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ENVIRO
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Information for
Problem
Spills

SULPHUR DIOXIDE

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

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

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of 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.

TABLE OF CONTENTS

		Page
FOREWORD		i
ACKNOWLEDGEMENTS		i
LIST OF FIGURES		vii
LIST OF TABLES		ix
1	SUMMARY	1
2	PHYSICAL AND CHEMICAL DATA	3
3	COMMERCE AND PRODUCTION	10
3.1	Grades, Purities	10
3.2	Domestic Manufacturers	10
3.3	Other Suppliers	10
3.4	Major Transportation Routes	10
3.5	Production Levels	11
3.6	Manufacture of Sulphur Dioxide	11
3.6.1	General	11
3.6.2	Manufacturing Process	11
3.7	Major Uses in Canada	11
3.8	Major Buyers in Canada	12
4	MATERIAL HANDLING AND COMPATIBILITY	13
4.1	Containers and Transportation Vessels	13
4.1.1	Bulk Shipment	13
4.1.1.1	Railway tank cars	13
4.1.1.2	Tank motor vehicles	16
4.1.1.3	Portable tanks	16
4.1.2	Cylinders	17
4.2	Off-loading	17
4.2.1	Off-loading Equipment and Procedures for Sulphur Dioxide Railway Tank Cars	17
4.2.2	Off-loading Cylinders	20
4.2.3	Specifications and Materials for Off-loading Equipment	20
4.3	Compatibility with Materials of Construction	21
5	CONTAMINANT TRANSPORT	26
5.1	General Summary	26
5.2	Leak Nomograms	26
5.2.1	Introduction	26
5.2.2	Nomograms	28
5.2.2.1	Bottom puncture - liquid venting	28
5.2.2.2	Top puncture - gas venting	28

		Page
5.2.3	Sample Calculations	31
5.3	Dispersion in the Air	31
5.3.1	Introduction	31
5.3.2	Vapour Dispersion Nomograms and Tables	32
5.3.2.1	Figure 17: Normalized vapour concentration versus downwind distance	32
5.3.2.2	Table 9: Maximum puff hazard half-widths	36
5.3.2.3	Figure 19: Puff travel time versus travel distance	39
5.3.3	Sample Calculation	39
5.4	Behaviour in Water	43
5.4.1	Introduction	43
5.4.2	Nomograms	43
5.4.2.1	Nomograms for non-tidal rivers	44
5.4.2.2	Nomograms for lakes or still water bodies	52
5.4.3	Sample Calculations	52
5.4.3.1	Pollutant concentration in non-tidal rivers	52
5.4.3.2	Average pollutant concentration in lakes or still water bodies	55
5.5	Subsurface Behaviour: Penetration into Soil	55
5.5.1	Mechanisms	55
5.5.2	Equations Describing Sulphur Dioxide Movement into Soil	56
5.5.3	Saturated Hydraulic Conductivity of Sulphur Dioxide in Soil	56
5.5.4	Soils	58
5.5.5	Penetration Nomograms	58
5.5.6	Sample Calculation	61
6	ENVIRONMENTAL DATA	62
6.1	Suggested or Regulated Limits	62
6.1.1	Water	62
6.1.2	Air	62
6.1.2.1	Canada	62
6.1.2.2	Other Countries	63
6.2	Aquatic Toxicity	63
6.2.1	U.S. Toxicity Rating	63
6.2.2	Measured Toxicities	63
6.2.3	Aquatic Studies	63
6.3	Mammalian Toxicology	64
6.4	Soils	64
6.5	Plants	65
6.5.1	Measured Effects	65
6.5.2	Comparative Tree Sensitivity	70
6.5.3	Plant Studies	72
6.6	Effect Studies	72
6.7	Long-term Fate and Effects	73
7	HUMAN HEALTH	74
7.1	Recommended Exposure Limits	74

		Page
7.2	Irritation Data	76
7.2.1	Skin Contact	76
7.2.2	Eye Contact	76
7.2.3	Respiratory Tract Irritation	77
7.3	Threshold Perception Properties	77
7.3.1	Odour	77
7.3.2	Taste	78
7.4	Long-term Studies	78
7.4.1	Inhalation	78
7.4.2	Ingestion	81
7.4.3	Skin Exposure	81
7.4.4	Carcinogenicity	81
7.5	Symptoms of Exposure	82
7.5.1	Inhalation	82
7.5.2	Ingestion	83
7.5.3	Eye Contact	83
7.5.4	Skin Contact	83
7.6	Human Toxicity to Decay or Combustion Products	83
7.6.1	Sulphurous Acid	83
8	CHEMICAL COMPATIBILITY	84
8.1	Compatibility of Sulphur Dioxide With Other Chemicals and Chemical Groups	85
9	COUNTERMEASURES	87
9.1	Recommended Handling Procedures	87
9.1.1	Fire Concerns	87
9.1.2	Fire Extinguishing Agents	87
9.1.3	Evacuation	87
9.1.4	Spill Actions Cleanup and Treatment	88
9.1.4.1	General	88
9.1.4.2	Spills on land or in water	88
9.1.5	Disposal	88
9.1.6	Protective Measures	88
9.1.7	Storage Precautions	90
10	PREVIOUS SPILL EXPERIENCE	91
10.1	General	91
10.2	Storage Tank Leak	91
10.3	Sulphur Dioxide from a Sulphur Burn	91
11	ANALYTICAL METHODS	93
11.1	Quantitative Method for the Detection of Sulphur Dioxide in Air	93
11.1.1	Titrimetric	93

		Page
11.2	Qualitative Method for the Detection of Sulphur Dioxide in Air	94
11.3	Quantitative Method for the Detection of Sulphur Dioxide in Water	94
11.3.1	Electrometric	94
11.4	Qualitative Method for the Detection of Sulphur Dioxide in Water	94
11.5	Quantitative Method for the Detection of Sulphur Dioxide in Soil	95
11.5.1	Ion Chromatography	95
11.6	Qualitative Method for the Detection of Sulphur Dioxide in Soil	95
12	REFERENCES AND BIBLIOGRAPHY	96
12.1	References	96
12.2	Bibliography	103

LIST OF FIGURES

Figure		Page
1	VAPOUR PRESSURE vs TEMPERATURE	6
2	LIQUID DENSITY vs TEMPERATURE	7
3	GAS DENSITY	7
4	VAPOUR VISCOSITY vs TEMPERATURE	8
5	LIQUID VISCOSITY vs TEMPERATURE	8
6	SOLUBILITY IN WATER vs TEMPERATURE	9
7	PHASE DIAGRAM	9
8	RAILWAY TANK CAR - CLASS 105A300W	14
9	COMMON GAS CYLINDERS	19
10	TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP	27
11	PERCENT REMAINING vs TIME	29
12	DISCHARGE RATE vs PUNCTURE SIZE	29
13	PERCENT REMAINING vs TIME	30
14	DISCHARGE RATE vs PUNCTURE SIZE	30
15	SCHEMATIC OF CONTAMINANT PUFF	33
16	FLOWCHART TO DETERMINE VAPOUR HAZARD ZONE	34
17	NORMALIZED VAPOUR CONCENTRATION vs DOWNWIND DISTANCE	35
18	CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m^3)	37
19	PUFF TRAVEL TIME vs TRAVEL DISTANCE	40
20	HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM	42
21	HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM	42
22	FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS	45
23	TIME vs DISTANCE	46

Figure		Page
24	HYDRAULIC RADIUS vs CHANNEL WIDTH	47
25	DIFFUSION COEFFICIENT vs HYDRAULIC RADIUS	48
26	ALPHA vs DIFFUSION COEFFICIENT	49
27	ALPHA vs DELTA	50
28	MAXIMUM CONCENTRATION vs DELTA	51
29	VOLUME vs RADIUS	53
30	AVERAGE CONCENTRATION vs VOLUME	54
31	SCHEMATIC SOIL TRANSPORT	57
32	FLOWCHART FOR NOMOGRAM USE	59
33	PENETRATION IN COARSE SAND	60

LIST OF TABLES

Table		Page
1	CONVERSION NOMOGRAMS	5
2	RAILWAY TANK CAR SPECIFICATIONS FOR SULPHUR DIOXIDE	13
3	TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A300W	15
4	PORTABLE TANK SPECIFICATIONS - TC51/CTC51	17
5	CYLINDER SPECIFICATIONS FOR SULPHUR DIOXIDE SERVICE	18
6	COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION	22
7	MATERIALS OF CONSTRUCTION	25
8	WEATHER CONDITIONS	36
9	MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR SULPHUR DIOXIDE)	38

1 SUMMARY

SULPHUR DIOXIDE (SO_2)

Colourless gas with a sharp, irritating odour.

SYNONYMS

Sulphurous Acid Anhydride, Sulphurous Anhydride, Sulphurous Oxide, Sulphur Dioxide Solution.

IDENTIFICATION NUMBER

UN. No. 1079; CAS No. 7446-09-5, 7782-99-2; OHM-TADS No. 7216914; STCC No. 4904290

GRADE & PURITIES

Commercial, 99.90 percent.

Refrigeration, 99.98 percent.

IMMEDIATE CONCERNS

Fire: Not combustible.

Human Health: Acutely toxic by inhalation.

Environment: Harmful to aquatic life in very low concentrations; toxic to animals, plants and soil organisms.

PHYSICAL PROPERTY DATA

Shipping state: liquid (liquefied gas)
State (15°C, 1 atm): gas
Boiling Point: -10.0°C
Melting Point: -72.7°C
Flammability: noncombustible
Vapour Pressure: 338 kPa (21°C)
Density: 1.379 g/mL (21°C) (liquid SO_2)

Solubility (in water): 22.8 g/100 mL (0°C)
Behaviour (in water): liquid sinks, boiling and dissolving to produce sulphurous acid
Behaviour (in air): gas is heavier than air
Odour Threshold Range: 0.1 to 3 ppm

ENVIRONMENTAL CONCERNS

Sulphur dioxide is toxic to aquatic life in low concentrations, generally below 10 mg/L. Concentrations above 1 ppm are injurious to plants.

HUMAN HEALTH

TLV®: 2 ppm (5 mg/m^3)
IDLH: 100 ppm

Exposure Effects

Inhalation: Gas is so irritating that it is unlikely that a person would remain exposed to dangerous levels unless unconscious or trapped.

Contact: Contact with liquefied product causes frostbite and severe skin and eye burns. Prolonged contact may cause blindness.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "POISON". Personnel involved should have full protective equipment. Stop the flow, 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 foam, dry chemical, carbon dioxide, water spray or fog to extinguish fires where sulphur dioxide is involved. Cool fire-exposed containers with water. Do not allow water to enter containers. Stay clear of tank ends. Containers may rupture and release toxic vapours in heat of fire.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Neutralize contaminated soil with lime, sodium bicarbonate or soda ash.

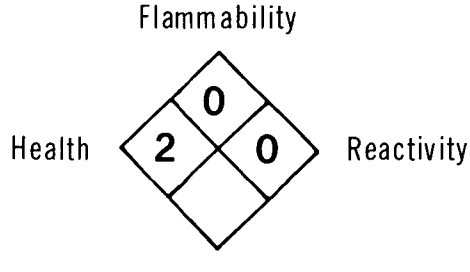
Water: Contain by damming or water diversion.

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

NAS HAZARD RATING

Category	Rating
Fire	0
Health	
Vapour	4
Liquid or Solid Irritant	1
Poison	4
Water Pollution	
Human Toxicity	0
Aquatic Toxicity	3
Aesthetic Effect	1
Reactivity	
Other Chemicals	1
Water	1
Self-reaction	0

NFPA HAZARD CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas. At low temperatures (<-10°C) or moderate pressures, is a colourless liquid (HCG 1981)
Usual shipping state	Shipped as a liquefied compressed gas under its own vapour pressure (HCG 1981)
Physical state at 15°C, 1 atm	Gas
Melting point	-72.7°C (CRC 1980), -75.8°C (Matheson 1980)
Boiling point	-10.0°C (HCG 1981)
Vapour pressure	338 kPa (21°C) (HCG 1981)

Densities

Density (liquid sulphur dioxide)	1.50 g/cm^3 (-20°C) (Kirk-Othmer 1983), 1.379 g/cm^3 (21°C) (HCG 1981)
Specific gravity	1.434 (liquid at 0°C) (HCG 1981)
Vapour density (air = 1)	2.263 (0°C) (Kirk-Othmer 1983), 2.262 (21°C) (HCG 1981)

Fire Properties

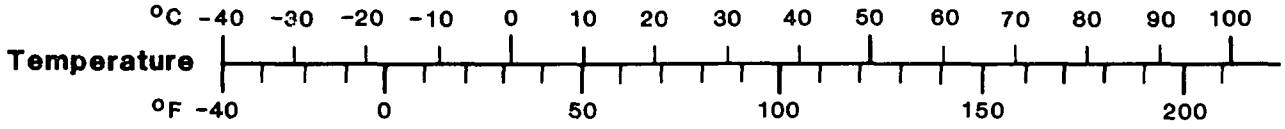
Flammability	Not combustible or flammable (NFPA 1978)

Other Properties

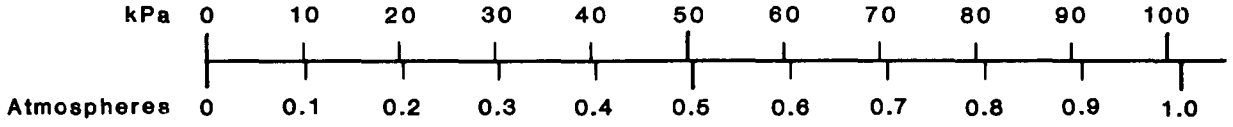
Molecular weight of pure substance	64.06 (CRC 1980)
Constituent components of typical commercial grade	Technical or commercial: >99.98 percent SO_2, <100 ppm H_2O; Refrigeration: >99.98 percent SO_2, <50 ppm H_2O (Kirk-Othmer 1983)
Molar volume	21.9 L/mole (Ullmann 1975)
Viscosity	Gas: 0.0124 mPa·s (18°C) (CRC 1980) Liquid: 0.368 mPa·s (0°C) (Ullmann 1975)
Latent heat of fusion	7.4 kJ/mole (-75.5°C) (HCG 1981)
Latent heat of sublimation	30.6 kJ/mole (est.)
Latent heat of vapourization	24.92 kJ/mole (-10°C) (Kirk-Othmer 1983)
Heat of formation	-296.8 kJ/mole (25°C) (JANAF 1971)
Entropy	248.1 J/(mole·°C) (25°C) (Kirk-Othmer 1983)

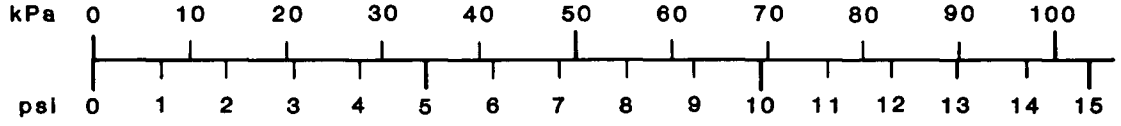
Ionization potential	12.33 eV (Rosenstock 1977)
Heat of solution	-14.0 kJ/mole (CHRIS 1978)
Heat capacity	
constant pressure (Cp)	39.8 J/(mole·°C) (25°C) (HCG 1981)
constant volume (Cv)	31.1 J/(mole·°C) (25°C) (HCG 1981), 30.932 J/(mole·°C) (25°) (Matheson 1980)
specific heat ratio (Cp/Cv)	1.29 (Matheson 1980)
Critical pressure	7870.4 kPa (HCG 1981) 7911 kPa (Kirk-Othmer 1983)
Critical temperature	157.6°C (Ullmann 1975; Kirk-Othmer 1983)
Coefficient of thermal expansion	384 x 10^{-3}/°C (Perry 1973)
Thermal conductivity	0.2214 W/(mole·K) (liquid at -25°C), 0.0088 W/(mole·K) (gas at 15°C) (Matheson 1980)
Saturation concentration	8840 gm^3 (21°C) (calc.)
Diffusivity	1.7 x 10^{-5} cm^2/s (in water, 25°C) (Perry 1973)
Surface tension	28.59 mN/m (liquid at -10°C) (Matheson 1980)
pH of aqueous solution	Produces a slightly acidic aqueous solution when combined with the water in the atmosphere or on land
Refractive index	1.0006 (gas at 25°C) (Matheson 1980)
Dielectic constant	1.0093 (gas at 20°C), 14.1 (liquid at 20°C) (Matheson 1980)
Dipole moment	1.16 D (25°C) (Bailar 1973)
Solubility	
In water	22.8 g/100 mL (0°C) (CRC 1980), 11.3 g/100 mL(20°C) (Matheson 1980), 0.58 g/100 mL (90°C) (CRC 1980)
In other common materials	Soluble in ethanol, acetic acid and sulphuric acid (CRC 1980). Moderately soluble in methanol, benzene, acetone and carbon tetrachloride (Ullmann 1975)
Vapour Weight to Volume Conversion Factor	1 ppm = 2.660 mg/m^3 (20°C) (Verschueren 1984)

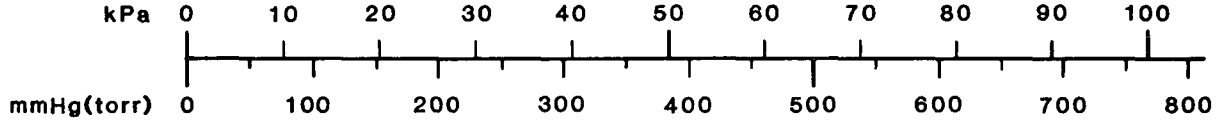
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

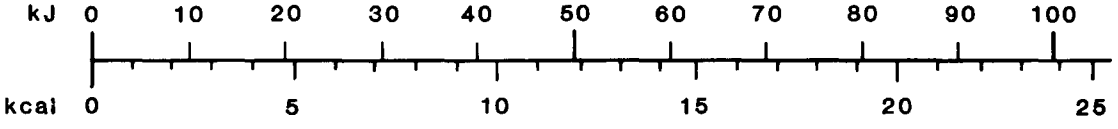
Dynamic 1 Pa·s = 1 000 centipoise (cP)

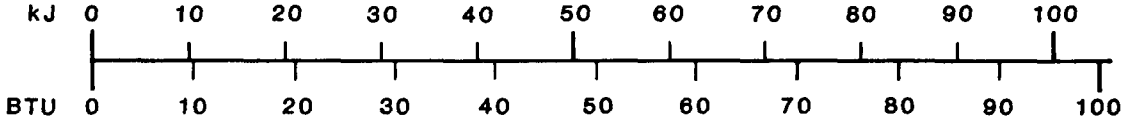
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





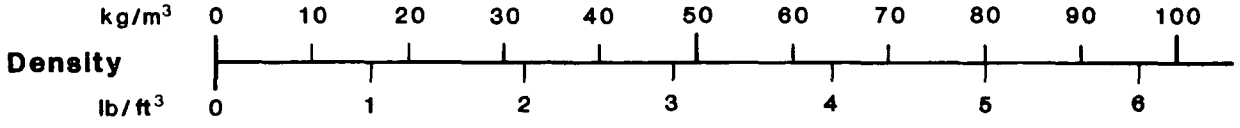


FIGURE 1

SULPHUR DIOXIDE

VAPOUR PRESSURE vs TEMPERATURE

Reference: Chem. Eng. 1974

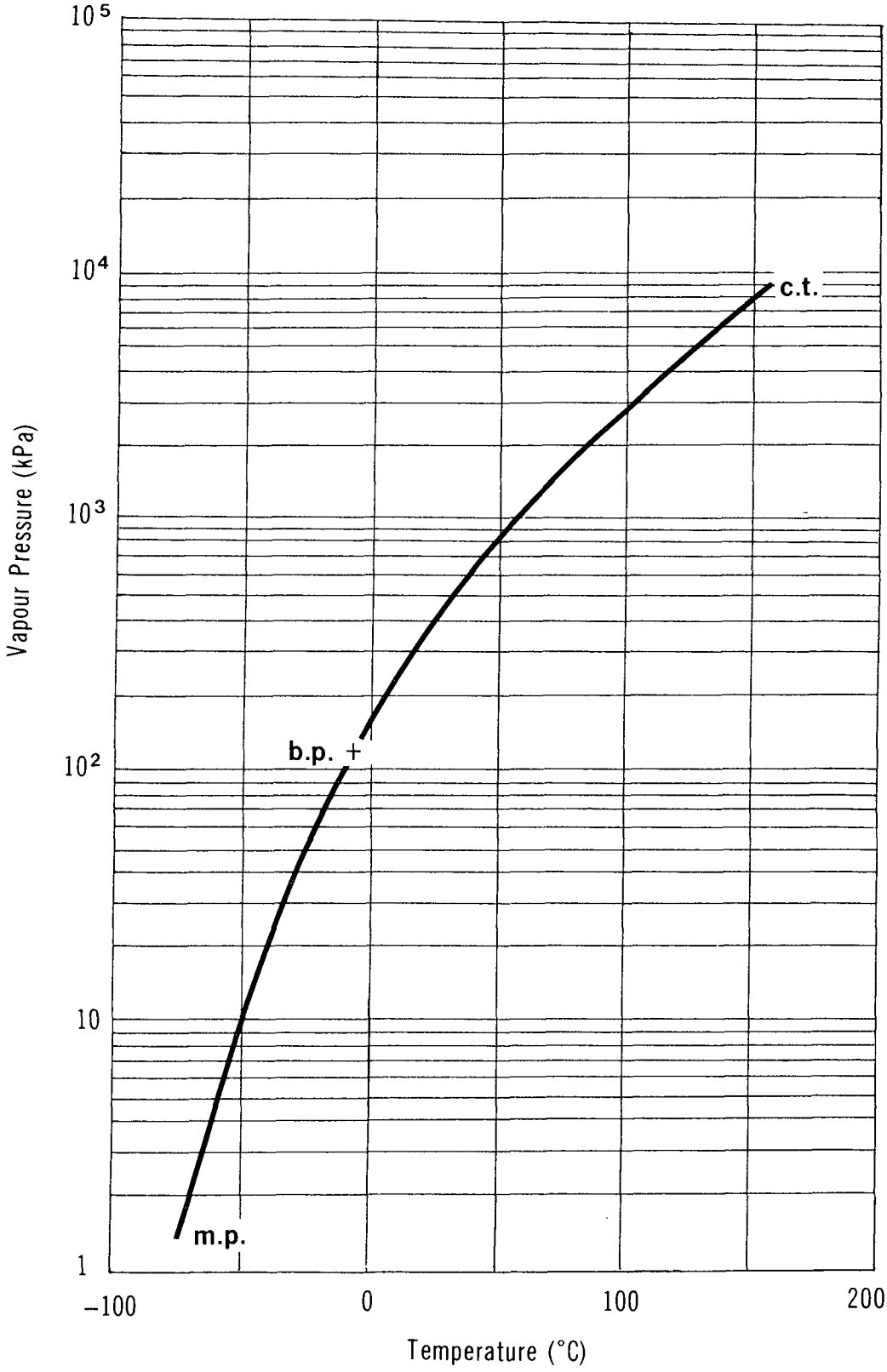


FIGURE 2

SULPHUR DIOXIDE

LIQUID DENSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

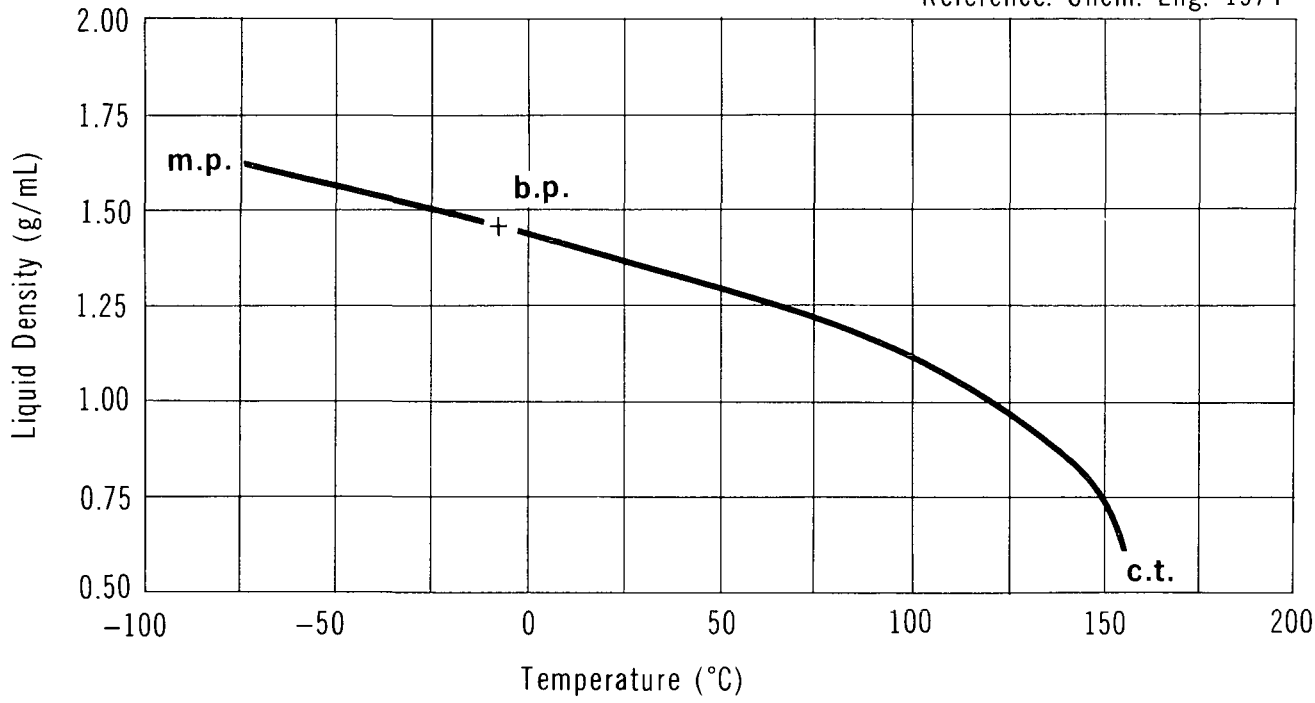


FIGURE 3

SULPHUR DIOXIDE

GAS DENSITY

Reference: MATHESON 1980

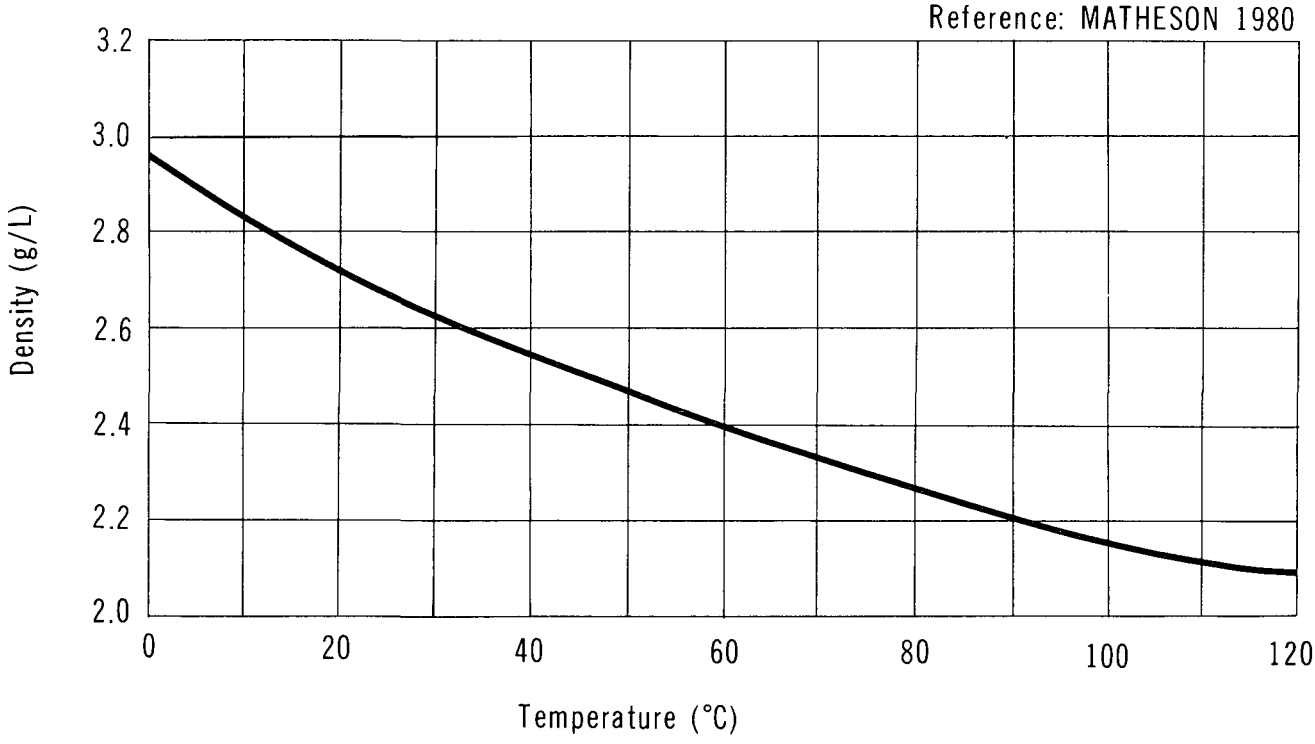


FIGURE 4

SULPHUR DIOXIDE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

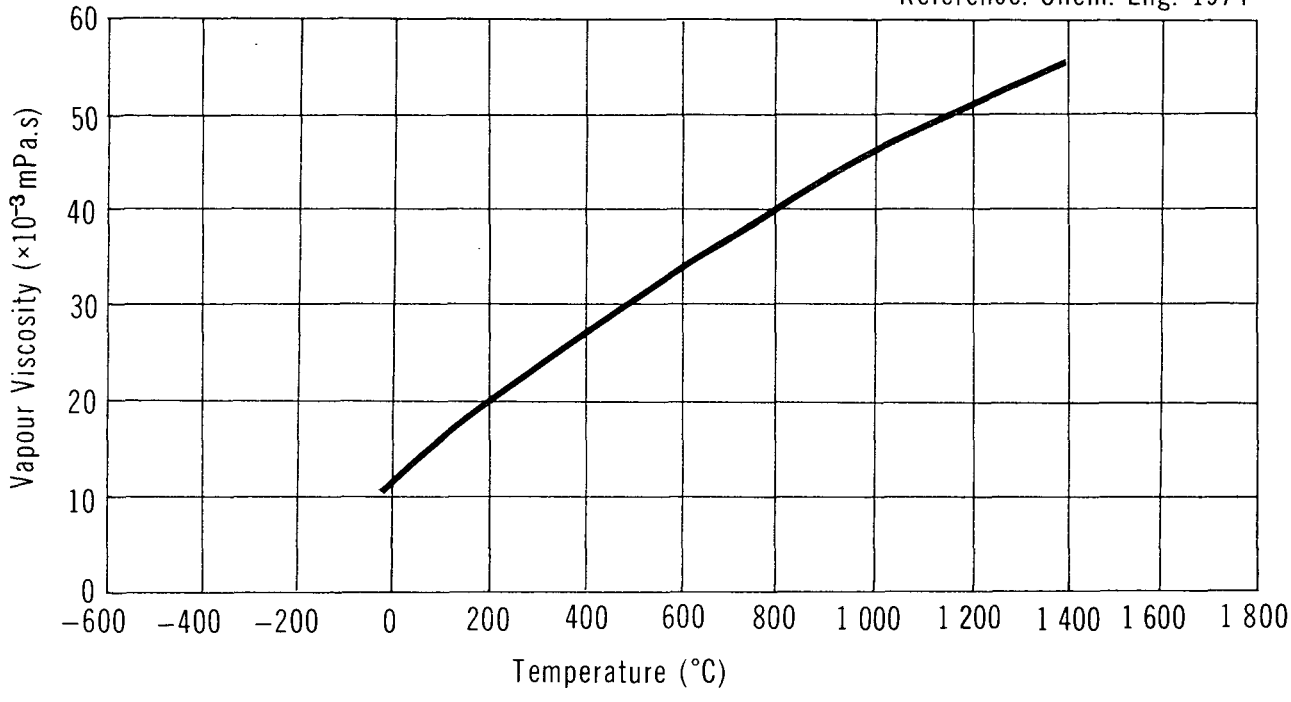


FIGURE 5

SULPHUR DIOXIDE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

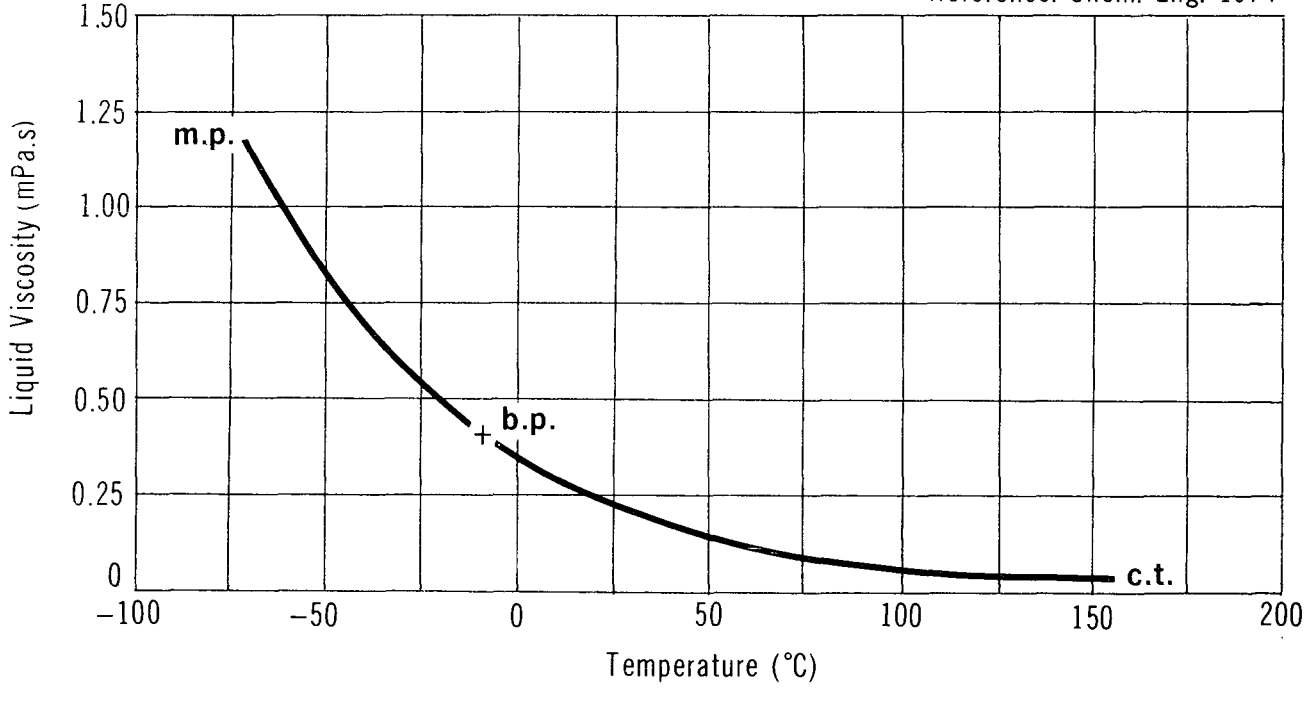


FIGURE 6

SULPHUR DIOXIDE

SOLUBILITY IN WATER vs TEMPERATURE

Reference: SEIDELL and LINKE 1965

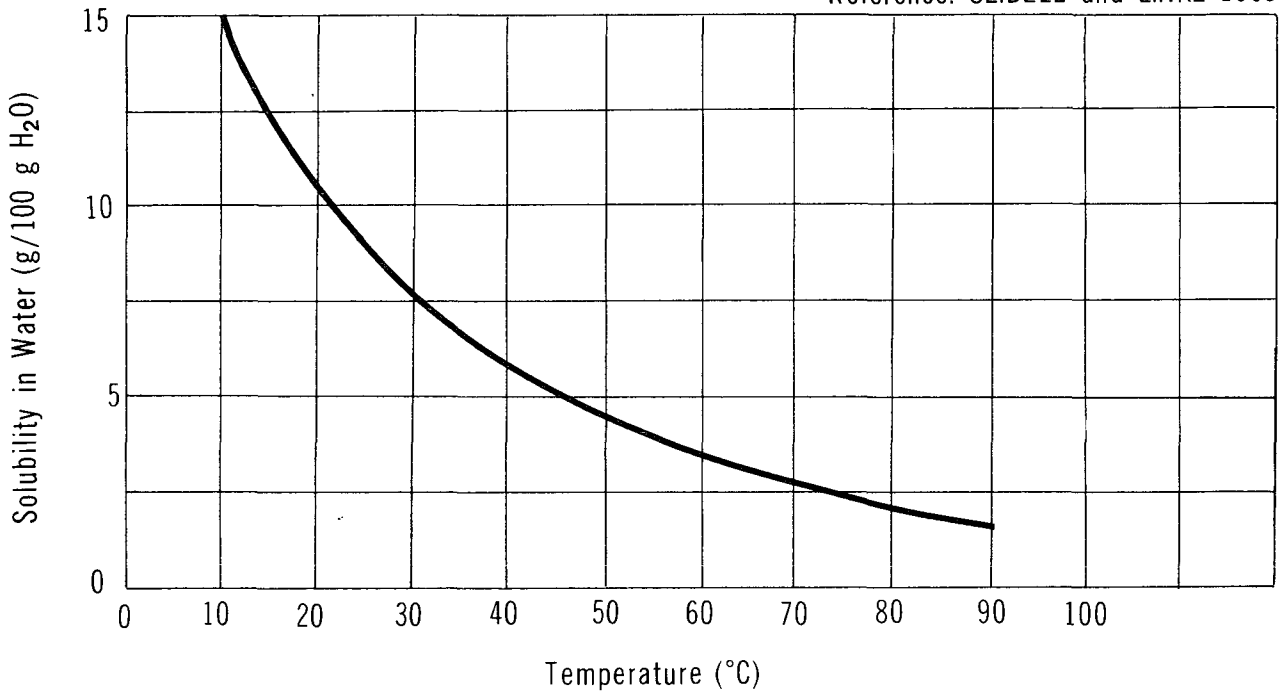
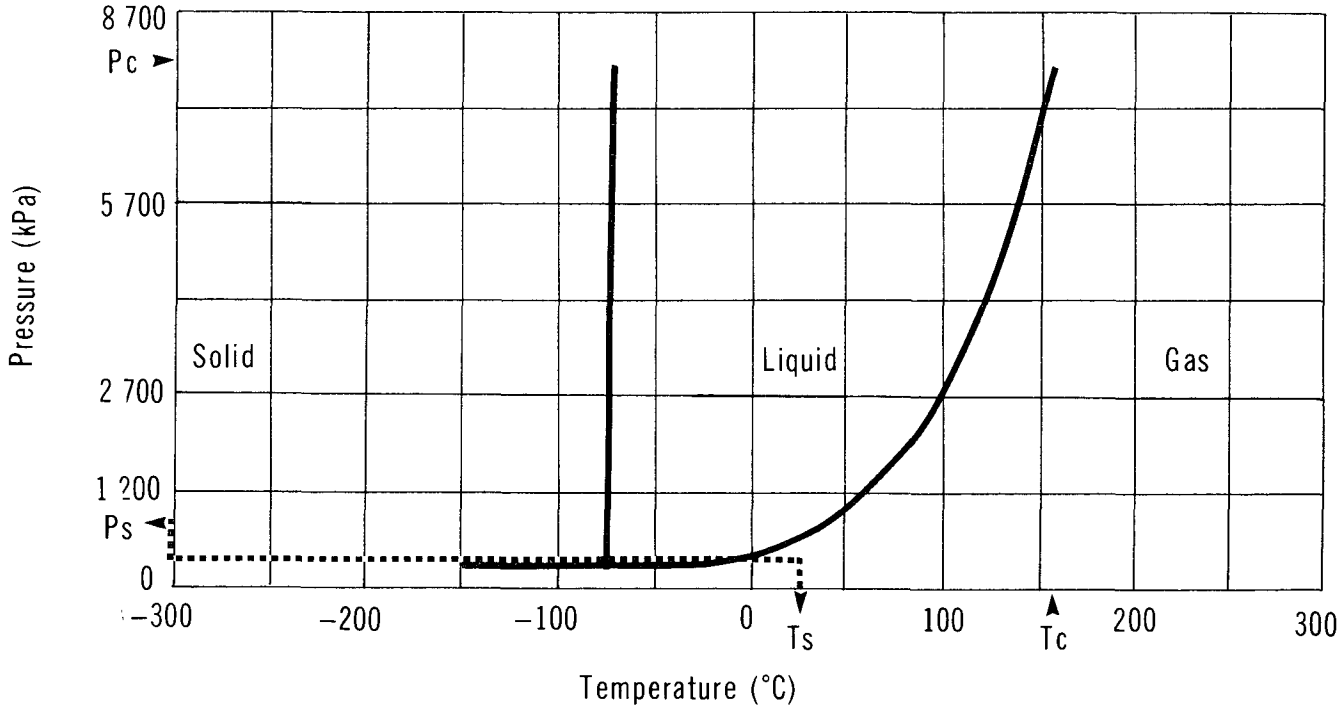


FIGURE 7

SULPHUR DIOXIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (HCG 1981; Kirk-Othmer 1983)

Sulphur dioxide is sold in technical or commercial grade, with >99.98 percent SO_2 and <100 ppm H_2O, and in refrigeration grade, with >99.98 percent SO_2 and <50 ppm H_2O. Sulphur dioxide is also frequently encountered as a combustion product from sulphur and sulphur-containing products.

3.2 Domestic Manufacturers (Corpus 1984; CCPA 1981)

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

Cominco
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

Inco Metals
Inco Ltd.
1 First Canadian Place, P.O. Box 44
Toronto, Ontario
M5X 1C4
(416) 361-7511

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

Canadian Liquid Air Co. Ltd.
1155 Sherbrooke Street West
Montreal, Quebec
H3A 1H8
(514) 842-5431

C-I-L Inc.
90 Sheppard Avenue East
Box 200, Station 'A'
North York, Ontario
M2N 6H2
(416) 229-7000

Matheson of Canada Ltd.
P.O. Box 89
Whitby, Ontario
L1N 5R9
(416) 668-3397

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

3.4 Major Transportation Routes

Current Canadian production of sulphur dioxide is located in Copper Cliff, Ontario, and in Trail, British Columbia. The product is shipped by tank cars, tank trucks or cylinders.

3.5 Production Levels (Corpus 1984)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1983)
Inco Metals, Copper Cliff, Ont.	110
Cominco, Trail, B.C.	55
TOTAL	165
Domestic Production (1983)	93.5
Imports (1982)	6.1
TOTAL	99.6

3.6 Manufacture of Sulphur Dioxide (FKC 1975; CCPA 1984)

3.6.1 General. In Canada, sulphur dioxide is a byproduct of the flash-smelting of metallic sulphide ores.

3.6.2 Manufacturing Process. Smelter gas containing about 75-80 percent sulphur dioxide is passed through a gas-cleaning system and a tower where it is dried by strong (98 percent) sulphuric acid. From the drying tower, the gas passes through a series of liquefaction processes consisting of compression, cooling, filtration (to remove oils) and separation of the liquid sulphur dioxide from the gas phase. Liquid sulphur dioxide from the first liquefaction process passes to storage, and the gas phase is compressed to higher pressures; the cooling, filtration and separation processes are repeated. The effluent gas from the final compression/refrigeration cycle is discharged with other waste gas streams.

Liquid sulphur dioxide may be stored under 3 to 10 atmosphere pressure, or at atmospheric pressure at -10°C, with refrigeration to condense evaporating gas.

3.7 Major Uses in Canada (Corpus 1984)

Sulphur dioxide is used in pulp bleaching, sulphite pulping, metal mining/refining, water treatment, and food processing. It can also be used in the production of sulphuric acid, sodium sulphate and sulphites. In 1983, 45 percent of domestic production was used for pulp bleaching, 27 percent was exported, 11 percent was used for sulphite bleaching, and 10 percent used for metal refining.

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

Abitibi-Price, Kenogami, Que.
Boise Cascade, Fort Frances, Ont.; New Castle, N.B.
BC Forest Products, Crofton, B.C.
B.C. Timber, Castelgar, Skeena, B.C.
Brunswick Mining & Smelting, Belledune, N.B.
Canadian Cellulose, Castlegar, N.B.
Canadian Copper Refiners, Montreal, Que.
Canadian Forest Products, Port Mellon, Que.
Canadian International Paper, La Tuque, Que.
Cariboo Pulp & Paper, Quesnel, B.C.
Consolidated-Bathurst, Bathurst, N.B.
Consolidated-Bathurst, Portage du Fort, Que.
Crestbrook Forest, Skookumchuk, B.C.
Domtar, Cornwall, Trenton, Ont.; Dolbeau, Que.
Donohue St. Felicien, St. Felicien, Que.
Eddy Forest Products, Espanola, Ont.
Great Lakes Forest, Dryden, Ont.
Intercontinental Pulp, Prince George, B.C.
James River Marathon, Marathon, Ont.
Kidd Creek Mines, Timmins, Ont.
MacMillan Bloedel, Powell R., Alberni, B.C.
Ontario Paper, Thorold, Ont.
New Brunswick International Paper, Dalhousie, N.B.
Prince Albert Pulp, Prince Albert, Sask.
Noranda Mines, Manitouwadge, Ont.
Nova Scotia Forest Industries, Port Hawkesbury, N.S.
St. Anne-Nackawic Pulp and Paper, Nackawic, N.B.
Scott Maritimes, New Glasgow, N.S.
Spruce Falls Power, Kapuskasing, Ont.
Tembec Forest Products, Temiskaming, Que.
Thurso Pulp & Paper, Thurso, Que.
Van Waters & Rogers, Vancouver, B.C.
Western Forest Products, Port Alice, Woodfibre, B.C.
Weyerhaeuser Canada, Kamloops, B.C.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Sulphur dioxide is shipped under pressure as a liquid in railway tank cars, tank motor vehicles and ton containers.

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of sulphur dioxide are listed in Table 2 (TCM 1979; RTDCR 1974).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS FOR SULPHUR DIOXIDE

CTC/DOT* Specification Number	Description
105A200W	Steel fusion-welded tank with manway nozzle. Insulated. Safety valve (1034 kPa, 200 psi) Top unloading arrangement required. Bottom outlet or washout prohibited.
105A300W	As 105A200W except with safety valve set at a maximum of 2070 kPa (300 psi).
105A500W	As 105A200W except with safety valve set at a maximum of 3450 kPa (500 psi).
106A500X	Multiple unit with removable steel uninsulated tanks mounted on underframe. Tanks have fusion-welded longitudinal tank seam and forge-welded head seams. Each tank equipped with loading and discharge valve and safety valve or vent set for pressure not exceeding 2588 kPa (375 psi). Popular name: "ton container".
110A500W	Same as 106A500X except tanks are totally fusion-welded.

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

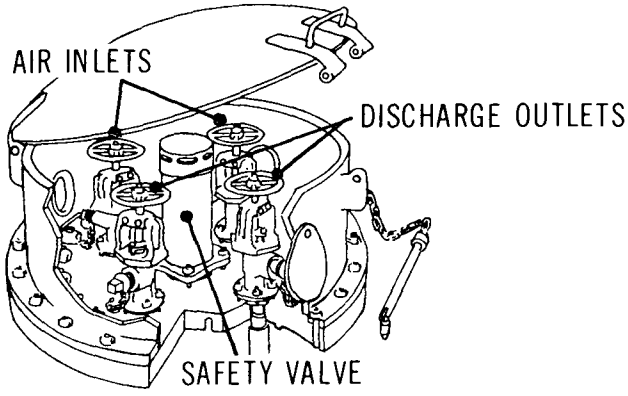
The liquid is usually shipped in CTC/DOT 105A300W railway tank cars as shown in Figure 8. Table 3 indicates railway tank car details associated with this drawing. Sulphur dioxide cars are never unloaded through bottom outlets; these are prohibited. The cars are unloaded from the top by compressor or dry air padding (MCA 1953).

FIGURE 8

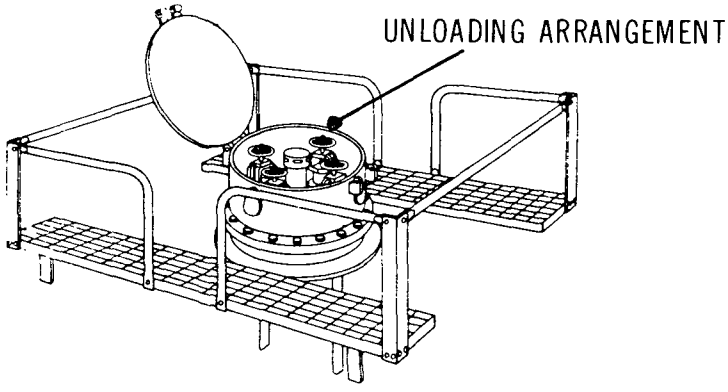
SULPHUR DIOXIDE

RAILWAY TANK CAR - CLASS 105A300W

(Reference: RTDCR 1974, TCM 1979)



Detail of top unloading arrangement



Detail of loading platform

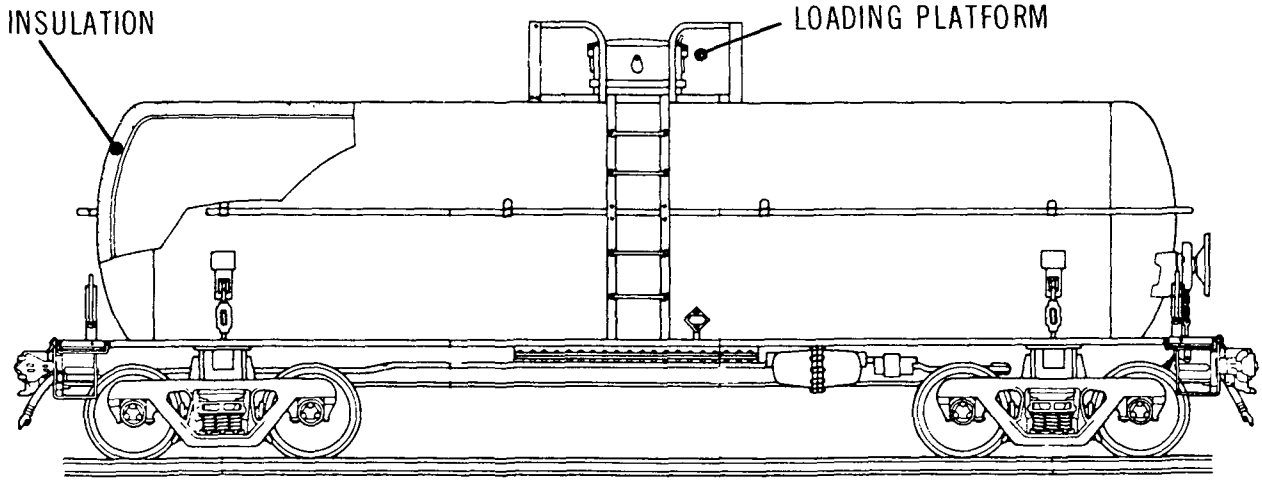


Illustration of tank car layout

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

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

The only opening permitted in the tank is a single manway located in the centre at the top. Cars are equipped with two discharge or liquid inlets or outlets and one or two vapour space outlets. These are either 25 mm (1 in) or 51 mm (2 in) fittings (MCA 1953; CCPA 1984). Under each liquid discharge is a 32 mm (1-1/4 in) eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a 32 mm (1-1/4 in) rising-ball, excess-flow valve designed to close when the rate of flow of liquid exceeds about 5400 kg/h (12 000 lb/h) for the 25 mm (1 in) fitting and 1300 kg/h (28 600 lb/h) for the 51 mm (2 in) fitting (CCPA 1984). This is a protective device designed to close automatically against the flow of liquid if the angle valve is broken off. The safety relief valve is of the spring-loaded type and is usually combined with a frangible disc.

Multiple unit tank cars described in Table 2 may also be used. The ton containers, up to 15 of which may be carried at one time on these tank cars, have fusible plugs at the ends designed to melt at 74°C. After removal from the rail car, the containers are emptied from a horizontal position, with the two outlet valves located above each other so that one eduction pipe dips into the liquid phase and the other into the gas phase (MCA 1953).

4.1.1.2 Tank motor vehicles. Sulphur dioxide is shipped by tank motor vehicles of various capacities (HCG 1981). Similar to railway tank cars, these highway tankers are unloaded from the top, usually the standpipe being extended down over the back of the tank. Dry air is used for unloading. The air inlet is usually a 25 mm (1 in) diameter male threaded connection located at the top of the trailer.

Sulphur dioxide is transported in highway tankers similar to the railway tankers used for similar service. Sulphur dioxide is authorized for shipment in tank motor vehicles conforming to Transport Canada Specification TC331; that is, a seamless or welded steel tank, insulated, minimum design pressure 1034 kPa (200 psi) and designed and constructed in accordance with the ASME Code (HCG 1981). For tanks exceeding 4.5 m^3 (1200 gal) water capacity, the minimum design pressure may be reduced to 862 kPa (125 psi) (HCG 1981).

4.1.1.3 Portable tanks. Portable tanks are occasionally used to transport small volumes of sulphur dioxide. The capacities and weights of tanks vary depending on requirements of the user. Unloading fittings and methods are similar to those discussed for railway tank cars and highway tankers. Portable tanks must conform to Transport

Canada Specification TC51 or Canadian Transport Commission Specification CTC51, described in Table 4 (RTDCR 1974).

TABLE 4 PORTABLE TANK SPECIFICATIONS - TC51/CTC51 (RTDCR 1974)

Construction	- steel, welded or seamless
	- fusion-welded tanks must be heat-treated after weld in accordance with ASME Code
Design pressure	- not less than the vapour pressure at 46°C (for sulphur dioxide, minimum 828 kPa (120 psi)
	- standard design 1550 kPa (225 psi) maximum pressure
Outlets	- firmly mounted to tank - typically 25 mm (1 in) outlet with pipe extending to bottom for liquid discharge and 25 mm (1 in) outlet to vapour space
Capacity	- not less than equivalent 453 kg (1000 lb) water, not more than 907 kg (2000 lb) water capacity equivalent
Fill density	- maximum to 125 percent by weight of the water capacity of the tank

4.1.2 Cylinders. In addition to bulk shipment, sulphur dioxide is also transported in cylinders. Approved cylinders are detailed in Table 5. Cylinders often employed for small quantity usage (e.g., in laboratories) are depicted in Figure 9.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Sulphur Dioxide Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1953):

- The storage tank must be checked to make sure that it will hold the contents of the car.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.

Proceed with off-loading as follows (MCA 1953):

- Connect one 25 mm (1 in) liquid unloading line to the discharge outlet and connect the 25 mm (1 in) air line. Air pressure must be reduced to 860 kPa (125 psi) for

TABLE 5 CYLINDER SPECIFICATIONS FOR SULPHUR DIOXIDE SERVICE (RTDCR 1974)

CTC/DOT* Specification Number	Construction	Capacity (water equivalent) or size	Service Pressure kPa (psi)
3A225	steel, seamless	<454 kg (1000 lb)	1552 (225)
3AA225	steel, seamless	<454 kg (1000 lb)	>3448 (500)
3B225	steel, seamless	<454 kg (1000 lb)	1552 (225)
4A225	steel, welded and brazed	<454 kg (1000 lb)	1552 (225)
4B225	steel, welded and brazed	<454 kg (1000 lb)	1552 (225)
4BA225	steel, welded and brazed	<454 kg (1000 lb)	1552 (225)
4BW225	steel, electric arc-welded longitudinal seam	<454 kg (1000 lb)	1552 (225)
4B240ET	steel, welded and brazed, made from electric resistance-welded tubing	<5.4 kg (12 lb) or 5460 cm^3 (333 in^3)	1655 (240)
3E1800	steel, seamless	diameter, <51 mm (<2 in); length, 610 mm (<2 ft)	12 414 (1800)
ICC 3 ICC 4 ICC 25 ICC 26-150 ICC 38 ICC 39			

* Canadian Transport Commission and Department of Transportation

unloading. A safety relief valve must be installed in the air line to release at 900 kPa (130 psi). Air must be dry and clean (CCPA 1984).

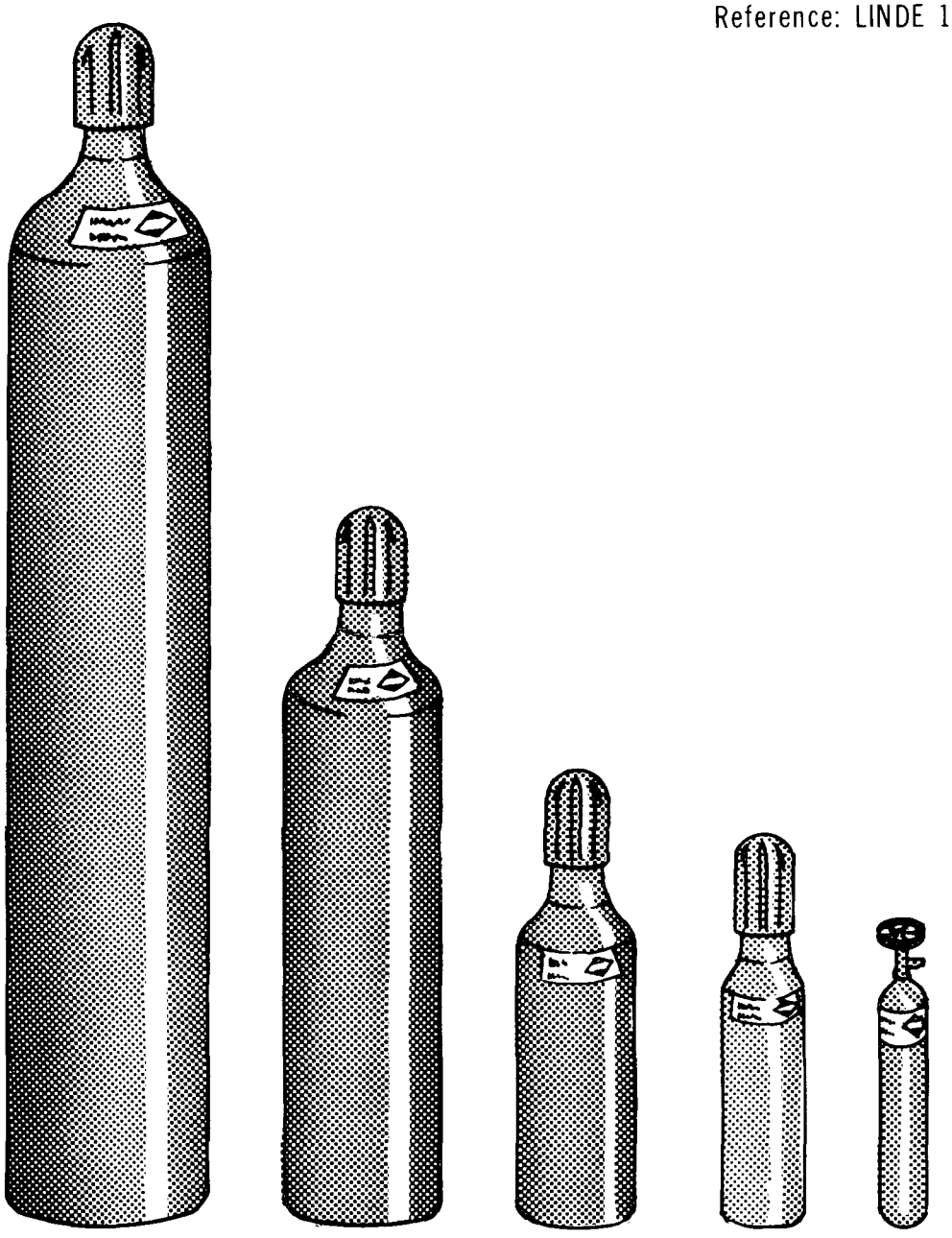
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure.
- Reverse the above procedure to close up the car.

FIGURE 9

SULPHUR DIOXIDE

COMMON GAS CYLINDERS

Reference: LINDE 1981



Industry designation		K	Q	G	F	LB
Approx. size	(mm)	229×1320	178×787	152×508	102×432	51×330
	(in)	9×52	7×31	6×20	4×17	2×13
Approx. weight (empty)	(kg)	60	29	13	5	1
	(lb)	132	65	29	10	4

- For off-loading by compressor, the suction side is connected to the top of the storage tank and the discharge side is connected to one of the gas valves on the tank car. One of the tank car liquid lines is then connected directly to the liquid line of the storage tank. When the compressor is started, a differential pressure of 207 kPa (30 psi) is sufficient to move the liquid sulphur dioxide to the storage tank (MCA 1953).

The general procedures for unloading of sulphur dioxide highway tankers are similar to those of railway tankers.

4.2.2 Off-loading Cylinders. The following points should be observed when handling and storing sulphur dioxide (anhydrous) cylinders (MCA 1953):

- Valve protection hoods should be in place.
- Cylinders should not be stored near ventilating systems.
- Store to minimize external corrosion.
- Store cylinders upright.
- Store full and empty cylinders separately.

Sulphur dioxide is withdrawn from the cylinder as a liquid when the cylinder is inverted and as a gas when the cylinder is upright (MCA 1953).

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading components discussed in this section along with specifications refer to those generally used in sulphur dioxide service. It is recognized that other materials may be used for particular applications as indicated in Table 6.

Schedule 40 carbon steel pipes and welding fittings are recommended for dry sulphur dioxide (HCG 1981). Welded, flanged joints should be used because threaded pipes and fittings tend to leak. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipeline should be tested with air pressures from 860 to 900 kPa (125 to 130 psi) and all leaks carefully stopped. The unloading line should be 25 mm (1 in) or 51 mm (2 in) pipe because this is the standard fitting on sulphur dioxide tank cars; process pipe may be almost any size. Pipe under 25 mm (1 in), however, is not recommended. Outdoor lines must be self-draining.

Stainless steel pipes and swivel joints may be used for flexible sections when handling sulphur dioxide. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Neoprene hoses serve adequately; however, at higher concentrations and temperatures, a Hypalon-lined hose is recommended (GF).

Quick acting ball or plug valves in "20" alloy or 316 stainless steel may be used for all room temperature concentrations (MCA 1953). Hypalon, asbestos, Teflon, or Neoprene (polychloroprene) gaskets can be used as a gasket material in most sulphur dioxide applications (GF; CCPA 1984). Lead gaskets are usually used in association with safety valves (MCA 1953).

A single-suction centrifugal pump with "20" alloy shaft and impeller and a high silicon cast iron casing is recommended for pumping. Hypalon is a good packing material (MCA 1953).

Welded heavy wall carbon steel or stainless steel storage tanks are commonly used for sulphur dioxide, anhydrous and aqueous. Tanks must conform to the ASME Code for Unfired Pressure Vessels. Each storage tank must be equipped with one or two approved safety valves set at 1550 kPa (225 psi) (MCA 1953).

4.3 Compatibility with Materials of Construction

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

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

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

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

TABLE 6 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Condition	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Gas, Wet	23		PVC II (DPPED 1967)	
	Liquid	23	Cast iron Carbon steel (Kirk-Othmer 1983)	PVC I (DPPED 1967)	PVC II (DPPED 1967)
	Liquid	24	PVDC (DCRG 1978) PE (MWPP 1978)		
	Gas, Dry or Wet	49	PE (DPPED 1967)		
	Gas, Dry or Wet	52	PVDC (DCRG 1978)		
	Gas, Dry	60	PVC I PVC II (DCRG 1967)		
			Cast iron Carbon steel (Kirk-Othmer 1983)		
	Gas, Wet	60		PVC I (DPPED 1967)	PVC II (DPPED 1967)
	Liquid	66			PVC I (DPPED 1967)
	Gas, Dry or Wet, Liquid	66	PVDF (DCRG 1978)		
	Gas, Dry or Wet	79	PP (DCRG 1978)		
	Gas, Wet	79	Chlorinated Polyether (DCRG 1978)		
	Liquid				Chlorinated Polyether (DCRG 1978)

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

Application	Chemical Condition	Chemical Temp. (°C)	Material of Construction: Recommended	Material of Construction: Conditional	Material of Construction: Not Recommended
1. Pipes and Fittings (Cont'd)					PVCI ABS (MWPP 1978)
	Gas		CS Cast Iron High Silicon (HCG 1981)		
2. Valves	Gas, Moist	21	SS 316 Alloy "20" (JSSV 1979)		
	Gas, Dry	302	SS 316 Alloy "20" (JSSV 1979)		
3. Pumps	Gas, Dry		Cast Iron High Silicon (MCA 1953)		
4. Storage	Gas, Dry		CS (MCA 1953; HCG 1981)		Zinc (HCG 1981)
	Gas, Wet		SS 316 Lead (HCG 1981)		
5. Others	Gas, Moist	20		SS 302 SS 304 SS 316 SS 410 SS 430 (ASS)	
	Wet	22	PVC (TPS 1978)		CPVC (TPS 1978)
	Dry	22	CPVC (TPS 1978)		
	Dry, Wet	23	PP (TPS 1978)		
	Moist, Aqueous	50	uPVC PE, PP NBR, IIR EPDM, CR CSM (GF)	FPM (GF)	POM NR (GF)

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

Application	Chemical Condition	Chemical Temp. (°C)	Material of Construction: Recommended	Material of Construction: Conditional	Material of Construction: Not Recommended
5. Others (Cont'd)	All, Moist, Aqueous	60	PE, PP NBR, IIR EPDM, CR CSM (GF)	uPVC FPM (GF)	POM NR (GF)
	All, Dry	60	uPVC PE, PP IIR, EPDM CR, FPM CSM (GF)	POM NBR (GF)	NR (GF)
	Dry	60	PVC (TPS 1978)		
	Wet	60			PVC (TPS 1978)
	Liquid, Technic-ally Pure	60	NBR, IIR EPDM, CR FPM, CSM (GF)	PE POM (GF)	uPVC NR (GF)
	Dry, Wet	66	PVDF (TPS 1978)		
	Dry, All	80	IIR EDPM CR, FPM CSM (GF)	PE, PP NBR (GF)	uPVC, POM NR (GF)
	Liquid	24 to 149	Glass (CDS 1967)		SBR (GPP)
	Liquid	24 to 204	Concrete (CDS 1967)		
	Liquid	f204		Concrete (CDS 1967)	
	Liquid	24	Wood (CDS 1967)		

TABLE 7 MATERIALS OF CONSTRUCTION

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

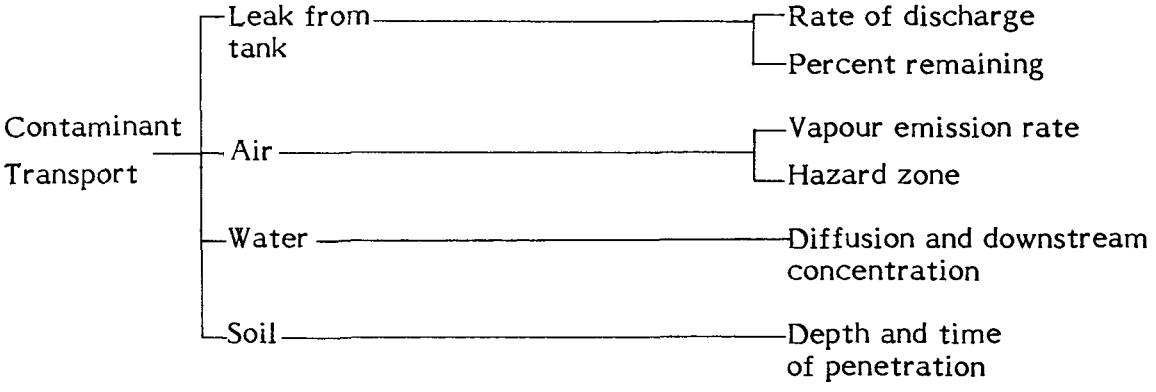
5 CONTAMINANT TRANSPORT

5.1 General Summary

Sulphur dioxide is commonly transported as a liquid under pressure in specially designed railway tank cars. When spilled on water, liquid sulphur dioxide sinks and boils, producing both contaminated water and a visible poisonous vapour cloud which tends to hug the surface and spread rather than lift off and disperse. It is moderately soluble and will dissolve readily in water.

Sulphur dioxide spills on soil surfaces will partly vaporize and partly adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport toward the groundwater table may cause environmental problems.

The following factors are considered for the transport of a sulphur dioxide 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. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Sulphur dioxide is commonly transported as a liquid under pressure at ambient temperature. While the capacities of the railway tank cars vary widely, one size has been chosen for development of the leak nomograms. It is

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

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

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 630 kPa.

The assumption of isothermal conditions will maximize the gas release rate from the tank and will be conservative for most cases.

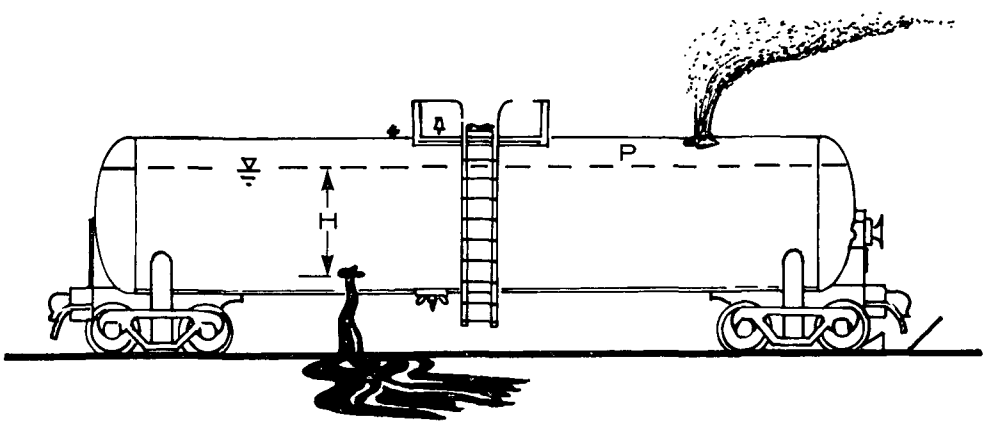


FIGURE 10 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid

release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of sulphur dioxide 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 sulphur dioxide at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time but also of the size and shape of the tank car.

Figure 12: Discharge rate versus puncture size. Figure 12 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 13: Percent remaining versus time. Figure 13 provides a means of estimating the percent of sulphur dioxide remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

As isothermal conditions have been assumed, the internal pressure and venting rate are constant. It should be noted that the isothermal assumptions will result in a very rapid release. Under actual conditions, this release may be much slower.

Figure 14: Discharge rate versus puncture size. Figure 14 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 14 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 630 kPa.

FIGURE 11

SULPHUR DIOXIDE

PERCENT REMAINING vs TIME

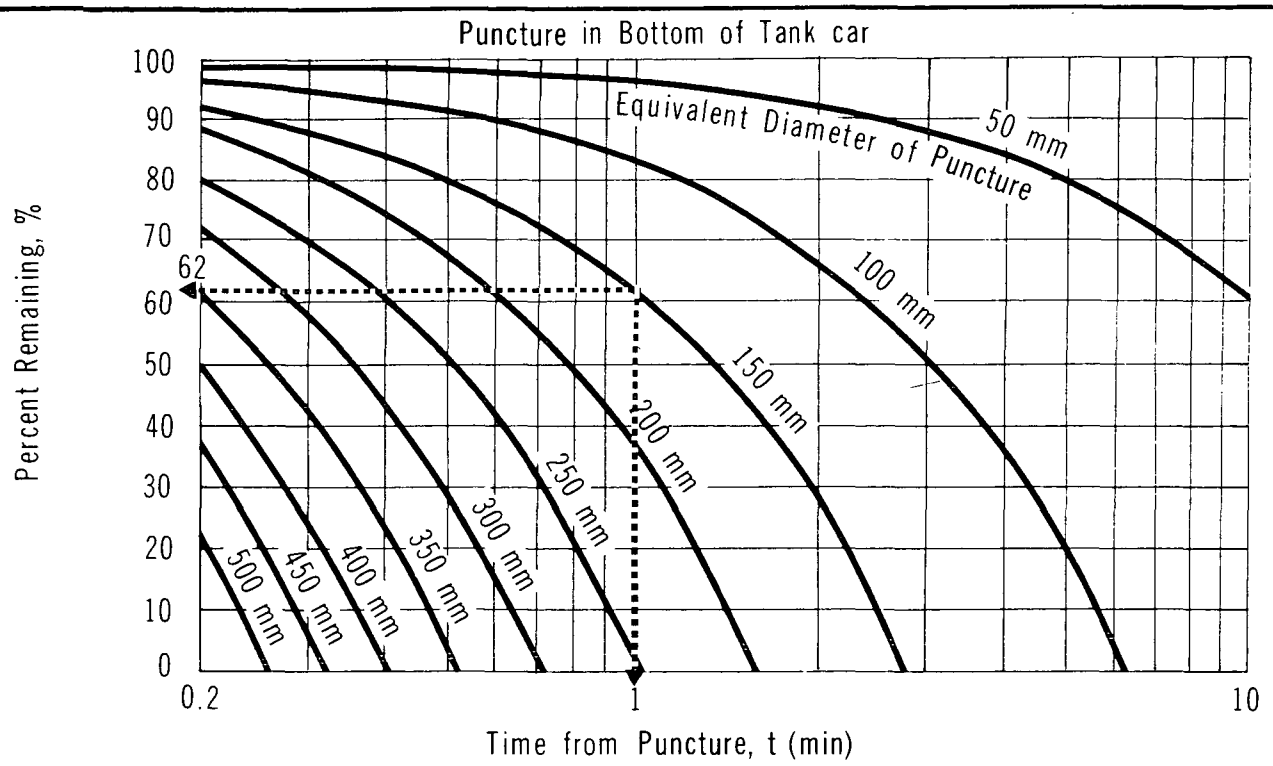


FIGURE 12

SULPHUR DIOXIDE

DISCHARGE RATE vs PUNCTURE SIZE

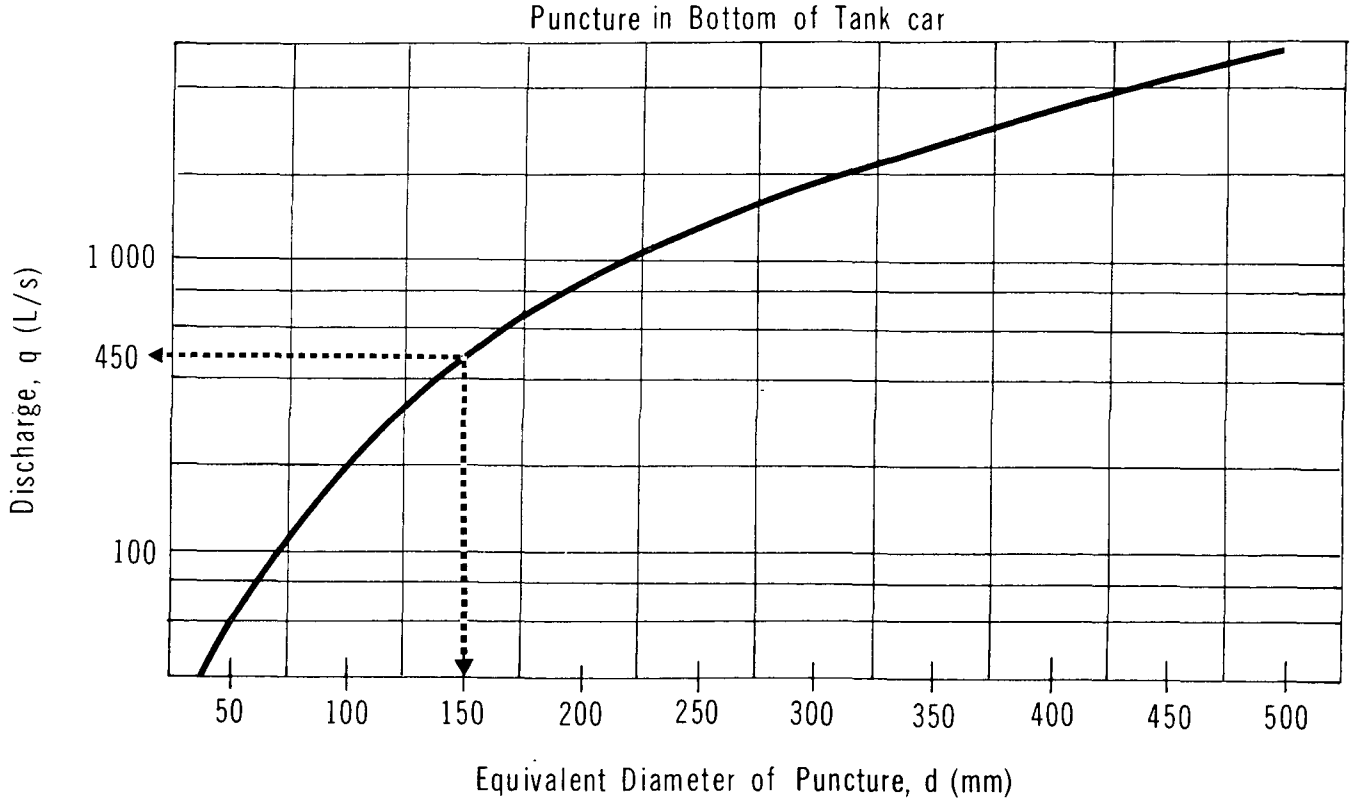


FIGURE 13

SULPHUR DIOXIDE

PERCENT REMAINING vs TIME

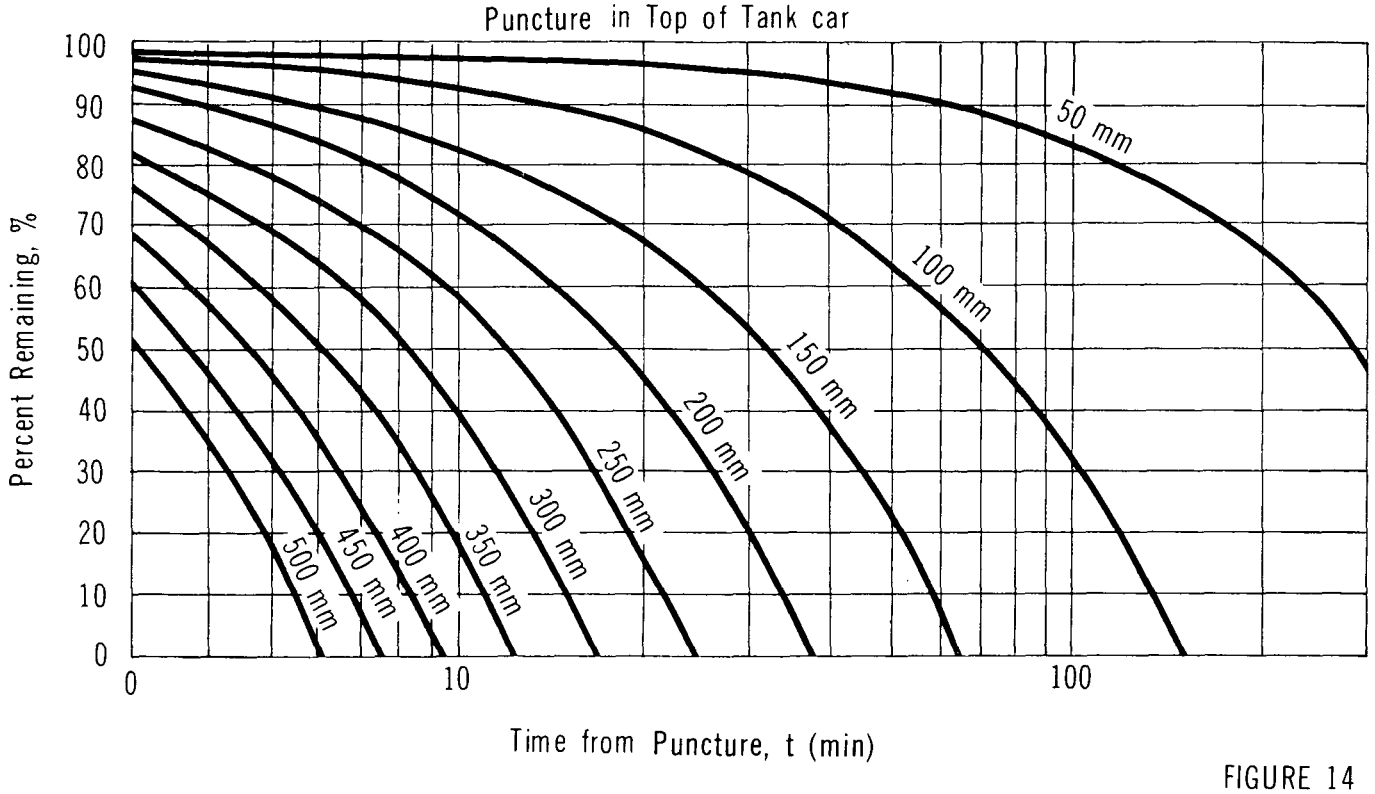
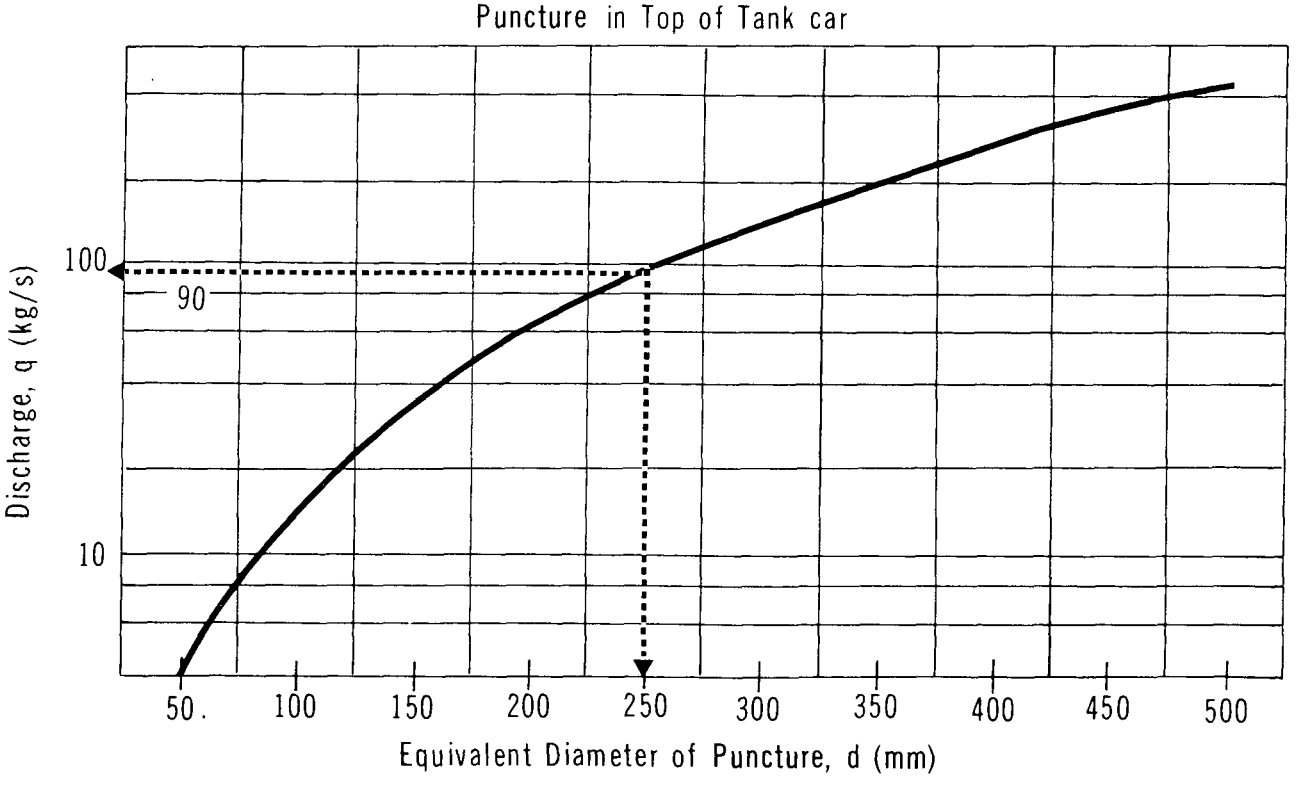


FIGURE 14

SULPHUR DIOXIDE

DISCHARGE RATE vs PUNCTURE SIZE



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with sulphur dioxide at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 1 minute and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate the amount remaining at t=1 min

- Use Figure 11
- With t=1 min and d=150 mm, the amount remaining is about 62 percent or 50 000 L

Step 2: Calculate the discharge rate

- Use Figure 12
- With d=150 mm, the instantaneous discharge rate (q) = 450 L/s

ii) Problem B

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

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 13
- With d=250 mm, the tank empties (0 percent remaining) in approximately 25 min

Step 2: Calculate the discharge rate

- Use Figure 14
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 90 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since sulphur dioxide under pressure is an extremely volatile liquid, vapour released from a liquid pool spilled on a ground or water surface vaporizes rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release is treated here.

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

Figure 15 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

Although no relevant spill information is available on the behaviour of a cloud of sulphur dioxide gas, it is expected that, in the initial period immediately after the spill, the cloud will behave as a denser-than-air gas. This is due primarily to the greater density of sulphur dioxide gas (2.2 times that of air at 20°C) and to the fact that the vapour cloud arising from the cold bulk liquid will be cold itself. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussion modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

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):

Table 8:	weather conditions
Figure 17:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 9:	maximum puff hazard half-widths
Figure 19:	vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 16 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 17: Normalized vapour concentration versus downwind distance. Figure 17 shows the relationship between the vapour concentration and the downwind

FIGURE 15

SULPHUR DIOXIDE

SCHEMATIC OF CONTAMINANT PUFF

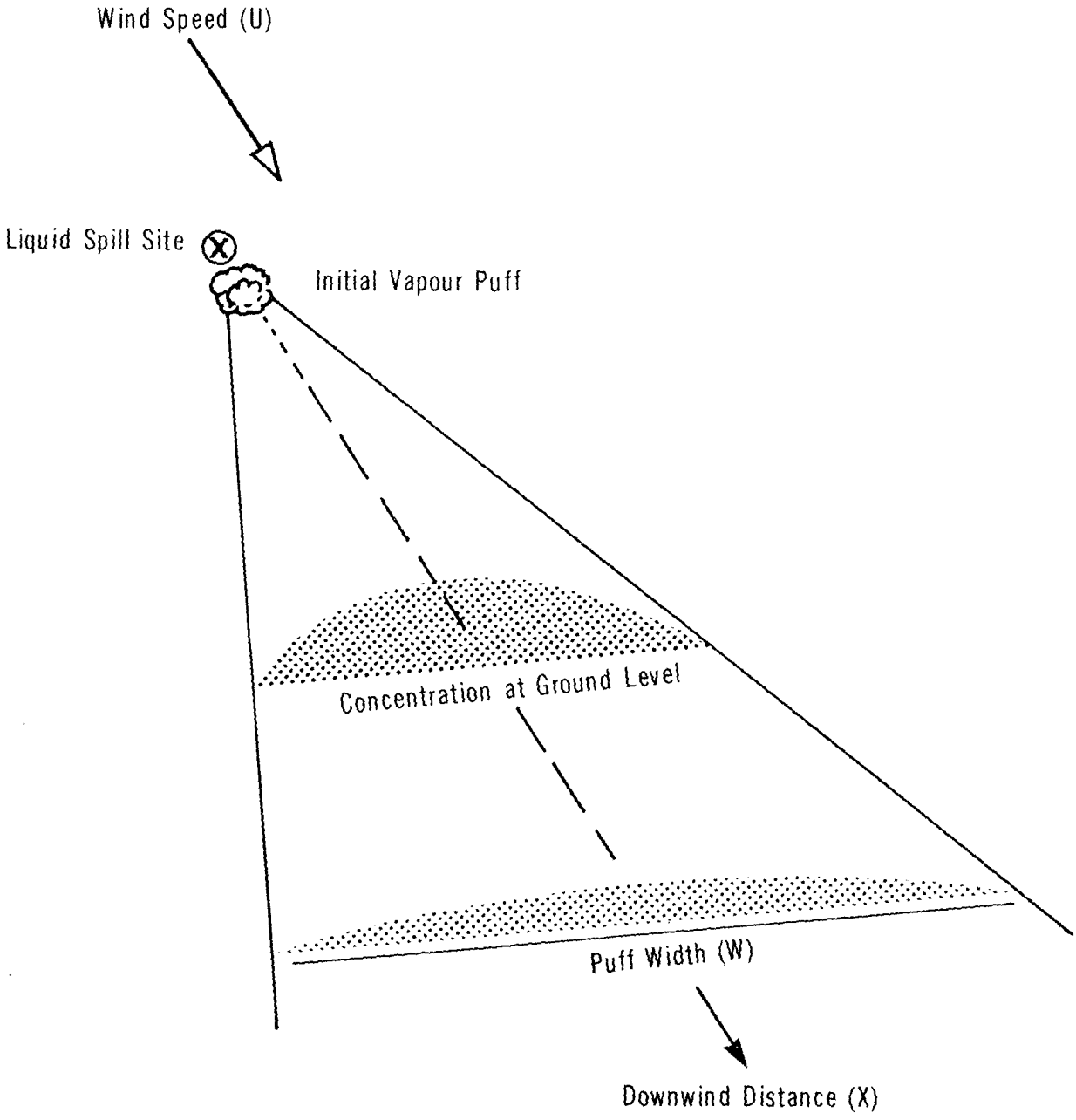


FIGURE 16

SULPHUR DIOXIDE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

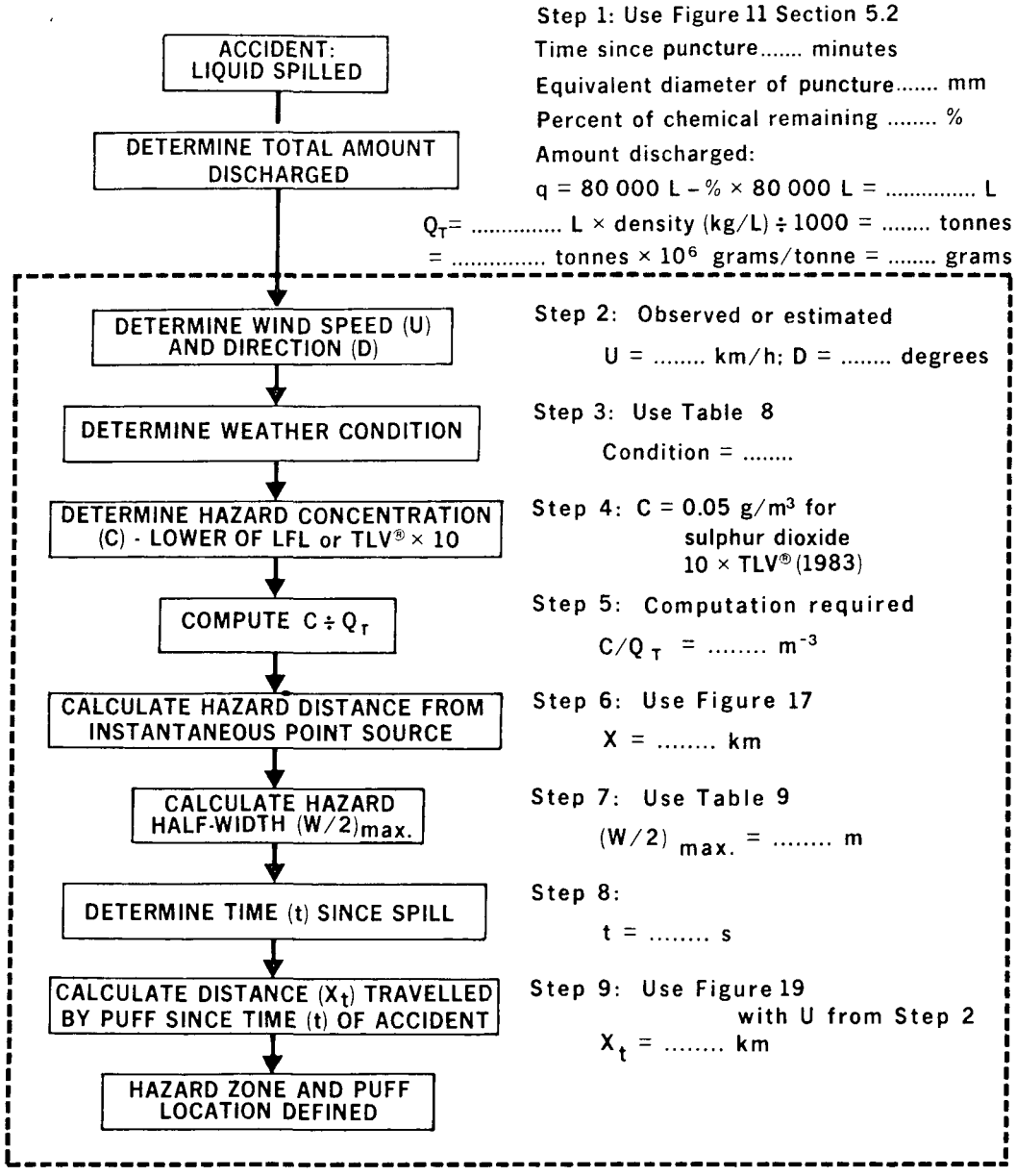
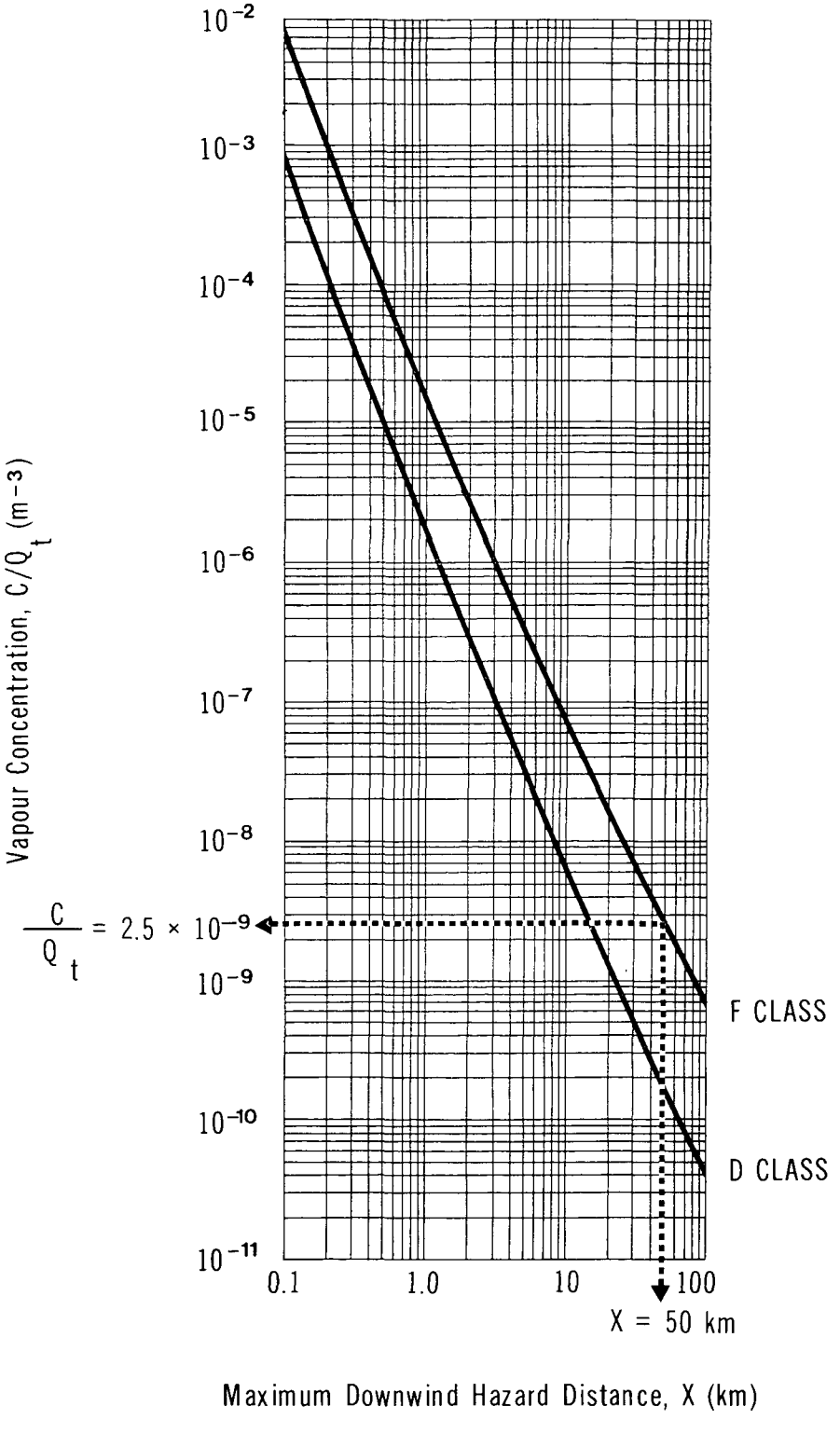


FIGURE 17

SULPHUR DIOXIDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 17, the weather condition must be determined from Table 8.

Table 8 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, downwind of the spill can be calculated from Figure 17 knowing:

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3), which for an inflammable vapour will be 10 x TLV®. Note: To convert the TLV®, in ppm, to a concentration in g/m^3, use Figure 18

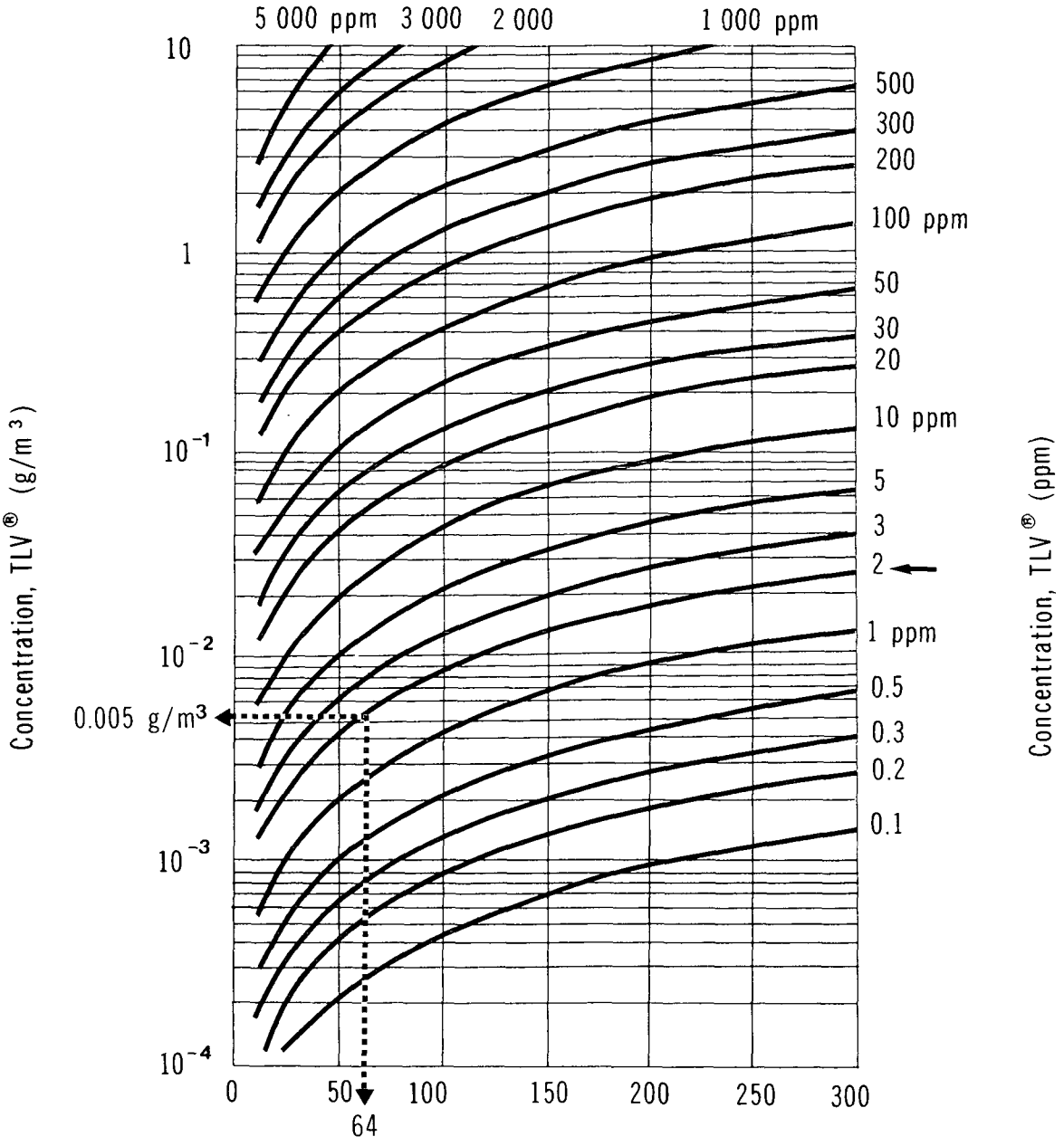
A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short-term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure; use of this value as the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

5.3.2.2 Table 9: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the sulphur dioxide Threshold

FIGURE 18

SULPHUR DIOXIDE

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



Example: Sulphur dioxide, MW = 64, TLV® = 2 ppm, then TLV® in g/m³ = 0.005

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

TABLE 9 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR SULPHUR DIOXIDE)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
1600	4020	(99.5 km)*	75	1860	(99.5 km)*
1500	3920		70	1805	
1250	3660		60	1690	
1000	3360		50	1565	
750	3010		40	1425	
500	2580		30	1260	
400	2365		25	1165	
300	2120	Q_T = 20 tonnes →	20	1060	→ $(W/2)_{max}$ = 1060 m
250	1980		15	935	
200	1815		10	790	
150	1625		5	585	
100	1395		2.5	440	
75	1250		1	305	
50	1070		0.5	235	
25	820		0.25	180	
20	755		0.1	125	
15	680		0.05	95	
10	590		0.01	50	
5	455				
2.5	350				
1	250				
0.5	195				
0.1	110				
0.05	85				
0.01	50				

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

Example: Under weather condition F and Q_T = 20 tonnes, the puff hazard half-width $(W/2)_{max}$ = 1060 m

Note: Above table is valid only for a sulphur dioxide concentration of 10 x TLV®, or 0.05 g/m^3.

Limit Value (TLV®) of 0.005 g/m^3, or 0.05 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the sulphur dioxide vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 9 is therefore only applicable for a sulphur dioxide hazard concentration limit of 10 x TLV®, or 0.05 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 1600 tonnes,

respectively. If the entire contents of an 80 000 L (17 600 Imp. gal) tank car spill, the mass spilled would be approximately 116 000 kg, or 116 tonnes. Therefore, under class D of Table 9, data are provided for up to 13 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 75 tonnes, respectively. Therefore, under class F of Table 9, data are provided for only about 65 percent of a standard rail car load.

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

5.3.2.3 Figure 19: Puff travel time versus travel distance. Figure 19 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

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

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

Problem:

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

Solution:

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

- Q_T = 20 tonnes or 2×10^7 g

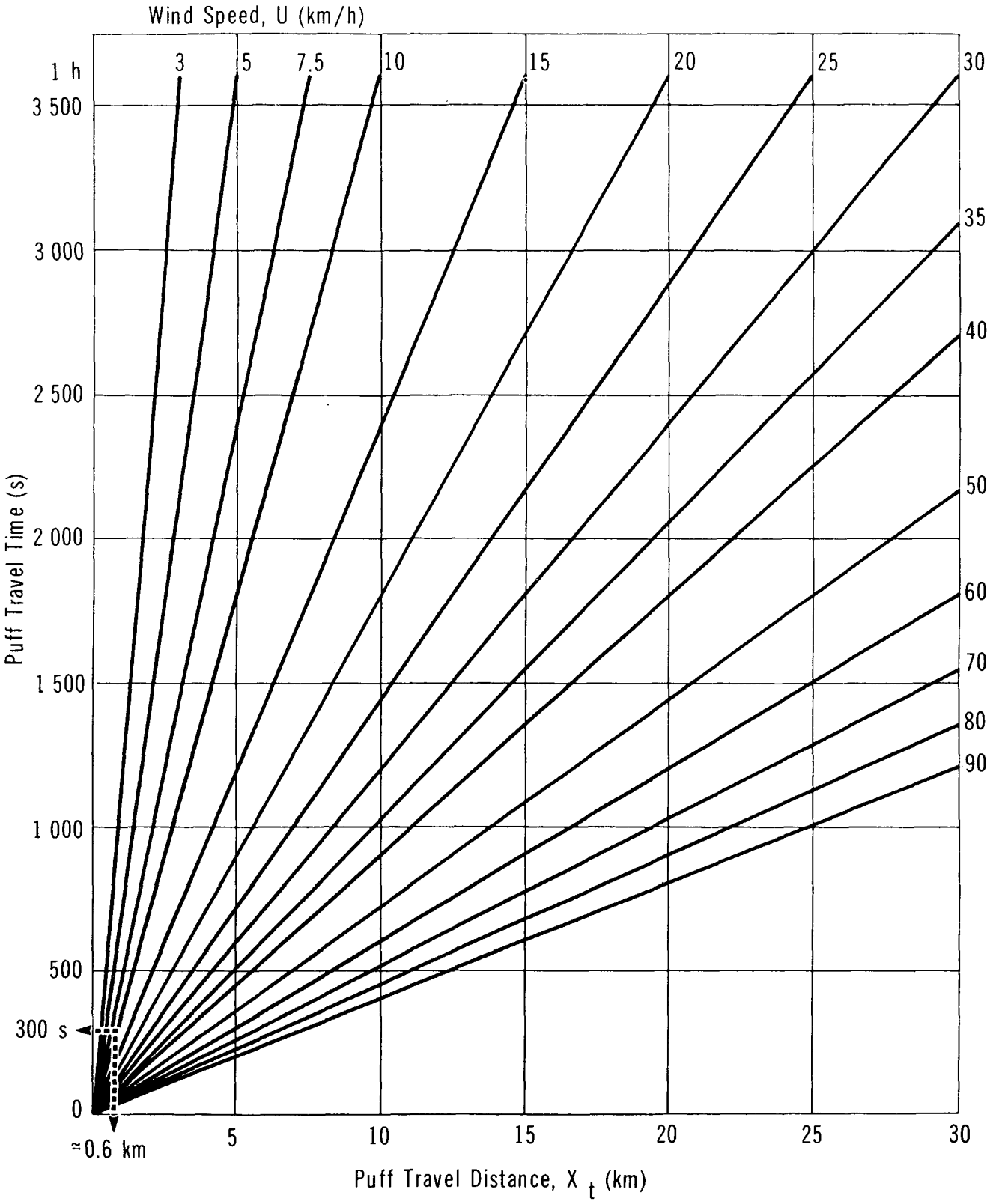
Step 2: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations

FIGURE 19

SULPHUR DIOXIDE

PUFF TRAVEL TIME VS TRAVEL DISTANCE



- Given: U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = Direction from which wind is blowing)

Step 3: Determine the weather condition

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

Step 4: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL; since sulphur dioxide vapours are flammable, this is 10 x TLV®
  C = 0.05 g/m^3 (TLV® = 0.005 g/m^3; no LFL)

Step 5: Compute C/Q_T

- $C/Q_T = \dfrac{0.05}{2 \times 10^7} = 2.5 \times 10^{-9}\ m^{-3}$

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

- From Figure 17, with $C/Q_T = 2.5 \times 10^{-9}\ m^{-3}$ and weather condition F, X ≃ 50 km

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

- Use Table 9
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 1060 m

Step 8: Determine the time since the spill

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

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

- Using Figure 19, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (1060 m) by the maximum hazard distance downwind of the instantaneous point source (50 km) along the direction of the wind, as shown in Figure 20
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 21
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 395 minutes before the puff reaches the maximum downwind hazard distance of 50 km

FIGURE 20

SULPHUR DIOXIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

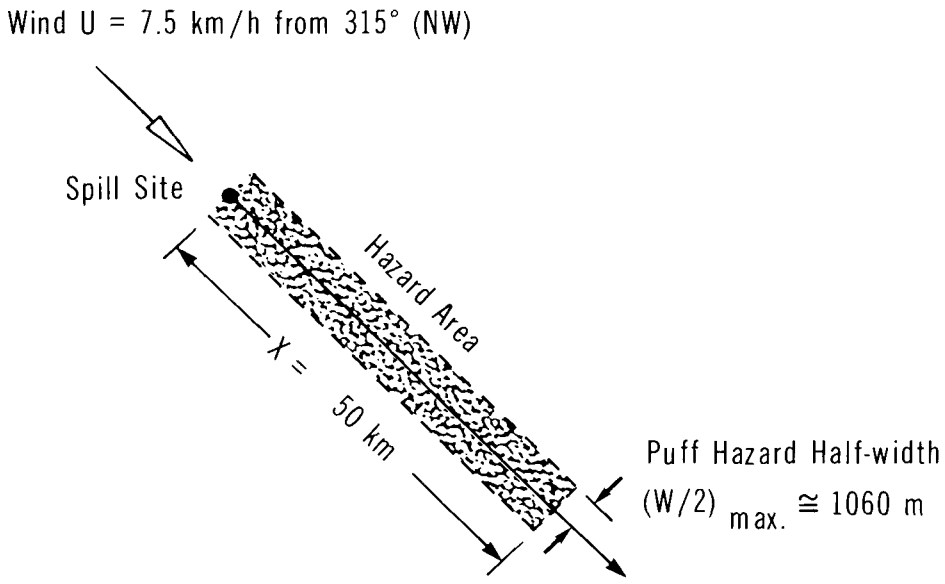
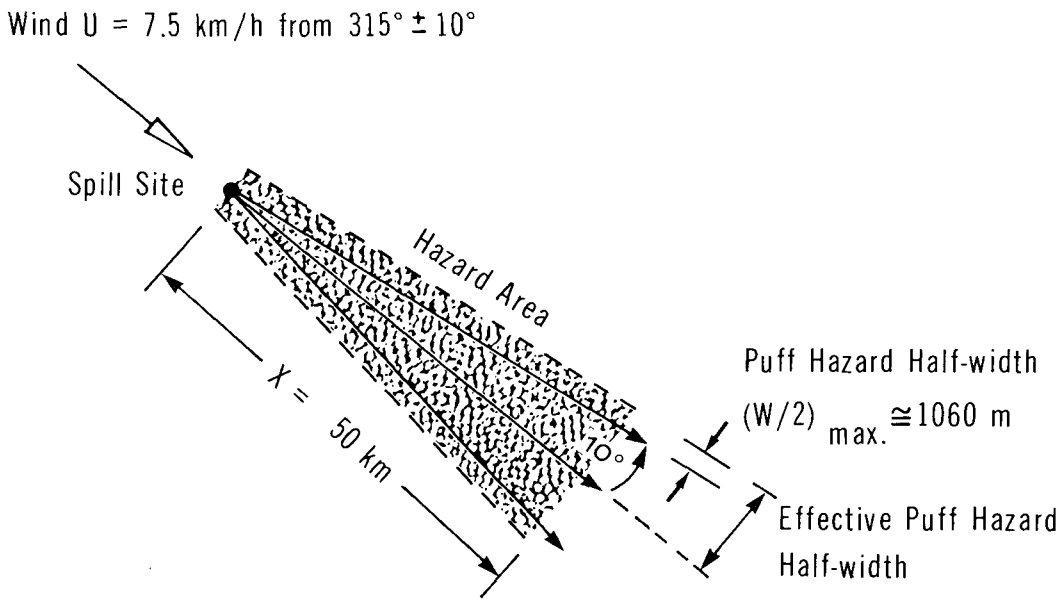


FIGURE 21

SULPHUR DIOXIDE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM



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

$= 50 \times 1000 \times \tan 10° + 1060$ m

$= 9880$ m or 9.9 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, sulphur dioxide will sink and boil, with some dissolution. Mixing of the water phase takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in a calm water mixing takes place by molecular diffusion.

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

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

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

Non-tidal Rivers

Figure 23:	time versus distance for a range of average stream velocities
Figure 24:	hydraulic radius versus channel width for a range of stream depths
Figure 25:	diffusion coefficient versus hydraulic radius for a range of average stream velocities
Figure 26:	alpha* versus diffusion coefficient for various time intervals
Figure 27:	alpha versus delta* for a range of spill sizes
Figure 28:	maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 29:	volume versus radius for the hazard zone for a range of lake depths
Figure 30:	average concentration versus volume for the hazard zone for a range of spill sizes

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

The flowchart in Figure 22 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figure 23 through 30) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 23: Time versus distance. Figure 23 presents a simple relationship between average velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 23.

Figure 24: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 24 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 25: Diffusion coefficient versus hydraulic radius. Figure 25 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 24 and the average stream velocity (U).

Figure 26: Alpha versus diffusion coefficient. Figure 26 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 27: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 27 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 28: Maximum concentration versus delta. Figure 28 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 28 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

FIGURE 22

SULPHUR DIOXIDE

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS

SPILL

DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

CALCULATE TIME (t) TO REACH POINT OF INTEREST

Step 2: Use Figure 23

t = _____ minutes

CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL

Step 3: Use Figure 24

r = _____ m

CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)

Step 4: Use Figure 25

E = _____ m^2/s

CALCULATE ALPHA (α) AT TIME (t)

Step 5: Use Figure 26

α = _____

CALCULATE DELTA (Δ) FOR SPILL MASS

Step 6: Use Figure 27

Δ = _____

COMPUTE A = W × d

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

A = W × d _____ m^2

CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 8: Use Figure 28

C = _____ ppm

FIGURE 23

SULPHUR DIOXIDE

TIME vs DISTANCE

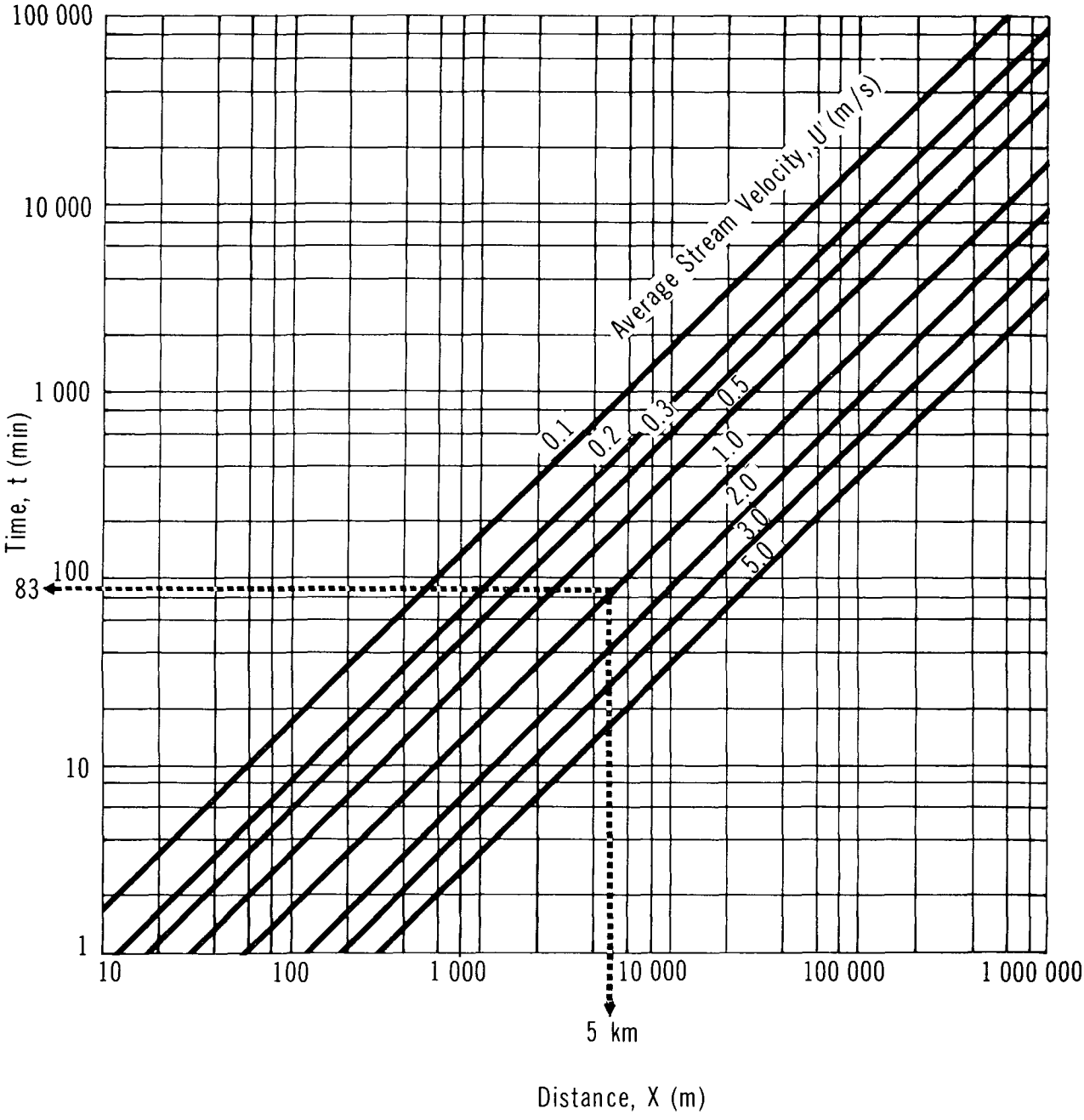


FIGURE 24

SULPHUR DIOXIDE

HYDRAULIC RADIUS VS CHANNEL WIDTH

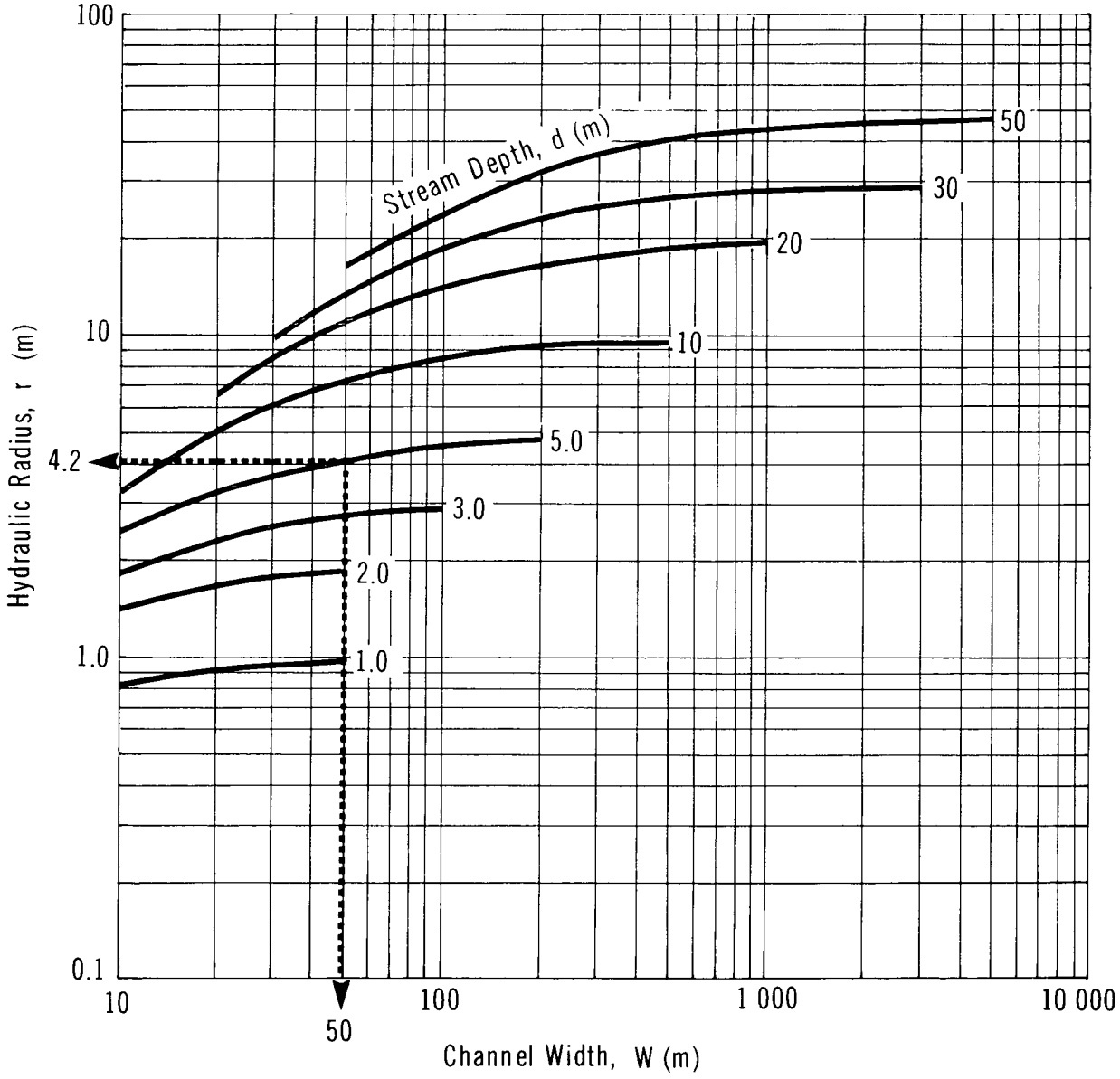


FIGURE 25

SULPHUR DIOXIDE

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

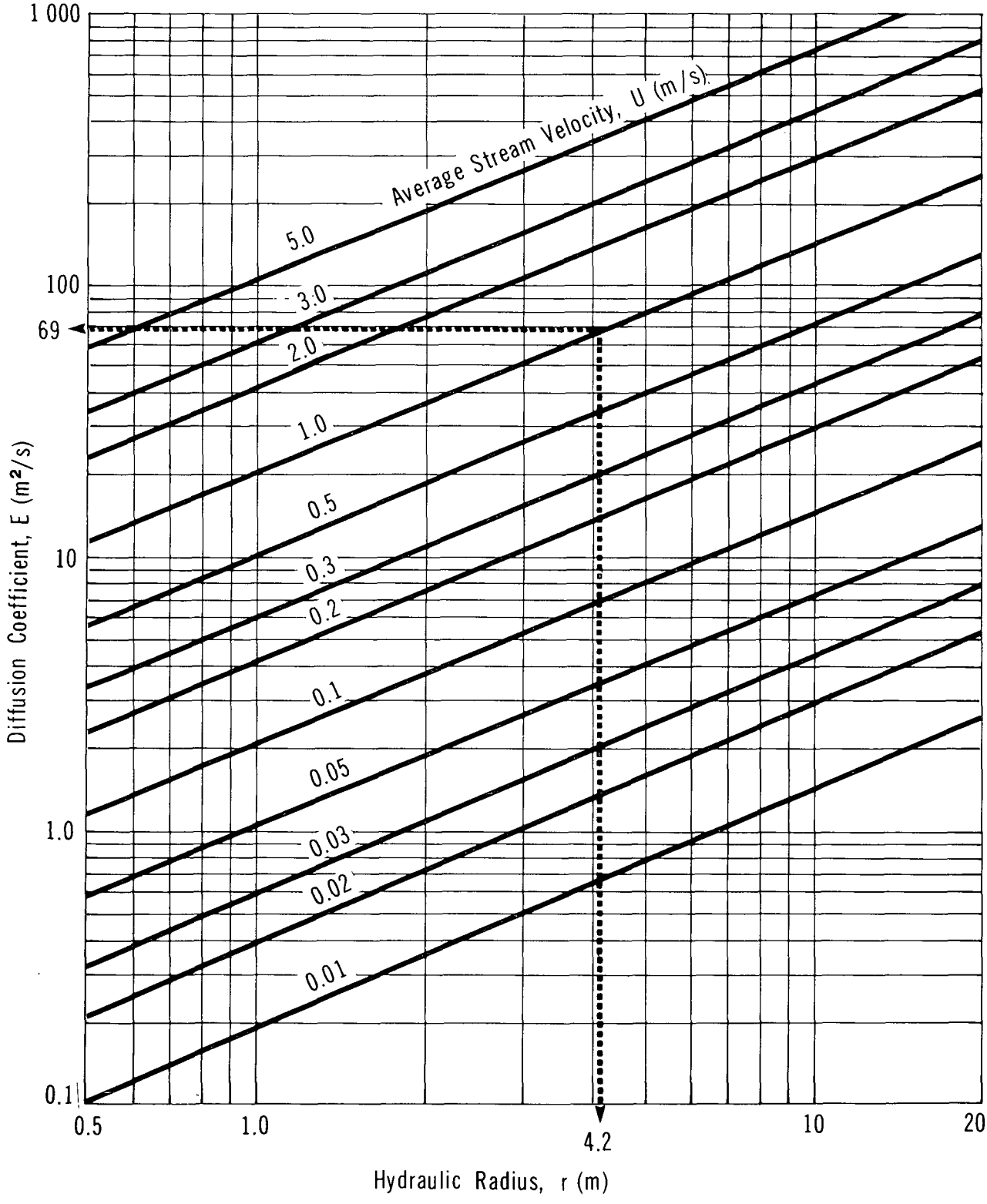


FIGURE 26

SULPHUR DIOXIDE

ALPHA vs DIFFUSION COEFFICIENT

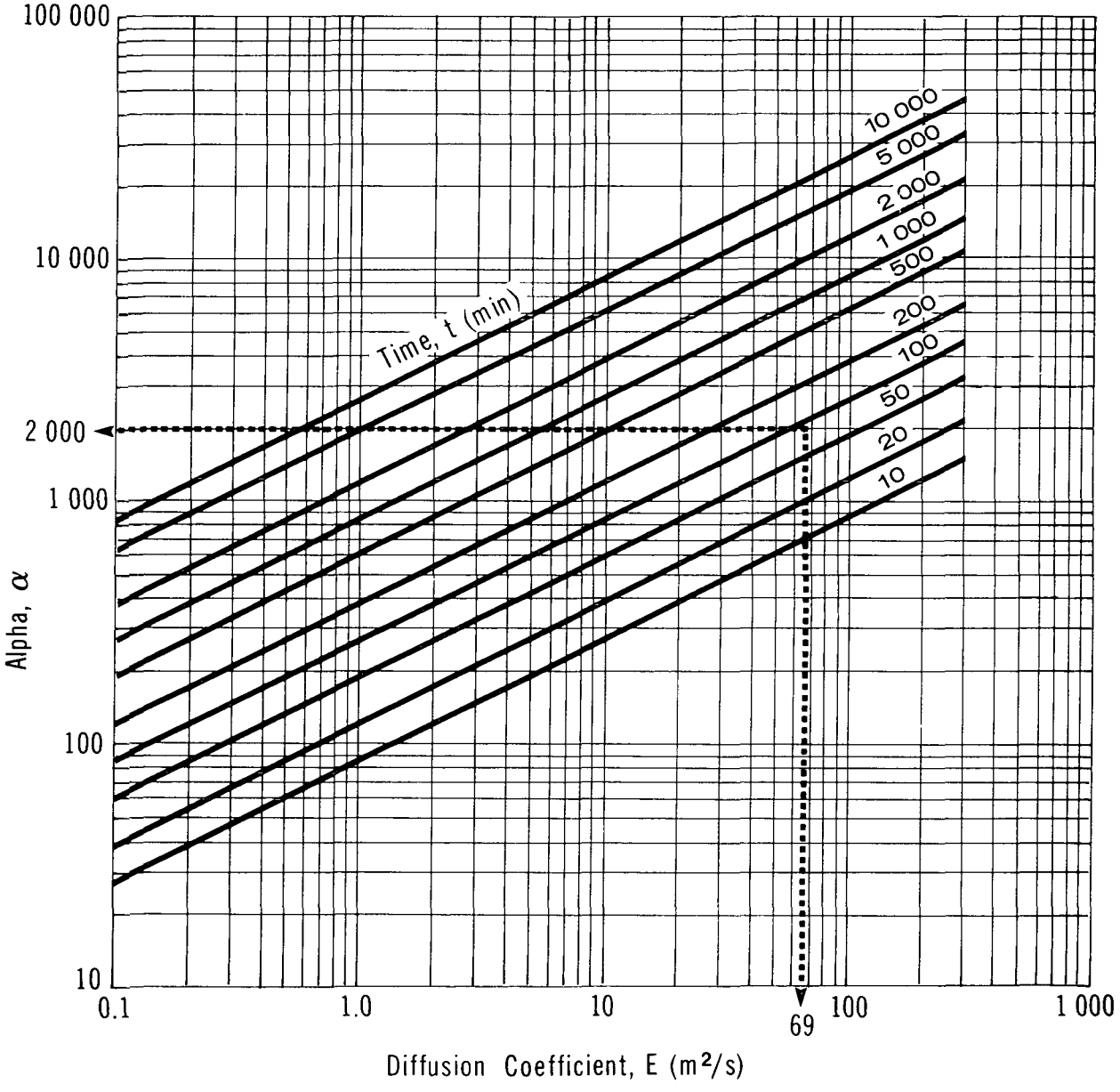


FIGURE 27

SULPHUR DIOXIDE

ALPHA vs DELTA

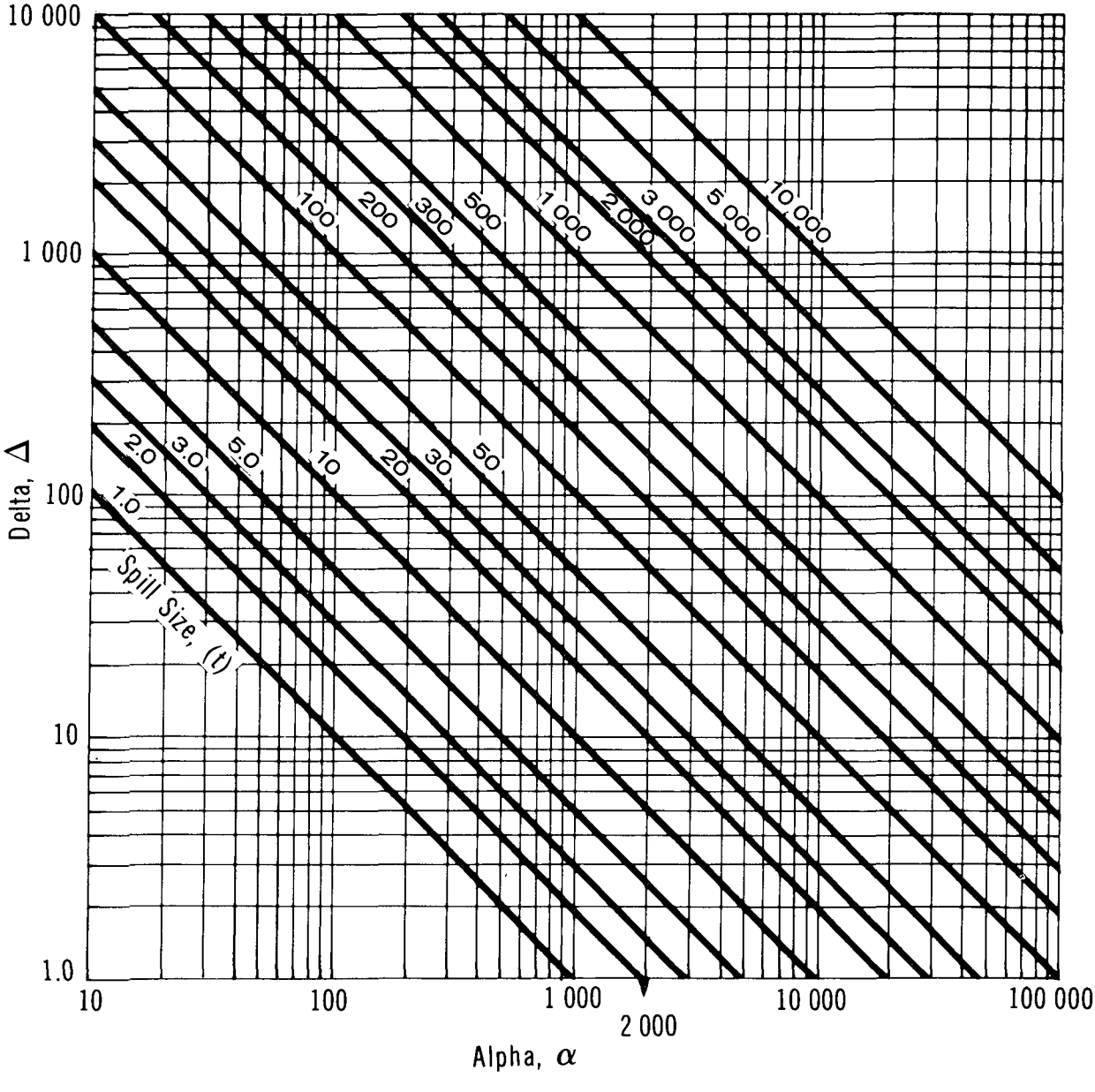
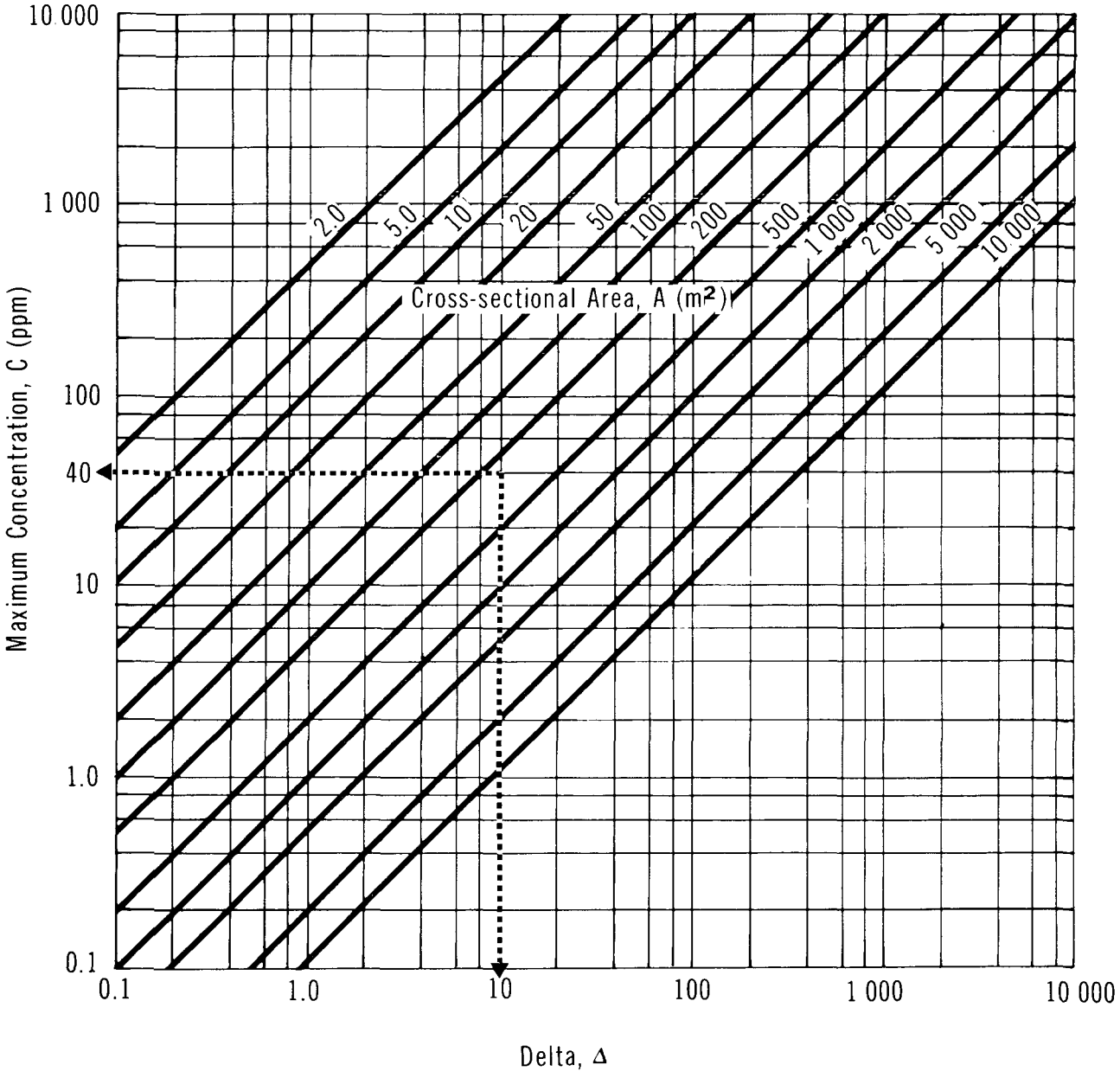


FIGURE 28

SULPHUR DIOXIDE

MAXIMUM CONCENTRATION vs DELTA



5.4.2.2 Nomograms for lakes or still water bodies.

Figure 29: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 29. The radius (r) represents the distance from the spill to the point of interest.

Figure 30: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 30 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

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

Solution

Step 1: Define parameters

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

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

- Use Figure 23
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 24
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 25
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

FIGURE 29

SULPHUR DIOXIDE

VOLUME vs RADIUS

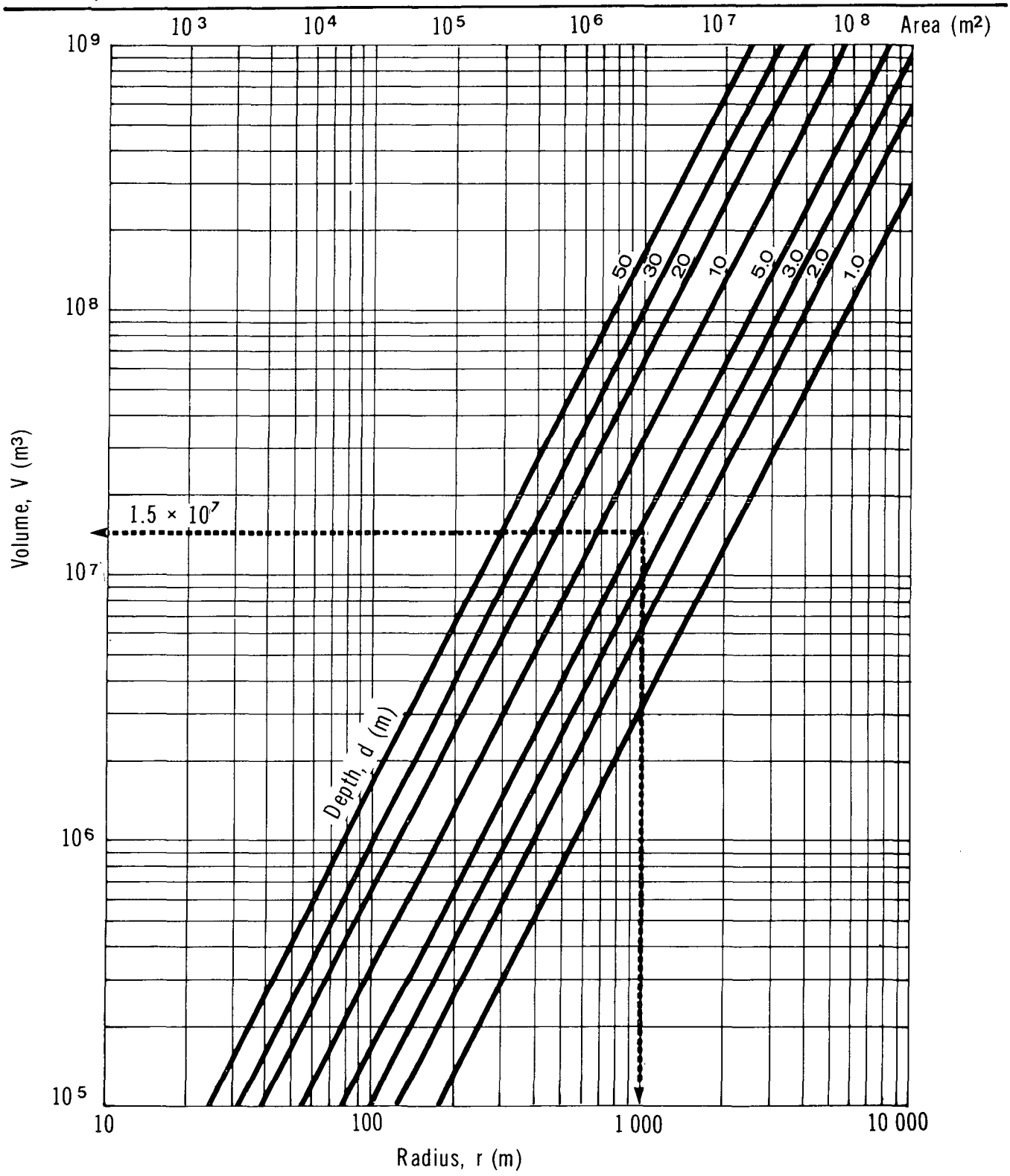
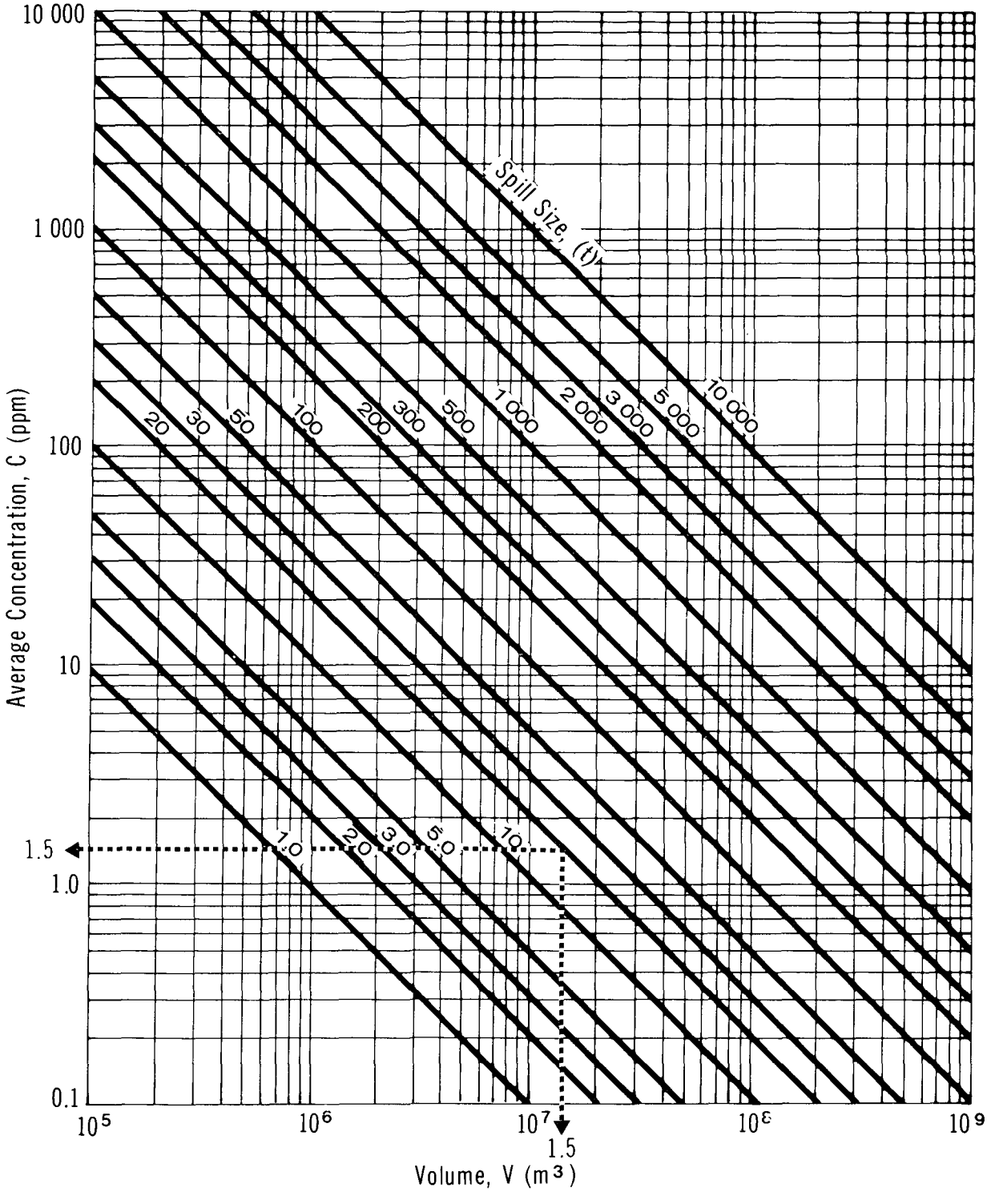


FIGURE 30

SULPHUR DIOXIDE

AVERAGE CONCENTRATION vs VOLUME



Step 5: Calculate alpha (α)

- Use Figure 26
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calculate delta (Δ)

- Use Figure 27
- With alpha (α) = 2000 and spill mass = 20 tonnes, delta (Δ) = 10

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

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

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

- Use Figure 28
- With Δ = 10 and A = 250 m^2, C = 40 ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of sulphur dioxide has occurred on a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 20 tonnes (sulphur dioxide)

Step 2: Determine the volume of water available for dilution

- Use Figure 29
- With r = 1000 m, d = 5 m, the volume is approximately $1.5 \times 10^7\ m^3$

Step 3: Determine the average concentration

- Use Figure 30
- With $V = 1.5 \times 10^7\ m^3$ and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. Sulphur dioxide has a boiling point of -10°C at a pressure of 1 atmosphere. Consequently, when it is spilled onto soil, extensive evaporation will occur. While most will be lost to evaporation, the balance will infiltrate the soil. Evaporation will continue within the soil but at a reduced rate.

Since sulphur dioxide is soluble in water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of chemical movement in the soil. Solutions in water have higher viscosities and lower mass densities than liquid sulphur dioxide. This will have the net effect of reducing the velocity of downward movement in the soil. It will also result in a decrease in the vapour pressure and reduce the rate of evaporation.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or pond and evaporate. For this work, the soils have been assumed to be at field capacity (the maximum amount the soil will hold after the excess has been drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport downward, liquid sulphur dioxide may interact with the soil as well as evaporate. However, it is assumed that sufficient material will remain to allow movement toward the groundwater table. Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and dispersion serving to reduce the concentration. This is shown schematically in Figure 31.

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

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

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

where: k = intrinsic permeability of soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa·s)

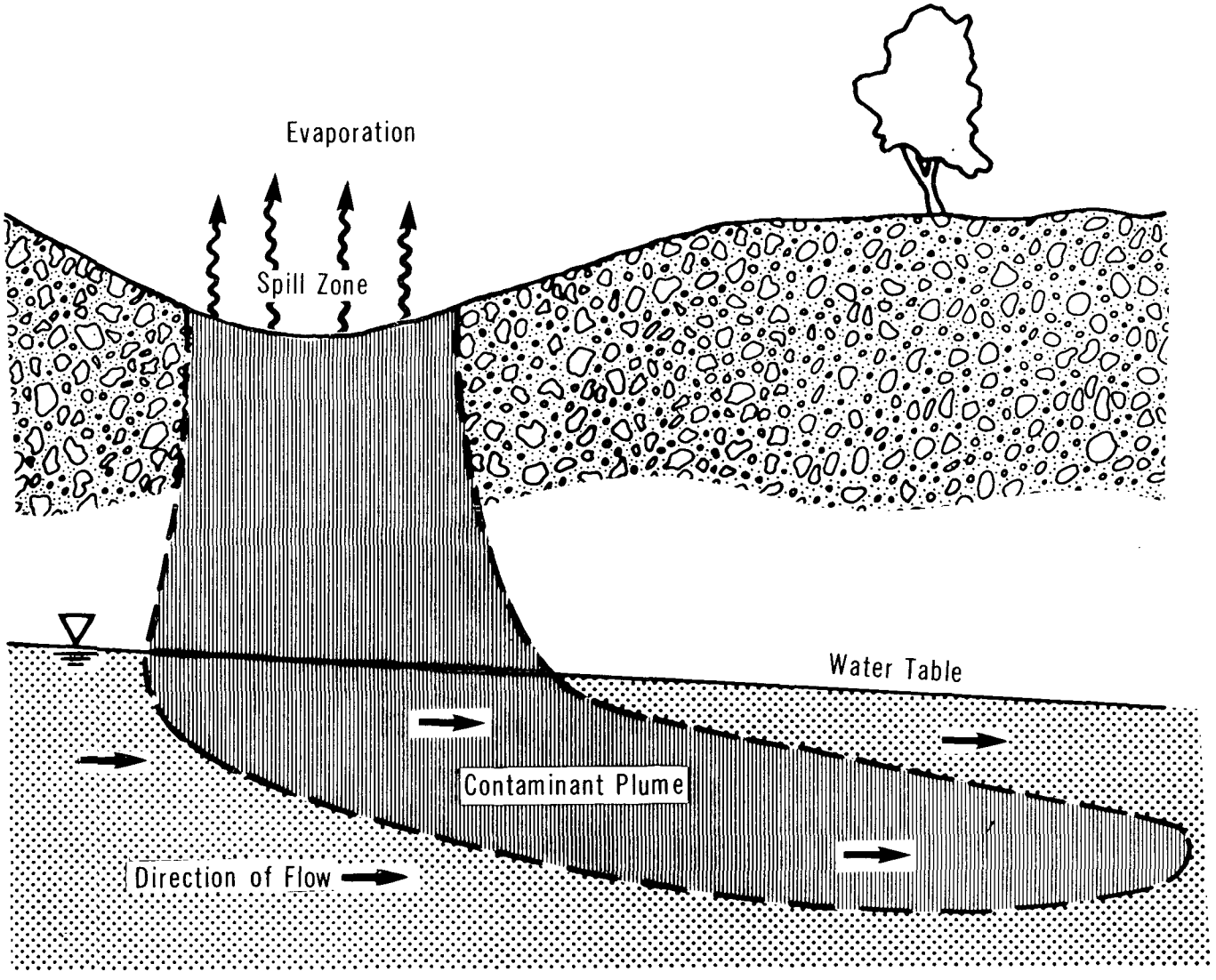
g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are liquid sulphur dioxide and water. The water calculations represent the extreme as the contaminant is diluted.

FIGURE 31

SULPHUR DIOXIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

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

–Field Capacity (θ_{fc}) = 0.075

Property	Liquid Sulphur Dioxide 20°C	Liquid Sulphur Dioxide 4°C	Water 20°C
Mass density (ρ), kg/m^3	1380	1440	998
Absolute viscosity (μ), Pa·s	0.3×10^{-3}	0.35×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(4.5 \times 10^7)k$	$(4.0 \times 10^7)k$	(0.98×10^7)

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	0.75	0.3	0.45

5.5.5 Penetration Nomograms. A nomogram for the penetration of liquid sulphur dioxide into the unsaturated zone above the groundwater table was prepared for coarse sand. Penetration times for the denser soils, silty sand and clay till, would be several orders of magnitude greater than for sand. Evaporation during this period would leave little or no contaminant for infiltration. Spills on these denser soils, therefore, should not result in groundwater pollution problems.

The nomogram presents penetration time (t_p) plotted against depth of penetration (B). The penetration depth should be considered as a maximum depth in time t_p because of the methods and assumptions used.

A flowchart for the use of the nomogram is presented in Figure 32. The nomogram is presented as Figure 33. The water lines on the nomogram represent the maximum penetration of water in time t_p. It is a limiting condition as sulphur dioxide becomes diluted with water.

FIGURE 32

SULPHUR DIOXIDE

FLOWCHART FOR NOMOGRAM USE

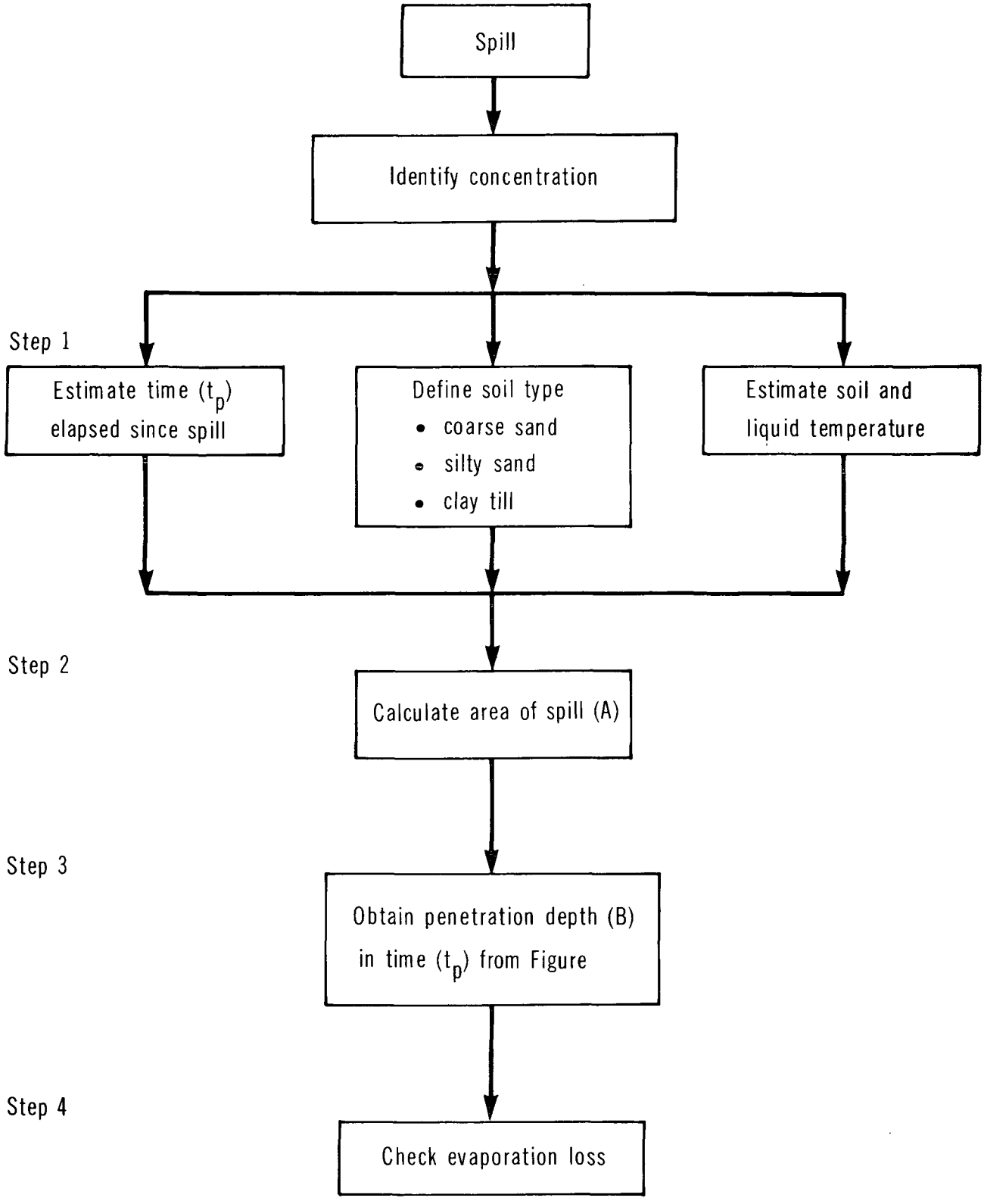
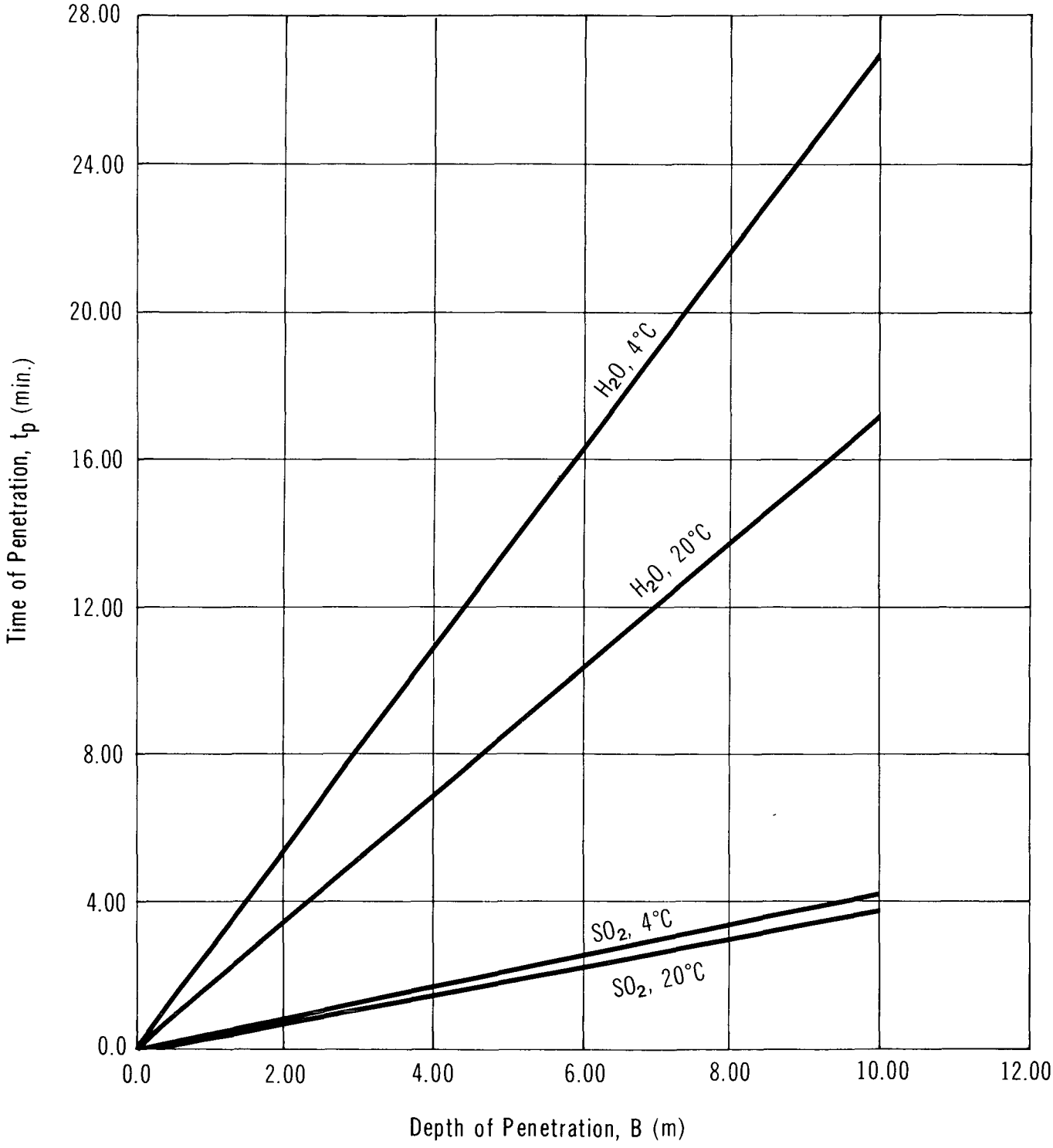


FIGURE 33

SULPHUR DIOXIDE

PENETRATION IN COARSE SAND



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

Solution

Step 1: Define parameters

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

Step 2: Calculate the area of the spill

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

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

- For coarse sand, B exceeds 10 m after 20 min
- Groundwater table could be reached in this time. The extent of evaporation would be important in reducing the extent of contamination.

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Not specifically regulated.

6.1.2 Air.

6.1.2.1 Canada. Ontario has specified an emission limit of 830 mg/m^3 of sulphur dioxide (half-hour average) (Ontario E.P. Act 1971). Other sulphur dioxide guidelines or limits are tabulated below.

Jurisdiction	Time (Hours)	Average Conc. (ppm)	Limit (10°C, 101 kPa) (mg/m^3)	Range of Quality	Reference
Ontario	1	0.25	690		Ontario E.P. Act 1971
	24	0.10	275		Ontario E.P. Act 1971
	1 year	0.02	55		Ontario E.P. Act 1971
Saskatchewan	1	0.17	450		CELC-Sask. 1980
	24	0.06	150		CELC-Sask. 1980
	1 year	0.01	30		CELC-Sask. 1980
New Brunswick	1		99	maximum permissible ground level concen-trations	CELC-NB 1980
	24		300		CELC-NB 1980
	1 year		60		CELC-NB 1980
Canada	1		0 to 450	at 25°C; desirable	CELC 1980
	24		0 to 150		CELC 1980
	1 year		0 to 30		CELC 1980
Canada	1		450 to 900	at 25°C acceptable at 25°C	CELC 1980
	24		150 to 300		CELC 1980
	1 year		30 to 60		CELC 1980
Canada	contin-uous 24 hour period		300 to 800	tolerable	CELC 1980
New Brunswick	1		500 ppm (v/v)	maximum allowable emission at stack conditions for recovery furnace	CELC-NB 1980

6.1.2.2 Other Countries. The 24-hour ambient air quality standard in the U.S. is 0.14 ppm (Goldstein 1979).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Sulphur dioxide is toxic to fish (OHM-TADS 1981). No RTECS rating is provided.

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
Fish Kill Data					
16	1	Sunfish	lethal		Wilber 1969
5	1	Trout	lethal		WQC 1963
1	2	Tench	lethal	as HSO_3^-	WQC 1963
Fish Toxicity Tests					
10	0.17	Trout	immobilized	tap	WQC 1963
Microorganisms					
5.0		Euglena (algae) family	increased concentration of chlorophyll, reduced rates of photosynthesis		DeKoning 1970
Vertebrates					
1 pph	15 min	Frogs	LC_{LO} (inhalation)		RTECS 1979

6.2.3 Aquatic Studies. Sulphur dioxide is very soluble in water, forming sulphurous acid (H_2SO_3). One study suggests that changes in the water type (carbonate to sulphate) are mainly responsible for damage to the biosystem (NRCC 1977).

6.3 Mammalian Toxicology

Conc. (ppm)	Time (hours)	Species	Result	Reference
3000	5 min	Mammals	LC_{LO} acute	RTECS 1979
80 to 160 g	daily	Cattle	gas caused anoxia	Garner
massive doses		Cattle	death	Garner
		Horse	poisoning; respiratory and circulatory disturbances	Garner
		Pigs	eye diseases and burns to respiratory tract	Garner
50	30 days 6 h/d	Rabbit	lethal (inhalation)	Sunshine 1969
500	4 min/d every other day for 2 weeks	Ground squirrel	adverse effects - endematous changes in lungs, trachea and heart	Rana 1979

Inhalation of 65 ppm of sulphur dioxide caused acute distention of stomach on the ninth day for one-third of animals exposed. Animals exposed to 100 ppm showed perforations of the stomach by the fourth day (Patty).

6.4 Soils.

Sulphur dioxide contamination of soils for prolonged periods will result in increased acidity and soluble sulphate content of the soil, reduced content of calcium and other bases, reduced activity of microorganisms (particularly nitrifiers and nitrogen-fixers), increased concentration of potentially toxic ions (aluminum, manganese), and an overall greater contribution of nutrients and potentially hazardous ions to surface and ground waters. One of the most serious hazards from atmospheric additions of sulphur dioxide is that of soil erosion following the death of the vegetative ground cover (NRCC 1977). One study of soil absorption showed that soil treated with even small amounts of SO_2 reduced soil pH (Chaudhry 1982).

6.5 Plants

Many plants are sensitive to SO_2 in the atmosphere and show damage at low concentrations. For broad-leaved plants, acute injury takes the form of lesions on both upper and lower surfaces, usually between the veins. Tissue near the veins is very resistant. Fully-expanded leaves are the most sensitive. High concentrations of SO_2 may also result in premature leaf dropping (Linzon 1978). In conifers, acute injury usually appears as a bright orange-red tip necrosis on current-year needles. Retardation of tip growth may also occur. Needle browning and subsequent drop may occur with severe exposures (Loman 1972; Gerhold 1979). Deciduous trees show SO_2 damage in the form of light chlorosis (bleaching) to almost complete necrosis of veins. The first symptoms of exposure are wetting of the leaf undersurface and light necrosis (Malhotra 1980). The nonvascular plants, e.g., lichens and bryophytes, are most sensitive because absorption takes place over the whole cuticle (NRCC 1977; Peterson 1977).

6.5.1 Measured Effects.

Concentration (ppm)	Exposure Time (hours)	Species	Result	Condition	Reference
Trees					
0.05	24 d	Beech tree (*Fagus* sp.)	injury	-	Linzon 1978
0.07	72	White pine (*Pinus* sp.)	injury	-	Linzon 1978
0.25	1	Eastern white pine (*Pinus strobus*)	foliage injury	-	Linzon 1978
0.25	2	Various pine species (Eastern, White, Jack, Loblolly, etc.)	foliage injury	-	Linzon 1978
0.03	1	Sensitive pine species	injury threshold	-	Linzon 1978
0.1	tns	White pine (*Pinus* sp.)	damage to sensitive clones	-	Felske 1980

Concentration (ppm)	Exposure Time (hours)	Species	Result	Condition	Reference
0.017	continuous	White pine (*Pinus* sp.)	continual exposure reduces growth	-	Felske 1980
1.0	1/2	Red pine (*Pinus resinosa*)	reduced chlorophyll in cotyledons	-	Linzon 1978
0.5	2	Red pine (*Pinus resinosa*)	reduced chlorophyll in cotyledons and decreased weight of primary needles	-	Linzon 1978
0.5	31 to 60 d	Scotch pine (*Pinus sylvestris*)	decreased photo-synthesis	-	Linzon 1978
0.14	12	Douglas Fir (*Pseudotsuga taxifolia*)	injury threshold	-	Linzon 1978
0.35	3	Trembling aspen (*Populus tremuloides*)	acute injury	-	Linzon 1978
0.03	4	Poplar (*Populus* sp.)	effects on pollen tube elongation	-	Linzon 1978
0.54	3	Mountain ash (*Sorbus* sp.)	injury threshold	-	Linzon 1978
2.0	2	Chinese elm (*Ulmus parvifolia*)	injury threshold	-	Linzon 1978
0.30	8	Western larch (*Larix occidentalis*)	injury threshold	-	Linzon 1978
0.95	1	Forest trees	acute injury threshold	-	Dreisinger 1970
0.55	2	Forest trees	acute injury threshold	-	Dreisinger 1970

Concentration (ppm)	Exposure Time (hours)	Species	Result	Condition	Reference
0.35	4	Forest trees	acute injury threshold	-	Dreisinger 1970
0.25	8	Forest trees	acute injury threshold	-	Dreisinger 1970
0.70	1	Forest trees	acute injury threshold to sensitive species	-	Dreisinger 1970
0.40	2	Forest trees	acute injury threshold to sensitive species	-	Dreisinger 1970
0.26	4	Forest trees	acute injury threshold to sensitive species	-	Dreisinger 1970
0.18	8	Forest trees	acute injury threshold to sensitive species	-	Dreisinger 1970
Crops, Flowers and Other Varieties					
0.2	tns	Alfalfa (*Medicago sativa*)	no apparent damage	-	Felske 1980
0.25	1	Alfalfa (*Medicago sativa*)	2 percent depression in CO_2 uptake	-	Linzon 1978
0.50	1	Alfalfa (*Medicago sativa*)	21 percent depression in CO_2 uptake	-	Linzon 1978

Concentration (ppm)	Exposure Time (hours)	Species	Result	Condition	Reference
0.70	1	Bean	decreased protein synthesis	-	Linzon 1978
0.25	1	Begonia	injury	humid conditions	Linzon 1978
0.25	4	Broccoli	injury threshold	-	Linzon 1978
0.07	14 d	Barley (*Hordeum vulgare*)	injury	-	Linzon 1978
0.66	1	Buckwheat (*Fagopyrum esculentum*)	injury	-	Linzon 1978
2.5	3	Chrysanthemum	injury threshold	-	Linzon 1978
0.20	2	Kentucky bluegrass (*Poa pratensis*)	moderate to severe injury	-	Linzon 1978
0.71	1	Lily	55 percent inhibition of pollen tube length	-	Linzon 1978
0.04	tns	Pea (*Pisum sativum*)	10 percent damage to crop	-	Felske 1980
0.05 to 0.12	4 to 8	Peanut (*Arachis hypogaea*)	injury	-	Linzon 1978
0.067	26 wk	Ryegrass (*Lolium* sp.)	depressed yield by 52 percent	-	Linzon 1978
2	4	Soybean (*Glycine max*)	necrotic lesions	-	Amundson 1981
0.1	continuous	Soybean (*Glycine max*)	12 percent decrease in yield	-	Amundson 1981
0.12 to 0.36	4 h/d, several days	Soybean (*Glycine max*)	some acute injury	-	Heggestad 1980
2.0	4	Weed species	injury	-	Linzon 1978

Concentration in Air (ppm)	Concentration in Water (ppm)	Time (hours)	Species	Effect	Reference
Lichens					
0.012	-	tns	Lichens generally	damage threshold	Felske 1980
0.83	9.1	24	*Cladina alpestris*	chlorophyll a reduction	Laurentian 1975
3	18	6	*Cladina alpestris*	chlorophyll a reduction	Laurentian 1975
<7	-	3	*Cladina alpestris*	chlorophyll a reduction	Laurentian 1975
0.57	7.2	1	*Cladina alpestris*	carbon 14 photosynthetic reduction	Laurentian 1975
2.45	16.5	1/6	*Cladina alpestris*	carbon 14 photosynthetic reduction	Laurentian 1975
0.75	8.5	3	*Cladina rangi-fernia*	effect on potassium levels	Laurentian 1975
-	6.2	1/6	*Cladina rangi-ferina*	effect on potassium levels	Laurentian 1975
5.7	-	1/6	*Cladina rangi-ferina*	no damage to carbon fix-ation	Laurentian 1975
1.4	-	1	*Cladina rangi-ferina*	no damage to carbon fix-ation	Laurentian 1975
5.7	-	1	*Cladina rangi-ferina*	carbon fix-ation dis-rupted	Laurentian 1975
2.2	-	3	*Cladina rangi-ferina*	no damage to pigmentation	Laurentian 1975
0.9	-	9	*Cladina rangi-ferina*	no damage to pigmentation	Laurentian 1975
9.9	-	3	*Cladina rangi-ferina*	pigmentation change	Laurentian 1975

Concentration in Air (ppm)	Concentration in Water (ppm)	Time (hours)	Species	Effect	Reference
3.2	-	6	*Cladina rangiferina*	pigmentation change	Laurentian 1975
2.2	-	24	*Cladina rangiferina*	pigmentation change	Laurentian 1975
-	35	3	*Umbilicaria muhlenbergii*	22 percent potassium loss	Laurentian 1975
-	75	3	*Umbilicaria muhlenbergii*	50 percent potassium loss	Laurentian 1975
-	125	1/4	*Umbilicaria muhlenbergii*	50 percent potassium loss	Laurentian 1975

6.5.2 Comparative Tree Sensitivity. The following is a ranking of a various tree sensitivities to SO_2 (Linzon 1978; Malhotra 1980; Davis 1976):

Sensitive (sensitivity 0.5-1.0 ppm SO_2, 1 h; 0.3-0.6 ppm SO_2, 3h)

Alpine fir (*Abies lasiocarpa*)

Black willow (*Salix nigra*)

Chinese elm (*Ulmus parvifolia*)

Douglas fir (*Pseudotsuga taxifolia*)

Eastern white pine (*Pinus strobus*)

Green alder (*Alnus crispa*)

Jack pine (*Pinus banksiana*)

Largetooth aspen (*Populus grandidentata*)

Lombardy poplar (*Populus nigra italica*)

Manitoba maple (*Acer negundo*)

Serviceberry (*Amelanchier alnifolia*)

Sumac (*Rhus* sp.)

Tamarack (*Larix laricina*)
Trembling aspen (*Populus tremuloides*)
Western larch (*Larix occidentalis*)
Western yellow pine (*Pinus ponderosa*)
White ash (*Fraxinus americana*)
White birch (*Betula papyrifera*)

Intermediate (sensitivity 1.0-2.0 ppm SO_2, 1 h; 0.6-0.8 ppm SO_2, 3h)

American elm (*Ulmus americana*)
Austrian pine (*Pinus nigra*)
Balsam fir (*Abies balsamea*)
Balsam poplar (*Populus balsamifera*)
Basswood (*Tilia* sp.)
Catalpa (*Catalpa* sp.)
Cherry (*Prunus* sp.)
Choke cherry (*Prunus virginiana*)
Dogwood (*Cornus* sp.)
Eastern cottonwood (*Populus* sp.)
Elm (*Ulmus* sp.)
Englemann's spruce (*Picea engelmannii*)
Lilac (*Syrina* sp.)
Locust (*Robinia pseudoacacia*)
Lodgepole pine (*Pinus contorta*)
Maple (common) (*Acer* sp.)
Mountain maple (*Acer spicatum*)
Ponderosa pine (*Pinus ponderosa*)
Red maple (*Acer rubrum*)
Red pine (*Pinus resinosa*)
Western hemlock (*Tsuga heterophylla*)
Western white pine (*Pinus monticola*)
White elm (*Ulmus americana*)
White oak (*Quercus alba*)
Willow (*Salix* sp.)
Witch hazel (*Hamamelis virginiana*)

Tolerant (sensitivity >2 ppm SO_2, 1 h; >0.8 ppm SO_2, 3 h)

Black spruce (*Picea mariana*)
Blue spruce (*Picea pungens*)
Carolina poplar (*Populus canadensis*)
Grand fir (*Abies grandis*)
Juniper (*Juniperus* sp.)
Linden (*Tilia* sp.)
Little-leaf linden (*Tilia cordata*)
London plane (*Platanus acerifolia*)
Red oak (*Quercus rubra*)
Silver maple (*Acer saccharinum*)
Sugar maple (*Acer saccharum*)
Western red cedar (*Thuja plicata*)
White cedar (*Thuja* sp.)
White spruce (*Picea glauca*)

6.5.3 Plant Studies. One study showed that plants derive a large portion of their sulphur requirements from atmospheric SO_2. Cotton derived 10 to 44 percent SO_2 from atmospheric sources, soybean derived 10 to 51 percent, and fescue derived 34 percent in a series of test runs (Noggle 1980). One study on the solubility and resulting effects inferred that dissolved but unreacted SO_2 is the most active species for initiating plant injury (Hocking 1977).

The diversity of lichens was found to be reduced in the vicinity of a gas plant (Case 1980). Small adaptation to higher levels of SO_2 has been noted (Horseman, 1977). Fumigation of the serviceberry plant (*Amelanchier alnifolia*) at 0.2 ppm caused deficiencies in selenium concentration and thus a potential for selenium deficiency diseases (Shaw 1980). A similar experiment using the serviceberry and red fescue grass (*Festuca rubra*) at 0.2 ppm and 0.1 ppm in the field showed the same selenium decreases (Shaw 1982).

6.6 Effect Studies

The primary effect of gaseous SO_2 is upon plants and other forms of life. The secondary effect is the deposition and absorption by soils, modifying the growing medium and bringing about changes to the soil microflora and microfauna (NRCC 1971). The fate and effects of acid rain have been reviewed by many authors (Nriagu 1978; Shriner 1980).

6.7 Long-term Fate and Effects

There is no potential for bioaccumulation or bioconcentration of sulphur dioxide (RTECS 1979). In the atmosphere, sulphur dioxide is converted to SO_3; in the presence of moisture, it is converted to sulphuric acid (H_2SO_4). This will reach the earth eventually in precipitation (NRCC 1977). The deposition of atmospheric SO_2 is 2 to 3 times as great over a forest as over grasslands (Shreffler 1978). Sulphur dioxide oxides to SO_3 as noted above; the rate of this oxidation is estimated to be 1 percent per hour in clean air and 2 percent per hour in fog (Kockmond 1976; Cheng 1971).

7 HUMAN HEALTH

Sulphur dioxide is considered to be a poison and a corrosive material (Sax 1981). Even at relatively low concentrations, it is highly irritating to the lungs and mucous membranes. Its principal toxic effects are due to the formation of sulphurous acid when sulphur dioxide comes into contact with water in various body fluids (Doc. TLV 1981). High concentrations of sulphur dioxide may cause respiratory paralysis and pulmonary edema. In addition, about 10 to 20 percent of the adult population is estimated to be hypersensitive to the adverse respiratory effects of sulphur dioxide (NIOSH/OSHA 1978); however, workers regularly exposed to the compound show an adaptation effect. Even though olfactory fatigue is a reported effect of exposure, the compound is so irritating that it is considered to have good warning properties (Sax 1981).

Sulphur dioxide may act as a promotor in the production of squamous cell carcinoma in the presence of other contaminants such as benzo(α)pyrene (NIOSH 1974). No data were found regarding its potential as a mutagenic or teratogenic agent.

Sulphur dioxide is an important air pollutant; its health effects on both occupationally and environmentally exposed populations have been widely studied. Due to the large number of studies showing supportive or complementary findings in relation to the toxicity of sulphur dioxide, only a representative sample of these studies has been reported; emphasis is placed on human exposure data and recently reported exposures. Animal data are generally reported in summary form only.

The toxicological data summarized here have been extracted from reliable standard reference sources. Several reviews of the toxicity of sulphur dioxide are available (Shriner 1980; Nriagu 1978). 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 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

The exposure standards for sulphur dioxide are based upon its respiratory effects. Canadian provincial guidelines are generally similar to those of the USA-ACGIH unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	2 ppm (5 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	5 ppm (13 mg/m^3)	NIOSH/OSHA 1978
Action Level (8 h)	USA-OSHA	1 ppm	Braker 1977
Permissible Exposure Limit (10 h)	USA-NIOSH	0.5 ppm (1.3 mg/m^3)	NIOSH/OSHA 1978
Permissible Concentration (8 h)	B.C.	5 ppm (13 mg/m^3)	B.C. 1980
Average Concentration (8 h)	Quebec	5 ppm (13 mg/m^3)	Quebec 1979
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	5 ppm (10 mg/m^3)	TLV 1983
Maximum Permissible Concentration (30 to 60 min)	-	50 to 100 ppm	Sax 1981
Other Human Toxicities			
IDLH	USA-NIOSH/OSHA	100 ppm	NIOSH Guide 1978
EEL (Emergency Exposure Limits)	-	150 ppm (5 min) 75 ppm (15 min) 50 ppm (30 min) 25 ppm (60 min)	NRCC 1977
LC_{LO} (1 min)	-	400 ppm	RTECS 1979
TC_{LO} (1 min)		4 ppm	RTECS 1979
TC_{LO} (5 d)	-	3 ppm	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 (Vapour Pressure, in mm Hg/TLV®, in ppm)

At 21°C, ITI = 1315.12 (2535 mm Hg/2 ppm)

At 21°C, ITI = 1.66×10^6

7.2 Irritation Data

7.2.1 Skin Contact. Data pertaining to skin irritation effects as a result of sulphur dioxide exposure are presented below. Sulphur dioxide has been reported to produce skin lesions through a mechanism believed to be systemic. These effects have been reported in Section 7.4.3.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Severe irritant of mucous membranes and skin due to rapidity with which it forms sulphurous acid on contact with moist membranes.	NIOSH/OSHA 1978
Unspecified (Liquid)	Severe burns resulting from its rapid evaporation which causes a "freezing effect".	CSC 1980
Unspecified	Skin irritation reported by workers exposed to SO_2 is aggravated by perspiration when sulphurous acid is formed in the perspiration.	Aleksieva 1972. IN NRCC 1977

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
8 to 50 ppm	Tearing, smarting and irritation of the eyes.	CSC 1980
>20 ppm	Smarting and tearing, irritation threshold.	GE 1979; Sax 1981
Unspecified (Liquid)	Severe burns resulting from its rapid evaporation which causes a "freezing effect". May result in some degree of blindness.	CSC 1980

Exposure Level (and Duration)	Effects	Reference
Unspecified	Corneal epithelium becomes gray and irregular, lids become swollen, vessels thrombosed, iritis.	TDB (on-line) 1981
SPECIES: Rabbit		
490 ppm (30 h)	Keratitis and corneal clouding.	TDB (on-line) 1981

7.2.3 Respiratory Tract Irritation.

Exposure Level (and Duration)	Effects	Reference
Low levels	Causes severe respiratory tract irritation even at low levels.	Coffin 1976; Gerhold 1976

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Sharp, pungent, like burning sulphur; deadens sense of smell (AAR 1981).

Odour Index: 941 293 (AAR 1981).

Parameter	Media	Concentration	Reference
Detection	-	0.3 to 1 ppm	Sax 1981
Recognition Threshold	in air	0.470 ppm	ASTM 1980
Odour Detection Threshold	in air	1.1 ppm	Amoore 1983
Odour Detection Threshold	in water	0.11 ppm	Amoore 1983

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Lower Taste Threshold	in air	0.3 ppm	Sax 1981
Upper Taste Threshold	in air	1.0 ppm	Sax 1981

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
400 ppm (1 min)	LC_{LO}	RTECS 1979
150 ppm	Can be endured only a few minutes due to eye irritation and the effects on the membranes of the nose, throat and lungs.	Braker 1977
1 to 25 ppm (7 to 8 h)	Significant changes in mucociliary flow rates at 5 and 25 ppm. No change in closing volumes was found.	Anderson et al. 1974. IN NRCC 1977
5 and 13 ppm	Initial cough and irritation occurred at 5 and 13 ppm, but subsided after 5 minutes of exposure.	NIOSH/OSHA 1978
1, 5 and 13 ppm	Mouth breathing at 13 ppm caused a 73 percent increase in pulmonary flow resistance; 5 ppm resulted in a 40 percent increase; 1 ppm produced no effects.	NIOSH/OSHA 1978
8 to 12 ppm	Throat irritation, coughing, constriction of the chest, lacrimation and smarting of the eyes.	Braker 1977

Exposure Level (and Duration)	Effects	Reference
4 ppm (1 min)	TC_{LO}	RTECS 1979
500 μg/m^3 daily average	Excess mortality and hospital admissions.	WHO 1972. IN NRCC 1977
250 to 500 μg/m^3 daily average	Worsening of patients with pulmonary disease.	WHO 1972. IN NRCC 1977
Unspecified (15 min) (confined space)	Eye inflammation, nausea, vomiting and abdominal pain, sore throat. After a delay, bronchitis; 1 out of 13 exposed died.	Hamilton and Hardy 1974. IN NRCC 1977
SPECIES: Rabbit		
198 to 200 ppm	Slowed cilia of trachea in vivo.	TDB (on-line) 1981
Species: Rat		
1000 ppm	LC_{LO}	AAR 1981
50 to 300 ppm (72 h)	Highest dosage produced considerable epithelial damage and almost complete destruction of goblet cells.	Doull 1980
SPECIES: Mouse		
6000 ppm (5 h)	LC_{LO}	AAR 1981
Chronic Exposures		
SPECIES: Human		
2 to 36 ppm	Increase in frequency of respiratory symptoms, cough, dyspnea on exertion and expectoration, and a significant reduction in maximum expiratory flow rate compared with those in an unexposed control group. The differences were more striking in workers under 50.	Skalpe 1964. IN NRCC 1977
20 to 30 ppm (3.8 to 12 yr)	The exposed group was found to have increased nasopharyngitis, alteration of taste and smell, increased dysphea on	Kehoe et al. 1932. IN NRCC 1977

Exposure Level (and Duration)	Effects	Reference
	exertion, and longer lasting colds.	
10 ppm (repeatedly)	Upper respiratory irritation and some nosebleeds. Symptoms does not occur at 5 ppm.	NIOSH/OSHA 1978
3 ppm (5 d)	TC_{LO}	RTECS 1979
100 $\mu g/m^3$ annual arithmetic mean)	Respiratory symptoms.	NRCC 1977
Unspecified	Associated with chronic bronchitis and excess mortality.	TDB (on-line) 1981
Unspecified	Inhibition of thyroid function and menstrual disorders in women.	TDB (on-line) 1981
Unspecified	Pneumosclerosis accompanied by emphysema. Nervous system disorders. Dental caries, peridental and gingival disorders. Rapid and painless dental destruction, loss of fillings, increased tooth sensitivity to temperature change.	TDB (on-line) 1981
Unspecified	A comparison between two groups of children (10 000, age 1 to 12 yr) in two locations, one of high ambient SO_2 levels and the other of low SO_2 levels, showed a significant increase in lower respiratory diseases in the high SO_2 area.	Hammer 1977
Unspecified	Soluble salts of such metals as manganese, ferrous iron, and vanadium potentiate response to SO_2 threshold when present at concentrations of 1 mg/m^3.	TDB (on-line) 1981
Unspecified	Bronchial asthma associated with chronic intermittent exposure. Predisposition to allergy.	Rommanoff 1939. IN NIOSH 1974

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Unspecified	Irritation to stomach if swallowed.	TDB (on-line) 1981
Unspecified	Ingestion unlikely. At room temperature, sulphur dioxide is a gas.	GE 1979
SPECIES: Cattle		
80 to 160 g (gas)	Anorexia. Massive doses were fatal.	TDB (on-line) 1981

7.4.3 Skin Exposure (Systemic Effects).

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Human		
Unspecified	Urticaria was present when worker did not use gas mask, absent when mask was used. Experimental exposure to 40 ppm for 1 hour caused new eruption.	Pirila 1954. IN NIOSH 1974

7.4.4 Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified (with arsenic)	Excess total mortality among arsenic-exposed smelter workers. As much as an 8-fold excess in instances of respiratory cancer as compared with that of the white male population in the	Lee and Fraumeni 1969. IN NIOSH 1974

Exposure Level (and Duration)	Effects	Reference
	same state. A gradient of effect was shown in proportion to the degree of sulphur dioxide exposure. Postulated that SO_2 and other industrial chemicals enhanced the suspected carcinogenic effect of arsenic.	
SPECIES: Rat		
10 ppm SO_2, (6 h/d, 5 d/wk followed by 10 mg/m^3 benzo(α)pyrene - 3.5 ppm SO_2 (1 h/d, 5 d/wk for 794 d)	Induction of squamous cell carcinoma in rats given inhalation exposures to sulphur dioxide in combination with benzo(α)pyrene, a known animal carcinogen. When sulphur dioxide was inhaled, it singly failed to produce a carcinoma. A "promoting" effect was suggested.	Laskin et al. 1970. IN NIOSH 1974

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 eyes, nose, throat and skin.
2. Cough.
3. Sneezing and lacrimation.
4. Rhinorrhea.
5. Anosmia (ITII 1981).
6. Reflex bronchoconstriction (NIOSH 1974).
7. Increased pulmonary resistance to air flow.
8. Bronchial asthma.
9. High pitched rales (NIOSH 1974).
10. Thoracic pain and striction (TDB (on-line) 1981).
11. Nasopharyngitis (ITII 1981).

12. Tracheitis (ITII 1981).
13. Laryngeal edema (ITII 1981).
14. Chemical bronchopneumonia (NIOSH 1974).
15. Pulmonary edema (TDB (on-line) 1981).
16. Cyanosis.
17. Systemic acidosis (TDB (on-line) 1981).
18. Asphyxia.
19. Death.

7.5.2 Ingestion.

1. Irritation to the stomach (TDB (on-line) 1981).

7.5.3 Eye Contact.

1. Irritation.
2. Lacrimation.
3. Keratitis (TDB (on-line) 1981).
4. Iritis (TDB (on-line) 1981).
5. Burns.
6. Corneal damage.
7. Blindness (CSC 1980).

7.5.4 Skin Contact.

1. Irritation.
2. Urticaria (NIOSH 1974).
3. Lesions.
4. Burns (NRCC 1977).

7.6 Human Toxicity to Decay or Combustion Products

Sulphur dioxide will react with water or steam to produce toxic and corrosive fumes such as sulphurous acid (TDB (on-line) 1981).

7.6.1 Sulphurous Acid. Sulphurous acid is a colourless, clear, acid liquid with a suffocating odour of sulphur dioxide. Symptoms of acute exposure may include irritation of mucous membranes, thoracic oppression and distress, and difficult breathing. There is no TLV® for sulphurous acid.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Sulphur Dioxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Water/Steam						•								Sax 1979
SPECIFIC/ CHEMICALS														
Acrolein	•			•										NFPA 1978
Aluminum		•												NFPA 1978
Barium Peroxide											•		Incandescence will occur.	Bretherick 1979
Cesium Acetylene Carbide											•		Incandescence will occur.	NFPA 1978
Cesium Monoxide											•		Incandescence will occur.	NFPA 1978
Chlorine Trifluoride			•											NFPA 1978
Chromium											•		Incandescence occurs.	NFPA 1978
Diethylzinc			•							•				Bretherick 1979
Ferrous Oxide											•		At 300°C incandescence occurs.	NFPA 1978
Fluorine			•											NFPA 1978
Lithium Acetylene Carbide Diamino		•												NFPA 1978
Lithium acetylide-Ammonia		•												Bretherick 1979

8.1 Compatibility of Sulphur Dioxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Manganese		•											Burns when heated in SO_2 vapour.	NFPA 1978
Potassium		•												Leleu 1975
Potassium Acetylene Carbide												•	Incandescence occurs.	NFPA 1978
Potassium Chlorate		•	•										Explosions occur if mixture is in ethanol or ether.	Bretherick 1979
Rubidium Carbide		•											When heated in SO_2 vapour.	NFPA 1978
Sodium											•			NFPA 1978
Sodium Carbide												•	Incandescence occurs.	NFPA 1978
Sodium Hydride			•											Bretherick 1979
Stannous Oxide												•	When heated in SO_2, incandescence occurs.	NFPA 1978
<u>CHEMICAL GROUPS</u>														
Chlorates		•	•										Chlorine peroxide is evolved and flashes at 60°C; can explode.	NFPA 1978

8.1 Compatibility of Sulphur Dioxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Metal Acetylides		•											Incandescence occurs.	Bretherick 1979
Metal Oxides		•											Incandescence also occurs, during heating in SO_2 gas.	Bretherick 1979

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be 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. Sulphur dioxide is a noncombustible gas (NFPA, 1978). Contact with some powdered metals and with alkali metals such as sodium or potassium may cause fires and explosions (NIOSH/OSHA, 1978). Containers may explode in heat of fire (US DOT, 1980).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture or explosion (US DOT, 1980; GE, 1979).

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

Move containers away from fire area if this can be done without risk. Stay away from tank ends (US DOT, 1980). Do not allow water to enter containers (Cities, 1979).

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

The following are recommended evacuation distances from immediate danger area of a spill, based on prevailing winds of 10 to 19 km/h (US DOT, 1978).

Approximate Size of Spill	Distance to Evacuate From Immediate Danger Area	For Maximum Safety Downwind Evacuation Area Should Be
20 m^2	65 m (84 paces)	480 m long, 320 m wide
35 m^2	90 m (120 paces)	805 m long, 480 m wide
55 m^2	115 m (150 paces)	1210 m long, 805 m wide
75 m^2	135 m (174 paces)	1210 m long, 805 m wide

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

9.1.4 Spill Actions Cleanup and Treatment.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact and inhalation (GE, 1979).

If container is leaking, move it to an open area, if possible and position the container so that the leak is at the top and only gaseous sulphur dioxide escapes rather than liquid (Cities 1979; MCA 1953). If possible, discharge the contents from the leaking container at a controlled rate into a large amount of water solution of 15 percent NaOH or other suitable alkali. The alkaline sulphite solution or slurry can be shipped for disposal or can be oxidized to inert sulphate salts with calcium hypochlorite for disposal (GE 1979).

9.1.4.2 Spills on land or in water. Contain if possible, by forming mechanical and/or chemical barriers to prevent spreading. Neutralize with lime or sodium bicarbonate (Pilie, 1975). The containing water can also be treated with a solution of soda ash followed by the addition of calcium hypochlorite (EPA, 1981). The following sorbents should also be considered in spill situations (Bauer, 1975): activated carbon and Amberlite IRA 400.

9.1.5 Disposal. Waste sulphur dioxide (which may be converted to sulphuric acid) must never be discharged directly into sewers or surface waters. Following treatment, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill.

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

If the spilled material is known to be sulphur dioxide:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent the skin from becoming frozen from contact with liquid sulphur dioxide or from contact with vessels containing liquid sulphur dioxide (NIOSH/OSHA, 1978).
- Splash-proof safety goggles are also recommended for eye protection (NIOSH/OSHA, 1978).
- Rubber is recommended for gloves, boots and protective suits (GE, 1979).
- Any clothing which becomes wet with liquid sulphur dioxide should be removed immediately and not reworn until the sulphur dioxide has evaporated (NIOSH/OSHA, 1978).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (NIOSH/OSHA, 1978).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where sulphur dioxide is present (NIOSH/OSHA, 1978).

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration	
20 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against sulphur dioxide.**
	Any supplied-air respirator.**
	Any self-contained breathing apparatus.**
100 ppm or less	A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against sulphur dioxide.
	A gas mask with a chin-style or a front- or back-mounted canister providing protection against sulphur dioxide.
	Any supplied-air respirator with a full facepiece, helmet, or hood.

Condition	Minimum Respiratory Protection* Required Above 5 ppm
	Any self-contained breathing apparatus with a full facepiece.
Greater than 100 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against sulphur dioxide.
	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.
** If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

9.1.7 Storage Precautions. Store cylinders in a cool, ventilated area (preferably fireproof); keep below 52°C. Protect from physical damage. Use check valve, trap, etc., in use to prevent "suck back" which could cause violent reaction within the cylinder (GE 1979). Never close all valves on a full line of liquid SO_2 unless protected by pressure relief (Cities 1979). Keep anhydrous sulphur dioxide away from chlorates (GE 1979).

10 PREVIOUS SPILL EXPERIENCE

10.1 General

A number of sulphur dioxide spills have been documented. The incident discussed here has been selected primarily because significant information, potentially useful in future spill circumstances, has been learned from it.

10.2 Storage Tank Leak (PC EQ 1982; World Information Services, 1981; Eco-Log Week 1981).

A 129 000 L storage tank containing liquid sulphur dioxide developed a leak in an eduction pipe and released sulphur dioxide which vaporized as it leaked to the atmosphere. The leak was probably due to corrosion of the 15-year-old fitting. The 150 plant employees and 250 families were evacuated from the area by fire officials about 1 hour after the leak was discovered. Transfer of the sulphur dioxide in the tank to a tank car began about 6 hours later.

During the transfer operation, a buildup of pressure occurred in the tank car, due to sulphur dioxide vaporizing. A vacuum truck equipped with a tank of absorbing solution containing aqueous sodium hydroxide was used to pump the excess sulphur dioxide gas (which was causing the pressure buildup) from the tank car and through the absorbing solution, neutralizing it. The transfer operation took about 1 day to complete. A total of 1000 L of sulphur dioxide was estimated to have leaked from the tank. Families and workers were allowed to return after air monitoring showed no detectable concentration of sulphur dioxide.

The authors feel that this incident illustrates the following point: if liquid under pressure is transferred from one vessel to another at different conditions, gas formation and pressure buildup may occur. In the above spill incident, a vacuum truck was used to relieve above-normal pressure formed during transfer. Passing the gas through an absorbing solution containing sodium hydroxide in water both reducing air contamination and affected disposal of the gas in a nonhazardous way. However, in similar cases, the absorbing liquid train must be arranged so that liquid is not "sucked back" into the tank car, possibly causing a pressure buildup.

10.3 Sulphur Dioxide from a Sulphur Burn (Hocking 1975).

A truck load of sulphur from a cleanup operation was dumped in a landfill near the town of Edson, Alberta, on August 8, 1974. The next day, the sulphur somehow

ignited, burned for about 5 hours, and smoldered for another 24 hours. The fire was partially extinguished by burial and partly by heavy rains. Forestry experts were called in to examine vegetative damage on August 13 and 21 and returned again September 13.

All vegetation 20 m downwind was totally and uniformly brown. Visual symptoms of damage were found as far downwind as 800 m. A total of 4 ha of vegetation was affected by the sulphur dioxide resulting from the burn. Re-examination of the area in the spring of 1975 showed that many of the species were recovering but that others were killed (e.g., white spruce up to 60 m downwind were dead). The area of damage in the spring was estimated to be 0.4 ha or 1/10 of that noted in the fall. The remainder of the vegetation had recovered or was replaced by new growth.

11 ANALYTICAL METHODS

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

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

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

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well. It should be noted that a number of standard tests for SO_2 have been published (EPS, 1974; EPS, 1975).

11.1 Quantitative Method for the Detection of Sulphur in Air

11.1.1 Titrimetric (NIOSH, 1978). A range of 6.6 to 26.8 mg/m^3 (2.52 to 10.23 ppm) of sulphur dioxide in air may be determined using bubbler collection followed by titration with barium perchlorate.

A known volume of air is drawn through a prefilter unit consisting of a 37 mm diameter cellulose-ester membrane filter of 0.8 μ pore size housed in a 2-piece cassette filter holder and a midget bubbler containing 15 mL of 0.3 N hydrogen peroxide. A sample size of 90 L at a flow of 1.0 L/min is recommended.

The sample is transferred to a 250 mL beaker. A 2 mL volume of 0.3 N hydrogen peroxide is used to rinse the bubbler and the rinses are transferred to the 250 mL beaker. A 100 mL volume of isopropanol is added and the pH of the solution adjusted to 3.5 with 1.8 percent perchloric acid. An 8 to 10 drop volume of Thorin indicator is then added and the sample titrated with 0.005 M barium perchlorate to a pink coloured endpoint. A blank determination must also be made.

11.2 Qualitative Method for the Detection of Sulphur Dioxide in Air

A range of 0.5 to 5 ppm of sulphur dioxide in air may be determined with the use of a Drager gas detector tube for sulphur dioxide. A known volume of air is drawn through a Drager gas detector tube for sulphur dioxide using a Drager multi-gas detector pump. A colour change of the blue indicating layer to white indicates sulphur dioxide. The colour change is based on the reaction between sulphur dioxide and iodine in the presence of starch (Leichnitz, 1979).

11.3 Quantitative Method for the Detection of Sulphur Dioxide in Water

11.3.1 Electrometric (ASTM, 1979). Concentrations greater than 6 mg/L (ppm) of sulphur dioxide as sulphite ion in water may be determined by titration using an electrometric indicator.

A minimum 2 L volume of representative sample is collected in an appropriate container. A 5 mL volume of 50 percent hydrochloric acid, 5 mL of potassium iodide (50 g/L), and 5 mL of 0.5 N potassium iodate are added and the sample is stirred at low speed. Several drops of starch indicator are added as well as the electrodes of a dead-stop electrometric titrator. The starch indicator is prepared by making a paste of 6 g arrowroot starch with cold water. The paste is then poured into 1 L of boiling water; 20 g of potassium hydroxide are added with stirring and the mixture is left to stand for 2 hours. A 6 mL volume of glacial acetic acid is added and the pH adjusted to 4.0 using concentrated hydrochloric acid. The mixture is stored in a glass-stoppered bottle.

The sample analysis continues as follows. The excess iodine chloride in the sample solution is titrated with 0.01 N sodium thiosulphite solution to an electrometric endpoint. A reagent blank must be titrated.

11.4 Qualitative Method for the Detection of Sulphur Dioxide in Water

Sulphur dioxide may be determined as sulphite ion in water. The sample is collected using the method described in Section 11.3.1. A 2 mL volume of sample is placed in a test tube and made basic by adding 6 M ammonium hydroxide, then adding 2 mL in excess. A 2 mL volume of 0.5 M tetraammine zinc nitrate solution is added. If a precipitate forms, it is discarded. A 3 mL volume of 4.4 M strontium nitrate is added to the supernatant. The mixture is stirred thoroughly and left to stand for 10 minutes. The supernatant is discarded. The precipitate is treated with 2 mL of 4.4 M strontium nitrate solution and the washings discarded. A 1 mL aliquot of 1 M barium chloride solution and 1 mL of 6 M hydrochloric acid are each added to the precipitate. The mixture is

centrifuged and any residue is discarded. The supernatant is decanted into a clean test tube. Drop-wise addition of 0.1 M iodine-potassium iodide is continued until the solution becomes very light yellow. The formation of a finely divided precipitate indicates sulphite (Welcher, 1955).

11.5 Quantitative Method for the Detection of Sulphur Dioxide in Soil

11.5.1 Ion Chromatography (Wetzel, 1978). Concentrations greater than 3 ppm of sulphur dioxide as sulphate ion may be determined using ion chromatography. A 5 g sample of soil is collected and extracted with 0.001 M lithium chloride solution, centrifuged, and filtered. The sample solution is injected into an ion chromatograph and quantitated using retention times and peak heights. The method is simple but requires specialized equipment.

11.6 Qualitative Method for the Detection of Sulphur Dioxide in Soil

Sulphur dioxide in soil may be determined as sulphate by precipitation. The sample is collected as in Section 11.5.1 and extracted. A 1 mL volume of sample is acidified with 6 M hydrochloric acid followed by 1 mL of 1 M barium chloride solution. A finely divided white precipitate indicates the presence of sulphate ion (Welcher, 1955).

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12.1 REFERENCES

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EnviroTIPS

Common Abbreviations

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