COMBUSTION TOXICITY ANALYSIS: ADVANCES USING A SPECIALIZED SAMPLING TECHNIQUE FOR FOURIER TRANSFORM INFRARED (FTIR) ANALYSIS

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ABSTRACT

The cone calorimeter as defined by ISO 5660, ASTM 1354, and NFPA 264A is used to assess the reaction to fire of almost any material that must be evaluated in the fire science field. Typical combustion gas analyses include oxygen, CO and CO2. Oxygen consumption is used to determine rate of heat release. Analysis of combustion gases other than oxygen, CO and CO2 has been attempted using filters to remove the solid smoke particles before analysis. This method has generated unreliable results due to the adsorption of many gas components on the active carbon particles deposited on the filters. A technique using Fourier Transform Infrared (FTIR) analysis without filtration will be disclosed and a discussion will be presented of the analytical results of toxic gases produced from various flame retarded polymeric materials. Use of such data in lethal toxic potency determinations is also reviewed.

INTRODUCTION

The cone calorimeter is an instrument used to assess the reaction to fire of materials that must be evaluated in the fire science field. The rate of heat release is the most important property obtained by cone calorimeter testing. To determine heat release rate cone calorimeters use the principle of oxygen consumption, that is for every kilogram of oxygen consumed by a burning material, 13.1 MJ of heat energy are released. Systems can optionally be equipped with carbon dioxide (CO_2) and carbon monoxide (CO) analysis equipment.

The capability of analyzing the combustion effluent gases for components in addition to CO_2 and CO make the cone calorimeter a much more versatile instrument for defining the fire safety of materials. This capability has been made possible through the coupling of the cone calorimeter with an integrated FTIR (Fourier Transform InfraRed) gas analysis system. This new technology uses a "DIRTY CELL"® for the FTIR cell and permits the analysis of all major combustion products on a real time concentration basis. These measurements can be used in further analyses to define Fractional Effective Dose (FED) and calculate lethal toxic potency (LC_{50}) of tested materials.

Many prior attempts have been made to combine FTIR analysis with the cone calorimeter. These attempts have utilized filtration of the combustion products before introduction of the FTIR cell. These filtration systems have been demonstrated to remove various components of combustion gases through absorption on the carbon (activated carbon) that is deposited on the filter media. This absorption produces questionable data on the amount of toxic materials in the combustion gases in such systems. The new "DIRTY CELL"® technology eliminates this problem. The new system, CTA/FTIR (Combustion Toxicology Analysis/Fourier Transform InfraRed), was developed at the request of customers by the Fire Science Products Group of Atlas Electric Devices Company. The first commercial units have been delivered and are operational.

DETECTION AND QUANTIFICATION

The analysis of multiple gases is possible with this newly developed system. The analysis software in the system is initially configured to detect and quantify the gases shown in Table 1. Also shown are the designed detection limits (parts per million) of the gases analyzed. Note that water (H_2O) is included in the table.

Table 1 CTA/FTIR Gas Species and Detection Limits

Gas Species	Range of Detection
CO	1 ppm to 2%
CO_2	300 ppm to 10%
HCN	5 ppm to 500 ppm
HCl	5 ppm to 5000 ppm
SO_2	15 ppm to 1%
NO	2 ppm to 2%
NO_2	15 ppm to 500 ppm
NO_x	5 ppm to 2%
HBr	5 ppm to 1000 ppm
HF	5 ppm to 5000 ppm
H_2O	5000 ppm to 10%
HC	25 ppm to 5000 ppm

Since the FTIR spectra are obtained and stored during the run, it is possible to use the spectra to quantify gases other than those shown in Table 1.

THE CTA/FTIR SYSTEM

The system is designed from the start to be compatible with the cone calorimeter and is attached to the cone calorimeter sampling system. The data acquisition system is integrated between the cone calorimeter and the FTIR gas analysis systems. Data from the two systems is merged and

presented in a spreadsheet format for ease of analysis and export of the data to other systems. Figure 1 shows the schematic of the gas sampling system from the cone calorimeter sampling ring through the FTIR exhaust system.

The CTA/FTIR system utilizes the following components:

FTIR Spectrometer
"Dirty Cell"™ Heated, Gas Cell
Heated Sample Line
MCT, N_2 Cooled Detector
"Omnic/QuantCom" Software
Pentium Computer
Control and Communication Software
Temperature, Pressure, and Flow Control

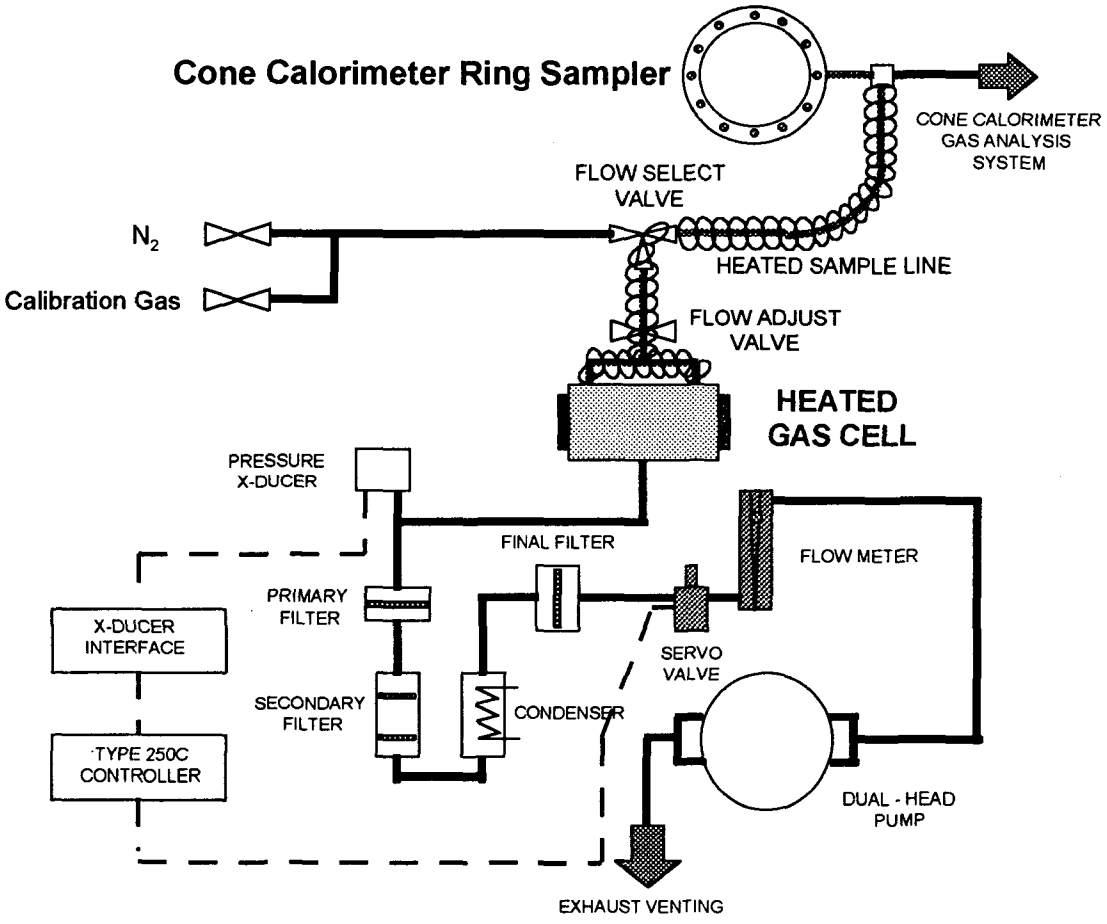

Figure 1 CTA/FTIR GAS SAMPLING SYSTEM

ANALYTICAL RESULTS OF TEST RUNS

The CTA/FTIR data is time coordinated with the cone calorimeter data. Shown in Table 2 is an example of the CTA/FTIR data taken at two specific times during the test. The material burned was polypropylene flame retarded with a brominated flame retardant and antimony oxide.

Table 2 CTA/FTIR GAS ANALYSIS

System ID **Atlas CTA/FTIR unit**
Title **950727A6**
Method Title **Atlas CTA 18 July 1995**

Time sec.	**CO** ppm	**CO_2** ppm	**HCN** ppm	**HCl** ppm	**NO** ppm	**NO_2** ppm	**HBr** ppm
151	1316.429	49648.14	8.819	1.142	3.755	1.488	136.687
152	1320.608	53342.19	-3.392	1.155	4.166	1.855	126.233
Time sec.	**HF** ppm	**H_2O** ppm	**HC** ppm	**SO_2** ppm	**CH_4** ppm	**C_2H_4** ppm	**NO_x** ppm
151	.0310	32982.8	162.321	1.583	2.617	501.414	5.243
152	0.336	33140.1	153.363	1.504	2.674	595.459	6.021

The data generated during this cone calorimeter test includes similar ppm readings at each second during the test. Test duration was 317 seconds with radiant heat flux at 50 kW/m^2.

Figure 2 below shows a graph of the heat release rate and the amount of hydrogen bromide in the combustion gas of this brominated polypropylene sample as a function of time. By integration of the area under the hydrogen bromide curve we can define the total amount of HBr evolved during the combustion.

The CTA/FTIR system can provide the concentrations of other gases present in the combustion gas and the total amounts evolved during the combustion can be similarly defined.

The ability of the CTA/FTIR system to discriminate between flame retardants can be of real assistance in defining differences in materials that by other physical tests and fire science evaluations are determined to be the same. If an aromatic bromine flame retardant and a cycloalphatic chlorine flame retardant are interchanged the CTA/FTIR would show the difference through the combustion gas analysis. In the case of the possible erroneous substitution of calcium carbonate for a metal hydrate FR the CTA/FTIR would show the increased evolution of CO_2 and the differences in water evolved. Similar discriminations could be made with other material interchanges.

All information needed to determine Fractional Effective Dose (FED) and calculate LC_{50} toxicity values for this material is available from the data generated using the CTA/FTIR system and the standard cone data. An explanation of this determination is further detailed below.

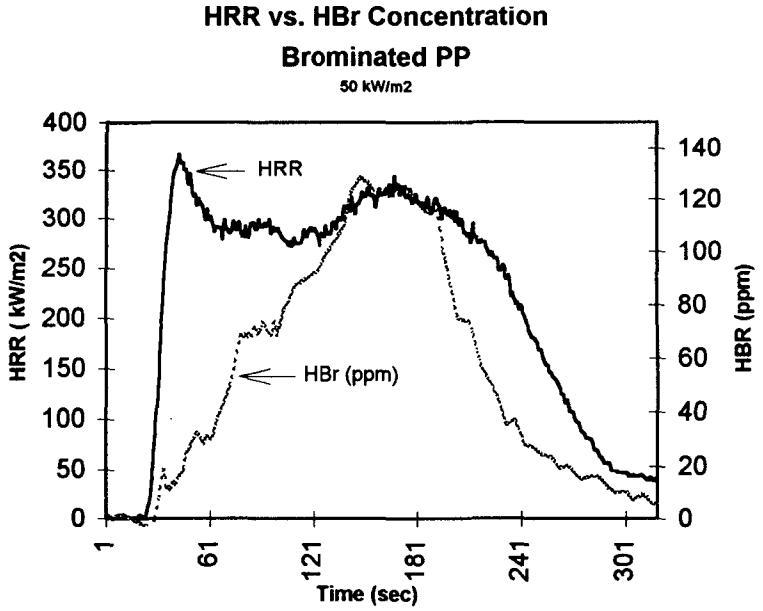

Figure 2 HEAT RELEASE RATE VERSUS HBr CONCENTRATION

The calculation shown here is an attempt to combine the toxic properties of the materials present in a gas into one toxicology evaluation. This method is used in other toxicological evaluation standards such as NFPA 269. In these standards a prediction of LC_{50} can be done without exposure of animals to the toxic materials. The lethal toxic potency may be predicted from the combustion atmosphere analytical data for CO, CO_2, O_2 and if present HCN, HCl, and HBr. This is accomplished through the use of fractional effective dose calculations. Fractional effective dose calculations are based on experimental data and take into account the toxicity of the various components of the combustion atmosphere. Equation 1 shows the calculation for FED.

$$FED = \frac{m[CO]}{[CO_2]-b} + \frac{21-[O_2]}{21-LC_{50}O_2} + \frac{[HCN]}{LC_{50}HCN} + \frac{[HCl]}{LC_{50}HCl} + \frac{[HBr]}{LC_{50}HBr} \quad (1)$$

In this equation the values for m and b are dependent on the CO_2 concentration. If the CO_2 concentration is less than 5% then m = -18 and b = 122,000; and if CO_2 concentration is above 5% then m = 23 and b = -38,600. The values for concentration are all in parts per million with the exception of O_2 which is in percent. The statistically determined LC_{50} values for the various components are:

O_2	5.4%
HCN	150 ppm
HCl	3700 ppm
HBr	3000 ppm

The LC_{50} value for the brominated polypropylene test sample is determined by equation 2

$$LC_{50} = \frac{\text{specimen mass loss}}{\text{FED x chamber volume}} \qquad (2)$$

When we entered the data on the polypropylene test sample into the FED and LC_{50} formulas we found the FED to be 0.124 and the LC_{50} to be 24.8.

It should be pointed out that the burning conditions are different between the cone calorimeter and other devices used to provide the toxic gases for analysis. The cone calorimeter is a well ventilated environment. As an example of different conditions, a test run according to NFPA 269 may be an oxygen deficient burn.

Results from another CTA/FTIR evaluation are shown in Figure 3. Specifically of interest in this evaluation was the amount of HCN produced while burning a sample of flexible polyurethane foam Again shown is the heat release rate and the amount of HCN in the combustion gas.

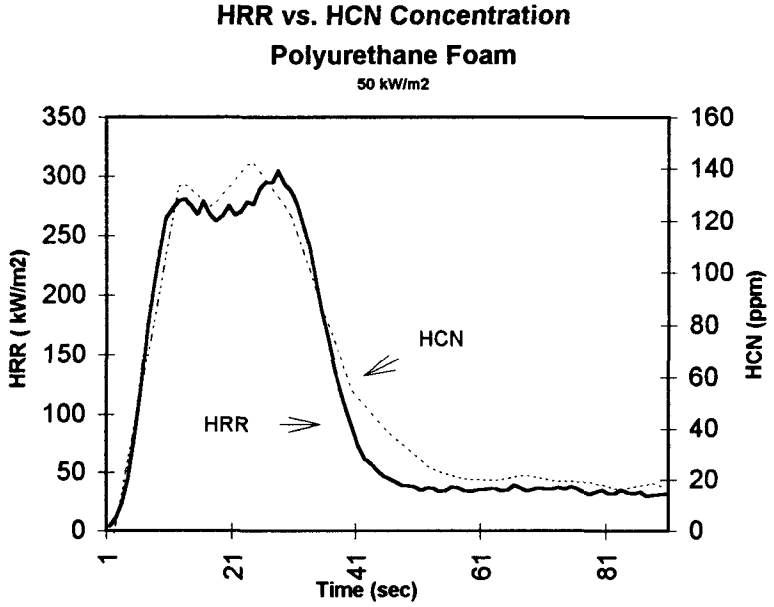

Figure 3 HEAT RELEASE RATE VERSUS HCN CONCENTRATION

The FED and LC_{50} for this sample were determined by using the data from the CTA/FTIR system and the regular cone data in the equations described above. The FED was 0.283 and the LC_{50} was 4.73.

These FED and LC_{50} values found for both the polypropylene and the polyurethane samples are consistent with the toxicology known for the two materials.

SIGNIFICANCE OF THIS TECHNOLOGY

The CTA/FTIR system provides data which when properly manipulated allows the user to define the total amount and average concentration of each toxic gas released during a test. It also

provides data on the production of these gases at any time during the test. This is a great advantage over the chemical analysis based methods of determining the concentrations of the toxic gases. The toxic gas production in various scenarios can be studied by varying the conditions of the cone calorimeter burn. These variations can include changing the incident heat and even the oxygen concentrations in the ambient air in the more sophisticated systems.

CONCLUSION

In this review we have demonstrated toxicity calculations. We have described a new technology which may address and eliminate the limitations of oxygen consumption theory upon which cone calorimeter testing is based. Specifically the heat release results from the oxygen consumption cone calorimeter can be refined by using the amount of water in the combustion gas to define how much water has been contributed from the modifiers in the sample formulations. When this refinement is made the rate of heat release based on oxygen consumption can be enhanced and corrected to reflect the actual heat release of the material.

Smoke in the fire science field is an all inclusive term. Smoke is made up of particulate and combustion gases. We have defined what is in the combustion gases and we have gained a greater understanding of the combustion process. We have provided a method to analyze for toxic gases produced in the combustion process and suggested a way to use these results in toxicological assessments.