RELATIVE EXTINGUISHMENT EFFECTIVENESS AND AGENT DECOMPOSITION PRODUCTS OF HALON ALTERNATIVE AGENTS

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ABSTRACT

Halon replacement candidates for the aircraft industry must be clean and effective extinguishing agents. Hand-held Halon 1211 extinguishers are required in transport category passenger compartments with a capacity of 31 or more passengers. Halon is used because of its effectiveness and low toxic gas hazard. Any replacement agent must demonstrate similar characteristics.

A simple apparatus was constructed to evaluate the effectiveness of Halon 1211, Halon 1301, CO_2 and several Halon replacement candidates. The agent is introduced into a standard 250 W (watt) methane flame until flame extinguishment. The flow of agent is then measured. Subsequently, agent is introduced into the small flame at a flow just below extinguishment to form a steady-state condition. The effluent gases from the flame are then measured with a magnetic sector mass spectrometer with analysis conducted for oxygen, carbon dioxide, water, hydrogen fluoride, hydrogen chloride, hydrogen bromide, and unreacted agent. Agents are then directly compared for effective volumetric flow to extinguish the standard flame. Agent weight equivalence and gas yields at extinguishment are then calculated.

BACKGROUND

The FAA has required Halon 1211 hand-held extinguishers in passenger category aircraft since 1986.[1] This regulation was an outgrowth of full-scale test results simulating a large in-flight seat fire to evaluate the effectiveness of hand held extinguishers, largely in response to the threat of a terrorist with combustible fluids. Halon 1211 was found to give superior performance, with acid gas and halon concentrations below harmful levels, while extinguishing gasoline ignited seat fires. Hazards associated with uncontrolled seat fires quickly exceeded transient hazards associated with Halon 1211 extinguishment.[2]

On March 17, 1991, a fire developed on Delta Airlines Flight 15, a Lockheed L-1011-385-3 on route from Frankfurt, Germany to Atlanta, Georgia. A flight attendant reported a fire on the left side of the aircraft towards the end 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 very effectively using three Halon 1211 extinguishers directed towards the source of the fire through return air vents located along the floor. The aircraft was diverted and made a safe landing at Goose Bay, Labrador, with no injuries to the 13 crew or 213 passengers.[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 fire scenario. Regulations state only that the hand-held extinguisher "must contain Halon 1211 (bromochloro - difluoromethane) or equivalent", and that it "must be designed to minimize the hazard of toxic gas concentration."

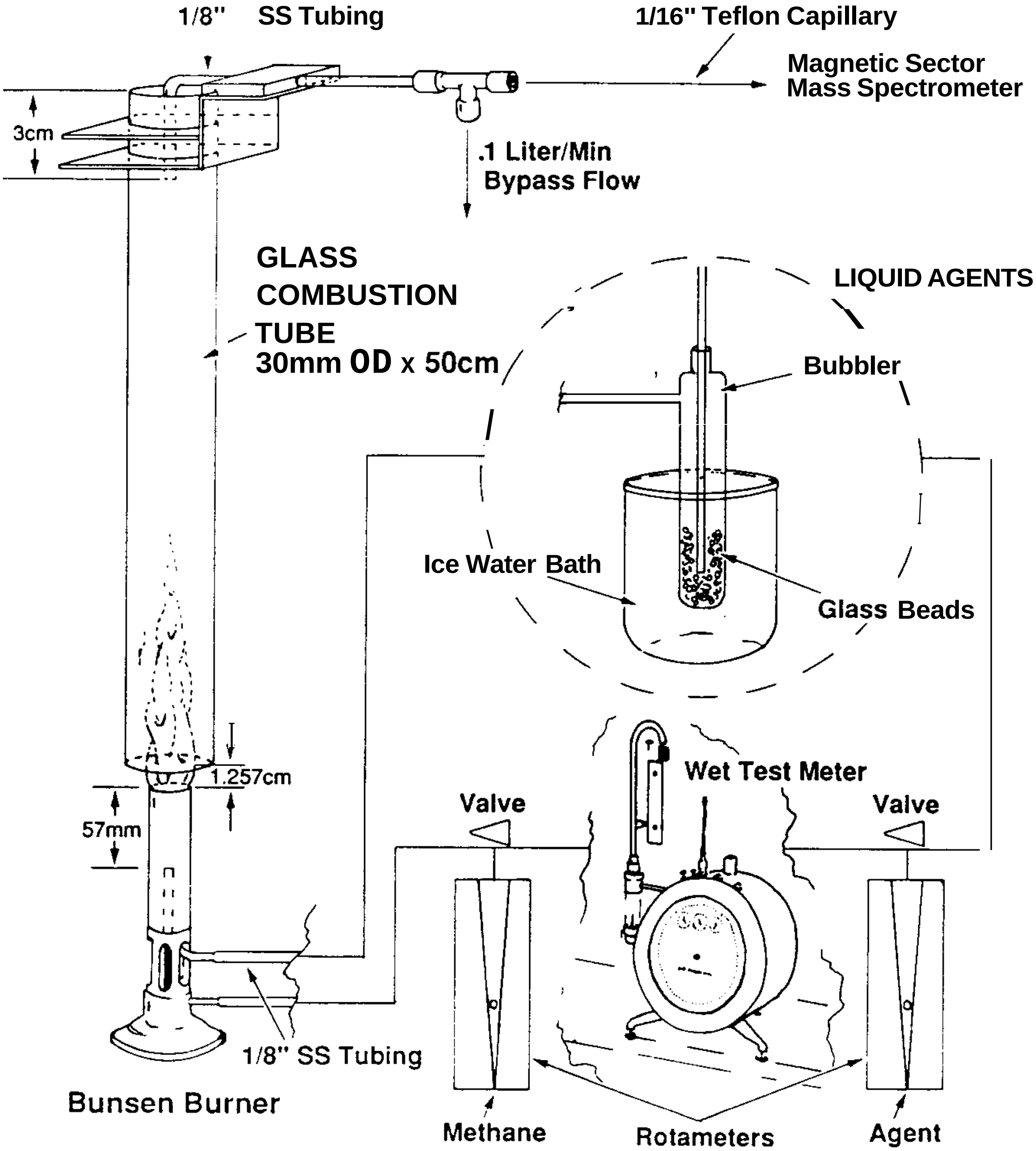
EXPERIMENTAL PROCEDURE

The criteria for a test to evaluate Halon and Halon substitute effectiveness and decomposition product generation should be simple, repeatable, and quantitative. The cup burner was not used because the concentration in air to cause extinguishment was not sought, as might be the case for calculating the amount of agent required to extinguish a room fire. Here the variable sought is volumetric flow of agent to extinguish a standardize fire, modeling the case of an extinguisher discharge at the base of a fire with excess air present. The standard fire was chosen to be a 250 W methane flame, as produced by a natural gas (.067 in. orifice) bunsen burner with flame retainer removed and the air inlets fully opened. UHP methane flow is calibrated using a Matheson rotameter to adjust delivery volume to a Precision Wet-Test Gas Meter. Net heat of combustion is 188.8 kW/mole and, after volume correction to STP, the nominal methane flow is .475 l/min. This produces a blue flame approximately 3 inches long. Extinguishing agent is delivered to the base of the flame with a 1/8 stainless steel tube bent into an L that enters the burner through the air inlet near the base. The tube is centered in the barrel of the Bunsen burner, 2 1/4 in. (57 mm) below the outlet. The effluent gases are contained by a combustion tube, 26 mm i.d. by 500 mm long, that is centered 12.57 mm above the outlet. Thus, the flame is almost completely contained within the combustion tube chimney with excess air freely diffusing around it. A 1/8 in. stainless steel tube is centered in the chimney 30 mm below the exit, and held in position by an aluminum sample probe assembly. Total flow through the probe is 100 ml/min as measured with a rotameter that has a vacuum pump connected to the outlet. The sample is analyzed using a Perkin-Elmer ICAMS (Industrial Central Air Monitoring System), a Magnetic Sector Mass Spectrometer (MSMS). Approximately 10 ml/min is drawn into the analyzer through a 1/16 in. Teflon TEF capillary. The Teflon capillary passes through a stainless steel tee, which is connected to the vacuum pump, into the sample probe where it is joined to the to the assembly. The assembly acts as a heat sink to prevent the Teflon from melting and to eliminate dead volume by drawing excess sample. A schematic drawing is shown in Figure 1.

A Magnetic Sector Mass Spectrometer analyses the sample by continuously drawing a tiny amount through the sample inlet into the device. A high energy electron beam fragments the molecules into ions which are accelerated and focused into a magnetic field. The radius of the path of the ions in the magnetic field is dependent on the mass to charge ratio of the particles. By varying the strength of the magnetic field, the various ions are

FIGURE 1

AGENT DECOMPOSITION PRODUCT GENERATOR



directed to a collector and measured. Analysis is conducted for m/e 28 (N_2), 32 and 33 (O_2), 18 (H_2O), 40 (Ar), 45 (CO_2), 19 (HF), 36 (HCl), 80 and 82 (HBr), and other ions appropriate for the spectrum of the Halons and Halon alternative agents. The system is configured for three agents using the base peak and two other peaks which are at least 10% of base and differentiate as much as possible between agents. A sophisticated program does the solution to the linear algebraic equations to determine the concentration of the individual sample components. Analysis time to scan for all of the ions is approximately 27 seconds.

Each agent is evaluated by slowly adding agent into the methane flame until the flame is extinguished and noting the flow on the rotameter. This is repeated several times until a consistent reading is obtained. The valve is then switched directing the agent flow to the wet test meter. A stopwatch is used to time a set volume. The volumetric flow is measured three times and the values averaged. The flame is then lit and agent metered into the flame at a rate just below that required for extinguishment. The analysis is started to determine a baseline and the probe assembly is then manually attached. Test duration is ten minutes, as timed with a stopwatch, at which point the probe is manually removed. The analysis is continued until the baseline condition is reestablished.

A somewhat different procedure is used for agents that are liquids at room temperature. An open tipped bubbler with nominal volume of 250 ml is adapted with Teflon Swagelok fittings and is inserted between the rotameter and the discharge tube into the Bunsen burner. The bubbler is filled with 3 mm glass beads about 30 mm above the dip tube and with agent about 50 mm above the beads. The bubbler is immersed into a Dewar flask filled with an ice and water mixture. Air is then metered into the bubbler by the rotameter, so a mixture of agent and air is discharged into the Bunsen burner. As before, the flow rate is increased slowly until extinguishment is reached. The wet test meter is used to measure the air flow going into the bubbler and the total flow of agent vapor and air leaving the bubbler. The difference in the two flows is the agent flow rate for extinguishment. The purpose of the beads and the ice/water bath is to make the concentration of agent vapor in air constant yet below the level where condensation will occur in the line between the bubbler and discharge into the flame. Therefore, the flame is extinguished by gaseous agent even when the agents are liquids at room temperature. This is shown in the inset of Figure 1.

RESULTS AND DISCUSSION

Agents evaluated by the above protocol are Halon 1211 (CF_2ClBr), Halon 1301 (CF_3Br), perfluorobutane (C_4F_{10}), HCF-23 (CHF_3), HBFC-22B1 (CF_2HBr) which are gases, and HCFC-123 (CF_3CHCl_2) and perfluorohexane (C_6F_{14}) which are liquids.

Table 1 shows the extinguishment flow rate expressed as ml/min gaseous agent, the flow rate during the analytical test, the decimal fraction of the test rate to extinguishment rate, and the flow rate in grams/min to extinguish the flame. Flow rate in grams/min during the analytical test can be calculated by multiplying the fraction times the mass flow at extinguishment.

TABLE 1 - EXTINGUISHMENT POTENTIAL

HALOCARBON NUMBER	FORMULA	EXTINGUISHMENT FLOW RATE (ml gas/min)	FLOW AT TEST (ml/min)	FRACTION	MASSFLOW (g/min)
GASEOUS AGENTS					
HALON 1211	CF_2ClBr	32.9	23.4	.71	.218
HALON 1301	CF_3Br	25.7	21.0	.81	.153
HBFC-22B1	CF_2HBr	28.7	19.5	.68	.151
HFC-23	CF_3H	523.	426.	.82	1.461
FC-3-1-10	C_4F_{10}	69.5	61.3	.88	.662
CARBON DIOXIDE	CO_2	736.	635.	.86	1.297
LIQUID AGENTS					
HCFC-123	CF_3CHCl_2	130.	92.8	.71	.796
FC-5-1-14	C_6F_{14}	71.5	60.4	.84	.968

There is some variability in the fraction of extinguishment flow rate used in the decomposition study because the flame must remain lit during analysis and the visible effects of different agents on the methane flame vary greatly. For example, HCFC-123 develops an intensely yellow and sooty flame which gradually diminishes as extinguishment is approached. HBFC-22B1 becomes only slightly yellow and remains virtually unchanged until it simply goes out. Perfluorohexane causes the flame to flicker and soot, while HFC-23 burns bright yellow and constant with no flickering.

Early into the experiments it was seen that, due to the high concentration of water in the exhaust, condensation in the line leading to the ICAMS would be a problem. Based on the stoichiometry of methane combustion, $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$, oxygen and carbon dioxide responded immediately and in proper proportion during probe attachment. However, water lagged badly in response and persisted after the probe was removed from the flame (Figure 2). It was seen however, that the height of the water peak approximated that expected from the stoichiometry and that the duration of the peak was proportional to the length of time the probe was attached to the combustion device. Not surprisingly, the acid gases, HF, HCl, and HBr, are retained in the water. The effect is that as the water peak begins to return to baseline, the acids elute as a peaks in the order HF, then HCl, then HBr, with some overlap (Figure 3). The yield of the acid gases is calculated by taking the concentration obtained every minute, summing the values during the course of elution, and dividing by the test duration, ten minutes. It was found experimentally that the yield of acid gases was independent of the time of the test. That is, although the peak concentration of the acid gas was approximately the same between tests of different duration, the integral of the acid gas peak was half as much for a five minute test, and double for a twenty minute test, but correction for the test duration gave the same yield. A ten minute test was selected as it was seen to give several points at

FIGURE 2

HALON 1211

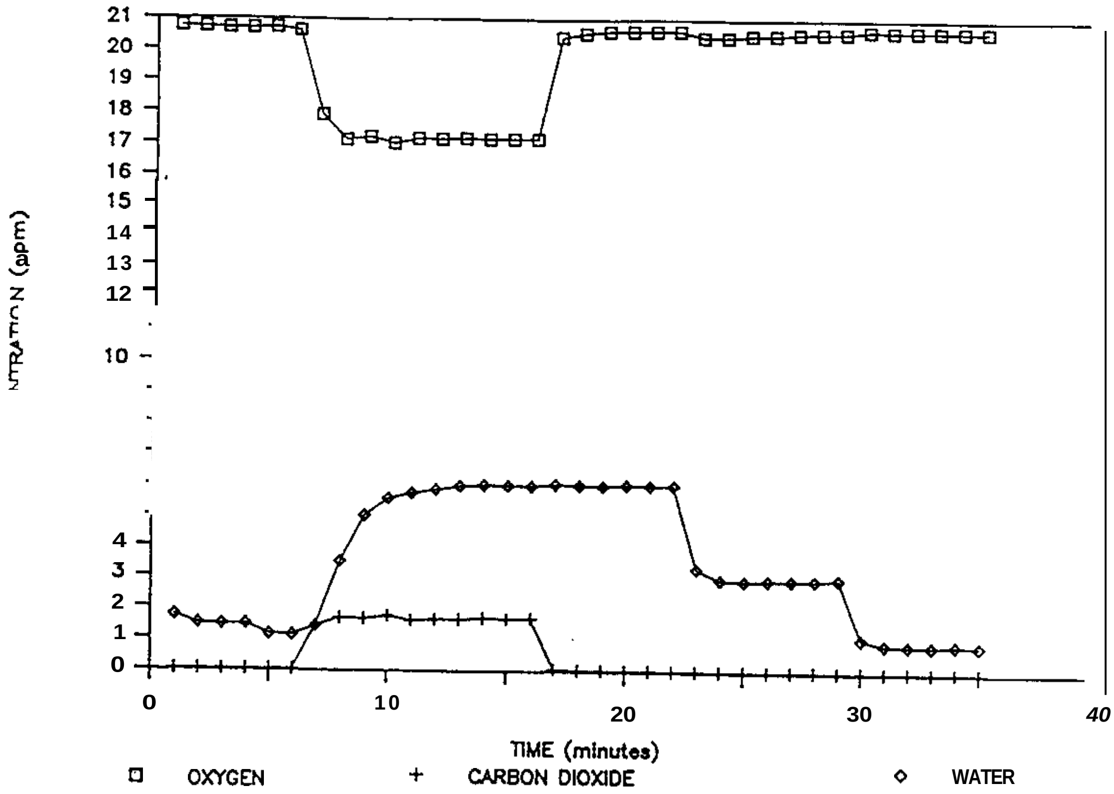
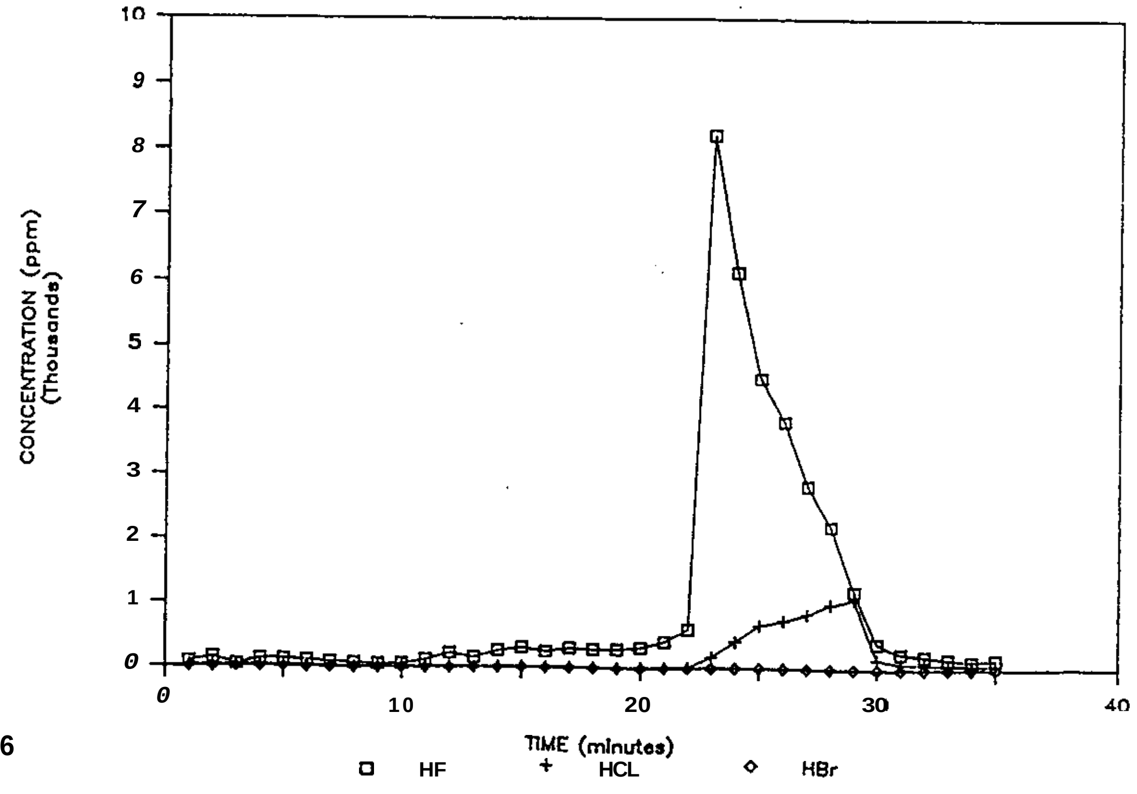


FIGURE 3

HALON 1211



the plateau and acceptable reproducibility between tests, yet result in a total test time under one hour.

Analytical results are presented in Table 2. Data can be presented in two ways: measuring the change in concentration from baseline or taking the area under the curve. For a perfect step change from baseline to test and back again, the results would be identical. In Table 2, oxygen, carbon dioxide, and water are presented as the change in concentration from baseline during the test. The integral under the curve for the ten minute test and the concentration step change during test are in general agreement with each other for oxygen and carbon dioxide, being about 10% larger for oxygen and +/- 5% for carbon dioxide. Average percent relative standard deviation between tests for the same agent is 8% for oxygen, 6% for carbon dioxide, and 14% for water. The integral under the curve for water was consistently much higher, generally about twice as large but in the instance of HFC-23 a factor of 3.8 times as much. Acid gases are presented as the integral under the curve in Table 2.

TABLE 2 - ANALYTICAL RESULTS

HALOCARBON NUMBER	O_2 (%)	CO_2 (%)	H_2O (%)	HF (%)	HCl (%)	HBr (%)
FLAME ONLY	-3.34	1.53	3.54	.046	.001	.0000
CO_2	-3.38	3.45	3.61	.038	.002	.0000
HALON 1301	-3.10	1.40	4.23	.225	.020	.0000
HALON 1211	-3.00	1.42	3.88	.289	.046	.0001
HBFC-22B1	-3.29	1.51	3.84	.504	.000	.0302
HFC-23	-5.65	2.90	1.45	16.00	.001	.0035
HCFC-123	-4.22	2.33	1.09	3.57	.632	.0015
FC-3-1-10	-2.71	1.42	1.86	2.51	.015	.016
FC-5-1-14	-5.29	3.24	1.51	6.15	.016	.023

Not shown in the table is that agent itself is almost completely consumed in the fire. Only trace quantities, between 10 to 100 ppm, were seen during the test, although a momentary flame out would show a sudden peak of several hundred or thousand ppm for that single sample. The only exception was HFC-23 which was seen at several hundred ppm, but flow rates of the agent were approaching that of the methane fuel itself.

The data show several interesting points. Notice that acid gas decomposition products are not in stoichiometric proportion to the halogen atoms on the agent molecule. Hydrogen fluoride is the dominant gas produced. Clearly fluorine is competing with oxygen for the consumption of active hydrogen in the reaction. Hydrogen bromide is seen in only small concentrations. The fate of the bromine is not clear, but it does not appear as unreacted agent or as the acid gas. Of some interest is that HCl is seen as a product from Halon 1301, since chlorine is not part of the molecule. Actually, the mass spectrometer is looking for m/e particles of mass 36, not specifically HCl. It is possible that what is actually present is H-O-F, which although it is not a stable compound may be present since both H_2O and F_2O exist. HF yields are quite high for many of the agents, so there may be a concentration process similar to what is seen where water integrals exceed the predicted step change.

The profiles of CO_2, H_2O, and O_2 show that carbon dioxide extinguishes the flame as CO_2 concentrations approach the same stoichiometric proportion as water production and oxygen consumption. The two Halons and perfluorobutane show a reduction of C02 production and oxygen consumption as the flame is extinguished. It seems that methane is having the hydrogens stripped from it by either fluorine or oxygen, and the carbon is left as a solid (soot). Other extinguishing agents show increased CO_2 and decreased O_2, implying that they are, in fact, flammable to an extent.

BIBLIOGRAPHY

1. Code of Federal Regulations, 14 CFR 25.851.

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