IN-SITU MONITORING OF TOTAL-FLOODING FIRE TESTS BY FTIR SPECTROSCOPY

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ABSTRACT

We discuss collection and analysis of in-situ Fourier transform infrared (FTIR) spectrometric measurements in intermediate scale flammable liquid storeroom fire tests. The majority of the test fires were fueled by a mixture of methanol and heptane, and were suppressed by 1,1,1,2,3,3,3-heptafluoropropane (HFP, HFC-227ea). **A** number of baseline tests were performed with no application of suppressant, and Halon 1301 **was** used in some tests for comparison with HFP. FTIR spectra were used primarily to determine concentrations of suppression agents and *of* acid gas byproducts, although concentrations of fuel vapor, carbon monoxide, and products of incomplete combustion could also be determined. The suppression agents and acid gases were also monitored by other techniques. Data obtained by the various methods are compared and the relative advantages and disadvantages of in-situ FTIR are discussed. In-situ measurements are free of effects of sampling probes and secondary reactions which can complicate extractive techniques. The FTIR results discussed here generally gave good agreement with other data sets collected during the test series. Nevertheless, interferences from gaseous combustion products, particulates, and water droplets need to be considered for reliable interpretation of in-situ test data. Data from representative tests are presented, showing the effect of these interferences, as well as other issues related to data analysis.

INTRODUCTION

Fourier Transform Infrared (FTIR) Spectroscopy, a widely used analytical technique, is able to detect and measure concentrations of many chemical species by measurement of their infrared spectra. Recently, we have employed FTIR, in conjunction with other methods, to measure concentrations of several species of interest in fire suppression tests involving halon alternative systems. The spectra were obtained in-situ, meaning that the absorption measurement was conducted inside the fire test chamber, rather than being extracted by means of a sampling probe *to* a beam path located outside the chamber. This approach has significant advantages for highly reactive analytes such as carbonyl fluoride (CF_2O) and hydrogen halides, which are likely to react or adsorb in a sampling tube. Since no sample preparation is done, the issue of visibility in the beam path arises, and the effects of particulates such as soot, water droplets (which were **used** in conjunction with HFP in some suppression tests), and other combustion products must be considered in collecting and analyzing the spectral data.

This paper discusses these and other issues that arise in employing FTIR as an analytical tool in fire tests. In the results discussed here, the testing protocol was in no way influenced by the goal of obtaining optimal FTIR data, but rather was dictated by the requirement of evaluating the performance *of* halon replacement and alternative suppression systems for a range of representative fire threats and operating conditions. The design and construction of the test chamber and testing protocol, as well as other instrumentation used, have been discussed elsewhere [1]. The purpose of this work is to discuss the capabilities and limitations of FTIR as an analytical tool in fire testing, based on our experience. Representative spectra and analyses are presented, but are meant to be illustrative of certain issues relevant to this application rather than to give a comprehensive picture of the test results and their implications regarding the design of nonhalon fire suppression systems. The overall conclusions and data analyses obtained from the test series are presented at this conference in a separate paper [2].

BACKGROUND ON INFRARED SPECTROSCOPY AND FOURIER TRANSFORM SPECTROMETERS

Most infrared spectra result from the deformation (stretching or bending) of chemical bonds in a molecule [3]. Most molecules exhibit infrared absorption; exceptions include monatomic gases (helium, argon, etc.) that contain no chemical bonds, and homonuclear diatomic molecules including N_2 and O_2. In the latter case chemical bonds exist but due to the symmetry of the molecule cannot be optically excited. When molecules absorb or emit infrared light, a transition occurs between two vibrational energy levels. The wavelength of the light absorbed or emitted is inversely proportional to the difference in energy between the two levels. For gas phase molecules, there is a fine structure superimposed on the vibrational transition. This structure is due to rotational states of the molecule. In condensed phases (solid or liquid), molecules cannot rotate freely and so the rotational structure is not discernable. One implication of this fact is that the details of an infrared absorption spectrum of a gas phase molecule will be very different from those of the same molecule in a condensed phase. Liquid water and water vapor have absorptions at roughly the same wavelengths, but the spectra are not at all similar. Likewise, gaseous hydrogen fluoride has a different (and much more identifiable) absorption spectrum than aqueous hydrofluoric acid. Infrared monitoring will generally not measure HF that has been absorbed into water droplets (either produced by the combustion process itself **or** added as a suppressant) and which may be present in the test region. In addition, condensed phases can attenuate light by scattering as well as by absorption, complicating data interpretation.

FTIR (Fourier Transform Infrared) refers to the principle by which the type of spectrometer discussed here collects spectra. The spectrometer contains a thermal infrared source whose emission is collimated and split into two beams. The two beams are recombined after reflecting off a pair of mirrors, one of which can be moved to adjust the relative path lengths traveled by the beams. After recombination, the IR beams are passed through the sample being studied and then focused onto a detector. Due to the wave properties of light, the two beams will exhibit interference effects as their relative path lengths are varied by translating the movable mirror (this optical setup is referred to as a Michelson interferometer). The intensity of the infrared beam at the detector as a function of the path length difference (referred to as the interferogram) **is** a Fourier transform of the IR intensity as a function of wavelength. The conversion of the signal from the tine *domain* (the detector signal as a function of time as the mirror is scanned) to thefrequency domain (signal vs. optical frequency or, equivalently, wavelength) is accomplished by a Fast Fourier Transform (FFT) algorithm on a data acquisition computer, which also controls the spectrometer operation. By comparing the spectrum obtained with a sample present to a baseline recorded with a purged optical path, the net absorbance of the sample can be determined. The spectrum of absorbance vs. wavelength is used to determine the presence and quantities of analytes in the test region.

A schematic of the spectrometer setup is shown in Figure 1. The spectrometer **(MIDAC** I2001) sits just outside the fire test compartment. The spectrometer has an external beam path. Light from the Michelson interferometer exits the spectrometer through one window, then enters approximately **1** m into the test chamber inside a 2.5-cm diameter tube with a reflective inner wall (referred to as a "light pipe"). The light pipe is enclosed inside an airtight housing, which provides mechanical support and protection from the fire environment. The light pipe and surrounding housing are purged with nitrogen during testing. The beam exits the tube and the enclosing pipe through a pair of windows. The outermost windows in contact with the compartment air are composed of barium fluoride to avoid chemical attack by HF. The beam then traverses 15 cm through the test chamber atmosphere before entering an identical tube that leads back to the spectrometer. The transmitted light is then collected by the infrared detector.

The advantage of recording spectra using the Fourier transform technique, compared to a dispersive monochromator (which allows a narrow spectral window, scanned with time, to reach a detector), is that the detector in the Fourier transform spectrometer simultaneously sees all wavelengths of light for the entire recording time. This means that for a given resolution and collection time, the photon throughput and hence the signal-to-noise ratio is greatly improved when using the transform method. This translates into the capability of obtaining spectral data in greatly reduced time, allowing determination of analyte concentrations with high time resolution. The fact that more mathematical manipulation is required to process the spectrum is not a significant disadvantage with current computational capabilities.

FTIR Setup in FLRS **1**

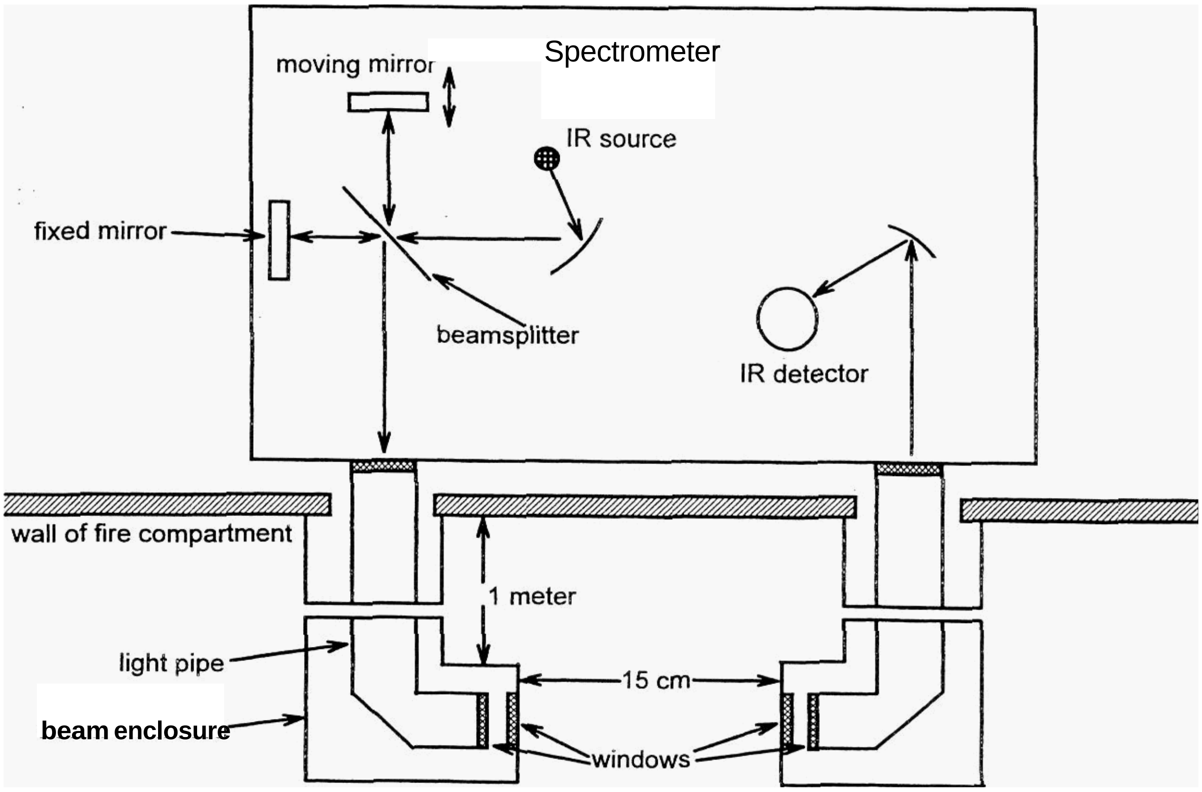

Figure 1. FTIR Spectrometer setup used for in-situ monitoring.

SPECTROMETER RESOLUTION AND DETERMINATION OF ANALYTE CONCENTRATIONS

The spectral resolution of an FTIR spectrometer is determined by the distance of travel of the movable mirror from the point of zero path difference for the two beams. Infrared spectra are typically plotted against inverse wavelength (referred to as "wavenumbers," usually written in units of cm^{-1}; this *is* proportional to the frequency of the light and to the transition energy in the molecule). The nominal resolution of a spectrometer is given by the inverse of the maximum path length difference. For a resolution of 0.5 cm^{-1}, the path length must be varied by 2 cm.

The actual resolution of a spectrum (for instance, the full-width half-maximum **(FWHM)** of a very narrow spectral feature) is not exactly the same as the nominal resolution, and depends to some extent on how the mathematical reconstruction of the spectrum is performed. In the Spectrometer, the interferogram of the molecule (which extends to infinity) is truncated at the limit of the mirror travel, i.e., is multiplied by a square wave function which is equal to unity up to the maximum path length difference, and is zero beyond. When the Fourier transform is performed, the resulting spectrum is the ***convolution*** of the spectrum of the molecule **as** it would appear in an infinitely high resolution spectrometer, and an ***instrument function,*** which in this case is the Fourier transform of the **square** wave function. The convolution is given by the relation:

$$S(\nu) = \int_{-\infty}^{\infty} I(\nu-\nu')S_m(\nu')d\nu' \tag{1}$$

where **S** is the intensity spectrum recorded by the spectrometer, S_m is the spectrum as it would appear through a spectrometer with infinite resolution, and **I** is the instrument function. For a square wave, I is given by

$$I(\nu) = \left|\frac{\sin(2\pi\nu D)}{\nu}\right| \tag{2}$$

Directly transforming the raw interferogram produces spurious subsidiary peaks slightly displaced from the real spectral feature. By multiplying the interferogram by some function that goes smoothly to zero at the limits of the mirror travel, the spurious peaks can be greatly reduced in intensity, but at a cost of slightly lower resolution. This procedure is referred to as *apodization.* One common apodization function is a triangle, which has a maximum value at the point of zero path difference for the two beams and goes linearly to zero at the limit of mirror travel. If triangular apodization is used, the instrument function is given by

$$I(\nu) = \frac{\sin^2(\pi\nu D)}{\nu^2 D} \tag{3}$$

With this instrument function, the FWHM of a narrow line for an ideal (i. e., perfectly aligned) spectrometer will be 89% of the nominal resolution [4].

The concentration of a molecule of interest is determined by converting the infrared spectrum to absorbance:

$$A(\nu) = \log_{10}\left(\frac{S_0(\nu)}{S(\nu)}\right) \tag{4}$$

where S and S_0 are the intensity spectra at a given frequency with and without the sample present, respectively. An absorbance of 1.0 means that 90% of the light has been absorbed: $(\log_{10}(100\%/10\%) = 1.0)$. The absorbance is proportional to the product of the analyte species' concentration and the absorption path length. Absorbances below about 0.02 are difficult to measure accurately unless a large number of scans are averaged, while absorbances greater than unity are also problematic because less than 10% of the light is getting to the detector. For this reason, FTIR inherently has a dynamic range of species concentrations limited to about *50*, although this can often be extended by using several spectral features having different absorption strengths, for different ranges of analyte concentration.

CALIBRATION PROCEDURE

The finite resolution of the spectrometer can introduce nonlinearities between the concentration and the apparent absorbance. This effect is most pronounced for diatomic molecules such as CO, HF, and other hydrogen halides, which generally exhibit sharp, non-overlapped lines, These sharp lines represent individual rotational transitions; the intrinsic line widths under standard conditions are typically about 0.05 cm^{-1}, much less than the resolution of most FTIR spectrometers. For a very sharp isolated line, the approximate effect of the convolution with the instrument function on the peak intensity is divided by the ratio of the spectrometer resolution to the molecular line width. Since this ratio is approximately 20 for a typical diatomic molecule viewed by a spectrometer at 1 cm^{-1} resolution, the true peak absorbance is liable to be almost 100% even when the ***apparent*** peak absorbance observed through the spectrometer is quite small.

If the molecular spectrum were converted to absorbance units ***before*** convolution with the spectrometer instrument function, the peak height of the convolved spectrum would still be proportional **to** concentration. In the spectrometer, however, the molecular spectrum is convolved before being converted into absorbance units via Eqn. **(4).** The two mathematical operations of convolution and absorbance transform will only commute (meaning that the final result will be independent of the order in which they are performed) if both are linear. The logarithmic transform, however, is only linear if the absorbance is $\ll 1$ for all frequencies. This is generally ***not*** the case for most diatomic molecules under typical concentrations and path lengths.

To simulate and account for the effect of this nonlinearity on determinations of species concentrations, spectral simulations were performed using the HITRAN database [5], which includes many molecules important in atmospheric chemistry, including carbon monoxide, all the hydrogen halides, carbonyl fluoride, methane, carbon dioxide, and water. The HITRAN calculation simulates the spectrum as it would appear through a spectrometer of infinite resolution, and takes into account effects of temperature and pressure on intensities and widths of spectral lines. The calculation is done in absorbance units, which then can be converted to any concentration and path length by multiplication by a constant of proportionality. To simulate the spectrum as it would appear on the real spectrometer, the calculated spectrum was converted to transmission:

$$A(\nu) = \log_{10}\left(\frac{S_0(\nu)}{S(\nu)}\right) \qquad (5)$$

where T is the transmission and A the absorbance. The transmission spectrum was then numerically convolved with the instrument function for the spectrometer. Ideally the instrument function should be given by Eqn. (3), but it was found that use of the ideal convolution function did not give a good reproduction of the experimental line shape. The actual line widths were somewhat greater than predicted, and varied somewhat with wavelength. Therefore, an empirical function of the form

$$I(\nu)=\frac{1}{(1+(\frac{\nu}{L})^2)^2} \qquad (6)$$

was used in the convolution, where the parameter L was adjusted to reproduce the FWHM line width of the experimental spectrum for the molecule being modeled.

After the convolution, the transmission spectrum was converted back into absorbance by inverting Eqn. **(5).** The HITRAN calculation, convolved spectrum, and experimental spectrum for carbon monoxide are shown in Figure 2. No scaling of the calculated or experimental spectra has been performed. The calculation gives good agreement with the absolute peak absorbances of the experimental spectrum. An analogous calculation and convolution for HF gave good agreement in intensity to a reference spectrum from the MIDAC spectral library.

Figure 3 shows peak absorbances of particular rotational lines of HF and CO as a function of concentration for the spectrometer operating at **1** cm^{-1} resolution. For CO, the absorbances from calibration spectra are also plotted. The plot shows the good agreement with the experimental measurements and the strong nonlinearity in the relationship between absorbance and concentration for these molecules.

For most polyatomic molecules the problem of nonlinearity is greatly alleviated. An example for carbonyl fluoride is shown in Figure **4.** Although the HITRAN calculation does show individual sharp lines, they are so numerous and so closely spaced that they almost run together. Consequently, the peak absorbances in the non-convolved and the convolved spectra only differ by about **30%.** Nonlinearity in absorbance at 1930 cm^{-1} vs. concentration is only a few percent up to an absorbance of 0.6.

For molecules such as CF_3Br and C_3HF_7, the individual rotational lines are unresolvable no matter how high the spectrometer resolution, and absorption spectra recorded at 0.5, **1,** and 2 cm^{-1} resolution look virtually identical. In such a case the convolution leaves the molecular spectrum essentially unchanged, so the effect of nonlinearity is negligible.

The point of considering nonlinearity is that many computational routines exist that fit an experimental spectrum to a series of reference spectra of analyte compounds and so determine the analytes' concentrations. Such routines generally assume linearity, which is reasonable for many compounds, ***but not most diatomics including HF and CO.*** Assuming linearity in these cases can lead to greatly inaccurate results. In our analysis of the FTIR data for HF and ***CO,*** we have used the relationship from Figure **3** to determine concentrations. For compounds such as Halon 1301 and HFP, where the nonlinearity is nil, we determined concentrations from the ratio of absorbances between the experimental and reference spectra.

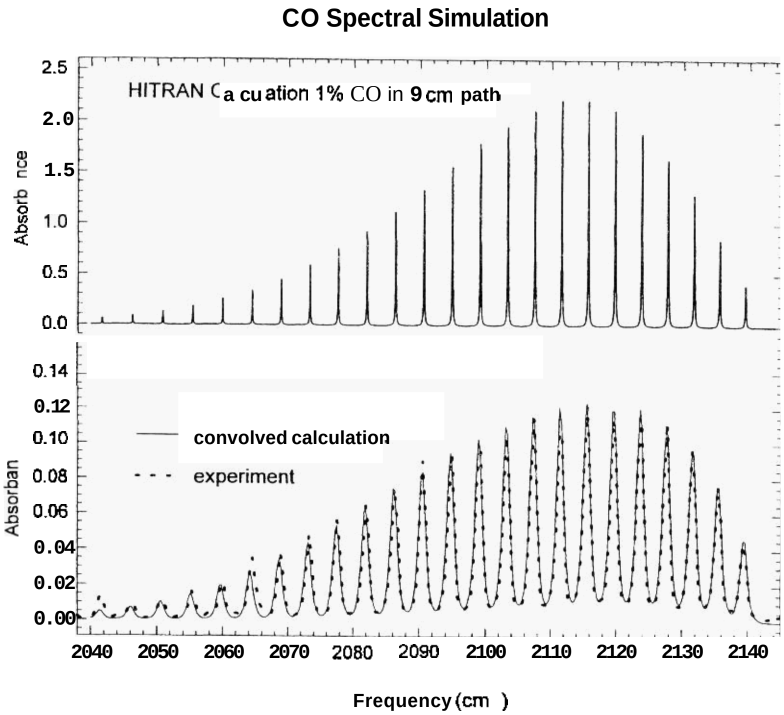

Figure 2. HITRAN calculation of carbon monoxide absorbance for a **1%** concentration under standard conditions for a 9 cm absorption path length (top); calculated absorbance after convolution with the instrument function defined in **Eqn.** (6) overlaid with experimental spectrum recorded under same conditions (bottom). In the experimental spectrum additional absorbances due to water vapor are present at **2042** cm^{-1} and 2065 cm^{-1}.

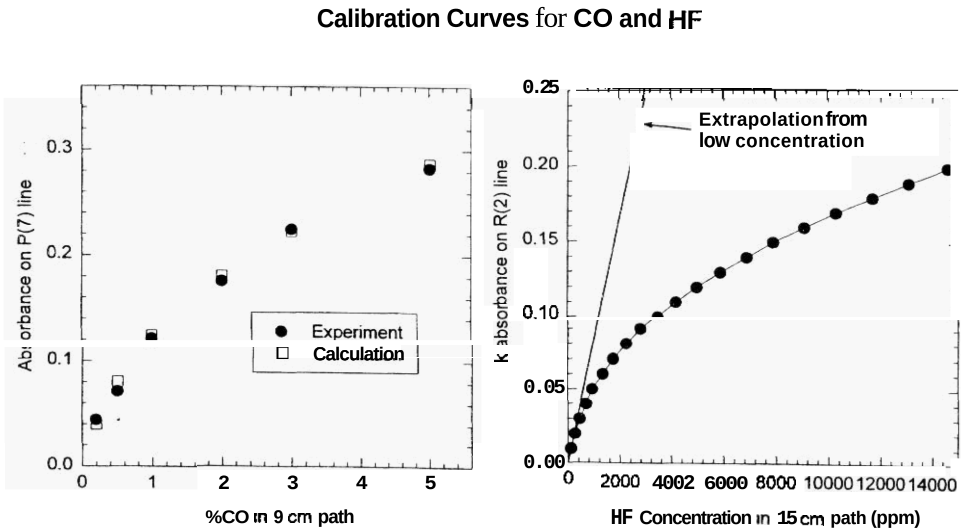

Figure **3.** Calculated apparent absorbances determined from convolved spectra for individual rotational lines of CO and HF for **a** spectrometer at 1 cm^{-1} resolution. The CO calculated values have been overlaid with experimental data points. The result obtained by extrapolating absorbances from low concentration measurements is shown on the HF plot.

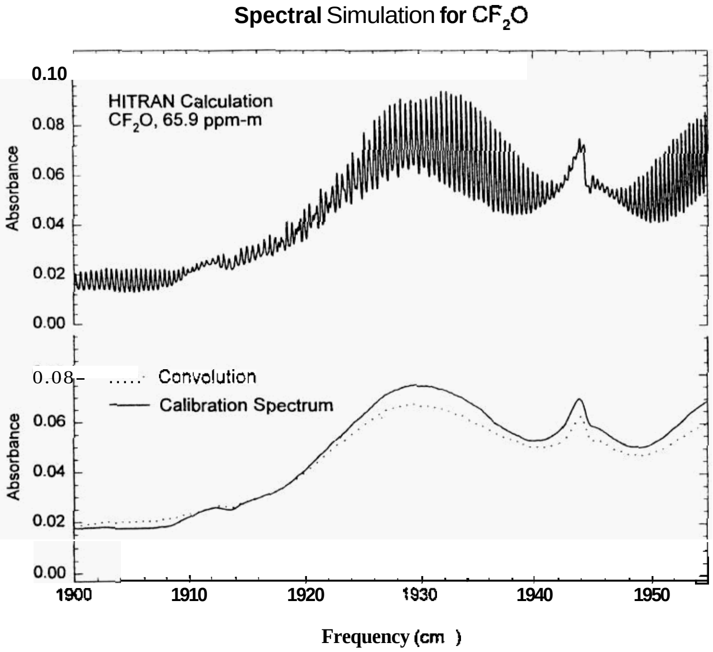

Figure 4. HITRAN calculated spectrum of carbonyl fluoride, calculated spectrum convolved with instrument function, and reference spectrum from MIDAC spectral library (reproduced by permission [8]).

INSTRUMENTATION AND TEST PROTOCOL

The tests described here were conducted at the Naval Research Laboratory Chesapeake Bay Detachment. The purpose of the tests was to evaluate the performance of halon alternative fire suppression systems under conditions that closely mimic fire threats in shipboard flammable liquid storage rooms. The tests were conducted in a 28-m^3 (1000-ft^3) chamber described in detail elsewhere [1,2]. The tests fall into two categories: baseline tests, in which the fire was allowed to bum itself out primarily by oxygen depletion, and suppression tests, in which the suppression agent was discharged to extinguish the fire before the oxygen had been severely depleted. **A** few cold discharge tests (with no fire) of the suppression agents were also performed ***to*** investigate the effect of different discharge system configurations on agent dispersal.

The majority of fire tests used liquid fuel consisting of 80% methanol and *20%* n-heptane. Two tests were performed with diesel fuel, and a few baseline tests (without suppression) were performed with burning cardboard. Of the suppression tests, the majority used 1,1,1,2,3,3,3-heptafluoropropane (HFP, HFC-227ea) as the suppression agent. **A** few tests were performed with Halon **1301** for comparison purposes. **Also** used on some tests was the NRL water spray cooling system [6], intended to mitigate the thermal effects of the fire and also to reduce the formation and persistence of acid byproducts.

The absorption path length used for the testing was 15 cm. This value was chosen to give a reasonable absorbance for HF at the concentrations expected based on previous test data (on the order of 5000 ppm). Since HF only **has** one absorption region in the operating range of typical FTIRs, there **is** not a choice of which spectral feature to use, and one must design the test setup around this molecule's absorbance.

The location of the FTIR beam path was located approximately 70 cm above the floor of the test chamber (which was essentially a cube 305 cm on a side). The liquid fuel fires had a vertically cascading flow of liquid fuel, and also a pan containing fuel on the compartment floor. The center of the fuel pan was displaced laterally from the FTIR measurement point by some 50 cm. Although the beam path was close to the fire, the spectral measurements did not sample the flame zone itself or the hot product gases immediately above it.

The spectrometer was operated at **a** resolution of 1 cm^{-1}. This choice of resolution was a compromise between several factors. At this resolution, an FTIR measurement could be obtained roughly every ***2.5*** sec, averaging two spectrometer scans per data point. Operating the spectrometer at its maximum resolution of 0.5 cm^{-1} would have reduced the effect of nonlinearity slightly, although by no means eliminated it. On the other hand, a higher spectral resolution would have entailed either reducing the time resolution by at least a factor of two (due to both the time to collect the interferogram and to perform the Fourier transform), or collecting only one scan per data point, reducing the signal-to-noise ratio, and increasing the minimal detectable concentrations of the analytes.

The spectrometer began recording spectra approximately **3** min before ignition of the fire, and continued collecting data at the maximum rate until the fire had extinguished (2 min after ignition for the suppression tests, roughly 4-5 min after ignition for the tests without suppression). For the remainder of the test (which entailed a hold time of typically 15 min, followed by ventilation of the test chamber and attempted reignition in the case of the suppression tests), the spectrometer performed a measurement every 15 sec. These measurements were based on an average of 20 spectra to obtain better concentration data since the time resolution was much **less** critical after fire extinguishment. The spectrometer gave a real-time concentration readout **for** specified analytes during the tests, although as discussed above, this should only be considered a relative measurement in the case of the diatomics. Each test produced approximately 30 MB of spectral data (archiving both the intensity spectra S and the absorbance spectra **A** to disk).

MONITORING STRATEGIES AND INTERFERENCES

The primary target molecules for the FTIR measurements were the suppressant agents HFP and Halon 1301, and the acid gases HF, CF_2O, and HBr.

The fluorocarbon suppressant agents have very strong IR absorption bands in the vicinity of 1000 cm^{-1} (it is because of this characteristic that fluorocarbons have high Global Warming Potentials). Using an absorption path length on the order of 15 cm, these absorption bands will cause complete extinction of the IR beam for agent concentrations on the order of several percent, precluding their use for quantitative measurements. Halon 1301 has a much weaker band at 1300 cm^{-1}, which has an absorbance of about 0.5 for typical test conditions. We used this feature for determination of concentrations, as it is a relatively isolated peak that shows little interference from other species under test conditions.

HFP has a number of relatively weak absorption **peaks** between 1400 cm^{-1} and 2400 cm^{-1}. Initially we tried to determine concentrations by comparing absorbances over several peaks in the region between 2490 cm^{-1} and 2672 cm^{-1}. This approach, however, proved problematic in tests where the spectrometer baseline drifted during the course of the test. Ultimately we determined concentrations using a single peak near 2050 cm^{-1}, which because it was relatively isolated, proved much less sensitive to baseline drifts. A comparison of the two protocols for concentration determination is shown in Figure 5. Both approaches gave nearly identical estimates for concentrations immediately after agent discharge. The method using the broader spectral region, however, calculated an agent concentration drop of nearly 40% prior to venting, which was not consistent with results from other test methods.

Determination of Agent Concentration During Fire Test

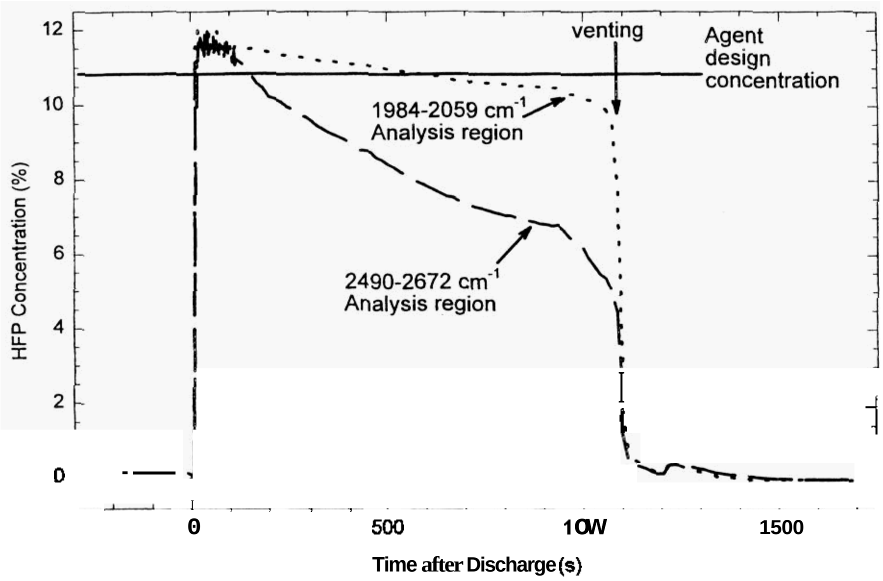

Figure 5. Concentration of HFP as a function of time during a fire suppression test. Two different spectral regions were used to determine concentrations. The apparent drop in concentrations during the hold time when the region near 2500 cm^{-1} was used is an artifact of baseline drift.

HF and CF_2O were monitored, respectively, at 4072 cm^{-1} and 1930 cm^{-1}, and quantities were determined based on the HITRAN simulation and convolution procedure. HBr was also monitored during suppressions using Halon 1301. HBr calibration curves were generated in an analogous manner to those for HF. In practice the spectral lines of HBr were barely detectable, due to a combination of factors. First, Halon 1301 generates considerably lower acid gas concentrations than does HFP. Secondly, there is a 3:1 stoichiometry ratio between fluorine and bromine in Halon 1301. Finally the molar absorption coefficient for HBr is about 10 times less than for HF. In the halon suppression tests, the highest HBr level measured had an absorbance of 0.005, corresponding to a concentration of about 400 ppm.

VISIBILITY AND SPECTRAL INTERFERENCES DURING FIRE TESTS

In the fire test series it was found that, in general, the most serious problem with transparency in the beam path was encountered in the tests without suppression. Since the fire was oxygen starved, the fire tended to produce a large amount of smoke even though the fuel was primarily methanol. For about the last minute before the fire extinguished and for about two minutes afterwards, the spectrometer had nearly complete obscuration across most of the spectrum. This was probably due to particulates, since transparency gradually returned during the hold time, even though the compartment was not vented. By the end of the 15-min hold time, molecular species produced by the oxygen starved combustion, including CO, CH_4, and C_2H_4, were evident.

In the tests with suppression, IR transparency was much better, even though the strong absorption bands of the agent caused complete attenuation in certain regions. To give a fair test of the agent's effectiveness, suppression was initiated before the fire had become severely oxygen depleted. Consequently, particulate formation was much less, even though some agents themselves have been found to enhance smoke production. Once again, the most serious obscuration was found just after fire extinguishment, with transparency gradually improving during the time interval before venting. The fire reignition after venting did not cause significant obscuration, since in this case the fire was being given a fresh oxygen supply.

Use of the water spray cooling system generally caused a much noisier background. This was particularly true for the spectral region used to detect HF, which lies adjacent to an absorption band of water. The noisier background reduced the signal/noise ratio, leading to significantly higher minimum detection limits as well as greater uncertainty in reported values.

Figure *6* shows an example of **a** spectrum from a fire test. The fuel in this case was diesel, which generates much more smoke than the methanol/heptane blend. The spectrum was recorded immediately after agent discharge (when transparency was at its poorest), and was averaged from only two scans. The absorption is about 90% at most wavelengths, and there are strong absorptions due to carbon dioxide and HFP, as well as absorption or scattering due to condensed phase entities. Nevertheless, the spectral features used to monitor HF, CF_2O, and HFP are clearly discernable above the background.

COMPARISON OF FTIR AND CHEMICAL ANALYSIS DATA FOR ACID GASES

Figure 7 compares graphs of acid gases as **a** function of time for a methanol/heptane fire suppressed by HFP. The initial peak at time zero corresponds to agent discharge and extinguishment of the fire. The subsequent rise of acid gases after 1900 seconds following agent discharge is due to reignition after compartment venting. The continuous acid analyzers (CAA) convert both HF and CF_2O to fluoride ion, which is measured by an ion specific electrode [7]. Therefore, the **FTIR** data were compared to the CAA data by counting all the fluorine in either the form of HF or CF_2O: twice the CF_2O concentration was added to the HF concentration. At the same time, the CAA can detect either gaseous HF or aqueous HF in water droplets, while the **FTIR** can only detect gas phase species.

In the plot the **FTIR** data are compared to averages from three CAAs at different points in the test chamber. The **FTIR** data have, if anything, better agreement with the averaged CAA data than the individual CAAs have with one another. The two data sets appear to be in reasonable agreement, although more definite conclusions cannot be made since compartment inhomogeneities may account for much of the observed variations. One trend that the data do appear to show is that the HF produced by the initial suppression seems to have greater persistence in the CAA data than in the FTIR data. Absorption of HF into droplets or particles could account for such a trend.

Comparison of FTIR and CAA data for acid gas concentrations

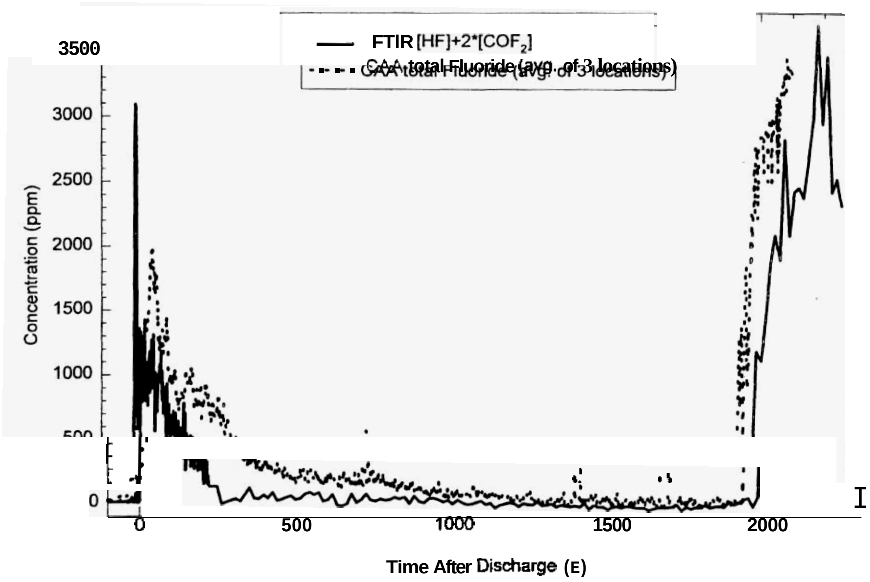

Figure *6*. Spectrum recorded during fire test using diesel fuel immediately after suppression of fire by HFP. The spectrum was recorded at 1 cm^{-1} resolution and was averaged from two scans. Spectral features used to monitor HF, CF_2O, and HFP **are** indicated by **arrows.**

Comparison of **FTIR** and **CAA** data for acid gas concentrations

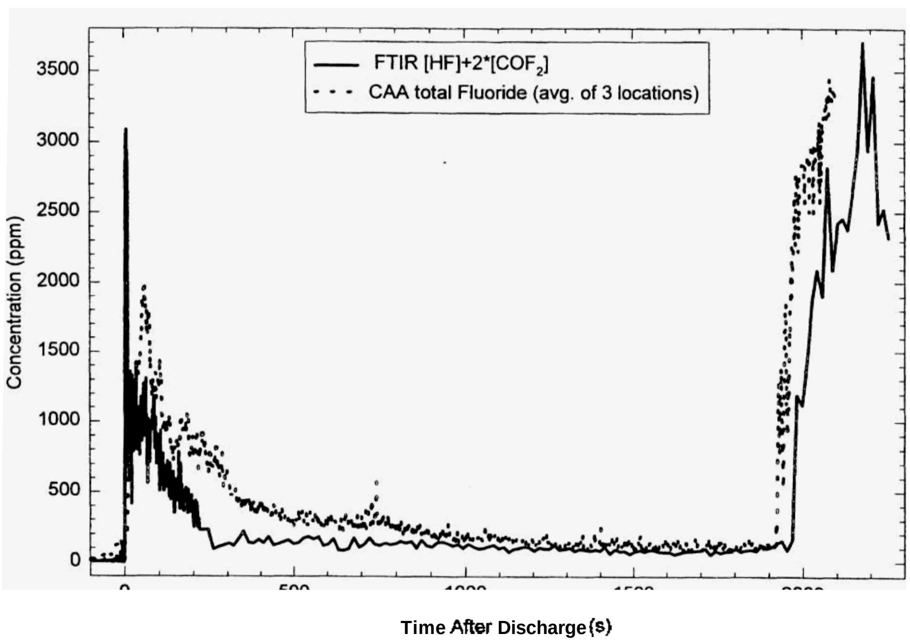

Figure 7. Comparison of FTIR and continuous acid analyzer data for acid gas concentrations as a function of time for a methanol/heptane **fire** suppressed by HFP. The secondary acid production at ca. 1900 sec following discharge is due to fire reignition.

For the test shown in Figure 7, the carbonyl fluoride peak concentrations were about 10-20% of those of the HF. For all the suppression tests performed, the ratio of CF_2O to HF was generally between 0.1 and 0.3. For "typical" fire suppression, roughly 30% of the fluorine from the reacted agent appears in the form of CF_2O.

CONCLUSIONS

FTIR spectroscopy is a versatile tool, which can detect and quantify many molecular species of importance for fire testing. When applied carefully, it can generate reliable data from in-situ measurements, which do not suffer from many of the uncertainties involved in sampling, especially for corrosive or reactive species. At the same time, FTIR has its own limitations, and is likely, in most cases, to supplement rather than replace other analysis methods. Furthermore, in a nonideal environment such as a fire test, care needs to be taken with many aspects of the data collection and analysis. FTIR spectrometers and data acquisition systems have become more automated in recent years, allowing a user to determine an analyte concentration without understanding what the instrument is measuring or how the analysis is being done. In a hostile and ill-characterized environment such as a fire test chamber, this approach is not recommended, especially when many of the species of greatest interest exhibit nonlinear absorbances due to finite resolution effects. With appropriate consideration to these pitfalls, FTIR can be successfully applied to the problem of fire testing.

ACKNOWLEDGMENTS

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