Sampling-Window Based Approach for Fire Gas Analysis of Rigid foams

by

Bryn Jones

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Mechanical Engineering

Waterloo, Ontario, Canada, 2013

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Bryn Jones, P. Eng.

Abstract

A sampling-window based approach was developed to collect and analyze the gases evolved during fire performance testing using the cone calorimeter. For this purpose, a Fourier Transform Intra-red (FTIR) Spectroscopy system and a Novatec analyzer were coupled to the cone calorimeter.

An experimental gas sampling apparatus was designed and constructed and a sampling-window based method was developed. The sampling-window based method was initially tested using blue Styrofoam samples, then a small number of intumescent materials were also examined. Using the new integrated system, spectral scans were taken with an FTIR using 30s, 45s and 60s sampling windows, during off-gasing, fire growth, steady heat release rate, and fire decay stages of cone calorimeter testing.

By focusing the sampling window on a specific stage of fire development the tests indicated that high concentrations of toxic gases were evolved during sample off-gasing, before ignition. In contrast to other methods that are designed to obtain total toxic gas yield over the full course of a cone calorimeter fire performance test, the sampling-window method here allows for a greater understanding of fire gas evolution at the various stages of fire growth and development.

With the cone calorimeter coupled with a preconfigured “out of the box” lightweight portable ambient air analyzer and the sampling-window based approach developed, the fire gases associated with the polystyrene (blue Styrofoam) could be identified along with a number of the fire gases typically associated with the intumescent foam.

For further analysis of fire gases produced, a calibrated, lab quality FTIR, with a higher resolution than the preconfigured “out of the box” lightweight portable ambient air analyzer may be required. However the system configuration and methodology would remain the same as developed here.

The sampling-window based approach developed is useful for use in the development of other gas sampling techniques and can be used with other complimentary techniques such as Gas Chromatography (GC) and Mass Spectroscopy (MS). In such a combined Cone Calorimeter-GC-MS system, the GC is used to separate the various fire gases while the MS is used to identify all the components at a molecular level, and provide a more concise analysis of evolved fire gases. It is therefore recommended that the GC-MS technique also be developed for the cone calorimeter and used to compliment the FTIR technique developed in this study.

Acknowledgements

The author wishes to express sincere gratitude to his supervisor, Dr. E.J. Weckman, for her valuable support and guidance throughout this program. Dr. E.J. Weckman, was instrumental in my decision to transfer from the M.Eng. course based program, to the M.A.Sc. research based program, at the University of Waterloo. Her continual support, encouragement, guidance, and technical assistance have all proven to be of extreme importance throughout this at time arduous nearly four-year process.

The assistance of Mr. G. Hitchman in support of carrying out the experimental portion of the program is greatly appreciated, as is the technical advice of D. Adeosun.

Additionally, thanks to the Department of Mechanical and Mechatronics Engineering at the University of Waterloo, and many of its faculty and staff are in order, as throughout both my undergraduate and graduate careers I have been provided with great learning opportunities both technical and otherwise which have proved extremely beneficial in both my personal life, and, in my professional engineering career.

Financial support for this research was provided by the Natural Sciences and Engineering Research Council of Canada and the Department of Mechanical and Mechatronics Engineering at the University of Waterloo.

There were times during my MASc I wanted nothing to do with my studies, as they were furthest from my mind while I focused on building my family and my career. Thankfully, my family,

friends and colleagues where there to keep me focused on my academics and provide emotional support during those trying times. For that I will always be grateful.

Lastly, and most importantly, I would like to thank my loving wife for her support. It is not possible to put into words how much you have helped me through school, work and life since I have met you. And to my wonderful children Payton and Avery who came into my life during this MASc research, I would like you to know how much more meaningful and enjoyable my life has become with you in it.

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Chapter 1 - Introduction

Flames, heat, smoke and toxic gases are produced during fires. Occupants in a building, depending on their location with respect to the fire enclosure, may be exposed to the combined effects of these hazards. Very few fire fatalities are a result of direct contact with the flames of the fire, however. Instead most occur due to exposure to smoke and toxic gases. Although the total number of fire deaths is actually declining, the percentage attributed to smoke inhalation has risen about 1% every year since 1979, exacerbated by the increased use of synthetic polymers in a wide variety of building applications [1]. The generation of smoke in the event of fire in polymeric materials, particularly in enclosed places, is a matter of great concern.

Determination of the toxicity of smoke is a necessary input in fire risk analysis, as it allows assessment of the potential severity of exposure, the likelihood of safe egress from a building and the probability of occupant survival in the event of a fire. The National Building Code of Canada (NBC) requires the selection of construction materials that meet the appropriate fire performance requirements for their application. Where fire performance certification is required within the clauses of the NBC, fire performance tests performed by industry recognized certification bodies, such as The Underwriters Laboratory of Canada (ULC), and, The Canadian Standards Association (CSA), are specified. In order to attain certification, the building construction materials are tested using standard fire test procedures, or they are tested under more realistic simulated fire conditions to determine the nature and yield of toxic combustion products in a given fire scenario. Full scale fire testing of all possible materials is cost-prohibitive; however, so it is necessary to develop valid bench-scale apparati and techniques, and standard operating procedures, so that combustion product yield data for new materials can be compared and validated against existing published data. Fire protection engineers are then able to approximate exposure levels, time available for egress and occupant survival in new building designs. At the same time, with enhanced test methods, manufacturers are able to design and test new building materials for improved fire performance characteristics.

As recently as 2003, the National Research Council of Canada indicated that [1], “our poor understanding of smoke and toxicity is a critical barrier to the further incorporation of polymers and their composites in building contents and structural applications”. In particular, polyurethane (PU) foams have been developed for many types and classes of products with applications in the building industry [2]. The present research is tailored to rigid foams often used as insulating panels. Unfortunately, PU and other rigid foams are inherently very flammable, leading to high rates of flame spread and heat release should they be ignited. Fire retardants (FRs) are generally added to PU products to reduce these hazards to acceptable levels, but addition of FRs generally leads to much higher yields of toxic gases than those measured in fires fuelled by non-FR foams [2]. For these products then, it is critical to develop methods by which to simultaneously evaluate fire performance and toxic gas yield in order to better understand their overall fire hazard, particularly during design and development of optimal FR PU foam products.

In assessing the overall fire performance of a material, the rate of heat release (HRR) is often considered the single most important fire property [1]. It provides an indication of the rate of fire growth, as well as the size a fire can attain, the time available for escape or fire suppression, and other parameters useful in defining fire hazard. There are many standard test procedures available to measure fire HRR [7]. Of these, the cone calorimeter, due to its accuracy and repeatability, is a common and well accepted test method for determining fire HRR, and also provides measured concentrations of carbon monoxide (CO) and carbon dioxide (CO_2) in the fire gases , two of the major gases produced during a fire.

When it comes to the fire effluents, fire safety engineers often assume that the only significant toxic product from combustion is carbon monoxide and that all burning items produce carbon monoxide at similar yield of 0.2 g/g [2]. In reality, the toxic fire gases that evolve depend on the chemical composition and molecular structure of the foam and any additives, such as blowing agents, fillers, stabilizers and cross linking agents. The type and formulation of flame retardants incorporated into a product further contribute to the nature and amounts of fire gases produced. Combustion conditions such as temperature, ventilation conditions, fire growth rate, humidity, ambient temperature conditions and moisture content of the sample may also affect the composition and yield of toxic gases observed. Finally, the types of toxic gas and their rates of release depend on the phase of fire development and heat release rate characteristics of the material.

In addition to carbon dioxide and carbon monoxide, some common fire gases that evolve from the combustion of fire retarded rigid foams include hydrogen chloride, nitrogen oxides, hydrogen cyanide, acrolein, formaldehyde and hydrogen sulphides [1]. Other gases may also be produced depending on the base chemical formulation of the rigid foam and chemical formulations of any fire retardant additives. Exposure to fire gases can produce two major toxic effects [1]:

i. asphyxia or narcosis, which causes central nervous system depression leading to incapacitation, unconsciousness and death; and

ii. irritation which causes acute discomfort of eyes, skin, mouth and/or immediate impairment of vision.

There is no universally accepted standard bench scale method to measure the toxicity of combustion products from rigid foams. Instead, the total yield of toxic gases produced during thermal decomposition of various foams under different conditions and the potential toxicity exposure in humans (by correlating the total yield of toxic gases produced to toxicity) has been examined by a number of researchers using a variety of methods. These include methods involving acute exposure of animals to exhaust gases issued from specimens of burning materials test [3-12], FTIR-cone calorimeter tests [13-16] and FTIR-laser pyrolysis tests [17]. Even when extensive chemical analyses have been performed on the combustion gases that evolve during fire performance testing of a material, the typical approach is to collect combustion gases throughout the entire fire performance test cycle, so the data reflect total gas yield across all stages from pre-ignition vaporization through to fire decay and flame out periods [3-17]. Such measurements provide integrated values of gas yield across the whole test, but do not provide an indication of in what stages certain species of fire gases are being generated.

Independent of the integrated nature of current measurements of fire gas yield, the FTIR method is emerging as an excellent tool for detailed study of the nature and yield of gases produced [13]. FTIR is one of many Infrared (IR) spectroscopic methods, in which a specific region of the electromagnetic spectrum is chosen, in this instance in the IR range, which is just below the visible region. The absorption spectrum of the fire gases is measured across the chosen spectral range and is used to distinguish individual chemical compounds. This can be done since each molecular compound generates a unique "fingerprint" resulting from absorption of particular frequencies of radiation by the molecular bonds [18]. The most pronounced absorption peak is at the resonant frequency for a particular bond in each species, so in an infrared spectrum, the strongest resonant frequencies are generally translated as large, intense peaks occurring at specific wavelengths. Known molecular spectra are then compared to measured library spectra to identify the gases present. The magnitude of a spectral peak is related to the concentrations of that gas.

In the present study, an experimental bench scale test apparatus was designed and constructed for use at the University of Waterloo Fire Lab. In this apparatus an FTIR system was interfaced to a cone calorimeter and a Novatec gas analyzer. The primary intent of the new UW apparatus is to develop techniques for analysis of fire gases evolved from FR and non-FR rigid foam samples tested under various heat flux conditions and during various phases of combustion.

This thesis focuses on the initial phases of interfacing and testing of this new apparatus. The objectives of the present research are:

1. to design and build an FTIR interface for the existing UW Fire Lab cone calorimeter using a preconfigured "out of the box" lightweight portable FTIR ambient air analyzer,
2. to develop a technique for sampling hot combustion gases at various stages of thermal degradation and combustion of materials during cone calorimeter testing,
3. to prove the system and technique using polystyrene (blue stryofoam) samples and then extend the system and technique to the study of intumescent rigid PU foam samples.

An extensive literature survey is included as Chapter II to provide the necessary background information on experimental techniques currently used in fire performance testing and fire gas analysis. Chapter III contains a description of the design and operation of the FTIR apparatus connected with the cone calorimeter, while results of testing and further refinement of the gas analysis technique using blue Styrofoam and intumescent foam samples is discussed in Chapter IV. Conclusions are in Chapter V, while considerations for improvements that could be made either to the experimental apparatus or to the operating technique are in Chapter VI. A brief treatment of FTIR theory, outlines of the calculations performed by the FTIR spectrometer and a more detailed experimental procedure are contained in Appendix A, B or C, respectively.

Chapter 2 - Literature

2.1 Fire Performance Testing Literature

It has been recorded that one of the primary driving forces in North America associated with the development of fire performance test methods was a number of sizable fires that destroyed large portions of major cities in America [19]. Fire events such as the great fires of New York City (December 16, 1835), Chicago (October 8-9, 1871), Boston (November 9, 1872), Baltimore (February 7, 1904), and the great San Francisco Fire (April 18, 1906) led to development of fire test methods, the standardization of those methods, and the enforcement of fire protection through building codes via component testing based on the standardized methods [19].

Early fire performance testing in North America generally consisted of testing at a large-scale. Full assemblies or buildings were burned and their fire performance was evaluated. The earliest fire testing in North America appears to have been related to the evaluation of fire protection systems in industrial facilities. For example, tests related to the fire performance of building materials for the Denver Equitable Building in 1890 included load, shock, fire and water and continuous fire testing [20]. The first known fire performance test method to be adopted as law in North America was the "fire-proofing" test method for floor arches used in buildings, established by the state of New York, in 1896. The city of New York included the state fire test requirements as part of the city building code in 1899 [20].

Two fire performance test methods that are still in use today were under development in 1903. The first test method was designed for the protection of urban buildings from fire including evaluations for ignition, fire spread, and penetration of exterior roofing materials. The second fire performance test method originated from recommendations after the 1903 London meeting of the International Fire Prevention Congress [21]. This test method dealt with the ability of building construction systems to endure fire exposure. In 1908, the American Society for Testing and Materials adopted their first fire performance test for floors, and in 1909 ASTM also adopted a fire performance test for partitions. In the 1940s, the danger associated with interior finishes was emphasized by fires such as the Coconut Grove night club fire (1942), the Winecoff, La Salle, and Canfield Hotel fires (1946), and the St. Anthony Hospital Fire [22]. All of these fires resulted in heavy losses of life and large financial loss from extensive property damage. As a result of these fires S. H. Ingberg (of NBS) and A. J. Steiner (of Underwriters Laboratories) took on the important challenge of developing a fire performance test method for measuring the fire performance of finishes and flooring materials. This work saw the development of a large flame-spread tunnel furnace which eventually became an Underwriters' Laboratory test method in 1944 and also became ASTM E84 (in 1950), and was adopted by NFPA as Standard No. 255. Test method ASTM E84 exposes a nominal 24-ft (7.32-m) long by 20-in. (508-mm) wide specimen to a controlled air flow and flaming fire exposure calibrated such that it will spread the flame along the entire length of a select grade red oak calibration specimen in 5 ½min. The oak is then replaced by the specimen under test and a flame spread index for the material is determined. The flame spread index indicates the relative rate at which flame will spread over the surface of the material, as compared with flame spread on asbestos-cement board, which is rated 0, and on red oak, which is rated 100.

Over the ensuing years, users of these large scale test methods became concerned about the cost of fabrication and testing of samples at large scale and development began on smaller-scale tests that could be used for assessing materials performance in fire. This resulted in two surface flammability tests that were much smaller than the large-scale tunnel test method. One test, similar to the ASTM E84 test (sample size 2' x 25'), only much smaller (sample size 14" x 8') was developed by the U.S. Department of Agriculture, Forest Products Laboratory, in 1951 [23]. The second test method was the surface flammability test using a radiant-panel method (sample size 6"x 18") developed by NBS [23]. These two tests have primarily been used to measure the surface flammability of wall and ceiling materials.

A study of a disastrous industrial plant fire by Factory Mutual Laboratories in 1953, where the insulated roof deck was a primary contributor, helped to uncover that not only surface flammability but heat release rate of building materials are critical parameters in determining fire behaviour [24]. Specifying the use of "non-combustible" materials is one of the several means by which codes attempt to regulate building materials to increase safety from fire. At the time the model building codes used one of two definitions to define "non-combustibility." These definitions were based on the following [25]:

i. Base material as defined by (i) with surface not more than 1/8-inch-thick with a flame spread rating of less than 50 by ASTM Method E 84; or

ii. Materials with a flame spread rating of less than 25 by ASTM Method E 84 inclusive of all surfaces that might be exposed by cutting.

Code officials recognized that many materials will not pass these requirements although they release only limited amounts of heat during the initial and the critical periods of exposure to fire. As a result of this new awareness in fire dynamics, in 1959, Factory Mutual Laboratories developed the first heat release rate calorimeter known to be located in North America. In addition, in 1959, Howard Emmons of Harvard University published an article which highlighted the need to quantify the "Total rate of energy release vs. time" and the "Space-distribution of energy release rate" [25]. These two efforts helped to raise to a high level of significance the use of heat release rate calorimetry as a fire performance test method.

It was not until the early 1970s that major strides in heat release rate calorimetry were made in North America. Two major efforts were underway at this time. One was led by E. E. Smith of the Ohio State University and the second was led by W. J. Parker of the U. S. National Bureau of Standards [26][27]. The "Smith Calorimeter or Ohio State Calorimeter" (also known as the "Ohio State University apparatus" or "OSU apparatus"), operated using differential thermocouples to measure temperature in the fire gas flow, and the "NBS Calorimeter", operated as a constant temperature device with the proportional lowering of a metered auxiliary fire gas flow equalling the heat release of the test sample [27]. Data from these two systems were logged by strip chart recorders. The heat release rates were then determined from the data. The "Smith Calorimeter" progressed through the standards process and eventually became the test instrument used for ASTM E906, Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using a Thermopile Method. Although these methods provided insight into the burning behaviour of materials, the convective enthalpy measured did not represent total energy release from the material as it did not account for the radiant heat losses to the apparatus walls.

In 1977, Beason and Alvares of Lawrence Livermore Laboratory reported that they experimented with a procedure using oxygen consumption to study the burning of wood and plastic cribs in a room with limited ventilation [28]. During the same time period, Parker of NBS was also using oxygen consumption techniques to investigate the fire dynamics inside the ASTM E84 tunnel test apparatus [29]. The techniques used by both efforts were based on the original work of W. M. Thornton who published a paper on the relation of oxygen to the heat of combustion of organic compounds [30]. In 1978, Clayton Huggett of the NBS focused an effort on defining a body of science necessary for the development of a oxygen calorimeter system. Huggett established the basis for the refinement and development of future test methods using oxygen consumption calorimetery. In concert, William Parker who was a colleague of Huggett at NBS, was putting the calorimeter concept into practice. Parker, with another colleague Darryl Sensenig a NBS Research Associate from Armstrong Cork Company, built and tested the first bench scale oxygen consumption heat release rate calorimeter [31].

In 1982, Babrauskas published a paper on the development of a bench-scale heat release rate calorimeter using the oxygen consumption technique [32]. This bench-scale heat release rate calorimeter was named the cone calorimeter. The oxygen consumption heat release rate measurement technique was further refined by Parker, Babrauskas, and others, and it has become a critical measurement tool amongst more than a dozen other small-scale, intermediate-scale, and large-scale fire test methods referenced in standards in North America and throughout the world [27, 30, 31, 34].

The first test method published describing the use of the Cone Calorimeter was a draft standard published by the American Society for Testing and Materials (ASTM) in 1986. It carried the designation of P 190 [26] and is now obsolete because ASTM subsequently published a full standard describing the Cone Calorimeter [27]. The full standard was first issued by ASTM in

1990 under the designation Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products using an Oxygen Consumption Calorimeter (ASTM E 1354-90). Slight amendments were made over the years, with the current edition being E 1354-11b [33].

The oxygen consumption method is based on the observation that the net heat of combustion is directly related to the amount of oxygen required for combustion [34]. The oxygen consumption method requires rate and accurate measurement of the mass flow of air into knowledge of the furnace fuel composition and mass flow and out of the exposure apparatus. Complete combustion is assumed (with end products of carbon dioxide and water vapor). The weight of material/heat of combustion method of measuring HRR consists of comparing the heat available for release before and after a test. The difference between the two end-point values is regarded as the heat released during the test. The heat available for release before a test is the weight of the specimen multiplied by its heat of combustion per unit weight. The heat available after a test is the sum of the weights of unburned specimen and char, each multiplied by their respective heats of combustion. The heat release is calculated by the following equation,

$$Q_{HRR} = EVO_2^i\left(\frac{\varphi}{\varphi(\alpha-1)+1}\right) \quad \text{[kW]} \qquad \text{[Eqn \#1]}$$

and,

$$\varphi = \frac{O_2^i(1-CO_2) - O_2(1-CO_2^i)}{O_2^i(1-CO_2-O_2)} \qquad \text{[Eqn \#2]}$$

where,

Q_{HRR}	heat release rate (kW)
E	heat release per volume of oxygen consumed, 17,200 (kJ/m^3) (vs. using 13,100 kJ/Kg)
V	volumetric flow rate through the exhaust duct, correcting to 25^{0}C (m^3/s)
φ	oxygen depletion factor
α	combustion expansion factor
O_2^i	initial value of oxygen analyzer reading, 0.2095 (mole fraction)
O_2	oxygen analyzer reading during test (mole fraction)
CO_2^i	initial value of carbon dioxide analyzer reading, assumed to be zero (mole fraction)
CO_2	carbon dioxide analyzer reading during test (mole fraction)

A Typical HRR/Temperature versus time curve based on oxygen consumption method for the various stages of fire growth is presented in *figure 2.1*.

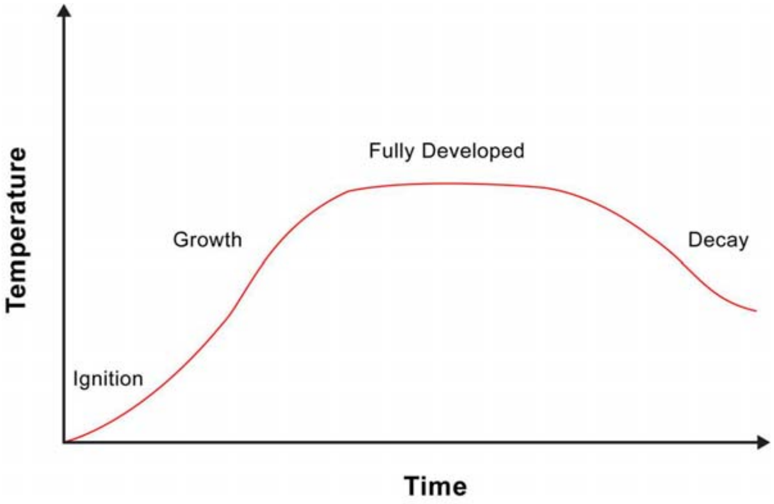

Figure 2.1: Schematic representing typical fire growth stages (www.nist.gov).

The fire development curve above shows the time history of a fuel limited or well ventilated fire. In other words, the fire growth is not limited by a lack of oxygen available to the fire. As more fuel becomes involved in the fire, the energy output or heat release rate continues to increase until all of the available fuel is burning (fully developed). Then as the fuel is burned away, the heat release rate begins to decay.

2.1.1 Use of Cone Calorimeter for Fire Performance Testing

The cone calorimeter is shown schematically in *figure 2.2.* The components of the cone calorimeter are described in detail in Chapter 3. The history of the use of the cone calorimeter for fire performance testing is described below.

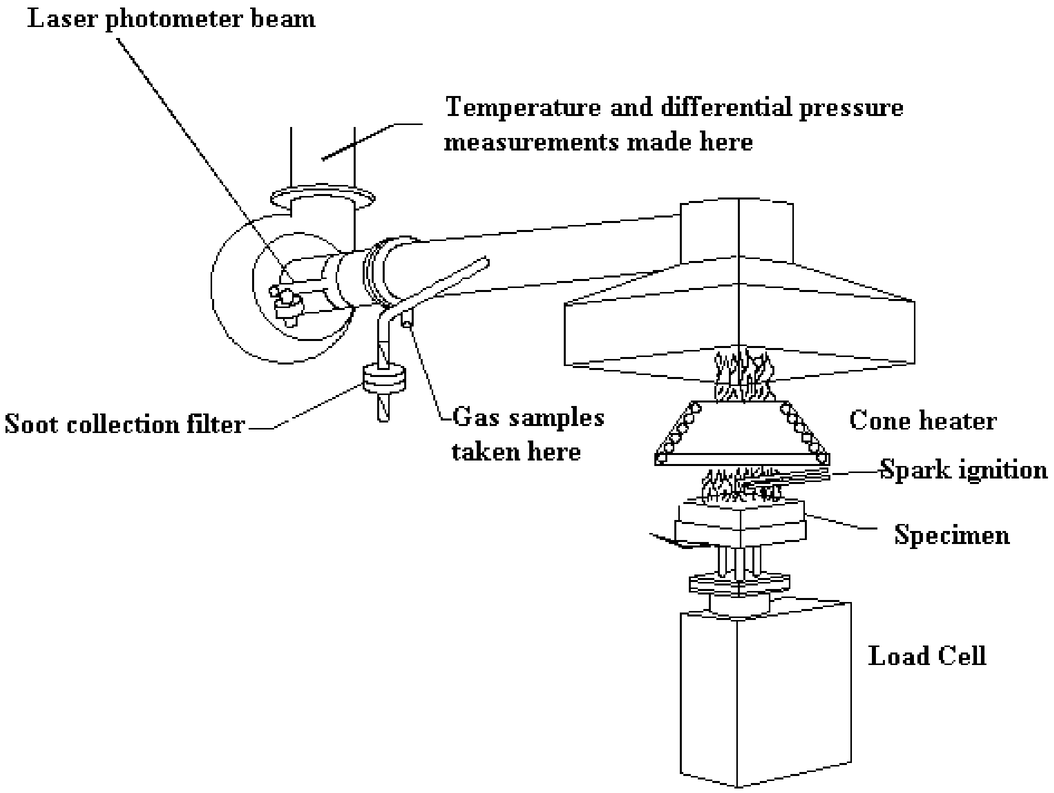

Figure 2.2 Schematic of the cone calorimeter

The earliest cone calorimeter study into fire performance of polyurethane foam specimens was reported in 1983 [11]. In that study, four polyurethane foams representing materials commercially used for furniture applications, were studied. Two of the foams had no fire retardants added, while two others were each similar to one of the foams, but one contained a bromine-based retardant and the other contained a phosphorous and chlorine based retardant. Both retarded products showed a very substantial increase (improvement) in time to ignition. The rates of heat release, both peak and average, however were not improved. At higher incident heat fluxes, the effect of the retardants on ignition time became small. Thus these products behaved in a manner similar to many other polymers where a small amount of retardant was added; where resistance to small ignition sources was noticeably improved, while actual fire performance, once ignited was not much changed. In addition, it was noted that the addition of fire retardant resulted in an increase in the total yield of CO.

In 1988, Drew and Jarvis conducted a systematic study of fire retarded polymers in the cone calorimeter [35] for which the specimens where specially prepared with varying controlled amounts of several different fire retardants. According to Babrauskas [36] this study was considered the most systematic study of fire retarded products tested in the cone calorimeter up to that point. The two base polymers used were polypropylene (PP) and polymethylmethacrylate (PMMA). The fire retardants were a series of organobromide/antimony oxide preparations. The decrease in heat release rate by the fire retardant additives on these two polymers was seen to be roughly linear; however, the increase in smoke and soot production was strongly non-linear. For example adding 5% retardant typically doubled the total yields for smoke and soot, while increasing the load to 15% gave only a small additional increase. The effect on CO and HC production was also non-linear, although somewhat less marked than that for soot. It was concluded that the systems under study were not suitable for commercial use since the modest benefits of reduced heat release rate were outweighed by the roughly doubled emissions of CO, HC, smoke and soot.

In 1990, Kallonen [13] from VTT (Technical Research Centre of Finland), used the cone calorimeter for fire performance and smoke analysis across a range of polymeric materials without fire retardant additives. In that study, Kallonen experimented on polyurethanes, polyvinylchloride and wool carpet. The aim of this preliminary investigation was to study applicability of FTIR spectrometry as a method for gas analysis during cone calorimeter fire testing of materials. Since these methods are directly applicable to the present work, further discussion of this work is contained in Section 2.3.

In 1993, a study into the combustion behaviour of polyurethane flexible foams (non fire rated) under cone calorimeter test conditions was conducted by Vanspeybroeck, Van Hess and Vandevelde [37]. One of the main objectives of this study was to determine the effects of cone calorimeter test variables on fire performance characteristics such as ignitability, heat release rate, effective heat of combustion and mass loss. The purpose was to define the effects of different operating procedures and to propose suitable test conditions for PU flexible foams. The results of this study indicated that when test procedures are closely followed, the repeatability of the test method within a single laboratory was good, with percentage standard deviations below

10% for measured values of effective heat of combustion, peak rate of heat release and mass loss rate.

In 1996, the new standard test method NT FIRE 047 was further described and critiqued in the Fire and Materials Journal by Bulien [15]. The experience with application and interpretation of the test method is reviewed in regard to mounting, calibration and use of the equipment. A cone calorimeter is applied as the fire test method in Bulien's study. Using the cone calorimeter allows variation of the radiant heat flux on the surface of the test material as well as (with the aid of optional equipment) testing at lower oxygen concentrations. This makes it possible to simulate fires with different heat release rates in conditions ranging from well-ventilated post-flashover fire to fires with different degrees of ventilation control [15]. Again since he employed FTIR analysis in his work, Bulien's study is described in greater detail in the review of the FTIR literature in Section 2.3.

In 1998, Checchin, Cecchini, Cellarosi and Sam of EniChem Research Centre reported that they experimented with the cone calorimeter for the evaluation of fire performance of polyurethane rigid foams for building insulation. The study, using cone calorimetry, demonstrated good sensitivity in discriminating the fire behaviour of different polyurethane foams, in particular in relation to changes in the fire performance of the polymer with modification of the base chemical structure and with respect to the use of conventional flame retardants [38]. One sample was a conventional brominated polyester polyol, one sample was a conventional non-reactive flame retardant dimethylmethylphosphonated (DMMP), one sample was prepared with a halogen free additive and one sample was prepared with a char forming additive. Two other samples were based on chemical structure modifications of the polymer aimed to increase both thermal and fire performances. The differences observed in measured fire performance characteristics support the choice of the cone calorimeter as a useful research tool for extensive studies on the fire behaviour of rigid foams.

More detailed cone calorimeter studies of PU foam fire performance have also been conducted by many others [39-42] to examine the effects of fire retardants on heat release rate, total heat released and effective heat of combustion. While they demonstrate the utility of the cone calorimeter for fire testing of foam they are not discussed further here since they are not directly relevant to this work.

An FTT cone calorimeter is available in the **University of Waterloo Fire Lab.** It can be used to measure heat release rate, total heat released and effective heat of combustion by the oxygen consumption principle. Results of calorimeter testing also provide values of mass loss rate, time to ignition, specific extinction area, and, optionally, carbon monoxide and carbon dioxide production during the burning of material specimens exposed to radiant heat flux from a conical heater across a range of values from 0 to 100 kW/m^2. In addition, the existing exhaust duct and gas sampling train connecting the sampling ring to the actual cone calorimeter instrument allows for gas samples to easily be extracted from the exhaust stream at a location where sufficient mixing is expected to have taken place to allow withdrawal of representative samples of the gases generated during testing. In this respect, the UW Cone Calorimeter provides an excellent platform from which to study species gas concentrations and toxic gas evolution from rigid PU foams.

2.2 Fire Gas Analysis Literature

In 1823, the danger associated with smoke inhalation during firefighting while aboard ships was recognized by Charles A. Deane, and as a result, he patented one of the first breathing apparatus' called the "Smoke Helmet" [43]. In North America, protection of occupants from potentially toxic fire gases typically was addressed for buildings in which large numbers of people were located. Therefore manufacturing plants and schools initially garnered the most attention. In 1918, Benjamin Richards of the National Fire Protection Association suggested that there should be standardization of fire protection for school buildings because, "The danger from smoke calls for special consideration from a life safety standpoint, so special care is necessary in planning exits" [44]. In 1933, George Ferguson described the significance of smoke and various fire gases to life safety in an article published in the NFPA Quarterly [45].

In 1964, a report was published describing the first fire performance test method that specifically attempted to address smoke hazards [46]. This test, developed by Rohm and Hass Co., of Philadelphia, PA, was designed to measure smoke density in relation to people's ability to view an exit sign in a smoky environment produced by a burning test material. In 1967, the U.S. NBS presented a paper on a similar fire performance test method for measuring smoke from burning materials [3]. This NBS test method was eventually adopted in 1979, by ASTM as ASTM E662, Standard Test Method for Specific Optical Density of Smoke Generated by Solid Materials [4]. The test is carried out in a constant-condition fume cupboard by introducing the material on a sample dish and heating from beneath with a small electric furnace (smouldering conditions) or with the same furnace together with a small ignition pilot flame (flaming conditions). The small furnace is set so that the sample receives 2.5 W/cm^2 thermal energy. The light transmission through the smoke, resulting from the decomposition or combustion of the sample, is detected by a photocell which senses a vertical beam of light passing through the smoke. The amount of light transmission passed during the test is expressed as the specific optical density value. In 1998, ASTM approved a new standard, making similar measurements, ASTM E1995, Standard Test Method for Measurement of Smoke Obscuration based on a light beam and photocell incorporated into a single closed chamber with a conical heat source [47].

In the 1970s, two fire test methods for fire gas toxicity emerged. One of these test methods grew from a NBS research grant to the University of Pittsburgh which resulted in a paper by Alarie and Barrow [4]. This test method is known as the “University of Pittsburgh Method” and is still in use today. The other fire toxicity test method began as a joint effort between the Southwest Research Institute (SwRI) and NBS. NBS further developed test method, and it was adopted by ASTM as ASTM E 1678-02 a test method for fire toxicity in 1995 [5].

The toxicity of the thermal degradation products from eight different rigid polyurethane foams with various fire retardant additives and blowing agents were evaluated with the University of Pittsburgh test method [10-12]. In contrast to the open cone calorimetry tests, this method uses a dynamic flow system in which materials are decomposed at a steadily increasing temperature in a Lindberg furnace. The material is allowed to decompose initially in a non-flaming mode and then to burn when the ignition temperature is reached. The decomposition products are fed into a glass exposure chamber in which four mice are exposed. Whole body plethysmographs are used to measure the respiration rate of the mice. This method proposes the use of three biological endpoints, for toxicity impact on the mice, all of which relate to the amount of material placed into the furnace. These biological endpoints are sensory irritation; measured as the concentration of smoke which produces a 50% decrease in the respiration rate of the animals, lethality; measured as the concentration of smoke which causes 50% of the animals to die during 30-minute exposure and a 10-minute post-exposure, and physiological stress; a mathematical approximation which represents the onset, recovery and degree of depression of the respiratory rate and includes the corresponding physiological adjustments for each mouse exposed (e.g. blood pressure and heart rate). The combustion gases produced for the rigid foams under various ventilation conditions were also examined using GC and MS and the following volatile compounds were identified though the concentration of each was not measured: acetaldehyde, HCN, ethane, propylene, toluene, monoisocyanate, propane, ethylene oxide, propylene oxide, acetone and formaldehyde.

The toxicities of many of the thermal degradation products from polymeric materials listed above, including rigid polyurethane foams, have been evaluated by a number of laboratories using the NBS toxicity test method [10-12]. This test method consists of three components; a combustion system, a chemical analysis system and an animal exposure system. The material under study is thermally decomposed in a 1000 ml cup furnace which is preheated to a temperature either 25 ^{0}C below the material's auto-ignition temperature (non-flaming decomposition) or 25 ^{0}C above the material's auto-ignition temperature (flaming decomposition). These two conditions, the non-flaming and flaming decomposition modes, at temperatures close to the auto-ignition temperature of the material are considered worst cases but still realistic fire conditions. Other regions and temperature regimes of fire development were not studied. All of the combustion products generated in the cup furnace go directly into the 200-l rectangular exposure chamber and remain there for the duration of the exposure. Carbon monoxide, carbon dioxide, oxygen, nitrogen gases and hydrogen cyanide are measured. Six rats are exposed head-only to the combustion atmospheres in each experiment. Blood samples are taken from two of the six animals to monitor the amount of carbon monoxide absorbed in the blood. Animals are exposed to the combustion atmospheres for 30 minutes and then observed during a 14 day post exposure period. The biological endpoint is the determination of the concentration of burning material that causes 50% of the animals to die in the 30 minute exposure and 14 day post exposure period. While animal testing provided useful results, analytical test methods were continually improving and could be applied to simulated fire scenarios precluding the necessity of animal exposure to toxic gases.

It has been known for thousands of years that combustion products from fires are toxic. However, many of the scientific tools and the knowledge needed to perform detailed chemical characterization and analysis of the toxic smoke and fire gases were not available until the 19th and 20th century, in which rapid advances in fire gas measurement technology were made. As new methods became available they have been applied to study fire performance of existing and newly formulated materials. Fire researchers have gradually developed new test methods that more accurately predict fire behaviour and fire gas toxicity in building fires. One of the most promising technologies that has been applied to qualitative and quantitative analysis of fire gas toxicity is Fourier Transform Infrared Spectroscopy (FTIR). This was chosen for use in the present research based on its promise in this area as will be discussed further in the next section.

2.2.1 FTIR Literature

In 1988, Babrauskas reported that even though the original design of the cone calorimeter was focused exclusively on the rate of heat release measurements it could also be used for ignitability testing and to monitor smoke emissions and soot production. The development of the cone calorimeter system for smoke and soot measurement was reportedly prompted by studies showing the various limitations of the widely used NBS smoke chamber [32]. The various analyzers for measuring combustion gases were added gradually, until the capability was achieved for making continuous measurements of O_2, CO, CO_2, H_2O, total hydrocarbons (HC), and HCl. Using the data from the cone calorimeter it was possible to distinguish with ease those fire retardant containing products which show modest improvements in performance from those which are either ineffective or are exceptionally successful. The capabilities to characterize gas yields are considered essential to studies of both product chemistry and fire toxicity [21].

A preliminary investigation into the application of FTIR for the analysis of smoke gases was presented in the Journal of Fire Sciences by Kallonen [13] from VTT (Technical Research Centre of Finland) in 1990. A FTIR spectrometer equipped with a long path gas cell was used in on-line (flow through gas) gas analysis in connection with a cone calorimeter. Spectra were acquired on a Michelson 100 FTIR by Bomem which was connected to a cone calorimeter through a heated sample line. It was noted in the study that if water is removed from the sample gas flow before analyzing some compounds soluble in water, such as HCN and HCl, may also be removed, whereas some compounds such as NO and NO_2 are not removed [13]. If the water is not removed however, it causes the analysis to be more complicated because of the presence of strong spectral interference.

In Kallonen's study a 30 cm long multiple pass gas cell with a path length of 7.2 m and resolution of 4 cm^{-1} was used. This was chosen considering the tradeoffs in resolution versus loss of intensity of the IR beam with increasing numbers of reflections of the beam on the mirror, and increase in response time with longer gas cell length. At a higher resolution the detection limit would be increased because of lower intensity and spectral acquisition would be slower because of increased number of data points.

It was concluded by Kallonen [13] that, after careful calibration, the precision of FTIR analysis can be the same as in commercial on-line (gas flow through) gas analyzers. The sensitivity of FTIR method is adequate for toxicity evaluations. The analysis results can be used as data in mathematical models to predict toxic effects in fires. The aim of this preliminary investigation was to study applicability of FTIR spectrometry as a gas analysis method in connection with cone calorimeter fire test method. Polyurethanes, polyvinylchloride and wool carpet were used as test samples. Concentrations of CO, CO_2, HCN, HCl and SO_2 in the smoke gases in the Cone Calorimeter exhaust duct were measured simultaneously. Single scan spectra were acquired over 25 or 28 second intervals during a test. The gas cell was 30 cm long, with multiple pass path and volume of 0.53 1iters. Sample gas flow of 21/min was used for the tests with polyurethanes, whereas 71/min was used for the tests with wool carpet and PVC. Spectra were acquired during a single scan in this study. The specific phase of fire development in which the sample was taken was not defined in the study. In addition, comparison of the results obtained by the FTIR with other gas analyzers was not conducted.

In May of 1993, out of Babrauskas' and Kallonen's work, a standard procedure known as NT Fire 047-Combustible Products: Smoke Gas Concentrations, Continuous FTIR Analysis, was developed by NTT in Finland and approved by NORDTEST [14]. This test method specifies a procedure for gas sampling and analysis that allows determination of the concentrations of combustion products, via FTIR spectroscopy using a Michelson Interferometer with a recommended resolution between 2 and 4 cm^{-1}. The method is applicable in connection with any fire test where combustion gases are collected in a representative way. Examples of such tests, as listed in NT Fire 047, are rate of heat release tests ISO 5660 or ASTM E1354 (cone calorimeter), ISO 9705 or NT Fire 025 (room/corner tests) and NT Fire 032 (Furniture calorimeter), NT Fire 036 (Pipe insulation) and NT Fire 043 (Large free hanging curtains and drapery materials).

The standard defines, in a general way, the testing apparatus, calibration methodologies, testing and analysis procedures, accuracy/sensitivity analysis and presentation of the results. In addition, the following stages of FTIR sampling are outlined [14]:

i. Smoke gas samples for the FTIR analysis are taken from a gas collecting systems (usually exhaust duct) drawn continuously through a heated sampling line to a heated IR absorption cell of a FTIR spectrometer.

ii. An infrared beam is directed through the gas absorption cell and at chosen time intervals (based on resolution) interferograms are obtained and converted into absorption spectra.

iii. The concentrations of the gases are calculated by integrating the area (or part of the area) of the characteristic absorption band for the compound seen in the absorption spectra of the sample and calibrating against spectra of normalized reference gas mixtures with known concentrations (usually singe or two gas mixtures in nitrogen, but for combustion gases, mixtures of several gases are best).

The FTIR technique is based on conversion of the measured interferogram into an absorption spectrum. The main component in any FTIR spectrometer is the interferometer shown in *figure 2.2*. In the interferometer, a beam from the irradiance source (in this case a heated wire) is projected to the beam splitter, which divides the beam into two (2) parts. The two beams are then reflected back to the beam splitter by mirrors. At the beam splitter the beams recombine and interfere either constructively or destructively depending on the distances between the mirrors. When the measurement beam travels through the gas cell, wavelengths that are characteristic of the compounds present in the gas cell are absorbed. The amount of absorption is related to the concentrations of the individual compounds present. The output at the detector is called the interferogram. Each point measured contains information about the intensity at all the wavelengths reaching the detector. A mathematical technique known as Fourier transformation is used to separate information on the intensity of individual wavelengths and the interferogram presented as a function of position is converted to a spectrum of the intensity of signal as a function of wave length (or wave number) or frequency. Further description of the theory of FTIR and its relevance to this study is outlined in Appendix A.

In 1996 [15], a critique of NT Fire 047 was conducted in which experience with application and interpretation of the test method is reviewed in regard to FTIR mounting, calibration and use of the equipment when interfaced to a cone calorimeter. A representative sample of smoke is collected over 20 second intervals for spectral analysis by the probe sampler in the exhaust duct of the cone calorimeter. The sample is filtered with glass microfiber filters to remove soot, then drawn to the gas cell of the FTIR system through a PTFE-tube heated to at least 130^0C. The gas cell is equivalently heated. From the gas cell, the sample passes through an ordinary, unheated PTFE tube and through a water-cooled pipe before the actual gas flow is measured. From this point, the gas passes through a vacuum pump and directly into the exhaust ventilation of the laboratory.

The work concludes that further revisions and development are required to the NT Fire 047 sections on apparatus, calibration routines, analysis procedures and expression of results. While, the work states that purchasing, mounting, learning and maintenance of FTIR equipment is time consuming and potentially cost prohibitive, it also suggests that the technique is probably the nearest one gets to analysing smoke from the burning materials using different scales and different fire testing equipment without changing the sampling set-up dramatically [15].

Of importance from this study were the conclusions on the practical use of the FTIR [48] since these provide guidance for the design of the present system. In particular, it was noted that development of instrument-specific calibration curves is better than seeking support through purchase libraries of spectra; that filtration of the smoke is required and presents a possible source of error as some of the fire gases may be filtered out and not reach the FTIR gas cell; that the capability of the FTIR software and the scanning rate of the FTIR system are of most importance in choosing an FTIR spectrometer for fire gas analysis and that strict laboratory safety precautions are required to avoid exposure of the personnel to toxic calibration or measurement of gases.

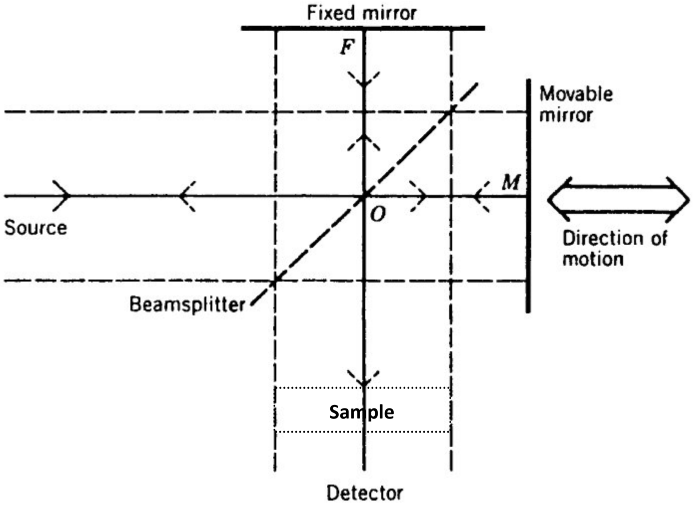

Figure 3.2: Schematic representation of interferometer

In 2000, FTIR was applied to the analysis of smoke and gases generated by thermal decomposition of polyurethane (PU) and fire retarded polyurethane coatings under various conditions [2]. A Nicolet FTIR spectrometer (NICOLET 710C) was attached to a standard cone calorimeter, and fire gases were extracted through the exhaust duct at a flow rate of 24 dm^3/min. Non-dispersive infrared detectors located at the end of the sampling line were used to quantify the concentration of CO_2 and CO (i.e. the FTIR was not used for quantitative analysis of CO_2 and CO), while a quantitative analysis of smoke opacity was made using a laser photometer. Samples of effluent gases were then extracted using a collection tube from the main extraction system at a rate of 8 dm^3/min and analysed by FTIR. A smoke filter removed soot particles from the gas sample before reaching the FTIR. The 4 meter long sampling line was maintained at a temperature of 183^0C to avoid cooling and condensation of the fire gases before analysis. Measurements were made for cone calorimeter testing in a range of conditions from low oxygen to highly oxidizing environments. As well as the carbon monoxide and carbon dioxide concentrations determined by the NDIR measurements, hydrogen cyanide, sulphur dioxide, nitrogen oxides, formaldehyde and some hydrocarbons were identified and quantified using a standard FTIR equipped with a DTGS detector at 4 cm^{-1} resolution and scanning time of 10 seconds. Results of the FTIR analysis indicated that flame retardants in PU foams significantly decreased the emission of toxic gases such as hydrogen cyanide and carbon monoxide during the degradation of the foam, while increasing smoke and soot production. This study showed that the FTIR technique is a powerful analytical tool for determining the total product yields during thermal decomposition or combustion [2].

More recently, a study was conducted into the effect of temperature and ventilation conditions on the toxic product yields from burning polymers using the Purser Furnace apparatus coupled with continuous in-line FTIR gas analysis [16]. The aim was to investigate the influence of equivalence ratio (fuel/oxygen ratio), temperature and material composition on the yields of toxic combustion gases. The relationship between temperature and ventilation conditions and the toxic product yields of four bulk polymers, low-density polyethylene, polystyrene, nylon 6.6 and polyvinyl chloride was examined. Fire gas samples are drawn continuously through heated lines and filter chambers to a mixing chamber and from there to a heated, folded path length gas cell of an FTIR spectrometer. Using a standard FTIR and scanning time of 10 seconds, the spectra of combustion products were collected during material decomposition at furnace temperatures of 650, 750 and 850 ^{0}C. The yields for each furnace condition are taken for a 5 minute sample period during the furnace steady-state period. Although PU foam was not studied, this research indicated that the use of FTIR allowed a wide range of combustion products to be analysed from different materials, when tested under different conditions of fire ventilation and temperature.

The results of the study indicated that the total toxic yields obtained from burning different materials were highly dependent upon the equivalence ratio as well as the chemical composition of the sample. The yields of most of the polymers tested were shown to be independent of the tube furnace temperature over the high temperature range used (650-850^{0}C).

As recently as 2009, polymer degradation studies were performed using laser pyrolysis-FTIR microanalysis [17]. In this study a new method (LP-FTIR) was introduced to promote a better understanding of polymer degradation, as well as the effect of flame-retardant additives on PU foams. The technique was based on FTIR analysis of gaseous products which originated from laser induced decomposition of ethylene vinyl acetate (EVA) and polypropylene (PP) in a combustion cell. The materials were also characterized using FTIR coupled with a cone calorimeter. Based on the results of the study, the new method and the conventional cone calorimeter-FTIR method were compared. It was concluded that with laser pyrolosis, specific degradation processes can be studied, while in the cone calorimeter thermal decomposition is less controllable particularly when the sample ignites. Instead the whole combustion process, from decomposition through flaming combustion to decay, takes place during cone calorimeter testing.

Based on review of the current literature, the conventional cone calorimeter-FTIR method has not been used extensively to study specific phases of combustion, but rather it has been applied to obtain average product gas compositions from the whole combustion process at a given temperature, radiant heat flux or under varying ventilation conditions. In the present study, a methodology is developed and presented for use at the **University of Waterloo Fire Lab** that interfaces an FTIR system to a standard cone calorimeter for detailed study of toxic gases evolved from rigid foam specimens during specific stages of testing, including thermal degradation (off-gasing) and flaming combustion, using appropriate sample windows.

Chapter 3 – Experimental Apparatus

In the first stage of this research, a Fourier Transform Infrared Spectroscopy (FTIR) system and additional gas analyzers were interfaced to the existing cone calorimeter at the **University of Waterloo Live Fire Research Facility** to develop a technique for fire gas analysis of rigid foams during various stages of thermal degradation and combustion under exposure to a constant heat flux. Physical descriptions of the main equipment and systems are contained in this chapter, followed by brief descriptions of the theory and principles behind their operation in the context of the present work.

3.1 Overview

Full scale fire tests of rigid foams are typically expensive, time-consuming, and require a high-level of technical expertise to perform. Bench-scale fire performance tests are feasible, but operate on much smaller scales. Work has been done at bench scale to study the toxic fire gases evolving from rigid foams using the conventional cone calorimeter-FTIR methods [13, 14, 15]. However, conventional cone calorimeter-FTIR methods typically are not applied to study different phases in the combustion of a sample but rather to measure concentrations of fire gas integrated across an entire cone calorimeter test for a given radiant incident heat flux. Such tests may also be run under varying ventilation conditions.

The primary purpose of the cone calorimeter-FTIR system developed in this research is to perform more detailed studies into the toxic gases evolved during specific stages of thermal degradation (off-gasing) and flaming combustion of samples being tested in the cone calorimeter. The fire gas analysis system developed in this work is based on integration of various gas analysis systems to the existing FTT cone calorimeter housed at the **University of Waterloo Fire Research Lab**. The controls and methodology established allow for a focused analysis, with the FTIR and gas analysis sample window limited to a particular phase during a conventional cone calorimeter fire performance test. In the following section, the cone calorimeter and its basis for operation will first be described, followed by those for the FTIR and other gas analysis and sampling systems used in this work.

3.2 Physical Description

3.2.1 Overview

A schematic of the final integrated design of gas analysis and cone calorimeter systems developed in this research is shown in *Figure 3.1*. It consists of two gas analysis systems based on Servomex analyzers and the FTIR spectrometer connected to a standard cone calorimeter which will be described in more detail in the following section. One of the two Servomex analysis systems in the sampling system for the FTT cone calorimeter and, as such, is connected directly to the cone calorimeter exhaust system. The others are the sensors in an independent combustion gas analysis system obtained from Novatech. All gas analysis systems are plumbed to allow calibration and zeroing of each analyzer with appropriate pure nitrogen, dry air and/or specialty calibration gas mixtures before measurement begins. Common zero reference values are thereby set to allow baseline comparisons between gas concentration data from the three different measurement systems, each of which is also described further in the sections below.

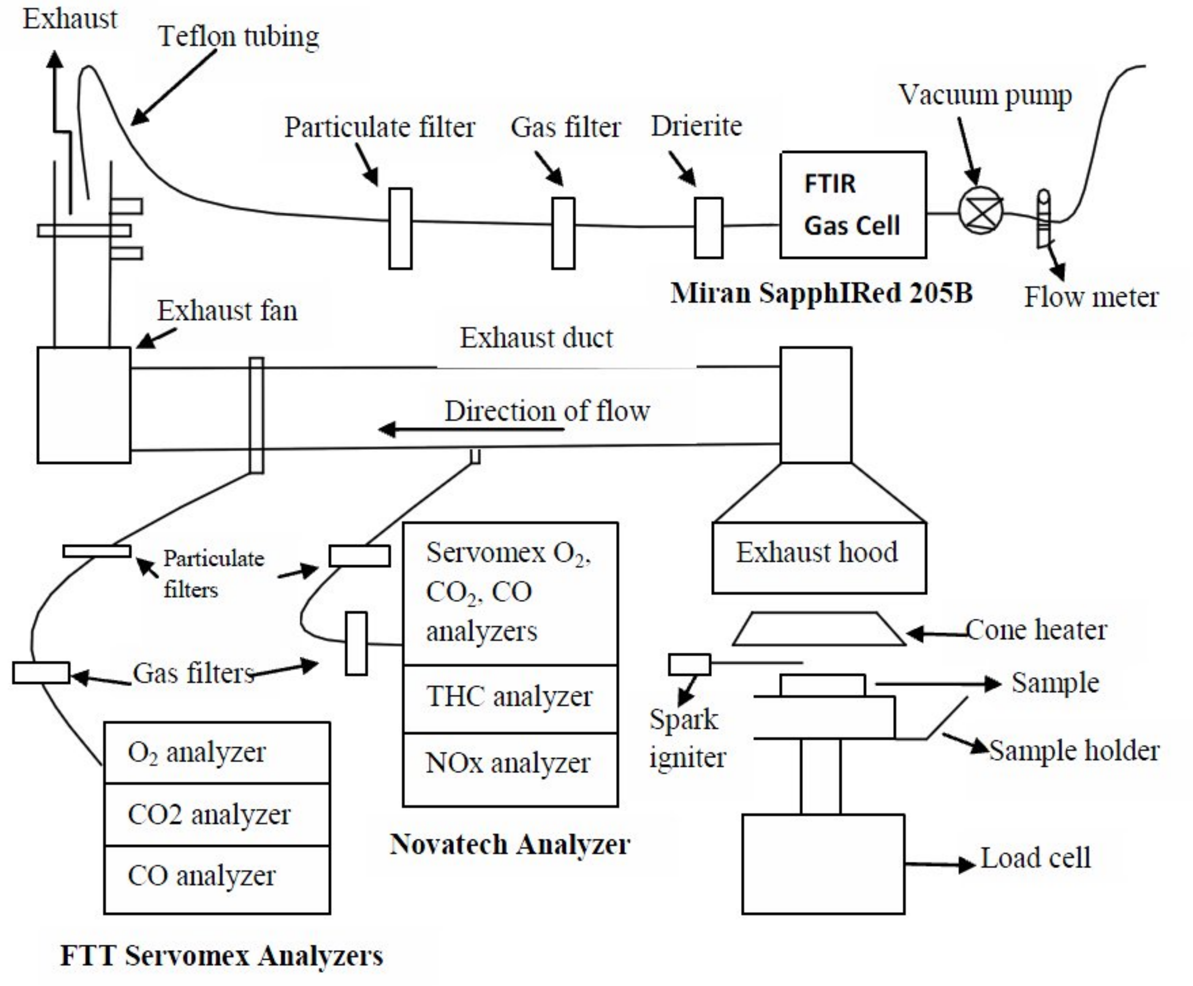

Figure 3.1 Schematic of the experimental apparatus

3.2.2 Cone Calorimeter

The cone calorimeter is shown schematically in *figure 3.2*. It consists of the cone heater, sample holder, load cell, exhaust system, gas sampling train and calibration and analysis systems. These are described in turn below.

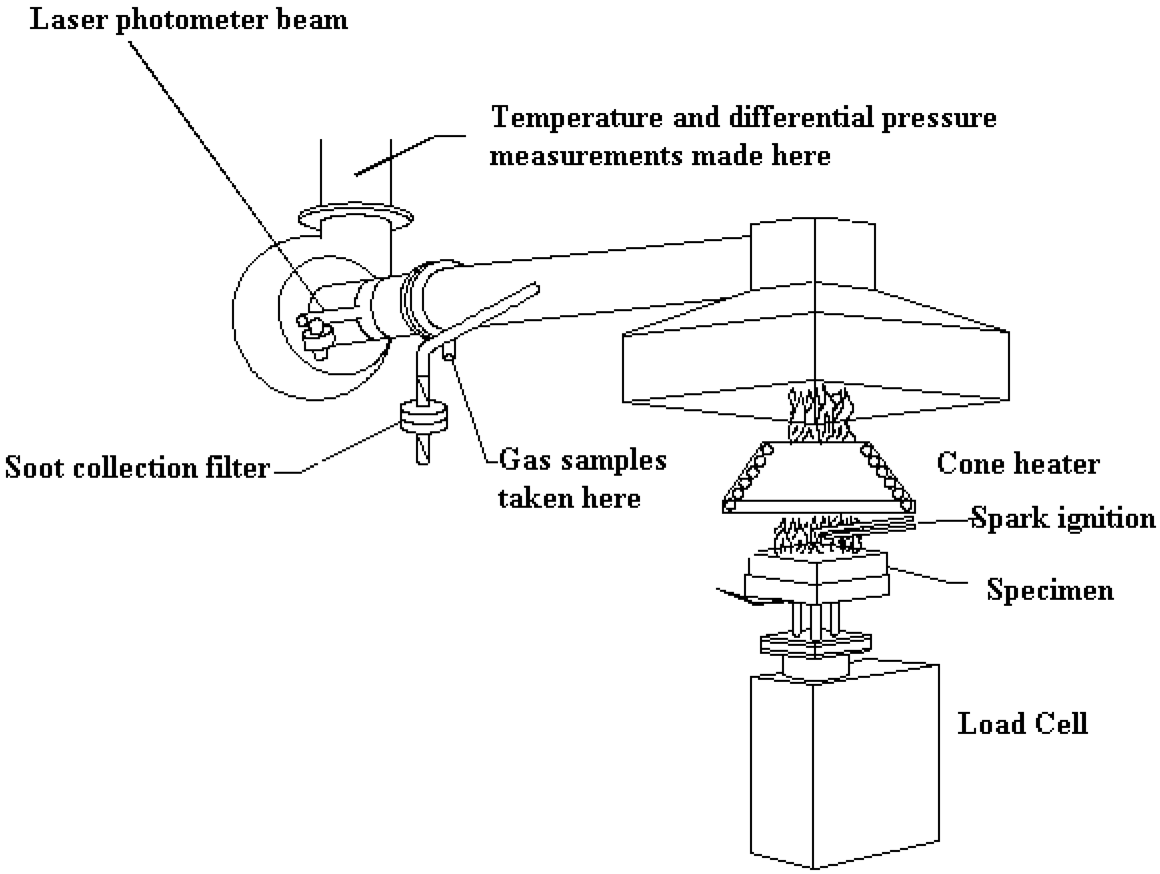

Figure 3.2 Schematic of the cone calorimeter

Central to a cone calorimeter is the cone heater, in which a heating element is wound in the form of a truncated cone. The heater is rated at 5000 kW (230 V) and has a maximum heat output of 100 kW/m2. For each experiment, the heater is set to a temperature that gives the desired heat flux at the surface of the specimen. The setting is checked during test calibration using a water cooled heat flux sensor placed at the surface of the specimen and the cone temperature further adjusted as needed. Temperature control is achieved using 3 type K thermocouples and a 3-term (PID) temperature controller.

Each 10 cm by 10 cm by 2.54 cm thick test specimen is mounted in a metal sample holder, which is placed a stain gauge based load cell. There are two types of sample holders. Depending on the specimen, the sample holder can have open or closed edges. For the experiments in this study the closed edge sample holder was used. The load cell has an accuracy of 0.1 g and total weight range of 2 kg and continuously records the weight of the sample during the experiment.

A 10 kV spark igniter, not shown in *figure 3.2*, is situated immediately above the sample surface below the cone heater. This ignites the flammable gases leaving the sample. The igniter, which ignites any flammable gases leaving the sample, is automatically positioned by a lever linked with the shutter mechanism. The shutter mechanism protects the sample area before the test. This ensures the initial mass measurement is stable and the operator has additional time for system checks before starting the test. This added time is very important for easily-ignitable samples, which would ignite prematurely if a shutter mechanism is not used. Once the whole sample surface is burning, the igniter is turned off and moved to the side.

Hot gases generated from the sample are collected into the extraction hood situated directly above the cone heater. A fan is mounted in the flue gas duct to set the flow rate of combustion products. The flow rate used in this study is 24 l/s. A gas sampling ring, situated before the fan, is used to sample exhaust gases which are then transferred to the gas analysis system in the cone calorimeter unit. The sampled gases are first passed through two filters to remove particles, then through a cold trap and a drying agent to remove water before they transferred to the gas analyzers. Between the gas sampling ring and the fan there is also a smoke measurement system. This measures the amount of smoke in the exhaust stream by determining the absorption of a laser beam., using photodiodes, and a 0.5 mW Helium Neon laser, with main and reference (compensating) photo detectors.

Since cone calorimeter measurements are based on the principle of oxygen consumption as measured in the exhaust gases, the main analyzer required is the paramagnetic oxygen analyser, which in the present system has a range of 0-25% oxygen. The heat release rate (HRR) of a burning sample is calculated using the oxygen concentrations with corrections made based on the concentrations of carbon dioxide and carbon monoxide in the flue gases. These are measured by the FTT Servomex paramagnetic oxygen, carbon dioxide and carbon monoxide analysers.

3.2.3 FTIR and Novatech Systems

In addition to the standard gas analyzers installed in the cone calorimeter to measure the concentrations of O_2 and CO_2/CO for calculation of heat release rate during the cone calorimeter tests, two other sets of gas analyzers were interfaced to the existing UW system. One is a *Novatech P-695* system consisting of a model *8800 Baseline* total hydrocarbon analyzer, *TML 41* NO/NO2/NOx analyzers and *Servomex 4900* IR CO/CO_2 and paramagnetic O_2 analyzers. The other system is a *Miran SapphIRe 205B* FTIR spectrometer which allows more detailed investigation of gases evolved during calorimeter testing. The *Novatech P-695* system, which is intended for monitoring gases during larger-scale furniture calorimeter and full-scale fire testing, is used here mainly to gain experience with its characteristics and operation; however, it also provides valuable comparison data for gases measured using the cone calorimeter analyzers, with some extension to the other major combustion gases present in the exhaust. The FTIR is intended for identification and analysis of a wide range of possible combustion products that are not otherwise accessible using the cone calorimeter or Novatech gas analysis systems. The use of an additional gas analyzer (Novatech P-695) for comparison with the FTIR and existing cone calorimeter gas analyzers is unique based on review of the current fire gas analysis literature.

The Novatech Analyzer system consists of three gas analyzer banks which are used to make species concentration measurements. One measures O_2, CO_2, and CO, while the others measure total hydrocarbons and nitrogen oxides respectively. These provide comparative data, to the cone calorimeter CO, CO2 and O2 data as well as information on total unburned hydrocarbons which cannot be measured with the FTIR gas analyzer.

The first gas analyzer bank in the Novatech system is the Servomex 4900 Series analyzer (O2, CO2 & CO) which utilizes independent non-dispersive IR analyzers for CO and CO_2 concentrations and a paramagnetic gas sensor for measuring O_2 concentration. The CO and CO_2 analyzers operate on the general principle of IR absorption. The O_2 analyzer operates on the paramagnetic principle, since O_2 has a relatively high magnetic susceptibility when compared to other gases and therefore is positively attracted into a magnetic field. All three work on the same principles as the analyzers in the cone calorimeter and when operated at the same sampling rate (1 Hz) provide directly comparable data.

The second gas analyzer bank in the Novatech system is the Model 8800H Heated Total Hydrocarbon Analyzer which measures the total concentration of hydrocarbons in the gas stream using an electronically flow controlled Flame Ionization Detector (FID). As a small sample of gas passes through the hydrogen and air flame in the detector, organic or hydrocarbon based gases in the sample are ionized and the freed electrons continuously collected on a biased electrode, producing an electrical signal proportional to the total amount of organic compounds in the flame.

The third and final gas analyzer bank is the Model TML 41 Nitrogen Oxides Analyzer which is used to measure the concentration of nitric oxide (NO) and nitrogen dioxide (NO_2) present in a sample of fire gas. The instrument uses chemiluminescence to directly measure the concentration of NO, a catalytic-reactive converter converts NO_2 in the sample gas to NO which is reported as NO_x which includes NO. The NO_2 concentration can then be calculated as the difference between the measured amounts of NO_x and NO.

The Novatech Analyzer is connected to a sampling port in the exhaust system of the cone calorimeter, through a sampling line that includes a particulate filter and gas filter which remove soot and heavy combustion products.

The Novatech analyzer continuously collects gas concentration data at a 1Hz sampling rate throughout each test. The unit is connected to a computer with an RS-232 cable. Using Microsoft Excel raw gas concentration data is uploaded and analyzed.

The FTIR system used in this research is a MIRAN SapphIRed-205B infrared spectrometer. It has a resolution of 4 cm^{-1} across a spectral range from 709 to 1298 cm^{-1} (14.1 - 7.7 μm) with a full spectral scan taking about 320 s to complete [48]. It is intended for use in monitoring ambient air quality in workplace environments for the purpose of detecting the presence of unwanted gases. The analyzer contains a MIRAN SapphIRe-XL single-beam infrared spectrophotometer, with a 2.2 l gas cell and a microcontroller that automatically controls the analysis, processes the measurement signal, and calculates the IR absorbance values for each line in the sample spectrum. Results can be displayed in parts per billion (ppb), parts per million (ppm), percent (%), mg/m^3, or absorbance units (AU) [48].

The SapphIRe-XL Analyzer can measure any compound having an absorbance in the wavelength region from 7.7 microns to 14.1 microns or at any of a limited series of fixed wavelength bands defined using band pass filters. In its current configuration there are a single continuously linear variable filter (7.7 to 14.1 microns) and seven fixed band filters. The seven fixed wavelengths are: water vapour (1.859 microns), general hydrocarbons (3.333 microns), formaldehyde (3.573 microns), a reference wavelength (4.004 microns), carbon dioxide (4.250 microns), nitrous oxide (4.500 microns), and carbon monoxide (4.620 microns). The FTIR can take continuous absorbance versus wave number output thereby allowing for multi-component analysis. In addition, its user library contains 120 single gas, factory calibrations in a standard library that can be used to identify specific gases within a larger gas sample.

FTIR gas concentration measurements are susceptible to changes in ambient temperature. In order to minimize these changes, a temperature sensor is installed inside the SapphIRE Analyser to measure the temperature of the incoming fire gases. In addition, there is an in-line temperature flux meter that measures the temperature of the fire gases in the sampling line. The temperature gauge in the SapphIRE Analyser is compared to the temperature at the zero point and a correction in the concentration calculation is made.

The FTIR system is connected to the soot mass sampling port on the cone calorimeter exhaust stack, from which exhaust gas is collected and passed via a sampling line through filters which remove soot and heavy combustion products and protect the FTIR from fouling. The sampled gas also passes through a drierite filter unit to prevent water vapor from condensing on the mirrors inside the FTIR gas cell. Since the gas sampling line is not heated and the gas cell itself has a limiting upper operating temperature of 50 ^{0}C, without drying the input sample condensation could occur in the FTIR during the analysis with detrimental impact on signal quality. In addition, changes in ambient humidity can significantly affect the accuracy of the calculation of measured values of gas concentration. When humidity levels rise or fall from the reference values, gas concentrations can either rise or fall respectively. The level of fluctuation is gas and wavelength dependent, but can be compensated for if the change in relative humidity is between +/- 20%. Finally, the drierite filter is important if there are compounds like HCl in the gas stream as they can mix with water and form highly acidic (corrosive) compounds like H_3O^+ which would damage the FTIR cell. Since the exact species in the exhaust gases are not know a priori in this work, the drierite filter was installed in the present system to minimize the potential impacts of these effects.

A single head diaphragm vacuum/pressure pump, 0.6 cfm and 115 VAC, attached to the outlet port of the of FTIR sampling system ensures a gas sample flow rate of 14 l/min, passing through the 2.2 l gas cell internal to the Gas Analyzer. A flow meter installed downstream of the vacuum pump allows confirmation of the required flow rate of 14 litres/minute (or 0.475 cfm on the flow meter used). This meter is also used for zero gas calibration using the same flow rate as would be observed during sampling. The 14 l/min flow rate was selected based on the manufacturer's recommendations. At a flow rate of approximately 14 liters/minute and a cell volume of approximately 2.2 l, the FTIR cell is provided about six volume changes of air each minute. According to the manufacturer, typically five volume changes of air is enough to purge the cell of the previous sample by 99%. For the FTIR analysis, the exhaust gases are collected in the FTIR sampling cell over a period of 60 seconds, after which the IR spectral scan begins. In the present configuration, gas is prevented from flowing through the sample cell during the spectral analysis by shutting off the vacuum pump and capping the outlet end of the sampling cell at the end of the 60 second sampling period.

During sample collection and after analysis is complete, the gas sample exhausts downstream of the flow meter. To prevent exposure to the potentially hazardous gases that may evolve from fire testing, the exhaust port is positioned inside the end of a 4” flexible hose (flexible dryer exhaust duct) that directs the sample exhaust to a mechanically ventilated exhaust hood.

To transfer data, the FTIR unit is connected to a computer with an RS-232 cable. Using Thermo connect and Thermo match software supplied by Thermo Environmental Instruments Inc (MIRAN SapphIRe Application Firmware Version 5.00.06) raw absorption spectral data is uploaded and analyzed.

For this research, all the above systems where integrated and the combined system was calibrated and the Experimental Procedure contained in Appendix D was developed for preliminary testing.

Chapter 4 – Experimental Results and Discussion

After the gas analysis system was connected and operational, a series of specimens of "blue Styrofoam" were tested in the cone calorimeter-FTIR system in order to set-up operating procedures and verify results. The procedures developed were then applied to probe the fire performance of, and species evolution from, a series of unknown rigid PU materials. The design and results of the test runs are presented and discussed in the following sections. Appendix C outlines the specific operating sequence and calibration routine that was developed for this research and followed prior to testing.

4.1 Blue Styrofoam

Initial tests were run to investigate the fire behaviour of five samples of "Blue Styrofoam", also known as extruded polystyrene, manufactured by DOW Corning. The samples were cut from a 1 inch thick x 24 inch x 96 inch sheet of material purchased locally. Styrofoam insulation is manufactured from polystyrene resin and extruded into rigid boards, with no flame retardants incorporated into the base formulation. To make the test samples, the Styrofoam insulation board is cut into standard 1 inch x 4 inch x 4 inch test samples (10 cm x 10 cm x 2.5 cm) for the cone calorimeter. The samples are conditioned in the laboratory for at least one week at temperatures between 20 – 22 ^{0}C and relative humidity levels between 28 – 25 % in order to minimize any effects of test temperature or sample relative humidity on the results [33]. Each sample is wrapped in aluminum foil with just enough overlap at the corners to contain any melted foam that could drip/pour over during a test. The test foam and aluminum foil assembly is then placed on a 12 mm thick ceramic board on the bottom tray of the standard cone calorimeter closed sided sample holder. All cone tests were conducted in accordance with ASTM E1354 (ISO 5660-1), with an incident heat flux of 50 kW/m^2 and spacing between the heater and sample of 25 mm [33]. This heat flux was chosen as it is the average heat flux for application of the ASTM E1354 (ISO 5660-1) standard and as such it was considered a good starting point for the experimental set-up.

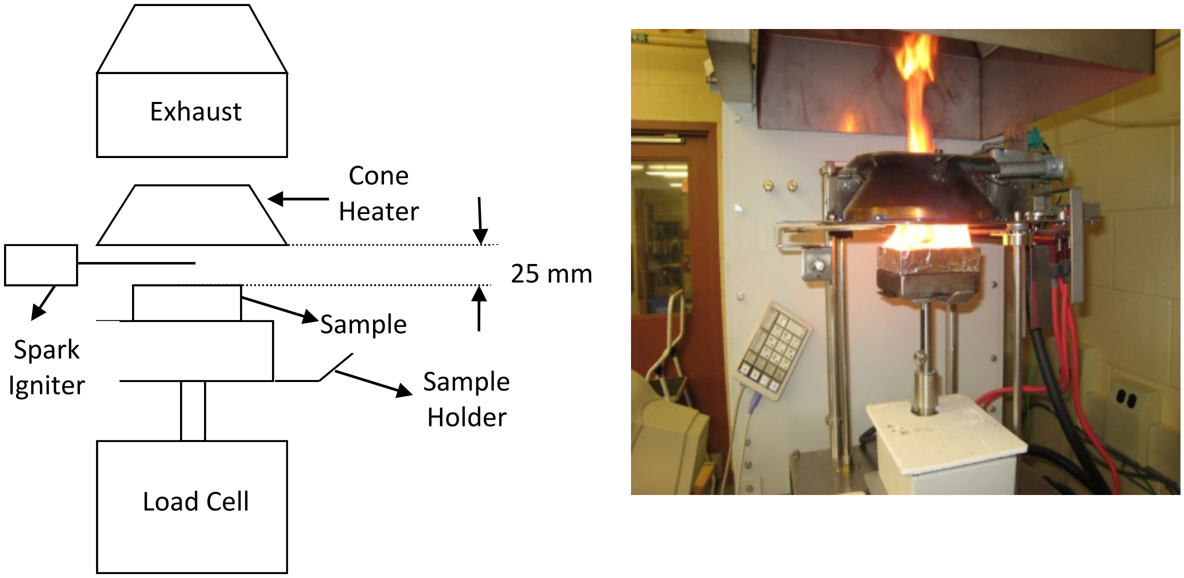

Figure 4.1: Sample set up in cone calorimeter for "blue Styrofoam" tests

A representative sample of "blue styrofoam" is first tested in the cone calorimeter in order to establish a timeline for ignition and heat release rate of the material. From this, times are set for sample collection within the representative stages of fire growth. A plot of HRR versus time for this initial test is shown in *figure 4.2*. HRR profiles for four subsequent tests are presented in *Figure 4.3* to show potential variation between the HRR profiles. It can be seen that in all cases, while initially being exposed to the incident heat flux, the sample undergoes a period of thermal decomposition (0 to 37 s on the plot) followed by ignition and a relatively rapid rise in HRR to a peak value of around 600 kW/m^2. Unlike the curve shown in f*igure 2.1*, blue Styrofoam does not undergo steady burning but instead the HRR decays again as the sample is consumed.

For later comparison, the main components in the chemical composition of blue Styrofoam are summarized in *Table 4.1* below.

Table 4.1: Chemical Composition of Blue Styrofoam [49]

Component	**CAS #**	**Amount**
2-Propenenitrile,polymer with ethenyl benzene	*9003-54-7*	*< 90.0 %*
Styrene, polymers	*9003-53-6*	*< 90.0 %*
1,1,1,2-Tetrafluoroethane	*811-97-2*	*>= 0.0 - < 10.0 %*
1-Chloro-1,1-difluoroethane		*>= 0.0 - < 10.0 %*
Copolymer mixture (trade secret)	*N/A*	*< 5.0 %*

Further, the MSDS sheet indicates that various toxic and/or irritating products might be produced during smouldering or flaming conditions, including CO, CO_2 and soot as well as hydrogen halides and trace amounts of acrylonitrile and hydrogen cyanide.

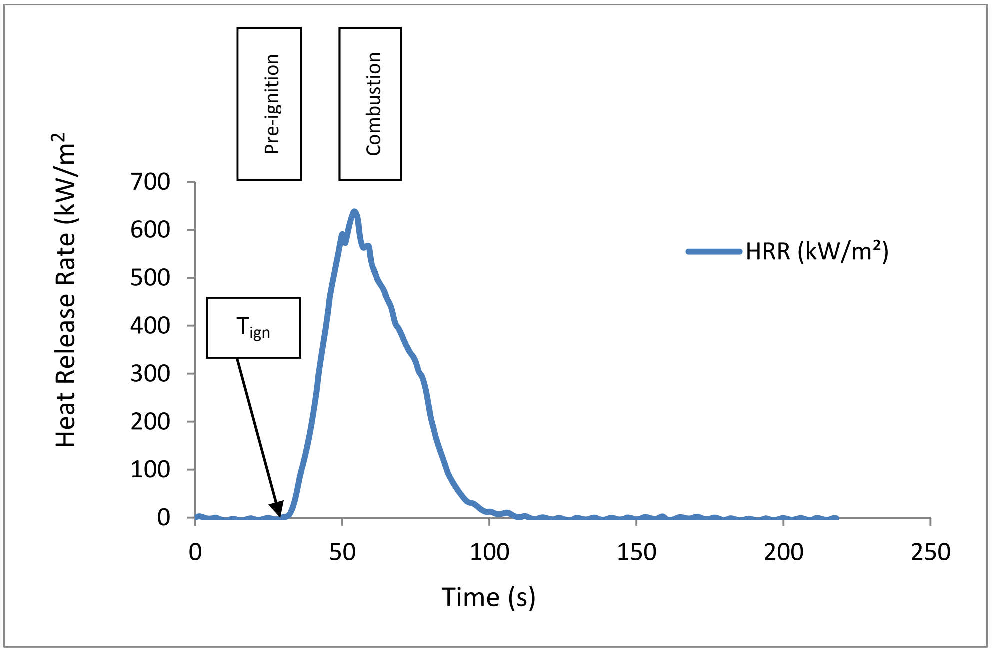

Figure 4.2: HRR profile from initial cone test for "blue Styrofoam" tests

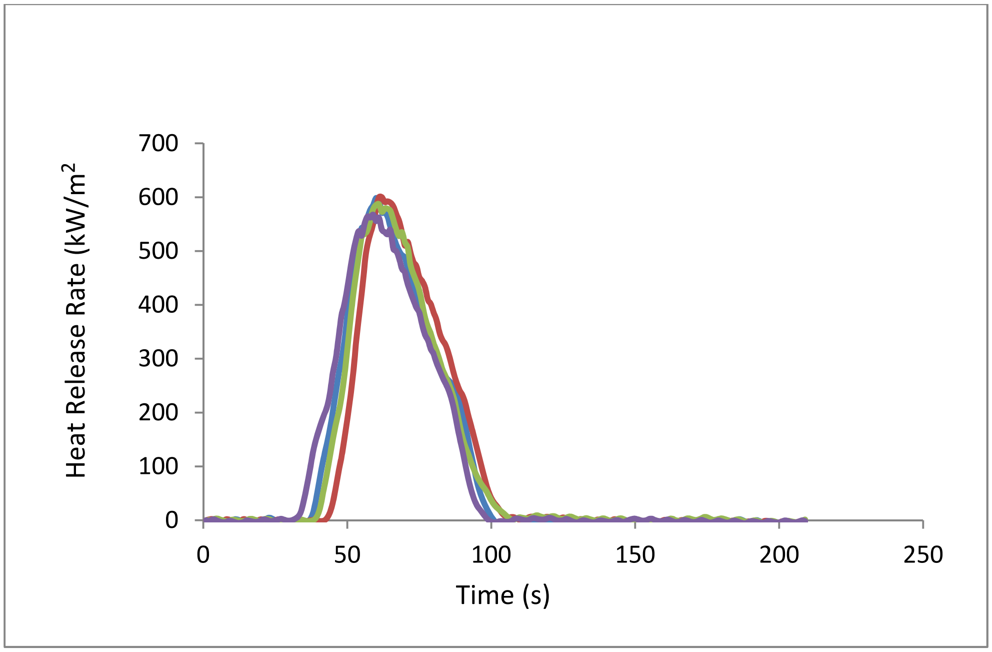

Figure 4.3: HRR profile for cone tests 1, 2, 3, and 4 for "blue Styrofoam" to show variance

The pre-ignition phase across all samples is between 0 seconds and around 37 seconds, and the combustion phase occurs between around 37 seconds to around 100 seconds. Gas sampling was therefore chosen to start at 0 seconds and 30 seconds, with sampling durations of 30 seconds, 45 seconds and 60 seconds in order to collect representative samples in these phases, in combination with the gases present during the transitions between the phases. A table summarizing the sampling start times and periods is shown as *Table 4.2* below.

Table 4.2: Summary of sampling start times and periods for blue Styrofoam tests

Test #	Start time (s)	Duration (s)
1	*0*	*30*
2	*0*	*45*
3	*0*	*60*
4	*30*	*60*

4.1.1 Test #1 – Blue Styrofoam (Pre-ignition)

The HRR profile for Test #1 is presented in *figure 4.4*. *figure 4.5* shows the plot of CO_2 versus time while *figure 4.6* contains the plot of CO versus time. The gas sampling period is superimposed on all of the plots for reference. As indicated, FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 30 seconds.

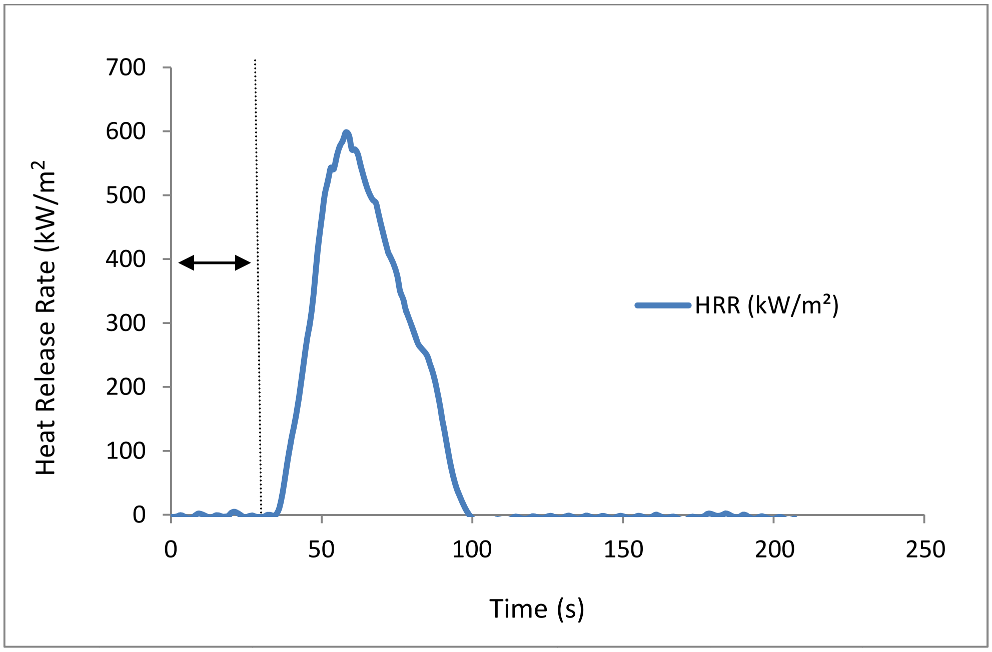

Figure 4.4: HRR profile from initial cone test for "blue Styrofoam" test #1

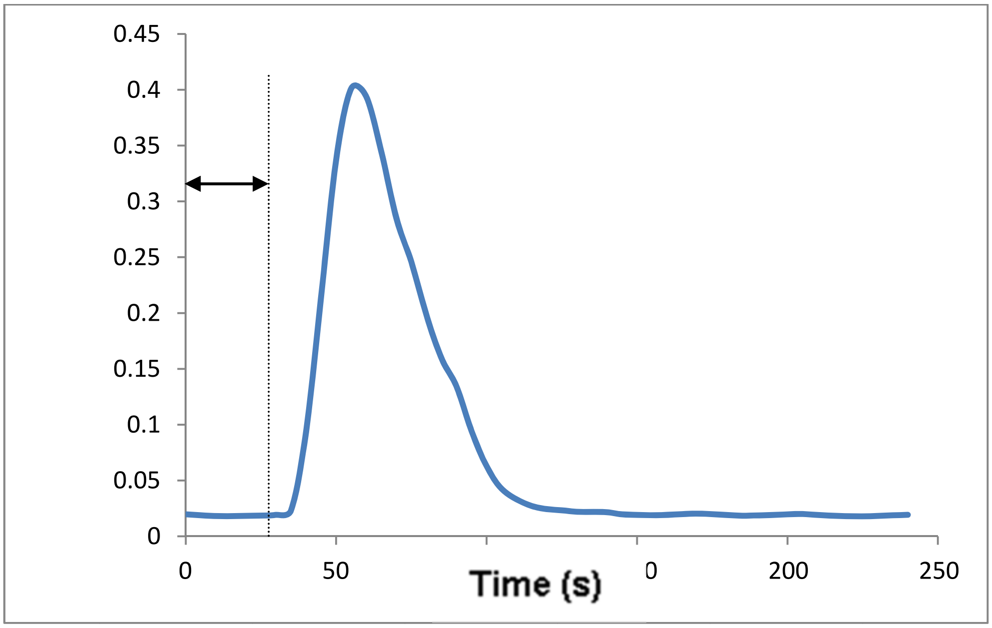

Figure 4.5: CO_2 concentration-time plots for blue Styrofoam test #1

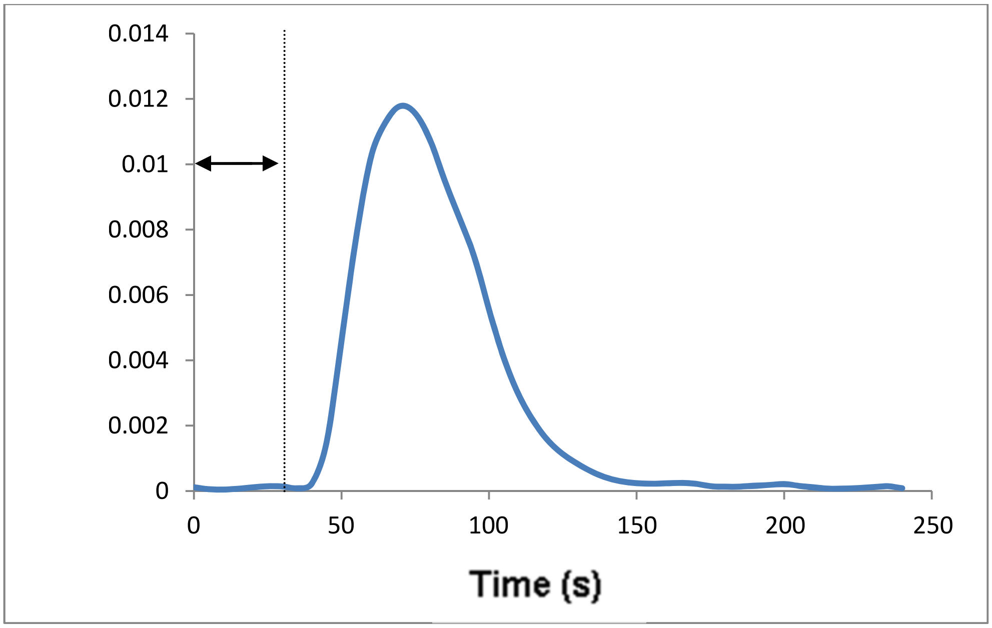

Figure 4.6: CO concentration-time plots for blue Styrofoam test #1

Substantial off-gassing was observed upon shutter opening, with ignition occurring at 37 seconds after the sample was exposed to the incident heat flux. Thus the gases collected and analyzed in this test were truly representative of blue Styrofoam off-gasing. As can be seen in all of the plots, the sampling period ended before a measured increase in HRR, CO or CO_2 concentration which would indicate ignition and combustion was taking place.

The infrared spectrum for test #1 is presented in *Figure 4.7*. It illustrates dominant peaks at wavelengths of 843 cm^{-1}, 970 cm^{-1}, 1087 cm^{-1}, 1166 cm^{-1} and 1270 cm^{-1}, believed to correspond to the compounds as listed in *Table 4.3* below.

Table 4.3: Potential compounds for test #1

Wavelength	***Compound***
843 cm^{-1}	Styrene (C_8H_8).
970 cm^{-1}	Acrylonitrile (CH_2CHCN)
1087 cm^{-1}	R-134A
1166 cm^{-1}	R-134A
1270 cm^{-1}	R-134A

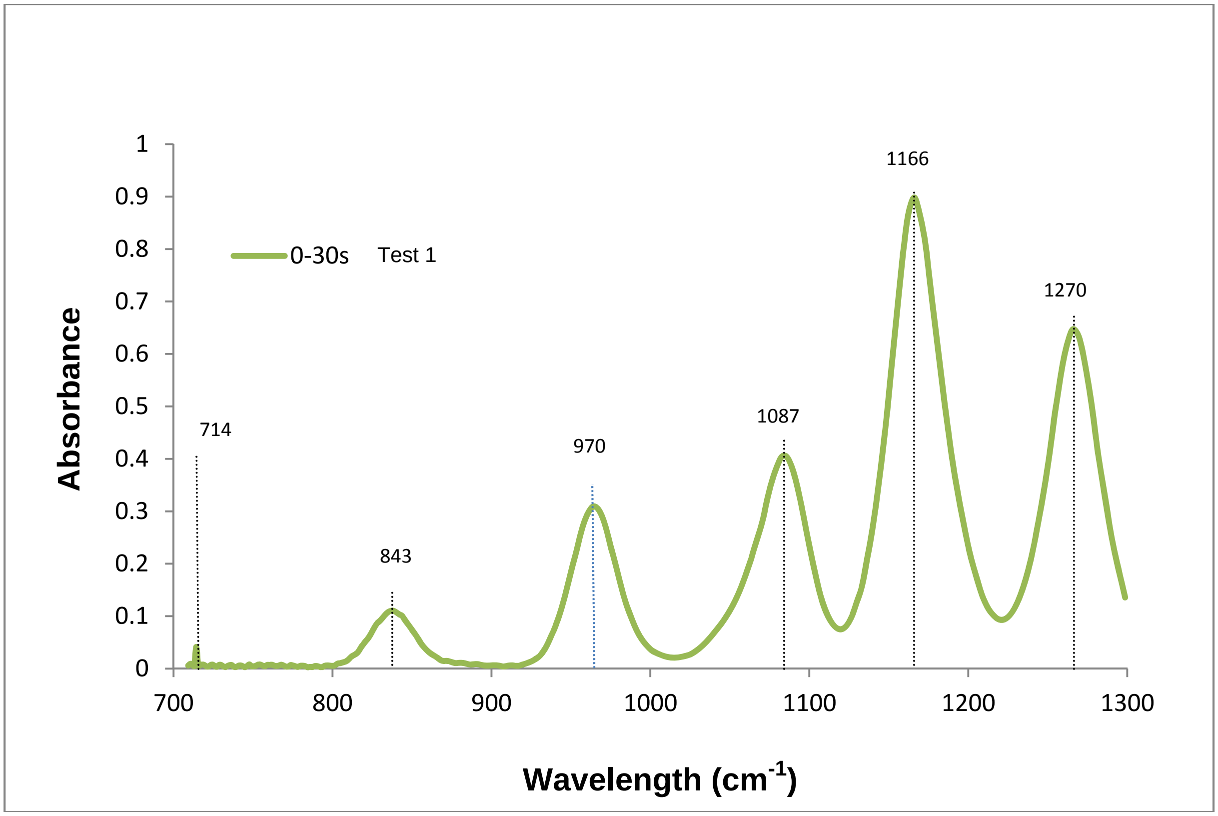

Figure 4.7: IR Spectrum for "blue Styrofoam" test #1

More detailed analysis of the spectrum using the Thermomatch library [56] confirmed the presence of 1,1,1,2 Tetraflouroethane (CH_2FCF_3) also known by its trade designation as R-134A which is used as a blowing agent in the manufacture of rigid foams, and Butyl Methyl Ether (CH_3C-CH_3-CH_3-OCH_3), Acrylonitrile (CH_2CHCN). The slight peak found at 714 cm^{-1} in the spectra is believed to be indicative of HCN. This peak is not clearly defined as it is hidden behind the strong CO_2 absorption peak at 700 cm^{-1}. Comparison of these results with Table 4.1 and the MSDS information confirmed that the FTIR was resolving various gaseous species in the exhaust samples and that the spectral indicate the presence of gases that are consistent with those expected during decomposition of a blue Styrofoam sample.

Further, the prevalence of organic gases representative of unburned materials is supported by the Total Hydrocarbon (HC)-time plot measured by the Servomex analyzer for test #1 and shown in *figure 4.8.*

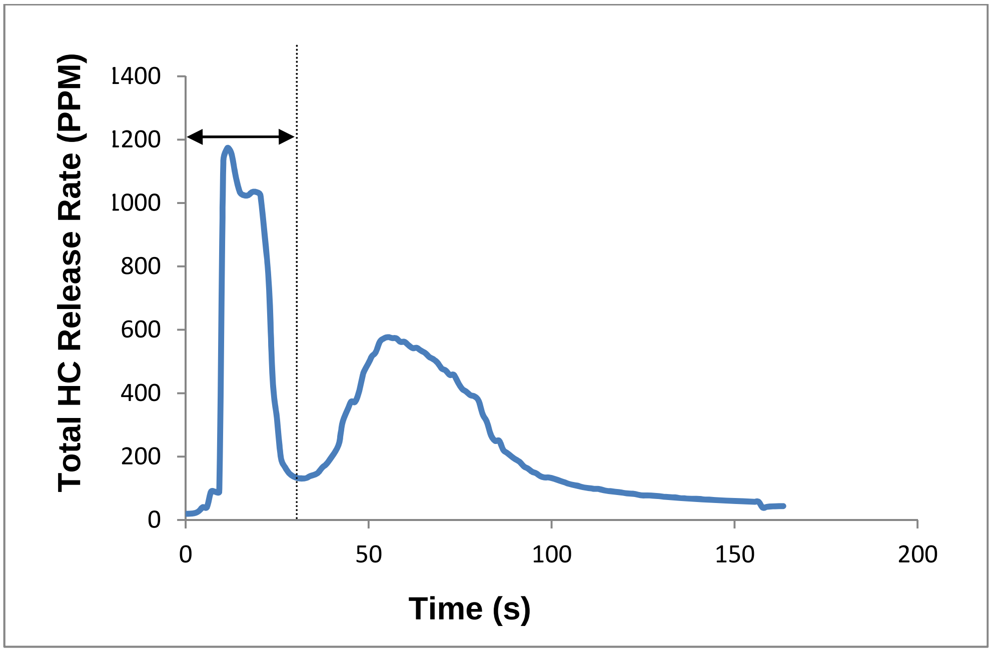

Figure 4.8: THC concentration-time plot sample regime for test # 1

There is clearly a large peak in total HCs during the period over which sampling takes place, further supporting the presence of organic vapours due to decomposition of the Styrofoam sample.

4.1.2 Test #2 - Blue Styrofoam (Pre-ignition plus 15 seconds)

The HRR-time, CO-time and CO_2 time profiles for test #2 are shown in *figures 4.9 through 4.11* with the test sampling time superimposed on top. FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 45 seconds, in an attempt to collect higher concentrations of the decomposition products as well as a sample of the gases produced in the time immediately after ignition.

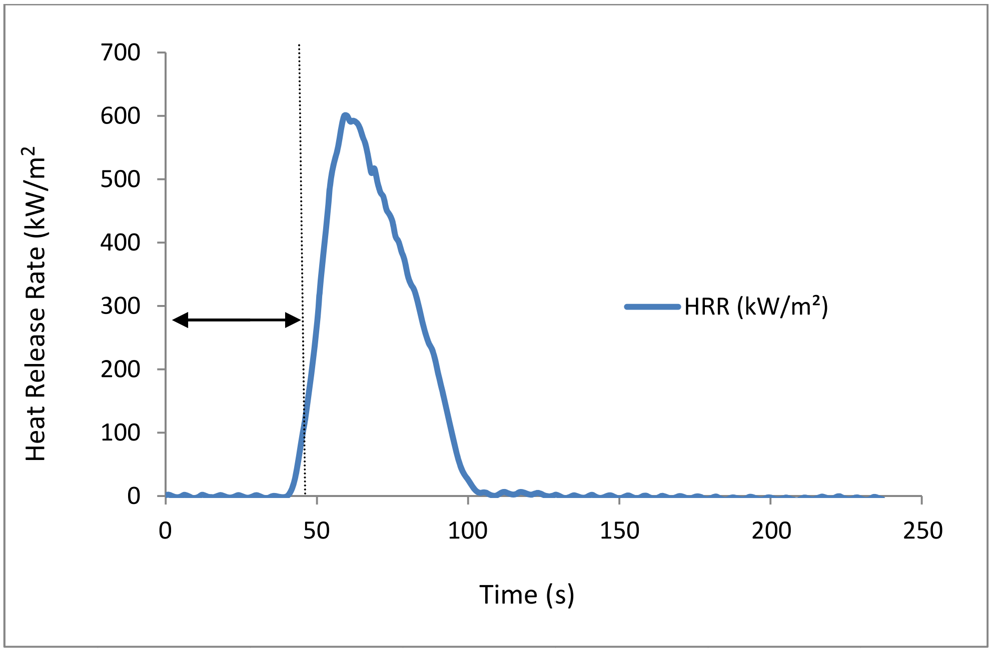

Figure 4.9: HRR profile from initial cone test for "blue styrofoam" test #2

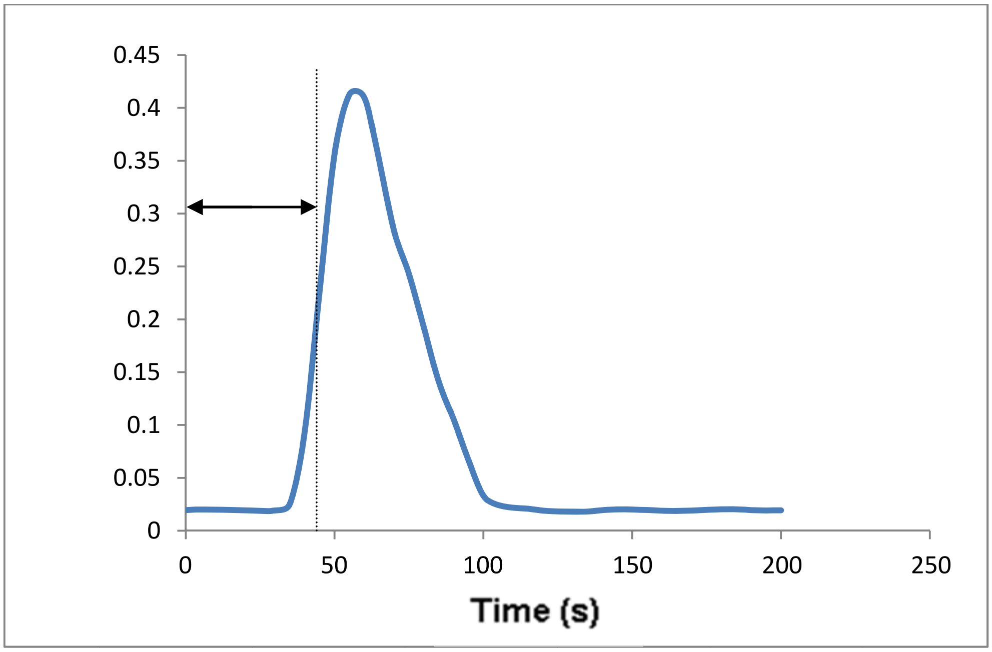

Figure 4.10: CO_2 concentration-time plots for blue Styrofoam test #2

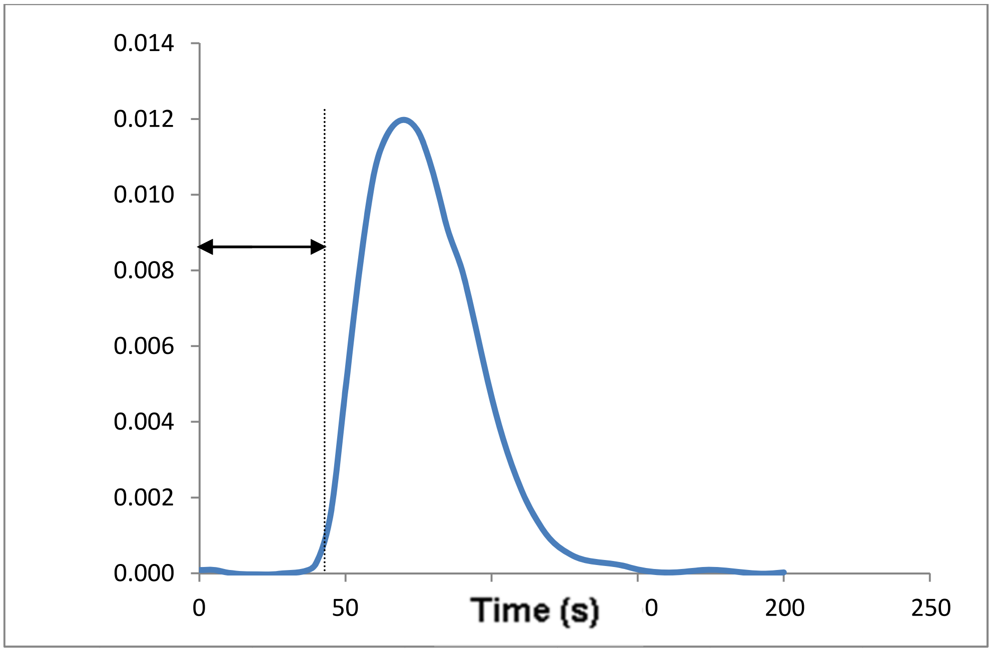

Figure 4.11: CO concentration-time plots for blue Styrofoam test #2

Again substantial off-gasing was observed upon shutter opening with ignition occurring around 35 seconds after shutter opening. Through the HRR, CO and CO_2 plots it can be noted that for this test, the sampling period extended beyond the point of ignition by about 10 seconds. As such, it is confirmed that gases from this test captured the thermal decomposition and initial burning of the Styrofoam sample.

Figure 4.12 contains the IR spectrum for test #2 overlaid on that from test #1 already shown as *Figure 4.7*.

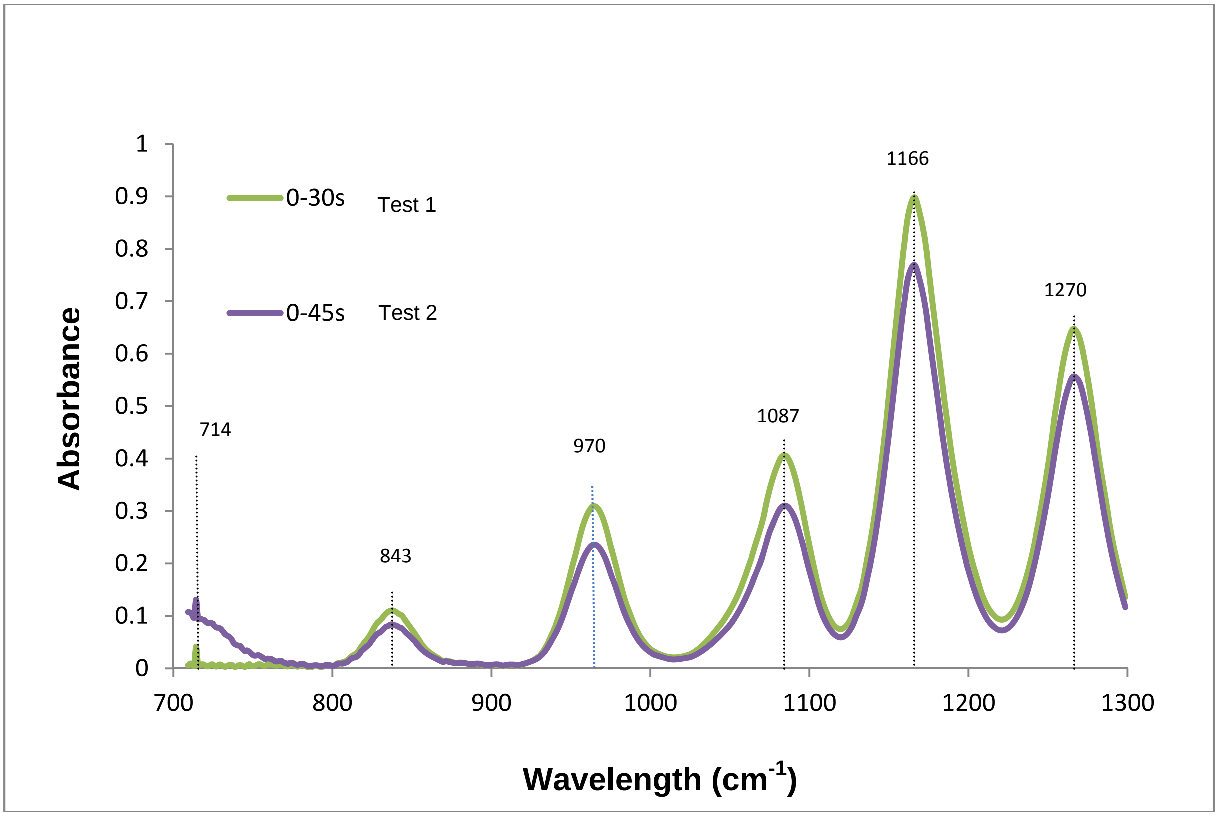

Figure 4.12: IR Spectrum for "blue Styrofoam" tests #1 and #2

The correspondence of the wavelengths for the main peaks is clear, indicating the presence of those compounds identified in test 1, table 4.3.

One notable difference in the IR spectra from tests #1 and #2 is the peak in the wavelength range between 700 and 775 cm^{-1}. This corresponds to the absorption peak for CO_2, and therefore is consistent with the fact that the sampling period for test #2 included gases from both sample decomposition and combustion. This is consistent with the overlaid time CO_2 trace which clearly shows that the sample time extended into the period when CO_2 was measured by the cone calorimeter as well. Due to the strong IR absorption of CO_2 and its high concentration during sample combustion, this peak will mask lesser peaks such as that for HCN which would be expected to appear at 714 cm^{-1}. This points to one weakness in applying FTIR to measurement of gases generated during burning of a cone calorimeter sample. Unless major combustion gases such as CO_2 can be removed from the sample before analysis, their strong absorption peaks in certain spectral regions will interfere with weaker signals produced by other important gases with absorption lines in those spectral regions.

4.1.3 Test #3 - Blue Styrofoam (Pre-ignition plus 30 seconds)

The HRR time profile for test #3 is presented in *Figure 4.13*, while CO_2 time and CO time plots are in *figures 4.14 and 4.15* respectively with the sampling period indicated on each plot. FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 60 seconds in an attempt to capture some gases typical of thermal decomposition but also those typical of the period from ignition through to the peak HRR from the sample.

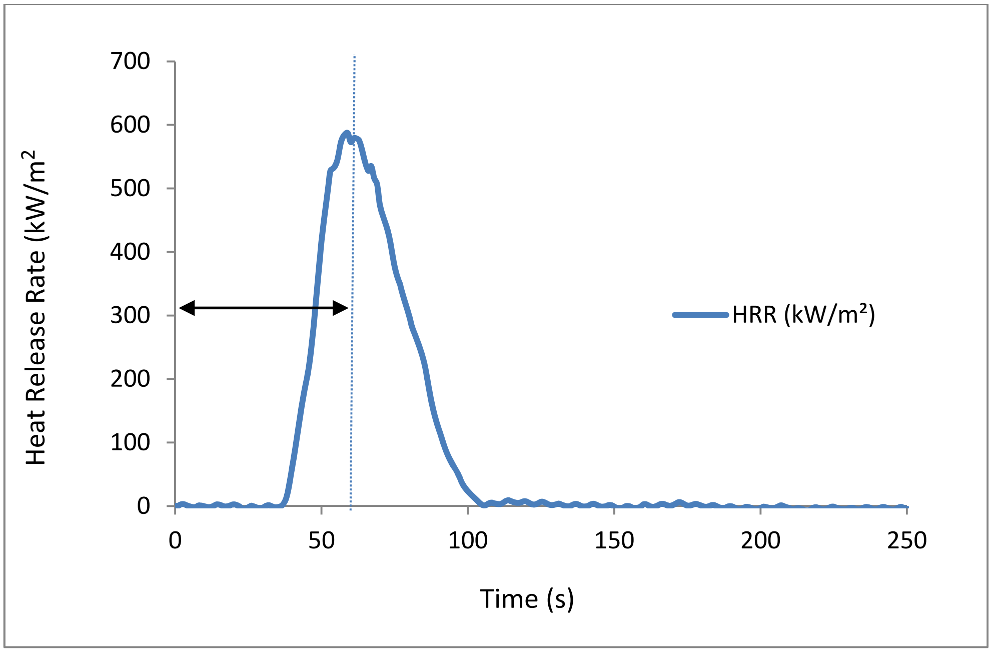

Figure 4.13: HRR profile from initial cone test for "blue styrofoam" test #3

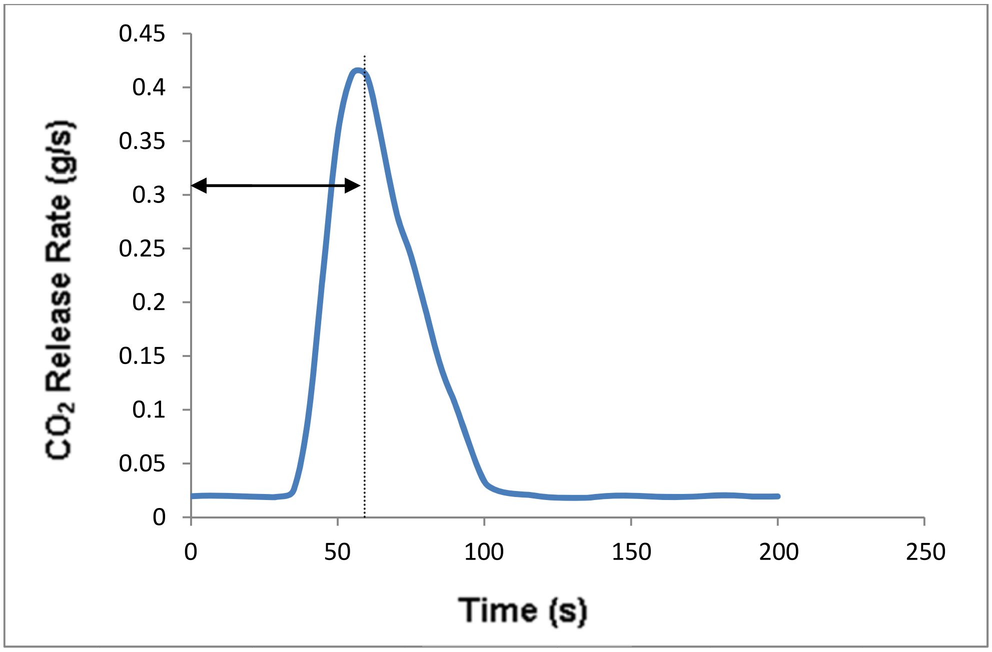

Figure 4.14: CO_2 concentration-time plots for "blue Styrofoam" test #3

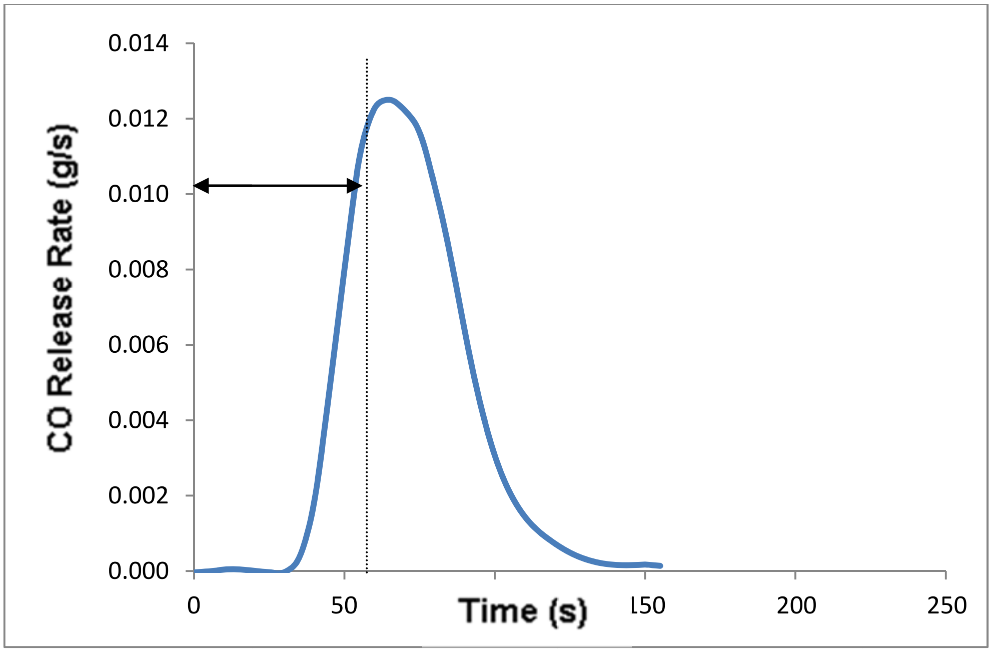

Figure 4.15: CO concentration-time plots for "blue Styrofoam" test #3

As in previous tests, substantial off-gassing was observed immediately upon shutter opening. Ignition occurred 34 seconds after shutter opening and sampling continued until 60 seconds when the HRR reach a value of 550 kW/m^2, just past its peak value. From *Figure 4.13,* due to the combustion of the sample it can be seen that the concentration of CO_2 reached a maximum of

0.42 g and CO of 0.012 g during sampling. Therefore this test captured the effects of initial burning and fire growth up to around the peak HRR (just before fire decay).

Evidence of the increased concentration of CO_2 is also in *figure 4.16* which contains the IR spectral plot from test #3 overlaid on those from tests #1 and #2. In this plot, the absorbance at 700 cm^{-1} is higher in the spectrum than those from either of the previous tests.

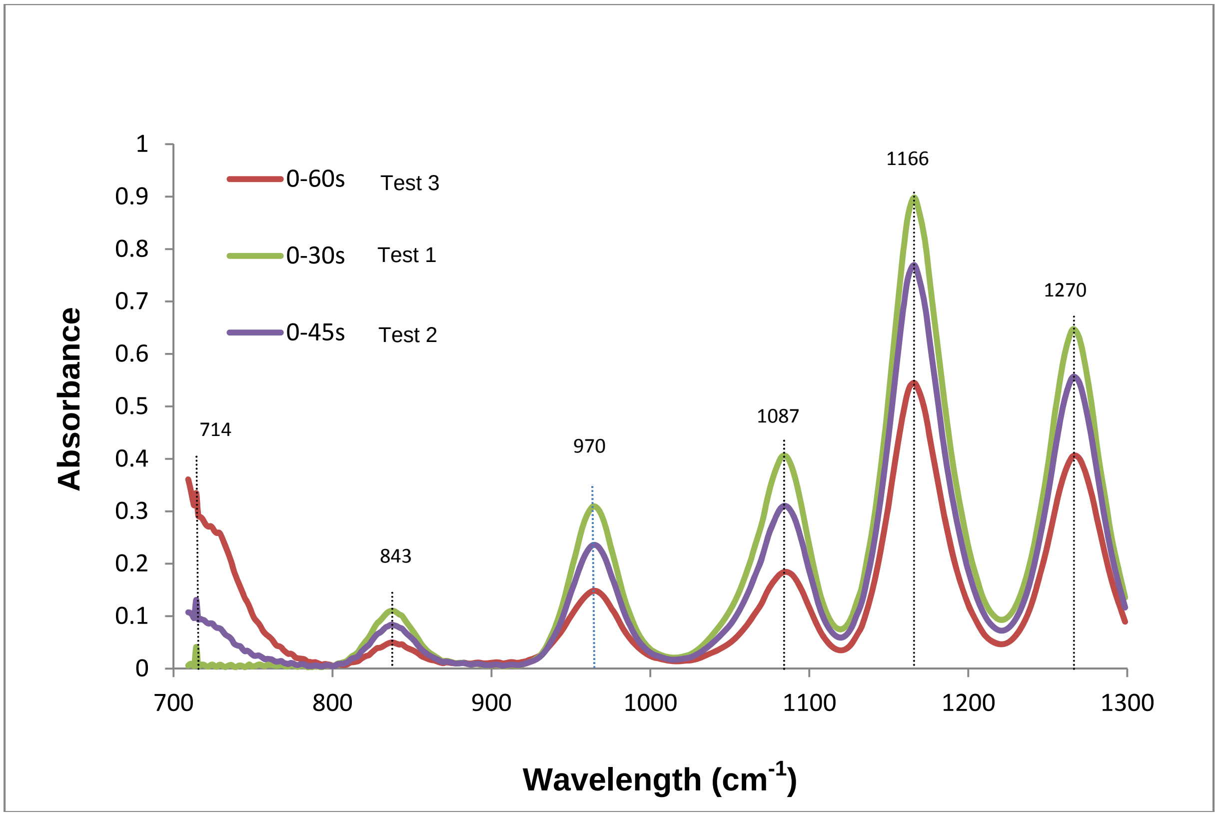

Figure 4.16: IR Spectrum for “Blue Styrofoam” tests #1 -#3

The other peaks listed in Table 4.3 are also present, though their magnitudes are lower than in test #1 or #2 due to the combined factors of spectral normalization and potentially reduced concentrations of the unburned HC represented by these peaks due to 26 seconds of post ignition sampling of burned combustion products. That the concentrations of gases might be different in the sample is also evidenced in figure 4.17, the plot of total HC-time where the sampling period for test #3 clearly includes gases from several distinct regions in the total HC versus time plot.

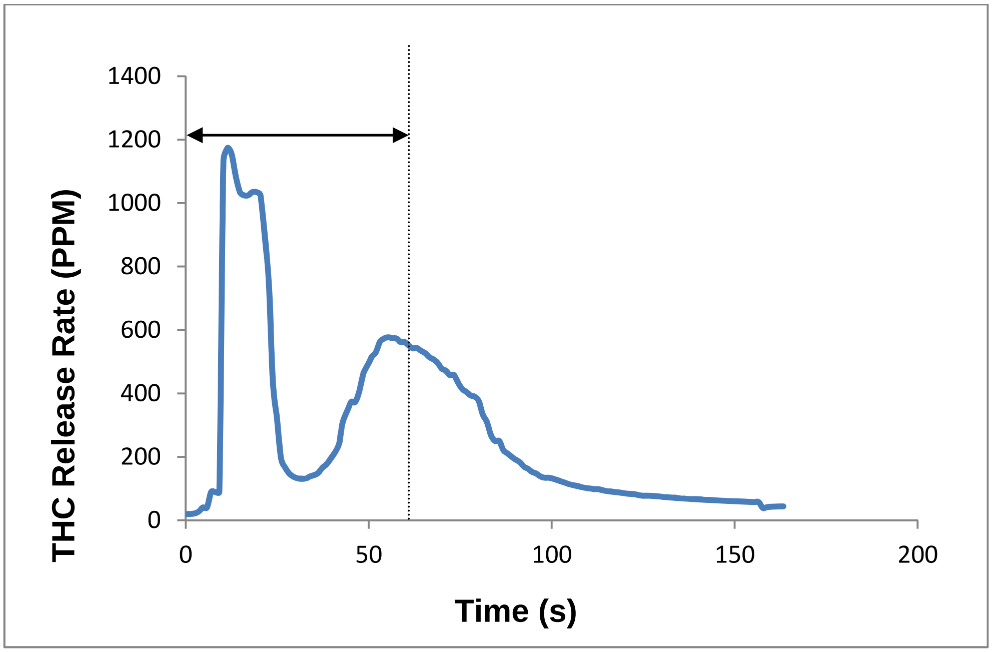

Figure 4.17: THC concentration-time plot sample regime for test # 3

Due to the 6 flushes of the spectrometer gas cell during a 60 second sampling period, the sample will be more biased towards the combustion products than those generated during pre-ignition thermal decomposition of the sample.

4.1.4 Test #4 - Blue Styrofoam (Post-ignition phase)

The HRR time profile from test #4 is presented in *Figure 4.18,* while those for CO_2 and CO are in *figures 4.19* and *4.20* respectively. For this test, FTIR sampling was initiated 30 seconds after the shutter on the cone heater was opened, and sampling lasted for 60 seconds in order to capture the gases generated during burning of the blue Styrofoam sample.

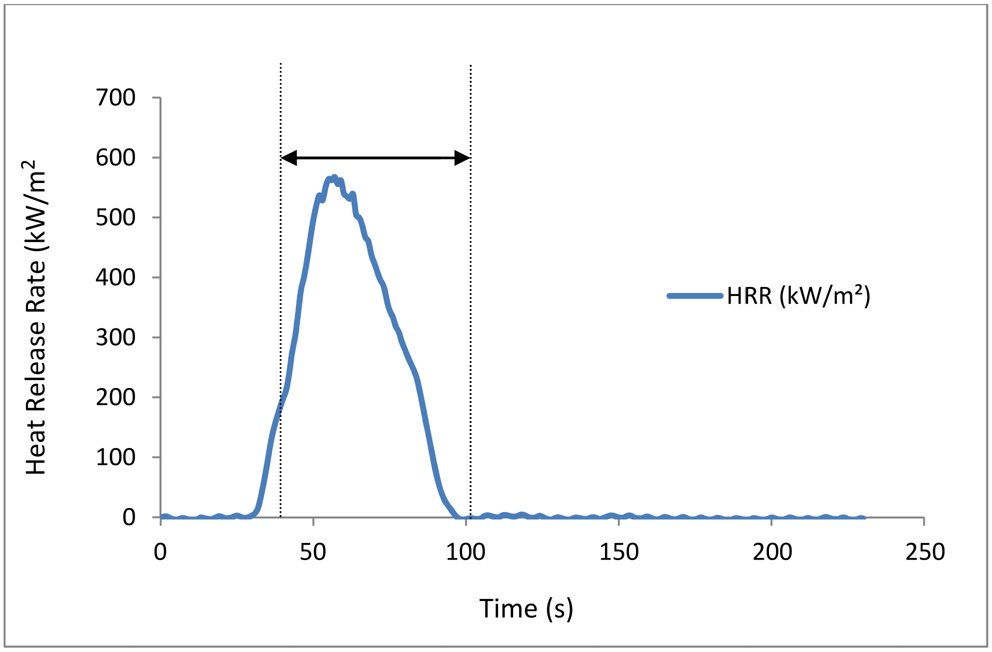

Figure 4.18: HRR profile from initial cone test for "blue Styrofoam" test #4

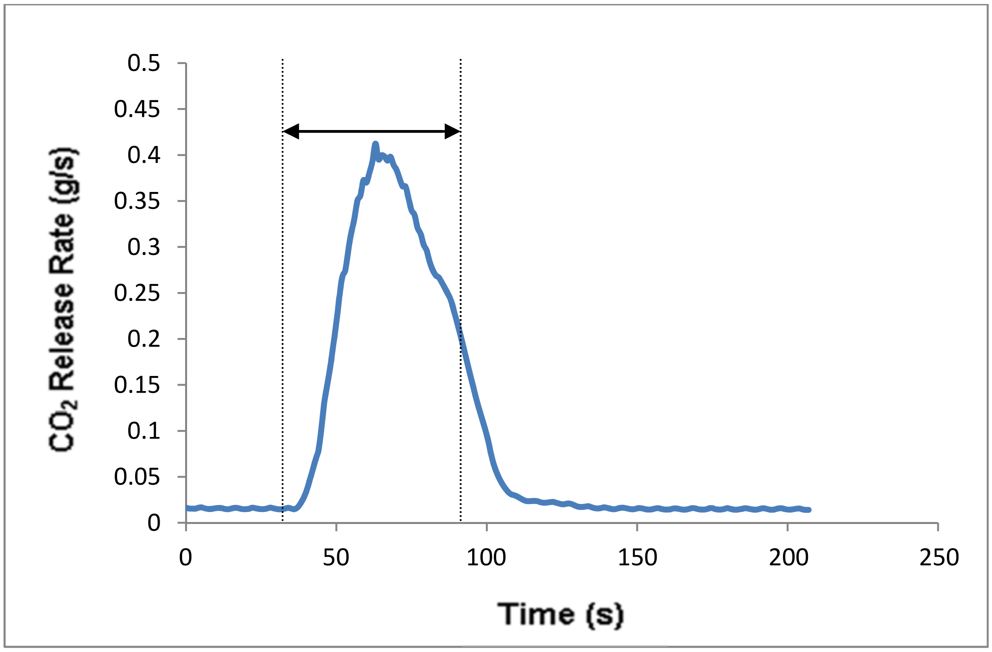

Figure 4.19: CO_2 *concentration-time plots for test #4*

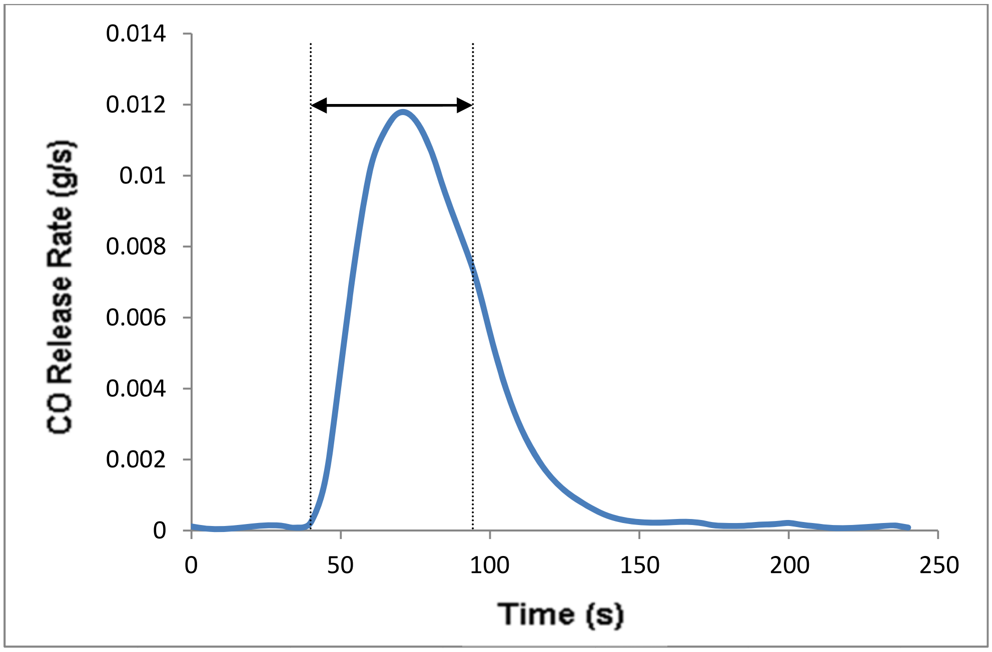

Figure 4.20: CO concentration-time plots for test #4

Substantial off-gassing was observed upon shutter opening and ignition occurred at 36 seconds after shutter opening. Therefore in this test, sampling was started 6 seconds before ignition and extended until approximately 10 seconds before the end of burning. Therefore this test captured the effects of initial burning, fire growth and fire decay (just before flame out).

The infrared spectra for test #4 is shown in *figure 4.21*.

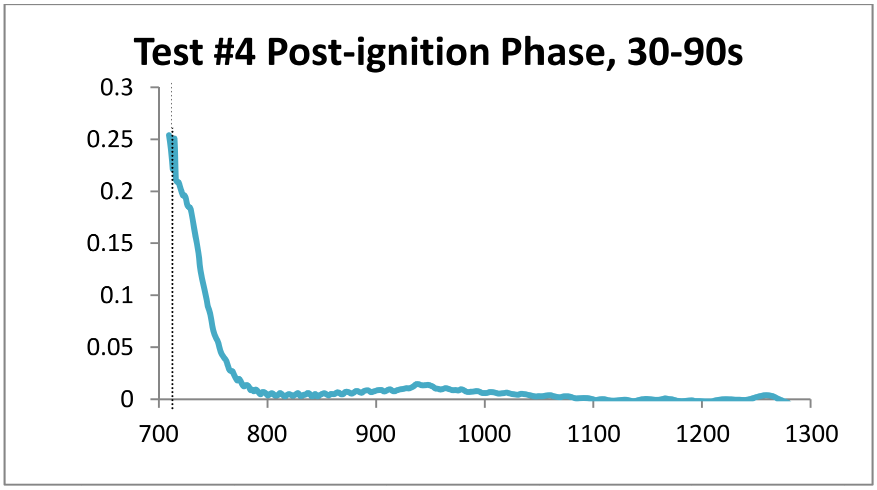

Figure 4.21 IR Spectrum for "blue Styrofoam" test #4

The slight peak found at 714 cm^{-1} in the spectra for test #4 is believed to be indicative of HCN. The peak is not clearly defined as it is hidden behind the strong CO_2 absorption peak at 700 cm^{-1}. None of the absorption peaks seen in test #1 through #3, except that for CO_2 and possibly HCN, are shown in the spectra for test #4. This lack of absorption peaks is due to the fact that sampling for test #4 starts after the large peak in the total HC-time plot shown in *figure 4.22.*

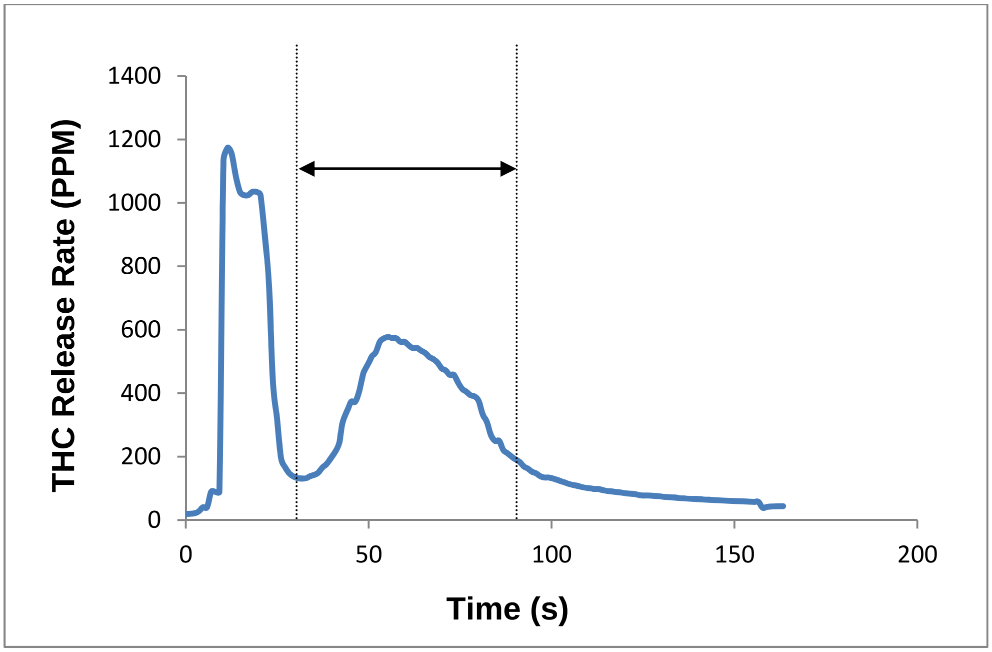

Figure 4.22: THC concentration-time plot sample regime for test # 4

Since the hydrocarbons generated during off-gas phase were not sampled, peaks corresponding to those *in figures 4.7, 4.12* and *4.16* and *Table 4.3* would not necessarily be expected to be present. The sample time was set to focus on the combustion phase, so the large CO_2 peak is expected as shown in *figure 4.19*, and possibly peaks corresponding to a different set of hydrocarbons. These are not evident however, likely due to CO_2 absorption swamping such other signals, but also because six flushes of the FTIR sample volume are used so the final sample composition is biased toward the combustion decay phase with low concentrations of UBHC (*figure 4.22*).

From the results of tests 1 through 4, it was shown that the integrated cone calorimeter-FTIR system and test procedures developed here could be used to examine the composition of gases at various stages during cone calorimeter testing. Comparison of the results with the MSDS information confirmed the presence of gases that are consistent with those expected during decomposition of a blue Styrofoam sample. The procedure was next applied to the more challenging problem of studying a series of rigid PU foams with intumescent FR additives that were supplied to the lab for fire performance tests.

4.2 Rigid Intumescent PU foam

In the second phase of testing, four samples of intumescent FR rigid foams manufactured in the Woodbridge Foam Corporation research laboratory using a high pressure foam production system, were examined. In these materials, flame retardants of types and levels used in commercial applications were incorporated into a proprietary high density base foam formulation to make samples representative of those currently available in the building industry. A key ingredient in these intumescent foams is expandable graphite which can cause the foam to expand to more than 100 times its original volume when exposed to heat. Expandable graphite additives also form a foamed char layer during combustion, with a worm-like structure that covers the entire burning surface of the fuel. The cellular charred layer on the surface thermally shields the underlying material from the cone heat flux, and acts as a physical barrier which slows down heat and mass transfer between the gas and the condensed phases [50]. The cumulative effect of this is normally a reduction in heat release rate, mass loss, smoke generation and toxic gas emission from the foam [50].

For the test described here, the foam was hand manufactured and poured into a 25.5 cm x 25.5 cm x 2.5 cm mold. The resultant slab was cut into standard 10 cm x 10 cm x 2.5 cm test samples for use in the cone calorimeter. The samples were conditioned in the laboratory for a least one week at temperatures between 20 – 22 ^{0}C and relative humidity levels between 28 – 25 %. Each sample is wrapped in aluminium foil with just enough overlap at the corners to contain any melted foam that may drip/pour over during a test. The test foam and aluminum foil assembly is then placed on a 12 mm thick ceramic board on the bottom tray of the standard cone calorimeter close sided sample holder. The cone calorimeter portion of the test was conducted in accordance with ASTM E1354 (ISO 5660-1), using various levels of cone heat flux for the different sample as outlined below.

For later comparison, *figure 4.23* below shows a representative infrared spectrum scan from the literature [48] taken during the combustion of rigid polyurethane foam at an incident heat flux of 50 kW/m^2 at 25 mm spacing in a cone calorimeter across that region of the spectrum in which absorption peaks for H_2O, CO_2, CO and HCN were identified.

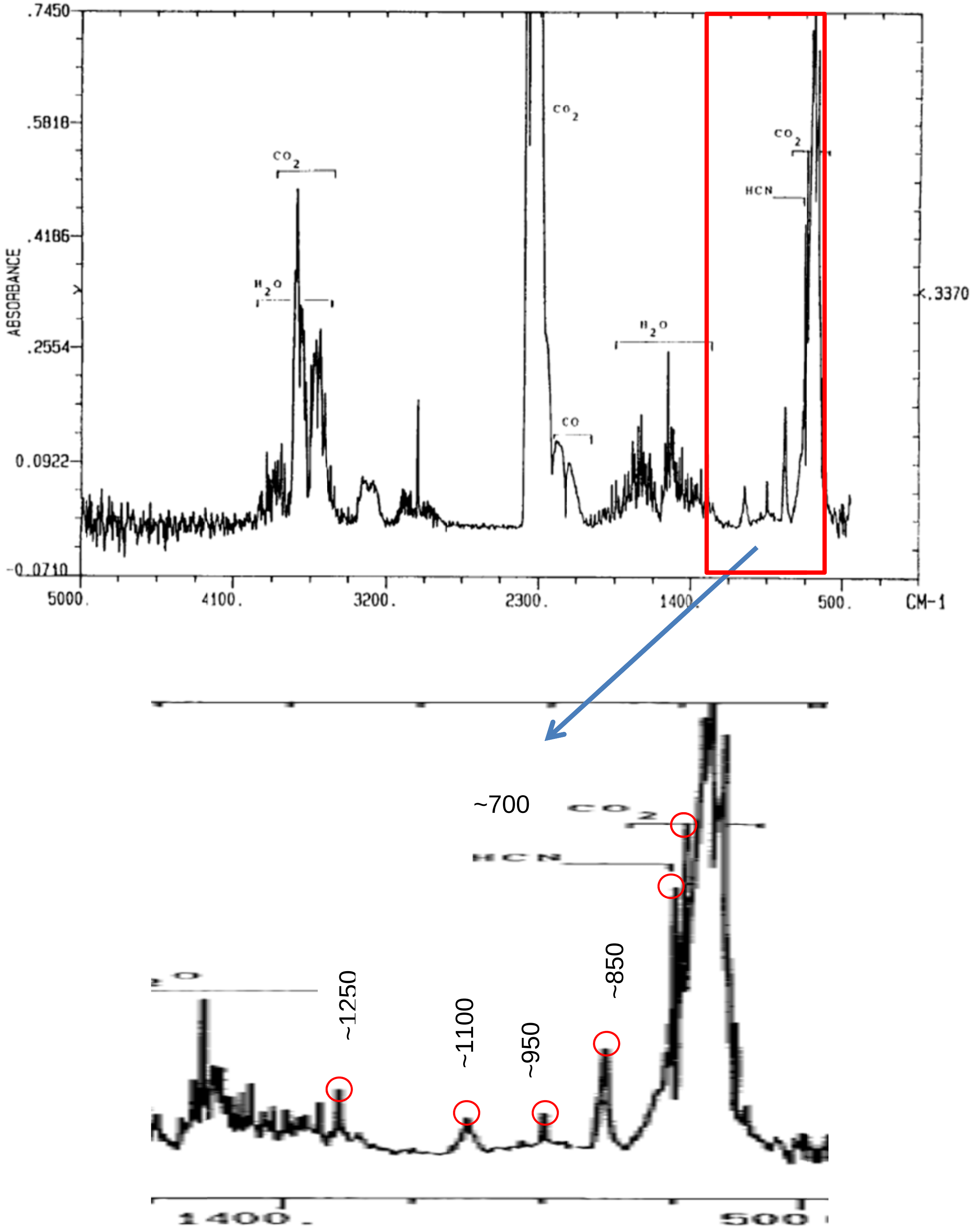

Figure 4.23 Infrared Spectrum for PUR1, 75s after ignition at 50 kW/m^2 [13]

A representative sample of intumescent foam was tested in the cone calorimeter in order to establish the baseline times for sample collection. The HRR-time curve is contained in *Figure 4.24,* while CO_2 and CO time traces from the Novatec system are in *figures 4.25 and 4.26* respectively. The plot of total HC-evolution with time is contained in *figure 4.27*.

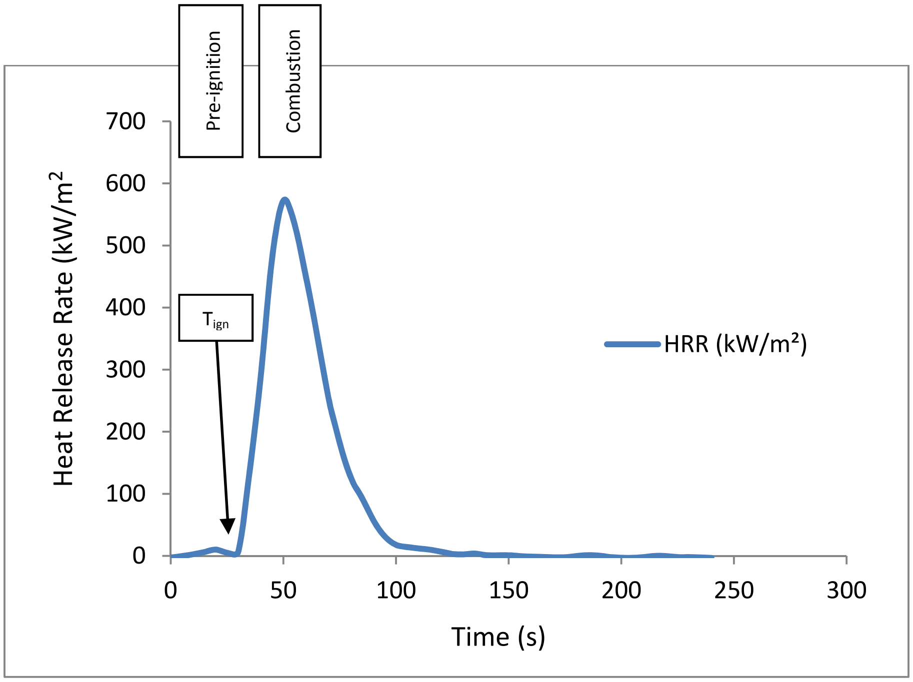

Figure 4.24 HRR profile from initial cone test for intumescent foam.

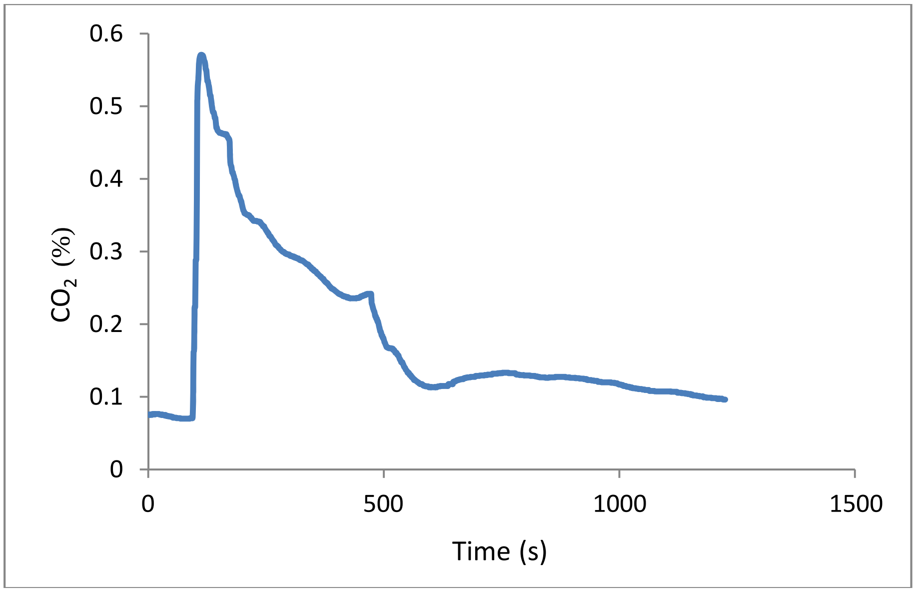

Figure 4.25: CO_2 concentration-time plot from initial cone test for intumescent foam

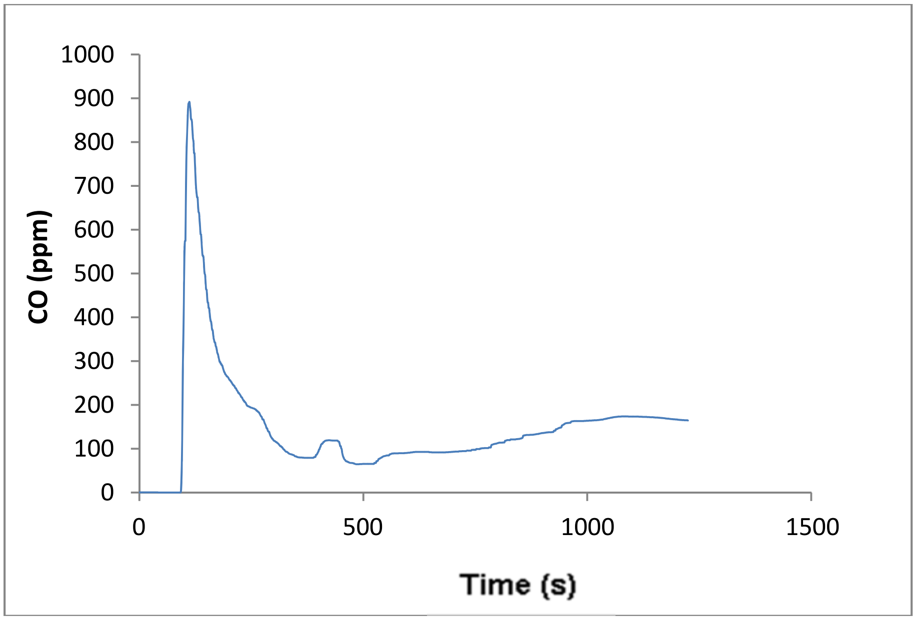

Figure 4.26: CO concentration-time plot from initial cone test for intumescent foam

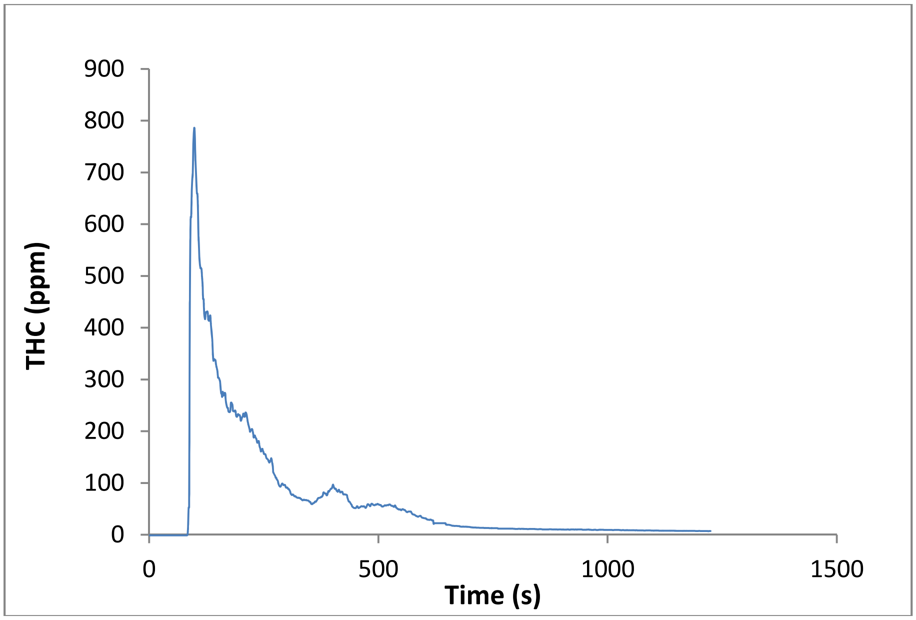

Figure 4.27: THC concentration-time plot for initial cone test for intumescent foam

Start of sampling, as well as the duration of the sampling window was selected based on the HRR profile produced by this initial cone calorimeter test (*figure 4.5*). Between 0 seconds and 30 seconds there is no notable heat being released or CO/CO_2 produced suggesting this phase involves thermal decomposition of the foam. Ignition takes place at around 30 seconds and the HRR, CO_2 and CO increase to about 60 seconds into the test, after which the combustion begins to decay. At around 100 seconds the sample is completely burned and the flames are out. Gas sampling was therefore chosen to start at 0 seconds, with sampling durations of 30 seconds and 60 seconds in order to collect representative samples in pre-ignition and combined pre-ignition and burning stages.

Table 4.4 below contains a summary of the sampling start times and periods.

Table 4.4: Summary of sampling start times and periods for intumescent foam tests

Test #	Start time (s)	Duration (s)
1	*0*	*60*
2	*0*	*30*
3	*0*	*60*
4	*0*	*30*

4.2.1 Test #1 - Rigid Intumescent foam

For test #1, the sample was exposed to a heat flux of 50 kW/m^2 with the standard spacing between the cone heater and sample surface of 25 mm. This heat flux was chosen because it corresponds to the evolved heat observed during an enclosure fire [43]. The sample ignited after 6 seconds of exposure to the heat flux, however due to the rapid expansion of the foam, the spark igniter was quickly embedded in the surface of the test foam sample.

Substantial off-gassing was observed upon shutter opening and in the short time before ignition was established. As indicated, FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 60 seconds. Thus the gases collected and analyzed in this test were truly representative of intumescent foam pre-ignition and burning.

The infrared spectrum for test #1 is presented in *Figure 4.28*. It illustrates dominant peaks at wavelengths of 714 cm^{-1}, 893 cm^{-1}, 950 cm^{-1}, 1067 cm^{-1}, 1163 cm^{-1} and 1262 cm^{-1}, believed to correspond to the compounds listed in *Table 4.5* below.

Table 4.5: Potential compounds for test #1	
Wavelength	***Compound***
893 cm^{-1}	1,4-dioxane
950 cm^{-1}	Ammonia
1067 cm^{-1}	1,4-dioxane
1163 cm^{-1}	Ethyl Formate (CH_3-CH_2-COOH)
1262 cm^{-1}	Dimethyl Carbonate (CH_3- COOO-CH_3)

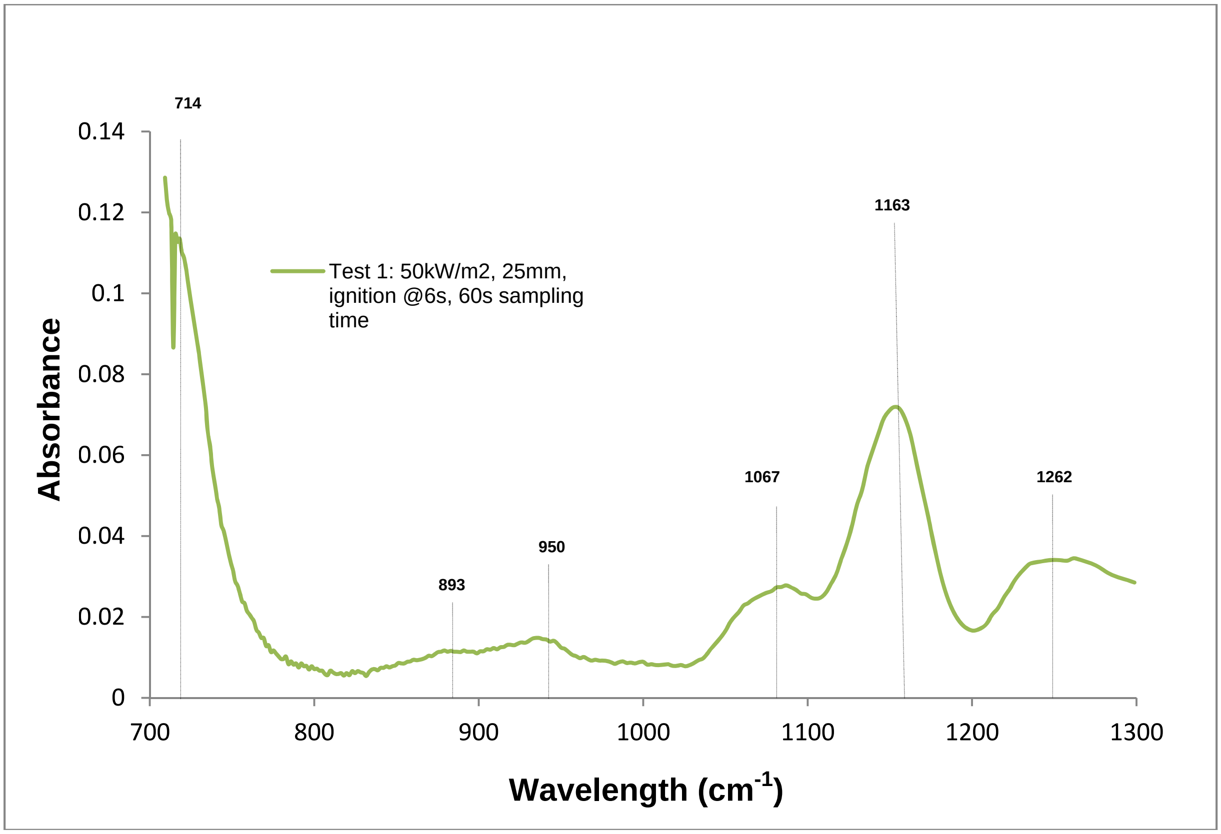

Figure 4.28 IR Spectrum for Intumescent foam test #1

Comparison of these results with Figure 4.23 indicates that the two intumescent foam samples exhibit similar absorption spectra. The same absorption peaks at 700 cm^{-1} for CO_2, 714 cm^{-1} for HCN, and around 850 cm^{-1}, and 1100 cm^{-1} for 1,4-dioxane, 950 cm^{-1} for ammonia, as well as at around 1150 cm^{-1} and 1250 cm^{-1} for unburned hydrocarbons similar to Ethyl Formate and

Dimethyl Carbonate can be observed in the wavelength spectra scan region 700 cm^{-1} – 1300 cm^{-1}.

More detailed analysis of the spectrum using the ThermoMatch library [56] confirm the presence of Ethyl Formate (CH_3-CH_2-COOH) and Dimethyl Carbonate (CH_3- COOO-CH_3) which are typically used in the manufacture of rigid foams. The wavelength spectral scan region 700 cm^{-1} – 1300 cm^{-1} is known to be representative of compounds with single bonds such as C-C, C-N and C-O [43]. The C-O bond has a strong absorption peak around 1100 cm^{-1}. In addition, compound groups such as phenols, alcohols, esters, ethers and carboxylic acids are found within the spectra wavelength range of 1000 cm^{-1} – 1300 cm^{-1} due to C-O stretch. More specifically, straight chain HC (alcohols) and ring compounds with C double bonds (phenols) are found within 1000 cm^{-1} – 1250 cm^{-1}. Carboxylic acids are known to be found within 1210 cm^{-1} – 1320 cm^{-1} with a COOH bond group. The slight peak found at 714 cm^{-1} is believed to be indicative of HCN. The peak is not as clearly defined as it is hidden behind the strong CO_2 absorption peak at 700 cm^{-1}.

4.2.2 Test #2 - Rigid Intumescent foam

For test #2, the sample was exposed to a heat flux of 50 kW/m^2. The spacing between the cone heater and the sample surface was again held at the standard value of 25 mm. FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 30s in an attempt to focus on capturing gases typical from the thermal decomposition period. Again substantial off-gassing was observed upon shutter opening. The spark igniter embedded in the surface of the expanded foam sample and ignition was not achieved during the sampling window.

Figure 4.29 contains the IR spectrum for test #2 overlaid on that from test #1 already shown as *figure 4.28.*

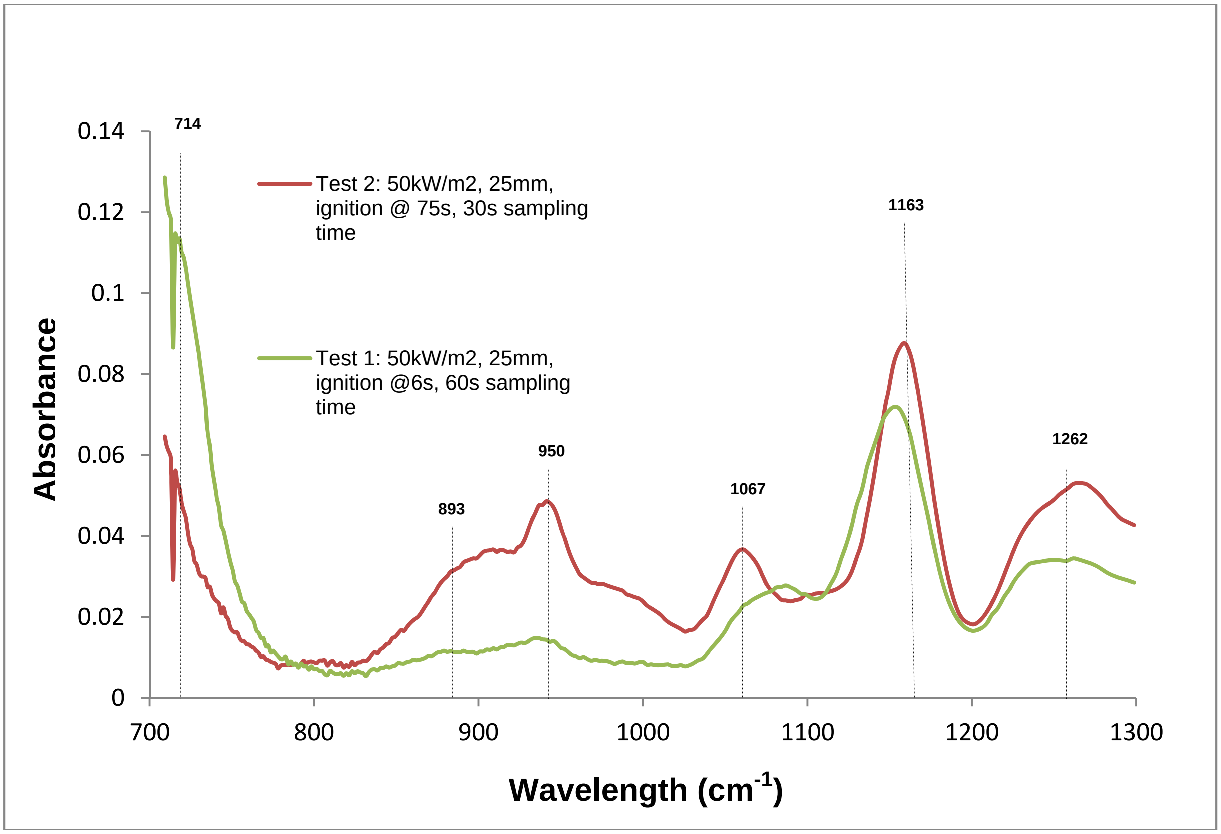

Figure 4.29 IR Spectrum for Intumescent foam tests #1 and #2

One notable difference in the IR spectra from tests #1 and #2 is the peak in the wavelength range between 700 and 775 cm^{-1}. This corresponds to the absorption peak for CO_2, and therefore is consistent with the fact that sampling test #1 included gases from both sample decomposition and combustion. Another notable difference in the IR spectra from tests #1 and #2 are the peaks in wavelength at 893 cm^{-1}, 950 cm^{-1} and 1067 cm^{-1} for test #2. The absorption peaks at 893 cm^{-1} and 1067 cm^{-1} may be attributed to 1,4-dioxane possibly produced through the condensation of diethylene glycol (which might be evolved from a depolycondensation reaction—degradation of

PU begins with scission of the urethane bonds to yield polyol and isocyanate) [2]. This is consistent with the fact that sampling test #2 only included gases from sample decomposition. The peak in wavelength at 950 cm^{-1} may be attributed to ammonia evolving from the thermal degradation of aammonium polyphosphate a typical phosphorus-based compound used in intumescent formulations [2]. Again, this is consistent with the fact that sampling test #2 only included gases from sample decomposition.

4.2.3 Test #3 - Rigid Intumescent foam

In order to avoid the spark igniter becoming buried in the rapidly expanding foam, the spacing between the cone heater and sample surface was increased to 56 mm for test #3 and #4. This corresponds to a calibrated surface heat flux of 40 kW/m^2, 20% lower than that used in the previous tests. FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 60 seconds in an attempt to capture some gases typical of thermal decomposition but also those typical of the period from ignition through to the burning period.

The infrared spectrum for test #3 is presented in *figure 4.30*. The correspondence of the wavelengths for the main peaks is clear, indicating the presence of those compounds identified in test #1, *Table 4.5*.

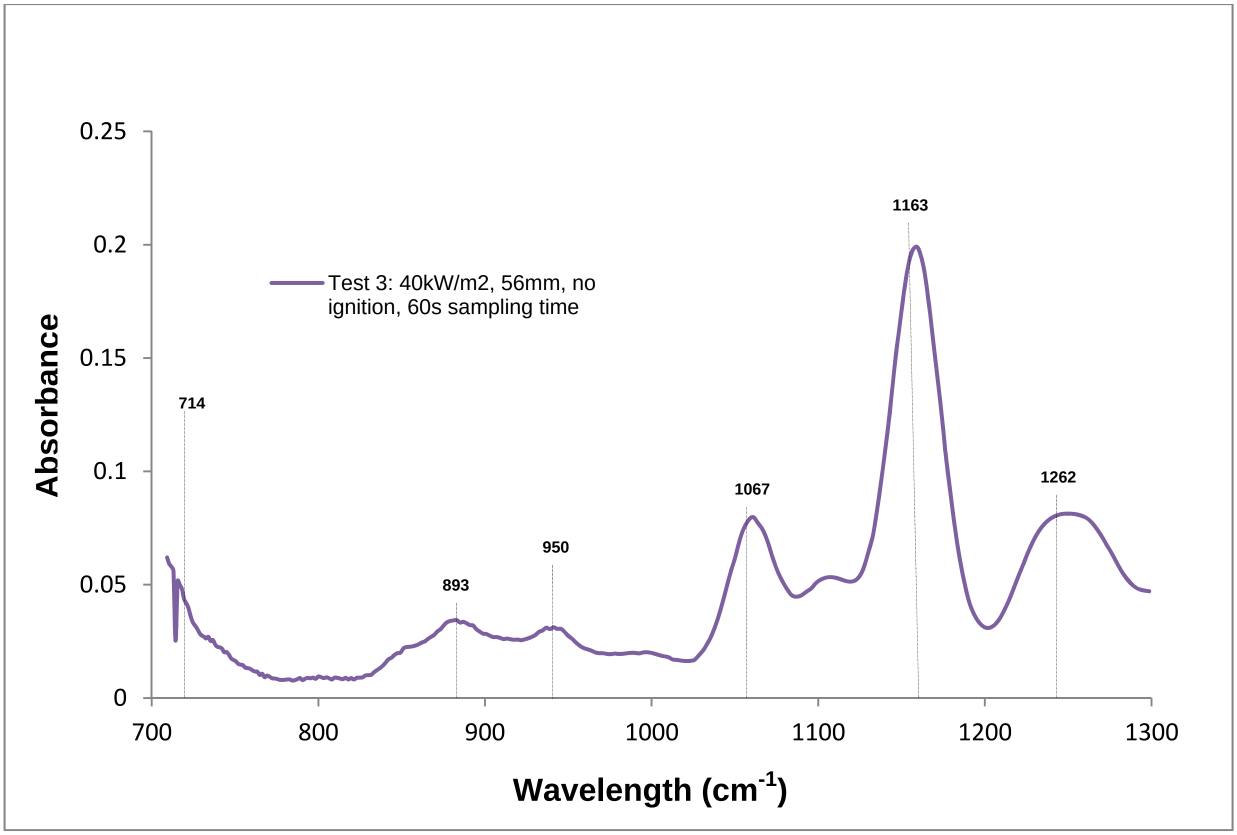

Figure 4.30 IR Spectrum for Intumescent foam test #3

As in previous tests, substantial off-gassing was observed immediately upon shutter opening. The spark igniter remained well above the surface of the foam; however ignition did not occur in this test. Therefore gases typical to burning were not captured.

4.2.4 Test #4 - Rigid Intumescent foam

For test sample #4, a heat flux of 40 kW/m^2 with the spacing between the cone heater and the intumescent foam surface of 56 mm was used. FTIR sampling was initiated as soon as the shutter on the cone heater was opened, and sampling lasted for 30 seconds in an attempt to focus on capturing gases typical of the thermal decomposition of the sample.

Figure 4.31 contains the IR spectrum for test #4 overlaid on that from test #3 already shown as f*igure 4.30*.

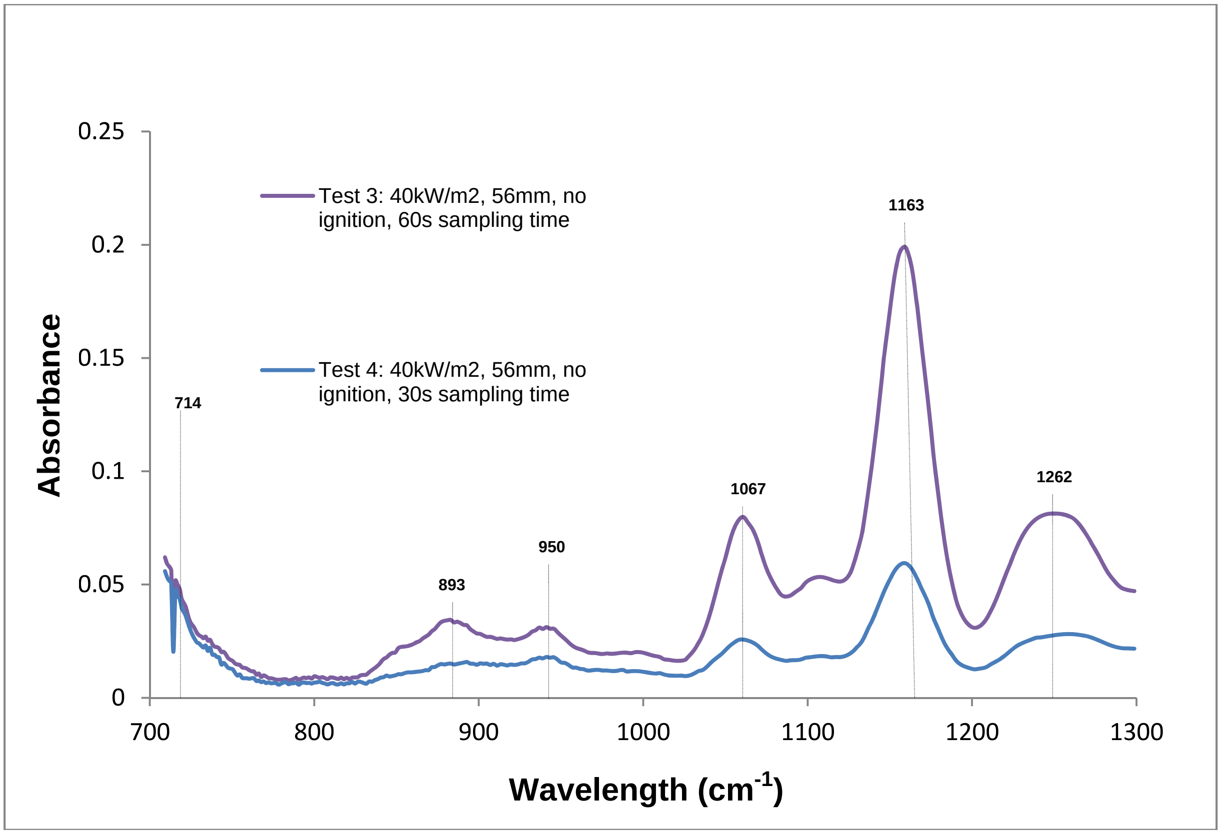

Figure 4.31 IR Spectrum for Intumescent foam tests #3 and #4

As in previous tests, substantial off-gassing was observed immediately upon shutter opening. The spark igniter remained well above the surface of the foam; however ignition did not occur in this test. Therefore, again gases typical to burning were not captured. In comparing the spectra peaks for test #3 and #4, the peaks are higher for test #3 due to the longer sample duration (60 s for test #3, compared to 30 s for test #4) which results in a sample containing higher concentrations of compounds typical of the pre-ignition phase.

Figure 4.32 contains the IR spectrum for test #1, #2, #3 and #4 overlaid on top of one another for comparison of the different sample durations and heat fluxes for all four tests.

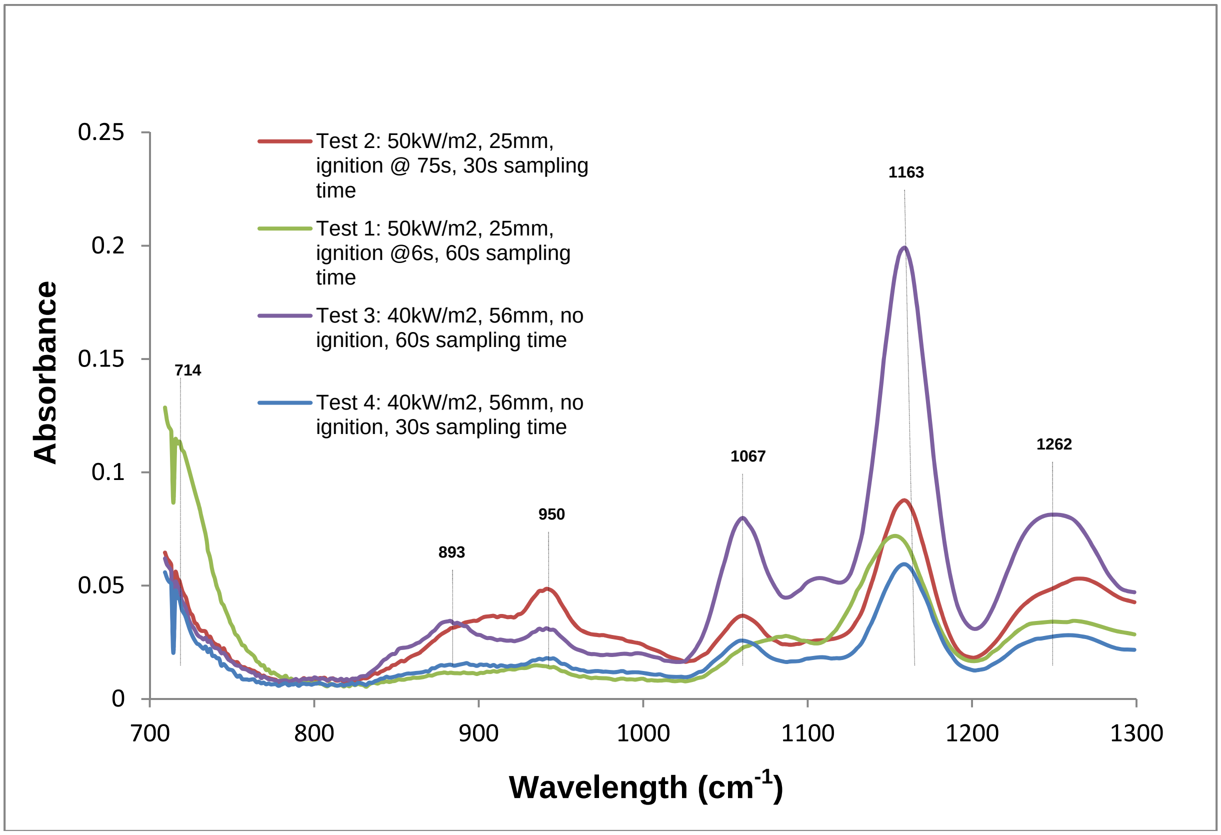

Figure 4.32 IR Spectrum for Intumescent foam tests #1, #2, #3 and #4

The spectrum for test #1 indicates the highest level of CO_2 absorption (700 cm^{-1}) since it captured samples containing representative CO_2 concentrations across all stages of the tests. This high level of CO_2 is because with carbon containing fuels (which includes the materials in this study), CO_2 is produced during combustion, and test #1 was the only test for which ignition and flaming combustion were included within the sampling window. For test #1 sampling was initiated at shutter opening, ignition started at 6 seconds and sampling lasted for 60 seconds.

In the case of test #2, ignition occurred at 75 seconds after shutter opening and the sampling window lasted only 30 seconds after shutter opening. In tests #3 and #4, ignition did not occur. Higher concentrations of thermal decomposition products were observed during off-gasing in proportion to the length of sampling window, as indicated by the highest peaks in test #3 where off-gassing was sampled for 60 seconds, at an incident heat flux of 40kW/m^2, followed by test #2 where off-gassing was sampled for 30 seconds, at an incident heat flux of 50kW/m^2.

In comparing the spectra peaks for test #2 and #4, the peaks are higher for test #2 due to the higher incident heat flux, (50kW/m^2 for test #2, compared to 40kW/m^2 for test #4) which results in higher levels of vapour generation during the pre-ignition phase. In comparing test #1 to test #4 the absorption peaks found at 1163 cm^{-1} and 1262 cm^{-1} are higher for test #1, even though the thermal decomposition gases were sampled longer for test #4 (6 seconds for test #1, compared to 30 seconds for test #4), the generation of what is believed to be Ethyl Formate ($C_3H_6O_2$) and Dimethyl Carbonate ($C_3H_6O_3$) is greater during the 6 second pre-ignition window for test #1 than during the 30 second pre-ignition window for test #4, likely due to the higher incident heat flux in test #1.

With the test procedure developed and verified using Blue Styrofoam it was shown that the FTIR-cone system could be used to examine composition of gases during thermal decomposition and burning for the more challenging problem of studying a series of rigid intumescent PU foams supplied to the lab.

Chapter 5 – Conclusions and Recommendations

An experimental test apparatus that allowed the use of Fourier Transform Infra-red (FTIR) Spectroscopy coupled with a cone calorimeter and a Servomex gas analyzer and a Novatech gas analyzer was designed and constructed. "Blue Styrofoam" foam samples were used to develop a sampling-window based gas analysis technique for the conventional cone calorimeter-FTIR apparatus that allows sampling and analysis of specific stages of thermal degredation and combustion phases. Following this, the sampling-window based approach was applied to a preliminary study of fire performance of intumescent PU foam samples. From the results of the tests and the observations made, several conclusions can be drawn,

1. With the sampling-window based approach, off gassing and other important stages of fire development can be studied using the conventional cone calorimeter coupled with a preconfigured "out of the box" lightweight portable ambient air analyzer.

2. With the apparatus and the test procedure developed, a subset of fire gases, including Styrene, Acrylonitrile, R-134A, Carbon Dioxide and Hydrogen Cyanide associated with thermal decomposition and combustion of polystyrene (blue Styrofoam) could be identified.

3. A subset of the fire gases, including 1, 4-Dioxane, Ammonia, Ethyl Formate and Dimethyl Carbonate typically associated with the thermal decomposition of intumescent foam could also be identified using the apparatus and the test procedure developed and verified using the polystyrene.

4. After some additional refinement of the methodologies established, sample off-gasses and flaming stages of fire development can be studied using the cone calorimeter-FTIR apparatus.
5. For further analysis of fire gases produced, a calibrated, lab quality FTIR, with a higher resolution than the preconfigured “out of the box” lightweight portable ambient air analyzer may be required. However the system configuration and methodology would remain the same as developed here.

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Appendix A – FTIR Spectroscopy Theory and the MIRAN SapphIR Infrared Analyzer

The analysis of chemical compounds involves identifying both the type of molecules that comprise these substances (qualitative) and the quantity of molecules present in a given sample cell (quantitative). The MIRAN SapphIR Infrared Analyzer measures concentrations of a wide range of chemical substances present under atmospheric conditions. To identify and measure various gases that enter the gas cell, a beam of infrared energy at a selected preset wavelength is sent through the sample and how much infrared energy passes through the sample (and conversely how much infrared energy gets absorbed) is measured.

All substances are made up of atoms and molecules. Molecules are made up of two or more atoms held together with chemical bonds. All molecules are constantly in motion. One type of molecular motion involves vibration of the atoms where they are bonded. These bonds can stretch or sway via molecular bending, where the bond angle changes and stretching (asymmetrical or symmetrical), where the bond length changes shown in *figures A.2, A.3 and A.4*. The degree of movement depends on the amount of energy contained in the atoms and their bonds. The bonds vibrate and sway at a particular frequency; specific wavelengths of infrared radiation can be absorbed by those bonds if that are at the same frequency.

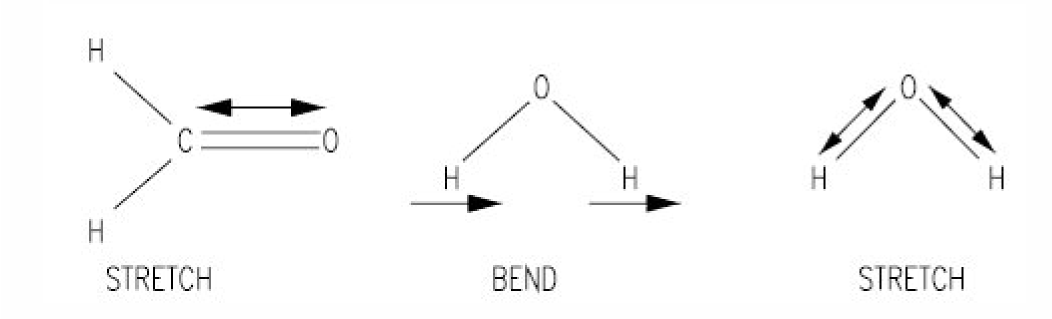

Figure A.1: Molecular bending and stretching involving either a change in bond length, stretching, or bond angle, bending

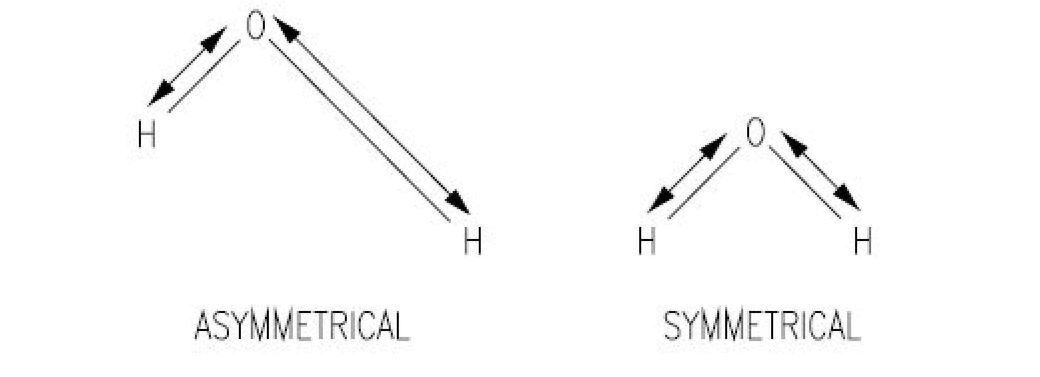

Figure A.2: Asymmetrical and Symmetrical stretching

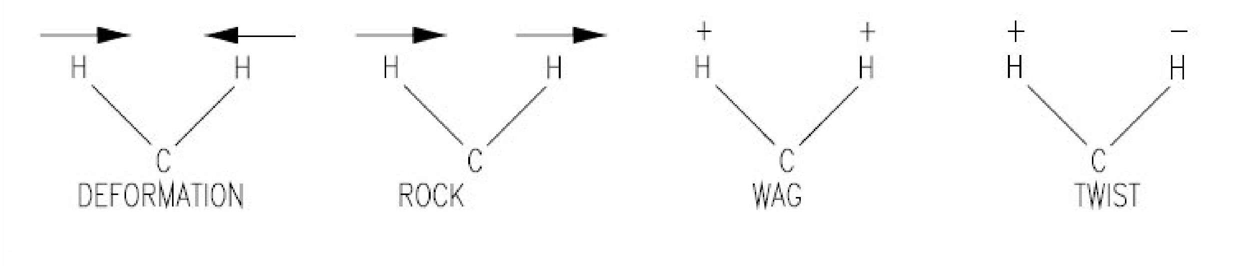

Figure A.3: Molecular bending

A spectrophotometer is an instrument used for recording variations in intensity of electromagnetic radiation at various frequencies. A diagram of the functional parts of the infrared spectrophotometer used in the SapphIRe Analyzer is shown in *figure A.5*.

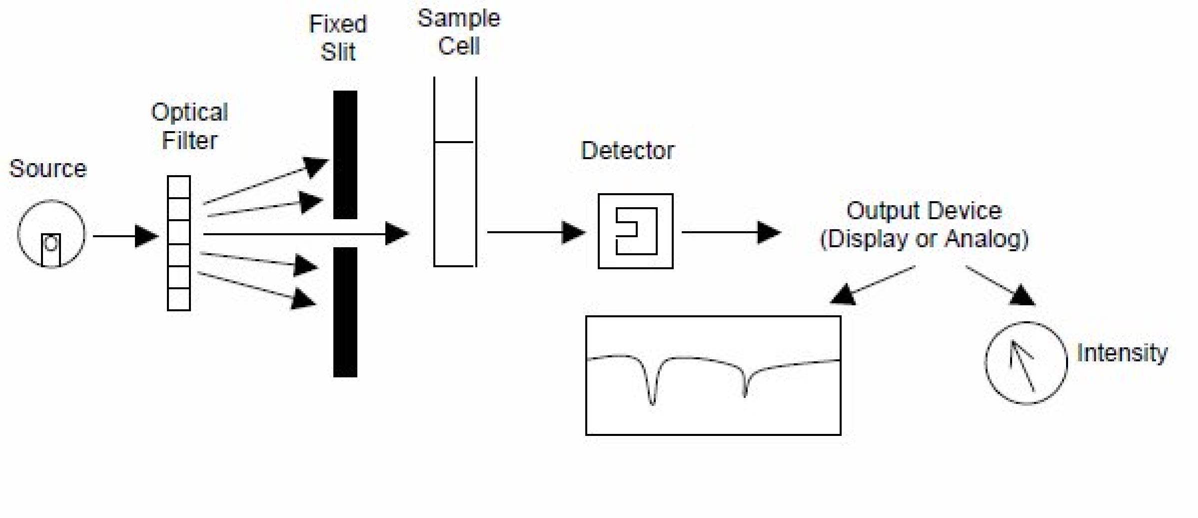

Figure A.4: SapphIRe Analyzer Spectrophotometer diagram

The source of infrared radiation is a heated wire. In the spectrophotometer, the source simultaneously emits radiation at all the infrared wavelengths. The wavelengths of radiation therefore cover nearly all the natural vibrational frequencies of organic compounds. The optical filter permits selection of a single, specific wavelength of infrared radiation to pass through the sample at a given time and continue on to reach the detector. The detector is a pyroelectric, heat-sensitive element used to measure infrared energy emerging from the sample cell.

The wavelength at which maximum energy is absorbed is called an absorption peak wavelength. The absorption peak is a narrow band of frequencies of energy that will be efficiently absorbed by the compounds in the gas sample cell. Most compounds demonstrate a number of absorption peaks dependent on the molecular bonds found in that molecule. By identifying characteristic primary and secondary absorption peaks specific to a particular compound and recording them for future reference, a library of infrared wavelength signatures (finger print) for a large number of gases can be maintained. The specific reference wavelength spectrum chosen for each compound depends on the specificity and intensity of the absorption peaks. The wavelength chosen for identification of a particular compound must be specific to that compound and distinguishable from other compounds that may be present in the gas sample cell, otherwise, some of the peaks for the main molecule will contain “shoulders” and demonstrate less intense peaks than expected. The wavelength chosen for analysis must exhibit an absorption level that is sufficiently intense to be measurable, taking into account the resolution and path length of the spectrometer and the concentration of the material. In general, higher absorption of infrared energy will occur for longer path lengths of the infrared beam and higher concentrations of a particular compound present in the gas sample cell. Intensity of absorption is typically measured in percent transmittance or in absorbance units (AU).

FTIR spectra records typically represent spectra as a plot of % transmittance versus frequency and wavelength. Transmittance is a measure of the difference between the intensity of the infrared energy entering the sample cell from the source, I_0 and the intensity of the infrared energy leaving the sample cell and reaching the detector, I. Percentage transmittance is therefore expressed as: $\%T = (I/I_0)x(100\%)$. The chart presented in *Figure A.6* is a typical spectrum that shows a measure of how much infrared energy has passed through the gas sample cell (high value) and has reached the detector (low value) depending on how much energy was absorbed by the gas.

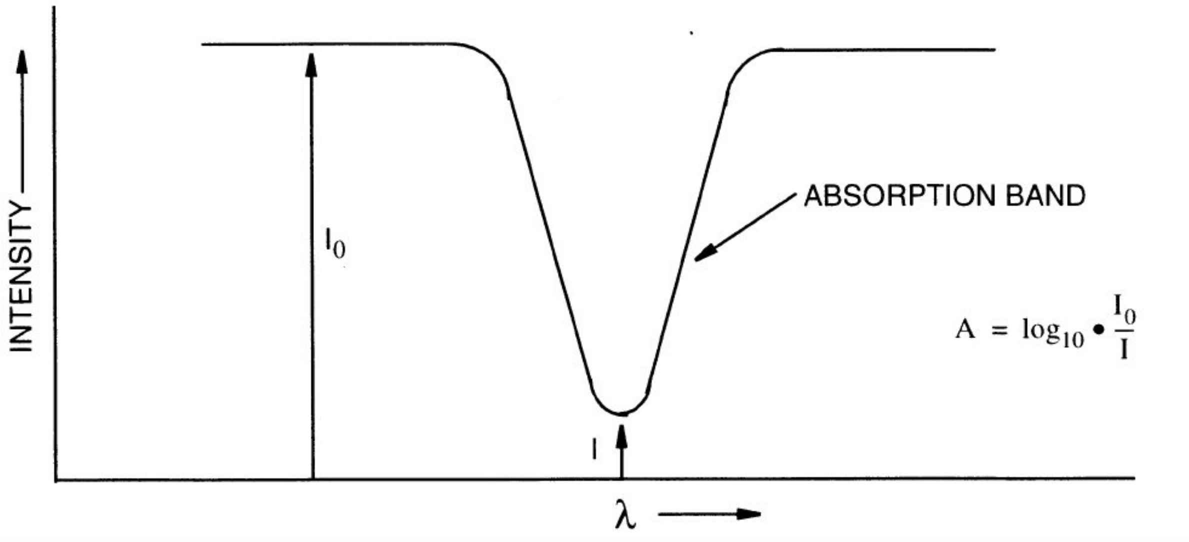

Figure A.5: Plot of Transmittance and Absorbance

The intensity of absorbance of infrared energy can also be represented in Absorbance Units (AU) expressed as a logarithm of the ratio of the intensity of infrared energy entering the cell versus infrared energy leaving the cell: $A = \log_{10}(I_0/I)$. Since percentage transmittance varies exponentially with the intensity of transmitted light, the resultant plot of absorption versus compound concentration is linear as shown in *Figure A.7*. Since both transmittance and absorbance are derived from the same ratio of intensity of infrared energy entering the cell versus infrared energy leaving the cell, we can substitute, $T = I/I_0$, and rearrange the Absorbance formula to yield, the relationship $A = \log_{10}(1/T)$. Thus absorbance, A is at 100% when the transmittance, T is 0.

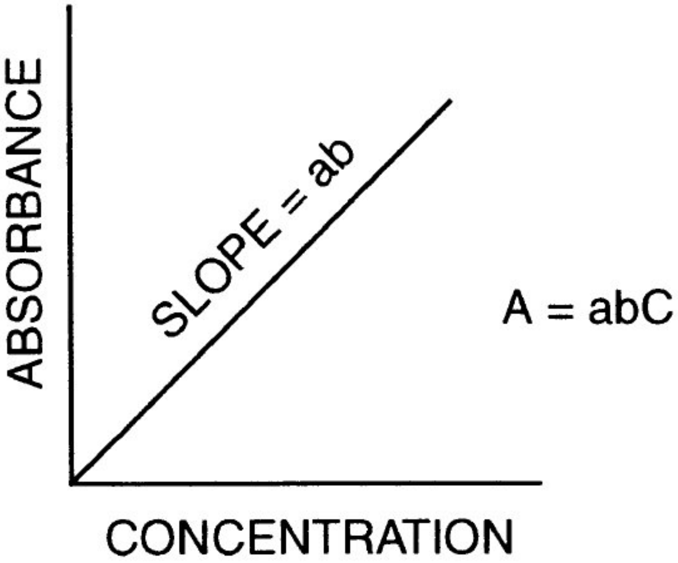

Figure A.6: Concentration versus Absorbance relationship

Appendix B – Calculations Performed by MIRAN

The Beer-Lambert Law describes the relationship between absorption and concentration. It states that the amount of energy absorbed by a molecule at a particular wavelength is directly proportional to the concentration of the sample of the material in the gas cell and to the infrared path length over which the energy travels through the sample cell. This relation is expressed as,

$$A = kCL \qquad \text{[Eqn \#B1]}$$

Where,

A – is the absorbance of the compounds in the sample gas and represents the amount of infrared energy absorbed by the molecules in the sample cell.

k – is a proportionality constant known as the absorptivity and is related to wavelengths absorbed by particular molecules (k is constant at a given wavelength).

C – is a measure of the concentration and it represents the quantity of a given gas in the sample cell.

L – is the infrared pathlength and is a measure of the distance that the infrared beam must travel in order to pass through the gas in the sample chamber.

At relatively low concentrations, the absorbance of a compound is typically directly proportional to the concentration averaged over the distance that the light travels through the sample. However at higher concentrations (for example above 20 ppm) the absorbance versus concentration relationship becomes nonlinear as shown in *figure B.1*

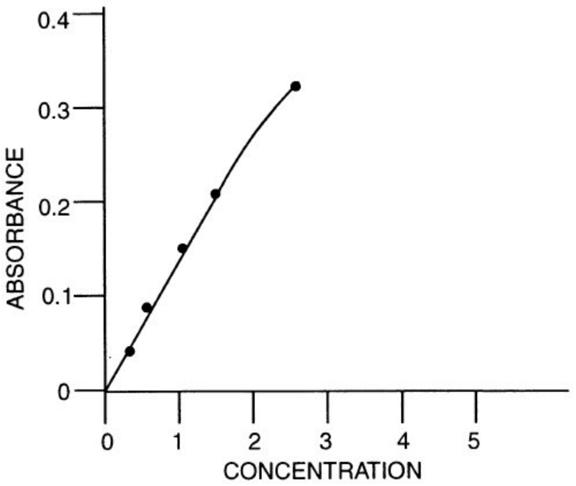

Figure B.1: *Absorbance vs Concentration relationship nonlinearity*

The nonlinearity of Beer-Lambert's law at higher concentrations is thought to be due to the interaction of gas molecules with one another in the gas sample cell. Collisions between the molecules as well as polymerization are the two phenomena thought to account for deviations from linearity [48].

The SapphIRE Analyzer is programmed to calculate concentration based on the Beer-Lambert equation with corrections for high concentrations of gases which compensate for the nonlinear relationship under these conditions. It accomplishes this by including a quadratic term in the formula that it uses for deriving the concentration levels from the absorbance values measured. For a number of gases the SapphIRE Analyzer has also been reprogrammed to resolve high and low concentration ranges.

In order to accurately calculate the concentration of the gas species, the absorbance value is fitted into the following quadratic equation:

$$C = QA^2 + PA + R \qquad \text{[Eqn \#B2]}$$

Where,

C – is the concentration of the gas species.

Q – is the Quadratic parameter

P – is the Linear parameter

R – is the Y –intercept (typically zero or very close to zero)

A – is the absorbance.

In order to improve the accuracy of the concentration measured there are between one and three calibration ranges; one for low concentrations where the concentration versus absorbance is relatively linear, one for higher concentrations where the concentration versus absorbance is less linear and one (optional) for even higher concentrations where the concentration versus absorbance is the least linear. Each calibration range will have its own set of calibration curve constants (P, Q values). The calibration constants will also depend on the particular gas being analyzed.

Given the nonlinearity of Beer-Lambert's relationship for high concentrations of gases, it is important to limit analytical work to the 0 – 1 AU range in order to achieve the highest degree of accuracy using the SapphIRE Analyser. The ability to alter the path length or the effective distance that the infrared radiation travels through the sample cell provides a convenient method for keeping absorbance values within these recommended limits. The concentrations of gas species identified by the SapphIRE that are expected to be in high concentrations may not be reliable (for example CO and CO_2 in the case of fire gas analysis) and it is recommended that other methods/equipment be employed for the quantification of those gases.

Appendix C – Experimental Procedures

The Miran 205B Series SapphIRe Portable Ambient Air Analyzer was configured and calibrated to collect samples from the cone calorimeter. The operating sequence is as follows,

PRELIMINARY SET-UP

Check Filters:

1. Visually inspect the filters. The condition of the filter cartridge can be observed through the filter casing, and the primary cylindrical tube filter turns black from soot accumulation on the inside of the filter.

2. Turn on vacuum/pressure pump. If the flow rate of the sample gas decreases below around 0.475 cfm, as indicated by the position of the metal float relative to the red line on the sliding markers of the flow meter installed downstream of the vacuum pump, it is time to change the cylindrical tube filter and check the disk filters. The filters are located on the sampling line from the cone calorimeter and are wall mounted above the gas analyzer equipment.

3. Change the filter medium by disconnecting the filter cartridge from the sampling line and unscrewing the cap. Remove the filter medium and replace with new medium. Screw cap back on unit and reconnect to sampling line. Make sure the filter is seating tightly on the bevelled housing and the O-rings are sufficiently lubricated with white lithium grease.

4. Turn on the vacuum/pressure pump and confirm that the 0.475 cfm reading on the flow meter has been achieved as a result of filter replacement. If the flow rate is still low after the filters have been change it may be a result of either loose/leaking connections on the sampling line or problems with the vacuum pump.

5. The filters must be changed as necessary: either when the flow rate of the sample gas drops or the filters are black with soot. New filter medium is stored in the cupboards below the window in the lab.

Check Drierite:

6. **WARNING:** RUNNING THE PUMP WITH DEPLETED DRIERITE WILL CONTAMINATE THE GAS CELL AND ANALYZER SENSORS. **NEVER RUN THE SAMPLING PUMP WITHOUT FRESH DRIERITE.**
7. Before handling Drierite, review the MSDS for this material.
8. Blue coloured Drierite is fresh and able to absorb moisture from the gas flow, whereas pink/purple coloured Drierite has absorbed all the moisture it can, and must be recharged before going further.
9. Locate the columns of Drierite on the gas analyser upstream of the sampling port. There should be more than half of blue coloured Drierite remaining in the top portion of the column.
10. Change the Drierite as necessary. Use the fume hood in the lab. Pour used Drierite into the jar marked ‘Needs Regenerating’. Fresh Drierite is in a ‘new’ jar or in the jar marked ‘Regenerated’.
11. When Drierite turns pink/purple in colour, regenerate it in a layer one or two granules thick in an oven for 1 hour at 210^{o} C. Pour the re-conditioned Drierite into

the jar labelled ‘Regenerated – Needs Sifting’. Sift the re-conditioned Drierite in small batches and then pour into the jar marked ‘Regenerated’. The colour indicator of Drierite will fade after baking it several times, so layer some new Drierite in each column downstream of the old Drierite to provide ongoing indication of moisture removal. Eventually, regenerated Drierite will become white, losing its color indicating ability, and ultimately its ability to absorb moisture. At this point is should be discarded.

SYSTEM START UP

Operator controls and display are located on the front panel of the gas analyzer.

12. On the gas analyser unit turn ON the ON/OFF power button.
13. Allow the gas analyzer unit at least five minutes to warm-up prior to configuration.
14. The gas analyzer includes an internal pump that can be used to pull sample gas into the gas cell. However, this internal pump is of insufficient size for this application and should be disabled. To disable the internal sample pump press the CONTROL key to set various analyzer features on/off. From the control menu confirm that the pump is disabled. The control menu should read, 2=Pump Enable. If not press 2 to disable the pump. Press Esc to Exit the control menu, and return to the main screen.

ZERO GAS CALIBRATION

For IR Spectroscopy, a zero gas calibration is performed using Nitrogen. With Nitrogen gas metered into the gas cell, the device is calibrated for zero ppm of carbon dioxide and zero ppm of carbon monoxide.

15. Disconnect the gas sampling line at the inlet sampling port of the gas analyzer and connect the Nitrogen gas line directly to the inlet sampling port.
16. Ensure the outlet port of the gas analyzer is open (uncapped).
17. Meter in gas from the Nitrogen tank. Adjust the flow rate on the tank so that the flow meter reads 0.475 CFM to match the flow rate that will be in the system when in sampling mode.

Zero for Carbon Dioxide:

From the main menu on the control, display press 2=Change gas. Select from the list CO2abbs (14.0). You may have to scroll the pages of the library with the arrow keys. In the standard library, there is more than one screen of choices, which can be selected by pressing the arrow keys or pressing the ENTER key to use the search mode and follow the screen prompts. Select the gas using the number keys or MENU and SELECT. Upon selection, the display responds “ACCEPTED” and returns to the Main Menu, showing the selected application in the left window.

18. From the main menu press 1=Analyze/Start.
19. To establish a new zero for carbon dioxide press 1=New Zero.
20. The control panel then displays the Install Chemical Filter screen, Press ENTER.
21. While the cell fills with zero air, the Zero Purge screen indicates the time remaining.
22. Wait while the zero measurement is taken. The screen displays the percent done. Once complete, the screen will display “Save this zero?”, press ENTER to save.
23. The instrument then displays the Install Particulate Filter screen, press ENTER.

24. Wait for the sample to fill the cell. The filling progress is shown on the display. Press ENTER to shortcut this procedure. If the purge is skipped, wait about 10 seconds for the cell to reach equilibrium. Press “1” to start logging as soon as the sample fill is complete. When the purge is complete, the display changes to the Analysis menu. The bands above and below the left portion of the display indicate that the analyzer is actively making measurements.
25. Wait while the unit analyzes the Nitrogen gas sample and confirm that the log values for CO2abb(14.0) are all around 0 ppm. Write the sample values for CO2abs (14.0) in the FTIR lab book including the date and time that the zero gas confirmation was conducted for this gas.

Zero for Carbon Monoxide:

26. From the main menu on the control display press 2=Change gas. Select from the list CO. Upon selection, the display responds “ACCEPTED” and returns to the Main Menu, showing the selected application in the left window.
27. From the main menu press 1=Analyze/Start.
28. To establish a new zero for carbon dioxide press 1=New Zero.
29. The control panel then displays the Install Chemical Filter screen, Press ENTER.
30. While the cell fills with zero air, the Zero Purge screen indicates the time remaining. Press ENTER to shortcut the purge.
31. Wait while the zero measurement is taken. The screen displays the percent done. Once complete the screen will display “Save this zero?”, press ENTER to save.
32. The instrument then displays the Install Particulate Filter screen, press ENTER.

33. Wait for the sample to fill the cell. Press ENTER to shortcut this procedure. Press “1” to start logging as soon as the sample fill is complete.
34. Wait to confirm that the log values for CO are all around 0 ppm. Write the sample values for CO in the FTIR lab book including the date and time that the zero gas confirmation was conducted for this gas.

SITE SET-UP

Before any data can be logged, a site must be created through the keypad of the SapphIRe and the logging parameters must be configured. This site holds all of the data that has been logged until a new site is created or the existing is site is erased.

35. From the main menu, select #3, Site Info, to access the Site Menu Display.
36. From the site menu - select # 1 (new site).
37. Enter the name of the site through the keypad. The site name may be up to twelve characters long (it is recommend to include the test date). Press **ENTER**.
38. The new site name is displayed on the left and the site menu is returned. Press **ESC** to return to the main menu.

LOGGING PARAMETERS

The Log function saves measurement values for later downloading to a PC or printer.

39. To change the logging characteristics, press **1** (Logging) from the Analysis Setup Menu.

40. To set the Log Mode, press **1** (Log mode) from the Log Menu. Then press 2 to specify a **single sample** per logging trigger . The display responds "-ACCEPTED-." Single sample mode is used so that once the desired sample window is collected in the gas cell and the scanning/logging is complete, the device ends the sampling cycle at which time the user confirms that the sample is valid.
41. To enter Log Interval, press **2** (Log interval) from the Log Menu.
42. Press 2 (1 cycle interval). The display now reads "-ACCEPTED-." This will return you to the analysis set up menu.

COMPENSATIONS

43. From the analysis set up menu press 3 to access the Compensations Menu. All compensations should be turned off for this experimental set-up. Press **1** to toggle Temperature compensation, 2 for Pressure, 3 for Reference, and 4 for Humidity. When finished, press **ENTER** to accept these selections. The display responds "-ACCEPTED-."
44. Press **ESC** to return to the main menu.

SPECTRUM SCAN PROCEEDURE

Prior to setting up the spectrum scan procedure it is important to determine the expected fire growth curve for the sample to be tested. From the curve, a time interval for gas sampling is established for the test. Depending on when the interval is planned a stop watch may be required to perform the test (i.e. it is not a visually confirmable fire event such as the start of ignition or the opening of the shutters on the cone calorimeter).

45. From the main menu on the control display press 2=Change gas. Select from the list Full Scan-L. You may have to scroll the pages of the library with the arrow keys. In the standard library, there is more than one screen of choices, which can be selected by pressing the arrow keys or pressing the ENTER key to use the search mode and follow the screen prompts. Select the gas using the number keys or MENU and SELECT. Upon selection, the display responds "ACCEPTED" and returns to the Main Menu, showing the selected application in the left window.
46. Wait for the start of the fire event/interval of interest (ex. at shutter opening) from the main menu press 1=Analyze/Start and then 1=Accept without re-zeroing and turn on the vacuum/pressure pump from the power bar switch.
47. The display screen with count down while the sample cell fills with gas.
48. Once the desired sample window duration has lapsed turn off the vacuum/pressure pump from the power bar and place the orange cap on the end of the exhaust port from the unit. Scanning and logging should start immediately following the countdown. This will be indicated on the display screen.
49. The unit display will scan through 1.859 to 14.100 microns.
50. Once the scan and logging is complete the test is complete and the unit is ready to transfer data to the PC.

DATA TRANSFER

51. From the analyzer's Main Menu, press **5** to access the Report/Data Menu.
52. From the Report/Data Menu, press **1** to select site.

53. Scroll down for the available sites and select the one that was recently created for this test (see section 4 of this SOP) by pressing **ENTER**. This will return you to the Report/Data Menu.
54. From the Report/Data Menu, press **3** to access the Data Transfer Menu.
55. Connect the analyzer to the computer with a serial communication cable. Verify that the baud rate on the analyzer and that on the computer match. A baud rate of 19200 is considered standard.
56. From the Data Transfer Menu, press **3** to send data to the computer.
57. On the computer (Smokebox) open the ThermoConnect software by double clicking on the desktop icon.
58. In the top left corner of ThermoConnect interface select receive data from device. The data will transfer. Progress will be indicated in the bottom left bar in the grey section.
59. Once the data is transferred windows will prompt the user to saVe the file. Assign a file name and hit save.
60. To access the data open the ThermoMatch software from the desktop icon.
61. In the top left corner of ThermoMatch interface open the newly saved scan file.