DOT/FAA/CT-94/59

FAA Technical Center
Atlantic City International Airport,
N.J. 08405

The Comparative Extinguishment Performance and Thermal Decomposition Products of Halon Alternative Agents

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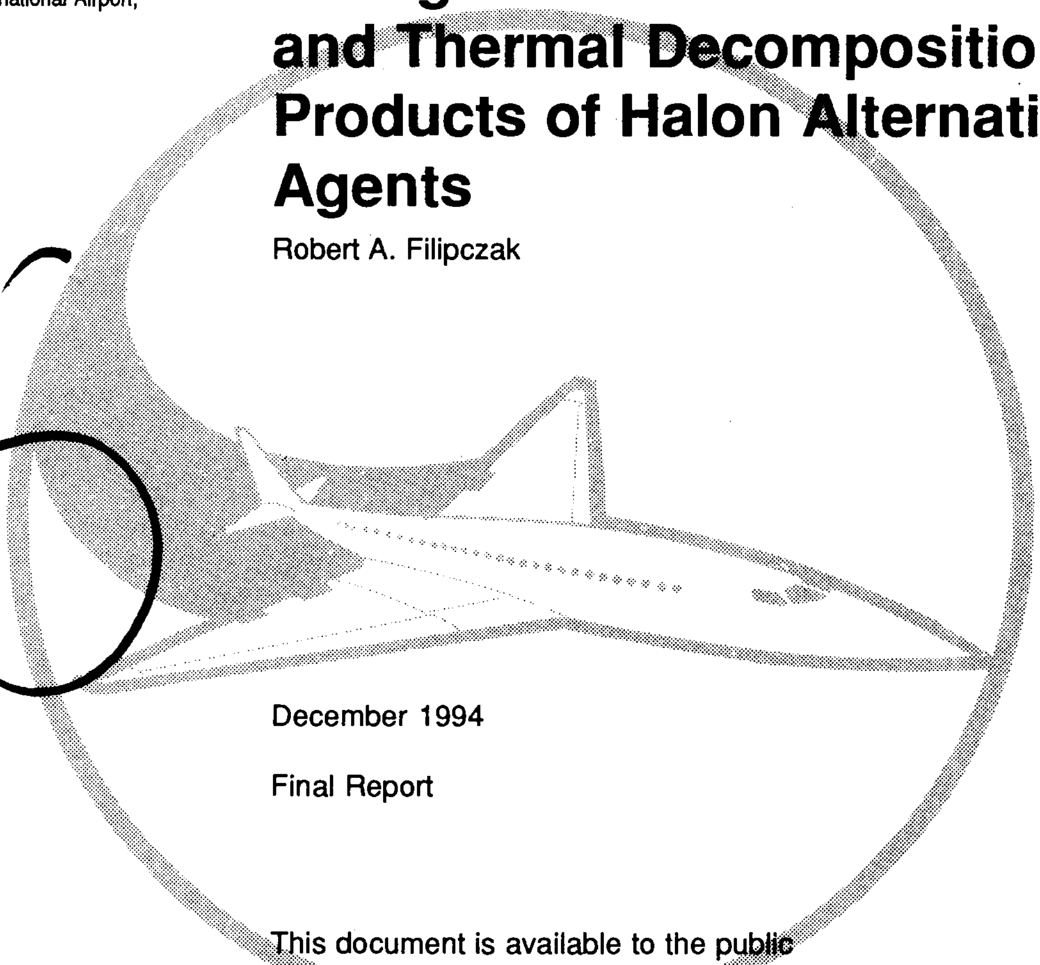

December 1994

Final Report

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U.S. Department of Transportation
Federal Aviation Administration

NOTICE

Technical Report Documentation Page

1. Report No. DOT/FAA/CT-94/59	**2. Government Accession No.**	**3. Recipient's Catalog No.**

4. Title and Subtitle THE COMPARATIVE EXTINGUISHMENT PERFORMANCE AND THERMAL DECOMPOSITION PRODUCTS OF HALON ALTERNATIVE AGENTS	**5. Report Date** December 1994 **6. Performing Organization Code** ACD-240
7. Author's) Robert A. Filipczak	**8. Performing Organization Report No.** DOT/FAA/CT-94/59
9. Performing Organization Name and Address Federal Aviation Administration Technical Center Atlantic City International Airport, N. J. 08405	**10. Work Unit No. (TRAIS)** **11. Contract or Grant No.**
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Technical Center Atlantic City International Airport, N. J. 08405	**13. Type of Report and Period Covered** **14. Sponsoring Agency Code**

15. Supplementary Notes

16. Abstract

Halon 1301, Halon 1211, and eleven alternative fire-fighting agents were compared for extinguishment effectiveness and thermal decomposition product generation, using a laboratory-scale test apparatus having methane as the fuel. Chemical analysis was conducted using a magnetic sector mass spectrometer with simultaneous measurement of oxygen consumption and carbon dioxide, water, and acid gas production. Chemical mechanisms are advanced to explain how halogenated hydrocarbons extinguish fires. The major conclusion was that the alternative agents were not as effective at fighting fires as Halons and that greater amounts of acid gases were produced during extinguishment. Hydrogen fluoride was found to be the predominant thermal decomposition product for all agents.

17. Key Words Halon Extinguishment Alternative Agent Mass Spectrometer	**18. Distribution Statement** This document is available to the public through the National Technical Information Service, Springfield, Va. 22161

19. Security Classif. (of this report) Unclassified	**20. Security Classif. (of this page)** Unclassified	**21. No. of Pages** 74	**22. Price**

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

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EXECUTIVE SUMMARY

A laboratory-scale test device was constructed to evaluate the fire-extinguishing effectiveness and toxic gas generation of Halon alternative agents. A methane flame, produced with a Bunsen burner, was extinguished by introducing a carefully measured flow of the candidate agent into the air inlets of the burner. Subsequently, a steady-state condition just below extinguishment was established and effluent gases were measured using a magnetic sector mass spectrometer. Halon 1211, Halon 1301, carbon dioxide, and eleven potential replacement agents were evaluated with this protocol. Possible mechanisms of the chemical interactions which cause extinguishment are advanced.

INTRODUCTION

PURPOSE.

The objective of this project was to experimentally evaluate Halons and potential replacement agents in terms of their relative fire extinguishment capability and agent decomposition product generation using a simple, laboratory-scale test method.

BACKGROUND.

The Federal Aviation Administration (FAA) has required Halon 1211 hand-held extinguishers for passenger category aircraft since 1986 (reference 1). This regulation was an outgrowth of a full-scale test program conducted in response to the threat posed by a terrorist with combustible fluids, e.g., gasoline. Halon was found to be effective "to extinguish a severe seat fire in a transport passenger cabin and safe in terms of agent decomposition (HF, HCl, and HBr) and neat agent concentration." (reference 2)

Subsequently, Halon 1211 demonstrated superior performance for a different fire scenario. On March 11, 1991, a fire developed below the floor of Delta Airlines Flight 15 en route from Frankfurt, Germany, to Atlanta, Georgia. A flight attendant reported a fire on the left side of the Lockheed L-1011-385-3 toward the rear of the cabin. At about the same time overheat warning lights for a pneumatic duct illuminated on the pilot's instrument panel. The fire was extinguished using three hand held Halon 1211 extinguishers directed toward the source through return air vents along the floor. The aircraft made a safe landing at Goose Bay, Labrador, with no injuries to the crew of 13 and 213 passengers. (reference 3) Because of the hidden nature of this electrical fire, it is believed that only a gaseous agent like Halon would be effective for this type of fire. Quite probably, many lives were saved due to Halon usage.

In addition to a general requirement for hand-held fire extinguishers , "an airplane with a passenger capacity of at least 31 or more <u>must contain Halon 1211</u> (bromochlorodifluoromethane) or equivalent, as the extinguishing agent." (reference 1) Regulations also require that "airplanes with a passenger capacity of 20 or more must be equipped with a built-in fire extinguisher for each disposal receptacle for towels, paper, or waste" (reference 4) and Class C cargo compartments must have "an approved built-in fire extinguishing system controllable from the pilot or flight station." (reference 5) While the latter two regulations do not specify an agent, industry practice has been to use Halon 1301.

The United States is a signatory to the Montreal Protocol, the international treaty to phase out ozone depleting substances. No halons may be produced after January 1, 1994. (reference 6) Because there is no immediately available replacement at the present time and sufficient Halon quantities exist for the short term, Halons will continue to be used but will be eventually phased out.

DISCUSSION

GENERAL.

A test device to evaluate Halons and Halon substitutes for comparative effectiveness and decomposition product generation should be simple, reproducible, and quantitative. The key parameter sought is the relative flow rate of agent to extinguish a standardized diffusion flame. The cup burner was not used because the high flow rate of air through the device would excessively dilute the gases to be measured. Additionally, the cup burner evaluates the agent concentration in air needed to stop combustion. This variable might be used to calculate the amount of agent to extinguish a room fire with a suppression system, but that is not the purpose here. Rather, the variable sought is the volumetric flow of agent needed to extinguish a standardized fire. This models discharge of an extinguisher at the base of a fuel fire where excess air is present.

TEST ARTICLE. The standard fire was chosen to be a 250-watt methane flame, as produced by a natural gas (0.067-inch orifice) Bunsen burner with flame retainer removed and air inlets fully open. Methane was selected because it is the simplest hydrocarbon fuel (CH_4), producing upon combustion two moles (gram molecular weights) of water and one mole of carbon dioxide for each mole of methane. Methane burns completely with no sooting as a simple diffusion flame, has a precisely known heat of combustion, and is fully gaseous from tank to burner, so no heat of vaporization effects are encountered which could result in irregular delivery to the burner. Ultra-high purity (UHP) methane flow was calibrated using a rotameter to adjust delivery volume to a Precision Wet Test Gas Meter. The net heat of combustion is 191.4 kcal/mole of methane. After volume correction from STP

(Standard temperature and pressure - 760 torr, 0° Centigrade) to ambient conditions the nominal methane flow rate was 0.475 liters/minute which produced a blue flame approximately 3 inches long. Kilowatts heat liberated by burning methane was calculated as follows:

$$\text{Kilowatts Heat Produced} = \frac{\text{liters}}{\text{min}} * \frac{191.4\ \text{kcal}}{\text{mole}} * \frac{273}{(T+273)} * \frac{p_a - \partial p_{H2O}}{760} * \frac{\text{kW*min}}{14.33\text{kcal}}$$

Where: liters per minute = methane flow at ambient, T = degrees C.
p_a = ambient pressure, and ∂p_{H2O} = partial pressure of water at T

Extinguishing agent was delivered to the base of the flame with a 1/8-inch stainless steel tube bent into an "L" that was inserted through the air inlets near the base of the Bunsen burner. The tube was centered in the barrel of the burner and was 2 1/4 inches (57 mm) below the outlet, thus methane and agent were mixed with air prior to combustion. The effluent gases produced by the burner were contained by a glass combustion tube, 26 mm i.d. by 500 mm long, situated 1/2 inch (12.7 mm) above the burner outlet. The flame was almost completely surrounded by the combustion tube and was visible during the experiment, with air freely diffusing around it. As was the case with methane, the extinguishing agent was metered using a rotameter that can be switched with a gas-tight ball valve to the wet test meter for precise measurement of the delivery volume. See Figure 1.

Gas concentrations were measured at the exhaust of the combustion tube chimney using a Perkin Elmer ICAMS (Industrial Central Air Monitoring System), a magnetic sector mass spectrometer. The inlet to ICAMS is a 1/16-inch Teflon FEP capillary tube which draws about 10 milliliters per minute of the sample gas mixture. The ICAMS capillary was attached to a sample probe assembly made of 1/8-inch stainless steel tubing which drew the sample gases from the combustion tube. The probe was held in place with a custom made aluminum adapter which has holes bored to the o.d. of the chimney so that it slides over the chimney and holds the probe in the geometric center of the chimney and 30 mm below the outlet. The aluminum adapter also served as a heat exchanger so that the combustion gases were cooled below the melting point of the Teflon capillary. To minimize dead volume and keep temperatures warm enough to prevent water condensation in the probe, the Teflon capillary passed through a 1/8-inch stainless steel Swagelok tee which drew a total sample of approximately 100 milliliters/minute, as measured with a rotameter connected to a vacuum pump. The unseparated gas mixture was analyzed for oxygen, nitrogen, water, carbon dioxide, argon, hydrogen fluoride, hydrogen chloride, hydrogen bromide, and unreacted extinguishing

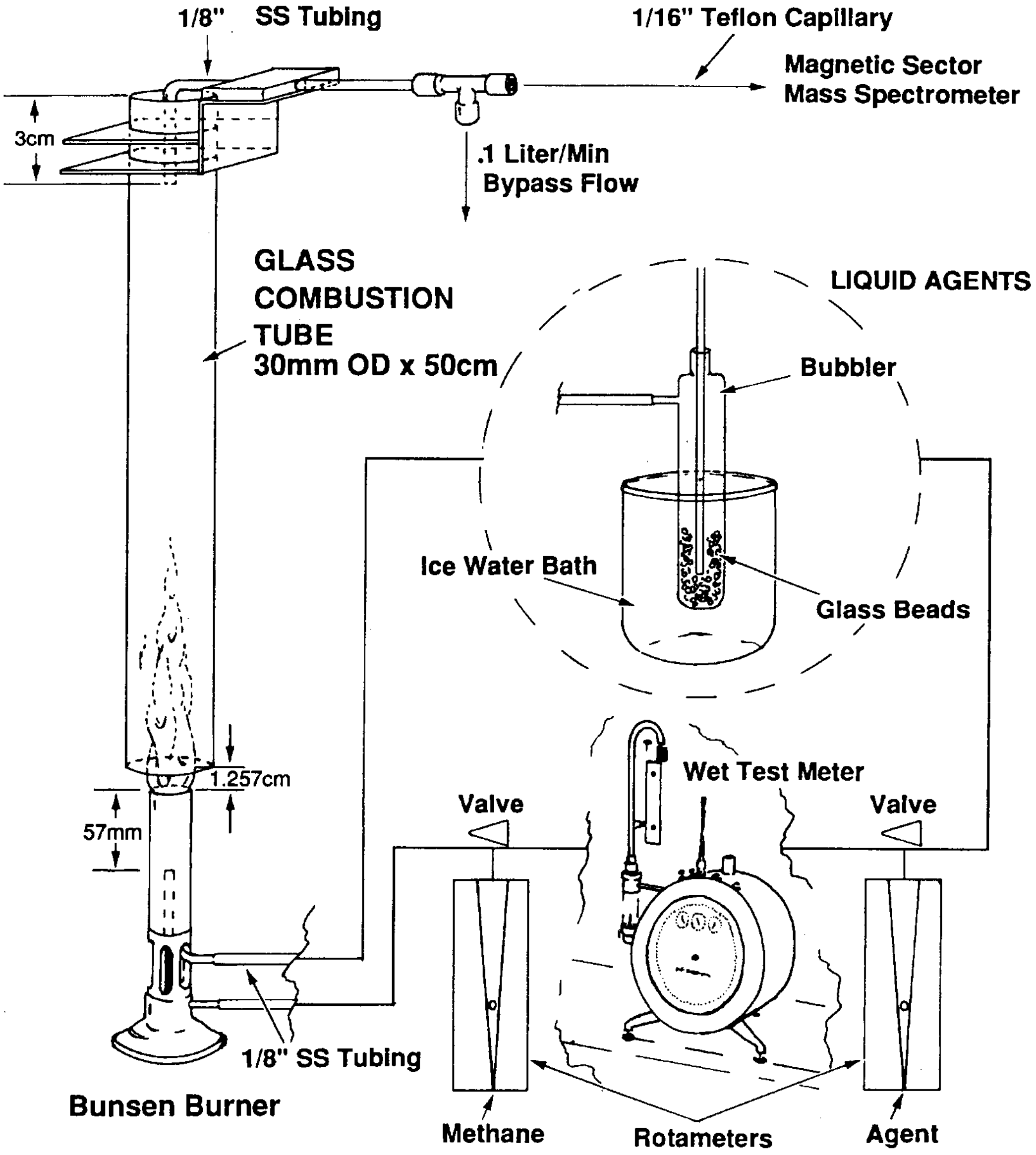

FIGURE 1. TEST APPARATUS

agents. In the investigative scan mode, ICAMS measured all ions from mass-to-charge ratio (m/z) 2 to 200 in units of ion counts per second. Configuration, calibration, and operation of ICAMS is explained in detail in appendix A.

TEST PROCEDURE. Methane flow was adjusted to produce a 250-watt flame. The extinguishing agent was slowly metered into the methane flame, with notes taken as to visible changes in the appearance of the flame. The agent flow rate was slowly increased until the flame is extinguished. The reading on the rotameter was noted and the valve was switched to direct flow to the wet test meter. A stopwatch was used to time the interval between volume readings on the dial of the wet test meter. This procedure was repeated three times, and the average flowrate of agent necessary for extinguishment calculated. To evaluate the decomposition products of the agent, flow was backed off about 10 percent from the extinguishment flow or until the flame just stayed continuously lit. The ICAMS data acquisition routine was started, and the background air analyzed for the baseline condition. ICAMS scanned all the masses of interest and issued a printout approximately every thirty seconds. After a few samples of background air, the probe was manually attached to the chimney. A stopwatch was started and the test was conducted for ten minutes, at which point the probe was removed from the chimney. The ICAMS was run until the measured concentrations returned to the baseline readings.

Agents that are liquids at room temperature were tested using a slightly different procedure. Heating the line and vaporizing liquid into the Bunsen burner would have been difficult. Instead, a Dewar flask was filled with ice and water. The liquid agent was added to a 250-ml bubbler, which has been filled with 3-mm glass beads about 30 mm above the dip tube. The agent was added until the level is about 50 mm above the glass beads. The bubbler was then immersed in the ice water until the temperature was equilibrated. Matheson zero air was then metered into the bubbler with the rotameter and the outlet of the bubbler was connected to the stainless steel tube entering the Bunsen burner air inlets. (See inset of figure 1) In this manner pure agent vapor and air were used to extinguish the flame. As above, the procedure was repeated three times, however it was necessary to measure the air flow entering the bubbler and the agent and air mixture leaving the bubbler with the wet test meter. The difference between the total flow and the air flow alone is equal to the agent flow. It was seen that air flow alone had no effect on the characteristics or analysis of the flame. At high air flows the only effect was that the methane air mixture was sufficiently flammable to flash down the barrel of the burner and stay lit in the air inlet region of the Bunsen burner. Since the agent vapor was produced at lower than room temperatures, agent condensation in the lines was not possible. The uniform temperature of the bath assured constant agent vapor pressure during the test. The glass beads in the bubbler were to assure high surface area for evaporation and mixing of the saturated agent/air mixture.

VISUAL OBSERVATIONS. Flame descriptions are presented below.

TABLE 1. VISUAL OBSERVATIONS OF FLAME

Agent	Observations
CO_2	No observable change until extinguishment
Halon 1211	Slight yellow color at top of flame, flickering near extinguishment, luminous tail above flame
Halon 1301	Slight yellow color at top of flame, no change except slightly sooty near extinguishment
HBFC-22B1 (FM-100)	Yellows near flame out
HFC-23 (Fluoroform)	Bright yellow flame at top, no flickering or sooting, yellow turns back to blue near out
HFC-125	Long, intense yellow, flickering flame, pops out suddenly at extinguishment
HFC-227EA (FM-200)	White turning to yellow, slow pulsing flame, no flickering or sooting
FC-3-1-10 (Perfluorobutane)	Intense yellow flame, gradually reduces in size until extinguishment
FC-4-1-12 (Perfluoropentane)	Yellow flickering flame at half flow, flame size reduces near extinguishment
FC-5-1-14 (Perfluorohexane)	Intense yellow, flickering flame, diminishes at extinguishment
HCFC-123	Intense yellow sooty flame at half flow, reduces in size and turns green near out
HCFC-124	Bright yellow, slowly pulsing flame, developing a long tail of soot
Halon 13001 (CF_3I)	Yellow flame within blue flame, no sooting of flame but noticeable faint purple, diffused smoke
Halon 37001 (C_3F_7I)	Inner yellow flame cone, sooting and flickering of flame, pronounced purple color of smoke

Flame response to the agents varied considerably, from little or no visible change as extinguishment was approached to heavy sooting and flickering of the flame. In general, visual effects were seen at flow rates about 25 percent of the amount required to extinguish, turning the flame from pale blue to bright yellow.

EXTINGUISHMENT RESULTS.

Extinguishment capability in this test protocol is presented as milliliters per minute of gaseous agent to extinguish a 250-watt methane flame produced by a Bunsen burner with free diffusion of room air. Since all agents were in gaseous form when they extinguished the flame, the mass flow of agent can be calculated by correcting the agent flow measured with the wet test meter for the molecular weight of the agent. Average ambient conditions used for the calculations were 22.5° C., 760 mm Hg, with water vapor partial pressure 20.4 mm Hg.

$$\text{Mass Flow rate (g/min)} = \frac{\text{ml/min gas @ ambient}}{24.92 * 10^3 \text{ ml /mole}} * \text{MW}$$

$$\text{Liters/mole of gas} = 22.41 \text{ l(STP)} \; \frac{295.7}{273.2} * \frac{760}{(760-20.4)} = 24.92 \text{ l/mole}$$

Analytical results were obtained with the agent flow rate just below that needed for extinguishment. Agent flow rates are presented in table 2.

TABLE 2. EXTINGUISHMENT PERFORMANCE

Agent	Formula	MW	Extinguishment Flow (ml gas/min)	Extinguishment Flow (g/min)	Test Flow (ml gas/min)	Fraction
HALON 1211	CF_2ClBr	165.4	32.9	0.218	23.4	0.71
HALON 1301	CF_3Br	148.9	25.7	0.153	21.0	0.81
HBFC-22B1	CF_2HBr	130.0	28.7	0.151	19.5	0.68
HFC-23	CF_3H	70.0	523.	1.469	426.0	0.82
HFC-125	C_2F_5H	120.0	122.2	0.588	112.4	0.92
HFC-227EA	C_3F_7H	170.0	92.3	0.629	90.5	0.98
HCFC-123	CF_3CHCl_2	152.9	130.0	0.797	92.8	0.71
HCFC-124	C_2HF_4Cl	136.5	114.7	0.628	99.2	0.86
FC 3-1-10	C_4F_{10}	238.0	69.5	0.663	61.3	0.88
FC 4-1-12	C_5F_{12}	288.0	172.6	1.994	151.2	0.88
FC 5-1-14	C_6F_{14}	338.0	71.5	0.969	60.4	0.84
HALON 13001	CF_3I	195.9	37.1	0.292	31.5	0.85
HALON 37001	C_3F_7I	295.9	66.3	0.787	52.1	0.79
CARBON DIOXIDE	CO_2	44.0	736.0	1.297	635.0	0.86

The test flow was the steady-state condition where the flame stayed continuously lit for purposes of analysis, and the fraction was test flow divided by extinguishment flow. There was some variability between agents in the fraction of extinguishment flow used for the decomposition study due to the visibly different effects the agent had on the flame. In general, flames that were constant or that diminished near extinguishment allowed testing at conditions closer to the extinguishment flow than flickering or sooty flames. Figure 2 shows the extinguishment flows and the flows at which the tests were conducted as stacked bar graphs in order of agent effectiveness.

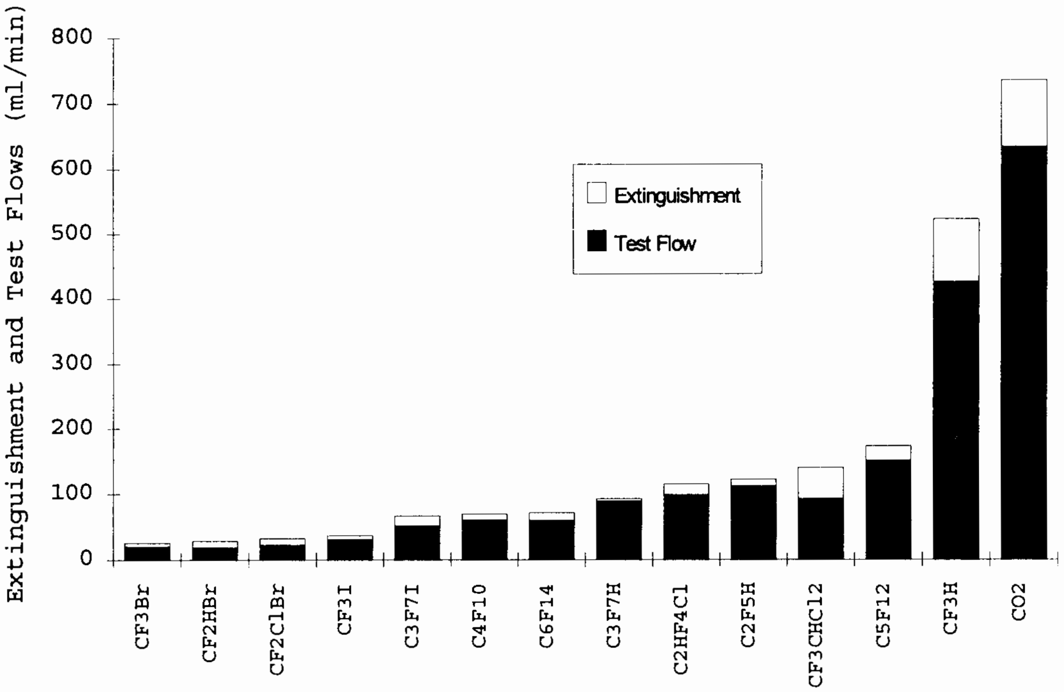

FIGURE 2. AGENT COMPARISON

There was not, nor would one expect, perfect correlation between the extinguishment flow for this test or the two tests described in NFPA 2001 Standard on Clean Agent Fire Extinguishing Systems, Inerting Concentrations or Flame Extinguishing Concentrations. (reference 7) The conspicuous outlying data point (Table 3) is HBFC-22B1 which performed better in this test than in either of the tests referred to in the NFPA document. The cup burner was designed to model the concentration in air necessary to extinguish a fire and thereby provide a means of calculating the amount of agent necessary to provide fire protection for a room of given size in a total flood application. Since this test and the cup burner both involve a fire with agent passing across it, there should be reasonable correlation. Figure 3 shows a comparison between this test and the cup burner, using Fenwal data from Table A-3-4.2.2 of the reference. Agreement between the cup burner and this test was better than that between the tests for extinguishment and inerting referenced in the NFPA document, the respective correlation coefficients being 0.904 and 0.687.

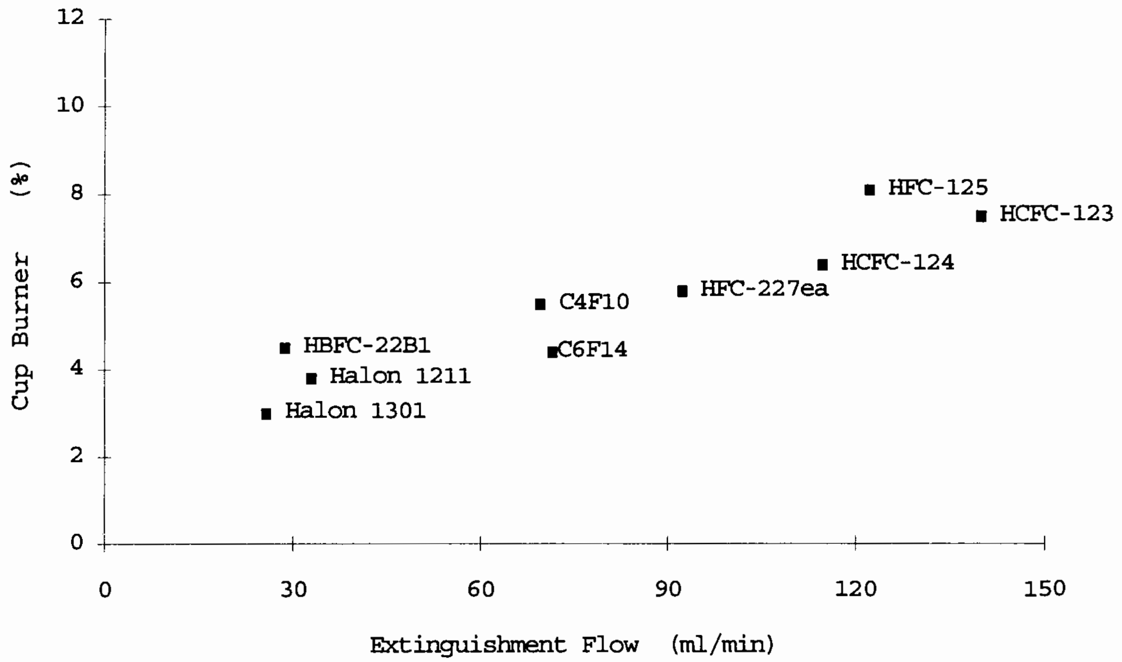

FIGURE 3. EXTINGUISHMENT FLOW VS CUP BURNER

Halon 1211, Halon 1301, and HBFC-22B1, which are halogenated bromomethanes containing at least two fluorine atoms, required essentially the same volumetric flow for extinguishment. It seems to make little difference in fire performance whether the remaining atom is hydrogen, fluorine, or chlorine. Replacing the bromine on Halon 1301 with iodine (Halon 13001) results in a superior fire fighting agent using this test as the evaluating criteria. This point will be discussed later, with possible mechanisms advanced that impart this quality. HFC-23 was the poorest performer of all the halogenated compounds tested in this and all other tests, being better than only CO_2. It is not clear why perfluoropentane performed so much poorer than perfluorobutane or perfluorohexane.

Table 3 lists the agents in order of extinguishment performance for this test, along with the values referenced in the NFPA 2001 Standards of Flame Extinguishing Concentration (Fenwal data) and Inerting Concentration (Senecal data) for comparative purposes.

TABLE 3. COMPARATIVE TEST PERFORMANCE

Agent	Extinguishment Flow (ml/min)	NFPA 2001 Extinguishment %	Inerting %
Halon 1301	25.7	3.0	6.7
HBFC-22B1	28.7	4.4	11.7
Halon 1211	32.9	3.8	-
Halon 13001	37.1	-	-
Halon 37001	66.3	-	-
Perfluorobutane	69.5	5.5	10.3
Perfluorohexane	71.5	4.4	7.3
HFC-227ea	92.3	5.8	11.3
HCFC-124	114.7	6.4	-
HFC-125	122.2	8.1	14.7
HCFC-123	130.0	7.5	-
Perfluoropentane	172.6	-	-
HFC-23	523.0	12.0	20.2
Carbon Dioxide	736.0	28.0	-

ANALYTICAL RESULTS.

Early into the experiments, it was seen that water condensation in the sample line leading to ICAMS would pose problems for real-time acid gas analysis. Examination of the flame alone showed immediate response to CO_2 and O_2 and in the stoichiometric proportions expected.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Water concentrations were seen to lag substantially and persisted at the high level long after the probe was removed from the chimney. After the initial lag, the water concentration went up and stabilized. CO_2 concentrations generally increased from ambient, 350 ppm, to about 1.5% (15,000 ppm), while ambient oxygen dropped from 20.9% to about 17.9%, or 3% consumption, and the water concentration shifted from 1.5% to 4.5%. This is consistent with the expected stoichiometry.

The water concentration, however, remained at the high level long after the probe was removed. Integrating the area under the time/concentration curve showed about twice as much water as expected using the assumption that the sample was collected uniformly and that dividing the area under the curve by the time the probe was attached should equal the amount of water production. With oxygen and carbon dioxide, using either the peak height or integral gave results within experimental error (< 10 percent RSD).

The concentration of water produced during the test, when added to the ambient background, was higher than saturation. This implies that some condensation was occurring in the line. Several different approaches were tried to eliminate this phenomena, including preheating the probe, changing or eliminating the bypass flow, sliding the capillary to ICAMS into and out of the probe for the test, and removing the capillary after the probe was removed from the chimney. The Teflon capillary itself was not heated because this would only shift the problem to the inlet of the mass spectrometer itself and possibly cause a serious instrument problem. (Changing a capillary is easy, decontaminating an inlet is not.) The phenomena of water lag persisting after probe removal was minimized when the bypass flow was approximately 100 ml/min (ICAMS inlet flow was approximately 10 ml/min) and the capillary was slid to where the 1/8-inch stainless steel probe met the aluminum probe holder. Here the probe holder itself was almost too hot to touch, but no melting of the Teflon capillary occurred.

The acid gases (hydrogen fluoride, hydrogen chloride, and hydrogen bromide) are very soluble in water and have boiling points much lower than water. In the presence of water, however, each acid forms a high boiling (120° C.) azeotrope. With the Halons, it was seen that the acid gases eluted as peaks after the probe was removed from the flame just as the elevated water concentrations began to return to ambient levels. The elution order was HF, HCl, and HBr. It was found experimentally that the yield of acid gases was independent of the time of the test. That is, when the analyses for the concentration of the acids were summed and then divided by the test interval, the resulting concentration was the same, within experimental error, regardless of test duration. Although the peak concentration was approximately the same between tests of different duration, or approached the same plateau, the total amount measured was directly proportional to the length of the test. A test duration of ten minutes was selected as the standard test, as this was seen to give several points at the plateau value, acceptable reproducibility, yet keep the total time for water and acid gases to elute from the capillary and return analyses to ambient condition to under one hour. Although the peak shape of the eluted acid would change, analytical results were +/- 15 percent. Ambient water levels also had no apparent effect.

For extinguishing agents other than the Halons, hydrogen fluoride concentrations were much higher and often were seen while the probe was attached. For HFC-23, ambient water actually dropped when the probe was attached due to high HF levels dehydrating room air. Water subsequently rose far above ambient and persisted for a long time. For C_3F_7I and HCFC-124 water concentrations dipped, then rose, showing only small changes in water concentrations from ambient.

Analytical results are presented in tables 4 and 5. Oxygen, carbon dioxide, water, and extinguishing agent results are shown in Table 4. Acid gas results are shown in table 5. (For more detail, see appendix B for a listing of the yields for each individual run. Appendix C shows the corresponding plots of all of the analytical data as a function of time.) Air gas results are given both in terms of the step change in concentration, or peak, and the yield, or area under the curve, during the ten-minute test. The numbers shown are the averages of three tests.

TABLE 4 - ANALYTICAL RESULTS - OXIDATION

Agent	O_2 (%)		CO_2 (%)		H_2O (%)		Agent
	Peak	Yield	Peak	Yield	Peak	Yield	Peak (ppm)
Flame only	-3.34	-3.38	1.53	1.54	3.54	7.48	-
Halon 1301	-2.85	-3.48	1.27	1.44	4.23	6.61	0
HBFC-22B1	-3.29	-3.31	1.51	1.41	3.84	6.46	15
Halon 1211	-3.00	-3.18	1.42	1.68	3.88	7.11	17
Halon 13001	-3.26	-3.49	1.50	1.50	2.50	4.23	0
Halon 37001	-3.78	-3.93	2.31	2.42	-	-	45
FC 3-1-10	-2.71	-3.43	1.42	1.45	1.86	3.27	20
FC 5-1-14	-4.86	-5.55	2.92	2.91	1.51	3.40	75
HFC-227EA	-2.66	-2.89	1.66	1.73	2.54	8.15	12
HCFC-124	-3.51	-3.57	1.12	1.11	0.30	0.35	0
HFC-125	-3.37	-3.69	2.01	2.05	1.97	5.72	27
HCFC-123	-4.22	-4.65	2.33	2.40	1.47	3.87	45
FC 4-1-12	-5.29	-5.34	4.32	4.35	2.05	2.69	0
HFC-23	-5.72	-7.11	2.90	3.04	1.45	5.53	350
Carbon Dioxide	-3.38	-3.34	3.45	3.47	3.61	6.45	-

The typical relative standard deviation between tests was approximately 10 percent for oxygen and carbon dioxide and 20 percent for water using either the step change or integral method. The integral and step change values are in general agreement for oxygen and carbon dioxide, with the oxygen integral generally 10 percent higher than the step change and carbon dioxide +/- 5 percent. As described above, the water yield (integral) was generally much greater than the peak change in concentration. The experimental work was carried out on humid summer days and dry winter ones, but there appeared to be no correlation between the yield-to-peak differences and the initial ambient water concentration. The extinguishing agent itself was almost completely consumed by the flame, except in the instance of HFC-23 where flow rates of agent are almost equal to the flow of the methane fuel. For any agent, if the flame was extinguished at any point in the test, ICAMS showed a peak of agent around several hundred parts per million. Any of these data points were disregarded and not averaged with the other values for the results shown in the table. Yield for agent was not reported since small ambient concentrations were often present in the trailer housing ICAMS and summing these values would be meaningless.

Table 5 shows the HF, HCl, and HBr yield calculated by summing the concentration values for each minute and dividing by 10, the number of minutes in the test. As mentioned above, some agents dehydrated the off-gas from the combustion device and HF concentrations were seen during the time the probe was attached to the combustion tube, although this was not the case for most agents. The peak was also quite variable although the area under the curve was reproducible. Therefore, reporting acid peak as well as yields was not done as it was with O_2, CO_2, and water.

TABLE 5. ANALYTICAL RESULTS - ACIDS

Agent	HF (%)	HCl (%)	HBr (%)	Water Ratio
Flame only	0.05	0.001	0.000	2.52
Halon 1301	0.19	0.014	0.000	1.57
HBFC-22B1	0.50	0.000	0.020	1.71
Halon 1211	0.29	0.046	0.000	1.98
Halon 13001	0.49	0.002	0.000	2.50
Halon 37001	1.14	0.062	0.001	1.00
FC 3-1-10	2.51	0.027	0.011	1.93
FC 5-1-14	6.15	0.016	0.017	2.23
HFC-227ea	0.59	0.005	0.000	3.36
HFC-125	1.95	0.038	0.001	1.97
HCFC-124	2.66	0.072	0.000	1.18
HCFC-123	3.57	0.632	0.002	2.63
FC 4-1-12	5.47	0.027	0.006	1.01
HFC-23	16.00	0.001	0.004	3.82
Carbon Dioxide	0.05	0.002	0.000	1.80

Some explanation is warranted as to the appearance of certain acid gases where they are not expected. For example, HFC-125 has substantial HCl reported, yet the chemical formula is C_2HF_5. An examination of the spectra shows that when HF is almost eluted, a peak of HCl appears. The ratio of m/z 36 to 38 is 3:1, just what was expected for hydrogen chloride. It therefore appears that there is a contaminant containing chlorine in HFC-125. The amount of HCl measured is just over one percent of the HF, consistent with contamination. Similarly, HBr is not expected in the decomposition products of FC 3-1-10, since the formula is C_4F_{10}. In this instance, HBr was seen in both the decomposition spectra and the neat agent in air, in the expected isotopic ratio for m/z 80 and 82 of 1:1, implying the contaminant is HBr itself. Surprisingly, very little HBr is seen for Halon 1211 and Halon 1301. This point is examined later. More about identification from isotopic ratios using ICAMS is discussed in appendix A.

Also listed in this table is the ratio of the peak water concentration to the yield of water obtained by integration of the area under the curve and dividing by test duration. Since it was seen that water yield exceeded the expected stoichiometry, it is expected that the same phenomena would occur with acids since they are soluble in water. That implies dividing the acid yield by the water ratio should allow back calculation of the true yield of the extinguishment reaction.

For example, HFC-23 or CHF_3 has a reported HF yield of 16.0%. Extinguishment flow of agent was 523 ml/min, compared to the methane fuel flow of 472 ml/min. That is about a 10 percent excess of a 1:1 ratio of agent to fuel. If the reaction is

$$CH_4 + CHF_3 + \frac{5}{2} O_2 \rightarrow 2CO_2 + 3\ HF + H_2O$$

This implies CO_2 concentration should be twice the water concentration and HF three times the water concentration. The peak concentration of CO_2 (2.90%) was in fact twice the water concentration (1.45%). Clearly, HF at 16.0% is much higher than predicted by stiochiometery. However, dividing 16.0 by the ratio of peak to yield of water, 5.53/1.45 the result is 4.19% or just under the three to one prediction. It seems reasonable that this reaction was just what was occurring. When sufficient fluorine was present to consume three of the four hydrogens on methane, flame propagation was terminated.

Similarly carbon dioxide seems to terminate the flaming reaction as soon as it is equal in concentration to oxygen being consumed and water being produced. In that case, we have CO_2 consuming the hydrogen and hydroxyl radicals to form H_2CO_3. Carbonic acid is a weak acid (commonly known as seltzer), although here it is in the gaseous form. Leftover oxygen radicals simply form molecular oxygen.

$$CH_4 + 2\ O_2 + CO_2 \rightarrow 2\ H_2CO_3$$

Extinguishment then occurred when active hydrogen containing particles were consumed by reactions that did not liberate sufficient energy to allow formation of more of these same particles.

Arguments for correcting the yield of acids for the other agents were less compelling, but seem reasonable. Note that HFC-23 had by far the largest water ratio for all extinguishing agents. In other cases, such as Halon 37001 and FC 4-1-12 (perfluoropentane) water concentration dipped when the probe was attached and later rose in a sine wave-like profile, so that there was very little correction for the water ratio. Figure 4 shows the yield for hydrogen fluoride, as measured directly, and the yield for hydrogen fluoride corrected for the water ratio. Table 6 compares the hydrogen fluoride production of the various agents at flows just below extinguishment. The last column of the table compares agents to Halon 1211 in terms of relative production of hydrogen fluoride during extinguishment of the

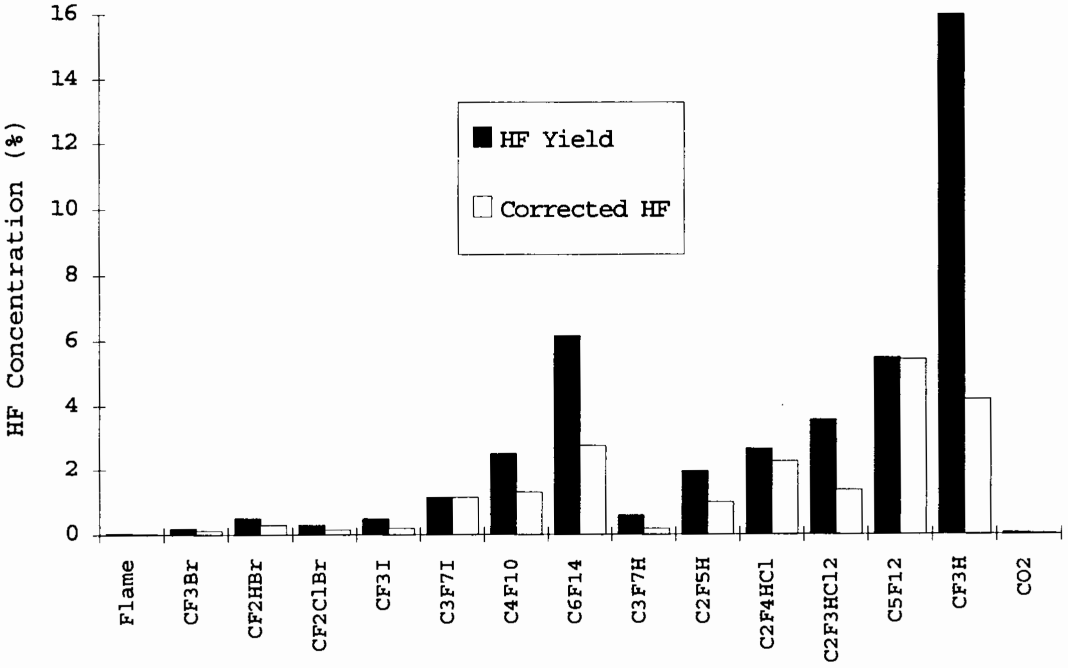

FIGURE 4. HYDROGEN FLUORIDE YIELD

standard fire. With the exceptions of HFC-227ea and Halon 13001, all potential replacements produced at least five times the amount of hydrogen fluoride as Halon 1211, the current hand-held aircraft extinguisher. The other agents may therefore have potential toxicity problems associated with their usage in confined space.

TABLE 6. HYDROGEN FLUORIDE PRODUCTION

Agent	HF Measured (%)	HF Corrected (%)	HF Relative to Halon 1211
Halon 1301	0.19	0.12	0.83
HBFC-22B1	0.50	0.29	2.00
Halon 1211	0.29	0.15	1.00
Halon 13001	0.49	0.20	1.34
Halon 37001	1.14	1.14	7.78
Perfluorobutane	2.51	1.30	8.88
Perfluorohexane	6.15	2.76	18.83
HFC-227ea	0.59	0.18	1.20
HCFC-124	2.66	2.25	15.39
HFC-125	1.95	0.99	6.76
HCFC-123	3.57	1.36	9.27
Perfluoropentane	5.47	5.42	36.98
HFC-23	16.00	4.19	28.60

OTHER DECOMPOSITION PRODUCTS.

ICAMS was used in investigative scan mode to determine other possible decomposition products. The investigative scan mode looked at all mass-to-charge particles, from m/z 2 to 200. To quantify any gas with ICAMS, the fragmentation pattern, or relative abundance of each m/z ion, and the response in terms of ion count per unit concentration must be known. This study has not attempted to quantify these decomposition products but did examine for m/z particles (ions) that were not due to the agent spectra or air gases. Since the hot exhaust was delivered into the spectrometer literally seconds after the combustion process, it was entirely possible to have had long-life free radicals measured. (Free radicals are reactive compounds which are electrically neutral but have unpaired electrons and do not follow the octet rule. That is, you can't put them in a bottle and store them on a shelf.)

The test procedure was to run an investigative scan five minutes into a test, at the rate of agent flow used for the normal 10-minute test. The scan for all masses took approximately 2 minutes. These spectra were compared to calibration spectra for neat agent in air. Peaks that were present during the test run but absent in the spectra of agent alone were noted. Where a peak overlapped the agent spectra, the base peak for the agent tested in the decomposition spectra was multiplied by the relative abundance fraction. If the difference was more than 20%, that peak was also noted. In this way the background for unreacted agent was subtracted. All agents but HCFC-124 were tested in this manner.

One species for which analysis was conducted due to its high toxicity was COF_2 (carbonyl fluoride) . This compound has a base peak at m/z 47 and a strong peak 55 percent of base at m/z 66. This decomposition product was found in the spectra for HFC-23, FC-3-1-10 (perfluorobutane) , FC-4-1-12 (perfluoropentane), and FC-5-14 (perfluorohexane). These peaks were also seen for Halon 1211 and C_3F_7I, although 66 was twice the abundance of 47 so the presence is not confirmed. M/z 66 was seen for HCFC-123, but the agent itself has a large peak at 47, so it is difficult to make any conclusion. The other agents did not show peaks of significant size at 47 and 66.

Similarly, $COCl_2$, or phosgene, was of interest. Phosgene has a base peak at m/z 63, with a large peak about 33 percent of base at m/z 65, and small peaks at m/z 98 and m/z 100. Halon 1211 did not show peaks necessary for phosgene but HCFC-123 had the necessary peaks and in approximately the correct proportions. All other compounds did not show the presence of phosgene. This was expected, however, since only Halon 1211 and HCFC-123 contain chlorine. (HCFC-124 was not tested.)

A point of interest, especially since it involves the Halons, is the question of the fate of bromine. HBr is a minor decomposition product present in much less abundance than HF, even allowing that there are two and three fluorine atoms for each bromine, respectively, on Halon 1211 and Halon 1301. Examination of the spectra for Halon 1211, Halon 1301, and HBFC-22B1 showed small peaks present at m/z 94, 96, 172, 174, and 176. Due to the fact that bromine is virtually unique in having two stable isotopes (79 and 81) in nearly identical concentrations , it was quite likely that bromomethane (m/z 94,96) and dibromomethane (m/z 172,174,176) were produced. Peaks were seen at 158, 160, and 162 just at the level of detection for the instrument. These were due to Br_2. This implies that a possible mechanism in the extinguishment of the flame is the combination of bromine atoms with methyl and methylene radicals produced during the combustion of methane, similar to the way fluorine combines with hydroxyl or hydrogen radicals. This additional mechanism may explain the superior fire-fighting performance of the Halons and also the low measured concentration of HBr.

CF_3I seemed to behave similarly. The agent alone has peaks at 196 and 177 due to molecular mass and CF_2I^+. The investigative scan for decomposition products does not show a peak at 177, but rather one at 178. This would seem to be CF_2HI, implying that this agent loses a fluorine while grabbing a hydrogen. CF_3I and C_3F_7I both have peaks at 142 that are not present in the agent spectra alone. This seems to be due to CH_3I, iodomethane, which implies that the agent reacts with a methyl radical, giving up an iodine. Because iodine has one isotope, 127, and this is the parent ion for the inorganic iodine compounds (HI, I_2) and is either parent or very large for the organic iodine compounds, it is impossible, with ICAMS, to tell if I_2 is formed.

BOND STRENGTH CALCULATIONS - REACTION MECHANISMS.

A simple examination of bond strength and the possible one step reactions provides insight as to why Halons extinguish fires. Work by Pauling (reference 8), Sanderson (reference 9) and others on the nature of the covalent bond and the theory of polar covalence have provided generally successful quantitative analysis of bond energy for organic compounds.

In the following analysis, each side of the elementary equations for possible reactions are balanced for the flow of energy into or out of the reactants and products. Breaking bonds requires energy (positive enthalpy change), forming bonds liberates energy (negative enthalpy change). Likely reactions are those with $-\Delta H$, that is exothermic reactions, which release chemical bond energy in the form of heat. Endothermic reactions require energy (+ΔH) and do not proceed spontaneously, but endothermic steps will occur if the net energy for several steps in the aggregate is negative. For the following arguments, the bond energies (reference 10) are converted to units of kcal/mole (kJ/mole*0.2390) are as given in table 7. Free radicals, molecules with unpaired electrons and not following the octet rule, are permitted as intermediates but not as final products of the reactions. Equations, of course, must be balanced.

TABLE 7 - BOND STRENGTH (kcal/mole)

Bond		Bond		Bond		Bond	
C-H	98.2	C-F	115.9	H-F	135.0	O-F	45.4
C=O	191.0	C-Cl	72.8	H-Cl	102.3	O-Cl	52.1
C-C	82.7	C-Br	68.1	H-Br	86.5	O-Br	48.0
C=C	143.9	C-I	50.9	H-I	70.5	O-I	48.0
O-H	109.7			F-F	37.0	Br-Br	45.5
O=O	118.1			Cl-Cl	57.3	I-I	35.6

METHANE COMBUSTION. For the combustion of methane, we will assume the reaction proceeds as follows:

									ΔH
CH_4	+	O_2	->	CH_3	+	O	+	OH	
98.2		118.1						-109.7	+106.6

In this reaction, methane reacts with oxygen to form a methyl radical, an oxygen radical, and a hydroxyl radical. One carbon-hydrogen bond is broken, requiring 98.2 kcal/mole, one oxygen-oxygen double bond is broken requiring 118.1 kcal/mole and one oxygen-hydrogen bond is formed liberating 109.7 kcal/mole. The total reaction is endothermic. This is expected since oxygen and methane will co-exist until sufficient heat of activation is present for the next exothermic steps to occur. When this point is reached, via a spark or ignition source, the combustion of methane proceeds spontaneously. That is, the net heat for the total reaction system is exothermic (-ΔH).

The next reaction is between the methyl radical and either the hydroxyl or oxygen radical.

							ΔH
CH_3	+	O	->	CH_2	+	OH	
98.2						-109.7	-11.5
CH_3	+	OH	->	CH_2	+	H_2O	
98.2						-109.7	-11.5

In both cases a carbon-hydrogen bond is broken, requiring 98.7 kcal/mole and an oxygen-hydrogen bond is formed, liberating 109.7 kcal/mole. The net energy is -11.5 kcal/mole, and proceeds spontaneously. CH_2 can likewise proceed to CH, or react with molecular oxygen. Clearly CH_2 reacting with oxygen is favored. The net reactions are:

							ΔH
CH_2	+	OH	->	CH	+	H_2O	-11.5
CH_2	+	O	->	CH	+	OH	-11.5
CH_2	+	O_2	->	COH_2	+	O	
		118.1		-191.0			-72.9
CH_2	+	O_2	->	COH	+	OH	
98.2		118.1		-191.0		-109.7	-84.4

The final reaction is COH and COH_2 reacting with oxygen or hydroxyl radical to form CO_2.

							ΔH
COH_2	+	O	->	CO	+	H_2O	
196.4						-219.4	-23.0
COH	+	OH	->	CO	+	H_2O	
98.2						-109.7	-11.5

The complete reaction for methane burning to water and carbon dioxide then is

CH_4 + O_2 -> CH_3 + O + OH	106.6	kcal/mole
CH_3 + OH -> CH_2 + H_2O	-11.5	kcal/mole
CH_2 + O_2 -> COH_2 + O	-72.9	kcal/mole
COH_2 + O -> CO + H_2O	-23.0	kcal/mole
CO + O -> CO_2	-191.0	kcal/mole
CH_4 + 2 O_2 -> CO_2 + 2 H_2O	-191.8	kcal/mole

Net heat for the total reaction of methane reacting with oxygen to form carbon dioxide and water is -191.8 kcal/mole. Notice that it matters little which actual path is followed, because the reality of the kinetics is that all are followed to some extent, the percent of which is affected by the net energy liberated and the availability of the species. Most reaction pathways examine OH and O reacting to form O_2 and H, and H reacting with itself to form H_2, and H_2 burning to form H_2O. All of these reactions undoubtedly take place, as the energy barriers are relatively small (10 kcal/mole), but the net effect is that oxygen is consumed and carbon dioxide and water are produced so these intermediates can be ignored for the purposes here. The important thing is that the equation be balanced and have no residual free radicals.

Literature values (reference 11) put the heat of combustion of methane at 210.8 kcal/mole. Note that the bomb calorimeter value listed in the literature is the gross heat of combustion. That is, bomb calorimetry has liquid water as the final reaction product, while the net heat of combustion subtracts the heat of vaporization of water for gaseous water as the final reaction product. Gaseous water is consistent with the value arrived at through bond strength calculations. The heat of vaporization of water (reference 12) is 9.7 kcal/mole, so the net heat of combustion is 210.8 - 2(9.7) = 191.4 kcal/mole, which was used earlier for the Bunsen burner flame calculations.

It should be noted that bond strength is not exactly uniform but varies with the molecular environment. That is, one would not expect the C-H bond to be exactly the same for methane as for all other compounds containing carbon hydrogen bonds. The argument here is somewhat simplistic, but the calculated heat of combustion is in excellent agreement with values measured in the bomb calorimeter.

MECHANISMS OF HALON EXTINGUISHMENT. It is clear from the above arguments that combustion is the process of net heat release which occurs during the formation of carbon-oxygen and oxygen-hydrogen bonds and the simultaneous destruction of oxygen-oxygen bonds and carbon-hydrogen bonds. The barrier to combustion is quite high, 106 kcal/mole, but once initiated almost twice that amount of energy is liberated.

The primary reactions driving combustion involve oxygen and hydroxyl free radicals. In examining how Halons work, consumption of the radicals responsible for the energy liberating steps is the obvious starting point. It is also reasonable to assume the weakest bond is the first one broken.

Using Halon 1301 the example, two steps are possible.

									ΔH
CF_3Br	+	OH	->	HBr	+	O	+	CF_3	
68.1		109.7		-86.5					91.3

							ΔH
CF_3Br	+	O	->	OBr	+	CF_3	
68.1				-48.0			20.1

Since the C-Br bond is the weakest (least energy required to break it), reactions between that bond and either the oxygen or hydroxyl free radicals are compared. Since the reaction with oxygen requires less energy, it is greatly favored.

Let's assume that BrO then reacts with OH to form HBr + O_2.

							ΔH
OBr	+	OH	->	HBr	+	O_2	
48.0		109.7		-86.5		-118.1	-46.9

Net reaction is (+ 20.1 - 46.9) = -26.8 Kcal/mole for:

$CF_3Br + OH + O \rightarrow CF_3 + HBr + O_2$

This ignores that empirically HF, not HBr, is seen as the major reaction product.

Looking at the bond strength table, an interesting point can be seen. If one compares the carbon-halogen bonds or the hydrogen-halogen bonds, the strength is in decreasing order from fluorine to iodine. The oxygen-halogen bonds, however, show that the fluorine-oxygen bond is weaker than either the chlorine-oxygen or bromine-oxygen bond. Including this in the possible reaction matrix, one finds that liberating HF is very favorable.

							ΔH
CF_3Br	+	O	->	OBr	+	CF_3	
68.1				-48.0			20.1
OBr	+	CF_3	->	OF	+	CF_2Br	
48.0		115.9		-45.4		-68.1	50.4
OF	+	OH	->	HF	+	O_2	
45.4		109.7		-135.0		-118.1	-98.0

While Halon reacting with an oxygen free radical and rearrangement of F with Br on the organic free radical both require energy, the amount liberated by producing HF more than compensates. Total energy liberated by the three steps is -27.5 kcal/mole.

Therefore, Halon 1301 consumes the OH and O free radicals from methane combustion to produce one HF and one O_2 for each removal of a fluorine atom on the Halon 1301 molecule.

$CF_3Br + 3\ O + 3\ OH \rightarrow 3\ HF + 3\ O_2 + CBr$

Net heat liberated is -82.5 kcal/mole.

The final step is reaction of CBr with oxygen. This reaction liberates a CO_2 and a bromine radical.

							ΔH
CBr	+	O_2	->	CO_2	+	Br	
65.9		118.1		-345.6			-161.6
Br	+	Br	->	Br_2			
				-46.3			-46.3
Br	+	CH_3	->	CH_3Br			
				-65.9			-65.9
OH	+	O	->	O_2	+	H	
109.7				-118.1			-8.4
H	+	Br	->	HBr			
				-86.5			-86.5

The Br free radical can then associate with another bromine or methyl free radical. Hydrogen radical can be present from OH and O combining, which in turn can form HBr. Notice that each of these reactions of Halon consumes the reactive particles that propagate the combustion process. Also, it should be mentioned that while OBr and OF are postulated as intermediates, the steps to arrive at them are highly endothermic and the steps removing them are highly exothermic. This implies that measuring the concentration during combustion would be difficult as the concentration at any moment of time would be extremely small.

The implications of this are rather surprising. First, Halon reactions liberate more heat than methane combustion during formation of HF and CO_2, -244.1 kcal/mole versus -191.4 kcal/mole. This still leaves a bromine free radical which has several possible fates, all exothermic reactions. Second, it consumes three pairs (OH and O) of free radicals per mole, more than liberated by all of the steps of methane combustion. It preferentially absorbs oxygen radical which would have continued to produce more hydroxyl free radicals as it reacts with other carbon-hydrogen bonds. Third, molecular bromine and bromomethane are theoretically predicted as reaction products. This was empirically confirmed by experimental measurement with the mass spectrometer.

One further point is that the specific bond dissociation energy for the C-Br bond in CH_3Br is found in the literature (reference 13) to be virtually the same strength, 70.0 +/- 1.2 kcal/mole, as the CF_3Br, 70.6 +/- 1.0 kcal/mole. This means Halons can absorb the reactive methyl radicals propagated by the flame as well. The dissociation energy of the carbon-halogen bond goes up a few kcal/mole comparing CF_4 and CH_3F, so this substitution is unfavorable. Thus, Halon substitutes that are fluorocarbons or hydrofluorocarbons do not have this competing reaction which also helps terminate combustion. For iodine, CF_3I has a slightly weaker bond dissociation energy than CH_3I so this substitution is favorable and it has a mechanism contributing to the effectiveness of that alternative agent.

HYDROFLUOROCARBON EXTINGUISHMENT. HFC replacement agents do not contain bromine so the reaction pathways will differ. HFC-23 (CHF_3), will be used as the example since it is the simplest of the hydrofluorocarbons. It is likely to undergo the following reactions:

							ΔH
CF_3H	+	O	->	CF_3	+	OH	
98.2						-109.7	-11.5
CF_3H	+	OH	->	CF_3	+	H_2O	
98.2						-109.7	-11.5

Notice that, unlike the Halons, either the O or OH radical yields the same reaction enthalpy rather than preference for O.

If the reaction begins with the O radical:

									ΔH
CF_3H	+	O	->	CF_3	+	OH			
98.2						-109.7			-11.5
CF_3	+	OH	->	CF_2	+	HF	+	O	
115.9		109.7				-135.0			90.6
CF_2	+	O	->	CF	+	OF			
115.9						-45.4			70.5
OF	+	OH	->	HF	+	O_2			
45.4		109.7		-135.0		-118.1			-98.0
CF	+	OH	->	HF	+	CO			
115.9		109.7		-135.0		-191.0			-100.4
CO	+	O	->	CO_2					
				-191.0					-191.0

The reaction started with O and consumes two OH and an additional O, liberating a total of -239.8 kcal/mole. This is less than Halon which liberated -244.1 and an additional bromine radical, so this reaction is not quite as favored. It also consumed only two, not three, of the hydroxyl and oxygen radicals produced by methane, so 50 percent more would be required for the same effect. Also, unlike Halon, OH an O radicals are liberated fire propagating intermediates.

It is more important to see the total outcome than the individual steps shown. Each of the intermediate reactions can occur with either an oxygen radical or a hydroxyl radical. The energy liberated for each step may change, but in the aggregate the energy change and products liberated are the same.

For example, if the reaction begins with OH radical.

							ΔH
CF_3H	+	OH	->	CF_3	+	H_2O	
98.2						-109.7	-11.5
CF_3	+	O	->	CF_2	+	OF	
115.9						-45.4	70.5

									ΔH
OF	+	OH	->	HF	+	O_2			
45.4		109.7		-135.0		-118.1			-98.0
CF_2	+	O	->	CF	+	OF			
115.9						-45.4			70.5
CF	+	O_2	->	CO	+	OF			
115.9		118.1		-191.0		-45.4			-2.4
OF	+	H_2O	->	HF	+	OH	+	O	
45.4		109.7		-135.0					20.1
OF	+	OH	->	HF	+	O_2			
45.4		109.7		-135.0		-118.1			-98.0
CO	+	O	->	CO_2					
				-191.0					-191.0

In this case, there are more steps and more bonds made and broken, but the outcome is still the same. Two OH and O radicals from methane combustion are consumed, the same amount of energy, -239.8 kcal/mole, in the aggregate, is liberated. Three moles of HF are formed for each mole of HCF-23 consumed. This agrees with the stoichiometry shown in Table 1 for HFC-23 for HF yield and the approximate 1:1 ratio of agent to methane.

It must also be kept in mind that the thermodynamics of the reactions shown are not the kinetics. That is, what goes on at the molecular level is dependent on the particles available for collision and the rate constants. For example, methane itself is combustible, with a known fixed heat of combustion. But, at concentrations, either sufficiently high or sufficiently low, no net reaction will occur and methane will not burn. In other words, far more detailed concentration data would be needed to predict agent effectiveness in an actual fire than presented here.

CONCLUSIONS

1. Halon 1211 and Halon 1301 are found to be the most effective extinguishing agents tested using this protocol. Halon 13001 (CF_3I) is the most effective agent of the alternatives not banned for ozone depletion potential or facing restriction for long atmospheric lifetime.

2. Agents tested using this method are examined in the vapor phase and demonstrate their effectiveness at the molecular level. This may not correlate with actual fire fighting performance where discharge pressure, type of fuel, heat of vaporization, hot surface re-ignition, and nozzle effects play a very important part in getting the agent into the reaction zone of the fire.

3. Hydrogen Fluoride is the predominant gas evolved during extinguishment of a fire with Halons and the alternative agents. Halon 1301 exhibited the lowest yield of hydrogen fluoride followed by Halon 1211.

4. HFC-227EA and Halon 13001 produced slightly higher levels of hydrogen fluoride than Halon 1211, although approximately three times more HFC-227EA or 13 percent more Halon 13001 is required for extinguishment.

5. Phosgene (carbonyl chloride) is detected in the decomposition spectrum of HCFC-123 but not Halon 1211. Because of the high toxicity of phosgene, HCFC-123 may not be a likely candidate extinguishing agent for enclosed habitable spaces. Carbonyl fluoride which is toxic, although much less so than phosgene, was seen in the decomposition spectra for the perfluorocarbons and HFC-23.

6. Bromine and iodine atoms on the agent molecule appear to have similar effects during extinguishment. Both consume methyl radicals generated by the fire. Halon 1211, Halon 1301, and HBFC 22B1 form bromomethane and dibromomethane. There also appears to be molecular bromine just at the level of detection. Similarly, iodomethane is seen when Halon 13001 is the extinguishing agent.

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APPENDIX A

ICAMS CONFIGURATION AND CALIBRATION

ICAMS (Industrial Central Air Monitoring System) is a magnetic sector mass spectrometer capable of measuring mass-to-charge ratio particles (m/z) 2 to 200. The unseparated gas mixture is drawn through the sample inlet of the instrument, where the sample is fragmented into positively charged particles, or ions, by a high energy beam of electrons. The ions are then accelerated by an electrical field and are focused into the magnetic sector of the instrument by the L2 lens, for which the voltage values are established for each m/z (mass-to-charge number) ion. The magnetic sector bends the path of the ions to a detector where they are quantified. This beam of ions appears as a peak within a window of fifteen magnetic settings, or B field values. ICAMS has two detectors, the electrometer and the PAD (Pulse Amplifier Discriminator). The PAD is more sensitive but can be damaged by high ion concentration, so that at detector saturation, approximately 10^6 counts per second, ICAMS automatically switches over to the electrometer. Each detector has its own magnetic settings, but the user is not aware nor needs to know which detector is used for quantitation. A cross calibration factor automatically corrects response for the proper detector. During initial set up, the B field is calibrated so that the ions are centered within the window of magnetic settings needed to direct the ions to the appropriate detector based on ion concentration. Similarly, the L2, or focus, is calibrated for maximum peak amplitude for that ion.

Each chemical compound which makes up the sample has a fragmentation pattern which is based on the molecular mass of the compound, its atomic composition, and the bond strength between the atoms. Each ion of the fragmentation pattern, or spectrum, is identified by its mass-to-charge ratio (m/z). For example, nitrogen has a molecular mass of 28 (N_2) and the predominant ion, or parent ion, is m/z 28 which involves simply the removal of a single electron from the molecule. It also has an ion at m/z 14 which comes from both splitting the nitrogen bond or the removal of two electrons from the molecule. The concentration of m/z 14 is less, however, than m/z 28. Since more energy is required to remove two electrons, this fragmentation is less likely to happen.

Most elements have more than one isotope. Oxygen (O_2), for example, has peaks at m/z 33 and 34, which are only a few tenths of a percent compared to the peak at m/z 32. These are due to $_8O^{17}$ and $_8O^{18}$ isotopes, which are naturally occurring. In the case of hydrogen bromide, the ratio is almost 50/50 for m/z 80 and 82 due to the isotopes of bromine.

Fluorine has only one isotope, m/z 19, but argon with a molecular weight of 40 has an isotope at 38 and a small peak at 19 (from the removal of two electrons), and water (H_2O) has a small 19 peak due to the oxygen isotope. These are important considerations for two reasons. First, argon and water are major constituents of room air so that even small fragmentation peaks are substantial. Second, fluorine is the most electronegative (meaning most reluctant to give up electrons) of all elements and has a greatly reduced response factor (counts per second per part per million) compared to nitrogen or any other ion. This means large concentrations of HF produce a relatively small change on a high background peak at m/z 19. Typically, HF concentrations as analyzed by ICAMS are +/- 200 ppm for the run conditions of these experiments.

More complex organic molecules have much more complicated fragmentation patterns. Each compound has a unique fragmentation pattern but compounds with similar chemical structures will have similar spectra. When configuring ICAMS for analysis of a compound, the spectra is examined. Fragmentation pattern ions that are 10 percent of the parent ion, or base peak, are considered suitable for analytical purposes. The idea is to find ions that are unique to a particular compound so that unambiguous identification is possible. If there is overlap between compounds, simultaneous linear equations are solved to best fit the fragmentation patterns of the compounds for which analysis is being conducted. ICAMS always conducts analysis for "possible stranger", that is, ions which are in excess of the linear combinations expected for analytes that are in the configuration. Since purely algebraic solutions are done, negative concentrations are also possible in the printout of the analysis, although this is clearly not realistic. It must be kept in mind that actual concentrations of the various analytes are prone to change during the cycle times required to measure all of the ion intensities and this will introduce some error to the data reduction routine used for quantitation.

Ordinarily, ICAMS is configured by the manufacturer for the analytes of interest, generally minor contaminants in breathable air. ICAMS was meant to function in a factory environment for OSHA (Occupational Safety and Health Act) compliance. Clearly, the use of ICAMS for these experiments is outside the norm and configuration is required in-house for several reasons. ICAMS can be configured for a maximum of 26 compounds, two of which are required to be nitrogen and "possible stranger". The more compounds that are in the configuration, the more ions (m/z particles) that must be analyzed during the scan. This increases the analysis time and the possibility that the ion intensities have shifted during the course of the scan due to changes in sample concentrations. ICAMS software will interpret these shifts as "possible stranger". Also, the ideal condition of having a unique mass to quantitate each compound becomes very unlikely when all compounds are essentially fluorocarbons and their decomposition products. In addition, ICAMS is configured for all analytes at the same time. As new compounds for fire-fighting appear on the market, they are to be included in this set of experiments without prior knowledge of their chemical composition and spectra. To keep analysis time under 30 seconds per sample and allow unambiguous identification of the compounds of interest, the configurations used in these experiments measure N_2, O_2, CO_2, Argon, Water, HF, HCl, HBr, and three halocarbon candidate agents. Several different configurations are saved on disk and can be loaded as needed to support other work of the Fire Safety Program at the FAA Technical Center. As new candidate agents or mixtures of agents emerge, additional configurations are added.

ICAMS must be chemically calibrated to give concentration output for the compounds of interest. The components of normal room air can be calculated directly from temperature, pressure, and percent relative humidity data. Based on room temperature, the saturation vapor pressure of water can be looked up in a table. Other components of air are looked up and normalized based on the ambient water concentration. Calculations are as follows:

Where p_a = ambient pressure
p_{H2O} = partial pressure of water @ RT

$$\text{Water Vapor Concentration (ppm)} = \frac{p_{H2O} * RH}{p_a} * 10^6$$

$$\text{Normalization Factor} = \frac{1{,}000{,}000 - \text{Water Vapor (ppm)}}{1{,}000{,}000}$$

ICAMS is then run in calibrate mode, inputting these concentrations and measuring the counts/second for each ion to determine the various response factors for all of the compounds. In the case of an analyte that overlaps an air peak, manual calculation and input to the scan matrix is done to arrive at the correct fragmentation pattern. The computer will automatically calculate the response factor with respect to nitrogen (S matrix), the fragmentation pattern for each analyte with respect to the base peak (H matrix), and the coefficients to the linear equations used to calculate all of the concentrations during run conditions (B matrix).

The Halon replacement agent concentrations are prepared using ultra-pure compressed air and pure agent, as mixed with a blending manifold. A rotameter is used to establish a precise flow for both agent and air. Ball valves are used to switch the flow to either the ICAMS calibration line or a wet test meter. Individual flows of air and agent through the rotameter are calibrated using a stopwatch to time a volume change on the wet test meter. The concentration is simply the flow of agent divided by the flow of agent and air. The two flows are joined with a Teflon tee about two feet before the calibration tee to insure adequate mixing. Typically, the blended concentration is approximately 2.5% or 25,000 ppm of agent in air, with total flow about 0.5 liters per minute.

Liquid agents are calibrated in a slightly different manner. The same manifold is used. However, instead of the agent being measured through the rotameter, air is measured through both rotameters. After calibration of pure air, a 250 milliliter bubbler is inserted after the rotameter in one of the lines leading to, but before the Teflon tee. Approximately 50 ml of the agent is added to the bubbler and it is immersed in a ice/water Dewar flask and allowed to equilibrate to 0° C. The bubbler is attached to the wet test meter and the total flow through the bubbler is measured. Agent flow is calculated by subtracting the air flow measured before the bubbler from the total flow after the bubbler. This is divided by the flow of pure air diluent plus the total flow through the bubbler.

The acid gases pose some problems not normally encountered. First, they are quite reactive and completely soluble in water, so the wet test meter cannot be used and rotameters must be down stream of the internal ICAMS calibration tee to verify flow. The all-Teflon construction of the sampling system is necessary so as not to have line losses and moisture must be avoided. Two separate methods were used for calibration and were found to be in good agreement. Lecture bottles of pure HF, HCl, and HBr were sampled using a 10 ml Series A-2 Precision Sampling Pressure-Lok gas chromatography syringe, by adapting a 1/4-inch Teflon tee with a gas chromatography septum. Air from the manifold was calibrated as usual with the wet test meter and the syringe was accurately discharged using a Sage syringe pump to meter the acid gas into the flowing air stream. The results were compared with those obtained using analyzed cylinders of HF and HCl in nitrogen purchased from Matheson Gas. It was seen that the syringe method produced samples that quickly stabilized at a counts/second value. On the other hand, the cylinder of HF (analyzed at 9500 ppm) required approximately 30 minutes to stabilize. The HCl cylinder showed similar lag problems, although much less severe. It was seen when connecting and disconnecting the capillary inlet to the ICAMS that concentration quickly fell to less than 100 ppm and quickly rose to the concentration at disconnect. This demonstrates that the problem is with the tank or regulator, not the sample lines. HBr calibration gases are not available, so only the syringe sampling calibration method was used. For consistency, the same acid gas calibration was used for all of the various configurations and repeated only when the filament, or source of the high energy electron beam, is replaced and B fields and L2 potentials require recalibration.

The various mass to charge particles used for identification of the compounds of interest are listed in table A-1.

TABLE A-1. ICAMS CONFIGURATION DATA

Compound	Sensitivity		m/z (Fraction of Base)	
Nitrogen	1.000	28	-	-
Oxygen	0.871	32	33 (0.000757)	-
Carbon Dioxide	1.465	44	-	-
Argon	1.514	40	38 (0.000550)	36 (0.00275)
Water	0.2789	18	19 (0.001120)	-
Hydrogen Fluoride	0.00310	19	-	-
Hydrogen Chloride	1.012	36	19 (0.000879)	-
Hydrogen Bromide	0.496	80	82 (0.975)	-
Halon 1211	1.513	85	87 (0.316)	69 (0.00056)
Halon 1301	1.539	69	129 (0.189)	85 (0.00027)
HFC-23	0.532	51	69 (0.779)	83 (0.00002)
HCFC-123	1.750	83	85 (0.662)	152 (0.164)
HCFC-124	1.207	67	101 (0.428)	117 (0.193)
HFC-125	1.065	51	69 (0.268)	101 (0.705)
HBFC-22B1 (FM-100)	1.598	51	81 (0.110)	132 (0.234)
HFC-227EA (FM-200)	2.011	69	51 (0.168)	151 (0.353)
Perfluorobutane	3.188	69	119 (0.173)	169 (0.016)
Perfluoropentane	3.502	69	119 (0.331)	169 (0.158)
Perfluorohexane	5.340	69	119 (0.266)	169 (0.201)
CF_3I	2.081	196	127 (0.520)	177 (0.201)
C_3F_7I	0.863	127	69 (0.974)	169 (0.794)

As mentioned above, all configurations contain the air gases and acid gases and a maximum of three extinguishing agents. For each compound, the table shows the sensitivity relative to nitrogen in terms of ion counts per second response per part per million composition. Each part per million concentration of nitrogen has approximately 500 ion counts per second, so a higher sensitivity number will provide a proportionately higher number of counts per second at the same concentration. Conversely, a lower sensitivity compound will have fewer counts per second for each unit of concentration. The mass to charge particles (m/z) used for the quantitation of each analyte is given. Where more than one ion is used, the percent response compared to the base peak is given in parentheses next to the mass number and is expressed as the decimal fraction.

Ordinarily, ICAMS is run in the normal mode, which outputs units of concentration only. For the purposes here, ICAMS is run in the Analyze Calibration Gas mode from the auxiliary menu. This is done so that all raw counts data are also printed out. With the raw data in hand, subsequent calculation of concentrations for each compound can be done manually to check what may seem to be anomalous readings of concentration, misidentification of compounds, or to use data reduction techniques other than the force-fit linear algebraic solutions (negative and/or high possible stranger concentrations).

APPENDIX B

MASS SPECTROMETRIC ANALYSIS - RESULTS

Flame only

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.40	1.50	7.31	210.20	0.57	-0.19	2.22	3.29
Test 2	-3.01	1.41	6.79	597.50	30.80	-0.18	3.51	1.93
Test 3	-3.73	1.71	8.34	588.33	-1.05	-0.37	3.57	2.34
Average	-3.38	1.54	7.48	465.34	10.11	-0.25	3.10	2.52
%RSD	10.80	10.00	10.54	47.50	-	-	24.60	27.68

Carbon Dioxide

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.30	3.27	6.14	876.07	48.88	-0.05	3.79	1.62
Test 2	-3.06	3.24	5.55	269.68	-2.22	0.09	3.68	1.51
Test 3	-3.68	3.92	7.66	385.05	4.14	0.21	3.37	2.27
Average	-3.34	3.48	6.45	510.26	16.93	0.08	3.61	1.80
%RSD	9.19	11.05	16.87	63.18	-	-	6.03	22.81

Halon 1301
(CF_3Br)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.21	1.39	6.43	1262.63	34.23	0.61	3.56	1.81
Test 2	-3.45	1.48	6.41	2063.10	199.30	0.29	4.30	1.49
Test 3	-3.18	1.45	6.92	2439.00	197.30	0.11	4.85	1.43
Average	-3.28	1.44	6.59	1921.58	143.61	0.34	4.24	1.57
%RSD	4.51	3.18	4.39	31.20	-	-	15.28	12.96

Halon 1211
(CF_2ClBr)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.60	1.80	6.74	2731.70	359.00	0.68	2.50	2.70
Test 2	-3.66	1.60	7.71	3078.90	505.60	0.54	4.31	1.79
Test 3	-3.79	1.65	6.50	2838.30	512.30	0.42	4.84	1.45
Average	-3.68	1.68	6.98	2882.97	458.97	0.55	3.88	1.98
%RSD	2.63	6.18	9.17	6.17	18.80	-	31.60	32.64

RESULTS - CONTINUED

HBFC-22B1
(CF_2BrH)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.56	1.61	6.15	5526.73	-0.31	0.20	3.72	1.65
Test 2	-2.96	1.58	6.27	5057.55	-1.46	245.88	4.39	1.43
Test 3	-3.42	1.65	6.98	4524.54	-1.44	359.57	3.40	2.05
Average	-3.31	1.61	6.47	5036.27	-1.07	201.88	3.84	1.71
%RSD	9.47	2.17	6.93	9.95	-	-	13.17	18.38

FC-3-1-10
(C_4F_{10})

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.47	1.53	3.61	21366.40	507.17	20.57	1.76	2.05
Test 2	-3.35	1.46	3.84	24650.75	192.05	148.96	1.95	1.97
Test 3	-3.47	1.37	3.27	29380.10	113.80	165.68	1.86	1.76
Average	-3.43	1.45	3.57	25132.42	271.01	111.74	1.86	1.93
%RSD	2.01	5.51	8.02	16.03	-	-	5.12	7.77

FC-4-1-12
(C_5F_{12})

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-5.85	4.49	0.46	69253.40	188.54	60.95	0.45	1.02
Test 2	-5.66	4.49	2.46	63562.93	236.34	24.90	2.41	1.02
Test 3	-4.51	4.07	2.91	31335.67	390.03	107.76	1.68	1.73
Average	-5.34	4.35	0.37	54717.33	271.64	64.54	1.25	1.35
%RSD	13.58	5.57	-	37.37	-	-	60.72	-

FC-5-1-14
(C_6F_{14})

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-5.34	2.71	3.14	63786.75	160.65	281.09	1.50	2.09
Test 2	-5.36	2.97	4.45	49176.40	124.20	52.91	1.72	2.59
Test 3	-5.94	3.04	2.61	71386.90	196.20	179.36	1.30	2.01
Average	-5.54	2.91	3.40	61450.02	160.35	171.12	1.51	2.23
%RSD	6.14	5.98	27.86	18.35	22.50	-	13.94	12.65

RESULTS - CONTINUED

HFC-23
(CF_3H)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-7.31	3.14	4.26	156056.00	9.93	40.95	1.24	3.44
Test 2	-6.37	2.95	4.01	141914.10	23.46	21.58	1.57	2.55
Test 3	-7.66	3.04	8.33	181931.00	8.64	43.80	1.55	5.48
Average	-7.11	3.04	5.53	159967.03	14.01	35.44	1.45	3.82
%RSD	9.37	3.12	43.91	12.68	-	-	12.73	39.29

HFC-125
(C_2F_5H)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.58	1.87	7.70	18563.95	274.94	2.90	4.04	1.91
Test 2	-3.56	2.13	4.60	18424.60	555.81	5.78	1.98	2.32
Test 3	-3.92	2.15	4.86	21605.84	327.74	7.75	2.91	1.67
Average	-3.69	2.05	5.72	19531.46	386.16	5.48	2.98	1.97
%RSD	5.49	7.62	30.06	9.20	38.70	-	34.66	16.71

HFC-227EA
(C_3F_7H)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-2.95	1.90	7.01	1289.93	63.58	2.16	2.86	2.45
Test 2	-2.88	1.65	6.71	7209.72	60.28	7.14	2.65	2.53
Test 3	-2.85	1.64	10.73	9274.43	32.91	0.99	2.10	5.11
Average	-2.89	1.73	8.15	5924.70	52.25	3.43	2.54	3.36
%RSD	1.77	8.51	27.47	69.96	32.35	-	15.47	44.99

HCFC-123
($C_2F_3Cl_2H$)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-5.10	2.65	3.55	42054.73	7061.07	15.90	1.21	2.93
Test 2	-4.56	2.45	3.25	36949.55	6498.82	17.75	1.09	2.98
Test 3	-4.30	2.40	3.87	28191.70	5400.64	13.35	1.47	2.63
Average	-4.65	2.50	3.56	35731.99	6320.17	15.67	1.26	2.85
%RSD	8.77	5.29	8.72	19.60	13.37	14.12	15.46	6.64

RESULTS - CONTINUED

HCFC-124
(C_2F_4ClH)

	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.68	1.15	0.33	29069.10	917.18	-20.85	0.29	1.14
Test 2	-3.62	0.95	0.15	27040.50	520.67	6.32	0.12	1.25
Test 3	-3.42	1.24	0.55	23560.90	730.50	-7.23	0.48	1.15
Average	-3.57	1.11	0.35	26556.83	722.78	-7.26	0.30	1.18
%RSD	3.77	13.33	58.35	10.49	27.49	-	60.70	5.15

HALON 13001
(CF_3I)

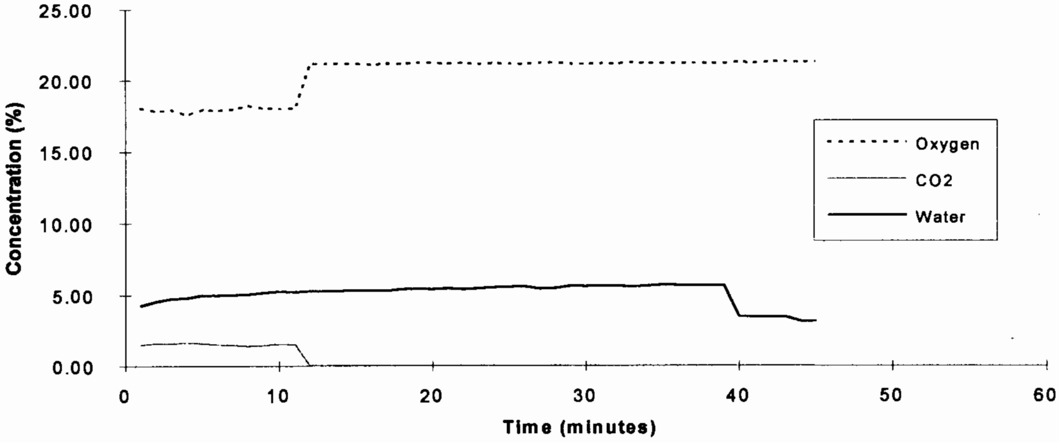
	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.50	1.44	4.15	4669.40	7.46	-0.09	2.62	1.55
Test 2	-3.69	1.55	4.06	5299.19	2.12	0.07	2.43	1.67
Test 3	-3.26	1.51	4.47	4848.40	-3.45	-0.08	2.45	1.82
Average	-3.49	1.50	4.23	4939.00	2.04	-0.04	2.50	1.68
%RSD	6.19	3.71	5.01	6.57	-	-	4.18	8.05

HALON 37001
(C_3F_7I)

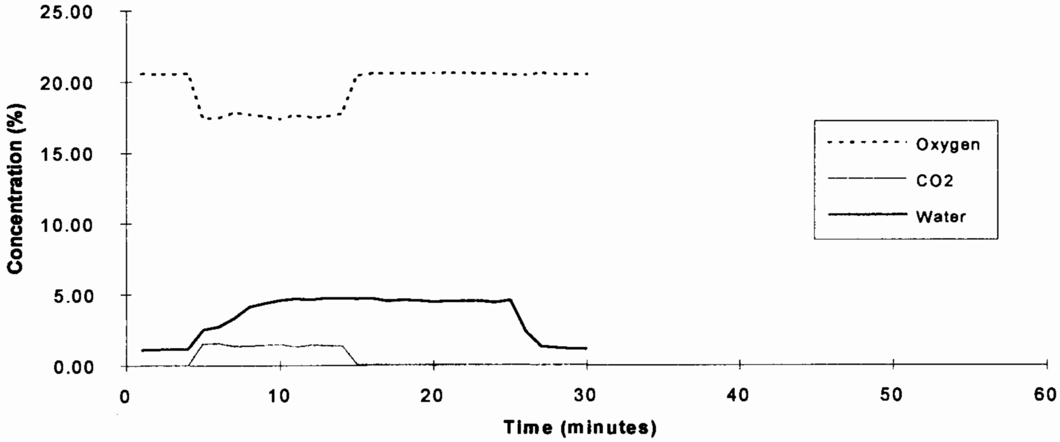
	O_2 (%)	CO_2 (%)	H_2O (%)	HF (ppm)	HCL (ppm)	HBr (ppm)	d[H_2O] (%)	H_2O ratio
Test 1	-3.73	2.40	4.56	11108.75	823.35	9.04	1.42	-
Test 2	-4.40	2.60	-4.29	11659.35	418.14	3.62	-0.69	-
Test 3	-3.67	2.26	2.11	11507.44	409.95	2.24	-0.10	-
Average	-3.93	2.42	-	11425.20	620.75	4.97	-	-
%RSD	10.30	7.06	-	2.49	46.17	-	-	-

APPENDIX C - TIME CONCENTRATION PROFILES

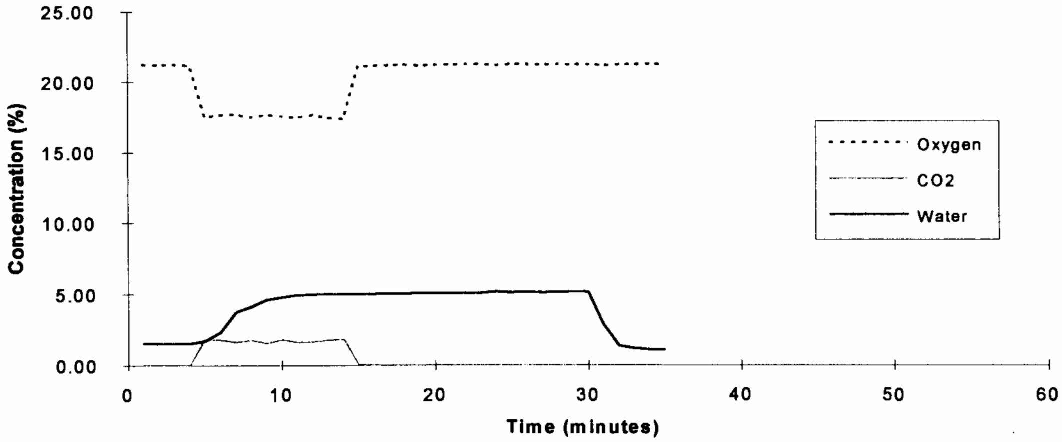
Flame only - Test 1



Flame only - Test 2



Flame only - Test 3



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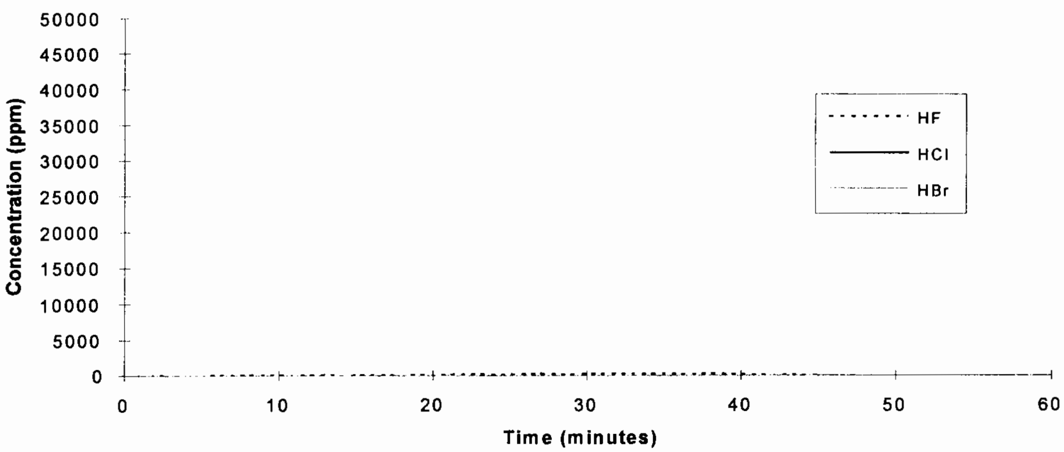
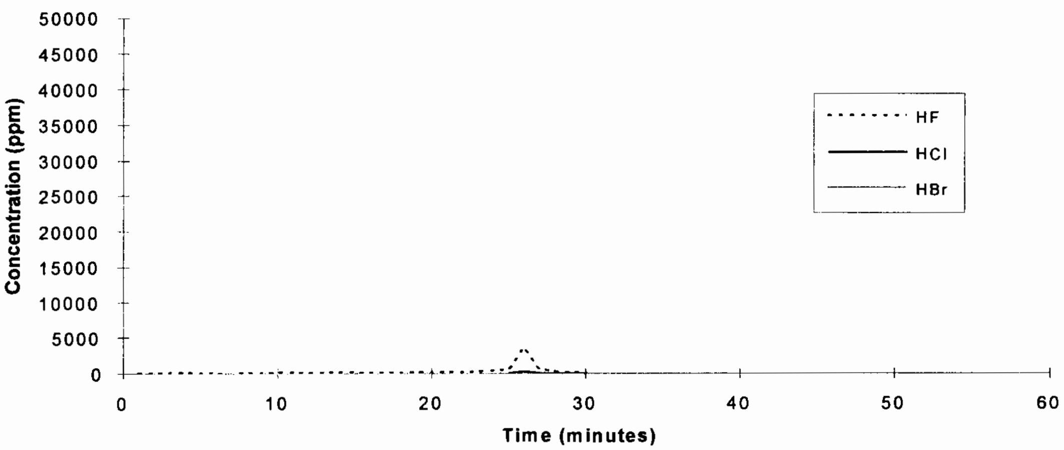
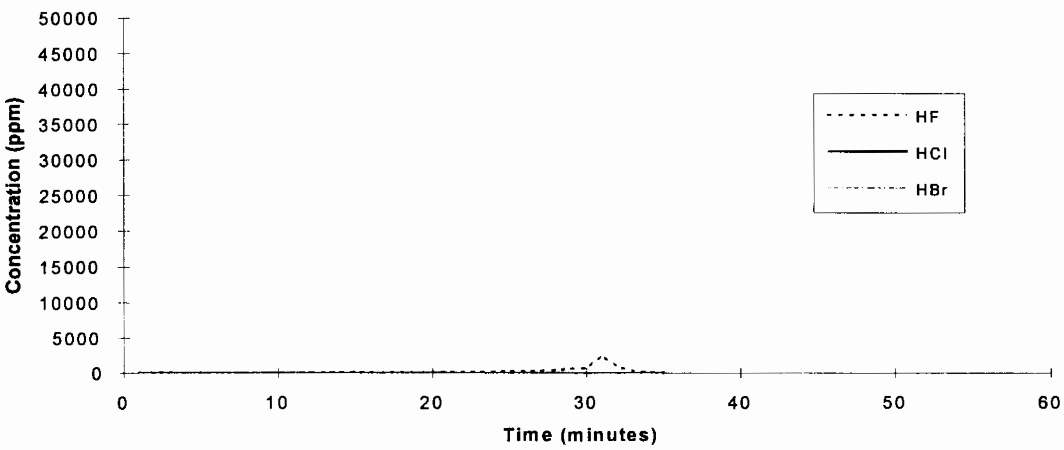


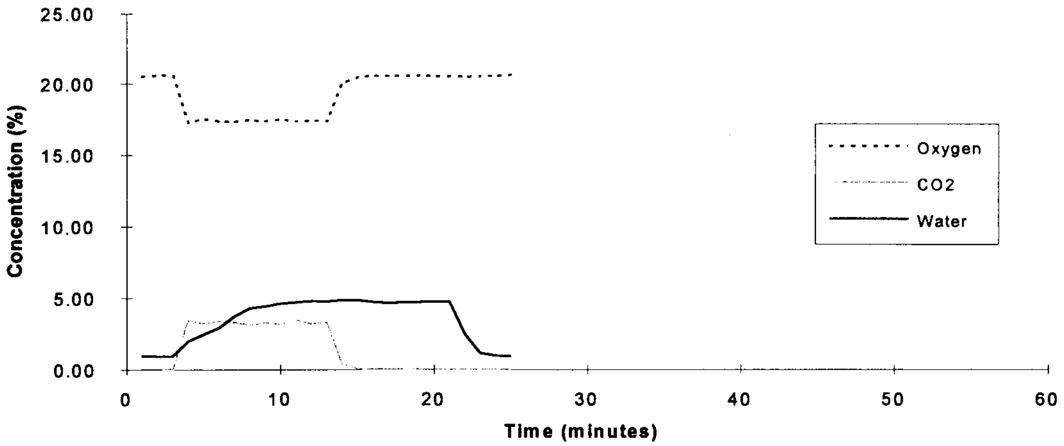
Flame only - Test 2



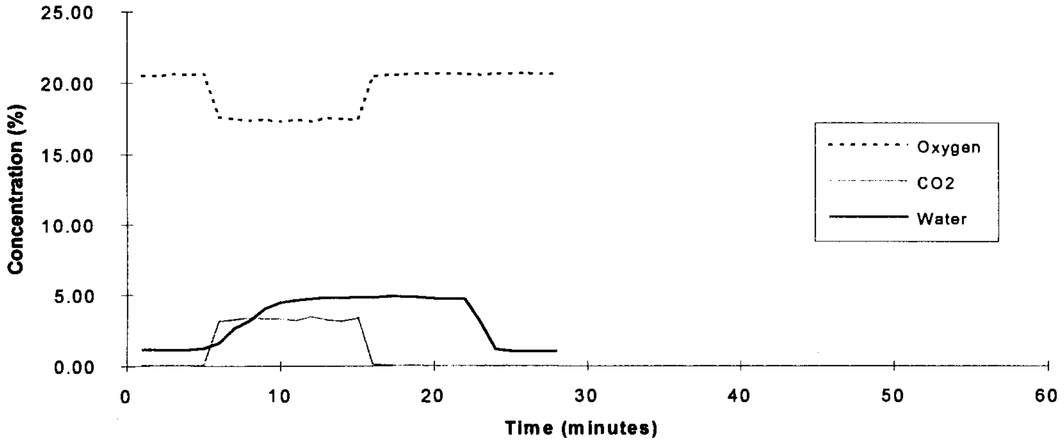
Flame only - Test3



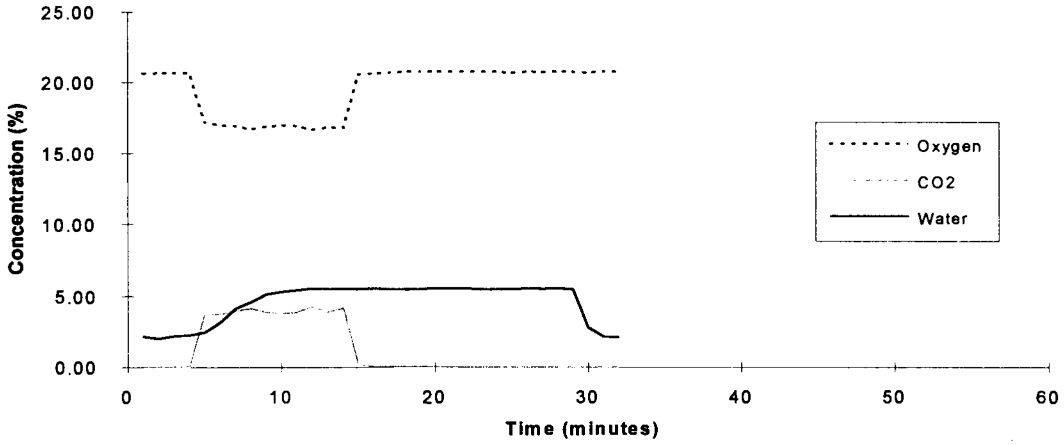
Carbon Dioxide - Test 1



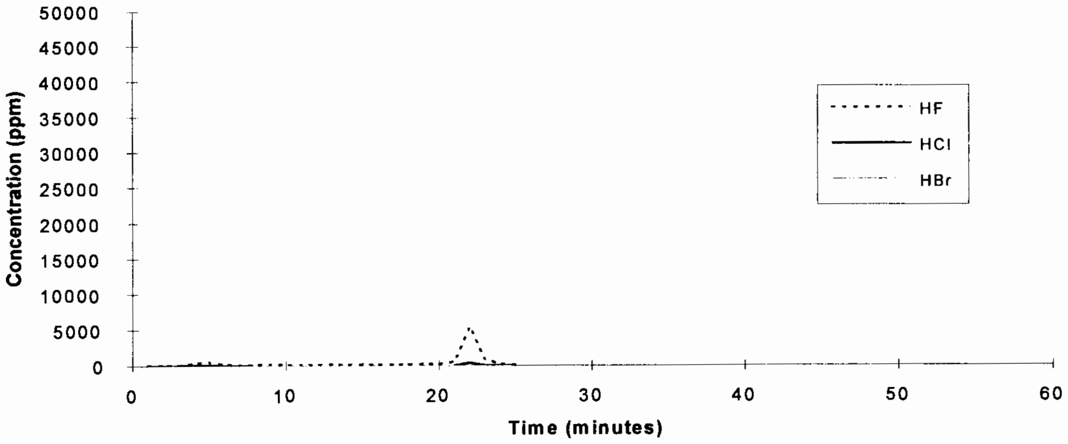
Carbon Dioxide - Test 2



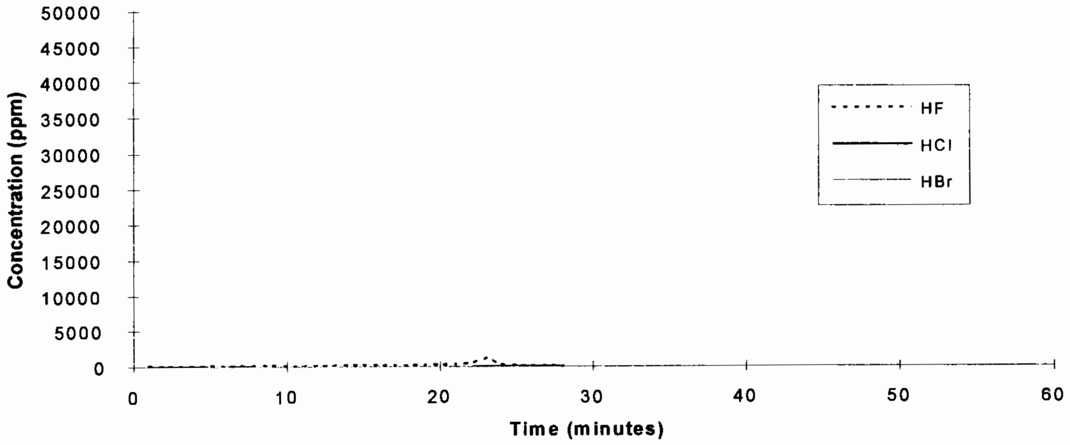
Carbon Dioxide - Test 3



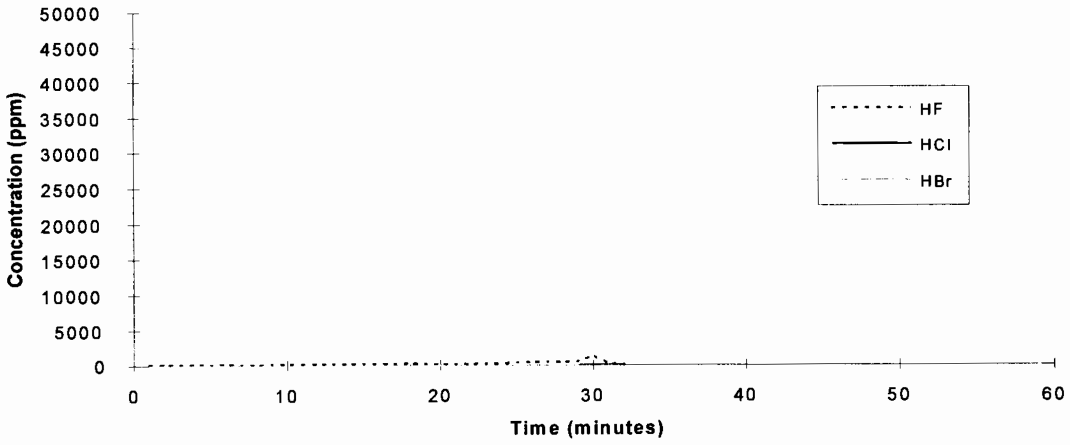
Carbon Dioxide- Test 1



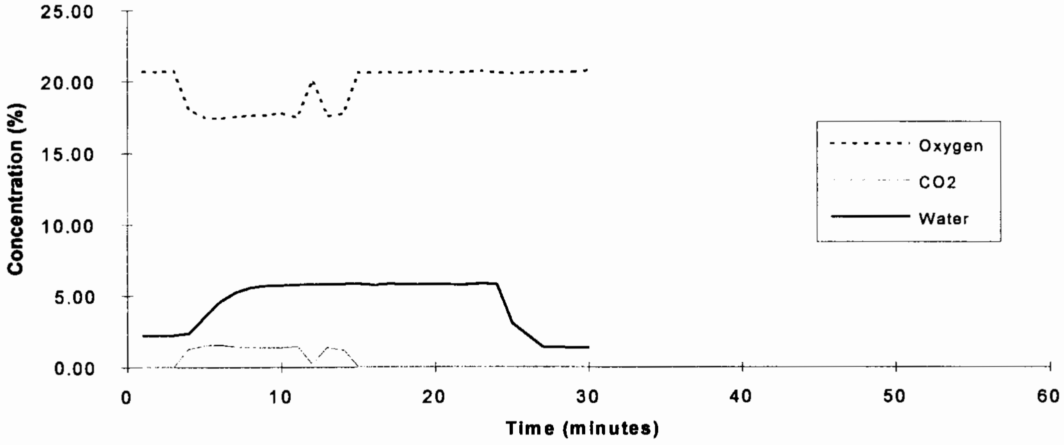
Carbon Dioxide- Test 2



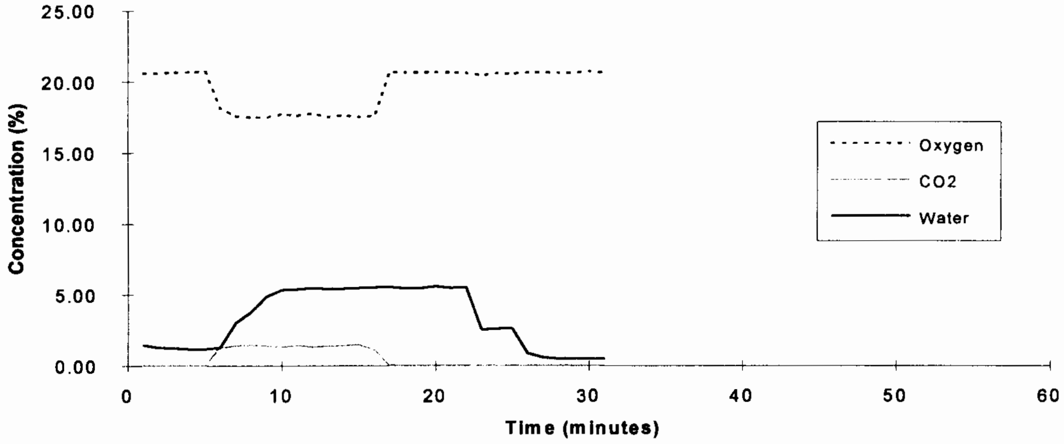
Carbon Dioxide- Test 3



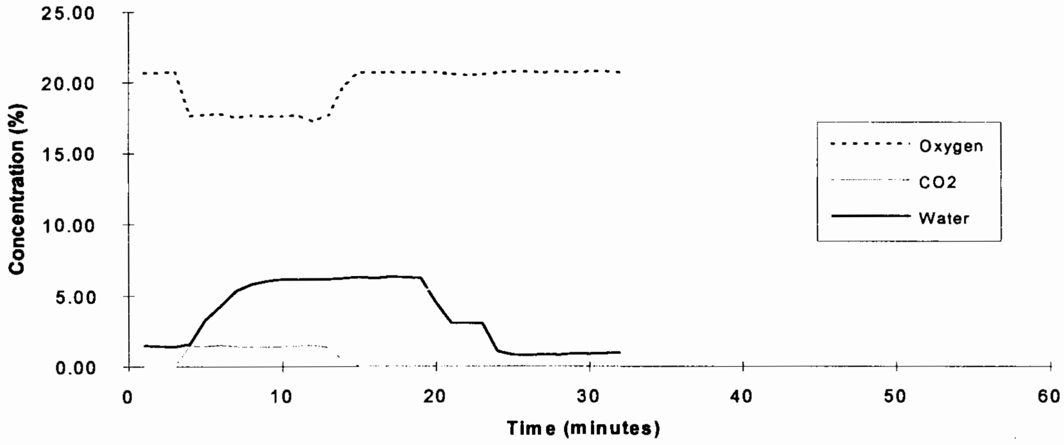
Halon 1301 - Test 1



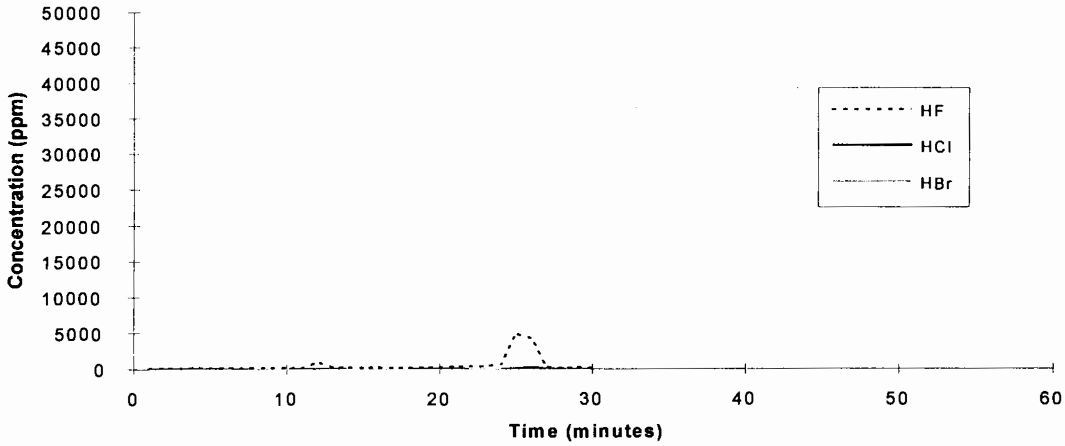
Halon 1301 - Test 2



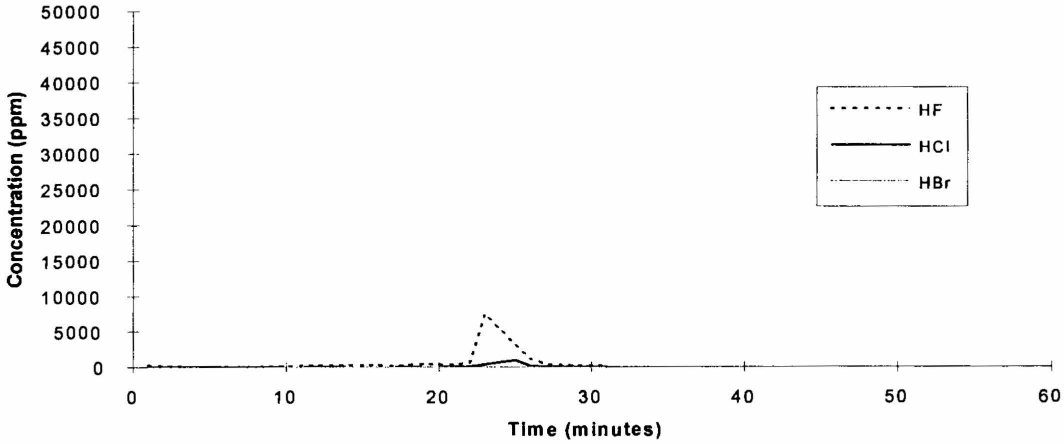
Halon 1301 - Test 3



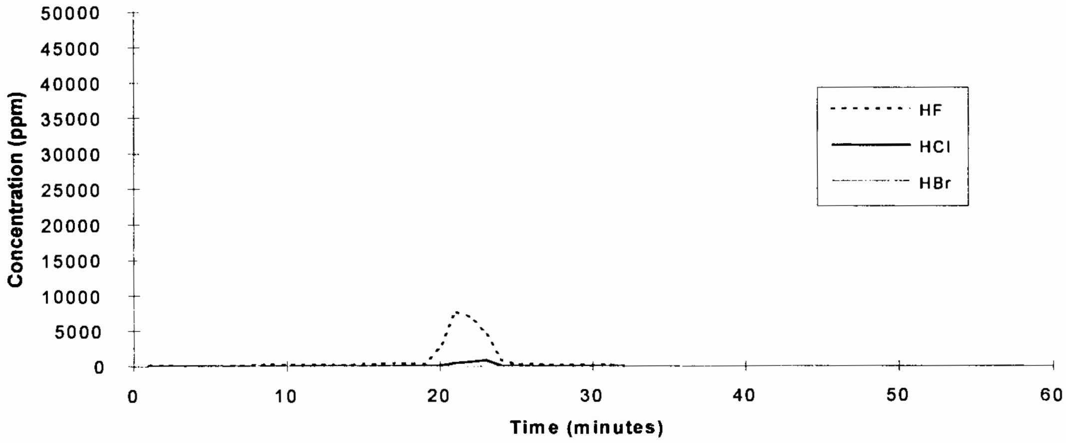
Halon 1301- Test 1

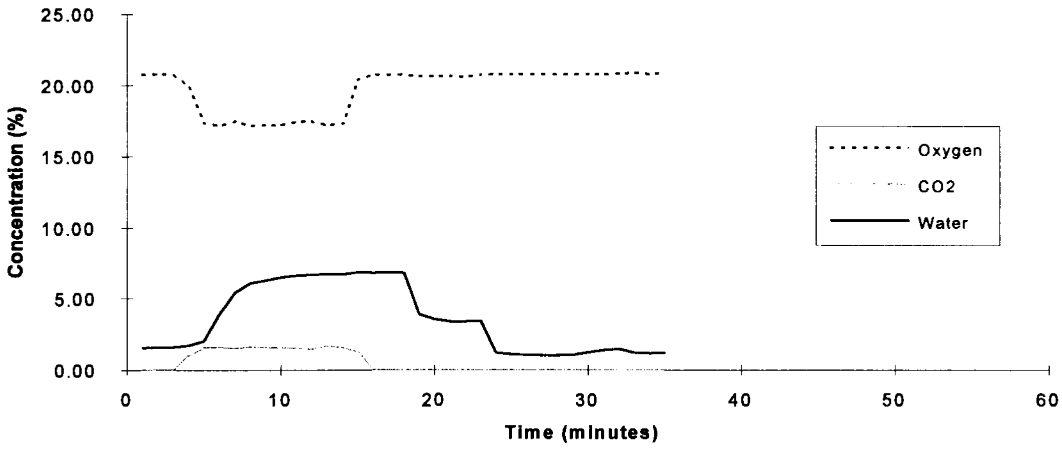


Halon 1301- Test 2

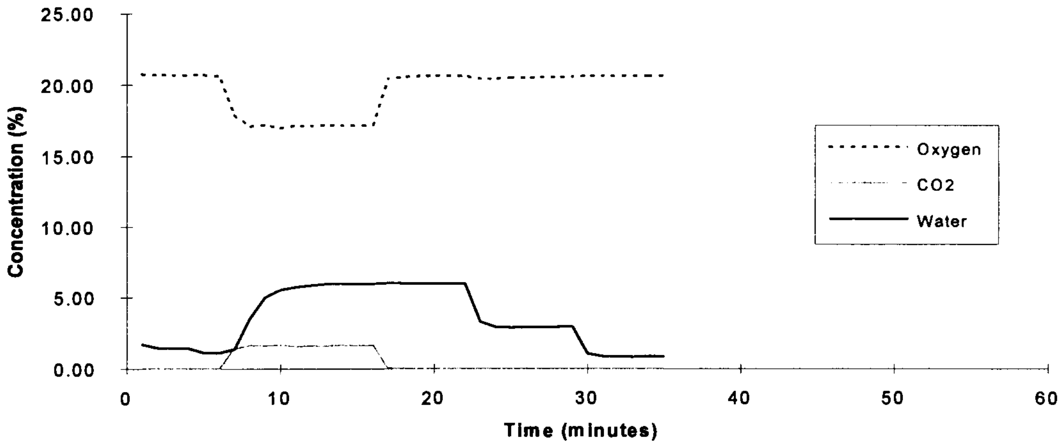


Halon 1301- Test 3

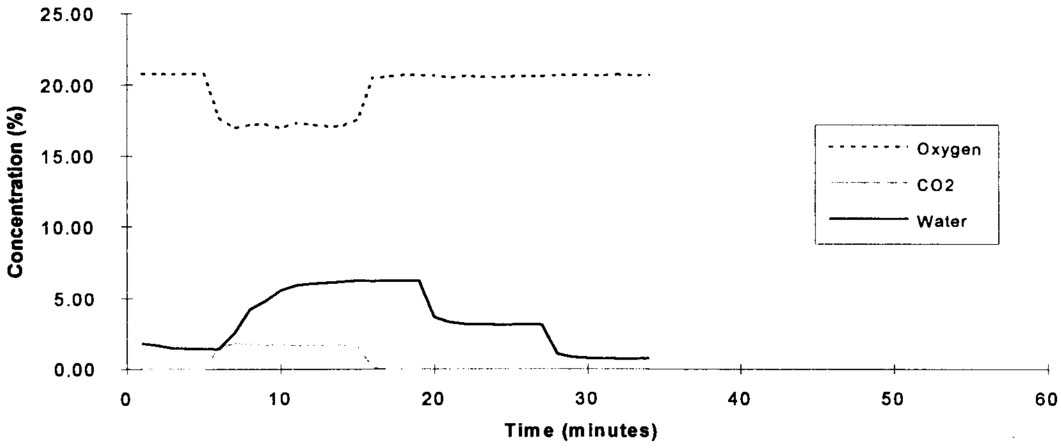




Halon 1211 - Test 1

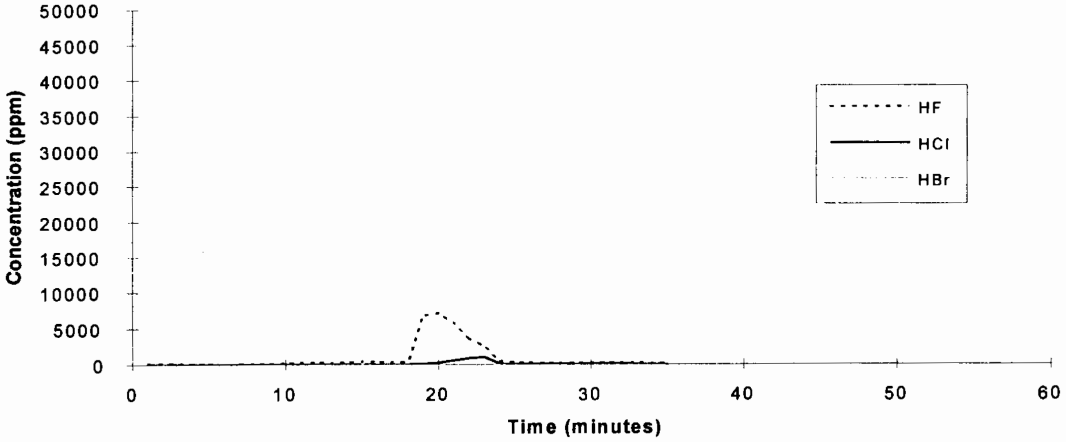


Halon 1211 - Test 2

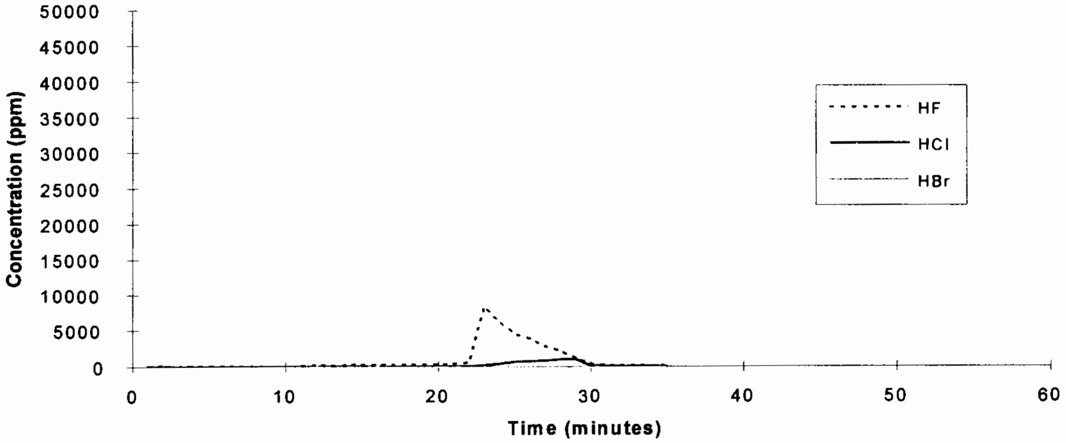


Halon 1211 - Test 3

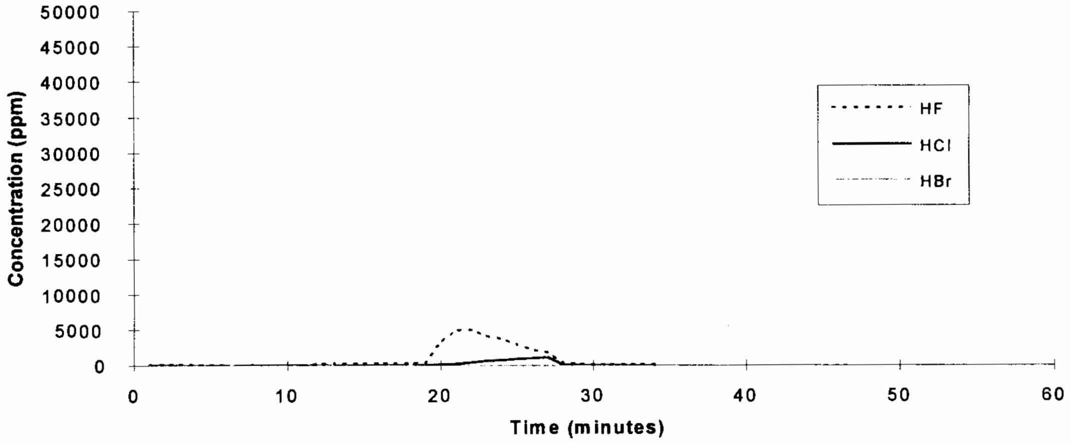
Halon 1211 - Test 1

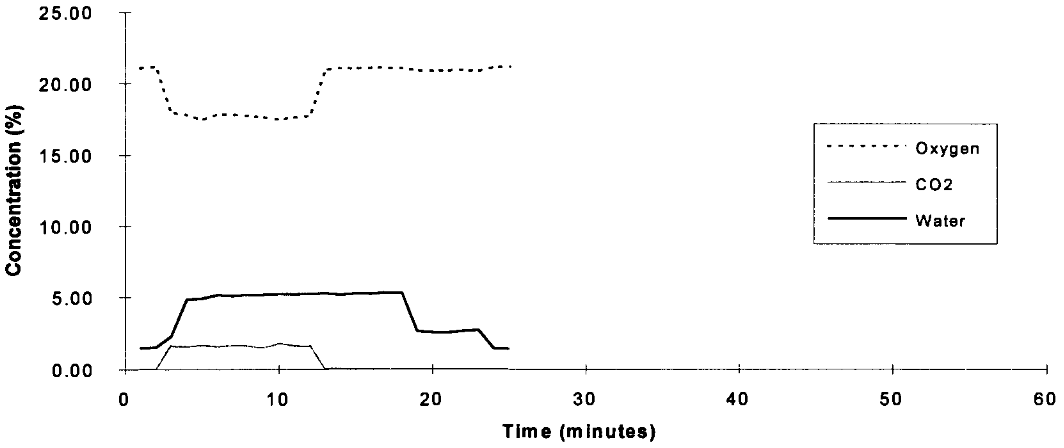


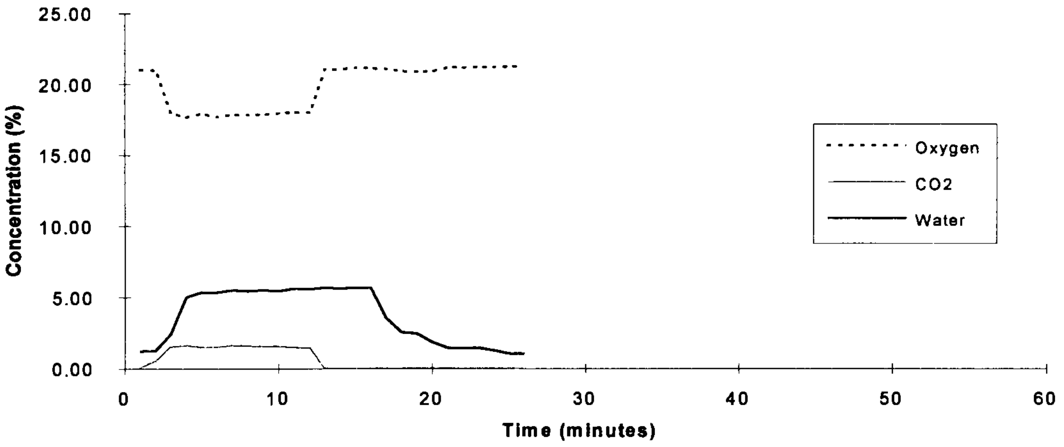
Halon 1211 - Test 2

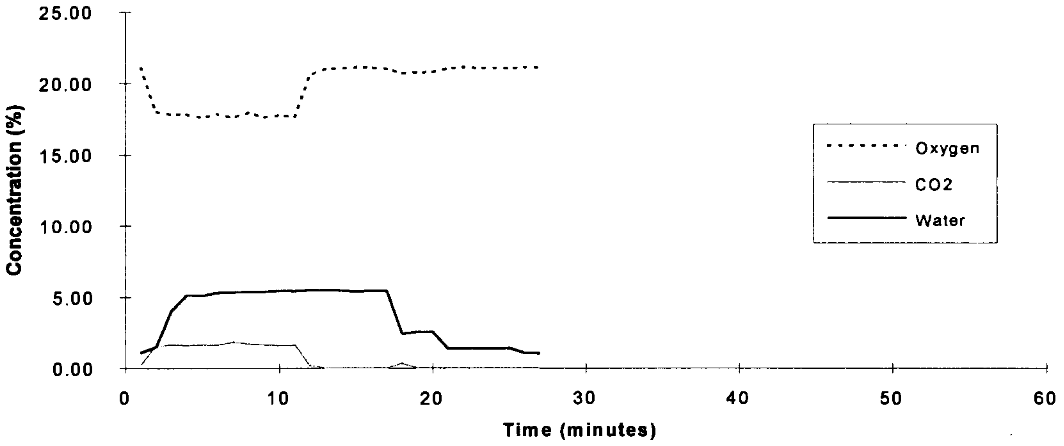


Halon 1211 - Test 3

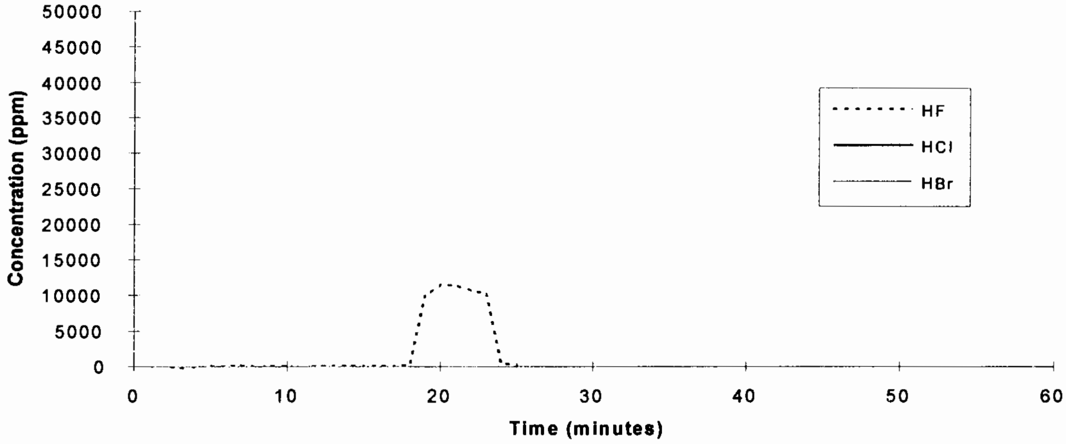



HBFC-22B1 - Test 1

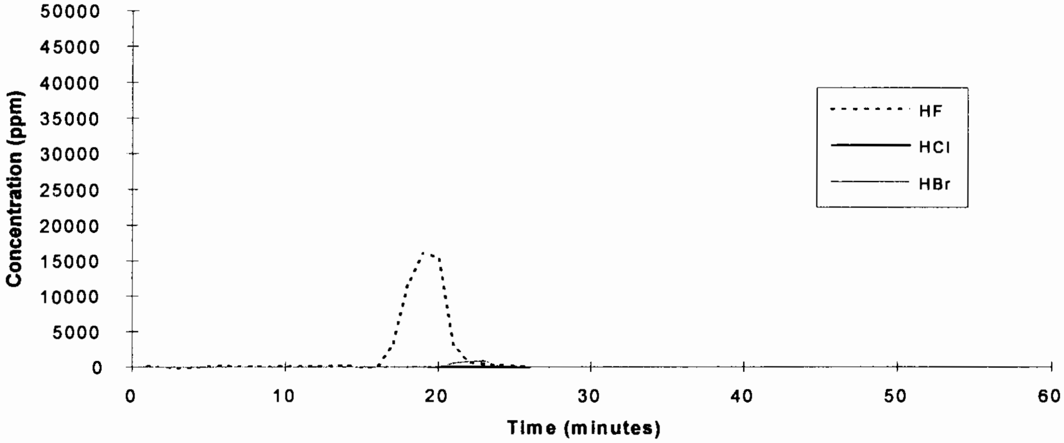

HBFC-22B1 - Test 2


HBFC-22B1 - Test 3

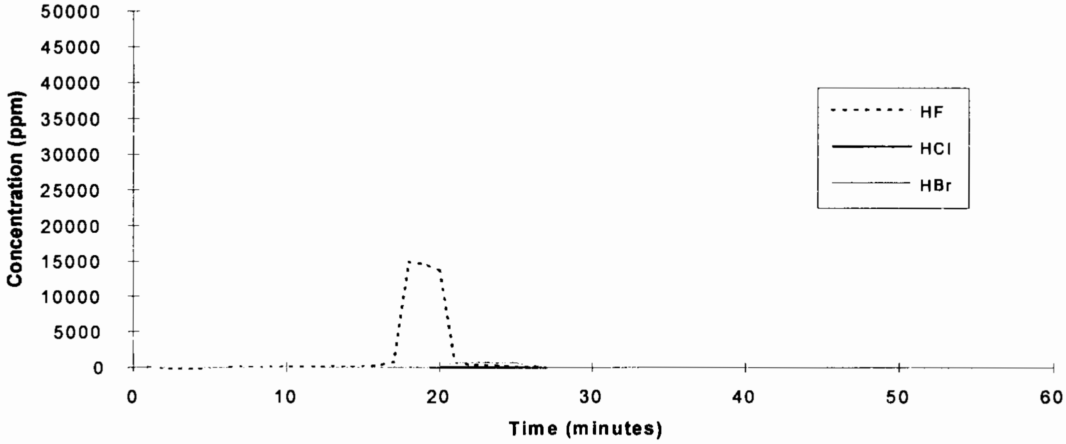
HBFC-22B1 - Test 1



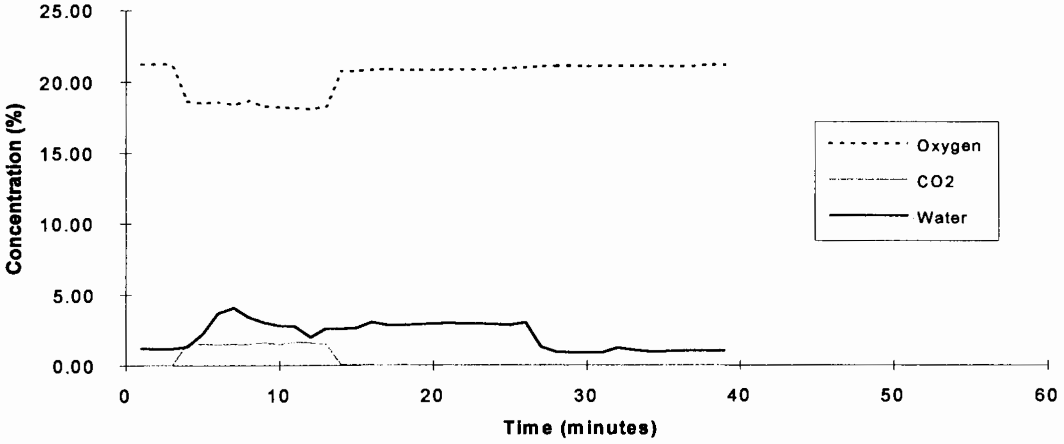
HBFC-22B1 - Test 2



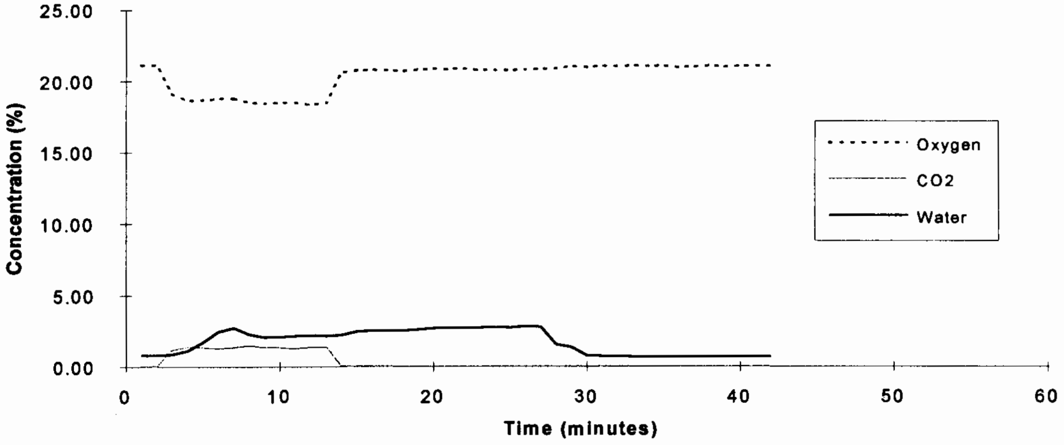
HBFC-22B1 - Test 3



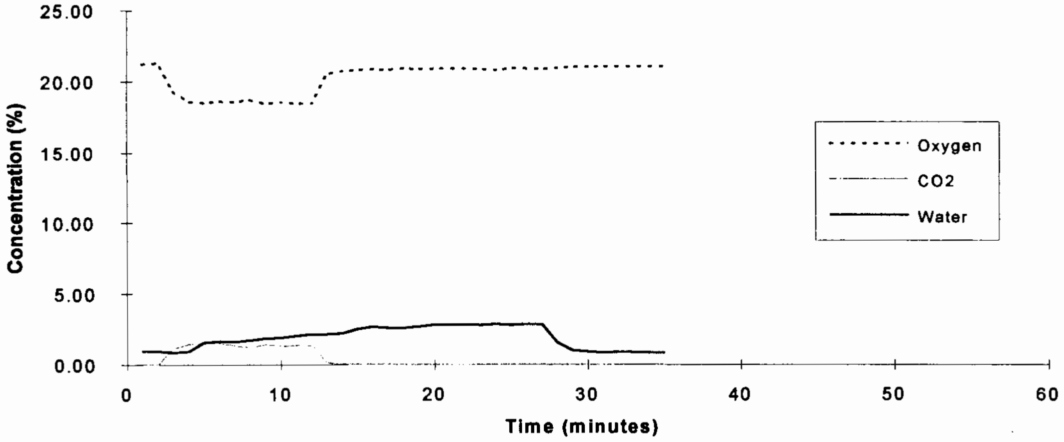
Perfluorobutane - Test 1

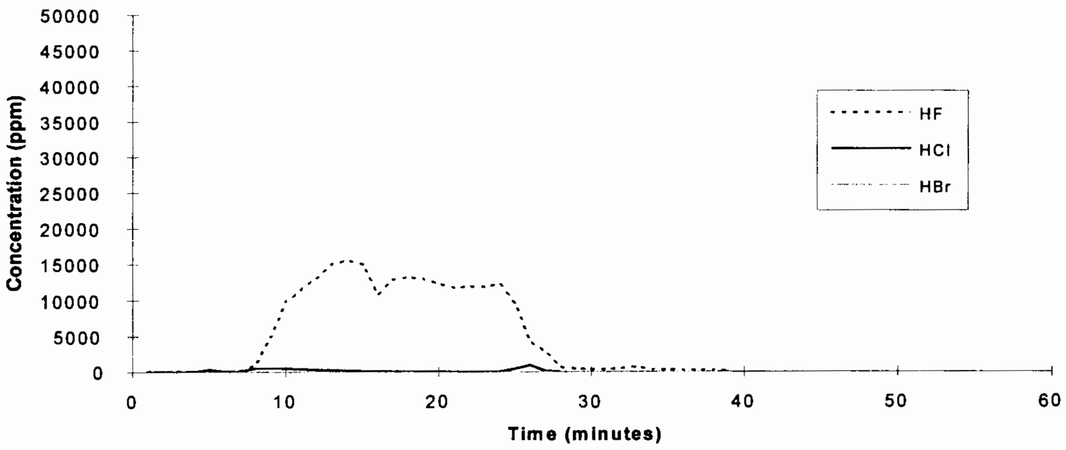


Perfluorobutane - Test 2

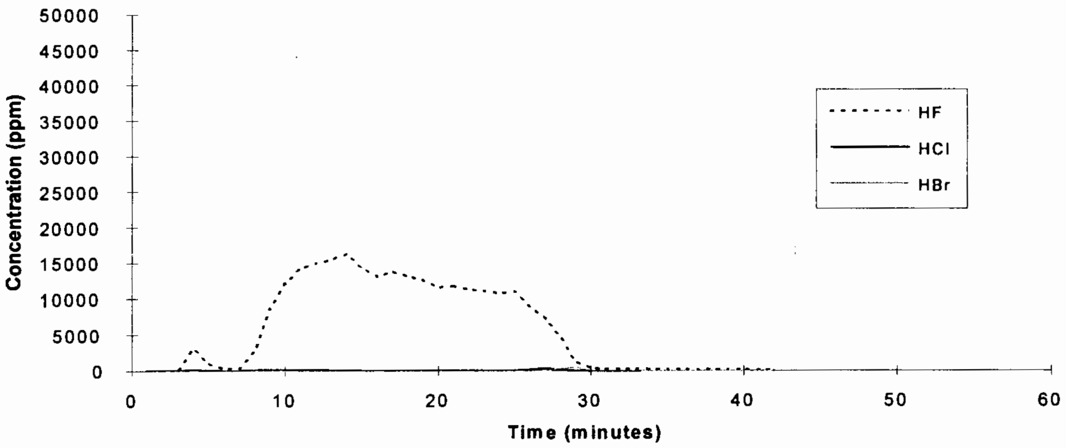


Perfluorobutane - Test 3

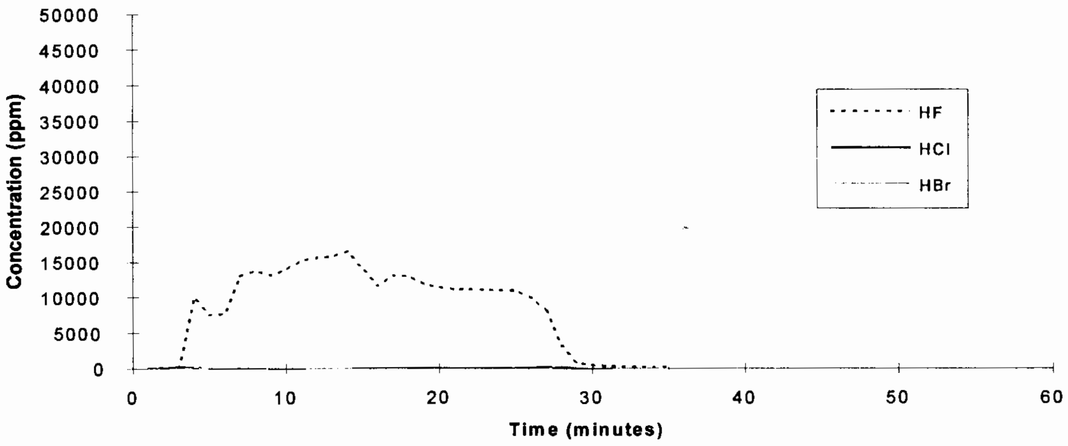




Perfluorobutane - Test 1

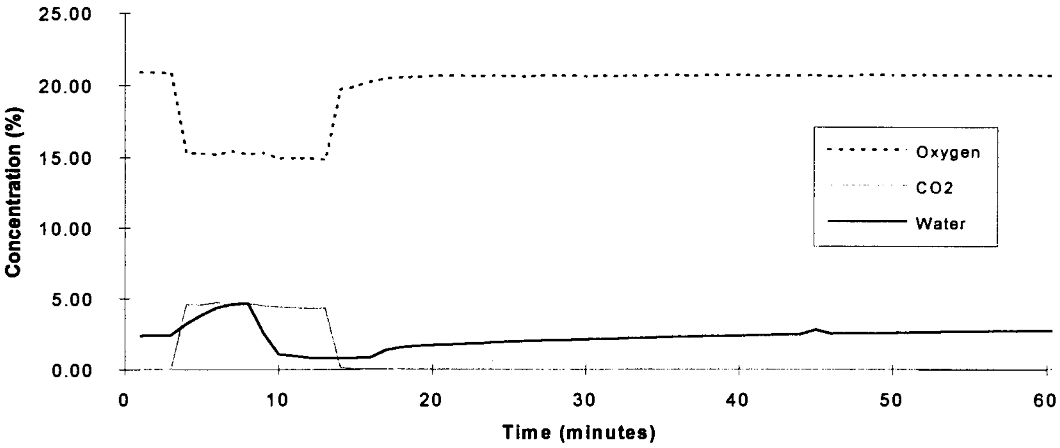


Perfluorobutane - Test 2

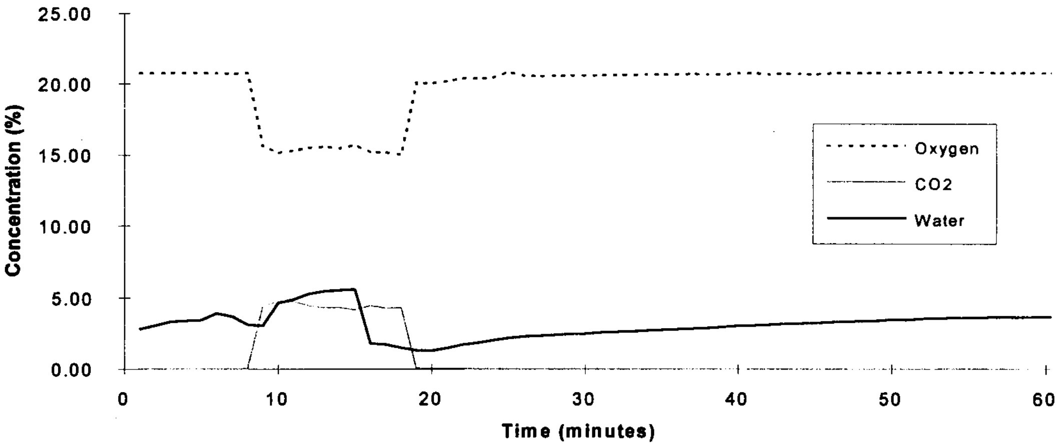


Perfluorobutane - Test 3

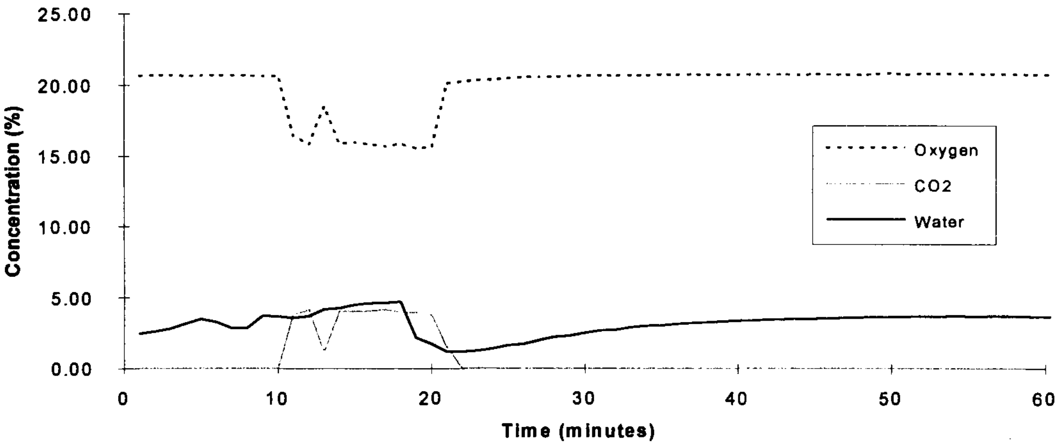
Perfluoropentane - Test 1

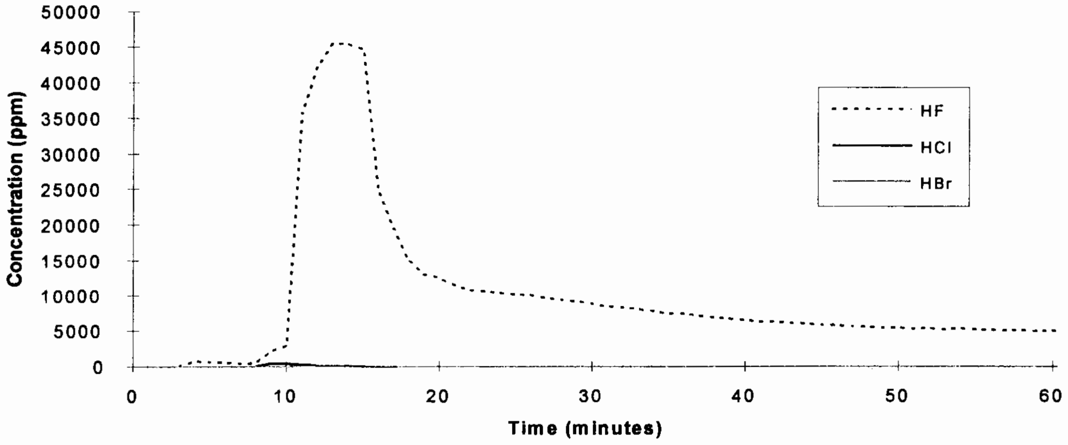


Perfluoropentane - Test 2

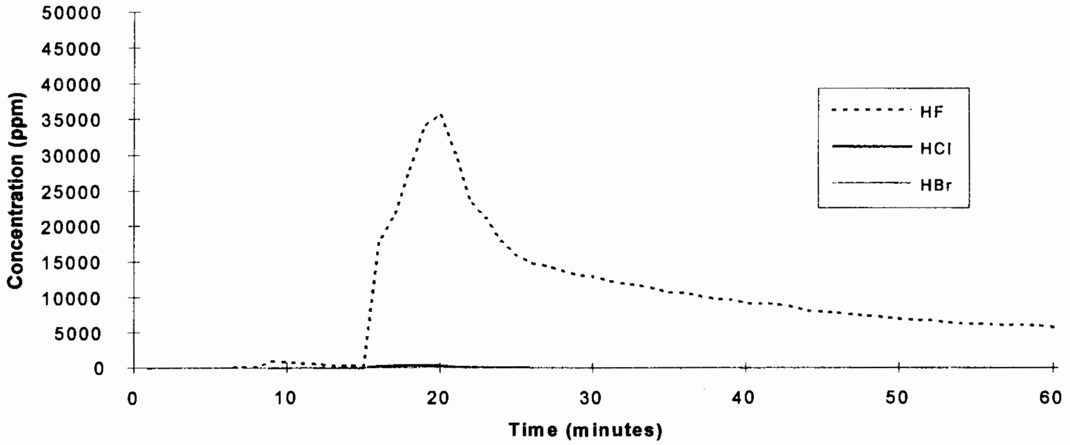


Perfluoropentane - Test 3

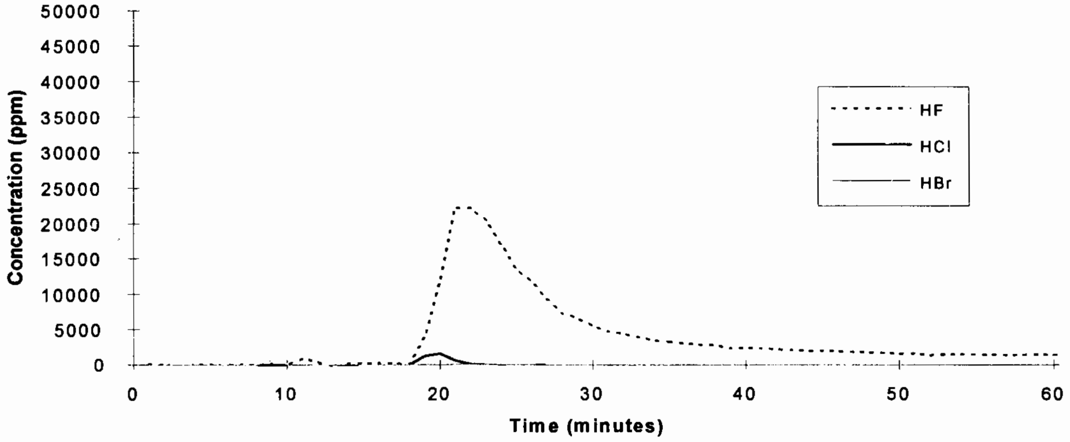




Perfluoropentane - Test 1

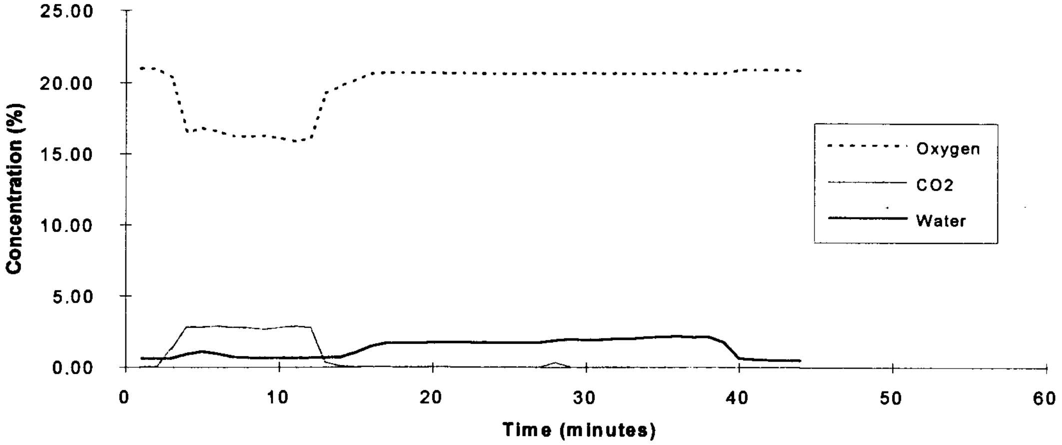


Perfluoropentane - Test 2

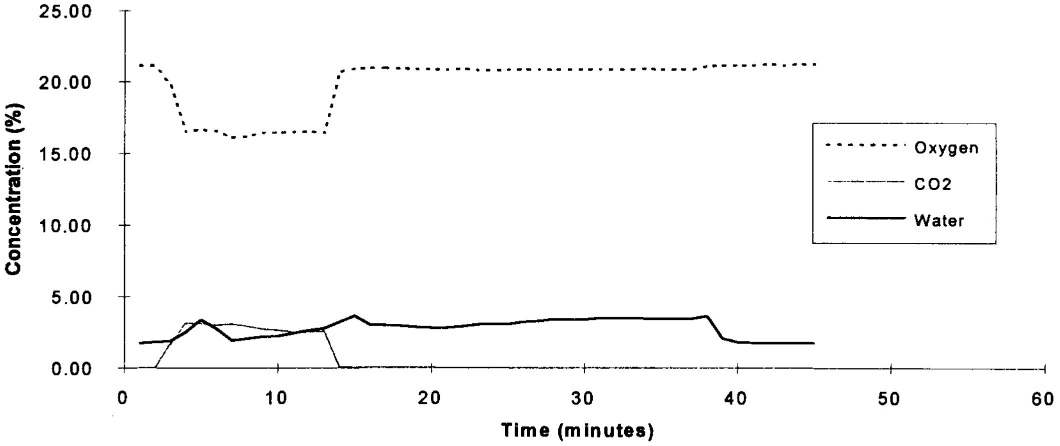


Perfluoropentane - Test 3

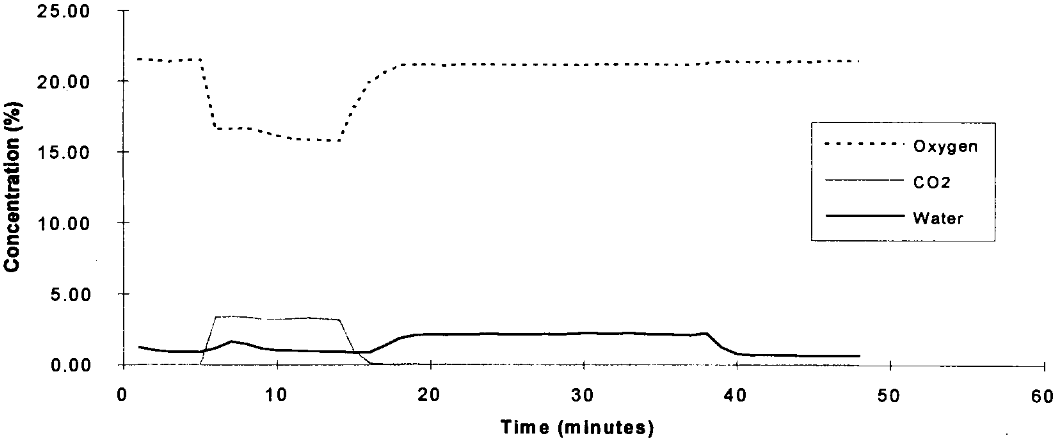
Perfluorohexane - Test 1



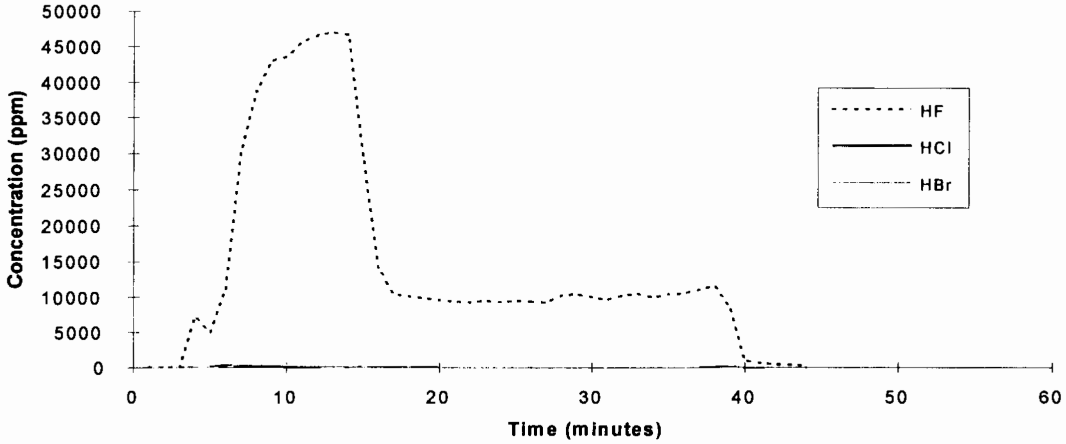
Perfluorohexane - Test 2



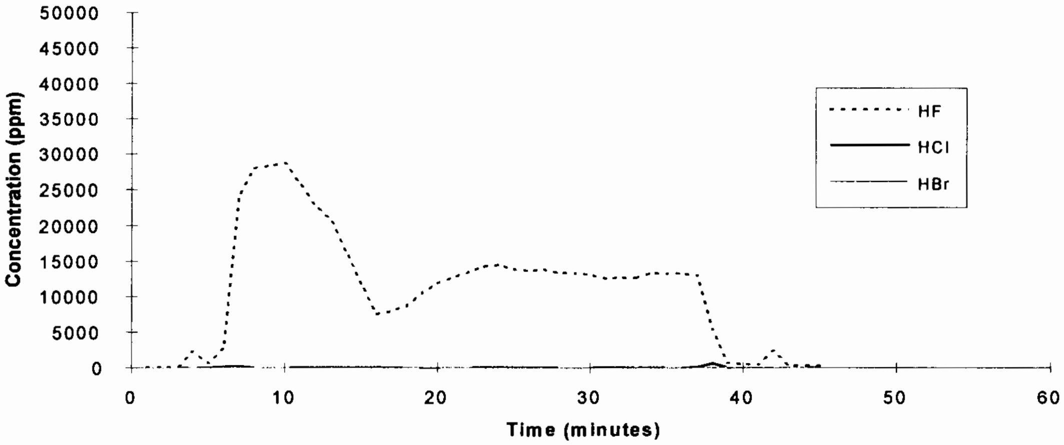
Perfluorohexane - Test 3



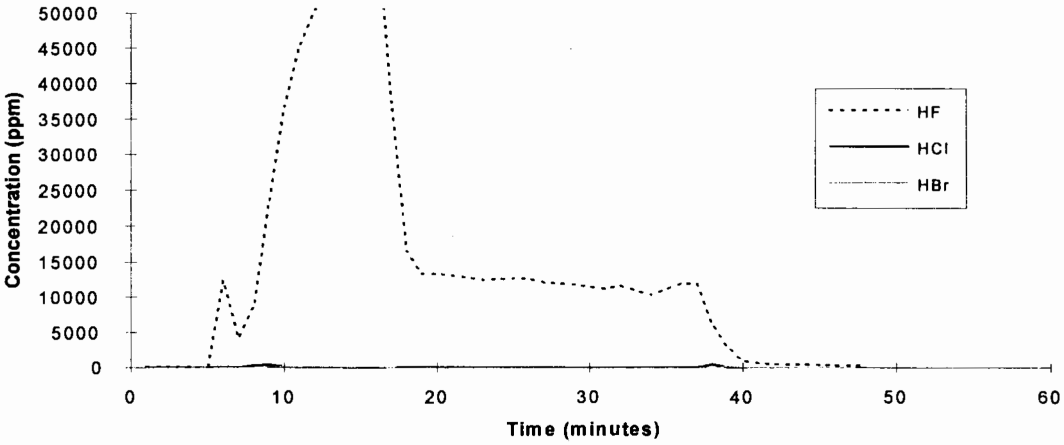
Perfluorohexane - Test 1

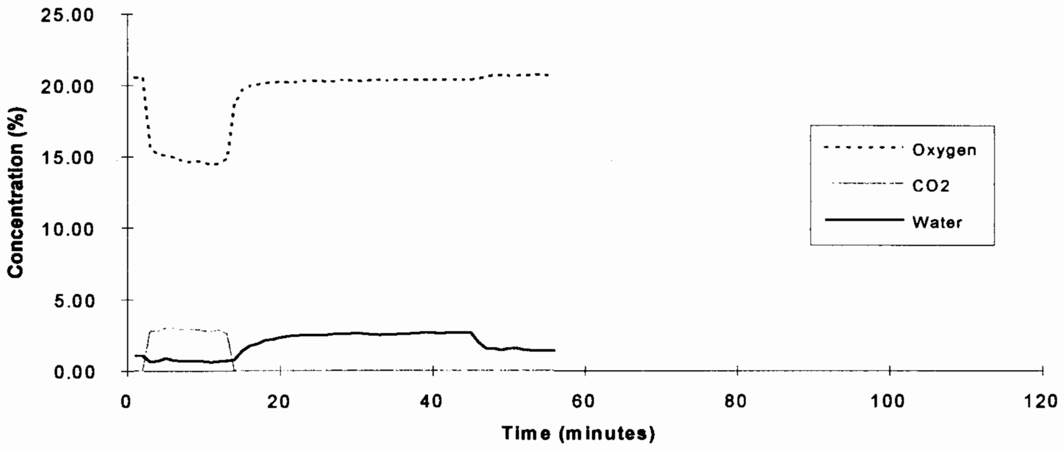


Perfluorohexane - Test 2

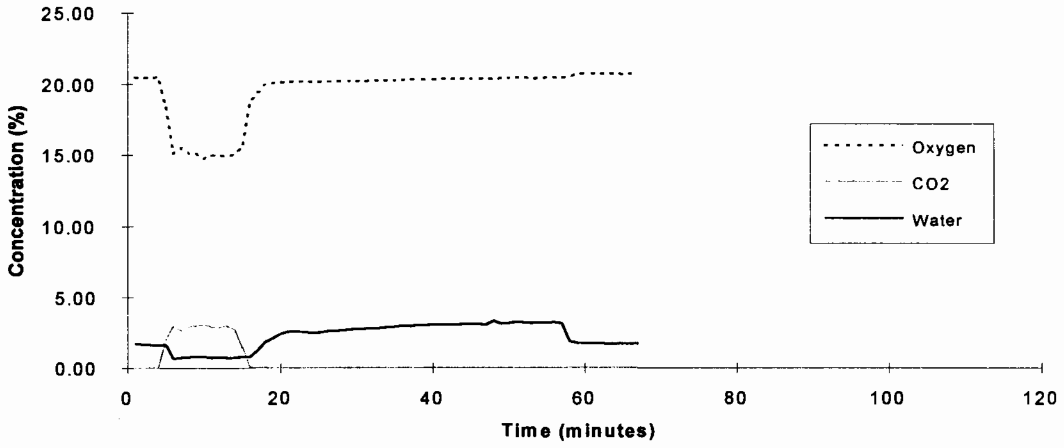


Perfluorohexane - Test 3

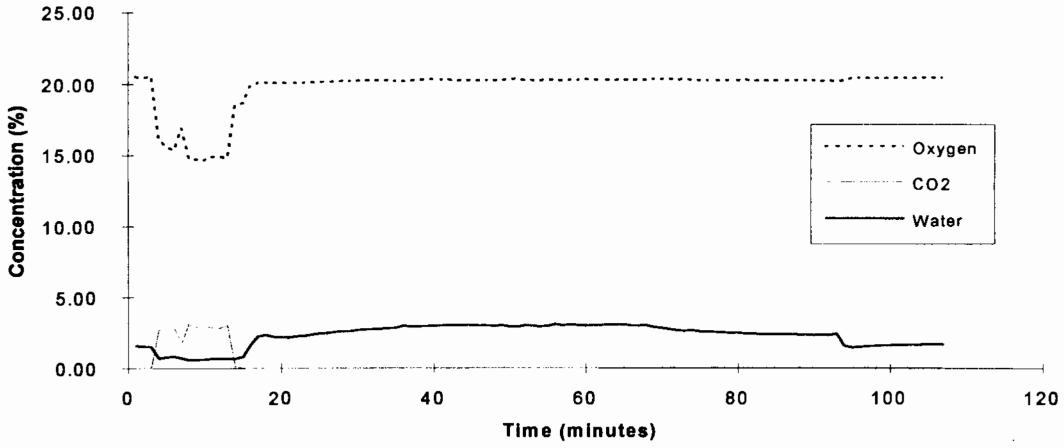




HFC 23 - Test 1

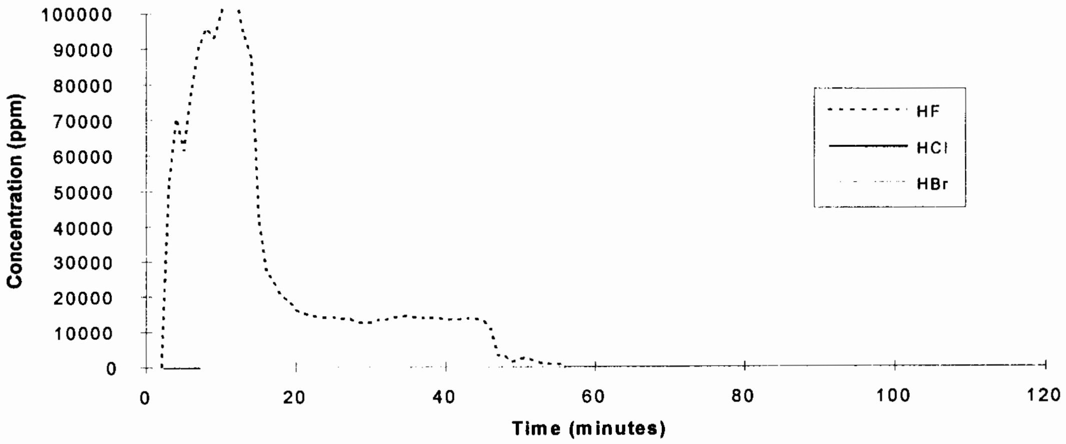


HFC 23 - Test 2

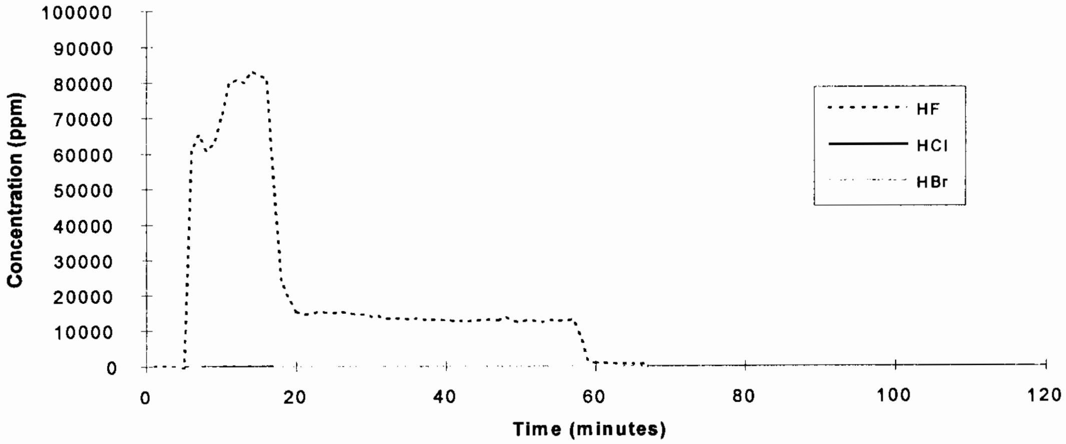


HFC 23 - Test 3

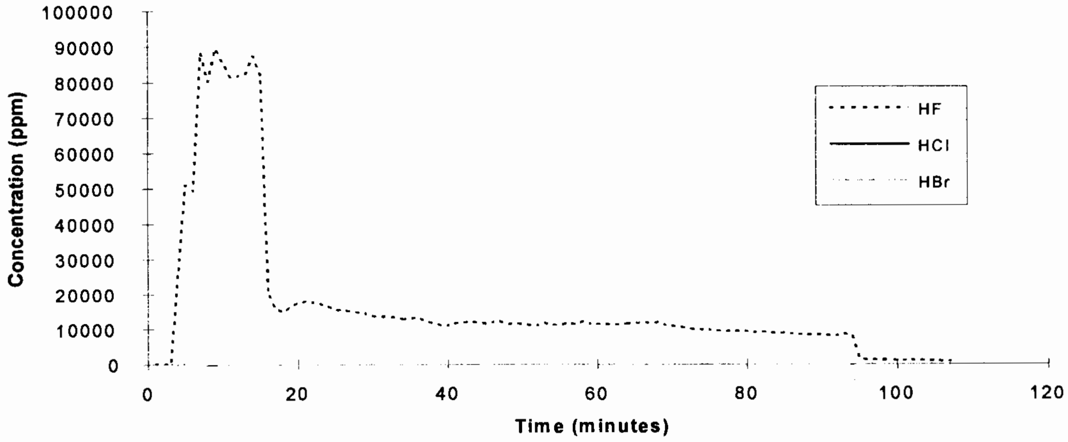
HFC 23 - Test 1



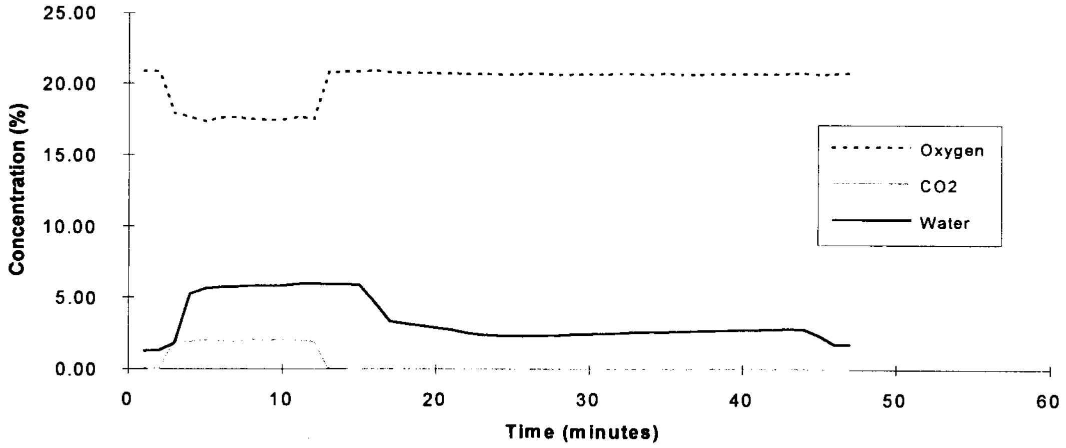
HFC 23 - Test 2



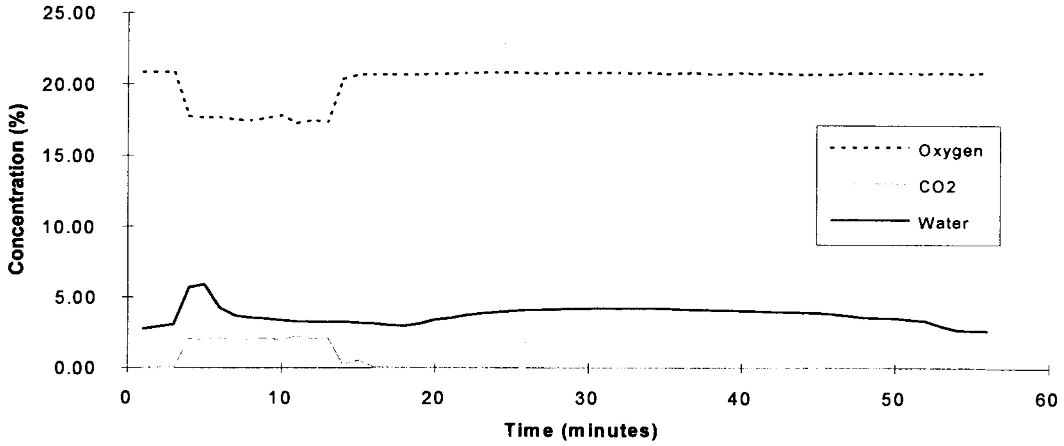
HFC 23 - Test 3



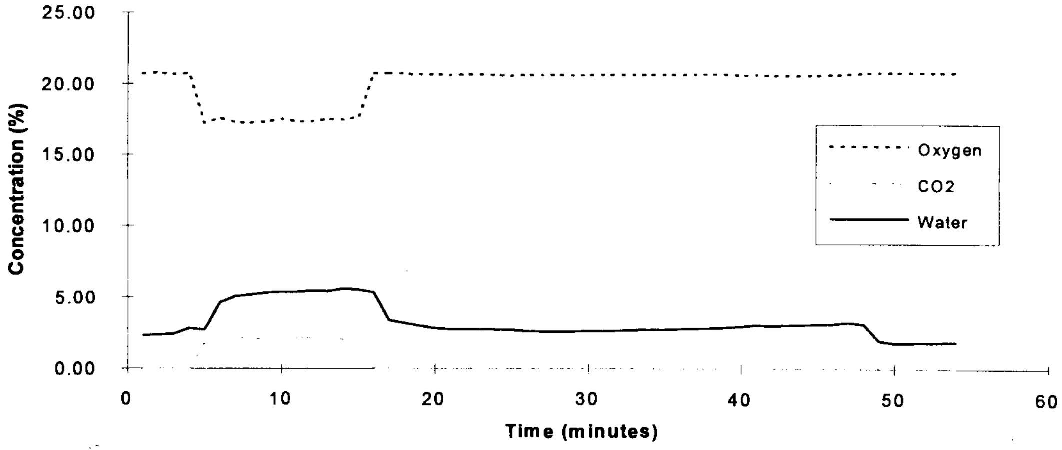
HFC -125 - Test 1



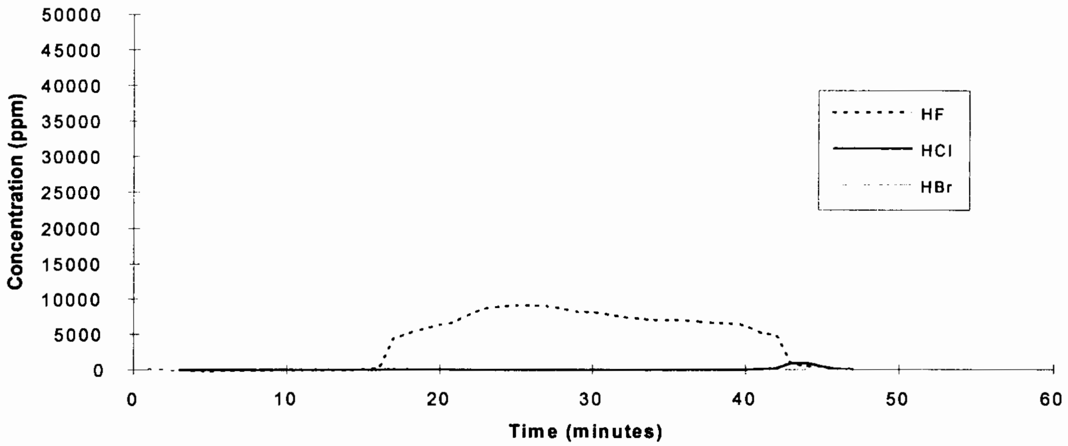
HFC -125 - Test 2



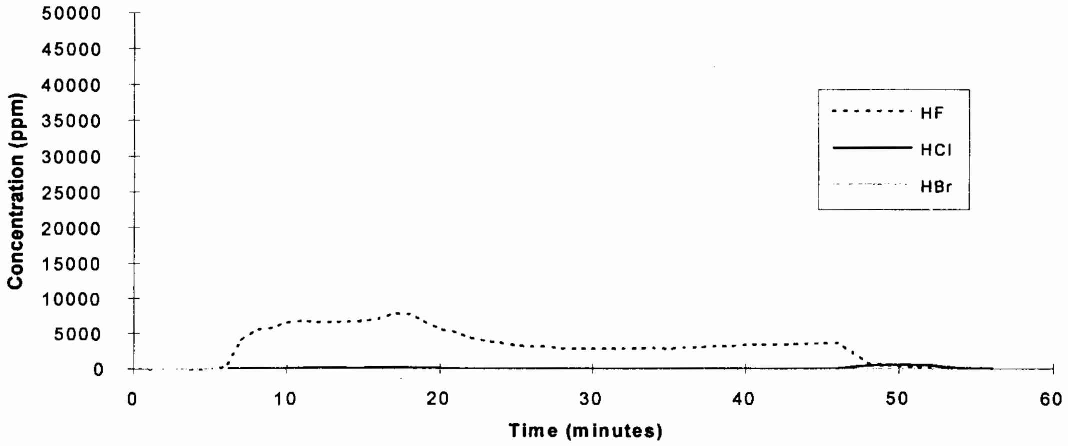
HFC -125 - Test 3



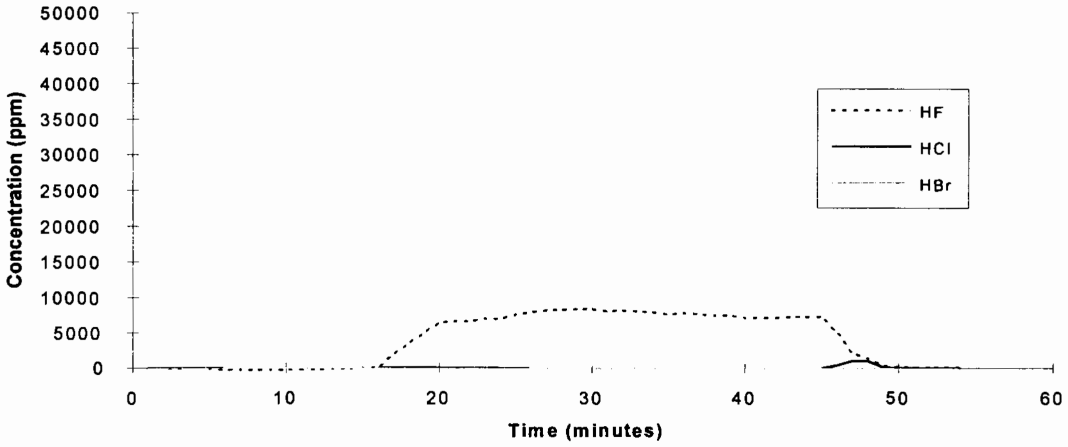
HFC-125 - Test 1

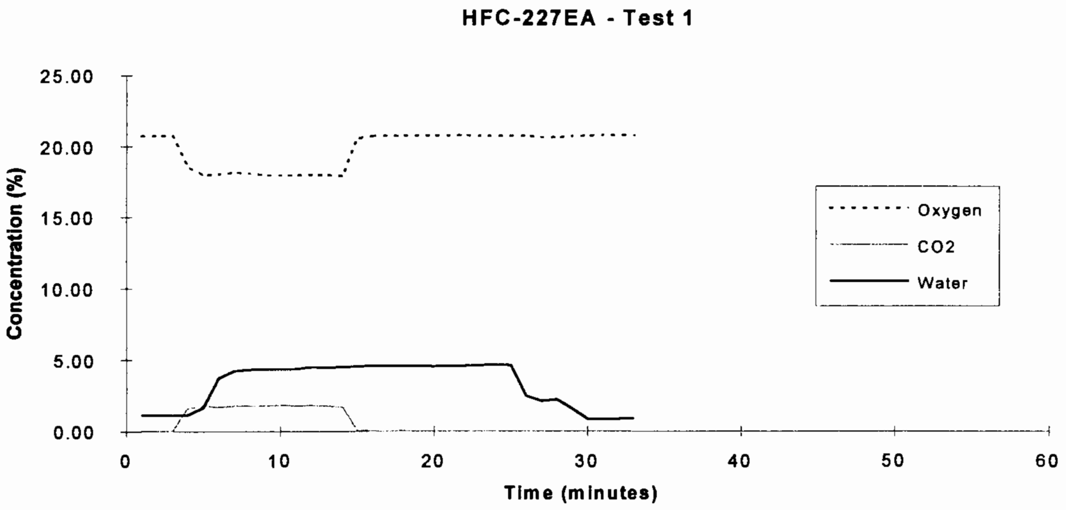


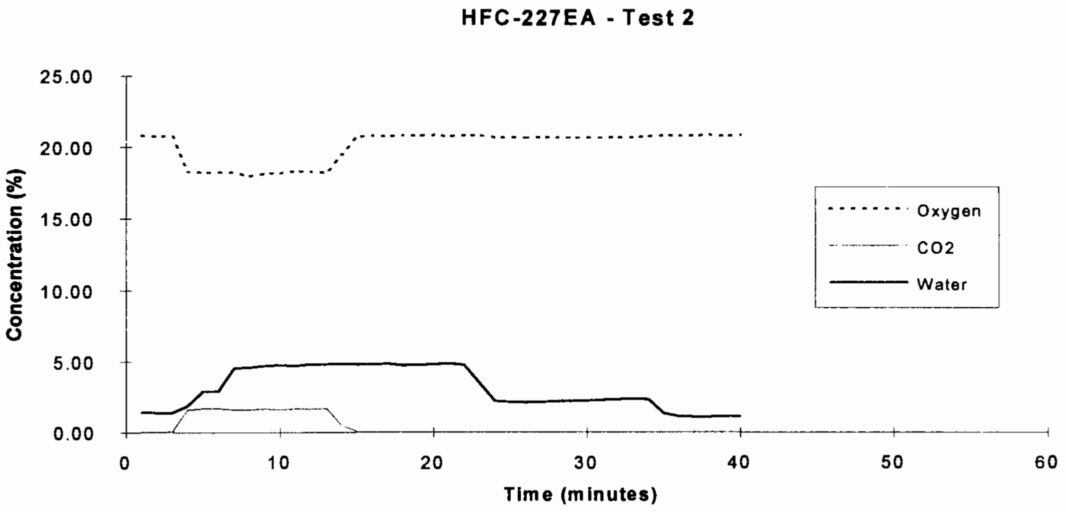
HFC-125 - Test 2

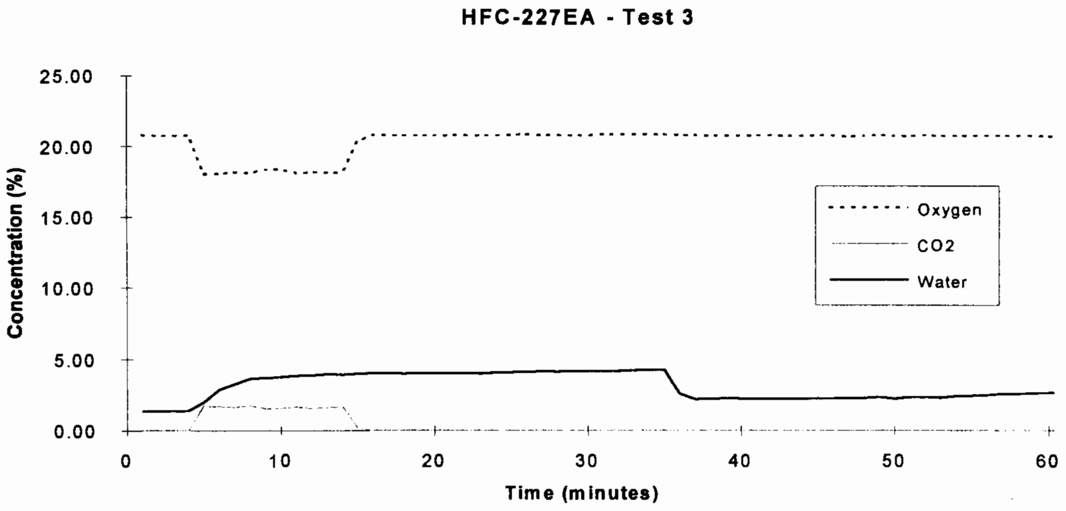


HFC-125 - Test 3

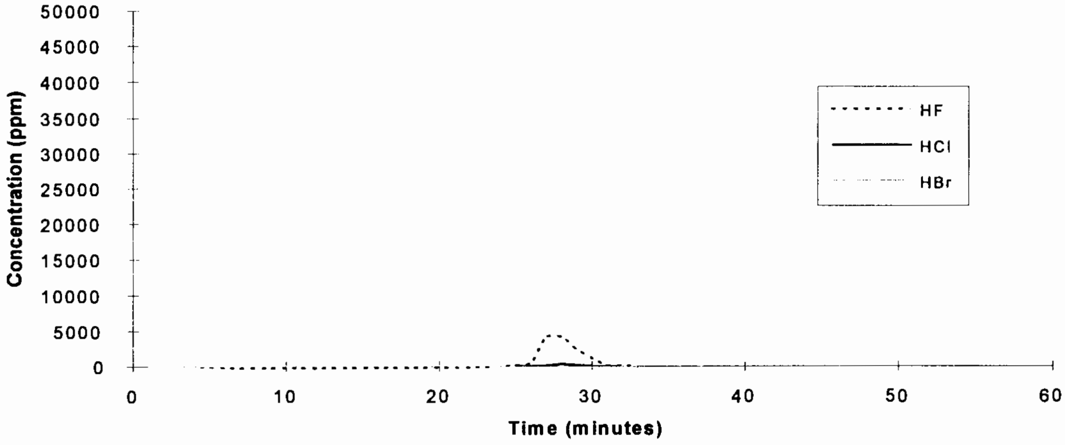



HFC-227EA - Test 1
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water

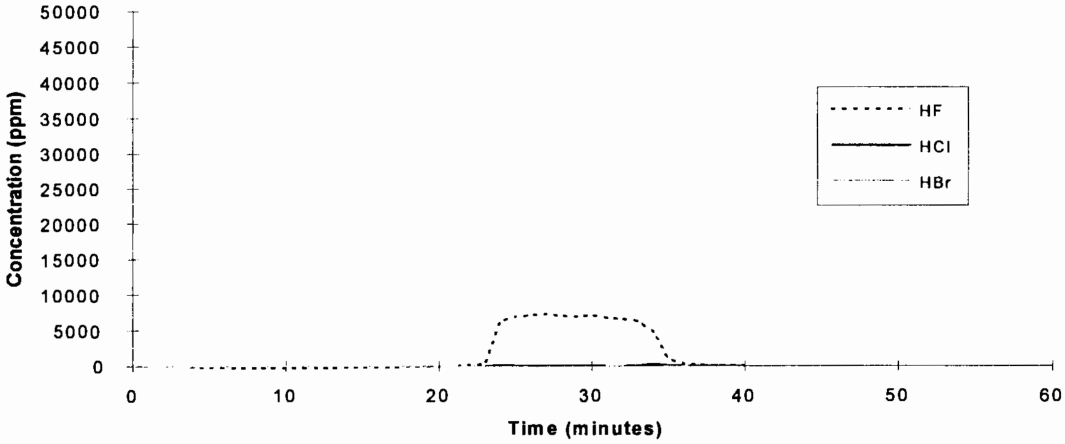

HFC-227EA - Test 2
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water


HFC-227EA - Test 3
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water

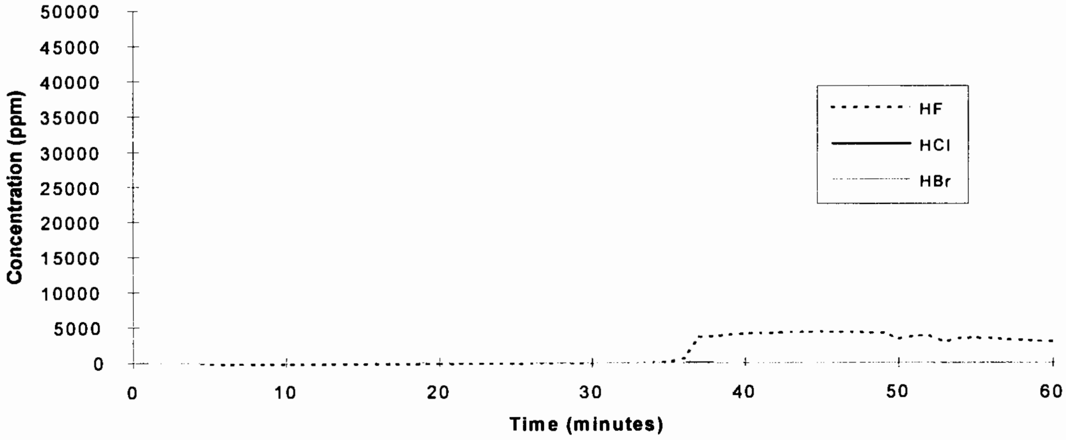
HFC-227EA - Test 1

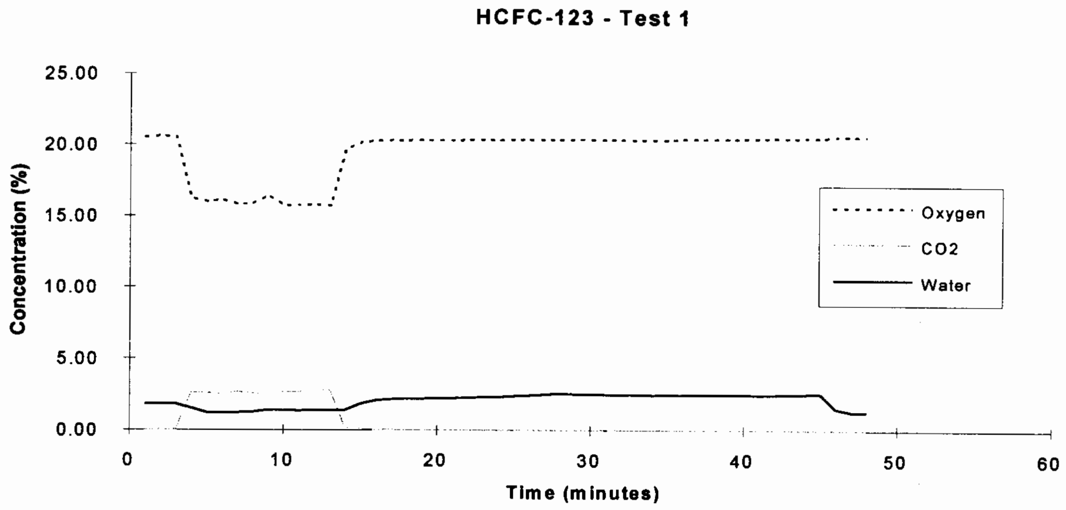


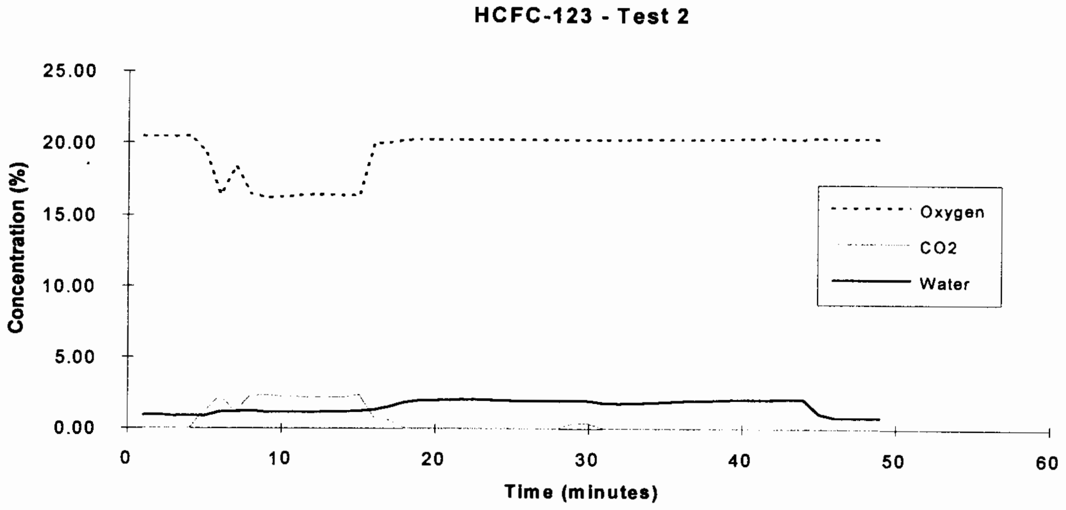
HFC-227EA - Test 2

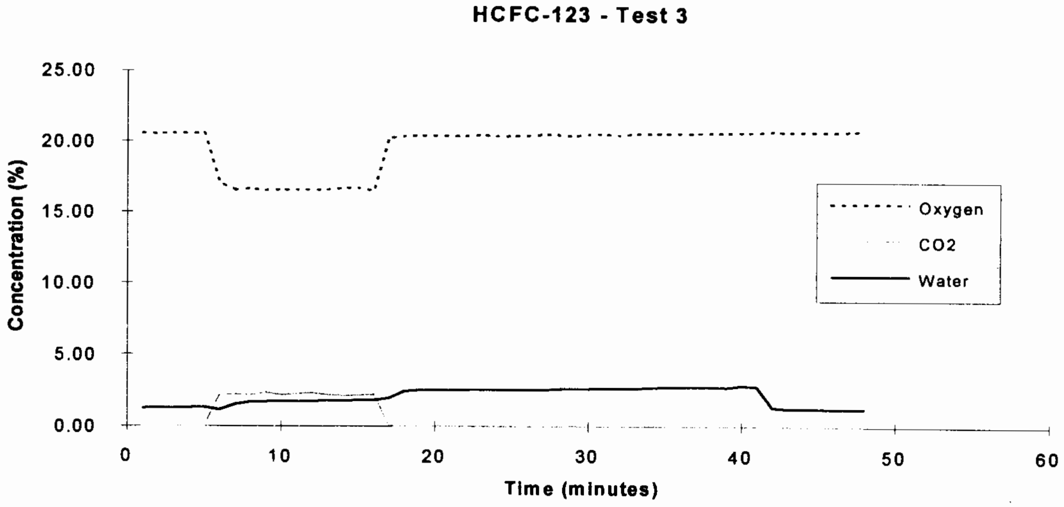


HFC-227EA - Test 3

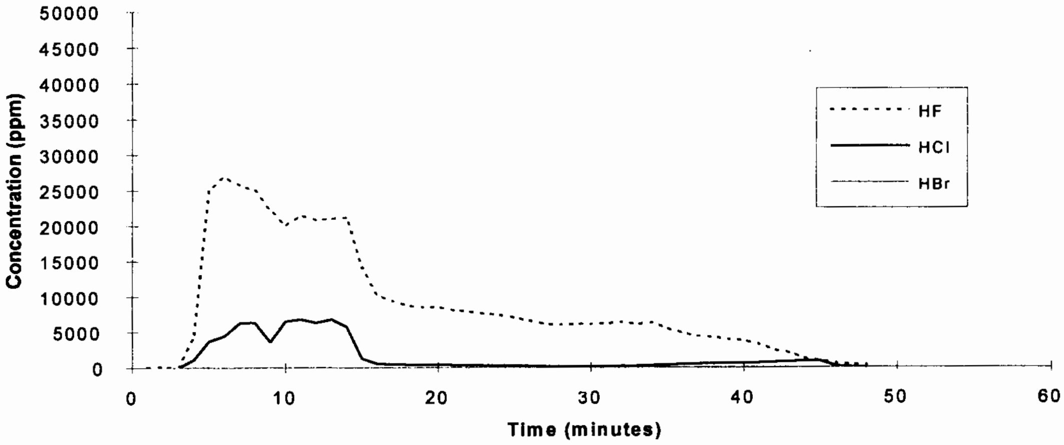



HCFC-123 - Test 1
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water

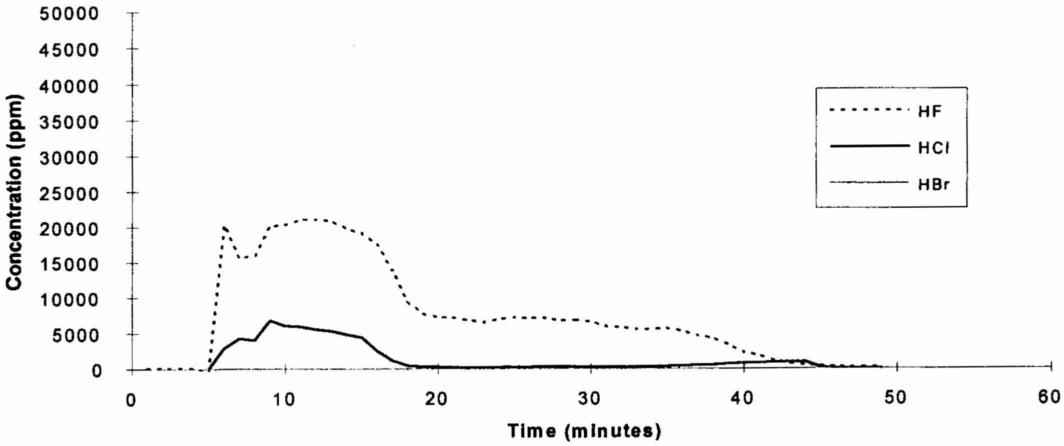

HCFC-123 - Test 2
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water


HCFC-123 - Test 3
Concentration (%)
25.00
20.00
15.00
10.00
5.00
0.00
0
10
20
30
40
50
60
Time (minutes)
Oxygen
CO2
Water

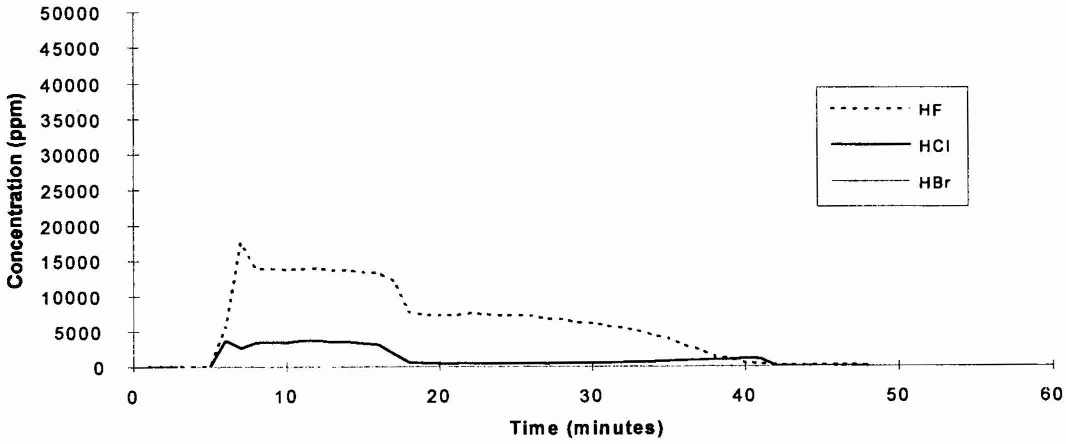
HCFC-123 - Test 1



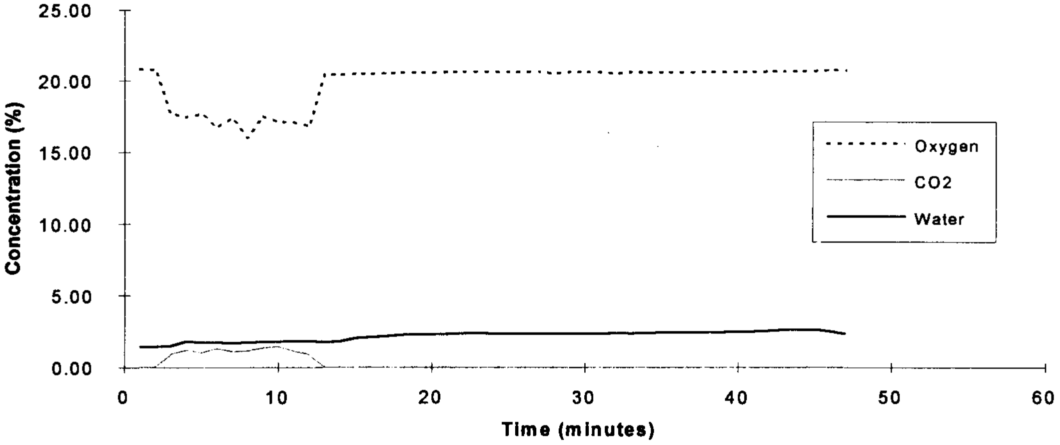
HCFC-123 - Test 2



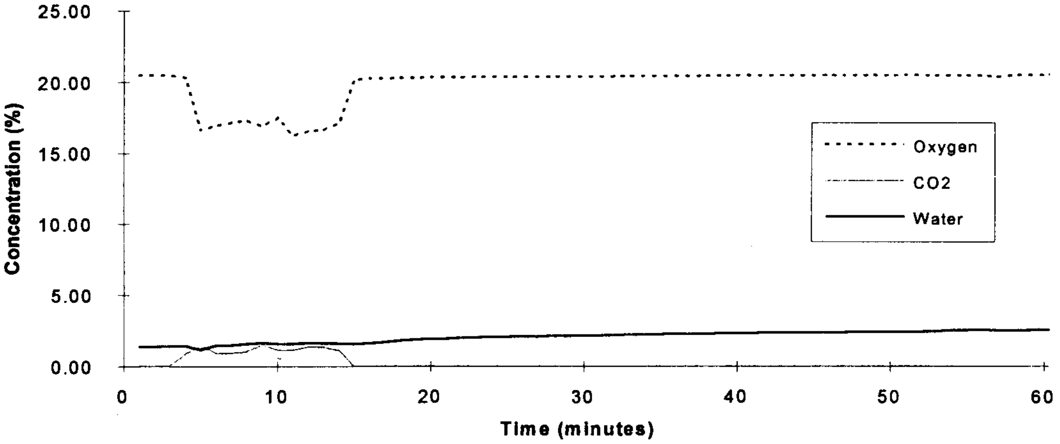
HCFC-123 - Test 3



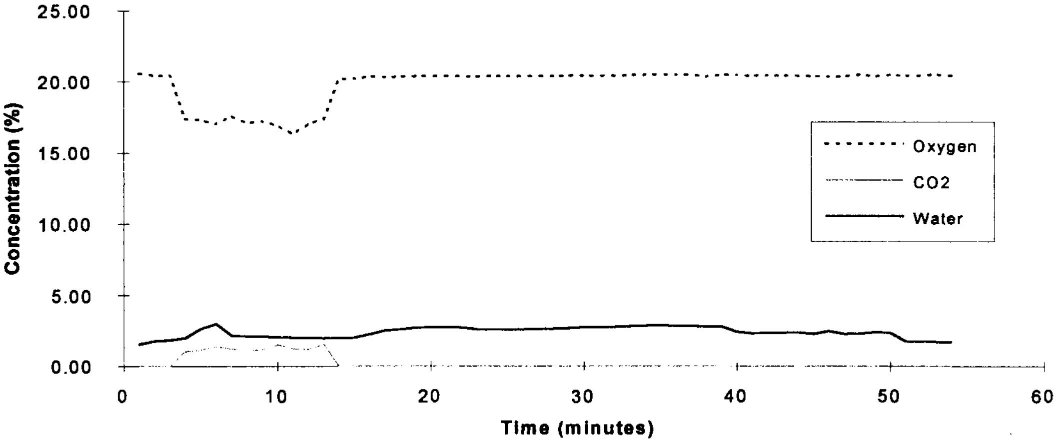
HCFC-124 - Test 1



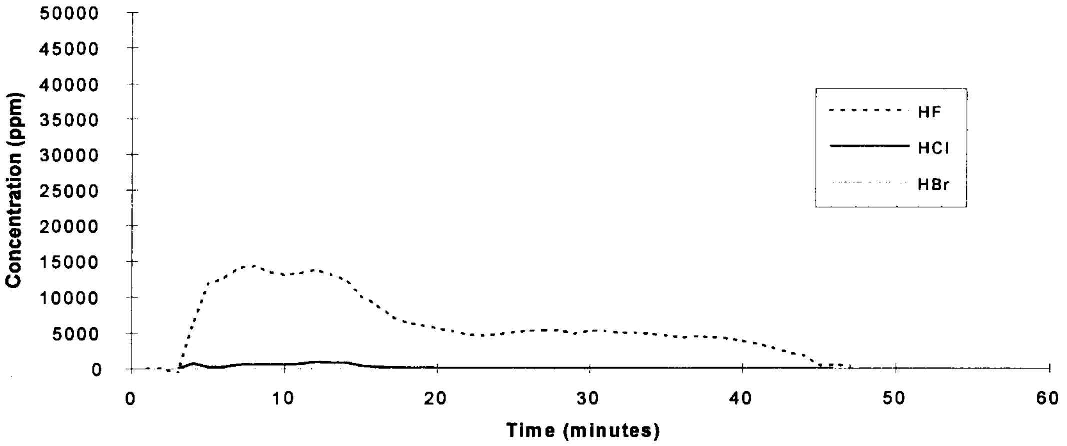
HCFC-124 - Test 2



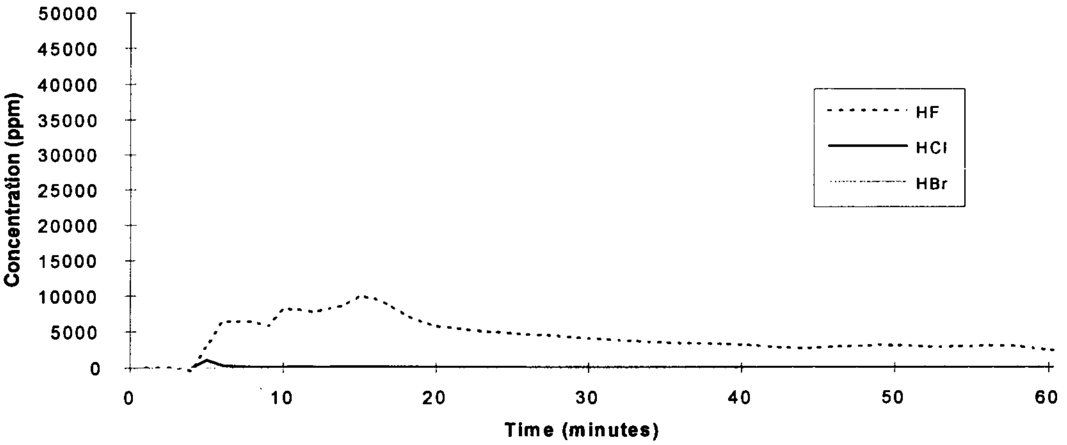
HCFC-124 - Test 3



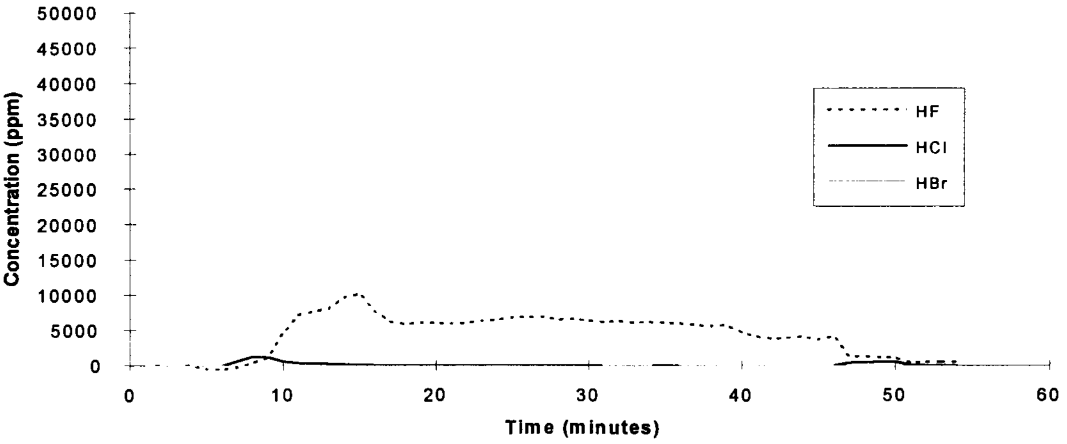
HCFC-124 - Test 1



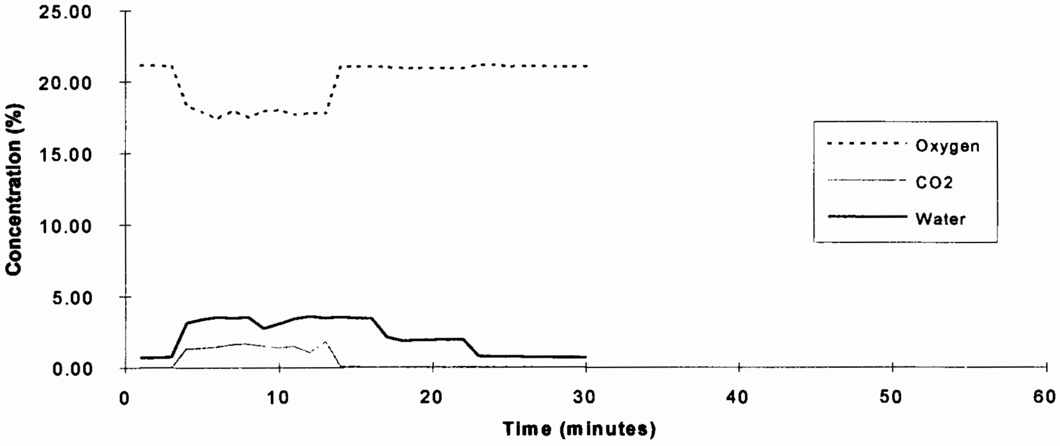
HCFC-124 - Test 2



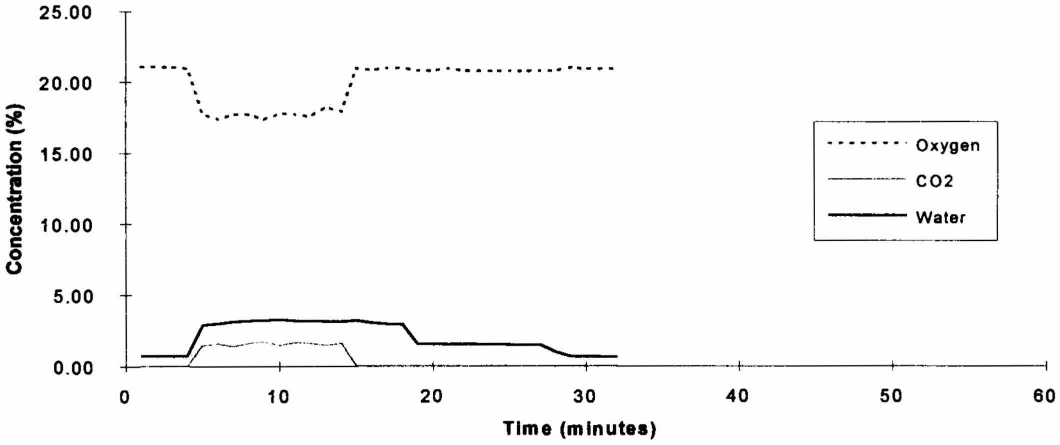
HCFC-124 - Test 3



CF3I - Test 1



CF3I - Test 2



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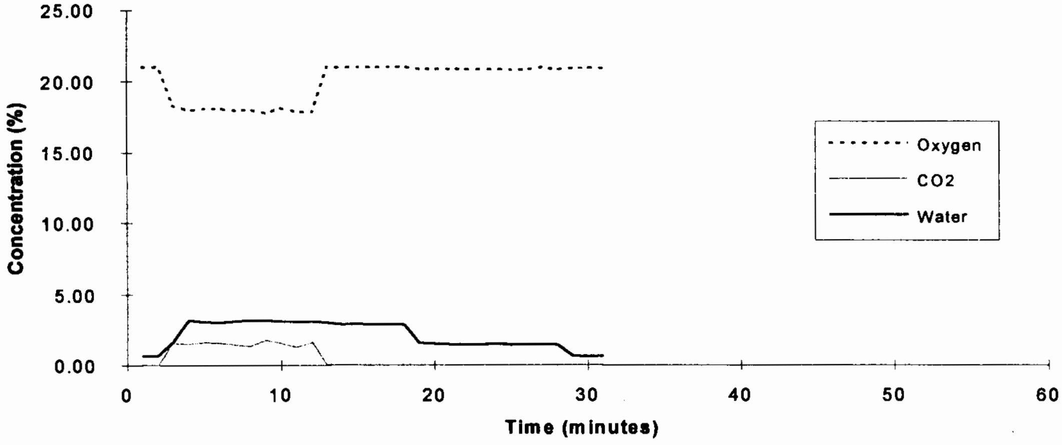

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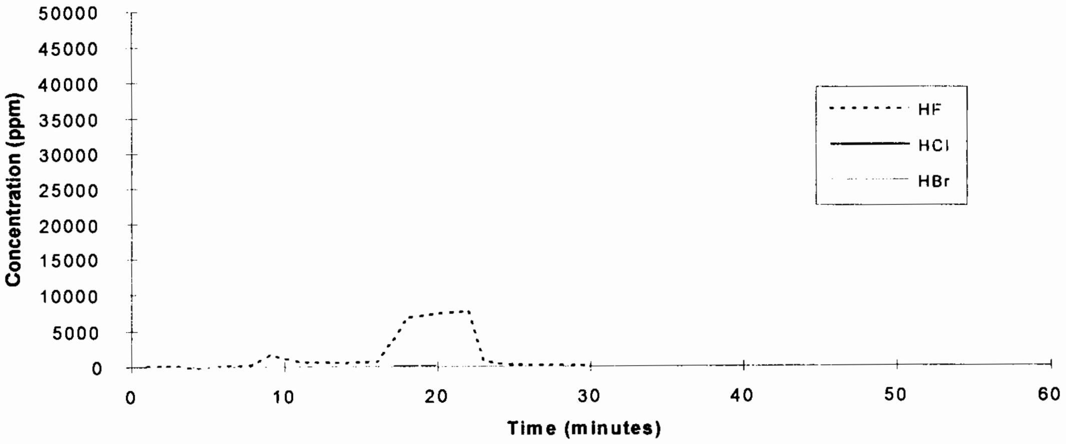

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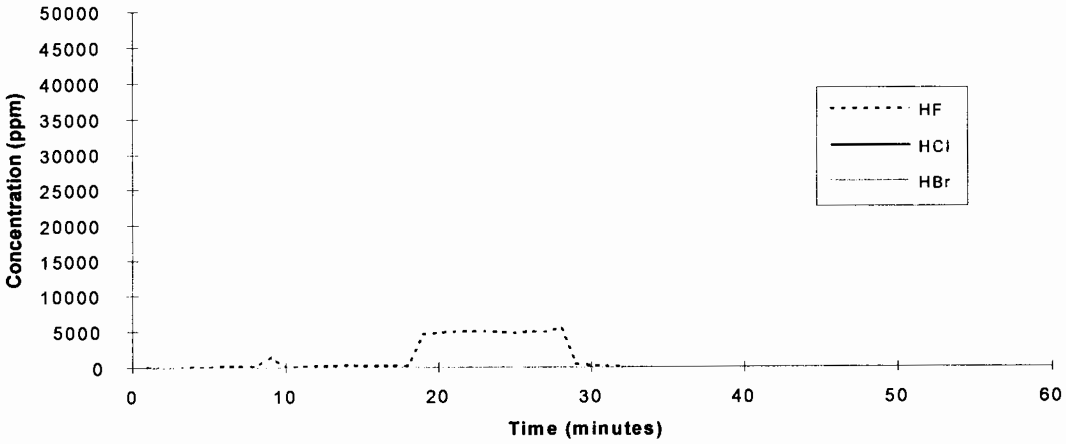

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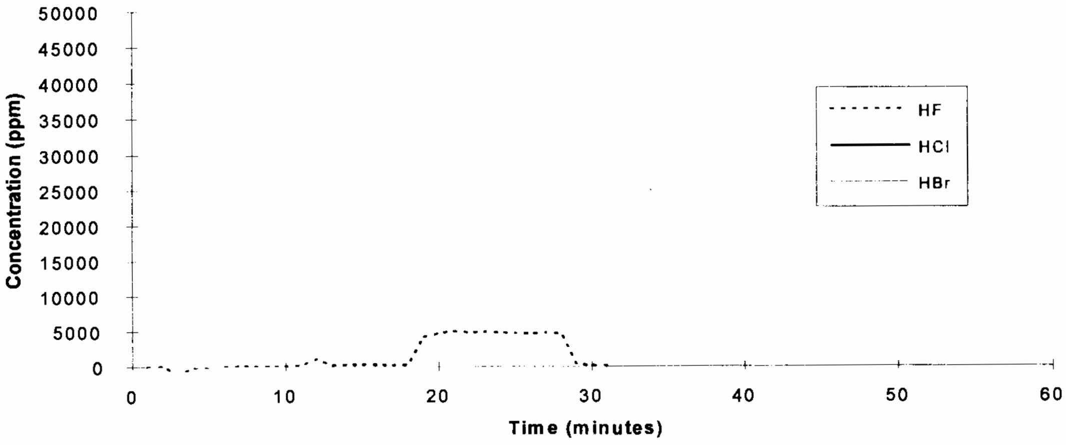
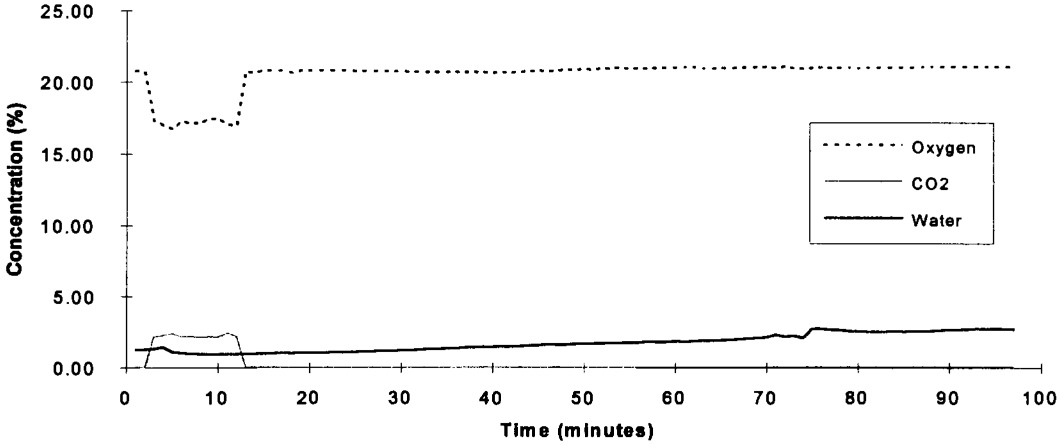


C3F7I - Test 1



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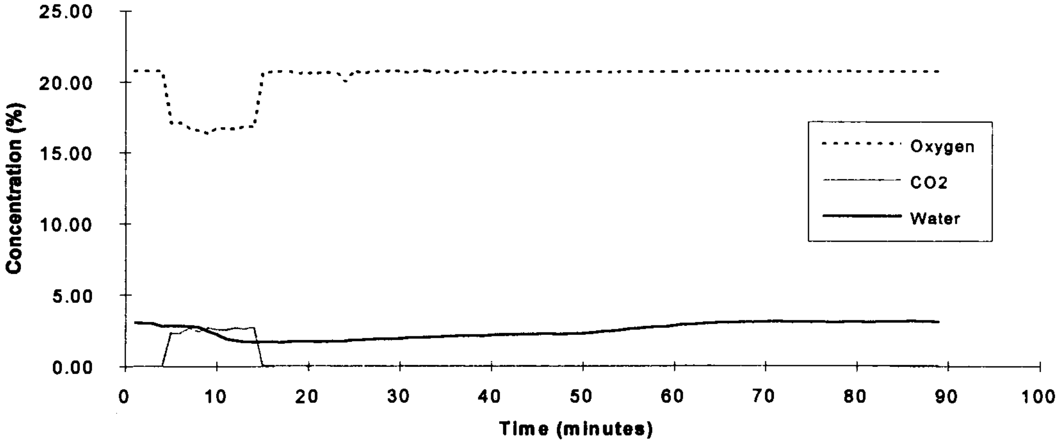

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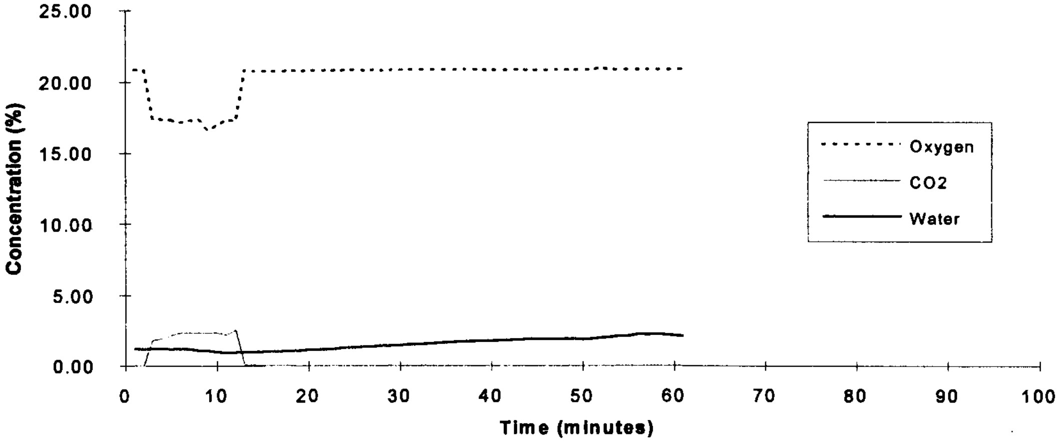

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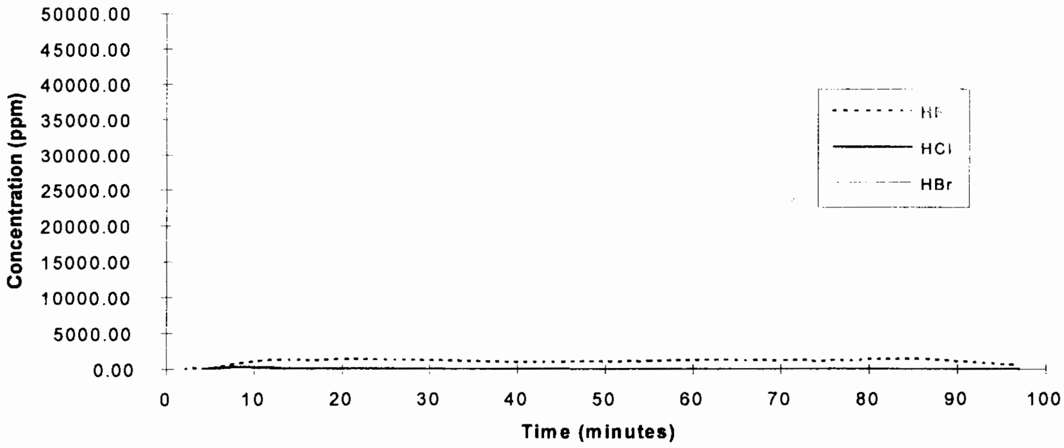

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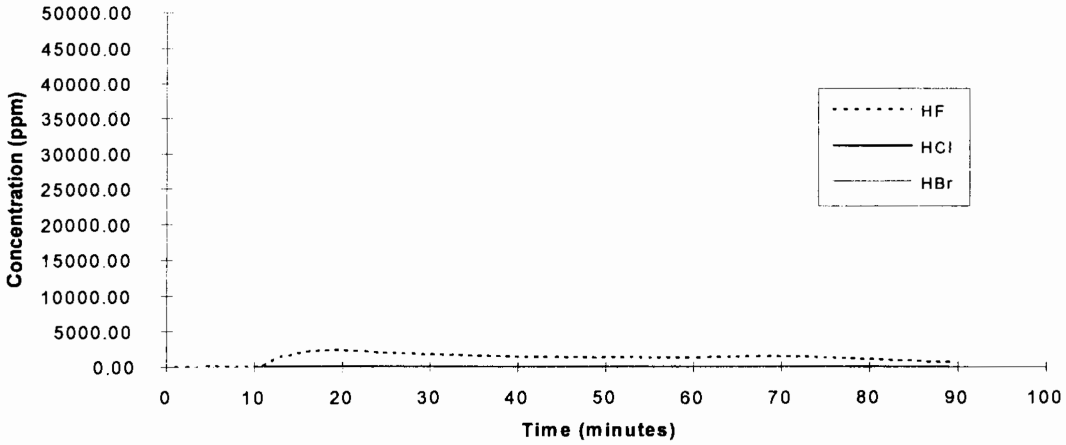

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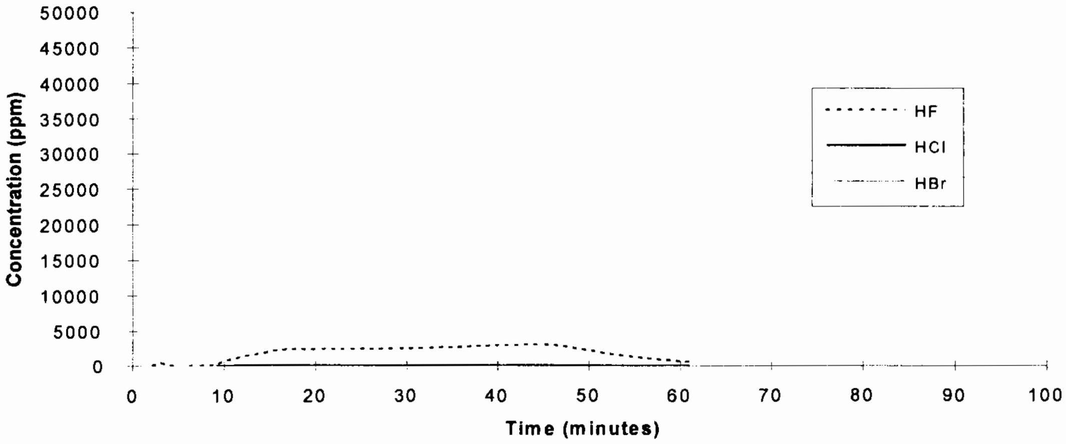

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