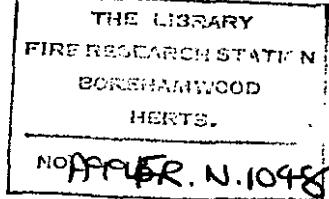


LIBRARY REFERENCE ONLY



Fire Research Note No 1048

THE INHALATION TOXICITY OF POLY-VINYL
CHLORIDE PYROLYSIS PRODUCTS

by

P C Bowes, J A G Edgington and R D Lynch

February 1976

FIRE
RESEARCH
STATION

53963

**Fire Research Station
BOREHAMWOOD
Hertfordshire WD6 2BL
Tel: 01 953 6177**

THE INHALATION TOXICITY OF POLY-VINYL CHLORIDE
PYROLYSIS PRODUCTS

by

P C Bowes¹, J A G Edgington² and R D Lynch²

SUMMARY

A limited study has been made of the toxic effects of hydrogen chloride, representing the major toxic component of the pyrolysis products of poly-vinyl chloride, in the presence of carbon monoxide generated by the combustion of a wood-based material (hardboard).

In the presence of the mixed gases, at concentrations within the range of approximately 2000–20,000 mg/m³, deaths among rats and guinea pigs exposed for 30 minutes were primarily due to carbon monoxide poisoning, but the hydrogen chloride was found to enhance the response to the carbon monoxide. However this enhancement occurred mainly at concentrations of hydrogen chloride which could be lethal when present alone.

There appears to be sufficient evidence available to indicate that the presence of hydrogen chloride at lethal concentrations in fire gases containing lethal concentrations of carbon monoxide could marginally increase the fatalities in fires. It is probable, however, that the most important effects of the presence of hydrogen chloride will accompany sub-lethal exposures, firstly because the highly irritant nature of the gas may result in more people being prevented from using escape routes in the early stages of fires in buildings by concentrations of fire gases and smoke which may be otherwise relatively harmless at the time and, secondly, because survivors may suffer long term, even permanent, injury from high concentrations of this gas. These are the aspects which appear most to require further study.

1. Fire Research Station
Melrose Avenue
Boreham Wood
Herts

2. Chemical Defence Establishment
Porton Down
Salisbury
Wilts

FOREWORD

This note reports part of a study of the toxicity of the combustion products of wood and plastics carried out at the Chemical Defence Establishment, Porton Down, under contract to the Fire Research Station.

It is intended that a complete account of the work under the contract, and discussion of its implications, will be published elsewhere. However, because of certain experimental difficulties and constraints, the results of the studies on poly-vinyl chloride pyrolysis products described here are less straightforward than those of the earlier studies of the series. It has therefore been considered desirable to devote part of the present Note (Part I) to a summary of the work and results which places it in the fire context, and also relates it to other published work. This part of the report is the responsibility of the Fire Research Station.

All enquiries concerning work described in this Note should be directed to the Fire Research Station.

THE INHALATION OF TOXICITY OF POLY-VINYL CHLORIDE
PYROLYSIS PRODUCTS

by

P C Bowes, J A G Edgington and R D Lynch

PART I. SUMMARY OF INVESTIGATION AND IMPLICATIONS OF RESULTS

by P C Bowes

INTRODUCTION

Commonly, pyrolysis or combustion of poly-vinyl chloride, PVC, in fires will occur in association with the combustion of wood or wood products present as the major combustible materials. Detailed analysis of the thermal decomposition products of PVC¹ and a toxicological study of the combustion products of wood² together indicate that hydrogen chloride and carbon monoxide are likely to be the principal toxic products in the fire gases and smoke from fires involving both PVC and wood or wood products.

Measurements of the concentrations of these gases, hydrogen chloride and carbon monoxide, produced during the course of fires in wood cribs in a full-scale compartment lined with PVC have shown³ that, with the larger loads of PVC (95 and 115 kg rigid PVC panels on a wall area of about 28 m²), the concentration of hydrogen chloride could reach values of 10³ to 10⁴ ppm (1.5 x 10³ to 1.5 x 10⁴ mg/m³) even after dilution with cold air sufficiently to reduce the temperature to a value of 120°C - which might be bearable for a short period by persons escaping from a burning building. The concentrations of carbon monoxide tended to be similar in order of magnitude but were commonly slightly lower than those of the hydrogen chloride. A preliminary assessment of the practical significance of these results was made using available toxicological data⁴ for the hydrogen chloride and carbon monoxide separately. However, toxicity measurements of the combined effects of these two gases were clearly desirable. A number of studies of the toxicity of PVC decomposition products to animals had been published (see Discussion) but none of these covered gas concentrations and exposure conditions directly relevant to the large-scale fire tests reported above³.

The present Note reports the results of toxicity trials, using rats and guinea pigs, in which attempts were made to achieve the high concentrations of both carbon monoxide and hydrogen chloride, in the presence of other gaseous combustion products and smoke, which had been observed in the large-scale fire tests with large loads of PVC. Full details of the trials are given in Part II of this report

and the Appendices. Here, in Part I, the experimental approach and the results are summarised and the implications of the results are discussed briefly.

EXPERIMENTAL PROCEDURE

As in the previous work reported in this series, rats and guinea pigs in groups of 15 were exposed for 30 minutes to the accumulated combustion products of the materials under test in a chamber with a volume of 10 m³. Five of each species were pre-selected at random before test for determinations of blood carboxy-haemoglobin on withdrawal. The remaining groups of 10 were examined for mortality and external damage on withdrawal and at intervals thereafter up to, usually, 24 hours. In order to remove complicating effects due to oxygen deficiency and high temperature, the oxygen concentration was restored to 21% and the temperature in the chamber was allowed to fall to near ambient values before the animals were introduced.

In order, further, to achieve combustion of the material under test, in a reasonably standard manner the Fire Propagation Test apparatus was used (with reduced ventilation as before²) to generate the combustion products.

The material initially selected for test was a hardboard faced with rigid PVC. The theoretical yield of hydrogen chloride from the PVC was known to be 50% by weight. In preliminary trials, however, it became apparent that, although sufficient of this material could be burned in the Fire Propagation Test apparatus to yield the required concentrations of carbon monoxide in the chamber, the concentration of hydrogen chloride produced was equivalent to only about 10% of the theoretical yield and was far too low. It was, moreover, not possible sufficiently to increase the yield of hydrogen chloride by including additional rigid PVC sheet with the PVC-faced hardboard.

It was clear that a large proportion of the available hydrogen chloride was being lost, either in the Fire Propagation Test apparatus itself or, perhaps, in condensed moisture on the walls of the chamber. The procedure finally adopted, therefore, was to burn the PVC-faced hardboard in quantities sufficient to provide the desired levels of carbon monoxide and to introduce hydrogen chloride gas into the chamber from a cylinder. Some control experiments were carried out using the hydrogen chloride gas alone.

The intended test procedure was to assess the effect of the hydrogen chloride in the combustion products by determining whether or not the observed mortality among

the animals could be accounted for by the carbon monoxide present. This involved determining LC_t₅₀ values with respect to the carbon monoxide in the combustion products at different levels of hydrogen chloride. In the event, it rapidly became evident that the high concentrations of hydrogen chloride used in the trials caused severe tissue damage and distress to the animals. Because of this, and because of the difficulty of achieving stable concentrations of hydrogen chloride in the atmosphere of the chamber, the full programme of tests was abandoned. Nevertheless, sufficient results were obtained to indicate at least in a qualitative way the possible effect of high concentrations of hydrogen chloride in the presence of carbon monoxide in fire atmospheres.

RESULTS

The observed mortalities for the rats and guinea pigs are given respectively in Tables 1 and 2 which include the exposures both to the combustion products of the PVC-faced hardboard with added hydrogen chloride gas and to hydrogen chloride gas alone. The entries are arranged in order of decreasing hydrogen chloride concentration. The mortalities, given as percentages rounded to the nearest integer, are listed for the time of withdrawal and for the final time of counting; the mortalities at intermediate times will be found in full in Part 2.

The sixth columns of Tables 1 and 2 give the range of expected mortalities, rounded as above, corresponding to the concentration of carbon monoxide when present. These expected mortalities are estimated from the 95 per cent confidence band of the probit regression line determined previously² for mortalities with respect to the concentration of carbon monoxide in the combustion products of wood; see Fig. 1*. These expected mortalities refer to a different population and any comparisons made will be subject to considerable reservation.

The final columns of the Tables give the mean values of the carboxy-haemoglobin (COHb) concentrations in the blood of the dead and live members of the pre-selected samples on withdrawal.

*Of the two series of results available², the one with the lowest variance on the slope has been selected for use here. On conclusion of this series of investigations, all results for exposure to carbon monoxide will be pooled to provide a measure of response which includes variance between populations. This may require some revision of the expected mortalities used here.

Table 1. Percentage mortalities of rats exposed for 30 m
to combustion products of PVC-faced hardboard
with added HCl gas and to HCl gas alone

HCl concentration mg/m ³	CO concentration mg/m ³	Mortality per cent ¹		Time of final count h	Expected mortality ¹ from CO alone	Carboxy-haemoglobin ²	
		Dead on withdrawal	At final count			Dead	Alive
22000	0	40	100	4	-	-	-
8000	5850	100	100	o/w	47-71	91.3 (5)	-
6650	0	0	100	24	-	-	-
4850	4410	80	100	24	19-52	98.6 (4)	47.5 (1)
3500	0	0	67	5	-	-	-
2520	5380	40	53	24	38-56	95.8 (4)	63.2 (1)

¹Rounded to nearest integer

²Mean per cent. Number of individuals in brackets

Table 2. Percentage mortalities of guinea pigs exposed for 30 m to combustion products of PVC-faced hardboard with added HCl gas and to HCl gas alone

HCl concentration mg/m ³	CO concentration mg/m ³	Mortality per cent ¹		Time of final count h	Expected mortality ¹ from CO alone	Carboxy-haemoglobin ²	
		Dead on withdrawal	At final count			Dead	Alive
22000	0	100	100	o/w	-	-	-
8000	5850	67	87	2	0	80.6 (7)	73.9 (3)
6650	0	80	100	24	-	-	-
4850	4410	53	80	72	0	68.1 (6)	56.6 (5)
3500	0	80	87	5	-	-	-
2520	5380	40	47	168	0	90.3 (4)	40.4 (1)

¹Rounded to nearest integer

²Mean per cent. Number of individuals in brackets.

Inspection of the Tables reveals the following features:

Rats

1. Contrary to the earlier trials with carbon monoxide alone² (when animals which were not dead on withdrawal generally survived), death following exposure to hydrogen chloride, with or without carbon monoxide, occurred over a protracted period following the half hour exposure.
2. At the higher concentrations of hydrogen chloride, down to 4850 mg/m³, 100 per cent mortality occurred within 24 hours or less whether carbon monoxide was present or not. However, when carbon monoxide was present together with the hydrogen chloride, the mortality on withdrawal was not only high but was higher than would have been expected from carbon monoxide alone.
3. Generally, as the concentration of hydrogen chloride decreased, there was a trend towards post-exposure deaths and, when the hydrogen chloride concentration was down to 2520 mg/m³, the mortality on withdrawal was within the range to be expected from the carbon monoxide alone (present at 5380 mg/m³). At these levels of carbon monoxide and hydrogen chloride, the increase in mortality within 24 hours of withdrawal became relatively small.
4. The high levels of carboxy-haemoglobin show that the high mortalities on withdrawal when carbon monoxide was present were due to this gas.

Guinea pigs

1. These animals are clearly more sensitive to hydrogen chloride than are rats. There is no marked increase in short term survival as exhibited by the rats towards the lower concentrations of hydrogen chloride in the range covered.
2. Whereas previously² guinea pigs have been found to be resistant to carbon monoxide, and the expected mortalities due to carbon monoxide at the concentrations used in the present trials are all zero, the mortalities observed here with carbon monoxide and hydrogen chloride present together are relatively high and are associated with high carboxy-haemoglobin levels in the dead animals.
3. The observed mortalities in the presence of hydrogen chloride and carbon monoxide together are, however, consistently lower than might be expected from the hydrogen chloride alone.

At the higher concentrations of hydrogen chloride, both the rats and guinea pigs suffered gross damage to airways and external tissues.

DISCUSSION

Results

Probably the most significant result from these trials is that, apart from toxic and otherwise damaging effects of its own, hydrogen chloride gas can enhance the response to carbon monoxide.

The trials have not been carried far enough to show to how low a concentration of carbon monoxide this enhancement will extend but, with rats, it appears to be of practical significance only over a relatively narrow band of hydrogen chloride concentrations with carbon monoxide concentrations in the neighbourhood of the LC₅₀ for this gas². Thus, at hydrogen chloride concentrations of 4850 mg/m³ and above, the effect of the enhanced response to carbon monoxide is merely to hasten death which is otherwise inevitable. At a hydrogen chloride concentration of 2520 mg/m³, and presumably below, the enhancement becomes insignificant and the long-term lethal effect of the hydrogen chloride becomes reduced.

The enhancement is most strongly marked with the guinea pigs. In the earlier studies on rats and guinea pigs exposed to the combustion products of wood², the carboxy-haemoglobin levels for the guinea pigs were found to be only about half those for the rats following exposures of 30 minutes with concentrations of carbon monoxide giving high rat mortalities. As pointed out in Part II, the enhancement of carbon monoxide toxicity by the hydrogen chloride is almost certainly due to excitement and overbreathing; for the guinea pigs this must be sufficient to double the carbon monoxide uptake during the 30 minutes exposure.

Comparison with other published work

Machle et al⁴ have reported 100 per cent mortality in rabbits and guinea pigs exposed for 30 minutes to hydrogen chloride gas at a concentration of 6500 mg/m³. The present observations are consistent with this. More recently, Darmer et al⁶ have published LC₅₀ values for 5 minute and 30 minute exposures of rats and mice to hydrogen chloride gas and to hydrochloric acid aerosol. The values obtained for the gas and the aerosol did not differ significantly. The LC₅₀ value obtained for the 30 minute exposure of rats to hydrogen chloride gas was as follows:

$$8300 \text{ mg/m}^3 \quad (7200-9700)$$

The figures in brackets are the 95 per cent confidence limits. By coincidence, the present trials include results for a hydrogen chloride gas concentration of 8000 mg/m³ but with carbon monoxide present as well. The observed mortality of 100 per cent (Table 1) is higher than would be expected from the hydrogen chloride gas alone but the extent to which the difference is attributable to the CO must be qualified by possible population differences.

With the object of determining the toxicity of hydrogen chloride gas with and without the presence of carbon monoxide, Higgins et al⁷ determined LC₅₀ values for 5 minute exposures of rats and mice to hydrogen chloride gas, using both untreated animals and animals which had been exposed to sub-lethal concentrations of carbon monoxide sufficient to raise their carboxy-haemoglobin levels to 25 per cent; for the rats, this involved a 5 minute exposure to a carbon monoxide concentration of 2200 mg/m³. Under these conditions there was no significant difference between the LC₅₀ values for exposure of the treated and untreated animals to hydrogen chloride and it was concluded that the sub-lethal dose of carbon monoxide did not enhance the response to the hydrogen chloride. The procedure used was, of course, incapable of revealing the enhancing effect of hydrogen chloride on the response to carbon monoxide which has been observed here.

In previous work on the exposure of animals to the pyrolysis or combustion products of PVC itself⁸⁻¹³, the animal response has been related to the weight of PVC pyrolysed⁸ and to the temperature of pyrolysis⁹⁻¹¹. Kishitani and Nakamura¹³ have measured concentrations of both hydrogen chloride and carbon monoxide but, otherwise, where gas analysis has been carried out at all, it has been restricted to carbon monoxide^{8,12}.

All authors agree in reporting that animal deaths were due predominantly to carbon monoxide but also that, under certain conditions, high mortalities occurred which were accompanied by low levels of carboxy-haemoglobin. In particular, Hofmann and Oettel^{9,10} pyrolysing PVC at a series of constant temperatures, observed high mortality ratios, 10/12 and 11/12, in rats exposed to the products in air with pyrolysis temperatures of 300°C and 400°C respectively. The carboxy-haemoglobin levels were low, being 25 per cent and 45 per cent respectively. At higher temperatures, namely 500°C and 600°C, mortality ratios were 12/12 and the carboxy haemoglobin levels were high, being 70 per cent and 76 per cent respectively. These results may be correlated with the pyrolysis studies of Sumi and Tsuchiya¹⁴ and of Woolley¹⁵ which show that the maximum possible yield of hydrogen chloride gas may be expected over the whole of the temperature range 300 to 600°C. However, the yield of carbon monoxide from PVC is highly temperature dependent over this

temperature range¹⁴. On a weight basis, the yield of carbon monoxide at 400°C is only about 0.6 per cent of the yield of hydrogen chloride while, at 600°C, the yield of carbon monoxide rises to 10 per cent of the hydrogen chloride. The high mortality ratio in the pyrolysis products at the lower temperatures is clearly associated predominantly with the presence of the hydrogen chloride gas. At the higher temperatures, where the mortality ratios are the maximum possible but only slightly higher than at the lower temperatures, the high carboxy-haemoglobin levels are consistent with the enhancement of response noted in the present work.

The lesions produced by the hydrogen chloride gas stem from its corrosiveness and details are given in references 5, 6, 8, 12 and 13. Here it is sufficient to note that death due to this gas is associated with severe tissue damage to the respiratory system. External tissue damage is generally as described in Part 2 of this Note. The gas must, of course, exert its principal effects dissolved in aqueous phase as hydrochloric acid.

CONCLUSIONS AND COMMENTS

The following conclusions apply to exposures of 30 minutes to hydrogen chloride and carbon monoxide, each at concentrations within the range of approximately 2000–20,000 mg/m³ in fire gases diluted and cooled by mixture with air sufficiently to remove possible effects of elevated temperature and oxygen deficiency.

1. The response of animals to hydrogen chloride observed in this work is consistent with the results of studies published elsewhere^{4–13}.
2. Deaths following exposure to HCl for 30 minutes occur over a protracted period, whereas animals not killed during exposure to carbon monoxide generally recover. HCl gas causes severe damage to internal and external tissues.
3. Deaths following exposure to a mixture of hydrogen chloride and carbon monoxide among other combustion products, and at the higher concentrations in the range studied, are generally associated with a high carboxy-haemoglobin concentration in the blood and are thus predominantly due to carbon monoxide poisoning.
4. The study has revealed that hydrogen chloride enhances the response to carbon monoxide but this is important mainly at concentrations of hydrogen chloride which are likely to produce high mortalities when this gas is present alone.

5. Broadly speaking, the observations reported here and elsewhere imply, in practice, that 'fire gases' containing both hydrogen chloride and carbon monoxide at concentrations in the range studied will be highly aggressive and probably more lethal than when hydrogen chloride is absent. A further implication is that the likelihood of successful resuscitation and recovery following the inhalation of carbon monoxide will be reduced by the presence of high concentrations of hydrogen chloride.

There appears to be sufficient evidence available to indicate that the presence of hydrogen chloride at lethal concentrations in fire gases containing lethal concentrations of carbon monoxide could marginally increase the fatalities in fires. It is probable, however, that the most important effects of the presence of hydrogen chloride will accompany sub-lethal exposures, firstly because the highly irritant nature of the gas may result in more people being prevented from using escape routes in the early stages of fires in buildings by concentrations of fire gases and smoke which may be otherwise relatively harmless at the time and, secondly, because survivors may suffer long term, even permanent, injury from high concentrations of this gas. These are the aspects which appear most to require further study.

It has been found here that hydrogen chloride in combustion products can be rapidly lost. This will be generally true in fires where the gas can react with alkaline surfaces in buildings (cement) or can dissolve in moisture condensing on cool surfaces. However, in estimating the probable hazard arising from a given loading and disposition of PVC in a building in the event of fire, it will be prudent to assume that most, if not all, of the available hydrogen chloride will appear in the fire gases - as has indeed been observed in experimental fires³.

Finally, it must be pointed out that a full assessment of the importance of the presence of hydrogen chloride in fire gases requires a knowledge of the variation in concentration with time during the development of a fire. This will not affect the above conclusions on the possible consequences of potentially lethal exposures to fire gases but will be crucial to consideration of the likelihood of people being trapped in the early stages of a fire.

THE INHALATION TOXICITY OF POLY-VINYL CHLORIDE
PYROLYSIS PRODUCTS

PART II. EXPERIMENTAL AND DETAILED RESULTS

by

J A G Edgington and R D Lynch

METHODS AND MATERIALS

Animals

As in reference 2 male rats and guinea-pigs were supplied by Allington Farm.

The weights for the animals were:-

Rats $207.2 \text{ g} \pm 12.7 \text{ g SD}$

Guinea-pigs $310.8 \text{ g} \pm 7.9 \text{ SD}$

Fifteen animals of each species were used for estimating mortality data, and five for carboxy-haemoglobin (COHb) estimation. As before, the animals intended for COHb estimation were allocated before the exposure.

The method for the estimation of COHb was again as in reference 2 to ensure continuity. Animals allocated for this estimation were killed with CO_2 if still surviving at the end of the exposure.

Materials

The PVC was in the form of either; (1) A PVC covered hardboard approximately $\frac{1}{8}$ in thick, in which the weight of plastic for each tile was about 40 g in a total of 210 g, and (2) rigid PVC sheet. The theoretical yield of hydrogen chloride from decomposition of the PVC was about 50 per cent by weight in both cases*.

In order to fit the pyrolysis equipment both materials were in the form of tiles approximately 22.5 x 22.5 cm.

In those experiments where HCl was added, it was either in the form of BDH AR grade hydrochloric acid, or BOC hydrogen chloride gas.

*Data supplied by Fire Research Station

Methods

The pyrolysis in all cases was carried out in the equipment specified in BS 476 : Pt 6 : 1968 as modified in reference 2.

Hydrochloric acid, when used, was sprayed into the chamber using a stainless steel 'Spraying System' (TM) nozzle driven by compressed air.

Hydrogen chloride gas was metered into the chamber via a reduction valve and a calibrated rotameter.

O₂, CO, CO₂ and temperatures were measured as in reference 2.

HCl was measured by drawing known volumes of air through sampling bubblers containing N NaOH, with subsequent estimation using a specific ion electrode against a calibration curve.

RESULTS

Before exposing any animals, attempts were made to mimic 'theoretical' HCl concentrations. See Appendices for full protocol. Essentially all the chlorine in PVC should appear as HCl during burning. However at the first attempt to burn PVC the following conditions obtained:

Total weight of 'tile' 1258 g

Total weight of PVC 240 g

Equivalent HCl content 120 g approximately

Theoretical HCl conc. in 10 m³ chamber 12 g/m³

Actual HCl conc. in 10 m³ chamber 0.21 g/m³ max

Appendix 1A

In order to increase the final HCl concentration higher loads of PVC were burnt without increasing the hardboard weight.

Total weight of 'tile' 1233 g

Total weight of PVC {240 g from 'tile' and
(890 g as solid PVC

Equivalent HCl content 565 g approximately

Theoretical HCl conc. in chamber 56 g/m³

Actual maximum conc. 3.1 g/m³

Appendix 1B

Upon examination after the equipment had cooled, about two thirds of the PVC was found unpyrolysed. Because of this a similar run was carried out using less plastic.

Total 'tile' weight 836 g

Total PVC weight (160 g from tiles
448 g as solid PVC)

Equivalent HCl 304 g

Equivalent theoretical HCl conc. in chamber 30.4 g/m³

Actual maximum HCl conc. 3.2 g/m³

Appendix 1C

It seemed from these runs that we would be unable to achieve the expected HCl concentrations even though the CO levels were satisfactory by just pyrolysing PVC and/or PVC covered hardboard. Because it was possible that either the chamber walls or the enormous amounts of water from the burn were scrubbing out the acid, two methods of increasing the HCl concentration by 'doping' were tried.

1. Concentrated hydrochloric acid was sprayed up in the chamber

a. as a test run without any pyrolysis
and

Appendix 1D

b. after the usual pyrolysis run, this gave the following results;

Total PVC weight 240 g

Equivalent HCl in PVC 120 g

Plus 360 ml HCl 130 g

Theoretical HCl conc. in 10 m³ chamber 15 g/m³

Actual maximum conc. 2.25 g/m³

Appendix 1E

2. As adding hydrochloric acid spray did not work, doping with HCl gas was tried.

a. with no PVC pyrolysis, with pure HCl metered into the chamber over a period of thirty minutes. A conc. of 12 mg/l was achieved on the first trial, and 13 mg/l on the second. Approximately 4 mols of HCl was passed into the chamber and this should have resulted in a maximum concentration of 15 g/m³. As this appeared successful a similar run with a PVC 'burn' was carried out.

Total tile weight 1260 g
Total PVC weight 240 g
Equivalent HCl due to PVC 120 g
Plus app. 15 mols HCl 5500 g
Theoretical HCl conc. 77 g/m³
Actual HCl conc. 18.2 g/m³

Appendix 1F

A repeat of this run gave a maximum concentration of 24 g/m³ HCl. As this was close to the hydrogen chloride concentration theoretically obtainable from the PVC input animal exposures were tried.

RUN 1 APPENDIX 2A

A load of 1253 g of PVC faced hardboard was burnt over a period of one hour. At the end of the burn the oxygen level in the chamber was raised to 20.95% from 18.1%, and the carbon monoxide level reduced from 0.95% to 0.46% by ventilation of the chamber. Hydrogen chloride gas was metered into the chamber to give a concentration equivalent to the complete dehydrochlorination of the 240 g of PVC contained in the plastic faced hardboard, ie 12 g/m³. In the event the maximum concentration of HCl obtained was 4.7 g/m³.

Animals (20 guinea-pigs and 20 rats) were then exposed in the chamber for 30 minutes, withdrawn and examined for effects. These runs were repeated, see Appendices 2B and C with the intention of obtaining enough data to provide the basis for a LC₅₀ estimation.

Because of the gross damage to the animals, see later, three control exposures to HCl only were carried out. See Appendices 3A-3C, plus one exposure to pyrolysed plastic only.

Only the major results of the animal exposures are listed here, for the full protocols see the Appendices.

1. PVC burns with added HCl

Run 1	Atmosphere analysis in mg/m ³
CO	5,380
CO ₂	14,640
HCl	2,520

Animal mortalities

	On withdrawal	+3 hours	+24 hours	+7 days
Rats	6/15	7/15	8/15	Rats sacrificed at +24 hours
Guinea-pigs	6/15	6/15	6/15	7/15

The rats were not, as originally intended, kept to one week's observation. Because of the gross damage to eyes, noses, mouth parts and hairless parts of the feet, on humanitarian grounds, surviving animals were killed.

Carboxy-haemoglobin results

Rats	1	95.8%	Dead on withdrawal from chamber
	2	49.9%	Alive o/w
	3	53.3%	"
	4	78.2%	"
	5	71.2%	"
Guinea-pigs	1	85.1%	Dead o/w
	2	85.5%	"
	3	94.1%	"
	4	96.5%	"
	5	40.4%	Alive o/w

RUN 2 APPENDIX 2B

Atmosphere concentrations in mg/m³

CO	4,410
CO ₂	17,100
HCl	4,850

Animal mortalities

	On withdrawal	+24 hours	+3 days
Rats	12/15	15/15	-
Guinea-pigs	8/15	10/15	12/15

Carboxy-haemoglobin results

Rats	1	102%	Dead o/w
	2	95.3%	"
	3	95.5%	"
	4	101.7%	"
	5	47.5%	Alive
Guinea-pigs	1	57.2%	Dead
	2	55.5%	Alive o/w
	3	56.0%	"
	4	39.4%	"
	5	84.6%	"

2. Besides guinea pigs 1-5 which had been pre-selected for COHb estimation advantage was taken of the high mortality figures to obtain further results.

Guinea-pigs	6	57.2%	Dead o/w
	7	72.4%	"
	8	90.9%	"
	9	53.3%	"
	10	77.7%	"

RUN 3 APPENDIX 2C

Atmosphere analysis in mg/m³

CO	5,850
CO ₂	17,020
HCl	8,000

Animal mortalities

	On withdrawal	+2 hours	
Rats	15/15		
Guinea-pigs	10/15	13/15	Remaining two guinea-pigs killed

Carboxy-haemoglobin results

Rats	1	82.9%	Dead o/w
	2	94.3%	"
	3	90.9%	"
	4	91.4%	"
	5	96.8%	"
Guinea-pigs	1	65.1%	Alive o/w
	2	94.3%	"
	3	62.4%	"
	4	85.3%	Dead o/w
	5	81.7%	"

Again dead guinea-pigs provided extra carboxy-haemoglobin results.

6	90.4%	Dead o/w
7	59.0%	"
8	80.7%	"
9	86.3%	"
10	80.8%	"

EXPOSURE TO PVC PYROLYSIS PRODUCTS ONLY, NO ADDED HCl APPENDIX 3D

Atmosphere analysis in mg/m³ for 30 minutes exposure

CO	5,970
CO ₂	18,430
HCl	160

Animal mortalities

	On withdrawal	+24 hours
Rats	12/15	12/15
Guinea-pigs	0/15	0/15

Carboxy-haemoglobin results

Rats	1	89.9%	Dead o/w
	2	96.0%	"
	3	92.6%	"
	4	98.0%	"
	5	48.2%	Alive o/w
Guinea-pigs	1	43.8%	Alive o/w
	2	44.3%	"
	3	49.4%	"
	4	45.5%	"
	5	46.8%	"

DISCUSSION

Under the conditions of our experiments, when no extra HCl was added to the chamber the effluent from burning PVC did not appear more toxic than pure CO gas. The table shows the CO toxicity from reference 2 as against the results from a single experiment using burning PVC faced hardboard.

	CO LC _t ₅₀ from Ref.2	Limits	
1.	CO/CO ₂ mixture	173,000 mg min/m ³	156,600 191,000
2.	Standard plywood burn	145,100 "	125,700 161,400
As against PVC faced hardboard burn (Appendix 3D)			
Mortality			
12/15 exposed animals for a Ct of 179,100 mg min/m ³ CO			

The single result and the atmospheric analysis quoted in the text is consistent with the COHb figures obtained in the rats and guinea-pigs.

If however, the levels of HCl in the chamber after doping are consistent with those concentrations found in a real fire, then a very different picture emerges. For the first time in any of our experiments guinea-pigs died with high COHb levels. Ignoring any toxicity of HCl, the level of COHb, both in the guinea-pig and rats appeared to be enhanced, and most, if not all, the immediate deaths can be attributed to CO poisoning. Added to this is the gross damage caused to all vulnerable tissues by the acid which, (a) almost certainly potentiates the CO toxicity by overbreathing due to excitement, (b) exerts some toxicity of its own as seen in the exposure to HCl only. Machle et al⁵ give a figure of approximately 200,000 mg min/m³ as killing all exposed rats.

We were unable to achieve a satisfactory LC_t₅₀ for HCl only, Cts in the same range gave similar results to Machle.

Added to the potentiation of the CO toxicity and the acute gross tissue damage, a second effect of the HCl, whether as the pure gas or admixed with burning PVC was the long term deaths. In our previous experiments² animals not dying acutely from CO exposure would normally survive. In the case of HCl exposure deaths occurred up to several days. We did not examine the cause of deaths, nor the time course for animals exposed to marginal concentrations of HCl, but, grossly, animals died through inanition, shock, and lung and airway involvement due to damage leading to chemical pneumonitis.

APPENDICES

1. A-F, are the protocols for the preliminary experiments without animals.
 2. A-C, animal exposures to HCl doped PVC pyrolysis effluent.
 3. A-C, animal exposures to HCl only
- D animal exposure to pyrolysed PVC faced hardboard only.

APPENDIX 1A

Six pieces of PVC faced hardboard (wt 1258 g) burnt in FRS apparatus*

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.93	17	17.6	
5'	.04		20.70	264	19.2	
10'	.15		20.50	349	19.0	
15'	.24	.20	20.30	350	19.0	1.64
20'	.38	.40	20.10	353	19.5	
25'	.48	.55	19.85	354	20.2	
30'	.60	.70	19.60	350	20.7	2.20
35'	.84	1.00	19.2	337	20.5	
45'	.90	1.10	19.0	332	20.7	2.34
50'	.95	1.25	18.8	333	20.7	
55'	1.00	1.35	18.6	333	20.5	
60'	1.02	1.45	18.4	334	20.7	2.34

HCl samples were taken as follows

Time	Conc. g/m ³
15'	0.16
30'	0.16
45'	0.21
60'	0.17

*Fire Propagation Test apparatus. Ed.

APPENDIX 1B

1233 g of PVC faced hardboard plus 892 g of solid PVC burnt in FRS apparatus

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.9	32	18.7	
5'	.02		20.9	196	20.2	
10'	.10		20.8	254	20.0	
15'	.15	.18	20.6	248	20.0	1.20
20'	.18	.30	20.4	213	21.0	
25'	.24	.35	20.3	180	20.7	
30'	.25	.35	20.2	157	20.5	1.76
40'	.30	.40	20.0	133	20.7	
45'	.32	.42	19.9	141	21.0	2.20
50'	.35	.48	19.8	139	21.0	
55'	.37	.50	19.7	136	21.3	
60'	.39	.50	19.7	133	21.0	2.37

HCl concentrations

Time	Conc. g/m ³
20'	1.93
40'	2.53
60'	3.10

Unburnt residue, 1465 g,
app. 2/3 of solid PVC
remained intact

APPENDIX 1C

836 g PVC faced hardboard plus 448 g solid PVC burnt

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.9	18	18.2	
5'	.08	.05	20.7	272	18.7	
10'	.175	.22	20.0	300	18.2	
15'	.20	.30	19.4	283	18.2	
20'	.27	.38	19.1	250	19.7	
25'	.40	.45	18.9	228	19.2	
30'	.56	.50	18.9	214	19.2	2.81
35'	.62	.54	18.8	195	19.7	
40'	.67	.58	18.7	176	19.7	
45'	.72	.62	18.7	160	19.7	3.21
50'	.74	.68	18.7	152	20.2	
55'	.72	.70	18.7	145	20.2	
60'	.72	.72	18.7	141	20.2	3.20

HCl concentrations

Time	Conc. g/m ³
30'	1.52
45'	1.93
60'	1.36

APPENDIX 1D

HCl spray trial in 10 m³ chamber, without pyrolysis of PVC.

360 ml of concentrated AR hydrochloric acid sprayed into chamber, using 'Spraying Systems' compressed air nozzle.

Sampled at +5' using 9.0 l/m sampling air flow through bubbler containing 10 ml N NaOH. Total sample = 18 litres.

Concentration 2.53 g/m³

APPENDIX 1E

1250 g PVC faced hardboard pyrolysed as before. At the end of the run, ie 60', the atmosphere analysis was

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
60'	.68	2.65	17.4	356	27.2	1.85

The power to the furnace was turned off, and 360 ml of conc. HCl was sprayed in the direction of the furnace.

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
65'	.66	2.2	17.3	339	25.7	
70'	.66	2.3	17.1	282	27.2	1.43
75'	.66	2.3	17.0	208	26.2	
80'	.66	2.4	16.9	177	26.2	1.27
85'	.66	2.4	16.9	157	25.7	
90'	.66	2.4	16.9	143	25.7	

Residue 430 g

HCl concentrations

Time	Conc. g/m ³
65'	2.25
75'	1.19
85'	0.90

APPENDIX 1F

PVC pyrolysis plus added HCl gas.

1260 g of PVC faced hardboard pyrolysed, at the end of the run, ie 60' the atmosphere analysis was

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
60'	.68	1.25	17.2	302	22.3	2.95

The power to the furnace was then turned off and HCl gas metered into the chamber over a period of 45'

HCl concentrations

Time	Conc. g/m ³
75'	5.3
85'	7.2
95'	12.8
105'	18.2

APPENDIX 2A

1253 g PVC faced hardboard burnt in FRS apparatus.

At the end of the burn, ie 60', the atmosphere analysis was

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
60'	.95	1.60	18.1	312	17.7	2.37

Energy inputs turned off.

CO reduced to 0.46% and O₂ raised to 20.9% by ventilation of chamber and O₂ addition

Time	CO%	CO ₂ %	O ₂ %
75'	.46	.82	20.9

At 75' HCl metered into chamber until z+90'

At 90' animals placed in chamber, until z+120'

Time	CO%	CO ₂ %	O ₂ %
90'	.46	.80	20.9
95'	.46	.80	20.9
100'	.46	.80	20.9
105'	.46	.80	20.9
110'	.46	.80	20.9
115'	.46	.80	20.9
120'	.46	.80	20.9

Residue at end of burn 403 g

HCl concentrations

Time	Conc. g/m ³
90'	2.3
100'	4.7
110'	2.0
120'	1.7

APPENDIX 2B

1260 g of PVC faced hardboard burnt

Atmosphere analysis

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.9	17	19.0	
5'	.03		20.8	243	21.5	
10'	.12	.20	20.4	330	21.3	
15'	.19	.40	20.2	317	21.8	1.10
20'	.26	.55	19.9	302	22.5	
25'	.32	.65	19.7	311	22.8	
30'	.38	.75	19.6	310	23.3	1.67
35'	.48	.85	19.5	297	23.3	
40'	.52	.95	19.3	289	23.8	
45'	.54	1.10	19.1	296	23.5	
50'	.56	1.25	19.0	273	23.0	
55'	.56	1.30	18.9	248	22.8	
60'	.56	1.40	18.7	243	21.5	1.53

NB At T = 40' energy input reduced due to fire bar failure.

At T = 60' CO reduced and O₂ raised and energy off.

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
75'	.34	.80	20.9	-	21.0	.63

2B Cont'd

HCl metered into chamber from T +75' to T +95'

Animals exposed to T +100' to T + 130'

Time	CO%	CO ₂ %	O ₂ %
100'	.35	.85	20.9
105'	.35	.85	20.9
110'	.36	.90	20.9
115'	.38	.95	20.8
120'	.39	.95	20.7
125'	.40	1.00	20.6
130'	.41	1.00	20.6

Unburnt residue 276 g

HCl concentrations

Time	Conc. g/m ³
100'	7.98
110'	3.84
120'	3.80
130'	3.73

APPENDIX 2C

1260 g of PVC faced hardboard burnt

Atmosphere analysis

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.9	17.0	16.7	
5'	.02		20.9	249	18.5	
10'	.13	.10	20.6	318	18.2	
15'	.22	.30	20.4	342	19.2	1.50
20'	.31	.40	20.1	356	20.2	
25'	.40	.65	19.8	358	20.2	
30'	.48	.75	19.6	363	20.2	2.40
35'	.56	.85	19.3	366	20.2	
40'	.64	1.00	19.0	377	20.0	
45'	.68	1.10	18.7	382	20.0	2.30
50'	.70	1.25	18.4	402	20.0	
55'	.72	1.35	18.2	402	20.5	
60'	.74	1.45	18.0	402	20.7	2.30

Energy input off at 60'

CO and O₂ levels adjusted

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
75'	.50	1.00	21.1	-	20.2	1.73

2C Cont'd

HCl metered into chamber from 75'-105'

Animals exposed from 105'-135'

Time	CO%	CO ₂ %	O ₂ %
105'	.52	1.00	21.0
110'	.50	.95	20.9
115'	.50	.95	20.9
120'	.50	.90	20.9
125'	.50	.90	20.9
130'	.50	.90	20.9

Unburnt residue 426 g

HCl concentrations

Time	Conc. g/m ³
104'	12.8
114'	6.7
124'	6.6
134'	5.9

APPENDIX 3A

Run 1 - HCl metered into chamber, and animals exposed for 30'

Time	HCl conc. g/m ³
5'	19.2
10'	25.9
20'	21.1
30'	22.8

Mean HCl concentration = 22.25 g/m³

HCl Ct: 667,500 mg min/m³

Animal mortalities:

	On withdrawal	+2 h	+4 h
Rats	6/15	11/15	15/15
Guinea pigs	15/15		

APPENDIX 3B

Run 2 - As above.

Time	HCl conc. g/m ³
5'	6.5
10'	6.7
20'	6.3
30'	7.1

Mean HCl concentration = 6.65 g/m³

HCl Ct: 199,500 mg min/m³

Animal mortalities:

	On withdrawal	+5 h	+24 h
Rats	0/15	10/15	15/15
Guinea pigs	12/15	12/15	15/15

APPENDIX 3C

Run 3 - As above

Time	HCl conc. g/m ³
5'	3.0
10'	3.4
20'	3.7
30'	3.9

Mean HCl concentration = 3.50 g/m³

HCl Ct: 105,000 mg min/m³

Animal mortalities:

	On withdrawal	+5 h
Rats	0/15	10/15
Guinea pigs	12/15	13/15

APPENDIX 3D

1230 g of PVC faced hardboard pyrolysed with no added HCl

Atmospheric analysis

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
0'			20.9	19	19.2	
5'	0.05		20.8	248	21.5	
10'	.16	.20	20.6	317	21.8	
15'	.25	.40	20.4	340	22.0	1.19
20'	.36	.60	20.1	345	22.3	
25'	.48	.75	19.9	350	22.3	
30'	.58	.90	19.6	353	22.5	1.75
35'	.68	1.10	19.3	349	22.7	
40'	.74	1.25	19.0	338	23.0	
45'	.80	1.30	18.9	327	23.3	1.81
50'	.84	1.40	18.7	329	22.5	
55'	.86	1.50	18.5	323	21.8	
60'	.88	1.65	18.3	305	21.5	1.74

Energy input off at 60'

CO and O₂ levels adjusted

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
75'	.50	.95	21.1	-	22.5	-

3D Cont'd

Animals exposed from 80-110'

Time	CO%	CO ₂ %	O ₂ %	Furnace °C	Chamber °C	Smoke g/m ³
80'	.50	.95	21.1	-	-	-
85'	.50	.95	21.0	-	-	-
90'	.50	.95	21.0	-	-	.92
95'	.51	1.00	20.9	-	-	-
100'	.52	1.05	20.9	-	-	.63
105'	.52	1.05	20.9	-	-	-
110'	.52	1.10	20.9	-	-	.62

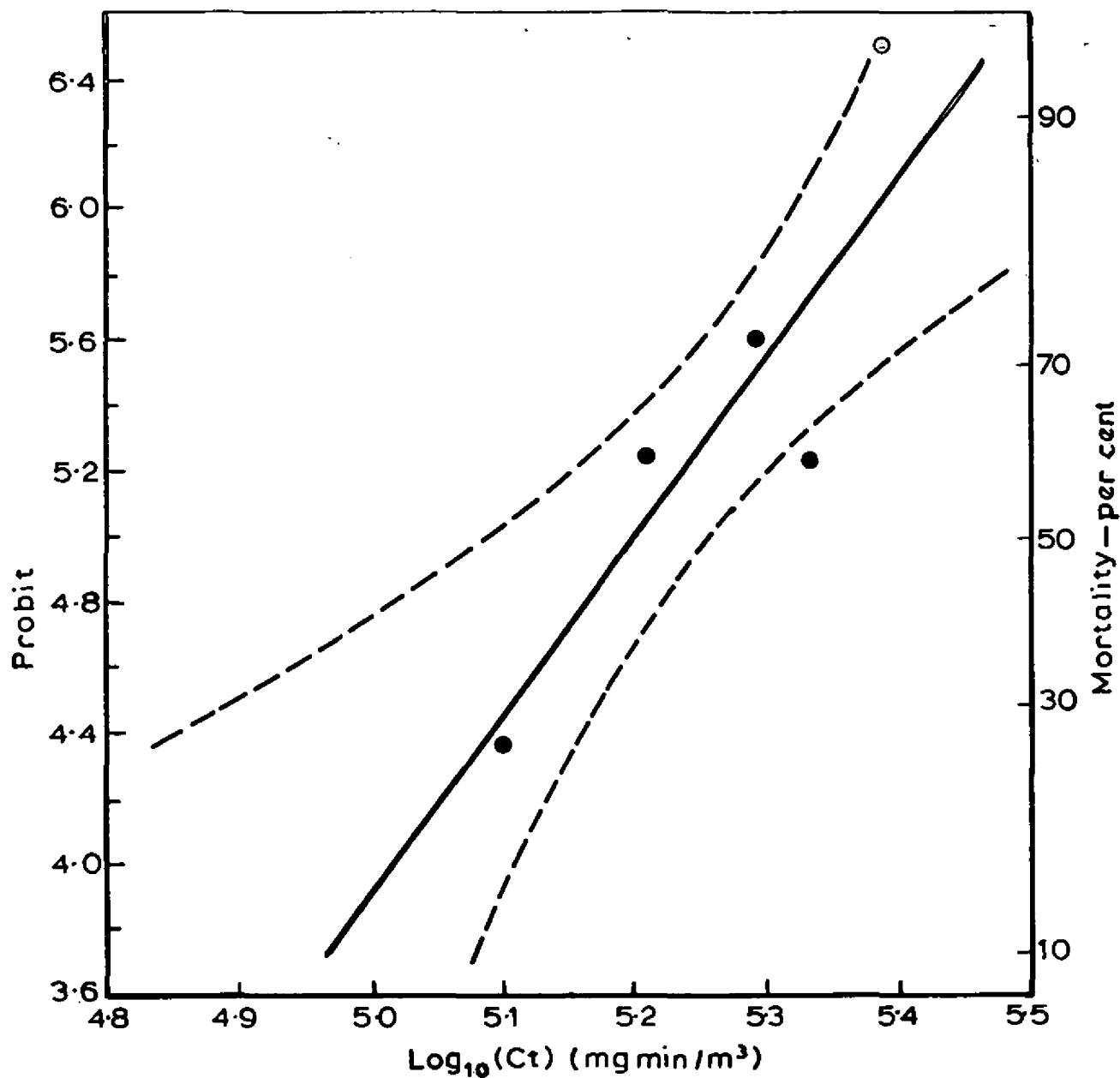
Residual matl. 306 g

HCl concentration app. 160 mg/m³

REFERENCES

1. WOOLLEY, W D. Br. Polym. J., 1971, 3, 186.
2. EDGINGTON, J A G and LYNCH, R. The acute inhalation toxicity of carbon monoxide from burning wood. Department of the Environment and Fire Offices' Committee Joint Fire Research Organization Fire Research Note No.1040 1975.
3. STARK, G W V and FIELD, P. Toxic gases and smoke from polyvinyl chloride in fires in the FRS full-scale test rig. Department of the Environment and Fire Offices' Committee Joint Fire Research Organisation Fire Research Note No.1030 1975.
4. HENDERSON, Y and HAGGARD, H W. Noxious gases and the principles of respiration influencing their action. Reinhold Publishing Corporation, New York, 1943.
5. MACHEL, W, KITZMILLER, K V, SCOTT, E W and TREON, J F. The effect of the inhalation of hydrogen chloride. J. Ind. Hyg. Toxicol. 1942 24 222.
6. DARMER, K J, KINKEAD, E R and DiPASQUALE, L C. Acute toxicity in rats and mice exposed to hydrogen chloride gas and aerosols. Amer. Ind. Hyg. Assoc. J. 1974, 35, 623.
7. HIGGINS, E A, FIORCA, V, THOMAS, A A and DAVIS, H V. Acute toxicity of brief exposures to HF, HCl, NO₂ and HCN with and without CO. Fire Technology 1972, 8, 120.
8. CORNISH, H H and ABAR, E L. Toxicity of pyrolysis products of vinyl plastics. Arch. Environ. Health 1969 19 15.
9. HOFMANN, H Th and OETTEL, H. Zur Relativen Toxizitat von Kunststoff-Verschwendungs-produkten am Beispiel von Hartschaumstoffen aus Polystyrol. Kunststoff-Rundschau 1968, 15 (6).
10. Idem. Comparative toxicity of thermal decomposition products. Modern Plastics. October 1969.
11. Hofmann, H Th and SAND, H. Further investigations into the relative toxicities of decomposition products. J. Fire and Flammability, Combustion Toxicology Supplement, 1974, 1, 250.
12. KISHITANI, K. Study on injurious properties of combustion products of building materials at initial stage of fire. J. Faculty of Engineering. University of Tokyo (B) 1971, 31 (1) 1.

13. KISHITANI, K and NAKAMURA, K. Toxicities of combustion products. J. Fire and Flammability. Combustion Toxicology Supplement 1974, 1, 104.
14. SUMI, K and TZUCHIYA, Y. Toxicity of decomposition products - polyvinyl chloride and wood. National Research Council, Canada. Division of Building Research, Building Research Note No.99 1975.
15. WOOLLEY, W D. Studies of the dehydrochlorination of PVC in nitrogen and air. Plastics and polymers 1972, 40 (148) 203.



C = Concentration of carbon monoxide mg/m³

t = 30 min

— Regression line

- - - 95 per cent confidence limits

Figure 1 Probit regression for mortalities of rats exposed 30 min to combustion products of wood (Ref 2)