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***Chapter 17: Fire Toxicity and its Assessment***

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### **17.1 Introduction**

The importance of the toxic effects of fire effluents has been rapidly increasing over the last 5 years. This chapter describes the types and effects of toxic effluents that fires produce, and the different methods that exist to assess fire toxicity, using animal exposure studies, laboratory scale and large scale generation of fire effluents, followed by a discussion on how different materials and fire conditions influence the generation of toxic products.

The majority of fire deaths result from the inhalation of toxic gases. The asphyxiant gases, carbon monoxide and hydrogen cyanide have yields which vary considerably with fire conditions, and this has proved difficult to replicate on a laboratory scale. In addition, fire gases contain respiratory irritants which inhibit breathing, causing flooding of the lungs. Coupled with the visual obscuration of smoke, the effects of irritants on the eyes and lungs can prevent escape, although the cause of death is almost always ascribed to asphyxiant gases, usually to carbon monoxide.

Recently two significant developments have raised the profile of fire toxicity. The first is the development of the steady state tube furnace (ISO TS 19700:2006) which has been shown to replicate the toxic product yields corresponding to the individual stages of fires. The second is the acceptance of performance based fire design as an alternative to prescriptive fire regulations, so that architects can specify the components within a building based on a safe escape time within which toxic and

irritant gas concentrations must not approach a lethal level (ISO 13571:2007).

### **17.2 Toxic components of fire effluents**

Fire gases contain a mixture of fully oxidised products, such as carbon dioxide (CO<sub>2</sub>), partially oxidised products, such as carbon monoxide (CO) and aldehydes, fuel and fuel degradation products, such as aliphatic or aromatic hydrocarbons, and other stable gas molecules, such as hydrogen halides (HCl, HBr) and hydrogen cyanide (HCN)<sup>1</sup>. The toxic hazards associated with fire and the inability of victims to escape from fire atmospheres is often considered in terms of major hazard factors: heat, smoke and toxic combustion products<sup>2</sup>. Heat, smoke and irritant gases may impair escape, and sometimes lung damage causes death in those managing to escape.

The main combustion products are divided into two classes: asphyxiant gases, which prevent oxygen uptake by cells, with loss of consciousness and ultimately death, and irritant gases which cause immediate incapacitation, mainly by effects on the eyes and upper respiratory tract, and longer term damage deeper in the lung. The effect of asphyxiants and deep lung irritants depend on the accumulated doses, the sum of each of the concentrations multiplied by the exposure time, for each product; upper respiratory tract irritants are believed to depend on the concentration alone<sup>3</sup>. The most common toxic components of fire effluent are presented in Table 17.1.

Asphyxiant gases	Irritant gases	Other components which should be monitored
Carbon monoxide (CO) Hydrogen cyanide (HCN)	Hydrogen Fluoride (HF) Hydrogen chloride (HCl) Hydrogen bromide (HBr) Nitrogen dioxide (NO <sub>2</sub> ) Sulphur dioxide (SO <sub>2</sub> ) Organo irritants	Oxygen (O <sub>2</sub> ) Carbon dioxide (CO <sub>2</sub> )

Table 17.1 List of main asphyxiant and irritant gases<sup>4</sup>

The specification of gases to be determined in particular standard tests is somewhat arbitrary, and may not adequately define the effluent toxicity<sup>4</sup>. There is also the potential for species to be present in the fire gas which have not been well-characterised in terms of chemical structure or toxicity and would be difficult to identify or to assess their toxic hazards, although the existence of important acute toxicants which have yet to be characterised is less likely than for toxicants with longer term or delayed effects.

Carbon dioxide content in fresh air varies 300 ppm to 600 ppm, depending on location, and is almost always present at higher levels in fire gases. Inhalation of carbon dioxide stimulates respiration rate, tidal volume and causes acidosis (an increase in the acidity of the blood). The result is an increase in inhalation of oxygen and toxic gases produced by the fire. It has moderate toxicity, in its own right, exposure to a 50,000 ppm (5%) concentration for 30-minutes produces signs of intoxication; above 70,000 ppm

unconsciousness results in a few minutes.

Oxygen depletion, also a feature of fire gases, can be lethal once oxygen concentration has fallen below tenable levels (~6%). However, from a fire toxicity perspective it is generally assumed that heat and other gases will have already prevented survival, while other toxicants such as CO or HCN, will be present in lethal quantities further from the fire where the oxygen depletion would not be considered harmful. However, oxygen depletion and high levels of CO<sub>2</sub> and CO would result from oxidative pyrolysis of biofuels in an enclosed storage facility, endangering people entering the enclosure.

### 17.2.1 Asphyxiant gases

Narcotic gases or asphyxiants cause a decrease in oxygen supplied to body tissue, resulting in central nervous system depression, with loss of consciousness and ultimately death. The severity of the effects increases with increasing dose<sup>2</sup>. The main asphyxiants, carbon monoxide and hydrogen cyanide have been widely studied and are the best understood<sup>5</sup>.

### **17.2.1.1 Carbon monoxide**

The toxic effect of carbon monoxide is characterised by a lowered oxygen-delivery capacity of the blood, even when a partial pressure of oxygen and the rate of blood flow rate are normal. Carbon monoxide binds to the haemoglobin in red blood cells resulting in the formation of carboxyhaemoglobin (COHb), with stability constant 200 times greater than that of oxyhaemoglobin, impeding the transport of oxygen from lungs to the body. This causes deterioration in mental and muscular performance. CO also combines with myoglobin in the muscle cells, impairing diffusion of oxygen to cardiac and skeletal muscles<sup>6</sup>. Carbon monoxide has a cumulative effect, from which the body takes time to recover. About 50% of blood carbon monoxide is eliminated in the first hour, while complete elimination takes from several hours to a few days. When inhaled, CO impairs an individual's ability to escape by decreasing the amount of oxygen, causing different effects at different concentrations of carbon monoxide (COHb) in the blood. At CO levels of 10 ppm for short periods, impairment of judgment and visual perception occur; exposure to 100 ppm causes dizziness, headache, and weariness; loss of consciousness occurs at 250 ppm; and inhalation of 1000 ppm results in rapid death. Chronic long-term exposures to low levels of carbon monoxide are suspected of causing disorders of the respiratory system and the heart<sup>7</sup>.

### **17.2.1.2 Hydrogen cyanide**

Hydrogen cyanide is approximately 25 times more toxic than carbon monoxide through the formation of the cyanide ion formed by hydrolysis in the blood<sup>2</sup>. Unlike carbon monoxide

which remains primarily in the blood, the cyanide ion is distributed throughout the extra-cellular fluid of tissues and organs<sup>5</sup>. Two mechanisms have been identified for the toxic effects of cyanide. The first is by combination with the ferric ion in mitochondrial cytochrome oxidase, preventing electron transport in the cytochrome system and inhibiting the use of oxygen by the cells. The second results in a brief stimulation, followed by severe depression, of respiratory frequency, accompanied by convulsions, respiratory arrest and death<sup>8</sup>. HCN also causes rapid incapacitation, preventing escape, and then, with CO, contributes to death from asphyxiation. One analysis of fire death data showed a recent decline in COHb and a rise in blood cyanide levels<sup>9</sup>, probably because of increased use of nitrogen-containing synthetic polymers. The uptake, distribution, metabolism and excretion of cyanide is much more complex than for CO and thus there is no simple and robust method for quantifying CN<sup>-</sup> in fire victims. Therefore the contribution of HCN to fire deaths is difficult to assess, and sometimes analysis for CN<sup>-</sup> only takes place when lethal concentrations of CO are absent.

### **17.2.2 Irritant gases**

In contrast to the well-defined effects of asphyxiant toxicants, the effects of exposure to irritants are much more complex. Incapacitating irritants and smoke can cause death indirectly by preventing escape from fire. Most irritant fire effluents produce signs and symptoms of both sensory and upper respiratory tract irritation, and of pulmonary irritation. However, in post-mortem analysis these are similar to the effects of heat exposure. Sensory and upper respiratory tract

irritation stimulates the trigeminal and vagus nerve receptors in the eyes, nose, throat and upper respiratory tract causing discomfort, then severe pain. The central nervous system's response to acidic and organic irritant gases in mice is to inhibit breathing, causing the respiration rate to fall to 10% of its normal value, while in primates and humans the same stimulus results in hyperventilation. The effects range from tears and reflex blinking of the eyes, pain in the nose, throat and chest, breath-holding, coughing, excessive secretion mucus, to bronchoconstriction and laryngeal spasms<sup>6</sup>. At sufficiently high concentrations, or when attached to submicron particles, such as soot, most irritants can penetrate deeper into the lungs, causing pulmonary irritation effects which may cause post-exposure respiratory distress and death, generally occurring from a few hours to several days after exposure, due to pulmonary oedema (flooding of the lungs)<sup>5</sup>.

### 17.2.2.1 Hydrogen halides

Hydrogen chloride (HCl) and hydrogen bromide (HBr) are strong acids which dissociate entirely in water. Both may be present in fire gas, for example from PVC or brominated flame retardants, and since the damage caused by the acidity is independent of the anion (Cl<sup>-</sup> or Br<sup>-</sup>). The current discussion focuses on HCl, it is also applicable to HBr.

Hydrogen chloride (HCl) is an acid gas which causes severe irritant effects at low concentrations (around 100 ppm) but only results in death at very high concentrations (in mice 2600 ppm, and in rats 4700 ppm for 30 minute exposures<sup>10</sup>). The difficulty in quantifying a threshold level for incapacitation, and the high levels of HCl evolved during decomposition of certain materials has led to a long-running controversy over the maximum atmospheric concentrations of HCl in fire gas from which escape is still possible.

Approximate Concentration /ppm	Exposure time	Effect	Ref
1 to 5		Limit of detection by odour	
≥5	Unspecified	Immediately irritating	[11]
>10	Occupational	Highly irritating, although workers develop some tolerance	[11]
10	Prolonged	Maximum tolerable	[13]
10 to 50	A few hours	Maximum tolerable	[13]
35	Short	Throat irritation	[13]
50-100	1 hour	Maximum tolerable	[13]
1000-2000	Short	Dangerous	[13]

Table 17.2 Inhalation exposure of humans to hydrogen chloride<sup>17</sup>

There is only one report of human exposure to HCl gas at concentrations relevant to fires<sup>12</sup>, which found that humans could tolerate exposure to 10 ppm HCl, while at 70 and 100 ppm humans had to leave the room because of intense irritation, coughing and chest pains, indicating that 100 ppm is intolerably irritating to humans. That data has led to guidelines<sup>13</sup> that the maximum concentration tolerable for 1 hour is between 50 and 100 ppm, and that 1000 to 2000 ppm is dangerous for even short exposures. These guidelines were corroborated using an animal model that correctly predicted intolerable irritation levels for humans for other inorganic gases such as sulphur dioxide, ammonia, chlorine, and a wide variety of organic chemicals, including formaldehyde, acrolein, etc.,<sup>14,15</sup> indicating that 300 ppm would be intolerable to humans<sup>16</sup>. Table 17.2 summarises the expected effects of HCl on humans<sup>17</sup> showing that concentrations of 50 to 100 ppm are barely tolerable for exposures up to an hour, while exposure to concentrations of 1000 ppm of HCl are dangerous, causing pulmonary oedema after only a few minutes exposure.

The physical manifestations of the action of HCl in rats, based on observations during one study<sup>18</sup>, seems to be primarily one of mechanical blockage of the upper airways caused by the extreme inflammatory and corrosive action of a strong mineral acid on these tissues. Post-mortem examination indicated almost total destruction from the nasal passage to the pharynx, but surprisingly little damage to airways below the trachea. Amongst obligatory nose-breathers, the lower sensitivity of rats than mice to HCl has been ascribed to differences in

their nasal passages. When a tube was used to bypass these passages, the response of rats occurred at similar concentrations to those of mice<sup>19</sup>. This has led to the suggestion that species that breathe through their mouth (such as humans, especially in the stressful situation of escaping from a fire) may be more sensitive to the effects of HCl than obligate nose-breathers, such as rodents<sup>17</sup>. In summary, a small amount of HCl causes incapacitation, preventing escape, but a much larger quantity is required to cause death directly.

#### **17.2.2.2 Nitrogen oxides**

Nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are non-flammable gases present in fire effluents. At high concentrations nitric oxide is rapidly oxidised in air to form nitrogen dioxide, however, at the concentrations found in fire gases, most of the nitric oxide remains unchanged. Nitrogen dioxide dissolves rapidly in water to form nitric and nitrous acid. At high concentrations these acids can cause pulmonary oedema and death<sup>20, 21</sup>. However, low concentrations of nitric oxide gas have been used to aid breathing in the treatment of respiratory disorders<sup>22</sup>. In the blood it combines with oxyhaemoglobin to form methaemoglobin, between 5 and 20 times faster than oxygen and the resulting compound breaks down slowly<sup>20</sup>, giving effects similar to hypoxia; it forms nitrates; and if the blood oxygen is low it can combine with haemoglobin to form nitrosohaemoglobin. Excessive levels of nitric oxide in blood have been shown to cause low blood pressure. However, it has been reported that tobacco smoke can contain up to 1000ppm of nitric oxide but this does not cause death<sup>20, 23</sup>.

### 17.2.2.3 Organo irritants

Large numbers of known irritant chemicals have been found to occur in fire atmospheres<sup>24,25</sup>. The irritant chemicals released in fires are formed during the pyrolysis and partial oxidation of materials, and the combinations of products from different materials are often remarkably similar<sup>25</sup>. However, for all organic materials and particularly for simple hydrocarbon polymers such as polypropylene or polyethylene, the main pyrolysis products, which consist of various hydrocarbon fragments, are innocuous<sup>6</sup>. Thus when polypropylene is pyrolysed in nitrogen the product such as ethylene, ethane, propene, cyclopropane, formaldehyde, butane, acetaldehyde, toluene, styrene are produced<sup>6</sup>, and such an atmosphere was found to have no effect upon primates<sup>24, 26</sup>. However, when these products are oxidized during nonflaming decomposition in air, some are converted to highly irritant products, and such atmospheres were indeed found to be highly irritant to both mice and primates. In reports of mouse exposure experiments, some fire retardant materials, which could be induced to flame only intermittently, with considerable smoke production, were found to produce atmospheres up to 300 times more irritant than the same polymer in its non-fire retardant state, which burned cleanly<sup>27</sup>. Table 17.3 shows some of more toxic, commonly encountered organic species in fire gas, with the concentration considered Immediately Dangerous to Health or Life (IDLH) (NIOSH)<sup>28</sup>.

Substance	IDLH Value / ppm
Acetaldehyde	2000
Acrolein	2
Carbon Monoxide	1200
Benzene	500
Crotonaldehyde	50
Formaldehyde	20
Phenol	250
Toluene	500

Table 17.3 Common organo irritants found in fire gas with IDLH Values<sup>28</sup>

### 17.2.2.4 Particulates

Death in fire may be caused either by gases which are directly toxic or which cause such irritation that they impair vision and breathing, preventing escape, or by smoke which not only impairs escape ability by visible obscuration, but also contains particulate matter which is sufficiently small to pose a respiratory hazard. In spite of large amounts of particulates generated in a fire, relatively few investigations have been made on the particles (size, distribution and composition) from such fires<sup>29</sup>.

The particle size distribution is dependent on the tested material, temperature and fire conditions. The particle size of the spherical droplets from smouldering combustion is generally of the order of 1µm, while the size of the irregular soot particulates from flaming combustion is often larger but much harder to determine and dependent on measuring technique and sampling position. The hazard areas for humans as a function of particle size are presented in Figure 17.1.

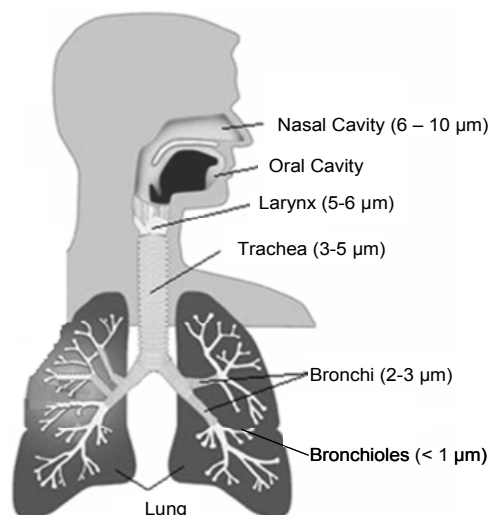


Figure 17.1 Particle deposition in respiratory system

The general effect of particulates is to cause fluid release and inflammation, preventing gas exchange. Inflammation of the terminal bronchioles can result in complete blockage. Oedema fluid disrupts the dispersion of the lung surfactant, causing collapse of the alveolae from higher surface tension of the fluid. The smallest particles ( $<0.5 \mu\text{m}$ ), penetrate into the lung interstitium (between the alveolar surface the blood capillaries), where they have been shown to be particularly dangerous, causing interstitial and luminal oedema. They can also transcend the air/blood barrier and enter the blood stream, triggering dangerous immune responses from the white blood cells, including polymer fume fever, and increased platelet stickiness leading to heart attacks.

Particulates, and other irritants can change lung efficiency expressed as compliance (how easily the lung opens in response to pressure reduction or how much stiffer is the lung tissue is becoming) and resistance (how easily air flows in and out of the lung or how much the airways are becoming blocked or flooded). Passage of oxygen through the blood gas barrier can only occur in the absence of fluid in the lungs<sup>30</sup>.

In addition the particulates can act as vehicles for transport of noxious molecules deep into the lungs. Some work has been reported on HCl, estimating that over an exposure time of 1 hour, about 2 mg of HCl would be deposited deep in the lungs by soot<sup>6</sup>.

### 17.2.3 Effect of toxicants on different species

There are a number of published papers presenting an estimation of toxic products by using animals as indicators of the toxicity<sup>1,21,31</sup>. Mice, rodents or primates are exposed to pure gas mixtures or fire gases to determine an incapacitation or lethality. However, there is no direct relationship between these data and the limits for humans. Some data indicates that the mechanism of toxicity of some gases is the same in rodents and humans. For other gases the response is known to be different<sup>6</sup>.

Chemical agent	Mice	Rats	Primates
CO (ppm)	3500	5300-6600	2500-4000
HCN (ppm)	165	110-200	170-230
HCl (ppm)	2600	3800	5000
Low oxygen (%)	6.7	7.5	6-7

Table 17.4 Comparison of  $LC_{50}$  (30 minutes exposure) for different animals<sup>31</sup>



Some literature suggests that the use of mice may not be reliable because of their very fast respiration rate and narrow airways. Differences between species such as respiratory rate and volume, may produce different relative results in toxicity tests. A paper by Hartzell<sup>31</sup> suggests that when considering acute lethal effects, primates may resist about 1.3 times greater concentrations of HCl and HCN than rats while rats resist about 1.6 times greater concentrations of CO. Nitric oxide also has different effects on different species. Exposure of rats to 1500ppm for 15 minutes and to 1000ppm for 30 minutes, and of lambs to 80ppm for 60 to 180 minutes does not cause adverse effects, but the exposure of rabbits to 5ppm for 14 days causes interstitial oedema. It is necessary to understand the accuracy and uncertainties of animal testing methods for fire hazard assessment. Table 17.4 presents and compares lethal toxic potencies of the most common fire effluents for different animal species<sup>31</sup>, showing considerable variation between species.

The effect of fire effluents on human life cannot be measured directly for legal and ethical reasons. It may be estimated from the effect on animals either directly, using animal exposure, or indirectly from tables of concentrations leading to a particular effect (such as the limit below that causing irreparable damage, death or incapacitation of 50% of the population etc.). In each case the data rely on the untested assumption that effects on animal subjects (usually rats) may be simply extrapolated to humans. For example, it has been reported<sup>21</sup> that rat data cannot be extrapolated to baboon data when

irritant gases are the principal toxicants.

#### **17.2.4 Estimation of fire effluent toxicity from chemical composition data**

Exposure to toxic fire effluents can lead to a combination of physiological and behavioural effects of which physical incapacitation, loss of motor coordination, disorientation are only a few. Furthermore, survivors of a fire may experience post-exposure effects, complications and burn injuries, leading to death or long term impairment. The major effects, such as incapacitation or death, may be predicted using existing rat lethality data, as described in ISO 13344<sup>32</sup> or more recently, based on the best available estimates of human toxicity thresholds as described in ISO 13571<sup>5</sup>, by quantifying the fire effluents in different fire conditions in small-scale tests, using only chemical analysis, without animal exposure.

The general approach in generating toxic potency data from chemical analysis is to assume additive behaviour of individual toxicants, and to express the concentration of each as its fraction of the lethal concentration for 50% of the population for a 30 minute exposure ( $LC_{50}$ ). Thus an FED equal to one indicates that the sum of concentrations of individual species will be lethal to 50% of the population over a 30 minute exposure. Two equations have been developed for the estimation of the FED for lethality from the chemical composition of the environment in the physical fire model. Each begins with the precept that the fractional lethal doses of most gases are additive, as developed by Tsuchiya<sup>33</sup>.

$$FED = \frac{m[CO]}{[CO_2]-b} + \frac{21-[O_2]}{21-LC_{50,O_2}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[HCl]}{LC_{50,HCl}} + \frac{[HBr]}{LC_{50,HBr}} + \dots$$

Equation 1 FED N-Gas model

Both equations have been taken from ISO 13344<sup>32</sup> and uses LC<sub>50</sub> values for lethality to provide reference data for the individual gases to calculate toxic potency, based on rats exposed for 30 minutes. The N-Gas model, in Equation 1 assumes that only the effect of the main toxicant CO is enhanced by the increase in respiration rate caused by high CO<sub>2</sub> concentrations, (expressed as a step function with one value of m and b for CO<sub>2</sub> concentrations below and another for those above 5%).

The Purser model, presented in Equation 2, uses V<sub>CO<sub>2</sub></sub> a multiplication factor for CO<sub>2</sub> driven by hyperventilation, therefore increasing the FED contribution from all the toxic species, and incorporates an acidosis factor A to account for toxicity of CO<sub>2</sub> in its own right<sup>32</sup>.

Both of these equations only relate to lethality, or *cause of death*. However, many people fail to escape from fires because of the incapacitating effect of smoke (obscuring visibility) and its irritant components which cause pain, preventing breathing or *reason for*

*death*. ISO 13571<sup>5</sup> considers the four major hazards from fire which may prevent escape (toxic gases, irritant gases, heat and smoke obscuration). It includes a calculation for prediction of incapacitation of humans exposed to fire effluents, indicating, in a non-normative appendix, that the effects of heat, smoke and toxicants may be estimated independently. Equations 2 and 3 have been taken from ISO 13571. They calculate the FED of asphyxiants, CO and HCN, and the Fractional Effective Concentration (FEC) of sensory irritants in the fire effluent which limit escape. Equation 2 represents the generally accepted case that there are only two significant asphyxiant fire gases CO and HCN. The FED value is calculated using the exposed dose relationship (concentration-time product, C·t) for CO. The lethal C·t product corresponds to the incapacitating dose (C·t) for CO of 35 000 µl l<sup>-1</sup>min, equal to around 1170 ppm for 30 minutes exposure) and an exponential relationship for HCN (because asphyxiation by HCN exposure does not fit a linear relationship).

$$FED = \left\{ \frac{[CO]}{LC_{50,CO}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[AGI]}{LC_{50,AGI}} + \frac{[OI]}{LC_{50,OI}} \dots \right\} \times V_{CO_2} + A + \frac{21-[O_2]}{21-5.4}$$

$$V_{CO_2} = 1 + \frac{\exp(0.14[CO_2]) - 1}{2}$$

[AGI] is the concentration of acid gas irritants

[OI] is the concentration of organic irritants

A is an acidosis factor equal to [CO<sub>2</sub>] × 0.05.

Equation 2 Purser model

$$FED = \sum_{t_1}^{t_2} \frac{[CO]}{35000} \Delta t + \sum_{t_1}^{t_2} \frac{\exp([HCN]/43)}{220} \Delta t$$

Equation 3 FED model for ISO 13571

$$FEC = \frac{[HCl]}{IC_{50, HCl}} + \frac{[HBr]}{IC_{50, HBr}} + \frac{[HF]}{IC_{50, HF}} + \frac{[SO_2]}{IC_{50, SO_2}} + \frac{[NO_2]}{IC_{50, NO_2}} + \frac{[acrolein]}{IC_{50, acrolein}} + \frac{[fomaldehyde]}{IC_{50, fomaldehyde}} + \sum \frac{[irritant]}{IC_{50, irritant}}$$

Equation 4 FEC model from ISO 13571

Equation 4 uses a similar principle to equation 1 to estimate the combined effect of all irritant gases.

The additive model is almost certainly an over simplification, because the effects occur in different organs (lungs, muscles, brain, etc.), although it is as likely to be an overestimate as an underestimate. However, more controversy surrounds the toxic potency values used in these models (Table 17.4 and Table 17.5). These range from direct application of rat lethality data for single gas exposures to humans, to estimates made by committees of experts<sup>5</sup>. Data exists to show that both simplifications are unjustified<sup>34,35</sup>. There are several gases where the additive methodology is known to be wrong. For example, at CO<sub>2</sub> concentrations of 5% (common in diluted fire effluents) the respiratory volume per minute (RMV) increases by a factor of 3 increasing the dose of fire gas inhaled. Purser's

model addresses this by applying a correction factor (itself a function of CO<sub>2</sub> concentration) to all the individual toxicant ratios, not just CO<sub>2</sub>. However ~50 ppm nitric oxide (usually present in fire gas) opens up the airways, allows improved respiration, but also greater exposure to other toxicants. HCN initially increases the respiration rate, and then severely suppresses it; irritant gases such as HCl suppress it by a factor of around 10 in stationary rats and mice<sup>36</sup>. There is also growing evidence that other chemical species present in fire gas (such as particulates and isocyanates), which are not normally included in these predictions of fire gas toxicity, can be some of, or even the most toxicologically significant species. However, while the FED and FEC values are valid relative to one another, the dilution factor of 1g /50 litres (or whatever) is arbitrary.

	<b>Concentration giving FED =1 using ISO 13344 / ppm</b>	<b>Concentration giving FEC/FED =1 using ISO 13571 / ppm</b>
CO	5700	1170
HCN	165	100
HCl	3800	1000
NO <sub>2</sub>	170	250

Table 17.5 Toxic gas concentrations leading to death (ISO 13344) and incapacitation impairing escape (ISO 13571)

### 17.2.5 Fire conditions on fire toxicity

Fire gases result from the pyrolysis, oxidative pyrolysis and flaming combustion of organic materials, and can comprise a complex mixture of many different compounds. The temperature and oxygen concentration vary significantly during a fire and between different fires, and as a consequence the gases produced in different stages of a fire may vary significantly. ISO have identified a number of different fire stages. While some real life fires may be represented by a single fire stage, other fires may pass through several different stages<sup>37</sup>.

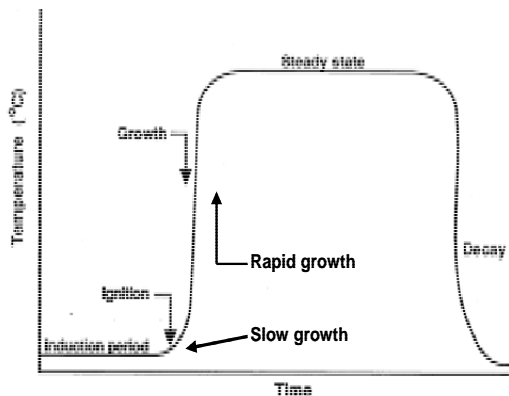


Figure 17.2 Schematic fire growth curve

The graph (Figure 17.2) illustrates a fire starting with a slow induction period, but once ignition is reached it grows very quickly until limited either by the access of oxygen or by the availability of the fuel.

The product yields are particularly dependent upon the composition of the polymeric material, the temperature and the ventilation conditions. Once the temperature of the surface is raised sufficiently (generally to around 300°C), then a process of thermal decomposition by oxidative pyrolysis begins. The products of non-flaming

decomposition tend to be rich in partly decomposed organic molecules (many of which are irritants), carbon monoxide and smoke particulates. This scenario presents a particular hazard to a sleeping subject in a small enclosure such as a closed bedroom which can reach a lethal dose over a number of hours<sup>6</sup>.

A useful concept in characterising or predicting the gas phase flaming combustion conditions, and the yields of products and hydrocarbons, is the equivalence ratio ( $\phi$ ), presented in Equation 5. If the amount of oxygen balances the amount of fuel exactly, then the conditions are said to be stoichiometric, and the equivalence ratio equal to 1. In the early stages of fire the equivalence ratio may be lower, when there is more than the stoichiometric amount of air available, and the conditions are well-ventilated, while in the later stages of a fire, when there is not enough air available and the conditions are under-ventilated, the equivalence ratio will be greater than 1. Toxic product yields have been shown to be highly dependent upon the fuel/oxygen ratio<sup>38</sup>, and this approach has led to a better understanding of the factors affecting fire toxicity.

$$\phi = \frac{\text{Actual fuel / Air ratio}}{\text{Stoichiometric fuel / Air ratio}}$$

#### Equation 5 Equivalence ratio

After ignition, fire development may occur in different ways, depending on the environmental conditions as well as on the arrangement of fuel. An early well-ventilated flaming fire is characterized by an equivalence ratio less than unity, and during the early stages is likely to be less than 0.5.

This means that there is always more than enough oxygen mixed with the fuel gases.

High yields of smoke, toxic and irritants are generated at temperatures around 600°C as the fire stage changes to under-ventilated flaming in an enclosure fire. A room occupant is exposed to a highly toxic effluent mixture capable of causing incapacitation and death from asphyxiation within a few minutes. They will also suffer from exposure to heat, with a possibility of burns.

The final category of flaming fire scenario in enclosures is the post-flashover under-ventilated flaming fire<sup>6</sup>. Flashover can occur when the upper-layer temperature is sufficiently high (around 800°C or above) to cause ignition of combustible materials. The effluent plume is similar in composition to that from a pre-flashover under-ventilated fire, fuel-rich ( $\phi$  between 1.5 and 5) combustion conditions, with very low oxygen concentrations, and high concentrations of asphyxiant gases (CO, HCN), organic irritants and smoke particles. Since the temperatures are higher and the conditions somewhat more extreme, the yields of toxic products may be somewhat higher than for pre-flashover under-ventilated fires. The heat release rate, and therefore the rate of effluent production, is very high. Post-flashover fires are therefore extremely hazardous because a large amount of hot toxic effluent plume material can rapidly fill extensive building spaces remote from the seat of the fire<sup>6</sup>. In the UK, and probably across Europe, where rooms and buildings tend to be smaller with less open layouts, most fire deaths (70% in 2006 in the UK) result from small

fires when the victim is in the room of fire origin. Conversely, in the US, only 21% of fire deaths occur in the room of origin of the fire, and 67% occur on another floor<sup>39</sup>. Thus, in the UK, flashover fires are not the major cause of fire fatalities, whereas in the US it is believed that 80% of fire deaths could be avoided if flashover could be prevented.

The classification of different fire stages shows that fire hazards, and particularly the toxic hazards, depend upon the combustion conditions. In buildings, the majority of fires which are hazardous to life are likely to involve under-ventilated flaming, either pre- or post-flashover. Since in the UK the majority of injuries and deaths from fire occur in domestic dwellings (77%), most deaths can be attributed to pre-flashover under-ventilated combustion. However the greatest numbers of deaths from single fire disasters will almost always be attributable to post-flashover conditions.

Fire effluent toxic potency is a function of the material and the fire conditions, and also the fire environment (enclosure, geometry and ventilation). In order to assess the fire hazard, toxic potency data must be relevant to the likelihood of particular end use fire situations. Such fires will develop through stages which have been defined by ISO<sup>37</sup>. The ISO fire stages, from non-flaming to well-ventilated flaming to under-ventilated flaming, have been characterised in terms of heat flux, temperature, oxygen availability, CO/CO<sub>2</sub> ratio, equivalence ratio  $\phi$ , and combustion efficiency. Details of this classification are given in Table 17.6.

To see how the predicted toxicity varies for different polymers and fire conditions<sup>40</sup>, the FED (calculated using ISO 13344<sup>32</sup>) is compared to the FED and FEC calculated using ISO 13571<sup>5</sup>.

Toxicities are expressed as the effluent generated from burning 1 g of material in 200 litres of air, based on an established standard<sup>41</sup>.

Organoirritants in the fire effluent (measured as the difference in CO<sub>2</sub> before and after passing over the secondary oxidiser) were considered collectively using an organic yield of 10 mg litre<sup>-1</sup> to result in incapacitation, as described by Purser<sup>6</sup>.

Fire Stage	Heat /kW m <sup>-2</sup>	Max Temp /°C		Oxygen %		Equiv- alence ratio $\phi$	$\frac{V_{CO_2}}{V_{CO}}$	Comb- ustion Efficie ncy %
		Fuel	Smoke	In	Out			
Non-flaming								
1a. Self sustained smouldering	n.a.	450 - 800	25 - 85	20	0 - 20	-	0.1 - 1	50-90
1b. Oxidative, external radiation	-	300 - 600		20	20	<1		
1c. Anaerobic external radiation	-	100 - 500		0	0	>>1		
Well ventilated flaming								
2. Well ventilated flaming	0 to 60	350 - 650	50 - 500	~20	0 - 20	<1	<0.05	>95
Under ventilated Flaming								
3a. Low vent. room fire	0 to 30	300 - 600	50-500	15 - 20	5 - 10	> 1	0.2 - 0.4	70 - 80
3b. Post flashover	50 to 150	350 - 650	>600	<15	<5	> 1	0.1 - 0.4	70 - 90

Table 17.6 ISO classification of fire stages, based on ISO TS 19706<sup>37</sup>

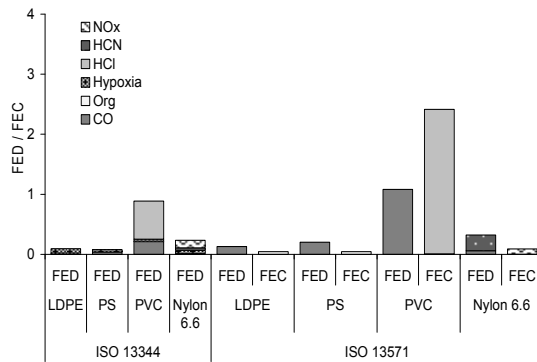


Figure 17.3 FED and FEC contribution for **well-ventilated conditions** from the principal fire gas toxicants determined in different polymers

The contribution to the FED and FEC from each of the principal fire gas toxicants was determined for different polymers, using the steady state tube furnace (described later). Figure 17.3 and 17.4 show a comparison of the fire hazard expressed as FED for lethality, estimated using the methodology presented in ISO 13344 (based on rat lethality data) compared with the FED for incapacitation from ISO 13571, which omits hypoxia, but includes a separate estimate of incapacitation (FEC), and lethality (FED), for low density of polyethylene (LDPE), polystyrene (PS), unplasticised polyvinyl chloride (PVC), and Nylon 6.6. For well-ventilated conditions this shows a generally low toxicity of products, with the exception of unplasticised PVC, which has a high yield of HCl resulting from the chain stripping of PVC, and of CO resulting from the inhibition of the oxidation of CO by the HCl. This shows the greater toxicological significance of HCl over CO from unplasticised PVC, and the much greater effect of the HCl when incapacitation preventing escape, not actual death is used as the end point. It is notable that this large FEC is obtained even though the  $IC_{50}$  value of

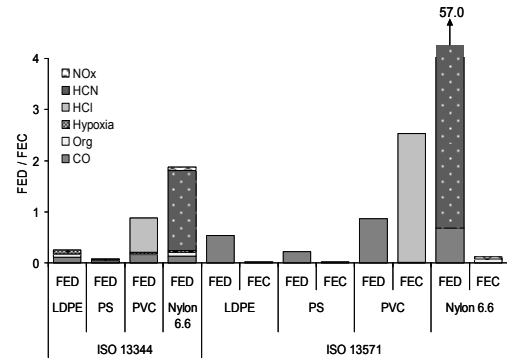


Figure 17.4 FED and FEC contribution for **under-ventilated conditions** from the principal fire gas toxicants determined in different polymers<sup>40</sup>

1000 ppm HCl is rather higher than that considered intolerable.

In addition, when Nylon 6.6 is burned in under-ventilated conditions there is a small but significant contribution from HCN, and its oxidation product  $NO_2$ . The lower level for incapacitation rather than lethality of CO and HCN gives higher values for these two toxicants using ISO 13571.

Instead of normalising the data to an arbitrary 1 g in 200 litres the fire toxicity of a material can be expressed as an  $LC_{50}$ , which in this case is the specimen mass  $M$  of a burning polymeric material which would yield an FED equal to one within a volume of  $1 \text{ m}^3$ . The relation to the FED from the N-Gas model is given in Equation 6.

$$LC_{50} = \frac{M}{FED \times V}$$

Equation 6 Relation of  $LC_{50}$  to FED

where  $V$  is the total volume of diluted fire effluent in  $\text{m}^3$  at STP. The accuracy of  $LC_{50}$  values determined in this manner is quoted as  $\pm 30\%$  if the concentrations of all the contributing

toxicants are measured and included<sup>42,43</sup>. Comparing the toxic potencies of different materials, the lower the LC<sub>50</sub> (the smaller the amount of materials necessary to reach the toxic potency) the more toxic the material is. LC<sub>50</sub> values should be referenced to the fire condition under which they were measured.

### **17.3 Assessment of fire toxicity**

Fire gas toxicity is an essential component of any fire hazard analysis. However, fire toxicity, like flammability, is both scenario and material dependent. Bench scale assessment of fire gas toxicity either adopts an integrative approach, where the material is burnt in a fixed volume of air, allowing the initially well-ventilated fire condition to become underventilated to an unknown degree, or the ventilation is controlled, so that individual fire stages may be replicated.

The ideal small-scale method for assessing fire toxicity must allow the toxic product yields from each fire stage to be determined, allowing assessment of each material under each fire condition. This appears to be the only way that the complexities of full scale burning behaviour can be realistically addressed on a bench scale.

#### **17.3.1 General requirements for bench scale generation of fire effluents**

Guidance on assessment of physical fire models has been published in ISO 16312-1<sup>44</sup>, and reviewed elsewhere<sup>45</sup>. In all fire smoke toxicity tests, specimens are decomposed by exposure to heat, resulting in “forced combustion” driven by an applied heat flux from a flame, radiant panel, etc..

Some tests use a pilot flame or spark igniter to facilitate ignition, while others rely on self-ignition of the sample. When flaming combustion occurs, this will increase the radiant heat flux back to the sample, typically between 2 and 10 times. This will have two significant effects on the fire effluent. First, the existence of flames will help to drive the combustion process to completion, by increasing the temperature and hence the reaction rates, which will tend to reduce the toxicity of the fire effluent (favouring CO<sub>2</sub> over CO and organic molecules). Secondly, the higher heat flux will pyrolyse more material at a greater rate, increasing the amount of material in the vapour phase, and reducing the concentration of oxygen, both of which will increase the toxicity of the fire effluent. Unfortunately, these effects are so large that, rather than cancelling each other out they can result in very large differences in the toxic product yield between different fire toxicity tests. Clearly, the presence or absence of flaming combustion is critical to the interpretation of the results from combustion toxicity assessments. In some conditions, specimens will either pyrolyse or self-ignite, but the scatter of results will be very large if flaming combustion is inconsistent. Once flaming is established, combustion will drive itself to completion (and hence the toxicity will be reduced), provided there is sufficient oxygen, and the flame is not quenched. If the flame is cooled rapidly, e.g. by excessive ventilation or a cool surface, the yield of toxic products will increase. Ultimately the value of the bench-scale toxicity assessment is dependent on its ability to predict large scale burning behaviour, and therefore validation must involve comparison with large scale test data.



Unfortunately most large scale test data have been obtained under well-ventilated conditions, and when data from under-ventilated fire scenarios, such as the ISO 9705 Room test, are made available the change of sample mass and the air flow to the fire during the test is not generally known. Of the standard methods used for toxicity assessment, there are three general types, well-ventilated or open methods, closed box tests, and tube furnaces.

### 17.3.2 Open tests

Most bench scale fire tests, such as the cone calorimeter, are open, and run in well-ventilated conditions. They are generally unsuitable for estimation of toxic product yields because the high degree of ventilation, coupled with the rapid quenching of fire gases, increasing the yield of products of incomplete combustion through premature flame quenching, rather than through underventilation<sup>46</sup>. This cancellation of errors may, in some circumstances, give yields closer to those of real fires, but open tests are not a reliable means of assessing fire toxicity for anything other than well-ventilated conditions.

The fire zone of the standard cone calorimeter apparatus<sup>47,48</sup> is well-ventilated but the apparatus has been modified for tests under oxygen-depleted conditions. Standardisation of the controlled atmosphere cone calorimeter is currently under discussion within ISO. This uses an enclosure around the specimen and radiator, and a controlled input flow of nitrogen and air, but has met with limited success. In some tests the effluent may continue to burn as it emerges from the chamber giving ultimately well-ventilated flaming. In others, under reduced oxygen

concentrations, the fuel lifts from the surface, and ignition does not occur<sup>49</sup>. The CO yields in the open cone calorimeter have been found to correlate with an equivalence ratio of 0.7 for a range of cable sheathing materials<sup>46, 50</sup>. The relatively high dilution of fire gases in, and stainless steel construction of, the hood and duct, may lead to difficulties in detecting some effluent components. Fire gases pass through the centre of conical heater, and then are quenched by the cold duct which may affect their composition.

### 17.3.3 Closed chamber tests

Closed cabinet tests and their operation may be likened to a small fire burning in a closed room. The specimen is decomposed by a heat source and the resulting effluent accumulates within the cabinet. The decomposition system is either mounted within the cabinet as in the aircraft<sup>51</sup> and maritime tests<sup>52</sup> or may be outside, connected to the cabinet by a short duct, as in ASTM E 1678<sup>53</sup>.

A direct consequence of the closed cabinet is that the fire effluent accumulates within the cabinet and the fire gas concentrations therefore increase as the specimen burns and the gases will change with oxygen depletion. For laminated or layered specimens, the effluent will also change as the flame burns through different layers. As the specimen decomposes, the hot effluent rises to the upper part of the chamber where it may accumulate or circulate around the chamber due to natural convection. Thus the product concentration will depend on where the gas samples are taken from, and the heat transfer from gas to the chamber walls altering the position of the smoke layer, which will recede away from cold walls. The

smoke density values will be unaffected provided a vertical light path is used. Although mixing fans are used in some smoke density tests, they are rarely used in toxicity tests probably because of their influence on the burning behaviour. Both the aircraft and maritime tests require the smoke to be sampled at specified times (although burning may have proceeded at different rates) from gas sampling probes in the geometric centre of the cabinet.

If the effluent is stratified, the gas sample is obviously unrepresentative, but if it is uniformly distributed, then the gas flowing into the fire zone may be oxygen depleted and fire gases may be recycled through the fire zone. These latter effects will be greater with thicker specimens which would be expected to generate more smoke, due to more complete consumption of oxygen and hence to under-ventilation.

Therefore, closed box tests give a complete product yield of burning from well-ventilated to under-ventilated conditions, but without giving any indication of how the yield varies with fire condition. They are not generally able to sustain flaming combustion in underventilated conditions where the toxic hazard is usually greatest. Another potential source of error may occur as the fire effluent is heated and excess pressure is released or stickier components within the effluent, such as hydrogen chloride are deposited onto the walls of the cabinet.

### **17.3.3.1 Tests based on the NBS Smoke Chamber ISO 5659-2<sup>54</sup>**

The smoke chamber (Figure 17.5) is a well-established piece of equipment, designed to monitor only the smoke evolution from burning materials, in order to minimise visible obscuration of escape routes during a fire. Its widespread acceptance has led to its use in a number of industry specific toxicity tests. The Aircraft test<sup>51</sup> (prEN 2824, 5 and 6, uses the vertical radiator and vertically mounted test specimen of ASTM E 662<sup>55</sup>) and is specified for components for passenger aircraft cabins (Figure 17.5). Airbus ABD 3 and Boeing BSS 7239<sup>51</sup> use the same apparatus but specify different gas analysis methods. The IMO test<sup>52</sup> is based on ISO 5659-2 using a conical heater, with the sample mounted horizontally on a load cell, and is used to specify materials and products for large passenger ships and high speed surface craft. A reduced version of this test is used in the UK for railway vehicles<sup>56</sup> as BS 6853, B2. The European specification (EN TS 45545-2<sup>57</sup>) uses the IMO toxicity test at 50kW/m<sup>2</sup> without the pilot igniter and with FTIR analysis to determine the toxicity of railway vehicle components. In the aircraft test, flaming conditions are generated by a series of small flames along the base of the vertical specimen, but in other tests it occurs when specimens are ignited by a single pilot flame or self ignite.

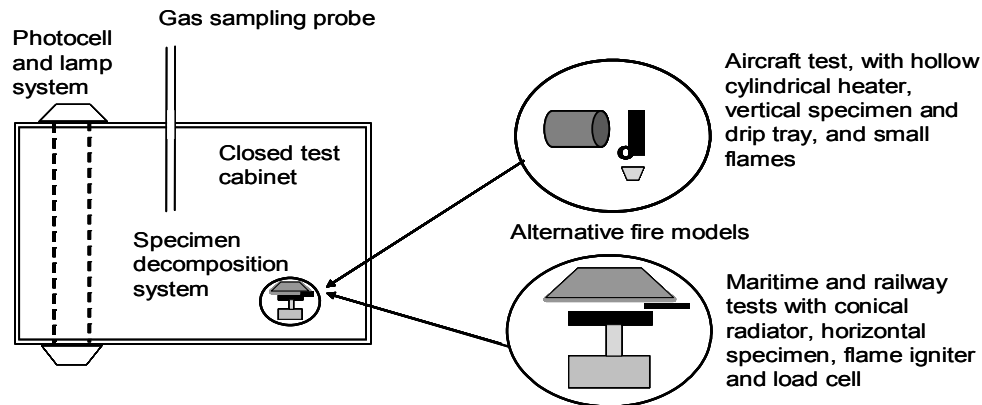


Figure 17.5 Diagram of fire smoke toxicity test based on NBS Smoke Chamber

In all of these tests, the specimens, 75 mm square and up to 25 mm thick, are exposed to radiant heat with and without a pilot flame(s). Decomposition takes place inside a closed cabinet of 0.51m<sup>3</sup>. There is no control of the air flow or oxygen concentration through the fire zone and the effluent is mixed by natural convection as it accumulates within the closed cabinet. Gases are sampled using probes mounted in the centre of the cabinet.

Flaming tests result in some oxygen depletion which can vary with the thermal stability and thickness of the specimen and also decreases with increasing test duration. The flaming fire stage is difficult to assess but may be related to ISO stage 2, well-ventilated and/or stage 3a, small-ventilated. The IMO tests at 50 kW m<sup>-2</sup> could possibly represent stage 3b, post-flashover flaming and may change from 2 to 3a or 3b during a test.

The advantages of these tests are that they use a widely available, standard smoke test apparatus, with the addition of simple gas sampling probes in the centre of the cabinet and relatively simple gas analysis systems to determine specified gases. The test specimen is heated from one side and

the effects of surface protection layers can be determined. The principal limitations are that the air supply to the fire zone is not controlled, and testing can cause oxygen depletion, which will change the toxic product yield by an unknown amount while effluent may be recycled through the fire zone. Alternatively, the effluent may stratify and gas samples may not be representative of the effluent generated. Specimens which drip in the aircraft test may give erroneous results if the liquid falls to the tray or cabinet floor and is not burned.

### 17.3.4 Flow-through tests

In these methods the specimen is thermally decomposed with or without flaming in a furnace over flowing air which drives the effluent to the gas determining or sampling systems.

#### 17.3.4.1 Simple tube furnace flow through test

The NF X 70-100 method<sup>58</sup> (Figure 17.6) was developed to estimate the toxicity of materials and products used in railway vehicles, initially in France. This is a small scale static tube furnace in which the test specimen (typically 1 gram or 0.1g for low density materials), is pushed, in a crucible, into the middle of the furnace tube and thermally decomposed, using furnace

temperatures of 400, 600 and 800°C to represent smouldering, well-ventilated and under-ventilated conditions in flowing air at 2 litres min<sup>-1</sup>, where they may pyrolyse and auto-ignite. For most materials at a temperature of 400°C they will not ignite, so the condition is 1b, oxidative pyrolysis. At a temperature of 600°C, the rate of pyrolysis may be fairly slow, giving a well-ventilated fire condition, whereas at 800°C the fire condition may be closer to under-ventilated as the rate of pyrolysis exceeds the stoichiometric air supply rate. The effluent is driven through gas detection systems, bags or bubblers for subsequent analysis.

This method is easy to use, uses simple equipment with specified operating conditions of temperature and air flow. It is increasingly used for fire toxicity testing of materials used for railway vehicles and is also included in prEN45545-2. The lack of requirement for flaming to be observed leaves the assignment of fire stage 2 to be assumed for most materials at 600°C and 3a or 3b for materials at 800°C. A practical

limitation is the number of replicate test runs needed to obtain sufficient samples for complete gas analysis.

#### 17.3.4.2 Steady state tube furnace methods

The steady state tube furnace ISO TS 19700<sup>59</sup> (also known as the Purser furnace) allows the possibility of controlling the fire conditions during burning. This forces combustion by feeding the sample into a furnace of increasing heat flux at a fixed rate, thus replicating each fire stage by steady state burning. The results are intended to form part of the input to ISO 13344<sup>32</sup>, ISO 13571<sup>5</sup> and fire risk assessments, which are specifically related to the ISO fire stages. The test uses the same apparatus as BS 7990<sup>60</sup> and IEC 60695-7-50 and -51<sup>61</sup> shown in Figure 17.7, with the air flow and temperature required to replicate each fire stage shown in Table 17.7. Alternatively, as a research tool, or to generate data for fire modeling, the yields can be determined at a fixed temperature as a function of the equivalence ratio  $\phi$ .

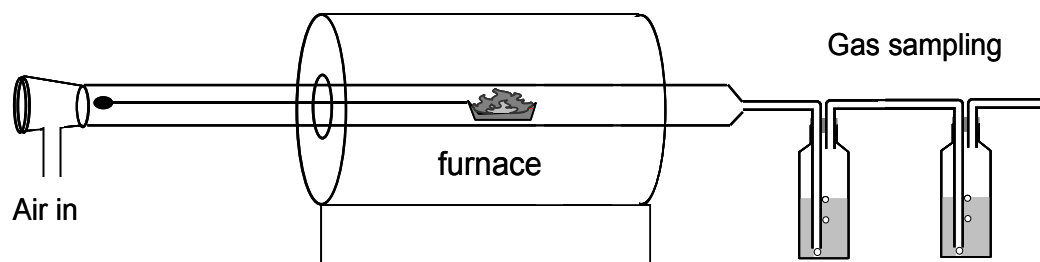


Figure 17.6 Schematic of NF X 70-100 test

Fire Type	Temperature /°C	BS 7990 Primary air flow /(l min <sup>-1</sup> )	ISO TS 19700 Primary air flow /(l min <sup>-1</sup> )	IEC 60695-7-50 Primary air flow /(l min <sup>-1</sup> )
1b Smouldering (non flaming fires)	350	2	2	1.1
2 Well ventilated	650	10*	10*	22.6

flaming				
3a Small under-ventilated flaming fires	650	Twice stoichiometric fuel/air ratio	Twice stoichiometric fuel/air ratio	-
3b Fully developed under ventilated fires	825	Twice stoichiometric fuel/air ratio	Twice stoichiometric fuel/air ratio	2.7

\* subject to verification of ventilation condition

*Table 17.7 Furnace conditions corresponding to characteristic stages of burning behaviour*

Adjustment of temperature, air flow or specimen introduction rate may be required to simulate a specified ISO fire stage. A strip specimen or pieces are spread in a silica boat over a length of 800 mm at a loading density of 25 mg mm<sup>-1</sup> and fed into a tube furnace at a rate of 1 g min<sup>-1</sup> with flowing air. Secondary air is added in a mixing chamber to give a total gas flow of 50 l min<sup>-1</sup> for analysis. The toxic potency of the effluent is assessed during the steady state burn period.

This method enables the toxic potency of a material of unknown composition to be determined under known, steady state fire conditions (temperature and equivalence ratio) which relate directly to the end-use fire hazard. The use of a high secondary air flow usually ensures that all the required gas samples can be taken during a single run. Smoke obscuration may also be determined. Unlike the closed box methods which may give toxic product data for a continuum of fire

stages, in this method a separate run is required for each fire stage. In addition to analysis of the gases specified in ISO 13344 (CO<sub>2</sub>, CO, O<sub>2</sub>, HCN, NO<sub>x</sub>, HCl, HBr, HF, SO<sub>2</sub>, acrolein and formaldehyde) there is a requirement to determine the total hydrocarbons. This may be achieved by passing part of the air-diluted test effluent through a secondary combustion furnace to allow the determination of the products of incomplete combustion even for materials of unknown composition. The ISO TS 19700 protocol allows determination of the equivalence ratio required for different fire stages, even for materials of unknown composition and thus enables the toxic potency of a material to be determined under known, steady state fire conditions (temperature and equivalence ratio) which relate directly to the end-use fire hazard. Crucially, this method has been shown to replicate the toxic product yields from large scale tests, see section 17.3.6.

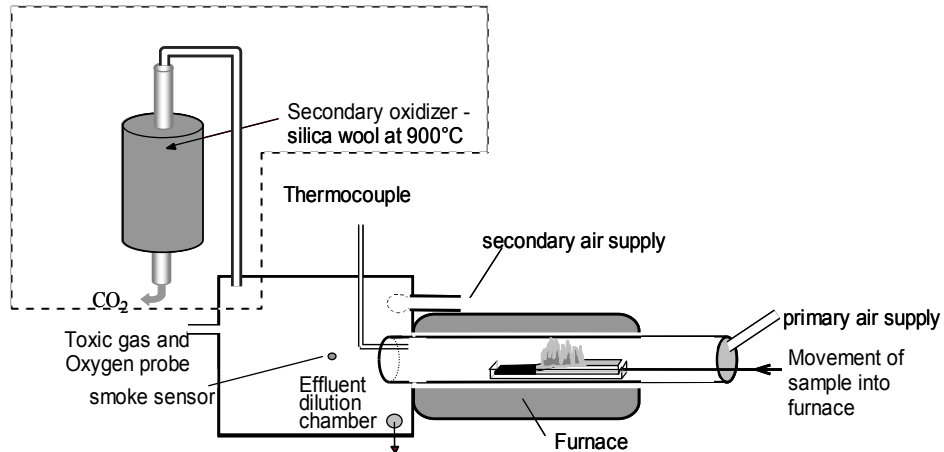


Figure 17.7 Diagram of apparatus of ISO TS 19700. The secondary oxidiser (inside dotted line) is for determination of total hydrocarbons in the ISO standard.

### 17.3.4.3 Fire propagation apparatus<sup>62</sup>

This method<sup>62</sup> shown in Figure 17.8 is also suited to obtaining toxicity data since the ventilation condition is well controlled, and the heat flux can be varied to force burning in underventilated conditions. The yield data have been published as a function of equivalence ratio, and have been used to calculate FED and LC<sub>50</sub> values<sup>63 64</sup>.

### 17.3.5. Correlation of different bench scale test data

The range of toxicity test methods is bound to produce different fire conditions, and hence different toxic product yields. Four test methods (NBS Smoke Chamber, NF X 70-100, Fire Propagation Apparatus and Steady State Tube Furnace) have been compared, primarily from published data<sup>65,66,67</sup> using the carbon monoxide yields and hydrocarbon yields (not

recorded in the NFX tests), which are both fairly good indicators of fire condition, for four materials (LDPE, PS, PVC and Nylon 6.6), at two fire conditions, well-ventilated and underventilated. The CO and hydrocarbon yields are shown in Figure 17.9 and 17.10.

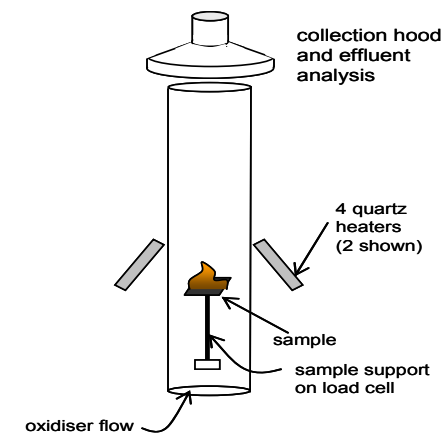


Figure 17.8 Fire propagation apparatus

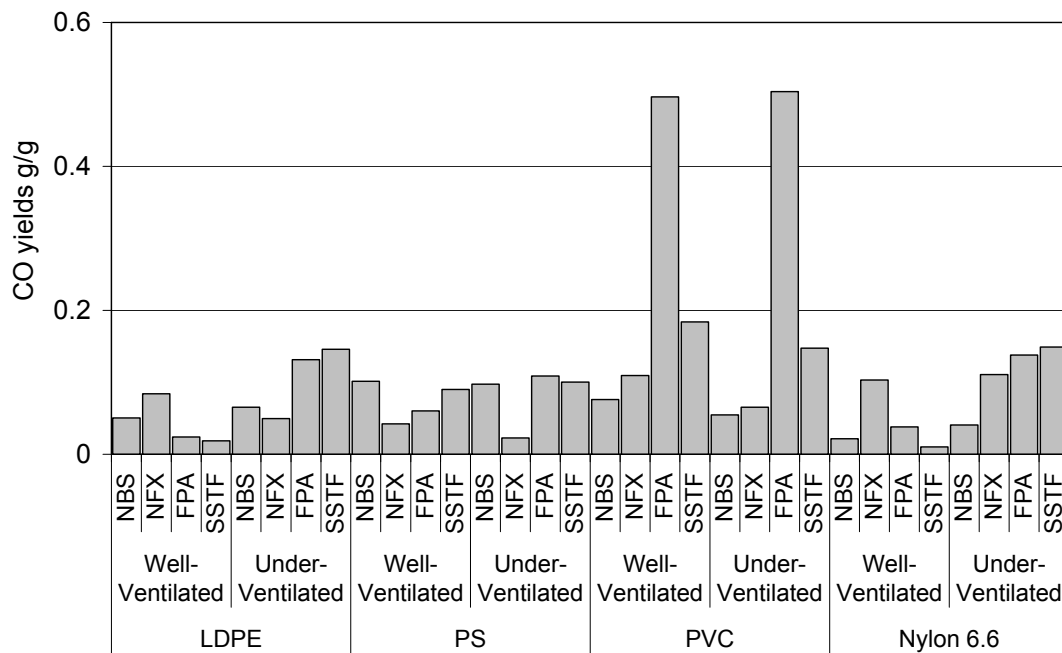


Figure 17.9 CO yields g/g for four polymers using four test methods at two fire conditions

For LDPE, the FPA (fire propagation apparatus) and SSTF (steady state tube furnace) show significant differences between the low CO yields of well-ventilated burning and the higher yields of under-ventilated fires. The NBS smoke chamber shows only a slight difference between the well-ventilated and under-ventilated fire conditions, while the NFX 70-100 gives the anomalous result of a higher CO yield for well-ventilated flaming than for under-ventilated. Although hydrocarbons are not always included in a toxicity assessment their presence is a good indicator of the fire condition. For LDPE, all the tests show a dramatic increase in hydrocarbon yields for under-ventilated combustion.

It has already been reported that the enhanced stability of the aromatic ring

in the decomposition products of polystyrene give higher CO yields in well-ventilated conditions and lower CO yields in under-ventilated conditions than aliphatic polymers such as LDPE<sup>68</sup>. This trend is observed in the fire propagation apparatus, and in the steady state tube furnace, but the reverse trend is seen in the NBS smoke chamber, and more markedly in the NFX 70-100. The hydrocarbon yields show very large differences for PS, with over half of the polymer being pyrolysed to hydrocarbons under well-ventilated conditions and about a quarter in under-ventilated conditions. Conversely, the FPA and SSTF show very low hydrocarbon yields under well-ventilated conditions, but high yields in under-ventilated conditions.

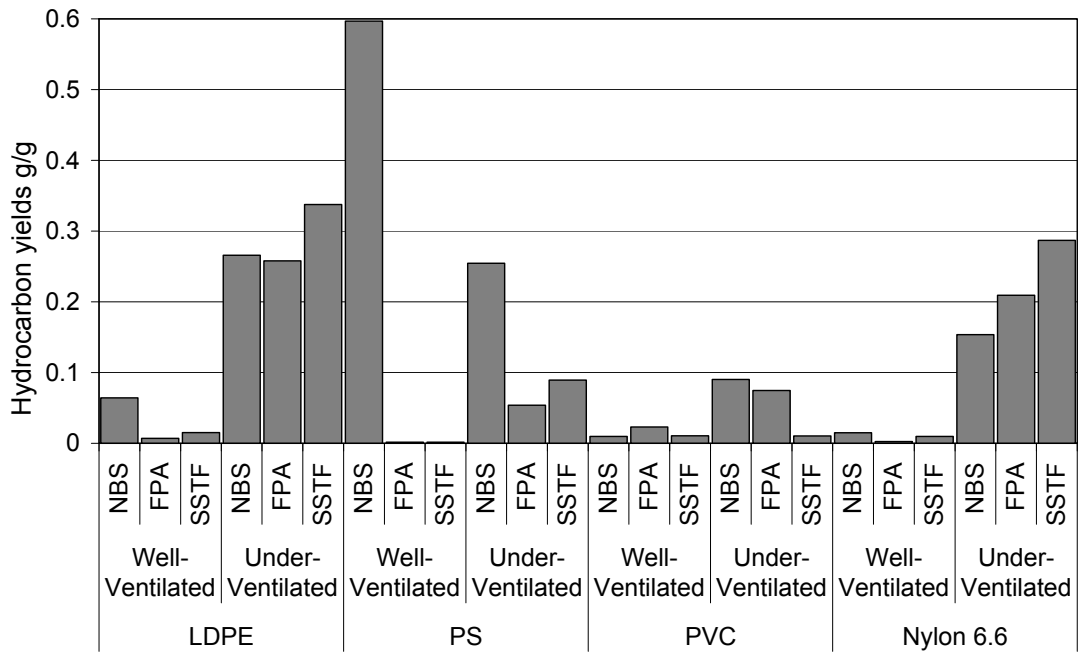


Figure 17.10 Hydrocarbon yields g/g for four polymers using four test methods at two fire conditions

For PVC, there is little difference between the CO yields for the two fire conditions for most of the tests, although the FPA gives much higher, consistent yield, while the other three tests give a lower yield for under-ventilated flaming. For hydrocarbons, there are significant increases in yield between the well-ventilated and under-ventilated flaming conditions for the NBS and FPA methods, but not for the SSTF.

For Nylon 6.6 all the tests show an increase in CO yield from well-ventilated to under-ventilated, although the values vary from very low (NBS and SSTF) to fairly high (NF X 70-100) for well-ventilated conditions, while all tests except the NBS smoke chamber are able to replicate the higher CO yields of under-ventilated combustion consistently for Nylon 6.6. For

hydrocarbons, a clear, consistent trend is observed between the low yields of well-ventilated combustion and the higher yields of under-ventilated combustion.

In summary, the FPA and the SSTF show consistent differentiation between well-ventilated and under-ventilated yields of CO and hydrocarbons for all materials (except for hydrocarbons from PVC in under-ventilated conditions). The NBS smoke chamber shows little differentiation between fire conditions, especially for CO yields, while the NF X 70-100 shows no consistency between fire condition and yield for the materials reported here.



### 17.3.6. Correlation of bench and large scale test data

The validity of a bench-scale study of fire behaviour is dependent on how it translates to the real scale. In general, real scale fires (both laboratory tests and unwanted fires) are poorly defined, and exhibit high sensitivity to a number of uncontrolled variables.

Full-scale and large-scale tests have demonstrated that toxic product yields are highly dependent on the combustion conditions. Fire stages and types can be characterised either in terms of CO/CO<sub>2</sub> ratio, or preferably in terms of equivalence ratio, which provide reasonably good predictive metrics for product yields.

Few studies have reported correlations between bench and large scale test data, and most of these have used the steady state tube furnace<sup>69,70,71</sup>.

Comparison of the yields of carbon monoxide from burning

polypropylene (Figure 17.11a) and nylon 6.6 (Figure 17.11b) show a strong dependence on equivalence ratio and consistency between bench and large-scale<sup>72</sup>. Figure 17.11b also includes data from the controlled atmosphere calorimeter, showing a failure to replicate the higher CO yields associated with underventilated fires. Both figures show much greater CO yields for underventilated burning, with a higher degree of scatter in those data points.

The large scale test data (from the ISO room corner test) show very good agreement with the steady state tube furnace data. It is notable that the controlled atmosphere cone shows higher CO yields in well-ventilated conditions and, crucially, lower CO yields in under-ventilated conditions. It has been reported<sup>73</sup> that correction can be applied to the calculation of equivalence ratio from the controlled atmosphere cone.

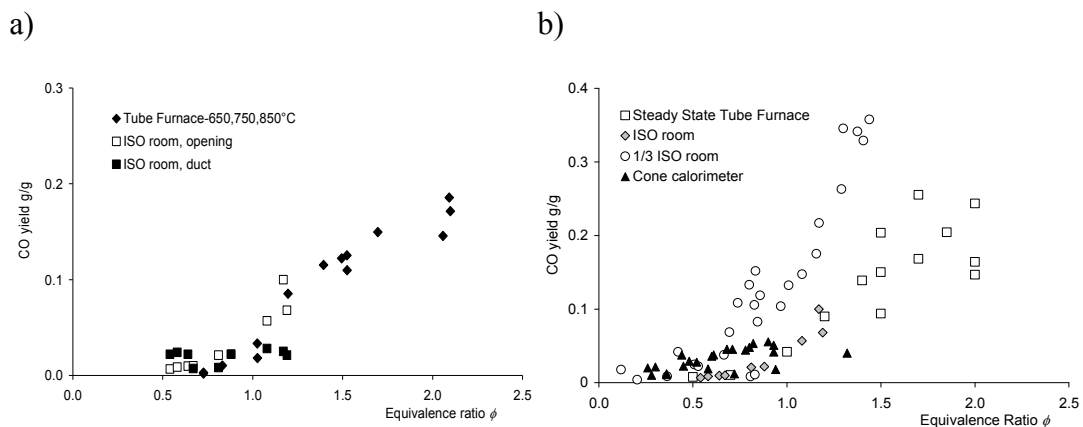


Figure 17.11 Comparison of CO yields as a function of equivalence ratio  $\phi$  for Polypropylene and Nylon 6.6 tested in the steady state tube furnace and the large scale ISO Room (left) and for Nylon 6.6 tested in the  $\frac{1}{3}$  ISO Room and controlled atmosphere Cone Calorimeter (right)<sup>71</sup>.

## 17.4 Conclusions

Fire toxicity, the largest cause of death in fires, is becoming better understood and tools now exist to assess those hazards. The effect of incapacitation on fire victims, rather than outright lethality, has generally been underplayed as the ultimate reason for the fire death, although witness accounts of fires frequently describe intolerable fumes. To a large extent this is because of the reliability and simplicity of ascribing a COHb level >50% to death by carbon monoxide poisoning. While it is entirely appropriate that forensic fire investigations need to establish that a victim was breathing at the time of the fire, it is wrong to assume that CO is the only, or indeed the major hazard, in all fire effluent.

The methods for estimation of FED and FEC allow materials developers to assess their products, and if the fire toxicity is likely to be high, to see which species are to blame and take remedial action. Since incapacitation in a fire will result in a fire death in the same way as lethality (unless the incapacitated victim is fortunate enough to be rescued) it is more appropriate to use the incapacitation methodology of ISO 13571 than the rat lethality methodology of ISO 13344.

There are a large number of different methods used for bench-scale assessment of combustion toxicity, and the applicability of test data to fire hazard assessment is not always clear. Obviously, toxic potency data should not be used in isolation but should either be a part of a classification scheme or as part of the input to fire risk and fire safety engineering assessments. It is important that

uncertainty or confidence limits should be used with toxic potency data, because they are often relatively large. Fire effluent toxic potency does not have a unique value but is a function of the material and the fire conditions, particularly temperature and oxygen availability in the fire zone, and also the fire environment (enclosure, geometry and ventilation). In order to assess the fire hazard, toxic potency data must be relevant to the end use fire situation, and the fire condition, which can be defined using the ISO classification of fire stages.

Globalisation of trade and relaxation of national barriers drive the need for international harmonisation of toxicity testing. ISO specifications and standards provide a common basis on which to determine toxic potency. A number of standard fire smoke toxicity tests are available and it is important to consider their relevance and limitations before selecting a method. Some of these tests do not appear to represent any fire stage; some represent several fire stages separately; others represent the progress of a fire through an indeterminate number of stages. Further, some test methods produce data which is a function of both the flammability of the specimen and the yield of toxic products, while others provide toxic product yield data which is independent of the burning behaviour. Finally, chemical methods of assessment provide a breakdown of the concentrations of individual toxicants, from which toxic potencies can be calculated, while the earlier animal based assays only give an overall estimate of the toxic potency of the fire smoke. Although it has been argued that animal based

methods are more likely to identify any new unusually high toxic potency products, provided the human and test animal responses are similar, it should be noted that there have only been two such instances<sup>24,74,75</sup> in the last three decades, and neither would be expected to be significant in a real fire.

The general trend has shifted from standard tests which include precise details of apparatus, procedure, method of assessment and specification of results, to more recent approaches which define the apparatus

and procedure necessary to obtain data relevant to end use fire situations. The later requires the involvement of suitably qualified personnel to define the necessary test conditions, effluent analyses, and to interpret results to ensure they are relevant to the end use application.

The steady state tube furnace (Purser furnace) has shown itself to be an excellent tool for generation of reliable data for different materials and fire conditions, for use in robust fire hazard assessments.

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