INTRODUCTION

In indirect coal liquefaction, coal-derived gases (hydrogen and carbon monoxide) are converted to liquids which have the potential for production of premium liquid fuels. A number of variations of the Fischer-Tropsch (F-T) process can be used in the liquefaction step. Although improvements are being made, these processes typically suffer from insufficient selectivity; hydrocarbons ranging from methane to high molecular weight paraffinic waxes are produced. Fischer-Tropsch product distributions can be given by the Anderson-Schultz-Flory polymerization law in which probability of chain growth is independent of carbon number. Although non-Anderson-Schultz-Flory selectivity has been reported in the literature and synthesis of catalysts to achieve high selectivity is an active area of research, it is likely that this problem with selectivity will persist, and upgrading of wax by-products will be required.

Although low molecular weight products from Fischer-Tropsch processes have been extensively characterized, this is not true for the high molecular weight waxes. Available information indicates that the wax composition depends on run conditions and can consist of very high molecular weight saturates, olefins, and oxygenates. Most previous work on analysis or characterization of Fischer-Tropsch waxes involved determination of average molecular composition such as degree of branching determined by nuclear magnetic resonance (NMR) spectroscopy or infrared (IR) (1-4), or determination of average molecular weight or molecular weight distribution by gas chromatography (GC) and/or gel permeation chromatography (GPC) (5-7). In other reported work, the analytical data were correlated with physical properties such as phase behavior (8) or degree of crystallinity (6,9-11). No references were found on the detailed composition of Fischer-Tropsch waxes.

Although much of the work on analysis of waxes from petroleum, tar sands, peat, coal, and plants has involved determination of average structures or functional groups, considerable work on detailed analysis of these other waxes has been reported including recent studies employing gas chromatography (GC) (12), GC/mass spectrometry (MS) (13), field ionization (FI) or field desorption (FD) MS (14), and chemical ionization (CI) MS (15). Many Fischer-Tropsch waxes contain significant quantities of compounds with insufficient volatility for analysis by GC or GC/MS, or by FIMS and CIMS using conventional batch inlet system sample introduction techniques. Combination of FIMS (or

CIMS) with sample introduction by probe microdistillation (PMD) extends the upper limit on compound boiling points from about 500° C to about 700° C. FDMS extends the upper limit much farther with considerable promise for analysis of wax components with molecular weights of about 2000 amu (14).

The objective of this project was to develop methods for the characterization of these high molecular weight waxes. Techniques developed will allow improved characterization of Fischer-Tropsch waxes, thereby leading to (1) improved understanding of the Fischer-Tropsch process and (2) improved understanding of the processing required to upgrade the waxes into higher value products.

EXPERIMENTAL SECTION

Sample Description and Preparation

The Fischer-Tropsch (F-T) waxes selected for development of the analytical techniques herein described were from two pilot plant units operated by Mobil and by Union Carbide. Two commercial waxes were also obtained but were not extensively analyzed. A wax produced in a commercial Arge fixed-bed reactor (Sasol) would have been a desirable candidate for analysis, but attempts to obtain this material were unsuccessful.

The Mobil sample (identified as Mobil wax #4) was a composite of runs CT-256-9, -11 and -12 made under their contract entitled "Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels." The runs were made in their slurry catalyst bench scale unit in the low methane + ethane high reactor-wax mode.

The Union Carbide wax was produced in a small fixed-bed bench-scale unit used in Union Carbide's development of bifunctional F-T catalysts (promoted cobalt intimately contacted with proprietary shape selective molecular sieves). Some initial analyses were run on the whole product, but most of the analyses were run on material which was topped (172° C, 1 mm Hg) with a spinning-band distillation apparatus to remove the lighter material (up to about C_{22}).

The two commercial waxes were hydrotreated Arge waxes (FT-200 and FT-300, upgraded by Huls of West Germany, and marketed in the United States by Durachem, Harrison, NY).

HPLC Instrumentation and Procedures

A Spectra-Physics 8000 liquid chromatograph was adapted for operation at elevated temperatures. The injection valve and the inlet tubing were maintained at 75° C with heating tape, the precolumn filter and column were placed in the SP8000 oven, and the detector was maintained at 60° C by a circulating water bath. A Waters R401 differential refractometer was the detector. The initial chromatographic column for neutral-polar separations was a semi-preparative size (1.0 cm i.d. x 25 cm) containing Davisil 710 silica gel (mean pore diameter, 60 Å; surface area, 480 m^2/g). The column was preconditioned by washing with ethyl ether and toluene. The initial mobile phase chosen was heptane.

In an attempt to minimize molecular size exclusion effects, a second column was packed with Davisil 643 silica (pore size, 150 Å; surface area, 300 m^2/g). The column tube (1.0 cm i.d. x 50 cm) was packed by the viscous slurry technique. Preconditioning and activation of the column were carried out by washing with ethyl ether and toluene in succession, with a final wash with heptane before use.

Preliminary column evaluations were carried out with heptane as eluant at temperatures ranging from 21° to 80° C with toluene, nonadecylbenzene, 1-dodecanol, and 1-tetradecanol as reference compounds. A second series of elution trials was made with 1 or 2% (vol) of 1-propanol in heptane as eluant. Wax samples were separated on the second column (packed with Davisil 643 silica) by injection of 0.1 to 0.4 grams of the sample (dissolved in heptane) on the column with 1% (vol) 1-propanol in heptane as eluant. The flow rate was 4 mL per min. Column temperature was either 65° or 80° C. Multiple separation runs were made to produce sufficient quantities of fractions for further separation and analyses.

Separation of the neutral fraction into alkanes and alkenes was accomplished using a silver-loaded, sulfonic-acid-bonded, wide-pore silica, semi-preparative column (1.0 cm i.d. x 50 cm) in the Spectra-Physics 8000 liquid chromatograph. The mobile phase was 0.5% (vol) toluene in heptane. Other

conditions were flow rate, 4 mL per min; column temperature, 60° or 80° C; and detector temperature, 60° C. Again, several separation runs were necessary to produce sufficient quantities of fractions for later experiments. A schematic showing the overall separation scheme and yields for the topped Union Carbide F-T wax is depicted in Figure 1.

NMR Data Acquisition

The solubility of Mobil wax #4 in common NMR solvents such as deuterated chloroform ($CDCl_3$) was very limited. A sample of the wax and n-decane (Aldrich Gold Label, 99+%) was weighed and sealed in a 10 mm NMR sample tube under vacuum. The sample was 28.77% Mobil wax #4 by weight. The NMR spectra, both proton and carbon-13, were obtained on the sample at a temperature of approximately 150° C (the temperature was controlled to ±0.3 C, but the precise sample temperature is unknown). At this temperature the wax and decane formed an apparent clear solution.

The proton and carbon-13 spectra were acquired using a JEOL GX270 wide-bore Fourier transform (FT) NMR spectrometer. The spectrometer operates at 270.17 MHz for protons and 67.94 MHz for carbon-13. The proton NMR spectral parameters for the Mobil wax solution were 4000 Hz spectral bandwidth and 8K points (the data set was zero-filled once before processing). A 45° pulse (11 us) was used with a 5.0-second delay between pulses. The carbon-13 spectral parameters for the solution were 16,025.6 Hz bandwidth and 16K points (zero-filled once before data processing). A 45° pulse (8 μs) was used with a 30-second delay between pulses. Gated decoupling during acquisition was used to achieve quantitative results. A total of 512 scans was accumulated for the proton spectra, and 2000 scans were accumulated for the carbon-13 spectra.

The proton and carbon-13 spectra of the neat n-decane, with a trace of tetramethylsilane (TMS), were also obtained to serve as a solvent blank. These spectra were obtained at a temperature of 27° C. The same spectral parameters were used for the neat decane spectra as specified above for the wax solution.

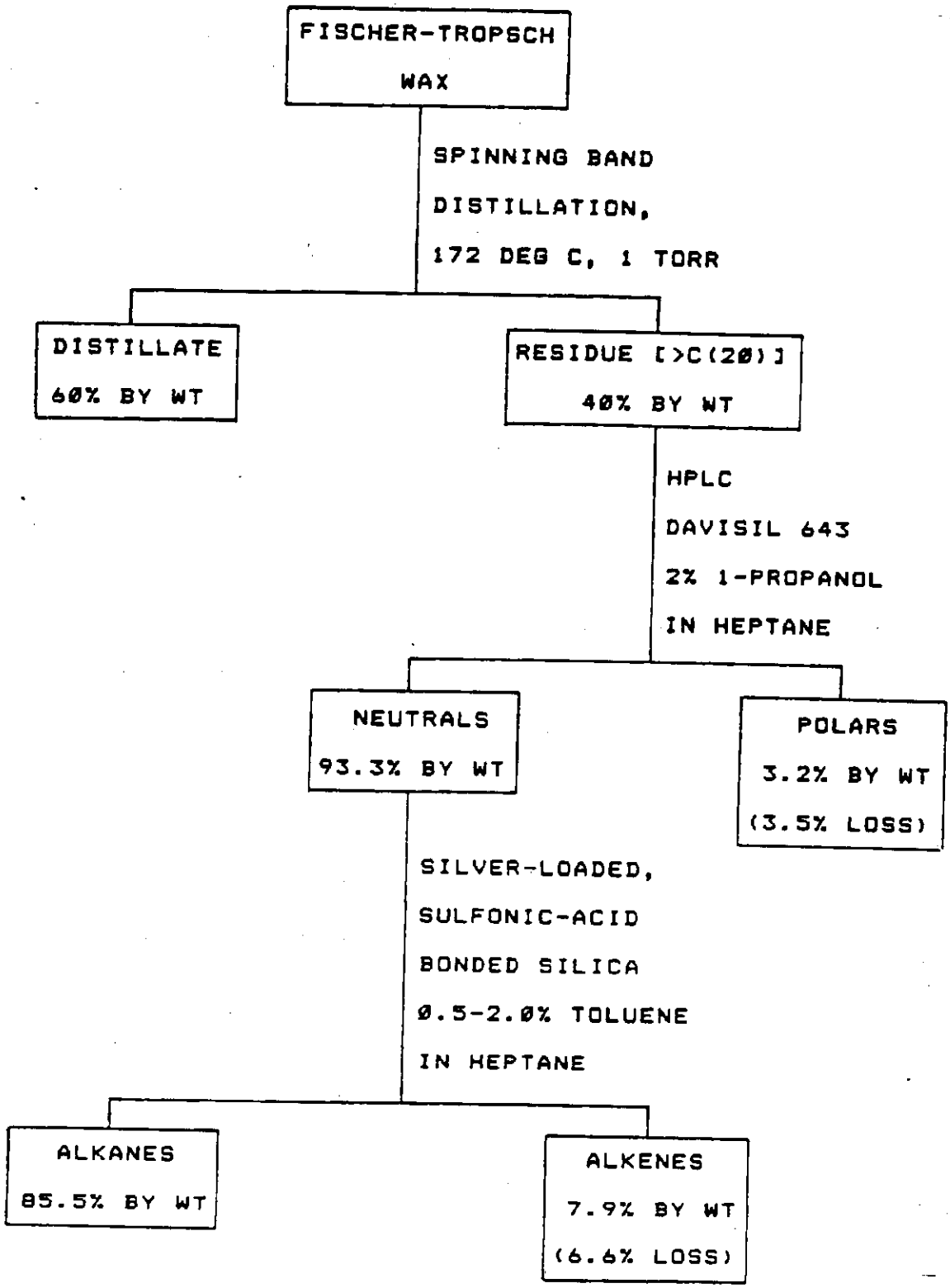


FIGURE 1. - Scheme for separation of Union Carbide Fischer-Tropsch wax.

Using the carbon-13 cross-polarization/magic angle spinning (CP/MAS) accessory, spectra of the neat wax in the solid phase were obtained. Several spectra at different sample spinning speeds varying from 3100 Hz to 4200 Hz were recorded to help differentiate spinning sidebands from true spectral peaks. The carbon-13 spectral parameters used for the solid wax sample were: 20,000 Hz spectral bandwidth, with 4K points. A 3.0-second delay between pulses was used. A 90° pulse (6.0 μs) with a 10 ms contact time was used for the CP/MAS sequence. A total of 19,660 scans was accumulated for each spectrum. Also, a spectrum of the empty Delrin sample rotor was obtained under the same experimental conditions to serve as a blank.

Alkane and alkene fractions separated from the Union Carbide wax were solubilized in hot CCl_4 (~65° C) and placed in a 5 mm C/H probe. The sample temperature was controlled at 60° C ± 0.2 during data acquisition in the spectrometer. A total of 64 scans was accumulated for the proton spectra using the single pulse, non-decoupled mode with a 62° pulse (11.0 μs) and a 5.0-second delay between pulses. The frequency bandwidth was 4000 Hz and 8K points were digitized. A total of 1200 scans was accumulated for the carbon-13 spectra using the single pulse, bilevel decoupling mode for proton decoupling. A 45° pulse (4.3 μs) with a 3.0-second delay between pulses was used, and a frequency bandwidth of 16,025.6 Hz with 16K points was digitized. The data were zero-filled once before transforming. Due to excellent spectrometer magnet stability, operation in the unlocked mode during the 70 minutes required for the carbon-13 data acquisition presented no problems.

Mass Spectral Data Acquisition

Mass spectral data were acquired on samples of the F-T waxes and separated fractions using a Kratos MS-50 high resolution mass spectrometer equipped with a high field magnet and a Kratos DS-55 data system, with sample introduction by probe microdistillation. Approximately 0.3 to 1.0 mg of sample was weighed in a capillary tube and placed in a quartz direct-introduction probe having a temperature range from -150° to +600° C (16,17). Typically, the wax samples were distilled into the ion source over a temperature range from about -70° to +300° C at a rate of 10° C/min. In later experiments, the temperature was increased by the temperature programmer at a variable rate to maintain constant ion current. Ionization was accomplished

via one of three different modes: 1) 70 eV electron impact, 2) low eV (approximately 10 eV or 20 eV) electron impact, or 3) field ionization. The ion source temperature was maintained at 300° C. Resolving powers from 5000 to 10,000 were achieved at scan rates of 10 seconds/decade (s/d) to 100 s/d. The mass range was typically 58 to 900 amu, with one experiment having a range from 58 to 1800 amu. Approximately 50 to 100 spectra were acquired in a typical run. Mass calibration was accomplished using perfluorokerosine (PFK) and PFK plus Ultramark 1621 for the 70 eV runs, a mixture of halogenated aromatics for the low eV runs, and a simple mixture of reference compounds along with prominent sample ions (after identification) for the field-ionization runs. Calibration mixtures were introduced through an all-glass heated inlet system (R. J. Brundfeldt, Inc., Bartlesville, OK) throughout the probe microdistillation mass spectral run. Samples were weighed before and after the experiment to determine the percentage distilled off the probe. The mass spectral data were processed using computer programs developed in part in this study and described in detail in Appendix A.

RESULTS AND DISCUSSIONS

For a preliminary determination of the molecular weight distributions in these samples, simulated distillations (SD) were run using a modified proposed ASTM lube oil method. Typical chromatograms are shown in Figures 2 and 3; weight percent distilled versus temperature data are summarized in Table 1. The first three peaks in the chromatograms shown in Figure 1 correspond to n-C_{10}, n-C_{11}, and n-C_{12} paraffins which were added as internal standards. The levels of material distilling below 1150° F (corresponding to n-C_{60}) were 42.6, 66.4 and 45.1% for Mobil wax #4, FT-200 and FT-300, respectively. The composite Mobil wax is a wide-boiling-range material with normal paraffins beginning at about carbon number 12. The FT-300 wax is conspicuous in the absence of significant paraffins below about C_{30}. The FT-200 wax appears to be a blend of a lower boiling paraffin fraction with the FT-300 or a similar wax based on the chromatograms alone.

The chromatogram of the topped Union Carbide wax, shown in Figure 3, clearly shows n-alkane peaks from C_{21} to C_{65}. Eighty-three percent of the material distills below 1150° F.

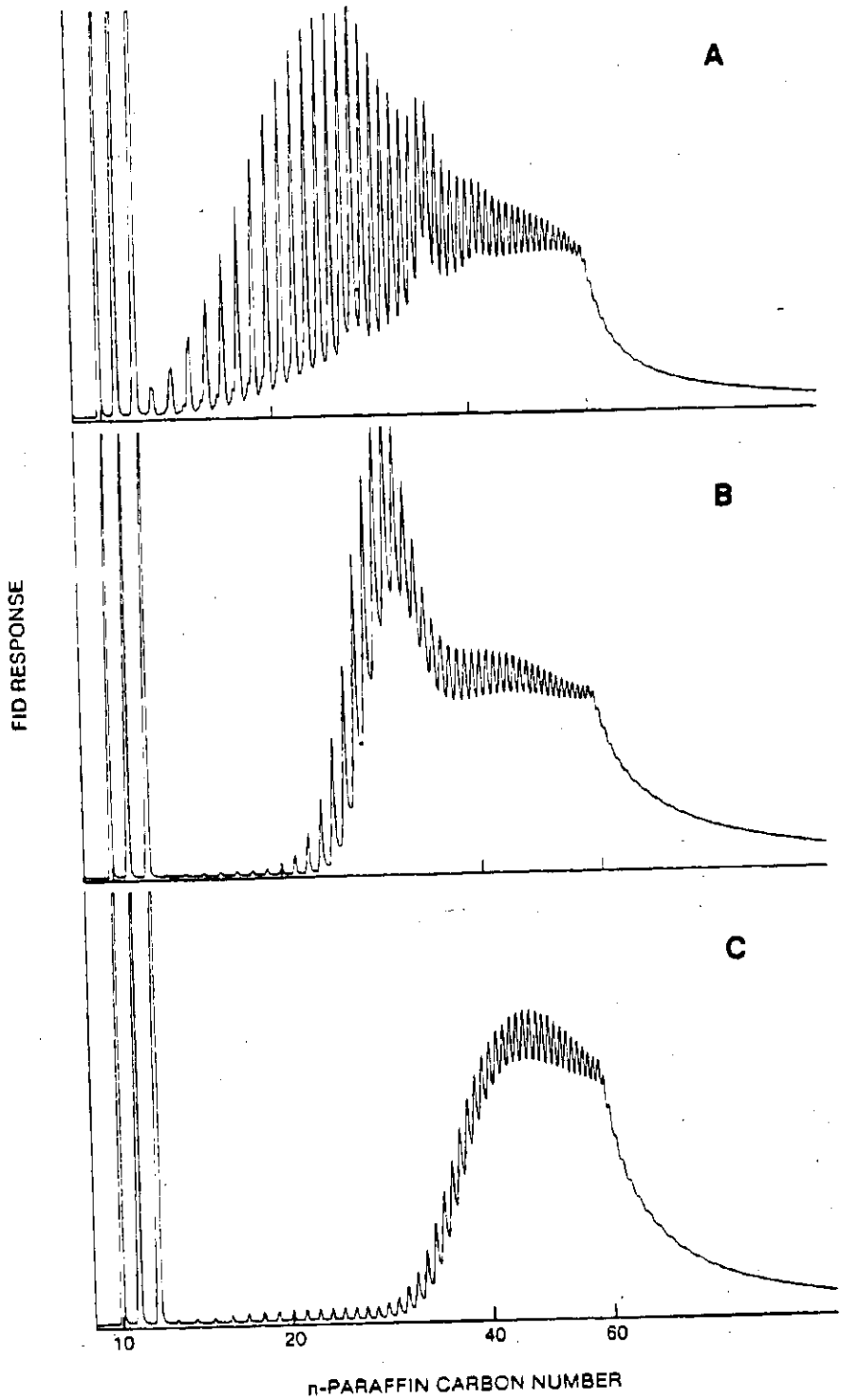


FIGURE 2. - Simulated distillation chromatograms for Fischer-Tropsch waxes; (A) Mobil #4 composite of runs CT-256-9, -11, and -12; (B) commercial FT-200; and (C) commercial FT-300. n-C_{10}, n-C_{11}, and n-C_{12} used as internal standards.

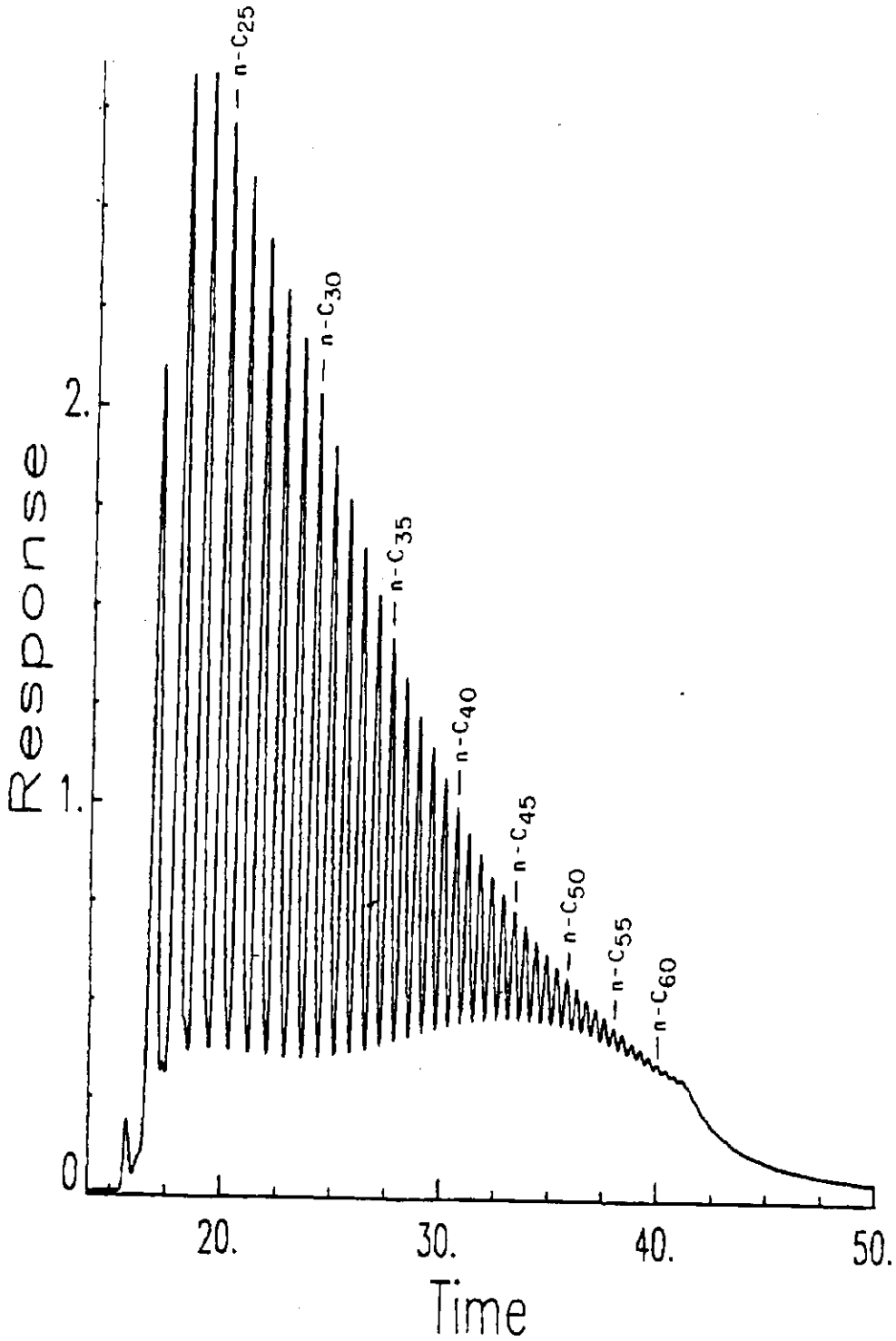


FIGURE 3. - Simulated distillation chromatogram of topped Union Carbide F-T wax.

TABLE 1. - Temperatures corresponding to percent off from simulated distillation of F-T wax samples using the Lube Oil method. Temperature in degrees centigrade.

Weight Percent Off	Mobil Wax #4	FT-200	FT-300	Topped Union Carbide Wax
IBP	251.7	390	234	364.3
1.0	290.3	402.3	436.2	366.3
5.0	344.9	419.9	498.6	377.9
10.0	388.9	428.9	520.2	387.5
15.0	417.0	434.9	537.6	396.5
20.0	441.8	442.9	553.4	406.7
25.0	473.7	448.6	568.9	419.4
30.0	497.9	455.3	584.6	431.5
35.0	533.7	461.8	600.7	442.1
40.0	581.2	471.0	617.7	453.6
45.0	621.9[1]	483.7	636.3[3]	479.8
50.0		502.5	636.5	496.2
55.0		525.2		509.7
60.0		551.3		529.3
65.0		590.4		547.9
70.0		608.1[2]		572.1
75.0				604.1
80.0				629.0[4]

[1]Endpoint, 42.6% distilled off.

[2]Endpoint, 66.4% distilled off.

[3]Endpoint, 45.1% distilled off.

[4]Endpoint, 82.8% distilled off.

Supercritical fluid chromatography (SFC), provided by Herbert E. Schwartz of Applied Biosystems, Santa Clara Division, was used to obtain data on higher molecular weight materials (18). The chromatogram for the Mobil wax, shown in Figure 4, clearly shows n-alkane peaks to C_{90} and beyond. The C_{50} n-alkane was added to the sample as a spike to aid in peak identification, and the attenuation was changed to a more sensitive level for the C_{52} and later peaks. These SFC results using a packed column system were considerably improved, particularly at the higher carbon numbers, over results for this sample using SFC with a capillary column.

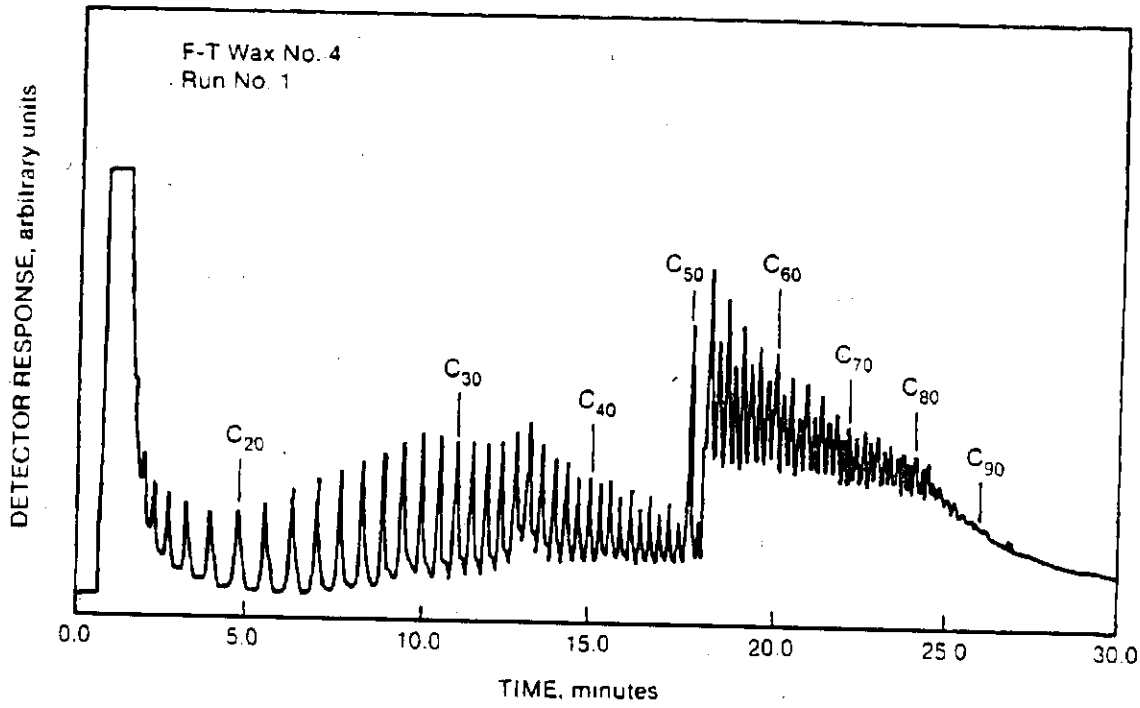


FIGURE 4. - Supercritical fluid chromatogram of Mobil wax #4 on packed column. Result from Santa Clara Analytical Division of Applied Biosystems. n-C_{50} was added as a spike, and the attenuation was changed at about 18 minutes.

The proposed lube oil method (packed-column, with 380° C maximum temperature) is limited to elution of sample below the boiling point of C_{60} (1150° F). As the SFC/SD profile shows, an additional 20 to 30% of the sample boiling point distribution can be obtained using methods such as SFC. An alternative method, high temperature GC, using special equipment that can reach an oven temperature of 450° C, has allowed elution of F-T waxes to C_{120}. It is presently unclear whether sample decomposition occurs at these high temperatures. SFC, which is typically performed below 150° C, appears to offer the promise of better boiling point information without the possibility of sample decomposition.

Fractionation of Waxes

Much of the fractionation of waxes which has been reported in the literature has involved separation by molecular weight, either by solubility or by

gel permeation chromatography. In contrast, we have attempted to separate by functionality using high performance liquid chromatography (HPLC). The objective was to obtain polar/oxygenate, alkene, and alkane fractions. This requires two separations: the first to separate the polar/oxygenates from the alkanes/alkenes and the second to separate the alkenes from the alkanes.

Due to the limited solubility of F-T waxes, a Spectra-Physics 8000 liquid chromatography instrument was adapted for operation at elevated temperatures. Solubility temperatures for the F-T waxes are indefinite since they are related to the desired concentration. Generally, temperatures of 60-80° C were used.

The Davisil 710 silica column was evaluated initially for the first stage of fractionation (i.e., separation of the polar materials from the neutrals or alkanes/alkenes). Table 2 shows capacity factors of toluene and nonadecylbenzene, both relative to hexadecane as unretained saturate. Temperatures are those maintained in the column oven.

TABLE 2. - Capacity factors on Davisil 710, heptane carrier

Temperature, °C	Toluene	Nonadecylbenzene
23	1.35	not determined
50	0.86	0.61
65	0.68	0.47
80	0.55	0.37

The capacity factor for toluene at 23° C is a normal value for chromatography on activated silica. At the higher temperatures, adsorption (and therefore resolution) of toluene diminishes. Nonadecylbenzene shows the same trend with temperature and also indicates the effect of a large alkyl group in reducing retention. Together, these observations may indicate potential problems in the separation of aliphatic and aromatic hydrocarbons and oxygenates in Fischer-Tropsch waxes. To investigate these potential problems, chromatograms of analytical sized samples of Mobil and Union Carbide wax were run at column temperatures of 80° C and 65° C, respectively.

The Mobil wax showed a single peak with first deflection from baseline at 5.2 min and peak at 7.4 min. For comparison, hexadecane showed first deflection at 7.3 min and peak at 7.5 min. This indicates a substantial effect of

molecular size exclusion in this sample that may interfere with adsorption of oxygenate functional groups within the pore space. The whole Union Carbide wax showed first deflection at 6.6 min and peak at 7.8 min with a small second peak at 8.8 min. For comparison at 65° C, hexadecane showed first deflection at 7.5 min and peak at 7.8 min. This indicates a relatively minor influence of molecular size exclusion in this wax.

In an attempt to minimize molecular size exclusion effects, the Davisil 643 silica column (with pore size 150 Å compared to 60 Å for the 710 silica) was prepared and evaluated. Table 3 summarizes results for toluene, nonadecylbenzene, and 1-tetradecanol using heptane and 2% (vol) of 1-propanol in heptane as carrier solvents at column temperatures ranging from 21° to 80° C. Tetradecanol was not eluted with heptane. However, the mixed 1-propanol/heptane solvent eluted the alcohol as a well-resolved, symmetrical peak while the two aromatic compounds were not separated from hexadecane. Separations of the topped Union Carbide and the Mobil waxes on this column also appeared to be satisfactory. A chromatogram of a typical separation of the Mobil wax is shown in Figure 5. After removal of the solvent, the neutral fraction accounted for about 93% of the wax sample and the polar fraction about 7%. Examination of the infrared spectrum of the neutral fraction indicated only aliphatic bands, although olefins could still be present at low concentrations. The infrared spectrum of the polar fraction indicated the presence of carbonyl groups corresponding to either esters or ketones, and OH corresponding to either alcohols or water. Further analyses of the fractions are discussed later.

TABLE 3. - Capacity factors on Davisil 643

Solvent	Temperature	Compound	Capacity factor, K' (relative to hexadecane)
Heptane	21	Toluene	0.73
Heptane	50	Toluene	0.44
Heptane	65	Toluene	0.33
Heptane	80	Toluene	0.27
Heptane	21	Nonadecylbenzene	0.51
Heptane	50	Nonadecylbenzene	0.29
Heptane	65	Nonadecylbenzene	0.22
Heptane	80	Nonadecylbenzene	0.18
2% (vol) 1-propanol in heptane	65	Toluene	0.00
	65	Nonadecylbenzene	0.00
	65	1-Tetradecanol	1.09

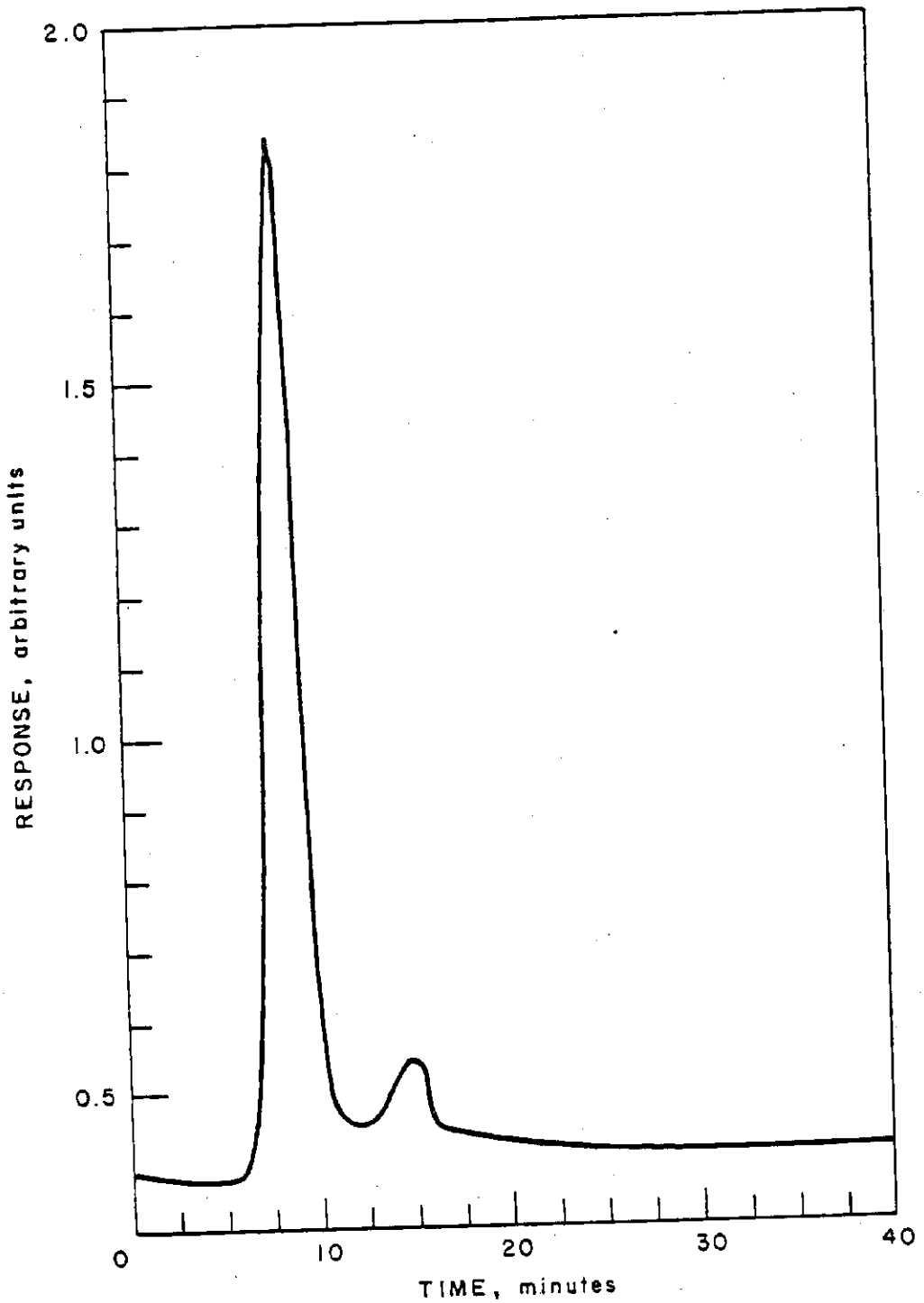


FIGURE 5. - Chromatogram of Mobil F-T wax #4 on Davisil 643. Solvent: 1% (vol) 1-propanol in heptane; flow: 4 mL/min; sample injected: approximately 0.35 g; column temperature: 80° C; refractive index detector temperature: 60° C.

The separation of alkenes was carried out on a silver-loaded, sulfonic-acid-bonded, wide-pore silica. The mobile phase for this separation was either 0.5% or 2% (vol) toluene in heptane. Both terminal and internal alkenes were retained on this column with hexadecene-1 eluting between the trans and cis forms of nonadecene-2. Molecular weight had only a minor effect on elution volumes. Butene-1 and methylpropene eluted at slightly higher volumes than hexadecene, while the isomers of octene-2 eluted at about the same volumes as nonadecene-2.

Neutral fractions from both the Mobil and Union Carbide waxes were separated into alkane and alkene fractions. A typical chromatogram for the topped Union Carbide neutral fraction is shown in Figure 6. Note that the cutpoint between alkanes and alkenes was taken immediately following the alkane peak. This results in a small amount of alkanes being included in the alkene fraction. A small unknown peak at ca. 11.5 min is included in the alkene fraction. Subsequent analysis of the alkene fraction shows the presence of low level oxygen-containing compounds. These compounds are probably diethers or esters and possibly could be obtained as a concentrate by isolation of the 11.5-min peak. The alkane fraction was obtained in 85.5% yield, the alkene fraction in 7.9% yield, and about 6.6% was lost, probably by deposition of more insoluble, high molecular weight components in the chromatographic system.

A schematic of the distillation and chromatographic procedures used for the Union Carbide F-T wax is shown in Figure 1. Analysis of the various fractions by high resolution mass spectrometry and by proton and carbon-13 NMR is discussed in the following sections.

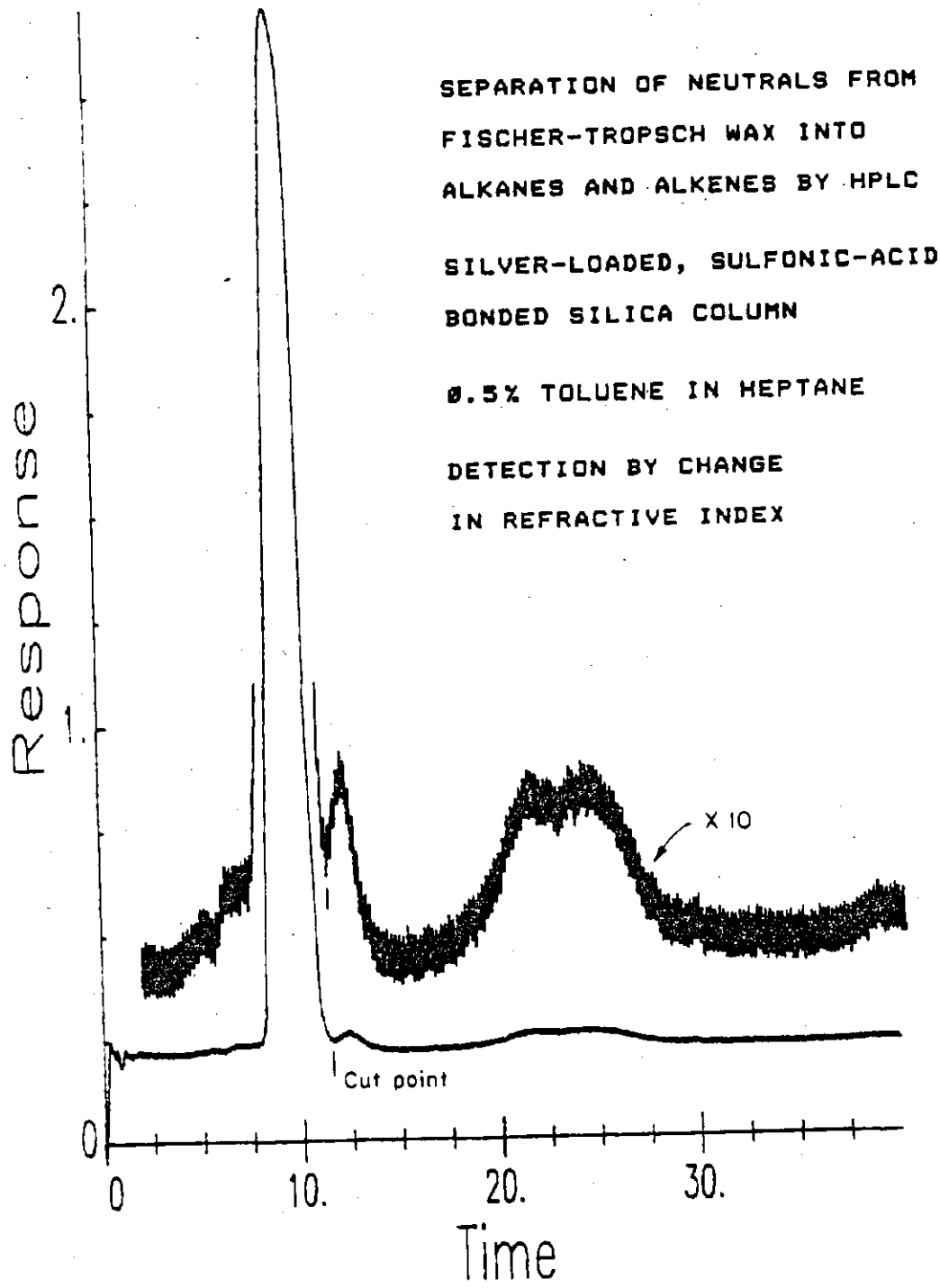


FIGURE 6. - Typical chromatogram for separation of Union Carbide F-T wax neutral fraction. Response in arbitrary units. Time in minutes.

Nuclear Magnetic Resonance Analysis

Nuclear magnetic resonance (NMR) spectroscopy was used for analysis of both whole and fractionated waxes. Due to limited solubility of the whole Mobil wax in common NMR solvents such as deuterated chloroform ($CDCl_3$), spectra were acquired on a solution of the wax (28.8 wt %) in n-decane at about 150° C. The proton NMR spectrum of the wax/decane mixture is shown in Figure 7. The spectrum shows two major bands: one at 0.9 ppm and the other at 1.4 ppm. The broadened, unresolved nature of the bands indicates the viscous nature of the sample even at 150° C. At high magnification the spectrum reveals several broad peaks in the region 4.8-6.0 ppm. This region represents olefinic protons in hydrocarbons. These peaks represent 0.17% of the total peak area. If the wax could be represented as a C_{60} alkane, the H/C ratio would be 2.03. The H/C ratio of decane is 2.20. For this sample, which is 28.77% wax, the proton peak area representing the wax would be 26.5% of the total. Because the proton spectrum of decane revealed no peaks in the olefinic region, then the 0.17% olefinic contribution represents 0.64% of the Mobil wax #4. The proton spectrum revealed no evidence of aromatic compounds in the wax (aromatic compounds would appear in the region 6.5-9.0 ppm).

The carbon-13 spectrum of the wax/decane mixture shown in Figure 8 reveals the typical appearance of a n-alkane structure. Normal alkanes of chain length C_9 or longer are characterized by a set of five peaks at 14.0, 23.0, 29.8, 30.2, and 32.5 ppm. There is evidence of two much smaller peaks at 28 ppm and 35 ppm. These peaks suggest some branching of the normal alkane structure with the branches, C_2 or longer. Cycloalkanes of five carbons or more have a carbon-13 chemical shift of 27-28 ppm. Thus, the peak at 28 ppm, suggestive of branched alkanes, could represent some contribution from small amounts of cycloalkanes. Its size appears larger than the peak at 35 ppm which would suggest the difference could represent the possible cycloalkanes. The carbon-13 spectrum of neat n-decane at high magnification, shown in Figure 9, shows several small peaks, barely evident at normal magnification, which indicate some branched isomers of n-decane are present. However, these are not prominent enough to account for the branching noted in the wax sample.

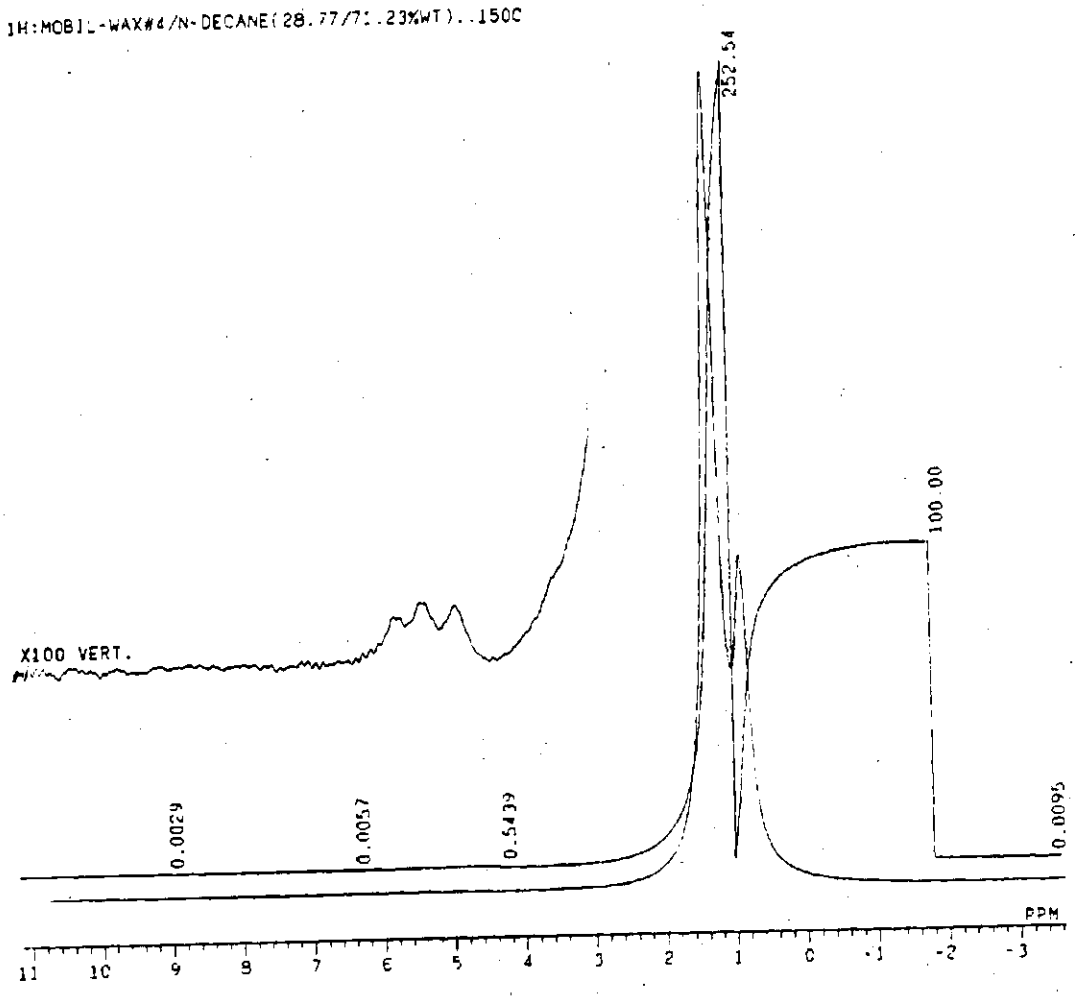


FIGURE 7. - Proton NMR spectrum of Mobil wax #4 in n-decane at 150° C. Also shown is the integral of the spectral peaks.

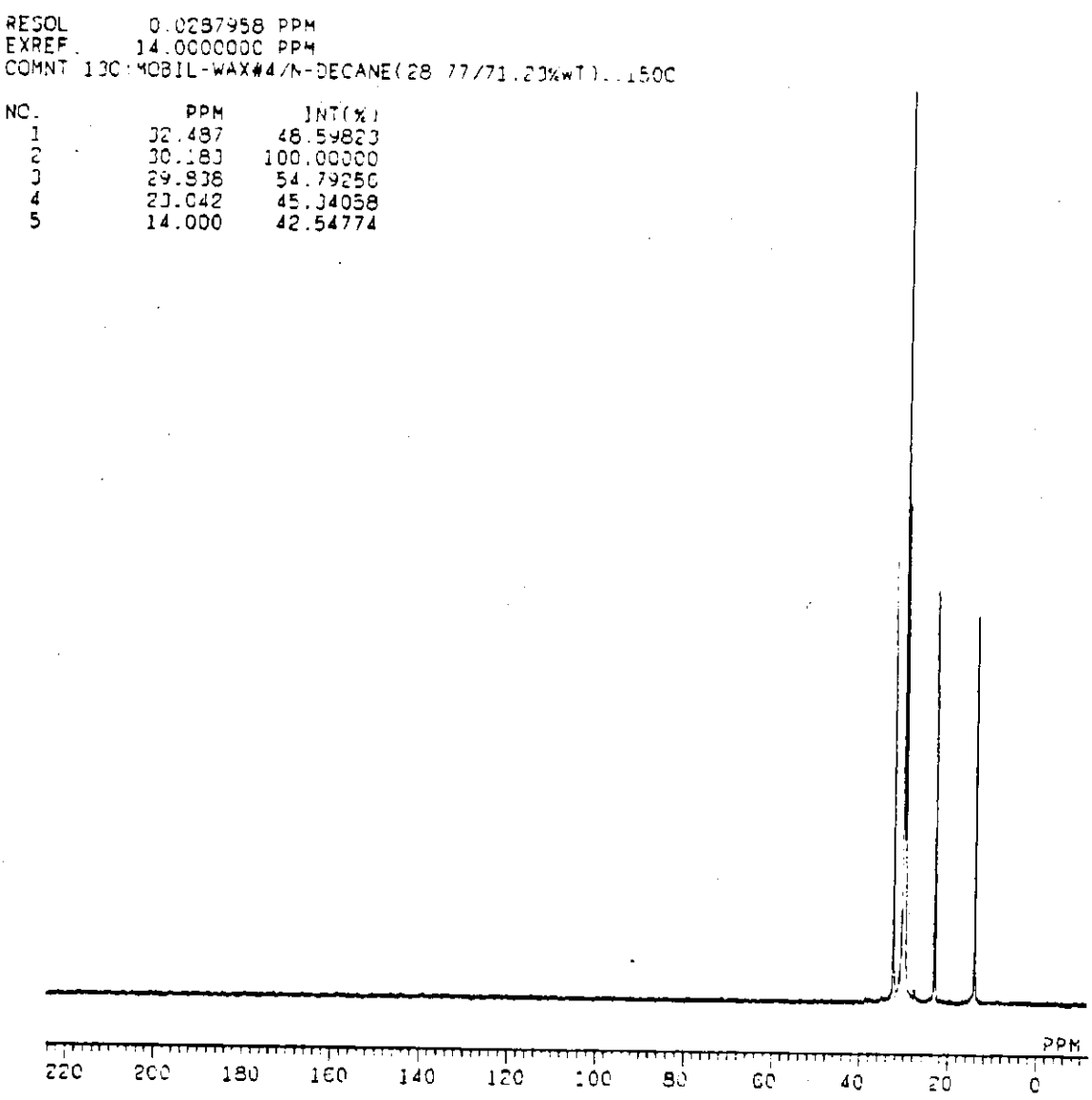


FIGURE 8. - Carbon-13 NMR spectrum of Mobil wax #4 in n-decane at 150° C.

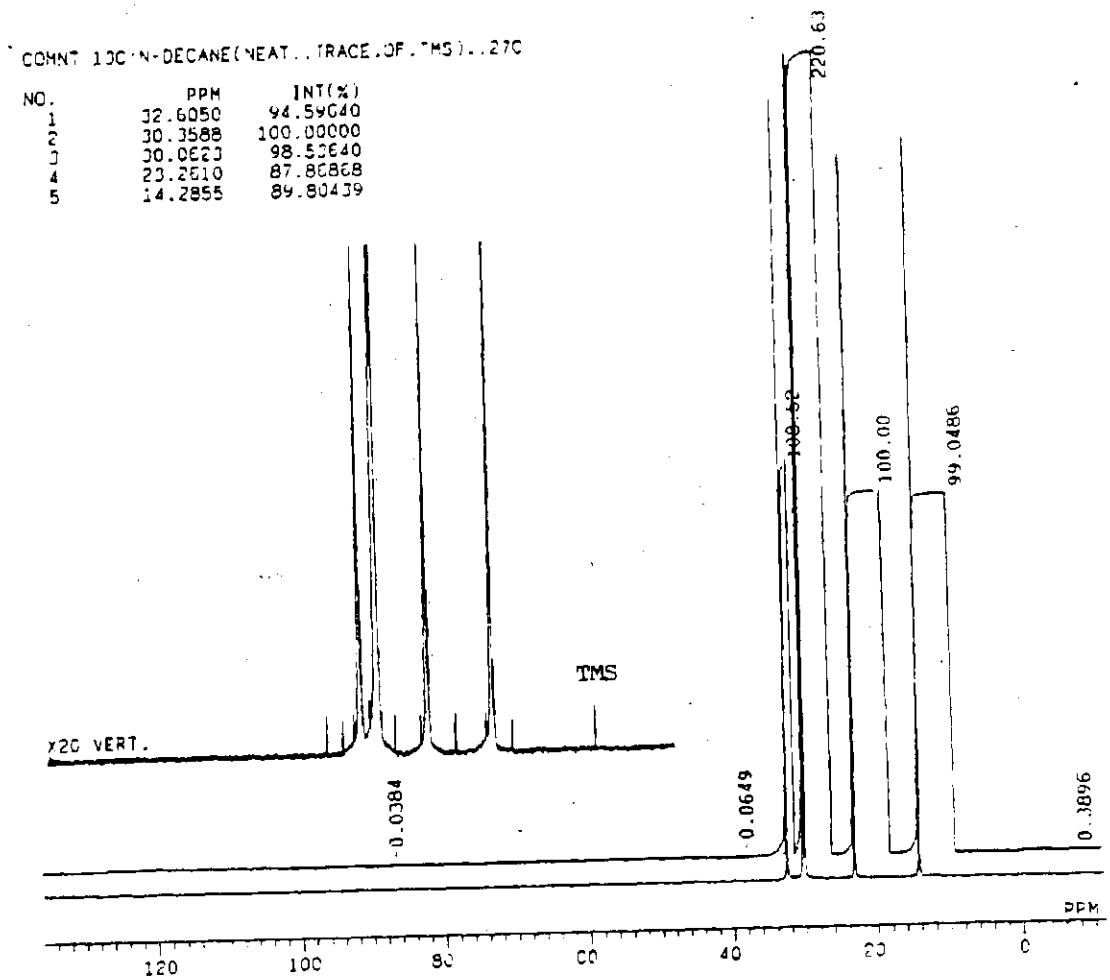


FIGURE 9. - Carbon-13 NMR spectrum of n-decane containing a trace of TMS at 27° C. Also shown is the integral of the spectral peaks (semi-quantitative).

The CP/MAS carbon-13 spectra of the solid wax sample, an example of which is shown as Figure 10, reveal that the wax is essentially a normal paraffin structure with prominent peaks at 14.1, 22.8, 29.9, and 32.1 ppm. The fifth peak associated with n-alkane structures discussed above is not resolved from the 29.9 ppm peak. Also, the peaks at 27.2 and 37.3 ppm characteristic of branched alkanes are more prominent in the solid sample spectrum. The other peaks in Figure 10 have been labeled as spinning sidebands (SB) or sample rotor (R) peaks if arising from these sources. There are several small peaks at 114, 124, and 138 ppm which are from the wax. These can be from either aromatic carbons or olefinic carbons which appear in the same region in the carbon-13 spectra. Because the proton spectra revealed no evidence of aromatic material, these peaks probably represent olefinic material.

No evidence of carbonyl structures other than those associated with the rotor spectrum could be found in the carbon-13 spectra. These peaks would be in the region 170-180 ppm for acid carbonyl carbons or 200-210 ppm for ketone carbonyl carbons. The lack of evidence for carbonyl in the NMR data is not surprising even though infrared data on the polar fraction from Mobil wax #4 showed carbonyl present. The low concentration observed in the IR (on the polar fraction) and possible interference in the NMR spectra from the rotor could explain the apparent inconsistency.

A summary of the conclusions derived from the NMR data on the Mobil wax follows:

1. Mobil wax #4 appears to be predominantly a mixture of normal alkanes with some branched alkane components. There are possibly small amounts of cycloalkanes present.
2. There appears to be some olefinic material present, representing 0.64% of the proton spectra area, evident also in the carbon-13 CP/MAS spectra.
3. No evidence of aromatic material or carbonyl material in the total wax was found.

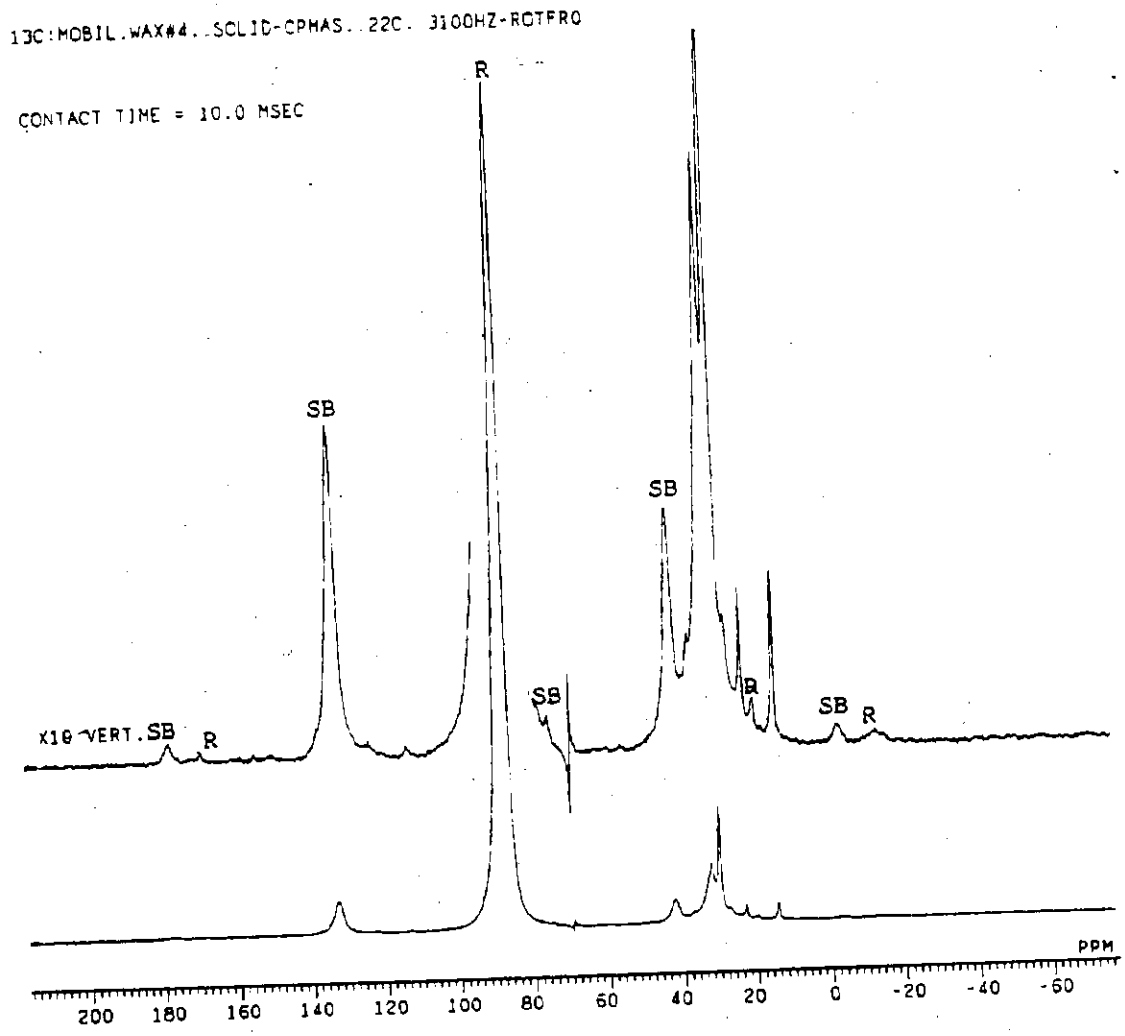


FIGURE 10. - Carbon-13 CP/MAS NMR spectrum of solid Mobil wax #4 at 22° C. Labeled peaks are spinning sidebands (SB) displaced 3100 Hz from the parent peak or Delrin rotor (R) peaks.

The alkane and alkene fractions separated from the topped Union Carbide wax were dissolved in hot CCl_4 and examined by proton and carbon-13 NMR. The proton and carbon-13 NMR spectra of the alkene fraction, shown in Figures 11 and 12, respectively, clearly show the presence of carbon-carbon double bonds in each case. These peaks are located at 4.8 to 5.8 ppm in the proton spectrum and 114-132 ppm in the carbon-13 spectrum (this is in the same region as aromatic carbon-13 signals, but the proton spectrum indicated no aromatic compounds were present.) As indicated in Figure 11, both terminal and internal carbon-carbon double bonds are present in the olefins detected. Approximate average molecular formulas calculated from the NMR data, assuming one double bond per molecule, are $C_{33}H_{66}$ for terminal olefins with an average of two methyl group branches and $C_{36}H_{72}$ for internal olefins. The carbon-13 data indicated that the paraffinic structures present are almost entirely normal alkyl groups. However, a few very small peaks in the region of 27-34 ppm could be indicative of some branching or could arise from carbon atoms adjacent to the double bonds. If the latter is correct, the position of the peaks indicates the internal olefins are mostly the trans-isomers. The approximate relative concentrations of terminal and internal olefins are 35 and 65 mol %, respectively. The small triplet peak at 4.0 ppm in the proton spectrum is in the region typical of oxygen compounds, either ether structures or possibly esters. This peak is from the hydrogens on the carbon alpha to the oxygen, and the triplet structure indicates the group in the beta position is a CH_2 group and not a methyl group. If it is an ester structure, then the group bonded to noncarbonyl oxygen is a normal propyl or larger group. The average molecular weight calculated on the basis of an average formula of $C_{35}H_{70}$ is 490. This value compares favorably with the simulated distillation results for the total sample, the topped Union Carbide wax, as the 50%-off temperature of 480° C corresponds approximately with the elution of the n-$C_{34}H_{70}$ alkane. This conclusion assumes the distribution of alkenes is approximately the same as the n-alkane distribution. The average molecular weight from the NMR data is somewhat less than the average molecular weight estimated from the mass spectral data for the alkenes, 585 amu.

These data taken together with the absence of detectable quantities of olefins in the proton NMR spectrum of the alkane fraction, shown in Figure 13, indicate a high quality separation of the Union Carbide topped wax neutrals into alkanes and alkenes.

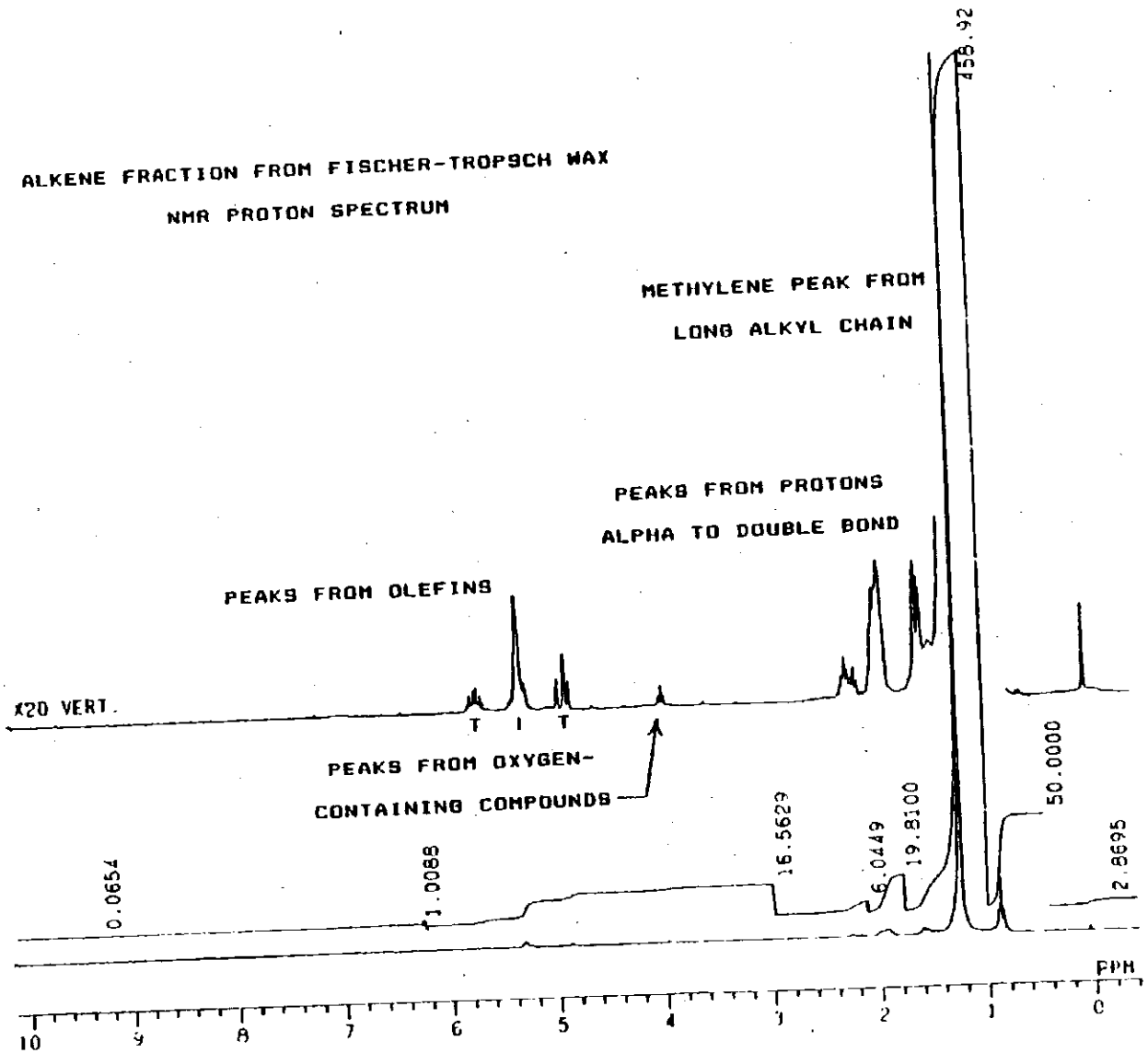
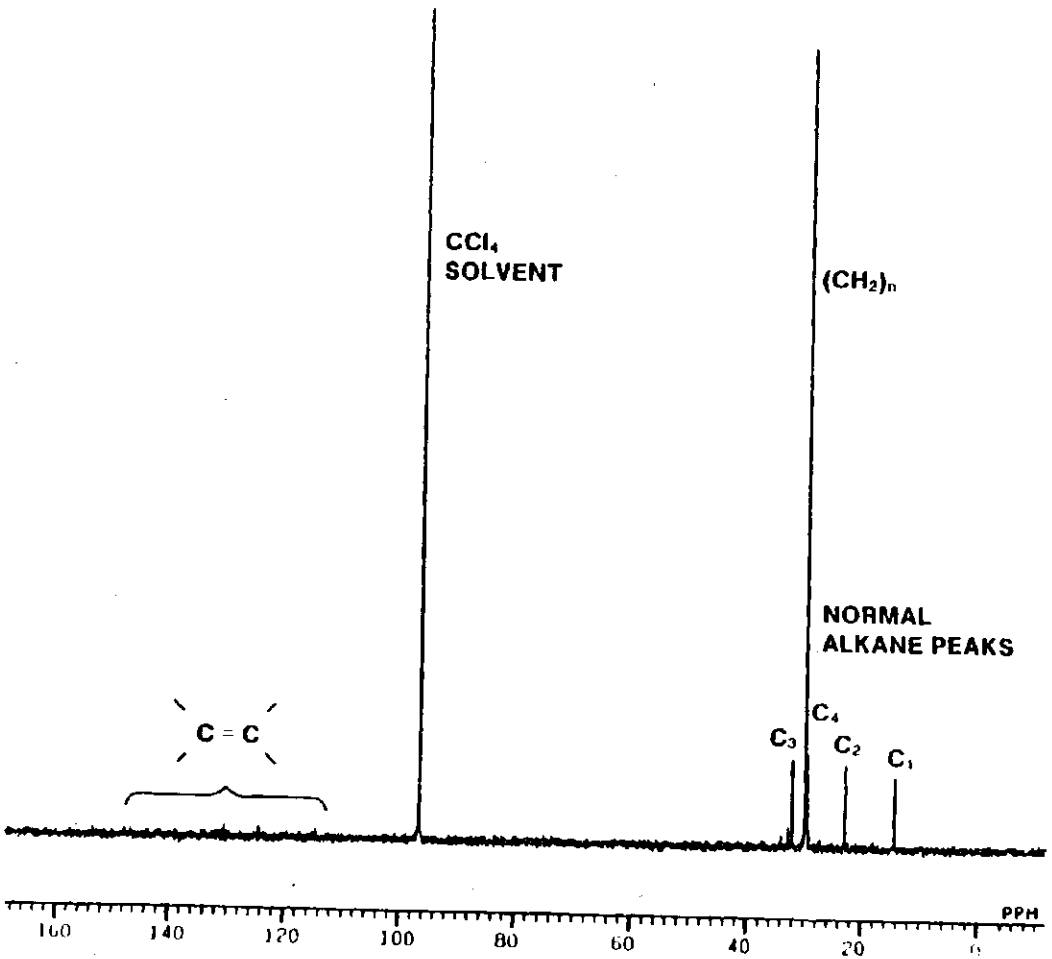


FIGURE 11. - Proton NMR spectrum of the topped Union Carbide F-T wax alkene fraction.



24-SEP-87 11:01:38
EXMOD SGBCM
OBNUC 13C
OBFRQ 67.80 MHZ
OBSET 135.00 KHZ
OBFIN 5660.0 HZ
POINT 32768
FREQU 16025.6 HZ
FILTR 8000 HZ
SCANS 1200
ACQTM 0.511 SEC
PD 3.000 SEC
PW1 4.3 US
ADBIT 12
IRNUC 1H
IRSET 112.00 KHZ
IRFIN 5600.0 HZ
IRATN 0
IRRPW 40 US
TEMP. 27.0 C
SPEED 15 HZ
SLVNT CDCL3
EXREF 96.50 PPM

FIGURE 12. - Carbon-13 NMR spectrum of the topped Union Carbide F-T wax alkene fraction.

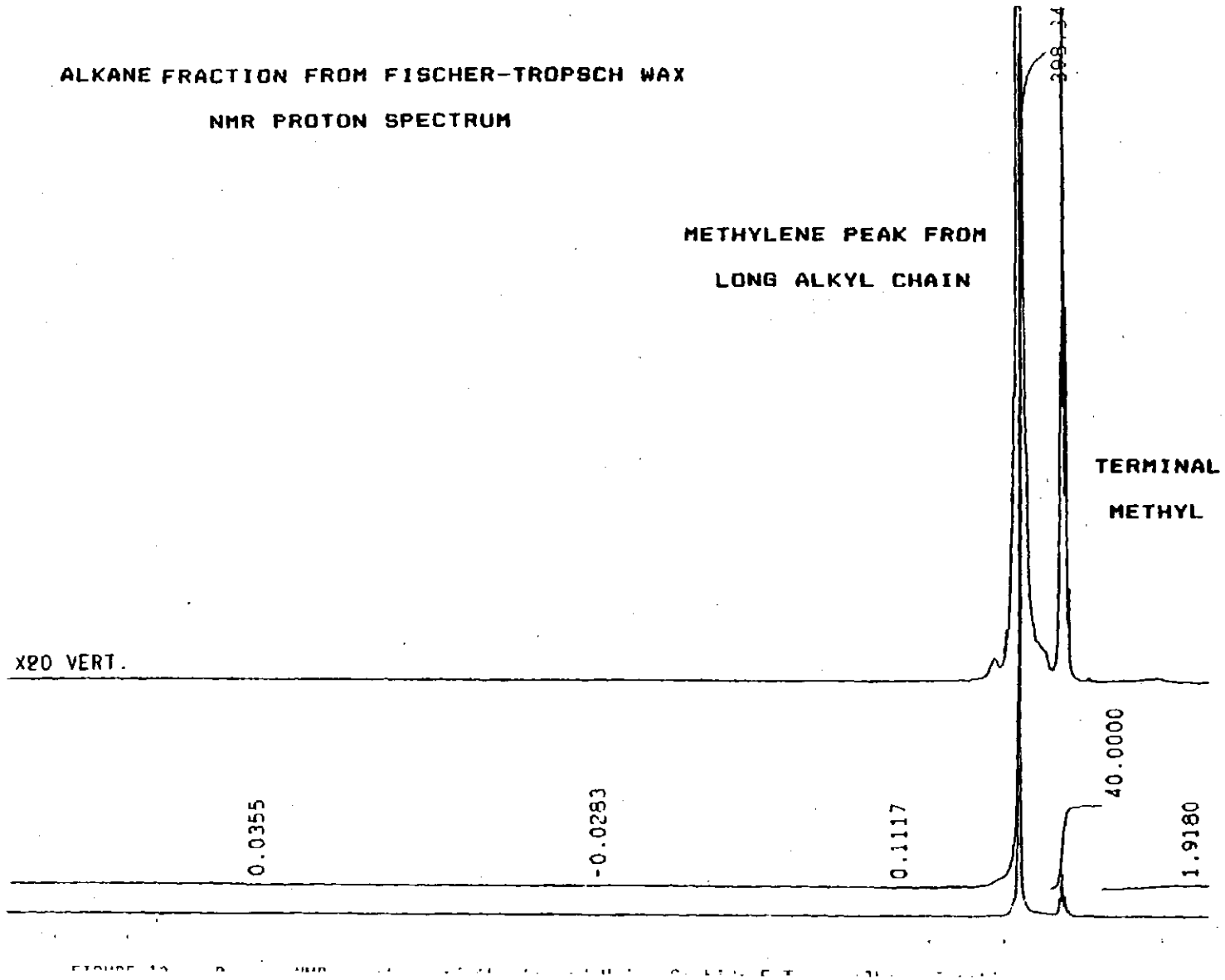

ALKANE FRACTION FROM FISCHER-TROPSCH WAX
NMR PROTON SPECTRUM
METHYLENE PEAK FROM
LONG ALKYL CHAIN
TERMINAL
METHYL
X20 VERT.
0.0355
-0.0283
0.1117
40.0000
1.9180

FIGURE 13 [illegible]

Mass Spectrometric Analysis

Samples of whole Mobil and Union Carbide waxes were analyzed by probe microdistillation mass spectrometry with ionization via high voltage (70 eV) electron impact, low voltage (ca. 10 eV) electron impact, and field ionization. Fractions separated from the waxes were analyzed primarily by PMD/MS in the field-ionization mode.

Electron-Impact Mode--Whole Wax. A preliminary probe microdistillation, 70 eV electron impact mass spectral run on the Mobil wax with the probe temperature programmed from 40° to 600° C produced spectra with peaks up to and beyond m/z = 1300 as shown in Figures 14 and 15. Most experiments were performed with a heating rate of about 10° C/min. The mass spectra were acquired at a resolving power of approximately 10,000. The spectra are characterized by intense ions at m/z 57, 71, 85, and 99, etc., which are characteristic of alkyl fragment ions. Intensities of ions beyond m/z 200 in Figure 14 are scaled up by a factor of 50, and only the upper mass regions are shown in the spectra in Figure 15 to show more clearly the progression toward higher m/z values as the probe temperature increased. Weights before and after the microdistillation indicated that the entire sample (>99%) vaporized.

The whole Union Carbide wax was analyzed by probe microdistillation low energy electron impact (ca. 10 eV) at a resolution of 10,000. Spectra were recorded up to a temperature of 325° C. At higher temperatures, the ion current dropped to zero, showing that all volatile components in the wax had distilled. The combination of probe microdistillation with low-energy electron impact gave very good spectra of the total wax sample, with 279 spectra being recorded over a mass range from 505 down to 55. The upper end of the mass range of sample components extended above 505 amu. Abundant molecular ions were observed for paraffins (C_nH_{2n+2} series) extending to m/z 380 and beyond, and also for hydrocarbons in the series C_nH_{2n} and C_nH_{2n-2}. Very weak ions were noted for compounds containing oxygen. Further work with the Union Carbide sample was concentrated on the topped and fractionated samples.

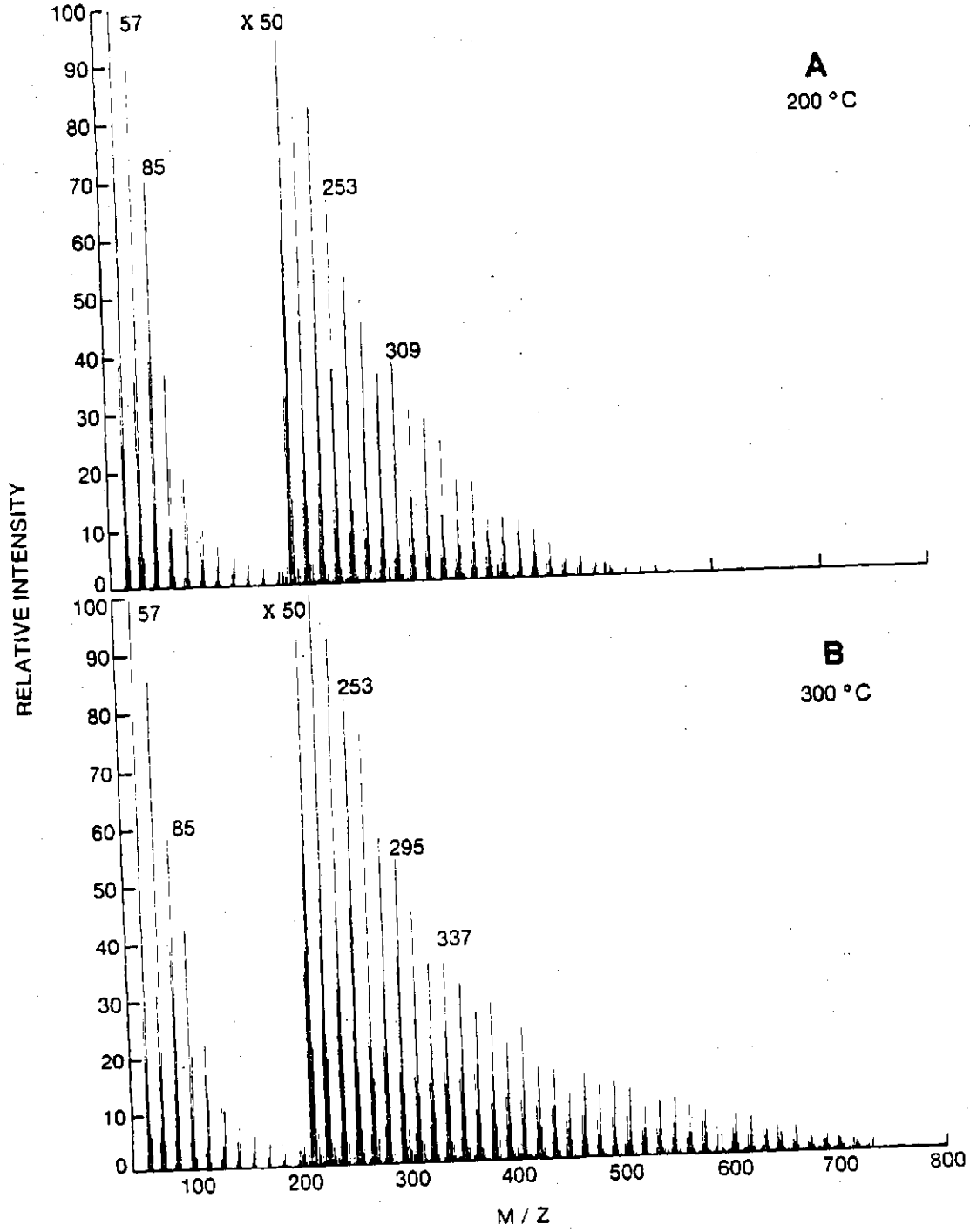


FIGURE 14. - Mass spectra recorded at probe temperatures of 200° C (A) and 300° C (B) in the probe microdistillation/mass spectrometric analysis of Mobil composite wax #4 (70 eV electron impact ionization; ion intensities at m/z >200 multiplied by 50).

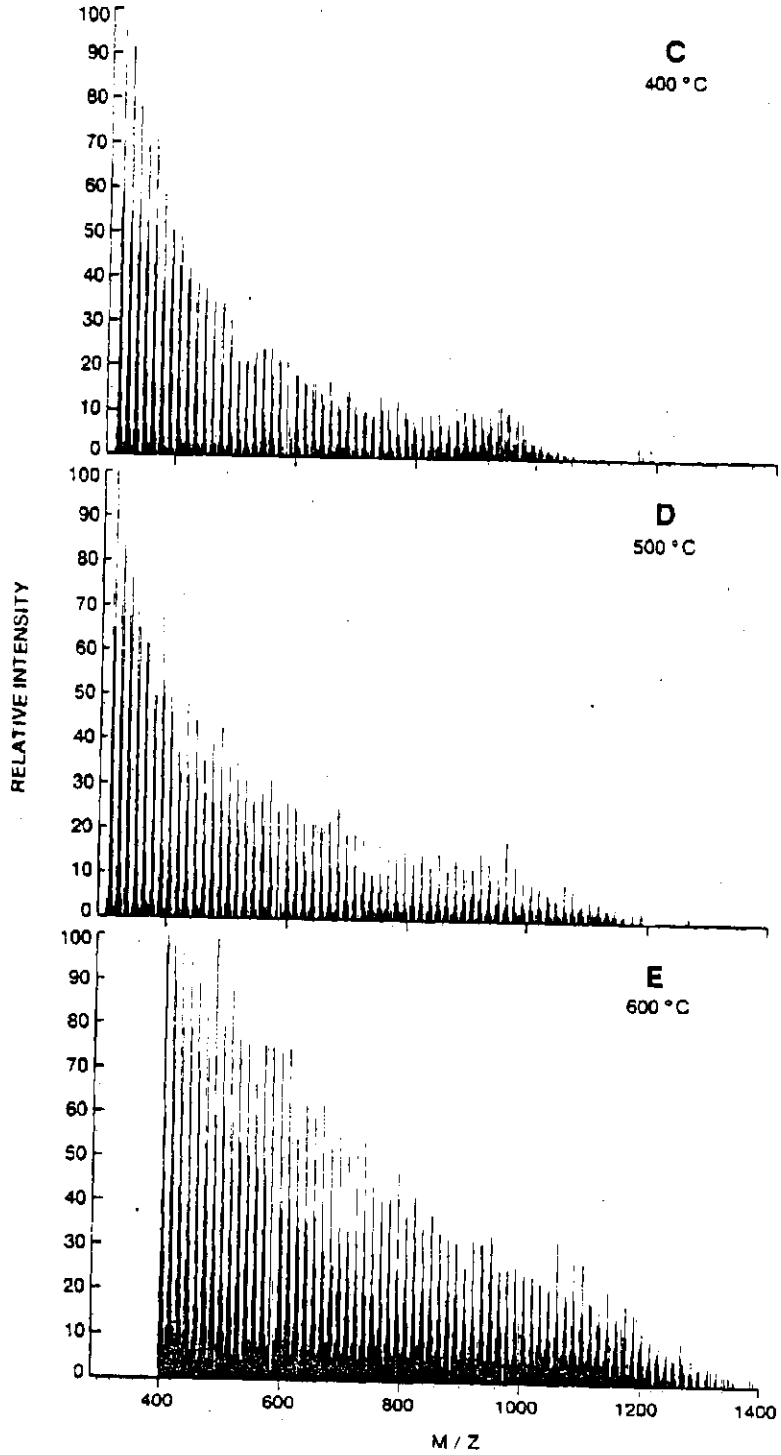


FIGURE 15. - Partial mass spectra recorded at probe temperatures of 400° C (C), 500° C (D), and 600° C (E) in the probe microdistillation/ mass spectrometric analysis of Mobil composite wax #4 (70 eV electron impact ionization; ion intensities normalized to largest peak in the mass range shown = 100%).

Field-Ionization Mode--Whole Wax. The initial run in the field-ionization mode was made with a sample of Mobil wax at about 5000 resolving power. As shown in Figure 16, the total ion current had gone through a maximum indicating either that most of the sample was distilled or that a decrease in sensitivity occurred as discussed in the next paragraph. Spectra acquired at four probe temperatures ranging from 264 to 359° C are shown in Figure 17. Since field ionization produces molecular ions almost entirely, the progression from lower to higher mass ions with increasing probe temperature is much more distinct than in the electron impact spectra. The spectra appear to consist primarily of ions in the homologous series corresponding to paraffins (C_nH_{2n+2}), olefins or cycloparaffins (C_nH_{2n}), and their isotope peaks.

As noted previously, the electron-impact mass spectra obtained on the whole Mobil wax show that the molecular-weight range of this wax extends beyond 1300 amu. The field ionization spectra of the wax do not show the range extending much beyond 1000 amu, but this apparent limitation is an artifact identified with the use of field ionization with sample introduction by probe microdistillation, particularly at probe temperatures exceeding 250° C. The phenomenon apparently is caused by sample molecules condensing on the surface of the emitter (razor blade) even though it is heated and the ion source temperature is maintained at 250° C. Although the field-ionization source used with the mass spectrometer permits the blade to be heated, no provision is made for measuring the blade temperature. Thus, finding the best combination of source temperature and blade-heater current is guesswork, and the optimum conditions may not be achieved. Future experiments with field ionization combined with probe microdistillation should be conducted with a conditioned wire emitter used in field desorption studies in place of the razor blade, because the wire emitter can be heated directly and its temperature more carefully controlled. In addition, very high molecular weight waxes, i.e., those having molecular weights greater than about 1500 amu, should be run by field desorption (FD) instead of field ionization. In the FD technique, the sample is deposited directly on the conditioned wire emitter, and the ions are formed and desorbed from the surface of the emitter. Thus, vaporization prior to ionization is not required, and a much higher molecular-weight range can be attained as compared to field ionization.

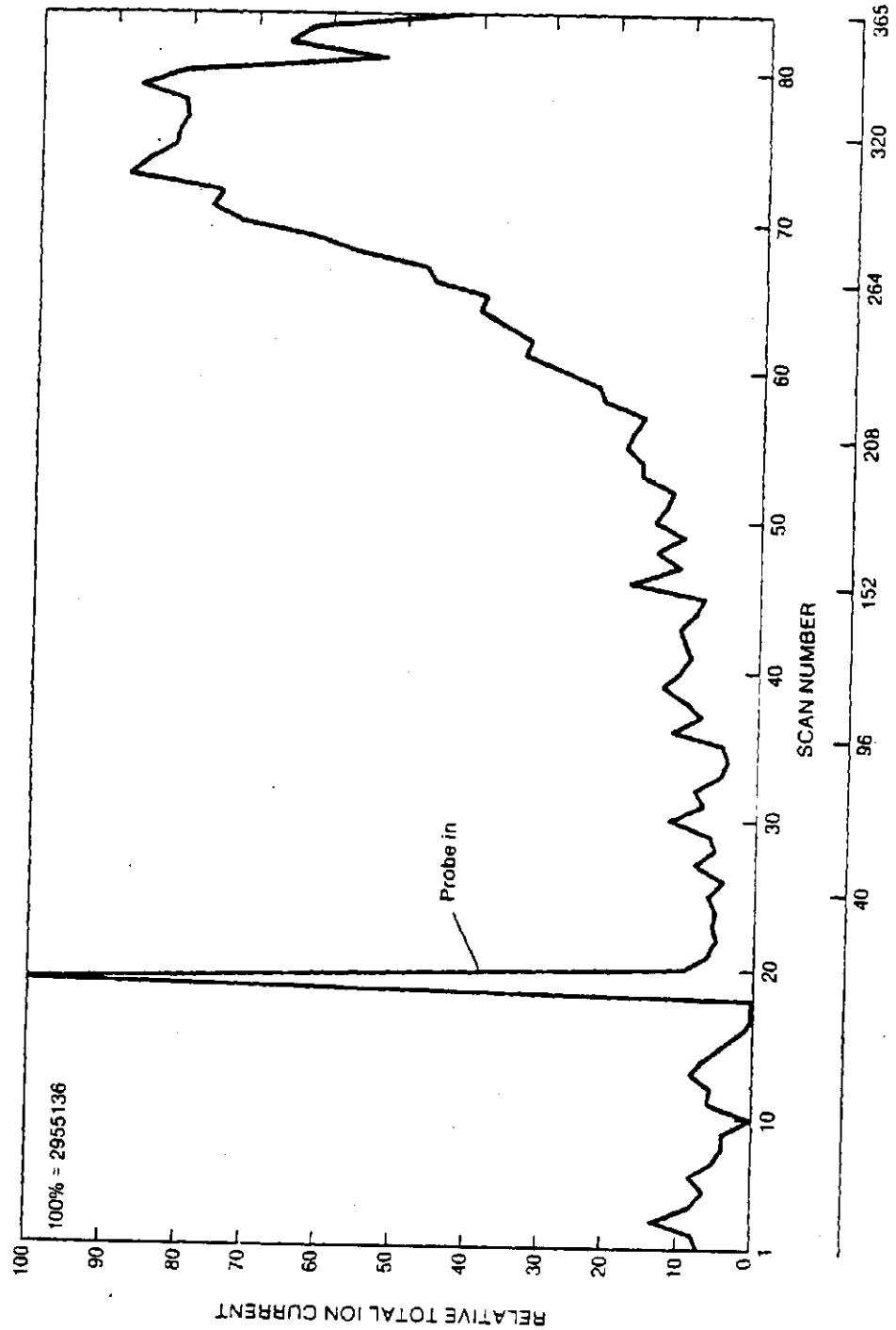


FIGURE 16. - Total ion current plot from the probe microdistillation/field ionization/mass spectrometric analysis of Mobil composite wax #4.

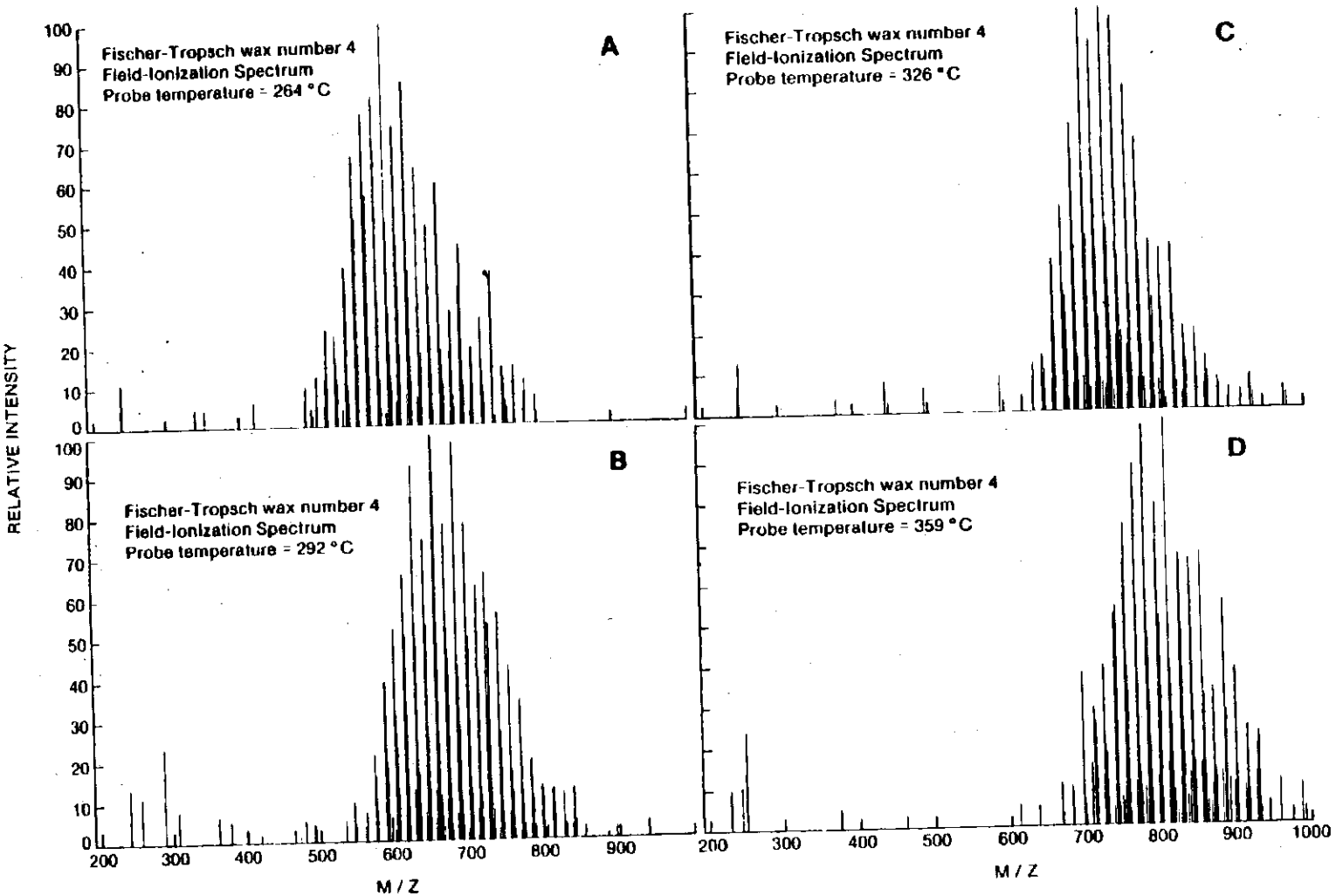


FIGURE 17. - Mass spectra recorded at probe temperatures of 264° C (A), 292° C (B), 326° C (C), and 359° C (D) in the probe microdistillation/field ionization/mass spectrometric analysis of Mobil composite wax #4.

Further experimentation with the field ionization source was conducted with the Union Carbide sample. A resolving power of 10,000 was achieved over a mass range of 1000 amu. The spectrum of scan 22 corresponding to a probe temperature of 124° C is shown in Figure 18. The ions at m/z 58 (acetone), 106 (p-xylene), and 240 (n-heptadecane) are from reference compounds introduced through the batch inlet system. Preliminary analysis indicated that small amounts of oxygenates are present in addition to large quantities of paraffins and smaller amounts of cycloparaffins or olefins. It is thus possible to detect the various compound classes in the field ionization mode without prior sample fractionation.

Field-Ionization Mode--Wax Fractions. Field ionization mass spectral data were acquired at about 8000 resolving power on the alkene, alkane, and polar fractions from the topped Union Carbide F-T wax. Results for the alkene fraction show a predominance of C_nH_{2n} molecular ions over the mass range from 308 to 882. These are presumed to be olefin molecular ions, rather than cycloparaffinic, based on the separation scheme and NMR data. Three mass spectra recorded at probe temperatures of 97, 141, and 195° C are shown in Figures 19, 20, and 21, respectively. These spectra were chosen as being representative of those from the early, middle, and late stages, respectively, of the probe microdistillation. Ions observed at m/z 244, 266, and 506 are from triphenylmethane, nonadecene, and hexatriacontane, respectively, used as mass markers; i.e., they do not arise from the alkene fraction. Excluding these ions, only those corresponding to elemental formulas C_nH_{2n} were observed in the lower temperature part of the distillation, as represented by scan 36, shown in Figure 19. In the spectrum of the intermediate part of the distillation (Figure 20), C_nH_{2n} ions are still dominant, although some low-intensity ions of elemental formula $C_nH_{2n}O_2$ were detected. The spectrum in Figure 21, scan 111 recorded near the end of the run at a temperature of 195° C, shows more complexity with molecular ions four mass units higher than the still dominant C_nH_{2n} ions. These higher mass ions have elemental compositions of $C_nH_{2n}O_2$, as determined from the high resolution output. Although not apparent in Figure 21, small molecular ions from paraffins or $C_nH_{2n}O$ compounds or both are present two mass units higher than the olefin peaks. At 8000 resolving power, these peaks are not distinguishable from the second isotope peaks of the olefins. However, calculations show that they have intensities about twice as large as those expected for the isotope peaks of the C_nH_{2n} ions.

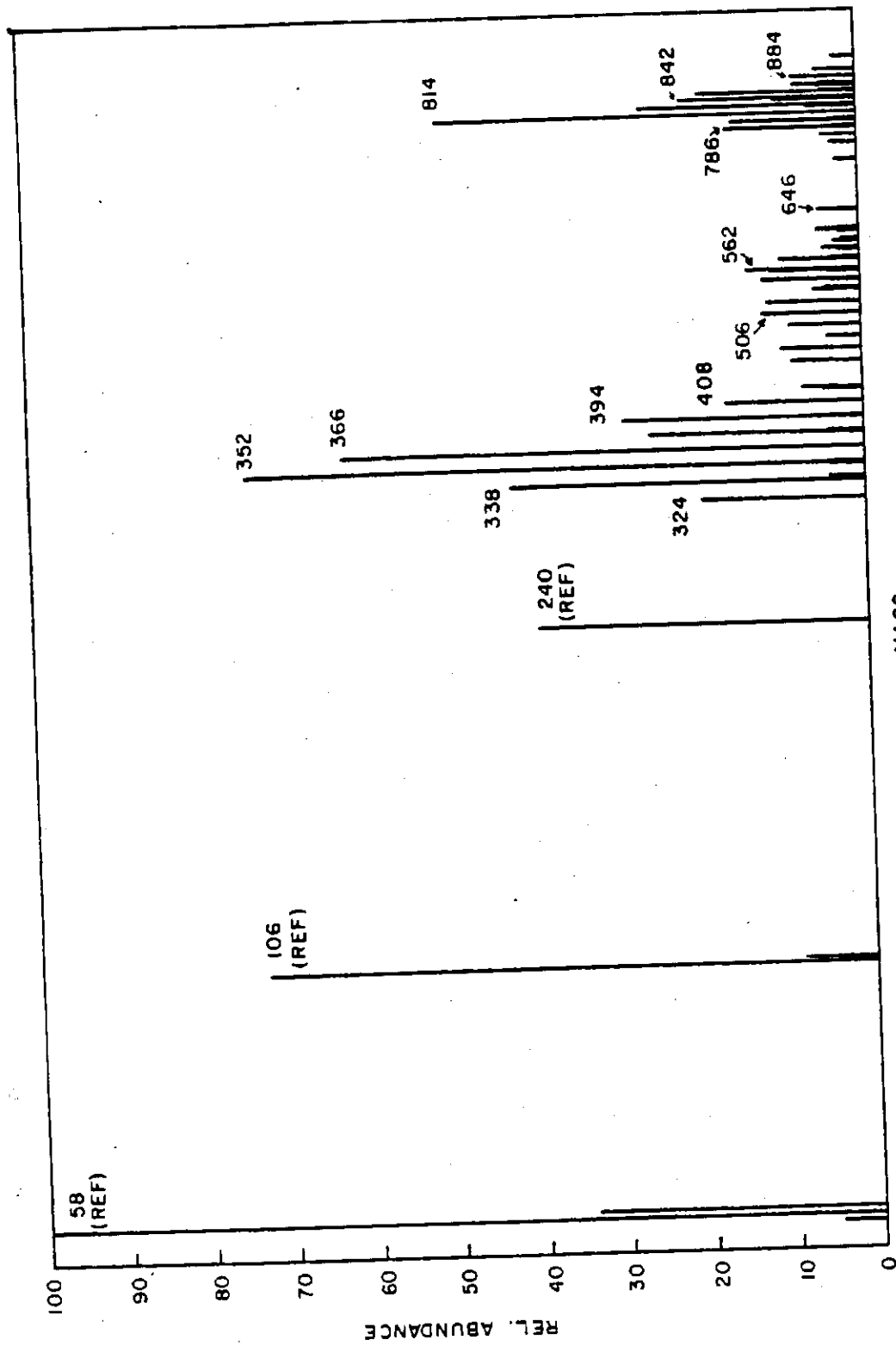


FIGURE 18. - Field ionization mass spectrum (scan 22, T = 124° C) from the probe microdistillation of Union Carbide F-T wax (as received). Scan rate: 100 sec/decade; 10,000 resolving power.

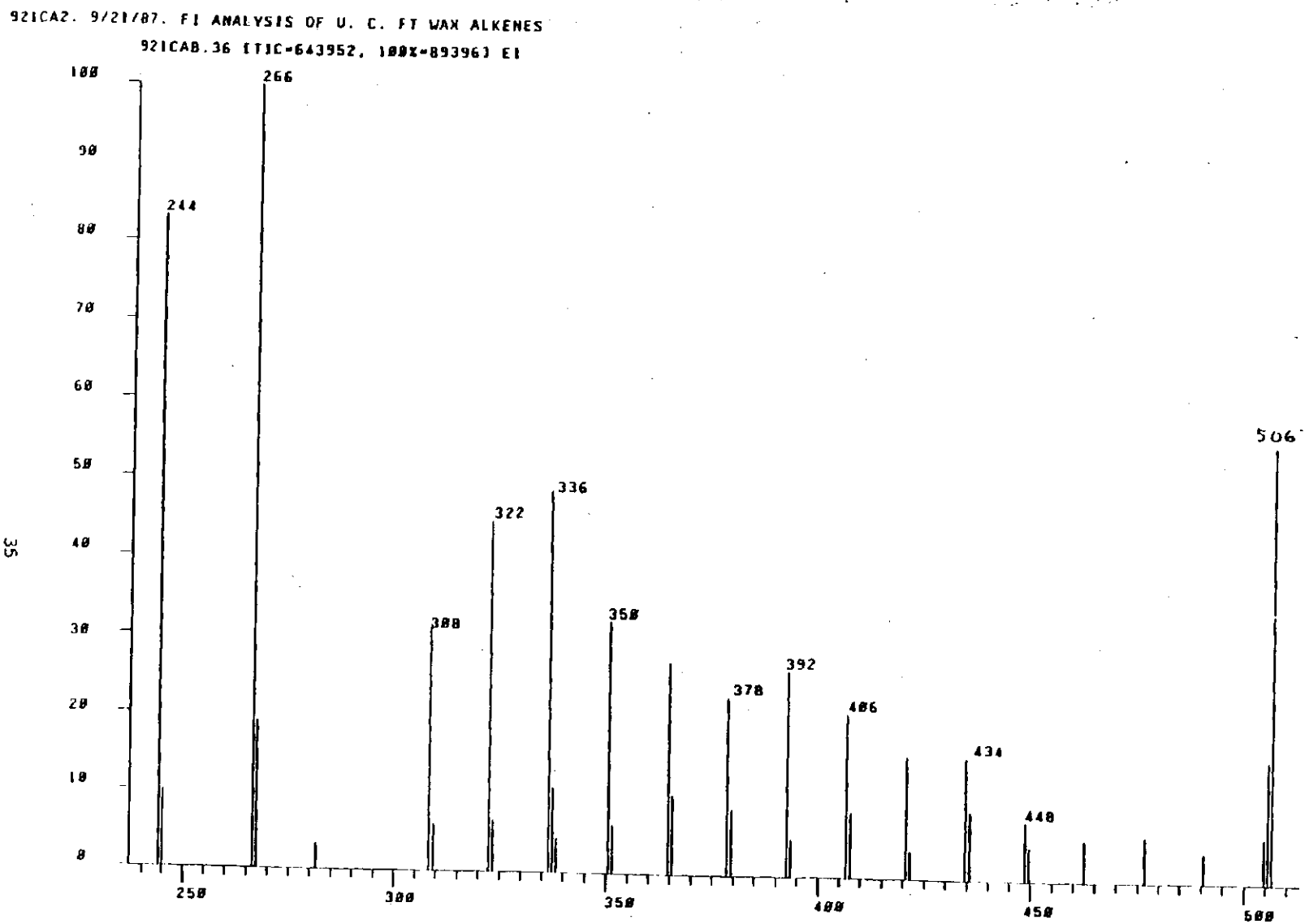


FIGURE 19. - Field ionization mass spectrum recorded at a probe temperature of 97° C during the probe microdistillation of an alkene fraction from from a topped Union Carbide Fischer-Tropsch wax. Peaks at m/z 244, 266, and 506 represent molecular ions of triphenylmethane, nonadecene, and hexatriacontane, respectively.

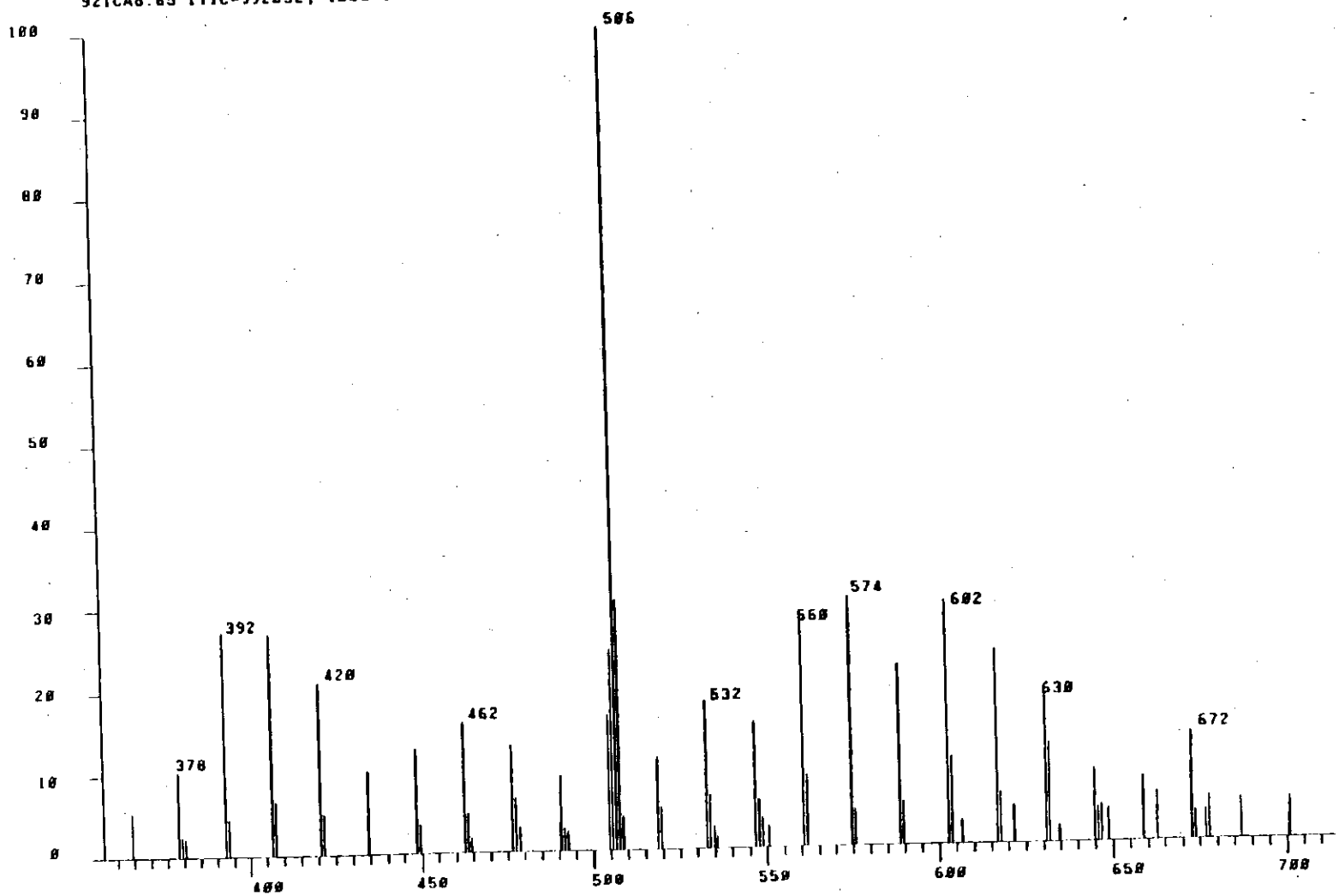


FIGURE 20. - Field ionization mass spectrum recorded at a probe temperature of 141° C during the probe microdistillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax.

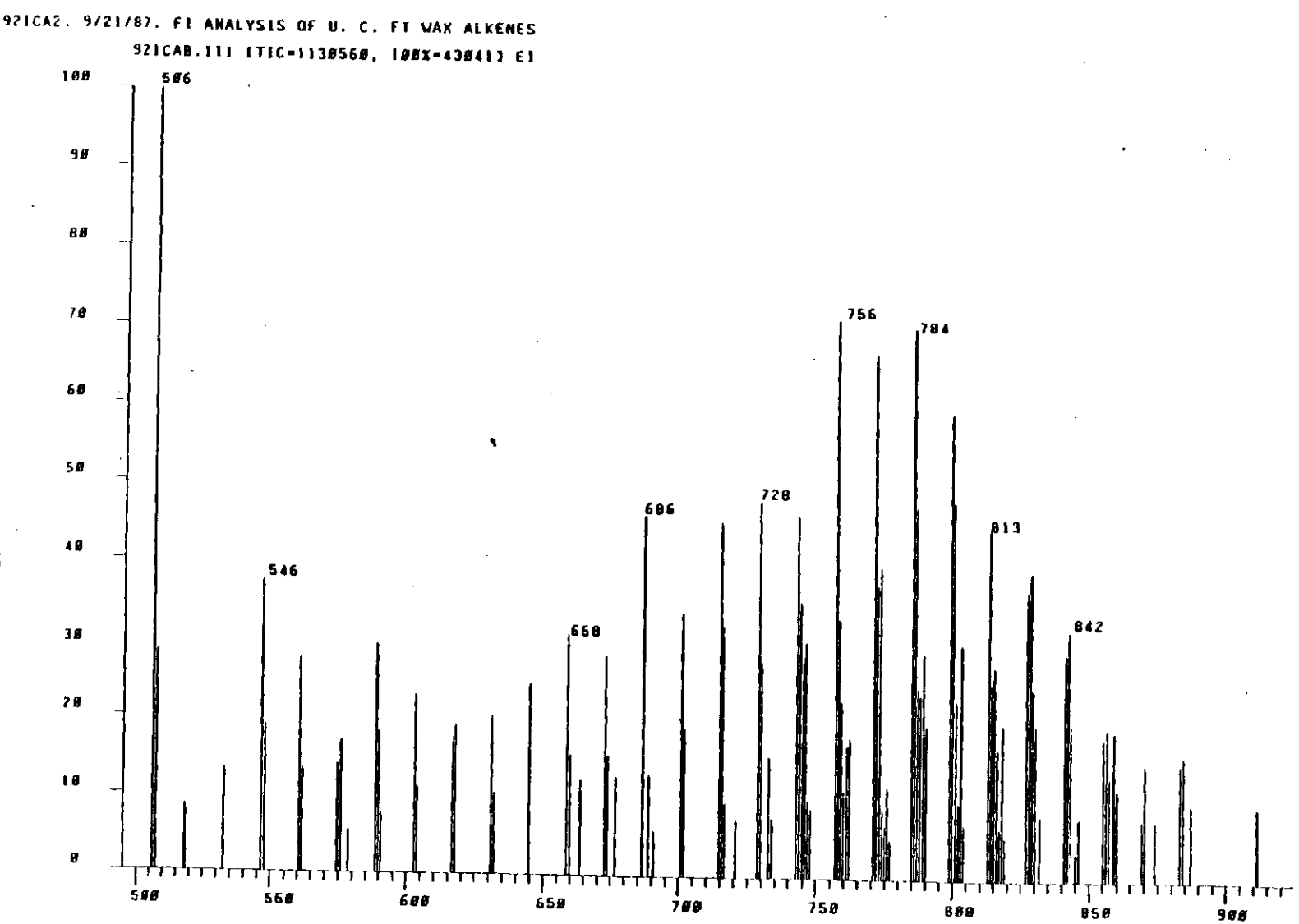


FIGURE 21. - Field ionization mass spectrum recorded at a probe temperature of 195° C during the probe microdistillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax. Peak at m/z 506 represents the molecular ion of hexatriacontane.

The most probable explanation for the abnormally large intensities is that the corresponding peaks represent unresolved multiplets from paraffins and $C_nH_{2n}O$ compounds; e.g., esters and/or cyclic or unsaturated ethers.

An elimination curve for the olefin molecular ion at m/z 658 and elemental formula $C_{47}H_{94}$ is shown in Figure 22. This curve, obtained from the statistical analysis of ion intensity versus distillation time was calculated with programs described in Appendix A. The curve is typical for fairly intense ions in the mass spectra. Data scatter is relatively high, but this is an unavoidable consequence of the low sensitivity encountered in field-ionization experiments.

Results of the type shown in Figure 22 are summarized in Table 4. All ions represented in the table have elemental compositions corresponding to olefins. The T_{IMAX} values are times in minutes corresponding to the maximum heights, IMAX/10000, of the elimination curves, and the values in the column labeled AREA/10000 are the areas under the curves. These values are proportional to the quantities of olefins present in the fraction, although sensitivity factors would be required to convert areas to quantitative results. Unit sensitivities were used in calculations for all compound types because experimentally determined values are generally not available for field-ionization experiments. The error limits (90% confidence intervals) are relatively high for most ions in the table because of the low ion intensities, noted above. Although not shown, an approximately linear relationship exists between the molecular-ion masses and T_{IMAX} values given in the table.

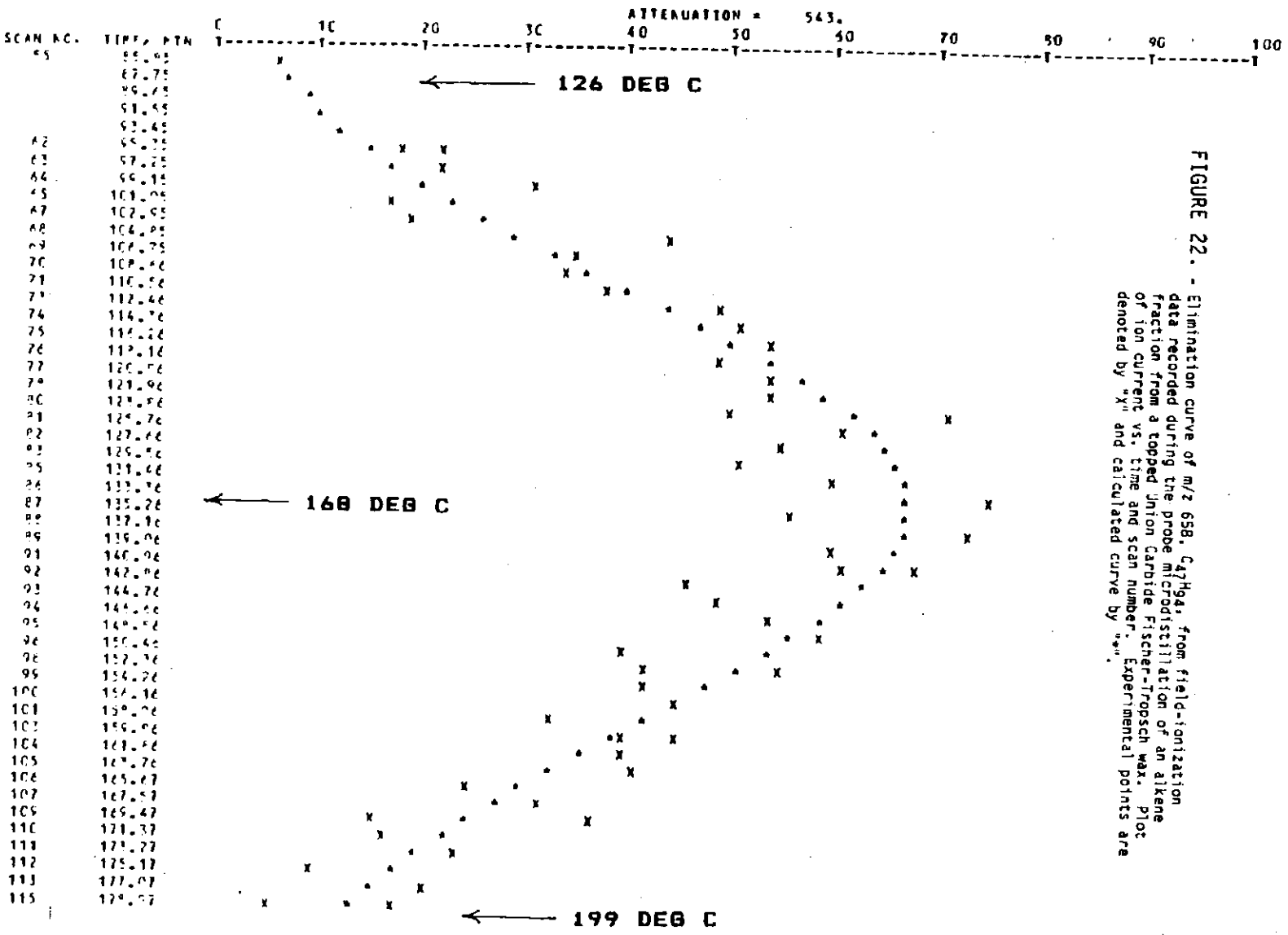


FIGURE 22. - Elimination curve of m/z 658, $C_{47}H_{94}$, from field-ionization data recorded during the probe microdistillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax. Plot of ion current vs. time and scan number. Experimental points are denoted by "X" and calculated curve by "*".

TABLE 4. - Output from program "ELMCRV" showing statistical results for C_nH_{2n} assignments from 94 scans recorded during the probe microdistillation of an alkene fraction from a topped Union Carbide F-T wax

921CAC. 10/14/87. FI ANALYSIS OF U. C. FT WAX ALKENES SCANS: 22-115

MAXIMUM PPM ERROR = 20.0 ELEMENTAL COMPOSITION: C(N)H(2N+Z)

STATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(IMAX), MIN	IMAX/10000	AREA/10000
0	322	50.71 +- 4.51	5.18 +-2.03	100.26 +- 41.70
0	336	49.06 +- 6.51	4.55 +-2.45	116.39 +- 81.71
0	350	49.92 +- 5.47	3.72 +-0.24	123.72 +- 9.97
0	630	121.65 +-29.34	3.71 +-3.54	212.63 +-203.61
0	658	135.03 +-22.29	3.67 +-2.86	202.82 +-158.75
0	672	129.68 +-39.09	4.07 +-4.07	215.66 +-216.99
0	700	136.46 +-36.00	4.23 +-3.74	218.82 +-194.17
0	714	145.17 +- 2.38	4.55 +-0.25	225.58 +- 16.93
0	728	147.92 +-40.59	4.42 +-4.19	215.97 +-205.94
0	770	163.32 +-33.77	3.99 +-3.22	169.60 +-139.67
0	784	172.34 +-17.14	3.44 +-3.00	131.93 +-120.99

SUM OF AREAS/10000 FROM STATISTICAL CALCULATIONS = 1933.37

NOTE: RESULTS FOR ODD-MASS IONS HAVE BEEN OMITTED

When data scatter is excessive, the ion intensity versus time values cannot be analyzed statistically. However, nonstatistical parameters can still be calculated to represent the elimination curves. By summing the time-intensity products and dividing by the sum of the intensities, the time centroids of the curves can be calculated. These values, labeled T_{CENTR} in Table 5, are given for the molecular ions whose intensities scattered too much for statistical analysis. The values under the column headings IMAX/10000 and T_{IMAX} are simply the maximum intensities and corresponding times for the given molecular ions. As data scatter becomes smaller, the T_{CENTR} and T_{IMAX} values tend to converge, as seen for m/z 644 in the zero Z series. Thus, the difference between T_{CENTR} and T_{IMAX} provides a measure of the scatter when the elimination curve data cannot be handled statistically.

TABLE 5. - Output from program "ELMCRV" showing nonstatistical results for C_nH_{2n} assignments from 94 scans recorded during the probe microdistillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax. Peaks in the +2 Z series represent unresolved multiplets consisting of alkane and $C_nH_{2n}O$ molecular ions and second isotope peaks from C_nH_{2n} molecular ions.

921CAC. 10/14/87. FI ANALYSIS OF U. C. FT WAX ALKENES SCANS: 22-115

MAXIMUM PPM ERROR = 20.0 ELEMENTAL COMPOSITION: C(N)H(2N+Z)

NONSTATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(CENTR), MIN	T(IMAX), MIN	IMAX/10000	AREA/10000
2	450	98.87	122.58	0.58	26.96
2	464	115.00	128.89	0.62	20.85
2	478	108.38	90.86	0.42	25.65
2	492	111.89	76.58	0.60	27.70
2	520	124.68	135.13	0.71	32.98
2	534	119.25	157.28	0.81	49.02
2	548	122.58	92.33	0.99	47.83
2	562	120.73	139.82	0.76	30.85
2	576	128.79	109.71	1.02	30.64
2	590	121.15	154.03	0.79	26.19
2	604	124.54	120.76	1.28	33.89
2	618	127.45	115.99	1.24	24.40
2	632	128.01	127.06	1.21	41.66
2	646	137.11	136.54	1.51	49.19
2	660	137.80	141.27	1.57	43.53
2	674	136.84	133.34	1.80	54.07
2	688	140.35	138.07	1.73	61.48
2	702	144.17	144.39	1.91	63.01
2	716	148.87	145.96	2.28	55.99
2	730	147.88	152.28	2.58	69.94
2	744	154.89	158.60	2.40	74.26
2	758	153.91	152.25	2.19	73.75
2	772	160.00	171.24	2.24	64.09
2	786	157.29	164.89	2.14	59.25
2	800	161.09	155.37	2.15	47.75
2	814	163.82	171.19	2.01	41.39
2	828	167.13	172.76	1.46	27.63
2	842	167.79	175.92	0.92	15.47
2	856	170.78	179.07	0.89	11.85

TABLE 5. - Output from program "ELMCRV" showing nonstatistical results for C_nH_{2n} assignments from 94 scans recorded during the probe micro-distillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax. Peaks in the +2 Z series represent unresolved multiplets consisting of alkane and $C_nH_{2n}O$ molecular ions and second isotope peaks from C_nH_{2n} molecular ions (cont'd).

921CAC. 10/14/87. FI ANALYSIS OF U. C. FT WAX ALKENES SCANS: 22-115

MAXIMUM PPM ERROR = 20.0 ELEMENTAL COMPOSITION: C(N)H(2N+Z)

NONSTATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(CENTR), MIN	T(IMAX), MIN	IMAX/10000	AREA/10000
0	308	59.14	54.79	3.51	47.59
0	364	74.36	54.66	3.56	121.93
0	378	77.22	64.13	3.97	132.67
0	392	82.05	65.68	3.60	143.59
0	406	87.75	110.00	3.48	137.75
0	420	91.08	106.80	3.43	150.46
0	434	94.61	114.69	2.97	144.47
0	448	98.36	124.17	2.96	153.49
0	462	104.28	130.48	3.04	149.95
0	476	106.54	136.79	3.16	169.77
0	490	112.80	143.10	3.54	171.27
0	504	114.55	150.99	3.49	221.33
0	518	118.79	147.80	3.20	188.01
0	532	120.85	82.86	2.99	187.65
0	546	124.01	98.67	3.01	201.57
0	560	123.53	97.07	3.46	201.12
0	574	125.47	101.80	3.48	182.44
0	588	127.71	125.53	3.20	187.54
0	602	127.72	128.68	3.82	190.24
0	616	130.39	115.99	4.16	200.74
0	644	132.85	131.79	4.10	194.85
0	686	140.68	145.99	4.55	209.40
0	742	150.16	155.43	5.20	177.71
0	756	152.03	157.00	4.83	167.20
0	798	158.45	163.29	4.43	118.66
0	812	158.45	169.61	3.14	91.17
0	826	161.93	172.77	2.70	67.84
0	840	161.44	172.75	2.18	51.73
0	854	164.51	172.74	1.96	38.92
0	868	166.52	163.22	1.36	21.28
0	882	171.05	167.96	0.93	10.39

SUM OF AREAS/10000 FROM NON-STATISTICAL CALCULATIONS = 5664.00

NOTE: RESULTS FOR ODD-MASS IONS HAVE BEEN OMITTED

Areas under the curves can always be calculated by adding the areas of trapezoids, and this method is used for nonstatistical analysis of the data. Values under the heading AREA/10000 in Table 5 were obtained this way and correspond to the elemental compositions specified by the Z numbers and molecular-ion masses. When combined, the results given in Tables 4 and 5 represent all of the olefin molecular ions together with the unresolved multiplets in the +2 hydrocarbon Z series detected in the alkene fraction. Thus, olefins with molecular masses ranging from 308 to 882 are present. Those giving elimination curves with the largest areas have corresponding masses in a range around MW 700. These olefins are not necessarily the most abundant in the fraction because sensitivities were not included in the calculations. In fact, the higher molecular-weight olefins may be weighted too much because their sensitivities may be large when compared with those for the lower molecular-weight compounds.

In Table 6, results, all of which are nonstatistical, are given for components having molecular ions of the type $C_nH_{2n}O_2$. Areas under the elimination curves are generally much smaller than those for the olefins when unit sensitivities are used in calculations for both compound types. In fact, the areas for the oxygen-containing compounds may be deceptively large because these types may have larger sensitivities when compared with those for olefins. This possibility is based on very limited data from other studies in our laboratory on relative sensitivities for compounds ionized by field ionization.

By summing the areas under the curves for olefins, alkanes, single oxygen and dioxygen compounds and normalizing to 100, approximate mole percentages for these types can be calculated. The alkene fraction from the topped Union Carbide F-T wax thus contains about 78.3% olefins, 7.6% alkanes plus $C_nH_{2n}O$ compounds, and 14.1% $C_nH_{2n}O_2$ compounds. A correction for isotopic contributions (two carbon-13 atoms) from the olefins was included in the calculations. The mass spectral data indicate a concentration of oxygenates in the alkene fraction higher than the NMR data suggest. However, if sensitivity factors were available for use in the calculations, agreement between the two data sets might be improved.

TABLE 6. - Output from program "ELMCRV" showing nonstatistical results for $C_nH_{2n}O_2$ assignments from 94 scans recorded during the probe microdistillation of an alkene fraction from a topped Union Carbide Fischer-Tropsch wax

921CAC. 10/14/87. FI ANALYSIS OF U. C. FT WAX ALKENES SCANS: 22-115

MAXIMUM PPM ERROR = 20.0 ELEMENTAL COMPOSITION: C(N)H(2N+Z)O(2)

NONSTATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(CENTR), MIN	T(IMAX), MIN	IMAX/10000	AREA/10000
0	508	116.09	120.90	0.36	17.84
0	536	109.40	87.60	0.51	27.40
0	550	120.51	112.92	0.72	33.10
0	564	131.93	168.32	0.65	29.87
0	578	130.53	149.30	0.84	40.67
0	592	131.57	116.03	0.63	38.64
0	606	130.33	104.92	1.33	37.63
0	620	129.22	153.99	1.03	38.82
0	634	125.61	131.81	1.18	38.07
0	648	132.95	163.46	1.02	46.78
0	662	138.18	146.02	1.47	58.74
0	676	141.33	146.01	1.62	66.78
0	690	145.04	131.74	1.72	53.28
0	704	145.00	145.97	1.73	58.97
0	718	147.29	144.37	2.22	78.88
0	732	151.07	157.03	2.30	65.03
0	746	149.77	160.18	1.92	71.16
0	760	158.36	161.75	2.93	73.91
0	774	159.37	175.99	2.75	71.92
0	788	161.80	171.22	2.81	61.67
0	802	162.10	174.37	2.82	47.72
0	816	165.09	168.02	2.09	46.43
0	830	167.95	179.10	2.05	28.32
0	844	168.50	169.58	0.92	14.87

SUM OF AREAS/10000 FROM NON-STATISTICAL CALCULATIONS = 1146.50

NOTE: RESULTS FOR IONS IN THE +2 Z SERIES HAVE BEEN OMITTED AS WELL AS ALL RESULTS FOR ODD-MASS IONS

Examination of the mass-spectral data from the alkane fraction of the topped F-T wax shows a predominance of molecular ions corresponding to elemental formulas C_nH_{2n+2} over a mass range from 296 to 688. Figures 23, 24, and 25 show the spectra of the alkane fraction recorded at probe temperatures of 103, 146, and 193° C, respectively. By comparing the spectra in Figures 19-21 with those in Figures 23-25, it is evident that, at approximately the same probe temperatures, the molecular ion intensities are distributed toward lower masses in the alkane spectra when compared with the distribution in the alkene spectra. The reason for this difference is not readily apparent, and additional experimental work would be required to provide an answer.

Examination of the high resolution mass spectra of the alkanes shows only very small molecular ions with elemental formulas C_nH_{2n} and virtually no molecular ions containing oxygen. This observation in combination with the NMR results indicates the separation of a high quality alkane fraction.

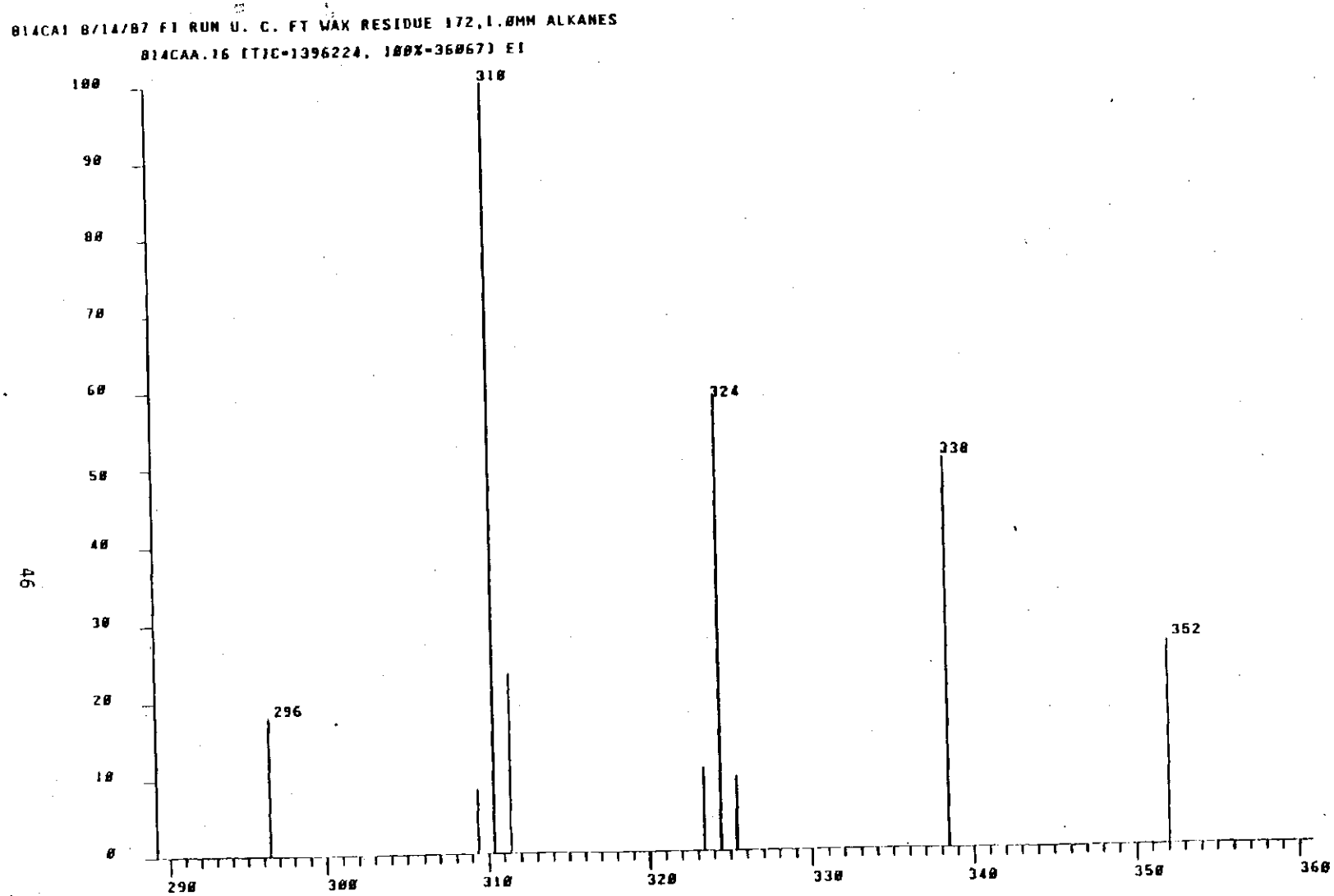


FIGURE 23. - Field ionization mass spectrum recorded at a probe temperature of 103° C during the probe microdistillation of an alkane fraction from a topped Union Carbide Fischer-Tropsch wax.

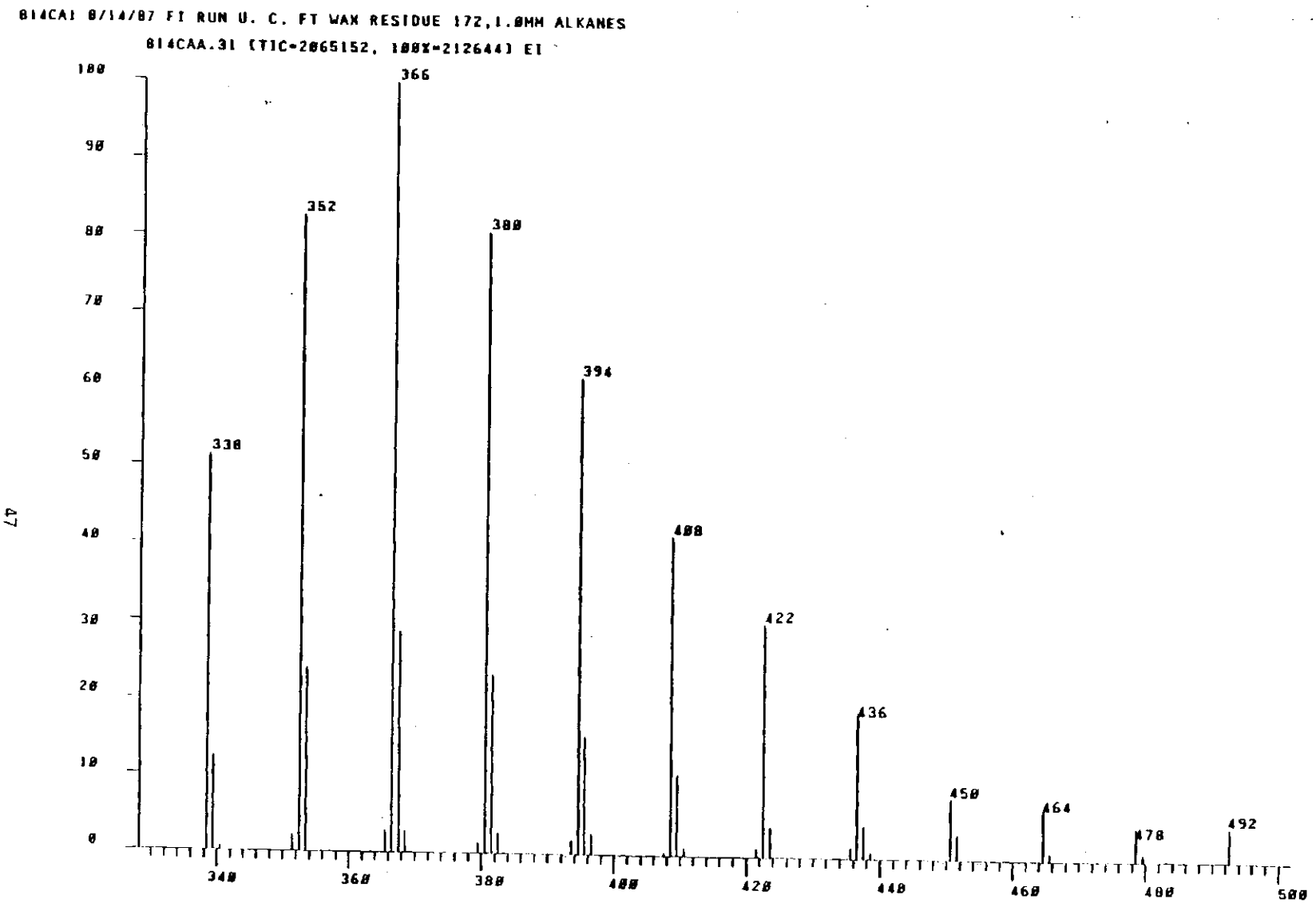


FIGURE 24. - Field ionization mass spectrum recorded at a probe temperature of 146° C during the probe microdistillation of an alkane

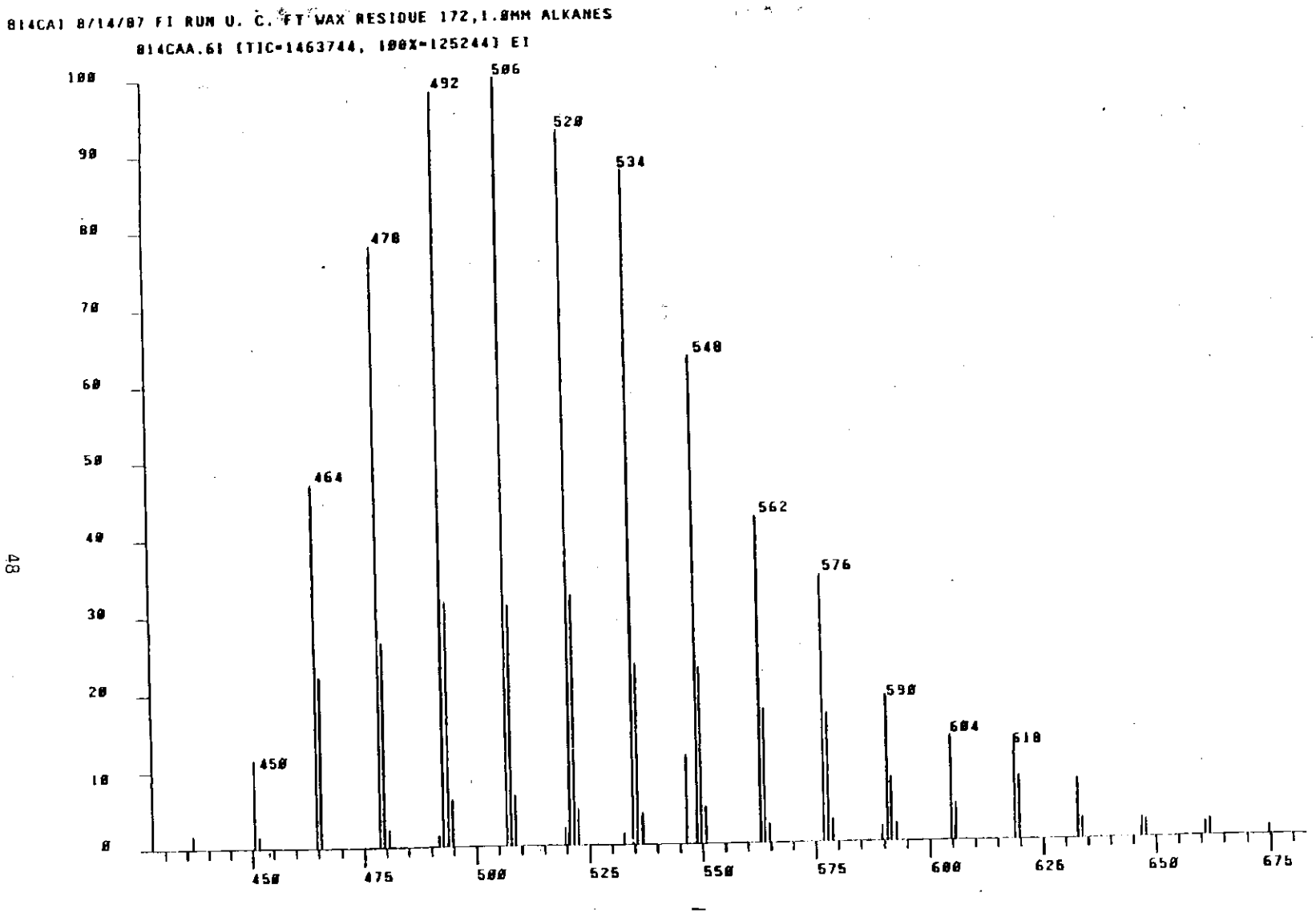


FIGURE 25. - Field ionization mass spectrum recorded at a probe temperature of 193° C during the probe microdistillation of an alkane fraction from a topped Union Carbide Fischer-Tropsch wax.

CONCLUSIONS

The NMR data indicate that the bulk of the waxes are normal alkane structures. There is evidence of minor branching and the presence of very low levels of cyclic structures. Also, data on the alkene fraction, available only in a small amount, hinted at some characteristics such as the internal olefins being mostly the trans-isomer. Using NMR techniques such as DEPT[1] and QUAT[2] and with the availability of a larger alkene fraction, a more detailed examination of these minor features and their characteristics could be obtained. These two techniques enable the acquisition of carbon-13 spectra containing peaks from only a single type of carbon species: CH_3-, $-CH_2-$, $>CH-$ or $-\overset{|}{C}-$.

The electron-impact mass spectral data obtained on the whole Mobil wax show that the molecular-weight range of this wax extends beyond 1300 amu. In contrast, the field-ionization spectra of the wax do not show the range extending much beyond 1000 amu. At probe temperatures exceeding 250° C, this latter observation is an artifact caused by sample molecules condensing on the surface of the razor blade emitter. The limitation can be avoided in future probe microdistillation experiments if field desorption emitters are used in place of razor blades. Very high molecular weight waxes, i.e., those having molecular weights greater than about 1500 amu, should be run under true field-desorption conditions by depositing the sample on the emitter and desorbing it at elevated temperature.

The mass spectral data from the alkane fraction of the topped Union Carbide F-T wax show a predominance of compounds having C_nH_{2n+2} elemental formulas over a mass range from 296 to 688. Only very small quantities of C_nH_{2n} compounds are present and virtually no compounds containing oxygen. These results together with those obtained from NMR showing no detectable olefins or oxygen-containing compounds in the fraction, provide conclusive evidence that the chromatographic separation scheme developed during the investigation produced an almost pure alkane fraction from the topped F-T wax.

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[1]DEPT - Distortionless enhancement by polarization transfer.
[2]QUAT - Quaternary only carbon-13 spectra - non-protonated carbons.

Based on the mass-spectral data, the alkene fraction from the topped Union Carbide wax contains about 78% olefins, 8% alkanes plus $C_nH_{2n}O$ compounds, and 14% $C_nH_{2n}O_2$ compounds. For the alkenes, the molecular-weight range extends from 308 to 882 amu. The range for the oxygen-containing compounds is less well defined, but it appears to extend at least to 844. The mass spectral data are in good qualitative agreement with the NMR data, except that the former indicate a concentration of oxygenates in the alkene fraction higher than the latter data suggest. If sensitivity factors were available for use in the calculations, agreement between the two data sets might be improved. Although some field-ionization sensitivities are available in the literature (19), this data base needs to be expanded, particularly with respect to compounds having molecular weights greater than 600 amu.

In spite of the presence of an unknown peak in the chromatogram showing the alkane-alkene separation of the topped Union Carbide wax, the separation is relatively clean according to the NMR and mass spectral results. The unknown peak may contain the oxygen compounds detected in the alkene fraction by NMR and MS. Based on the separations scheme, NMR, and MS data, such compounds could be unsaturated ethers and esters or unsaturated diethers. Isolation and analysis of this peak would be desirable and could provide some very interesting results to add to those already obtained on the Union Carbide wax.

In summary, the results obtained to date on the Mobil and Union Carbide waxes show that viable experimental methods have been developed to analyze these materials. The procedures, based on chromatographic separations, nuclear magnetic resonance spectroscopy, and mass spectrometry, have been refined to the point where they can be employed with confidence in spite of the fact that difficult obstacles had to be overcome during their development. Over the course of the investigation, these obstacles have been identified with the properties of the waxes themselves; i.e., high molecular weight, low volatility, and low solubility. Additional work on the Union Carbide and Mobil F-T waxes and similar F-T waxes is needed to establish the general utility and quality of the separation procedure and to make further refinements in the mass spectrometric method of analysis.

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