FLAME EXTINGUISHMENT BY METAL CONTAINING AGENTS

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INTRODUCTION

More than a generation ago, it was discovered that very small amounts of iron pentacarbonyl have a dramatic effect on flames. Lask and Wagner reported that addition of 0.017 percent $Fe(CO)_5$ to a stoichiometric hexane-air flame reduced the flame velocity by 30%.[1] Stimulated by this initial result, Bonne, Jost and Wagner extended the investigation of the inhibiting effect of $Fe(CO)_5$, and studied both methane-oxygen and methane-air flames.' Here are some of the key findings of this latter work.

(1) $Fe(CO)_5$ more effectively inhibits hexane/air flames than hydrogen/air flames. Conversely, bromine is a more effective inhibiting agent in the latter than in the former; it is of interest to note in passing that the ·Br atoms are known to inhibit flames by catalytically recombining ·H atoms.

(2) $Fe(CO)_5$ is less effective in methane/oxygen flames than in methane/air flames.

(3) $Fe(CO)_5$ is more effective in atmospheric pressure flames than in low pressure flames.

(4) By comparison with uninhibited flames, flames inhibited with $Fe(CO)_5$ have significantly lower OH radical concentrations in the recombination zone, especially at distances greater than 2 cm above the burner in 60-torr flames.

(5) In flames inhibited with $Fe(CO)_5$, the concentration of Fe atoms peaks at about the same place as ·OH, ·CH and C_2 molecules (about 0.5 cm above the burner); the emission spectrum of iron atoms does not track with the concentration, peaks at a greater distance above the burner, about 1.3 cm, and falls off very slowly with increasing distance above the burner.

(6) The emission spectrum of the FeO molecule has two maxima in $Fe(CO)_5$-inhibited flames: about 0.5 cm and about 3.3 cm above the burner.

Taken as a whole, these results suggest, but do not conclusively prove, that the mechanism of catalytic inhibition by $Fe(CO)_5$ may be different from that exhibited by the Br atom. Interesting candidates include ·H + OH recombination and even O + O recombination.

The effect of $Fe(CO)_5$ on premixed flames is being reinvestigated both at the National Institute of Standards and Technology (NIST[3] and in our own laboratories. Linteris and Gmurczyk recently reported a set of experiments in which premixed methane/air and propane/air flames were inhibited by $Fe(CO)_5$; these authors reported a 20% reduction in burning rate with an $Fe(CO)_5$ mole fraction of 24 ppm, but that, for $Fe(CO)_5$ concentrations above about 100 ppm, additional amounts of $Fe(CO)_5$ did not seem to be effective in contributing to further extinguishment of the flame.

More recently, the work on $Fe(CO)_5$ has been extended to include investigation of its behavior in counterflow diffusion flames: Results of this work were presented by Linteris and Reinelt at this meeting: These workers confirmed that the effect on a flame is quite dependent on the stoichiometry of the flame and on the location of the flame with respect to the stagnation plane. With the flame on the fuel side of the stagnation plane, the $Fe(CO)_5$ has negligible effect when added to either stream. When the flame is on the oxidizer side, addition of $Fe(CO)_5$ to the fuel stream results in an apparent promotion of combustion, while addition of $Fe(CO)_5$ to the oxidizer side results in inhibition similar to that observed in the premixed flame. These results with the counterflow diffusion flame add credence to the suggestion that the extinguishing mechanism involves the direct interaction of the $Fe(CO)_5$ with the oxidizer, and that the mechanism must be quite different from that exhibited by Halon 1301.

EXPERIMENTAL

Figure 1 illustrates the key components of the experiment. The Sapphire 0-7 burner is a modified laboratory Meker burner (diameter = 3.7 cm). The heat absorbed by the burner is carried off by ethylene glycol, circulated at a measured flow rate by a gear pump through a cooling loop (3/16" copper tubing) silver soldered to the outside of the burner rim. The increase in the temperature of the ethylene glycol is measured by a pair of thermocouples located in the cooling loop just below the points of attachment of the loop to the burner rim. The temperature at the center of the burner surface was sensed by a thermocouple spot-welded to the grid. The entire burner was insulated and resistively heated to prevent condensation of the slightly volatile extinguishing agents. A nitrogen sheath was used to minimize recirculation of the burned gases into the flame. Methane, "air" (21% O_2, 89% N_2), and the extinguishing agent were premixed. In typical experiments, the total flow rate

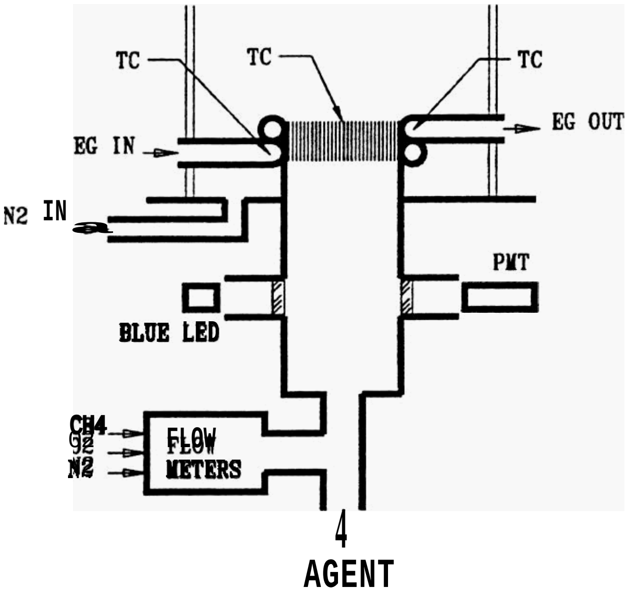
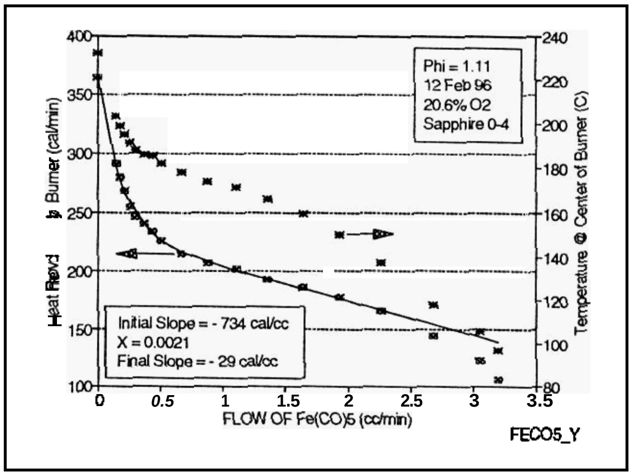


Figure 1. Schematic Diagram of the Sapphire 0-7 Burner

RESULTS

Catalytic Extinguishment. The experiment which most convincingly demonstrates the fact that the iron-containing extinguishants catalytically inhibit the flame is the experiment in which the heat removed by the burner is studied as a function of the amount of extinguishing agent added to the premixed gases. **A** typical result is shown in Figure 2. In a typical data set (and this set is characteristic), the heat removed by the burner (HRBB) shows a



incremental additions of agent, followed by a linear decrease, and terminated by extinguishment (flameout). The data are easily treated by first fitting data for relatively large flow rates to a linear equation, and then fitting the residual data for small flow rates to an exponential equation of the form $y = a + b e$. The exponential form of the behavior at small flow rates is characteristic of catalytic quenching. For comparison with data for other agents (a physical agent and a catalytic agent), the reader is referred to Appendix **A.** The slope of the curve at any point is a measure of the effectiveness of the agent at that point. The following, essentially meaningless, calculation illustrates the dramatic effect that small amounts of $Fe(CO)_5$ have on the flame. From the initial slope, and the fact that about 20% of the total heat in the flame is removed by the Sapphire 0-7 burner, it can be estimated that the impact on the reduction of the heat in the flame is on the order of 4×10^5 kJ/mol $Fe(CO)_5$. (For comparison, the heat of complete atomization of $Fe(CO)_5$ is only 6.0×10^4 kJ/mol.) Even with the final slope of -29 cal/cc, the effectiveness of this iron-containing compound is quite significant. (For comparison, if one dissociates the $Fe(CO)_5$ into Fe(g) and CO(g) and adds the energy required to bring these gas-phase species to a temperature near that of the flame, one would expect to observe a slope of about -6 cal/cc.)

It should be noted, in this regard, that extinguishment was routinely observed in $Fe(CO)_5$ experiments. Typical $Fe(CO)_5$ volume percentages at which extinguishment was observed ranged from 0.05% to 0.08%. In the experiment illustrated by Figure 2, the higher flow rates of $Fe(CO)_5$ resulted in significant buildup of deposits on the surface of the burner; these deposits doubtless insulated the burner and caused the HRBB to be smaller than it would have been in the absence of these deposits. In this regard, note the "tail-off," beginning with an $Fe(CO)_5$ flow rate of 2 cc/min.

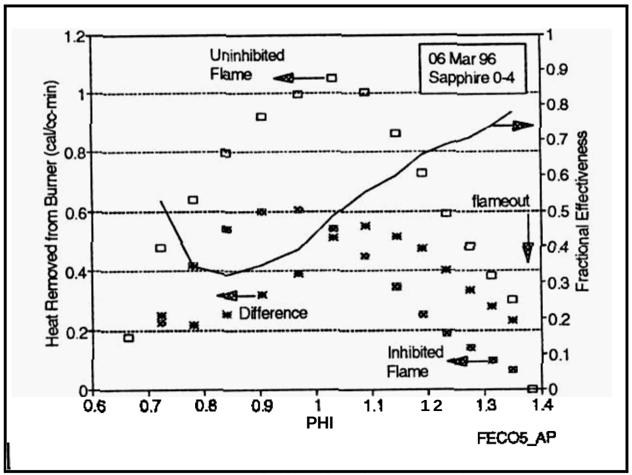


Figure 3. Inhibition of a Methane-Air Flame by 4.00 cc/min $Fe(CO)_5$

Effect *of* the Carbonyl Moieties. To examine the possible effect of the CO fragments on the overall extinguishment effectiveness, the concentrations of all the gases except methane were fixed, and the fuel/oxidizer equivalence ratio, ϕ, was "scanned by varying the flow rate of methane from the lean inflammability limit to the rich inflammability limit. The results of a typical experiment are shown in Figure 3. As expected, the HRBB for the uninhibited flame has its maximum at the stoichiometric ratio. By contrast, the peak for the inhibited flame is on the fuel-lean side (and the peak of the difference curve is on the fuel-rich side). Thus, it is clear that, while the $Fe(CO)_5$ contributes to the net extinguishment of the flame at all values of ϕ, it extinguishes fuel-rich flames more effectively than fuel-lean flames. This is reminiscent of for Fe(CO)$_5$ at several different concentrations. Figure 4 illustrates the effectiveness of Fe(CO)$_5$ by plotting the decrease in heat absorbed by the burner as a function of ϕ, and Figure 5 collects the Fractional Effectiveness data for the same experiments. It is especially instructive to compare the results in Figure 4 with a similar set of results for a typical physical extinguishing agent such as CF$_4$; see Appendix B for representative GF, data. While the decrease in heat absorbed by the burner is essentially independent of ϕ for CF, the distinct peak near ϕ = 1.1 for the Fe(CO)$_5$ is clearly indicative of the catalytic quenching mechanism at work in this compound. It may be necessary to obtain detailed concentration profiles (by mass spectrometry and other techniques) and model the system with a complete kinetics model in order to completely elucidate

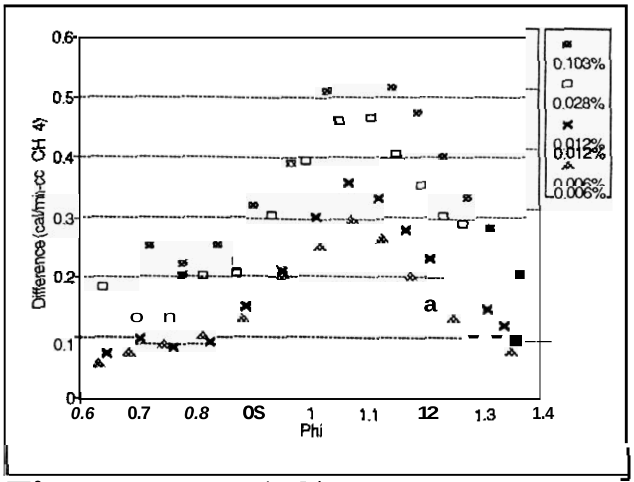
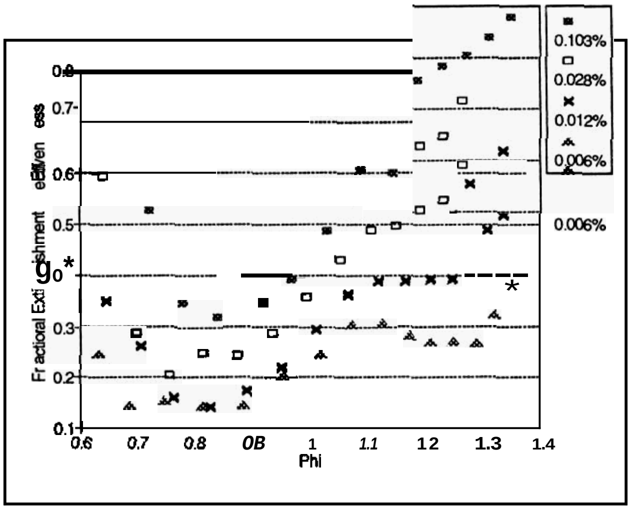


Figure 4. Fe(CO)$_5$ Extinguishment Effectiveness

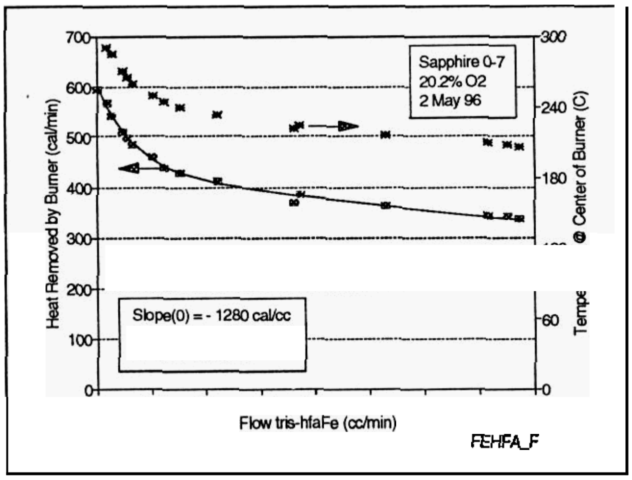
atoms, as noted above) displays a similar, though not as marked, maximum near the same value of ϕ; see Appendix B for representative results.

The requirement for a set of follow-on experiments with a compound lacking the CO moieties is clearly indicated. Although initial experiments with $Fe(hfa)_3$ have been completed (see the next paragraph), the critical experiments (in which the HRBB is studied as a function of ϕ for a fixed amount of $Fe(hfa)_3$ have not yet been done.



apparent that the results are nearly identical with those for $Fe(CO)_5$, clearly indicating that the iron in the agent is involved in the inhibition. While the slopes of the curves are larger than those for $Fe(CO)_5$, it should be noted that small experimental uncertainties can

date, it has was not been possible to



$Fe(CO)_5$ (less than 0.5 cc/min in Figure 2), the flame is observed to be orange and the spectrum is dominated by emission by the FeO molecule;[8] see Figure 7. As the amount of $Fe(CO)_5$ is increased, luminous particles begin to appear in the flame and the spectrum begins to be dominated by the broad feature illustrated in Figure 8. With relatively large amounts of added $Fe(CO)_5$, the spectrum is entirely dominated by the broad emission, though the absolute intensity of the FeO emission appears to remain constant. This broad, intense emission is assigned to chemiluminescence of a species closely related to the FeO molecule, based on the observation that the feature is structured (has three maxima) and lies slightly to the red (at longer wavelengths) of the FeO emission bands. The broad feature clearly is not black-body radiation, which would not be structured, and would have a maximum

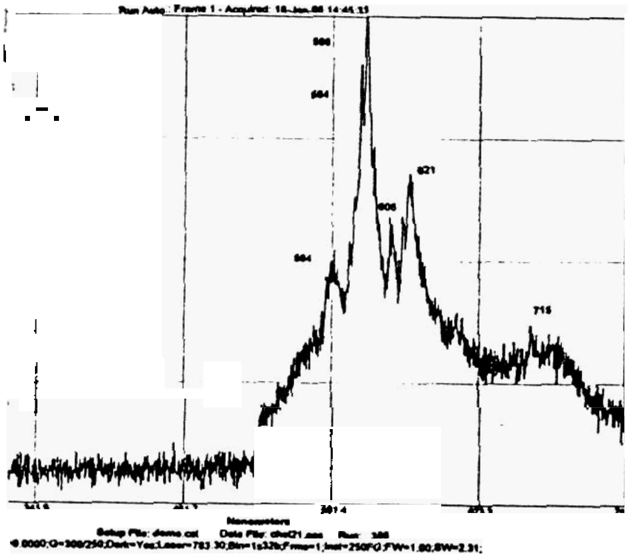


Figure 7. Emission Spectrum at **Low Concentrations of $Fe(CO)_5$**

compounds catalytically inhibit flames, and that the important catalytic species involves the iron atom. The collective data are consistent with the following proposed description of the extinguishment by these agents. At low concentrations of agent, the FeO molecule is the primary species, and is

aerosols, possibly in concert with amorphous carbon (soot precursors) in the form of FeO seeded particles. It appears that the inhibition chemistry still involves the FeO molecule: however, the FeO molecule is perturbed by the environment in the aerosol particle, and the spectrum is shifted in the (expected)

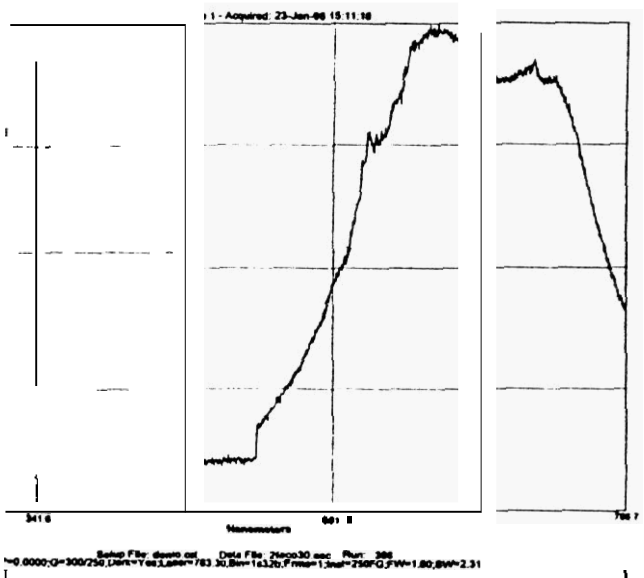


Figure 8. Emission Spectrum at **High Concentrations of $Fe(CO)_5$**

direction of longer wavelengths. Moreover, since many of the FeO molecules are now trapped in internal sites in the aerosol particles, relatively few are available on the surface of the particles to contribute to the inhibition of the flame.

Although this description is consistent with all observations to date, other possibilities cannot yet be ruled out conclusively, and several additional questions are of great interest.

(1) The possible role of the Fe atom cannot be ruled out.

(2) It is not known whether the fact that iron has several possible oxidation states, two of which (2+ and 3+) **very** easily accessible, is important. Experiments with metals having only one easily accessible oxidation state should provide insight into this question.

(3) Since the aggregation of the FeO molecules is clearly associated with reduced effectiveness, it may be asked whether there is some technique by which aggregation may be reduced or delayed. Does the onset and/or degree of aggregation depend on the nature of the precursor?

(4) Another source of iron in flames is an aqueous aerosol containing $Fe(NO_3)_3$. Preliminary experiments with aerosols demonstrate that FeO is generated in the flame, just as it is by the $Fe(CO)_5$ and $Fe(hfa)_3$ precursors[9]. Can this aerosol lead to an effective extinguishing system?

(5) Do metals other than iron, such as manganese or titanium, have similar catalytic inhibition mechanisms?

The answers to these and related questions are the objectives of continuing investigations in our laboratories.

ACKNOWLEDGEMENTS

This work was supported by the Air Force Office of Scientific Research, Contract NO. F49620-94-1-0241.

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APPENDIX A
Comparison of Physical and Catalytic Chemical Agents

Figure A-1 illustrates results typical of a physical extinguishing agent, while Figure A-2 shows results typical of a catalytic chemical extinguishing agent. Note especially the straight line exhibited by the nitrogen and the exponential curve displayed by the Halon 1301.

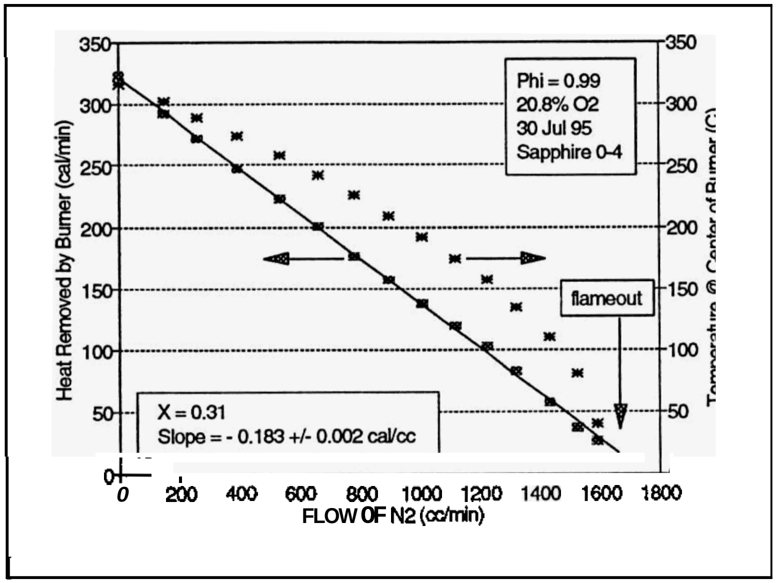

Figure A-1. Inhibition of a Methane-Air Flame by N

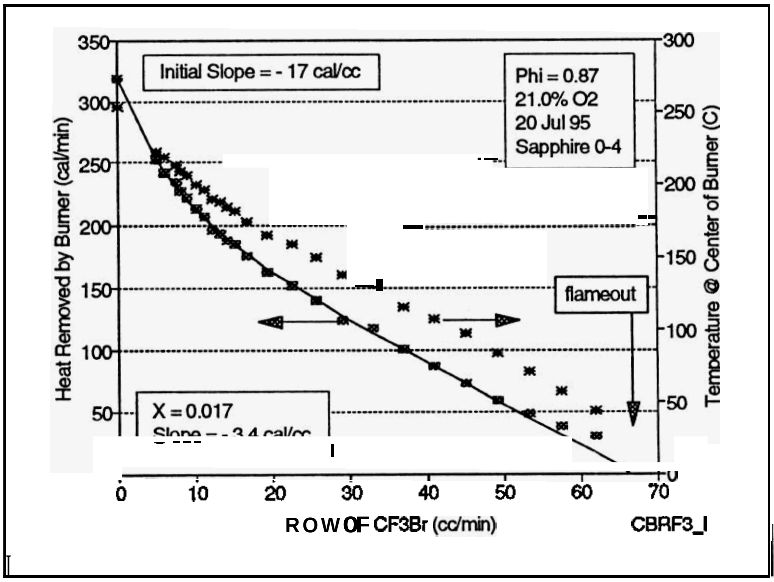

Figure A-2. Inhibition of a Methane-Air Flame by Halon 1301

APPENDIX B
Comparative Data for CF_4 and CF_3Br

Plotted in these two figures (as a function of the fuel-oxidizer equivalence ratio, ϕ) is the magnitude by which the agent reduces the amount of heat removed by the burner. Note that, in the experiments with CF_4 (a typical physical extinguishing agent which reacts chemically with the flame only reluctantly), the magnitude of the reduction in the heat removed by the burner is nearly independent of ϕ. By contrast , Halon 1301, in which abstraction of the Br by a hydrogen atom is facile, shows a modest, but distinct, maximum near ϕ = 1.1.

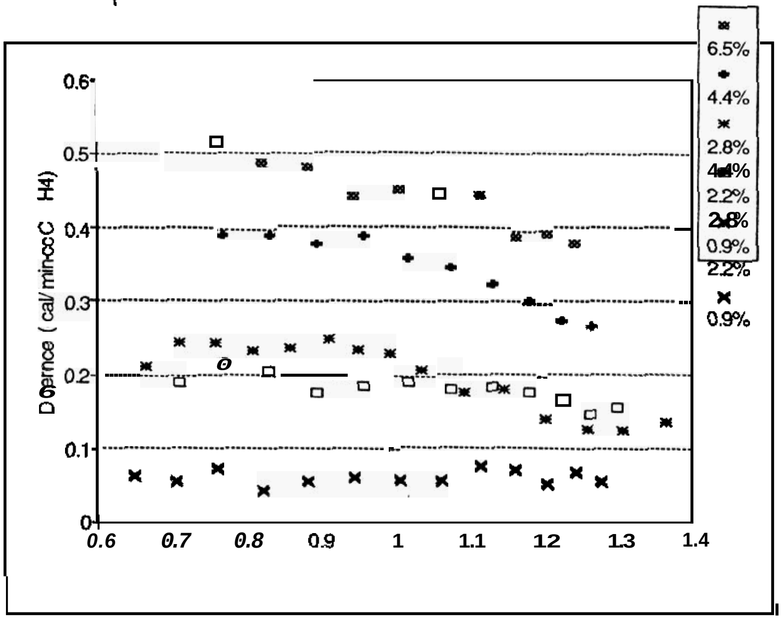

Figure B-1. CF_4 Extinguishment Effectiveness

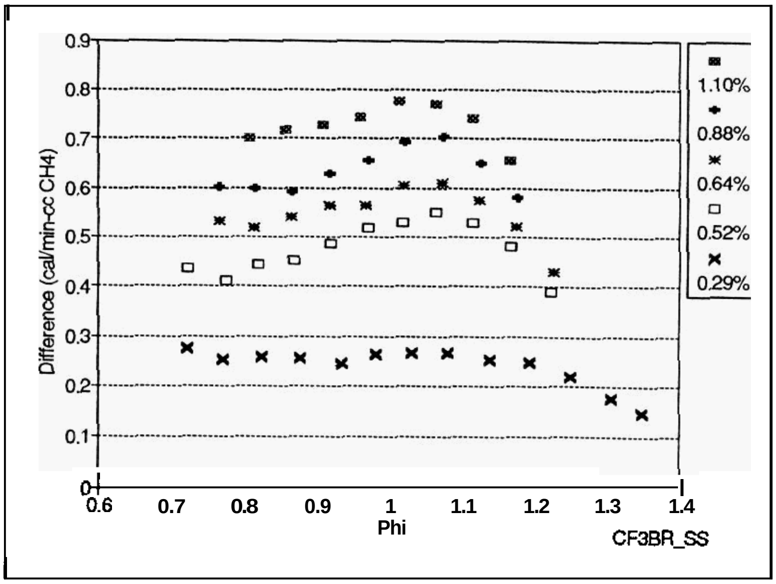

Figure B-2. Halon-1301 Extinguishment Effectiveness