

# Hydrogen Chloride in Fires

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## ABSTRACT

ISO 13571:2007 describes the calculation of safe escape time using yields of asphyxiant and irritant gases for performance based design. Hydrogen chloride (HCl) gas is an incapacitating irritant, reported to be intolerable at concentrations above 100 ppm, but lethal to rats only at concentrations around 5000ppm for a 30 minute exposure. It is evolved from burning PVC, and other chlorine containing plastics. The experimental evidence of the concentration/dose effects on a range of animal species has been reviewed, and concludes that the HCl concentration leading to incapacitation of 1000 ppm, used in ISO 13571, is rather too high to ensure safe escape. Experimental data is presented from burning unplasticised PVC, plasticized PVC cable, and LDPE to show that HCl interferes with the flame chemistry, particularly the conversion of CO to CO<sub>2</sub>, further increasing the hazard from the fire effluent. The product yields are used to estimate the fire effluent toxicity, comparing the standard based on rat lethality, ISO 13344 with the newer standard, which also takes the effect of incapacitating irritants into account, showing the large contribution of HCl to the fire hazard. Finally, the relationship between the toxicity and a simple analysis of effluent acidity (EN 50297-2-3) is discussed.

**KEYWORDS:** fire chemistry, toxicity, egress

## INTRODUCTION

The prediction of the hazards to life of people from exposure to fire effluents, including heat, smoke and toxic gases, is an important part of fire hazard assessment and fire safety engineering. The acceptance of ISO 13571 [1] provides the tools to assess hazard to life during escape from a fire for performance based design, and establishes a framework against which the fire safety provided by regulatory codes can be quantified. Specifically, it describes methods for calculation of the time available for escape, which it defines as the interval between ignition and when the conditions become untenable, preventing occupants from taking effective action to accomplish their own escape. It describes such incapacitation as resulting from:

- a) exposure to radiant and convected heat;
- b) inhalation of asphyxiant gases, such as carbon monoxide (CO) and hydrogen cyanide (HCN);
- c) exposure to sensory/upper-respiratory irritants, including acid gases and organo-irritants;
- d) visual obscuration due to smoke.

The aim of this study is to consider the hazards associated with hydrogen chloride (HCl) in fire effluents and the extent to which they contribute to the overall prediction of fire toxicity. First, it is necessary to review the available information on the effects of exposure to HCl on human and animal subjects. Then, using polyvinyl chloride (PVC) as an example with well-characterised decomposition and combustion products, the effects of HCl as a component of fire gas are considered. How this information may be input into sets of equations for predicting the fire gas toxicity is described. However, for substances such as HCl, which can deposit rapidly, not only on walls and surfaces of enclosures, but also on water droplets and smoke particles, the transport of HCl in fire effluents must also be considered. A method for quantifying the yields of toxic products in fire effluents as a function of fire condition is described, alongside a method adopted by the European Commission for classification of cable materials according to the acidity of their decomposition products. Experimental data is reported showing the influence of HCl on the CO yield under different fire conditions, and how these combinations of toxicants translate into an overall estimation of the toxicity. Finally, a relationship between the European acidity classification and the fire toxicity for a number of electric cables burned under well-ventilated conditions is reported.

Sensory irritants cause painful effects to the eyes, upper respiratory tract, and to the lungs. The ratio between the concentrations producing severe irritation and death is typically between 15 and 500 [2]. Moreover, experiments exposing human subjects to CS gas (2-chlorobenzalmalononitrile) [3], which produces similar symptoms to HCl exposure, indicate that a gradual increase in concentration would allow subjects to tolerate a concentration which would be unbearable when subjected to immediate exposure. It has been argued both that sensory irritants will provide a stimulus to encourage escape [4], or that they will make escape extremely difficult [5]. Given the range of responses of human fire victims, it is likely that some individuals will respond by furthering their efforts to escape, while others, feeling unable to see or breathe, will be trapped. This raises the question as to what is an acceptable proportion of a population we can allow to be trapped in a fire, and what concentration of irritant gas will produce this?

### EFFECTS OF HCl ON HUMAN SUBJECTS

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, rats 4700 ppm for 30 minute exposures [6]). 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.

There is only one report of human exposure to HCl gas at concentrations relevant to fires [7], 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 [8] 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 properly 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., [9], [10] indicating that 300 ppm would be intolerable to humans [11].

Table 1 summarises the expected effects of HCl on humans [12] confirming 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 would be dangerous, causing lung oedema after only a few minutes exposure.

Table 1. Inhalation exposure of humans to hydrogen chloride [12].

Approximate Concentration /ppm	Exposure time	Effect	Ref
1 to 5		Limit of detection by odour	
≥5	Unspecified	Immediately irritating	[13]
>10	Occupational	Highly irritating, although workers develop some tolerance	[13]
10	Prolonged	Maximum tolerable	[8]
10 to 50	A few hours	Maximum tolerable	[8]
35	Short	Throat irritation	[8]
50-100	1 hour	Maximum tolerable	[8]
1000-2000	Short	Dangerous	[8]

However, it has also been argued that sensory irritancy is dependent on concentration, not dose [14]. Since the response, like a blinding light or deafening sound is practically instantaneous, the exposure times in Table 1 may be inappropriate.

### EFFECTS OF HCl ON ANIMAL SUBJECTS

A number of methods have been used to indicate incapacity [15], [16]. While lethality studies inevitably provide the most reproducible end point, behavioural end-points for incapacity are more difficult to define, and are generally too close to death, or require extensive training [15], [17]. A number of studies have

been undertaken exposing animals to HCl to address the issue of HCl in fire gases. These studies are compromised by the difficulty in relating irritancy suffered by the animal to a human equivalent, the difficulty in defining the point at which incapacitation occurs, and by the apparent tolerance developed during the period of exposure. In mammals, the trigeminal and vagus nerves respond to acidic irritant gases, in mice this leads to a fall in respiration rate to 10% of its normal value, while in primates and humans [2], as the lungs become flooded with pulmonary fluid, their decreased efficiency results in hyperventilation.

The guinea-pig has been proposed as the most appropriate model to use to study the effect of HCl because this animal, like humans, is known to develop laryngeal and bronchial spasms leading to suffocation [18]. Guinea-pigs have been exposed to HCl at rest and during moderate exercise [19]. Incapacitation occurred very quickly (60 s) at 600 ppm during exercise followed by death due to suffocation, as suggested [18]. In contrast, in one study when mice were exposed to various HCl concentrations in motorised wheels [20], incapacitation resulted from exposure to 20 000 ppm HCl between 5 and 15 minutes, and at 10 000 ppm from 17 minutes upwards.

Crane et al. observed that much higher HCl concentrations (e.g. 13 000 ppm lead to incapacitation in 30 minutes and death in 36 minutes) were required for incapacitation of rats, also on a motorised wheel [21]. The mechanism of action for HCl in rats, based on observations during this study, seems to be primarily one of mechanical blockage of the upper airways caused by the extreme inflammatory and corrosive action of this 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 [22]. This has led to the suggestion that species that breathe through their mouth (humans, especially in the stressful situation of escaping from a fire) may be more sensitive to the effects of HCl than obligate nasal breathers, such as rodents [12].

Much of the controversy surrounding survivable HCl concentrations revolves around two studies in which baboons were exposed to dry HCl. The first study focussed on a simple escape paradigm [23], the second measured their respiratory changes [24]. The baboons used for the first test series were trained for 5 to 8 weeks to respond with 95% success by distinguishing a correct white lever in response to a white light, from an incorrect red lever and red light, "encouraged" by a sound, and then an electric shock. Both those animals which operated the lever and escaped within 10 seconds (avoid result), and those which received the electric shock and escaped within the next 20 seconds (escape result), were considered to have escaped, and not to be incapacitated by exposure to the gas. While the irritant gas may adversely affect breathing, general well-being and the recognition of a light, it will not directly affect recognition of the sound or the electric shocks until the effects are very extreme. Indeed, there is no need to see the light as there is a 50% chance of pressing the correct lever and escaping at the first attempt. In one test at high concentrations, the incorrect lever was pushed 8 times before the correct one was pushed resulting in an escape.

Test data show that the baboons were adversely affected by HCl concentrations above 940 to 2 780 ppm. Even higher concentrations did not prevent their escape but did adversely affect their reaction times and performance. Although the two highest concentrations did not prevent escape, these animals subsequently died from their exposure to HCl, (classified as an escape result in the test). Understandably, each HCl exposure test only involved a single baboon, thus the results are not from replicated tests. This must be considered when interpreting such results. Many of the relative standard deviation values given in the baboon study are large and greater than 50% making it very difficult to draw meaningful conclusions from the data. Since the response of a population to an irritant would follow a log-normal distribution[1] with a wide range at its base, it is very difficult to see where to fit individual results into that distribution.

With the exception of the lowest HCl concentration (190 ppm), the baboons were all reported to cough and froth at the mouth at the lower concentrations, with profuse salivation, blinking, rubbing of the eyes and shaking of the head at the higher concentrations.

## **PVC DECOMPOSITION AND COMBUSTION**

At elevated temperatures (200-300°C) PVC undergoes a dehydrochlorination reaction to release hydrogen chloride and forms a conjugated polyene [25] which undergoes further rearrangements and product

elimination at higher temperatures to produce a complex pattern of hydrocarbons with aromatic materials predominating. Approximately 70 compounds [26] including benzene, toluene, xylene, indene, and naphthalene have been identified, but among these HCl is the principal toxicant. There has sometimes been an assumption that the chlorine content of burning PVC is quantitatively converted into HCl but this is not generally the case. Although some chlorine will always appear as HCl, other chlorine containing gas or vapour species will be produced while, in some formulations, some chlorine may remain in the char. For example calcium carbonate, a common filler in PVC, will react with HCl to produce non-volatile calcium chloride. A number of chlorine containing species have been identified from large-scale fires burning a high proportion of PVC, including mono- and dichlorobenzenes and other chloro-aromatic and chloro-aliphatic hydrocarbons [27]. Evidence exists to show that, depending on the fire situation, as much as 20% of the chlorine may exist in an organic form [28].

## EFFECTS OF PVC DECOMPOSITION AND COMBUSTION PRODUCTS ON ANIMAL SUBJECTS

When Swiss-Webster mice were exposed for 3 to 5 minutes and the sensory irritation response (measured as the change in respiratory rate) was compared with similar experiments using HCl [11], the PVC products were more potent sensory irritants than HCl. In a comparison of the irritant effects of PVC from flaming and non-flaming with corresponding amounts of HCl alone, it was found for baboons that the respiratory rate, tidal volume and minute volume all increased dramatically, again indicating the presence of other respiratory irritants in PVC fire effluents [29].

## PREDICTION OF FIRE EFFLUENT TOXICITY

The majority of UK deaths in fire are attributed to inhalation of toxic gases [30]. Carbon monoxide and hydrogen chloride are the principle toxicants from burning unplasticised PVC [31] (uPVC). There is a large variation in the responses to animal exposure to HCl and PVC fire effluents. In order to predict the escape time, it is necessary to estimate the fire toxicity, either directly from animal exposure experiments which are unacceptable in the European Union [32], or by chemical quantification of the major toxicologically significant products. ISO have published two standard methods for estimating the fire effluent toxicity from fire effluent composition. One is based on rat lethality data (ISO 13344 [33]) but which gives no indication as to how this data may be extrapolated to human exposure, while the other, which includes sensory irritants, is based on consensus estimates of human exposure limits (ISO 13571 [1]). The general approach 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 (LC<sub>50</sub>). Thus a Fractional Effective Dose (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.

$$\text{FED} = \frac{m[\text{CO}]}{[\text{CO}_2]-b} + \frac{21-[\text{O}_2]}{21-\text{LC}_{50,\text{O}_2}} + \frac{[\text{HCN}]}{\text{LC}_{50,\text{HCN}}} + \frac{[\text{HCl}]}{\text{LC}_{50,\text{HCl}}} + \frac{[\text{HBr}]}{\text{LC}_{50,\text{HBr}}} + \dots \quad (1)$$

Equation 1, from ISO 13344, referred to as the N-Gas model, uses this approach. However, in the first term the effect of the CO is enhanced by the increase in respiration rate caused by high concentrations of CO<sub>2</sub>, (expressed as a step function with one value of constants *m* and *b* for CO<sub>2</sub> concentrations below 5% and another for those above 5%). The equation also includes a term for oxygen depletion, although it is generally accepted that death from other fire gas components is inevitable if the fire gas is so undiluted that the contribution from hypoxia is significant. The HCN, HCl and HBr terms are the ratio of the gas concentration to the lethal concentration of HCN, HCl or HBr. The HCl concentration of 3500 ppm given in the standard is for rat lethality, not incapacitation.

ISO 13571 considers the four major hazards from fire which may prevent escape (toxic gases, irritant gases, heat and smoke obscuration). In essence, it describes the calculation of data relating to the incapacitation of humans exposed to fire effluents. However, it gives no indication as to how these may be combined, except by a general assumption, in a non-normative appendix, that the effects may be estimated independently. Equations 2 and 3 have been taken from ISO 13571. They calculate the FED of

asphyxiants and the Fractional Effective Concentration (FEC) of sensory irritants for the fire effluent which limits 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 (35 000 corresponds to the incapacitating dose (C-t) for CO of 35 000  $\mu\text{l l}^{-1}\text{min}$ , equal to around 5 500 ppm for 30 minutes exposure) and an exponential relationship for HCN (because asphyxiation by HCN exposure does not fit a linear relationship).

$$\text{FED} = \sum_{t_1}^{t_2} \frac{[\text{CO}]}{35000} \Delta t + \sum_{t_1}^{t_2} \frac{\exp([\text{HCN}]/43)}{220} \Delta t \quad (2)$$

$$\text{FEC} = \frac{[\text{HCl}]}{\text{IC}_{50, \text{HCl}}} + \frac{[\text{HBr}]}{\text{IC}_{50, \text{HBr}}} + \frac{[\text{HF}]}{\text{IC}_{50, \text{HF}}} + \frac{[\text{SO}_2]}{\text{IC}_{50, \text{SO}_2}} + \frac{[\text{NO}_2]}{\text{IC}_{50, \text{NO}_2}} + \frac{[\text{acrolein}]}{\text{IC}_{50, \text{acrolein}}} + \frac{[\text{fomaldehyde}]}{\text{IC}_{50, \text{fomaldehyde}}} + \sum \frac{[\text{irritant}]}{\text{IC}_{50, \text{irritant}}} \quad (3)$$

Equation 3 uses a similar principle to equation 1 to estimate the combined effect of all irritant gases.

Of particular relevance to this study is the value used for the  $\text{IC}_{50, \text{HCl}}$  which is given as 1000  $\mu\text{l l}^{-1}$  or 1000 ppm, in contrast to the estimates of intolerable pain to eyes, nose, throat and chest at 100 ppm discussed earlier and to the 3500 ppm required for rat lethality given in ISO 13344.

### Fire Effluent Movement

An important aspect in the assurance of fire safety is the transport of narcotic and irritant gases in various parts of the building remote from the fire. As smoke moves away from the fire source within a building, it gradually cools and is diluted by the entrainment of air. The concentrations of fire gases remote from a fire may therefore be significantly less than those close to the fire. In most cases, however, they remain present in the same proportions below 600°C. The two principle exceptions are the equilibrium between NO and NO<sub>2</sub> and gases which deposit during transport. For species such as HCl whose absorption is dependent on the surface coating of the enclosure this can result in significant losses. Figure 1 shows the rate of decay for HCl, HCN, SO<sub>2</sub> and NO<sub>x</sub> in a closed cabinet [27]. Two sets of data are shown for HCl, one for a polypropylene (PP) cabinet and one for a mineral fibreboard (MFB) cabinet. The gases were generated by burning materials inside the cabinet where they were retained and the gas concentrations measured.

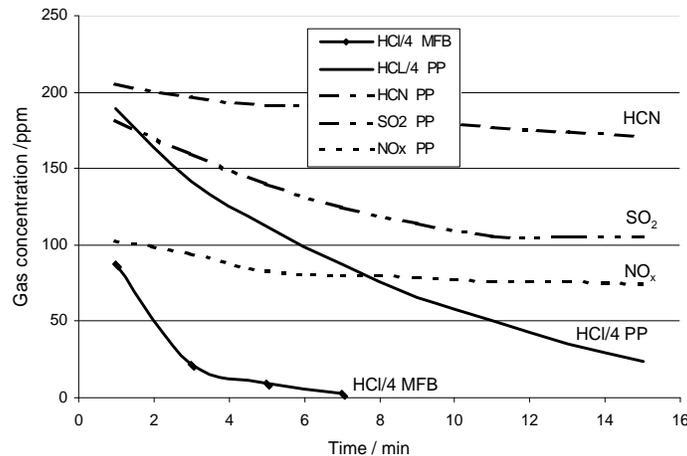


Fig. 1. Decay of fire gases in closed polypropylene cabinet (1.3 m<sup>3</sup>) and for HCl also in a mineral fibreboard cabinet.

In another study, the concentration of dry HCl travelling at 1 m s<sup>-1</sup> along 120 m of ventilation ducting 30 x 30 cm was investigated as a function of wall lining. Unfortunately, all the experiments reported included

some unpainted gypsum board, and the surface aspect ratio of the duct is unrepresentative of a typical corridor. The fall in HCl concentration was initially rapid, but then recovered depending on the amount of unpainted gypsum board. However, it was noted that the ability of all materials to absorb HCl diminished during the 30 minute run, and the experiments were conducted at room temperature, maximizing the adsorption of HCl [34].

In some of the animal exposure experiments reported earlier, HCl concentrations were monitored at the point of exposure, in others there are varying degrees of uncertainty as to how much HCl was lost during transport to the subject. It should also be noted that most animals were exposed to dry HCl whereas all fire gases contain condensable water vapour. As the fire gases cool, this water may be present as droplets into which the HCl will dissolve. A further complication arises from the tendency of HCl to deposit on coalescing soot particles. Although studies in rats and mice have shown similar responses to HCl aerosols and vapour, the wider respiratory tract of humans and anticipated mouth-breathing may affect this adversely, since droplets have the capacity to penetrate much deeper into the lung than water soluble gases, such as HCl in a similar way to the PM-10 particles (of  $\sim 10\mu\text{m}$  diameter) present in some polluted urban atmospheres.

The data available for HCl shows that for humans breathing becomes painful and difficult at 100 ppm. For many individuals this pain will reduce the perceived chances of a successful escape. Since most fire victims are not the healthy adults of animal exposure experiments, this may increase the proportion of victims who are trapped by such incapacitating irritants. The animal exposure studies indicate significant differences between species and between experimental protocols. In particular, HCl exposure appears more survivable by resting subjects than those engaged in physical activity. HCl exposure during exercise ultimately results in suffocation by animals, who are unable to breathe. The concentrations of HCl resulting directly in death are much higher than those which will effectively prevent escape, and the more sophisticated approach, which considers both asphyxiation and incapacitation described in ISO 13571 takes this into account. The effect of HCl in fire gases is complicated by its transport, resulting in a reduction through adsorption on surfaces, but enhanced by deposition onto water droplets and soot, where it can penetrate deep into the lung. As a first approximation, it could be assumed that these two opposing effects might balance each other out.

## **EXPERIMENTAL**

### **Bench-Scale Determination of Toxic Product Yields in Fire Effluents**

To quantify the yields of HCl, carbon monoxide and organo-irritants from burning PVC, the ISO TS 19700 steady state tube furnace (Purser furnace) [35] was used to generate fire effluent under controlled conditions. The apparatus may be set up to burn material at a particular equivalence ratio  $\phi$  (the actual fuel/air ratio divided by the stoichiometric fuel/air ratio), from well-ventilated burning through to forcing a steady state during under-ventilated burning. It does so by feeding the sample and air into a tube furnace at fixed rates, so that the flame front is held stationary relative to the furnace. This enables it to provide reliable data on the product yields as a function of equivalence ratio. Unlike a “flammability test” where a material’s chemistry dictates the rate of burning, in the steady state tube furnace all materials are burned at the same fixed rate.

The apparatus is described elsewhere [36], and shown in Fig. 2 with the addition of a secondary oxidiser. Samples are fed into the furnace in a silica boat, travelling at a mass feed rate of  $1\text{ g min}^{-1}$ . By varying the primary air flow rate different fire conditions were created at known equivalence ratios. Continuous analysis of oxygen depletion and yields of carbon dioxide, carbon monoxide and smoke were determined for each fire condition, at furnace temperatures between  $650\text{-}800^\circ\text{C}$ , as previously reported [37]. For the PVC containing materials, hydrogen chloride was collected by drawing a metered volume of fire effluent through three bubblers containing deionised water, and determined using a titrimetric method [37]. In addition, organics were determined, as products of incomplete combustion, by further oxidation at  $900^\circ\text{C}$  in excess air over silica wool, as the difference between secondary  $\text{CO}_2$  and primary  $\text{CO}$  and  $\text{CO}_2$ .

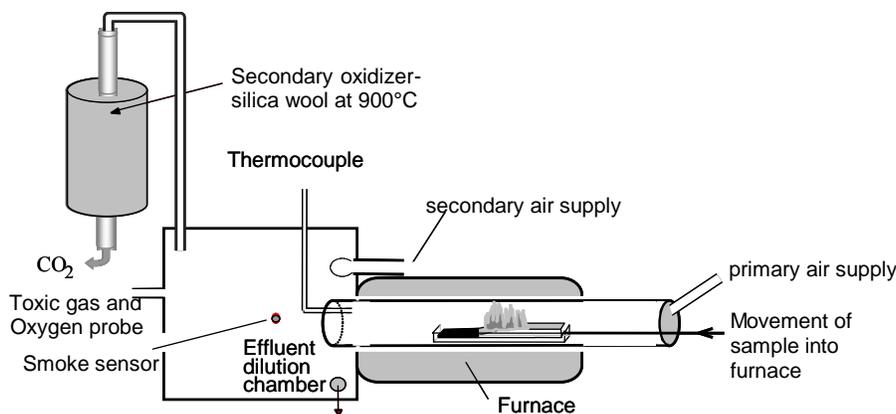


Fig. 2. The steady state tube furnace apparatus (Purser furnace).

### The Acid Gas Test - EN 50297-2-3:1998 [38]

This test has been incorporated into the Euroclassification of cables as part of the Construction Products Directive, introducing an additional acidity classification. This standard uses a simpler apparatus (Fig. 3) in which a static sample is decomposed in a stream of flowing air in the middle of the tube furnace, above 935°C, and the effluent is collected in bubblers prior to analysis. The acidity of the effluent solution is quantified in terms of pH and conductivity. In aqueous solution, acids dissociate to give hydrogen ions  $H^+$ , which give rise to the acidity, measured as pH, the negative logarithm of the hydrogen ion concentration.

In essence, this test identifies the presence of PVC or other halogenated materials in a cable formulation, allowing the two main types of cables used in buildings (PVC based and low smoke zero halogen (LSZH)) to be distinguished.

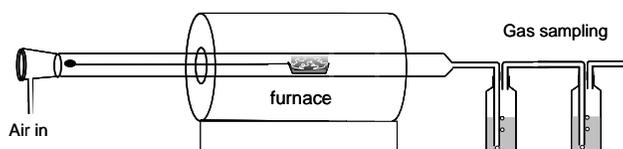


Fig. 3. The EN 50267-2-3 test apparatus.

### Materials

Commercial grades of Low Density Polyethylene (LDPE) and unplasticised PVC (uPVC) were used in pellet form, and the cable samples were used whole. The PVC cable reported in Fig. 4 and Fig. 5 was a commercial formulation which contained PVC, plasticiser and chalk in approximately equal proportions. The cable results shown in Fig. 6 represent a typical selection of widely used PVC and LSZH energy and data cables, and have been described elsewhere [39].

### RESULTS

Fire gas toxicity is a function of both the material composition and the fire conditions. For most materials the fire toxicity increases with decrease in ventilation, but for uPVC there is little change. For clarity, the results presented in Fig. 5 and Fig. 6 refer only to well-ventilated fires. Toxicities are expressed as the effluent generated from burning 1 g of material in 200 litres of air, based on an established standard [40]. Organoirritants in the fire effluent (measured as the difference in  $CO_2$  before and after passing over the secondary oxidiser) were considered collectively using an organic yield of  $10 \text{ mg litre}^{-1}$  to result in incapacitation, as described by Purser [2].

## CO Yield from PVC

In order to investigate another effect of HCl, as an inhibitor of gas phase combustion, reducing the heat release and hence flammability, a series of experiments were conducted on uPVC, PVC cable, and for comparison on LDPE at different equivalence ratios. Each data point represents a separate experimental run, obtained under different ventilation conditions, at furnace temperatures of 650 and 750°C.

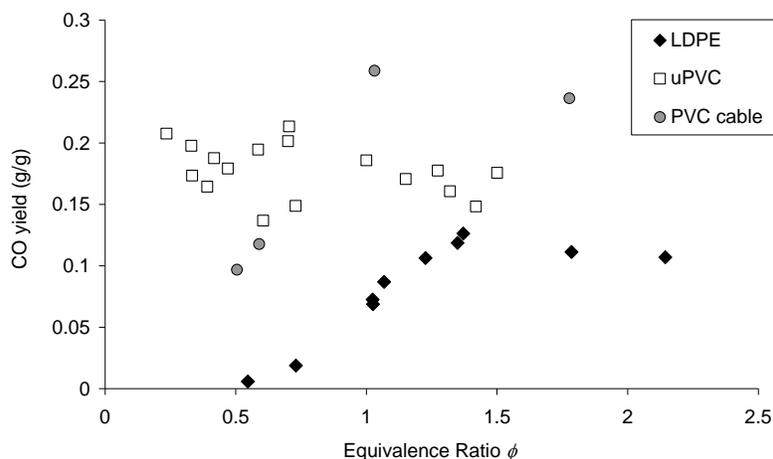
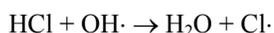
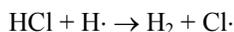


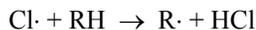
Fig. 4. CO yield for LDPE, uPVC and PVC cable burning in the steady state tube furnace (650-800°C).

Figure 4 shows the CO yield from UPVC, PVC cable and LDPE as a function of equivalence ratio for the steady state tube furnace. For LDPE and most other common polymers, the CO yield is very low until  $\phi = 0.7$ , then it starts to rise rapidly until  $\phi = 1.5$ , when it usually levels out. This is evident in this data both for LDPE and also for PVC cable. Conversely, for uPVC, a consistently high CO yield is observed even under the most well-ventilated fire conditions, and aside from some scatter in the data, there appears to be a slight reduction in the CO yield as the flaming becomes under-ventilated.

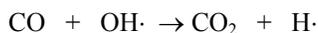
PVC forms more CO than simple hydrocarbon polymers under well-ventilated conditions because HCl interferes with the radical chain mechanism [41]:



The high-energy  $\text{H}\cdot$  and  $\text{OH}\cdot$  radicals are removed by reaction with HCl and replaced with lower-energy  $\text{Cl}\cdot$  radicals, which are able to leave the flame without further reaction, or be regenerated by reaction with a hydrocarbon:



Crucially, removal of  $\text{OH}\cdot$  (and also  $\text{H}\cdot$  which generates  $\text{OH}\cdot$ ) prevents the conversion of CO to  $\text{CO}_2$



This reaction is responsible for around half of the heat release. Thus inhibition of flame reactions leads to a higher proportion of products of incomplete combustion, particularly CO, but reduces the heat release. It is interesting to note the higher yields of CO in under-ventilated conditions for the plasticised PVC (~20% Cl content) is higher than that of uPVC (~60% Cl).

## Comparison of Toxic Effects Predicted by ISO 13344 and ISO 13571

Figure 5 shows a comparison of the fire hazard expressed as FED estimated by ISO 13344 (based on rat lethality data) with that from ISO 13571, which omits hypoxia, but includes a separate estimation of incapacitation (FEC), and lethality (FED), for uPVC, a plasticised PVC cable formulation and LDPE. For uPVC this shows the greater toxicological significance of HCl over CO, 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 using the high  $IC_{50}$  value of 1000 ppm HCl.

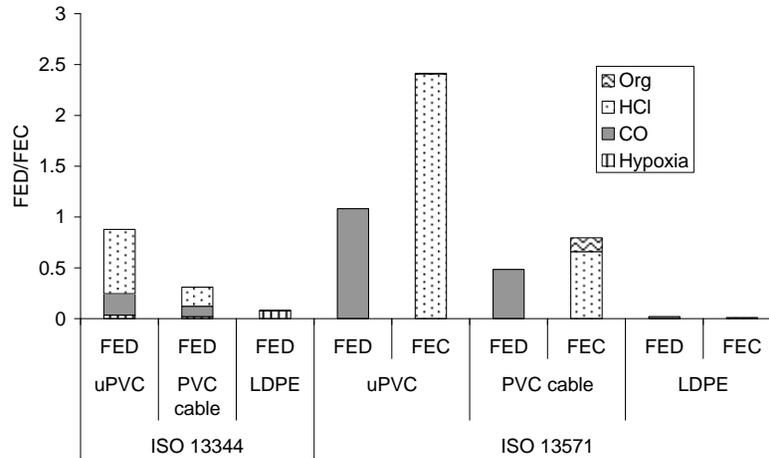


Fig. 5. Comparison of toxic fire hazard assessment from ISO 13344 (based on rat lethality) and ISO 13571 (based on estimates of human incapacitation (FEC) or death (FED)).

In order to demonstrate the relationship between HCl evolution and the overall toxicity (as quantified using ISO 13344), a series of standard commercial cables were burnt under well-ventilated conditions. The same cables were also decomposed in a small static tube furnace (Fig. 3) and the acidity of the effluent quantified using the EN 50297-2-3 acidity classification method. The results are shown in Fig. 6.

### Fire Toxicity of Electric Cables

The relationship between toxicity (expressed as FED) and acidity (expressed as pH) is shown in Fig. 6. For the cables tested, the same two groups appear on the figure. One group gave high pH values (low acidity), greater than 4, and correspondingly low toxicity, while the other gave pH values of 2.5 or less with correspondingly higher toxicity. The change in pH corresponds to a 50 fold difference in the acidic content.

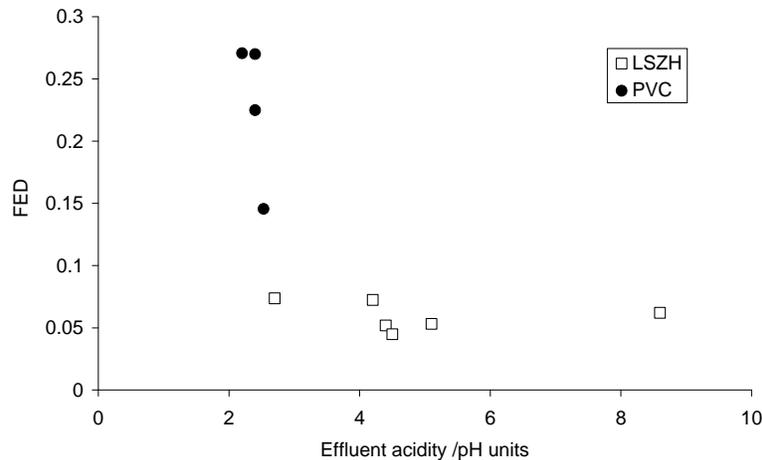


Fig. 6. Variation in toxicity with effluent pH for standard cables

In both the pH and toxicity measurements, the four members of the high acidity (low pH) and high toxicity group contained PVC and all those in the low toxicity and low acidity group were low smoke zero halogen (LSZH) formulations. For most of the cables tested, the acidity classification is a simple way of discriminating between the two common cable types (LSZH and PVC). For 9 out of 10 of these cables, this

classification coincides with increased toxicity. However, there are a wide variety of formulations within the two broad types, including many variants which were not part of this study. Although the results give a clear indication of the link, one specific cable fell outside these groups, producing quite a strongly acidic effluent (pH 2.7), but very low FED values. Moreover, analysis of the cable shows that it is in fact completely halogen-free and therefore the acid-generating effluent must be non-halogen.

## CONCLUSIONS

HCl presents two significant hazards in fires, by causing incapacitation through sensory irritancy (leading to painful breathing, swelling of the airways, and ultimately death), and by inhibiting the conversion of CO to CO<sub>2</sub>. The concentration causing incapacitation, and thus preventing escape, is much lower than that causing death directly; it is considered intolerable to humans at 100 ppm although a value of 1000 ppm given for incapacitation in the ISO 13571 standard. Assigning a “safe level” of HCl in fire effluents is fraught with difficulties. Incapacitation, preventing escape from a fire, is not quantifiable in animal subjects in the same way as lethality. There is a wide range of responses within a group of animals, and wider differences between different test groups, both within a species and between species. Given the range of physiological and psychological responses of humans to fire effluents, the fire safety community needs to be confident that the level deemed to cause incapacitation will not endanger lives in fires. Transport effects, both in animal exposure studies and in real fires add more uncertainty to the prediction of the time before HCl will cause incapacitation.

The results demonstrate the increased yield of two of the most easily quantified fire effluents, CO and HCl, when uPVC is burning, compared with LDPE. They also show differences in the fire chemistry (from increased CO yield). This manifests itself as a significant increase in the overall estimation of fire toxicity for well-ventilated burning, and, more surprisingly higher CO yields for PVC cable than for the purer uPVC under conditions of reduced ventilation. As an indicator of incomplete combustion, increased CO yields may be accompanied by the formation of other hazardous organic and organohalogen species, including chloro-aliphatics and mono- and dichlorobenzenes, many of which are more potent sensory irritants than HCl alone. The effects of these species is corroborated by the difference in response of animal subjects to fire effluents containing HCl to exposure to HCl alone. The effect of chlorine on the yields of all toxic and irritant species in different PVC formulations needs to be investigated before more general conclusions can be drawn about the influence of HCl on fire toxicity. Once these effects have been quantified, and the factors affecting HCl’s contribution to the overall fire toxicity understood, it may be that HCl can be used as a marker for a range of fire toxicants. This could lead to a demonstrable relationship between acidity and toxicity, allowing the acidity classification [38] to be used to discriminate between cables of higher and lower fire toxicity.

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