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Toxic Gas Measurement in Inhibited Flames Using Tunable Diode Laser Spectroscopy

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Introduction

The investigations at the Army Research Laboratory (ARL) into Halon inhibition of flames began several years ago as a project' to elucidate mechanisms of suppression using low pressure premixed flames. This investigation was expanded to include atmospheric pressure counterflow diffision flames, and was further expanded by an ongoing collaboration with the Aberdeen Test Center (ATC) to evaluate new test methods and equipment for suppression of real fires. Since beginning these investigations, we have also been measuring production of toxic gases during and following Halon inhibition of flames. The purpose of this paper is to provide an overview to this aspect of the work, and to describe some recent results, using new laser-based diagnostics, of toxic gas production during Halon inhibition of real fires in ordinary and demanding environments.

The fire types investigated for production of toxic gases during inhibition by Halons range from laboratory-scale controlled flames to air-fed jet fuel (JP8) pan fires. Laboratory controlled flames include low pressure premixed CH_4/O_2 and CH_4/air flames and atmospheric pressure CH_4/O_2 and CH_4/air counterflow diffusion flames[2,3]. Real fires include open-air JP8 pan fires and confined JP8 pan **fires.** Gas production was measured using optical dignostics including mid-infrared tunable diode lasers (MIR-TDL), near-infrared tunable diode lasers (NIR-TDL), and Fourier transform infrared (FT-IR) absorption and emission spectroscopy. Inhibitants investigated include CF_3Br (Halon 1301), C_3F_7H (FM-200), $C_3F_6H_2$ **(FE-36),** C_2F_5H **(FE-25),** CF_3H **(FE-13),** C_2F_5H (HFC-125), and CF_4.

Laboratow-Scale Fires

Initial measurements in our lab using FT-IR spectroscopy to measure spectra through low pressure (20 torr) premixed CH_4/O_2 flames inhibited by up to 15% CF_3Br showed no evidence of CF_2O formation, even though calculations indicated[4] that CF_2O should be formed in small amounts. Figure **1** is an FT-IR emission spectrum of gases present **10** mm above the burner surface of a 17 torr premixed CH_4/O_2 flame to which 3% CF_3Br has been added. Although significant amounts of HF are detected near 4000 cm^{-1}, there is no evidence of CF_2O gas (strongest feature near 1900 cm^{-1}) at any height within the flame. Figure 2 shows the FT-IR absorbtion spectrum measured through an atmospheric pressure counterflow diffusion CH_4/air flame inhibited by **1.3%** CF_3Br. In this spectrum, formation of CF_2O gas is measured near **1900** cm^{-1}, as well as CO **(2100 cm^{-1}), HBr** (2700 cm^{-1}), and HF (4000 cm^{-1}). The reason that more species are observed in the atmospheric pressure counterflow diffusion flame than in the low pressure premixed flame is because the peak temperature in the counterflow diffusion CH_4/air flame is several hundred Kelvins lower[3] than in the low pressure CH_4/O_2 flame. Species generated in the lower temperature flame are not oxidized as rapidly as in the low pressure CH_4/O_2 flame. This allows a buildup of concentrations of CF_2O, CO, and HBr in the counterflow diffusion CH_4/air flame. These gases may then be measured easily using an optical diagnostic (FT-IR) employing **a** resolution (0.5 cm^{-1}) much larger than a typical ro-vibrational linewidth' of the species of interest (-0.05 cm^{-1} for CO).

These initial studies using FT-IR spectroscopy provided spectroscopic evidence that gas production during Halon inhibition of fires was highly dependent on the fire type and conditions. In our investigations aimed at validating flame modeling calculations', we used the low pressure flame because at low pressure, flame zones are expanded, and more information is available from optical measurements using our finite spatial resolution (typically 1 mm). However, for measurements of species at low concentrations within the low pressure flame, we are limited by the optical resolution of most commercial FT-IR spectrometers (usually on the order of 0.5 cm^{-1}).

To overcome these resolution/sensitivity limitations, we employ tunable diode laser absorption spectroscopy using phase sensitive detection. The instrumental methods employed in using such derivative-based spectroscopies have been well characterized in the literature'. The principle advantages of the technique are high resolution (typically better than 0.0005 cm^{-1}), increased sensitivity because of the use of phase sensitive detection, and at high laser modulation frequencies, low source noise. Figure **3** shows 2nd derivative mid-infrared tunable diode laser (MIR-TDL) absorption spectra near 1265 cm^{-1} of a 21 torr $CH_4/O_2/Ar$ premixed gas flame to which 5% CF_3Br has been added. The features in each spectrum in Figure **3** are from absorption of the laser radiation by CF_2O. This figure shows the increase in sensitivity (relative to FT-IR) afforded by the use of the tunable diode laser, and also shows the increase in CF_2O formation as flame conditions change from rich to lean. This portion of the spectrum was chosen because in this region the radicals $CF_2\cdot$ and $CF_3\cdot$ also have vibrational fundamentals'. Figure **4** shows successive MIR-TDL absorption spectra, measured as a function of height above the burner surface, over this same region in a rich, 21 torr, $CH_4/O_2/Ar$ flame to which 5% CF_3Br has been added. The arrows in Figure **4** indicate features which we believe are due to absorption of laser radiation by the $CF_3\cdot$ radical. The successive spectra show an increase, followed by a decline, with height above the burner surface, for the two features believed to be due to the $CF_3\cdot$ radical. This observation is consistent with predictions from flame model calculations of fluorine inhibited flames'.

Real-Scale Fires

Measurement **of** gases produced during real scale fire testing was performed at the Aberdeen Test Center (ATC). The fires investigated all used JP8 as fuel. JP8 is a turbine engine fuel composed of long chain (C_n, $n>5$) hydrocarbons. Figure 5 shows the FT-IR absorbance spectrum of gases removed from the vicinity of the fire during inhibition of the fire by Halon 1301 (CF_3Br). Evident from this spectrum are features due to HF, HCI, HBr, CO, and CF_2O, as well as other species participating in the combustion. Most noticable is the difference between species present in this fire versus those observed in the laboratory-scale fires. Most significant are the prominent features due to HBr and CF_2O. **We** believe the HCI present in the flame arises from chlorine impurities in the CF_3Br. The optically determined concentrations of gases present during inhibition of JP8 pan fires by CF_3Br (Halon 1301) and C_3F_7H **(FM-200)** have recently been reported by **us** elsewhere''.

Figure *6* shows a schematic of the facility for measuring gases produced during suppression of JP8 fires occurring within the crew compartment of an Army personnel carrier. For testing of fire inhibition by Halons in occupied areas, it is important to measure the time evolution of any toxic gases produced during the inhibition event. For this reason, tunable diode laser spectroscopy was chosen to be one of the diagnostics employed during testing. HF was selected as the most important gas to monitor, since HF typically has the highest partial pressure of any of the Halon flame decomposition products.

The HF diagnostic used a near-infrared tunable diode laser operating at **7665** cm^{-1}. This frequency corresponds to the frequency of the **P(2)** line of the first overtone of the fundamental HF vibration. There are several reasons to use diode lasers operating in the near-infrared. **For** HF diagnostics, however, the most important **is** that mid-infrared diode lasers operating at the fundamental frequency (near 4000 cm^{-1}) are not yet available. Other reasons for using a near infrared tunable diode laser-based diagnostic include ease of transmission of the laser radiation through fibers, operation at temperatures attainable with thermoelectric coolers **(–270K),** low cost of detectors, and ability to significantly reduce laser output noise through the use of kHz modulation techniques''.

Figure **7** is a graph of HF gas production (in pppm - parts per million meter) versus time immediately after release of **3.4** kg of C_3F_7H (FM-200) into a JP8 fuel pan fire (area **~0.25** m^2) burning within the closed crew compartment of a Bradley Fighting Vehicle. The Halon was dispersed into the fire in approximately 1 **s.** Fire extinguishment was immediate. Figure 8 is a graph of HF gas production (in pptm - parts per thousand meter) versus time for an identical test, except that the fire was not extinguished by the Halon. To the best of our knowledge, the only difference between tests is a slight change in position of the nozzle of the cannister from which the Halon is dispersed. From Figures 7 and 8, it may be seen that peak HF production in the fire not extinguished by the Halon is approximately 50 times higher than in the fire in which extinguishment by the Halon occurred immediately. The dip in HF concentration in Figure **8** near 40 seconds marks the time at which the back-up CO_2 extinguishment system was used to put out the fire.

Conclusion

We believe that optically-based measurements can provide virtually all diagnostic information necessary for determination and analysis of mechanisms and efficiencies of Halon fire inhibitants We have shown that production of toxic gases associated with fire inhibition by Halons, particularly HF and CF_2O, is highly dependent on the type and conditions of the fire being investigated. Finally, we have shown that HF production is extremely dependent on whether or not fire suppression is accomplished immediately after application of Halon inhibitant. We are currently exploring the application of the diagnostic techniques mentioned in this report to more types of fires, and extending the methods development to even more extreme environmental conditions.

Acknowledgement

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1. The project was originally funded under the auspices of the Strategic Environmental Research and Development Program of the **U.S.** Department of Defense.

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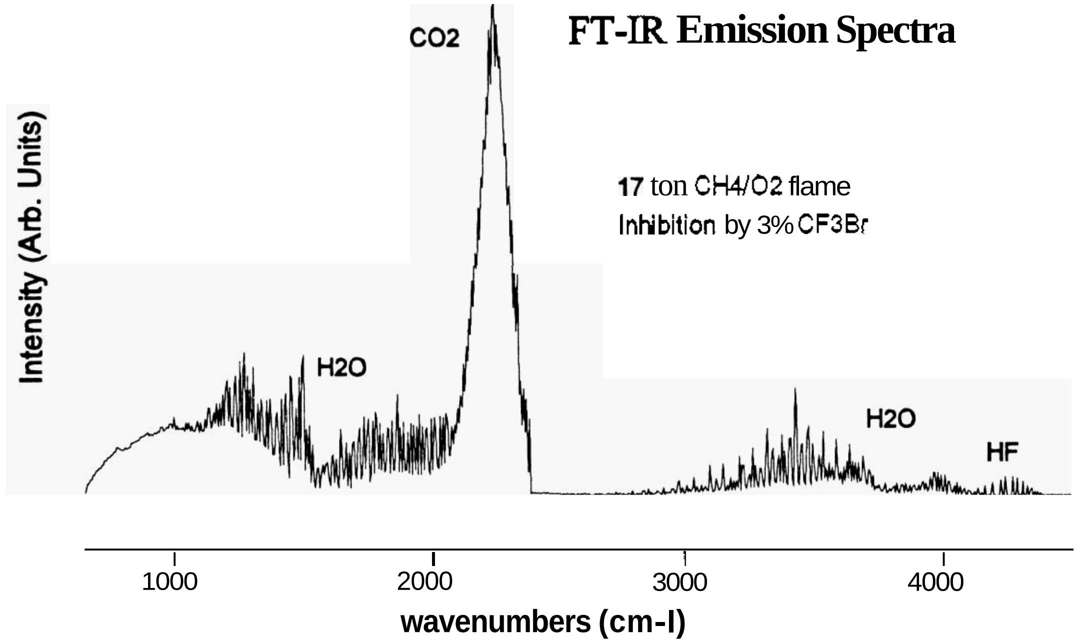

Figure 1: The FT-IR emission spectrum **of** gases present 10 mm above the burner surface of a **17** torr premixed gas CH_4/O_2 flame to which **3%** CF_3Br has been added.

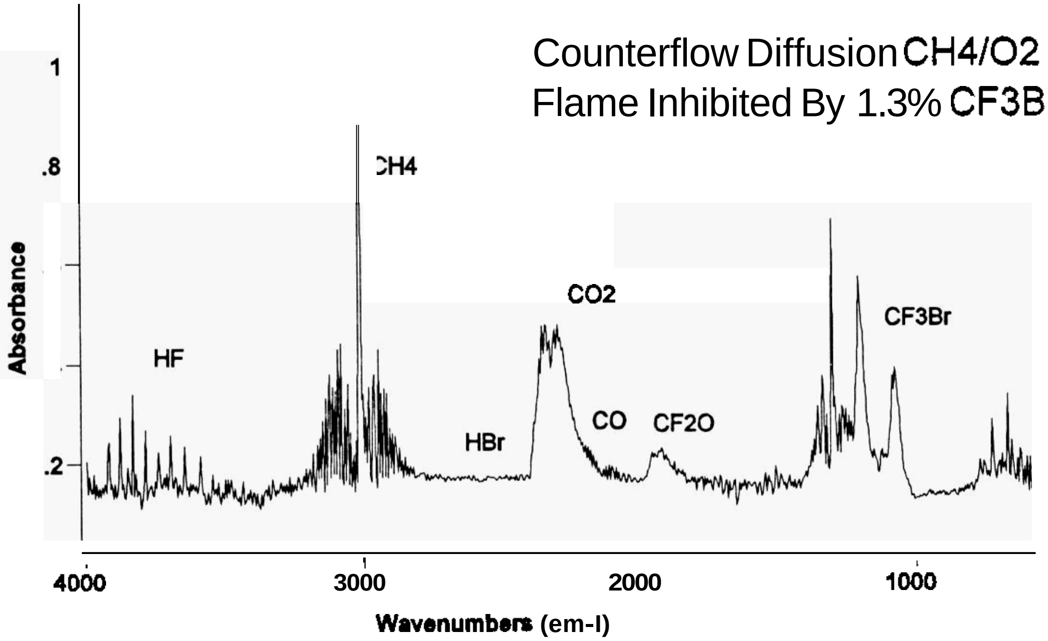

Figure 2: The FT-IR absortion spectrum measured through an atmospheric pressure counterflow diffusion CH_4/air flame inhibited by 1.3% CF_3Br.

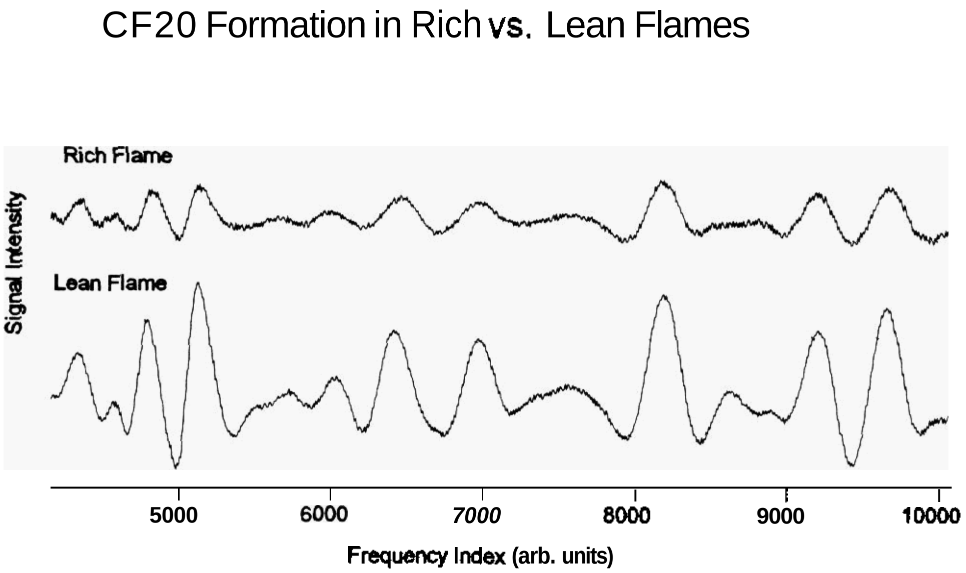

Figure 3: Second derivative mid-infrared tunable diode laser (MIR-TDL) absorption spectra near 1265 cm^{-1} of a 21 torr $CH_4/O_2/Ar$ premixed gas flame to which 5% CF_3Br has been added. All features shown are due to CF_2O. Spectra measured 2 mm above burner surface.

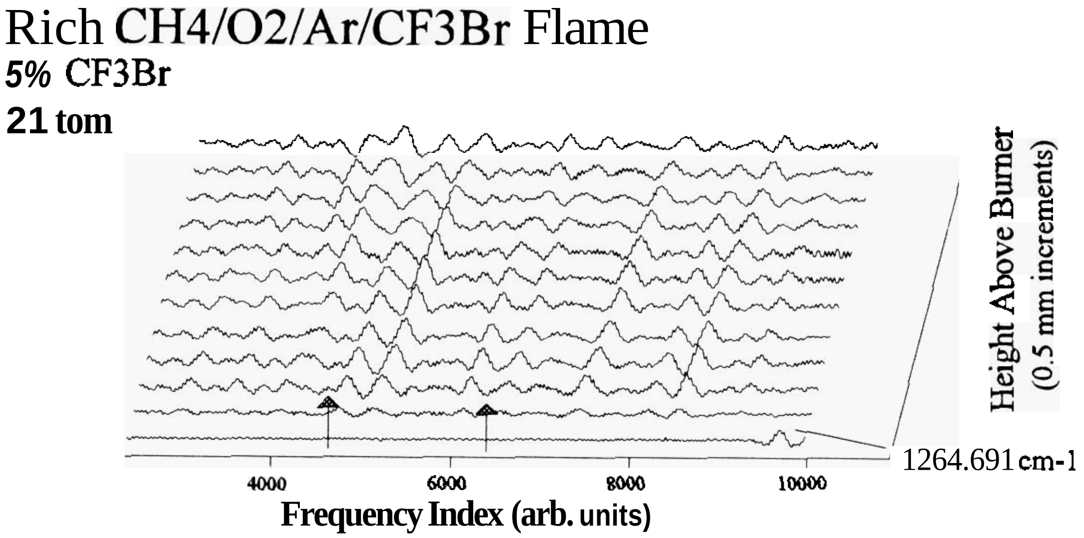

Figure 4: Second derivative mid-infrared tunable diode laser (MIR-TDL) absorption spectra in a rich $CH_4/O_2/Ar$ flame to which 5% CF_3Br has been added, measured as a function of height above the burner surface. Arrows indicate absorption features due to $CF_3\cdot$.

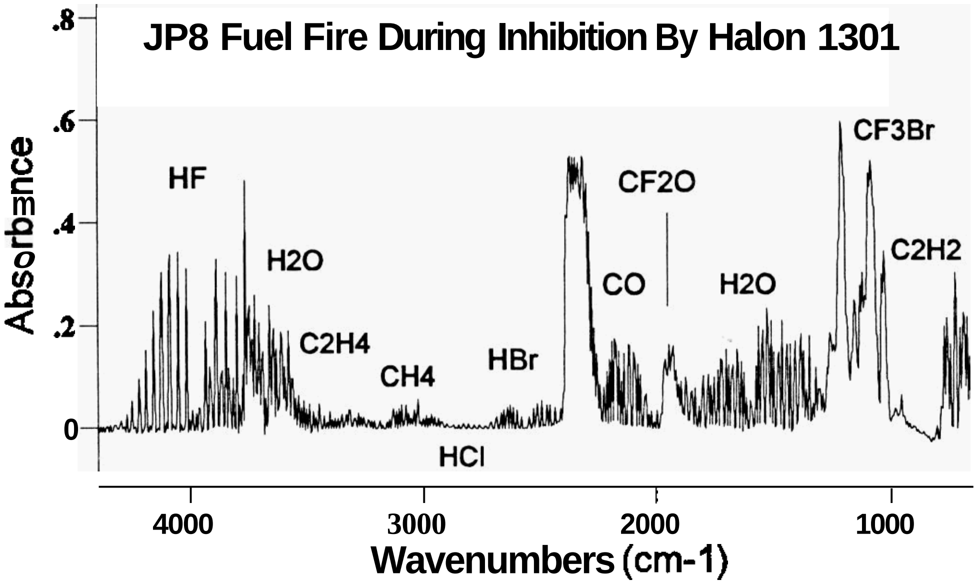

Figure 5: The FT-IR absorbance spectrum of gas removed from the vicinity of a JP8 fuel pool fire during inhibition by CF_3Br (Halon 1301).

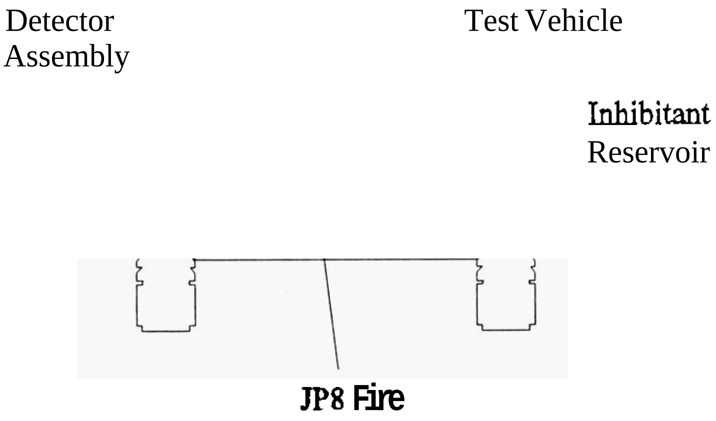

Figure 6: A schematic of the test facility for measuring gases produced during suppression of JP8 fuel pool fires occurring within crew compartments of Army vehicles. The detector assembly consists of an extractive FT-IR probe and an in-situ NIR diode laser emitter-detector assembly.

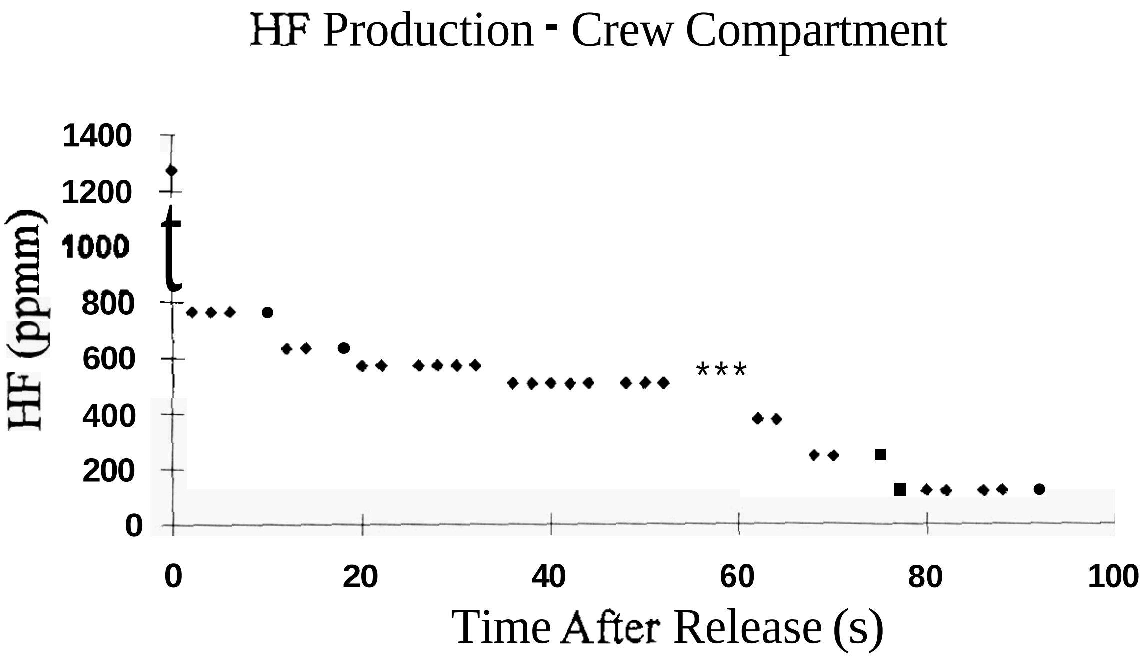

Figure 7: **A** graph of HF production (ppmm - parts per million meter) versus time after release of C_3F_7H inhibitant (FM-200) for a JP8 fuel pool fire occurring within a Bradley Fighting Vehicle. For this test, the inhibitant extinguished the fire.

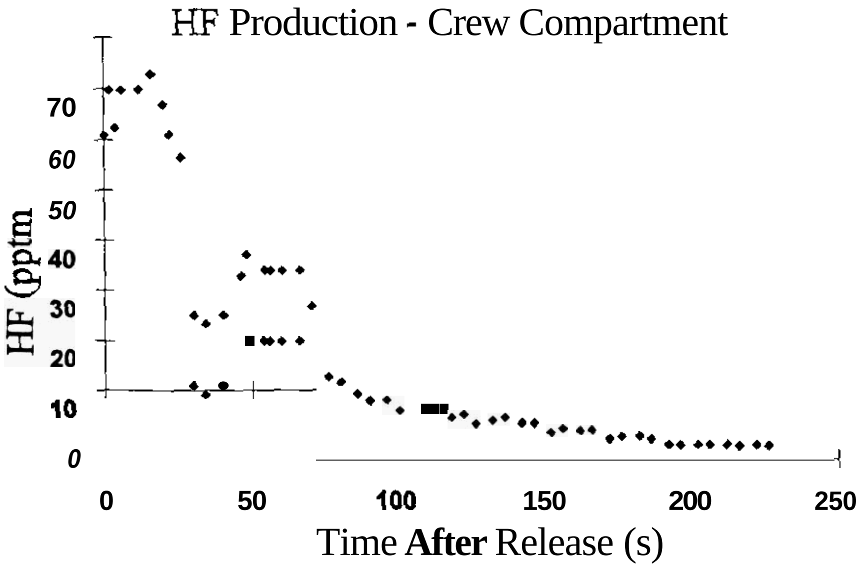

Figure 8: **A** graph of HF gas production (pptm - parts per thousand meter) versus time immediately after release of C_3F_7H (FM-200) into a JP8 fuel pool fire burning within the closed crew compartment of a Bradley Fighting Vehicle. Unlike the data shown in Figure **7,** for this test the fire was not extinguished by the inhibitant. The dip in HF concentration near 40 s is due to activation of the back-up CO, extinguisher system.