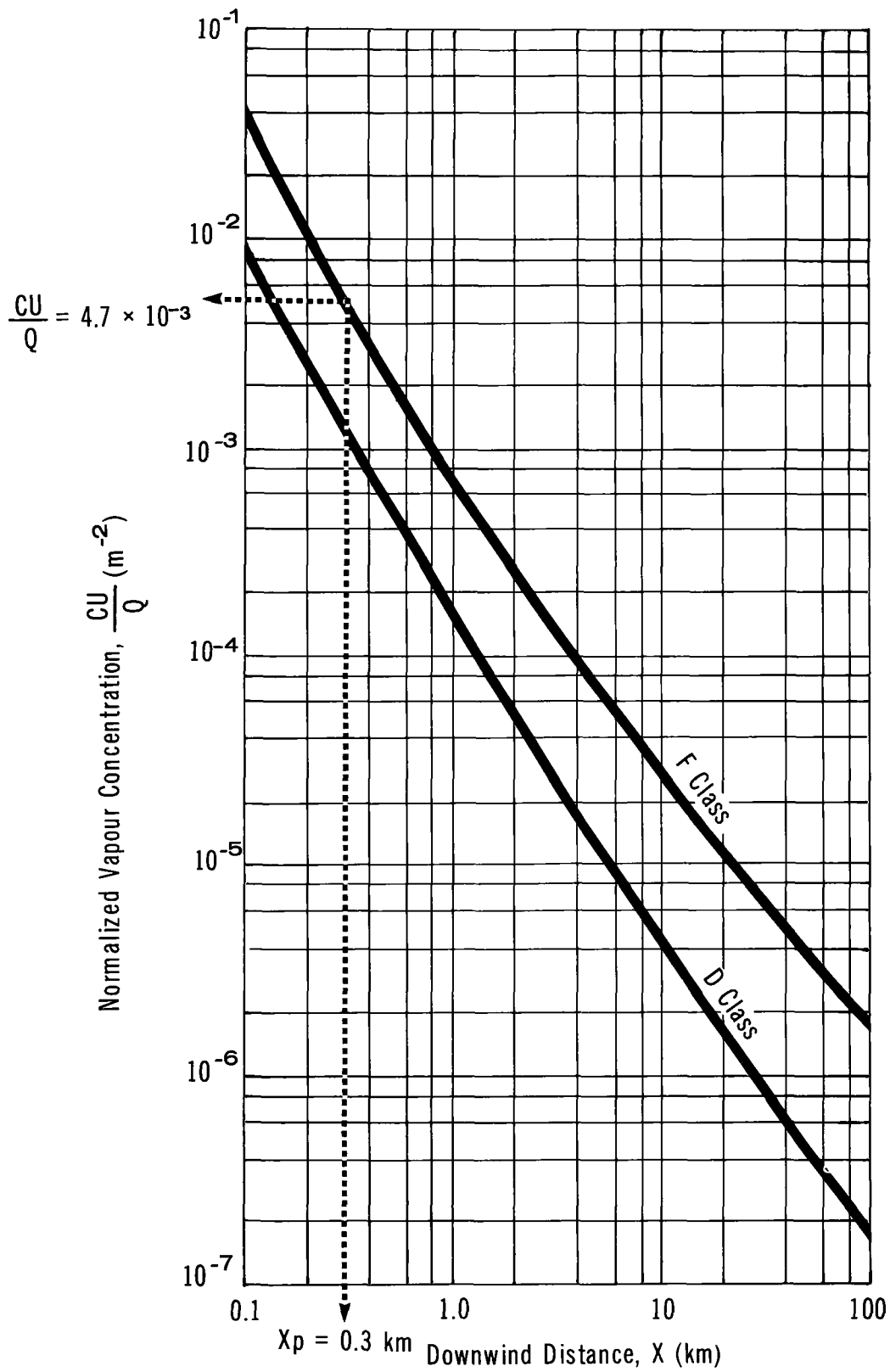
TABLE 7 WEATHER CONDITIONS

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

Use: The maximum hazard distance, X_p , downwind of the spill can be calculated from Figure 9 knowing:

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

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NORMALIZED VAPOUR CONCENTRATION
VS DOWNWIND DISTANCE

- the weather condition
- the hazard concentration limit, C , which is the lower value of 10 times the Threshold Limit Value (TLV[®], in g/m³), or the Lower Flammability Limit (LFL, in g/m³). Note: To convert the TLV[®] (in ppm) and the LFL (in percent by volume) to concentrations in g/m³, use Figures 10 and 11. Since the TLV[®] x 10 produces the Lower Value, it will be used throughout this manual

A hazard concentration limit of 10 times the TLV[®] has been chosen as an example; it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV[®] is a workplace standard for long-term exposure; use of this value as the hazard limit would result in unrealistically large hazard zones.

Since the TLV[®] for naphtha takes into account the fact that the aromatic hydrocarbon content is normally about 10 percent or less, the user may consider using a lower value for the TLV[®] should a naphtha with a higher aromatic content (and thus more hazardous) be modelled.

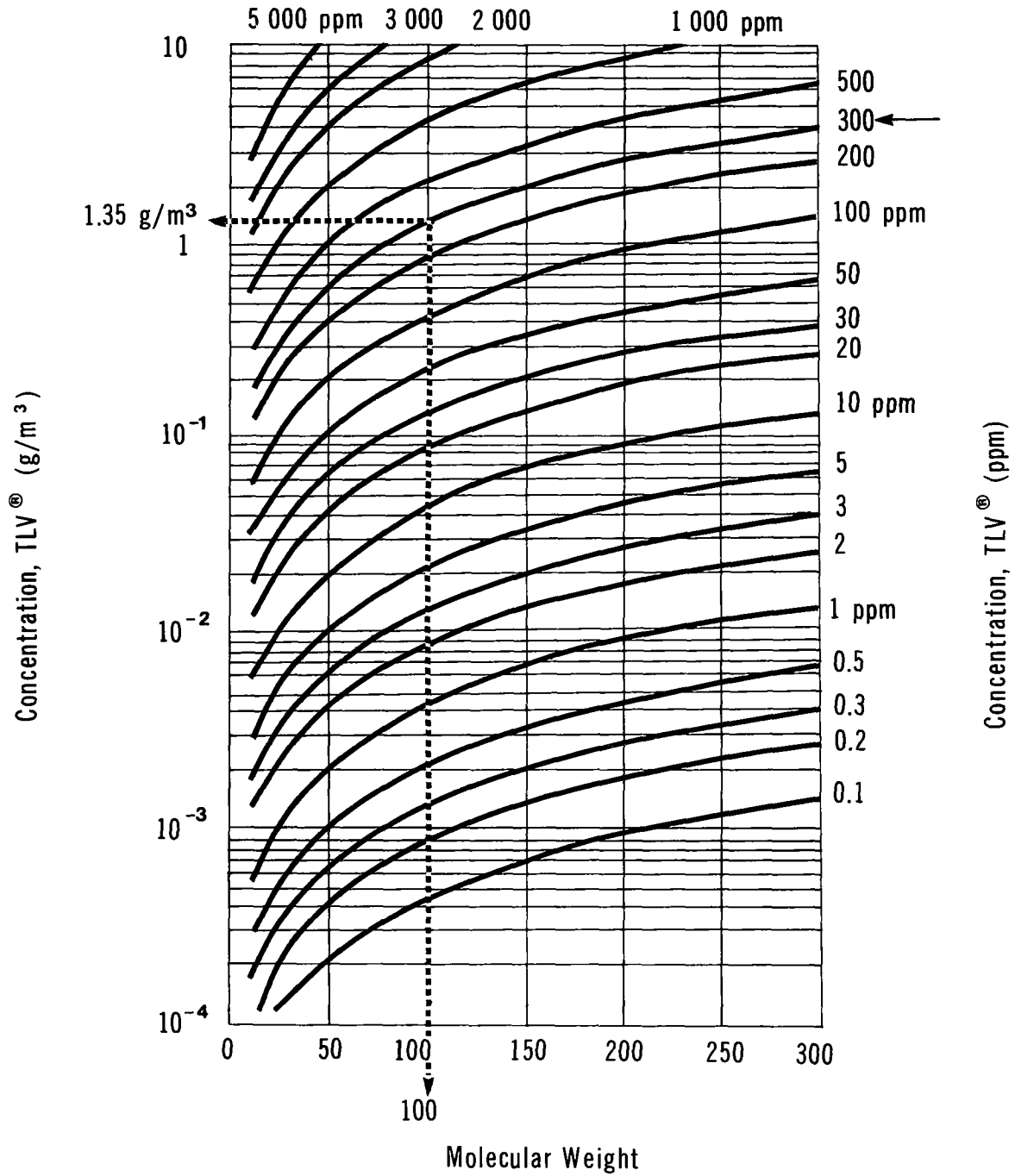
5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{\max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the naphtha Threshold Limit Value (TLV[®]) of 1.35 g/m³, or 13.5 g/m³. The maximum plume hazard half-width represents the maximum half-width of the naphtha vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV[®]. Table 8 is therefore only applicable for a naphtha hazard concentration limit of 10 x TLV[®], or 13.5 g/m³. 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 3 to 30 m/s. The range of vapour emission rates (Q) used was 150 000 to 80 000 000 g/s, corresponding to naphtha spills in the range of about 1000 to greater than 1 500 000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 60 300 kg or approximately 60 tonnes. Therefore, under class D of Table 8, data are provided for up to greater than 25 000 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 vapour emission rates (Q) used was 15 000 to 8 000 000 g/s, corresponding to

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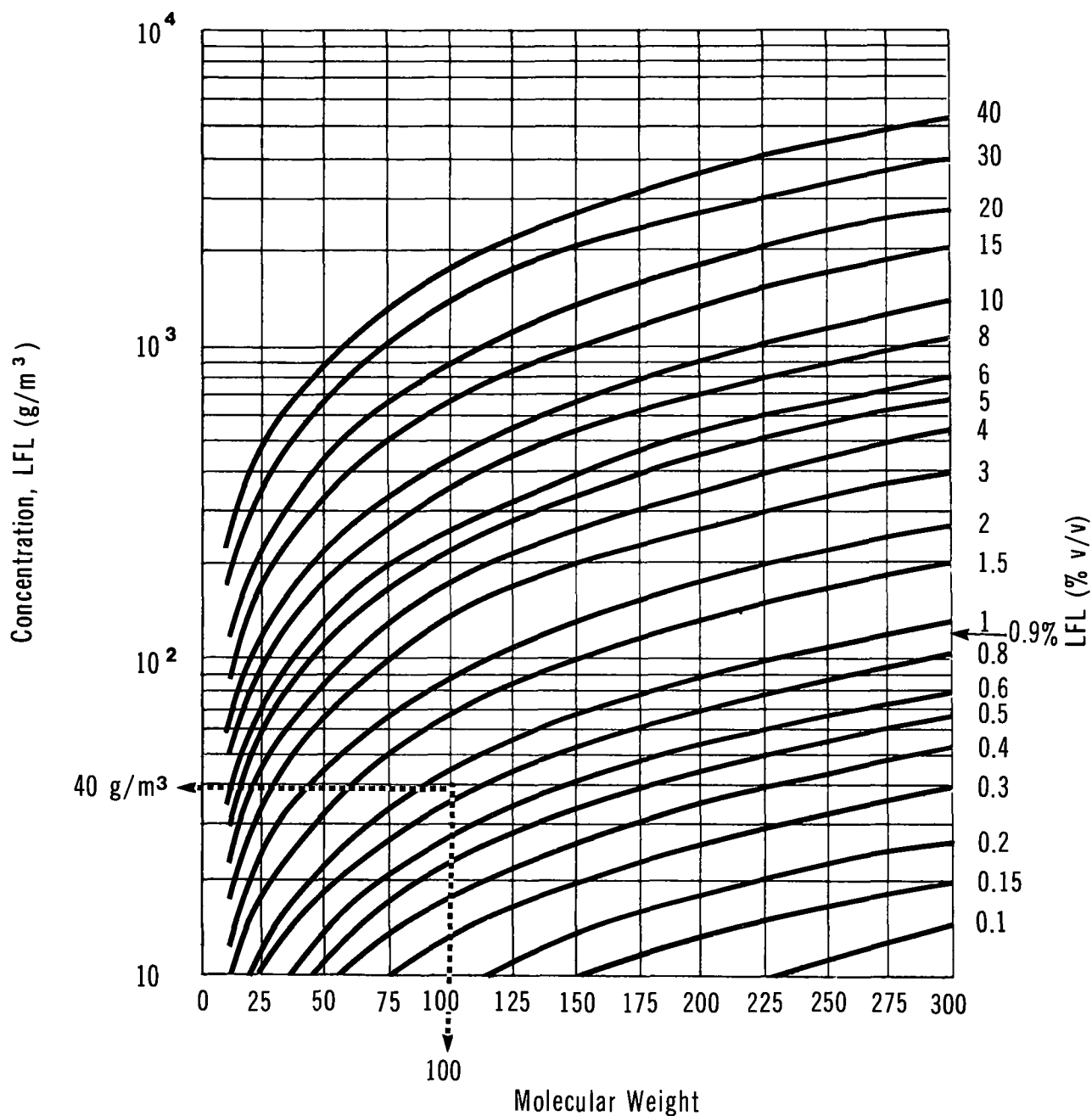
CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Example: Naphtha, MW = 100 (est), TLV® = 300 ppm
 then TLV® in g/m³ = 1.35

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

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**CONVERSION OF LOWER FLAMMABILITY
LIMIT (LFL) UNITS (volume % to g/m^3)**


Example: Naphtha, MW = 100 (est), LFL = 0.9%
then LFL in $\text{g}/\text{m}^3 = 40$

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

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR NAPHTHA 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)	
80 000 000	3090	(96.7 km)*	8 000 000	1420	(99.5 km)*
60 000 000	2590		7 000 000	1285	
50 000 000	2310		6 000 000	1145	
40 000 000	2015		5 000 000	1000	
30 000 000	1685		4 000 000	845	
20 000 000	1310		3 000 000	680	
10 000 000	855		2 000 000	505	
5 000 000	560		1 000 000	310	
2 500 000	375		750 000	255	
1 500 000	280		500 000	200	
1 000 000	220		250 000	130	
750 000	185		100 000	70	
500 000	145		75 000	60	
250 000	95		50 000	45	
100 000	60		25 000	31	
75 000	50		10 000	19	
50 000	40	Q/U = 2850 →	5 000	13	→ (W/2) _{max} = 13 m
25 000	28				
10 000	17				
5 000	12				

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

Example: A spill releasing naphtha vapour at the rate of $Q = 6 \times 10^3$ g/s under weather condition F and a wind speed $U = 2.1$ m/s means $Q/U = 2850$ g/m which results in a maximum plume hazard half-width $(W/2)_{\max} = 13$ m.

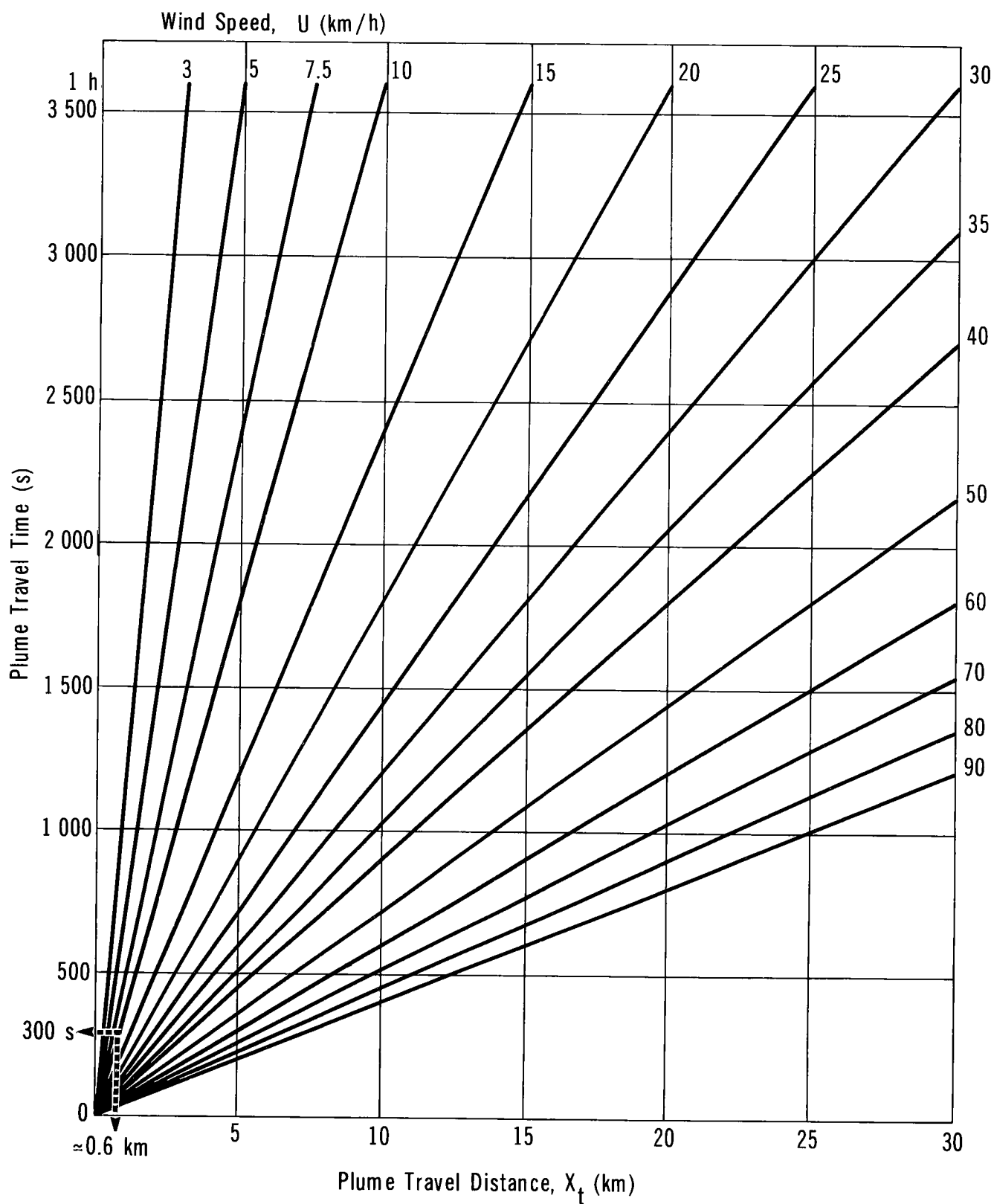
Note: Above table is valid only for a naphtha concentration of $10 \times \text{TLV}^{\circ}$, or 13.5 g/m³.

naphtha spills in the range of about 80 to 125 000 tonnes, respectively. Therefore, under class F of Table 8, data are provided for up to 2000 times a standard rail car load (see note as per class D above).

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 12: Plume travel time versus travel distance. Figure 12 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.

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**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 naphtha. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of naphtha 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 the observed (measured) pool radius, if possible; if not, use the maximum radius from Figure 13, Section 5.4. Note that use of this value, which applies specifically to spills on water, will result in an exaggerated pool radius on land.
- Radius (r) = 50 m + 1000 = 0.05 km

Step 3: Calculate the vapour emission rate (Q) at $T = 20^\circ\text{C}$

- From Figure 8, for $r = 50$ m and $T = 20^\circ\text{C}$, $Q = 6 \times 10^3$ g/s

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

- Use available weather information, preferably on-site observations
- Given: $U = 7.5$ km/h, then $U = 7.5 \div 3.6 = 2.1$ m/s
 $D = \text{NW or } 315^\circ$ ($D = \text{Direction from which wind is blowing}$)

Step 5: Determine the weather condition

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

- Step 6:** Determine the hazard concentration limit (C)
- This is the lower of 10 times the TLV^o, or the LFL, so for naphtha
 $C = 13.5 \text{ g/m}^3$ (TLV^o = 1.35 g/m^3 ; LFL = 40 g/m^3)
- Step 7:** Compute CU/Q
- $$\text{CU/Q} = \frac{13.5 \times 2.1}{6 \times 10^3} = 4.7 \times 10^{-3} \text{ m}^{-2}$$
- Step 8:** Calculate the downwind distance (X_p) from the virtual point source
- From Figure 9, with $\text{CU/Q} = 4.7 \times 10^{-3} \text{ m}^{-2}$ and weather condition F,
 $X_p \approx 0.3 \text{ km}$
- Step 9:** Calculate the hazard distance (X_a) downwind of the area source
- With $X_p = 0.3 \text{ km}$ and $r = 0.05 \text{ km}$, then
 $X_a = X_p - 10 r = 0.3 \text{ km} - 10 (0.05 \text{ km}) = -0.2 \text{ km}$
 - A negative value indicates that there is no hazard downwind of the pool

Subsequent steps leading to the mapping of the hazard zone are not given since there is no downwind hazard zone indicated from a 20 tonne spill of naphtha for the example case given. It is therefore necessary to refer to the Introduction Manual to map the hazard zone should another spill situation produce a hazard distance in Step 9 above.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, naphtha will vaporize and at the same time spread on the surface. Because it is insoluble, none will dissolve in the water; however, it will evaporate until it is removed. This is assumed for nomogram preparation.

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). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

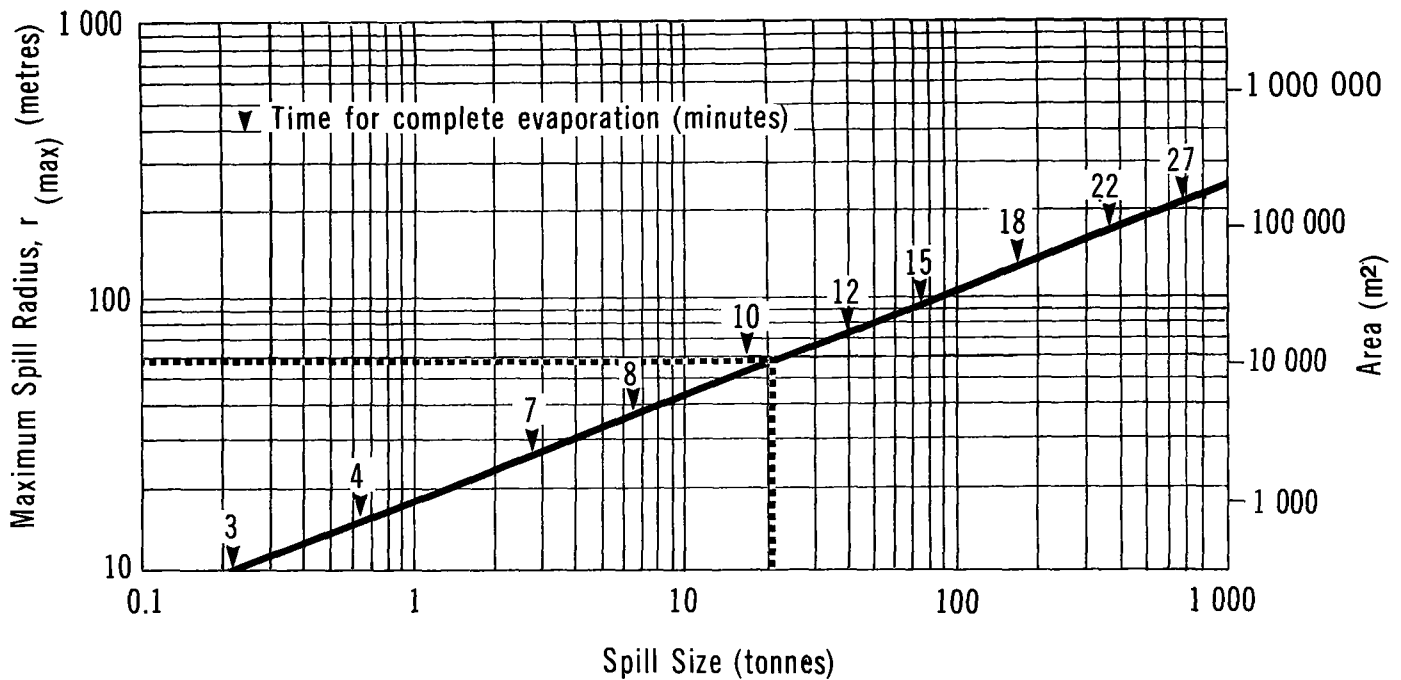
The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purpose of the nomogram presented, the water temperature has been taken at 20°C, representing a reasonable maximum for surface water bodies. This condition maximizes the spill size.

5.4.2 Nomogram for Spreading on Still Water. Figure 13 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 13 provides a simple means of estimating the maximum spill radius for naphtha, 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 liquid spilled on water (Raj 1974). The arrow points 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.

FIGURE 13

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MAXIMUM SPILL RADIUS vs SPILL SIZE

5.4.3 Sample Calculation. A 20 tonne spill of VM & P naphtha has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

Solution

- Use Figure 13
- With spill mass = 20 tonnes, $r_{max} = 60$ m
- Time for complete evaporation is about 10.5 minutes

If other naphtha grades are spilled, there will be differences in some of the transport properties. Using the same logic, for instance, a 20 tonne spill of coal tar naphtha (a less volatile mixture) would be expected to have $r_{\max} = 200$ m and an evaporation time of about 80 minutes.

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Introduction. Naphtha has a low solubility in water. Consequently, when spilled onto soil, its infiltration and transport downward through the soil involve multi-phase phenomena. The phases of concern are naphtha as a liquid, water, soil, and gas or vapours.

Unfortunately, sufficient data do not exist to permit a detailed assessment of immiscible contaminant transport in a specific circumstance. A few extensive field investigations have been carried out, especially involving spills of oil, gasoline and PCBs. Consequently, it is necessary to simplify the soil and groundwater conditions and to express contaminant behaviour through analogy to these more extensively studied materials.

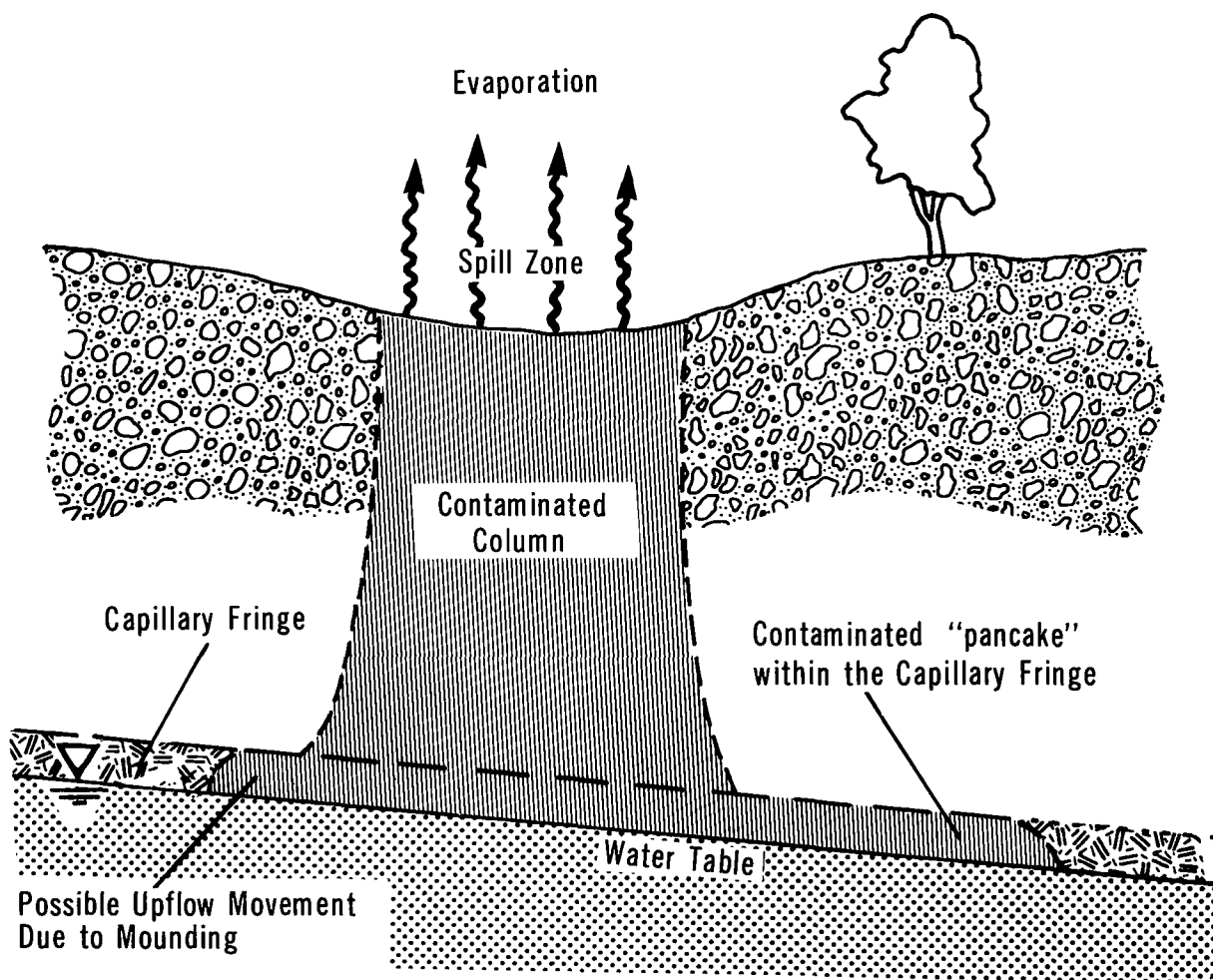
A pattern for the downward movement of immiscible fluids such as naphtha in soil has been prepared by comparison to oil spilled onto soil surfaces (Blokker 1971; Freeze and Cherry 1979). It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled naphtha fills the pores at the soil surface and begins to penetrate downward. It is assumed that naphtha moves downward through the soil as a saturated slug but leaving behind a constant amount (S_0) of naphtha within the soil pores.

Downward transport will continue until the volume of naphtha spilled per unit area (B_0) equals the amount retained in the soil as S_0 . Some lateral spreading may occur due to capillary action. If B_0 is greater than the volume that can be retained as S_0 above the groundwater table, the excess naphtha 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 naphtha, S_0 . This is shown schematically in Figure 14.

5.5.2 Equations Describing Naphtha 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.

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SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m²

–Field Capacity (θ_{fc}) = 0.075

5.5.3 Saturated Hydraulic Conductivity of Naphtha in Soil. The saturated hydraulic conductivity (K_0), in m/s, is given by:

$$K_0 = \frac{(\rho g)k}{\mu}$$

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

The appropriate properties of naphtha and water are given in the chart below. The water condition is used to simulate the movement of a low viscosity liquid.

Property	Naphtha		Water 20°C
	20°C	10°C	
Mass density (ρ) kg/m^3	866	869	998
Absolute viscosity (μ), Pa·s	5.7×10^{-3}	9.2×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(0.15 \times 10^7)k$	$(0.093 \times 10^7)k$	$(0.98 \times 10^7)k$

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

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fC}), m^3/m^3	0.075	0.3	0.45
Residual fraction (S_0), m^3/m^3	0.05	0.1	0.2

5.5.5 Penetration Nomograms. Nomograms for the penetration of naphtha into the unsaturated zone above the groundwater table were prepared for each soil. The

nomograms show the total depth of naphtha penetration (B) versus penetration time (t_p) for various volumes spilled per unit area of soil (B_0). Temperatures of 10°C and 20°C were used. Calculations were based on the equations developed in the Introduction Manual:

$$v = -K_0 \frac{(dh)}{(dl)} \qquad t_p = \frac{B}{v}$$

$$\frac{dh}{dl} = -1 \qquad B = \frac{B_0}{nS_0}$$

A flowchart for use of the nomograms is shown in Figure 15. The nomograms are presented as Figures 16, 17 and 18.

5.5.6 Sample Calculation. A 20 tonne spill of naphtha has occurred on coarse sandy soil. The temperature is 20°C; the spill radius is approximately 15.7 m. Calculate the depth and time of penetration.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20^\circ\text{C}$
- Mass density $\rho = 866 \text{ kg/m}^3$
- $r = 15.7 \text{ m}$

Step 2: Calculate the volume and area of spill

- $V = \frac{M}{\rho} = \frac{2 \times 10^4 \text{ kg}}{866 \text{ kg/m}^3} = 23.1 \text{ m}^3$
- $A = \pi r^2 = 770 \text{ m}^2$

Step 3: Calculate the volumetric loading B_0

- $B_0 = \frac{V}{A} = \frac{23.1}{770} = 0.03 \text{ m}^3/\text{m}^2$

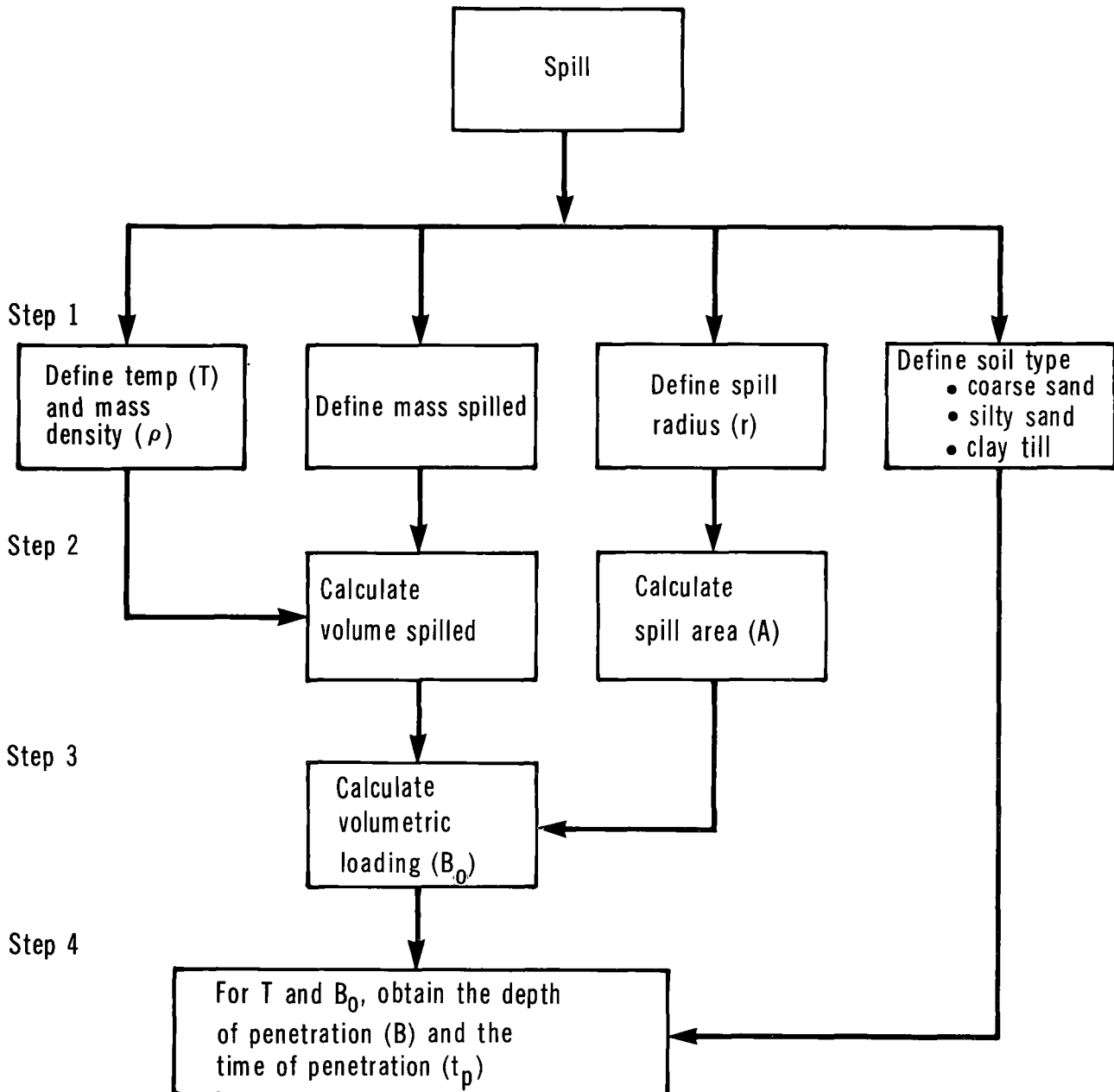
Step 4: Estimate the depth of penetration (B) and the time of penetration (t_p)

- For coarse sand, $B_0 = 0.03 \text{ m}^3/\text{m}^2$
- $B = 1.7 \text{ m}$, $t_p = 17.5 \text{ min}$

Note: Since extensive evaporation may have occurred during this time, penetration estimated will be the worst case

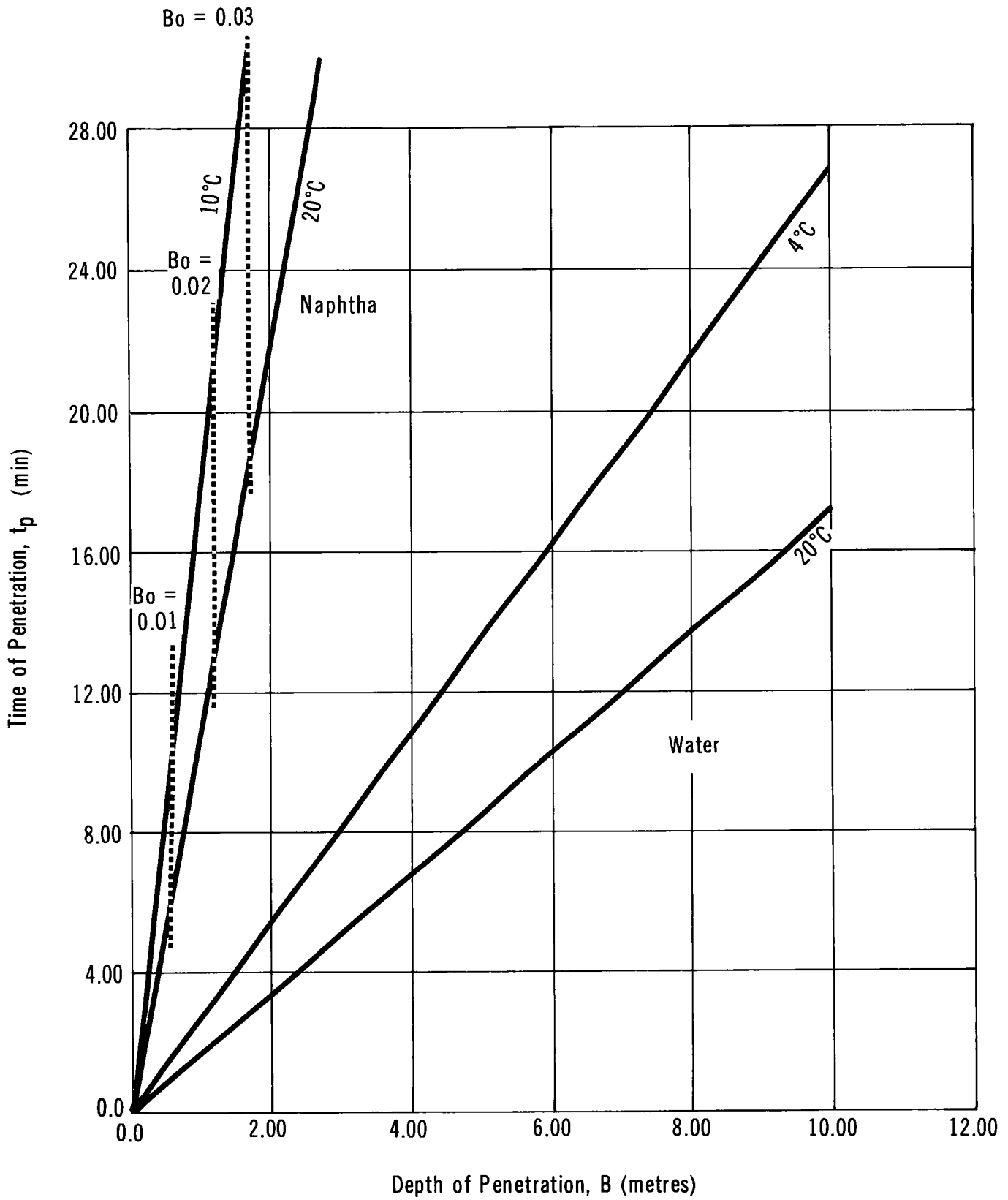
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FLOWCHART FOR NOMOGRAM USE



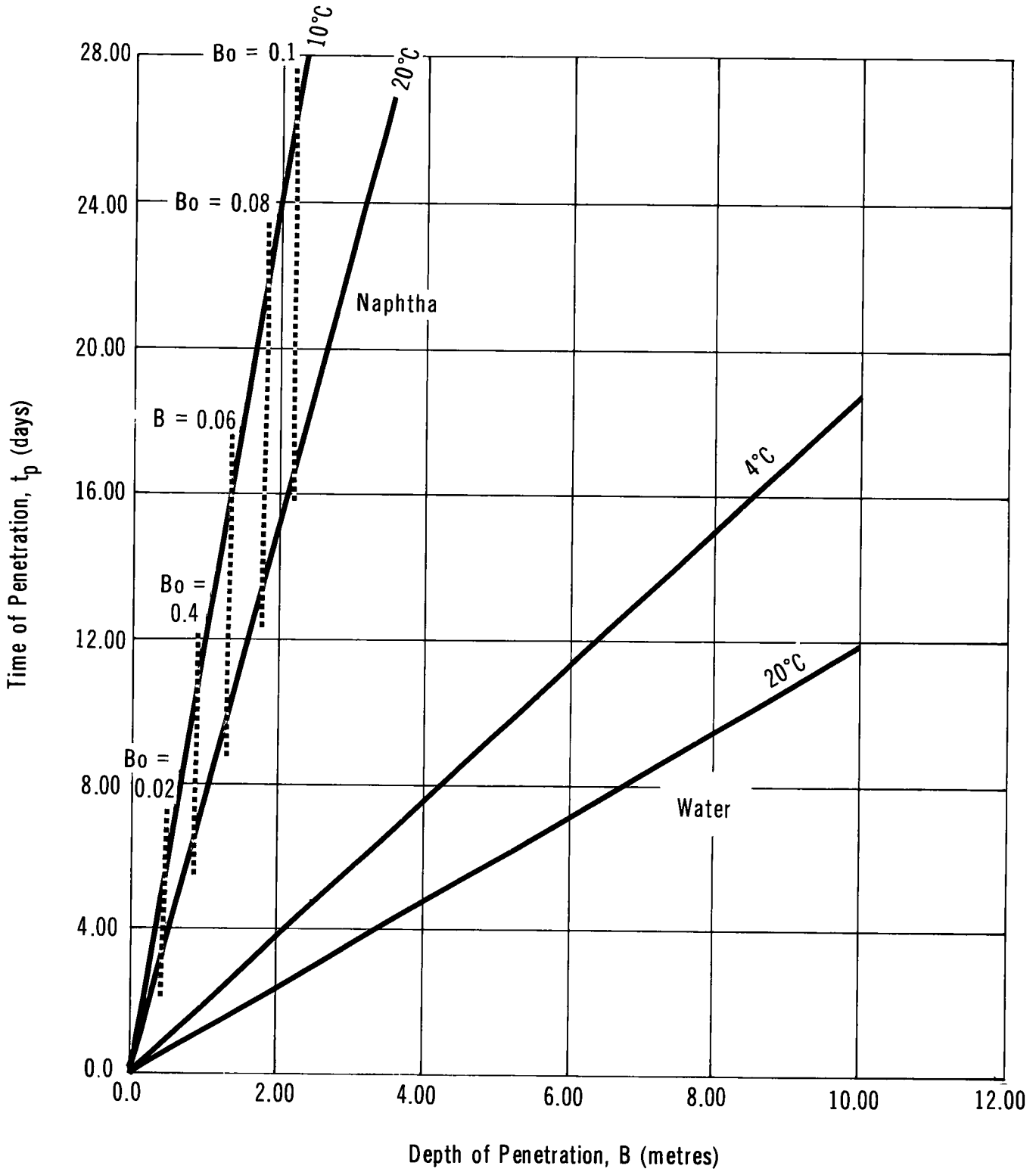
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PENETRATION IN COARSE SAND



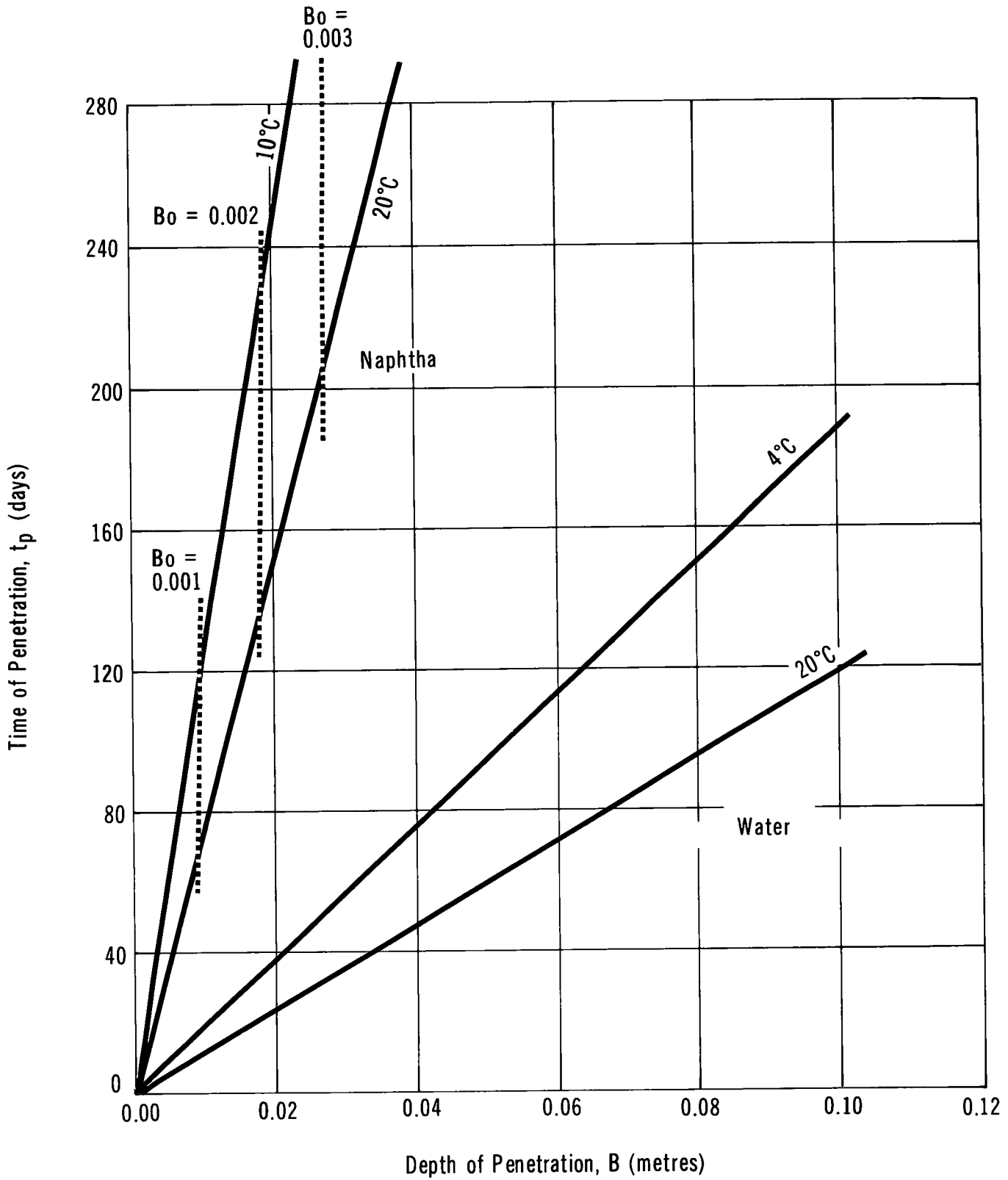
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PENETRATION IN SILTY SAND



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PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Although naphtha is not specifically regulated, "oils and petrochemicals" (which includes naphthas) should not be present in concentrations detectable by odour, film, sheen or discolouration, or cause tainting of edible aquatic organisms (Water Management Goals 1978).

6.1.2 Air. No specific limits.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. A TL_m96 of over 1000 ppm has been assigned to "petroleum spirits" including mineral spirits, solvent naphtha, and VM & P naphtha (RTECS 1979).

6.2.2 Measured Toxicities. "Naphtha" is variously cited as containing mostly pentane and hexane (WQC 1963) or, depending on type, heptane and octane (VM & P); nonane, decane, and 15 percent trimethyl benzene (Mineral Spirits); toluene, xylene and higher boilers, possibly with benzene (coal tar) (Alliance 1980).

Although naphtha has not been extensively tested for aquatic toxicity, many of its components have. Some representative toxicities are listed below.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Kill Data</u>					
Pentane >60	-	White roach	lethal	20.2°C	WQC 1963
Heptane 30	1-4	White roach	lethal	21°C	WQC 1963
<u>Fish Toxicity Tests</u>					
Octane					
100	96	Young coho salmon (<i>Oncorhynchus kisutch</i>)	no significant mortalities	8°C arti- ficial sea- water	Verschueren 1977

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Heptane					
100	96	Young coho salmon (<i>Oncorhynchus kisutch</i>)	no significant mortalities	8°C artificial seawater	Verschueren 1977
4	24	Goldfish (<i>Carassius auratus</i>)	LD ₅₀	modified ASTM D1345	Verschueren 1977
Hexane					
4	24	Goldfish (<i>Carassius auratus</i>)	LD ₅₀	modified ASTM D1345	Verschueren 1977
100	96	Young coho salmon (<i>Oncorhynchus kisutch</i>)	no mortalities	8°C, artificial seawater	Verschueren 1977
Toluene					
24	24-96	Bluegill (<i>Lepomis macrochirus</i>)	TL _m		Verschueren 1977
10	24-96	Young coho salmon (<i>Oncorhynchus kisutch</i>)	no significant mortality	artificial seawater, 8°C	Verschueren 1977
50	24	Young coho salmon (<i>Oncorhynchus kisutch</i>)	90 percent mortality	artificial seawater, 8°C	Verschueren 1977
o-Xylene					
13	24	Goldfish (<i>Carassius auratus</i>)	LD ₅₀	modified ASTM D1345	Verschueren 1977
10	24-96	Young coho salmon (<i>Oncorhynchus kisutch</i>)	no significant mortality	8°C artificial seawater	Verschueren 1977

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Microorganisms</u>					
Toluene					
120	-	Algae (<i>Scenedesmus</i>)	LD ₀ (no effect level)		Verschueren 1977
<i>o</i> -Xylene					
55		<i>Chlorella vulgaris</i>	50 percent reduction in cell numbers	20°C	Verschueren 1977
<u>Invertebrates</u>					
Toluene					
60	-	Daphnia	LD ₀ (no effect level)		Verschueren 1977
100 to 1000	24	<i>Daphnia magna</i>	TL _m		Verschueren 1977

6.3 Effect Studies

The estimated threshold level for producing tainting in fish flesh is 0.1 mg/L (WQC 1972).

6.4 Degradation

BOD (kg/kg)	% Theo.	Days	Seed	Method	Reference
n-Decane	4.7	1	-	-	Verschueren 1977
n-Nonane	1.1	1	-	-	Verschueren 1977
Mesitylene	3	5	-	-	Verschueren 1977
Toluene					
0.86	-	5	-	-	Verschueren 1977

BOD (kg/kg)	% Theo.	Days	Seed	Method	Reference
1.23	-	5	standard diluted sewage, acclimated	-	Verschuere 1977
Xylene					
0.64	-	5	-	-	Verschuere 1977

6.5 Long-term Fate and Effects

The constituents of naphthas both biodegrade (at varying rates) and volatilize, so that environmental persistence is not expected. No food chain concentration effects have been cited.

7 HUMAN HEALTH

Naphtha is a general term describing petroleum distillates that consist of various mixtures of predominantly aliphatic hydrocarbons (C₅ to C₁₃), boiling over the range 30-238°C.

This section includes a summary of toxicity information for refined petroleum solvents more volatile than kerosene, as identified in NIOSH (1977). The list includes petroleum ether, rubber solvent, varnish makers' and painters' naphtha (VM & P naphtha), mineral spirits, and Stoddard solvent. Wherever possible, information pertinent to a particular chemical in this group has been specifically identified.

These petroleum solvents have similar toxic effects on humans. The most volatile fractions may induce cardiac arrest while the higher-boiling components are pulmonary irritants. All have been reported to cause central nervous system depression.

Toxicity summaries of "naphtha", in general, were not found in the literature, although some information on specific classes such as Stoddard solvent (Doc. TLV 1981) and groupings of compounds such as refined petroleum solvents was available in review form. In addition, relevant toxicity data concerning pure single component chemicals found in these mixtures (such as heptane or octane) have been reported in Table 9.

Concerning potential carcinogenicity, mutagenicity or teratogenicity, the 1977 NIOSH Criteria Document draws the following conclusion: "There is no present reason for suggesting that these solvents, if they are free of carcinogenic aromatics such as benzene, would cause cancer, birth defects or germicidal mutations."

The toxicological data summarized here have been extracted from standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity, teratogenicity and carcinogenicity, 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

Due to the differing groupings of compounds by different standard-setting agencies, it is not possible to summarize the basis for the standards individually. The ACGIH-TLV®s refer to Stoddard solvents (excluding 140 Flash aliphatic solvent), VM & P naphtha (ligroin), and rubber solvent (naphtha). The Stoddard solvent standard was designed primarily to prevent irritative and narcotic effects of the vapours and to prevent

TABLE 9 SUMMARY OF REFINED PETROLEUM SOLVENTS AS REFERRED TO IN THIS REPORT WHEN CITING NIOSH (1977)

(adapted from NIOSH 1977)

Names and Synonyms	Boiling Range (°C)	Physical Appearance and Odour	Predominant Species
<u>Petroleum ether</u> , benzin, benzine, petroleum benzin, canadol, light ligroin, Skellysolve	30-60	Clear colourless liquid; sweet ethereal odour	C ₅ to C ₆ ; primarily pentane and isohexane; typically contains no aromatics
<u>Rubber solvent</u> , benzine, lacquer diluent	45-125	Clear colourless liquid; pleasant aromatic odour	C ₅ to C ₈ ; 70-90 percent paraffins 11-22 percent naphthenes 9-22 percent aromatics
<u>VM & P Naphtha</u> , benzine, Naphtha 76, ligroin, high boiling petroleum ether	95-160	Clear water-white to yellow liquid; pleasant aromatic odour	C ₇ to C ₁₁ ; 45-60 percent paraffins 30-45 percent naphthenes 5-13 percent aromatics
<u>Mineral Spirits</u> , white spirits, petroleum spirits and light petrol (sometimes Stoddard solvent)	150-200	Clear, colourless; pleasant sweetish odour	C ₉ to C ₁₂ ; 30-65 percent paraffins 15-55 percent naphthenes 10-30 percent aromatic hydrocarbons
<u>Stoddard solvent</u> , mineral spirits	160-210	Clear colourless liquid	C ₉ to C ₁₁ ; 30-50 percent straight and branched chain paraffins 30-40 percent naphthenes 10-20 percent aromatic hydrocarbons

kidney injury (reported as questionable) (Doc. TLV 1981). The standard for VM & P naphtha and the rubber solvent standard are based upon prevention of irritation effects. The NIOSH standard has been set for unrefined petroleum solvents including kerosene with a total aromatic content less than 20 percent. This standard is based upon eye, nose and throat irritation effects, and on the potential for causing dermatitis and adverse central nervous system effects. Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
<u>Time-weighted Averages (TWA)</u>			
TLV® (8 h)	USA-ACGIH	Varnish makers' and painters' naphtha (VM & P naphtha): 300 ppm (1350 mg/m ³)	TLV 1983
TLV® (8 h)	USA-ACGIH	Stoddard solvent: 100 ppm (525 mg/m ³)	TLV 1983
TLV® (8 h)	USA-ACGIH	Rubber solvent (naphtha): 400 ppm (1600 mg/m ³)	TLV 1983
PEL (8 h)	USA-OSHA	Petroleum distillates mixture (naphtha): 500 ppm (2000 mg/m ³)	NIOSH Guide 1978
TWAEC (40 h/wk)	Ontario	Varnish makers' and painters' naphtha: 1350 mg/m ³	Ontario 1981
TWAEC (40 h/wk)	Ontario	Rubber solvent: 1600 mg/m ³	Ontario 1981
TWAEC (40 h/wk)	Ontario	Stoddard solvent: 575 mg/m ³	Ontario 1981
Permissible Concentration (8 h)	British Columbia	Stoddard solvent: 100 ppm (575 mg/m ³)	B.C. 1980
TWA (10 h)	USA-NIOSH	Petroleum ether, Rubber solvent, Varnish makers' and painters' naphtha, Mineral spirits and Stoddard solvent: 350 mg/m ³	NIOSH 1977
Action level (10 h)	USA-NIOSH	Petroleum distillates mixture (naphtha): 200 mg/m ³	NIOSH 1977
<u>Short-term Exposure Limits (STEL)</u>			
STEL (15 min)	USA-ACGIH	Varnish makers' and painters' naphtha (VM & P naphtha): 400 ppm (1800 mg/m ³)	TLV 1983
STEL (15 min)	USA-ACGIH	Stoddard solvent: 200 ppm (1050 mg/m ³)	TLV 1983
Ceiling (15 min)	USA-NIOSH	Petroleum ether, Rubber solvent, Varnish makers' and painters' naphtha, Mineral spirits, Stoddard solvent: 1800 mg/m ³	NIOSH 1977
Permissible Concentration (15 min)	British Columbia	Stoddard solvent: 125 ppm (720 mg/m ³)	B.C. 1980

Guideline (Time)	Origin	Recommended Level	Reference
Short-term Inhalation (30 min)	-	Naphtha (Stoddard solvent): 500 ppm	CHRIS 1978
STEC (15 min, not more than 4/d, only after 60 min have elapsed from the time of last previous exposure to such concentration)	Ontario	Stoddard solvent: 720 mg/m ³	Ontario 1981
STEC (15 min, not more than 4/d, only after 60 min have elapsed from the time of last previous exposure to such concentration)	Ontario	Varnish makers' and painters' naphtha: 1800 mg/m ³	Ontario 1981
<u>Other Human Toxicities</u>			
IDLH		Stoddard solvent: 5000 ppm	NIOSH Guide 1978
LD _{LO}		Petroleum spirits: 1470 mg/kg	RTECS 1979
LC _{LO}		140 Flash aliphatic solvent	RTECS 1979

Inhalation Toxicity Index

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

$$ITI = 1315.12 (\text{Vapour Pressure, in mm Hg/TLV}^\circ, \text{ in ppm})$$

For Rubber Solvent

$$\begin{aligned} \text{At } 20^\circ\text{C, ITI} &= 1315.12 (125 \text{ mm Hg}/400 \text{ ppm}) \\ &= 4.1 \times 10^2 \end{aligned}$$

For Stoddard Solvent

$$\begin{aligned} \text{At } 20^\circ\text{C, ITI} &= 1315.12 (5.9 \text{ mm Hg}/100 \text{ ppm}) \\ &= 77.6 \end{aligned}$$

For VM & P naphtha

At 20°C, ITI = 1315.12 (21.9 mm Hg/300 ppm)
= 96.0

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	References
SPECIES: Human	Dermal single contact may cause erythema, blistering and cellular damage; naphthas may have allergic potential. Repeated applications may cause dermatitis and lesions.	Patty 1981
Unspecified	Stoddard solvent causes defatting, drying, scaling of the skin on direct contact, and possible development of dermatitis.	Patty 1981
1 mL (10-30 min)	Skin irritation, peeling of skin, water vapour loss from injured skin. (Petroleum ether)	Spirit et al. 1970. IN NIOSH 1977
SPECIES: Rats		
461 ppm	Skin irritation of extremities (140 Flash aliphatic solvent).	Carpenter et al. Part IV 1975. IN NIOSH 1977

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
880 ppm (15 min)	Irritation (Petroleum spirits).	RTECS 1979
470 ppm (15 min)	Irritation (Stoddard solvent).	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
430 ppm	Produced slight eye irritation (Rubber solvent).	Doc. TLV 1981
150 ppm (15 min)	Slight eye irritation (Stoddard solvent).	Doc. TLV 1981
Unspecified	Produced no effect on the human eye (Stoddard solvent).	Patty 1981
SPECIES: Rat		
9800 ppm (4 h)	Eye irritation (Rubber sol- vent).	Carpenter et al. Part IV 1975. <u>IN</u> NIOSH 1977
800 ppm (8 h)	Eye irritation (Stoddard sol- vent).	Carpenter et al. Part III 1975. <u>IN</u> NIOSH 1977

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristic: Kerosene-like (Stoddard solvent) (Doc. TLV 1981).
Gasoline-like (CHRIS 1978).

Parameter	Media	Concentration	Reference
Odour detected (10 s) (by all subjects)	in air	160 ppm (640 mg/m ³) (Rubber solvent)	Carpenter et al. Part IV 1975. <u>IN</u> NIOSH 1977
Odour detected (10 s) (by 9/12 subjects)	in air	16 ppm (64 mg/ m ³) (Rubber solvent)	Carpenter et al. Part IV 1975. <u>IN</u> NIOSH 1977
Odour detected (10 s) (by 2/12 subjects)	in air	1.6 ppm (6.4 mg/m ³) (Rubber solvent)	Carpenter et al. Part IV 1975. <u>IN</u> NIOSH 1977
Odour detected (10 s) (by all subjects)	in air	15 ppm (70 mg/ m ³) (VM & P naphtha)	Carpenter et al. Part II 1975. <u>IN</u> NIOSH 1977
Odour detected (10 s) (by 11/12 subjects)	in air	1.5 ppm (7 mg/ m ³) (VM & P naphtha)	Carpenter et al. Part II 1975. <u>IN</u> NIOSH 1977

Parameter	Media	Concentration	Reference
Odour detected (by 2/12 subjects)	in air	1.5 ppm (0.7 mg/m ³) (VM & P naphtha)	Carpenter et al. Part II 1975. <u>IN NIOSH 1977</u>
Odour detected	in air	0.6 ppm (0.4 mg/m ³) (140 Flash aliphatic solvent)	Carpenter et al. Part IV 1975. <u>IN NIOSH 1977</u>

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposures</u>		
SPECIES: Human		
4000 mg/m ³ (50 min)	Prolonged reaction time, probable impaired short-term memory (Mineral spirits).	Gamberale et al. 1975. <u>IN NIOSH 1977</u>
2500 mg/m ³	Severe nausea, vertigo (Mineral spirits).	Astrand et al. 1975. <u>IN NIOSH 1977</u>
625 to 2500 mg/m ³ (2 h)	No effects on perceptual speed, reaction time, short-term memory, numerical ability, and manual dexterity (Mineral spirits).	Gamberale et al. 1975. <u>IN NIOSH 1977</u>
2000 ppm (15 min)	Olfactory fatigue in 6/7 subjects; light headedness, reddening of the sclera, eye, nose and throat irritation (Rubber solvent).	Carpenter et al. Part IV 1975. <u>IN NIOSH 1977</u>
1700 ppm (15 min)	Olfactory fatigue in 7/7 subjects; eye, nose and throat irritation and reddening of the sclera, light headedness (Rubber solvent).	Carpenter et al. Part IV 1975. <u>IN NIOSH 1977</u>
880 ppm (15 min)	Olfactory fatigue in 6/7, eye irritation in 3/7, throat irritation in 4/7 (VM & P naphtha).	Carpenter et al. Part II 1975. <u>IN NIOSH 1977</u>

Exposure Level (and Duration)	Effects	Reference
780 ppm (15 min)	Olfactory fatigue in 5/7 subjects, throat, eye and nose irritation (Rubber solvent).	Carpenter et al. Part IV 1975 <u>IN NIOSH 1977</u>
660 ppm (15 min)	Olfactory fatigue in 6/7, eye irritation in 2/7, throat irritation in 1/7 (VM & P naphtha).	Carpenter et al. Part II 1975. <u>IN NIOSH 1977</u>
600 mg/m ³ (8 h) 500 mg/m ³	Irritation (Petroleum spirits). Severe nausea, vertigo (Mineral spirits).	RTECS 1979 Gamberale et al. 1975. <u>IN NIOSH 1977</u>
470 ppm (15 min) (2700 mg/m ³)	Eye irritation in 6/6, olfactory fatigue in 5/6, dizziness in 2/6, throat irritation in 1/6 (Stoddard solvents).	Carpenter et al. Part III 1975. <u>IN NIOSH 1977</u>
450 ppm (15 min)	Olfactory fatigue in 5/7, eye and throat irritation in 2/7 (VM & P naphtha).	Carpenter et al. Part II 1975. <u>IN NIOSH 1977</u>
300 ppm (15 min)	Olfactory fatigue in 3/7, throat irritation in 2/7, eye irritation in 1/7 (VM & P naphtha).	Carpenter et al. Part II 1975. <u>IN NIOSH 1977</u>
150 ppm (15 min) (850 mg/m ³)	Olfactory fatigue in 6/6, eye irritation in 1/6 (Stoddard solvent).	Carpenter et al. Part III 1975. <u>IN NIOSH 1977</u>
24 ppm (15 min) (140 mg/m ³)	Olfactory fatigue in all subjects (Stoddard solvent).	Carpenter et al. Part III 1975. <u>IN NIOSH 1977</u>
17 ppm (15 min)	LC _{LO} (140 Flash aliphatic solvent).	RTECS 1979
"Large concentrations"	Causes disturbances similar to those observed with benzene (Rubber solvent).	Patty 1981
SPECIES: Dog		
1400 ppm (8 h)	Spasms and death (Stoddard solvent).	Doc. TLV 1981
SPECIES: Cat		
1400 ppm (8 h)	Spasms and death (Stoddard solvent).	Doc. TLV 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
2800 to 24 200 ppm (8 h)	Motor incoordination was observed at 5300 ppm. Convulsions and death occurred in all subjects (Rubber solvent).	Doc. TLV 1981
15 000 ppm (4 h)	LC ₅₀ (Rubber solvent).	Doc. TLV 1981
3400 ppm (4 h)	LC ₅₀ (Petroleum spirits).	RTECS 1979
2800 ppm (8 h)	No toxic signs observed (Rubber solvent).	Doc. TLV 1981
SPECIES: Mouse		
50 000 mg/m ³	LC _{LO} (Petroleum spirits).	RTECS 1979
Chronic Exposures (Inhalation and Skin Contact)		
SPECIES: Human		
Unspecified	Reversible and irreversible CNS effects, myocardial and hematopoietic effects. Myelotoxic effects and hypoplasia have been ascribed to benzene content of the solvents.	Patty 1981
Unspecified	Numerous reports of neurotoxic effects, polyneuropathy, loss of appetite, muscle weakness, impairment of motor action, and paresthesia (Petroleum ether).	Patty 1981
Unspecified	Chronic inhalation exposure in humans has resulted in hepatic and hematopoietic changes (Stoddard solvent).	Patty 1981
Unspecified (2 to 3 times/mo for 2 yr)	Excessive uterine bleeding, purplish discolourations of skin, moderate marrow hypoplasia, death. Victim spot-cleaned rugs with Stoddard-like solvent and carbon tetrachloride.	Scott et al. 1959. <u>IN</u> NIOSH 1977
Unspecified (4 to 5 times/wk for 6 mo)	Fatigue, moderate marrow hypoplasia, death. Student washed hands in Stoddard solvent.	Scott et al. 1959. <u>IN</u> NIOSH 1977

Exposure Level (and Duration)	Effects	Reference
Unspecified (2 yr)	Purplish discolorations of skin, fatigue, palor, marked marrow hypoplasia, death. Man washed hands in Stoddard solvent.	Scott et al. 1959. <u>IN</u> NIOSH 1977
Unspecified (20 yr)	Slight reduction of all formed elements in the blood (Stoddard solvent).	Scott et al. 1959. <u>IN</u> NIOSH 1977

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	On ingestion, aspiration into the lungs may occur, causing pneumonitis, pulmonary edema and hemorrhage (Stoddard solvent).	Patty 1981

7.4.3 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mammal		
2500 mg/kg	LD _{LO} (Benzin).	RTECS 1979
SPECIES: Rat		
8560 mg/kg	LD _{LO} (Petroleum spirits).	RTECS 1979

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	In six of eight recorded deaths, findings in rubber workers included myeloid leukemia in a nonsignificant number of cases.	Patty 1981
Unspecified	None of the petroleum solvents has carcinogenic potential although some may aid in the translocation of carcinogenic agents by the solvent effect.	Patty 1981
Unspecified	Demonstrated an association between leukemia and jobs entailing exposure to solvents. The exact etiologic agent was not identified. Other potential carcinogenic agents were also present.	McMichael et al. 1975 <u>IN NIOSH 1977</u>
Unspecified	Epidermoid carcinoma. Multiple exposures to various solvents and greases. Etiologic agent unknown.	Downing 1952. <u>IN NIOSH 1978</u>

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 the respiratory tract.
2. Headache.
3. Nausea.
4. Vomiting.
5. Intoxication.
6. Olfactory fatigue (NIOSH 1977).
7. Reddening of the sclera (NIOSH 1977).
8. Pallor (CHRIS 1978).

9. CNS depression.
10. Hematopoietic effects (NIOSH 1978).
11. Polyneuropathy (Patty 1981).
12. Purplish discoloration of the skin (NIOSH 1977).
13. Hepatic changes (Patty 1981).
14. Hemorrhages into vital organs (Sax 1981).
15. Excessive uterine bleeding (NIOSH 1977).
16. Coma.
17. Death.

7.5.2 Ingestion.

1. Burning sensation (Sax 1981).
2. Vomiting (Sax 1981).
3. Diarrhea (Sax 1981).
4. Drowsiness (Sax 1981).
5. Pulmonary edema (Sax 1981).

7.5.3 Skin Contact.

1. Irritation.
2. Erythema.
3. Blistering (Patty 1981).
4. Defatting (NIOSH 1978).
5. Drying and cracking.
6. Dermatitis (Patty 1981).

7.5.4 Eye Contact.

1. Irritation.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Naphtha 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	PRESSURIZATION OF VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>GENERAL</u>														
Fire		•	•										Flammable liquid, slight explosion hazard.	Sax 1984
Heat		•											Flammable liquid. Moderate fire hazard and slight explosion hazard.	Sax 1984
<u>CHEMICAL GROUPS</u>														
Explosives				•					•					EPA 600/2-80-076
Oxidizing Agents	•	•	•			•								EPA 600/2-80-076
Reducing Agents		•		•									Hydrogen gas may be formed.	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. Naphtha is a flammable liquid. Its vapours can flow along surfaces to distant ignition sources and flash back. Burning can produce toxic vapours and gases, including carbon monoxide and carbon dioxide (GE 1978). Containers may explode in heat of fire (ERG 1980).

9.1.2 Fire Extinguishing Agents. Water may not be effective in putting out fire, but should be used to cool fire-exposed containers. Do not direct a stream of water into burning liquid, for it will scatter the fire (GE 1978).

Small fires: Dry chemical, CO₂, water spray or alcohol foam.

Large fires: Water spray, fog or alcohol foam.

Move containers from the 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). Smothering is recommended to put out the fire (GE 1978).

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 (GE 1978). Cellosize and Hycar, as absorbent materials, have shown possible application for vapour suppression and/or containment of naphtha in spill situations (ICI 1982).

9.1.3.2 Spills on land. Contain if possible. Remove liquid with pumps or vacuum equipment, then remove residual by adsorbing on vermiculite, sand or other sorbent material and shovel into covered metal containers for recovery or disposal. Use nonsparking tools for scraping up spilled material (GE 1978).

Soil surface sealants such as Callery Chemical Resin 115 and Ashland Chemical EP 65-86/88 may be also used to prevent penetration of naphtha in soil (Lafornera 1978).

9.1.3.3 Spills in water. Contain if possible by using booms and recover spilled material with oil spill equipment (CG-D-38-76). The following sorbents can also be used in spill situations (CG-D-38-76): activated carbon, polyurethane foam, polyolefin fibres, cellulose fibres, and polypropylene fibres.

9.1.4 Disposal. Waste naphtha must never be discharged directly into sewers or surface waters. Absorbed material may be burned in an open pit, away from buildings and people. Scrap liquid may also be atomized in an approved incinerator. Large amounts of waste liquid may be reprocessed for use or disposed of via a licensed solvent disposal company. Scrap liquid can be diluted with fuel oil for incineration in boiler (GE 1978). Certain disposal procedures (e.g., open burning) may require environmental authorities' approval.

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 naphtha:

- Impervious rubber or plastic gloves should be worn to limit skin contact and safety goggles to prevent eye contact with liquid. A face shield, protective clothing, boots, etc., may also be required to limit skin contact where splashing of solvent is probable (GE 1978).
- The following clothing materials showed penetration times of about 1 hour for mineral spirits: neoprene and polyvinyl chloride. Natural rubber showed penetration times of less than 1 hour. For VM & P naphtha, nitrile and polyvinyl alcohol showed penetration times greater than 1 hour. Neoprene, chlorinated polyethylene and Viton showed penetration times of about 1 hour. Butyl rubber, natural rubber and polyvinyl chloride showed penetration times of less than 1 hour (Little 1983).
- The following chemical suit materials are recommended for protection against naphtha (EE-20): cloropel (excellent resistance) and butyl (good resistance).
- For emergency and nonroutine conditions, an approved organic cartridge respirator is suitable for use up to 3500 mg/m^3 (or about 780 ppm). Full face protection is needed above 3500 mg/m^3 ; an approved gas mask with organic vapour canister is

suitable up to 17 500 mg/m³ (or about 3900 ppm). For unknown concentrations or those above 17 500 mg/m³, air-supplied or self-contained type respirators are required (GE 1978).

- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1978).

9.1.6 Storage Precautions. Store in tightly closed containers in a cool, well-ventilated area. Keep away from sources of heat, sources of ignition, and oxidizing agents. Protect containers against physical damage. Electrically bond and ground containers for liquid transfers to prevent static sparks. Use metal safety cans for small amounts of solvent. No smoking in areas of storage, handling, or use of this material (GE 1978).

10 PREVIOUS SPILL EXPERIENCE

10.1 General

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.

10.2 Pipeline Rupture (HMIR 1980)

An undetermined amount of naphtha was released and caught fire when a 30 cm pipeline carrying the material ruptured. Response personnel were able to shut off the flow of naphtha through the pipe, although the pipe contents continued to leak out the hole. Firefighters sprayed more than 87 000 L of chemical foam/water mixture on the fire, taking some 2 hours to extinguish it. In the meantime, about 50 residents were evacuated from the vicinity of the spill area. After the fire was extinguished, vacuum trucks were used to collect pools of naphtha remaining in the area. Two days after the incident, the evacuated residents were allowed to return to their homes.

Six houses and ten automobiles were destroyed by the fire, and four persons were seriously burned. Several firefighters reported a feeling of lightheadedness from breathing the naphtha fumes and others suffered rashes on their skin from exposure to the naphtha. A light sheen of naphtha was observed on a nearby watercourse but it dissipated quickly, not requiring cleanup.

It should be noted that even though naphtha is sometimes used as a fuel for heating or cooking purposes, it does not imply that protective equipment need not be worn in spill circumstances.

The fire-smothering effect of the chemical foam and water mixture proved to be an acceptable and effective means of extinguishing the naphtha fire.

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 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 Naphtha in Air

11.1.1 **Gas Chromatography** (NIOSH 1977). A range of 193 to 809 mg/m³ of naphtha in air may be determined by gas chromatography.

A known volume of air is drawn through a 7 cm x 6 mm O.D. charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The first section contains 100 mg whereas the second section 50 mg. A silanized glass wool plug is recommended.

The charcoal tube sample is scored before the first section of charcoal and broken. The larger section of charcoal is transferred to a 2 mL stoppered sample container containing 1.0 mL of carbon disulphide. The same operation is performed with the backup section. The sample should be allowed to desorb for 30 minutes.

A 5 µL aliquot of sample is injected into a suitable gas chromatograph equipped with a flame ionization detector. The sample concentration is determined using a suitable electronic integrator which measures peak areas in conjunction with a calibration curve. Typical gas chromatograph operating conditions are: helium carrier gas flow at 30 mL/min, hydrogen gas flow at 35 mL/min, air flow at 400 mL/min, injector temperature at 225°C, detector temperature at 250°C, column temperature at 80°C, and

a 6 ft. x 1/8 in. stainless steel column packed with 1.5 percent OV-101 on 100/120 mesh Chromosorb W.

11.2 Qualitative Method for the Detection of Naphtha in Air

The sample is collected and desorbed as in Section 11.1.1. The sample is scanned on a suitable I.R. spectrophotometer from 4000 to 667 cm^{-1} using suitable cells. The presence of characteristic absorption bands on the chromatogram indicates naphtha (ASTM 1979).

11.3 Quantitative Method for the Detection of Naphtha in Water

11.3.1 Infrared Spectrophotometry (ASTM 1979). This method is used for waterborne oils but may be used for naphtha. A suitable volume of representative sample is collected in a narrow mouth borosilicate glass container with a TFE-fluorocarbon cap. The container air is displaced with nitrogen gas and the sample stored in the dark during transportation.

The sample is transferred to a 1 L separatory funnel; a suitable extractant (e.g., Freon[®] 113, or methylene chloride) may be added if the concentration is suspected to be low. The phases are allowed to separate. The aqueous phase is discarded and the oil phase transferred to a 12.5 mL centrifuge tube. A 5 g mass of anhydrous magnesium sulphate is added and the mixture centrifuged for 10 minutes with a relative centrifugal force between 500 and 800 g. The supernatant is decanted into a suitable container.

The supernatant is scanned on a suitable I.R. spectrophotometer from 4000 to 667 cm^{-1} using suitable cells. The sample concentration is determined using a calibration curve.

11.4 Qualitative Method for the Detection of Naphtha in Water

The sample is collected, separated, dried and centrifuged as in Section 11.3.1. The sample is scanned on a suitable I.R. spectrophotometer from 4000 to 667 cm^{-1} using suitable cells. The presence of characteristic absorption bands on the chromatogram indicates naphtha (ASTM 1979).

11.5 Quantitative Method for the Detection of Naphtha in Soil

11.5.1 Infrared Spectrophotometry (AWWA 1981). Concentrations greater than 40 ppm of naphtha in soil may be determined by 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 naphtha. Three extractions using 30 mL of Freon® each time are carried out. The extracts are combined in a 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®. The sample is scanned on a suitable infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Naphtha in Soil

The sample is collected and extracted as in Section 11.5.1. The sample is scanned on a suitable double-beam recording infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells and Freon®113 in the reference cell. The presence of characteristic absorbance bands on the chromatogram indicates the presence of naphtha (AWWA 1981).

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

