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Formation of Hydrogen Cyanide in Fires

A Literature and Experimental Investigation

BRANDFORSK Project 510-991

SP Swedish National Testing and Research Institute
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Abstract

A study has been made of the role of CO and HCN in the escape of fire victims. The mechanism by which both compounds affect their victims and the existence of synergy effects (as both are often present in fires) are discussed based on literature data.

Further, a literature study is conducted into the present state of the art concerning the most probable cause of death for victims of fatal fires. Evidence of CO poisoning is discussed together with similar evidence concerning HCN poisoning. It is concluded that insufficient data is available concerning HCN concentrations in fire victims to rule out HCN poisoning as a compounding factor, together with CO poisoning, in the fire fatalities investigated. Indeed, in those cases where HCN measurements have been made these have often been sufficiently high to hamper egress of fire victims, and in some cases to be fatal.

Finally, a pilot laboratory investigation was made using a selection of nitrogen containing material commonly found in domestic environments. The aim of this investigation was to obtain an indication of under which conditions one would expect these materials to emit both CO and HCN in a fire. In this context both non-flaming (i.e., pyrolysing) conditions and flaming (i.e., fire) conditions were studied. The materials chosen for this part of the study were: wool, nylon, synthetic rubber, melamine and polyurethane foam.

The laboratory experiments showed that all material containing nitrogen in its chemical structure readily gave rise to HCN. While the results of these bench scale experiments cannot readily be extrapolated to large-scale behaviour they do indicate that under pyrolysing conditions and in the presence of restricted oxygen availability one should expect significant amounts of HCN and CO. As HCN is approximately 35 times as acutely toxic as CO this would imply that HCN might well be an important factor in reducing the ability for fire victims to leave the scene of the fire.

Based on the results of this study it has been concluded that greater attention should be paid to HCN as an incapacitating agent and potentially as a cause of death in fires, together with CO.

Key words: fire, HCN, CO, toxicity, DIN furnace

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Preface

This report concerning the production of hydrogen cyanide in fires has been financed by the support of the Swedish Fire Research Board (BRANDFORSK, Project 510-991).

The authors would like to acknowledge the assistance of the BRANDFORSK reference group for their comments on the content and disposition of the report. Special thanks are also extended to Professor David Purser whose input has been invaluable.

Sammanfattning

Följande rapport sammanfattar en utredning om hur kolmonoxid (CO) och cyanväte (HCN) kan påverka brandoffers möjlighet till flykt. Ämnenas toxiska mekanismer och en möjlig existens av synergi mellan ämnena diskuteras baserat på litteraturdata.

I litteraturstudien diskuteras vilka de mest troliga dödsorsakerna i bränder är, och bevis för förgiftning av HCN respektive CO, som lagts fram i tidigare undersökningar, diskuteras. En slutsats rörande de data som finns tillhands, som behandlar koncentrationerna av HCN uppmätta i brandoffer, är att de data som finns är för otillräckliga för att kunna bevisa att HCN försvårar situationen i en brand. I de fall där HCN har mätts har dock koncentrationen oftast varit tillräckligt hög för att förhindra flykt från brandplatsen, och ibland tillräckligt hög för att vara dödande.

En undersökning i liten skala utfördes med kväveinnehållande material som är vanliga i bostäder. Materialen genomgick nedbrytning i en DIN-ugn, och brandgaserna som bildades analyserades med hjälp av en FTIR-utrustning. Målet för undersökningen var att få fram indikationer för under vilka brandförhållanden man kan förvänta sig att materialen i fråga utsöndrar både HCN och CO. Både flammande och icke flammande brandförhållanden (pyrolys) undersöktes. Materialen som valdes för projektet var: ull, nylon, syntetgummi, melamine och polyuretanskum. Alla dessa material innehåller kväve i sin kemiska struktur.

Resultaten från experimenten visar att alla de material som undersöktes kan bilda HCN när de bryts ner. Fastän resultaten från de småskaliga försöken inte kan extrapoleras till att visa hur materialen skulle bete sig under storskaliga förhållanden, indikerar de att man kan förvänta sig att stora mängder HCN och CO bildas. HCN är ungefär 35 gånger mer toxisk än vad CO är, vilket innebär att HCN kan minska chanserna för ett brandoffer att undkomma en brand markant.

Baserat på resultaten från denna undersökning blir slutsatsen att större uppmärksamhet bör läggas på HCN på grund av dess toxiska egenskaper i brandgaser, speciellt mot den fara som HCN potentiellt utgör tillsammans med CO.

Nyckelord: brand, HCN, CO, toxicitet, DIN-ugn

1 Introduction

Of the toxic gases generated by fire carbon monoxide (CO) has been assumed to be the greatest killer of people in connection to fires. Increasingly one has realised that other more toxic gases, which are also produced in fires, may be responsible for an unknown percentage of fire deaths due to smoke inhalation [1]. One of the most toxic gases in this context is hydrogen cyanide (HCN), which is extremely dangerous for humans to inhale. The "Immediately Dangerous to Life and Health" (IDHL) level for CO, for example, is 1200 ppm while that for HCN is 50 ppm [2].

In fires HCN is mainly produced through the combustion of nitrogen-containing materials, such as synthetic rubber, wool, nylon, polyurethane (PUR) and melamine. Numerous laboratory tests show the existence of the hydrogen cyanide in fire gases [3]. Especially, during the under-ventilated combustion and at the relatively high temperatures found in fires, large amounts of both CO and HCN may be produced. While the list above is by no means exhaustive, many of the building and lining materials and furniture used in our homes and industries include the common substances listed above. Thus many of the building and lining materials and furniture used in our homes and industries contain the potential to produce large amounts of CO and HCN in a fire.

In fires, the HCN is formed in the reaction zone from fuels containing nitrogen (N) and hydrogen (H) atoms. However, HCN may be consumed if there is sufficient oxygen in the mixture and if the temperature is sufficiently high, making further oxidation of HCN possible. This oxidation can lead to a variety of compounds including equally undesirable compounds, such as oxides of nitrogen (so called NO_x), although under ideal conditions should ultimately lead to CO_2, H_2O and N_2. Most commonly in fires, however, CO would be a major product of the oxidation of HCN.

Although HCN is a narcotic gas like CO it has been suggested that HCN is about 35 times more toxic than CO [4]. The influence of HCN on the victim is relatively quick because it is carried rapidly to the brain by blood. The most important determinant of incapacitation with HCN is the rate of uptake, which is directly related to the concentration of HCN in the air the victim is breathing. This is dealt with in more detail in the next chapter.

It has been speculated that HCN is generally not found in the blood of fire victims essentially for two reasons. The first reason is that traditionally one has concentrated on identifying and quantifying the amount of CO in the blood of fire victims. Thus, this may be a case of not having found HCN because it has not been looked for. In the literature there is ample evidence available that shows a wide variation in the concentration of carboxyhaemoglobin (COHb) necessary to cause death. Thus, the amount of COHb claimed to be responsible for the death of fire victims may range from 30% to 70% [5, 6]. This would indicate that in at least some cases where COHb has been assigned the cause of death there might well have been other important contributing factors.

The second reason is that the mode of action of HCN is different to that of CO. As HCN does not follow Habers rule [5] very low concentrations are actually required to prompt a toxic reaction. This toxic reaction will generally not be death but unconsciousness. The person effected would essentially be unable to escape from the scene of the fire and would continue to breath, thereby inhaling increasing amount of CO and possibly eventually actually die from CO inhalation. Technically speaking the cause of death may well be CO poisoning but arguably had the person not been incapacitated by the HCN in the first place then they could have escaped from the fire and avoided the CO poisoning.

Thus, the death has been reported to be poisoning due to CO even though the real reason to the death could be the incapacitation due to HCN.

A potent modern day example of the importance of fire gases in causing the death of fire victims is the Gothenburg Disco fire in 1998. In this fire most of the 63 victims died due to toxic gases and not due to heat from fire. The fuel in this fire consisted of material that could potentially generate large amounts of HCN. Indeed, the report from this incident indicates that HCN was an important factor in the fatalities [7].

This study does not intend to consider the full range of material combinations prevalent in an enclosure fire. Nor does it intend to consider real scale product or full room fire tests. Rather this study intends to establish the importance of HCN emissions relative to CO emissions from a series of materials commonly used either as building material or in the production of e. g. upholstered furniture used in domestic applications. Thus a series of small scale tests have been conducted on five types of material chosen firstly for the presence of nitrogen in their chemical structure and secondly for their relevance as material present in domestic applications.

The specific materials included in this study were: wool, nylon, synthetic rubber, melamine and polyurethane-foam. None of the materials were combustion modified through the use of a flame retardant additive. The first four materials were compact, with approximately the same intrinsic density, while the fifth material (a foam) had a significantly lower density. This lead to the use of a lower weight of the fifth material in the laboratory tests. The reason for the choice of this low-density material was two-fold. Availability was a factor in the choice of material in all cases and the low-density polyurethane foam was readily available. Secondly, polyurethane foam is a common product in upholstered furniture – an important source of emissions in domestic fires.

As the aim is to investigate the importance of HCN emissions relative to CO emissions it was determined to conduct bench scale laboratory tests. The specific test method chosen was the DIN 53436 tube furnace. In these tests the generation rate of HCN and CO from the combustion of the 5 selected fuels at two ventilation rates (100 mg fuel / l air, and 400 mg/l) was studied for up to three different temperatures (350 °C, 650 °C and 900 °C). The selection of the ventilation rates and temperatures was based on both the ISO 9122-1 standard defining different types of burning behaviour and experience from other research projects [8, 9]. The aim was to establish the product distribution behaviour for these materials both under well-ventilated and poorly ventilated conditions in the presence of flaming and non-flaming conditions. In all cases (with the exception of the polyurethane foam) it was possible to obtain flaming burning conditions with combustion of all combustible material under well-ventilated conditions at the two highest selected temperatures. Further no major difference was seen between the results obtained for these two temperatures. For a variety of reasons that are discussed in more detail in Chapter 4 this was not possible in all cases to conduct the full experimental series at the lowest temperature. Thus, in the case of the vitiated experiments it was determined that only one of the two highest temperatures would be run and the lowest temperature would be eliminated.

The reason to focus on HCN is clear. It is important as a potential killer or escape inhibitor in fires but as we presently lack a concrete comparison between the CO producing potential of common material relative to their HCN producing potential it has been difficult to establish the relative importance of HCN compared to that of CO. This is of particular importance as we become more acquainted with computer modelling using, for example, Computational Fluid Dynamics (CFD). In recent years it has become more common to use CFD methods to model fire behaviour in complicated situations as an alternative to time consuming and costly experiments. In recognition of the importance of CO, production models have been developed to calculate the production of CO as the fire being modelled develops. This study has, therefore, also been conceived to determine whether calculation of the production of CO using CFD is sufficient to establish the toxic hazard posed by any given enclosure fire, or whether it is necessary to model other species, such as HCN, as well.

As a starting point for this study a literature study has been conducted to establish what has been done previously in this field. The results of this work are summarised in Chapter 2. This includes a description of the toxic behaviour of both CO and HCN. The specific fire experiments conducted in this study, to investigate the relative importance of CO and HCN, are described in Chapter 3 and the results reported in Chapter 4. A final discussion of the results and conclusions of this study are presented in Chapter 5 with suggestions for future work summarized in Chapter 6.

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2 Literature survey

2.1 Previous toxicity studies

A large body of information is available in the literature concerning the toxicity of CO in fires. In fact, many fire deaths are attributed to CO poisoning. We have not attempted to cover all available data but have focused on reviewing a small number of treatises on this topic that have themselves reviewed previous data [1-3]. It is clear from this work that CO is without doubt one of the most important acute toxicants produced in fire gases. As most material present in our work and domestic environments is organically based, and fires generally produce large amounts of CO, it will remain an important species from a toxicological point of view. This work does not aim to contend this.

There is, however, a growing body of evidence that suggests that while CO may often be sufficient to account for fire fatalities it is not generally working alone. A variety of species are being considered in models that have been developed in the past 5-10 years aimed at defining which species contribute to the toxicity of fire gases and to which degree [4-6]. Indeed, there is some human evidence that in cases where nitrogen containing organic material is burning (such as with upholstered furniture or mattresses made of polyurethane) HCN poisoning is an important factor in fire deaths [7].

Human data is abundant for CO, both from fire and non-fire victims. The carboxyhaemoglobin content in the blood of fire victims is often determined in order to establish cause of death. This information provides a body of data important in establishing our knowledge of the acute toxicity of CO. A description of the mechanism of the toxicity of CO is summarized in section 2.1.1 together with the relevant reference material.

In contrast human data is difficult to obtain for HCN. This is due to the fact that while fire victims have often been tested for COHb content in their blood the HCN content has generally not been investigated. This is exacerbated by the fact that HCN is released from blood after death. Thus, it is generally necessary to rely on animal data. A description of the mechanism of HCN toxicity is summarized in 2.1.2.

The relative toxicity of CO and HCN and their action together is discussed in section 2.1.3. Finally, a presentation is made of selected modern experimental data that is available concerning the relative production of CO and HCN from fires in section 2.2.

2.1.1 Toxicity of CO

Under optimal conditions haemoglobin in the blood is used to transport oxygen to the body. This transport is essential for the life of any breathing organism. The toxicity of CO lies in that it combines with haemoglobin in the blood to form carboxyhaemoglobin (COHb).

Carbon monoxide combines preferentially with hemoglobin to produce COHb, displacing oxygen and reducing systemic arterial oxygen (O_2) content. The CO binds reversibly to hemoglobin with an affinity 200- 230 times that of oxygen [8]. Consequently, relatively minute concentrations of the gas in the environment can result in toxic concentrations in human blood. Possible mechanisms of toxicity include:

- Decrease in the oxygen carrying capacity of blood.
- Alteration of the dissociation characteristics of oxyhaemoglobin, further decreasing oxygen delivery to the tissues.
- Decrease in cellular respiration.
- Binding to myoglobin, potentially causing myocardial and skeletal muscle dysfunction.

The most clear-cut mechanism by which CO toxicity occurs is competitive binding to the hemoglobin heme groups. This effect is magnified by the allosteric properties of the hemoglobin molecule. Its tetrameric structure undergoes a conformational change when CO is bound at one of the four heme sites, with a resulting increase in the affinity of the remaining heme groups for oxygen. This not only shifts the oxygen-hemoglobin dissociation curve to the left, but also distorts its sigmoidal shape towards a hyperbola. The net result is a hemoglobin molecule that is poorly equipped to release oxygen at the tissue level. The decreased oxygen delivery is then sensed centrally, stimulating ventilatory efforts and increasing minute ventilation. The latter will increase uptake of CO and raise COHb levels, further shifting the oxygen-hemoglobin dissociation curve to the left.

Interestingly, fetal hemoglobin binds CO more avidly than hemoglobin A, and with slow transplacental transport, fetal levels decrease much more slowly than in the mother. This accounts for the occurrence of occasional fetal death in nonfatal maternal exposures [9].

Carbon monoxide combines readily with haemoglobin to form COHb and the CO is not readily released. Thus the amount of COHb increases steadily as CO is inhaled up to well defined saturation levels that depend on the concentration in the inspired air [10]. The toxicity of CO is, therefore, dependent on the accumulated dose of COHb, usually expressed as the percentage of the total haemoglobin present as COHb.

Table 1 summarizes the effects generally expected from exposure to CO. One should, however, keep in mind that it is very difficult to set exact boundaries between the various effects as while death is expected at COHb concentrations of 50-70% it can occur at much lower concentrations in susceptible subjects.

Table 1 Summary of effect of exposure to CO [11].

Concentration (% in air)	Effect
10%	Asymptomatic or may have headaches
20%	dizziness, nausea, and syncope
30%	visual disturbance
40%	confusion and syncope
50%	seizures and coma
60%	cardiopulmonary dysfunction and death

Separating out the role of CO from other toxic gases is a difficult task [2]. A study of the deaths that occurred in fire accidents during the period 1972-1977, resulted in the estimation that smoke inhalation accounted for roughly three-quarters of all fire deaths. This result was calculated by assuming that CO-poisoning was the most likely cause of death

[12]. In a previous statistical analysis [1] it has been indicated that it is, generally, unnecessary to search for any other toxicant in fire atmospheres when the COHb level lies between 20 and 50%. Thus, as the effect of other toxicants in fire atmospheres has been assumed to be very small in many cases other toxicants have not been studied. This implies that we may have traditionally attributed deaths to CO poisoning due to lack of contradictory evidence when other factors may have been important.

Factors affecting the toxic potential of CO

Traditionally, 50% COHb has been considered the threshold level for human lethality. This has often lead to the assumption that if the COHb level in the victims blood is less than 50%, CO poisoning could not have been the sole cause of death [1]. Other factors causing the death could, for instance, have been oxygen deprivation, shock, burns or other toxic gas, such as HCN [2]. A universal 50% COHb lethality threshold, however, does not exist. Nearly 20% of exposed individuals died from CO poisoning (city gas and exhaust gas) at blood COHb levels less than 50% COHb [3]. Indeed it has been proposed that any blood COHb value > 20% can produce lethality [1]. It is, however, well documented that shorter and higher CO exposures can lead to higher COHb level than longer and lower exposures. A longer exposure allows CO to penetrate more deeply into bodily processes [2]. This is illustrated in Figure 1.

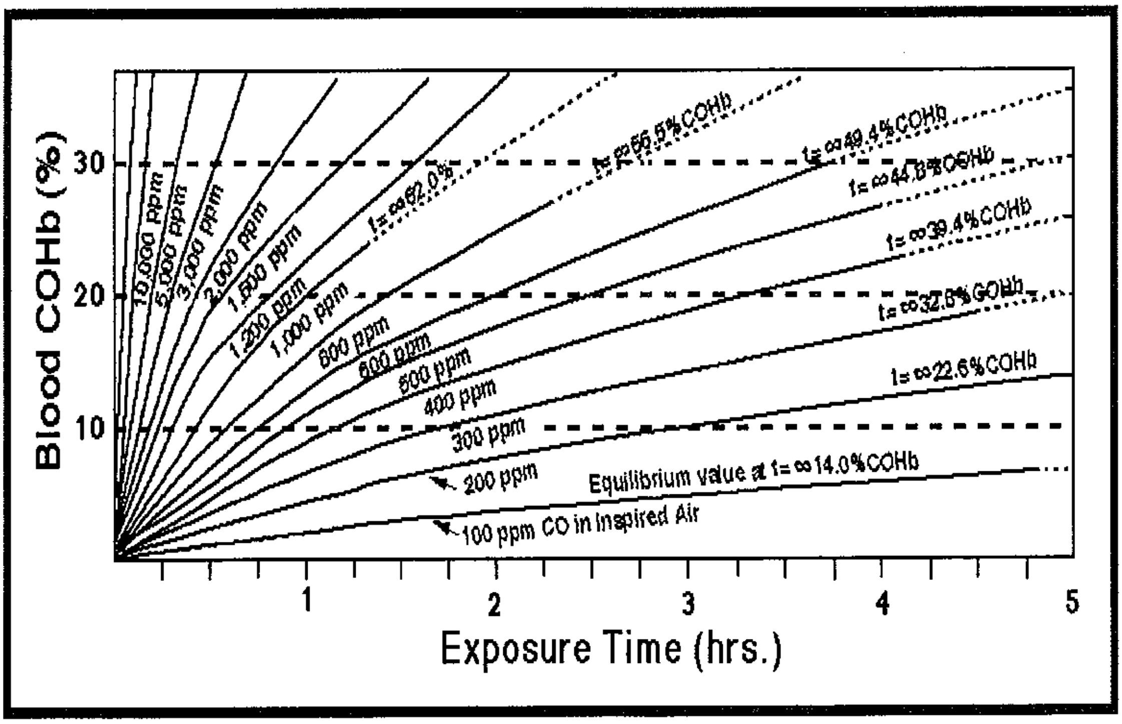


Figure 1 Uptake of CO by humans under resting conditions. COHb saturation after infinite exposure time is shown on each line. Redrawn from [10].

The lethal level of CO has a strong dependence on the characteristics of the victim (e.g., people with cardiovascular diseases are more sensitive to CO than healthy individuals [1, 3]). The most important factors, however, seem to be the age and the physical condition of the victim, although such factors as blood-alcohol levels also have an influence.

When different individuals are exposed to the same atmosphere, their COHb levels can be very different. Victims found lying next to each other can have highly varied COHb values [2]. One may survive, while the other one, for no apparent reason, dies. Survivors may have COHb levels well above 50%, while others, deceased, have well below 50% [1]. Fire victims tend to have lower COHb levels than comparable non-fire victims (i.e. gas heater exposures or suicides)[2, 3]. The lower value for fire victims may indicate that some other factor (or factors) effect fire victims. For fire victims, increased age and impairment were strongly associated with low COHb levels. Factors such as compounding toxicants have not been documented in the same detail at this point.

According to [3], alcohol use is pervasive in CO fatalities. Approximately 33% of all CO poisoning fire fatalities had blood alcohol levels above 0,05%. Approximately 28% of the victims with blood-alcohol level between 0,05% and 0,29%, had blood COHb values less than 60%. However, victims with blood-alcohol level above 0,30%, 46% had COHb values less than 60%. One can therefore conclude that low blood-alcohol levels (between 0,05% and 0,29%) increase the possibility of surviving a fire, while blood-alcohol levels above 0,30% decreases survivability. Given the diversity of the database it is, however, difficult to interpret these results as details of many contributing factors (such as age, sickness, access to escape etc) are not provided.

2.1.2 Toxicity of HCN

HCN is, despite its secondary role relative to CO, considered to be one of the most toxic gases produced in fires. It inhibits cellular oxidative processes, by inactivating cytochrome oxidase enzymes, and may slightly interfere with the binding of oxygen with haemoglobin. The gas, which has a smell of almonds, is produced when any material containing nitrogen is subjected to combustion or pyrolysis. The amount of HCN produced depends both on heating temperature and air supply, but the production is roughly proportional to the nitrogen content in the material [13].

Hydrogen cyanide is one of the most acutely toxic components of the thermal degradation products of nitrogen-containing polymeric materials. At a concentration of 300 ppm death can follow within a few minutes [14], while the concentration of CO has to be about 25 as high to kill you [15]. One toxicological study, for example, showed that deaths (of mice) would first occur when the CO concentration was about 4000 ppm [16].

Table 2 summarizes the effects generally expected from exposure to HCN. One should, however, keep in mind that it is very difficult to set exact boundaries between the various effects as various symptoms can occur at much lower concentrations in susceptible subjects.

Table 2 Summary of effect of exposure to HCN [17].

Concentration (ppm HCN in air)	Effect
10	NOAL
20-40	Slight symptoms after several hours
50-60	Max. amount that can be inhaled for up to 1 hour without serious disturbance
120-150	Dangerous in 30-60 min
3000	Rapidly fatal

Hydrogen cyanide has been found in the blood of both fatal [18] and non-fatal [19] victims. In many cases lethal COHb levels were measured in the fatal victims [18]. Thus, when discussing the toxicology of HCN, the combined effect of CO and HCN should also be considered. HCN is found frequently in blood samples from victims of fire gases, and high levels of HCN are usually present with high CO levels [2]. Although, in many cases the HCN component may have no significant effect in terms of lethality, due to its effect at low doses it may be very important for incapacitation. One should also keep in mind that it is difficult to relate blood cyanide levels from samples collected after a fire to the actual HCN exposure as the dynamics of uptake and release of HCN in the blood is not fully understood [6].

Evidence from primate experiments [20], indicate that when HCN is inhaled for short periods at air concentrations of 150-200 ppm, loss of consciousness results from a high transient plasma cyanide concentration The HCN uptake is then greatly reduced when the subject looses concentration and the cyanide plasma disperses through the bodily fluids, leaving a low immediate post-exposure blood concentration. Finally, cyanide decomposes rapidly in dead bodies [21], with an approx. half-life of 1-2 days, which further confounds the issue.

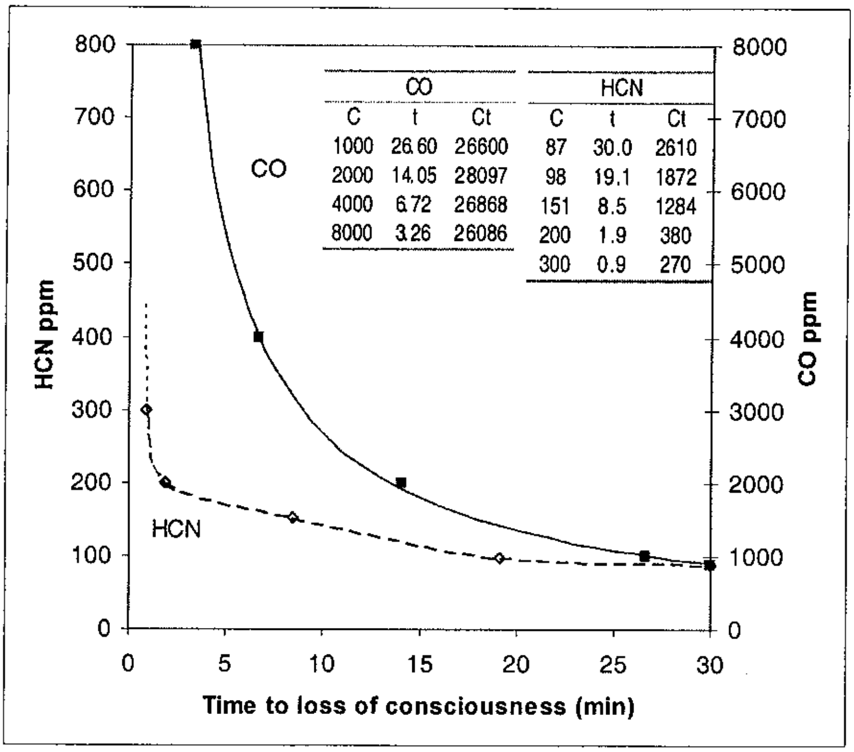
It is thought that hydrogen cyanide produces intracellular hypoxic poisoning due to the binding of the cyanide anion to the ferric iron in the mitochondial cytochrome oxidase [22]. Impaired oxidative phosphorylation results in the depletion of cellular high energy phosphate stores and lactic acidosis. The rate of cellular dysfunction and death are determined by the rate of entry of cyanide into the body. Based on this mode of toxicity the antidote for cyanide poisoning has traditionally been aimed at dissociating cyanide from the cytochrome oxidase by instilling an agent into the circulation, which has a higher affinity for cyanide than the ferric iron moiety of the oxidase. Provision of supplementary oxygen is an additional treatment [22]. Oxygen administered at ambient pressures diminishes the effect of low doses of cyanide, while hyperbaric oxygen (2,0 – 2,8 ATA) decreases the mortality from even high doses of cyanide.

2.1.3 Toxicity of HCN relative to CO

Ultimately the effect of HCN poisoning is similar to that of CO poisoning (for example both are considered narcotic toxicants causing disorientation and unconsciousness) although the pattern of toxicity in the early stages is quite different. The onset of CO poisoning is slow and insidious while that of HCN poisoning may be rapid and dramatic with unconsciousness resulting [6]. This seems to be due to the occurrence of a period of hyperventilation at some time within a 30 minutes exposure to even relatively low concentrations of HCN (80 ppm). The hyperventilation effectively increases the actual HCN exposure resulting in unconsciousness within 1 to 5 minutes. In the case of primate experiments it was seen that after the period of hyperventilation, and ensuing unconsciousness, the rate of ventilation decreased which lead to a slowing of the demise of the creature (see the discussion in Section 2.1.2).

On theoretical grounds little interaction is expected between CO and HCN. CO diminishes the carriage of oxygen in the blood and its delivery to the tissues, while HCN diminishes the ability to use the oxygen once it is delivered to the tissue [6]. One would, therefore, expect that one or the other of these gases would constitute the rate limiting step depending on their relative concentrations. The consensus view is, however, that there is some additive effect between these two gases. Experiments in primates [23], indicate that the time to incapacitation by HCN is slightly reduced by the presence of near toxic concentrations of CO. Similarly, the rate of uptake of CO may be increased by the hyperventilatory effect of HCN. In general it may be best to assume that these two species are additive in terms of toxic effect in order to avoid underestimating their combined effect.

In evaluating the relative importance of the toxicity of HCN and CO in fire gases one must consider the relative time/concentration behavior of the two species. In the case of CO the time/concentration behavior follows Habers rule. This implies that a small increase in the concentration of CO leads to a small decrease in the time to incapacitation. In the case of HCN this behavior is not seen. A small increase in the concentration of HCN causes a large decrease in the time to incapacitation for the victim. This is illustrated for primates in Figure 2. This behavior is one possible explanation for the relative importance of HCN in incapacitation of fire victims. The disproportionately large effect of low doses of HCN would explain their rapid influence. The state of unconsciousness this low concentration effect induces would allow the victim to remain alive in the fire environment – alive but unable to leave the fire scene unassisted.



CO			HCN		
C	t	Ct	C	t	Ct
1000	26.60	26600	87	30.0	2610
2000	14.05	28097	98	19.1	1872
4000	6.72	26868	151	8.5	1284
8000	3.26	26086	200	1.9	380
			300	0.9	270

Figure 2 *Comparison of the relationship between time to incapacitation and concentration for HCN and CO exposures in primate's [6].*

2.2 Experimental emissions studies

Once again this work is intended to provide an understanding of the state of the art of emissions studies concerning the evolution of toxic species such as CO and HCN from fires. The references are by no means exhaustive as the literature concerning emissions of CO from fires is prolific. In the case of HCN emissions far less work has been done but the available emissions data in the literature is too extensive to review fully here.

Numerous studies have been made regarding at which temperature HCN starts to develop, and how the production depends on the atmosphere (i.e. the pyrolysis conditions) [13, 14, 16, 23, 24]. The combustion atmosphere does not effect the initial production of HCN significantly [14]. HCN is produced both under flaming and non-flaming conditions. In the majority of experiments, however, flaming condition produced higher concentrations of HCN. These results can be understood by considering fundamental combustion mechanisms for the production of HCN from fuel bound nitrogen [25, 26]. HCN is produced in the early stages of combustion of fuel containing nitrogen. Under conditions with ample oxygen availability this HCN is converted to NO_x or N_2, depending on the temperature and other parameters. Under conditions with poor oxygen availability, such as in vitiated fires, this conversion may not take place.

Thus, HCN probably develops early in a fire, as the fire grows one would expect the importance of HCN to decrease as the concentration of CO produced increases. As the fire approaches flashover and becomes vitiated the concentration of HCN may increase again but at this stage the CO production is significant and it probably represents the greatest risk. There is evidence in the literature that different building practice and dwelling tradition in different countries affects the potential for harm in pre- or post-flashover fires.

According to one part of the literature [13], lethality from smoke inhalation is less frequent in pre-flashover fires, fire deaths from smoke inhalation occur predominantly after the fires have progressed beyond flashover. Based in part on these results it has been stated that the toxicants produced at or after flashover are most lethal [15]. US fire statistics show that 69% of all fire deaths are associated with post-flashover fires, with the vast majority of deaths occurring outside the room of fire origin. Such statistics are, however, highly dependent on national traits, e.g., whether it is customary or not to keep doors closed within the dwelling unit [27]. In the UK, for instance, fatal fires are much more likely to be confined to the room of origin, since it is much more common to keep the doors closed between rooms in a dwelling [15]. One should also consider that post-flashover fires are generally large fires and therefore often represent a greater risk than the small fires. Small fires can, however, represent a great risk (as seen in the UK) if they are sufficiently vitiated and therefore produce significant amounts of toxic species per g burned material.

A number of large research projects investigating the combustion behavior of furniture have established that the production of HCN from polyurethane foam in furniture represents a significant risk [28, 29]. This work, together with medical reports from furniture and mattress fires [7, 30-32] confirms the importance of the emission of HCN on the incapacitation and possible death of fire victims.

The concentration of CO in ventilation controlled post-flashover fires is determined by oxygen availability (ventilation), mass loading and geometrical variables, but is largely unaffected by the chemical composition of the fuel [23]. However, during the early stages of a room fire (before flash over), the CO yield in the room fire depends a great deal on the chemistry of the fuel being burned, and therefore on the material itself. The yield will be similar to those seen in various small-scale tests. This is not surprising, since a small room fire can be of the same scale as the burning specimen in a small-scale test. For greater burning rates in the room fire (as the fuel/air ratio increases), however, the CO yield tends to become independent of the chemical nature of the fuel being burned, and only being dependent on the global equivalence ratio (φ) [23], defined as below:

$$\text{Global equivalence ratio} = \varphi = ((\text{kg fuel})/(\text{kg air}))/((\text{kg fuel})/(\text{kg air}))_{\text{stoich}},$$

where "stoich" indicates the stoichiometric fuel:air ratio. A global equivalence ratio that is <1 implies that the combustion process is fuel lean (more oxygen present than is needed for a complete combustion), whiles an equivalence ratio that is >1 implies that the combustion process is fuel rich (less oxygen present than required for stoichiometric combustion). When the fire reaches this size (ventilation controlled, post-flashover fires), small-scale tests no longer may predict CO yields. This means that the results from the small scale tests cannot be used to predict toxic fire hazard for ventilation controlled post-flashover fires, unless CO yields are calculated by analogy with full scale fire test results [1].

2.3 References

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3 Experimental Description

3.1 Test apparatus

The test apparatus used was a *DIN-furnace*, as described in *DIN 53 436* [1]. This furnace was connected to a *FTIR* instrument: *BOMEM MB 100* equipped with a *DTGS* detector. The gas cell in the FTIR was an *Infrared Analysis M-38H-NK AU.* The program used for the analysis was *GRAMS/386 v 3.01b (Galactic Industries Corporation).*

To ensure that the correct air -flow was maintained, a mass digital flow meter was connected to the system before the air entered the DIN furnace. A filter was attached immediately after the DIN furnace to remove particles as these could disturb the FTIR analysis. This filter was heated to 180 °C to eliminate condensation of water out of the fire gases before they were transported to the FTIR for analysis. A second pump was used to transport the fire gases to the analysis equipment. A schematic representation of the experimental apparatus is shown in Figure 3.

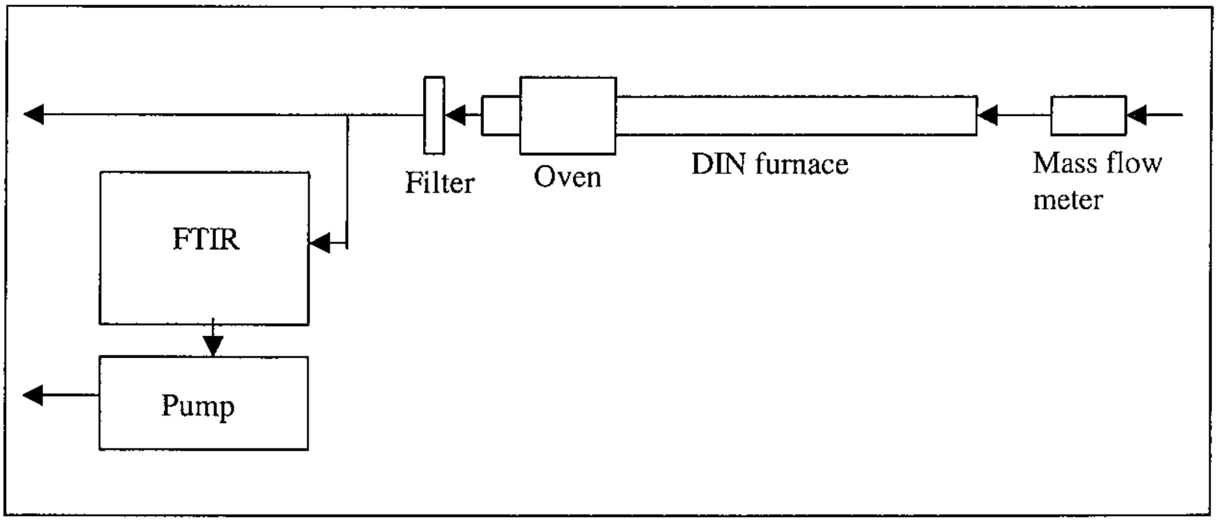

Figure 3 Schematic representation of experimental apparatus.

The most important parameters defining the FTIR instrument used in these experiments are summarised in Table 3.

Table 3 Important parameters defining the FTIR instrument used in these experiments.

Gas Cell		**Spectrometer**	
Path length	4,8 m	Spectrometer type	Bomem MB100
Path length range	0,4-8,0 m	Resolution	4 cm^{-1}
Gas cell volume	0,922 l	Resolution range	1-128 cm^{-1}
Window type	KBr	Detector	DTGS
Working temp.	150 °C	Wavenumber range	6000-350 cm^{-1}
Temp. Range	≤ 200 °C	Apodization	cosine
Thermocouple pos.	Internal	Number of scans	3
Heating device	Heating jacket	Scan time	3 s
Working pressure	≈ 1 atm	Measurement interval	15 s

3.2 Test method

The test method used was a modified version of the DIN 53 436 standard [1]. The method was modified to satisfy the relationship between the sample mass and the airflow specified in Table 4. The calibration procedure and the equipment used were those prescribed in DIN 53 436.

The airflow was 2.5 l/min (150 l/h), of which 2.0 l/min were transported to the FTIR analysis equipment using a pump. The product gases were transported from the DIN-furnace to the FTIR in a heated sampling tube maintained at 150 °C. The temperature in the gas cell in the FTIR was also maintained at 150 °C in accordance with recommendations for use of FTIR in fire experiments obtained from the SAFIR project [2].

The aim of these experiments was to investigate the effect of degree of ventilation and the type of combustion, on the product distribution from the chosen products. Thus, based on ISO 9122:1 and experience of using the DIN oven in tests run for the TOXFIRE project [3] it was determined that well-ventilated combustion would be best represented using an air flow rate relative to sample loading of 100 mg sample/l air. Similarly, vitiated conditions were modelling using a loading of 400 mg sample/l air. Flaming combustion was determined probable at a temperature of 650 °C and certain at 900 °C (provided sufficient oxygen is available). Non-flaming combustion was determined probable at 350 °C. Thus, these 3 temperatures were selected for the test series. As seen in the results described in Chapter 4, all three temperatures were not viable for all tests. This is discussed in more detail in the next chapter.

The motivation for this choice of parameters was that in a real fire it goes through several stages where the relative importance of CO and HCN would be expected to vary. By selecting one set of parameters we would be effectively studying only one stage during a fire. In the initial stages of a fire one would expect temperatures to be low and ventilation to be good. As the fire progresses it will pass through a stage where the temperature is high but the ventilation is still good. A high temperature and poor ventilation best represent the next stage, while the final stage is best represented by a low temperature and poor ventilation. By investigating various combinations of temperature and ventilation we hope to cover all of these stages in the fire development.

Those tests specified as 400 mg/l air the amount of oxygen in the gas flow was reduced using nitrogen, instead of increasing the weight of the sample. The air was diluted to a concentration of oxygen four times smaller (5%) than in air. The gas used in the test specified as 100 mg/l air was pure air, no nitrogen was added. The length of the sample was 20 cm, since the speed of the oven is 1 cm/min and that it was assumed that 20 min would be sufficient when trying to reach a steady state. Due to the airflow, the sampling time, the length of the sample, and the specified relation 100 mg/l air, the sample weight was determined as 5.00 g. The width of the sample was 1.5 cm. The height of the samples varied due to the varying densities of the samples.

Exceptions from the procedure were the PUR-material, and when the experiment had to be stopped due to low pressure in the FTIR analysis cell. Due to its low density, the PUR sample had to be very large if 5.00 g was to be used. This was solved by reducing the weight and reducing the concentration of oxygen to reach the specified 100 mg/l air. The amount of sample was 1.25 g and the concentration of air was 5%. To obtain the specified 400 mg/l air, the oxygen concentration had to be reduced to 1.25% using nitrogen gas, rather than increasing the weight of the sample.

Soot was retained in the filter during the experiments, resulting in a pressure drop. When this pressure drop was too large, i.e., when the pressure reached approximately 850 Pa, the accuracy of the analysis results was reduced. A large pressure drop was avoided by reducing the weight of some samples. The specific experimental start conditions for each experiment are summarised in Table 4.

Table 4 Weight of samples used in the experiments.

	Material	**Temperature (°C)**	**Weight of sample (g)**
100 mg/l	Nylon	All temps.	5.00 g
	Wool	All temps.	5.00 g
	Melamine	All temps.	5.00 g
	Synthetic rubber	650	2.50 g
	Synthetic rubber	900	5.00 g
	PUR	350	0.50 g
	PUR	650 and 900	1.25 g
400 mg/l	Nylon	650	5.00 g
	Wool	650	5.00 g
	Melamine	650	2.50 g
	Synthetic rubber	650	2.50 g
	PUR	650	1.25 g

3.3 Test procedure

Before the test was started, a nitrogen gas flow of 2 l/min was started streaming through the FTIR cell for some minutes, to ensure that the cell did not contain any contaminants from previous experiments. The gas flow through the system was started and controlled with the mass flow meter. The oven was started, and when the temperature specified for the experiment was reached, the pump was started, and connected to the quartz tube when the pump flow had been controlled. The heater for the filter was started and set to 180 °C. The sample was placed on the sample boat, 10.0 cm from the end of the boat closest to the oven, and then inserted in the quartz tube. The boat was placed with its front edge in line with the edge of the furnace. When the heater for the filter had reached 180 °C, the oven and the FTIR analysis program were started. The experiment continued until the sample was fully combusted and the analysis results had reached a stable value near its starting values, or, when no fully developed combustion occurred, the oven had fully passed the sample in the boat. When the stop criteria had been reached, the FTIR program was turned off and the oven was turned off and returned to its start position. The pump was turned off and the nitrogen gas was connected to the FTIR gas cell. The nitrogen gas flow was maintained for a further 5 minutes. The heater to the filter was turned off. The airflow was maintained until the quartz tube had reached a temperature so that the sample boat could be removed from the oven and the remains of the sample could be weighed. All experimental results are summarised in the next chapter.

3.4 References

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4 Results

The total amount of combustion gases produced was calculated from the time when the amount of combustion gases began to increase and had passed the detection limit. The approximate detection limits for the various species studied in this project are summarised in Table 5. Generally, this was after about 10 minutes, when the oven reached the specimen. All the analysis results collected thereafter were used in the yield calculations, including the results collected after the sample was totally combusted. This was due to the fact that combustion gases could remain in the DIN furnace despite the cessation of combustion, on their way to the FTIR, and therefore had not been analysed.

Table 5 Detection limits for various species measured using FTIR.

Species	**Detection limit (ppm)**
CO	10
HCN	2
NH_3	2
SO_2	2
NO	10
NO_2	2

The figures in this chapter show the time period where the produced amounts of combustion gases were calculated. The combustion gases shown in each figure are not the only gases that were detected during the experiments. The reason for not showing the analysis results for all of the gases is that some spectra were severely compromised by the disturbance of other interfering species.

During some of the experiments, a yellow deposition was found on the inside of the quartz tube behind the oven, sometimes followed by a decrease in the quantity of some of the gases being analysed. Whether the decrease in concentration was due to the formation of the deposition or due to reaction kinetics is not known. This question could have been addressed by analysing the chemical composition of the deposition, but due to the limitations of this project this was not done. In light of the fact that the aim of the experiments is to establish some guidelines concerning the relative importance of HCN production relative to that of CO it was not deemed necessary to resolve this issue. Should more quantitative information be required it would be advisable to use a different experimental set up to avoid the production of this deposition in the first place.

The amount of material combusted in the well-ventilated experiments in summarised in Table 6, while the amount of material combusted in the vitiated experiments is summarised in Table 7.

Table 6 Amount of material combusted in each of the well ventilated experiments, i.e. corresponding to a sample amount relative to air flow of 100 mg/l air flow.

Material	**Temperature (°C)**	**Before (g)**	**After (g)**	**Combusted (g)**
Nylon	350	4,99	4,64	0,35
	650	5,03	0,00	5,03
	900	5,00	0,00	5,00
Wool	350	4,98	2,63	2,35
	650	5,02	0,11	4,91
	900	4,98	0,03	4,95
Melamine	350	5,00	1,51	3,49
	650	5,00	0,24	4,76
	900	5,00	0,03	4,97
Synthetic rubber	650	2,52	0,15	2,37
	650	5,03	1,04	3,99
	900	5,04	0,54	4,50
PUR	350	0,52	0,30	0,22
	650	1,25	0,00	1,25
	900	1,27	0,07	1,20

Table 7 Amount of material combusted in each of the vitiated experiments, i.e. corresponding to a sample amount relative to air flow of 400 mg/l air flow.

Material	**Temperature (°C)**	**Before (g)**	**After (g)**	**Combusted (g)**
Nylon	650	5,03	0,05	4,98
Wool	650	5,01	0,75	4,26
Melamine	650	2,51	0,03	2,48
Synthetic rubber	650	2,41	1,07	1,34
PUR	650	1,29	0,33	0,96

The yields of the various combustion products studied using the FTIR in the well-ventilated experiments are summarised in Table 8, while the yields of the various combustion products studied using the FTIR in the vitiated experiments are summarised in Table 9.

Table 8 Yield 100 mg/l air flow (g product/g sample combusted).

Material		**350 °C**	**650 °C**	**900 °C**
Wool	CO	0.013 g/g	0.064 g/g	0.0006 g/g
	HCN	0.018 g/g	0.006 g/g	0.00004 g/g
	NH_3	0.039 g/g	0.001 g/g	0.00003 g/g
	SO_2	0.016 g/g	0.030 g/g	0.032 g/g
	NO	-	0.003 g/g	0.0035 g/g
	NO_2	-	0.001 g/g	0.0001 g/g
Nylon	CO	0.012 g/g	0.03 g/g	0.031 g/g
	HCN	-	0.005 g/g	0.011 g/g
	NH_3	0.081 g/g	0.001 g/g	0.001 g/g
	SO_2	0.005 g/g	0.001 g/g	-
	NO_2	0.004 g/g	-	-
Synthetic rubber	CO	-	0.134 g/g	0.027 g/g
	NH_3	-	0.0005 g/g	0.0005 g/g
	SO_2	-	0.017 g/g	0.015 g/g
	NO	-	0.007 g/g	0.003 g/g
	NO_2	-	0.001 g/g	0.0004 g/g
Melamine	NH_3	0.002 g/g	0.017 g/g	0.017 g/g
	HCN	-	0.001 g/g	0.033 g/g
PUR-foam	CO	0.012 g/g	0.895 g/g	0.002 g/g
	HCN	-	0.003 g/g	0.0001 g/g
	NH_3	-	0.001 g/g	0.0002 g/g
	SO_2	0.025 g/g	-	-
	NO	-	-	0.011 g/g
	NO_2	0.004 g/g	0.002 g/g	-

Table 9 Yield (g product/g sample combusted) 100 mg /l air flow and 400 mg/ l air flow at 650 °C.

Material		**100 mg/litre air**	**400 mg/litre air**
Wool	CO	0.064 g/g	0.044 g/g
	HCN	0.006 g/g	0.023 g/g
	NH_3	0.001 g/g	0.022 g/g
	SO_2	0.030 g/g	0.012 g/g
	NO	0.003 g/g	-
	NO_2	0.001 g/g	-
Nylon	CO	0.03 g/g	0.172 g/g
	HCN	0.005 g/g	0.018 g/g
	NH_3	0.0001 g/g	-
	SO_2	0.0001 g/g	-
	NO_2	-	0.004 g/g
Synthetic Rubber	CO	0.134 g/g	0.171 g/g
	HCN	-	0.010 g/g
	NH_3	0.0005 g/g	0.006 g/g
	SO_2	0.017 g/g	0.020 g/g
	NO	0.007 g/g	-
	NO_2	0.001 g/g	0.005 g/g
Melamine	HCN	0.001 g/g	0.001 g/g
	NH_3	0.017 g/g	0.023 g/g
PUR-foam	CO	0.895 g/g	0.881 g/g
	HCN	0.003 g/g	0.001 g/g
	NH_3	0.001 g/g	0.001 g/g
	SO_2	-	0.025 g/g
	NO	-	-
	NO_2	0.002 g/g	0.004 g/g

The individual results for each material are presented in the following sections.

4.1 Polyurethane

Due to the low density of PUR, the weight of the sample and the oxygen concentration had to be scaled down by a factor 4 reduce the volume of the sample. Since both the material and the oxygen amount were diminished by the same factor, the defined ratio between oxygen and was nominally equivalent to the other experiments. Examination of the ratio between CO_2 and CO, however, shows that even in the case of well-ventilated combustion a large proportion of the combustion products were not fully oxidised. The well-ventilated and vitiated experiments are presented separately.

4.1.1 Well-ventilated experiments

The amount of material combusted in the well-ventilated experiments for each temperature studied is summarised in Table 10. The specific species concentrations for each experiment are then summarised for each temperature individually.

Table 10 Amount of PUR combusted in each of the well-ventilated PUR experiments.

Temperature (°C)	Before (g)	After (g)	Combusted (g)
350	0,52	0,30	0,22
650	1,25	0,00	1,25
900	1,27	0,07	1,20

Well- ventilated, 350 °C

No fully developed fire occurred during the experiment. The sample turned black and reduced in size, but no flaming combustion was observed. As seen in Table 10, only 0.22 g was actually combusted. It should be noted, however, that the experiment was stopped after 27 minutes due to a very low pressure in the FTIR cell due to soot blockage of the filter. The yields of the various species measured are summarised in Table 11. Note that no detectable HCN was found.

Table 11 Yield (g produced/ g sample combusted) of CO, SO_2 and NO_2 from PUR combusted at 350 °C.

CO	0.012 g/g
SO_2	0.011 g/g
NO_2	0.002 g/g

The species production profiles are summarised in Appendix 1. These figures illustrate the fact that a period of steady state combustion behaviour was established for approximately 10 minutes, with the production of minimal amounts of the species measured. Towards the end of the experiment some increased combustion is seen probably due to the fact that the furnace had largely passed the sample and a slight increase in the oxygen availability was seen. This could have been compounded by the increase in the surface area at this point due to exposure of the end of the sample to the heat from the furnace.

Well- ventilated, 650 °C

No flaming combustion occurred during the experiment. The sample first turned black, and thereafter turned into white ash. The yields of the various species measured are summarised in Table 12.

Table 12 Yield (g produced/ g sample combusted) of CO, HCN, NH_3 and NO_2 from PUR combusted at 650 °C.

CO	0.895 g/g
HCN	0.003 g/g
NH_3	0.002 g/g
NO_2	0.002 g/g

The species production profiles are summarised in Appendix 1. These figures illustrate the fact that a period of steady state combustion behaviour was established for approximately 20 minutes, as desired.

Large amounts of both CO and HCN are produced in the experiment.

Well- ventilated, 900 °C

The results from this experiment indicate that only very small amounts of products of incomplete combustion were formed. Neither CO nor HCN were formed to any large degree as shown in Table 13. Thus in the case of a well-developed fire (i.e., high temperature) with ample supply of oxygen optimal combustion conditions are approached and CO and HCN are both oxidised. In the case of CO the main product will be CO_2 whereas in the case of HCN the products will include H_2O, CO_2 and oxides of nitrogen. This is seen by the production of a higher concentration of NO in this experiment relative to the previous experiment and the stable and high production of CO_2.

These conditions probably do not mirror typical conditions in a fire. In the case of a high temperature one would expect to have vitiated conditions. The yields of the various species detected are summarised in Table 13.

Table 13 Yield (g produced/ g sample combusted) of CO, HCN, NH_3 and NO from PUR combusted at 900 °C.

CO	0.002 g/g
HCN	0.0001 g/g
NH_3	0.0003 g/g
NO	0.01 g/g

4.1.2 Vitiated experiments

In all cases only one vitiated experiment was conducted at 650 °C per material. This temperature was chosen as it gave the most stable behaviour in the case of the well-ventilated experiments. Unfortunately, no flaming combustion was observed. The sample melted and started to boil, giving off small clouds of gases. The amount of material combusted is summarised in Table 14.

Table 14 Amount of PUR combusted in the vitiated experiment.

Temperature (°C)	**Before (g)**	**After (g)**	**Combusted (g)**
650	1,29	0,33	0,96

The yields of the various species measured in this experiment are summarised in Table 15. This shows that while substantial amounts of CO were produced only small quantities of HCN were produced. Thus, one would expect that under vitiated conditions in the fire gases one should be in most danger from the concentration of CO.

Table 15 Yield (g produced/ g sample combusted) of CO, HCN, NH_3, SO_2 and NO_2 from PUR combusted at 650 °C.

CO	0.881 g/g
HCN	0.001 g/g
NH_3	0.001 g/g
SO_2	0.011 g/g
NO_2	0.002 g/g

The breathing behaviour observed is seen in the shape of the curves summarised in Appendix 1. This behaviour is not unusual in vitiated fires due to the low oxygen availability. The behaviour is a reflection of the build up of pyrolysis gases that ignite and use up the available oxygen. When the oxygen is sufficiently depleted the combustion ceases as new pyrolysis gases build up while oxygen levels are also replenished. This cycle of depletion and replenishment is repeated as long as fuel remains.

Large amounts of both CO and HCN are produced in the experiment.

4.2 Nylon

4.2.1 Well-ventilated experiments

The amount of material combusted in the well-ventilated Nylon experiments is summarised in Table 16. Flaming combustion occurred at 650 °C and 900 °C, with full combustion of the Nylon present. In the case of 350 °C, however, no ignition of the sample occurred with a very small reduction in the weight of the sample in the experiment.

Table 16 Amount of Nylon combusted in the well-ventilated experiment.

Material	Temperature (°C)	Before (g)	After (g)	Combusted (g)
Nylon	350	4,99	4,64	0,35
	650	5,03	0,00	5,03
	900	5,00	0,00	5,00

Well-ventilated, 350 °C

No flaming combustion occurred during this test, i.e., the sample did not ignite. The sample melted, forming a hard, thick deposit in the sample boat. The weight loss, as seen in Table 16, was low during this experiment. The yields of the various species quantified in the experiment are summarised in Table 17. Note that no detectable HCN was found.

Table 17 Yield (g produced/ g sample combusted) of CO, NH_3, SO_2 and NO_2 from Nylon combusted at 350 °C.

CO	0.012 g/g
NH_3	0.133 g/g
SO_2	0.002 g/g
NO_2	0.003 g/g

The species profiles are summarised in Appendix 1. These figures illustrate the fact that a period of steady state was established for approximately 20 minutes (between 28 to 48 minutes).

Well-ventilated, 650 °C

In contrast to the previous experiment this sample was fully combusted during the experiment (see Table 16). The fire behaviour during this experiment varied. When the furnace reached the sample it began to burn, although the combustion diminished shortly afterwards due to charring of the sample with cessation of the flame resulting. This flaming/non-flaming behaviour was witnessed on at least two occasions as seen in the species concentration profiles (see Appendix 1). Further the flame spread was prone to be faster than the progression of the furnace. This has no doubt contributed to the unsteady behaviour of the species profiles.

Table 18 Yield (g produced/ g sample combusted) of CO, HCN, NH_3, and SO_2 from Nylon combusted at 650 °C.

CO	0.03 g/g
HCN	0.005 g/g
NH_3	0.0011 g/g
SO_2	0.0005 g/g

Large amounts of both CO and HCN are produced in the experiment.

Well-ventilated, 900 °C
As in the previous experiment this sample was fully combusted. The flame moved along the sample faster than the progression of the furnace. Therefore the behaviour of the fire was not constant during the experiment. This behaviour is shown in the species concentration profiles (see Appendix 1).

The yields of the various species quantified in this experiment are summarised in Table 19.

Table 19 Yield (g produced/ g sample combusted) of CO, HCN, and NH_3 from Nylon combusted at 900 °C.

CO	0.031 g/g
HCN	0.011 g/g
NH_3	0.002 g/g

Large amounts of both CO and HCN are produced in the experiment.

4.2.2 Vitiated experiments

Vitiated, 650 °C
No flaming combustion was observed. The sample melted and boiled, periodically giving off small clouds of smoke as described for the vitiated PUR experiment. When the experiment was finished, the sample had been totally transformed into ash. The amount of material combusted in this experiment is summarised in Table 20. The yield of the various species quantified in this experiment are summarised in Table 21.

Table 20 Amount of Nylon combusted in the vitiated experiment.

Temperature (°C)	Before (g)	After (g)	Combusted (g)
650	5,03	0,05	4,98

Table 21 Yield (g produced/ g sample combusted) of CO, HCN, and NO_2 from Nylon combusted at 650 °C.

CO	0.172 g/g
HCN	0.018 g/g
NO_2	0.002 g/g

The concentration verses time curves for CO and NO_2 show that approximately steady state was maintained throughout the majority of the experiment (see Appendix 1). This behaviour was accompanied by the production of large amounts of CO and HCN (see Appendix 1). The results for the concentration of HCN should be seen as semi-quantitative as the concentration of HCN was outside of the calibrated range of the spectrometer. This meant that in such cases it was necessary to extrapolate well outside of the known range of the instrument. To diminish this error, these peaks were set to zero. In any case this behaviour indicates that large amounts of HCN were produced in this experiment.

Large amounts of both CO and HCN are produced in the experiment.

4.3 Melamine

Only ammonia and hydrogen cyanide were detected during these experiments. Since the amount of carbon dioxide detected was at the background level, and that no carbon monoxide above the detection limit was detected, very little oxidative combustion seems to have taken place. This could also be concluded from the observations made during the experiments. No flaming combustion was observed. Instead the material was vaporised or seemed to sublime before it entered the oven and condensed on the inside of the quartz tube after the furnace or on the filter. The condensed material was not analysed. As very little CO was detected it is reasonable to assume that the HCN detected represents the most important acute toxicological hazard from melamine combusted under these conditions.

4.3.1 Well-ventilated experiments

The amount of material combusted in each of the three well-ventilated Melamine experiments is summarised in Table 22.

Table 22 Amount of Melamine combusted in the well-ventilated experiments.

Temperature (°C)	Before (g)	After (g)	Combusted (g)
350	5,00	1,51	3,49
650	5,00	0,24	4,76
900	5,00	0,03	4,97

Well-ventilated, 350 °C

No flaming combustion was observed in this experiment. A white aerosol was emitted from the melamine. Directly after the furnace, the aerosol crystallised, and a white powder was formed on the bottom of the quartz tube. The yield of NH_3 is summarised in Table 23. The NH_3 concentration profile is shown in Appendix 1.

Table 23 Yield (g produced/ g sample combusted) of NH_3 from Melamine combusted at 350 °C.

NH_3	0.002 g/g

Well-ventilated, 650 °C

No flaming combustion was observed in this experiment. The sample melted and boiled and a yellow deposit was formed about 10 cm behind the furnace. The yield of NH_3 and HCN is summarised in Table 24. The species concentration profiles verses time for NH_3 and HCN are shown in Appendix 1. Apart from an initial burst of HCN at the start of the experiment steady state seems to have been established throughout much of the experiment.

Table 24 Yield (g produced/ g sample combusted) of NH_3 and HCN from Melamine combusted at 650 °C.

NH_3	0.026 g/g
HCN	0.001 g/g

Well-ventilated, 900 °C

No flaming combustion was observed in this experiment. The sample melted and boiled and white gas was formed which left a yellow deposit. A lot of condensation was formed after the furnace, forming a yellow and green deposit on the inside of the quartz tube. The yield of NH_3 is summarised in Table 25. The species concentration profile verses time for NH_3 and HCN are shown in Appendix 1. The steady nature of the curve indicates that steady state was established for approximately 20 minutes.

Table 25 Yield (g produced/ g sample combusted) from Melamine combusted at 900 °C.

NH_3	0.017 g/g
HCN	0.033 g/g

4.3.2 Vitiated experiment

No flaming combustion was observed. A white aerosol was formed inside the furnace, with the deposition of a yellow green powder after the furnace, inside of the tube. The amount of Melamine combusted is summarised in
Table *26*.

Table 26 Amount of Melamine combusted in the vitiated experiment.

Temperature (°C)	**Before (g)**	**After (g)**	**Combusted (g)**
650	2,51	0,03	2,48

The yield of NH_3 and HCN from this experiment is summarised in Table 28. The concentration verses time profiles are summarised in Appendix 1. As was the case in the well-ventilated experiment conducted at 650 °C, inspection of the curves shows that apart from an initial burst of HCN the species production is stable. This indicates that a quasi-steady state was established for approximately 20 minutes (between 15-45 minutes).

Table 28 Yield (g produced/ g sample combusted) of NH_3 and HCN from Melamine combusted at 650 °C.

NH_3	0.037 g/g
HCN	0.001 g/g

4.4 Wool

4.4.1 Well-ventilated experiments

The amount of material combusted in the well-ventilated Wool experiments is summarised in Table 29. Flaming combustion was noted for 650 °C and 900 °C but not at 350 °C. A yellow gas was emitted at 350 °C and 650 °C, but not at 900 °C. After the experiments at 650 °C and 900 °C, the remains consisted of ash, but after the one at 350 °C the sample was essentially intact.

Table 29 Amount of Wool combusted in the well-ventilated experiments.

Temperature (°C)	Before (g)	After (g)	Combusted (g)
350	4,98	2,63	2,35
650	5,02	0,11	4,91
900	4,98	0,03	4,95

Well-ventilated, 350 °C

No flaming combustion occurred during this experiment. Yellow smoke was released 20 minutes after the experiment had been started. The sample was essentially unchanged after completion of the experiment, except that the sample had melted at the end that first entered the furnace and a cavity had been formed inside the sample due to gas emissions.

The yield of the various species quantified in this experiment are summarised in Table 30. The species concentration verses time profiles are shown in Appendix 1. From these figures it is apparent that a steady state period was established for approximately 15 minutes (between 24 and 39 minutes).

Table 30 Yield (g produced/ g sample combusted) of CO, HCN, NH_3 and SO_2 from Wool combusted at 350 °C.

CO	0.013 g/g
HCN	0.018 g/g
NH_3	0.064 g/g
SO_2	0.007 g/g

Large amounts of both CO and HCN are produced in the experiment.

Well-ventilated, 650 °C

Flaming combustion was observed. A yellow gas was emitted, and the sample started to melt, before flaming combustion began. When flaming combustion began, the yellow gas disappeared. As this gas was seen throughout the previous experiment, where no flaming appeared, it is assumed that this contains pyrolysis products that are then removed through oxidative combustion.

The yield of the various species quantified in this experiment is summarised in Table 31. The concentration verses time profiles for these species are shown in Appendix 1. From these figures one can see that apart from some boundary effects (with an initial burst of some species at the beginning and/or end of the experiment) a period of steady state seems to have been established (between approximately 20-35 minutes).

Well-ventilated, 650 °C
The fire behaviour varied during this experiment. The sample swelled before it ignited, producing large amounts of CO, then self-extinguished. This cycle was repeated three times. Between the three cycles the sample glowed, and at the end of the experiment the sample had turned to ash.

The yield of the various species quantified in this experiment are summarised in Table 36. The concentration verses time profiles for the various species are shown in Appendix 1. As can be seen in these figures no steady state behaviour could be established. This is due to the cyclic nature of the combustion behaviour of this material under these conditions.

Table 36 Yield (g produced/ g sample combusted) of CO, NH_3, SO_2, NO and NO_2 from Synthetic Rubber combusted at 650 °C.

CO	0.134 g/g
NH_3	0.001 g/g
SO_2	0.008 g/g
NO	0.006 g/g
NO_2	0.001 g/g
HCN	0.002 g/g

Well-ventilated, 900 °C
As in the case of the previous experiment the fire behaviour this experiment was unstable. The flame front was moving along the sample in front of the oven. Due to this, the fire was extinguished, and ignited, several times.

The yield of the various species quantified in this experiment are summarised in Table 37. The concentration verses time profiles for the various species are shown in Appendix 1. As can be seen in these figures no steady state behaviour could be established. This is due to the cyclic nature of the combustion behaviour of this material under these conditions.

Table 37 Yield (g produced/ g sample combusted) of CO, NH_3, SO_2, NO and NO_2 from Synthetic Rubber combusted at 900 °C.

CO	0.027 g/g
NH_3	0.001 g/g
SO_2	0.007 g/g
NO	0.003 g/g
NO_2	0.0002 g/g
HCN	0.006 g/g

4.5.2 Vitiated experiments

No flaming combustion was observed. The sample swelled with the emission of small clouds of smoke. The amount of material combusted in this experiment is summarised in Table 39.

The yield of various species quantified in this experiment is summarised in Table 40. The concentration verses time profiles are summarised in Appendix 1. Inspection of the curves shows that the species production is reasonably stable. This indicates that a steady state was established for approximately 15 minutes (between 15-30 minutes).

Table 39 Amount of Synthetic Rubber combusted in the vitiated experiment.

Temperature (°C)	**Before (g)**	**After (g)**	**Combusted (g)**
650	2,41	1,07	1,34

Table 40 Yield (g produced/ g sample combusted) of CO, HCN, NH_3, SO_2 and NO_2 from Synthetic Rubber combusted at 650 °C.

CO	0.171 g/g
HCN	0.011 g/g
NH_3	0.010 g/g
SO_2	0.009 g/g
NO_2	0.003 g/g

Large amounts of both CO and HCN are produced in the experiment.

5 Discussion and Conclusion

A literature study has been conducted into the present state of the art concerning the most probable cause of death for victims of fatal fires. It is concluded that insufficient data is available concerning HCN concentrations in fire victims to rule out HCN poisoning as a compounding factor, together with CO poisoning, in the fire fatalities investigated. Indeed, in those cases where HCN measurements have been made these have often been sufficiently high to hamper egress of fire victims, and in some cases to be fatal.

Further, a pilot laboratory investigation has been made using a selection of nitrogen containing material commonly found in domestic environments: wool, nylon, synthetic rubber, melamine and polyurethane-foam. The aim of this investigation was to obtain an indication of under which conditions one would expect these materials to emit both CO and HCN in a fire. In this context both non-flaming (i.e., pyrolysing) conditions and flaming (i.e., fire) conditions were studied.

The laboratory experiments showed that all materials tested readily gave rise to HCN. While the results of these bench scale experiments cannot readily be extrapolated to large-scale behaviour they do indicate that under pyrolysing conditions and in the presence of restricted oxygen availability one should expect significant amounts of HCN and CO. As HCN is approximately 35 times as acutely toxic as CO this would imply that HCN might be an important factor in reducing the ability of fire victims to leave the scene of the fire.

Based on the results of this study it has been concluded that greater attention should be paid to HCN as an incapacitating agent and potentially as a cause of death in fires, together with CO.

6 Future Work

The results show the question of formation of HCN in fires is complicated. We know that materials containing nitrogen in their chemical structure will generate HCN and under which conditions; but, are we able to say which materials we should avoid in particular buildings? In real room fire situations, the emission of HCN is largely dependent on the combustion behaviour, ventilation factor and how the fuel is available to burn.

In a previous BRANDFORSK project (project number 607 971) the detailed chemistry concerning about 2000 elementary reaction steps including more than 100 components, was used successively together with a CFD program (SOFIE) to model the production of CO in an enclosure fire [1]. The results of this project shows that even very complicated chemical models can be used together with CFD models, provided one applies the right techniques. The technique used in the previous project focuses on the 10 most important species and forms a flamelet library.

In the same way, detailed flamelet chemistry calculations may be performed for HCN chemistry. The existing chemical reaction scheme for heptane can be used with additional reactions involving the nitrogen (N) for HCN formation and destruction. The calculation of flamelet profiles for HCN could then be conducted in the same manner as those for CO. The distribution of HCN in the fire room and to surrounding compartments could then be mapped using the same CFD technique used previously.

Based on the results of this project it is important to extend the CFD work conducted in the previous BRANDFORSK project modelling CO to include the production and destruction of HCN. A series of CFD calculations including flamelet modelling of HCN and CO together with appropriate validation experiments would provide a basis for fire risk modelling using toxicity and fire egress models that goes beyond what has been done previously.

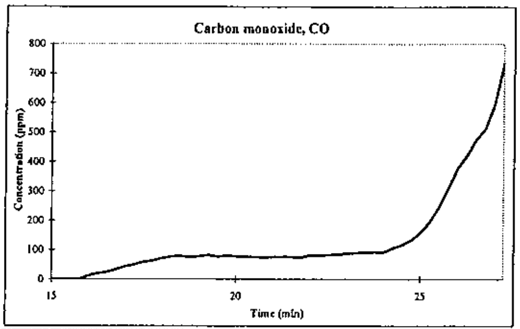
6.1 References

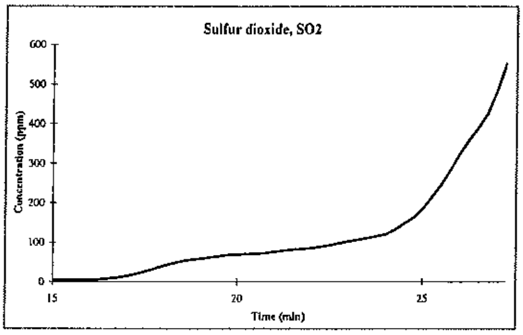
[1] Tuovinen, H. and Simonson, M., "Incorporation of Detailed Chemistry into CFD Modeling of Compartment Fires", SP-Report 1999:03 (1999).

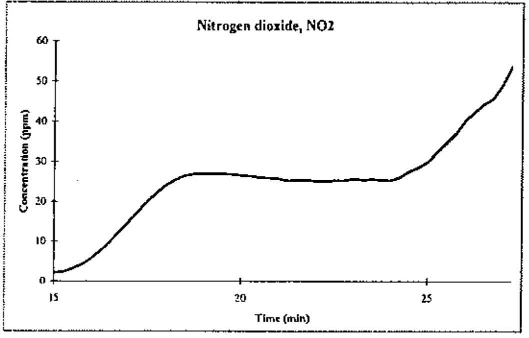
Appendix 1: Time resolved species profiles from DIN-furnace experiments.

Polyurethane Foam

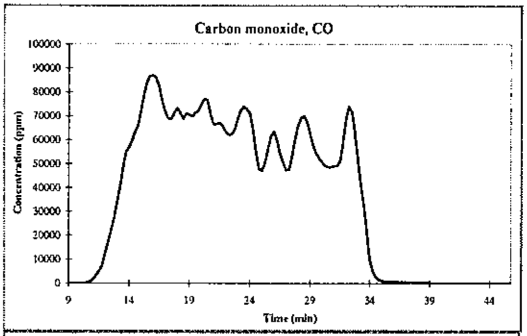
Well-ventilated, 350 °C

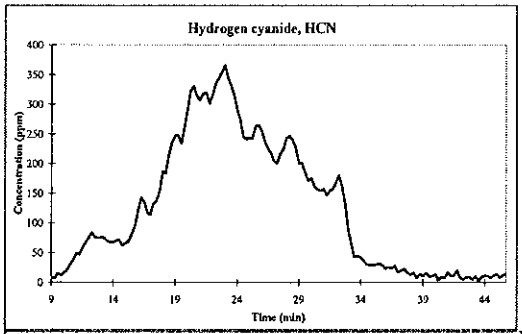


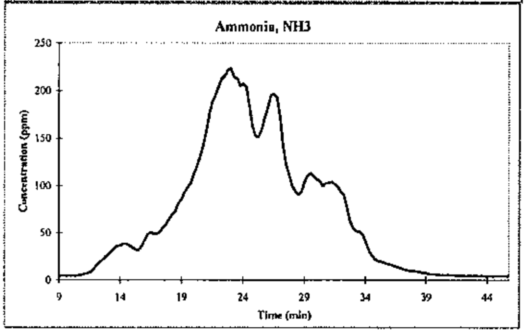


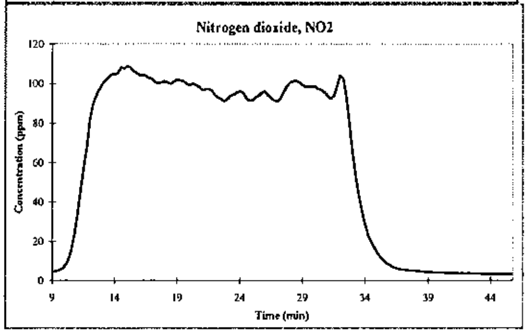


Well-ventilated, 650 °C

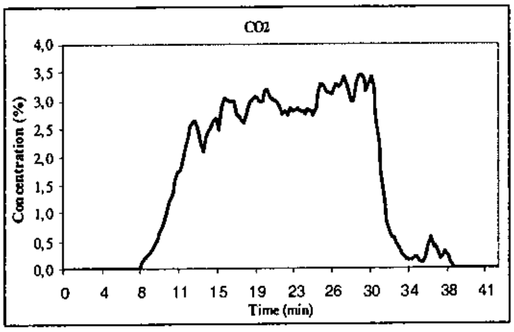


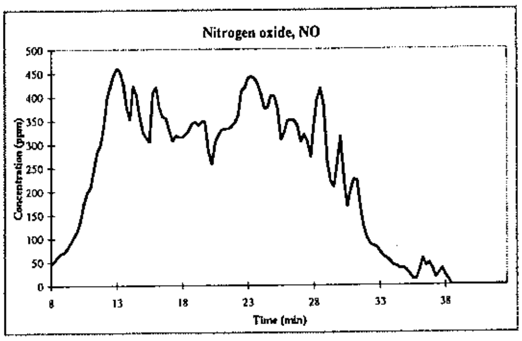




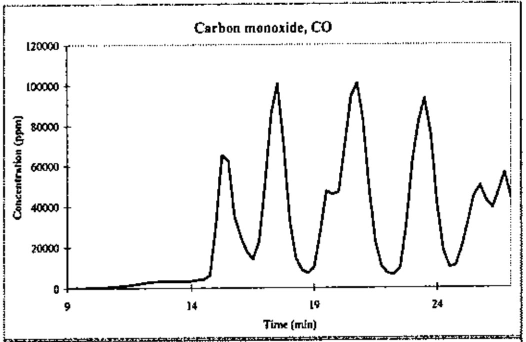


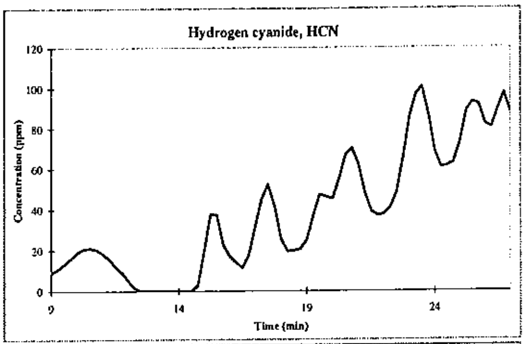
Well-ventilated, 900 °C

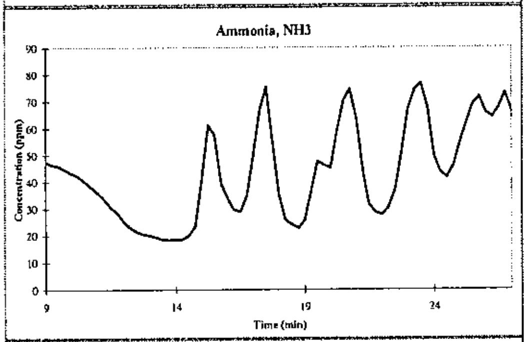


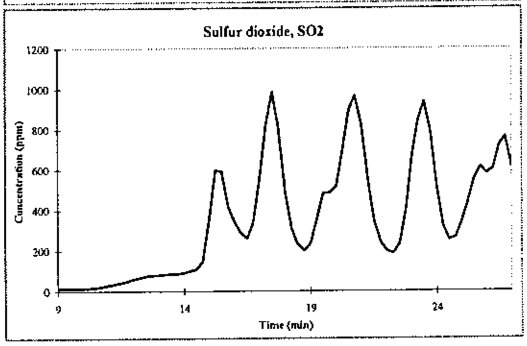


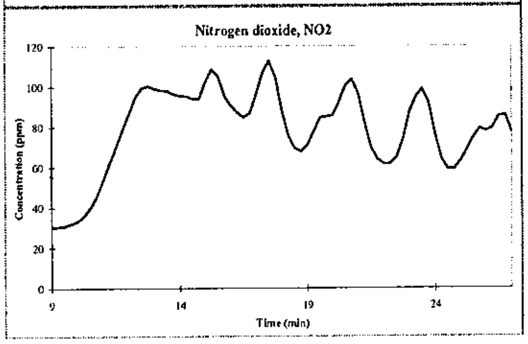
Vitiated, 650 °C





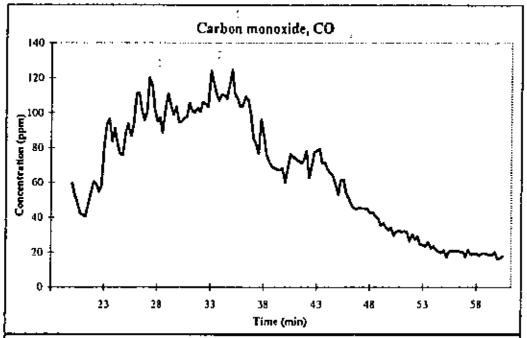


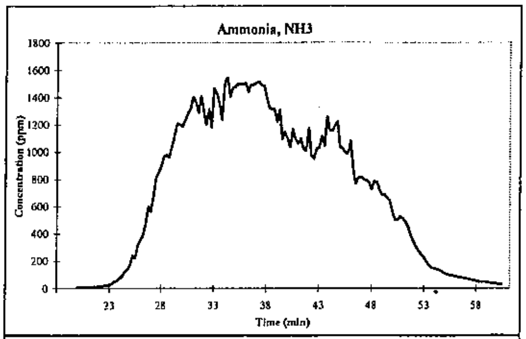


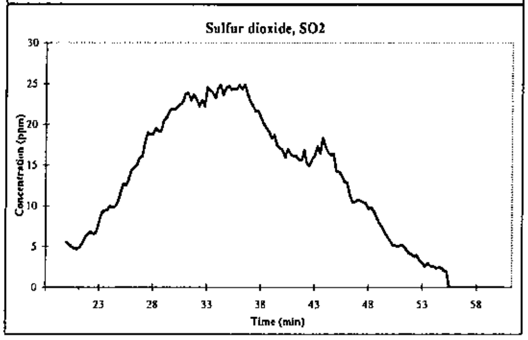


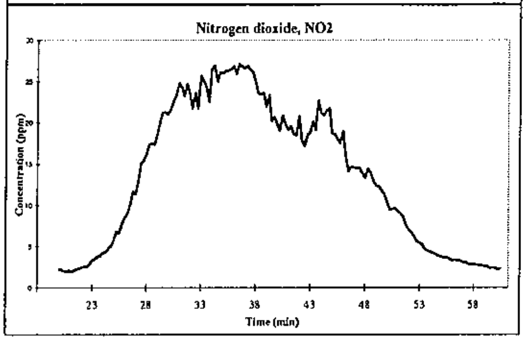
Nylon

Well-ventilated, 350 °C

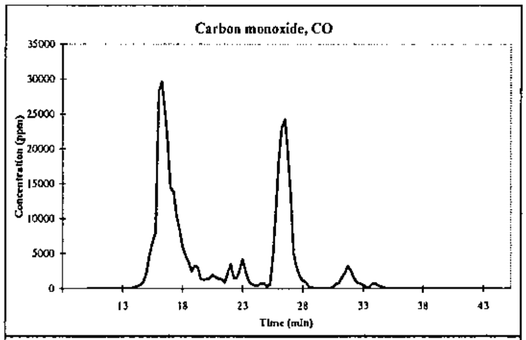


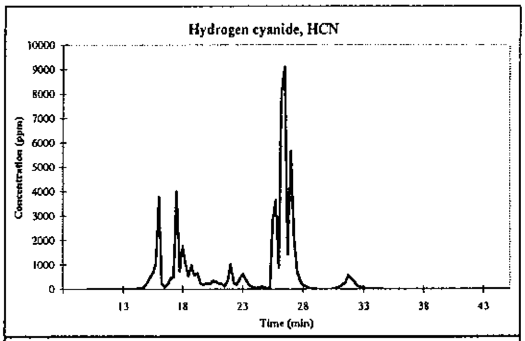


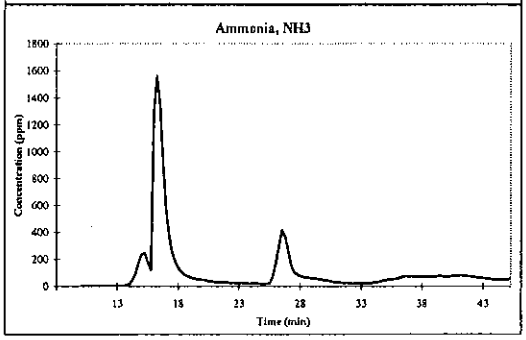


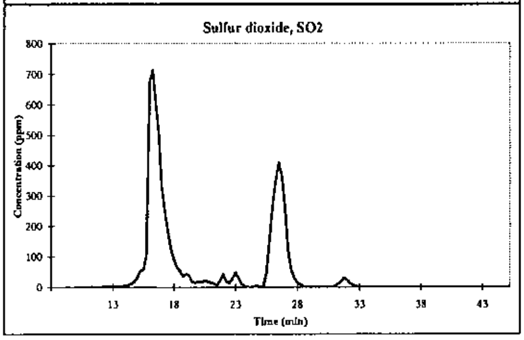


Well-ventilated, 650 °C

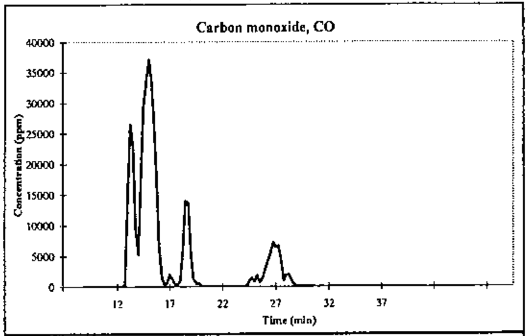


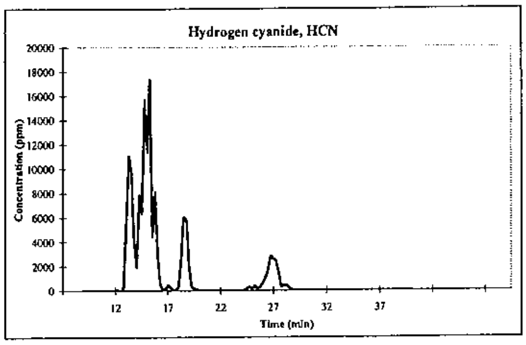


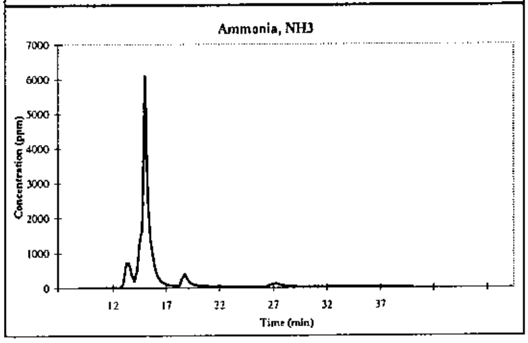




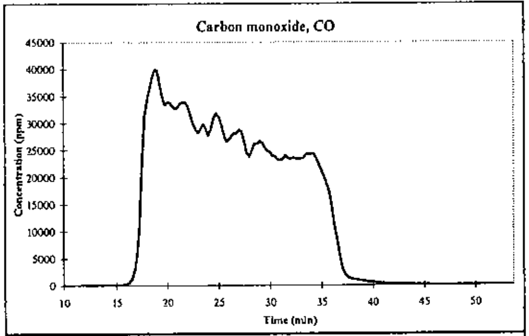
Well-ventilated, 900 °C

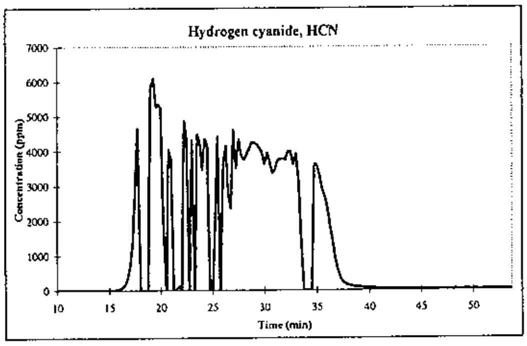


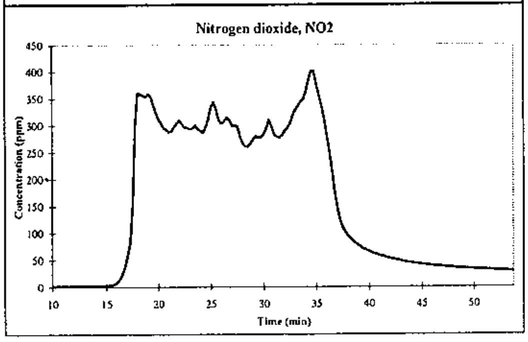




Vitiated, 650 °C

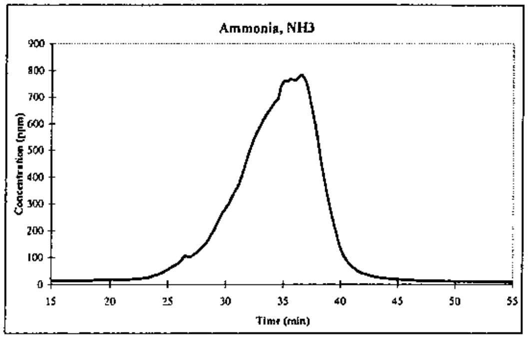




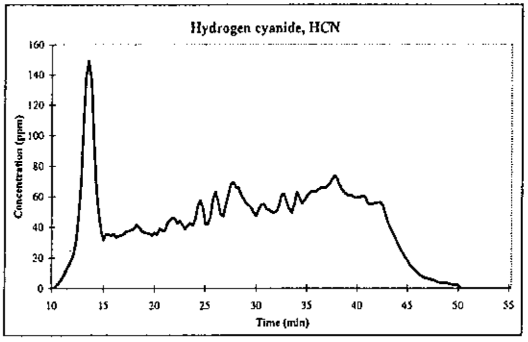


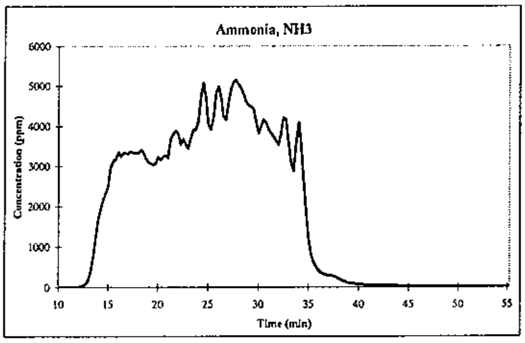
Melamine

Well-ventilated, 350 °C

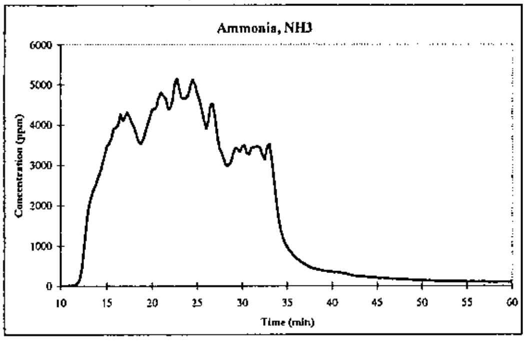


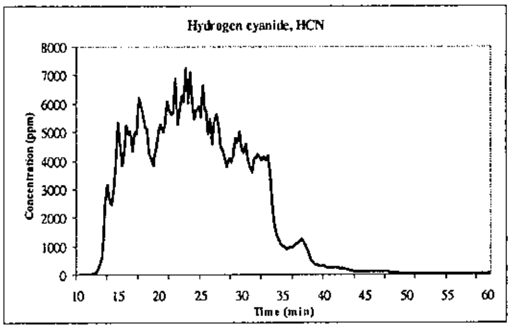
Well-ventilated, 650 °C



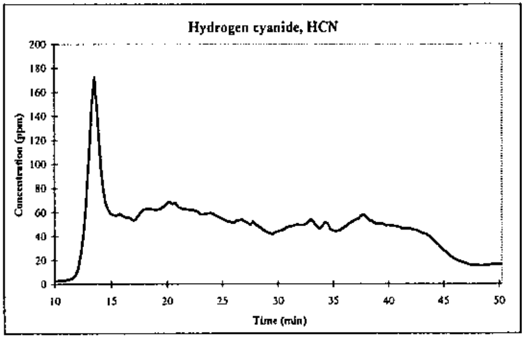


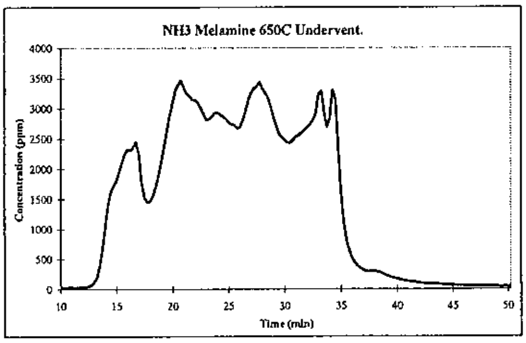
Well-ventilated, 900 °C





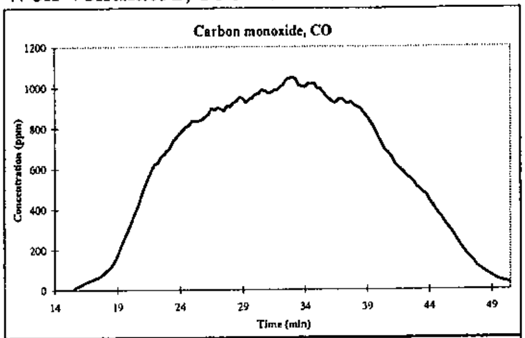
Vitiated, 650 °C

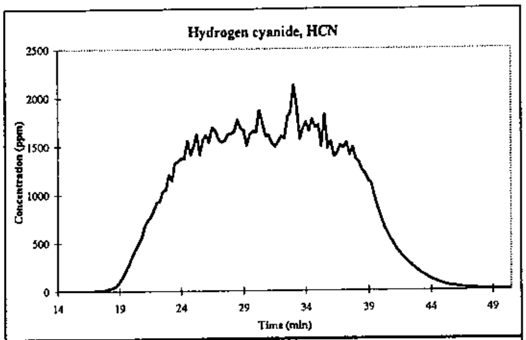


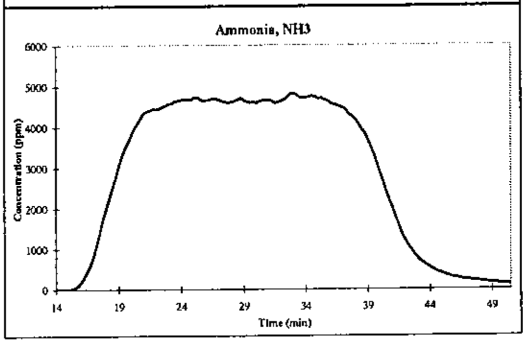


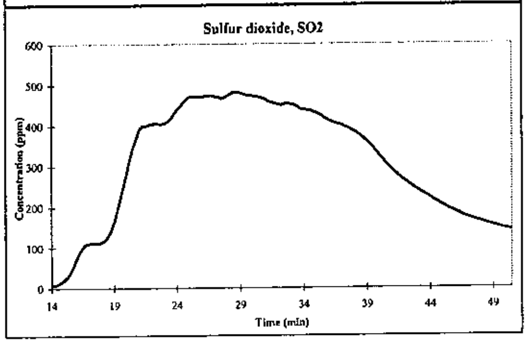
Wool

Well-ventilated, 350 °C

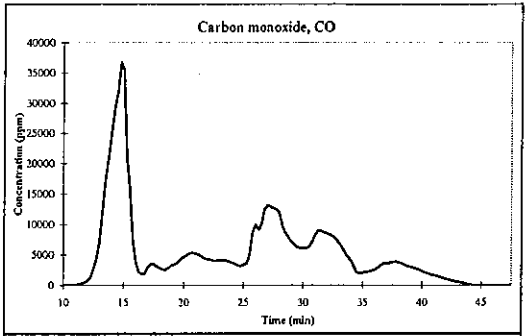


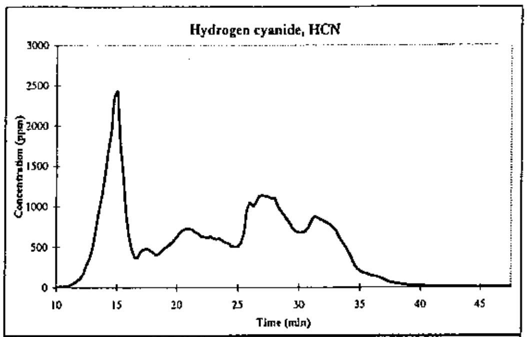


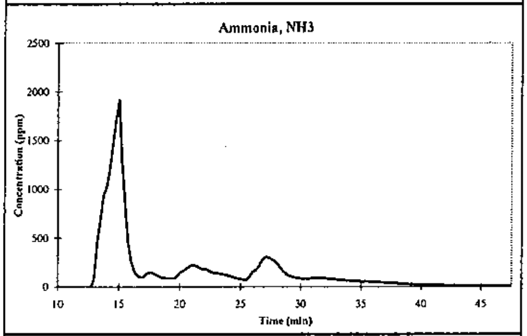


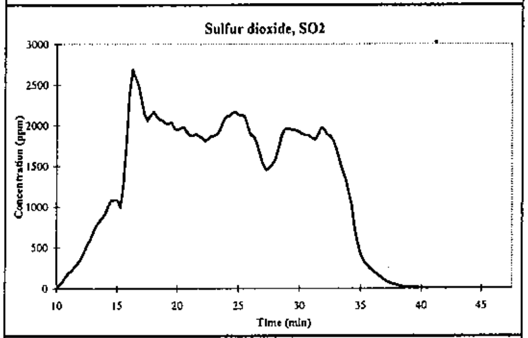


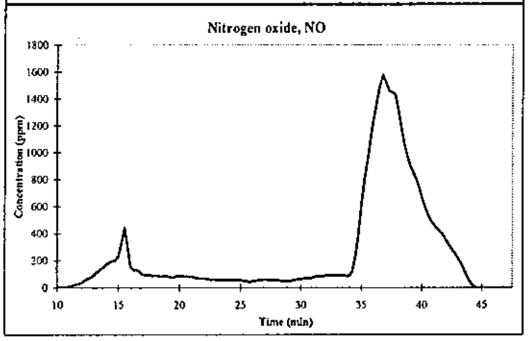
Well-ventilated, 650 °C

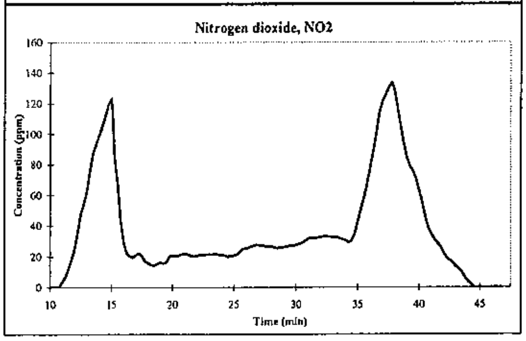




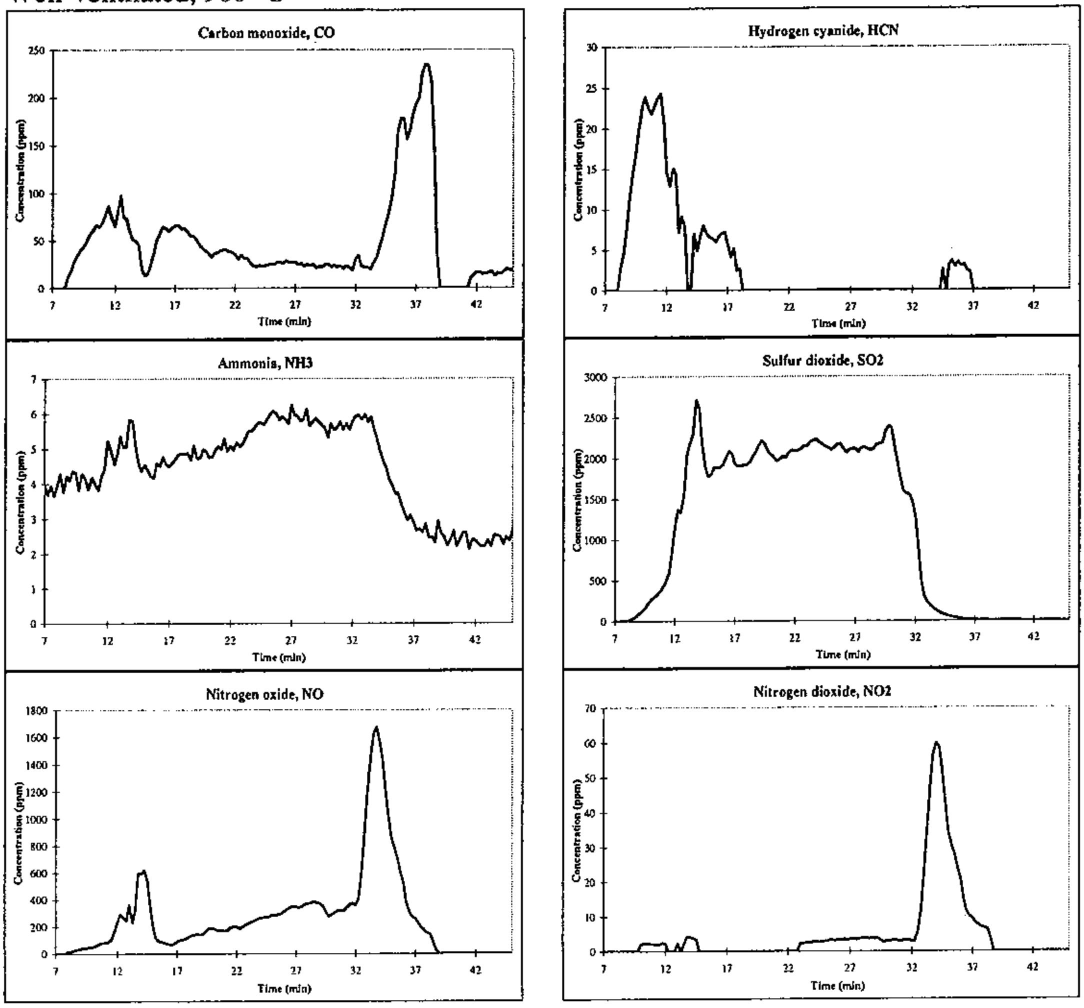




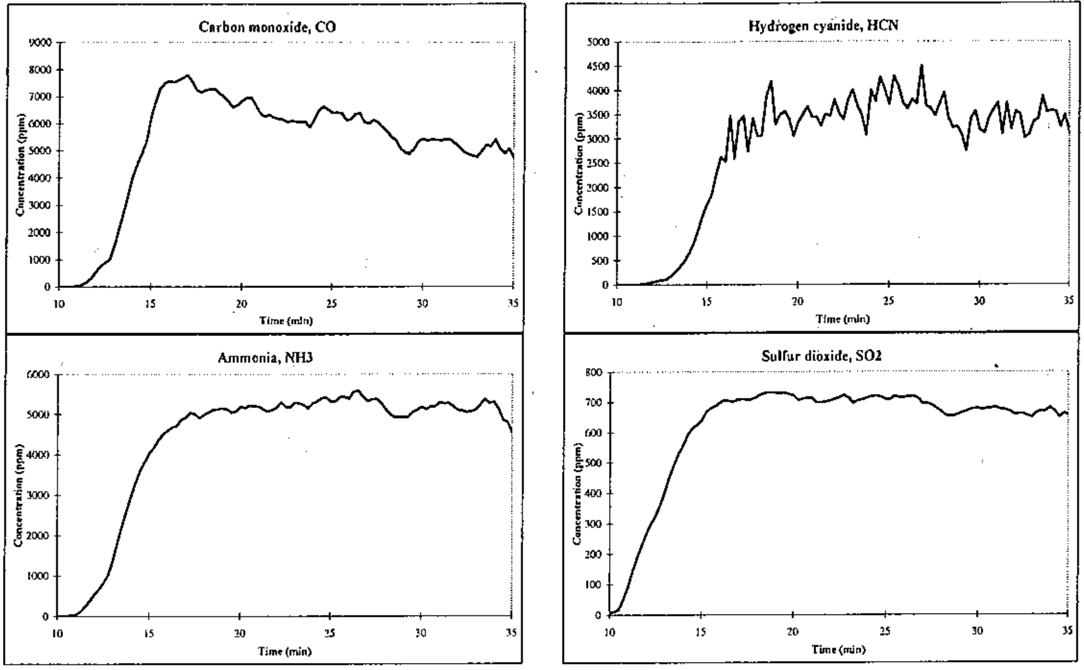




Well-ventilated, 900 °C

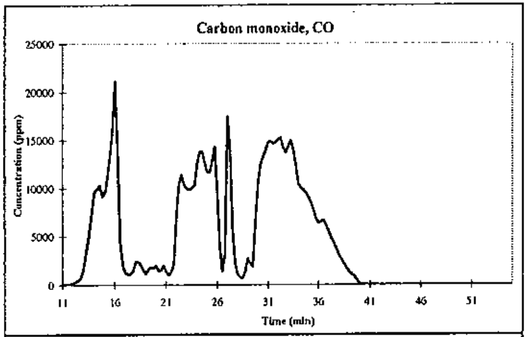


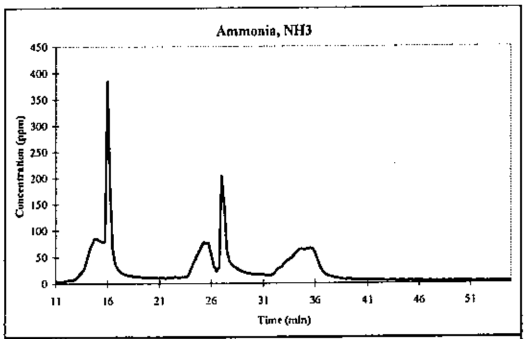
Vitiated, 650 °C

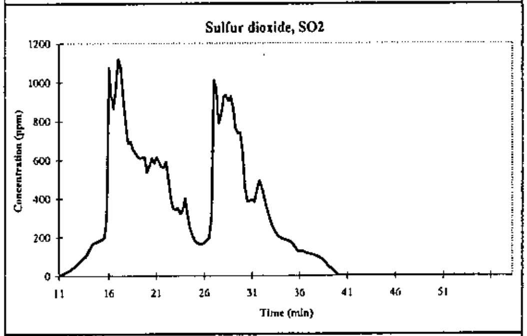


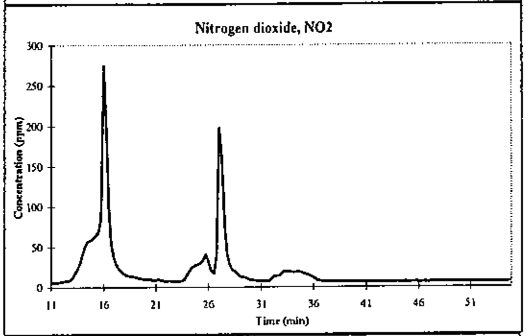
Synthetic Rubber

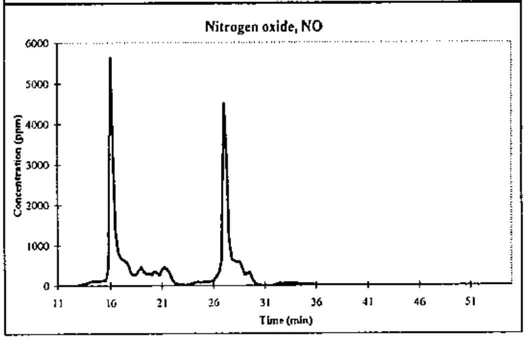
Well-ventilated, 650 °C

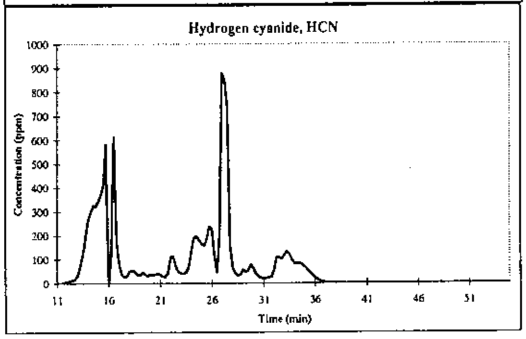




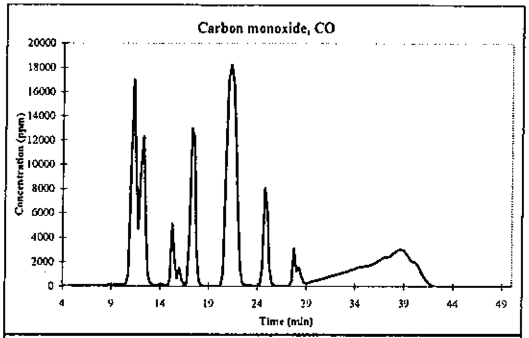


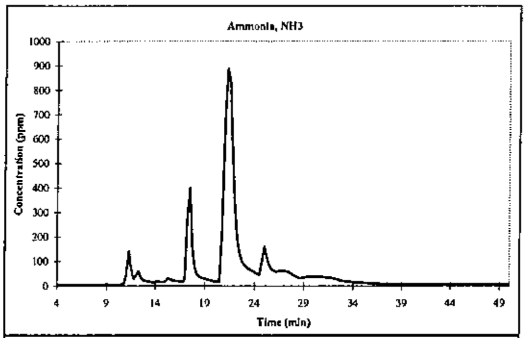


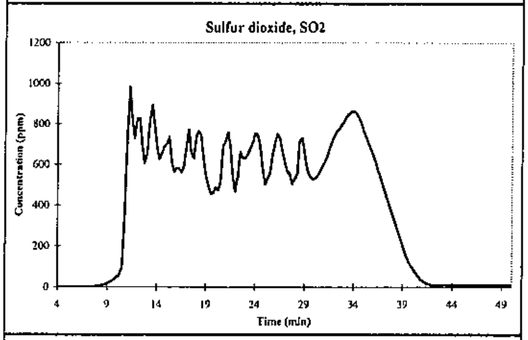


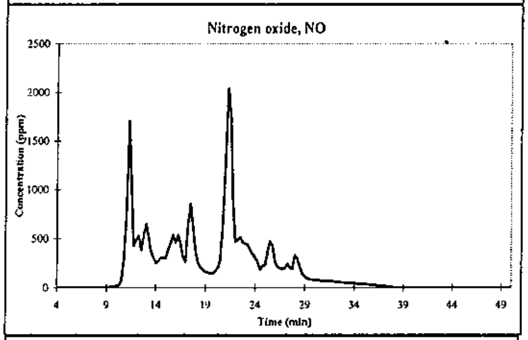


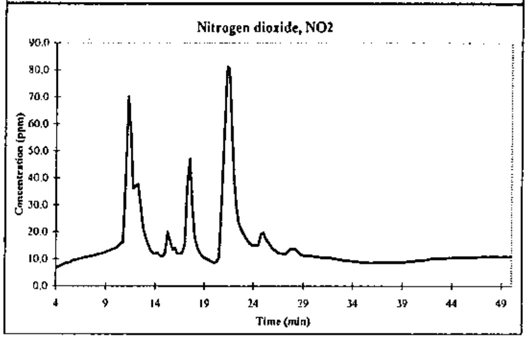
Well-ventilated, 900 °C

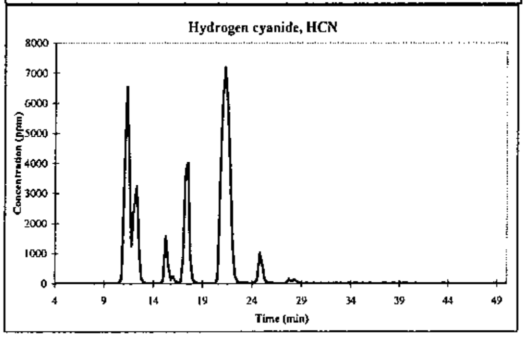




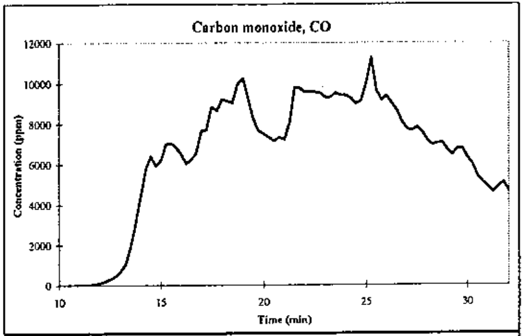


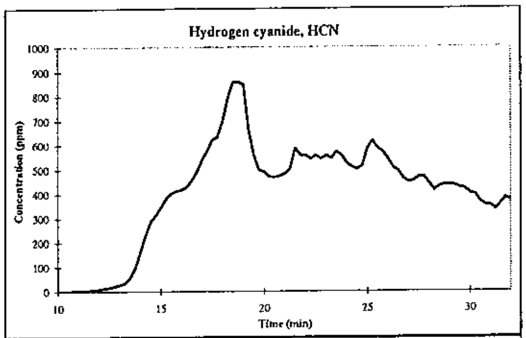


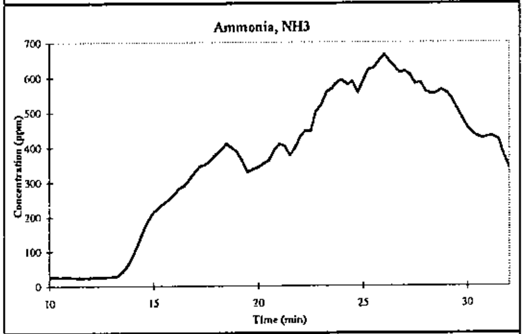


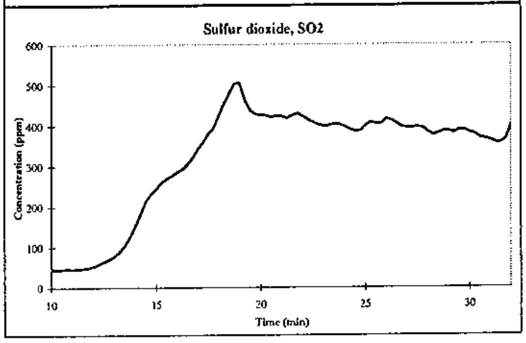


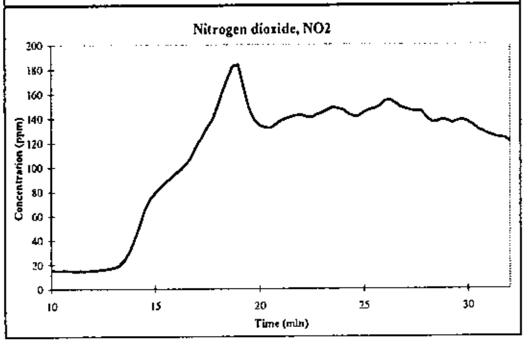
Vitiated, 650 °C


Carbon monoxide, CO


Hydrogen cyanide, HCN


Ammonia, NH3


Sulfur dioxide, SO2


Nitrogen dioxide, NO2

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