\OPTIMIZATION OF CAPILLARY GC-FTIR FOR COMPLEX SAMPLE ANALYSIS

by

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INTRODUCTION

The gas chromatography/infrared (GC-IR) method of analysis, while not new, has only recently improved to the point where complex, real world samples can effectively be studied. To perform such an analysis, a highly efficient separating mode (gas chromatography) must be interfaced to an infrared detection system which is capable of rapid scanning and computerized data handling.

The advent of modern Fourier transform infrared (FTIR) spectrometers offers improvements and advantages over conventional dispersive infrared spectrophotometers for detecting eluting components from a gas chromatograph[1]. Increased optical throughput, rapid-scanning of the IR region and dedicated high-speed computers make possible routine high-resolution infrared spectra. The effluent from a gas chromatographic separation can be directed through a heated lightpipe placed in the path of the infrared beam and FTIR spectra of GC fractions obtained as they elute from the GC column. Nitrogen-cooled Hg-Cd-Te (MCT) detectors and advanced lightpipe designs are particularly responsible for the improvement in IR sensitivity. Coupled with the recent development of highly efficient capillary columns as the separation mode, valuable gas phase spectra for even complex "real-world" samples should be obtainable. At present, narrow bore fused silica capillary columns give the most efficient separations in gas chromatography.

The major objectives of this research are the separation and

identification of components in aviation jet fuel samples by GC-FTIR. Optimum conditions and parameters will be established for proper capillary gas chromatography. The interfacing of capillary GC with FTIR presents some unique situations with respect to both chromatography and detection. Two Nicolet FTIR optical benches, with respective GC hardware, will be used in assessing those conditions/ parameters needed for state-of-the-art GC-FTIR. In addition, gas chromatography-mass spectrometry data for the same jet fuel samples will be presented in an effort to compare directly information obtainable from both spectroscopic methods. A fused silica capillary column is used to achieve the maximum separation of components. Sensitivities from both GC-FTIR and GC-MS will be directly compared for the same sample components isolated using on-the-fly methods.

Characterization and identification of components in aviation jet fuels are of interest to the United States Air Force in that compounds may be present that are carcinogenic and/or have appreciable heteroatom (alcohols, ethers, etc.) character. Since concentration of highly branched alkanes can generally improve fuel performance (e.g. high octane number), the presence of such aliphatics should be significant. Finally, identification of decomposition products due to fuel instability would be of interest with respect to storage of such aviation products.

HISTORICAL

Because of recent advances in both gas chromatography and FTIR, optimizing the GC-FTIR experiment has been of obvious concern to many researchers. A review of these developments and advances should give a better understanding of how the research reported here relates to other work and how the GC-FTIR technique could be applied to complex real-world samples.

While packed column gas chromatography offered reasonable separation of sample components, the development in 1957 of open tubular capillary columns[2] initiated the evolution of GC columns with higher efficiency and lower resistance to gas flow. The open tubular design consequently resulted in a lower pressure drop across the column. Another pioneer, D. H. Desty, (1958) applied "open tubulars" (so-called because a thin film of stationary phase is deposited on the walls of a thin open tube) to the separation of petroleum products[3]. Desty et al. also contributed to capillary column technology by suggesting a simple design for a machine which could draw and coil glass capillary tubing[13].

Holasz and Horvath initiated the development of support coated open tubular (SCOT) columns[4] which were found to be more efficient than packed columns. Although the stationary phase is coated on a support (as in packed columns), the center of the tube is still open. L. V. Azarraga was one of the first to use SCOT columns with on-line FTIR detection for analysis of environmental samples[5]. SCOT columns, while

providing capillary efficiency, also afforded a sample loading compatible with the existing GC-FTIR sensitivity. D. M. Hembree, et al. resorted to GC separations using a SCOT column but used cryogenic trapping of fractions from the chromatographic run for final off-line FTIR analysis. Solvent refined coal (SRC) fractions were the "real, complex samples" used to illustrate GC-FTIR[11]. Such samples were commonly too complex for sufficient separation by SCOT columns followed by on-line FTIR detection.

Therefore, while SCOT columns offered needed sample loading and enhanced capillary efficiency, work resumed to develop what has come to be known as WCOT (Wall coated open tubular) capillary columns. These columns were found to have unmatched separating capability. Instead of a support, the stationary phase is coated on the smooth wall of the capillary, thus the name WCOT. Azarraga first presented preliminary WCOT capillary GC-FTIR results in 1976[9].

K. M. Shafer boasts that "the first on-the-fly GC-FTIR spectra ever obtained using WCOT (glass) capillary columns"[7] was achieved in his laboratory. Shafer found the 0.5 mm i.d. x 40 m glass column gave better separations than a SCOT column, but not as good as other more narrow bore WCOT columns. Despite his claim, Shafer's separation of a wastewater sample provided only a small number of separated components. Shafer was not able to use columns less than 0.5 mm i.d. because of the comparably limited sample capacity, again relating back to FTIR detection limitations. Later, Shafer and Cooke et al. developed the methodology to compare GC-FTIR and GC-MS data directly, thereby

elucidating more effectively various components. Since WCOT columns were commonly used in GC-MS, a 0.5 mm i.d. glass WCOT with 0.8 μm stationary film thickness was tested in the GC-FTIR experiment and favorable detection limits achieved.[8] Environmental sample data from both FTIR and MS could then be more readily compared due to similar chromatographic conditions. Finally, Rossiter has achieved an on-line spectrum of 20 ng of isobutylmethacrylate by using a short (6 cm) lightpipe[12]. In an effort to demonstrate on-line GC-FTIR with the short lightpipe, a jet fuel sample was separated by gas chromatography. The wide bore WCOT glass capillary column, however, provided only marginal separation of the complex fuel sample.

Although glass capillaries (WCOT) can be very useful for separating complex mixtures, the soda lime which is commonly used to manufacture these columns can be brittle and often difficult to work with. Column end straightening by a torch can cause a loss of column deactivation which can lead to tailing peaks.

Dandeneau and Zerenner have shown that capillary WCOT columns made from fused silica (SiO_2) are not only easier to deactivate but are flexible enough to bend even though fused silica is inherently straight[10]. These workers found that fused silica was unexcelled in inertness to all functional groups tested. Flexible and rugged, fused silica columns can be inserted directly into injection ports, through transfer lines and detector fittings. Such columns are available with inner diameters of 0.35-0.2 mm. Film thicknesses for these columns can be as high as 1.2 μm for maximum sample capacity (commonly 500 ng per component).

Using an OV-101 fused silica capillary of narrow bore (0.2 mm i.d. x 50 m), Azarraga in 1981 analyzed environmental samples by GC/FTIR prepared from waste effluents of the printing and ink industry[6]. Preconcentration using a SCOT capillary column combined with cold trapping was necessary, however, prior to separation on the fused silica column.

Recently, Griffiths has used wide bore fused silica (>0.3 mm i.d.) with 0.5 μm film thickness in the further development of capillary GC-FTIR techniques[14]. His efforts have concentrated on the principal problem with capillary GC-FTIR, its "chemical dynamic range", i.e. the difference between the maximum quantity of any component able to be injected onto a column without degradation of GC performance to the minimum amount yielding an observable infrared spectrum. He has discussed the "problem" in terms of the choice between narrow-bore fused silica columns coated with thin (0.2-0.3 μm) layers of stationary phase to wider bore glass columns with much thicker (0.8-1.2 μm) layers of stationary phase. He has indicated, though, that few separations of truely complex samples using fused silica columns coupled with FTIR detection have been shown.

Garlock et al. have demonstrated the use of narrow as well as wide bore fused silica columns in separating coal derived products (SRC), perfumes, essential oils and a few jet fuels derived from kerosene. For less than 100 ng, narrow bore (0.25 mm i.d.) columns were usable. However, for maximum sample loading 0.3 mm i.d. columns with 1.0 μm film thickness were required. A colleague has indicated that fused

silica columns handled overloading reasonably well[15]. A 36 cm x 1.4 mm diameter lightpipe was used in their experiments along with a narrow band MCT detector resulting in a sensitive on-the-fly GC-FTIR technique.

Shafer and Jakobsen have shown success in coupling a narrow bore fused silica column (0.25 mm i.d.) with FTIR and have achieved acceptable detection limits. They also have interfaced a mass spectrometer in series with the GC-FTIR[16]. (It should be noted that the last three references (14-16) have not appeared in publication at the time of this writing).

In light of the several methods and developments just cited, a combination of the best gas chromatographic separation available with optimal FTIR conditions should lead to a hyphenated method capable of producing quality infrared spectra on-the-fly for even very complex samples. The greater part of this research is an attempt to determine those parameters necessary to separate, characterize and identify components in aviation jet fuels. Emphasis will center around final quality IR spectra that can be identified by the EPA vapor phase library search routines available in the Nicolet FTIR data base. No prior pretreatment or preconcentration of samples is to be envisioned. Because the majority of components in jet fuels do not contain strong absorbing groups (i.e., like isobutylmethacrylate), proper optimization of all parameters will be critical. Two optimized GC-FTIR systems using different lightpipe designs and MCT detectors will be compared in light of the requirements necessary to analyze these complex samples.

In reference to the actual jet fuel samples to be analyzed, LC-NMR by Dorn, et al. has been used to characterize both qualitatively and quantitatively major classes of compounds present. Data showing percent alkanes, monoaromatics and dicyclic aromatics are presented. Their data also indicate the presence of alkenes in these Air Force jet fuels[18]. In general, no prior pretreatment was used before analysis.

EXPERIMENTAL

Equipment:

Two GC-FTIR configurations were used in assessing a "best system". In our laboratory we have a Nicolet series 6000 FTIR with a liquid nitrogen cooled Hg-Cd-Te detector capable of scanning the IR region 4000-400 cm^{-1}. The Michelson interferometer has a maximum mirror velocity of 3.130 cm/sec although 0.586 cm/sec is the recommended value for MCT detectors. The Nicolet 6000 FTIR uses a single disc drive with 8-sector cartidges and is controlled by a Nicolet IR-80 data processor. Cylindrical lightpipe arrangements of both 2mm i.d. x 6 cm and 3 mm i.d. x 6 cm stainless steel were supplied by the Accuspec Corp. Each lightpipe was placed in the cell holder normally used for LC cells. An Accuspec Compact GC with auxillary microvolume thermal conductivity detector (TCD) fitted for capillary columns was used. Available columns included a 25 m wide-bore glass capillary (OV-101), a 0.32 mm i.d. x 25 m CP-sil 5 and a 0.35 mm i.d. x 60 m DB-5 fused silica capillary (the latter two columns being bonded phases). A home-made on-column injector was fitted to the Accuspec GC to make use

of the Carlo-Erba 0.23 mm o.d. syringe needle design. As general practice, the effluent from the column was transferred to the lightpipe via a heated transfer line and returned by narrow bore heated tubing to the TCD heated block in the GC. In the case where fused silica was used, the column was fed through the transfer line up to the IR lightpipe.

Also available was a dual-beam Nicolet 7199 system with GC 7000 external bench, 40 cm x 1 mm i.d. gold plated lightpipe, and narrow band (4000-700 cm^{-1}) MCT-A^{+} detector. The GC employed in this study was from Hewlett Packard and was fitted with capillary split-splitless injectors. For data storage, dual disc drives (and a storage module capable of holding 5000 8 cm^{-1} file spectra) were utilized. The capillary column available at Nicolet was a 60 m x 0.3 mm i.d. DB-1 bonded phase fused silica interfaced to the 40 cm lightpipe by 0.7 mm i.d. glass lined tubing.

The Nicolet 6000 in our laboratory had available nitrogen purging for the IR bench while only compressed "dried" air was available at Nicolet for the 7199 system.

A Varian MAT 112 Electron Impact mass spectrometer was interfaced to the Accuspec GC and DB-5 fused silica column. The source voltage was 70 eV and the operating temperature was 240°C. The Varian-MAT 620/L-100 computer uses 32 sector hard disk cartridges to store accumulated data. A ten inch heated transfer line brought the effluent directly into the mass spectrometer and no make-up gas was used (flow rate ~2 ml/min).

Jet fuel samples were provided by Major D. D. Potter from the Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH. Samples were received and stored in teflon-tape-sealed 100 mL glass bottles and resealed after each opening.

The standard mixtures used in these experiments were as follows:

TABLE 1

STANDARD MIXTURE USED WITH MODEL 36
LIGHTPIPE AND NICOLET 6000 FTIR

Compound	bp(°C)	Quantity (μL)
m-xylene	138	20
nonane	150	30
cumene	152	15
p-ethyl toluene	162	30
decane	174	15
indan	176	1
trans-decalin	185	30
undecane	195	10
1,2,3,4-tetra-methylbenzene	205	1
dodecane	216	15
tridecane	232	10

(Component mixture diluted to 3.0 ml with n-octane)

TABLE 2

STANDARD MIXTURE USED WITH 40cm
LIGHTPIPE AND NICOLET 7199 FTIR

Component	bp(°C)	Quantity (µL)
methylcyclopentane	72	10
2,4-dimethylpentane	81	10
2,3-dimethylpentane	90	7.5
iso-octane	99	10
2,5-dimethylhexane	108	5
2-methylheptane	116	7
1,2-dimethylcyclohexane		
cis-	130	10
trans-	123	
p-xylene	138	1.5
m-xylene	139	5
o-xylene	144	10
nonane	150	10
m-ethyltoluene	159	5
p-ethyltoluene	162	2
o-ethyltoluene	164	5
tert-butylcyclohexane	171	5
indan	176	7
trans-decalin	185	5
cis-decalin	193	2
tetralin	207	4
isopropylcyclohexane	155	3

(Component mixture diluted to 10.0 mL with n-hexane)

TABLE 3

STANDARD MIXTURE USED WITH
ACCUSPEC GC AND VARIAN MAT MASS SPECTROMETER

Component	Quantity (μL)
hexane	10
methylcyclopentane	5
2,4-dimethylpentane	10
2,3-dimethylpentane	7
heptane	10
2,5-dimethylhexane	5
2-methylheptane	7
1,2-dimethylcyclohexane (cis and trans)	10
m-xylene	5
o-xylene	10
isopropylcyclohexane	3
m-ethyltoluene	5
p-ethyltoluene	2
o-ethyltoluene	5
tert-butylcyclohexane	5
indan	7
trans-decalin	5
cis-decalin	2
tetralin	4

(Component mixture diluted to 10.0 mL with tridecane)

RESULTS AND DISCUSSION

Column Selection and Interface Considerations:

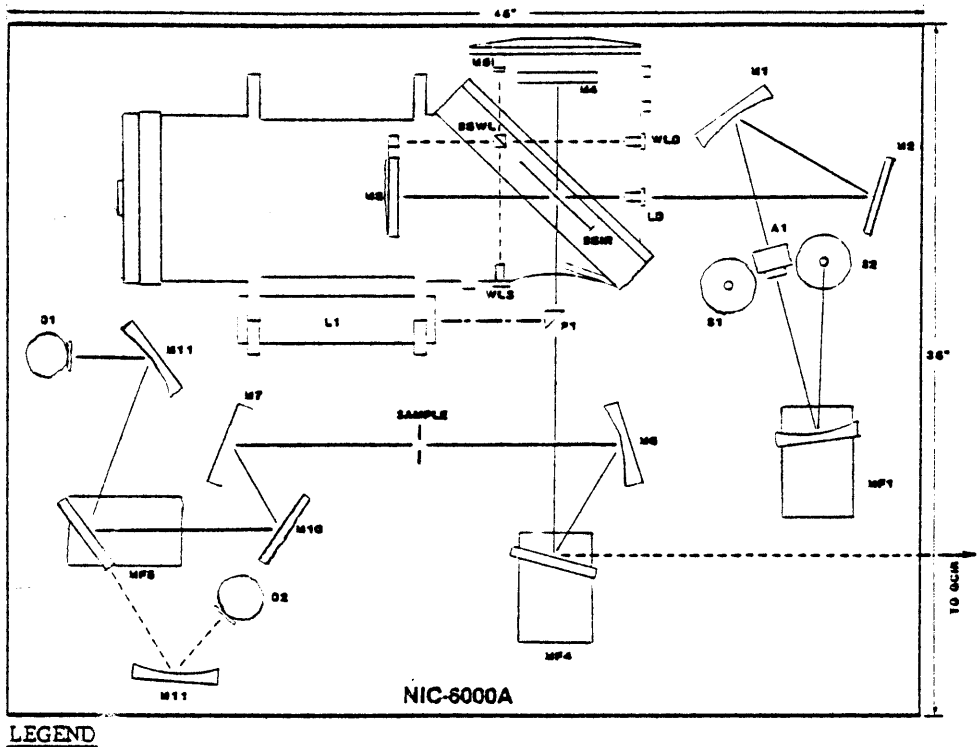
Historically, many kinds of gas chromatography columns have been used with FTIR. Packed column use is relatively straightforward since peaks are generally broad (relative to capillary columns). Sample loading and IR detection are generally not a problem. Several other columns have been tested for their separating power with reference to jet fuel samples.

Preliminary experiments used a twelve foot stainless steel Apiezon L packed column (2 mm i.d.) with an Accuspec polished stainless steel lightpipe (Model 36) of dimension 3 mm i.d. x 6 cm. An Accuspec Compact GC fitted with heated injectors designed for packed columns was used. The GC cell was placed in the sample compartment of the Nicolet 6000 bench which normally holds a 1 mm (or less) pathlength liquid chromatography cell (Figure 1). Using the adjusting screws of the IR cell, the Model 36 was optimized for the 3 mm infrared beam. To properly align the cell, the IR signal is monitored by observing an oscilloscope signal from the center burst of the interferogram as the instrument scans. The effects of the longer pathlength cell (relative to an LC cell) were soon realized as defocusing of the IR beam resulted in decreased throughput of infrared signal. It was also determined that for complex jet fuel samples, packed column efficiency was not adequate for the separation desired.

An OV-101 wide bore glass capillary column (25 meters) was then

OPTICAL LAYOUTS

NIC-6000A Single Beam FT-IR Spectrometer



LEGEND

S1, S2	Alternate source positions
MF1	Computer controlled source selection mirror, spherical 4.5" E.F.L.
A1	Computer controlled aperture
M1	Collimating off-axis parabolic mirror, 8.2" E.F.L.
M2	Flat mirror
M3	Moving mirror assembly
M4	Fixed mirror (I.R. beam and reference laser)
M5	Fixed mirror (white light)
BSWL	White light beamsplitter
BSIR	Infrared/reference laser beamsplitter
LD	Centerline reference laser detector
WLD	White light detector
WLS	White light source
L1	Reference laser
P1	Centerline laser prism
MF4	2-position, computer controlled flat mirror
M6	Sample focusing mirror, off-axis parabola, 9.3" E.F.L.
M7	Sample collection mirror, off-axis parabola, 9.3" E.F.L.
M10	Flat mirror
MF5	2-position, computer controlled, detector selection mirror, flat
M11	Detector focusing mirror, off axis parabola, 3.5" E.F.L.
D1, D2	Alternate detector positions

FIGURE 1. Nicolet 6000 Optical Layout

made available by the Accuspec Corp. along with a compact GC fitted with split-splitless capillary injector and a heated lightpipe of dimensions 2 mm i.d. x 6 cm (to cut down on dead volume). Operating in the splitless mode, injections of less than 0.2 µl of jet fuel were made. Separations were markedly improved relative to the packed column.

Optimization of the IR signal, however, now became more critical as less sample passed through the cell. Also, the smaller diameter of the lightpipe decreased the signal throughput considerably. As standard operating procedure, the cell was adjusted to an optimum position, the MCT-B detector then moved until maximum signal was achieved, and finally the interferometer mirrors were aligned for maximum final signal. Most of the time this alignment was done with the cell at room temperature to simplify the procedure. A jet fuel, VN77-11 JP-4, was selected and separated with the path of the effluent being column - IR cell - microvolume TCD. The column-IR-TCD route was chosen to minimize any band broadening which might occur due to the TCD dead volume.

The instrumental parameters and temperature program are given on the real-time CHEMIGRAM for the jet fuel separation carried-out on the 25 meter OV-101 glass capillary (Figure 2). Given the required amount of sample injected for IR detection, this separation was not considered adequate and a slight column overloading was observed. Since the objective of the separation was to isolate low concentration components, we considered the glass column to have too low a sample

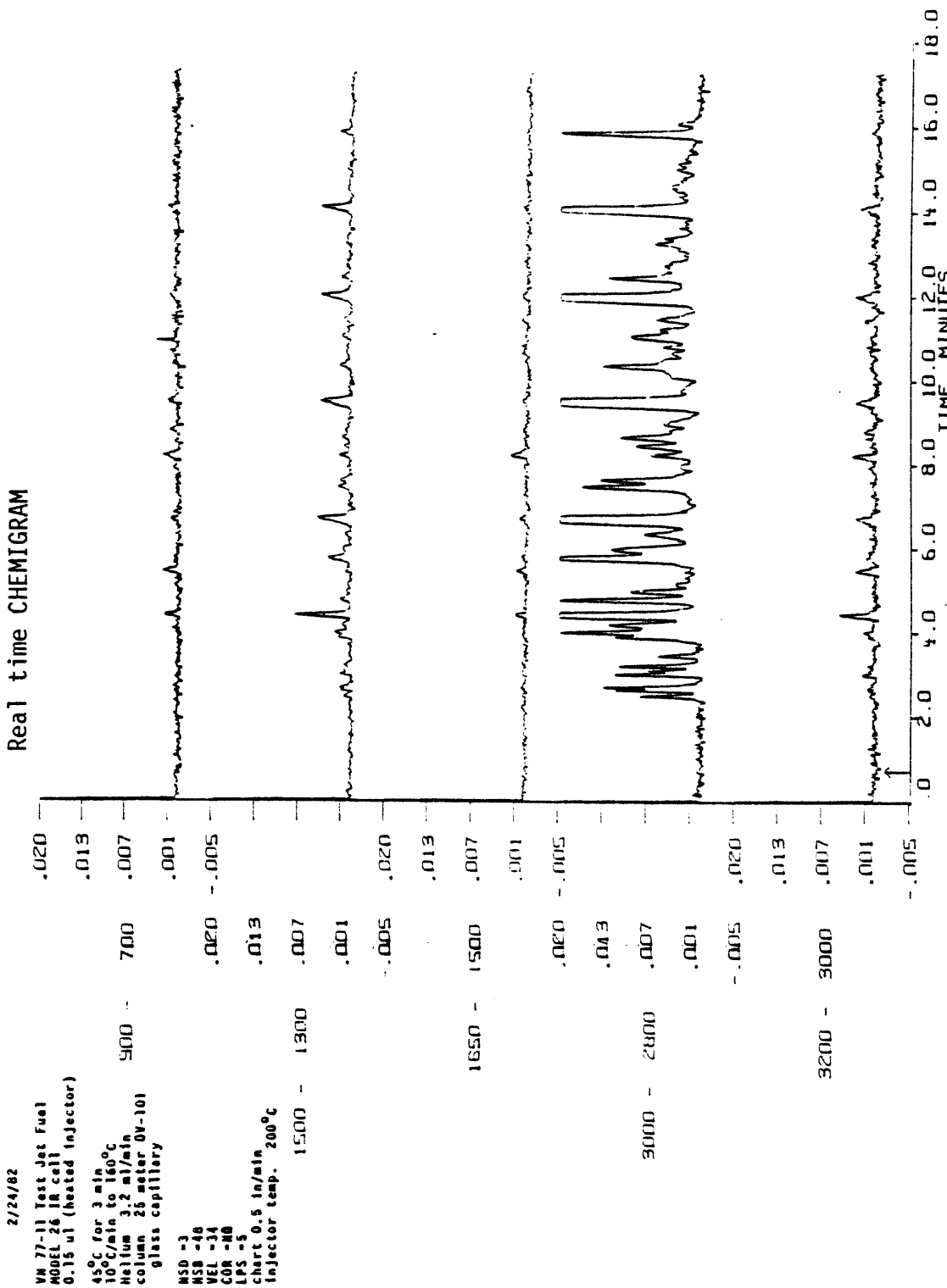

Real time CHEMIGRAM
2/24/82
VH 77-11 Test Jet Fuel
MODEL 26 IR cell
0.15 ul (heated injector)
45°C for 3 min
10°C/min to 160°C
Helium 3.2 ml/min
column 25 meter OV-101
glass capillary
NSD -3
NSB -48
VEL -34
COR -88
LPS -5
chart 0.5 in/min
injector temp. 200°C
1500 - 1300
900 - 700
1650 - 1500
3000 - 2800
3200 - 3000
.020
.013
.007
.001
-.005
TIME, MINUTES
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0

FIGURE 2

capacity and only fair chromatographic efficiency. Handling of the rigid glass column was also considered unnecessarily awkward, and the column connections were somewhat difficult. In addition, overlapping (coeluting) peaks meant that identification by spectral matching using the EPA vapor phase library could become tedious.

Upon reviewing the literature and chromatography supply catalogs, WCOT (Wall Coated Open Tubular) fused silica capillary columns seemed to provide the best separating efficiency. Fused silica was chosen over narrower bore glass because of the flexibility and durability of fused silica. Longer lengths of column would also be easier to handle. With fused silica, the column could be inserted through the heated transfer line up to or very near the IR cell thus minimizing dead volume (critical in capillary chromatography). Although fused silica is durable, sharp right angle bends are not feasible without threat of breakage. Construction, therefore, of a curved, heated, 15 inch transfer line (exiting through the top of the GC) was needed to reach the Model 26 cell.

After experimenting with a 25 m x 0.32 mm i.d. CP-SIL-5 (methylsiloxane) bonded phase fused silica capillary column, it was decided to go to a longer (60 meter) column for a maximum separation. The 60 m x 0.35 mm i.d. DB-5 column proved to be adequate for separating selected jet fuels. A column any longer than 60 meters might have caused handling problems in the GC oven, and the cost of such an extremely long column would have been prohibitive. The DB-5

column from J & W Scientific is capable of generating over 175,000 theoretical plates. With its 1.0 micron film thickness, column sample capacity was about 500 ng per component (recommended). The methyl-phenyl-vinylsiloxane character of the DB-5 column also offered possible functional group interaction leading to further discriminatory separation. An additional advantage of the bonded phase was that relatively large amounts of solvent(s) could be injected without damage to the stationary phase. Upper temperature limits of 325 to 350°C made the bonded phase with fused silica a prime choice.

One important consequence of switching to fused silica over glass columns was that a make-up gas (helium) had to be used to retain chromatographic separation as the effluent passes through the relatively large dead volume of the lightpipe. For the Model 26 this dead volume was about 190 µl. The wide bore glass column used previously was run with a helium flow rate of about 3.2 ml/min and no make-up gas. Because narrower fused silica columns are rarely used with flow rates above 2 ml/min and because the eluting peaks may be very close together, a total flow of 5 ml/min including make-up helium was used through the lightpipe. The make-up gas was supplied by a tee at the exit of the column from the oven. The gas was passed through the same transfer line as the column effluent, thus forcing the eluting components through the cell. A heated return line from the lightpipe brought the effluent back to the microvolume thermal conductivity detector in the GC.

Finally, an adequate injection technique was required for the capillary column. The idea of "on-column" injection, whether cold or heated, was considered to be the most reliable and reproducible method. Sample discrimination (i.e. relating to inconsistent vaporization of high boiling components) could be eliminated by switching from standard vaporizing injection methods to on-column. S. Trestianu and Carlo Erba Instruments have presented valuable information on this injection technique[20]. For jet fuel samples, instant vaporization may become a major problem in higher boiling fractions. Since no commercial on-column injector would fit the Accuspec GC, one was designed based on the use of the Carlo Erba (0.23 mm o.d.) syringe needle (See Figure 3). This homemade injector design required an extra-long syringe needle (11.5 cm), but the assembly has been successfully used with wide bore (>0.3 mm i.d.) as well as narrow bore (0.25 mm i.d.) fused silica columns. Injection is made at a point inside the oven while retaining an unimpaired helium carrier gas flow rate. Because a mass-flow sensitive microvolume TCD was used, any changes in flow would be immediately apparent. In summary, on-column injection was chosen in order that a more quantitative and higher sample loading could be employed.

Samples:

As a preliminary screening, 10 jet fuels were separated with the fused silica column to determine their complexity and boiling point ranges. The microvolume (~20 µL) TCD was directly connected to

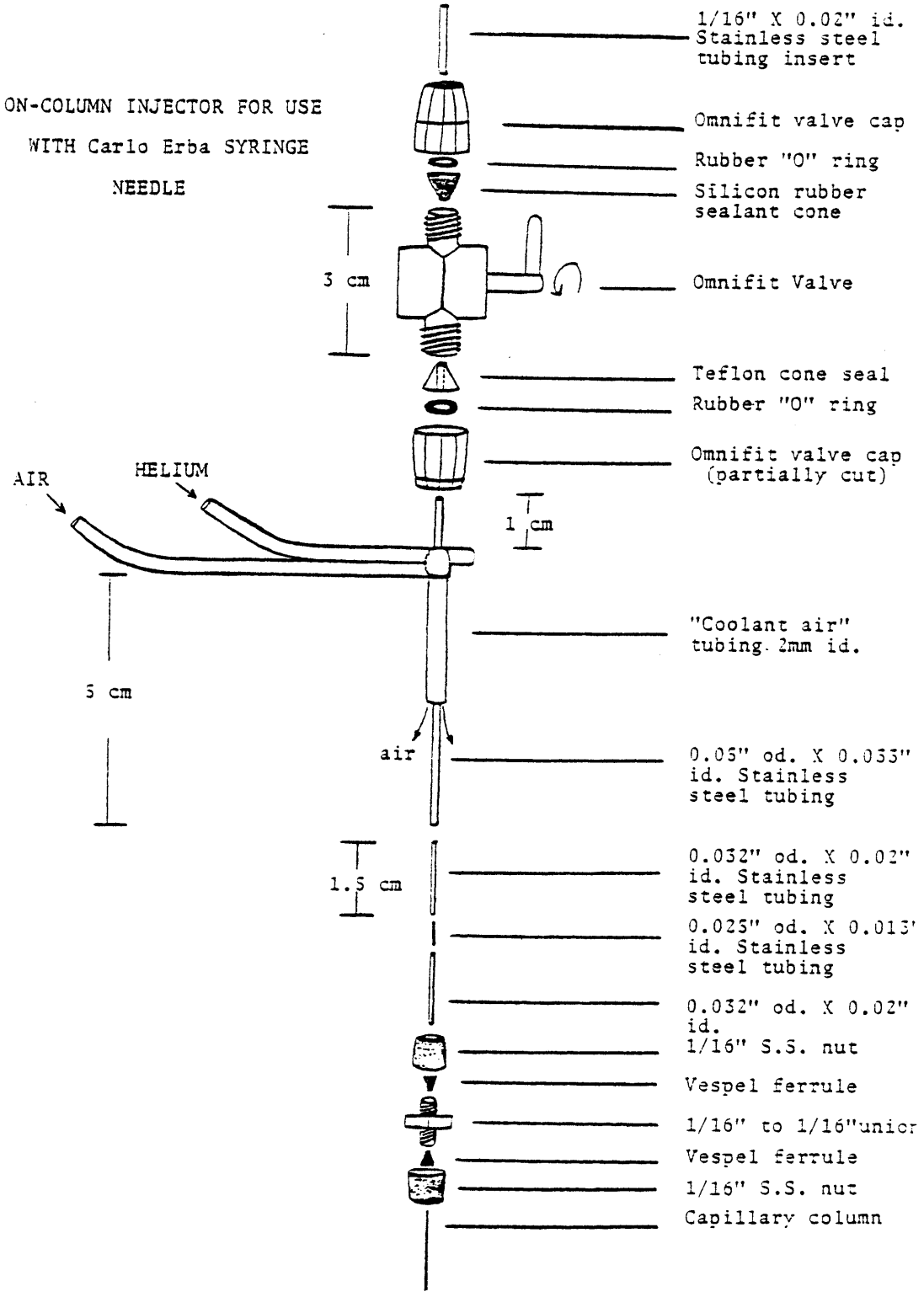

ON-COLUMN INJECTOR FOR USE
WITH Carlo Erba SYRINGE
NEEDLE
1/16" X 0.02" id. Stainless steel tubing insert
Omnifit valve cap
Rubber "O" ring
Silicon rubber sealant cone
3 cm
Omnifit Valve
Teflon cone seal
Rubber "O" ring
Omnifit valve cap (partially cut)
AIR
HELIUM
1 cm
"Coolant air" tubing. 2mm id.
5 cm
air
0.05" od. X 0.033" id. Stainless steel tubing
1.5 cm
0.032" od. X 0.02" id. Stainless steel tubing
0.025" od. X 0.013" id. Stainless steel tubing
0.032" od. X 0.02" id.
1/16" S.S. nut
Vespel ferrule
1/16" to 1/16"unior
Vespel ferrule
1/16" S.S. nut
Capillary column

FIGURE 3

the column outlet to monitor these "ideal, no dead volume" separations. Figure 4 illustrates such a separation on the 60 meter DB-5 fused silica column. More information on these fuels was made available by Dorn et al.[8] who previously employed ^{1}H and ^{13}C LC-NMR to characterize these jet fuels. The alkane, monoaromatic, polyaromatic and (possible) alkene content reported by Dorn was considered in selecting a few samples for GC-FTIR analysis. Three of the ten fuel samples were chosen for GC-FTIR analysis. One test jet fuel (VN-77-11 JP-4 from shale oil) contained mostly alkanes, a second (VN-80-39 Aromatic Blend) contained mostly monoaromatics, and a third (VN-80-40 Aromatic Blending Stock) was 68% polyaromatic in character.

The fused silica capillary column provided the necessary efficiency for separating these samples. The on-column injector allowed more sample to be injected onto the column (as compared to the heated injector) with minimal overloading characteristics. Also, dilutions could be made of the sample to lower sample loading thereby increasing chromatographic resolution. A phenomena called the "solvent effect" could invariably be utilized in which peaks are sharpened due to the slow-moving plug of low boiling solvent[22,23].

Instrument and Associated Parameters:

Having delineated the mode of chromatography, injection technique and pertinent samples, attention is now turned to the FTIR instrument and associated parameters. In capillary GC-FTIR, aside from chromatography, the two major considerations to be faced are those of optical

100
90
80
70
60
50
40
30
20
10
0
60°C

throughput and detector sensitivity. Throughput relates to the intensity of the infrared beam which is allowed to pass through the heated lightpipe to the MCT detector. Sensitivity relates to the detector response for a given amount of sample vapor. Lightpipe length and diameter affect throughput and sensitivity since a long, narrow lightpipe will allow less IR radiation through, but because of the longer pathlength sensitivity may be increased. For long, narrow lightpipes a reflective (but inert) surface is required for maximum throughput. Azarraga has described the requirements and method for attaining higher reflective lightpipes using a gold coating[17].

For our Nicolet 6000 setup, the Accuspec IR cells were considered short enough that the abscence of gold coating would not result in an appreciable loss in throughput. For work using the 60 meter fused silica capillary, the 2 mm i.d. x 6 cm Model 26 lightpipe was chosen initially to reduce dead volume (190 µl instead of 400 µl for the Model 36).

As stated previously, the procedure for achieving the best throughput was to 1) align the cell, 2) modify the position of the MCT detector and 3) tune (align) the interferometer mirrors. However, before such alignments can be pursued certain FTIR instrument parameters must be established. These parameters are collected in a specified PARAMETER FILE which is stored in the computer (See Table 4).

TABLE 4

GC-FTIR

INSTRUMENT PARAMETERS

PRF

AFN	=	HG
APT	=	FL
BDL	=	10
COR	=	MD
DFN	=	20
FIT	=	YS
FSZ	=	2816
GAN	=	1
HPS	=	1
LPS	=	6
MIR	=	SB
NDP	=	2048
NPD	=	200
NPT	=	1024
NSB	=	40
NSD	=	10
NSS	=	10
NSK	=	0
NTP	=	4096
PTS	=	3
SGH	=	8
SGL	=	1
SMO	=	NO
SSP	=	2
VEL	=	50

.

One of these important parameters, mirror velocity, (VEL) was set to 50. At VEL=50, a rapid-scan mode is employed where rapid acquisition of interferograms occurs. For fused silica capillary GC, rapid data collection is essential because of narrow peak widths and closely spaced peaks. Using VEL=50 (or higher), however, creates a source of noise due to instrumental vibration. Although the FTIR bench has a very heavy base plate and vibration damping feet, vibration patterns can cause problems in data collection. COR (correlation) is the parameter used to circumvent excessively noisy conditions. By a more or less trial and error method, the COR is set to different values until enough "bad data collects" are thrown out to achieve a smooth flowing scan rate. Values of COR include NO (no correlation; all scans collected) up to a correlation factor of 32 (HI). Care must be taken when setting COR, as excessively noisy conditions can affect the overall data collect time frame which may simulate a slower scan rate altogether. Under such conditions pertinent information on unresolved peaks may be lost. As a consequence of the rapid scan mode only 2048 data points are normally collected per scan, corresponding to an 8 cm^{-1} resolution spectra. Therefore, a file size (FSZ) of 2816 is needed to contain those points.

To achieve the best possible signal to noise ratio, a maximum number of scans must be coadded and ratioed to a series of coadded background scans. Experimentally, ten scans coadded (NSD) into a data file would take about 1 second when ratioed to 40 coadded background scans (NSB). The real time CHEMIGRAM is the limiting factor when

wanting to collect and ratio data because of computer data-acquisition and storage limitations. The absolute maximum number of background scans capable of being ratioed to one-half that value of sample scans is 54 (e.g. 27 sample scans). Since NSD must be a factor of 2, 4, 8, etc. less than NSB (by design), then this maximum would not be useful for rapid data file collect situations (i.e. 27/2 does not exist for the CHEMIGRAM program since it is not a whole number). Ideally, in the rapid scan mode, several data files can be collected per second. However, the S/N would suffer due to a minimum of scans being coadded.

Data collection can be manipulated, therefore, according to what the complexity of the sample happens to be. As always, peak width will affect the scan rate in that more than one file shall define a component peak. For less complex samples, either a slower scan rate can be used or more scans can be coadded for better S/N. Both procedures will save on storage space on the computer disk. Also, instead of saving every file, a threshold value (absorbance) can be entered in the computer where only those files which contain absorbing compounds will be stored (barring excessive random noise).

Finally, the aperture (APT) of the infrared beam can be stepped-down depending on how much throughput is needed. Typically, a full aperture is used for maximum signal throughput. One other fine-tune parameter is the use of low pass and high pass 4-pole Butterworth noise filters. Since optimal LPS and HPS filter settings are a function of mirror VEL, the manufacturer's values are normally used (Table 4). A

consequence of using such filters is usually less signal throughput, however. After the velocity, aperture and associated parameters have been set, the signal throughput can be fully optimized with an oscilloscope as described previously at the beginning of Column Selection and Interface Considerations.

Using the Model 26 lightpipe, MCT-B detector and a nitrogen gas purge for the IR bench, no more than 6 volts throughput was possible for an IR cell temperature of 270°C. As a point of reference, 25 volts throughput is possible when no lightpipe is in the path of the infrared beam. The 270°C lightpipe temperature was chosen since it is the highest recommended temperature possible for the cell (before the teflon seals begin to soften) and because gas chromatographic comparisons were desired when using higher boiling mixtures.

GC/FTIR Results:

Preliminary screening of the jet fuels using the 60 meter DB-5 column and Accuspec GC with microvolume TCD, directly, indicated that Aromatic Blending Stock VN-80-39 was a relatively simple fuel. Also, due to its previously suggested overall monoaromatic character[18], this sample was considered to be an interesting fuel to examine. Five infrared windows were chosen in obtaining the real time CHEMIGRAM. Regions 3200-3030, 1650-1500 and 950-650 cm^{-1} give characteristic aromatic absorbances while regions 3000-2800 and 1500-1300 cm^{-1} give information regarding aliphatic C-H stretching and bending vibrations (See Figure 5). Instrument parameters are given on the CHEMIGRAM, and the information from each selected IR window region confirms

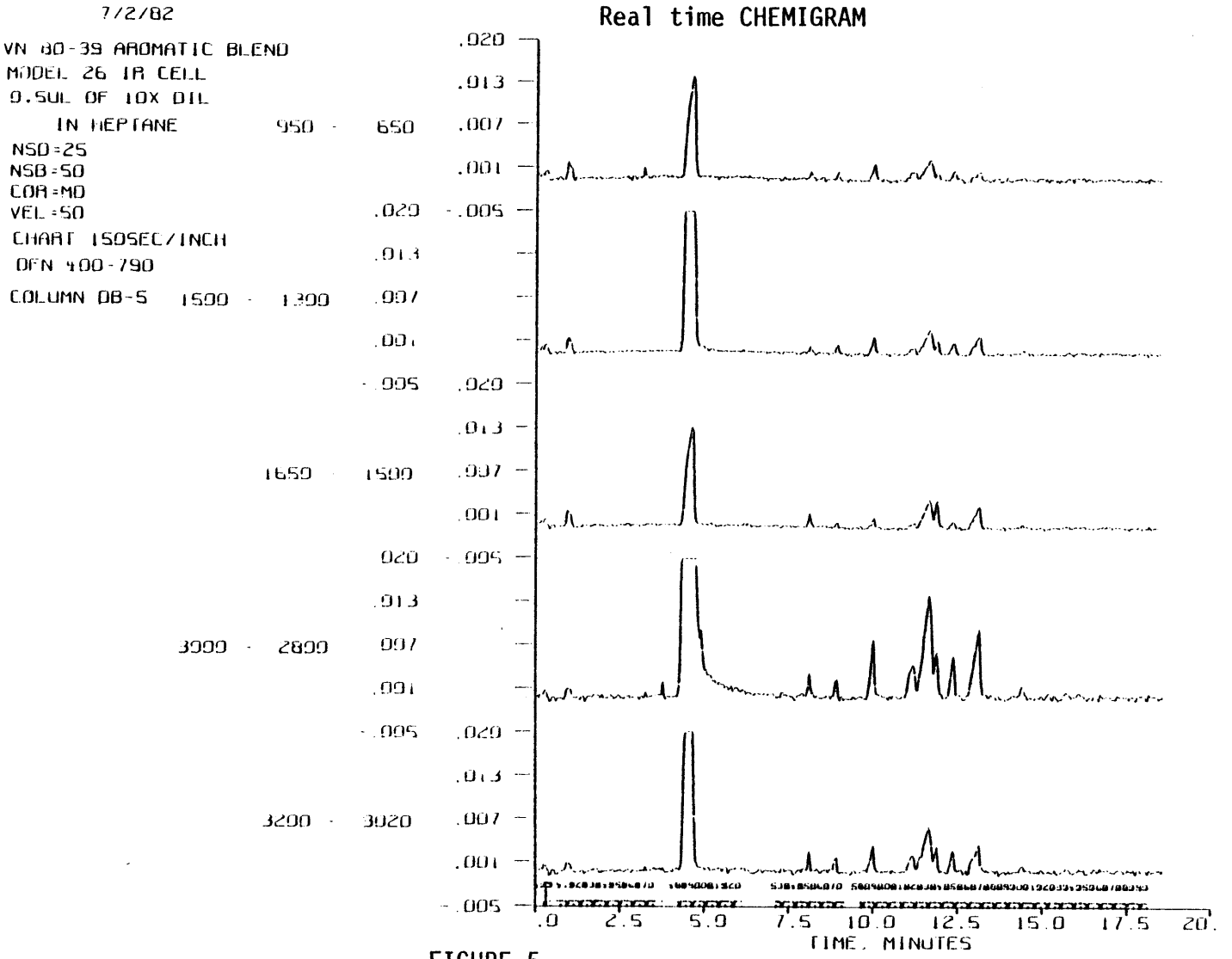

7/2/82
VN 80-39 AROMATIC BLEND
MODEL 26 IR CELL
0.5UL OF 10X DIL
IN HEPTANE
950 - 650
NSD=25
NSB=50
COR=MD
VEL=50
CHART 150SEC/INCH
DFN 400-790
COLUMN DB-5
1500 - 1390
1650 - 1500
3000 - 2800
3200 - 3020
Real time CHEMIGRAM
.020
.013
.007
.001
-.005
TIME, MINUTES
.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.

FIGURE 5

immediately the expected aromatic character. All window regions show a very strong absorbance for the heptane solvent because of the relatively large amount present. The TCD trace of this same separation indicates similar chromatography and relative peak intensities (Figure 6). The first three peaks in the TCD trace are assigned to air, freon (syringe cleaning fluid) and a hexane impurity, respectively.

Before Fourier transforming the jet fuel data to absorbance spectra, a chromatographic reconstruction based on this infrared information can be generated. Infrared window regions can be specified, whereby the resulting reconstruction is functional group specific, or the entire region 4000-400 cm^{-1} may be chosen, most often done using the Gram-Schmidt orthogonalization[21] (See Figures 7-8).

An extensive mathematical explanation pertaining to the generation of reconstructed chromatograms has been given by Hohne, et al.[24]. Briefly, the Gram-Schmidt reconstruction is a collection of orthogonal distances from a set of basis files (taken while no absorbing compounds are present) to each successive scan in the GC run. Compounds absorbing light (infrared) in the lightpipe change the shape of the interferogram. The change in shape increases the distance from the interferogram segment to the basis set. A plot of these distances appears as a set of peaks in the reconstruction. Whereas the Gram-Schmidt reconstruction uses infrared information from 4000-400 cm^{-1}, specified IR window region reconstructs may give more useful information. Although the specified reconstructed chromatogram gives a reconstruct based on chemical class, this classification is not 100%

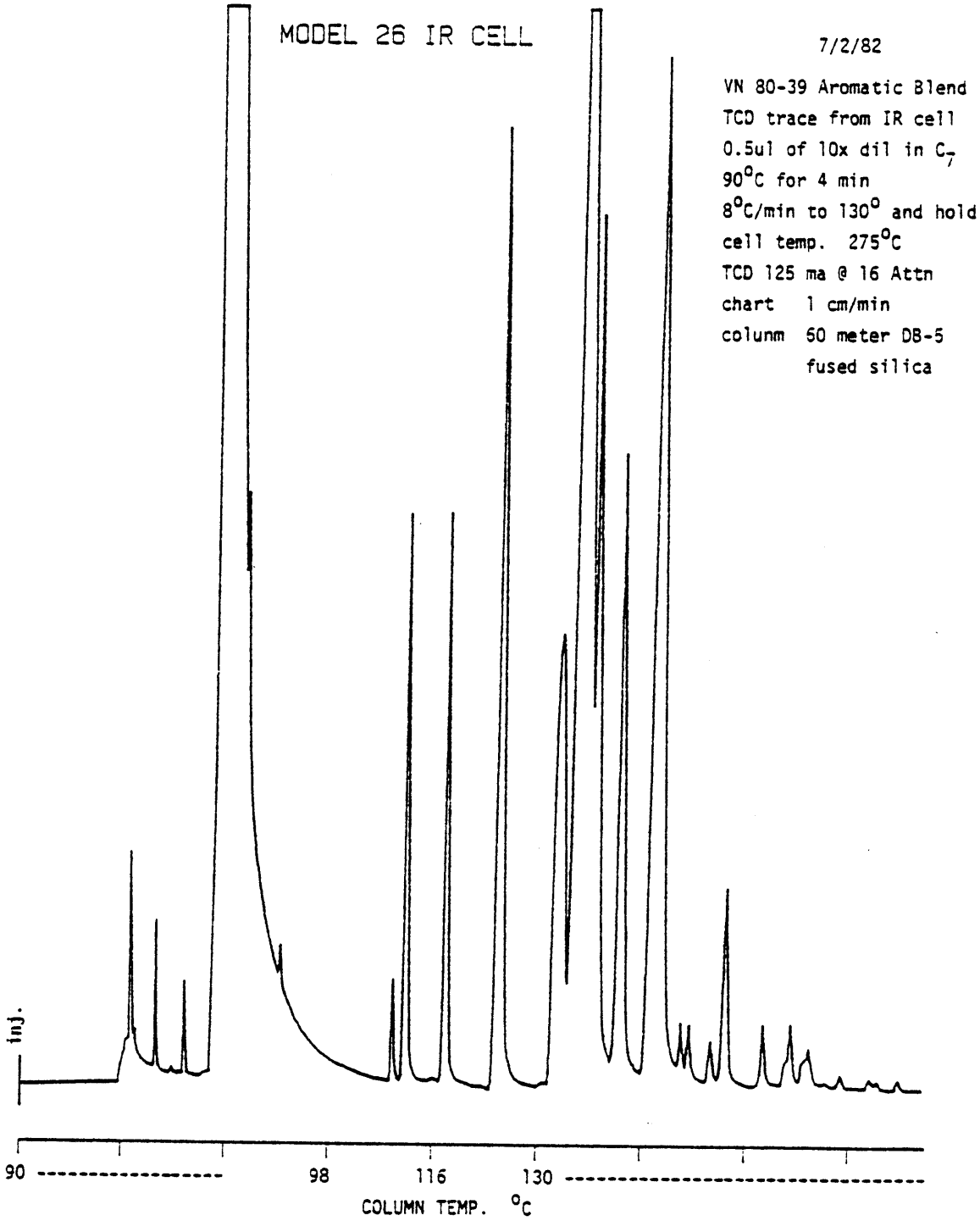

MODEL 26 IR CELL
7/2/82
VN 80-39 Aromatic Blend
TCD trace from IR cell
0.5ul of 10x dil in C7
90°C for 4 min
8°C/min to 130° and hold
cell temp. 275°C
TCD 125 ma @ 16 Attn
chart 1 cm/min
column 60 meter DB-5
fused silica
inj.
90
98
116
130
COLUMN TEMP. °C

FIGURE 6

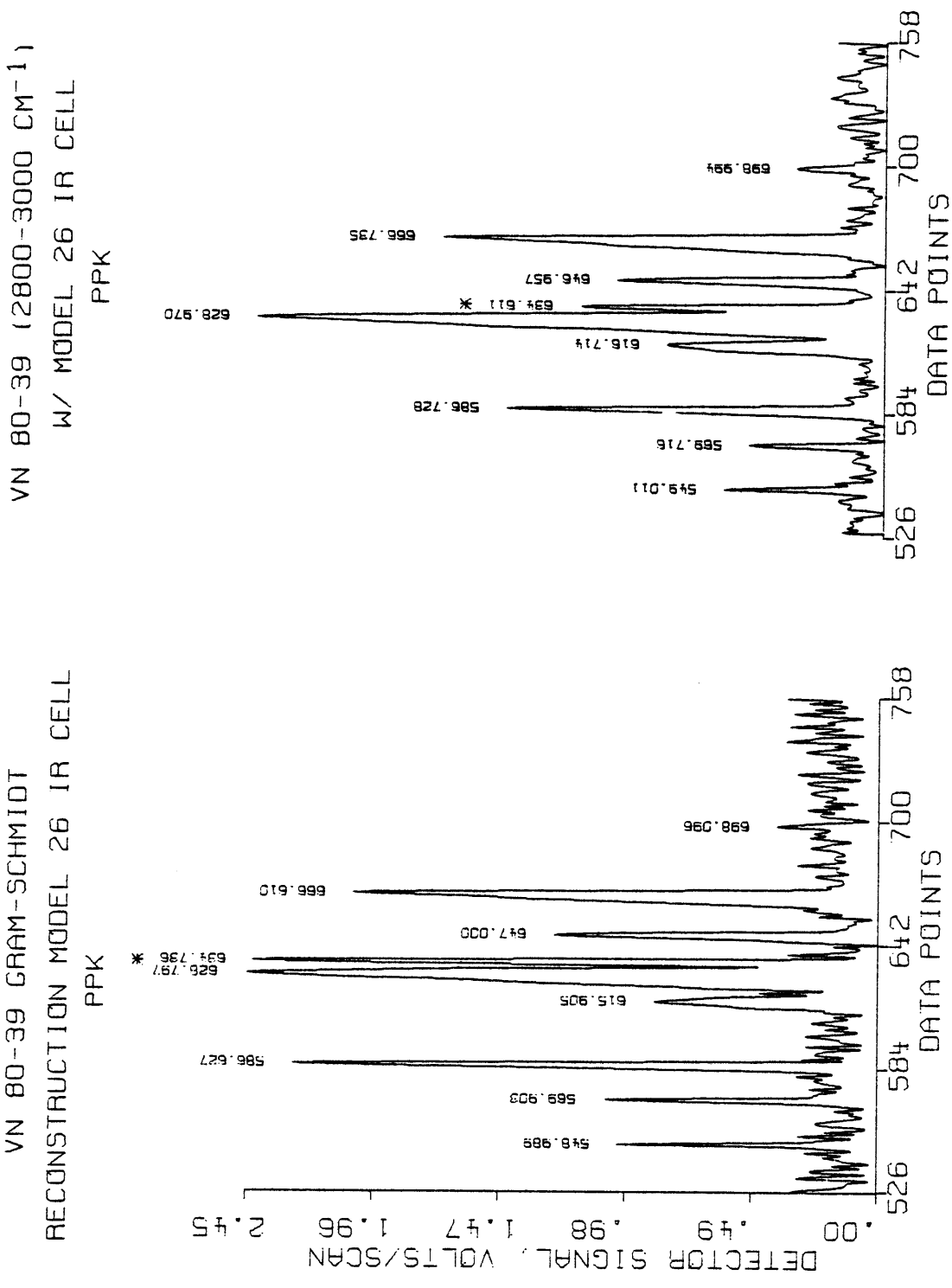

VN 80-39 GRAM-SCHMIDT
RECONSTRUCTION MODEL 26 IR CELL
PPK
VN 80-39 (2800-3000 CM-1)
W/ MODEL 26 IR CELL
PPK
DETECTOR SIGNAL, VOLTS/SCAN
.00
.49
.98
1.47
1.96
2.45
526
584
642
700
758
DATA POINTS
548.989
569.903
586.627
615.905
626.797
634.736
647.000
666.610
698.096
549.011
569.716
586.728
616.714
628.970
634.611
646.957
666.735
698.994

FIGURE 7

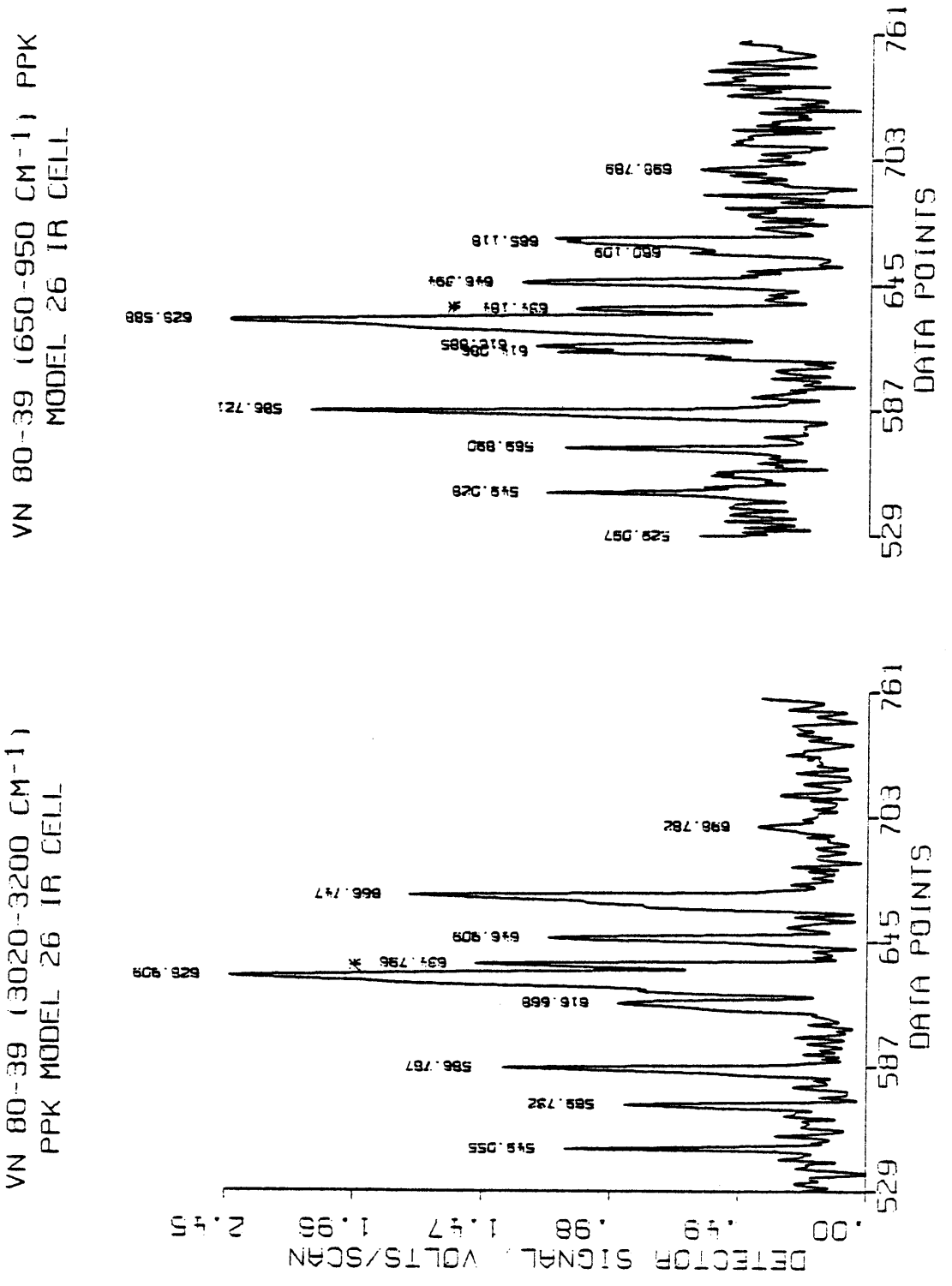

VN 80-39 (3020-3200 CM-1)
PPK MODEL 26 IR CELL
DETECTOR SIGNAL, VOLTS/SCAN
.00
.49
.98
1.47
1.95
2.45
529
587
645
703
761
DATA POINTS
545.055
589.732
586.767
616.668
626.909
634.796
646.909
666.747
698.782
VN 80-39 (650-950 CM-1) PPK
MODEL 26 IR CELL
529.097
549.028
569.880
586.721
626.588
634.184
646.094
660.109
665.118
698.789
529
587
645
703
761
DATA POINTS

FIGURE 8

accurate. The inconsistency present is that no IR frequency exists where all compounds in a particular class absorb and no compounds not belonging to that class do not absorb. For this reason, class-specific reconstructions are only used as an aid in interpretation.

Comparison of the specified reconstructed chromatograms obtained from the interferometric data of VN-80-39 indicate a range of noise levels, particularly in the aromatic window regions 3200-3020 and 950-650 cm^{-1}. The region 3200-3020 cm^{-1} represents aromatic ring C-H stretching bands, and the 950-650 cm^{-1} region contains information concerning out-of-plane C-H bending vibrations. Problems with S/N may be partially explained by reviewing the response curve for the MCT detector over the 4000-400 cm^{-1} region. The overall response of the detector is found to be nonlinear in nature, where maximum throughput and S/N are achieved around 1600 cm^{-1}. A single beam spectrum of the infrared background (Figure 9) can illustrate this nonlinear response where at lower areas in the spectrum S/N is generally decreased. As an example, the loss of sensitivity in the IR for aromatic compounds can be due partially to this response curve. In reviewing the response curve, one can see that the typical aromatic absorption regions (3200-3020 cm^{-1} and 950-650 cm^{-1}) are at relative low points. Even though moderate IR absorption may occur in these regions, overall sensitivity is hindered by a low signal response. In spite of the low response for the region 3000-2800 cm^{-1}, aliphatic C-H stretching vibrations (indicative of alkanes) still give good signal-to-noise since these infrared bands are so stable and intense. Problems with

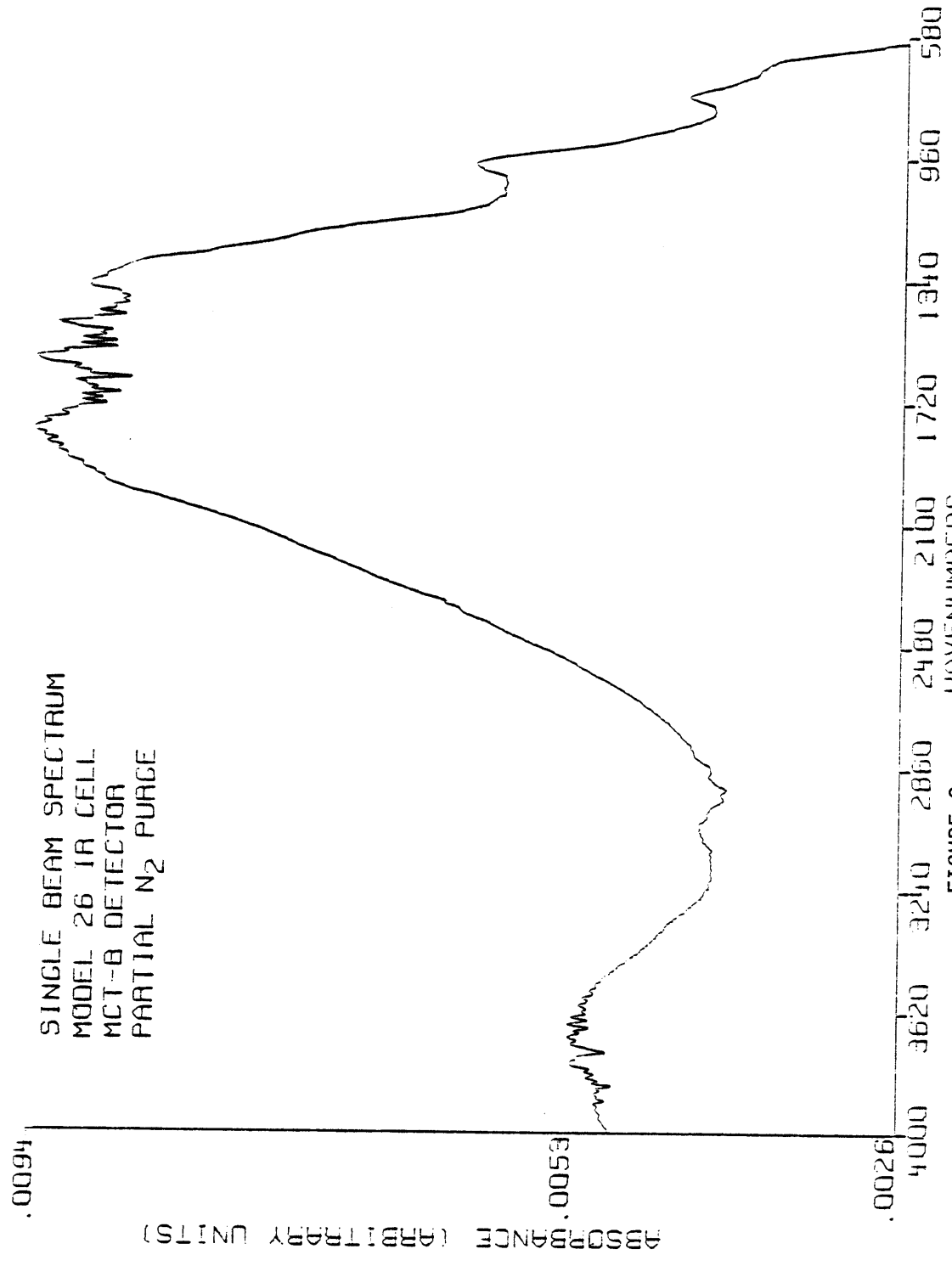

SINGLE BEAM SPECTRUM
MODEL 26 IR CELL
MCT-B DETECTOR
PARTIAL N_2 PURGE
.0094
.0053
.0026
ABSORBANCE (ARBITRARY UNITS)
4000
3620
3240
2860
2480
2100
1720
1340
960
580
WAVENUMBERS

FIGURE 9

signal-to-noise and throughput are therefore dependent on the overall absorbance characteristics of of the species being examined. Of course, loss of throughput and signal-to-noise can also be related back to the short, narrow 2 mm i.d. x 6 cm lightpipe. The narrow bore (relative to the IR beam diameter) will cut down on throughput, and the short length may not provide the optimal cell pathlength necessary for sufficient sensitivity. Also, from looking at Figure 9 one can see that spectral interference from background CO_2 and water at around 1600 and 3600 cm^{-1}, respectively, may occur. Although a constant nitrogen purge (transparent in the IR) of the optical bench is provided, changes in trace CO_2 and water levels remain a problem. Spectral subtractions would appear to alleviate such lingering background absorptions except that these levels may change significantly from the beginning to the end of a long gas chromato-graphic run.

After generating reconstructs of the chromatographic run (including the Gram-Schmidt reconstruct) the data are transformed to absorbance spectra using 4096 transformed points (NTP) ratioed to a transformed background file. Use of 4096 transform points ensures that the data file is zero filled from the end of the interferogram (NDP) to the end of the transform block. The 8 cm^{-1} resolution spectra from such a transform can then be spectrally compared to the EPA (Environmental Protection Agency) vapor phase library for tentative identification.

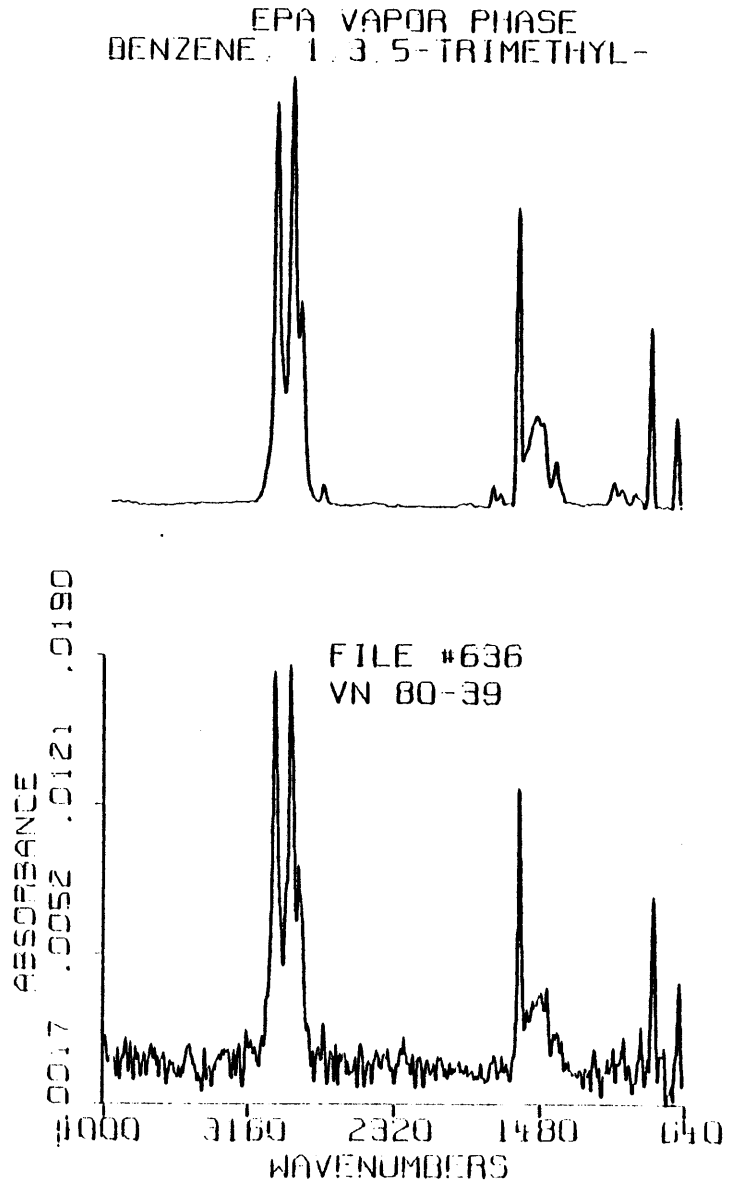
Using the Nicolet computer, selected absorbance file spectra from VN-80-39 (Aromatic Blend) were software matched to EPA library file

spectra. A major peak at file #636 taken during the separation was used to illustrate the search and retrieval system. The location of this chromatographic peak is starred (*) in each of the four reconstructs (Figures 7-8).

A description and understanding of the search and retrieval software is needed to fully appreciate its capabilities. Lowry et al. have fully described the search software and function for the Nicolet FTIR[19]. Briefly, the search routine uses any one of four algorithms and involves actual comparison of the sample spectrum with each member of the EPA search file. The EPA file contains 3300 component spectra of 16 cm^{-1} resolution. Two algorithms, AB and SQ, use absolute difference and least squares approaches, respectively. The least squares metric (SQ) tends to weigh large differences in the spectra more than the absolute value calculation. In other words, one large difference between the sample and a reference spectrum is worse than an equivalent number of small ones. Two other algorithms, AD and SD, utilize the first derivatives of the sample spectrum and EPA file spectrum. The first derivative can use absolute or least squares metrics also. Advantages of the first derivative searches are to minimize the effects of sloping base line and/or excessive noise.

In operation, the search routine normalizes the sample spectrum to one absorbance unit and reduces it to 16 cm^{-1} resolution, although the original spectrum is not destroyed (i.e. 8 cm^{-1}). The search may cover the entire range 4000-400 cm^{-1} or it may be selectively specified by

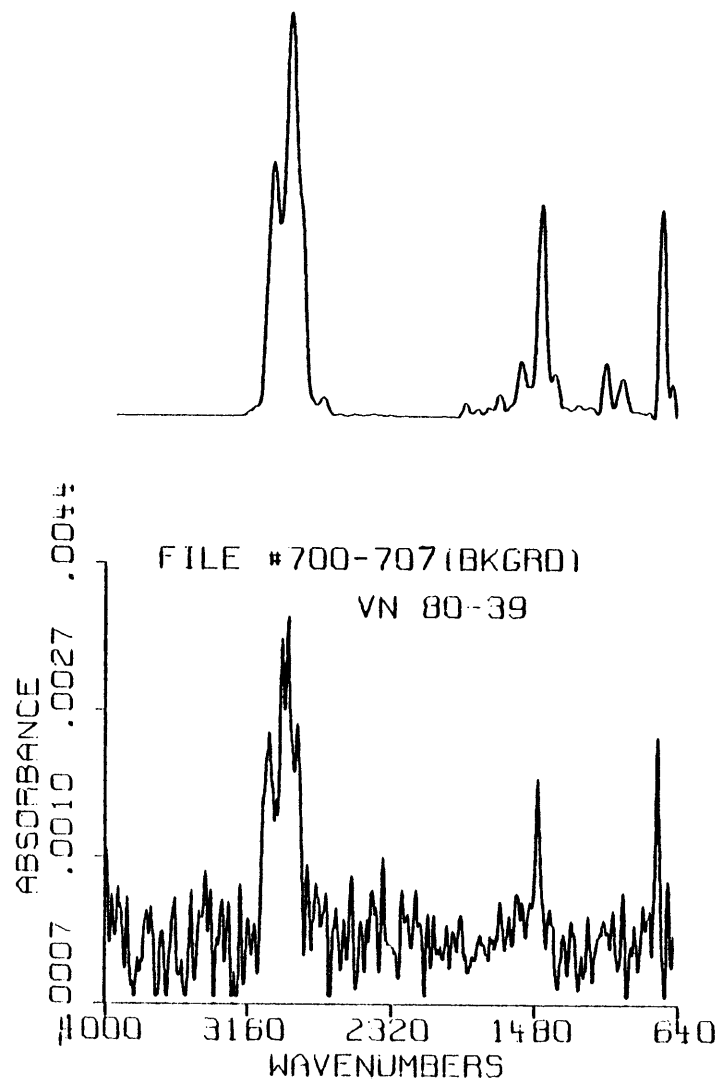
blanking out certain regions of the spectrum where excessive noise or background compounds (such as carbon dioxide and water) may occur. Typically, the region 650-400 cm^{-1} is blanked where little or no information is expected for that region. This region also has the worst S/N ratio of the entire IR spectrum due to low throughput. One should realize, however, that blanking too many regions can lead to inaccurate searches since vital information may not be entered. Usually, when excessive blanking is done, several compounds having a variety of functional groups may be retrieved because of the limited spectral range available. For instance, blanking of the amine absorption region may still give amines as possible matches since other wavenumber regions may be similar. In the search "RESULTS", the possible compound names (HITS) are given with each HIT location number in the EPA vapor phase library. The number below and to the right of the EPA file number indicates the match similarity (Figure 10). A smaller number coincides with a better match where zero (0) is a perfect match. Typical "match values" range from 50 to 3000 depending on the noise level of the sample spectrum. Each match listed beneath the first is the second, third, fourth, etc. "best match". Up to 32 "best matches" can be listed. The general rule adopted is that if the first "match value" is one half of the second "match value" (for the SQ algorithm in particular) then a reasonable amount of certainty can be expected. A spectral search for a minor component, file spectrum #700, from VN-80-39 gives a high match value due to the low S/N (Figure 11).



MODEL 26 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 650
 LOW LIMIT 3500
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1



EPA VAPOR PHASE
   POSSIBLE HITS
   799     BENZENE, 1,3,5-TRIMETHYL-,
     295     1R C E
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
    1763     1R B C E
    75     BENZENE, 1,2,4-TRIMETHYL-,
    2247     1R B D
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
    2650     1R B C D
   222     3,5-LUTIDINE
    2672     T6NJ C E
  1190     BENZENE, HEXAMETHYL-,
    2722     U 6-R
  1107     BENZENE, 1,2,4,5-TETRAMETHYL-,
    2731     1R B D E
   457     2-BUTENE, 2,3-DIMETHYL-,
    2802     1Y&UY
  2476     BENZENE, 1-ETHYL-3-METHYL-,
    2865     2R C
  1600     CUMENE, 3,5-DIMETHYL-,
    3017     1YR C E

EPA ↑ ↑
    Match Value
```

FIGURE 10



MODEL 26 IR CELL

```
SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 670
 LOW LIMIT 3500
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   923     BENZENE, 1,2,3-TRIMETHYL-,
     2533     1R B C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
     3188     2R C
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
     3475     1R B C D
  1190     BENZENE, HEXAMETHYL-,
     3865     U 6-R
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
     3927     1R B C E
  2666     OCTANE, 3,6-DIPHENYL-,
     4137     2YR&2YR&2
    41     2-BUTENE, 2-METHYL-,
     4178     YU2
    75     BENZENE, 1,2,4-TRIMETHYL-,
     4187     1R B D
   902     BENZENE, BUTYL-,
     4324     4R
  2489     TOLUENE, O-ETHYL-,
     4329     2R B
```

FIGURE 11

Even so, most of the other choices listed indicate a substituted benzene compound. An SQ algorithm was used in the search and a spectral subtraction done prior to the search. The background file spectrum #707 is subtracted from file spectrum #700 to eliminate CO_2 and water. The presence of these background compounds do affect the search results. A search of a major component, file spectrum #636, gives a more certain match with the other choices again being very similar, i.e. substituted benzenes (Figure 10). It is evident that different substitution on benzene does give rise to different absorption patterns.

Recalling that the search routine reduces the sample file spectrum from 8 cm^{-1} to 16 cm^{-1}, temporarily, Figures 12 and 13 illustrate the actual 16 cm^{-1} spectra which were being matched. An obvious shortcoming of the present search system is that the same signal-to-noise ratios are not shared by both sample and EPA files. In addition, although normalized to an absorbance of 1.0, the actual spectrometer conditions under which the EPA library was formulated are not known. Most likely, a maximum number of scans was taken and coadded to produce a relatively noise-free spectrum. Also, overtone IR bands indicate that the EPA standards were concentrated to some extent. Both of these procedures can lead to library spectra which may not represent on-the-fly conditions, making spectral matching ambiguous when low S/N and overlapping GC peaks are encountered. Problems arise particularly when searching alkanes because of limited infrared information. One advantage of the present search system, however, is that additional

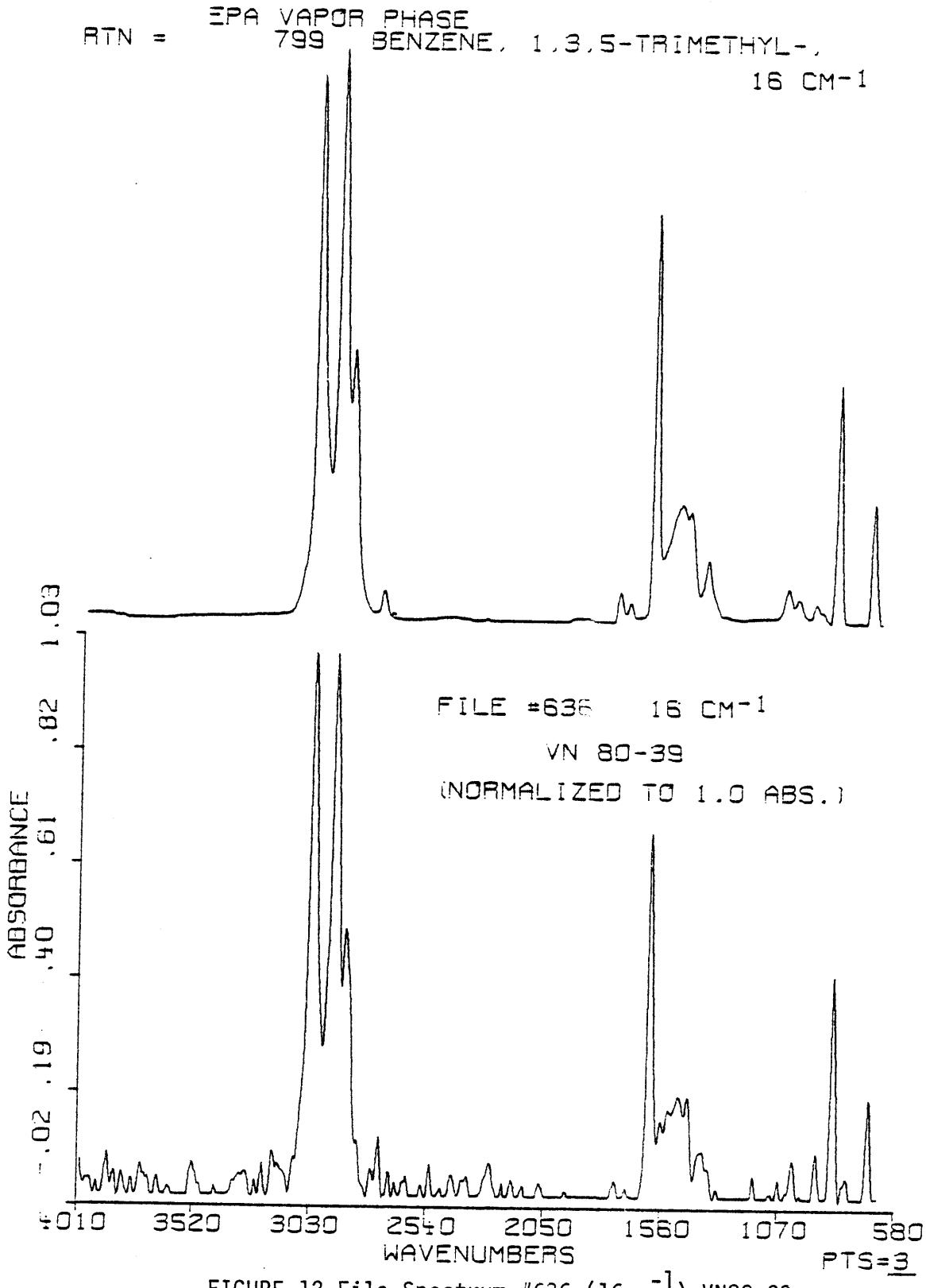


FIGURE 12. File Spectrum #636 ($16cm^{-1}$) VN80-39

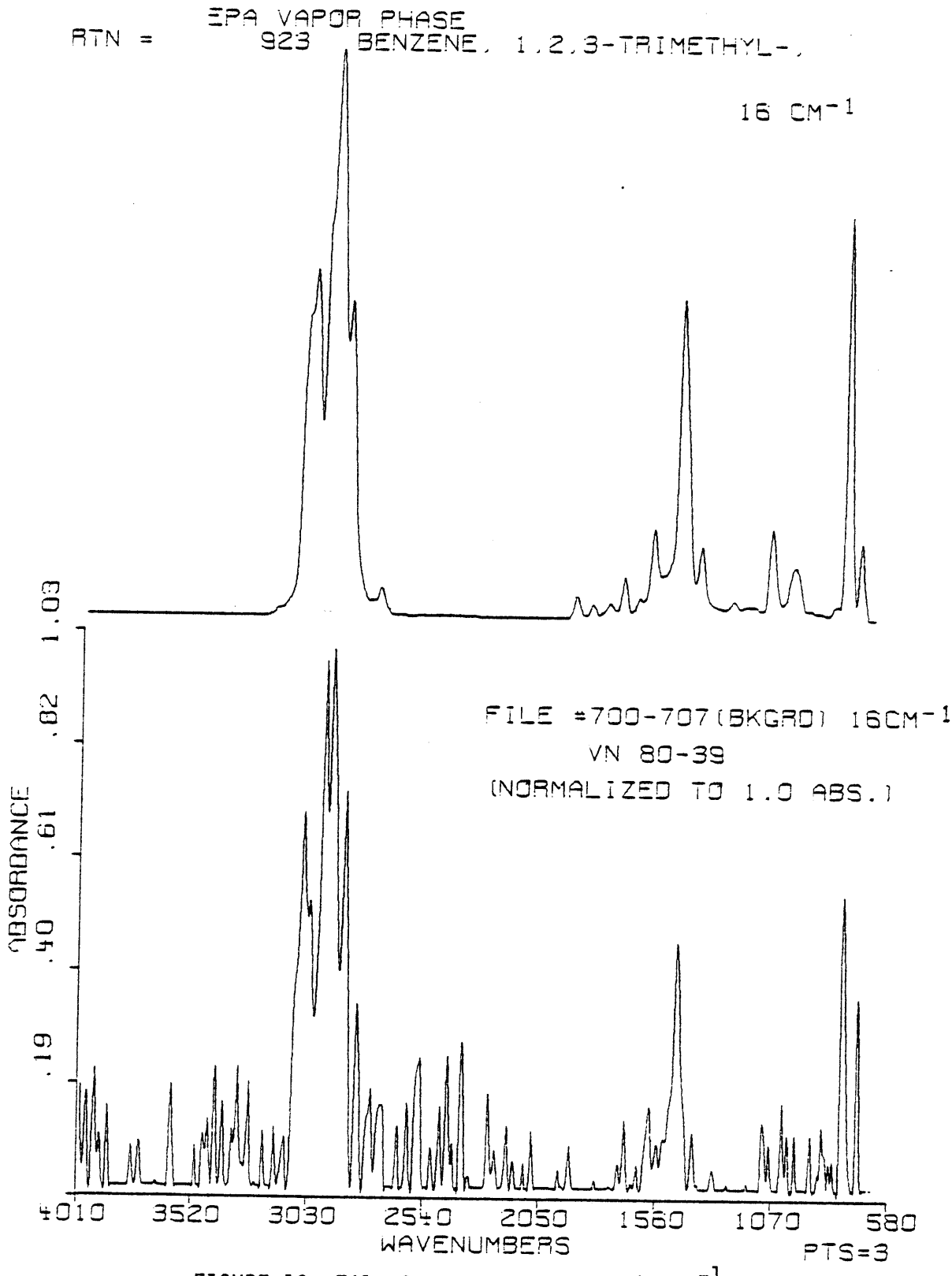


FIGURE 13. File Spectrum #700-707 ($16cm^{-1}$)

spectra may be added to the library (for instance straight chain alkanes) which may more closely mimic on-the-fly conditions. From an examination of the infrared file spectra taken during the separation of VN-80-39 with the Model 26 IR cell, it appears that better infrared detection is needed if truely complex samples composed of a wide concentration range of individual components are to be analyzed. The spectral matching results from the library searches confirm the need for a more optimum system. One idea was to increase the throughput of IR signal by increasing the lightpipe inner diameter from 2 mm to 3 mm (Model 36). A consequence of this change was a doubling of dead volume from 0.2 ml to 0.4 ml. Use of the same make-up gas (He) at 5 ml/min, however, was found to cause not much more band broadening than the Model 26 cell. For example, a thermal conductivity trace (positioned after IR cell) using the 60 meter DB-5 column and Model 36 lightpipe of VN-80-39 indicates little additional band broadening over the Model 26 (Figure 14). Figure 15 illustrates the spectrum and search results for a major peak in the VN-80-39 separation using the wider bore lightpipe with the same sample volume injected. This spectrum corresponds to the same component peak searched using the Model 26 cell, (compare Figure 10 with 15). Slightly lower noise levels are seen with the Model 36 cell although overall S/N is about the same with both cells. A dilution effect is most likely occurring when using the Model 36 due to its relatively large dead volume and swift 5 ml/min make-up helium gas. Although the component absorbance is less with the Model 36 cell, the

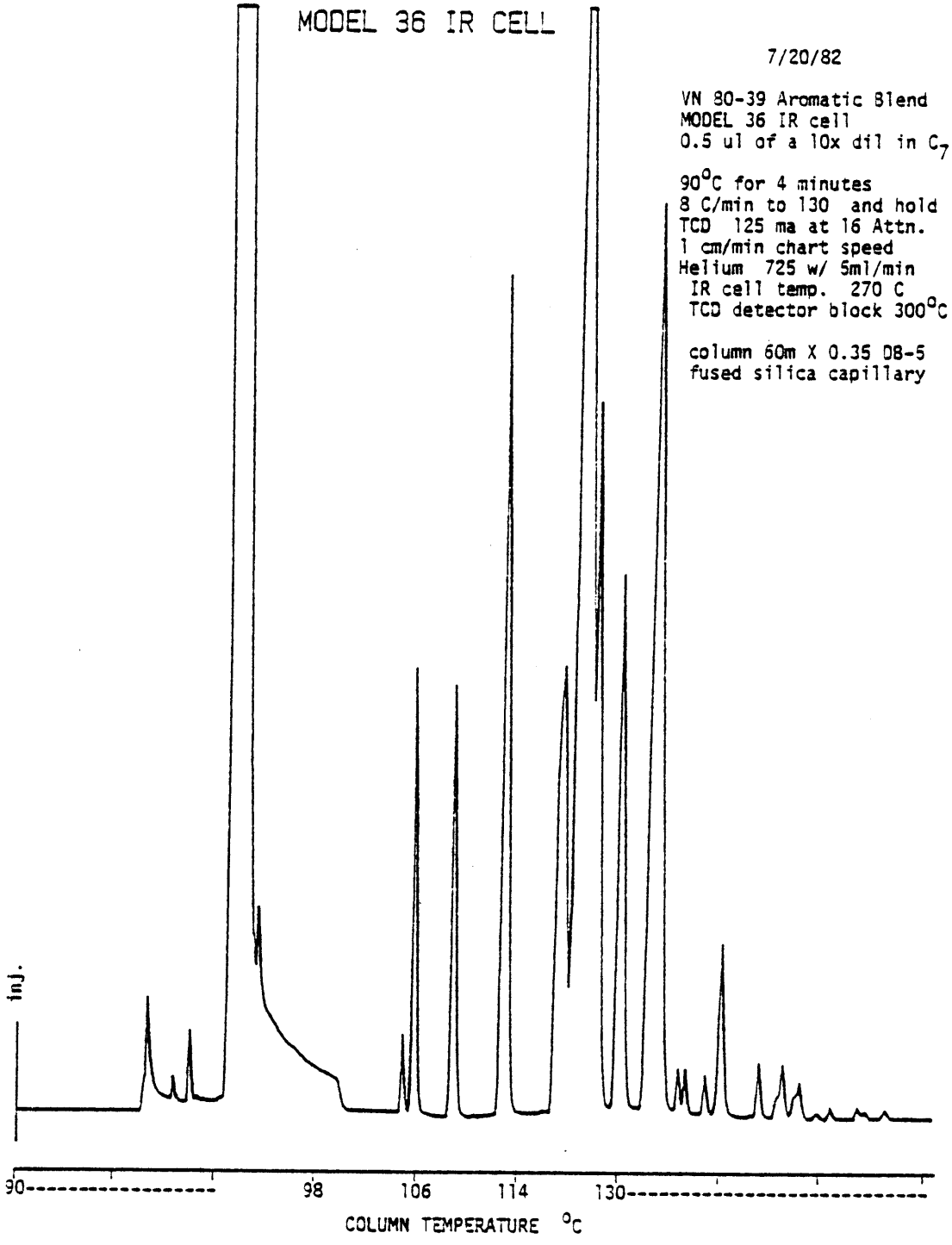
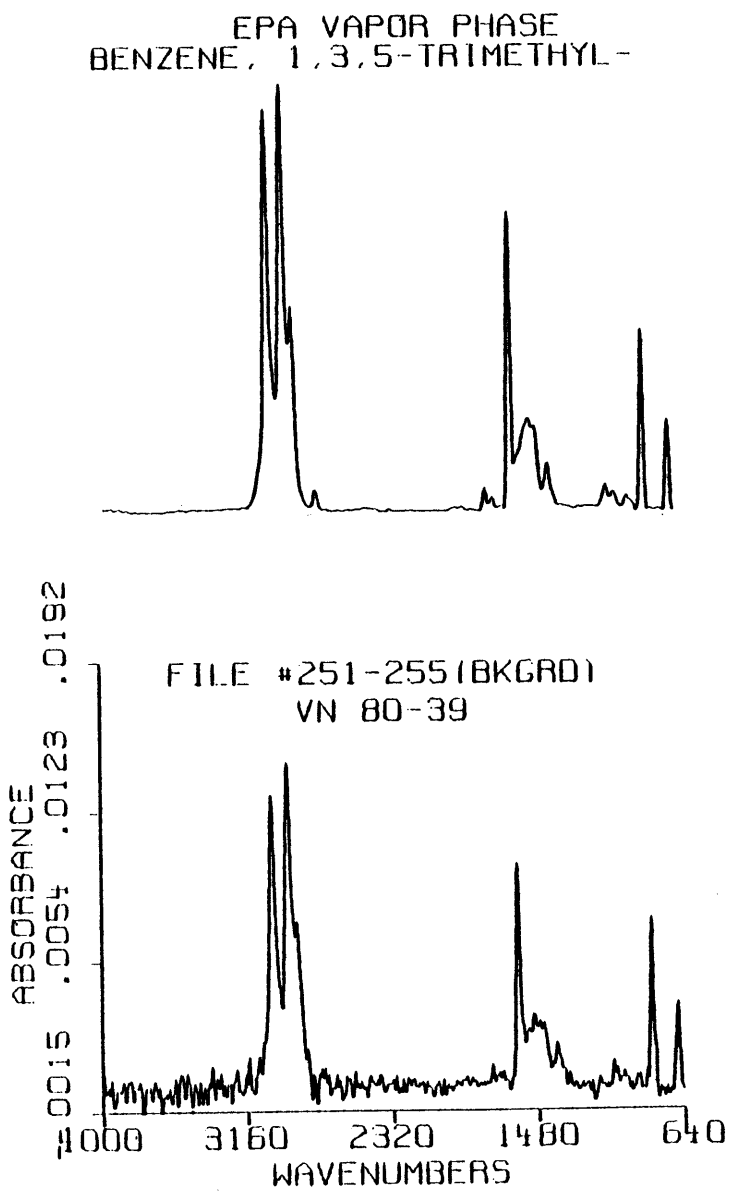


FIGURE 14. TCD trace



MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 650
 LOW LIMIT 3500
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

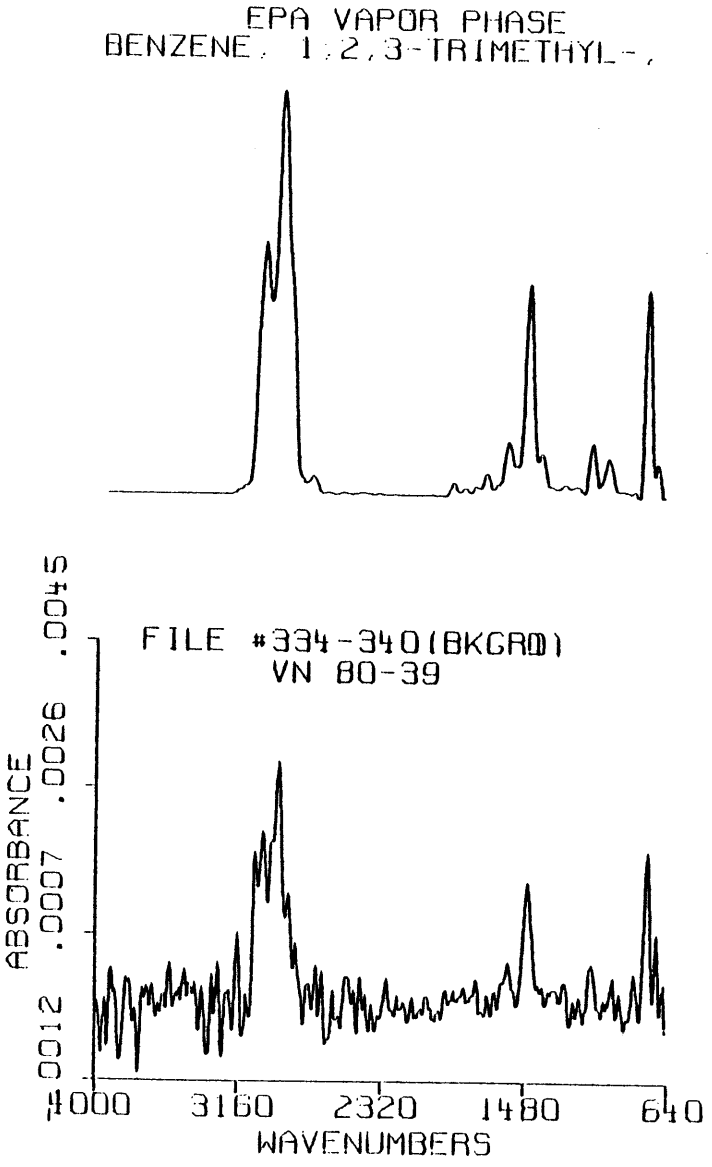
```
EPA VAPOR PHASE
   POSSIBLE HITS
   799     BENZENE, 1,3,5-TRIMETHYL-,
     274     1R C E
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
    1807     1R B C E
    75     BENZENE, 1,2,4-TRIMETHYL-,
     2306     1R B D
   457     2-BUTENE, 2,3-DIMETHYL-,
     2718     1Y&UY
  1190     BENZENE, HEXAMETHYL-,
     2740     U 6-R
   222     3,5-LUTIDINE
     2756     T6NJ C E
  1107     BENZENE, 1,2,4,5-TETRAMETHYL-,
     2763     1R B D E
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
     2820     1R B C D
   103     2,4-HEXADIENE, 2,5-DIMETHYL-,
     2874     1Y&U2UY
    41     2-BUTENE, 2-METHYL-,
     3083     YU2
```

FIGURE 15

reduction in random noise benefits library search efforts. The same type of phenomena is seen for a minor component in the separation at file spectrum #334 using the Model 36 (Figure 16). The corresponding peak spectrum from using the Model 26 lightpipe (Figure 11) is much noisier than its Model 36 counterpart although S/N is roughly equivalent. Therefore, with very low concentration components, overall noise levels will greatly affect the reliability of the library search.

One other advantage of the Model 36 is that manipulation of the IR lightpipe for optimization of the infrared signal is easier than for the Model 26, due to its wider inner bore. In addition, twice the throughput (13 volts at 270°C) was attainable using the wider 3 mm x 6 cm lightpipe (Model 36) over the 2 mm i.d. cell.

To pursue a more complex sample, a test Jet Fuel derived from shale oil (VN-77-11) was separated on the 60 meter DB-5 fused silica column with FTIR detection through the Model 36 IR cell. A Gram-Schmidt reconstruction for VN-77-11 (Figure 17) indicates good separation despite the additional IR cell dead volume. A good signal to noise ratio is achieved with only 0.25 µl of jet fuel sample injected. An EPA library search of one minor component, file spectrum #136, illustrates a good match followed by very similar second and fourth choices (Figure 18). Another search, file spectrum #224, gives excellent S/N and a confident search listing for the larger alkane peak (Figure 19). Good signal to noise for these components of the sample may be explained by the strong absorption character of alkanes (in



MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 650
 LOW LIMIT 3500
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   923     BENZENE, 1,2,3-TRIMETHYL-,
     2145     1R B C
  2476 .   BENZENE, 1-ETHYL-3-METHYL-,
     3508     2R C
    78     M-XYLENE
     3656     1R C
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
     3920     1R B C D
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
     4111     1R B C E
    75     BENZENE, 1,2,4-TRIMETHYL-,
     4401     1R B D
  1190     BENZENE, HEXAMETHYL-,
     4489     U 6-R
  2489     TOLUENE, O-ETHYL-,
     4497     2R B
  1549     PYRIDINE, 2-PENTYL-,
     4552     T&U B5
  2666     OCTANE, 3,6-DIPHENYL-,
     4586     2YR&2YR&2
```

FIGURE 16

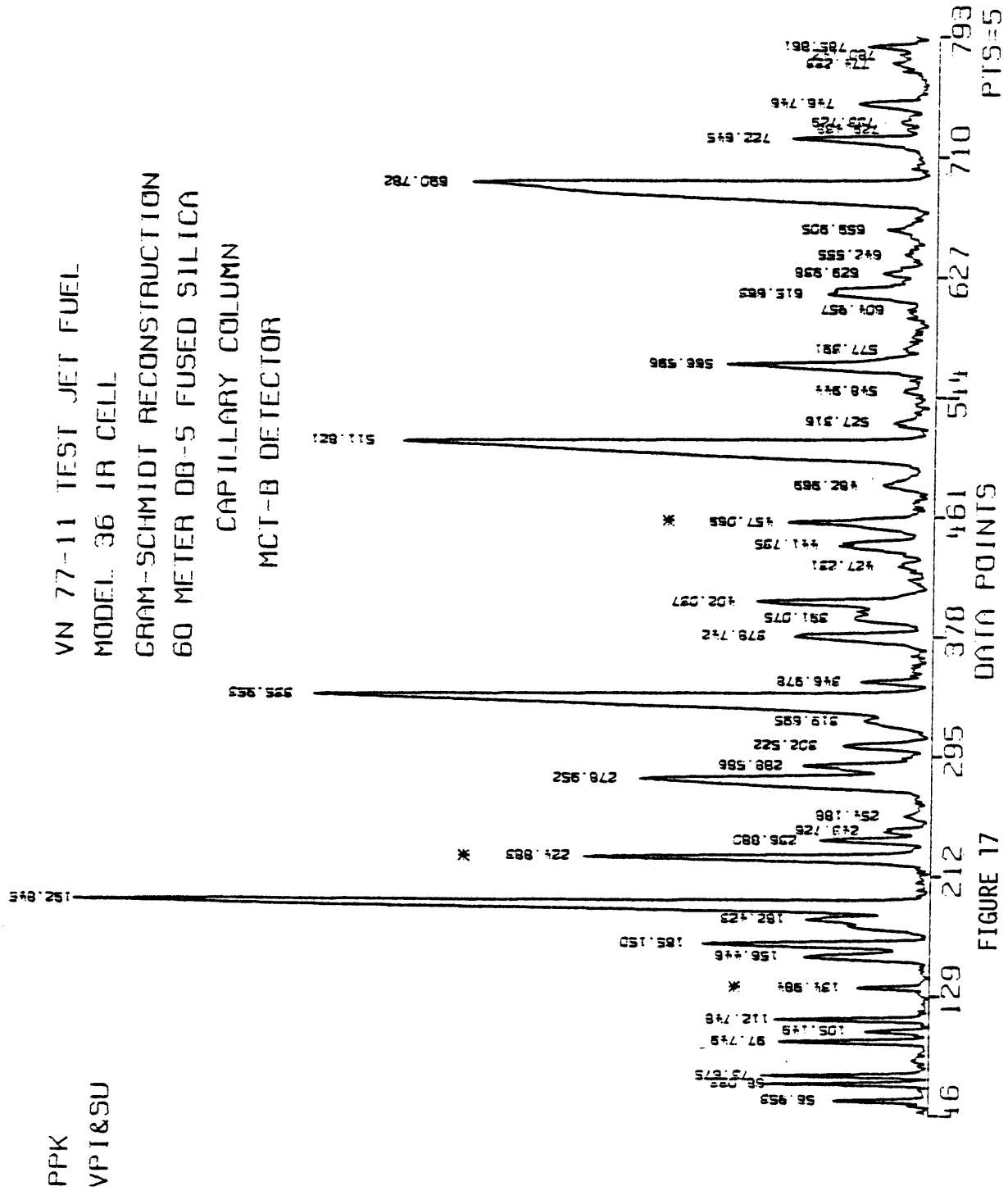
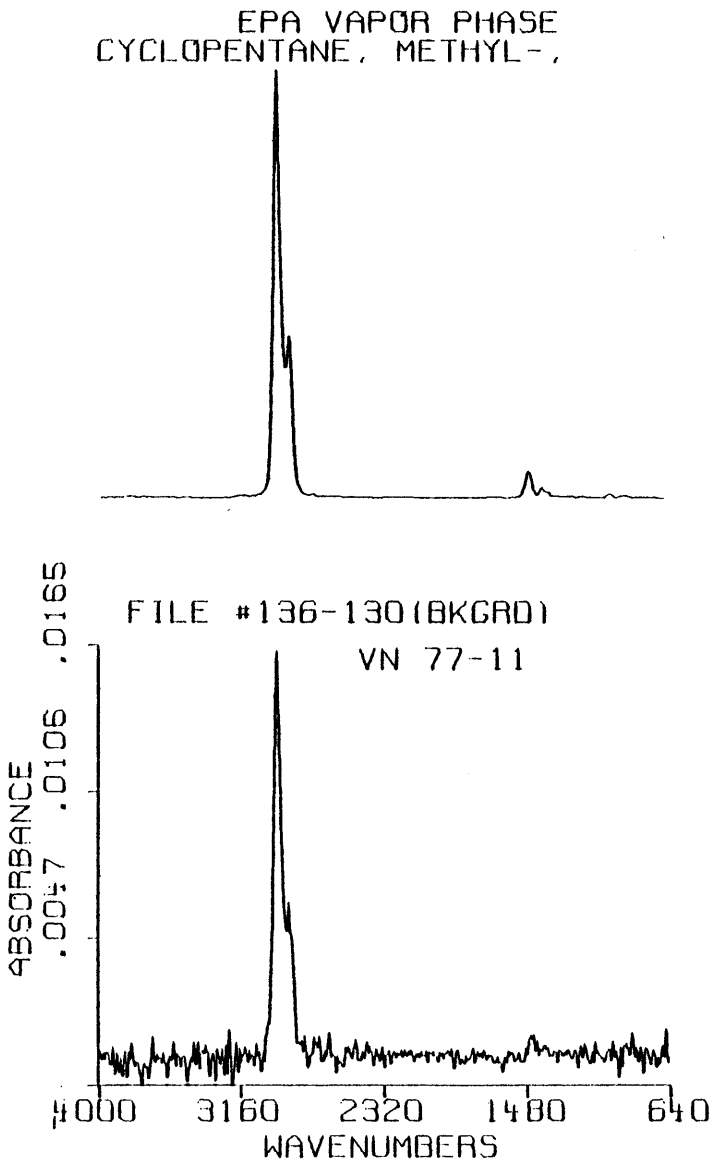

PPK
VPI&SU
VN 77-11 TEST JET FUEL
MODEL 36 IR CELL
GRAM-SCHMIDT RECONSTRUCTION
60 METER DB-5 FUSED SILICA
CAPILLARY COLUMN
MCT-B DETECTOR
46
129
212
295
378
461
544
627
710
793
DATA POINTS
PTS=5

FIGURE 17

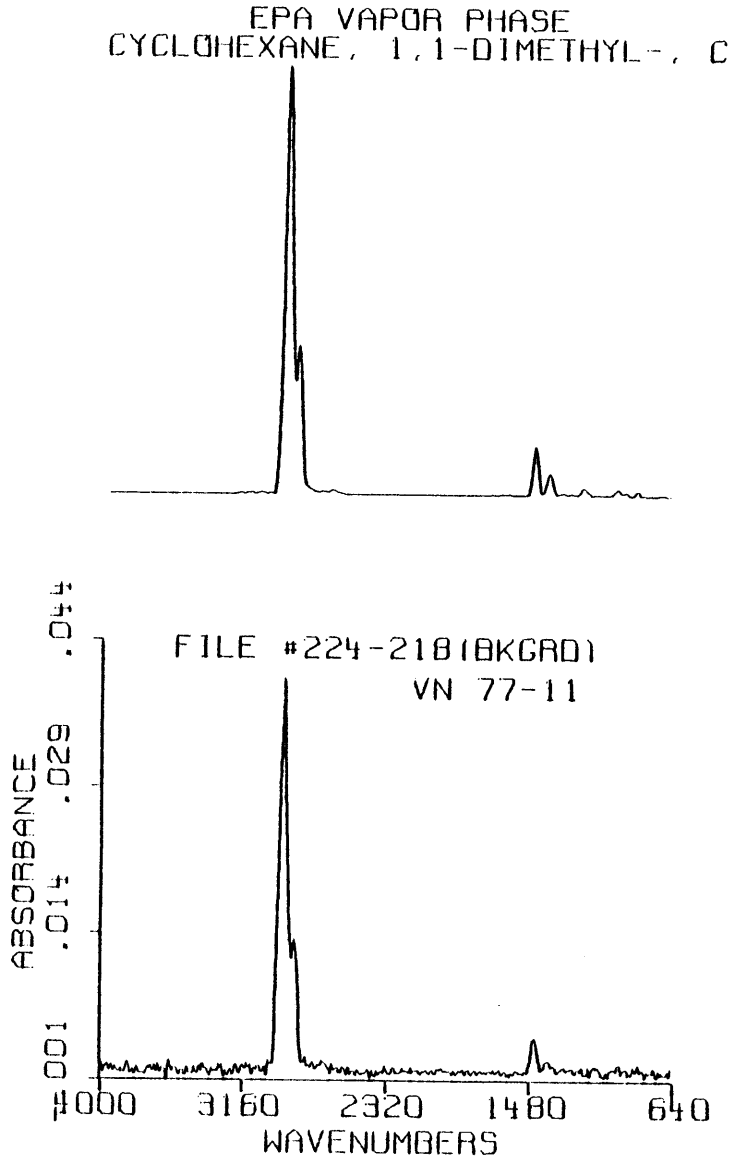


MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 650
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

```
EPA VAPOR PHASE
   POSSIBLE HITS
    45     CYCLOPENTANE, METHYL-,
     101      L5TJ A
  2480     CYCLOPENTANE
     173      L5TJ
  2494     HEPTANE, 2,2-DIMETHYL-,
     183      5X
  2583     CYCLOPENTANE, BUTYL-,
     244      L5TJ A4
   922     HEPTANE, 3,3-DIMETHYL-,
     254      4X2
    47     BUTANE, 2-METHYL-,
     291      2Y
  2930     ISOBUTANE
     292      1Y
  2907     BUTANE
     328      4H
    43     HEXANE, 2,2,5-TRIMETHYL-,
     346      1Y&2X
   802     HEXANE, 2,2,4-TRIMETHYL-,
     367      2Y&1X
```

FIGURE 18



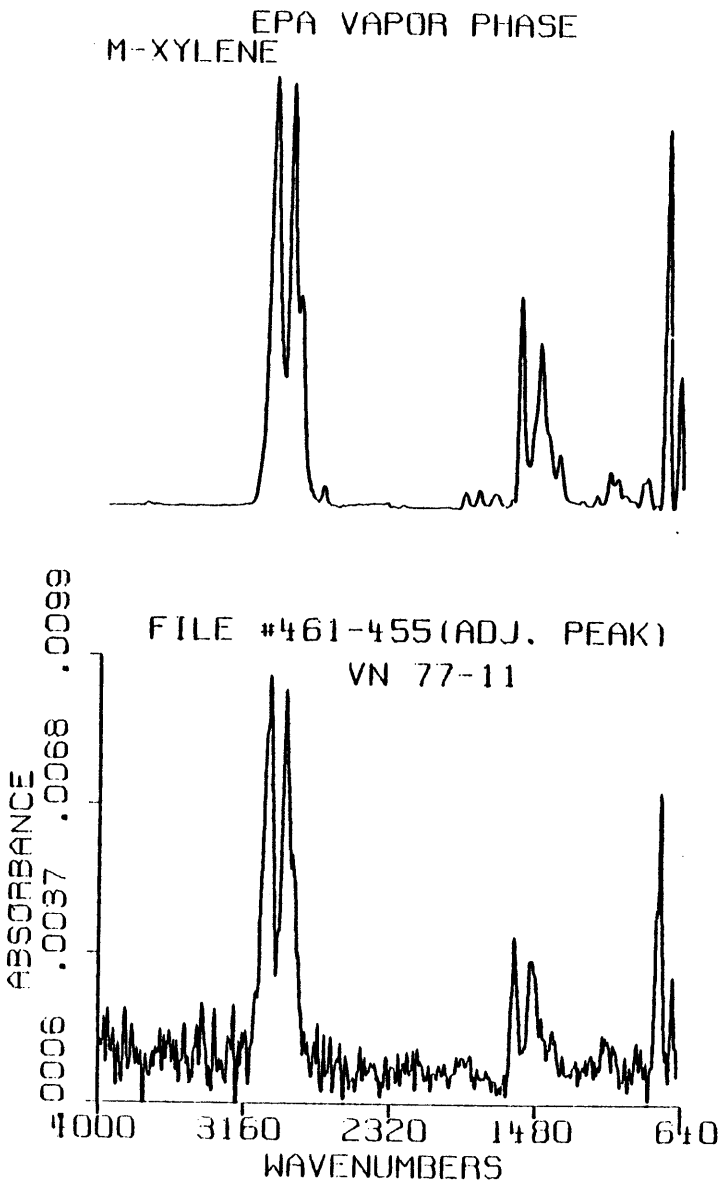
MODEL 36 IR CELL

```
.SRG
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 700
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

```
EPA VAPOR PHASE
   POSSIBLE HITS
  646     CYCLOHEXANE, 1,1-DIMETHYL-, C
      48     L6J A A
 2553     HEPTADECANE, 6,9,12-TRIPROPYL-,
     155     5Y3&2 2Y3
  121     CYCLOHEXANE, CIS-1,3-DIMETHYL-,
     173     L6TJ A C -C
 2206     UNDECANENITRILE
     176     NC10
 2554     HEPTADECANE, 6,12-DIETHYL-9-
     176     5Y2&2 2Y5
 2155     OCTYL DISULFIDE
     178     8S38
  887     NONANE
     179     9H
 2555     HEXADECANE, 6,11-DIPENTYL-,
     179     5Y5&2 2
  895     OCTANE
     181     8H
 1768     CYCLOHEXENE, 1-METHYL-,
     193     L6UTJ A
```

FIGURE 19

particular the C-H stretching vibrations) coupled with better throughput of the Model 36 cell. A third component showing absorbance in all five monitored IR window regions of the CHEMIGRAM (i.e. 3200-3020, 3000-2800, 1650-1500, 1500-1300 and 950-700 cm^{-1}) appears to be the co-elution of an aromatic and an aliphatic material. Subtraction of file spectrum #455 from #461 yields the spectrum shown in Figure 20. A spectral search using the SQ algorithm and select blanking identified the component tentatively as m-xylene. Here-in lies a true advantage of FTIR when coeluting peaks occur. The subtraction technique can subtract the absorbances of one spectrum from another. The actual subtraction can be performed so that 100% of one file spectrum is subtracted out of another. In addition, different percentages of spectrum A can be subtracted from spectrum B. The software allows increments of about 1% to be subtracted either plus or minus. With such a capability, co-eluting peaks (which may be present in different concentrations) can be subtracted in such a manner as to give a final spectrum conducive to library searching. While the subtraction of one component from another may lead to some arbitrary spectrum, this result should always be viewed with caution. Ambiguous and sometimes faulty conclusions can occur. For the subtracted peak in question, however, further evidence to be given later will support the present hypothesis. This test jet fuel was found to be a good example of a predominantly alkane-type mixture which agrees with the 85% alkane content previously determined by Dorn et al. with LC-NMR[18].

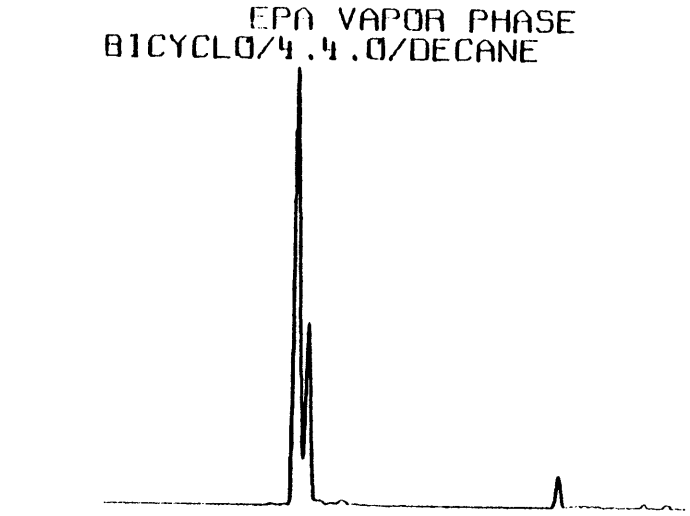


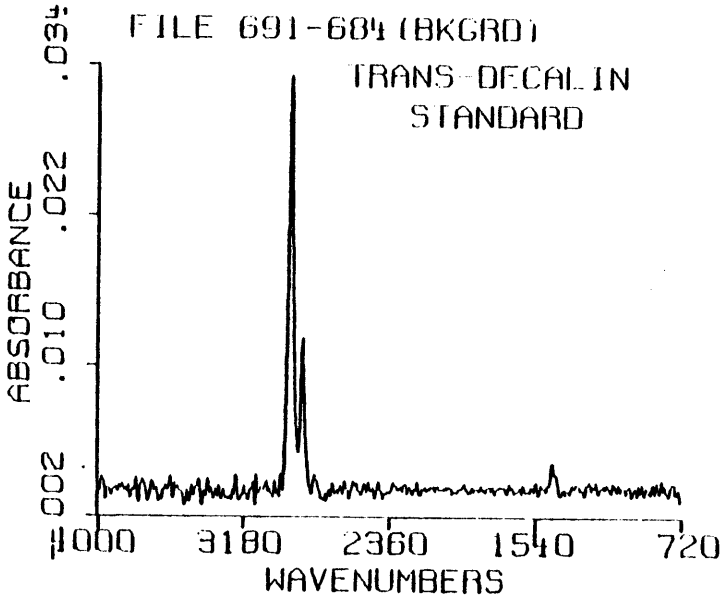
MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 660
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
     1655      1R C
   923      BENZENE, 1,2,3-TRIMETHYL-,
     3212      1R B C
   871      P-XYLENE
     3279      1R D
  2476      BENZENE, 1-ETHYL-3-METHYL-,
     3824      2R C
  2222      BENZYLAMINE, 2,5-DIMETHYL-,
     3941      21R B E
    75      BENZENE, 1,2,4-TRIMETHYL-,
     3964      1R B D
   799      BENZENE, 1,3,5-TRIMETHYL-,
     4157      1R C E
   342      BITOLYL, M,MPR-,
     4368      1R CR C
  2200      ETHANETHIOL, 2-/BENZYLAMINO/-,
     4387      SH2N1R
  2470      2,4-HEXADIENE
     4408      2U2U2

.
```

FIGURE 20

To get an idea of the detection limits possible for this GC-FTIR configuration, a twelve component mixture of alkanes, cyclic aliphatics and aromatics was separated chromatographically using the DB-5 column and Model 36 cell. Concentration ranges varied from 1.7 µg injected of trans-decalin down to about 60 ng of indan. The indan was invariably lost in the background noise but decane (730 ng), trans-decalin (1.7 µg) and m-xylene (1.15 µg) gave reasonable S/N spectra. The spectrum (Figure 21), taken at the peak maximum, gave good response and a "confident" match for trans-decalin (note the position of cis-decalin isomer in the listing). The m-xylene component, however, showed considerably less IR response due to weaker aromatic-type absorbance. The high (1108) "match value" demonstrates a low S/N although 1.15 µg had been injected (Figure 22). Injection of 730 ng of decane shows strong absorbance around 2900 cm^{-1} but the library search is not very reliable due to so little infrared information (Figure 23). In the decane search results, the number one and two matches are standard spectra taken on-the-fly from previous chromatographic runs and then added to the library. Here, an example of the need for spectra representing real on-the-fly conditions is shown. Such representative library spectra are needed more for straight-chain hydrocarbons than for perhaps any other class of compounds. Spectral matching for these straight-chain aliphatics demands the most from the search software. Low S/N conditions often result in ambiguous matching in which reliable identification becomes impossible.

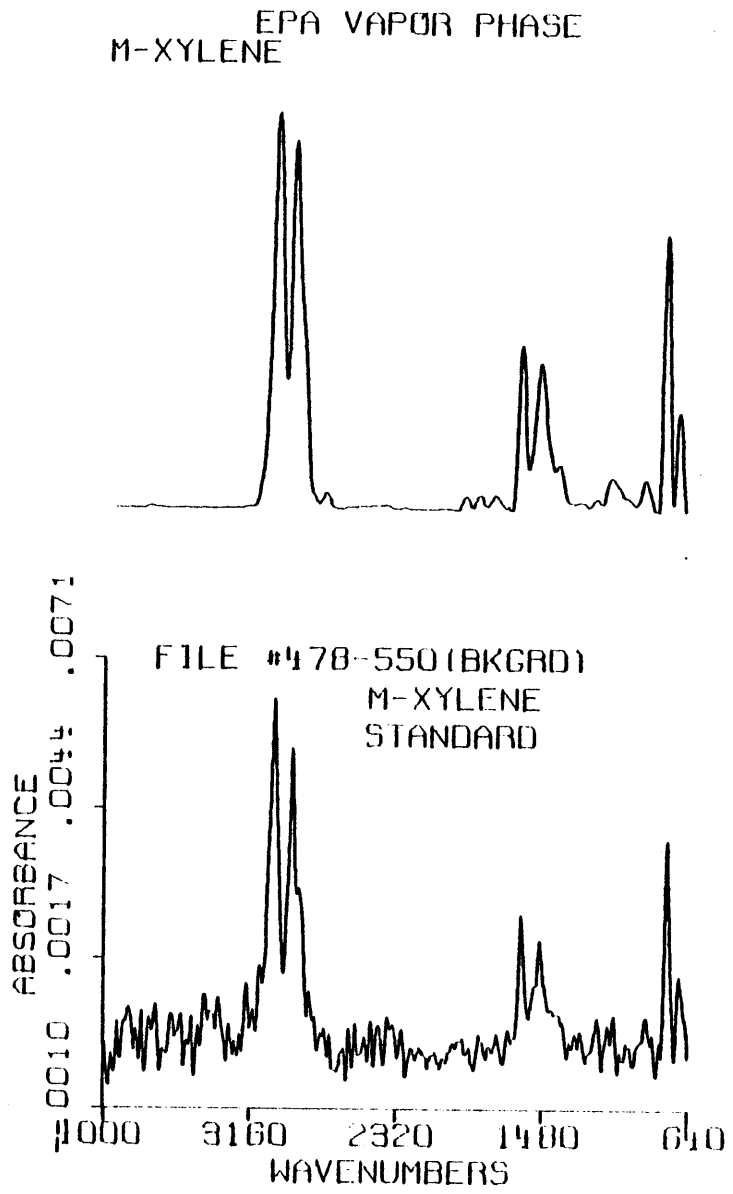




MODEL 36 IR CELL

```
SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 750
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   241     BICYCLO/4.4.0/DECANE
        66     L66TJ
   446     CYCLOOCTANE
       137     L8TJ
  2576     METHYLAMINE, 1-CYCLOHEPTYL-,
       149     L7TJ A12
  1312     PENTACOSANE
       161     25H
  2314     NONADECYLAMINE
       165     Z19
  1038     NAPHTHALENE, DECAHYDRO-, CIS-,
       184     L66TJ
   137     CYCLOHEXANE, PENTYL-, C
       197     L6TJ A5
  1276     TRICOSANE
       198     23H
  2316     PENTADECYLAMINE
       208     Z15
   417     CYCLOHEXANE, ETHYL-,
       210     L6TJ A2
```

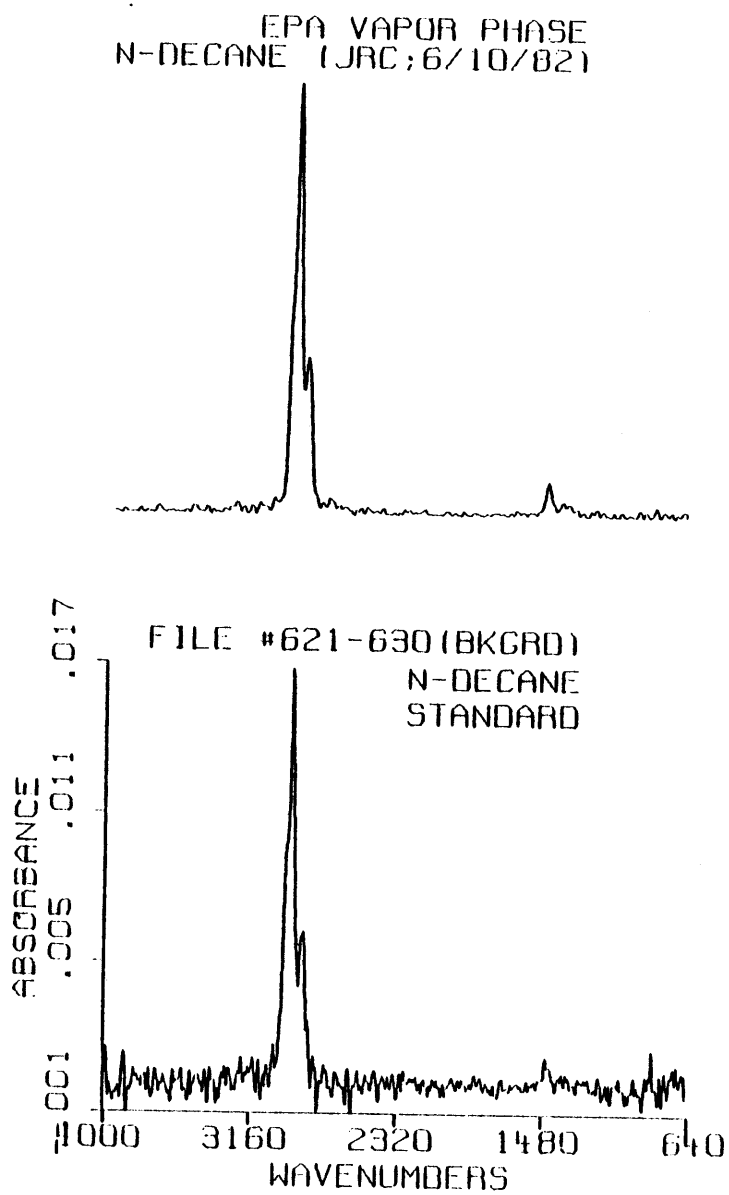
FIGURE 21



MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 640
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
    1108     1R C
   342     BITOLYL, M,MPR-,
    2447     1R CR C
   923     BENZENE, 1,2,3-TRIMETHYL-,
    2915     1R B C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
    2988     2R C
   799     BENZENE, 1,3,5-TRIMETHYL-,
    3069     1R C E
   871     P-XYLENE
    3430     1R D
    75     BENZENE, 1,2,4-TRIMETHYL-,
    3491     1R B D
   222     3,5-LUTIDINE
    3589     T6NJ C E
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
    3678     1R B C E
  2610     HEXANE, 1,3,5-TRIPHENYL-,
    3708     1YR&1YR&2R
```

FIGURE 22



MODEL 36 IR CELL

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 750
 LOW LIMIT 3700
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
  3301     N-DECANE (JRC;6/10/82)
      120
  3302     N-UNDECANE (JRC;6/10/82)
      137
   887     NONANE
      160     9H
  2554     HEPTADECANE, 6,12-DIETHYL-9-
      160     5Y2&2 2Y5
  2553     HEPTADECANE, 6,9,12-TRIPROPYL-,
      161     5Y3&2 2Y3
   895     OCTANE
      169     8H
  2555     HEXADECANE, 6,11-DIPENTYL-,
      184     5Y5&2 2
   415     DECANE
      186     10H
  2155     OCTYL DISULFIDE
      187     8S8
  2343     AMMONIUM BROMIDE, TETRAHEPTYL-,
      188     7 4K &E &4/7

.SRA = 50
```

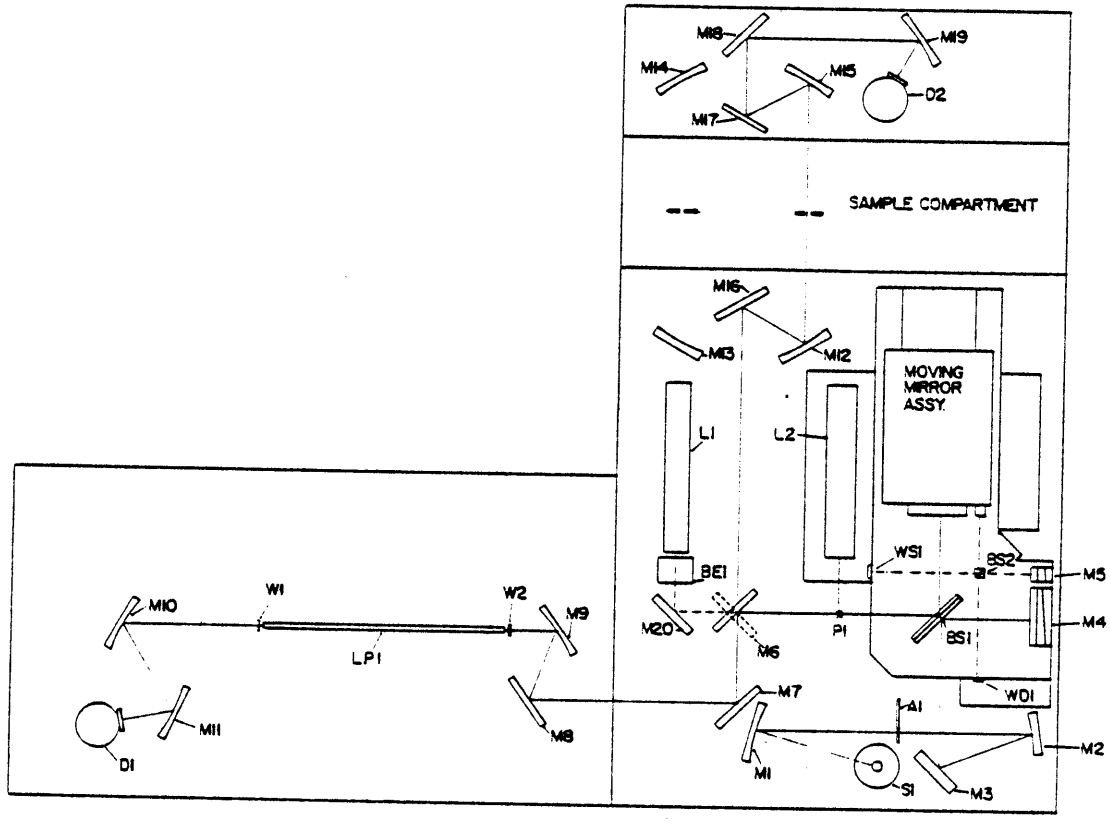
FIGURE 23

Thus far, the overall data indicate that a 3 mm x 6 cm lightpipe combined with a MCT-B detector (4000-400 cm^{-1}) can provide reasonable capillary GC-FTIR data for complex mixtures. The interfacing of fused silica capillary columns to such a system is feasible and sample loadings of over 1 microgram appear to be handled well by such a narrow bore column. A 0.5 µg detection limit can be envisioned for weakly absorbing aromatics although a point is reached where low S/N can lead to ambiguous and often inaccurate library search results. A somewhat lower limit, around 200 ng, is possible for branched and cyclic aliphatics, although lack of infrared spectral information may lead to unreliable search results.

Although our Nicolet 6000 arrangement could achieve reasonable capillary GC-FTIR, a more sensitive system was made available for testing at the Nicolet Instrument Corporation, Madison, WI.

The system, a Nicolet 7199 dual-beam FTIR, was interfaced to an external GC lightpipe and detector bench which included a 40 cm x 1 mm i.d. lightpipe and narrow range MCT-A^+ liquid nitrogen cooled detector (4000-700 cm^{-1}) (See Figure 24). A Hewlett-Packard gas chromatograph with split injection was fitted with a DB-1 0.35 mm i.d. x 60 meter fused silica capillary column.

In an effort to compare the overall performance of both 6000 and 7199 Nicolet GC-FTIR systems, test jet fuel VN-77-11 was again used and a similar temperature program run. For this fuel, the effects of the DB-1 column vs. the DB-5 on retention time were considered minimal since VN-77-11 is mainly of aliphatic character. (The DB-5 is actually



LEGEND

S1	- Source
M1	- Spherical Mirror, 4.5" E.F.L.
A1	- Aperture and Chopper
M2	- Spherical Mirror, 9.0" E.F.L.
M3	- Flat Mirror
BS1	- Beamsplitter and Compensator
BS2	- White Light Beamsplitter
M4	- Fixed Mirror
M5	- White Light Mirror
P1	- Centerline Laser Prism
M6	- 4-Position, Computer-Controlled Flat Mirror
M7, M8	- Flat Mirror
M9, M11	- Off-Axis Parabolic Mirror, 3.5" E.F.L.
W1, W2	- KBr windows
LP1	-3.0 x 420 mm Gold-lined Pyrex Light-Pipe
M10	- Off-Axis Parabolic Mirror, 9.3" E.F.L.
D1	- HgCdTe Detector and Dewar
M16, M17	- 2-Position, Computer-Controlled Flat Mirrors
M12, M13, M14, M15	- Off-Axis Parabolic Mirror, 9.3" E.F.L.
M18	- Flat Mirror
M19	- Off-Axis Parabolic Mirror, 3.5" E.F.L.
D2	- IR Detector
L2	- Centerline Laser
L1	- Alignment Laser
BE1	- Beam Expander
M20	- Flat Mirror
WS1	- White Light Source
WD1	- White Light Detector

White Light Beam
Infrared Beam
Laser Beam

FIGURE 24. Nicolet 7199 Optical Layout

a methyl-phenyl-vinyl polysiloxane (bonded phase) while the DB-1 has only methyl character). The splitter was set to 30 ml/min helium making the split-ratio approximately 1:15. A make-up gas (He) was used to bring the total flow rate through the lightpipe to 4 ml/min. The flame ionization detector was not used due to the problems of re-directing the helium gas to a make-up tee.

The major operating parameters for this experiment are given below:

```
VEL = 50        injector temperature 260°C
COR = IN        lightpipe temperature 270°C
NSD = 10
NSB = 40
APT = FL
GAN = 1
```

The amount of fuel injected was 0.2 µl, with the amount actually going to the column being approximately 0.013 µl. The dual computer disc drive for this system made available almost 1600 8 cm^{-1} data files to store the IR scans. No files are lost as a result of automatically switching to the second data disk cartridge. The throughput for this system was about 7.7 volts with a GAN=1. This throughput is only slightly more than achieved with the Model 26 lightpipe with MCT-B detector, although in terms of sensitivity the longer lightpipe and short range (4000-700 cm^{-1}) detector should give better response. The chromatographic parameters and IR windows monitored are given on the CHEMIGRAM and again the data indicate mostly aliphatic character (Figure 25). A reconstructed chromatogram of the infrared region 2800-3000 cm^{-1} (aliphatic C-H) illustrates the separation possible

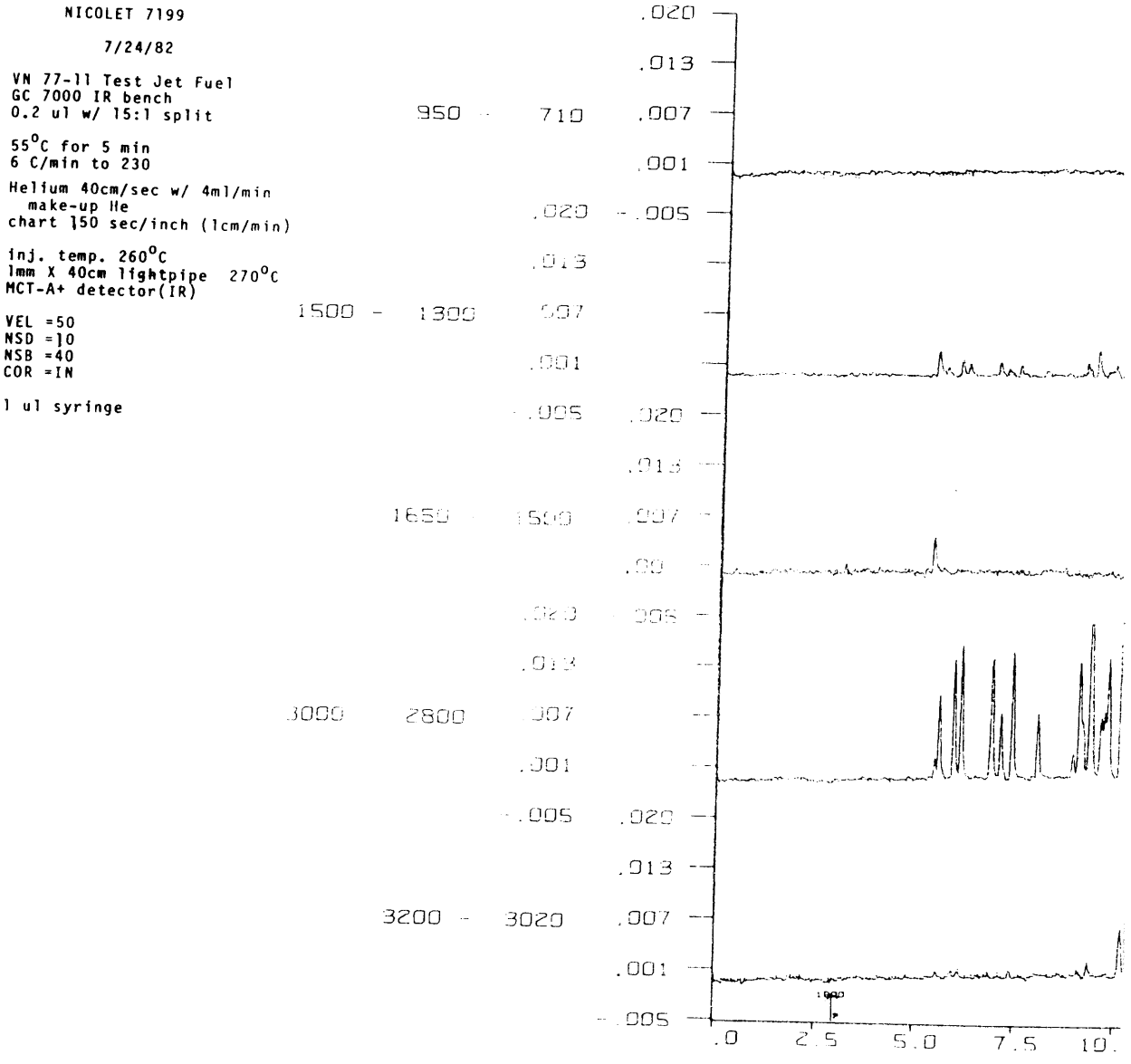
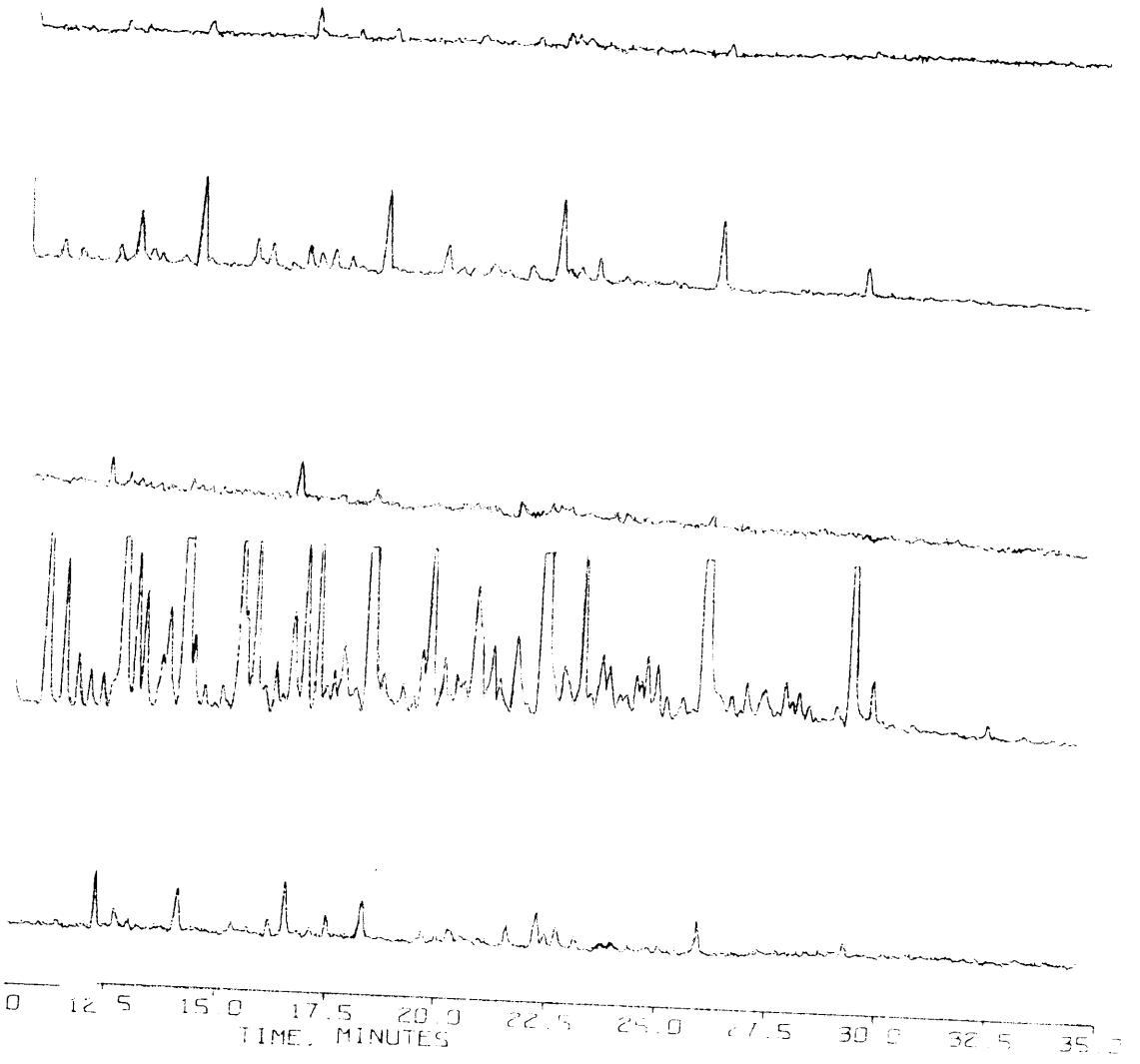


FIGURE 25. CHEMIGRAM of VN-77-11 Separated on DB-1 fused silica column (7199 System)


0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
TIME, MINUTES

on fused silica columns with FTIR detection when no overloading is caused and when the infrared response is enhanced (Figure 26). Figure 27 is a single beam spectrum showing the response curve and, in particular, the IR cutoff at 700 cm^{-1} for the MCT-A^+ detector. For this highly sensitive system, CO_2 is easily distinguishable in light of the "dried air" used as the purge.

Figure 28 shows again the aliphatic region reconstructed chromatogram for VN-77-11 with a peak-picking routine used to locate components on the data disk. Only half of the total run is shown in order that a less confusing plot may be presented. Each peak picked by this routine is chosen according to a y-axis threshold value set by the user. The "starred" peaks will be spectrally matched and interpreted using the EPA library system.

A minor peak giving rise to file spectrum #184 was spectrally searched using the least squares algorithm SQ. This specific peak corresponds to the one previously searched when the Accuspec Model 36 lightpipe and Nicolet 6000 FTIR were used (Figure 18). Because of the excessive CO_2 and water vapor present (and because of the sensitivity now available) the regions 2300-2400 cm^{-1} and 3700-4000 cm^{-1} were blanked out. Also, the region below 700 cm^{-1} was, of course, blanked corresponding to the detector cut-off. The library search identifies the peak component as methyl cyclopentane (Figure 29) with a moderate certainty. This finding confirms the earlier analysis although the actual amount being detected is much smaller in the current 7199 system experiment.

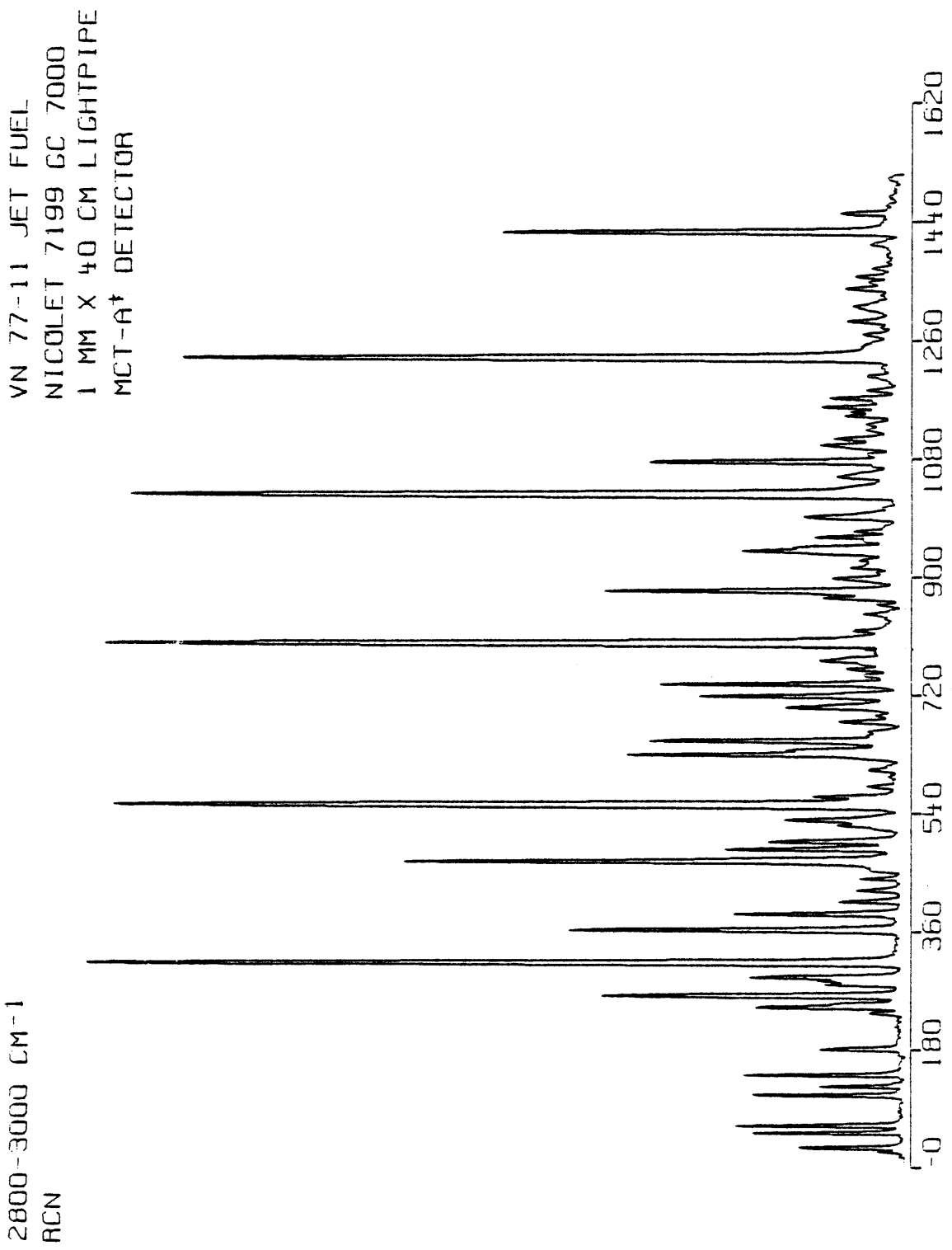

VN 77-11 JET FUEL
NICOLET 7199 GC 7000
1 MM X 40 CM LIGHTPIPE
MCT-A* DETECTOR
2800-3000 CM-1
RCN
-0
180
360
540
720
900
1080
1260
1440
1620
DATA POINTS

FIGURE 26

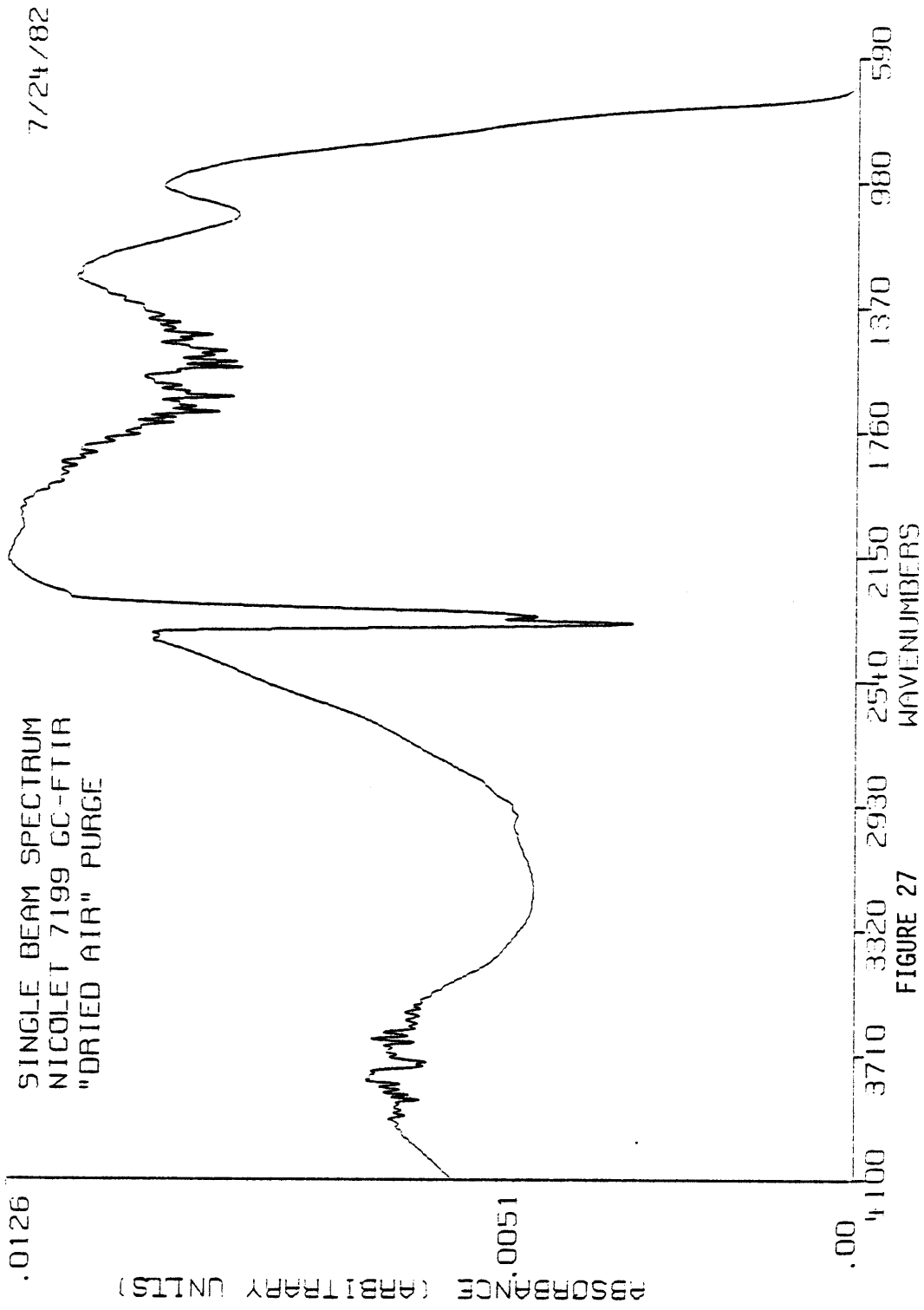

7/24/82
SINGLE BEAM SPECTRUM
NICOLET 7199 GC-FTIR
"DRIED AIR" PURGE
.0126
.0051
.00
ABSORBANCE (ARBITRARY UNITS)
4100
3710
3320
2930
2540
2150
1760
1370
980
590
WAVENUMBERS

FIGURE 27

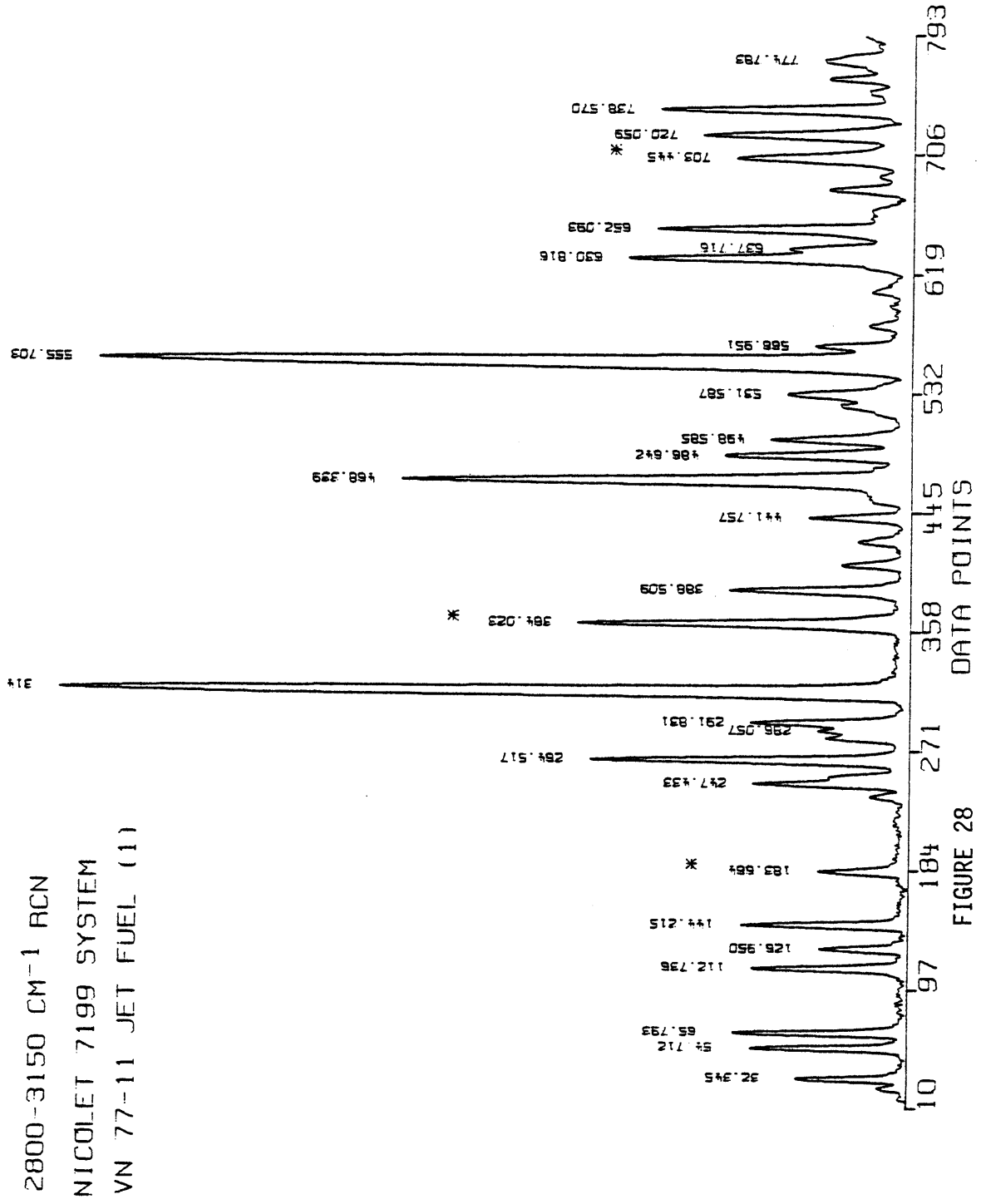
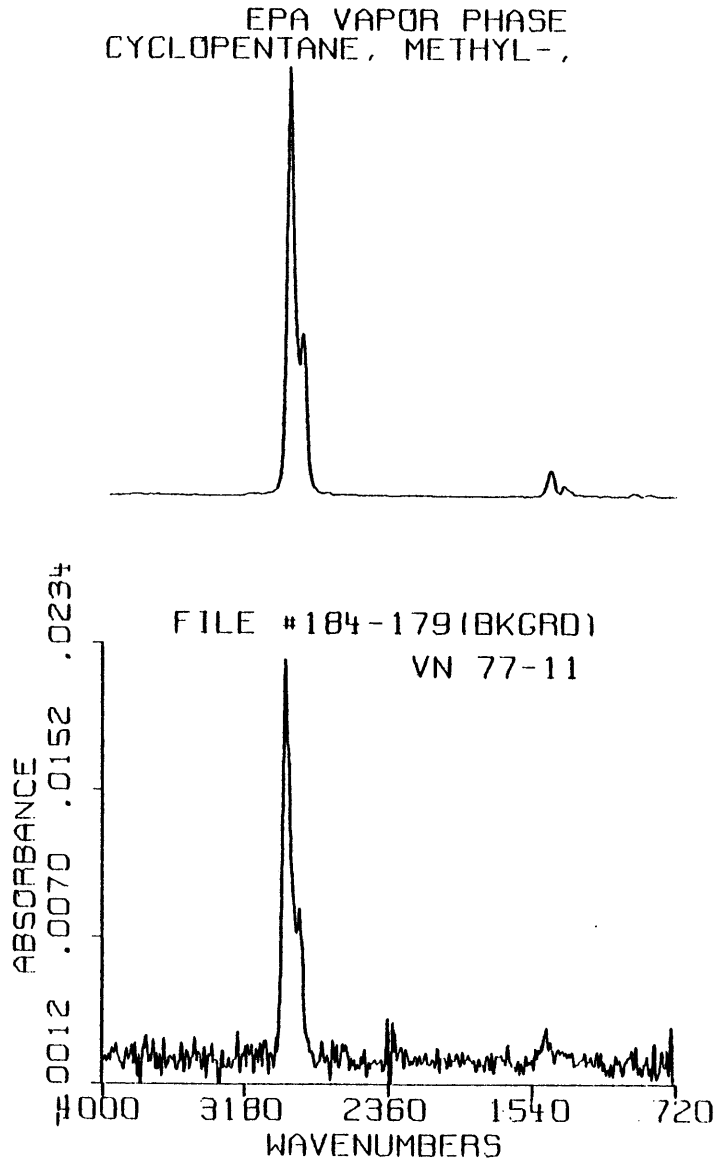

2800-3150 CM-1 RCN
NICOLET 7199 SYSTEM
VN 77-11 JET FUEL (1)
10
97
184
271
358
445
532
619
706
793
DATA POINTS
32.345
54.712
65.793
112.736
126.950
144.215
183.664
247.433
264.517
291.831
296.057
314
384.023
388.509
441.757
468.399
486.642
498.585
531.587
555.703
566.951
630.816
637.716
652.093
703.445
720.059
738.570
774.783

FIGURE 28



NICOLET 7199 SYSTEM

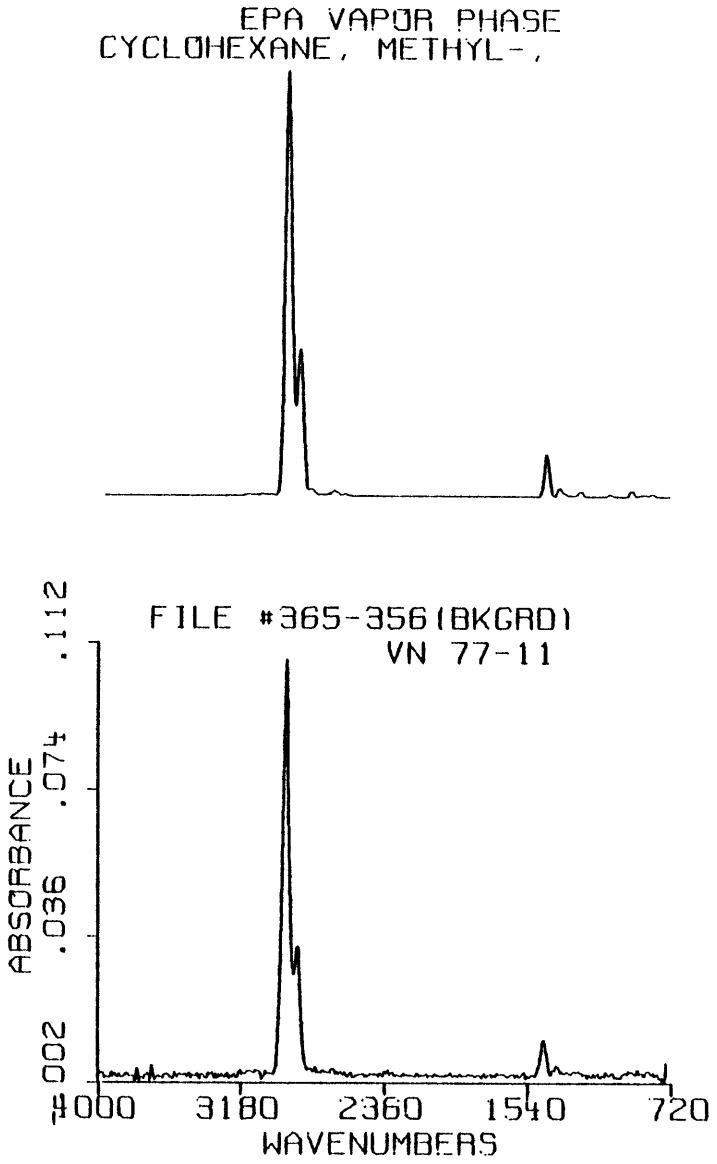
```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 750
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
    45    CYCLOPENTANE, METHYL-,
      84     L5TJ A
  2494    HEPTANE, 2,2-DIMETHYL-,
     118     5X
    43    HEXANE, 2,2,5-TRIMETHYL-,
     172     1Y&2X
   802    HEXANE, 2,2,4-TRIMETHYL-,
     185     2Y&1X
   922    HEPTANE, 3,3-DIMETHYL-,
     189     4X2
  2480    CYCLOPENTANE
     193     L5TJ
  2491    HEXANE, 2,5-DIMETHYL-,
     193     1Y2Y
   381    ISOOCTANE (ISO-CALLED)
     198     1Y&1X
  2930    ISOBUTANE
     219     1Y
    38    PENTANE, 2,4-DIMETHYL-,
     226     1Y&1Y
```

FIGURE 29

The superior sensitivity of the Nicolet 7199 (40 cm lightpipe) system is realized when one considers that a 1.4x increase in total absorbance is being seen for approximately 20 times less sample when compared with the best Nicolet 6000 (6 cm lightpipe) system. Numerically, the library search results with the 7199 system are roughly the same as the previous analysis, which may be due to baseline problems caused by an inconsistent "dried air" purge or fluctuations in the long 40 cm lightpipe temperature.

A search of file spectrum #365 corresponding to the same peak component as Figure 19 yields a match this time differing only by one methyl group (Figure 30). For this component the IR response is over 2 times that of the previous analysis (for 20 times less sample), and the library search match value of 21 is very convincing. Coeluting peaks may account for the discrepancy in identification between the "best" 6000 and 7199 systems, since the latter configuration gives a more resolved separation.

This greater sensitivity is manifested for the third "starred" peak in the reconstruction. File spectrum #703 (after subtracting out background water and CO_2 (i.e. file spectrum #694) was spectrally searched and found to closely resemble m-xylene (Figure 31). An indepth file by file inspection of the entire peak centered around file #703 revealed that two and possibly three classes of compounds were co-eluting in this peak. In an effort to isolate the aromatic component in this peak, file spectrum #703 had subtracted from it file spectrum #698 which was still within the peak envelope. This subtraction, while



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 750
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

```
EPA VAPOR PHASE
   POSSIBLE HITS
    12    CYCLOHEXANE, METHYL-,
      21    L6TJ A
  3128    CYCLODODECANE
      54    L-12-TJ
   647    CYCLOHEXANE, ISOBUTYL-, C
      74    L6J A1Y
   646    CYCLOHEXANE, 1,1-DIMETHYL-, C
      80    L6J A A
   733    THIOPYRAN, TETRAHYDRO-,
      99    T6STJ
  2556    HEXADECANE, 6-(3,6,7,8-TETRAHYDRO
     103    L66&TJ CY1O&5
   136    CYCLOHEXANE, PROPYL-, C
     110    L6TJ A3
   982    CYCLODODECENE
     115    L12 AUTJ
   417    CYCLOHEXANE, ETHYL-,
     118    L6TJ A2
   234    CYCLOHEXANE, TRANS-1,2-DIMETHYL-,
     119    L6TJ A B -T
```

FIGURE 30

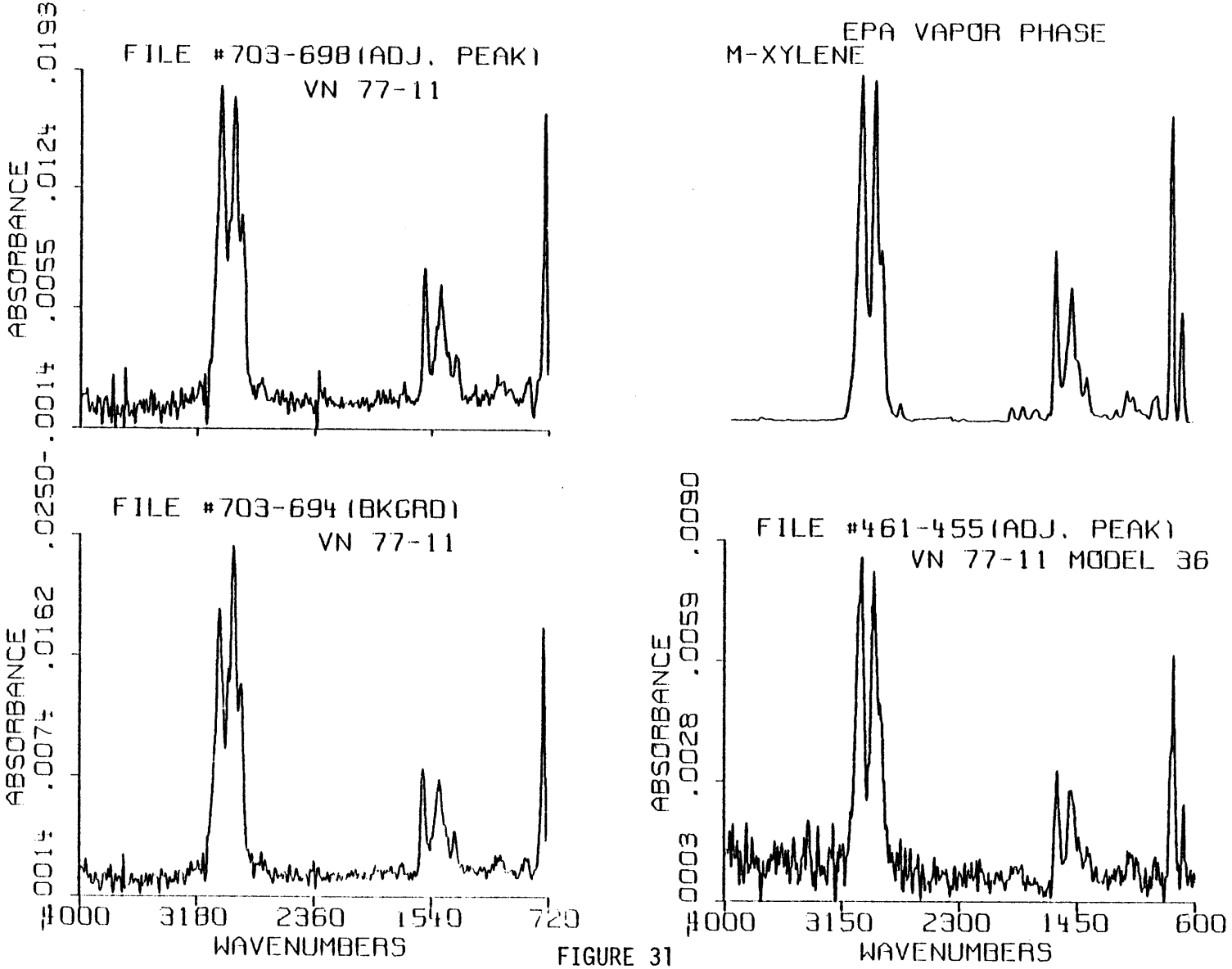

FILE #703-698(ADJ. PEAK)
VN 77-11
ABSORBANCE
.0193
.0124
.0055
-.0014
-.0250
EPA VAPOR PHASE
M-XYLENE
FILE #703-694(BKGRD)
VN 77-11
ABSORBANCE
.0162
.0074
.0014
FILE #461-455(ADJ. PEAK)
VN 77-11 MODEL 36
ABSORBANCE
.0090
.0059
.0028
.0003
4000
3180
2360
1540
720
3150
2300
1450
600
WAVENUMBERS

FIGURE 31

not as straight-forward as a simple background subtraction yielded a spectrum more closely matching (visually) the EPA library file spectrum of m-xylene. Particular attention is drawn to relative IR band heights in Figure 31. Comparison of the relative infrared band heights from these subtractions to the EPA file spectrum of m-xylene (Figure 31) confirms the assumption of co-eluting components. Further confirmation for the presence of m-xylene in VN-77-11 is shown in Figure 31, using the data collected when using the Nicolet 6000 (Model 36 lightpipe) system. A subtraction of file spectrum #455 from file spectrum #461 (both within the peak envelope) resulted in a spectrum and search results (Table 5) identifying m-xylene as present.

An important point to be made concerning spectral subtractions in complex mixture separations is that even though fused silica capillaries have a high degree of separating power, coeluting compounds are still very possible. CHEMIGRAM interpretation and specified IR window reconstructs, however, can help in determining the presence of underlying components.

The aromatic blend VN-80-39 jet fuel was next separated chromatographically employing the Nicolet 7199 system, and data was compared with the results from work with our Nicolet 6000 system. Figure 32 shows the Gram-Schmidt reconstruction for both GC-FTIR systems using the same temperature program and linear gas velocity. One difference between the two analyses was that 5 times less sample was injected into the 7199 GC-FTIR system. From a comparison of the reconstructed chromatograms, more information can be retrieved from the

TABLE 5

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 735
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

a)

a) File #703-698(Adj.Peak)
VN 77-11 Nicolet 7199

```
EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
      371     1R C
   923     BENZENE, 1,2,3-TRIMETHYL-,
     1499     1R B C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
     2388     2R C
  2668     BUTANE, 1,3-DIPHENYL-, /PLUS/-,
     2985     1YR&2R
   342     BITOLYL, M,MPR-,
     2998     1R CR C
  2669     BUTANE, 1,3-DIPHENYL-, /MINUS/-,
     3060     1YR&2R
   871     P-XYLENE
     3136     1R D
    75     BENZENE, 1,2,4-TRIMETHYL-,
     3200     1R B D
  2610     HEXANE, 1,3,5-TRIPHENYL-,
     3235     1YR&1YR&2R
  2222     BENZYLAMINE, 2,5-DIMETHYL-,
     3337     2IR B E
```

SPECTRAL SEARCH LISTINGS
(SQ ALGORITHM)

b) File #703-694(Bkgrd)
VN 77-11 Nicolet 7199

c) File #461-455(Adj.Peak)
Model 36 IR cell

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 745
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

b)

```
EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
      583     1R C
   923     BENZENE, 1,2,3-TRIMETHYL-,
      881     1R B C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
     1372     2R C
    75     BENZENE, 1,2,4-TRIMETHYL-,
     1954     1R B D
  2668     BUTANE, 1,3-DIPHENYL-, /PLUS/-,
     1966     1YR&2R
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
     1998     1R B C D
  2669     BUTANE, 1,3-DIPHENYL-, /MINUS/-,
     2063     1YR&2R
   806     O-XYLENE
     2094     1R B
  1190     BENZENE, HEXAMETHYL-,
     2127     U 6-R
  2610     HEXANE, 1,3,5-TRIPHENYL-,
     2148     1YR&1YR&2R
```

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 650
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1
```

c)

```
EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
      1646     1R C
   923     BENZENE, 1,2,3-TRIMETHYL-,
      3222     1R B C
   871     P-XYLENE
      3275     1R D
  2476     BENZENE, 1-ETHYL-3-METHYL-,
      3826     2R C
  2222     BENZYLAMINE, 2,5-DIMETHYL-,
      3946     2IR B E
    75     BENZENE, 1,2,4-TRIMETHYL-,
      3966     1R B D
   799     BENZENE, 1,3,5-TRIMETHYL-,
      4148     1R C E
   342     BITOLYL, M,MPR-,
      4334     1R CR C
  2200     ETHANETHIOL, 2-/BENZYLAMINO/
      4392     SH2M1R
  2470     2,4-HEXADIENE
      4409     2U2U2
```

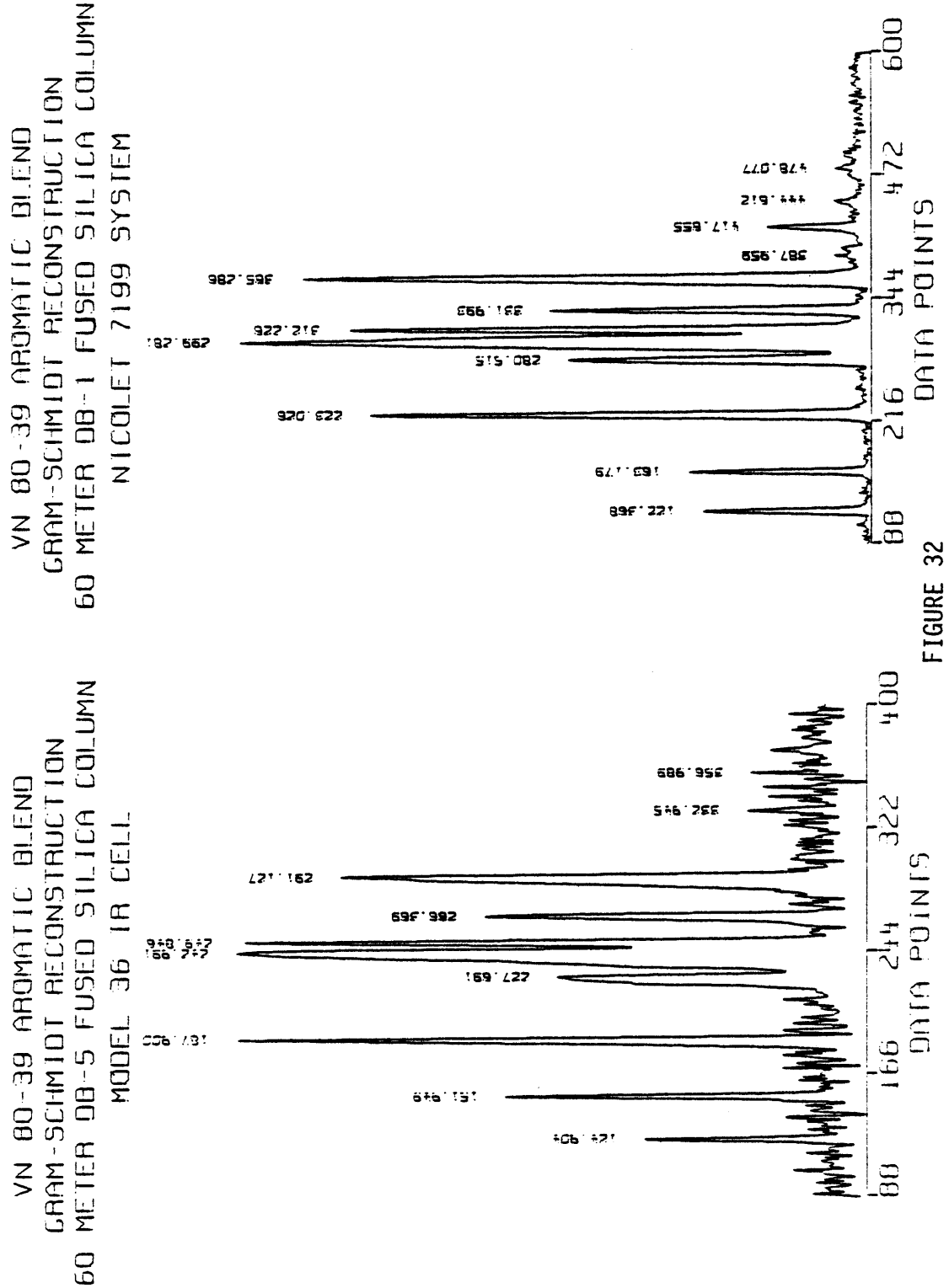
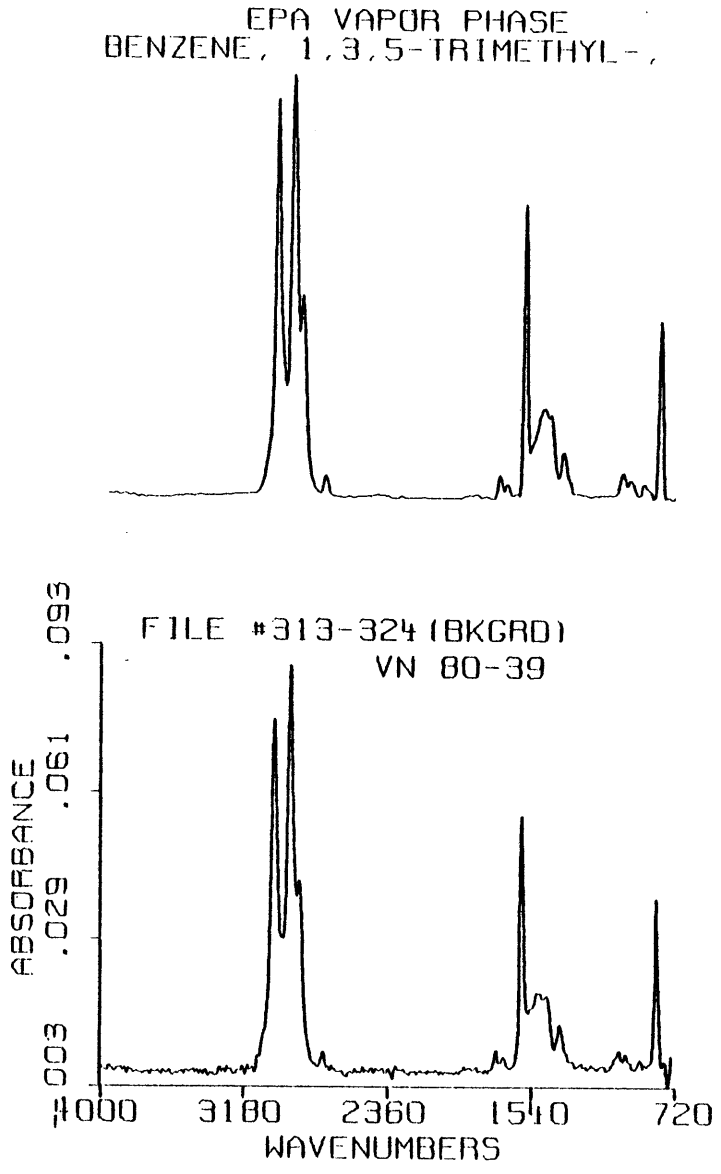

VN 80-39 AROMATIC BLEND
GRAM-SCHMIDT RECONSTRUCTION
60 METER DB-5 FUSED SILICA COLUMN
MODEL 36 IR CELL
DATA POINTS
VN 80-39 AROMATIC BLEND
GRAM-SCHMIDT RECONSTRUCTION
60 METER DB-1 FUSED SILICA COLUMN
NICOLET 7199 SYSTEM
DATA POINTS

FIGURE 32

7199 run as compared to the 6000 run in which some components were lost in the more noisy baseline. Spectral searches of identical peaks as before revealed less noisier spectra. A noticeable improvement in spectral matching, however, was apparent only for the component of low concentration (Figures 33, 34, 15, 16). In any case, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene were again identified for the major and minor peaks, respectively.

To gain more insight as to the actual sensitivity of the Nicolet 7199 GC-FTIR system, a standard mixture of aliphatics and aromatics (Table 2) at low concentration was separated chromatographically, spectrally searched and identifed. For 0.5 µl of actual injection, concentrations ranged from 65 ng to 440 ng per select component. Figure 35 illustrates the separation of this standard (complex) mixture.

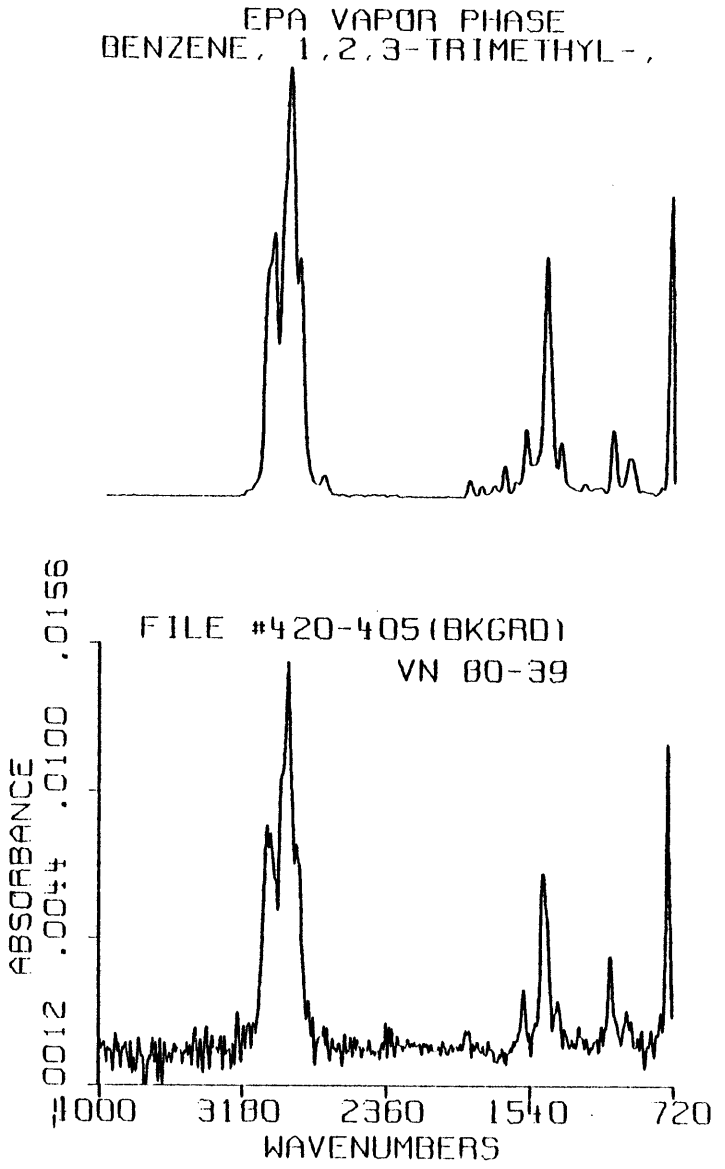
When referring to detection limits and reporting such for GC-FTIR, one must keep in mind that 65 ng of an aromatic hydrocarbon species will have a total absorbance intensity different from an alkane hydrocarbon and certainly less than a component such as isobutylmethacrylate which is a very strong infrared absorber. It is not the purpose here of setting actual "detection limits" for classes of compounds but merely to correlate overall absorbance with an estimated amount of material. One might then, upon reviewing the spectrum of a complex jet fuel, estimate a range, for example, less than one microgram or even speculate low nanogram levels. For about 65 ng of p-xylene, Figure 36 indicates a total absorbance of less than



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 730
 LOW LIMIT 3700
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   799     BENZENE, 1,3,5-TRIMETHYL-,
     262     1R C E
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
    1311     1R B C E
    75     BENZENE, 1,2,4-TRIMETHYL-,
    1771     1R B D
   457     2-BUTENE, 2,3-DIMETHYL-,
    2042     1Y&UY
  1107     BENZENE, 1,2,4,5-TETRAMETHYL-,
    2149     1R B D E
   222     3,5-LUTIDINE
    2169     T6NJ C E
   103     2,4-HEXADIENE, 2,5-DIMETHYL-,
    2179     1Y&U2UY
  1190     BENZENE, HEXAMETHYL-,
    2198     U 6-R
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
    2279     1R B C D
    41     2-BUTENE, 2-METHYL-,
    2335     YU2
```

FIGURE 33



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF NONE
 LOW LIMIT 400
HIGH LIMIT 730
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT 3700
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   923     BENZENE, 1,2,3-TRIMETHYL-,
      304     1R B C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
     1863     2R C
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
     1886     1R B C D
  2668     BUTANE, 1,3-DIPHENYL-, /PLUS/-,
     2101     1YR&2R
    78     M-XYLENE
     2108     1R C
  1190     BENZENE, HEXAMETHYL-,
     2132     U 6-R
  2610     HEXANE, 1,3,5-TRIPHENYL-,
     2241     1YR&1YR&2R
  2669     BUTANE, 1,3-DIPHENYL-, /MINUS/-,
     2252     1YR&2R
  2486     BENZENE, PROPYL-,
     2300     3R
  2666     OCTANE, 3,6-DIPHENYL-,
     2340     2YR&2YR&2
```

FIGURE 34

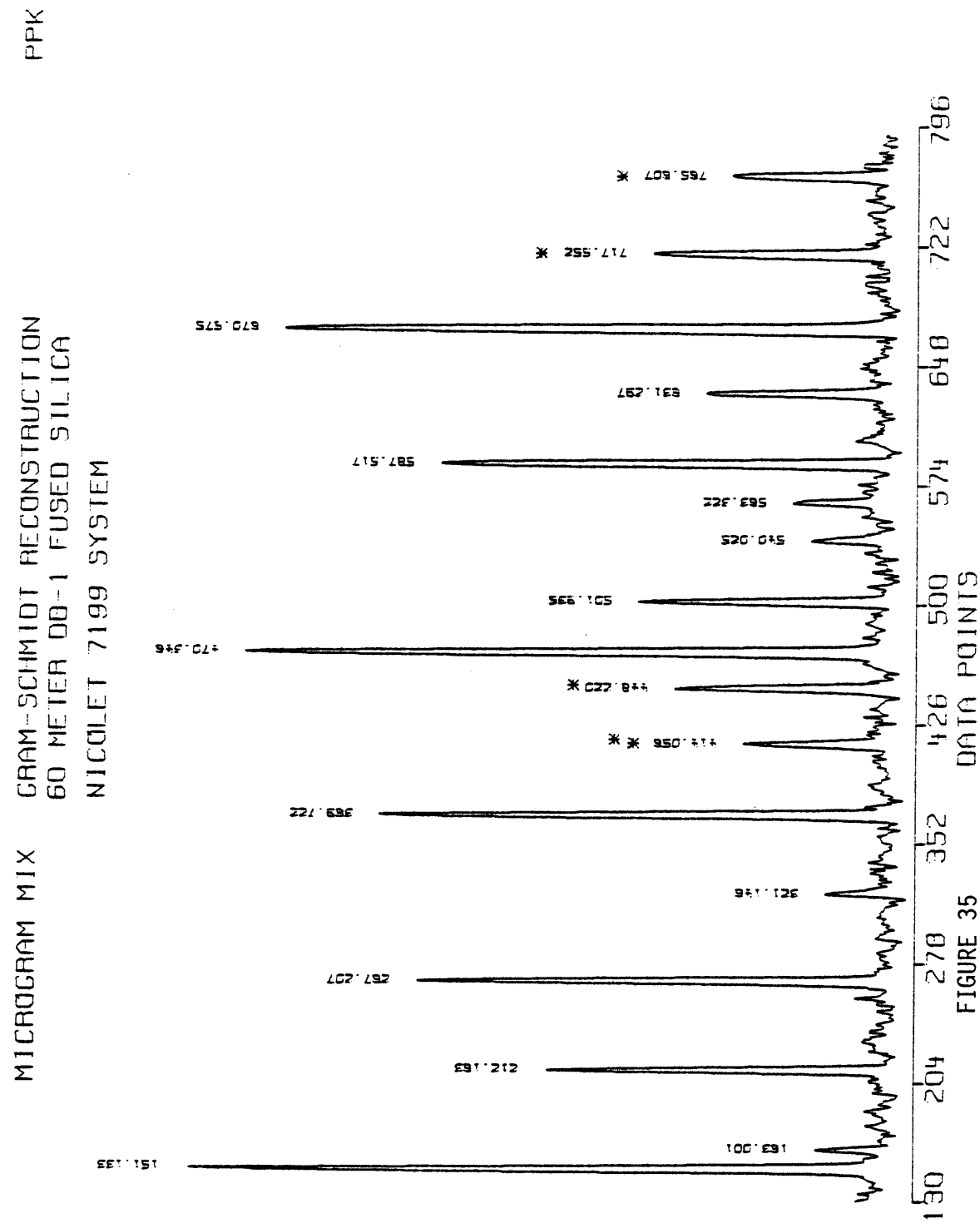
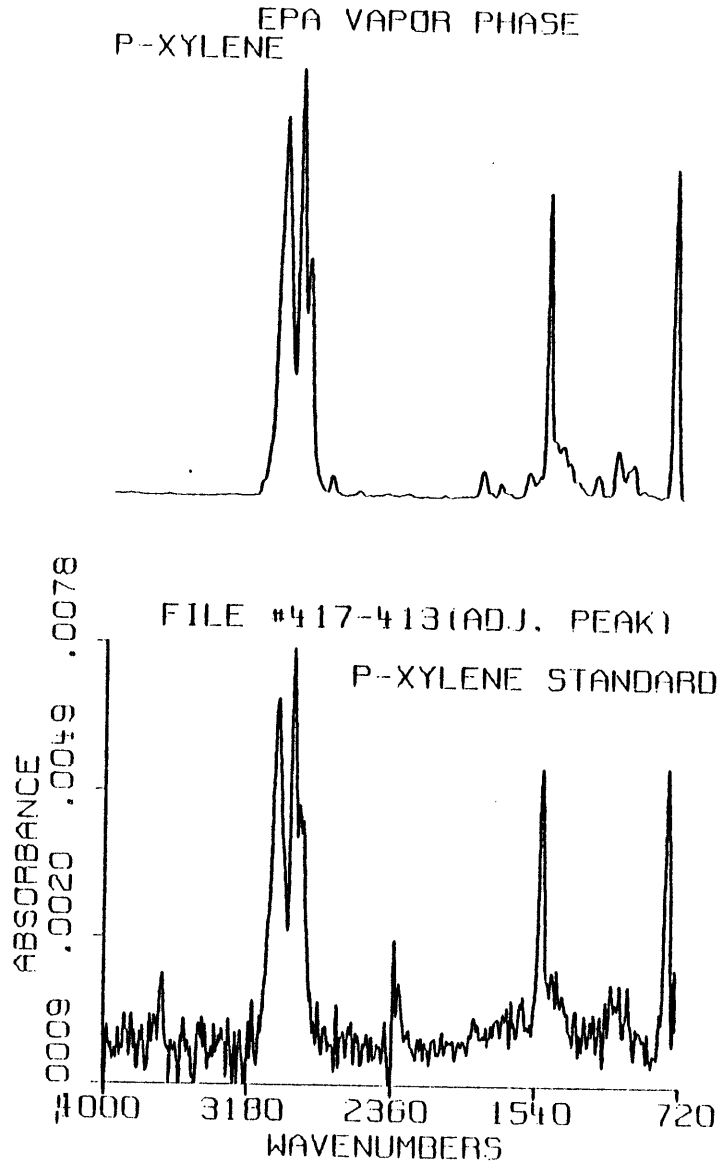

MICROGRAM MIX
GRAM-SCHMIDT RECONSTRUCTION
60 METER DB-1 FUSED SILICA
NICOLET 7199 SYSTEM
PPK
151.133
163.001
212.163
267.207
321.136
369.122
414.056
448.220
470.346
501.935
540.025
563.422
587.517
631.297
670.575
717.552
765.607
130
204
278
352
426
500
574
648
722
796
DATA POINTS

FIGURE 35



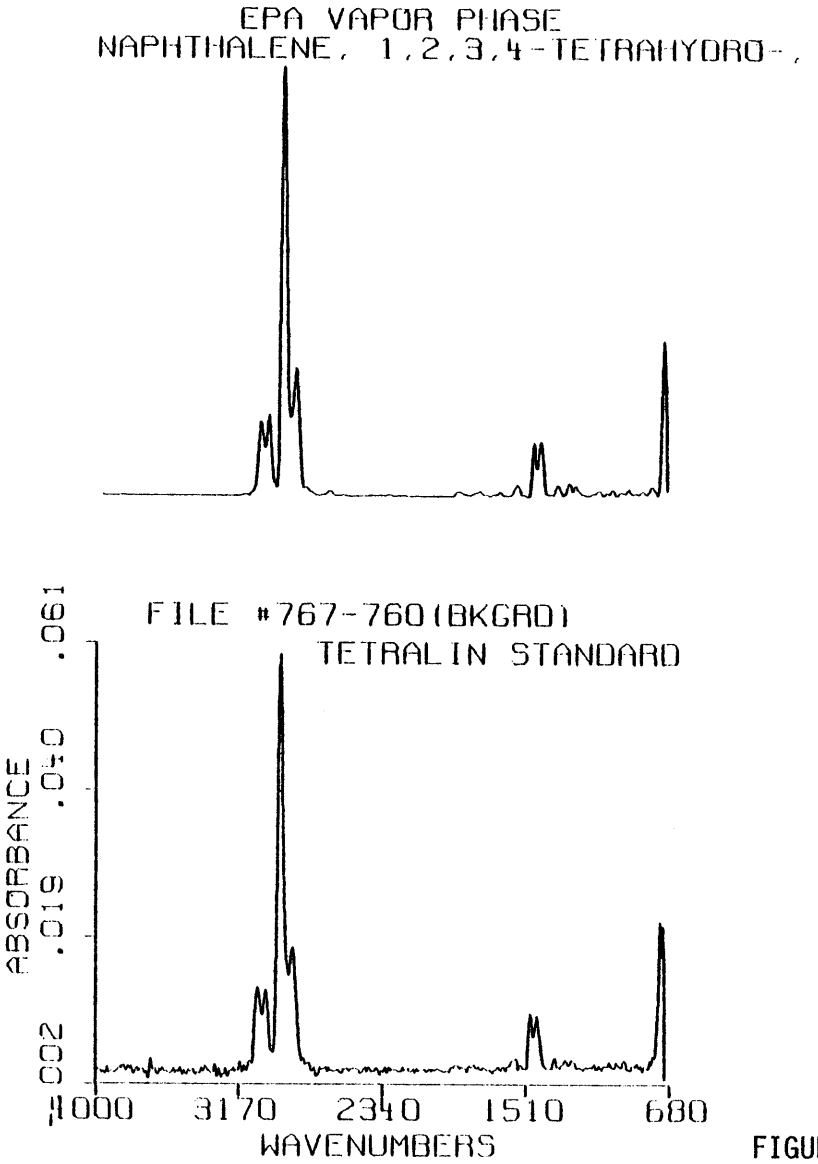

```
.SRO
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 730
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   871     P-XYLENE
     495      1R D
    75     BENZENE, 1,2,4-TRIMETHYL-,
    1360     1R B D
  2222     BENZYLAMINE, 2,5-DIMETHYL-,
    2173     2IR B E
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
    2318     1R B C D
  2431     BIPHENYL, 4,4PR-DIMETHYL-,
    2328     1R DR D
  2200     ETHANETHIOL, 2-/BENZYLAMINO/-,
    2612     SH2M1R
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
    2769     1R B C E
  2476     BENZENE, 1-ETHYL-3-METHYL-,
    2905     2R C
  1190     BENZENE, HEXAMETHYL-,
    2915     U 6-R
  1107     BENZENE, 1,2,4,5-TETRAMETHYL-,
    2951     1R B D E
```

FIGURE 36

0.01 units. S/N, even at this concentration, appears quite good and the "match value" is reasonable considering the low S/N. For tetralin, 195 ng provides a substantial S/N; while 90 ng of cis-decalin is "virtually" noiseless (Figures 37, 38). The match value in each case is exceedingly low. In general, as aliphatic character increases, S/N ratio increases. However, information content can be reduced to the point where straight chain alkanes offer little individual IR distinction.

Probably one of the most significant advantages of infrared spectroscopy is its ability to distinguish between isomers, particularly substituted aromatics. Figure 39 illustrates these differences for two xylenes (o,m) chromatographed with the Nicolet 7199 system. Quantitatively these spectra represent 215 ng of m-xylene and 440 ng of o-xylene. Comparison of these spectra to the p-xylene isomer spectrum (Figure 37) again illustrates the differences in IR absorbance indicative of aromatic substitution. In checking the spectral match list (Table 6) for file spectrum #449 minus background, one notes that the para and meta isomers are not even listed in the top ten but o-xylene has the best match value. A similar situation is observed for file spectrum #414 minus background. Meta-xylene is the best match. O-xylene is not listed while p-xylene is an unlikely choice.

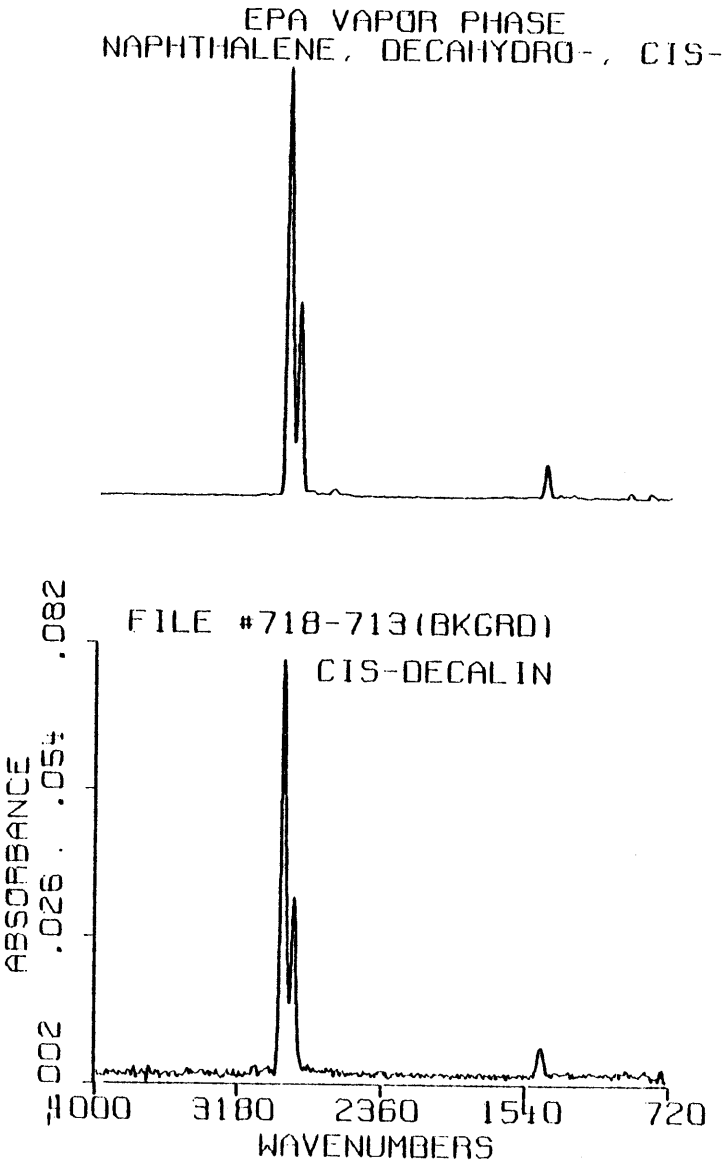
A more complex aromatic blend VN-80-40 was also analyzed using the Nicolet 7199 GC-FTIR system. For such a sample, even a slight column over-loading can lead to badly tailing chromatographic peaks, more so than for predominantly aliphatic samples. A reconstructed



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 710
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   910     NAPHTHALENE, 1,2,3,4-TETRAHYDRO-,
       92     L66&TJ
  1008     TOLUENE, O-/1-CYCLOHEXEN-1-YL/-,
      219     L6UTJ AR B
  2168     CYCLOHEXANOL, 1-O-TOLYL-,
      408     L6TJ AQ AR B
  1574     HEXANE, 1-PHENYL-,
      451     6R
   336     ACENAPHTHENE, 2A,3,4,5-TETRAHYDRO
      512     L566 1A LT&TJ
  2510     OCTANE, 1-PHENYL-,
      516     8R
   917     BENZENE, PENTYL-,
      520     5R
  1222     NONANE, 1,9-DICHLORO-,
      528     69G
   322     DECANE, 1,10-DICHLORO-,
      550     G10G
    14     BENZENE, TETRAHYDRO-,
      555     L6UTJ
```

FIGURE 37




```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 735
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
  1038    NAPHTHALENE, DECAHYDRO-, CIS-,
       34    L66TJ
   241    BICYCLO/4.4.0/DECANE
       85    L66TJ
   446    CYCLOOCTANE
      115    L8TJ
   169    CYCLOHEXANE, BUTYL-, C
      120    L6TJ A4
   982    CYCLODODECENE
      120    L12 AUTJ
   417    CYCLOHEXANE, ETHYL-,
      124    L6TJ A2
   137    CYCLOHEXANE, PENTYL-, C
      128    L6TJ A5
  3128    CYCLODODECANE
      130    L-12-TJ
   136    CYCLOHEXANE, PROPYL-, C
      132    L6TJ A3
  3253    FLUORENE, DODECAHYDRO-,
      139    L656TJ

.
```

FIGURE 38

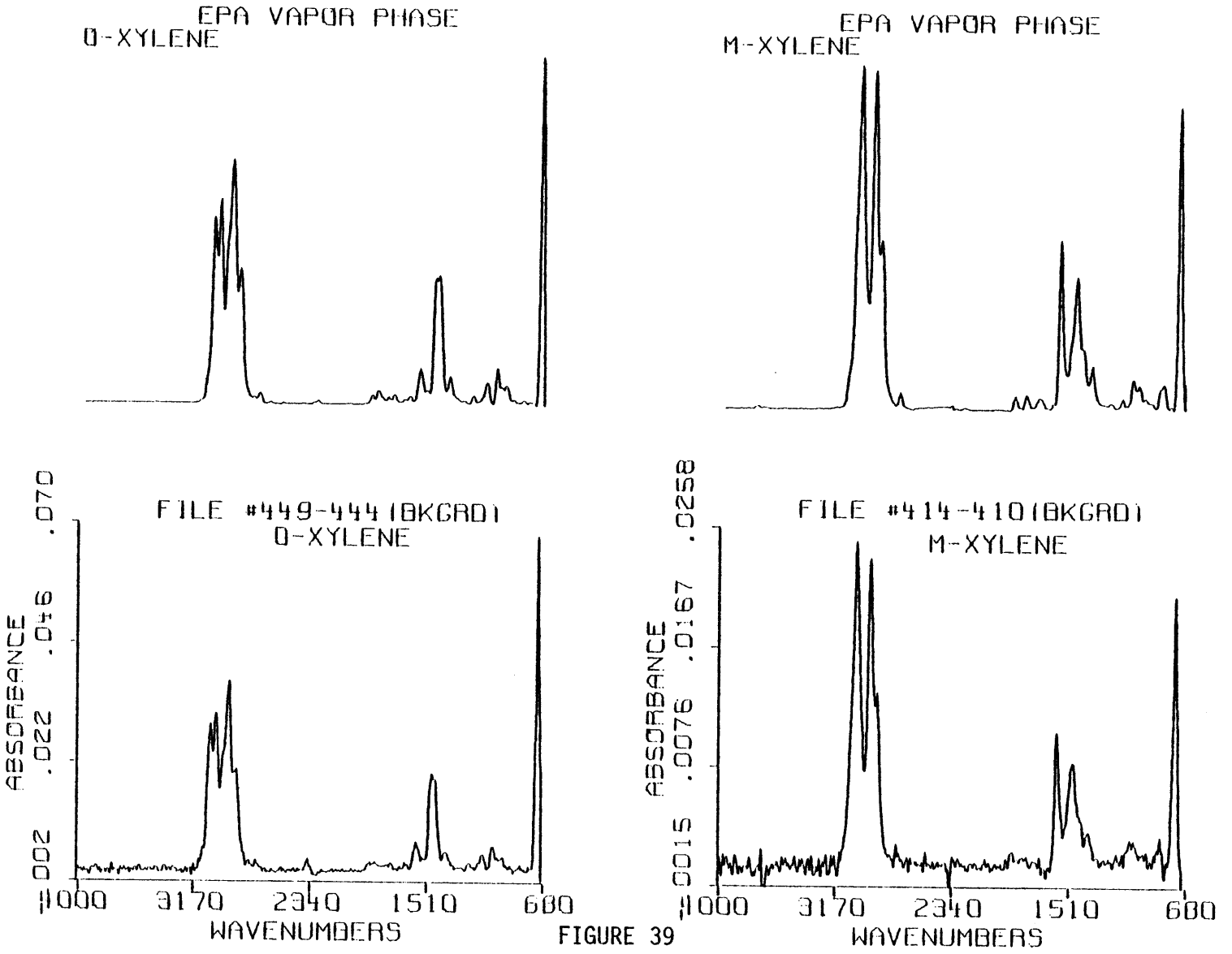

EPA VAPOR PHASE
O-XYLENE
EPA VAPOR PHASE
M-XYLENE
FILE #449-444(BKGRD)
O-XYLENE
ABSORBANCE
.070
.046
.022
.002
4000
3170
2340
1510
600
WAVENUMBERS
FILE #414-410(BKGRD)
M-XYLENE
ABSORBANCE
.0258
.0167
.0076
.0015
4000
3170
2340
1510
600
WAVENUMBERS

FIGURE 39

TABLE 6

NICOLET 7199 FTIR SYSTEM

O-XYLENE STANDARD SEARCH LIST

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 710
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   806     O-XYLENE
      106      1R B
   795     SULFIDE, PHENYL 3-PHENYLPROPYL,
     1232      RS3R
  2609     BUTANE, 1-BROMO-2,4-DIPHENYL-,
     1342      E1YR&2R
  2686     PROPANE, 1,3-DIPHENYL-,
     1391      R3R
  2610     HEXANE, 1,3,5-TRIPHENYL-,
     1404      1YR&1YR&2R
  2489     TOLUENE, O-ETHYL-,
     1522      2R B
    26     BENZENE, METHYL-,
     1557      1R
  1938     ISOQUINOLINE, 1,2,3,4-TETRAHYDRO-
     1591      T66 CMT&J
  2669     BUTANE, 1,3-DIPHENYL-, /MINUS/-,
     1593      1YR&2R
  2668     BUTANE, 1,3-DIPHENYL-, /PLUS/-,
     1658      1YR&2R
```

M-XYLENE STANDARD SEARCH LIST

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 712
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
    78     M-XYLENE
     220      1R C
   923     BENZENE, 1,2,3-TRIMETHYL-,
    1805      1R B C
   342     BITOLYL, M,MPR-,
    1874      1R CR C
  2476     BENZENE, 1-ETHYL-3-METHYL-,
    2304      2R C
  2610     HEXANE, 1,3,5-TRIPHENYL-,
    2350      1YR&1YR&2R
   871     P-XYLENE
    2423      1R D
   799     BENZENE, 1,3,5-TRIMETHYL-,
    2525      1R C E
    75     BENZENE, 1,2,4-TRIMETHYL-,
    2594      1R B D
  2668     BUTANE, 1,3-DIPHENYL-, /PLUS/-,
    2735      1YR&2R
  2669     BUTANE, 1,3-DIPHENYL-, /MINUS/-,
    2751      1YR&2R
```

chromatogram of the region characteristic of aromatics, 3020-3200 cm^{-1}, accurately illustrates the wide range of aromatic components (both mono-and polyaromatic) detected for 0.025 µL of sample injected (Figure 40). The transformed spectrum for a minor monoaromatic component, file #322, gives reasonable S/N and a good match with 1,2,4-trimethylbenzene (Figure 41). Although VN-80-40 is highly complex, three polyaromatics make up the bulk of this sample. One of these compounds has been tentatively identified as 1-methylnaphthalene. Figure 42 (file spectrum #892 minus background) shows the excellent match achieved by the search system from both visual and numerical comparisons.

The fuel product (VN-80-40) was also run on our Nicolet 6000 system with the Model 26 cell. Lack of sensitivity resulted in badly tailing peaks from the column overloading needed to detect the minor constituents. The three polyaromatics were, however, identified as a result of their high concentration and high corresponding S/N. They were found to be naphthalene, 2-methylnaphthalene and 1-methylnaphthalene. These findings agree with spectral matches using the more sensitive 7199 system (Figures 43-45). It should be noted, however, that considerably less sample was used in the 7199 case. Although these polyaromatics differ in structure by only one methyl group, infrared absorbance spectra of each are dissimilar both visually and spectroscopically. This observation points out the unique advantages of FTIR detection in the gas phase.

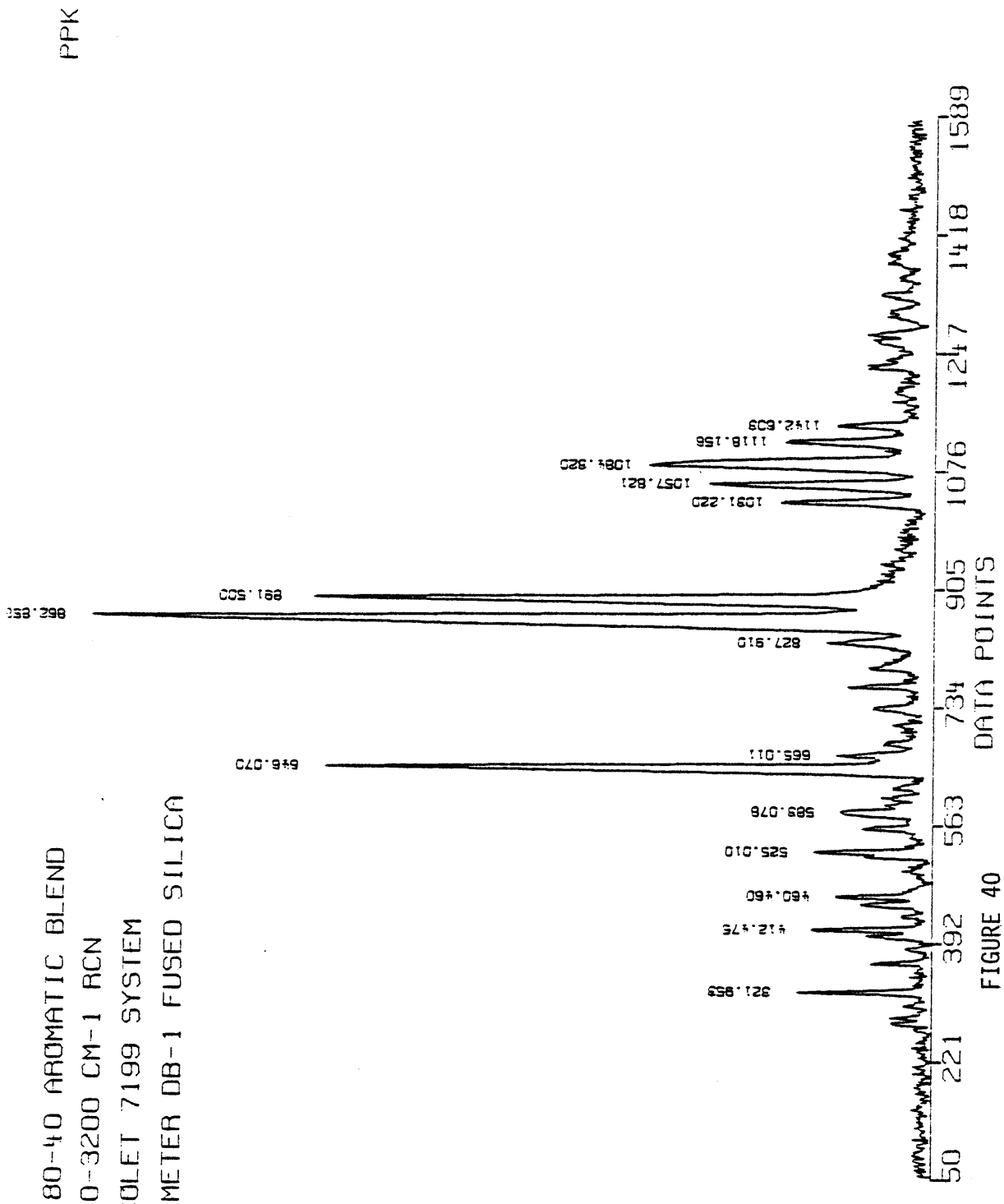
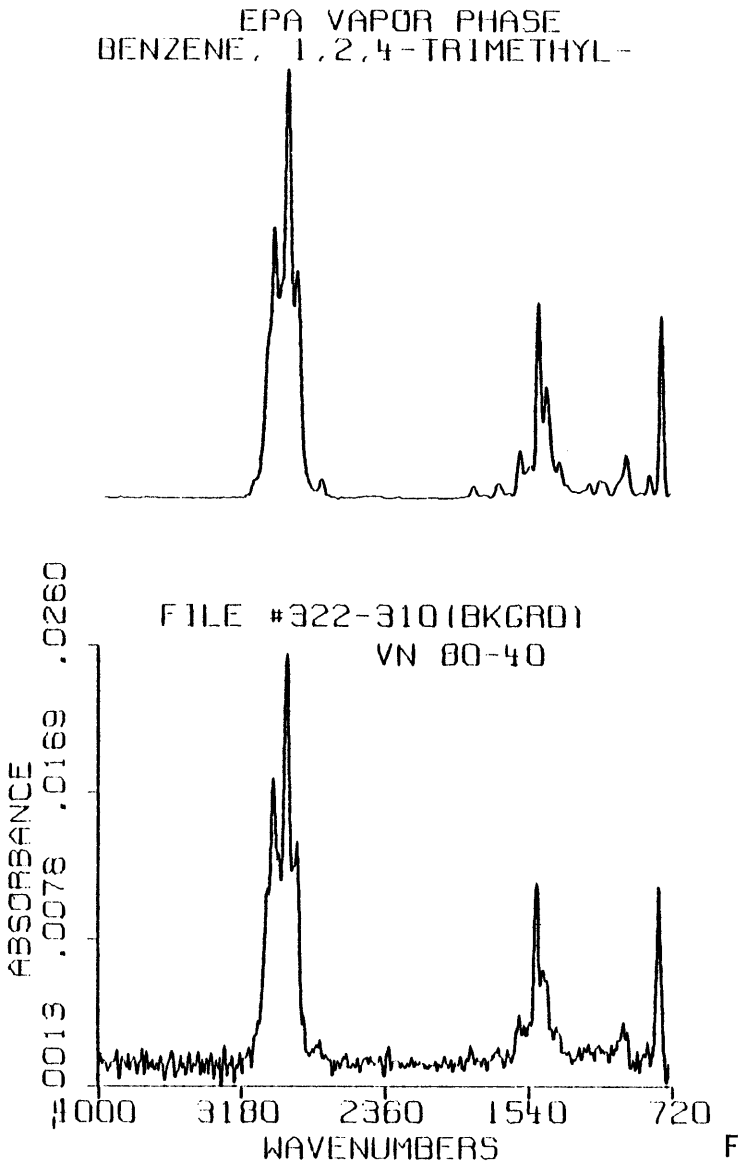

PPK
VN 80-40 AROMATIC BLEND
3020-3200 CM-1 RCN
NICOLET 7199 SYSTEM
60 METER DB-1 FUSED SILICA
50
221
392
563
734
905
1076
1247
1418
1589
DATA POINTS
321.959
412.476
460.460
525.010
589.078
665.011
827.910
891.500
1091.220
1057.821
1118.156
1142.638

FIGURE 40



NICOLET 7199 SYSTEM

```
.SRG
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 740
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
    75     BENZENE, 1,2,4-TRIMETHYL-,
      156     1R B D
   914     BENZENE, 1,2,3,4-TETRAMETHYL-,
      635     1R B C D
  2498     BENZENE, 1,2,3,5-TETRAMETHYL-,
      653     1R B C E
  1107     BENZENE, 1,2,4,5-TETRAMETHYL-,
      754     1R B D E
    41     2-BUTENE, 2-METHYL-,
     1044     YU2
  1190     BENZENE, HEXAMETHYL-,
     1115     U 6-R
   103     2,4-HEXADIENE, 2,5-DIMETHYL-,
     1398     1Y&U2UY
  2308     PROPANE, 2,2-BIS(3,4-XYLYL)-,
     1448     1R B EXR C D
   457     2-BUTENE, 2,3-DIMETHYL-,
     1454     1Y&UY
  2222     BENZYLAMINE, 2,5-DIMETHYL-,
     1563     Z1R B E
```

FIGURE 41

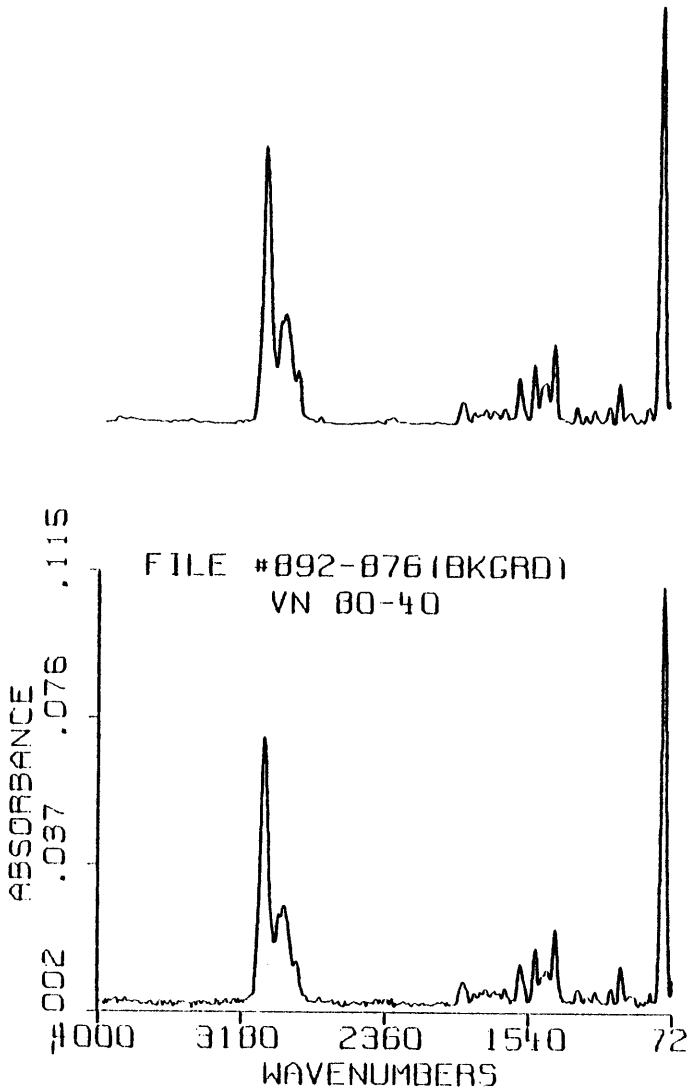


FIGURE 42

NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 720
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   798     NAPHTHALENE, 1-METHYL-,
       76      L66J B
   175     NAPHTHALENE, 1-ETHYL-,
      701      L66J B2
  1357     NAPHTHALENE
      737      L66J
  1493     1-NAPHTHALENESULFONIC ACID, DIHYD
      981      L66J BSWQ &QH &QH
  1254     NAPHTHALENE, 1,5-DIMETHYL-,
     1012      L66J B G
   330     NAPHTHALENE, 1-/CHLOROMETHYL/-,
     1090      L66J B1G
  2518     1-NAPHTHALENECARBONITRILE
     1179      L66J BCN
  1331     AZOBENZENE
     1613      RNVNR
   172     QUINOLINE, 8-METHYL-,
     1745      T66 BNJ J
   876     M-TOLUNITRILE
     1774      NCR C
```

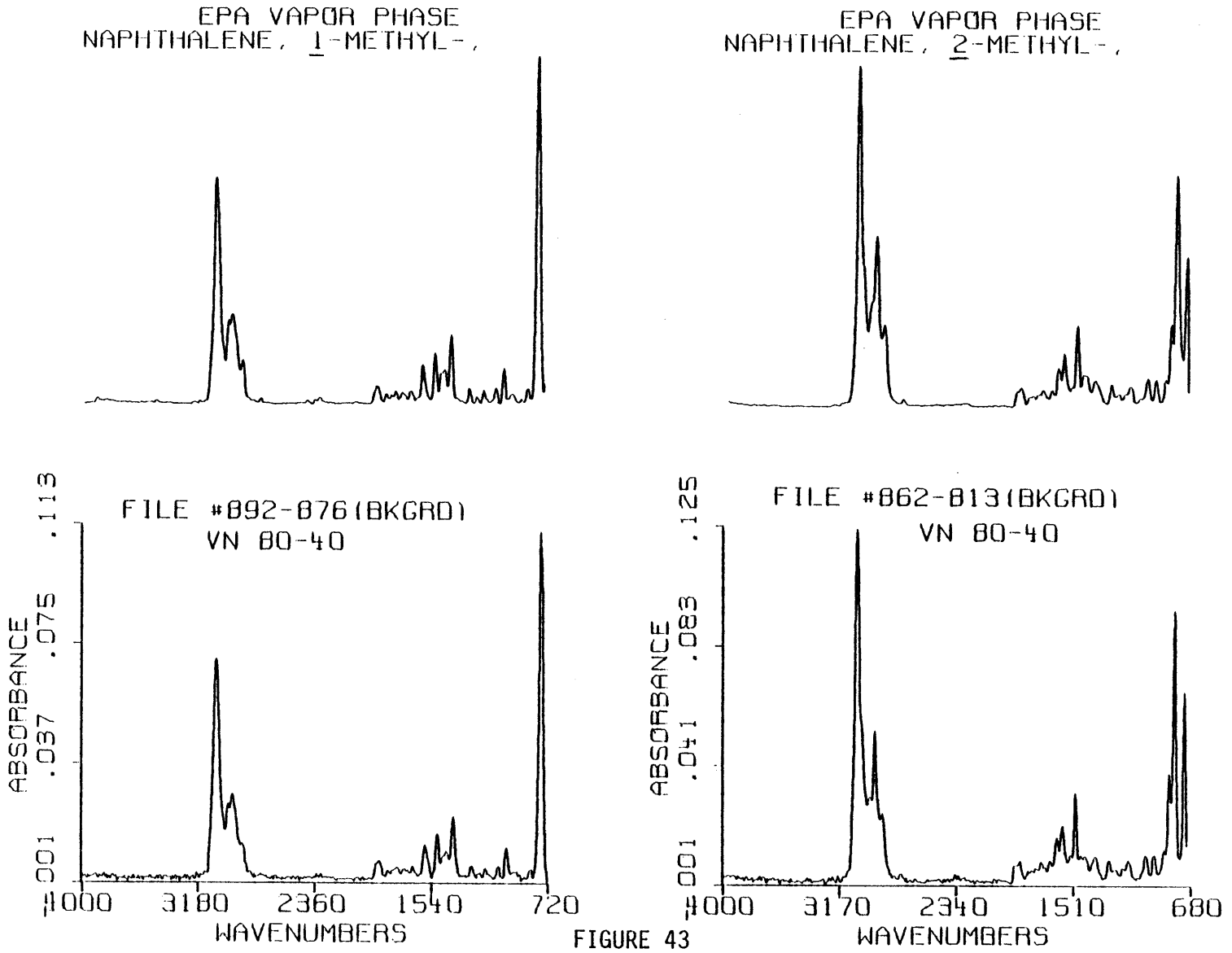
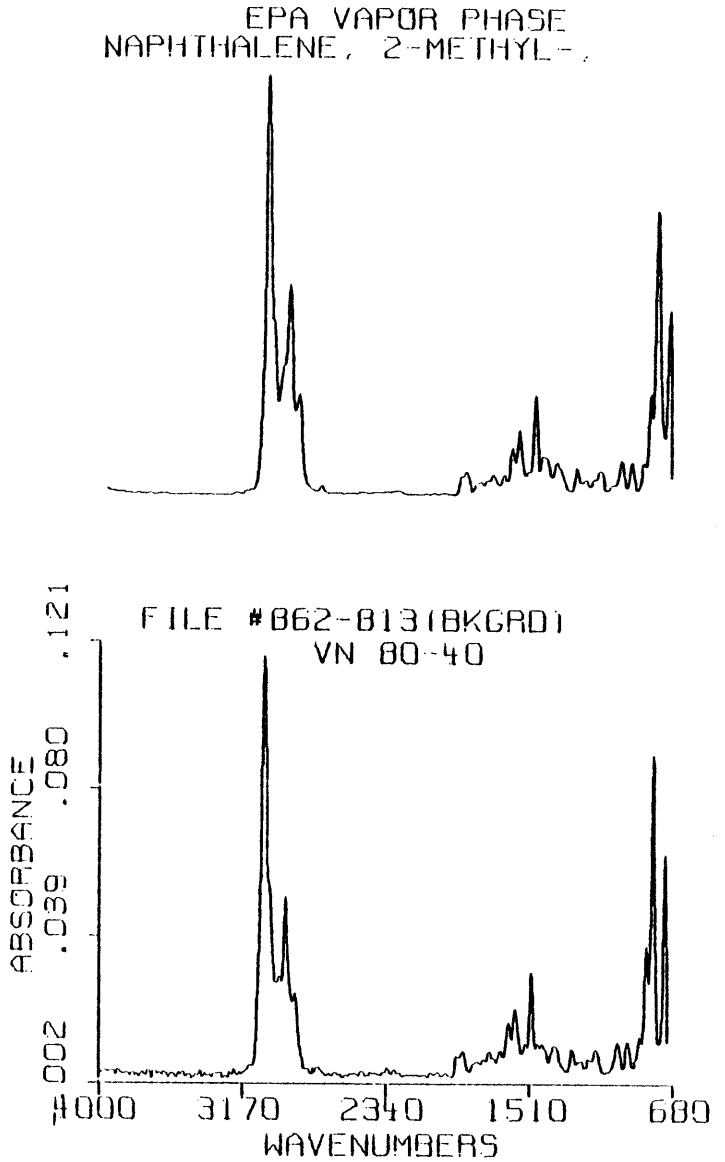

EPA VAPOR PHASE
NAPHTHALENE, 1-METHYL-,
EPA VAPOR PHASE
NAPHTHALENE, 2-METHYL-,
FILE #892-876(BKGRD)
VN 80-40
ABSORBANCE
.001
.037
.075
.113
4000
3180
2360
1540
720
WAVENUMBERS
FILE #862-813(BKGRD)
VN 80-40
ABSORBANCE
.001
.041
.083
.125
4000
3170
2340
1510
680
WAVENUMBERS

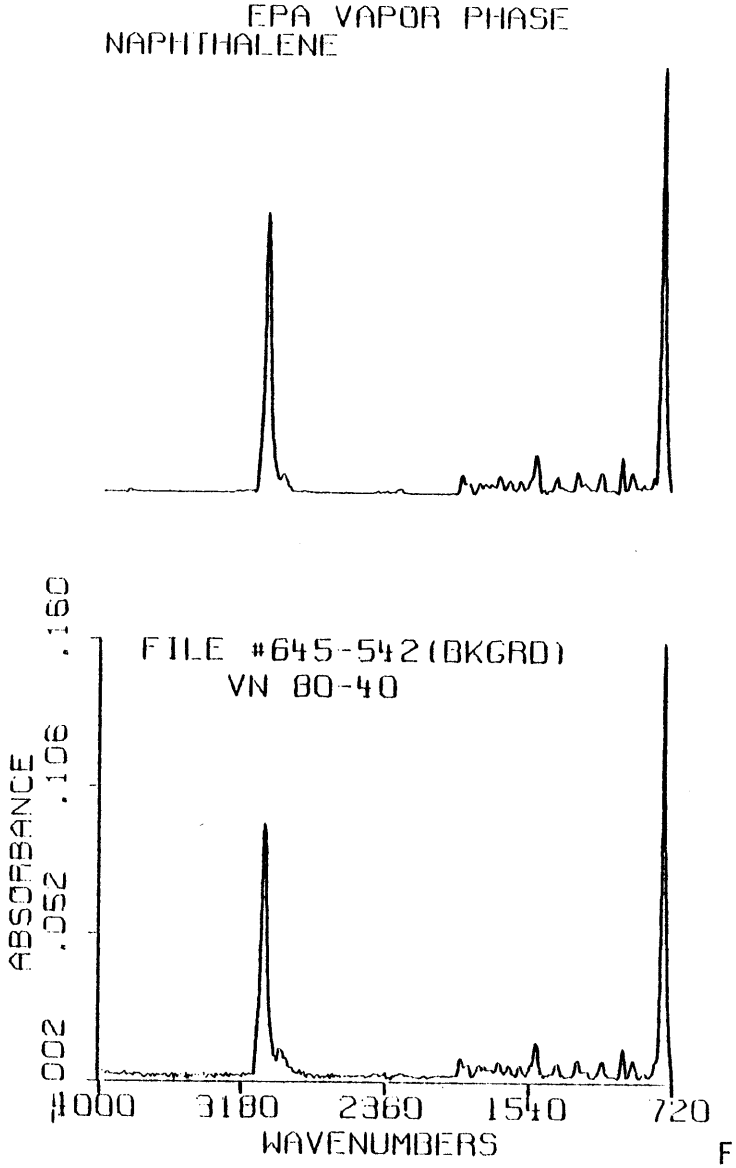
FIGURE 43



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 712
 LOW LIMIT 2300
HIGH LIMIT 2400
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
  2514     NAPHTHALENE, 2-METHYL-,
      185     L66J C
  2201     NAPHTHALENE, 1-CHLORO-2-METHYL-,
     1764     L66J BG C
  2513     NAPHTHALENE, 2-ETHYL-,
     1796     L66J C2
   334     NAPHTHALENE, 1-BROMO-2-METHYL-,
     1845     L66J BE C
  1713     ISOQUINOLINE
     1951     T66 CNJ
  1264     PHENANTHRENE, 3-METHYL-,
     2109     L B666J D
  1101     PHENANTHRENE
     2413     L B666J
   172     QUINOLINE, 8-METHYL-,
     2430     T66 BNJ J
  1852     ETHYLAMINE, 1,2-DIPHENYL-,
     2450     ZYR&1R
   855     1-BENZAZINE
     2456     T66 BNJ
```

FIGURE 44



NICOLET 7199 SYSTEM

```
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 725
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
  1357    NAPHTHALENE
       49    L66J
  1493    1-NAPHTHALENESULFONIC ACID, DIHYD
      467    L66J BSWQ &QH &QH
   330    NAPHTHALENE, 1-/CHLOROMETHYL/-,
      494    L66J B1G
   798    NAPHTHALENE, 1-METHYL-,
      596    L66J B
  2518    1-NAPHTHALENECARBONITRILE
     1006    L66J BCN
  1254    NAPHTHALENE, 1,5-DIMETHYL-,
     1262    L66J B G
  1331    AZOBENZENE
     1264    RNVNR
   175    NAPHTHALENE, 1-ETHYL-,
     1532    L66J B2
   325    PROPANE, 1,1,2-TRICHLORO-,
     1732    GYGYG
   837    METHANE, BROMOTRICHLORO-,
     1743    GXEGG

.
```

FIGURE 45

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

COMPARISONS

Comparison of GC-FTIR to GC-MS was conducted by analysis of test fuel VN-77-11, aromatic blend VN-80-40, and a standard mixture. The Accuspec GC with DB-5 fused silica column was interfaced to a Varian MAT 112 electron impact mass spectrometer by a short, heated transfer line. The same or very similar injection volumes as used for the 7199 GC-FTIR analysis were approximated. Since on-column injection was used in the GC-MS experiment, a dilution of the sample was necessary since sample volumes of less than 0.1 µl were not possible.

The VN-77-11 test fuel was run with the source pressure at about 1.5×10^{-5} torr. The GC effluent was directed into the mass spectrometer without a separator. A 2 ml/min linear flow rate of helium carrier gas accounts for the relatively high source pressure. All fittings in the interface were tested with argon gas to detect leaks prior to using the mass spectrometer. With knowledge to the total alkane character of this fuel and estimated molecular weight maximum, a mass/charge scan range of 50-180 was used. This scan range resulted in approximately 1 (130 m/e total) scan per second. The sample was diluted ten-fold in tetradecane to avoid solvent interferences. One consequence of using a lower boiling solvent would have been loss of volatile sample data. In addition, the relatively large amount of diluting solvent was found to cause the ionization source pressure to exceed 10^{-4} torr, thus causing a temporary system shutdown. The large C_{14} peak is, however, not as sharp due to retention band broadening and

causes no problems. A listing of the temperature program and associated parameters are given on the total ion reconstructed chromatogram (Figure 46). For clarity, Figure 46 shows only half of the total sample detected. For 0.02 µL of actual sample injected, the MS trace shows a response for some trace components not adequately detected by the 7199 GC-FTIR system. In reference to detection limit comparisons, about twice as much sample was injected into the GC-MS as was injected into the GC-FTIR (0.02 µL vs. ~0.013 µL), although the amount associated with the FTIR may be more or less, since quantitation using the injection splitter is not as certain as on-column injection.

The mass/charge versus ion intensity plot for spectrum #1756 confirms the earlier FTIR peak identification as methylcyclopentane (Figure 47a). Recalling earlier FTIR analyses, the component eluting and giving rise to spectrum #1921 had been identified as methylcyclohexane (7199 system) or 1,1-dimethylcyclohexane (Model 36). Mass spectral data indicate a molecular ion of 98 for this peak component and a splitting pattern similar to methylcyclohexane (Figure 47b). In this example, mass spectrometry is very useful in defining the overall molecular weight of the molecule.

Due to the difference in column bonded phases used for the 7199 FTIR and GC-MS analyses, confirmation of m-xylene found earlier by FTIR was more elusive. The m/e versus intensity plot for spectrum #2266 does <u>not</u> indicate the expected strong intensity at m/e=91 for m-xylene (Figure 48). As was mentioned earlier, because jet fuel VN-77-11 was of mainly aliphatic character (85%) only "minimal" differences in retention

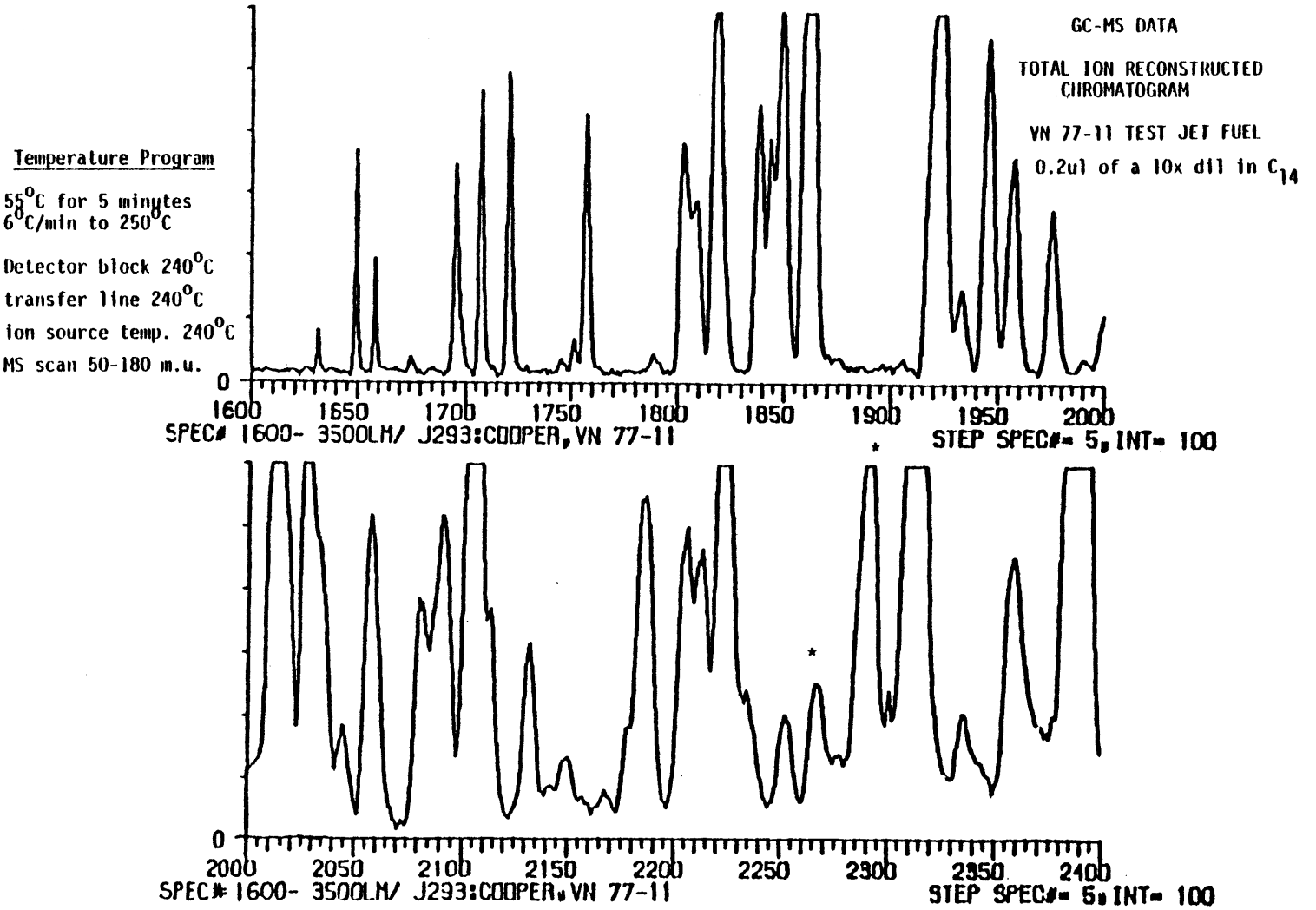
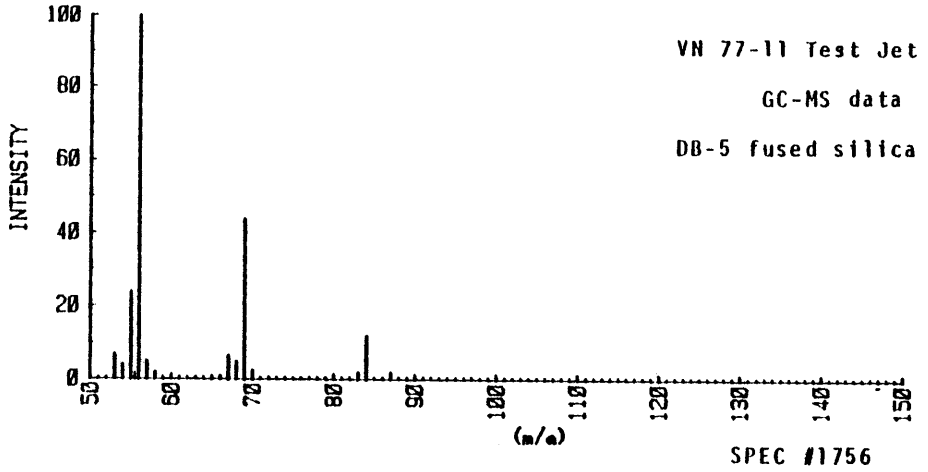

Temperature Program
55°C for 5 minutes
6°C/min to 250°C
Detector block 240°C
transfer line 240°C
ion source temp. 240°C
MS scan 50-180 m.u.
GC-MS DATA
TOTAL ION RECONSTRUCTED CHROMATOGRAM
VN 77-11 TEST JET FUEL
0.2ul of a 10x dil in C14
0
1600 1650 1700 1750 1800 1850 1900 1950 2000
SPEC# 1600- 3500LM/ J293:COOPER, VN 77-11
STEP SPEC#= 5, INT= 100
0
2000 2050 2100 2150 2200 2250 2300 2350 2400
SPEC# 1600- 3500LM/ J293:COOPER, VN 77-11
STEP SPEC#= 5, INT= 100

FIGURE 46



VN 77-11 Test Jet Fuel

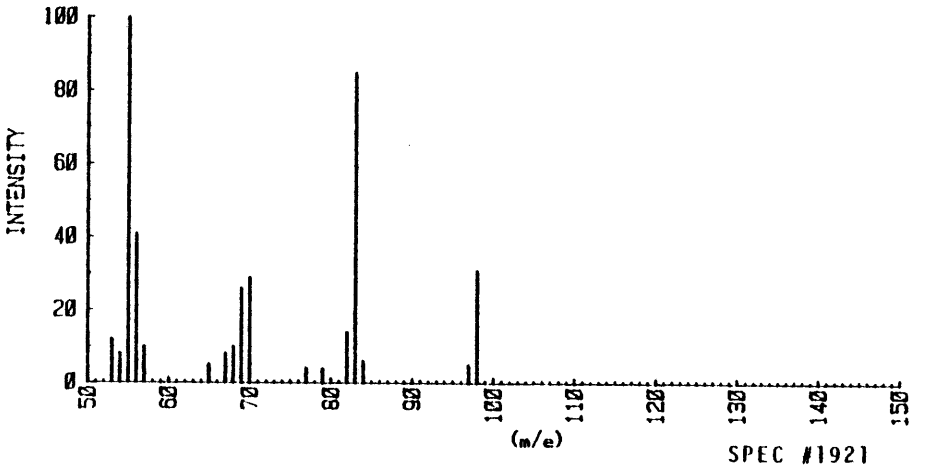
GC-MS data

DB-5 fused silica column

methylcyclopentane

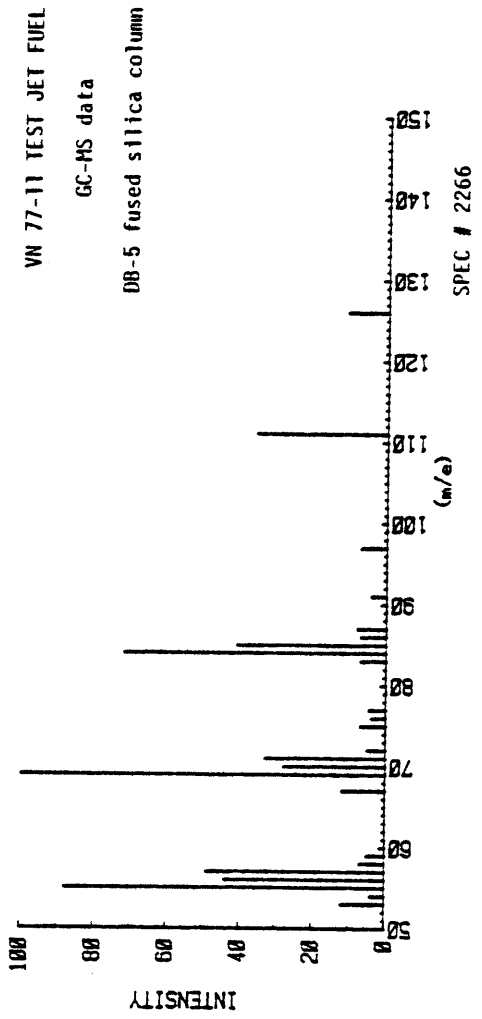
%	100	64	33	29	25	25	23	15
m/e	56	41	69	42	55	39	27	84

FIGURE 47a



methylcyclohexane

FIGURE 47b


VN 77-11 TEST JET FUEL
GC-MS data
DB-5 fused silica column
SPEC # 2266
INTENSITY
(m/e)

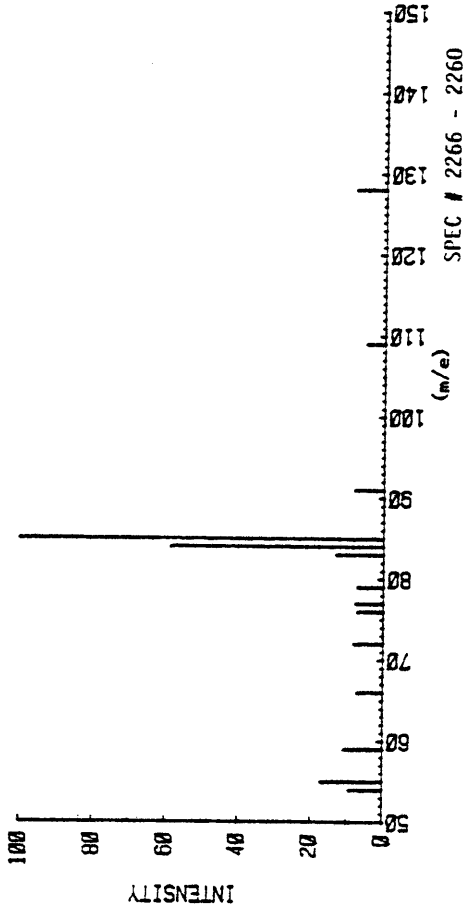

SPECTRAL SUBTRACTION
SPEC # 2266 - 2260
INTENSITY
(m/e)

FIGURE 48

times were to be expected. In looking for the m-xylene component, however, by GC-MS (using the DB-5 column) significant retention time shifts were observed, particularly for the aromatic m-xylene. In Figure 49 sections of the GC-FTIR Gram-Schmidt reconstruction for VN-77-11 near the m-xylene location are presented to illustrate these retention time differences for chromatography on the DB-1 and DB-5 capillary columns. The starred peaks for each section of the respective chromatogram correspond to the tentatively identified m-xylene. These sections originate from FTIR chromatograms previously run using the Model 36 IR cell and for the Nicolet 7199 IR system. The GC-MS data for the corresponding section of chromatogram added more uncertainty in locating the m-xylene since two individual peaks showed mass spectra indicative of a xylene compound (Figure 50). These peaks are located at mass spectrum #2291 and #2315 in the GC-MS total ion reconstructed chromatogram (Figure 46). The starred peaks indicate the component peaks of interest in the first half of the total ion chromatogram (presented for clarity). Since the splitting patterns and molecular ion masses for all three isomers of xylene (o, m, p) are nearly identical, an identification by GC-MS alone could not be made. An exhaustive file by file search of each FTIR run could find no other xylene near the m-xylene peak. Due to the fact that the mass spectrometer is more sensitive to aromatics than is FTIR, no confirmation could be made concerning the second aromatic "xylene-type" component. In the mass spectrum, because of the relative chemical stability of the aromatic xylene molecule (compared to an alkane),

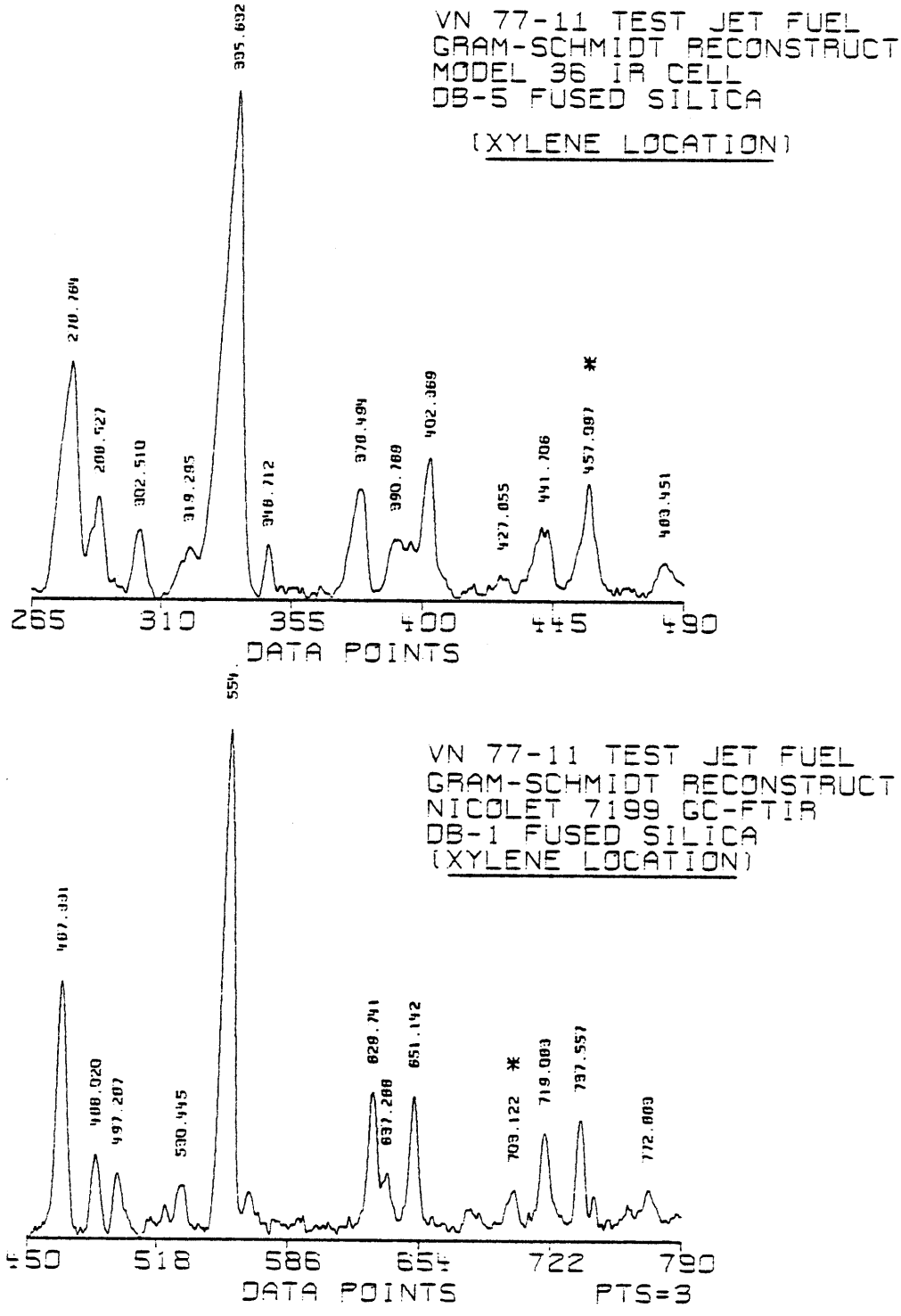

VN 77-11 TEST JET FUEL
GRAM-SCHMIDT RECONSTRUCT
MODEL 36 IR CELL
DB-5 FUSED SILICA
(XYLENE LOCATION)
335.692
210.764
208.527
302.510
319.295
348.712
370.494
390.789
402.369
427.855
441.706
457.997
483.451
265
310
355
400
445
490
DATA POINTS
554.
VN 77-11 TEST JET FUEL
GRAM-SCHMIDT RECONSTRUCT
NICOLET 7199 GC-FTIR
DB-1 FUSED SILICA
(XYLENE LOCATION)
407.391
408.020
497.207
530.445
629.741
637.288
651.142
709.122
719.083
737.557
772.883
450
518
586
654
722
790
DATA POINTS
PTS=3

FIGURE 49

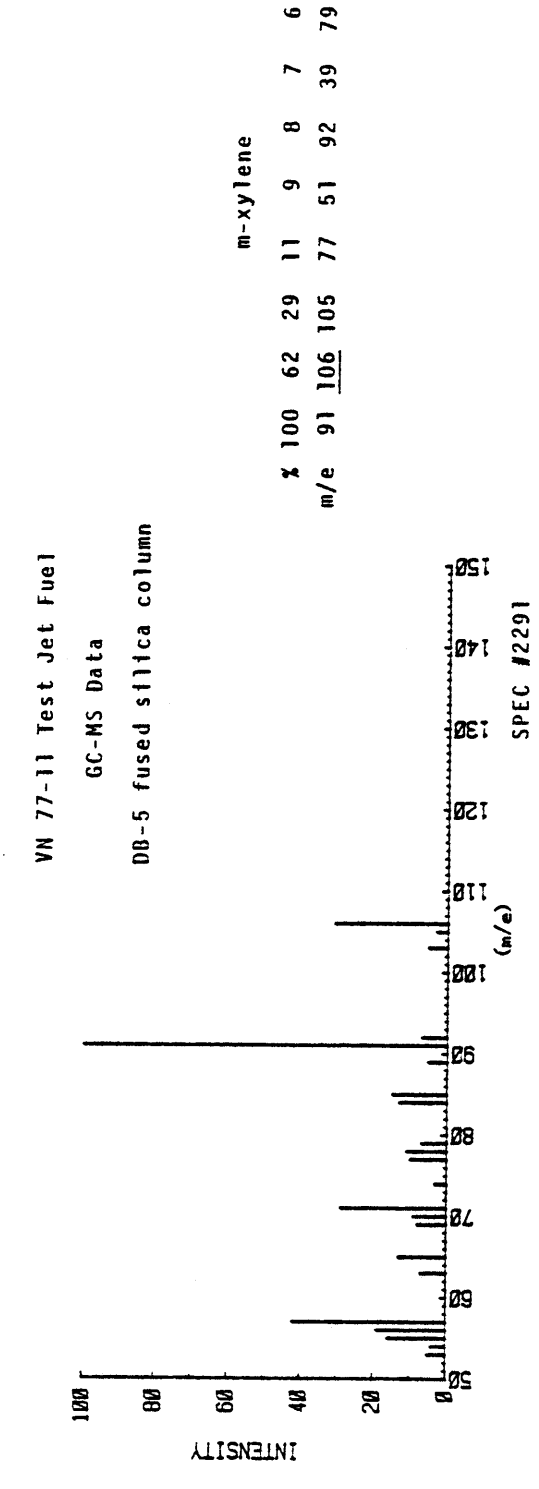

VN 77-11 Test Jet Fuel
GC-MS Data
DB-5 fused silica column
m-xylene
m/e % 100 62 29 11 9 8 7 6
91 106 105 77 51 92 39 79
SPEC #2291
SPEC #2315
INTENSITY
(m/e)

FIGURE 50

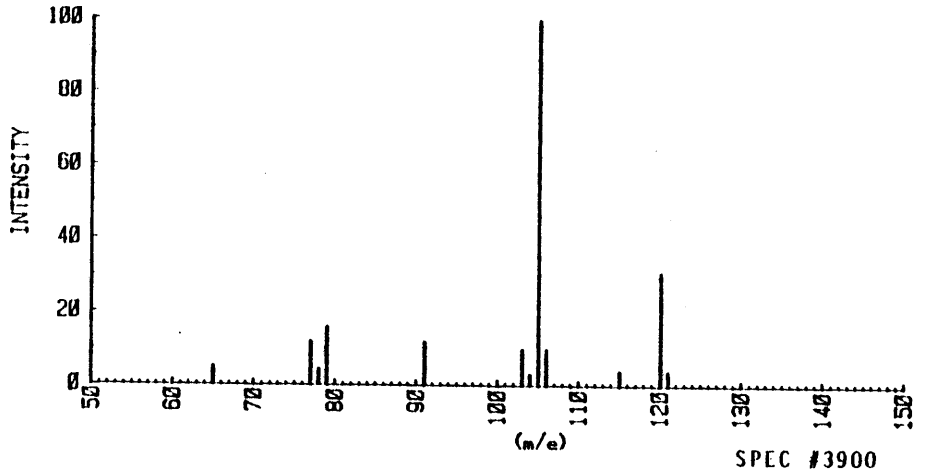
co-elution of a xylene with an alkane would still give an intense aromatic molecular ion intensity. Although a combination of GC-MS and GC-FTIR data may appear incomprehesible, the information which is discernable should not go without some merit. By having access to both sets of data one can surmise that an aromatic xylene is present according to the mass spectrum, and further, that this xylene can be distinguished from other xylene isomers by its characteristic infrared absorbance spectrum.

Another illustration of the mass spectrometer's sensitivity toward aromatics can be seen for spectrum #3900 (Figure 51) which corresponds to the starred component in VN-80-40 (Figure 52). Using a sample dilution of 10x in THF, a 0.02 µL equivalent was injected onto the GC-MS as compared to 0.023 µL (calculated) for the GC-FTIR Nicolet 7199 experiment. A good total ion intensity can be seen for this very low concentration component (Figure 52, starred peak). The splitting pattern and a molecular ion of 120 indicate that this compound is a substituted benzene, possibly o-ethyltoluene or isopropylbenzene. An FTIR library search of file spectrum #286, the corresponding peak, from VN-80-40 yielded uncertain results due to the poor S/N and baseline inconsistencies (Figure 53). Neither o-ethyltoluene nor isopropylbenzene are listed for the FTIR search although toluene-3,5-diisopropyl is listed as the second match using the AB algorithm. The spectrum of this match is, however, not very similar at all to the sample spectrum. Visually, however, the compound resembles 1,3,5-trimethylbenzene. Quite possibly, the two

VN 80-40 Aromatic Blend

GC-MS data

DB-5 fused silica column



o-ethyl toluene

%	100	31	10	10	9	9	7	6
m/e	105	120	77	91	106	79	44	103

isopropyl benzene

%	100	27	13	11	9	9	8	5
m/e	105	120	77	79	106	51	103	91

FIGURE 51

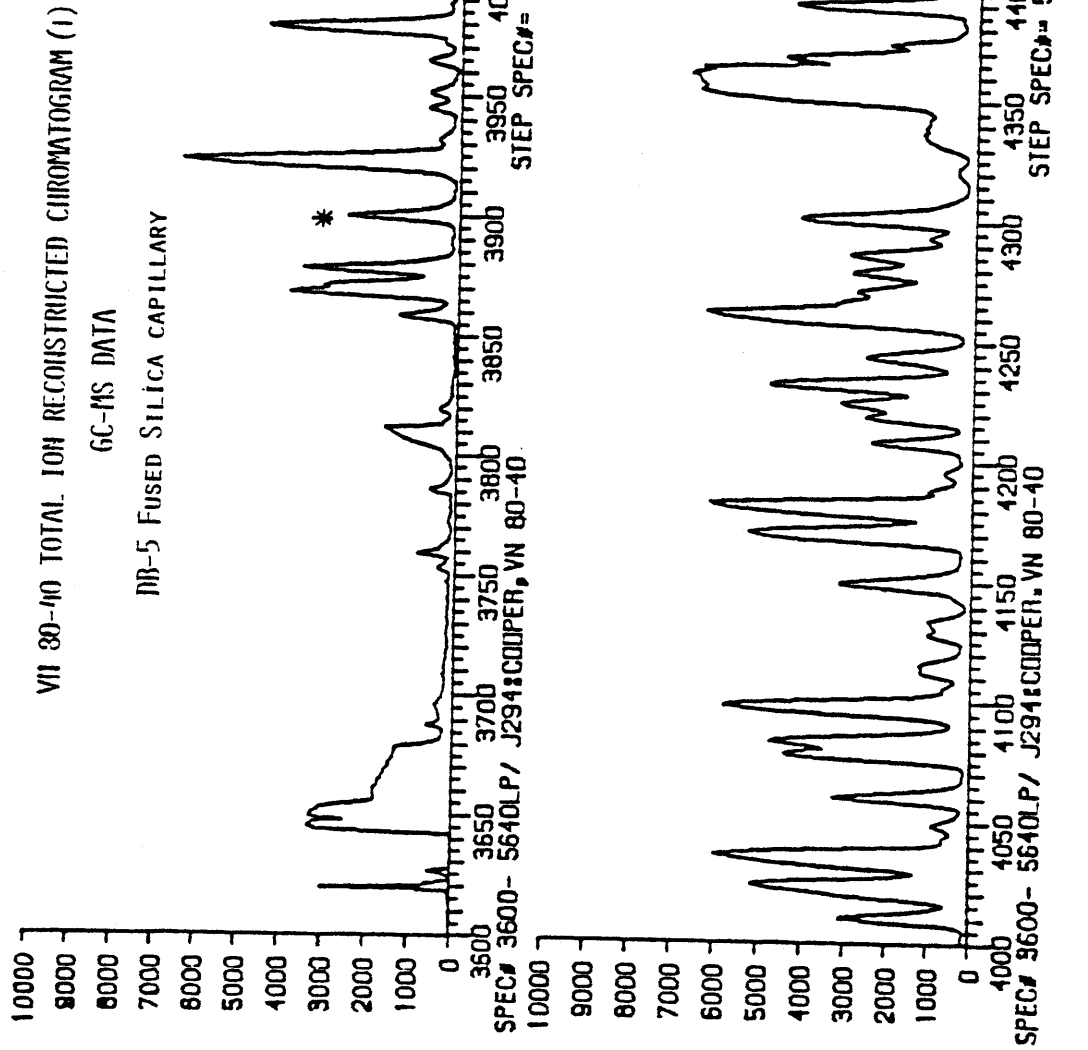

VII 80-40 TOTAL ION RECONSTRUCTED CHROMATOGRAM (1)
GC-MS DATA
DB-5 FUSED SILICA CAPILLARY
SPEC# 3600- 5640LP/ J294:COOPER, VN 80-40
STEP SPEC#= 5, INT=1000
SPEC# 9600- 5640LP/ J294:COOPER, VN 80-40
STEP SPEC#= 5, INT=1000

FIGURE 52a

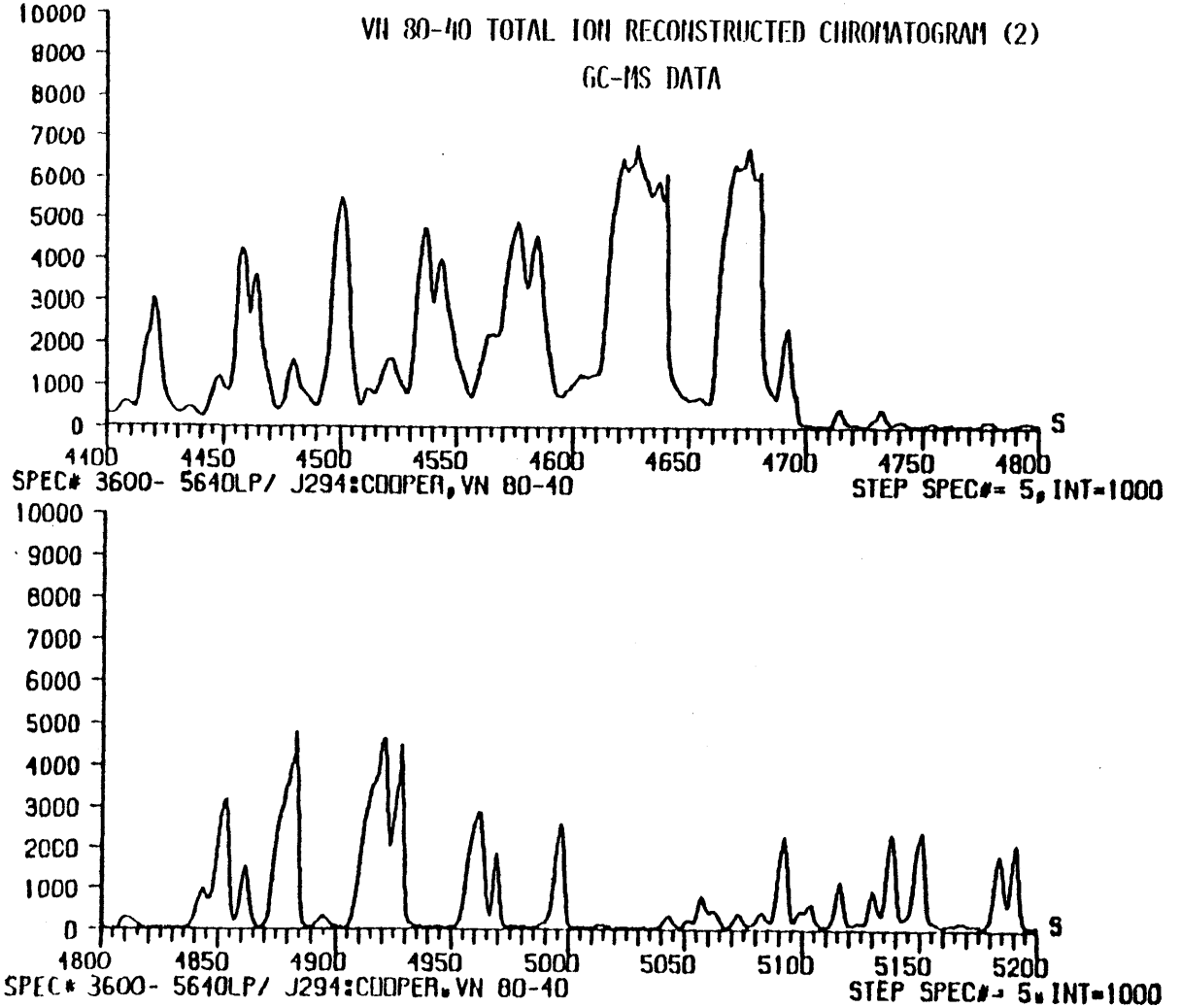

VN 80-40 TOTAL ION RECONSTRUCTED CHROMATOGRAM (2)
GC-MS DATA
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
4400
4450
4500
4550
4600
4650
4700
4750
4800
S
SPEC# 3600- 5640LP/ J294:COOPER,VN 80-40
STEP SPEC#= 5, INT=1000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
4800
4850
4900
4950
5000
5050
5100
5150
5200
S
SPEC# 3600- 5640LP/ J294:COOPER,VN 80-40
STEP SPEC#= 5, INT=1000

FIGURE 52b

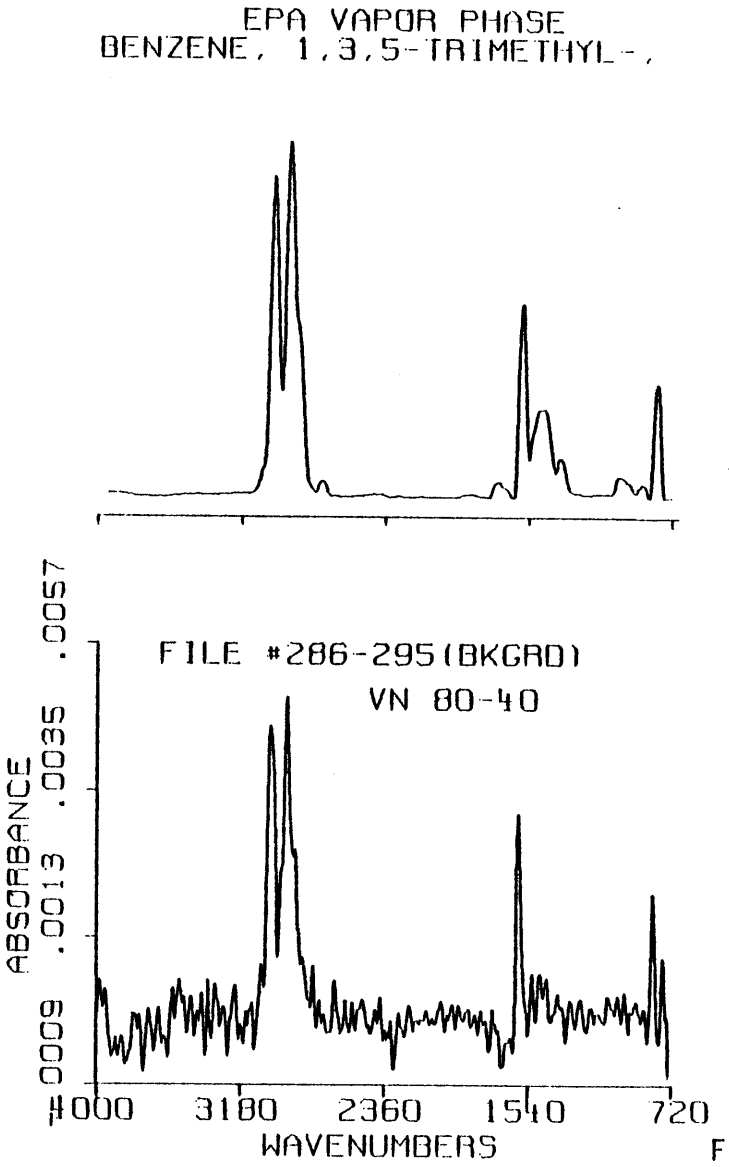


FIGURE 53

NICOLET 7199 GC-FTIR

```
SPA = AB
.SRQ
ENTER SKIP REGIONS, NEGATIVE NO. IF DONE
 LOW LIMIT 400
HIGH LIMIT 740
 LOW LIMIT 3600
HIGH LIMIT 4000
 LOW LIMIT -1
MAX FOR SCALING, NEG IF AUTO -1


EPA VAPOR PHASE
   POSSIBLE HITS
   371    BROMOFORM
      201    EYEE
  1026    TOLUENE, 3,5-DIISOPROPYL-,
      210    YR CY E
   907    BENZENE, CYCLOHEXYL-,
      212    L6TJ AR
  1960    METHANOL, TRI-2-NORBORNYL-,
      217    L55 ATJ 3/CXQ
   374    ETHANE, 1,2-DICHLORO-,
      219    G2G
   302    ETHANE, 1,1,1-TRICHLORO-,
      222    GXGG
  2654    BICYCLO/6.1.0/NONANE, 9,9-DIBROMO
      223    L38TJ BE BE
   402 .  BICYCLOHEXYL
      224    L6TJ A- 2
  2708    CYCLOHEXANECARBONITRILE, 1-PHENYL
      224    L6TJ ACN AR
  2759    HEXADECANE, 1,2-EPOXY-,
      224    T3OTJ B14
  1176    TETRACOSANE
      225    24H
  2655    CYCLOHEXANECARBONITRILE,
      225    L6TJ ACN AR D
   668    CYCLOHEXANETHIOL
      226    L6TJ ASH
  2721    1-OCTADECANETHIOL
      226    SH18
   420    CYCLOHEXANE, /2-BROMOETHYL/-,
      227    L6TJ A2E
```

aforementioned compounds are simply not in the FTIR library search file.

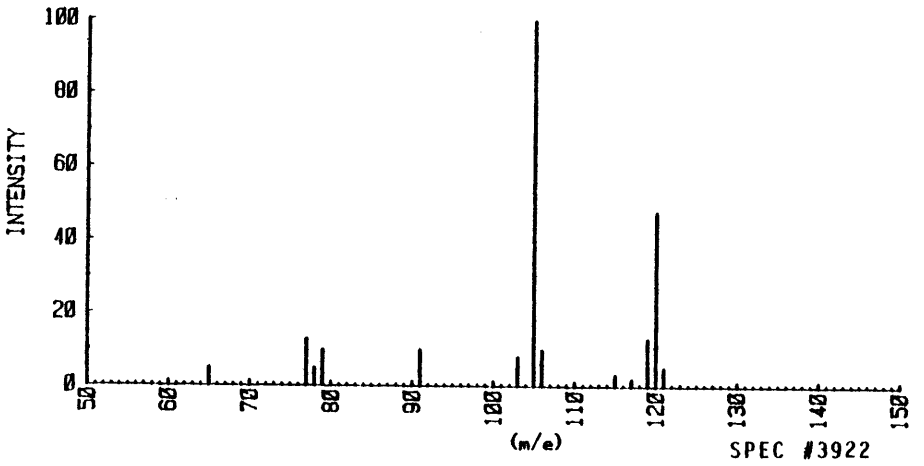
On the positive side of GC-FTIR methodology, Figure 54 confirms the presence of a trisubstituted benzene, although the corresponding GC-MS information cannot be certain as to which one. GC-FTIR has previously identified the VN-80-40 component as 1,2,4-trimethylbenzene (Figure 41) because of the difference in infrared absorbance patterns of trisubstituted benzenes. Figure 55 shows that the mass spectral data for two substituted polyaromatic hydrocarbons are indistinguishable by GC-MS. The assignment of spectrum #4670 to 1-methylnaphthalene and spectrum #4620 to 2-methylnaphthalene was only possible after reviewing previous GC-FTIR data for VN-80-40. The distinction between these two isomers in their infrared absorbance patterns has already been established and need not be repeated (Figure 43). Herein lies a significant advantage of GC-FTIR over GC-MS. While isomer analysis using GC-MS is often ambiguous, the often profound differences in absorbance spectra for a series of very similar isomers usually lead to a confident identification by GC-FTIR.

Since the Varian MAT mass spectrometer did not have available a library file, a 20 component standard mixture similar to the one used with the GC-FTIR experiments was separated by gas chromatography and individual mass spectra analyzed. The standards were used to check the calibration and accuracy of GC-MS data. For each component in the mixture an accurate m/e vs. intensity plot was observed which

VN 80-40 Aromatic Blend

GC-MS data

DB-5 fused silica column



1,2,4-trimethyl benzene

%	100	59	15	10	9	8	6	6
m/e	105	120	119	77	106	91	121	79

1,2,3-trimethyl benzene

%	100	54	12	10	9	8	7	6
m/e	105	120	119	77	106	91	79	39

1,3,5-trimethyl benzene

%	100	62	15	11	9	8	6	6
m/e	105	120	119	77	106	91	121	79

FIGURE 54

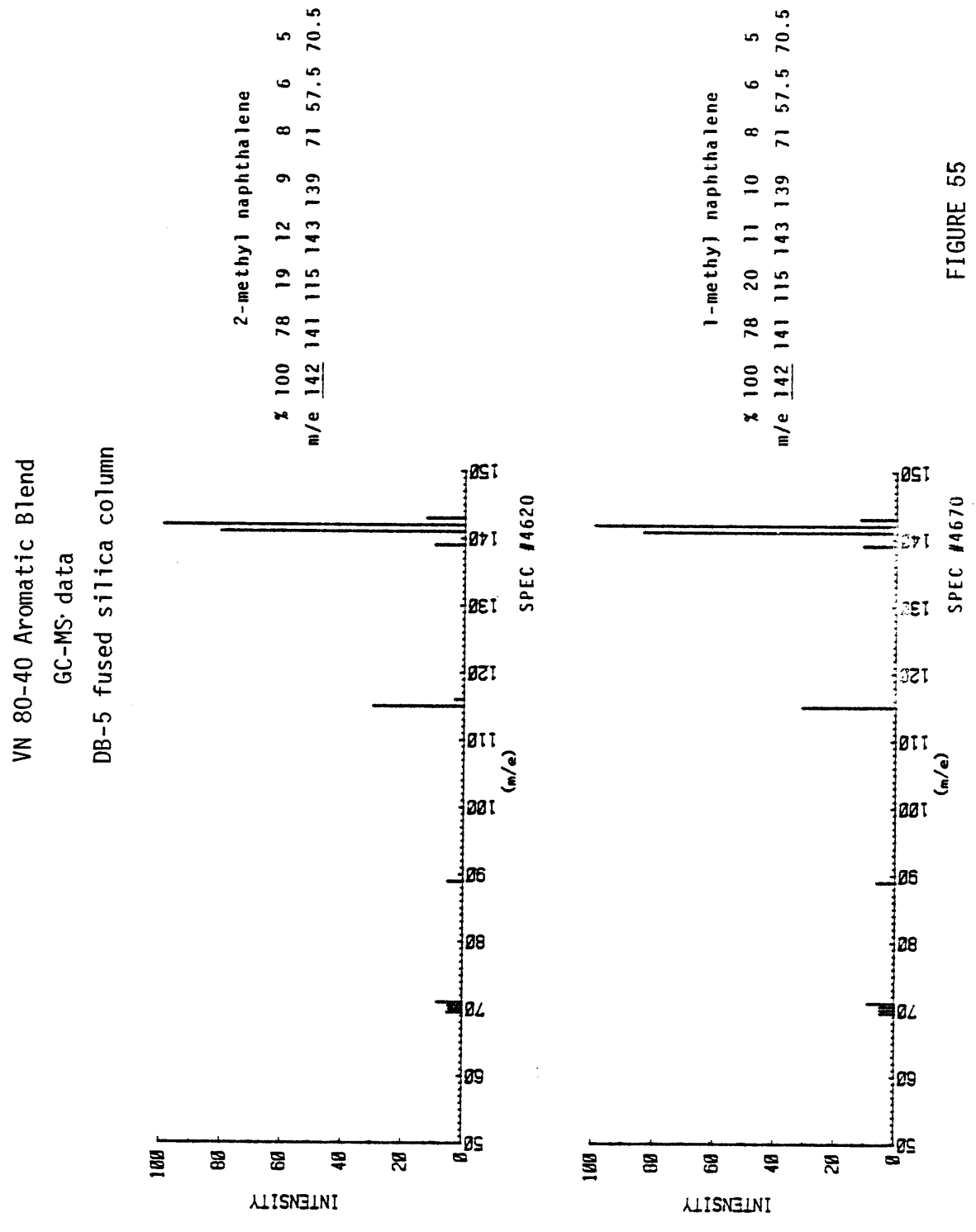

VN 80-40 Aromatic Blend
GC-MS data
DB-5 fused silica column
2-methyl naphthalene
% 100 78 19 12 9 8 6 5
m/e 142 141 115 143 139 71 57.5 70.5
SPEC #4620
INTENSITY
(m/e)
1-methyl naphthalene
% 100 78 20 11 10 8 6 5
m/e 142 141 115 143 139 71 57.5 70.5
SPEC #4670
INTENSITY
(m/e)

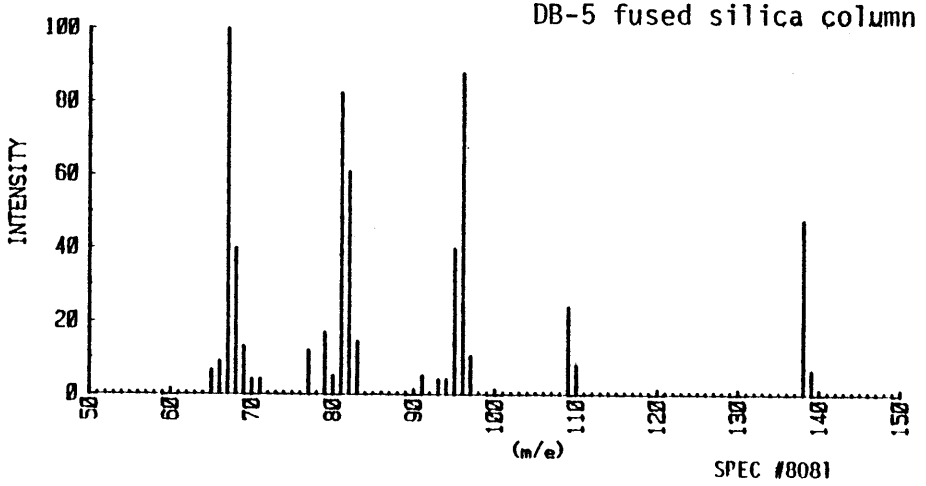
FIGURE 55

corresponded well to values listed in the Eight Peak Index of Mass Spectra tables[25]. Although relative m/e intensities did not generally match up perfectly, acceptable matches were possible taking into consideration the probable differences in instrument parameters such as source current, internal pressure and mode of ionization used to generate the reference data. It is quite common to see several mass spectral listings for the same compound, although the experimental conditions are not given. Two examples of standards that were run are given in Figure 56 with respective index entries. The mass spectra represent 25 ng of cis-decalin and 65 ng of o-ethyl-toluene. The listings to the right of each spectrum are the tabulated m/e intensities as referenced in Eight Peak Index of Mass Spectra[25]. The m-ethyltoluene listing (1-methyl-3-ethylbenzene) is included to illustrate the near identical spectral data obtainable for these isomers using GC-MS.

STANDARD MIXTURE

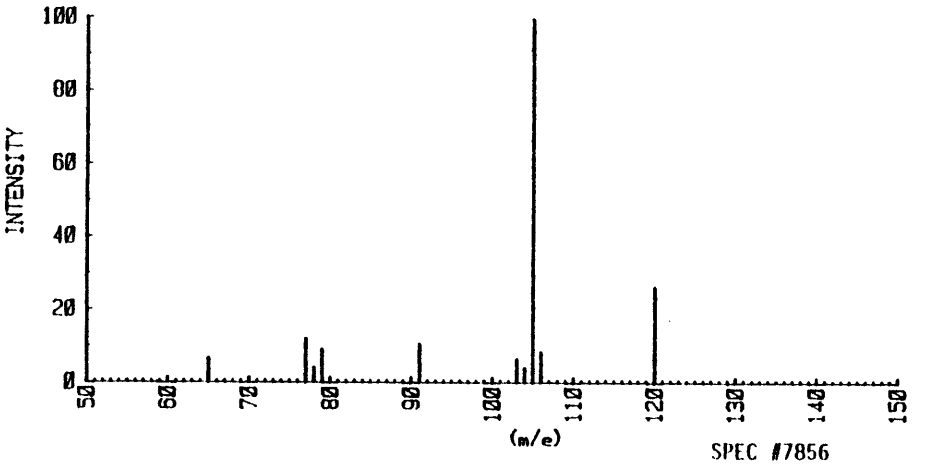
GC-MS data

DB-5 fused silica column



cis-decalin

%	100	91	87	86	60	56	48	47
m/e	67	41	81	96	82	95	39	138



o-ethyl toluene

%	100	29	9	9	9	8	6	6
m/e	105	120	77	91	106	79	39	103

m-ethyl toluene

%	100	29	9	9	9	8	6	6
m/e	105	120	91	77	106	79	39	51

FIGURE 56

CONCLUSIONS

The research accomplished thus far has shown that given optimum conditions and state-of-the-art equipment high quality infrared data can be generated from the separation of complex mixtures. While the focus has been on characterizing and identifying relatively non-polar compounds in jet fuel products, progress is anticipated in the detection of trace intermediate and/or polar compounds by GC-FTIR. Since fused silica capillary efficiency can be fully utilized, maximum resolution can, again, be achieved with more polar heteroatom containing compounds.

When designing and assembling the hardware necessary for GC-FTIR, attention should be focused on several aspects. Proper matching of lightpipe and MCT detector can give sensitivity in the low nanogram range. Shorter lightpipes with less dead volume may limit band broadening and increase throughput, but the loss in sensitivity may be more critical. While the Model 36 has 420 μL of dead volume and the 40 cm x 1 mm gold lightpipe has ~310 μL, band broadening appears to be minimal for both when a make-up gas of 4 to 5 mL/min is used. For use with gas chromatography, the MCT-B detector is generally not sensitive enough. No doubt with a longer, narrower lightpipe than the Model 36 (6 cm x 3 mm i.d.) throughput for an MCT-B would be unrealistically limited. A wider spectral range (4000-400 cm^{-1}) in the MCT-B case is however, certainly one advantage over the more narrow range MCT-A+ (4000-700 cm^{-1}) when infrared information is available below 700 cm^{-1}.

For less ambiguous and/or confusing infrared data, several FTIR scans per component peak should be attempted. The use of a rapid-scan mode which allows coadding of data in a time frame approaching fractions of a second is necessary when separating multicomponent mixtures on capillary columns. For best S/N, as many scans as possible should be coadded and ratioed against a background file. At a VEL of 50 (rapid-scan), 10 scans coadded and ratioed to 40 coadded background scans takes close to 1 second for real time "on-the-fly" data acquisitions. A one second per data file time frame is very useful for interpreting coeluting components although data storage space can be used up rapidly.

Interferences from atmospheric gases plague the FTIR experimental results either from masking essential IR regions or from creating an unstable, changing baseline throughout the experiment. Standing vibrations whether caused from the interferometer itself or externally can lead to eradict baselines and ruined data. The process of subtracting out such anomalies is many times a source of irreproducible errors and may change the actual spectral results. Base-line correcting of spectra can also lead to confusing "match results" when using the spectral search routines.

FTIR as a selective detector is very powerful in elucidating functionality, often by simply monitoring the real time on-the-fly CHEMIGRAM. User specified infrared windows can be used to selectively assemble chromatograms based solely on functional group infrared

absorbance. In comparing capillary GC-FTIR with GC-MS, one realizes the respective advantages of each as a separate analytical tool. Together, one method can fill the information void left by the other. For analysis of jet fuel type samples, molecular weight and splitting patterns from MS analysis can be an asset when extremely low quantities of unknown make FTIR detection difficult. In the analysis of aliphatic hydrocarbons, limited GC-FTIR spectral information can sometimes lead to ambiguous identifications. The mass information of GC-MS can be invaluable here also. When concerned with isomer analysis, whether for aliphatic or aromatic species, infrared absorbance differences are as varied as substitution patterns. Gas phase FTIR can readily distinguish most isomers whereas, mass spectral information is often ambiguous.

In reference to possible detection limits with the FTIR systems used, the 7199 system is at least 20 or more times as sensitive as the Nicolet 6000 (Model 36) system. The combination of a longer, narrower lightpipe and a detector giving better S/N account for this difference in performance. While the dual-beam characteristics of the 7199 do not add to this difference, use of a properly designed effluent transfer system from GC to lightpipe is very important. Use of an external lightpipe and detector bench is convenient to use and temperature control of the transfer system can be more adequately managed. For an optimized GC-FTIR system, tens of nanograms of a weakly absorbing aromatic component can be readily detected. Generally, the GC-MS

sensitivities are related to stability of the parent (molecular) ion. Aromatics can, therefore, be detected at much lower concentrations than FTIR because of the benzene ring stability. Roughly an order of magnitude can separate MS sensitivity from FTIR for these weak absorbers. For other compounds this discrepancy will close rapidly depending on the intensity and stability of molecular bending and stretching infrared absorbing vibrations.

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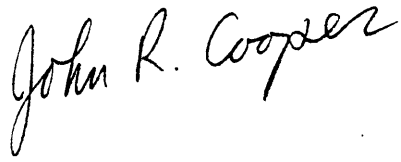
VITA

John R. Cooper was born on the 3rd day of July, 1957 in District Heights, Maryland. He received his high school diploma from Suitland Senior High School in 1975 and a Bachelor of Science degree from Lynchburg College, Lynchburg, Virginia in 1979 with a major in chemistry. After working for a small analytical laboratory in Silver Spring, Maryland for 15 months, he came to Virginia Polytechnic Institute and State University to pursue an advanced degree in Chemistry. Completion of the requirements for the degree of Master of Science was accomplished in September, 1982.



OPTIMIZATION OF CAPILLARY GC/FTIR FOR COMPLEX SAMPLE ANALYSIS

by

John R. Cooper

(ABSTRACT)

Optimization of capillary gas chromatography-Fourier Transform Infrared (GC-FTIR) spectrometry has been accomplished by studying various columns, lightpipe designs, FTIR detectors and spectroscopic parameters. For adequate separation of complex samples the efficiency of WCOT (Wall Coated Open Tubular) fused silica capillary columns was found to be unmatched by packed columns or wide bore glass capillaries. A consequence of using more narrow bore columns, however, is lower sample capacity and less IR detectability. Two 6 cm lightpipes and a more narrow 40 cm lightpipe were compared with respect to both optical throughput and eluent band broadening. FTIR spectroscopic parameters such as mirror velocity and number of scans coadded were examined in order to achieve an optimum signal to noise ratio. The complexity of a particular sample has been shown to dictate certain spectroscopic parameters. The sensitivity differences of two liquid-nitrogen cooled FTIR detectors used in the GC-FTIR experiments have been determined with reference to using them with either a long or short lightpipe.

The capability of optimized capillary GC-FTIR has been demonstrated in the analysis of model compound mixtures and complex petroleum products including test aviation jet fuels. Major attention

was given to the detection and identification of aliphatic and aromatic components in the highly complex samples. Computerized library search routines have been used to tentatively identify eluting components by infrared spectral matching to quality vapor phase library file spectra. Gas chromatography-mass spectrometry (GC-MS) data are also included for the same jet fuel samples to directly compare extent of information provided and relative spectroscopic sensitivities.