A SURVEY OF TECHNIQUES FOR FIRE SUPPRESSANT STUDIES

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INTRODUCTION

Fire suppressant studies have included field and laboratory experiments analyzing the compounds produced when a candidate fire suppressant is used to extinguish a fire or flame. It would seem beneficial at this time to review the results obtained to date along with instrumentation used and to discuss what additional information and techniques might be useful (Table 1). Techniques such as FTIR spectroscopy, mass spectroscopy and various gas chromatography techniques have proven useful in these studies in the analyses of toxic volatile gases and trace organic compounds. However, one aspect of fire suppression which has not been extensively studied experimentally is the role of free radicals. A study of the decay of OH and other free radicals could provide data useful in building a model of suppressant action and in selecting the most efficient fire suppressants.

Table 1: Instrumental Approaches for Decomposition Product Analysis

ANALYTICAL METHOD	SPECIES DETECTED
OPTICAL SPECTROSCOPY	
Infrared (FTIR)	IR Active Heteronuclear Molecules.
Fluorescence (LIF)	Free Radicals, Molecules.
Raman	IR Active Molecules, Homonuclear Molecules.
UV-Vis	Free Radicals, Molecules Atomic Species, Metals.
OTHER ANALYTICAL TECHNIQUES	
Gas Chromatography (GC)	Organic Cmpds, Halogenated Organics.
Mass Spectroscopy (MS)	Organic Cmpds, Inorganic Cmpds.

TECHNIQUES IN CURRENT FIRE SUPPRESSION STUDIES

FTIR Spectroscopy

Almost any compound having covalent bonds, whether organic or inorganic, will be found to absorb radiation in the infrared region of the electromagnetic spectrum [1]. If a dipole exists as in A-B type molecules, energy is absorbed when the frequency of the radiation and the frequency of the vibration coincide. Symmetric bonds like those of Br_2 or I_2 will not absorb infrared radiation because they do not have a dipole moment.

Over the past several years, FTIR spectroscopy has been used in field and laboratory studies to analyze the compounds produced when fire suppressants are applied to a fire [2,3]. There are several reasons why this technique was chosen [2]:

1. Infrared spectroscopy allows the simultaneous determination of a variety of compounds;
2. Spectra can be obtained rapidly, without the use of sampling bags or cylinders, minimizing concerns with absorption or contamination;
3. Unexpected products can be readily identified; and
4. It can be easily adapted to field studies due to the development of hardened process spectrometers.

Both field and laboratory studies have identified the halogen acids (HF, for example), COF_2 and CO as toxic by-products when a fire is suppressed by Halons or haolgenated organic compounds.

FTIR spectroscopy has proven its usefulness in both the laboratory and in the field. More importantly, the results from the field and laboratory agreed as far as what compounds were detected during a fire suppression event. This would suggest that laboratory studies could be used to screen candidate fire suppressants for not only their effectiveness as fire suppressants but also for the formation of toxic compounds. In addition, with time resolved FTIR, it is possible to follow the production and decay of the major compounds produced in a fire suppression event. This information could also help in elucidating possible mechanisms of fire suppression.

Other Analytical Techniques

When it is necessary to analyze a wide variety of molecular compounds at very low concentrations, additional techniques are needed. These techniques have included mass spectrometry as well as gas chromatography coupled with various types of detectors.

Gas chromatography (GC) is a columnar separation technique based on the differential interaction of volatilized sample components with a liquid or solid stationary phase [4]. As sample components are transported through a column containing the stationary phase by a mobile inert carrier gas, they distribute themselves between the two phases. Any component that is weakly retained by the stationary phase will be propelled to the end of the column at nearly the velocity of

Table 2. Detectors in Gas Chromatography

DETECTOR	THEORY OF DETECTION	COMPOUNDS DETECTED
Mass Selective (MSD)	Ionized compounds are separated by m/e ratio by applied magnetic field and detected by electron multiplier	Wide range of organic and inorganic compounds
Flame Ionization (FID)	Organic compound in H_2 flame yields ions in proportion to mass of carbon it contains	Majority of organic compounds
Electron Capture (ECD)	Compounds capturing emitted electrons reduce the number of electrons collected at the anode	Especially effective for halogenated organics
OTHERS		
Thermal Conductivity (TCD)	Conductivity change in carrier gas due to presence of analyte	Wide range of organic compounds
Photoionization (PID)	Ionizable molecules absorb photons	Alkenes, Alkynes Aromatic cmpds

the carrier gas. A component that interacts strongly with the stationary phase will emerge bands at the end of the column. When the components elute from a GC column, they can be monitored by a variety of detectors.

Table 2 lists the most common GC detectors in fire suppression studies which include mass selective detectors (MSD), flame ionization detectors (FID) and electron capture detectors (ECD). These techniques have been used to determine the concentration profiles of the stable by-products of combustion and fire suppression. The GC/MS method has been particularly useful in determining a wide range of volatile and semi-volatile organic compounds produced during suppression events. These compounds include polyaromatic compounds, dioxins, furans and the simple halogenated organic compounds. Results from field studies showed significant levels of benzene, toluene and halocarbons but none exceeded the IDLH (immediately dangerous to life and health) levels. Likewise, SVOC and dioxin/furan results indicated less than IDLH levels of some PAHs and dioxins/furans.

Other GC techniques used include GC/FID and GC/ECD. As suggested in Table 2 both of these detectors are somewhat compound selective. The FID is particularly ideal for pure hydrocarbons. Its sensitivity decreases for substituted hydrocarbons such as halogenated organics. The ECD, however, is especially suited for these types of compuonds and would give complementary information to the FID. Also included in the table are two additional GC detectors which could prove useful in certain aspects of fire suppression studies.

Mass spectrometry can also be used directly on-line without the compound separation performed by GC. This direct MS method is currently only feasible in laboratory experiments. This method has been used in past laboratory studies by drawing combustion products from a laboratory burner into a mass spectrometer by a feflon capillary [5]. The masses monitored corresponded to N_2, O_2, H_2O, Ar, CO_2, HF, HCl and HBr.

ADDITIONAL OPTICAL TECHNIQUES FOR FIRE SUPPRESSION STUDIES

The techniques used to date have produced important information on the toxic by-products of fire suppression, an important consideration in the study of Halon alternatives. Also important in the suppression of fires is the free radical mechanisms which are necessary to maintain a fire. To date, few laboratory studies have been conducted to determine their behavior in fire suppression. The suppression of free radicals is the major mechanism in the suppression of fires by halons. It will probably be an important mechanism for some of the halon alternatives that are now being considered. To illustrate this action let us represent the halogen active in fire suppression in CF_3Cl, CF_3Br and CF_3I by X. The interaction of CF_3X with hydrocarbons typically leads to the acid HX. This acid can dramatically deplete OH radicals by transforming them to less reactive H_2 and O_2 molecules by many passages through the reaction loop

$$HX + OH \dashrightarrow XO + H_2$$

$$XO + OH \dashrightarrow HX + O_2$$

The rates of these reactions are very fast, so that the OH radical pool can be quickly exhausted. This lowers the overall rate of chain branching in the fire chemistry and can lead to the suppression of a hydrocarbon fire. It is with these facts in mind that we discuss the following optical techniques.

For an overview of other possible analytical instrumentation techniques, there is applicable information in the studies of combustion flames. Most of these studies analyze the mechanism by which fuel burns by using spectroscopic techniques to directly probe the flame or by sampling the gases in the flame with subsequent detection. Following is a discussion of optical techniques that have been important in the study of flames.

Most of the spectroscopic techniques used in these studies detect molecular species as well as radicals and sometimes atoms. One of the more common spectroscopic techniques is laser induced fluoroescence (LIF). Fluorescence may occur after a quantum of radiation has excited an outer electron in a molecule to a higher level. The fluorescence is detected by photomultiplier tubes (PMT) and a fast transient digitizer, for example. Experimental conditions are controlled by a computer.

Fluorescence studies include detection of radicals in combustion flames as well as calculation of reaction rates and mechanisms of reaction. Table 3 includes a list of combustion intermediates which can be detected by LIF. This enables the measurements of relative species concentrations in the same spatial volume making it easier to deduce probable reaction mechanisms in flames. Fluorescence studies have also been devoted to studying concentrations of the important reactant OH radical in combustion chemistry [6].

Table 3. Combustion Intermediates Detected by LIF

OH
CH CN C_2
NH NH_2 NO NO_2 HNO
S_2 SH SO SO_2
CS CS_2
CH_3O $CH_{2}0$ C_2O
HCN

Raman techniques have also been used to study flames. Raman spectroscopy is an important mode of gaining information about molecules based upon the scattering of monochromatic light. Incident radiation induces an oscillating dipole in molecules. The incident radiation can then interact with molecular motions such as vibrations with the result that some oscillating dipoles radiate at new wavelengths and give Raman Scattering [4]. Raman spectroscopy is usually limited to the detection of major constituents because the scattering cross sections are small resulting in low signal levels. However, the list of major constituents would be long since the number of infrared active molecules is large. Unlike FTIR, this list would also include homonuclear compounds such as Br_2 and I_2, two probable by-products of Halon fire suppression events.

Coherent Anti-Stokes Raman Spectroscopy (CARS) is a special kind of Raman spectroscopy that is also used in combustion studies. Anti-Stokes scattering occurs when an electron is excited from a ground state to an excited state via a virtual state. The scattered photon is a coherent beam of high intensity and small divergence, yielding high signal levels as well as a high degree of discrimination against a background flame. Thus CARS is suitable for use in flame chemistry [4,7].

These optical techniques could contribute in several areas to fire suppression studies. With LIF spectroscopy, radical intermediates in combustion processes as well as radicals important in fire suppression could be detected. This information would make it possible to understand the important mechanisms of fire suppression and may help in finding an effective replacement for halon suppressants. The techniques based on Raman spectroscopy could be especially useful in detecting homonuclear compounds such as Br_2, I_2, etc. Since Br_2 and I_2 are most likely decomposition products during a fire suppression event, the detection of these compounds could also prove useful in elucidating reaction mechanisms. However, while laboratory studies of fire suppression events using LIF and Raman techniques is feasible, these techniques have not been proven to be field capable. In addition, these techniques all require lasers as an intense monochromatic source. This fact limits the number of different compounds or radicals that could be detected.

Multi-channel UV-Vis Spectroscopy and Fire

UV-Vis spectroscopy, applied in past military and space programs [8,9], eventually led to the recognition and quantification of the stratospheric ozone depletion problem. The ozone depletion potential of Halons is one of the major reasons alternatives are now actively being sought. Since UV-Vis spectroscopy can contribute to the selection of alternatives it would seem that we have come full circle.

With UV-Vis spectoscopy, it is possible to use the flame as an emission source to directly determine the behavior of free radicals in a flame. Of particular importance are the strong intensities of the spectra of OH, CH, CN, NO, NH, NH_3, CH_3, C_2H_2, C_6H_6, HNO_2, CH_2O, CHO and CHOOH. The fact that free radicals tend to be strongly represented in electronic emissions of flames [8-15] should be very advantageous in fire and fire suppressant studies. Our past spectroscopic experiments with diffusion flames and with flames into which particles have been injected [16-18] also show a strong black body continuum at longer wavelengths (>500 nm).

In Multichannel Spectroscopy, the grating is fixed and a linear array of charge coupled devices is used as detectors; each viewing a different wavelength at the exit aperture. Typical arrays have 128, 256, 512 and 1024 elements. Thus these numbers of point spectra can be recorded simultaneously; the major advantage over scanning monochromators. Array based spectrometers also have the potential for better stability and reproducibility than scanning spectrometers since they have no moving parts.

Figures 1 and 2 [from reference 19 and 20] illustrate the type of data possible using current multichannel UV-Vis spectroscopy. Figure 1 shows how intensely the radicals emit in a premixed propane (390 ml/min) and air (7.2 L/min) flame. The most intense peaks are from the radicals OH, CH and C_2. Figure 2(a) illustrates the changes that occur when propane is not premixed with air. Under these diffusion conditions, the temperature of the flame is cooler and a bright yellow as opposed to the blue color of the hotter flame. Not only do the counts decrease dramatically, but the Planck continuum rises above 500 nm, as previously observed [13,16-18]. Figure 2(b) is the same diffusion flame as in Figure 2(a) but with 94 ml/min of Halon 1211 premixed whth the fuel. The biggest change with the added suppressant is the increase in the continuum.

Another possible advantage to the multichannel UV-Vis system discussed here is that he time variation of the free radicals might be recorded as the fire is put out. It is not unreasonable to anticipate that the emission data will contain useful information that will help in assessing the effectiveness of the fire suppressant and to show the transient molecules formed during the quenching of the fire. A great advantage of the ultraviolet-visible spectral region is that it should serve equally well for halon suppressant or aerosol suppressant studies since metals, such as sodium, lead and other strong emitters, if present in the fuel or suppressant, would be expected to be observed in the emissions.[21,22].

With the help of a continuum light source with strong MUV intensities such as a high pressure xenon arc or a deuterium lamp, we might also use the same spectral system to study absorption by the gases exiting the flame. This might also give an immediate indication of the product gases generated in the fuel-suppressant fire chemistry.

The major advantages of MUVV is the immediate and fast time information that might be gained with respect to specific species represented in the hot parts of the fire in emissions or in the colder parts of the fire in absorption. Of particular importance in halon replacement studies would be the clarification of the free radical chain branching mechanisms. The fast time changes in OH, CH and other free radicals in a fire suppression event might provide data useful in building a model of suppressant action. With such a model and a rapid data collection system, information might be provided for choosing efficient strategies for suppressing fires.

Conclusions

The study of fire suppressants has taken on increasing importance due to the enforcement of the Montreal Protocol. Halocarbons previously used as fire suppressants are being phased out because of their high ozone depletion potential (ODP) and/or their high global warming potential (GWP). FTIR spectroscopy has been especially useful in this area as a means to study major toxic compounds produced during a fire suppression event. The advantages of FTIR include the rapid, simultaneous detection of compounds in the ppm range and it's easy adaptability for field studies.

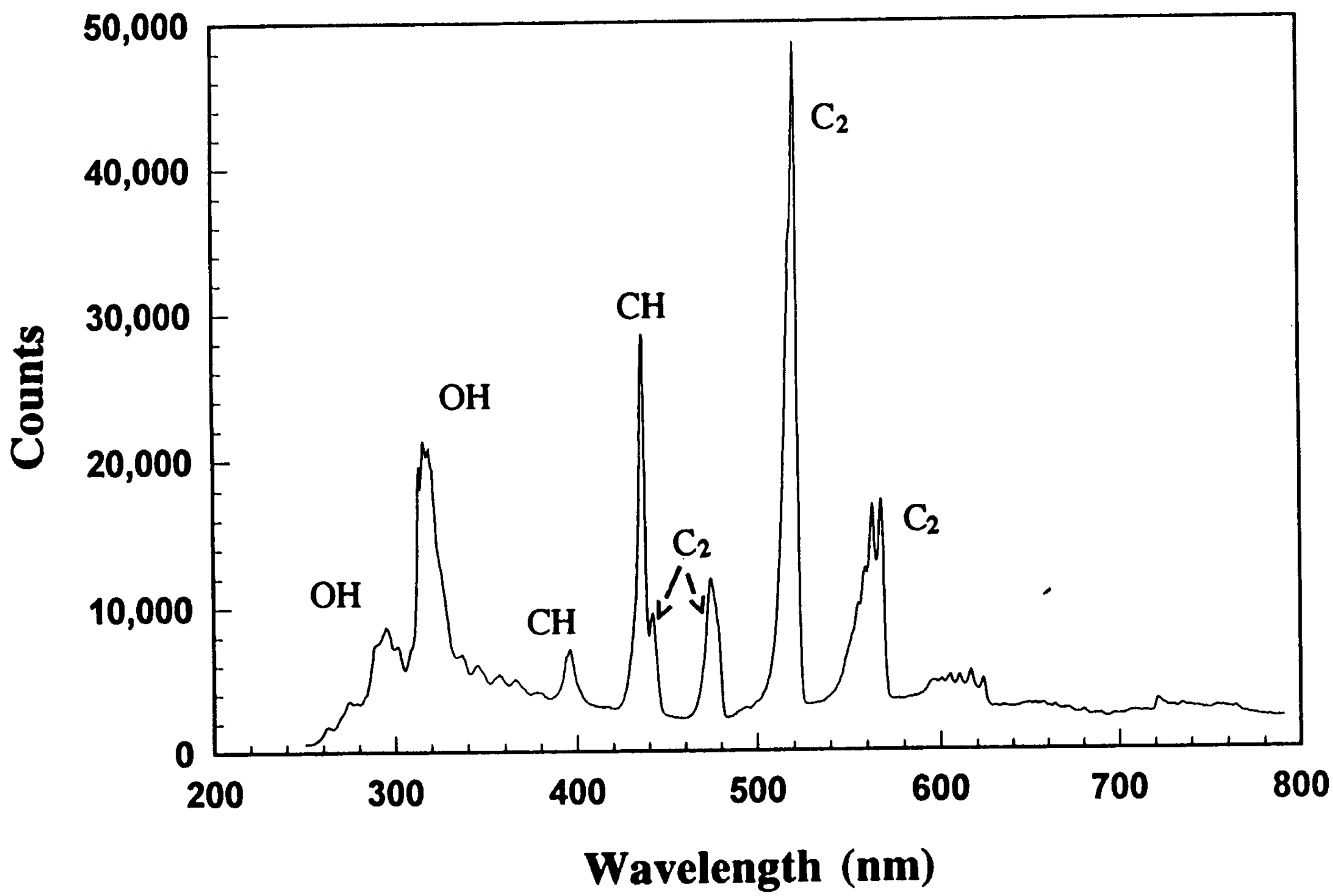

Figure 1. Spectra of major radicals obtained from a premixed propane (390 ml/min) and air (7.2 L/min) flame. This spectra was obtained from a 0.125 m spectrometer with a 400 line/mm grating and an exposure time of 0.4 s [from reference 19 and 20].

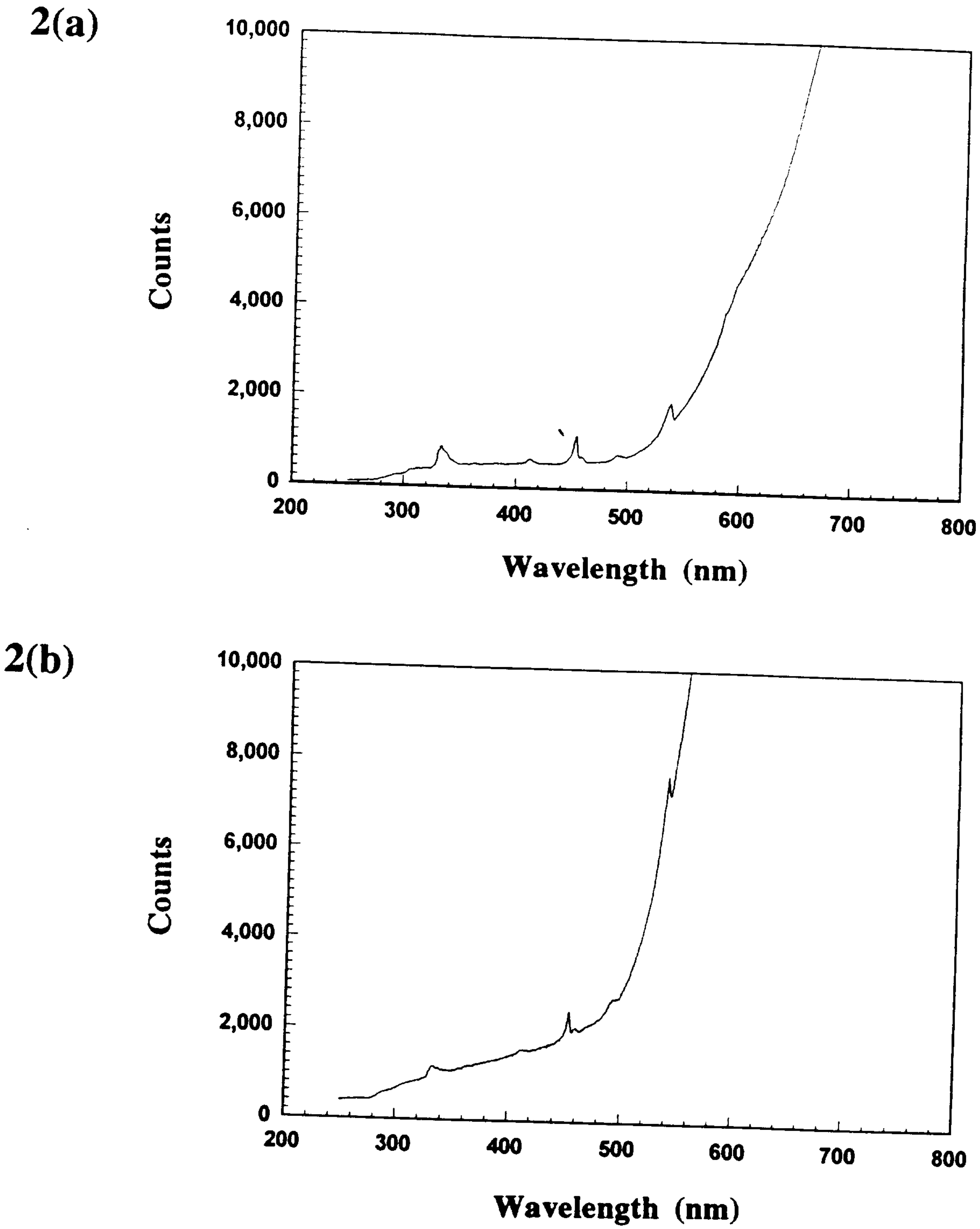

Figure 2. (a) Spectra obtained from a propane difusion flame. The intensity of the free radical emissions decreases because of the cooler flame. The bright yellow flame is also associated with a Planck continuum rising above 500 nm. Conditions are as in Figure 1 but with a 0.1 s exposure; (b) Spectra obtained from a premixed propane/Halon 1211 (94 ml/min) flame. Notice that the background and continuum increase with the addition of the suppressant. All other conditions as in (a) [from reference 19 and 20].

If FTIR is coupled with additional sampling and GC separation techniques, a relatively complete list of compounds produced during fire suppression is obtained.

However, the chemistry not revealed by these techniques is the free radical chemistry important in combustion and fire suppression. This chemistry is probably the most important mechanism in fire suppression and largely determines how effective a material is at suppressing a fire. These radicals are active in the UV-Vis region of the electromagnetic spectrum and are detectable at ppb levels. Another advantage of using MUV-Vis spectroscopy is that it should work for aerosol fire suppressants as well as halon suppressants. It would seem that augmenting currently used techniques with MUV-Vis techniques could contribute to an improved understanding of fire suppression mechanisms and aid in the selection of alternatives to halon.

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