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ABSTRACT

Electrical cable fires may occur as part of a fire load and this was simulated using a pine wood crib fire in a compartment with PVC cables laid as a single layer on top of the crib. The aim was to trace the HCL yield under a mixed fuel compartment fire. A 1.6 m^3 compartment fire was used under fixed ventilation conditions. The 3.0 kg pine wood crib, with 0.25kg of 12 PVC cables 100mm long in a bundle placed in the centre of the crib, was burnt with 21 air changes an hour, simulating a restricted ventilated compartment fire. Toxic gases were measured using the Temet Gasmet heated FTIR, calibrated for 60 species including all the fire toxic gases. The HCl yields were similar to those in cone calorimeter tests for 40 kw/m^2. The toxic gases were high during the flaming phase of the fire where the peak temperatures and peak heat release occurred. The long smouldering phase of the pine wood crib fire had low concentrations of toxicity. The fire toxicity was dominated by the toxic products from the wood fire and the HCL from the PVC fire was a minor contributor. However, in the PVC cable fire tests on the cone calorimeter it was found that the peak yield (per g of PVC) of acrolein and formaldehyde were 0.055 and 0.035, respectively and were the dominant toxic gases for PVC cable fires and hence the PVC cables would have contributed to the yields of acrolein and formaldehyde in the combined wood crib and PVC cable fire. For the wood crib alone the acrolein and formaldehyde peak yields were 0.008 and 0.014 g/g respectively. The present results show much higher yields and this is because of the significant contribution to their formation from the presence of the PVC cables. The role of PVC cables in acrolein and formaldehyde formation has not previously been recognised.

KEYWORDS: Fire Toxicity, PVC, HCl, aldehydes, irritant gases..

INTRODUCTION

The majority of deaths in fires (66%) are due to the effects of toxic gases rather than flames [1]. PVC is the second largest contribution after wood to fires in non-domestic premises [2] and its use in electrical cable insulation is one of the main sources of PVC in fires. It has been estimated that there are 250m of electrical cable per house (50m per room) and 140 fires/million km cable/year [3]. Electrical cable fires may occur as part of a fire load for a fire that has started elsewhere and spread to ignite the cables externally. This is simulated in the present work with a mixed wood and PVC cable fire. Cable fires may also start through an electrical fault that results in overheating of the cable and ignition of the sheaf. Such fires are more dangerous in that electrical cables tend not to be in view and often in air starved service ducts. Thus, the fire can spread unnoticed until it ignites other material or the electric supply to the building fails as a consequence. Sundstrom [4] has reviewed methods of testing of cables for their fire resistance and concluded that current tests concentrate on fire propagation rates and not on toxicity.

However, he concludes that the future must address the toxicity issue and the measurement requirements, as reliable test methods are lacking.

Mangs et al. [5] have developed a new method for determining flame propagation speeds in electrical cable samples in the form of 2m long rods in an enclosure with heated air supply. 13mm OD PVC cable flame propagation rates were measured at 6mm/s at 100°C. This equipment [5] has a smoke offtake from the enclosure that could be used for toxic gas measurements, but was not used [5]. The equipment of Manga et al. [5] is, at atmospheric temperature, a laboratory scale version of the EN 50399 [6] equipment for the classification of electrical cables within the European construction products regulations. The EN 50399 equipment consists of a 1m wide by 2m deep cross section vertical tunnel with 4m height, with the cables mounted on the rear 1m wide wall on a vertical ladder or cable tray and ignited at the bottom with a 20.5 kW propane burner, which generated 900°C above the burner at the ignition point of the cables [7]. Heat losses led to a rapid temperature fall to 250°C by 450mm above the burner. The test is well ventilated by entrainment of air from a floor slot by the door, but there is no specific control of the air ventilation or the compartment equivalence ratio. It has the conventional cone calorimeter collection of the diluted products of the test section from which the HRR is derived by oxygen consumption calorimetry. This system is also used to determine smoke production by obscuration but there has been, to our knowledge, no publication of toxic gas measurements from this equipment, as its prime use is to determine flame propagation rates along the cable. Forsth et al. [7] showed that this equipment with three 12mm OD electrical cables (Euroclass Dca) had a peak HRR of 40 kW and that the HRR from the cable fire led to peak temperatures of 800°C 450mm above the burner outlet at the same time as the peak HRR. Most of the compartment was at a much lower temperature than those vertically above the fire. Similar compartment temperature conditions were achieved in the present work.

The authors [8] have investigated the toxic gases release from burning PVC electrical cables on the freely ventilated cone calorimeter. This showed that acrolein and formaldehyde were more important toxic gases than HCL and that CO was of little importance. TGA analysis was used to show that the HCL yield at temperatures up to 450°C was 42% and this increased to 52% at 500°C, which is close to the theoretical yield of 58%. In the cone calorimeter burning with 40 kW/m^2 radiant heating the peak HCL yield was 30%, although the temperature of the combustion is not known in the cone calorimeter. In the present work the same PVC electrical cables were burnt together with a wood crib, where the PVC cables were 8% of the fire load. The aim was to trace the HCL yield under a mixed fuel compartment fire and to investigate whether the PVC cable fire high yield of aldehydes also resulted in higher aldehydes in the wood/PVC fire compared with wood cribs alone, for the same compartment ventilation.

PREVIOUS WORK ON TOXIC YIELDS FROM ELECTRIC CABLE FIRES

Several investigators have measured toxic yields in PVC fires. These are summarised in Table 1, which also gives the measurement method and identifies which were cable fires. The present results are included for comparison plus for HCl the theoretical yield, assuming that all the chlorine is emitted as HCl from the fire. The HCl yields are also given in Table 1 as a % of the theoretical yield and this shows that in most experimental fires, less than half of the chlorine in PVC is released as HCl, implying either measurement problems or that much of the original chlorine remains in the char. The key measurement problem is the loss of HCl by solution in water condensed from the fire product gases. Fully heated sampling systems are required for on line measurement, as used in the present work. There is no evidence of other significant chlorine products from PVC fires [10]. The HCl yields of Al-Sayeh [8] were much closer to the

theoretical possibly due to their use of a heated FTIR with no sample line losses of HCl. Table 1 also shows the CO yields and there was little correlation between these and the HCl yields.

Purser [14] showed that in most fires the main toxic products are CO, HCN and irritant or acidic gases. The authors [15-20] have used heated FTIR for toxic gas analysis in small scale enclosed fires in a 1.6 m^3 fire facility with air starved fires for various fire loads. These results

Table 1 HCl and CO yields for PVC fires.

Author	Ref.	Method	CO Yield g/g	HCl Yield g/g	% Max Yield HCL
Theoretical		PVC C$_2$H$_3$Cl		0.58	100
Babrauskas	9	NBS Cup Furnace	0.09 – 0.11	0.2 – 0.3	34-52
Babrauskas	9	SwRI/NIST	0.086 – 0.090	0.21 – 0.26	36-45
Babrauskas	9	Cone Calorimeter 35, 50, 75 kW/m^2	0.066 – 0.076	0.3 – 0.32	52-55
Babrauskas	12	Real Scale Fires PVC board	0.19 - 0.47	0.09-0.22	16-38
Persson and Simonson	2	Large scale fire	0.116	0.32	55
Bowes	10	Pyrolysis of 1kg of rigid PVC in 1m^3 furnace		0.09	16
Blomqvist	11	Vertical cable fire test with FTIR	0.04-0.13	0.045-0.13	8 -22
Hull et al.	12	ISO Purser Furnace FTIR	0.025 -0.12	0.11-0.15	19-26
Hull et al.	13	Purser Furnace	0.23-0.46	0.15	26
Al-Sayegh et al.	8	Cone Calorimeter + FTIR, PVC cables	0.09-0.12	0.2 – 0.5	34-86

showed that the overall fire toxicity was dominated by relatively few species: CO, NO$_2$, SO$_2$, HCN, HCl, benzene, formaldehyde and acrolein.

EXPERIMENTAL METHODS

A 1.6 m^3 enclosed fire compartment was used that has been described in previous publications [15-20]. It had a 1.4m by 0.96m floor (1.344 m^2 floor area used in the HRR as MJ/m^2). It was similar to that used by Bundy et al. [21]. This was operated with a fixed air ventilation rate of 40 kg/hr (11 g/s), which gave 21 air changes per hour (ACH), which is a restricted ventilated fire, typical of a fire with a door or window partially open. The fire load rested on a flat metal plate on the floor of the chamber supported on load cells in the air plenum chamber under the fire compartment. The air was fed into the plenum chamber and then into the fire compartment through four slots at the edge of the compartment. The fire gases flowed along the flat metal ceiling to exit the compartment through a small gap between the edge of the ceiling and the compartment walls. The fire products then flowed along the rear of the ceiling to exit through a 140mm diameter short chimney discharge and gas samples were taken from this location using a water cooled sample 'X' probe with 40 sample holes on centres of equal area and this gas sample was the mean composition of the ceiling gases. The compartment had horizontal and vertical thermocouples arrays to determine the fire compartment mean ceiling temperature.

This mean raw fire ceiling exit gas flow was sampled via a 180°C heated sample line and passed to a 180°C heated filter and pump and then to a heated FID for total hydrocarbon analysis and to a heated chemiluminescence NOx analyser. From the heated pump and filter unit a second sample line was passed to a 2°C water condenser and the sample gas then went to NDIR analysers for CO and CO_2 and a paramagnetic analyser for oxygen. An independent 180°C heated sample line from the same raw gas sample point was passed to a heated TEMET GASMET CR-Series portable FTIR which was used for acidic and irritant toxic gas analysis. This had a separate heated sample line, filter and pump and the FTIR sample cell was also heated at 180°C so all analysis was on a hot wet basis and no acidic gases were lost by condensation. The FTIR was calibrated for over 50 species, including most of the toxic gases of interest in fire toxicity. The FTIR had a liquid nitrogen cooled detector and this gave at least 2ppm resolution on all species. The gas analysis were time aligned to the same event in the fire, to take account of the gas sample line delay of about 10s, which was a small proportion of the 600s main fire time.

PINE WOOD CRIBS

The pine wood crib weighed 3.0 kg (51 MJ) and was constructed of 50 19mm square pine wood sticks 300mm long. The bottom layer had two side sticks and there were then 12 layers of 4 equi-spaced sticks per layer with alternate layers with sticks in the opposite direction to the layer above and below. The total height was 247mm and the sticks were spaced with 75mm gaps between the sticks. 12 PVC standard domestic power cables 100mm long were placed in a bundle in the centre of the top of the crib. The PVC cables weighed 0.512kg with the copper cores and 0.250kg of PVC coating (5MJ), this was 7.7% of the total fire mass load and 8.9% of the total fire thermal load. The cables had the copper cores in place at the start of the fire, which was started using 50ml of ethanol at the bottom of the crib in the centre, the two bottom pine sticks allowed a central gap to insert the tray of ethanol into the centre. The CHON analysis of the pine wood was 47.2 % C, 47.1 % O and 5.7 % H, which give the chemical formula as $CH_{1.44}O_{0.75}$. The stoichiometric A/F ratio for this composition is 5.34/1. At the 40 kg/hr air flow rate into the compartment and with 3.0MJ/kg of air HRR, the fire HRR should be 33 kW (22.3 kW/m^2) and it should take 1530s to burn all the fire load. The result below show that the fire duration was in agreement with these predications but the peak HRR was 67% of the above and this difference was due to the poor combustion efficiency with very high CO and HC at the peak HRR.

FIRE DEVELOPMENT

The mass loss of the 3.512kg initial fire load as a function of time with 21ACH ventilation is shown in Fig. 1. The final weight, if all the wood and PVC coating burnt, was that of the copper wires at 0.262kg. The main fire mass loss was over the first 600s but there was a continuing slow mass loss after this to 0.650kg after 1400s and 0.400kg after 4000s, so that there was 0.138kg of flammable material left and most of this was observed to be char on the PVC cables. TGA studies [8] of PVC cables in air and nitrogen showed that at 900°C 30% of the original PVC cable coating remained as a char (excluding the copper core). For the present 0.250kg of PVC fire load this would leave 0.075kg of char, the remaining weight was the ash from the pine wood, 2.1% pine ash was measured which was 0.063g, giving a total weight of 138g.

The compartment ceiling temperatures from the rear of the ceiling to the front are shown as a function of time in Fig. 2. This shows that above the fire there were two peak temperatures of 500°C at 240s and 540°C at 740s, after which the fire cooled. In the ceiling plane at 90° to the above, the peak temperature was 785°C at 215s and 684°C at 770s. Comparison with Fig. 1

shows that the period between 215 and 770s was the time period for the main mass loss in the fire and it will be shown below that most of the fire toxicity occurred in this time period.

The NOx emissions (by chemiluminescence) are shown as a function of time in Fig. 3. This shows a sharp peak in NOx at 210s close to the first peak in the central ceiling temperature in Fig. 2. NOx emissions are created at the flame front in the flaming combustion fire phase [22]. Thus it can be assumed that the first peak in the central ceiling temperature in Fig. 2 was due to flaming combustion. At the later peak central ceiling temperature at 740 – 785s the NOx in Fig. 3 was very low and was not caused by flaming combustion, but by smouldering combustion in the char burn out phase of the fire. The second peak ceiling temperature was caused by the caused by the accumulation of heat release in the compartment from the flaming combustion phase with char heat release adding to the temperature. It will be shown below that the peak fire toxicity occurred at around 500s in the middle of the period of high central peak ceiling temperatures. At the peak temperature time the fire global equivalence ratio by carbon balance was 2.0.
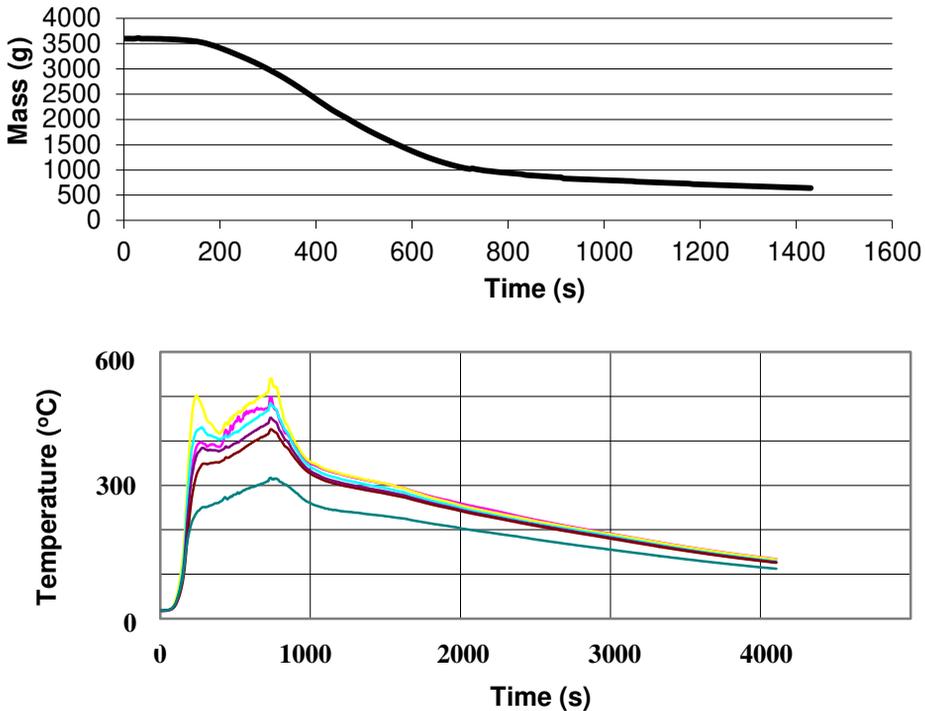
Figure 2. Ceiling temperatures from centre (top) to the compartment wall (bottom)

NOx ppm   **THC ppm**   **O_2 %**
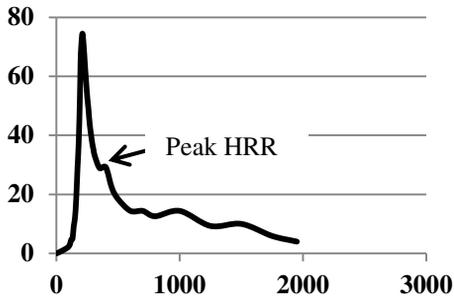
Figure 3. NOx **emissions v. time**
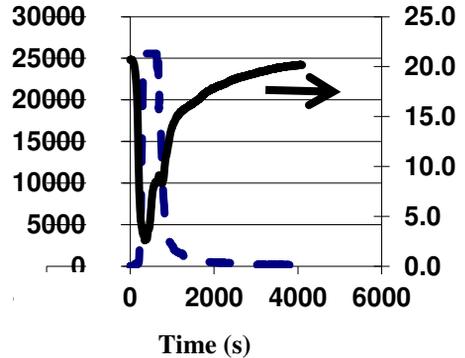
Figure 4. THC ppm and O$_2$ v. time

OXYGEN, THC, CO AND HRR

The mean compartment ceiling exit oxygen concentration is shown as a function of time in Fig. 4 together with the total unburnt hydrocarbons (THC) measured by heated flame ionisation detection (FID). The minimum oxygen occurred at 340s with a value of 2.6%. This raw gas oxygen measurement was used to determine the heat release rate (HRR) by oxygen mass consumption, using the compartment metered air mass flow of 40 kg/h together with the measured ss loss rate of the fire load to xhaust mass flow rate as a function of time. This HRR, norm compartment of 1.344 m^2, is shown in Fig. 5, which has the inverse shape to the ceiling oxygen level in Fig. 4. The peak HRR was 14.9 kW/m^2 and also occurred at 340s from the start of the fire. Figs 4 and 5 show that the slow smouldering combustion continued for 4000s with a low HRR. The peak HRR occurred 130s after the peak

NOx, where the NOx was 29 ppm and occurred at a trend change in the NOx profile, as shown in Fig. 3. The peak HRR was close to the midpoint of the fire mass loss in Fig. 1. Fig. 4 also shows the THC emissions peaked at the time period of the minimum O$_2$ and peak HRR. The values were very high (off scale on the FID) and show that the combustion efficiency was poor.
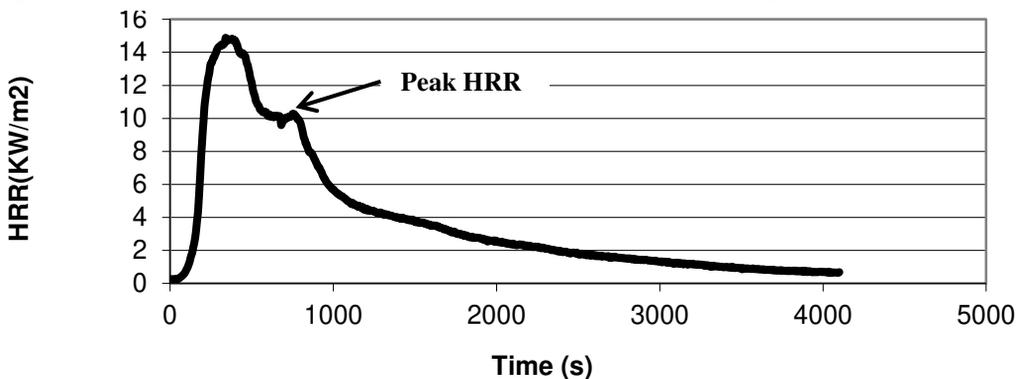
Figure 5. HRR by oxygen mass consumption v. time

CO AND ACROLEIN YIELDS

CO Yield g/g
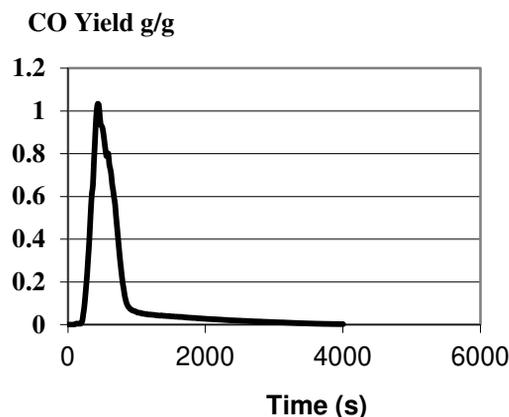
Acrolein Yield g/kg

Figure 6. CO yield g/g v. time
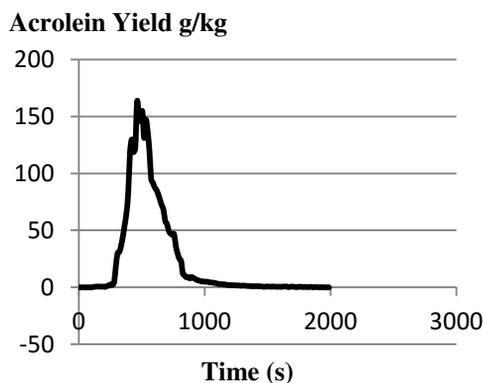
Figure 7. Acrolein Yield g/kg v. time

Fig. 6 shows the CO yield as a function of time. The peak CO yield was 1.0 g/g at 420 – 450s from the start of the fire. This is a very high yield and is much higher than the peak yield of 0.22 g/g for the pine wood crib alone at 21 ACH [20], although the two tests were not exactly the same as a 4.8 kg crib was used without the cables present [20]. The CO yields without the PVC cables present were comparable with the results of Alarifi et al. [23] for a full scale compartment fire with the door open, where CO yields were 0.26 g/g for a $\varnothing_{global}$ of 1.9 and peak fire ceiling temperature of 700°C. The PVC sheathed cables tested on a cone calorimeter had a peak CO yield of 0.125g/g, which is also lower than in the present work. The peak CO yield occurs in the middle of the fire load mass consumption, but well after the peak HRR at 340s. The high CO yield in the present work was due to the presence of the PVC sheathed cables. The release of HCl from the cables could act as a fire retardant on the wood fire combustion leading to higher CO and THC than for the fires with no PVC present.

Fig 7 shows the yield of acrolein, which is the most toxic gas on an impairment of escape basis. The peak yield was very high at 163 g/kg compared with 89 g/kg in the previous work [20] with no PVC cables present. The peak acrolein yield occurred at 462s, just after the peak CO yield. The other major toxic gas was formaldehyde and this had a peak yield of 100 g/kg at 616 – 650s, which was significantly after the peak acrolein yield. The formaldehyde was generated towards the end of the mass consumption of the fire load and just after the second peak in the ceiling temperature in Fig. 2. In the higher temperature full scale compartment fires of Alarifi et al. [23] acrolein yields were only 1g/kg and this was due to the higher temperatures at the higher ventilation in a compartment with an open door,.

HCL YIELD

The yield of HCl is shown in Fig. 8 in terms of the yield in g of HCl per g of PVC, not per g of total fire load as in the previous definitions of yields in Figs. 6 and 7. The HCl was expressed in this way so that it could be compared with the yields in the literature reviewed in Table 1. There were two peaks in the yield with 0.29 and 0.33 g/g. These values of yield were very close to those determined for the same PVC sheathed cables tested in the cone calorimeter [8] and are in
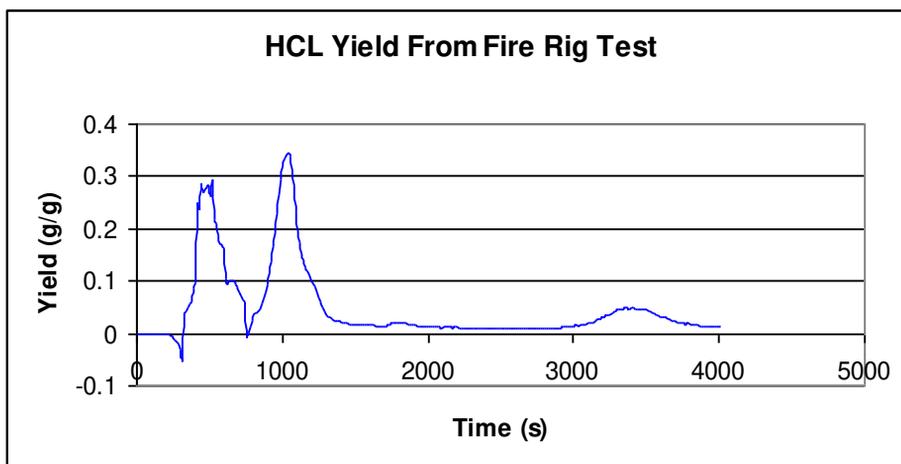
Figure 8. HCl Yield g/g_{HCl}

the upper range of the values in Table 1. This indicates that the cone calorimeter is a good small scale test method for toxic gas yield determinations. The two peaks in HCl yield occurred at 500s and 1050s and the first was in the main combustion phase of the wood after the end of flaming combustion, but the second was in the char burn out phase. TGA analysis [8] of PVC heated in N_2 and air showed two periods of weight loss at $450 – 500^oC$ and $750 – 800^oC$, with the second HCl yield coming from the PVC cable char and the first from the release of gaseous HCl. The two peaks for HCl yield in the present work are due to the same release mechanisms, as the second peak is in the char burn out phase of the fire.

TOTAL TOXICITY N RATIO

The authors have previously shown [8, 15-20] that the COSHH 15 mins. toxicity assessment procedures give a procedure for predicting the no harm exposure to toxic gases, that is similar to the no impairment of escape criteria in AEGL-2, which is a 10 minute exposure method. If this is used together with that of LC_{50} for 50% deaths after 30 minutes, then the measured emissions can be assessed for total toxicity in terms of impairment of escape and deaths. All the 60 species of gases analysed by the FTIR were evaluated for their toxic limits and the measured values were divided by the $COSHH_{15min}$ or LC_{50} limits to give an 'n' value for that gas. All the'n' values for all species were then added to give the total toxicity ratio N. Details of this procedure have been given in previous publications [8, 15–20]. The n/N ratios for each species enables the most important toxic species to be determined and in the present work these were acrolein, formaldehyde, CO, HCl and HCN which accounted for 90%+ of the LC_{50} and $COSHH_{15min}$

Figs. 9and 10 show that N varies in the fire in a very similar way for both the $COSHH_{15min}$ and LC_{50} methods of toxic gas assessement. For both methods of assessment the peak values of N are very high. N is the required dilution of the fire gases before they are safe. The peak toxicity occurs at about 500s for both methods of assessment of N, which is close to the peak CO and acrolein yield times. The increase in N at around 900-1000s was due to the second peak in the HCl yield and to formaldehyde.
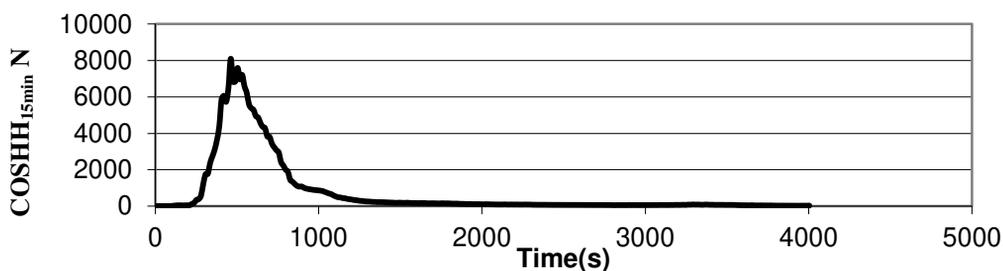
Figure 9. $COSHH_{15min}$ N v. time
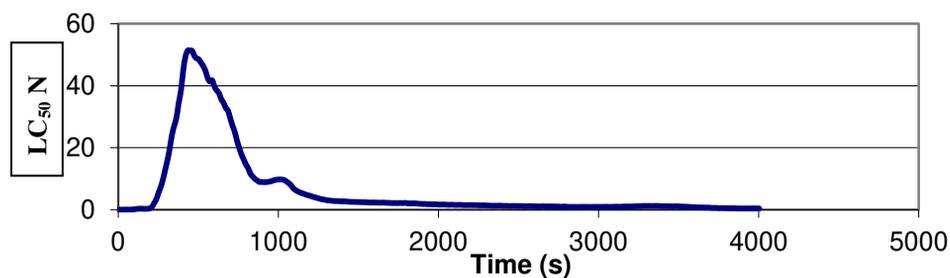
Figure 10. LC_{50} N v time

Table 2. The Contribution of the major toxic gases to the total toxicity N.

Toxic gas	LC_{50}	$COSHH_{15\,MIN}$
CO	64%	7%
Acrolein	15%	69%
Formaldehyde	15%	13%
HCl	0.4%	2%
HCN	6%	5%
Total	100%	96%

CONCLUSIONS

1. The contribution of the major toxic gases to the overall toxicity is summarised in Table 2 for both methods of toxic gas assessment. The key difference in the two methods is that LC_{50} places much more emphasis on CO as a cause of death, but it is not an irritant or acidic gas and does not impair escape. Acrolein is much more important in delaying escape as an irritant gas, but it is not important in terms of deaths in fires. The role of formaldehyde and HCN was similar for both methods of assessment.

2. In a compartment fire with 21ACH ventilation the combustion of a wood crib with 8% of the fire load from PVC cables, the peak yield of HCl from the cables was 0.33 g/g in good agreement with measurements on a cone calorimeter and with the literature.
3. The compartment fire toxicity was dominated by the toxic gases CO, acrolein and formaldehyde which were all produced by the wood combustion. The contribution of HCl was 2%.
4. Unless PVC dominates the fire load, the contribution of HCl to the fire toxicity is likely to be small in compartment fires.
5. There was evidence that the presence of PVC sheathed cables retarded the rate of fire development and decreased the combustion efficiency with large emissions of CO and THC and higher acrolein and formaldehyde yields than had been found in similar pine crib fires with no PVC present. This was due to the well known fire retardant influence of halogens.

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