

Hazards of Combustion Products

QUANTIFYING THE COMBUSTION PRODUCT HAZARD ON THE BASIS OF TEST RESULTS

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Abstract

In any countries where fire death causes have been studied in detail, it invariably is found that most of the fire fatalities are due the inhalation of toxic combustion gases. In the toxicology community, the toxicity of inhalable substances is normally assessed by the use the variable “LC₅₀.” Thus, some regulatory entities have considered it appropriate to identify this LC₅₀ variable as a suitable test result by which to categorize, control, or limit the combustion product hazard of various materials or products.

Such a strategy is technically unsound and does not capture the essence of the hazard that is intended to be regulated. This is because it does not quantify the amount of toxic gases that are being released from the combustion of the product in question. Even gases which are highly toxic per-gram, can be easily tolerated if the amount released is small. Conversely, even gases which have a fairly limited toxic potency will not be acceptable, if they are generated in great profusion. By endeavouring to control solely the LC₅₀, this essential principle is overlooked.

Test results are examined for a diverse collection of products where the toxicity was characterized extensively in both bench-scale and full-scale tests. It is shown that (a) the essential characteristics of the full-scale combustion product toxic hazard are adequately described by using the full-scale heat release rate (HRR) as the primary variable; and (b) that the contribution of the measured LC₅₀ values to the assessment of the full-scale combustion product hazard is so small that it can be disregarded. From the manufacturer’s point of view, the same conclusion holds: the successful strategy to reduce the fire hazard of a product is to reduce its HRR, not to endeavour to improve its LC₅₀ value. The above conclusions are pertinent to building products and to most other industry sectors, with the exception of storage of hazardous chemicals. The latter is not within the scope of treatment here, but it is recommended that specific toxic hazard analyses be performed if the fire threat of such situations is to be properly assessed. This is because chemicals might potentially be encountered which produce exceedingly toxic substances when involved in fire, of a much worse order of magnitude than what occurs in fires in other types of occupancies.

Keywords: Cone Calorimeter; DIN 53 436 test; fire hazard analysis; fire toxicity; ISO 5660 test; pipe insulation; room-corner fire tests; sandwich panels; wall insulation.

Introduction

The measurement of combustion product toxicity in full-scale tends to be costly and difficult. Consequently, it is rarely done for research [1][2][3] and very rarely for actual evaluation of products. Instead, has been more common to attempt to use bench-scale data in product assessment, even when its relation to full-scale performance is not yet established. Typically, the variable selected has been the *toxic potency*, denoted as LC₅₀. This can most simply be visualized as a ‘per-gram toxicity,’ since the variable is not affected by the burning rate of the product nor by the amount of product present. Its units are (g m⁻³) and the scale is an *inverse* one, since the LC₅₀ represents the amount of substance to be dispersed into 1 m³ in order to cause a 50% probability of lethality.

Hazards of Combustion Products

In the U.S. a few years ago the legislature of one large State [4] mandated product testing for toxic fire hazard, wherein the only variable to be reported was the bench-scale LC_{50} (albeit an LC_{50} with a non-standard definition). Furthermore, the State officials specifically encouraged [5] users to evaluate products by ranking them on the bench-scale LC_{50} scale. Fortunately, the regulation was eventually rescinded* [6], but not before significant efforts were consumed in an unproductive activity. This lesson was not sufficiently learned world-wide, and it is important to develop the understanding why this was an unfruitful strategy. Superficially, it is a simple strategy, easily amenable to the regulator, and therefore with some intrinsic attraction. Thus, it is essential to examine in detail why it is technically unsound.

Internationally, ISO 13344 [7], was the first normative international standard to address the issue of fire toxicity when the first edition was issued in 1996. It mandated that the user select from one of eight bench-scale tests for toxic potency, as listed in the non-normative ISO TR 9122-4 [8]. The user was instructed to conduct product tests, measure the toxic gases evolved, and quantify the toxic effect by reporting the LC_{50} . The standard contained *caveats* against solely relying on the reported result for assessing product hazard. However, it did not provide any information on suitable computational techniques for assessing the toxic fire hazards in real-fire situations, nor did it point the user towards other numerical data which need collecting. The standard is now in its second edition (2004), but the limitations also remain in the new edition.

In simple terms, one can consider that the toxic impact on a potential victim in a fire is comprised of two factors: a rate and an intensity. This is true in general for the delivery of any dispersed substance or quantity. In the case of combustion toxicity, the rate is the burning rate. This would most precisely be described in units of kg/s, which is termed mass loss rate (MLR). MLR is generally not reported in large-scale tests. This primarily is because, if the large-scale test is a room test, the material or product which will often be of interest is something that can be put on walls or on the ceiling. In such a case, it becomes very difficult to actually make an MLR measurement. By contrast, HRR measurements are very well established [9] and these are routinely made in such tests. The HRR (kW) can be expressed as $HRR = MLR \times \Delta h_{c,eff}$, where MLR = mass loss rate ($kg\ s^{-1}$), and $\Delta h_{c,eff}$ = effective heat of combustion ($kJ\ kg^{-1}$). The gamut of values encompassed by HRR would be identical to that of MLR if $\Delta h_{c,eff}$ were a constant. It is not, but the data spread is not large; cellulosic combustibles are typically around 12 – 15 $MJ\ kg^{-1}$, while plastics are generally 20 – 40 $MJ\ kg^{-1}$. Conceptually, then,

$$\text{Toxic hazard} \propto MLR \times (\text{per-gram-toxicity})$$

This expression combines the rate (MLR) and the intensity (per-gram-toxicity) to give an expression of the rate at which the hazard is evolved. Now, in inhalation toxicology, the primary ‘intensity’ variable is termed LC_{50} and it has the units of concentration, $g\ m^{-3}$. The term is so denoted because it represents the concentration that is lethal, at the 50% level of probability. This scale is an *inverse* one, in other words, the lower the number the more toxic is the substance. Thus, we can write per-gram-toxicity = $1/LC_{50}$. Putting this together,

$$\text{Toxic hazard} \propto MLR \times (\text{per-gram-toxicity}) = \frac{HRR}{\Delta h_{c,eff}} \times \frac{1}{LC_{50}}$$

And, accepting that $\Delta h_{c,eff}$ does not vary by much among practical combustibles,

$$\text{Toxic hazard} \propto \frac{HRR}{LC_{50}}$$

Now the question to be determined is: Does one of these two variables show a wide spread of data, and the other a small spread? If this is true, then it will make hazard assessment much easier, since only one variable needs to be taken into account. This question can be answered by looking at experimental data.

* The City of New York also had a similar regulation but this has not yet been rescinded.

Hazards of Combustion Products

NIST studies

The earliest study [10] on this question was published by Babrauskas in 1992. In that study, some 1980s data obtained by NIST were examined. The HRR for an assortment of furniture items had been studied in full scale. The range of peak HRR values found is shown in Figure 1. From best to worst, a range of 100:1 was found. Figure 1 also shows the range of toxic potencies (LC_{50}) that was found. Due to availability of data, the LC_{50} range that was studied comprised not just furniture materials, but all products tested at NIST up to that time. This LC_{50} range is approximately 4:1. This gave the first indication of where the problem was, versus where it was not. A follow-on study examined the effect of room fire conditions [11]. After extensive research at NIST, it was found that post-flashover fires show some very specific carbon monoxide (CO) generation traits [12]. While CO yields in small, free-burning fires are highly variable, all types of combustibles tested in post-flashover fires produce a very large yield of CO. That post-flashover CO yield is essentially constant among fuel types and is invariably close to 0.20 kg CO produced/kg fuel burned. Consequently, since CO is a dominant toxicant in most fires, the range of LC_{50} values shrinks further, if post-flashover fires are considered. It must be emphasized that the pertinent combustion conditions refer to the room where the combustion products are being *generated*, not necessarily the room where the potential victims are located. Fires, quite clearly, get greatly more hazardous when post-flashover conditions are reached and an analysis of US fire statistics has shown that smoke inhalation deaths occur predominantly after fires have progressed beyond flashover [13]. Consequently, the second study [11] showed that, in post-flashover fires, the range of LC_{50} values is even smaller, less than 3:1.

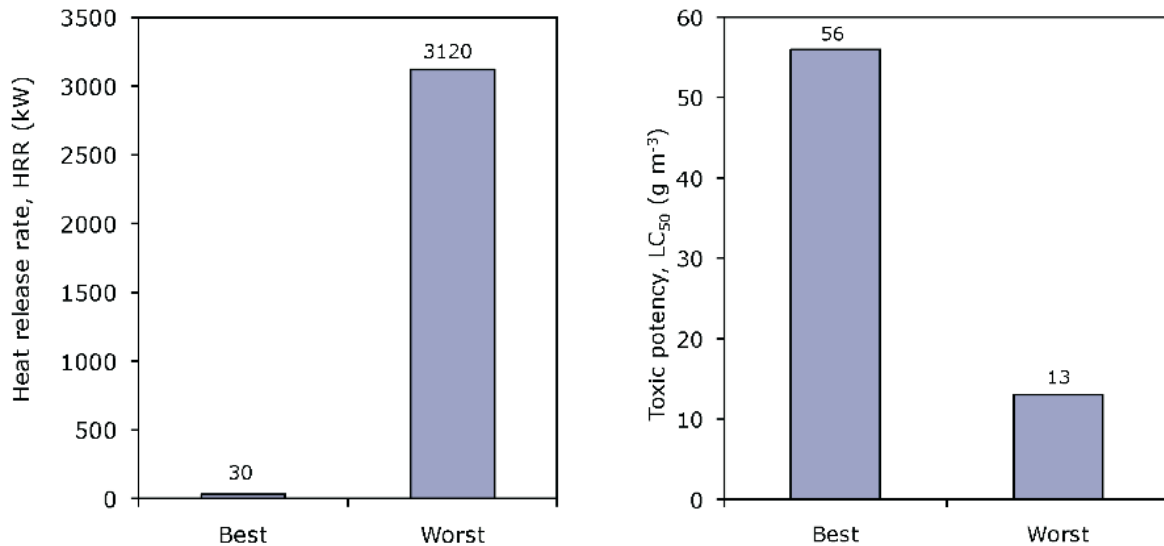


Figure 1 Comparison of importance of variables in assessing toxic fire hazard, 1992 study. The HRR data were full-scale, but the LC_{50} data were bench-scale; these results were not corrected for CO effect in room fires. The LC_{50} range would further shrink if this correction were made.

The above results for LC_{50} were obtained in bench-scale studies. Thus, the question then arises: Would full-scale measurements of LC_{50} show a different picture, perhaps with much greater spread in LC_{50} results? The data shown in Table 1 are from Babrauskas et al. [14] and Braun et al. [15] and indicate more similarities than differences, with most values being clustered in the range of 30 – 60 $g\ m^{-3}$, which is a very modest 2:1 spread.

Hazards of Combustion Products

Table 1 Range of LC₅₀ values found in full-scale room tests at NIST

Product	Full-scale LC ₅₀ (g m ⁻³)	Ref.
Douglas fir	> 70	[14]
rigid polyurethane foam	30 – 40	[14]
PVC	35 - 45	[14]
cork board	> 32	[15]
laminare (melamine formaldehyde plastic face, vermiculite core)	39	[15]
wood particleboard	44 – 60	[15]

Another very interesting finding was from a full-scale study at NIST where a wide mix of plastic products was present in the same test room [16]. Values of LC₅₀ were not derived in that test but, instead, the ratio of CO toxicity to total toxicity was derived for 7 different room tests. These results ranged from 0.27 to 0.54, which is a small range (2:1) and again confirms that actual toxic hazard is overwhelmingly driven by ‘rate’ (HRR) and not by ‘intensity’ (LC₅₀).

Recently, NIST published a collection of bench-scale (only) LC₅₀ data [17]. This was grouped into 3 categories: well-ventilated combustion, ventilation-limited combustion, and oxidative pyrolysis. This grouping is important since, if one extrapolates to full-scale, it suggests what the MLR might be and consequently what the overall toxic hazard is to be expected. Oxidative pyrolysis should represent no significant hazard since it means that, under these conditions, the substance itself is not combusting; instead, some chemical reactions are forced by heating it externally. In such situations the full-scale MLR will be vanishingly small, consequently the hazard is also necessarily equally small. Ventilation-limited combustion is of most interest. This corresponds, in full-scale, to post-flashover fires, where MLR is the highest that it will be. Well-ventilated combustion, in terms of full-scale fire hazard, will comprise a lower level of hazard, since it corresponds either to early room fire burning, where MLR is still low, or else environments which are so well-ventilated that flashover will never be attained. But in the latter case, the toxic hazard will not be high, since—apart from all other factors—there will be copious dilution before the combustion products reach the potential victim. The NIST summary statistics are shown in Table 2. For ventilation-limited combustion, the 95% confidence intervals represent a data spread of 2.6:1. While well-ventilated combustion data spread is roughly 10:1, the range is much smaller when considering only the combustibles which (a) might be found in use in larger quantities, and (b) may be expected to undergo of self-sustained combustion (if a material is likely to burn only when exposed to a large ongoing fire, then its contribution will be small). Finally, it must be remembered that a good deal of the data spread in bench-scale results is due to unusual combustion conditions in such tests that do not correspond to full-scale reality; this can be seen by comparing the data spread in Table 1 to that in Table 2.

Table 2 Statistical summary of bench-scale LC₅₀ database compiled by NIST

Condition	Mean LC ₅₀ (g m ⁻³)	LC ₅₀ 95% confidence intervals (g m ⁻³)
Ventilation-limited combustion	24.4	15.8 – 40.3
Well-ventilated combustion	30.1	5.1 – 58.0
Oxidative pyrolysis	27.8	1.6 – 78.4

An early study at NIST [14] found a fair (half-an-order-of-magnitude) agreement between bench-scale and full-scale LC₅₀ results when using animals. Use of animals for fire hazard assessment purposes is not acceptable in Europe. However, even in the US, animal-based testing has been discontinued at the institutions that used to be doing such testing. As will be shown below, when considering solely

Hazards of Combustion Products

chemical-analysis based LC₅₀ testing, the agreement between bench-scale and full-scale results is too poor to be useful.

An extensive European study

Some time later, an extensive series of products was tested at SP in Sweden [18][19][20] where full-scale fire test results were accompanied by bench-scale toxic potency measurements. These parallel series of test results can be treated as a database to relationships among the full-scale hazard parameters and also investigate predictability from bench-scale toxic potency data. The database exhibits suitable consistency, since the full-scale tests were all conducted in the same test room, with the same door opening, and using the same instrumentation. It also shows necessary diversity, since the products examined covered a wide range of fire performance, from minimal involvement, to dangerous conditions requiring manual extinguishment. This meant that both freely-burning and oxygen-limited fires were encompassed. The products were also mounted in several different ways within the test room. Taken together, the resulting data collection represents a wide mix of product compositions, geometric arrangements, and ventilation conditions. Using this reference data, various bench-scale test methods could then be examined for their potential utility in assessing the full-scale combustion product hazard. Analysis was facilitated by the fact that the same instrumentation and the same equations were used for examining toxicity in full-scale and in bench-scale tests.

FULL-SCALE TESTS. All full-scale tests done in the ISO 9705 [21] room test, which is configured to examine the fire behaviour of products used for the inside surfaces of rooms. However, this test room has subsequently become very widely used within the fire science profession, and nowadays it is by no means restricted to treating wall-surface lining materials. Three different types of building products were examined in these tests: pipe insulation, sandwich panels, and wall insulation. For pipe insulation, Nordtest method NT FIRE 036 [22] was followed; this method uses the basic arrangement of the ISO 9705 room, but provides specific instructions for product mounting. The product is mounted in a tight-packed array covering the entire room ceiling; no product is applied to walls. The gas burner used in the NT FIRE 036 test is not the standard ISO 9705 burner, but is designed for pipe insulation tests and provided an output of 150 kW for 15 min. Further details on the pipe insulation tests are given in [18].

Sandwich panels are most commonly used to construct self-supporting offices, cold stores, and other industrial spaces. When a fire occurs in such a room, it can often break out through the panel joints and burn on both sides of the enclosure. To collect the entire toxic gas output, the test specimens were constructed as a 'room-within-a-room' by erecting them within the ISO 9705 room. The specimens were spaced out 5 cm from the test room walls to avoid unrepresentative heat sink effects. The ignition burner used an output of 100 kW for 10 min, after which it was raised to 300 kW for 10 additional min. Further details on the methods and materials are given in [19].

Wall insulation products were tested using the ISO 9705 test method. The products were applied to both the walls and ceiling. Here, the scenario envisions the fire hazard of buildings in the process of construction, renovation, demolition, or whenever the thermal insulation is not covered up by a wall board. The ignition burner used an output of 100 kW for 10 min, after which it was raised to 300 kW for 10 additional min. One wall product was tested in a variant whereby it was applied only to the walls. Further details on wall insulation tests are given in [20].

All of the products tested are identified in Table 3. The products were obtained in the European marketplace and were selected to cover a wide range of chemical compositions. The products were not examined for performance under any regulatory scheme and the results are not intended to reflect acceptance limits for any jurisdiction. The specimens are coded *P* for pipe insulations, *S* for sandwich panels, and *W* for wall insulations. The ISO 9705 (or NT FIRE 036, in the case of pipe insulation)

Hazards of Combustion Products

procedures envision a fixed specimen exposure time. In the case of some products, however, excessive fire development occurred, threatening laboratory safety. These products had to be extinguished before the full test time (15 min for pipe insulation, 20 min for other products) elapsed.

BENCH-SCALE TESTS. For bench-scale toxicity testing, ISO offered eight methods ISO TR 9122-4 [8] and now twelve in ISO TR 16312-2 [23]. Of these, two were chosen: the DIN 53 436 tube furnace [24] and the ISO 5660 Cone Calorimeter [25]. The DIN tube furnace was operated at two conditions: 500 and 700°C. Cone Calorimeter tests were run at two irradiances, 35 and 50 kW m⁻². In addition, those specimens having metallic facings were tested both ways, with and without the facing. For brevity and consistency, only tests without facings are tabulated here. The previous studies made comparisons for faced products between the two test conditions; some differences were significant, but a systematic trend was not observed.

GAS ANALYSIS INSTRUMENTATION. For these experiments, no animals were used and toxicity was quantified by gas analysis. The gases analyzed included CO, CO₂, O₂, NO, NO₂, total unburned hydrocarbons (TUHC), HCl, HCN, and HBr. The gas analysis employed dedicated gas analyzers and FTIR methods [18]. The gas analysis was done with the same instrumentation and procedures for both the full-scale and the bench-scale experiments.

Table 3 The products tested in the SP test series

Code	Product description	Metallic face	Thick. (mm)	Density (a) (kg m ⁻³)
P2	synthetic rubber foam	no	20	70
P3	high density rock wool	al. foil	40	130
P4	phenolic foam	al. foil	25	33
P5	polyethylene foam	no	20	25
S1	polyurethane foam	steel sheet (b)	80	35
S2	rock wool	steel sheet (b)	100	120
S3	polystyrene foam	steel sheet (b)	100	20
W1	polystyrene foam	no	50	16
W2	polyurethane foam	no	40	34
W3	light density rock wool	no	50	29
W4	high density rock wool	no	47	145
W5	polyisocyanurate foam	al. foil	46	32
W6	polystyrene foam (walls only)	no	50	16
(a) excluding any facings				
(b) steel sheets had a decorative plastic film				

RESULTS. To perform an evaluation of the toxic fire hazard, under ISO 13344 the basic analysis is done by use of the *Fractional Effective Dose* (FED) principle. This principle, arithmetically, simply represents that the toxic effects of various gases are linearly additive. The expression for additivity selected for the present work was:

$$FED = \frac{[CO]}{5000} + \frac{[HCN]}{150} + \frac{[HCl]}{3800} + \frac{[HBr]}{3000} + \frac{[NO]}{1000} + \frac{[NO_2]}{200}$$

where the terms in brackets denoted individual gas concentrations (ppmv) and the denominators represent LC₅₀ values[†] (ppmv) for the same gases. The ISO 9705 test room, however, does not represent actual dimensions and air flow situation of a real building volume into which the gases are to be distributed in order to compute specific concentrations. The analysis, then starts with total *production* of the various gas

[†] The LC₅₀ is usually expressed on a mass basis in units of g m⁻³, but can also be expressed on a volume basis as ppmv or μL/L. Conversion between the two types of units can be done on the basis of the Ideal Gas Law.

Hazards of Combustion Products

species, as measured in the ISO 9705 room (units in grams). This must be distributed into some specified total air volume. Lacking design information on a specific building, this is arbitrary and a single value of $V = 100 \text{ m}^3$ was used for all full-scale results[‡] (note that several different values of volume were used in references [18][19][20]). The LC_{50} values for the individual gas components are time-dependent, and here the values used are for a 30 min exposure. The bench-scale data were analyzed in an identical manner, except that here $V = 0.01 \text{ m}^3$ was assigned. Effective values of LC_{50} for the combustion products were computed using Eq. 4 of ISO 13344-2004:

$$LC_{50} = \frac{\Delta m}{FED \times V}$$

Unlike for pure gases, the values of LC_{50} for combustion product mixtures are customarily expressed in units of (g m^{-3}) . The results are given in Table 4. In addition to the toxicity measures, this table provides some basic fire performance measures, including heat release rate (HRR) and mass loss.

Table 4 Results from full-scale and bench-scale testing

Code	Full-scale			FED					LC ₅₀				
	Pk. HRR (kW)	F/O (s)	Δm_{f-s} (kg)	room	D500	D700	C35	C50	room	D500	D700	C35	C50
P2	52	∞	4.7	2.0	35.6	84.1	52.0	101.2	23.7	8.5	4.8	13.7	11.1
P3	40	∞	0.1	0.1	4.4	5.4	6.7	6.3	5.8	3.2	2.6	13.4	6.4
P4	1490	600	9.9	3.0	90.9	4.4	24.3	3.1	33.3	5.0	114.0	16.9	248.0
P5	217	∞	0.6	0.2	14.6	11.5	8.2	10.3	29.5	34.4	42.6	75.6	66.0
S1	> 5992	702	> 16.4	>13.7	62.3	58.1	94.4	104.2	12.0	5.6	8.4	13.5	13.2
S2	288	∞	2.7	1.9	7.5	7.6	30.2	25.0	13.9	3.3	3.0	4.3	7.6
S3	> 5639	736	> 9.5	>20.5	2.5	13.7	19.2	18.2	4.6	146.0	26.5	45.3	50.0
W1	> 6142	70	> 6.5	>1.8	2.0	6.2	12.2	13.6	36.3	130.0	43.0	58.2	53.7
W2	> 8942	12	> 11.3	>4.1	220.6	17.8	86.2	100.1	27.8	1.8	28.0	10.1	12.9
W3	329	∞	0.7	0.7	5.1	3.5	0.0	9.9	10.7	3.9	5.4	—	6.1
W4	378	∞	1.6	2.6	7.0	8.3	0.0	17.4	6.2	2.6	2.4	—	12.1
W5	2604	630	27.7	24.8	134.7	19.2	29.0	130.5	11.2	3.0	24.0	11.7	8.2
W6	3483	73	10.2	3.6	2.0	6.2	12.2	13.6	28.6	130.0	43.0	58.2	53.7

In the above table, the shaded entries indicate specimens where the fire in the ISO 9705 room had to be manually extinguished due to excessively large fire conditions. F/O denotes the time at which flashover was reached (if ever) in the room fire test. Δm_{f-s} is the mass lost during test. The values of FED are dimensionless, with higher numbers indicating greater hazard. D500 represents the results of the DIN 53 436 testing at a temperature of 500°C, while D700 denotes 700°C; C35 denotes Cone Calorimeter results taken at an irradiance of 35 kW m⁻², while C50 is for 50 kW m⁻² irradiance. The values of LC_{50} are in (g m^{-3}) .

Qualitative analysis. The primary hazard indicator can be taken to be the occurrence of flashover. When flashover occurs, tenability of a space is normally considered precluded. The products which did not lead to flashover are, of course, safer than those which did. For the products which did lead to flashover, shorter flashover times, again, indicate greater hazard. The highest hazard category can be assigned to those products where the room fire had to be manually extinguished due to laboratory safety concerns

[‡] The volume that is chosen is immaterial, as it does not affect the correlation between bench- and full-scale results.

Hazards of Combustion Products

about excessive fire size. Other variables affecting fire hazard include the peak HRR and the amount of specimen burned. The toxic fire hazard is expressed as the FED.

The first question which might be asked is how, if at all, are these variables related. The simplest relationship should be one of grouping, or rank ordering. In Table 5 we examine each of the measured variables from Table 4 and identify two groups of specimens for each variable: the best and the worst performing product, on that particular measuring scale. The number of specimens included in each group is not always constant, due to natural clustering of data.

Table 5 The best and worst performers for each variable

Variable	Best specimens	Worst specimens
Peak HRR	P2 P3 P5 S2 W3 W4	S1 S3 W1 W2 W6
Flashover time	P2 P3 P5 S2 W3 W4	S1 W2 W6
Mass lost	P2 P3 P5 S2 W3 W4	S1 S3 W1 W2 W5
FED: Full-scale	P2 P3 P5 S2 W3 W4	S1 S3 W1 W2 W5
FED: D500	P3 S2 W1 W3 W4 W6	P2 P4 S1 W2 W5
FED: D700	P3 P4 S2 W3 W4 W6	P2 S1 W2 W5
FED: C35	P3 P5 W1 W3 W4 W6	P2 P4 S1 S2 W2 W5
FED: C50	P3 P4 P5 W1 W3 W6	P2 S1 W2 W5
LC ₅₀ : Full-scale	P2 P4 P5 W1 W2 W6	P3 S3 W4
LC ₅₀ : D500	P5 S3 W1 W6	P3 S2 W2 W3 W4 W5
LC ₅₀ : D700	P4 P5 W1 W6	P2 P3 S2 W3 W4
LC ₅₀ : C35	P5 S3 W1 W6	P2 P3 S1 S2 W2 W5
LC ₅₀ : C50	P4 P5 S3 W1 W6	P3 S2 W3 W5

Considering first the relationship among the four full-scale variables (excluding LC₅₀), it is noteworthy that the five best-performing products are identical for each variable—HRR, flashover, mass loss, and FED. The worst-performing specimens vary slightly. In no case, however, does any specimen show up in the Best group by one full-scale performance measure and in the Worst group by another. For some purposes, the fire safety objective may not require fully quantitative computations. It may be sufficient to simply select products which are ‘among the better performing specimens’ rather than ‘among the worst.’ For such tasks, using *any* of the four full-scale measures from the present database would result in the same decision.

Turning now to bench-scale issues, one finds that *every* bench-scale variable tabulated above would misclassify the full-scale product performance. Indeed, a large fraction of the specimens flagged as Worst by the bench-scale variables turn out to be in the Best group, according to all full-scale results. Furthermore, one were to choose products ranked in the Best group for any of the bench-scale variables, then one would invariably end up including products which show up in the Worst group according to full-scale tests. These findings imply that procedures for classifying product acceptability on the basis of bench-scale LC₅₀ values are unpromising, even if the hazard to be addressed is solely toxicity (i.e., full-scale FED) and not any other fire aspects. Finally, we note that full-scale LC₅₀ values mis-rank the product hazard from toxicity, which is represented by the full-scale FED.

Hazards of Combustion Products

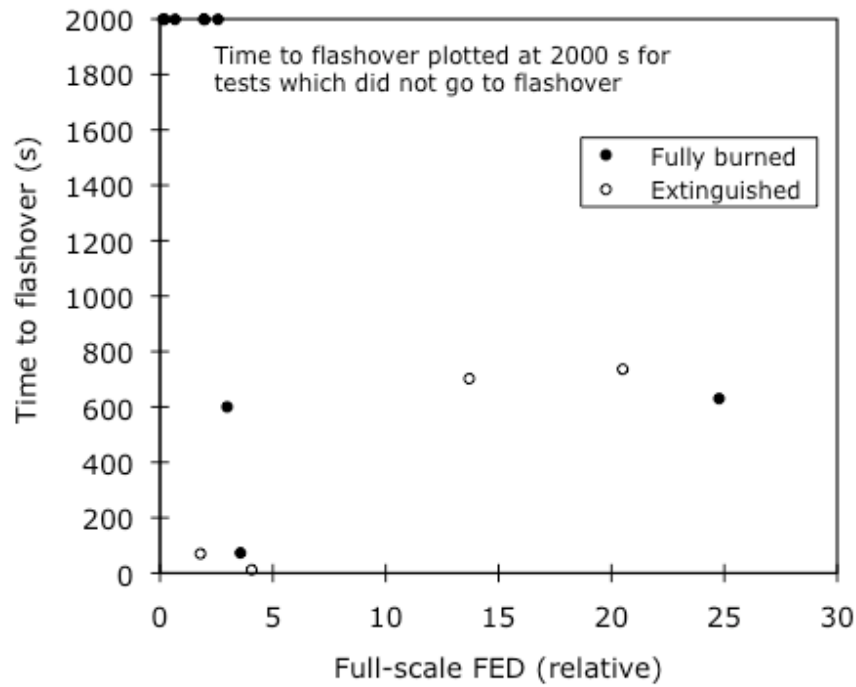


Figure 2 The relation between FED and flashover time

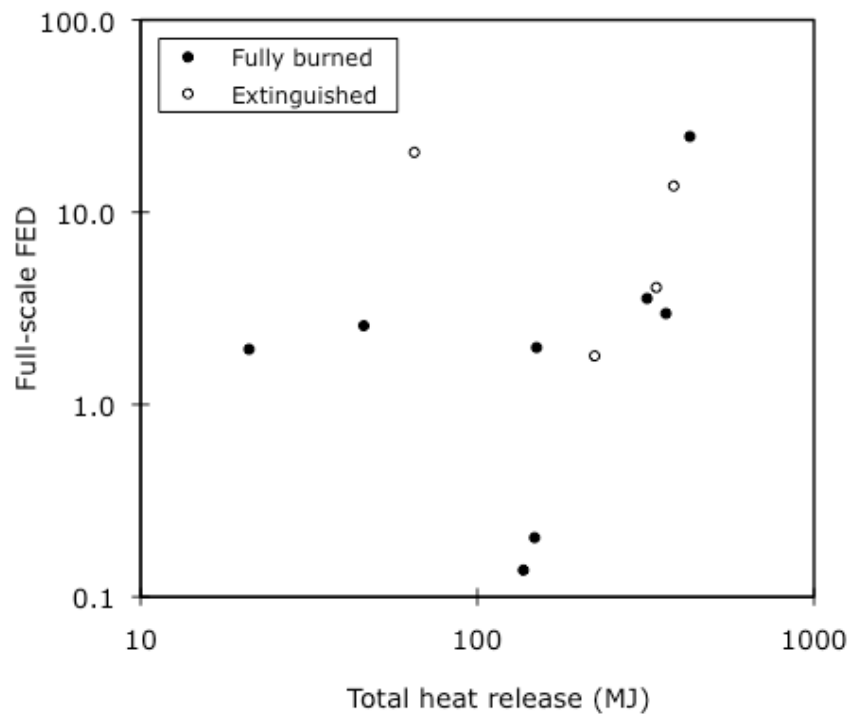


Figure 3 Comparison of full-scale total heat release and FED

Hazards of Combustion Products

Quantitative analysis. The above results indicate that behaviour of products in full-scale fires is roughly similar, regardless of which hazard component is being studied. It is of interest to see whether such conclusions can be refined quantitatively. Using the measure of total combustion product as the FED, one can first examine to what extent the full-scale FED is correlated with time to flashover. This is indicated in Figure 2.

The relation is seen to be only very rough. High values of FED are associated with occurrence of flashover, while low FED values predominate for the non-flashover cases. Beyond this, quantitative conclusions are difficult. The hazard measures being compared here are, of course, of different types, one being a time-to-event the other being proportional to an amount of substance. To compare on a more similar basis, among the hazard variables of the room, one can select the total heat release. The results are shown in Figure 3.

The relationship is only slightly better on such a basis, however. Next, a regression was tried for the full-scale LC_{50} against each of the four bench-scale LC_{50} measurements (DIN furnace and Cone Calorimeter, each at two conditions). Presumably, the reason that the ISO 13344 specifies that the bench-scale LC_{50} are to be measured is that they are considered to be applicable to the full-scale fire situation. Certainly the most elementary relation would be that *full-scale* $LC_{50} \propto$ *bench-scale* LC_{50} . The four regressions attempted, however, each returned $R^2 < 0$, indicating no correlation.

A straightforward quantitative model for the toxicity effects in full-scale fires can be expressed as:

$$FED_{f-s} = \frac{\Delta m_{f-s}}{V \cdot LC_{50(f-s)}}$$

This uses the same fundamental definition of FED as found in Eq. 4 of ISO 13344, but explicitly applied to the full-scale situation. Leaving aside the design variable V , this requires that Δm_{f-s} and $LC_{50(f-s)}$ be predicted. To obtain Δm_{f-s} requires having a fire model which can predict how much mass loss will be sustained by the product in a full-scale scenario. Mass loss models are only rarely attempted; models for the HRR are more often found, although even those can only be found in the literature for a very few cases (as discussed in a preceding chapter of this book), and not including any of the present product categories. While it might at least have been hypothesized that estimating $LC_{50(f-s)}$ values on the basis of bench-scale testing would be possible, the non-correlation results above prove otherwise.

It is of concern then that, lacking such prediction tools, a user will simply construct the model:

$$\text{full - scale toxic fire hazard} \propto \frac{1}{LC_{50(b-s)}}$$

This concern is not merely hypothetical, due to the US precedent already discussed. The nature of the full-scale toxic fire hazard was not spelled out by those regulators, although for consistency we can take it as the full-scale FED. A comparison of such a prediction against actual measured full-scale FED values is shown in Figure 4. The bench-scale LC_{50} was taken from the Cone Calorimeter using an irradiance of 50 kW m⁻². It can readily be seen that such a ‘user-accessible’ model does not succeed in predicting the full-scale results. Significantly better results can be obtained by taking the model:

$$FED_{f-s} = \frac{\Delta m_{f-s}}{V \cdot LC_{50(b-s)}}$$

Hazards of Combustion Products

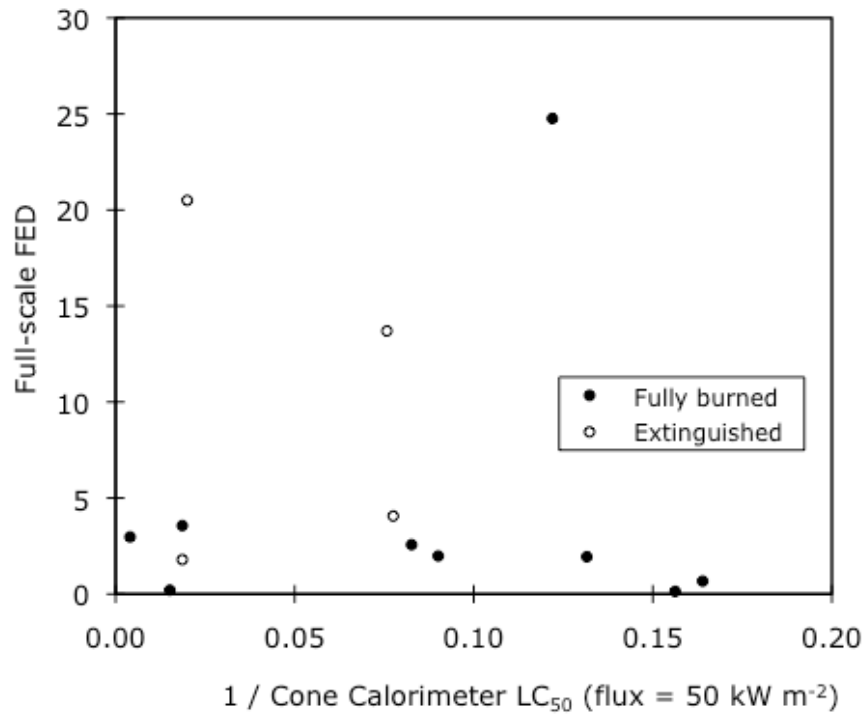


Figure 4 Non-prediction of full-scale results by use of a simple model

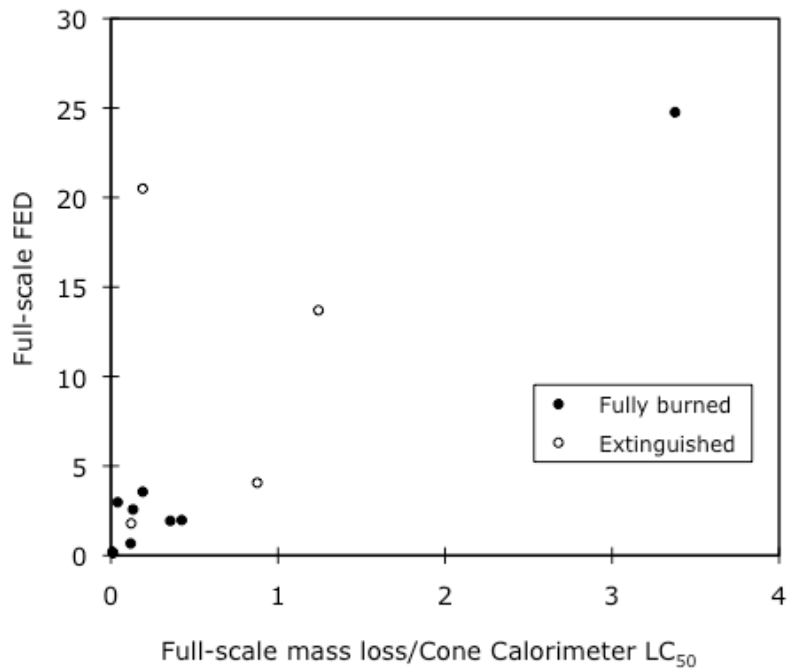


Figure 5 The use of an improved model

Hazards of Combustion Products

This is indicated in Figure 5. Such a model, however, is simply hindsight, rather than prediction. The reason is that the values of Δm_{f-s} are obtainable only from the full-scale test itself. Thus, there is no way to actually use such an equation for predictions, except for the few cases in which the mass loss rate can be predicted, as mentioned earlier.

It should be noted that, for simplicity, the analysis above focused on total production quantities of toxic substances. In some situations, it can be anticipated that production *rates* rather than total quantities will govern. The modeling implications, however, for this case would be no more favourable, since methods for predicting full-scale mass loss rate no more exist than do predictive methods for mass loss amount.

DISCUSSION. The bench-scale tests for obtaining LC_{50} values require that certain test conditions be defined. These are furnace temperature for the DIN 53 436 test and irradiance for the Cone Calorimeter. For the European test series here, in each case two different conditions were selected. These were intended to be similar to customarily used values [26] or to common recommendations [27]. The LC_{50} values obtained tended to vary significantly between the two test conditions. Correlations between LC_{50} values reported at each of the two test conditions were attempted for both the DIN 53 436 and the Cone Calorimeter tests. In both cases, the regression showed $R^2 < 0$. This indicates that the toxic effects change substantially when different, yet equally reasonable, test conditions are selected.

To examine the predictive power of the bench-scale LC_{50} measurement, the quotient $LC_{50} (\text{bench-scale})/LC_{50} (\text{full-scale})$ was computed, and the values are given in Table 6. As discussed above, for animal-based testing, research at NIST showed a fair agreement to full-scale values. Here, Table 6 shows that for chemical-analysis based LC_{50} determinations, there is such a poor agreement that it does not represent a useful correlation. It can also be noted that here the bench-scale LC_{50} values, for both test methods, averaged significantly higher (1.45 to 3.36 times) than LC_{50} values for full-scale fires, meaning that the bench-scale results tended to be systematically less toxic (mean ratio > 1) than in the full-scale. It is of interest that this includes even the low temperature (500°C) condition in the DIN furnace. The 500°C test condition is often associated with ‘non-flaming’ fires, and claims are sometimes made that such conditions can lead to especially toxic combustion products.

Table 6 Descriptive statistics for the bench-scale/full-scale LC_{50} ratio

$LC_{50} (\text{bench-scale}) / LC_{50} (\text{full-scale})$	D500	D700	C35	C50
maximum	31.50	5.72	9.78	10.80
minimum	0.06	0.20	0.31	0.46
mean	3.36	1.45	2.02	2.37
std. deviation	8.57	1.57	2.69	3.13
coefficient of variation	2.55	1.08	1.33	1.32

The standard deviations of the bench-scale/full-scale ratio were high in all cases, but especially for the DIN 500°C tests. Apart from that condition, the remaining three test conditions were similarly predictive (or non-predictive) of the full-scale results. While, for any particular product category one or another bench-scale testing protocol might prove better suited, the fact remains that without the hindsight of full-scale test results, there would be no means of selecting the ‘right’ conditions.

As stated earlier, reduction of the combustion products hazard can stem from one of two sources: (1) improvements in the mass loss behaviour; or (2) improvements in the LC_{50} . An important question which the data in the present database can help answer is: What is more fruitful to attempt: reduce the burning rate, or improve the LC_{50} characteristics? Table 7 presents statistics to help answer this question.

Hazards of Combustion Products

Table 7 Variations in full-scale performance among the products tested

Performance measure	Ratio (Worst / Best)
Mass loss amount (kg)	277
FED (—)	248
Peak HRR (kW)	224
LC ₅₀ (g m ⁻³)	8

The implications are clear. It is demonstrably feasible to make products with superior mass loss, HRR, or non-flashover characteristics. But it is unrealistic, in view of the present experience, to seek much improvement by trying to raise the LC₅₀.

An additional point arises concerning the bench-scale LC₅₀ variable. Table 8 compares the range of product diversity in the present full-scale fire tests, versus the ranges reported from the bench-scale procedures (we omit the DIN 500°C condition, due to its especially poor predictivity). These results indicate that all of the bench-scale protocols seriously overestimate the differences in toxic potency. This overestimation is on the order of 3- to 4-fold. This conclusion is very similar to what was found at NIST (compare Table 1 and Table 2).

Table 8 The variation in the LC₅₀ variable in full-scale and in bench-scale

Test method	Ratio (Worst / Best)
Full-scale	8
DIN, 700°C	28
Cone Calorimeter, 35 kW m ⁻²	31
Cone Calorimeter, 50 kW m ⁻²	23

Summary of guidance

The hazard of combustion products can be accurately characterized by conducting full-scale tests, accompanied by extensive (e.g., FTIR) chemical instrumentation and analysis. This is a costly and difficult exercise and is only appropriate for major research programmes, not for standardized testing of products or materials.

HRR tests are now well-enough standardized and routine, so they can be used for testing free-standing articles. In fact, the US Consumer Product Safety Commission recently enacted a regulation whereby exactly this type of testing is now mandated for mattresses [28]. No specific toxicological data need to be sought from such testing, since the full-scale combustion product hazard is very closely linked to the peak HRR.

In case of materials or products that are used in bulk, such a strategy is not ideal. Materials intended, for example, for wall or ceiling linings may, in the actual end-use environment, show up as an area of 1 m², or 1000 m². Thus, ideally, they will be tested in a bench-scale test, then a hazard analysis is performed where modeling of the HRR for the end-use situation is done using the bench-scale test data. The previous chapter in this book discusses details of the state of the art. It suffices to test and model only the HRR, since additional data on LC₅₀ would not contribute significantly towards making the hazard analysis more accurate.

Wall/ceiling linings may be tested using the ISO 9705 standard in the scale of the ISO 9705 room. While costlier than bench-scale testing, this is now common enough in laboratories that it can be done routinely. Note, however, that such testing, while suitable for rank-ordering purposes, cannot quantify the hazard in rooms of significantly larger size, nor can it describe the hazard if the material is to be used more sparingly than as a total covering for all the wall surfaces.

Hazards of Combustion Products

Bench-scale LC₅₀ tests do not have a useful role in product hazard regulation. Used by themselves, the results would be grossly misleading, if intended to provide an estimate or ranking of full-scale combustion product hazard. Even as an adjunct to HRR testing, such testing would not make a positive contribution. There are several reasons for this: (a) bench-scale LC₅₀ results differ widely, when comparing different ISO 13344-recommended test methods; (b) the relation between bench-scale and full-scale results, when not using animals, is notably poor ($R^2 < 0$); (c) the range of fire performance (the span from best to worst) is very broad for HRR (or MLR) and is very narrow for LC₅₀.

There is a very broad span between the best and the worst performance, as concerns the full-scale burning-rate related variables. But there is only a very small range over which full-scale LC₅₀ values range. This indicates that product improvements are likely to show up only as reduced burning rates, not as improved LC₅₀ values.

Finally, it is important to emphasize that present results and the guidance given here should not be extended to the evaluation of toxicity hazards of chemical warehouses. In principle, materials of any conceivable toxicity—even rare substances of extreme toxicity—can be encountered in a chemical warehouse. A large European research project [29] examined the toxicity issues involved such chemical warehouse fires.

References

- [1] Braun, E., Levin, B. C., Paabo, M., Gurman, J. L., Holt, T., and Steel, J. S., Fire Toxicity Scaling (NBSIR 87-3510), [U.S.] Natl. Bur. Stand., Gaithersburg, MD (1987).
- [2] Braun, E., Levin, B. C., Paabo, M., Gurman, J. L., Clark, H. M., and Yoklavich, M. F., Large-Scale Compartment Fire Toxicity Study: Comparison With Small-Scale Toxicity Test Results (NBSIR 88-3764), [U.S.] Natl. Bur. Stand., Gaithersburg, MD (1988).
- [3] Babrauskas, V., Levin, B. C., Gann, R. G., Paabo, M., Harris, R. H. jr., Peacock, R. D., and Yusa, S., Toxic Potency Measurement for Fire Hazard Analysis (Special Publication 827). Natl. Inst. Stand. and Technology, Gaithersburg (1991).
- [4] New York State Uniform Fire Prevention and Building Code, Article 15, Part 1120: Combustion Toxicity Testing (9 NYCRR 1120).
- [5] McGarry, F. A., Towards a Safer Built Environment: New York State's Building Materials and Finishes Fire Gas Toxicity Data File, in *Proc. Recent Advances in Flame Retardancy of Polymeric Materials—Materials, Applications, Industry Developments, Markets*, Business Communications Co., Inc., Norwalk, CT (1990).
- [6] Amendment to Rescind Requirements for Combustion/Toxicity Testing, 9 NYCRR 719.1, 741.1, 773.1 and Part 1120, *New York State Register* (18 Nov. 1998).
- [7] Determination of the Lethal Toxic Potency of Fire Effluents (ISO 13344), International Organization for Standardization, Geneva (1996).
- [8] Toxicity Testing of Fire Effluents – Part 4 : The fire model (furnaces and combustion apparatus used in small-scale testing), ISO TR 9122-4, International Organization for Standardization, Geneva (1993).
- [9] Babrauskas, V., and Grayson, S. J., eds., **Heat Release in Fires**, E&FN Spon, London (1992).
- [10] Babrauskas, V., Toxicity, Fire Hazard and Upholstered Furniture, pp. 125-133 in *3rd European Conf. on Furniture Flammability (EUOFF)*, Brussels, Interscience Communications Ltd, London (1992).
- [11] Babrauskas, V., Toxic Fire Hazards: Control by Limiting Toxic Potency or Control by Limiting Burning Rate?, pp. 239-250 in *Flame Retardants '94*, Interscience Communications Ltd., London (1994).

Hazards of Combustion Products

- [12] Babrauskas, V., The Generation of CO in Bench-scale Fire Tests and the Prediction for Real-scale Fires, *Fire and Materials* **19**, 205-213 (1995).
- [13] Gann, R. G., Babrauskas, V., Peacock, R. D., and Hall, J. R., jr., Fire Conditions for Smoke Toxicity Measurement, *Fire and Materials* **18**, 193-199 (1994).
- [14] Babrauskas, V., Harris, R. H., Jr., Braun, E., Levin, B. C., Paabo, M., and Gann, R. G., The Role of Bench-Scale Test Data in Assessing Full-Scale Fire Toxicity (NIST Tech. Note 1284), Natl. Inst. Stand. and Technol., Gaithersburg MD (1991).
- [15] Braun, E., Levin, B. C., Harris, R. H. jr., and Gann, R. G., Real Scale Fire Test Data for Bench-Scale Fire Toxicity Test Method Correlation: Series II, unpublished report, Nat. Inst. Stand. and Technol., Gaithersburg MD (1997).
- [16] Babrauskas, V., Harris, R. H., Jr., Gann, R. G., Levin, B. C., Lee, B. T., Peacock, R. D., Paabo, M., Twilley, W., Yoklavich, M. F., and Clark, H. M., Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749), [U. S.] Natl. Bur. Stand. (1988).
- [17] Neviasser, J. L., and Gann, R. G., Evaluation of Toxic Potency Values for Smoke from Products and Materials, *Fire Technology* **40**, 177-199 (2004).
- [18] Babrauskas, V., Toxic Fire Hazard Comparison of Pipe Insulations: The Realism of Full-scale Testing Contrasted with Assessments from Bench-scale Toxic Potency Data Alone, pp. 439-452 in *Asiaflam '95*, Interscience Communications Ltd, London (1995).
- [19] Babrauskas, V., Sandwich Panel Fire Performance in Full-scale and Bench-scale Fire Tests, *Fire and Materials* **21**, 53-65 (1997).
- [20] Babrauskas, V. Wall Insulation Products: Full-Scale Tests Versus Evaluation from Bench-Scale Toxic Potency Data, pp. 257-274 In *Interflam '96*, Interscience Communications Ltd, London (1996).
- [21] Full Scale Room Test for Surface Products (ISO 9705), International Organization for Standardization, Geneva (1993).
- [22] Pipe Insulation: Fire Spread and Smoke Production—Full-scale Test (NT FIRE 036), Nordtest, Espoo (1988).
- [23] Guidance for assessing the validity of physical fire models for obtaining fire effluent toxicity data for fire hazard and risk assessment. Part 2: Evaluation of individual physical fire models (TR 16312-2), International Organization for Standardization, Geneva (2007).
- [24] Erzeugung thermischer Zersetzungsprodukte von Werkstoffen unter Luftzufuhr und ihre toxikologische Prüfung. Teil 1: Zersetzungsgerät und Bestimmung der Versuchstemperatur (1981). Teil 2: Prüfung Verfahren zur thermischen Zersetzung (1986). Teil 3: Verfahren zur inhalationstoxikologischen Untersuchung (1989). Deutsches Institut für Normung, Berlin.
- [25] Reaction-to-fire tests -- Heat release, smoke production and mass loss rate -- Part 1: Heat release rate (cone calorimeter method), ISO 5660-1, International Organization for Standardization, Geneva (2002).
- [26] Kallonen, R., Von Wright, A., Tikkanen, L, and Kaustia, K., Toxicity of Fire Effluents from Textiles and Upholstery Materials, *J. of Fire Sciences* **3**, 145-160 (1985).
- [27] Babrauskas, V., Specimen Heat Fluxes for Bench-scale Heat Release Rate Testing, *Fire and Materials* **19**, 243-252 (1995).
- [28] Standard for the flammability (open flame) of mattress sets (16 CFR 1633), Code of Federal Regulations, Government Printing Office, Washington.
- [29] Smith-Hansen, L., The COMBUSTION and TOXFIRE Projects, pp. 43-58 in **Industrial Fires II**, S. T. Cole and P. J. Wicks, eds. Report EUR 15967-EN. European Commission, Luxembourg (1995).

HAZARDS OF COMBUSTION PRODUCTS:

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