

# MEASUREMENT OF CARBONYL FLUORIDE, HYDROGEN FLUORIDE, AND OTHER COMBUSTION BYPRODUCTS DURING FIRE SUPPRESSION TESTING BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

Craig S. Miser, and W. Randolph Davis  
Aberdeen Test Center, Aberdeen Proving Ground, MD  
and

Kevin L. McNesby, Army Research Laboratory, Steven H. Hoke  
U. S. Army Center for Health Promotion and Preventative Medicine  
and

Michael K. Leonnig, Sci-Tech, Services Inc.

## ABSTRACT

The Fourier transform infrared (**FTIR**) spectrometer is used for gathering toxic byproduct data in real fire situations using Halon replacement candidate systems. **A** unique approach is used to obtain carbonyl fluoride calibration data. Hydrogen fluoride can be measured in all systems; carbonyl fluoride can be measured in most systems. Several other methodologies are used simultaneously to measure hydrogen fluoride, and these data are compared. Further work will be done to refine this methodology and in-situ measurement will be employed in the future.

## INTRODUCTION

The United States Army is committed to replacing its halon-based fire suppression systems. Evaluation of candidate replacement systems is a complex problem that requires the analytical measurement of chemical byproducts. Factors such as agent dispersion, extinguishment time, and bottle configuration can all affect the nature and quantity of the gaseous byproducts. Hydrofluorocarbon (HFC) based replacement systems, such as hexafluoropropane, heptafluoropropane, and octafluoropropane, stoichiometrically contain about twice the fluorine of Halon 1301 systems. These HFC-based systems also have extinguishing concentrations roughly twice that of Halon 1301, according to conventional cup burner data [1]. These factors combine to produce systems with about four times more total fluorine. This causes great concern for the production **of** carbonyl fluoride ( $\text{CF}_2\text{O}$ ) and hydrogen fluoride (HF) as toxic byproducts [2]. These byproducts have extremely low, short-term exposure limits (STEL) of **5** and **3** parts per million (ppm), respectively [3]. These extremely low exposure limits make  $\text{CF}_2\text{O}$  and HF high priority analytes during the evaluation of candidate systems **for** occupied spaces.

To test candidate replacement systems a hull penetration threat scenario has been developed. This scenario places a fuel cell in the path of a shape charge **jet**, which results in a heated fuel spray fire. Live fire shape charge penetration tests are very expensive and time consuming; therefore, a pressurized fuel spray simulator has been developed for fast repetitive testing (Figure 1). This apparatus consists of a fuel pressurization chamber, a spray nozzle, and an igniter. This simulator produces a **less** intense fire than that of the shape charge penetration (Figure 2), but it has proven to be a valuable tool when evaluating the potential of replacement systems and multiple configurations. Promising systems are then tested with a full shape charge penetration.

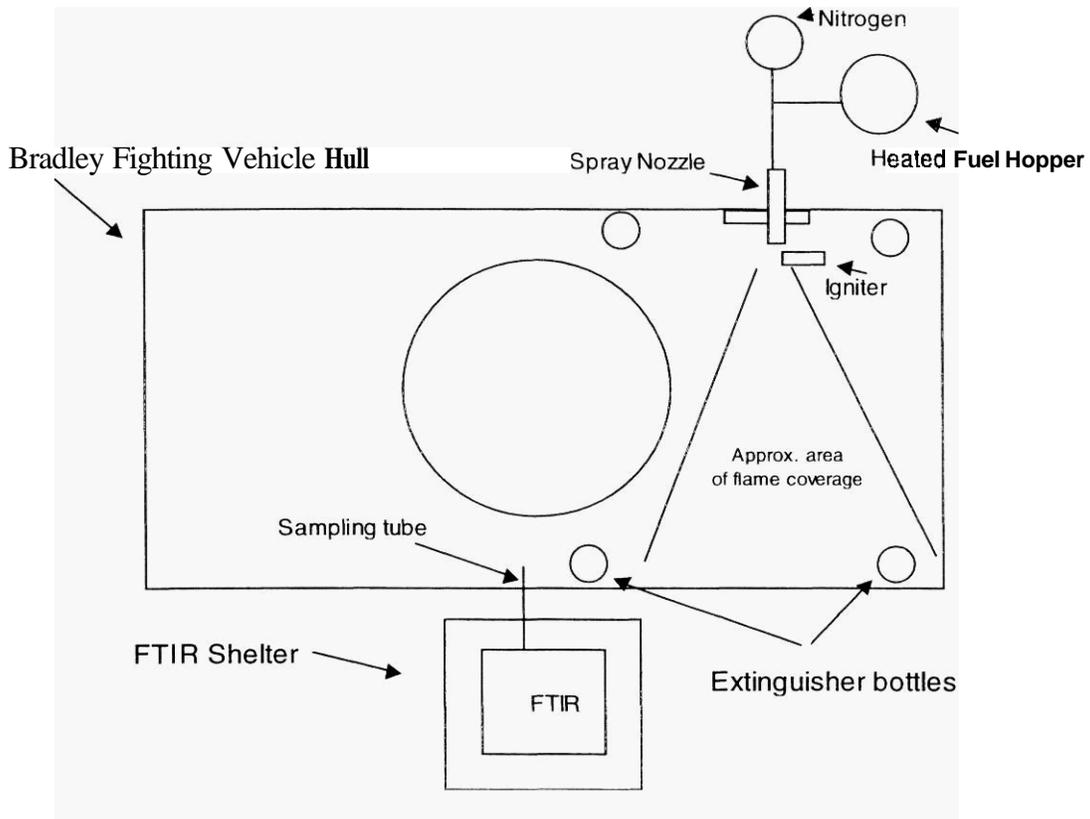


Figure 1. Schematic of the heated fuel spray (fireball) simulator.

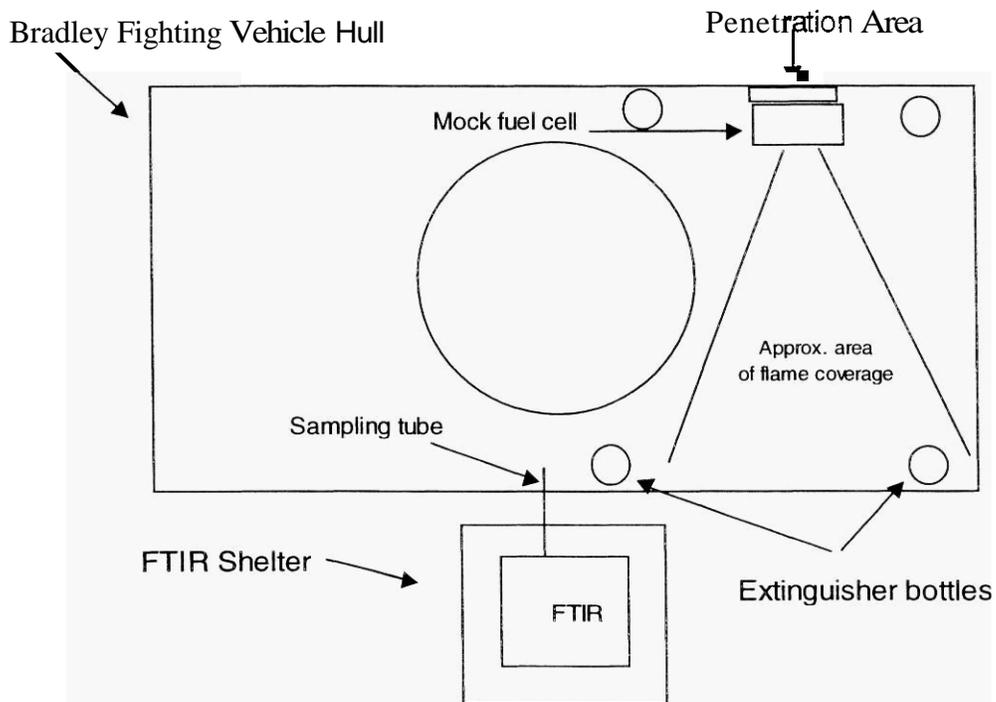


Figure 2. Schematic of the shape penetration.

Traditionally HF has been a difficult gas to measure because of its reactivity. Therefore, several techniques are currently used to measure toxic byproducts in this scenario. To maintain credible data, two National Institute of Safety and Health (NIOSH) approved methodologies have been employed in sorbent tube and impinger analysis. These methods, however, only produce dose or time-weighted-average (TWA) results. To more thoroughly investigate this environment, time-resolved techniques are necessary. Three time-resolved techniques available for measuring HF include an ion selective electrode monitor, Fourier transform infrared (FTIR) spectroscopy, and tunable diode laser (TDL) spectroscopy [4,5]. Each one of these methodologies has advantages to its use and they collectively provide an excellent view of the toxic byproducts. Although this paper will focus on the FTIR technique, the other methodologies will be used for comparative purposes [6].

## EXPERIMENTAL

A Midac Corporation G-5001-FH with zinc selenide interferometer optics is used with a multipass 10-m gas cell and a liquid nitrogen cooled mercury-cadmium-telluride detector. The gas cell is heated to 105 °C and it has a 2.3-liter volume. An Alcatel Pascal rotary vane pump is used to sample through the gas cell at a rate of 17 liters/min. A ¼-in piece of stainless steel tubing approximately 2 ft long is placed into the vehicle as shown in Figure 1. A piece of ¼-in polypropylene tubing is then used to complete the tubing to the FTIR inlet valve. A schematic diagram of the FTIR sampling train is shown in Figure 3.

All data presented are generated from spray fires with the fireball simulator. Generally, the fires are extinguished in 250 ms. The FTIR sampling pump is started approximately 3 sec prior to ignition and continues to sample for 5 min. Large quantities of soot and other particulates are produced during each fire, so all sampling train parts including the cell are cleaned every two or three trials. Cell throughput and line pressure are used as criteria for cleaning. The sample train was cleaned after every powder containing system.

Calibrations for HF and CF<sub>2</sub>O were done in the field with the FTIR system configuration intact. A commercially available cylinder of HF from Matheson Gas Products was cross-checked for accuracy by impingers and sorbent tubes (1465 ppm). This cylinder was diluted with nitrogen and mixed by mass flow controllers to produce various concentrations (Figure 4). Carbonyl fluoride is not available as a premixed pressurized gas; therefore, an alternative approach was taken. A lecture bottle containing 97 % pure CF<sub>2</sub>O was used in conjunction with a permeation tube device (Kin-Tek Inc.). The permeation tube has a maximum output of 2.5 liters/min, so a mass flow controller was used to bring the total flow up to 20 liters/min with nitrogen (Figure 5). This technique provides an accurate dilution of CF<sub>2</sub>O, but it severely limits the available concentration range.

A reference spectrum for CF<sub>2</sub>O and HF are shown in Figures 6 and 7, respectively. For CF<sub>2</sub>O the broader peaks at 1800, 1200, and 900 cm<sup>-1</sup> are obscured by agent absorptions during fire testing, so the sharp peak at 774 cm<sup>-1</sup> is used for quantification. Likewise, the p-branch peaks in the HF spectrum from 3700-3900 cm<sup>-1</sup> are obscured by water vapor. Some agent overtone absorptions interfere with the higher energy r-branch peaks; therefore, peaks R1-R3 are used for quantification. Figures 8 and 9 show the calibration curves produced for CF<sub>2</sub>O and HF, respectively. The corrected absorbance represents an absorbance normalized with respect to line pressure.

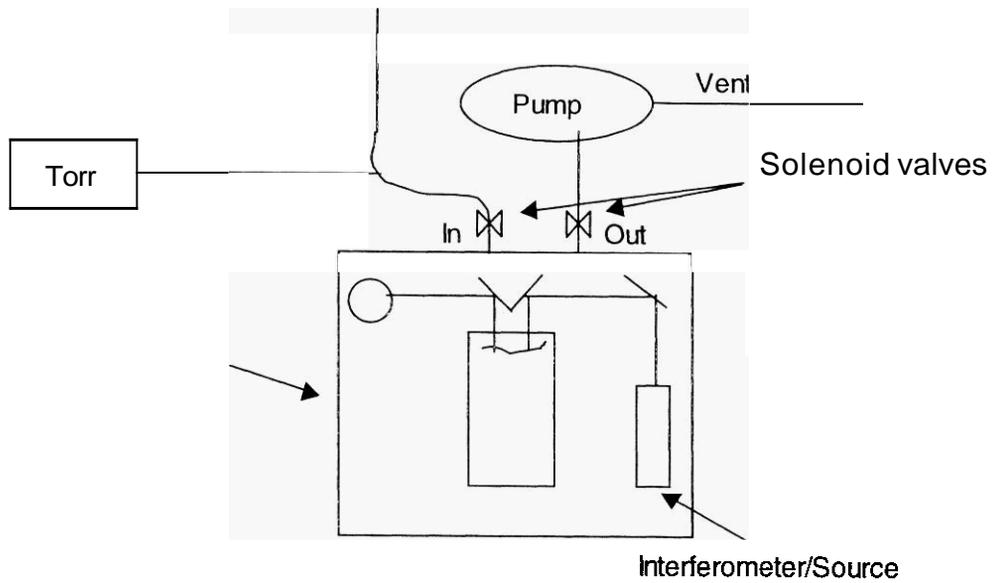


Figure 3. Schematic layout of the FTIR sampling train.

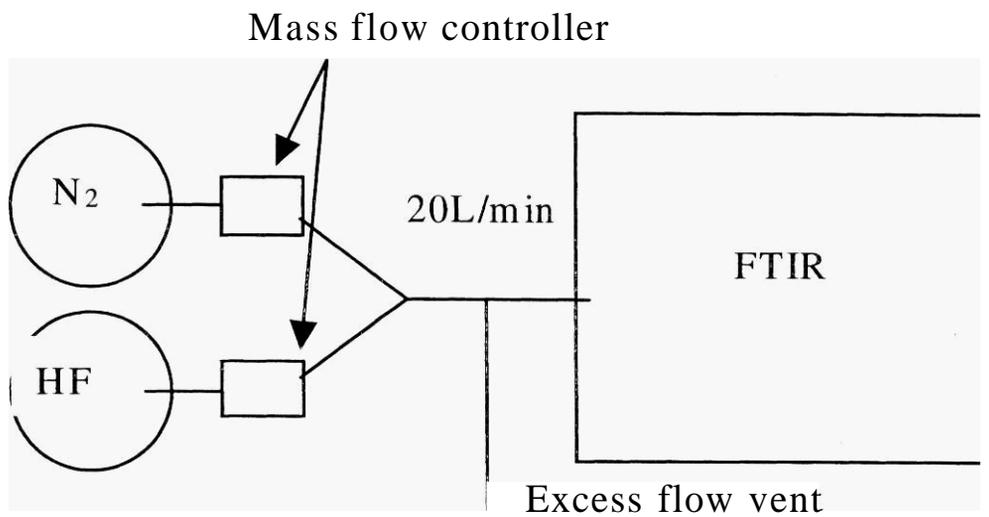
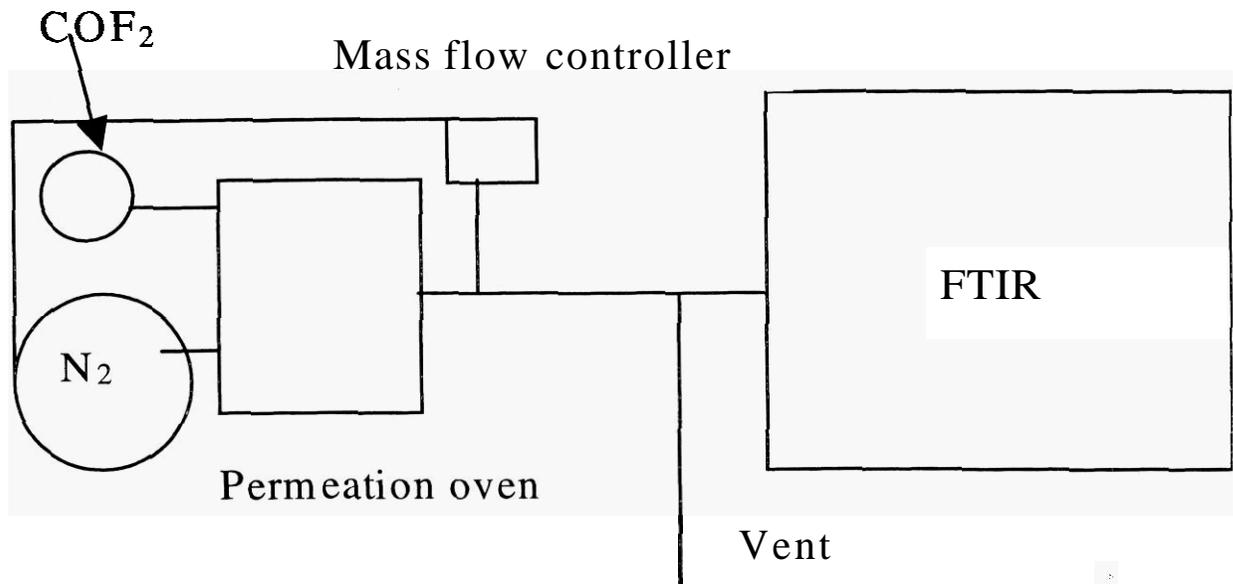
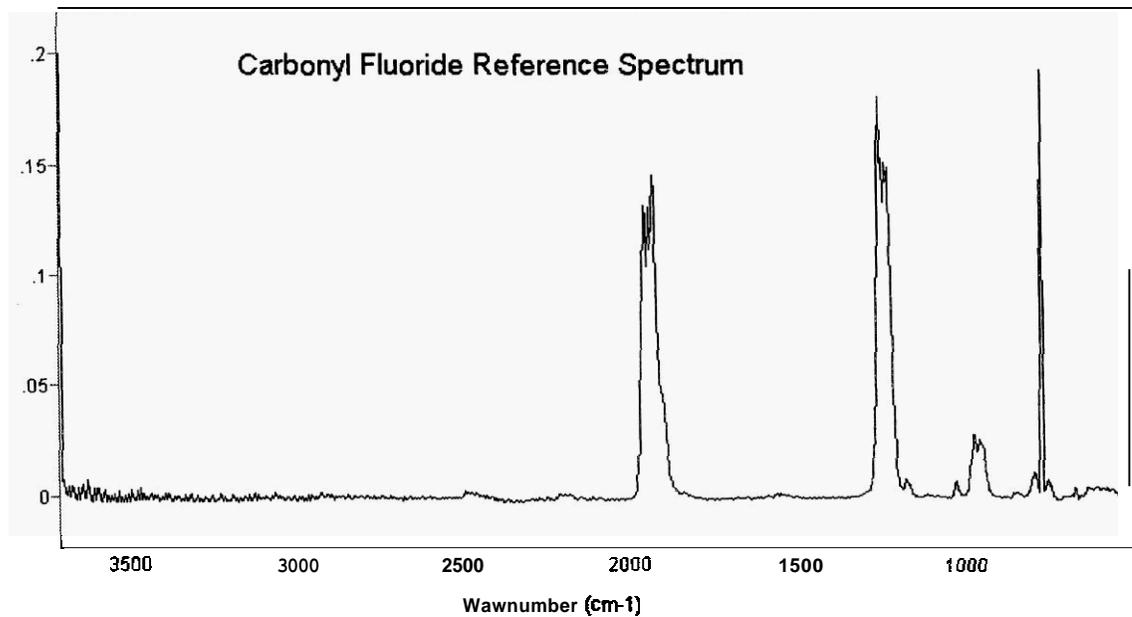


Figure 4. Schematic of the HF calibration.



**Figure 5.** Schematic of the  $\text{CF}_2\text{O}$  calibration.



Carbonyl fluoride, 100 ppm-meters in 1 atm.  $\text{N}_2$ ; 25 C.

**Figure 6.**  $\text{CF}_2\text{O}$  reference spectrum.

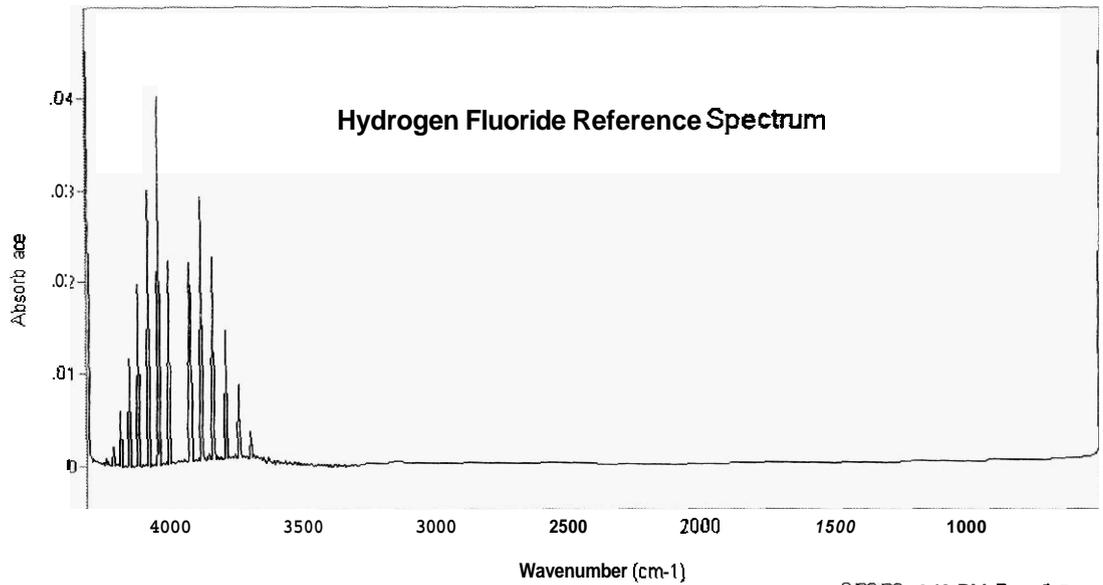


Figure 7. HF reference spectrum.

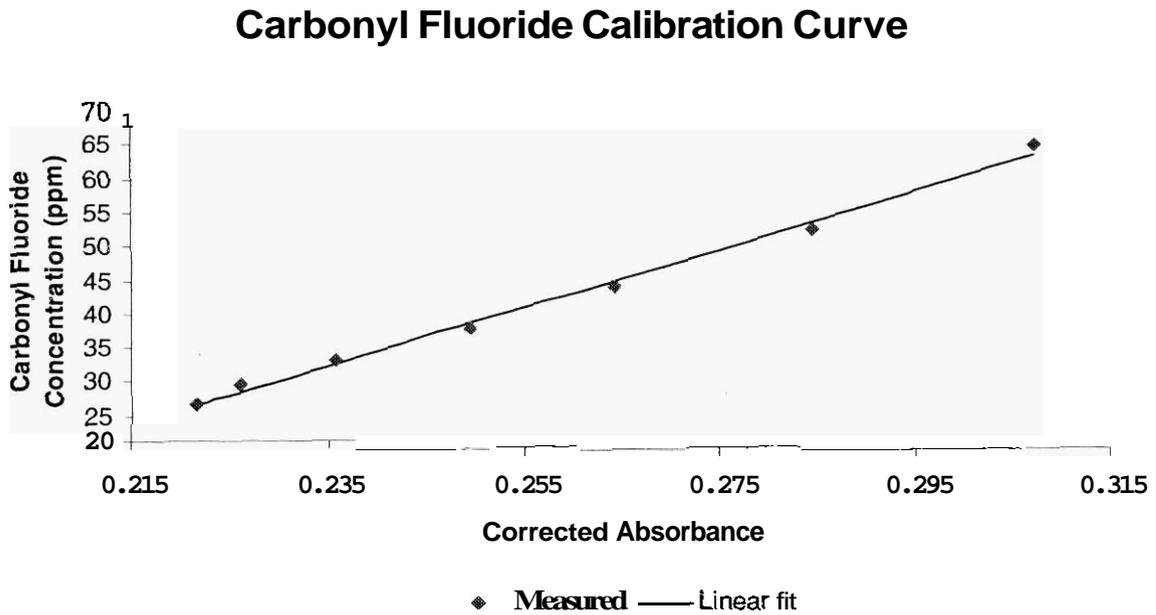


Figure 8. CF<sub>2</sub>O calibration curve.

### Hydrogen Fluoride Calibration Curve

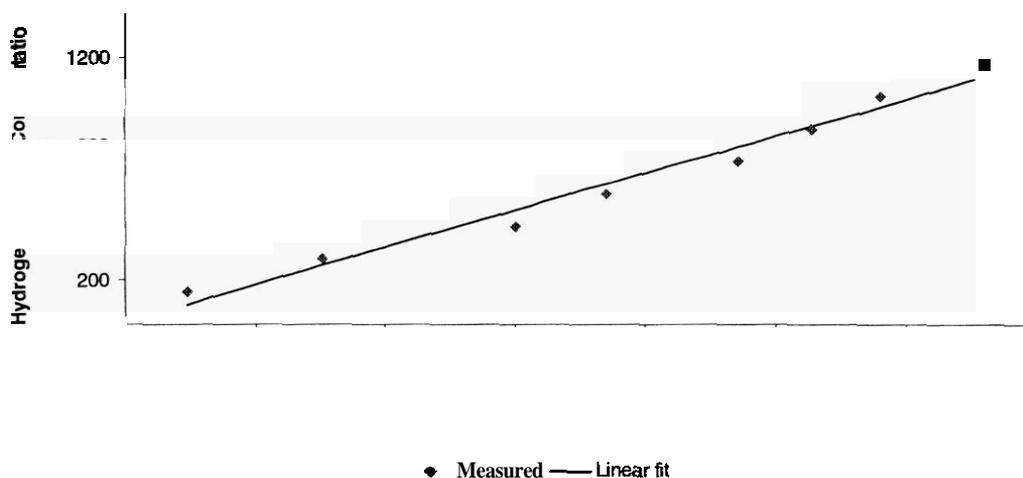


Figure 9. HF calibration curve.

After the suppression event, spectra are acquired every 1.5 sec at  $0.5 \text{ cm}^{-1}$  resolution. Galactic GRAMS software is used for acquisition of the multi-spectra file. This file is then split into individual spectra and analyzed with Midac Autoquant software. Autoquant uses a single point calibration file for quantification. The quantitative results are then corrected for the actual sampling pressure as compared to the calibration sampling pressure.

## RESULTS AND DISCUSSION

A spectrum from a Halon 1301 extinguished fire is shown in Figure 10. This spectrum reveals a clear view of the hydrogen fluoride R-branch. Carbon monoxide, water vapor, JP-8 fuel vapor, carbon dioxide, and Halon 1301 are visible in large quantities. Carbonyl fluoride is difficult to see because of spectral interferences around its major absorptions.

Figure 11 shows a spectrum of a hexafluoropropane extinguished fire. Spectral overtones dominate the spectrum between  $4200$  and  $4500 \text{ cm}^{-1}$ . Hydrogen fluoride R-branch rovibrational lines can be clearly seen. Small hydrocarbon fragments acetylene, ethylene, and methane are produced from inefficient burning. Water vapor, JP-8 fuel vapor, carbon dioxide, and agent are seen in very large quantities. A small spectral window around  $774 \text{ cm}^{-1}$  allows for carbonyl fluoride detection even though there is significant baseline liftoff.

A spectrum from a heptafluoropropane extinguished fire is shown in Figure 12. Spectral overtones from heptafluoropropane interfere with the hydrogen fluoride r-branch between  $4150$  and  $4300 \text{ cm}^{-1}$ . Water vapor, carbon dioxide, JP-8 fuel vapor, and agent are again present in large quantities. Acetylene, ethylene, and methane are present in visible quantities. Although there is significant baseline lift-off, carbonyl fluoride can be seen at  $774 \text{ cm}^{-1}$ .

Figure 13 shows a spectrum of an octafluoropropane extinguished fire. The hydrogen fluoride r-branch is free of interference although the p-branch is significantly obscured by water vapor.

The hydrocarbon fragments and JP-8 fuel vapor are not as prevalent in this spectrum, but this is due to a less intense fire and not the function of the agent itself. Carbonyl fluoride is obscured at  $774\text{ cm}^{-1}$ .

A concentration plot is shown in Figure 14 for a Halon 1301 extinguished fire. This  $\text{CF}_2\text{O}$  quantification is highly questionable because of the previously mentioned spectral interferences with Halon 1301. When compared to other trials, this fire reveals an odd shape for HF production. This information can be used to help diagnose extinguishing problems like nozzle configurations, bottle valve problems, or reflash. Figures 15 and 16 show concentration plots for hexafluoropropane and heptafluoropropane, respectively. Figure 17 represents the concentrations produced from a fire extinguished with heptafluoropropane with ammonium polyphosphate (APP) added powder. APP is a fire retarding agent, which is suspected to reduce HF production by free radical scavenging. A concentration plot for an octafluoropropane extinguished fire is shown in Figure 18. The erratic behavior of the  $\text{CF}_2\text{O}$  concentration is a product of the spectral interference discussed earlier.

The FTIR data acquired have been compared to other techniques in order to validate their results. Figure 19 shows sorbent tube, impinger, real-time ion selective electrode (ISE), and FTIR data. The non-FTIR based techniques are fluoride ion sensitive; therefore, in order to compare the data the  $\text{CF}_2\text{O}$  concentration has been multiplied by two and added to the HF concentration to produce a simulated fluoride result. The sorbent tube, impinger, and RT-ISE techniques are sensitive to aerosolized HF and other potential fluorine containing species. Although it is difficult to compare these data, there seems to be reasonable correlation.

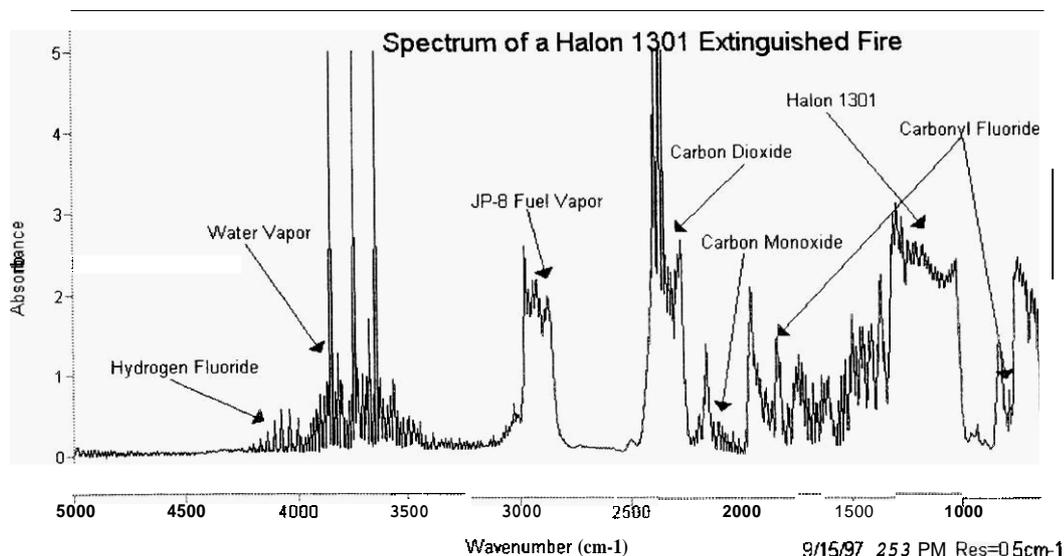


Figure 10. Spectrum of a Halon 1301 extinguished fire.

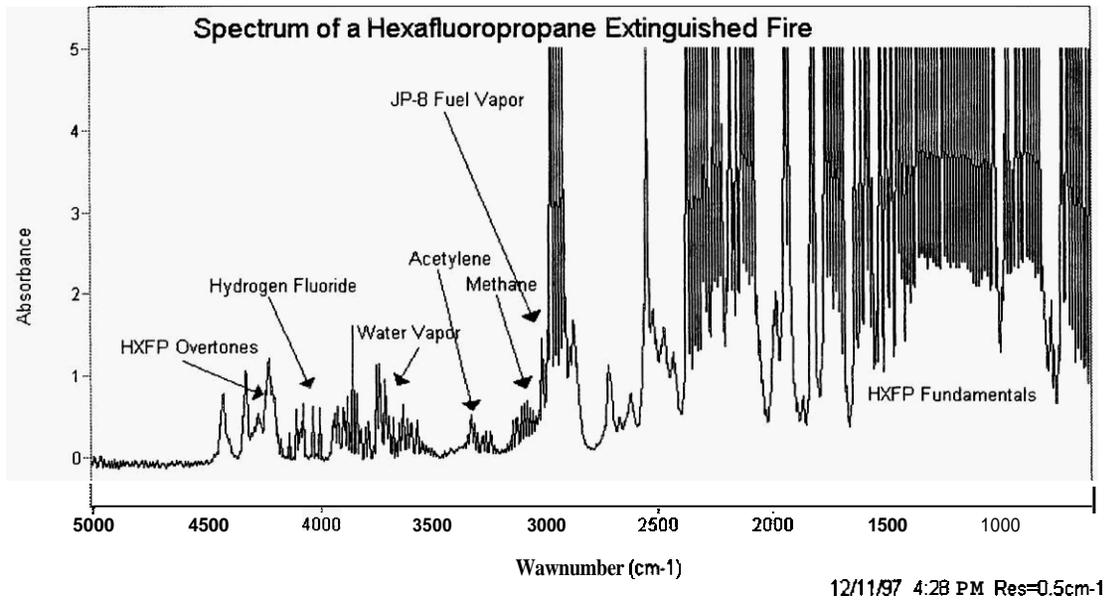


Figure 11. Spectrum of a hexafluoropropane extinguished fire.

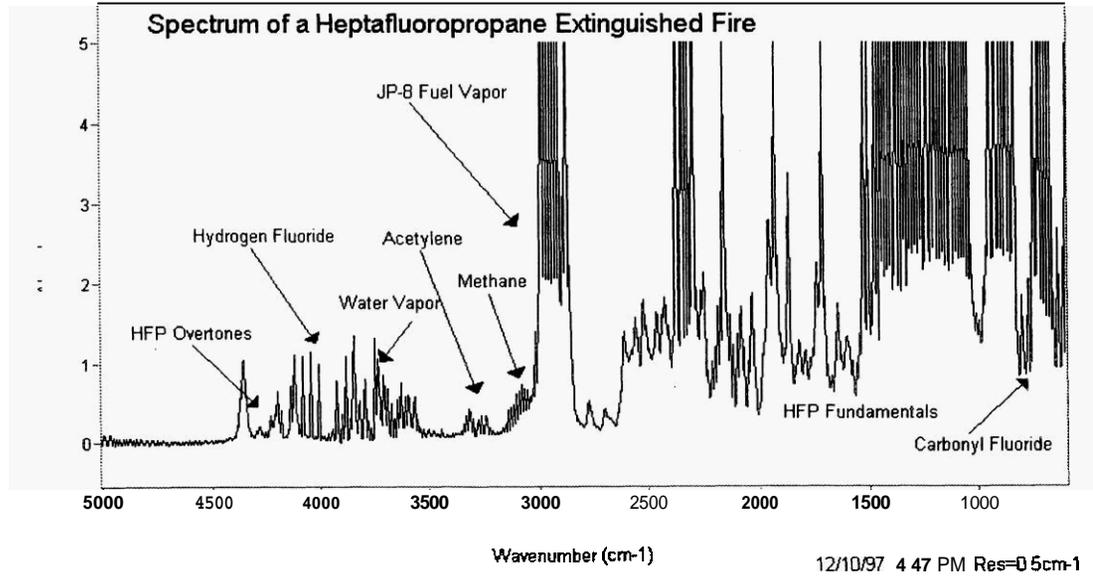
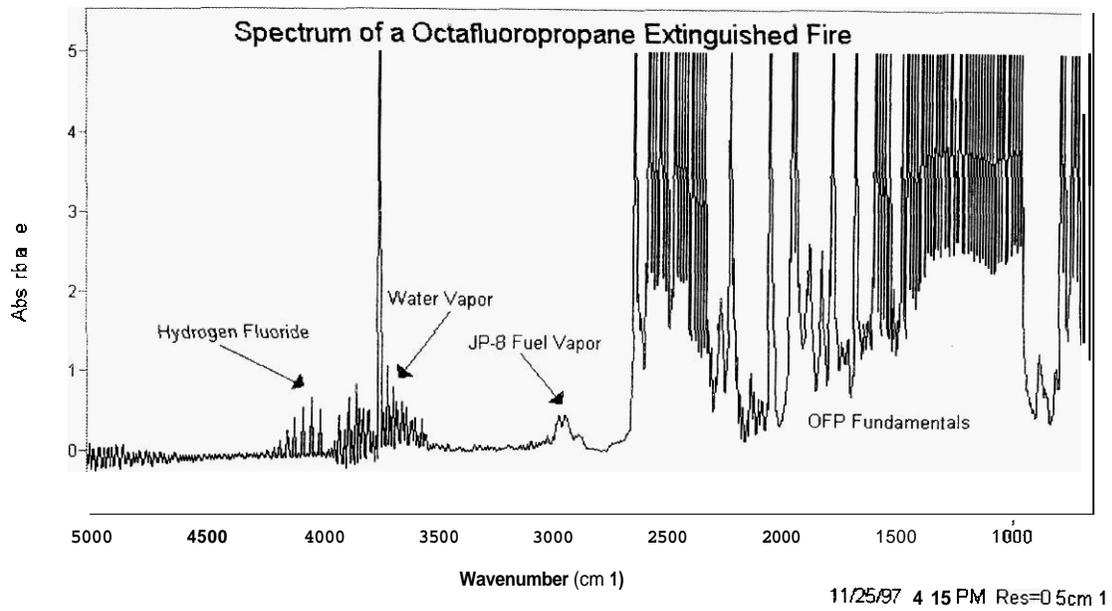
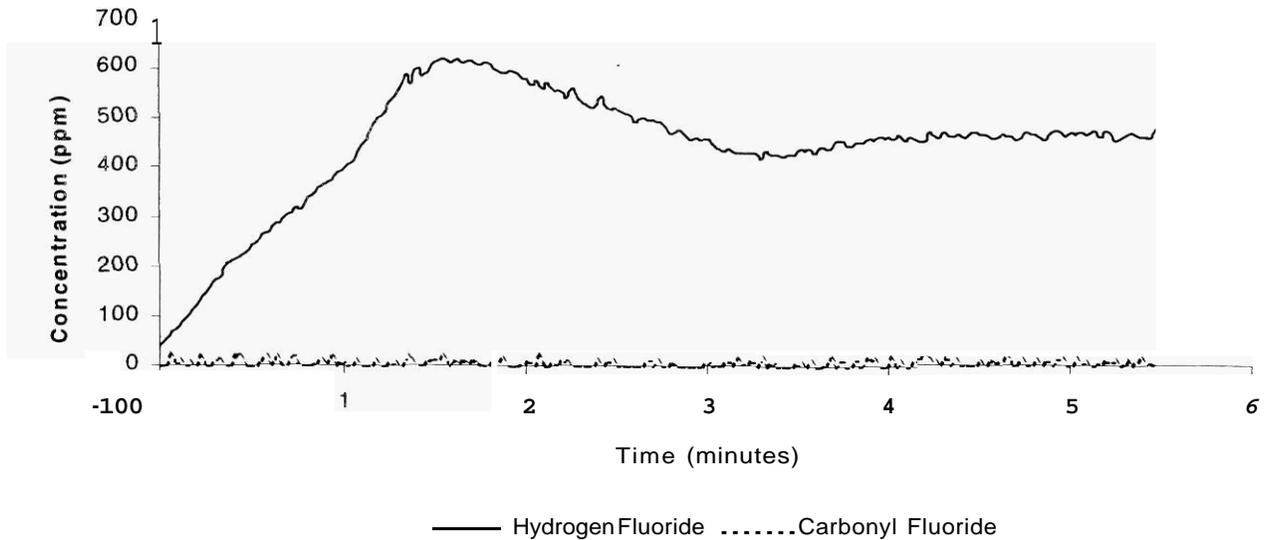


Figure 12. Spectrum of heptafluoropropane extinguished fire.

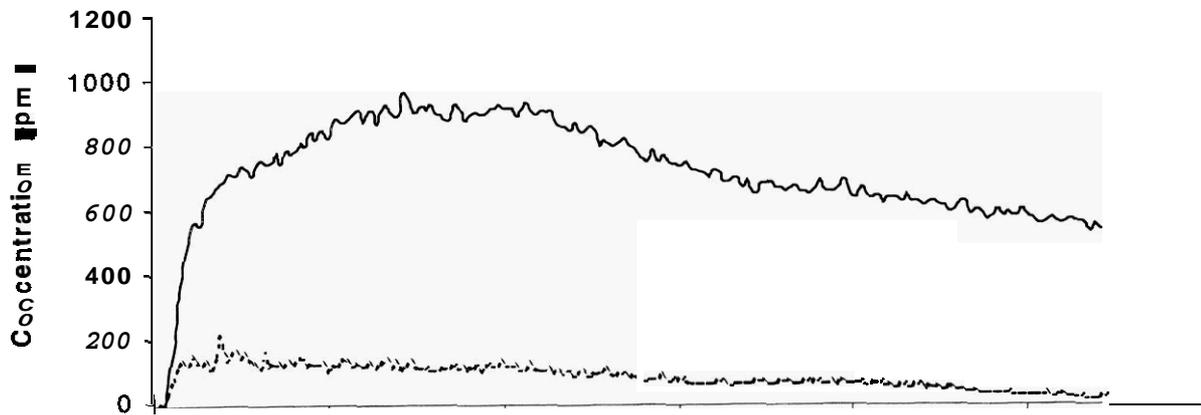


**Figure 13. Spectrum of an octafluoropropane extinguished fire.**

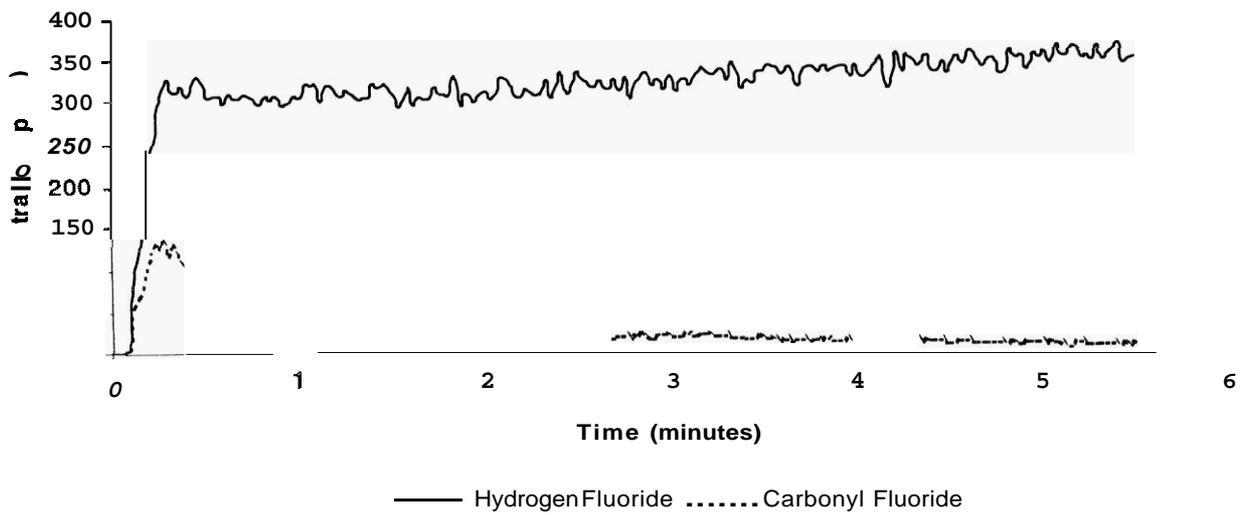
**Toxic Byproducts -Halon 1301 Extinguished Fire**



**Figure 14. Halon 1301 concentration plot.**



**Toxic Byproducts - Heptafluoropropane Extinguished Fire**



**Figure 16. Heptafluoropropane concentration plot.**

**Toxic Byproducts - Heptafluoropropane with Ammonium Polyphosphate Powder Extinguished Fire**

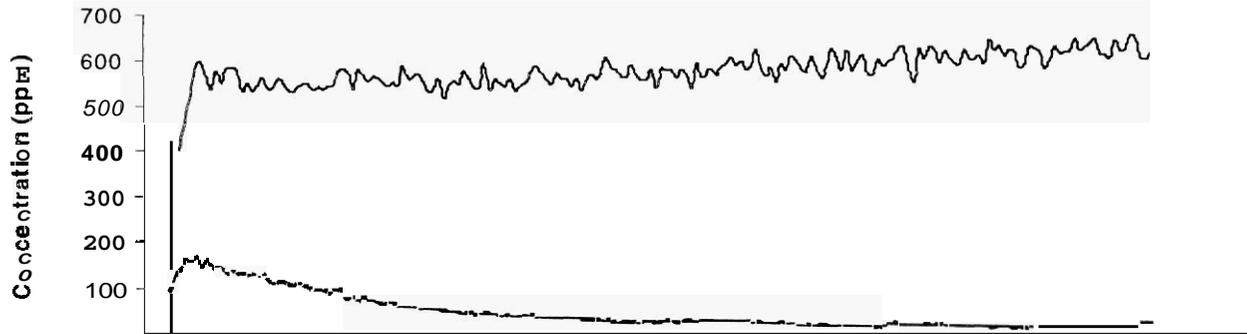


Figure 17. HFP/APP concentration plot.

**Toxic Byproducts - Octafluoropropane Extinguished Fire**

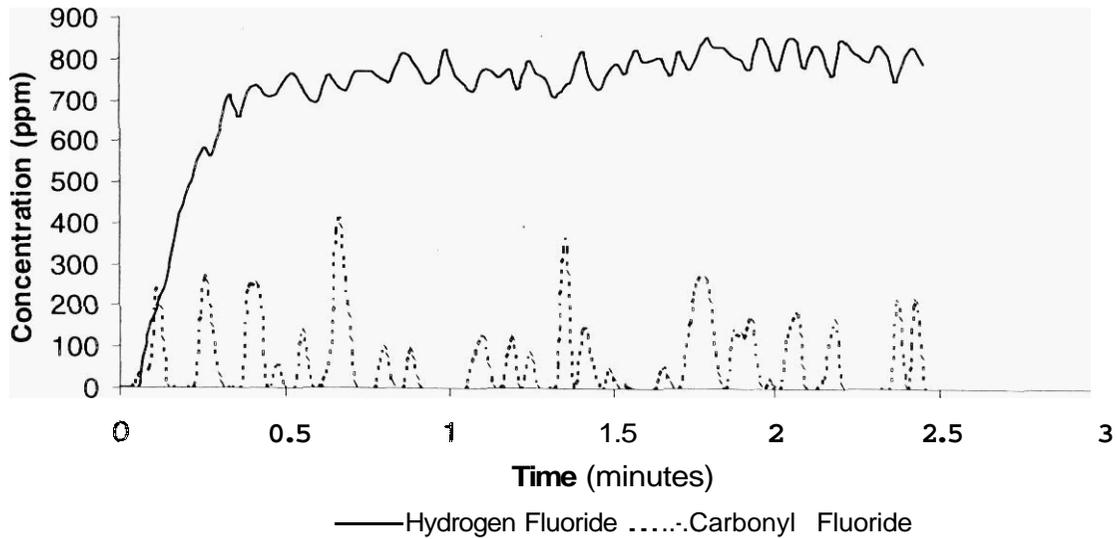
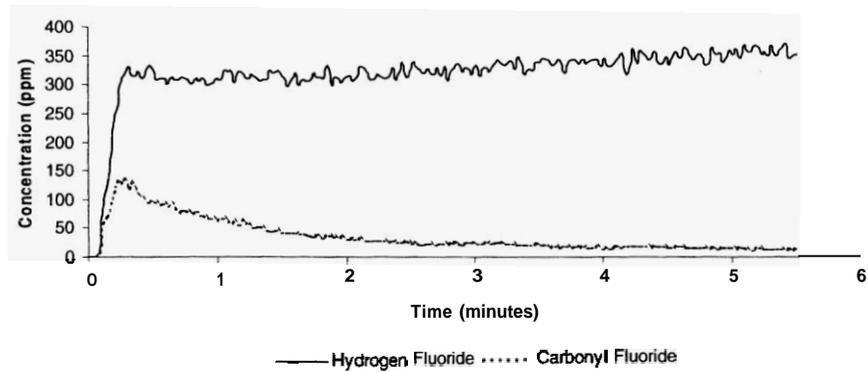


Figure 18. Octafluoropropane concentration plot

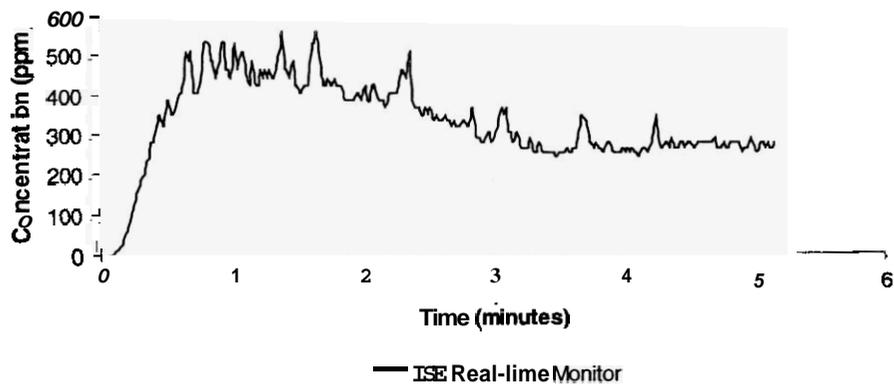
**Sorbent Tube 2-min TWA: 750 Dm**

**Toxic Byproducts - Heptafluoropropane Extinguished Fire**

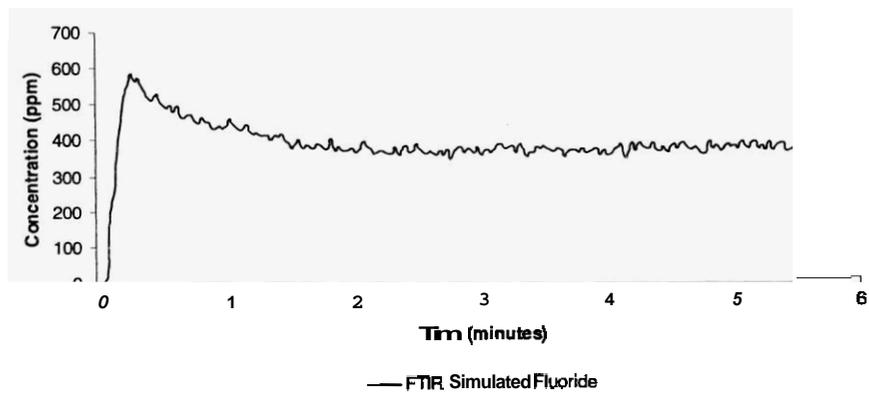


**Impinger 2-min TWA: 625 ppm**

**Ion Selective Electrode - HFP Ext. Fire**



**FTIR Simulated Fluoride - HFP Ext Fire**



**Figure 19. Comparison data for multiple techniques.**

## CONCLUSIONS AND FURTHER WORK

The FTIR technique is limited by spectral properties, which are fundamental problems that must be managed because they can not be changed. This technique provides a powerful tool to identify and quantify the gaseous species produced by an extinguished fire. The quantities of these species vary based on fire-out time. Fire-out times are controlled by factors such as nozzle configuration, bottle alignment, and the amount of agent. The FTIR has proven useful in determining good, satisfactory, and failure tests with respect to toxic byproducts. Further work is required to refine the FTIR technique. The first approach to improve the FTIR analysis will be to change to a 10-cm cell, which will reduce the intensity of the stronger absorbing species such as agent, water vapor, carbon dioxide, and fuel vapor. This will, in **turn**, open **larger** spectral windows, effectively reduce interferences, and allow for quantification of these strong absorbers.

The FTIR has provided quantitative results, which are comparable with NIOSH approved techniques for HF and CF<sub>2</sub>O. We will continue to produce quantitative results for other species to assess completely the health risks for these occupied spaces. Further work will be done to characterize CF<sub>2</sub>O response for the fluoride selective techniques. Specific laboratory studies will determine adsorption efficiency and hydrolysis rates. In-situ tunable diode laser measurements will ensue for oxygen (O<sub>2</sub>) and HF. These measurements will help to determine chemical effects of O<sub>2</sub> depletion and the interdependency of CF<sub>2</sub>O, HF, and O<sub>2</sub>. There are also plans to implement a fiber optic **gas** transmission probe that will allow for the in-situ measure of CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CF<sub>2</sub>O, and extinguishing agent.

## REFERENCES

1. S. P. Baldwin et al., "Cup Burner Values in Intermediate Size Fire Evaluation," *Proceedings of the 1992 International CFC and Halon Alternatives Conference*.
2. S. H. Modiano, K. L. McNesby, P. E. Marsh, W. Bolt, and C. Herud, "Quantitative Measurements by Fourier Transform Infrared Spectroscopy of Toxic Gas Production During Inhibition of JP-8 Fires by CF<sub>3</sub>Br and C<sub>3</sub>F<sub>7</sub>H," *Applied Optics*, 35, 4004-4008 (1996).
3. *1997 Threshold Limit Values for Chemical Substances and Biological Exposure Indices*, The American Conference of Governmental Industrial Hygienist, Cincinnati, OH.
4. K. L. McNesby, R.G. Daniel, A.W. Miziolek, S. H. Modiano, "Optical Measurement of Toxic Gases Produced During Firefighting Using Halons," *Applied Spect.*, 51, 678-683.
5. S. H. Hoke and C. Herud, "Performance Evaluation of Halogen Acid Gas Analyzer," *Proceedings of the 1996 Halon Options Technical Working Conference*, pp. 577-584.
6. S. H. Hoke, M. Clay, K. L. McNesby, C. S. Miser, M. K. Leonnig, S. Polyanski, C. Herud, W. Bolt, "Comparative Methods for Measuring Hydrogen Fluoride Gas as a Fire Suppression By-Product," *Proceedings of the 1997 Halon Options Technical Working Conference*.