



Project Summary

Continuous Performance Monitoring Techniques for Hazardous Waste Incinerators

Rachel K. Nihart, John C. Kramlich, Gary S. Samuelsen, and
W. Randall Seeker

The report gives results of a study to determine the feasibility of an incinerator performance measuring methodology based on real-time continuous exhaust measurements of combustion intermediates; i.e., carbon monoxide, total hydrocarbons, and methane. The key issue was the correlation that exists between destruction and removal efficiency (DRE) and these intermediates. The study consisted of five steps:

1. A review of methods for monitoring intermediate species in the exhaust gases.
2. Selection of instruments for evaluation.
3. Evaluation of the instruments for response and potential interferences.
4. An experiment in which test organic compounds were incinerated in a laboratory-scale turbulent diffusion spray flame.
5. An analysis of the exhaust gas for both destruction efficiency (DE) of the waste compounds and the emission of intermediate species over a range of operating conditions from high- to low-efficiency operation.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, 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

A number of programs sponsored by the U.S. Environmental Protection Agency (EPA) have shown that thermal destruction is an effective technique for eliminating organic hazardous waste. Both field tests of operating incinerators and bench scale tests on turbulent diffusion spray flames have indicated that properly operated incinerators are very efficient. They have been found to destroy compounds to typically >99.99% destruction and removal efficiency (DRE) when operated correctly. However, there is currently no way to continuously monitor the DRE performance of the hazardous waste incinerator.

More than 300 organic wastes have been identified by the EPA as being hazardous. A particular waste stream may consist of a number of these compounds, and assurance must be given that the incinerator is not releasing any of them during normal operation. Because of the wide range of compounds and the low concentration levels that need to be measured, direct real-time continuous monitoring is beyond the state-of-the-art of measuring techniques. EPA's licensing procedure requires that high efficiency operation (DRE >99.99%) be demonstrated prior to operation for a selected set of constituents in the waste stream. After licensing, the incinerator is maintained within the range of operating conditions stipulated in the permit. During

routine operation, it is desirable to monitor the destruction efficiency (DE) of the unit and thereby allow corrective action to be initiated at the onset of unsafe performance. Methods available to measure specific hazardous waste compounds that are used during licensing trial burns (e.g., organic trapping and gas chromatography separation and analysis) are suitable for routine performance monitoring. They are both skill- and labor-intensive, noncontinuous, and the results are not immediately available after sampling.

Thus, there is a need for the development of an indirect real-time continuous monitoring methodology for hazardous waste incinerator performance. A number of indirect methodologies have been proposed. For this discussion, the potential methodologies can be categorized as:

- Tracer measurements (within waste stream composition or added).
- System parameter measurements (pressure, temperature, flow rate).
- Combustion intermediate species measurements (e.g., CO, hydrocarbons).
- Combustion product measurements (CO₂, O₂, NO_x).

Methodologies which rely on these measurements are largely untested and not completely developed. This study will concentrate on the use of intermediate species as a measure of incinerator performance since they appear most feasible at this time. Field tested and relatively low cost instrumentation is commercially available for several of the stable species.

Combustion of Organics

The combustion of organic molecules is a complex series of elementary reaction steps involving a myriad of intermediate species. For example, to completely describe the oxidation of the simplest organic (methane) requires more than 100 reactions and involves 25 intermediate species. For more complex organics, the numbers increase geometrically with the molecular weight. However, only a few of the species are stable; e.g., lower molecular weight hydrocarbons, methane (CH₄), carbon monoxide (CO), and formaldehyde. Also, these stable intermediates are common to the combustion of most organic compounds including hazardous waste and auxiliary fuels.

Organics burn in a complex series of fundamental reaction steps that eventually lead through CO as the principal intermediate before the completely oxidized state (CO₂) is reached. CO is a thermally stable compound, compared to hazardous waste organics. Since it is an intermediate, large amounts of CO are produced in the flame zone that will be eventually destroyed if mixing is good. If mixing is poor, CO can escape the flame by mechanisms of thermal quenching. Excessive CO emissions usually reflect poor mixing or incorrectly set combustion air. The CO level measured in the stack depends on many factors; e.g., waste properties, spray nozzle design and operation, combustion air mixing pattern, and incinerator chamber design. CO can be measured continuously, using nondispersive infrared analyzers, to concentrations of a few parts per million (ppm).

Exhaust emissions of hydrocarbons have three sources: (1) the unburned hazardous organic constituents due to a low DE, (2) unburned hydrocarbons from the auxiliary fuel, and (3) intermediate hydrocarbons generated during the combustion of the hazardous waste and auxiliary fuel. Which of these is dominant depends on the operating condition of the incinerator. However, the dominant source is likely the intermediate and, in particular, the light intermediates such as methane that are typically more thermally stable than the hazardous and fuel constituents. Total hydrocarbons can be measured with a flame ionization detector (FID) down to a few ppm, while CH₄ can be measured with similar sensitivity using a nondispersive infrared analyzer (NDIR). Formaldehyde, another hydrocarbon intermediate, is somewhat less stable than CO or CH₄ and no suitable instrumentation is currently available for routine continuous monitoring.

Study Objective

The objective of this study is to determine the feasibility of an incinerator performance monitoring methodology based on real-time continuous exhaust measurements of combustion intermediates, specifically: CO, total hydrocarbons, and CH₄. The key issue is the correlation between destruction and removal efficiency (DRE) and these intermediates. The study involved five steps:

1. A review of methods for monitoring intermediate species in exhaust gases.
2. Selection of instruments for evaluation.

3. An evaluation of the instrument response and potential interference.
4. An experiment in which a set of organic compounds are incinerated in a laboratory-scale turbulent diffusive spray flame.
5. Analysis of the exhaust gas for DE of the waste compounds and emission of intermediate species over a range of operating conditions from high- to low-efficiency operation.

Study Approach

This approach was designed to determine if correlation exists between the level of combustion intermediates and the DE in the turbulent spray flame. A turbulent flame reactor (TFR) can be operated under conditions where DE are very high (>99.999%). The conditions investigated covered a range of low-efficiency conditions and failure modes: fuel rich, excessively lean, poor atomization quality, and flame quench. These failure modes were considered to be representative of practical operation conditions that might exist in liquid injection incinerators.

The exhaust concentrations of the ten hazardous waste compounds were measured along with the concentrations of ten hydrocarbons, CH₄, and CO for each of the conditions delineated above in order to assess the correlation between DE and the concentration of intermediate species. The test compounds were mixed 1:1 by mass with diesel fuel and introduced to the reactor. The compounds used were acrylonitrile, benzene, chloroform, and chlorobenzene—were selected because they are EPA-listed hazardous organic compounds and because they are expected to represent a broad range of incinerability behavior.

The purpose of this study was to determine the feasibility of utilizing real-time continuous exhaust measurements of combustion intermediates as a way to monitor incinerator performance. The key issue was to determine if a direct correlation exists between DE and intermediate species concentration measurements. DE was based on exhaust measurements for specific input waste compounds using a Tenax cartridge for capture and gas chromatography, flame

*This report distinguishes between waste destruction efficiency (DE) and waste destruction and removal efficiency (DRE). DE is based on measurement of input and output concentrations of a species across a thermal treatment reactor but upstream of any control device which removes that species from the flow exhaust.

ionization detection for sample analysis. The intermediate species measurements were selected to be continuous and real-time. A comparison of the potential intermediate measurements with the availability of commercial instruments resulted in the selection of a Beckman 402 Total Hydrocarbon Analyzer (THC), a Beckman 864 NDIR methane analyzer, and an Anarad AR-500 NDIR CO analyzer. The response of each instrument was compared to DE measurements from a turbulent spray flame in order to experimentally determine if flame zone correlation exists.

The TFR was designed so that the processes controlling DE in the flame (e.g., atomization quality, ballistic transport, turbulent mixing, flame quench, and flame-surface impingement) simulate those that control DE in the flame zone of a liquid injection incinerator. The cold walls of the TFR were designed to emphasize flame zone performance by quenching post-flame reactions. As such, the TFR data do not directly address how post-flame processes such as afterburners and gas cleaning equipment affect the flame-zone correlations.

The data presented are cross-plotted to produce the DE/continuous monitoring correlations shown in Figure 1. These represent a broad range of operating conditions from high flame efficiency to low DE failure conditions. Two general correlations were observed between DE and the intermediate species measurements:

1. **THC and CH₄:** The correlation between DE, THC, and CH₄ is nearly proportional; i.e., a linear increase in the intermediate concentration corresponds to a proportional increase in the hazardous component concentration.
2. **CO:** The CO correlation indicates that a significant increase in CO emissions is necessary before the exhaust concentration of waste compounds increases substantially.

Fundamental combustion kinetic studies (e.g., laminar flat-flames) indicate that hydrocarbon flames can be divided into two partially overlapping regions. In the first, hydrocarbon fuel is rapidly consumed by reaction with flame radicals (O, H, OH) to produce CO and water. In the second region, the CO is oxidized to CO₂ at a relatively slow rate. The flame can be made to operate inefficiently by, for example, a reduction in temperature or the addition of flame inhibiting compounds. The first manifestation of

this inefficiency is the release of CO because the hydrocarbon destruction reactions remain sufficiently fast to quantitatively remove organic molecules. It is only after the flame has become extremely inefficient that hydrocarbons are released, by which time the CO emissions are substantial.

Although a direct comparison between laminar flat-flame and turbulent flame results is difficult due to the fundamental difference between the processes, the reactions occurring in each are the same. These reactions are simply superimposed on different fluid dynamic backgrounds. Thus, a qualitative explanation for the flame zone correlations observed here would include:

- Since the hydrocarbon intermediates and the model waste compounds are made up of organic molecules, the flame destruction rate of each is similar, at least relative to the slower CO destruction rate.
- Decreased flame efficiency is evidenced by CO release while hydrocarbon intermediates and the waste compounds are still quantitatively destroyed.
- Further decreases in flame efficiency bring about a concurrent release of hydrocarbon intermediate and organic wastes due to the (relative to CO) similarity in their flame destruction rates.

Conclusions

These data support the following conclusions:

- A turbulent spray flame operating without afterburners or postflame gas cleaning can achieve a DE of 99.99%. This implies that careful design of efficient burners can cause the flame zone of a liquid injection incinerator to perform most, if not all, of the legally required waste destruction.
- The data indicate that flame conditions which minimize CO, THC, and CH₄ emissions result in optimum waste DE. This indicates that maximum flame efficiency, defined by the release of fuel and fuel fragments, also results in maximum waste destruction.
- Less than optimum DE performance was accompanied by an increased release of intermediate species. This means that, for all conditions examined in this study, a change in DE toward lower efficiency was always accompanied by an increase in CO, THC, and CH₄.

- The range of conditions for optimum flame performance, as defined by CO, THC, and CH₄, was found to be less than or equal to the range for high DE. This means that, under some conditions, the flame performance could decrease without a significant decrease in DE.
- CO was found to increase significantly under some conditions in which the DE remained high.

Application of these results to the continuous monitoring behavior of a full-scale incinerator requires some assessment of how the postflame zone process, such as afterburners or scrubbers, affect the flame zone correlations. Due to the very low solubility of hydrocarbons and CO in aqueous solutions, incinerator scrubbing systems would not be expected to alter the continuous monitoring correlations for organic wastes. However, the afterburner may be expected to impact the postflame zone correlations. The aliphatic hydrocarbons that make up the bulk of THC, in particular CH₄, are generally equally or more resistant to nonflame thermal destruction than the waste compounds upon which thermal testing has been performed. This indicates that monitoring THC and CH₄ approach is potentially more conservative than indicated by the flame measurements. Thermal testing has not been performed on CO. However, detailed chemical kinetic predictions indicate that the nonflame thermal destruction rate of CO is approximately the same as that for hydrocarbons (as opposed to the flame destruction rates in which the hydrocarbons predominate). Thus, no large alteration of the flame zone correlation would be expected.

The correlations shown in Figure 1 suggest that CO is possibly an overly conservative indicator of flame performance. That is, an incinerator shutdown procedure based on response of a CO monitor may be environmentally safe but economically impractical. The results of this study suggest the following approach to incinerator monitoring and control:

- Use CO as an indicator of flame performance, but not as an incinerator shutdown criterion. This should provide a way to tune the flame operating parameters.
- Use THC as a shutdown alarm to indicate potential waste compound release.

Use of these two instruments in tandem provides, through CO, a way to tune for flame efficiency and, through THC, a way

to indicate incipient waste emission and direct shutdown.

Quality Assurance/Quality Control requirements are applicable to this project. The data contained in this report are NOT supported by QA/QC documentation as required by the U.S. Environmental Protection Agency's Quality Assurance Policy.

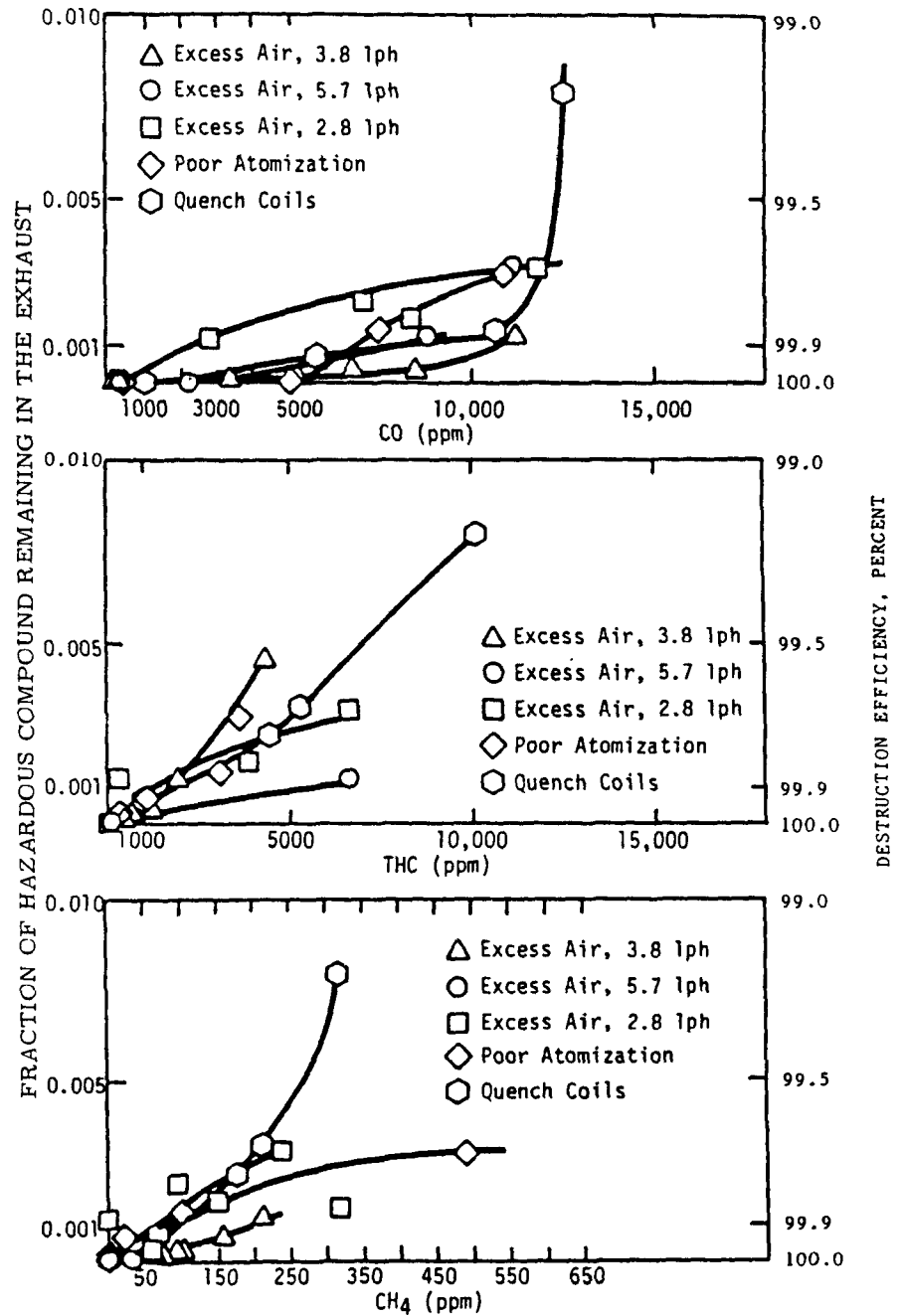


Figure 1. Fraction of hazardous compound remaining in the exhaust as a function of intermediate species concentrations.

R. Nihart, J. Kramlich, G. Samuelsen, and W. Seeker are with Energy and Environmental Research Corp., Irvine, CA 92714-4190.

W. Steven Lanier is the EPA Project Officer (see below).

The complete report, entitled "Continuous Performance Monitoring Techniques for Hazardous Waste Incinerators," (Order No. PB 89-195 192/AS; Cost: \$15.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Air and Energy Engineering Research Laboratory

U.S. Environmental Protection Agency

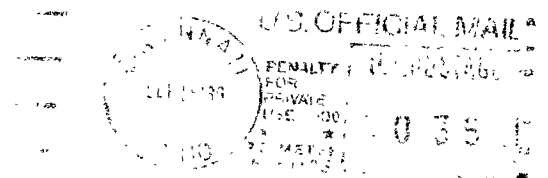
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S2-89/021



000085833 PS
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604