



## Project Summary

# Report for Non-Flame Hazardous Waste Thermal Destruction

A laboratory apparatus, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system, has been used to investigate the impact of key factors of the post-flame zone in the combustion process upon the effluent decomposition products. The results from thermal treatment of various organic compounds showed that:

(1) Very good reproducibility under similar test conditions was obtained for effluent composition/concentration from initial thermal treatment tests, of a solid, pentachloronitrobenzene, and a volatile organic, chloroform.

(2) Thermal decomposition profiles of individual organic compounds introduced as the feed material to the system provided DE (Destruction Efficiency) values for each compound.

(3) Products of Incomplete Combustion (PICs) were generated, sometimes in major quantity, that accounted for a large portion of the elemental composition of the feed material.

(4) Test series concentrating on the thermal treatment of chloroform showed major differences in PIC generation as a result of different atmospheres (rich oxygen and reduced oxygen). It appeared that several hundred degrees (°C) higher temperature would be needed to attain the same degree of destruction of the more refractory PICs in the reduced oxygen atmosphere as was shown in the rich oxygen case.

*This Project Summary was developed by EPA's Hazardous Waste Engineering 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

In the thermal destruction of hazardous organic waste material, the interactions of the gaseous components in the post-flame or the non-flame zone of the combustion process make an important contribution to the overall results. The thermal decomposition in those zones can range from simple pyrolysis in an oxygen-deficient atmosphere as might occur in an incinerator or a boiler, to a thermal-oxidative treatment with a considerable excess of oxygen as can occur for example in a liquid injection incinerator supported by a secondary combustion zone or supply of air.

A laboratory unit, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC), has been used to investigate key thermal decomposition factors of the post-flame zone, such as temperature and atmosphere in the reactor zone, and their impact upon the effluent decomposition products. The TDU-GC was developed at the University of Dayton Research Institute (UDRI) and has been applied by Institute personnel over the past several years to study many organic compounds.

The TDU-GC at EPA's Center Hill Facility has been used to develop thermal decomposition profiles for various organic compounds as well as to study some of the compounds in depth for the purpose of evaluating several factors of the decomposition process and of PIC (Product of Incomplete Combustion) formation.

## Experimental Procedure

The principal equipment used in this study was the Thermal Decomposition Unit-Gas Chromatograph system, a closed in-line system consisting of two basic units, (1) the thermal reactor and (2) the analyzer, a gas chromatograph. These units are shown in the basic schematic illustration, Figure 1. The experimental procedure used was as follows:

1. The thermal reactor incorporates a capillary quartz tube within a furnace with three heating zones that are independently controlled to produce temperatures up to 1150°C in the central zone for thermally decomposing the sample compound in its gaseous state.

A tubular quartz extension at the entrance of the furnace transfers the feed gas from the larger-bore sample insertion chamber. That chamber is fitted with any one of several probes adapted to handle gas, liquid or solid samples. A temperature programmer controls the heating jacket on the insertion chamber, for converting the liquid and solid samples to the vapor phase at selected elevated temperatures. The vapor or gas is conveyed to the reactor by a controlled flow of carrier gas which is selected according to the nature of the atmosphere required in the high-temperature zone of the reactor. According to the temperature and pressure measured in the reactor tube, the carrier gas flow is regulated at the instrument console to result in a precise residence time of the vaporized/gaseous sample in the closely controlled high-temperature zone.

The gaseous emission from the reactor pass through a capillary tube into a in-line tubular trap controlled to sub-ambient temperatures as low as -50°C and colder. The trap is located inside the wall of the gas chromatograph (GC) and is a very short (several mm) section of the extension of the GC capillary column into the 30:1 splitter tubing.

2. The gas chromatograph is fitted with a fused silica capillary column leading to a flame ionization detector (FID). Heating the trap transfers, via the 30:1 splitter, the smaller stream of trapped emissions sample to the front end of the capillary column which itself is at the sub-ambient temperature. Upon injection of the sample into the GC, as initiated by the switch on the supporting computer, the temperature program for the capillary column controls the separation of the components of the reactor emissions sample and their ensuing detection and measurement by the FID.

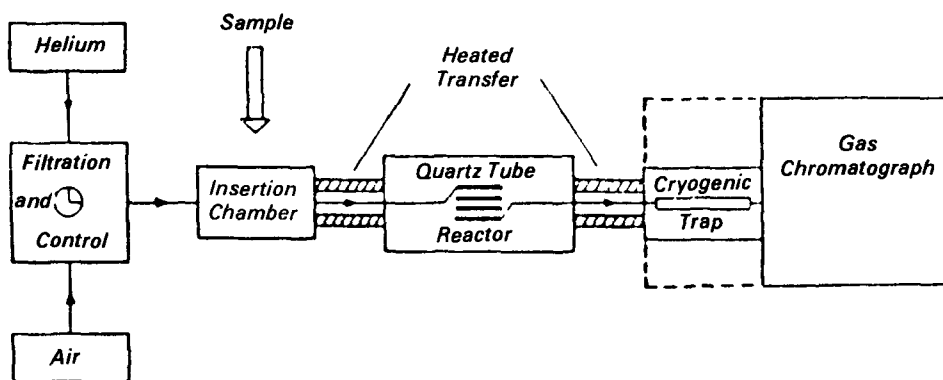


Figure 1. Basic schematic of TDU-GC system.

The computer, coupled with a recorder, provides a means of storing the output from the FID and of depicting it in a chromatogram as well as in a tabulation of the various peak areas.

3. The Principal Organic Hazardous Constituent (POHC) material under investigation was introduced into the insertion chamber as a gas, liquid or solid.

The more volatile, low molecular weight compounds were generally fed by syringe to the TDU-GC system as gaseous samples prepared at known concentrations.

For various organic liquids, nanoliter quantities were injected directly into the insertion chamber where the sample was converted to the vapor form by a programmed temperature increase that provided transfer by the carrier gas into the thermal reactor.

4. Samples of organic solids were deposited as measured amounts in solution onto the end of the "solids" probe. Evaporation of the solvent left a residue which in the confines of the insertion chamber was transformed to the vapor state for transfer into the thermal reactor by the carrier gas.

## Results

Thermal decomposition profiles were obtained for various organic compounds. In the process of the thermal decomposition of the POHC (feed) material, various PICs formed and in turn decomposed with temperature increase in the reactor. In some cases, the major PICs were identified and then quantified through subsequent calibration runs. Where unidentified PICs were included in the plots, for lack of calibration runs that would help quantify those components, their peak area counts obtained from the analysis step were treated as being equivalent to the counts of the POHC material in the plot presentations.

Through a major effort expended on the study of the thermal treatment of chloroform, the effects of atmospheric (rich oxygen and reduced oxygen) type were presented in plots, percent conversion vs. temperature. The changes in PIC formation—peak level temperature of DE, and rates of formation/decomposition—were readily depicted through comparison of the plot for the different reactor atmospheric conditions.

In most every case, the temperature range investigated extended beyond the point for 99.99% DE (Destruction Efficiency) of the POHC (feed) material.

## Discussion

The early test runs, with perchloronitrobenzene (PCNB) and with pure chloroform, were made primarily to check for inter-laboratory reproducibility. The PCNB results from the present study yielded a decomposition curve for PCNB that closely matched that reported by UDRI; the formation/decomposition profile of the PIC, hexachlorobenzene, also closely matched that reported by UDRI. The results for the thermal treatment of chloroform showed very good agreement with those presented by UDRI as reported for some of their earlier work with toxic organic compounds. The three major PICs of the current study, which were identified as hexachloroethane, tetrachloroethylene and carbon tetrachloride apparently were the same as the three unidentified PICs presented in the UDRI plot.

In a study of a chloroform-heptane mixture (3 weight percent chloroform) the effective masking of the GC peak for chloroform and its products by the heptane source pollutants limited the results to simply a decomposition profile for heptane, with a  $T_{99.0}(2)$  of 675°C.

(temperature for 99.0 percent destruction of heptane at 2.0 seconds residence time).

Thermal treatment of monochlorobenzene, trichloroethylene and Freon-113 indicated a  $T_{99.99}(2)$  of 850, 875, and 810°C, respectively, for those compounds.

Some remarkable differences in PIC emissions concentrations were noted when chloroform was exposed to high temperatures under highly oxidative (Figure 2) and under reduced oxygen (Figure 3) atmospheres:

(1) Tetrachloroethylene,  $C_2Cl_4$ , was far more refractory under the reduced oxygen condition. Its presence persisted in large amount throughout the higher temperatures investigated. At the 850°C level, there still was about 15 mol percent of the compound present in the emissions, in sharp contrast to the mere 0.4 percent in the rich oxygen atmosphere case.

(2) Carbon tetrachloride,  $CCl_4$ , also persisted through the higher temperatures much more in the reduced oxygen atmosphere.

(3) Hexachloroethane,  $C_2Cl_6$ , was more readily formed in the high oxygen atmosphere than in the reduced oxygen case.

(4) Pentachloroethane,  $C_2HCl_5$ , appeared in trace amounts in the reduced oxygen runs, but was not detected in the rich oxygen series.

(5) The POHC chloroform had a slightly higher value of about 635°C for the 99.99% DE point in the reduced oxygen atmosphere as compared to about 610°C in the rich oxygen case.

Only perchlorinated compounds were being formed in significant/detectable amounts in the reduced oxygen atmosphere, with both tetrachloroethylene and carbon tetrachloride persisting through the higher temperatures.

Tetrachloroethylene was also produced in considerable quantity as a PIC when carbon tetrachloride was exposed as a feed, to high temperature treatment.

## Conclusions and Recommendations

The Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system has been used to evaluate the non-flame thermal decomposition of various organic compounds associated with the incineration of toxic/hazardous organic waste substances.

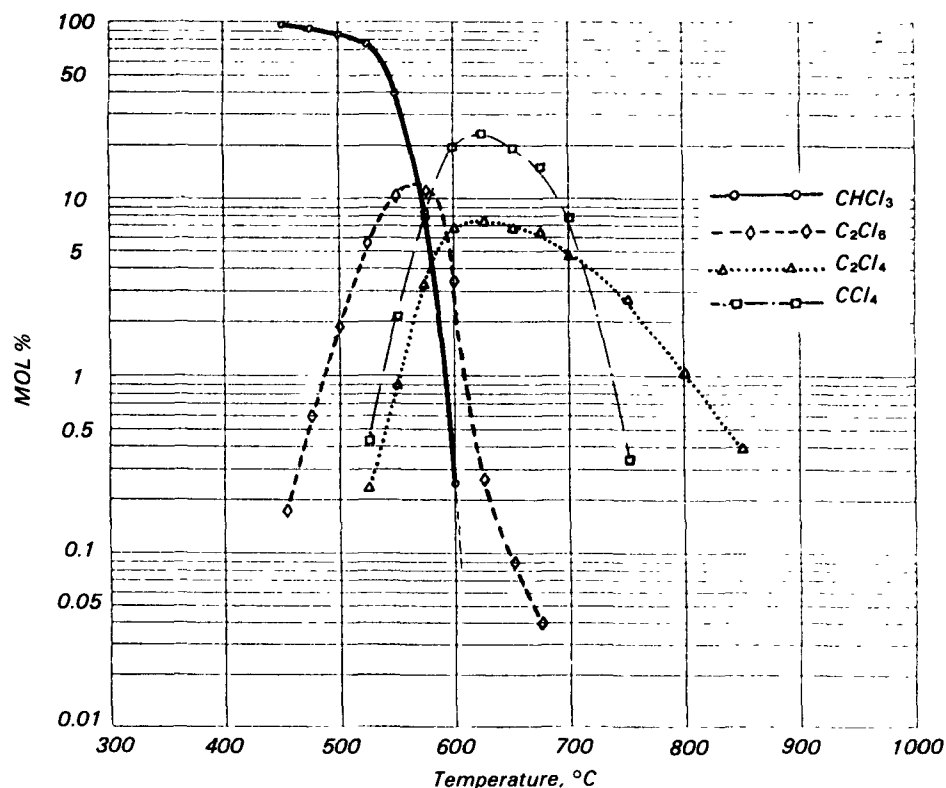


Figure 2. Thermal treatment of chloroform  $CHCl_3$  (vapor feed, air carrier gas).  $\left[ \begin{matrix} \bar{t}_r = 2.0 \text{ sec} \\ \phi = \sim 0.05 \end{matrix} \right]$

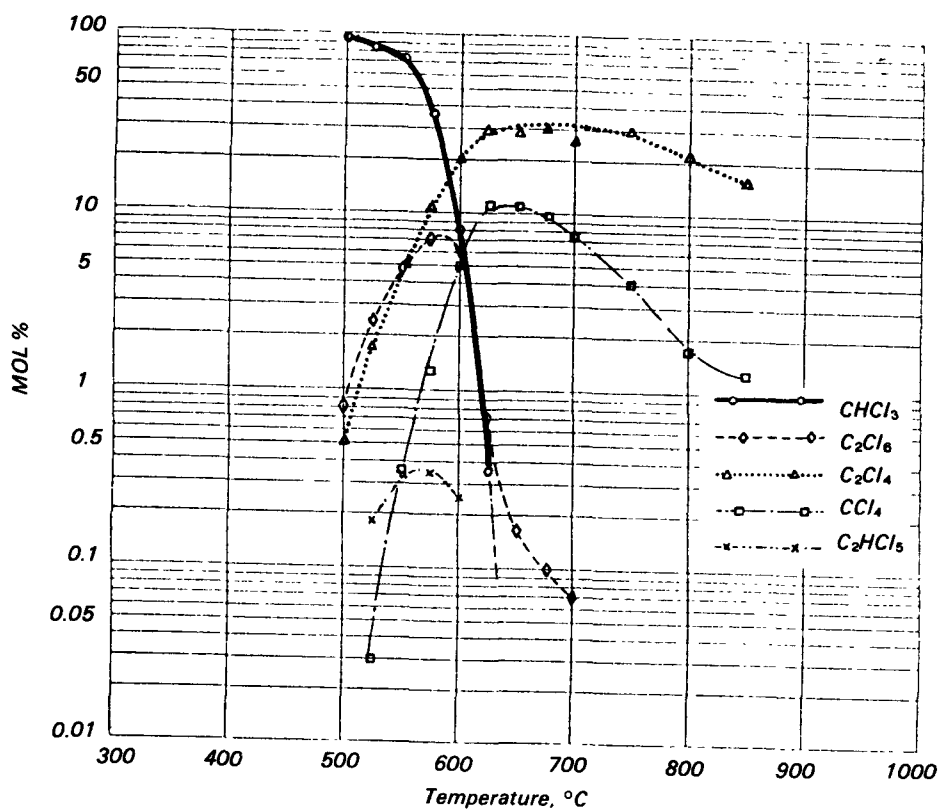
The system has been used successfully to demonstrate reproducibility of results consistent with the findings of other investigations using similar equipment.

From the experience with heptane as a component in the feed, it appears necessary, for accurate measurement of the effects of feed composition, to limit mixtures for study to a very few, perhaps only two, compounds that are individually "clean" in any GC analysis.

In the study of oxygen/organic-compound ratio, the oxygen in a large amount had a very significant effect upon the composition of the emissions under the test conditions used. Perchlorinated compounds were totally dominant in the reduced oxygen atmosphere; in the rich oxygen atmosphere, those compounds were far more readily being eliminated. It appears that a temperature several hundred degrees (°C) higher is needed in a reduced oxygen atmosphere to obtain the same destruction level of PICs that was observed for the oxygen-rich atmosphere. Also, the generation/production levels of the PICs

varied with the oxygen concentration levels. Clearly, the mechanisms/rates for PIC formation were different in those different atmospheres. In the oxygen-rich atmosphere, there were no hydrogen-containing organic compounds detected in significant amounts.

For more fully characterizing the thermal reactor emissions with respect to PICs, more extensive procedures involving additional instrumentation is needed to identify and quantify PIC compounds. A Mass Selective Detector (MSD) dedicated to the TDU-GC system is the instrument of choice, both for accuracy of determinations and for volume of work (data) that can be expected.



**Figure 3.** Thermal treatment of chloroform  $\text{CHCl}_3$   $\left[ \bar{t}_r = 2.0 \text{ sec} \right]$   
(vapor feed, nitrogen carrier gas).  $\left[ \phi = \sim 0.76 \right]$

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The complete report, entitled "Report for Non-Flame Hazardous Waste Thermal Destruction," (Order No. PB 87-130 274/AS; Cost: \$11.95, subject to change) will be available only from:

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