# Chapter 2

# Combustion Products and Their Effects on Life Safety

Revised by

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Along with heat, the burning of every combustible material or product\* produces smoke—gases and aerosols that, in sufficiently high concentration, present hazards to people in the vicinity. Products near those already burning may also contribute to the smoke as they decompose from exposure to the heat from the fire. Predominant among the hazards, which generally occur simultaneously, are the following:

- Sensory irritation of the upper and/or lower respiratory tract, which can affect speed of movement and the ability to negotiate escape and, at higher exposures, can lead to incapacitation or death
- Central nervous system depression resulting from inhalation of asphyxiant fire gases, which can, in ascending exposures, lead to impaired judgment, disorientation, loss of motor coordination, unconsciousness, and, ultimately, death
- Thermal effects, including hyperthermia and thermal burns of the skin and respiratory tract

Exposure to these hazards is often prolonged by eye irritation and diminished visibility due to smoke obscuration, which can affect the ability of occupants to see and negotiate escape routes efficiently. Survivors from a fire may also experience postexposure complications that can lead to delayed health effects or even death.

The *nature and concentration* of the generated smoke depends on a variety of factors. These include the quantity of the product that is burning, whether the product is flaming or pyrolyzing, the ventilation in the area, and distance from the fire. Thus, smoke toxicity is not a singular property of a product.

The *threat to people* from the heat and smoke depends on additional factors, including the entire ensemble of burning products, the location of people relative to the fire, the locations of exits from the burning enclosure and the paths to those exits, the time (in the fire growth history) at which people are in the vicinity of the fire-generated atmosphere, and individual susceptibility of each person to the components of the smoke. Thus, the hazard and risk to people from exposure to the fire effluent (heat and smoke) from a burning product is also not a singular property of the product.

See also Section 2, Chapter 3, "Flammability Hazard of Materials"; Section 4, Chapter 2, "Calculation Methods for Egress Prediction"; and Section 6, Chapter 3, "Concepts and Protocols of Fire Testing."

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#### **Key Terms**

asphyxiant, available safe egress time (ASET), carbon dioxide, carbon monoxide, combustion product, cup furnace test, fractional effective dose, hydrogen cyanide, irritant, LC<sub>50</sub>, mass loss model, N-gas model product of combustion, pyrolysis, radiant panel test, required safe exit time (RSET), smoke, Station Nightclub fire, stoichiometric, supertoxicant, test, toxic gas model, toxicity, University of Pittsburgh (UPITT) device

<sup>\*</sup>In this chapter, *product* refers to a finished commercial item, and *material* refers to a single substance. Thus, for example, a chair (the product) is composed of several materials (e.g., a wooden frame, polyurethane padding, cotton batting, an aramid fire barrier, and a polyester/cotton cover fabric).

#### FIRE AND COMBUSTIBLE MATERIALS

# Pyrolysis and Combustion

Almost all polymeric materials, both natural (e.g., wood) and synthetic (e.g., polyurethane or nylon), can undergo pyrolysis and/or combustion. Pyrolysis is defined as a "process of simultaneous phase and chemical species change caused by heat," with combustion being defined as "a chemical process of oxidation that occurs at a rate fast enough to produce temperature rise and usually light, either as a glow or flame." The processes of pyrolysis and combustion have both physical and chemical aspects.<sup>2</sup>

Polymeric materials, on exposure to sufficient thermal energy, typically first undergo phase change, such as melting in the case of thermoplastics, followed by chemical decomposition. These are endothermic processes, resulting in the production of volatile low-molecular-weight products, which may or may not then undergo actual combustion.

If pyrolysis produces gases that are themselves combustible, flaming may occur if the following exist in the same volume:

- Sufficient oxidizing agent (air)
- · An ignition source of sufficient intensity
- Sufficient gaseous fuel vapors or volatiles

The nature of the gases generated by the pyrolysis can have a significant effect on when and whether ignition takes place. For example, a material that contains a readily volatile fire retardant may not ignite until the fire retardant has been sufficiently depleted. Should the fire retardant and the host polymer continuously volatilize until the polymer is depleted, ignition may be prevented altogether.

For the process of combustion to be self-sustaining, it is necessary for the burning gases to impart sufficient heat energy to the material to continue the production of ignitable volatiles. The process is a continuous feedback loop: heat transferred to the material causes the generation of flammable volatiles, these volatiles react with oxygen in the air to generate heat, and a part of this heat is transferred back to the material to continue the process. The chemical oxidation processes for flaming combustion of organic materials are generally quite exothermic, with more than enough energy being produced to continue the pyrolysis and bond-breaking processes if the heat transfer is efficient and heat losses to the environment are not too great.

Smoldering is a different form of combustion occurring only in certain porous materials. Here, air diffuses into the pores of the material and reacts directly with the interior surfaces of the pores. The combustion products from this slower process are typically quite different from those from flaming combustion. They are, however, a significant cause of fire deaths when a person is close to the smoldering product, as can occur following cigarette ignition of a bed or piece of upholstered furniture.<sup>3</sup>

# Flammability Properties of Materials and Products

It is difficult to generalize the flammability properties of materials, since fire performance is influenced by a number of factors, including the chemical composition and structure of the material, the use of additives in formulated systems, and even the conditions of the fire. Highly crosslinked thermoset polymers normally burn less readily than thermoplastics. Cellular plastics (foams) generally burn quite readily due to their large surface area and good thermal insulating properties, which prevent dissipation of heat. Polymer systems containing halogen atoms (e.g., polyvinyl chloride [PVC]) burn with difficulty; however, the addition of plasticizers increases the propensity of these polymer systems to burn. Fire-retardant additives, which include organic halogen and phosphorus-containing compounds and several metal oxides and hydrates, are employed to increase resistance to ignition and/or lower burning rates of polymer systems.4 However, inherently fire-resistant polymers and polymer systems containing fire-retardant additives will still burn under sufficiently severe thermal conditions.

#### **GENERATION OF FIRE GASES**

Smoke is commonly defined as "the airborne solid and liquid particulates and gases evolved when a material undergoes pyrolysis or combustion." The particulates and aerosols produced affect occupants' visibility as they attempt to escape from a fire; this will be addressed in a later portion of this chapter. Consideration will be given first to the formation and toxicity of the gases commonly produced in fires.

#### Carbon Dioxide

In well-ventilated flaming fires, nearly all the carbon lost from the combustibles is converted to carbon dioxide (CO<sub>2</sub>). Even in postflashover fires, the fraction of carbon conversion to CO<sub>2</sub> is fairly high. Thus, the yield\* of CO2 has been used to estimate the burning rate of products when a direct measurement of mass loss is not possible. Carbon dioxide is also generated in smoldering fires, but the generated carbon monoxide is far more hazardous.

#### Carbon Monoxide

Carbon monoxide (CO) is produced from both smoldering and flaming combustion. The production of CO from smoldering fires is quite slow, but these fires are not accompanied by vigorous mixing and diluting of the combustion products with room air. Thus, lethal concentrations of CO can be generated in the immediate vicinity of the ignition within 10 minutes. Lethal concentrations of CO elsewhere in the room may take 1 to 3 hours. By then, smoldering may have ceased or may have undergone transition to flaming combustion.<sup>5</sup>

The production of CO from flaming combustion is a gas phase process. The fuel vapor or carbon-containing decomposition products react in a complex sequence with the oxygen in the air to form carbon monoxide. Subsequent reaction further oxidizes the CO to CO<sub>2</sub>. The completeness of this process is largely dependent on the local supply of oxygen. Oxygen available to

<sup>\*</sup>The yield of a fire-generated gas is defined as the mass of the gas produced divided by the mass of the combustibles consumed in the burning. A parallel definition applies to the overall yield of smoke.

a fire can be limited either by lowering the oxygen concentration in the incoming air supply or by reducing the volume flow of air to a fire. The formation of CO is related to the fuel-to-air equivalence ratio,6 which is defined as

$$\phi = \frac{\text{(kg fuel/kg air)}}{\text{(kg fuel/kg air)}_{\text{stoich}}}$$
(1)

where "stoich" denotes conditions at which the ratio between fuel and oxygen is that required for complete combustion, with no excess oxygen. Thus, when  $\phi = 1$ , exact stoichiometric conditions exist between fuel and air. For values of  $\phi$  < 1, the fire is fuel-lean and well ventilated; for values of  $\phi > 1$ , the fire is fuelrich and ventilation controlled. These latter conditions ( $\phi > 1$ ) are ones that favor the formation of CO.

Studies have shown that under well-ventilated conditions ( $\phi$  < 0.5), yields of CO are very low, typically less than 0.01.<sup>6</sup> Above equivalence ratios of about 0.5, the yield of CO increases rapidly as the value of φ increases. For compartments of moderate size and ventilation, this rise in the yield of CO occurs near the point of flashover. Flashover occurs when the thermal environment is sufficiently intense that many or all the combustibles in the compartment burst into flame. The result is a high density of combustible vapors, a decrease in the oxygen within the compartment, and thus a sharp increase in  $\phi$ . This is the same condition that favors generation of CO. According to NFPA 269, Standard Test Method for Developing Toxic Potency Data for Use in Fire Hazard Modeling, once of reaches a value greater than about 1.5, the CO yield becomes rather constant at about 0.2 kg CO/kg fuel consumed, with the production rate being dependent principally on the mass burning rate. For a sufficiently large fire whose flame radiative heat flux and mass generation rate of material vapor have approached their asymptotic values, the mass burning rate remains rather constant, and, thus, the CO production rate is also fairly constant (until the fuel supply becomes depleted). These phenomena have been observed with large-scale fire tests involving fully furnished rooms.<sup>8</sup>

The ratio of the concentrations of carbon dioxide to carbon monoxide, often used as a descriptive characteristic of a fire, depends more on the ventilation conditions of the fire than on the nature of the materials being burned. Studies of the dependence of CO2/CO ratios on the equivalence ratio show that for well-ventilated fires (i.e.,  $\phi \ll 1$ ), essentially all the fuel carbon is oxidized to CO<sub>2</sub> and the ratio exceeds 20.<sup>10</sup> Once the equivalence ratio has exceeded that associated with flashover, indicating a fuel-rich or ventilation controlled fire, the CO<sub>2</sub>/CO ratio reaches a plateau at about 2 to 10.6,10 The bases for this range have not been established.

# Hydrogen Cyanide

The generation of hydrogen cyanide (HCN) is both materialdependent and temperature-dependent. In smoldering fires and pyrolysis from flaming fires, HCN can be produced by decomposition of some nitrogen-containing polymers. HCN can be generated from nitrogen-containing polymers during flaming combustion as well. In neither case is there evidence of toxicologically significant HCN formation by fixation of the nitrogen in the air. In contrast to CO, there have been insufficient

studies on HCN to enable quantitative prediction of its formation in fires. If sufficient oxygen is present, oxides of nitrogen (NO<sub>x</sub>) may also be formed from nitrogen-containing materials. Although one study reported NO<sub>r</sub> production from nitrogencontaining fuels to be far less than that for HCN, there are conflicting data in the literature. 11 HCN has also been seen to be oxidized to NO, when flames extended from a flashed-over room and continued to burn outside the doorway.<sup>12</sup>

# Halogen Acids

Polymer systems containing halogen atoms (fluorine, chlorine, or bromine) result in the formation of the halogen acids-hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr), the production of which is largely material-dependent as long as thermal decomposition temperatures are reached. The halogen acids are formed in the pyrolysis component of the combustion process and are not oxidized further. Thus, the halogen acids are produced even if flaming combustion does not occur. Since the production efficiencies for the formation of HF, HCl, and HBr are close to being unity, maximum yields might be expected in fires. For example, HCl is readily evolved from polyvinyl chloride (PVC) at temperatures of about 437 to 527°F (225 to 275°C). Since HCl can be released before significant carbon from the material is combusted, the mass yield of HCl can exceed the stoichiometric value early in the material's decomposition. Nonetheless, the maximum possible concentrations of halogen acids are generally not encountered. Far lower yields have been found from PVC that contains a high fraction of calcium carbonate filler. <sup>13</sup> Presumably, this reflects reaction with the chlorine atoms to form (solid) calcium chloride, which is thermally stable under ordinary fire conditions. Furthermore, halogen acid concentrations decay rather quickly in the presence of adsorptive surfaces<sup>14</sup> and water droplets present in most fire effluents at temperatures below 212°F (100°C).

#### **Organic Irritants**

Pyrolysis and/or incomplete combustion of organic materials can lead to a wide variety of organic irritant species. Those considered to be the most important toxicologically are formaldehyde, unsaturated aldehydes (especially acrolein), and isocyanates (from nitrogen-containing polymers<sup>15</sup>). The first two result from partial oxidation of the carbon in the material. (Further oxidation leads to the formation of CO and then CO<sub>2</sub>.) Acrolein, in particular, has been demonstrated to be present in many fire atmospheres. 16 It is also formed from the smoldering of all cellulosic materials and from the oxidative pyrolysis of polyethylenes.<sup>17</sup>

#### Other Gases and Aerosols

Depending on the composition of the combusting products, additional toxic components of smoke can be produced in a fire. For example, phosphorus-containing fire retardants can result in phosphoric acid aerosol, and sulfur-containing polymers can generate sulfur oxides. There is yet no predictive capability for the yields of such species.

#### **TOXICITY OF FIRE GASES**

Fire gas toxicants are usually considered as belonging to one of three basic classes:

- 1. Asphyxiants, or narcosis-producing toxicants
- 2. Sensory/upper respiratory irritants or pulmonary irritants
- 3. Toxicants exhibiting other or unusual effects; although always a possibility, this class has few documented examples

The toxicological effects of smoke produced from fires usually involve relatively high concentrations of toxicants inhaled over quite short periods of time. Thus, many criteria commonly used in conventional toxicology to describe hazardous conditions, such as threshold limit values (TLVs<sup>18</sup>) and occupational long-term exposure values, are normally of little use in combustion toxicology.

This section addresses the toxicity of the major fire gases in a largely descriptive manner. It also provides guidance on limiting criteria for exposure of humans in fires.

#### **Asphyxiants**

In combustion toxicology, the term *narcosis* refers to the effects of asphyxiant toxicants that are capable of resulting in central nervous system depression, with loss of consciousness and ultimately death. Effects of these toxicants depend on the accumulated dose, that is, both concentration and duration of the exposure. The severity of the effects increases with increasing dose.

Carbon Monoxide. The toxic effects of carbon monoxide are those of anemic hypoxia.<sup>19</sup> Hypoxia refers to the condition in which there is an inadequate supply of oxygen  $(O_2)$  to body tissue, with anemic hypoxia being characterized by a lowered oxygen-carrying capacity of the blood, even when the arterial partial pressure of O<sub>2</sub> and the rate of blood flow are normal. This is due to competition between O<sub>2</sub> and CO for the heme-binding sites of hemoglobin, with the affinity of hemoglobin for CO being about 250 times greater than that for O<sub>2</sub>. <sup>19</sup> Even partial conversion of hemoglobin to carboxyhemoglobin (COHb) significantly reduces the oxygen-transport capability of the blood such that serious toxic signs and symptoms are produced. Additionally, partial conversion of hemoglobin to COHb causes oxygen that is bonded as oxyhemoglobin (HbO2) to be more tightly held and less available to body tissues. The extent to which blood hemoglobin is converted to COHb can readily be measured in a clinical laboratory and is expressed as percentage of COHb saturation. An ISO standard for these measurements is being processed in ISO TC 92/SC 3.<sup>20</sup>

The signs and symptoms produced by exposure to CO are directly related to the percentage of blood hemoglobin that is converted to COHb.<sup>21</sup> Deaths of humans exposed to CO produced in fires have been associated with COHb saturations ranging from 1 to 99 percent.<sup>22</sup> Although most deaths have been reported to be in the 50 to 70 percent COHb range, both lower and higher values are not unusual.<sup>23,24</sup> Low COHb values in fire victims may be due to preexisting physiological conditions,

such as pulmonary insufficiency or cardiovascular disease, which may have already compromised the individual. The high oxygen demand resulting from physical exertion may also cause a person to succumb to low COHb saturation. High COHb values at death may be attributed to the low oxygen demand of a person either at rest or at quite low physical activity. There is no specific COHb saturation below which one would be expected to live and above which death would occur. As with essentially all biological responses, there is a distribution of COHb saturations associated with death.<sup>24</sup> Sometimes, in the case of even a single exposure, permanent harm may result from hypoxic damage to neural structures. 19 The peak incidence of such delayed neurological impairment is with the elderly.<sup>25</sup>

Binding of O<sub>2</sub> and CO with hemoglobin occurs as an equilibrium, with both association and dissociation taking place.<sup>19</sup> Thus, CO and hemoglobin are in equilibrium with COHb, with the concentration of COHb being dependent on the partial pressure (or concentration) of CO in the atmosphere. Each concentration of CO is associated with an equilibrium COHb saturation, or, stated another way, for any given value of COHb saturation there is a minimum concentration of CO that will attain it. At any given O2 concentration, higher equilibrium COHb saturations can be obtained only by increasing the concentration of CO.

The competition between O<sub>2</sub> and CO for bonding sites on hemoglobin is defined by the Haldane equation:<sup>19</sup>

$$\frac{\text{(COHb)}}{\text{(HbO}_2)} = M \frac{(P_{\text{CO}})}{(P_{\text{O}_2})} \tag{2}$$

where

 $(COHb)/(HbO_2)$  = Ratio of carboxyhemoglobin to oxyhemoglobin

 $(P_{CO})/(P_{O_2})$  = Ratio of the respective partial pressures (or concentrations)

> M = A constant that is, to some extent, species dependent

The Haldane equation is commonly used to calculate the CO concentration that would be in equilibrium with any given COHb saturation.

The time required for a human subject to attain a given COHb saturation can be approximated from the Stewart-Peterson equation:<sup>26</sup>

% COHb = 
$$(3.32 \times 10^{-5})(CO)^{1.036}(RMV)(t)$$
 (3)

where

(CO) = CO concentration  $(\mu L/L)^*$ 

RMV = Respiratory minute volume (L/min)

t = Exposure time (min)

At rest, the RMV for humans averages approximately 8.5 L/ min,<sup>23</sup> but may increase during strenuous activity to as much as

<sup>\*</sup>The concentration in µL/L is numerically equal to the frequently used unit of "ppm." The use of the latter unit is discouraged.

100 L/min. Curves showing the relationship between CO concentration and time of exposure for various COHb saturation values for humans have been constructed using the Stewart-Peterson equation.<sup>27</sup>

Studies using rats have shown that elevated temperatures have an exacerbating effect on CO intoxication, 28 possibly through increased rate of respiration. This is likely to occur with humans as well. The obvious treatment for persons exposed to CO is to provide for inhalation of fresh air or even pure oxygen. For example, the half-recovery time in terms of blood COHb levels for resting adults breathing air at 1 atmosphere is 320 minutes.<sup>19</sup> When oxygen is given at 1 atmosphere, the time is reduced to 80 minutes.

Hydrogen Cyanide. Hydrogen cyanide (HCN), whose lethal dose is approximately 25 times smaller than that of carbon monoxide, is a very rapidly acting toxicant.<sup>29</sup> The action of HCN is due to the cyanide ion, which is formed by hydrolysis in the blood. Unlike CO, which remains primarily in the blood, cyanide ions are distributed throughout the body water and make contact with the cells of tissues and organs. Cyanide ions readily react with the enzyme cytochrome oxidase to form a cytochrome oxidase-CN complex and also with methemoglobin to form cyanomethemoglobin. If the concentration of cyanide ions is not sufficiently great to cause death, the ions are slowly released from the complexes with cytochrome oxidase and methemoglobin and converted to thiocyanate ions by the enzyme rhodanese. This detoxification process, along with the fact that cyanide is distributed throughout the body, makes correlation of blood cyanide content with actual exposure to HCN difficult.

Cytochrome oxidase occupies a central role in the utilization of oxygen in practically all cells. Its inhibition rapidly leads to loss of cellular functions (cytotoxic hypoxia) and then to cell death. In contrast to CO, cyanide ions do not decrease the availability of oxygen but rather prevent the utilization of oxygen by cells. The heart and brain are particularly susceptible to this inhibition of cellular respiration, with bradycardia, cardiac arrhythmia, and EEG brain wave activity, indicative of central nervous system depression, having been reported in studies using monkeys.<sup>30</sup> Although cardiac irregularities are often noted in HCN intoxication, the heart tends to outlast respiration, and death is usually due to respiratory arrest of central nervous system origin.

A complication resulting from the inhalation of HCN is one of respiratory stimulation or hyperventilation, <sup>23</sup> presumably due to the body's regulating chemoreceptor cells responding to a need for oxygen. This causes a more rapid uptake of not only HCN but also other toxicants that may be present. The hyperventilatory effect of HCN may also account for its rather steep dose-response relationship.

Data relating symptoms in humans to various concentrations of HCN are very limited. One widely referenced descriptive account of HCN intoxication of humans reports that 50 μL/L may be tolerated for 30 to 60 minutes without difficulty, 100  $\mu$ L/L for that same period is likely to be fatal, 130  $\mu$ L/L may be fatal after 30 minutes, and 181 µL/L may be fatal after 10 minutes.<sup>31</sup>

The role of HCN as a causative agent in human fire fatalities is considerably less clear than that of CO. Documented cases are rare in which HCN alone can be shown to be the primary toxicant. Blood can be analyzed for cyanide, but the procedure is more complex than that for CO, and the reliability of the results is dependent on proper blood storage conditions prior to analysis. Analyses should be interpreted with caution, with consideration given to the analytical method used, the blood storage history, and the past performance of the responsible laboratory. It is generally held that blood cyanide concentrations greater than 1.0 µg/ml are indicative of possibly significant toxicological effects due to inhalation of HCN.<sup>22,32</sup> Blood cyanide levels greater than 3.0 µg/ml are generally considered to be lethal. Significant concentrations of blood cyanide are normally found associated with carboxyhemoglobin saturation due to inhalation of CO.<sup>32,33</sup> The contribution of each to death often cannot be determined with confidence. There is no evidence for synergism between HCN and CO, and it is generally agreed that these two toxicants are additive in their effects. 34,35

**Carbon Dioxide.** Carbon dioxide  $(CO_2)$  is quite low in its own toxicological potency and is not, by itself, normally considered to be significant as a toxicant in fire atmospheres. However, it does stimulate both the rate and depth of breathing, thereby increasing the RMV. The RMV, increasing about 50 percent with only 2 percent CO<sub>2</sub>, may be as much as 8 to 10 times normal in the presence of 10 percent CO<sub>2</sub>. Such respiratory stimulation causes accelerated inhalation of other toxicants leading, for example, to an increased rate of formation of blood COHb from inhalation of CO. However, the same equilibrium COHb saturation of blood is reached as in the absence of CO<sub>2</sub>.<sup>36</sup>

Increased incidence of lethality of rats has also been reported with combinations of CO and CO<sub>2</sub> particularly occurring after the exposure period.<sup>37</sup> This effect may be associated with the combined insult of respiratory acidosis (caused by CO<sub>2</sub>) and metabolic acidosis (caused by CO), a condition from which the rodent has difficulty recovering postexposure. Whether or not this latter effect of CO2 also occurs with people has not been determined.

**Oxygen Depletion.** Since oxygen is consumed in the combustion process, oxygen depletion or vitiation must also be considered a toxic component of smoke. When oxygen drops from its usual level of nearly 21 percent in air to approximately 17 percent, a person's motor coordination may be impaired. When oxygen drops to the range of 14 to 10 percent, a person can be still conscious but may exercise faulty judgment and will be quickly fatigued. In the range of 10 to 6 percent, a person loses consciousness and must be revived with fresh air or oxygen within a few minutes to prevent death.<sup>38</sup> During periods of exertion, increased oxygen demands may result in oxygen deficiency symptoms at higher oxygen levels.

#### **Irritants**

Both inorganic irritants (e.g., halogen acids and those formed from nitrogen oxides) and organic irritants (e.g., aldehydes) can be formed in fires. Irritant effects, produced from exposure to essentially all fire atmospheres, are normally considered by combustion toxicologists as being of two types:

- 1. Sensory irritation, including irritation of the eyes and the upper respiratory tract
- 2. Pulmonary irritation affecting the lungs

Most fire irritants produce signs and symptoms characteristic of both sensory and pulmonary irritation.

Eye irritation, an immediate effect that depends primarily on the concentration of an irritant,<sup>39</sup> may significantly impair a person's escape from a fire. Nerve endings in the cornea are stimulated, causing pain, reflex blinking, and tearing. Severe irritation may also lead to subsequent eye damage. Victims may shut their eyes, partially alleviating these effects; however, this action may also impair their escape from a fire.

Airborne irritants also enter the upper respiratory tract, causing burning sensations in the nose, mouth, and throat, along with the secretion of mucus. These sensory effects are also primarily related to the concentration of the irritant and do not normally increase in severity as the exposure time is increased.<sup>39</sup>

Following signs of initial sensory irritation, significant amounts of inhaled irritants may also be quickly taken into the lungs, with the symptoms of pulmonary or lung irritation being exhibited. Lung irritation is often characterized by coughing, bronchoconstriction, and increased pulmonary flow resistance. Tissue inflammation and damage, pulmonary edema, and subsequent death may follow exposure to high concentrations, usually within 6 to 48 hours. Inhalation of pulmonary irritants also appears to increase susceptibility to postexposure bacterial infection. Unlike sensory irritation, the effects of pulmonary irritation are dependent both on the concentration of the irritant and on the duration of the exposure.

**Halogen Acids.** The halogen acids have received particular attention, with the most prevalent case being hydrogen chloride (HCl) resulting from the decomposition of polyvinyl chloride (PVC). HCl is both a potent sensory irritant and a strong pulmonary irritant. Volume fractions as low as 75 to 100 µL/L are extremely irritating to the eyes and the upper respiratory tract, suggesting possible impairment of physical activity such as is needed for escape. 40 Although HCl was found not to be physically incapacitating to baboons subjected to volume fractions up to 17,000 µL/L for 5 minutes, postexposure deaths were reported from doses that did not appear to incapacitate.<sup>41</sup> Comparable studies have not been conducted using actual PVC smoke.

Another study, using baboons exposed for 15 minutes to (flaming) PVC smoke containing 5000 µL/L HCl, did not show any smoke-related impairment of pulmonary function when tested at 3, 90, 180, and 360 days postexposure. 42 Lesions to mucosal surfaces of the mouth were observed, however, along with evidence of bronchoconstriction and lowered PaO2 (arterial oxygen) levels during the exposure.

Considerable controversy has existed as to what concentration of HCl may be hazardous to humans. It is questionable whether data from numerous studies with rodents can be directly extrapolated to humans because of significant anatomical differences between the respiratory tracts of the rodent and the primate which, in turn, result in very different responses to HCl. Rodents exhibit a decrease in respiratory rate and minute volume on exposure to HCl, whereas these values have been shown to increase for primates.<sup>43</sup> Interestingly, exposure doses (concentrations × time) of HCl causing postexposure lethality in rats are in the same range as those that have resulted in postexposure deaths of baboons. 44 However, the data for baboons are very limited, and the comparison made is rather subjective. From studies using exposure of baboons, HCl would not appear to be physically incapacitating, nor would it seem to produce significant chronic respiratory complications after short exposures to volume fractions of 5000 µL/L and below. Although acute symptoms, ranging from severe discomfort to noticeable upper respiratory tissue damage, may be experienced, significant pulmonary function changes would not be expected except at higher concentrations.

It would still be prudent, however, to recognize that HCl is likely to be dangerous to humans at concentrations far below those indicated from studies using baboons. Evidence of bronchoconstriction and markedly lowered PaO2 levels from inhalation of HCl were observed with baboons, 45 suggesting a potential for adverse effects with humans. Furthermore, persons having preexisting compromised pulmonary function may be more susceptible than healthy individuals.

Fire-retardant additives based on chlorine or bromine are also sources of halogen acids in fires. Fluoropolymers are a major source of HF. Although studies using the halogen acids HF and HBr have been very limited, it would appear that these acid gases exhibit irritant effects similar to those of HCl at comparable concentrations.<sup>23</sup>

The determination of incapacitation threshold criteria for the initial effect of the halogen acids (and for irritant gases in general) has involved considerable controversy, since very few controlled studies have been made that relate to the effects of human exposure. Most information has been only anecdotal. Taking expert cognizance of relevant published information, ISO 13571 suggests the following incapacitating volume fractions:<sup>46</sup>  $F_{\rm HCl}$  = 1000 µL/L,  $F_{\rm HBr}$  = 1000 µL/L, and  $F_{\rm HF}$  = 500 µL/L. These are for use in Equation (7) on p. 6-20.

Nitrogen Oxides. Nitrogen dioxide (NO<sub>2</sub>) and nitric oxide (NO) are the major components of a mixture of nitrogen oxides usually referred to as NO<sub>r</sub>. Nitric oxide is only about onefifth as potent as NO2.11 Studies on rats exposed to NO2 under the conditions of smoke toxicity test methods indicate NO2 to have a lethal toxic potency comparable to HCN.<sup>47</sup> In contrast to HCN, the toxicity of NO<sub>x</sub> is primarily due to its properties as a pulmonary irritant, with lethality of rats being postexposure, usually within one day. A consensus (ISO 13571) incapacitating volume fraction is  $F_{NO_2} = 250 \,\mu\text{L/L}$ .

Other Inorganic Irritants. As indicated above, the presence of other atoms in the burning materials can lead to the generation of inorganic oxides and acids, which behave as irritants as well. The toxic effects of these gases are likely to be additive with the irritants discussed above. A consensus value for the incapacitating volume fraction of SO<sub>2</sub> is 150 µL/L. Consensus values for other inorganic irritants have not yet been determined.

Organic Irritants. Although numerous organic irritants may be produced in fires, only acrolein has received significant attention in combustion toxicology. It is deemed to be the most potent of the organic irritants. Volume fractions of acrolein as low as a few µL/L are extremely irritating to the eyes and upper respiratory tract. Interestingly, studies with baboons showed that volume fractions up to 2780 μL/L (5700 g/m<sup>3</sup>) for 5 minutes were not physically incapacitating during exposure. 41 Pulmonary complications caused by that and even lower concentrations resulted in death within hours after the exposure, however. Values of incapacitating volume fractions for acrolein and formaldehyde are 30 μL/L and 250 μL/L, respectively. 46 However, given the results of the baboon studies, this figure for acrolein seems conservative.

# Supertoxicants

Concern regarding potential "supertoxicants" (materials generating smoke of extremely high potency) in fire atmospheres was prevalent in the 1970s and 1980s. With more experience in the testing of materials, this concern has diminished, since there have been few documented examples. One involved the formation of a neurotoxin from the thermal decomposition of a noncommercial rigid polyurethane foam, 48 whereas another concerned the extreme toxic potency exhibited by polytetrafluoroethylene in some laboratory tests. The latter eventually came to be regarded as largely an artifact of the test methods. 49 For most materials and products it is now widely accepted that smoke toxicity can, to a large extent, be explained both qualitatively and quantitatively on the basis of a small number of common toxic gases. 50,51 A protocol for identifying a supertoxicant is presented below in the section Test Methods for Toxicity of Smoke.

# QUANTIFICATION OF TOXIC POTENCY

# The LC<sub>50</sub>

The standard in combustion toxicology for quantifying the toxic potency of individual fire gases or of smoke has mostly been the LC<sub>50</sub> for 30 minute exposure of rats.<sup>52,53</sup> The LC<sub>50</sub> is defined as the volume fraction of toxic gas in  $\mu L/L$  or smoke in g/m<sup>3</sup> statistically calculated from concentration-response data to produce lethality in 50 percent of test animals within a specified exposure and postexposure time.\* The IC50 is similarly defined for incapacitation. It is significant that consensus among experts has been to recognize that the rat is a reasonably acceptable animal model for human exposure to smoke when the principal effects are due to inhalation of asphyxiant toxicants.<sup>27,54</sup> Over the years, LC50 values have been experimentally determined for rodent (and less frequently, other laboratory animals) exposure to individual fire gases,<sup>54</sup> as well as for many materials and products.55

# Lethal Toxic Potency from Chemical Analysis

Although individual fire gas toxicants may exert quite different physiological effects through different mechanisms, when present in a mixture each may result in a certain degree of compromise experienced by an exposed subject. It should not be unexpected that varying degrees of a partially compromised condition may be roughly additive in contributing to death. The extensive bank of rodent lethality data became useful in the development of a strategy for calculating smoke LC50 values from combustion analytical data without the need for exposure of animals. As early as 1972, Tsuchiya and Sumi proposed that a toxicity index could be constructed from the sum of terms for all the gases generated by a fire. Each term was the ratio of the actual concentration of the gas divided by the concentration fatal to a person in a 30 minute exposure. 56 Three further developments made this concept tractable for estimating lethal toxic potency.

# **Additivity Studies**

The additive effects of combustion gases were demonstrated in a number of studies using rodents. 34,35 As a result, it is now fairly well agreed that the asphyxiants CO and HCN are additive. Furthermore, analysis of data from experiments exposing rats to mixtures of HCN and CO, and also mixtures of HCl and HCN, suggests that their effects leading to lethality may also be approximately additive. 57,58

#### Fractional Effective Dose (FED)

The additive effects of fire gases was advanced to include consideration of variable exposure time. This strategy is commonly referred to as the fractional effective dose (FED) methodology. 34,59,60 The FED is "the ratio of the Ct product (concentration x time) for a gaseous toxicant produced in a given test to that Ct product of the toxicant that has been statistically determined from independent experimental data to produce lethality in 50 percent of test animals within a specified exposure and postexposure time."53

The additivity of FEDs has become a useful tool in combustion toxicology for the calculation of lethal toxic potencies from combustion product analysis data, as well as for the assessment of potential toxic hazards to humans.<sup>51</sup> Mathematically, the principle is expressed as

$$FED = \sum_{i=1}^{n} \sum_{t_{i}}^{t_{2}} \frac{C_{i}}{(Ct)_{i}} \Delta t$$
 (4)

where

 $C_i$  = Concentration of toxic component i

 $(Ct)_i$  = Specific dose (concentration × time) required to produce lethality

t = Time increment (min)

When the accumulated FED = 1, it is expected that the mixture of gaseous toxicants would be lethal to 50 percent of exposed animals, that is, the  $LC_{50}$ .

<sup>\*&</sup>quot;Within a specified exposure" refers to the time interval during which the animals can inhale the gas or smoke. A "specified postexposure time" refers to a length of time after that, when the animals are breathing fresh air.

#### N-Gas Model

The combustion of the complex formulations used in commercial products generates hundreds of different gases. The evaluation of the FED values and the nature of the combination of those FED values would have been a daunting, if not insurmountable, task. Researchers at the National Institute of Standards and Technology (NIST) proposed the N-gas model. This concept suggests that the toxic potency of most commercial products could be estimated from the contributions of a small number, N, of the combustion gases. 35,51 The results of rat exposure experiments to single and mixed gases were compared with experiments in which rats were exposed to the gases generated by the combustion of a number of materials. The mean FED value corresponding to the LC<sub>50</sub> was 1.07, using the "N-gas" calculation, with 95 percent confidence limits of 0.20.61 This provided substantial support for this concept.

Two equations have been developed to fit rodent data.<sup>52</sup> The first, Equation 5, was developed empirically by Levin and coworkers<sup>9</sup> from exposure of laboratory rats to individual and mixed gases:

$$FED = \frac{m \cdot f_{CO}}{f_{CO_2} - b} + \frac{21 - f_{O_2}}{(21 - 5.4)} + \frac{f_{HCN}}{150} + \frac{f_{HCl}}{3700} + \frac{f_{HBr}}{3000}$$
 (5)

where m and b are, respectively, the slope and intercept of the interactive curve of CO and CO2, which depicts the increasing toxicity of CO as CO<sub>2</sub> concentration increases. The values of m and b depend on the volume fraction of  $CO_2$ . If  $f_{CO_2} \le 0.05$ , m = -18 and b = 122,000. If  $f_{CO_2} > 0.05$ , m = 23 and b = -38,600. Confirmatory work using this model has been published by

The terms  $f_{\rm r}$  are the volume fractions of those species in μL/L, except for O<sub>2</sub> and CO<sub>2</sub>, where the volume fractions are in volume percent.

The second, Equation 6, was developed by Purser, 62 fitting the rat LC<sub>50</sub> data obtained mainly by Levin et al. 61,63 and Kaplan and Hartzell.27

$$FED = \left(\frac{f_{CO}}{LC_{50,CO}} + \frac{f_{CN}}{LC_{50,HCN}} + \frac{f_X}{LC_{50,X}} + \frac{f_Y}{LC_{50,Y}}\right) V_{CO_2} + A + \frac{21 - f_{O_2}}{(21 - 5.4)}$$
(6)

where, in addition to the definitions for Equation 5,

 $f_{\rm CN}$  = The volume fraction of HCN in  $\mu$ L/L, corrected for the presence of other nitriles and the protective effect of  $NO_2$ , and is equal to  $f_{HCN}$  +  $f_{\text{total organic nitriles}} - f_{\text{NO}_2}$ 

 $LC_{50 \text{ X}}$  = The  $LC_{50}$  of each acid gas irritant in  $\mu L/L$ 

 $LC_{50 \text{ Y}}$  = The  $LC_{50}$  of each organic irritant in  $\mu L/L$ 

 $V_{\rm CO_2}$  = A multiplication factor for  $\rm CO_2$ -driven hyperventilation equal to 1 + e[(0.14  $\cdot$  CO<sub>2</sub>%) – 1]/2

 $A = \text{An acidosis factor equal to } f_{\text{CO}_2} \times 0.05$ 

The 30 minute  $LC_{50}$  values used in Equation 6 are given in Table  $6.2.1.^{54}$ 

Between the two equations, there are small numerical differences in the LC50 values for HCN, HCl, and HBr. These differences are within the uncertainties of the experiments from which the values were derived.

There are also functional form variations in the way CO,  $CO_2$ , and depleted  $O_2$  are included in the two equations. These variations will lead to modest differences in the calculated values of the FED. A reasonable estimate of agreement between the two equation calculations is  $\pm 30$  percent for FED values  $\approx 1$ .

#### Sublethal Effects of Fire Smoke

Smoke inhalation can lead to a succession of sublethal effects that each can affect how readily a person can find safety from a fire. For nearly all of these, there are few quantitative data from controlled experiments or actual fire experience for the degree to which these effects alter the ability of laboratory animals or people to escape from a fire. Although tests have been developed for assessment of incapacitation due to sensory irritation, <sup>64</sup> they have not received significant use. This is due, at least in part, to a lack of validation between the tests and actual effects on humans. This has led the experts assigned to ISO TC92 SC3 to affirm that the focus should be on incapacitation. <sup>10</sup> Incapacitation is defined as the inability to take action to accomplish an escape from a fire.

Some measurements have been made of incapacitation on rodents.<sup>27</sup> A literature review of the animal exposure data for CO and HCN showed that the concentrations that caused incapacitation were one-third to one-half those that resulted in death.<sup>27</sup> A subsequent review was performed of the literature of the animal exposure data for exposure of animals to combustion smoke from a wide variety of materials and products.<sup>55</sup> The mean value of the ratios of the IC<sub>50</sub> to the LC<sub>50</sub> and the standard deviation were 0.50 and 0.21, respectively.

Although considerable attention was once directed toward incapacitation studies, testing for smoke toxicity ultimately made no such assessment. Incapacitation is simply inferred from lethality data, with combustion toxicologists generally regarding incapacitating exposure doses to be about one-third to one-half of those required for lethality.<sup>27</sup>

**TABLE 6.2.1** 30 Minute LC<sub>50</sub> Values for Rats

Combustion Product	30 min LC <sub>50</sub> (μL/L)
СО	5700
HCN	165
HC1	3800
HBr	3800
HF	2900
$SO_2$	1400
$NO_2$	170
Acrolein	150
Formaldehyde	750

Source: Data from International Organization for Standardization.

#### TEST METHODS FOR TOXICITY OF SMOKE

# **Evolution of Testing**

In the 1970s and 1980s, the dominant philosophy was that smoke toxicity was a property of a material and that control of this property was the proper approach to improving life safety in fires. Accordingly, a number of bench-scale apparatus were developed to measure the toxicity of smoke produced from the burning of materials and, sometimes, products.<sup>65</sup> These tests exposed a sample of a material or a finished product to a thermal exposure that was deemed appropriate to simulate a fire. Multiple rats or, less commonly, mice were exposed to the combustion products. Sufficient experiments were performed to estimate the LC<sub>50</sub> for a 30 minute exposure and frequently within a postexposure period of up to 14 days. The LC<sub>50</sub> values were expressed in units of g/m<sup>3</sup>, that is, grams of the test specimen that were consumed (and presumed to be present as smoke) per unit exposure chamber volume (for closed box apparatus) or total air flow (for flow-through apparatus). One test method, The University of Pittsburgh (UPITT) device, expresses the LC<sub>50</sub> only as grams of material subjected to the test protocol, which is not a true expression of concentration. In general, care should be taken in comparing LC<sub>50</sub> values obtained from different test methods to ensure that the basis for reporting data is the same.

Although this type of testing may have led some manufacturers to not market certain products, regulation on this basis was limited. For a number of years, the state of New York required the testing and filing of test data for certain construction and finish materials using the "LC50" value from the UPITT method. However, when it became widely recognized that the results of such testing were often irrelevant to the toxic hazards of real fires, the regulation was repealed and most of the laboratory testing ceased. At present, there are no laboratories conducting nonproprietary animal tests for smoke toxicity on a routine basis.

In recent decades, there has been growing resistance to the routine use of laboratory animals for testing products, whether this be for skin care or fire safety. This has resulted in a move toward the N-gas concept. Unfortunately, there were, and continue to be, some regulations based on limiting the concentration of one or more gases generated using a particular test apparatus. As noted in the introduction to this chapter, this is not likely to help achieve a desired level of fire safety, since the gas yields are not singular properties of a product.

More recently, there has been enhanced awareness that the proper use of smoke toxic potency data is as input to a fire hazard or risk assessment, rather than stand-alone pass/fail testing of materials or products. 10 The values to be used are the yields of the toxic gases. This is the mass of the gas generated divided by the combusted mass of the test specimen. Less commonly, the calculations use the specimen mass subjected to the test conditions. (These values will be identical if the specimen is completely combusted with no residue.)

Per NFPA 269 and ASTM E1678-02,53 there is now a protocol that balances the need for accuracy in toxic potency measurement while minimizing the use of laboratory animals. In this method, the measured concentrations of the principal

toxicants that are generated when a test specimen is combusted are used to estimate the LC<sub>50</sub> using the N-gas equation. Rats are then exposed to smoke at concentrations 30 percent below and 30 percent above this value. If the animal mortality agrees with the predicted LC<sub>50</sub>, then it is presumed that the smoke is "normal" and the estimated value is used. This will generally be the case for a product whose chemistry is similar to other products for which the animal confirmation test was successful. If the smoke is unusually toxic to rats, then additional research or testing is warranted.

The question then arises as to which of the many tests available gives toxic potency values that are "right." ISO 16312-1 describes the characteristics of the ideal fire effluent toxicity test method:66

- The combustor (or physical fire model) replicates one or more fire stages (radiative pyrolysis, well-ventilated flam-
- The test specimens are representative of as-used products.\*
- The apparatus itself does not affect the results.
- The apparatus is straightforward to use.
- The method generates gas/smoke yields and specimen mass loss data.
- The method has demonstrated accuracy relative to realscale fires.
- The results are repeatable and reproducible.

The standard then provides criteria to evaluate a real method. ISO/TR 16312-2 (not a Standard, but a Technical Report that presents the ISO TC 92/SC 3 assigned experts' appraisal) applies these criteria to twelve test methods in use today.<sup>67</sup>

The following sections present the essential features of some of the tests whose data are most likely to appear in the published literature or which are more commonly used for the regulation of materials and products. For a broader coverage of the many apparatus that have been developed over the years, the reader is referred to more complete compilations. <sup>66,67</sup>

#### **Cup Furnace Test**

The cup furnace test, <sup>68</sup> described in Figure 6.2.1, combusts a test specimen in a quartz beaker (the "cup"); the effluent rises and expands to fill an 0.2 m<sup>3</sup> closed box. Data for both nonflaming and flaming combustion are obtained by conducting tests just below and just above the autoignition temperature of the specimen, respectively. In each test, six rats are held in tubular restrainers, with their heads inside the box. They inhale the smoke for 30 minutes and then are observed for the following 14 days. Multiple experiments are conducted, with varying masses of the test specimen placed in the cup furnace, leading

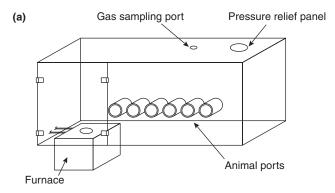
<sup>\*</sup>This may be the most difficult of the characteristics with which to comply. Some test methods can accommodate a specimen prepared to resemble, as much as possible, a product in its form of use as it would be exposed in a fire. Other test methods require, or can only accommodate, a ground or crumpled specimen. The latter is less representative of a product having complex construction (e.g., layers of different materials). These two approaches may yield different results for the toxicity of smoke produced by a product.

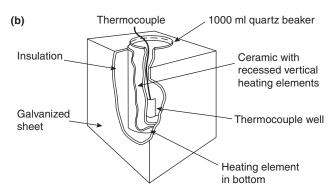
to different concentrations of smoke in the box. The number of animal deaths per test is plotted against the smoke concentration (specimen mass in the furnace divided by the box volume). Statistical analysis of the data then generates an estimate of the LC<sub>50</sub> (30 minute exposure plus 14 day postexposure period). Chemical analysis of the principal toxicants enables a second estimation of the  $LC_{50}$  using Equation 5 for FED = 1. The use of rats can be minimized by using the animal check test protocol as noted above under "Evolution of Testing."

Extensive data on individual fire gases, combinations of those gases, materials, and products have been produced using this method. The data can be found in the references to Levin and coworkers in the bibliography of this chapter. This method is no longer in use since the radiant furnace apparatus (discussed next) manifests a more fire-like exposure of the test specimen. However, the data from the cup furnace method are still widely referenced.

#### Radiant Furnace Test

The radiant furnace test<sup>53</sup> uses the same 0.2 m<sup>3</sup> box as the cup burner test. However, the cup furnace is replaced by an assembly that applies a fixed radiant flux to the test specimen, as shown in Figure 6.2.2.<sup>69</sup> A spark source is used to ignite the fuel vapors. The test is particularly applicable to layered products, such as furniture or wall coverings. In the operation of the method, a test specimen up to 10 cm by 15 cm by 5 cm thick is exposed to





**FIGURE 6.2.1** Schematic of the Cup Furnace Apparatus. (a) Orientation of furnace to exposure box. (b) Details of cup furnace. (Source: National Institute of Standards and Technology)

a radiative flux of 50 kW/m<sup>2</sup> for 15 minutes. The smoke enters the box through the center hole of a three-slot chimney. Air from the box is recirculated to the combustion zone through the two outer slots. The rat exposures and gas analyses are the same as with the cup furnace test. Successive tests are performed, with the top surface area of the specimen being varied to vary the concentration of smoke in the box.

The lethal toxic potency, LC<sub>50</sub>, of the smoke from the test specimen is predicted from the combustion atmosphere analytical data by first calculating the FED for the test. The 30 minute LC50 is then calculated as that specimen mass loss that would yield FED = 1 within a chamber volume of 1 m<sup>3</sup> from the equation:

$$LC_{50} = \frac{\text{Specimen mass loss}}{\text{FED} \times \text{Chamber volume}}$$
 (7)

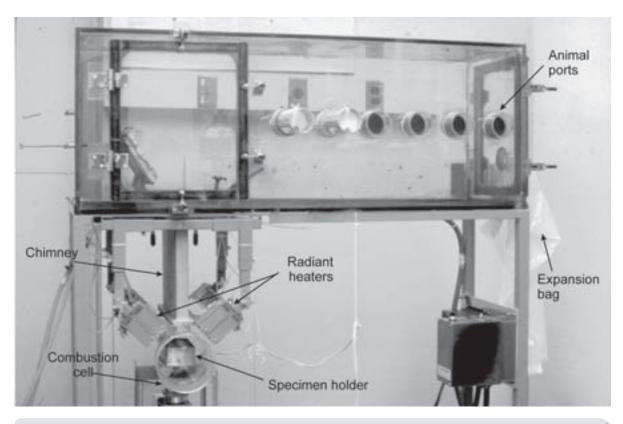
where the specimen mass loss is in grams and the chamber volume is  $0.2 \text{ m}^3$ . The resulting LC<sub>50</sub> has the units of g/m<sup>3</sup>. The predicted LC50 is then confirmed in limited tests using rats to ensure that the monitored toxicants account for the observed toxic effects.

The apparatus and procedures have been standardized (identically) as ASTM E1678, Standard Test Method for Measuring Smoke Toxicity for Use in Fire Hazard Analysis<sup>53</sup> and NFPA 269, Standard Test Method for Developing Toxic Potency Data for Use in Fire Hazard Modeling. Both standards also provide for a mathematical adjustment of experimental LC50 values in order to make them appropriate for the toxic hazard assessment of oxygen-vitiated, postflashover fires.

The test results have been compared to results from roomscale postflashover fires.<sup>70</sup> Prior to performing the comparison, an adjustment was made to the CO yield. Following flashover, the oxygen concentration in a room drops precipitously. Were this condition replicated in the current test, the animals would succumb to the reduced oxygen, regardless of the effects of the other gases in the smoke. A literature search indicated that postflashover fires typically generate yields of CO of about 0.2 kg CO per kg fuel consumed. This yield is substituted for the CO yield determined in the tests. For five different criteria, the bench-scale apparatus produced results consistent with the room-scale data. Accuracy to within a factor of three was established as both attainable and practical.

# University of Pittsburgh (UPITT) Test

The UPITT test,<sup>71</sup> shown in Figure 6.2.3, exposes four mice per test to fire effluent produced in a flow-through system from the 68°F (20°C) per minute ramped heating of a specimen in a box or muffle furnace. Exposures are for 30 minutes, starting when 1 percent of the sample weight has been lost. The animals are also observed for 10 minutes following the exposure to the combustion gases. Animal measurements include concentrationresponse for lethality and time-to-death. Although the results are reported as LC<sub>50</sub> values, the values are actually the weight of test specimen charged to the furnace, rather than actual concentrations of smoke, which varies considerably during a test. Thus, "LC50" values obtained from this test are not directly comparable to those from other methods. Between 1987 and 1998, this



**FIGURE 6.2.2** ASTM E1678/NFPA 269 Test Apparatus (Source: National Institute of Standards and Technology)

test was required by the state of New York for certain construction and finish materials. No acceptance levels or criteria for classification of materials were ever set. During the years over which testing was conducted, LC50 values were reported and filed with the state of New York for over 15,000 products.<sup>72</sup>

There are a number of differences between real-scale fires and the conditions in this apparatus. There is no ignition source, so the samples autoignite or don't, depending on the mix of gases generated, the point in the temperature ramp, and the sufficiency of the oxygen at that point. Furthermore, it is not clear

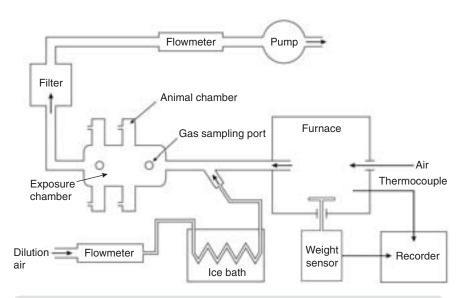


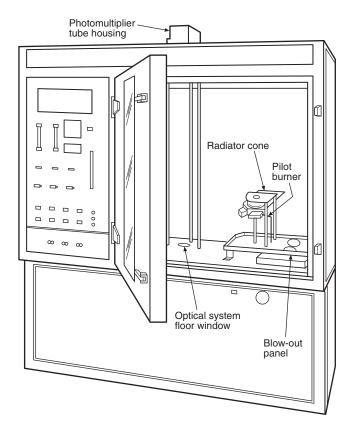
FIGURE 6.2.3 Schematic of the University of Pittsburgh Apparatus (Source: National Institute of Standards and Technology)

when the combustion conditions in the furnace resemble preflashover burning, postflashover burning, or neither. Because the combustion gases flow past the mice, the mice can be exposed to some gases in series, rather than concurrently.

#### **Closed Cabinet Toxicity Test**

The closed cabinet toxicity test is illustrated in Figure 6.2.4. This apparatus, standardized in NFPA 270, Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber, and ISO 5659-2,<sup>73</sup> was designed for measurement of smoke optical density. However, with the addition of gas concentration measurements, it is used by the International Maritime Organization and the European Union, among others, as an acceptance test based on gas concentrations.

In a test, a planar test specimen, 7.5 cm by 7.5 cm by up to 2.5 cm thick, is exposed to a radiant flux of either 25 kW/m<sup>2</sup> or 50 kW/m<sup>2</sup> for 10 minutes. A pilot flame is standard, but provision is made for testing without the pilot flame. The combustion products accumulate in the 0.5 m<sup>3</sup> chamber. Combustion products are sampled through a probe whose tip is located at the geometric center of the chamber. Should the concentration



**FIGURE 6.2.4** Typical Arrangement of the Closed Cabinet Test Chamber (Source: NFPA 270, Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber, 2002 ed., Figure 4.1)

of any of the specified fires gases exceed a prescribed limit, the material or product fails the test.

During the course of a test, the air in the chamber becomes vitiated, and the generation rates of the combustion products evolve. 74 Thus, it is not clear what stage of a fire is being replicated. It follows that the use of the gas concentration data are of questionable value as an indicator of fire safety. There have been no reported comparisons of data from this apparatus with data from real-scale fire tests of the same materials or products.

#### **Tube Furnaces**

There are a number of designs of these apparatus in use around the world. Two are described here, the first because of the data that have been generated, the second because of its potential as an ISO standard.

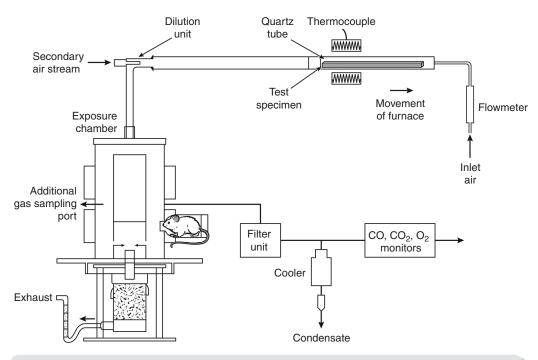
The DIN 53436 Test, developed by the German Standards Institution and shown in Figure 6.2.5, is characterized by the use of a moving cylindrical tube furnace operating at a constant temperature in the range of 392 to 1832°F (200 to 1000°C).<sup>75</sup> The furnace is programmed to travel the length of a quartz tube containing the sample, which has a volume of about 40 mL. Decomposition, taking place in an air stream countercurrent to the direction of furnace travel, is intended to result in the continuous flow of fire effluents of constant composition. The standard procedure includes exposure of 10 rats to the effluent and measurement of the gases generated.

This test device, used in six European countries, offers a rather wide range of well-controlled combustion conditions. Ratios of CO<sub>2</sub>/CO can be made to vary widely, depending on the air flow used. Thus, both well-ventilated and ventilationlimited fires may be simulated. Specimens may undergo either flaming or nonflaming combustion, depending on the imposed heat flux.

Combustion product analytical data obtained from the DIN 53436 test have been used for the calculation of LC<sub>50</sub> values using the FED principle, as well as the N-gas method described in connection with the ASTM E1678 test. <sup>76</sup> Comparisons between calculated and experimental LC50 values for over 30 materials tested revealed fairly good correlation and predictability, giving additional credibility to the concept that lethal toxic potency can largely be attributed to a small number of major toxic gases.

The tube furnace used in ISO/TS 19700<sup>77</sup> is larger in diameter (4.3 cm) than the DIN furnace. It is described in Figure 6.2.6. The test specimen fills a boat that is at least 0.8 m long. The boat is driven through a tube furnace at a set temperature, 660°F (350°C) for oxidative pyrolysis, 1200°F (650°C) for well-ventilated flaming combustion, and 1520°F (825°C) for postflashover combustion. The fixed sample speed and the variable air flow though the tube allows predetermination of the equivalence ratio. There is a small open box at the exit end of the tube from which the effluent gases are sampled. The box can be adapted for exposing laboratory animals. The apparatus is identical to the tube furnace in BS 7990;<sup>78</sup> there is a less well-defined version that has been adopted by the International Electrotechnical Commission.

Because of the wide variation in tube furnaces, ISO/TS 19700 was developed to encourage broad construction of uni-

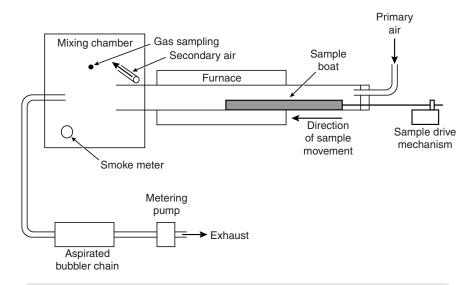


**FIGURE 6.2.5** Schematic of the DIN 53436 Tube Furnace (Source: National Institute of Standards and Technology)

form devices. A correlation has been found between CO yields in real-scale fire tests and those from the tube furnace.<sup>79</sup>

#### **ESTIMATION OF TOXIC HAZARD IN FIRES**

The fundamental principle in designing for the safety of people in fires is to provide sufficient time for them to escape or find a place of refuge before being overcome by the flames, heat, or smoke. In quantitative terms, the objective is for ASET to be greater than RSET. ASET, the *available safe egress time*, is the interval between the time of ignition of the fire and the time at which an individual is incapacitated. RSET, the *required safe egress time*, is the time it takes that individual to find a safe location. Each person may have a different value for each of these terms, depending on such factors as his/her starting location, physical condition, and susceptibility to smoke. The magnitude of the difference between ASET and RSET is an indicator of the degree of safety being provided.



**FIGURE 6.2.6** Schematic of the ISO/TS 19700 Tube Furnace (Source: National Institute of Standards and Technology)

A fire simultaneously generates gases, heat, and aerosols. Each of these three can lead to a state in which a person cannot effect his or her own escape, which is the definition of incapacitation. Typically, one estimates an independent ASET value for flames, heat, or smoke.\* The limiting hazard is the effluent component that leads to the shortest value of ASET.

The following sections summarize the consensus of the assigned experts to ISO TC 92/SC 3 regarding the best representation of incapacitating levels of these three threats. Additional information may be found in ISO 13571.<sup>46</sup>

## Response of People to Fire Gases

The modeling of this component of toxic hazard assessment can take either of two forms, depending on the nature of available input data. <sup>80</sup> In each case, a person moves from a location at the time of ignition to a final location (which may be a site of safety or a site of incapacitation), passing through a time-varying field of combustion products. In some simplified calculations, the person remains in a fixed location. The tenability of various locations is then examined as a function of time following ignition of the fire. There are very few data on exposures of an hour or more. Thus, using the following information for estimation of incapacitation or lethality due to long exposures to very low levels of heat and smoke is not advised.

#### Toxic Gas Model

The toxic gas model is most useful in considering fires where the time varying concentrations of the individual fire gases can be simulated using a fire growth and effluent spread model, such as the Fire Dynamics Simulator (FDS).81† The effects of asphyxiant toxicants and sensory/upper respiratory irritants are considered separately. This is because effects due to asphyxiants are related to their accumulated exposure dose (concentration × time), whereas the initial effects due to sensory/upper respiratory irritants are related largely to their concentration. Thus, the model also requires as input the exposure dose for each asphyxiant and concentration for each irritant that would be expected to cause incapacitation. These latter values are obtained from exposure of laboratory animals, with the results then being extrapolated to people. ISO 13571 contains consensus estimates of the incapacitating values and two equations, one for the effects of asphyxiant gases and one for the effects of irritant gases.

The modeling of the asphyxiant gases involves the same FED concept used to calculate  $LC_{50}$  values from analytical data. As before, incremental exposure doses of each gas are accumulated over time, with the incremental time interval being at the discretion of the modeler. However, rather than determining the accumulated FED by integration over 30 minutes, here the

exposure doses of the gases are accumulated until the time at which a chosen FED criterion is reached. <sup>46</sup> For example, the time required to reach FED = 1 can be defined as the most frequently expected time for incapacitation to occur. ISO 13571 indicates lower FED criteria could provide safety for a larger fraction of the population at large, as well as for the subpopulations that are more sensitive to fire smoke. <sup>46</sup>

The FED equation for incapacitation due to asphyxiants is

FED = 
$$\sum_{t_1}^{t_2} \frac{\text{[CO]}}{35,000 \,\mu\text{L/L} \cdot \text{min}} \Delta t + \sum_{t_1}^{t_2} \frac{\exp(\text{[HCN]/43})}{220 \,\text{min}} \Delta t$$
 (8)

where CO and HCN volume fractions are in  $\mu$ L/L. Equation 8 is derived from actual incapacitation experiments using nonhuman primates. <sup>23,41</sup> It is most applicable when oxygen volume fractions are not lower than 0.13, and CO<sub>2</sub> volume fractions do not exceed 0.02.

The sensory/upper respiratory irritant component of toxic hazard is addressed in a somewhat analogous manner, with the exception that instantaneous concentrations, rather than accumulated doses, are used. For irritants, the time at which the total fractional effective concentration (FEC) becomes equal to 1 is the time at which the average person will become incapacitated.

A generic equation for incapacitation due to sensory/upper respiratory irritants is

$$FEC = \frac{f_{HCl}}{F_{HCl}} + \frac{f_{HBr}}{F_{HBr}} + \frac{f_{HF}}{F_{HF}} + \frac{f_{SO_2}}{F_{SO_2}} + \frac{f_{NO_2}}{F_{NO_2}} + \frac{f_{acrolein}}{F_{acrolein}} + \frac{f_{formaldehyde}}{F_{formaldehyde}} + 3 \frac{f_{irritant}}{F_{irritant}}$$
(9)

where irritant volume fractions are in  $\mu$ L/L. Consensus values of the denominator constants, F, were given in the prior section of this chapter.

#### Mass Loss Model

For many combustibles, there are no data and no predictive capability for the yields of the toxic gases as a function of time. However, if an  $LC_{50}$  or an  $IC_{50}$  value has been measured, a simulation of toxic hazard is still possible. Rather than generating individual gases and then distributing them throughout the building, this model distributes a single "gas," the combusted mass from the burning fuels. The basic FED concept is then employed, giving Equation  $10^{.46}$ 

$$FED = \sum_{i=1}^{n} \sum_{t_{1}}^{t_{2}} \frac{\Delta m}{V(Ct_{i})} \Delta t$$
 (10)

where

 $\Delta m$  = Average accumulated mass loss (g) over the time increment,  $\Delta t$ 

 $V = \text{Volume (m}^3)$  into which fire effluents are dispersed

 $\Delta t$  = Time increment (min)

 $(Ct_i) = \frac{1}{2}(LCt)_i \text{ in } g \cdot m^{-3} \cdot \text{min as determined from test methods (e.g., NFPA 269)}$ 

<sup>\*</sup>Although it is likely that the three components of the fire effluent act in combination to retard the escape process, there are very few data on which to base the quantification of the interactions. Thus, for example, it is not known whether or how elevated temperature affects a person's ability to find his or her way through dense smoke.

<sup>&</sup>lt;sup>†</sup>FDS, as well as all current "fire" models, does not contain the chemistry to predict the generation rates of fire gases or aerosols. The yields of these species are input parameters, and the computational model distributes the species around the building.

As with the toxic gas model, the time required to reach FED = 1 can be defined as the most frequently expected time for incapacitation to occur for the person of median susceptibility to fire smoke. The mass loss model represents a considerable simplification for assessment of the life-threatening effects of combustion atmospheres:

- It combines the effects of irritant and asphyxiant gases. Although there are data to indicate the additive effect of HCl and CO on the lethality for rats, there are no published data to verify this (or any other mode of combination) for people.
- It also presumes that the two types of gases stay in the same proportion to each other as they spread away from the fire. In this sense, the mass loss model is conservative, because the acid gases, for instance, are likely to stick to surfaces. Their concentrations thus diminish relative to those of the narcotic gases as one gets farther from the fire.

# Further Simplification

An even further simplification employs a "generic"  $LCt_{50}$ value for lethal toxic potency when combustible fuel in a fire consists of a mixture of materials and products that are unidentified as to their nature and relative quantity. Suggested "generic" LCt<sub>50</sub> values are 900 g/m<sup>3</sup>·min for well-ventilated, preflashover fires and 450 g/m<sup>3</sup>·min for vitiated, postflashover fires. <sup>46</sup> For incapacitation, values of  $(Ct_i)$  in Equation 8 then become 450 g/m<sup>3</sup> min for well-ventilated, preflashover fires and 220 g/m<sup>3</sup>·min for vitiated, postflashover fires. It is cautioned that these "generic" LCt<sub>50</sub> values represent only an approximation and their use should be subject to expert toxicological and engineering judgment.

Whereas compiled data of laboratory determination of LC<sub>50</sub> values have a mean value of about 30 g/m<sup>3</sup> for wellventilated combustion, the measured values range from about 5 to 60 g/m<sup>3</sup>.<sup>55</sup> Thus, there are some materials whose smoke is over five times as potent as the average material. Fortunately, flaming fires of toxicological importance generally involve a mixture of materials, and it is infrequent that such large fires would be dominated by a single product whose smoke is of very high toxicity. Nonetheless, the person performing the hazard or risk analysis should be aware of the presence of such materials.

# Variability of Human Responses to Fire Gases

The variability of the responses of people to the toxicological insults of fires is best represented by a statistical distribution that takes into account their varying susceptibilities. The overall human population contains a number of subpopulations that exhibit a greater than average sensitivity to fire gas toxicants. The largest of such subpopulations are the very young, the elderly, and those who suffer from compromised respiratory systems (e.g., asthmatics). Infants and young children are particularly susceptible to asphyxiant toxicants due to a greater volume of air inhaled per minute relative to their body weight. The elderly, particularly those with compromised cardiovascular systems, are also especially susceptible to asphyxiant toxicants. Asthmatics, along with sufferers of other lung conditions such as

chronic bronchitis and reactive airways dysfunction syndrome, are particularly susceptible to bronchoconstriction from even brief exposure to low concentrations of irritants, with collapse and sometimes even death resulting. To provide a degree of protection to these more vulnerable subpopulations, safe levels for exposure of the human population to fire gas toxicants must always be significantly lower than those that might cause incapacitation or other adverse effects with healthy young adults.

According to the methodology described, FED and/or FEC values of 1.0 are associated with sublethal effects that would incapacitate persons of average susceptibility. In the absence of information to the contrary, a log-normal distribution of human responses is a reasonable choice, with FED and/or FEC values of 1.0 corresponding to the median value of the distribution. (Half the population would be more susceptible to an insult and half would be less susceptible.) Statistics then show that at FED and/or FEC criteria of 0.3, 11.4 percent of the population would be susceptible to less severe exposures (lower than 0.3) and, therefore, be statistically subject to incapacitation.<sup>82</sup>

Lower criteria would reduce that portion of the population. These would be appropriate for occupancies in which the people are expected to be more susceptible to heat and smoke or for whom escape is more difficult and thus might take longer. Examples of such occupancies are hospitals and schools for very young children. Note, however, that there is no criterion so low as to be statistically safe for all people. For proper balance between the effects of narcotic and irritant gases, the FEC and FED threshold criteria should be equal.

A consequence of the statistical distribution of human responses resulting from exposure of people to smoke atmospheres is that the distributions for two such responses, such as incapacitation and death, may overlap. This gives rise to a probability that some may die without others even being incapacitated. It is known that this occurs in real fires.

#### Extrapolation of Rodent Data to Humans

The propensity for smoke to have the same effects on humans in fires can only be inferred to the extent that the rat or mouse can be correlated with humans as a biological system. As a result of comparisons of rodent data with limited human and nonhuman primate data, the use of the rat as an acceptable model for human exposure, at least for the asphyxiant gases, has received general endorsement among smoke toxicologists.54 The 30 minute exposure time for animals in laboratory smoke toxicity tests is considered by some to be rather long compared to most human exposures to smoke in fires. Traditional extrapolation of toxic potency test data for shorter exposures has presumed that the product of lethal concentration and exposure time is a constant.

A recent publication<sup>83</sup> provides an estimation method for relating the normal rat lethality data to incapacitation values for smoke-sensitive people:

- For materials and products that do not generate strong acid gases, assume that CO (as a surrogate for asphyxiants) is the primary toxicant and use one-fourth the 30 minute rat LC<sub>50</sub> as the 5 minute human IC<sub>sens</sub>.
- · For materials and products that do generate strong acid gases, narcotic gases still generally account for the majority

of the combined incapacitating effect of narcotic and irritant gases. Based on the relative generation rates of CO and HCl cited above, one could use one-fifth of the 30 minute rat LC<sub>50</sub> as the 5 minute human IC<sub>sens</sub>.

Because the narcotic component dominates the IC<sub>sens</sub> values, the use of  $C^2t$  as a time scaling formula is preferred.

Gann<sup>83</sup> estimates that, for an unknown mixture of combustibles, a generic value for the concentration of smoke that would incapacitate a rat of average sensitivity in 30 minutes would be  $30 \text{ g/m}^3 \pm 20 \text{ g/m}^3$  for a well-ventilated flaming fire and 15  $g/m^3 \pm 3$   $g/m^3$  for a postflashover fire. Incorporating the above guidance leads to corresponding values for the concentration of smoke that would incapacitate smoke-sensitive people in 5 minutes: 6 g/m<sup>3</sup> for a well-ventilated fire and 3 g/m<sup>3</sup> for an underventilated postflashover fire. The user of these values needs to be mindful of three key factors:

- 1. There is a wide range of smoke toxicity values reported for various materials. Some of these have significantly higher or lower values than these generic values.
- 2. These generic values are estimated with significant assumptions in their derivations. An estimated uncertainty is about a factor of two.
- 3. People involved in fires are often excited and physically active. Both of these can increase the intake of the smokeladen air and increase its toxic potency. At present, there is no quantitative literature on these effects or any way to apply them to the population as a whole.

#### Response of People to Heat

The burning of most materials is an exothermic chemical oxidation process. Enthalpy from the process is evolved as heat, which possesses both convective (hot gases) and radiative components, each measured as a heat flux (kW/m<sup>2</sup>).

Heat produced from a fire presents significant physical danger to humans in three basic ways: burns to the skin, hyperthermia or heat stroke, and respiratory tract burns. Before skin can absorb sufficient heat to raise its surface temperature, the body's heat-dissipating capabilities must be defeated. The body dissipates heat by evaporative cooling (perspiration) and by circulation of blood. If the total heat energy reacting with the body surpasses the capability of the physiological defense processes to compensate, a series of events can occur, ranging from minor injury to death. Up to a critical exposure, one can reasonably tolerate excess heat, but above that exposure, tolerance decreases exponentially.

For radiant heat, there is a threshold radiant flux below which significant heating of the skin is prevented, but above which quite rapid heating occurs. The tenability limit for exposure of skin to radiant heat is approximately 2.5 kW/m<sup>2</sup>, below which exposure can be tolerated for 30 minutes or longer without significant consequences. <sup>23,46</sup> Above this threshold, the time to burning of skin decreases very rapidly to about 20 seconds and less. Clothing offers a degree of protection and increases tolerance times.

Skin tissue burns commonly are classified as first-, second-, or third-degree. First-degree burns involve only the outer layer of the skin and are characterized by abnormal redness, pain, and sometimes a small accumulation of fluid underneath the outer layer. Second-degree burns penetrate more deeply into the skin. The burned area is moist and pink, the skin blisters, and there is usually a considerable amount of subcutaneous fluid accumulation. Third-degree burns usually are dry, charred, or pearly white. If a large percentage of the body skin tissue has suffered third-degree burns, postexposure consequences may be extremely critical, often leading to death. A relationship for time (min) to the second-degree burning of skin due to radiant flux, q (kW/m<sup>2</sup>), is shown in Equation 11.84

$$t_{\rm I,rad} = 6.9q^{-1.56}$$
 (11)

The effects of exposure to convective heat are also a strong inverse exponential function of temperature. An empirical relationship between temperature and the time to incapacitation is shown in Equation 12.85

$$t_{\rm I,conv} = 4.1 \times 10^8 \ T^{-3.61}$$
 (12)

where  $t_{\text{Lconv}}$  is the time (min) to thermal collapse and T (°C) is the temperature at the skin surface.

Thermal tolerance data for unprotected skin of humans suggest a limit of about 248°F (120°C) for convected heat, above which considerable pain is quickly incurred along with the production of burns within a few minutes or less.<sup>23</sup> Depending on the length of exposure, convective heat below this temperature may still result in hyperthermia. Hyperthermia occurs if the body absorbs heat faster than it can be dissipated by evaporation of surface moisture and outward radiation. The entire body temperature is thereby elevated sufficiently above normal to cause damage to the central nervous system and, possibly, death.

Thermal burns to the respiratory tract from inhalation of air containing less than 10 percent by volume of water vapor do not occur in the absence of burns to the skin or face. Thus, tenability limits with regard to skin burns are normally lower than for burns to the respiratory tract.

Moisture can be present in a fire environment as the result of natural humidity, from the combustion itself, and from the application of water for extinguishment. The effects of exposure to heated air are greatly exacerbated by the presence of moisture. With higher moisture content, transfer of heat energy is more efficient and the body is less able to rid itself of the heat burden. If excessive heat is conducted rapidly to the lungs, a serious decline in blood pressure may result, along with capillary blood vessel collapse leading to circulatory failure. Severe heat may also cause fluid buildup in the lungs.

In fire tests conducted by the National Research Council of Canada, 300°F (149°C) was taken as the maximum survivable breathing air temperature.86 A temperature this high can be endured for only a short period and not at all in the presence of moisture. The city of Los Angeles selected 150°F (66°C) at 1.5 m above the floor as the design temperature beyond which teachers and children could not be expected to enter a corridor from a relatively cool room.<sup>87</sup> This selection assumed exposure to dry air and only for the brief period of time necessary to reach exits.

# Response of People to Visible Smoke

In addition to fire gases, smoke also consists of particulate matter, formed from the burning of most materials under the conditions of incomplete combustion, and suspended liquid droplets known as aerosols. Since the average size of the particulates and aerosols is about the same as the wavelength of visible light, light is scattered and vision through smoke can be obscured. Petroleum-derived materials, especially those from aromatic hydrocarbons, are particularly prone to the formation of dark, sooty smoke. There is, however, no established relationship between the color of the smoke and the toxicity of fire gases that may be present.

Since smoke obscures the passage of light, visibility to exits may be hampered, impairing escape from a fire. The development of quantities of smoke sufficient to impair egress can be very rapid and usually is the first hazard to occur in a fire. As evidenced in nearly every one of the Los Angeles school fire tests, smoke in the corridors arising from fires in the basement reached untenable levels before temperatures attained hazardous condition.<sup>87</sup> Smoke was therefore the principal hazard. Although smoke frequently provides an early warning of fire, it also limits visibility because of its blinding and irritating effects, slowing escape.

Obscuration of vision due to smoke is related to its concentration and is usually expressed as optical density per meter, OD (m<sup>-1</sup>). Visibility is, then, the reciprocal of the OD. People's response to obscuration of vision and its detrimental effects on the speed of movement and way-finding efficiency is highly variable. Visibility requirements for escape depend to a large extent on the size of an enclosure and occupants' familiarity with escape routes. Suggested OD limits for impairment of egress have ranged from 0.5 m<sup>-1</sup> (2 m visibility),<sup>88</sup> for occupants of small rooms who are familiar with escape routes, down to about 0.065 m<sup>-1</sup> (15 m visibility), <sup>89</sup> for large enclosures in which occupants are unfamiliar with their surroundings.

For visible smoke, the equivalent of toxicological incapacitation for fire gases is an inability to orient oneself with one's surroundings. This is the equivalent to not being able to see one's hand in front of one's face. ISO 13571 estimates that this occurs when a person is confronted with a fuel mass loss concentration of 20 g/m<sup>3</sup> for well-ventilated fires and 10 g/m<sup>3</sup> for underventilated fires. 46 This is based on a minimum detectible contrast of 0.0290 for a distance of 0.5 m, published smoke yields, 91,92 and a generic value of the mass specific extinction coefficient of the smoke<sup>91</sup> of 10 m<sup>2</sup>/g. At these high smoke densities, the presence of light-reflecting or light-emitting exit signs does not change the incapacitation criterion significantly. The equivalent smoke optical density is 1.7 m<sup>-1</sup>.

The analog to people who are sensitive to the inhalation of fire gases is people who require a higher degree of contrast to discern an object against a background. If one intended to provide the same additional degree of protection as with, for example, the FED value of 0.3, the incapacitating concentrations of smoke would be 15 g/m<sup>3</sup> for well-ventilated fires and 7 g/m<sup>3</sup> for underventilated fires. This reflects the logarithmic dependence on the capacity for visual perception.

Smoke particulates and aerosols also can be harmful when inhaled, and long exposure may cause damage to the respiratory system. Also, smoke particulates often are of a sufficiently small size that enable them to be inhaled deeply into the lungs, where adsorbed toxicants may produce damage to the respiratory system. These effects have not been sufficiently studied to enable a full understanding of their consequences.

# DEVELOPMENT OF TOXIC HAZARDS IN FULL-SCALE FIRES

#### Importance of Full-Scale Experiments

While lab-scale tests and fire models can provide valuable insight into ignition and fire growth, full-scale experiments are still necessary to understand and validate critical fire phenomena. Full-scale fire reconstructions can document many important interactions within a fire environment not captured by small-scale tests or fire models. These interactions can include how fuel density can impact fire growth, how the thermal feedback from a hot smoke layer may increase the pyrolysis of the fuel, how specific fuels may generate toxic gases in vitiated smoke layers, or how the lack of ventilation can limit fire development. Full-scale experiments or reconstructions are often used to better understand the development of toxic hazards in specific fire incidents, especially scenarios with unusual conditions. An example of an incident that exhibited some unusual conditions, including rapid fire growth, quick smoke layer development, and multiple toxic gas species, was a fire that occurred on February 20, 2003, in the Station Nightclub in West Warwick, Rhode Island.

# Reconstruction of Station Nightclub Fire

Full-scale experiments were conducted at NIST to reconstruct the fire and better understand how the toxic hazard may have developed that night in the Station Nightclub. 93 During a band performance at the nightclub, pyrotechnics ignited polyurethane foam insulation that lined the walls and ceiling of the band platform. The fire spread quickly along the walls and ceiling area over the dance floor. Smoke was visible in the exit doorways in a little more than 1 minute, and flames were observed breaking through a portion of the roof in less than 5 minutes. Egress from the nightclub, which was not equipped with sprinklers, was hampered by crowding at the main entrance to the building. One hundred people lost their lives in the fire.

In order to characterize the fire growth and spread in the early stage of the fire, two real-scale mockup experiments reconstructed approximately 20 percent of the nightclub with polyurethane foam covered walls, a drummer's alcove, a raised platform, carpeting, and wood paneling. Figure 6.2.7 shows the dimensions of the mock-up floor plan and Figure 6.2.8 compares the test compartment to a floor plan of the nightclub. Full-scale data, including gas temperatures, heat fluxes, and gas concentrations, provided insight as to how quickly the toxic hazards, in particular, the generation of CO and HCN, can develop during the early stages of a fire.

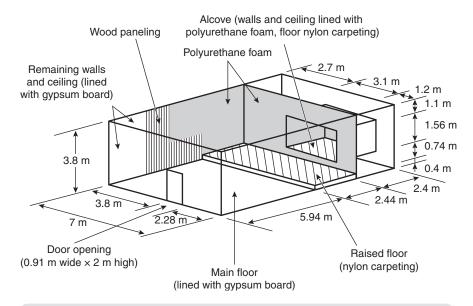


FIGURE 6.2.7 Isometric View of Test Compartment and Fuels (Source: National Institute of Standards and Technology)

A physical mock-up was created at the NIST Large Fire Laboratory with overall floor dimensions of the test room of 10.8 m by 7.0 m, and a ceiling height of 3.8 m. A single opening, 0.91 m wide and 2.0 m high was located in the wall opposite the alcove. The test area was constructed with a structural steel

frame, lined with two layers of 12 mm thick calcium silicate board, covered with 12 mm thick gypsum board. The walls of the alcove and the raised floor area had 5.2 mm thick plywood paneling installed over the gypsum board. The paneling had a flame spread index of 200 or less, as tested by ASTM E84, Stan-

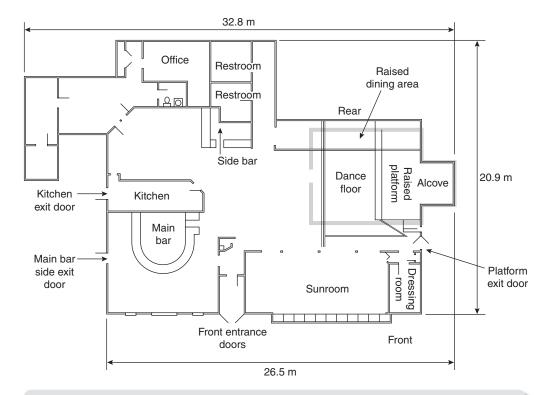


FIGURE 6.2.8 Full-Scale Mock-Up Floor Plan Versus Station Nightclub Floor Plan (Source: National Institute of Standards and Technology)

dard Test Method for Surface Burning Characteristics of Building Materials, 94 according to the manufacturer. The plywood paneling extended 3.6 m from the raised floor along the rear wall of the test area. The rear wall was adjacent to the platform on the right as one stands on the platform facing the audience (stage-right). A non-fire-retardant, ether-based polyurethane foam was glued over the paneling in the alcove and along the walls on both sides of the alcove opening and to the rear wall. The flat side of the foam was mounted next to the plywood and the convoluted side was left exposed. The foam was installed from the top of the wall down to 1.35 m above the floor. It was also applied to the ceiling of the alcove and extended for 2.4 m from the raised floor along the rear wall.

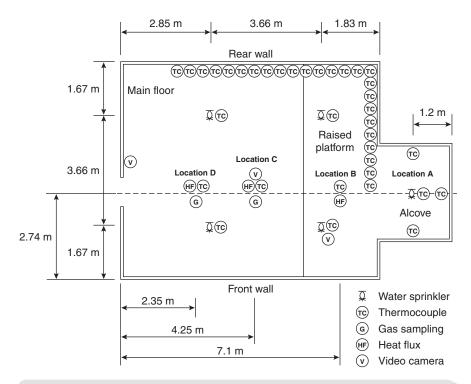
The test room (Figure 6.2.9) was equipped with thermocouples, video cameras, heat flux gauges, bidirectional probes, and gas extraction probes to measure CO, CO<sub>2</sub>, O<sub>2</sub>, and HCN. In addition, fixed temperature and rate-of-rise heat detectors were installed, as were sprinklers. Data for 194 channels were recorded at 1 second intervals. Ignition of the foam was initiated simultaneously using electric matches at two locations on the outer corners of the alcove, 1.66 m above the raised floor area. The fire gases that emerged from the open door on the end of the test room were captured in the hood of the oxygen depletion calorimeter. The succession of video frames in Figure 6.2.10 show how rapidly the fire spreads during the first 90 seconds.

Data were collected at several locations as indicated in Figure 6.2.9. Selected data (collected at Location D, on the centerline of the doorway and 6 m from the front of the drummer's

alcove) including gas concentrations (O2, CO, CO2, and HCN), gas temperatures, and heat fluxes, are presented in Figures 6.2.11 and 6.2.12. As can be seen in Figure 6.2.10, the fire was ignited at two locations on either side of the drummer's alcove. The fire spread up the polyurethane foam wall lining on both sides of the alcove and within 60 seconds the alcove was fully involved. The smoke layer continued to descend quickly and. within 90 seconds, the layer was near the floor of the mock-up compartment.

In less than 90 seconds, conditions at Location D and 1.4 m above the floor included gas temperatures exceeding 750°F (400°C), total heat flux in excess of 30 kW/m<sup>2</sup>, O<sub>2</sub> volume fractions below 0.05, and HCN and CO volume fractions greater than 0.0015 and 0.03, respectively. The tenability of the compartment deteriorated quickly due to high temperature, high heat flux, O<sub>2</sub> depletion, and toxic concentrations of HCN and CO. Exceeding the tenability limit does not imply that any or all occupants who are present in that environment will succumb due to a particular limit exceeded. The length of time exposed, the rate of change of the environmental conditions, the individual's starting location, his/her breathing rate, and the susceptibility of the individual all play a role. Occupants in this compartment would have likely have had less than 11/2 minutes to escape safely from this rapidly growing fire.

A second mock-up experiment was also conducted and was a duplicate of the first except that automatic water sprinklers were installed and charged. Sprinkler heads began to activate in less than 30 seconds and quickly controlled the fire growth. Throughout the second experiment, conditions in the compartment at



**FIGURE 6.2.9** Schematic Floor Plan with Instrumentation Positions (Source: National Institute of Standards and Technology)

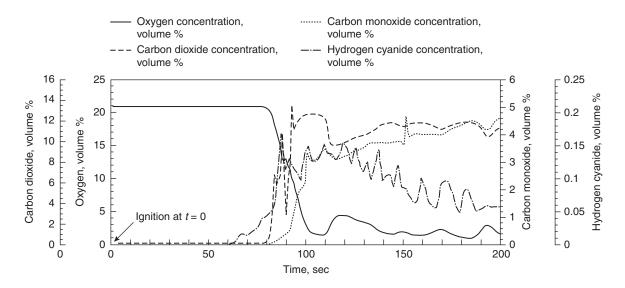


FIGURE 6.2.10 Still Frames Taken from Video of Full-Scale Mock-Up Experiments. Time after ignition is indicated in lower left of each frame. (Source: National Institute of Standards and Technology)

Location D remained tenable in terms of temperature, heat flux, O<sub>2</sub> depletion, and concentrations of HCN and CO.

## **SUMMARY**

All combustibles produce heat and smoke that, in sufficiently high concentration, may be hazardous to life safety. Incapacitation can result from exposure to the asphyxiant gases, irritant gases, and heat. Irritant gases and visible smoke can reduce a person's ability to find and negotiate escape routes efficiently. Survivors of the acute effects of exposure during a fire may also experience serious postexposure health effects. Responses of people to the effects of exposure to the combustion products of fire vary considerably. This is due both to the degree of physi-



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FIGURE 6.2.11 Gas Concentrations Measured at Location D During First 200 Seconds of Unsprinklered Mock-Up Experiment. Gas sampling probe was located 1.4 m above the floor. Ignition occurred at t = 0. (Source: National Institute of Standards and Technology)

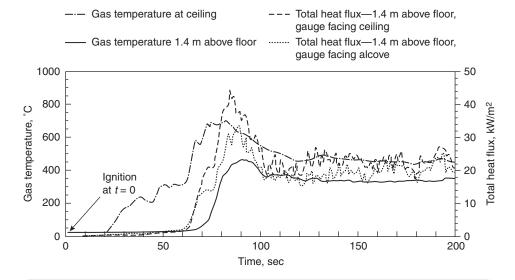


FIGURE 6.2.12 Gas Temperatures and Total Heat Fluxes Measured at Location D During First 200 Seconds of Unsprinklered Mock-Up Experiment. Ignition occurred at t = 0. (Source: National Institute of Standards and Technology)

cal activity during exposure and to the vulnerability of certain subpopulations. Techniques are available for estimating the fire environments that can led to incapacitation of building occupants. The understanding for estimating other sublethal effects and postexposure harm is not yet developed.

The testing of materials and products in the laboratory does not, in itself, address their toxic hazards when involved in fires. Numerous other factors, including their heat release and mass burning rates, contribution of other combustibles present, size and configuration of the enclosure, ventilation, smoke transport, the nature of the occupants, and occupant movement also affect toxic fire hazard. These factors must all be considered in concert.

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#### NFPA Codes, Standards, and Recommended Practices

Reference to the following NFPA codes, standards, and recommended practices will provide further information on combustion products and their effects on life safety discussed in this chapter. (See the latest version of The NFPA Catalog for availability of current editions of the following documents.)

- NFPA 269, Standard Test Method for Developing Toxic Potency Data for Use in Fire Hazard Modeling
- NFPA 270, Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber

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