CHAPTER 24

CHEMICALS

On December 3, 1988, in Bhopal, India, during the predawn hours, methyl isocyanate gas leaked from a chemical plant and settled over a 15-square mile area populated by more than 200,000 people. This "devil's day," as termed by the local people, left more than 2,500 dead and approximately 20,000 injured. The injuries often included damage to eyes and mild to severe pulmonary disorders.

In Michigan in 1973, an estimated 1,000 lb of polybrominated biphenyl (PBB), a flame-retardant chemical, were accidentally mixed into livestock feed. The feed was distributed to farms throughout the state and found its way into millions of animals. As a result, the state ordered the destruction of more than 30,000 cattle, 1,400 sheep, 5,900 swine, and 1.5 million chickens. Researchers found PBB in 97% of tissue samples taken from human adults across the state.

Chemicals are the basic elements of life and the world around us. Chemical products fill our homes. Materials made from chemicals are elements of our cars, clothing, furniture, tools, and other things we come in contact with daily. Most chemicals are not dangerous. Many chemicals and compounds are beneficial to humans; others are dangerous and may cause harm.

Today, however, public concern over chemicals is at an all-time high. There are more books written about chemicals and the dangers of chemicals for people than about any other subject covered in this book. Is the concern valid? Are people unnecessarily afraid of chemicals? Certainly events like those cited raise public concern. There are many other events involving chemicals: Love Canal, New York, Times Beach, Missouri, and Institute, West Virginia, to list a few.

The purpose of this chapter is to explore the hazards and controls for dangerous chemicals, not to pass judgment on these public issues. Readers should form their own opinions.

There are more than 3,000,000 registered compounds. About 60,000 compounds have significant economic value and are in the marketplace, and an estimated 700 to 1,000 new compounds enter the marketplace each year. There are published exposure standards for approximately 500 chemical compounds and the National Institute for Occupational Safety and Health (NIOSH) has compiled a list of 5,000 chemicals that have some inherent hazard. When considering the hazards of chemicals, several factors are important:

1. compounds that have known hazards may not be hazardous at low concentrations
2. compounds that are not normally dangerous may become so for certain uses
3. some compounds become dangerous when combined with other compounds

Like other hazards, there is much to learn about some of these chemicals, their use, and disposal.

Safety and Health for Engineers, Second Edition, by Roger L. Brauer

This chapter cannot cover all the compounds important for safety and health and all the conditions in which they may be found or used. This discussion focuses on an understanding of chemical hazards.

24-1 CHEMICAL REGULATIONS AND STANDARDS

Indoors

Concern about indoor air quality continues to grow. Several federal agencies regulate chemicals in indoor air. OSHA regulates the workplace, the Environmental Protection Agency (EPA) regulates some public places, and the Department of Transportation (DOT) regulates public transportation, such as aircraft, trucking, and railways. Many local governments have additional laws and regulations, and some individual organizations have standards for indoor air quality. For example, in 1987 and 1988, many local government organizations and companies banned smoking in public places and workplaces or restricted it to particular areas. In the late 1990s, people became concerned with molds and their effects on people (see Chapter 26), so that a number of state governments have begun regulating mold inspectors.

For many years, the American Conference of Governmental Industrial Hygienists (ACGIH) has published standards for exposures to hazardous materials in the workplace. The American Industrial Hygiene Association (AIHA) also publishes guidelines for exposures to certain materials.

For a long time, little attention was given to indoor air quality other than for workplaces. However, some organizations have begun to address the problem. In the 1930s and even earlier, the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) recommended ventilation rates for indoor space, and their recommendations were incorporated into many building codes. Energy conservation in buildings, reduced ventilation rates, and tighter construction that limits air infiltration produced a renewed interest in indoor air. ASHRAE, the American Institute of Architects, and other organizations held conferences on indoor air quality. The American Society for Testing and Materials (ASTM) has an indoor air subcommittee. Indoor air quality will remain an active topic for some time and will result in new standards.

The American Institute of Chemical Engineers (AIChE) and its Center for Chemical Process Safety (CCPS) provide a variety of publications on the identification and control of hazards in chemical process plants and facilities.

Outdoors

For outdoor environments, there are many laws and regulations governing air and water quality and the handling and disposal of hazardous material. In addition, there are laws governing the cleanup of sites containing hazardous materials. Some of the environmental laws have expired before Congress resolved additional provisions under renewal acts.

Air Congress passed the Clean Air Act in 1970 and renewed it in 1977 and 1991. Its purposes are to

1. protect and enhance the quality of the nation's air
2. initiate and accelerate research to achieve prevention and control of air pollution
3. provide technical and financial assistance to state and local governments for air pollution prevention and control programs

4. encourage and assist the development and operation of regional air pollution prevention and control programs

Water Congress passed several laws affecting water quality, including the Clean Water Act of 1972, which set limits on toxic discharges of industry, and created a large public works program to build sewage treatment plants. The Safe Drinking Water Act of 1974 (and modified in 1992) sets standards for the taste, color, and appearance of public drinking water and maximum limits for certain chemicals and bacteria it contains. The Federal Water Pollution Control Act of 1977 (and modified in 1992) extended previous regulation of water quality. The Marine Protection, Research and Sanctuary Act of 1972 banned ocean dumping of radioactive, biological, and chemical warfare wastes. It established a permit system for ocean dumping of other wastes, such as sewage sludge and dredged materials.

Control of Hazardous Materials The Federal Insecticide, Fungicide and Rodenticide Act of 1972 (and modified in 1994) required all pesticides to be registered and required manufacturers to submit detailed information about pesticide ingredients and safe use. The Resource Conservation and Recovery Act of 1976 (often referred to as RCRA and modified in 1992) authorized regulation of the generation, treatment, storage, and disposal of hazardous wastes. It established a manifest system for tracking hazardous materials from creation to disposal or use and it eliminated open landfills. The Toxic Substances Control Act (often called TSCA) was passed in 1976 and was modified in 1992. It required testing of new chemicals for safety before they reach the marketplace. The Hazardous Materials Transportation Act (discussed in Chapter 14) controls the packaging, labeling, and transportation of hazardous materials.

Cleanup In 1980, Congress passed the Comprehensive Environmental Response, Compensation and Liability Act (sometimes called CERCLA, modified in 1992), which addressed the cleanup of existing hazardous waste sites. This Superfund bill required industry to contribute to the cost of cleaning up sites containing hazardous materials. An EPA survey of states identified approximately 35,000 hazardous waste sites. In 1986, Congress passed the Superfund Amendments and Reauthorization Act (called SARA), which extended the Superfund and hazardous waste site cleanup.

Right-to-Know Public demand for more information about the dangers of particular chemicals led to federal and state right-to-know laws. Under the Emergency Planning and Community Right-to-Know Act of 1986 (also known as SARA Title III and amended in 1992), employers must inform employees within and citizens outside a plant about the dangers of chemicals at the site. Material safety data sheets (MSDSs) standardize the information and give details about chemicals or compounds and applicable protection from harm when exposed to them (see Figure 24-1). SARA Title III also covers labeling and storage requirements and allows states to pass right-to-know laws that require emergency planning for communities around a plant.

Companies analyze process plant safety and develop emergency response plans that they coordinate with local police, fire departments and other organizations in a neighboring community. The analysis and emergency response plans cover both exposures within the plants and in the surrounding community.

Products

There are also regulations covering chemicals in certain products. For example, food additives and coloring agents fall under the control of the Food and Drug Administration

Material Safety Data Sheet May be used to comply with OSHA's Hazard Communication Standard, 29 CFR 1910 1200. Standard must be consulted for specific requirements.	**U.S. Department of Labor** Occupational Safety and Health Administration (Non-Mandatory Form) Form Approved OMB No. 1218-0072
IDENTITY *(as Used on Label and List)*	*Note: Blank spaces are not permitted. If any item is not applicable or no information is available, the space must be marked to indicate that.*

Section I

Manufacturer's name	Emergency Telephone Number
Address *(Number, Street, City, State and ZIP Code)*	Telephone Number for Information
	Date Prepared
	Signature of Preparer *(optional)*

Section II—Hazardous Ingredients/Identity Information

Hazardous Components (Specific Chemical Identity, Common Name(s))	OSHA PEL	ACGIH TLV	Other Limits Recommended	% (optional)

Section III—Physical/Chemical Characteristics

Boiling Point		Specific Gravity (H_20 = 1)	
Vapor Pressure (mm Hg)		Melting Point	
Vapor Density (AIR = 1)		Evaporation Rate (Butyl Acetate = 1)	
Solubility in Water			
Appearance and Odor			

Section IV—Fire and Explosion Hazard Data

Flash Point (Method Used)	Flammable Limits	LEL	UEL
Extinguishing Media			
Special Fire Fighting Procedures			
Unusual Fire and Explosion Hazards			

(Reproduce locally) OSHA 174 Sept. 1985

Figure 24-1. OSHA format for material safety data sheets.

(FDA), which also controls certain chemicals in cosmetics. The Consumer Products Safety Commission (CPSC) regulates the chemicals in a variety of consumer products.

One action of the CPSC that garnered much public attention involved the recall and banning of children's sleepwear that contained a fire-retardant material known as TRIS. After pressure to prevent the horrors of sleepwear (particularly dacron) burning and melting into the skin of children, Congress required a fire retardant for the sleepwear. TRIS was the material most often used. Not only was it an effective fire retardant, but it also retained properties in the clothing that made the sleepwear soft and saleable. However, it was suspected of being a cancer-causing agent. Before researchers could complete health studies to establish if TRIS was a carcinogen, Congress, facing public pressure to protect children's health, pressured the CPSC to act. The Commission tried to balance eco-

Section V—Reactivity Data

Stability	Unstable		Conditions to Avoid
	Stable		

Incompatibility *(Materials to Avoid)*

Hazardous Decomposition or Byproducts

Hazardous Polymerization	May Occur		Conditions to Avoid
	Will Not Occur		

Section VI—Health Hazard Data

Route(s) of Entry	Inhalation?	Skin?	Ingestion?

Health Hazards *(Acute and Chronic)*

Carcinogenicity	NTP?	IARC Monographs?	OSHA Regulated?

Signs and Symptoms of Exposure

Medical Conditions
Generally Aggravated by Exposure

Emergency and First Aid Procedures

Section VII—Precautions for Safe Handling and Use

Steps to Be Taken in Case Material Is Released or Spilled

Waste Disposal Method

Precautions to Be Taken in Handling and Storing

Other Precautions

Section VII—Control Measures

Respiratory Protection *(Specify Type)*

Ventilation	Local Exhaust	Special
	Mechanical *(General)*	Other

Protective Gloves	Eye Protection

Other Protective Clothing or Equipment

Work/Hygienic Practices

Figure 24-1. *continued*

nomic, health, and political factors. TRIS retained the feel necessary to induce customers to buy sleepwear, whereas other additives gave fabric a coarse feel. With each washing, the TRIS content of sleepwear decreased about 50% so that a few washings would remove any potentially dangerous levels from already purchased clothing. The sleepwear industry was a collection of small firms dedicated to producing this clothing. The CPSC ultimately decided to recall TRIS-treated sleepwear. The action seriously harmed the industry, while protecting children against an undetermined hazard. Sleepwear with flame-retardant protection as required by law was no longer available, so as an alternative, many parents purchased non–fire-retardant insulated underwear. The problem was back to where it started.

Processes

Chemical engineers and other specialists work on the safety of equipment, systems, and processes for the manufacture of chemicals, petroleum, and other products. The processes may use heat, pressure, chemical reactions, and other methods to achieve the end product after several stages in the process. Many processes are based on continuous and controlled flow of materials, rather than batch approaches. Part of the design responsibility is to reduce or eliminate risks in the processes and to include sensors, warning systems, automated or manual system adjustments, or shutdown when processes go outside the acceptable range of operating parameters.

OSHA has established a performance standard[1] for evaluating the hazards and risks of such processes and defining controls for the hazards. A number of states have enacted similar process safety standards and regulations. The Center for Process Safety and the American Institute of Chemical Engineers have publications and references that help achieve safe processes. Those involved in process safety often apply techniques and methods associated with system safety (covered in Chapter 36).

Workplaces

There are several standards for exposures to chemicals on the job, for levels of contaminants in drinking water and in air, for use of chemicals in consumer products (cosmetics, food, etc.), and for agricultural purposes. One should refer to appropriate federal agencies for current exposure standards for chemicals. This discussion focuses on standards for workers.

For many years, the ACGIH has published a booklet[2] listing the recommended exposure limits for workers. It is intended as a guide to help limit harmful chemical exposures for workers; it does not distinguish safe from harmful environments. The threshold limit values (TLVs) include exposures to airborne particulates and gases or vapors. An ACGIH committee updates the TLV Guide annually. Changes result from careful review of research literature and monitoring of reported experience. The ACGIH also publishes documentation for recommendations found in the TLV Guide.

Early OSHA standards listed permissible exposure limits (PEL) for workers. Both ACGIH and OSHA standards generally are based on 8-hr time-weighted averages (TWA). The TWAs allow for reasonable exposure excursions during a workday. For particular chemicals, ACGIH lists ceiling limits: these concentrations are never to be exceeded. The TLVs have a “skin” notation for substances that are easily absorbed through the skin. For many years, ACGIH’s TLV Guide has included a second set of time-weighted average exposure limits based on a 15-min exposure period. These are short-term exposure limits (STEL).

In January 1989, OSHA completed initial rule-making on a new table of exposure standards for more than 400 substances.[3] Appendix A contains a sample of the current OSHA exposure standards. The final rule-making report includes justification for the exposure limits for substances. The main difference between ACGIH and OSHA exposure standards is a legal consideration: ACGIH standards are recommended practice for industrial hygienists practicing in industry, whereas OSHA standards are enforceable as government regulations. Since initial publication, OSHA has been working on updates to its exposure standards, including a more global update. However, the process of changing them has been very slow.

Mixtures Some people are exposed to more than one substance during an 8-hr period, either as independent substances or mixtures. In some cases, the combination of chemicals involved in the exposures may have independent effects. In other cases, the chemicals may react with each other and have a synergistic effect. When exposures involve two or more hazardous substances that act on the same organ, one should address combined effects. When there is little or no information about combined effects, the additive effect should be considered. One can evaluate additive effects by using

$$X = \frac{C_1}{T_1} + \frac{C_2}{T_2} + \cdots + \frac{C_n}{T_n}, \tag{24-1}$$

where

C_x is the atmospheric concentration of a substance and

T_x is the threshold limit value.

If $X < 1$, the mixture does not exceed the TLV; if $X > 1$, the mixture exceeds the TLV.

Example 24-1 During an 8-hr workday, a worker is exposed to the following mixture of substances: acetic acid, 4 ppm; stoddard solvent, 150 ppm; ethyl ether, 230 ppm. From the OSHA permissible exposure limits (Appendix A), the allowable exposures for these substances are 10, 500, and 400 ppm, respectively.

Applying Equation 24-1,

$$X = \frac{4}{10} + \frac{150}{500} + \frac{230}{400} = 1.275.$$

Because $X > 1$, the mixture exceeds the threshold limit value.

Biological Exposure Indices Biological monitoring consists of an assessment of overall exposure to chemicals that are present in a workplace through measurement of appropriate determinants in biological specimens collected from workers. Biological determinants can be the chemical itself or its metabolite(s) or a characteristic reversible biochemical change induced by the chemical. Appropriate measurements are made on exhaled air, urine, blood, or other biological specimens. Biological exposure indices (BEIs) serve as reference values. They represent the levels of determinants that are most likely to be observed in specimens collected from a healthy worker who has been exposed to chemicals to the same extent as a worker with inhalation exposure to the TLV-TWA. BEIs published by ACGIH are reference values intended as guidelines for the evaluation of potential health hazards in the practice of industrial hygiene. BEIs apply to 8-hr exposures, 5 days a week. Individual differences may account for occasional measurements above BEIs, but if a sample exceeds a BEI consistently, there is cause for investigation of the workplace. BEIs should be used as a backup check on exposures, not the primary means for determining if a hazard exists.

24-2 HAZARDS

Chapter 9 introduced hazard recognition and control. The discussion notes that one must know at least three items of information about an agent to determine if it is hazardous:

1. what the agent is and what form it is in
2. the concentration
3. the duration and form of exposure

Having this information available is particularly important when seeking to understand hazards and controls for chemicals.

The main hazards for chemicals are (1) health effects, (2) fires and explosions, and (3) reactivity with other materials. This chapter mainly discusses health effects, and Chapters 16 and 17 discussed fire and explosion hazards. Reactivity refers to the relative stability of a material: in a fire, a material may become unstable from the heat or products of combustion; some materials may be sensitive to mechanical disturbance from pressure or physical impact; and extinguishing agents, such as water, can react with certain materials. A reaction may involve releases of large amounts of energy and the release may be sudden, as in an explosion.

Classification

There are several ways to classify hazardous materials. Chapter 14 discussed the DOT classification and labeling of hazardous materials, including chemicals. In the United States, a commonly used classification scheme for hazardous chemicals is that of NFPA 704.[4] A diamond-shaped symbol, divided into quadrants, conveys health, flammability, and reactivity information (see Chapter 16).

Identification

There are several ways to identify chemicals. Each chemical or compound has a chemical name and chemical formula. Examples are ozone (O_3) and methyl isocyanate (CH_3NCO). The Chemical Abstract Service has a registration system for assigning unique identifying numbers in the format xxx-xx-x: ozone and methyl isocyanate are 10028-15-6 and 624-83-9, respectively. NIOSH maintains the Registry of Toxic Effects of Chemical Substances (RTECS), which assigns each chemical a unique number: RS8225000 and NQ9450000 denote ozone and methyl isocyanate. As noted in Chapter 14, DOT has an identifying number for hazardous materials. Numbering systems for procurement purposes, such as the federal National Stock Number, also identify chemicals.

Type of Airborne Contaminants

There are two main forms of airborne contaminants: particulates and gases or vapors. Particulates include dusts, fumes, smoke, aerosols, and mists that are classified additionally by size and chemical makeup. Shape also can be important. Some particulates are fibrous, having long, thin shapes, whereas others may be more spherical and have a fairly uniform cross section. Figure 25-5 provides size characteristics of some airborne contaminants.

Dusts Dusts are airborne solids, typically ranging in size from 0.1 to 25 μm. Dusts larger than 5 μm settle out in relatively still air because of the force of gravity. Many dusts are created by processes that break materials into small sizes, such as grinding and mixing.

Fumes Fumes are fine solids less than 1 μm in size that are often formed by condensation of vapors. For example, heating of lead vaporizes some lead material that quickly condenses to small, solid particles.

Smoke Smoke is carbon or soot particles, generally less than 0.1 μm in size, that results from incomplete combustion of carbonaceous material.

Aerosols Aerosols are airborne solid or liquid particulates dispersed in air.

Mists Mists are fine liquid droplets suspended in or falling through air. Mist is generated by condensation from the gaseous to the liquid state or by breaking up of liquid into fine particles through atomizing, splashing, or foaming.

Gases A state of matter separate from solids and liquids.

Vapors The gaseous phase of a substance that is liquid at normal temperature and pressure.

Health Effects

Health effects for different chemicals vary considerably. The likelihood and degree of damage depend on type and form of substance, the type and rate of exposure, and what happens to the substance in the body. Most hazardous materials affect particular organs of the body. For example, some damage tissue, such as skin and eyes, on contact, some affect respiration, some damage nerves and other elements of the central nervous system, and some affect oxygen transport of the blood or other blood functions. Often general symptoms, such as headache and nausea, are confused with symptoms of other diseases. Chemical exposures may not be recognized immediately as the cause.

Some effects of chemicals appear as behavioral changes. For example, lead exposure may lead to forgetfulness, hallucinations, and lethargy. Again, behavioral symptoms resulting from chemical damage often are confused with other causes.

Latency Period Some chemicals have immediate effects. An example is strong acid or caustic contacting tissue and destroying it. These are sometimes called chemical burns, because they exhibit properties similar to thermal damage of tissue. Other chemicals may not manifest their effects for some time. The delay between exposure and observable effect is a latency period. Some carcinogens have a latency period as long as 20 to 40 yr.

Acute Versus Chronic Exposures Exposures can be acute or chronic. For some chemicals, disease or effects do not appear until after repeated exposures; in other cases, a single exposure may be sufficient to induce effects. Some materials will not cause significant permanent damage with a single exposure; some may. Others may not cause permanent damage at all.

Local Versus Systemic Effects Local effects occur when substances cause injury to skin, eyes, or respiratory tract after one or more exposures. Systemic effects occur when substances enter the body and produce damage to organs or biological functions. The effects may be behavioral or physical. Examples of damage include kidney dysfunctions or failures, clotting of blood, damage to liver tissue, and ulcerations in the digestive tract.

Asphyxiants Asphyxiant materials do not have direct effects on the body or its organs, but they do displace oxygen in a breathing atmosphere. The reduced oxygen content affects the partial pressure of oxygen and inhibits oxygen transport in the blood (see Chapter 19). Some asphyxiants may interfere with oxygen transport or breathing in other ways.

Nuisance Dusts Some materials are simply a nuisance. They may cause irritation, coughing, or similar symptoms, but have no long-term effects. Certain dusts are classified as nuisance dusts.

Individual Differences Not everyone exhibits the same effects or degree of effects from a chemical exposure. Two people may have the same exposure, but only one may have a reaction. Some people are allergic to certain materials in their environment. The allergic reaction may be inherited or may develop during life. Some people become sensitized to a substance. Initially, they do not react to an exposure, but then suddenly they show reactions. Removal of the substance may stop the reaction. However, a single, subsequent exposure after sensitization usually produces the reaction.

Pneumoconiosis Pneumoconiosis is a disease of the lungs resulting from the inhalation of various kinds of dusts and other particles. The term means dusty lung. The disease has several names depending on the material one is exposed to. Table 24-1 lists several forms of pneumoconiosis.

There are other forms of lung disorders related to exposures to hazardous materials. Fibrosis is the formation of scar tissue, which forms when the body attempts to engulf foreign material that lodges in the lung. Bronchitis is the overproduction of mucus, which often results in coughing. Asthma is the constriction of the bronchial tubes caused by a histamine reaction to some toxin that produces swelling. Hives on the skin is a similar reaction.

Carcinogens A substance that produces cancer in animals or humans under certain quantified exposures is a carcinogen. Some define a carcinogen as any agent that increases tumor induction in humans or animals. Even the induction of benign tumors may be enough to characterize a substance as a carcinogen. Irreversibility and a long latency period after the initial exposure to a carcinogenic agent characterize carcinogenesis. There are specific tests to determine when a material is to be classified a carcinogen or a suspected carcinogen.

Mutagens A mutagen is any substance that causes changes in the genetic structure in a current generation of animals or humans such that it can cause cancer or some mutation in a later generation. Mutations may not show up until several generations later. Mutagens cause inheritable changes in the chromosomes, changes that may not be observable deformities. Radiation, for example, has been associated with sterility.

Teratogens A teratogen is any substance that causes malformations or serious deviations from the normal in a human or animal fetus. Congenital malformations or abnor-

TABLE 24-1 Types of Pneumonconiosis

Disease	Material Inhaled
Asbestosis	Asbestos fibers
Silicosis	Free silica (SIO_2) dust from mining, sandblasting, quarrying, and in ash from volcanic eruptions
Berylliosis	Beryllium particles
Byssinosis	Cotton dust
Metal fume fever	Particulates of zinc, magnesium, copper, and their oxides (other metals have also been known to produce metal fume fever)
Siderosis	Iron oxide (often from welding and mining)
Kaolinosis	Kaolin (china clay) dust from grinding and handling
Mica pneumoconiosis	Mica dust from grinding
Bauxite pneumoconiosis (Shaver's disease)	Aluminum oxide fumes from smelting bauxite

malities in offspring resulting from exposure of a mother or fetus to some agent is teratogenesis. Typically, there is no exposure effect on the mother. Teratogens interfere with normal embryonic development.

24-3 TOXICOLOGY

Toxicity is the capacity of a material to produce injury or harm after it reaches a site in or on the body where harm can result. In contrast, a health hazard is the possibility that exposure to a toxic material will cause harm under ordinary use circumstances or when a specific quantity is used under particular conditions. Toxicology is the science that deals with the nature and effects of poisons. Tables 24-2 and 24-3 summarize some toxicity rating schemes.

Sources of Data

There are many publications that list toxic properties of chemical substances. One of the primary references is *Dangerous Properties of Industrial Materials*, edited by N. I. Sax. This publication lists toxicity and other data for more than 18,000 substances. Another primary reference is *Patty's Industrial Hygiene and Toxicology*. This long-standing, multivolume publication includes discussions of evaluation and control methods as well as toxicity data. The OSHA Hazard Communication Standard[5] requires that chemical manufacturers and importers provide customers with material safety data sheets (MSDSs). These data sheets are good sources of information about the toxicity and other physical, chemical, and hazardous properties of chemicals.

There are also some computer accessible data banks of toxicity data for substances. The most noteworthy ones are the National Library of Medicine's Hazardous Substances Data Bank and the NIOSH Registry of Toxic Effects of Chemicals and the NIOSH Pocket Guide to Chemical Hazards.[6] Also there are computer data banks and CD-ROM collections of MSDSs, many available over the Internet.

Routes of Entry

There are three main routes of entry for hazardous substances into the body: inhalation, ingestion, and absorption through the skin. An occasional route of entry is injection. The most common route of entry in work environments is by inhalation. As soon as materials enter the body and reach the blood, they can be distributed throughout the body. Some materials have an affinity for certain kinds of tissue, and consequently, concentrate in particular organs.

Inhalation During respiration, airborne gases and particulates are carried into the upper respiratory system and lungs. The body may absorb the materials into the bloodstream or may encapsulate the materials in the lung tissue. The inhaled materials or portions of them may be exhaled as well.

Figure 24-2 illustrates the structure of the respiratory system. Air passes through the pharynx and trachea to the bronchi, bronchioles, and ultimately to the terminal air sacks or alveoli, where inhaled gases may enter the blood stream.

Gases and vapors disperse with oxygen and nitrogen in normal air. Consequently, hazardous gases will travel with normal air deep into the lungs. Depending on solubility and other properties, a gas may go into solution in the blood or may attach to red cells or elements of the blood. The blood transports the material to other tissues in the body for

TABLE 24-2 Toxicity Rating System[a]

Rating	Description
U	**Unknown.** Insufficient data are available to enable a valid assessment of toxic hazard to be made.
0	**None, no toxicity.** This rating applies to chemicals that (a) produce no toxic effects under any conditions of normal usage or (b) require overwhelming doses to produce any toxic effects in humans.
1	**Low, slight toxicity.** The rating is characterized under four types of exposure: (a) *Acute local*. Chemicals that on a single exposure lasting seconds, minutes, or hours cause only slight effects on the skin or mucous membranes or eyes, regardless of the extent of exposure. (b) *Acute systemic*. Chemicals that can enter the body by inhalation, ingestion, or dermal contact and produce only slight toxic effects, regardless of the duration of exposure or after the ingestion of a single dose, regardless of the amount absorbed or the extent of the exposure. (c) *Chronic local.* Chemicals that on repeated or continuous exposure covering days, months, or years cause only slight and reversible damage to the skin or mucous membranes. The extent of the exposure can be great or small. (d) *Chronic systemic.* Chemicals that on repeated or continuous exposure covering days, months, or years cause slight and usually reversible toxic effects on the skin, mucous membranes, or eyes. The exposure can be by ingestion, inhalation, or skin contact and may be great or small. Slightly toxic chemicals produce changes readily reversible once the exposure ceases with or without medical intervention.
2	**Moderate toxicity.** Chemicals may cause reversible or irreversible changes in the human body not necessarily sever enough to cause serious physical impairment or threten life. Ratings are characterized under four types of exposure: (a) *Acute local.* Chemicals that on a single exposure lasting seconds, minutes or hours produce moderate toxicity to the skin, mucous membranes, or eyes. The effects can be the result of an intense exposure for seconds or a moderate exposure for hours. (b) *Acute systemic.* Chemicals that after being absorbed by inhalation, ingestion, or skin contact produce moderate toxicity after a single exposure lasting seconds, minutes, or hours or after the ingestion of a single dose. (c) *Chronic local.* Chemicals that on continuous or repeated exposure over days, months, or years cause moderate toxicity to the skin, mucous membranes, or eyes. (d) *Chronic systemic.* Chemicals that on absorption by ingestion, inhalation, or skin contact cause moderate toxicity after continuous or repeated exposures over days, months, or years.
3	**High, severe toxicity.** Ratings are characterized under four types of exposure: (a) *Acute local.* Chemicals that on a single exposure covering seconds or minutes can cause injury to the skin, mucous membranes, or eyes of sufficient severity to threaten life, cause permanent physical impairment, or cause disfigurement. (b) *Acute systemic*. Chemicals that after a single exposure by inhalation, ingestion, or skin contact cause injury of sufficient severity to threaten life. The exposure may last seconds, minutes, or hours or may be a single ingestion. (c) *Chronic local*. Chemicals that on continuous or repeated exposures covering days, months, or years can cause injury to the skin, mucous membranes, or eyes of sufficient severity to threaten life or produce permanent impairment, disfigurement, or irreversible change. (d) *Chronic systemic*. Chemicals that on continuous or repeated exposures by inhalation, ingestion, or dermal contact to small amounts for days, months, or years can produce death or serious physical impairment.

[a] From Sax, N. I., *Dangerous Properties of Industrial Materials*, 7th ed., Van Nostrand Reinhold, New York, 1988.

TABLE 24-3 Degree of Toxicity Ratings

Toxicity Rating	Probable Lethal Dose for a 70-kg Human	Experimental LD_{50}: Dose per kg of Body Weight
Dangerously toxic	A taste	<1.0 mg
Seriously toxic	A teaspoonful	1–50 mg
Highly toxic	An ounce	50–500 mg
Moderately toxic	A pint	0.5–5 g
Slightly toxic	A quart	5–15 g
Extremely low toxicity	More than a quart	>15 g

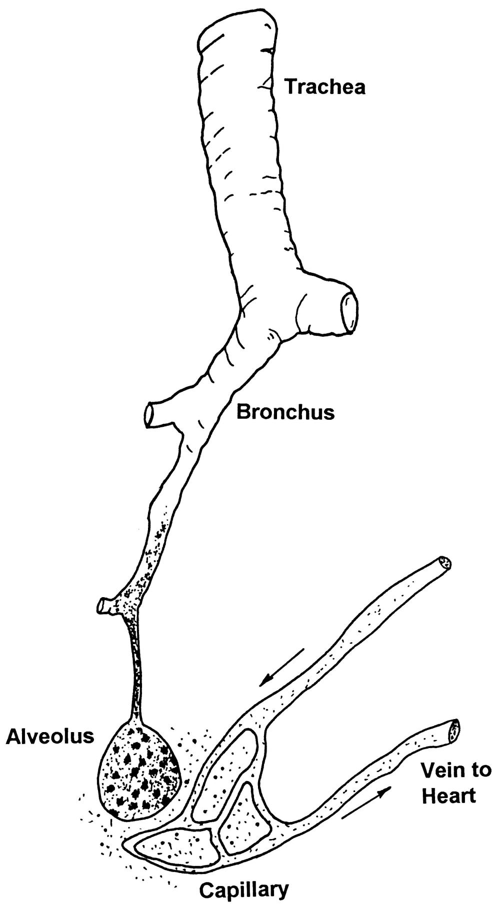

Figure 24-2. General structure of the human respiratory system.

which there may be more affinity. For example, carbon monoxide forms a bond with the hemoglobin of the red cells more readily than oxygen. In addition, because it does not release from the hemoglobin easily, the red cells are unavailable to bond with oxygen, and therefore become ineffective in transporting oxygen throughout the body.

Although gases and vapors move freely with inhaled air, particulates may not reach the alveoli. Because of their mass or shape, larger particulates (generally those larger than 5–7 μm in diameter) are not able to make sharp turns with air movement. They impinge on the mucus membrane of the upper respiratory tract and the cilia, which line the mucus membrane, move the foreign matter upward along the respiratory tract in a cleaning process. The foreign material is expectorated or swallowed. Smaller particulates (less than 5–7 μm in diameter) do reach the alveoli. Because particulates smaller than 0.5 μm tend to remain airborne, they are likely to pass from the lungs as one exhales. Those between approximately 0.5 and 5 to 7 μm have a good chance of lodging in the alveoli.

Ingestion Ingestion involves eating or drinking materials. Ingested materials are absorbed into the blood after traveling to the intestinal tract. Although people ingest little toxic material directly from work environments, often food is contaminated by hands or from contaminated eating areas. Some toxic material may be ingested from material originally inhaled and moved through ciliary action to the throat, where it is swallowed.

Absorption through the Skin Some materials enter the bloodstream through the skin. The skin may be abraded or have lesions that foster absorption, although many materials are absorbed directly through intact skin. Elevated skin temperature or moisture on the skin may enhance cutaneous absorption. Some skin areas, such as the back of the hand and follicle-rich areas, exhibit higher absorption rates than areas like the palm of the hand and the forearms.

Injection Materials may be injected purposely or accidentally. Accidental injection is more important for occupational settings. Refer to the discussion of injection injuries in Chapter 19.

Direct Contact with Tissue

Beside the three main routes of entry, some materials may be harmful in direct contact with external tissue.

Dermatitis There are many forms of skin disorders, many of which result from exposures to chemicals. Dermatitis is a general term for skin disorders. Some forms of dermatitis exhibit reddening; others involve cracking, sores, acne, and other disorders. Some forms of dermatitis, called contact dermatitis, result from direct contact with a substance that may be in gaseous, liquid, or solid form and may be a direct irritant or an allergen. Chloracne results from chlorinated naphthalenes and polyphenyls acting on sebaceous glands. The acne-like appearance can appear on skin of the hands and arms, as well as other areas of the body.

Eye Irritation Substances may contact eyes or tissues around the eyes and cause irritation or more severe injury. Conjunctivitis is an inflammation of the conjunctiva, the delicate membrane that lines the eyelids and covers the exposed surface of the eyeball.

24-4 TOXICOLOGICAL DATA

Methods for Assessing Toxicity

Toxicity data for substances come from many sources, most often from controlled studies. Because all chemicals can be toxic, the studies manage not only the amount of chemical involved, but also the conditions of exposure. Nearly all substances fail to exhibit effects at very low exposure levels, but at some level, effects begin to appear. This suggests a threshold level for effects, above which increased concentrations will produce more severe effects. Also, as exposure levels increase, the effects are likely to occur in a larger portion of the population. One cannot assume that the relationship between exposure and effects is linear.

Human Experimentation One way to collect data on toxicity of materials is through experimentation with humans. In general, society does not condone human experimentation, but on occasion, particularly when there is a strong national concern for some disease or illness, society may accept human testing of substances for medical treatment of terminally ill patients who approve. When a pharmaceutical substance appears to have high benefit and relatively little risk as a result of many other tests, the FDA may approve testing in humans. Because there is virtually no opportunity to perform general testing of substances for toxicity on humans, toxicity data must come from other than human tests.

Human Experience Sometimes accidental exposures provide opportunities to compile data on the toxicity of a substance. The exposures may be acute or chronic. In accidental exposures, there is no control over the exposure, so the difficulty is knowing what the exposure level actually was. Researchers must estimate exposure levels and conditions from limited information using epidemiological procedures. (Epidemiology is the study of disease in human populations.) After a pattern of disease appears that could be related to some exposure, further testing may result. For example, workers exposed to certain pesticides exhibited similar disease patterns that stimulated further testing, which ultimately lowered exposure standards and even led to a ban on certain materials.

Animal Studies Most toxicity data come from controlled and replicated animal studies. The physiology of animal species varies from humans, and as one moves farther away from humans in the zoological chain, the meaningfulness of test results is less valid for generalization to humans. However, standard tests and methods for rating toxicity help estimate human effects. Controlled breeding and raising of test species also helps improve reliability and comparability of results.

A problem in toxicity testing involves time. Some substances produce disease in a portion of a population after a long latency period or chronic exposures. To replicate slow exposures or wait for latency periods would be very expensive. As a result, many toxicity test procedures involve high-dose rates. Measures for controlled doses to experimental animal populations are quantities per unit body weight, per unit of skin area, or per unit of volume of inspired air. Toxicity theories assume that the product of the concentration and the time of exposure has a linear or near linear relationship with the effects. This assumption has been the source of much debate.

Studies report toxicity data for animal populations in various units. One unit is lethal concentration (LC), which applies to airborne concentrations. Another unit of measure is lethal dose (LD), which involves ingestion, injection, or other means of applying a substance. Effects are often reported as the portion of the exposed population that dies as a result of the controlled exposure. A subscript indicates the portion that died. For example, LD_{50} means that 50% of a test population died of a particular dose; LC_{10} means that 10% died of an inhaled concentration. The designation "toxic concentration—lethal" is the lowest published lethal concentration. Similarly, "toxic dose—lethal" is the lowest published lethal dose. Other notations in toxicity tables indicate effects on skin, blood, nervous system, muscles, or other tissue and organs. Notations also indicate whether a substance produces irritation or mutagenic, carcinogenic, teratogenic, or other effects.

Microorganism Testing Because animal testing is expensive and time consuming, researchers have developed some short-term tests for chemical toxicity, many of which involve bioassays of microorganisms. Studies monitor the growth patterns of particular bacteria and contrast bacteria exposed to a chemical compared with unexposed samples.

These tests may help screen substances rapidly for particular characteristics. In general, short-term tests have limitations. They do not include variables that animal studies do in the mathematical models for generalizing test results to humans. For example, one of the notable short-term tests for carcinogens is the Ames test. The procedure uses Salmonella and the results involve dose, but not time or duration of exposure. In addition, the Ames test has been criticized for its lack of reliability. It demonstrates high correlations between certain known carcinogens and human experience, whereas correlations between test results for other carcinogens relative to human experience are low.

24-5 CONTROLS

There are three classes of controls for protecting people from exposure to hazardous materials in the workplace:

1. engineering controls
2. work practices and administrative controls
3. personal protective equipment

One should consider these controls in the order presented, as discussed in Chapter 9.

Engineering Controls

Engineering controls include process changes and substitution of nonhazardous substances, enclosing a source, isolation of a worker, and the use of ventilation.

Substitution By replacing a hazardous material with a nonhazardous one, the danger of exposure to a hazardous material can be eliminated. Even a less hazardous material may form a desirable control by substitution. If the proposed alternate material does not perform as well as the original material, substitution may not be a desirable solution.

Isolation Isolation uses a barrier between a source of contaminants and workers. Often, enclosing the process equipment that generates a contaminant provides the barrier. The enclosure usually involves an exhaust ventilation system as well. Sometimes there is a port with built-in gloves that a worker's hands can slip into to allow the worker located on one side of the enclosure to perform some function inside the enclosure. This setup is called a glove box. In other cases, workers are located in an enclosure with a controlled, uncontaminated atmosphere from which they can see an operation and control it remotely. The separation prevents potential exposures to contaminants. Placing workers in an enclosure may not be desirable if the workers must enter the contaminated process area frequently. They may fail to protect themselves as they move from the protected area to the unprotected or to decontaminate them selves when returning from the unprotected area. Another form of isolation is separating hazardous operations from nonhazardous ones.

Ventilation Ventilation is useful for airborne contaminants. There are two types of ventilation for controlling hazardous substances: one is general ventilation or dilution ventilation, and the second is local exhaust ventilation. Chapter 25 gives details on ventilation.

In general ventilation, one moves fresh outside air into the general work space to dilute or displace contaminants. The goal is to keep concentrations at or below allowable levels. There are several limitations for general ventilation:

1. It normally requires movement of large volumes of air.
2. The outdoor air may already be contaminated and not fresh or clean.

3. Heating, cooling, or dehumidifying outdoor air is costly.
4. The general movement may not dilute substances at all locations in a space to keep air quality within limits everywhere.

Local exhaust ventilation requires much smaller volumes of air than general ventilation. Local exhaust systems capture contaminants at or near their source, before hazardous substances reach the breathing zone of people, and moves the air to locations where people will not be present. To avoid violation of air pollution standards or exposure of more people, exhausted air may need treatment to remove and collect contaminants.

Work Practices and Administrative Controls

Work practices and administrative controls include housekeeping procedures, materials handling or transfer procedures, leak detection programs, training, modifying the work, and personal hygiene. Administrative controls may involve several controls organized into programs.

Housekeeping Housekeeping activities include removal of dust accumulation and rapid cleanup of spills. Regular removal of hazardous dust from floors, walls, or other surfaces is important. Otherwise, the material can become airborne and can pose greater danger. Removal should avoid dispersing a material into the air. Therefore, vacuum cleaning equipment that properly traps the contaminants should be used. Sweeping, compressed air, or blowers should not be used to remove dust from surfaces because they will cause material to become airborne. In some operations, spraying water on materials may eliminate sources of dust.

Materials Handling or Transfer Procedures Loading and unloading of materials can cause materials to become airborne, thereby exposing workers to hazardous levels of the materials. For example, transferring liquid into an empty tank truck or car will displace residual or evolving vapors from the container. Pouring or dumping dusts or dusty materials into open containers or on piles may generate a great amount of airborne dust. These transfer operations may require closed transfer systems or exhaust systems to prevent exposures of workers or others.

Another form of control involving materials transfer is use of containers to collect overfill spills or leaking material between transfers. For example, one could place a drip pan under a fill spout for liquid material.

Leak Detection Programs Leak detection may involve visual inspections and automatic sensor devices, as well as scheduled inspections of valves, piping, and other potential sources for leaks. Quick repair will minimize potential exposures. Sensor systems for particular materials can determine if a hazardous material is airborne and can trigger visual or audio alarms. The signal should initate corrective action or the system should automatically shut down a process.

Training Proper training of workers and supervisors is necessary to supplement other controls. OSHA standards and some state right-to-know laws require training workers to understand the hazards associated with materials they may encounter on their jobs and how to protect themselves from those hazards.

Modifying the Work One can reduce the exposure of a person by limiting the duration of exposure. Keeping the exposure time during a day or longer period low by having more workers share an activity will ensure that any one worker remains below the exposure limits. Exposing additional workers may not be an appropriate procedure.

Personal Hygiene Personal hygiene involves cleaning skin that becomes contaminated during normal work activity or as the result of a spill or accident. One should evaluate carefully which soaps, waterless hand cleaners, washing facilities, and emergency showers provide the proper cleaning agents to remove particular contaminants. If there is a possibility for contamination and injury of eyes, there should be emergency eyewash fountains. Workers may need places to change clothes to prevent carrying hazardous materials home or outside a controlled area. People should not eat or drink in areas where there are toxic materials.

Personal Protective Equipment

Use of personal protective equipment may be necessary when adequate engineering controls, work practices, or administrative reforms cannot be achieved. Maintenance workers and those involved in spill cleanup activities usually need personal protective equipment. Other controls may be too expensive or difficult to achieve for such operations. Depending on the hazards associated with certain substances, personal protective equipment may involve eye and face protection, protective clothing, protective creams and lotions, respiratory protection, or other equipment. Chapter 28 discusses personal protective equipment in more detail.

24-6 MEASUREMENT

To determine what chemicals are present in the air, water, or solids, one must collect samples and analyze them. Analysis will also provide data on quantity or concentration of the contaminants. Gases and vapors require different collection and analysis procedures than do particulates. Some methods help determine if a worker's exposure exceeds the 8-hr TWA; others find out if a contaminant is present and how much its concentration varies over time. The kind of assessment needed will vary. There are laboratory instruments intended for highly accurate analysis. There are field instruments for quick assessment of conditions. There are instruments attached to workers (personal samplers or dosimeters) to monitor exposures. Also, there are automatic sensor, analysis, and alarm systems intended to monitor releases and to warn people to evacuate or to correct faulty equipment or conditions. Many of the instruments must be calibrated regularly to ensure accurate assessment. There are a wide range of collection procedures and devices. This discussion is a limited review of collection and analysis equipment.

OSHA and NIOSH have published sampling and analysis procedures appropriate for particular substances.[7] ASTM has standards on instrumentation, sampling, and analytical procedures. ACGIH publishes a book, *Air Sampling Instruments*, and there are many other treatises on the subject. With technological changes in instrument design and features, there are also changes in their use and the methods associated with making assessments.

Sampling for Gases and Vapors

There are short- and long-term sampling devices for gases and vapors. Some short-term samples are grab samples. Short-term samples involve drawing air into an evacuated, contaminant-free container (plastic, glass, or stainless steel) or pumping a sample into an evacuated container or through an impregnated filter paper or gas detection tube. Most often one uses a small hand pump or squeeze bulb.

There are many kinds of glass detection tubes that contain material designed to change color when they react to particular contaminants. This method is called colorimetry. This form of sampling and analysis device gives quick indications of the presence and concentration of substances. The glass tubes are sealed until used. The user breaks the ends off to allow air to pass through the tube and its indicator material. A scale on the tube or the hand pump holder gives a quantitative reading. One must know what substances to test for before selecting the proper indicator tube.

Continuous or long-term samples require more elaborate equipment. Sample times are typically 15 to 30 min. Some systems continually sample many ports or sensors to detect if a leak or release of hazardous material occurs. Portable, powered air-sampling pumps draw air through a variety of collecting devices. They are calibrated so that one knows the volume of air drawn through the collection device. Some collectors contain an absorbent material (charcoal or silica gel) that accumulates the substance. After collection, samples are analyzed in a variety of ways to assess the type and concentration of contaminants.

There are a variety of portable devices that give direct readings of certain gases or vapors. There are oxygen meters, combustible gas meters that indicate the presence of particular flammable gases, and portable infrared analyzers and gas chromatographs for assessing many different materials.

Chemical Analysis

There are many ways to identify a type of contaminant and to assess concentration. The proper method depends on the form of the material, type of material, and collection method used. Colorimetric methods cause a reactive material to produce a color in proportion to the quantity of a substance that is present. Ion exchange methods separate elements by passing a sample through calibrated columns of eluting agents. Gravimetric methods weigh the presence of a substance collected or the product of a reaction. Volumetric methods involve reaction with definite volumes of standard solutions or reagents. Gas chromatography measures the length of time materials take to pass through a column of detector material. X-ray diffraction produces a unique spectrum when a beam of x-rays impinges on a crystalline sample. X-ray fluorescence is a similar technique. Spectroscopy involves affecting a sample with carbon arc, infrared radiation, electron beams, or high-temperature flame. Each spectroscopy process produces a spectrum that gives a unique signature for particular materials.

Sampling for Particulates

Particulates may be liquids or solids, and most often air passes through a collection device to obtain a sample of particulates. Collection may involve filtration, impactors, impingers, or other devices. The method used depends on the information desired and other factors, such as particle mechanics in an airstream.

There are a variety of special filtration devices for air sampling. Impactors involve a sudden change in direction for an airstream. The airborne particulates impact on a surface because they cannot change direction because of their mass. There are single or multi-staged impactors. Impingers move air through a small opening, causing materials to impinge on a plate (or the bottom of a collector tube) immersed in a liquid. The particles become trapped and can be analyzed various ways.

Some other devices are centrifugal separators, electrostatic precipitators, particle sizers, and counters. Centrifugal separators cause air to spin. Because of their mass, the particulates move to the outside of the rotating air column, where they are collected or removed from the column. Electrostatic precipitators place a charge on particulates in an airstream passing through the device. The charged particles move to collection surfaces with an opposite charge and lodge there. Some analysis requires knowing the number of particles per volume of air in a gas stream or the distribution of particles by size. There are several kinds of instruments for obtaining particle size, the number of particulates, or the distribution by size. Some of these instruments can obtain data as air passes through the device.

24-7 CONFINED SPACES

Confined spaces are enclosures having limited means of access and egress. They can be storage tanks, tank cars, pressure vessels, boilers, bins, silos, and similar enclosures that have access through a manhole or door. Open pits, vaults, and vessels with limited ventilation, as well as underground utility tunnels, storm sewers, pipelines, septic tanks, and similar containers are also confined spaces. Some partial enclosures, such as railroad boxcars, can be confined spaces.

A long time ago, miners sent a canary into a mine. If the canary returned, it was assumed that the atmosphere was satisfactory for workers; if the canary did not return, it was assumed the atmosphere was not suitable for workers. Too often, workers are sent into confined spaces and become the canaries that do not return. Today, confined spaces require special procedures to ensure that they are safe before people enter or work in them.

Hazards

There are three main hazards of confined spaces. The first is oxygen deficiency. Oxygen-deficient atmospheres are those with less than 18% oxygen. This reduced concentration can result from other gases mixed in air that reduce the normal 21% of oxygen in the atmosphere. Another way that oxygen deficiencies arise is the presence of heavier-than-air gases that settle in a closed container, especially where there is no opening at the bottom. Heavier-than-air gases also create problems when there is little ventilation and mixing of gases within a confined space. Some confined spaces have oxygen-depleting bacteria, have oxidation processes (such as rusting) that consume available oxygen, or have combustion.

The second hazard of confined spaces is flammable and combustible gases, vapors, or dusts. Sources of heat or spark may ignite these materials, and a fire or an explosion may result. The gases may result from residual fuels, methane produced by decay (anaerobic bacteria), or heavier-than-air vapors that flow into the space.

The third hazard is toxicity. The toxic materials may have direct effects, such as pulmonary paralysis from hydrogen sulfide. They can be asphyxiants, such as carbon monoxide, that interrupt oxygen transport or they can be irritants at very low concentrations and lethal at higher levels.

Another hazard of confined spaces is a pressurized atmosphere that can produce injury when opened. Confined spaces may contain moving parts that can cause injury if external controls are not locked out and tagged out. There also may be hazards from electrical equipment or dangers from ducts, pipes, or drains that connect to sources of hazardous materials.

Controls

Before entry, one must evaluate a confined space for hazards. It should be depressurized, connections to potentially hazardous materials must be isolated and sealed, energy sources must be locked out and tagged out, stored energy must be released or controlled to prevent inadvertent release, and the atmosphere must be tested for oxygen content, toxic materials, and flammable gases and vapors. Atmospheric testing must not be limited to locations near the entry because often there are widely varying conditions resulting from layering of gases.

Ventilation systems for confined spaces can achieve several purposes. They must provide adequate breathable air supplies unless workers wear self-contained breathing equipment. Often confined spaces are vented with elevated oxygen levels to produce breathable mixtures. The ventilation also must reduce flammable hazards to 10% or less of lower flammable limits. The intake for the ventilation system must not take in exhausted contaminants.

If heated processes, such as open flames, welding, and cutting, are used in a confined space, precautions for fire protection and removal of smoke and fumes are necessary. If workers use solvents for cleaning, the hazards of the materials must be assessed and suitable precautions must be taken. Electrical equipment should use low voltage.

Activities in a confined space may create noise, ionizing radiation, or heat or cold hazards. Precautions for these must be in place.

Workers involved inside confined spaces or in support of confined space activities must be trained in the hazards associated with the operations. They must learn what procedures to follow before entry, during occupancy, and in emergencies; they must know rescue procedures; and they must know what protective or rescue equipment is required and how to use it.

There should be at least two workers involved in confined space work, one of whom should be an observer. The observer is the prime rescue person and cannot enter the space without a replacement observer. With proper planning, rescue can be completed without a second person entering the space. Use of lifelines and harnesses or belts is critical.

Before beginning work in a confined space, workers should receive entry permits. A confined space permit system requires the identification of the space as hazardous and includes an evaluation of the potential hazards. Supervisors and safety specialists must each agree and attest that all preentry evaluations and procedures are complete and that the space is ready for safe entry. Work should be thoroughly planned, workers trained, and emergency procedures and equipment in place.

Standards

OSHA has established a standard for confined spaces which require a permit for entry.[8] The standards establishes procedures for determining whether a confined space poses any hazard for which the employer must issue a permit after providing the necessary protection to any workers who may enter it. The American National Standards Institute has a standard on working in tanks and other confined spaces.[9]

EXERCISES

1. A worker is exposed to naphthalene vapor on the job. Based on OSHA permissible exposure limits, what is the allowable concentration for

(a) an 8-hr day?

(b) a 15-min period?

Is there any danger of absorbing the material through the skin?

2. A worker is exposed to silica dust (crystalline quartz). What is the allowable exposure (based on OSHA standards) if the substance is respirable?

3. During an 8-hr day, workers in one plant are exposed to a mixture of three chemical vapors considered to have additive effects: nitrobenzene, 0.3 ppm; ethyl acetate, 100 ppm; 2-butanone, 75 ppm. Is the OSHA exposure standard for the mixture exceeded?
4. A city has an infestation of mosquitos. There is a public fear of meningitis, and demands for the city to take some remedial action grow. A city worker sprays neighborhoods with malathion mixed with kerosene. What dangers, if any, are there for the worker? What are the exposure limits, if any apply?
5. A worker in a pharmaceutical plant helps produce iodine. What OSHA standard applies to this worker for an 8-hr day? Is the standard a time-weighted average (TWA)?
6. Locate an organization that has activities involving confined space entry. After reviewing the OSHA confined space entry standard, develop a written procedure for
   (a) a permit required confined space
   (b) a confined space for which a permit is not required
7. A worker is exposed to methyl formate during an 8-hr shift with the following exposures: 2 hr at 150 ppm, 2 hr at 75 ppm, and 4 hr at 50 ppm. Based on OSHA permissible exposure limits and associated computational procedures, what is the 8-hr time-weighted average limit? Is the exposure for the shift acceptable?

REVIEW QUESTIONS

1. Approximately how many chemical compounds are there? How many have economic value? How many have some inherent hazard? How many have published exposure standards?
2. What federal agency regulates the use of chemicals related to the following:
   (a) outdoor air quality
   (b) water quality
   (c) public transportation
   (d) the workplace
   (e) indoor air quality
   (f) consumer products
3. What do the following acts address or what significant elements do they cover?
   (a) Clean Air Act
   (b) Clean Water Act
   (c) Safe Drinking Water Act
   (d) Federal Water Pollution Control Act
   (e) Marine Protection, Research and Sanctuary Act
   (f) Federal Insecticide, Fungicide and Rodenticide Act
   (g) Resource Conservation and Recovery Act
   (h) Toxic Substances Control Act
   (i) Hazardous Materials Transportation Act

(j) Comprehensive Environmental Response, Compensation and Liability Act
(k) Superfund Amendments and Reauthorization Act
(l) Emergency Planning and Community Right-to-Know Act

4. What are the three main types of hazards for chemicals?

5. What are the two major forms of airborne contaminants?

6. Define the following:
- **(a)** dusts
- **(b)** fumes
- **(c)** smoke
- **(d)** aerosols
- **(e)** mists
- **(f)** gases
- **(g)** vapors

7. What is a latency period for a health effect?

8. Compare acute and chronic exposures.

9. What is the difference between local and systemic effects from chemicals?

10. What is an asphyxiant?

11. What is a nuisance dust?

12. What are some individual differences among people who are exposed to chemicals?

13. What are the following?
- **(a)** pneumoconiosis
- **(b)** carcinogen
- **(e)** mutagen
- **(d)** teratogen
- **(p)** dermatitis
- **(f)** chloracne
- **(g)** conjunctivitis

14. What are the three main routes of entry into the body for chemicals?

15. Name and briefly explain four methods for assessing toxic properties of chemicals.

16. Explain the following:
- **(a)** LD_{50}
- **(b)** LC_{10}
- **(c)** TCL
- **(d)** TDL

17. Define the following related to chemical exposure standards:
- **(a)** PEL
- **(b)** STEL
- **(c)** TWA
- **(d)** TLV
- **(e)** “skin” notation

(f) ceiling value

(g) BEI

18. Name and briefly explain three engineering controls for chemicals.
19. Name and briefly explain six work practices and administrative methods for controlling exposures to chemicals.
20. Why is personal protective equipment a last choice method for controlling exposures to chemicals?
21. Briefly explain the following:

(a) grab sample

(b) colorimetry

(c) long-term sampling for gases and vapors

(d) impinger

(e) centrifugal separator

(f) electrostatic precipitator

NOTES

1 29 CFR 1910.119, Process Safety Management of Highly Hazardous Chemicals.

2 *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, annual.

3 *Federal Register*, Volume 54, No. 12, Book 2, pp. 2329–2984, January 19, 1989.

4 NFPA 704, *Identification of the Hazards of Materials*, National Fire Protection Association, Quincy, MA.

5 29 CFR 1910.1200.

6 *NIOSH Pocket Guide to Chemical Hazards and Other Databases*, U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2002-440, June 2002.

7 See *Federal Register*, Vol. 54, No. 12, Book 2, pp. 2960–2983, January 19, 1989, for recommended procedures. Also see Schlecht, P. C., and O'Connor, P. F., *NIOSH Manual of Analytical Methods*, 4th ed., DHHS (NIOSH) Publication 94-113, and supplements available from the Superintendent of Documents, Washington, DC.

8 29 CFR 1910.146, Permit-Required Confined Spaces.

9 ANSI Z117.1, *Safety Requirements for Confined Spaces.*

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