Flame Velocimetry Measurements of Inhibited Methane/Oxygen Flames Using Pulsed Flame Velocimetry

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ABSTRACT

Knowledge of flame velocities is an important factor in the design and construction of many devices involving combustion phenomena. We report here results of flame velocity measurements obtained using pulsed flame velocimetry, a new technique that may be useful for Halon replacement research. The method developed here is based on and is an extension of the pulsed flame photometer detector developed at Tel Aviv University.

Flame velocities for burning methane/oxygen mixtures to which a small amount of inhibitant has been added are determined using pulsed flame velocimetry. Results are compared to flame velocities measured for similar mixtures using other techniques. Relative flame velocities for burning methane/oxygen mixtures doped with small amounts of inhibitants are compared with flame inhibition efficiencies. The utility of flame velocities determined using pulsed flame velocimetry as a predictive technique for inhibitor efficiency studies is discussed.

INTRODUCTION

One of the great successes in firefighting technology over the past several decades has been the development and use of Halon 1301 (CF_3Br) and Halon 1211 (CF_2ClBr) as fire extinguishing agents. These halogenated hydrocarbons have been shown to be highly effective in extinguishing fires in critical situations by virtue of the their flame inhibiting characteristics, non-toxicity prior to use and relative non-toxicity during and following use, and because ancillary damage caused by their presence after extinguishment is minimized. Critical uses range from extinguishing fuel fires in military vehicles while preserving crew safety, to safe and non-damaging extinguishment of electrical fires in large computer facilities. Unfortunately, Halons 1301 and 1211 have been implicated as participants in stratospheric ozone depletion', and their production and sale have been banned by international agreement' as of 1 January 1994. Because of this, there is a concerted effort underway to find environmentally friendly yet effective substitutes for these fire inhibitants' for which production has been halted.

There is a large body of literature devoted to the investigation of the mechanism by which certain additives, or diluents, affect combusting systems[4,5]. We define a diluent as any dopant (i.e. inhibitor, suppressant, retardant, extinguisher, negative catalyst, accelerant, fuel/oxidizer added to a combusting system, etc.) to the existing flame system, regardless of the effect on the system. For investigations of flame inhibitant performance, scenarios range from studies of inhibitant effectiveness on large fires fueled by liquid hydrocarbons burning in air, to inhibitor effect on laminar low pressure pre-mixed gas flames. Unfortunately, these studies have shown that the effectiveness of a particular fire inhibitant may vary depending on the type of combusting system being investigated[6]. For most real fires, the conditions within the combusting region may vary from highly diffusion-limited fuel rich combustion to locally premixed stoichiometric combustion. The inhibitor therefore needs to be effective over a wide range of macroscopic combustion parameters.

BACKGROUND

A macroscopic effect of adding a diluent to a premixed volume of gas through which a combustion wave is propagating is to alter the flame velocity'. The flame velocity is highly dependent of the fuel/oxidizer equivalence ratio, defined here for the uninhibited flame as the ratio of mixture volume percent fbel divided by mixture volume percent oxidizer to the stoichiometric balanced chemical equation coefficient of fuel divided by the coefficient of oxidizer. For the flames studied here, this equation is $CH_4 + 2O_2 = CO_2 + 2H_2O$. By this convention, a fuel rich flame will have an equivalence ratio greater than one and a fuel lean flame will have an equivalence ratio less than one. Depending on the equivalence ratio, and whether the diluent might be classed as inert, or an additional fuel or oxidizer, or an inhibitant, or any combination of these classifications, this change in flame velocity can be positive or negative. For the case of a diluent which may be classed as an inhibitant, the overall effect is to lower the flame velocity, with incremental addition of inhibitant eventually resulting in extinction of the flame.

All diluents will have an effect by virtue of the increase they bring to the heat capacity of the premixed gas[3]. The higher heat capacity of the mixture upon addition of a diluent initially removes energy from the flame. The energy removal lowers the flame temperature, reducing the rate of elementary chemical reactions responsible for flame propagation. This inhibitory effect is a physical manifestation. The secondary effect of the diluent is dependent upon whether the temperature and constituents within the flame enable the diluent to become a participant in the combustion chemistry. When the chemical reaction of the diluent with the premixed gas in the flame promotes flame velocity to the extent that the physical reduction of the flame velocity is overcome, the diluent may be classed as a fbel. When the diluent does not participate in the combustion chemistry, or when the diluent does participate and diluent generated species interfere or suppress generation of species important to flame propagation, the diluent may be classed as an inhibitant.

Measurement of the speed of a laminar flame propagating through a premixed gas is most often accomplished using the total area method from a schlieren image of a flame supported by a Bunsen-type burner*. When operated in a vertical configuration, the premixed gas exits fiom the burner tube orifice and is confined from above by a stationary conical combustion wave. Except

for the base and the tip of the cone, the wave is usually considered to be planar. Schlieren images of the height of the inner edge of the cone are used to geometrically calculate the area of the cone. The burning velocity is calculated by dividing the gas flow rate by the area of the combustion cone. Burning velocities calculated in this way for many different fuel/oxidizer systems can be a means of verifying flame kinetic mechanisms used in adiabatic laminar flame computer models[9].

We report here the development of a new device which uses pulsed flame velocimetry (PFV) to measure the degree to which an inhibitor decreases flame speed. The device is based upon the pulsed flame detection method developed at Tel Aviv University that was applied in a pulsed flame photometer detector by Cheskis et al[10a] and in a combined pulsed flame photometer and ionization detector as described by Tzanani and Amirav[10b]. Results of flame velocity measurements using this device show good correlation with previous results of flame velocity measurements, and good correlation with previous results of extinguishment studies. The new device is simple, inexpensive to build and operate, and provides repeatable results. The device is especially well suited to studies of flame inhibition by Halons because it relies on a non-optical technique, minimizing equipment cost and potential damage to sensitive optics from exposure to hot acid gases.

EXPERIMENTAL

The pulsed flame velocimeter consists of a rectangular aluminum block, 10 cm in length, with a square cross section of 25 cm^2 (see Figure 1). A 0.5 cm diameter circular cross section cavity has been bored down the center and the length of the Al block. Bored into one side of the block and into the central cavity (normal to the cavity axis) are three one cm diameter holes which house an igniter and two charge collectors. The igniter is positioned in the hole nearest the cavity exit. At the cavity end farthest away from the igniter (resistively heated Pt wire), is a plug with a small aperture allowing a flow of gas to pass into the cavity. BNC-type charge collectors, separated by 50 mm, are positioned in the remaining holes normal to the cavity axis. The entire apparatus is encased in heating tape and temperature is controlled and monitored (Omega Engineering) using Pt-Pt/10%Rh thermocouples embedded at opposite ends of the device. It is assumed that during operation, no temperature gradients exist within the aluminum block. Device temperature measured by thermocouples embedded in opposite ends of the device always agreed to within **2K.**

To operate the device, a premixed fuel\oxidizer\inhibitant gas is allowed to pass through the aperture into the cavity end furthest from the igniter. When the flowing column of gas reaches the heating element, the gas ignites and the combustion wave traverses the tube toward the rear of the device, passing the two charge collectors, which are connected in series. As the combustion wave passes each charge collector, a small voltage is generated which is recorded on a digital oscilloscope (LeCroy Industries), enabling calculation of flame velocity. When the combustion wave reaches the gas entrance aperture, combustion is quenched by a flame arrestor placed in the mouth of the aperture. A fresh sample of gas continuously flows into the device, exhausting the burned gas in the cavity, and the process repeats itself (see Figure **2).** Gas flow velocity is negligible compared to flame velocity. Each time the velocimeter operates, a small flame is observed at the open end of the device. Depending on device temperature (see below) total flow

rates varied from **0.214** to 0.3 liters/min, providing a flame repetition rate of approximately *2 Hz .*
Gas flow was controlled using calibrated gas flow controllers (MKS Industries). The
fuel/oxidizer equivalence ratio found to give most repeatable operation was 0.35. At equivalence
ratios higher (more rich) than this value, measured flame velocities showed increased scatter.

Prior to electrically controlling the device temperature, for methane/oxygen flames, steady
operation at a total flow of **0.214** liters per minute causes the device temperature to remain at
approximately 355K. For Halon inhibited flames, lower temperatures of the pulsed flame caused
this temperature to vary, depending on inhibitant. For this reason, and to minimize reactions of
acid gases with condensed water vapor on the walls of the cavity, the device was heated to and
maintained at a temperature of 385K. The tradeoff for operation at this temperature was that the
velocimeter would not function properly at this temperature at an equivalence ratio higher than
0.35. We believe that modification of the gas entry aperture (to minimize turbulence and increase
quenching efficiency) will enable operation at a greater range of equivalence ratios.

The average value of the flow rate of the premixed gas through the velocimeter was *3.6*
cm^{3}s^{-1}. This means that for a cavity length of 10 cm and a cavity diameter of 0.5 cm, the
expected pulsed flame frequency is **1.8 Hz ,** and considering the velocimeter temperature of 355K
(gas expansion), the pulsed flame frequency is expected to be **2.2 Hz**. This value is in close
agreement with the **−2** Hz operational frequency observed.

Gases were not preheated prior to entering the velocimeter. Each reported flame velocity
represents the summed average of 100 repetitions of the device. Measured flame velocity in tubes
has been shown to be angle sensitive'', so all data reported here were measured with the cavity
tilted approximately 10 degrees above horizontal, with the open end of the cavity directed slightly
upward. It was found that for flames inhibited by Halons, generation of HF gas caused the Pt
filament to burnout after only a few hundred repetitions. For the experiments using Halon
inhibitants, the Pt igniter was replaced by a methane/air flame positioned approximately **1** mm
away from the open end of the cavity.

All experiments were conducted at atmospheric pressure, Comparisons of flame speeds
for uninhibited methane/oxygen flames showed the method of ignition to have a negligible effect,
with the flame ignited measurements yielding a slightly higher flame speed than the glow ignited
measurements, possibly because the flame at the cavity entrance caused excess heating of the gas
just prior to flame ignition. No difference in flame velocities in neat methane/oxygen mixtures
was seen when the Pt filament was exchanged for a Kanthal AF-1 wire filament or for a Nichrome
filament. When the Pt filament was used, decreasing filament current after the device was
warmed to operating temperature caused the device to stop operating, indicating that the Pt
filament was not igniting the gas catalytically. All gases were supplied by Matheson, Inc., and
were used without further purification.

RESULTS and DISCUSSION

Figure 3 shows the measured flame velocity for uninhibited flames as a function of
equivalence ratio for the pulsed flame velocimeter with the velocimeter temperature at 355 K.

Total flow rates varied from 0.06 to 0.3 liters/min. At 385 K, the device would not operate at an equivalence ratio higher than 0.35. At 385 K and at values of the equivalence ratio above 0.35, the flame would stabilize at the aperture through which gases entered the cavity, negating any attempts to measure flame velocities.

Figure 3 shows flame velocities for methane/oxygen flames as a function of equivalence ratio measured with the PFV and calculated using the adiabatic laminar flame code for a premixed gas temperature of 355 K. The flame speed of a premixed methane/oxygen flame was calculated using computer codes developed at the Sandia National Laboratories[12]. The flame speed is calculated for a freely propagating flame at an initial temperature of 355 K at one atmosphere pressure. For the calculations, the GRIMECH12 kinetic mechanism of methane combustion was employed. For each equivalence ratio in Figure 3, calculated laminar adiabatic flame velocities are less than what is measured using the PFV[12].

The explanation for this difference is as follows. Figure 4 shows a drawing of the appearance of the flame front in a horizontally positioned tube containing a premixed flammable gas when the tube is closed at one end and ignited at the open end[13]. Gas flow near the walls of the cavity is slower than near the axis of the cavity because of viscous drag. Because expanding gas cannot escape from the closed end of the tube, gas flows opposite to the direction of the combustion wave near the walls of the cavity. The asymmetry of the combustion wave is caused by buoyancy of the hot gases within the tube. The flame velocity relative to the tube is equal to the sum of the normal flame velocity and the horizontal component of the cold gas velocity near the most advanced flame point in Figure 4. The flame velocity measured by the velocimeter (the velocity relative to the cavity) may be given by":

$$V = A V_{lam} / \pi R^2$$

where V is the measured flame velocity, V_{lam} is the calculated laminar adiabatic flame speed, A is the area of the flame surface, and R is the radius of the cross section of the cavity. While not accounting for heat losses to the walls of the device as a function of the flame surface, or accounting for the asymmetry of the flame front with regard to the cavity axis, this equation does show how measured velocities in the PFV may be higher than those calculated using adiabatic flame codes. We believe the scatter in the experimental data in Figure 3 at high flame velocity (high equivalence ratio) is caused by turbulence due to elongation and asymmetry of the flame front.

Figure 5 shows measured flame velocities for a premixed methane/oxygen flame inhibited by CF_3Br as a function of percent volume CF_3Br at two different device temperatures. From this figure it may be seen that heat transfer from the walls of the cavity to the premixed gas has an important effect on measured flame speed. The slight sigmoid shape of the data at low levels of inhibitant concentration is common to all data measured using the device. At this time we do not have an explanation for this behavior. We estimate the error in flame speeds measured with a fuel/oxidizer equivalence ratio of 0.35 to be approximately 10%.

From the previous discussion, it may be argued that the velocimeter measurements differ

from total area method measurements in several ways. By the nature of the design, the premixed gas is mixed with burned gas prior to reaching the igniter. Because the igniter represents a constant energy source, the premixed gas will dilute the burned gas in the cavity until a flammability limit is reached, at which time the velocimeter will operate. Recently, some experiments were conducted in which flame velocity was measured as a hnction of distance from the igniter, using a velocimeter equipped with optical ports through which OH emission (from the flame front) was monitored. It was found that over the length of the device, the flame velocity was constant to within a few percent. Since this would not be the case if mixing of the premixture with burned gases were important, we have concluded that this is not a major source of error in the data. *Also,* it has been shown in Figure 5 that the temperature of the walls of the cavity play a significant role in determining flame velocity, possibly because the temperature influences the asymmetry of the flame front, or influences heterogeneous chemistry occurring on the tube walls.

Figure 6 shows flame speeds of premixed methane/oxygen flames inhibited by Ar, CF_2H_2, CF_3H, and CF, as a function of volume percent inhibitant. Inhibition of flames by Ar is assumed to occur via a purely physical mechanism. The effect of addition of CF_2H_2 to the premixed gas is to act as a fuel. After only a few percent addition of CF_2H_2, the effective equivalence ratio of the premixed gas was raised beyond 0.35 to the extent that the velocimeter ceased to operate, with the $CH_4/O_2/CF_2H_2$ flame burning at the aperture entrance to the cavity. CF_3H was found to be superior to Ar as a flame speed inhibitant on a percent volume basis, and CF, was found to be slightly superior as a flame speed inhibitant to CF_3H. This result is in contrast to laminar flame speed calculations[9] and to measurements of flame speeds using the total area method for methane/air flames inhibited by the fluoromethanes. Laminar adiabatic methane/air flame modeling calculations predict that CF, acts as an inhibitant only by changing the heat capacity of the combusting mixture (physical mechanism). CF_3H, however, is a good source of the CF, radical, which may react via the mechanism[14]:

$$CF, + OH = CF_2O + HF$$
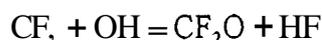
This reaction acts as an OH scavenger, so for methandair flames, CF_3H is expected to inhibit combustion via chemical and physical mechanisms.

We believe that for methane/oxygen flames, CF, participates in flame inhibition via both physical and chemical mechanisms. Figure 7 shows the infrared spectrum measured through the flame zone of an atmospheric pressure counterflow diffision burner for a methane/air and a methane/oxygen flame to which 1.3% CF, (by volume of total flow) has been added. Formation of HF (near 3500 cm^{-1} in the spectrum of the inhibited methane/oxygen flame) indicates cleavage of the C-F bond in CF,. No HF formation is observable in the infrared spectrum of the methane/air flame inhibited by CF,. We believe the difference between the PFV measurements using inhibited methane/oxygen flames and total area method measurements of methane/air flame speeds for CF_3H inhibited flames relative to CF, inhibited flames may be due to the lower flame temperatures in the methandair flames. Laminar flame calculations[12] for premixed methane/oxygen/CF_4 and methane/air/CF_4 flames show peak temperatures for the two flames differing by approximately 700K ($T_{CH4/air/CF4} < T_{CH4/O2/CF4}$).

Figure 8 shows flame speeds of the inhibited methane/oxygen flame (phi=0.35) as a fbnction of weight percent inhibitant. It has been suggested[17] that flammabilities of fuel/oxidizer/halocarbon gas mixtures are dependent on the weight percent of halocarbon in the mixture. From Figure 8, it may be seen that when flame speed reduction is plotted versus weight percent inhibitant, inhibition efficiency among the fluorocarbons becomes more equal than when expressed on a volume percent basis. This indicates that flame speed reduction via a physical mechanism is important when flame inhibition is measured using the PFV. The fact that CF_2H_2 acts as a fuel indicates that the device is also sensitive to diluents which may participate in flame chemistry. *Also,* it may be seen that on a weight percent basis up to approximately 20 percent, CF_3H and CF_4 cause similar flame speed reductions.

Figure 9 shows flame speeds of the methane/oxygen flame (phi=0.35) inhibited by Ar, CF_4, and by CF_3Br (Halon 1301) as a function of volume percent inhibitant. Of all inhibitants examined in this study, CF_3Br was the most effective on a percent volume basis in reducing flame velocity. Figure 10 shows the data in Figure 9 plotted on a weight percent basis. From this figure, it may be seen that CF_3Br is still the "best" flame speed reducer examined in this study, but that the difference in flame speed reduction between methane/oxygen flames (phi=0.35) doped with CF_3Br or CF_4 when examined on an inhibitant weight percent basis is less than what is observed when the flame speed reduction is examined on an inhibitant volume percent basis.

CONCLUSION

Using the pulsed flame velocimeter, it is possible to measure the effect of various diluents on flame speed in a flame propagating in a tube containing a premixed methane/oxygen gas mixture. Results of measurements using the pulsed flame velocimeter of flame speed reduction in methane/oxygen mixtures by various Halons are qualitatively similar to measurements of flame speed obtained using the total area method. The device holds promise as a fast, efficient, and inexpensive tool by which flame inhibitor efficiency may be measured. However, more measurements on a wide variety of inhibitors need to be done before the device can become a complement to the many other test methods available for predicting flame inhibitor efficiency. Measurements are currently under way using a new series of inhibitors, and the device has been redesigned to allow operation at higher fuel/oxidizer equivalence ratios.

ACKNOWLEDGEMENT

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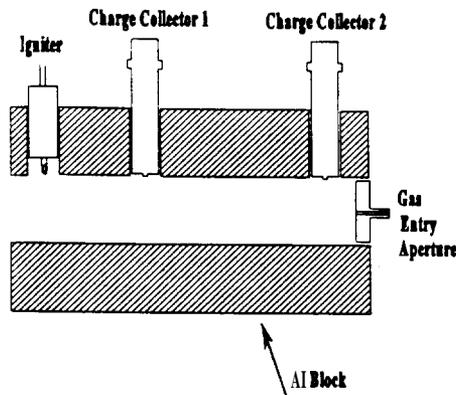
Figure 1: Cross sectional view of the Pulsed Flame Velocimeter (PFV) showing the igniter, charge collectors, and gas entry aperture.
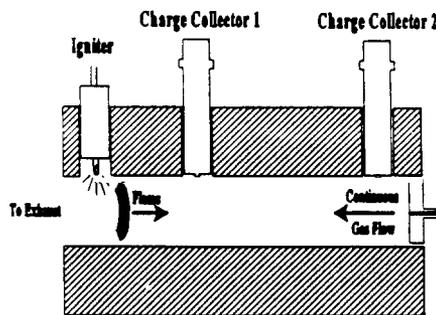
Figure 2: Cross sectional view of the PFV during operation. The fuel/oxidizer gas mixture flows continuously. Gas flow rates are negligible compared to flame velocities.
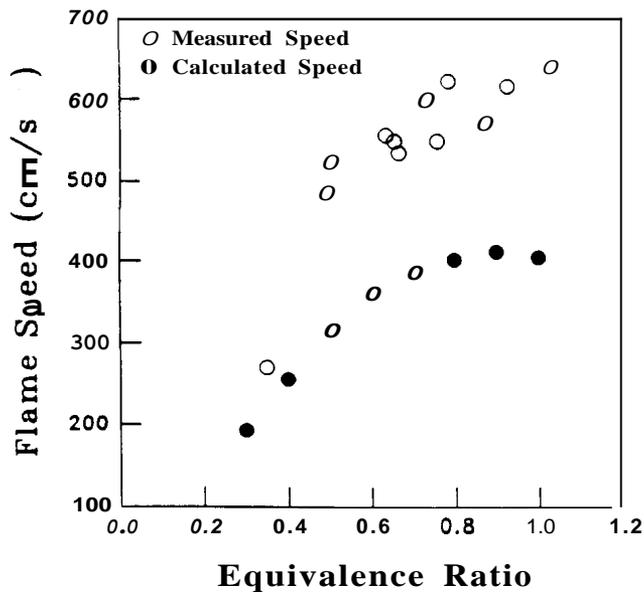
Figure 3: Flame velocity as a function of equivalence ratio measured with the PFV, and calculated using the **SANDIA** laminar flame code. The premixed gas temperature **is** 355K.
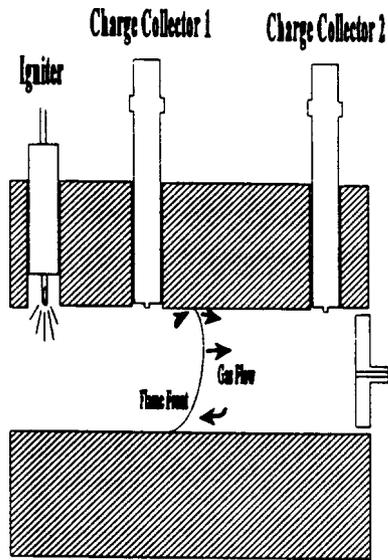
Figure **4:** Approximate appearance of the flame front and gas motion in a horizontal tube closed at one end and containing a premixed fuel/oxidizer gas after ignition at the open end. Note **gas** buoyancy effects and asymmetry of flame front with respect to the cavity **axis.** This figure is adapted from reference **13.**
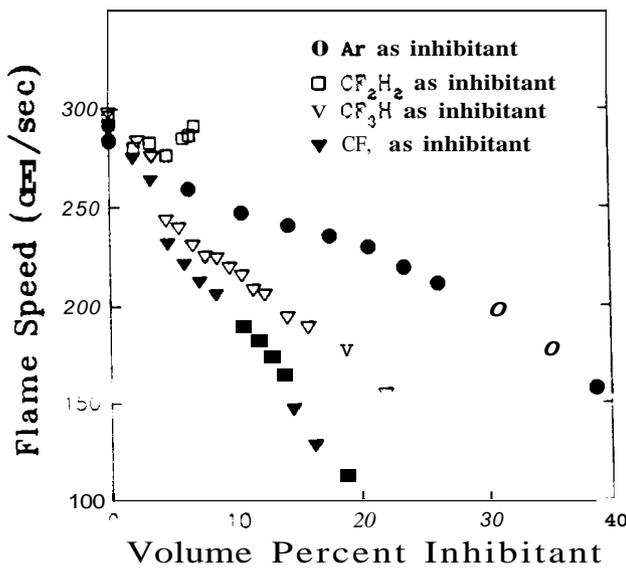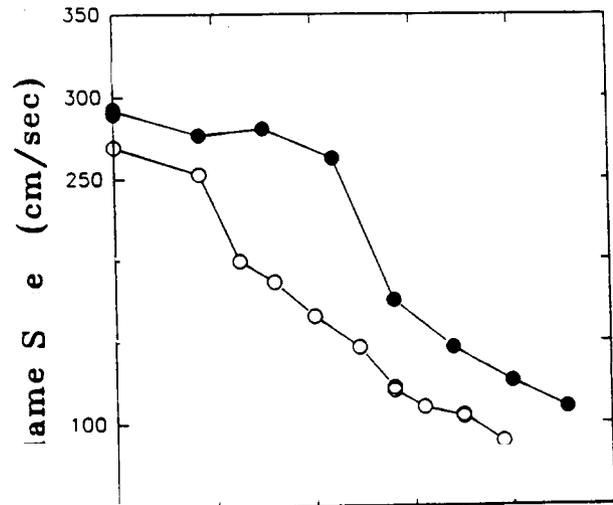
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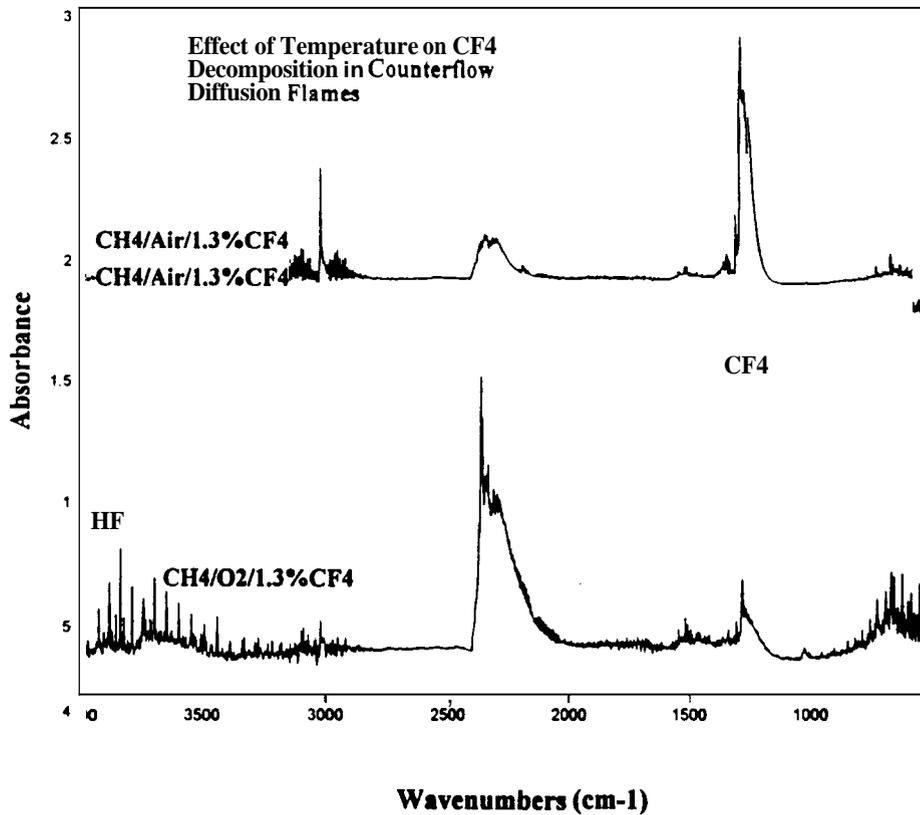
Figure **7:** Infrared spectra measured through the flame region of an atmospheric pressure counterflow difision burner for methane/oxygen and methandair flames doped with **1.3%** (by volume) CF,.
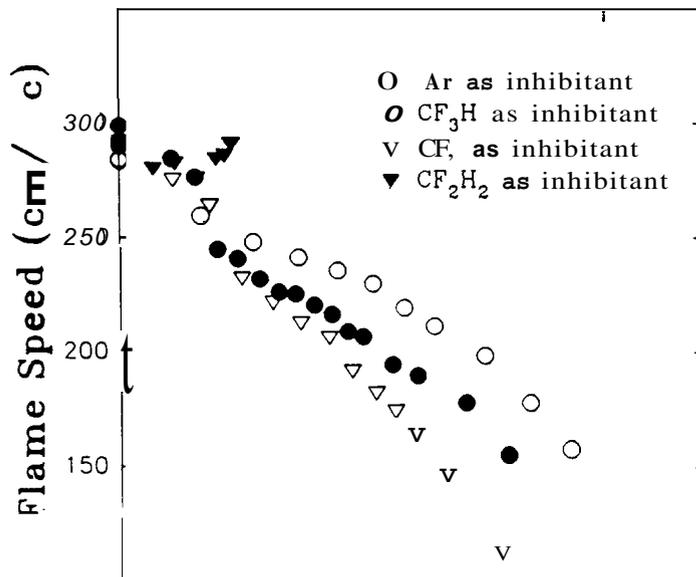
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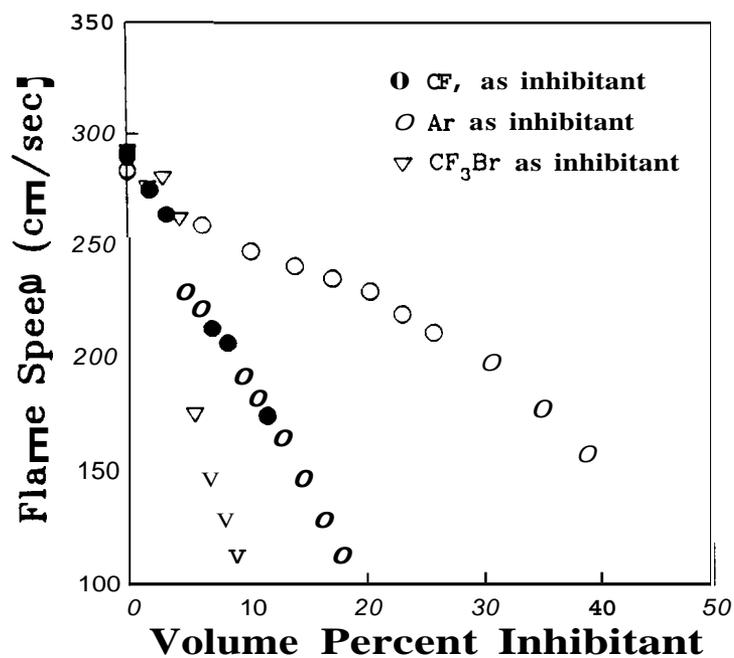
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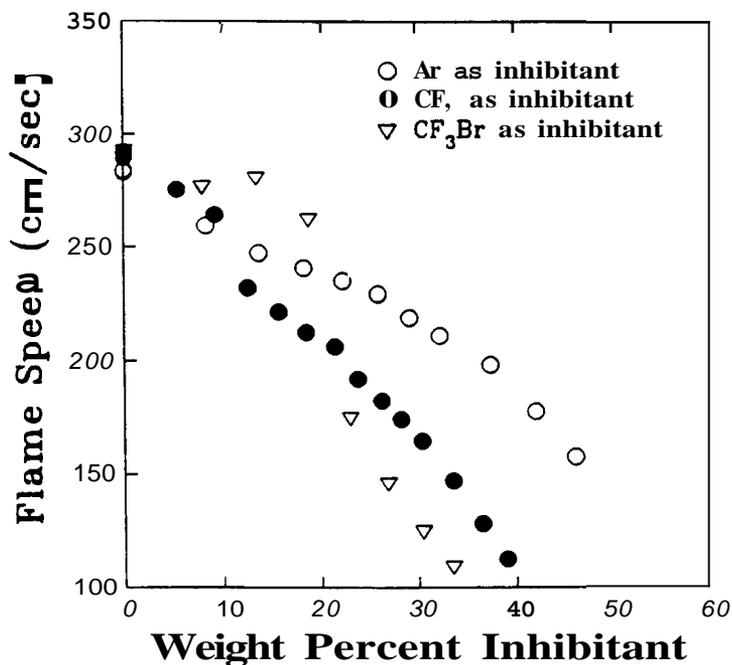
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