Evaluation of Alternative Agents for Halon 1301 in Total Flooding Fire Suppression Systems

– Thermal Decomposition Product Testing –

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Introduction

Halon 1301 has been the agent of choice for the protection of sensitive equipment or in other situations where the collateral damage caused by the use of deluge sprinkler systems is intolerable. The link of Halon 1301 to stratospheric ozone depletion [1-3] has launched an intensive search for alternative agents.

An alternative agent candidate would have to retain many of the performance features of Halon 1301 in order to successfully fill the same niche. These features include nontoxicity, relatively low effective concentrations, nonresidue forming, and low production of toxic thermal decomposition products.

With the exception of thermally inert agents like carbon dioxide and nitrogen, fire suppression agents decompose as a result of exposure to the fire. For most of the proposed alternatives, the primary decomposition products are hydrofluoric acid, HF, and carbonyl fluoride, COF_2.

Two series of tests are being conducted in order to quantify the production of HF and COF_2 in total flooding fire protection systems in terms of discharge times, fire sizes, and enclosure volumes. This work is part of an evaluation of proposed alternative agents sponsored by the National Aeronautics and Space Administration.

Proposed Alternative Agents

Five proposed alternative agents were included in this investigation. They were trifluoromethane, CHF_3 (FE-13), pentafluoroethane, C_2HF_5 (FE-25), heptafluoropropane, C_3HF_7 (FM-200), perfluoropropane, C_3F_8 (PFC 38), and perfluorobutane, C_4F_{10} (PFC 410). FE-13 and FE-25 were proposed by E.I. du Pont de Nemours and Company. FE-25 has been restricted to unoccupied applications by du Pont due to cardiac sensitization concerns. FM-200 was proposed by Great Lakes Chemical Corporation. Both PFC 38 and PFC **410** were proposed by 3M Corporation. Selected physical and chemical properties of these alternatives are given in Table **1** [4-7].

Extinguishing concentration determined for each of these proposed agents are given in Table 1 [8]. With the exception of PFC 38, these concentrations were obtained from the Naval Research Laboratory as determined using their cup burner with n-heptane. **The** concentration for PFC 38 was determined by ratio with PFC 410 using concentrations determined by **3M** Corporation.

Test **Apparatus**

Two enclosures have been utilized in thermal decomposition testing to date. The majority of these tests have been conducted in a 1.2 m^3 (**41.8** ft^3) enclosure constructed from 1.2-cm (0.5-in.) thick polycarbonate sheet reinforced with an angle iron frame. Access to the enclosure was gained by four 23 cm (9 in.) square openings that were sealed during testing with an overlapping polycarbonate panel. **Air** flow through the enclosure was accomplished by means of a 280 L/min (10 cfm) blower and controlled by two **3.8** cm (1.5 in.) normally open solenoid valves.

The agent was discharged from a stainless steel cylinder with an internal volume of 0.5, 1.0, or 2.25 L (0.018, 0.035, or 0.079 ft^3) depending on which proposed agent or Halon 1301 was used (0.5 L cylinder for Halon 1301, 2.25 L cylinder for FE-13, and 1.0 L cylinder for the remaining agents). Discharge was actuated with a quarter-turn ball valve

Table 1

	Halon 1301	Perfluorobutane	FM-200
Chemical Formula	$CBrF_3$	C_4F_{10}	C_3HF_7
Molecular Weight	149	238	170.03
Normal Boiling Point	−57.8°C	−2.2°C	−16.4°C
Vapor Pressure, MPa	1.47 at 21°C	0.330 at 32°C	0.405 at 21°C
Critical Temperature	67°C	113.2°C	101.7°C
Critical Pressure	3.97 MPa	2.32 MPa	2.91 MPa
Vapor Density, kg/m^3	6.26 at 21°C and 0.101 MPa	9.94 at 25°C and 0.101 MPa	7.26 at 21°C and 0.101 MPa
Liquid Density, kg/m^3	1567 at 21°C	1517 at 20°C	1403 at 21°C
% Volume Extinguishment (n-Heptane)			
NRL Cup Burner	3.1	5.2	6.6
With 20% Safety	3.7	6.2	7.9

	FE-13	FE-25	Perfluoropropane
Chemical Formula	CHF_3	CF_3CHF_2	C_3F_8
Molecular Weight	70.01	120.02	188.02
Normal Boiling Point	−82.0°C	−48.5°C	−36.7°C
Vapor Pressure, MPa	4.59 at 25°C	1.31 at 25°C	0.79 at 21°C
Critical Temperature	25.9°C	66.3°C	71.9°C
Critical Pressure	4.83 MPa	3.59 MPa	2.68 MPa
Vapor Density, kg/m^3	2.93 at 21°C and 0.101 MPa	4.97 at 21°C and 0.101 MPa	8.01 at 21°C and 0.101 MPa
Liquid Density, kg/m^3	670 at 25°C	1249 at 25°C	1352 at 20°C
% Volume Extinguishment (n-Heptane)			
NRL Cup Burner	12.0	9.1	6*
With 20% Safety	14.4	10.9	7.2

* Estimated value.

with flow through 0.63 cm (0.25 in.) steel pipe. The agent discharged into the enclosure 0.45 m (1.5 ft) from the top on one side through a Bete 0° NF series nozzle. The flow rate and discharge time were varied by changing the orifice size.

Three square stainless steel pans were used in the small enclosure. They were 5, 7.5, and 10 cm (2, 3, and 4 in.) on a side. These pans correspond to n-heptane fire sues of 0.79, 1.9 and 4.0 kW as determined using a cone calorimeter with the three-minute average heat release rate after ignition used.

The larger enclosure was constructed with two layers of 1.2 cm (0.5 in.) gypsum wallboard over 5 x 10 cm (2 x 4 in.) wood framing. It has three **60** x 90 cm (2 x 3 ft) polycarbonate windows, and access is gained through a steel door with magnetized seals. Air flow in the enclosure was accomplished by means of a 56.6 m^3/min (2000 cfm) blower through 36 x 50 cm (14 x 20 in.) ducts with the **flow** controlled by two sets of 50 cm (20 in.) steel louvers.

In the large enclosure, the agent was discharged from Fike Halon 1301 cylinders with the cylinder actuated by a quarter-turn ball valve. The cylinders had internal volumes of 7, 26, and 42 L (0.25, 0.92, and 1.5 ft^3). The agent flowed through a simple pipe network constructed of 2.5 cm (1 in.) NPT pipe terminating at a Fenwal 360" pendant nozzle model 31-194119. The network included a section of flexible pipe to allow the cylinder weight to be monitored during discharge and a section of polycarbonate tubing to facilitate the visual observation of the flow regime.

Two steel square pans, 25 and 38 cm (10 and 15 in.) on a side, were used in the larger scale **tests.** These correspond to n-heptane fires sizes of 78 and 250 kW **as** estimated **by** then following equation [10]:

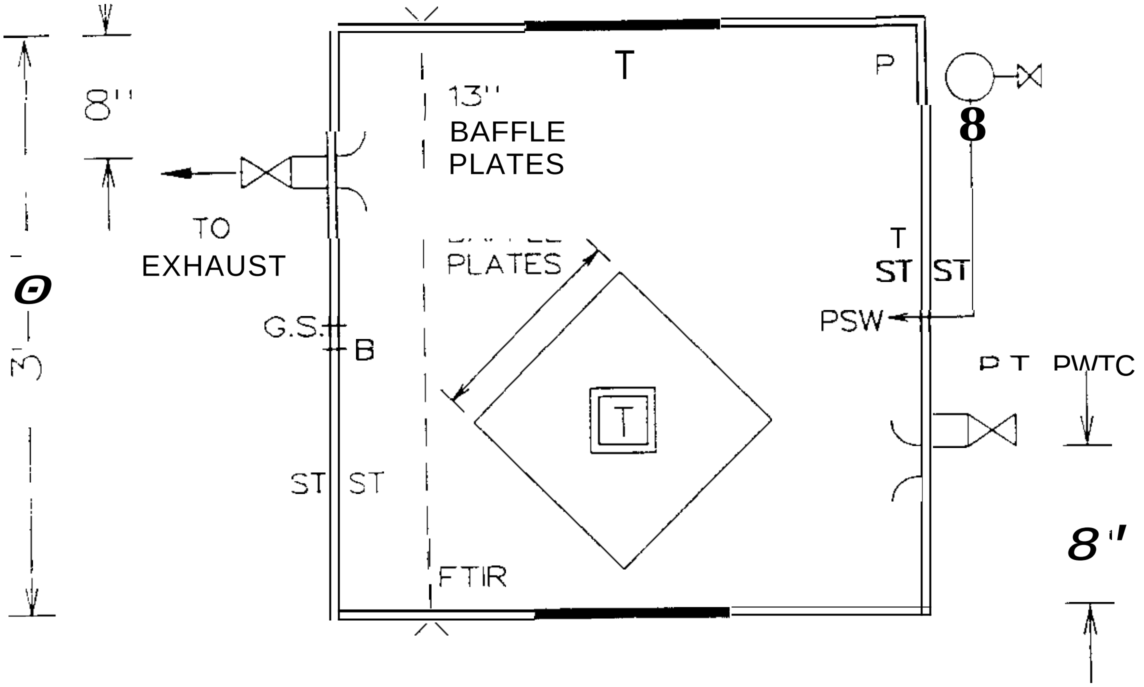
$$Q = mA_f\Delta H_c = A_f\Delta H_c m^{*}(1 - \exp(-kD))$$

where A_f is the pan area in m^2, ΔH_c is the heat of combustion in kJ/kg (44,600 kJ/kg for n-heptane), m is the mass loss rate per unit area in kg/m^2, m^* is the mass burning rate per unit area for an infinite diameter pool (0.101 kg/m^2 for n-heptane), k is the extinction/absorption coefficient for the flame in m^{-1} (1.1 m^{-1} for n-heptane), and D is the diameter of the pool in m which was taken as the diameter of a circle with the same area as the square pan used. When this method was used to estimate the fire sizes in the small box, the fire sizes are overstated for the 7.5 and 10 cm (3 and 4 in.) pans.

Instrumentation

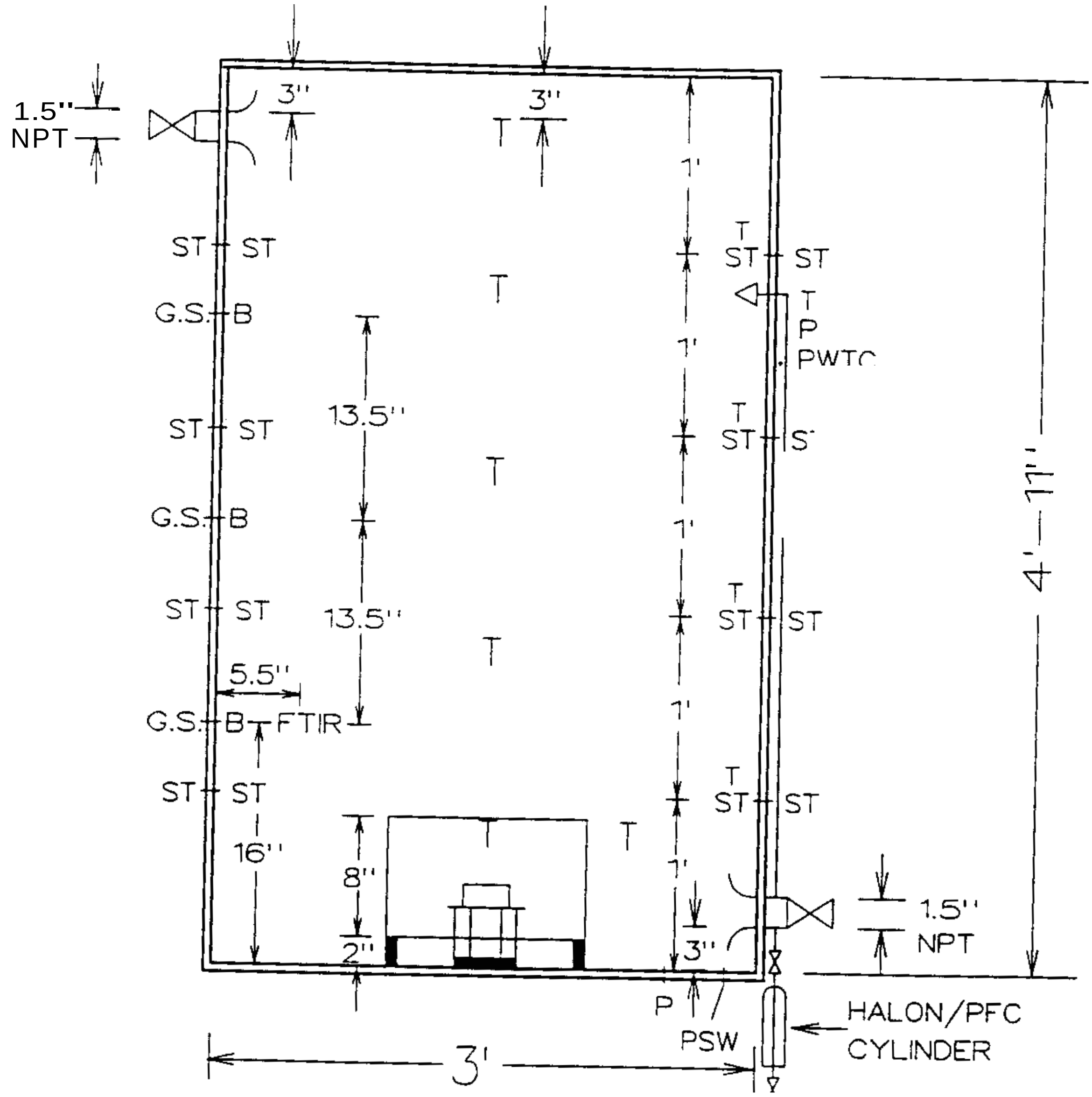
Schematics of the instrumentation for both enclosures can be found in Figures 1 through 4. The temperature in both enclosures were monitored using exposed junction type K thermocouples. In the small enclosures, the temperature in the enclosure was monitored by ten inconel-sheathed exposed junction thermocouples in two vertical trees and by four wafer type k thermocouples. The interior surface of the enclosure was monitored with eight wafer type K thermocouples in two vertical trees, and four wafer type K thermocouples were used to monitor the exterior surface. The pressure inside the enclosure was monitored by an Omega Engineering Model PX 181 pressure transducer with a range of 0-103 kPag (0-15 psig). In the larger enclosure, 23 fiberglass-braided type K thermocouples in three vertical trees were utilized to monitor the enclosure temperature with three more embedded into the gypsum wall. A Lucas-Schaevitz Model P3091 with a range of –4.9 - 4.9 kPag (–0.72 - 0.72 psig) was used to monitor the pressure in the larger enclosure. The exhaust flow from the larger enclosure was monitored with two MKS Baratron Model 223B pressure transducers with a range of –133 - 133 Pag (-0.019 - 0.019 psig) in combination with two exposed junction inconel-sheathed thermocouples.

In both enclosures, the temperature of the flowing agent was monitored by two exposed junction inconel-sheathed thermocouple, and two wafer type K thermocouples were used to monitor the exterior surface temperature of the discharge pipe. Two



T	THERMOCOUPLE	PWTC	PIPE WALL THERMOCOUPLE
ST	SURFACE THERMOCOUPLE	G.S.	GRAB SAMPLE (3M METHOD)
P	PRESSURE TRANSDUCER	B	BUBBLER (GREAT LAKES METHOD)
PSW	PRESSURE SWITCH	FTIR	IR BEAM PATH

Plan View



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PSW	PRESSURE SWITCH		
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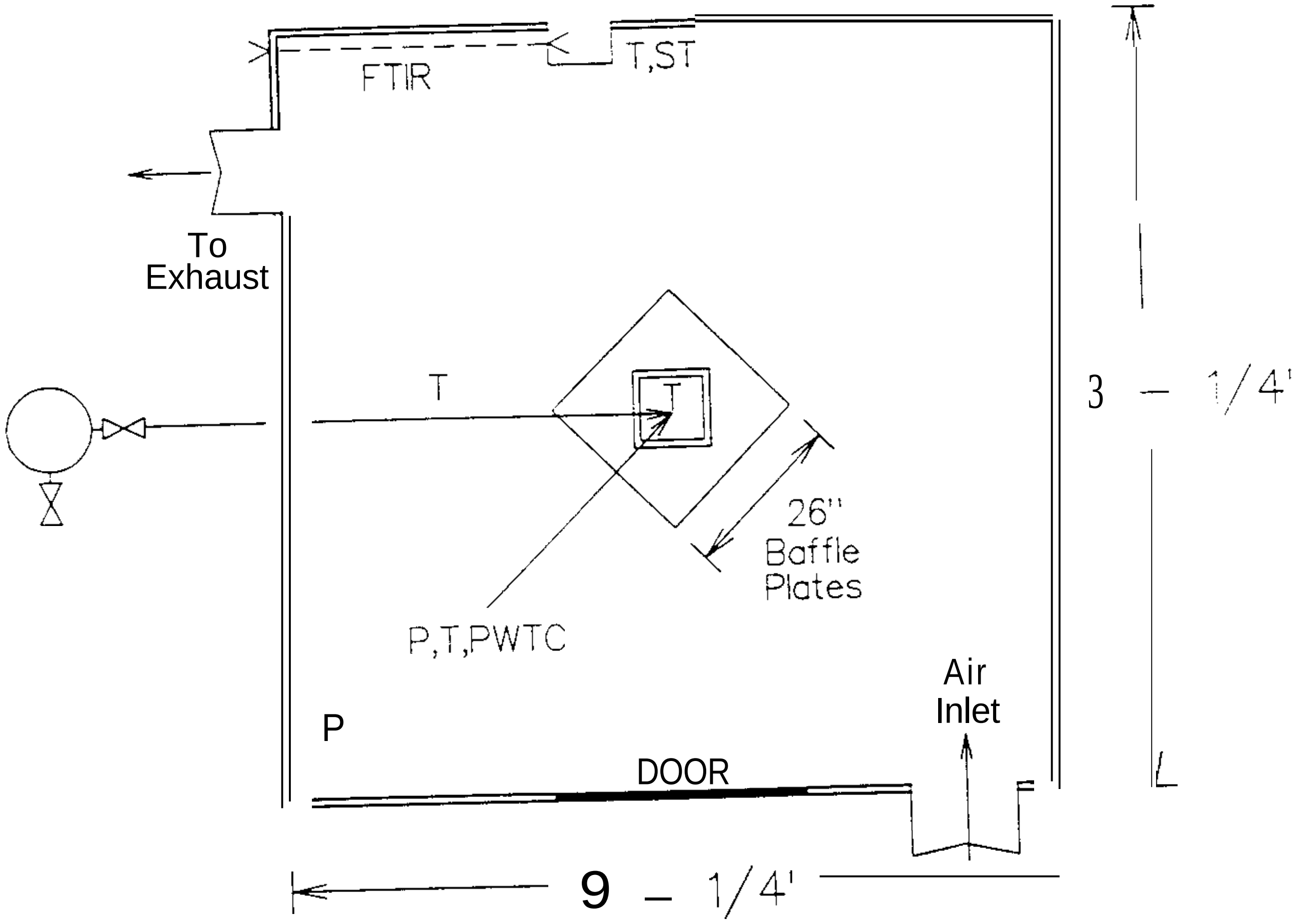
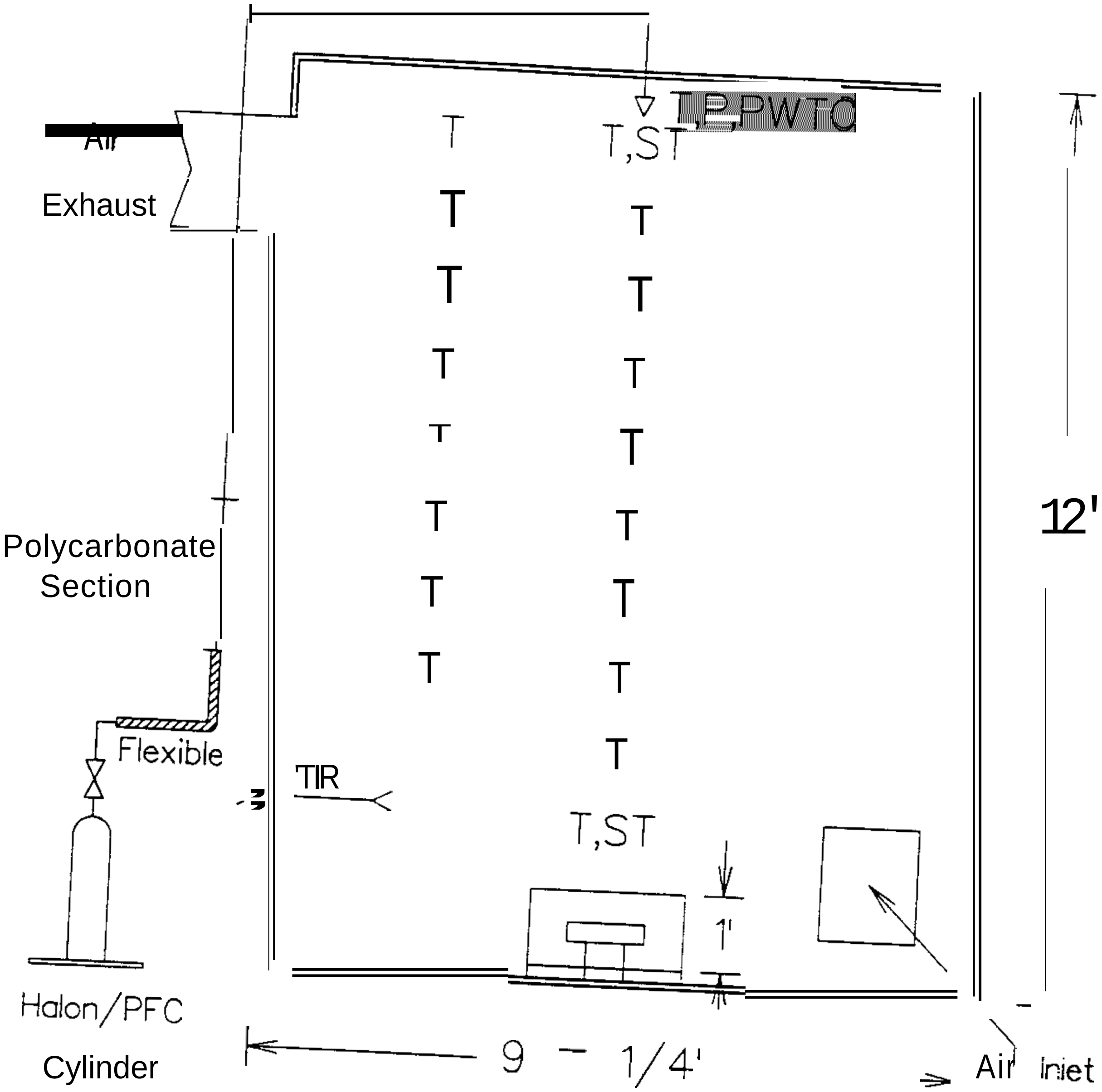
Elevation **View**



Plan View Large Box



Elevation **View** Large **Box**

Transmetric Model **P21AB** vented-gage pressure transducers with a range of 0 - 6.9 MPag (0 - 1000 psig) were used to monitor the pressure of the discharging agent.

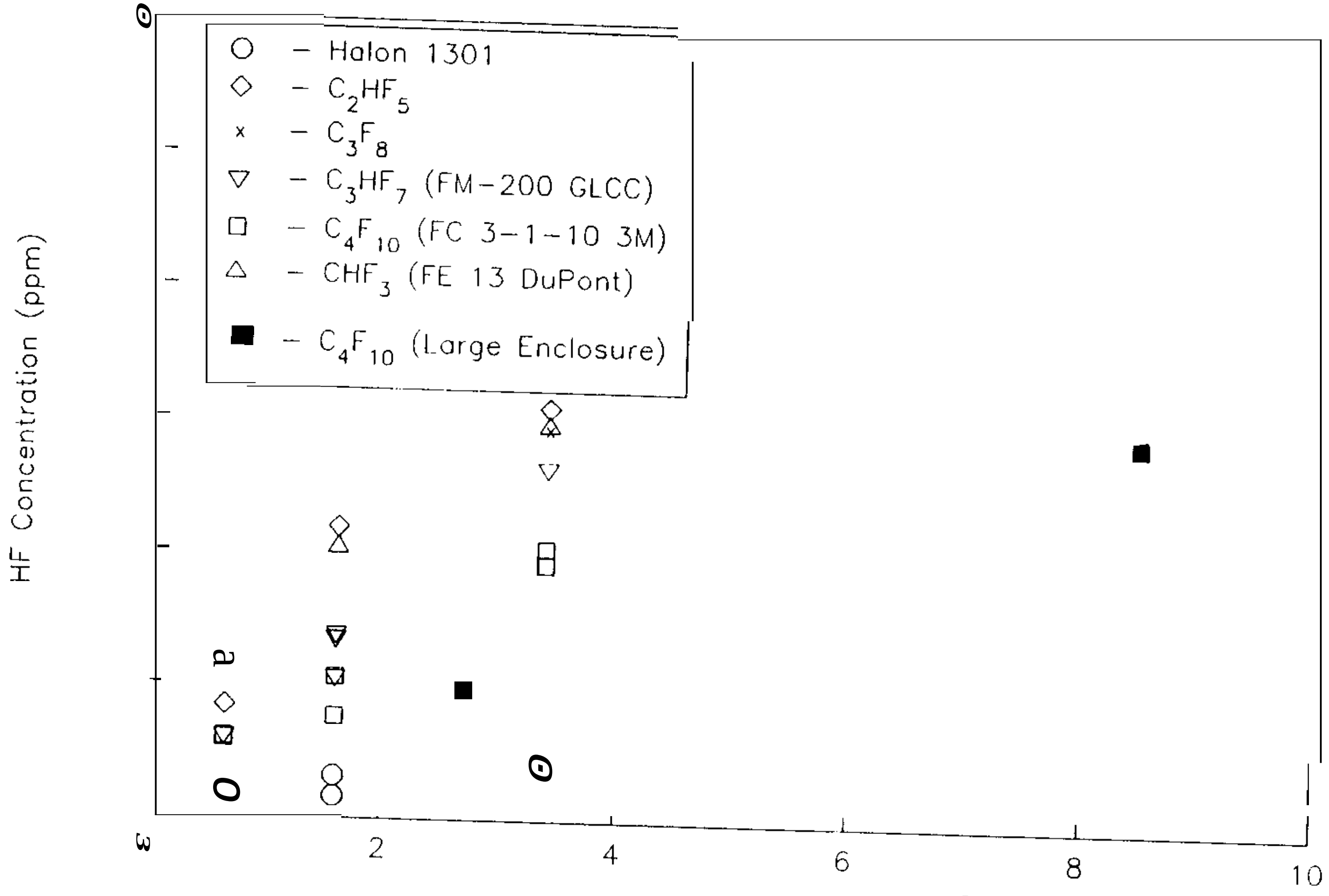
A KVB/Analect Diamond **20** Fourier Transform Infrared Spectrometer (FTIR) was installed with a light pipe system utilizing calcium fluoride (CaF_2) windows to monitor gas concentrations in situ. Two ion specific electrode methods were utilized to measure the hydrogen fluoride concentration in the smaller enclosure. These methods were similar to those used by Great Lakes Chemical Corporation **[6]** and **3M** Corporation [9], and were used primarily to allow for direct comparison with their results. In the large enclosure, a Servomex **540A** paramagnetic oxygen analyzer and a Horiba VIR **510** carbon dioxide analyzer were installed.

Test Procedure

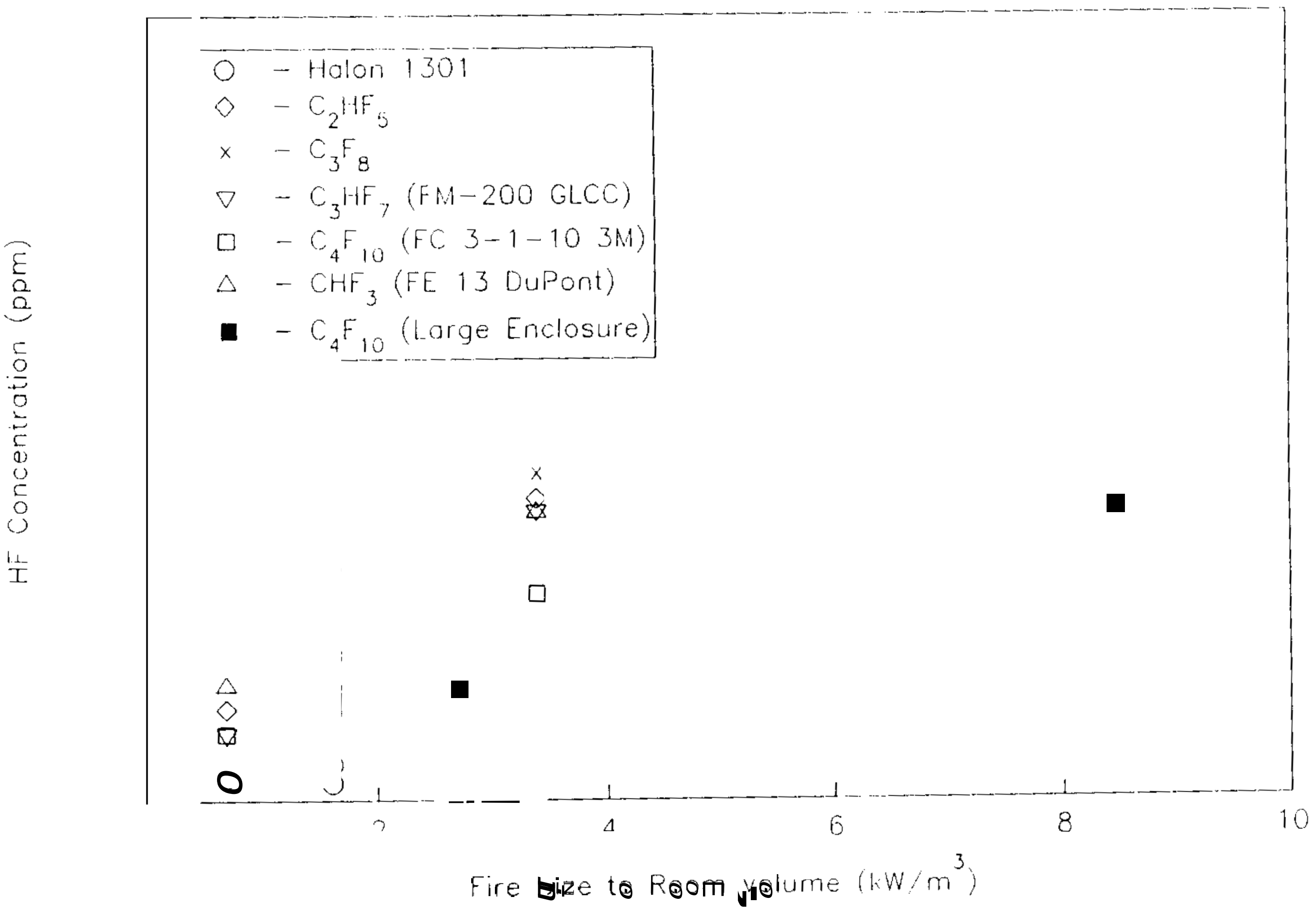
Once the pan was ignited, FTIR data collection was begun, and the fire was allowed to burn for 60 seconds with the blower operating. After this preburn period, the blower was turned off, the enclosure was isolated, and the agent cylinder was discharged. The extinguishment time was recorded by tripping a flag when the fire was observed to be out. In the small box, thirty seconds following the beginning of agent discharge, the bubbler **pump** was started, drawing 0.2 L/min through the bubblers and grab samples were taken. After ten minutes, the bubblers were stopped, and the enclosure was purged. In the larger enclosure, the enclosure was isolated for six minutes instead of ten.

Results **and Discussion**

HF concentrations were determined by comparison with spectra obtained with known concentrations. The HF concentrations implied by the absorbances at wavenumbers **4003, 4041,** and **4077** cm^{-1} were averaged together. Figures 5 and ***6*** show the maximum and time weighted average HF concentration over the time period the enclosure was isolated **as** a function of the fire size normalized by the room volume. The error associated with the estimated fire size could account for the offset of the large



Maximum HF concentration resulting from extinguishing n-heptane fires with a nominal total discharge time of 15 seconds



erage HF concentration resulting from extinguishing n–heptane fires with nominal total discharge time of 15 seconds enclosure data and the small box. HF concentrations determined using the ion specific electrode method developed by 3M Corporation is shown in Figure 7. As can be seen from these figures, the agreement between the 3M method and the FTIR is good.

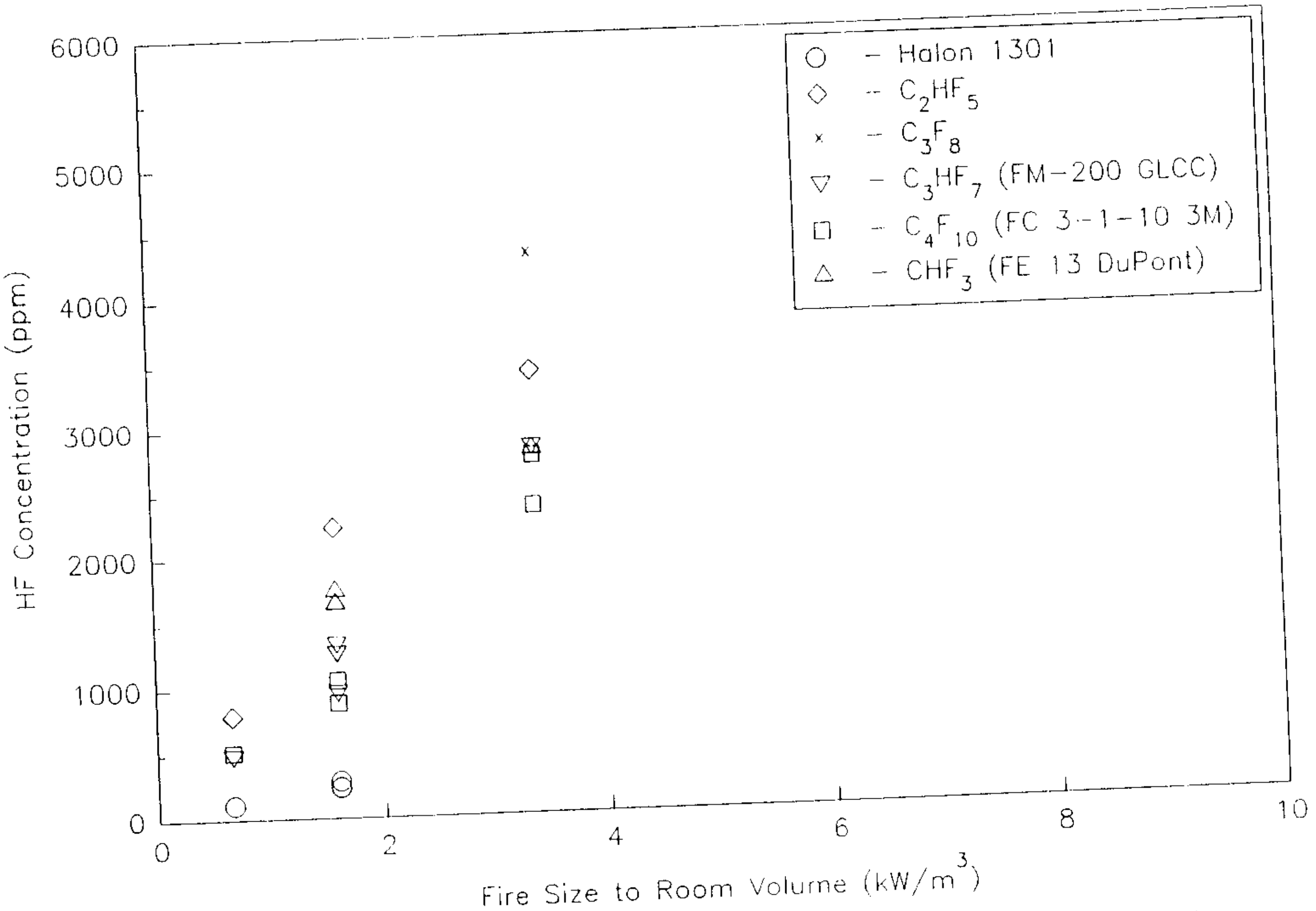
Figures 8 through 10 show the maximum and average HF determined by the FTIR and that determined by the 3M Method as a function of discharge time for the 4 kW fires in the small box.

Figures 11 through 14 show the maximum and average absorbance due to carbonyl fluoride (COF_2) at 1931 cm^{-1} as a function of the fire size to room volume ratio and as a function of the total discharge time. These figures imply the same type of relationships for COF_2 as was shown for HF. However, there appears to be a greater ratio of COF_2 formed to HF formed in the large enclosure than in the small enclosure. This increase could well be due to nonlinearity in the absorbance to concentration conversion. No quantification of these COF, results has been done due to a lack of sufficient calibration spectra.

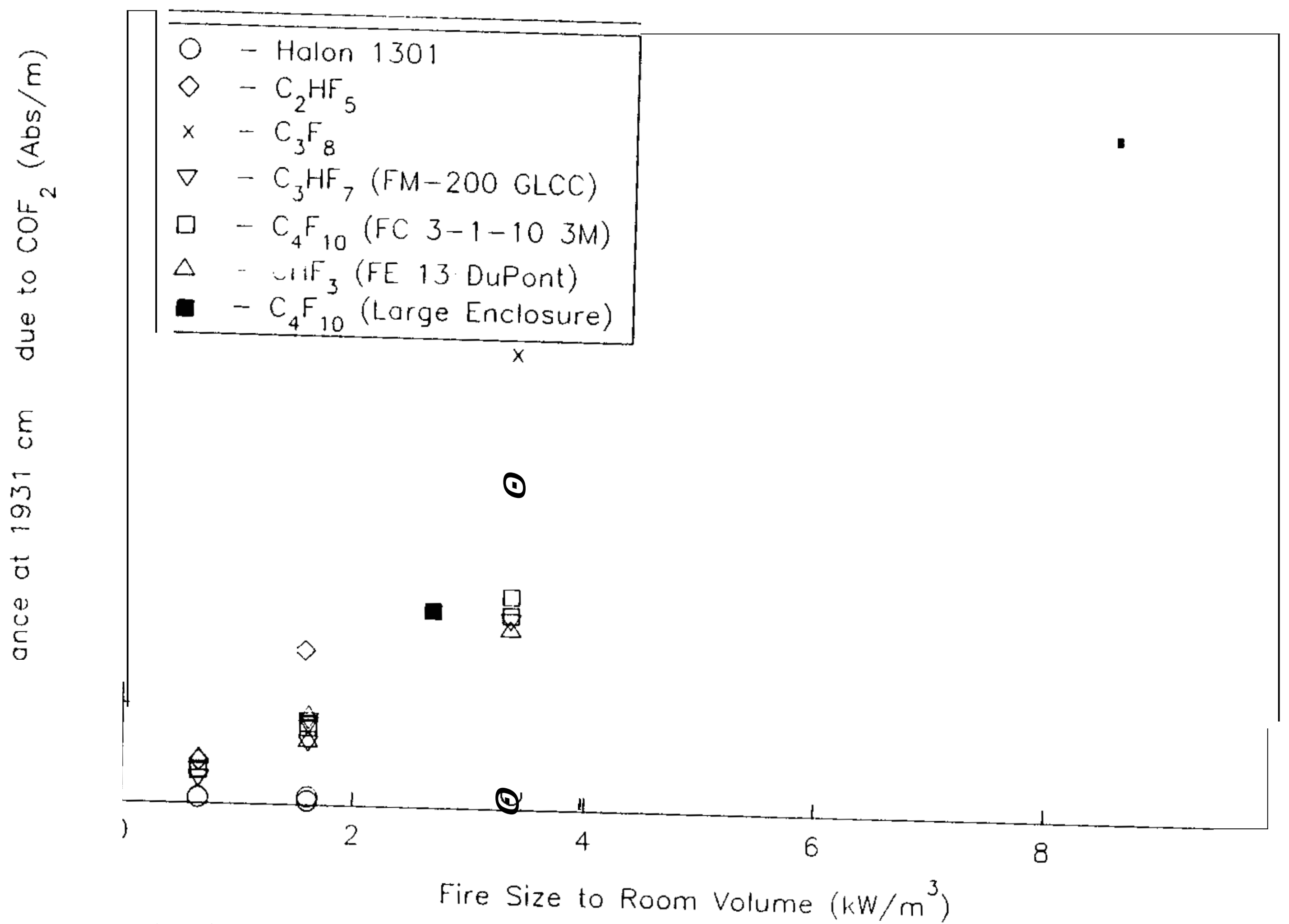
The generated concentrations of HF and those implied for COF_2 show a need to avoid the test conditions in a protected space in terms of the fire sue to room volume ratio. Sax lists the LC_{50} for HF as 1276 ppm for 30 minutes for inhalation when testing with rats [11], and this concentration is met or exceeded in many of these tests. The need for quick detection and rapid extinguishment is clearly stated.

Conclusions

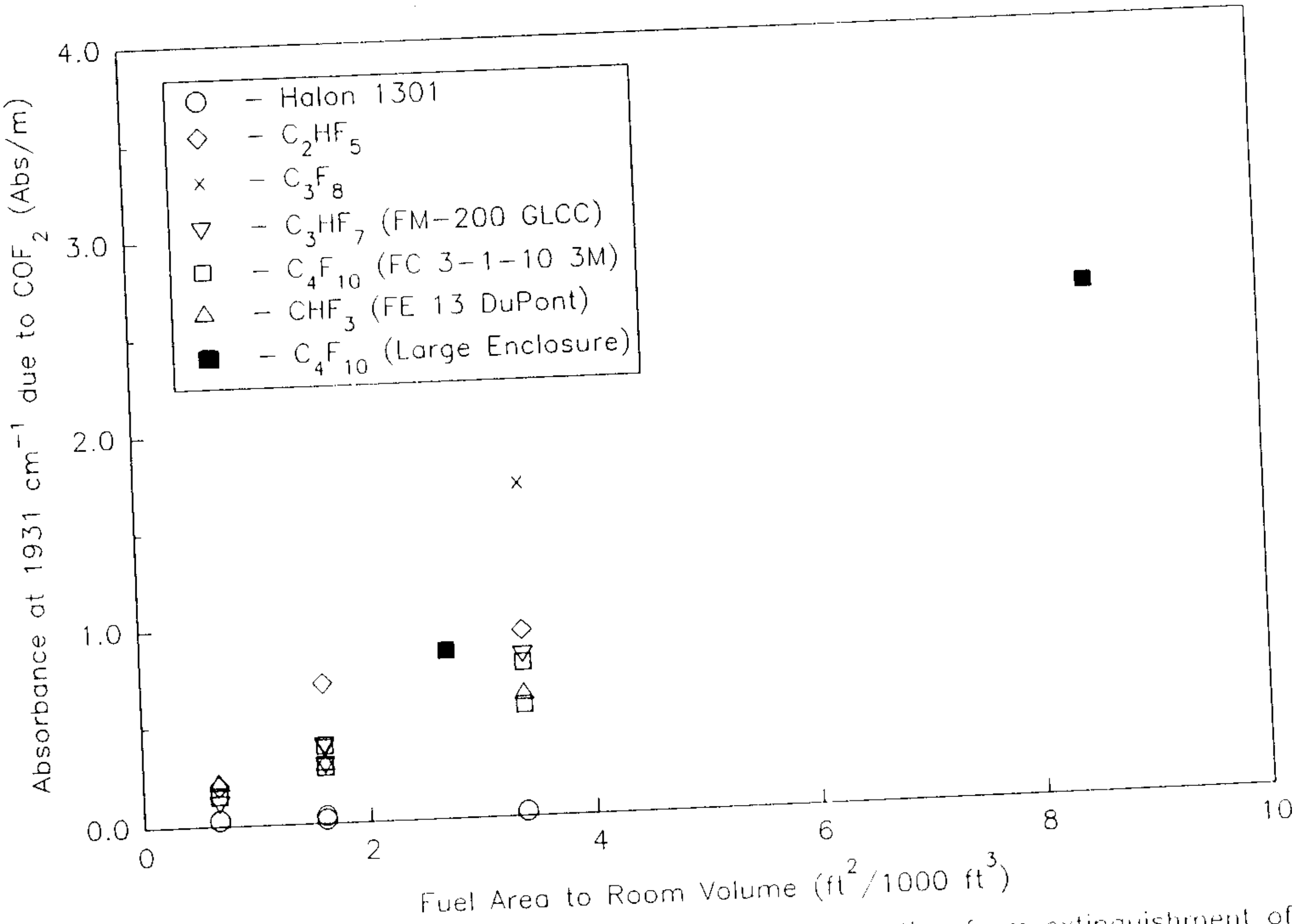
These tests have shown strong relationships between the amount of thermal decomposition products formed, the total discharge time and the fire size to volume ratio. These relationships appear to be linear or nearly linear with the intercepts at the origin.



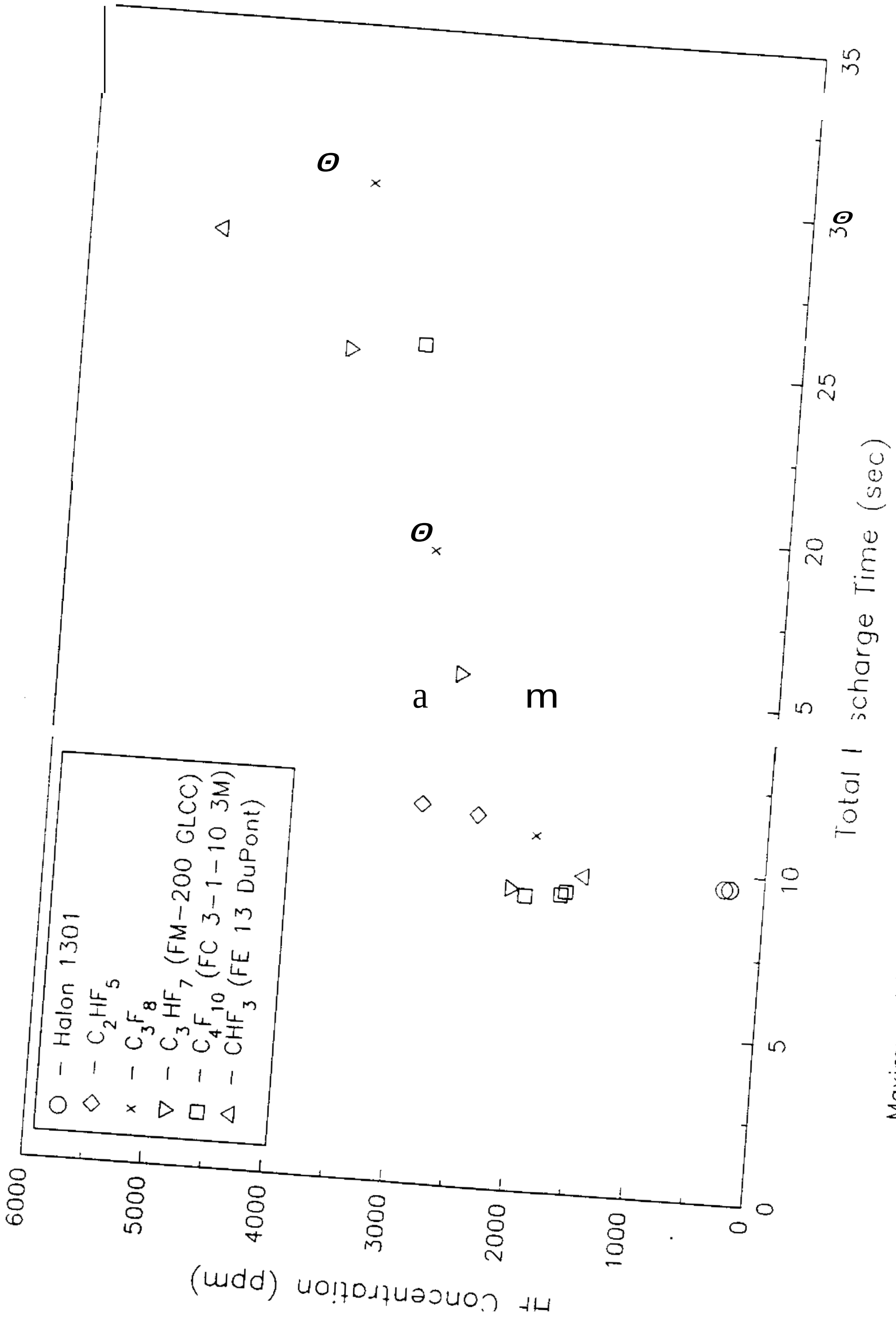
HF concentration resulting from extinguishing n–heptane fires with a nominal total discharge time of 15 seconds as determined by 3M method (grab/ISE)



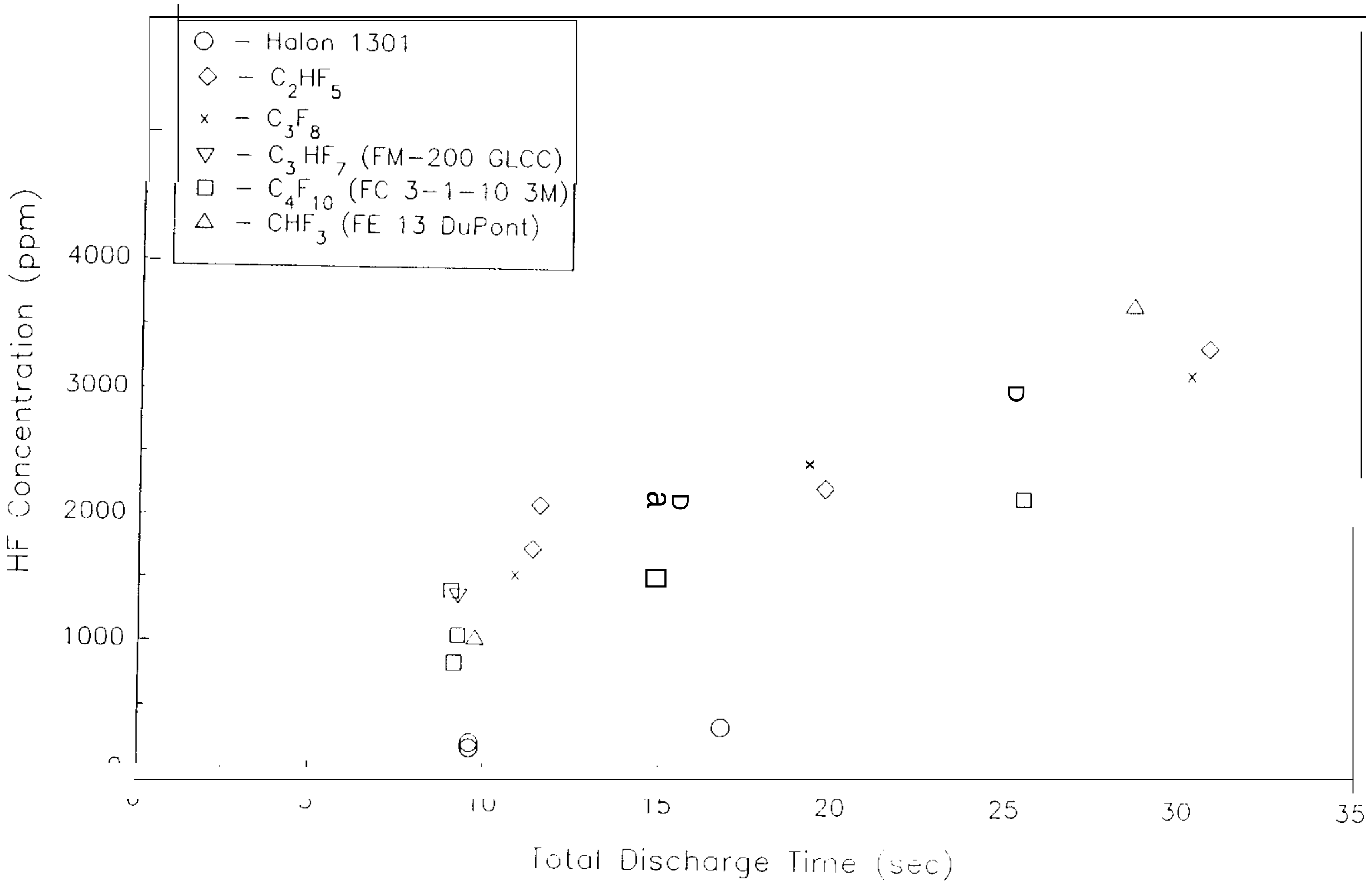
Maximum Absorbance due to carbonyl fluoride resulting from extinguishm
n-heptane with nominal 15 second total discharae time



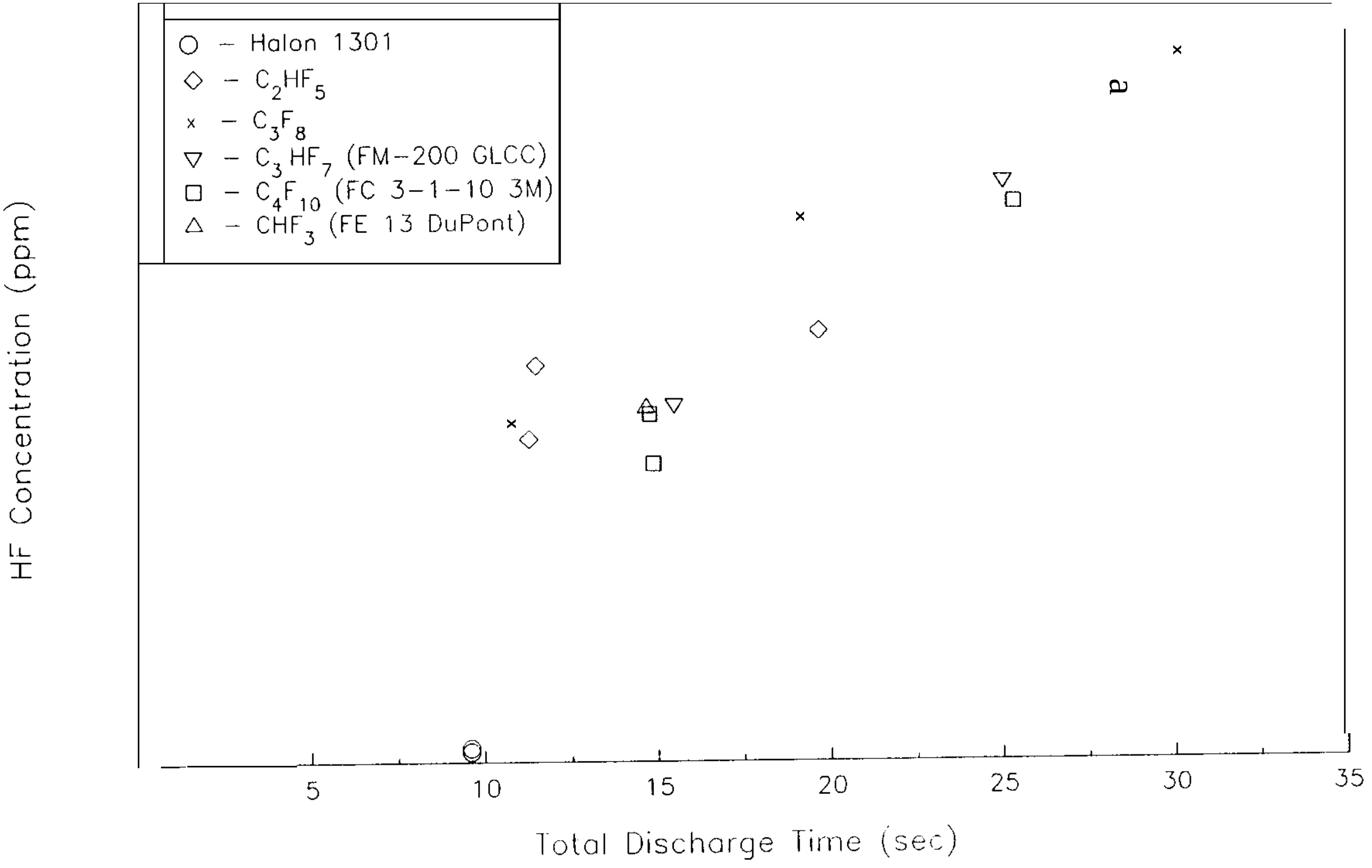
Average absorbance due to carbonyl fluoride resulting from extinguishment of n-heptane with nominal 15 second total discharge time



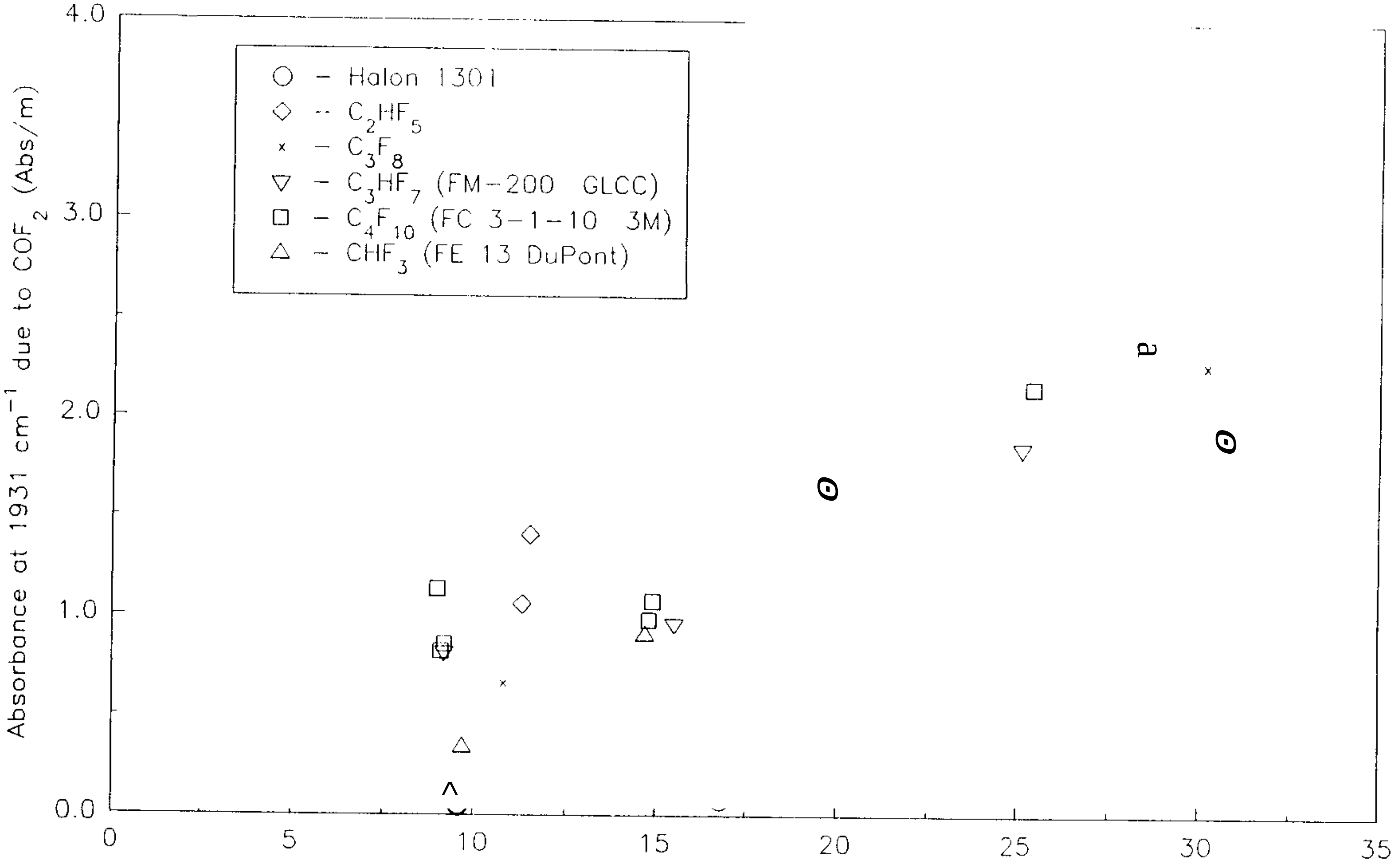
Maximum HF concentration res ting from extinguishment of 4.0 kW heptane fires.



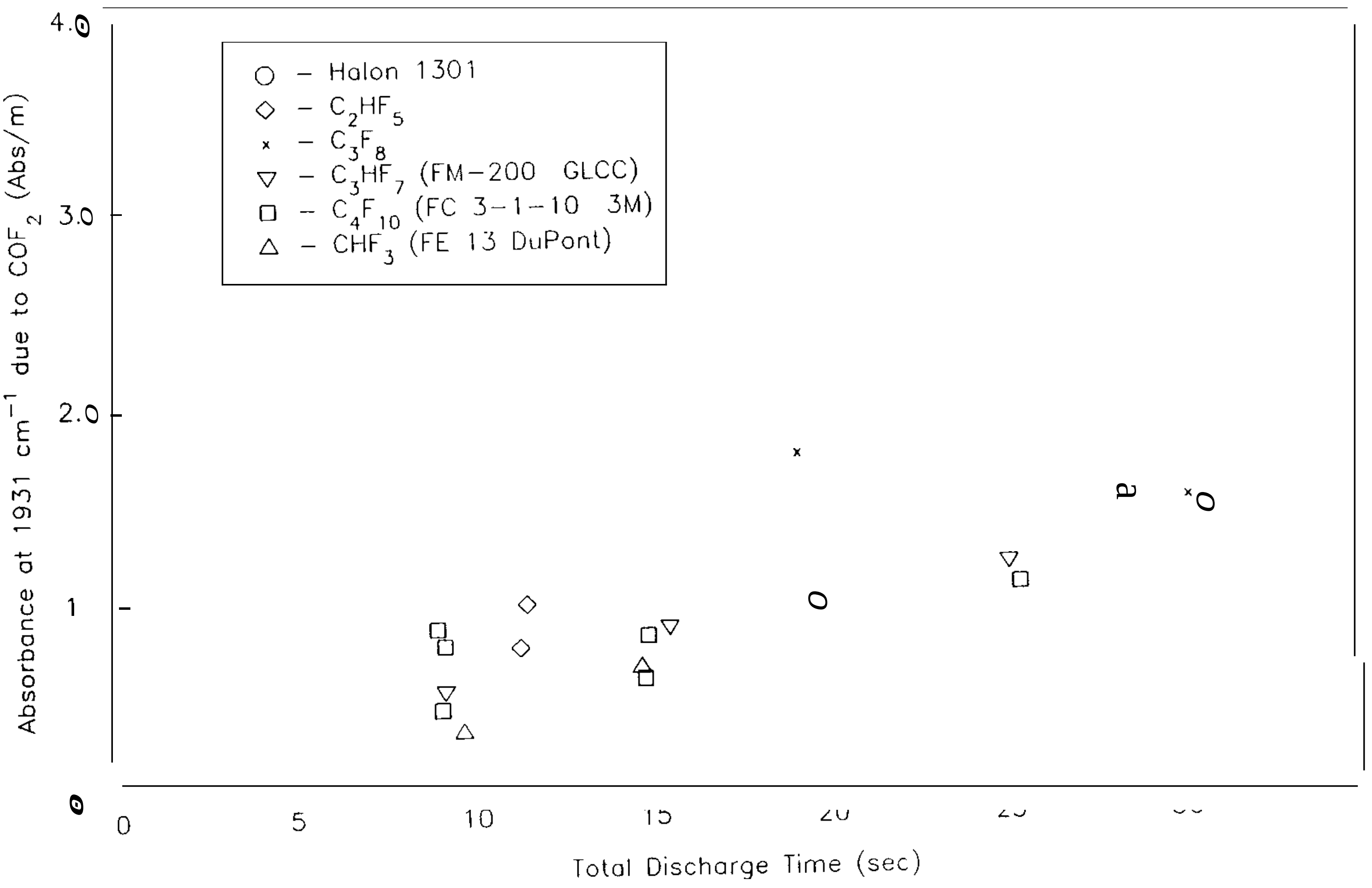
Average HF concentration resulting from extinguishment of 4.0 kW heptane fires.



HF concentration resulting from extinguishment of 4.0 kW heptane fires.
as determined by 3M method (Grab/ISE)



Maximum COF_2 Absorbance resulting from extinguishment of 4.0 kW heptane fires.



Average COF_2 Absorbance resulting from extinguishment of 4.0 kW fires.

These relationships and the generated concentrations demonstrate the need to detect while they are still small and to extinguish them rapidly.

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