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TOXIC GASES AND SMOKE FROM POLYVINYL CHLORIDE IN FIRES - STATISTICAL ANALYSIS OF TEST RESULTS

by

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SUMMARY

In order to assess quantitatively the products of combustion due to plastics, large scale tests were conducted at the Fire Research Station. The three factors investigated were crib load, weight of PVC and width of ventilation opening. Two levels of each factor were considered. The observations presented for statistical analysis were maximum temperature, maximum concentrations of carbon dioxide and carbon monoxide and minimum oxygen. Classical analysis of variance was not possible especially in view of the fact that the observations were extreme values. A suitable technique has been developed and described in this note for comparing the two levels of one factor at constant levels of all other factors. Suggestions are given for further experimentation and statistical analysis.

Department of the Environment and Fire Offices' Committee
Joint Fire Research Organization

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INTRODUCTION

A major part of combustible material in buildings, particularly dwellings, is cellulosic in origin. However, during the past few years synthetic plastics have been increasingly used, augmenting and replacing cellulosic materials. The involvement of plastics in fires in buildings may alter the amount and composition of the products of combustion, viz smoke and toxic gases.

In order to assess quantitatively the products of combustion due to plastics, large scale tests were conducted at the Fire Research Station. A complete description of the test rig used, data recorded and other details of these tests is given in a separate Fire Research Note[1]. In this note the statistical analysis of the test results is discussed. It was necessary to develop a suitable technique for this purpose since the observations were presented as extreme (maximum or minimum) values. Classical methods of analysis of variance are not applicable to such data.

TEST CONDITIONS

The test rig consisted of compartment and corridor. The end of the corridor close to the compartment was sealed and the other end left unrestricted. The only opening in the compartment was that communicating with the corridor and extending to ceiling height. Air for combustion and the resultant smoke and fire gases passed through the corridor, entering the compartment through this opening, the width of which was either 240 mm or 700 mm.

The basic fire loads of wood consisted of cribs of sticks laid so as to form a stack of square base to give weights of 120.5 and 241 kg. For those tests in which it was present, 95 kg of rigid PVC sheet was attached to the walls of the compartment by mushroom-headed nails.

Conditions of test did not permit full control of the moisture content of the fuels and the compartment but the compartment was heated before tests to above ambient temperature for a time sufficient to dry out the cellulosic adhesive and in most tests to reduce the moisture content of the wood to less than 12 per cent.

VARIABLES MEASURED

The temperature of the fire gases was measured 150 mm below the ceiling at the opening between the compartment and at 2 m intervals along the corridor to 10 m away at the open end of the corridor. Recording was maintained throughout the main flaming period and continued until the temperature at the compartment opening was less than 300°C.

Samples of fire gases were withdrawn through internally lacquered stainless steel sampling tubes which were heated resistively to at least 150°C, and collected for subsequent analysis. Samples were collected from the opening between compartment and corridor and 10 m away at the open end of the corridor. Separate tubes were used for the measurement of concentrations of oxygen, carbon dioxide and carbon monoxide. Concentration of nitrogen, speed of entry of air into the corridor and the optical density of the smoke plume were other variables measured but these are not included in this analysis.

RESULTS

The tests were not designed statistically. Hence out of 14 tests conducted only 10 are amenable for some form of statistical analysis. Extreme values for gas concentrations and temperatures recorded in these 10 tests are given in Appendix 1 together with test conditions (factors).

ANALYSIS OF RESULTS

It is known[2] that extreme values have highly skewed probability distributions and that such observations cannot be transformed to follow the normal distribution. Also the tests did not fit into any standard experimental design and were small in number. For these reasons it is impossible to carry out the classical analysis of variance and test the significance of the interactions as well. Hence it became necessary to develop a special test of significance which would take into consideration the extreme value nature of the population. This test and the mathematics leading to it are described in Appendix 2. The following is an example of their application.

For any given variable the test could be applied to compare two levels of one factor at fixed levels of other factors. Consider the following table.

Table 1

Maximum temperature at vent position

Levels of other factors (kg)		Vent width levels (V) 240 mm	700 mm
L (Load)	P (PVC)	Maximum temperature (x)	Maximum temperature (x)
120.5	0	870	925
120.5	95	950	975
241	0	960	1100
241	95	1010	1020
103.5) 137.5)	0	960	1070

It is assumed that the scale parameter 'a' is the same for all the observations. For the 10 observations, viz maximum temperature (x), the standard deviation (σ_x) is 68.06. According to Gumbel[2] the standard deviation of y (σ_y) for N = 10 is 0.9497. Hence, from equation (6) in Appendix 2 the estimated value of 'a' is

$$a = \frac{0.9497}{68.06} = 0.0139$$

Also the averages of the maximum temperatures for the two vent levels are

$$\bar{x}_{240} = \tfrac{1}{5}(870 + \ldots .\ 960) = 950$$

$$\bar{x}_{700} = \tfrac{1}{5}(925 + \ldots .\ 1070) = 1018$$

The value of $\bar{y}$ for N = 5 obtained from (3) and (5), Appendix 2, is 0.4588. Hence, from (7), Appendix 2,

$$b_{240} = 950 - \frac{0.4588}{0.0139} = 917$$

$$b_{700} = 1018 - \frac{0.4588}{0.0139} = 985$$

The 'y' values and the 'z' test statistic have been calculated using equations (2) and (17), Appendix 2. These values are shown in the following table.

Table 2

Reduced values y and z

Levels of other factors (kg)		Vent width levels (V) 240 mm	700 mm	$Z = \left\{ \left\| y_{240} - y_{700} \right\| \div 2 \right\}$
L (Load)	P (PVC)	y values	y values	
120.5	0	-0.6533	-0.8340	0.0904
120.5	95	0.4587	-0.1390	0.2989
241	0	0.5977	1.5985	0.5004
241	95	1.2927	0.4865	0.4031
103.5) 137.5)	0	0.5977	1.1815	0.2919

For (2,2) degrees of freedom (Appendix 2) the Table value of 'z' for 10 per cent level of significance is 1.0986. In all the 5 cases the observed Z values shown in Table 2 were less than the theoretical value 1.0986. Hence, for any fixed levels of other factors the difference between maximum temperatures for the two levels of ventilation was not significantly different from the difference between the average of all maximum temperatures for the two levels of ventilation irrespective of the levels of the other factors. This would imply that there was no significant difference between the maximum temperature at the vent position for the two ventilation levels for any fixed level of other factors; hence the interactions LV and PV are not likely to be significant. As mentioned in Appendix 2 it is not possible to test at this stage the significance of the overall difference between the average maximum temperatures at the two levels of ventilation $(\bar{x}_{240} - \bar{x}_{700})$.

Two more tables similar to Table 1 could be formed for maximum temperature for comparing load and PVC levels. Hence, in all there are 24 tables corresponding to the eight variables for which measurements were made and recorded in Appendix 1. Each table has at least three comparisons. The comparisons which led to significant differences at the 25 per cent level or less are summarised in Table 3.

Table 3

Significant comparisons

Measurement	Factors compared	Fixed factors	Z	Significance level per cent
Max temp vent	P_0 v P_{95}	L_{241} + V_{700}	0.689	21
Max CO_2 vent	V_{240} v V_{700}	P_{95} + L_{241}	0.898	15
" " "	P_0 v P_{95}	L_{241} + V_{240}	0.563	25
Max CO vent	V_{240} v V_{700}	P_0 + L_{241}	0.726	19
" " "	P_0 v P_{95}	$L_{120.5}$ + V_{240}	1.066	11
" " "	P_0 v P_{95}	L_{241} + V_{700}	0.936	14
" " "	$L_{120.5}$ v L_{241}	P_{95} + V_{240}	0.971	13
" " "	$L_{120.5}$ v L_{241}	P_0 + V_{700}	0.842	16
Min O vent (Test 7 excl)	P_0 v P_{95}	$L_{120.5}$ + V_{240}	0.702	20
Max CO_2 corr.	P_0 v P_{95}	L_{241} + V_{700}	0.589	24
Max CO corr.	V_{240} v V_{700}	$L_{120.5}$ + P_{95}	0.581	24
" " "	P_0 v P_{95}	$L_{120.5}$ + V_{240}	0.578	24
Min O corr.	P_0 v P_{95}	L_{241} + V_{700}	0.731	19
" " "	$L_{120.5}$ v L_{241}	P_{95} + V_{700}	0.597	24

DISCUSSION

For the reasons mentioned earlier it was not possible to carry out the usual analysis of variance. Hence, in order to get some tentative ideas about significant comparisons a test of significance is developed and applied in this note. For strengthening the conclusions, further experimentation and research on the following lines would be needed.

Future tests could be planned to fit into a 2^3 factorial design with the three factors, ventilation, crib load and weight of PVC. The eight tests already done (excluding tests 6 and 9 shown in Appendix 1) and analysed in this note, should be augmented with two more replications each of 8 tests. With 24 tests in all it would be possible to develop an analysis of variance using extreme values and draw meaningful conclusions on the interactions of the factors examined.

A graphical analysis revealed that the variables as such (without any transformation) belong to exponential type distributions as first approximations. However, it is advisable to have this result confirmed either by a detailed study of the stochastic processes governing the variables or by an empirical method using sufficient data. In the latter case, measurements on the variables taken at various times and points during each test could be used.

In regard to the statistical theory, further research is required to develop an analysis of variance model for extreme observations. The eight variables measured could be expected to have correlations between them. Such correlations would yield further useful information about the toxic effects of PVC. Hence, research into statistical methods concerning bivariate or multivariate extremes would also be necessary.

CONCLUSIONS

None of the comparisons were significant at the conventional probability level of 5 per cent. However, in view of the small number of tests conducted, it is advisable to base the preliminary conclusions at a higher level, say, 25 per cent. Table 3 shows the factors at certain fixed levels of other factors which are likely to affect the variables studied. For example, it may be seen from Table 3 that in a fire there are significant effects on the maximum temperature, carbon monoxide and carbon dioxide all measured at the vent position with and without PVC while the crib load is held at 241 kg. At present, it is not possible to judge the significance of the difference between the overall (mean) values for the two levels of any factor. Further experimentation and analysis are necessary to draw final conclusions.

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2. GUMBEL, E J. Statistics of extremes. Columbia University Press, 1958.

APPENDIX 1

TEST RESULTS

Test No	1	2	3	4	5	6	7	8	9	10
Factors (Conditions) Load (L) crib	120.5	120.5	120.5	120.5	241	103.5	241	241	103.5	241
kg wall						137.5			137.5	
PVC (P) kg	0	95	0	95	0	0	95	0	0	95
Vent (V) mm	240	240	700	700	240	240	240	700	700	700
Observations (variables) Max Temp Vent	870	950	925	975	960	960	1010	1100	1070	1020
" Corr	300	300	420	430	380	570	340	635	680	550
Max CO_2 Vent	18.8	14.6	17.7	16.4	14.2	12.9	6.4	13.7	12.1	14.5
Max CO Vent	0.2	4.6	1.1	2.0	3.5	4.8	1.8	6.0	2.4	1.9
Min O Vent	2.3	4.8	2.8	1.4	8.2	6.8	-	5.0	7.2	4.5
Max CO_2 Corr	7.0	6.0	9.1	7.7	8.2	11.4	-	14.1	13.1	7.3
Max CO Corr	0.8	2.3	0.3	0.35	2.7	1.1	-	1.6	1.3	1.8
Min O Corr	14.5	13.8	12.2	11.8	11.9	9.2	-	7.0	7.1	12.8

APPENDIX 2

EXTREME VALUE THEORY AND TEST OF SIGNIFICANCE

Extreme value distributions

The theory of extreme values is concerned with the statistical analysis of maximum or minimum values. Its application to fire losses has been investigated in Fire Research Note 837[1] and subsequent notes and papers.

The first step is to identify the nature of the parent probability distribution. This is the distribution of probabilities with which a variable would take different values at different times during each test. The exact nature of this distribution would depend upon the physical, stochastic and other factors governing the changes of the variable over time. However, it is reasonable to expect a variable either in original units or in transferred scale to follow a distribution of the exponential type. This type[2] includes well known distributions like normal, gamma, chisquare logistic and the simple exponential function.

The test observations subjected to statistical analysis were extreme values ie maximum (or minimum) from parent distributions of exponential type. Maximum values are known to have the following probability density function[2]

$$\varphi(y) = e^{-y-e^{-y}}\, dy \qquad -\infty \leqslant y \leqslant \infty \qquad (1)$$

where

$$y = a(x-b) \qquad (2)$$

The maximum value is denoted by the variable x. The parameters a and b are constants depending upon the variable.

There is a simple graphical method to test whether the observed maximum values fit the distribution in expression (1). Suppose there are N observations available for the maximum, say, x_i (i = 1,....N). If they are arranged in increasing order let R_i be the rank of x_i. The empirical value of the cumulative frequency of x_i is

$$\Phi(x_i) = \frac{R_i}{N+1} \qquad (i = 1, \cdots N) \tag{3}$$

The value of y_i corresponding to x_i is given by

$$\begin{aligned} \Phi(x_i) &= \Phi(y_i) \\ &= \int_{-\infty}^{y_i} e^{-y-e^{-y}}\, dy \\ &= e^{-e^{-y_i}} \end{aligned} \tag{4}$$

Hence from (3) and (4)

$$y_i = -\log_e \left[-\log_e \left\{ \frac{R_i}{N+1} \right\} \right] \tag{5}$$

The values of y_i for different Φ have been tabulated by the National Bureau of Standards[3]. If the points (y_i, x_i), $i = 1, \ldots N$ plotted on a graph show approximately a straight line relationship then the assumption that observations x_i are maximum values from an exponential type distribution is justified. (If not, it is likely that transformed values of x_i have a linear regression with y_i).

The parameters a and b could be estimated from (2) either graphically or by the method of least squares. If the method of moments is used the estimated values are given by

$$a = \frac{\sigma_y}{\sigma_x} \tag{6}$$

and

$$b = \bar{x} - \frac{\bar{y}}{a} \tag{7}$$

where $\bar{x}$ and σ_x are the average and standard deviation of x_i and $\bar{y}$ and σ_y the average and standard deviation of y_i for the N values given by (5).

If N is large the following asymptotic values[2] could be used

$$\bar{y} = 0.5772$$

$$\sigma^2 = 1.6449$$

In the case of the minimum value denoted by x'_i the density function is

$$\varphi(y') = e^{y' - e^{y'}} \qquad (8)$$

with

$$y' = a'(x' - b') \qquad (9)$$

We also have the cumulative frequency of x'_i as

$$\Phi(x'_i) = \frac{R'_i}{N+1} \qquad (10)$$

where R'_i is the rank of x'_i in an arrangement in increasing order. The value of y'_i corresponding to x'_i is given by

$$\Phi(x'_i) = \Phi(y'_i)$$

$$= \int_{-\infty}^{y'_i} e^{y - e^{y}} \, dy$$

$$= 1 - e^{-e^{y'_i}} \qquad (11)$$

so that from (10) and (11)

$$1 - \Phi(x'_i) = e^{-e^{y'_i}}$$ or

$$y'_i = \log_e \left[- \log_e \left\{ \frac{N + 1 - R'_i}{N+1} \right\} \right] \qquad (12)$$

The method of estimation of a' and b' is similar to the method for a and b pertaining to the maximum values x_i. For large N the average value of y'_i is given by − 0.5772 but the variance is 1.6449.

Test of significance

From (1) it may be deduced that the transformed variable

$$\xi = 2e^{y} \tag{13}$$

has the distribution

$$f(\xi) = \frac{1}{2} e^{-\frac{\xi}{2}} \tag{14}$$

which is a chisquared distribution with 2 degrees of freedom. For (n-1) degrees of freedom the chisquared distribution is[4]

$$f(\chi^2) = \frac{1}{2^{\frac{n-1}{2}}\,\Gamma\left(\frac{n-1}{2}\right)} e^{-\frac{\chi^2}{2}} (\chi^2)^{\frac{n-3}{2}} d(\chi^2) \tag{15}$$

The ratio

$$F = \frac{\chi_1^2/(n_1-1)}{\chi_2^2/(n_2-1)}$$

of two chisquared variables χ_1^2 and χ_2^2 with (n_1-1) and (n_2-1) degrees of freedom respectively has the well known 'F' distribution[4]. The variable

$$z = \frac{1}{2}\log F \tag{16}$$

has the z distribution which has been tabulated[5] for selected probability points. For any probability level see Appendix 3.

In the case of the maximum value

$$n_1 - 1 = n_2 - 1 = 2 \qquad \text{From (13) and (16)}$$

$$z = (y_2 - y_1)/2 \tag{17}$$

has the z distribution with two degrees of freedom for both y_2 and y_1 pertaining to two maximum values x_2 and x_1 from two different populations. As in a 'F' test the values y_2 and y_1 should be so taken that $\xi_1 = 2e^{-y_1}$ is greater than $\xi_2 = 2e^{-y_2}$.

Suppose we wish to test whether x_2 is significantly different from x_1. It may be assumed that the two random variables have the same parameter 'a' but different location parameters b_1 and b_2. By considering replicated observations the parameters a, b_1 and b_2 should be first estimated by one of the methods described earlier. Then for each pair of values (x_1, x_2) calculate y_1 and y_2 from (2) and Z using (17). For (2, 2) degrees of freedom the table value of Z is 1.0986 for 10 per cent level. Significance of the difference between y_2 and y_1 at this level would occur if the observed value of Z is greater than the table value. Similarly significance at other levels of probability could be tested

From (2) and (7)

$$(x_2 - x_1) = (b_2 - b_1) + \frac{(y_2 - y_1)}{a}$$

$$= (\bar{x}_2 - \bar{x}_1) + \frac{(y_2 - y_1)}{a}$$

Hence if the difference $(y_2 - y_1)$ is significantly different from zero it would imply that the difference $(x_2 - x_1)$ is significantly different from the overall difference $(\bar{x}_2 - \bar{x}_1)$. At the present stage it is difficult to construct a technique to test the difference between $\bar{x}_2$ and $\bar{x}_1$.

In the case of the minimum value x', from (8), the transformed variable

$$\xi' = 2e^{y'}$$

has the chisquared distribution with 2 degrees of freedom. The test for the difference between y'_2 and y'_1 is similar to the test for y_2 and y_1. The random variables y'_2 and y'_1 would correspond to two minimum values x'_2 and x'_1 from two independent populations. The test statistic is

$$Z' = (y'_1 - y'_2)/2$$

if $\xi'_1 = 2e^{y'_1}$ is greater than $\xi'_2 = 2e^{y'_2}$ or

$$Z' = (y'_2 - y'_1)/2$$

if $\xi'_2 > \xi'_1$

APPENDIX 3

Fisher and Yates[5] tabulate values of the Z statistic at only a few probability points. For the purposes of the significance test described in Appendix 2, the values of the Z statistic with two and two degrees of freedom only are required. These can be obtained easily for any probability level as follows:

The F statistic with m and n d.f. has the probability density function

$$h(F) = \frac{\Gamma\left(\frac{m+n}{2}\right)}{\Gamma\left(\frac{m}{2}\right) . \Gamma\left(\frac{n}{2}\right)} \cdot \frac{\left(\frac{m}{n}\right)^{\frac{m}{2}} F^{\frac{m-2}{2}}}{\left(1 + \frac{m}{n}F\right)^{\frac{m+n}{2}}} dF \quad , F > 0$$

Let $\omega = \dfrac{\frac{m}{n}F}{1 + \frac{m}{n}F}$ then $dF = \dfrac{n}{m} \dfrac{1}{(1-\omega)^2} d\omega$

so that $$g(\omega) = \frac{\Gamma\left(\frac{m+n}{2}\right)}{\Gamma\left(\frac{m}{2}\right) \Gamma\left(\frac{n}{2}\right)} \omega^{\frac{m-2}{2}} (1-\omega)^{\frac{n-2}{2}} d\omega$$

i.e. $$\omega \sim \beta\left(\frac{m}{2}, \frac{n}{2}\right) \qquad 0 \leqslant \omega \leqslant 1$$

$\therefore$ letting $m = n = 2$ gives $g(w) = 1 \qquad 0 \leqslant w \leqslant 1$

Hence, the α % point of the w-distribution is given by

$$\omega = 1 - \alpha$$

so that $$F_{2,2,\alpha} = \frac{1-\alpha}{\alpha}$$

$$\therefore \qquad Z_{2,2,\alpha} = \frac{1}{2} \log_e \left\{ \frac{1-\alpha}{\alpha} \right\}$$

Using this, the values of $Z_{2,2,\alpha}$, $\alpha = 0.01(0.01)0.25$ have been calculated, and are shown in Table 1.

Table 1

Critical values of $Z_{2,2,\alpha}$, $\alpha = 0.01(0.01)0.25$

α x 100	$Z_{2,2,\alpha}$	α x 100	$Z_{2,2,\alpha}$
1	2.298	14	0.908
2	1.946	15	0.867
3	1.738	16	0.829
4	1.589	17	0.793
5	1.472	18	0.758
6	1.376	19	0.725
7	1.293	20	0.693
8	1.221	21	0.662
9	1.157	22	0.633
10	1.099	23	0.604
11	1.045	24	0.576
12	0.996	25	0.549
13	0.950		

REFERENCES FOR APPENDICES 2 AND 3

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