

# Assessment of Smoke Toxicity of Building Materials

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## Abstract

In this paper, tests and standards on assessing smoke toxicity of materials will be reviewed first. Toxic potency data such as EC<sub>50</sub>, LC<sub>50</sub>, IC<sub>50</sub>, LT<sub>50</sub> and IT<sub>50</sub> are briefly introduced and criticized for suitability to use. Whether LC<sub>50</sub> is a good toxic potency parameter will be discussed.

Preliminary tests on some of these toxic data for selected building materials commonly used will be assessed. Two groups of materials, i.e. timber and plastics are investigated by standard tests to determine LC<sub>50</sub> and the fractional exposure dose (FED). Results indicated that polyvinyl chloride (PVC) was very toxic in having the smallest value of LC<sub>50</sub>. Poly(methyl methacrylate) (PMMA) got a higher value of LC<sub>50</sub> and appeared to be not so toxic. Wood did not give so much smoke in testing with a cone calorimeter. Suitability of using the tested results for assessing building materials will then be discussed.

In addition, smoke toxicity of some of these samples were assessed by a cone calorimeter. Results among the tests are also compared. Samples tested are timber, PMMA and PVC. Similar burning characteristics were observed.

Recommendations are made on how to include smoke toxicity in the local codes. This will be useful while in implementing engineering performance-based fire codes.

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## 1. Introduction

Smoke is believed to be the main threat to life safety in an accidental building fire. However, toxicity of smoke had not yet been put in building codes and regulations [e.g. 1-4] for fire safety provisions in Hong Kong, and many countries in the Far East. One of the main reasons is because toxicity depends not only on the materials that burn, but also on how the materials are burning. Burning carbon-containing materials would give much higher concentration of carbon monoxide if the combustion is incomplete, say due to inadequate air or cooling of the burning objects, say by water mist. It is difficult to study toxicity of smoke, but no excuse not paying effort to review and investigate how to put into fire codes.

There are many new architectural features such as those for green or sustainable buildings [e.g. 5]. New materials with polymer-based composites such as reinforced fibres with thermoplastic or thermosetting matrices are commonly used. Despite of ease of ignition, using those materials with good thermal insulation might give shorter flashover time. This was clearly demonstrated [e.g. 6] by those big air-conditioned buses in the past 3 years. New style of living such as staying longer time indoor would change the fire safety objectives. Note that designs for green or sustainable buildings gave some fire safety problems since 1998. There had been arguments and debates in many new projects.

In addition to the big accidental fires such as the two big old highrise building fires, tunnel fire and bus fires in Hong Kong, the number of non-accidental fires appeared to be increasing in the past few years. These included the arson bank fire,

arson karaoke fire and a recent arson underground railway train vehicle fire in Hong Kong; World Trade Centre terrorist attack fire the South Korean underground railway arson fire. All these suggested the hidden threat on fire safety must be dealt with urgently. Of all the complex fire phenomena, smoke toxicity emitted from having combustibles is a key element.

In this paper, tests and standards on assessing smoke toxicity of materials will be reviewed. Toxic potency data [7-9] such as  $EC_{50}$ ,  $LC_{50}$ ,  $IC_{50}$ ,  $LT_{50}$  and  $IT_{50}$  are introduced and criticized. Whether  $LC_{50}$  is a good toxic potency parameter will be discussed. Preliminary tests on some of these toxic data for two groups of selected building materials commonly used will be assessed.

## 2. Smoke Hazards

In an accidental fire, harm is caused by falls, heat, suffocation or smoke inhalation. As analyzed on US fire deaths in the 1970s [e.g. 7], 48% of victims had lethal carboxyhaemoglobin levels; and 26% of victims had carboxyhemoglobin level from 30 to 50%. Other conditions like cyanide exposure or preexisting heart diseases were deemed sufficient in combination with the sub-lethal carboxyhemoglobin levels to cause death. In fact, smoke is confirmed to be the major cause of harm. Smoke inhalation accounted for roughly three-quarters of all fire deaths. The effects on human included making victims incapacitated to escape by reducing egress speed, making wrong decision to select a longer egress path due to eye and lung irritation, visual obscuration and decreased mental acuity. These effects were brought by the toxicants inside the smoke.

Smoke toxicants can be divided into two types as reviewed before [10-12]:

- The first type is called asphyxiants or narcosis-producing toxicants, which can cause central nervous system depression, loss of consciousness or ultimately death. Effects depend upon the accumulated dose. Major asphyxiants include carbon monoxide (CO), hydrogen cyanide (HCN) and carbon dioxide (CO<sub>2</sub>).
- The second type is irritants which would lead to sensory irritation and pulmonary irritation. Sensory irritation mainly refers to the irritations of eyes and the upper respiratory tract. Hydrogen chloride (HCl) is the most important halogen acid which is formed from thermal decomposition of polyvinyl chloride (PVC). HCl is both a potent sensory irritant and also a strong pulmonary irritant. Upon burning, fire retardants based on halogen such as chlorine or bromine would also give halogen acids including hydrogen bromide (HBr).

In the past 30 years, different test methods were developed to determine the toxic potency of smoke released from different materials during combustion. But different fire scenarios were used in developing test methods in different laboratories. Calculation methods are different and even different gas species are analyzed.

### 3. Parameters on Smoke Toxicity

Common toxic potency data [e.g. 7] included:

- Effect concentration EC<sub>50</sub> which is used for any observed response of the animals.

EC<sub>50</sub> means the concentration of a sample that cause 50% effect (e.g. immobilization) in a standard toxicity test on the specified species over the specific period of time.

- The concentration LC<sub>50</sub> of materials or fire effluent that produces death in 50% of the animals for a specified exposure time.

LC<sub>50</sub> means the concentration of a sample cause 50% mortality in a standard toxicity test on the specified species over the specified species over the specific period of time.

- The concentration IC<sub>50</sub> necessary to incapacitate 50% of the animals for a specified exposure time.

IC<sub>50</sub> means the concentration of a sample cause 50% inhibition of activity in a standard toxicity test on the specified species over the specified species over the specific period of time.

- The mean time to death LT<sub>50</sub> and the time-to-incapacitation IT<sub>50</sub> used for fixed concentration of toxic gases.

LT<sub>50</sub> is the mean time to death and IT<sub>50</sub> is the mean time to incapacitation. Both are commonly used in toxicology also. LT<sub>50</sub> and IC<sub>50</sub> can be achieved by plotting the curve of percentage of lethal or incapacitation in log scale.

EC<sub>50</sub>, LC<sub>50</sub>, IC<sub>50</sub>, LT<sub>50</sub> and IT<sub>50</sub> are typical examples on measuring toxic potency. These measures are commonly used in toxicology. Testing conditions can be roughly divided into two types: fixed test period and fixed smoke concentration. EC<sub>50</sub>, LC<sub>50</sub> and IC<sub>50</sub> are the measure of the concentration of smoke to have different effects to human being in a fixed period of time. LT<sub>50</sub> and IT<sub>50</sub> are statistical method to get a mean time to a human effect at a certain constant concentration of smoke.

Typical values of 30-min LC<sub>50</sub> for CO, HCN, HCl and HBr (denoted by LC<sub>50CO</sub>, LC<sub>50HCN</sub>, LC<sub>50HCl</sub> and LC<sub>50HBr</sub>) as quoted in NFPA 269 are 5700 ppm, 150 ppm, 3700 ppm and 3000 ppm respectively.

Studying smoke toxicity has become a worldwide hot topic recently. International Organization for Standardization (ISO) had developed a standard 'ISO 13344 Determination of the Lethal Toxic Potency of Fire Effluents' in 1996 [8], which is only a general summary of the calculation method for determining LC<sub>50</sub>.

Smoke toxicity was also studied in the Sichuen Fire Research Institute and the Tsinghua University in China. A joint new national 973 fire project in this topic was started two years ago [13]. Results obtained are very useful as reference for the legislation on selecting building materials.

All the above had not yet appear in the prescriptive fire codes [1-4] of Hong Kong, nor considered in the fire engineering approach of fire safety design. Apart from a preliminary study [10-12], there is not yet systematical investigational works on smoke toxicity. In fact, these smoke toxicity tests should be applied for assessing local materials. Obviously, this is not possible without a detailed study.

#### 4. Fractional effective exposure dose (FED)

Tests on smoke toxicity can either be based on 'material' or 'chemical gases identified to cause troubles'. As the amount of those gases librated depends on the burning process, test based on those gases identified under some fire scenarios will be useful. Based on that, a concept

known as the N-Gas Model was developed by the National Institute of Standards and Technology (NIST) on the toxic potency of smoke in the NFPA 269 'Standard Test Method for Developing Toxic Potency Data for Use in Fire Hazard Modeling' [14] and ASTM E 1678 'Standard Test Method for Measuring Smoke Toxicity for Use in Fire Hazard Analysis' [15].

In following ASTM E1678, Fractional effective exposure dose (FED) is defined as "the ratio of the concentration and time product for a gaseous toxicant produced in a given test to that product of the toxicant that has been statistically determined from independent experimental data to produce lethality in 50% of test animals within a specified exposure and post-exposure period". FED can be expressed mathematically as:

$$FED = \sum_{i=1}^n \int_{t_0}^t \frac{c_i}{(ct)_i} dt \quad (1)$$

where

$c_i$  is the concentration of the  $i^{\text{th}}$  toxic component

$(ct)_i$  is the specific exposure dose (concentration-time product) required to produce the toxicological effect

When FED equal to 1, the mixture of the gaseous toxicants would be lethal to 50% of the exposed animals.

Mathematically, if the exposure time can be cancelled, the FED becomes the ratio of the average concentration of a gaseous toxicant to its LC<sub>50</sub> value for the same exposure time.

Tests on the physical aspects in NFPA 269/ASTM E 1678 are suitable for fire hazard assessment while implementing engineering performance-based fire code.

Transient concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, HCl, HCN and HBr denoted by [O<sub>2</sub>], [CO<sub>2</sub>], [CO], [HCl], [HCN] and [HBr] of the smoke generated from a sample will be measured in the chamber. The concentration-time (in ppm/min) product can then be deduced by integrating the area under the measured concentration-time curves.

FED can then be written as:

$$\text{FED} = \frac{m[\text{CO}]}{[\text{CO}_2] - b} + \frac{21 - [\text{O}_2]}{21 - \text{LC}_{50\text{O}_2}} + \frac{[\text{HCN}]}{\text{LC}_{50\text{HCN}}} + \frac{[\text{HCl}]}{\text{LC}_{50\text{HCl}}} + \frac{[\text{HBr}]}{\text{LC}_{50\text{HBr}}} \quad (2)$$

where

$$m = \begin{cases} -18 & [\text{CO}_2] < 5\% \\ 23 & [\text{CO}_2] > 5\% \end{cases} \quad (2a)$$

$$b = \begin{cases} 122000 & [\text{CO}_2] < 5\% \\ -38600 & [\text{CO}_2] > 5\% \end{cases} \quad (2b)$$

## 5. Preliminary Experimental Studies with NFPA 269/ASTM E1678

Preliminary tests following NFPA 269/ASTM E 1678 were carried out by a modified setup designed for local use. Physical aspects of the experiment were carried out at the first stage.

Two groups of selected samples are assessed:

- Timber: Pine, beech, maple, teak and oak;
- Plastics: PVC, PMMA sheets;

Samples of the testing specimen were placed at the combustion cell under the electric heater for 15 minutes. The specimen is either ignited by itself or by an igniter under the action of a 28.5 kWm<sup>-2</sup> heat flux emitted by the electric heaters. The electric heaters were turned off after 15 minutes. The gas components inside the animal exposure chamber were analyzed for 30 minutes by two gas analyzers on measuring [O<sub>2</sub>], [CO], [CO<sub>2</sub>]; and [HBr], [HCl] and [HCN] respectively.

As HCl and HBr cannot be distinguished by the gas sensor in this study, concentrations of them were combined. But as values of the 30-min LC<sub>50</sub> for both HCl and HBr are taken to be the same, i.e. 3800 ppm, the formula to calculate LC<sub>50</sub> can be revised as:

$$\text{FED} = \frac{m[\text{CO}]}{[\text{CO}_2] - b} + \frac{21 - [\text{O}_2]}{21 - 5.4\%} + \frac{[\text{HCN}]}{150\text{ppm}} + \frac{[\text{HCl}] \text{ or } [\text{HBr}]}{3800\text{ppm}} \quad (3)$$

LC<sub>50</sub> of product specimen can be estimated in this test rig by:

$$\text{LC}_{50} = \frac{\text{specimen mass loss}}{\text{FED} \times \text{chamber volume}} \quad (4)$$

For post-flashover fire, LC<sub>50</sub> calculated by the above equation would be corrected for hazard assessment. As CO is the major specie in smoke, the corrected LC<sub>50</sub> (denoted by LC<sub>50(corr)</sub>) will be calculated from the one without correction through [CO] and mass loss when FED is 1.1.

## 6. Results on NFPA 269/ASTM E1678

After conducting a series of experiments, transient concentrations of carbon monoxide from burning the two groups of samples are shown in Fig. 1 together for comparison.

Burning under the tested conditions, the pine sample got the highest peak [CO] of over 4000 ppm.

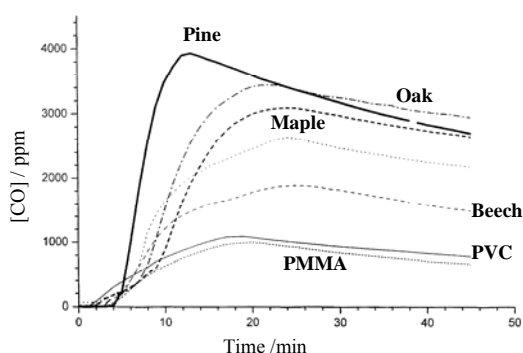


Fig. 1: Carbon monoxide concentration

Except PVC and pine samples, no HBr/HCl and HCN were emitted from the other samples. Transient [HBr] (with [HCl]) and [HCN] for PVC and pine samples are shown in Figs. 2 and 3. Burning the PVC sample would give [HBr], [HCl] and [HCN] up to 150 ppm. These gases are very corrosive and destructed the rubber and plastic tubings in the rig. Care must be taken in burning PVC.

Values of  $LC_{50}$  of these two groups of building materials were determined as shown in Table 1.

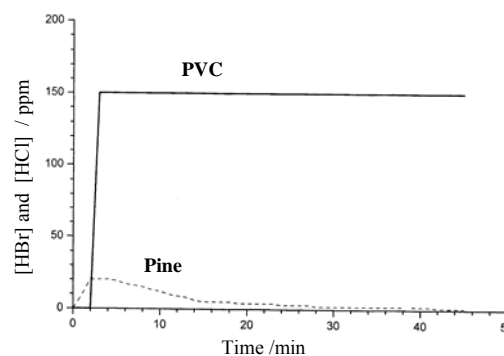


Fig. 2: Hydrogen bromide concentration

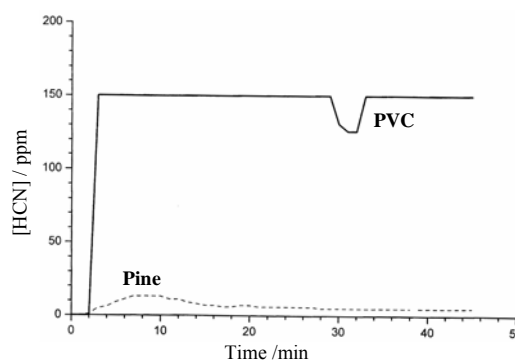


Fig. 3: Hydrogen cyanide concentration

The results showed that the value of  $LC_{50}$  of PVC is the smallest, indicating that the largest amount of toxic gas was released from burning PVC when comparing with other test materials. As shown in Fig. 2, HBr/HCl concentrations of 150 ppm was released while burning

Table 1: Testing results on smoke

Groups	Materials	NFPA 69/ASTM E1678		Cone calorimeter ISO 5660-1				
		FED	$LC_{50}/\text{gm}^{-3}$	TSR	pk[CO]	FED	Mass lost m/g	$LC_{50}/\text{gm}^{-3}$
Timber	Beech	0.80	147	126	243	0.049	52.3	27
	Maple	0.66	107					
	Teak	0.75	99					
	Oak	0.80	108					
Plastics	PMMA	0.15	256	337	111	0.022	69.8	79
	PVC	1.20	31	422	446	0.089	12.4	35

PVC. That might be due to dehydrochlorination of the PVC polymer chain would emit HCl of temperature from 200 to 350°C, and with maximum HCl emitted at 250 to 300°C. Under this condition, 90% of the chlorine atoms of the PVC polymer would be converted into HCl as reported [16].

The value of  $LC_{50}$  of PMMA is the largest among the tested samples. Combustion products of burning PMMA were only carbon monoxide and carbon dioxide, without other toxic components. A possible explanation is due to the relative simple polymer structure of PMMA, containing only carbon, hydrogen and oxygen atoms  $[CH_2C(CH_3)COOCH_3]_n$ . Almost complete combustion might be resulted and the whole test specimen was burnt out.

Burning behaviors of different wood samples were quite similar and so the values of  $LC_{50}$  of them were roughly the same except pine. This might be due to the similar micro-structure of wood as having cellulose, hemi-cellulose and lignin.

As PVC sheets have the lowest value of  $LC_{50}$ , it will be the most 'toxic' upon burning among the nine samples tested. Pine wood is the second one, then followed by teak, maple, oak, beech and then PMMA. The above is just a direct comparison on the measured  $LC_{50}$  values.

It is difficult to determine all the parameters to get FED of 1.1 as many samples would be required. In this study, the FED = 1.1 condition of PVC was conducted. The  $LC_{50(corr)}$  calculated is  $14.3 \text{ gm}^{-3}$ . Note that values of  $LC_{50(corr)}$  of PVC reported in the literature was about  $17.5 \text{ gm}^{-3}$ , calculated from the measured value [9] of  $13.73 \text{ gm}^{-3}$ .

All these demonstrated that the experimental results of this study are quite consistent with others available in the literature.

## 7. Cone Calorimeter with ISO 5660-1

Samples of wood, PVC, and PMMA are tested with a cone calorimeter [17] to study their fire behaviour. Flashover heat flux of  $20 \text{ kWm}^{-2}$  was applied. As PVC [9] is very difficult to ignite under  $20 \text{ kWm}^{-2}$ , higher heat flux of  $50 \text{ kWm}^{-2}$  was applied. As shown in Fig. 4 on the [CO] curve, more CO was emitted by PVC. Further, key parameters can be deduced [9] by the measured transient [CO],  $[CO_2]$ , smoke release rate  $S_R$  (in  $\text{s}^{-1}$ ) and smoke extinction area SEA (in  $\text{m}^2$ ) curves.

Smoke parameters are:

- Total smoke released at the end of the test, TSR (a non-dimensional quantity), calculated by integrating the  $S_R$  curve over the burning time  $t_B$ :

$$TSR = \int_0^{t_B} S_R dt \quad (5)$$

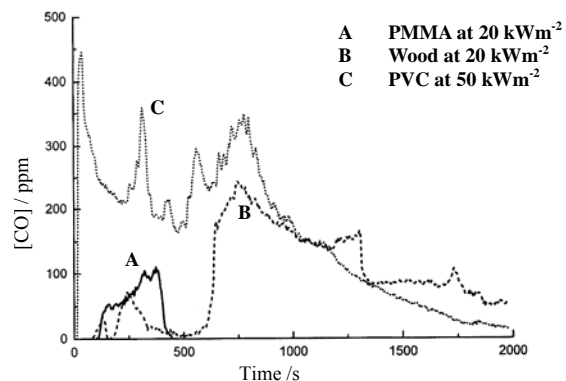


Fig. 4: Experimental rig.

- The peak Fractional Effective Dose (FED):

Under ISO 13344, basic analysis is carried out by FED in assuming that toxic effects to be linearly additive.

$$\text{FED} = \frac{[\text{CO}]}{5000} + \frac{[\text{HCN}]}{150} + \frac{[\text{HCl}]}{3800} + \frac{[\text{HBr}]}{3000} + \frac{[\text{NO}]}{1000} + \frac{[\text{NO}_2]}{200} \quad (6)$$

LC<sub>50</sub> are time-dependent, values for each chemical specie (such as 5000 for CO) used are the average LC<sub>50</sub> over 30 minutes.

Since only CO and CO<sub>2</sub> were measured and toxic potency LC<sub>50</sub> for CO<sub>2</sub> is much greater than LC<sub>50</sub> for CO (i.e. 5000 ppm) [18], FED was calculated [19,20] from the peak concentration of CO denoted by pk[CO] in the cone calorimeter by:

$$\text{FED} = \frac{\text{pk}[\text{O}]}{5000} \quad (7)$$

Values of TSR, pk[CO] and FED (from LC<sub>50</sub> in ppm, not yet converted to the units appropriate) for testing the two groups of samples are shown in Table 1.

## 8. Discussion

Thermal decomposition or combustion of combustibles gives a fire effluent atmosphere, causing toxic hazards, either in low or high concentration. As reviewed by Hartzell [21], there are at least three levels of engineering approach to protect occupants against a fire:

- Level 1: Prevention of ignition, but no effective method is available.
- Level 2: Active and passive fire protection with efficient evacuation, if ignition occurs.

- Level 3: Consequence to be not so serious of exposure to fire, if occurs.

Hazard analysis on the life threat components of fire is required on the level 3 protection in above. This is related to the toxicity of fire effluent resulted from agreed fire scenarios derived from specific fire safety goals.

As discussed by Babrauskas [22], LC<sub>50</sub> is commonly used in assessing smoke toxicity in products. Toxic effect might cause from two factors on burning real products:

- Real-scale mass loss rate
- Real-scale LC<sub>50</sub>

It was found from a developed database that LC<sub>50</sub> in actual fires would not be deviated much from LC<sub>50</sub> determined by bench-scale tests. However, the mass loss rates in a real fire and a bench-scale test varied significantly. Therefore, the burning rate should be reduced, rather than making the effluent less toxic. Anyway, another point of concern is how the materials will burn, as incomplete combustion of polymer will give higher levels of carbon monoxide.

LC<sub>50</sub> can be used as a ‘toxic potency’ parameters to account for combustion product toxicity. It can be viewed as ‘per-gram toxicity’ (in gm<sup>-3</sup>), not affected by the burning rate of the product nor by the amount of product present. The scale is an ‘inverse’ one as this is the amount of substance dispersed to a unit square volume to cause a 50% probability of lethality. Bench-scale LC<sub>50</sub> was commonly used. The recent standard ISO 13344 is the first normative international standard on smoke toxicity.

Toxic gases would be dispersed into some specific total air volume V. If there



is no design information on the building volume, an arbitrary value of 100m<sup>3</sup> was used for full-scale burning tests, and 0.01 m<sup>3</sup> for bench-scale test.

Effective values of LC<sub>50</sub> for the combustion products can be calculated in ISO 13344, in a fashion similar to equation (4) in terms of FED (with appropriate units), V and the mass lost Δm as:

$$LC_{50} = \frac{\Delta m}{FED \times V} \quad (8)$$

Values of full-scale FED for room tests and from the cone calorimeter are very different, say 0.1 and 6.7 respectively on a sample tested by Babrauskas [22]. But LC<sub>50</sub> are similar, with values 5.8 and 6.4 respectively. Perhaps, varying the space volume is the key.

Values of LC<sub>50</sub> on the timber, PMMA and PVC tested by the cone calorimeter were calculated with a correction factor of 4000 as shown in Table 1.

## 9. Codes Review

Fire safety provisions on active fire safety systems and passive building construction in Hong Kong follow four prescriptive fire codes [1-4]:

- Codes of Practice for Minimum Fire Service Installations and Equipment and Inspection, Testing and Maintenance of Installations and Equipment
- Code of Practice for Fire Resisting Construction
- Code of Practice for the Provision of Means of Escape in Case of Fire
- Code of Practice for the Provision of Means of Access for Firefighting and Rescue Purposes

Fire safety objectives of the local fire codes are on life safety. There are concerns on how to evacuate building occupants as soon as possible, explaining only why there are fire resistance requirement and protected corridors, lobbies and staircases.

In designing fire safety provisions, normally the fire load density is considered as the value specified in those local fire codes. This gives only the total heat released when all the combustibles are burnt out. No information on smoke toxicity is specified in the local fire codes yet. Results as in above should be specified as burning small samples of PVC as in the test will give out very toxic gases. This can be considered on implementing engineering performance-based fire codes or fire engineering approach in Hong Kong [23].

However, health effects nor post-exposure effects of the smoke products to the occupants are not yet included. Note that statistical fire records indicated that many fire victims were due to smoke toxicants. Therefore, smoke toxicity should be added to local fire codes.

As proposed by Babrauskas [22], taking full-scale value for FED in terms of the burning mass loss Δm<sub>f-s</sub>, volume V (something unknown) and LC<sub>50</sub> for real-scale fires as:

$$FED_{f-s} = \frac{\Delta m_{f-s}}{V \cdot LC_{50(f-s)}} \quad (9)$$

The mass loss Δm<sub>f-s</sub> can be predicted by a fire model. Assuming bench-scale measured LC<sub>50</sub> is correlated with LC<sub>50(f-s)</sub>, real-scale toxic fire hazard in a building is then inversely proportional to LC<sub>50</sub>.

From this study, it is observed that the PVC sample tested has the lowest LC<sub>50</sub> among the others. However, this sample is commonly used as building and finishing material for piping, flooring and electrical insulation in Hong Kong. Results of the experiments suggested that the use of that type of PVC sample should be limited and if possible, replaced with others. The toxic gases released by PVC during combustion are harmful to human beings. PMMA samples tested might be better as shown in the measured LC<sub>50</sub>. The materials might be less harmful upon burning.

## 10. Conclusions

The toxic potency parameter LC<sub>50</sub> is proposed to quantify the toxicity of smoke, due to chemical species CO, CO<sub>2</sub> and HCN on narcosis-producing toxicants, and HCl and HBr on irritants. Values on LC<sub>50</sub> are very useful in assessing materials while setting up design guides or regulations in selecting materials, and implementing engineering performance-based fire codes [23,24].

Values of FED and LC<sub>50</sub> can be worked together with fire models in studying consequences of different fire scenarios due to different combustible.

The current paper is only a preliminary report on a modification of the standard test NFPA 269/ASTM E1678. 'Toxic potency' of two group samples of common building materials were assessed.

Further works should be carried out.

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