

# REAL-TIME ANALYSIS OF HALON DEGRADATION PRODUCTS

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## ABSTRACT

The Army uses Halon 1301, bromotrifluoromethane, and Halon 1211, bromochlorodifluoromethane, as fire suppression agents on board armored vehicles. When these agents are used to extinguish a fire, thermal degradation can produce hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen cyanide (HCN), and hydrogen bromide (HBr) gases. A multigas analyzer is being developed to measure these gases in real-time using a continuous-flow miniature impinger and flow-through ion-selective electrodes.

## INTRODUCTION

When fire suppression agents such as Halon 1301, bromotrifluoromethane, and Halon 1211, bromochlorodifluoromethane are used on board armored vehicles to extinguish a fire, thermal degradation of these agents and other combat materials can produce hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen cyanide (HCN), and hydrogen bromide (HBr) gases which can be more hazardous than the fire that produced them. The HCN is produced primarily from the burning of on board ammunition and polymeric materials. Due to the reactivity of these gases, they need to be trapped or analyzed immediately. Trapping gas samples for later analysis only provides a time weighted average of the concentration and does not account for concentration excursions which may be extremely high but only last for a few seconds. In order to accurately assess exposure levels and potential health hazards, as well as reduce testing time and costs, accurate measurements of these toxic gases need to be made on a real-time basis.

A multigas analyzer is being developed to measure HCl, HF, HCN, and HBr gases

which are produced in the crew compartments of combat vehicles during live fire or fire extinguishing system testing. These toxic gases are extracted from air using a continuous flow miniature impinger where they are subsequently analyzed in real time using ion-selective micro flow through electrodes. In order to minimize the size of the instrumentation, reduce reagent consumption, and provide for rapid response, a continuous miniature impinger and micro flow through electrodes have been developed for the anions of each of the above acids.

## EXPERIMENTAL

The overall schematic diagram of the multigas analyzer is shown in figure 1. Three channels are used because the ionic strength adjusters for individual electrodes are incompatible with various other electrodes.

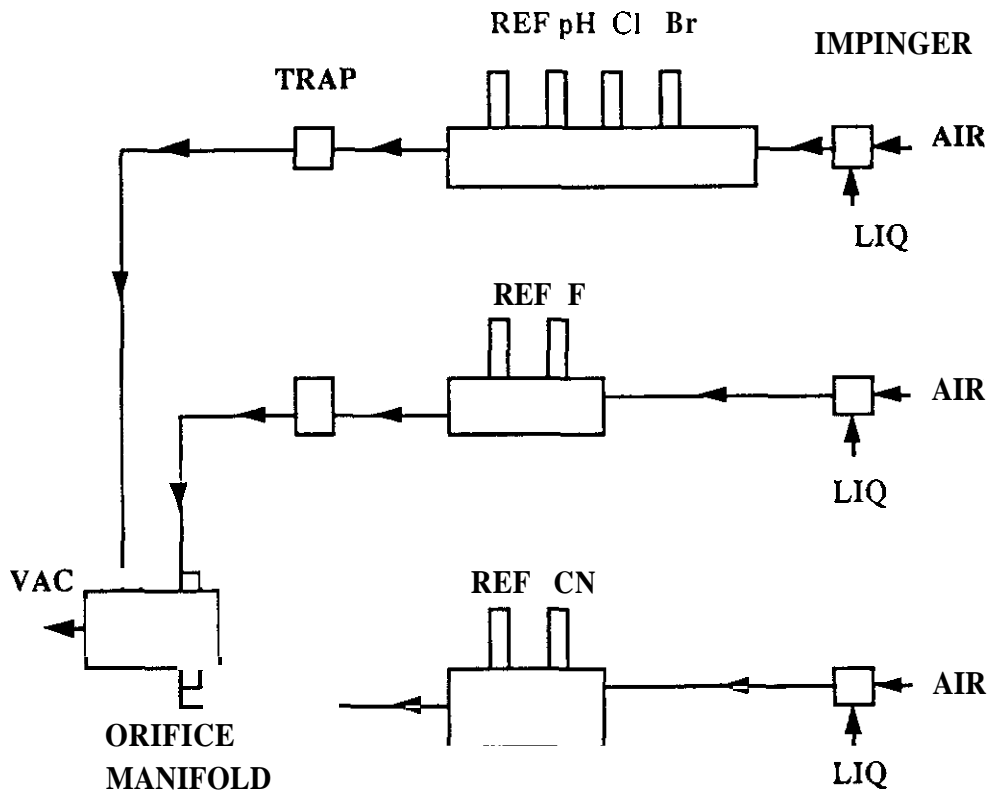


Figure 1. Schematic diagram of multigas analyzer.

**Miniature impinger.** Air is pulled through a miniature impinger (figure 2 ), which was designed and fabricated in-house, at about 3 L/min. by means of an external vacuum.

STAINLESS STEEL

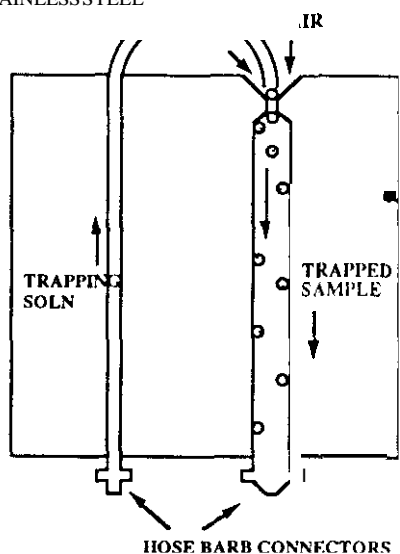
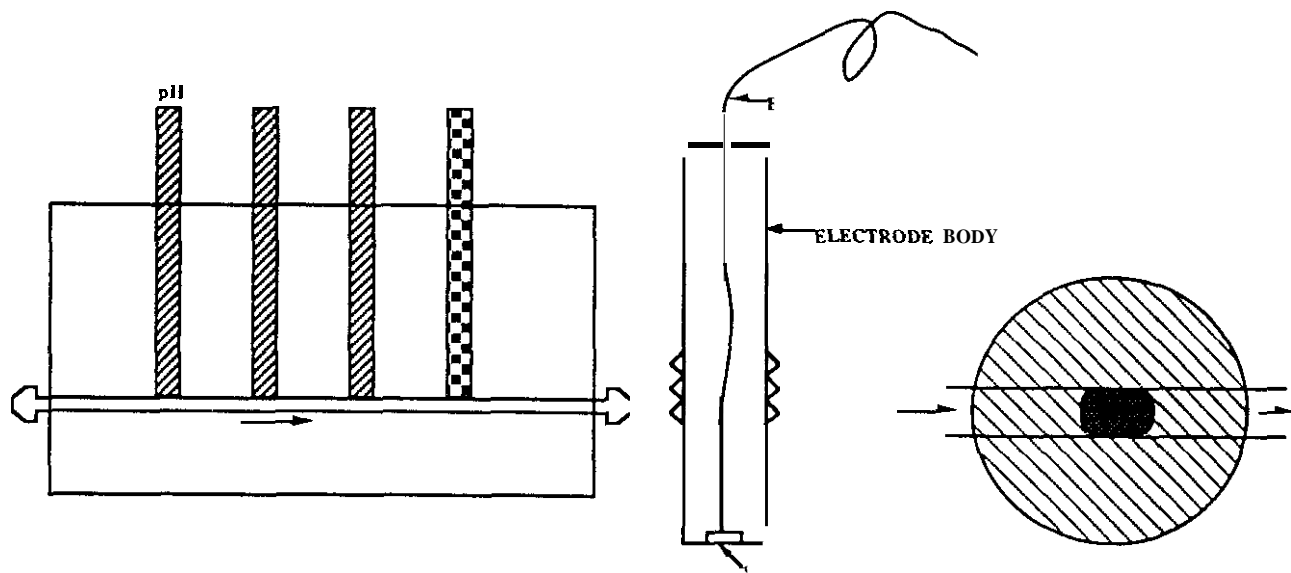


Figure 2. Miniature impinger with minimal surface interaction.

The impinger has been designed to keep interactions between the gas being sampled and the surface of the impinger at a minimum. By using longer lengths of connecting tubing, sampling can be conducted at locations remote to the multigas analyzer such as in a breathing zone area.



**Flow through electrodes.** The flow through electrodes are mounted in a plastic tube which is inserted into a flow cell as shown in figure 3. All electrodes are flat surface-mounted and removable for easy maintenance and replacement. All flow cells are fabricated in-house from Lexan<sup>®</sup> and microelectrode inserts are fabricated by Microelectrodes, Inc., (Londonderry, NH). The reference electrodes are mounted downstream to avoid ionic strength effects from the liquid/liquid junction.

The liquid/liquid junction has been specially designed to reduce electrical noise produced by the turbulent flow of the air/liquid sample through the system.

**Trapping solutions.** The trapping solutions not only serve to extract the toxic gas, but they also serve as an ionic strength adjuster and to reduce interferences. All chemicals used to prepare trapping solutions and standards were of reagent grade quality or better. For the chloride, bromide, and pH electrodes, a 0.1 M NaNO<sub>3</sub> solution was prepared. The cyanide electrode required a 0.1 M NaOH trapping solution. A total ionic strength adjuster buffer (TISAB 111, Orion Research Incorporated, Cambridge, MA) was used for the fluoride electrode. To all trapping solutions and standards 200 μL of polyoxyethylenesorbitanmonolaurate (Tween 20) (Sigma Chemical Company, St. Louis, MO) was added as a non-ionic surfactant.

**Calibration container.** Once the multigas analyzer is calibrated, only trapping solution is needed to monitor the atmosphere; therefore, calibration standards are housed in a separate container. Before and after atmospheric sampling, the multigas analyzer is connected to the standards container and calibrated with at least three concentrations of standard for each parameter. A standard select valve allows the operator to move quickly from one standard to the next. Housing the calibration standards in a separate container conserves space in the multigas analyzer.

## RESULTS

Ideally it would be convenient to include all of the electrodes in a single cell and thus use only one sampling channel; however, this is not possible because the trapping solutions used for each of the electrodes are not compatible with the other electrodes. It is possible to use a single cell for the chloride, bromide, and pH electrodes. The pH is measured to verify that the gas is acidic and not just a salt aerosol. Figure 4 shows the response curve of the pH and chloride electrode to standards containing HCl and to a short exposure of HCl gas.

The ability of the individual components of the multigas analyzer to efficiently extract and detect various gases and aerosols is shown on table 1. Few commercially available gas analyzers claim to respond to both gases and aerosols in real time.

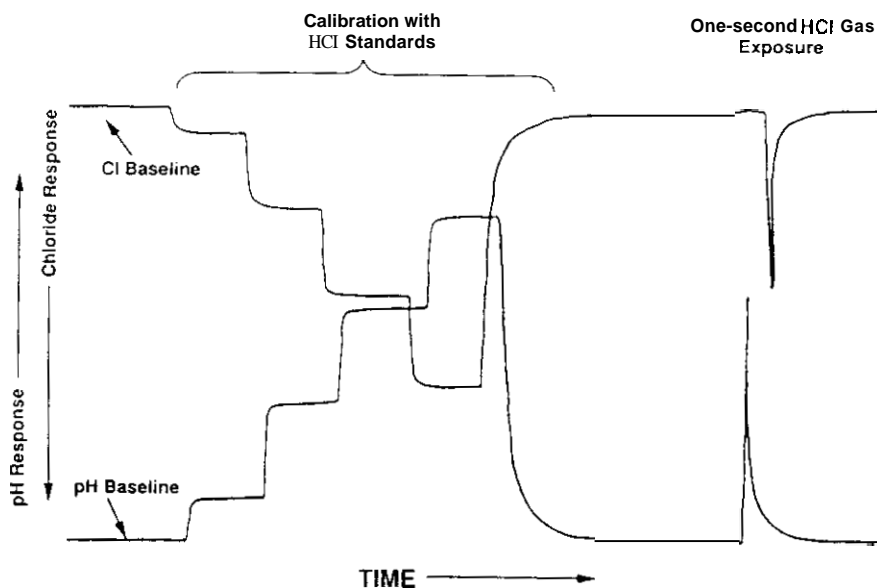


Figure 4. Response of multigas analyzer to standards and hydrogen chloride gas.

Air Toxic	Multigas Analyzer mg/m <sup>3</sup>	Midget Impinger mg/m <sup>3</sup>
Hydrogen Chloride	1.1	1.1
	2.7	2.4
	5.6	4.8
	6.1	6.2
	22	24
	145	152
Hydrogen Fluoride	300	430
	1050	1050
	2130	2020
	6400	6970
Hydrogen Bromide (aerosol)	9.9	17.2
	97	123
Hydrogen Cyanide	2.5	2.9

## DISCUSSION

Although the total multigas analyzer has not yet been completely assembled, the individual components appear to function properly. The sampling part of the analyzer will measure about 30 cm x 30 cm x 10 cm and weigh about 13 kg (with armored case). A three-point calibration for each of the sensing electrodes will take from 8-10 min and the response time of the multigas analyzer will be on the order of 0.5 sec. The response range of the analyzer to liquid standards indicates that response to the toxic gases in air will range from the threshold limit values up to several thousand ppm.

The flow cell described above was only recently designed to address erosion and electrode surface poisoning problems. When an electrode becomes badly eroded it can be replaced in a matter of seconds. In most cases the electrode can be removed, the surface refurbished, and replaced within minutes. With the previous design the electrode surface could not be polished and as a result the entire electrode flow cell had to be replaced.

Silver chloride is slowly lost from the Ag/AgCl surface through dissolution. When this happens the electrode loses Nernstian response and must be replaced. Replacement of the Ag/AgCl electrode with a  $\text{Ag}_2\text{S}/\text{AgCl}$  electrode promises to add service life.

## CONCLUSION

The various components of a multigas analyzer to perform real-time monitoring of halon degradation products have been developed and tested. Most of these components had not previously been available as off-the-shelf items. In the near future the components will be assembled in a hardened vessel and tested under live fire conditions.

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