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Project Summary

Description and Operation of a Thermal Decomposition Unit-Gas Chromatographic System

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Controlled high-temperature incineration is recognized as one of the most promising methods for the permanent disposal of industrial organic wastes. However, before acceptable incineration procedures can be fully implemented, information is needed concerning the thermal decomposition properties of the immense variety of organic materials. In response to this need, laboratory-scale thermal instrumentation has been designed and developed for experimentally determining the high-temperature gas-phase decomposition properties of toxic organic substances. A thermal decomposition unit-gas chromatographic (TDU-GC) system has been designed and assembled to provide data rapidly and safely on the gas-phase thermal decomposition behavior of organic substances. This system has been designed to accommodate a wide variety of organic materials which range from pure substances to complex industrial organic waste mixtures. Data obtained with the TDU-GC can provide guidance with respect to the eventual incineration of numerous industrial organic wastes.

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

Numerous procedures have been proposed for the disposal of the vast quantities of industrial organic wastes that are produced annually. One of the most promising methods for the permanent disposal of hazardous organic wastes is controlled high-temperature incineration. Before this disposal technology can be developed fully, more precise information is needed concerning the high-temperature decomposition properties of an immense variety of organic materials. Accordingly, there are many advantages to generating such basic gas-phase thermal decomposition data in the laboratory, where conditions can be precisely adjusted and easily controlled. Once the thermal decomposition properties of a particular material have been characterized in the laboratory, the preliminary decision can be made as to whether high-temperature incineration is a viable disposal route for that material.

Appropriate incineration of toxic organic wastes requires very high temperatures, sufficient gas-phase residence time, ample quantities of oxygen, and extensive gas-phase mixing. With the use of laboratory-scale instrumentation, a wide variety of environmentally important organic compounds can be studied with respect to their thermal decomposition behavior. Laboratory-scale studies are especially suited for identifying and studying the parameters and variables that affect gas-phase high-temperature decomposition behavior.

At the University of Dayton Research Institute, two thermal decomposition unit-gas chromatographic (TDU-GC) systems have been designed and assembled for conducting laboratory-scale thermal decomposition studies with various organic materials. Figure 1 shows a block diagram of the TDU-GC

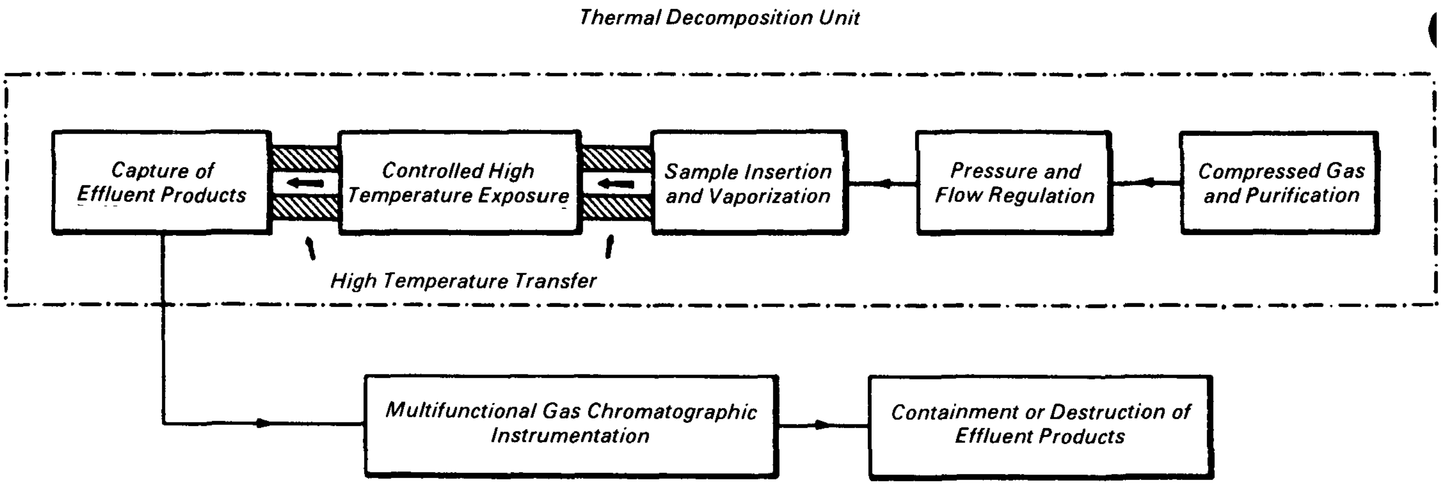

Figure 1. *Block diagram of TDU-GC.*

system, and Figure 2 is an artist's rendering of the system. The TDU-GC has been designed for measuring the thermal decomposition properties of a wide range of organic samples—gases, liquids, solids, and even polymers. Thermal decomposition tests can be conducted relatively easily with the TDU-GC after suitable familiarization and experience.

The TDU-GC is a continuous system that can be viewed as two in-line instrumental stations or units. The primary function of the thermal decomposition unit (TDU), that is, the first station of the system, is to subject gas-phase molecules to well-defined thermal exposures. The GC portion of this system, that is, the second in-line station, serves to capture, separate, and analyze the various chemical constituents that have passed through the TDU.

One of the distinct advantages in conducting thermal decomposition experiments using the laboratory-scale TDU-GC is that each molecule is subjected to essentially the same thermal exposure. Also, the sample insertion section of the TDU-GC was designed to be as versatile as possible and there are numerous modes for inserting samples into the system.

One major requirement with respect to sample handling with the TDU-GC is that substances leaving the sample insertion chamber must be in the gas phase. Therefore, TDU-GC samples are either volatilized or thermally degraded in the sample insertion chamber. Also, the rate at which molecules are admitted into the high-temperature reactor is an important factor in thermal decomposition studies. In addition to the sample handling requirements, there are three basic criteria that must be met for proper transport of gas-phase samples. Material inertness and uniformity are important, and, therefore, fused quartz was used as the tubing material for sample transport in the TDU-GC. The second basic requirement for good transport involves the continual gas sweeping of the transfer tubing. The selection of transport temperature and the maintenance of uniform temperature along the transport path constitutes the third criterion for proper transfer of sample. Each of these criteria was given special attention in the design of the TDU-GC system.

One of the most important components of the TDU-GC system is the high-temperature reactor. The design considerations and the thermal reactor assembly details are found in a previous report on the development of a thermal decomposition analytical system (see EPA-600/2-80-098). Using the multiple folded racetrack reactor design, as shown in Figure 3, sample molecules encounter essentially isothermal conditions during their traverse through the reactor due to the averaging of the existing subtle longitudinal temperature gradients. A temperature versus time profile for gas-

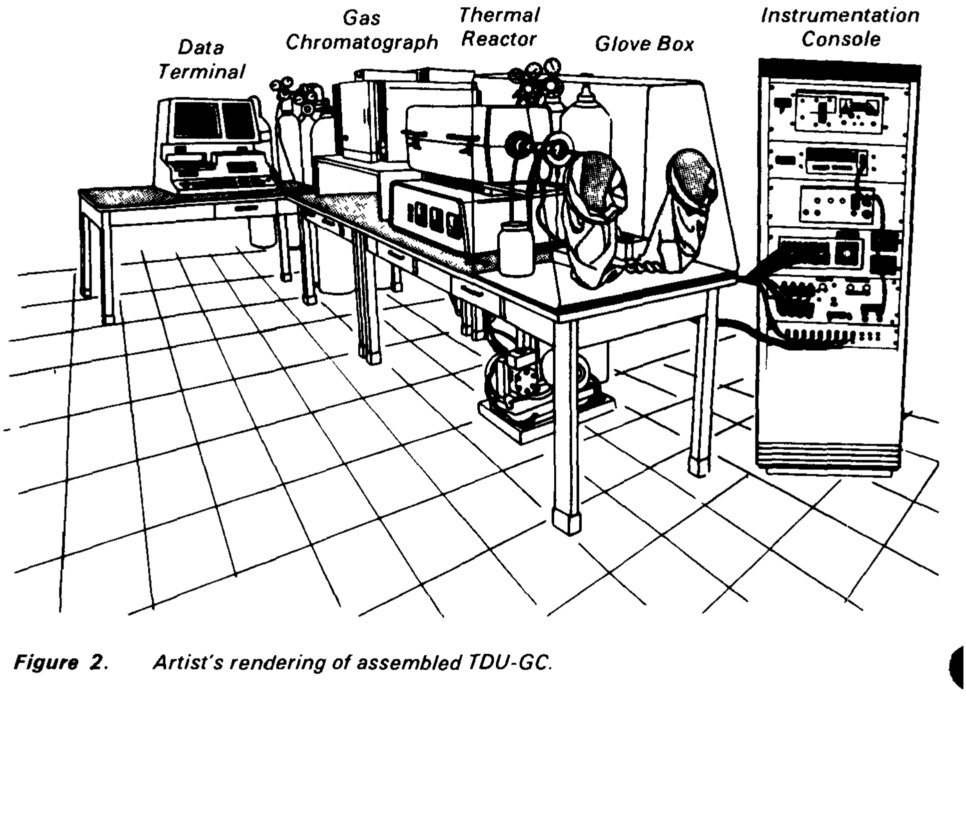

Figure 2. *Artist's rendering of assembled TDU-GC.*

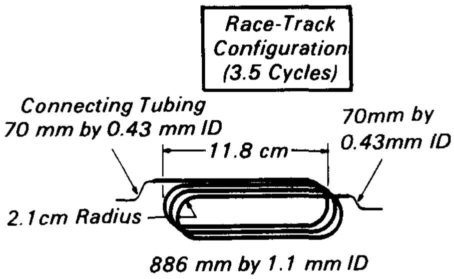

Figure 3. *Detail of Quartz Tube Reactor*

phase molecules is shown in Figure 4. The high-temperature unit selected for heating the quartz thermal reactor assembly employed a three-zone furnace of hinged construction that was designed for continuous operation at temperatures up to 1200°C.

In the TDU-GC, the effluent from the high-temperature reactor is swept through the heated exit transfer line after which it is cryogenically cooled. The entire flowpath is then purged with an inert carrier gas, where upon the collected sample is subsequently passed into a high-resolution gas chromatograph.

The assembled TDU-GC system includes a versatile modular instrumentation console which is used to monitor and control the many experimental variables, such as reactor temperature, gas flow rate, transport temperatures, and pressure. The gas flow control module of this console is an especially important component as it has direct interaction with the high-temperature reactor.

Laboratory-scale thermal decomposition experiments rely strongly on the analysis of the chemical compounds that emerge from the high-temperature reactor. Accordingly, the primary function of the GC located in the TDU-GC assembly is to separate the constituents of the various complicated chemical mixtures. Another vital function of the TDU-GC separation column is to trap cryogenically the condensable products that emerge from the high-temperature reactor.

Test samples that are to be introduced into the TDU-GC can be prepared in their final form within the confines of the glove box that surrounds the entrance to the sample insertion region of the TDU-GC. Sampling procedures have been developed for gaseous samples, highly volatile liquid samples, low volatility liquid samples, and also solid organic samples. For low volatility organic samples, a microliter syringe can be used for sample introduction; however, in most cases, the sample of interest will have to be diluted with a suitable solvent.

With the TDU-GC system, precise thermal decomposition experiments can be conducted using a wide assortment of pure organic substances or highly complex industrial organic waste mixtures. Figure 5 shows a chromatogram of an extremely complex organic waste mixture which was examined using a TDU-GC. The skeletal chromatogram presented in Figure 6 gives an indication of the relatively few stable compounds from that complex sample which survived a 2 0 second 690°C exposure while in a flowing air atmosphere.

Although the TDU-GC is especially suited for complex organic mixtures it can also be used to:

a) establish the thermal decomposition profile of a substance;
b) determine the residence time effects and associated kinetic behavior;
c) investigate different gaseous atmospheres, pressure effects, and other related thermal decomposition variables;
d) collect data for prediction of thermal decomposition behavior; and
e) provide guidance for larger scale thermal disposal operations.

The TDU-GC system that is located in the Environmental Chemistry Laboratory at the University of Dayton has been in operation since early 1982. Maintenance and troubleshooting procedures have been established for the TDU-GC systems.

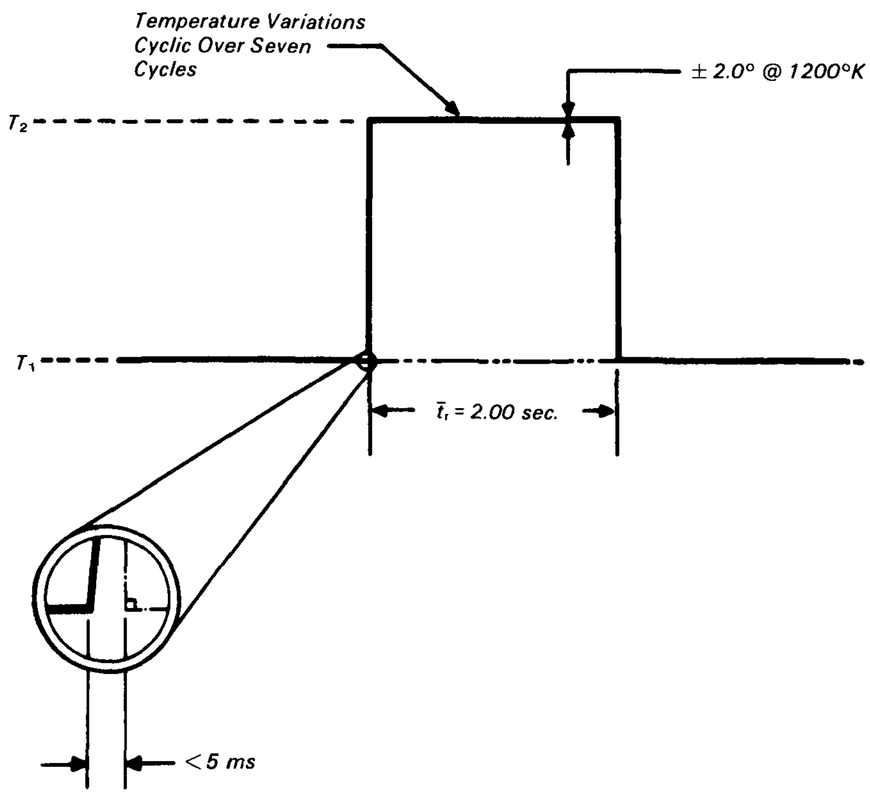

Figure 4. *Square wave profile of gas-phase temperature versus time.*

Conclusions

The TDU-GC laboratory system has the following specific features incorporated into its design:

- With the closed continuous design concept and the gloved-boxed sample entry of this system, toxic samples can be safely tested.
- Samples can be subjected to a very precise thermal exposure in the TDU-GC. At selected reactor temperatures ranging from 200°C to 1150°C, the maximum temperature variation is less than ±2°C
- The TDU-GC is capable of subjecting a sample to a precise mean residence time ranging from 0.25 to 5.0 seconds. In addition, this system provides a narrow Gaussian residence time distribution.
- With the flexibility designed into the TDU-GC, thermal decomposition studies can be conducted using pure organic substances or complex organic mixtures, and only small quantities of sample are needed

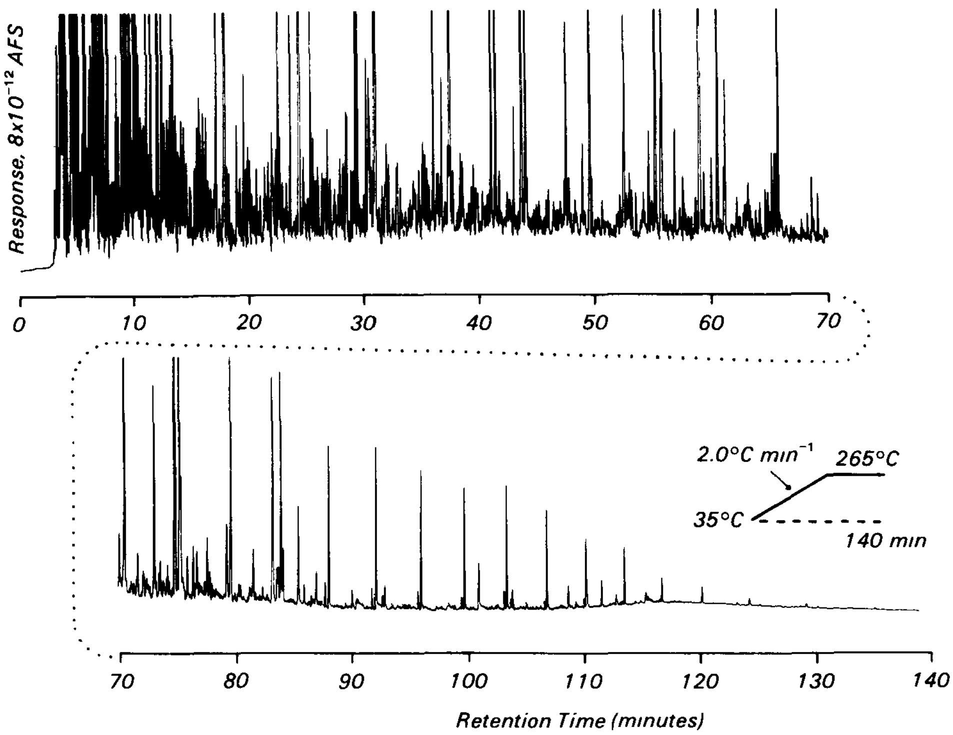

Figure 5. *HRGC chromatogram of composited waste sample.*

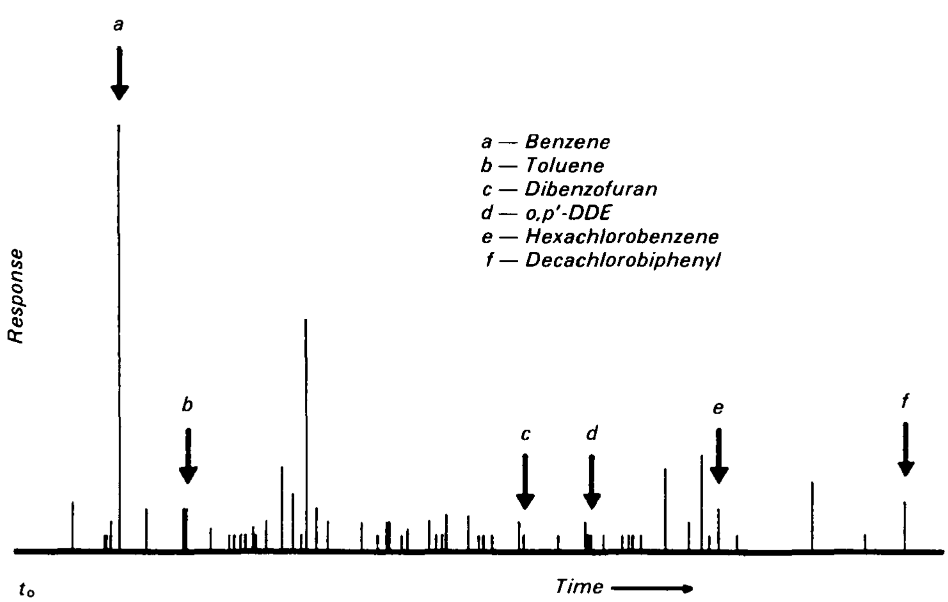

Figure 6. *Skeletal TDU-GC chromatogram of the composited waste effluent.*

(micrograms). Samples can be either gases, liquids, or solids. In addition, these samples can be subjected to thermal decomposition studies in any of a wide variety of atmospheres.

- Analyses of the thermal decomposition products are performed through the use of a versatile high-resolution gas chromatograph and a variety of sensitive detectors.
- The TDU-GC can provide fundamental thermal decomposition data rapidly and economically.

Recommendations

In view of the numerous industrial organic compounds and mixtures that need to be subjected to permanent disposal, it is recommended that the high-temperature gas-phase thermal decomposition behavior of these organic materials be evaluated using the laboratory-scale thermal decomposition unit-gas chromatographic (TDU-GC) system. This thermal instrumentation system has been designed for the efficient examination and safe handling of a wide variety of organic substances. It is recommended that laboratory-scale data be obtained prior to subjecting large quantities of complex organic mixtures to controlled high-temperature incineration.

It is further recommended that the TDU-GC be utilized for data base generation such as studying the thermal decomposition behavior of hazardous organic compounds and determining the formaton of products of incomplete combustion (PICs). As many variations in conditions can occur throughout the various areas of a large incineration system, it is recommended that the effects of different incineration variables be studied using the TDU-GC system.

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***Richard A. Carnes** is the EPA Project Officer (see below).*
The complete report, entitled "Description and Operation of a Thermal Decomposition Unit-Gas Chromatographic System," (Order No. PB 84-246 362; Cost: $16.00, subject to change) will be available only from:
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