A FLAME IONISATION DETECTOR AS A SCREENING TOOL FOR HALON ALTERNATIVES

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ABSTRACT

A standard flame ionisation detector (FID) of the type used in gas chromatography experiments has been modified **to** enable extinguishing concentrations **to** be determined for a range of fire extinguishing agents. Good agreement with cup-burner extinguishing concentrations has been obtained for a variety of halon alternatives. The fact that only small quantities of these compounds (<2 g) are required for the test makes it an ideal tool for the assessment of novel compounds, which may be available in only small quantities.

INTRODUCTION

The search for nonozone-depleting alternatives to the halon gases has resulted in consideration of a wide variety of chemical types. These include chemicals containing bromine that degrade before reaching the stratosphere often referred to as “tropodegradable bromocarbons” [1], phosphorus [2–4], and metal [5, 6] containing compounds, amongst others. Assessment of the efficiency of halon alternatives is commonly carried out using the cup-burner apparatus [7] that measures the concentration in air at which a compound extinguishes a fuel/air diffusion flame. A drawback with this apparatus is the quantity of agent required to obtain an extinguishing concentration (50 to 100 g per test). Although the apparatus can be scaled down [8], it is still not appropriate for establishing extinguishing concentrations of some novel agents that are available in only small quantities.

In our laboratories we have modified a standard FID, a detector commonly used for the quantification of organic compounds in gas chromatography experiments. to measure the extinguishing concentration of a number of potential halon alternatives. Extinguishing concentrations can be obtained using very low quantities of agents (< 2 g) and the apparatus can be configured at very low cost from a standard detector. The objective of the work is to develop an effective screening tool for halon alternatives research using low agent quantities.

FLAME IONISATION DETECTOR

The FID is based on the measurement of changes in the number of ions generated in a hydrogen/air diffusion flame due to the presence of trace quantities of organic compounds and was first described by McWilliam in 1958 [9]. It is still the most commonly used detector for the quantification of organic compounds in gas chromatography experiments today. **A** schematic diagram of a FID is shown in Figure 1.

Investigations of the mechanism of ion formation in flames are still being reported but the basic processes are now quite well understood. The basic reactions in the hydrogen/air flame can be described by Eqs. 1, 2, and 3.

$$H + O_2 = OH + O \qquad (1)$$

$$O + H_2 = OH + H \qquad (2)$$

$$OH + H_2 = H_2O + H \qquad (3)$$

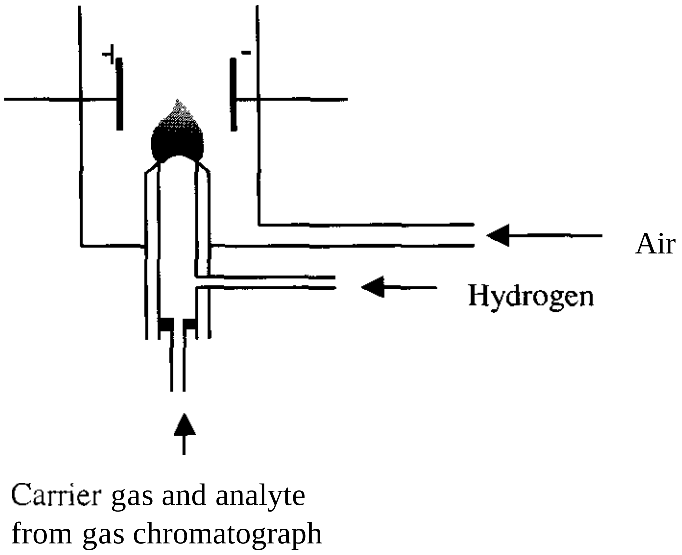

Figure 1. Flame ionisation detector.

In the flame reaction zone, the radicals formed react exothermically as shown in Eqs. 4 and 5.

$$H + H + Z = H_2 + Z \qquad (4)$$

$$OH + H + Z = H_2O + Z \qquad (5)$$

The heat generated by these reactions cracks any organic compounds present.

The ion formation process has also been studied in detail. It has been shown that the greatest number of ions exist outside the hottest part of the flame, hence thermionisation processes cannot account for the ion yield. The energy of the photons generated by the flame is also not great enough to ionise organic compounds. In 1955 the concept of chemionisation (reactions between neutral atomic excited states and organic molecules in their ground state) was proposed to account for the ion yield from flames. This is represented by **Eq.** 6 below. The close proportionality of the FID signal to the number of carbon atoms in the molecule indicates that organic molecules are fully fragmented prior to chemionisation.

$$CH + O = CHO^{+} + e \qquad (6)$$

It is noted that the detector yields a response for compounds that do not contain any hydrogen, hence it is likely that hydrogenation precedes ionisation. Experiments in which organic compounds are added to either the air or the fuel [10] indicate that heat is conducted from the reaction zone by the hydrogen and that hydrogenation occurs in the pre-reaction zone of the flame. If the compound is added in the air (the intended configuration for our experiments), the detector response is expected to be considerably lower and not proportional to the number of carbon atoms. This is significant for the present study and is a much **less** studied detector configuration.

The role of ions is not thought to be a key factor in the extinguishment process with halogen-containing compounds [11], however, throughout this work FID signals were recorded as **a** function of agent concentration and a number of interesting observations were made. It is proposed that the study of ions may reveal information indirectly about extinguishment mechanisms.

EXPERIMENTAL

A Hewlett Packard HP 5890 Series II gas chromatograph fitted with a FID was used in this study. The fuel line (normally hydrogen in gas chromatography experiments) was doped with methane in order to emulate the processes occurring in the hydrocarbon flame of the cup-burner apparatus. This gave a high hut stable background ion signal. The chromatography column connection to the FID was blocked off and the air inlet re-routed so that it passed through the gas chromatography oven. This enabled agents that were liquids at room temperature to be added to the air at a controlled temperature. All gas flows to the detector were controlled using mass flow controllers (MKS Inc.). Agents that were liquids at room temperature were injected into the air stream using a syringe-driving pump (Model A-99, supplied by Razel Sci. Inst., Inc.). A Luer lock syringe connected to a capillary tube (0.1 mm diameter) using a Valco Ltd. zero dead volume fitting was passed through the side of the gas chromatograph into the oven and connected to the air line using a Swagelock tee piece with a graphite ferrule seal. During liquid injection the oven was set to the boiling point of the agent to ensure evaporation and to keep it in the vapour phase. The liquid density. syringe size and syringe driving pump motor speed fixed the mass ilow-rate of the injected liquid. The volume concentration of the agents in the air stream was calculated using the assumption that the agents behaved as ideal gases in their vapour state [12]. The FID was operated at 250 ºC. A schematic of the experimental set-up is shown in Figure 2.

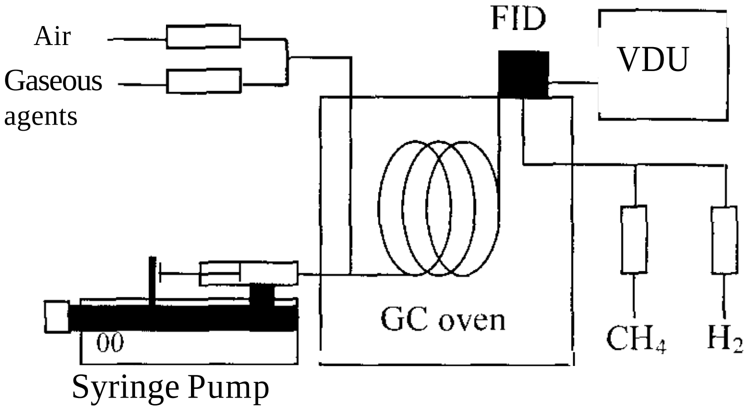

Figure 2. Schematic diagram of the FID apparatus.

The FID signal was displayed on a monitor using the Hewlctt-Packard Chemstation software, and the detector signal was recorded manually in a notebook. A modification to the ion collection system was made to improve the linearity of response in ion signal. Initially, sudden large changes in the FID signal had been observed using the standard Hewlett-Packard FID geometry. The standard electrode was replaced with a 0.5 mm platinum electrode placed closer to the flame as shown in Figure **3.** This resulted in a more steady change in the FID signals with agent concentration, but had no effect on the extinguishing concentrations observed.

The approach to the test was to fix the extinguishing concentration of Halon 1301 to its cup-burner value (approximately 3.0%) and then observe how a range of other agents compared to

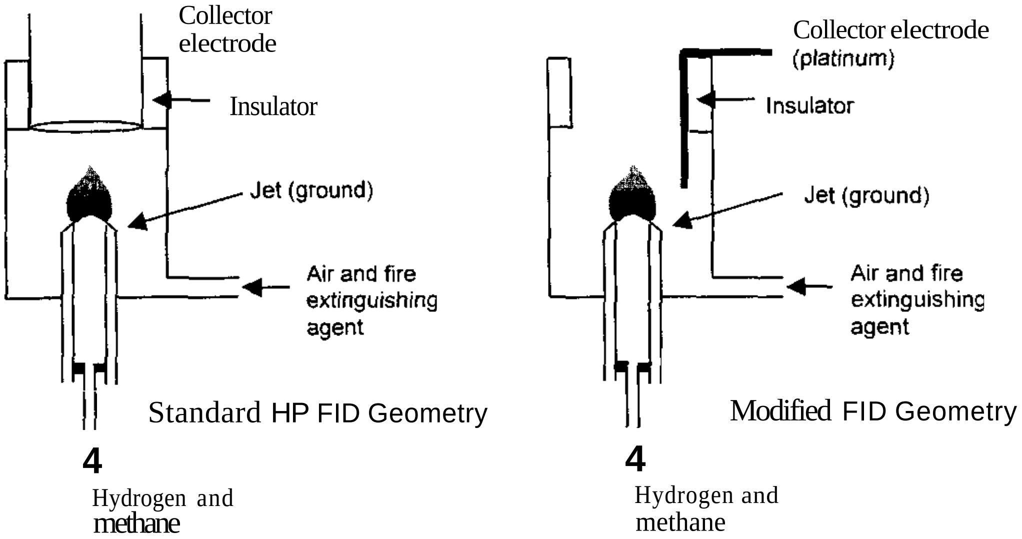

Figure 3. Modification to FID electrode geometry.

the known hierarchy of cup-burner values. Preliminary work identified that the extinguishing concentration depended principally on the hydrogen flow. The optimisation process led to the following gas flows being used: hydrogen = 15 cm^3 min^{-1}, methane = 38 cm^3 min^{-1} and air = 400 cm^3 min^{-1}. This gave an overall flame stoichiometry of 1.0. These gas flows were used for all the experiments reported in this paper. The fuel/air mixture was ignited and the detector signal allowed to settle. Agent was then added to the air stream in increments and the detector signal recorded after each addition. This process was continued until flame extinguishment was achieved as noted by a sudden drop in the ion signal to zero.

RESULTS

Extinguishing concentrations obtained for a number of halon alternatives using the FID are given in Table 1 along with their corresponding NMERI cup-burner values [13, 14]. The data demonstrate extremely good agreement between the FID test and cup-burner values. These results are the average of at least three readings recorded over a period of two weeks during which time the FID was not cleaned.

The work was extended to a study of more novel halon alternatives many of which were available in only very small quantities. These compounds were liquids at room temperature and the syringe injection technique described in the experimental section was used to generate the vapours. The results from the study of a range of halogen-containing liquids. used to evaluate the performance of the system with liquid agents, and some “tropodegradable bromocarbons” (shown in italics) are shown in Table 2.

The results for liquid agents demonstrate reasonable agreement with cup-burner values with the exception of dibromomethane and bromochloromethane (Halon 1011) where the FID extinguishing concentrations are approximately double that of the cup-burner values. These two compounds contain both bromine and hydrogen but no fluorine, which may be significant and will be studied further.

TABLE 1. COMPARISON OF FID EXTINGUISHING CONCENTRATIONS WITH CUP BURNER VALUES FOR GASEOUS AGENTS.

	Extinguishing Concentration / vol%	
Agent	Cup Burner	FID
Bromotrifluoromethane (Halon 1301)	2.9	2.x ± 0.2
Bromochlorodifluoromethane (Halon 1211)	3.2	3.5 ± 0.1
Dichlorodifluoromethane (Freon 12)	6.1	1.7 ± 0.1
Perfluoroethane	7.6	8.6 ± 0.1
Perfluoropropane	7.x	7.7 ± 0.1
1,1,1,2 Tetrafluoroethane (R134a)	10.5	9.8 ± 0.3
Trifluoromethane (HFC 23)	12.6	11.6 ± 0.5
Carbon dioxide	20.4	18.8 ± 0.4
Nitrogen	28.0	26.9 ± 0.1
Argon	38.0	38.4 ± 1.0

TABLE 2. COMPARISON OF FID EXTINGUISHING CONCENTRATIONS WITH CUP BURNER VALUES FOR LIQUIDS.

Compound	Extinguishing Concentration / vol%	
	Cup Burner	FID
Dibromodifluoromethane	2.2	2.0 ± 0.1
Dibromomethane	1.3	2.3 ± 0.2
Bromochloromethane (Halon 1011)	2.1	5.5 ± 0.3
3-Bromo-1,1,1-trifluoropropanol	4.1	3.0 ± 0.2
2-Bromo-3,3,3-trifluoro-1-propene	2.6	4.0 ± 0.2
4-Bromo-3,3,4,4-tetrafluoro-1-butene	3.5	5.3 ± 0.2
2-Bromo-3,3,3,4,4-pentafluoro-1-butene	4.1	2.5 ± 0.2
Chloroform	1.2	x.3 ± 0.4
Dichloromethane	14.1	14.1 ± 1.0
1,2,2-trichloro-1,1,2-trifluoroethane	6.2	6.4 ± 0.3
Perfluorohexane	4.4	5.1 ± 0.3

A number of methods have been used to study the mechanism of extinguishment of commonly available and novel extinguishing agents. These range from indirect measurements based on flame temperature to more direct measurements of radicals in flames. Despite the fact that ion chemistry is not thought to be important in flame suppression with halocarbons [11], the FID signal could be used to obtain information indirectly about the chemical mechanisms operating for different agents and may be important for other compound classes. The ion signals from our experiments were plotted as a function of agent concentration to investigate this possibility. Plots for the gaseous agents are shown in Figure 4. All the gaseous agents showed a non-linear relationship between ion signal and concentration with the exception of Halons 1301 and 1211. The halons gave a linear relationship with a distinctive high rate of reduction in ion signal.

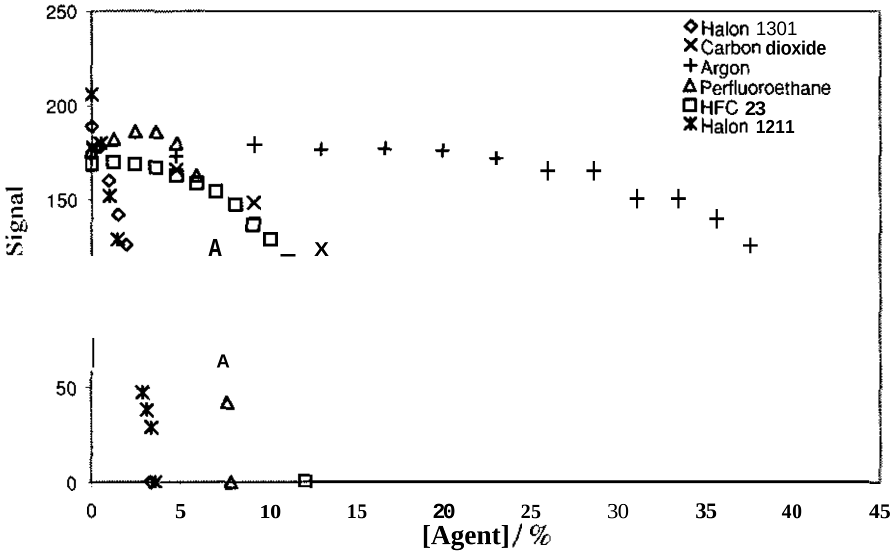

Figure 4. FID signals against agent concentration for gaseous agents.

The bromine-containing liquids, like the halons, gave a linear relationship between ion signal and agent concentration as plotted in Figure 5. Liquids that did not contain bromine gave a characteristic non-linear relationship between the ion signal and the agent concentration as shown in Figure 6.

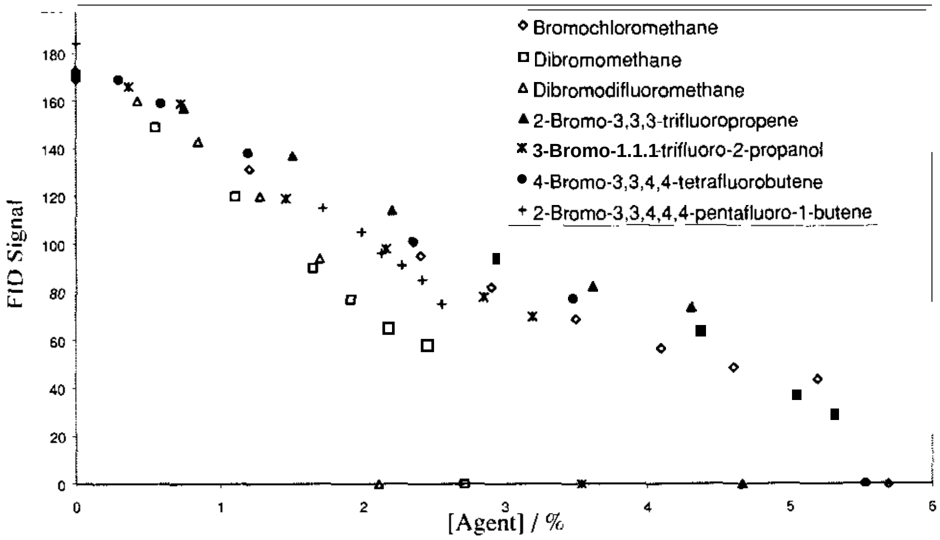

Figure 5. FID signals against agent concentration for bromine-containing liquids.

An interesting possibility of this work would be to extrapolate to the extinguishing concentration from the initial rate of change in the ion signals observed. This could enable rapid screening of small quantities of compounds using a gas chromatography separation prior to the analysis. Clearly, the behaviour of the different compound classes studied in our work demonstrates that, although this is unfeasible for agents of widely different chemical type, it may be possible for

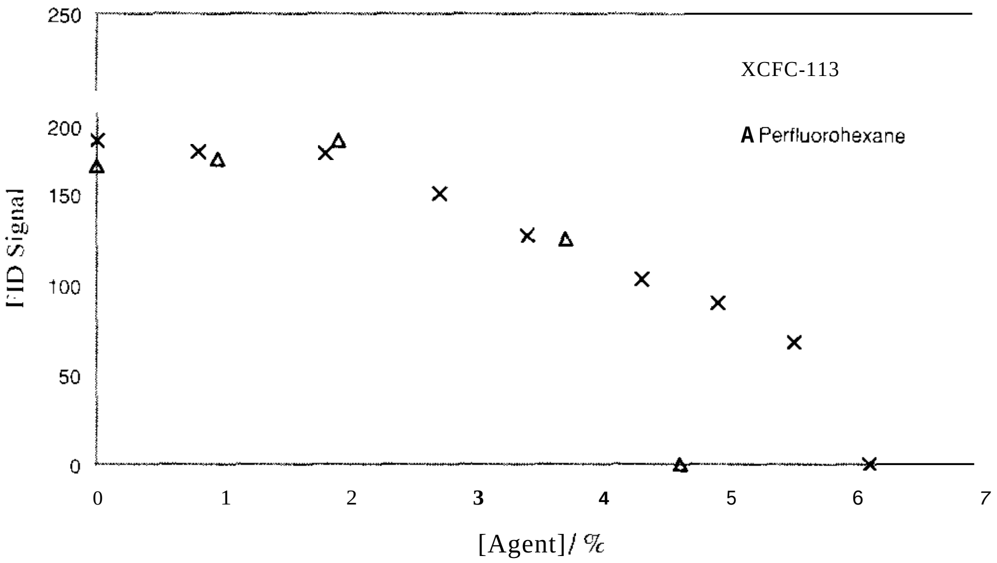

Figure 6. FID signal against agent concentration for bromine-free liquids.

closely similar compounds to be studied in this way. Data for such compounds are currently being studied in more detail.

Statistical data for this test have been collected (Table 3). These data show that the results are more reproducible for agents added in the gaseous phase and suggest imperfections in the vapour delivery system. Possible implications of a poor vapour generation system are flash evaporation and/or insufficient mixing of the agents with air resulting in either pockets of vapour rich air, or perhaps aerosol generation. Either of these would result in lower than expected extinguishing concentrations. This was not generally a feature of our experiments. Further investigation of vapour delivery using liquid agents is proposed in the Discussion section of this paper.

TABLE 3. STATISTICAL DATA FOR FID TEST.

Compound	Sample Population	Average Extinguishing Concentration / vol%	Standard Deviation	Coefficient of Variation /%
Halon 1301	24	2.x	0.3	9.6
Halon 1011	3X	5.0	0.9	17.4
Dibromodifluoromethane	10	2.1	0.3	**16.6**
2-Bromo-3,3,3-trifluoro-1-propene	17	3.9	0.8	20.6
4-Bromo-3,3,4,4- tetrafluoro-1-butene	9	4.4	0.7	16.7
2-Bromo-3,3,4,4,4-pentafluoro-1-butene	12	2.5	(1.4	15.7

Another range of compounds being considered as halon replacements are phosphorus-containing compounds (PCC). The flame suppression potential of a number of PCCs has been evaluated in our laboratories previously using pre-mixed flames **[IS]**. These were shown to be up to twice as effective as Halon 1301. These compounds and some additional fluorinated phosphate derivatives have been studied using the FID test. Extinguishing concentrations for these compounds are shown in Table 4.

TABLE **4.** PCCS STUDIED USING THE FID.

Phosporus-Containing Compound No. and Name	Structure	FID Extinguishing Concentration / vol%
1. Trimethyl phosphate	$O = P(OCH_3)_3$	0.6-2.8
2. Dimethyl methylphosphonate	$O = P(CH_3)(OCH_3)_2$	0.7
3. Diethyl methylphosphonate	$O = P(CH_3)(OC_2H_5)_2$	0.9
4. Dimethyltrifluoroethyl phosphate	$O = P(OCH_3)_2(OCH_2CF_3)$	0.7
5. Diethyltrifluoroethyl phosphate	$O = P(OC_2H_5)_2(OCH_2CF_3)$	0.7
6. Diethylpentafluoropropyl phosphate	$O = P(OC_2H_5)_2(OCH_2CF_2CF_3)$	0.7
7. **Diethylhexafluoroisopropyl**phosphate	$O = P(OC_2H_5)_2(OCH_2(CF_3)_2)$	0.7
8. Diethylheptafluorobutylphosphate	$O = P(OC_2H_5)_2(OCH_2CF_2CF_2CF_3)$	0.6
9. Diethyloctafluoropentyl phosphate	$O = P(OC_2H_5)_2(OCH_2CF_2CF_2CF_2CF_2H)$	1.1
10. Bis(2,2,2-trifluoroethyl)-2,2,3,3,3-pentafluoropropyl phosphate	$O = P(OCH_2CF_3)_2(OCH_2CF_2CF_3)$	0.7
11. Tris(2,2,2-trifluoroethyl) phosphate	$O = P(OCH_2CF_3)_3$	0.8
12. Tris(2,2,3,3,3-pentafluoro-1-propyl) phosphate	$O = P(OCH_2CF_2CF_3)_3$	1.0
13. Tris(2,2,3,3,4,4,4-heptafluoro-1-butyl) phosphate	$O = P(OCH_2CF_2CF_2CF_3)_3$	1.8

The results for the recently studied fluorinated phosphates (Compounds 10 to 13 [Table 4]) provide further evidence that it is the phosphorus in these compounds that makes them effective. The boiling points of Compounds 10 and 11 were 196 and 187 °C, respectively. This compares favourably with Compounds 4 to 9 studied previously that had boiling points in excess of 250 °C. **A** plot of FID signal against agent concentration for two of these compounds is shown in Fig**ure** 7. These data show that these compounds are extremely effective at removing ions/electrons from the flame under the conditions used. Nevertheless, they are no more effective than similar compounds containing a significant fuel content such as dimethyl methylphosphonate.

All the PCCs studied showed an impressive reduction in FID signal at very low concentrations. Direct measurements of ions in hydrocarbon flames doped with PCCs have been made by Goodings et al. [16] using mass spectrometry. This showed alkyl esters of phosphates and phosphites as extremely efficient scavengers of electrons in hydrocarbon flames when added at low concentration (< 0.1 mole%). The results presented here for extinguishment of diffusion flames confirm the findings of other workers **[3]** who have shown PCCs to be two to four times more effective than Halon 1301.

DISCUSSION

The rate of ion signal reduction with agent concentration is in general a good indicator of agent efficiency in these experiments with the exception of fully fluorinated compounds. This does not mean that ion chemistry is important in the extinguishing mechanism for any of the compounds studied as many of them have also been shown to have direct effects on radical concentrations in

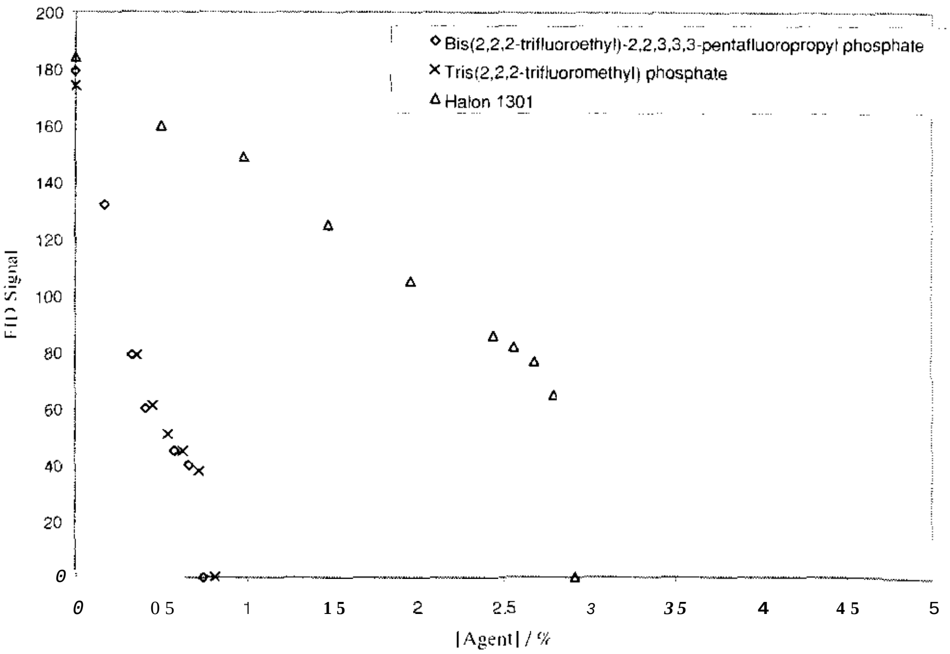

Figure 7. FID signal against agent concentration for PCCs.

flames. The agent delivery system for liquid agents in our experiments needs to be characterised more fully. However, a balance will be sought between increasing the complexity of the system and maintaining a test that enables low agent quantity and a high throughput. Further work will involve continued study of compounds that have given FID extinguishing concentrations significantly different from their cup-burner values. If this behaviour is a feature of chemistry then a larger database of similar compounds will be required to have confidence in the FID results. An alternative approach would be to use a fuel which is closer to that used in the cup-burner such as pure methane, propane or butane. Heptane could also be considered.

CONCLUSIONS

Good correlation between FID extinguishing concentrations and cup-burner values has been obtained for a range of halon alternatives using a modified flame ionisation detector as a burner. This concept gives a ready-made platform for flame extinguishing experiments using very low quantities of chemicals. The FID can therefore be used as an effective screening tool for evaluating novel fire extinguishing agents. For example, a number of tropodegradable bromocarbons and phosphorus-containing compounds have been studied with low quantities of agent (<2 g/test). Interesting data on the effect of different compounds on ion chemistry in flames have also been obtained, which could be studied in more detail. A number of phosphorus-containing compounds have been shown to be some two to four times more effective than Halon 1301 in the FID test. These results agree with those of other workers and provide further evidence that it is the presence of phosphorus in the molecule that is important in determining their extinguishing behaviour.

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