Performance Evaluation Of A Halogen Acid Gas Analyzer

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ABSTRACT

Real-time monitoring instrumentation has been developed to measure halogen acid gases and their aerosols resulting from the thermal breakdown of halogenated fire suppression agents under live fire testing conditions. This halogen acid gas analyzer is designed to measure HF, HCl, HBr, and HI simultaneously. Linear response is indicated from laboratory generated gases and aerosols of each of the acids from a few mg/m^3 to several thousand mg/m^3. It has the capability of extending the extraction module up to 2 m from the monitor, thus minimizing instrumentation losses should the test conditions become too hostile.

INTRODUCTION

Many of the current fire suppression agents, as well as the candidates for replacing these agents, contain halogens. In combat situations the crew of an armored vehicle may not be able to exit the vehicle in case of fire; therefore, when these agents are used to extinguish the fire, large quantities of halogen acid gas and aerosol may be produced, which can be as life threatening in close quarters as the fire itself. In order to accurately assess exposure levels and potential health hazards, support Congressionally mandated live fire tests, and reduce testing time and costs, accurate measurements of these toxic gases need to be made on a real-time basis. The thermal degradation of halogenated organic fire suppression compounds can produce **HF** (hydrogen fluoride), HCI (hydrogen chloride), HBr (hydrogen bromide), or HI (hydrogen iodide) gases.

Sampling of these gases through tubing can lead to severe sample losses.[1] Trapping gas samples for later analysis provides a time weighted average of the concentration and does not detect concentration excursions that may be extremely high but only last for a few seconds. These excursions can cause performance decrements and adverse health effects. To determine the concentration of these reactive gases, they must be trapped or analyzed immediately.

Many of the components of this analyzer were not off-the-shelf items and had to be developed. Because of the space constraints inside the crew compartments of armored vehicles, attempts have been made to size down the instrumentation used to measure these air toxics. In order to minimize the size of the instrumentation, reduce reagent consumption, and provide for rapid response, micro flow-through electrodes were developed to detect the anions of each of the above acids. A minimal surface continuous impinger that is an integral part of the analyzer was developed in this laboratory and is described in more detail elsewhere.* This report provides a performance evaluation of a halon acid gas analyzer developed by the Army to provide real-time analysis of halogen acid gases and aerosols with minimal opportunity for the gas phase to interact with surfaces prior to analysis.

EXPERIMENTAL

Description of Analyzer. The halogen acid gas analyzer holds up to four analytical channels and thus can analyze up to four different halogen acid gases at the same time. The signals from the electrodes are amplified and sent to a digital readout on the analyzer and to an output connector where they are stored on a data logger or go into a computer where the data are manipulated with the results of concentration vs. time being shown in real time on a computer screen. Because live fire testing creates a hostile environment, the halogen acid gas analyzer described in this report has the capability of locating the continuous impinger up to 2 m from the analyzer. A 1/4 in i.d. sample line transports the trapped sample from

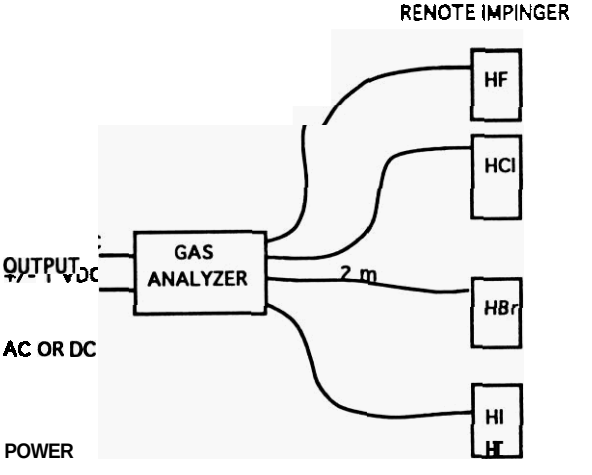
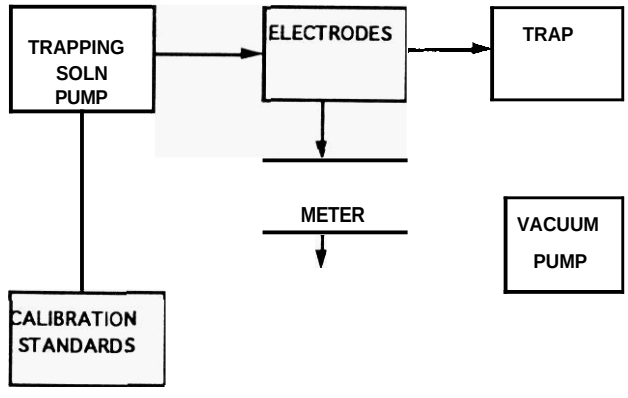


Figure 1. Analyzer configured to measure four gases remotely.

the fire is extinguished in a few milliseconds, thus the plastic

effected.



is camed through a pair of wires running parallel to the sample line.

Fluid Movement. Trapping solution is delivered to the continuous impinger at a rate of 3 mL/min using a miniature solenoid pump . The controller for the variable flow solenoid pump was fabricated in-house. An air flow of 2.5 L/min. through the system is obtained by a variable flow personal monitoring pump or by using a critical orifice (0.025 in.) and a vacuum source of 17 in. of Hg or greater. *An* air filter was placed downstream from the waste trap to prevent aerosols from entering the vacuum pump or critical orifice. This vacuum source located external to the analyzer draws sample air into the continuous impinger where the halogen acid gases and aerosols are immediately extracted into the aqueous phase of the trapping solution. The resulting mixture

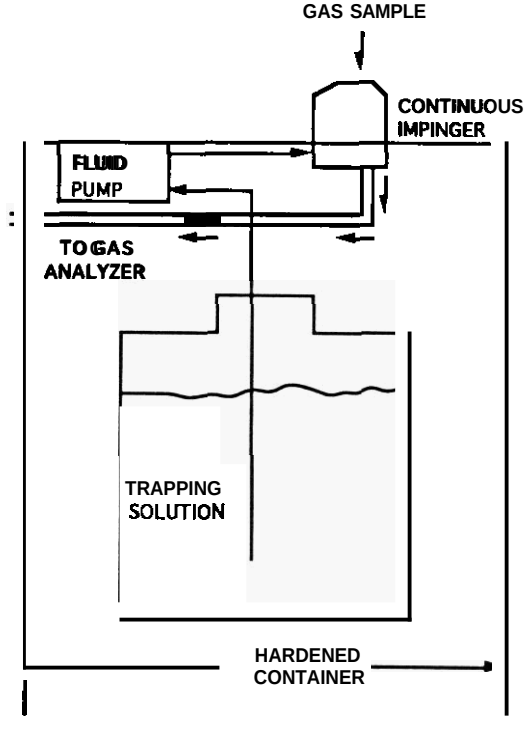
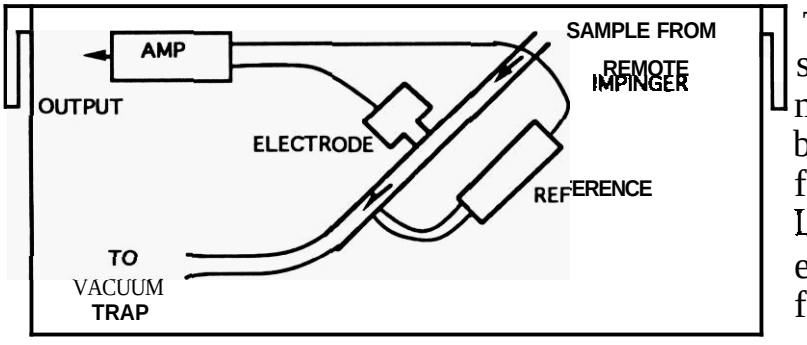


Figure 3. Components of remote continuous impinger.



The flow cell of the ion-selective electrodes measure about 2.4 mm i.d. by 16 mm. The solid state fluoride electrode uses a LaF_3 crystal as a sensor embedded in the wall of the flow cell. It can easily be

Calibration. Each of the channels is calibrated using external standards of the ion of interest. The standards are administered to the analyzer through a detachable tube on the inlet side of the solenoid pump. It takes about five minutes to perform a three point calibration. Since they operate independently all four of the channels can be calibrated simultaneously.

Sampling and Analysis. To validate concentrations of gases and aerosols midget impingers are used in conjunction with ion chromatography. Plastic impingers were used to collect HF gas samples and glass impingers equipped with fritted glass nozzles had to be used to collect aerosol samples.

Gas and Aerosol Generation. Hydrogen fluoride, hydrogen chloride, and hydrogen bromide gases in N_2 were obtained from a local supplier. They were diluted to various levels with house nitrogen using Sierra electronic flow controllers. Hydrogen iodide gas was not commercially available and had to be generated by a controlled chemical reaction between KI and H_3PO_4 developed under contract by the University of Florida.[3] Aerosols of the sodium salts were generated with a medication nebulizer that was operated at 13 psi and 5.8 LPM and measured with a Grimm model 1.104 real-time aerosol monitor.

RESULTS AND DISCUSSION

The halogen acid gas analyzer has been extensively tested under laboratory conditions using both gases and aerosols. To validate concentrations of gases and aerosols midget impingers were used in conjunction with ion chromatography. Plastic impingers were used to collect HF gas samples and glass impingers equipped with fritted glass nozzles had to be used to collect aerosol samples. As indicated on table1 good agreement was obtained between the two methods.

All of the electrodes exhibited good Nernstian response (slope about -57 mV/ten-fold change in concentration) from a few mg/L to several thousand mg/L. Figure 5 shows the response of the halogen acid gas analyzer to an episodic exposure of HCl gas followed by HCl standards. In this case a glass flow-through electrode was also used to monitor change of pH in the sample. Figure 6 shows field data indicating HF as a thermal degradation product from extinguishing a fire using FM-200.

Erosion problems with the chloride electrode have been addressed by applying a thicker layer of AgCl on to the Ag wire of the electrode and by making the electrode tip disposable thus greatly reducing the overall cost of the electrode.

With the continuous impinger located remotely (about 6 ft.) form the halogen acid gas analyzer, there is a 15-sec delay in response. With the continuous impinger a short distance from the analyzer, response begins in less than a second.

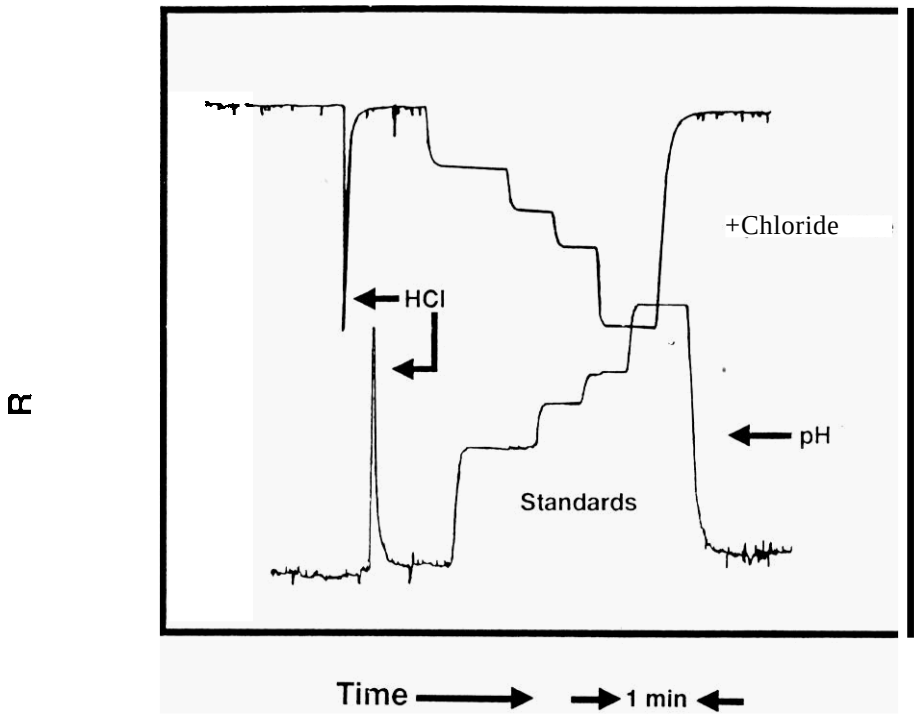


Figure **5.** Response of the halogen acid gas analyzer to **an** episodic exposure of HCl gas and HCl standards.

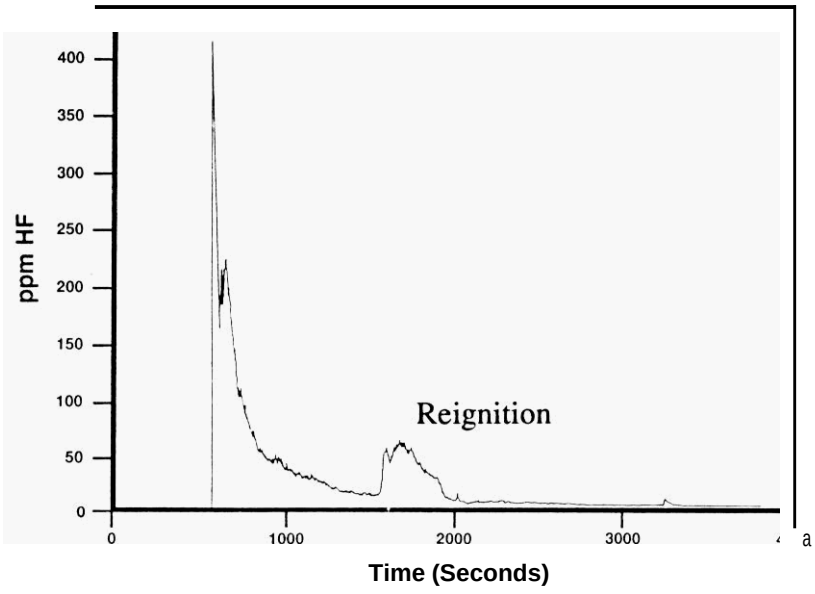


Figure 6. Concentration profile of HF resulting form FM-200 (C_3HF_7) being used to extinguish **a** fire.

Table 1. Comparison of halogen acid gas analyzer and midget impinger results for gases and aerosols. **All** values are reported in mg/m^3.

	HF		HCl		HBr		HI	
Phase	Impinger	Analyzer	Impinger	Analyzer	Impinger	Analyzer	Impinger	Analyzer
Gas	2.4	2.3	16.1	16.8	32.3	34.5	38.5	42.4
	4.5	4.0	48.7	47.8	55.2	60.8	48.4	51.9
	57	59	59.2	61.6	324	273	68.1	75.2
					766	816		
Aerosol	149	144	77.7	77.1	8.4	9.0	84	64
			165	164	45.5	43.3	219	200
					61.8	62.0		
					151	134		

CONCLUSION

This real-time halogen acid gas analyzer has become a useful tool in evaluating halon replacement fire extinguishing candidates and assessing the potential health hazards associated with the thermal breakdown of halogenated fire suppression agents. It is anticipated that this analyzer will find use in monitoring the atmosphere from the demilitarization of perchlorate based solid rocket fuel and in compliance monitoring to trap air toxics in hostile environments such as inside the stack of a hazardous waste incinerator.

ACKNOWLEDGMENT

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