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Fourier Transform Infrared Analysis of Combustion Gases

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Final Report

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16. Abstract

The Federal Aviation Administration (FAA) has developed a unique extractive Fourier Transform Infrared (FTIR) system to analyze rapidly changing moist fire gas concentrations as a function of time. The system was designed to eliminate numerous errors generated by state-of-the-art FTIR systems for fire gas analysis. In addition, the path length, cell volume, sample flow rate, and system temperature were optimized to provide a rapid response and a sufficient dynamic range to detect gas concentrations generated in the cone calorimeter. A nonlinear classical least squares method was developed to analyze the FTIR data and generate the concentration histories and confidence limits of the 16 fire gases. Results of the technique are presented for flaming and nonflaming combustion tests of a mix of six common plastics.

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EXECUTIVE SUMMARY

The objective of this work was to develop an infrared spectroscopy sampling system and method to quantify the evolution of combustion gases in flaming and nonflaming combustion. This system was designed to support the unique requirements of the Federal Aviation Administration's cargo fire detection project and toxicity evaluations of combustion gases generated from burning materials. Both projects require an analytical system with a fast response and high accuracy.

The cargo fire protection project requires concentration-time profiles of many gases produced in the early stages of cargo compartment fire development. The patterns of response will aid in the selection and development of improved cargo smoke and fire detectors. The ultimate goals are to shorten detection times, improve reliability and sensitivity of detectors, and to discriminate between real and spurious signals for detection of cargo compartment fires.

Toxicity monitoring requires quantitative evaluation of a wide variety of toxic gases over a wide concentration range, operational simplicity, and an estimate of the reliability of each gas measurement as a function of time. These requirements ensure a valid toxicity assessment for each material.

The analytical Fourier Transform Infrared (FTIR) gas monitoring system was demonstrated for flaming and nonflaming conditions for a mixture containing six common plastics. Excellent agreement was obtained for replicate tests in both the flaming and nonflaming mode. The accuracy was confirmed by reasonable agreement between the CO and CO_2 levels determined by the FTIR method and the in-line nondispersive infrared (NDIR) gas analyzers. The classical least squares errors and calibration errors were presented for both the flaming and nonflaming tests for 16 gases.

INTRODUCTION

The Federal Aviation Administration's (FAA) Fire Safety Section has a need to obtain the concentration-time profiles of a wide variety of gases produced in the early stages of cargo compartment fire development. The patterns of response will aid in the selection and development of improved cargo smoke and fire detectors [1-3]. The ultimate goals are to shorten detection times, improve reliability and sensitivity of detectors, and to discriminate between real and spurious signals for detection of cargo compartment fires.

Fourier Transform Infrared Spectroscopy (FTIR) has been shown to be a useful tool in characterizing multiple fire gas concentrations [4-12]. However, numerous errors are generated in state-of-the-art FTIR systems [4, 10]. An extractive FTIR sampling and analytical system was designed to minimize these errors.

The sampling system is heated to approximately 170°C to prevent absorption losses of water-soluble gases on moist surfaces. The sample is prewarmed prior to contact with the filter to prevent condensation on the filter medium. The sampling system is designed to provide a 6 second 90-percent response time from baseline (t_{90}) for cone calorimeter sampling. This system maintains a constant flow through the sample cell as the filter starts to clog (as the filter backpressure increases). The sampling system contains a calibration gas generation system for chemicals that are liquid at room temperature.

A piecewise linear curvilinear fit was used to generate calibration curves for each gas. A curvilinear fit is needed because the Mercury Cadmium Telluride (MCT) detector exhibits a nonlinear response for many of the gases to be measured in this study.

A specialized Classical Least Squares (CLS) technique was selected. Spectral shapes can change markedly with increasing concentrations of a given gas. This technique accounts for the change of spectral shapes of each calibration gas with concentration. This enables accurate quantification of each gas in its selected analysis region when there is a common absorbance with other gases defined in the method. This works well, in theory, for complex mixtures of gases over a wide range of concentrations. Many (CLS) routines are based on the shape of one spectrum per gas. This particular CLS technique is based on the best fitting calibration spectrum for each gas in the method.

Errors, calculated from the residuals for that gas, are provided alongside gas concentrations as a function of time. This expedites the process of developing a valid FTIR method of analysis for a mix of overlapping fire gas spectra. This also enables the analyst to determine the validity of fire gas measurements for each gas, method, and fire test.

The Analytical FTIR system was demonstrated under flaming and nonflaming conditions for a mix of six common plastics. Excellent agreement was obtained for replicate tests in both the flaming and nonflaming mode. The accuracy was confirmed by reasonable agreement between the CO and CO_2 levels determined by the FTIR method and the nondispersive infrared (NDIR) gas analyzers.

EXPERIMENTAL

MATERIALS.

A smoke generation source representative of the composition of combustible materials in passenger luggage articles was formulated to provide a reproducible and realistic fire signature in nonflaming and flaming combustion for use in developing an FAA cargo detection standard [13]. The specimen consists of thermoplastic polymer beads commonly found in consumer products contained in luggage articles [14]: polyamide (nylon 6,6), polyethylene (PE), polyvinylchloride (PVC), polystyrene (PS), thermoplastic urethane (TPU), and polybutyleneterephthalate (PBT). The polymers were all available commercially in the form of extruded pellets (3-6 mm nominal dimensions). Table 1 lists the plastics and their proportions in the specimen.

TABLE 1. COMPOSITION OF A MIXED RESIN SPECIMEN

Component Material	Tradename	Parts by Weight
Polyamide (nylon 66)	Dupont Zytal 101	1
Polyethylene (HDPE)	Dow 08454	1
Polystyrene (PS)	HiVal 5308	1
Polyvinylchloride, rigid (PVC)	Geon 8700	2
Thermoplastic polyurethane (TPU)	Dow 101	1
Polybutyleneterephthalate (PBT)	DuPont Crastin 600	1

The smoldering test specimen consists of two mixed resin plaques, which are fabricated separately, and then thermally consolidated under heat and pressure to form a porous sandwich structure containing the embedded resistance heating element. Figure 1 shows the specimen and fabrication process and also shows the frictionless electrical connection to the variable power supply, preventing spurious forces from affecting the mass loss rate measurements during smoldering and flaming combustion.

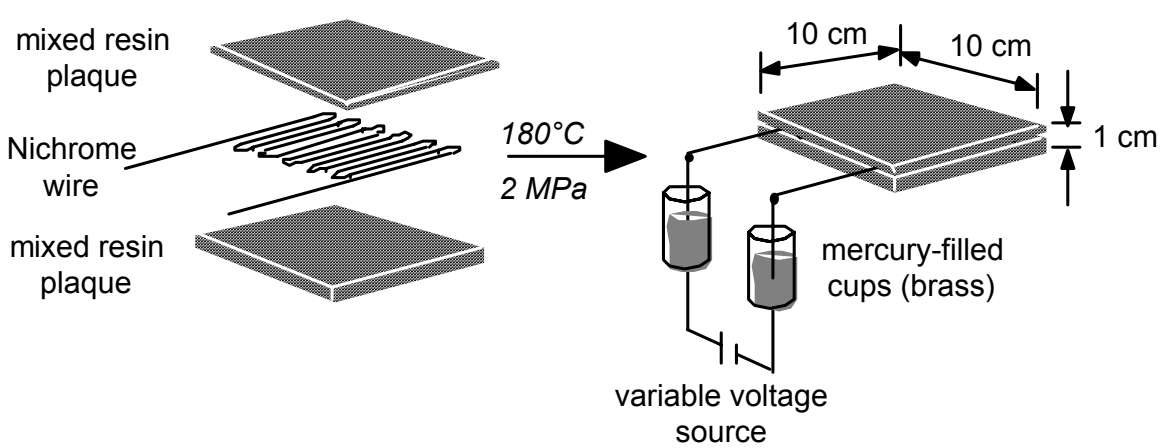

FIGURE 1. SMOLDERING SPECIMEN FABRICATION

METHODS.

FIRE CALORIMETRY METHOD. An oxygen consumption fire calorimeter (Atlas Electric Devices) was used to measure the release rate of heat and visible smoke, as well as mass loss [15]. The test specimen is 100 mm square. It can be subjected to external heat fluxes up to 100kW/m^2. A spark igniter can be used to ignite the evolved gases. Heat release rate due to gas phase combustion is determined by measuring oxygen depletion of the air drawn past the burning specimen into an exhaust duct where a laser system measures visible light obscuration of the smoke. Production of carbon dioxide, carbon monoxide, and specimen mass loss are measured during the test, allowing calculation of the effective (mass based) quantities during the test. The test procedure consisted of placing the mixed plastic specimen in a close fitting 0.76-mm-thick stainless steel pan set in a 1.27-cm-thick calcium silicate board sample holder. Insulated copper lead wires connect the heater wire to the mercury filled cups, which are, in turn, connected to a variable ac voltage supply (VARIAC), which is set at no load to 42 Vac. One minute of baseline data was recorded before the electrical heater circuit was energized. Heating was maintained to the end of the test. A nitrogen FTIR background was obtained prior to each combustion test. Gas concentrations are reported relative to the average concentrations obtained during the first 40 seconds of baseline data.

Nonflaming Tests. Nonflaming tests were conducted on the mixed resin test specimen without the external radiant (cone) heater or the spark igniter in order to generate smoke under simulated smoldering conditions. The embedded Nichrome™ wire heater provided sufficient internal heat generation at 483 watts to thermally decompose the test specimen into volatile fuel gases. Flaming combustion would only occur if a spark or flame ignited the fuel gases.

Flaming Combustion Tests. Flaming combustion of the mixed plastic test specimen was initiated instantly and reproducibly by using an accelerant (2 milliliters of heptane) and a spark igniter. The test procedure was to pour the heptane on the test specimen, acquire 60 seconds of baseline data, and then activate the 483-watt internal heater and spark igniter to initiate immediate flaming combustion.

INFRARED SPECTROSCOPY OF COMBUSTION GASES.

Extractive Fourier Transform Infrared Combustion Gas Sampling System. Figure 2 is a schematic of the sampling system. The 0.064-cm (1/4-inch) heated, Teflon-lined stainless steel tubing draws from the ring sampler of the cone calorimeter. The entire sampling system from the probe to a point a few inches downstream of the sample cell is heated to approximately 170°C. The fire gas sample is continuously drawn through the heated sample line at a flow rate of approximately 11 liters per minute and passes through a series of filters into the bellows pump head. A needle valve at the inlet to the analyzer is set to provide a flow rate of 5.0 liters per minute through the sample cell. A cooling coil of 0.064-cm (1/4-inch) copper tubing and a high-capacity filter protect the flow meter downstream of the sample cell. A back-pressure regulator maintains the inlet pressure to the analyzer at a constant pressure, enabling a constant flow rate through the 160-ml sample cell. This ensures a constant system response time throughout a fire test, and from test to test, as particulates buildup in the filters. The back-pressure regulator output bypasses the analyzer. A high system flow rate of 11 liters per minute results in a short

sample line delay and a fast system response. A vacuum/pressure gauge monitors the filter for clogging and serves as a system check to monitor the filter housing for leaks after filter replacement. Valves can be set to pressurize the filter with nitrogen to check for leaks.

The coarse filter is composed of layers of fine glass wool and 3-mm glass beads. The second filter houses a 7.5-cm glass fiber filter with a porosity of 1 micron. Glass filters have been shown to have a low retention for hydrochloric acid (HCl) [4]. This glass filter material is not recommended for high frequency (HF) analysis. Tetrafluoroethylene (TFE) membrane filters can be used in place of the second filter when HF is expected as a decomposition product.

The sample line is cleaned periodically by backflushing it with 150-psi house air. The line is checked for clearance by blowing a 4-mm crumpled paper ball through the line.

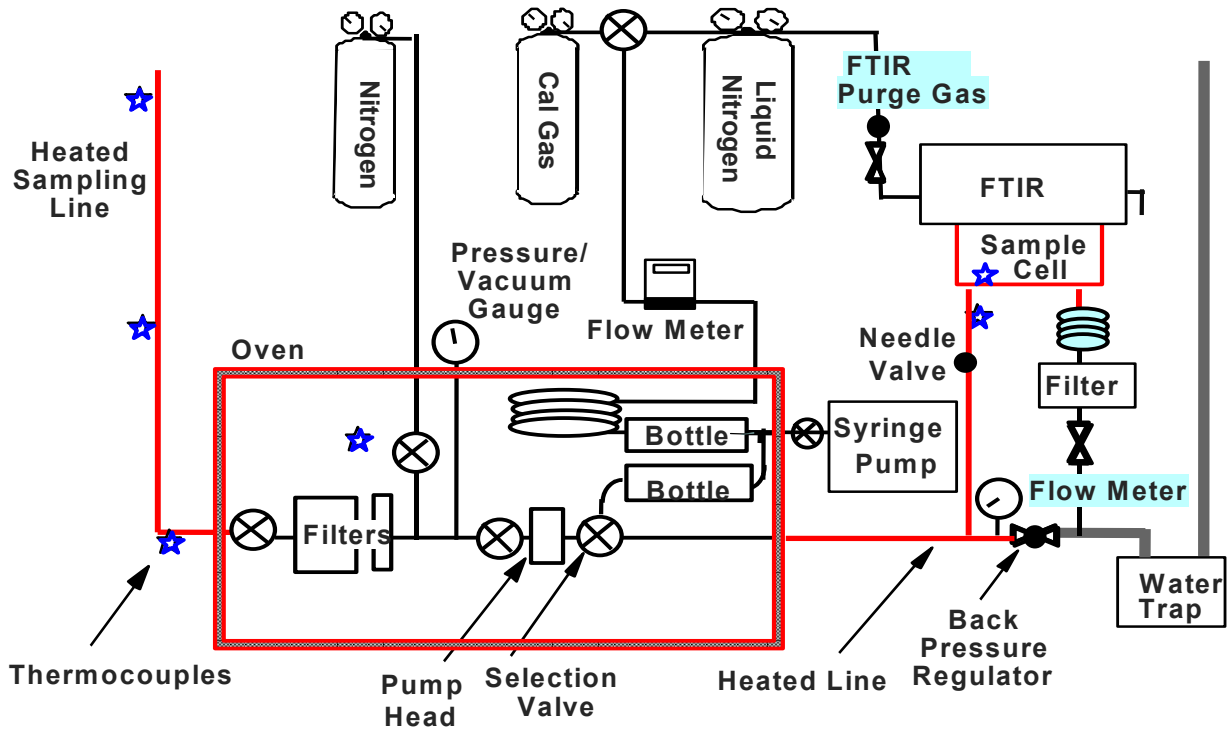

FIGURE 2. FTIR SAMPLING SYSTEM

A 3-way valve, downstream of the sample pump, can select either a calibration gas or a combustion gas input to the sample cell. The calibration gas flows from the gas cylinder through a heated 4-m Teflon-lined 0.64-cm (1/4-inch) stainless steel coil and two heated 150-milliliter Teflon-lined stainless steel expansion and mixing bottles. This enables preheating the calibration gas for analysis. It also serves to preheat the diluent gas stream allowing continuous generation of calibration gases for chemicals that are liquid at room temperature. A pure liquid is introduced into the second expansion bottle by a programmable syringe pump. The syringe is connected to the mixing bottle by an 8 cm length of narrow bore polyimide tubing. The diluent nitrogen gas flow rate is monitored by a mass flow meter. The sampling system also allows accurate metering of water into the calibration gas flow to check a method for accurate prediction of gas concentrations measured using spectral regions where water absorbs.

Note that the calibration gas and the sample stream are preheated through 4 meters of Teflon-lined stainless steel tubing prior to coming in contact with the first filter. This prevents condensation of water onto the filter medium and the resulting line delay effects for water soluble gases such as HCl. Line delays are seen with the state-of-the-art extractive heated sampling systems for FTIR smoke gas analysis of water soluble gases [4]. Nonheated lines produce major line delays [16].

There are four separate heating circuits in the sampling system, controlled at 170°C. The temperature circuits are the sample line leading to the oven, the tubing leading from the oven to the analyzer, and the gas cell. All tubing in the sampling system is either Teflon-lined 316 stainless steel or perfluoroalkoxy (PFA) Teflon. All valves and connectors are 316 stainless steel. The tubing diameter is 0.64 cm (1/4 inch) with the exception of the point where the analyzer output meets the bypass flow to the end of the exhaust line. The exhaust line diameter is 1.27 cm (1/2 inch). All valves in the heated zone have spring-loaded TFE seals and are rated for 230°C.

Figures 3 and 4 show the FTIR sampling system alongside the cone calorimeter. Figure 5 shows the contents of the oven.

FIGURE 3. FTIR SAMPLING SYSTEM ALONGSIDE THE CONE CALORIMETER

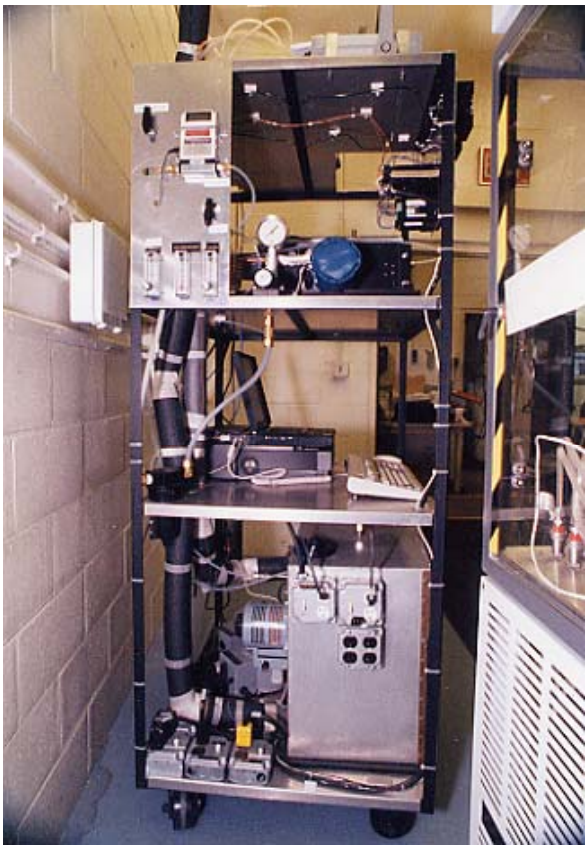

FIGURE 4. FTIR SAMPLING SYSTEM ALONGSIDE THE CONE CALORIMETER—SIDE VIEW

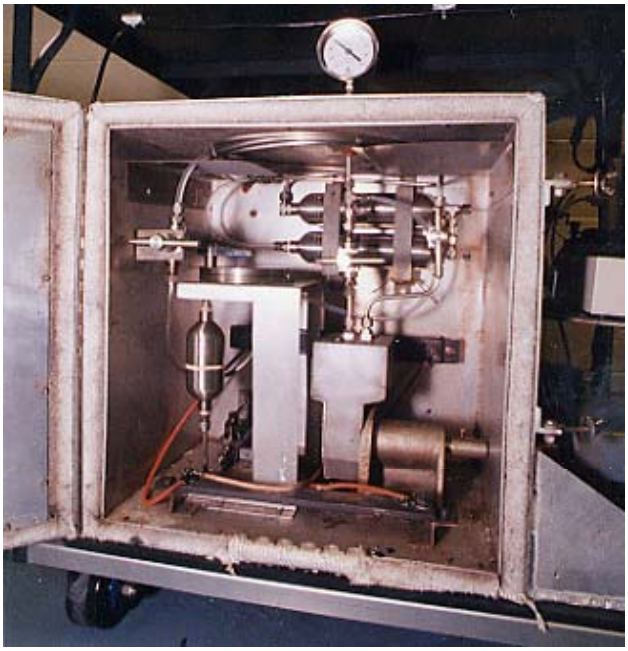

FIGURE 5. FTIR SAMPLING SYSTEM—OVEN

Spectrometer and Data Acquisition. A Midac Model I2001F FTIR Spectrometer* with a 4-meter cell was used for all tests. The sample cell is nickel, the mirrors are coated with gold, and the windows are zinc selenide (ZnSe). The cell volume is approximately 160 ml. The interferometer, beamsplitter, and windows are constructed of ZnSe with a germanium coating for moisture protection. The detector is a liquid nitrogen-cooled MCT detector. All interface optics are gold coated for high light throughput and corrosion resistance. The sample cell has a horizontal orientation to minimize buildup of soot on the cell mirrors.

All tests were conducted in an extractive mode at 0.5-cm^{-1} resolution, with five scans averaged every 8.5 seconds. The cell's temperature and pressure were monitored and used to correct gas concentration and error data. The 170°C, 0.5-cm^{-1} calibration spectra were supplied by the FTIR manufacturer for all gases except water. A 40-meter temperature-controlled line was used to heat and introduce the calibration gases into the cell. The 170°C, 0.5-cm^{-1} water calibration spectra were prepared in-house at the William J. Hughes Technical Center, using a syringe calibration system, built into the sampling system, with a flow rate of 1-2 lpm through the cell.

Data was collected, analyzed, and plotted using commercial software: Midac's Autoquant software Version 3.1, Nicolet's OMNIC E.S.P. 5.1, and Microsoft's Excel 97. Spectral bands for 16 gases were selected to have minimal common absorbance. Another requirement for spectral band selection is that it must have a low absorbance, so that the calibration is linear over a wide concentration range. Broad nonoverlapping bands were selected when possible.

Method of Analysis. The method defines the 16 gases to be analyzed and identifies the spectral bands for applying the CLS method to each gas within the 650 cm^{-1} to 4500 cm^{-1} spectral region. Different spectral bands were used for CO_2, C_2H_2, and water at some concentration ranges to enable quantification of the higher concentration ranges in spectral regions that exhibit the best linearity.

Spectra are selected for each gas to define each piecewise linear calibration curve. The minimum number of absorbance spectra needed to obtain accurate calibration curves are selected. All calibration spectra and test spectra were obtained at a unit gain. Triangular apodization was used throughout. A Mertz phase correct and a resolution of 0.5 cm^{-1} was used. The method creates a spreadsheet with the time profiles of the concentration and error (residuals) data for the 16 gases defined in the method. A macro was written to interpolate between the FTIR data to obtain a 1-Hz output. Another macro combines fire calorimeter and FTIR data into one spreadsheet. The method includes the following gases: CO, CO_2, $COCl_2$ (phosgene), COF_2, HBr, HCl, HCN, HF, NO, NO_2, SO_2, CH_4 (methane), C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), and H_2O. The spectra for these gases are shown in figures 6 and 7.

* Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure. Such identification does not imply that the material or equipment is the best available for the purpose or endorsement by the FAA.

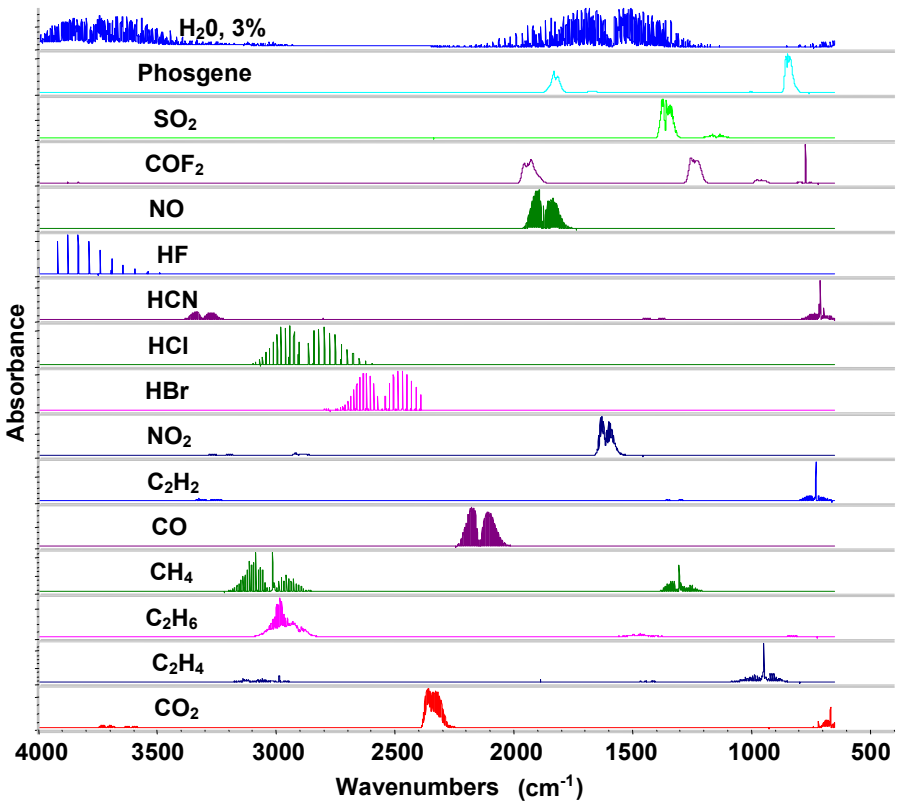

FIGURE 6. FTIR CALIBRATION SPECTRA OF 16 GASES AT 170°C—FULL-SCALE

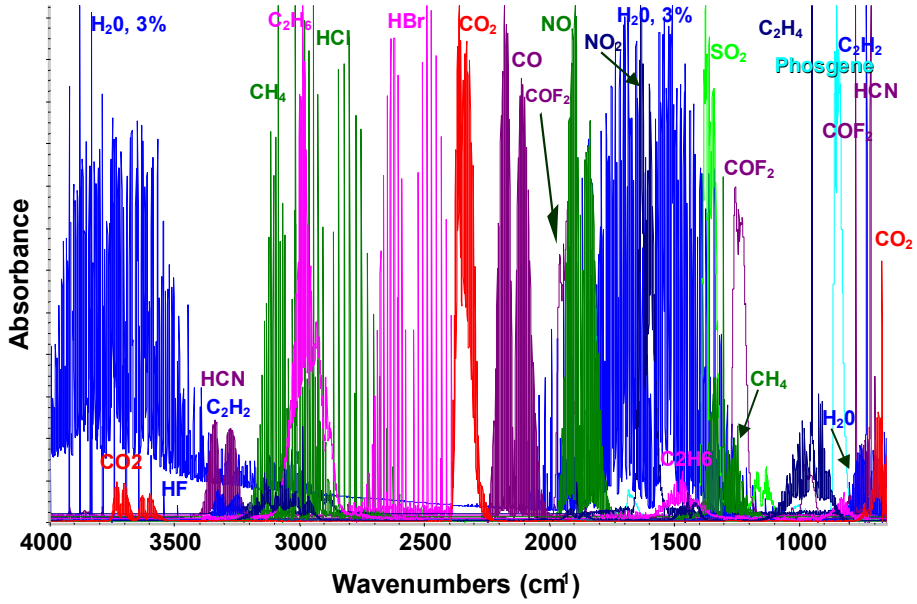

FIGURE 7. OVERLAID FTIR CALIBRATION SPECTRA OF 16 GASES AT 170°C—FULL SCALE

It can be seen from figure 7 that there are many overlapping peaks for these sixteen gases. It is desirable to select a wide band when possible, from baseline to baseline, with no absorption for gases that are not in the method.

An example of submethod development can be illustrated by examining the NO spectrum. The absorbance spectrum for NO is buried under the water spectrum in figure 8. Two-percent water is the maximum concentration measured in these fire tests.

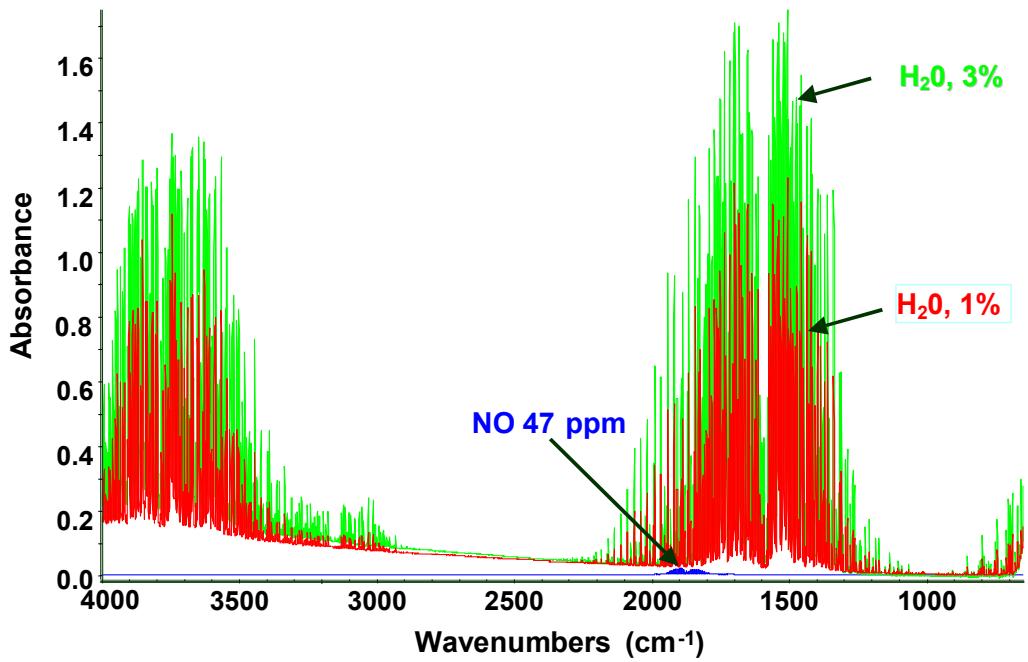

FIGURE 8. FTIR CALIBRATION SPECTRA OF H_2O AND NO

A narrow spectral region from 1899.2 to 1905.5 cm^{-1} was selected to quantify NO as indicated in figures 9 and 10. Figure 11 illustrates the value of the CLS method's automatic selection of the closest fitting H_2O spectra to calculate the NO concentration for the gas spectra of the flaming plastic specimen. The CLS method selects the closest matching water spectral shape in this spectral region. This more accurately defines the contribution of NO to the absorbance in this region, resulting in more accurate measurement of NO.

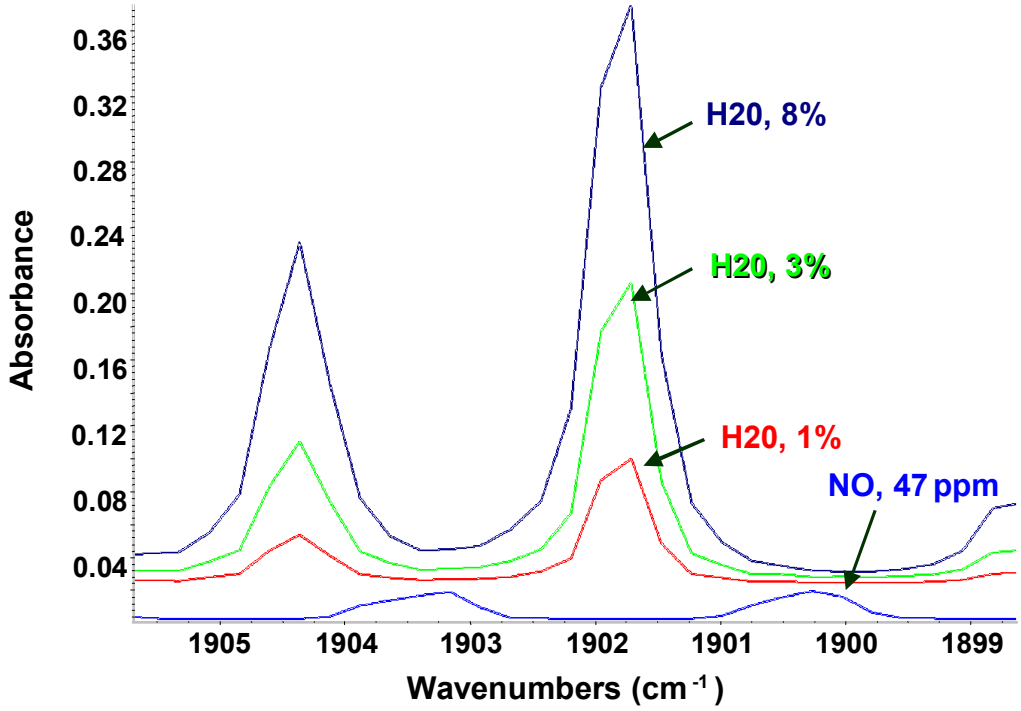

FIGURE 9. FTIR CALIBRATION SPECTRA OF H_2O AND NO—REGION SELECTED FOR NO ANALYSIS

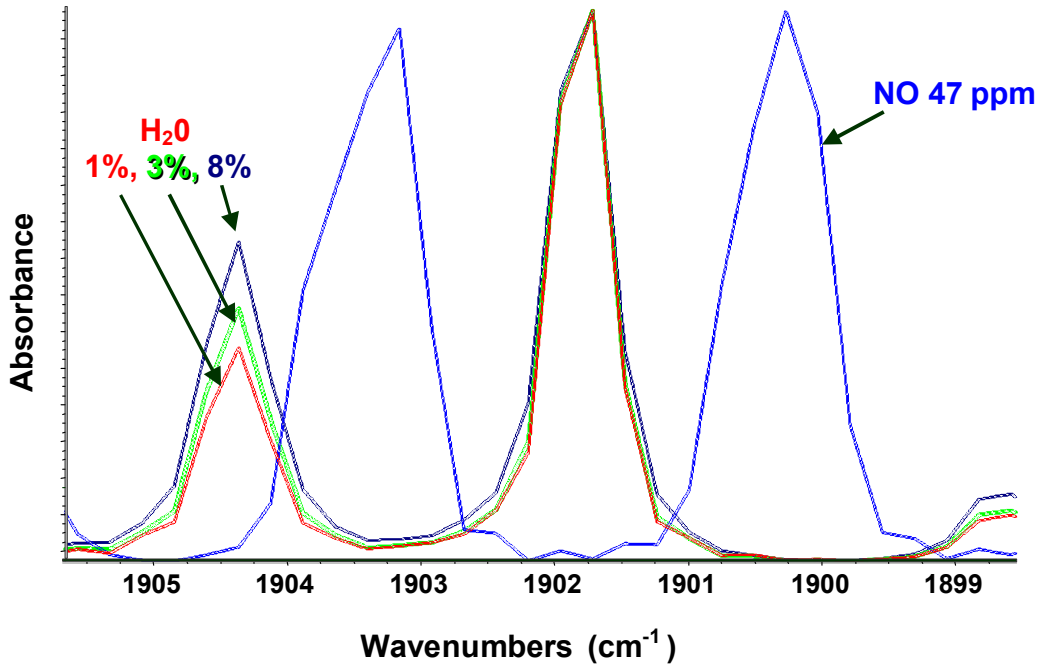

FIGURE 10. FTIR CALIBRATION SPECTRA OF H_2O AND NO—FULL SCALE

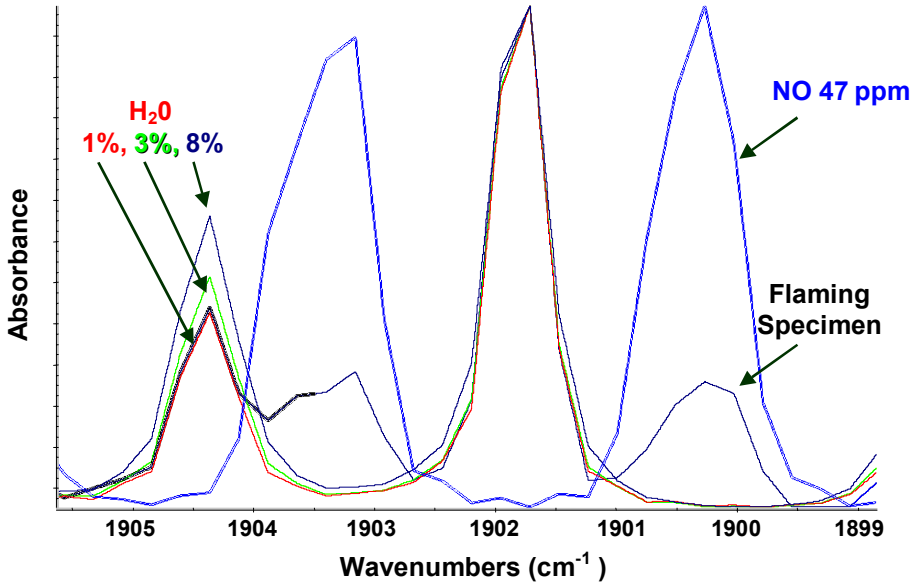

FIGURE 11. FTIR CALIBRATION SPECTRA OF H_2O, NO, AND FLAMING SPECIMEN SPECTRUM—FULL SCALE

System Dynamics. After correcting for transit delays, the system response time (90% of ultimate response) is 4 seconds when calibration gas is introduced at the inlet to the 12-foot heated sampling line leading to the oven. The system response time is 6 seconds when the calibration gas is introduced at the center of the cone at the nominal airflow rate of 0.020 m^3/second. This is shown in figures 12 and 13.

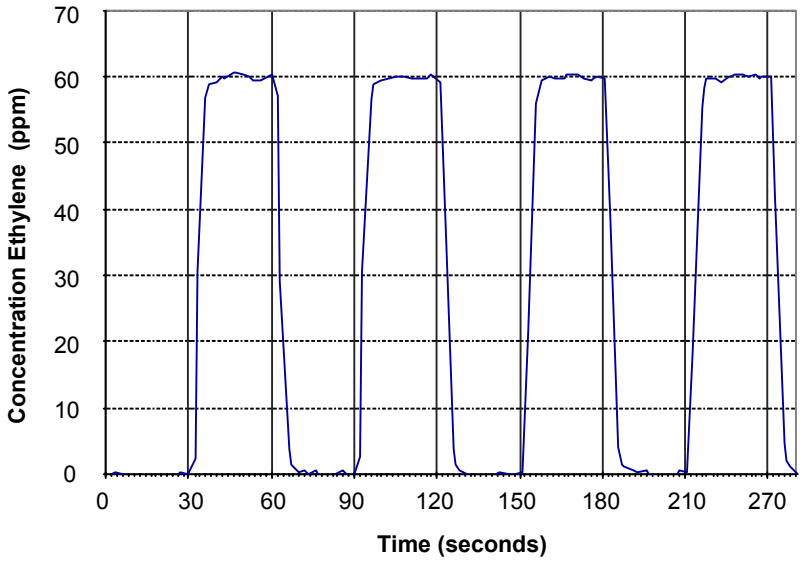

FIGURE 12. DYNAMIC RESPONSE OF THE FTIR SYSTEM WHEN CALIBRATION GAS IS INTRODUCED AT THE HEATED SAMPLING LINE INLET

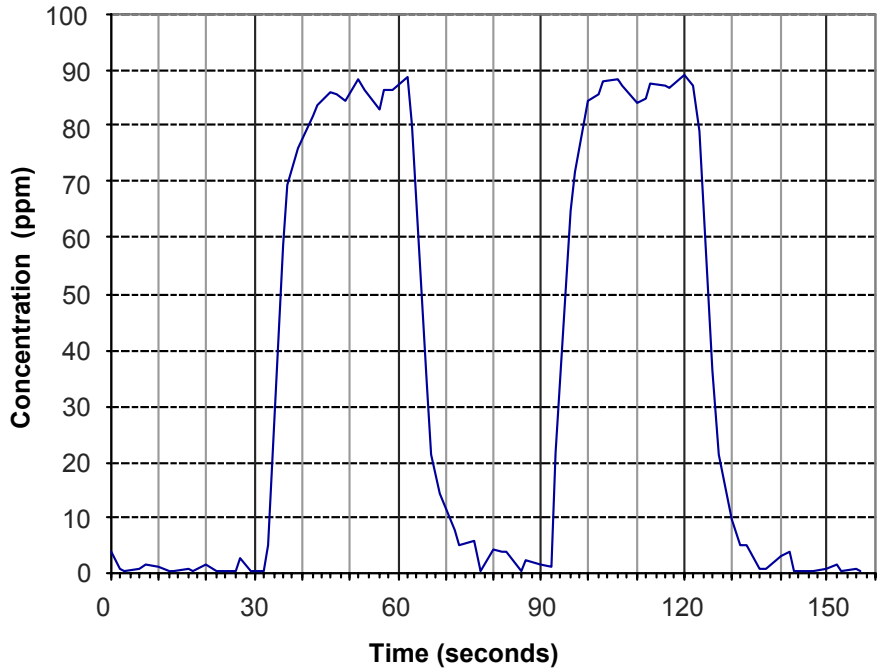

FIGURE 13. DYNAMIC RESPONSE OF THE FTIR SYSTEM WHEN CALIBRATION GAS IS INTRODUCED FROM THE CENTER OF THE CONE

Error Analysis.

Calibration Errors. The fit for the calibrations is point to point. This poses a problem in achieving high accuracy for fire gas analysis, as there is a limit to the number of spectra that can be included in a method. This "fit" error for the 16-gas method falls within ±10% for each gas within the measurement range of the combustion gases measured. This was demonstrated by running the method in the batch mode using calibration spectra for each gas and comparing the calculated concentration with the actual reported concentration for that calibration spectra.

Classical Least Squares Errors. The residuals for each gas from the CLS technique are used by the method to automatically calculate the corresponding CLS errors. These errors indicate the validity of the results as a function of time into the test. Gas concentrations are reported that are at least five times greater than the corresponding CLS error.

RESULTS AND DISCUSSION

NONFLAMING COMBUSTION TEST.

Figure 14 shows the spectra obtained 171 seconds into the tests for the nonflaming and flaming mixed plastic specimens. Additional gases are present for these 171 second samples; however, they need to be viewed at higher resolutions to be seen.

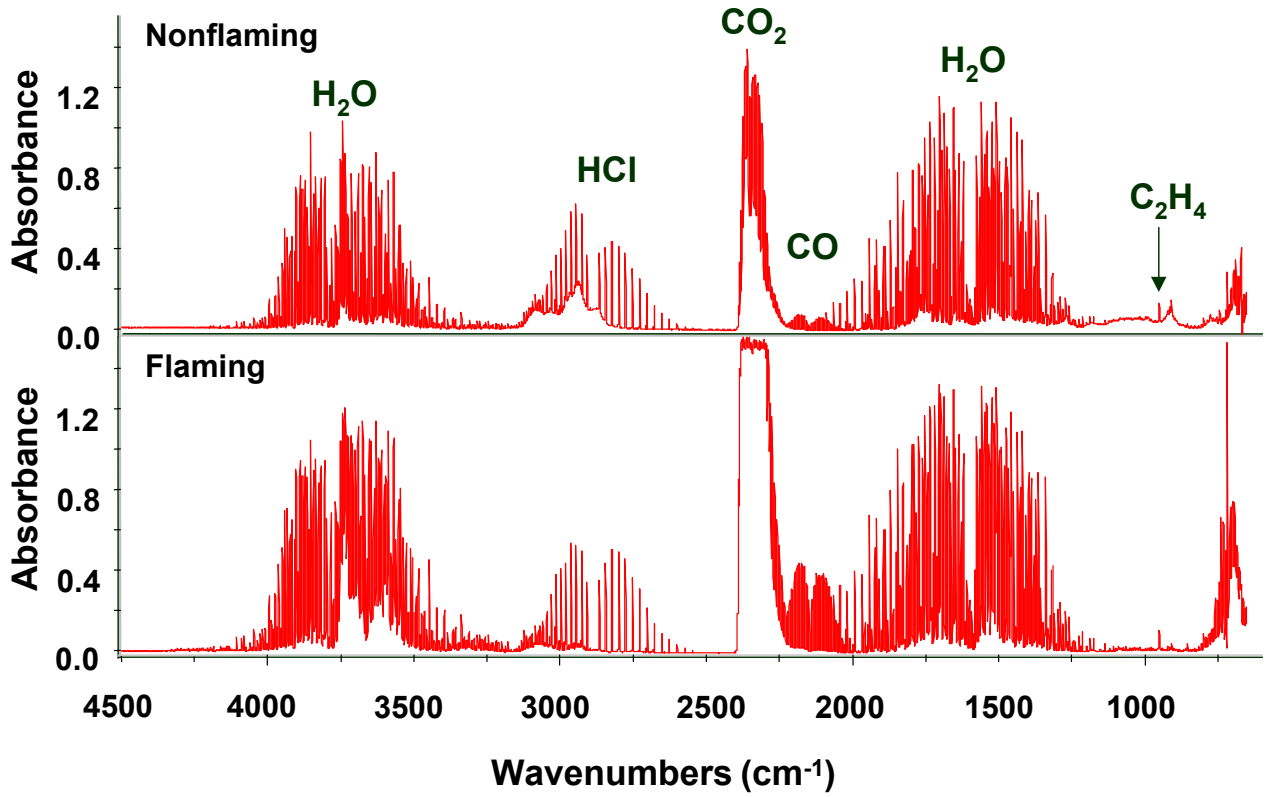

FIGURE 14. FTIR SPECTRA OF NONFLAMING AND FLAMING MIXED PLASTIC SPECIMENS AT 171 SECONDS

Figure 15 shows the chemical signatures of the gases CO, CO_2, HCN, HCl, C_2H_4, and CH_4, detected in the cone calorimeter for duplicate nonflaming tests of the mixed plastic test specimen. The gas generation rate increases with time for CO, methane, ethylene, and HCN. Hydrochloric acid (from the PVC) is relatively high, while carbon dioxide and carbon monoxide levels are comparable in the absence of gas phase combustion. Reproducibility is seen to be excellent and the accuracy was confirmed by the reasonable agreement between CO and CO_2 levels determined by the FTIR method and the cone NDIR gas analyzers (figure 16).

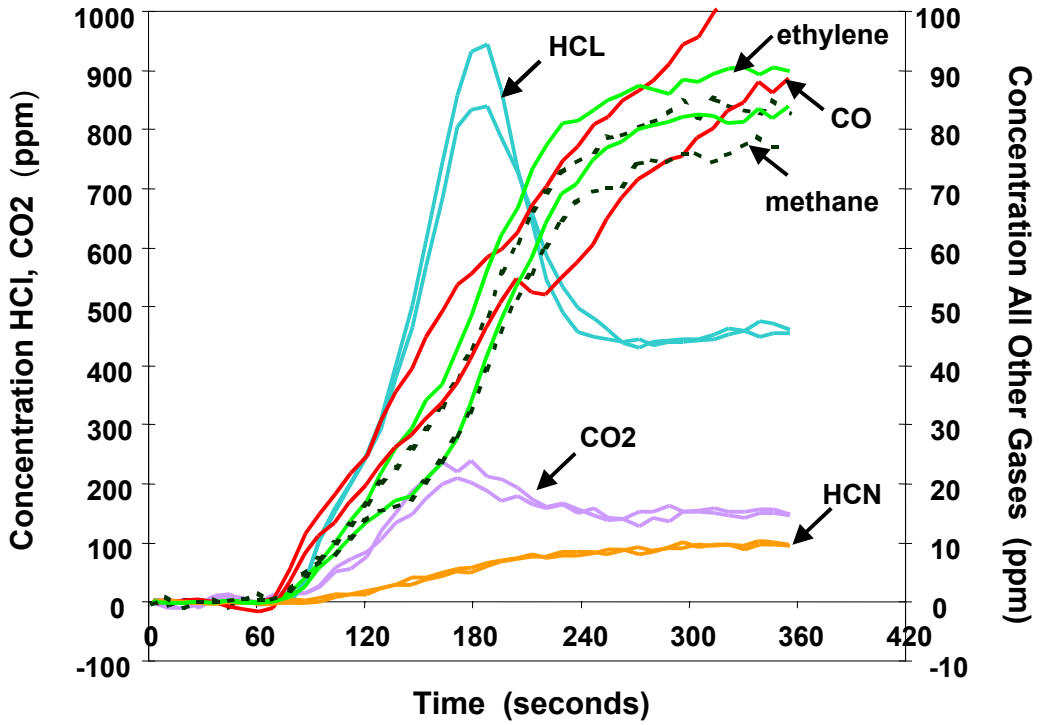

FIGURE 15. FIRE GAS HISTORIES FOR DUPLICATE NONFLAMING TESTS OF MIXED PLASTIC SPECIMEN

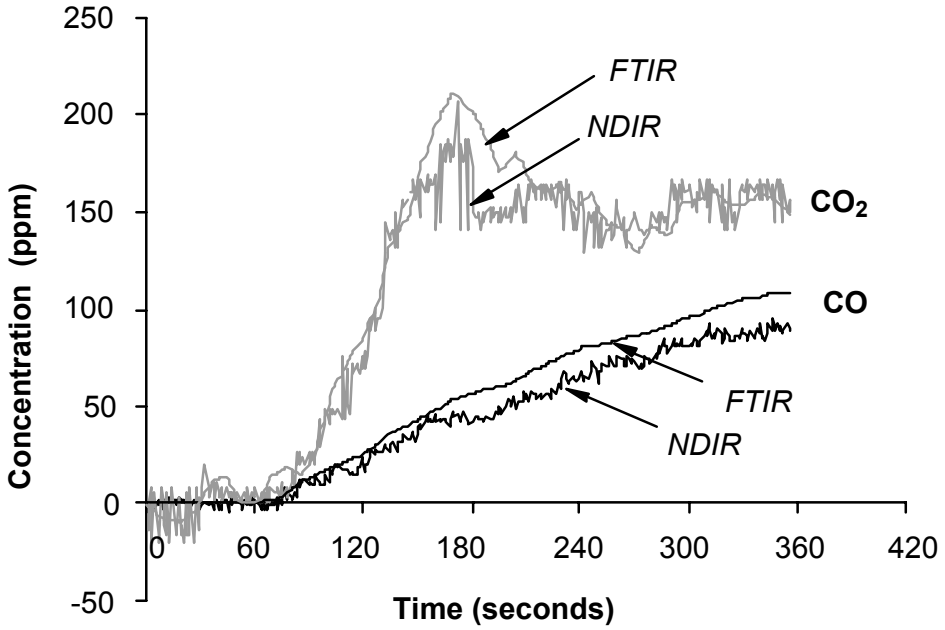

FIGURE 16. COMPARISON OF FTIR AND NDIR NONFLAMING PROFILES

The noise level for water (water is not reported) was quite high in the nonflaming tests (as were the residuals), so that water is probably not suitable for use as the sole analyte gas for early detection of smoldering combustion using FTIR-based detectors. COF_2 and SO_2 also had high residuals and the concentrations were not reported. The residuals for nonflaming combustion of the mixed resin specimen at 171 seconds are listed in table 2.

TABLE 2. RESIDUALS FOR A NONFLAMING SPECIMEN AT 171 SECONDS

Gas	Concentration (ppm)	± Error (ppm)	Error (%)
CO	53.6	0.7	1.3
CO_2	210.5	39.2	18.6
$COCl_2$	-0.1	0.1	
COF_2	8.3	2.2	26.5*
HBr	-0.2	1.2	
HCl	805.3	14.4	1.8
HCN	5.6	0.9	16.1
HF	0.0	1.3	
NO	-0.3	-6.5	
NO_2	-0.0	-6.5	
SO_2	6.4	3.3	51.6*
CH_4	37.6	0.4	1.1
C_2H_2	-1.0	0.2	
C_2H_4	42.9	0.4	0.9
C_2H_6	0.0	2.7	
Water	267.2	572.7	214.0*

*Gases with residuals exceeding 20 percent are not reported.

FLAMING COMBUSTION TEST.

Figure 17 shows the chemical signatures of CO, CO_2, H_2O, HCl, HCN, NO, C_2H_4, and C_2H_2 for duplicate flaming combustion tests of the mixed resin specimen. Reproducibility of the test is again seen to be excellent. The accuracy was confirmed by the reasonable agreement between CO and CO_2 levels determined by the FTIR method and the cone gas analyzers (figure 18). The CO_2/CO ratio of about 12/1 is characteristic of well-ventilated flaming combustion of halogen (e.g., PVC) containing materials (6) but is at least an order of magnitude below what is typically observed for hydrocarbon polymers. Acetylene, NO, and water are produced only in the flaming combustion tests. Note that the HCl curve does not lag behind the other gas curves as it does in most heated FTIR sampling systems for fire gases [4]. The sample stream was prewarmed prior to contact with the first filter, avoiding condensation of water on the filter medium and line delay effects due to the water solubility of HCl.

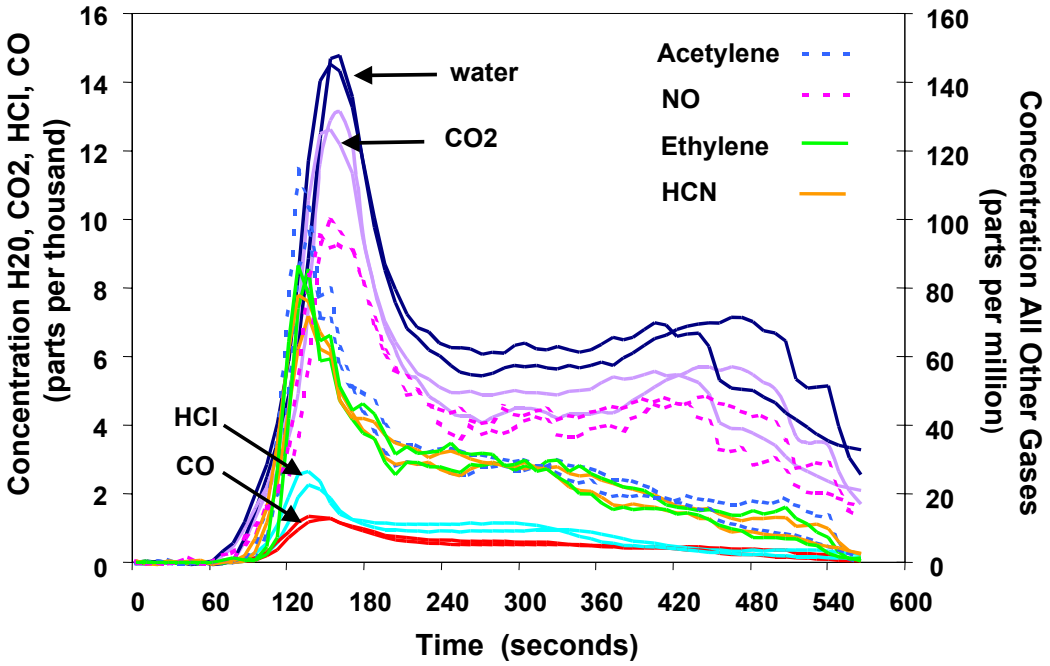

FIGURE 17. FIRE GASES FOR DUPLICATE FLAMING TESTS OF MIXED PLASTIC SPECIMEN

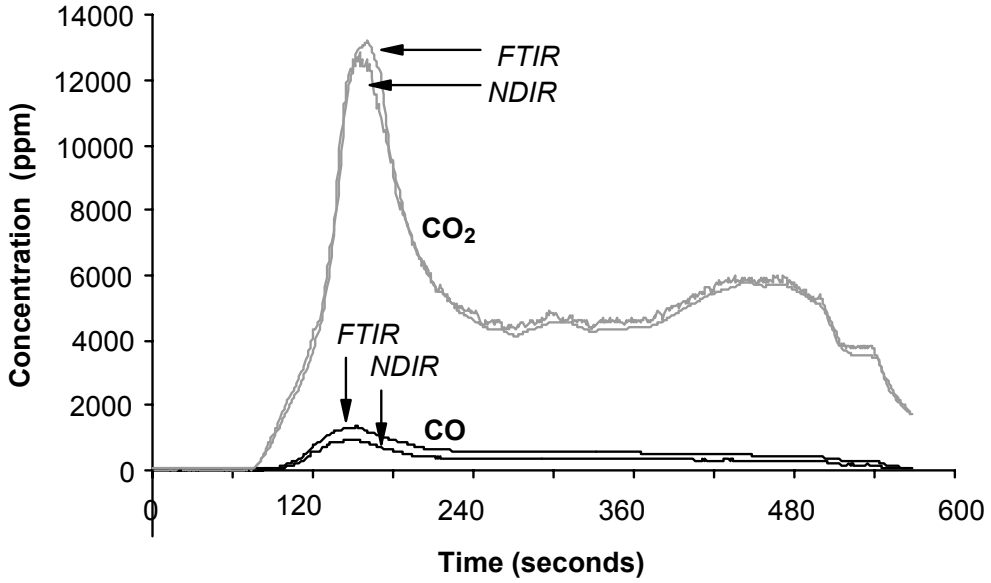

FIGURE 18. COMPARISON OF FTIR AND NDIR FLAMING PROFILES

SO_2 and CH_4 had high residuals and the concentrations were not reported. The residuals for flaming combustion of the mixed resin specimen at 171 seconds are listed in table 3.

TABLE 3. RESIDUALS FOR A FLAMING SPECIMEN AT 171 SECONDS

Gas	Concentration (ppm)	± Error (ppm)	Error (%)
CO	1025.9	5.5	0.5
CO_2	12182.3	1031.8	8.5
$COCl_2$	0.1	0.1	
COF_2	-0.4	1.3	
HBr	0.0	1.0	
HCl	1236.9	24.6	2.0
HCN	43.8	1.3	3.0
HF	0	1.7	
NO	90.9	11.2	12.4
NO_2	-0.1	11.2	
SO_2	2.5	4.8	192.0*
CH_4	40.6	32.7	80.5*
C_2H_2	50.1	0.5	1.0
C_2H_4	41.6	0.5	1.2
C_2H_6	-1.0	4.6	
Water	13578.6	203.6	1.5

*Gases with residuals exceeding 20 percent are not reported.

CONCLUSIONS

An FTIR system for monitoring fire gas concentrations was demonstrated using flaming and nonflaming conditions for a specimen containing a mixture of six common plastics. Excellent agreement was obtained for replicate tests in both the flaming and nonflaming mode. The accuracy was confirmed by reasonable agreement between the CO and CO_2 levels determined by the FTIR method and the NDIR cone gas analyzers.

This analytical system provides the capability of quantifying fire gas concentration histories along with an estimate of the reliability of the measurement during routine fire testing. A fast system response and good selectivity have been demonstrated for 16 fire gases.

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