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PERSONAL PROTECTIVE EQUIPMENT FOR SPILL SITUATIONS

*Merv Fingas
Emergencies Science Division
Environmental Technology
Centre
Environment Canada
Ottawa, Ontario*

Introduction

People responding to and cleaning up spills are exposed to toxic chemicals that could cause serious illness or injury. The wearing of personal protective equipment is very important in spill situations as it prevents exposure to these chemicals.

Such equipment is even more important in those accidental chemical spills that do not occur in the workplace. Those who respond to such spills often don't know what chemicals they will encounter or at what concentrations. They also don't

know what the actual spill site will be like or what other dangers may be present there.

Toxic chemicals can enter the unprotected human body by inhalation, ingestion, and permeation through the skin.

Ingestion occurs when absorbed contaminants are transferred to the mouth by eating, smoking, or other forms of contact with the mouth.

Permeation is a process whereby some chemicals readily pass through the skin.

The most common types of protective devices necessary for spill response are **protective clothing** and **respiratory protective devices** or respirators. Respirators protect against inhalation and the various types of protective clothing protect against permeation and ingestion of chemicals.

There is a notable lack of standards and guidelines for selecting and using personal protective equipment for emergency chemical spills. Most existing standards are written for spills in the workplace and may not deal with the multiple hazards of accidental chemical spills that occur away from the workplace.

This article is a review of the types of personal protective equipment best used by those who respond to accidental chemical spills, particularly such spills that occur outside the workplace. It looks at factors to consider in selecting protective clothing and respirators, the different levels of response for chemical spills, the most often spilled chemicals, and the basic components of a chemical spill response program.

Respiratory Protective Devices

There are several well-known guidelines for selecting respiratory equipment for use in workplace spills (NIOSH, OSHA, U.S. CG, U.S. EPA, 1985; CSA, 1993). Other publications deal with selecting respiratory equipment for emergency spill situations (U.S. EPA, 1988; Fingas, 1987).

The difference between selecting a respirator for use in an emergency spill situation as opposed to the workplace is that maximum protection must often be used in emergency spill situations to deal with the potential presence of high concentrations of chemicals.

A wide variety of respiratory devices is available, some of which are listed in Table 1. These devices consist of a facepiece which either covers the entire face or just the nose and mouth. The facepiece is connected to either an air-source or an air-purifying device.

The basic types of respirators are **air-purifying respirators** and **supplied-air respirators**, which include the **self-contained breathing apparatus** or **SCBA**.

Air-purifying respirators use filters and/or sorbents to remove contaminants. The filters remove particulates. Small particulates (less than 10 μm) are removed by high-efficiency filters, referred to as HEPA. Sorbents consist of materials, such as charcoal, that absorb gaseous chemicals.

Supplied-air respirators supply air from air lines or tanks

rather than using ambient air. These respirators provide better protection for users in highly contaminated or oxygen-deficient atmospheres. In fact, the SCBA or self-contained breathing apparatus is the most commonly used form of respiratory protection in the initial phases of a spill as it provides the highest protection against the inhalation of chemical contaminants.

Table 1 also lists a protection factor which is the ratio of the concentration of contaminant outside the facepiece to the concentration of contaminant inside the facepiece. The protection factors presented in the table represent an average value for a large number of individuals. Such values can be much lower, however, if the

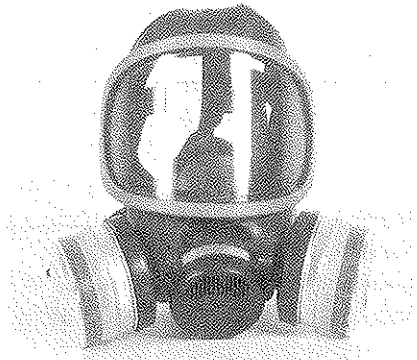
facepiece does not fit properly. A beard, for example, can cause leakage around a facepiece, reducing protection by as much as a factor of 10.

Protection factors are important criteria for selecting respiratory protective devices. The protection factor must be high enough to reduce the contaminant inside the facepiece to an acceptable level, usually referred to as the Threshold Limit Value or TLV.

The Threshold Limit Values for some commonly spilled chemicals are listed in Table 2. These values are used in the following manner. A spill of a substance with a TLV of 5 ppm, where according to calculations, concentrations at the spill scene could rise as high as 5000 ppm, would require a respirator with a

Table 1 Respiratory Protective Devices and Associated Protection Factors

Respirator	Protection Factor
Air-purifying Respirators - Particulate	
Single-use mask	5
Half facepiece mask	10
Full facepiece mask	50 (100)
Air-purifying Respirators - Gas-absorbing	
Half facepiece	10
Full facepiece	50 (100)
Supplied-air Respirators	
Demand half facepiece mask	50
Pressure-demand half facepiece mask	1,000
Pressure-demand full facepiece mask	2,000
SCBAs (Self-contained Breathing Apparatus)	
Open-circuit demand	50
Open-circuit pressure demand	10,000
Closed-circuit, oxygen-supplied type (all are full facepiece)	50



A full facepiece respirator.

protection factor of at least 1000. For a safety factor of 2, a protection factor of 2000 would be required.

Pressure-demand SCBAs, which have a protection factor of about 10,000, represent the ultimate in safety and are generally used at spill scenes because the exact substance and amount of contaminants are not known until measurements have been made.

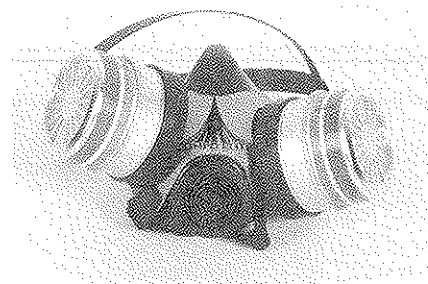
Air-purifying respirators are limited in the concentrations that they can handle or absorb. The top level at which an air-purifying respirator is useful is referred to as the "Immediately Dangerous to Life and Health" level or IDLH. This is also the level at which a chemical can cause severe damage. The IDLH level represents the value at which one must either switch from an air-purifying respirator to an air-supplying respirator, or escape from the environment. The IDLH values for some commonly spilled chemicals are also listed in Table 2.

Another requirement for air-purifying respirators is that they be used at contaminant concentrations less than the specified Maximum Use

Table 2 Threshold Concern Values for Frequently Spilled Chemicals

Chemical	TLV	IDLH
Acetic acid	10	1,000
Acetic anhydride	5	1,000
Acetone	500	20,000
Ammonia	25	500
Asbestos	0.5-2 f/cc	
Chlordane	0.5 mg/m ³ (s)	500 mg/m ³
Chlorine	0.5	30
Chlorine dioxide	0.1	10
Chromic acid	0.5 mg/m ³ (g)	30 mg/m ³
Copper sulphate	1 mg/m ³ (g)	
Diethylamine	10	2,000
Dimethylamine	10	2,000
Ethanol	1,000	
Ethyl acrylate	5	2,000
Ethyl benzene	100	2,000
Ethyl chloride	100 (s)	20,000
Ethylene glycol	50	80
Formaldehyde	0.3 (c)	
Hexane	50	5,000
Hydrazine	0.01 (s)	
Hydrogen peroxide	1	75
Hydrogen sulphide	10	300
Hydrochloric acid	5 (c)	100
Hydrofluoric acid	3 (c)	30
Isopropanol	400	12,000
Lead oxide	0.05 mg/m ³ (g)	
Mercury	0.01 mg/m ³ (s)	28 mg/m ³
Methanol	200 (s)	25,000
Methyl ethyl ketone	200	
Naphthalene	10	500
Nitric acid	2	100
Nitrogen dioxide	3	50
Pentachlorophenol	0.5 (s)	150 mg/m ³
Perchloroethylene	25	
Phenol	5 (s)	250
Phosphoric acid	1 mg/m ³	
Phosphorus	0.2	
Phthalic anhydride	1	10,000
Polychlorobiphenyls	0.5 (s)	
Potassium hydroxide	2 mg/m ³ (c)	
Pyridine	5	3,600
Sodium cyanide	5 mg/m ³ (g,s,c)	50 mg/m ³ (g)
Sodium hydroxide	2 mg/m ³ (c)	250 mg/m ³
Styrene	20 (s)	5,000
Sulphur dioxide	2	100
Sulphuric acid	1 mg/m ³	80 mg/m ³
Terphenyls	0.5 (c)	3,500 mg/m ³
Tetraethyl lead	0.1 mg/m ³ (g,s)	40 mg/m ³
Titanium dioxide	10 mg/m ³	
Toluene	50 (s)	2,000
Toluene diisocyanate	0.005	10
Trichloroethane	10 (s)	
Vinyl acetate	10	
Vinyl chloride	5	
Xylene	100	1,000
2,4 -D	10 mg/m ³	

Notes All values in ppm except as noted s - value for skin contact
f/cc - value in fibres per cc c - a 'ceiling' or maximum value
g - a value for generic substance or class used



A half facepiece respirator.

Concentration (MUC). The MUC is based on the capability of the sorbent in air-purifying respirators to deal with high concentrations of materials.

The following guidelines can simplify the selection process for respiratory protection devices for use at a spill scene.

1. The SCBA should be used for entry into an unknown situation, if unknown or high levels of a toxic chemical are present, or if there is any possibility of an oxygen shortage.
2. The air-purifying respirator can be used when the situation is stable and the levels of chemicals are below the IDLH, with very little possibility of them rising.

Regardless of which respirator is used, the selection should be verified by taking measurements and calculating concentrations inside the facepiece.

Protective Clothing

Protective clothing includes coveralls, gas-tight or totally encapsulated chemical protection suits (TECPSs), gloves, boots, goggles, and other such items worn to

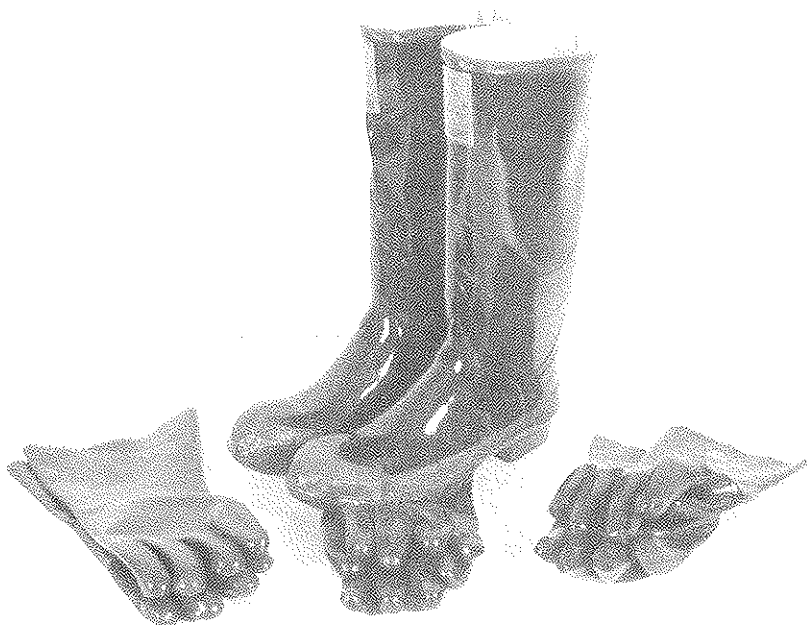
prevent the chemicals from contacting the skin or eyes.

Totally encapsulated suits are worn when the contaminant is unknown or when vapours that can penetrate the skin or skin-attacking chemicals are present. With chemicals that are corrosive or absorbed as liquids through the skin, protection is required to prevent contact with the substance itself. Some chemicals pose both dangers.

Boots and gloves are the most frequently used protective clothing and the ones that most often come into contact with chemicals. They should therefore be selected carefully. Disposable coveralls made of treated cellulose or polypropylene fabrics are now frequently used at spill scenes and are very useful for minimizing contact with the substance.

Goggles are sometimes used at spill scenes if there is a danger of material getting into eyes and respirators with face guards are not worn. Splash guards are also sometimes used, but are not recommended as they were originally designed to protect construction workers and welders from flying sparks and objects projected directly at the guard. In the case of liquid spills, however, the materials are often at ground level and the open area at the bottom of the splash guard can actually direct liquids towards the face. Hard hats and ear protectors should be used as required in any situation.

Chemicals can pass through protective clothing by either penetrating into openings in the clothing, by degrading or breaking down the material, or by permeating the material. For the purpose of spill response, permeation is the primary



Boots and gloves are the most important component of chemical protective clothing as they are most likely to come into contact with the chemical.

means of entry into materials. The following provides more detail on these three processes.

Penetration occurs when liquid or gaseous chemicals flow through closures, seams, pin holes, or other openings in the clothing. Penetration can occur regardless of the type of material selected, although some types of material are tougher and more resistant to puncturing from abrasion or pinholing, depending on the type of conditions the clothing is subjected to.

Degradation is the deterioration of clothing material caused by the action of the chemical. Degradation may change bulk properties such as tensile strength or cause small areas of the material to dissolve. In the

past, most data on a material's resistance to chemicals was related to degradation as there were no standards for measuring other types of chemical intrusion. Many different measurements were lumped together and termed "chemical compatibility".

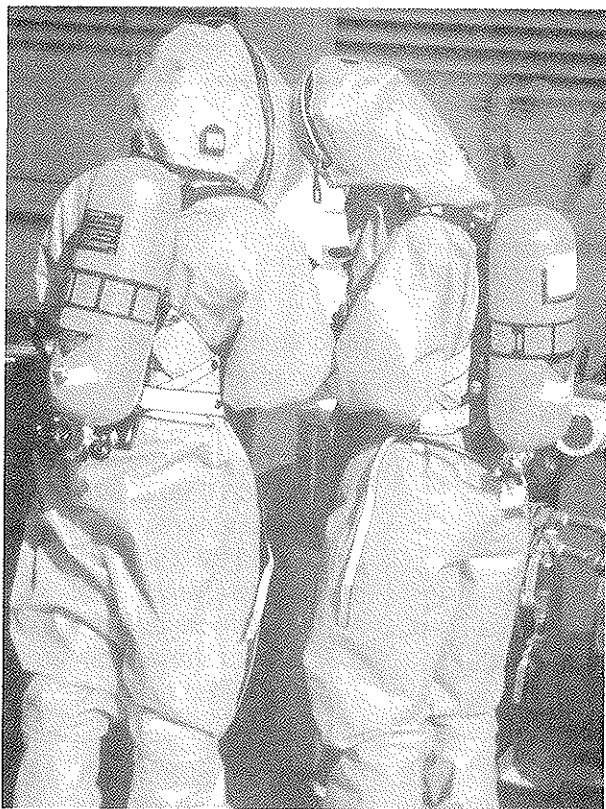
Permeation is the process by which molecules of liquid or gaseous chemicals move through clothing material. For the purpose of spill response, it is the most important indicator of the usefulness of a particular clothing material. Permeation data on the specific material used to manufacture the clothing should be obtained whenever possible.

Some chemicals can permeate through clothing material in only a few seconds. If these chemicals are toxic, then the clothing material is obviously not useful for chemical protection. Material with permeation times of less than 30 minutes has little application in spill response as this is the time usually spent in an encapsulated suit. In some cases, however, there is no material with a long enough permeation time and the material with the best permeation time possible would have to be used.

Permeation times vary for different

chemicals, at different temperatures, and if other solvents are present. It has been found, for example, that a mixture of chemicals can sometimes penetrate clothing material much faster than any one of the chemicals alone. Permeation times also vary with the thickness of the material, with thicker material having a longer permeation time. In fact, thickness is such an important factor that material, such as that used in light clothing, could have significant permeation in thin sheets of .05 cm, but be much less permeable when the material is .5 cm thick. Therefore, in very thick synthetic materials such as are used in SCBA facepieces, permeation may not be a serious concern. Permeation times may also vary with material fabrication. Other differences may be due to erroneous data. It is therefore important to verify the permeation data provided for a given material with more than one source.

Existing data on permeation are primarily measured using the ASTM (American Society for Testing and Materials) procedure. A standard test cell is used which consists of two spherical halves. The clothing material to be tested is placed as a divider between these two halves. The challenge liquid is placed on one side, with air on the other side. The air is then monitored and breakthrough occurs when the chemical can be measured in the air space. As the clothing material is completely immersed in the challenge liquid, the test provides a conservative measure.



A team working in level A gear. It is important to work in 'buddy' groups of two or three.

Table 3 Permeation Times for Clothing Materials (in minutes)

Chemical	Material							
	BETEX*	Butyl	Rubber**	Neoprene	Nitrile	PVC	Teflon	Viton
Acetic acid	>360	180	120	360	360	180	>480	120
Acetic anhydride	>360	>240	3	210	X	4	>180	X
Ammonia, anhydrous	>360	>480	2 (V)	>180	250 (V)	15 (V)	>300	
Ammonium hydroxide	>360	>480	120	360	360	180		>60
Benzene	15	30 (V)	3 (V)	12 (V)	15 (V)	1 (V)	>200	9 (V)
Chlorine	>360	>480	>480	>480	>480	30	>300	>480
Ethylene glycol	>360	>480	360	360	360	360	>480	
Formaldehyde	>360	>480	60	120	>360	70 (V)	>180	>480
Hexane	5	15 (V)	5	50 (V)	360	30	>300	>480
Hydrogen peroxide	>360		>360	6	>360	>360		
Hydrochloric acid	300	>480	360	>360	360	360	>480	>480
Hydrofluoric acid	>480	>480	150 (V)	360	120 (V)	360	>480	>480
Methanol	100	>480	15	10 (V)	180 (V)	2 (V)	>480	60
Nitric acid	>360	>480	360	150	100 (V)	240		60
Pentachlorophenol				6-360 (V)	>360	180		>480
Perchloroethylene	20	4 (V)	X	15 (V)	40 (V)	15 (V)	>180	>480
Phenol	>480	>480	60 (V)	180	60	20 (V)	>180	>480
Polychlorinated bp's		>480	60	>480	150 (V)		>480	>480
Sodium hydroxide	>360	>480	360	360	360	>360	>480	>480
Sodium hypochlorite	>360		360	360	360	360		
Styrene	10	30 (V)	1 (V)	12	30	30	>240	>180
Sulphuric acid	>360	>480	80	>360	10 (V)	10 (V)		>240
Toluene	<10	10 (V)	5 (V)	10 (V)	20 (V)	10 (V)	>180	>180
Toluene diisocyanate		>480	7 (V)	0-240 (V)	240	480	>480	>480
Vinyl chloride					300			260
Xylenes	10	30 (V)	2 (V)	4 (V)	60 (V)	1 (V)	>180	>60

Legend

* BETEX = Butyl on neoprene

** Rubber = natural rubber

Blank indicates no testing performed

V indicates highly variable data

X indicates that material should not be used, usually because it degrades

The time it takes for some commonly spilled chemicals to permeate some typical clothing materials is presented in Table 3. Data are compiled from the American Conference of Industrial Hygienists and from a standard reference on the subject (Schwope *et al.*, 1987; Forsberg and Keith, 1995). The eight materials listed in the table are commonly used in totally encapsulated suits and protective gloves. Permeation data are very important for selecting these types of clothing.

Totally encapsulated**chemical protection suits**

must be selected carefully. The following are a few guidelines to assist in selecting totally encapsulated chemical protection suits.

1. There are few standards governing the manufacture of totally encapsulated suits. Existing standards apply primarily to suits for firefighters. The buyer must therefore be careful to ensure that the suit

purchased is appropriate for use in chemical spill response.

2. It must be ensured that any permeation data provided by the manufacturer are generated by a standard method, preferably the ASTM method, and that the data are for the actual material in the suit to be purchased.
3. Suits that interfere with the facepiece of the SCBA should not be purchased.



A response team making the first entry using level A.

Response Levels

The way of responding to chemical spills has been organized into four levels based on the type of chemical spilled. These levels of response and the appropriate protective equipment for each level are shown in Table 4. These levels are commonly accepted among spill response organizations, including Environment Canada, the United States

Environmental Protection Agency, and the United States Coast Guard.

Level A is a situation in which high or unknown levels of chemicals may be present, some of which may permeate or otherwise attack the skin. Level A requires that a self-contained breathing apparatus, a totally encapsulated or gas-tight suit, and gloves be worn.

Level B involves a situation where it is known that no skin-permeating or damaging chemicals are present, or where high levels of contaminant may be present that a standard air-purifying device would not protect against. There are a variety of acceptable options for protective equipment and clothing, but basically, this level requires that an SCBA and splash-tight clothing, such as rainsuits or firefighter's bunker gear, and gloves are worn.

Such practice is dangerous and contravenes most occupational health laws.

4. As gas-tight suits are sometimes made of several materials, permeation of the weakest material is the limiting factor. The permeation time of each type of material should therefore be measured, as well as the joints between each material. To simplify the amount of data required, avoid suits made of more than one type of material.
5. The suit should allow access to the controls of the SCBA, whether the SCBA is worn inside or outside the suit. Many responders prefer that the SCBA be worn outside the suit to ensure that they have access to the controls. The question of whether the SCBA should be

worn inside or outside the suit is still controversial. Sales staff may indicate that suits with built-in face masks are not safe or legal, but this is not correct.

6. When dealing with sales staff of companies that manufacture totally encapsulated suits, caution must be taken. Many of these sales staff may not be familiar with the respiratory protection required for spill response, safety requirements at spill scenes, and permeation data for suit materials.
7. If possible, other users of the suit should be surveyed to ensure that the suit has performed well in chemical spill situations.

Level C response is often used by cleanup crews when the situation has stabilized and concentrations are known and are not likely to rise above the capability of the respirator. No skin-permeating materials are present. This level requires respirators and protective clothing, which most typically consists of liquid-repellant coveralls made of polypropylene or treated cellulose, which are proving more comfortable than Tyvek, and gloves.

Level D response is applicable to spills where there are no airborne contaminants of concern and there is minimal likelihood of harm by contact with the spilled material. Many organizations provide treated cotton coveralls or similar garb for working in such frequently occurring situations.

The Spill Situation

The target chemical is a very important consideration when selecting protection equipment. While it is not possible to be prepared for all types of chemical spills, it is possible to be prepared for the most frequent ones.

Some common chemicals spilled from 1974 to 1993 and the frequency and volume of these spills are shown in Table 5 (Fingas *et al.*, 1991, 1996).

There has been a national database on chemical spills in Canada for several years which is useful in assessing priorities (Beach, 1982; Fingas, 1987).

Looking at total spills, only about 40 materials have been spilled more than 10 times and about 150 materials have been spilled

Table 4 Levels of Spill Response

Level	Situation	Protective Equipment
A	Entry into unknown or high levels of skin-permeating chemicals	SCBA and totally encapsulated or gas-tight suit
B	High concentrations - no skin-permeating chemicals present	SCBA and splash-tight clothing
C	Known levels of non-skin-permeating chemicals	Respirator and liquid-repellant coveralls
D	Chemicals well below danger levels	Coveralls or street clothing

more than 3 times. According to the database, about 5% of the incidents are single or one-time incidents with a low probability of repeat. About 90% of the incidents are spills of high-volume production industrial chemicals. Fifty substances account for about 80% of the

spills and 100 substances for about 90% of the spills. Less common chemicals account for only a small number of spills.

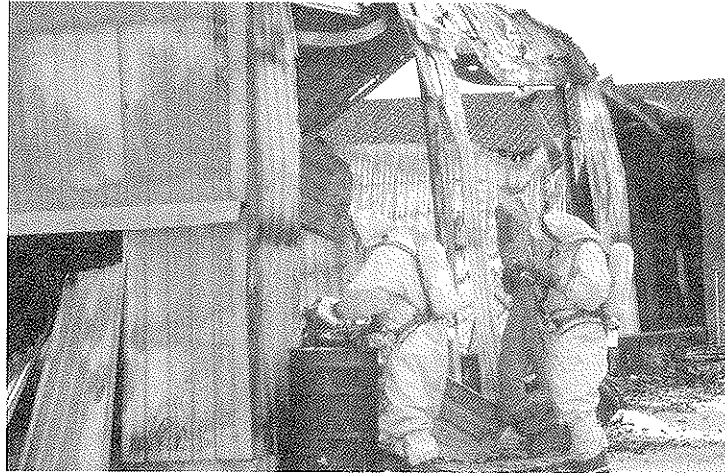
A priority list of spill substances has been prepared using spill and toxicity data. The highest priority chemicals and the

Table 5 Frequently Spilled Substances (from 1974 to 1993)

Chemical	Spill Numbers	Spill Volume (t)
PCBs	334	89
Sulphuric acid	155	13,000
Hydrochloric acid	123	3,300
Ammonia	107	470
Sodium hydroxide	92	8,200
Sulphur	68	70,000
Ammonium nitrate	63	4,200
Fenitrothion	49	100
Nitric acid	48	140
2,4-dichlorophenoxyacetic acid (2,4-D)	37	130
Chlorine	36	120
Potassium chloride	31	12,000
Ethylene glycol	31	590
Vinyl chloride	31	180
Styrene	24	5,000
Sodium chlorate	23	7,700
Calcium chloride	20	3,700

protective equipment to be used with them are summarized in Table 6. The table includes statistics on the number of spills occurring from 1974 to 1993, the volume of these spills (in tons), and the annual supply volume of these chemicals in Canada (in millions of tons).

It is important to stress that the protection levels listed in Table 6 are for typical spill situations. When chemicals and/or their concentrations are unknown or when entering enclosed or confined spaces, SCBAs and totally encapsulated suits must be worn. Once chemical concentrations are known and



Members of this response team are using a variety of analytical equipment as they make their first entry at a spill scene.

Table 6 Priority Chemicals and Protection for Spills (1974 to 1993)

Chemical	Spill Numbers	Spill Volume (t)	Supply Volume (mt)	Respiratory Protection	Clothing
Ammonia	107	470	3,700	SCBA	TECPS
Chlorine	36	120	1,700	SCBA	TECPS
Tetraethyl lead	4	72	26	respirator	splash-tight clothing
Styrene	24	5,000	630	respirator	splash-tight clothing
PCBs	334	89		respirator	splash-tight clothing
Sulphuric acid	155	13,000	3,700	SCBA	TECPS
Sodium cyanide	3	83	12	SCBA	splash-tight clothing
Hydrochloric acid	123	3,300	170	SCBA	TECPS
Potassium chloride	31	12,000		respirator	-
Pentachlorophenol	19	110	1.5	respirator	splash-tight clothing
Phenol	10	14	68	respirator	splash-tight clothing
Zinc sulphate	3	68	1,500	respirator	-
Phosphorus	16	46	68	respirator	splash-tight clothing
Toluene	13	110	430	respirator	splash-tight clothing
Copper sulphate	5	23	24	respirator	splash-tight clothing
Sodium chloride	12	1,400	12,000	-	-
Calcium chloride	20	3,700	340	-	-
Sodium hydroxide	92	8,200	1,800	respirator	splash-tight clothing
Sodium chlorate	23	7,700	440	respirator	splash-tight clothing
Ammonium sulphate	8	260	330	-	-
Ammonium hydroxide	15	130		respirator	splash-tight clothing
Benzene	12	14	740	respirator	splash-tight clothing

Note: Respiratory protection and clothes are specified for normal spill situations. Self-contained breathing apparatus (SCBA) and totally encapsulated chemical protection suits (TECPS) should be worn for entry into unknown situations and confined spaces.

the situation is under control, however, lower levels of protection may be possible.

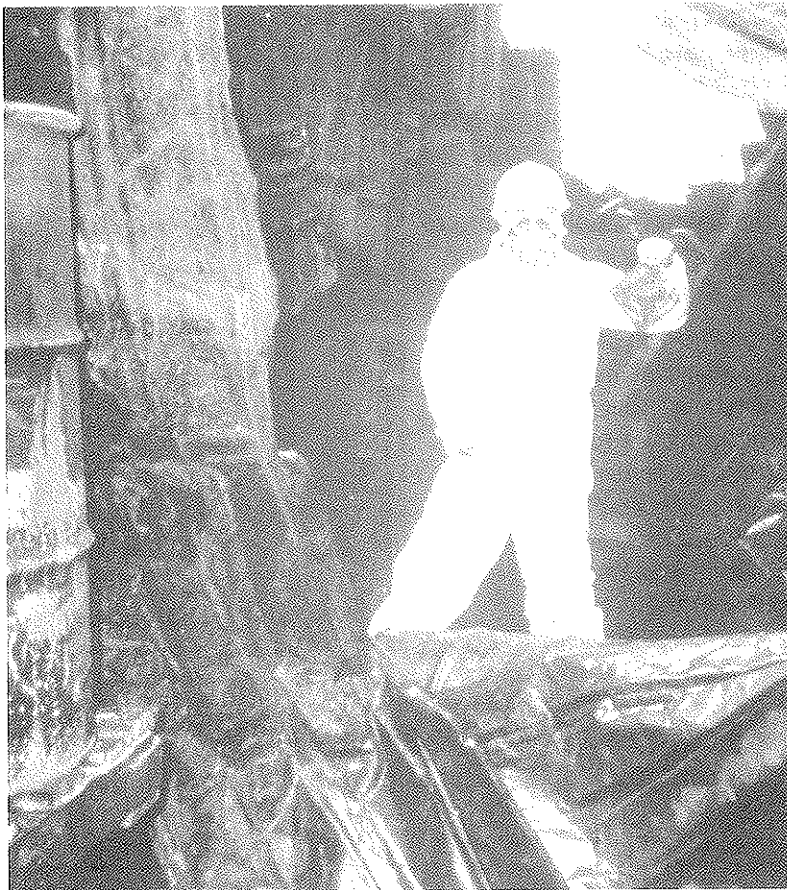
Confined spaces are areas with poor air circulation where gas concentrations can rise far beyond danger levels and there is a high potential for oxygen deficiency. There is also the danger of entrapment and fire. Confined spaces include sewers, closed rooms, and silos. Special occupational health and safety rules govern entering and working in confined spaces.

Chemical Spill Response Program

In spill response organizations, a good chemical spill response program includes medical testing, training, retraining, and practice. Purchasing, maintaining, upgrading, and replacing equipment are also part of such a program. One person in the organization should be responsible for developing, coordinating, and supervising the program.

A body of literature is available to assist in establishing a recognized and systematic program (NIOSH, OSHA, U.S. CG, U.S. EPA, 1985; CSA, 1993). The program should focus on carrying out a carefully developed policy concerning procedures for entering a spill site and minimum requirements for training and equipment.

Organizations such as Environment Canada and the U.S. Environmental Protection Agency have had such



A spill responder in level C has retrieved a label from a chemical drum.



Training is very important for first responders. These trainees pose 'incognito' for a group shot.

programs and policies for many years. For example, anyone entering a spill site must have a minimum of one week of training in the use of the appropriate equipment and a refresher course of at least two days must be taken every year.

Spill responders at Environment Canada are issued with an SCBA and a totally encapsulated suit with all the accessories. This equipment is signed out by employees and kept until they leave the program. The equipment is repaired and replaced on a regular basis.

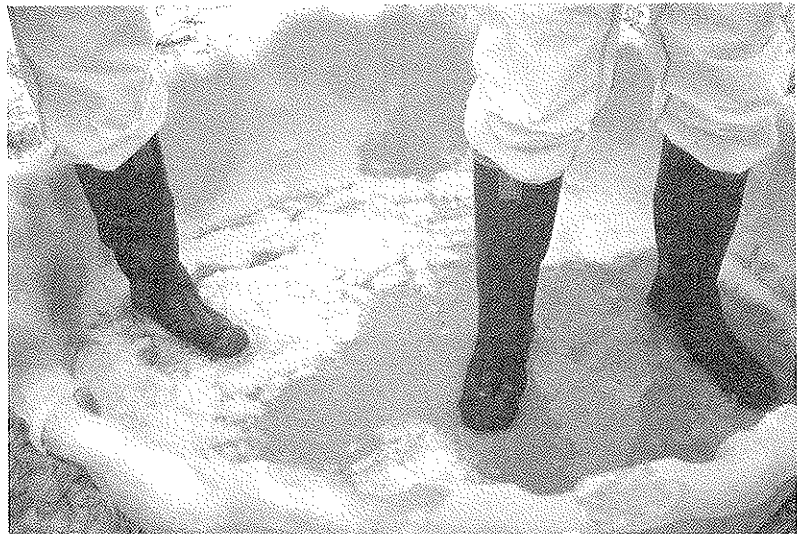
Training at regular intervals is also important. Any response organization should require at least 40 hours of training before an individual can enter a site. Annual refresher courses are also required.

Conclusion

It is important to recognize that first-responders are generally like first-aiders. They perform limited emergency duties at the site but rely on specialists, such as professionals in chemistry and site remediation, for further advice and follow-up action. Response organizations should build up a network of information sources for this purpose. Just as first-aiders do not perform surgery at the site, those who respond to chemical spills should not perform tasks beyond their training and capability.



Trainees in level B practice using a simulated spill.



Clothing, especially boots, usually requires decontamination after a spill response.

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The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have more than 2500 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

Dr. M.F. Fingas
 Technical Editor
 Emergencies Science Division
 Environmental Technology
 Centre
 Environment Canada
 Ottawa, Ontario
 K1A 0H3

Phone: (613) 998-9622

Fax: (613) 991-9485

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Phone: (819) 953-5750

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