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Correlation analysis of cone calorimetry test data assessment of the procedure with tests of different polymers

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Abstract Correlation algorithms are used to analyse the relationship amongst heat release rate, carbon dioxide and carbon monoxide generated in cone calorimetry test of material flammability. These correlation algorithms include Pearson's correlation, Spearman's rank correlation and Kendall's rank correlation. Cone test data of seven materials are analysed. These materials are two kinds of polyvinyl chloride wall panel, glass-reinforced plastics, vinyl panel, polymethyl methacrylate, polyurethane and two types of expanded polystyrene foam. Correlation coefficients are calculated for cone calorimeter results from tests at 50 kW m^{-2} of these materials. The distribution of the coefficients would be used to discriminate the test materials according to the so-called FO-categories which can help to predict the time to flashover.

Keywords Correlation analysis · Cone calorimetry · Flashover prediction · Material fire safety

Introduction

Fire is a complex phenomenon. Its behaviour and effects depend upon a variety of factors which are inter-related in an intricate way. The behaviour of materials and products in a fire will depend on the characteristics of the particular fire, the way the materials are used and the environment in which they are exposed [1]. To clarify the fire safety of material, one should consider all aspects of the fire performance of the material in terms of heat release, flame spread, smoke production and toxicity and its contribution to the propagation of fire.

Many test standards have been developed to evaluate material's fire performance. These standards could be classified based on test scale. Small or bench scale tests include ISO 5660/ASTM E1354, UL94, ASTM D2863, ASTM E662, ASTM E162/3675 and ASTM E1678. Room scale tests include ISO9705, SBI/EN13823, ASTM E1623 and ASTM E114-74, whilst large scale tests include NFPA 265, and Steiner tunnel/UL 1256.

One of the most commonly used parameter to characterize fire behaviour of material is heat release rate (HRR), the term HRR is defined as the amount of calorific energy released per unit time by a material during combustion under specified test conditions. It is one of the fundamental properties of fire and should almost always be taken into account in any assessment of fire hazard since it significantly affects the development of the fire [1]. HRR is one of the properties of cone calorimetry. As for a large number of materials, the amount of energy release per unit mass of O_2 consumed or per unit mass of CO_2 produced is relatively constant. This method relies on oxygen consumption or carbon dioxide and carbon monoxide generation measurements [2]. From the measurement of the oxygen consumption, HRR is determined by the oxygen concentration and the flow rate in the exhaust product stream. Cone calorimeter according to ISO 5660 is the first choice equipment used for measuring of HRR of materials [3–5]; many models have been developed based on HRR to classify the fire safety performance of materials [6–8].

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The products of combustion have internal relations amongst each other would display correlation facts in signals. The objective of the research on the correlation between HRR and CO\CO$_2$ might be useful in material and product evaluations, mathematical modelling, design purposes or development and research.

Test procedure and materials

Test procedure

All the tests were performed with the cone calorimeter in State Key Laboratory of Fire Safety Science of China, in University of Science and Technology of China. This calorimeter is based on 'the oxygen consumption method', and meets all existing standards including ISO5660 and ASTM E1354. The cone is a Standard Cone Calorimeter from Fire Testing Technology Limited, UK.

The tested materials were two kinds of polyvinyl chloride (PVC) wall panel, glass-reinforced plastics (GRP), vinyl panel, polymethyl methacrylate (PMMA), polyurethane (PU) and two types of expanded polystyrene (EPS) foam. All material samples were treated according to the guided procedure of cone test with a surface area of 100 × 100 mm, and were exposed in the horizontal orientation with the standard pilot operating at an irradiance level of 50 kW m^{-2}. Samples were tested with the use of an edge frame to retain the specimen as allowed in the standard. The edge frame reduces the test surface area to 0.008836 m^2, and this is the area used in calculations. The bottom of each sample was hold by aluminium foil and packed to the appropriate test level height using asbestos pad.

Material description

Cone test results of eight kinds of materials are analysed. These materials are two kinds of PVC wall panel, GRP, vinyl panel, PMMA, PU and two types of EPS foam.

PVC is a vinyl polymer constructed of repeating vinyl groups (ethenyls) having one hydrogen replaced by chloride. PVC is the third most widely produced plastic. The PVC samples tested in this article are rigid PVC.

GRP is a fibre-reinforced polymer made of a plastic matrix reinforced by fine fibres of glass. The GRP panel consists of tissue layer, chopped strand mat, woven roving and resin.

Vinyl products are widely encountered in home and industrial applications as cover materials, pipes and fitting, household and automotive electrical applications, as well. The vinyl panel sample used here is a kind of vinyl-based lining material with an average density 1,152 kg m^{-3} (100 × 100 mm and 2 mm thickness) provided commercially by a Plastic Company.

PMMA is the synthetic polymer of methyl methacrylate and is always used as standard material to calibrate cone calorimeters [9].

PU is any polymer composed of a chain of organic units joined by carbamate (urethane) links. PU polymer is a combustible solid and can be ignited if exposed to an open flame. PU exposure decomposition from fire can produce mainly carbon monoxide, and trace nitrogen oxides and hydrogen cyanide. A kind of PU foam, which was used as filling material for sandwich panels, was tested by cone calorimeter and the data was used in this article.

EPS is combustible. As EPS is heated it softens, and at about 150 °C it begins to shrink. Continued heating will melt it to liquid and then a combustible gas will form above 200 °C. This gas can be ignited at temperatures between 360 and 380 °C, and will self-ignite around 500 °C. When burning, it produces 40–45 MJ kg^{-1} of heat. Gases released during combustion are predominantly CO and CO$_2$.

Fire safety classification of materials

Östman and Tsantaridis [7] presented a regression model for prediction of time to flashover in the room corner test based on empirical data. Cone calorimeter results from tests at 50 kW m^{-2} are used as input data to this model, which also requires information about mean density of the tested product. The regression model is expressed in the following equation

$$t_{\mathrm{FO}} = 0.07\frac{t_{\mathrm{ig}}^{0.25}\rho^{1.7}}{\mathrm{THR}_{300}^{1.3}} + 60, \quad (1)$$

where t_{FO} is the time to flashover in the room corner test, t_{ig} is the time to ignition in the cone calorimeter at 50 kW m^{-2}, THR_{300} is the total heat release during 300 s after ignition at 50 kW m^{-2} and ρ is the mean density. t_{FO} is used to determine surface material belongs to a so-called FO-categories which can help to predict the time to flashover. The FO-categories grouping is based on ISO room corner tests. A propane burner placed in a corner exposes the test material to a HRR of 100 kW for 10 min and then 300 kW for the next 10 min. The test is terminated if flashover has been reached; otherwise the total testing time is 20 min. A set of separation criteria for grouping products according to the time to flashover (t_{FO}) based on above ISO room test. These criteria divide the tested products into four groups, the so-called FO-categories [8] 1 to 4.

Surface material belongs to which category is determined by application of the following set of rules:

- FO-category 1: products not reaching flashover during 1,200 s of testing time.

- FO-category 2: 600 s $\le t_{FO} < 1{,}200$ s
- FO-category 3: 120 s $\le t_{FO} < 600$ s
- FO-category 4: $t_{FO} < 120$ s.

According to calculated t_{FO} for all samples less than 50 kW m^{-2}, the FO-categories of these materials are listed in Table 1.

Correlation algorithms

There are a number of coefficients which are appropriate to use under different circumstances. Amongst them, the most frequently used one is Pearson's product moment correlation coefficient, which is sensitive only to a linear relationship between two variables (which may exist even if one is a nonlinear function of the other). It is obtained by dividing the covariance of the two variables by the product of their standard deviations. The population correlation coefficient $\rho_{X,Y}$ between two random variables X and Y with expected values μ_X and μ_Y and standard deviations σ_X and σ_Y is defined as:

$$\rho_{X,Y} = \mathrm{corr}(X,Y) = \frac{\mathrm{cov}(X,Y)}{\sigma_X \sigma_Y} = \frac{E[(X-\mu_X)(Y-\mu_Y)]}{\sigma_X \sigma_Y}, \tag{2}$$

where E is the expected value operator, cov means covariance, and, corr a widely used alternative notation for Pearson's correlation. The Pearson correlation is defined only if both of the standard deviations are finite and both of them are nonzero.

If we have a series of n measurements of X and Y written as x_i and y_i where $i = 1, 2, \ldots, n$, then the sample correlation coefficient can be used to estimate the population Pearson correlation r between X and Y. The sample correlation coefficient is written as:

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{(n-1)s_x s_y} = \frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2 \sum_{i=1}^{n}(y_i-\bar{y})^2}} \tag{3}$$

where x and y are the sample means of X and Y, and s_x and s_y are the sample standard deviations of X and Y.

This can also be written as:

$$r_{xy} = \frac{\sum x_i y_i - n\bar{x}\bar{y}}{(n-1)s_x s_y} = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{\sqrt{n\sum x_i^2 - (\sum x_i)^2}\sqrt{n\sum y_i^2 - (\sum y_i)^2}}. \tag{4}$$

Rank correlation coefficients, such as Spearman's rank correlation coefficient and Kendall's rank correlation coefficient measure the extent to which, as one variable increases, the other variable tends to increase, without requiring that increase to be represented by a linear relationship.

Spearman rank correlation coefficient

Spearman Rank correlation coefficient is a non-parametric measure; therefore it is suitable for data that is not normally distributed. It works better in detecting a non-linear relationship between two variables.

The Spearman correlation coefficient is defined as the Pearson correlation coefficient between the ranked variables. The n raw scores X_i, Y_i are converted to ranks x_i, y_i, and ρ_S is computed from these:

$$\rho_S = \frac{\sum(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum(x_i-\bar{x})^2\sum(y_i-\bar{y})^2}}. \tag{5}$$

Tied values are assigned a rank equal to the average of their positions in the ascending order of the values. In the Table 2, notice how the rank of values that are the same is the mean of what their ranks would otherwise be:

In applications where ties are known to be absent, a simpler procedure can be used to calculate ρ_S. Differences $d_i = x_i - y_i$ between the ranks of each observation on the two variables are calculated, and ρ_S is given by:

$$\rho_S = 1 - \frac{6\sum d_i^2}{n(n^2-1)}. \tag{6}$$

Because statistical rank is just the ordinal number of a value in a list, Spearman rank correlation coefficient can be computed even when actual values of the variables are unknown.

Table 1 FO-category of materials

Material	Label	Density/kg m^{-3}	FO-categories
PVC-wall panel	PVC	1,649	FO-category 1
PVC-wall panel	WP	1,632	FO-category 1
GRP panel	GRP	1,578	FO-category 3
Vinyl panel	VP	1,152	FO-category 3
PMMA	PMMA	1,180	FO-category 4
Sandwich panel filling	PU	31.3	FO-category 4
Low density EPS foam	EPS-L	12.8	FO-category 4
High density EPS foam	EPS-H	32.6	FO-category 4

Table 2 Rank of values

Variable X_i	Position in the descending order	Rank x_i
0.8	5	5
1.2	4	3.5
1.2	3	3.5
2.3	2	2
18	1	1

Kendall correlation coefficient

Kendall correlation coefficient, or Kendall tau, is equivalent to Spearman *R* in terms of their assumptions and statistical power. However, Kendall correlation coefficient has a more intuitive interpretation. And its algebraic structure is simpler. Furthermore, it does not require ordering of the data before the computation.

Kendall correlation coefficient can be computed by

$$r_K = \frac{2(C - D)}{n(n-1)} \tag{7}$$

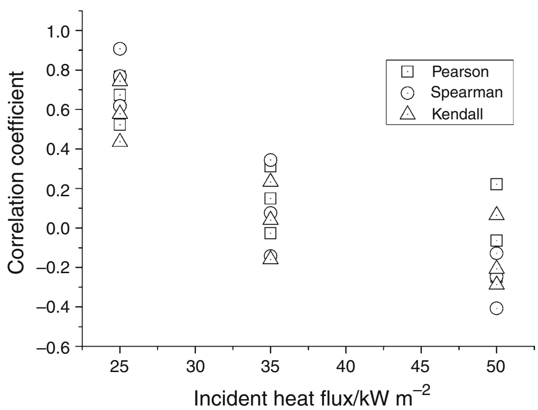

Fig. 1 Correlation coefficient of HRR and CO of PVC samples

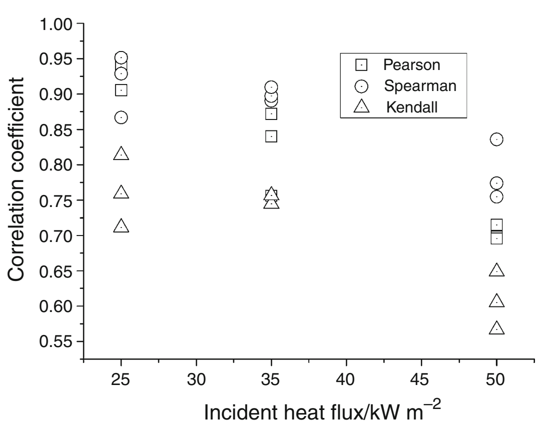

Fig. 2 Correlation coefficient of HRR and CO_2 of PVC samples

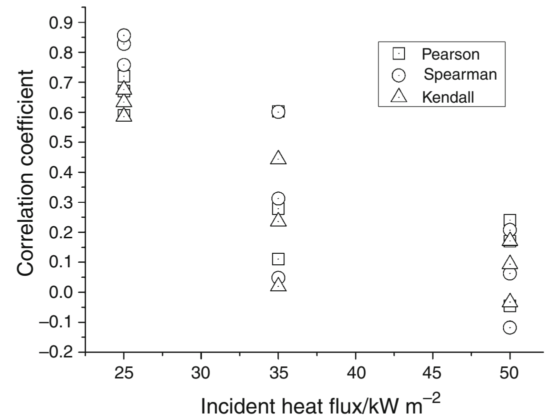

Fig. 3 Correlation coefficient of CO and CO_2 of PVC samples

where *C* is the number of concordant pairs (pairs of observations that have the same signs) and *D* is the number of discordant pairs (pairs of observations that have opposite signs).

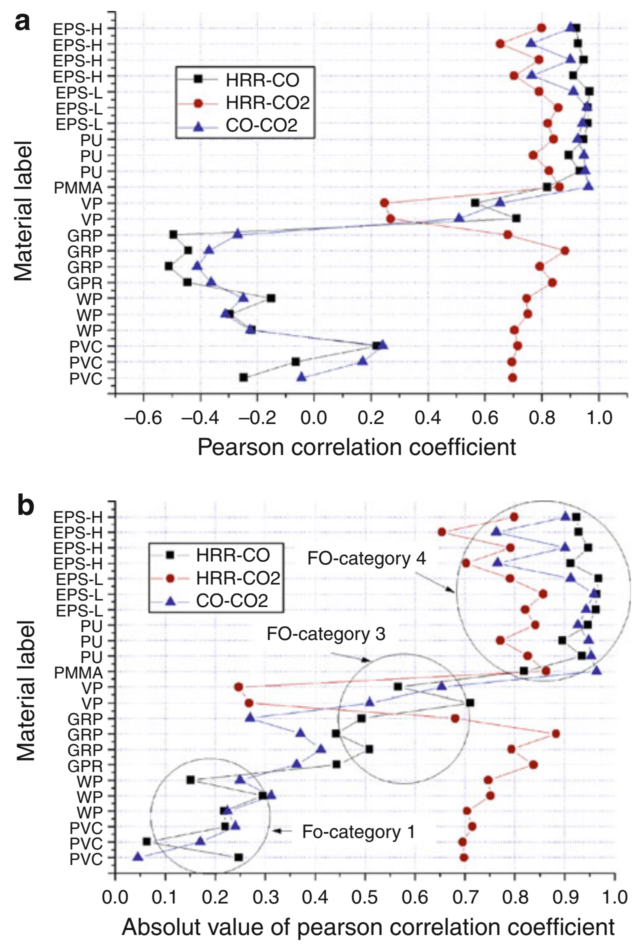

Fig. 4 **a** Pearson correlation coefficients of materials. **b** Absolute value of Pearson correlation coefficients of materials

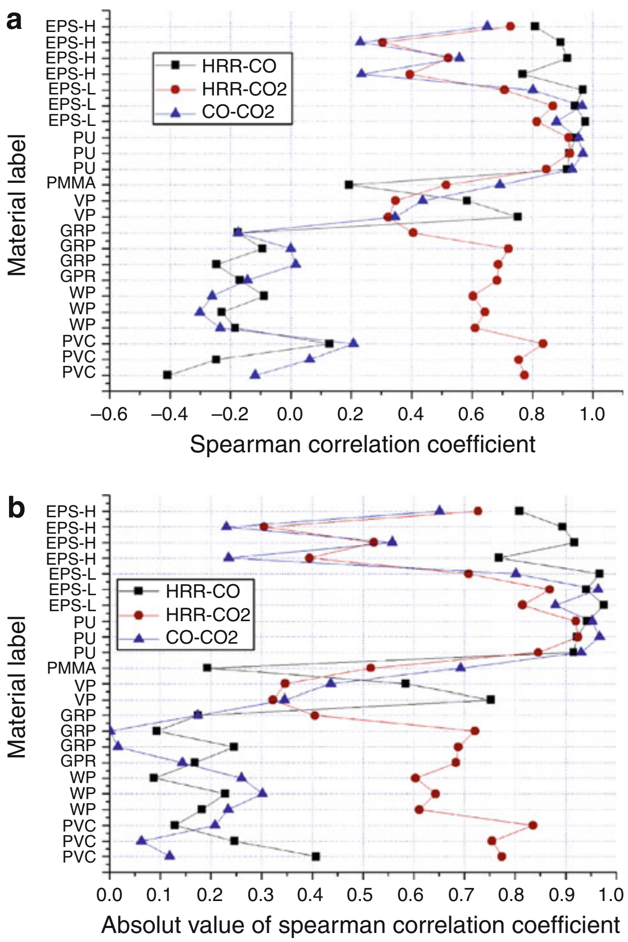

Fig. 5 **a** Spearman correlation coefficients of materials. **b** Absolute value of Spearman correlation coefficients of materials

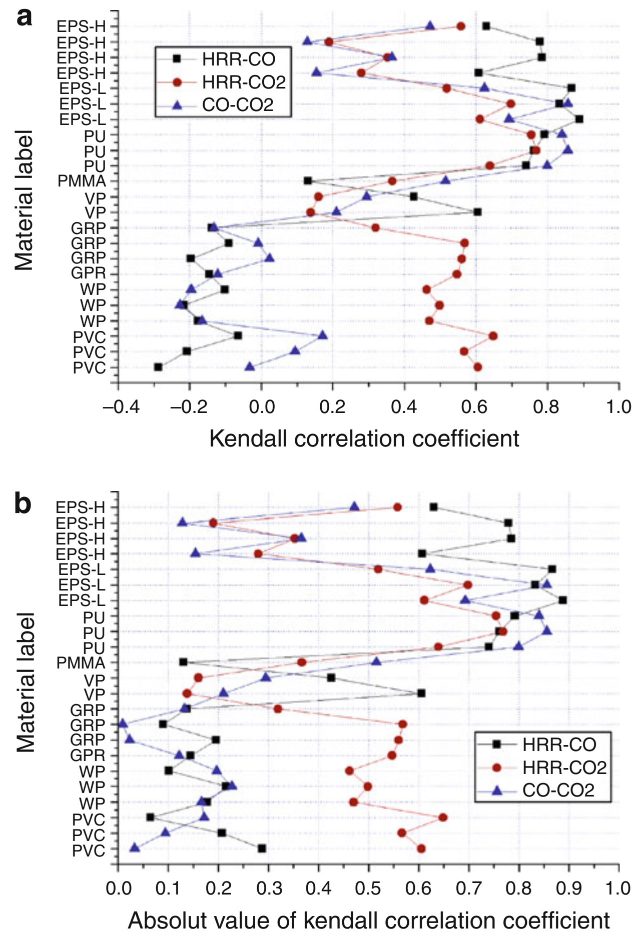

Fig. 6 **a** Kendall correlation coefficients of materials. **b** Absolute value of Kendall correlation coefficients of materials

Analysis and results

Single material under different heat flux

Figures 1, 2 and 3 illustrate the calculated correlation coefficients of HRR–CO, HRR–CO_2 and CO–CO_2 for all PVC tests. From Fig. 1, higher correlation between HRR and CO could be seen clearly in lower incident heat flux, and the tendency is obvious. In Fig. 2, the results are scattered, no evident tendency is displayed. But in Fig. 3, the correlation coefficients again decrease with the increase of incident heat flux for CO–CO_2. From the overall analysis of all correlation coefficients, the Spearman coefficients have higher values whilst Kendall coefficients are lower.

Multi materials under 50-kW m^{-2}-incident heat flux

The Figs. 4, 5 and 6 are the summary of Pearson, Spearman and Kendall correlation coefficients calculated for all the materials listed in Table 1 under the incident heat flux 50 kW m^{-2}. The correlation coefficients of HRR–CO and CO–CO_2 have close relation with the FO-categories of materials, especially in Fig. 4b where all three types of the tested materials are clearly classified.

FO-category 1 materials, such as WP and PVC in these tests, have lower HRR–CO and CO–CO_2 correlation coefficients, whilst FO-category 4 materials, such as EPS and PU in these tests, have higher HRR–CO and CO–CO_2 correlation coefficients. The HRR–CO_2 correlation coefficients do not have close relation with the FO-categories of materials, at least for the materials tested in this article. With the comparison of the three algorithms for calculating correlation coefficients, the Pearson's, as shown in Fig. 4a, b, illustrates a better function in classification of materials than Spearman's and Kendall's.

Conclusions

Above analysis illustrates that the correlation between HRR and other combustion products could be used to classify the FO-categories of materials. HRR has close relationship with exhaust gases, and for cone calorimeter tests it can be assumed that the exhaust gases consist primarily of nitrogen, oxygen, CO_2, water vapour and CO; thus, measurements of these gases can be used to determine the actual expansion. The correlation analysis could be used in identifying the relationship between internal combustion procedure and external signal characteristics. Construct the correlation between the energy output (HRR) and exhaust material yield of combustion will help the research on the dynamic procedure of combustion. But the generation of CO and CO_2 is different for materials, for example some materials generate CO and CO_2 both during pyrolysis and combustion, some are not. This would influence the analysis result of correlation calculation. Correlation analysis could be used in data mining of cone calorimeter data to derive more useful information on studying of fire behaviour of materials.

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References

1. ISO 5660-1:2002 Reaction-to-fire tests—heat release, smoke production and mass loss rate—part 1: heat release rate (cone calorimeter method).
2. Biteau H, Steinhaus T, Simeoni A, Schemel C, Marlair G, Bal N, Torero JL. Calculation methods for the heat release rate of materials of unknown composition. Proceedings of the 9th International Symposium on Fire Safety Science, vol 9. 2009. p. 1165–1176.
3. Kim J, Lee J-H, Kim S. Estimating the fire behavior of wood flooring using a cone calorimeter. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-1902-1.
4. Lomakin SM, Dubnikova IL, Shchegolikhin AN, Zaikov GE, Kozlowski R, et al. Thermal degradation and combustion behavior of the polyethylene/clay nanocomposite prepared by melt intercalation. J Therm Anal Calorim. 2008;94:719–26.
5. Janowska G, Kucharska-Jastrząbek A, Rybiński P. Thermal stability, flammability and fire hazard of butadiene-acrylonitrile rubber nanocomposites. J Therm Anal Calorim. 2011;103:1039–46.
6. Capote JA, Alvear D, Abreu O, Lázaro M, Puente E. Modelling pyrolysis of medium density Polyethylene. Int Rev Chem Eng. 2010;7:884–90.
7. Östman BA-L, Tsantaridis LD. Correlation between cone calorimeter data and time to flashover in the room fire test. Fire Mater. 1994;18:205–9.
8. Hansen AH, Hovde PJ. Prediction of time to flashover in the ISO 9705 room corner test based on cone calorimeter test results. Fire Mater. 2002;26:77–86.
9. Lindholm J, Brink A, Hupa M. Cone calorimeter-a tool for measuring heat release rate. SNCI, 6th Topical Meeting, measuring techniques in combustion, Göteburg, Sweden; 2008.