DECOMPOSITION PRODUCT ANALYSIS DURING INTERMEDIATE-SCALE (645 FT^3) AND LABORATORY SCALE (6.18 FT^3) TESTING OF NFPA 2001 AGENTS

BY

Douglas S. Dierdorf, Ted A. Moore, and Stephanie R. Skaggs
Center for Global Environmental Technologies
New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque, New Mexico, USA 87131

INTRODUCTION

A number of agents are being developed as near-term replacements for Halon 1301 and are being considered for inclusion in the NFPA 2001 standard. While the agent list is extensive, only four halocarbon agents appear to meet the key toxicological requirement for use in occupied areas. That is that the **No Observed Adverse Effect Level (NOAEL)** for cardiac sensitization is greater than the proposed design concentration for a total flood system. The four agents that are likely to meet this requirement are listed in Table 1.

Table 1. List of Likely NFPA 2001 Agents

Halocarbon Number	Trade Name	Manufacturer
HFC-23	FE-13	DuPont
HFC-227ea	FM-200	Great Lakes Chemical
FC-3-1-10	PFC-410	3M Corporation
R-595	NAF-SIII	North American Fire Guardian

Earlier studies of the decomposition products from some of these agents[1,2] have shown that substantially larger quantities of toxic products, especially HF and COF_2 are formed during the extinction process than with Halon 1301. For this reason it was necessary to develop methods to determine the quantities of decomposition products formed during prototypical total flood extinguishment testing. Using these methods the formation of decomposition products during experiments can be determined.

EXPERIMENTAL CONSIDERATIONS

Two test chambers have been constructed to evaluate replacement agents in a total flooding fire scenario. The Laboratory Extinguishment and Emissions Test Chamber is shown in Figure 1. This chamber is approximately 22 inches per side, with a total volume of 6.18 ft^3. This chamber is constructed of steel and aluminum components which have been nickel plated to minimize reactions with decomposition gases. The other chamber is part of the NMERI Field Test Facility, and has been described elsewhere.[3]

FTIR spectroscopy was chosen as the method of chemical analysis for several reasons:

- Infrared spectroscopy allows the simultaneous determination of a variety of compounds.

- Spectra can be obtained rapidly, without the use of sampling bags or cylinders, minimizing concerns with absorption or contamination.
- Unexpected products can be readily identified.

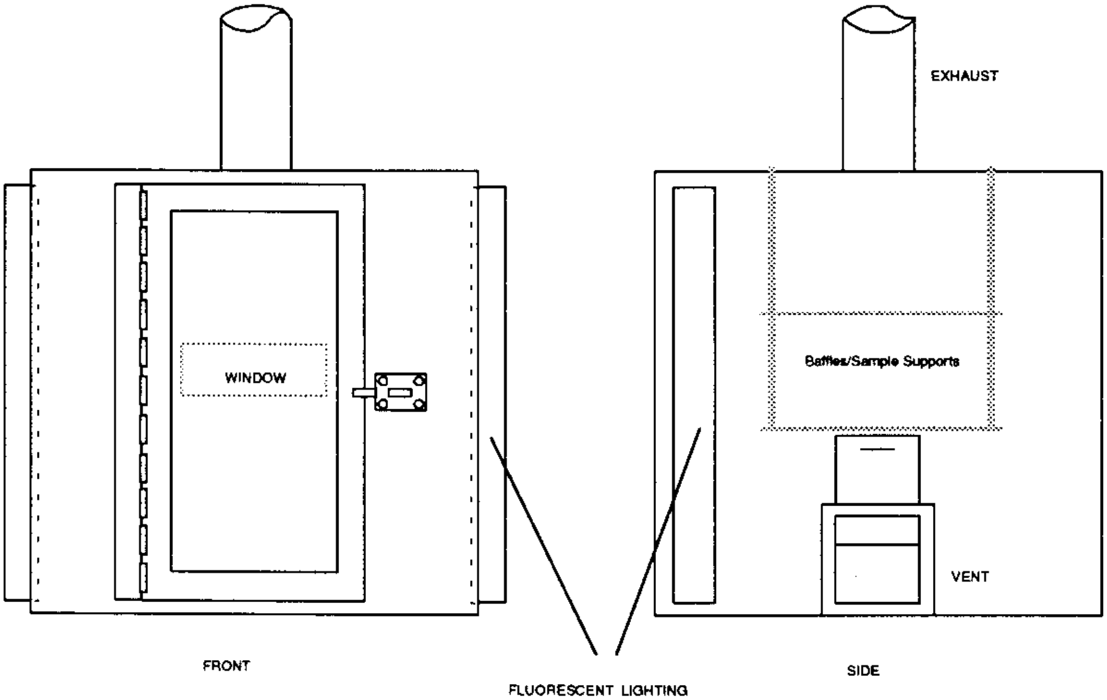

Figure 1. Diagram of the Laboratory Extinguishment and Emissions Test Chamber (LEETC)

Experiments in the LEETC were conducted in three different modes of operation, using NMERI's Perkin Elmer System 2000 FTIR Spectrometer, which is outfitted with optional (0.2 cm^{-1}) high resolution, time resolved infrared (TRIR), and infrared emission hardware and software. An Axiot optical system is used to transfer the infrared beam in various sampling configurations. In this work all spectra were recorded a 2 cm^{-1} resolution. Figure 2 shows schematically the three experimental modes. Comparison spectra are shown in Figure 3.

Spectrum A, recorded in the external absorption mode, is conventional in all respects. The intensities, band positions, and peak widths are in agreement with literature values. Because of the controlled sample conditions available in this mode, the concentrations of each of the constituent gases can be calculated with good precision. The primary concern with this experimental mode is the possible interaction of combustion gases with the sampling system. Figure 4 shows assignments of some key peaks for HFC-227ea and its decomposition products. Spectra for the experiments in the field test chamber were also collected in the external mode.

Spectrum B, recorded in the *in situ* absorption mode, shows some of the advantages and disadvantages of this mode when compared with the external mode. Note, particularly the increased complexity of the HF region from 4300 to 3600 cm^{-1}. This results from the "hot" bands of excited hydrogen fluoride produced by the interaction of the extinguishing agent and the flame. Also of interest is the broadening of the carbon dioxide band at about 2360 cm^{-1}. These features are only observable in the *in situ* mode and provide significant information about the detailed interaction of the agent and flame. The use of this information is discussed in the following section on time resolved infrared (TRIR) spectroscopy . These "hot" spectral features complicate the determination of quantitative concentrations and are quite dependent on the movement of the flame in response to air currents.

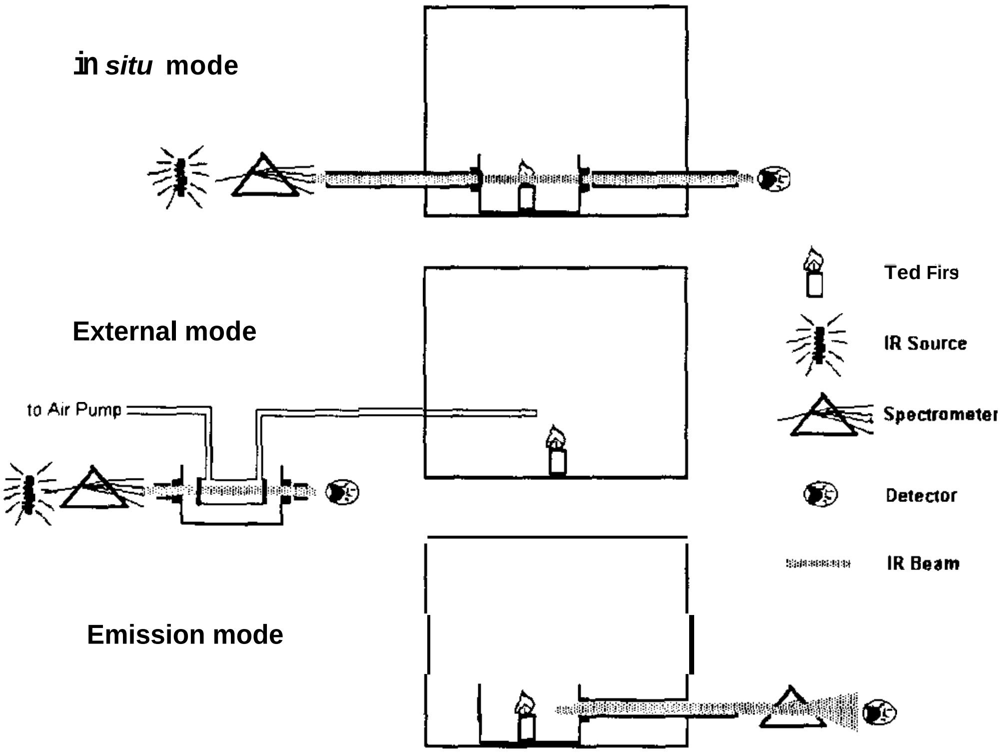

Figure 2. Schematic diagram of FTIR experimental modes

Spectrum C was recorded in the emission mode. This mode clearly shows the effect of the excited molecules whose emissions are the primary features of the spectrum. Black body radiation creates an overall emission background. An interesting feature of this spectrum is the series of downward oriented **peaks** below 1500 cm^{-1}. These result from the absorption **of** energy by the agent in the space between the flame and the IR window. The lack of agent emission peaks suggests that the agent is entirely consumed by the flame. A detailed spectroscopic study of flame-agent interactions was beyond the scope of this study, but would yield valuable information useful in designing second generation agents and minimizing decomposition products.

A special feature of the NMERI FTIR spectrometer is its ability to collect spectra at very high data rates. At low resolution, 16 cm^{-1}, 20 spectra per second can be collected. This resolution is not adequate for detailed gas-phase spectroscopy, which is often performed at resolutions **of** 0.2 cm^{-1}. This resolution is far too high to enable **spectra** collection in a time resolved **mode. For** these experiments a compromise resolution of *2* cm^{-1} was chosen allowing a data acquisition rate of approximately **2.5 spectra** per second. Figure *5* **shows** an example of a time resolved "stack" plot produced from the spectra recorded during an extinguishment experiment.

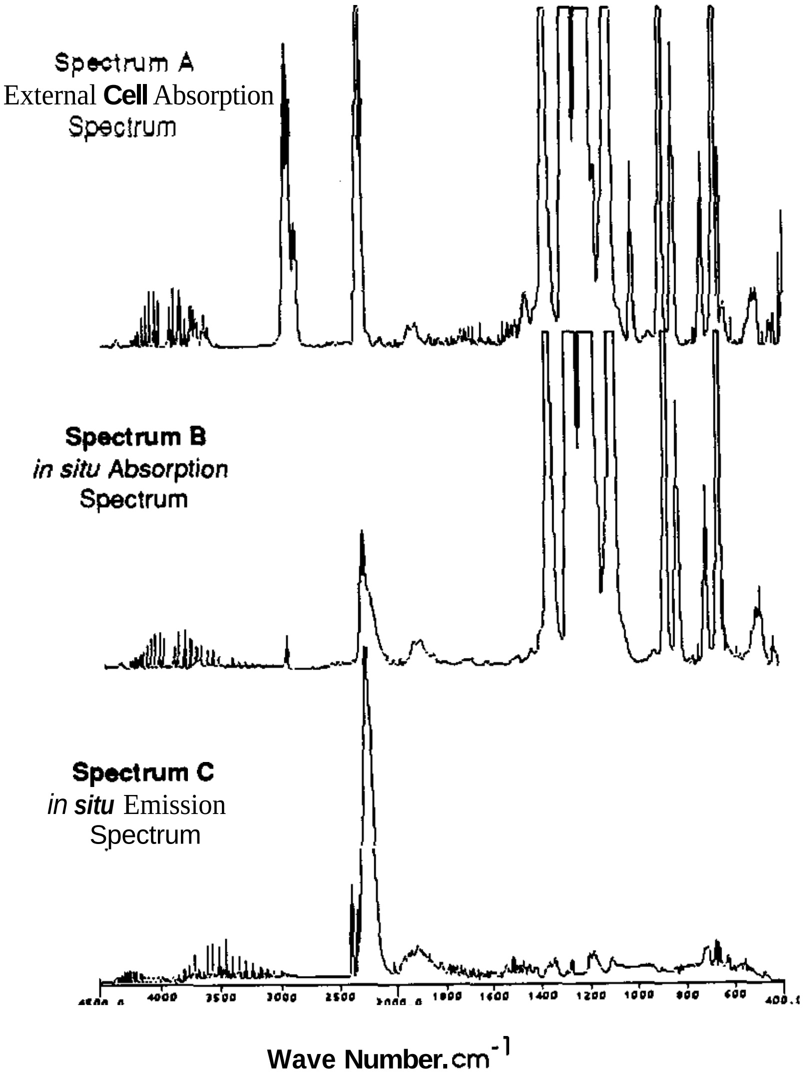

Figure 3. Representative spectra during agent discharge in each experimental mode. HFC-227ea

RESULTS

Laboratory Scale

The **LEETC** experiments provide an interesting qualitative comparison of three replacement agents, and Halon **1301.** Figures 6 and 7 show time resolved plots of typical extinguishment experiments in the HF/Hydrocarbon and $CO_2/CO/COF_2$ regions respectively. Several distinctive features are apparent in these spectra.

1. HF and COF_2 concentrations rise and fall rapidly during extinguishment. This is an effect of the observations being made in the flame region. **Also,** the rise and fall occurs as the agent and flame interact followed by diffusion of the products into the total chamber volume.
2. The sudden appearance of heptane absorptions indicates extinction of the flame.

3. **Distinctive differences exist between Halon 1301 and the other agents.**

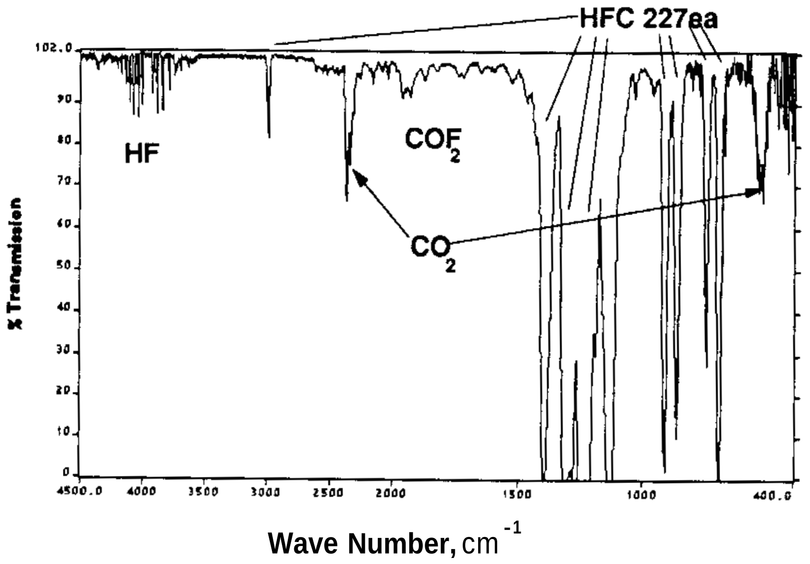

Figure 4. Typical Spectral Assignments

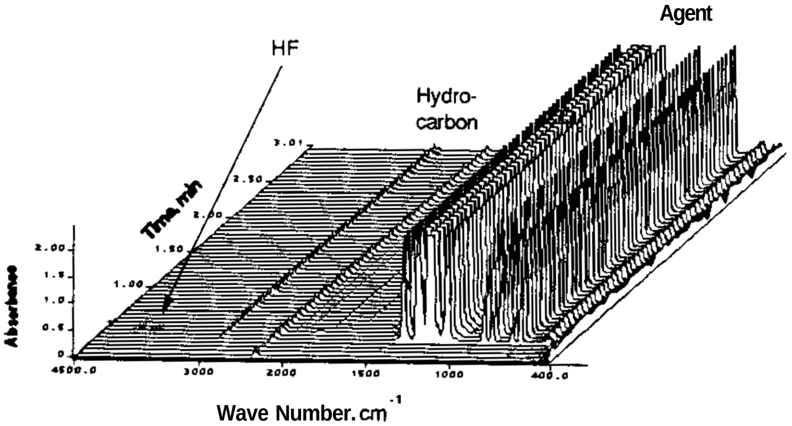

Figure 5. Time resolved stack plot for an entire extinguistiment experiment

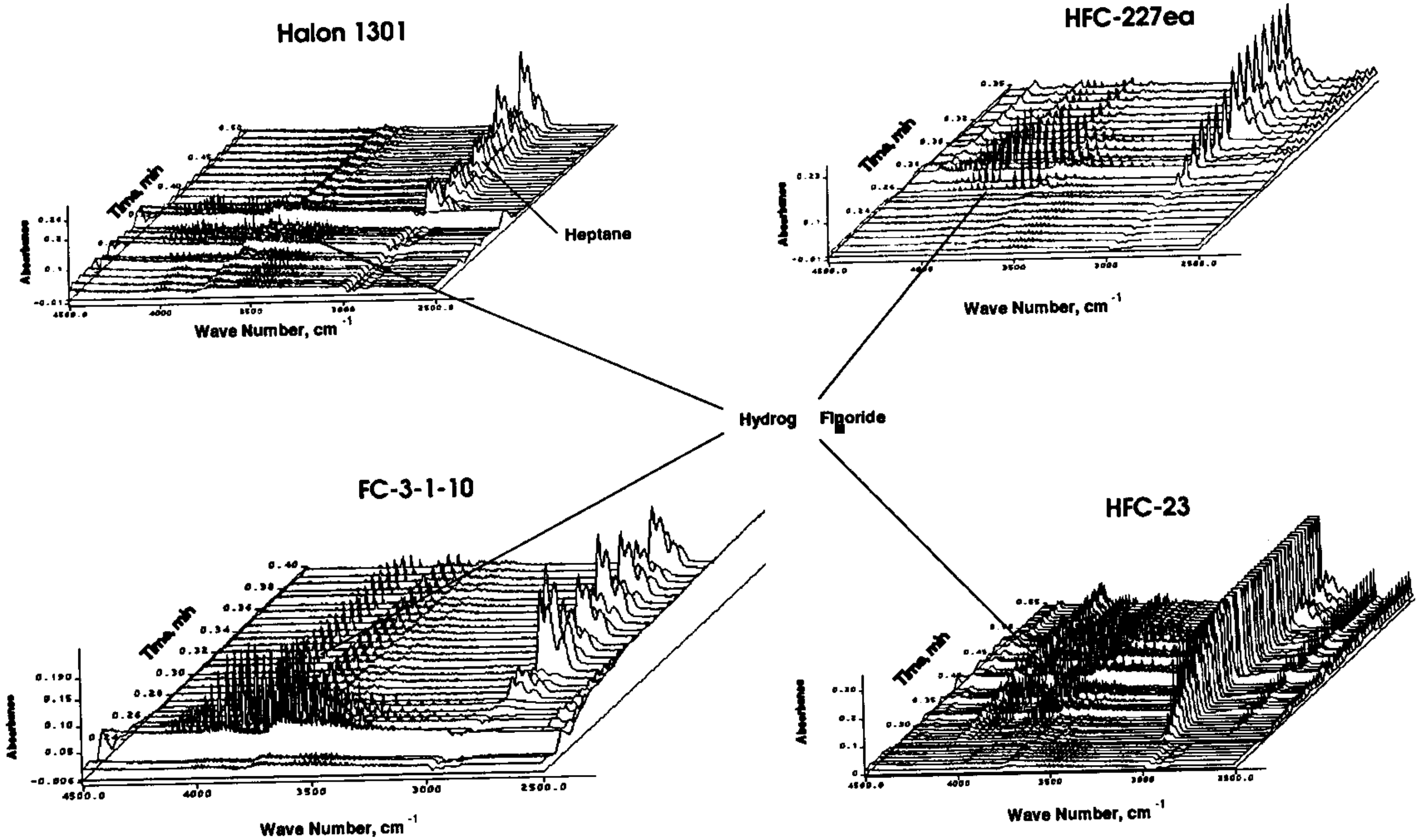

Figure 6. Comparison plots of various agents in the LEETC *in situ* mode experiments. The relatively intense HF peaks appearing during the extinguishment event include "hot" bands originating from excited vibrational states. Note the relative intensity of the HF peaks in the replacement agents compared to Halon 1301. Also note the appearance of additional hydrocarbon bands immediately after extinction, these bands are characteristic of the heptane fuel.

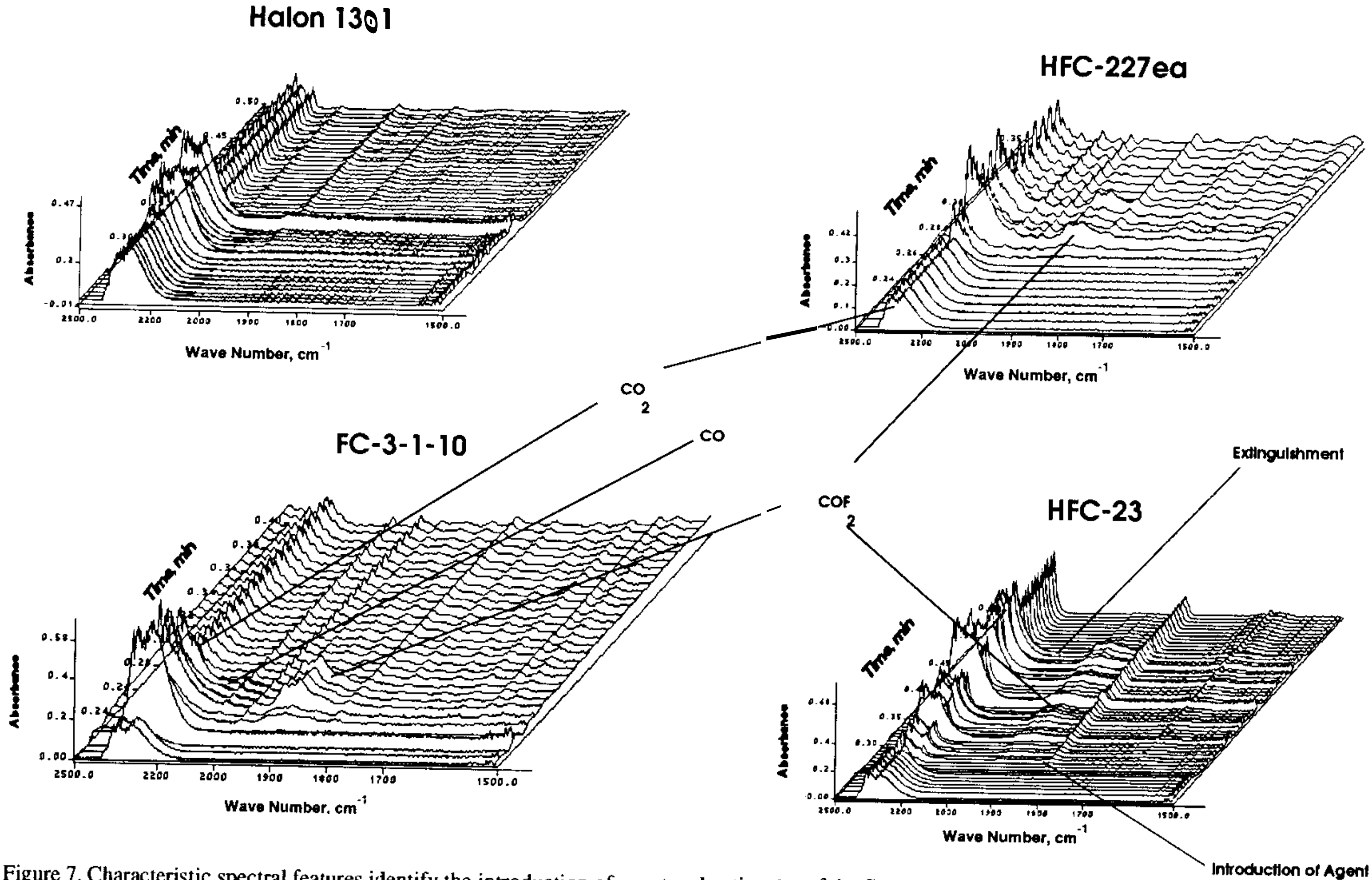

Figure 7. Characteristic spectral features identify the introduction of agent and extinction of the flame. Note the similar features in the other TRIR stack plots.

In another set of experiments, much larger tires were examined using the external sampling mode. In one of these experiments, an unusual set of peaks appeared in the stack plot shown in Figure 8.

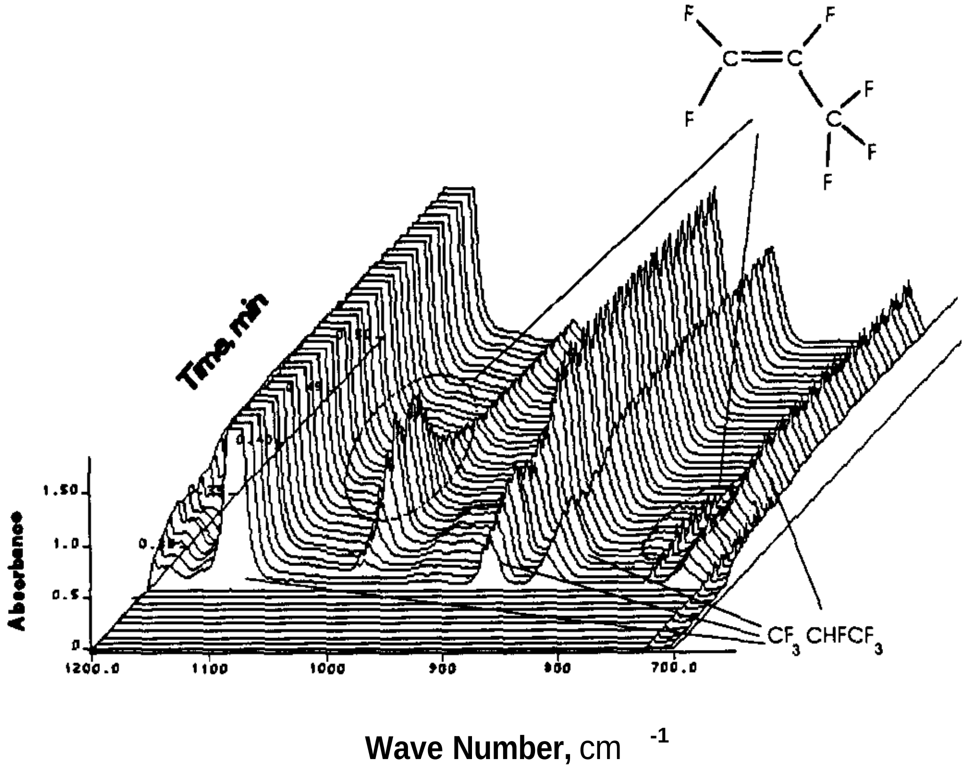

Figure 8. Peaks highlighted by TRIR in a test of HFC-227ea were identified by comparison to reference spectra.

The new peaks were identified by comparison to reference spectra! The new decomposition product, perfluoropropene ($CF_3CF{=}CF_2$) is the expected product formed by dehydrohalogenation:

Reaction 1. $CF_3CFHCF_3 \Rightarrow CF_3CF{=}CF_2 + HF$

This kind of analysis provides important information about actual combustion/extinguishment machanisms. Also, agents may form potentially harmful combustion products which are not identifiable when measured by traditional analysis methods (ie. grab samples and gas chromatography). For example, examination of key industrial hygiene literature[5] indicates that perfluoropropane is only moderately toxic. However, other products which might be derived from hydrofluoropropanes, and butanes could create much more serious toxicological problems.

Field Scale

Detailed examination of the decomposition product formation in the field scale (645 ft^3) is beyond the scope of this paper, however Figures 9 and 10 present some summary results. Figure 9 shows the HF formation with a variety of agents at different tire sizes and short extinguishment times (< 20 seconds.) Fire sizes are indicated in terms of the tire pan surface area to chamber volume ratio in units of

ft^2 per 1000 ft^3. While this ratio has been commonly used in the past, there is no theoretical basis to confirm its validity. It should be noted that the 0.62 $ft^2/1000\ ft^3$ fires were in the intermediate scale chamber and the 0.69 $ft^2/1000\ ft^3$ fires were in the LEETC. Figure 10 indicates that the variation in the 0.62 $ft^2/1000\ ft^3$ fires appears to be an effect of the time required for extinction. Long extinguishment times allow greater quantities of agent to interact with the flame and form higher concentrations of combustion products. The diagonal lines show the fits which are obtained for Halon 1301, and all of the other agents combined. Individual plots for single agents did not vary greatly.

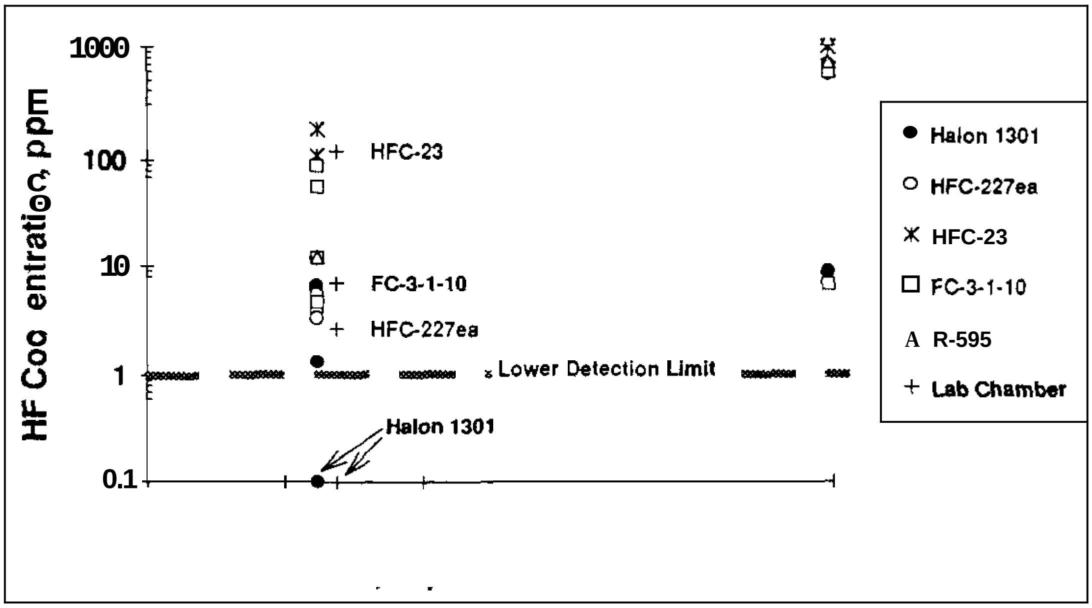

Figure 9. HF concentration as a function of fire size for fires extinguished in less than 20 seconds. Note at small fire sizes there is a large variation in HF formation.

CONCLUSIONS

LEETC testing in various FTIR modes indicates the power of FTIR as a method for determining the decomposition product formation during extinguishment. This power is enhanced by the use of time resolved techniques to sample at high frequency during the extinguishment event. Of special note was the direct observation of $CF_3C{=}CF_2$ during experiments with HFC-227ea.

Intermediate field scale testing of NFPA 2001 agents indicates an approximate 10 fold increase in HF production versus Halon 1301. This decomposition product formation for the new agents is also much more dependent on the time to extinguish and fire size than in the Halon 1301 case.

ACKNOWLEDGMENTS

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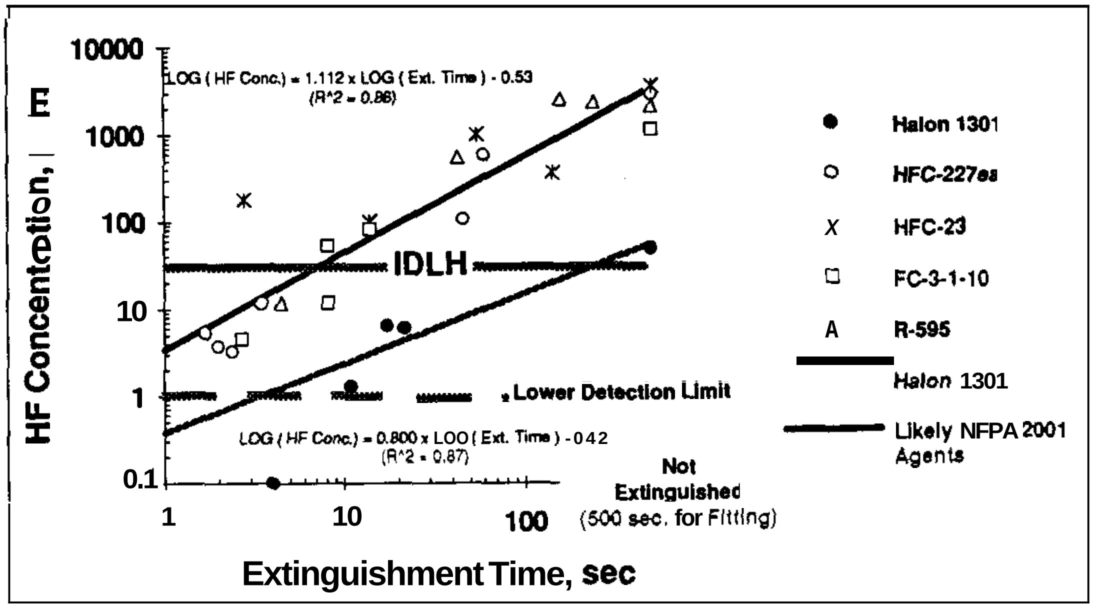

Figure 10. HF concentration as a function of extinguishment time for 0.62 $ft^2/1000\ ft^3$ fires in the intermediates scale test chamber. IDLH = Immediately Dangerous to Life and Health.

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