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HIGH-TEMPERATURE LUBRICANT ANALYSES
USING THE SYSTEM FOR THERMAL DIAGNOSTIC
STUDIES (STDS)- A FEASIBILITY STUDY

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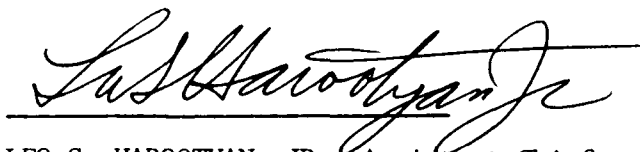


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assembly, and the associated instrumental chemical analyses consisted of tandem high-resolution gas chromatography, mass spectrometry, and Fourier transform IR spectroscopy. Laboratory experiments were conducted on the four different lubricants with respect to thermal exposure, the effects of residence time, and behavior in different gaseous environments. Comparisons were then made with respect to the relative stability of the various lubricants. The major conclusion from this investigation was that the STDS mode of experimental evaluation provided new capabilities and insights into the study of the thermal degradation behavior of lubricant samples.

FOREWORD

This report was prepared by the Environmental Sciences Group within the Research Institute of the University of Dayton, located in Dayton, Ohio 45469-0001. The study reported herein was conducted under Task 22 of the Scholarly Research Program for Contract F33615-84-C-2411, which was sponsored by the Aero Propulsion and Power Laboratory, Wright Research and Development Center, Wright-Patterson Air Force Base, Ohio 45433-6563.

This investigation consisted of a feasibility study which addressed the use of specially designed laboratory instrumentation for experimentally evaluating the high-temperature stability behavior of different lubricants. Although this particular investigation was initiated in the summer of 1987, subsequent work with this same type of laboratory equipment was performed under Scholarly Research Program F33615-87-C-2714.

The Project Officers for this effort were Lt. Charles Kelly and Edward Pitzer (WRDC/POSL). The final phase of this work was completed within the Lubricants Branch, Bldg. 490 at Wright-Patterson Air Force Base, Ohio 45433-6563.



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SECTION 1

INTRODUCTION

The high-speed and high-performance aircraft of the future will generate considerably greater temperatures throughout various portions of the aircraft. Consequently, fuels, lubricants, hydraulic fluids, and many other organic materials and composites will need to withstand these elevated temperatures. Although research into enhanced heat dissipation mechanisms is on-going, and progress will undoubtedly be made in the ability to dissipate some of this increased thermal burden, it is still envisioned that many of these different organic materials will be subjected to much greater thermal stress than in previous aircraft.

Ester-based lubricants have essentially fulfilled the task of providing lubrication for the turbine engines that are currently used in commercial and military aircraft. Some of the classes of compounds considered for future higher-speed aircraft are liquid lubricants such as polyphenylethers, perfluoro ethers, and silahydrocarbons. It is anticipated that these liquid organics will experience temperatures in excess of 600°F. Solid lubricants such as oxythiomolybdates are also being considered for these high-performance aircraft, and their surface temperatures may approach 1600°F. A considerable amount of laboratory research is anticipated with respect to establishing desired lubrication formulations for these future aircraft.

Consequently, much attention will be given to the long-term thermal exposure aspects of lubricants.

Current test methods for evaluating thermal behavior and oxidation stability need to be expanded to provide more definitive information with respect to evaluating the physicochemical characteristics of these lubricants at elevated temperatures.

Extensive laboratory-scale examinations of the thermal stability of organic substances have occurred with halogenated hydrocarbons. However, much of this work has been done with lower molecular weight species and the bulk of the studies have centered around determining the ease of thermal destruction of the organic species. It is anticipated that the application of the same instrumental technology can be used for determining the long-term thermal exposure and thermal degradation behavior of the organic lubricants.

Research and development activities have been directed towards applying the STDS mainframe system (and various associated test-cell assemblies) to the task of testing and evaluating the thermal and oxidative stability of different lubricant specimens. The influences of such parameters as exposure temperature, residence time, and oxygen concentration relative to the degradation of lubricant samples need to be determined.

The goal of this research study is to determine the feasibility of using thermal instrumentation studies technology,

as represented by a System for Thermal Diagnostic Studies (STDS),
for the evaluation of high-temperature stability of advanced
turbine engine lubricants.

SECTION 2

LUBRICANT SAMPLE SELECTION

The samples selected for use in this feasibility study were carefully chosen. Lubricants used for future hypersonic aircraft must possess considerable thermal stability and be capable of resisting high-temperature oxidation. Therefore, this study was initiated to instrumentally examine, in some detail, the thermal decomposition characteristics of a candidate lubricant for these higher-temperature exposures. Other candidates of different chemical classes were also evaluated with respect to thermal exposure behavior.

To permit comparisons with respect to testing and transporting these high-molecular-weight organic materials, one of the ester-type lubricants was subjected to similar thermal testing.

The handling and introduction of these lubricant samples were accomplished in both their concentrated forms and with the subject lubricant dissolved in a suitable solvent. The lubricants were investigated as individual samples, i.e., they were not mixed in any way prior to thermal testing or instrumental analysis.

The samples selected for this feasibility study are shown in Table 2.1.

TABLE 2.1

LIST OF LUBRICANT SAMPLES

LUBRICANT DESIGNATION	GENERAL DESCRIPTION	SELECTED SOLVENT
ATL-8001	Polyol Ester	Toluene
0-67-0	Polyphenylether	Toluene
0-66-26	Fluorinated Mixture	Fluorinet FC-72
TEL-1004	Ester Mixture	Toluene
Flombin Z-60	Fluorinated Mixture	Fluorinet FC-72

SECTION 3

BRIEF REVIEW OF LUBRICANT THERMAL TESTING

There have been numerous methods and techniques developed for studying the behavior and corrosivity of liquid lubricants, and most specifically the turbine engine lubricants. Most of these test methods have been applied to the synthetic based lubricants, e.g., diesters and polyol esters. Test equipment and special apparatus have been used in research activities involving other chemical classes of lubricants, particularly the fluorinated materials.

Special laboratory tests are performed in conjunction with examinations of wear characteristics, hot-wall exposures for localized oxidation, and other attributes as defined in specifications MIL-7808 and MIL-23699. A method for examining the stability of lubricants in an oxidizing environment was developed by Wohltjen et al [1], and this particular apparatus bubbles oxygen through a sample containing reservoir that is maintained at pre-selected temperatures. This equipment is used to predict the stable lifetime of the sample lubricant while under oxidizing conditions.

In research with some of the linear polyperfluoroalkylether based lubricants [2], a glassware assembly was used for investigating the corrosive oxidation characteristics of various experimental lubricants at elevated temperatures. Several other types of laboratory-scale equipment have been used for examining the thermal behavior of lubricants, and these include a recording

tensiometer [3], a macrooxidation cell [4], a stirred flow microreactor [5], a microoxidation apparatus [6], an oxidation degradation apparatus which uses electronic gas sensing equipment [7], and an apparatus that used chemiluminescence devices [8]. Several of these pieces of laboratory equipment can also be used for investigating catalytic effects upon lubricant degradation.

Although some of this test equipment is incorporated into procurement specifications, many of the methods are empirical or of an exploratory nature and are used primarily in activities concerned with developing new materials.

The relatively recent introduction of highly sensitive instrumental analysis equipment now permits extensive examinations of thermal degradation of organic materials using extremely small amounts of sample. In addition, the increased use of the various hyphenated instrumental techniques [9] allows considerable versatility in designing and custom fabricating special test equipment. Practically any type of thermal degradation condition can now be examined using the appropriate analytical instrumentation.

SECTION 4

SEARCH OF RELEVANT INSTRUMENTAL ANALYSIS TECHNIQUES

In the study of thermal behavior and degradation characteristics of a lubricant, the classical thermal analysis techniques [10] are of key importance. Thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and instrumental combinations thereof, play an important role in defining the thermal characteristics of a sample.

Although evolved gas detection (EGD) and evolved gas analyses (EGA) techniques have been applied with many of the classical thermal analysis procedures, it is only recently through the advent of the quadrupole mass spectrometer (MS) and the Fourier transform infrared (FTIR) spectrophotometer that high sensitivity and much needed additional analytical diagnostics have become available. These now provide the wealth of information required for examining extremely complex thermal decompositions.

In most cases, the complexity of reaction products is so complicated that some form of separation technique is needed to simplify the eventual analytical task of the various spectroscopies. The separation of these complex mixtures and effluents is usually accomplished by the various chromatographic methods. Gas chromatography (GC), liquid chromatography (LC), thin-layer chromatography (TLC), and even gel permeation chromatography (GPC) have been applied to lubricant type samples.

Most recently the newly introduced supercritical fluid chromatography (SFC) has been applied to the separation of lubricant mixture constituents. Practically every one of these chromatographic procedures have been married to downstream instrumental analysis techniques, e.g., MS, IR, chemiluminescence procedures, atomic adsorption, etc.

The three most promising chromatographies that can be invoked for the complex lubricants under consideration are high-resolution gas chromatography (HRGC), high-performance liquid chromatography (HPLC), and SFC. Each of these chromatographic separation procedures is experiencing considerable growth, and major advances are occurring frequently within the practices of these techniques.

Of the most immediate interest is the latest high-temperature version of HRGC. This technique is finding significant application in separating high-molecular-weight materials, e.g., up to 1500 Daltons. Although SFC does not possess (as of yet) the resolution capabilities of HRGC, it is capable of eluting higher molecular weight substances, particularly materials that are thermally labile, or of a polar and adsorptive nature.

Both HRGC and SFC are being interfaced with MS and FTIR instruments. Highly versatile multidimensional chromatography procedures can be implemented with either HRGC or SFC, and even combinations thereof.

SECTION 5

GAS CHROMATOGRAPHIC OPEN TUBULAR COLUMN REQUIREMENTS FOR LUBRICANT SAMPLES

The thermal degradation testing of organic materials relies heavily upon detailed instrumental analyses of the parent material and its various thermal decomposition products. It is therefore of primary importance that these different substances be successfully transported to the analytical station. This transport from the high-temperature test region to the inlet of the analytical station is very important and considerable design considerations have addressed this particular transfer topic. Of even greater importance is the successful migration of the complex mixture through the analytical flowpath, i.e., the chromatographic column and other downstream stations.

In earlier studies [11-15], a criterion was established for the applicability of certain samples to extensive thermal decomposition testing. In short, if a material can be successfully admitted to and migrated through a GC column, it is amenable to examination by a variety of thermal instrumentation testing procedures. Thus, the importance of the behavior within the GC column is clearly seen.

At the present time, there are four slightly different types of open tubular columns (OTCs) that can handle high-molecular-weight organic substances. The first of these OTC types, i.e., the polyimide clad fused silica OTC is the most established, although it is the one most restricted with respect to high-temperature operation.

With the advent of the flexible fused silica tubing with the polyimide outer coating [16] and the development of bonded stationary phases, it has been possible to operate a phenylmethylsilicone phase (5% phenyl) column up to temperatures near 350°C. Very efficient columns have been made using this stationary phase and tubing material. Indeed, this column type and combination possesses one of the widest usable temperature ranges that is commercially available. Typically, it can be operated with very high efficiency from -60°C to 350°C. Also, it has been shown that uniform thin film phases can be placed within this column interior.

The second OTC type that has been considered used the recently introduced [17] aluminum-clad fused silica tubing arrangement. Versions of these columns have been operated at temperatures up to 500°C and have eluted very high-molecular-weight organic substances. The aluminum-clad fused silica OTC is still undergoing development and the availability of different stationary phases, tubing diameters, and film thickness is limited at the present time. It is a common opinion that there are still some development activities that must take place before this particular OTC will receive extensive usage within the analytical chromatography community.

The third OTC type considered was a high-temperature polyimide outer coated fused silica column contained within a braided stainless steel or "armored" outer covering. These OTCs contained somewhat polar stationary phases that could be exposed to temperatures in the vicinity of 360°C. They have been used

for the analysis of triglyceride containing samples, such as butter fat, soybean oil, and even coffee oils. One of the disadvantages of this particular type of column is that it has an elevated low-temperature limit. Specifically, it cannot be used at temperatures less than 250°C as the stationary phase at temperatures below this value loses its liquid partitioning quality and thereby extremely inefficient migration of solutes is experienced.

The fourth type of OTC considered for high-temperature GC operation uses a material other than fused silica, i.e., Pyrex and other glasses, for the wall material. This tubing is then coated with OH-terminated polysiloxane stationary phases. This fourth type of OTC assembly has only recently been announced and considerable development activities are probably ahead for this particular high-temperature OTC. However, this column has been used in efficiently migrating substances approaching 1200 Daltons. This was accomplished at temperatures near 420°C.

At temperatures above approximately 450°C, thermal fragmentation of certain gas-phase materials could be encountered. In fact, there are many thermally labile samples and compounds that one would like to examine by HRGC. Unfortunately, in some situations, what has been injected into the entrance of a long OTC is not the same mixture of solute constituents that elutes from the exit of the very high-temperature OTC assemblies.

The OTC selected for most of the work in this study was of the first type described above. Specifically, most of the work was conducted with 12 to 15 meter length OTCs of internal diameter ranging from 0.20 to 0.32 mm, and in most cases, very thin films of stationary phase were used, e.g., 0.1 microns of phenylmethylsilicone. After the thorough conditioning of these OTCs, operation could be performed up to 330°C.

In many cases, other temperature limitations were invoked by the associated instrumentation, such as the interface in the MS, the upper temperature limit of the IR cell, etc. It is anticipated that future high-temperature GC work with OTCs will be conducted routinely at a final programmed temperature of approximately 450°C.

SECTION 6

INSTRUMENTAL ANALYSIS AND TESTING METHODS

Before a sample can be subjected to a series of thermal decomposition experiments using a system for thermal diagnostic studies (STDS), it is necessary to determine that the sample can be efficiently chromatographed using the system's GC equipment. Specifically, when the molecular weights of the parent material and the various decomposition products are in the range of 400 to 900 Daltons, it is necessary to give considerable attention to the gas chromatographic assembly.

The present status of analytical instrumentation is such that some materials can be handled with special gas chromatographs but cannot, as of yet, be transported and analyzed with commercially available GC-MS systems. This is a situation that undoubtedly will change in the future.

In this study, considerable effort was devoted to obtaining HRGC separations of various lubricant samples. Much attention was given to the sample insertion process and the modification of the GC oven interior so that non-distorted solute zones could be migrated and detected. Also, transport to the active region of the detector was enhanced by improving the flowpath at the OTC exit region, which has been shown to be crucial for high-molecular-weight solutes. To accomplish this enhanced performance, a previously modified GC system was further revised for handling these lubricant samples.

There is currently little doubt that the best carrier gas for most HRGC separations is hydrogen. It is the only carrier that can permit high linear gas velocities with programmed temperature operation (which is definitely needed for broad-molecular-weight-range samples). Although hydrogen gas can be admitted to a GC assembly with a high degree of cleanliness, i.e., with extremely low levels of contaminants, such as, oxygen, water, etc., it does have operational drawbacks. The chromatographer must take many precautions to protect against an accidental release or generation of an explosive situation whereby hydrogen gas leaks into the high-temperature interior of a GC assembly, e.g., the confined column oven with its exposed heating elements.

Figure 6.1 is the schematic of the HRGC assembly used for this exploratory work. Note that there are three protective features for limiting the flow of hydrogen (even under accidental conditions) to the high-temperature GC oven. At no time could there be more than $80 \text{ cm}^3 \text{ min}^{-1}$ of hydrogen getting past the injector of the chromatographic assembly. This would occur only if the OTC were to break downstream of the injector and within the GC oven. The convenient use of hydrogen and helium carrier gases was facilitated through the utilization of a slightly revised kit from the Restek Corporation (#20410).

It should also be noted in this HRGC schematic that a modified Hewlett Packard on-column injector was used. The previous on-column injector that had been used initially for investigating these lubricant samples produced continual

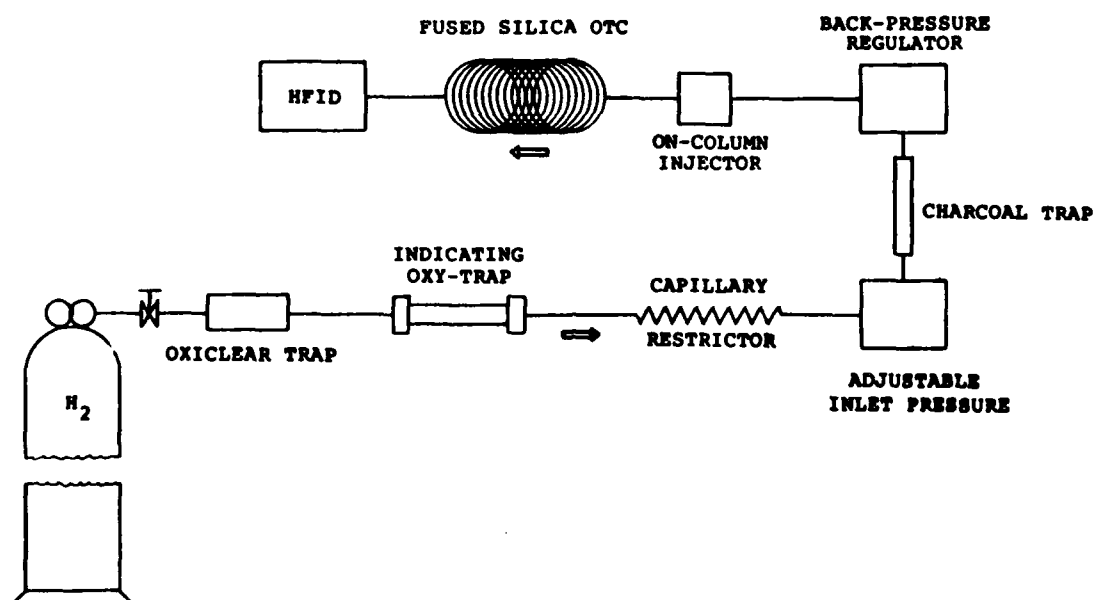


Figure 6.1. Schematic of High-Temperature High-Resolution Gas Chromatographic Assembly.

contamination from siloxane substances that were inadvertently admitted with each injection. Early work showed that these silicone contaminants were coming from a seal that surrounded the syringe needle during the on-column injection process. As it was practically impossible to remove the source of contamination, a modified on-column injector was employed which used a duck-bill valve for sealing around the syringe needle during the insertion process. Subsequently, no contaminant or out-gasing components were observed in blank chromatograms programmed up to 330°C.

Figure 6.2 is a photograph of the interior of a modified Varian 3700 GC instrument. The fused silica OTC is seen in the left-hand side of the photograph. An aluminum buffer plate has been firmly positioned in the rear of the oven compartment to intercept line-of-sight radiant energy transfer to the fused silica OTC. Previous work has shown that radiant energy transfer with polyimide coated fused silica OTCs can produce distorted solute zones. Since an important aspect of this work was to thoroughly examine the lubricant samples and even detect isomeric formations, efforts were made to migrate these lubricant constituents with no distortion.

Figure 6.3 shows the various components that eventually went into this HRGC assembly for migrating solute zones without distortion. A thin-wall aluminum container is seen along with the OTC, stainless steel braiding, woven glass tape, and a modified detector insert. The installation of these various components is shown in Figure 6.4. The fused silica OTC has been placed within the aluminum container and the braided stainless

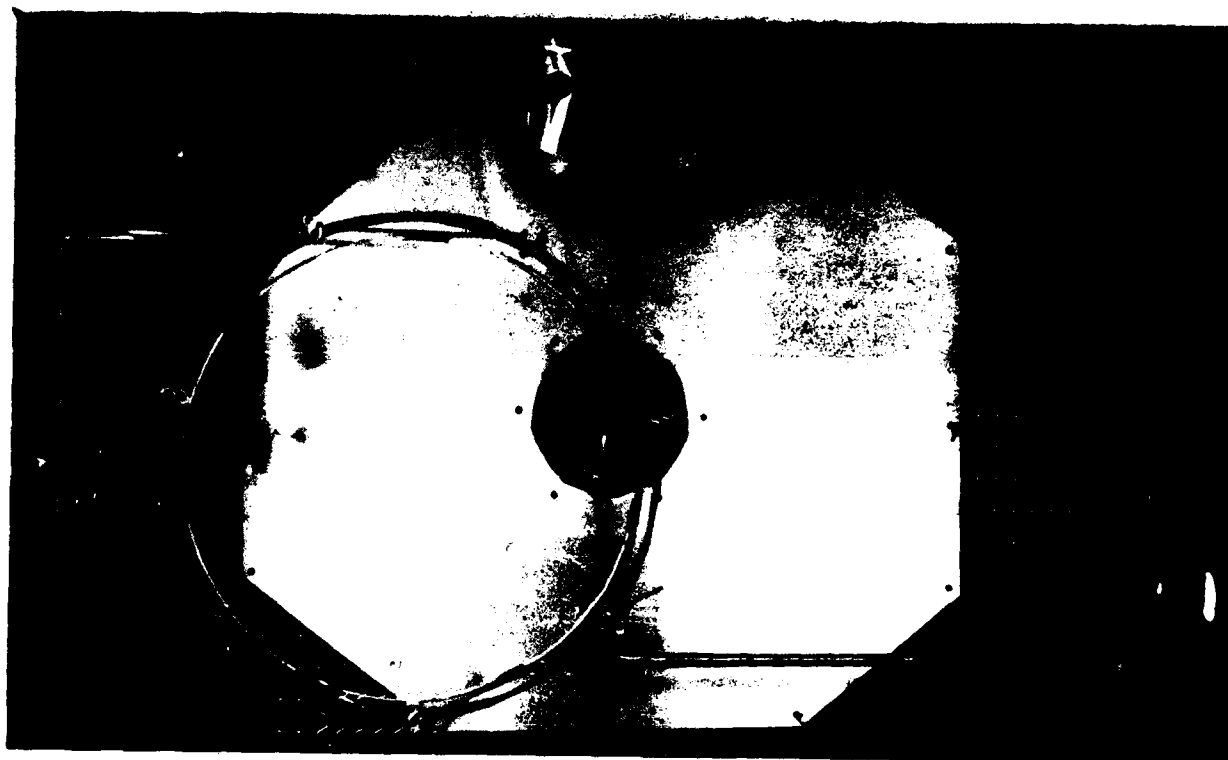


Figure 6.2. Photograph of Gas Chromatographic Oven Interior.

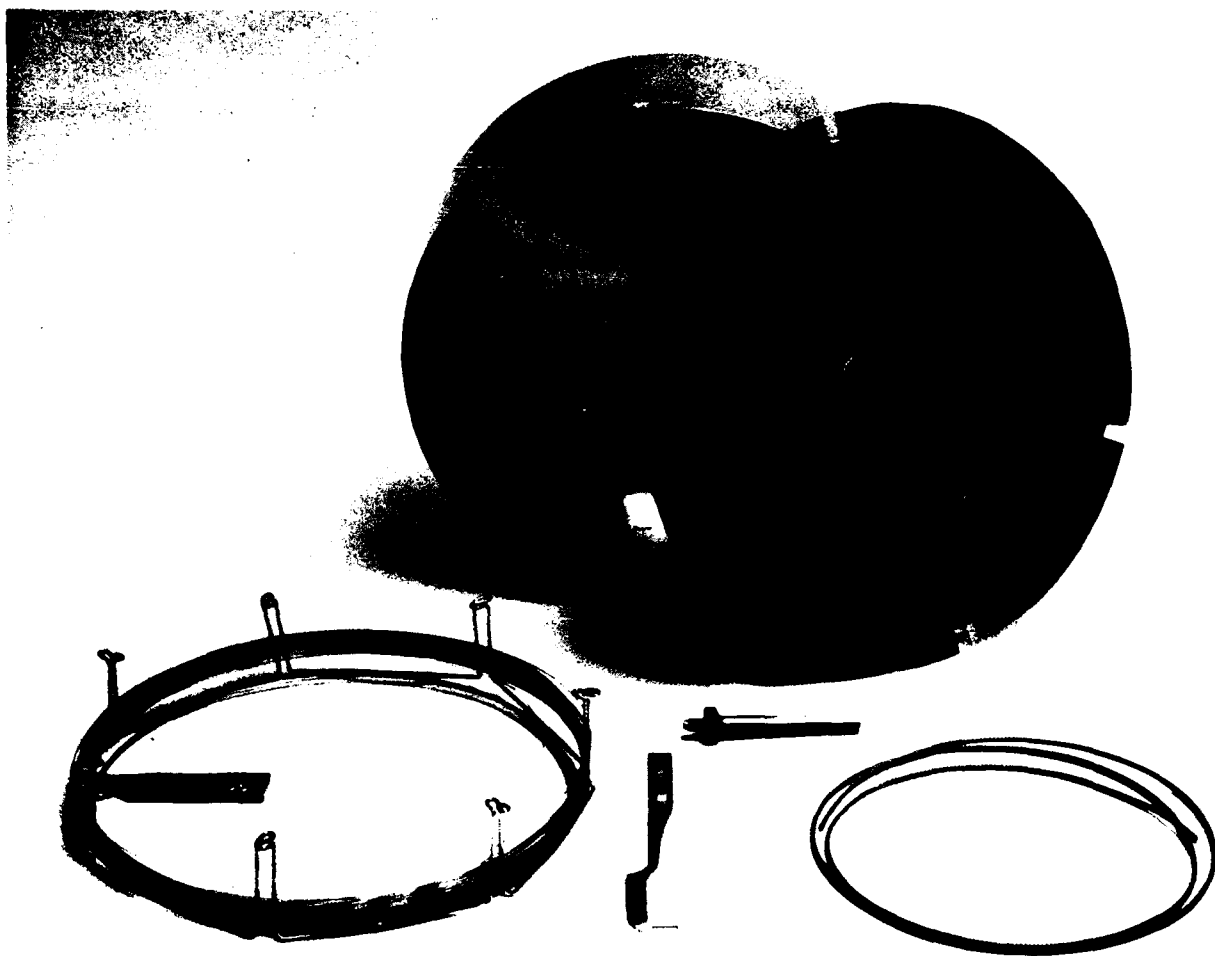


Figure 6.3. Photograph of Column Oven Components.

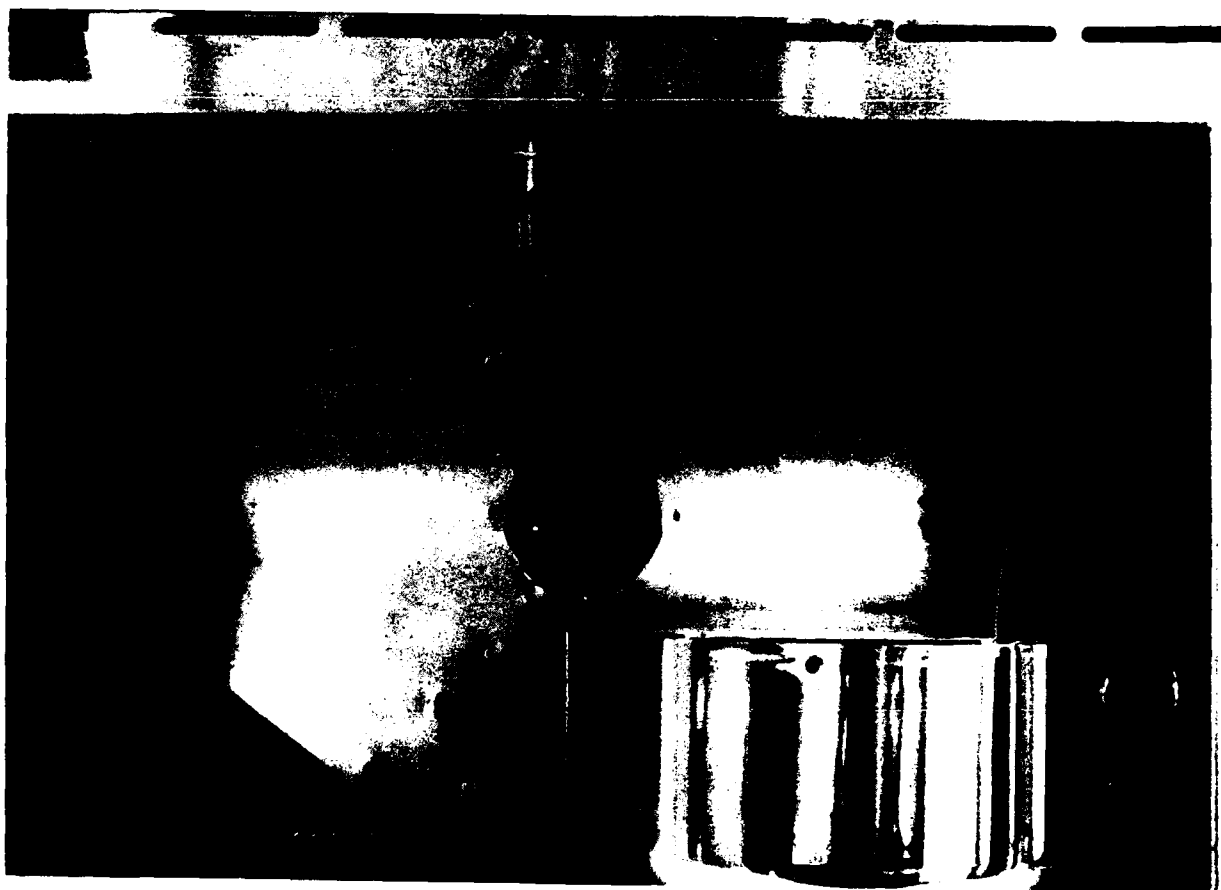


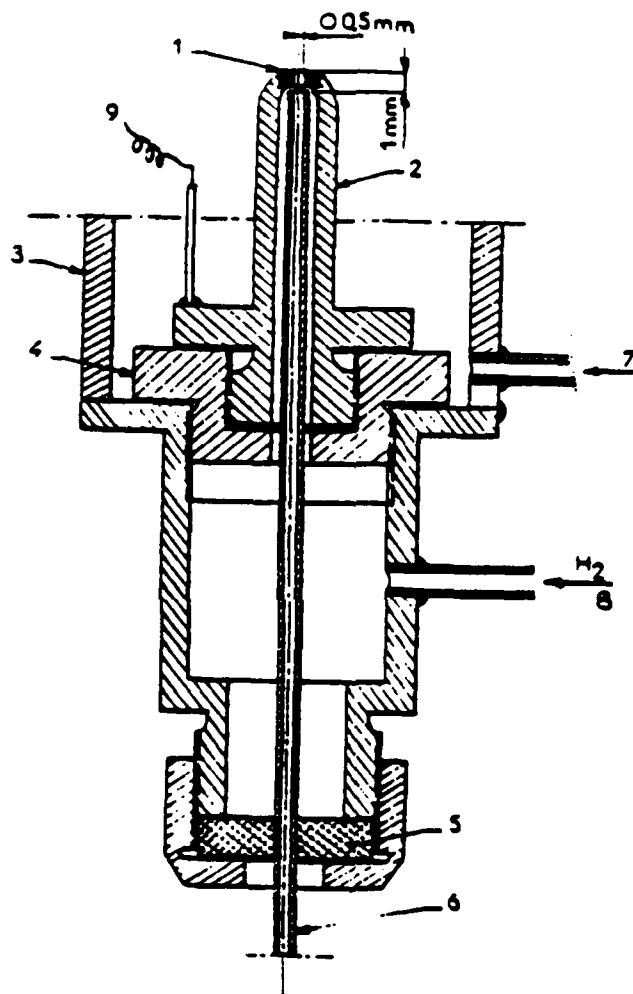
Figure 6.4. Installation of Components in HRGC Oven.

steel sleeving covers the entrance and exit regions of the fused silica OTC leading to and from the aluminum container. By employing a detector insert which permits good thermal transfer from the detector base into the oven interior, and by insulating this device with the woven glass tape (and then covering it with an aluminum outer sleeve) it was possible to have good thermal control of the OTC exit right up to the point of emergence at the detector tip. This is an important aspect in eluting distortion-free solute zones of high-molecular weight.

A schematic of a preferred design of such an ideal detector interior is shown in Figure 6.5. This particular design is attributed to Guiochon et al., although in their work [18] this detector was used specifically for obtaining rapid detection of solutes.

Most of the HRGC separations conducted in this study were performed using relatively short OTCs (12 to 15 meters) that possessed small inside diameters (0.20 to 0.25 mm) and used small film thicknesses (approximately 0.1 microns). The stationary phase used was a bonded phenylmethylsilicone that was equivalent to SE-54 silicone. The GC conditions under which most of the separations were accomplished are shown in Figures 6.6.

As it was anticipated that many of these lubricant samples would contain very high-molecular-weight materials, a Kovats' indices standard was prepared and combined with a paraffin wax sample that contained normal paraffins ranging from $n\text{-C}_{25}$ to greater than $n\text{-C}_{40}$. A chromatogram of this particular sample is



Cut section of the flame ionization burner.
 1. Platinum tip. 2. Burner body. 3. FID housing. 4. Insulating Teflon base. 5. Septum. 6. Capillary column. 7. Air. 8. Hydrogen. 9. Polarization voltage (+ 120 V).

Figure 6.5. Interior of Well-Designed Hydrogen Flame Ionization Detector (see Ref. 18).

GAS CHROMATOGRAPHIC CONDITIONS		
Instrument	Varian 3700	
Analyst	W. Rubey	
Date	July 1987	
Column:		
type and description	WCOTC	
tubing material	Fused Silica	
tubing length	15.0	m
tubing inside diameter	0.25	mm
Stationary phase	DB-5 Phenylmethylsilicone	
film thickness	0.1	µm
Carrier gas	Hydrogen	
inlet pressure	1.5	abs atmo
linear velocity	~100	cm sec ⁻¹
outlet flow	~2.0	cm ³ min ⁻¹
Detector:		
type	HFID	
range	10 ⁻¹² AFS	
attenuation	32 & 64	
Detector gas flows:		
hydrogen	30	cm ³ min ⁻¹
air	300	cm ³ min ⁻¹
column outlet supplement	30	cm ³ min ⁻¹
Output signal recording:		
full scale read out	1.0	mv
chart advance rate	1.0	cm min ⁻¹
Sample:		
description	noted	
solvent	Toluene	
concentration in solvent	100 PPM	
injection sample size	0.5	µl
split ratio	0	
Temperatures:		
injector	45	°C
column:		
initial	45	°C
initial hold	4.0	min
final	320	°C
program rate	8.0	°C min ⁻¹
detector	330	°C

Figure 6.6. Gas Chromatographic Conditions for High-Temperature HRGC Assembly.

shown in Figure 6.7, and the four major peaks correspond to normal paraffins of C_{28} , C_{30} , C_{32} , and C_{34} , respectively. It was found that most of the lubricant constituents would be eluted from this particular OTC with Kovats' indices ranging from approximately $I = 2800$ to 4500 .

The chromatogram shown in Figure 6.8 corresponds to the TEL-1004 sample, and in this particular case, the lubricant had been diluted to approximately 100 ppm (by volume) in reagent grade toluene. The numerous early peaks observed in this chromatogram are due to impurities in the toluene solvent. Again, the temperature programming of these chromatograms was accomplished from 45°C to 320°C .

Figure 6.9 is a chromatogram of the 0-67-0 lubricant as again dissolved in a toluene solvent. Here, we see well-shaped solute zone profiles corresponding to the three polyphenylether isomers. Although some contaminants were observed, their concentrations were very small.

Figure 6.10 is a chromatogram obtained from the ATL-8001 sample and in all cases it is very similar to the earlier chromatogram of Figure 6.8. However, in this latter chromatogram there is a peak (shown by the arrow in the enlarged view of Figure 6.10.1) that was not present in the earlier TEL-1004 sample.

It is important to notice in both the chromatograms of Figures 6.8 and 6.10 that the reproducibility of these GC tracings shows that although these are undoubtedly homologous

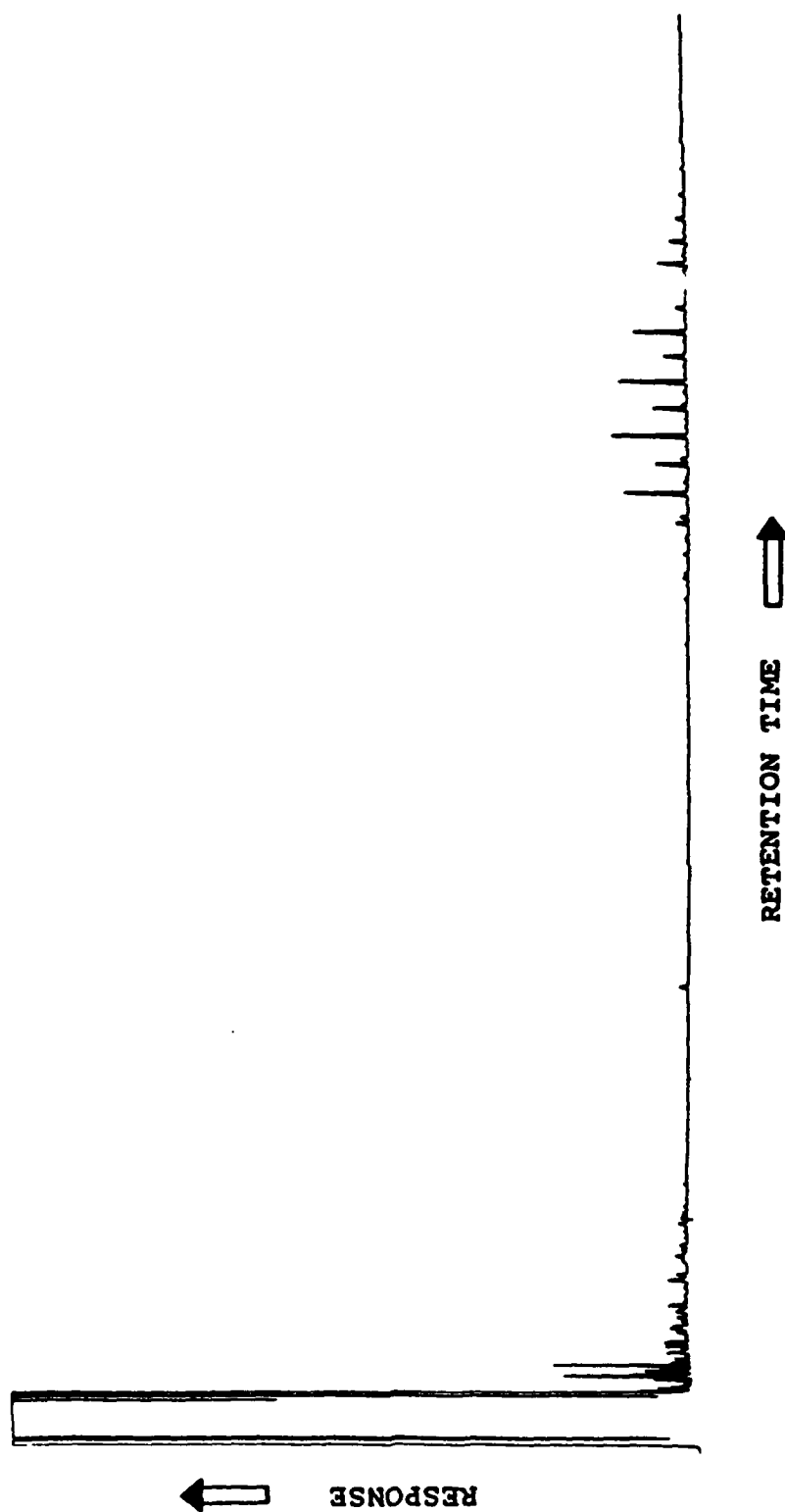


Figure 6.7. Chromatogram of Kovats' Indices Sample.

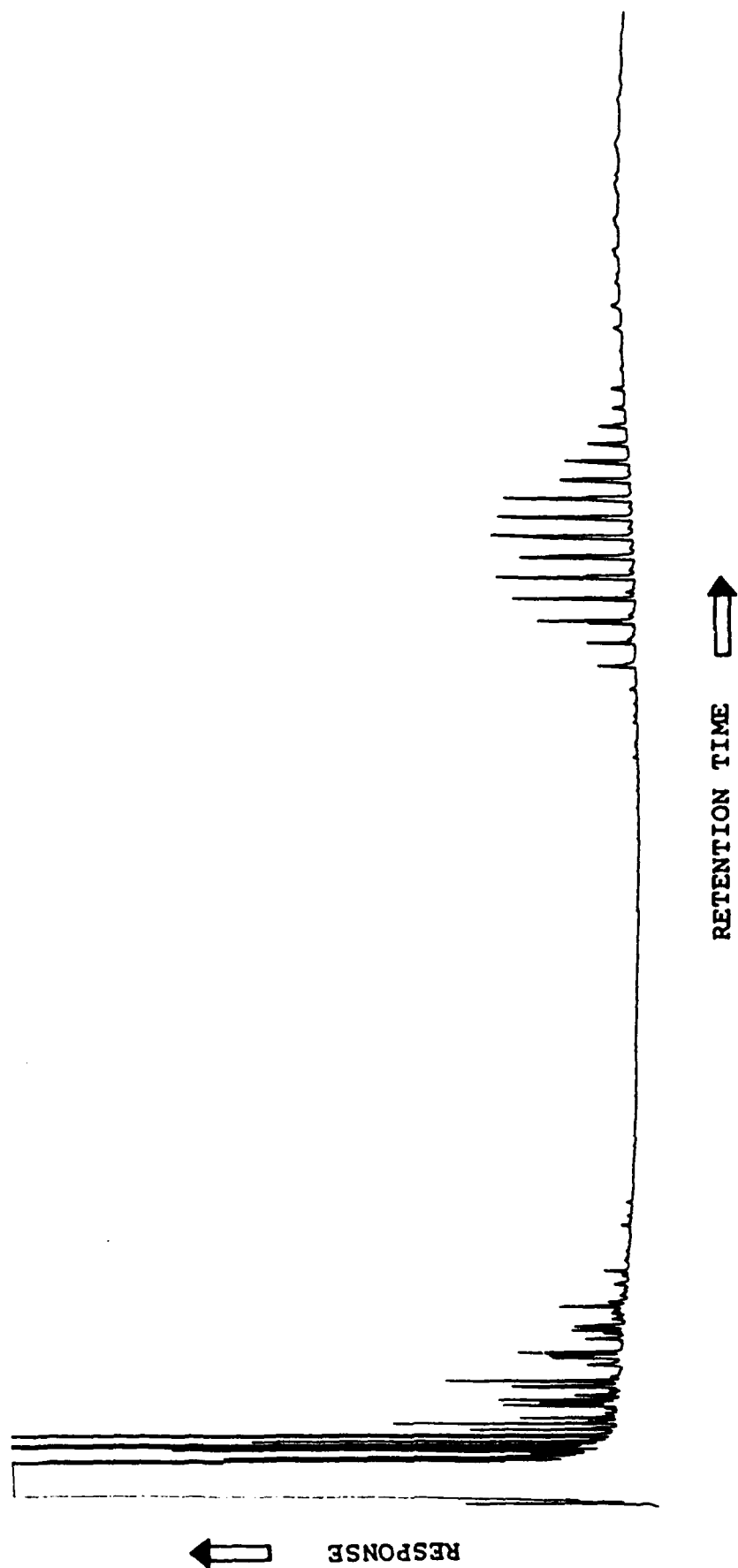


Figure 6.8. Gas Chromatogram of TEL-1004 Lubricant.

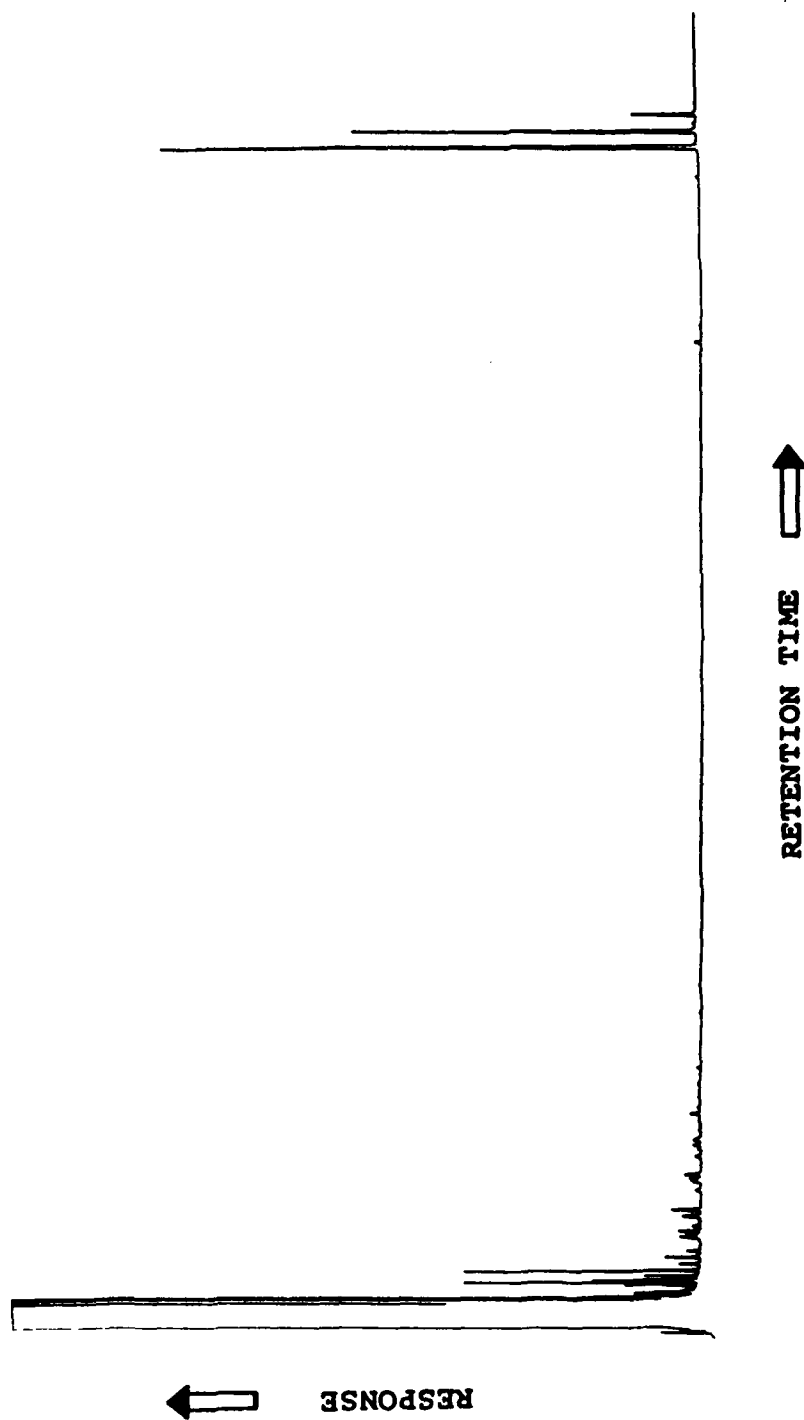


Figure 6.9. Gas Chromatogram of 0-67-0 Lubricant.

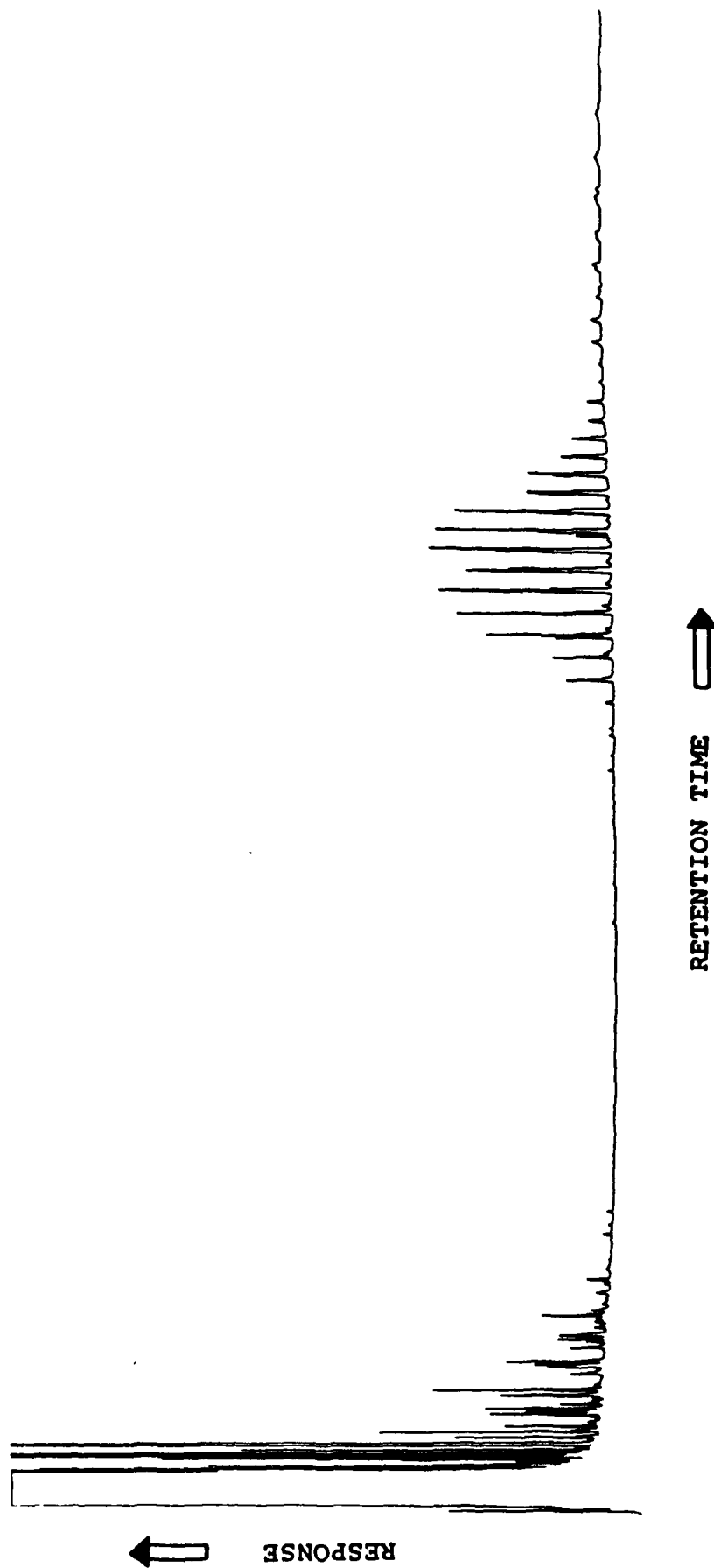


Figure 6.10. Gas Chromatogram of ATL-8001 Lubricant.

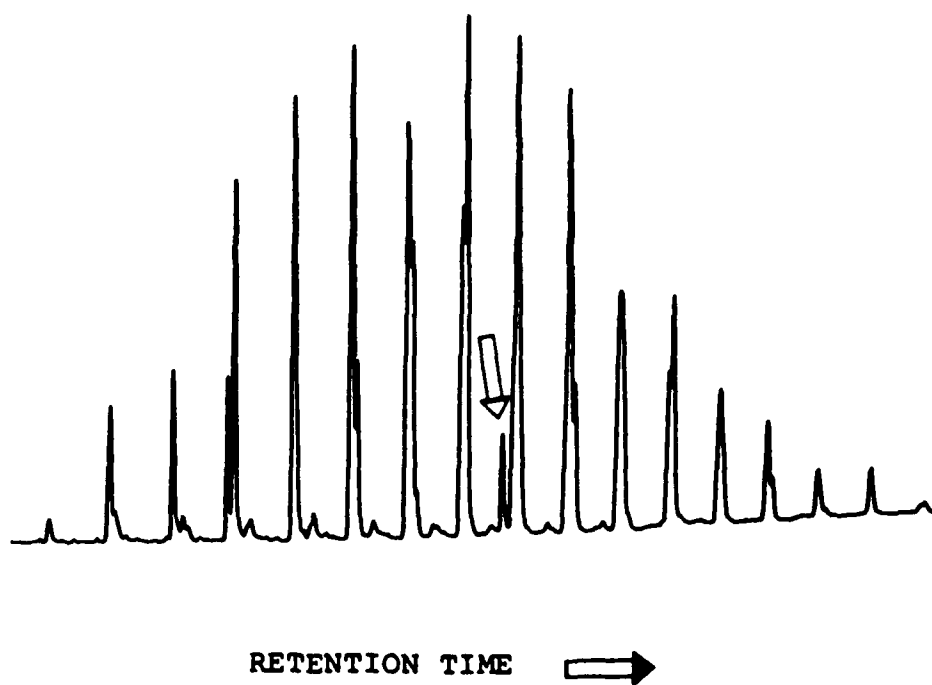


Figure 6.10.1. Enlarged View of Gas Chromatogram of ATL-8001 Lubricant.

series of constituents, the chromatographic resolution is sufficient to indicate the presence of isomeric species with each major constituent. With this high-temperature GC arrangement, these chromatographic patterns were also highly repeatable as the output signals from the modified hydrogen flame ionization detector were especially distortion-free. Again, these are analog signal output recordings, and not digitized profiles like the output data from the GC-MS assembly discussed later in this report.

Although other lubricant samples, i.e., the fluorinated samples, were admitted to the high-temperature HRGC assembly, practically no discernible response for solutes was indicated, as this work was conducted exclusively with the hydrogen flame ionization detector. Later it was learned that responses of these fluorinated materials to the HFID are extremely low and in many cases erratic, whereas the mass spectrometer could readily detect the solutes in these lubricants.

One of the objectives of this feasibility study was to determine the applicability [19,20] of the System for Thermal Diagnostic Studies (STDS) for evaluating the thermal degradation characteristics of high performance lubricants. A block diagram of the STDS is shown in Figure 6.11 and an artist's rendering of the full system is shown in Figure 6.12. The operational procedure for tests with the STDS involving these particular lubricant samples is presented in separate reports [21,22]. Figure 6.13 shows the gas chromatographic conditions that were used for the various GC-MS analyses conducted both from sample

System for Thermal Diagnostic Studies (STDS)

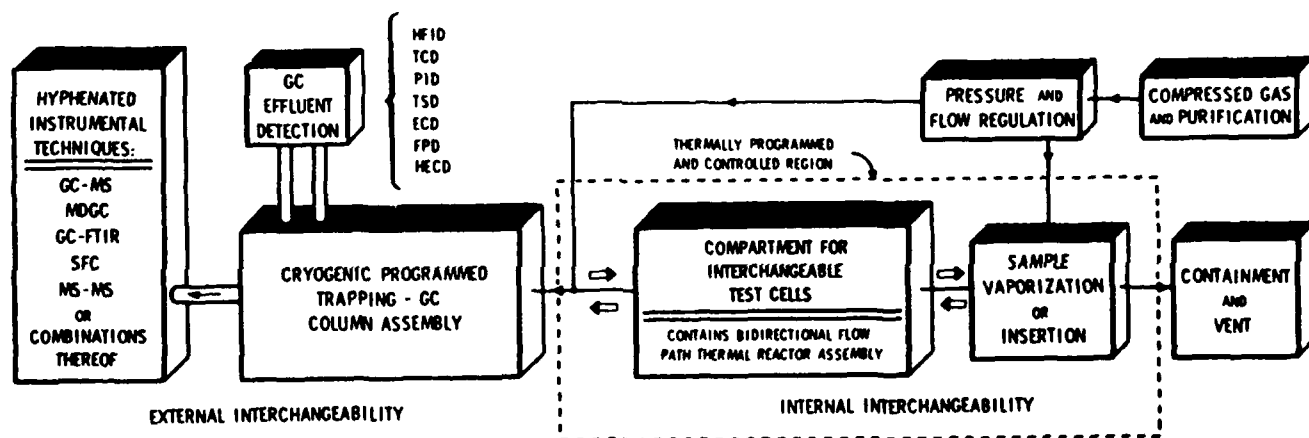


Figure 6.11. Block Diagram of the System for Thermal Diagnostic Studies (STDS).

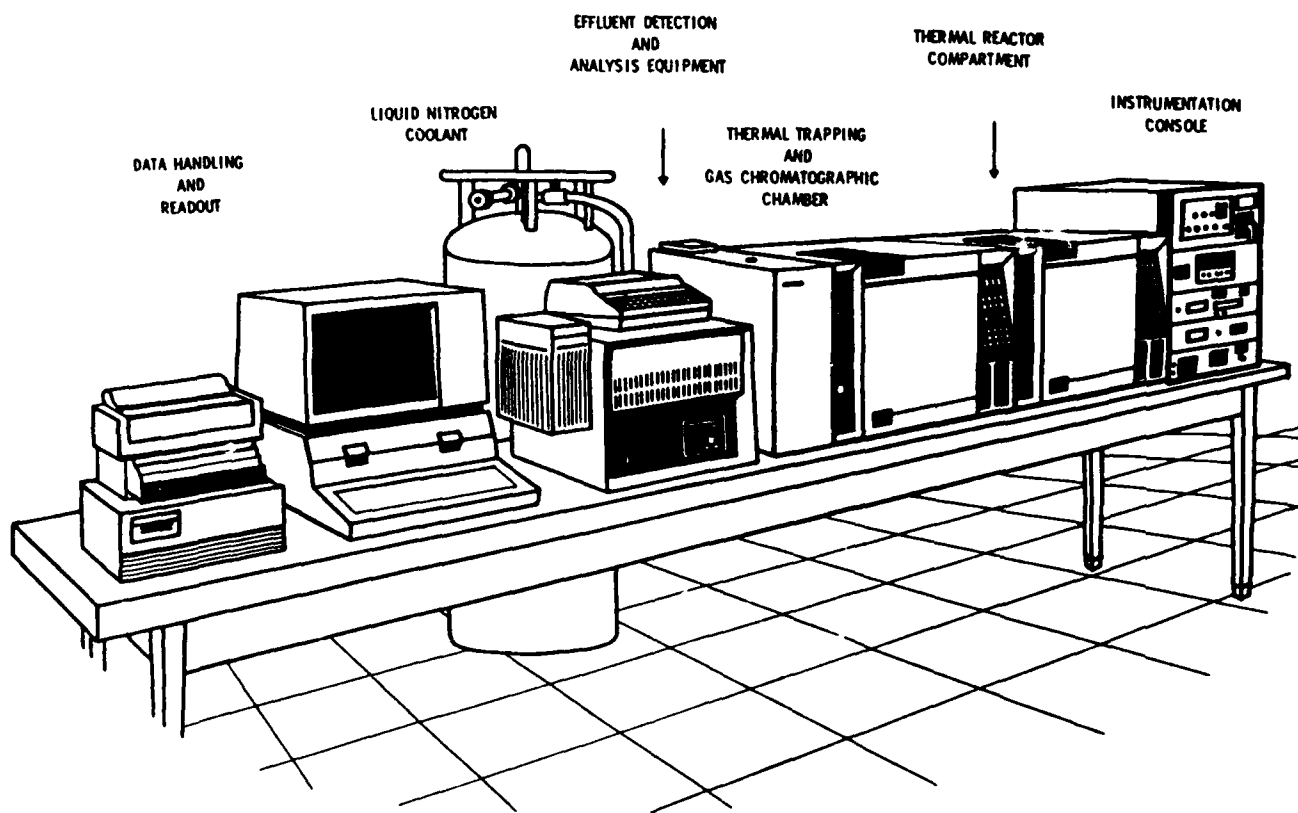


Figure 6.12. Artists' Rendering of Complete STDS.

GAS CHROMATOGRAPHIC CONDITIONS		
Instrument	HP-5890/5970B	
Analyst	W. Rubey	
Date	September 1987	
Column:		
type and description	WCOTC	
tubing material	Fused silica	
tubing length	12.0	m
tubing inside diameter	0.20	mm
Stationary phase	BP-5 Phenylmethylsilicone	
film thickness	0.10	um
Carrier gas	Helium	
inlet pressure	1.4	abs atmo
linear velocity	~30	cm sec ⁻¹
outlet flow	~1.0	cm ³ min ⁻¹
Detector:		
type	MSD	
range	-	
attenuation	-	
Detector gas flows:		
hydrogen	-	cm ³ min ⁻¹
air	-	cm ³ min ⁻¹
column outlet supplement	-	cm ³ min ⁻¹
Output signal recording:		
full scale read out	-	mv
chart advance rate	-	cm min ⁻¹
Sample:		
description	0-67-0	
solvent	Toluene	
concentration in solvent	1.0%	
injection sample size	1.0	ul
split ratio	1 to 60	
Temperatures:		
injector	300	°C
column:		
initial	50	°C
initial hold	1.0	min
final	300	°C
program rate	8.0	°C min ⁻¹
detector	-	°C

Figure 6.13. Gas Chromatographic Conditions for GC-MS Analyses.

injections into the GC-MS portions of the STDS, and full analyses that were conducted throughout the thermal decomposition testing of the lubricants using the STDS.

SECTION 7

TESTING OF VARIOUS LUBRICANT SAMPLES WITH STDS

The five lubricant samples listed in Table 2.1 were dissolved in their respective solvents and injected into the GC-MS portion of the STDS. Injections were accomplished using a Hamilton 701 syringe, and 1.0 microliters of a 1.0% (v/v) solution were inserted into a 300°C splitter injector adjusted to produce a 60 to 1.0 split.

One of the objectives was to compare chromatograms with those obtained using the high-temperature HRGC assembly and to determine if the fluorinated substances could be successfully migrated through the OTC used within the GC-MS assembly. Figure 7.1 is the GC-MS reconstructed tracing for the ATL-8001 sample. The polyphenylether sample is shown in Figure 7.2. Figure 7.3 is a reconstructed chromatogram corresponding to the 0-66-26 lubricant sample.

Figure 7.4 shows the reconstructed GC-MS output from the Z-60 sample and this particular material would probably best be chromatographed using one of the high-temperature polar stationary phase columns used for the triglyceride analyses. It indeed contains high-molecular-weight material not readily separated on the non-polar phenylmethylsilicone OTC, although it is evident in Figure 7.4 that this material can be transported at these STDS temperatures, e.g., 300°C. The chromatogram shown in Figure 7.5 was obtained with the TEL-1004 lubricant, and

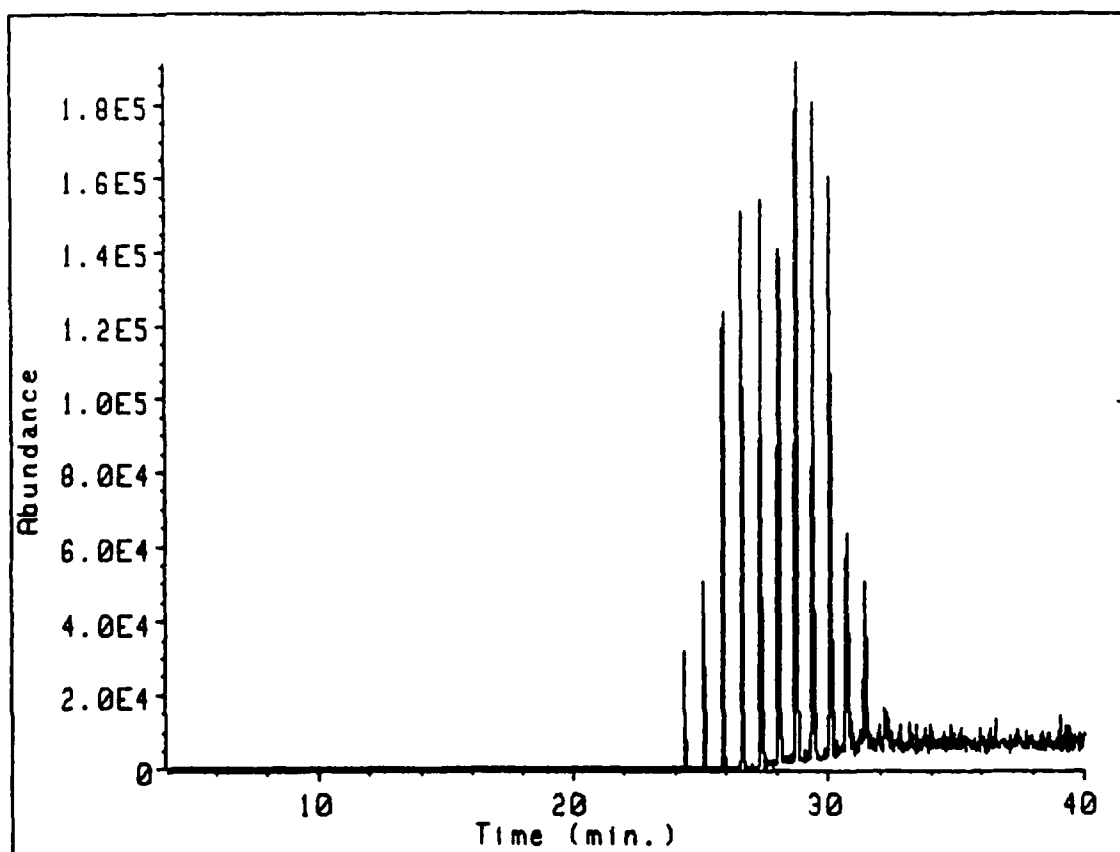


Figure 7.1. GC-MS Chromatogram of ATL-8001 Lubricant.

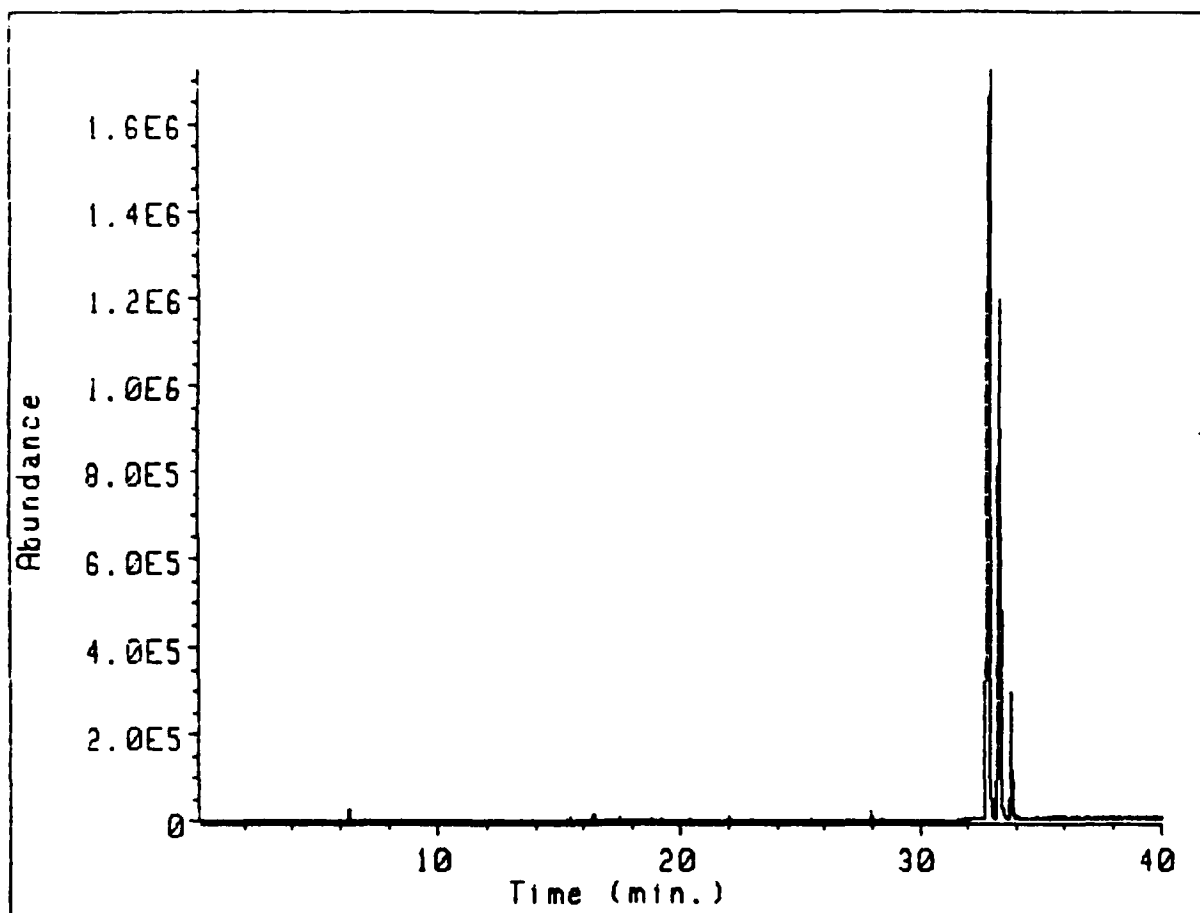


Figure 7.2. GC-MS Chromatogram of 0-67-0 Lubricant.

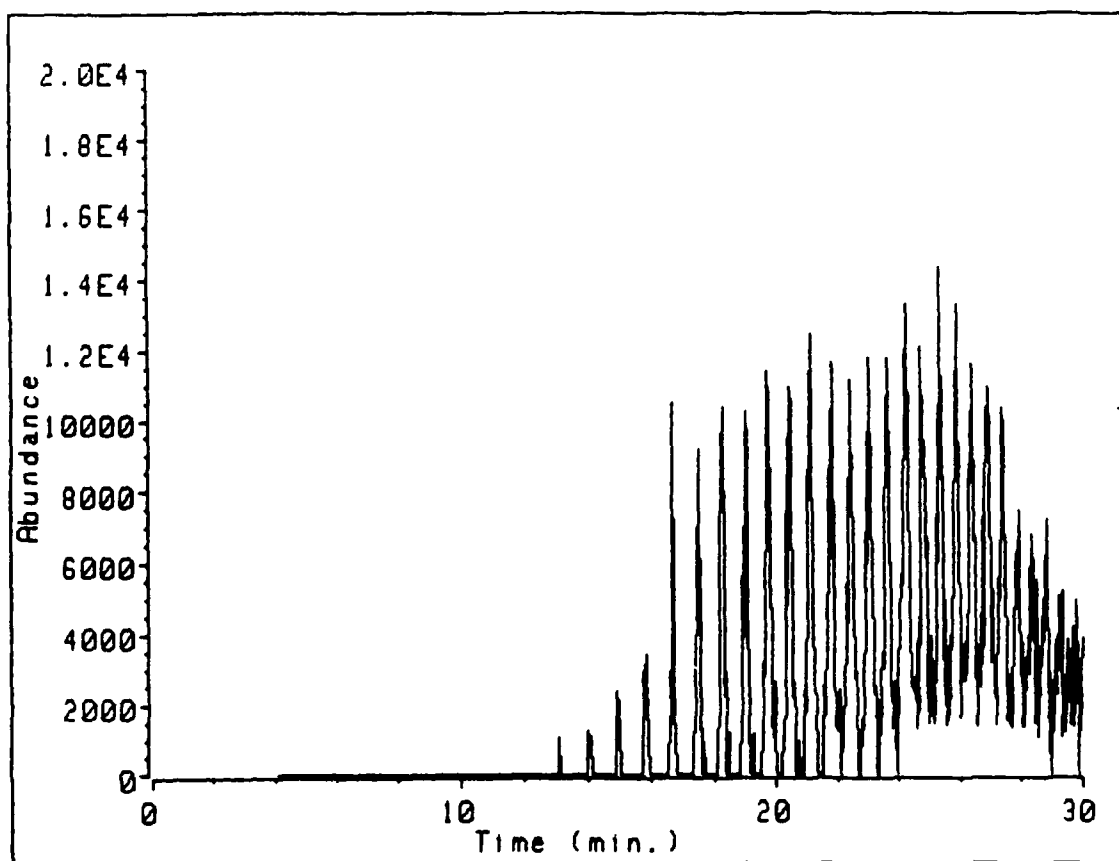


Figure 7.3. GC-MS Chromatogram of 0-66-26 Lubricant.

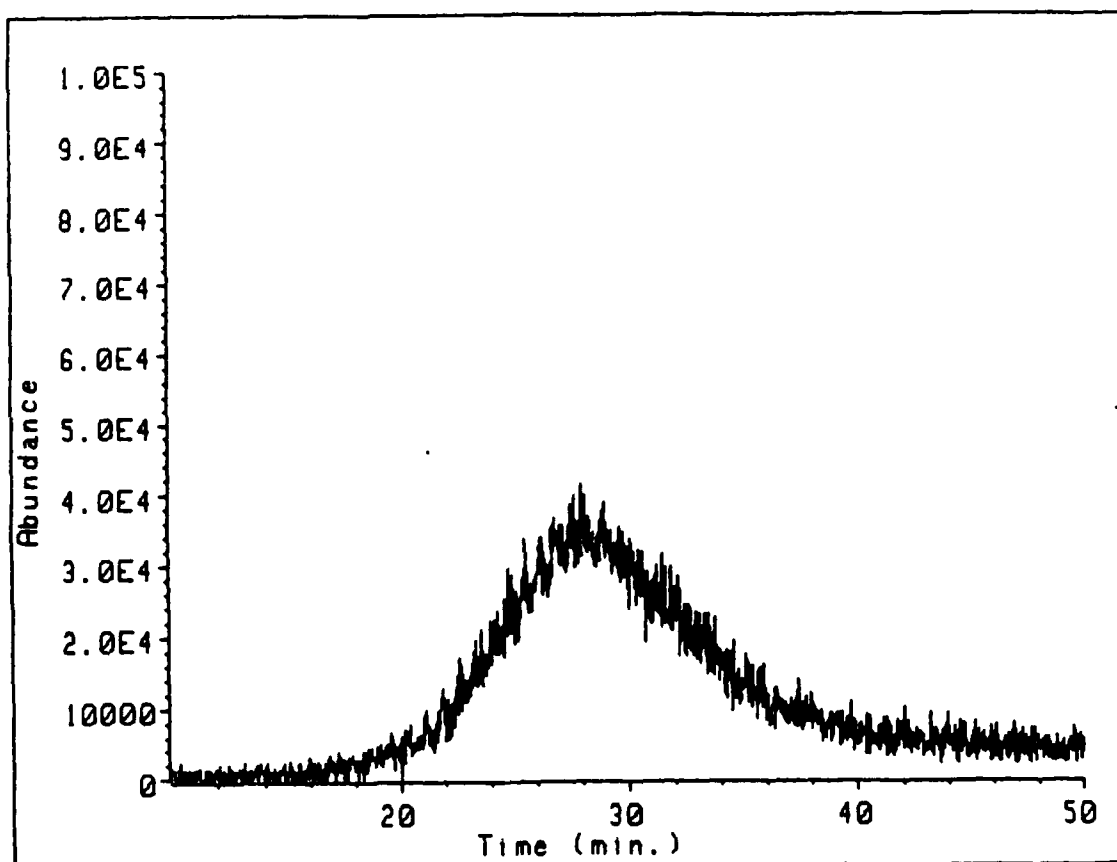


Figure 7.4. GC-MS Chromatogram of Z-60 Lubricant.

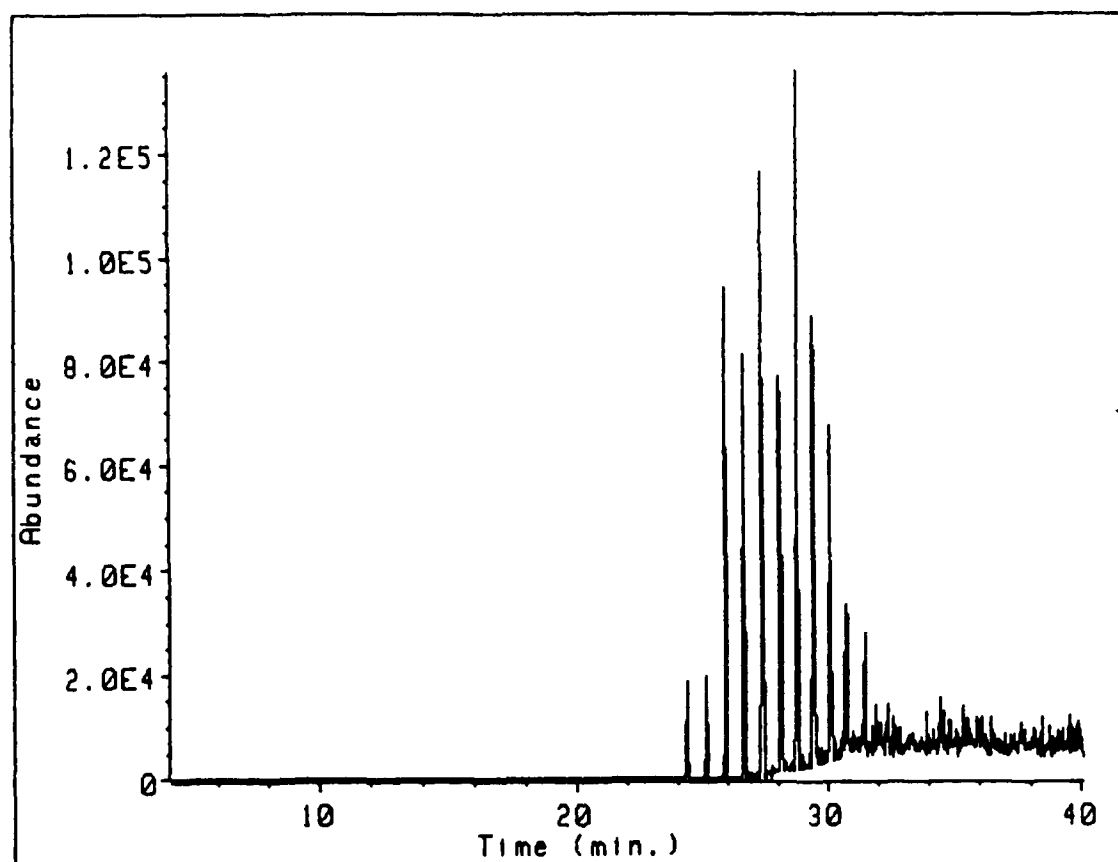


Figure 7.5. GC-MS Chromatogram of TEL-1004 Lubricant.

again, it is very similar to the reconstructed digitized output tracing shown in Figure 7.1.

The lubricant selected for major examination in this study was the polyphenylether, i.e., lubricant sample 0-67-0. However, to obtain some background comparative data with another well established lubricant, thermal decomposition experiments were conducted with the ATL-8001 sample. Figure 7.6 shows the resulting GC-MS output tracing from a 0.02 μ l injection of ATL-8001. This was accomplished using 0.5 microliter full-scale syringe, and no solvent was included with this sample insertion. The sample was transported through the STDS using the operational procedure described in Reference 22, and the series of homologous solutes emerging at around 30 minutes is seen. There are some low-level species eluting at times earlier than 27 minutes, and indeed, some thermal fragmentation had occurred with this ester lubricant sample during this exposure. The test conditions were as follows: nitrogen atmosphere, 2.0 second gas-phase mean residence time, and 350°C exposure temperature. Figure 7.7 shows the GC output corresponding to a 400°C exposure (with other experimental variables as before). It is seen in this output that considerable degradation has occurred (37.4% remaining) and numerous volatile species generated. Also, there is a shift in the pattern of ester solutes. Figure 7.8 shows a continuation of this behavior, as there is now only 4.34% of the original material remaining, and the complexity of the early portion of the chromatogram has increased. This reconstructed chromatogram resulted from a 450°C exposure.

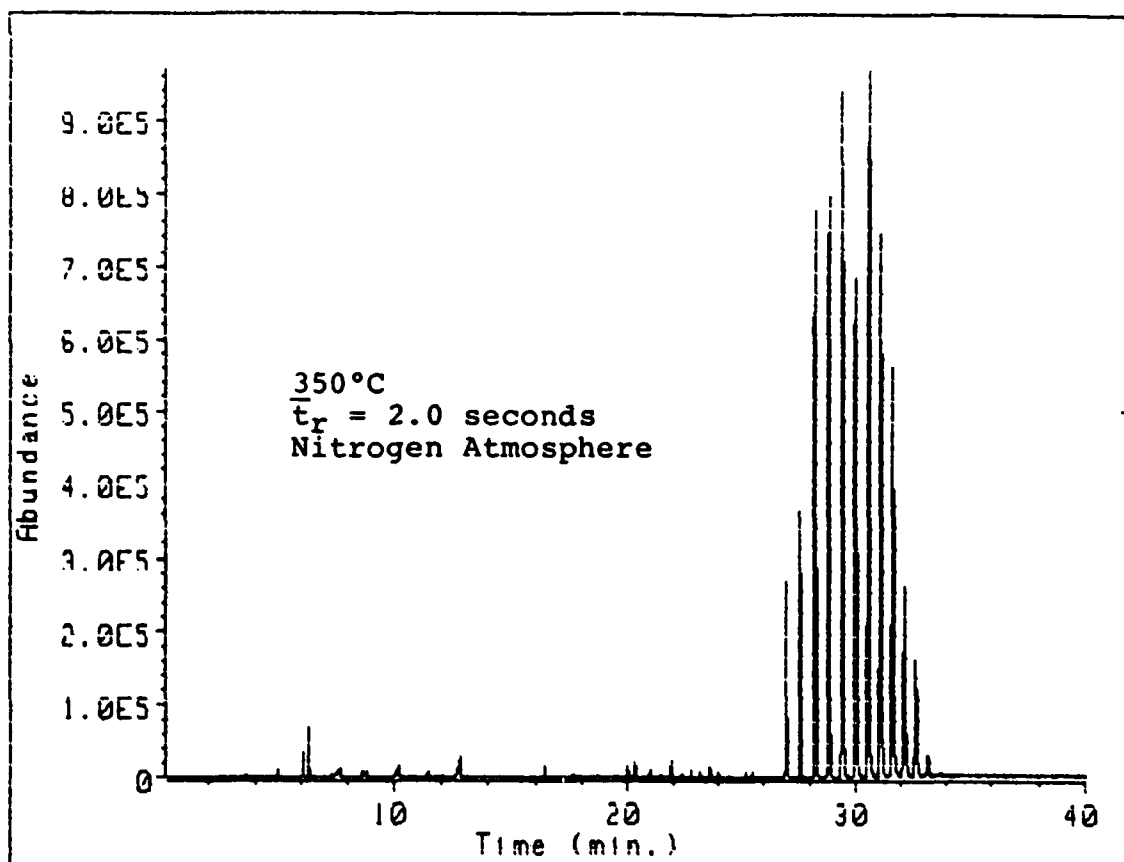


Figure 7.6. STDS Output from ATL-8001 Lubricant at 350°C.

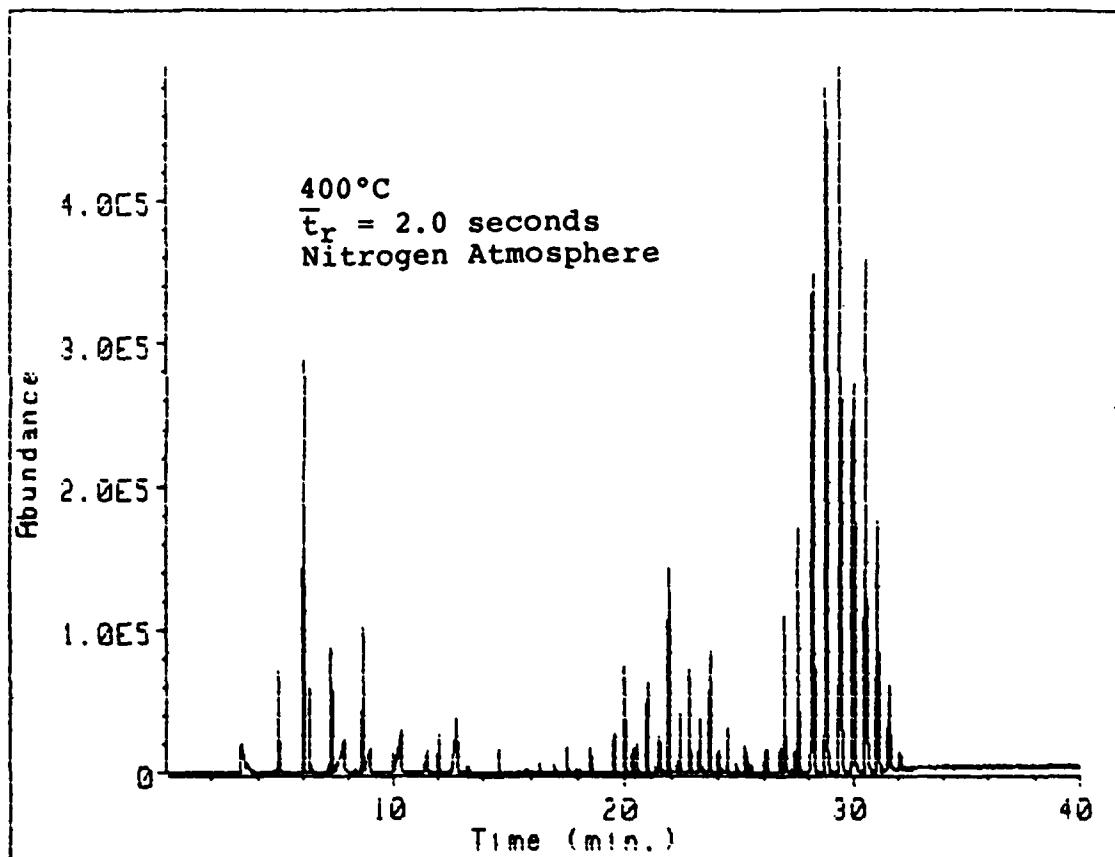


Figure 7.7. STDS Output from ATL-8001 Lubricant at 400°C.

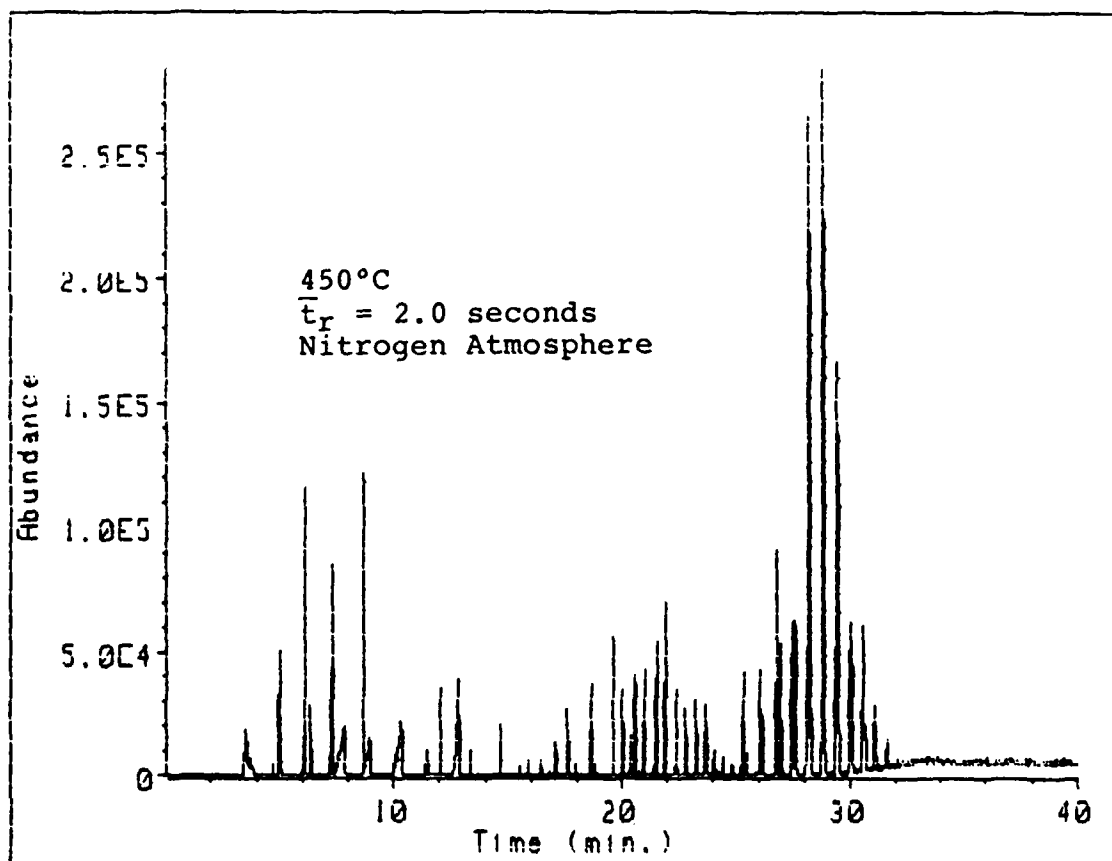


Figure 7.8. STDS Output from ATL-8001 Lubricant at 450°C.

One interesting point observed from this series of output tracings is that the heavier ester substances degraded more rapidly than the lower-molecular-weight constituents. The portion of materials remaining after 30 minutes elution is much smaller than that shown in chromatogram 7.6. The thermal decomposition curve for this ATL-8001 lubricant is shown in the next section, where its thermal stability in nitrogen is compared to that of the polyphenylether lubricant which was tested in both air and pure nitrogen atmospheres.

SECTION 8

THERMAL TESTING OF POLYPHENYLETHER LUBRICANT WITH STDS

A series of 23 experiments was conducted using the STDS with the quartz tubular reactor test-cell assembly. The thermal decomposition behavior of the 0-67-0 sample was examined over the temperature range of 300°C to 800°C. Its behavior was evaluated when subjected to a flowing dry air environment and when pure nitrogen was used as the gaseous media in the high-temperature test-cell assembly. These experiments were conducted with GC-MS serving as the effluent analysis technique. The elapsed instrument time for a single experiment was 70 minutes, and the thermal trapping/gas chromatographic compartment was maintained at -60°C during each of those experiments.

Figure 8.1 shows a GC-MS output tracing which served as one of the quantitative standards for measuring the extent of thermal decomposition of the parent lubricant material. The various numerical integrated response data were plotted as a measure of the response associated with the largest of the polyphenylether isomers, i.e., the "m,m,m" isomer. Figure 8.2 shows the reconstructed GC tracing and the numerical integrated response data for the experiments that were conducted at 650°C with flowing nitrogen and a 2.0 second mean residence time. These are the kind of data used for generating the thermal decomposition profiles of the parent material and also for plotting the relative concentrations of the various thermal decomposition products.

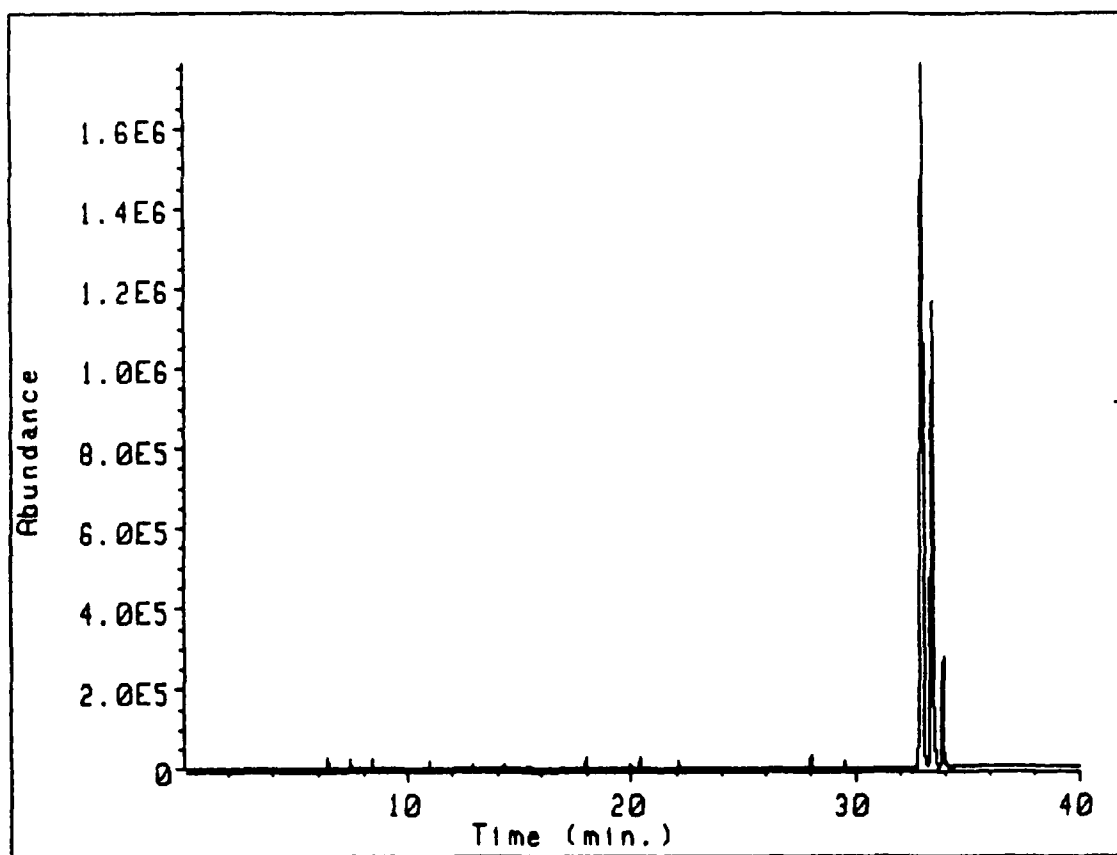
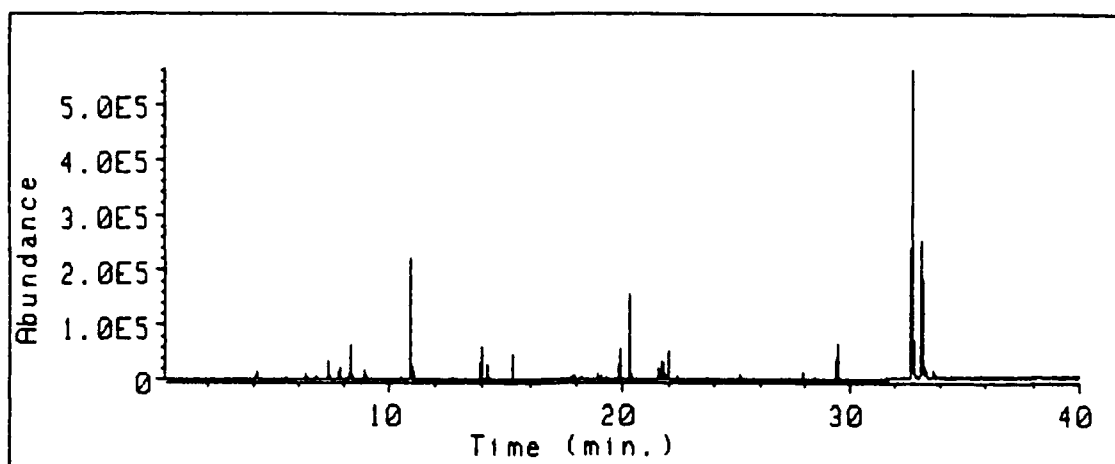


Figure 8.1. STDS Output from 0-67-0 Lubricant.



TIC of DATA:PPE009.D

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	4.170	BB	0.083	709317	4.080	4.256
2	6.357	BH	0.040	144579	6.286	6.400
3	6.747	BH	0.024	95054	6.681	6.775
4	7.331	BH	0.039	740949	7.264	7.420
5	7.825	BH	0.040	495318	7.743	7.899
6	8.324	BH	0.054	1367998	8.221	8.388
7	8.937	BH	0.040	403069	8.856	8.992
8	10.895	BH	0.036	4317599	10.813	10.984
9	11.018	PH	0.043	398238	10.984	11.063
10	13.944	BH	0.041	978396	13.893	13.991
11	14.194	BH	0.042	458061	14.122	14.237
12	15.255	BH	0.051	889500	15.204	15.319
13	17.911	BH	0.053	301978	17.858	17.962
14	18.946	BH	0.042	315946	18.899	18.993
15	19.073	PH	0.055	171938	18.993	19.117
16	19.890	BH	0.037	1307464	19.784	19.950
17	20.309	BH	0.044	4246469	20.179	20.387
18	21.566	BH	0.038	486331	21.449	21.636
19	21.713	BH	0.042	940502	21.667	21.782
20	21.857	BH	0.038	230856	21.813	21.927
21	25.141	BH	0.046	202902	25.091	25.185
22	27.942	BH	0.037	292977	27.838	27.984
23	29.443	BH	0.044	1837161	29.316	29.587
24	32.740	PH	0.059	19654754	32.652	32.967
25	33.176	PV	0.054	8925924	33.090	33.315
26	33.367	VV	0.080	612675	33.315	33.487
27	33.679	PV	0.060	321884	33.594	33.743

Figure 8.2. STDS Typical Output Data.

Figure 8.3 shows two reconstructed chromatograms of the thermal decomposition products. The upper tracing corresponds to the products formed in a flowing air environment, and the lower set corresponds to the products formed in nitrogen. Although the exposure temperatures were slightly different (upper tracing 600°C, and lower tracing 650°C) the composition of the generated gaseous species was relatively similar. One exception was the appearance of phthalic acid anhydride occurring in the air environment thermal decomposition.

Figure 8.4 is a thermal decomposition plot that shows the degradation of the ATL-8001 lubricant in nitrogen and the 0-67-0 polyphenylether in the two different gaseous environments. An interpretation of this thermal decomposition behavior is given in the latter portion of this section.

Figure 8.5 is an example of the MS readout that identifies the various thermal decomposition products, and many of these identifications are made via the NBS mass spectral library which is contained within the MS instrumentation. In this figure, the identification of benzaldehyde is a rather straight-forward interpretation from the MS displayed file data. Table 8.1 is a listing of the stable thermal decomposition products observed during the course of these studies with 0-67-0. These compounds were observed in large concentrations from the GC-MS data as shown in Figure 8.3.

Figure 8.6 is a re-drawn curve (on a different scale) of the thermal decomposition behavior of 0-67-0 in flowing air. Also, on this same graph the product concentrations are shown at three

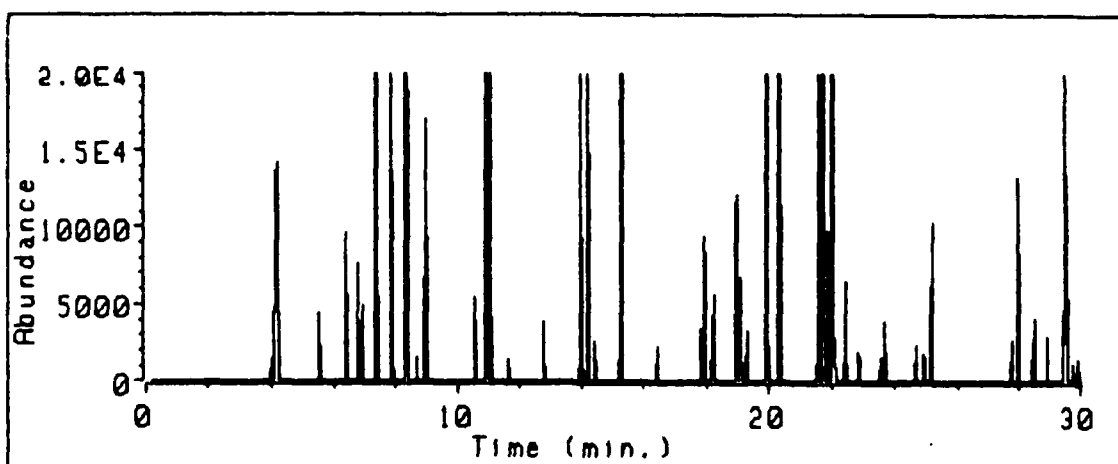
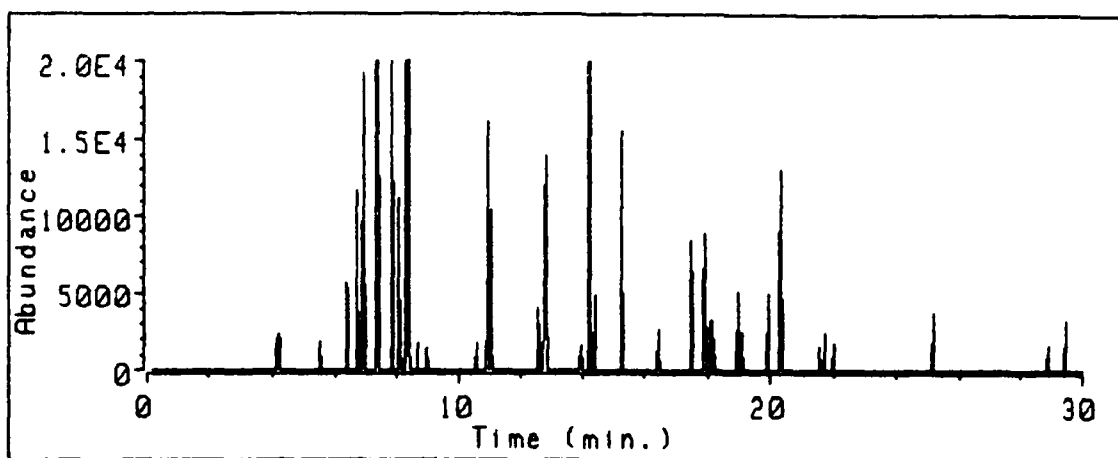


Figure 8.3. Reconstructed GC-MS Output of Thermal Decomposition Products from 0-67-0 Lubricant.

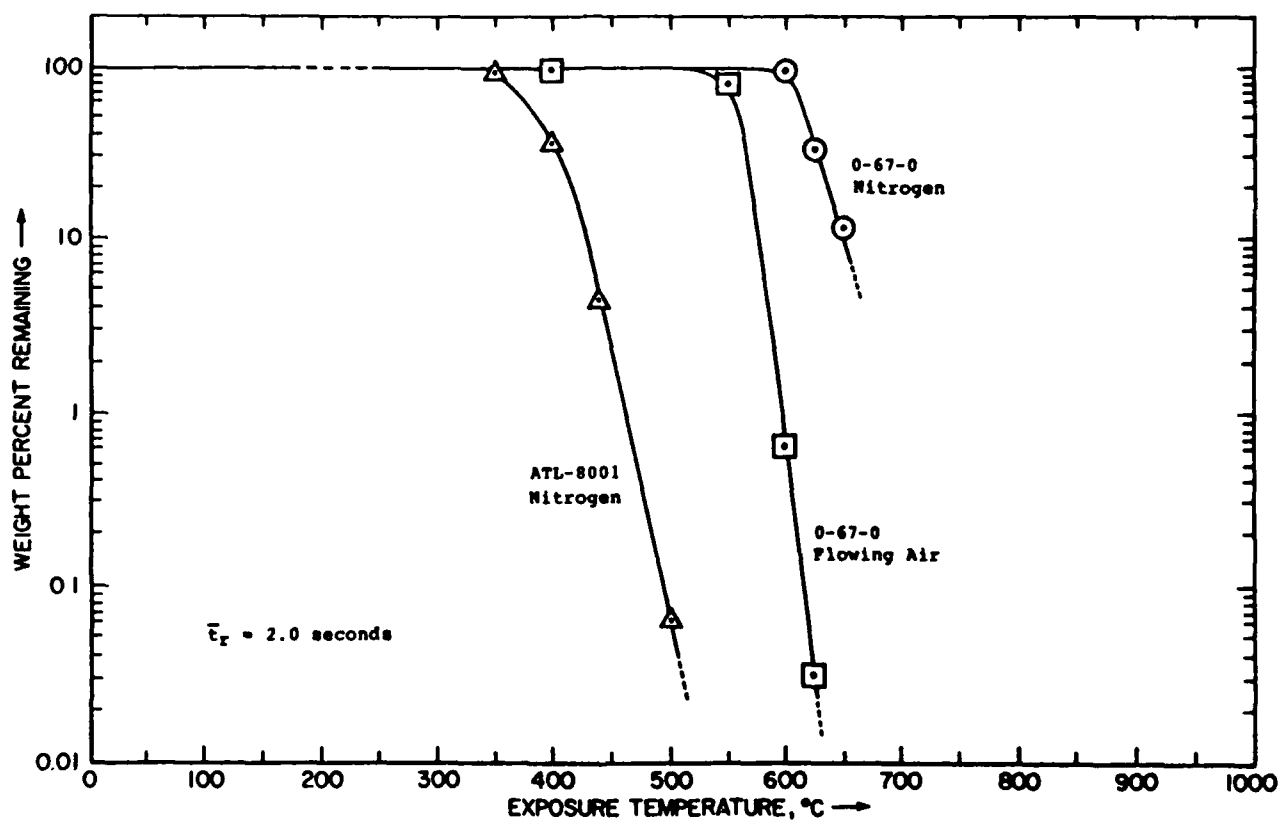


Figure 8.4. Thermal Decomposition Plots for ATL-8001 and 0-67-0 Lubricants.

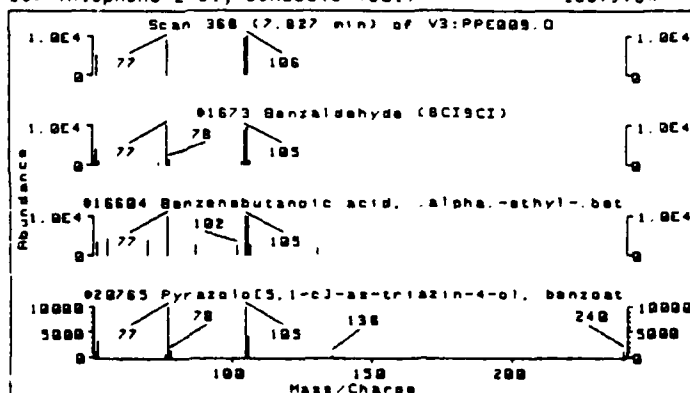
LIBRARY SEARCH RESULTS

Scan 368 (7.827 min) of V3:PPE009.D

Library file: NBS_REVE.L

Library name: NBS MASS SPECTRAL DATABASE

	CAS #	Library Index #	Match Quality
1: Benzaldehyde (8C19CI)	100527	1673	9842
2: Benzenebutanoic acid, .alpha.-ethyl-.bet	55822894	16604	9242
3: Pyrazolo[5,1-c]-as-triazin-4-ol, benzoat	28464484	20765	9217
4: 1,2,4-Trioxolane, 3-phenyl- (8C19CI)	23253307	7569	9056
5: 1,2-Benzenedioxaldehyde (9CI)	643799	4669	9020
6: 1,2,4-Trioxolane, 3,5-diphenyl- (9CI9CI)	23888155	19426	9013
7: Ethanone, 1,2-diphenyl- (9CI)	451401	14865	8908
8: Benzoic acid, 2-(phenylmethyl)hydrazide	1215527	19138	8887
9: Oxaziridine, 2-methyl-3-phenyl- (8C19CI)	3400122	4748	8753
10: Thiophene-2-ol, benzoate (8CI)	16693984	15934	8743



GRAPHICS
[DE]

T: null.
Z: Set of 3 MS
Y: TIC of V3:PPE009.D
X: Set of 4 MS

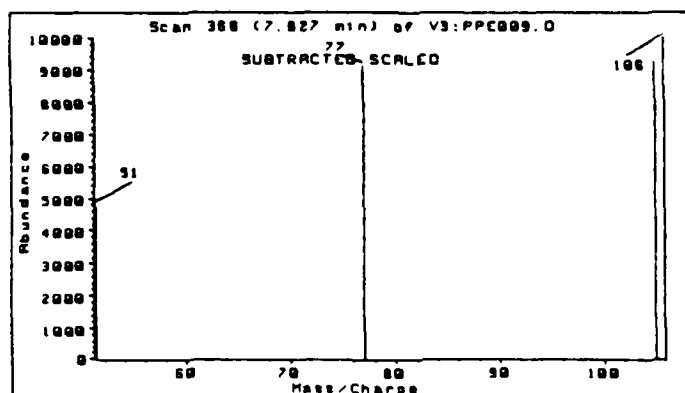


Figure 8.5. Example of MS Output for Compound Identification.

TABLE 8.1

THERMAL DECOMPOSITION PRODUCTS
(Tentative Identification)

maleic anhydride
2,5-cyclohexadiene-1,4-dione
Benzaldehyde
phenol
naphthalene
phthalic acid anhydride
2-propenal, 3-phenyl
dibenzofuran
2-phenyl naphthanol

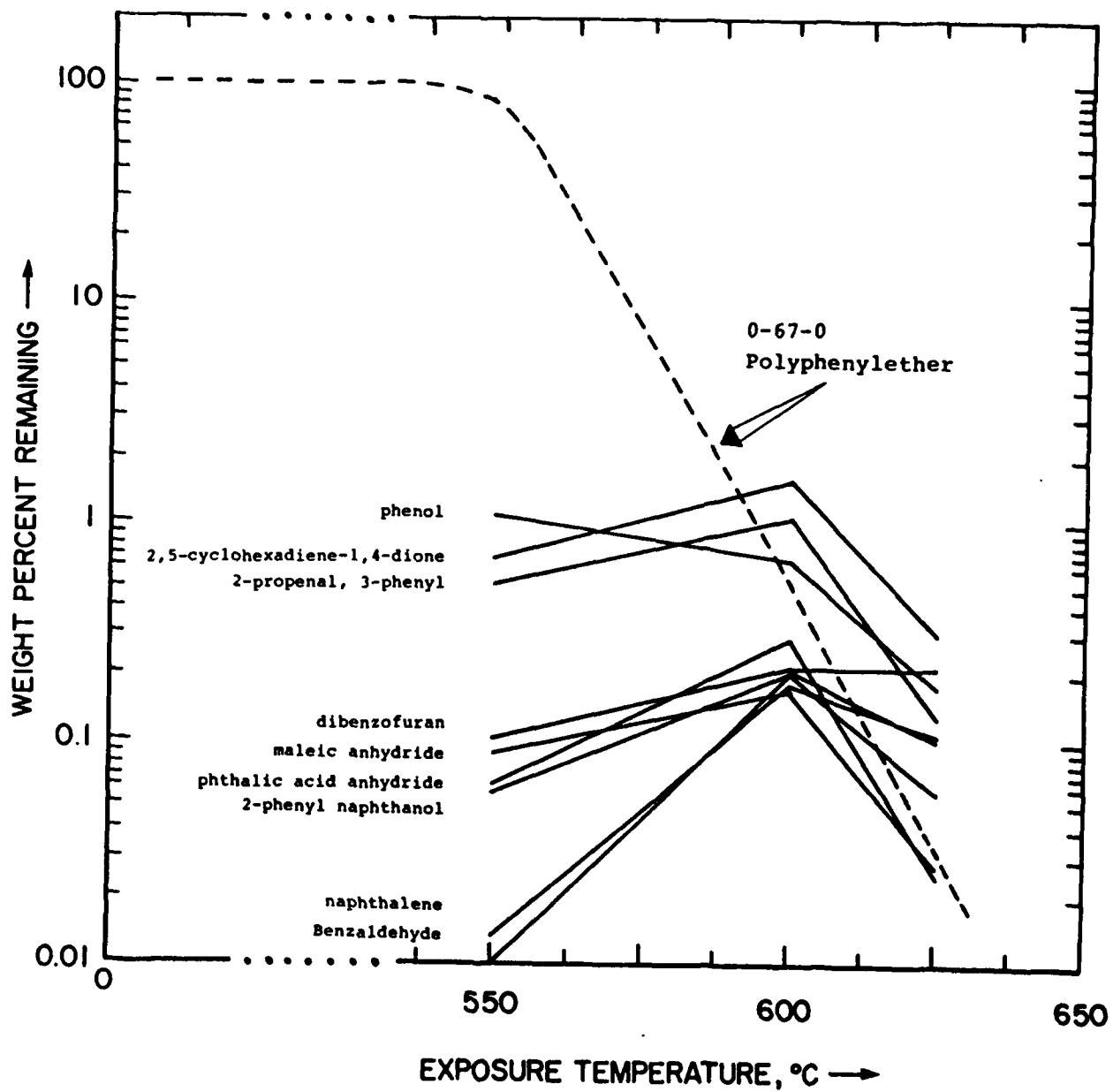


Figure 8.6. Thermal Decomposition Profile for 0-67-0 in Flowing Air.

different exposure temperatures, i.e., the compounds listed in Table 8.1. From past experience, it has generally been observed that the major concentrations of thermal degradation products occur during the steepest decline of the semi-log plotting of the thermal decomposition of the parent material. This is usually the situation when the thermal decomposition is complex, and certainly this is the case with the polyphenylether sample.

The thermal decomposition at different gas-phase residence times was examined, and these tests were conducted at 625°C in flowing nitrogen. It is shown in the semi-log plotting of Figure 8.7 that indeed the gas-phase residence time has a profound impact upon the thermal decomposition of the 0-67-0 lubricant. It was also of interest to note in this study that the thermal stabilities of the three isomers were different. The most stable of the three was the "m,m,m" isomer, and the least stable was the "p,m,p" isomer.

From these STDS generated data with the polyphenylethers, an assessment was made of the global thermal degradation pathways for the 0-67-0 lubricant. This assessment can be summarized as follows:

For the polyphenylether investigated, the lowest bond dissociation energy is suspected to be the C-O sigma bond (~70 kcal/mole). The thermal decomposition data for polyphenylether in air indicated rapid destruction over a small temperature band of ~550-630°C. When the flowing gas stream was changed to dry nitrogen, the temperature band of thermal degradation shifted to

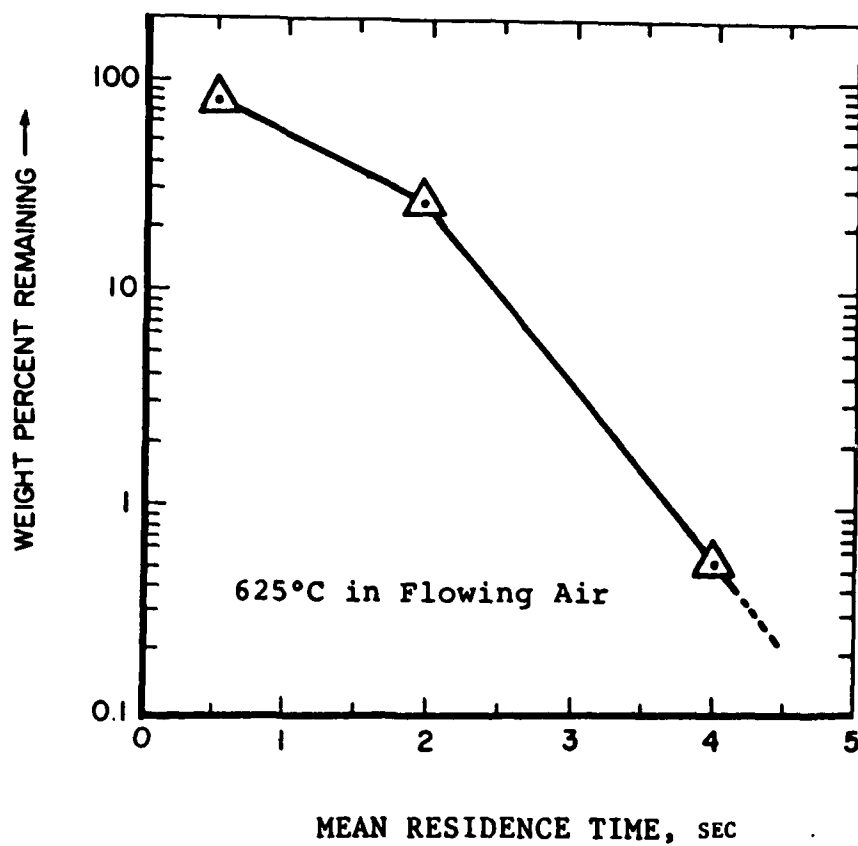


Figure 8.7. Gas-Phase Residence Time Influence on Thermal Decomposition of 0-67-0 Lubricant.

slightly higher temperatures (~600-700°C). The lower degradation temperature for the oxygen-rich data may be due to O atom abstraction and addition reactions as the concentration of these species is much higher under these conditions. Thus, it is doubtful that the kinetics of this reaction are first-order in nature for the conditions of this experiment.

Examination of thermal degradation products indicated that the nature of the products was nearly constant, regardless of the oxygen concentration. The complexity of the major products formed (including single and multi-ring aromatics and oxygen-containing alicyclic and aromatic compounds) suggests that a complex mechanism, involving C-O bond cleavage yielding O atoms and other larger electron deficient molecules, followed by rapid radical-molecular addition and abstraction reactions, may be occurring. In essence, a radical chain mechanism may be responsible for the extremely rapid decay of this lubricant over a temperature bandwidth of approximately 50°C. A full-scale kinetic study of the oxidative and pyrolytic degradation of this material (including quantitation of thermal reaction products) is required in lieu of further speculation with regard to mechanistic pathways.

SECTION 9

ANALYSIS OF LUBRICANT CONSTITUENTS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

Although HRGC and mass spectrometry are individually very powerful analytical tools, their coupling (i.e., GC-MS) has produced an analytical capability of extraordinary power. Even so, there are many situations where additional information is required and IR spectroscopy [23-26] can provide much of the needed additional chemical data.

High-performance hyphenated instrumental analysis systems are being offered [27-29] by a few instrument suppliers, and it was of interest to determine if FTIR could provide additional analytical information with respect to lubricant analysis. Eventually, FTIR could be used in the sophisticated analytical instrumentation that would be utilized for characterizing the thermal decomposition behavior of lubricant samples.

Accordingly, two replicate samples of a mixture containing the 0-67-0 lubricant were analyzed using a Hewlett Packard 5890A/5965A GC-FTIR system. The instrumental conditions used for conducting these tests were as follows:

Injection Port: splitless, 0.5 min purge delay, 300°C

GC column: BP5, 12 m, 0.2 mm i.d., 0.1 micron film
thickness

Carrier Gas: helium (1.15 mL/min through the column,
12 psi head pressure)

GC Program: 40°C (1 min) to 300°C(20 min) @20°C/min

Transfer line B: (sample in) 300°C, (5 psi head pressure
of make-up nitrogen)

Transfer line A: (sample out) 300°C, (3 psi head pressure
of make-up nitrogen, making the total flow
out of A = 1.86 mL/min)

Flow Cell: 300°C

Acquisition Delay: 0.1 min

Pre-peak Storage: 2 seconds

Post-peak Storage: 5 seconds

Initial Storage Threshold: 0:0 response units

The objectives of this study were twofold: 1) to test whether the samples in question could be chromatographed and transported through the system successfully, and 2) to determine whether the IR data obtained could be conclusive enough to distinguish between isomers where MS data had failed.

As can be seen in the following chromatograms and IR scans (see Figures 9.1 through 9.4), the three isomers were baseline resolved despite the overloaded peak shapes. They also appeared to elute in the order of most to least concentrated.

Inspection of the IR spectra data showed three quite different compounds. Notice the increase in abundance of the 1600 cm^{-1} peak relative to the 1450 cm^{-1} peak with the increase of para ether linkages in the polymer. This is logical since peaks in this area are a result of C to C double bond ring stretching. As the polymer contains more and more para linkages the ring system becomes even more rigid and locked into a

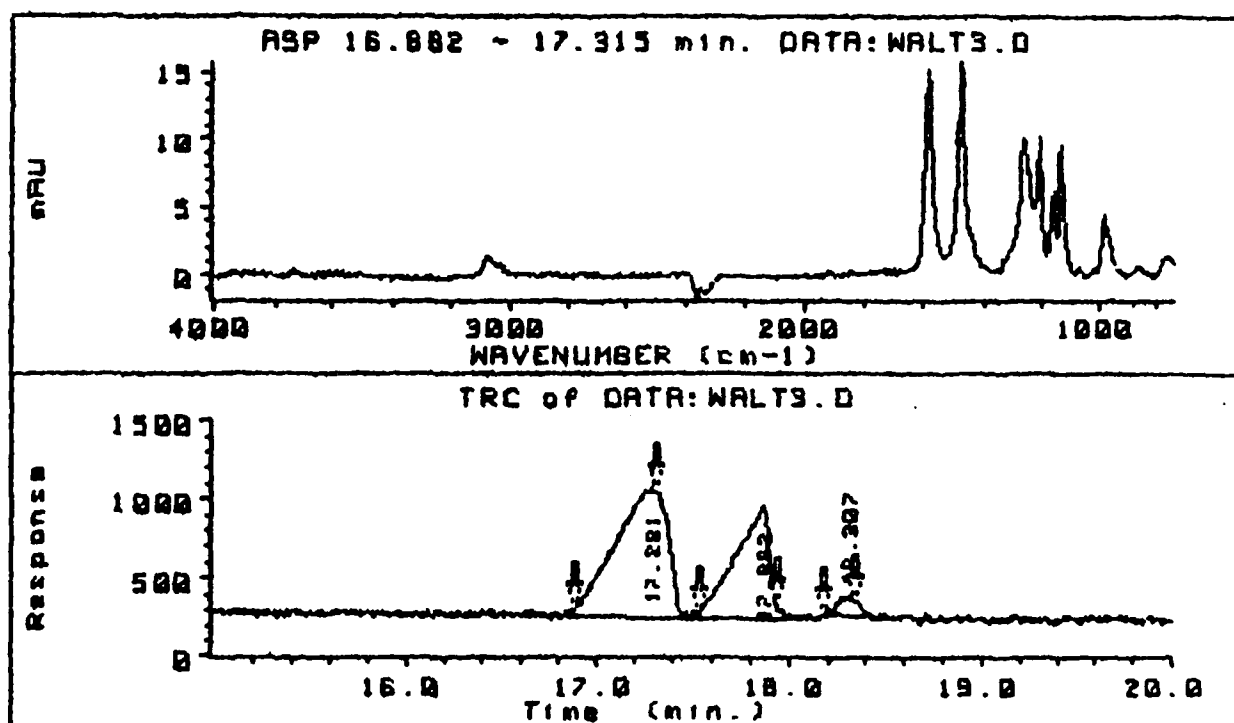


Figure 9.1. GC-FTIR Output for 0-67-0 "m,m,m" isomer.

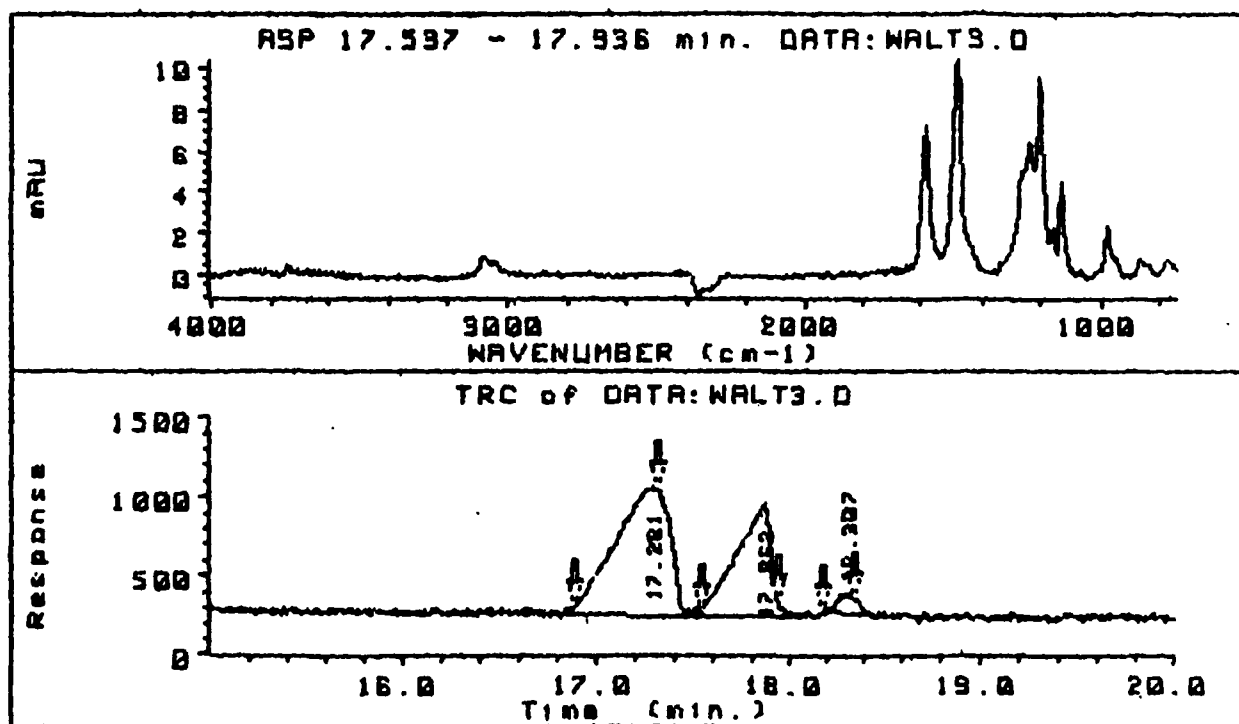


Figure 9.2. GC-FTIR Output for 0-67-0 "m,m,p" Isomer.

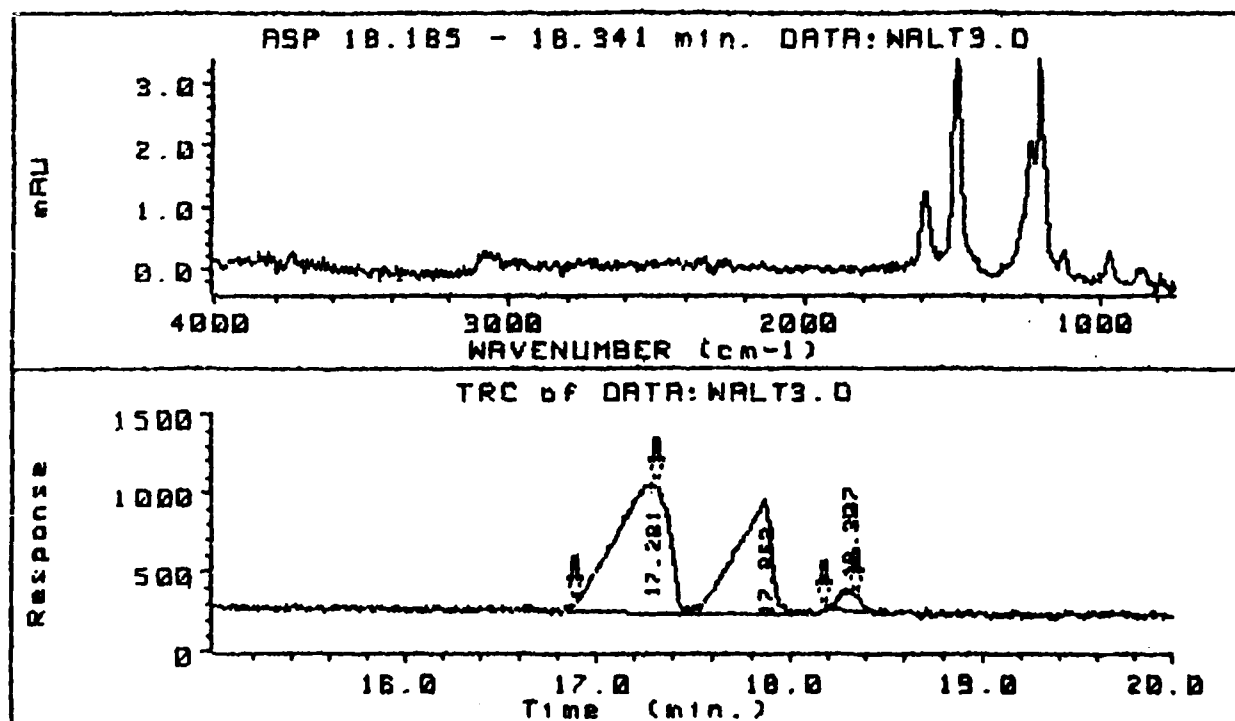


Figure 9.3. GC-FTIR Output for 0-67-0 "f,m,p" Isomer.

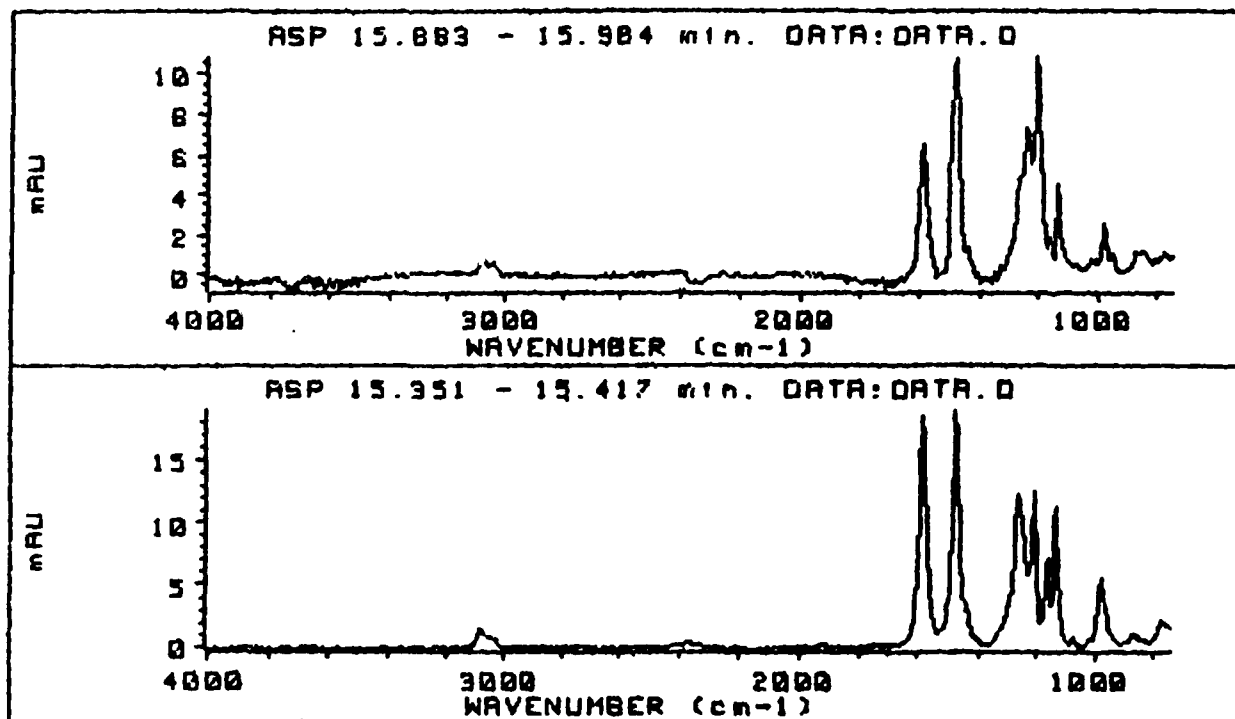


Figure 9.4. Repeats of FTIR Scans of 0-67-0 "m,m,p" and "m,m,m" Isomers under Different GC Conditions.

particular x,y,z planar configuration. For example, the m,m,m-isomer is the most flexible in terms of allowing bond stretching around the ring. Because of this, a greater relative abundance of the 1600 cm^{-1} peak is seen. As soon as para linkages are added into the polymer and with more frequency, the ability of the carbon bonds to stretch in many configurations is decreased. They are "locked in" and their position is limited much as the stability of a ladder increases with an increasing number of rungs.

Another distinguishing area in the IR spectrum of these compounds is the region between 1000 and 1400 cm^{-1} . The region for C-O-C asymmetric stretching is around 1250 cm^{-1} . Again, it is logical to conclude that the differences in ether linkages among the isomers would give rise to differences in this area of their spectrum as well. The m,m,m- isomer shows the greatest splitting of peaks in this region, while the p,m,p- isomer shows the least. The important observation here is that there is a difference in the spectra of this region and that this difference is reproducible.

Based upon the results of this initial examination, it appears that the study of high-molecular-weight lubricants similar to those tested here would benefit from GC-FTIR data. The use of this FTIR technique could augment information, and in many cases it could provide valuable analytical data where GC-MS techniques were insufficient.

SECTION 10

CONCEPTUALIZED INVERSE GAS CHROMATOGRAPHY TEST-CELL ASSEMBLY

Inverse gas chromatography (IGC) has been applied [30-32] to studies of nonvolatile substances that were in different physical forms, e.g., fibers, gels, particles, crystals, thin films, etc. Low volatility fluids, such as lubricants and hydraulic fluids can also be examined using various inverse chromatography procedures.

Another mode, known as reaction gas chromatography [33], can be coupled with IGC to examine degradation behaviors at moderate temperatures and also to examine various specimens under different manners of chemical attack, e.g., water, oxygen, acids, etc.

An IGC test-cell assembly for use in the STDS would require that the sample be held in place and then various gaseous media be permitted to percolate through, or flow over, the sample. This type of testing would not involve the elevated extreme temperatures that are customarily associated with thermal degradation of lubricant specimens. Actual thermal exposures would generally be conducted at temperatures where the specimen's vapor pressure would be very small, generally less than 5 mm of mercury.

IGC finds special application with samples such as polymeric materials, crystalline solid additives, or lubricant constituents that are in the solid phase. Analytical and physical analysis

techniques using IGC have been largely overlooked since the general procedure was first presented in the 1960s. However, with the introduction of new gaseous extraction techniques, e.g., supercritical fluid extraction, procedures such as IGC will probably be developed for vastly improved analyses and characterizations of materials.

SECTION 11

CONCEPTUALIZED LIQUID-PHASE TEST-CELL ASSEMBLY

Throughout this feasibility study attention was given to the thermal decomposition behavior of lubricant samples that were subjected to high-temperature gas-phase degradations. The thermal decomposition behavior of a lubricant that remains in the liquid phase can also be tested using a specially designed test-cell assembly. Again, the liquid sample would be subjected to different thermal exposures where temperature, mean residence time, pressure, and contacting materials were controlled or varied at will.

A liquid-phase test-cell assembly would require special high pressure pumping and various types of valves for stream switching. Periodic samplings would subject a small microliter quantity of the liquid to in-line chemical analyses using high-resolution gas chromatography and the hyphenated techniques of mass spectrometry or Fourier transform infrared spectroscopy, or even atomic emission spectroscopy. The ability to detect gaseous and low-volatility constituents within the lubricant sample would be available and, with the very sensitive in-line analytical instrumentation, these types of compounds could be detected at extremely low concentration levels. Often they are key indicators for the early onset of thermal decomposition or structural degradation.

A considerable amount of versatility can be incorporated into a liquid-phase test-cell assembly. For example, after a

fluid has been examined with respect to its thermal decomposition behavior, various formed deposits can also be analyzed with respect to quantity, composition, and subsequent degradation.

SECTION 12

CONCLUSIONS AND RECOMMENDATIONS

The major objective of this study was to determine the feasibility of using STDS technology to evaluate the high-temperature thermal decomposition properties of current and future Air Force lubricants. In this respect, the study was a complete success - all lubricants investigated were successfully transported, thermally exposed, and analyzed by the STDS. The applicability of gas-phase STDS testing for evaluating the thermal stability aspects of the lubrication process (a high-pressure liquid-phase phenomenon) is an important question. In other studies of multiphase organic material thermal stabilities, it has been shown that the limiting process is the gas-phase thermal degradation behavior. In addition to the investigation of liquid-phase test cells for the STDS, there may be a direct relationship between liquid and vapor-phase decomposition properties. One of the interesting results of this work is the relative instability of the ester lubricant compared to the polyphenylether. This finding would seem to reinforce established liquid-phase testing.

Thus, the feasibility of using the STDS for high-temperature lubricants has been shown. A number of other important conclusions and observations may be derived from this work:

- 1) An extremely successful method was developed for the separation of isomeric mixtures of high-molecular-weight lubricants using high-resolution gas

chromatography. This enhanced separation may allow a more exact determination of the relationship between lubricant composition and properties.

- 2) The gas-phase thermal decomposition of isomers of the same compound can be different. Note that the "m,m,p" and "p,m,p" isomers of the polyphenylether lubricant are more thermally fragile than the "m,m,m" isomer. If these isomers could be separated on a large scale, a single isomer of the polyphenylether may be significantly more thermally stable than the three component mixture.
- 3) This study demonstrates the obvious importance of the decomposition atmosphere. The STDS can be used to investigate the benefits of lubricant systems inerting.
- 4) The analysis of lubricants by in-line GC-FTIR is extremely valuable in determining structural differences in lubricant isomers.
- 5) Residence time at temperature has a very definite effect on thermal stability. This type of information will be of importance to lubricant system designers.
- 6) Products of thermal decomposition can be quickly and accurately identified. It may be possible to find

lubricant candidates whose thermal reaction products may also have good lubricant qualities.

Thus, considerable information has been derived from this feasibility study. More in-depth work needs to be undertaken to develop other test-cell assemblies (e.g., liquid-phase and solid-phase test cells) for future lubricant materials. The effect of metals and lubricant contaminants on thermal stability needs to be examined experimentally. Finally, more detailed experiments should be carried out for each lubricant candidate to completely elucidate their thermal decomposition behavior.

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