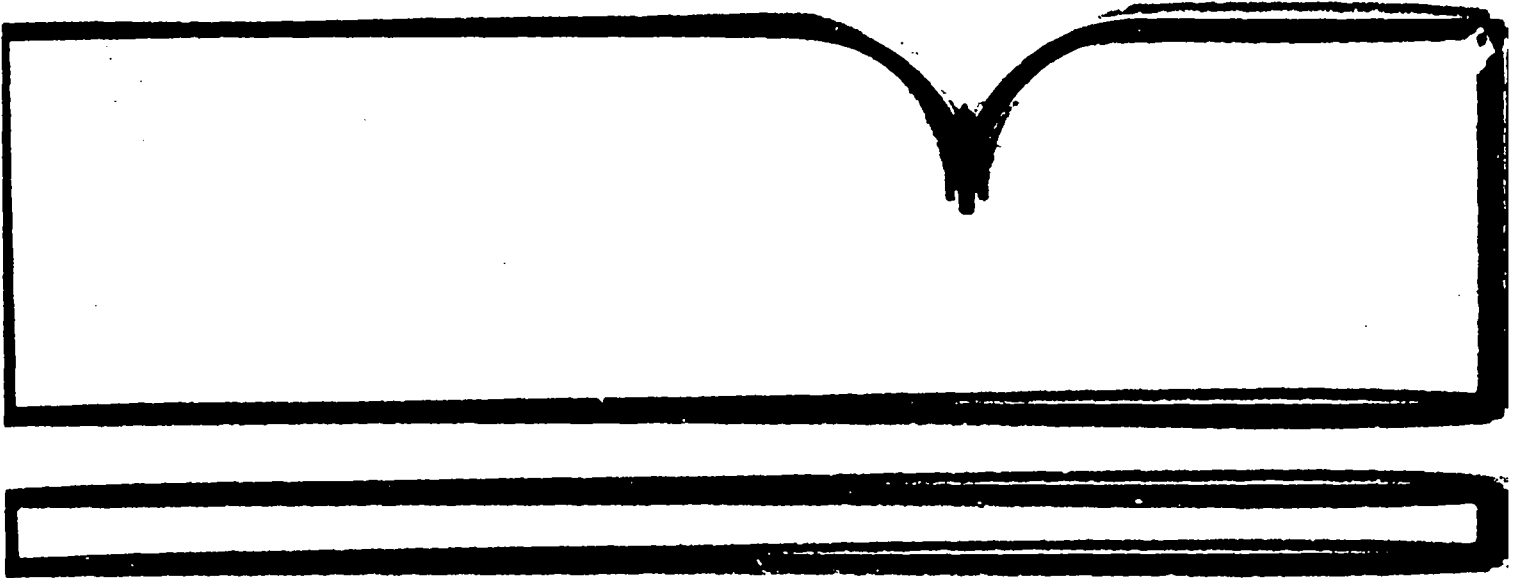


**Formation of PICs (Products of
Incomplete Combustion) from the
Combustion of Chlorinated Materials**

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Cincinnati, OH**

Apr 88



THE FORMATION OF PICs FROM THE COMBUSTION OF CHLORINATED MATERIALS

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ABSTRACT

The formation of unwanted Products of Incomplete Combustion (PICs) from the incineration of hazardous wastes under sub-optimal conditions must be avoided if incineration is to be effectively used to treat hazardous wastes. Studies of the thermal behavior of chlorinated C₁s (methanes) and C₂s (ethanes and ethenes) in non-flame, flat-flame, and shock tube devices have yielded results which offer a plausible explanation for the formation of certain PICs. To determine whether the same results are obtained in a larger, more complicated device, two mixtures of chlorinated methanes and two mixtures of chlorinated ethanes and ethenes were burned under "high" and "low" oxygen conditions in a Turbulent Flame Reactor (TFR). Results of these tests indicate that the earlier test results predict some of the emissions observed from the TFR. Soot formation affects the emissions of volatile organic chemicals in ways not predicted by the earlier studies however.

Introduction

Public acceptance of hazardous waste incineration is complicated by the fact that toxic byproducts (also known as Products of Incomplete Combustion or PICs) can sometimes form from materials fed to incinerators. Although they are formed in small quantities, these materials can sometimes (though not always) be more toxic than the original chemicals fed to the incinerator for disposal. This is a cause for concern. To address this concern studies have been undertaken to determine how best to minimize the formation of these compounds.

The Problem

Studying the formation of PICs in hazardous waste incinerators is complicated by three factors. First, the waste stream fed to most incinerators is a multi-component, and sometimes even a multi-phase, mixture of organic and inorganic materials. Second, the combustion chemistry of each component of the feed stream consists of multi-step free radical chain reaction mechanisms which can result in the formation of a variety of reaction products. The relative amounts of reaction products which ultimately form depends on the conditions existing within the incinerator at the time the waste is incinerated. Third, the conditions existing within the incinerator are neither precisely known nor controlled. That is, while incinerator operating temperature and oxygen level may be known well enough for process control purposes, localized fluctuations in these and other parameters which may result in PIC formation may not be discernable using conventional measurement techniques. Sorting through these complications first requires an understanding of the combustion chemistry of the most likely components of the hazardous waste feed streams fed to incinerators.

Chlorinated organic compounds are most often found in hazardous waste streams fed to incinerators. Short chain chlorinated hydrocarbons, specifically chlorinated methanes and ethenes, have been studied most extensively in non-flame thermal destruction units, flat-flame burners and shock tubes (1,2,3,4,5,6,7,8). Each of these three experimental devices has rather uniform and predictable temperature and oxygen concentration profiles. Their

predictability and controllability makes these devices significantly different from field-scale combustion devices for reasons mentioned above. Nevertheless, results from these studies provide a logical starting point for this effort.

The Approach

To see how well the results of studies of chlorinated compounds using these small-scale devices compared to a more realistic combustion environment, four mixtures of chlorinated methanes, ethanes and ethenes were burned in a Turbulent Flame Reactor (TFR) under "high" and "low" oxygen conditions. The gaseous emissions were collected and characterized. These data were then compared with the results of the earlier studies to determine if temperature and concentration gradients and also localized fluctuations affected the type and quantity of PICs formed.

Tables 1 and 2 list the experimental mixtures used and also the test conditions evaluated. The large amount of heptane added to each mixture was required to sustain combustion in the TFR. Although the presence of this material undoubtedly affected the combustion of the test chemicals fed, it does represent a somewhat more realistic situation than in the smaller devices. The "high" and "low" oxygen levels were chosen because they represented the limits of flame stability for the device. Even though the "low" oxygen condition was still on the average an oxidative condition (115% theoretical air), fuel/air mixing was apparently inefficient enough to result in excessive soot formation.

Table 1. Experimental Test Mixtures and Composition

	<u>Composition</u>	<u>Mass</u> (grams)	<u>Moles</u>	<u>Properties</u>			
				<u>Mol %</u>	<u>Cl/H</u> (excluding heptane)	<u>Wt% Cl</u>	<u>Mol% Cl</u>
Mixture 1A:	CH ₂ Cl ₂	5.682	.0668	.25	6.4	6.65	.87
	CHCl ₃	78.47	.66	2.49			
	CCl ₄	113.642	.74	2.80			
	C ₇ H ₁₆	2500	25.00	94.46			
Mixture 1B:	CH ₂ Cl ₂	55.05	.6476	2.42	2.0	6.03	.78
	CHCl ₃	118.0	.9874	3.70			
	CCl ₄	11.8	.07662	.3065			
	C ₇ H ₁₆	2500	25.00	93.57			
Mixture 2A:	C ₂ H ₂ Cl ₄	8.311	.04947	.18	6.4	6.18	.84
	C ₂ HCl ₃	83.5	.635	2.41			
	C ₂ Cl ₄	107.7	.648	2.46			
	C ₇ H ₁₆	2500	25.00	94.95			
Mixture 2B:	C ₂ H ₂ Cl ₄	7.8816	.0469	.70	12.48	6.40	.84
	C ₂ HCl ₃	39.01	.2966	1.13			
	C ₂ Cl ₄	157.63	.9496	3.61			
	C ₇ H ₁₆	2500	25.00	95.08			

Table 2. Experimental Test Conditions

<u>Test</u>	<u>Mixtures</u>	<u>O₂ Level %</u>	<u>Temperature (Exhaust) °F</u>	<u>Average CO Level (ppm)</u>
1	1A & 1B	6.0-6.3	930	550
2	1A & 1B	4.0	888	50
3	2A & 2B	6.6-6.8	940	450
4	2A & 2B	3.5	910	200

Figure 1 shows the TFR and Figures 2 and 3 show the sampling trains employed. Limitations in both the TFR and in the sampling trains affected the type and amount of information obtainable. The TFR, which is described in detail elsewhere, was designed to enhance the formation and emission of combustion byproducts (9). Turbulent diffusion flames with large fuel, oxygen, and temperature gradients enhance the formation of soot and other combustion byproducts. The TFR's water-cooled walls cooled the post-flame combustion gases inhibiting further breakdown of these byproducts. While low temperature and low oxygen concentrations represent conditions that are likely to enhance PIC formation, the TFR exaggerates these conditions resulting in higher levels of these emissions than might ordinarily occur.

The TFR's exhaust gases were sampled for CO, CO₂ and O₂ using the continuous monitors described in Figure 2. Since the sampling was done only at the exhaust duct, only concentrations at this point were determined. The non-uniformities in combustion gas composition within the TFR, which may be responsible for the formation and emission of organic materials, could not be measured using these devices.

The Tenax sampling system described in Figure 3 could only reliably sample materials whose boiling points ranged from 40°C to 160°C. Other materials including many polycyclic aromatic hydrocarbons (PAHs) and semi-volatile organic compounds could not be sampled using this method. Soot was not sampled.

Results Observed

Several qualitative, yet key, results were obtained from this study. These are as follows:

1. The observed emissions could be explained, in part, by combining the results of the studies mentioned above.
2. The formation of soot significantly affected the formation of volatile emissions.
3. PIC formation, and indeed, organic emissions in general, were not directly correlated with exhaust temperature or carbon monoxide emissions.

Characterization of Emissions

Figures 4 and 5 show the mass emissions for the chlorinated methanes under "high" and "low" oxygen conditions. Figures 6 and 7 show the emissions for the chlorinated ethanes and ethenes under similar conditions. All four sets of results show some similarities. First, the predominant volatile emission was the fully chlorinated derivative of the test chemicals fed. In the case of the chloromethanes, carbon tetrachloride was the main emission.

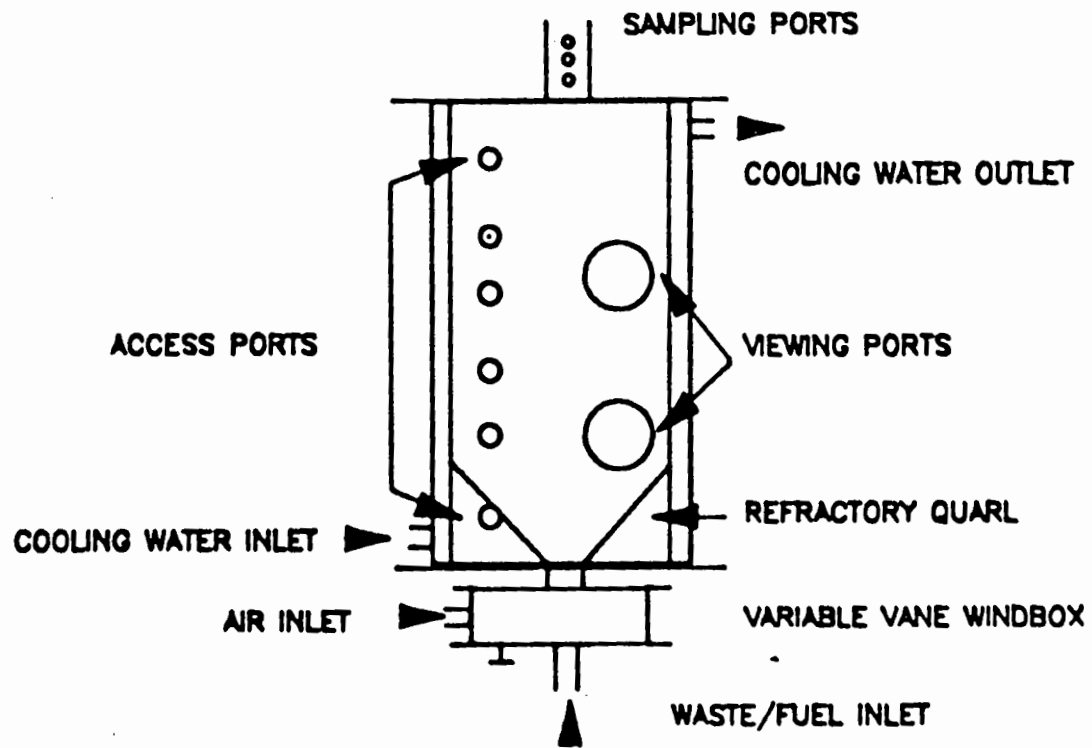


FIGURE 1 Turbulent Flame Reactor

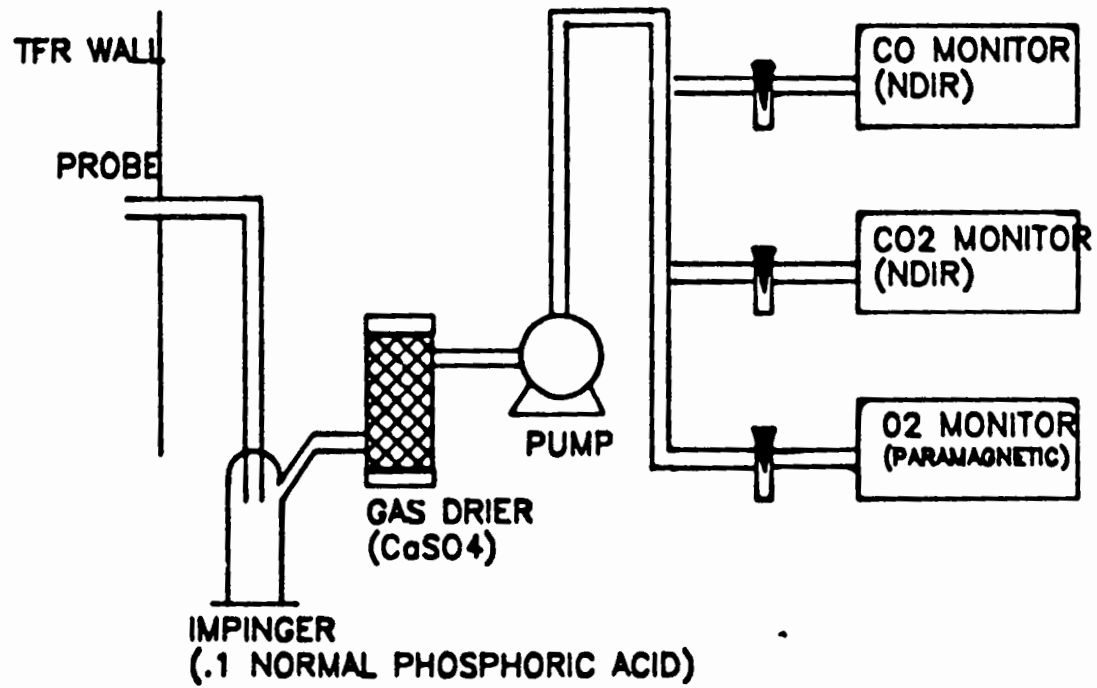


FIGURE 2 Continuous Monitors

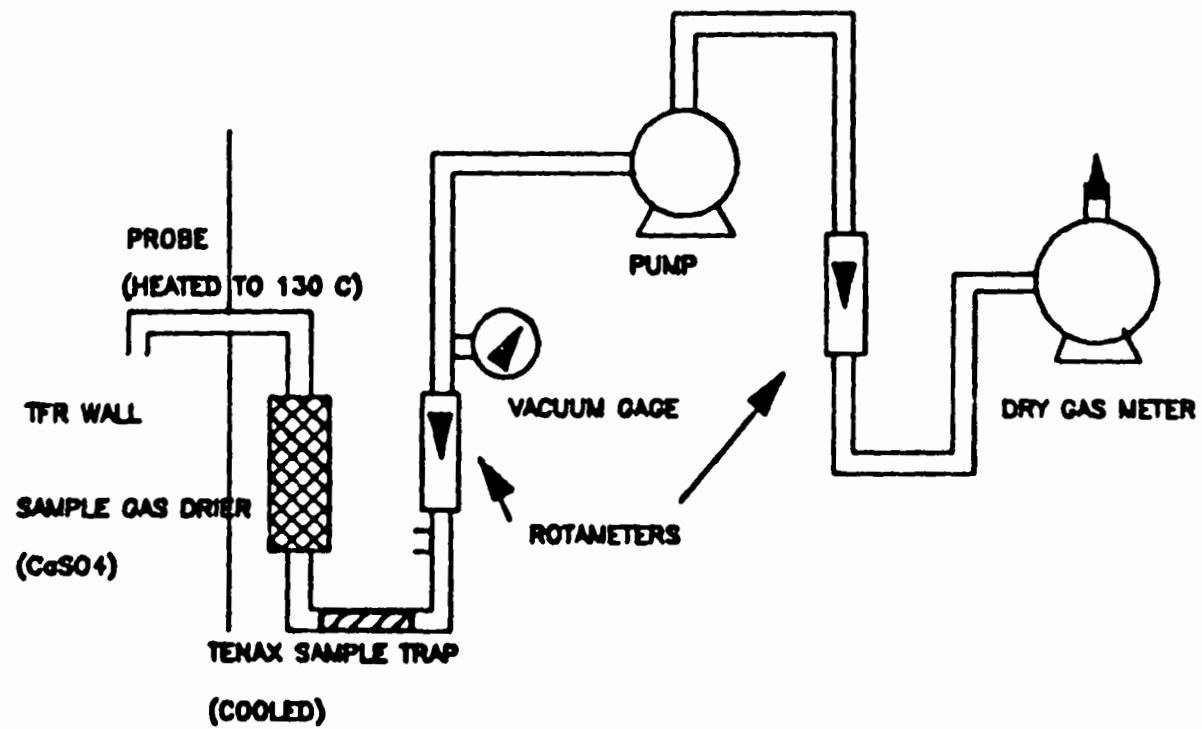
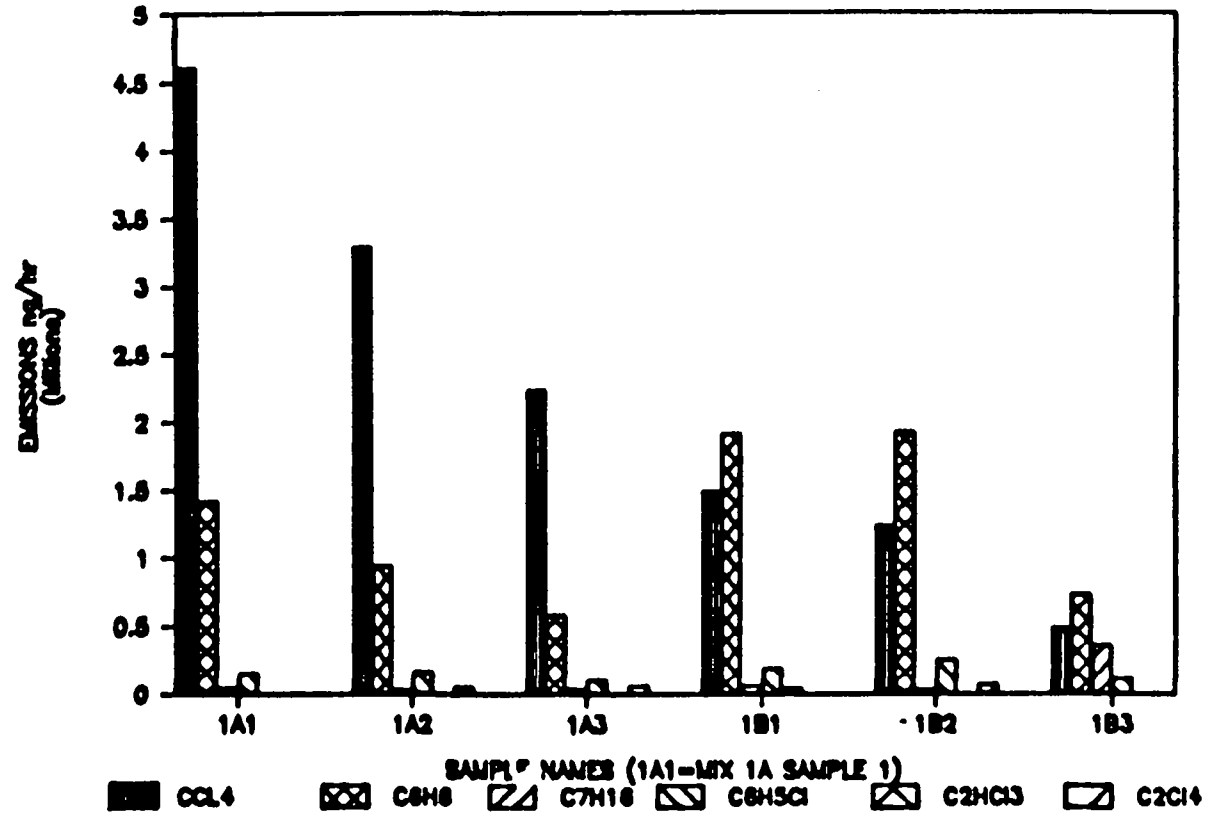
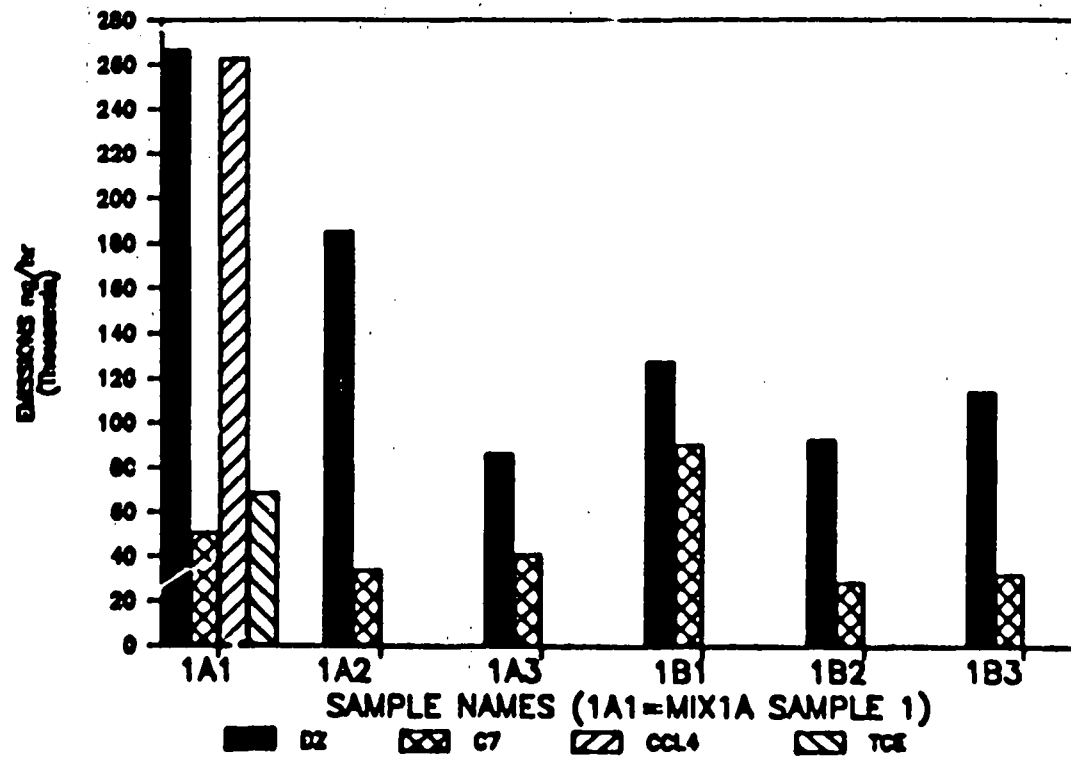


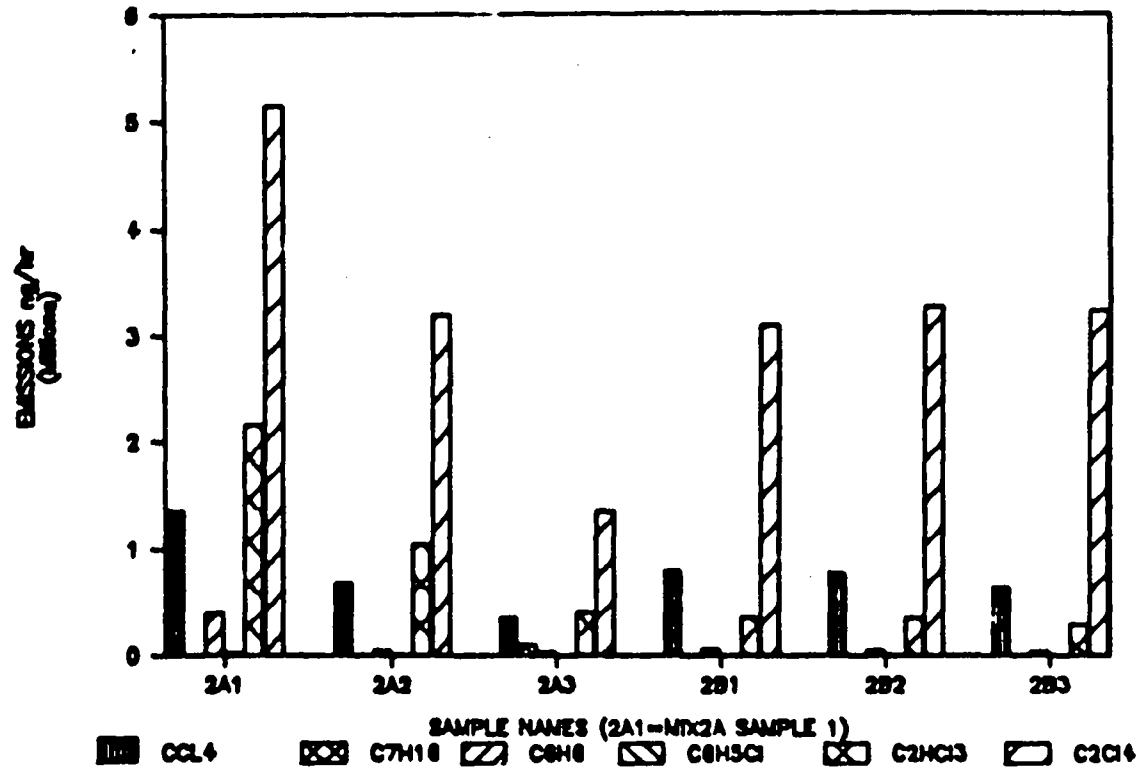
FIGURE 3 Tenax Sampling Train



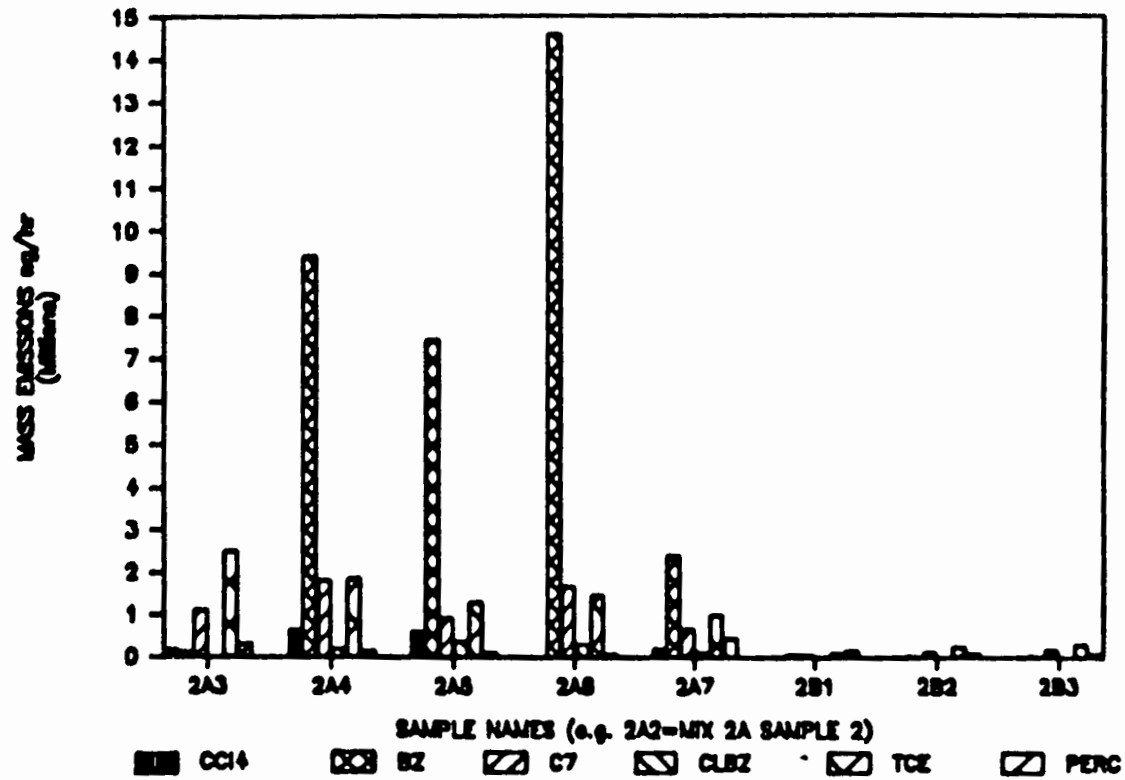
**FIGURE 4 Mass Emissions, Chloromethanes
High Oxygen Tests**



**FIGURE 5 Mass Emissions, Chloromethanes
Low Oxygen Tests**



**FIGURE 6 Mass Emissions, Chlorinated C2s
High Oxygen Tests**



**FIGURE 7 Mass Emissions, Chlorinated C2s
Low Oxygen Tests**

In the case of the chlorinated C₂s it was tetrachloroethylene. Perchlorinated compounds are often observed as stable intermediates in the combustion of chlorinated hydrocarbons as indicated by the results of some of the studies mentioned above (6,7,8,10).

The prevalence of perhalogenated organic compounds in the exhaust results, in part, from how chlorine atoms affect the combustion of hydrocarbons. Chlorine abstraction, followed by molecular fragmentation, is an important pathway for the combustion of chlorinated hydrocarbons under oxidative conditions (11). Even when present in relatively small amounts, chlorine, in the form of Cl· and ClO· radicals, can become the most abundant reactive species present in the combustion environment. This is true even under oxidative conditions where OH would be expected to predominate (3,12). The presence of chlorine radicals further alters the combustion of chlorinated hydrocarbons by preferentially abstracting hydrogen from chlorinated hydrocarbons. In the case of the chlorinated C₁ and C₂ compounds studied here, these reactions result in the formation of fully chlorinated intermediates. If these chlorinated intermediates fail to react further it is possible that they will react with the abundant Cl· and ClO· radicals to ultimately form a fully chlorinated and quite stable intermediate. Non-flame studies of chloromethanes support this theory (3). In these studies, carbon tetrachloride appeared to be more thermally stable when treated in a mixture than when treated separately, a result that was attributed to carbon tetrachloride reforming from the other mixture components. A similar set of chemical reactions seems to also be occurring when chlorinated C₂s are burned under oxidative conditions.

Under oxygen deficient conditions the observed emissions were quite different and appeared to be greatly affected by the formation of soot. As mentioned earlier, soot was the major emission under these conditions. Although we did not quantify it, the soot formed in such large amounts that it rapidly coated all of the viewports. Unexpectedly, the amounts of volatile emissions produced under these conditions were much less than under oxidative conditions. Benzene, a side product of soot formation, was among the most abundant volatile emissions observed. Chlorinated hydrocarbons tend to form soot more readily than other organic chemicals (13). This is because, under oxygen deficient conditions, chlorinated hydrocarbons tend to decompose via the elimination of HCl from the parent molecule. Repeated HCl elimination results in the formation of unsaturated radicals which can condense into large polycyclic aromatic hydrocarbons and, ultimately, soot (13). Chlorocarbons with H:Cl ratios of 1 form soot the easiest (ibid).

The sooting tendency of these chlorocarbons was observed during the tests on mixture 1B which contained a relatively high level of methylene chloride (CH₂Cl₂) for which H:Cl=1. Even under oxidative conditions large quantities of soot were formed similar to the oxygen deficient conditions. Results of the volatile organic sampling showed that benzene was also produced in very large amounts.

When chlorinated C₂s were tested in the TFR under "low" oxygen conditions, trichloroethylene was observed in significant amounts. This was likely caused by the elimination of HCl from the 1,1,2,2-tetrachloroethane that was present in test mixtures 2A and 2B.

Under conditions leading to the formation of large amounts of soot, volatile emissions decreased. This was unexpected. Short chain pyrolysis products were expected to be observed. It is unclear at this point whether the feed materials formed soot instead of short chain pyrolysis products or

whether the short chain products that were formed adsorbed onto the soot that was formed. There is evidence from other researchers that suggests that soot does adsorb volatile compounds present in the combustion environment (14,15).

Finally, Figures 8 and 9 show the volatile emissions observed plotted against the carbon monoxide level and exhaust temperature respectively. No correlations are visually apparent. There are two explanations that account for this. First, it is likely that a number of factors not necessarily related to either exhaust temperature or carbon monoxide level account for the emissions observed. Secondly, fluctuations in temperature or in carbon monoxide level which would bear on the emission of specific volatile organic chemicals, are perhaps too transient and localized to be detected by the measurement techniques employed in this study.

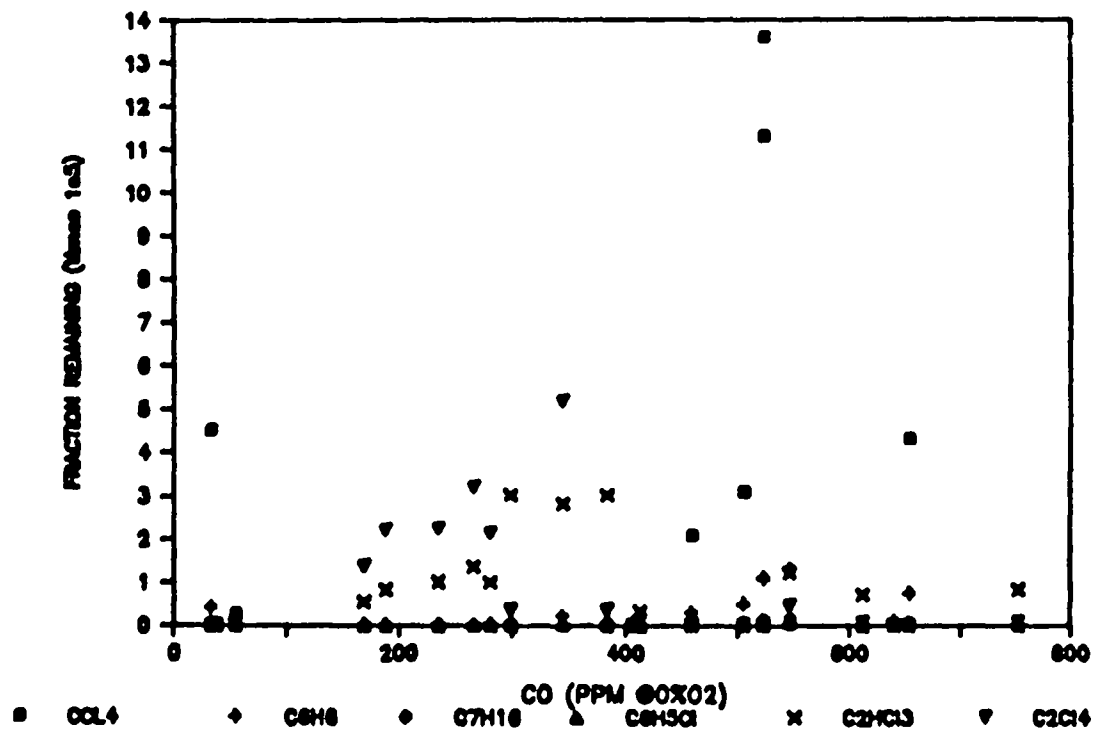
Conclusions

In summary, this study supported several conclusions. First, the results of studies of the combustion of chlorinated C₁s and C₂s in non-flame, flatflame, and shock tube devices were consistent with the emissions from the TFR. Second, the formation of large amounts of soot affected the emissions of volatile organic chemicals in unexpected ways that are not fully understood. Third, the emissions observed did not seem to correlate with temperature or carbon monoxide level in the exhaust.

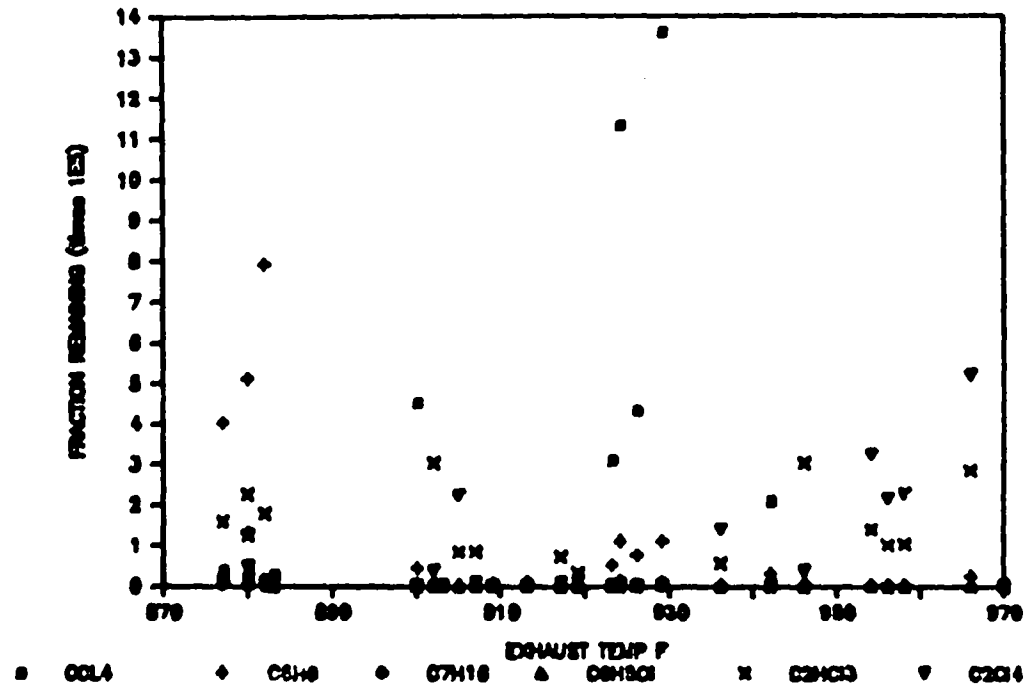
More research is needed in this area. Further studies of the combustion chemistry of individual compounds and simple mixtures would aid in the understanding of PIC formation. In addition, studies of the effect of soot formation on the emission of volatile organic chemicals is needed in order to determine the fate and transport of these materials. Finally, additional evaluations of temperature, carbon monoxide level, and other potential combustion indicators is needed to determine if there is a practical way to continuously monitor the combustion process. Taken together, these studies will help to evaluate the extent to which incineration can be applied as a disposal technique for hazardous waste.

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**FIGURE 8 CO Level vs. Fraction Remaining
(Fraction Remaining-Exhaust Rate/Feed Rate)**



**FIGURE 9 Exhaust Temperature vs. Fraction Remaining
(Fraction Remaining=Exhaust Rate/Feed Rate)**

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