COMPARISON OF METHODS FOR MEASURING HYDROGEN FLUORIDE GAS AS A FIRE SUPPRESSION BY-PRODUCT

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ABSTRACT

Halon 1301 (CF_3Br) and many of its replacement candidates produce hydrogen fluoride (HF) gas as a thermal degradation product during fire suppression. HF gas is a toxic irritant and its concentration needs to be measured accurately and in real-time as part of the overall evaluation of fluorine-containing fire suppressant agents. Since HF is extremely reactive, determining an accurate HF gas concentration is challenging. This paper is a status report of a study designed to compare the results of measurements of HF gas concentrations in the laboratory and under field conditions using several different types of instrumentation.

Both real-time and time-weighted-average methods are used to measure HF gas concentrations. The time-weighted-average methods include sorbent tubes and midget impingers recommended by NIOSH[1], and scrubber tubes developed by the Army[2]. Real-time instrumentation includes a Fourier transform infrared (FT-IR) spectrometer, a near-infrared tunable diode laser (NIR-TDL), and a hydrogen fluoride monitor which uses ion-selective electrodes (ISE) for detection. A Plexiglas(R) flow chamber was constructed to enable measurement of HF gas by FT-IR, NIR-TDL and ISE simultaneously at a fixed flow chamber location. The flow chamber measurements are to be used as a calibration for field measurements using the different measuring techniques. Field measurements are conducted inside a crew compartment test fixture where fires are generated and extinguished.

INTRODUCTION

Current (Halon 1301 (CF_3Br)) and replacement candidate non-ozone-depleting fire inhibitants (e.g. FM-200 (C_3F_7H)) produce significant quantities of hydrogen fluoride (HF) gas during fire fighting[3]. Because these agents may be deployed in occupied spaces, quantitative measurement of HF gas produced during the inhibition event is required prior to certification of a candidate replacement agent. Because HF is a highly reactive gas, in-situ, real-time methods of measurement are preferred over grab-sampling techniques. This paper is a status report of a comparative study that evaluates various techniques for measuring HF under controlled laboratory conditions and under reproducible fire suppression operations.

EXPERIMENTAL

Laboratow-Based Testing

In the laboratory, experiments are conducted in a Plexiglas$^{(R)}$ flow chamber employing optical and impinger ports allowing for simultaneous measurement of HF gas by FT-IR spectroscopy, NIR-TDL absorbance spectroscopy, and using an ISE-equipped HF monitor. The radial positioning of the ports allows sampling at the same longitudinal position in the flow chamber (Figure 1). These experiments provide calibration curves and limits of detection for HF gas measurement using these techniques.

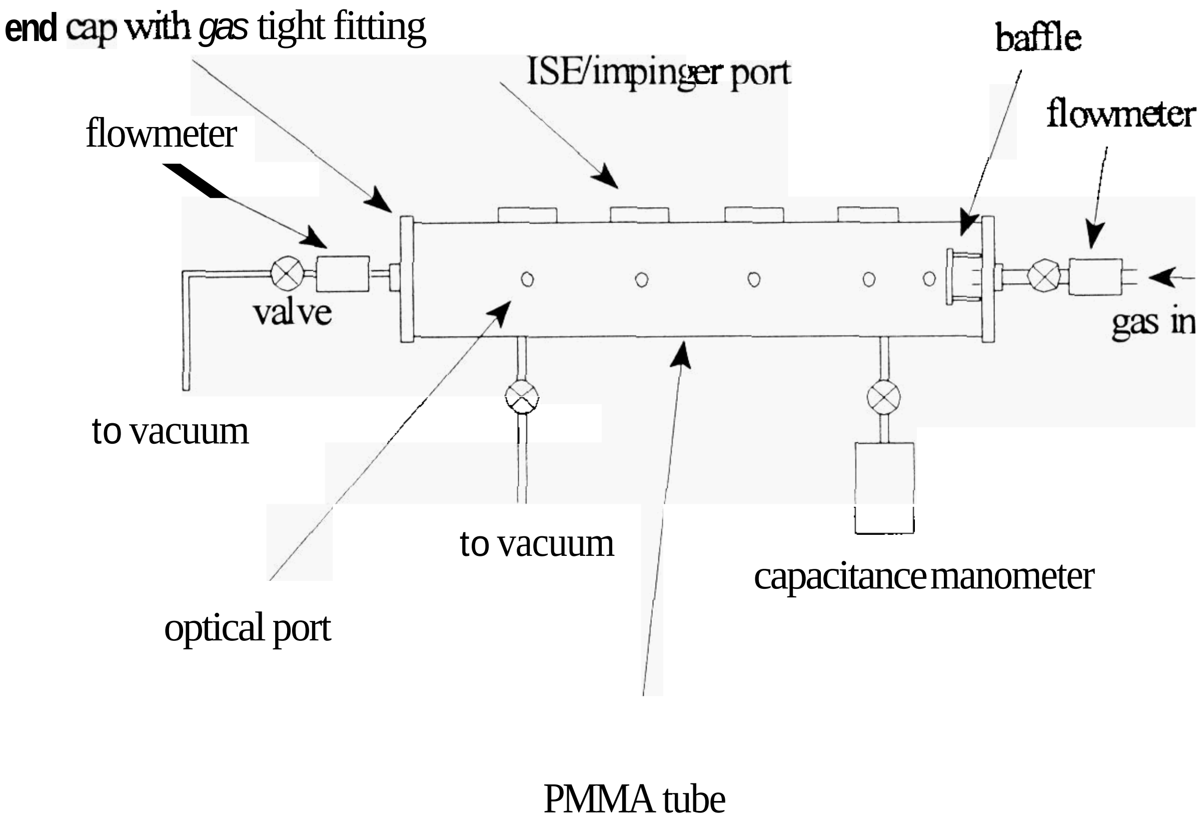

Figure 1: The flow tube used for simultaneous measurement of HF gas using FTIR spectroscopy, NIR-TDL absorption spectroscopy, and the ISE-equipped HF monitor

Prior to entering the flow chamber, a known HF/nitrogen gas mixture is mixed at a “tee” with dry nitrogen (Matheson, Inc.) using a flow controller (Tylan, Inc.) to generate a range of HF concentrations while maintaining the total flow through the chamber at 10 liters per minute. All laboratory-based experiments are conducted at room temperature and atmospheric pressure. Gases are exhausted from the flow chamber using a vacuum pump (Alcatel).

FT-IR spectra are measured using a Midac Corporation Model G FT-IR spectrometer equipped with zinc selenide (ZnSe) optics and using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. For the laboratory-based experiments, the spectrometer is disassembled and then rebuilt around optical ports built into the flow chamber. Near-infrared spectra are measured using a tunable diode laser (NIR-TDL) spectrometer system (thermoelectrically cooled InGaAsP distributed feedback laser source coupled to a GIUN-lens tipped fiber optic, emitting laser radiation at 7665 cm^{-1}), manufactured by Southwest Sciences, Inc. The laser radiation is detected by a room temperature InSb photodiode detector . The laser frequency corresponds to the frequency of the **P(2)** line of the first overtone of the fundamental HF vibration. The laser is scanned at 50 Hz over the spectral region of interest (approximately 0.05 cm^{-1} on either side of 7665 cm^{-1}) and frequency modulated at 50 KHz during each scan through the spectral region of interest. Detector output is demodulated at 100 KHz (SRS Inc. Model 850 Lock-In Amplifier), and digitized using an oscilloscope (Lecroy 9360). Since the flow chamber material is transparent at 7665 cm^{-1}, the line-of-sight passes directly through the walls of the flow chamber.

The HF monitor (M. M. Smith Co.) employs an impinger to continuously flow the gas being sampled (2 liters/min impinger flow) into an aqueous trapping solution. The trapping solution is pumped through a fluoride electrode flow cell where fluoride ion is continuously monitored. The continuous impinger is designed to minimize interaction between the HF gas and any surfaces prior to being extracted and converted to fluoride ion.

To determine absolute values of concentrations of HF (in the cylinders purchased from Matheson) prior to dilution in the laboratory based experiments, three time-weighted-average **(TWA)** sampling techniques are used. The first technique uses silica-gel sorbent tubes (SKC, Inc.). HF gas present in the sample gas is adsorbed onto the surface of the silica gel, and then extracted at the conclusion of sampling using a basic solution. The second technique uses midget impingers constructed of 50-mL plastic centrifuge tubes filled with a basic buffer solution. The sample gas is bubbled through the solution, converting HF gas to fluoride ion. The third technique uses scrubber tubes, consisting of plastic tubes filled with glass beads coated with a 0.5 M NaOH solution. HF gas flowing through the tube is converted to fluoride ion. Sampling time for each technique was 120 seconds. Gas flow rate through each device is 0.2 liters per minute. The fluoride ion contained in the eluent from each of the time weighted average techniques is analyzed using an ion chromatograph (Dionex Corporation).

Field-Based Testing

Field-based measurements are performed in a crew compartment test fixture within a ballistic hull and turret of an ex-Bradley Fighting Vehicle. Small scale (– 1MW) JP-8/air fires in the crew compartment test fixture are produced using a spray nozzle and pump similar to those used in an oil fired furnace to supply fuel. Ignition is accomplished using an electric glow plug. After ignition, the fire is allowed to bum uninhibited for 30 seconds. After this time has elapsed, suppression agent is metered into the fire at a rate fast enough to produce ample amounts of HF for measurement while not extinguishing the fire.

Each of the techniques used in the laboratory-based measurements is used in the field-based tests, with some necessary modifications. Because of the harsh environment, FT-IR spectra are measured by continuously withdrawing gas samples through a heated probe placed within the crew compartment test fixture, and flowing **this** gas sample through a heated multipass optical cell placed within the beam path of the externally-located spectrometer. The distance from the sampling location to the spectrometer is approximately **3** meters.

For measurements of HF gas concentration using the NIR-TDL, near-infrared laser radiation is conducted to the crew compartment test fixture using a GRIN-lens tipped optical fiber. The collimated laser radiation is detected using a room temperature InSb photodiode. The path length from the **GRIN** lens to detector is **13** cm. For HF gas measurements employing the ISE, the impinger protrudes through the inner wall of the crew compartment test fixture. **A** 3-ft. section of tubing is used to transport the trapping solution to the fluoride electrode flow cell. The **FT-IR** gas sample probe, the "pitch and catch" optical NIR-TDL assembly, and the ISE impinger port are all located within a volume of approximately **0.03** m^3 within the crew compartment test fixture.

RESULTS AND DISCUSSION

Calibration curves for each technique from the laboratory-based measurements are used to calculate HF concentrations measured under firefighting conditions. In order to obtain an absolute calibration, we use time weighted average measurements described above to determine the "true" HF concentration in a commercially-supplied test mixture cylinder, and assume that the flow control mixture system is inert to HF gas. For the field-based measurements, some variance between the techniques is to be expected because even within the small volume which contains the various sampling probes, the assumption of a well-stirred reactor may not be valid.

Table 1 shows results of measurements of HF concentration (ppm) in commercially prepared cylinders (Matheson, Inc.) of HF in nitrogen. Table 1 shows that there is disagreement between measured values of HF concentration and values reported by the supplier. Additionally, for the HF/Nitrogen cylinder specified by the manufacturer at **5423** ppm HF, we believe the sorbent tubes have become saturated. The actual HF concentration in the tank specified by the manufacturer as **5423** ppm HF has been taken to be the average of the HF concentrations measured using the impinger and the HF monitor (11580 ppm HF). The accuracy of this value is approximately ±10%.

MANUFACTURER VALUE	IMPINGER	SORBENT TUBES	HF MONITOR
96	46	64	57
904	1447	1477	1675
5423	11464	5579	11702
712	1303	1212	1741

Table 1: A comparison of manufacturer specified HF in Nitrogen concentrations (ppm) **versus** concentrations measured (ppm) using impinger tubes, sorbent tubes, and the ISE-equipped HF monitor for four commercially prepared gas cylinders.

Figure **2** shows a plot of instrument response versus calculated concentration for simultaneous HF measurement using the FT-IR spectrometer, **NIR-TDL** absorption spectroscopy, and the ISE-equipped HF monitor, as measured in the **flow** tube apparatus described in Figure **1.**

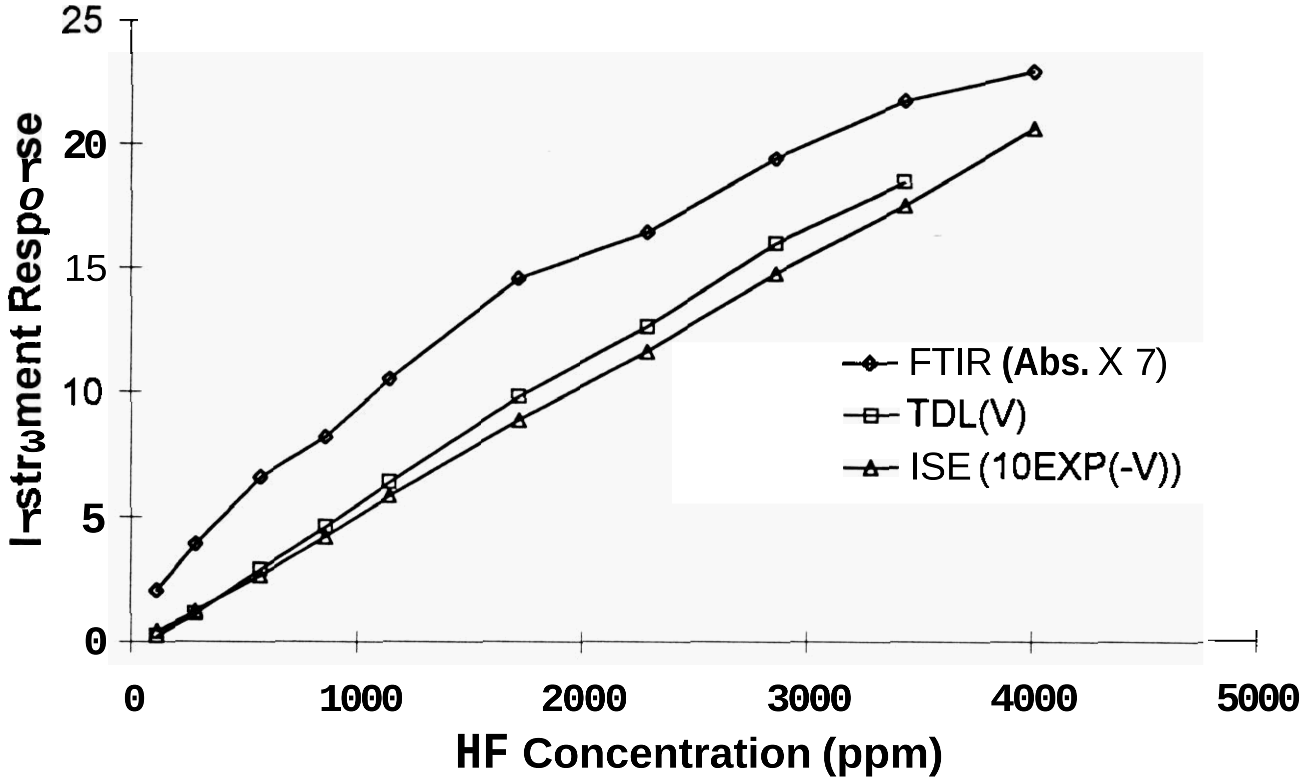

Figure 2: Instrument response for HF measurements **versus** calculated HF concentration (ppm) using a FT-IR spectrometer, a NIR-TDL, and an ISE-equipped HF monitor, using the test fixture shown in Figure 1.

The value used for HF absorbance from the FT-IR spectrum was the integrated area of the absorbance of the R-branch in the fundamental absorption band of HF near 4000 cm^{-1}. The nonlinearity of the FT-IR instrument response versus HF concentration is due to the instrument resolution (0.5 cm^{-1}) being larger than the HF linewidth (– 0.1 cm^{-1}). For measurements made using the NIR-TDL, instrument response is the trough-to-peak height of the 2nd derivative lineshape corresponding to the P(2) line of the first overtone transition of HF near 7665 cm^{-1}. For the ISE-equipped HF monitor, the instrument response is proportional to the negative of the log of the fluoride ion concentration.

Test Method	Impinger	Sorbent Tube	ISE-equipped HF Monitor
Controlled Burn 1	1356	889	1879
Controlled Burn 2	1262	1186	1184

CONCLUSION

Preliminary measurements have demonstrated the linear response of FT-IR spectrometry, NIR-TDL absorption spectroscopy, and an ISE-equipped HF monitor to measurement of HF gas from 100 ppm to 4000 ppm under laboratory conditions. We are currently conducting field testing of these techniques for the measurement of HF gas produced during real firefighting using fluorine-containing fire inhibitants.

ACKNOWLEDGMENT

The authors wish to thank Mr. Steven J. McCormick of the U.S. Army Tank Automotive Command, and the Next Generation Fire Suppression Technology Program of the Department of Defense, for financial support of this project.

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