AGENT DECOMPOSITION PRODUCTS OF HALON ALTERNATIVE AGENTS

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ABSTRACT

Hand-held Halon 1211 extinguishers have been required in passenger category aircraft since 1986, initially in response to the threat of a terrorist with combustible liquids. Since that time, these'extinguishers have proven very effective in fighting and suppressing hidden fires. A replacement agent must demonstrate similar characteristics of effectiveness and low toxicity for both the neat agent and its decomposition products.

Halon alternative agents are compared in terms of their relative extinguishment effectiveness and acid gas production during extinguishment of a standard 250 Watt methane flame. A simple apparatus was constructed using a Bunsen burner and two rotameters to accurately meter methane and agent flow rates to form a steady-state condition just below flame extinguishment. Effluent gases are measured with a magnetic sector mass spectrometer, with analyses conducted for oxygen, carbon dioxide, water, hydrogen fluoride, hydrogen chloride, hydrogen bromide, and unreacted agent. Spectra were also subsequently examined for m/z (mass to charge ratio) particles not present in the neat agent spectra, to attempt identification of additional possible decomposition products. Agents examined were: HFC-23, HFC-125, HCFC-123, HCFC-124, HFC-227ea, HBFC-22B1, FC-3-1-10 (perfluorobutane), FC-4-1-12 (perfluoropentane), FC-5-1-14 (perfluorohexane),Halon 13001 (CF_3I), Halon 37001 (C_3F_7I), as well as Halon 1211, Halon 1301 and CO_2.

BACKGROUND

The Federal Aviation Administration (FAA) has required Halon 1211 hand held extinguishers for passenger category aircraft since 1986.[1] The referenced regulation states that "an airplane with a passenger capacity of at least 31 or more must contain Halon 1211 (bromochlorodifluoromethane) or equivalent, as the extinguishing agent." This regulation was an outgrowth of the full-scale testing program developed in response to the threat posed to the flying public by a terrorist with combustible fluids, e.g. gasoline. Halon was found to be an effective fire fighting agent "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."[2] Subsequent to the making of that rule, Halon 1211 has demonstrated utility for fighting hidden fires. In one instance, three Halon 1211 hand-held extinguishers were discharged into the return air vents located along the floor during an in-flight fire on a Lockheed L1011-385-3.[3] Halon effectively extinguished this electrical fire located in the cheek area of the aircraft. Without a gaseous agent like Halon that is capable of diffusing into obstructed areas, it is quite possible the aircraft and passenger would have been lost.

Regulations also require that for "airplanes with a passenger capacity of 20 or more: (b) Each lavatory must be equipped with a built-in fire extinguisher for each disposal receptacle for towels, paper or waste"[4] and that Class C cargo compartments must have "an approved built-in fire extinguishing system controllable from the pilot or flight station."[5] While the later two regulations do not specify the 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 substance. No halons may be produced after January 1, 1994. Because there is no suitable substitute at the present time, but sufficient quantities existent for the short term, Halons will continue to be used in aircraft but will be phased out as soon as practical.

This research is to examine the issues of equivalency to Halon in terms of effectiveness and relative amounts of decomposition products.

EQUIPMENT DESCRIPTION

The test device to compare Halons and potential replacements should be reproducible and quantitative. The standard fire was chosen to be a 250 Watt methane flame, as produced with a natural gas Bunsen burner (.067 in. orifice, air inlets fully open, flame retainer removed).

The extinguishing agent is delivered to the base of the flame with a 1/8 stainless steel tube that enters through the air inlet near the bottom of the burner. Methane and agent are metered with two Matheson Tube Cube Flowmeters (150 mm). Flow rates are calibrated using a Precision Wet Test Gas Meter. At nominal ambient conditions, the methane flow rate is approximately .475 liters per minute, which produces a blue flame approximately 3 in. long. The flame and effluent gases are contained within a glass combustion tube, 26 mm i.d. by 500 mm long, situated 12.57 mm above the burner outlet.

Gas concentrations exiting the combustion tube are measured using a Perkin-Elmer **ICAMS** (Industrial Central Air Monitoring System), a magnetic sector mass spectrometer. The sample probe consists of a 1/8 in. stainless steel tube, held in the center of the tube 30 mm below the top of the combustion tube 'chimney' with a custom made aluminum adapter. The inlet to the **ICAMS** is a **1/16** in. Teflon FEP capillary which draws approximately 10 ml. per minute of the sample gas. This capillary passes through a 1/8 Swagelok stainless steel tee into the probe, with the other leg of the tee attached to a flowmeter and vacuum pump used to draw a total flow of 100 ml/min. through the probe. The aluminum adapter acts as a heat sink to prevent the Teflon capillary from melting with the bypass eliminating dead volume and minimizing condensation. ICAMS measures the distribution of m/z (mass to charge ratio) particles called for in the configuration and solves the set of linear equations for the fragmentation pattern of each gas to report the concentrations in the unseparated mixture.[6]

The test procedure calls for slowly metering agent into the flame with the flowmeter. When the flame is extinguished a ball valve is switched to direct the agent flow to **a** wet test meter. **A** stopwatch is used to time an appropriate volume, and the flow rate is calculated. The flame is then reignited and agent is introduced at a flow rate slightly below that needed for extinguishment. A baseline for room air **is** established by **ICAMS** and the probe **is** manually attached by sliding it onto the combustion **tube.** The test is run for ten minutes, at which point the probe is manually removed. Measurements continue to be made with ICAMS until the concentration of the gases return to baseline. The agent flow rate at the reduced setting is measured with the wet test meter. This procedure is repeated three times and the values for flow rate and gas concentrations are averaged.

The procedure differs slightly for agents that are liquids at room temperature. In this instance, the agent is poured into a bubbler that is immersed in a Dewar flask filled with an ice and water mixture. This allows the vapor pressure of the liquid to equilibrate. The bubbler is inserted into the system between the rotameter used for agent flow and the tube delivering agent to the base of the Bunsen burner. Air is then slowly metered into the bubbler with the flowmeter until the saturated vapor/air mixture extinguishes the flame. The wet test meter is then used to measure the flow rate of air enfering the bubbler and the flow of the saturated agent/air mixture leaving the bubbler. The difference in these two flows is the flow of agent alone. As before, the flow for the test is reduced to a rate slightly below that needed for extinguishment.

TEST RESULTS

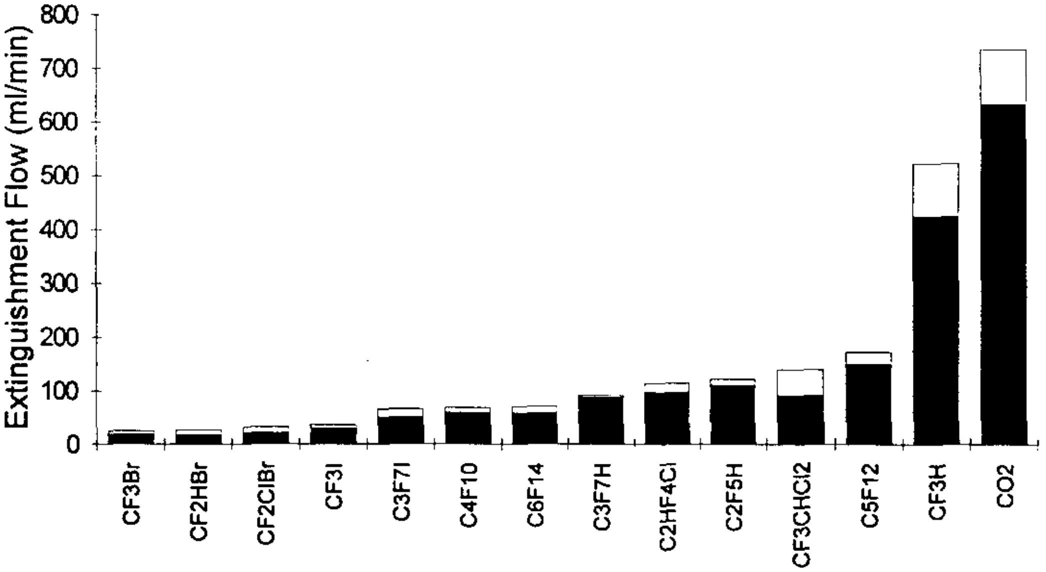
In addition to Halon 1211, Halon 1301, and CO_2, the prime candidates for use as fire extinguishing agents can be grouped into the categories of HFCs, HCFCs, perfluorocarbons, and iodocarbons. The various agents examined in the test are listed in Table 1. As discussed above agent comparison is done in terms of comparative volumetric flow rates to extinguish a standard flame.

TABLE 1 - Extinguishment Performance

Agent	Formula	MW	Extinguishment Flow		Test Flow	Fraction
			(ml gas/min)	(g/min)	(ml gas/min)	
HALON 1211	CF_2ClBr	165.4	32.9	.218	23.4	.71
HALON 1301	CF_3Br	148.9	25.7	.153	21.0	.82
Carbon Dioxide	CO_2	44.0	736.	1.297	635.	.86
HBFC-22B1	CF_2HBr	130.0	28.7	.151	19.5	.68
HFC-227EA	C_3F_7H	170.0	92.3	.629	89.5	.97
HFC-23	CF_3H	70.0	523.	1.469	426.	.81
HCFC-123	CF_3CHCl_2	152.9	139.9	.797	92.8	.66
HCFC-124	C_2HF_4Cl	136.5	114.7	.628	99.2	.86
HFC-125	C_2F_5H	120.0	122.2	.588	112.4	.92
FC 3-1-10	C_4F_{10}	238.0	69.5	.663	61.3	.88
FC 4-1-12	C_5F_{12}	288.0	172.6	1.994	151.2	.88
FC 5-1-14	C_6F_{14}	338.0	71.5	.969	60.4	.84
HALON 13001	CF_3I	195.9	37.1	.292	31.5	.85
HALON 37001	C_3F_7I	295.9	66.3	.787	52.1	.79

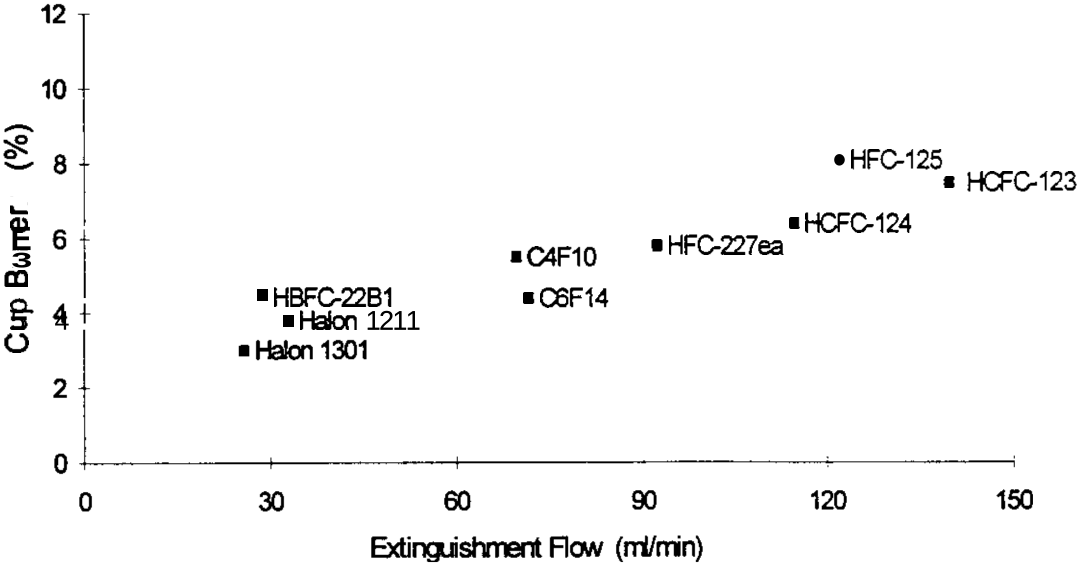
The tests to measure the production of carbon dioxide, water, and acid gases, as well as consumption of oxygen are done at flow rates just below extinguishment. The last column of the table lists the decimal fraction of flow used for the test compared to that required for extinguishment. Figure 1 represents the extinguishment and test flows as stacked bar graphs. In terms of extinguishment effectiveness the agents group themselves with Halon 1211, Halon 1301, CF_3I, and HBFC-22B1 requiring approximately 30 ml/min. for extinguishment. Perfluorobutane (C_4F_{10}), perfluorohexane (C_6F_{14}), and C_3F_7I require approximately twice the volumetric flow. The HFCs and HCFCs require three to four times the flow compared to the Halons. HFC-23 (CF_3H) performs only somewhat better than CO_2, but may be important as a propellant for other agents because all of the other candidate agents would be fully miscible in the liquid phase inside the extinguisher or holding tank. Using it as a blending agent to increase and unify discharge pressure may have utility.

Figure 1 - *Agent* Comparison



The cup burner, NFPA 2001, was not used for this study because the high flow rate, 40 liter/min., would excessively dilute the stream of decomposition products. Additionally, the variable sought with the cup burner is the effective concentration of agent in air necessary to extinguish a fire. This is used to calculate the total weight of agent needed to be effective in a total flood or room fire scenario. The results of this test seek an agent to fuel ratio, where air is freely allowed to diffuse around the fire. Since both tests involve agent flow across a fire, it is reasonable that there should be correlation between methods. Where values are available [7], the agents examined with this test are compared to cup burner results, shown in Figure 2.

Figure 2 - Extinguishment Flow vs Cup Burner



The r^2 value of the linear regression line through the data points (correlation coefficient) is .9043. By comparison the r^2 comparing NFPA 2001 inerting concentration to the cup burner is .6871.

ACID GAS PRODUCTION

Initial tests showed that water would be a problem. For the flame alone, it was seen that CO2 production and oxygen consumption closely agreed with the stoichoimetry expected for a methane flame. When the probe was attached to the apparatus, oxygen concentration decreased approximately 3% from 20.5% to 17.5%, while CO2 went from

350 ppm to 15,000 ppm (1.5%).The concentrations returned to baseline as soon as the probe was removed.

This is accurately represented by the equation;

$$CH_4 + 2\ O_2 = C02 + 2\ H_2O$$

Water, however, lagged badly in response and persisted long after the probe was removed. The shift in concentration (Δ) was approximately that expected. Nominal room concentrations of air are 15,000 ppm and the peak concentrations went to about 45,000 ppm. Unlike CO_2 and oxygen, which showed virtually the same result whether the shift in concentration was used or the integral (values summed over the ten minute test' divided by the time the probe was attached), water integrals were larger by a factor of two.

When Halon extinguishing agents were used, a similar effect was seen. During the test and while the probe was attached to the apparatus, HF was not seen. However, HF was measured as the water concentrations returned to baseline. It was experimentally determined the the total amount of HF, measured by summing the values during elution, was directly proportional to the duration the probe was attached to the combustion apparatus. That is, the reported HF for a five minute test was half that for a ten minute test, which in turn was half the amount of a twenty minute test. The peak concentration of HF was approximately the same for different duration tests. A ten minute test was established as the standard since it gave a sufficient number of points to define the elution curve yet kept total test time for baseline, probe attachment, and water elution under one hour. Acid yields are reported as the sum of measured concentration values divided by 10, the test duration.

With other'agents varying effects were seen. Acid gas production and the water ratio, or integral divided by concentration shift, for all of the agents examined are listed in Table 2. Most HFCs showed water increasing when the probe was attached, decreasing somewhat after the probe was removed with acid gases eluting later as the water concentrations returned to baseline. While the peak shape might change significantly from test to test, the integral values were generally +/- 15% relative standard deviation.

HCFCs and perfluorocarbons showed small changes in water concentrations as the probe was attached but increasing concentrations after removal. Water peak to integral ratios were similar to Halons and HFCs.

TABLE 2 - Acid Gas Yields

AGENT	HF (%)	HCl (%)	HBr (%)	Water Ratio
Flame only	0.05	0.001	0	2.52
Halon 1301	0.19	0.014	0	1.57
HBFC-22B1	0.5	0	0.02	1.71
Halon 1211	0.29	0.b46	0	1.98
Halon 13001	0.49	0.002	0	2.50
Halon 37001	1.14	0.062	0.001	1.00
Perfluorobutane	2.51	0.027	0.011	1.93
Perfluorohexane	6.15	0.016	0.017	2.23
HFC-227ea	0.59	0.005	0	3.36
HFC-125	1.95	0.038	0.001	1.97
HCFC-124	2.66	0.072	0	1.18
HCFC-123	3.57	0.632	0.002	2.63
Perfluoropentane	5.47	0.027	0.004	1.01
HFC-23	16	0.001	0.004	3.82
Carbon Dioxide	0.05	0.002	0	1.80

HFC-23 (CF_3H) reduced the ambient concentration of water to less than half the baseline (dehydration), with high water and HF concentrations persisting long after the probe was removed. HF concentrations were very high, around 160,000 ppm, greatly exceeding the expected stoichiometry. The flow rate of agent, 523 ml/min, is about 10% in excess of a one to one ratio with methane. C02 production is approximately 3%, water concentration shift is 1.5%. This implies the likely reaction is;

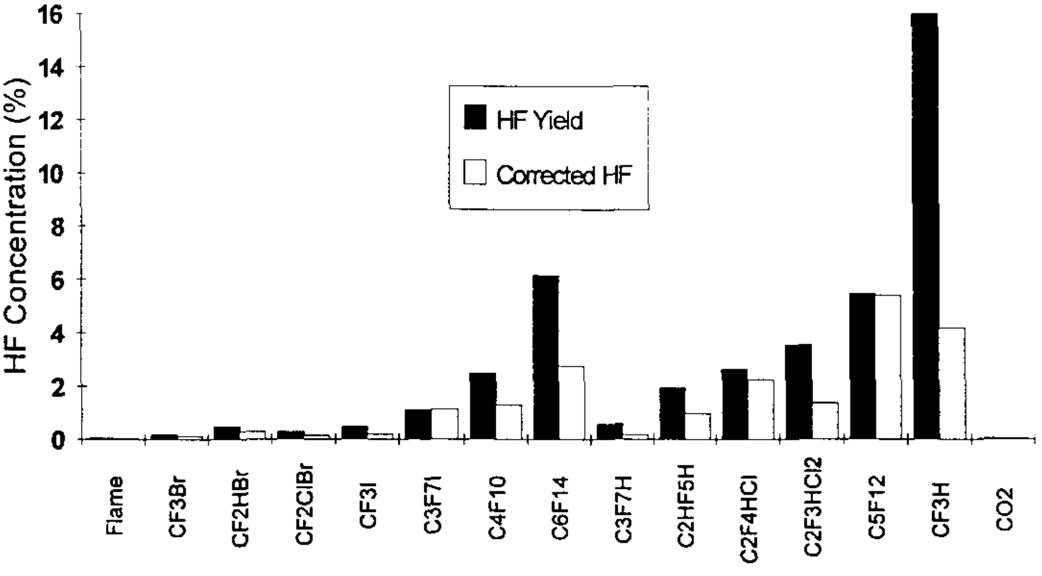
$$CH_4 + CHF_3 + \frac{5}{2} O_2 \text{ -> } 2CO_2 + 3\ HF + H_2O$$

The water integral is much larger, having a ratio of 3.82, or nearly twice that of other agents. Assuming that acids 'concentrate to the same extent, dividing by that ratio should be the correct yeild. In fact, if each HF concentration is divided by the water ratio, the mean HF yeild is 4.5%. This is exactly what is expected assuming the above reaction is taking place. This implies the method of extinguishment is that fluorine acts as a scavenger for the reactive hydrogen and hydroxyl free radicals formed during combustion. When the fluorine concentration is sufficient to grab three of the hydrogens on methane, the reaction releases insufficient energy for propagation, and extinguishment occurs.

HCFC-124, perfluoropentane (C_5F_{12}), and Halon 37001 (C_3F_7I) show little to no change in water concentration from ambient, with perfluoropentane showing a small dip when the probe is attached and a small rise above ambient when it is removed. C_3F_7I showed apparent shifts in ambient concentration and no definite trend, so the water ratio was set to one.

The HF yields, produced at an agent flow just below extinguishment, are shown below. Values which are corrected for water ratio are compared in Figure 3.

Figure 3 - Hydrogen Fluoride Yields



Interestingly, a similar phenomena seems to occur with C02 as the extinguishing agent Oxygen consumption is approximately 3%, as is the case with the flame alone. Water concentration shift is similarly 3%. As C02 concentration exceeds 3%, extinguishment occurs. This implies the reaction is:

$$CH_4 + 2\ O_2 + CO2 \rightarrow 2\ H_2CO_3$$

H_2CO_3, carbonic acid, is a weak acid formed by the interaction of carbon dioxide and water. It is commonly known as seltzer. Extinguishment is probably due to the interaction of unpaired electrons on CO_2 with the reactive hydroxyl radicals.

OTHER DECOMPOSITION PRODUCTS

ICAMS is used in investigative scan mode to determine other possible decomposition products. Investigative scan mode looks 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 will not attempt to quantify these decomposition products but will examine for m/z particles (ions) that are not due to the pure agent spectra or air gases. Since the hot exhaust is delivered into the spectrometer literally seconds after the combustion process, it is entirely possible to have 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 is to run an investigative scan 5 minutes into a test, at the rate of agent flow used for the normal 10 minute test. The scan for all masses takes approximately 2 minutes. These spectra are compared to calibration spectra for neat agent in air. Peaks that are present during the test run which are absent in the spectra of agent alone are noted. Where a peak overlaps the agent alone spectra, the base peak for the agent tested in the decomposition spectra is multiplied by the relative abundance fraction. If the difference is more than 20%, that peak is also noted. In this way the background for unreacted agent is subtracted. All agents but HCFC-124 were tested in this manner.

One species examined for was COF_2, or carbonyl fluoride, due to its high toxicity. This compound has a base peak at 47 and a strong peak 55% of base at 66. This possible decomposition product was noted in the spectra for HFC-23, perfluorobutane perfluoropentane, and perfluorohexane. These peaks were also seen for Halon 1211 and C_3F_7I, although 66 was twice the abundance of 47. 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 63, with a large peak about 33% of base at 65, and small peaks at 98 and 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 fluorines per bromine respectively for Halon 1211 and Halon 1301. Examination of the spectra for Halon 1211, Halon 1301, and HBFC-22B1 show 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 is quite likely that bromomethane and dibromomethane are produced. This implies that a possible mechanism in the extinguishment of the flame is the combination of bromine with methyl radicals produced by the combustion of methane, similar to the way fluorine combines with active hydrogens. This may explain the superior fire fighting performance of the Halons, and also the low measured concentration of HBr.

CF_3I seems 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. These would seem to be due to CH_3I, iodomethane, which implies that the agent reacts with a methyl radical, giving up an iodine.

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