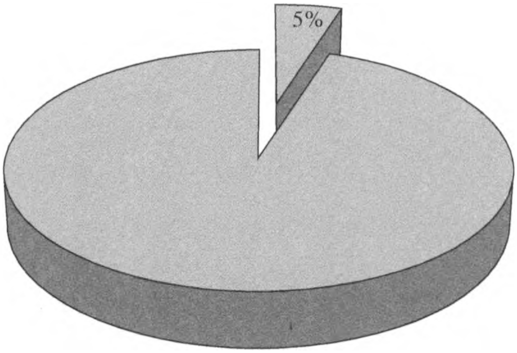
CHAPTER 9

Health and Toxic Substances



Percentage of OSHA General Industry citations addressing this subject

Health hazards carry a great deal of impact because the potential harm to exposed employees is great and the cost of correction of a single health hazard can run into millions of dollars. Industrial hygienists have been saying for many years that health hazards deserve more attention, and in response to this pressure, a shift from safety toward health activities has been evident almost since OSHA began. At first, OSHA did not have a sufficient cadre of qualified health professionals to assess health hazards, so the natural focus was on safety. However, the proportion of health specialists has increased a great deal since the early days of OSHA.

Health hazards will always tend to be more subtle to detect than safety hazards, by the very definitions of *health* and *safety*. As was noted in Chapter 1, health deals with the long-term chronic exposure effects, whereas safety deals with the more obvious acute effects that do their damage immediately.

BASELINE EXAMINATIONS

Almost everyone has taken a preemployment physical examination, but few understand the importance of the physical examination to the overall safety and health program. Each employee's baseline health status is established by this examination.

This status is important in placing the employee in the right job and in detecting any health deterioration due to job exposures. Occupational health exposures are perhaps the most important reason for preemployment physical examinations because of the chronic nature of health hazards. If an employee already has emphysema or some other lung disorder, it is essential that this fact be established at the time of employment. The same can be said of hearing impairment, as will be discussed in Chapter 10.

TOXIC SUBSTANCES

Exposure to toxic substances is the classic "health problem," and this topic will be used to model the entire subject of health and environmental control. The choice of words is important here. For instance, the term *hazardous materials* is sometimes used to refer to toxic substances, but the term *hazardous* is a much more general term that would include such safety hazards as presented by flammable and combustible liquids and explosives. This book follows popular convention, which tends to associate the term *materials* with safety hazards and the term *substances* with health hazards. Chapter 11 deals almost exclusively with safety hazards.

The safety and health manager needs to have a general knowledge of what various types of toxic substances can do to the body. Such general knowledge will be useful in convincing workers and management alike that toxic substances must be controlled for the health of the workers as well as to avoid OSHA citation. The discussion in this chapter will describe some of the various types of toxic substances by considering their effects on the body.

Irritants

Irritants inflame the surfaces of the parts of the body by their corrosive action. Some irritants affect the skin, but more of them affect the moister surfaces, especially the lungs. Even a weak irritant to the upper respiratory tract will be easily detectable by the victim, but irritants to the lower respiratory tract may go unnoticed.

When the irritant is some type of dust, the lung disease that results is called *pneumoconiosis*. This is a general term that includes reactions to simple nuisance dusts as well as fibrosis, a more serious reaction that includes the development of fibrous scar tissue that impairs the efficiency of the lungs. Examples of pneumoconioses include siderosis (from iron oxide dust), stannosis (from tin dust), byssinosis (from cotton dust), and aluminosis (from aluminum dust). The more dangerous fibroses are asbestosis (from asbestos fibers) and silicosis (from silica).

Everyone is familiar with the strong odor of ammonia. Ammonia gas and moisture on the mucous membranes of the body combine to form ammonium hydroxide, a strongly caustic agent. It is easy to understand why this would irritate and injure the delicate tissues of the nose, trachea, lungs, and other parts of the body with which it might come in contact. By similar logic, any of the gases that combine with water to produce acids would be irritants, as would airborne particles of the acids themselves.

Plating operations easily impart acid mists to the air, since the plating tanks are often splashing, hot, and acidic. Particularly offensive is chromic acid mist, which causes an ominous-sounding malady, *chrome holes*. Chromic acid also destroys the nasal septum—the tissue that separates the two nostrils.

Another well-known irritant is chlorine gas, a widely used industrial chemical. Chlorine's halogen relatives, fluorine and bromine, are also irritants, especially fluorine, the strongest of all halogens. Even the soluble salts of fluorine are poisonous. Less well known are those substances that are irritants deep within the lungs, such as the oxides of nitrogen and phosgene. Phosgene is best known as a chemical warfare gas, which is evidence of its toxicity. However, phosgene can also be generated inadvertently in the workplace when chlorinated hydrocarbon solvents are exposed to welding radiation.

Chronic exposure to such irritants over a long period can cause scar tissue to develop in the lungs. Some of these substances do not produce an appreciable immediate irritant effect, but are dangerous in the long run. The most notorious of these scarring agents is asbestos fibers. Coal dust is also a scarring agent. Scarring agents are in the form of tiny solid particles, and their action on the lungs is mechanical, as contrasted with the systemic poisons discussed in the next section.

Systemic Poisons

More insidious than irritants are poisons that attack vital organs or systems of organs, sometimes by toxic mechanisms that are not understood. The chlorinated hydrocarbons common in solvents and degreasers, for example, are blamed for liver damage.

Perhaps the best-known systemic poison found in occupational settings is lead. Lead is disappearing from paint pigments because of its reputation as a poison. An author of this book formerly worked in a tetraethyl lead plant, and decades ago the workers in that plant had a high awareness of what lead can do to the body. Lead attacks the blood, the digestive system, and the central nervous system, including the brain. Autopsies have also shown damage to kidneys, liver, and reproductive systems. Other toxic metals are mercury, cadmium, and manganese. Magnesium, sometimes confused with manganese, is less toxic.

Another important systemic poison is carbon disulfide. Carbon disulfide is unusual in that its hazards are extreme from the standpoint of both safety (fire and explosions) and health. It is widely used in industry as a solvent, a disinfectant, and an insecticide. As a systemic poison, carbon disulfide attacks the central nervous system. Methyl alcohol (methanol), a popular solvent, also is a systemic poison to the central nervous system, but is a much milder poison than is carbon disulfide. Indeed, methanol is even acceptable in small quantities as a food additive! Methyl alcohol is also a fire and explosion hazard.

Depressants

Certain substances act as depressants or narcotics on the central nervous system and as such can actually be useful as medical anesthetics. Unlike the systemic poisons discussed earlier, the effect of the action of depressants on the central nervous system is usually temporary. However, some substances, such as methyl alcohol, are both systemic poisons and depressants. Besides affecting health, depressants can have an adverse effect on safety because they interfere with the concentration of workers who operate machinery.

The most familiar depressant is *ethyl alcohol* (the "drinking" variety of alcohol), sometimes called *ethanol* in industry. Its harmful effects as an industrial hazard are minimal compared with its effects from drinking it. In fact, ethanol's greatest on-the-job hazard is without a doubt from "voluntary ingestion" from bottles brought on the premises by employees. Ethanol is not as toxic as methanol.

Acetylene, the most widely used fuel gas for welding, is a narcotic, but its health dangers are minimal compared with its safety hazard as highly flammable and explosive. Acetylene has been used in medical anesthesia.

Benzene is a very popular industrial chemical used principally as a solvent. Benzene acts as a depressant on the central nervous system, an irritant, and a systemic poison, and has recently been recognized as causing leukemia. In addition, benzene is a dangerous fire and explosion hazard. OSHA has a video that dramatically depicts the hospital-bed testimony of a young benzene worker who is dying from leukemia.

Asphyxiants

Asphyxiants prevent oxygen from reaching the body's cells, and in the general sense, any gas can be an asphyxiant if there is enough of it to crowd out the essential proportion of oxygen in the air. Many people have committed suicide by breathing natural gas, which is essentially methane. However, methane is merely a simple asphyxiant, in that it displaces the proportion of oxygen in inhaled air. Methane can be encountered in industrial environments, as it is a product of fermentation. Other simple asphyxiants commonly encountered are the inert gases such as argon, helium, and nitrogen used in welding.

It may seem incorrect to classify nitrogen as an air contaminant and an asphyxiant when it is the principal constituent (78%) of normal air. However, too much nitrogen will reduce the normal proportion of oxygen (21%) in the air. Any proportion of oxygen less than 19.5% is considered oxygen deficient. Oxygen deficiency is very dangerous, a more serious condition than most people think. Case Study 9.1 is an accident description quoted from federal records of workplace fatalities (Fatal Facts, 1988).

CASE STUDY 9.1

A contract employee was assigned to sandblast the inside of a reactor vessel during turnaround activities at a petrochemical refinery. Instead of relying on the contract company's own air compressors, in accordance with the contractor's policy, the contract foreperson connected the employee's supplied air respirator to a hose containing what he thought was plant air, but was actually nitrogen. Both hoses were identical except for markings at the shutoff valve. The worker entered the vessel, descended to the bottom, placed the respirator hood on his head, and was overcome.

The cause of death in this accident case study was oxygen deficiency, and the irony is that the worker was breathing nearly pure nitrogen, the primary constituent of normal air. Oxygen deficiency is a serious hazard to consider when workers must enter a tank, vessel, or other confined space. Many fatalities occur every year in just this way. OSHA focused on confined space entry in the 1990s, and this topic will be covered in detail in Chapter 12.

In another case study (Case Study 9.2), we find a hazard in which a seemingly innocuous use of nitrogen can lead to trouble.

CASE STUDY 9.2

NITROGEN AS A HAZARD

An electrician found moisture in an electrical box. As a precaution, he decided to attach a nitrogen drop to the box to eliminate the moisture and prevent an accidental ignition due to arcing in the box. The problem was that the nitrogen filled up the box and then quietly propagated through the electrical conduit system to other areas of the plant, including various confined spaces, such as operating line pulpits, mezzanines, crane cabs, and other areas in which operators were present. In one pulpit, workers began to complain of being overly tired. The oxygen level was tested and found to be much below safe minimums. The workers were being quietly asphyxiated by the relatively benign nitrogen that was entering their workspaces through the electrical conduit system. The same thing can happen with argon, a well-known inerting agent for welding operations.

The accident described in Case Study 9.2 took place in a large steel mill. The same or similar situations have developed in other types of plants. Fortunately, in the steel mill case, the plant was alert to safety and health problems. Management took worker complaints seriously and the breathing air was tested, which led to the solution of the problem before something more serious happened. By observing this case study and eliminating the practice that leads to nitrogen propagation throughout the electrical conduit system, future accidents or hazardous situations of this type can be avoided.

Carbon dioxide is one of the most important simple asphyxiants, although in normal quantities it is a harmless constituent of air. Fire is the primary source of dangerous industrial concentrations of carbon dioxide. Carbon dioxide is heavier than air, which causes it to accumulate in low, confined spaces, increasing its hazard potential. Confined spaces have a great deal of hazard potential, not only for carbon dioxide, but for all air contaminants.

The asphyxiants discussed so far are *simple asphyxiants*, essentially nontoxic substances that replace the essential oxygen content in the air. The other type of asphyxiant is the *chemical asphyxiant*, which interferes with the oxygenation of the blood in the lungs or of the body's tissues. The most notorious chemical asphyxiant is carbon monoxide, a substance for which blood hemoglobin has a stronger affinity than it does for oxygen (over 200 times the affinity). The resulting compound, carboxyhemoglobin, is a very stable substance that prohibits the life-critical exchange of oxygen and carbon dioxide by their vehicle, blood hemoglobin.

Added to the dangers of carbon monoxide is the fact that its presence is so difficult to detect without instruments. Although other contaminants which may be found with it may have odors, carbon monoxide itself is odorless. It is also colorless, tasteless, and nonirritating. None of the senses are capable of warning the victim. The best defense against carbon monoxide is to know its source and control worker exposure to it. The most common source is engine exhaust, and that includes gas- or LPG-powered forklifts. Another dangerous source is unvented gas heaters. This is not to say that forklifts and gas heaters should not be used indoors at all, but that personnel should be aware of the danger and take precautions to test the atmosphere.

Another well-known chemical asphyxiant is hydrogen cyanide, an industrial insecticide, but better known as the gas formerly used widely in prison execution chambers. The gas is formed by dropping sodium cyanide pellets into a small container of acid. Some work places have the potential for becoming execution chambers. In a workplace inspection in California, a laboratory was found in which strong acids in glass bottles were stored on shelves located directly above sodium cyanide salts!

Carcinogens

Carcinogens are substances that are known to cause or are suspected to cause cancer. A great deal of attention has been given to carcinogenesis since the advent of OSHA, but the source of the emphasis is not OSHA alone. NIOSH, the Consumer Product Safety Commission (CPSC), and other agencies have focused on carcinogens. Public awareness is high, and many workers and consumers alike are becoming very cautious about exposure to carcinogens. One of the frightening things about carcinogens is that cancer has such a long latency period. Sometimes a lapse of 20 or even 30 years occurs between exposure and the appearance of a cancerous tumor.

New carcinogens are being labeled every year, and many of the substances indicted are very commonly used industrial materials, such as benzene and vinyl chloride. The familiar saying "Everything I do is either illegal, immoral, or fattening" might be modified to include "or causes cancer." So many substances have been indicted by laboratory tests on animals that it is possible that a sort of complacency could be developing in the minds of the public.

Vinyl chloride, mentioned earlier as a type of carcinogen, is extremely dangerous from many aspects. It is a severe explosion hazard, and when it burns, it is very difficult to extinguish. Added to this is the hazard of highly toxic phosgene being liberated during vinyl chloride fires. Acute skin exposures can result in injury from skin freezing due to rapid evaporation of vinyl chloride. Chronic inhalation is now recognized to cause a form of cancer of the liver, angiosarcoma. Vinyl chloride is also believed to be a teratogen, a type of substance that affects a fetus (see next section).

Before discussing teratogens, a distinction should be made between the extremely hazardous vinyl chloride and polyvinyl chloride (PVC). PVC is a type of plastic synthesized by polymerizing the unstable vinyl chloride monomer into the stable polyvinyl chloride polymer. Figure 9.1 illustrates the arrangement of the atoms in the dangerous vinyl chloride monomer and in the harmless and very stable polyvinyl chloride polymer.

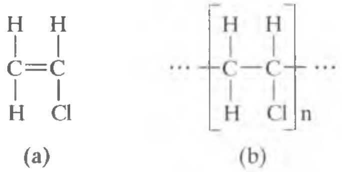


FIGURE 9.1

Comparison of the vinyl chloride molecule with the polyvinyl chloride molecule: (a) vinyl chloride monomer; (b) polyvinyl chloride polymer.

Teratogens

Teratogens affect the fetus, so their toxic effect is indirect. Women should be careful about exposures to certain substances during pregnancy, especially in the first trimester (first 3 months). Teratogens should not be confused with mutagens, substances that attack the chromosomes and thus the species instead of the individual. Teratogens do their damage after conception but before birth, whereas *mutagens* do their damage before conception. Mutagens can affect the chromosomes of either potential fathers or potential mothers.

Several well-known teratogens are alcohol and illegal drugs. Significant attention has been given to substance abuse during pregnancy. Most women know to avoid alcohol during pregnancy. The Centers for Disease Control and Prevention state that fetal alcohol syndrome can include mental retardation, birth defects, abnormal facial features, growth problems, problems with the central nervous system, trouble remembering and/or learning, vision or hearing problems, and behavior problems. According to the National Women's Health Information Center (Pregnancy and Substance Abuse, 2009), illegal drugs may cause underweight babies, birth defects, or withdrawal symptoms after birth.

A tricky legal question is whether an industry can prohibit women of childbearing age from working in jobs in which they may be exposed to teratogens. The question is whether this constitutes sex discrimination. The affirmative contingent says that the teratogens must be controlled by the industry so that pregnant women can have a safe and equal opportunity to work in the same jobs as those offered to men. The negative contingent says that it makes more economic, safety, and social sense to employ women in other jobs during pregnancy.

Routes of Entry

The term *toxic substance* can be considered synonymous with the term *poison*, a word familiar to all of us who were taught as children not to eat or drink poison. Poison is even in our fairy tales, such as "Snow White and the Seven Dwarfs." It may be true that the greatest danger from poisons in the home is from ingestion (swallowing), but on the job, the greatest danger is from breathing. In fact, it has been said that the order of importance of routes of entry into the body for toxic substances on the job is the exact opposite as the order at home, as shown in Figure 9.2.

The various routes of entry into the body for toxic substances are more related than most workers realize. Inhalation of toxic substances results in accumulations on the mucous membranes; mucus is later coughed up, and some of it is inevitably swallowed. Skin contact with toxic materials can also result in ingestion as substances become embedded beneath fingernails and on hands that later come into contact with food. Toxic dusts in the air are also picked up in the hair and are later deposited on the pillow during sleep and thus gain entry into the body indirectly.

Routes	Importance	
of entry	At home	At work
Ingestion	Most important	Least important
Skin contact	Of moderate importance	Of moderate importance
Inhalation	Least important	Most important

FIGURE 9.2

Toxic substances' routes of entry into the body. Note reverse sequence of importance at work versus at home.

From knowledge of routes of entry for toxic substances, it is easy to see the importance of sanitation. Some of the principles of sanitation discussed in Chapter 7 take on more importance when toxic substances are considered. Proper storage of food and the availability of shower and washing facilities may be essential in the control of the quantities of toxic substances entering the worker's body.

One other route of entry into the body should be mentioned before closing this section: the eyes. Although the eyes are not considered a principal route of entry, it should be noted that the eyes are particularly sensitive to toxic substances. Especially with the advent of the hazard of exposure to the HIV virus and AIDS, more attention has been given to the eyes as a route of entry. Examples of hazardous occupations with respect to exposure to HIV through the eyes are dental technicians and dentists.

Air Contaminants

The greatest concern with toxic substances in the workplace is with air contamination, and this is as it should be (as shown in Figure 9.2). Air contaminants take on many physical forms, and most people confuse these forms in everyday language. The safety and health manager should know the difference, for instance, between vapors and fumes. Although air is essentially a combination of gases, the *contamination* of that air can consist of any of the three states of matter: solids, liquids, or gases.

Gases easily contaminate the air because air consists of gases and gases readily mix. The most familiar toxic gas is carbon monoxide. Also dangerous in the industrial environment are hydrogen sulfide and chlorine. Even "harmless" gases, such as carbon dioxide and inert nitrogen, can become dangerous if allowed to accumulate in large quantities so that they become asphyxiants by crowding life-giving oxygen out of the air.

Vapors are also gases, but these substances are normally liquids or even perhaps solids that release small quantities of gases into the surrounding air. Some of our most useful industrial liquids, such as gasoline and solvents, have a strong tendency to release vapors.

Mists are really tiny droplets of liquids, so small that they remain suspended in the air for long periods, as in clouds. Since liquids are heavier than air, they eventually settle out or coalesce into larger droplets, which fall in the manner of rain. Long before that happens, however, mists can be inhaled by the worker. Fine mists are generated as vapors condense into clouds. Coarse mists are produced by splashing or atomizing operations, such as from machine tool cutting oils or from electroplating. Pesticide spray is also usually a mist.

Dusts are recognized as solid particles. Technically speaking, dust particles range in size from 0.1 to 25 μm (0.000004 to 0.001 inch) in diameter. Everyone is exposed to dust, and some dust is relatively harmless. Dangerous dusts include asbestos, lead, coal, cotton, and radioactive dusts. Silica dust from grinding operations is also becoming recognized as a hazard, although ordinary earth dust is principally silica. Asbestos dust particles are fiber shaped rather than round, which contributes to their hazard.

Fumes are also solid particles, but are generally too fine to be called dusts. Actually, the sizes for classifying fume particles and dusts overlap, as can be seen in Figure 9.3. While dust particles are typically finely divided by mechanical means, fumes are formed by the resolidification of vapors from very hot processes such as welding. Chemical reactions can also produce fumes, but gases and vapors, although

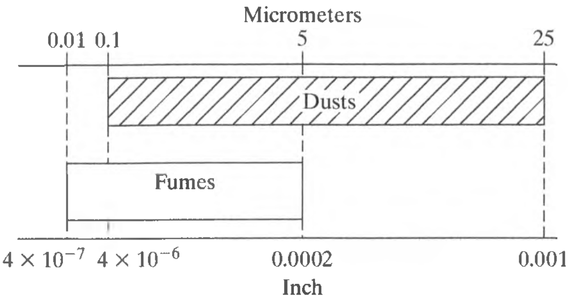


FIGURE 9.3

Comparison of dust and fume particle sizes (not to scale).

also produced by chemical processes, are not to be confused with fumes. Metal fumes are the most dangerous, especially those of the heavy metals.

Particulates make up a general classification that includes all forms of both solid and liquid air contaminants (i.e., dusts, fumes, and mists). Particle sizes thus can vary greatly; some are visible to the naked eye, but most are not. The tiniest invisible particles are actually submicroscopic large molecules, such as complicated organic gas molecules.

It is probably already obvious that industry and technology do not eliminate exposures to toxic substances; they merely control these exposures to keep them within acceptable levels. It is both naïve and unnecessary for the safety and health manager to adopt a strategy of complete elimination of worker exposure to toxic substances. There is no known poison to which a human being cannot be exposed without significant harm, provided that the exposure is tiny enough and distributed over a long-enough interval for the body to assimilate or counteract it. On the other hand, even the mildest of poisons can become lethal if the worker is constantly exposed to it in massive doses—the kind that can be found in industrial exposures, more so than in any other environment.

Threshold Limit Values

Since no poison is lethal in small enough doses, and all poisons are lethal in large enough doses, no clear-cut line separates the harmful from the benign worker environment. However, some line has to be drawn to serve as a basis for action to control toxic substances. Particularly with regard to airborne contaminants, it becomes necessary to identify some levels of concentration below which one need not worry about worker exposures. Thus, the term *threshold limit value* (TLV) evolved and refers to the level of concentration below which the worker could be exposed to during the entire workday without significant harm. The TLV varies drastically with the toxicity of the contaminant, of course, and every toxic substance has its own TLV.

So far, this discussion of TLVs is in a generic sense, and thus every toxic substance has a TLV even if it is unknown and even if no one knows that the particular substance is toxic. However, for *known* toxic substances, there is a *listed TLV*, which is a value agreed on by a committee of the American Conference of Governmental Industrial Hygienists (ACGIH) and is listed in the *TLV booklet*. When the abbreviation TLV is used instead of spelling out the words *threshold limit value*, the ACGIH listed value is usually the meaning intended.

Just because a committee decides on the TLV for a given substance, it does not mean that employers must control worker environments to comply with that level.

Some TLVs are based on hard scientific data and are very robust criteria for action. Others are based on much more sketchy data, and thus professional judgment is necessary to determine the actions that should be taken to control the worker environment. The TLVs themselves may change from year to year as more information becomes available. Thus, to be strictly correct, one should refer to the date of the list when naming a given TLV, for example, "the 2003 TLV for carbon monoxide was . . . ." Incidentally, when TLVs change, their levels usually decrease as new information about hazards is uncovered.

Recommended Exposure Levels

NIOSH, too, has a role in recommending exposure levels for possible adoption by OSHA as mandatory limits. Although OSHA relies primarily on the ACGIH list of Threshold Limit Values for initiating the promulgation process for new exposure limits, Congress set up the NIOSH agency to perform research and make recommendations to OSHA for new standards. NIOSH has devised a designation "Recommended Exposure Levels" (RELs) for suggested limits of exposure to substances it considers harmful. However, until OSHA adopts the REL as a mandatory limit for exposure to a particular substance, employers are not obligated to adhere to the REL.

An example substance for which NIOSH has taken employee exposure seriously is metal working fluid (MWF). When machining operations are performed to shape or cut metal product components, "cutting oils" (MWFs) are used to lubricate the interface between the tool and the material. The MWFs also cool the process and assist in removing the chips from the work. Later the oily metal components are often subjected to a degreasing process to remove the oils before final assembly. Invariably the oils become airborne during the machining and degreasing processes. Various types of oils are used for MWFs, some natural and some synthetic. Research is still underway to determine what harm these oils do to the worker when exposed. NIOSH has taken the position that atmospheric exposure above 0.5 mg/m^3 is harmful and has set an REL at that level for a time-weighted average over a worker shift. The concept of controlling averages for a full shift will be explained later in this chapter. Although NIOSH issued the REL for MWFs in 1998, OSHA still had not promulgated a corresponding mandatory limit as of 2008. As explained in Chapter 4, in the promulgation process OSHA must justify the rule to the public, giving all interested parties an opportunity to support or object to the rule, considering not only the harmful effects of the hazard, but also the cost of complying with a mandatory rule.

Permissible Exposure Limits

The focus of this book is on what enforcement agencies require, not what ACGIH lists or what NIOSH recommends, but the three are definitely related. At OSHA's beginning, when it was permitted to adopt national-consensus standards without formal promulgation, the agency adopted hundreds of TLVs, most of which represented the TLV levels published in 1968 by ACGIH. Since the OSHA-published list assumed a regulatory character, the term *permissible exposure limit* (PEL) was used to distinguish between the OSHA-prescribed level and the ACGIH term *TLV*. For the most part, PELs have remained static, as OSHA has had difficulty getting the public to accept stricter and stricter levels of control. However, the TLVs remain dynamic, as ACGIH continues to revise the list whenever the collective professional judgment of the committee determines that a new TLV should be added to the list or an old one adjusted, usually downward.

Over the years, the disparity between the OSHA PELs and the ACGIH TLVs grew to such proportions that OSHA decided on a bold plan to revise all of the PELs in a single promulgation, instead of painstakingly revising each in substance-specific rulemaking. Thus, in 1989, OSHA added 164 new listings to the air contaminants list and at the same time tightened the PELs on 212 substances that were already on the list. OSHA laid its groundwork carefully because behind each of the new PELs (which they labeled *final limits*) were backup *transitional limits* at the old PEL levels. The transitional limits were to remain in effect during a specified implementation period. Then as a legal safety measure, OSHA added a footnote that retained the transitional limits in case opponents of the new PELs were able to mount a court challenge and strike down the new rules.

Because this move was so comprehensive and revolutionary, opponents to the new PELs seemed unable to cope with so many changes at once—so the strategy seemed to work. However, the victory was an illusion, because nearly four years later, in 1992, the Eleventh Circuit Court of Appeals vacated the entire PEL list revision, in what Labar (Labar, 1993) said was "perhaps the agency's biggest defeat in its 22-year history." A stunned OSHA was expected to appeal to the U.S. Supreme Court, but in 1993, it announced that the U.S. Solicitor General would not attempt to appeal. OSHA was compelled to prove to the public that each new PEL and each tightening of each existing PEL would be justified. OSHA had no choice but to return to its original list of 264 PELs adopted by the national-consensus process in 1971.

The entire table of PELs, as revised back to its earlier state in 1993, is included in this book. as Appendices A.1, A.2, and A.3, which correspond to OSHA's designations Z.1, Z.2, and Z.3, respectively. Appendix Table A.1 is the main table and contains most of the PELs, listed alphabetically by substance name, with *CAS No.* (Chemical Abstracts Service) for reference. A common mistake is to ignore the hazard when the substance is not listed in the main table, but a few of the most hazardous and frequently encountered substances in industrial exposures are those found in the second table, Appendix Table A.2. This table has its origins in a version formerly (prior to OSHA) published by ANSI for certain substances. Appendix Table A.3 is for mineral dusts, which are considered separately because solid particles are sampled and measured by different means than are toxic gases, mists, and vapors.

MEASURES OF EXPOSURE

The tables of Appendix A.1 are long and complicated, and the many columns specified for each toxic substance warrant explanation. The reason for this complication is that it is difficult to measure levels of contamination of the atmosphere in the workplace. The problem is compounded by the various physical states—solid particles, liquid droplets, mists, gaseous molecules—in which the contaminant can exist in the atmosphere.

Further, the medical data incriminating a particular poison may point to danger in a single short-term exposure or may suggest deleterious effects from long-term exposures.

Time-Weighted Averages

The most popular measure of air-contaminant exposures is the *time-weighted average* (TWA). The PELs are understood to be TWAs unless otherwise specified. The TWA is a computed weighted-average concentration over an 8-hour shift. Such a calculation recognizes that concentrations of air contaminants change over time and that it is sometimes permissible for a workplace concentration to exceed the permitted value if at other times during the workday the exposure is sufficiently lower than the permitted value, such that the average exposure for the workshift is lower than the specified level.

The following formula is used to compute the TWA:

$$E = \frac{\sum_{i=1}^{n} C_i T_i}{8} = \frac{C_1 T_1 + C_2 T_2 + \cdots + C_n T_n}{8}, \tag{9.1}$$

where E = equivalent 8-hour time-weighted-average concentration
C_i = observed concentration of the contaminant in time period i
T_i = length of time period i
n = number of time periods studied

The calculation will now be illustrated in Case Study 9.3.

CASE STUDY 9.3

Calculate the 8-hour, full shift TWA for the concentrations shown.

Time period, i	Observed concentration, C_i	Length of period, T_i (hours)	$C_i \times T_i$
1	2	$1\frac{1}{2}$	3
2	4	$2\frac{1}{2}$	10
3	7	1	7
4	5	2	10
5	3	1	3
Total		8	$33 = \sum_{i=1}^{5} C_i T_i$

Solution

$$E = \frac{33}{8} = 4.125$$

The Case Study 9.3 calculation shown is quite adequate if there is only one toxic substance present in the industrial atmosphere. However, mixtures present a different problem. Suppose, for instance, that an industrial atmospheric TWA concentration of nitric acid was barely below the specified PEL of 5 mg per cubic meter. Suppose further that the same atmosphere showed TWA concentrations of just under the prescribed limits of 1 mg per cubic meter for sulfuric acid and 25 mg per cubic meter for acetic acid *at the same time*. Taken separately, none of these three acid concentrations violates the standard, but common sense says that the three concentrations present at the same time are dangerous.

The synergistic effect of combinations of toxic substances is a complicated subject. Most research has concentrated on direct effects of substances acting alone. Some mixtures of contaminants would tend to neutralize each other and be beneficial. For instance, caustics mixed with acids may produce benign salts. In the example just described, however, the three acids working together are bound to have a combined effect. For some mixtures, the combined effect may be far worse than the sum of the individual effects.

OSHA takes a moderate approach by requiring simple combinations of toxic substances to be considered, but generally ignores the complex synergistic effects. The method is to sum the ratios of concentrations of each substance to its own PEL. The resulting sum should not exceed unity. The following formula summarizes the computation:

$$E_m = \sum_{i=1}^{n} \frac{C_i}{L_i} = \frac{C_1}{L_1} + \frac{C_2}{L_2} + \cdots + \frac{C_n}{L_n}, \tag{9.2}$$

where E_m = calculated equivalent ratio for the entire mixture
C_i = concentration of contaminant i
L_i = permissible exposure level (PEL) for contaminant i
n = number of contaminants present in the atmosphere

E_m is not permitted to exceed 1. The calculation is demonstrated in Case Study 9.4.

CASE STUDY 9.4

An industrial process produces exposure in accordance with the following table:

	Nitric acid	Sulfuric acid	Acetic acid
Contaminant, i	1	2	3
Concentration, C_i	4	0.9	22
Limit, L_i	5	1	25

Solution

$$E_m = \sum_{i=1}^{3} \frac{C_i}{L_i} = \frac{4}{5} + \frac{0.9}{1} + \frac{22}{25} = 2.58$$

Since 2.58 > 1, the concentration of the mixture exceeds the PEL, even though the individual PELs are not exceeded.

Ceiling Levels and STELs

Most of the PELs listed in the main table (Appendix A.1) are to be considered TWAs, but for some substances, the concern is for short-term exposures. A "ceiling" value, sometimes abbreviated *C* or *MAC* for *maximum acceptable ceiling*, is an exposure limit that should *never* be exceeded. Another convention is to specify an *STEL, short-term exposure limit*, recognizing the danger of acute exposures, but allowing short excursions above a level that on an 8-hour-shift basis would clearly be hazardous. The STEL states a maximum concentration permitted for a specified duration, usually 15 minutes. For instance, Table A.2 lists the following PELs for toluene:

TOLUENE

TWA	200 ppm
MAC	300 ppm
STEL	500 ppm for 10 minutes

Note that the STEL for toluene is much higher than the MAC. One would think that the STEL would lie somewhere between the TWA and the MAC, but the standards consistently list STELs higher than MACs. This suggests that if the exposure duration is shorter than the duration specified by the STEL, there is no limit to the allowable concentration! This seems to be a contradiction of the definition of the MAC, but in reality it is not feasible to measure the concentration for so short a time period except for "grab samples," a very unreliable method of measurement. Indeed, even the STELs are often impractical to check with current state-of-the-art instruments, so STELs are sometimes ignored by industry and enforcement officials alike.

The bottom line takeaway is that measurement in terms of averages can be tricky. One can be exposed to 400 ppm of toluene in one hour and 100 ppm over the next two. The time-weighted average for the three hours is still at the PEL of 200 ppm. Therefore, OSHA had to determine a way to put limits around concentration exposures for some chemicals even though a TWA might be at or below the PEL. The ceiling here would ensure that even though 400 ppm for an hour would work for the TWA, it exceeds the MAC of 300 ppm and is not permitted due to the dangers such a concentration at any time might present. Recognizing the STEL, OSHA does make some small exceptions where an exposure of 500 ppm or less might be allowed, but only for a very short period of time, in this case 10 minutes.

Units

Regardless of the type of limit against which the exposure is being measured, the analyst must be concerned with the units of the measure. For most of the substances in Appendix A.1, the table lists for each limit a pair of values, which are really two different measures of the same limit expressed in different units. Gases are usually more conveniently measured by volume, and thus the first column, labeled p/m (parts per million), is usually used for these substances. Liquids and some solids are more conveniently measured by weight, and thus the second column, labeled mg/m^3 (milligrams of particulate per cubic meter), is preferred for these substances. If the molecular weight of the substance is known, conversion can be made by using the formula

$$\mathrm{p/m} = \frac{\mathrm{mg/m^3} \times 24.45}{\mathrm{MW}},$$

where MW is the molecular weight of the substances. Parts per million is usually abbreviated ppm rather than p/m.

Action Levels

One other level, the action level (AL), deserves mention. If control measures are taken only after TLVs are exceeded, it may be too late to prevent serious harm and also perhaps too late to prevent citation by authorities. ALs are somewhat of a preventive measure, which anticipates the problem before TLVs or other measures are exceeded. ALs are set arbitrarily at one-half PEL. A great deal of statistical and instrumentation variation prevents precisely accurate surveys. The difference between the AL and the PEL provides a margin for error to ensure that worker exposures do not exceed the PEL, by implementing controls before PELs are reached.

STANDARDS COMPLETION PROJECT

The preceding sections have described the method of enforcement of, and compliance with, standards prescribed for hundreds of toxic substances covered by PELs listed in tabular form. This is OSHA's general approach to air contaminants and applies to a large majority of substances that can be found in the workplace environment. However, for a few substances, OSHA has taken a more comprehensive approach by issuing detailed standards, each of which is devoted to the control of one particular hazardous substance. The standards for these substances have been formulated as a series, and all the standards in the series have been issued several years after the passage of the OSHA act. This means that the standards were scrutinized by the public promulgation procedures and survived the controversy of opposing factions. Several of the substances experienced stormy promulgation, including the invoking of "emergency temporary" promulgation procedures and subsequent court challenges. Much of the background research to justify the issuance of these separate standards for individual substances was conducted by NIOSH. The effort has been called the *standards completion project* because it has been envisioned by some that every toxic substance should eventually have its own unique standard instead of simply being included in a list of TLVs. A list of standards completed, along with the associated PEL for each substance covered, appears in Table 9.1. As the table shows, some of these substances are extremely hazardous and no PEL is specified. For these substances, the standard is very specific regarding handling procedures to be followed, personal protective respirators to be used, and other precautionary measures.

OSHA standard 1910.130 has to do with bloodborne pathogens and is not included in Table 9.1. There is no question that bloodborne pathogens are toxic, but the standards completion list refers to toxic substances that were originally listed in the air contaminants list but for which full standards have since been promulgated. The standard for bloodborne pathogens does not belong in the list because it was not included in the

TABLE 9.1 OSHA Standards for Specific Toxic Substances ("Standards Completion Project")

Substance	Permissible exposure limit (PEL) TWA
1910.1001 Asbestos	0.1 fiber/cm^3 (longer than 5 μm) Ceiling: 1 fiber/cm^3 (longer than 5 μm)
1910.1002 Coal tar pitch volatiles	0.2 mg/m^3
1910.1003 13 Carcinogens (4-Nitrobiphenyl, etc.)	Extremely hazardous. Refer to standard
1910.1004 α-Naphthylamine	Carcinogen (see 1910.1003)
1910.1005 (Reserved)	
1910.1006 Methyl chloromethyl ether	Carcinogen (see 1910.1003)
1910.1007 3,3-Dichlorobenzidine (and its salts)	Carcinogen (see 1910.1003)
1910.1008 bis-Chloromethyl ether	Carcinogen (see 1910.1003)
1910.1009 β-Naphthylamine	Carcinogen (see 1910.1003)
1910.1010 Benzidine	Carcinogen (see 1910.1003)
1910.1011 4-Aminodiphenyl	Carcinogen (see 1910.1003)
1910.1012 Ethyleneimine	Carcinogen (see 1910.1003)
1910.1013 β-Propiolactone	Carcinogen (see 1910.1003)
1910.1014 2-Acetylaminofluorene	Carcinogen (see 1910.1003)
1910.1015 4-Dimethylaminoazobenzene	Carcinogen (see 1910.1003)
1910.1016 *N*-nitrosodimethylamine	Carcinogen (see 1910.1003)
1910.1017 Vinyl chloride	1 ppm STEL 5 ppm/15 minutes
1910.1018 Inorganic arsenic	10 μg/m^3
1910.1024 Beryllium	0.2 μg/m^3
1910.1025 Lead	50 μg/m^3
1910.1026 Chromium (VI)	5 μg/m^3
1910.1027 Cadmium	5 μg/m^3
1910.1028 Benzene	1 ppm STEL: 5 ppm/15 minutes
1910.1029 Coke oven emissions	150 μg/m^3
1910.1030 Blood-borne pathogens	Exposure control plan requirement. Refer to standard
1910.1043 Cotton dust	200–750 μg/m^3 (depending on process; see standard for details)
1910.1044 1.2-Dibromo-3-chloropropane	1 ppb (parts per billion)
1910.1045 Acrylonitrile	2 ppm ceiling: 10 ppm/15 minutes
1910.1047 Ethylene oxide	1 ppm excursion: 5 ppm/15 minutes
1910.1048 Formaldehyde	0.75 ppm STEL: 2 ppm/15 minutes
1910.1050 Methylenedianiline	10 ppb STEL: 100 ppb/15 minutes
1910.1051 1,3-Butadiene	1 ppm STEL: 5 ppm/15 minutes
1910.1052 Methylene chloride	25 ppm STEL: 125 ppm/15 minutes
1910.1053 Respirable crystalline silica	50 μg/m^3

Source: OSHA Safety and Health Standards (29 CFR 1910).

original air contaminants list, and indeed, the principal exposure to bloodborne pathogens is not through the air.

DETECTING CONTAMINANTS

It is nice to have a list of toxic substances with permissible exposure levels for each, but more is needed to determine whether a problem exists. There are simply too many substances on the list to keep tabs on all possibilities. Safety and health managers need to have knowledge of the processes within their plants so that they know where to look or at least whom to ask. Air sampling and testing are the way to determine concentrations as accurately as possible, but before the test is done, some suspicion of possible contamination needs to be provided by other evidence.

One of the most common ways a potential problem is first detected is by the sense of smell. People seem to believe that they can smell an air contaminant, and they *usually* can smell either the toxic substance or some odorous agent that may accompany toxic substances. However, sense of smell is not enough to detect some of the most dangerous contaminants. The most notorious example is carbon monoxide. But carbon dioxide, nitrogen, and methane are also essentially odorless and can be dangerous simply by displacing the oxygen in the air. Some readers will question the statement that methane is odorless because they know that methane is the principal ingredient in natural gas. However, the odor in "natural" gas is from a stenching agent deliberately introduced as a safety precaution so that people can detect leaks by sense of smell. Even hydrogen sulfide, a gas that is both dangerous and has a very strong rotten odor, cannot be detected reliably by sense of smell. The odor is so foul that it quickly overcomes the olfactory system, and victims begin to block out the smell sensation so that they are not aware of the degree of their exposure.

Another approach is to examine technical literature to determine which industries might release what substances. Table 9.2 provides some information from NIOSH literature regarding possible contaminants in various industries.

TABLE 9.2 Potentially Hazardous Operations and Air Contaminants

Process type	Contaminant type	Contaminant examples
Hot operations		
Welding	Gases (g)	Chromates (p)
Chemical reactions	Particulates (p)	Zinc and compounds (p)
Soldering	(dust, fumes, mists)	Manganese and compounds (p)
Melting		Metal oxides (p)
Molding		Carbon monoxide (g)
Burning		Ozone (g)
		Cadmium oxide (p)
		Fluorides (p)
		Lead (p)
		Vinyl chloride (g)

Process type	Contaminant type	Contaminant examples
Liquid operations		
Painting	Vapors (v)	Benzene (v)
Degreasing	Gases (g)	Trichloroethylene (v)
Dipping	Mists (m)	Methylene chloride (v)
Spraying		1,1,1-Trichloroethylene (v)
Brushing		Hydrochloric acid (m)
Coating		Sulfuric acid (m)
Etching		Hydrogen chloride (g)
Cleaning		Cyanide salts (m)
Dry cleaning		Chromic acid (m)
Pickling		Hydrogen cyanide (g)
Plating		TDI, MDI (v)
Mixing		Hydrogen sulfide (g)
Galvanizing		Sulfur dioxide (g)
Chemical reactions		Carbon tetrachloride (v)
Solid operations		
Pouring	Dusts	Cement
Mixing		Quartz (free silica)
Separations		Fibrous glass
Extraction		
Crushing		
Conveying		
Loading		
Bagging		
Pressurized spraying		
Cleaning parts	Vapors (v)	Organic solvents (v)
Applying pesticides	Dusts (d)	Chlordane (m)
Degreasing	Mists (m)	Parathion (m)
Sandblasting		Trichloroethylene (v)
Painting		1,1,1-Trichloroethane (v)
		Methylene chloride (v)
		Quartz (free silica, d)
Shaping operations		
Cutting	Dusts	Asbestos
Grinding		Beryllium
Filing		Uranium
Milling		Zinc
Molding		Lead
Sawing		
Drilling		

Source: NIOSH (Occupational Diseases: A Guide to Their Recognition, 1951).

Yet another approach is to analyze the processes within the plant to determine potential leaks into the industrial atmosphere. Such an analysis can become quite technical and involves not only an understanding of the machines, pumps, valves, sumps, and tanks, but also a knowledge of the materials used, quantities, intermediate phases, volatilities, and other characteristics that affect the amount of contaminant that becomes airborne. A chemical engineering qualitative flow process chart (see also Chapter 6) and perhaps a quantitative flow process chart may be necessary to determine whether air-contaminant potentials are present. The safety and health manager should not hesitate to involve a chemical engineer in the analysis of potential air contaminations. A technical analysis at this phase may preclude a lot of expensive and laborious sampling experiments later.

Measurement Strategy

Once the existence of an air-contamination risk has been determined, a procedure is needed to go about taking samples, measuring employee exposures, and instituting controls. NIOSH recommends a strategy for this purpose, which is displayed in the form of a decision chart in Figure 9.4.

Measurement Instruments

Federal regulation by both OSHA and EPA of permissible exposure levels for toxic substances in the atmosphere has stimulated the electronics and instrumentation industries to develop new and more precise instruments for determining concentrations. Interest in parts per million is shifting toward closer scrutiny to detect parts per *billion*.

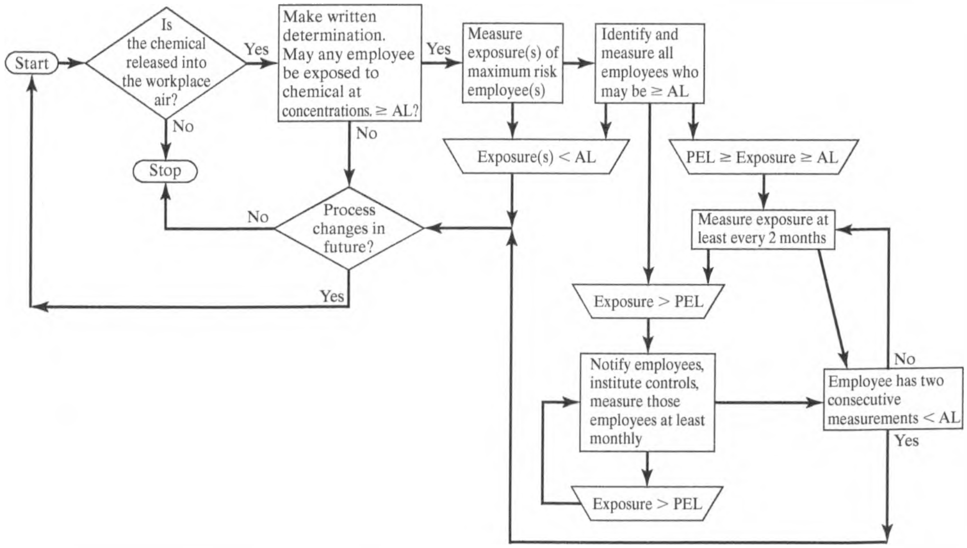


FIGURE 9.4

NIOSH exposure measurement strategy. Each individual substance's health standard should be consulted for detailed requirements: AL, action level; PEL, permissible exposure limit.

Such demands are pressing the physics of the instruments, which can result in large-scale inaccuracies.

With such demands by high technology on atmospheric measurement devices, one would think that air-contamination monitoring would be a new field. However, historically there have been other, more crude means for monitoring breathing air. Animals formerly were used to test for toxic gases or oxygen deficiency. A canary or a mouse in a cage was often carried into mines. If the animal died, the workers were alerted to the hazard. A flame safety lamp was used to test for oxygen deficiency; the flame would die if the oxygen proportion in the atmosphere was too low. A brighter burning lamp was supposed to be an indication of the presence of methane.

These methods were crude, but they did provide some essential indications—for *acute* exposures. With the recognition of threshold limit values and the rise in importance of chronic exposures, the canary test and the flame test became totally inadequate. By the time the canary developed cancer or scarred lung tissue, the workers would also be victimized. Furthermore, animal life spans are too short to deal with the chronic effect to which humans might be susceptible.

Today, there are basically four approaches to measuring air-contaminant exposures:

1. Direct-reading instruments
2. Sampling with detector tubes
3. Sampling with subsequent laboratory analysis
4. Dosimeters

For a few commonly encountered problems, such as oxygen deficiency and natural-gas leaks, devices have been invented that are capable of metering and registering actual concentrations on a display such as a digital readout. Such a direct-reading instrument is sometimes essential for confined space entry when it is necessary to obtain an on-the-spot reading to determine whether an atmosphere is safe from dangerous acute exposures. So convenient are the direct-reading instruments that instrument manufacturers are constantly trying to press the frontiers of physics to devise and patent new instruments for measuring concentrations of as many varieties of air contaminants as possible.

Less precise than direct-reading instruments, but still feasible for on-site assessment of existing concentrations, is the drawing of a sample of the atmosphere through the "detector tube" that contains a chemical that reacts to the suspected contaminant if present. The procedure is to use a hand bellows pump to draw an air sample of known volume through a glass tube that contains a reagent that changes color in the presence of the target contaminant. Both qualitative and quantitative determinations are possible because the length and intensity of the color band are related to the quantitative concentration of the contaminant in question. Sometimes such tubes are used for quick screening for potential problems, with subsequent sampling and laboratory analysis for exact quantitative measurement. Case Study 9.5 serves to demonstrate the method of using a detector tube to reveal an air contaminant, in this case acetaldehyde.

CASE STUDY 9.5

DETECTOR TUBE TEST

A detector tube is used for testing atmospheric concentrations of acetaldehyde. The following specifications apply to this tube:

Standard measuring range	100–1000 ppm
Number of strokes	20
Standard deviation	±15–20%
Color change	Orange to brownish green

The problem is to determine whether this detector tube can be used to test for the PEL or AL for acetaldehyde.

Solution

Appendix A.1 reveals that the PEL for acetaldehyde is 200 ppm. This concentration is within the range of sensitivities for the tube specified. The tube is also capable of detecting concentrations of 100 ppm, which is the AL for acetaldehyde. The method is to snap off the ends of the glass tube and attach it in-line to a flexible tube attached to a pump. The pump is actuated for 20 strokes. The color band that appears in the tube reveals the approximate concentration of acetaldehyde. There is some error associated with the experiment, and other petroleum hydrocarbon impurities can sometimes contaminate the results. Still, the test is widely used to assess suspected problem areas.

For more obscure contaminants and for rarer concentrations there is no choice; sampling devices and laboratory analysis must be used. Either these devices pump a prescribed quantity of air past a filter or a sorbent that collects the contaminant, or they merely collect a precise volume of the air itself. The filter, the sorbent, or the air sample is then sent to a laboratory for analysis.

Dosimeters are the most convenient device of all, especially for gathering TWA data. A dosimeter is a small collector worn on the worker's body or clothing and that collects a time-weighted-average exposure over a specified time period, such as a full shift. Unfortunately, accurate dosimeters are still beyond the state of the art for most toxic substances.

Nanotechnology

The twenty-first century has seen increased attention to nanomanufacturing that deals with particles on the nanometer scale (10^{-6} mm). On this scale there is speculation about manipulating matter on the molecular or atomic level. Nanotechnology, or "nanotech," offers immense potential in terms of applications in vital fields, such as energy, medicine, and electronics. At the same time nanotech opens the door to a new paradigm of concern for worker safety and health and raises questions about how these tiny particles might propagate throughout the body. Another concern is for the fibrous nature of some nanoparticles. The dangers of asbestos fibers are well known. Might it be possible that nanofibers are even more dangerous than asbestos fibers in leading to lung diseases such as mesothelioma? For instance, an example nanoparticle is the carbon nanotube. Nanotubes have very large length-to-diameter ratios on the order of from 10,000,000 to 1 to 40,000,000 to 1. Compare this ratio with asbestos fiber aspect ratios of 3 to 1 to 10 to 1. Figure 9.5 is an artist's conception of a comparison of asbestos fibers with carbon nanotubes. Although such a particle comparison has never been seen under a microscope, the artist's conception is based upon known ratios of size and length-to-diameter ratios. It is true that both particles are fibers, but considering the enormous disparity in size and length-to-diameter ratios, do the hazard mechanisms bear any resemblance at all? In truth, no one knows as of early twenty-first century science, but the safety and health manager can be sure that the scientists are at work trying to reach logical conclusions, supported with nanotech research studies. It is possible that carbon nanotubes will be found to be even more hazardous than asbestos fibers or possibly not dangerous at all, so the wise safety and health manager will keep abreast of new scientific developments in this field.

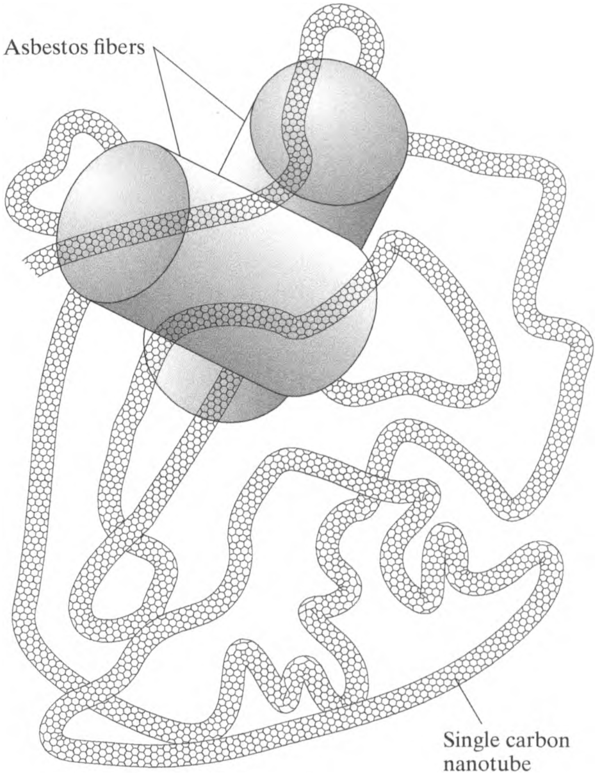


FIGURE 9.5

Artist's conception of a comparison between asbestos fibers and carbon nanotubes.

Exposure Comparisons

Before leaving the subject of exposures to toxic contaminants, it is appropriate to put the whole subject in perspective by comparing the levels of exposures due to industrial pollution and those encountered in our everyday personal lives. The focus in the closing decades of the twentieth century was on the outdoor pollution of the environment by industrial sources of emission. The focus in the twenty-first century may well be on indoor pollution—not necessarily only that within factories, but also in our homes and everyday environment. Researchers Ott and Roberts (Ott, 1998) have concentrated, not on the *emissions* of highly toxic substances, but on the *levels* to which humans are exposed to such substances in their daily activities. Some of their conclusions have been surprising:

> Most citizens were very likely to have the greatest contact with potentially toxic pollutants not outside but inside the places they usually consider to be essentially unpolluted, such as homes, offices and automobiles. The exposures arising from the sources normally targeted by environmental laws—Superfund sites, factories, local industry—was negligible by comparison.
>
> Even in the New Jersey cities of Bayonne and Elizabeth, both of which have an abundance of chemical processing plants, the levels of 11 volatile organic compounds proved much higher indoors than out. (Concentrations of the other volatile compounds tested were found to be insignificant in both settings.) The chief sources appeared to be ordinary consumer products, such as air fresheners and cleaning compounds, and various building materials.

This chapter used benzene as an example of a toxic substance associated with serious health risks such as leukemia. Benzene is of such concern that it is one of the few contaminants for which comprehensive standards have been promulgated in the OSHA "standards completion project." However, research by Wallace (Wallace, 1995) has shown that it is not industrial, but personal, exposures to benzene that are responsible for the major portion of the exposure. According to his calculations, 45% of the total U.S. exposures to benzene are from smoking (or breathing smoke exhaled by others)! Another 36% are from inhaling gasoline vapors or from using various common products (such as glues), and another 16% from miscellaneous home sources. All three of these sources of benzene exposure taken together add up to 97% of total U.S. exposures. That leaves only 3% of the average person's benzene exposure from industrial pollution. In light of these statistics, is it any wonder that emphasis on air contaminants in the twenty-first century is shifting away from industrial pollution to everyday, personal exposures?

Fatigue and Worker Safety

Toxic substances are not the only element in the field of worker safety and health factors. In the year 2016, workplace environmental specialists began to show increased interest in the role that fatigue might play in safety in the workplace. The National Safety Council hosted a "Fatigue Blue Ribbon Panel" that year. Matthew Hallowell, Associate Professor at University of Colorado Boulder, reported in 2016 that fatigue effects include slower reaction time, more errors, and decreased cognitive ability (Trotto, 2017). David Lombardi, research scientist at Liberty Mutual, stated to the NSC Blue Ribbon Panel that risk among night shift workers was 31 percent higher than for morning shift workers and that the risk became worse with repeated consecutive night shifts. On the positive side, Lombardi reported significant injury risk decreases after workers were given rest breaks. Using data from a National Health Interview Survey, Lombardi reported that the annual injury incidence rate per 100 workers who get 7–8 hours sleep per day is 2.27; for workers who usually get less than 5 hours of sleep per day that incidence rate deteriorates to 7.89 per 100 U.S. workers (Lombardi, 2016)!

SUMMARY

Exposure to toxic substances is the classic health problem, but workplace exposures are different in nature from what most people think of as poisons. Off the job, poisons are thought of as deadly potions that are ingested. On the job, poisons may be deadly, but their entry into the body is usually through the lungs in minute concentrations, and the effects may take years to recognize. A notable exception is oxygen deficiency, which can have quick and fatal outcomes. The ways that poisons affect the human body can be somewhat classified into seven categories: irritants, systemic poisons, depressants, asphyxiants, carcinogens, teratogens, and mutagens. Each of the seven types of poisons can be mild or deadly, depending on concentration. Many substances fall into several of the seven categories.

An important first step in getting control of health hazards is to make effective use of baseline examinations for all new employees. Such examinations determine any preexisting health conditions that might be aggravated by workplace exposure to toxins. The examinations also permit measurement of deterioration of the worker's health, if any, during the period of employment.

Measuring the deterioration of worker's health during the period of employment provides valuable information, but even more worthwhile is the measurement of toxic exposures before they do their damage. This chapter has explored the science and instrumentation to measure tiny concentrations of toxic substances in industrial atmospheres. It has also introduced the system of standards against which these concentrations are compared. The most important standards for air contaminants are the permissible exposure levels (PELs). Most of the PELs are for 8-hour time-weighted-average (TWA) exposures. Some toxic substances are so dangerous as to require setting a ceiling (C) maximum concentration. Action levels (ALs) are derived from the PELs and indicate when air contaminants are reaching levels that need control before limits are exceeded. Special formulas are needed for considering the combined effects of multiple contaminants.

Having studied toxic substances, their effects on the human body, and the methods and standards for the measurement of their concentrations in industrial atmospheres, Chapter 10 will now consider ways that the industrial environment can be controlled to minimize the effects of these substances. In addition, Chapter 10 will introduce the hazard of industrial noise and its control.

EXERCISES AND STUDY QUESTIONS

9.1 Besides being a good basis for placement of employees in appropriate jobs for their physical characteristics, what is a secondary reason for baseline physical examinations?

9.2 How would you distinguish between the terms *toxic substances* and *hazardous materials*?

9.3 Identify the seven principal classes of toxic substances.

9.4 What is the technical name for the "drinking" variety of alcohol? To what toxic substance class does it belong?

9.5 Identify the three principal routes for toxins to enter the body.

9.6 Identify a career field in which workers are particularly vulnerable to contamination from biohazard exposure to the eyes.

9.7 What is the "standards completion project?" Name at least two common substances that are covered by such standards.

9.8 Name at least three common, odorless gases that can be dangerous.

9.9 What extremely foul-smelling toxic gas has the potential of overcoming a person's olfactory system? What does *olfactory* mean?

9.10 Explain the relationship between AL and PEL. What do these terms represent?

9.11 What is the definition of the word *fumes*?

9.12 How much carbon monoxide in the air is permissible, given a normal (0.033%) concentration of carbon dioxide (and no other contaminants)?

9.13 Air samples show an industrial atmosphere to contain 0.001% methyl styrene during the morning half of the shift and 0.015% during the afternoon half. Calculate the TWA. Assuming that no other contaminants are present, does the exposure exceed the PEL? Does it exceed the AL?

9.14 Air samples show the following contaminant concentrations in an 8-hour shift (from 8:00 A.M. to 4:00 P.M.):

- **(1)** Trifluorobromomethane, 0.1% from 11:00 A.M. to 2:00 P.M.
- **(2)** Propane, 0.05% all day
- **(3)** Phosgene, 1 part per million at 2:00 P.M., with a duration of 15 minutes
    - **(a)** Assuming that no other contaminants are present, does the full-shift atmosphere meet OSHA standards?
    - **(b)** To *exactly* meet OSHA standards, how much more or less time for the phosgene exposure would be permissible provided other contaminants remain as previously stated?

9.15 Two color detector tubes for testing for atmospheric concentrations of nitrogen dioxide have the following specifications:

Tube A standard measuring range:
    5 to 25 ppm (using 2 pump strokes)
    0.5 to 10 ppm (using 5 pump strokes)
Tube B standard measuring range:
    5 to 100 ppm (using 5 pump strokes)
    2 to 50 ppm (using 10 pump strokes)

Which tube provides the greater precision for the test? Which tube would be preferable for checking for concentrations close to the PEL? How many pump strokes should be used? Which tube would be preferable for checking for concentrations close to the AL? How many pump strokes should be used?

9.16 A particular gas welding process in a confined space is suspected of producing dangerous concentrations of carbon monoxide, carbon dioxide, iron oxide particulate, and manganese fumes. Atmospheric sampling produces the following exposure data:

Period	CO (ppm)	CO_2 (ppm)	Iron oxide (mg/m^3)	Manganese (mg/m^3)
8:00 A.M.–10:00 A.M.	10	1000	1	1
10:00 A.M.–12:00 noon	20	1000	4	1
12:00 noon–1:00 P.M.	25	1000	2	0
1:00 P.M.–4:00 P.M.	30	1000	3	1

Do calculations to determine whether the combined exposure represents an OSHA violation.

9.17 Name at least five pneumoconioses. Which are most dangerous?

9.18 How do fibroses differ from other pneumoconioses?

9.19 Name the two basic classes of asphyxiants and give examples of each.

9.20 Explain the following terms:

(a) Mutagen
(b) Carcinogen
(c) Teratogen

9.21 In what ways are the threats of poisons at work different from those at home?

9.22 What is the difference between *fumes* and *vapors*?

9.23 Compare the particle sizes of the following substances:

(a) Zinc oxide fumes
(b) Tobacco smoke
(c) Diameter of human hair
(d) Bacteria

9.24 Explain the following terms:

(a) *TLV*
(b) *PEL*
(c) *TWA*
(d) *MAC*
(e) *STEL*
(f) *AL*

9.25 Name some traditional methods of detecting the presence of dangerous air contaminants and explain advantages and disadvantages of each.

9.26 Name three basic approaches to measuring air-contaminant exposures.

9.27 Suppose that an industrial process produces the following air-contaminant concentration for the periods shown:

Period	Methanol (ppm)	Nitric oxide (ppm)	Sulfur dioxide (ppm)
8:00 A.M.–10:00 A.M.	50	5	0
10:00 A.M.–11:00 A.M.	150	10	1
11:00 A.M.–1:00 P.M.	100	5	1
1:00 P.M.–4:00 P.M.	200	10	1

Taken collectively, would these concentrations exceed permissible exposure levels?

9.28 In Exercise 9.27, suppose that the solvent ethanol could serve to replace the methanol in this process, but at the expense of double the concentrations of the solvent in the atmosphere. Would this help or hinder matters? Explain.

9.29 Two solvents, benzene and chlorobenzene, are under consideration by process engineers for use in a plant for which you have responsibility for safety and health management. What information can you provide to the process engineers regarding the comparative hazards of these two solvents?

9.30 A man and woman spill a bottle of 150 proof rum on the kitchen floor in their small one-bedroom apartment. The total apartment area is 600 square feet and has standard 8-foot ceilings. By the time they clean up the spill, approximately 5 cubic feet of alcohol vapor has entered the air through evaporation. Noting the strong smell of alcohol in the air, they open the window and, feeling drowsy, go to bed and sleep all night (8 hours). The open window permits a gradual dilution of the alcohol in the air, and by morning, the concentration of alcohol in the air is down to 500 parts per million. Assuming a constant rate of decline in alcohol content of the air all night, was the alcohol concentration a hazard? If the exposure had been occupational, would PELs have been exceeded?

9.31 In Exercise 9.30, the couple's original intent was to bake rum cake. Had they gone ahead and made the cake, suppose that the hot oven had caused an additional 25 cubic feet of alcohol vapor to be liberated into the apartment. How would this concentration compare with the PEL?

9.32 A direct-reading gas detector tube is available for sampling concentrations of the toxic gas sulfur dioxide. Tube 5H is specified for concentrations in the range of 0.05 to 8.0% and tube 5M is for concentrations in the range 20 to 3600 ppm. Which tube is the more sensitive of the two tubes?

9.33 The following gas detector tubes are available for direct reading of concentrations of the toxic gas hydrogen sulfide:

Tube	Concentration
4HT	1–40%
4HH	0.1–4.0%
4H	10–3200 ppm
4M	12.5–500 ppm
4L	1–240 ppm
4LL	0.25–60 ppm

Which of these tubes would be satisfactory for detecting the OSHA-specified ceiling concentration for hydrogen sulfide? Of the satisfactory tubes, which one tests the narrowest range of concentrations?

9.34 A detector tube is available for testing concentrations of isopropyl acetate in the range 0.05 to 0.75%. Would this tube be capable of detecting concentrations at the OSHA PEL? Would it be a satisfactory device for testing whether the AL was exceeded?

9.35 A particle of coal is determined in the laboratory to have a diameter of 17 μm. What is the diameter in centimeters? Calculate the diameter in inches. Is the particle classified as dust or fume?

9.36 Consider the following concentrations of air contaminants observed together on the same day:

Contaminant	TWA (ppm)
Isopropyl ether	200
Ethyl benzene	40
Chlorobenzene	25
Chlorobromomethane	50

Taken separately, do any of the concentrations exceed the PEL for that substance? the AL? Taken as a whole, does the mixture exceed the PEL? the AL?

9.37 Historically, do TLVs tend to become higher or lower over time? Why?

9.38 Which set of values tends to remain more static, PELs or TLVs? Why?

9.39 Identify three negative effects shown by research to be associated with fatigue in the workplace.

9.40 In general, which shift has been shown to be safer, day or night?

9.41 Compare injury incidence rates for workers who get adequate sleep (7–8 hours per day) to rates for workers who get only 5 hours of sleep.

9.42 What problem is associated with using dosimeters to measure time-weighted average exposures?

9.43 Compare the nature of poisons on the job and off the job.

9.44 **Design Case Study.** A process engineer proposes a new solvent that will reduce the quantities required by the process and significantly reduce the quantities of solvent vapors released into the air inside the plant. The new solvent is perchloroethylene, and it is expected to reduce the solvent vapors absorbed into the plant air by 20% by volume as compared to the old solvent (Stoddard solvent). You are called in as a Certified Safety Professional to evaluate the proposed change to the process. Do you support the proposed process change? Explain your position.

9.45 **Case Study: Rayon Manufacturing Plant.** Measurements are taken and airborne contaminant concentrations are as shown in Table 9.3. Determine which of the substances are listed by OSHA as having PEL limits and perform computations to determine whether the given exposures, taken separately and together, exceed OSHA PELs and ALs.

9.46 **Design Case Study.** Process design engineers for the rayon manufacturing plant in Exercise 9.45 suggest introducing a new process that uses the solvent formaldehyde. Preliminary evaluations suggest that the new process will add a slight amount of formaldehyde vapors to the plant atmosphere, perhaps 1 part per million by volume, in addition to current levels of the other air contaminants listed in Table 9.3. The plant engineer has had the foresight to invite the safety and health manager to join the design team for an additional perspective into the design process. Perform calculations and evaluate the potential impact of the new process proposal on the safety and health of the workers in the plant. What recommendation would you make to the design team?

TABLE 9.3 Exposure Levels

	Morning exposures (4 hour)	Afternoon exposures (4 hour)
Acetic anhydride	0.5 ppm	1 ppm
Sodium hydroxide	0.2 mg/m^3	0.3 mg/m^3
Ammonium sulfide	3 ppm	4 ppm
Calcium bisulfide	5 ppm	8 ppm
Carbon disulfide	4 ppm	6 ppm
Sodium sulfide	0.7 mg/m^3	0.8 mg/m^3
Sodium sulfite	0.5 mg/m^3	0.5 mg/m^3

RESEARCH EXERCISES

9.47 Mercury and its compounds are toxic materials addressed in this chapter. In 1995, an industrial release of mercury compounds into a river in Russia threatened the health of people in the area and environmental damage to the Arctic Ocean. Research the particulars of this accident and the extent of the damage. Why is the Arctic Ocean more vulnerable to damage from this type of accident than would be more temperate oceans?

9.48 On January 10, 1997, OSHA issued a final rule on methylene chloride. Research this standard to determine the following:

- **(a)** The standard number
- **(b)** The effective date of the standard
- **(c)** The date of the end of the implementation (start-up) phase
- **(d)** The 8-hour TWA PEL
- **(e)** The STEL
- **(f)** The length of time exposure records must be kept

9.49 Study the impact of the methylene chloride standard. How many lives per year are expected to be saved as a result of the promulgation of this standard? How much will cancer risks be cut for workers who use this solvent? How much will worker exposures be decreased? How many workers use methylene chloride?

9.50 In 2017, OSHA revised the Crystalline Silica in Construction rule. With the change in PEL, how many workers are exposed to levels higher than the PEL?

9.51 Do a search on the Internet to determine currently known diameters and lengths of typical carbon nanotubes. Compute the aspect ratio for these dimensions.

9.52 If the diameter of a carbon nanotube is represented as a line of width 1/100 of an inch in Figure 9.5, how long should the curvy line be drawn in the artist's illustration to represent the correct aspect ratio (length to diameter) for a carbon nanotube?

9.53 Do a search on the Internet to determine currently known diameters of asbestos fibers and carbon nanotubes. Calculate the ratio between these diameters. Using this information, carefully examine Figure 9.5 to determine whether the artist used reasonable dimensions to compare asbestos fibers with carbon nanotubes.

9.54 OSHA PELs are based off averages for exposure. How do the STEL and ceiling limits act as controls around use of averages? Identify several examples of chemicals that have such limits and why they are important.

STANDARDS RESEARCH QUESTIONS

9.55 This chapter listed all of the chemicals identified in the "standards completion project." Use the Companion Website database to determine which of these chemicals generates the most OSHA citation activity.

9.56 Study the OSHA General Industry standard for dealing with toxic air contaminants in general. Find the provision that requires air contaminants to be held within their respective PELs. Determine the frequency of citation of this provision using the database on the Companion Website. Determine the average dollar level of proposed penalties for violation of this provision.

9.57 Find the provision of the OSHA standard that deals with mixtures of various toxic air contaminants. Use this standard to verify Equation (9.2) in this chapter.