



## Project Summary

# Laboratory-Scale Flame-Mode Hazardous Waste Thermal Destruction Research

J. C. Kramlich, M. P. Heap, J. H. Pohl, E. M. Poncelet, G. C. Samuelsen,  
and W. R. Seeker

This program was performed to generate fundamental flame-mode data on the incinerability of hazardous waste compounds. Other objectives included the comparison of flame and nonflame data, and the development of guidelines for future work on the development of an acceptable incinerability ranking methodology.

Two reactor systems were selected to provide flexibility in simulating the failure conditions that can occur in liquid injection incinerators. In the microspray reactor the reaction characteristics of single droplets of waste compounds were studied. The turbulent flame reactor consisted of a swirl-stabilized turbulent spray flame in which the waste compounds were doped into an auxiliary fuel. In this reactor the effect of flame parameters such as stoichiometry, atomization quality, and quench phenomenon were studied. The approach was to establish conditions that yielded high destruction efficiencies, and then to perturb the flame by changing one or more flame parameters until incomplete destruction occurred. The waste compound concentration was then measured at the reactor exit to establish the ranking. Five test compounds were utilized: acrylonitrile, benzene, chlorobenzene, chloroform, and 1,2-dichloroethane.

The results indicated that when operated under conditions of optimal combustion efficiency flames were capable of high waste destruction efficiency. Under off-optimum conditions the destruction efficiencies were typically 90-99.9 percent. No single ranking procedure adequately described the

rankings observed under all conditions. Rather, the flame rankings were condition-dependent. These data indicate that a realistic incinerability ranking methodology must be a synthesis of waste properties and system-dependent parameters.

*This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Permitting procedures for hazardous waste incinerators are defined by the Resource Conservation and Recovery Act (RCRA). A permit to operate is issued after a trial burn has been executed or other appropriate test data obtained which demonstrate that the incinerator satisfactorily converts hazardous waste into non-hazardous compounds when operated under specified conditions. Satisfactory conversion is defined in terms of destruction and removal efficiency (DRE). However, since most hazardous waste streams contain many compounds, a trial burn which involves the measurement of all of them would be prohibitively expensive. Consequently, the trial burn involves the measurement of a subset of compounds (the principal organic hazardous constituents—POHC's) which are present in the input stream. If the DRE of these POHC's is 99.99 percent or greater, and certain other conditions are met (e.g., chlorine and particulate matter removal

and emissions standards), then a permit to operate is granted. Thus, the burden of responsibility rests with the permit writer who must select the subset of compounds (POHC's) based upon concentration and incinerability. This constitutes the final report of a project which was carried out to examine methods of ranking incinerability and to compare flame with nonflame waste destruction.

Several procedures have been proposed to rank incinerability, namely:

- The heat of combustion.
- Autoignition temperature (AIT).
- A computational approach based upon AIT, compound structure, and other compound-dependent parameters.
- The temperature necessary for a given destruction level within a given time under dilute premixed conditions ( $T_{99.99}$ ).
- Susceptibility of the compound-bound structure to attack by flame radicals.

These procedures have their merits, but fail to take into account all the conditions which may exist in actual incinerators. The heat of combustion, for example, of a particular compound may be insignificant if it is present in small quantities and is mixed with an auxiliary fuel. In addition, some of these procedures do not consider processes and reactions that occur in flames. The times and temperatures which exist under nonflame experimental conditions may be inappropriate for large-scale diffusion flames.

The concept of incinerability is used to describe the relative degree of difficulty of incineration of the various hazardous organic constituents present in a given waste stream. If, during the trial burn, it is demonstrated that compounds most difficult to destroy have a DRE greater than 99.99 percent, then it is assumed that compounds ranked more incinerable under the accepted hierarchy will be destroyed at the same or greater DRE than the difficult compounds. Thus, there is a need for some ranking methodology that will aid the permit writer in his selection of difficult compounds. If the ranking methodology is in error, or is not applicable to a particular system, then a condition could exist wherein a POHC was destroyed satisfactorily, but other hazardous compounds in the waste stream were not destroyed sufficiently. Under these circumstances, a trial burn designed to measure only the POHC may have incorrectly demonstrated the satisfactory operation of the incinerator.

Because of the nature of flames, waste compounds which experience a flame environment are rapidly and completely destroyed. This can be demonstrated by considering nonflame thermal decomposition data obtained under dilute premixed conditions. As an example, nonflame data indicates that chlorobenzene will decompose to 99.99 percent of its original concentration in 1 sec at 1038°K. At typical flame temperatures (approximately 2000°K), the time required to obtain the same destruction level is much smaller ( $<10^{-13}$  sec. using the same thermal decomposition data) than the typical 0.10 sec. flame residence time.

Thus, nonflame thermal decomposition data obtained under dilute premixed conditions indicate that temperatures much lower than those encountered in typical incinerator flames will destroy all the organic hazardous waste compounds which have been tested to date. Also, because of high reactant concentrations in flames, free radicals which must be present to propagate the flame will contribute to destruction of the compounds in the flame. These free radicals will increase the rate of decomposition above those predicted from dilute decomposition kinetics. Under ideal flame conditions, in which all of the waste is exposed to flame temperatures, the concept of incinerability has little significance since all hazardous compounds would be expected to be completely destroyed.

Incomplete destruction of a hazardous waste compound in an actual incinerator must be caused by conditions that allow some of the material to escape or bypass the flame, since organic compounds are destroyed rapidly in a flame environment. Most incinerators include long residence time hold-up zones or afterburners to destroy material that has not completely reacted in the flame zone. Thus, incinerability would be expected to be influenced not only by the chemical properties of the compound, but also by its physical properties and their interaction with the incinerator operating conditions because these may influence the failure mode. The term "failure mode" is used to describe those conditions that might occur in a practical incinerator, which preclude complete processing of the waste material by a high-temperature turbulent diffusion flame. Thus, the term in the present context does not include conditions that may affect other parts of an incinerator (e.g., afterburner or scrubber). It is important to evaluate incinerability under conditions that simulate

those failure modes which could occur in practice.

Various phenomena account for the failure of turbulent diffusion flames, typical of those used in liquid injection incinerators, to completely destroy a liquid waste. The destruction efficiency in the flame may be less than quantitative (100 percent) because of any of the following reasons:

1. *Atomization Parameters.* When the waste material is injected as a liquid that must be atomized, poor destruction efficiency can result from inappropriate atomization. (a) Droplets that are too large to evaporate may be produced. (b) Their trajectory may be such that they penetrate the flame zone and ignition does not occur. (c) Droplets that are too small may promote concentrated evaporation zones which produce fuel-rich pockets.
2. *Mixing Parameters.* In a turbulent diffusion flame the reactants are supplied separately and reactant contacting takes place via turbulent mixing. Poor mixing can result in low destruction efficiencies because the waste material may not be mixed with oxygen before it escapes from the flame region.
3. *Thermal Parameters.* The destruction efficiency may be low because flame temperatures are too low. This can occur if the calorific value of the waste/auxiliary-fuel mixture is low or heat removal rates are high.
4. *Quenching Parameters.* The reactants can be quenched before destruction is complete by heterogeneous or homogenous phenomena. Quench rates are high due to mixing with excessive excess air levels in fuel injection systems in which the flame impinges on an aqueous jet, or the flame may contact a relatively cool surface.

Consequently, it is essential to investigate the concept of incinerability in flames under conditions that could account for a failure to completely destroy the waste compound and under conditions that are typical of real systems.

The primary goal of this study was to compare the proposed incinerability ranking procedures with those measured under flame conditions typical of liquid injection incinerators. The approach utilized was to measure the exhaust com-

pound concentration under different simulated failure modes and to compare the ordering of the compounds to those given by several incinerability ranking procedures. Two reactors were required to simulate failure conditions for all the parameters expected to influence incinerator performance; i.e., thermal atomization, mixing, and quenching. A microspray reactor consisting of a laminar premixed flat-flame into which test compounds were injected was used to investigate thermal parameters. A subscale turbulent diffusion spray flame was used to investigate atomization, mixing, and quenching parameters. Secondary goals included the generation of fundamental flame-mode destruction data necessary to compare flame and nonflame decomposition. The results are primarily a means of guiding future experimental work, since further work is necessary to select a reasonable ranking protocol.

## Experimental Approach

Extensive investigations are being carried out at the University of Dayton Research Institute under EPA sponsorship to define the kinetics of waste decomposition in post-flame regions. The emphasis of the present study was on the flame zone itself and the impact of failure conditions associated with mixing, thermal, quenching, and atomization parameters on the relative destruction of five compounds. These compounds were selected because they represented a broad range of incinerability as defined by existing ranking procedures, and because data within each of the procedures were available for the compounds. The study was restricted to conditions typical of liquid injection incinerators. No attempt was made to include phenomena associated with waste destruction in beds such as those that exist in fluidized beds, rotary kilns, or hearth incinerators. Two flame reactors were used to study destruction efficiency under different conditions:

1. **Microspray Reactor.** In the microspray reactor, monodisperse waste droplets were injected into a hot, uniform post-flame gas. These experiments investigated the destruction efficiency (DE) behavior and ranking that resulted from individual droplet evaporation and flame decomposition reactions. The experiment was designed to bridge the gap between the nonflame thermal decomposition experiments and the turbulent flame data. As such, it included two processes in addition

to the thermal decomposition experiments: droplet vaporization dynamics and flame reactions. The data were used for the following purposes:

- To determine what portion of the turbulent flame rankings was due to laminar flame and evaporation processes.
  - To compare flame (microspray) with nonflame (thermal decomposition) destruction on a fundamental level without the complicating influence of turbulence.
2. **Turbulent Flame Reactor.** A turbulent flame reactor (TFR) was used to investigate DE and ranking in a turbulent spray diffusion flame. The TFR was operated under conditions to simulate many of the processes occurring in the flame zone of a liquid injection incinerator; these could be exaggerated to simulate different failure modes.

Five compounds (chloroform, acrylonitrile, benzene, chlorobenzene, and 1,2-dichloroethane) were selected as representative of liquid organic hazardous wastes. All the compounds are listed in the 1980 RCRA regulations, Part 261, Appendix VIII (*Federal Register*: May 19, 1980). The compounds were chosen to represent a broad range of incinerability based on the most commonly proposed ranking procedures. They cover greater than 90 percent of the range in heats of combustion for the listed compounds (.13 to 10.14 kcal/gm). Since a direct comparison between nonflame thermal decomposition rankings and the flame-mode destruction was an objective of this study, compounds were selected for testing for which nonflame data were available. In addition, the selection also took into account the NBS ranking system, a range of autoignition temperatures and a variety of molecular structures. Two compounds, a highly chlorinated methane and a chlorinated ethane, are aromatic; another compound contains nitrogen.

Compound DE was measured in the reactor exhaust by adsorption onto Tenax-GC, followed by thermal desorption and flame ionization gas chromatographic analysis. The use of Tenax for concentrating the sample provided the necessary rapid turnover of samples with sufficient separation and sensitivity. The breakthrough volumes of all the test compounds were directly measured and were found to be greater than the utilized sample volumes. Benzene and 1,2-dichloroethane

were not separable by the column and hence mixtures containing both compounds were avoided.

## Microspray Results

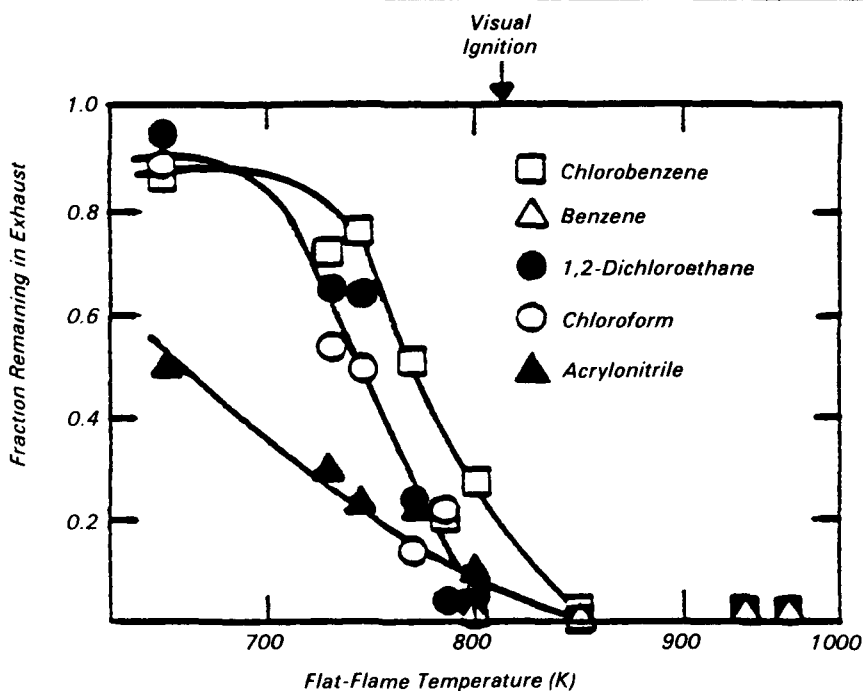
The microspray was used to investigate the impact of thermal parameters for two conditions:

- Fuel-lean—excess oxygen available to oxidize test compounds.
- Fuel-rich—insufficient oxygen available to oxidize test compounds.

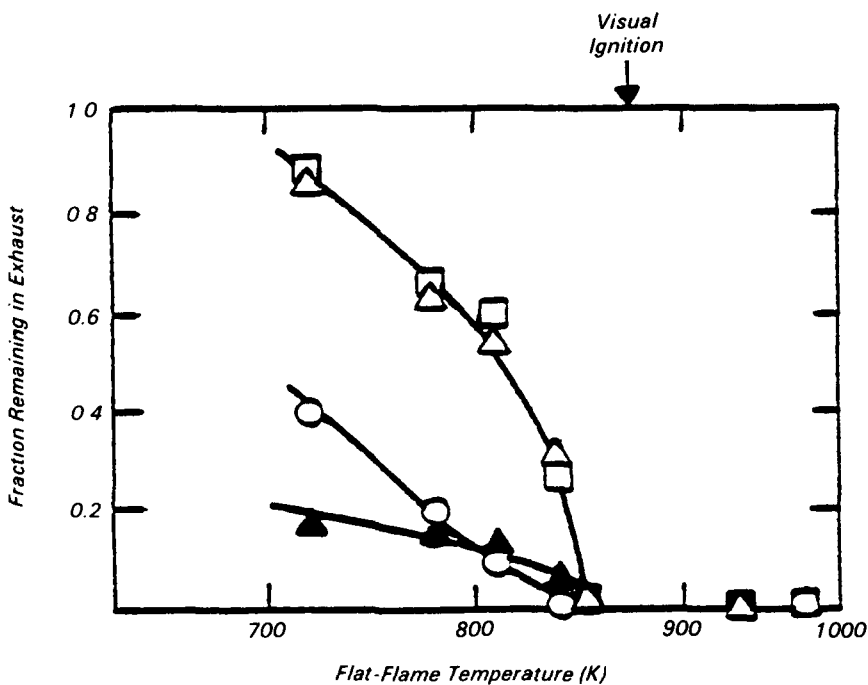
In addition, the effect of using pure compounds was compared with that for mixtures of compounds. The other failure mode parameters (atomization, quenching, and mixing) cannot be effectively investigated in the microspray reactor and were investigated in the turbulent flame reactor.

Figure 1 presents data for two mixtures of four compounds shown separately in Figures 1(a) and 1(b). In these tests, 38  $\mu\text{m}$  droplets of the two mixtures were injected separately into a lean (10 percent excess oxygen)  $\text{H}_2/\text{air}/\text{N}_2$  flame with different flat-flame temperatures. Exhaust concentrations of the individual test compounds were measured and the data are shown in Figure 1 in terms of the fraction of each compound remaining versus the measured flat-flame temperature. This temperature is determined by extrapolating the axial temperature measurements to the burner face and is the highest temperature of the flat-flame gas. Under these excess oxygen conditions, flames were observed to surround each individual droplet for both mixtures for flat-flame temperatures in excess of 850°K. However, the minimum droplet ignition temperature was observed at slightly lower temperatures for the 1,2-dichloroethane mixture, probably due to the substitution of compounds. When the flat-flame temperature is greater than the ignition temperature of the specific compound mixture, the exhaust concentration of the test compounds were below the detection limit of the analytical technique which indicated a destruction level in excess of 99.995 percent.

Calculations using nonflame kinetics indicate that almost no decomposition should occur below 800°K for the residence times (~1 sec.) available in the microspray reactor. However, as shown in Figure 1, significant destruction was measured at flat-flame temperatures below 800°K. This destruction at low flat-flame temperatures is probably due to a



(a) Mixture Containing Dichloroethane, Chlorobenzene, Chloroform and Acrylonitrile



(b) Mixture Containing Benzene, Chlorobenzene, Chloroform and Acrylonitrile

**Figure 1.** Fraction of test compound remaining in exhaust when 38  $\mu\text{m}$  droplets of mixtures of compounds were injected into lean (10 percent excess oxygen)  $\text{H}_2/\text{air}/\text{H}_2$  flames as a function of flame temperature.

local increase in temperature around droplets and flame radical attack. For gas temperatures at and above the point at which the individual droplets were ob-

served to support flames, all the compounds were destroyed, but below the ignition temperature the fraction destroyed depended upon the compound. At

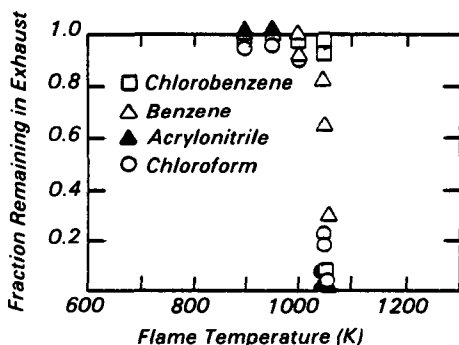
low flat-flame temperatures for the dichloroethane mixture, the ranking from highest to lowest concentration was: chlorobenzene, dichloroethane, chloroform, and acrylonitrile. At flat-flame temperatures just below the droplet ignition point, again chlorobenzene was found to be the most difficult compound to be eliminated but the other compounds showed some rearrangement in ranking; however, the effect of compound type is small. When benzene was substituted for dichloroethane (Figure 1(a)), chlorobenzene remained the most prominent compound in the exhaust followed by benzene, chloroform, and acrylonitrile. Again, just below ignition there was some reordering of compounds with chloroform becoming the easiest to eliminate.

These data indicate that for single droplet oxidative conditions where the flame temperature is too low for droplet ignition, a particular order of compounds does exist in terms of the fraction remaining in the exhaust. This order is chlorobenzene, benzene, 1,2-dichloroethane, chloroform, and acrylonitrile. However, this order changes as the temperatures reach the ignition point. The ordering just below ignition is identical to the ordering suggested by  $T_{99.99}$  and autoignition temperature.

When 38  $\mu\text{m}$  droplets of pure compounds were injected into oxygen-rich, fuel-lean flame products, the droplets were observed to ignite at different temperatures. For example, visual ignition for chloroform droplets was observed at 860°K, while dichloroethane ignited at 850°K, acrylonitrile at 800°K, and chlorobenzene at 740°K. Benzene had the lowest ignition temperature and was observed to ignite at temperatures below 600°K. For pure compounds, the destruction is controlled by droplet ignition. The observed ignition temperature does not agree with any proposed incinerability ranking procedures, although the heat of combustion criteria is almost the same with the exception that acrylonitrile and chlorobenzene are reversed. A potential explanation for this behavior is that the ability to support droplet flames is determined, to first order, by the heat release available upon droplet combustion ( $\Delta H_c$ ). Although second order effects may modify the rankings, for pure droplets the ranking appears to be dominated by heat of combustion.

The absence of oxygen was the third failure mode investigated with microspray reactor. Droplets of equal molar mixtures of compounds were injected into fuel-rich

(stoichiometric ratio = 0.83)  $H_2$ /air/ $N_2$  flames of different temperatures. In these tests, the oxygen was rapidly and completely consumed by the hydrogen in the flat-flame so that no oxygen was available to oxidize the test compounds. The fraction of each compound remaining in the exhaust as a function of the flat-flame temperature is shown in Figure 2. Even with mixtures, the temperature, 1050°K, required to destroy the compounds was found to be very similar to the  $T_{99.99}$  temperatures of the individual compounds (920 to 1037°K); and were much higher than those required if droplet ignition occurred (Figure 1). The fractional destruction was strongly dependent upon flame temperature. In fact, the data show that a very small change in flame temperature above 1050°K produced a substantial change in the compound concentrations, particularly for benzene. A difference between the compounds was observed only at a temperature just below the flat-flame temperature required for complete destruction. At that temperature, the compound that was most predominant was chlorobenzene, followed by benzene, chloroform, and acrylonitrile. This ranking was identical to that measured for the low temperature oxidation data (Figure 1). The nonflame  $T_{99.99}$  did identify the temperature range required for complete destruction and the most predominant compounds (chlorobenzene and benzene); however, acrylonitrile and chloroform are reversed from the  $T_{99.99}$  ranking.



**Figure 2.** Fraction of test compound remaining in exhaust when 38  $\mu$ m droplets of mixtures of compounds were injected into rich (stoichiometric ratio = 0.83)  $H_2$ /air/ $N_2$  flame as a function of flame temperature. Incinerability order at 1050°K (highest to lowest concentration) is chlorobenzene, benzene, acrylonitrile, and chloroform.

## Turbulent Flame Reactor Results

The turbulent flame reactor was operated and tested under a number of conditions. However, many of these conditions resulted in high destruction efficiency of all the test compounds. Only those parameters resulting in significant deterioration of destruction efficiency are presented. The conditions investigated in the turbulent flame reactor that had a strong influence on destruction efficiency were primarily associated with three failure parameters:

- Atomization parameters—poor atomization quality.
- Combustion parameters—high excess air
  - low excess air
  - low heat release
- Mixing (or turbulence)—swirl
  - air velocity

Those parameters found to be of less importance included burner velocity, fuel type (No. 2 fuel oil), and concentration of hazardous waste compounds (from 3 to 25 percent).

It was generally found that exhaust concentration measurements of carbon monoxide (CO) and total hydrocarbons were good indicators of flame performance and compound destruction efficiency. The exhaust CO level in particular appeared to be well correlated with the exhaust concentration of the test compounds. This result was expected since the high heat removal rates in the TFR emphasize flame performance over post-flame reaction. Since CO is an intermediate in the oxidation of hydrocarbons to carbon dioxide ( $CO_2$ ), it is directly linked with combustion efficiency. Therefore, an examination of the relative CO levels for each failure condition indicates the overall combustion efficiency which can be compared to the destruction efficiency of the hazardous waste compounds. The relationship between exhaust CO, total hydrocarbons measured by the flame ionization detector, and destruction efficiency measured for a mixture of compounds is shown in Figure 3. The maximum DRE (>99.995 percent) was measured at 30-40 percent excess air, which corresponded to the minimum in both exhaust CO and hydrocarbon.

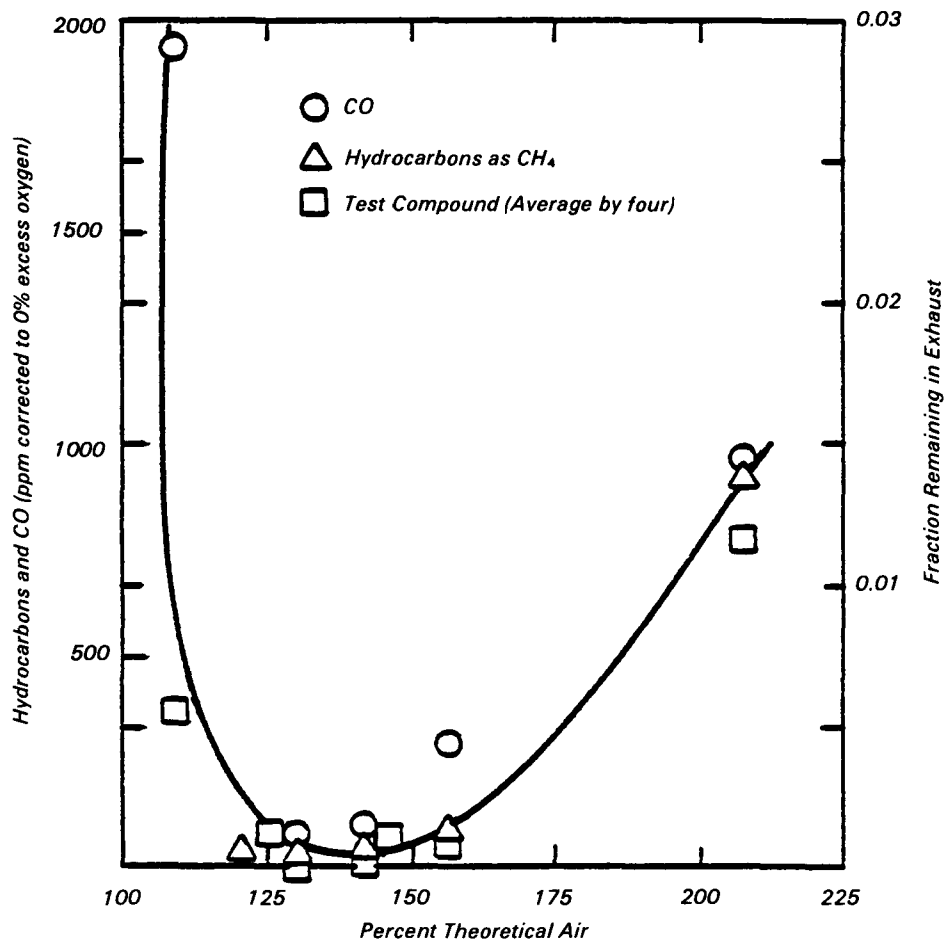
Figure 4 presents data obtained with the TFR at high heat-release rates (44 kW). Very high destruction levels (>99.995 percent) were measured for all

compounds at 20 percent excess air at this heat-release rate with the exception of benzene. It is possible that benzene was a product of incomplete combustion of either the auxiliary fuel or one of the test compounds (e.g., chlorobenzene). The actual source of the benzene, whether it is a product of incomplete combustion or an indication of incomplete benzene destruction, has not been determined. Benzene is a possible intermediate in the formation of soot which was observed in the flame in the form of luminosity, especially at low excess air levels. Because of the relatively large amounts of heptane present (97 percent), only a small conversion of heptane to benzene is required to account for the exhaust levels of benzene measured at this low excess air condition. However, the benzene could also be the result of a chlorobenzene reaction.

At higher excess air levels (>150 percent) theoretical air, the exhaust concentrations of CO and the test compounds increased. This is probably due to lower flame temperatures and increased quenching, which can occur when large amounts of unheated air are present. The lowest DRE level obtained for these heat-release rates (44 kW) was 99.9 percent. The compound differences were small but measurable at 150 percent theoretical air. The ranking from highest to lowest concentration was: chloroform, acrylonitrile, benzene, and chlorobenzene. This particular order, which was found to exist for a number of failure conditions tested with the turbulent flame reactor, does not agree with any of the proposed rankings, although the heat of combustion did identify the most predominant compound (chloroform).

The data obtained at low heat-release rates (24-42 kW) are shown in Figure 5. This data set was achieved by lowering the fuel flow rate from the nominal operating conditions, while maintaining the air flow constant. This drop in load and increase in theoretical air resulted in a significant increase in the fraction of waste compounds in the exhaust. Under this failure conditions, chloroform and benzene had similar high exhaust concentrations, followed by 1,2-dichloroethane and similar low exhaust concentrations for acrylonitrile and chlorobenzene.

The data presented in Figure 6 indicate that atomization parameters had significant impact upon compound destruction. In these tests, a nozzle designed for 1.5 gal/min was operated at .75 gal/min dropping the pressure from 161 psig to 40 psig. This increases the mean droplet



**Figure 3.** Exhaust CO and total hydrocarbons and fraction of test compound remaining in exhaust as a function of theoretical air (constant air velocity, variable load, equal molar mixture of chloroform, benzene, chlorobenzene, and acrylonitrile added 3 percent by weight to heptane).

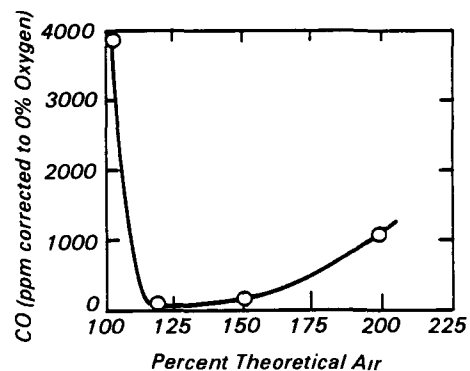
size, affects fuel air mixing, and may cause some of the large droplets to escape the flame. The highest compound exhaust concentrations were measured under these poor atomization conditions. However, the order of compounds was found to be identical to other failure conditions for the TFR, such as high excess air at high loads, low excess air at low loads, and quench coils. The chloroform was found to be the most predominant compound followed by benzene, acrylonitrile, and chlorobenzene.

A water-cooled copper coil was placed directly within the flame in the TFR to provide an extreme case of flame-quenching in order to investigate destruction efficiencies under this mode of failure. In this failure condition test, the coil acted to cool the flame and supplied a surface area for reactants to quench. The presence of the quench surface increased

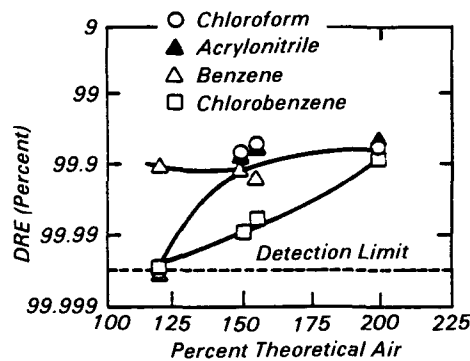
both CO and the test compound concentration (Figure 7). The dashed line for the uncooled data was derived from Figure 5. The order of the compounds was similar to other failure conditions with chloroform being the most predominant and chlorobenzene the least predominant compound in the exhaust. However, the positions of acrylonitrile and benzene were reversed from the order found in other failure modes.

### Discussion

The combustion of hydrocarbon fuels in turbulent diffusion flames results in relatively high flame-zone temperatures (between 1600-2000°K) and residence times are on the order of 0.1 seconds. If the waste compounds investigated in this study experience these conditions, then they would be quantitatively destroyed.



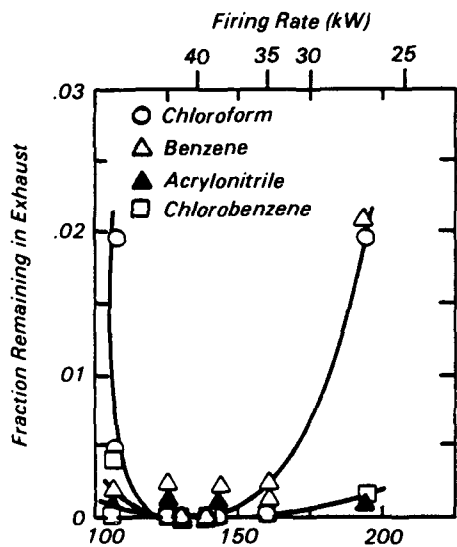
(a) Exhaust CO Concentration



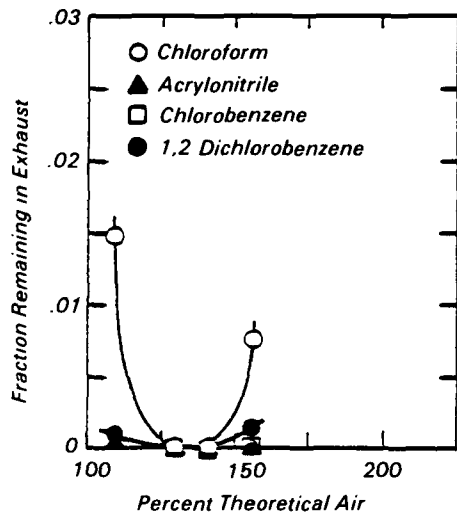
(b) Destruction and Removal Efficiency

**Figure 4.** Impact of theoretical air on CO and DRE from turbulent flame reactor. Incinerability order at 150 percent T.A. is chloroform, acrylonitrile, benzene, and chlorobenzene (constant load = 48 kW; variable air flow rate and burner velocity; equal molar mixture of compounds added 3 percent by weight to heptane)

The results of this study agree with this hypothesis. Turbulent diffusion spray flames and a laminar reactor burning single droplets were capable of destruction efficiencies greater than 99.995 percent. In the case of the turbulent flame reactor under optimized conditions (stable flame, low CO, and total hydrocarbon), the compounds were destroyed mainly in the flame because post-flame decomposition was minimized due to the fact that the flame was contained by cold walls. Consequently, it can be concluded that a flame is an extremely efficient mode of destroying waste compounds and the concept of incinerability under these conditions has little value. If everything is destroyed it is not possible to rank compounds in terms of difficulty or ease of destruction. Consequently, a series of



(a) Mixture Containing Benzene, Chlorobenzene, Chloroform and Acrylonitrile

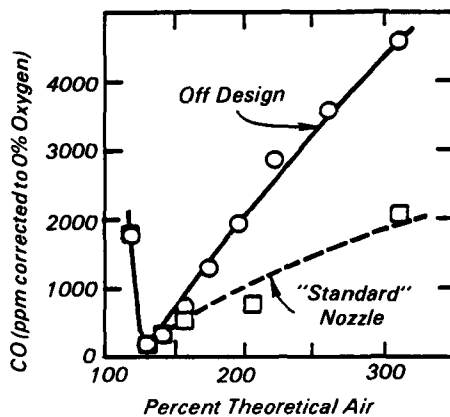


(b) Mixture Containing Dichloroethane, Chlorobenzene, Chloroform and Acrylonitrile

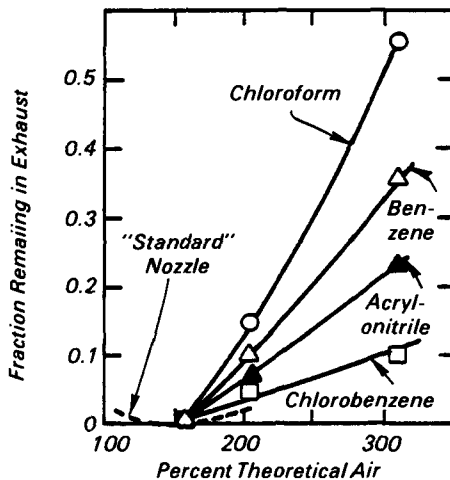
**Figure 5.** Impact of theoretical air and load on fraction of test compounds remaining in exhaust of turbulent flame reactor (constant air velocity, variable load 24-42 kW; equal molar mixture of compounds added 3 percent by weight to heptane).

experiments were designed to assess incinerability under several limiting conditions that might typify the failure modes of practical liquid injection incinerators.

The microspray reactor investigated those conditions associated with single droplet combustion in the absence of complications due to turbulent mixing. It was selected in order to study thermal effects separated from turbulent mixing



(a) Carbon Monoxide

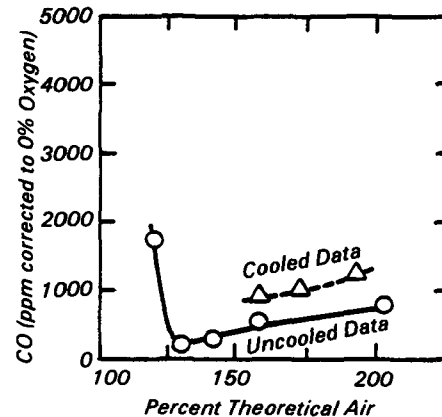


(b) Test Compound Data with Standard Nozzle and Off Design Nozzle

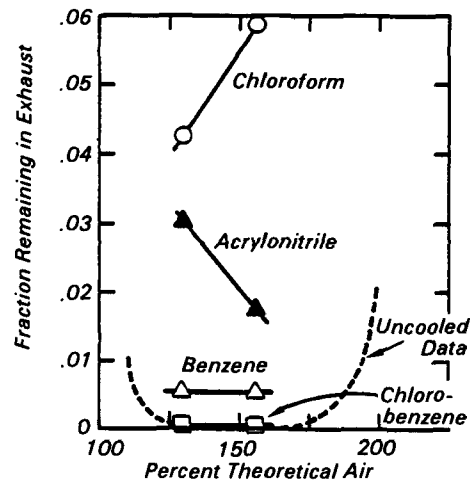
**Figure 6.** Impact of atomization quality on CO and fraction of test compounds remaining in exhaust of turbulent flame reactor (constant air velocity, variable load: 16-42 kW; equal molar mixture of compounds added 3 percent by weight to heptane).

and atomization. The temperature required to ignite droplets of hazardous waste under oxygen-rich conditions in the laminar premixed flat-flame reactor was found to be low (850°K) in comparison to typical flame temperatures (1500-2000°K). Above the ignition temperature, the droplets were visually observed to ignite and the compounds tested were quantitatively (>99.995 percent) destroyed. Even in the absence of oxygen, the microspray data were consistent with the high destruction efficiencies achievable in a turbulent diffusion spray flame environment.

The TFR was operated at high heat removal rates by operating with water-



(a) Carbon Monoxide



(b) Test Compound Data with and without Cooling Coil.

**Figure 7.** Impact of cooling coil placed in flame on CO and fraction of test compound remaining in exhaust of turbulent flame reactor. (Constant air velocity; load = 32 kW equal molar mixture of compounds added 3 percent by weight to heptane).

cooled walls in order to minimize post-flame reactions and mixtures up to 25 percent by weight of the test compounds were investigated. Even in the absence of significant post-flame decomposition, destruction efficiencies which corresponded to the detection limits of the analytical systems (99.995 percent) were achieved for all the compounds tested. In the turbulent flame reactor, a direct relationship was observed between overall combustion efficiency as indicated by exhaust CO and hydrocarbon emissions and the destruction of the test compounds. Conditions that minimized the CO concentration in the exhaust gases also maximized destruction efficiency.

Under all failure conditions investigated, exhaust CO concentration increased when the test compound concentration increased. These results suggest the feasibility of using exhaust CO and potentially total hydrocarbons to monitor the performance of liquid injection incinerators once the conditions giving the maximum destruction efficiency have been defined.

The incinerability or ordering of the compounds was found to depend on the actual failure condition which caused the inefficiency. When both the microspray and the turbulent flame reactor were operated under conditions that simulated failure modes of practical incinerators, measurable differences in the destruction efficiency of the five test compounds were obtained. For example, chlorobenzene was the most difficult to eliminate in the microspray when the temperature was too low to ignite the droplets, but was the least difficult to eliminate for a variety of failure conditions in the TFR, such as poor atomization quality.

Figure 8 presents a series of bar graphs which allow a comparison between incinerability as defined by the various failure modes and the rankings indicated by procedures based upon  $T_{99.99}$ , heat of combustion, the NBS method, and AIT. The bar graph shows the concentrations measured in the experiment normalized so that the most predominant compound shows full-scale and the lesser concentrations are expressed as a percentage of that maximum concentration. This approach gives an indication of the measured magnitude of the difference in destruction efficiency between compounds. A comparison of these relative concentration measurements with proposed incinerability ranking techniques demonstrates that none of the proposed techniques agree with the data for all failure conditions. However, some of the ranking procedures were found to be appropriate for specific failure conditions. For example, the nonflame thermal destruction ( $T_{99.99}$ ) and AIT procedures both agreed with the compound concentration measurements when the temperature was below droplet ignition temperature and under oxygen-deficient conditions. Heat of combustion was found to correlate the pure compound data when the microspray was operated below droplet ignition temperature. In most instances, chloroform was the most difficult compound to incinerate for the failure conditions investigated with the TFR, and this was anticipated by only one of the four ranking techniques: heat of combustion.

Although measurable differences in the destruction efficiency of the five test compounds were obtained, the differences were not large under any of the conditions tested. For the most part, the variation in the concentration (between highest and lowest) of the compounds in the exhaust was typically of the order of five, although variations larger than ten were measured under some circumstances. This suggests that the selection of POHC may not be very critical because the differences between compounds are small. If the permit writer selects three compounds based upon two or more ranking techniques, and it is demonstrated that their DRE is greater than 99.99 percent, then it is very unlikely that any other compounds will be destroyed to a significantly lesser degree.

This study has identified the differences between compound destruction efficiency caused by failure conditions associated with the flame zone. High destruction efficiencies have been demonstrated in the flame alone. However, many incinerators are equipped with post-flame hold-up zones and afterburners in order to achieve additional thermal decomposition of compounds which escape the flame zone. In order for an incinerator to fail to destroy a compound, the material must both escape the flame and the temperature be too low in the post-flame hold-up zone to destroy the compound (less than  $T_{99.99}$ ). The differences in the concentration of compounds in the exhaust of the incinerators is associated with both the flame and nonflame zones. The thermal decomposition which occurs in the post-flame zone can alter the ranking in the exhaust. As an example, consider a flame zone in which the DE of chloroform and chlorobenzene was 95 percent and 99 percent, respectively (a flame ranking consistent with the data of Figures 6 or 7). Utilizing nonflame kinetics and a 1.0 sec isothermal post-flame zone for post-flame temperatures below about 870°K, the flame zone ranking will persist in the exhaust. Above 1008°K both compounds are destroyed to 99.99 percent DE. Hence, there are potential situations, dependent on incinerator conditions, for either a flame zone or a post-flame ranking to prevail within a given unit.

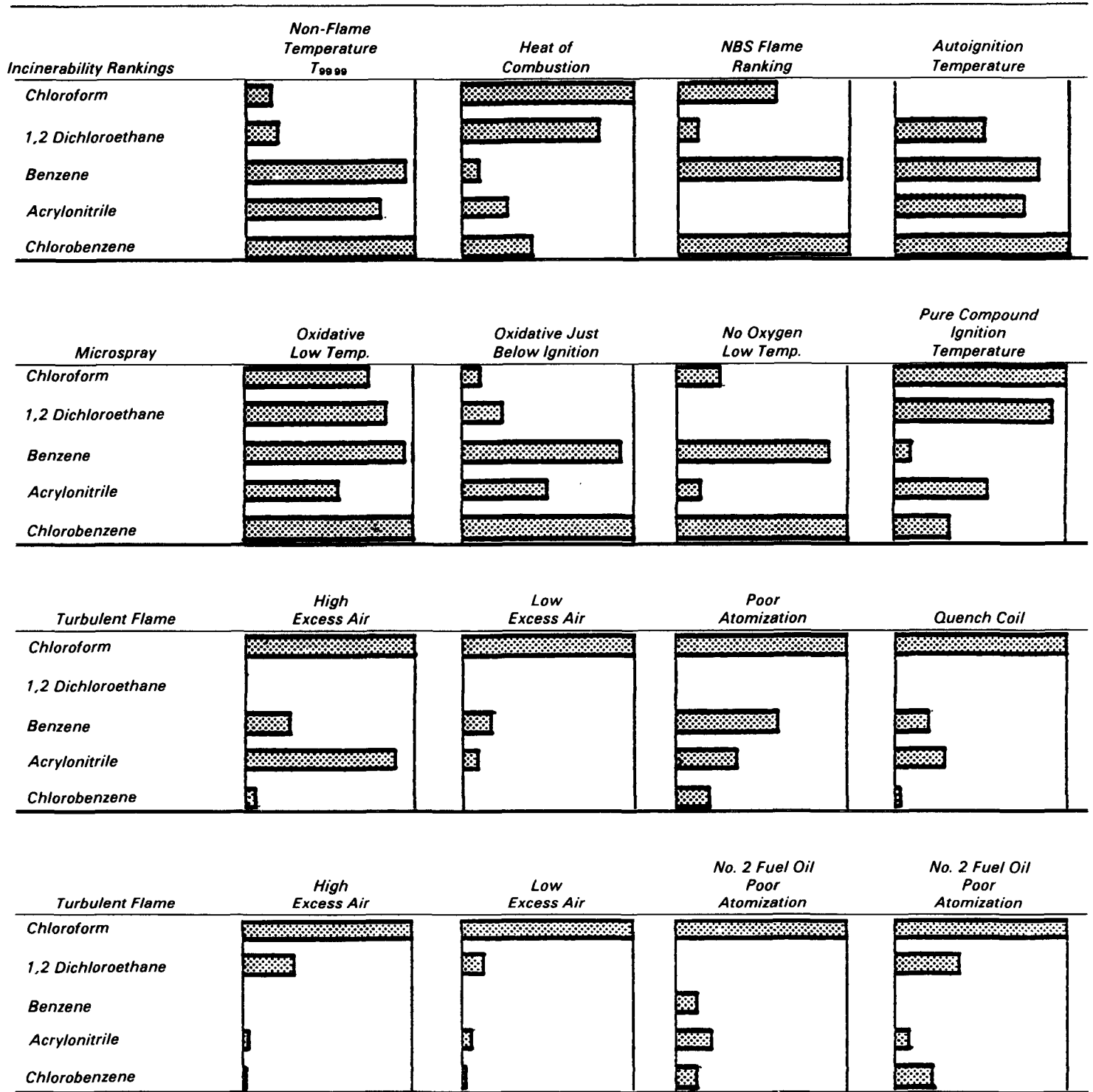
It was not the purpose of this study to ascertain why destruction efficiency under flame conditions can be compound and failure mode specific. More detailed measurements, such as fundamental kinetic flame studies, are necessary to provide a full explanation of the causes of the rankings. It could be associated with

flame inhibition due to the presence of halogens, which are known to reduce burning rates. Under quenching conditions, these effects could be enhanced. The formation of products of incomplete combustion (PIC's), as a consequence of the partial destruction of the waste compound, was not investigated. An alternate method of assessing incinerability could be based upon the potential to form PIC's, which are themselves hazardous.

## Conclusions

1. Under optimum conditions, flames are capable of destroying hazardous waste compounds with very high efficiencies (greater than 99.995 percent) without the need for long residence time, high-temperature post-flame zones, or afterburners.
2. Reduced flame destruction efficiencies are the result of operation under some failure mode, such as poor atomization, poor mixing, or flame quenching.
3. Incinerability, or ordering of compounds in terms of their relative destruction efficiency, is dependent on the actual failure condition which caused the inefficiency.
4. Optimum conditions for destruction of hazardous waste compounds in turbulent diffusion spray flames correspond to minimal exhaust CO and total hydrocarbons.
5. No one incinerability ranking system appears to predict correctly the relative destruction efficiency of the five compounds tested for all failure conditions investigated. However, several rankings did correctly predict relative DE for specific failure conditions.
6. More data are required on other compounds and on other failure conditions more appropriate to different types of hazardous waste incinerators to fully determine the limitations of incinerability ranking systems and to develop an appropriate incinerability ranking methodology.
7. Future experimental effort should be directed toward extending the compound data base beyond the current five, and in particular, the extension of experimental capabilities to consider additional failure modes (e.g., those associated with post-flame thermal processes of afterburners).





**Figure 8.** Comparison of proposed ranking techniques and concentration measured in the experiments under flame failure conditions normalized to most predominant compound shows full scale.

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*J. C. Kramlich, M. P. Heap, J. H. Pohl, E. M. Poncelet, G. S. Samuelson, and W. R. Seeker are with EERC, Irvine, Ca 92714-4190.*

*C. C. Lee is the EPA Project Officer (see below).*

*The complete report, entitled "Laboratory-Scale Flame-Mode Hazardous Waste Thermal Destruction Research," (Order No. PB 84-184 902; Cost: \$16.00, subject to change) will be available only from:*

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*The EPA Project Officer can be contacted at:*

*Industrial Environmental Research Laboratory*

*U.S. Environmental Protection Agency*

*Cincinnati, OH 45268*

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