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COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION

Characterization of Coal-Derived Materials by Field Desorption Mass Spectrometry, Two-Dimensional Nuclear Magnetic Resonance, Supercritical Fluid Extraction, and Supercritical Fluid Chromatography/Mass Spectrometry

Topical Report

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Richland, Washington

and

CONSOL, Inc.
Library, Pennsylvania

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PROJECT ASSESSMENT

Introduction

Under contract from the DOE (Contract No. DE-AC06-RLO1830), and in association with CONSOL Inc. (DOE Contract No. DE-AC22-89PC89883), Battelle, Pacific Northwest Laboratory (PNL) evaluated four principal and several complementary techniques for the analysis of non-distillable direct coal liquefaction materials in support of process development. Field desorption mass spectrometry (FDMS) and nuclear magnetic resonance (NMR) spectroscopic methods were examined for potential usefulness as techniques to elucidate the chemical structure of residual (non-distillable) direct coal liquefaction derived materials. Supercritical fluid extraction (SFE) and supercritical fluid chromatography/mass spectrometry (SFC/MS) were evaluated for effectiveness in compound-class separation and identification of residual materials. Liquid chromatography (including microcolumn) separation techniques, gas chromatography/mass spectrometry (GC/MS), mass spectrometry/mass spectrometry (MS/MS), and GC/Fourier transform infrared (FTIR) spectroscopy methods were applied to supercritical fluid extracts. The full report authored by the PNL researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the methods for application to coal liquefaction materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of CONSOL's contract.

Summary

This study demonstrated the feasibility of using FDMS, NMR, SFE, and SFC/MS for the examination of the tetrahydrofuran-soluble portion of the 850°F$^+$ distillation resid materials derived from direct coal liquefaction. In addition, liquid chromatographic (LC) separations were employed to preseparate the resids prior to analysis by NMR and FDMS methods. Other techniques, including microcolumn LC separations, GC/MS, GC/FTIR, and MS/MS, were tested with the supercritical fluid extracts of the THF-soluble distillation resids.

A heteronuclear correlation (HETCOR) spectroscopy two-dimensional (2-D) NMR technique was applied without success to the THF-soluble distillation resids. Spectral-editing NMR techniques yielded some information on the aromatic cluster size and degree of aliphatic substitution in the THF-soluble resid samples.

FDMS analysis of the THF-soluble portion of the distillation resids showed differences in the molecular weight ranges and intensities of the prominent ions, and ratios of those ions, in samples obtained from different feed coals and in samples from different stages in the direct liquefaction process.

Supercritical fluid extraction reproducibly separated the THF-soluble resids with high extraction efficiency (>80%). The SFE fractions were successfully analyzed by FDMS and GC/FTIR, although no useful structural information was obtained. SFC of the unfractionated THF-soluble resids was not successful; there was very little or no peak resolution in the chromatograms. However, SFC did resolve some components of the SFE fractions. SFC/MS was not successful; this was primarily attributed to equipment limitations, such as a poorly performing SFC-MS interface, and not the technique. The MS/MS method, employing desorption chemical ionization, was demonstrated with one of the SFE extracts. The MS/MS experiment was performed on the m/z 277 ion, chosen because it was presumed to be m/z (276 H^+); m/z 276 was found to be a prominent peak in the FDMS study. Although the results obtained were not those for the predicted structure of the m/z 277 ion, the method appears to be promising.

Program Description

This report describes the work performed at PNL under a contract from the U.S. DOE (Contract No. DE-AC06-76RLO1830) in association with CONSOL Inc., Research and Development. CONSOL's contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction process development facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

PNL used field desorption mass spectrometry (FDMS) and various NMR techniques to analyze the THF-soluble portion of 850°F$^+$ distillation resids. 2-D NMR and NMR spectral editing techniques, which rely on the unique polarization parameters between the proton and carbon nuclei, were applied to the THF-soluble resids. These techniques included the attached proton test (APT) and distortionless enhancement by polarization transfer (DEPT). The resid materials, which are solids at room temperature, were analyzed as THF solutions. The samples analyzed by FDMS and NMR were produced at the Wilsonville pilot plant. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic or catalytic/catalytic). Samples from Wilsonville were taken from three locations: between the reactors, after the second-stage reactor, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. All of the Wilsonville samples were composites of samples taken over long periods of single runs.

Separation techniques, including SFE, SFC, SFC/MS, high pressure liquid chromatography (HPLC), microcolumn liquid chromatography, open column liquid chromatography, gas chromatography/Fourier transform infrared (GC/FTIR) spectroscopy, MS/MS and GC/MS were applied to THF-soluble materials obtained from two facilities. Four of the samples analyzed by these methods were identical to those analyzed by FDMS and NMR. Two additional samples, which represent single run periods, were obtained from the HRI process development unit. The HRI samples were chosen to represent two methods of pretreating the coal before it is fed to the liquefaction system.

The FDMS experimental procedure is described on page 7 of the attached report, the NMR experiments are described on page 15, and the separation techniques are described on pages 23-26.

Participant's Major Findings

The following principal observations were reported by PNL for the application to coal liquefaction materials of Field desorption mass spectrometry (FDMS), nuclear magnetic resonance (NMR) spectroscopy, and the assorted separation techniques inclusive of supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC), and high pressure liquid chromatography (HPLC), microcolumn liquid chromatography, and open column liquid chromatography. An expanded discussion can be found in the attached report, pages 6 through 31.

The FDMS technique shows that all the resid samples examined have roughly the same molecular weight distribution; the bulk of the material is within the range of 200 to 600 Da. However, many of the samples exhibited peaks as high as 3500 Da. PNL reports that the molecular weights of resid samples obtained at different locations in the liquefaction process increases slightly in the order: second-stage product sample < recycle oil sample < interstage oil sample for each set of samples produced during different runs at the Wilsonville Advanced Two-Stage Liquefaction Facility. Tentative structures were assigned to several prominent ions in the 200 to 400 Da range (e.g., m/z 242, 276, 308, and 316). The prominent peaks and their assignments agreed with previous published field-ionization mass spectroscopy work on the same samples.[1] It was noted by PNL that the ratios of these ions differ among the various samples.

Application of the heteronuclear correlation (HETCOR) spectroscopy technique, also referred to as 2-D NMR, was not successful with the whole resid samples. This is due to the lack of peak resolution obtained in both the component ^{13}C- and ^{1}H-NMR spectra. In an exploratory test, PNL found that it is possible to improve the resolution by preliminary separation of the resid samples by supercritical-fluid techniques and open column liquid chromatography. DEPT and APT techniques are used to determine the distribution of carbon types. The experiments can distinguish between protonated and non-protonated aromatic carbon, and the amount of methyl, methylene, and methine carbon. The DEPT and APT spectra of the samples examined by PNL (Nos. 2, 3, and 4), show very little aliphatic methine (mono-protonated) carbon to be present.

Supercritical fluid extraction gave high extraction efficiencies for four samples (>80% in all cases) with the THF-soluble resid samples. However, HPLC of the whole THF-soluble resids and supercritical fluid chromatography of the SFE fractions were not successful; only broad, unresolved peaks were observed. The SFE fractions were further separated by open column liquid chromatography followed by HPLC. Although peak resolution was greatly improved, the separated components were not characterized. GC/FTIR of the SFE fractions was performed; however, no compound identifications could be made. GC/MS of a nonpolar (hexane-eluted) HPLC fraction of an isopropyl alcohol/CO_2 SFE fraction of one HRI filter liquid was reported. Some of the identified structures are consistent with the prominent ions identified by FDMS of the parent THF-soluble resid.

The SFE fractions also were analyzed by electrospray mass spectrometry and desorption chemical ionization (DCI) MS/MS of selected ions from the electrospray MS analyses. As most of the compounds in the SFE fractions were not ionizable by electrospray ionization, this technique appears to have little potential for use with these samples. The DCI MS/MS technique, while not fully explored in this study, showed potential for further analysis of single ions in the complex MS spectra. The SFE fractions also were examined by FDMS. The different SFE fractions consist of materials with distinctly different molecular weight ranges.

CONSOL Evaluation

The FDMS technique appears to have potential for the analysis of the coal-derived resids. A number of unresolved issues remain to be addressed before the method can be unconditionally recommended. One issue concerns the limitation placed upon the analysis by the introduction into the mass spectrometer of only the solubility portion of the samples. Alternate mass spectral techniques also have limitations: field ionization (FI) MS is limited by sample volatility, plasma desorption (PD) MS is limited by the ability of the experimenter in creating a thin film of sample material. Which of these constraints is more restrictive is not obvious. A second issue is the potential for different FDMS responses to various compound types in complicated mixtures that have a wide range of molecular weights (such as in a resid); this also must be determined before the FDMS method could be routinely used for process development application.

The use of 2-D NMR techniques and the various NMR spectral editing techniques for coal derived resids appears feasible and potentially useful for structure determination if the samples are first separated into sufficiently specific compound class fractions. Such separations, as demonstrated in this work, were performed fairly well by a series of techniques: supercritical extraction with various organic fluids, followed by liquid chromatographic methods. The resultant information from such extensive and labor-intensive work was not fully evaluated by PNL, although such an evaluation would be required before the use of such a complicated scheme could be recommended as a process development tool.

The different techniques employed in this work require large capital investment for the equipment. Some costs reported by PNL to CONSOL follow. The high-resolution mass spectrometer with FD capabilities costs approximately $800,000. A supercritical fluid extraction system costs about $60,000. A supercritical fluid chromatograph/mass spectrometer costs on the order of $300,000. A high-resolution NMR costs approximately $300,000. The expendable supplies used in this contract for the supercritical fluid systems (e.g., columns, solvents and gases), cost about $5,000. The open column chromatography experiments, as performed in this work, used about $5,000 worth of supplies (columns, packing, and solvents). Each of the experimental procedures requires 1 - 2 hours to prepare and run a sample.

Further Development

Each of the analytical techniques demonstrated in this study can be further developed for use in the analysis of direct coal liquefaction derived resid materials. Suggestions made by the PNL research group include: 1) further examination of the specific hydrocarbons, some of which were tentatively identified by FDMS, that have prominent ion intensities, 2) identification of specific compounds that have molecular weights greater than 300 Da., 3) the analysis of all process streams in the direct liquefaction process by various NMR techniques, including HETCOR, DEPT, APT, and quantitative proton and carbon NMR, 4) application of PNL's ultra-high pressure NMR cell for the in situ analysis of supercritical fluid extracts from coal liquefaction resids, and 5) expanded use of separation techniques, especially supercritical fluid techniques, as hyphenated methods (i.e. SFC-MS, SFC-FTIR, and SFE-desorption chemical ionization (DCI) MS) for the analyses of the resid materials. Other research directions based on this work that are worthy of note include: 1) a detailed comparison of the results and usefulness of FDMS, FIMS and ^{252}Cf-PDMS for process development, and 2) development of a systematic separation and analysis scheme for non-distillable coal-derived resids utilizing the methods demonstrated in this study.

Contractor's Statement of Work

In order to better elucidate the composition of the non-distillable residuum portion of coal liquefaction streams as it relates to conversion activity, a number of novel techniques will be applied to coal liquefaction process derived materials. These techniques include field desorption mass spectrometry (FDMS), two dimensional nuclear magnetic resonance spectroscopy (2D-NMR), and supercritical fluid extraction (SFE) coupled with supercritical fluid chromatography (SFC). FDMS is noted for its ability to directly analyze high molecular weight materials. 2D-NMR is a powerful method for obtaining organic structural information. SFE is useful for compound class separations, especially of high molecular weight materials. SFE, followed by SFC with mass spectral detection, is useful for the analysis of compounds with high molecular weight and limited volatility. It is, therefore, a promising technique for analysis of coal derived materials.

Field desorption mass spectrometry (FDMS) will be used for resid characterization. A potential advantage of FDMS over other mass spectrometric methods is that high molecular weight samples can be ionized directly from the condensed phase without the need for vaporization by heating. The application of FDMS to a reasonably large sample set (12 samples) will allow a demonstration of the value of this technique. These samples have been selected (see attached list) so that the utility of FDMS for addressing the issue of resid reactivity can be evaluated. The twelve samples will be supplied to PNL with the following information (as available): elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, resid reactivity data (calculated), and the full history of the sample (plant, process conditions, age, and storage conditions). All samples are non-distillable residual materials which may contain insoluble organic matter (IOM) and ash. Sample size will be at least 0.5g. Most samples will be brittle pitch-like materials that will be supplied as approximately -8 mesh (2.4 mm) pieces.

Supercritical fluid extraction-supercritical fluid chromatography (SFE-SFC) is a combined technique which may prove useful for the separation of the high molecular weight, polar materials found in coal liquefaction process streams. These materials are primary candidates for retrogressive reactions leading to poor conversion in coal liquefaction. The extraction will provide a rough compound class separation. With the use of mass spectrometric detection, supercritical fluid chromatography can be used to detect compounds with molecular weights in excess of 600 daltons. The method is not amenable to solids-containing samples and, therefore, a sample set has been selected which contains only the tetrahydrofuran (THF) soluble portion of distillation resids and filtered liquids from different process streams. Six samples will be supplied to PNL for supercritical fluid chromatography. Each will be supplied with the following information (as available): elemental analyses, phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Sample size will be nominally 1 g.

Two dimensional NMR (2D-NMR) will be used to obtain structural information of the heavy materials found in coal liquids. The technique is only amenable to liquid or soluble material. Consol will supply to PNL THF-soluble portions of four distillation resids for 2D-NMR. These materials will be supplied with the following information (as available): elemental analyses, phenolic -OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Sample size will be nominally 0.5 g.

References

1. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization, Topical Report", DOE/PC 89883-39, January 1992.

COAL LIQUEFACTION PROCESS STREAMS
CHARACTERIZATION AND EVALUATION

CHARACTERIZATION OF COAL-DERIVED MATERIALS BY FIELD DESORPTION MASS SPECTROMETRY, TWO-DIMENSIONAL NUCLEAR MAGNETIC RESONANCE, SUPERCRITICAL FLUID EXTRACTION, AND SUPERCRITICAL FLUID CHROMATOGRAPHY/MASS SPECTROMETRY

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CONTENTS

ILLUSTRATIONS

TABLES

GLOSSARY

2-D NMR	Two dimensional-nuclear magnetic resonance
APT	Attached proton test
C/C	Catalytic/catalytic
CI	Chemical ionization
CID	Collision induced dissociation
CsI	Cesium iodide
DCI	Desorption Chemical Ionization
DEPT	Distortionless enhancement by polarization transfer
EI	Electron impact
EPA	Environmental Protection Agency
FAB	Fast atom bombardment
FDMS	Field Desorption Mass Spectrometry
FI	Field ionization
FL	Filter Liquid
GC	Gas chromatography
GC/FTIR	Gas chromatography/Fourier transform infrared spectrometry
GC/MS	Gas chromatography/mass spectrometry
GC/MSD	Gas chromatography/mass selective detector
HET2DJ	Heteronuclear two-dimensional J-spectroscopy
HETCOR	Heteronuclear correlation spectroscopy
HOM2DJ	Homonulear two-dimensional J-spectroscopy
HOMCOR	Homonuclear correlation spectroscopy
HPLC	High performance liquid chromatography
INEPT	Insensitive nucleus enhancement by polarization transfer
IPA	Isopropanol
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
PAH	Polycyclic aromatic hydrocarbons
PNL	Pacific Northwest Laboratory
RIC	Reconstructed ion chromatogram
SFC	Supercritical fluid chromatography
SFC/MS	Supercritical fluid chromatography/mass spectrometry
SFE	Supercritical fluid extraction
SRC	Solvent refined coal
T/C	Thermal/catalytic
THF	Tetrahydrofuran
W	Wilsonville

EXECUTIVE SUMMARY

Pacific Northwest Laboratory (PNL) has analyzed a series of coal-derived residual oils by field desorption mass spectrometry (FDMS) and two-dimensional nuclear magnetic resonance (2D-NMR) to better elucidate the composition of the non-distillable residuum portion of coal liquefaction streams as it relates to conversion activity. Supercritical fluid extraction and supercritical fluid chromatography/mass spectrometry (SFC/MS) have also been evaluated for compound class separation and identification. The results of the analyses are briefly summarized in Table 1.

Twelve coal-derived samples, taken from the Wilsonville facility at three different locations during each of four runs to represent different degrees of coal processing, have been analyzed by FDMS. The molecular weight distributions obtained by FDMS are similar for all of the samples analyzed. The molecular weight ranges are between 200 and 800 Da. There are, however, subtle differences that exist between samples. Qualitatively, there appears to be a slight increase in the molecular weight in going from the product oil, to the recycle oil, to the interstage oil for each set of samples. For some samples, there is also a difference between the ratio of extracted ions for a specific mass range, e.g., 400 to 500 Da, and the total ion intensity. In addition, the ratio of the intensities for several of the predominant ions varies for many of the samples. Tentative structures for several of the predominant ions m/z 242, 276, 308, and 316 have been assigned. Mass spectra for the above listed ions have been obtained by supercritical fluid fractionation of one of the samples, followed by open column chromatographic separations, with subsequent analysis by gas chromatography/mass spectrometry. The tentative structures are consistent with the observed mass spectra. Other methylated homologues have also been tentatively assigned.

For several of the Pittsburgh seam and Wyodak samples, field desorption (FD) spectra were difficult to obtain, possibly due to suppression of the signal from higher molecular weight material or degree of solubility in THF. However, for the most part, there was good agreement between the results obtained by FD and field ionization

(FI) studies conducted by SRI (1). The results also provide clear evidence for the value of FDMS analysis of coal-derived resids.

Field desorption mass spectrometry has also shown a clear molecular weight distribution difference between supercritical fluid fractionated high molecular weight resids. Desorption chemical ionization (DCI), a technique similar to both FD and FIMS except chemical ionization is utilized rather than electron impact ionization, has also provided information on both the coal-derived resids and also the supercritical fluid-fractionated resids.

Quantitative proton and ^{13}C solution spectra were collected at 300 MHz and 75 MHz on four THF-soluble portions of the distillation resid. The coal liquefaction residues were found to contain aromaticities, f_a, from 52-74%. Distortionless enhancement by polarization transfer (DEPT), Heteronuclear Correlation Spectroscopy (HETCOR) and the Attached Proton Test (APT) were used to determine the distribution of the functional groups throughout these coal products. The failure of the HETCOR experiments on the coal liquefaction residues is, in part, caused by the lack of peak definition in both the ^{13}C and ^{1}H NMR spectra of these samples. A comparison of the spectra obtained in this study with those of solvent refined coal (SRC) distillate products show a large difference in NMR signal type. In order to effectively apply two-dimensional NMR techniques to coal products, fractionation of the products is necessary. As an example, the samples may be fractionated with the utilization of supercritical fluids prior to NMR analysis. Preliminary results obtained in a study employing fractionation by supercritical fluids, followed by separation with open column chromatography, and subsequent NMR analysis show significant improvement in resolution compared to NMR analysis of the original material.

Four of the six samples (17-20) provided by Consol were extracted with supercritical propane, pentane, pentane/methanol, pentane/THF, and pentane/acetic acid in a sequential manner. The summation of the weights of all of the extracts and the residue added up to 99+% of the material placed in the extraction cell for each sample. The total amount extracted by the non-polar solvents, propane and pentane, was fairly constant at 43.6 to 44.8 wt %. The last two samples, HRI filter liquid samples, were extracted with supercritical fluid carbon dioxide with a modifier of 10%

isopropanol. Approximate extraction efficiencies were 20-30% for both of the last two samples. Supercritical fluid chromatography (SFC) was attempted on the extracts, but met with little success. Only a broad, unresolved hump was present; there was no indication of any separation or resolution of components for any of the samples. Both packed and capillary column SFC were attempted using supercritical propane, pentane, and modified pentane but little difference in resolution was observed.

Supercritical fluid chromatography/mass spectrometry has been used to analyze complex hydrocarbon mixtures. Mass spectral data were obtained and the preliminary results are very promising; however, more work needs to be directed toward instrument development. We do feel that SFC/MS warrants further attention for the analysis of the high molecular weight resid samples.

Supercritical fluid extraction with subsequent analysis by electrospray mass spectrometry appears to be of little use for these types of samples. However, supercritical fluid extraction and fractionation followed by desorption chemical ionization (DCI) mass spectrometry or FD holds promise for providing additional structural information. Preliminary results of the pentane and pentane/methanol fractions by FD showed different molecular weight distributions. Fractionation by supercritical fluid extraction with subsequent analysis by NMR may also provide structural information on the coal liquefaction products. In addition, preliminary results from microcolumn separations and open column separations with subsequent mass spectrometry analysis indicate that further insight into structure elucidation or compound class identification in the resids may be possible.

INTRODUCTION

Under a subcontract from Consolidation Coal Company (CONSOL Inc.), Pacific Northwest Laborary (PNL)[a] has analyzed a series of coal liquefaction products by field desorption mass spectrometry (FDMS), two-dimensional nuclear magnetic resonance (2D-NMR), and tested the feasibility of supercritical fluid extraction and supercritical fluid chromatography/mass spectrometry for compound class separation and identification. The purpose of this work was to provide a bridge between direct coal liquefaction process development and analytical chemistry. Well-documented samples were provided by CONSOL to apply methodology to a sufficient number and range of samples to identify the value of the method to process understanding and development. Analytical methods of interest were chosen which are novel only in that they have not been fully demonstrated for application to coal liquefaction. The intention of this project was not to foster development of completely new analytical techniques, but to fully exploit the potential of existing but currently underutilized techniques. The further intent of this project was not merely to collect data, but to assist process development efforts. One of PNL's goals was to attempt to elucidate the composition of the non-distillable residuum portion of the coal liquefaction streams as it relates to conversion activity.

The project consisted of three tasks which are listed below:

TASK 1	Field Desorption Mass Spectrometry
TASK 2	Two-dimensional Nuclear Magnetic Resonance of as received THF soluble resids
TASK 3	Supercritical Fluid Extraction and Supercritical Fluid Chromatography/ Mass Spectrometry of THF soluble resids

The samples provided by CONSOL and the corresponding analytical techniques are listed in Table 2.

[a] Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

TASK 1. FIELD DESORPTION MASS SPECTROMETRY OF RESIDS

INTRODUCTION

Field desorption mass spectrometry (FDMS) is a valuable analytical tool because of its advantage in producing high molecular ion abundances. FDMS has proven itself to be an excellent technique for the screening and profiling of complex samples. The number of components, their molecular weights, and even their approximate relative abundances can readily be obtained. Field desorption has been particularly useful in studies of biologically significant molecules, providing in many cases the first unequivocal verification of structure. The technique has been applied to antibiotics, peptides, nucleosides, nucleotides, oligosaccharides, and carotenoids (2). In addition, FD has been applied to a Lummus Crest, Inc. (LCI) Arab heavy resid and a coprocessed coal and heavy oil (3).

Field desorption is an alternative method of producing ions from neutral molecules. In this procedure a sample is deposited (from solution) onto a specially prepared emitter consisting of a 10 micron tungsten wire on which has been grown carbon dendrites, or alternatively, single crystal silicon needles. In either case, the tips of the emitter's microstructure exhibit submicron radii of curvature. After coating with sample, the emitter is introduced into the mass spectrometer and exposed to voltages which produce field strengths on the order of 10^8 V/cm at the needle-like tips. The exact nature of the ionization process in field desorption is a matter of intensive study. At least in some instances, it appears that coating the anode with sample simply serves to provide a reservoir of sample very near the site that ionization occurs as in field ionization. In addition, at such field strengths, the molecular orbitals of the sample molecules are distorted to such an extent that there exists a finite probability of an electron moving from the molecule to the emitter substrate. This process is termed electron tunneling. Loss of an electron converts the sample molecule to a surface-bound positive ion. Under the influence of the high field, these surface-bound ions are evaporated from the surface and formed into an ion beam. The ion beam is then mass analyzed in exactly the same way as for any other form of mass spectrometry.

Field desorption has the advantage of imparting very little energy to a sample molecule in the process of producing an ion. The technique is, therefore, far more likely to produce an intact molecular ion than is electron impact. It should be noted that the presence in a sample of acids or alkali metal salts can lead to the preferential formation of ions by protonation or alkali ion attachment. Many samples require that the emitter be resistively heated in order to obtain ion emission. The exact temperatures reached are unknown because the structures are so small, but the effect of temperature is to transfer sample from locations deep within the emitter structure out to the fine points where ion emission is occurring. Based on the thermal changes observed in sensitive samples, it is clear that the temperatures are much lower than those required to obtain electron impact spectra.

EXPERIMENTAL

The analyses were performed on a high resolution magnetic sector instrument. The mass spectrometer was scanned from 0-4000 amu and 40 s scan slope at approximately 35 s/scan. The resolution was 1000 and the instrument was calibrated from 133 to 5000 with CsI. A small portion of each sample was dissolved in tetrahydrofuran (THF) and placed on a silicon emitter. The ramp rate was 4mA/min up to 50 mA. The ion source was maintained at ambient temperatures. Mass spectra were acquired at about every 35 sec across the desorption profile and individual scans in the desorption profile were summed to create a time-integrated mass spectrum representing the overall sample composition. Typical total scan time was 5-10 min.

Solubility estimates were measured by taking approximately 0.2 g of sample, dissolving in THF, centrifuging, removing the THF soluble material, drying the residue, and weighing the undissolved material. The weight of the undissolved material compared to the weight of the starting material produced an estimate of the THF soluble material.

RESULTS

Figures 1 and 2 are spectra from two of the samples, sample 5 (Illinois No.6, Wilsonville (W); Run 250, Thermal/Catalytic (T/C), product oil resid) and sample 6 (Illinois No. 6, W; Run 250; T/C, recycle oil resid), respectively. Figures 3-4 show the extracted molecular weight ranges for sample 5 and sample 6. Figures 5-6 show the spectra of samples 8 (Illinois No. 6, W, Run 257, Catalytic/Catalytic (C/C), product oil resid) and 10 (Illinois No. 6, W, Run 257, C/C, interstage oil resid) in the mass range of 200-400 Da, respectively. The spectra were not ^{13}C corrected. The FD mass spectra of all the samples are included in Appendix A.

Table 3 lists the estimates of THF solubility for all the samples examined by FDMS.

DISCUSSION

The FD spectra for all the samples were similar in that the molecular weight distributions were typically in the range of 200 to 600 Da. There are, however, small differences that exist between samples. As an example; in a qualitative sense, there is a difference among samples 5,6, and 7, the product oil resid, recycle oil resid, and the interstage oil resid, respectively. In going from the product oil resid to the recycle oil resid, there is a slight shift to a higher molecular weight distribution. The base peak, the most intense ion, in sample 5 is m/z 426 and for sample 6, m/z 559 is the base peak. There appears to be very little difference between sample 6, recycle oil resid, and sample 7, the interstage oil resid. The base peak in sample 6 is m/z 559 and for sample 7, m/z 571 is the base peak.

There are also small differences among samples 8,9, and 10. The molecular weight distribution for sample 8 is almost identical to sample 10. Sample 9, recycle oil resid, is somewhat different than both sample 8 and 9. However, the base peak for sample 8 was m/z 364, sample 9 was m/z 863, and sample 10 was 490.

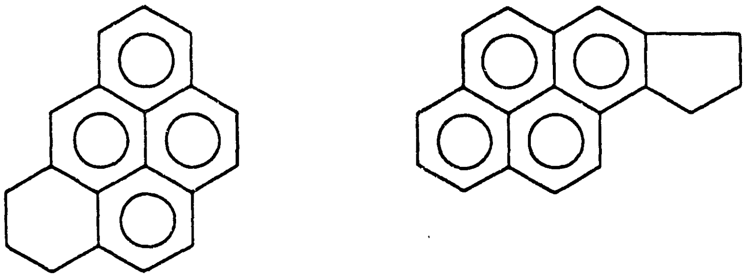
Differences also exist among the thermal/catalytic samples from Illinois No.6 and the catalytic/catalytic samples. There is a slight difference in molecular weight distribution between samples 5 and 8. The base peak for sample 5 is m/z 426, and for sample 8 m/z 364 is the base peak. For samples 6 and 9, there is a distinct difference in molecular weight distribution. The molecular weight distribution is centered around 400 Da for sample 9 and approximately 550 Da for sample 6. Again, the base peaks are m/z 863 and m/z 559, for samples 6 and 9, respectively. The differences between sample 7 and 10 are not as dramatic. The molecular weight distribution is centered around 450 to 550 Da for both samples. However, the base peak for sample 7 is m/z 571 and m/z 490 for sample 10.

Samples 11, 12, and 13 , Wyodak starting coal, provided the most unique field desorption mass spectra. Sample 11 has no real distinct molecular weight distribution; there is approximately equal intensity of ions from 200 to 4000 Da. Sample 12 appears to have a distribution centered around 300 to 350 Da and another centered around approximately 450 Da. The base peak is m/z 451. The mass spectrum for sample 13 has the lowest intensity, corresponding to the lowest solubility in THF (See Table 3). The base peak for sample 13 is also m/z 450 Da.

Samples 14, 15, and 16 have very similar molecular weight distributions centered at approximately 500 Da. However, the base peaks for samples 14, 15, and 16 are m/z 552, 350, and 276, respectively.

Corrections for background intensities of all other components that may exist at the specific masses were not included. This may not be a large factor for a peak at 242 Da; the correction may be larger for a component at 300-350 Da. Therefore, in a semiquantitative manner, the ratio of the various mass ranges to the total ion intensity varies for some of the samples. As an example, as shown in Figures 3 and 4, the ratios of the ion intensity at 400 to 500 Da to the total ion intensity are slightly different. The ratios for sample 5 for the various mass ranges are 400 to 500- 0.41, 500 to 600- 0.30, 600 to 700- 0.18, 700 to 900- 0.22, 900 to 1100- 0.10, 1100 to 1300- 0.06, and 1300 to 1500- 0.04. For sample 6, the ratios for the same mass ranges are 0.17, 0.25, 0.20, 0.28, 0.16, 0.08, 0.06.

There are several prominent ions, in the range 200 to 400 Da, present in the FD spectra of many of the samples. The major ions include m/z 242, 276, 282, 300, 308, 316, 330, 354, 380, and 382. Several of these peaks are similar to those identified by Sullivan et al. (4) as showing an increase during hydrotreating of petroleum vacuum gas oil fractions. In addition, these components may be related to the difficulty of catalytic/thermal breakdown to smaller species. As a result, the structures of these prominent ions becomes very important. As an example, in sample 8 (Figure 5), the first prominent peak is m/z 242. Tentative structures for m/z 242 and other ions are shown below:

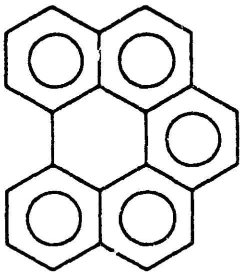


MW 242

pentacylcopyrene

The structure of this component is probably pentacyclopyrene. Peaks at m/z 256 and 270 are possibly the methylated pentacyclopyrenes.

The next peak, m/z 276, may be benzo[ghi]perylene with m/z at 290 and 304 designated as the methylated benzo[ghi]perylenes. The structure of benzo[ghi]perylene is shown below.

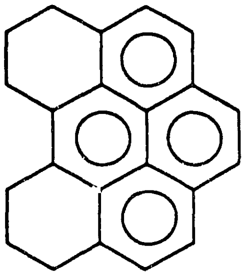


MW 276

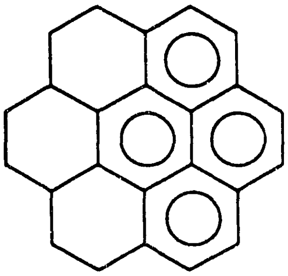
benzo[ghi]perylene

The peak at m/z 276 is a prominent ion in the mass spectra of the Pittsburgh resid samples 11 and 12, the recycle oil resid and interstage oil resid, respectively. In addition, the intensity of m/z 276 is higher in the Pittsburgh resids, both the recycle oil resid and the interstage oil resid, than for the other samples. However, the intensity of m/z 276 in the product oil resid is only approximately 20%. The intensity of m/z 276 in the interstage oil resid (Illinois No.6; Run 257; C/C) is approximately 20%, but m/z 276 is 75% for the product oil resid (Illinois No. 6; run 257; C/C). The catalytic/catalytic run of Illinois No. 6 (Run 257) produced more m/z 276 by a factor of 3 to 4 more than the thermal/catalytic run of Illinois No.6 (Run 250).

The peak at m/z 282, of almost equal intensity of m/z 276, is probably hexacylopyrene. The methylated hexacyclopyrenes are assigned as m/z 296 and 310. The peak at m/z 308 is possibly heptacyclopyrene. The tentative structures for m/z 282 and 308 are shown below.

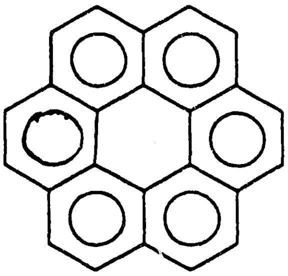


MW 282
hexacyclopyrene

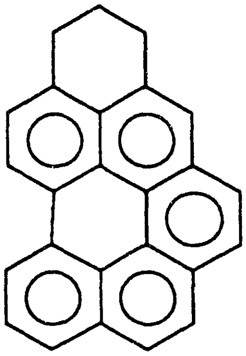


MW 308
heptacyclopyrene

Peaks at m/z 300 and 316 have been assigned the following tentative structures.



MW 300



MW 316

coronene

Similar compounds have been identified by Sullivan et al. utilizing high performance liquid chromatography (HPLC) separation with subsequent field ionization mass spectrometry (4). Malhotra and McMillen found similar components by field ionization mass spectrometry (1). Boduszynski et al. also utilized liquid chromatography/field ionization mass spectrometry to analyze high-boiling and nondistillable coal liquids (5). Mass spectra of many of the low, <350, m/z components have been obtained by PNL utilizing supercritical fluid extraction, followed by open column chromatographic separation, with subsequent analysis by mass spectrometry. The structures are consistent with the observed mass spectra. This will also be discussed in more detail under Task 3- Supercritical Fluid Extraction and Supercritical Fluid Chromatography/ Mass Spectrometry of THF soluble resids.

The intensities for m/z 242, 252, and 276 in the FD spectrum of sample 10 (Figure 6) are considerably less than that for the corresponding product oil resid (Figure 5). For sample 10, m/z 242 is approximately 8%, 252 is 10%, and 276 is 15%. M/Z 242 is approximately 30%, 252 is 5%, and 276 is 80% for sample 8, the corresponding product oil resid. The ratios of the intensities for m/z 256/242, 300/276, 316/242 are also quite different for these two samples. For sample 8, the ratio for the intensities for m/z 256/242 is approximately 2.0, m/z 300/276 is approximately 0.45, and 316/242 is 1.0. However, for sample 10, the ratio of the intensities for m/z 256/242 is approximately 1.0, m/z 300/276 is 1.1, and 316/242 is approximately 6.0. These may reflect differences in processing and should be examined in greater detail for these as well as the other samples.

The FD spectrum of sample 13 (Wyodak, W; Run 251-II; T/C; interstage oil resid) is shown in Figure 7. This sample was interesting because of the limited solubility in THF and the large amount of suspended material. The estimated solubility in THF was approximately 55%. The estimated solubilities for the other samples are listed in Table 3. However, the FD spectrum looks very similar to the others, but with much lower intensity.

FURTHER STUDIES

There are qualitative differences between many of the samples. Many of the predominant ions tentatively identified have very different intensities and the ratios of intensities of the major ions vary. These differences should be examined in more detail. The identity of many of the hydrocarbons and others that are yet unidentified may affect the reaction chemistry in coal processing. There should also be an emphasis on the identification of hydrocarbons with higher molecular weights than 350 Da.

In addition, there should be an emphasis placed on the utilization of FD and DCI for fractionated resids, for example supercritical fluid extracts.

TASK 2. TWO-DIMENSIONAL NMR

INTRODUCTION

Spectral editing and two dimensional NMR techniques on fossil fuel derived samples can yield valuable structural information not obtainable by normal ^1H or ^{13}C NMR techniques. While the normal, one-dimensional, NMR techniques yield statistical information and can yield quantitative structural distributions, important structural information can be obtained using spectral editing and two-dimensional NMR methods on fossil fuel products. Spectral NMR editing techniques include: INEPT (Insensitive Nucleus Enhancement by Polarization Transfer); APT (Attached Proton Test); DEPT (Distortionless Enhancement by Polarization Transfer); as well as other methods. These spectral editing methods use the unique polarization transfer parameters between the proton and the carbon nucleus for each carbon functionality to yield the desired spectra. Spectral editing techniques are extremely important for determining the actual carbon functionality distribution around the ^{13}C NMR boundaries for each specific functional group. For example, the DEPT experiment can be used for the determination of overlap between the methyl and methylene regions. More importantly, this experiment can differentiate between protonated and non-protonated aromatic carbons which unfortunately can appear in similar regions of the ^{13}C NMR spectrum. Spectral editing techniques can also be used to determine the amount of methyl, methylene, and non-protonated carbons for narrow fractions of fossil fuel products.

Two-dimensional NMR techniques such as HETCOR (Heteronuclear Correlation Spectroscopy), HOMCOR (Homonuclear Correlation Spectroscopy), HET2DJ (Heteronuclear two-Dimensional J-Spectroscopy), and HOM2DJ (Homonuclear two-Dimensional J-Spectroscopy) are also used to uncover information buried in unusual spectral regions. These techniques can also be used to determine the hybridization about the carbon atoms , similar to the spectral editing techniques. The ^{13}C HOMCOR experiment has been used to determine carbon-carbon connectivities and thereby the structure of complicated biological molecules. The

HETCOR experiment allows the correlation between protons and carbons detected by the NMR method. The two-dimensional J-coupling resolved spectroscopies yield spectra which show the coupling constants on each nuclei of interest. These techniques also yield information on connectivity and hybridization.

The NMR techniques discussed above have been successfully utilized in determining structures of complicated biological molecules and have also been applied to fossil fuels and their products with varying degrees of success. The best results with fossil fuel derived materials using two-dimensional and spectral editing techniques have come while investigating fractionated products. The types of information to be gained using these advanced NMR techniques on fossil fuel fractions include: uncovering "buried" structural information; determining carbon-hydrogen connectivities; determining the degree of protonation on each type of carbon; and the hybridization of each carbon. We have proposed to use spectral editing and two-dimensional NMR techniques along with conventional one-dimensional methods to investigate fractionated coal products to determine structural information important in the liquefaction process.

EXPERIMENTAL

All NMR spectra were collected on a Varian VXR-300 NMR spectrometer. The THF soluble coal residues, approximately 30-100 mg, were dissolved in 1 mL of 99+% deuterated THF which contained tetramethylsilane (TMS) as an NMR chemical shift standard. The NMR spectra were collected with 0.5 mL of these samples in a 5 mm NMR tube. The proton NMR spectra were collected at 300 MHz using a 3000 Hz spectral window with a 2.5 s acquisition time. The ^{13}C NMR spectra were obtained at 75 MHz with a 16,000 Hz spectral window, a 0.374 s acquisition time and a 100 s recycle time. Gated decoupling was used along with the long recycle time to suppress the nuclear Overhauser effect (NOE) and improve quantitation. The DEPT (6), APT (7a-c) and HETCOR (8a-b) experiments were conducted using the standard respective pulse sequences. The samples studied were designated sample 1 as run 257, C/C, 2nd stage product; sample 2 as run 257, C/C; interstage oil; sample 3 as run 259, C/C, 2nd stage product; and sample 4 as run 259, C/C, interstage oil. Samples 1 and 2 are derived from Illinois No.6 coal and samples 3 and 4 from Pittsburgh seam coal.

RESULTS

Figure 8 is a ^{13}C NMR spectrum of sample 4, Illinois No.6, run 259, C/C, interstage oil, in d_8-THF. The remaining ^{13}C NMR spectra are in Appendix B. The two large offscale peaks shown in the figures are the carbon signals from the THF solvent. The sharp resonance at 0 ppm is due to the added TMS. All of the other resonances are due to the coal products. The results from the ^{13}C NMR experiments are shown in Table 4 . The integral regions depicted in the figures and shown in the table correspond to known carbon functionalities (8a-b). The column headed f_a is the fraction of the carbon which is aromatic as determined by the NMR technique, and is defined as the amount of carbon signal between 90 and 220 ppm divided by the total carbon signal. The functional group distribution data in Table 4 show that Illinois No.6 samples, 1 and 2, are very similar to one another but the Pittsburgh samples, 3 and 4, are very different.

The proton NMR results are shown in Table 5. Figure 9 is a proton NMR spectrum of sample 4. Other proton NMR spectra have been placed in Appendix B. The two separate resonances from the THF solvent appear at 3.6 ppm and at 1.6 ppm and are small compared to the coal resonances. The large offscale peak at 0 ppm is due to the added TMS chemical shift standard. The integral regions depicted are again selected for functional group analysis (9a-b).

The DEPT spectra for sample 4 (Pittsburgh seam, run 259,C/C, interstage oil) are shown in Figures 10-12. DEPT spectra for sample 3 (run 259, C/C, 2nd stage product) are in Appendix B. The large sharp peak centered at 0 ppm is TMS and the negative peak is from the THF solvent while the other signal from the THF has been nulled. Figure 10 shows the spectrum obtained when only the methyl carbons are examined. Figure 11 demonstrates the ability to probe only the methine carbons while Figure 12 shows the spectrum obtained when only protonated carbons were selected.

The APT spectra for sample 2 (Illinois No.6, C/C, interstage oil) shown in Figures 13 and 14 demonstrate the abilities of this technique. Parameters in the APT experiment can be selected so that only specific types of carbons are "tickled" by polarization transfer. The phase of the resulting spectrum can be either positive or negative. Figure 13 shows the spectrum resulting from the use of a general APT parameter which allows observation of all carbons while differentiating them. The non-protonated and the methylene (CH_2) carbons appear as positive peaks in the spectrum while metine (CH) and methyl (CH_3) are negative. The two large off-scale peaks are due to to d_8 -THF which is mainly deuterated and behaves as non-protonated carbons. The regions denoted by the various types of APT signals are in good agreement with the expected results.

The APT spectrum in Figure 14 shows the results of selected excitation of only the quaternary carbons from sample 2, C/C, interstage oil. The parameters selected for this APT spectrum allow excitation of only the quaternary carbons. The results of this experiment show good agreement with those from Figure 13 with only the non-protonated carbons showing signals. Again, the two large off-scale peaks are due to deuterated THF solvent. This spectrum also shows the ability to observe only slected carbon types, but this spectrum also demonstrates some of the drawbacks of this technique. The negative peak in the protonated aromatic region, around 130 ppm, shows that the polarization transfer is not always selective. Some spill over from the proton transfer can and does occur. However, this spectrum does demonstrate the absence of non-protonated aliphatic carbons.

No HETCOR spectra of these samples are shown since only the solvent peaks were resolved using this technique.

DISCUSSION

The quantitative ^{13}C and proton NMR spectra obtained for each coal product can be used with the elemental analysis to construct a model structure for each coal liquefaction residue. The quantitative ^{13}C NMR spectra of samples 1 and 2 show relatively similar functional group distributions. The differences can probably be interpreted as being within experimental error. The analysis of the functional group distributions show large differences between samples 3 and 4. The analysis of the functional group distributions show large differences between the aromaticities, f_a, of samples 3 ($f_a = 67\%$) and sample 4 ($f_a = 74\%$). The per cent of phenolic and protonated aromatic carbons is the same but the biggest differences between the two samples is the percentage of non-protonated carbons, sample 3 is 17.5% and sample 4 is 24%. The difference in the non-protonated aromatics could be due to more cross linking between the aromatic rings or more polyaromatic ring structures in sample 4 than in sample 3. The methylene functionalities is also significantly different between the two samples. The higher methylene group fraction in sample 3 can be interpreted as being due to longer aliphatic chains between the aromatic rings than for sample 4. The residues from the Illinois No. 6 coal, f_a= 52-55%, are distinctly different that the Pittsburgh seam coal, f_a= 67-74%, with a much higher percentage of the Pittsburgh seam coal being protonated aromatic, approximately 45%, to approximately 32% for the Illinois No. 6 coal samples.

Comparison of the non-protonated aromatic carbons for the two Pittsburgh residue fractions with the almost identical proton distribution from NMR (See Table 5) and the similar elemental analysis for the two samples leads to the conclusion that sample 4 has larger aromatic cluster size than does sample 3, not just more branch points for a attachment of aliphatic groups. This result is consistent with the fact that sample 3 is the 2nd stage product and sample 4 is the interstage oil. The aromatic cluster size is defined as the number of fused aromatic rings held together in one structure. Rough calculations using the elemental analysis as well as the carbon and proton NMR results show that sample 3 has on the average roughly 1.2 rings per aromatic group while sample 4 has 2 rings per aromatic group.

The DEPT spectra of samples 3 and 4 also show very little aliphatic methine, mono-protonated, carbon present in these samples. The APT spectra of sample 2 also show that there is almost no methine aliphatic carbon. The DEPT and the APT spectra confirm the chemical shift regions used for functional group analysis. Those carbons which are designated as being from protonated aromatic carbons correlate well with the DEPT and APT spectra showing only methine carbons.

The DEPT spectra of sample 3 show that careful consideration must be given to the quality of the data obtained with this experimental technique. The DEPT spectra of this particular sample do not show just the functional groups selected. There is some polarization transfer between carbon functionalities in the material. The errors associated with the DEPT can usually be compensated as is shown in the DEPT spectra of sample 4. The DEPT and APT spectra of coals and coal products are not quantitative unless extreme measures are taken in calibrating the experiments. The DEPT and the APT NMR experiments should be used to identify carbon containing functional groups and not for quantification.

The proton NMR experiments can be used in conjunction with the elemental analysis and the carbon NMR results to determine the type and amount of aliphatic materials present. The results from the analyses of these materials show a relatively small amount of free methylene protons which implies a short aliphatic chain length between aromatic centers. This result is intuitive because the materials studied are expected to be of relatively low molecular weight due to their solubility in THF. This is also substantiated by the results obtained from field desorption mass spectrometry. For the most part, these results from proton NMR agree with results obtained by Burke et al. (10) and Winshel et al. (11), particularly for samples 3 and 4. However, the differences in results obtained on samples 1 and 2, both aromatic and methyl percentages, may be attributed to integration over slightly different ppm region or choice of solvent.

The failure of the HETCOR experiments on the coal liquefaction residues is ,in part, caused by the lack of peak definition in both the ^{13}C and the ^{1}H NMR spectra of these samples. The comparison of the spectra obtained in this study with those of SRC distillate products show the large difference in NMR signal type. In order to apply 2-dimensional techniques to coal products effectively fractionation of the products by distillation is necessary.

FUTURE STUDIES

Due to the lack of resolution, the HETCOR experiments were not successful for the coal residues in this study. However, HETCOR is very useful for distillate products as shown with the SRC distillate in Figures 15-17. The HETCOR experiment allows direct correlation between the carbon NMR resonances and the proton NMR resonances. Perhaps most importantly this technique allows the identification of resonances which do not fall into the broad chemical shift ranges which usually define such functionalities. For example, in Figure 17 there is a correlation, cross peak, with a 1 ppm proton NMR resonance (usually a free methyl group) and 31 ppm in the ^{13}C NMR spectrum (which usually corresponds to a methylene). This cross peak shows that for this distillate fraction some methyl resonances are shifted out of their normal chemical shift range and into the methylene region. These types of results can seriously skew the functional groups distributions if quantitative results are needed for mechanistic determinations. While we were unable analyze the residues utilizing HETCOR , we would be able to use this technique on distillable fractions.

Quantitative solid ^{13}C NMR of coals and insoluble coal products has been pioneered at PNL (12a-c). This technique yields valuable structural information about insoluble coal fraction as well as the initial coal. To reach significant conclusions about the value of the coal liquids produced, the change between the starting coal and the product must be determined. We are currently using a 300 MHz NMR spectrometer with a 80 mg sample capacity, but we are in the process of purchasing a 100 MHz spectrometer with a 2.5 g sample capacity. The large sample size will allow for more-quantitative NMR spectra with better signal-to-noise to be obtained. The increased signal to noise will be especially important to determine the fate of the minor functional groups in coal during liquefaction as well as decreasing the time needed for each spectrum. A solid proton NMR technique, CRAMPS, will also be available this summer with the new instrument.

The coal liquefaction process should be examined from start to finish with quantitative NMR techniques. The experiments will include 2-dimensional techniques such as HETCOR, polarization experiments such as DEPT, as well as quantitative proton and carbon NMR on soluble fractions. Insoluble fractions will be examined by quantitative solid carbon NMR as well as dipolar-dephasing experiments (which are similar to the DEPT solution experiments) and solid proton NMR by CRAMPS.

In addition, PNL staff have recently developed a new, inexpensive, ultra-high pressure NMR cell that allows the observation of proton and ^{13}C NMR spectroscopy in supercritical fluids. The chemical shift and relaxation time pressure dependence of ethylene up to 45,000 psi have been observed. The capability of observing dilute samples is currently being developed. The high pressure NMR cell fits in any NMR spectrometer and allows the use of all the usual spectral editing and two-dimensional NMR techniques. Signals from coal liquid fractions extracted with supercritical fluids should be observable (13).

TASK 3. SUPERCRITICAL FLUID EXTRACTION AND SUPERCRITICAL FLUID CHROMATOGRAPHY/MASS SPECTROMETRY

INTRODUCTION

Supercritical fluids are not liquids, but have liquid-like densities and solvating power. At ambient temperatures and pressures greater than the critical point, supercritical fluids are gas-like and compressible. Their advantage as an extraction fluid and as a mobile phase in separations arises because they exhibit gas-like transfer properties while maintaining solvation characteristics of liquids. Supercritical fluids have several properties that may make them useful for the rapid and quantitative extraction and recovery of organic components from environmental matrices. Solvent strength is directly related to density. Solvating properties of a supercritical fluid toward a particular species can be easily modified by changing the extraction pressure, and to a lesser extent, the temperature. Supercritical fluids with different polarities are also available, and the polarity of a supercritical fluid can be changed by the use of solvent modifiers. The ability to select and change the solvent strength of a supercritical fluid is important for optimizing the extraction conditions for a particular analyte species from a particular matrix. The use of different extraction pressures, solvent modifiers, and solvents with varying polarities is particularly valuable in allowing class-selective extraction. Many supercritical solvents are sufficiently volatile that the concentration of the extracted species can be performed at ambient or even subambient temperatures. This reduces the amount of solvent that requires disposal. The supercritical fluids used in this study are also pure, inert, and nontoxic. In addition, the utilization of supercritical fluid extraction insures that the degradation of compounds found in the original mixture and analytical loss from the extraction procedure will be minimal.

A supercritical pentane system equipped with fluorescence detection has been used for the analysis of a polyaromatic hydrocarbon (PAH) standard with up to nine condensed aromatic rings. The system was also used to separate high-molecular weight carbon blacks, coal tars, and coal-derived vacuum still bottoms (14). The vacuum still bottoms had a molecular weight range of 200-800 Da, as determined by field desorption mass spectrometry.

In supercritical fluid chromatography (SFC), the chromatographic mobile phase, which can be either an inorganic or organic medium, is subjected to temperatures and pressures near or above its critical parameters. A supercritical fluid has chemical, chromatographic, and physical properties intermediate between those of a gas and a liquid and can be used to perform separation of novolatile and high-molecular weight polycyclic aromatic compounds. PNL has developed methods of introducing the supercritical fluid into a mass spectrometer. A number of modifications of this technique, including the introduction of capillary chromatographic effluent as well as direct injection techniques have been designed. Applications of supercritical fluid extraction, supercritical fluid chromatography, and the instrumentation used for capillary SFC/MS and for the direct injection techniques have been described elsewhere (15). Hawthorne and Miller (16) reported a simple SFC/MS capillary direct interfacing method which allowed a single quadrupole mass spectrometer to be used for GC/MS and SFC/MS with minimal conversion time. Methane chemical ionization (CI) spectra of PAHs and heteroatom-containing PAHs were obtained.

EXPERIMENTAL

Supercritical Extraction

The general supercritical extraction method is described in reference 17 (17). Samples 17 (Illinois No. 6, W; Run 257; C/C; recycle stream), 18 (Illinois No. 6, W; Run 257; C/C; interstage stream), 19 (Pittsburgh seam, W; Run 259; C/C; recycle stream), and 20 (Pittsburgh seam, W; Run 259; C/C; interstage stream) were extracted sequentially with a series of supercritical fluids. In this case, propane and pentane both modified and unmodified were used as the fluids. The modifiers used in this portion of the project were methanol, tetrahydrofuran (THF), and acetic acid at a concentration of 10 volume %. For each experiment, approximately 0.1 g of sample was placed into the stainless steel extraction cell. The cell was heated to 150°C, and supercritical propane was introduced into the cell at 400 atmospheres. The propane/extractants exited the extraction cell via a 100-µm fused-silica capillary. The propane/extractants were bubbled through pentane. The exact flow rate of the propane/extractants was not determined but is estimated to be on the order of several liters per minute. The propane extractions were performed for 15 min. After the propane extractions, pentane at 300 °C and 400 atm was used as the extraction medium. After 15 min of extraction, the fluid was changed to 10 % methanol in pentane and the extraction again was repeated for 15 minutes. The next fluid used was 10 % tetrahydrofuran (THF) in pentane. The final fluid used was 10 % acetic acid (HOAc) in pentane. Each extract was collected in pentane and dried. The resulting extract was then weighed then redissolved in THF for further analysis.

Samples 21 (Black Thunder, HRI; CC-2 [227-57], first stage, FL) and 22 (Black Thunder HRI; CC-5 [227-62], first stage; FL) were extracted with supercritical fluid CO_2 with 10% isopropanol as a modifier. At that per cent modifier and pressure, there is still only one phase. This is illustrated in Figure 18. The specific supercritical fluids utilized for extraction of the samples are summarized in Table 6.

Supercritical Fluid Chromatography

Standard SFC conditions were used with the working fluids being either propane or pentane, typically 1900 psi. The oven temperature was 150°C or 250°C, respectively, and detection was by a ISCO UV detector set at 300 nm. Columns were either 1mm packed columns using 5 µm silica (Brownlee) or 50 µm capillary column coated with 5% phenyl/methyl silicon (Lee Scientific).

HPLC

High pressure liquid chromatography was performed on a Waters modular HPLC. The detector used was a Waters 494 variable wavelength UV detector set at 270 nm. A 4.6 mm X 250 mm Alltech C_{18} column was used for all analyses. Elution solvents were water, acetonitrile and tetrahydrofuran. The elution gradient started at 50:50 water:acetonitrile, proceeding to 100% acetonitrile in 10 min, and then to 100 % THF in 10 min.

Microcolumn Liquid Chromatography

Microcolumn liquid chromatography was used as a separation technique using an ISCO syringe pump and an in-house modified fluorescence detector. The column employed was a Phase Separation 1mm X 250 mm with C_{18} coating on 5 µm Si particles. Fluorescence excitation was at 270 nm and emission was monitored at 300 nm to 700 nm. Flow rates for all experiments were 50 µl/min. All solvents used were "LC" grade or better and filtered through a 4.5 µm filter before use.

Open column chromatography

Open column chromatography was performed on the SFEs in the following manner. Pasteur pipets were filled with approximately 2 g of either 50 µm neutral alumina or 50 µm silica. The columns were wetted with 10 column volumes of hexane. The SFEs were added drop wise to the hexane. Five column volumes of hexane were passed through the loaded columns. Methylene chloride was next passed through the column, followed by THF, and finally methanol.

Mass Spectrometric Analyses

Mass spectrometric analysis was performed on a TAGA 6000 using an in-house built electrospray interface. Complete description of the interface and standard conditions for the analysis can be found in reference 18. MS/MS analyses were performed using argon as the collision gas at an approximate thickness of 10^{14} molecules/cm^2 (18). The pentane and pentane/methanol fractions were also examined by field desorption mass spectrometry and desorption chemical ionization.

Sample 22 was extracted with supercritical CO_2/10% isopropanol and then separated with open column chromatography using alumina, florisil, and silica in that order with hexane as the eluting solvent. The resulting hexane fraction was analyzed by gas chromatography/mass selective detector (GC/MSD) . The column was a 200 µm film thickness, 30m, methyl-silicon column (Lee Scientific) with the following temperature program: 100° C for five min., 100-300° C at 10° C/min, and then 300° C for 20 min. In addition, an aluminum-clad, fused-silica column (Quadrex) was used because of its higher temperature limit (420° C- 440° C). Spectra can be found in Appendix C.

SFC/MS

The SFC/MS analyses were performed with a Hewlett-Packard Model 5988A GC/MS. The interfacing of the SFC column to the mass spectrometer was achieved by inserting the column through the transfer line until the restrictor tip of the column extended to approximately 1 mm of the end of the interface probe similar to that employed by Hawthorne and Miller (16). No modifications of the commercially supplied GC/MS interface were made. The source temperature and the interface probe temperature were held at 270° C. A Superbond (Lee Scientific) column (SB-octyle-50, 10 m X 100 µm i.d., 0.25 µm film thickness) was utilized in these studies. Supercritical fluid propane was used as the mobile phase at a column temperature of 120° C.

Methane CI mass spectra were obtained with an ion source housing pressure of 2 X 10^{-4} torr. The ionizing voltage was typically 100 eV and the scan rate was 450 amu/sec with a multiplier voltage of 2500. The scan range was typically 100-800 amu.

GC/FTIR

A Nicolet 740 FTIR with a HP 5890 GC was used for all experiments. A Supelco SPB-1 250 micron X 0.25 micron X 30 m column was temperature programmed from 50 °C to 320 °C @ 10 °C/min. On-column injection of 1 to 3 mL of each extract was used for each analysis.

RESULTS

Figure 19 shows the results of duplicate supercritical extractions of sample 17. The extraction efficiency was typical of the first four samples.

An example of the Gram-Schmidt reconstruction from GC/FTIR analysis of one of the components in the propane extract of sample 17 can be seen in Figure 20. The corresponding infrared spectrum can be seen in Figure 21. The remaining spectra are in Appendix C.

Figures 22-26 show the electrospray mass spectra for the SFEs from sample 17. A collision induced dissociation (CID) spectrum of the prevalent ion in the spectra for all of the extracts, m/z 538, is shown in Figure 27. FD spectra of the supercritical fluid pentane and pentane/methanol extracts are shown in Figures 28-29 . A desorption chemical ionization spectrum (methane) is shown in Figure 30 for the pentane/methanol fraction. A MS/MS study was done with m/z 277 and the results are shown in Figure 31.

An example of SFC for sample 17 is illustrated in Figure 32.

Fractions obtained from the open column separations of the SFEs were further separated using microcolumn HPLC. The results of one such separation can be seen in Figure 33.

Mass spectra for several of the components obtained by open column chromatography of the SFEs from sample 22 are shown in Figures 34-36.

DISCUSSION

The results from the SFE experiments with sample 17 indicate that it is possible to reproducibly extract the samples. Using a variety of supercritical fluids it was possible to crudely fractionate the sample (See Table 7). It is interesting to note that the total amount extracted during each experiment with sample 17, 84.1 wt% and 85.3 wt%, are almost the same. Also, the total amount extracted by propane and pentane, 43.6 wt% and 44.8 wt % are almost the same. The results for the extractions of samples 18, 19, and 20 and duplicates are also shown in Table 7. Efficiencies greater than 100% reflect inability to completely dry the extract and obtain a proper weight. The color of the extracts from the more polar fluids (methanol or THF modified fluids) was much darker than from either propane or pentane extracts even when taken to near dryness. This is not a concentration effect as evidenced by the fact that more material was present in either the propane or pentane extracts than in any of the modified extracts. The efficiency for the CO_2/10% isopropanol extraction of samples 21 and 22 is estimated to be 20 to 30%.

SFC was attempted on the extracts from sample 17 but only a broad "hump" was observed, no individual "peaks". This is illustrated in Figure 32. Similar spectra were obtained for the other extracts. Both capillary and packed column SFC were attempted using both supercritical propane and pentane; however, little difference in the resolution was observed. Standard HPLC was attempted on the extracts using a 4.5 mm X 250 mm C_{18} column and UV detection. The results of these experiments were the same as observed for the SFC experiments. Only broad unresolved humps were observed. No conditions could be found that would separate the compounds present in any of the extracts.

It was felt that the samples were too complex to separate using a single chromatographic method. Open column chromatography has been used extensively to class fractionate PAH samples, therefore it was felt that this approach might help solve the problem of poor or incomplete chromatographic resolution. Each extract was passed first through the alumina open column, then the silica gel column, thus producing 16 separate fractions from each SFE fluid. Most of the material was present in the methylene chloride fraction of the silica gel column. Actual percentages of each fraction were not obtained. Again the more polar phases in the open column separation gave the darker fractions.

Fractions obtained from the open column separations of the SFEs were further separated using microcolumn HPLC. The chromatogram in Figure 33 is from the least polar of all of the samples; many of the compounds are separated. The peak shape observed in the chromatograms was improved when acetic acid was added to the elution solvents. This indicates that the compounds are acidic and that the acetic acid acted as an ion suppressing agent for that particular sample. Other than the fact that the observed compounds fluoresce under the experimental conditions, little can be said concerning their identity. It is assumed that they are PAHs, but no direct experimental evidence has been obtained to support this supposition.

Many of the components of the SFEs were analyzed by gas chromatography/Fourier transform infrared spectrometry (GC/FTIR). However, none of the compounds observed in the extract were present in the Environmental Protection Agency (EPA) gas phase spectral library.

The results of electrospray mass spectrometric analysis of the SFEs can be seen in Figures 22-26 . The propane extract is the most complicated spectrum, and the 10% HOAc/pentane extract is the simplest. The major ion observed in most extracts is m/z 538. No compounds are immediately assignable to the ions observed; therefore, MS/MS was attempted on the major ions. Only the 538 amu ion produced a CID spectrum (Figure 27). In all other cases no ions other than the parent ion was observed in the resulting spectrum. This results are interpreted to mean that all other major ions observed in the spectrum are PAHs ,and therefore not amenable to CID under the conditions that can be produced in a standard triple quadruple mass spectrometer. The CID spectrum of the 538 amu ion suggests that the compound may be a substituted cyclopentadienephenanthrene. This assignment could not be verified due to the lack of standards. The results indicate that the electrospray ionization technique used to introduce the extracts into the mass spectrometer is a powerful technique but it has been shown to be highly selective. Many compounds are not ionizable by electrospray ionization; as a result, electrospray ionization does not appear to be a very useful form of ionization detection for these types of molecules.

The mass spectra obtained from sample 22 after supercritical fluid extraction followed by open column separations, are shown in Figures 34-36 . Some of the structures that were tentatively identified in the FD study are consistent with the mass spectra observed for some of the predominant ions.

A total ion chromatogram of the supercritical fluid propane/mass spectrometry of one of the extracts is shown in Figure 37. The mass spectrum, the sum of 30 scans, is illustrated in Figure 38. Although the chromatography leaves something to be desired, it was felt that improvement in the restrictor would improve the chromatography and mass spectral data.

FURTHER STUDIES

The major problems in analyzing the samples of high molecular weight resids appears to be twofold; (1)separating the multitude of compounds present and (2) determining their identity. While it can be said that these are the standard problems encountered in analytical chemistry, these samples are particularly difficult due to their complexity. However, these problems appear to be solvable by applying a variety of both novel and traditional techniques.

Our results indicate that supercritical fluid extraction is a very successful first step for the fractionation of coal-derived products into less complex mixtures for analysis. In addition, it was possible to class fractionate the sample to a level where individual compounds were resolvable by microcolumn HPLC after using a combination of supercritical fluid extraction and traditional open column chromatography.

The results from the analysis of the extracts indicate that fractionation and identification of components is possible. The infrared spectra and mass spectrometric analysis agree in general; both analytical techniques indicate that the extracts consist of a multitude of similar PAHs and polar substituted PAHs. Although few if any standards exist for these compounds, tentative identifications were made on several of the major ions observed in the FD spectra. The major analytical techniques used in this part of the project, infrared spectroscopy and mass spectrometry employed sample introduction techniques which may not be appropriate for these samples. Gas chromatography does not typically work well on extremely polar compounds or very high molecular weight materials. It is possible that many of the compounds present in the various extracts and fractions thermally decompose before they can be eluted through the gas chromatograph. Thus, the results of these analyses could be biased. It is possible that many of the compounds present in the extracts and fractions never reached the spectrometers due to discrimination in the separation/sample introduction part of the instrument. However, mass spectra for several of the dominant ions of lower molecular weight, <300, observed in the FD spectra were obtained by separation by open column techniques followed by GC/MS. For these reasons, SFC/MS would have been the method of choice for the analysis of these types of components, particularly the higher molecular weight PAHs. However, due to instrumental problems we were unable to complete this analysis. Progress is being made in addressing these problems and this technique should receive additional attention. Other techniques such as LC/MS and SFC/FTIR may provide information concerning structure elucidation or compound class identification in the resids.

The FD spectra of the pentane and pentane/methanol extractions clearly indicate the usefulness of fractionation with subsequent mass spectrometric analysis. The utilization of desorption chemical ionization of fractionated extractions also demands further attention. The quantitation of specific components in these fractionated samples may provide additional information to assess reactivity and process differences.

CONCLUSIONS AND RECOMMENDATIONS

It is certainly apparent from our studies that one analytical technique is not capable of providing a complete characterization or an identification of all the components in the resids. However, a combination of analytical instrumental techniques and separation methodology is capable of providing additional insight into the composition of the resids.

Field desorption mass spectrometry has provided very useful information about the coal-derived samples. FDMS has shown qualitative differences in the molecular ranges, intensities of the predominant ions, and ratios of the intensities of the major ions. These qualitative differences should be examined in greater detail. FDMS has also shown molecular weight distribution differences between the supercritical fluid extracts.

Due to the complexity of the samples and lack of peak resolution, 2-D NMR has provided little useful information on the resids. However, a preliminary study employing fractionation by supercritical fluids, followed by separation with open column chromatography, has shown significant improvement in resolution compared with NMR analysis of the original material. The possibility of the utilization of 2-D NMR for characterization of the resids certainly exists with prior fractionation. This area should also be investigated further.

The results from the supercritical fluid extraction experiments indicate that it is a valuable technique to reproducibly extract the samples with high efficiency and to crudely fractionate the material. The use of the supercritical fluid series of propane, pentane, pentane/methanol, pentane/THF, and pentane/HOAc should be applied to samples 21 and 22. Also, the use of CO_2/10% isopropanol should be applied to samples 17-20.

Several of the supercritical fluid extracts have been analyzed by FD and 2D-NMR. The FD results showed a difference in molecular weight distribution between the supercritical fluid pentane and pentane/methanol extracts. In addition, the 2-D

NMR results indicate much better resolution than for the original material. Further effort should be directed for the use of these techniques on fractionated materials.

Microcolumn technology has been described by Novotny (19,20), Yang (21), and others (22-24). This technique utilizes fused silica tubing that is slurry packed with 5-µm particles to provide columns that approach separation efficiencies of 100,000 theoretical plates (25). High resolution microcolumn HPLC has been applied to a variety of complex environmental and biological samples allowing for separations that cannot be achieved within the resolution constraints imposed by columns of conventional dimensions. Harvey and Campbell have utilized microcolumn techniques for the separation of taxol, a taxane diterpene amide produced by the Pacific yew tree (26). This separation was a definite improvement over conventional LC techniques. In addition to the enhanced resolution, microcolumn separations offer a number of inherent advantages including minute sample requirements, enhanced mass flow detection sensitivity, and the feasibility of utilizing expensive "exotic " mobile phases (20). More importantly, the low flow rates characteristic of microcolumn HPLC greatly simplify introduction of the column eluate to mass spectrometric analyzers (27). The technique of microcolumn separations with prior fractionation by supercritical fluid extraction and open column chromatography has been applied to the resids. Preliminary results show many of the components are separated. This is another area that deserves further attention. In addition, fast atom bombardment (FAB) has been utilized for the identification of nitrogen-containing compounds in fossil fuels (28). Microcolumn separation techniques with FAB (continuous flow FAB) may provide additional structural information about the resids.

Supercritical fluid chromatography was applied to several of the supercritical fluid extracted resids. Only a broad peak was observed, no individual or resolved peaks. Both packed and capillary SFC were attempted ; however, little difference in resolution was observed. Preliminary results of a study with SFEs, further fractionated by open column chromatography, and followed by SFC showed marked improvement in resolution of components.

In view of the fact that our group is responsible for many and varied programs with different analytical requirements, it is virtually impossible to have a dedicated

SFC/MS. As a result, we have adapted a simple SFC/MS interface which allows a single instrument to be interconverted routinely between GC/MS and SFC/MS with a minimum of time. This interface is similar to the one reported by Hawthorne and Miller (6). Although our initial attempts at SFC/MS on the extracted resids were not totally successful, this area should also be examined in more detail. Improvement in the restrictor would certainly improve the chromatography and mass spectral results.

MS/MS methods should also be a technique for consideration. In the MS/MS method, a sample is ionized with the first mass spectrometer (MS1) and an ion beam (precursor ions) obtained by mass analysis are sent to a high vacuum MS/MS interface used to introduce them into the second mass spectrometer (MS2). The precursor ions are introduced into a collision cell filled with gas, and changed to secondary ions (daughter ions) by the gas collision method. Obtained daughter ions are subjected to mass analysis by MS2. Mass spectra of a mixture include many peaks of molecular ions and their fragment ions. Therefore, their spectra are complicated, making correct molecular weight determination and structural analysis difficult. When the MS/MS system is used in such a case, it is possible to introduce some of their precursor ion beams into the MS2 and thereby obtain the pure daughter ion spectral pattern. By comparing the mixed spectrum obtained by the MS1 and the daughter ion spectrum by MS2, the compoents in the sample can be identified. MS/MS was utilized with desorption chemical ionization on one of SFE extracts; MS/MS was performed on m/z 277 which was presumably m/z (276 + H). Although the spectrum observed was not what one would expect from the structure predicted for m/z 277(M+ H), further experimentation might prove fruitful. MS/MS techniques have been used on studies of the SRC process (29,30).

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Table 1

SUMMARY OF RESULTS

Samples	Technique	Comments
1 & 2- Illinois #6, W; Run 257; C/C, 2nd Stage Product & Interstage Oil	^{1}H/^{13}C 2D-NMR	Lack of resolution; Prior fractionation by SFE improves resolution.
3 & 4-Pittsburgh Seam, W; Run 259; 2nd Stage Product & Interstage Oil		
5,6,7,- Illinois #6, W; Run 250; T/C; M.WProduct, Recycle, Interstage oil	FDMS	Provides M.W. Distribution; Intensity of major ions varies; and ratios of intensities of ions different for FD of SFEs; Tentative structures of major ions.
8,9,10-Illinois #6, W; Run 257;C/C; Product, Recycle, Interstage oils		
11,12,13-Wyodak, W; Run 251-II; T/C; Product, Recycle, Interstage Oils		
14,15,16-Pittsburgh Seam, W; Run 259; Product, Recycle, Interstage Oils		
17 & 18- Illinois #6, W; Run 257; C/C; Recyle and Interstage Stream	SFE,SFC	Very good extraction efficiency, method for fractionation.
19 & 20-Pittsburgh, W; Run 259; C/C; Recycle and Interstage Stream		

Samples	Techniques	Comments
21 && 22-Black Thunder, HRI; CC-2 (227-57) & (227-62)		SFC- unresolved peak Extraction with supercritical CO_2/ isopropanol

Table 2

SAMPLES

Ref. No.	Coal Feed	Source/Conditions	Comments
$^1H/^{13}C$ 2D-NMR			
1	Illinois No.6	W; Run 257; C/C	2nd Stage Product
2	Illinois No.6	W; Run 257; C/C	Interstage Oil
3	Pittsburgh seam	W; Run 259; C/C	2nd Stage Product
4	Pittsburgh seam	W; Run 259; C/C	Interstage Oil
FDMS			
5	Illinois No.6	W; Run 250; T/C	Product Oil Resid
6	Illinois No.6	W; Run 250; T/C	Recycle Oil Resid
7	Illinois No.6	W; Run 250; T/C	Interstage Oil Resid
8	Illinois No.6	W; Run 257; C/C	Product Oil Resid
9	Illinois No.6	W; Run 257; C/C	Recycle Oil Resid
10	Illinois No.6	W; Run 257; C/C	Interstage Oil Resid
11	Wyodak	W; Run 251-II; T/C	Product Oil Resid
12	Wyodak	W; Run 251-II; T/C	Recycle Oil Resid
13	Wyodak	W; Run 251-II; T/C	Interstage Oil Resid
14	Pittsburgh seam	W; Run 259; C/C	Product Oil Resid
15	Pittsburgh seam	W; Run 259; C/C	Recycle Oil Resid
16	Pittsburgh seam	W; Run 259; C/C	Interstage Oil Resid
Supercritical Fluid Separation			
17	Illinois No.6	W; 257; C/C	Recycle Stream
18	Illinois No.6	W; 257; C/C	Interstage Stream
19	Pittsburgh seam	W; 259; C/C	Recycle Stream
20	Pittsburgh seam	W; 259; C/C	Interstage Stream
21	Black Thunder	HRI; CC-2 (227-57)	First Stage; FL
22	Black Thunder	HRI; CC-5 (227-62)	First Stage; FL

Notes:

- T/C = thermal/catalytic; C/C = catalytic/catalytic; W = Wilsonville; FL = Filter Liquid
- Samples 1-4 and 17-20 are THF-soluble portions of the distillation resid.

Table 3
Estimated Solublities in THF of Samples Analyzed by Field Desorption Mass Spectrometry

Sample #	Estimated Solubility in THF(%)
5	95
6	98
7	98
8	86
9	93
10	96
11	71
12	65
13	55
14	87
15	82
16	88

Table 4

Quantitative ^{13}C NMR in THF of Coal Liquefaction Residues

		Type of Carbon %				
Sample #	f_a	Phenolic	Non-Protonated Aromatic	Protonated Aromatic	Methylene	Methyl
1	52%	3.7%	18.4%	30.1%	35.2%	12.5%
2	55%	3.5%	17.2%	34.6%	33.8%	10.9%
3	67%	3.6%	17.5%	45.9%	25.3%	7.8%
4	74%	3.0%	24.0%	46.7%	19.5%	6.8%

PPM REGIONS, ^{13}C NMR

Phenol	145-165
Non-protonated aromatic	145-130
Protonated aromatic	130-90
Methylene	50-22
Methyl	22-0

f_a = Carbon Signal 90-165 ppm/Total Carbon Signal

Table 5

Proton NMR of Coal Liquefaction Residues

Sample #	Aromatic	Aliphatic (α-to-Aromatic)	Methylene	Aliphatic (ß-to-Aromatic)	Methyl
1	27.4%	16.3%	14.9%	24.0%	17.4%
2	27.7%	22.0%	15.0%	22.6%	12.7%
3	34.3%	25.9%	15.0%	15.3%	9.65%
3	34.3%	25.0%	14.4%	16.2%	10.1%

PPM REGIONS, ^{1}H NMR

Aromatic	9-6.3
Aliphatic α–to-aromatic	3.4-2
Methylene	2-1.4
Aliphatic β-to-aromatic	1.4-1
Methyl	1-0

Table 6

Summary of Sequence of Supercritical Fluid Extraction for Samples

Sample #	Propane	Pentane	Pen/MeOH	Pen/THF	Pen/HOAc	CO_2/IPA
17	X	X	X	X	X	
18	X	X	X	X	X	
19	X	X	X	X	X	
20	X	X	X	X	X	
21						X
22						X

Table 7

Extraction Efficiencies for Samples 17-22 and Duplicates

Sample #	Propane	Pentane	Pen/MeOH	Pen/THF	Pen/HOAc	Res.	%Rec.
17	21	23	27	9	4	16	100
17	14	31	20	13	8	15	101
18	22	28	19.4	6.9	25.3	12	113.5
18	18	24	26.8	18.8	21.9	26.2	114
19	28	23	12.3	17.3	3.3	3	87.3
19	36	36	5.9	3.5	4.5	2.3	88
20	34	32	10.6	42.5	7.5	0	127
20	36	30	7.6	15.4	5.9	4.5	99
21*						76	100
22*						77	100

* Samples were extracted with supercritical fluid CO_2/10% isopropanol and recoveries are only estimates. Approximately 24% was extracted from sample 21 and 23% from sample 22.

Figure 1. Field Desorption Mass Spectrum of Illinois No. 6, W; Run 250; T/C;Product Oil Resid

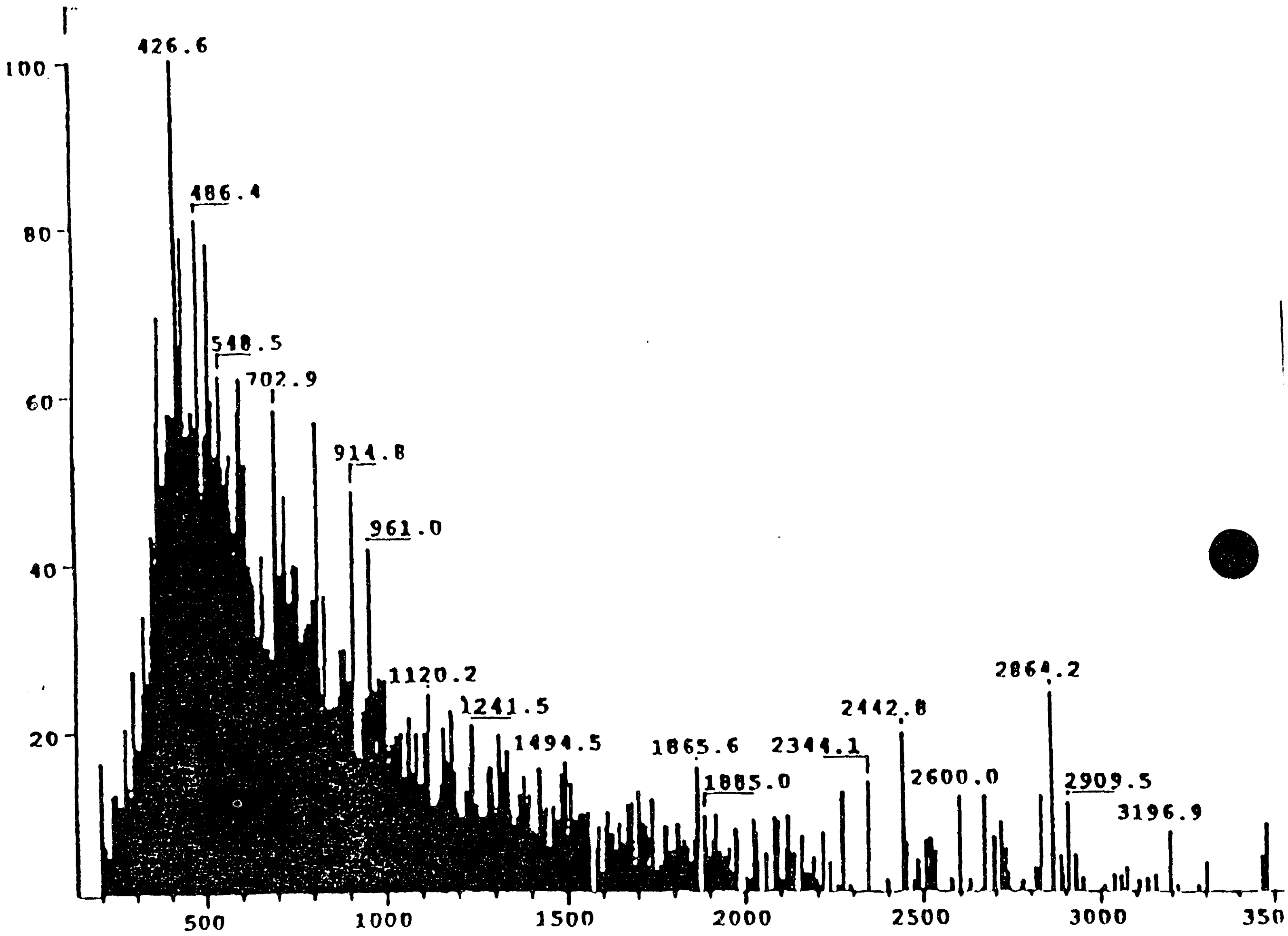


Figure 2. Field Desorption Mass Spectrum of Illinois No. 6, W; Run 250; T/C; Recycle Oil Resid

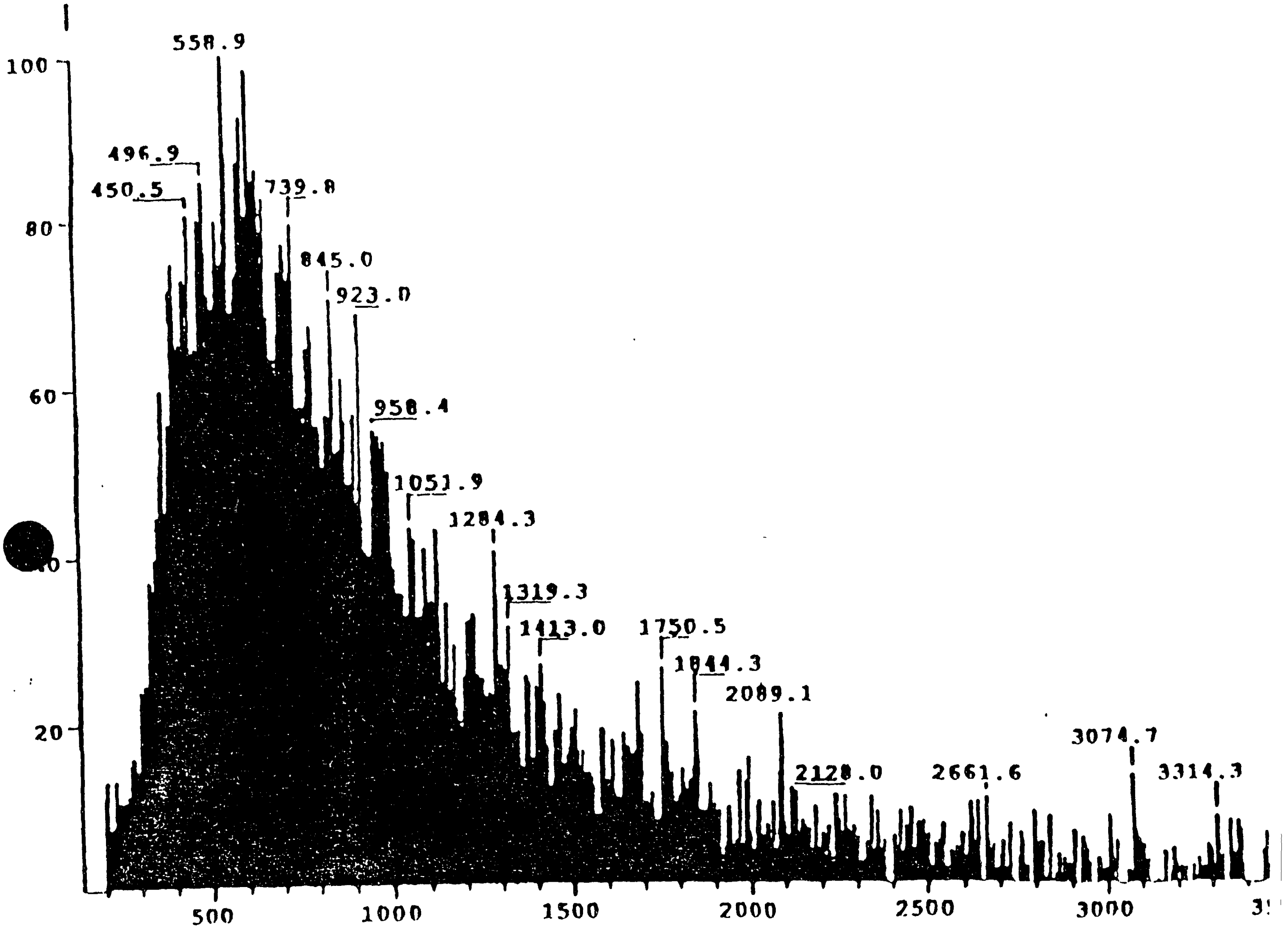


Figure 3. Extracted Ions of Various Mass Ranges for Illinois No. 6, W; Run 250; T/C;Product Oil Resid

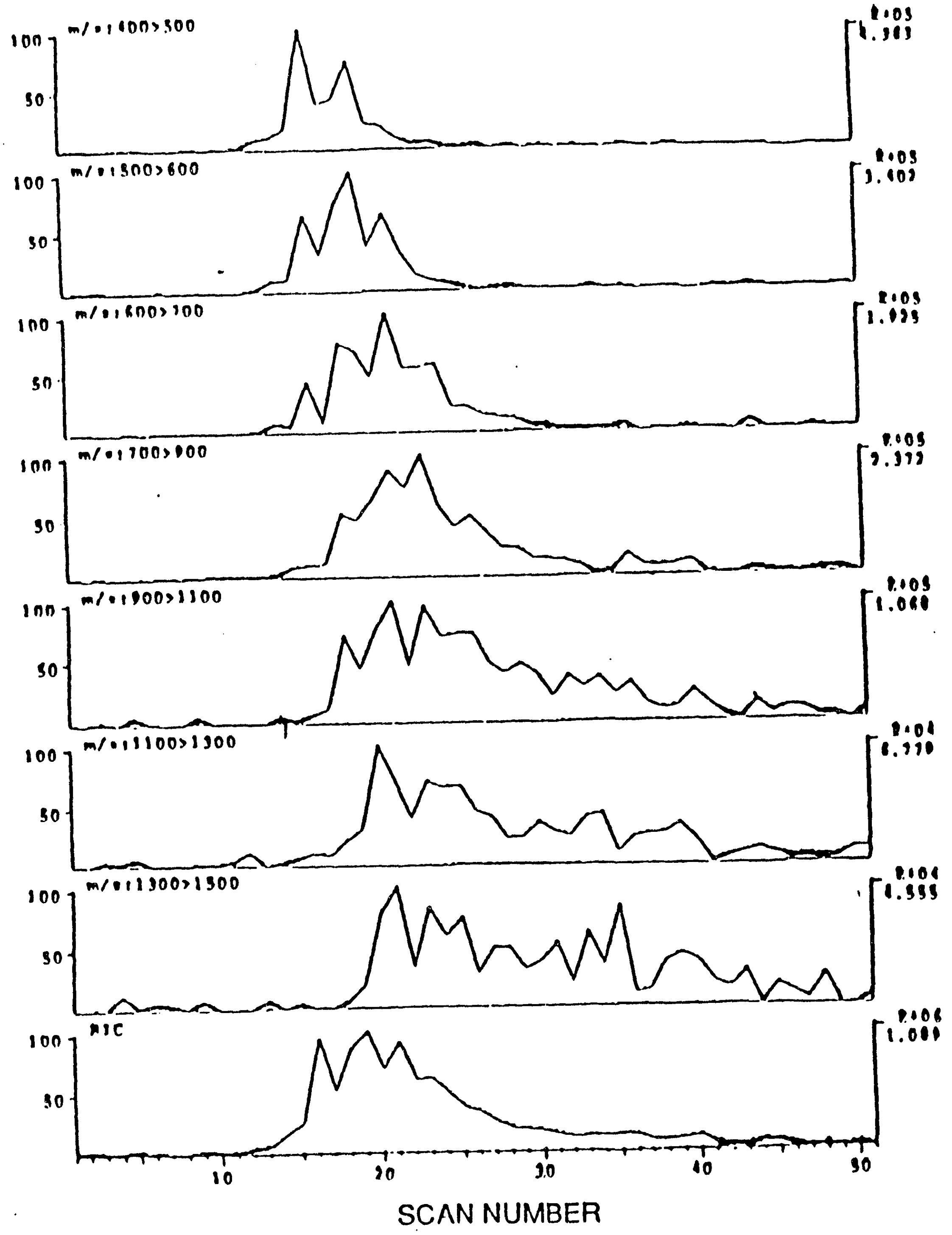


Figure 4. Extracted Ions of Various Mass Ranges for Illinois No. 6, W; Run 250; T/C; Recycle Oil Resid

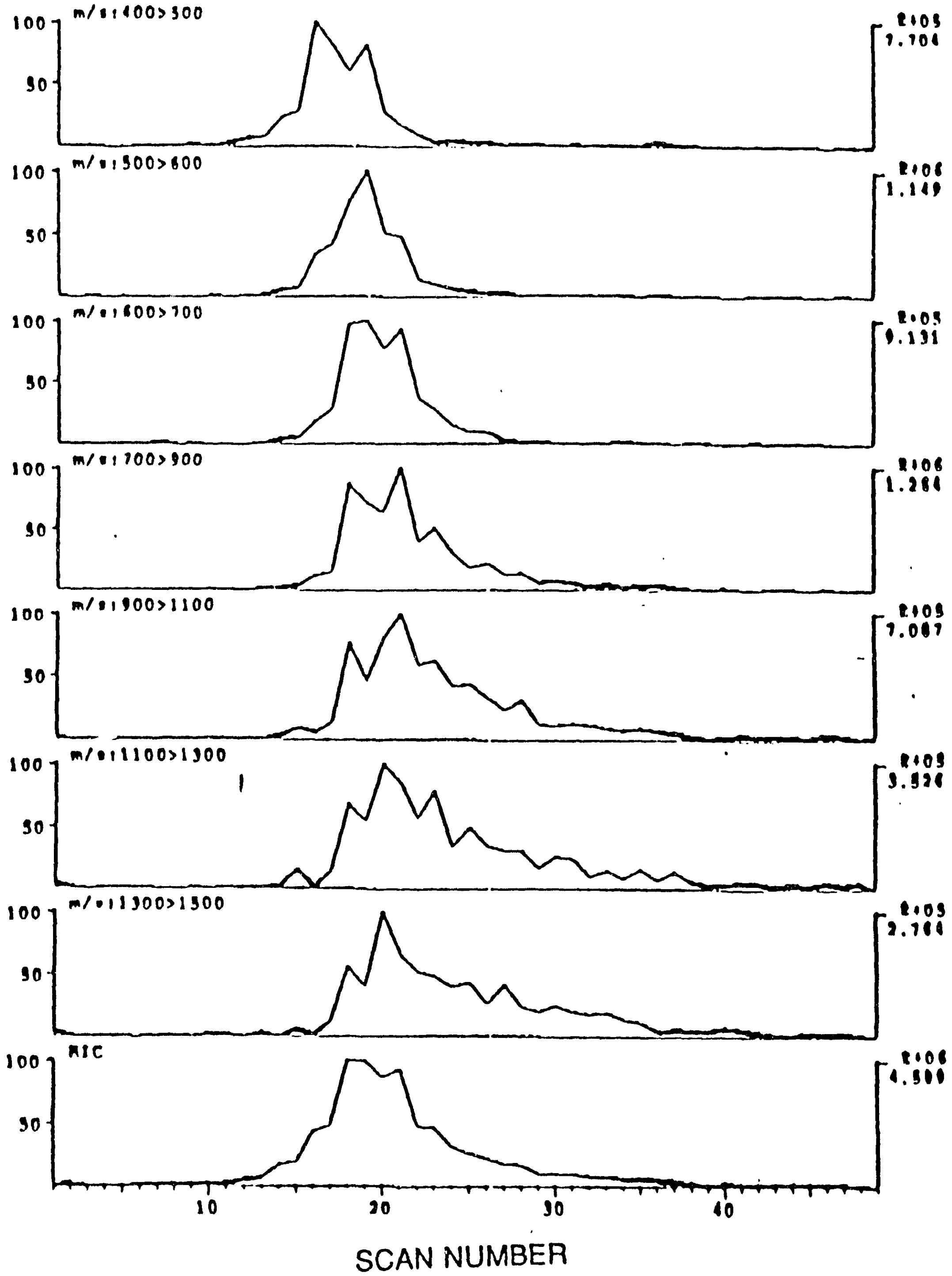


Figure 5. Field Desorption Mass Spectrum, Expanded Mass Range of 200-500 Da for Illinois No. 6, W; Run 257, C/C; Product Oil Resid

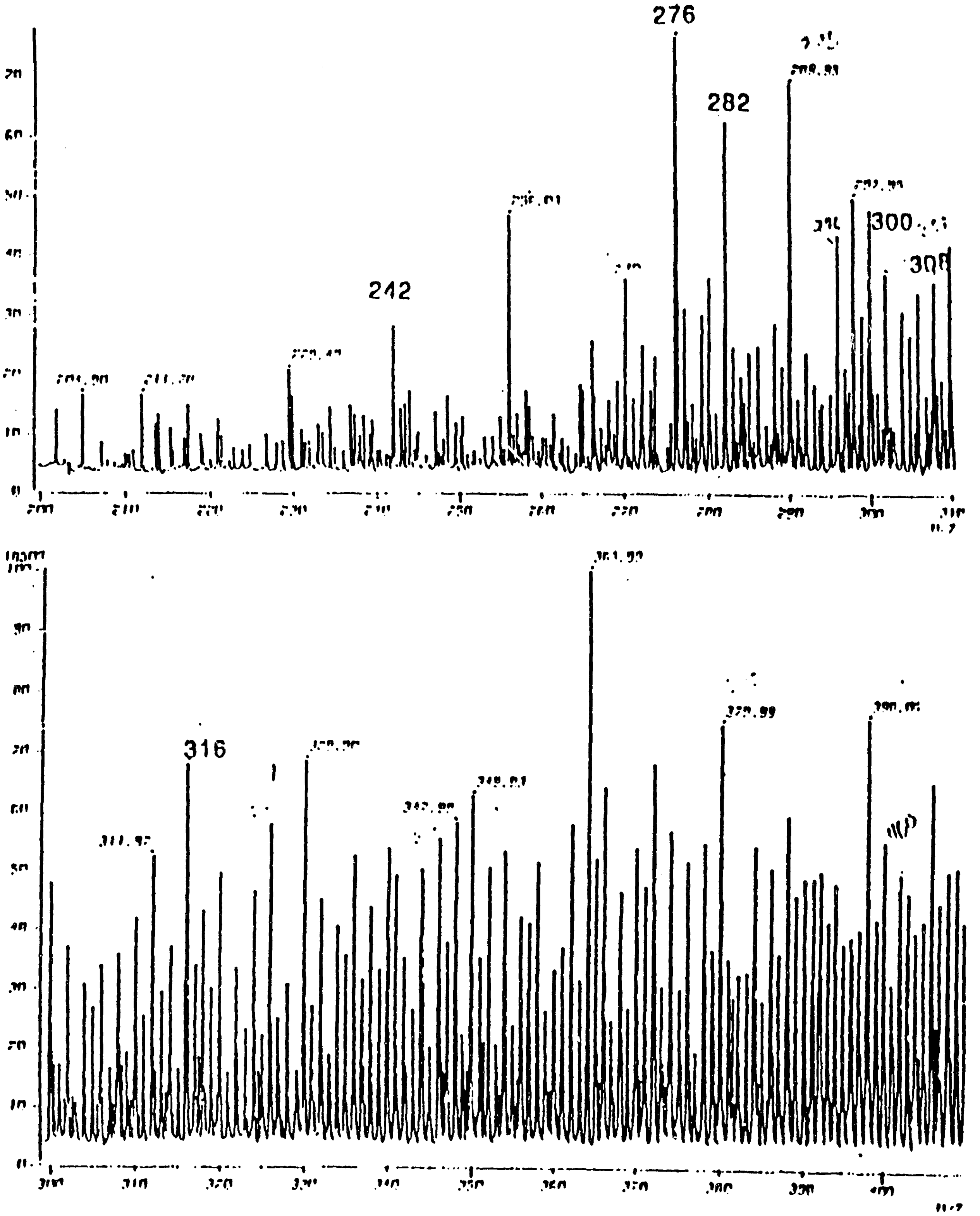


Figure 6. Field Desorption Mass Spectrum, Expanded Mass Range of 200-500 Da for Illinois No. 6, W; Run 257; C/C; Interstage Oil Resid

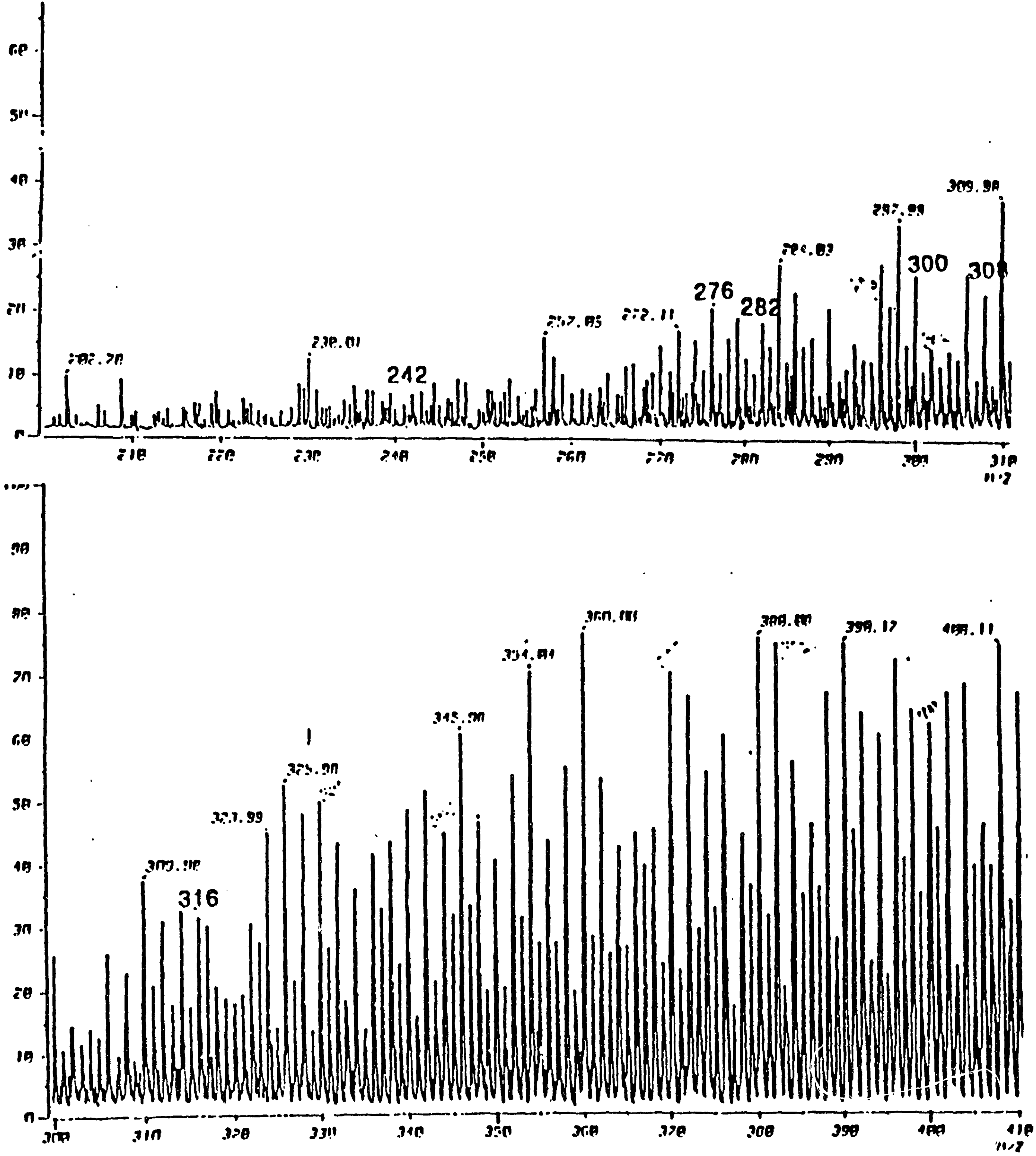


Figure 7. Field Desorption Mass Spectrum of Sample 13, Wyodak, W; Run 251-II; T/C; Interstage Oil Resid

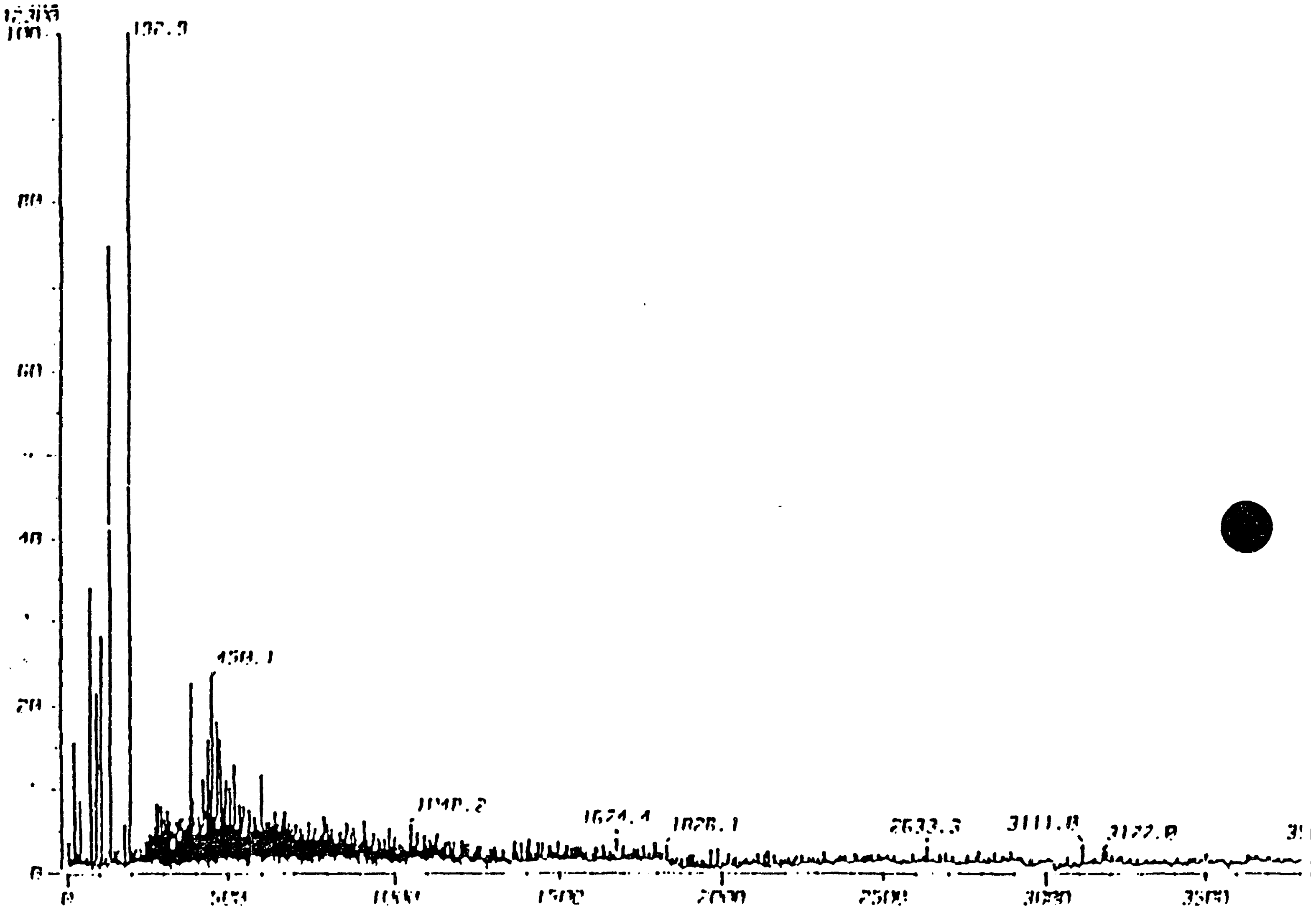


Figure 8. Quantitative ^{13}C NMR Spectrum of Sample 4, run 259, in d_8-THF

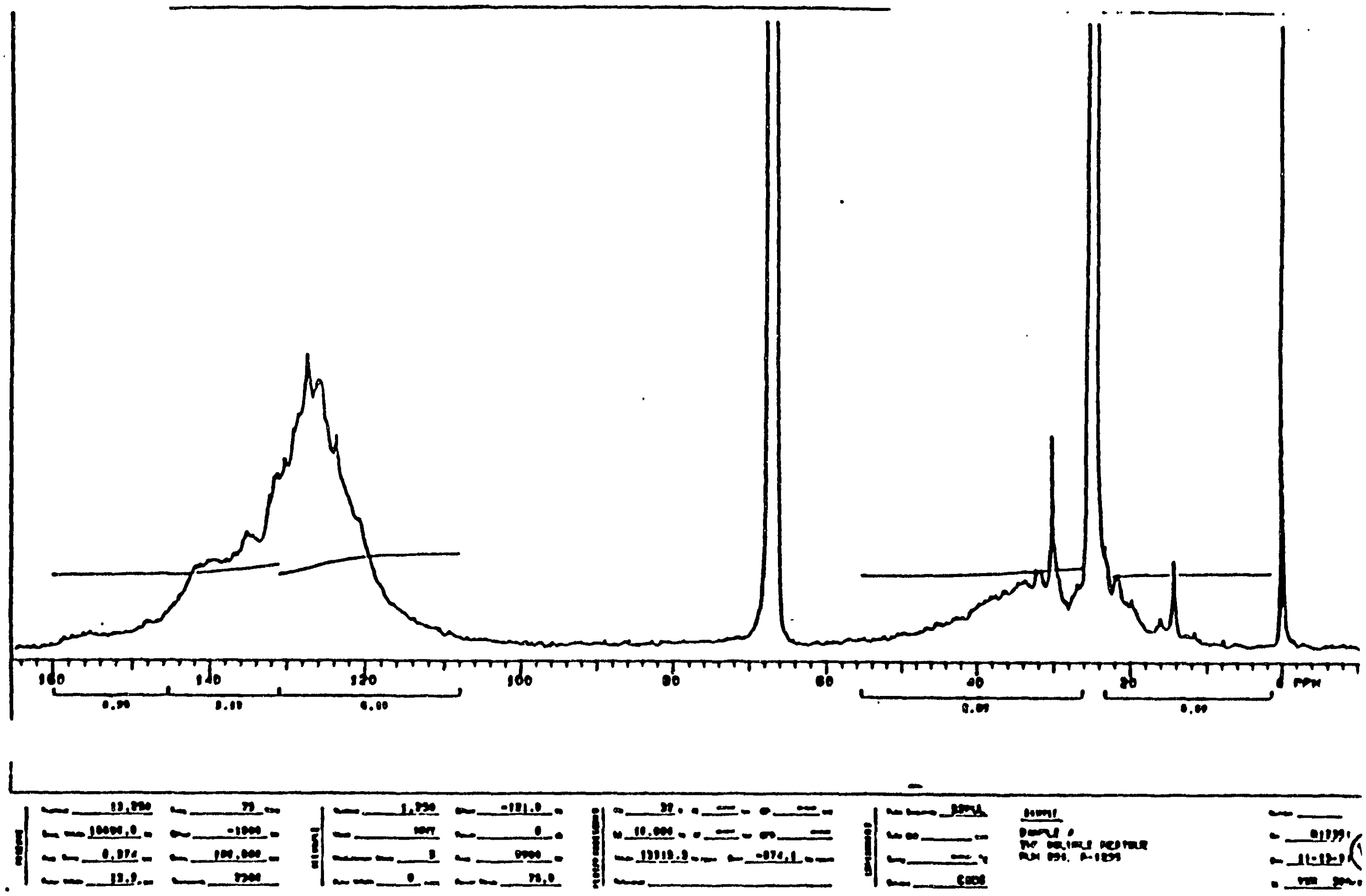


Figure 9. Proton NMR Spectrum of Sample 4, run 259, in d_8-THF

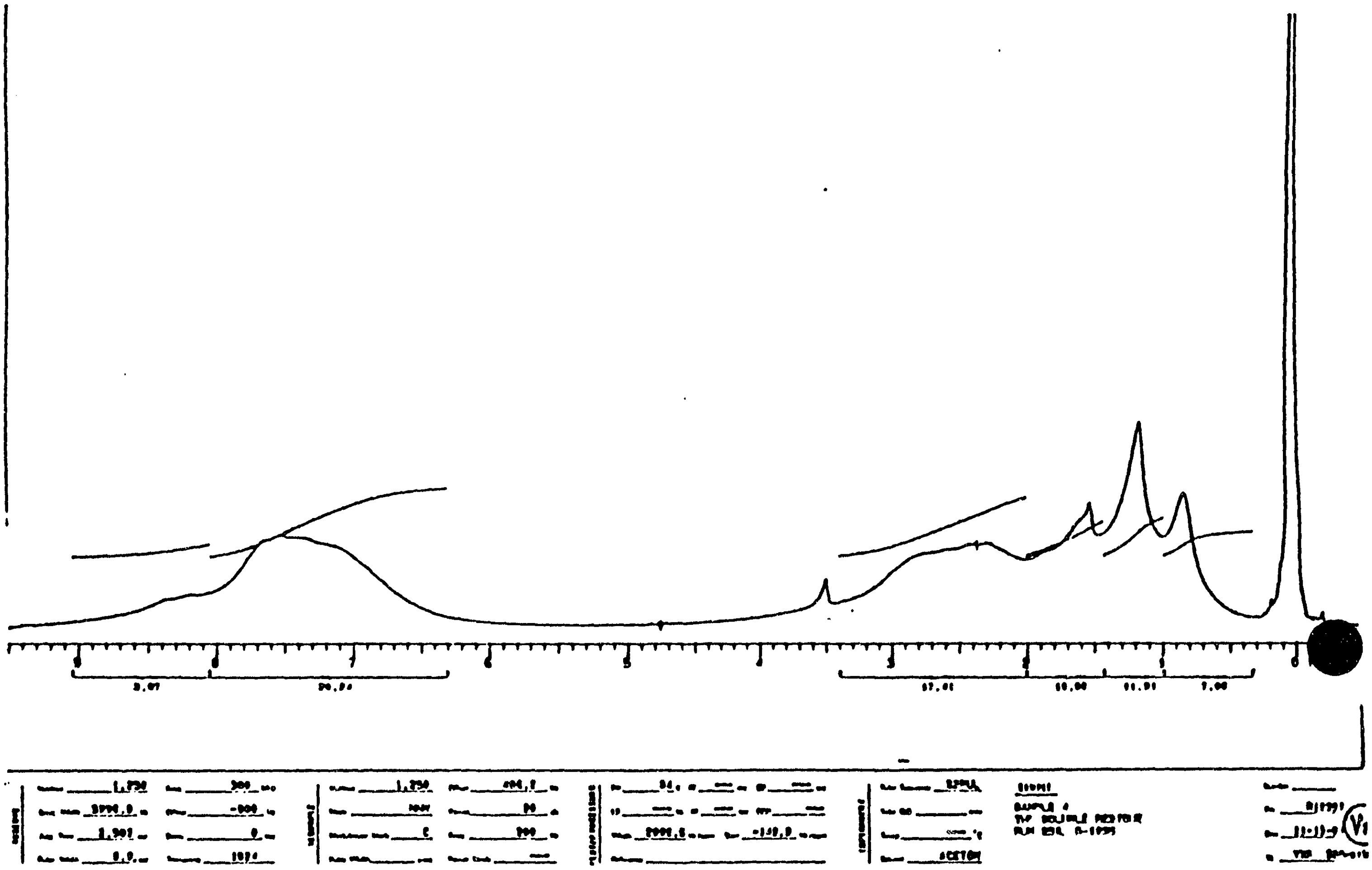


Figure 10. DEPT Spectrum of Sample 4, run 259, in d_8-THF Showing Selective Excitation of only Methyl Carbons

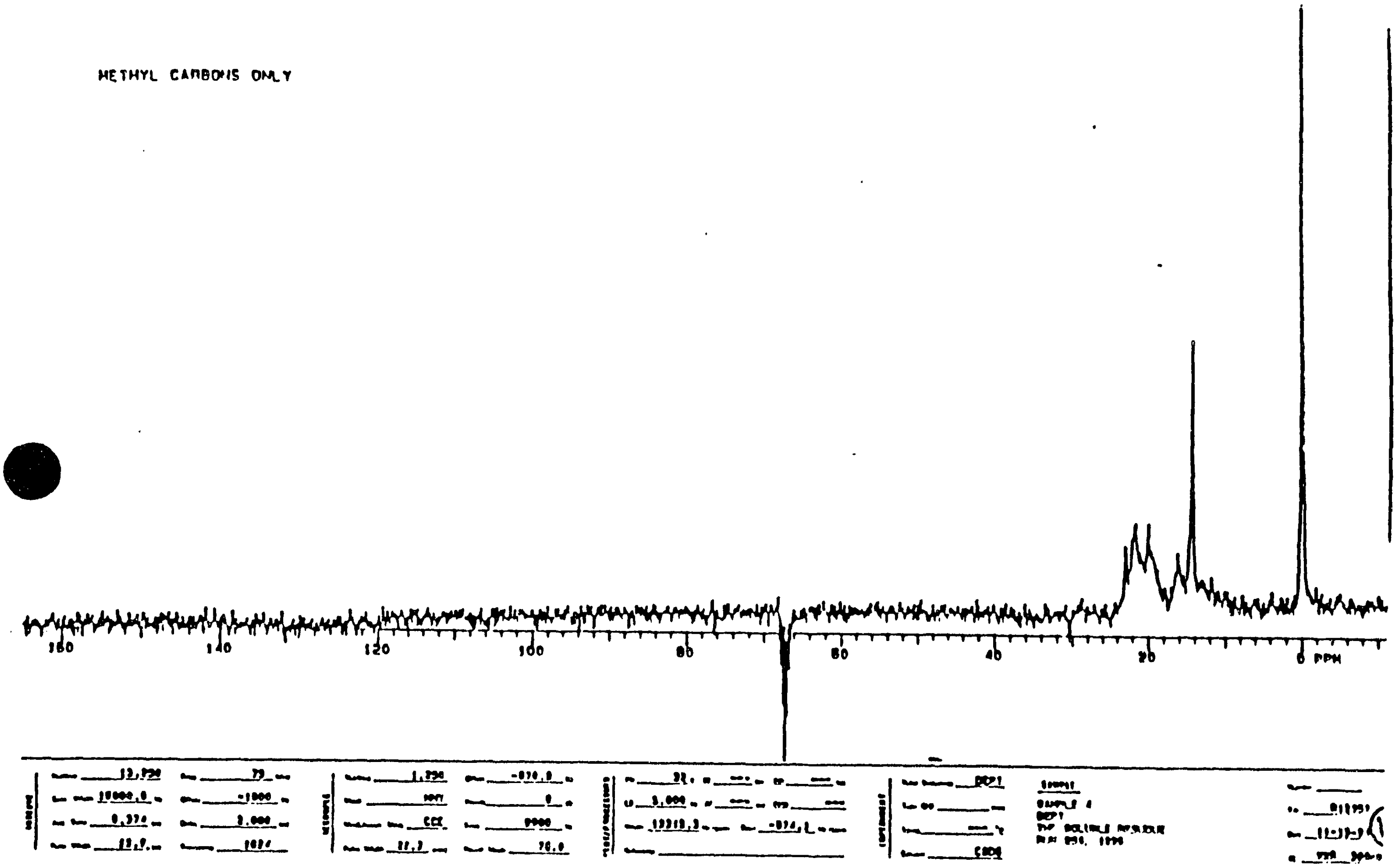


Figure 11. DEPT Spectrum of Sample 4, run 259, in d_8-THF Showing Selective Excitation of only Methine Carbons

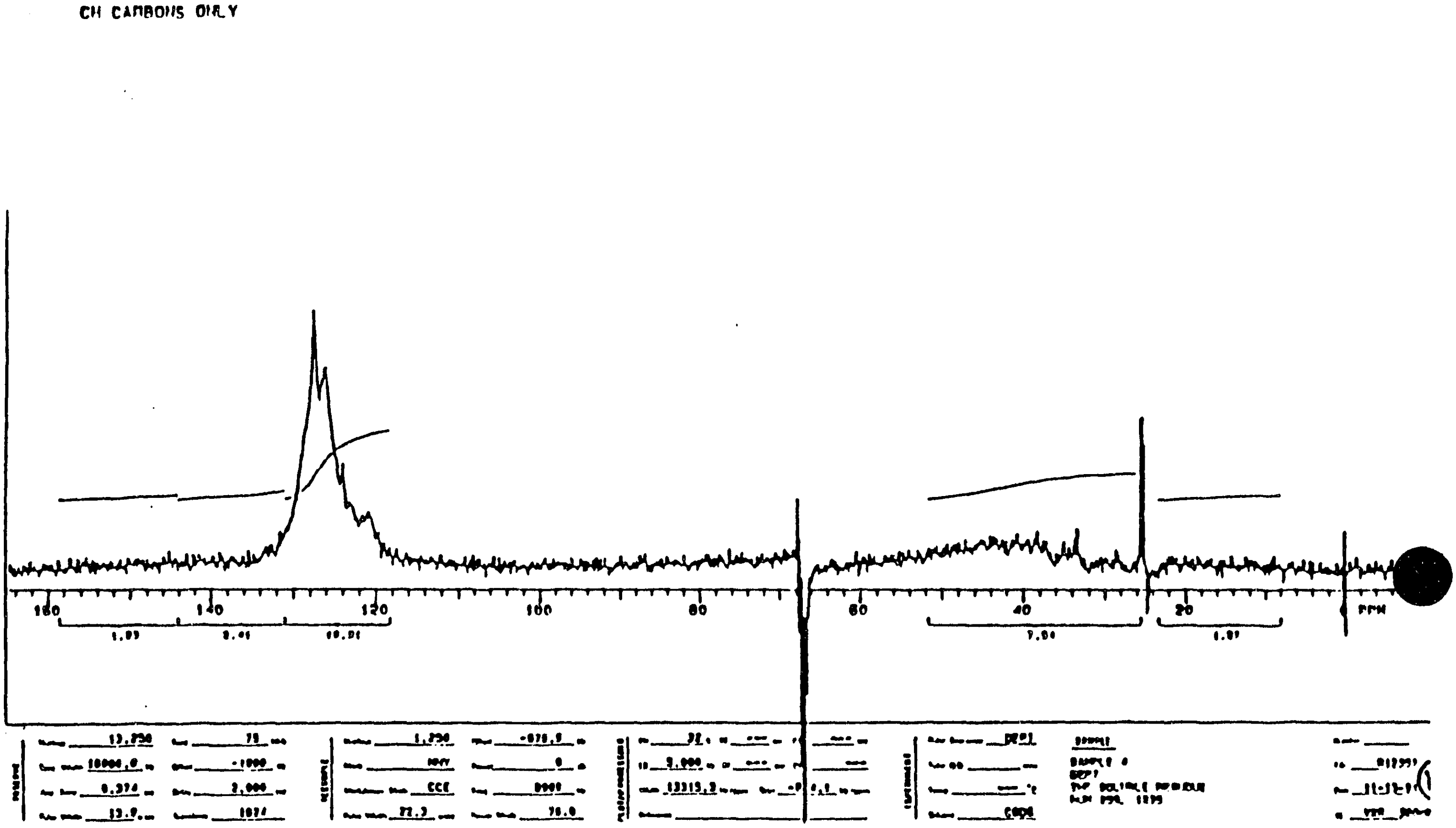


Figure 12. DEPT Spectrum of Sample 4, run 259, in d_8-THF Showing Selective Excitation of only Protonated Carbons

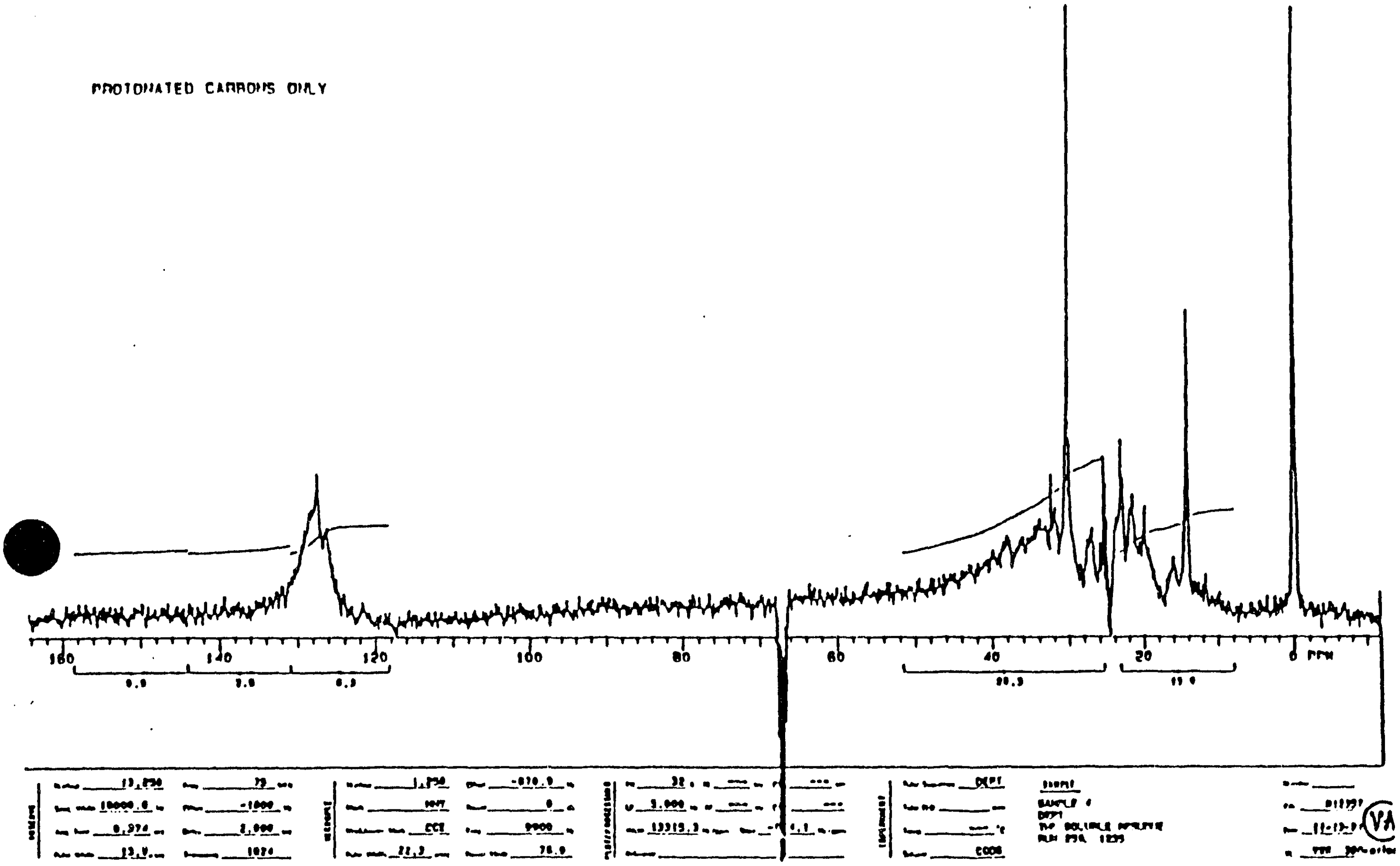


Figure 13. APT Spectrum of Sample 2, run 257, in d_8-THF. In this spectrum the quaternary and methylene carbons are up while the methine and methyl carbons are inverted

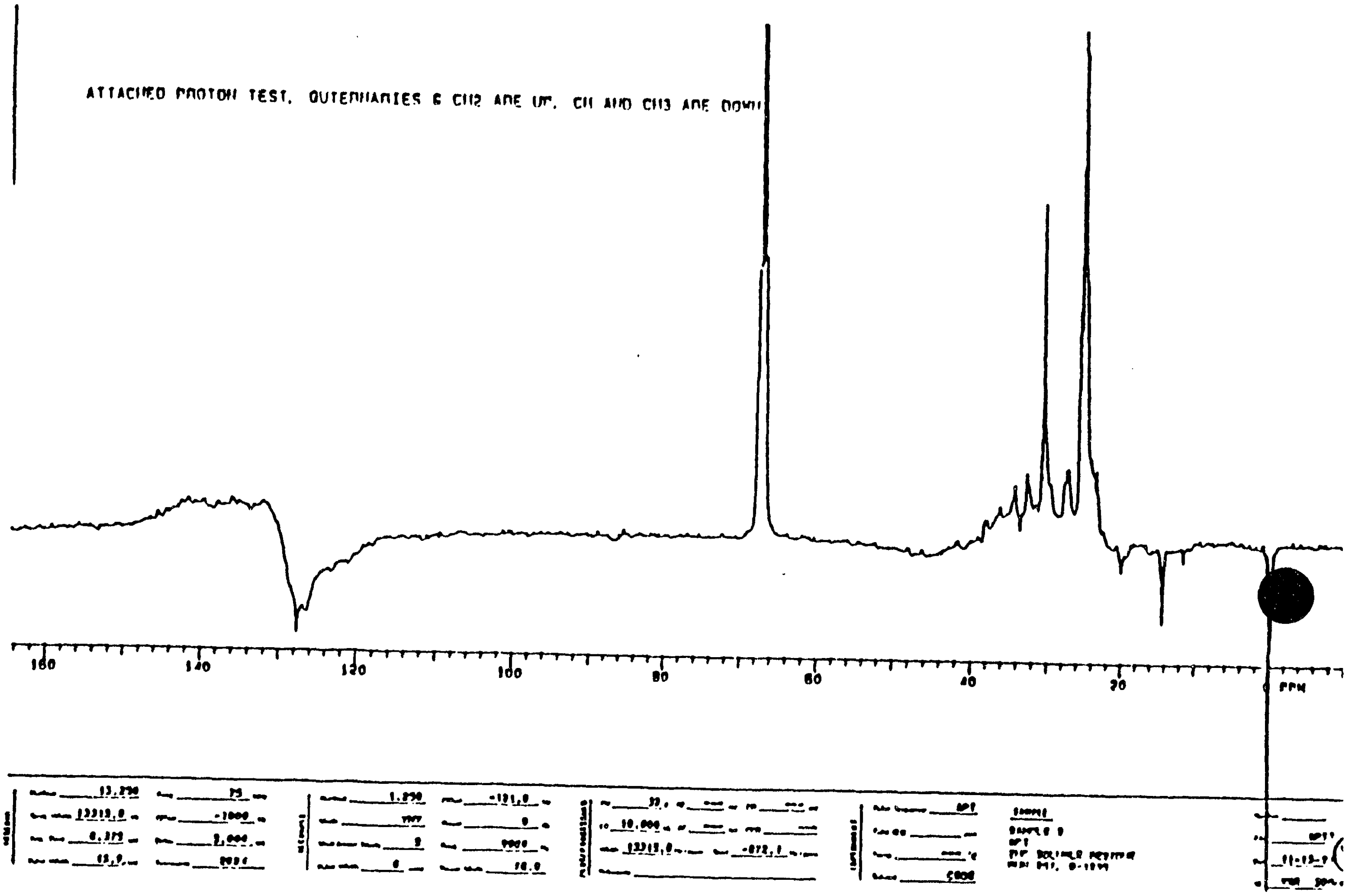


Figure 14. APT Spectrum of Sample 2, run 257, in d_8-THF. In this spectrum only the quaternary carbons are excited

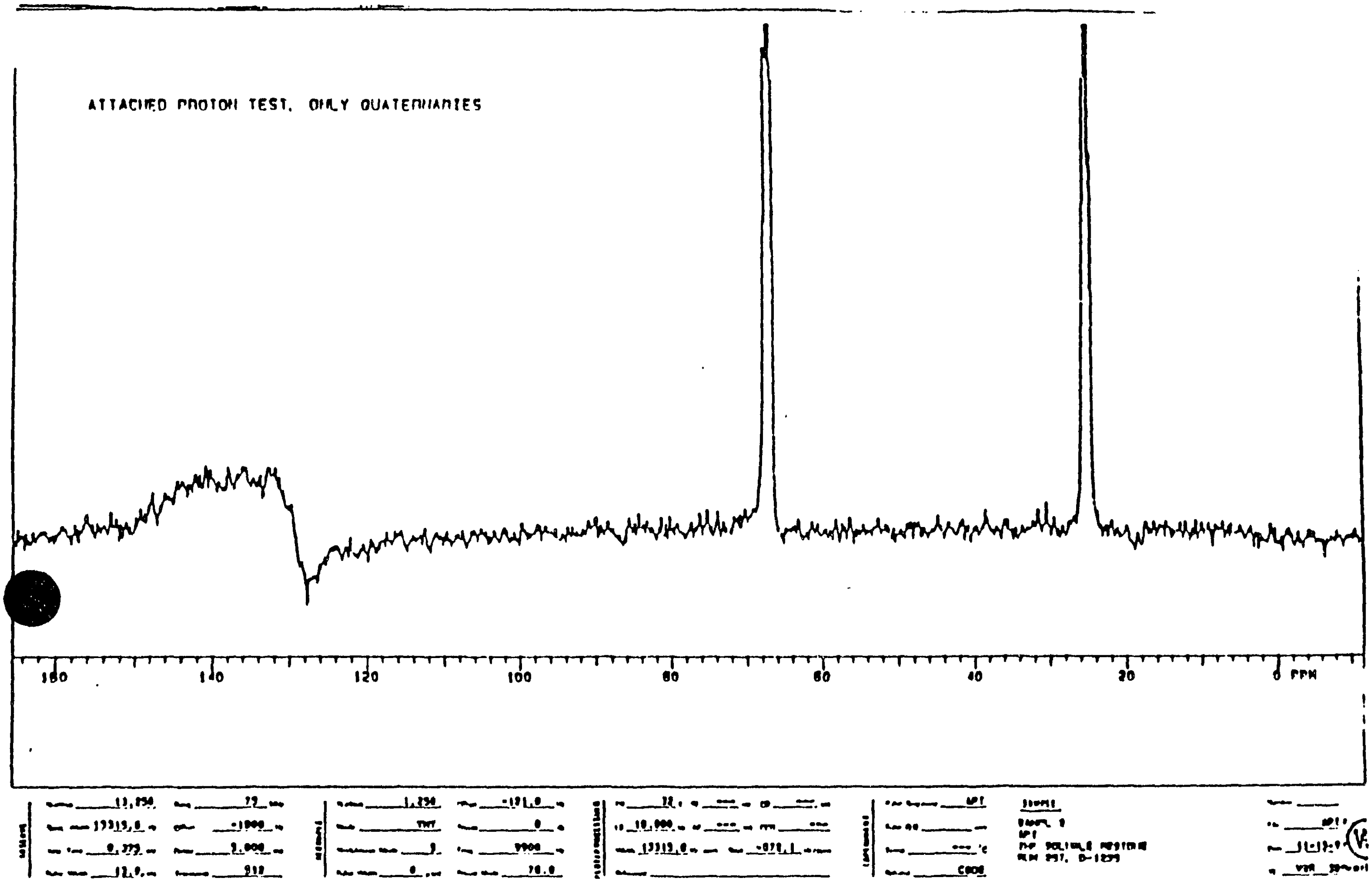


Figure 15. Quantitative ^{13}C NMR Spectra of a Heavy and a Middle Distillate of SRC II in $CDCl_3$

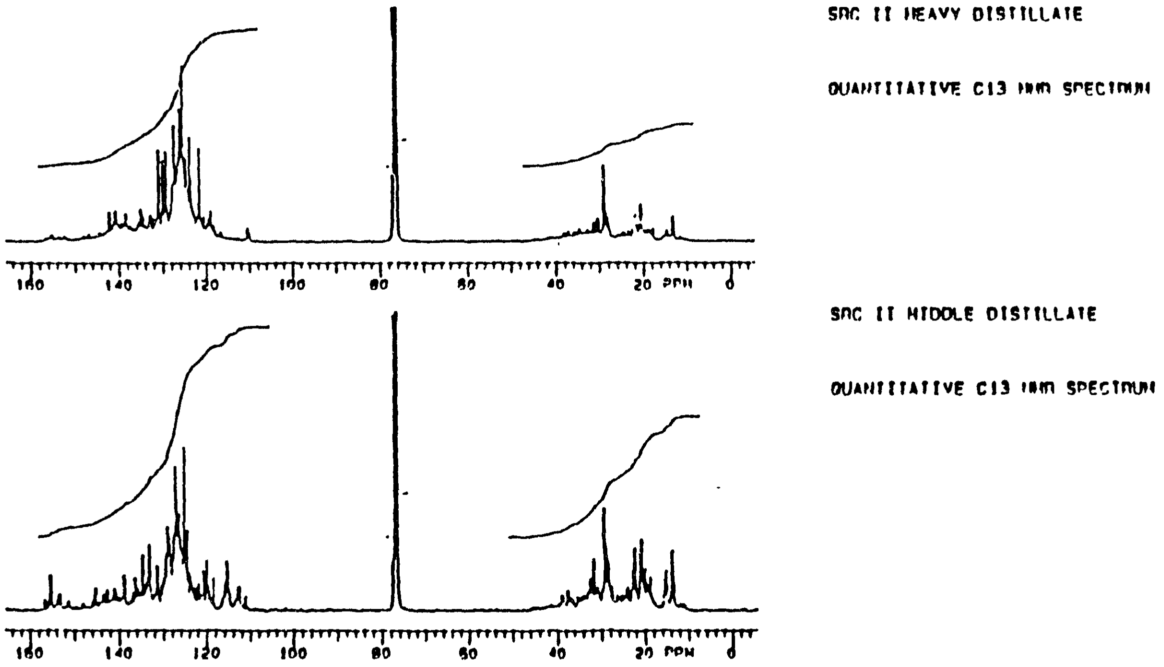


Figure 16. HETCOR Spectrum Centered Around the Protonated Aromatic Region of a Middle Distillate of SRC II in $CDCl_3$

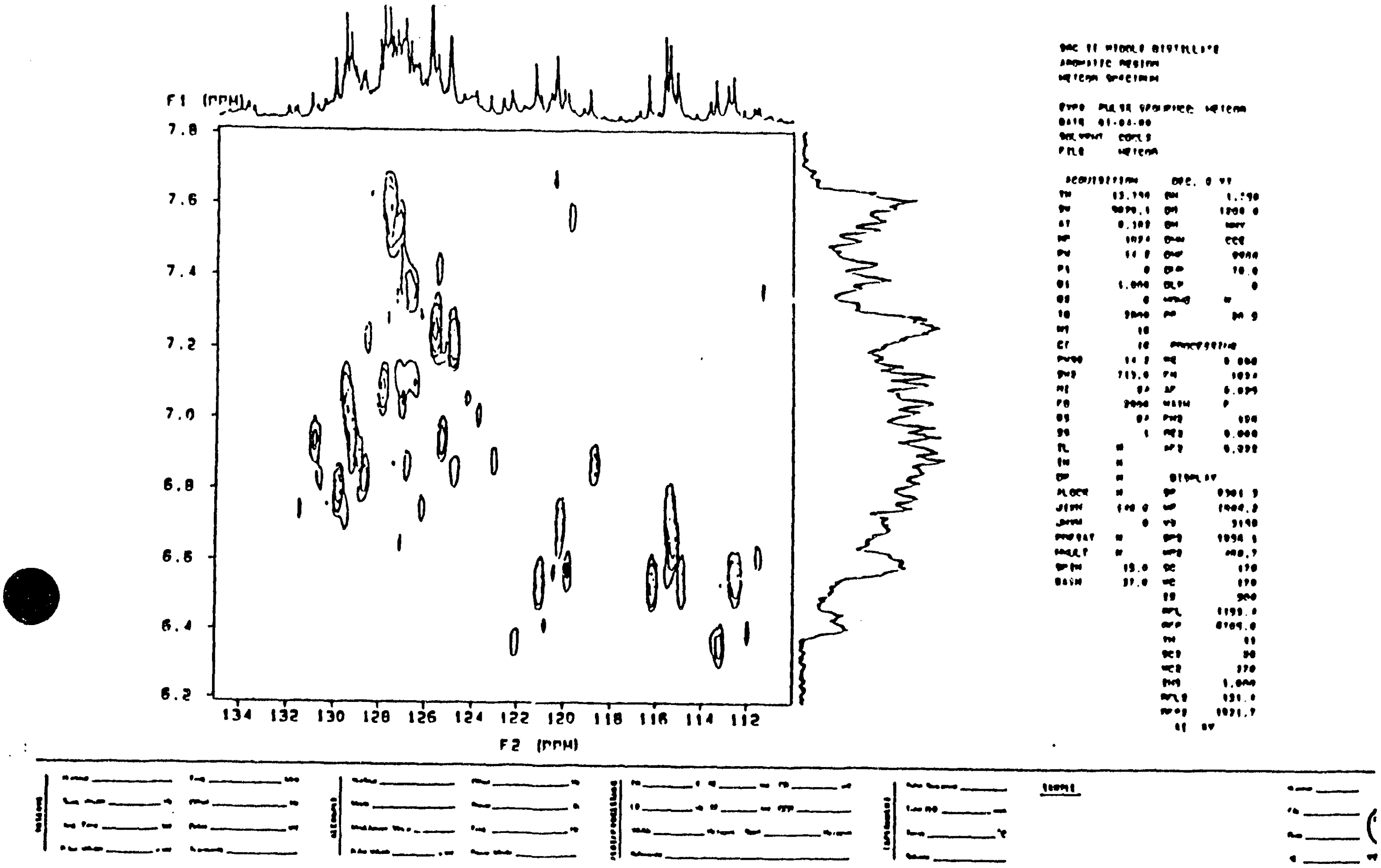


Figure 17. A HETCOR Spectrum of the Aliphatic Region of a Middle Distillate of SRC II in CDCl3

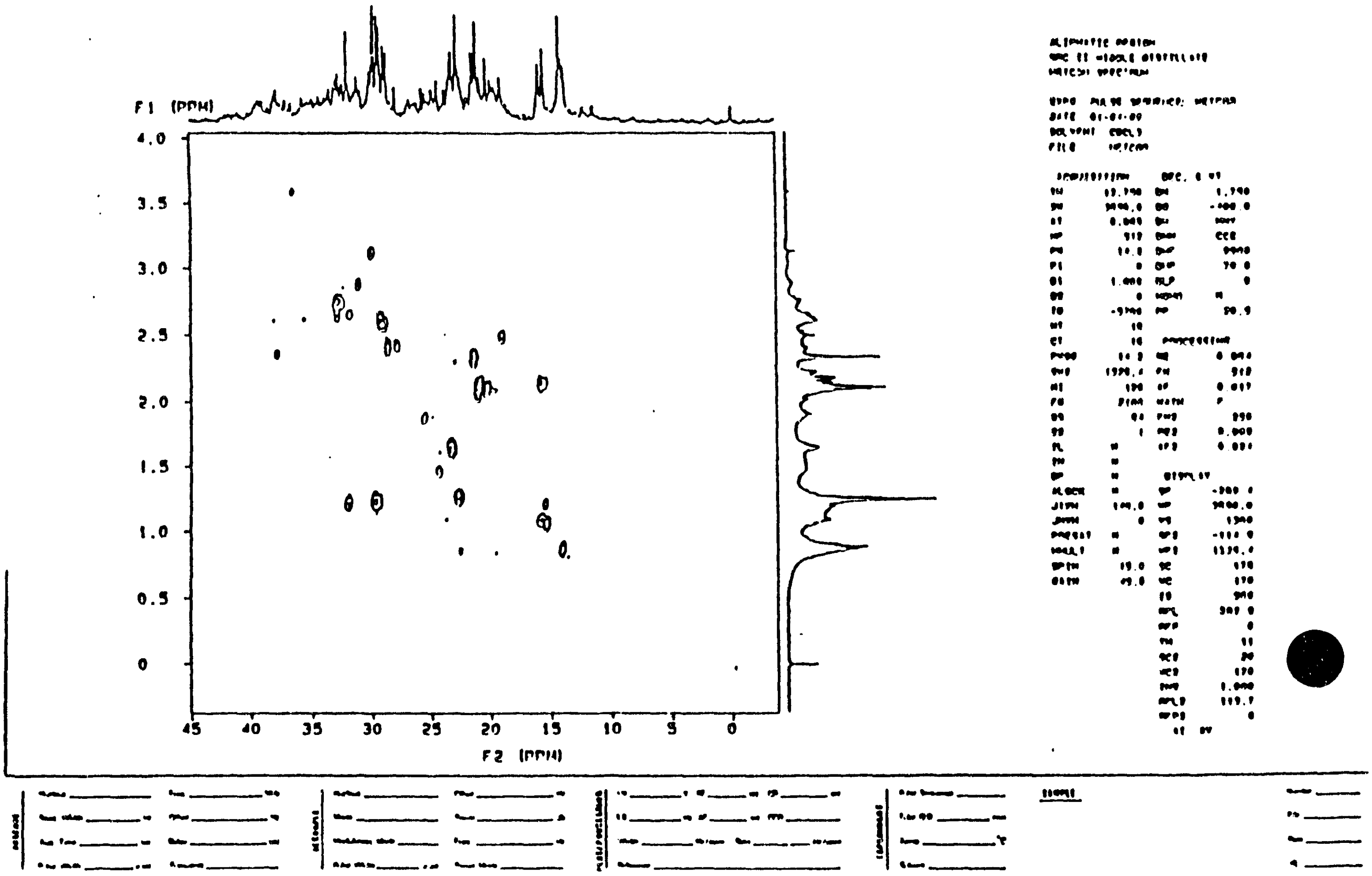


Figure 18. Equilibrium Phase Compositions in the Methanol-Carbon Dioxide Binary System (Reference 31)

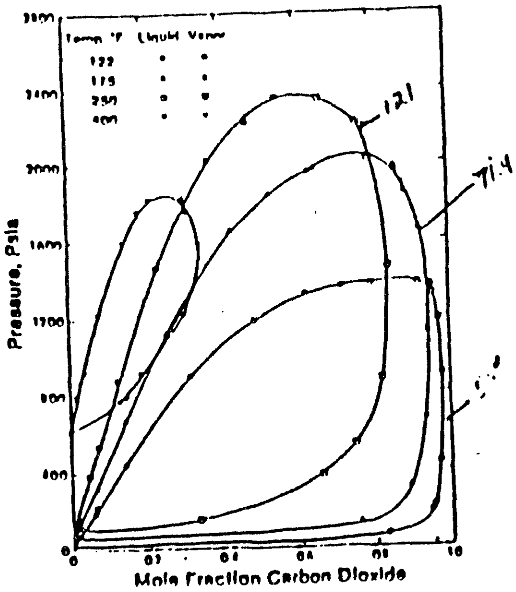


Figure 19. Results of Supercritical Fluid Extraction of Sample 17 (Illinois No. 6, W; 257; C/C; Recycle Stream

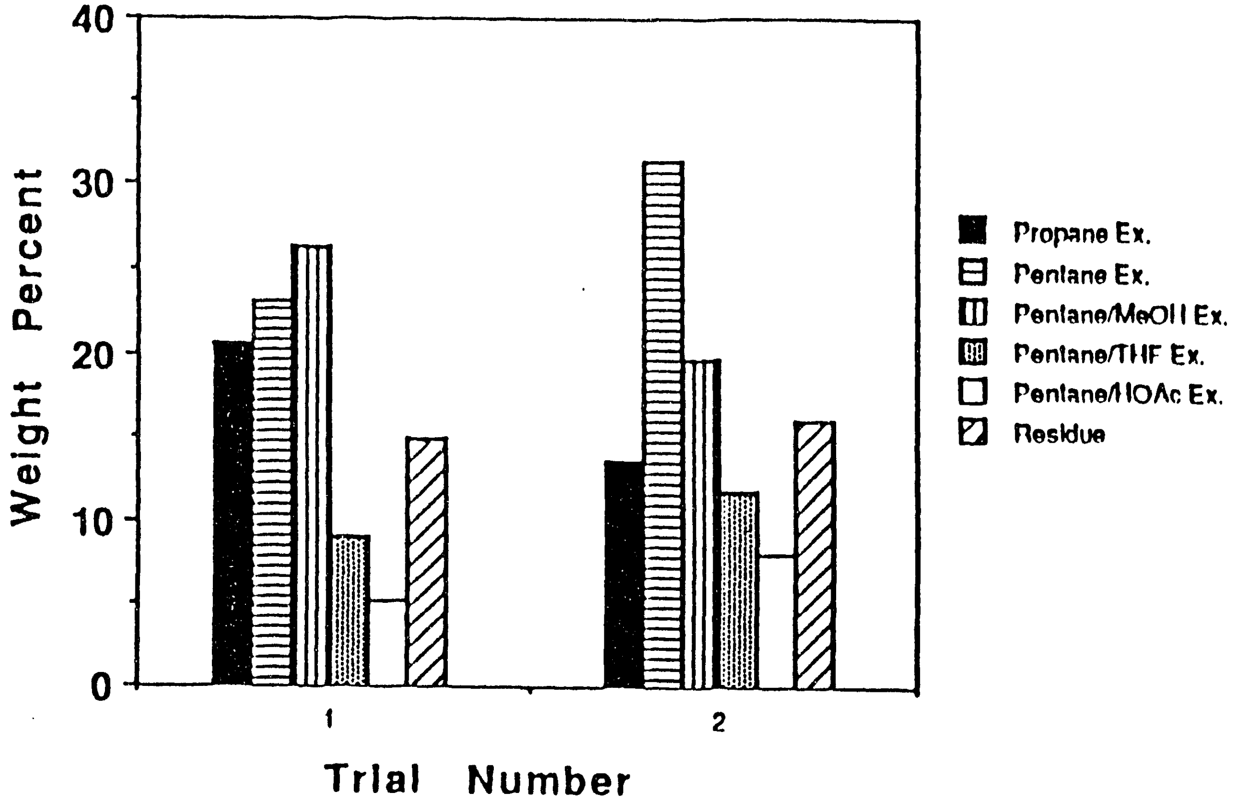


Figure 20. Grahm-Schmidt Reconstruction of GC/FTIR Analysis of a Propane Extract of Sample 17

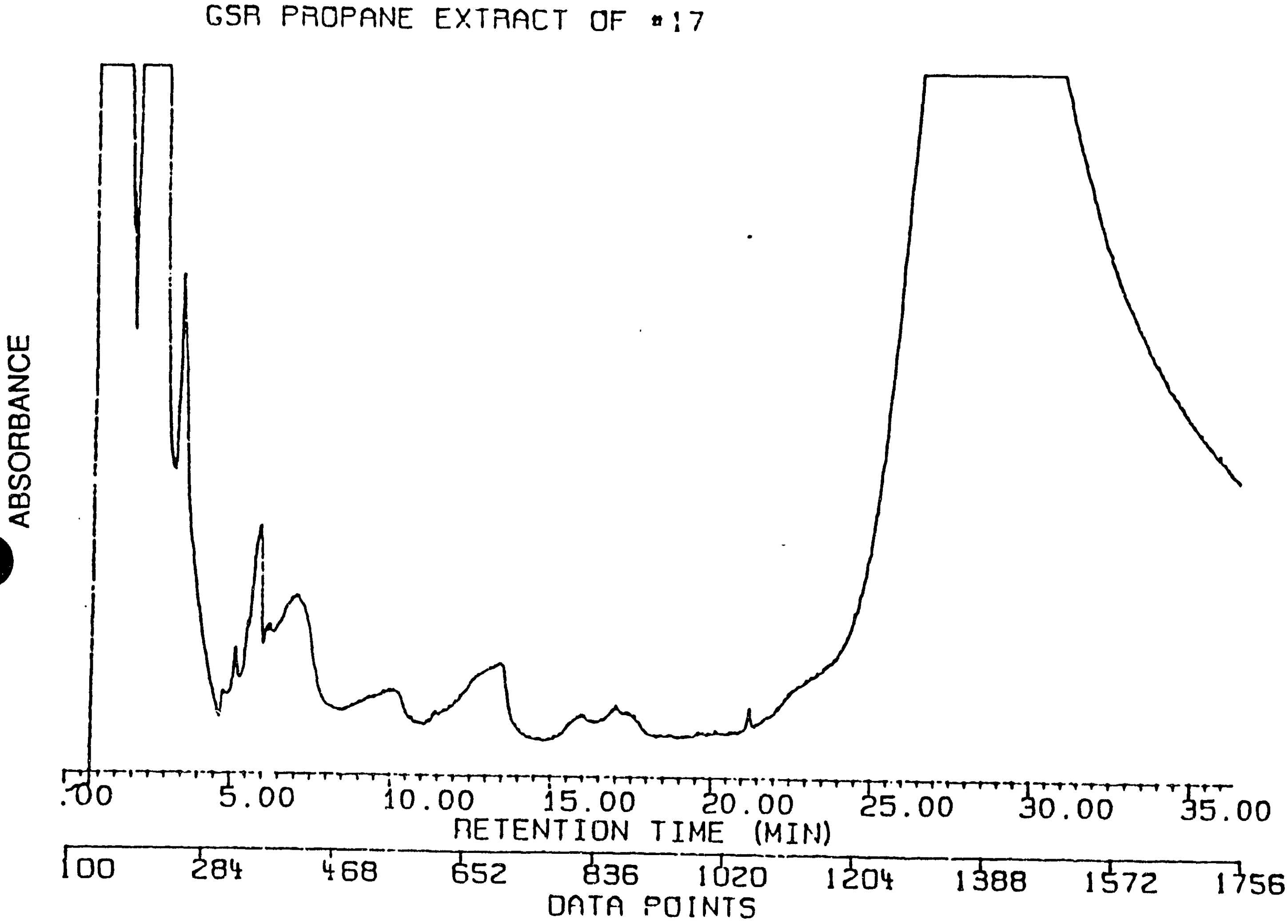


Figure 21. Infrared Spectrum of the Second Peak Observed in Figure 20 along with the Best Library Spectrum found in the Aldrich Vapor Library

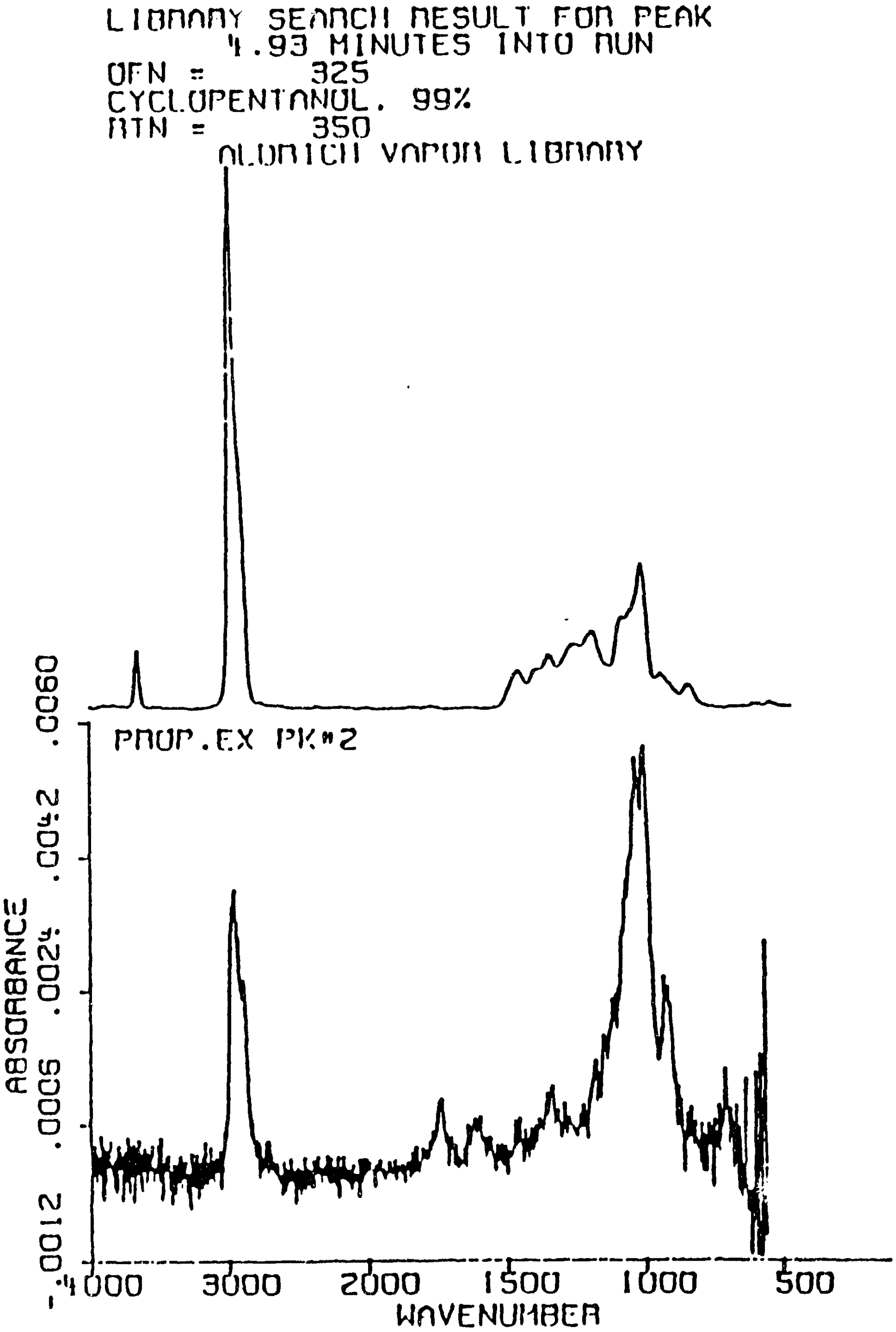


Figure 22. Electrospray Ionization Mass Spectrum of the Propane Extract from Sample 17. Flow rate into the electrospray interface was 0.5 µL/min. Extract was dissolved in 20% acetic acid, 10% water, and 70% THF with 0.012 M KH_2PO_4 added

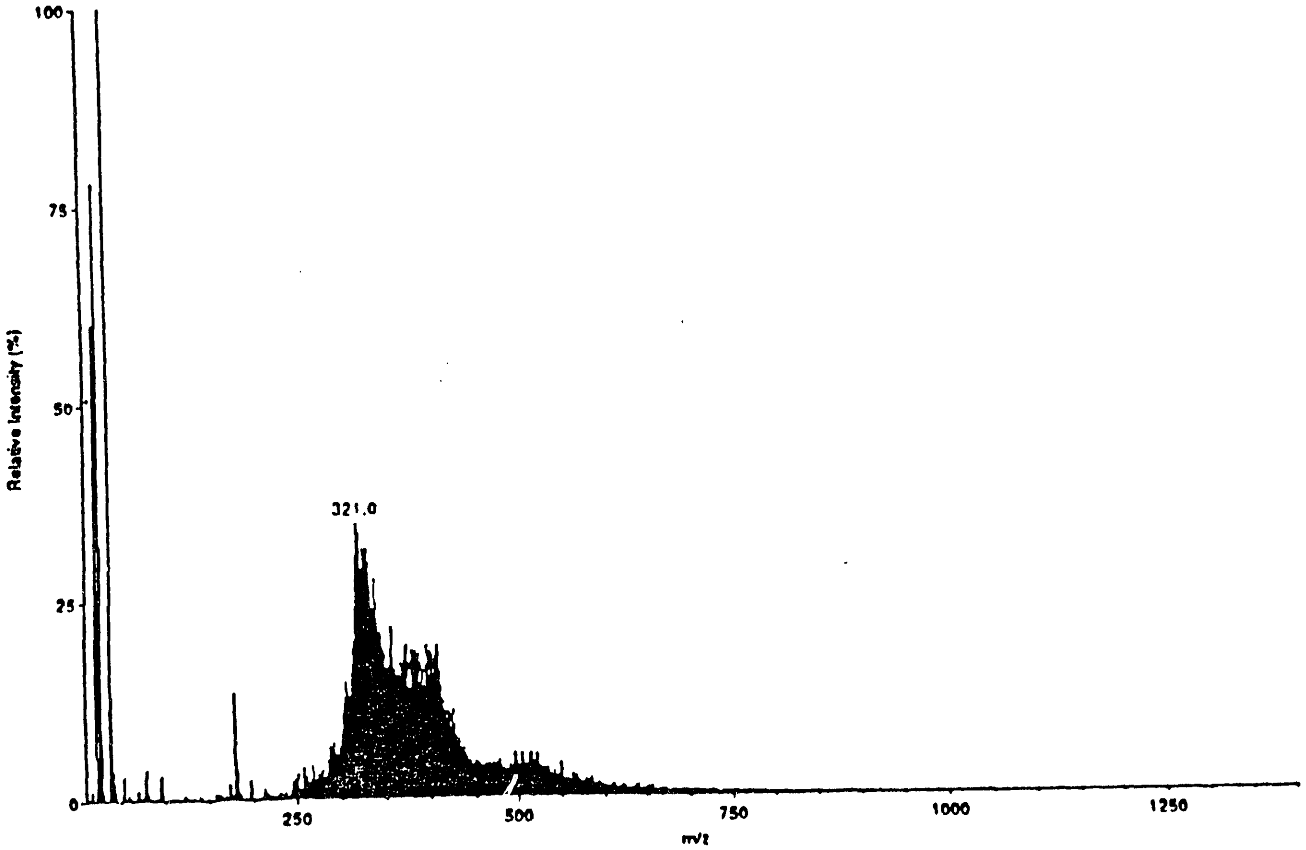


Figure 23. Electrospray Ionization Mass Spectrum of the Pentane Extract from Sample 17. Flow rate into the electrospray interfa was 0.5 µL/min. Extract was dissolved in 20% acetic acid, 10% water, and 70% THF with 0.012 M KH_2PO_4 added

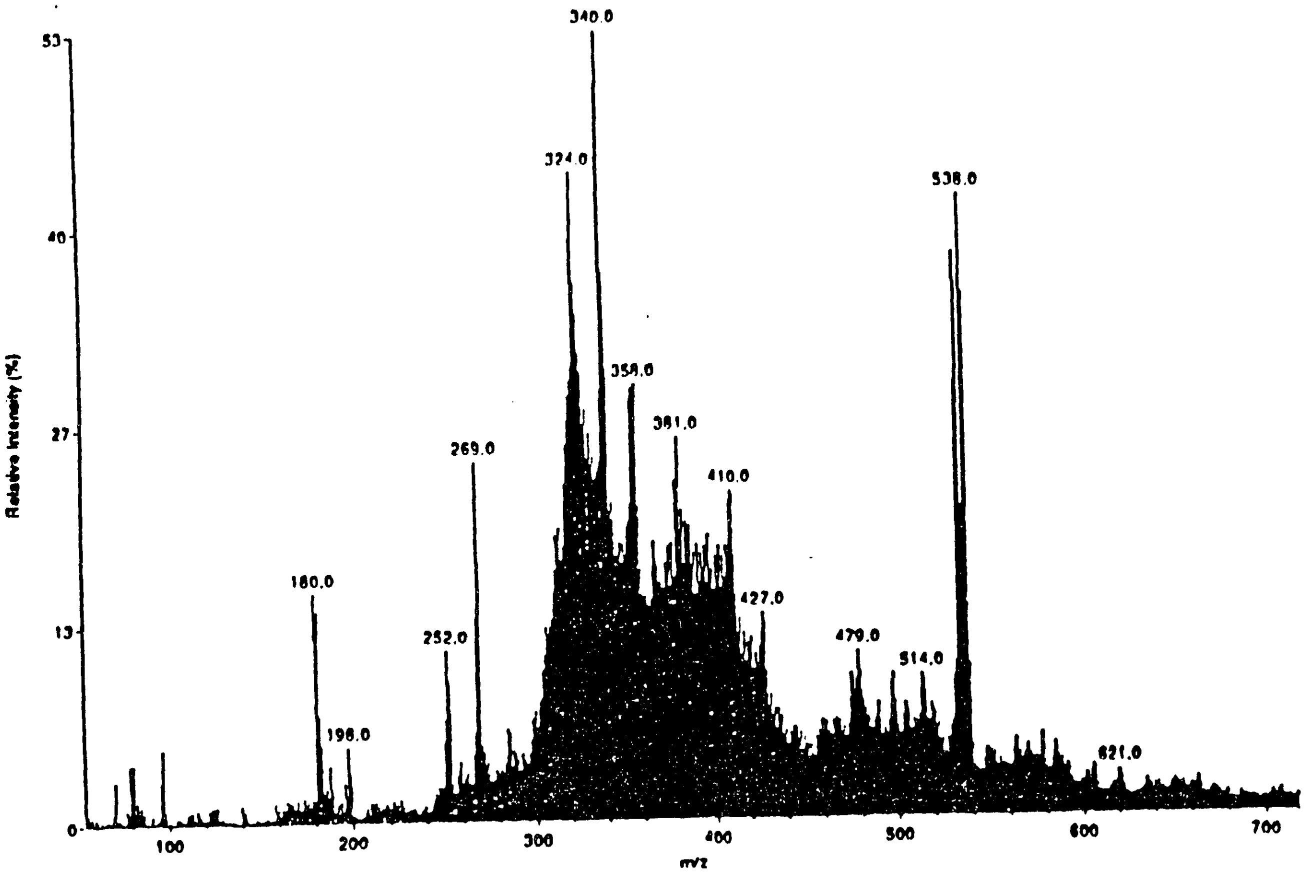


Figure 24. Electrospray Ionization Mass Spectrum of the Pentane/Methanol Extract from Sample 17. Flow rate into the electrospray interface was 0.5 µL/min. Extract was dissolved in 20% acetic acid, 10% water, and 70% THF with 0.012 M KH_2PO_4 added

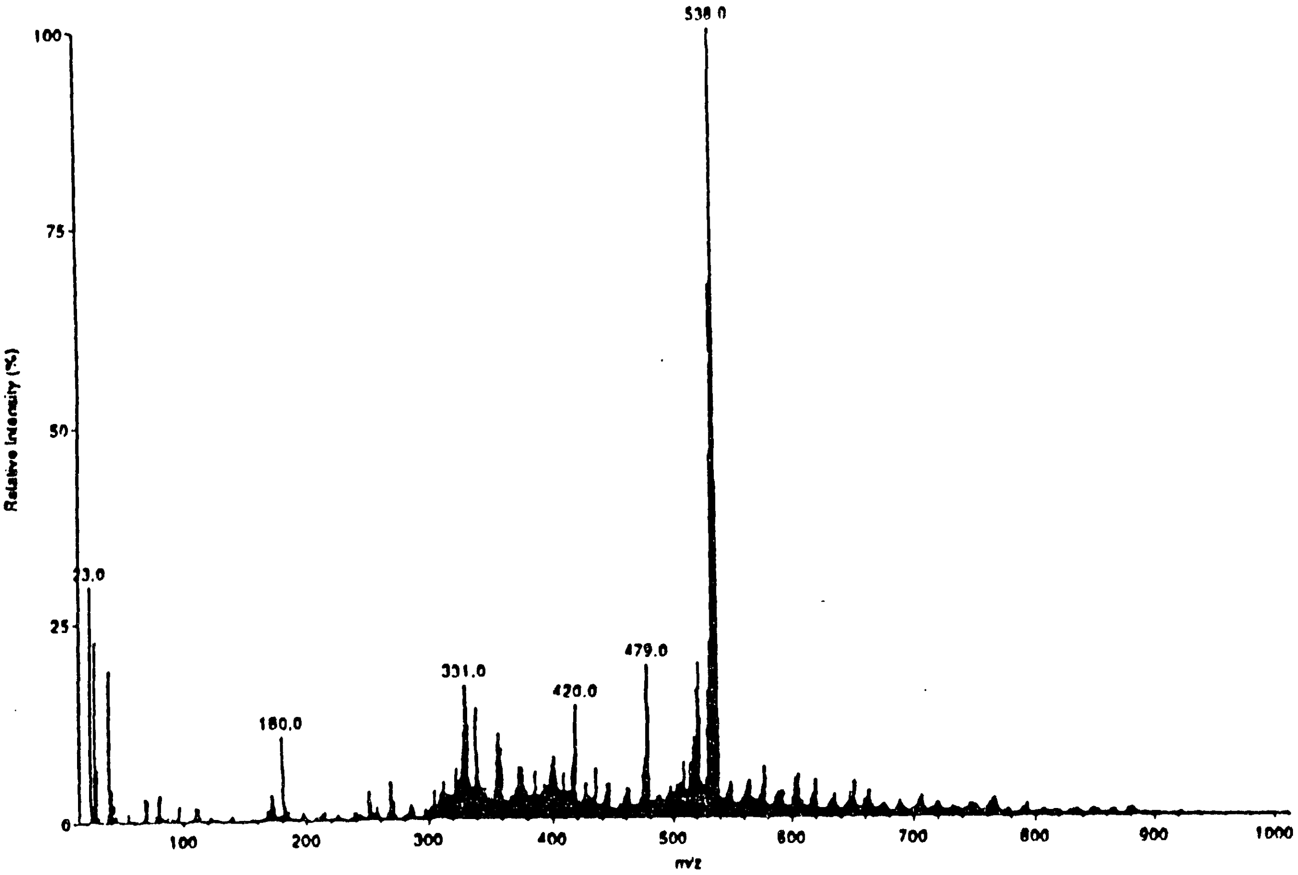


Figure 25. Electrospray Ionization Mass Spectrum of the Pentane/THF Extract from Sample #17. Flow rate into the electrospray interface was 0.5 µL/min. Extract was dissolved in 20% acetic acid, 10% water, and 70% THF with 0.012 M KH_2PO_4 added

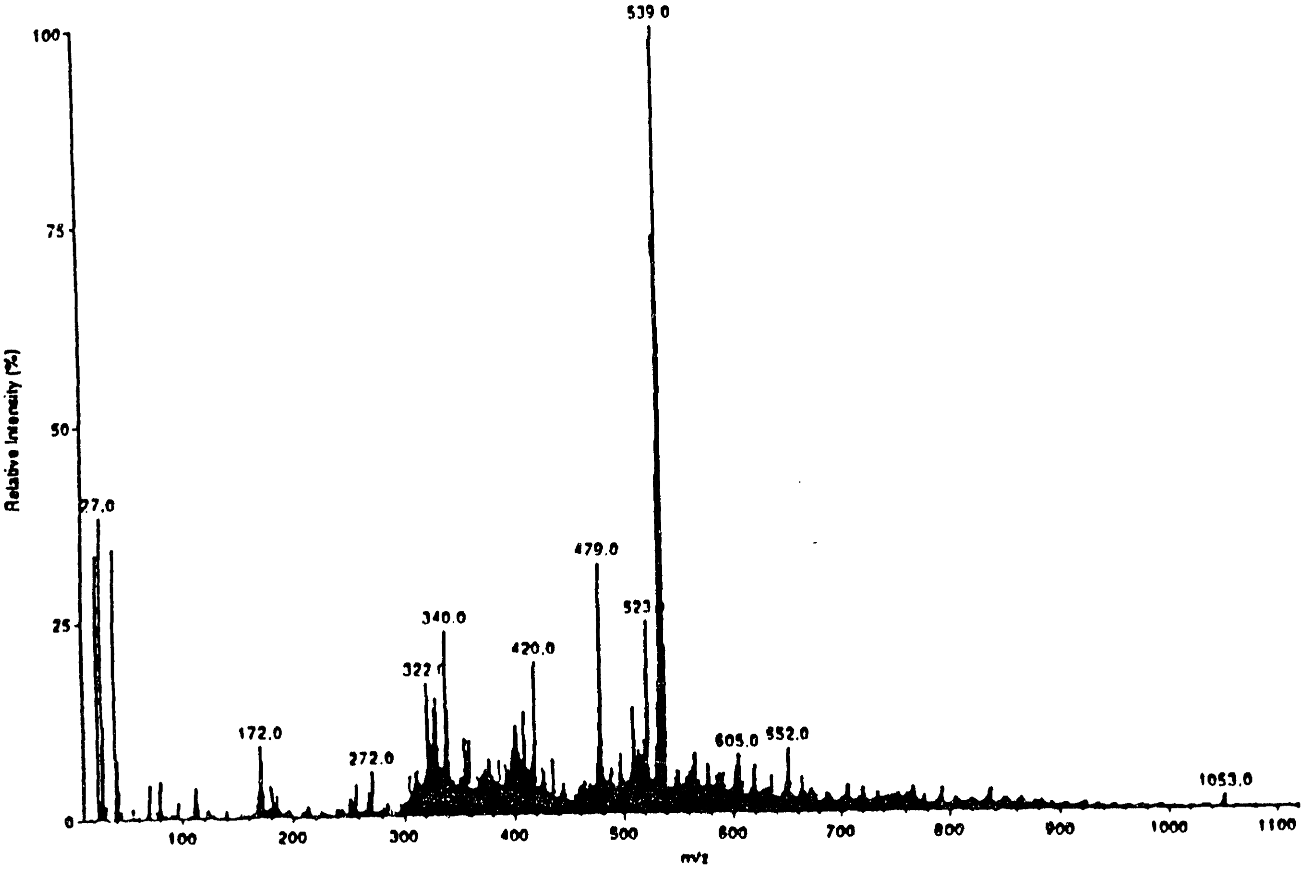


Figure 26. Electrospray Ionization Mass Spectrum of the Pentane/Acetic Acid Extract from Sample #17. Flow rate into the electrospray interface was 0.5 µL/min. Extract was dissolved in 20% acetic acid, 10% water, and 70% THF with 0.012 M KH_2PO_4 added

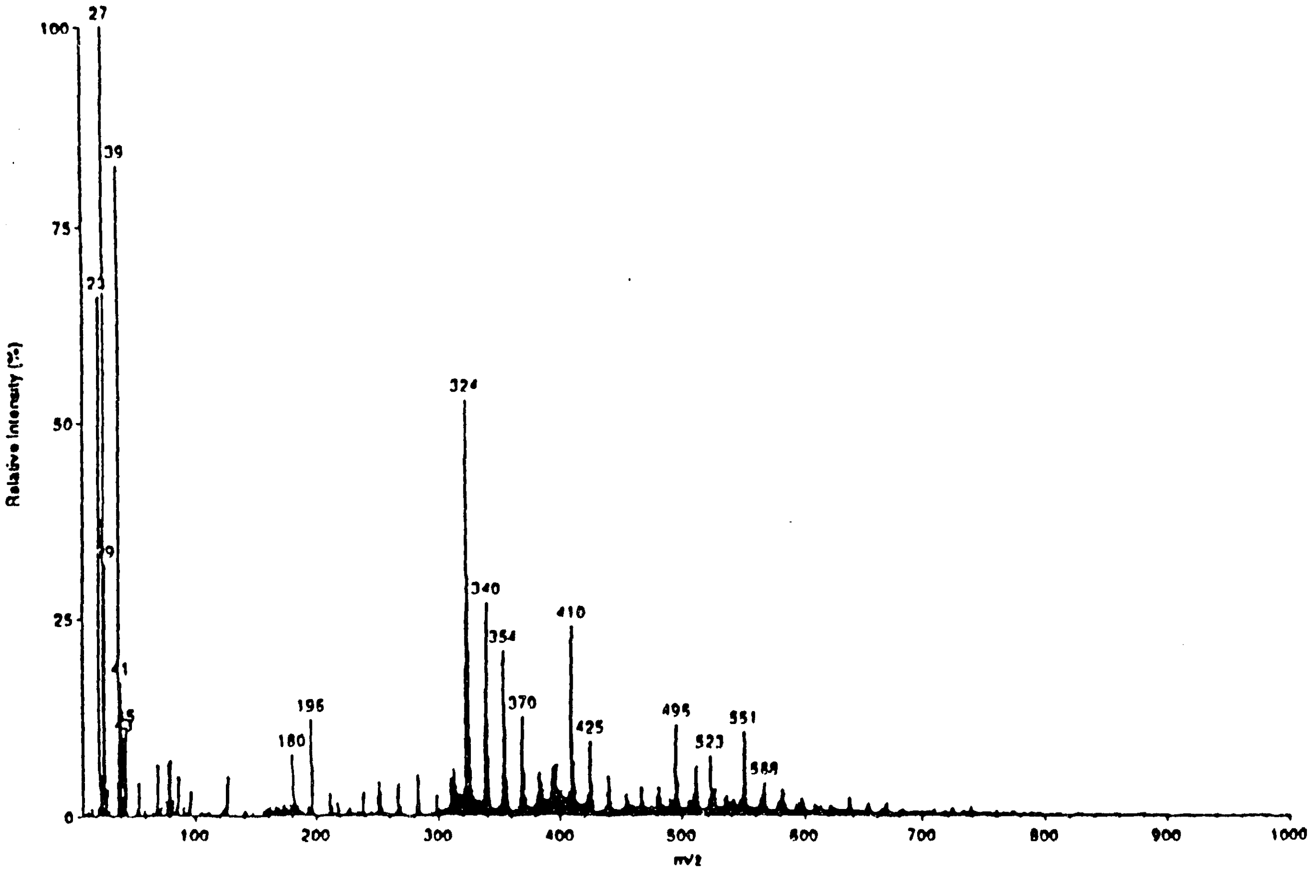


Figure 27. Electrospray Ionization CID Spectrum of ion m/z 538 Observed in Pentane/THF Extract from Sample 17. The collision gas used was argon

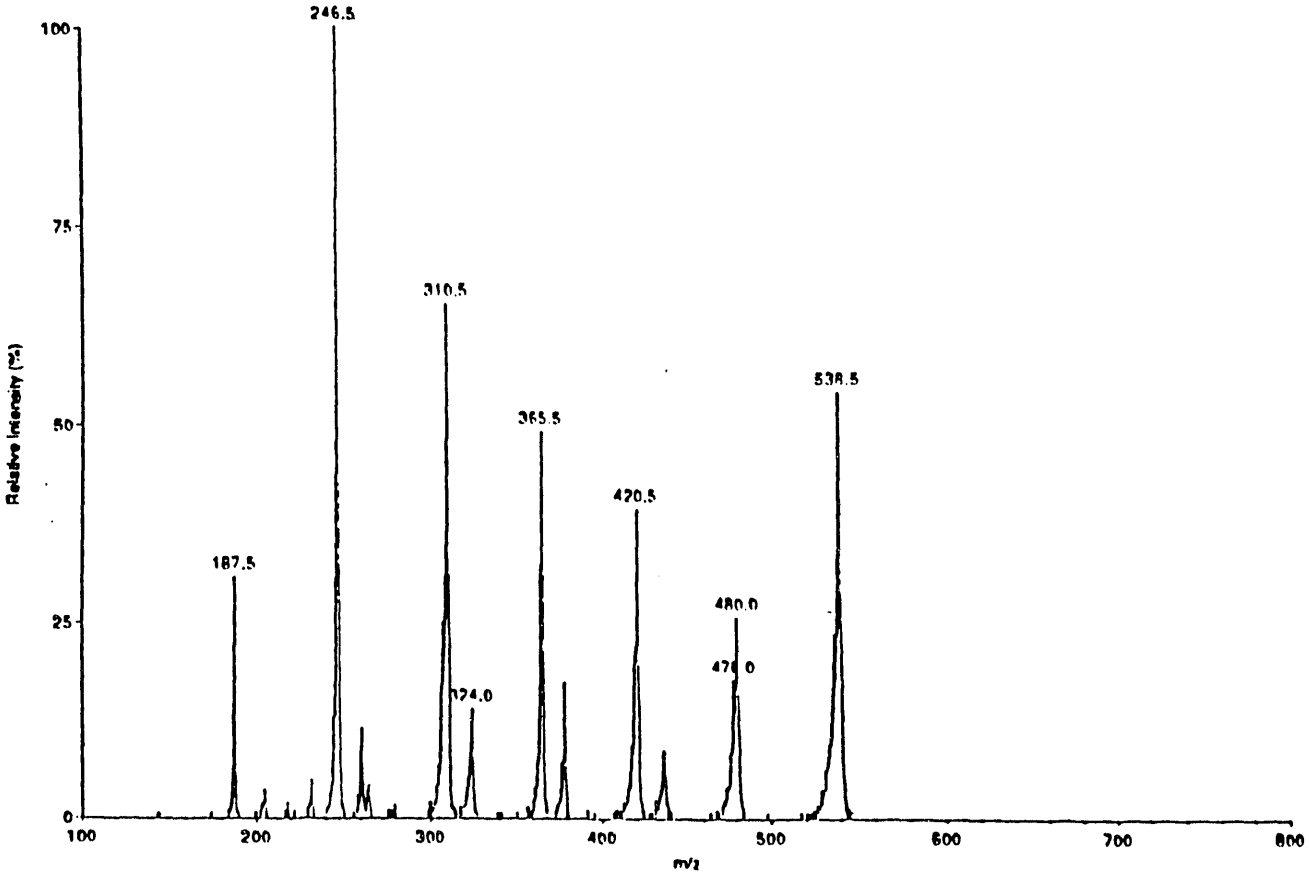


Figure 28. Field Desorption Mass Spectrum of Supercritical Fluid Pentane from Sample 17

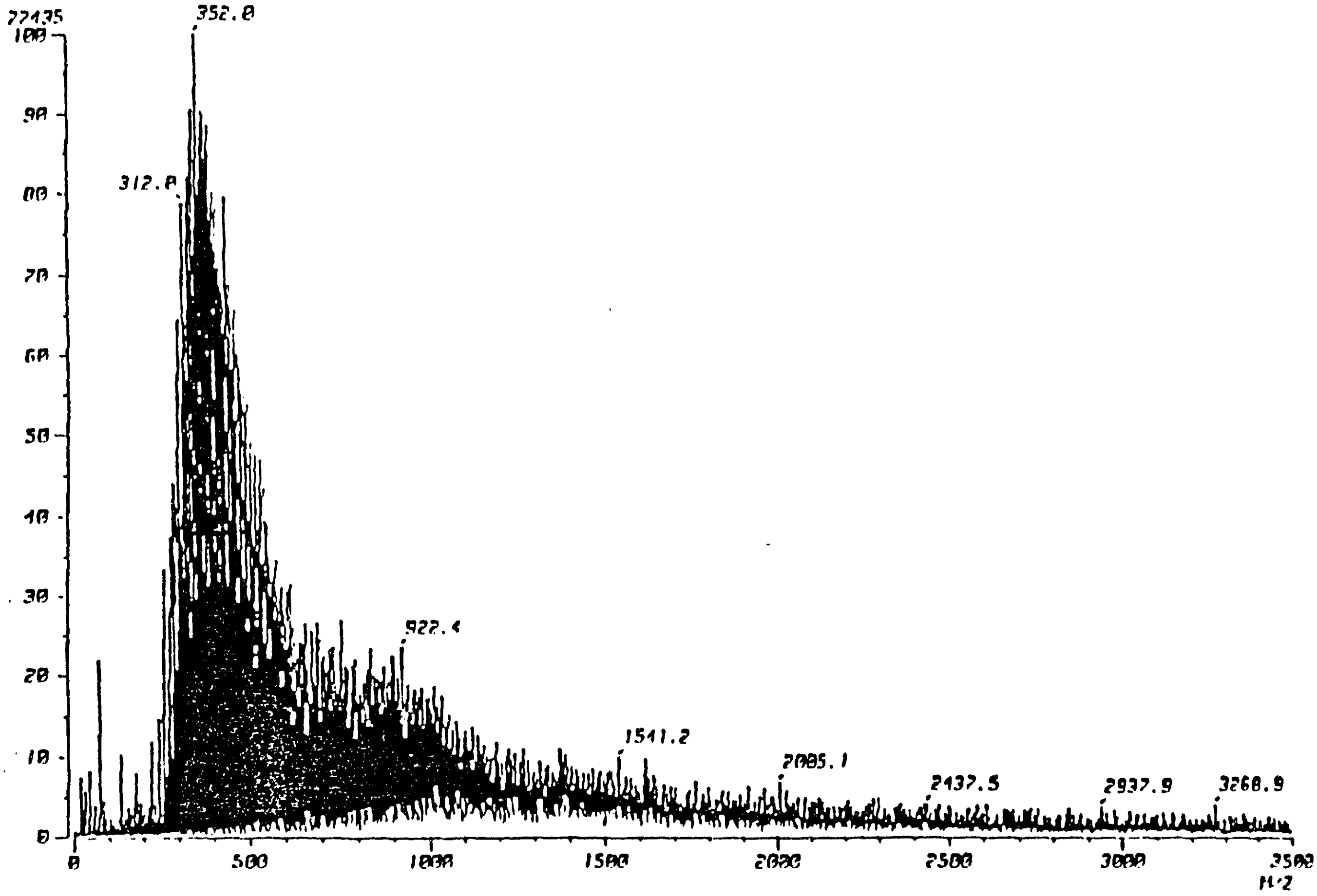


Figure 29. Field Desorption Mass Spectrum of Supercritical Fluid Pentane/Methanol from Sample 17

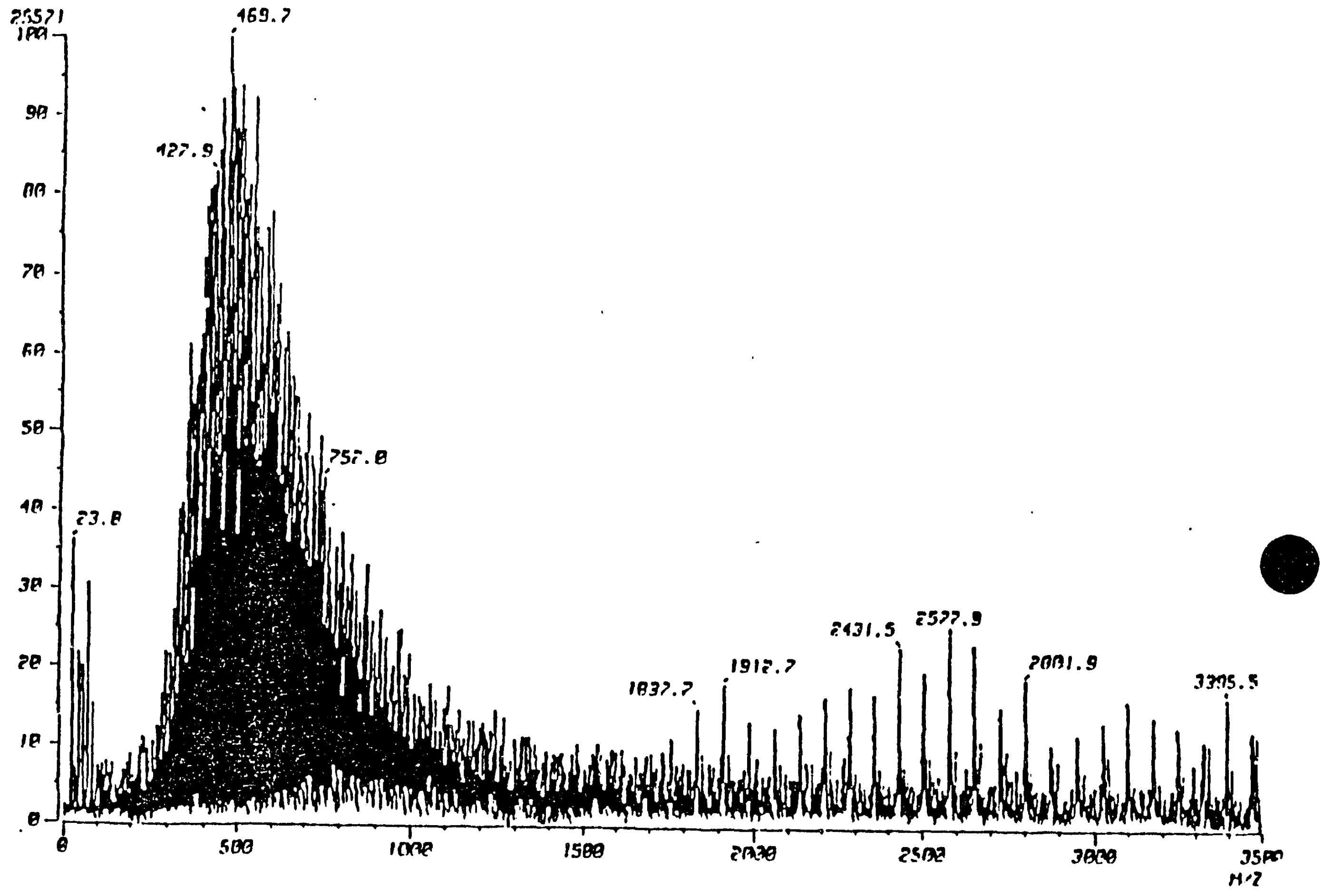


Figure 30. Desorption Chemical Ionization Mass Spectrum of Pentane/Methanol Extract of Sample 17

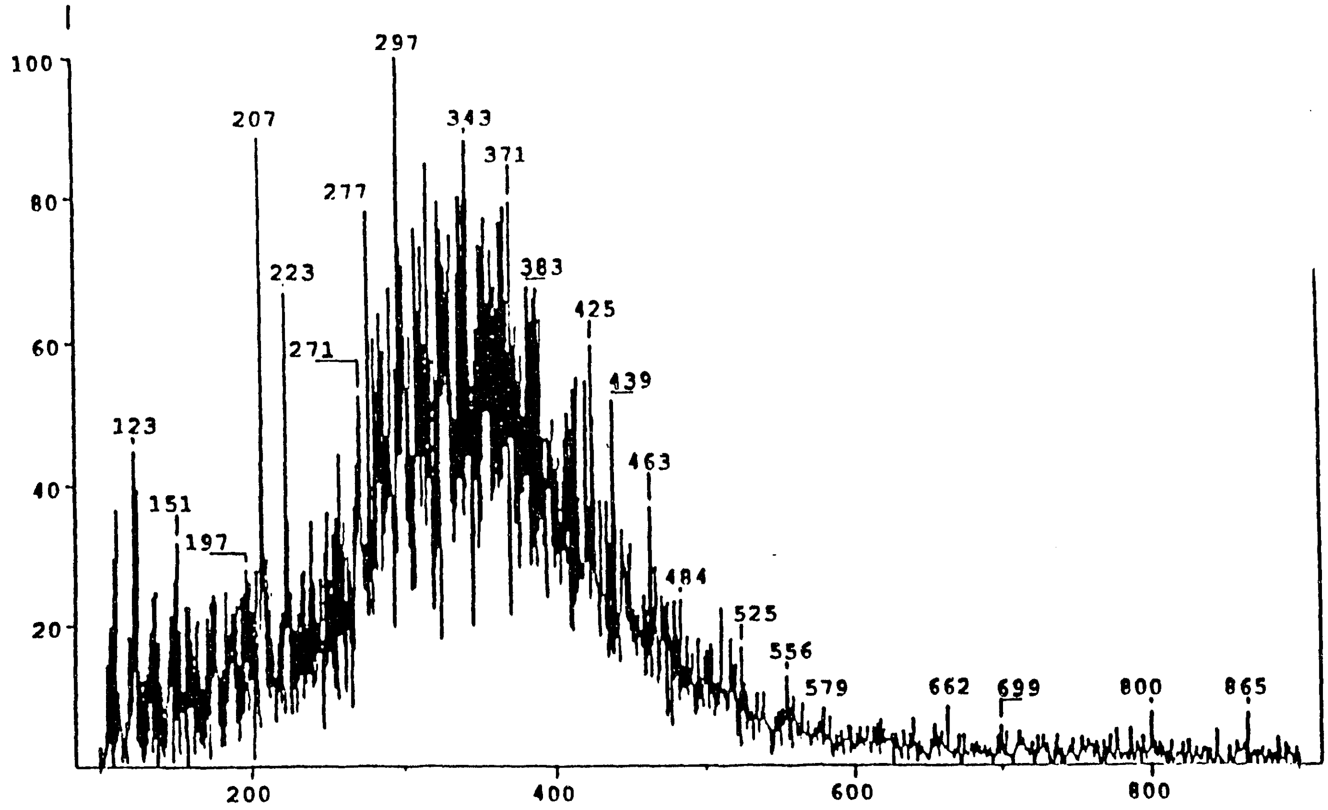


Figure 31. CID Spectrum of M/Z 277 from DCI Spectrum of Pentane/Methanol Extract of Sample 17

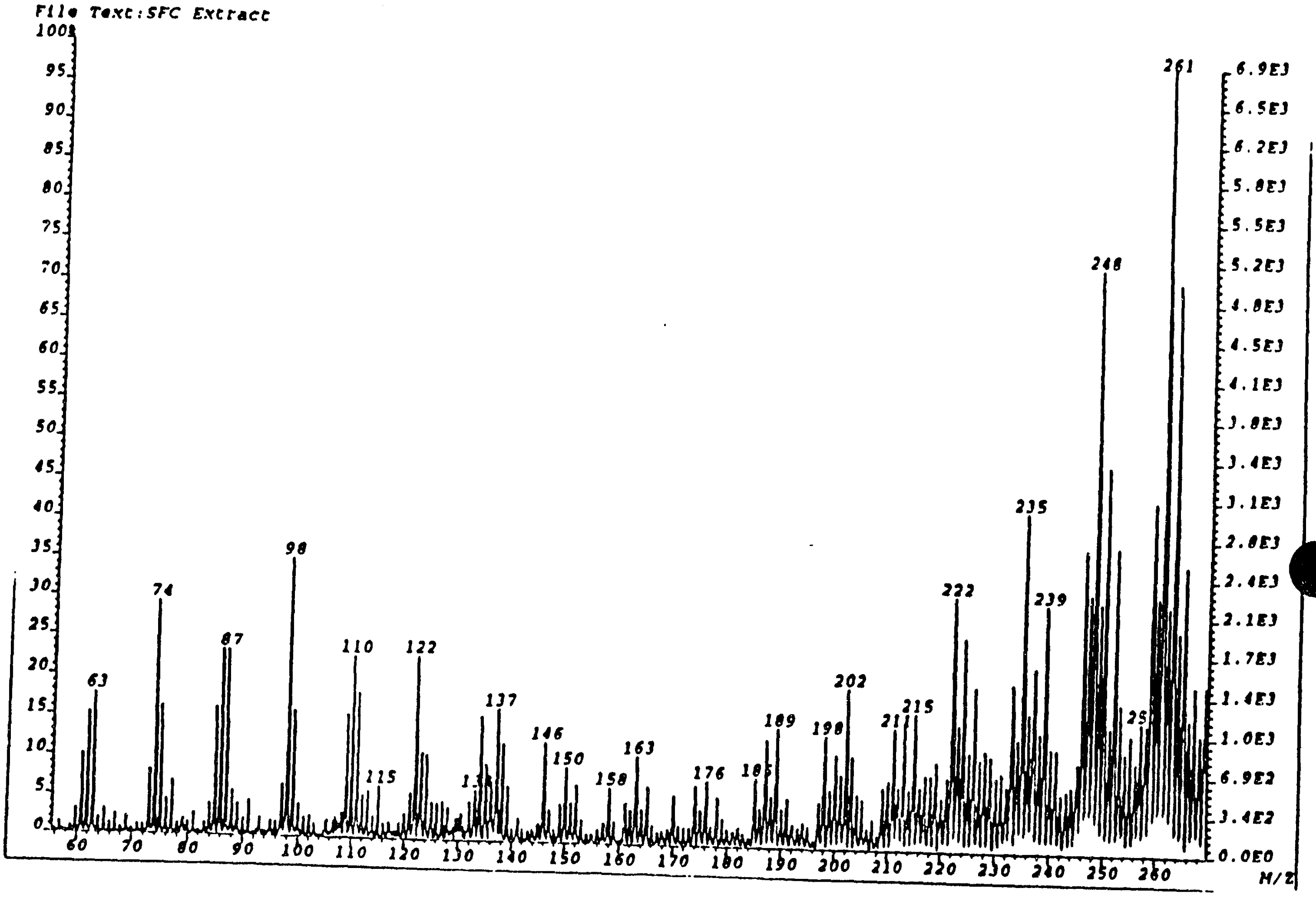


Figure 32. Supercritical Fluid Chromatography of Sample 17

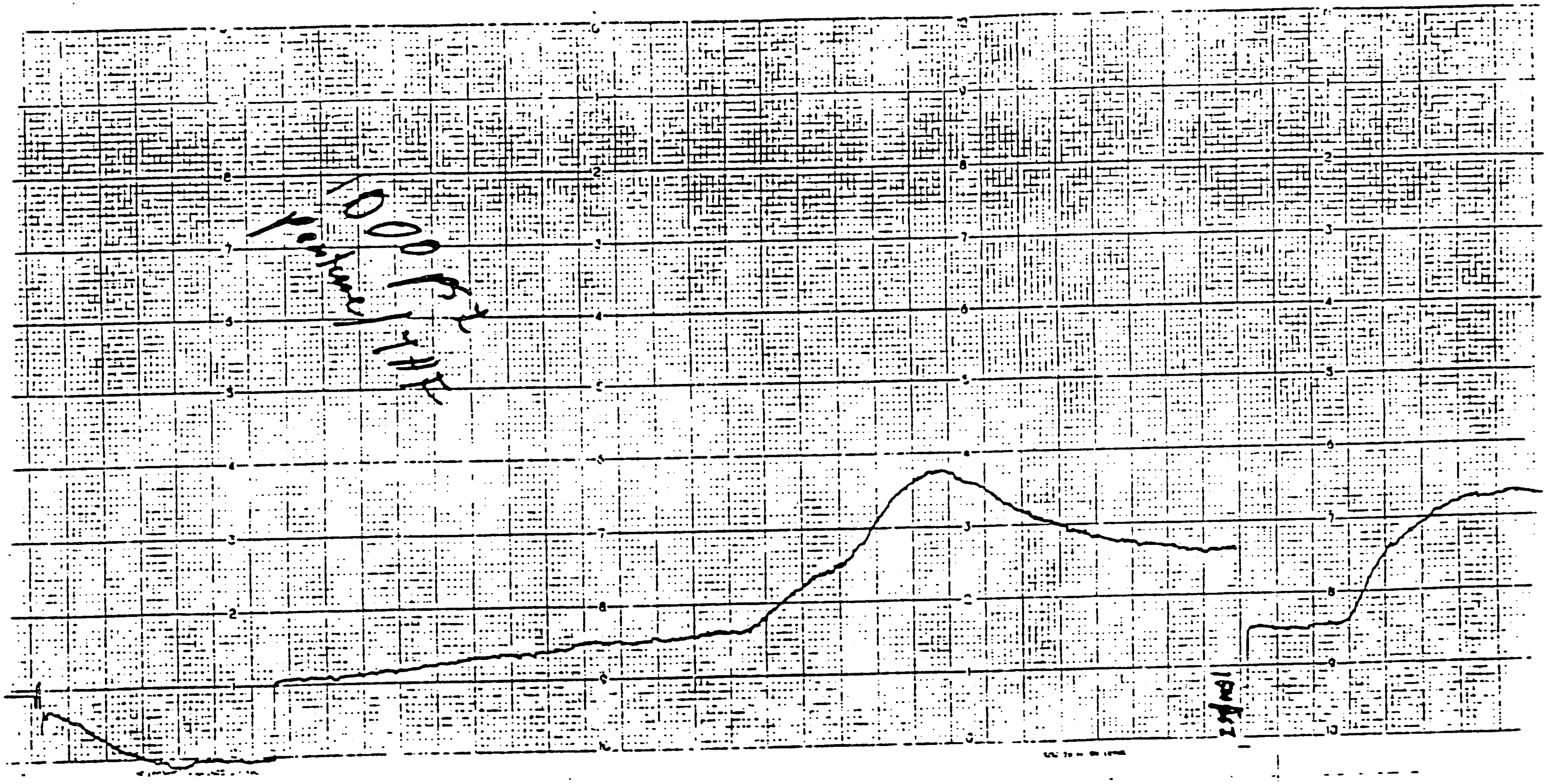
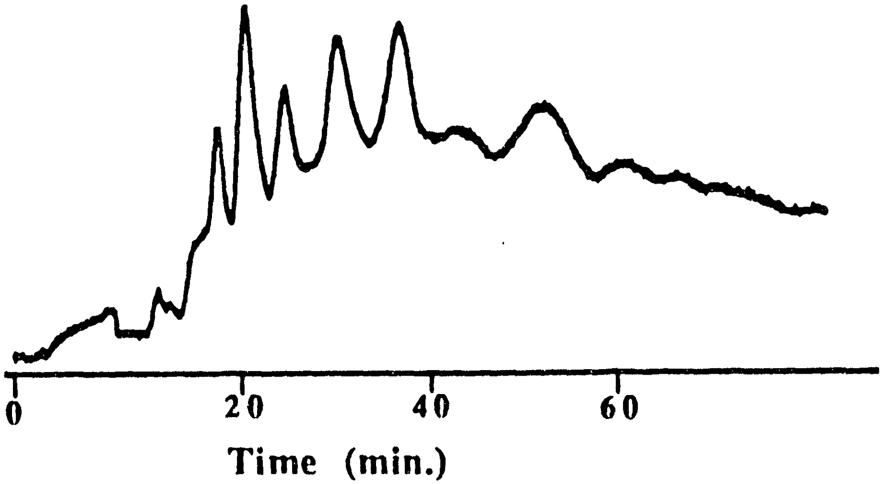


Figure 33. Microcolumn HPLC Chromatogram of the Pentane SFE, Hexane/Alumina, Hexane/Silica Fraction from Sample 17



Microbore HPLC chromatogram of the pentane SFE, hexane/alumina, hexane/silica fraction. Fluorescence detection with excitation set at 246 nm and emission monitored at 370 nm. Elution solvent is 16.7 % acetic acid, 16.7 % THF and 66.6 % acetonitrile. Flow rate = 50 µl/min.

Figure 34. Mass Spectrum of m/z 276 from Sample 22

```
File:            C:\CHEMPC\DATA\JIM15.D
Operator:        W ROBINS
Date Acquired:   31 Mar 92    1:15 pm
Method File:     JIMASS1.M
Sample Name:                       22. HEXANE AL2O3,FLUOROSIL, SIO2
Misc Info:                         250 MICRON SE54
ALS vial:        1
```

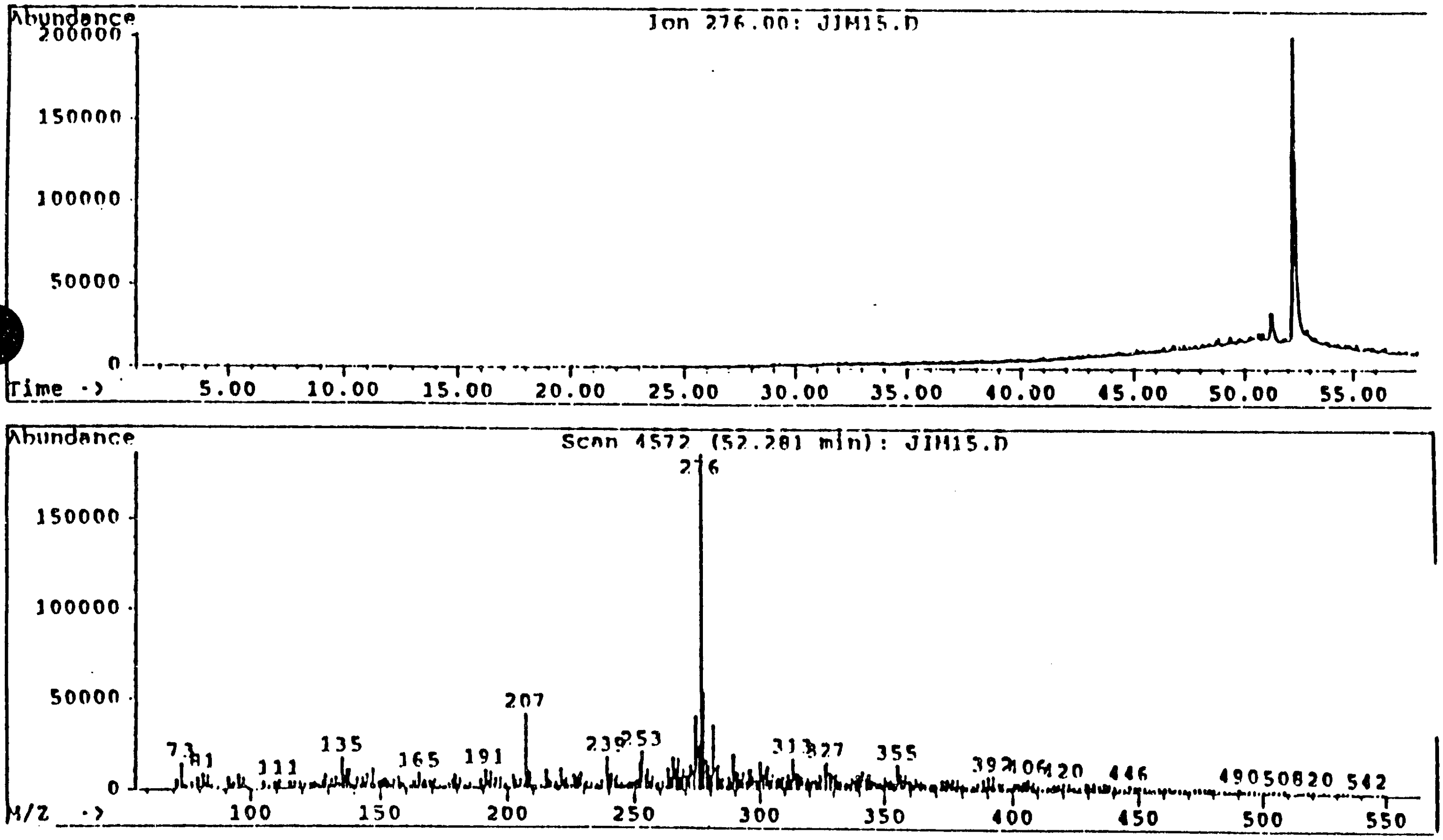


Figure 35. Mass Spectrum of m/z 242 from Sample 22

```
File:            C:\CHEMPC\DATA\JIM15.D
Operator:        W ROBINS
Date Acquired:   31 Mar 92    1:15 pm
Method File:     JIMASS1.M
Sample Name:                       22, HEXANE AL2O3,FLUOROSIL, SIO2
Misc Info:                         250 MICRON SE54
ALS vial:        1
```

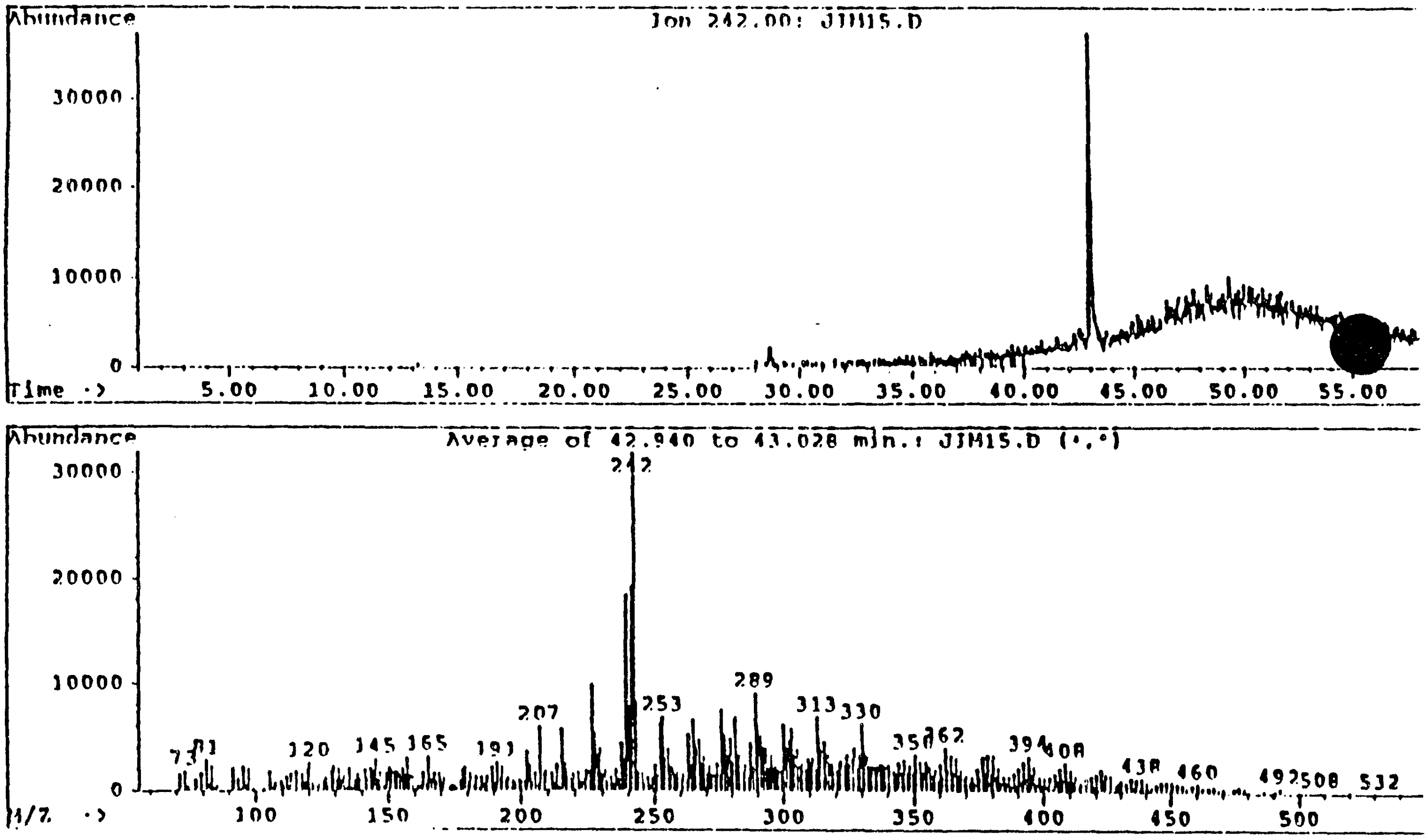


Figure 36. Mass Spectrum of m/z 300 from Sample 22

```
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Operator:       W ROBINS
Date Acquired:  31 Mar 92    1:15 pm
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Misc Info:                            250 MICRON SE54
ALS vial:       1
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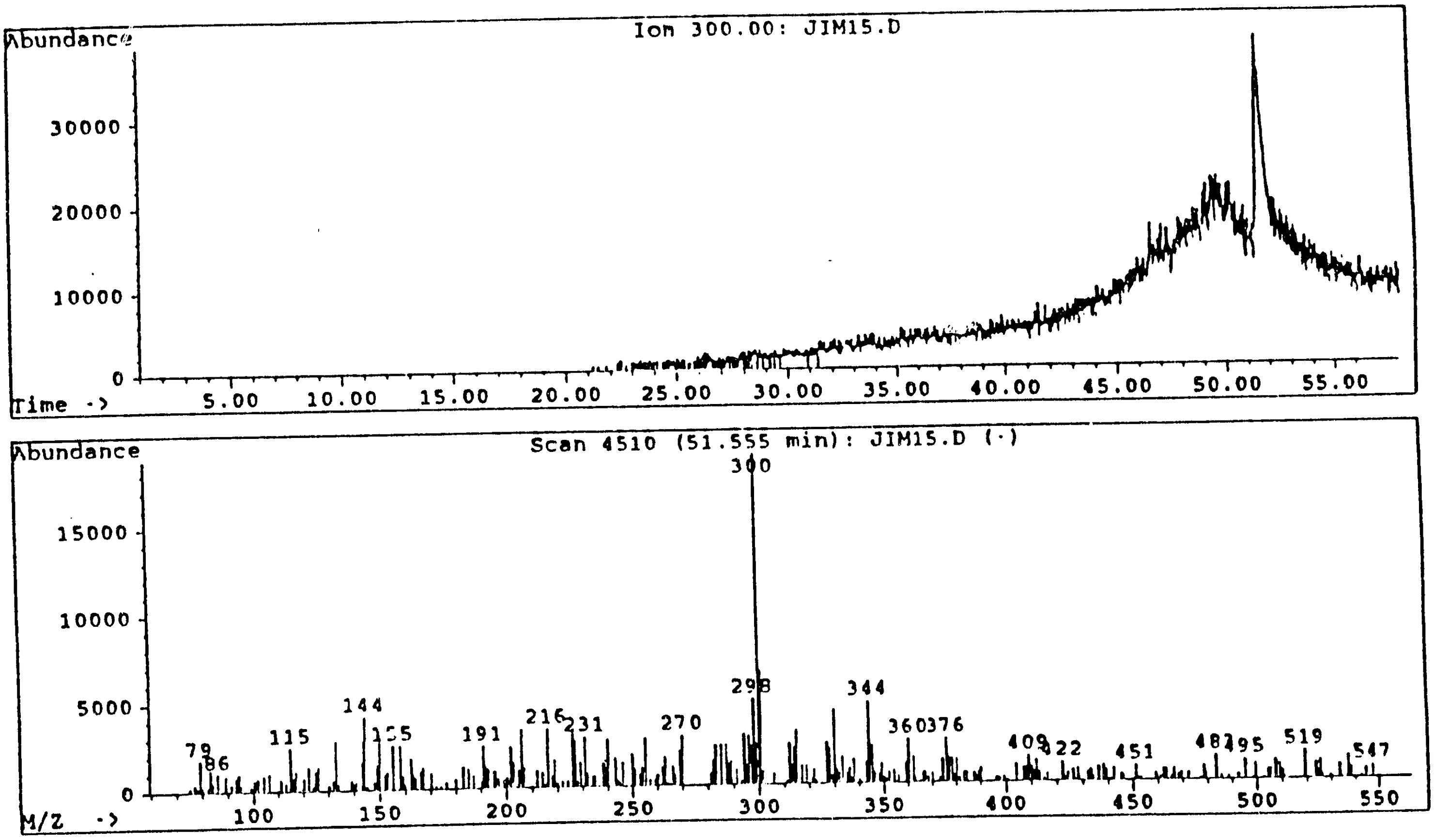


Figure 37. Total Ion Chromatogram of Supercritical Fluid Propane/Mass Spectrometry of Sample 17

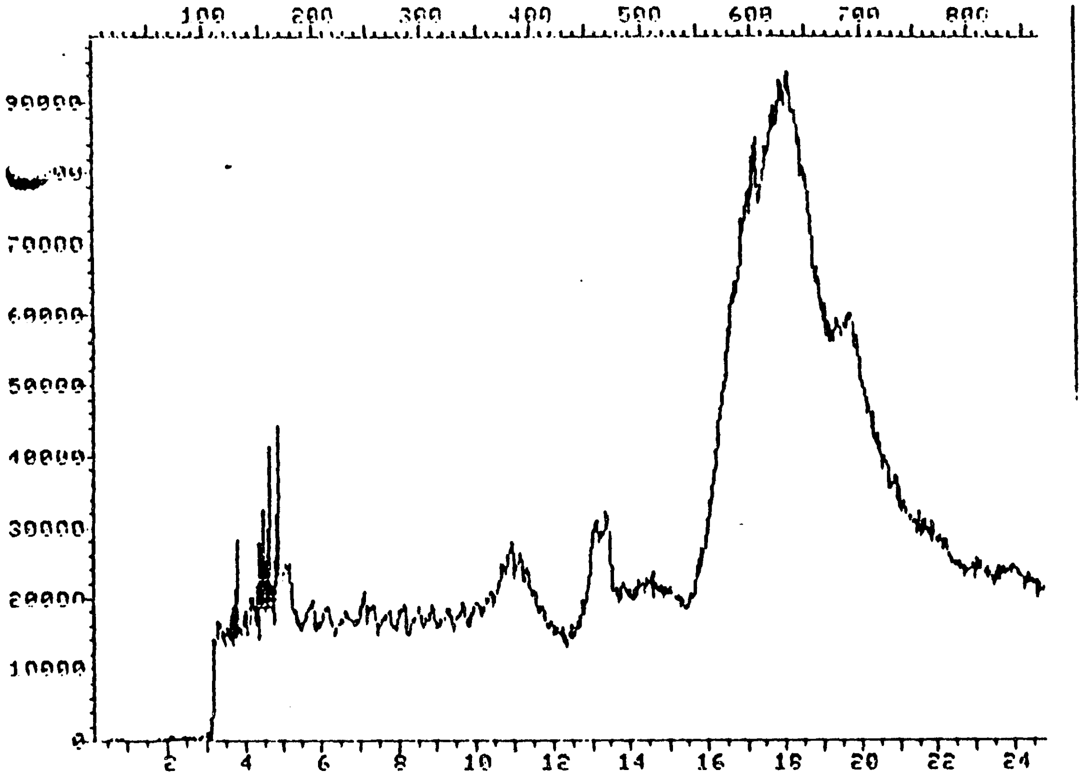
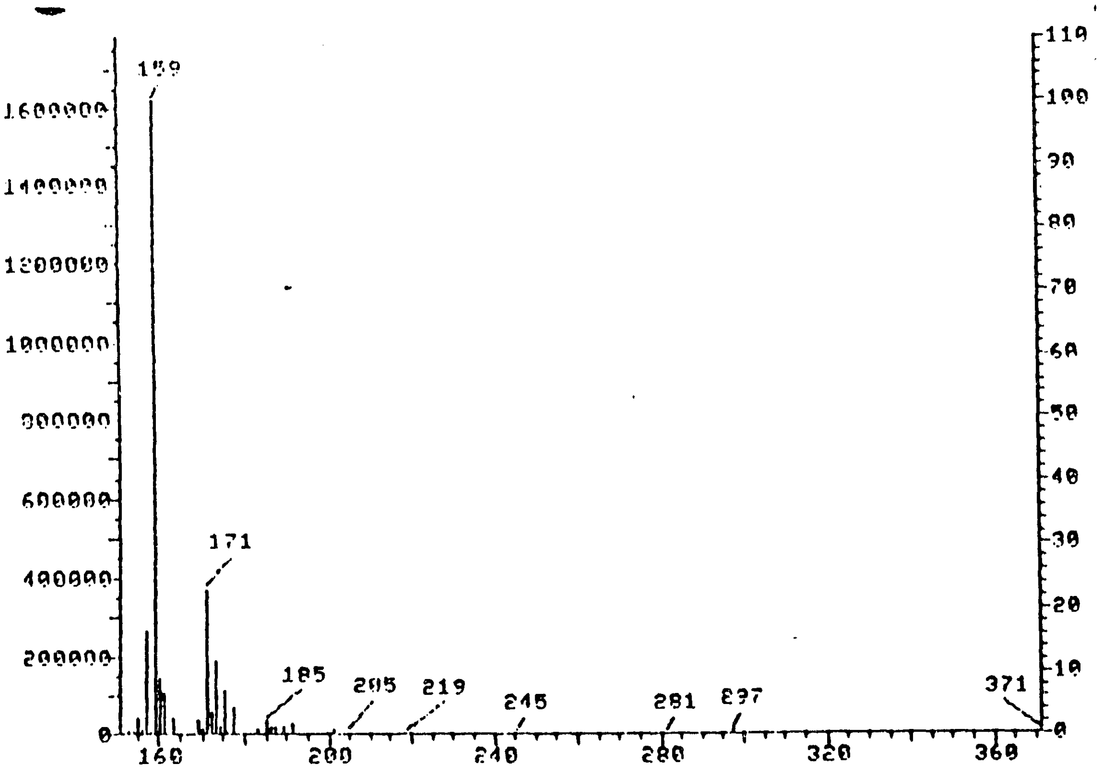


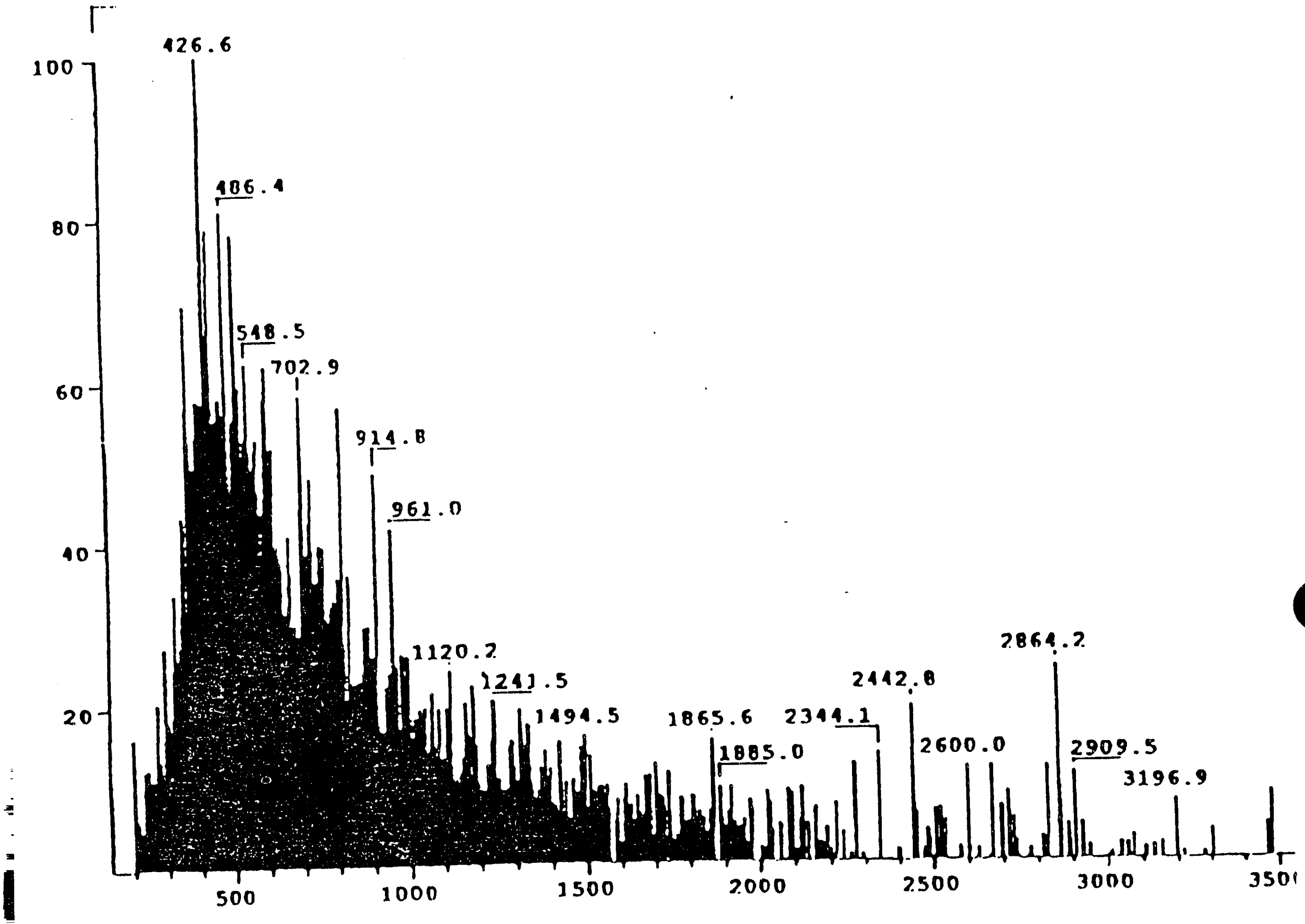
Figure 38. Mass Spectrum of SFC/MS (Propane) of Sample 17



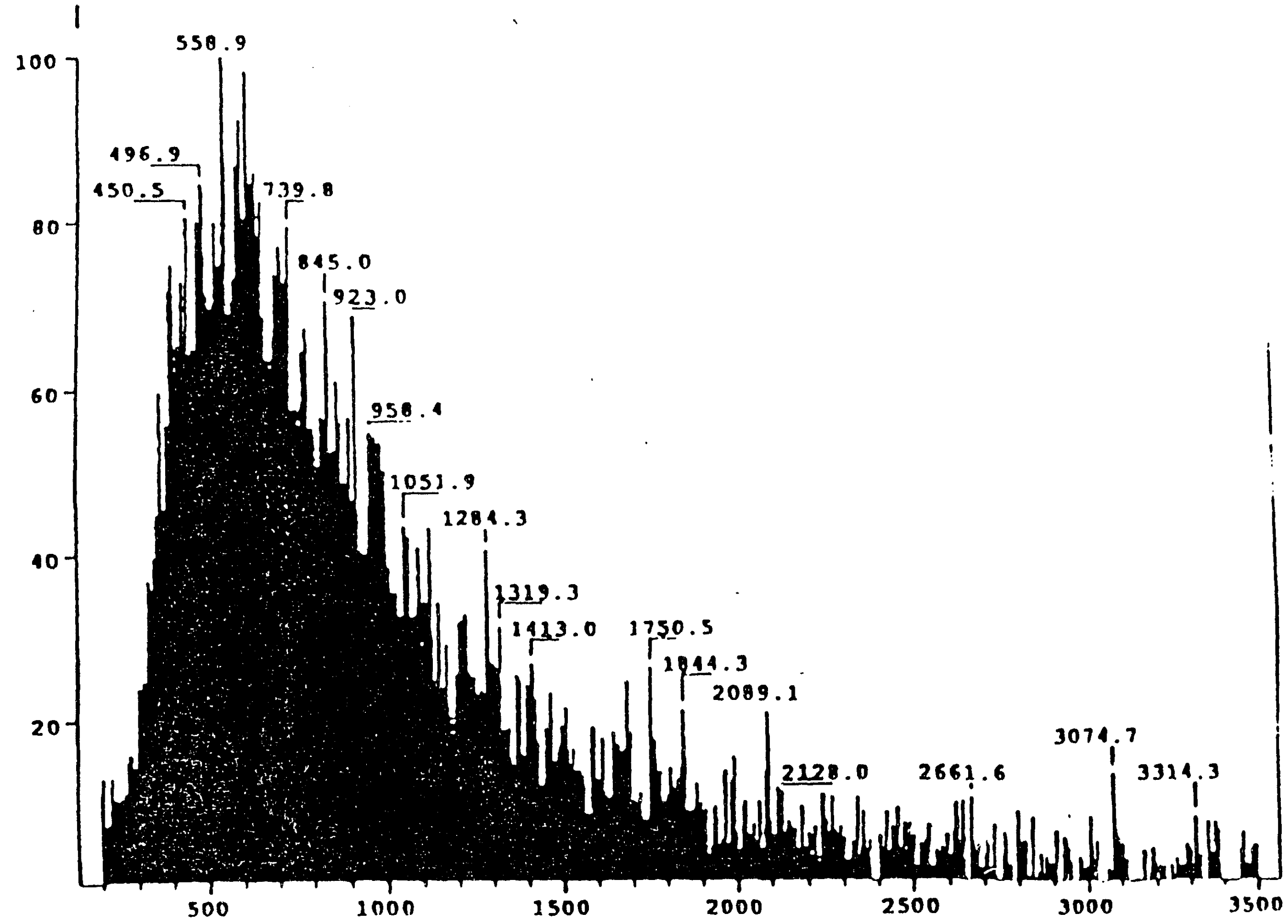
APPENDIX A.

FDMS SPECTRA FOR 12 SAMPLES

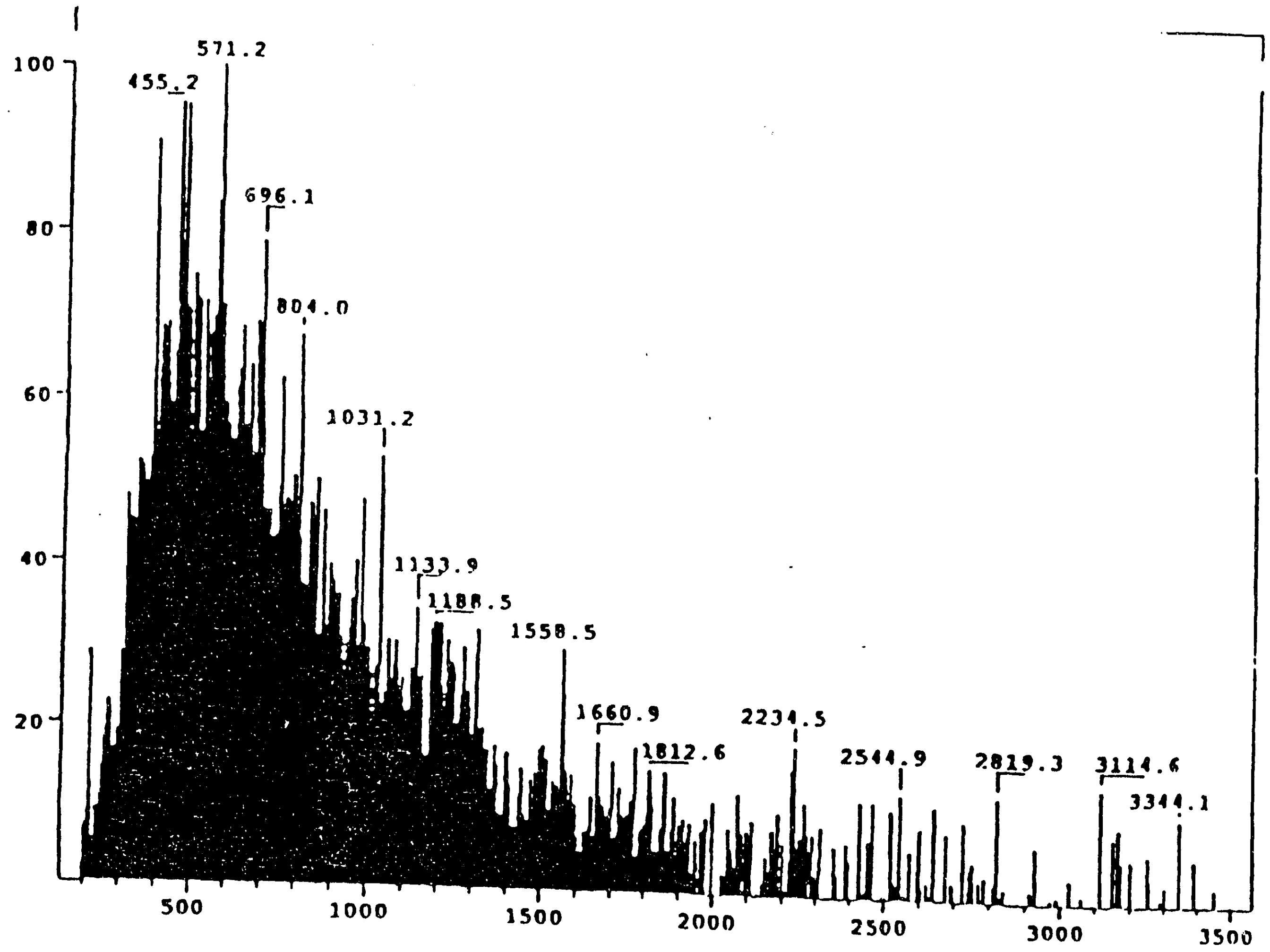
Field Desorption Spectrum of Illinois No.6, W; run 250; T/C, Product Oil Resid



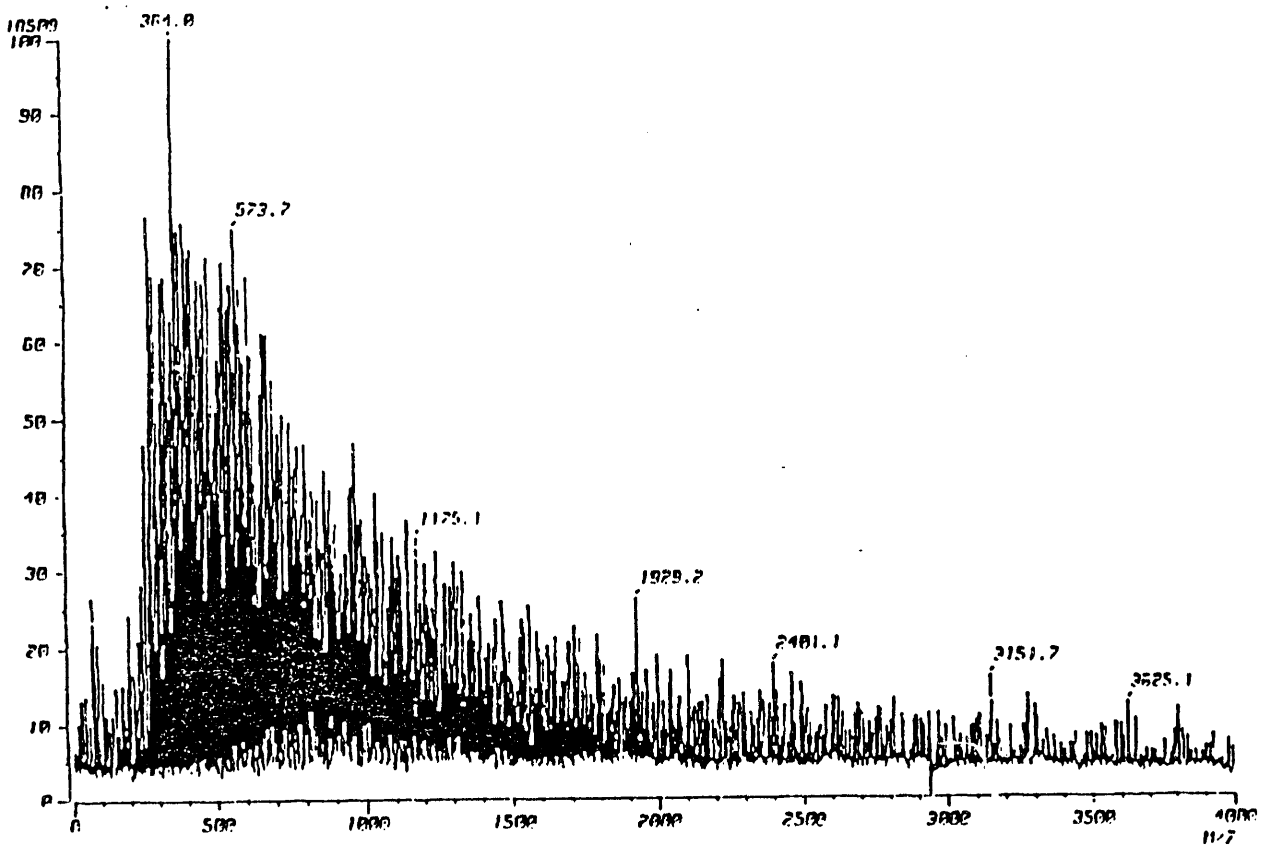
Field Desorption Spectrum of Illinois No.6, W; run 250; T/C, Recycle Oil Resid



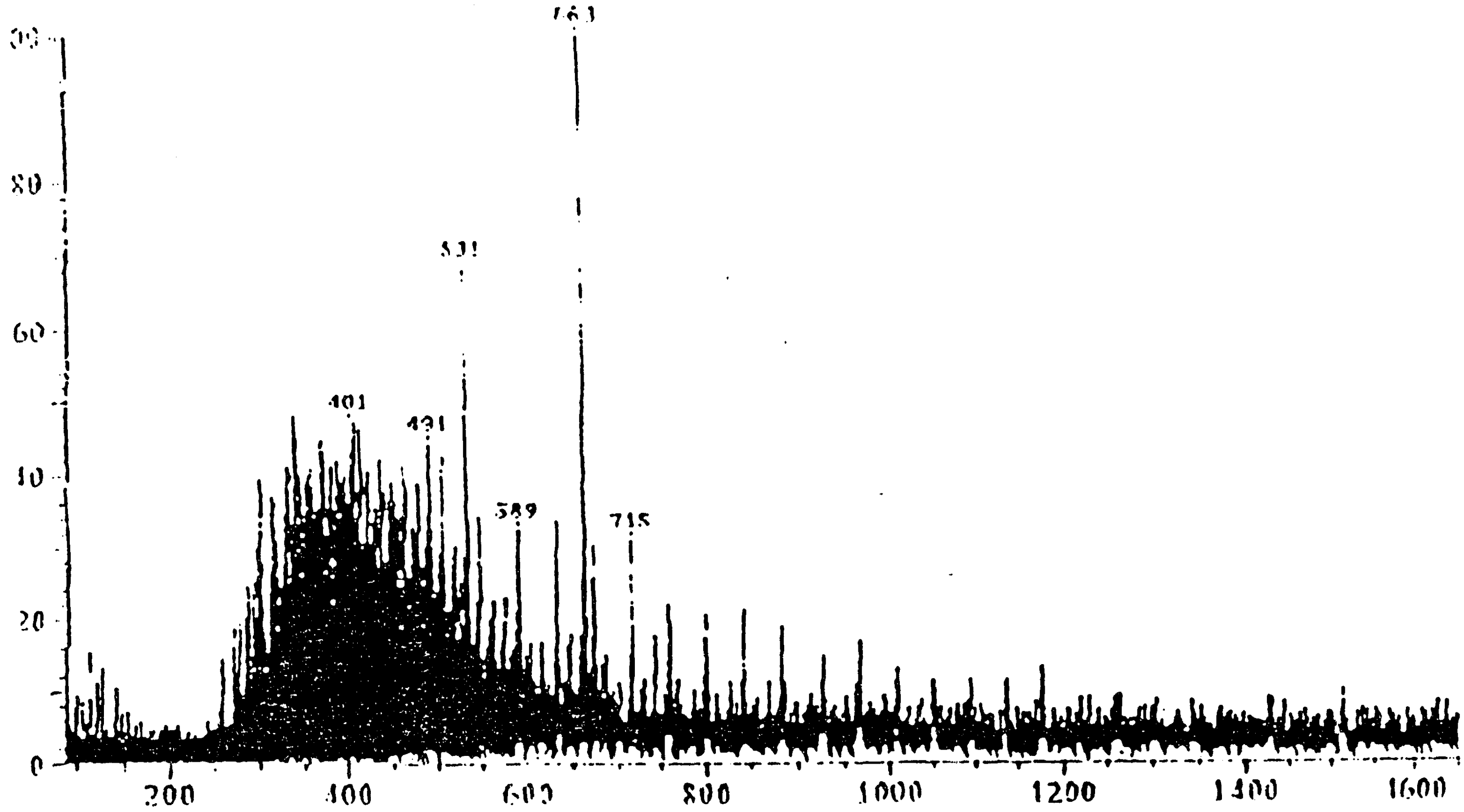
Field Desorption Spectrum of Illinois No.6, W; run 250; T/C, Interstage Oil Resid



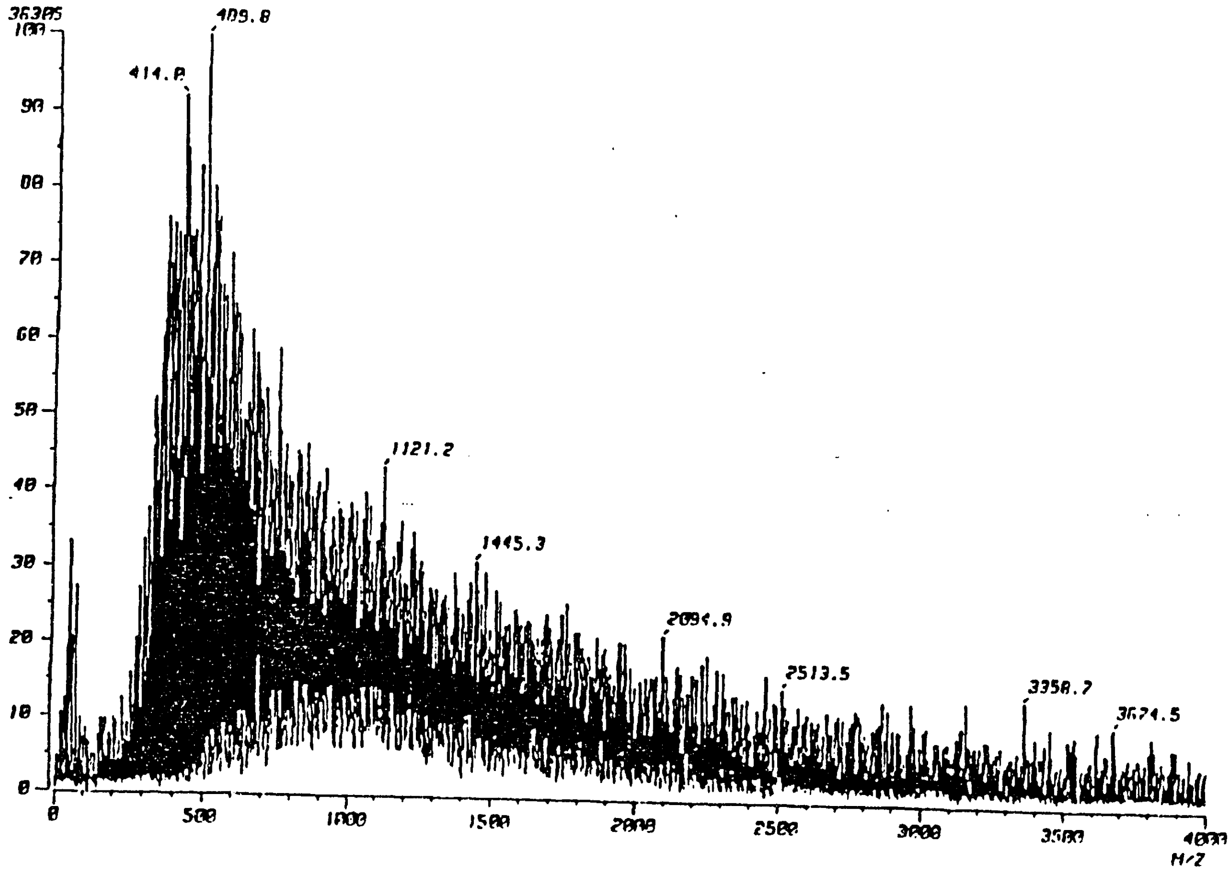
Field Desorption Spectrum of Illinois No.6, W; Run 257; C/C, Product Oil Resid



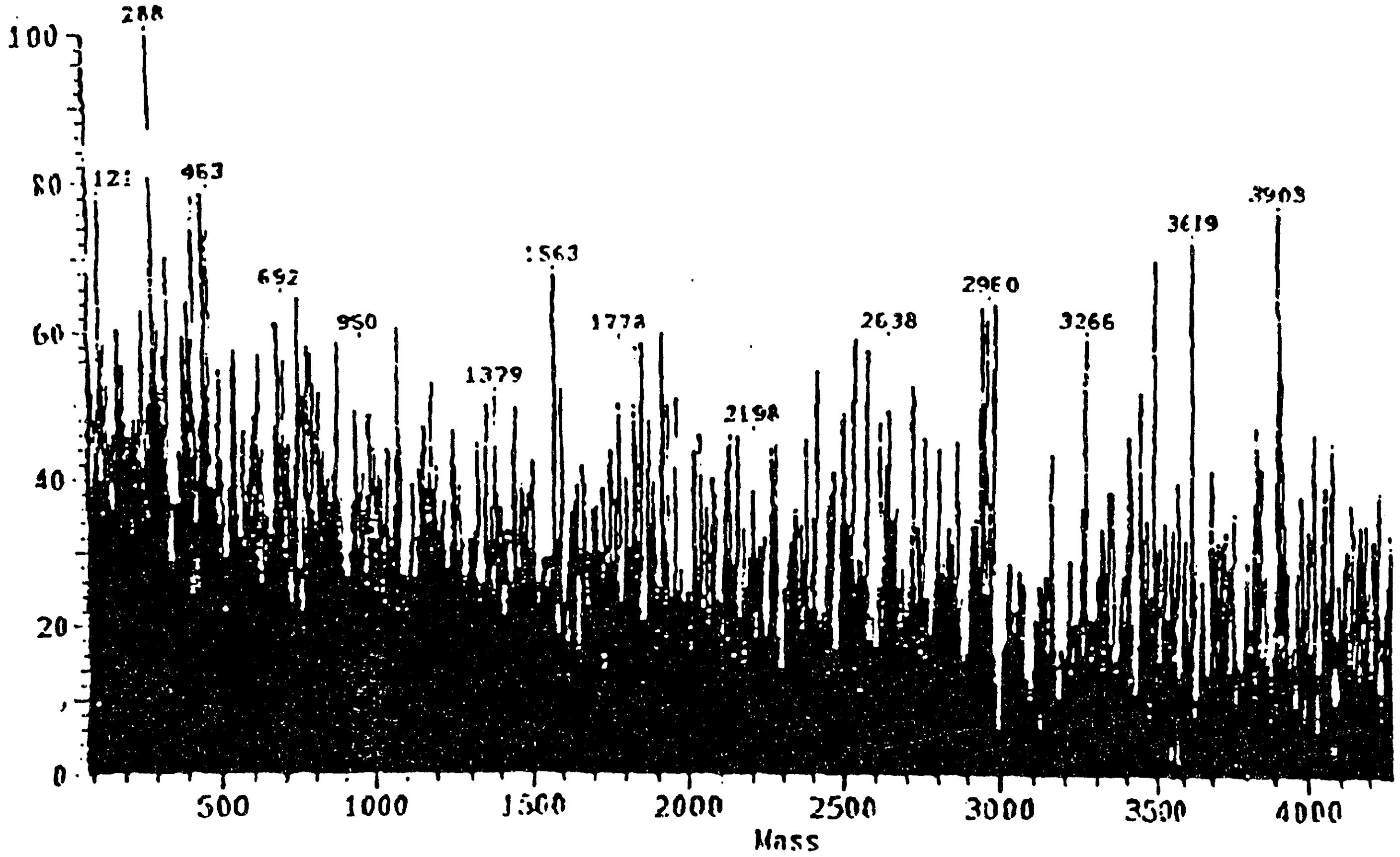
Field Desorption Spectrum of Illinois No 6, W; run 257; C/C, Recyle Oil Resid



Field Desorption Spectrum of Illinois No.6, W; Run 257; C/C, Interstage Oil Resid

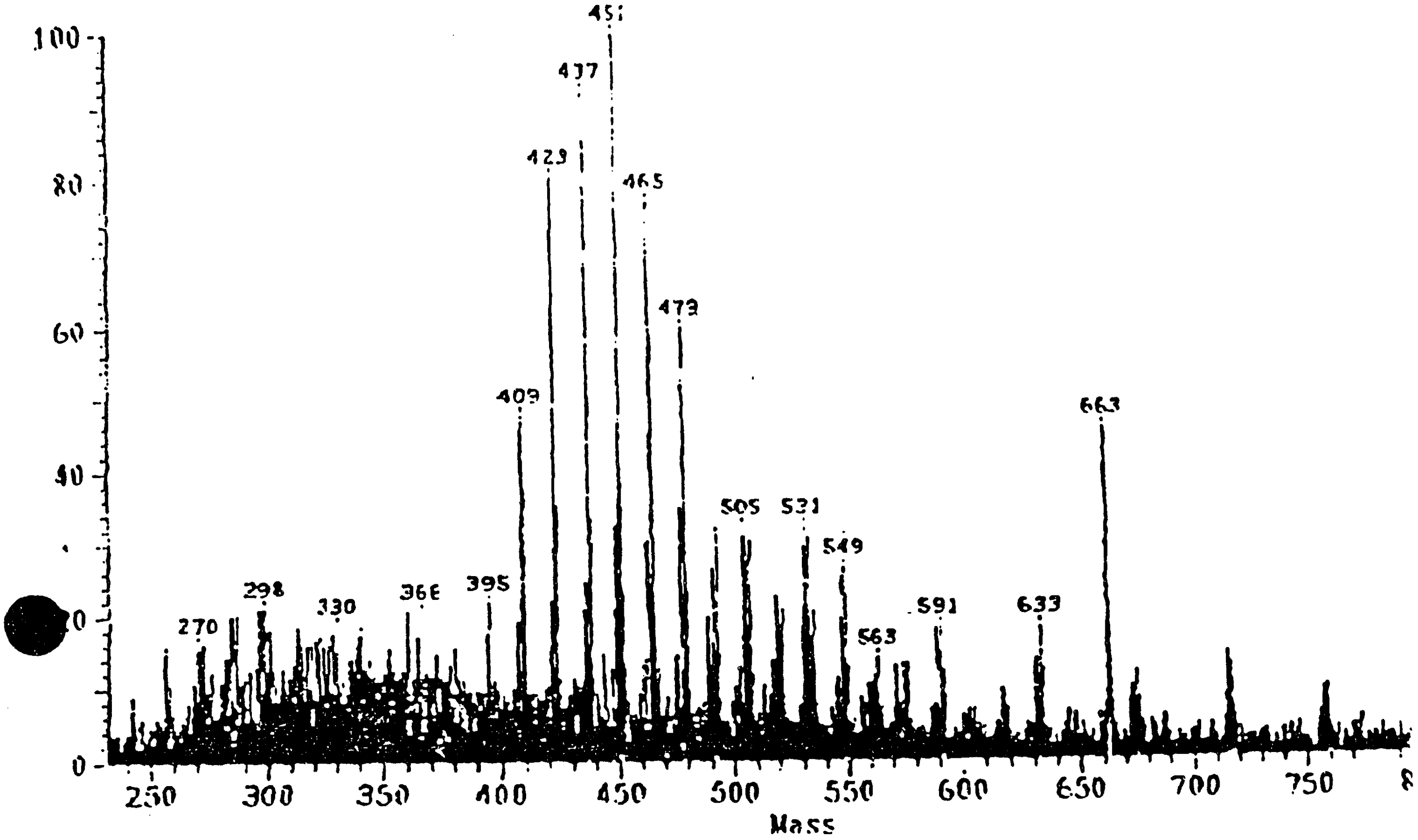


Field Desorption Spectrum of Wyodak, W; Run 251-II; T/C; Product Oil Resid

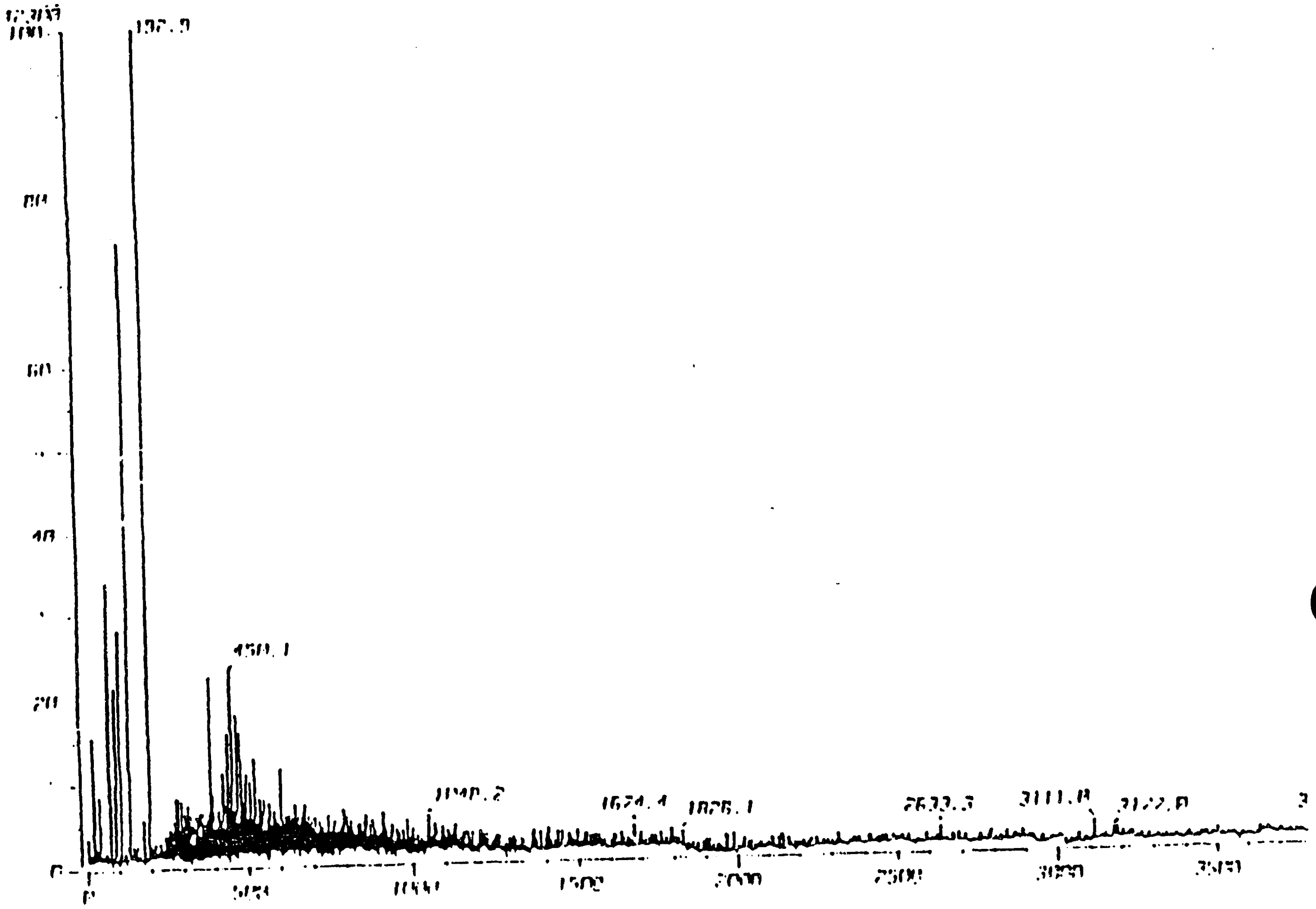


(11)

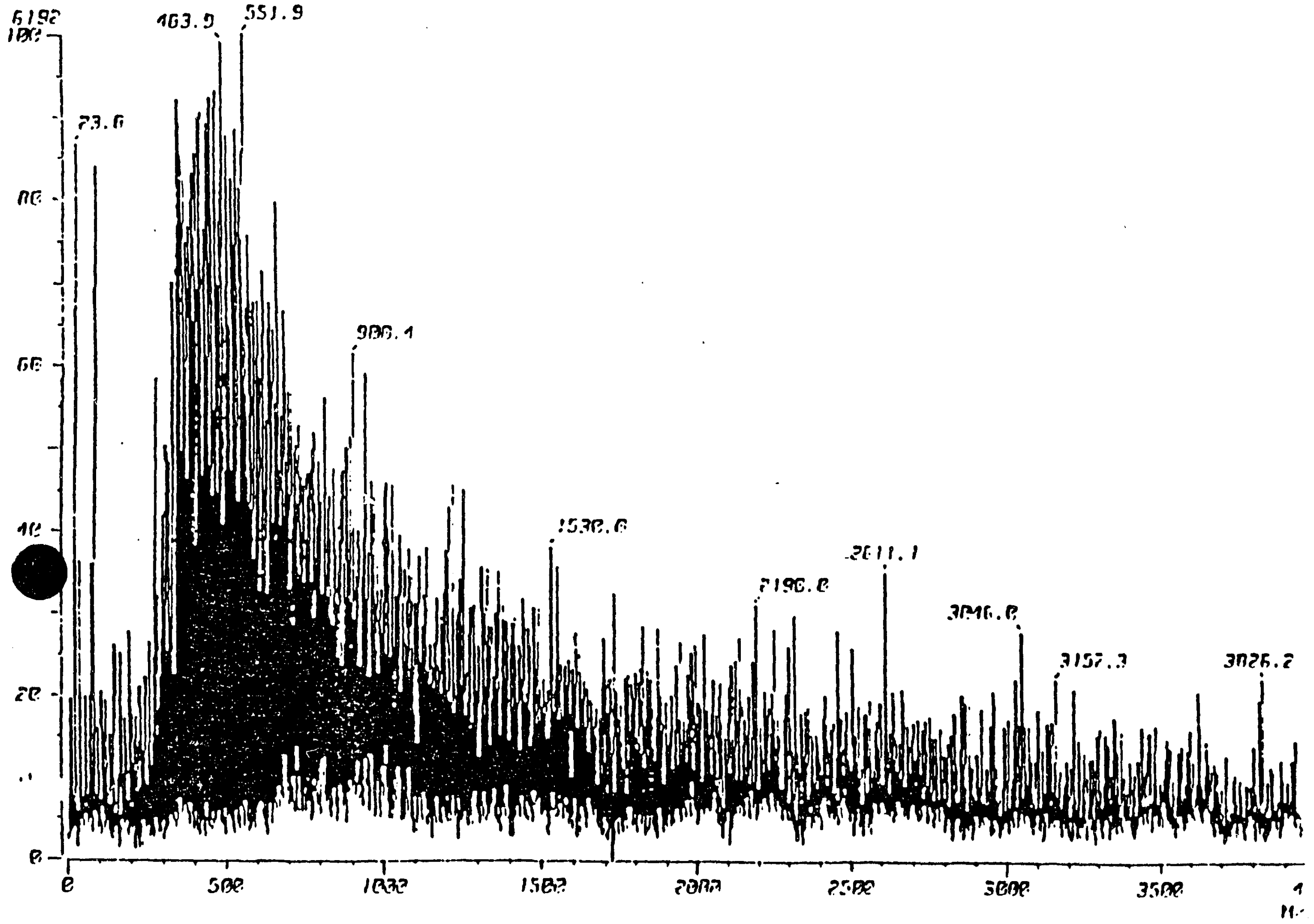
Field Desorption Spectrum of Wyodak, W; Run 251-II; T/C; Recycle Oil Resid



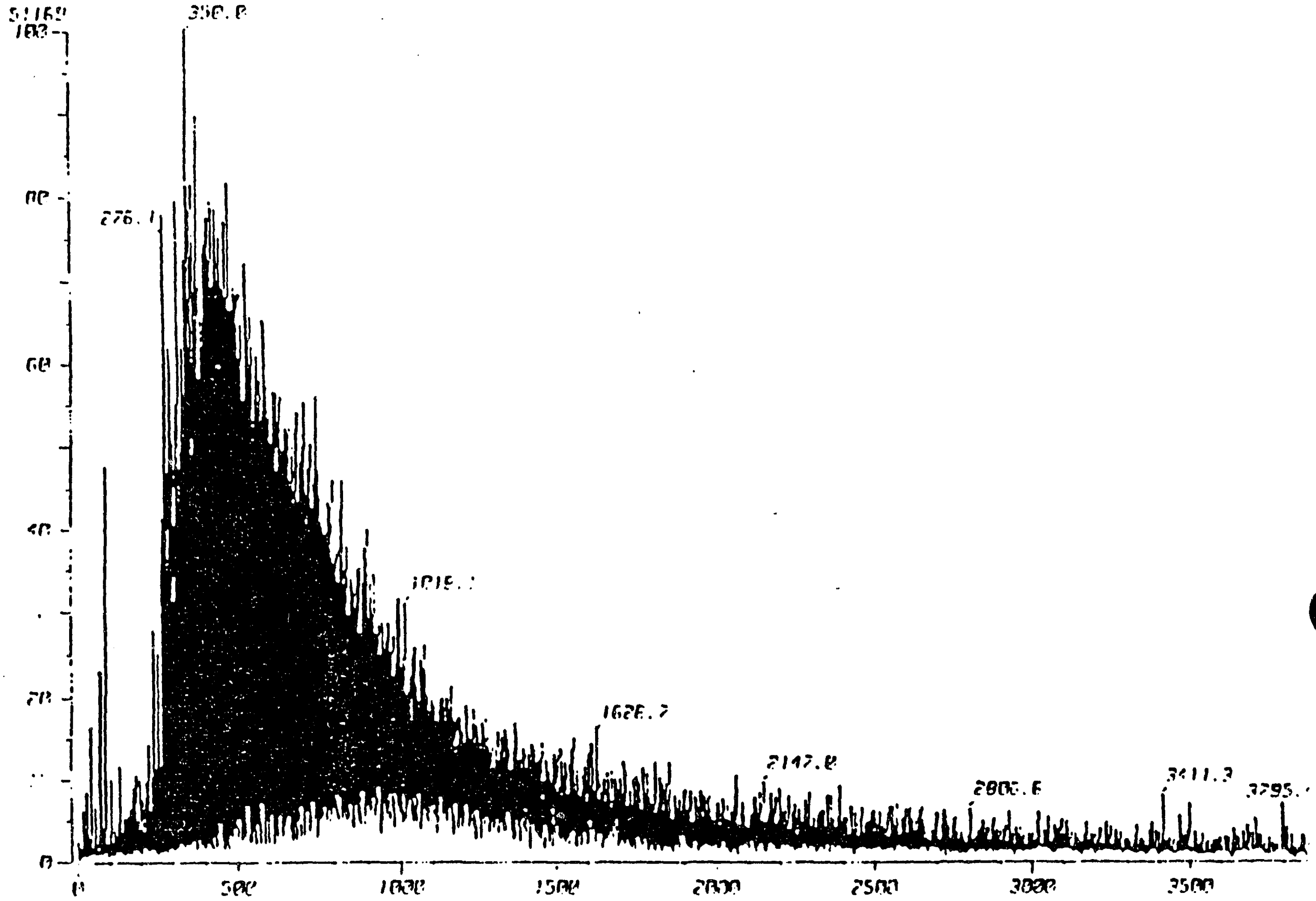
Field Desorption Spectrum of Wyodak, W; Run 251-II; T/C; Interstage Oil Resid



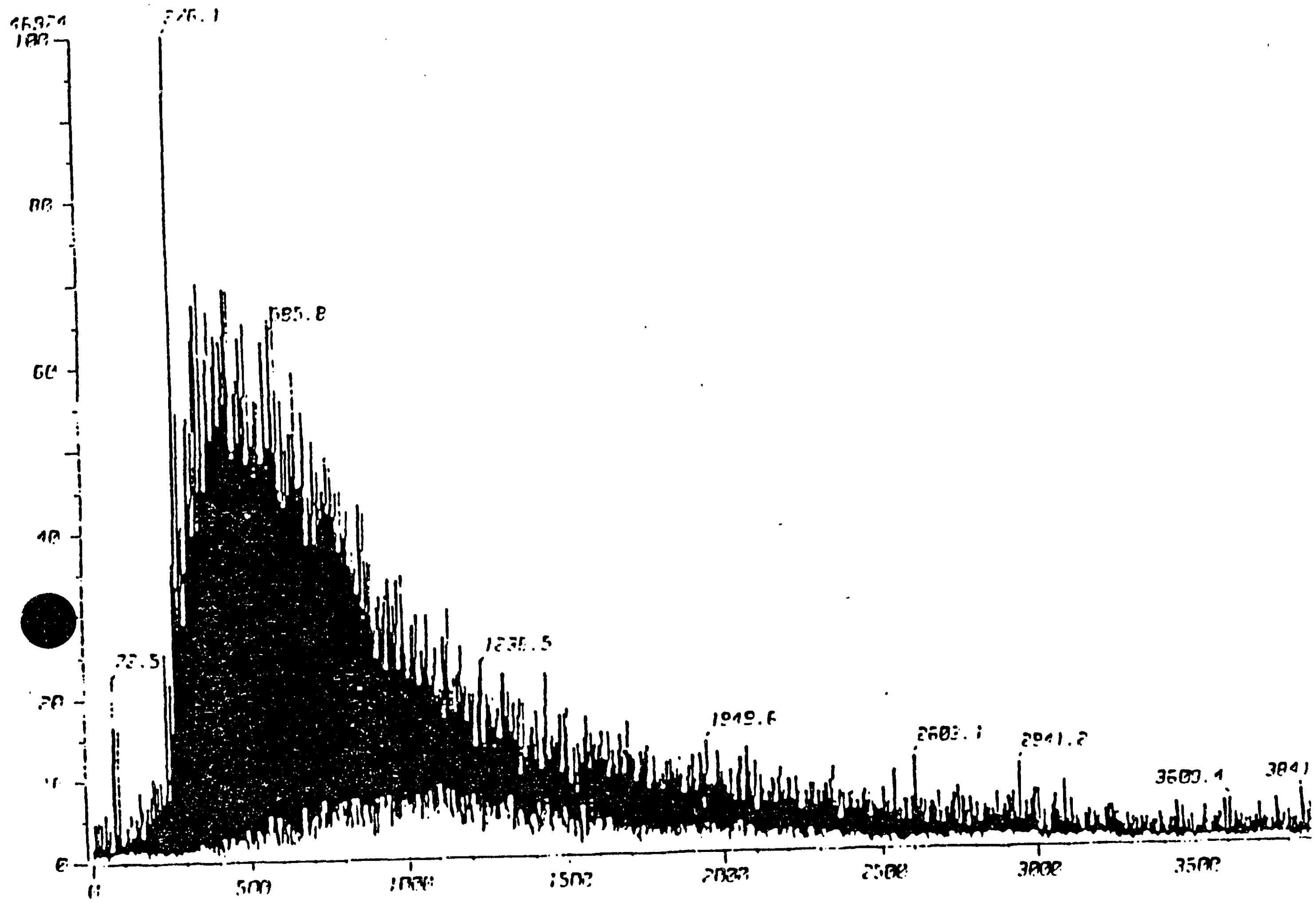
Field Desorption Spectrum Pittsburgh Seam, W; Run 259; C/C; Product Oil Resid



Field Desorption Spectrum Pittsburgh Seam, W; Run 259; C/C; Recycle Oil Resid

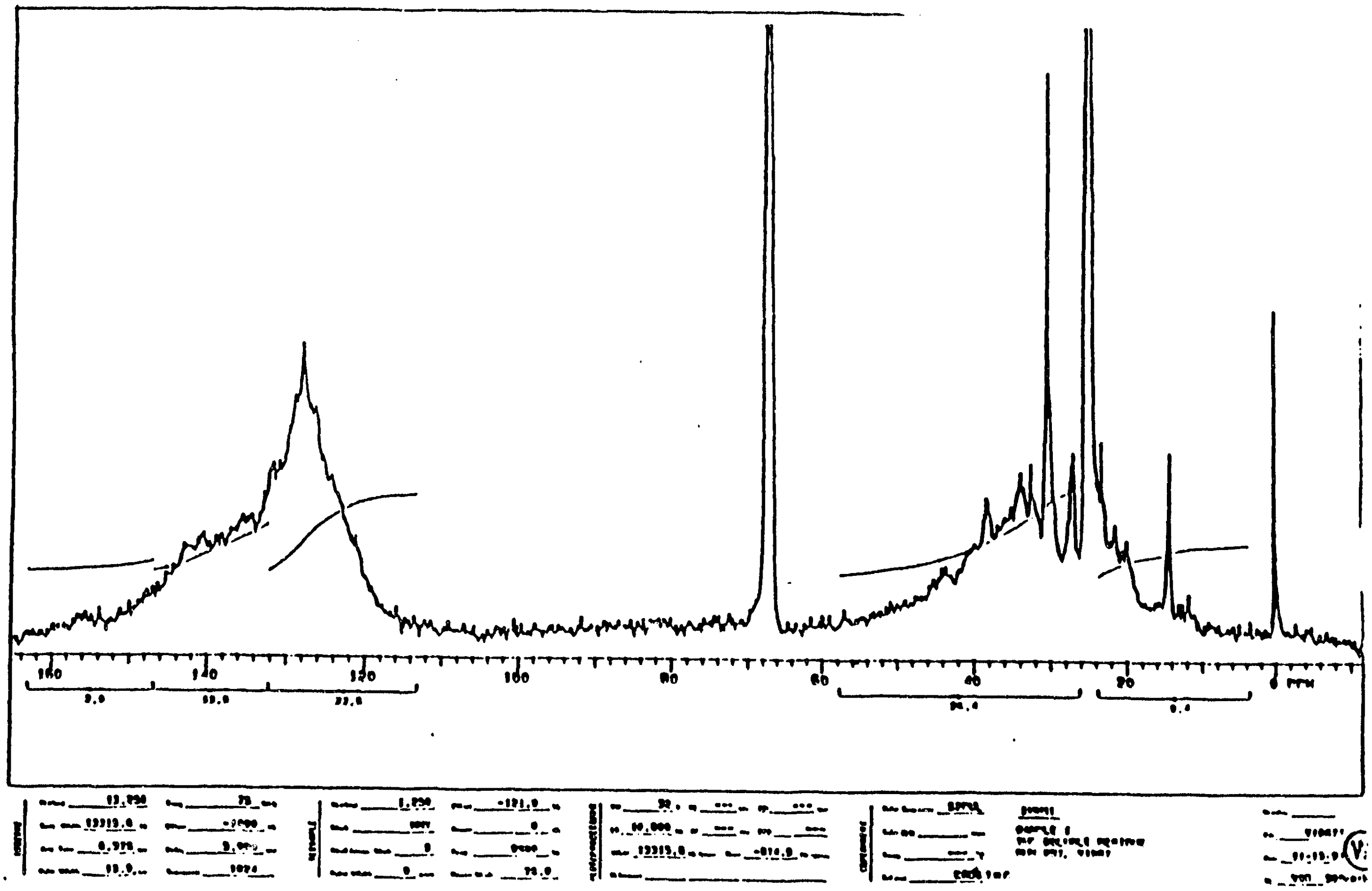


Field Desorption Spectrum Pittsburgh Seam, W; Run 259; C/C; Interstage Oil Resid

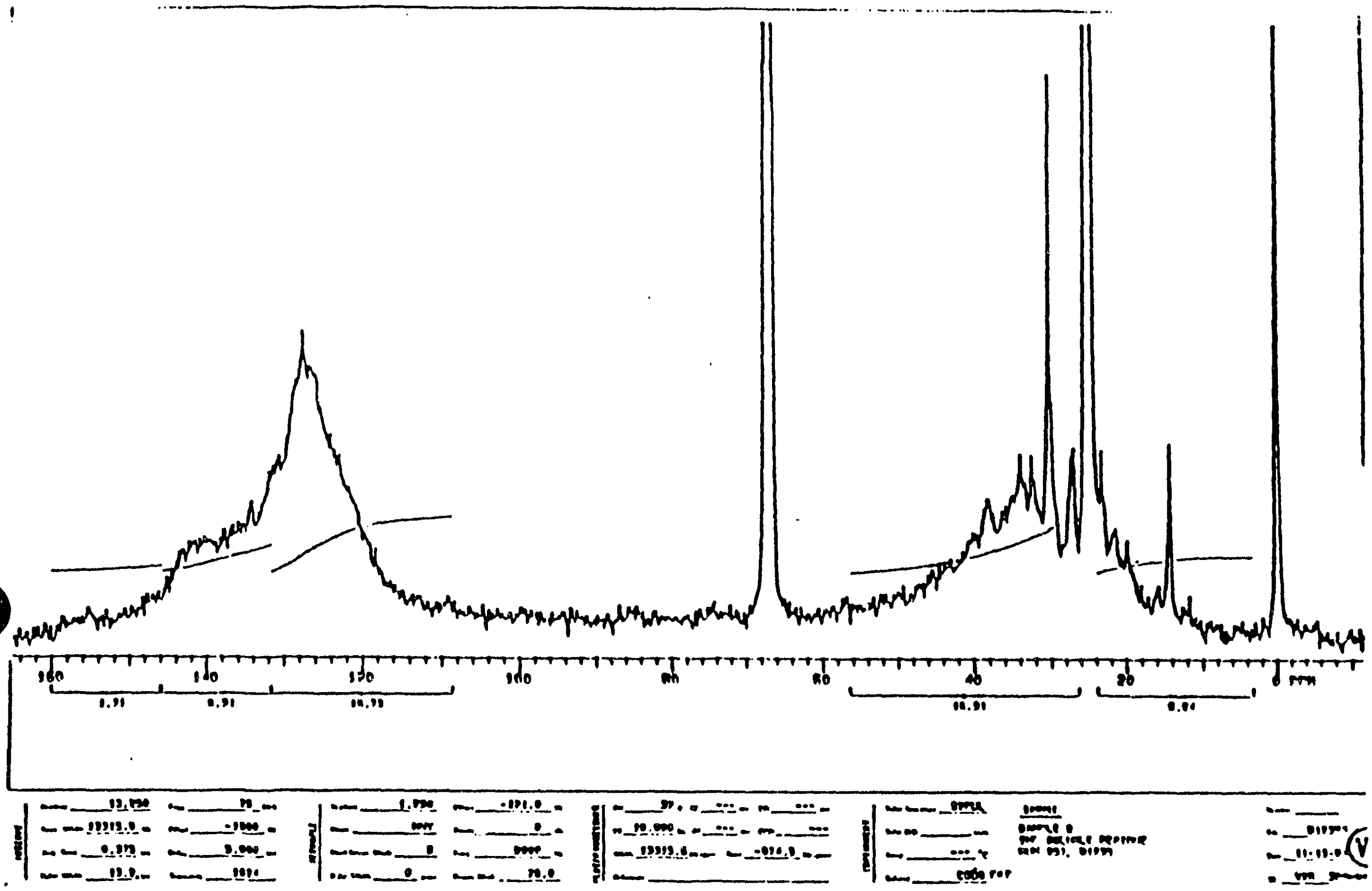


APPENDIX B.
TWO-DIMENSIONAL NMR DATA

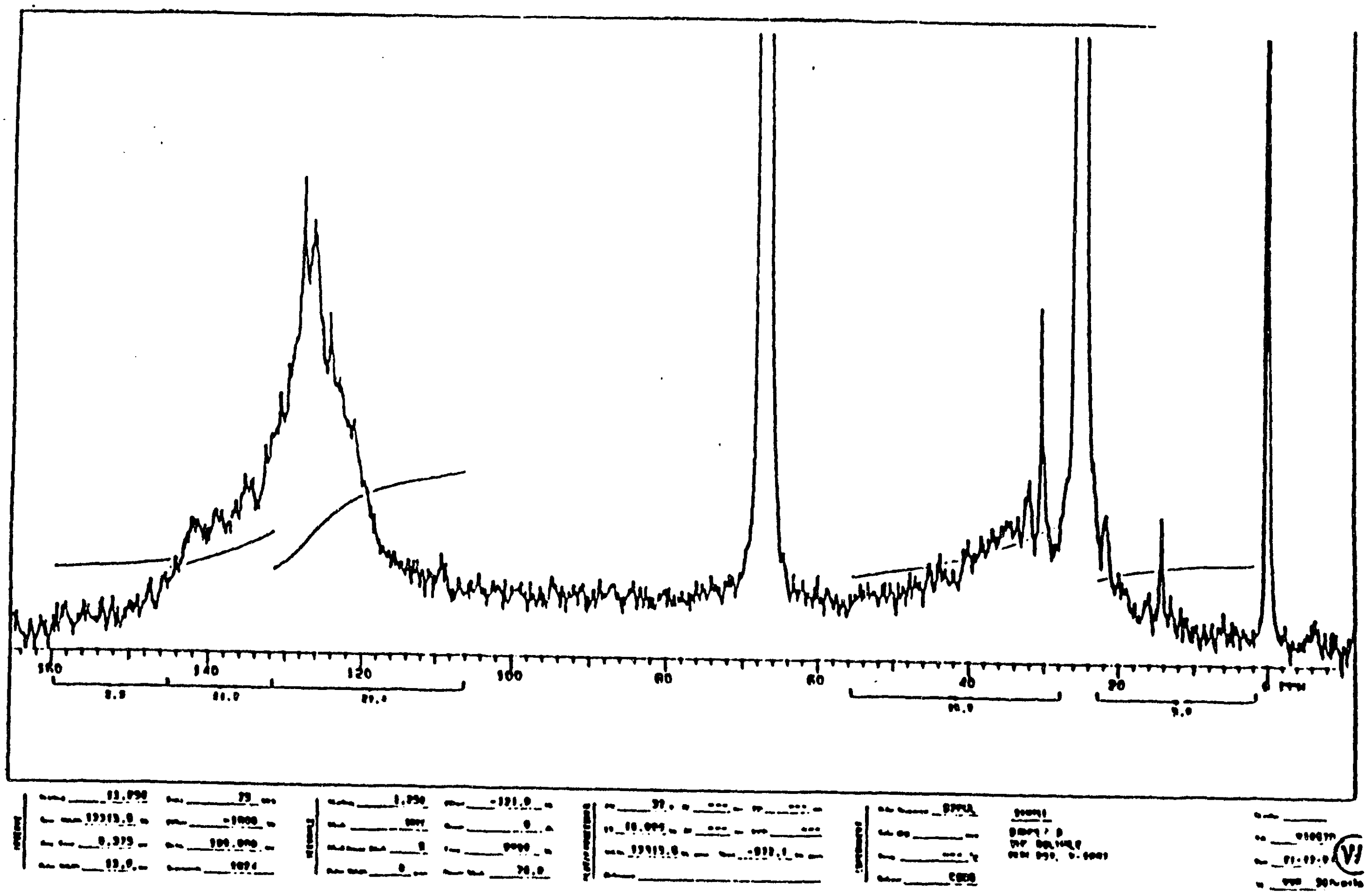
Quantitative ^{13}C NMR spectrum of sample 1, run 257, in d_8-THF.



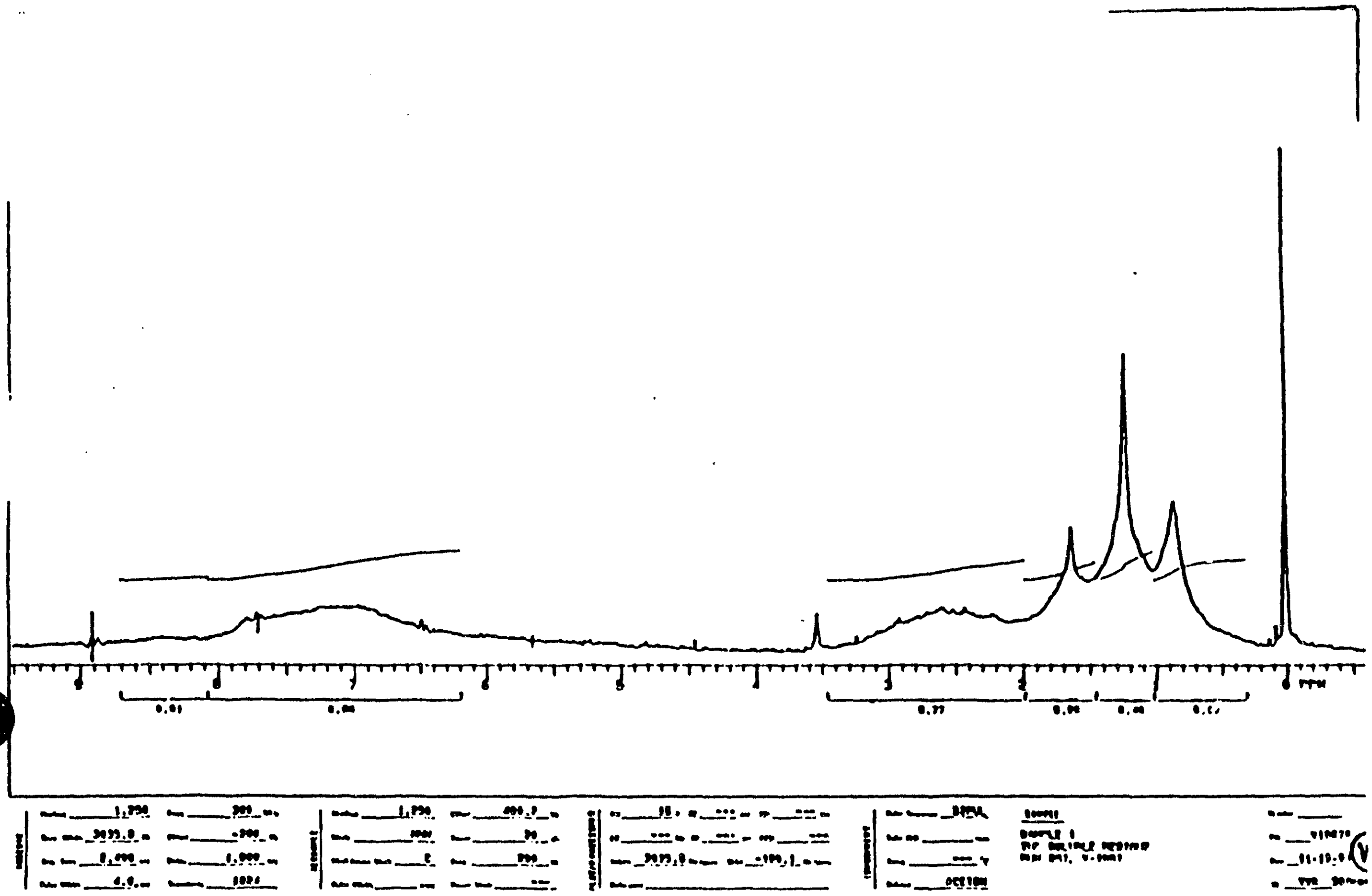
Quantitative ^{13}C NMR spectrum of sample 2, Run 257, in d_8-THF.



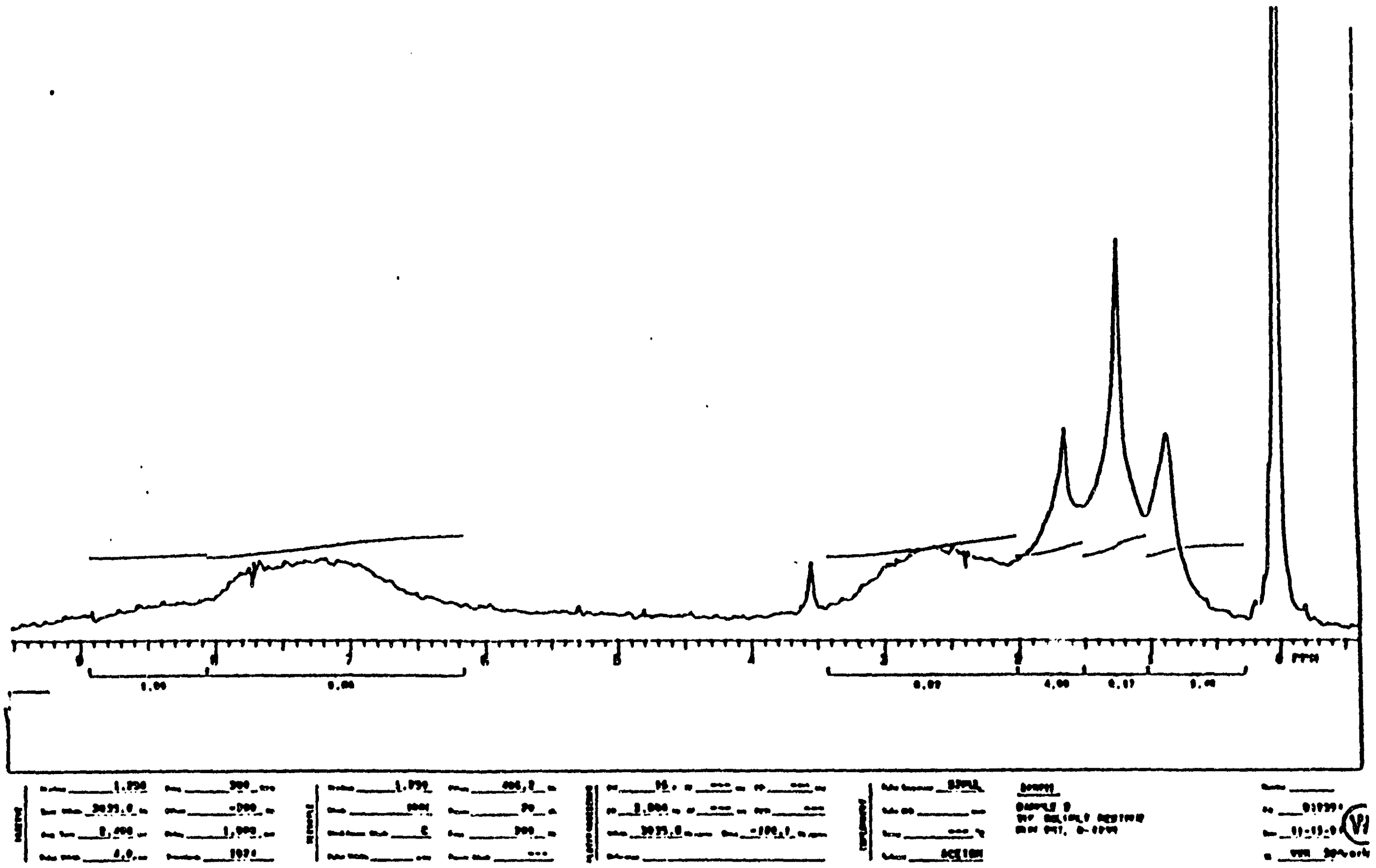
Quantitative ^{13}C NMR spectrum of sample 3, run 259, in d_8-THF.



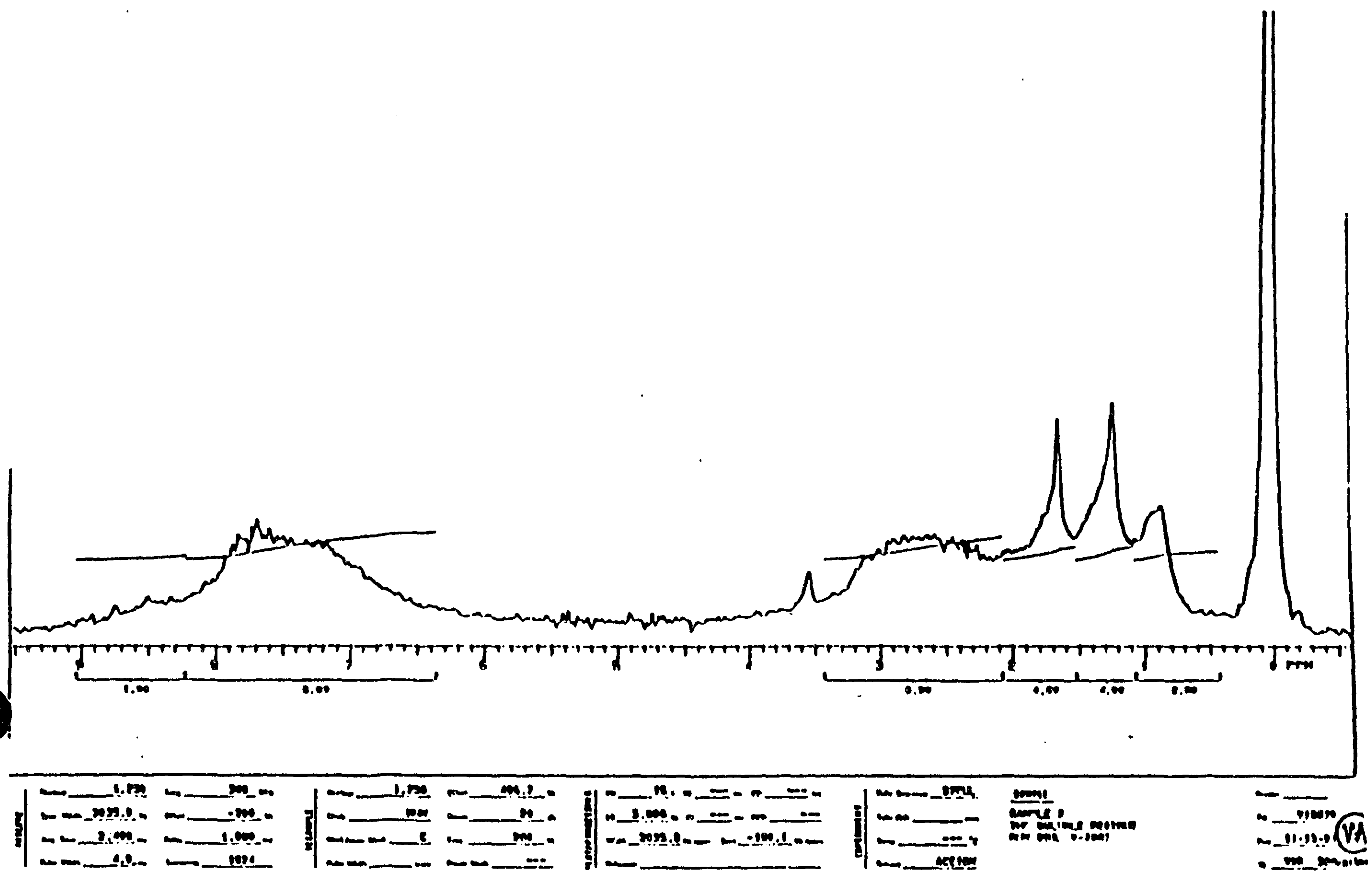
Proton NMR spectrum of sample 1, run 257, in d_8-THF.



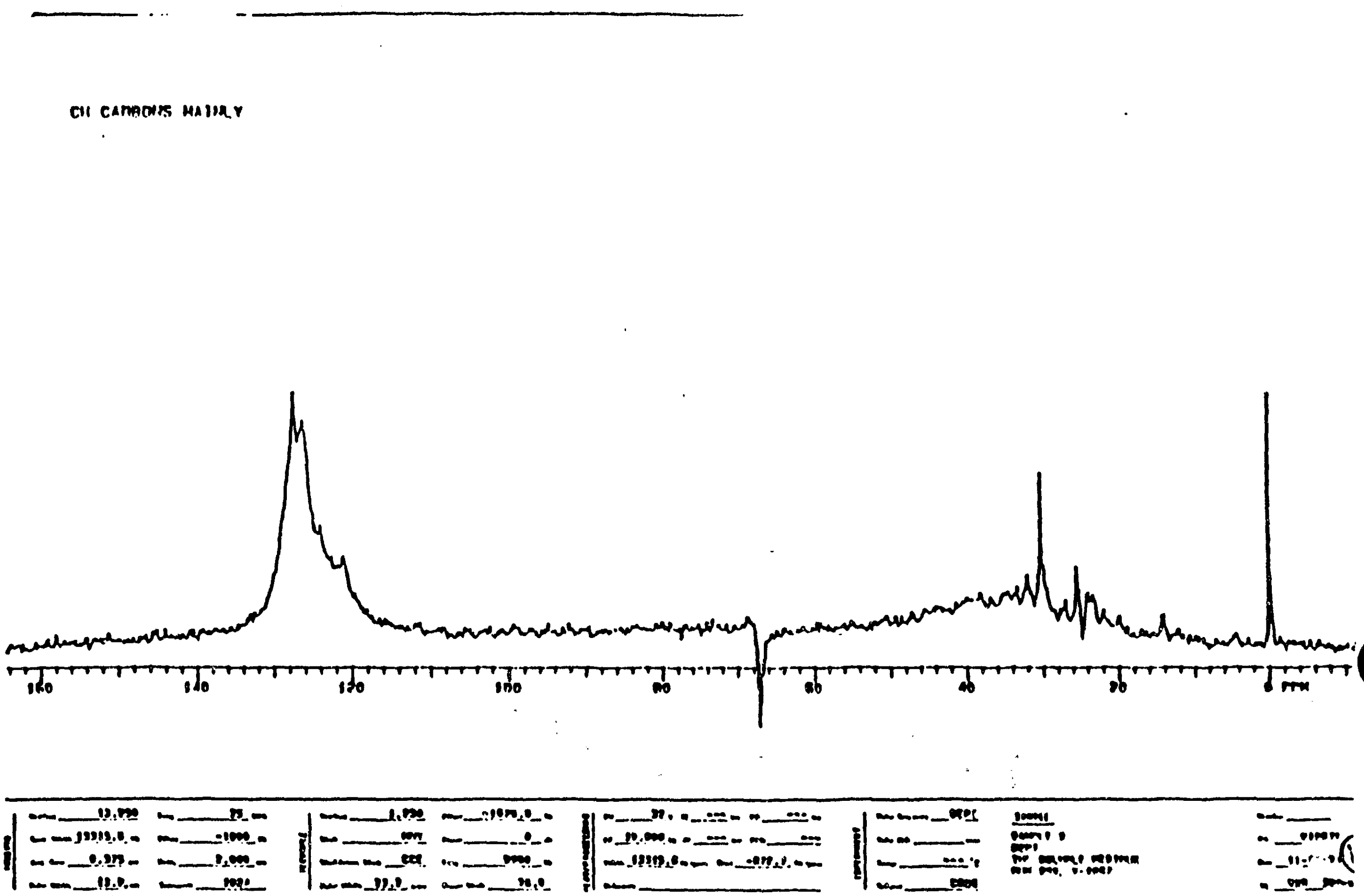
Proton NMR spectrum of sample 2, Run 257, in d_8-THF.



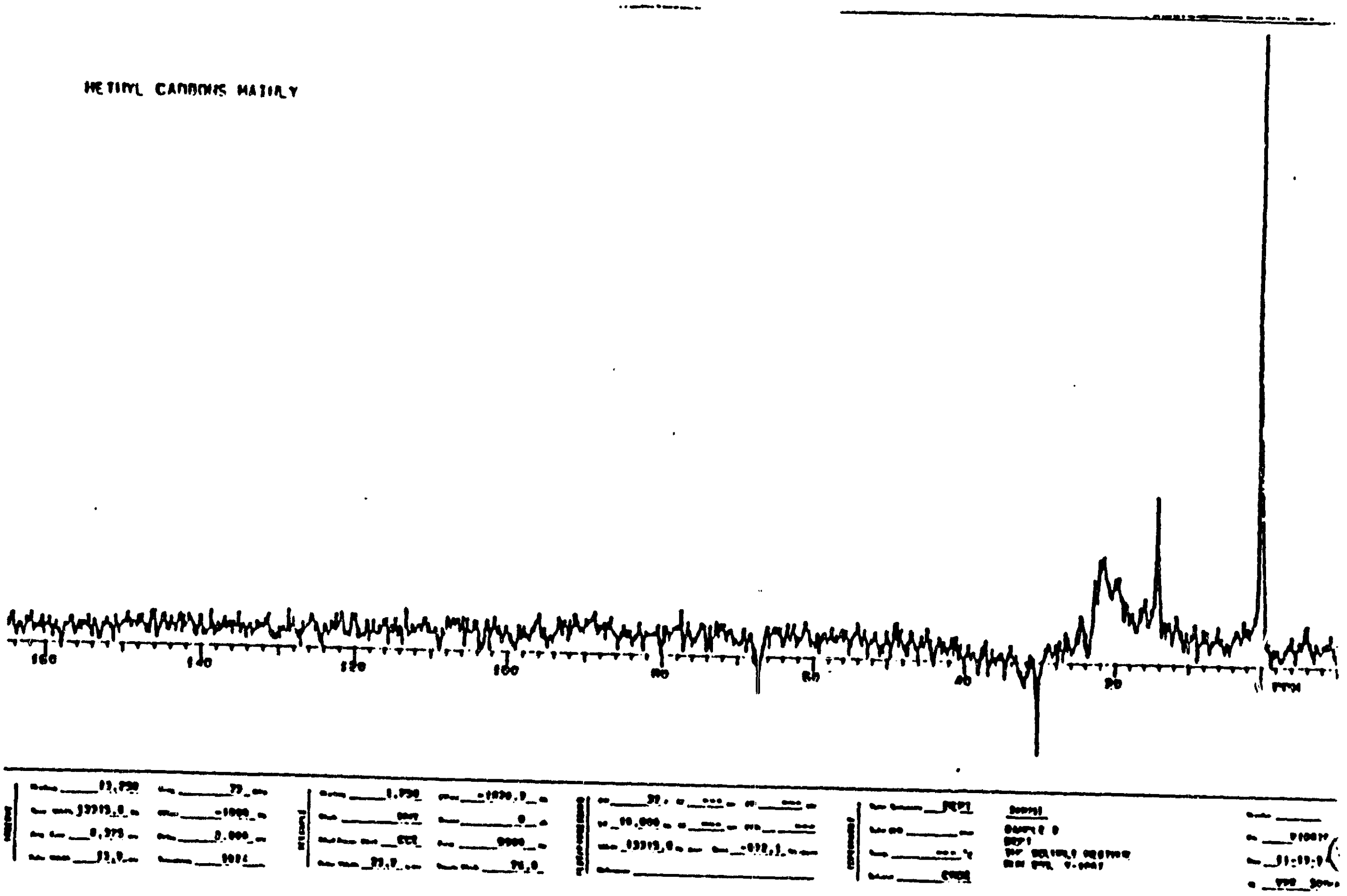
Proton NMR spectrum of sample 3, run 259, in d_8-THF.



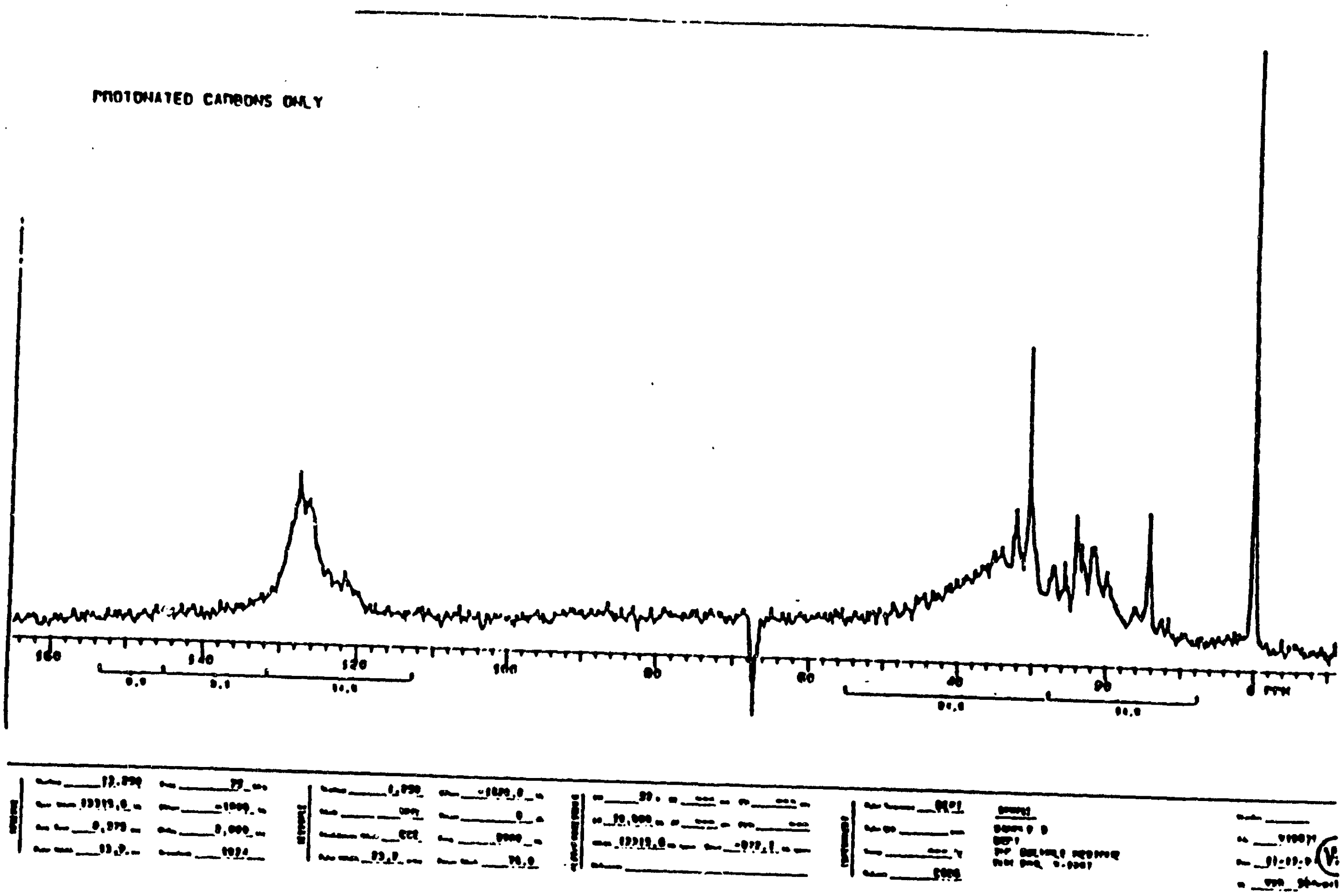
DEPT spectrum of sample 3, run 259, in d_8-THF showing selective excitation of mainly methine carbons.



DEPT spectrum of sample 3, run 259, in d_8-THF showing selective excitation of mainly methyl carbons.



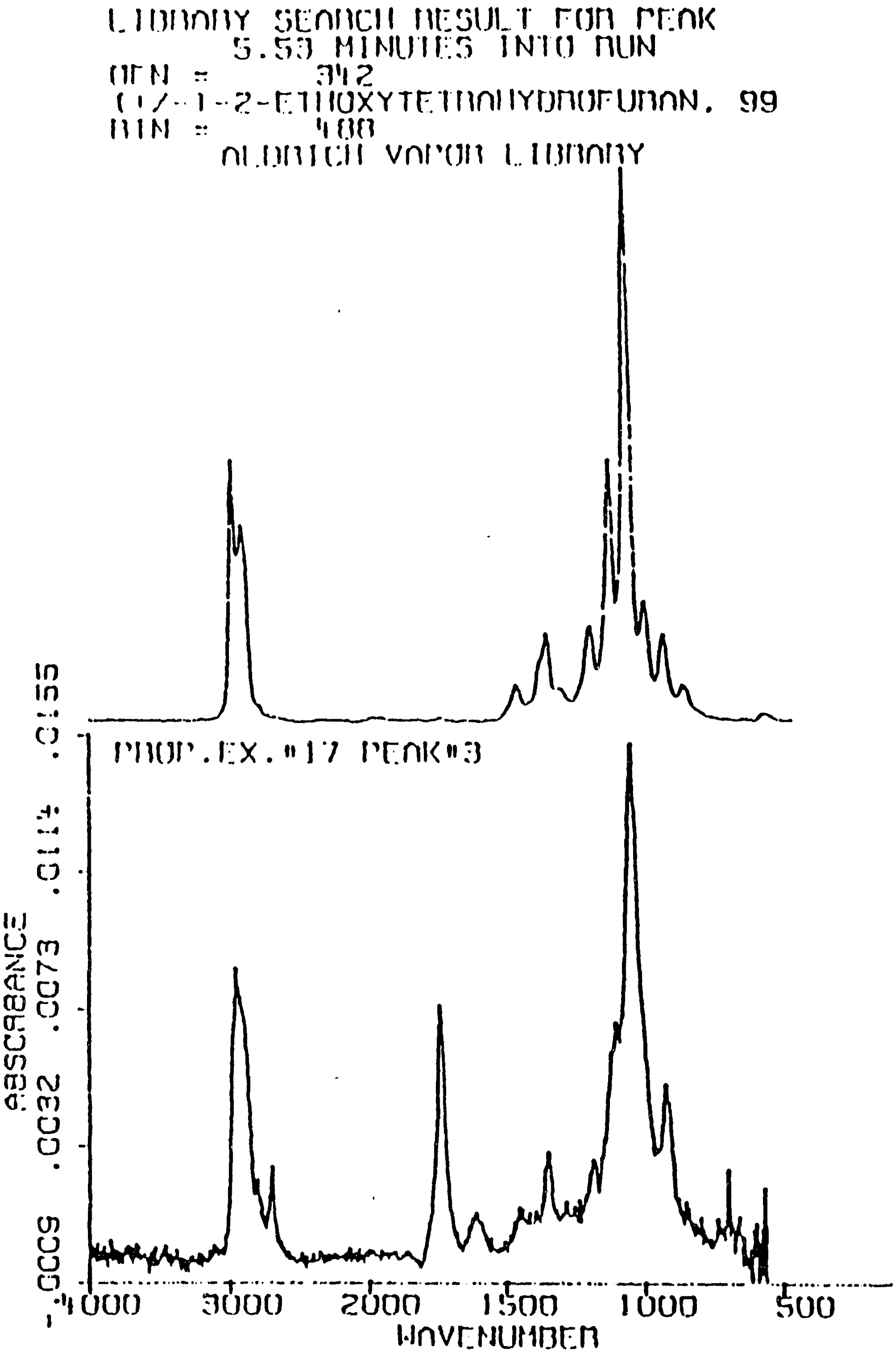
DEPT spectrum of sample 3, run 259, in d_8-THF showing selective excitation of only protonated carbons.



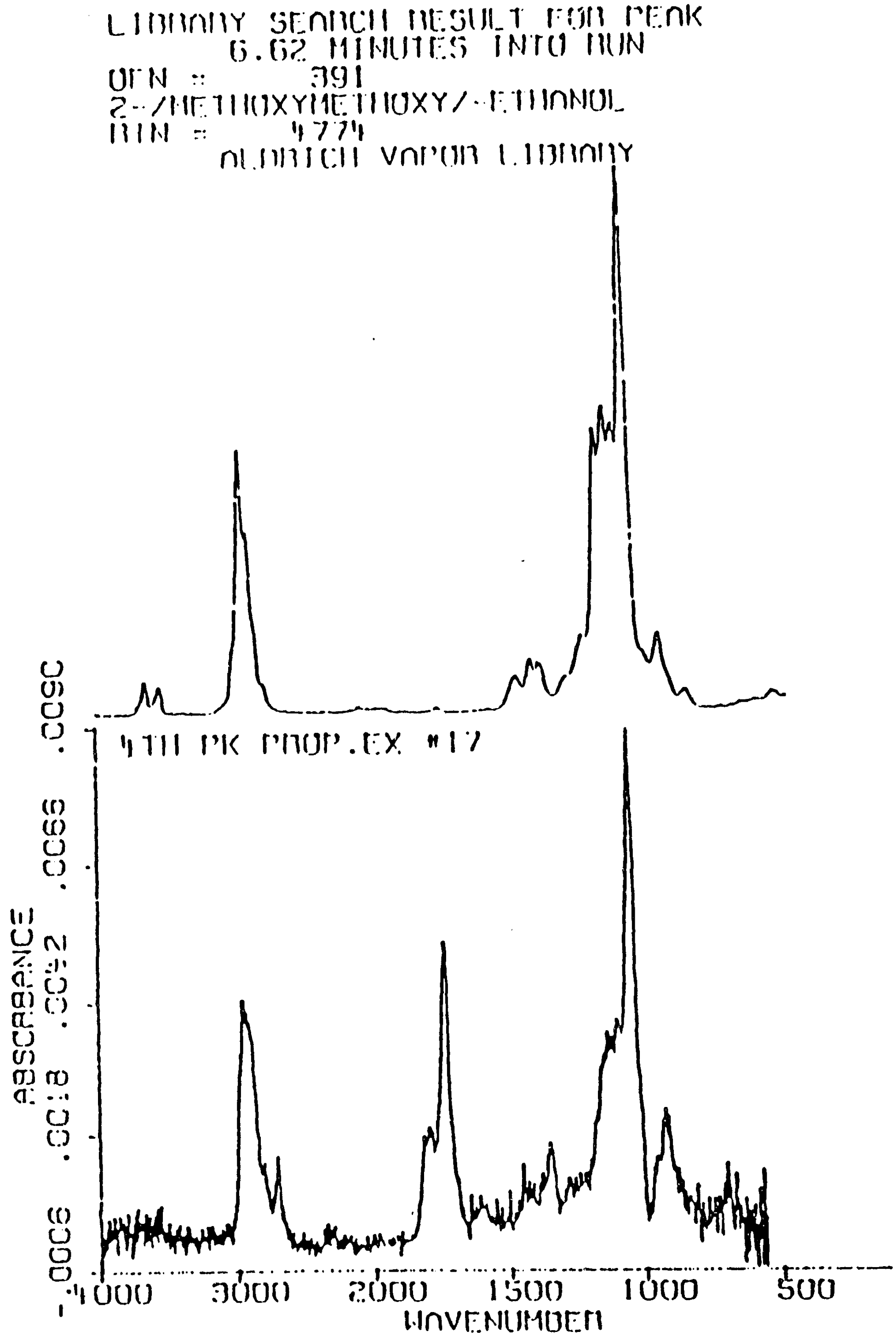
APPENDIX C.

SUPERCRITICAL FLUID CHROMATOGRAPHY DATA

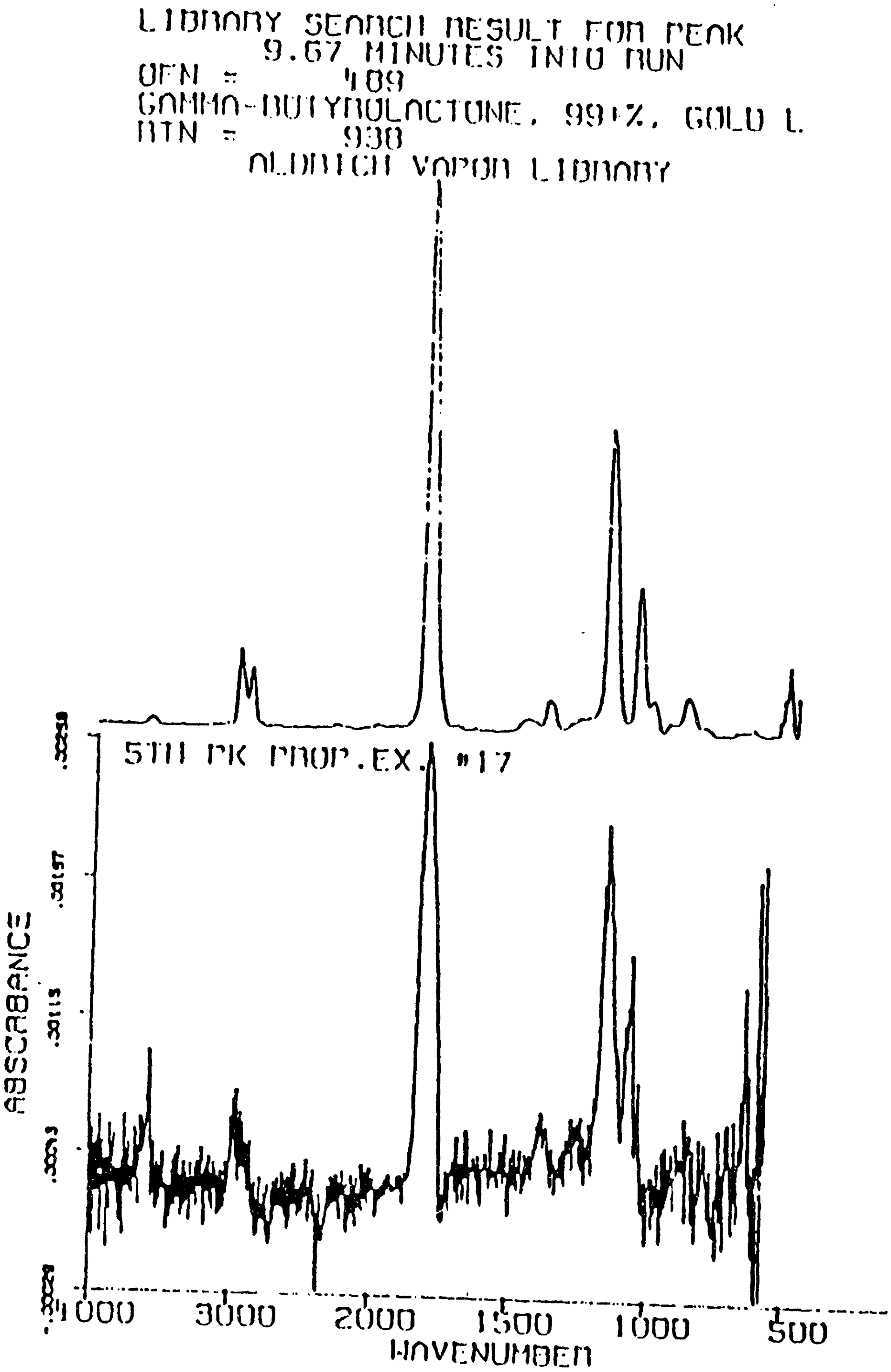
Infrared spectrum of the third peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



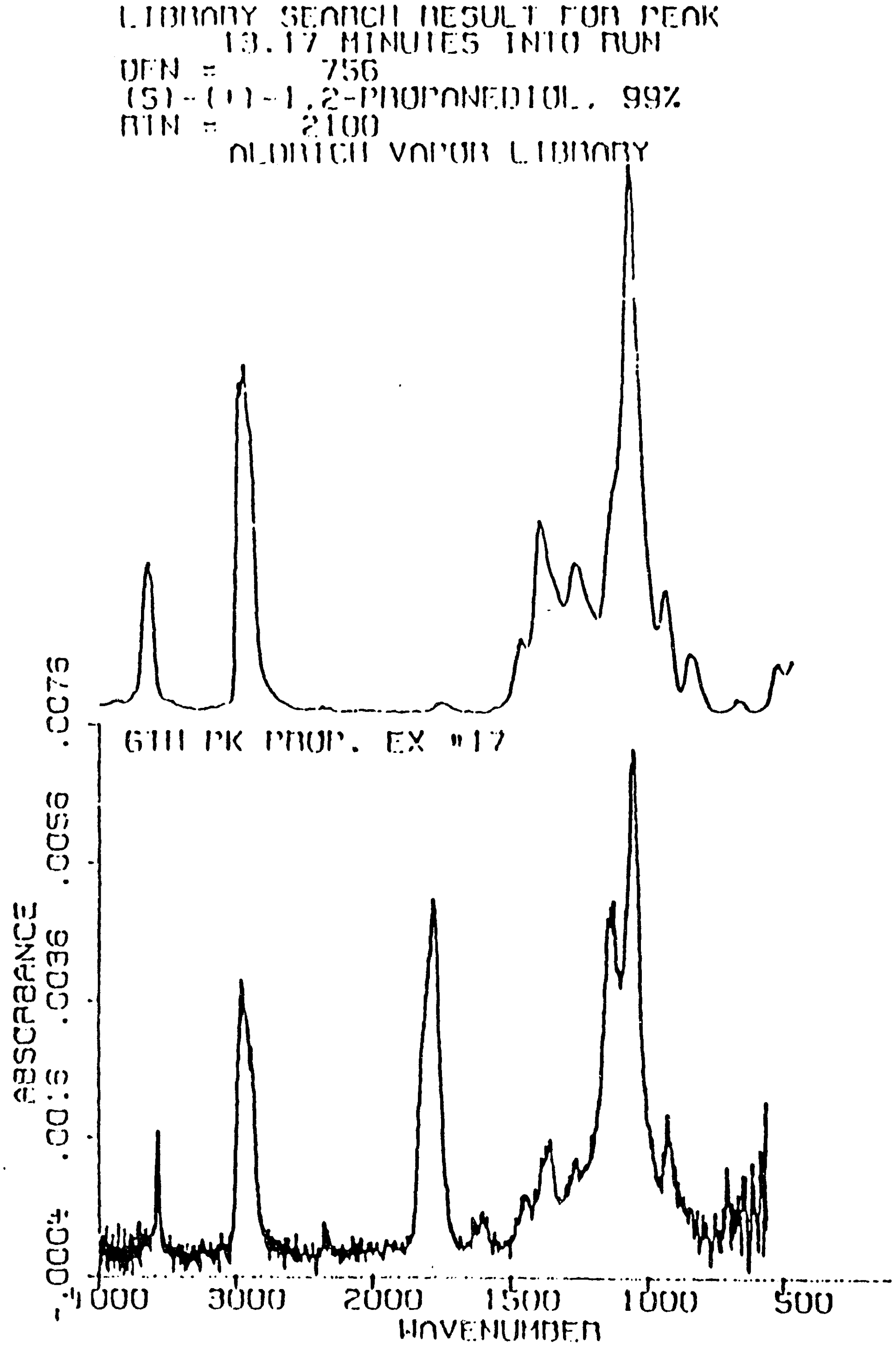
Infrared spectrum of the fourth peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



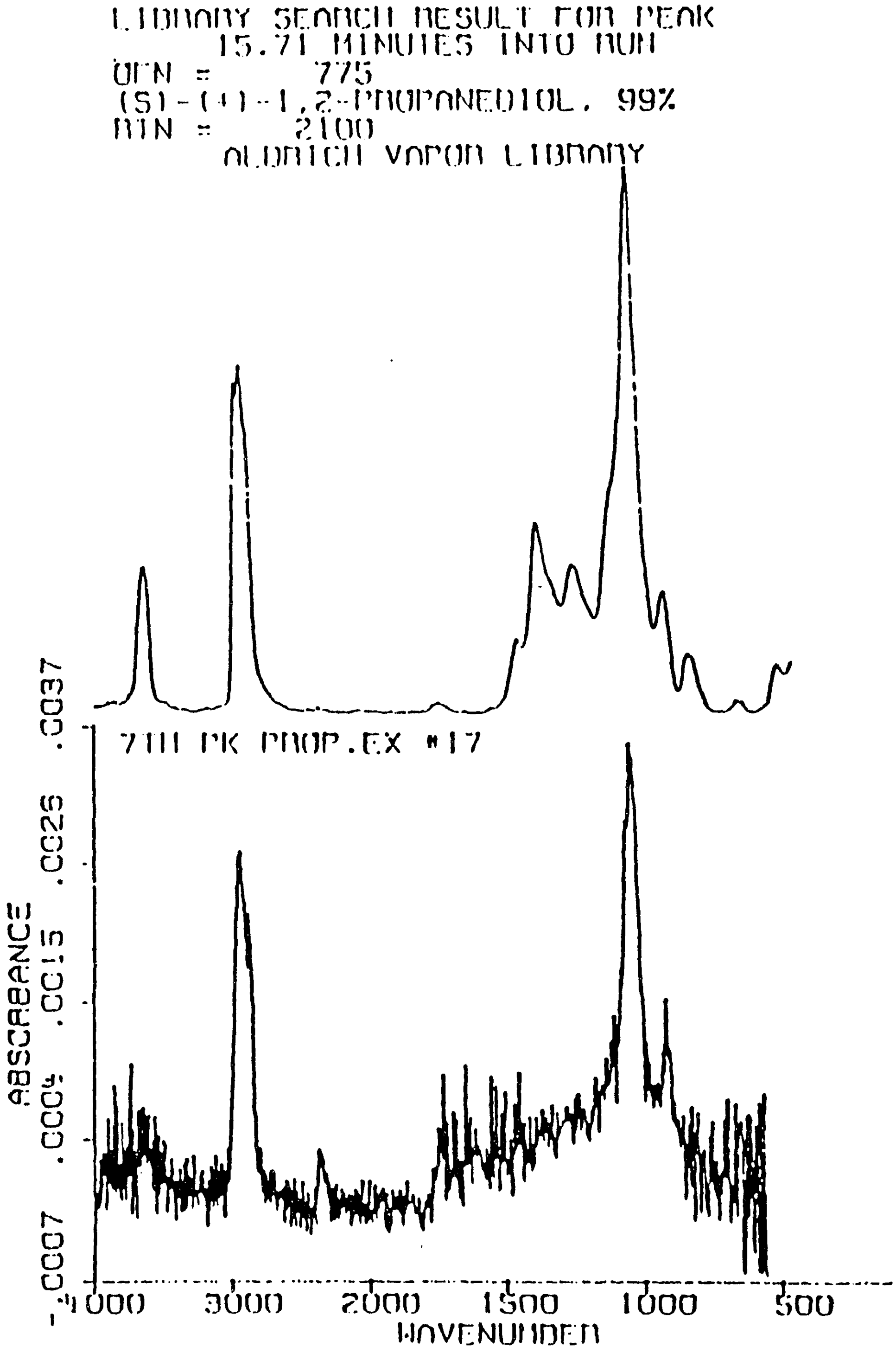
Infrared spectrum of the fifth peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



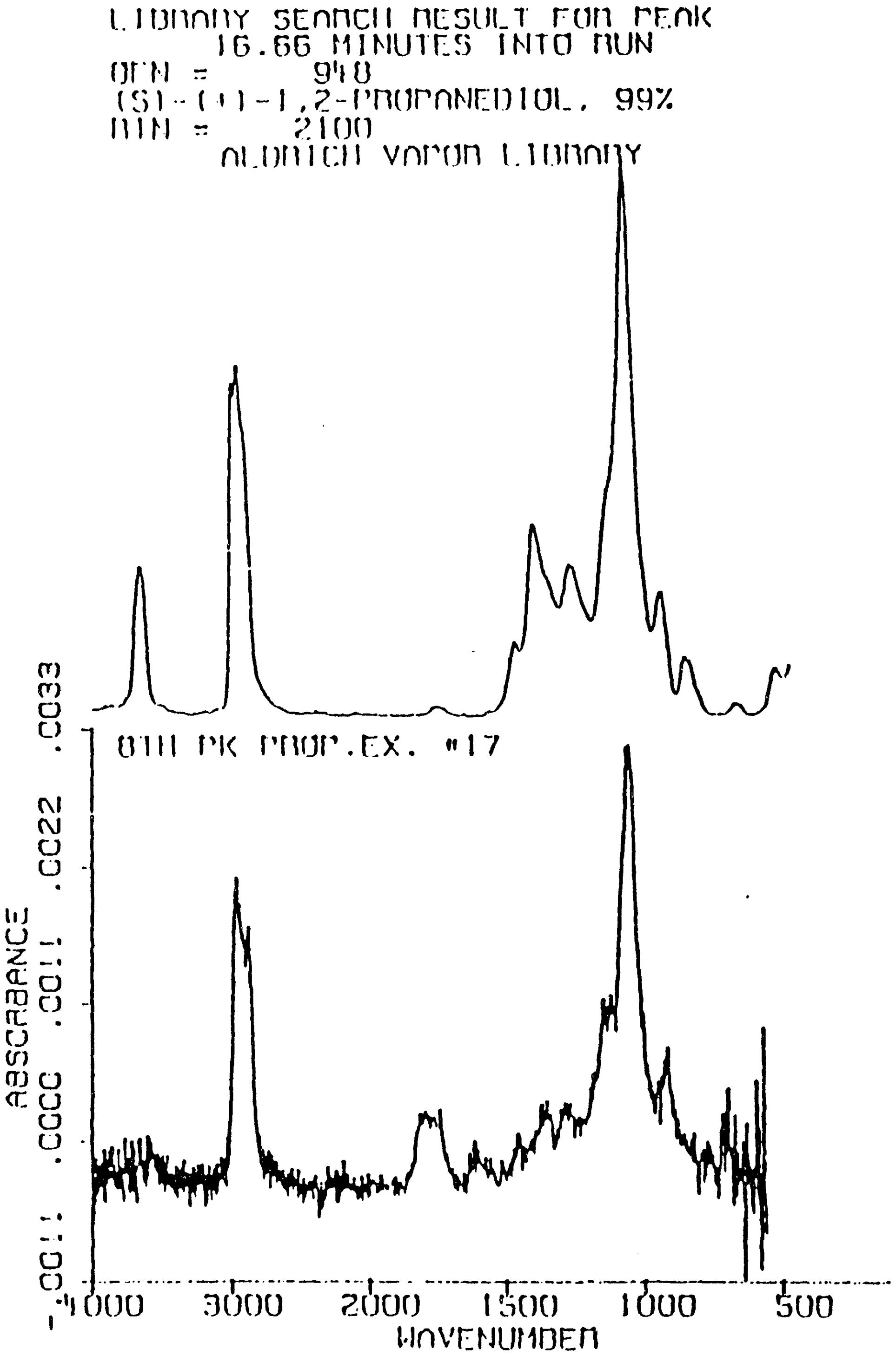
Infrared spectrum of the sixth peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



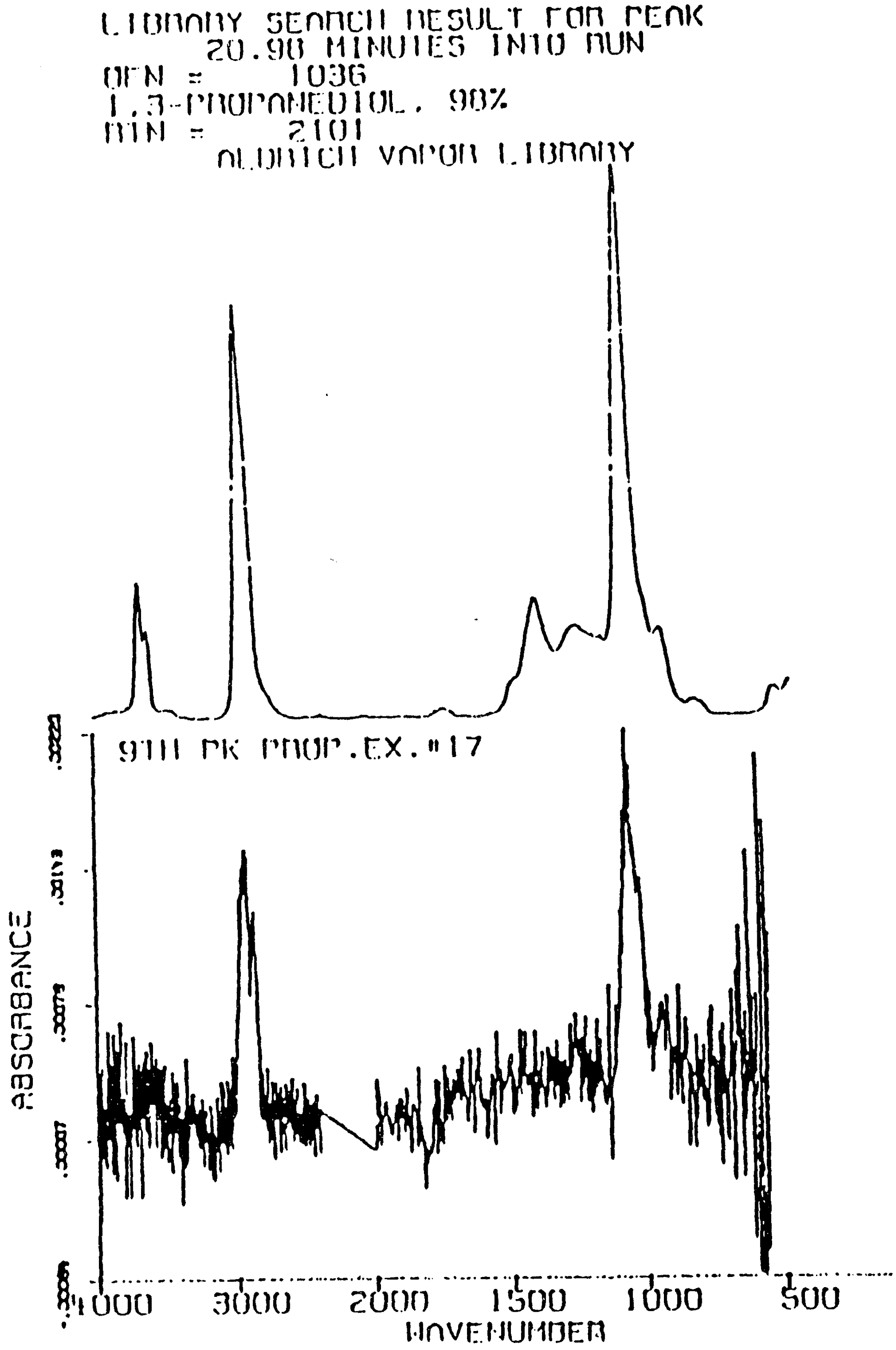
Infrared spectrum of the seventh peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



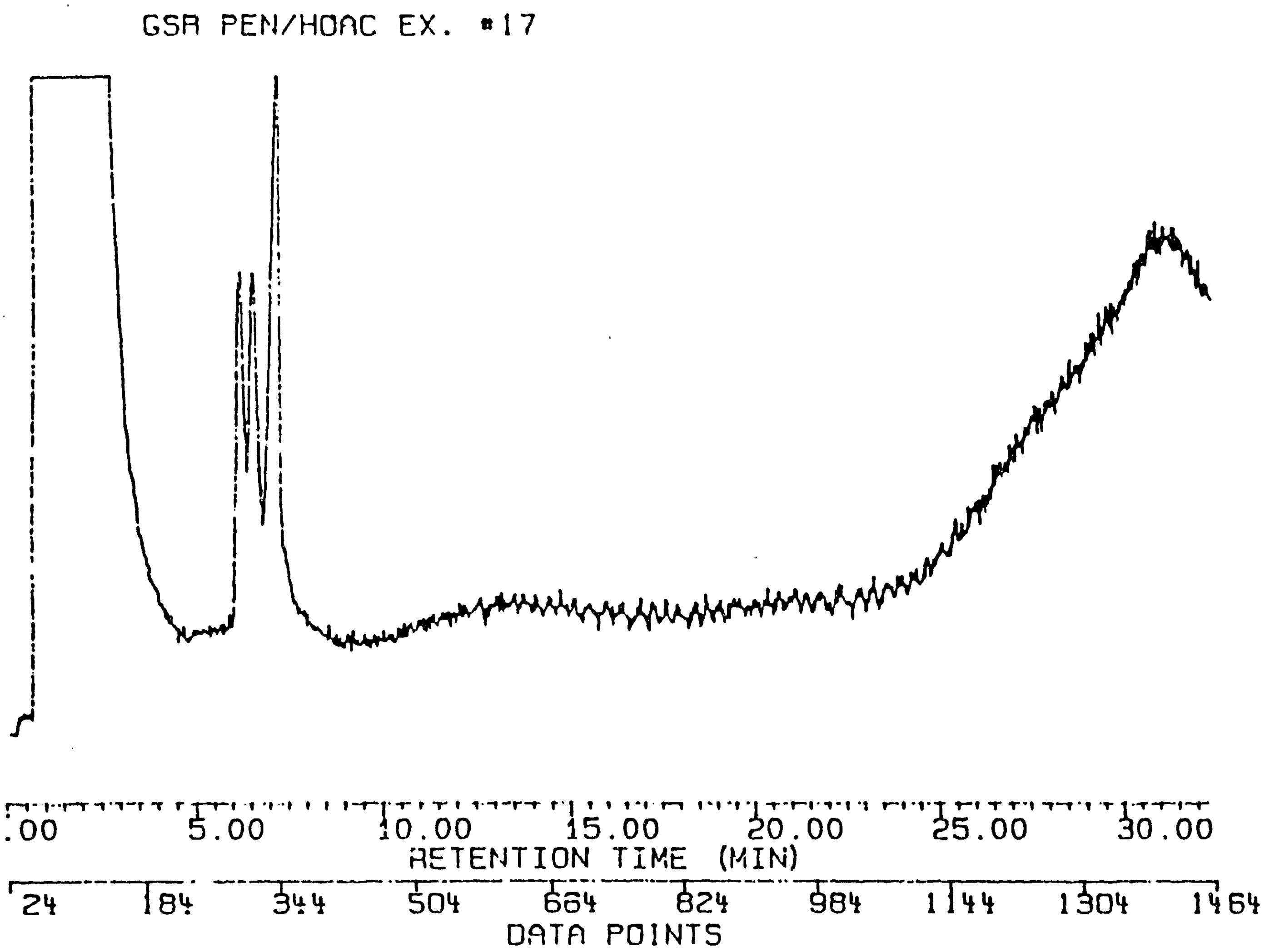
Infrared spectrum of the eighth peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



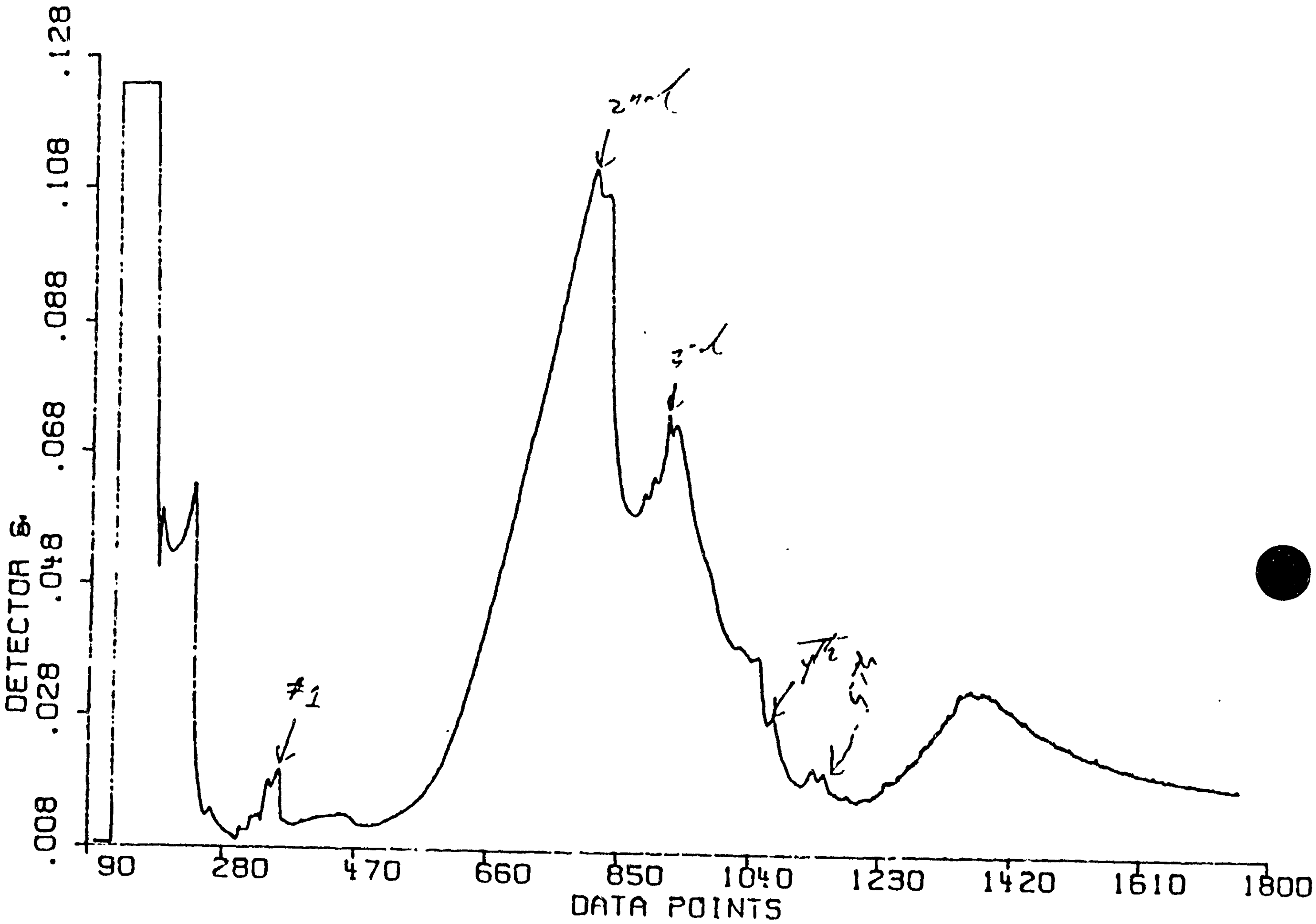
Infrared spectrum of the ninth peak in Figure 20 along with the best library spectrum found in the Aldrich Vapor Library.



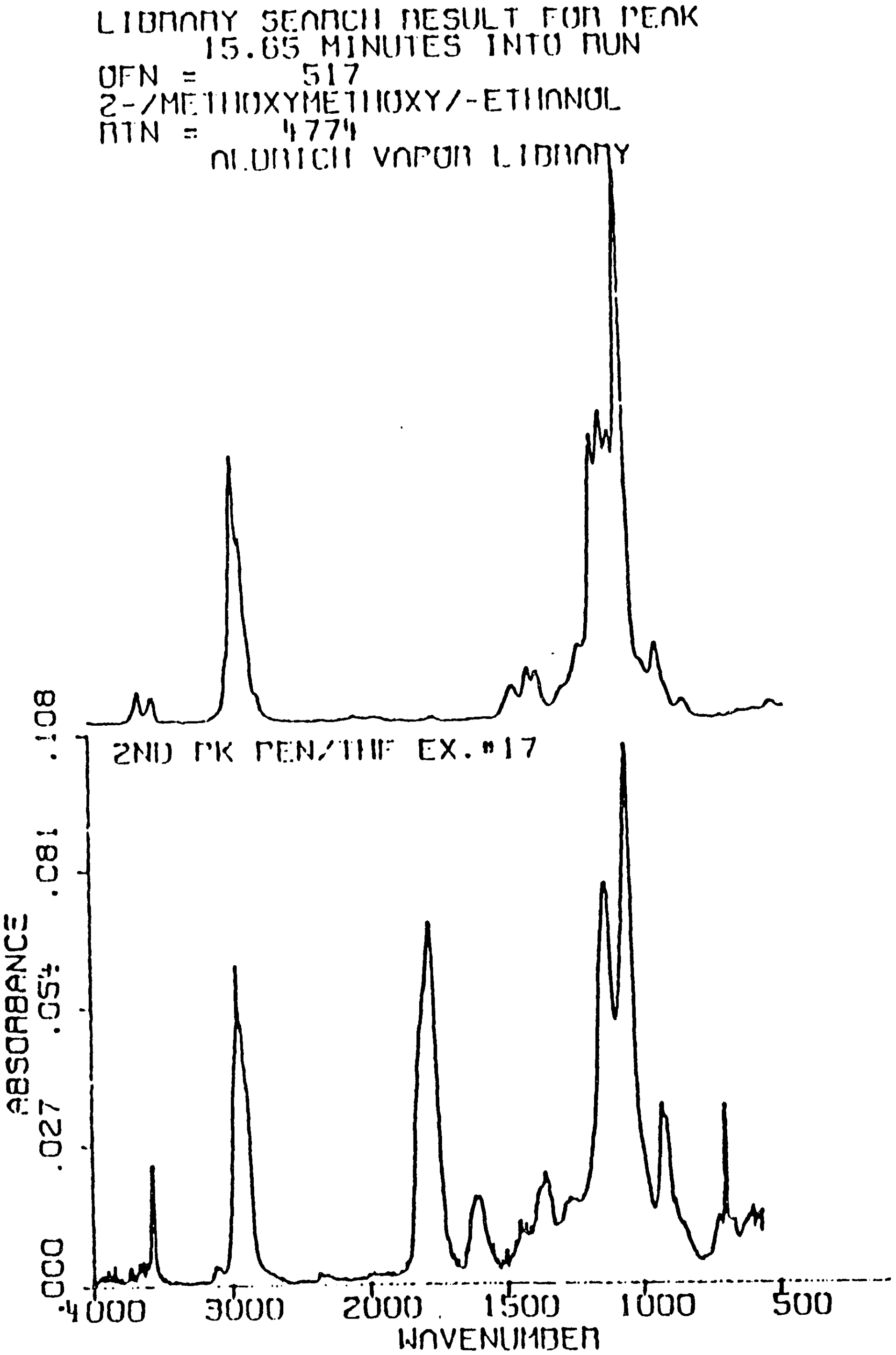
Grahm-Schmidt reconstruction of GC/FTIR analysis of a pentane/acetic acid extract from sample #17.



Grahm-Schmidt reconstruction of GC/FTIR analysis of a pentane/THF extract from sample #17.



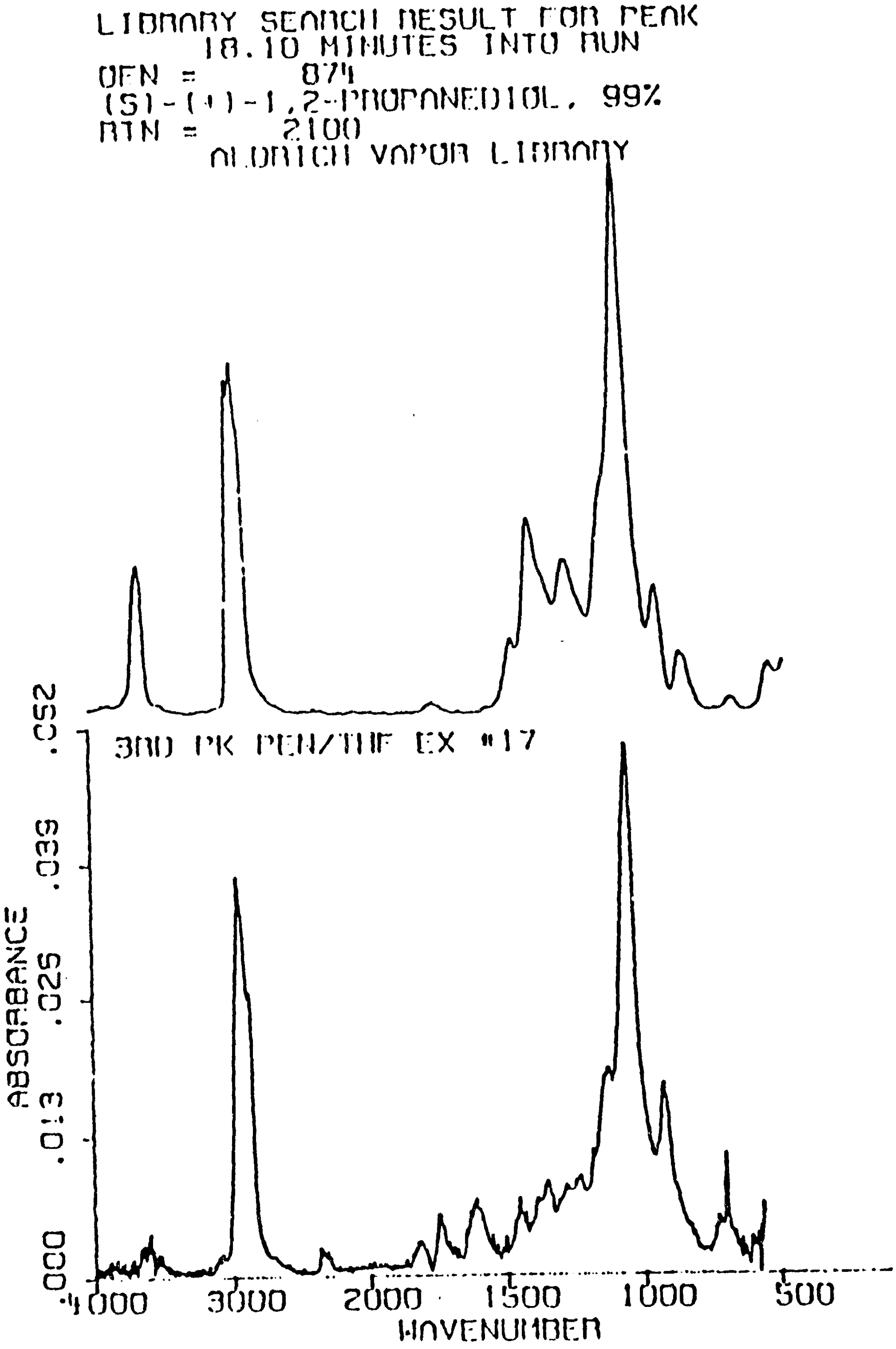
Infrared spectrum of the second peak observed in pentane/THF extract along with the best library spectrum found in the Aldrich Vapor Library.



```
LIBRARY SEARCH RESULT FOR PEAK
     15.65 MINUTES INTO RUN
OFN =        517
2-/METHOXYMETHOXY/-ETHANOL
RTN =      4774
     ALDRICH VAPOR LIBRARY
```

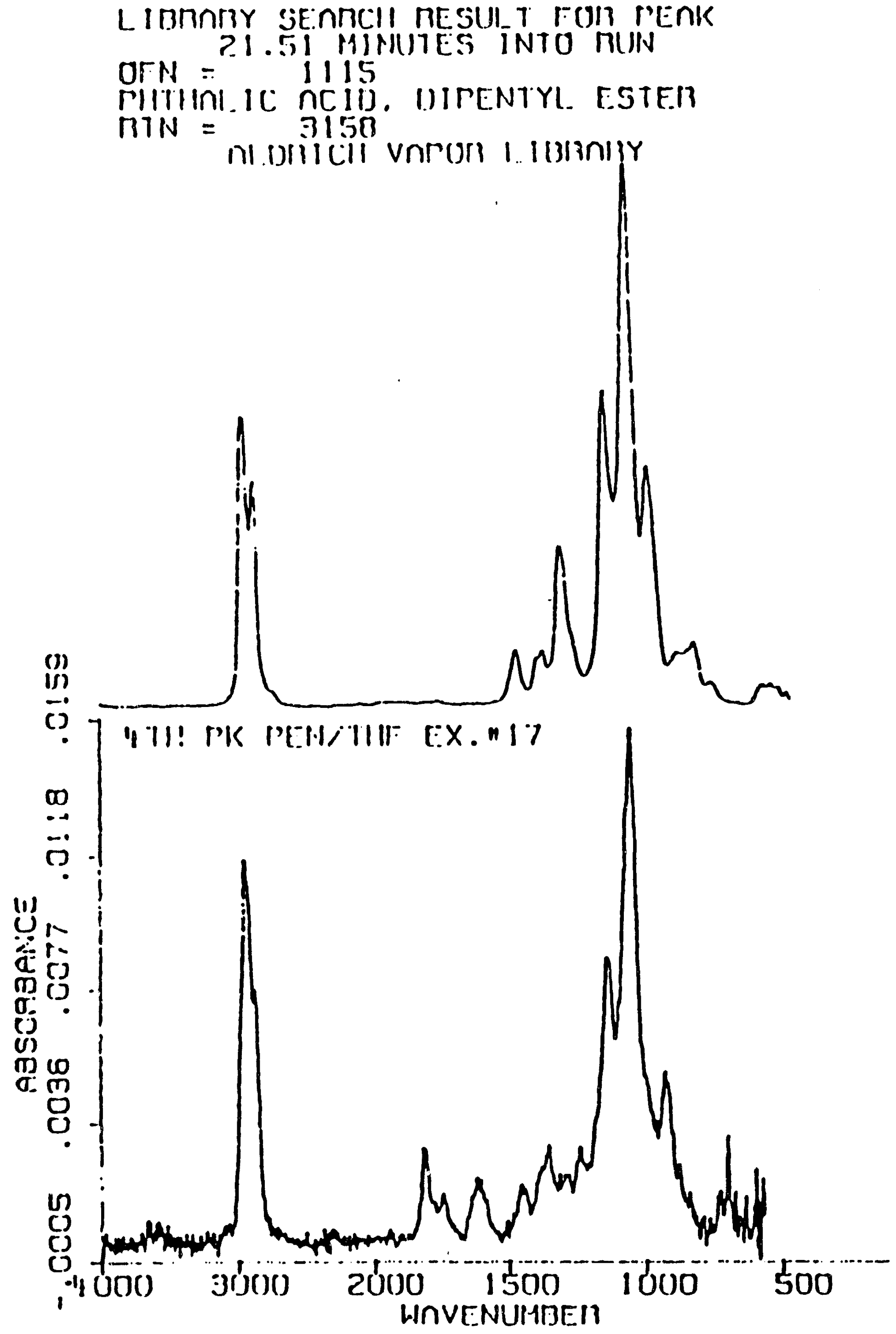
2ND PK PEN/THF EX.#17

Infrared spectrum of the third peak observed in pentane/THF extract along with the best library spectrum found in the Aldrich Vapor Library.



[redacted]

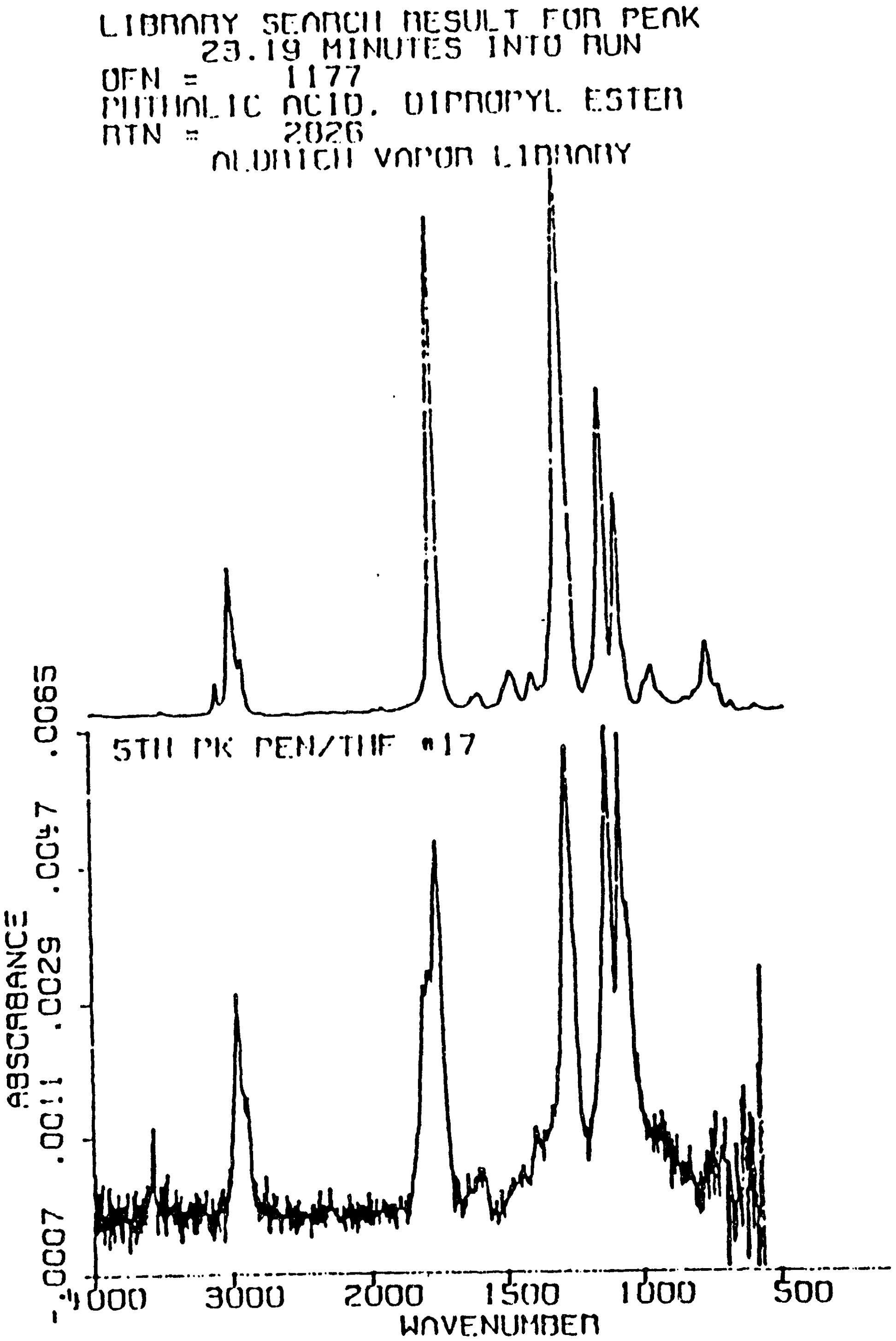
Infrared spectrum of the fourth peak observed in pentane/THF extract along with the best library spectrum found in the Aldrich Vapor Library.



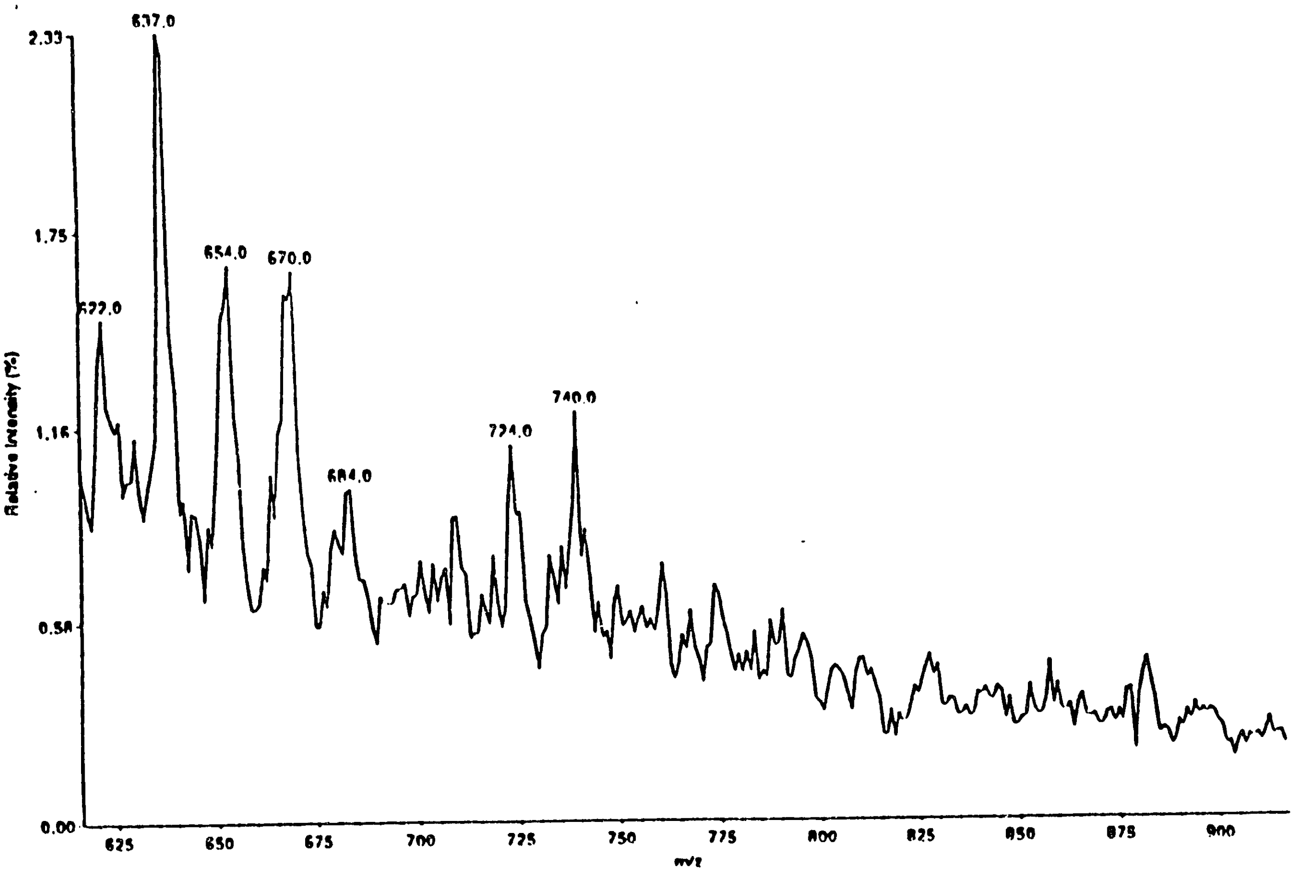
LIBRARY SEARCH RESULT FOR PEAK
21.51 MINUTES INTO RUN
OFN = 1115
PHTHALIC ACID, DIPENTYL ESTER
RIN = 3150
ALDRICH VAPOR LIBRARY

4TH PK PEN/THF EX.#17

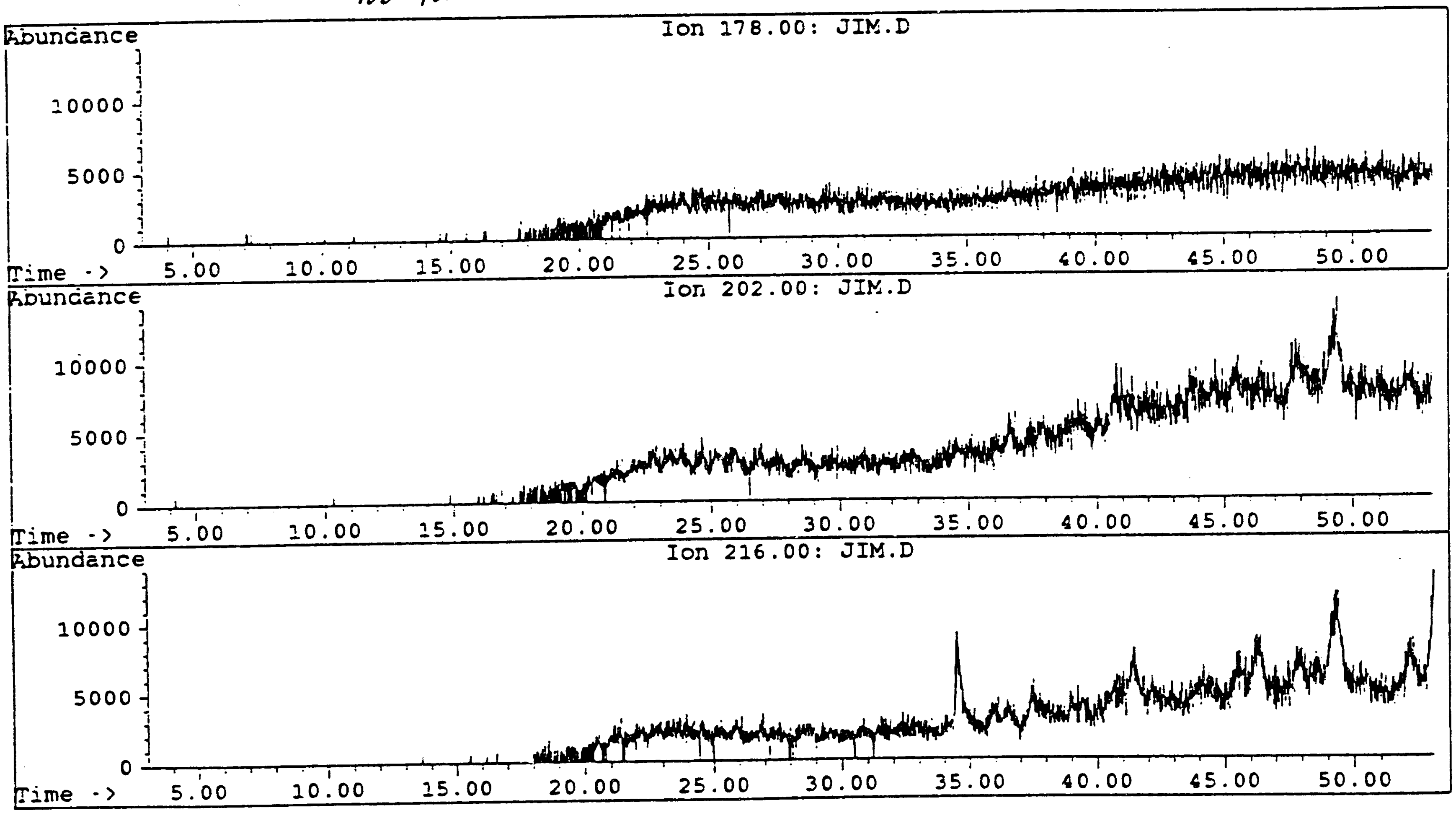
Infrared spectrum of the fifth peak observed in pentane/THF extract along with the best library spectrum found in the Aldrich Vapor Library.



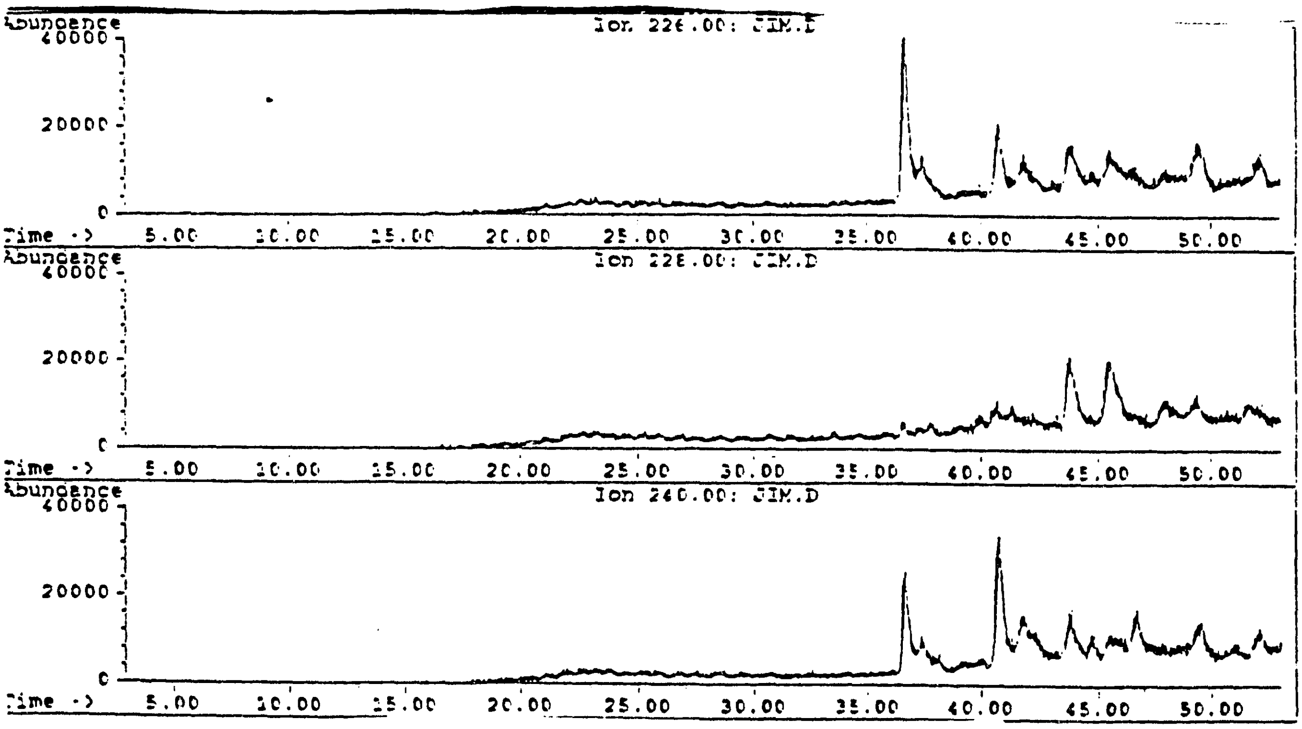
Electrospray Ionization mass spectrum of the high m/z ions in Figure 24.



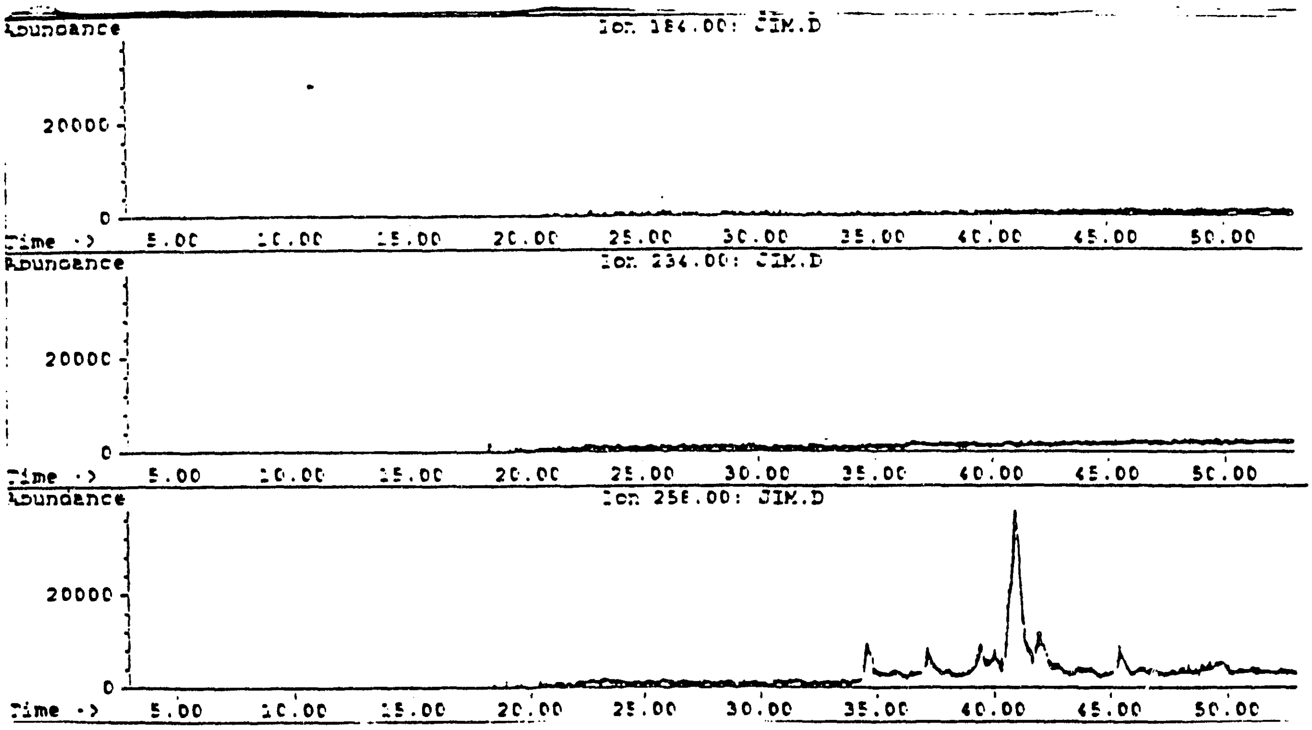
File: C:\CHEMPC\DATA\JIM.D
Operator:
Date Acquired: 20 Mar 92 9:07 am CO$_2$/10% IPA SFE
Method File: DEFAULT.M
Sample Name: Hexane, AL2O3, FLOUROSIL, SiO2 Sample 2a
Misc Info:
ALS vial: 1 200µm × 30m 100 Methyl Lee Scientific
100 for 5min 100 → 290 @ 10°C/min 280 for 20min.



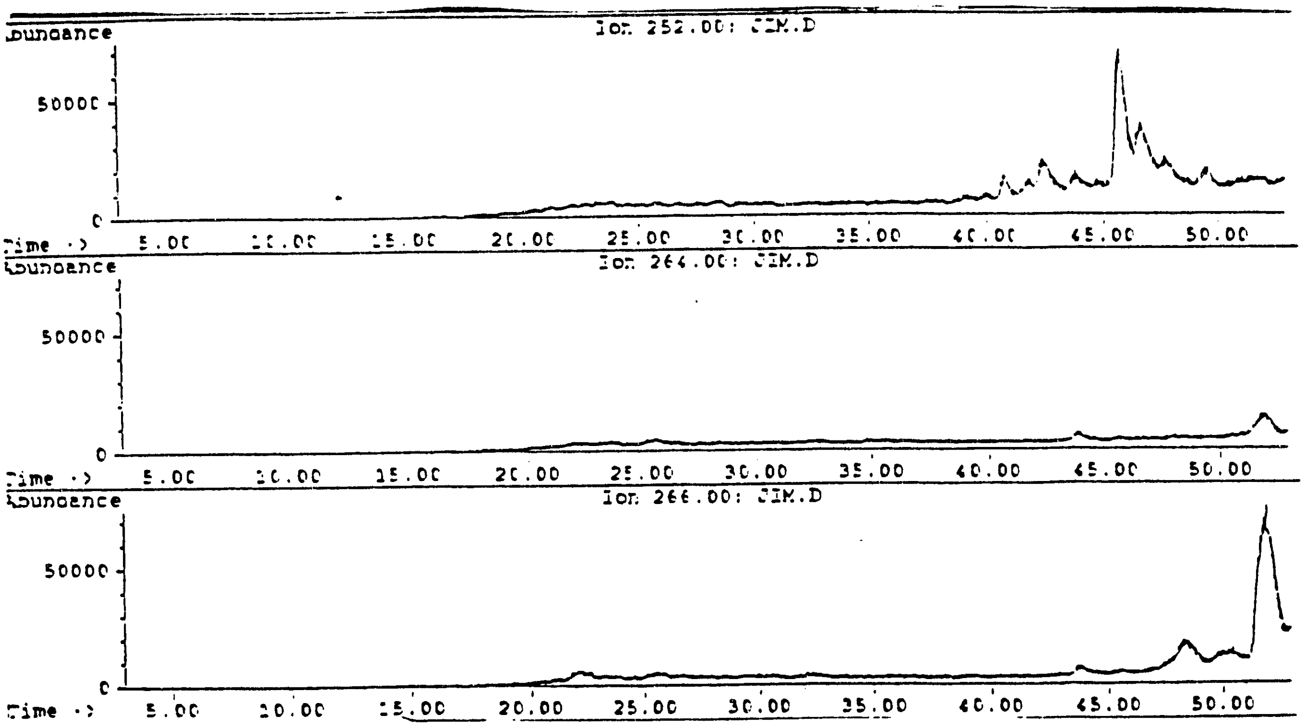
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 226, 228, and 240. Sample 22 was extracted with supercritical fluid CO_2/10% isopropanol.



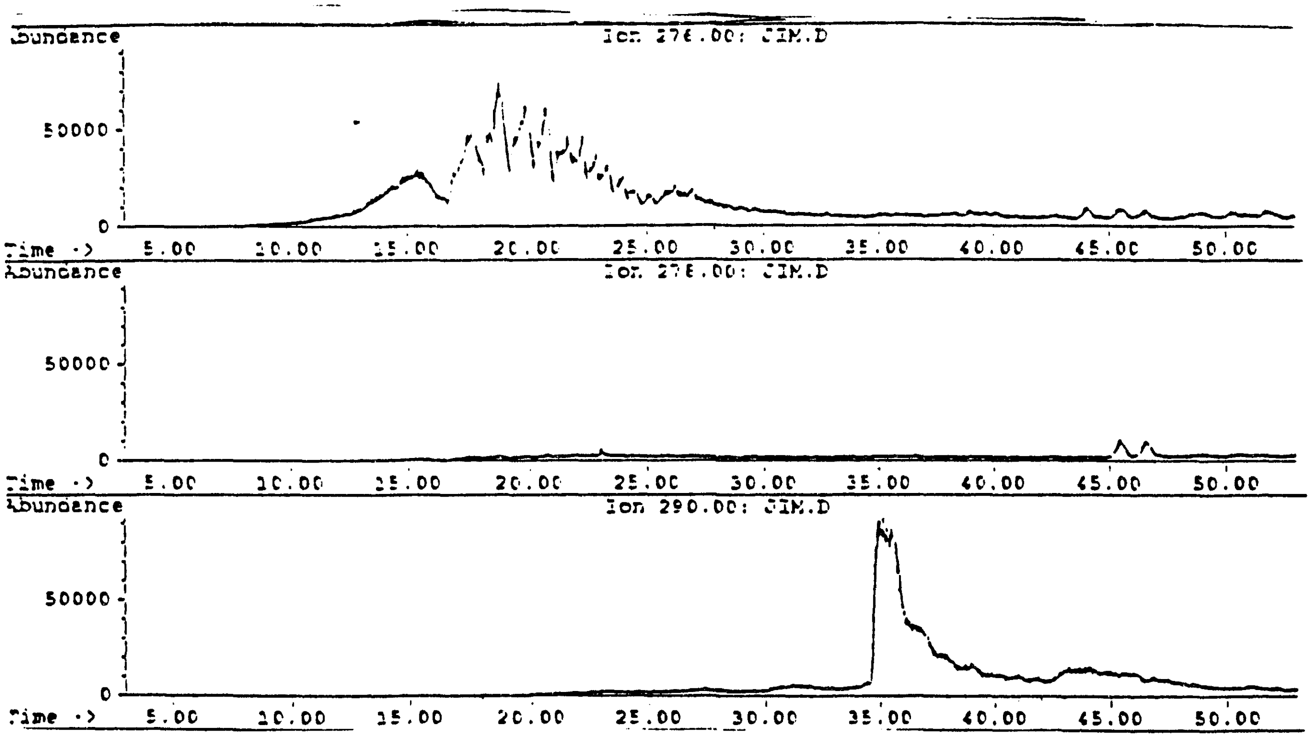
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 184, 234, and 258.



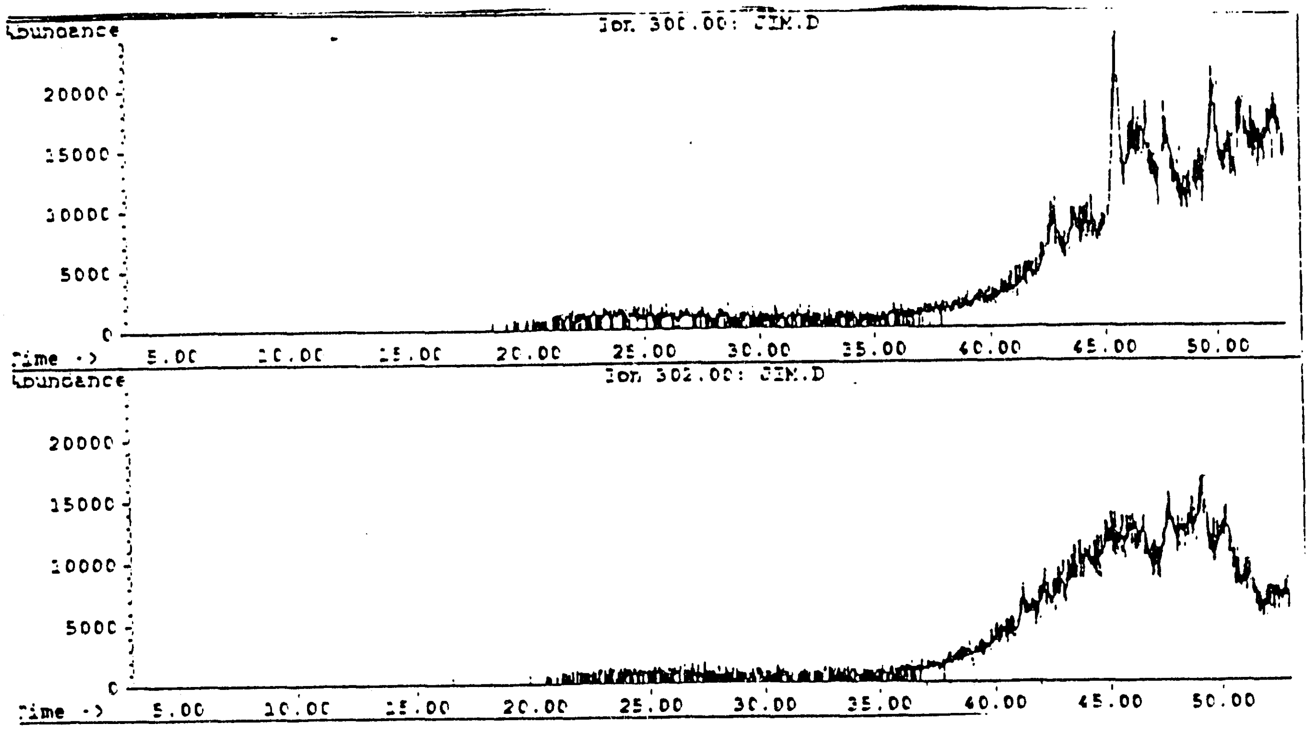
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 252, 264, and 266.



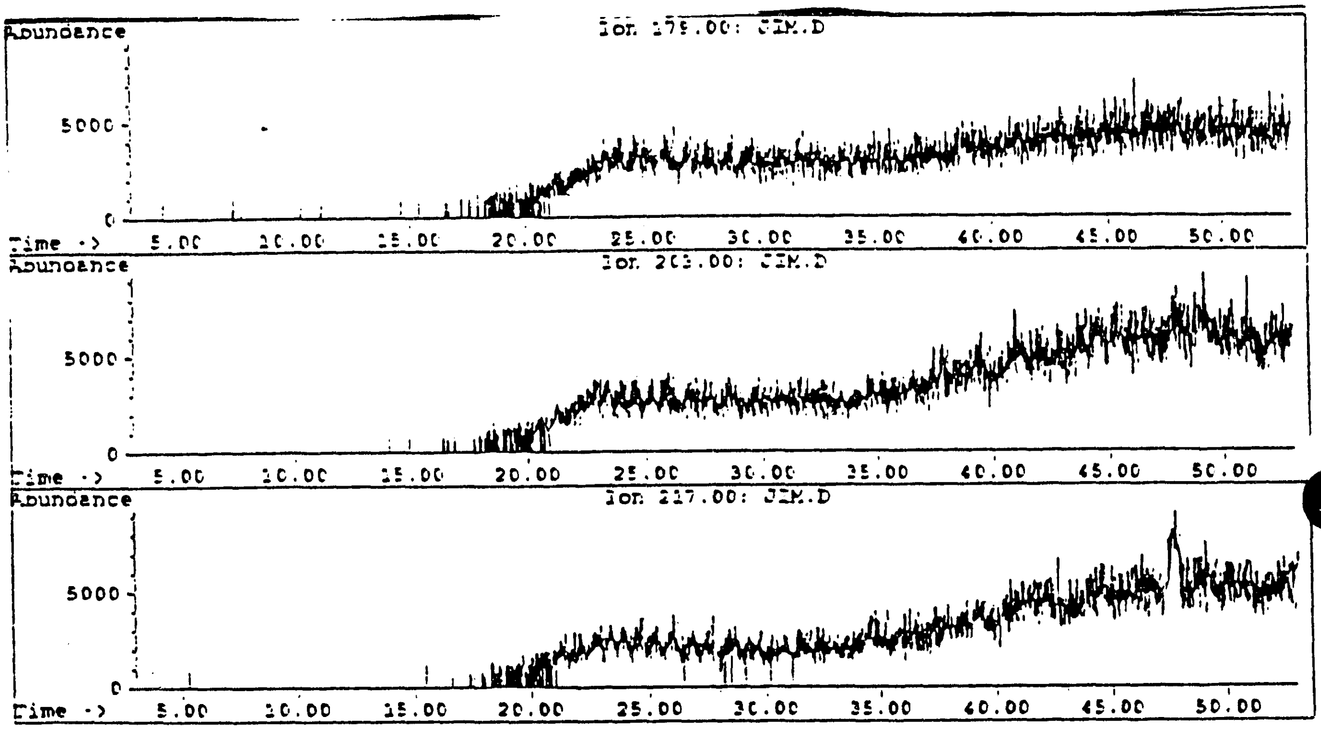
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 276, 278, and 290.



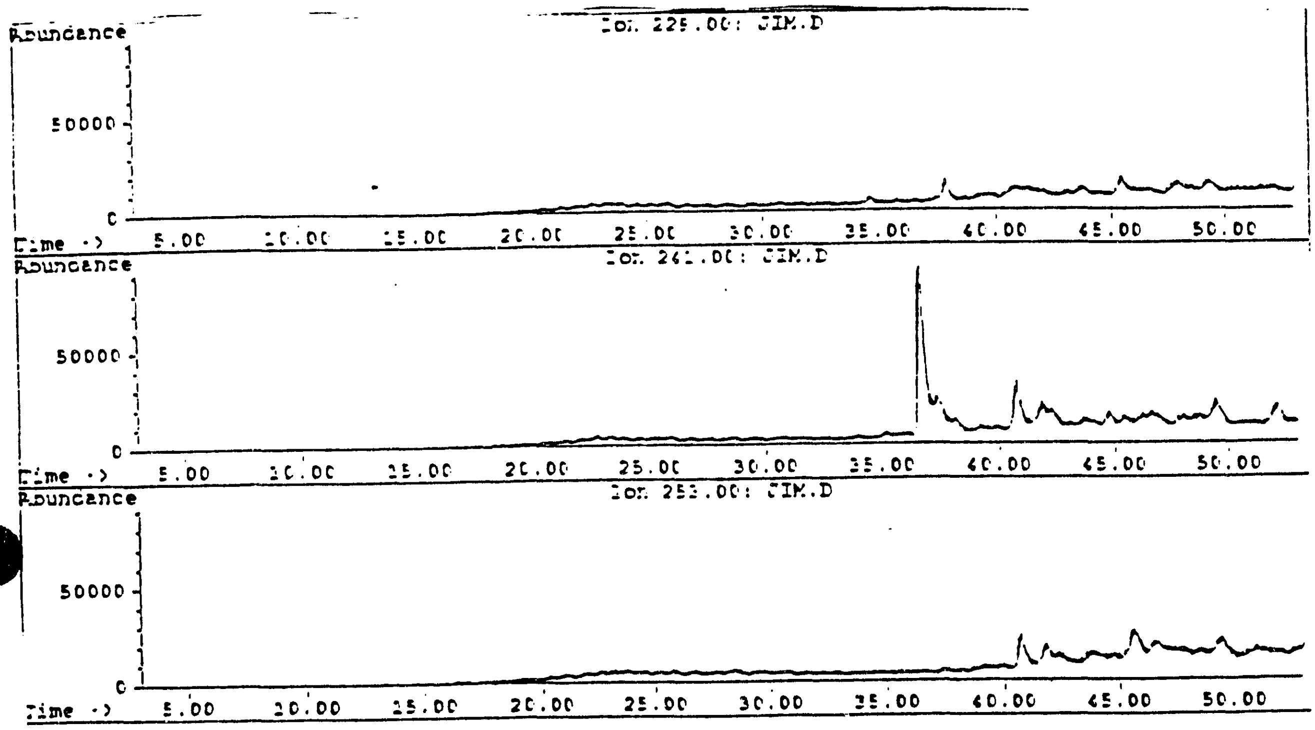
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 300 and 302.



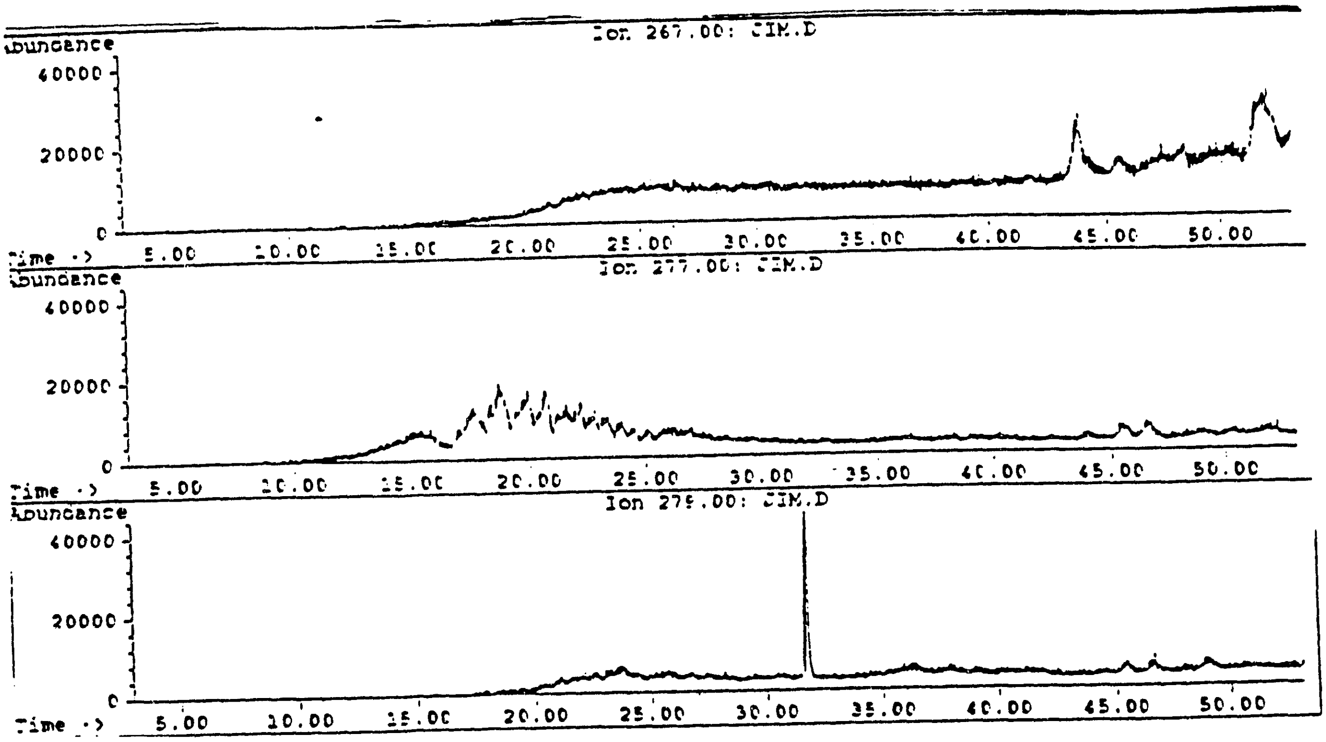
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 179, 203, and 217.



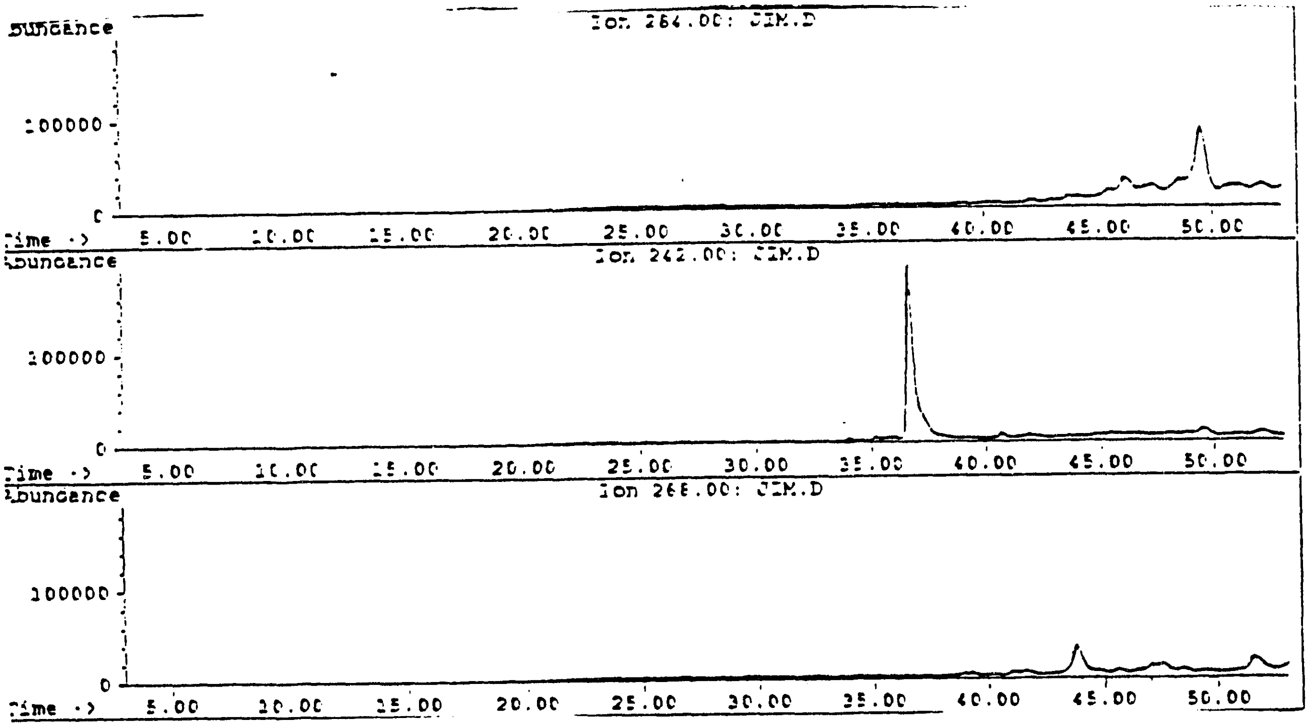
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 229, 241, and 253.



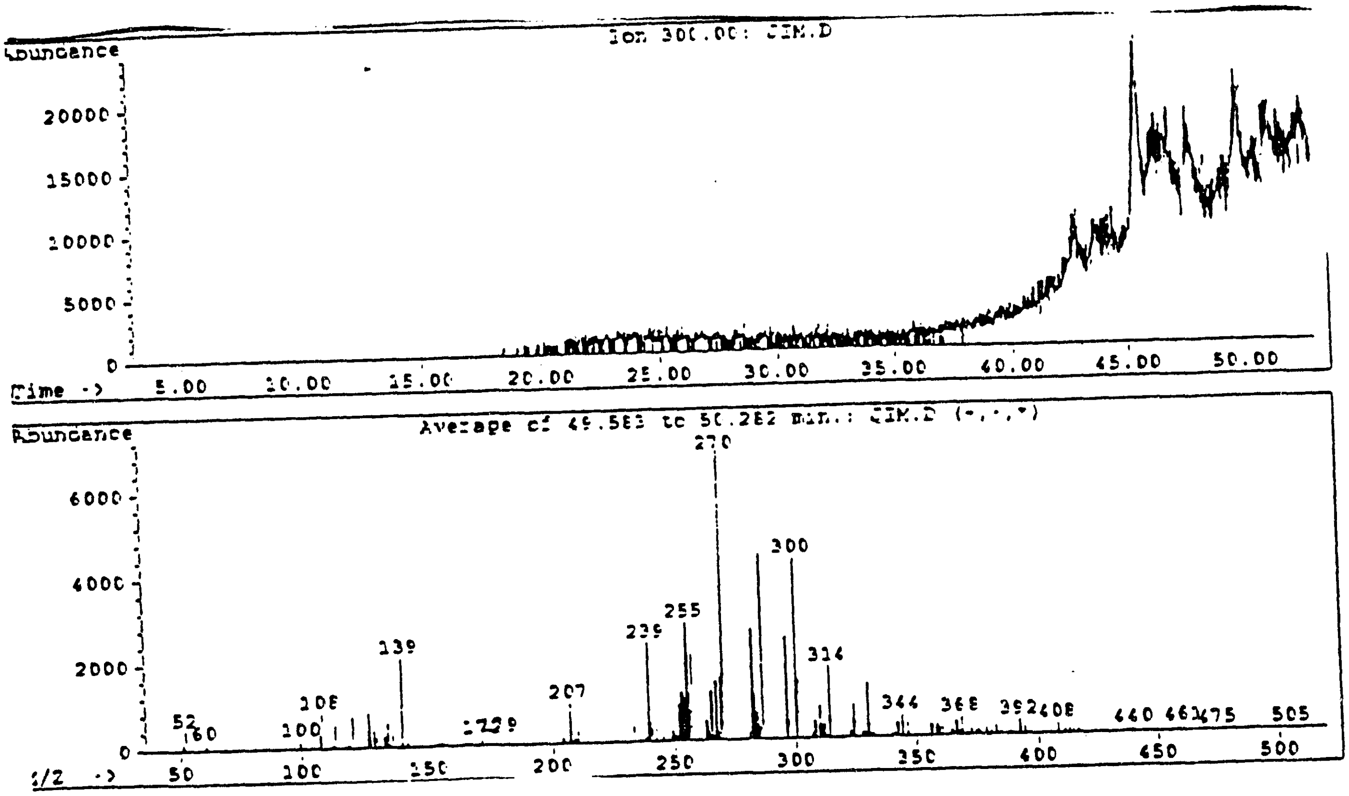
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 267, 277, and 279.

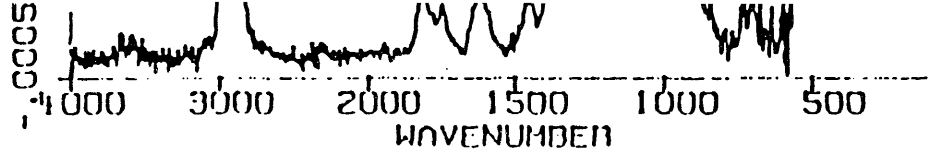


Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 284, 242, and 268.

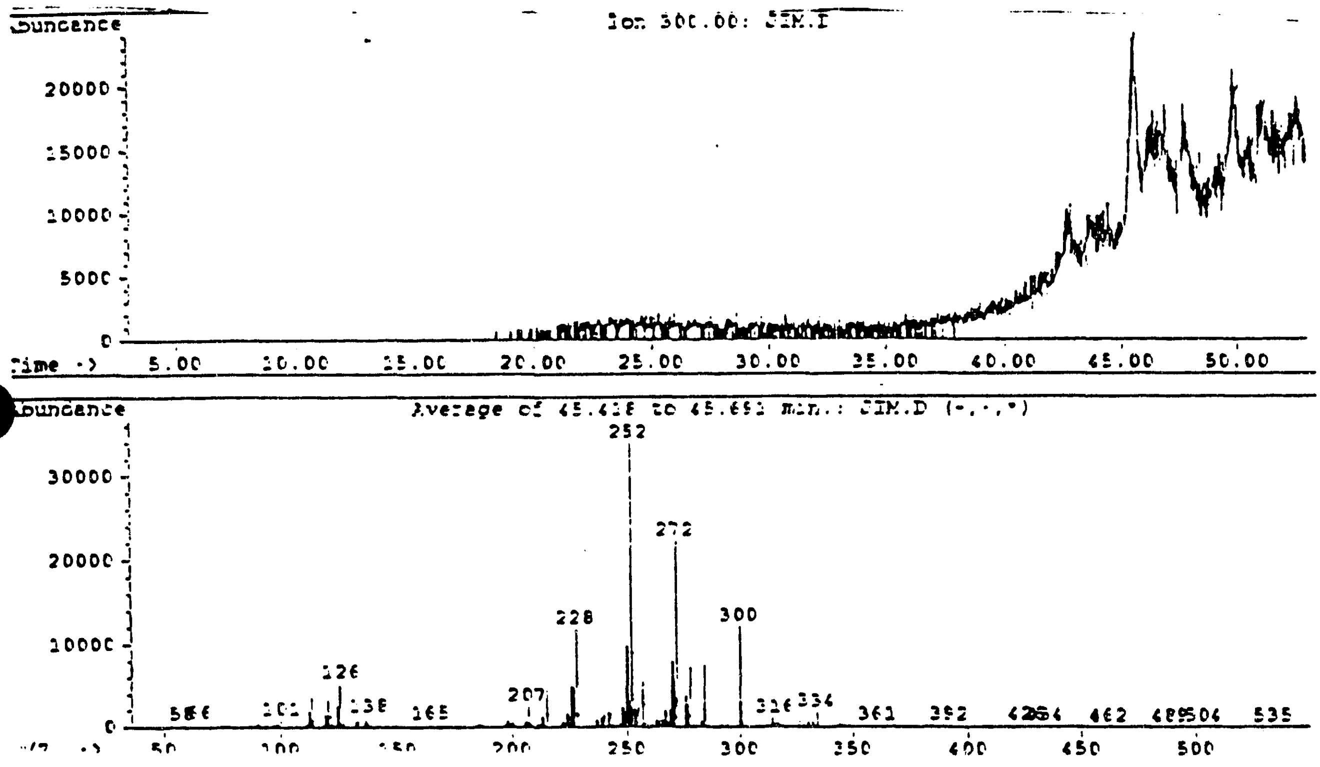


Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 300 and Corresponding Mass Spectrum Averaged from 49.5 to 50.3 min.

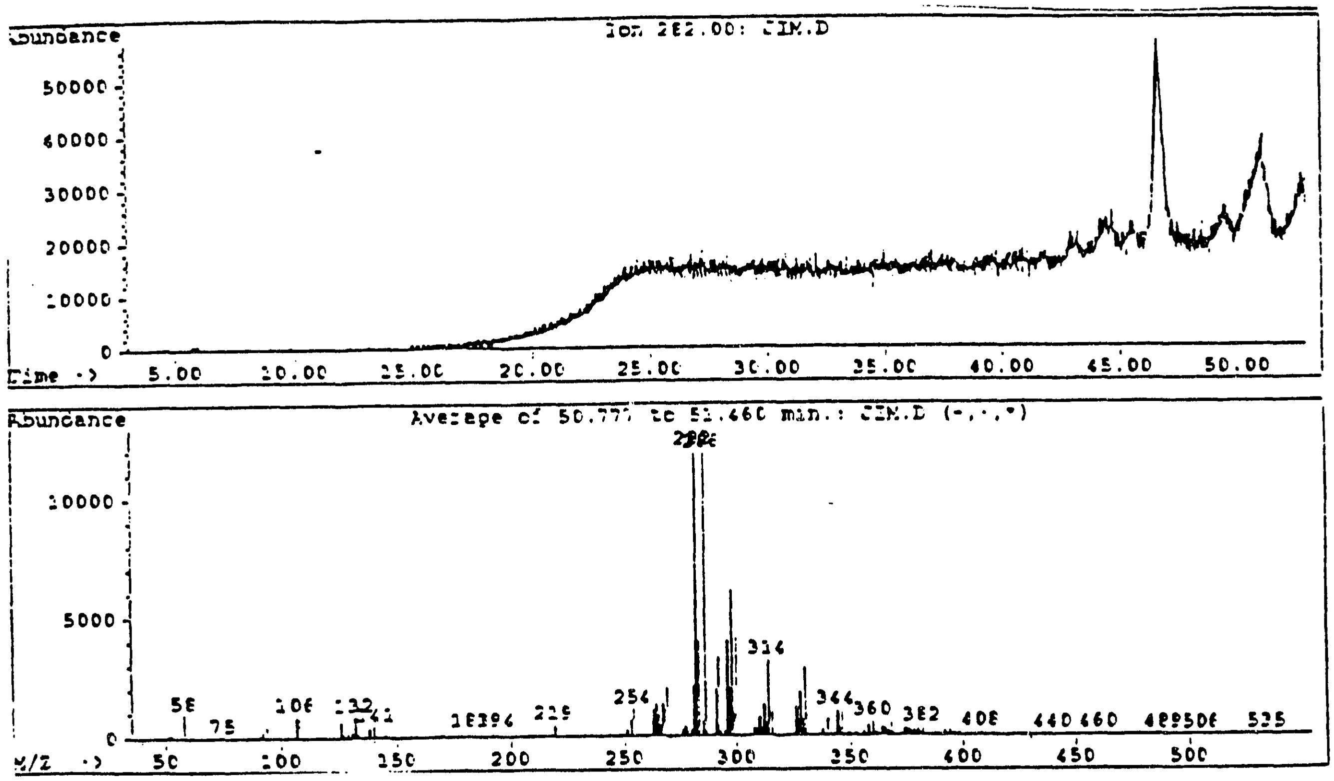




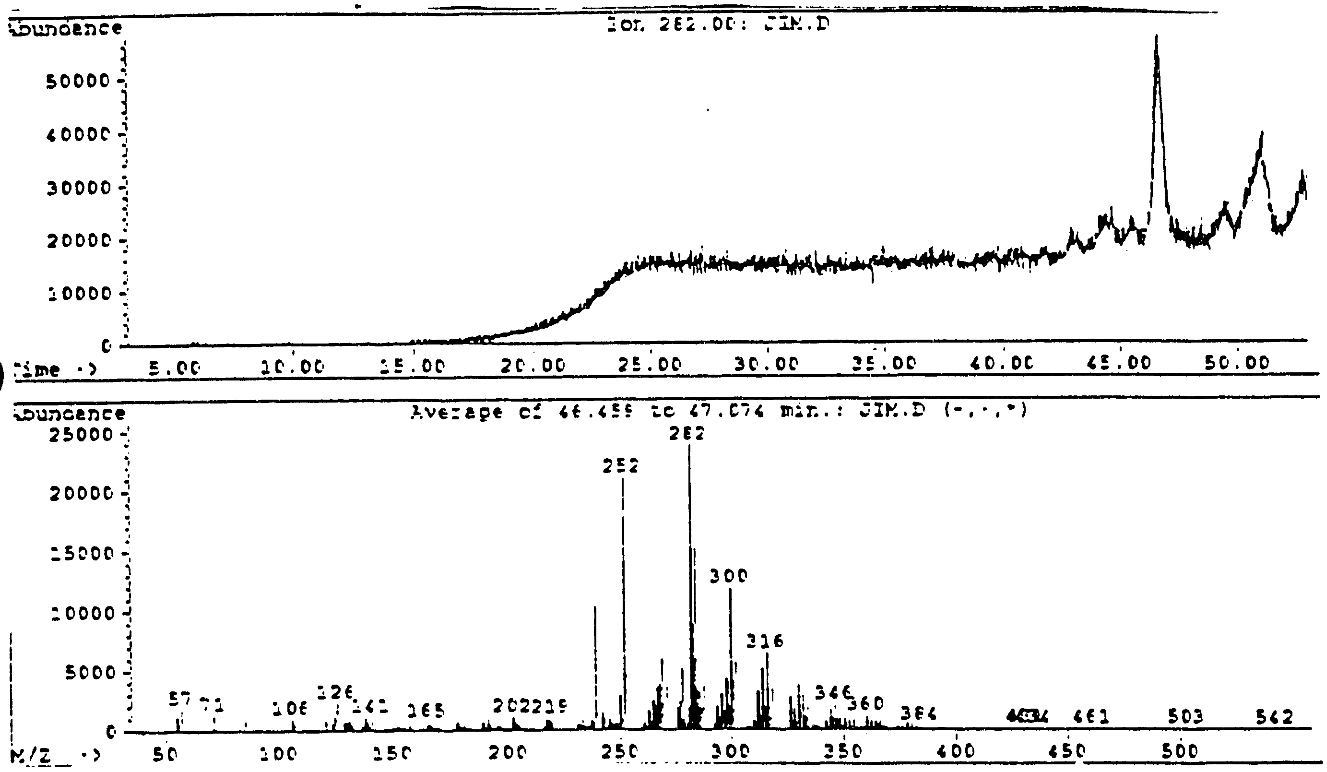
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 300 and Corresponding Mass Spectrum Averaged from 45.4 to 45.7 min.



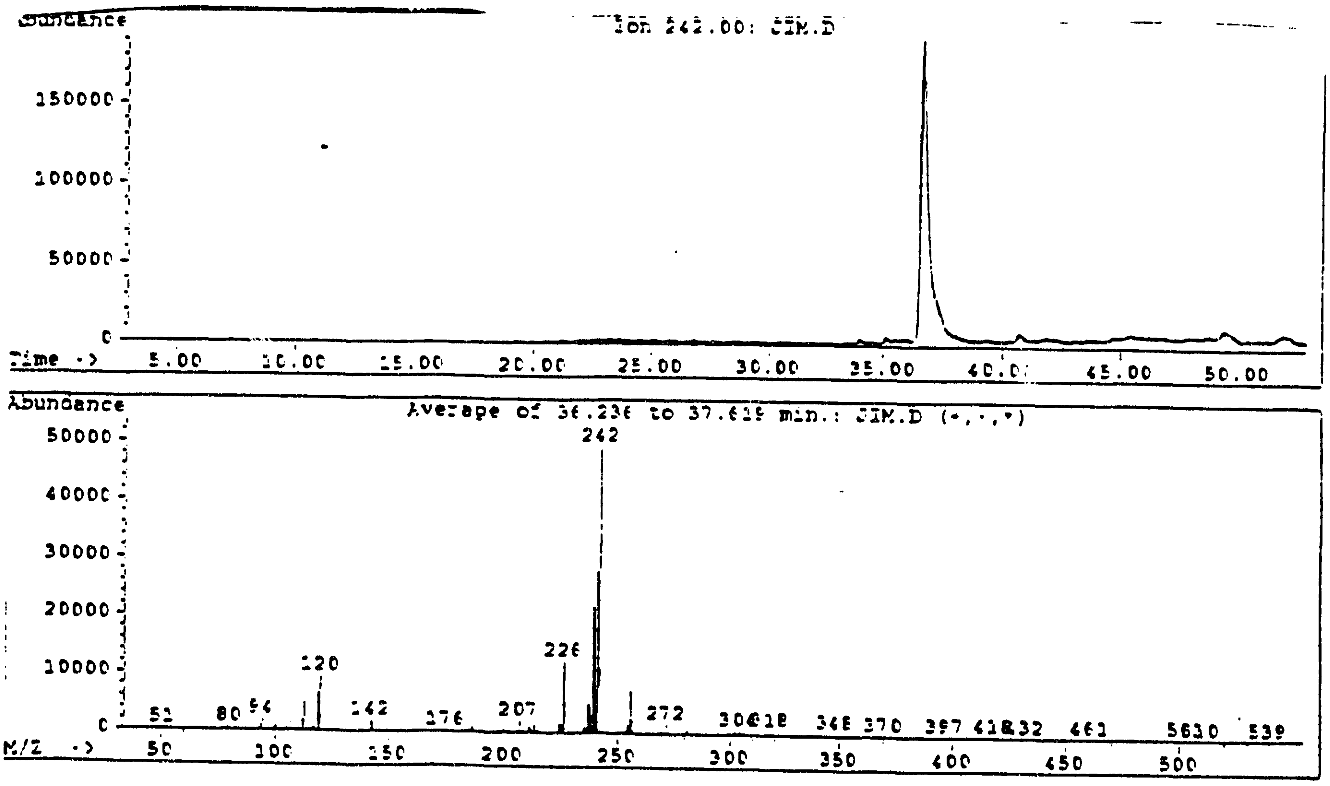
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogramof m/z 282 and Corresponding Mass Spectrum Averaged from 50.8 to 51.5 min.



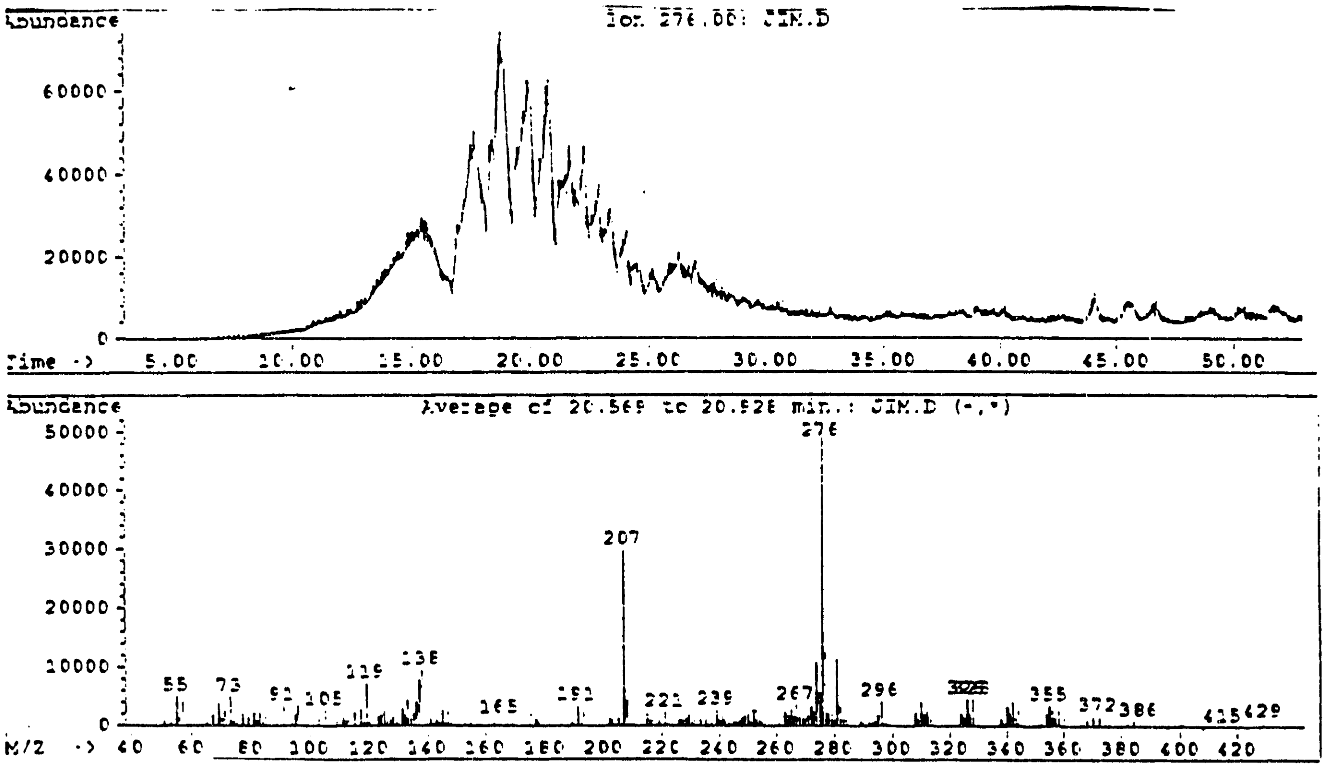
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 282 and Corresponding Mass Spectrum Averaged from 46.5 to 47.1 min.



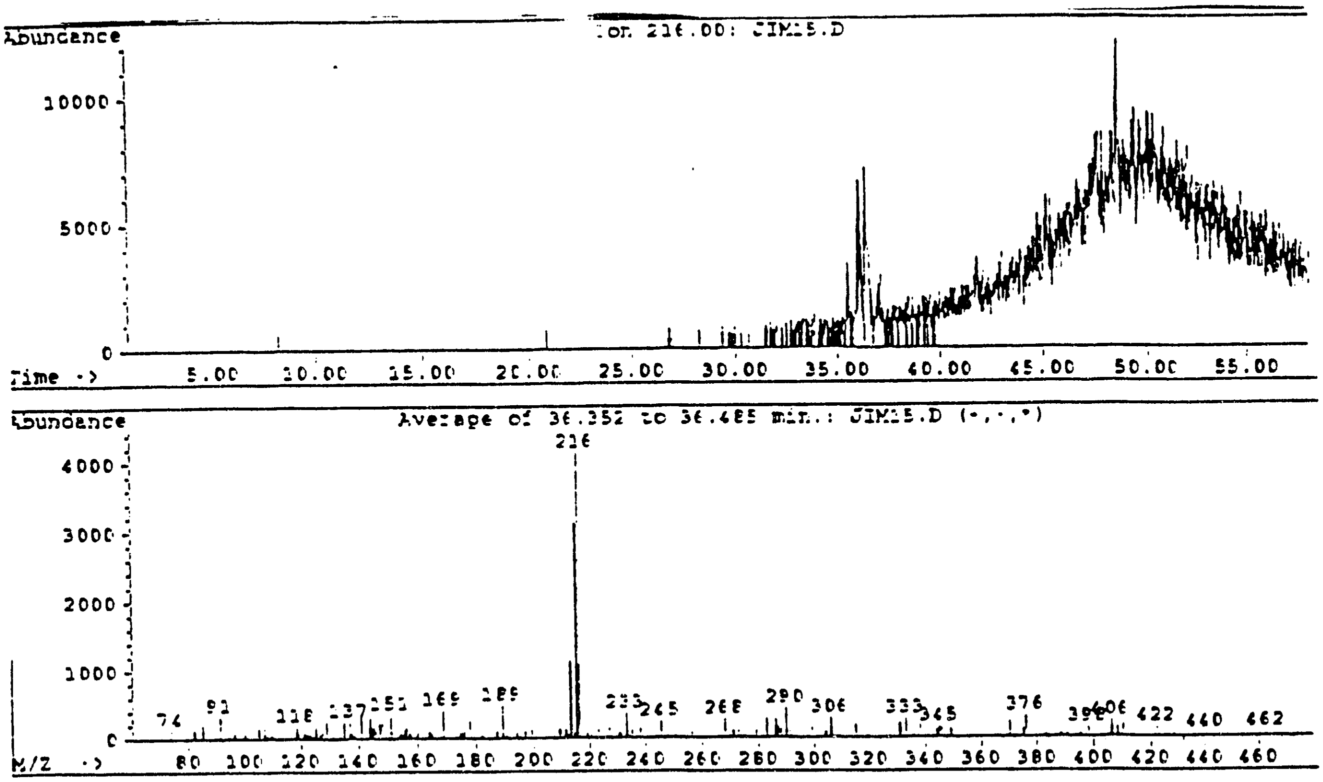
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 242 and Corresponding Mass Spectrum.



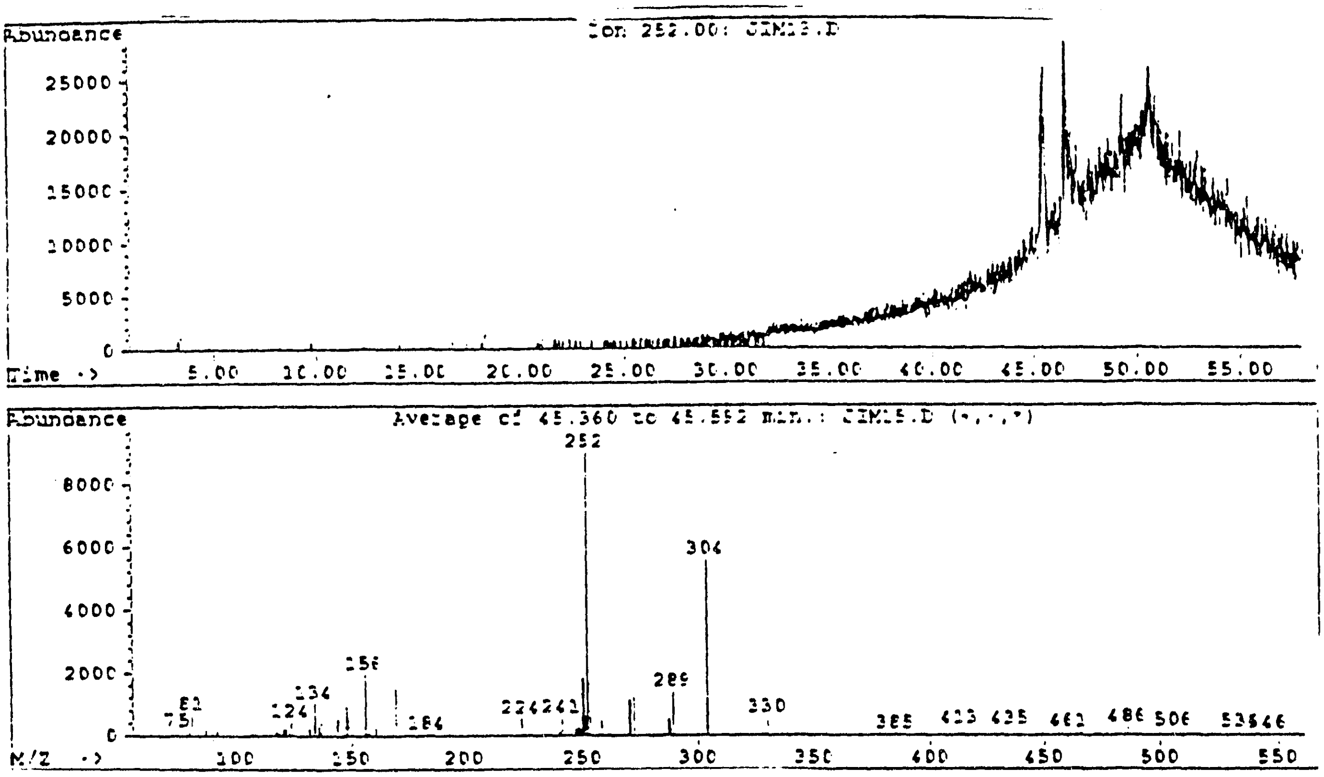
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 276 and Corresponding Mass Spectrum.



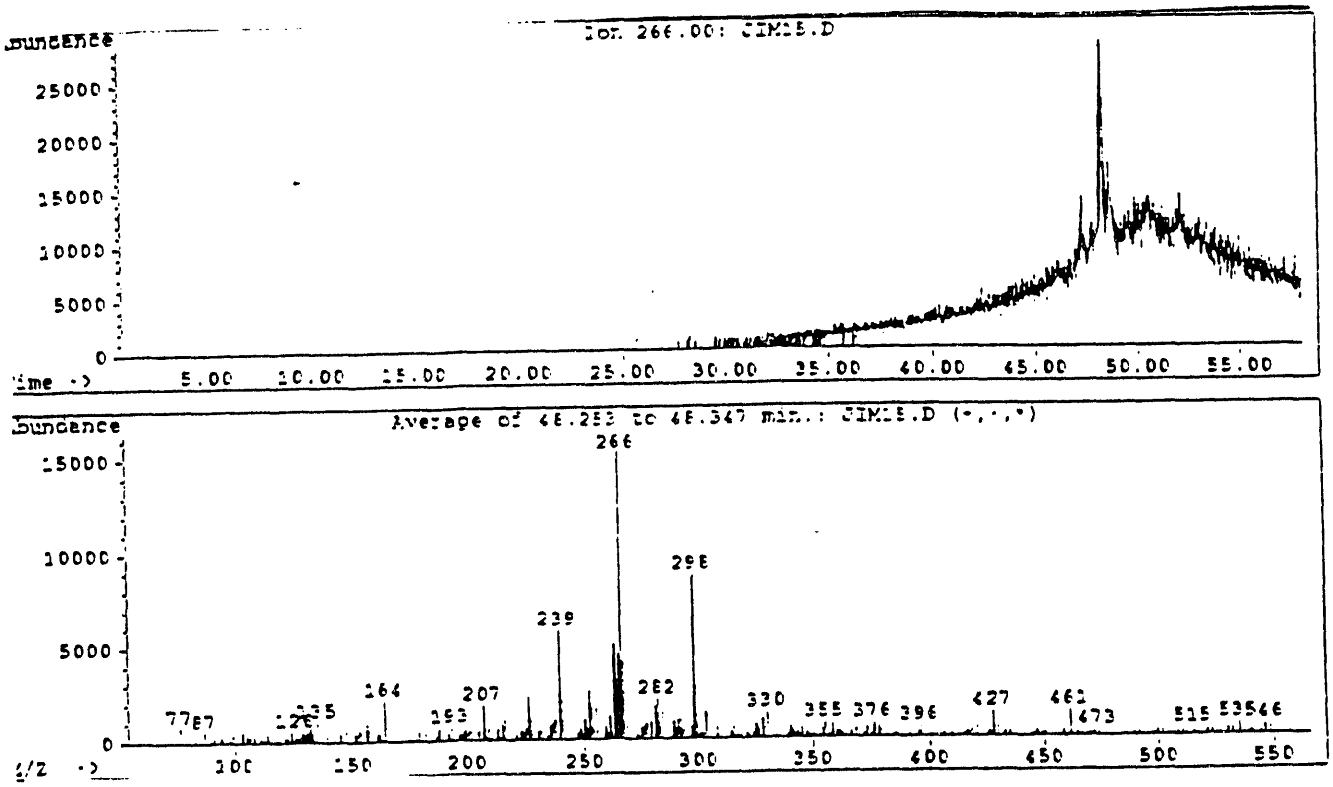
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 216 and Corresponding Mass Spectrum.



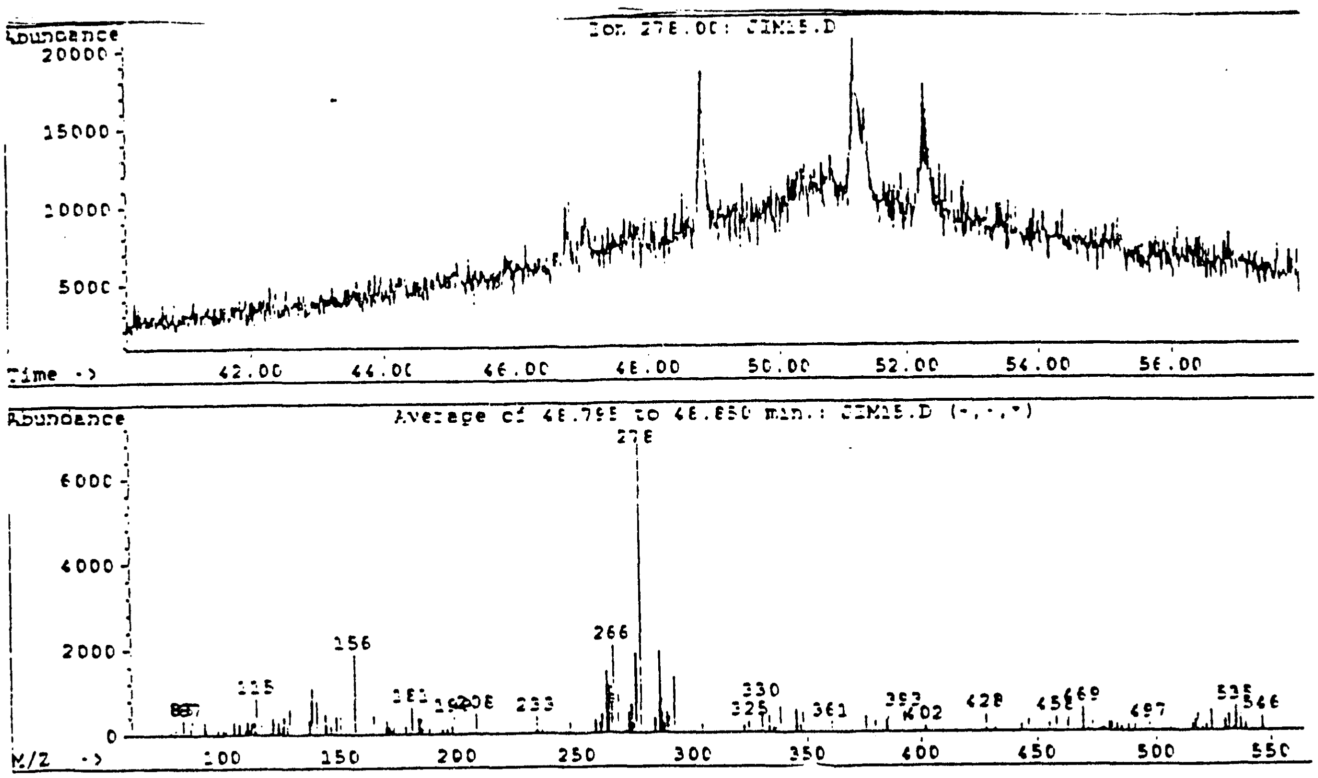
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 252 and Corresponding Mass Spectrum.



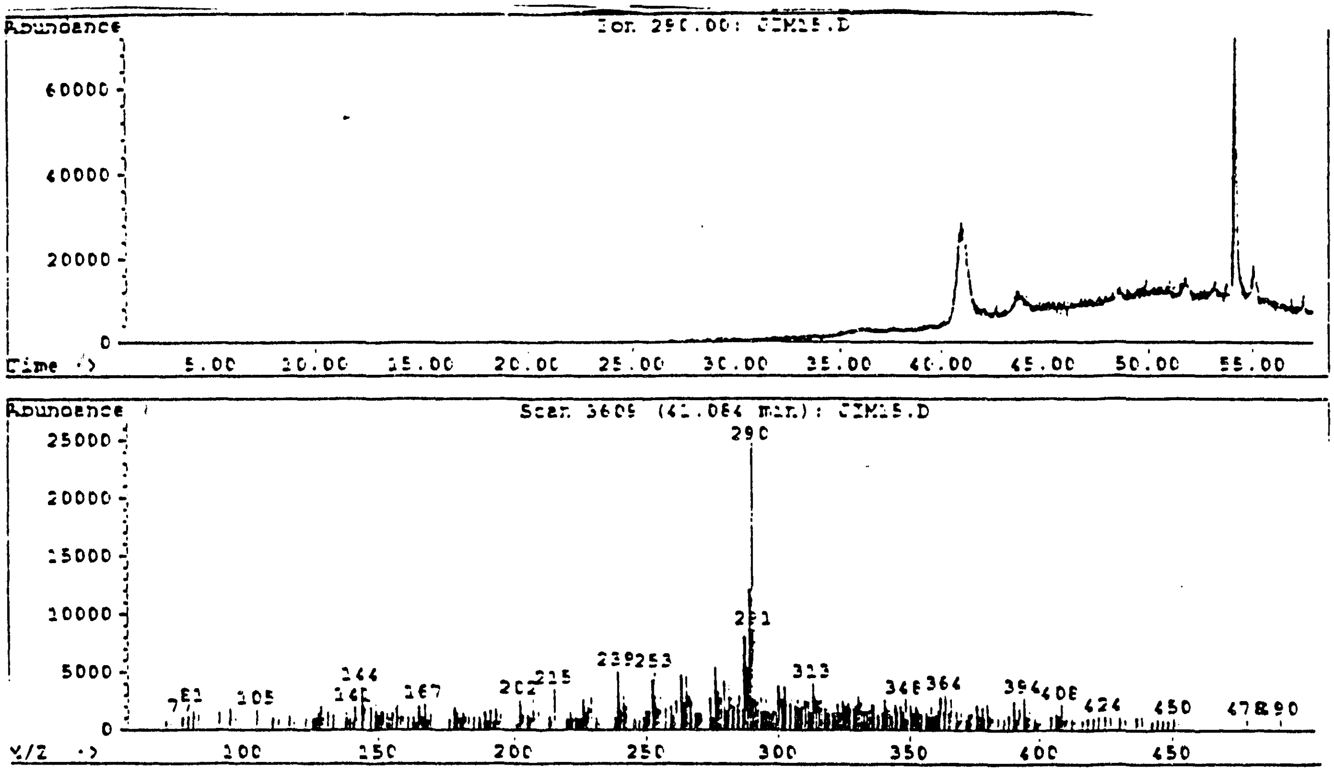
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 266 and Corresponding Mass Spectrum.



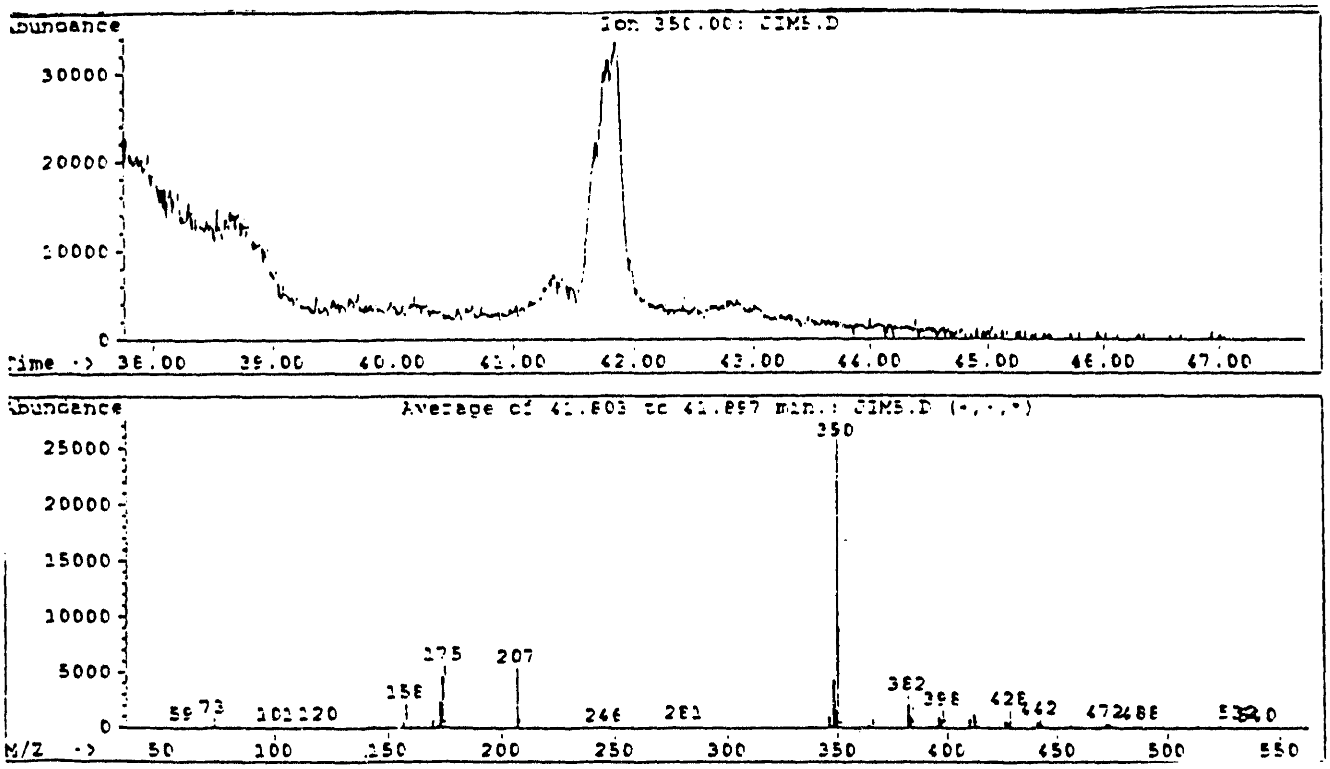
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 278 and Corresponding Mass Spectrum.



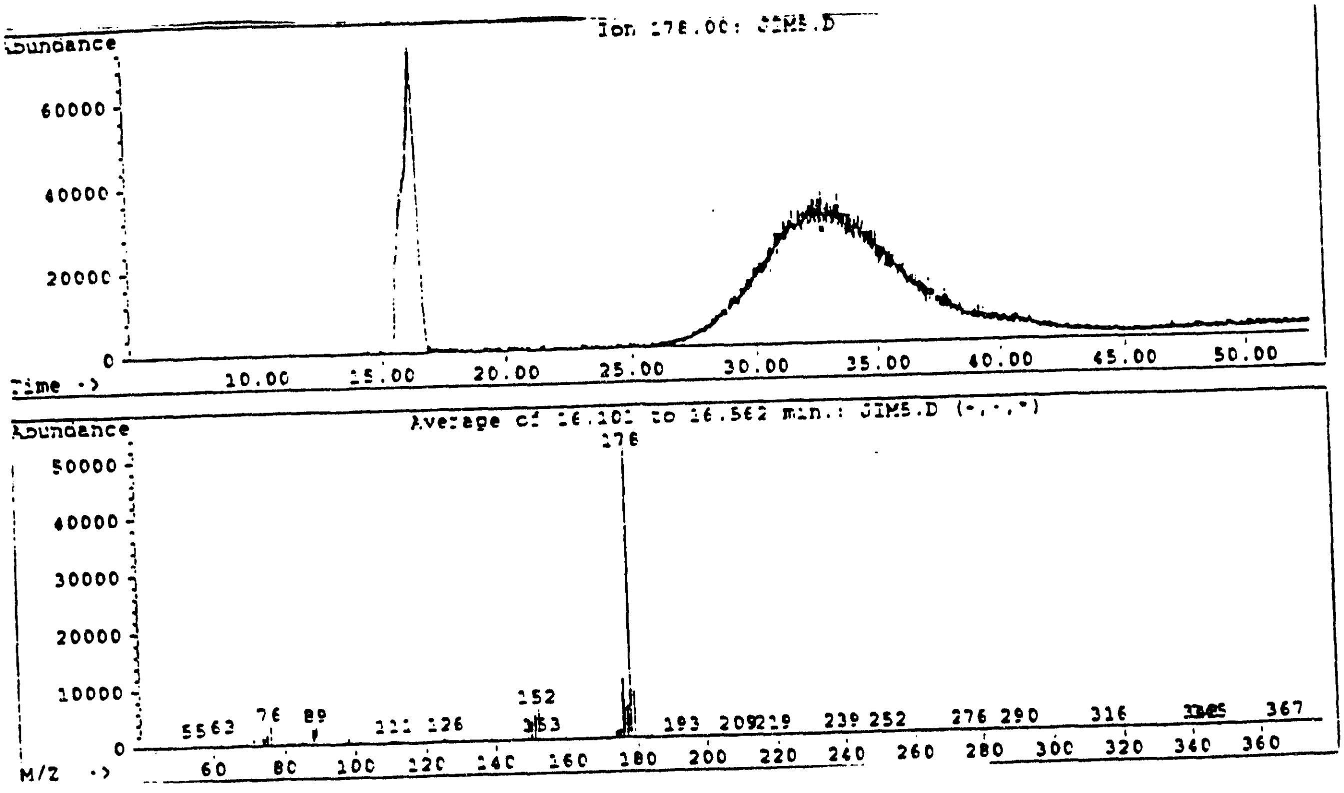
Sample 22 GC/MSD (with SE-54 column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 290 and Corresponding Mass Spectrum.



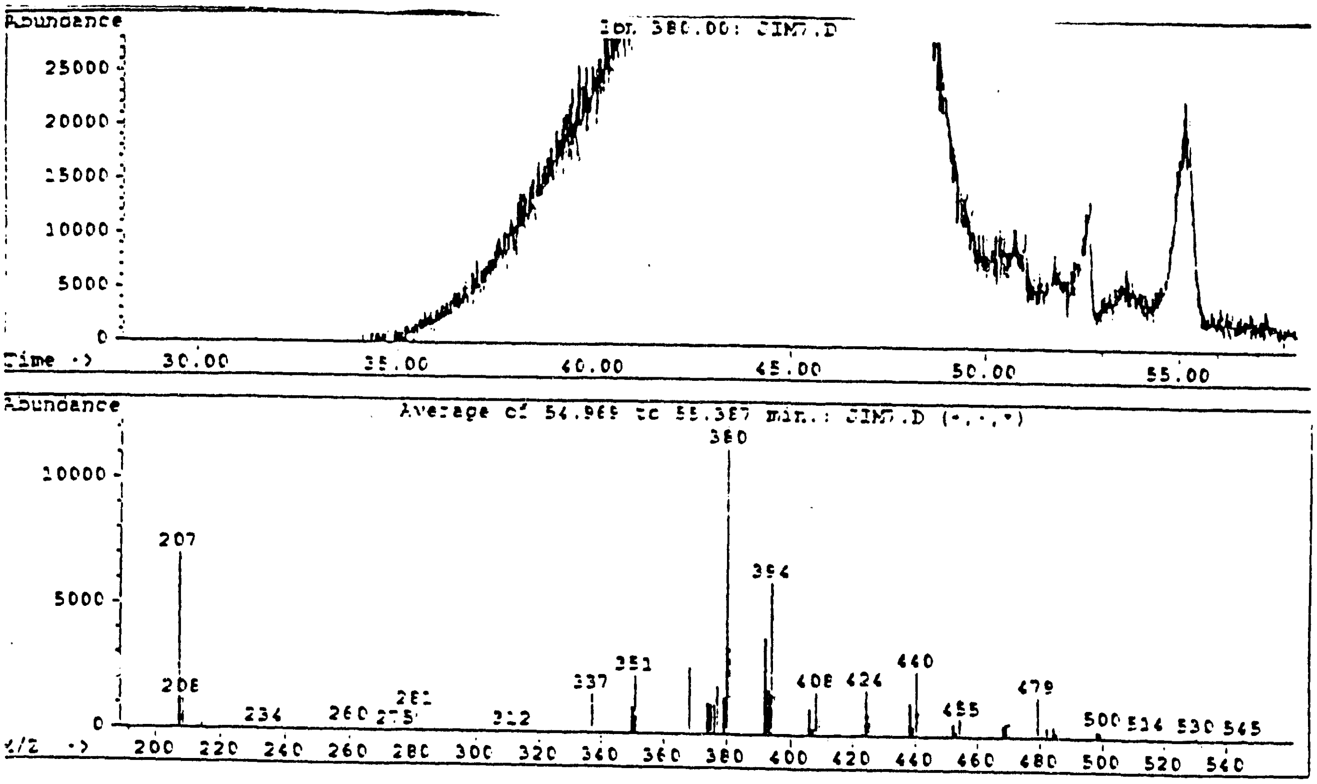
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 350 and Corresponding Mass Spectrum .



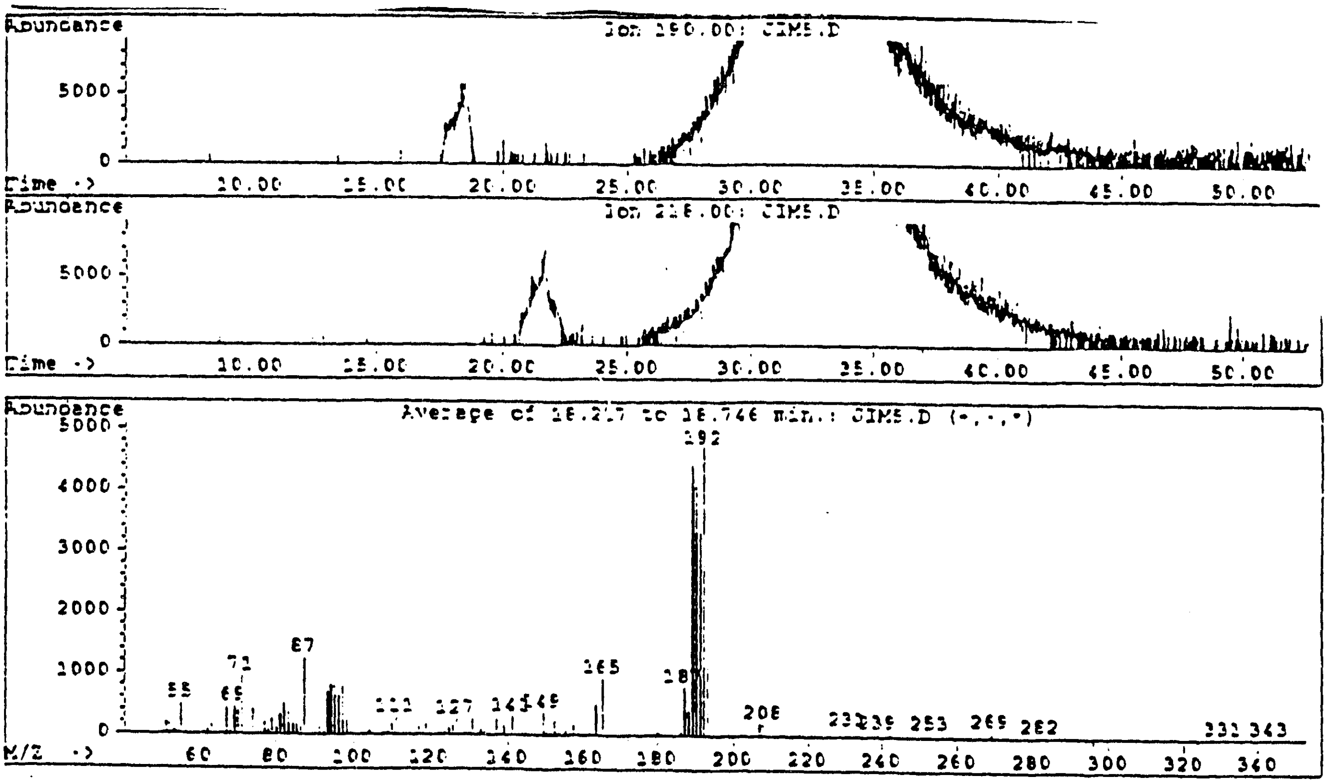
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 178 and Corresponding Mass Spectrum .



Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogramof m/z 380 and Corresponding Mass Spectrum .

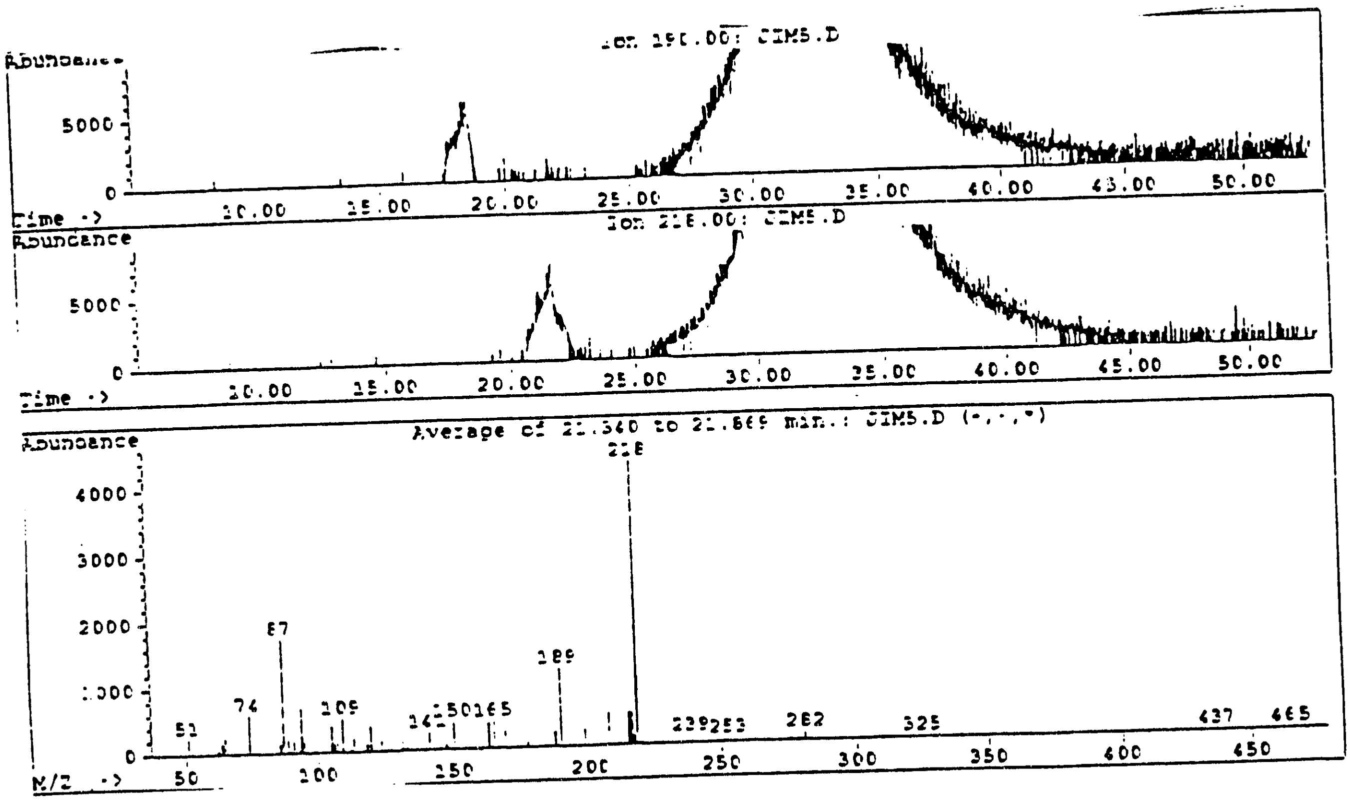


Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 190 and 218 and Corresponding Mass Spectrum Averaged from 18.2 to 18.5 min.

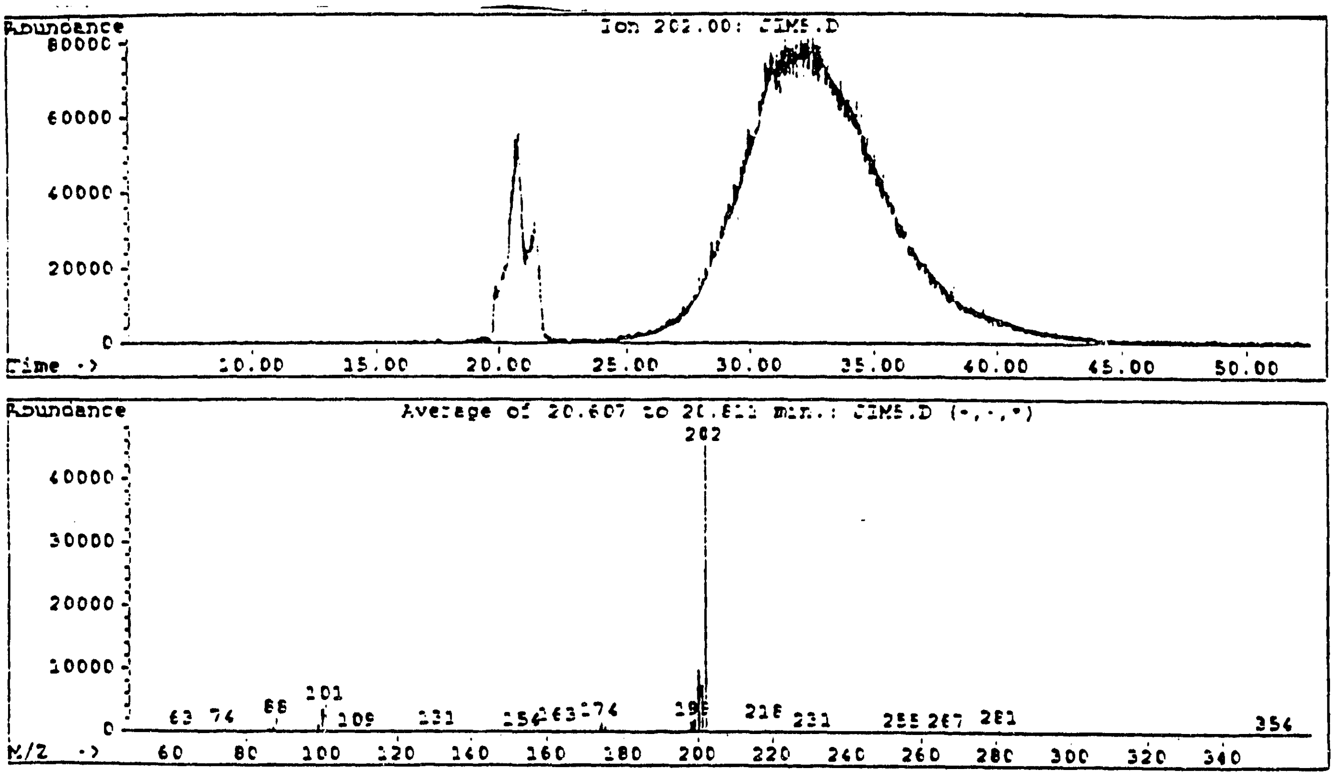


[redacted]

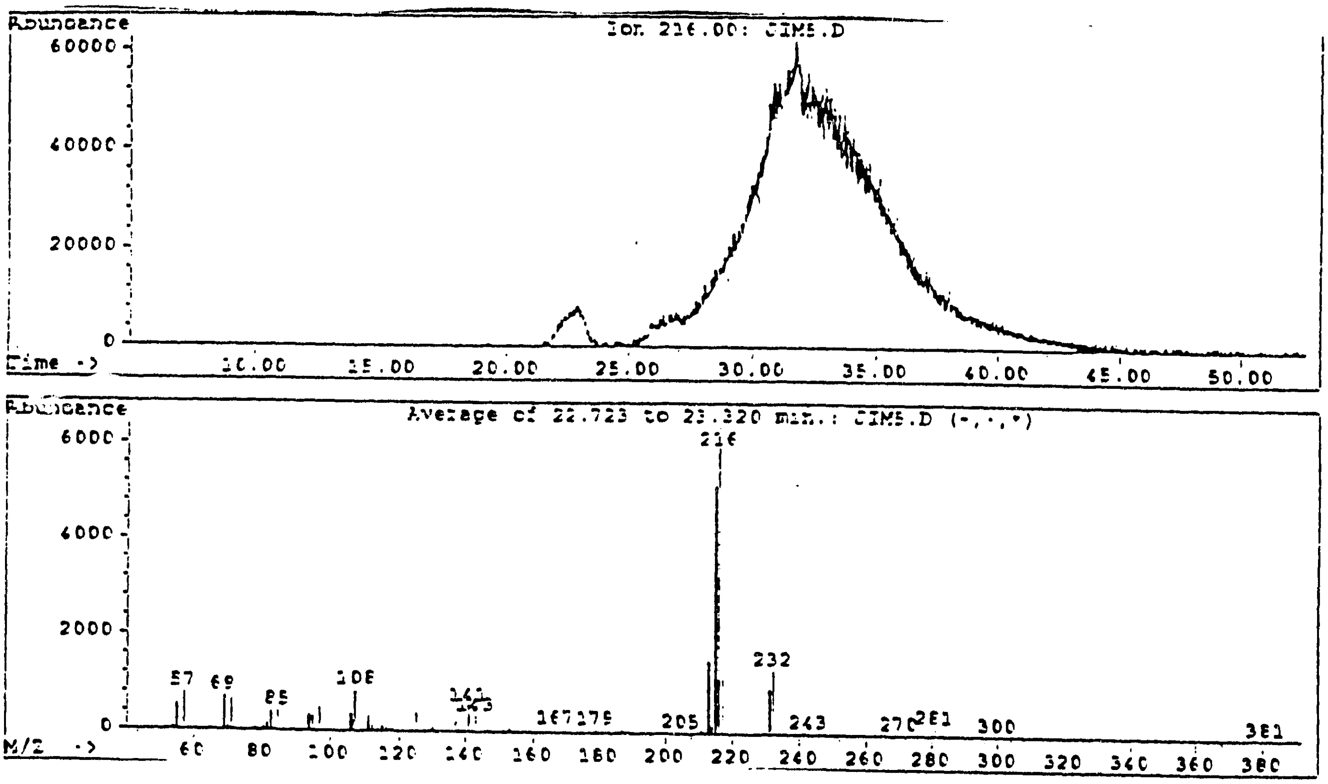
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 190 and 218 and Corresponding Mass Spectrum Averaged from 21.3 to 21.9 min.



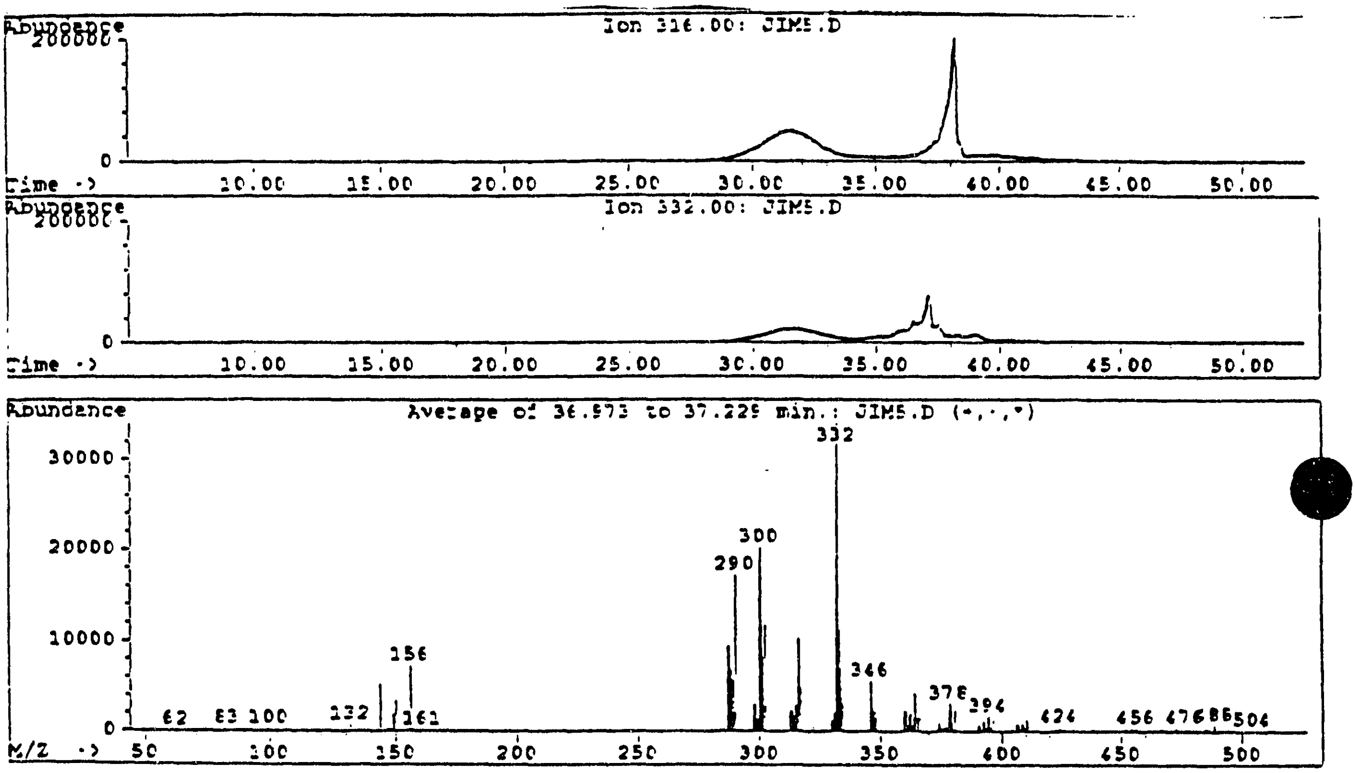
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 202 and Corresponding Mass Spectrum.



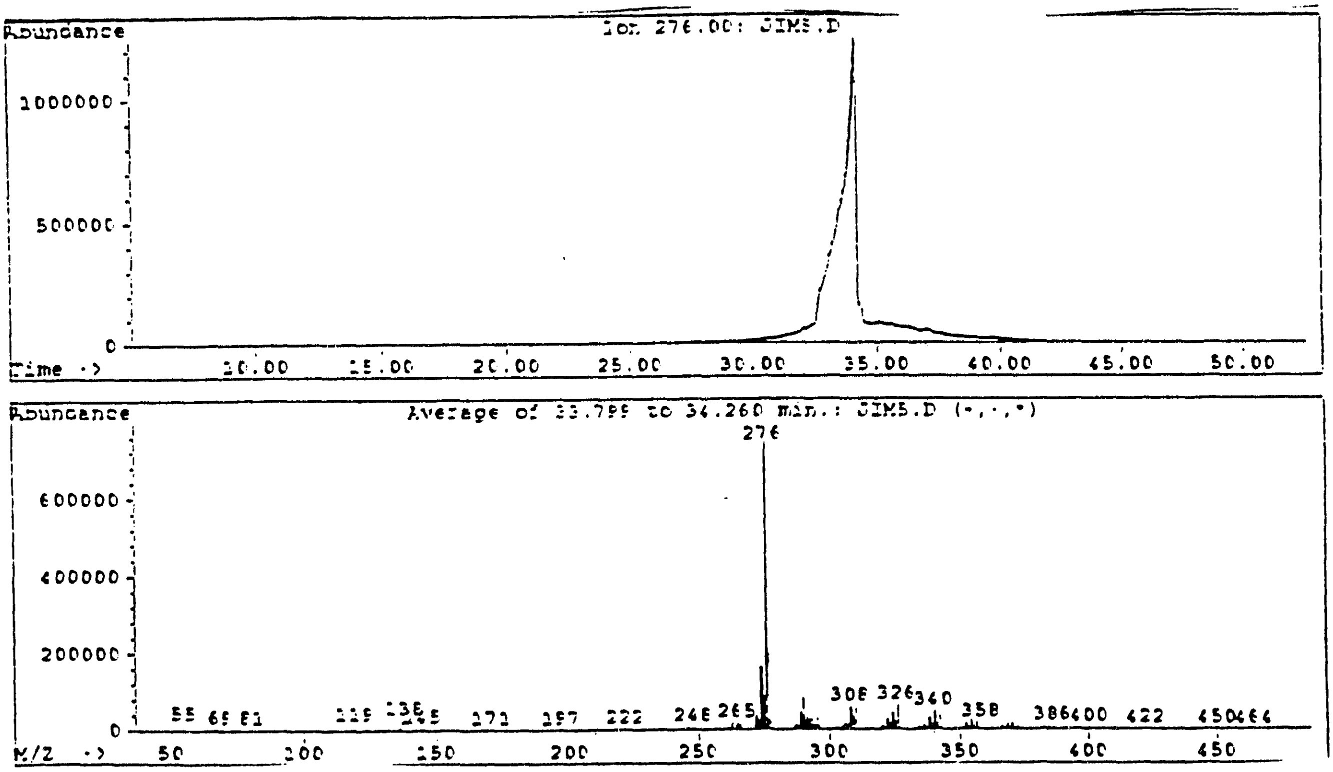
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 216 and Corresponding Mass Spectrum.



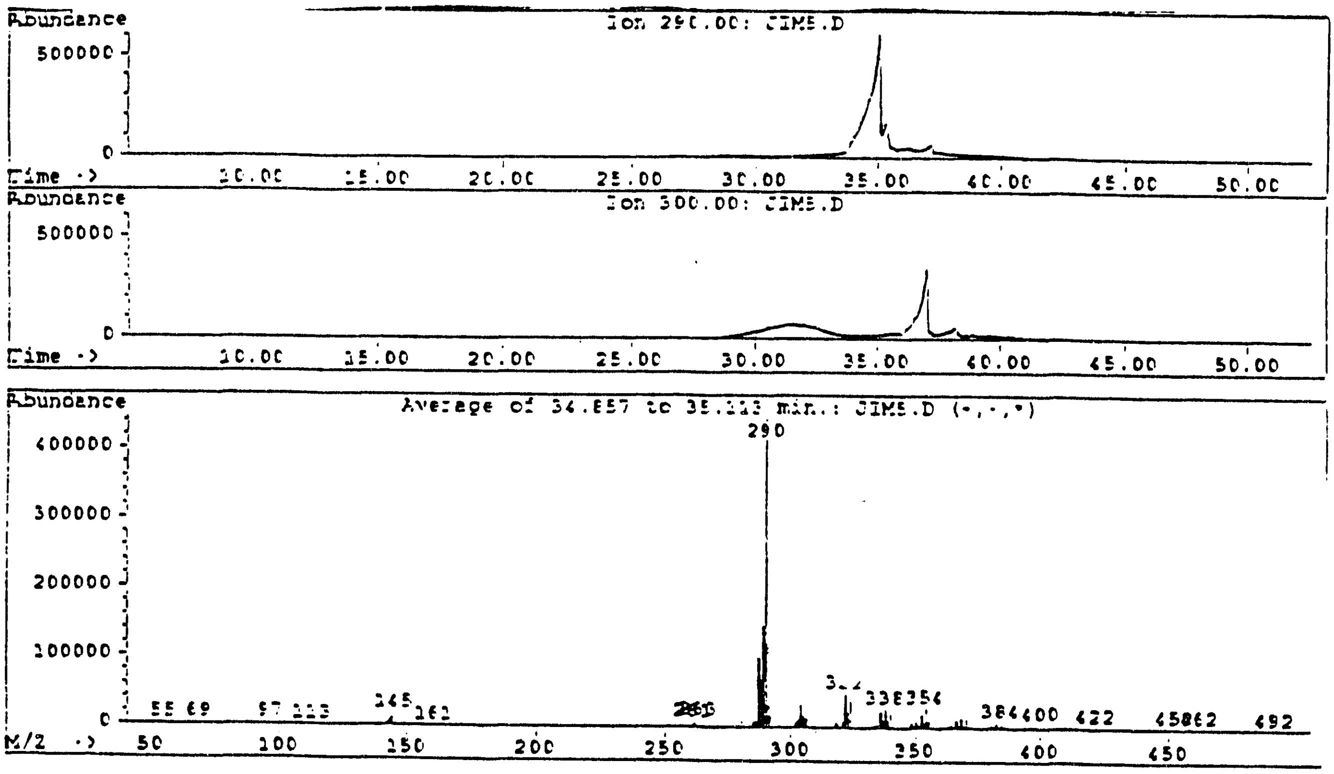
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 316 and 332 and Corresponding Mass Spectrum Averaged from 37.0 to 37.2 min.



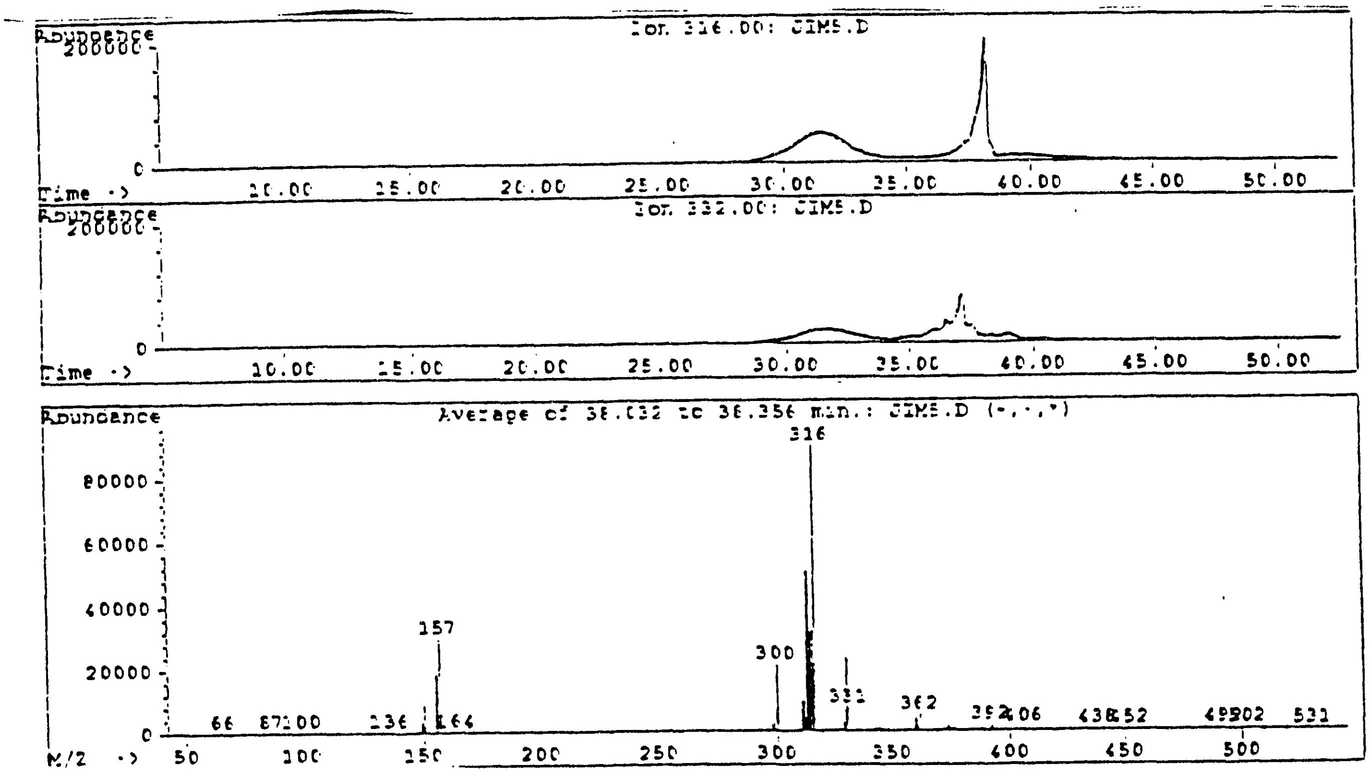
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 276 and Corresponding Mass Spectrum.



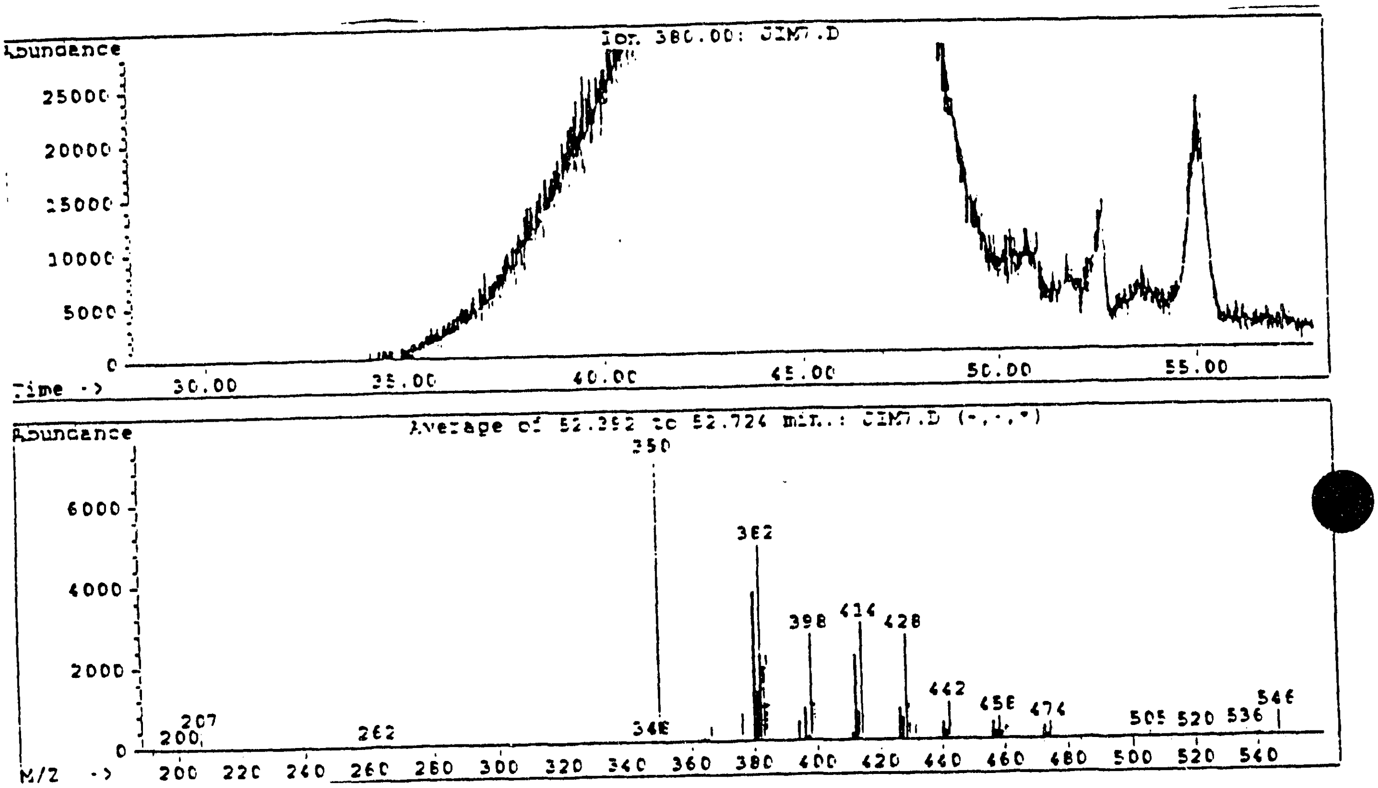
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 290 and 300 and Corresponding Mass Spectrum Averaged from 34.9 to 35.1 min.



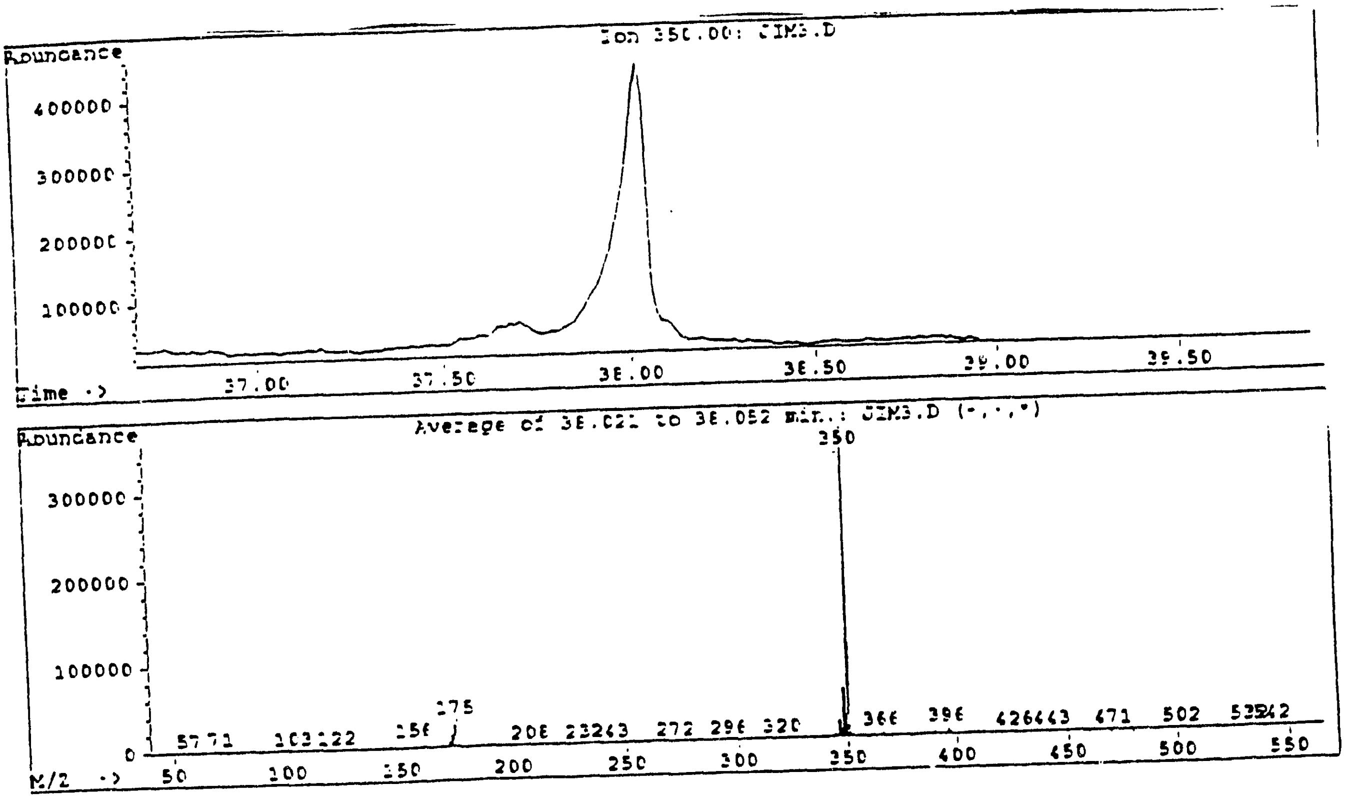
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatograms of m/z 316 and 332 and Corresponding Mass Spectrum Averaged from 38.0 to 38.4 min.



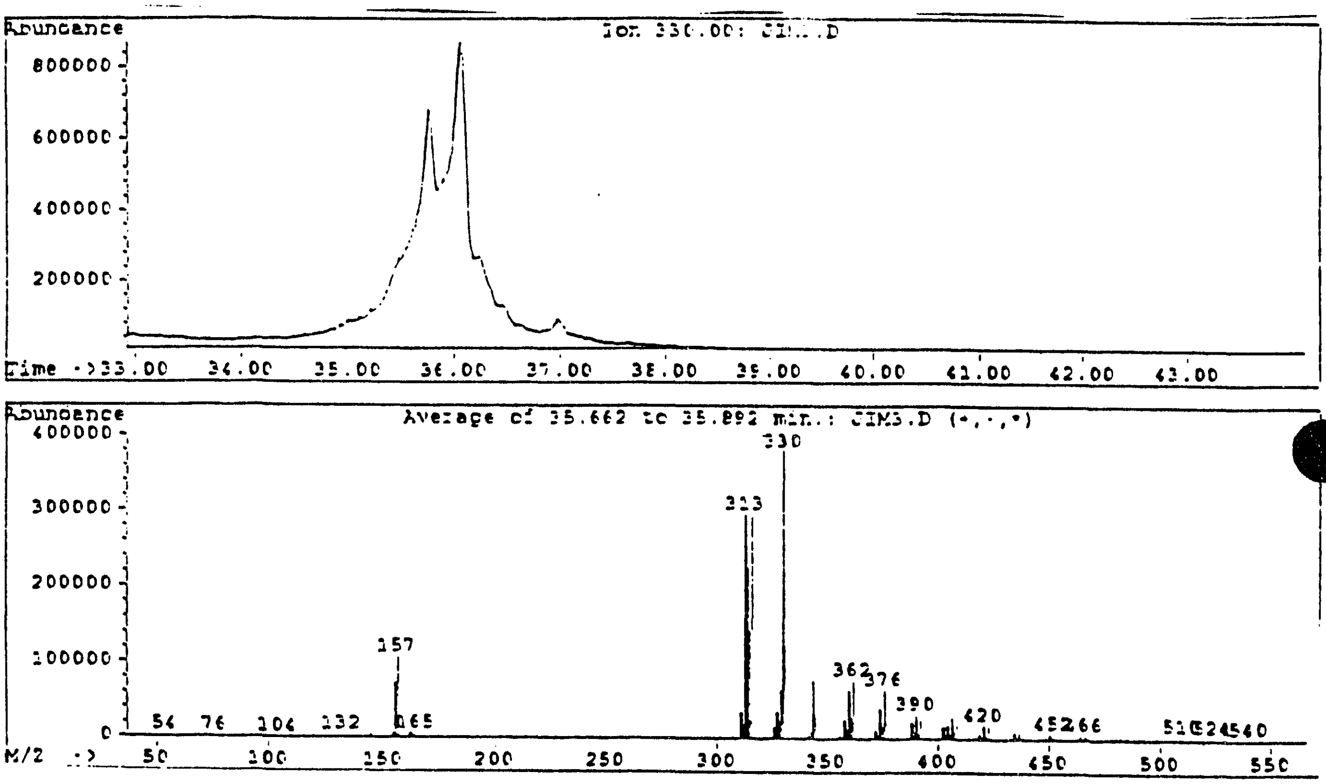
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 380 and Corresponding Mass Spectrum Averaged from 52.4 to 52.7 min.



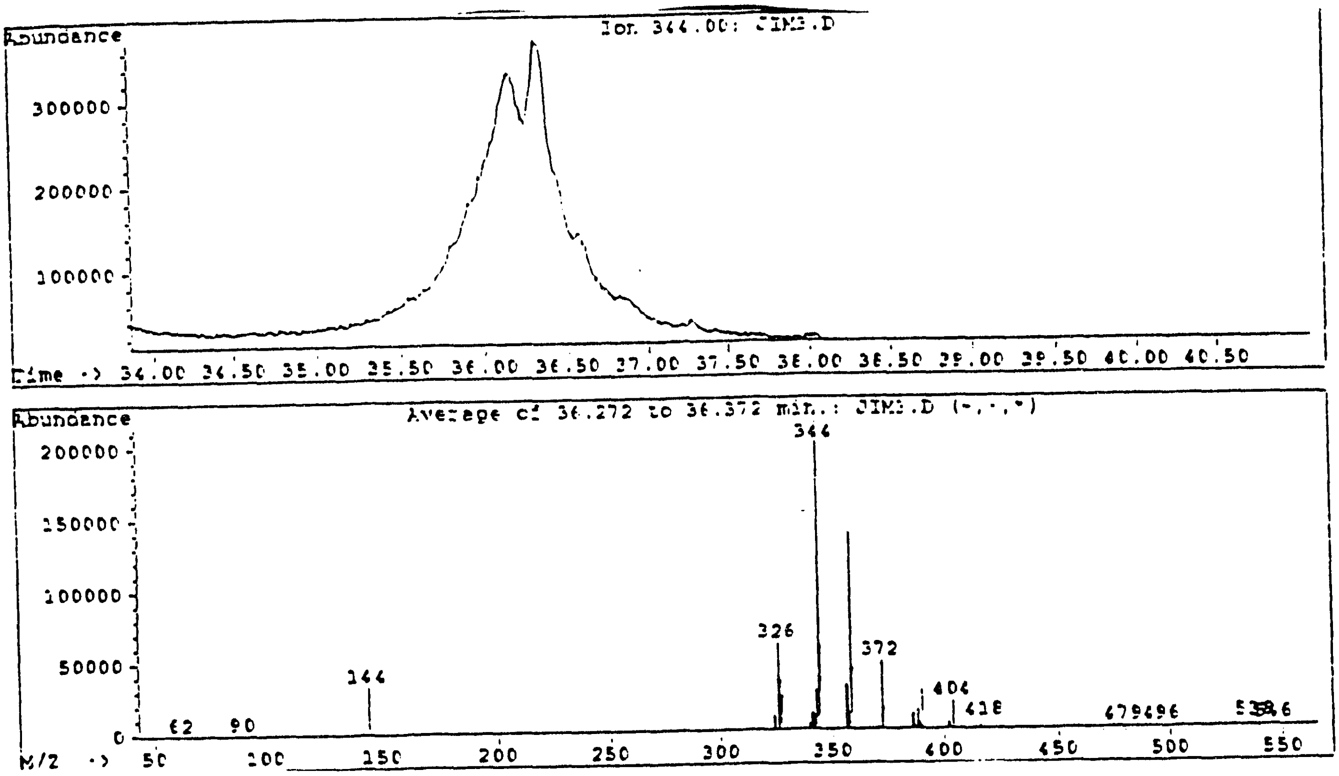
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 350 and Corresponding Mass Spectrum Averaged from 38.0 to 38.1 min.



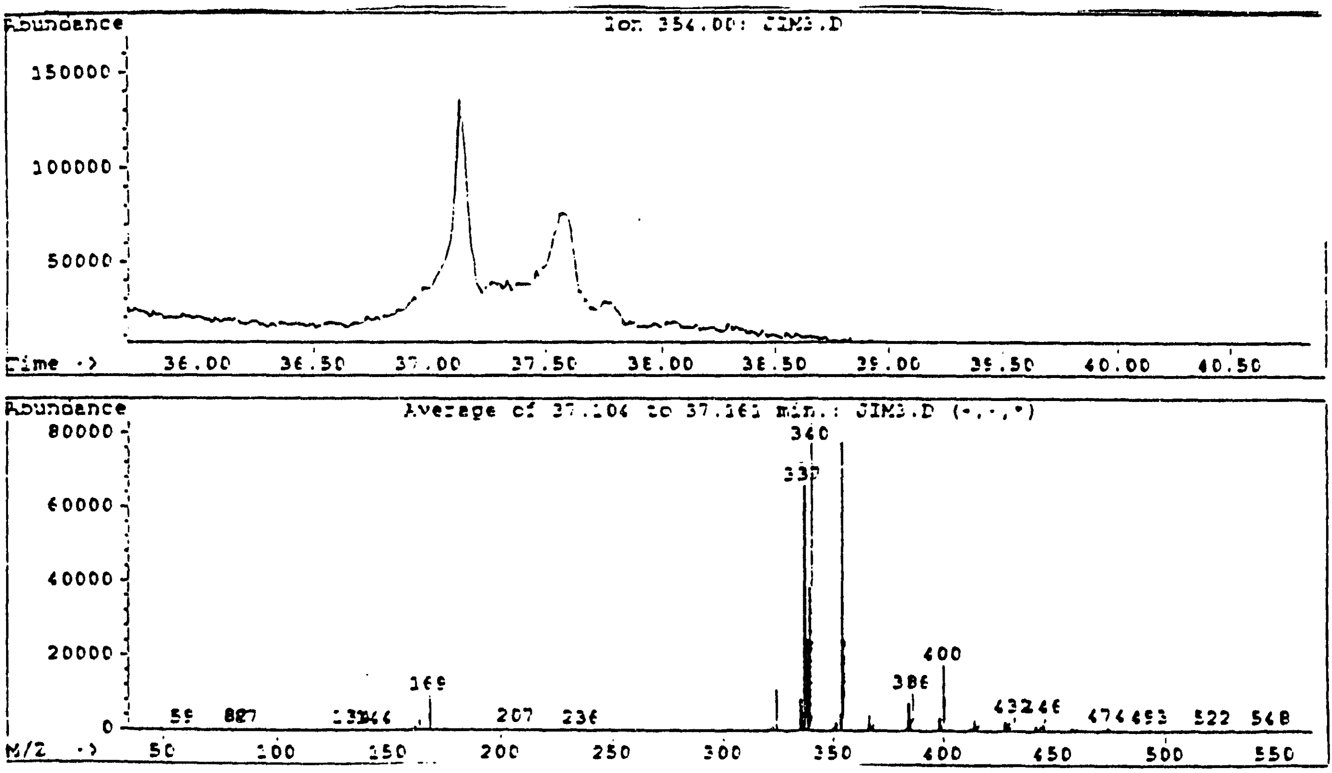
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 330 and Corresponding Mass Spectrum.



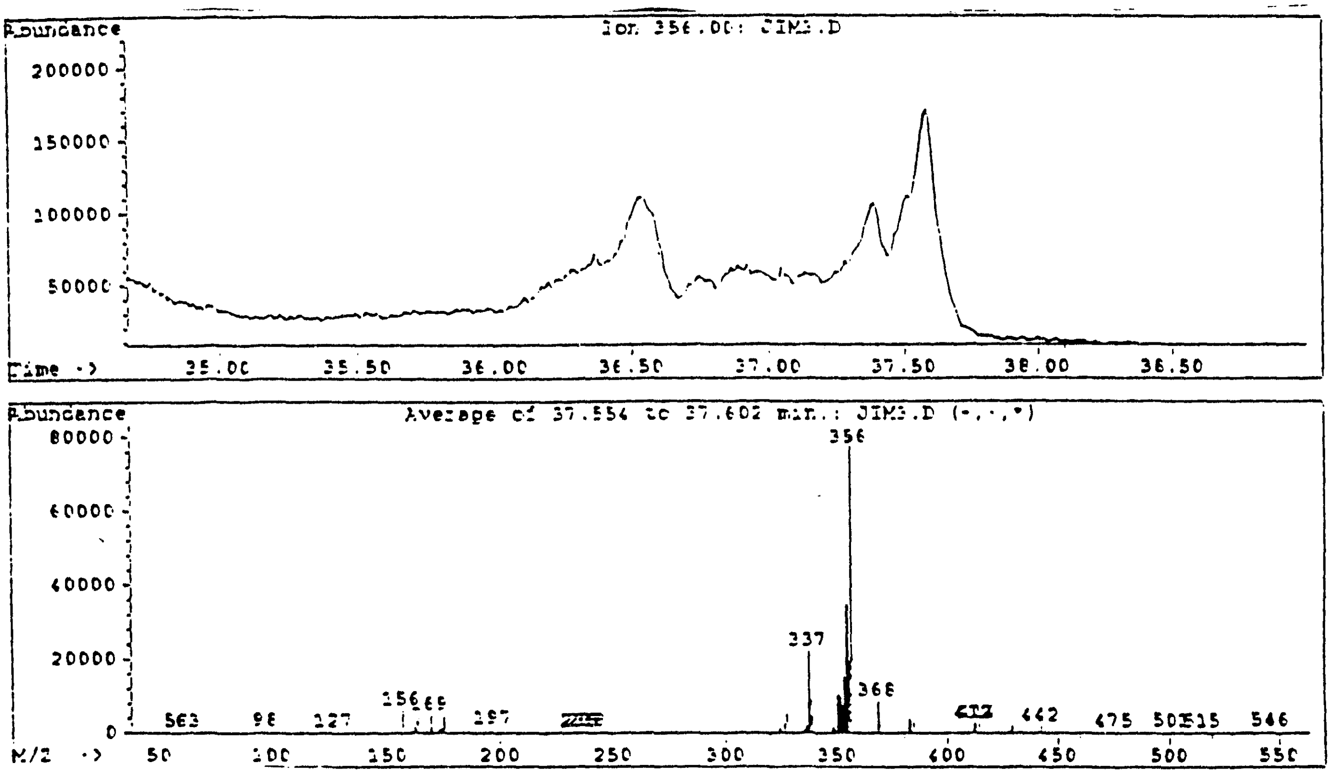
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 344 and Corresponding Mass Spectrum Averaged from 36.3 to 36.4 min.



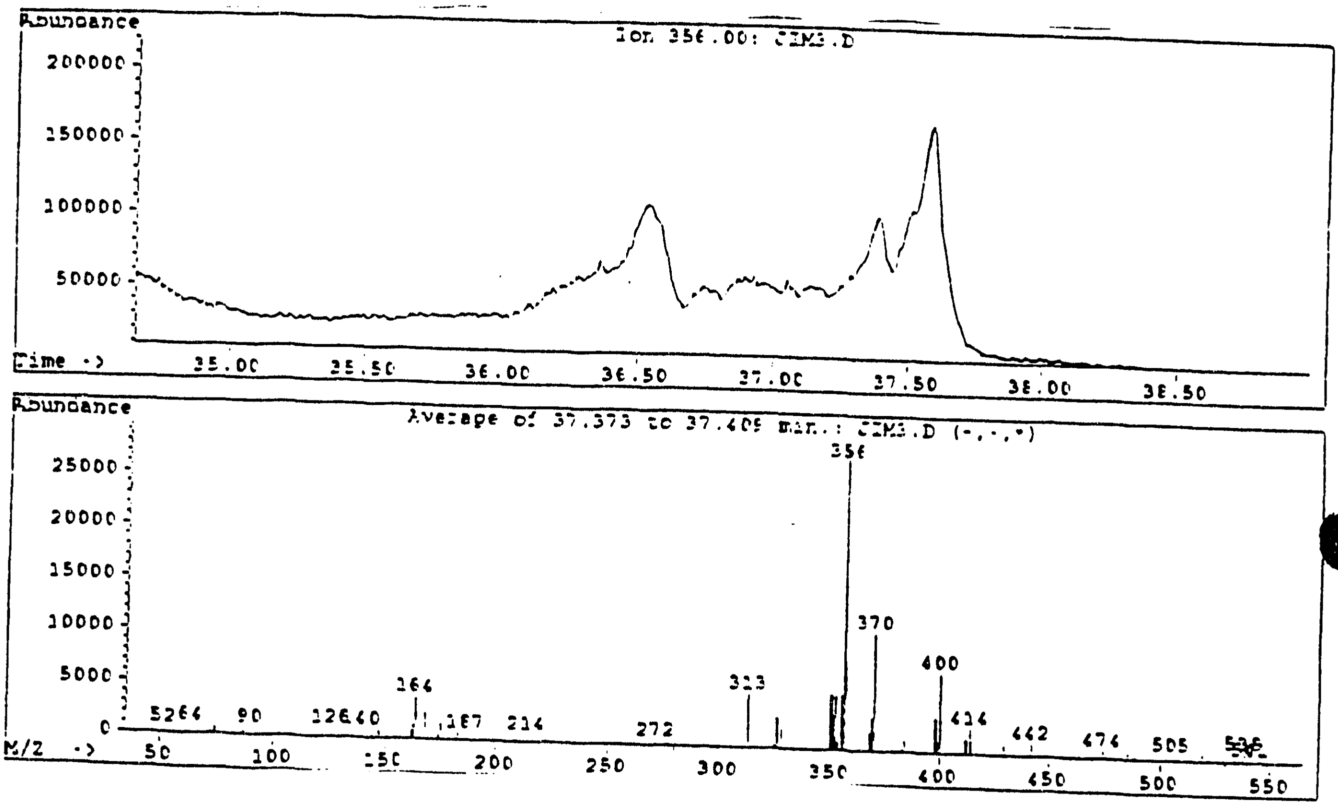
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 354 and Corresponding Mass Spectrum Averaged from 37.1 to 37.2 min.



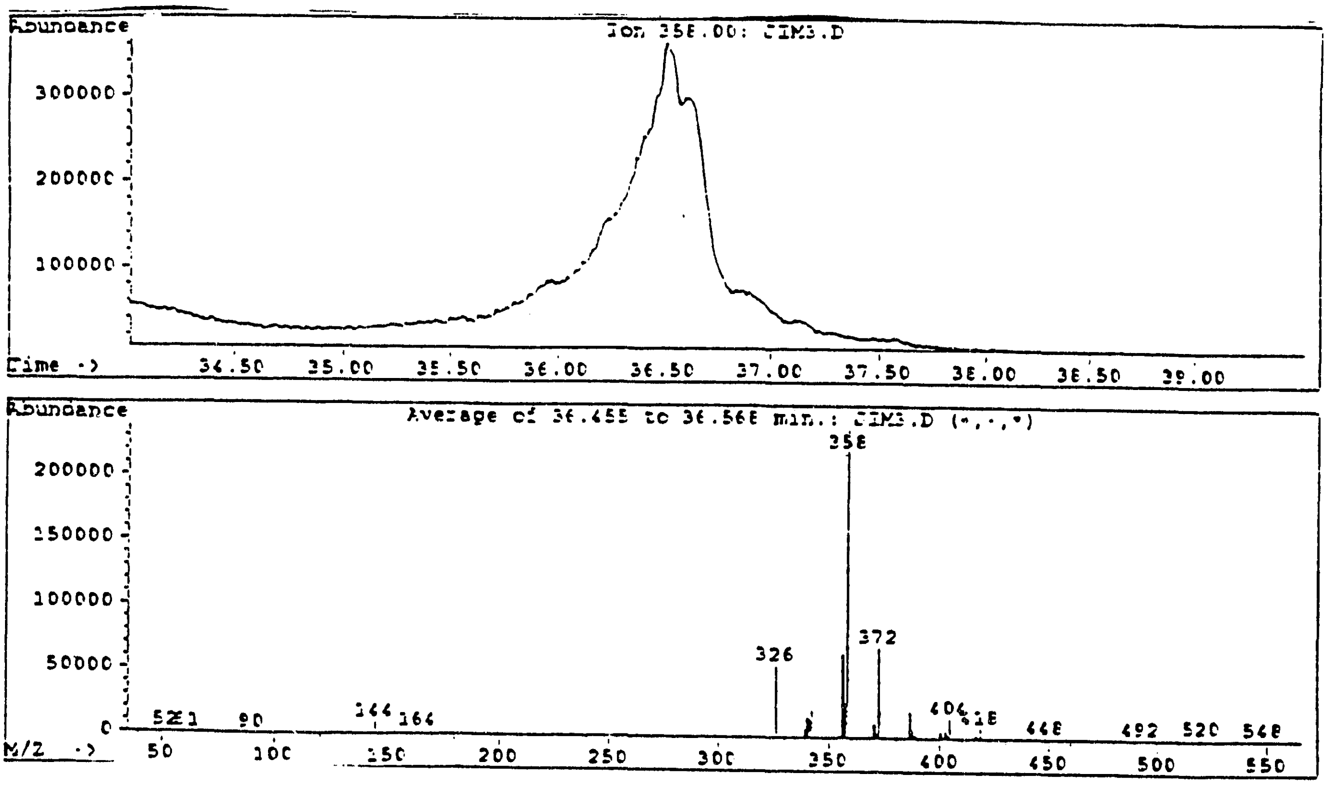
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 356 and Corresponding Mass Spectrum Averaged from 37.5 to 37.6 min.



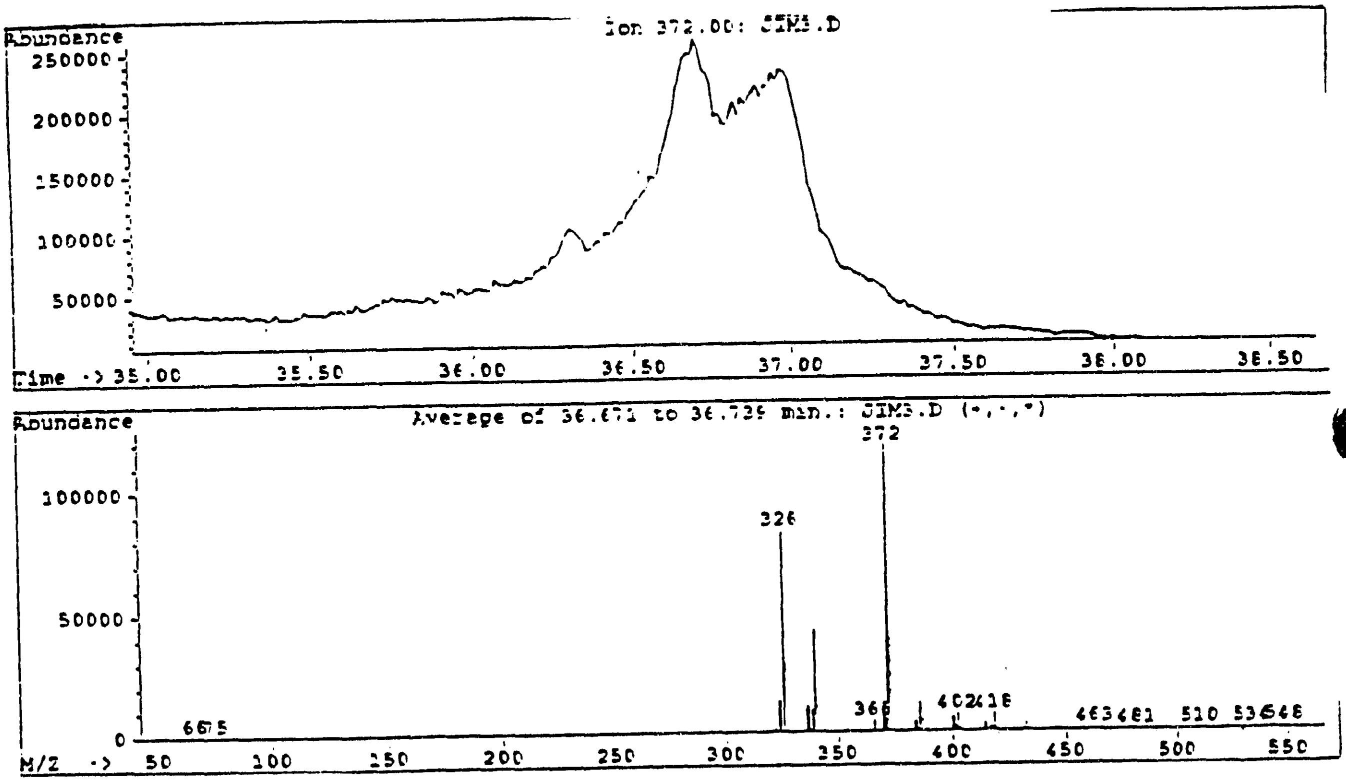
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 356 and Corresponding Mass Spectrum Averaged from 37.3 to 37.4 min.



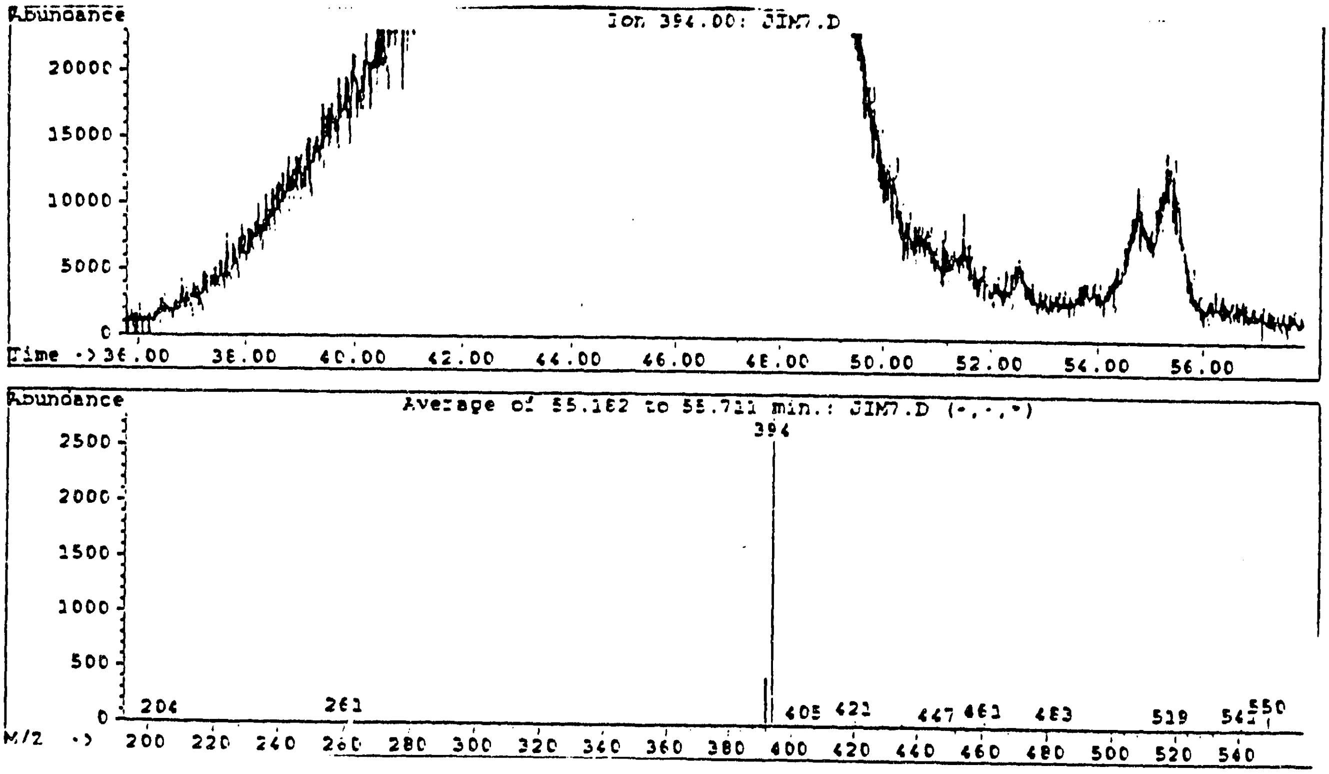
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 358 and Corresponding Mass Spectrum Averaged from 36.5 to 36.6 min.



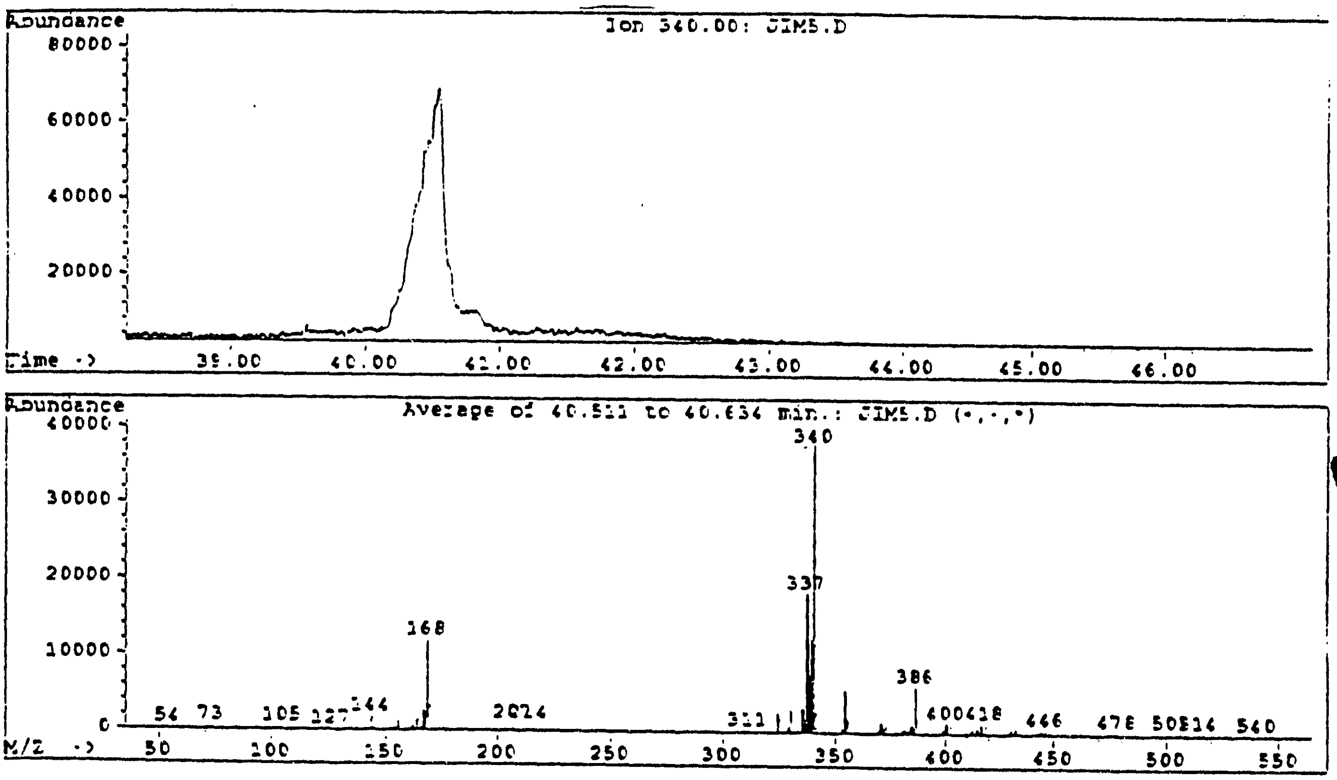
Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 372 and Corresponding Mass Spectrum Averaged from 37.5 to 37.6 min.



Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 394 and Corresponding Mass Spectrum.



Sample 22 GC/MSD (with Al clad Quadrex column) of Hexane Fraction from Open Column Chromatography (alumina, florisil, silica) of Supercritical Fluid Extract. Extracted Single Ion Chromatogram of m/z 340 and Corresponding Mass Spectrum.



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