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Identification of Organosulfur Compounds in Illinois Coal

Mandy N. Amin

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IDENTIFICATION OF ORGANOSULFUR

COMPOUNDS IN ILLINOIS COAL

(TITLE)

BY

MANDY N. AMIN

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IDENTIFICATION OF ORGANOSULFUR

COMPOUNDS IN ILLINOIS COAL

BY

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ABSTRACT

The goal of this research was to identify representative organosulfur compounds in Illinois coal which are removed by a mild, chemical desulfurization procedure. Pyridine was used to extract three raw Illinois coals. Coal with a significant amount of elemental sulfur was treated with 1:1 HCl/HF followed by lithium aluminum hydride before pyridine extraction. Pyridine soluble extracts were extracted with tetrahydrofuran. Nickel boride desulfurization was performed on the soluble extracts of the three coals. The before and after desulfurized THF soluble extracts were fractionated and purified by liquid chromatography and the eluents were analyzed by gas chromatography/mass spectrometry to characterize the sulfur compounds and to determine if the identified compounds reacted during the desulfurization.

Elemental analyses for C, H, and S in both the before and after desulfurized THF soluble extracts were obtained and the percentage of sulfur loss due to nickel boride desulfurization was calculated for each coal. Percentage of sulfur loss for Illinois Basin Coal #101, Argonne Premium Coal Sample Program #301, and Illinois Basin Coal #108 were 26.74%, 24.75%, and 38.07% respectively for the first

desulfurization. For the second desulfurization, they were 8.41%, 35.13%, and 33.03% for Illinois Basin Coal #101, Argonne Premium Coal Sample #301, and Illinois Basin Coal #108 respectively.

The organosulfur compounds identified include 1,2-Benzisothiazole (C_7H_5NS) in IBC-#101, Dibenzothiophene ($C_{12}H_8S$) in Arg-#301, and a compound with empirical formula ($C_{16}H_{18}O_2S$) in IBC-#108. The concentration of Dibenzothiophene decreased after the desulfurization.

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Chapter I

INTRODUCTION

Coal is a combustible rock.¹ From a more chemical point of view, coal is an aggregate of heterogeneous substances composed of organic and inorganic materials.² Organic coal material is formed from plant debris which have undergone geochemical alteration over a period of up to several hundred million years under the influence of pressure and temperature caused by overlying sediments.³ Inorganic materials in coal are primarily mineral matter such as clay, silica and iron pyrites.² As the result of its origin, coal is an almost non-volatile, insoluble, non-crystalline, extremely complex mixture of organic molecules and inorganic minerals varying considerably in size and structure.³ According to the ASTM (American Society of Testing and Materials) system used in the U.S.,⁴ there are mainly four classes of coal: Lignitic, Subbituminous, Bituminous and Anthracitic coal with increasing carbon content and heating value. The structure of coal can be viewed as consisting of hydroaromatic structures with aromaticity increasing from low-rank to high-rank coals.⁵ The heteroatoms oxygen, nitrogen, and sulfur are present in coal in variable amounts.⁵

Total production of coal throughout the world increased

more than fivefold, from about 180 million tons in 1865 to 930 million tons in 1905. World consumption of coal was almost constant during the years between 1912 and 1970, rising during the war years and falling during the great depression and the recessions of the 1950s.⁴ Then coal production increased again during the 1970s as a result of increasing industrialization in previously underdeveloped countries and as a result of increased use of coal caused by the oil price shocks.⁴ Even though the near disintegration of OPEC as a serious world political force and sharp drops in the price of crude oil have caused the increased use predicted for coal in the late 1970s and 1980s to be somewhat faded, growth in coal use is expected, not only since supplies of oil and gas will become quite limited, but also because of the concern of relying on energy imported from politically unstable regions of the world.⁴ In addition, as new processes for more efficient coal burning and conversion to synthetic fuels or chemicals become available, the options for using coal will become more attractive.⁴

Coal is an abundantly available energy source⁵ and the U.S. has a quarter of the world's proven reserves in coal. The full utilization of this energy resource is limited however. One of the reasons for that is the environmental concern resulting from the release of sulfur-containing

pollutants during coal processing and utilization. Sulfur occurs in coal as organic sulfur, as inorganic sulfates and as pyrites.⁶ Organic sulfur is distributed throughout the entire coal.⁵ Organic sulfur is the predominant form of sulfur in low-sulfur coals, but both the organic and pyritic sulfur content increase as the total sulfur increases.⁶ While the amount of pyritic sulfur varies considerably, the amount of organic sulfur does not vary much with the class.⁶

The commonly accepted method for determining sulfur forms in coal is ASTM Method D-2492.⁷ In this method, total sulfur is determined by heating a coal sample with MgO and Na₂CO₃ at 800°C followed by addition of hot water to remove the sulfur. The solution is then made acidic, oxidized and the sulfur content is precipitated as barium sulfate. The sulfate sulfur is determined by extracting -60mesh (250μm) coal with hot dilute HCl and determining the sulfate sulfur gravimetrically as BaSO₄. Pyritic sulfur is determined by extracting the HCl-treated coal with hot 2M HNO₃ for 30 minutes, or overnight with 2M HNO₃ at room temperature, and determining the iron present in the extract. The pyritic sulfur in coal is calculated from the iron content, assuming that all the extracted iron came from FeS₂ in the coal. Organic sulfur is then calculated as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur. Elemental sulfur, if present, is counted as organic

sulfur in this sulfur analysis method. ASTM-D2492 has proved to be useful and reasonably accurate for practical purposes for most coal.

Removing all the sulfur from coal in an economically practical way before combustion or processing has been a long sought goal. Since pyrites and other minerals are much more dense than organic material in coal, these materials can be separated by physical methods⁸ such as floatation, gravity separation, electrostatic or magnetic methods.⁹ Because organic sulfur is chemically bound into the organic matrix of coal and can not be removed by physical cleaning processes⁶, chemical treatment is required to remove the organic sulfur.¹⁰

Lack of information on types of organic sulfur present in coal contributes to the lack of development of efficient organic desulfurization processes. Better characterization of the organic sulfur forms is needed to improve the design of desulfurization technologies. There have been many selective chemical reactions and related techniques introduced in the area of coal model compound desulfurization and much progress has been made. These techniques include single electron transfer reactions;¹¹ reduction by hyperthermophilic archaebacteria;¹² use of hydroxide ion as the single electron reducing agent;¹³ and

reactions with soluble metallic reagents.¹⁴ But the disadvantage of the model compound chemical desulfurization strategy is that of the model compound(s) being completely representative. If the real structures of the organic sulfur in coal can be determined, the right model compounds can be chosen for studies and more useful chemical desulfurization reactions can be developed.

Even though there have been many recent studies of organic sulfur in coal, only a few sulfur compounds have been identified as existing in whole coal. Much of the research has been done on the analysis of coal extracts^{15,16} and pyrolysis^{17,18} products to obtain this information. The sulfur species from pyrolysis processes may be highly modified and account for only a very small percentage of the total sulfur in the coal. It can be very misleading to characterize the whole coal by extrapolation of the data from these analyses. ASTM procedures along with direct methods such as SEM-EDX (scanning electron microscopy with energy-dispersive X-ray analysis),^{19,20} TEM (transmission electron microscopy)²¹ and electron probe microanalysis²² provide excellent data on the forms and amount of sulfur in coal but provide no data on the molecular structure of organosulfur components.²³ Other approaches that have been used to characterize the organic sulfur in coal are programmed temperature reduction (PTR)^{20,24,25,26,27} and

programmed temperature oxidation (PTO)^{28,29}. Both methods rely on differences in reactivity of the different sulfur species. However these methods involve the use of high temperatures which are destructive to the coal structure. In addition, complex reactions may occur during these destructive methods of analysis, resulting in compounds which are not present in the original coal.

Further new techniques include Curie-Point analysis,³⁰ X-ray absorption fine structure (XAFS) spectroscopy,^{31,32,33} and X-ray photoelectron spectroscopy (XPS).^{34,35} XAFS spectroscopy determines the electronic structure and atomic environment of an element by analysis of the fine structure associated with an X-ray absorption edge of that element. The spectra are normally divided into two regions. The region within about 20-50 eV of the absorption edge is called the X-ray absorption near-edge structure, or XANES. The peaks and other structure in this region are derived primarily from two sources: photoelectron transitions to vacant, bound levels and low-energy scattering resonances. The XANES spectra are quite sensitive to the detailed nature of the electronic bonding and can frequently serve as fingerprints to identify different compounds or types of bonding. The extended X-ray absorption fine structure, or EXAFS, is the oscillatory structure that begins at 30-50 eV above the edge and extends to fairly high energies (-500-

1000 eV). These oscillations arise from interference between the outgoing and backscattered photoelectron wave functions and can be analyzed by means of Fourier transformation methods in terms of interatomic distances and coordination numbers for the atomic neighbor shells. These methods do provide some information regarding organic sulfur species in coal. Huffman et al.³² demonstrated that XAFS spectroscopy is an excellent method for direct, non destructive investigation of the molecular structure of organic sulfur in coal and coal derivatives, and desulfurized coals³³.

Following early studies of sulfur in coal using XAFS by Hussain et al.³⁶ and Spiro et al.³⁷, several groups have developed methods for quantitative analysis of XANES spectra of sulfur in coal. Gorbaty et al.³⁸ have developed a sulfur K edge X-ray absorption spectroscopic method for the direct determination and quantification of sulfidic and thiophenic forms of organically bound sulfur in coal samples by analyzing the third derivatives of XANES spectra. Huffman et al.³⁹ reported that they developed a method for quantitative analysis of all major forms of sulfur (pyrite, organic sulfide, thiophene, sulfoxide, sulfone, and sulfate) in coal from sulfur K-edge XAFS spectroscopy. The method was based on least-squares analysis of the XANES into a series of peaks that represent 1s \rightarrow np photoelectron

transitions. The method was used to determine the sulfur forms in the Argonne Premium Coal Sample Bank (APCSB) coals. They observed that the percentage of organic sulfide content generally increases with decreasing coal rank, although thiophenic sulfur is the dominant organic sulfur form, regardless of coal rank. In their investigation of new methods for the desulfurization of the organic compounds in coal using XANES spectroscopic analysis, Stock et al. and Gorbaty et al.⁴⁰ have been able to determine that 65% of the organically bound sulfur compound have aromatic character and about 35% sulfidic character in Illinois No. 6 coal from the Argonne Premium Coal Sample Program (APCSP #3) supporting the previous finding of Gorbaty et al.⁴¹. Their results also support the suggestions of Attar, Calkins, and Hippo and their associates that certain bituminous coal contain appreciable quantities of sulfide sulfur compounds.^{17,42,43}

In sulfur speciation of desulfurized coals, Huffman et al.³³ have applied a least square analysis method³⁹ of the XANES region of sulfur K edge X-ray absorption fine structure in a number of desulfurized coals prepared from different desulfurization procedures. A reasonable quantitative speciation of the change in the sulfur forms resulting from the various treatments was achieved in all cases.

XPS is an appropriate technique for the direct non-destructive determination of the proportions of thiophenic and aliphatic-sulfidic sulphur in coal. Kelemen et al.³⁵, by using XPS, were able to determine that thiophenic sulfur is the major form of the organic sulfur species in unoxidized Illinois No.6 coal. In their work, the complication that arose from the presence of inorganic sulfur components in coals in interpretation of XPS spectra for speciating organic sulfur forms has been solved by monitoring the influence of inorganic components and sample charging in detail. Since XPS derives the signal from the external surface and XANES data can be acquired for the bulk, important information about materials can be gained by combining these techniques as both methods have been developed to characterize and approximately quantify the forms of organically bound sulfur in coals.

Another direct, non-destructive technique that has been used in studying the organic sulfur in coal is very high frequency electron paramagnetic resonance (VHF-EPR) and Clarkson et al. have concluded that it can provide information about the nature and the concentration of heteroatomic species in coal.^{44,45} VHF-EPR is a magnetic resonance method that is capable of analyzing for the organic sulfur in whole coal, separated macerals, treated and desulfurized coals, as well as in materials produced

from coals (e.g. liquefaction and pyrolysis products).⁴⁶

These non-destructive spectroscopic methods such as XANES and very high field EPR show great promise for determining the major classes of organosulfur functional groups present in coal or coal products. However, at the resolution available now or in the next few years, these methods are not able to identify individual compounds.

While it is important to know the nature of sulfur species present in coal in order to improve the design of desulfurization processes, it is more important to know the identity and the reactivity of the actual sulfur compounds in coal. In identification and characterization of the organic sulfur compounds in coal-derived materials, sulfur-containing polycyclic aromatic compounds (S-PAC) have been studied extensively. Nishioka et al.^{47,48} have been able to describe the most abundant structures found for S-PAC in coal-derived materials and some structural correlations between the PASHs (polycyclic aromatic sulfur heterocycles) and PAHs (polycyclic aromatic hydrocarbons) have been observed as noted by Karcher et al.⁴⁹ and Burchill et al.⁵⁰ A coal tar (a medium crude coke-oven tar from an unknown feedstock) obtained from the National Bureau of Standards was studied by Nishioka and Lee using capillary GC and GC-MS. It was concluded that the structures and relative

abundances of the major PACs containing a single heteroatom are analogous to those of the major PAHs and that the major PACs containing two heteroatoms could be structurally derived from the major PACs containing a single heteroatom.⁴⁸

It is more difficult to study the organic sulfur compounds in unprocessed coals because of the low extractabilities of most coal matrices. Nevertheless there has been some work done on coal extracts. The nature of the organosulfur compounds extracted by perchloroethylene and tetrahydrofuran from Illinois #6 samples of the Argonne Premium Coal Sample Program (APCS), Argonne Premium Coal Sample Program #3 and Illinois Basin Coal Sample Program (IBCSP) #5 has been studied by Karl Vorres using sulfur sensitive gas chromatography and GC/MS. The organic sulfur compounds identified include substituted thiophenes, benzothiophenes, dibenzothiophene, thiazoles, benzothiazoles.⁵¹ Also it was noted that the concentrations of sulfur species in whole coal extracts were too low to be observed with the GC/MS. However, the concentration in the various chromatographic fractions was high enough for identification of sulfur species in some of the fractions as in the case of pristine APCS #3. While a whole coal extract of PCE showed no indication of a sulfur compound, the sample after fractionation showed evidence of sulfur compounds in

three of the fractions (PAC, N-PAC, H-PAH). Using GC-MS, Lee et al.⁵² have identified individual compounds in isolated sulfur fractions of solvent extract of five different coals of different rank from the Argonne National Laboratory namely, Illinois #6, Pittsburgh #8, Upper Freeport, Pocahontas #3 coal and Wyodak subbituminous coal. They found that condensed thiophenic compounds, dibenzothiophene, benzo[b]naphtho[2,3-d]thiophene, and their alkylated derivatives are the major constituents in all five S-PAC fractions. In addition, some diaryl sulfides along with the condensed thiophenic compounds were found in the high volatile bituminous Illinois #6 coal. These diaryl sulfides are assumed to be intermediates in the conversion of cyclic sulfides and/or thiols to condensed thiophenes. However, aromatic thiols were not found in any of their S-PAC fractions.

The purpose of this thesis work was to identify representative organosulfur compounds which are removed by nickel boride desulfurization⁵³. Demineralized or physically cleaned coals were Soxhlet extracted⁵⁴ with pyridine to isolate as much of the organosulfur compounds as possible and the pyridine extracts then extracted with distilled THF. The THF soluble portions, concentrated by rotary evaporation, were fractionated and purified by chromatography on a neutral alumina column packed in hexane.

Elution with hexane followed by toluene gave aliphatic and aromatic hydrocarbon fractions containing non-polar organosulfur compounds. The hexane and toluene fractions eluting from the column were concentrated by rotary evaporation and analyzed by gas chromatography/mass spectrometry.

After the sulfur compounds were characterized, the parent extracts were desulfurized using nickel boride desulfurization, fractionated and again analyzed for organosulfur content to determine if the identified compounds reacted during the chemical treatment. This was done by first identifying a hydrocarbon with similar retention time in the GC/MS which was inert in desulfurization reaction and then by determining relative areas of GC peaks for the sulfur compound to that of the nearby identified hydrocarbon.

Another analysis done on both THF soluble coal extracts and desulfurized THF soluble coal extracts was elemental analysis of carbon, hydrogen, and sulfur. This kind of measurement is often referred to as the ultimate analysis of coal. Using mole ratios S/C and H/C for the THF (Tetrahydrofuran) soluble fraction and desulfurized product fraction, the percentage of sulfur loss due to nickel boride desulfurization reaction was calculated for each coal used

in this research.

With the advancement of instrumentation technology, it is promising that more of the individual organosulfur compounds in coals would be identified. Along with that process, better desulfurization methods would be developed and hence it is hopeful that coal will be a much more clean and efficient energy source in the future.

Chapter II

EXPERIMENTAL SECTION

A. Coal Samples

The following coal samples were used in this work.

IBC-#101: Herrin (Illinois No. 6) coal obtained in 1983 from a commercial preparation plant in west central Illinois. It has the highest organic sulfur content of any coal in the program and exhibits one of the lowest pyritic sulfur values for a conventionally-washed coal.

Arg-#301: Illinois No. 6 Seam High Volatile Bituminous coal obtained in 1985 (Argonne Premium Coal Sample Program). It was blanketed with Argon at the mine.

IBC-#108: State-of-the-art, physically-cleaned blend of Herrin (No. 6) and Springfield (No. 5) coal (80% and 20%, respectively). It is a micronized coal with low pyritic sulfur. It was produced by an advanced froth flotation process (microbubble column flotation) in 1988. It is delivered to requesters as a filter cake (approximately 45% moisture).

B. Coal Drying Procedure

In this study, coal drying means the sample was dried to constant weight in an Abderhalden apparatus with concentrated H_2SO_4 as desiccant at 100°C and 0.05 Torr. The constant weight is defined as such that the weight difference between two successive times is less than $\pm 0.2\%$. This drying procedure will be referred to as "Standard Condition"⁵⁴ in this work. The drying process usually takes four to six hours depending on the weight of the samples.

C. Solvent Purification

Pyridine

Pyridine was dried over potassium hydroxide overnight and then over barium oxide overnight. The dried pyridine was transferred to a round bottom flask and barium oxide was added. The solution was heated at reflux for at least half an hour followed by the distillation over BaO under a nitrogen atmosphere.

Tetrahydrofuran

Tetrahydrofuran was distilled from sodium and benzophenone after the solution had been heated at reflux to produce a dark blue color. The distillation was carried out under a nitrogen atmosphere.

D. Pyridine Extraction

Dry coal (Standard Condition) was extracted using a known method^{54,55} with distilled, nitrogen-purged pyridine in a Soxhlet apparatus under an argon atmosphere as follows: Soxhlet thimbles were washed with the solvents to be used, in this case pyridine, and dried to constant weight under standard condition. Solvents were dried and distilled under a nitrogen atmosphere, and purged with a stream of nitrogen gas before use. For samples weighing 5-10g, a 43mm×123mm Whatman cellulose thimble and a 500mL round bottom flask with 400mL pyridine solvent were used in the Soxhlet extraction. The extraction lasted until the siphoning solvent was colorless, taking 4-7 days usually. The coal residue was washed with 80% methanol/water in the Soxhlet apparatus twice to remove the pyridine, each washing taking two hours. The soluble extract was filtered through a 0.45 μ m Nylon membrane filter. The pyridine solvent in the soluble fraction was removed on a rotary evaporator by changing the round bottom flask to a 250mL size in the last step of rotavapping to dryness. The viscous extract in the 250mL round bottom flask was washed twice for one hour each with 80% methanol/water under nitrogen with magnetic stirring to remove the remaining pyridine. Filtration through a 0.45 μ m Nylon membrane filter was done after each washing. Both extract and residue were dried under vacuum for over night before the weights were determined.

E. THF Extraction

Dry pyridine extract (Standard Condition) was re-extracted using purified THF in a round bottom flask under nitrogen for at least 18 hours maintaining the temperature between 50-60°C. Heating was provided with an electrically heated oil bath. The mixture was filtered through a 0.45 μ m Nylon membrane filter. The material left on the filter was let sit in half the amount of THF used in extraction for half an hour before the filtration was continued. THF solvent in the extract was removed on a rotary evaporator and the extract dried under Standard Condition before determining the weight. For samples weighing 1-2.5g, a 100mL round bottom flask with 60-85mL of THF was used. For samples weighing 4g, as in the case of the pyridine extract of IBC-#108, a 250mL round bottom flask with 200mL of THF was used.

F. Nickel Boride Desulfurization

Dry THF soluble coal extract was desulfurized using a published method⁵³ which uses nickel boride as the reagent in desulfurization. In this method nickel boride is the active material formed by sodium borohydride reduction of aqueous nickel chloride in ethanol. For the model compound, DBT (dibenzothiophene), the solvent used was ethanol. For the THF soluble extracts, the solvent used was THF/EtOH. A 25mL, three-neck, round bottom flask was fitted with a

magnetic stirrer, thermometer, condenser and rubber septum, and the top of the condenser was closed with a rubber balloon. In the normal addition procedure, the solvent, the sample and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were added to the flask. The flask was closed with a rubber septum and the contents were heated to 50-60°C with an electrically heated oil bath. To the stirred reaction mixture, 4.8M NaBH_4 in 95% aqueous ethanol was added drop wise via syringe over 45 minutes. The hydrogen gas produced inflated the balloon and was slowly consumed over an additional one hour of heating. For 0.147g of DBT(0.08mmole), 10mL of ethanol, 0.380g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.60mmole) and 2mL of 4.8M NaBH_4 (9.6mmole) in aqueous ethanol was used. The hot reaction mixture was filtered through a plug of glass wool into a separatory funnel and 10mL of cold water was added. The cooled reaction mixture was extracted with dichloromethane and brine solution (saturated NaCl solution). The combined extracts were dried over anhydrous sodium sulfate, filtered through glass wool and diluted in a 25mL volumetric flask for GC/MS analysis. In the reverse addition procedure, an aqueous solution of nickel salt was added drop wise via syringe to the mixture of borohydride, solvent and sulfur compound over an hour.

For the THF soluble coal fractions, 300-700mg samples of the coal extract were used and only the reverse addition

method was used. Either a 100mL or 250mL round bottom flask was used depending on the amount of the THF coal sample extract used. The hot reaction mixture was filtered through a 0.45 μ m Nylon membrane filter and the volume reduced to 4mL on a rotary evaporator. Purified THF (50-75mL) was added and the mixture was magnetically stirred for half an hour. Finally the mixture was filtered through a 0.45 μ m Nylon membrane filter, rotavapped to dryness, and then dried under Standard Condition before determining the weight.

Depending on the amount of THF extract used in desulfurization, the amount of solvent, NaBH₄, and NiCl₂·6H₂O were increased proportionally relative to the amount used for model compound DBT.

G. Storage of Coal Samples

All the dry coal samples (Standard Condition) including the extracts and residues were used in extraction or in chromatography either immediately after standard drying or stored in a nitrogen-flushed glove bag prior to use. The nitrogen in the glove bag was refreshed periodically.

H. Alumina Chromatography

Alumina Chromatography⁵⁶ was used to fractionate the THF soluble coal fractions and the desulfurized THF soluble coal fractions. In sample preparation, the extract was

,dissolved in THF and adsorbed into the neutral alumina (Brockman Activity I) as received from Aldrich by rotavapping the mixture to dryness on a rotary evaporator. For the THF soluble coal fractions, the amounts used were 0.1675g, 0.3442g, and 0.3503g for IBC-#101, Arg-#301, and IBC-#108, respectively. For desulfurized THF soluble coal fractions, the amount used were 0.1970g, 0.3805g, and 0.3037g for Illinois Basin Coal #101, Argonne Premiun Coal Sample #301, and Illinois Basin Coal #108, respectively. They were absorbed into 2-5g of alumina.

In column preparation, a column having an internal diameter of 11mm was used. The packing material alumina used was as received from Aldrich. The column was wet packed by filling the column 2/3 full with hexane before adding the alumina. The amount of 6.5-7.5g of Alumina was used in packing the column. After packing the column, the excess hexane was drained out, leaving 3-4mL of hexane at the top for the sample.

In adding the sample, the sample flask was rinsed with a few drops of THF onto the column. A thin layer of sand was placed on top of the sample which was allowed to absorb for 15 minutes before the sample was eluted with 27mL of hexane and then with 55mL of toluene. The hexane fraction was collected till the last of hexane reached the top of the

column. Then 4mL of the eluent collected in a graduated cylinder after the addition of toluene started was combined with previously collected hexane fraction. The toluene fraction was collected until the last of the eluent after adding 5mL of toluene into the column in addition to the 55mL used in the chromatography.

In this chromatography, HPLC grade hexane and toluene, and purified THF were used. All solvents were purged with nitrogen prior to use.

I. GC/MS Sample Preparation

In the sample preparation of the desulfurized DBT, 1mL of a 25mL solution in dichloromethane was transferred into a 10mL volumetric flask and diluted to make a 10mL solution using methanol. Then a 1mL sample was diluted in another 10mL volumetric flask to make a 10mL solution, again in methanol. The sample was transferred to a 2mL size Hewlett Packard GC vial filling it at least 3/4 full with the sample.

In the sample preparation of the eluents from the alumina chromatography of the THF soluble coal samples and the desulfurized THF soluble coal samples, the eluents were filtered through a 0.45 μ m Nylon membrane filter and the volume reduced to 2mL by rotary evaporation. The samples

were transferred directly into the GC vials.

J. GC/MS Column Calibration and Method Development

The GC/MS instrument used in this work was an Hewlett Packard 5890A/5971A. The capillary column was an HP-5MS (30m x 0.25mm i.d.) and the carrier gas was helium. The injection size was 3/10 μ L. Total ion chromatograms (TIC) were obtained and the GC peak identities were determined using the Wiley Library Search Program.

In the calibration of the column, a standard n-alkanes mixture (D2887 Quantitative Calibration Mix - Catalog No. 4-8882) and a standard PAH mixture (Polynuclear Aromatic Hydrocarbons mixture 610-M - Catalog No. 4-8743) from SUPELCO were used.

The D2887 Quantitative Calibration Mix consists of the following n-paraffins in the proportions (%W/W) indicated:

Hexane	6	Octadecane	5
Heptane	6	Eicosane	2
Octane	8	Tetracosane	2
Nonane	8	Octacosane	1
Decane	12	Dotricontane	1
Undecane	12	Hexatricosane	1
Dodecane	12	Tetracontane	1

Tetradecane	12	Tetratetracontane	1
Hexadecane	10		

The Polynuclear Aromatic Hydrocarbons Mixture 610-M contains the following components in methanol: methylene chloride (50:50):

Component	$\mu\text{g/ml}$
Acenaphthene	1000
Fluoranthene	200
Naphthalene	1000
Benzo(a)anthracene	100
Benzo(a)pyrene	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Chrysene (93%)	100
Acenaphthylene	2000
Anthracene	100
Benzo(ghi)perylene	200
Fluorene	200
Phenanthrene	100
Dibenzo(a,h)anthracene	200
Indeno(1,2,3-cd)pyrene	100
Pyrene	100

Both standard mixtures were analyzed with methods

"Toluene.M" and "Mlee.M" (see section "L" of experimental section for method information). While the PAH mixture was analyzed as received by the Supelco, n-alkanes mixture was diluted with methylene chloride before it was analyzed.

K. Methods used in GC/MS Analyses

In analyzing the desulfurized DBT, the "DHBMLEE" method was used. (See section "L" of experimental section for method information.)

For all the hexane fractions of before and after the desulfurized THF soluble extract of IBC-#101, Arg-#301 and IBC-#108, the "MODHMLEE" method was used. (See section "L" of experimental section for method information.)

For all the toluene fractions of the same coal samples, the "MODTMLEE" method was used. (See section "L" of experimental section for method information.)

L. Method Information

i) Method "Toluene.M"

ACQUISITION PARAMETERS

General Information

- - - - -

Inlet	: GC
Tune File	: ATUNE.U
Acquisition Mode	: Scan

MS Information

- - - - -

Solvent Delay : 3.00 min

EM Absolute : False

EMV Offset : 0.0

Resulting Voltage : 1823.5

[Scan Parameters]

Low Mass : 40

High Mass : 400

Threshold : 300

Sampling # : 2 A/D Samples 4

Scan Group : 2

Start Time : 15.00

Low Mass : 40

High Mass : 550

Threshold : 300

Sampling # : 2 A/D Samples 4

Scan Group : 3

Start Time : 30.00

Low Mass : 40

High Mass : 650

Threshold : 300

Sampling # : 2 A/D Samples 4

[Real Time Plot Parameters]

Time Window : 20 min

Ionize Real Time Display : False

Plot 1 type : Total ion

Scale minimum : 0

Scale maximum : 2000000

Plot 2 type : No plot

GC Inlet Information

- - - - -

[Inlet A Temperature Program Information]

Oven Track : Off

Inlet A Off

[Inlet B Temperature Program Information]

Oven Track : Off

Initial Temp : 250°C

Initial Time : 480.00 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Inlet A Pressure Program Information]

Constant Flow : Off
Initial Pres. : 3.0 psi
Initial Time : 480.00 min

Level	Rate (psi/min)	Final Pres.(psi)	Final Time(min)
1	0		

Total Program Time : 480.00 min
Pressure Units : psi

[Inlet A Flow Settings]

Column length : 30.00 m
Column diameter : 0.250 mm
Gas : He
Vacuum compensation : On
Pressure : 1.8 psi
Flow : 0.0 ml/min
Linear velocity : 0.0 cm/sec

[Inlet B Pressure Program Information]

Constant Flow : On 12.0 psi at 75°C
Pressure Units : psi

[Inlet B flow settings]

Column length : 30.00 m
Column diameter : 0.250 mm
Gas : He
Vacuum compensation : On
Pressure : 0.0 psi
Flow : 0.0 ml/min
Linear velocity : 0.0 cm/sec
Split flow : 7 ml/min

[Auxiliary Channel C Information]

Comment:

Pressure Program:
Initial Pres. : 0.0 psi
Initial Time : 480.00 min

Level	Rate (psi/min)	Final Pres. (psi)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel D Information]

Comment:

Pressure Program:
Initial Pres. : 0.0 psi
Initial Time : 480.00 min

Level	Rate (psi/min)	Final Pres. (psi)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel E Information]

Comment:

Pressure Program:
Initial Pres. : 0.0 Psi
Initial Time : 480.00 min

Level	Rate (psi/min)	Final Pres. (psi)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel F Information]

Comment:

Pressure Program:
Initial Pres. : 0.0 psi
Initial Time : 480.00 min

Level	Rate (psi/min)	Final Pres. (psi)	Final Time (min)
1	0		

Total Program Time: 480.00 min

GC Temperature Information

- - - - -

[GC Zone Temperatures]

Inj. A : 250°C Off
Inj. B : 250°C
Det. A : 50°C Off
Det. B : 330°C
Aux. : 280°C Off

[Oven Parameters]

Oven Equib Time : 0.50 min
Oven Max : 325°C
Oven : On
Cryo : Off
Ambient : 25°C
Cryo Blast : Off

[Oven Program]

Initial Temp. : 75°C
Initial Time : 2.00 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	10.00	120	0.00
2	5.00	320	2.00
3	0.00		

Next Run Time : 48.50 min

Injector Information

- - - - -

Injector Source : Auto
Injection Location : Rear

Sample Washes : 2
Sample Pumps : 2
Sample Volume : 1 stop(s)
Viscosity Delay : 0 sec
Solvent A Washes : 3
Solvent B Washes : 2
On column : No

[Purge Information]

Purge A/B	Init. value	On Time	Off Time
A	On	0.50	0.00
B	On	0.00	0.00

DATA ANALYSIS PARAMETERS

- - - - -

Percent Report Settings

- - - - -

Sort By: Signal

Output Destination

Screen: No
Printer: Yes
File: No

Integration Events: AutoIntegrate

General Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

- - - - -

Peak Location of Unknown: Apex

Library to Search Minimum Quality
C:\DATABASE\WILEY138.L 0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination

Screen: No
Printer: Yes
File: No

Generate Report During Run method: No

Quantitative Report Settings

- - - - -

Report Type: Summary

Output Destination

Screen: Yes
Printer: No
File: No

Generate Report During Run Method: No

Calibration Last Updated:

Reference Window: 10.00 Percent
Non-Reference Window: 5.00 Percent
Correlation window: 0.02 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

ii) Method " MLEE.M"

Method information for this method is the same as the previous method except for the following parameters:

ACQUISITION PARAMETERS

MS Information
- - - - -

Solvent Delay : 6.00 min
EM Absolute : False
EMV Offset : 0.0
Resulting Voltage : 1823.5

[Scan Parameters]

Low Mass : 40
High Mass : 500
Threshold : 300
Sampling # : 2 A/D Samples 4

Scan Group : 2
Start Time : 20.00
Low Mass : 40
High Mass : 650
Threshold : 300
Sampling # : 2 A/D Samples 4

[Real Time Plot Parameters]

Time Window : 20 min
Ionize Real Time Display : False
Plot 1 type : Total ion
Scale minimum : 0

Scale maximum : 1000000
Plot 2 type : No plot

GC Inlet Information

- - - - -

[Inlet B Pressure Program Information]

Constant Flow : On 10.0 psi at 80°C
Pressure Units : psi

GC Temperature Information

- - - - -

[GC Zone Temperature]

Inj. A : 250°C Off
Inj. B : 250°C
Det. A : 50°C Off
Det. B : 280°C
Aux. : 280°C Off

[Oven Parameters]

Oven Equib time : 0.50 min
Oven Max : 295°C
Oven : On
Cryo : Off
Ambient : 25°C
Cryo Blast : Off

[Oven Program]

Initial Temp. : 80°C
Initial Time : 1.00 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	4.00	280	6.00
2	0.00		

Next Run Time : 57.00 min

DATA ANALYSIS PARAMETERS

- - - - -

Same as for method "Toluene.M".

iii) Method "DHBMLEE.M"

Method information for this method is the same as
"MLEE.M" method except for the following parameters:

ACQUISITION PARAMETERS

MS Information

- - - - -

Solvent Delay 3.00 min

GC Temperature Information

- - - - -

[Oven Parameters]

Oven Max : 300°C

[Oven Program]

Initial Temp. : 80°C

Initial Time : 2.50 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	30.00	220	6.00
2	0.00		

Next Run Time : 13.17 min

DATA ANALYSIS PARAMETERS

- - - - -

Same as for method "Toluene.M".

iv) Method "MODHMLEE.M"

Method information for this method is the same as
"MLEE.M" method except for the following parameters:

ACQUISITION PARAMETERS

GC Temperature Information

- - - - -
[GC Zone Temperature]

Inj. A : 250°C Off
Inj. B : 250°C
Det. A : 50°C Off
Det. B : 280°C
Aux. : 280°C Off

[Oven Parameters]

Oven Equib time : 0.50 min
Oven Max : 295°C
Oven : On
Cryo : Off
Ambient : 25°C
Cryo Blast : Off

[Oven Program]

Initial Temp. : 80°C
Initial Time : 1.00 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	4.00	220	0.00
2	2.50	280	8.00
3	0.00		

Next Run Time : 68.00 min

DATA ANALYSIS PARAMETERS

- - - - -

Same as for method "Toluene.M".

v) Method " MODTMLEE.M"

Method information for this method is the same as
"MODHMLEE.M" method except for the following parameters:

ACQUISITION PARAMETERS

GC Temperature Information

- - - - -

[Oven Program]

Initial Temp. : 80°C
Initial Time : 2.00 min

Level	Rate (°C/min)	Final Temp. (°C)	Final Time (min)
1	4.00	115	0.00
2	3.00	185	0.00
3	5.00	280	5.00

Next Run Time : 58.08 min

DATA ANALYSIS PARAMETERS

- - - - -

Same as for method "Toluene.M".

M. Elemental Analysis

All the elemental analysis work was done by
Galbraith Laboratories Inc., Knoxville, TN.

Chapter III

Results and Discussion

1. GC/MS Column Calibration Results

The calibration results of both the standard alkane and the PAH compounds indicate that this GC/MS instrument can identify the hydrocarbon compounds very accurately.

i) GC no. with Method used and Tuning Type before the Run

<u>Std. Mix</u>	<u>GC no.</u>	<u>Method</u>	<u>Tuning type</u>
n-alkanes	1.NALKSTD4	TOLUENE	Mid Mass Autotune
	2.NALKSTM	MLEE	Max Sensitivity Autotune
PAH	3.PAHSTD2	TOLUENE	Mid Mass Autotune
	4.PAHSTM	MLEE	Max Sensitivity Autotune
	5.PAHSDM	MLEE	Std Spectra Autotune

Note: The PAH sample run by the "Mlee" method for both Maximum Sensitivity Autotune and Standard Spectra Autotune give the same retention times.

ii) Retention Times of Standard n-alkanes Mixture

<u>Compounds</u>	<u>No. of C</u>	<u>M.W</u>	<u>B.P</u>	<u>Ret. Time(min)</u>	
				<u>TOLUENE</u>	<u>MLEE</u>
Hexane	6	86	69	-	-
Heptane	7	100	98.4	-	-
Octane	8	114	125.6	-	-

Nonane	9	128	151	-	4.34
Decane	10	142	174	4.39	6.66
Undecane	11	156	196	5.84	9.56
Dodecane	12	170	216.2	7.31	12.78
Tetradecane	14	198	252.3	10.96	19.18
Hexadecane	16	226	286.8	15.04	25.11
Octadecane	18	254	317	19.05	30.49
Eicosane	20	282	220	22.85	35.37
Tetracosane	24	338	391	29.73	-
Octacosane	28	394	278	35.63	43.93
Dotricontane	32	450	467	40.85	-
Hexatricontane	36	506	265	45.37	-
Tetracontane	40	562	-	50.15	63.85
Tetratetracontane	44	618	-	-	-

For the TIC of standard alkane sample run by the "Toluene" method, see Fig. 1.1, Fig. 1.2, and Fig. 1.3 which also show the mass spectra of decane, eicosane, and dodecane, respectively.

For the same sample run by the "Mlee" method, see Fig. 2.1 and Fig. 2.2 which also show the mass spectra of tetracontane and octacosane, respectively.

iii) Retention Times of Standard PAH Mixture

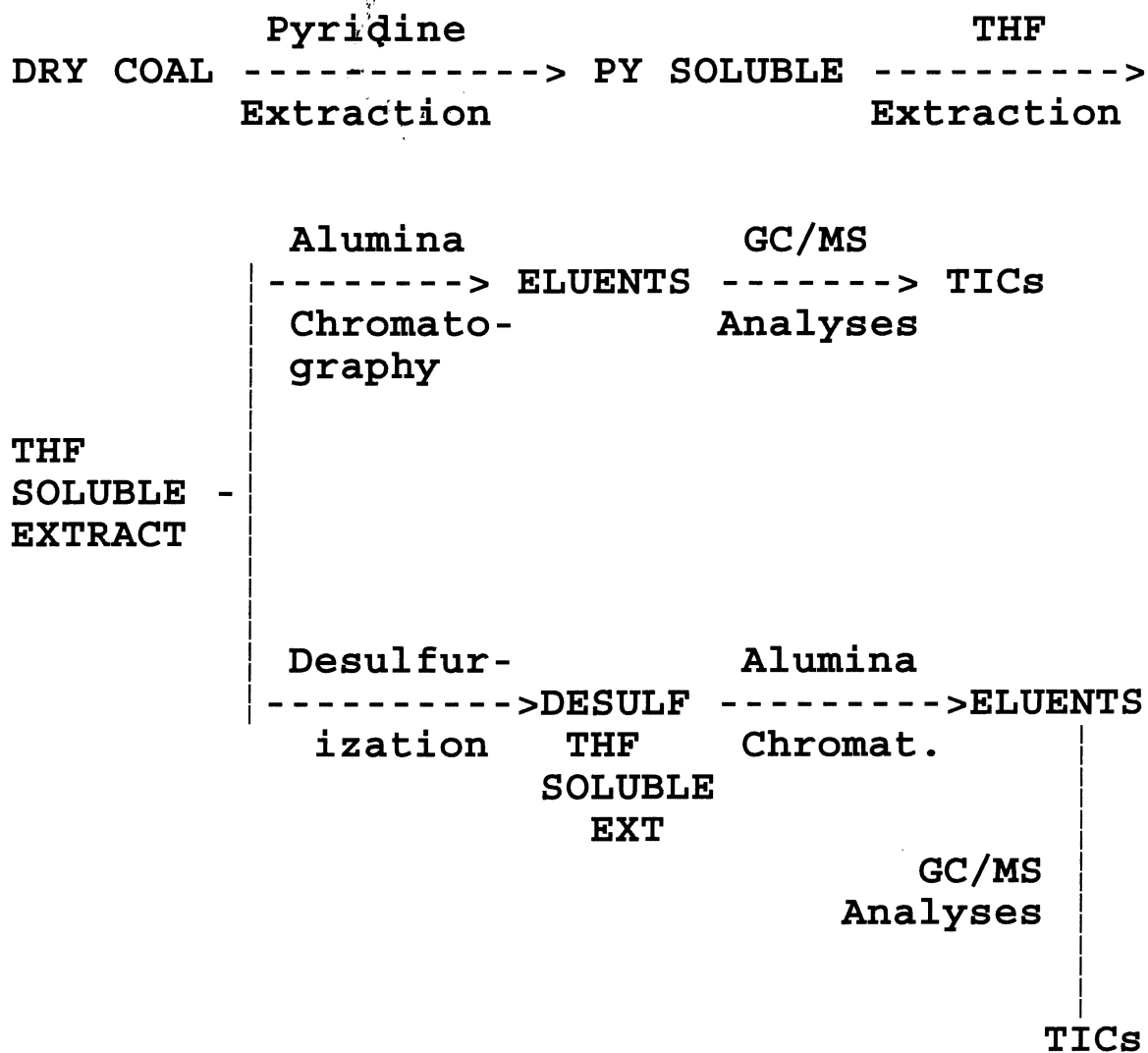
	<u>Compounds</u>	<u>M.W</u>	<u>B.P</u>	<u>Ret. Time (min)</u>	
				<u>TOLUENE</u>	<u>MLEE</u>
1.	Acenaphthene	154	279	12.68	21.79
2.	Fluoranthene	202	bp ₆₀ 250-1	23.88	36.58
3.	Naphthalene	128	218	7.15	12.32
4.	Benzo(a)anthracene	228	-	30.41	44.71
				or	or
				30.58	44.94
5.	Benzo(a)pyrene	252	bp ₁₀ 310-2	35.09	50.57
				or	or
				35.19	50.68
				or	or
				36.29	52.02
6.	Benzo(b)fluoranthene	252	-	Same as above	
7.	Benzo(k)fluoranthene	252	480	Same as above	
8.	Chrysene (93%)	228	448	30.41	44.71
				or	or
				30.58	44.94
9.	Acenaphthylene	152	bp ₂₈ 156-60	12.01	20.77
10.	Anthracene	178	340	18.77	30.05
11.	Benzo(ghi)perylene	276	-	41.22	58.07
12.	Fluorene	166	295	14.64	24.52
13.	Phenanthrene	178	340	18.58	29.81
14.	Dibenzo(a,h)anthracene	278	-	40.56	57.31
15.	Indeno(1,2,3-cd)pyrene	276	-	40.36	57.08

24.82 37.71

39

Scheme 1

Sample Preparation of Coal Samples for GC/MS Analyses



Sample Preparation of Desulfurized Model Compound DBT for GC/MS Analyses

GC/MS
-----> TICs
Analyses

41

2. Pyridine Extraction

From Table 1 and Fig. 6, for all three coal samples, i.e. Illinois Basin Coal #101, Argonne Premium Coal Sample #301, and Illinois Basin Coal #108, for the first experiment, the soluble coal fractions obtained from pyridine extractions account for 18.79%, 32.88%, and 16.87% of the dry coals, respectively. For the second experiment (second extraction for IBC-#108), they account for 18.86%, 36.78%, and 14.68% of the dry coals, respectively. So Argonne Premium Coal #301 has the highest extractibility among these three coals for pyridine extraction.

Argonne Premium Coal Sample #301 (The pristine (un-oxidized) parent of Illinis Basin Coal #105) was treated with acid followed by lithium aluminum hydride) before extracting with pyridine. This process was performed to remove oxidized pyrite which is the source of the elemental sulfur (S_8).

The acid demineralization used was a modification of standard methods.⁵⁸ Coal (10g) was placed in a 250mL RB flask containing a magnetic stirring bar along with 50mL of 25% HCl. An ice-filled cold finger condenser was connected to the flask and the exit attached to a nitrogen gas system. The stirred reaction mixture was heated to 100°C for two hours, cooled, filtered and washed with deionized water

until the wash water pH was above 5.5, and dried overnight under a slow flow of nitrogen. The sample was then placed in a 500mL heavy polyethylene tube containing 50mL of 48% HF and heated to 70°C for two hours. After cooling, the product was collected by vacuum filtration and washed with deionized water until the pH of the wash water was above 5.5. Then the product was dried under standard condition. The variation used 25% HCl and 48% HF mixed 1:1 in a single acid demineralization. Pyrite was removed by lithium aluminum hydride reduction using the method of Khun, et al.⁵⁸

3. THF Extraction

From Table 2 and Fig. 7, for the three pyridine soluble coal extracts from Illinois Basin Coal #101, Argonne Premium Coal Sample #301, and Illinois Basin Coal #108, the soluble coal fractions obtained from the THF extractions account for 49.92%, 41.86%, and 51.62% of the pyridine soluble extracts, respectively and 5.22%, 10.28%, and 6.67% of the dry coals, respectively for the first experiment. For the second experiment, they account for 65.74% and 50.45% of the pyridine soluble extracts, respectively and 7.15% and 12.15% of the dry coal, respectively for Illinois Basin Coal #101 and Argonne Premium Coal Sample #301. For Illinois Basin Coal #108, the same THF soluble extract was used for the second desulfurization and hence no second pyridine and THF

extraction was done for this coal.

4. Desulfurization

From Table 3 and Fig. 8, for all three coals, namely Illinois Basin Coal #101, Argonne Premium Coal Sample #301, and Illinois Basin Coal #108, the desulfurized THF soluble fractions account for 82.05%, 61.07%, and 54.01% of the THF soluble extracts, respectively for the first desulfurization. For the second desulfurization, they account for 41.36%, 52.33%, and 53.76% of the THF soluble extracts, respectively.

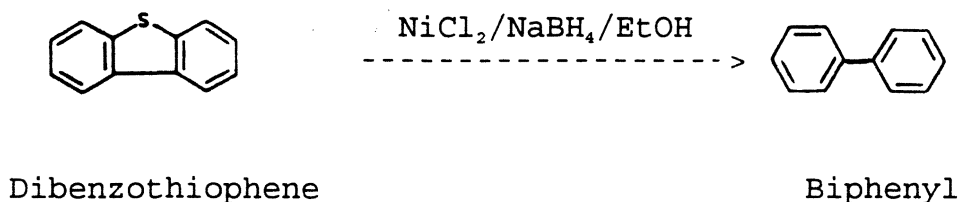
The reason the yield is large in the case of Illinois Basin Coal #101 (the first experiment) is that in working up the mixture after desulfurization, the filtered, rotavapped extract was not redissolved in THF and refiltered again as for the other desulfurizations before rotavapping to dryness since it would be alumina chromatographed with hexane and then with toluene, and any compound too polar to go through the GC column used would not be carried into the samples.

5. GC/MS Analyses

(i) Analyses of Model Compound

The desulfurized DBT samples obtained from both of the normal and the reverse addition procedures of Nickel Boride Desulfurization⁵³ were analyzed by the "DHBMLEE" method and

the retention times for DBT and Biphenyl were found to be 8.45 min and 6.58 min, respectively. See Fig. 10(a) and Fig. 10(b) for the TICs of desulfurized model compound DBT for the normal and the reverse addition procedures, respectively.



In the normal addition procedure of nickel boride desulfurization of the model compound DBT, 23% of dibenzothiophene (0.184mmoles) was converted to biphenyl. In the reverse addition procedure, 46% of dibenzothiophene (0.369mmoles) was converted to biphenyl. The calculation of the amount of conversion to biphenyl was based on the area percent report of the Total Ion Chromatogram. See Table 4 for the area percent report corresponding to TICs of desulfurized model compound dibenzothiophene for the normal addition and the reverse addition procedures.

From Table 4 and Fig. 9, it is easy to determine that the reverse addition procedure of nickel boride desulfurization removes sulfur (organic sulfur) from the model compound dibenzithiophene more effectively, and hence

this procedure was applied in desulfurization of THF soluble coal extracts of Illinois Basin Coal #101, Argonne Premium Coal Sample #301, and Illinois Basin Coal #108.

(ii) Analyses of Coal Samples

The GC/MS analyses of coal samples showed that the peaks observed were typical of the aliphatic and aromatic species present in coal samples. This GC/MS can identify the hydrocarbons common in all three coals at very similar retention times. Among the sulfur compounds identified was Dibenzothiophene, the most frequently observed and the most abundant as stated in Karl Vorres' paper⁵¹.

1) Analyses of Chromatographic Eluents of THF Soluble

Fractions of Illinois Basin Coal #101

In hexane fractions, no sulfur containing compound was identified in either the before or after desulfurization samples. For the first experiment, see Fig. 11.1 and Fig. 11.2 for the TICs of the THF soluble extract, and Fig. 13.1 and Fig. 13.2 (also shows the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.375 min with quality match 91) for the TICs of the desulfurized THF soluble extract.

For the second experiment, see Fig. 15 (also show the mass spectrum of pentadecane,2,6,10,14-tetramethyl

identified at 23.393 min with quality match 91) for the TIC of the THF soluble extract, and Fig. 17.1 and Fig. 17.2 (also shows the mass spectrum of tetratetracontane identified at 35.249 min) for the TICs of the desulfurized THF soluble extract.

The following is a list of some hydrocarbons identified in hexane fractions of Illinois Basin Coal #101.

For the first experiment,

<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before: Not identified	-	-
After: 23.208min(1680)	352(72)	Pentacosane
Before: Not identified	-	-
After: 23.375min(1693)	268(91)	Pentadecane, 2,6,10,14-tetramethyl
Before: 28.393min(2085)	619(62)	Tetratetracontane (M.W. for this would be 618)
After: Not identified	-	-
Before: 28.675min(2107)	192(89)	Anthracene, 2-methyl
After: 28.634min(2104)	192(87)	Penanthrene, 1-methyl

Before:	Not identified	-	-
After:	30.734min(2268)	212(81)	Pentadecane
	- (80)	Tetratetracontane

For the second experiment,

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	23.393min(1694)	268(91)	Pentadecane, 2,6,10,14-tetramethyl
After:	Not identified	-	-
Before:	Not Identified	-	-
After:	35.249min(2621)	479(53)	Tetratetracontane (M.W. for this would be 618)
Before:	Not Identified	-	-
After:	35.479min(2639)	467(76)	Dotriacontane (M.W. for this would be 450)

In the toluene fractions, for the first experiment, at average retention times of 10.387 to 10.409 min, a compound with an empirical formula of C_7H_5NS (M.W. 135) (given name by the Library - 1,2-Benzisothiazole) was identified with a low quality match of 47 in the THF soluble extract. See Fig 12.2 for the mass spectrum of C_7H_5NS .

For the TICs of toluene fraction of the THF soluble

extract for the first experiment, see Fig. 12.1, Fig.12.2 (also shows the mass spectrum of C_7H_5NS), Fig. 12.3 (also shows the mass spectrum of naphthalene identified at 9.224 min), Fig. 12.4 (also shows the mass spectrum of naphthalene,2-methyl identified at 12.471 min), and Fig. 12.5 (also shows the mass spectrum of heptadecane identified at 19.502 min).

No sulfur containing compound was identified in the toluene fraction of the desulfurized THF soluble extract of the first experiment. For the TICs of the toluene fraction of the desulfurized THF soluble extract for the first experiment, see Fig. 14.1 and Fig. 14.2.

For the second experiment, at average retention time of 10.362 to 10.422 min, the Library identified Silane, trichloro methyl (M.W. 140) with a very low quality match of 17 in the THF soluble extract while no compound was identified at the same retention time for the desulfurized THF soluble fraction.

<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
<u>(Averaged)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before: 10.387 to 10.409	135 (47)	1,2-Benzisothiazole (C_7H_5NS)
After: Not identified	-	-

For the second experiment,
 Before: 10.362 to 10.422 140(17) Silane, trichloro methyl
 After: Not identified - -

For the TICs of the toluene fraction of the THF soluble extract for the second experiment, see Fig. 16.1 (also shows the mass spectrum of hexadecane identified at 19.485 min) and Fig. 16.2.

For the TICs of the toluene fraction of the desulfurized THF soluble extract for second experiment, see Fig. 18.1 and Fig. 18.2 (also shows the mass spectra of dodecane identified at 9.607 min with quality match 90).

The following is a list of some hydrocarbons identified in toluene fraction of IBC-#101.

For the first experiment,

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	9.224min(327)	128(91)	Naphthalene
After:	Not identified	-	-
Before:	9.576min(363)	133(72)	Hexadecane
			(M.W. for this would be 226)
After:	Not identified	-	-

Before:	9.606min(366)	170 (60)	Dodecane
After:	Not identified	-	-
Before:	10.007min(407)	184 (78)	Undecane, 2, 5-dimethyl
After:	Not identified	-	-
Before:	12.471min(659)	142 (91)	Naphthalene, 2-Methyl
After:	Not identified	-	
Before:	12.647min(677)	184 (91)	Tridecane
	12.667min(679)	184 (94)	Tridecane
After:	Not identified	-	-
Before:	13.019min(715)	142 (91)	Naphthalene, 1-methyl
After:	Not identified	-	-
Before:	16.001min(1020)	198 (94)	Tetradecane
After:	Not identified	-	-
Before:	16.578min(1079)	156 (91)	Naphthalene, 2, 3-dimethyl
After:	Not identified	-	-
Before:	19.502min(1378)	240 (83)	Heptadecane
After:	Not identified	-	-

Before:	23.081min(1670)	366(83)	Hexacosane
	198(83)	Tetradecane
	226(83)	Hexadecane
After:	Not identified	-	-

For the second experiment,

	<u>Ret. Time</u> (Scan)	<u>Given M.W</u> (Qual.)	<u>Name Given by</u> the Library
Before:	9.594min(364)	170(70)	Dodecane
After:	9.607min(366)	170(90)	Dodecane
Before:	9.996min(405)	184(83)	Undecane, 2,6-dimethyl
After:	Not identified	-	-
Before	12.484min(659)	142(93)	Naphthalene, 1-methyl
After:	Not identified	-	-
Before:	12.641min(675)	184(91)	Tridecane
	12.661min(677)	184(93)	Tridecane
After:	Not identified	-	-
Before:	13.004min(712)	142(95)	Naphthalene, 1-methyl
After:	Not identified	-	-
Before:	15.168min(933)	212(72)	Dodecane, 2,6,11-trimethyl

After:	Not identified	-	-
Before:	16.010min(1019)	198(91)	Tetradecane
After:	15.985min(1018)	198(93)	Tetradecane
Before:	16.578min(1077)	156(98)	Naphthalene,1,2-dimethyl
After:	Not identified	-	-
Before:	19.485min(1374)	296(86)	Hexadecane
			(M.W. for this would be 226)
After:	Not identified	-	-
Before:	26.756min(1955)	268(64)	Heptadecane,2,6-dimethyl
After:	Not identified	-	-

2) Analyses of Chromatographic Eluents of the THF Soluble Fractions of Argonne Premium Coal #301

In the hexane fractions of the first experiment, a compound with the empirical formula $C_{12}H_8S$ (M.W 184 - dibenzothiophene) was identified at the retention time 24.440 min with a quality match of 80 in the THF soluble extract while it was identified at retention time 24.446 min with quality match of 81 in desulfurized THF soluble extract. See Figures 19.2 and 21.2 for the mass spectrum of the dibenzothiophene identified in the hexane fractions of the before and after desulfurized THF soluble fraction of

Argonne Premium Coal Sample #301 for the first experiment, respectively.

In the hexane fractions of the second experiment, this compound was identified at a retention time 24.475 min with quality match 80 and at a retention time 24.485 min with quality match 90 for the before and after desulfurized THF soluble extracts, respectively. See Figures 23.4 and 25.4 for the mass spectrum of the dibenzothiophene identified in the hexane fractions of the before and after desulfurized THF soluble fraction of Argonne Premium Coal Sample #301 for the second experiment, respectively.

<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
For the first experiment,		
Before: 24.440min(1776)	184(80)	Dibenzothiophene
After: 24.446min(1776)	184(81)	Same as above
For the second experiment,		
Before: 24.475min(1777)	184(80)	1-Thiaphenylene
.....	184(50)	Dibenzothiophene
After: 24.485min(1777)	184(90)	1-Thiaphenylene
.....	184(87)	Dibenzothiophene

The m/z 184 mass peak is highly abundant in all four mass spectra of the dibenzothiophene. See Fig. 19.2, Fig.

21.2, Fig. 23.4, and Fig. 25.4.

While the quality match given for the dibenzothiophene in the before and after desulfurized analyses for the first experiment and the after desulfurized sample for the second experiment were high, the quality match for it in the before desulfurized sample, for the second experiment was not as high, indicating that this GC/MS might not be sensitive enough.

For the first experiment, for the TICs of the hexane fraction of the THF soluble extract, see Fig. 19.1, Fig. 19.2 (also shows the mass spectrum of the dibenzothiophene identified at 24.440 min), Fig. 19.3 (also shows the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.390 minute), Fig. 19.4 (also shows the mass spectrum of phenanthrene identified at 25.131 minute), and Fig. 19.5.

For the first experiment, for the TICs of the hexane fraction of the desulfurized THF soluble extract, see Fig. 21.1, Fig. 21.2 (also shows the mass spectrum of DBT identified at 24.446 minute) , Fig. 21.3 (also shows the mass spectra of pentadecane,2,6,10,14-tetramethyl identified at 23.382 min), and Fig. 21.4.

For the second experiment, for the TIC of the hexane

fraction of the THF soluble extract, see Fig. 23.1, Fig. 23.2 (also shows the mass spectrum of 1H-indene,2,3-dihydro-1,1,2,3,3-pentamethyl identified 18.230 min), Fig. 23.3 (also show the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.399 min), Fig. 23.4 (also shows the mass spectrum of DBT identified at 24.475 min), and Fig. 23.5.

For the second experiment, for the TICs of the desulfurized THF soluble extract, see Fig. 25.1, Fig. 25.2 (also shows the mass spectrum of 1H-indene,2,3-dihydro,1,1,2,3,3-pentamethyl identified at 18.241 min), Fig. 25.3 (also shows the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.407 min), Fig. 25.4 (also shows the mass spectrum of dibenzothiophene identified at 24.485 min), and Fig. 25.5.

The following is a list of some hydrocarbons identified in the hexane fractions of Argonne Premium Coal Sample #301.

For the first experiment,

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	12.068min(618)	142(90)	Naphthalene,2-methyl
After:	12.048min(616)	142(90)	Naphthalene,2-methyl

Before:	15.236min(942)	156 (97)	Naphthalene,1,5-dimethyl
After:	15.216min(940)	156 (97)	Naphthalene,1,3-dimethyl
Before:	17.613min(1185)	282 (72)	Eicosane
After:	17.603min(1184)	212 (47)	Pentadecane
	17.613min(1185)	282 (43)	Eicosane
Before:	18.229min(1248)	188 (90)	1,1,3,3,5-pentamethyl- 2,3-dihydro indene
After:	18.200min(1245)	188 (94)	Same as above
Before:	18.445min(1270)	170 (96)	Naphthalene,2,3,6- trimethyl
After:	18.445min(1270)	170 (97)	Same as above
Before:	22.790min(1646)	184 (90)	Azulene,7-ethyl-1,4- dimethyl
After:	22.780min(1646)	184 (94)	Same as above
Before:	23.211min(1680)	310 (70)	Docosane
After:	23.220min(1681)	310 (60)	Docosane
Before:	23.390min(1694)	268 (91)	Pentadecane, 2,6,10,14- tetramethyl
After:	23.390min(1694)	268 (91)	Same as above

Before:	24.030min(1744)	184 (91)	Naphthalene, 1-methyl-7-
			(1-methyl ethyl)
	184 (76)	Azulene, 7-ethyl-1,4-
			dimethyl
After:	24.030min(1744)	184 (89)	Same as above
Before:	25.131min(1830)	178 (90)	Phenanthrene
After:	25.139min(1830)	178 (87)	Phenanthrene
Before:	25.848min(1886)	394 (76)	Octacosane
	198 (72)	Tetradecane
After:	25.844min(1885)	394 (87)	Octacosane
Before:	26.078min(1904)	352 (62)	Pentacosane
After:	26.088min(1904)	212 (89)	Pentadecane

For the second experiment,

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	8.872min(291)	170 (87)	Dodecane
After:	8.833min(287)	170 (93)	Dodecane
Before:	11.739min(584)	184 (90)	Tridecane
After:	11.709min(581)	184 (93)	Tridecane

Before:	12.101min(621)	142(87)	Naphthalene,2-methyl
After:	12.081min(619)	142(87)	Naphthalene,2-methyl
Before:	15.263min(944)	156(97)	Naphthalene,2,3-dimethyl
After:	15.243min(942)	156(97)	Naphthalene,1,3-dimethyl
Before:	16.536min(1074)	296(80)	Heptadecane, 2,6,10,15-tetramethyl
After:	16.526min(1073)	296(72)	Heptadecane, 2,6,10,14-tetramethyl
Before:	18.230min(1247)	188(94)	1-H indene,2,3-dihydro-1,1,2,3,3-pentamethyl
After:	18.241min(1248)	188(91)	Same as above
	18.231min(1247)	188(93)	1,1,3,3,5-pentamethyl-2,3-dihydro indene
Before:	18.485min(1273)	170(96)	Naphthalene,1,6,7-trimethyl
After:	18.476min(1272)	170(98)	Naphthalene,1,4,6-trimethyl
Before:	18.936min(1319)	170(95)	Same as above
After:	18.907min(1316)	170(98)	Same as above

Before:	19.004min(1326)	170(93)	Azulene, 2,4,6-trimethyl
After:	19.005min(1326)	170(95)	Naphthalene, 1,4,6-trimethyl
Before:	19.416min(1368)	170(98)	Same as above
After:	19.397min(1366)	170(98)	Same as above
Before:	19.475min(1374)	170(98)	Same as above
After:	19.466min(1373)	170(98)	Same as above
Before:	20.080min(1434)	170(97)	Same as above
After:	20.098min(1435)	170(98)	Same as above
Before:	20.503min(1467)	184(90)	Tridecane
After:	20.495min(1466)	184(96)	Tridecane
Before:	22.387min(1614)	184(89)	Azulene, 7-ethyl-1,4-dimethyl
After:	22.393min(1614)	184(93)	Same as above
Before:	23.232min(1680)	394(58)	Octacosane
	23.245min(1681)	226(62)	Hexadecane
After:	23.239min(1680)	198(96)	Tetradecane
	23.252min(1681)	282(58)	Eicosane

Before:	23.399min(1693)	268 (91)	Pentadecane, 2, 6, 10, 14-
			tetramethyl
	23.412min(1694)	268 (91)
After:	23.407min(1693)	268 (90)	Same as above
Before:	24.078min(1746)	184 (89)	Azulene, 7-ethyl-1, 4-
			dimethyl
After:	24.061min(1744)	184 (93)	Naphthalene, 1-methyl-7-
			(1-methyl ethyl)
Before:	25.180min(1832)	178 (96)	Anthracene
	178 (94)	Phenanthrene
	178 (95)	9H-Fluorene, 9-
			methylene
	178 (83)	Anthracene
After:	25.190min(1832)	178 (96)	Anthracene
	178 (96)	9H-Fluorene, 9-methylene
	178 (96)	Phenanthrene
Before:	25.872min(1887)	198 (96)	Tetradecane
	198 (70)	Tetradecane
	282 (68)	Eicosane
	394 (68)	Octacosane
After:	25.871min(1885)	198 (96)	Tetradecane
	352 (87)	Pentacosane
	184 (87)	Tridecane
	198 (87)	Tetradecane

Before:	26.103min(1904)	212(64)	Dodecane,2,6,11-trimethyl
After:	26.115min(1904)	212(70)	Pentadecane
	619(68)	Tetratetracontane
			(M.W. for this would be 618)
	366(68)	Hexacosane
	394(68)	Octacosane
Before:	28.204min(2068)	192(52)	Phenanthrene,9-methyl
After:	Not identified	-	-
Before:	28.807min(2115)	192(64)	Anthracene,2-methyl
After:	28.812min(2114)	192(91)	Same as above

Among all the identified good quality match nearby hydrocarbon compounds in the hexane fractions of both before and after desulfurization, the signal of a branched alkane pentadecane,2,4,10,14-tetramethyl (M.W. 268) was used as a standard to determine the relative area of GC peak for dibenzothiophene in the before and after desulfurized THF soluble extract in order to determine whether the identified sulfur compound dibenzothiophene was desulfurized during the nickel boride desulfurization⁵³ process. It was found that this desulfurization process did desulfurize dibenzothiophene but whether the amount of dibenzothiophene was greatly reduced or not is difficult to say. See Table 5.1 and Table 5.2 for data on area percent ratio comparison

for the first and the second experiment, respectively.

The reason pentadecane,2,4,10,14-tetramethyl was chosen as a standard was that it was found to be the most inert hydrocarbon during the nickel boride desulfurization⁵³. This conclusion was based on the fact that when the area ratios of good quality match hydrocarbons between the before and after desulfurized THF soluble extracts were compared, the difference in ratio is the least for this compound.

In the toluene fractions, no sulfur containing organic compound was identified. For the first experiment, see Fig. 20. and Fig. 22 for the TICs of the before and after desulfurized THF soluble extract, respectively.

For the second experiment, see Fig. 24.1, Fig. 24.2 (also shows the mass spectrum of Dodecane identified at 9.599 min), and Fig. 24.3 (also shows the mass spectrum tetradecane identified at 16.002 min) for the THF soluble extract, and Fig. 26.1, Fig. 26.2 (also shows the mass spectrum of dodecane identified at 9.584 min), and Fig. 26.3 (also shows the mass spectrum of tridecane identified at 12.635 min) for the after desulfurized THF soluble extract.

The following is a list of some hydrocarbons identified in the toluene fractions of Argonne Premium Coal Sample #301.

For the second experiment,

	<u>Ret. Time</u> <u>(Scan)</u>	<u>Given M.W</u> <u>(Qual.)</u>	<u>Name Given by</u> <u>the Library</u>
Before:	6.857min(85)	156(94)	Undecane
After:	6.865min(86)	156(81)	Undecane
Before:	9.599min(365)	170(91)	Dodecane
After:	9.594min(365)	170(87)	Dodecane
Before:	12.643min(676)	184(94)	Tridecane
After:	12.635min(676)	184(94)	Tridecane
Before:	16.011min(1020)	198(94)	Tetradecane
After:	15.99min(1019)	198(95)	Tetradecane

3) Analyses of Chromatographic Eluents of the THF Soluble Fractions of Illinois Basin Coal #108

For this coal, desulfurization was done twice to the same THF soluble extract. In the hexane fractions, among all the identified hydrocarbons, pentadecane, 2,4,10,14-tetramethyl (M.W. 268) was identified in all three samples with quality match 97 for the THF soluble extract and the first desulfurized THF soluble extract, and with quality

match 90 for the second desulfurized THF extract. The retention times were 23.441 min, 23.427 min, and 23.399 min, for the THF soluble extract, the first desulfurized THF soluble extract, and the second desulfurized THF soluble extract, respectively. See Figure 27.3, Figure 29.3, and Figure 31.3 for the mass spectrum of this alkane for the before desulfurized THF soluble extract, the first desulfurized THF soluble extract, and the second desulfurized THF soluble extract, respectively.

For the TICs of the hexane fraction of the THF soluble extract, see Fig. 27.1, Fig. 27.2 (also shows the mass spectrum of pentadecane identified at 17.646 min), Fig. 27.3 (also shows the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.441 min), Fig. 27.4 (also show the mass spectrum of decane,2-methyl identified at 67.501 min), and Fig. 27.5.

For the TICs of the hexane fraction of the first desulfurized THF soluble extract, see Fig. 29.1, Fig. 29.2 (also shows the mass spectrum of pentadecane identified at 17.629 min), Fig. 29.3 (also show the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.427 min), Fig. 29.4 (also shows the mass spectrum of decane,2-methyl identified at 67.475 min), and Fig. 29.5.

For the TICs of the hexane fractions of the second desulfurized THF soluble extract, see Fig. 31.1, Fig. 31.2 (also shows the mass spectrum of pentadecane identified at 17.626 min), Fig. 31.3 (also shows the mass spectrum of pentadecane,2,6,10,14-tetramethyl identified at 23.399 min), Fig. 31.4 (also shows the mass spectrum of hexatriacontane identified at 67.504,min), and Fig. 31.5.

The following is a list of some hydrocarbons identified in hexane fractions of before and after desulfurization of Illinois Basin Coal #108.

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Name Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	8.846min(288)	170(81)	Dodecane
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	11.73min(582)	240(86)	Heptadecane
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	12.083min(618)	142(93)	Naphthalene,2-methyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-

Before:	14.807min(885)	156 (97)	Naphthalene2,6- dimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	15.260min(941)	156 (97)	Naphthalene,1,3- dimethyl
After (1st):	N/I	-	-
After (2nd) :	N/I	-	-
Before:	17.646min(1183)	212 (97)	Pentadecane
After (1st):	17.629min(1183)	212 (93)	Same as above
After (2nd):	17.626min(1183)	212 (96)	Same as above
Before:	18.229min(1242)	188 (91)	1,1,4,5,6- Pentamethyl- 2,3-dihydro indene
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	18.367min(1256)	170 (96)	Naphthalene,2,3,6- trimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-

Before:	18.466min(1266)	170 (97)	Naphthalene,2,3,6-trimethyl
After(1st):	N/I	-	-
After(2nd):	N/I	-	-
Before:	18.940min(1314)	170 (98)	Naphthalene,1,4,6-trimethyl
After(1st):	N/I	-	-
After(2nd):	N/I	-	-
Before:	19.019min(1322)	170 (96)	Naphthalene,1,6,7-trimethyl
After(1st):	N/I	-	-
After(2nd):	N/I	-	-
Before:	20.525min(1462)	226 (96)	Hexadecane
After(1st):	N/I	-	-
After(2nd):	N/I	-	-
Before:	22.834min(1641)	184 (91)	Azulene,7-ethyl-1,4-dimethyl
After(1st):	N/I	-	-
After(2nd):	N/I	-	-

Before:	23.260min(1674)	240 (96)	Heptadecane
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	23.441min(1688)	268 (97)	Pentadecane, 2,6,10,14- tetramethyl
After (1st):	23.427min(1690)	268 (97)	Same as above
After (2nd):	23.399min(1689)	268 (90)	Same as above
Before:	24.074min(1737)	184 (89)	Azulene,7-ethyl- 1,4 dimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	24.410min(1763)	619 (68)	Tetratetracontane (M.W. for this would be 618)
	507 (68)	Hexatriacontane (M.W. for this would be 506)
After (1st):	24.420min(1767)	198 (46)	Tetradecane
After (2nd):	24.417min(1767)	184 (38)	Tridecane

Before:	25.198min(1824)	178 (96)	Anthracene
	178 (96)	Phenanthrene
	178 (96)	9H-Fluorene, 9-methylene
After (1st):	25.180min(1826)	178 (96)	Phenanthrene
After (2nd):	25.178min(1826)	178 (96)	Anthracene
	178 (96)	Phenanthrene
Before:	25.896min(1878)	254 (96)	Octadecane
	212 (94)	Pentadecane
After (1st):	25.864min(1879)	254 (96)	Octadecane
After (2nd):	N/I	-	-
Before:	26.116min(1895)	212 (91)	Dodecane, 2, 7, 10-trimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	28.211min(2057)	192 (95)	Phenanthrene, 9-methyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	28.820min(2104)	192 (95)	Anthracene, 9-methyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-

Before:	31.437min(2306)	206(96)	Phenanthrene, 2, 5-dimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	36.509min(2697)	216(95)	Pyrene, 1-methyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	38.484min(2849)	230(91)	Pyrene, 1, 3-dimethyl
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	40.811min(3028)	228(92)	Chrysene
After (1st):	N/I	-	-
After (2nd):	N/I	-	-
Before:	67.476min(5074)	619(46)	Tetratetracontane
		(M.W. for this would be 618)	
	67.501min(5076)	156	Decane, 2-methyl
After (1st):	67.475min(5087)	156(76)	Decane, 2-methyl
After (2nd):	67.504min(5087)	507(46)	Hexatricontane
		(M.W. for this would be 506)	

Note: N/I stands for not identified.

For the organosulfur compounds, in the hexane fraction of the THF soluble extract, at retention time 43.855 min, a compound with an empirical formula of $C_{16}H_{18}O_2S$ (M.W. 274) was identified with Wiley Library quality match of 64. The second best match was a compound with an empirical formula of $C_{13}H_{11}NO_2S$ (M.W. 245) with quality match 44 (see Fig. 27.5 for the mass spectrum).

In the hexane fraction of the first desulfurization of the THF soluble extract, at retention time 43.794 min, a compound with an empirical formula of $C_{13}H_{11}NO_2S$, which was the second best match for the THF soluble extract, was identified with a low quality match of 30 as the best match (see Fig. 29.5 for the mass spectrum).

In the hexane fraction of the second desulfurization of the same THF soluble extract, at retention time 43.813 min, a compound with an empirical formula $C_9H_{13}BrNO_3S$ was identified as the second best match. The quality match was 27. The best match was a compound with an empirical formula $C_9H_{13}NO_3$ and the quality match was 30 (see Fig. 31.5 for the mass spectrum).

	<u>Ret. Time</u>	<u>Given M.W</u>	<u>Formula Given by</u>
	<u>(Scan)</u>	<u>(Qual.)</u>	<u>the Library</u>
Before:	43.855min(3262)	274 (64)	$C_{16}H_{18}O_2S$
		245 (44)	$C_{13}H_{11}NO_2S$

1st Des: 43.794min(3264)	245 (30)	Same as above
	209 (25)	$C_9H_{11}N_3O_3$
2nd Des: 43.813min(3265)	183 (30)	$C_9H_{13}NO_3$
	289 (27)	$C_9H_8BrNO_3S$

Since the compound of interest does not have Br and the quality match in the second desulfurization was so low, it may mean that the organosulfur compound was removed by the desulfurization and the computer could not find a real match.

When the toluene fractions were analyzed, none of the sulfur containing compounds was identified in samples of either the before or after desulfurization. For the TICs of the THF soluble extract, see Fig. 28.1, Fig 28.2 (also shows the mass spectrum of chrysene identified at 43.364 min), and Fig 28.3 (also shows the mass spectrum of benz(e)acephenanthrylene identified at 51.611 min).

For the first desulfurized THF soluble extract, see Fig. 30.1, Fig. 30.2 (also shows the mass spectrum of chrysene identified at 45.352 minute), and Fig 30.3 (also shows the mass spectrum of benz(e)acephenanthrylene identified at 51.616 min).

For the second desulfurized THF soluble extract, see

Fig. 32.1, Fig. 32.2, and Fig. 32.3.

A few polycyclic aromatic hydrocarbons were identified in toluene fractions of Illinois Basin Coal #108. The following is a list of them.

	<u>Ret. Time</u> <u>(Scan)</u>	<u>Given M.W</u> <u>(Qual.)</u>	<u>Name Given by</u> <u>the Library</u>
Before:	45.364min(3412)	228(96)	Chrysene
After (1st):	45.352min(3409)	228(93)	Chrysene
After (2nd):	N/I	-	-
Before:	51.611min(3898)	252(95)	Benz(e)acephenanthrylene
	252(95)	Perylene
	252(90)	Benzo(a)pyrene
After (1st):	51.616min(3895)	252(97)	Benz(a)acephenanthrylene
	252(95)	Benzo(k)fluoranthene
	252(92)	Benzo(a)pyrene
2nd After:	N/I	-	-

While identification of the PAH compounds in the toluene factions of Illinois Basin Coal #108 with high quality match was accomplished, this GC/MS seems to be not sensitive enough to differentiate the possible sulfur

compound identified in the hexane fractions.

In Illinois Basin Coal #101, while the quality match of identified hydrocarbons were good, quality match of the identified sulfur compound 1,2-Benzisothiazole (C_7H_5NS) was quite low - only 47 and no other organosulfur compound was identified with good quality match indicating that the GC/MS system we are using might not be not sensitive enough to identify the abundant organosulfur content of this coal.

For Argonne Premium Coal #301, from the hexane fractions, the comparison result of the area ratios of DBT and pentadecane,2,6,10,14-tetramethyl shows that even though it was obvious that the dibenzothiophene was desulfurized during the nickel boride desulfurization⁵⁴, the current GC/MS cannot provide enough information to determine whether the amount of dibenzothiophene was greatly reduced or not.

In the hexane fractions of all three coals, the molecular weight for tetratetracontane given by the GC/MS was 619 instead of 618. The reason for that could be in the spectrometer, a very stable $[M+H]^+$ ion was formed by the hydrogen abstraction of the molecule. This type of ion for tetratetracontane is $CH_3-(CH_2)_{42}-CH_3-H^+$. It might also be that the resolution of the spectrometer was not good enough at that mass to tell the difference between 618 and 619. In

the case of hexatriacontane, given as an equally best match as tetratetracontane in Illinois Basin Coal #108, this type of ion is $\text{CH}_3-(\text{CH}_2)_{34}-\text{CH}_3-\text{H}^+$.

6. Elemental Analysis

Elemental analyses for carbon, hydrogen and sulfur were obtained for the THF soluble extracts and the desulfurized THF soluble extracts. The results are listed in Table 6.

For Argonne Premium Coal #301 and Illinois Basin Coal #108 coals, the weight percentages of carbon in desulfurized product fractions are a little higher than that of the THF soluble fraction which means the coal samples were protected very well from air oxidation during the experiment.

The weight percentages of sulfur in the THF soluble extracts of Illinois Basin Coal #101 are 70% and 64% of that of the original coal for the first and second experiment, respectively. The weight percentages of sulfur in the THF soluble extracts of the demineralized Argonne Premium Coal Sample #301 are 87% and 86% of that of the organic fraction of the original coal for the first and second experiment, respectively. The weight percentage of sulfur in the THF soluble extract of Illinois Basin Coal #108 is 73% of that of the original coal. See Table 7 for the data.

Considering the facts that Illinois Basin Coal #101 has seventy percent of its sulfur content in organic form and Illinois Basin Coal #108 has very low pyrite, the THF extraction of pyridine soluble fraction of coal samples was a valid procedure to isolate as much of organosulfur compounds as possible from the original coal.

Percent sulfur loss due to nickel boride desulfurization was determined from elemental analyses results and the results are listed in Table 8. For Illinois Basin Coal #101, it accounts for 26.74% and 18.41% for the first and second experiment, respectively. For Argonne Premium Coal Sample #301, it accounts for 24.75% and 35.13% for the first and second experiments, respectively. For Illinois Basin Coal #108, it accounts for 38.07% and 33.03% for the first and second desulfurization, respectively.

Also from Table 8, H/C mole ratio increase in most of the product fractions indicates that some hydrocarbons in the THF soluble extracts were reduced during nickel boride desulfurization as expected.

In summary, elemental analysis results provided the information pertaining to sulfur amount as expected.

Chapter IV

CONCLUSION

From the before to after desulfurization of the THF soluble extract of the coal samples, some of the hydrocarbons remain the same while others are chemically reduced, proving that nickel boride desulfurization⁵³ applied here is a reducing agent. Also, elemental analysis results support that nickel boride⁵³ desulfurizes the organosulfur compounds in coals.

What we are dealing with in identification of organosulfur compounds in coal is very subtle due to the complex nature of coal. Hence, it is very difficult to know how concentrated the sample must be in order to be able to identify more of the organosulfur compounds.

If a change in concentration during the preparation of the samples for GC/MS analyses is the main reason for not being able to identify more of the organosulfur compounds, then a more sensitive Mass Spectrometer should be the next step. There may also be some other effects that we have not considered, which might cause changes in concentration of organosulfur compounds in these samples.

Nevertheless, considering the facts that the standard

hydrocarbons are identified very accurately and the hydrocarbons identified in coal samples are consistent in their information, the conclusion is that the applied method of using mass spectrometry in conjunction with gas chromatography to possibly identify extremely small amounts of individual organosulfur compounds in complex mixtures like coal extracts is valid. This is especially true since this technique has already contributed enormously to our knowledge of low-molecular-weight compounds extractable from coal⁵².

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Table 1. Data on Pyridine Extraction

	IBC-#101		Arg-#301*		IBC-#108	
	First	Second	First	Second	First	Second
Start Coal g	10.0367	10.5832	10.4241	10.6166	10.0600	20.6016
Py Extract g	1.8859	1.9965	3.4270	3.9043	1.6975	3.0252
Wt % Extract	18.79	18.86	32.88	36.78	16.87	14.68
PY Residue	8.0984	8.6466	6.6252	6.6386	8.6874	16.3403
WT % Residue	80.69	81.70	63.56	62.53	86.35	79.32
Material Balance	99.48	100.56	96.44	99.31	103.22	93.99
Wt % Extract (Lit. Value)	N/A		22.4 ^{**1}		N/A	

* Demineralized coal

** Data for the oxidized version i.e. the sample had exposure to air for short period during processing but was stored under nitrogen

¹ See Reference No.55

Note: During the Soxhlet extraction of IBC-#108 with pyridine, for the second extraction, the joints of the soxhlets connected to the neck of round bottom flasks were blocked due to the tearing of the thimbles and hence it was needed to stop the extraction and clear the coal from the joint of the soxhlet. Extraction was continued afterward. Also during the Abderhalden drying of the extract in the first experiment, it was suspected that some of the Sulfuric acid used as the desiccant have got to the extract and hence the extract was washed again and dried again under standard condition.

Table 2. Data on THF Extraction

	IBC-#101 First Second		Arg-#301 First Second		IBC-#108
Py Extract g	1.0502	1.1513	2.5602	2.5565	4.0301
THF Soluble g	0.5243	0.7569	1.0718	1.2897	2.0805
% THF Soluble (of PY Extract)	49.92	65.74	41.86	50.45	51.62
% THF Soluble (of dry coal)	5.22	7.15	10.28	12.15	6.67
% THF Soluble (of dry coal and of Lit. Value)	N/A		14.63 ^{**1}		N/A

** Data for the oxidized version i.e. the sample had exposure to air for short period during processing but was stored under nitrogen

¹ See Reference No.55

Table 3. Data on Desulfurization

	IBC-#101		Arg-#301		IBC-#108	
	First	Second	First	Second	First	Second
THF Soluble g	0.2997	0.3316	0.6868	0.6859	0.6902	0.6878
Solvent	EtOH	THF/EtOH	THF/EtOH	THF/EtOH	THF/EtOH	THF/EtOH
Ext. Recovered g	0.2459	0.1359	0.4194	0.3590	0.3728	0.3698
% of Ext. Recovered	82.05	41.36	61.07	52.33	54.01	53.76

Table 4. Area percent report from TICs of desulfurized DBT and percent DBT converted to Biphenyl

Desulfurization Procedures	Ret. Time (min)	Compd.	Area	% Converted to Biphenyl	Amount of DBT converted (mmoles)
Normal Addition	6.585	BP	5274398	23%	0.184
	8.452	DBT	16856350		
Reverse Addition	6.580	BP	1184709	46%	0.369
	8.450	DBT	1383722		

Table 5.1 Area Percent Ratio Comparison for Arg-#301
(the first exp.)

	Area Percent of DBT	Area Percent of Std. Peak	Area % Ratio of DBT & Std. Alkane
Before	868618	5862344	0.148173
After	2103169/2	8878068	0.11845

Table 5.2 Area Percent Ratio Comparison for Arg-#301
(the second exp.)

	Area Percent of DBT	Area Percent of Std. Peak	Area % Ratio of DBT & Std. Alkane
Before	1768601	14730862	0.12006
After	2873188	18929981	0.15177

Table 6. Elemental Analysis Results, Atomic Ratios and %S Loss

Coal	Sample	% C	% H	% S
IBC-#101* dry coal	Moisture Free	69.20	5.10	4.4
IBC-#101*** (1st Exp)	THF Sol. Frac: De-S-Product	78.78 65.72	6.60 6.54	3.06 1.87
IBC-#101 ¹ *** (2nd Exp)	THF Sol. Frac: De-S-Product	79.40 74.96	6.91 7.56	2.83 2.18
Arg-#301** dry coal	Moisture & Ash Free	77.67	5.00	2.38 ¹
Arg-#301 ^{***,2} (1st Exp)	THF Sol. Frac: De-S-Product	79.13 79.37	6.34 6.99	2.08 1.57
Arg-#301 ^{***,2} (2nd Exp)	THF Sol. Frac: De-S-Product	79.88 80.49	5.99 6.63	2.05 1.34
IBC-#108* dry coal	Moisture Free	76.00	5.20	2.70
IBC-#108*** (1st Desulf)	THF Sol. Frac: De-S-Product	80.01 80.91	6.36 7.26	1.98 1.24
IBC-#108*** (2nd Desulf)	THF Sol. Frac: De-S-Product	80.01 80.60	6.36 6.95	1.98 1.34

* average analyses of Twelve IBCSP Lots (moisture free values)
data from Illinois Basin Coal Sample Program (1993 Annual Report of
Illinois Clean Coal Institute)

** moisture and ash free sample
data from User Handbook for Argonne Premium Coal Sample Program (October
1, 1989 U.S. Dept. of Energy)

*** moisture and ash free lab samples

¹ organic sulfur (total S=4.83%)

² demineralized sample

Table 7. Wt % of sulfur in the feed coal samples (THF soluble extracts) as percent of the original coal

	% S in orig. coal	%S in feed coal	Wt % of S in feed coal as of the orig. coal
IBC-#101 (1st exp)	4.4*	3.06***	70
IBC-#101 (2nd exp)	4.4*	2.83***	64
Arg-#301 (1st exp)	2.38**,1	2.38***,2	87
Arg-#301 (2nd exp)	2.38**,1	2.05***,2	86
IBC-#108	2.70*	1.98***	73

* average analyses of Twelve IBCSP Lots (moisture free values)
data from Illinois Basin Coal Sample Program (1993 Annual
Report of Illinois Clean Coal Institute)

** moisture and ash free sample
data from User Handbook for Argonne Premium Coal Sample
Program (October 1, 1989 U.S. Dept. of Energy)

*** moisture and ash free lab samples

¹ organic sulfur (total S=4.83%)

² demineralized sample

Table 8 % Desulfurization calculated from Elemental Analysis Results

Coal	THF Sol. H/C	Frac: S/C	De-S-Product H/C	Frac: S/C	% Desulfurized
IBC-#101 (1st Exp)	0.9984	0.0146	1.1859	0.0107	26.74
IBC-#101 (2nd Exp)	1.0371	0.0134	1.2019	0.0109	18.41
Arg-#301 (1st Exp)	0.9548	0.0098	1.0495	0.0074	24.75
Arg-#301 (2nd Exp)	0.8936	0.0096	0.9816	0.0062	35.13
IBC-#108 (1st Desulf)	0.9473	0.0093	1.0693	0.0057	38.07
IBC-#108 (2nd Desulf)	0.9473	0.0093	1.0276	0.0062	33.03

Note: H/C and S/C are mole ratio.

Figure 1.1. TIC of n-alkanes run by method "TOLUENE" after "Mid Mass Autotune" and the mass spectrum of Decane

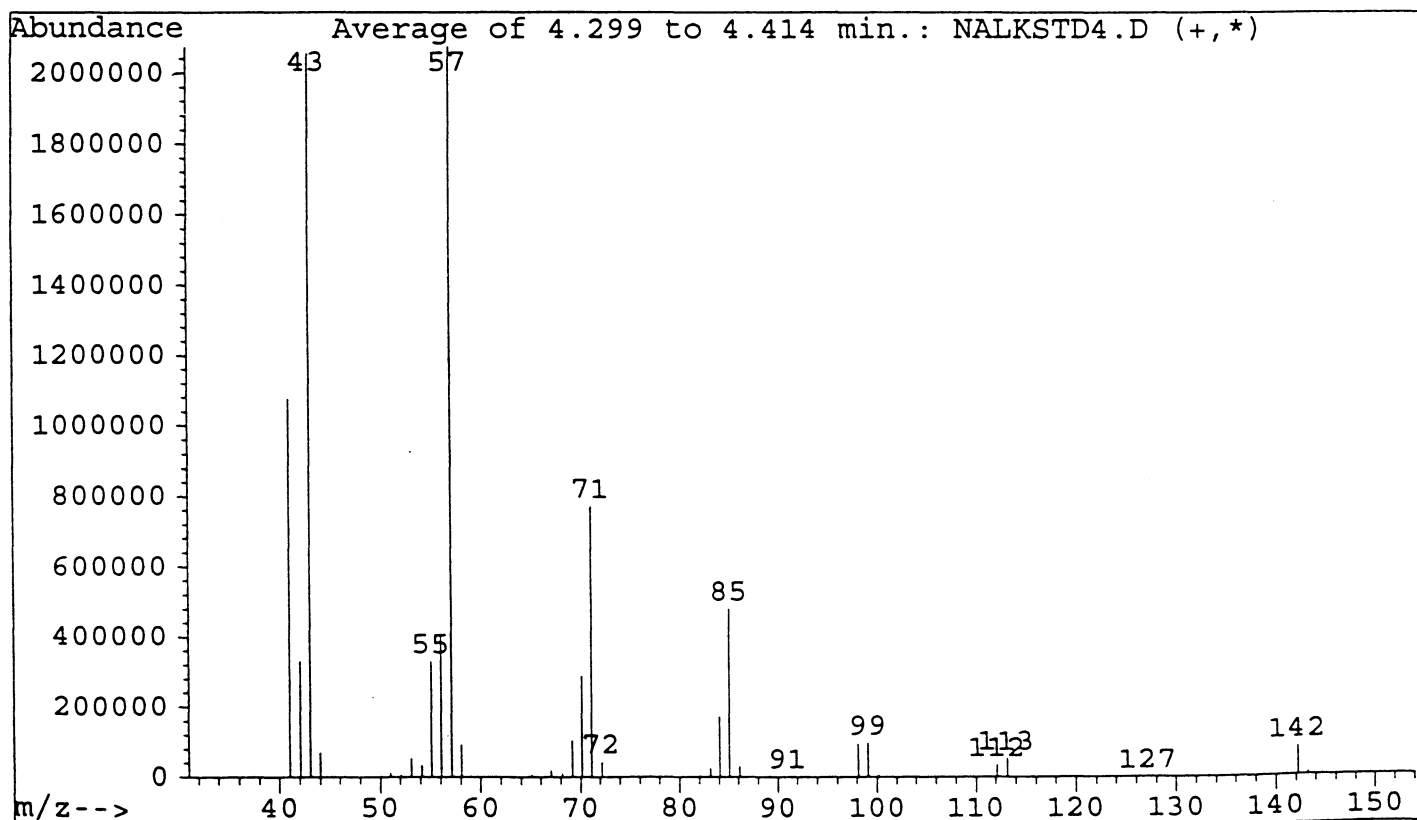
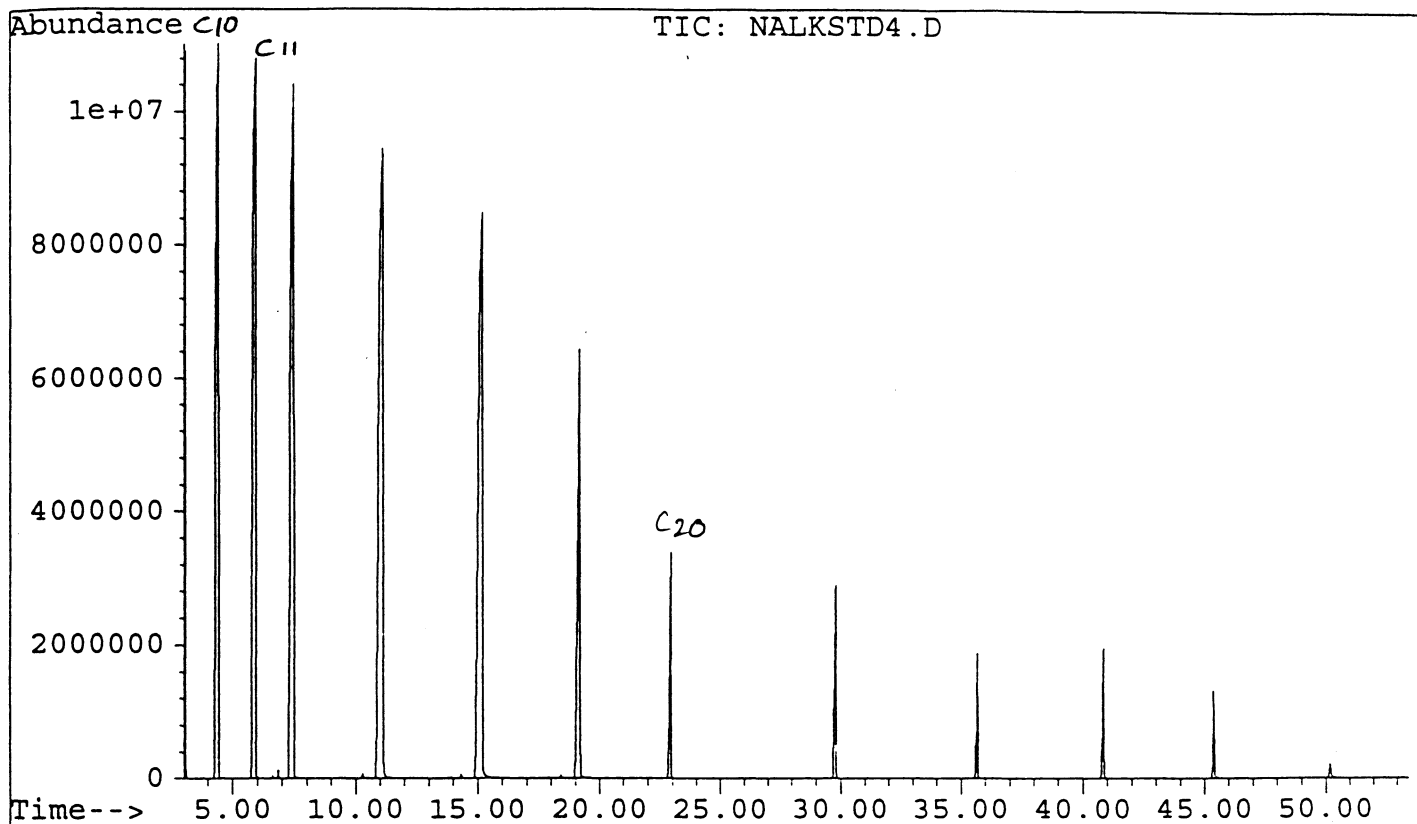


Figure 1.2. TIC of n-alkanes run by method "TOLUENE" after "Mid Mass Autotune" and the mass spectrum of Eicosane

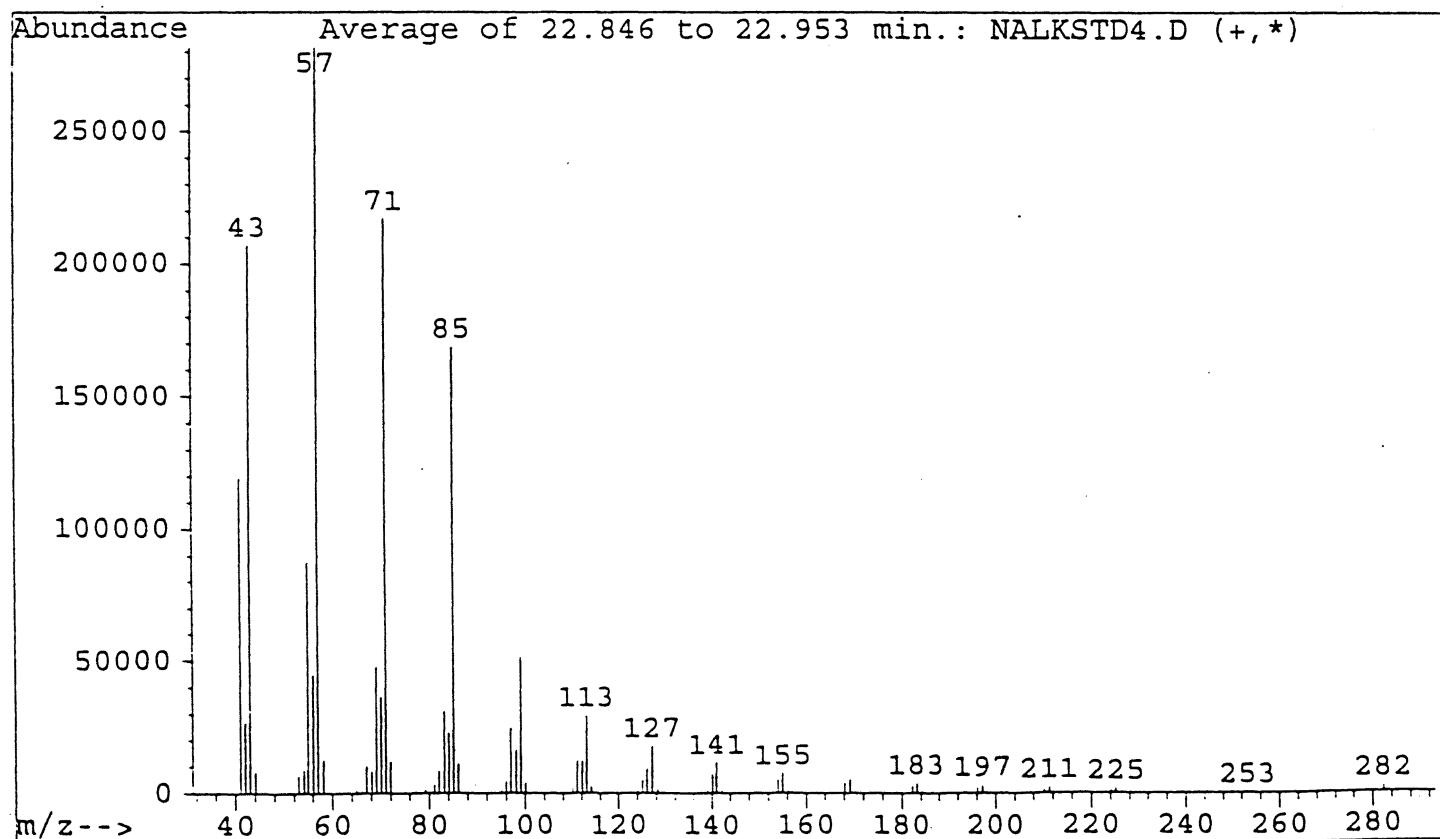
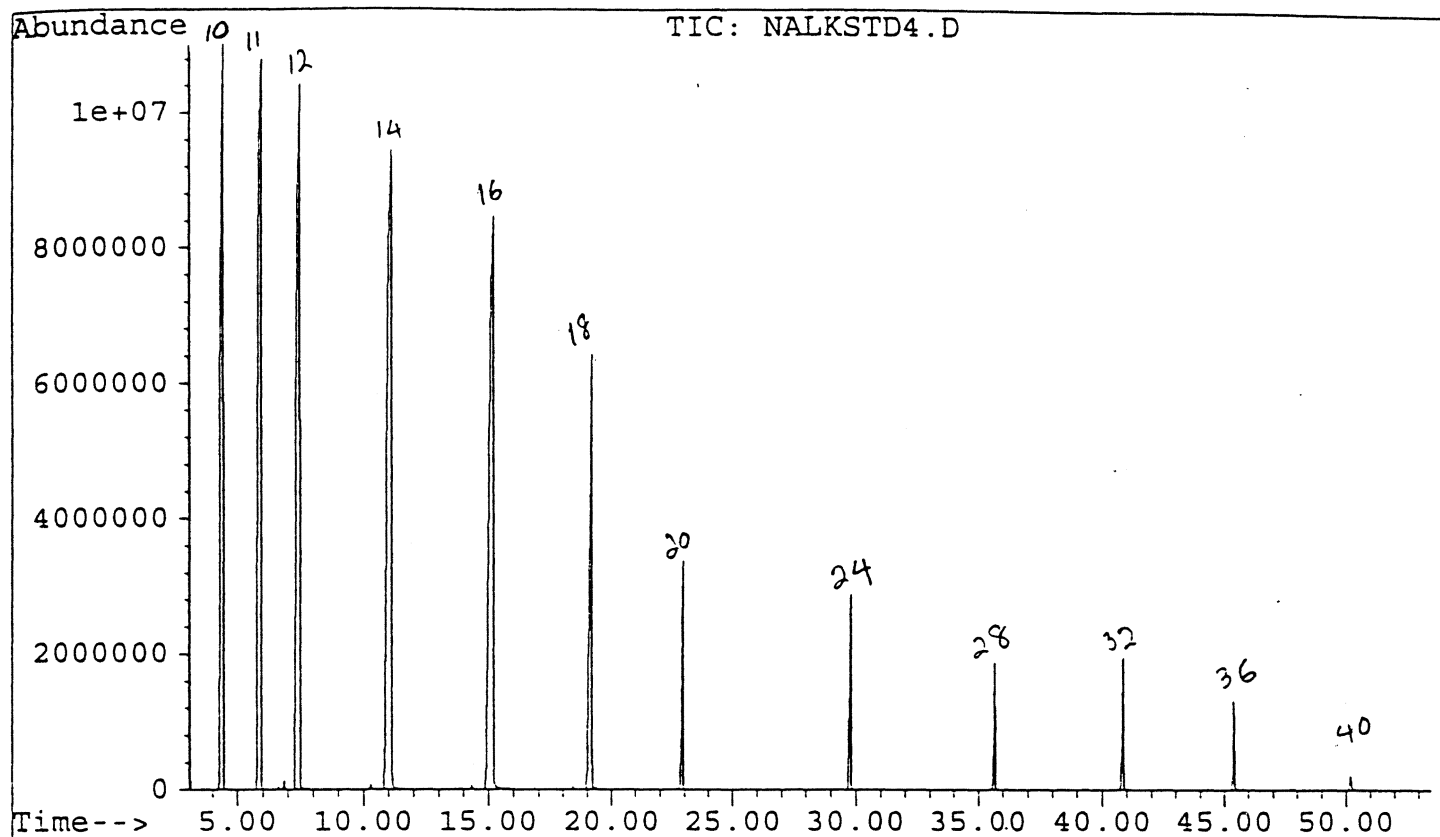


Figure 1.3. TIC of n-alkanes run by method "TOLUENE" after "Mid Mass Autotune" and the mass spectrum of Dodecane

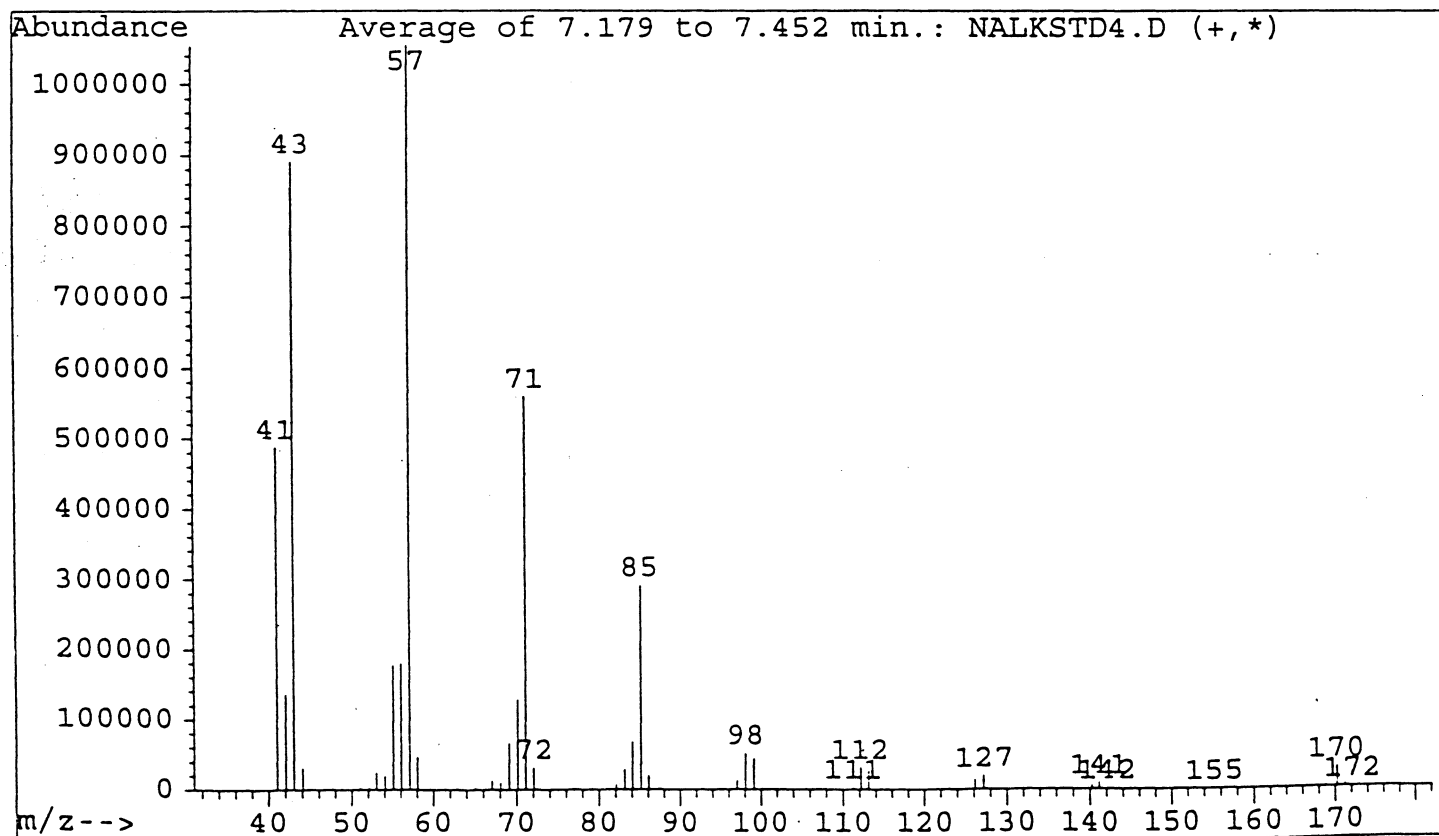
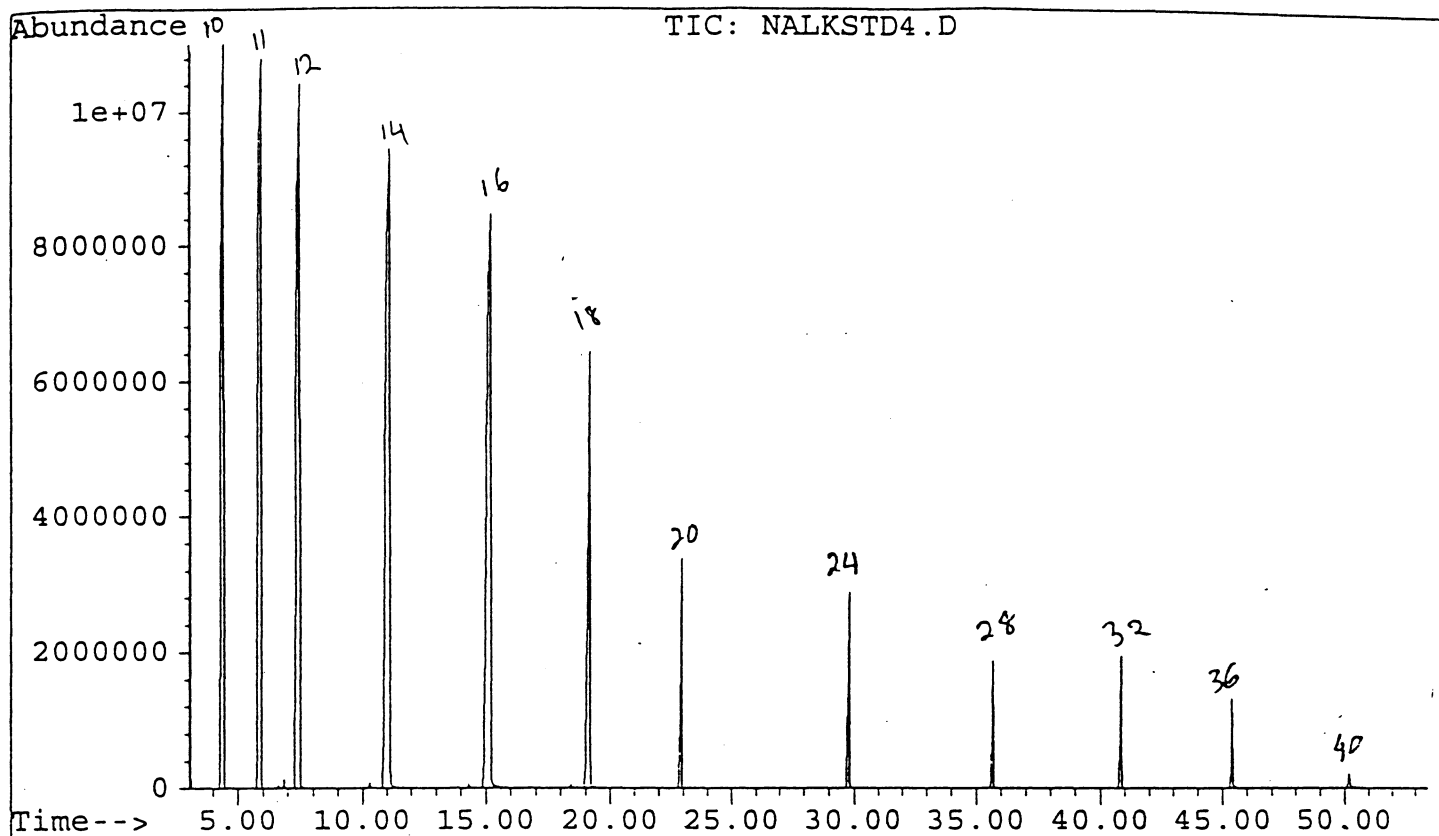


Figure 2.1. TIC of n-alkanes run by method "MLEE" after "Max sensitivity Autotune" and the mass spectrum of Tetracontane

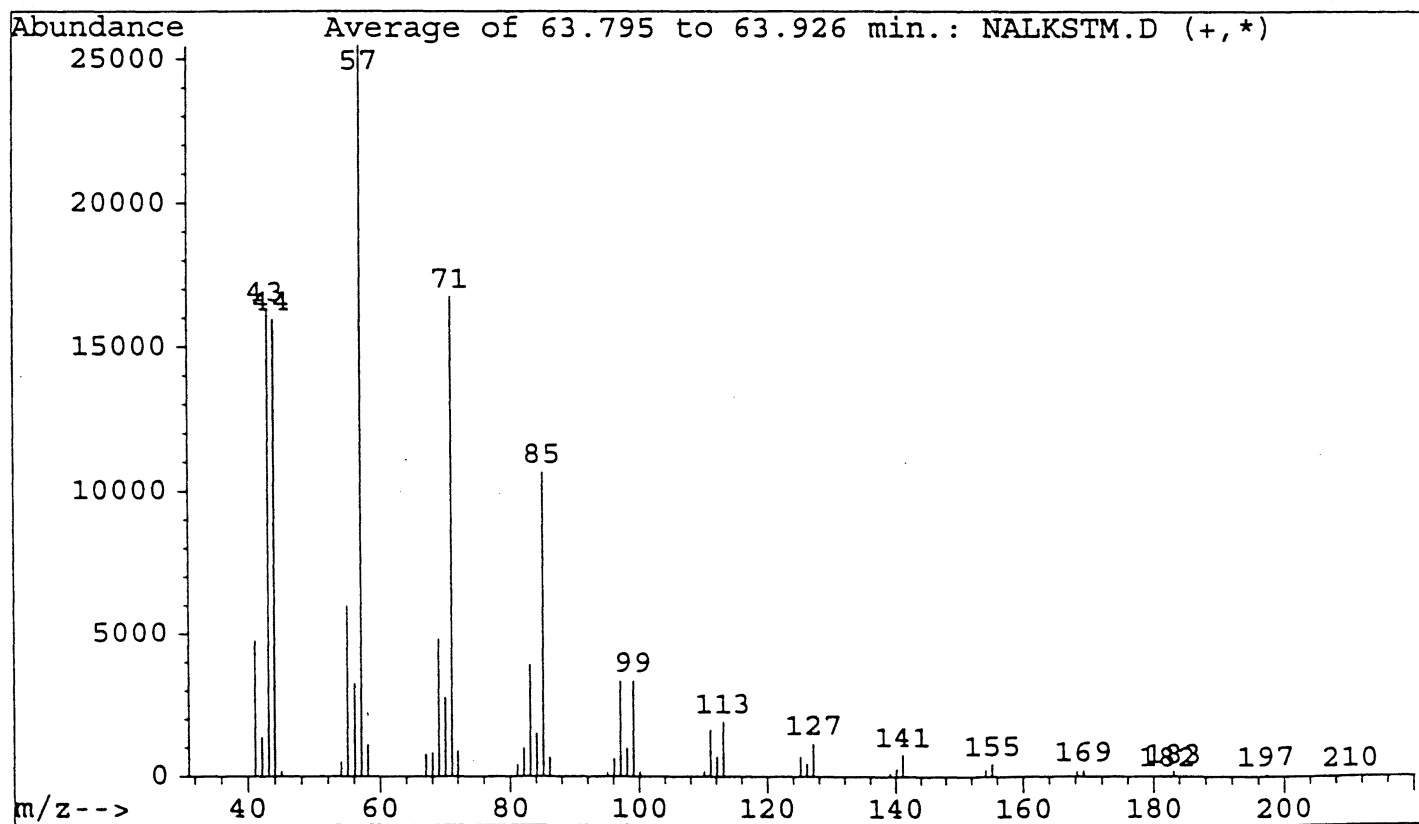
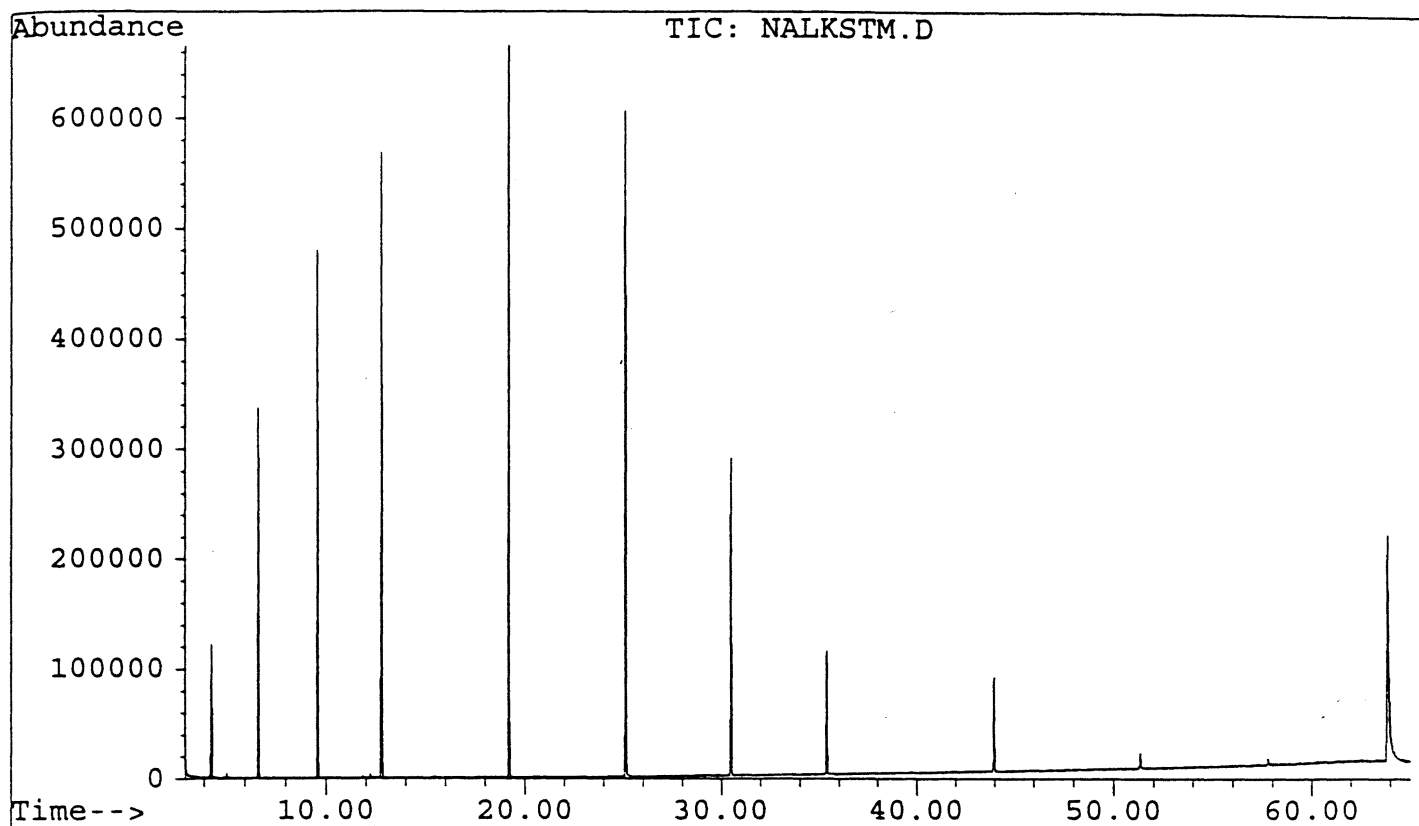


Figure 2.2. TIC of n-alkanes run by method "MLEE" after "Max Sensitivity Autotune" and the mass spectrum of Octacosane

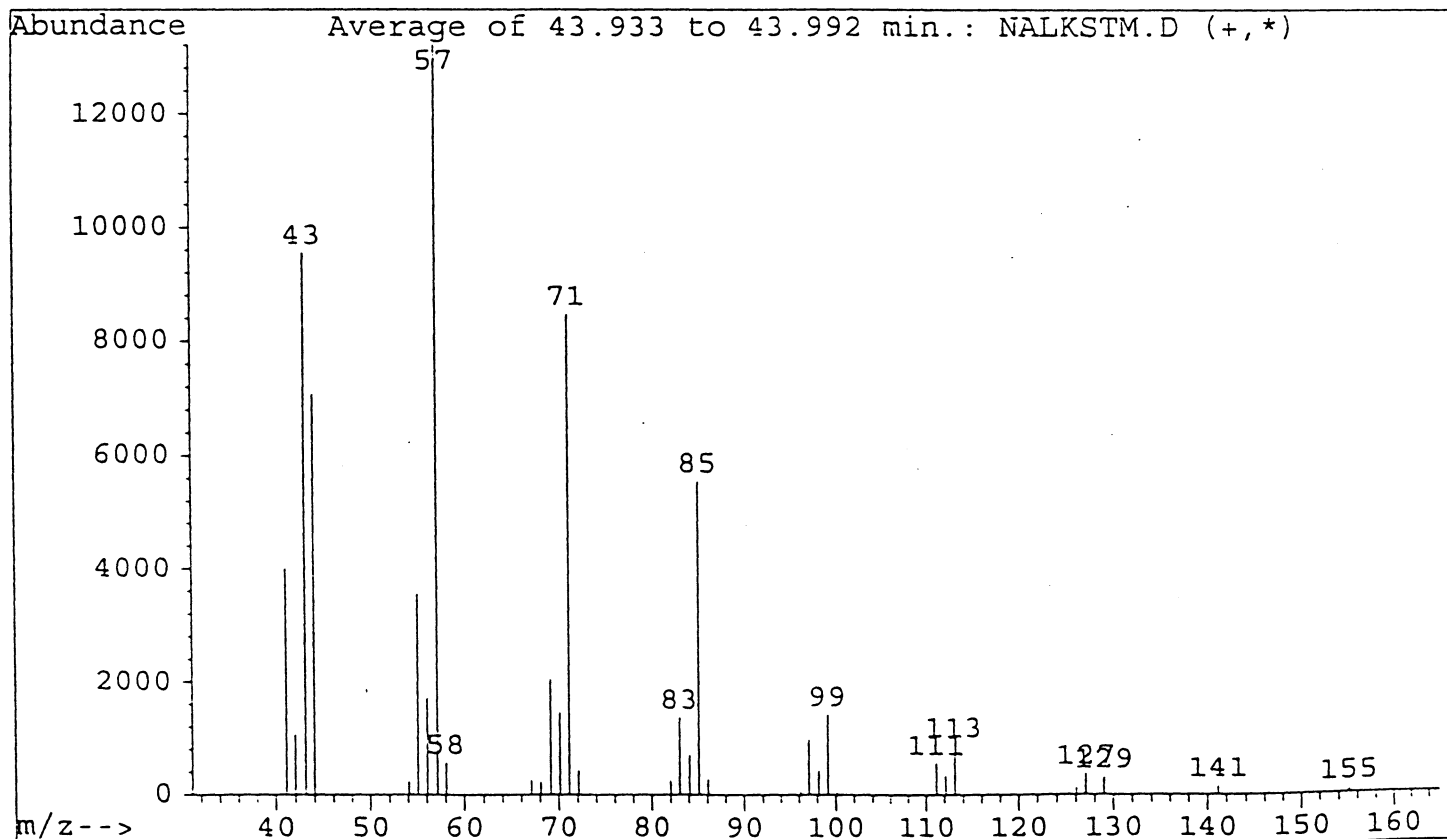
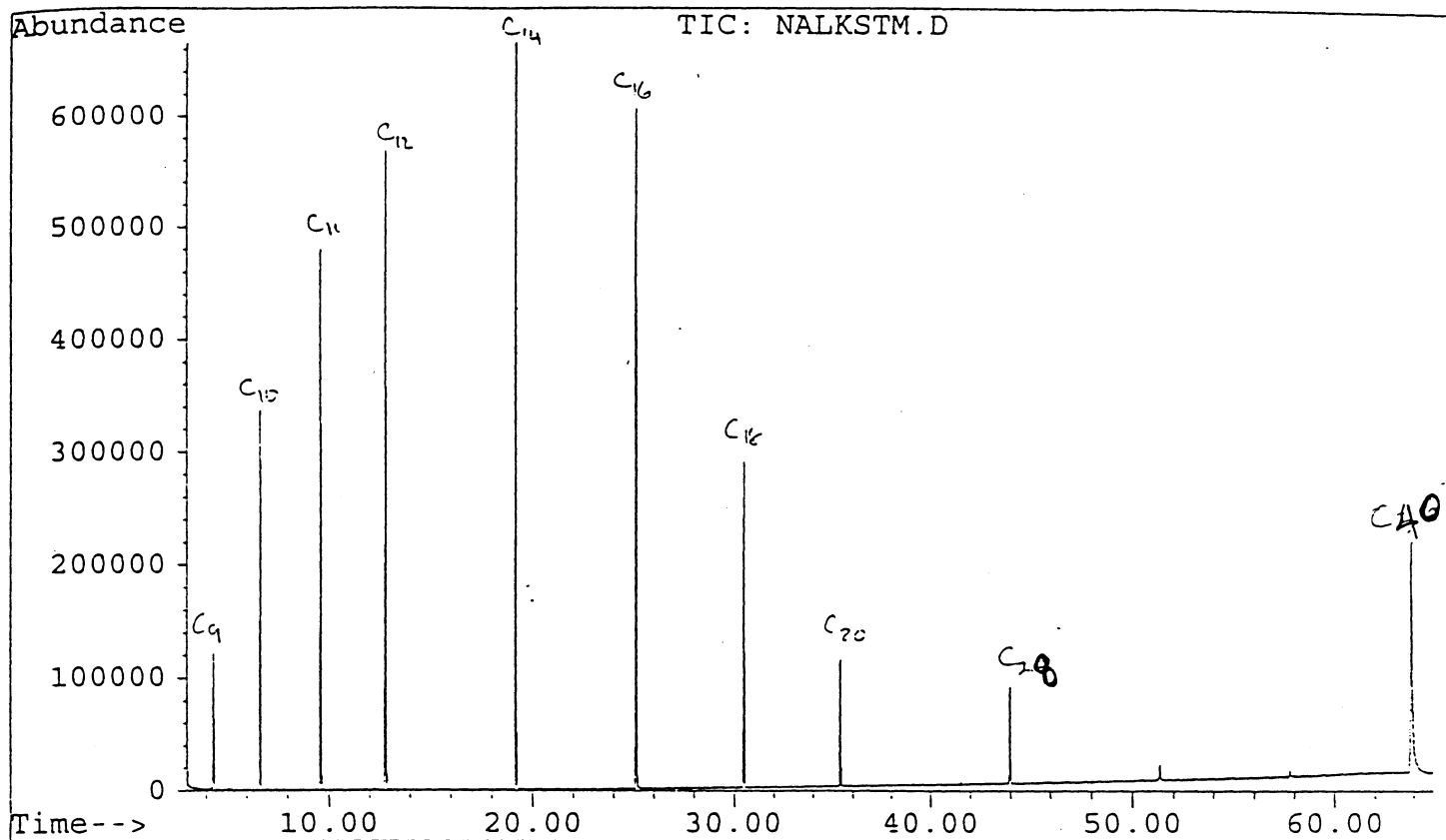


Figure 3.

TIC of PAH mixture run by method "TOLUENE" after
"Mid Mass Autotune" and the mass spectrum of
Pyrene

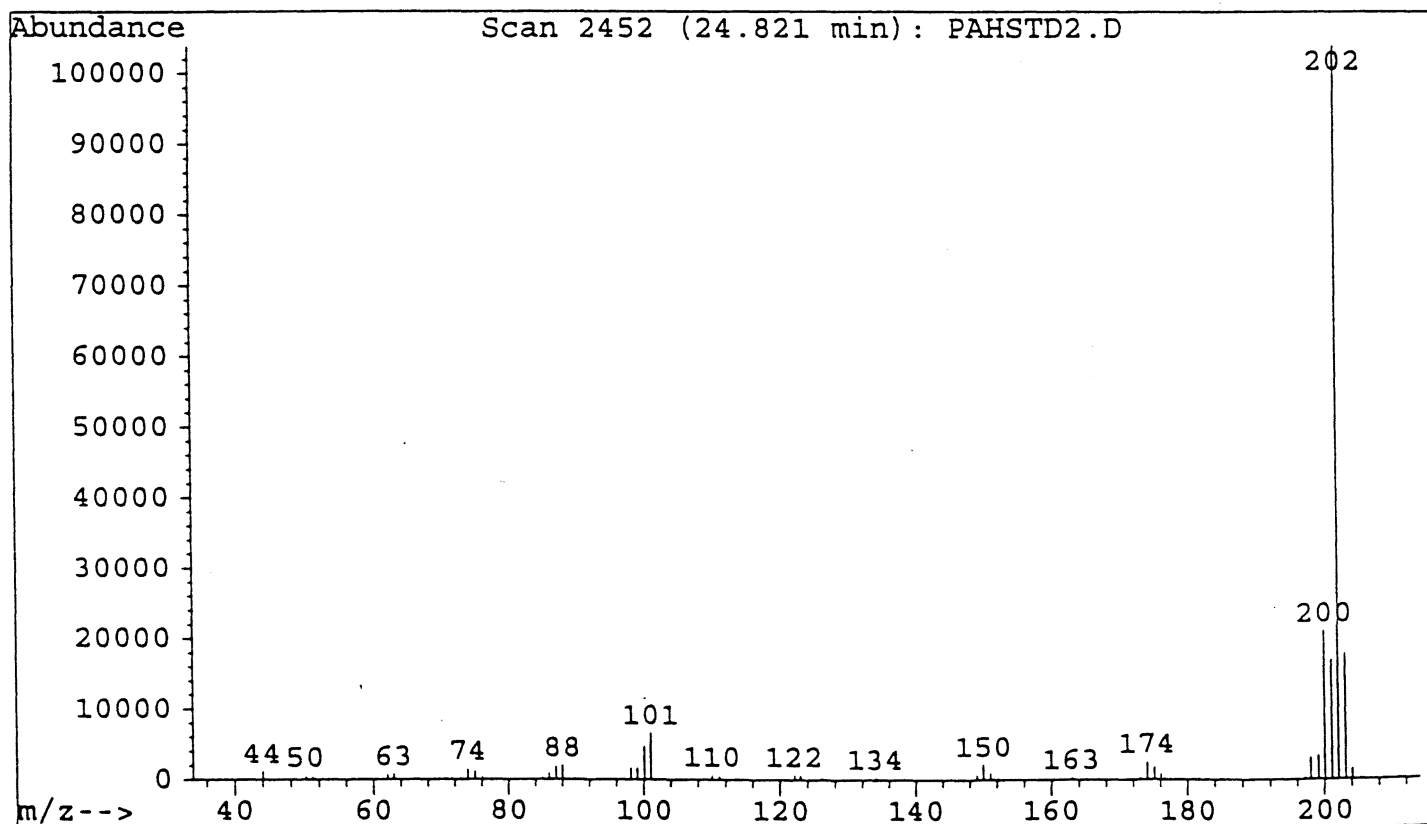
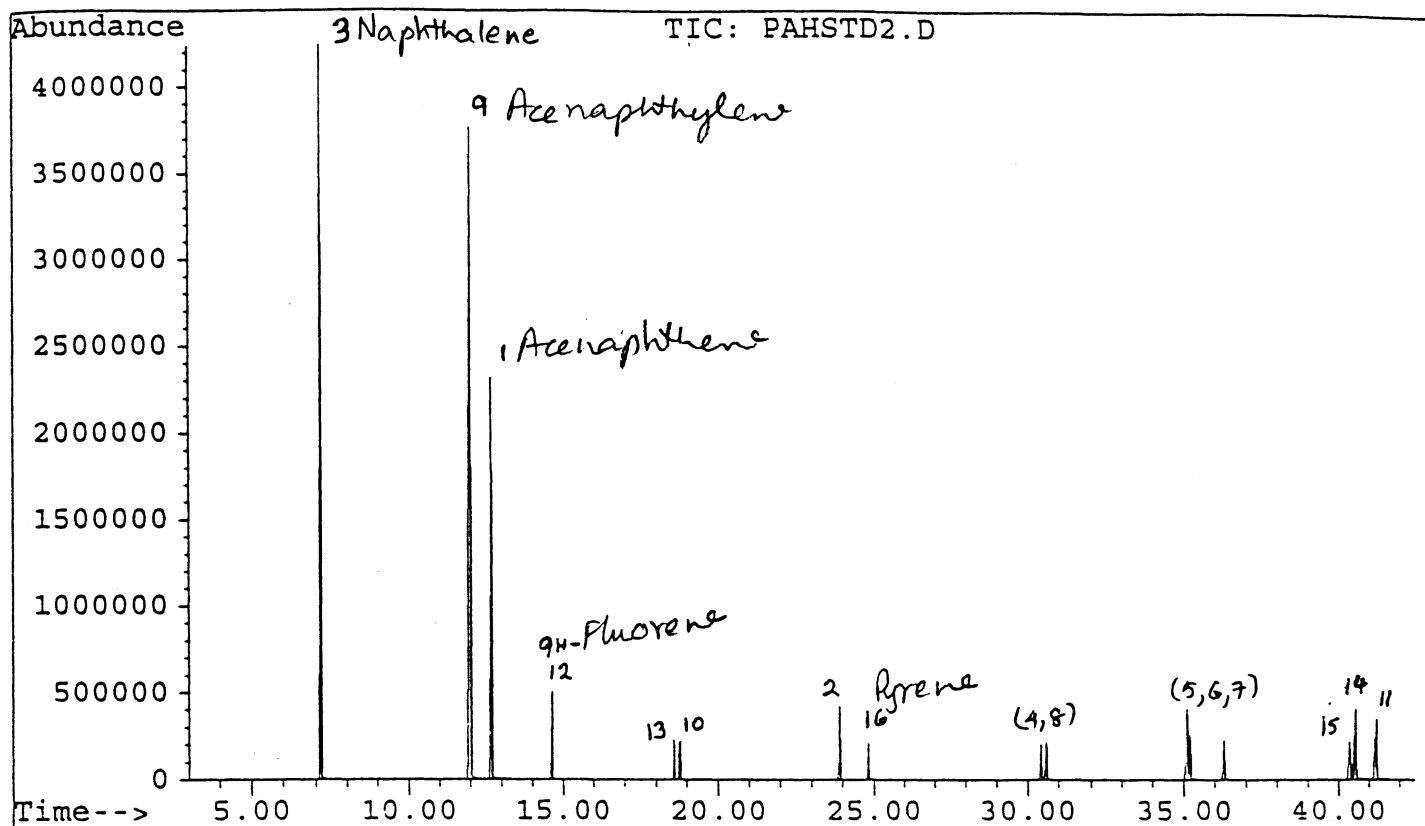


Figure 4.

TIC of PAH mixture run by method "MLEE" after
 "Max Sensitivity Autotune" and the mass spectrum
 of Naphthalene

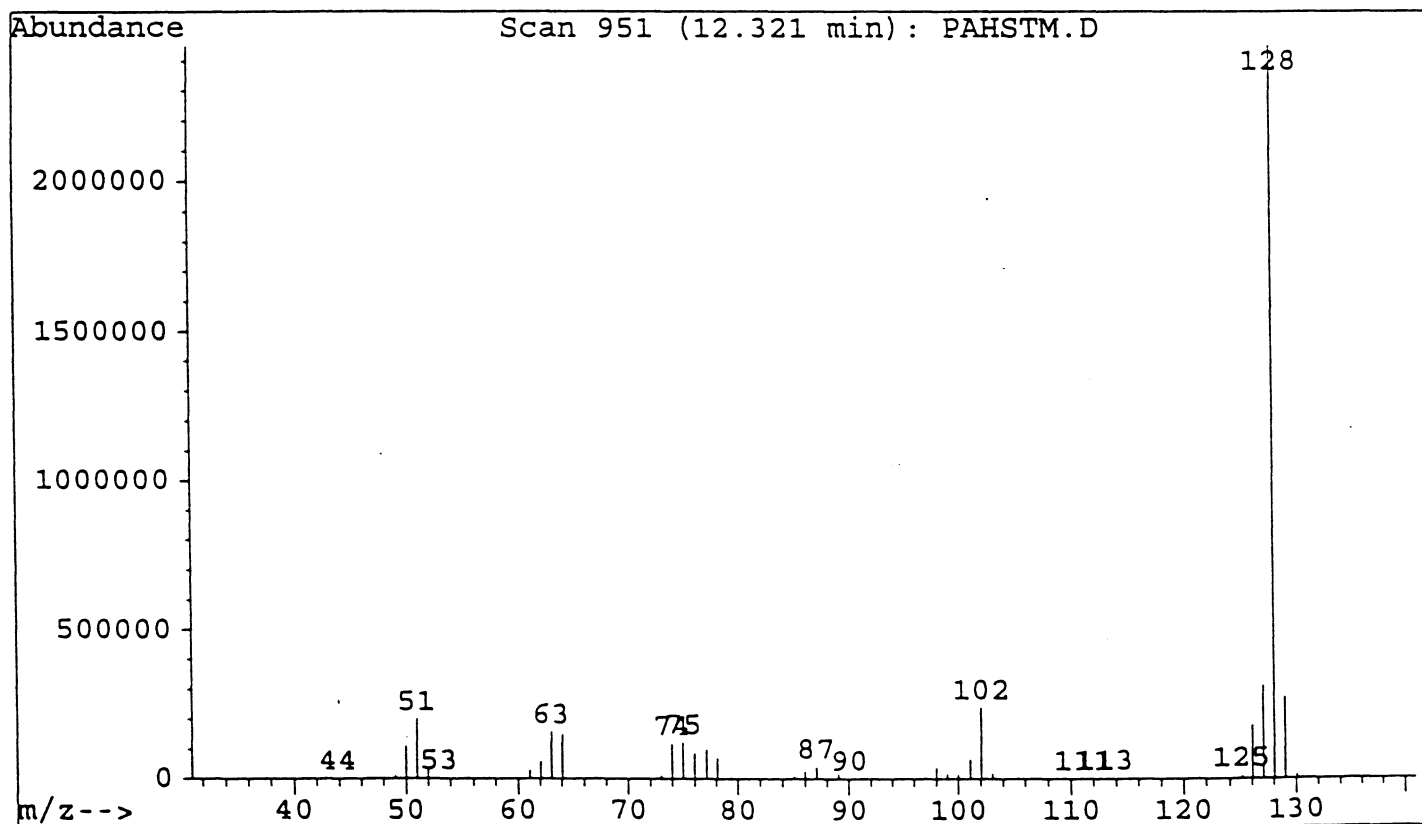
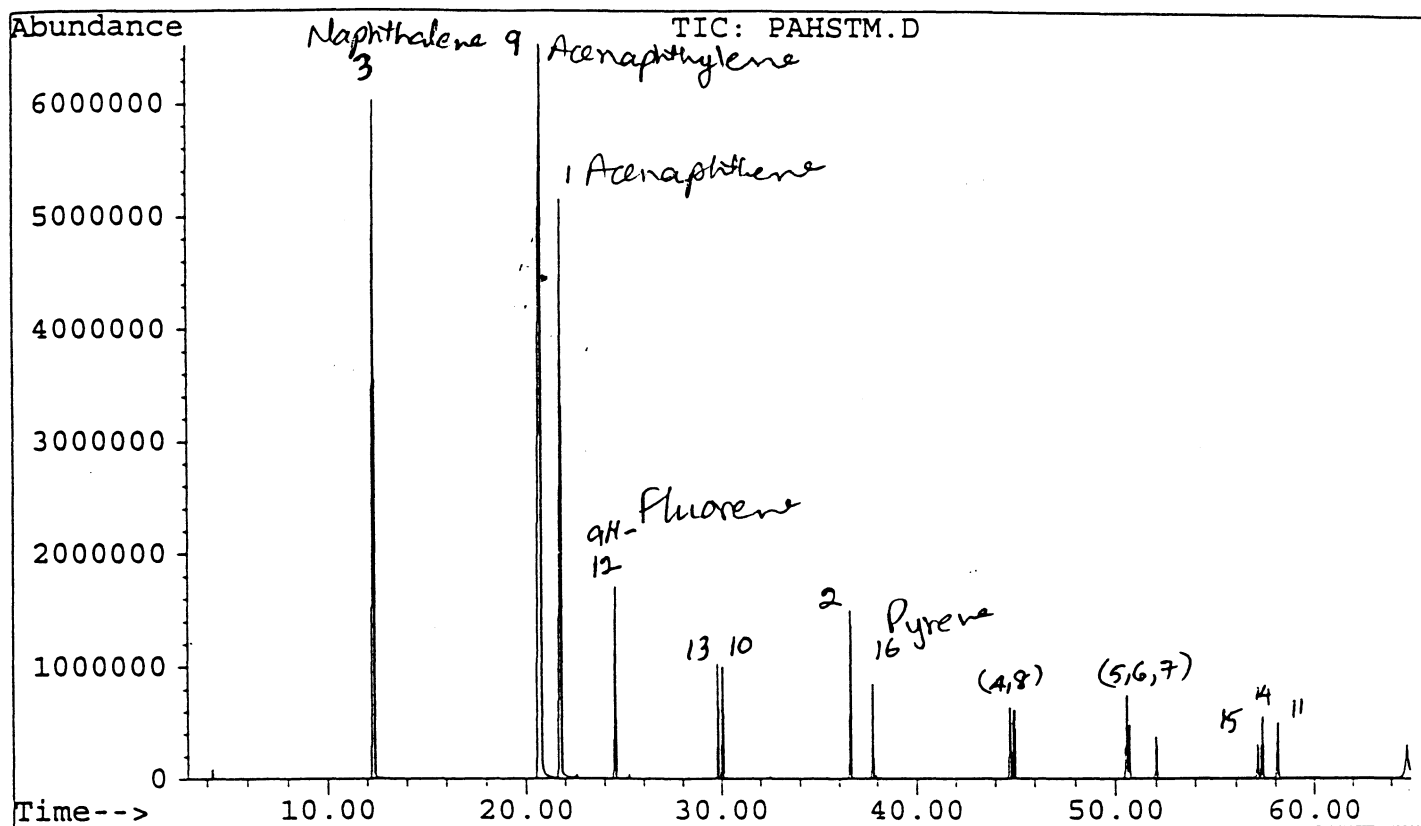


Figure 5. TIC of PAH mixture run by method "MLEE" after "Std. Spectra Autotune" and the mass spectrum of Naphthalene

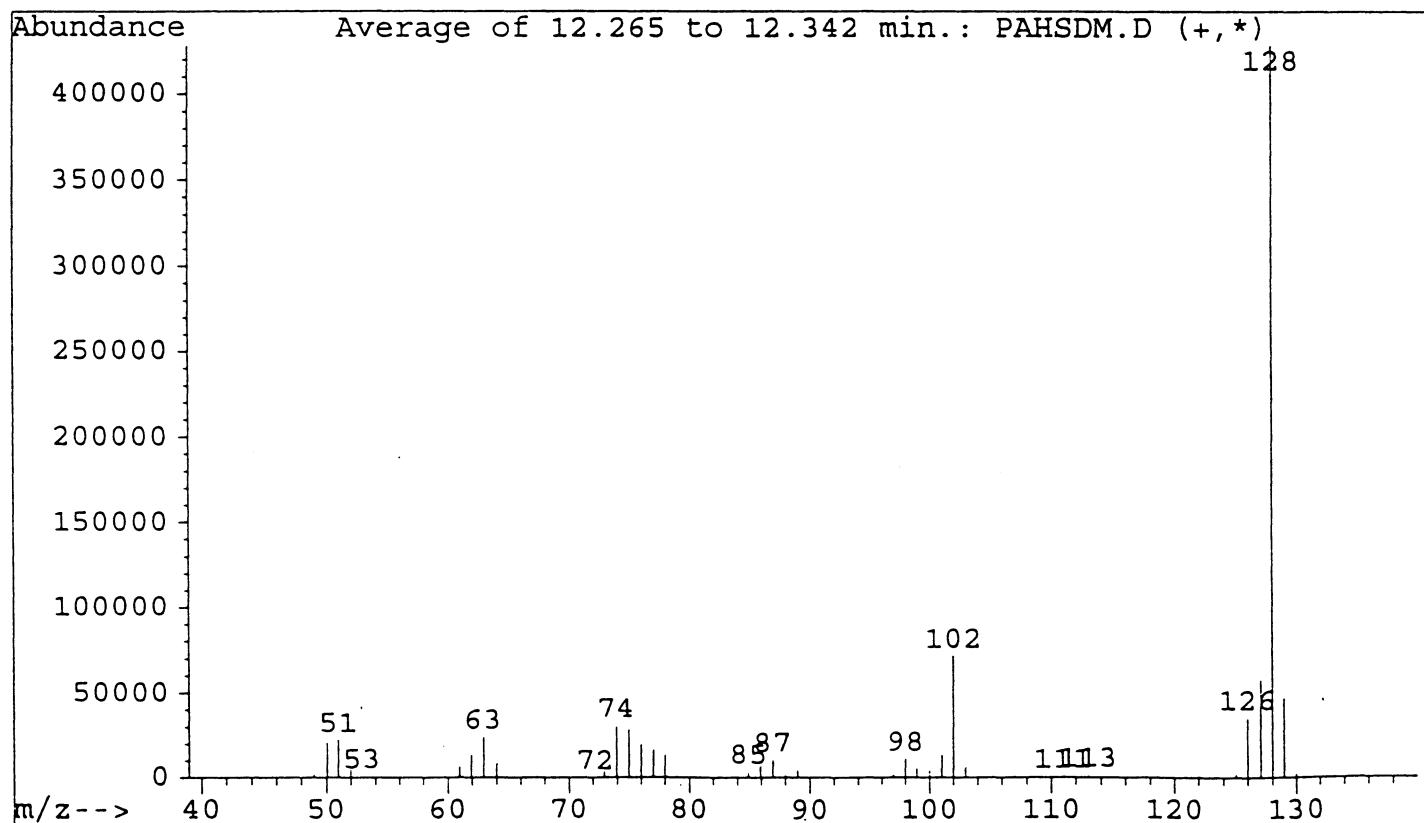
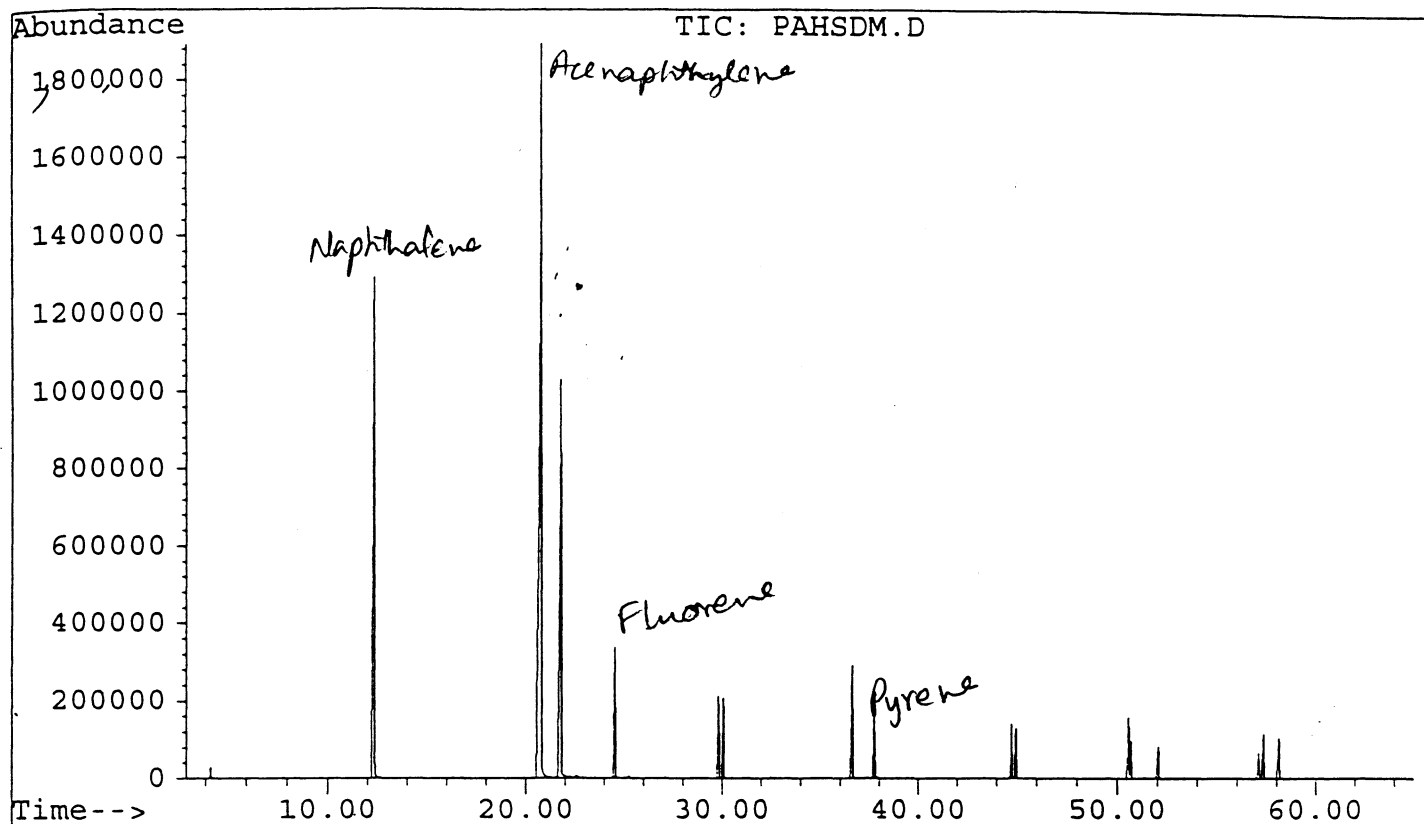


Figure 6. PYRIDINE EXTRACTION YIELD

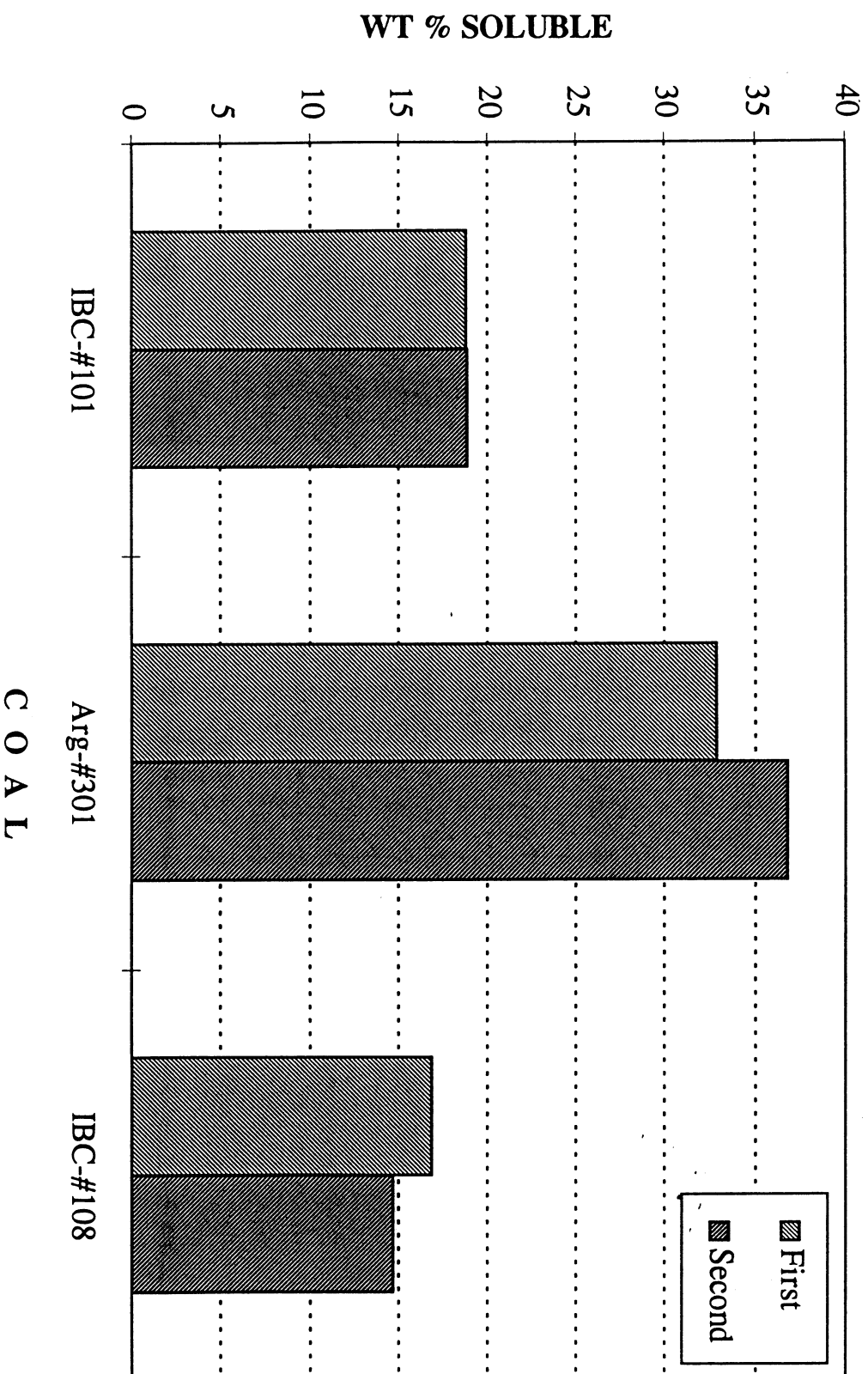


Figure 7. THF EXTRACTION YIELD

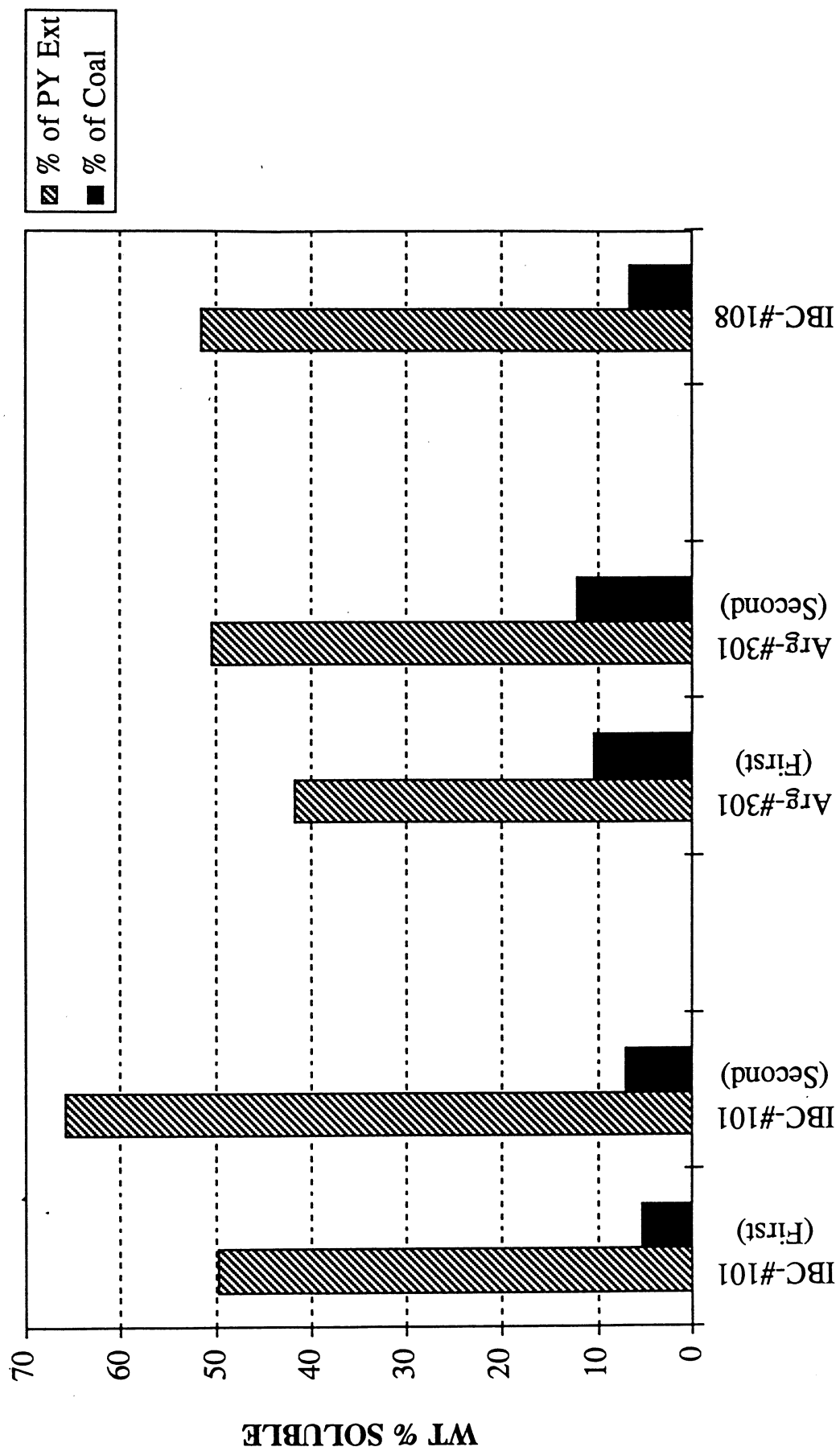


Figure 8. % OF EXTRACT RECOVERED

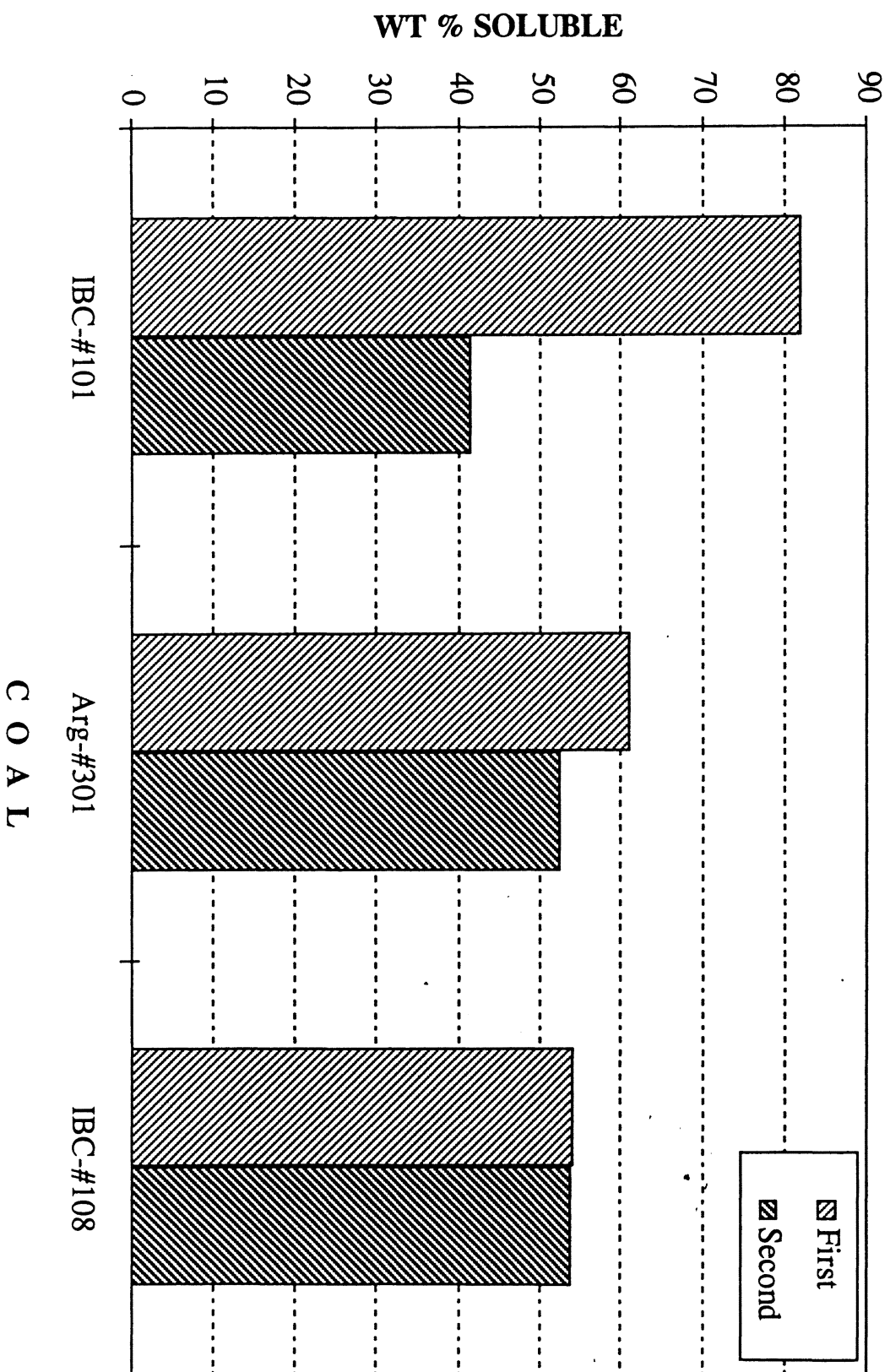


Figure 9. DESULFURIZATION OF MODEL COMPOUND DBT

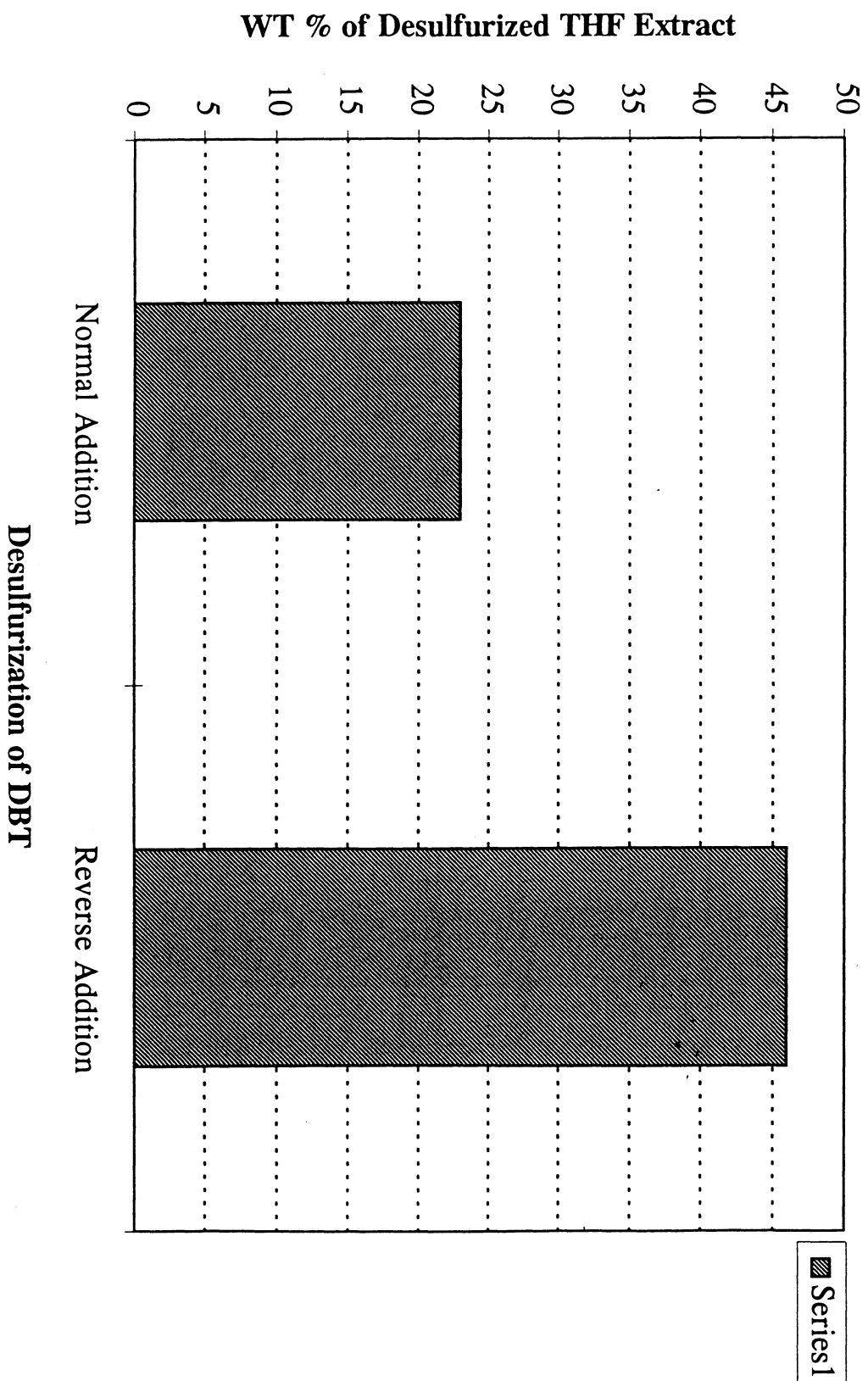


Figure 10(a). TIC of Desulfurized DBT (normal addition) run by method "DHBMLEE" and the mass spectrum of DBT

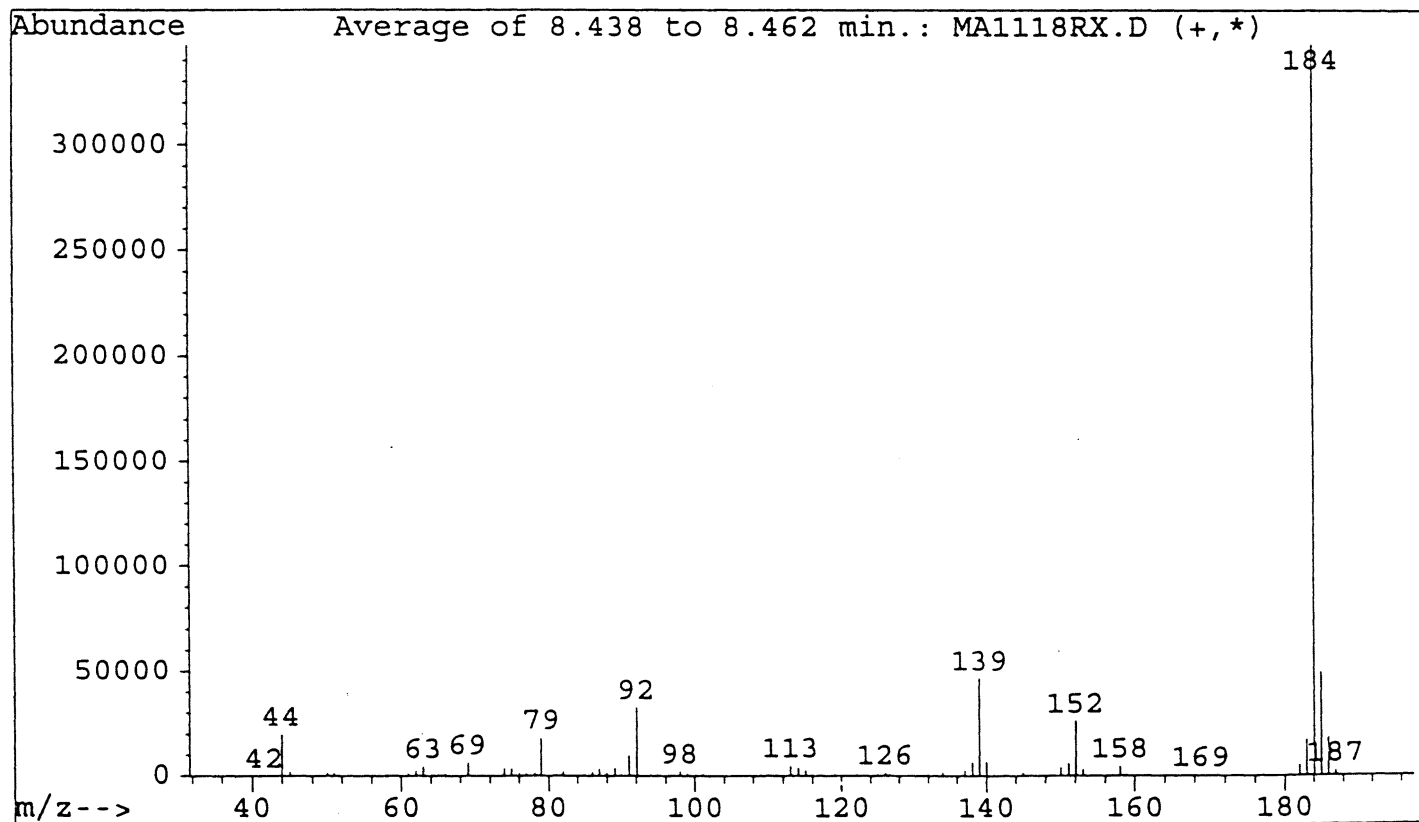
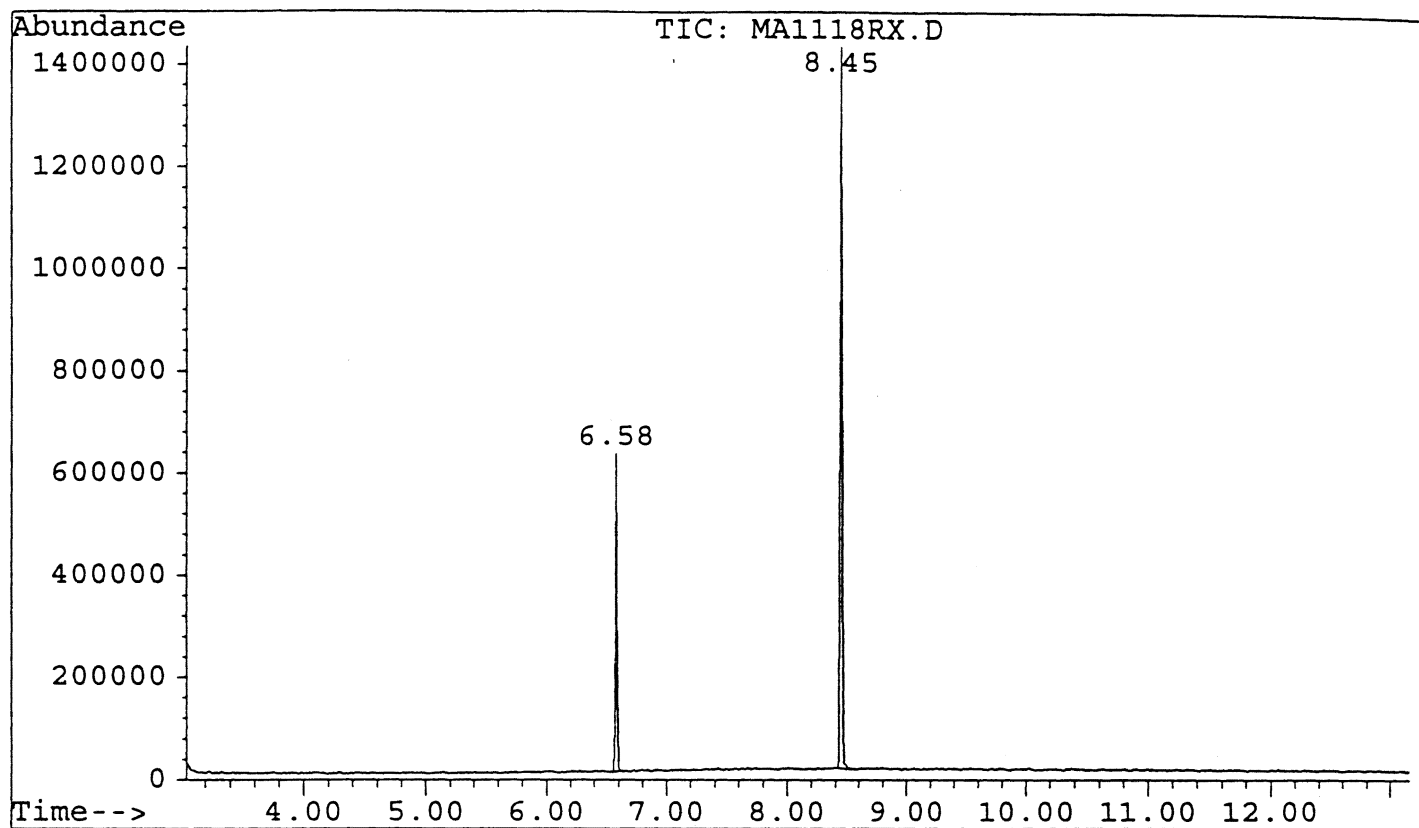


Figure 10(b). TIC of Desulfurized DBT (reverse addition) run by method "DHBMLEE" and the mass spectrum of Biphenyl

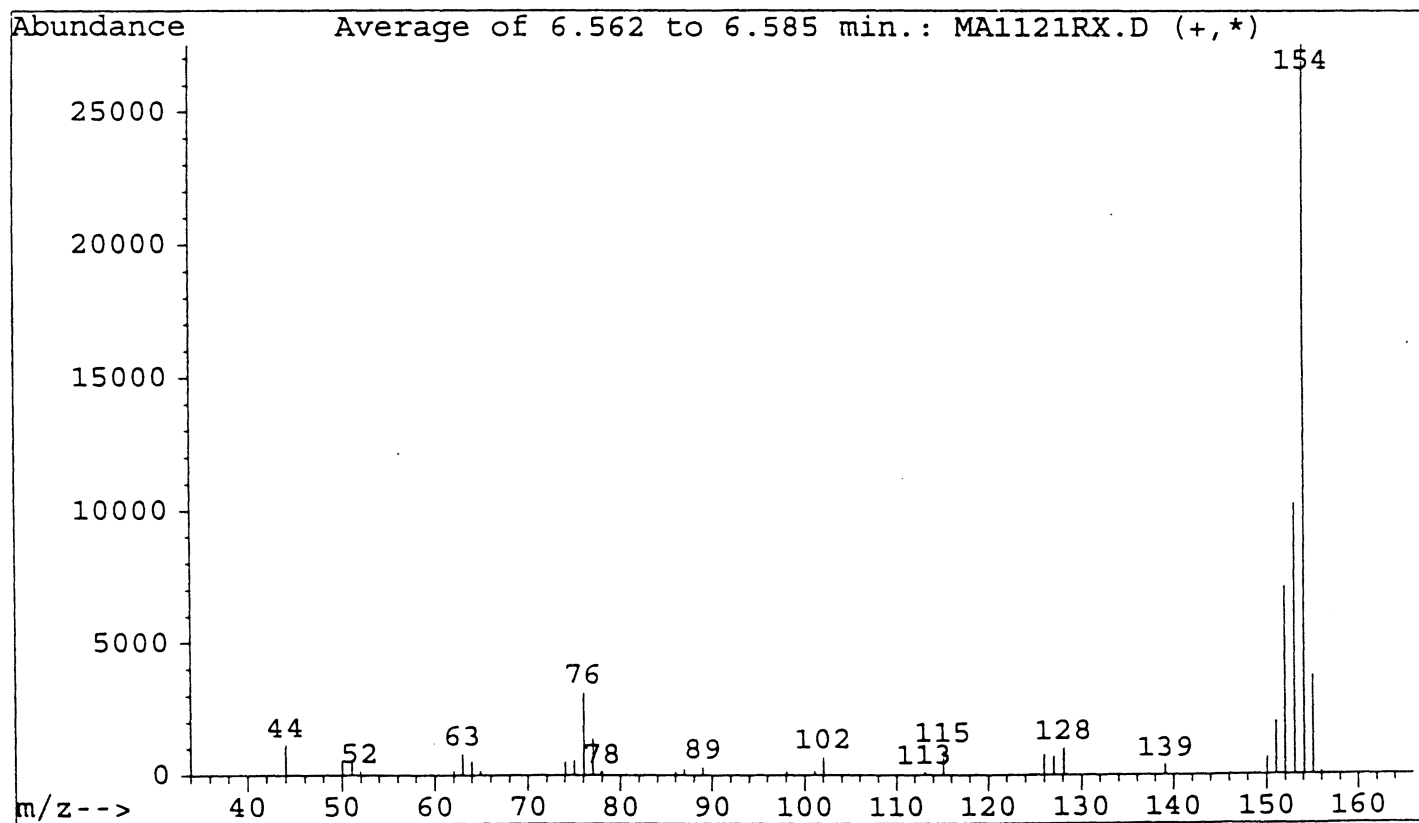
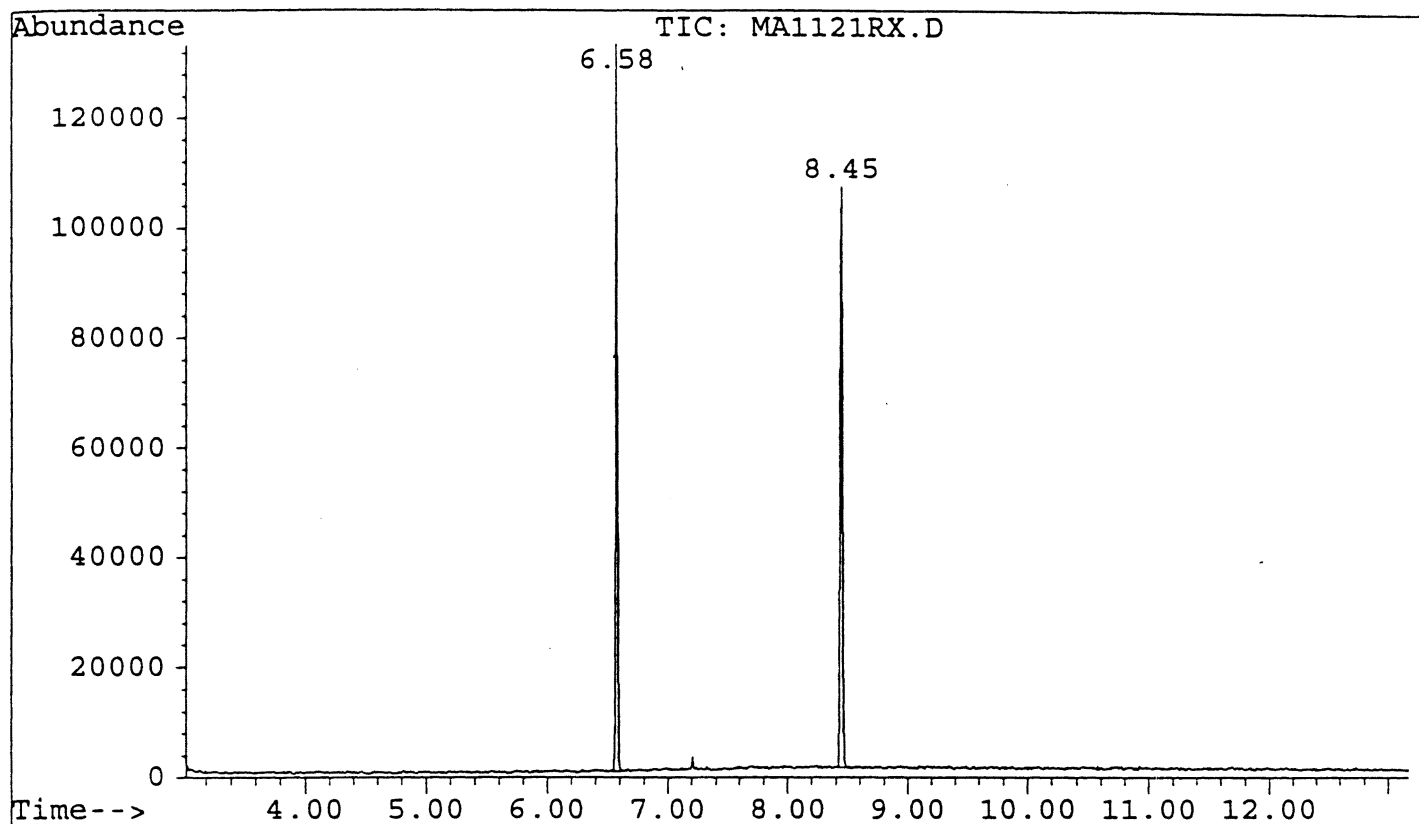


Figure 11.1. TIC of hexane fraction of before desulfurized sample of IBC-#101 (the 1st exp.)

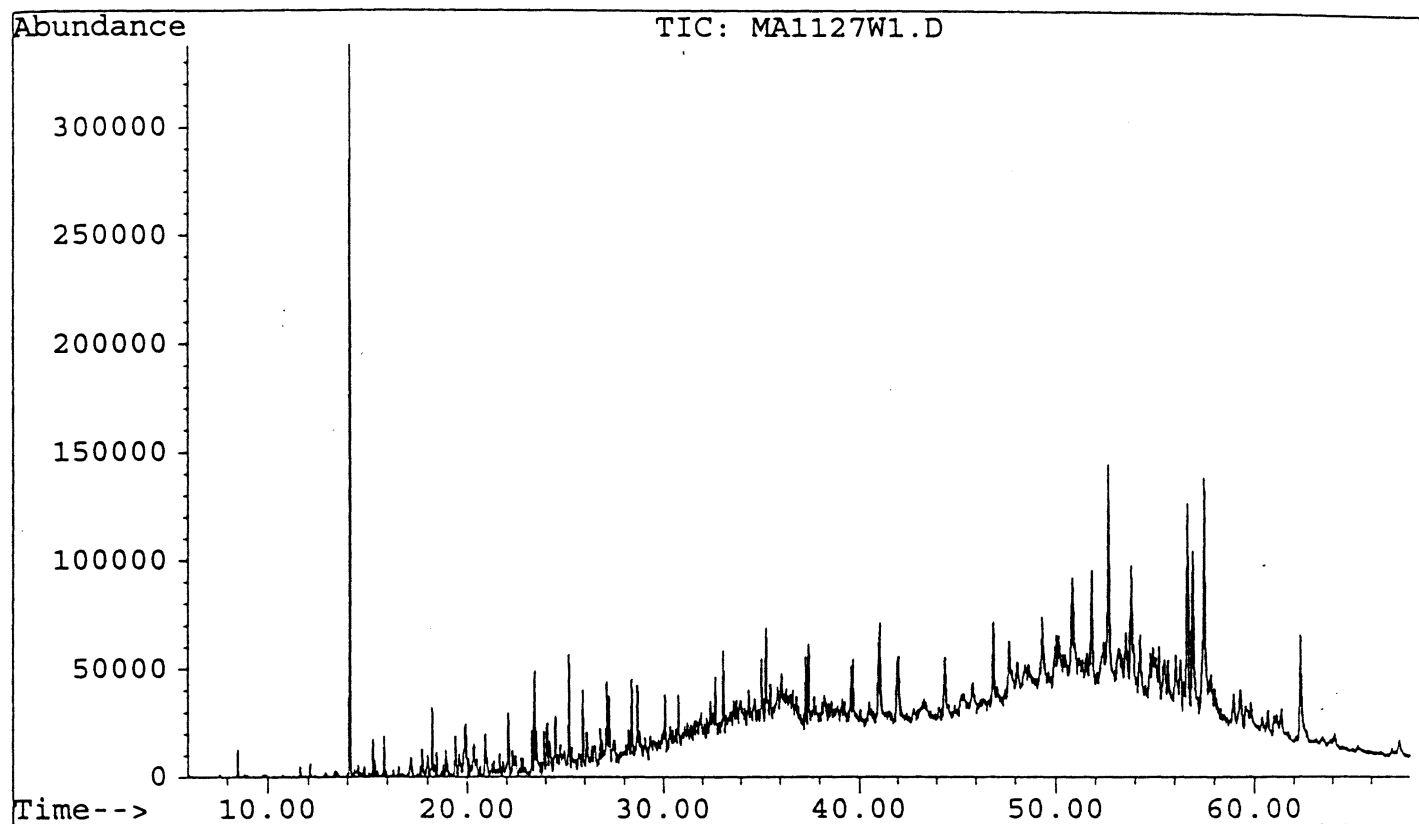


Figure 11.2. TIC of hexane fraction of before desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 23.6-30.6 min

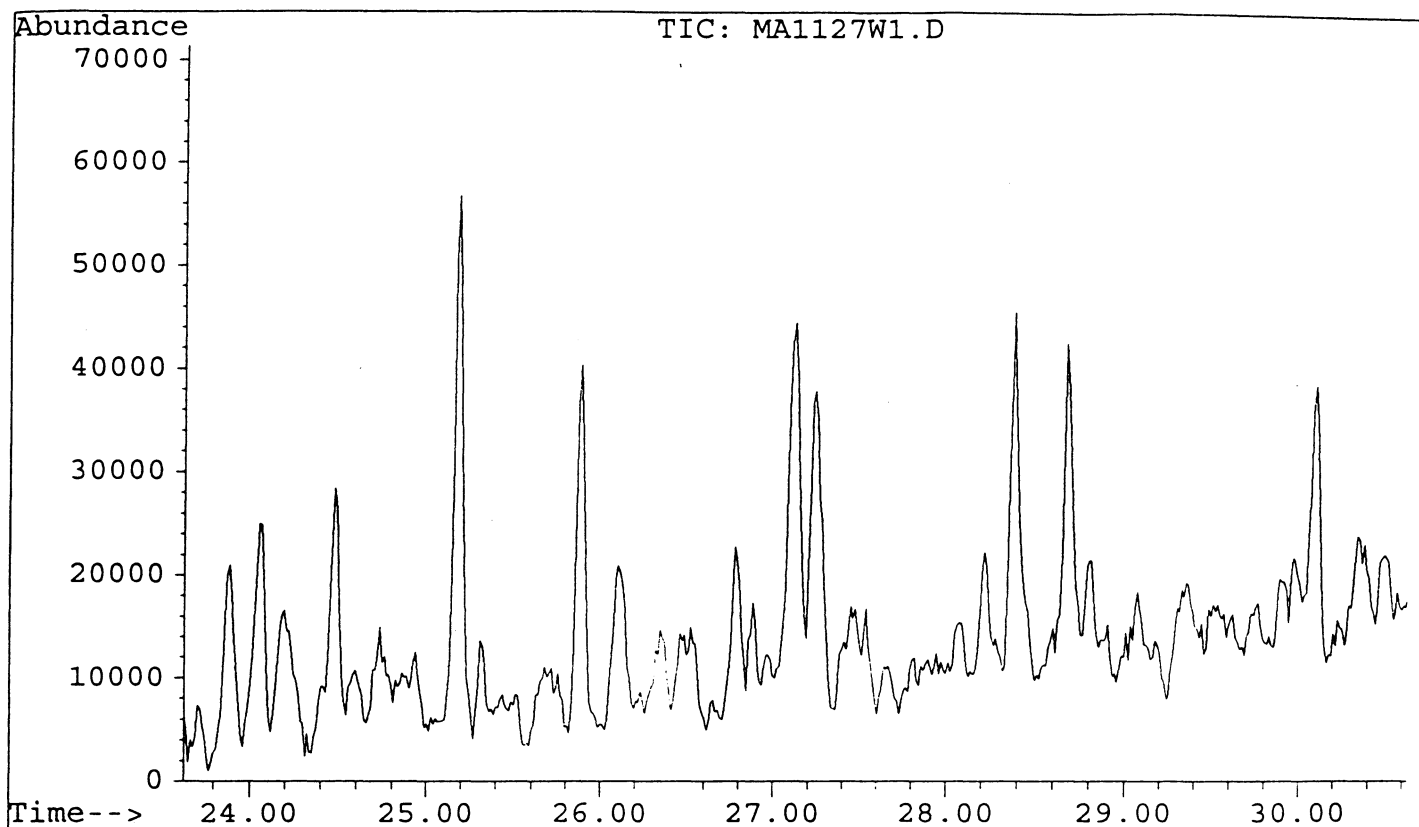


Figure 12.1. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 1st exp.)

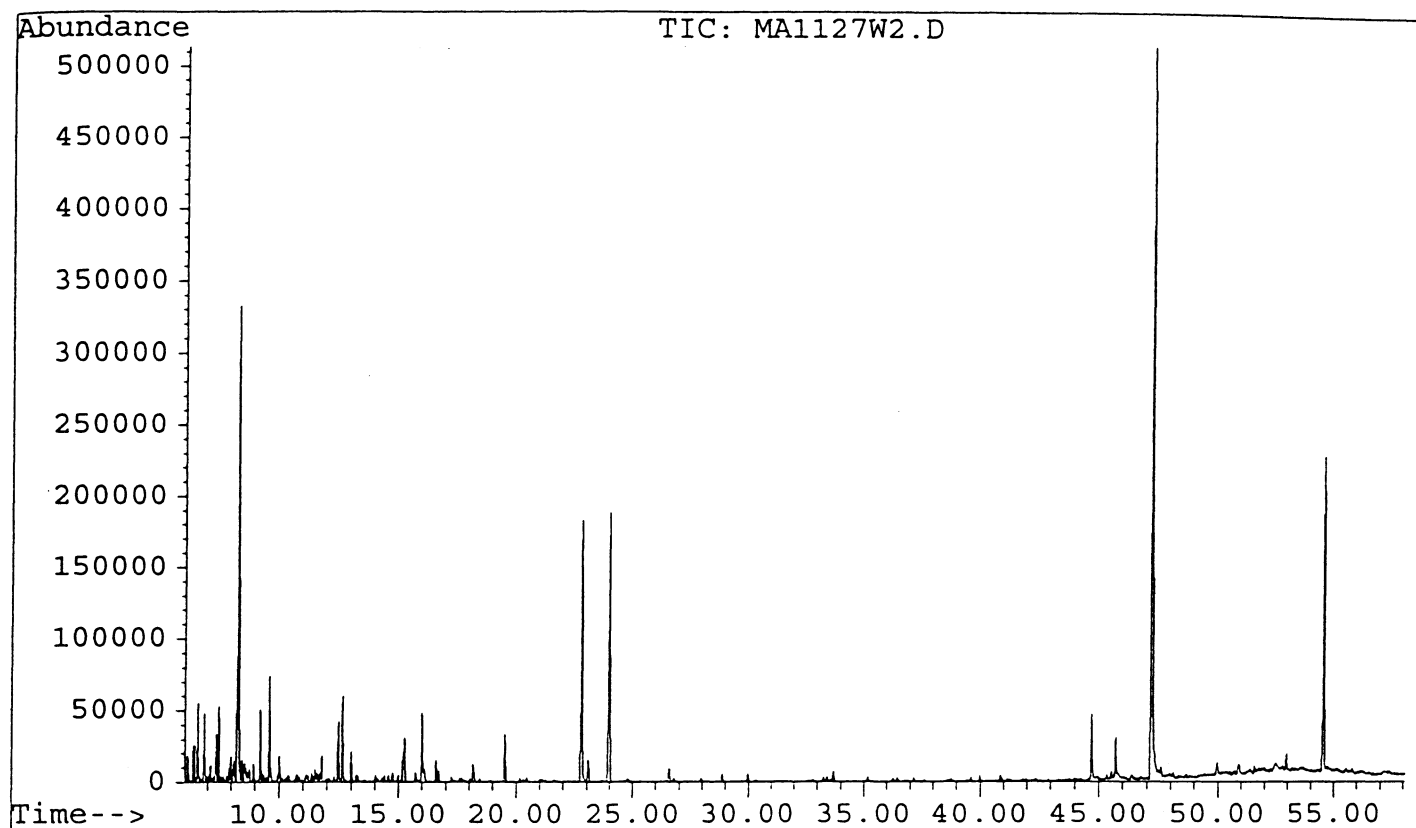


Figure 12.2. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 10-12 min and the mass spectrum of 1,2-Benzisothiazole

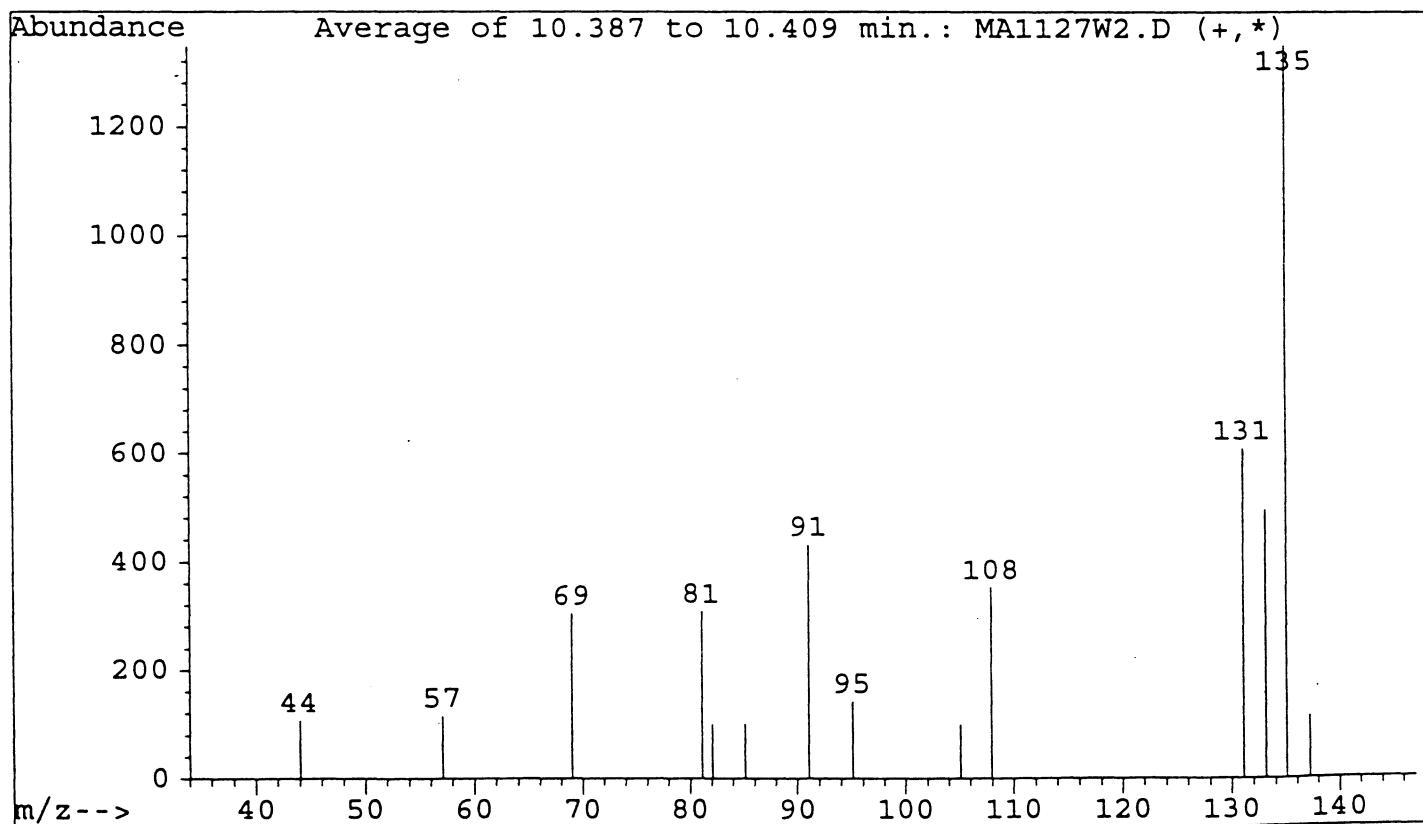
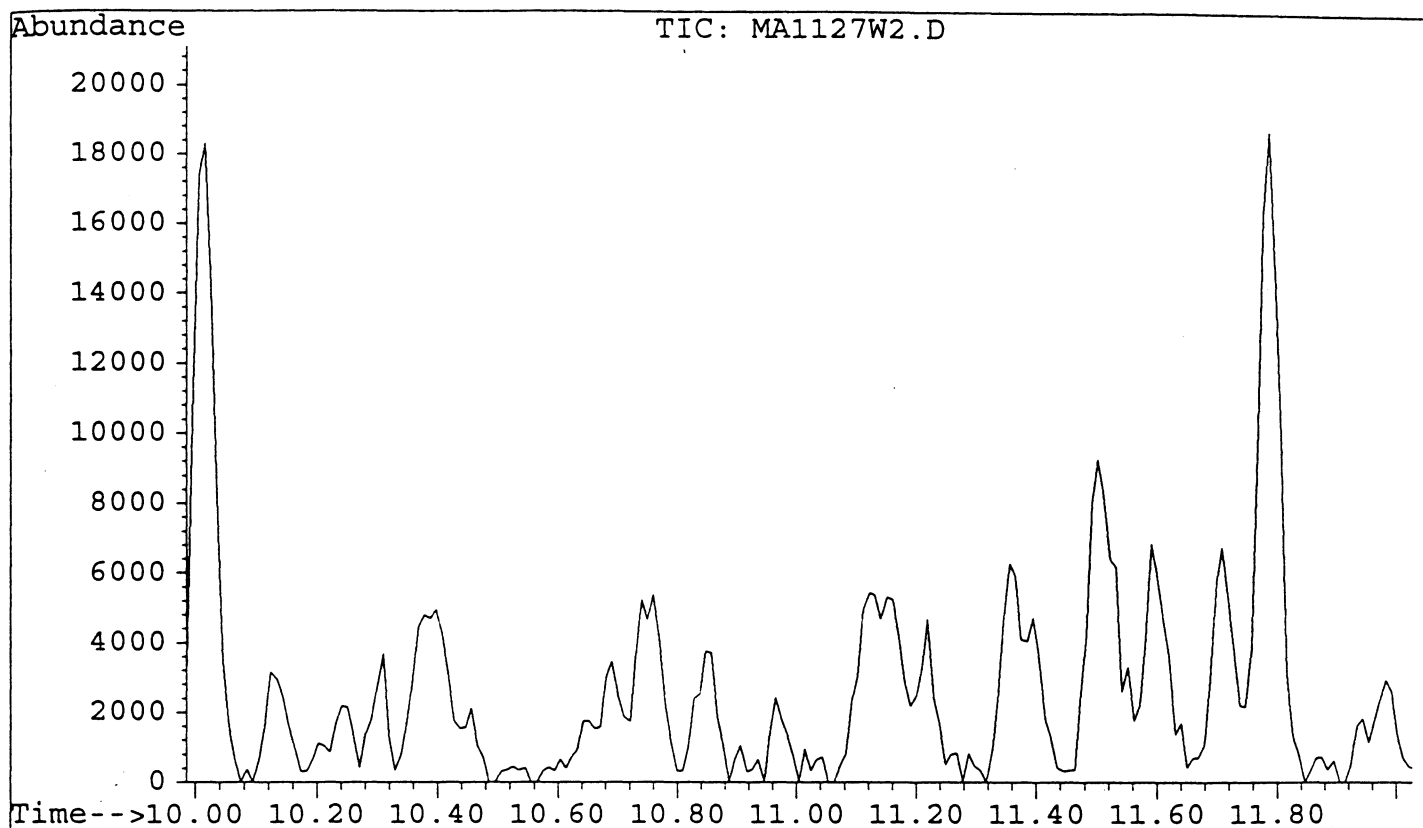


Figure 12.3. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 6.0-10.2 min and the mass spectrum of Naphthalene

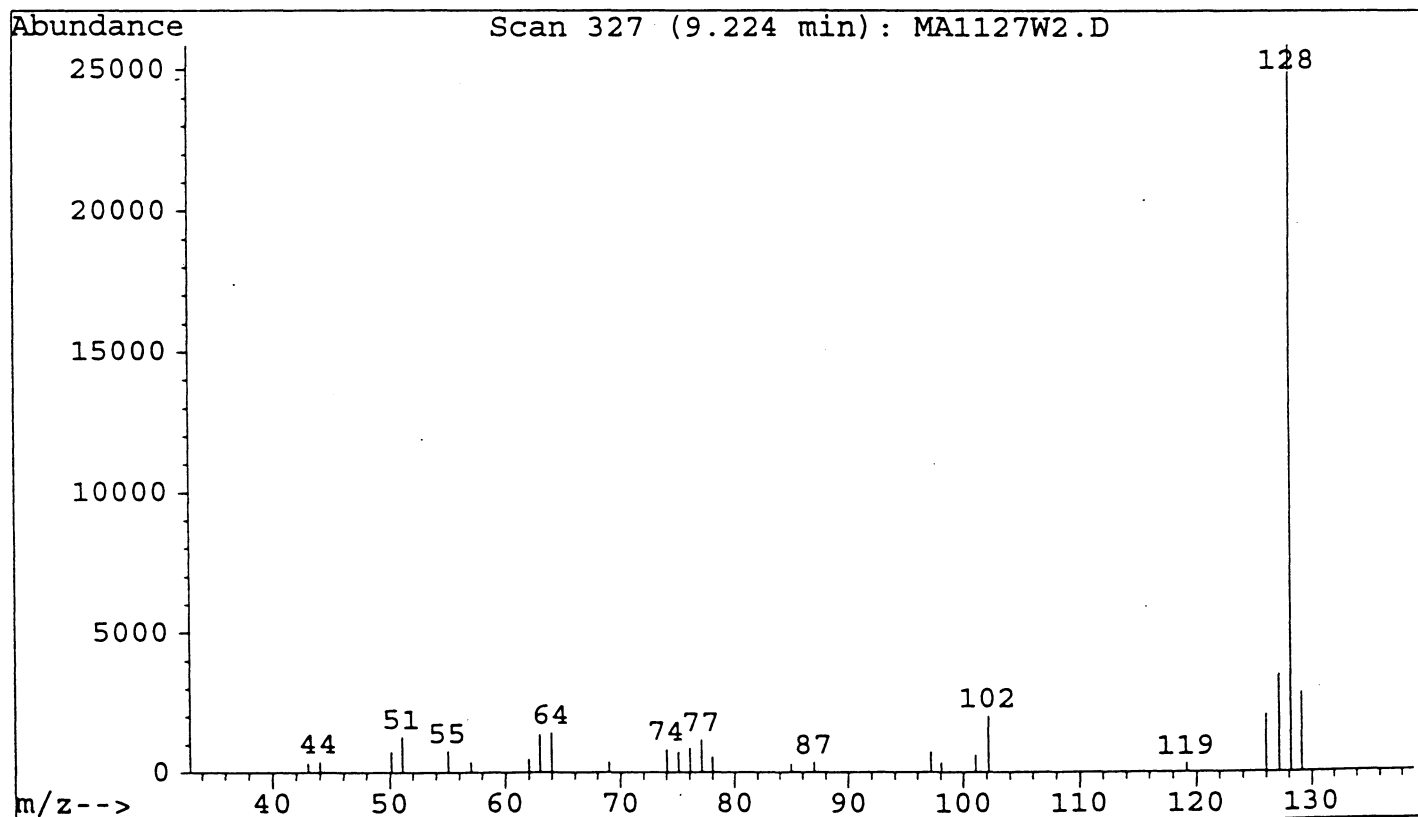
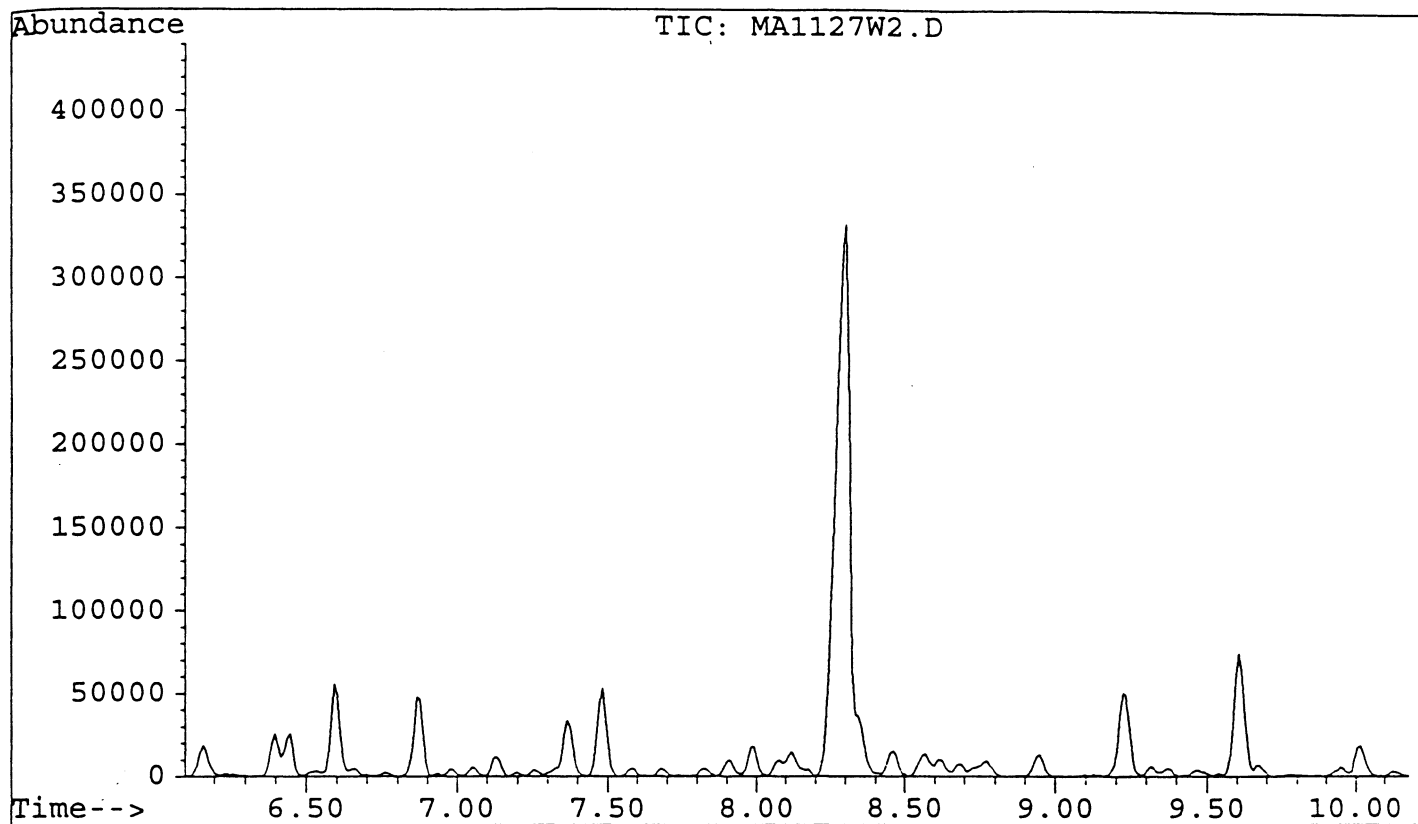


Figure 12.4. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 8.4-22.4 min and the mass spectrum of Naphthalne,2-methyl

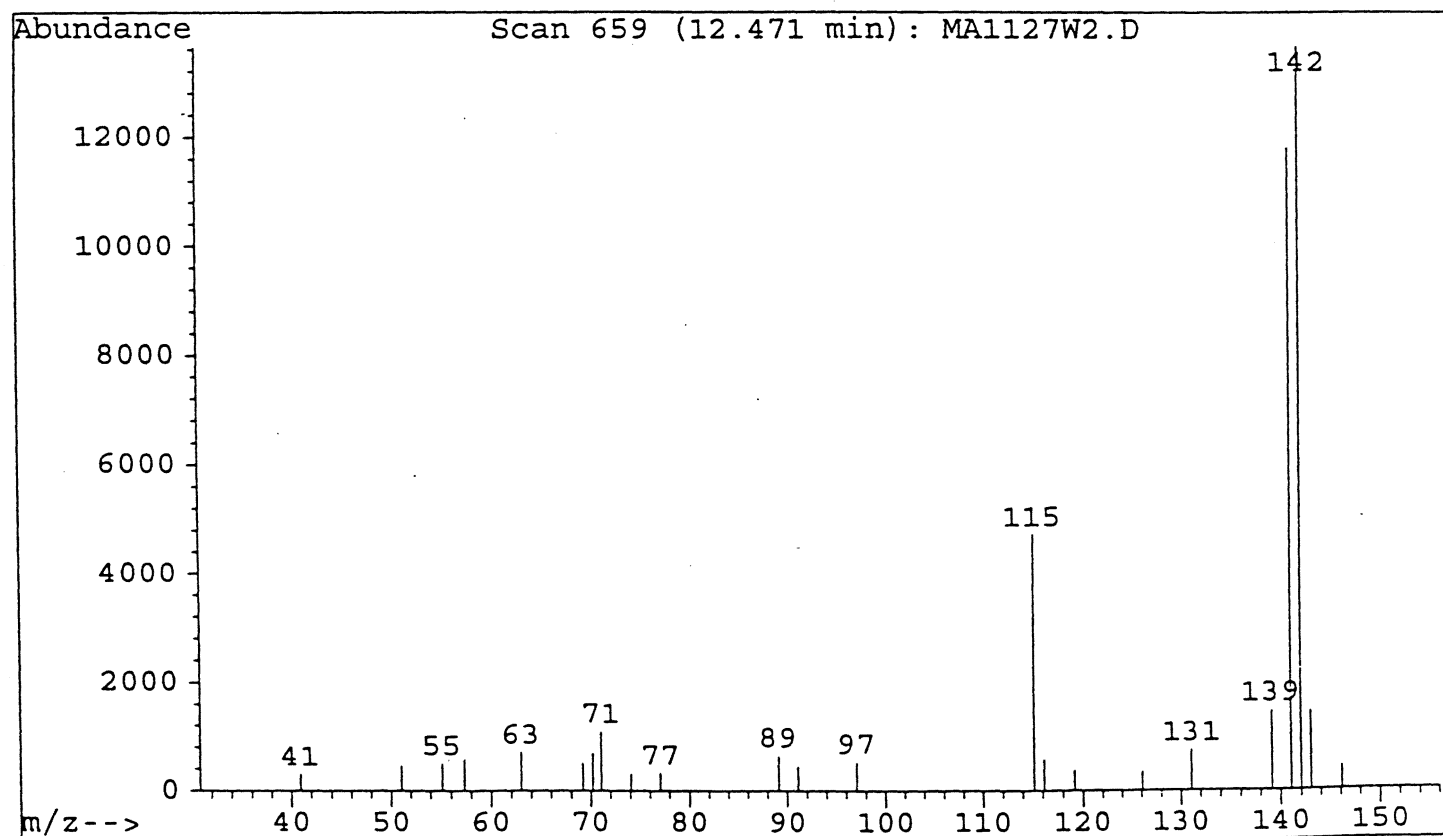
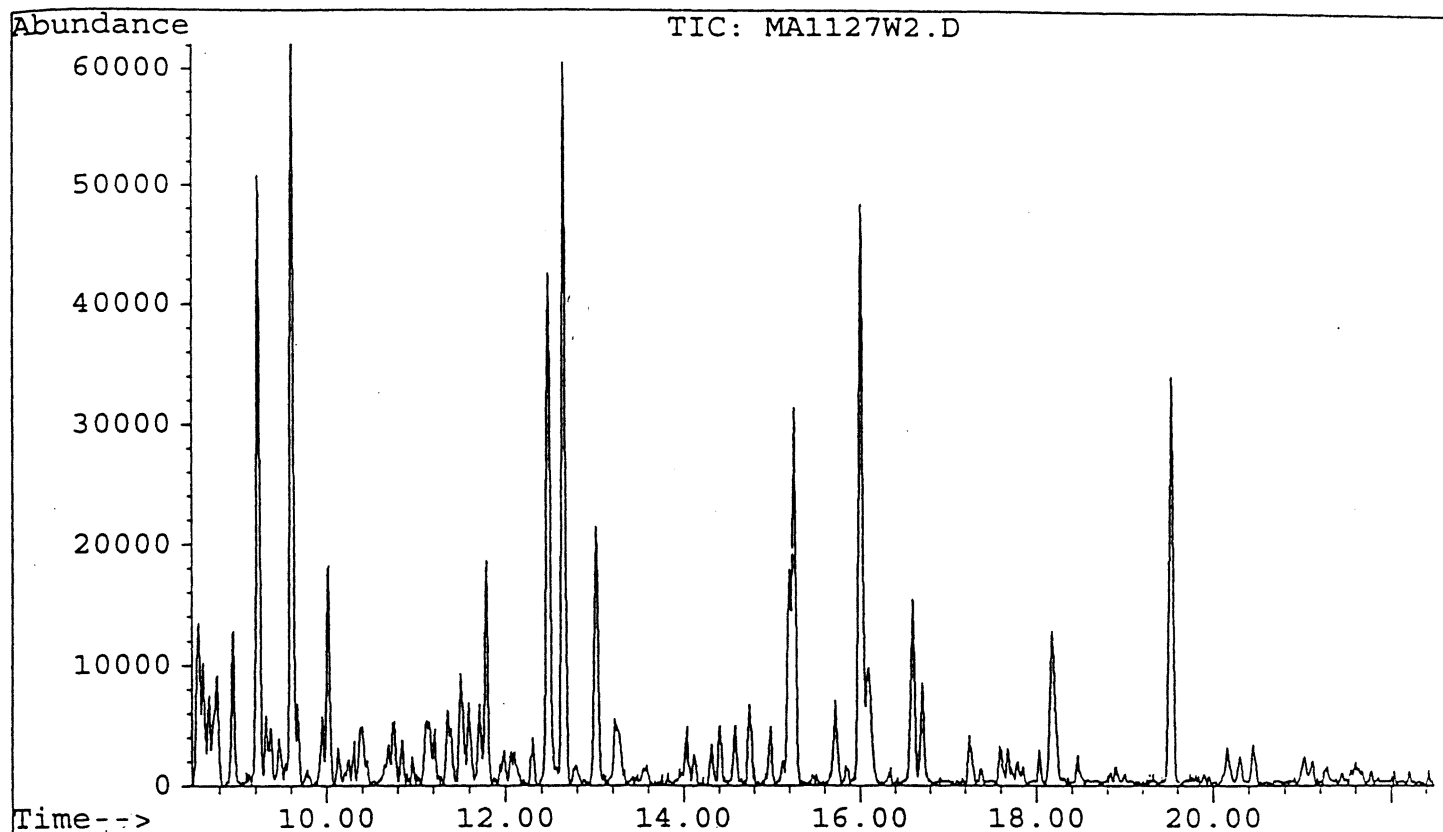


Figure 12.5. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 8.4-22.4 min and the mass spectrum of Heptadecane

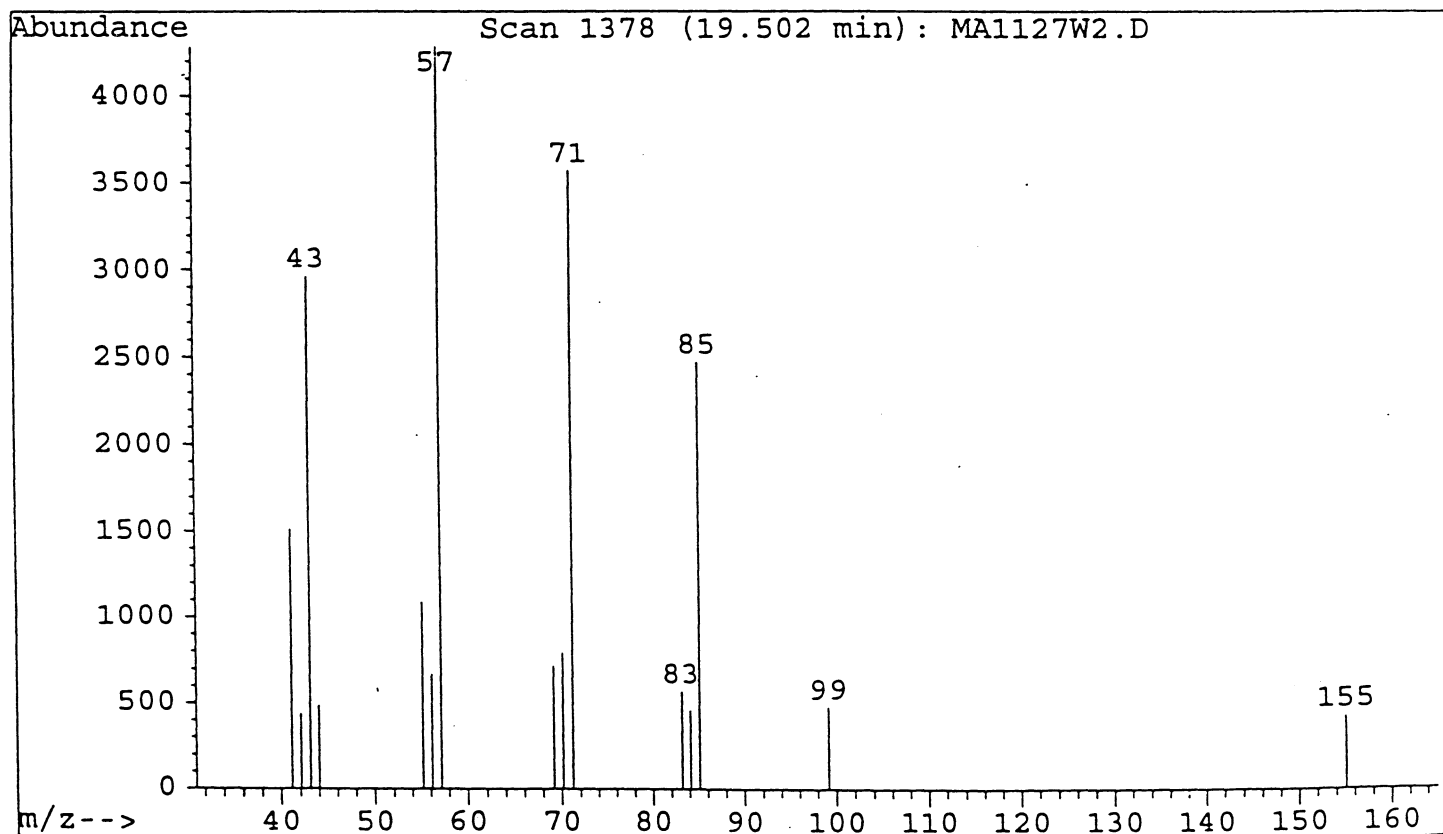
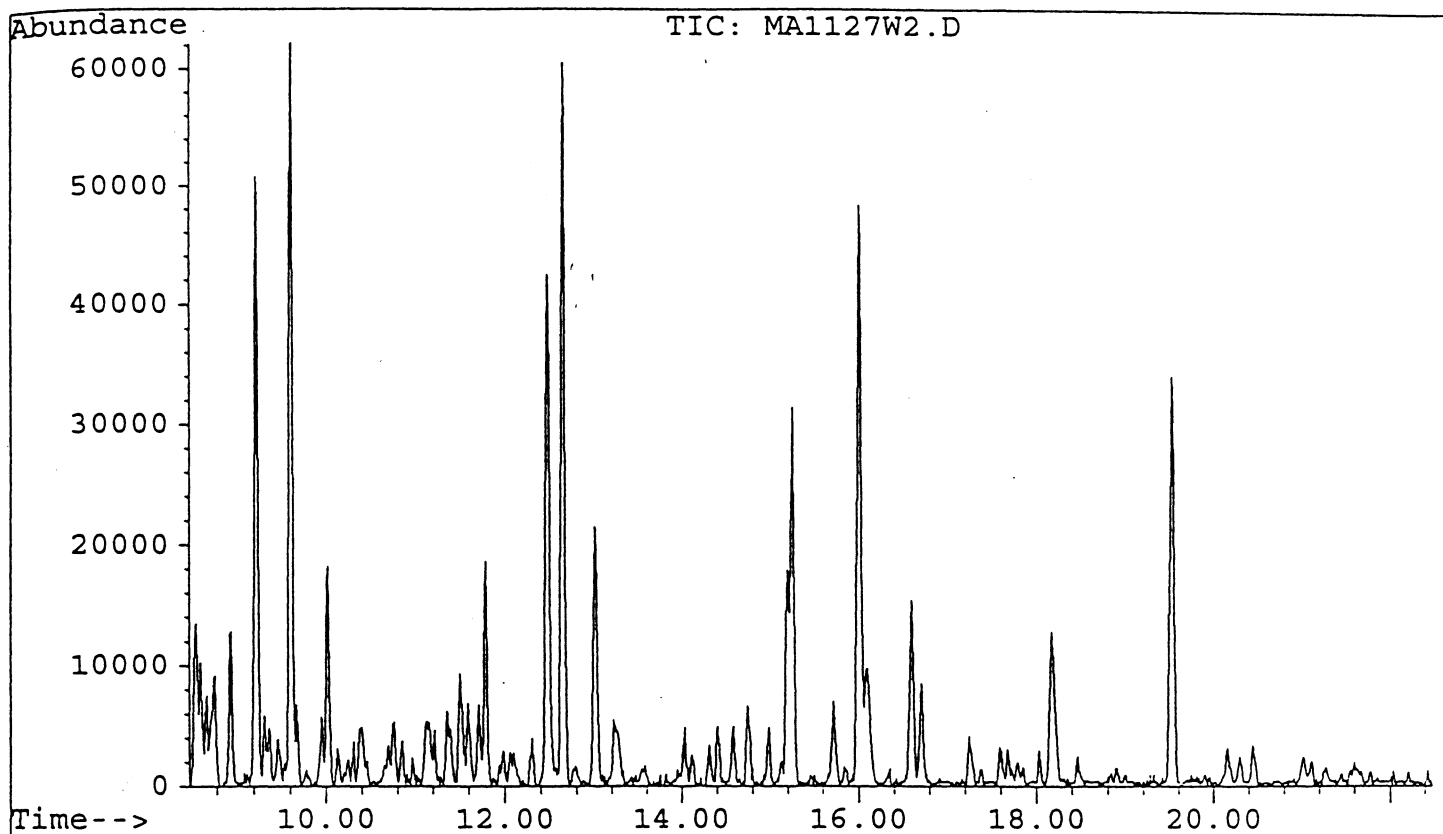


Figure 13.1. TIC of hexane fraction of after desulfurized sample of IBC-#101 (the 1st exp.)

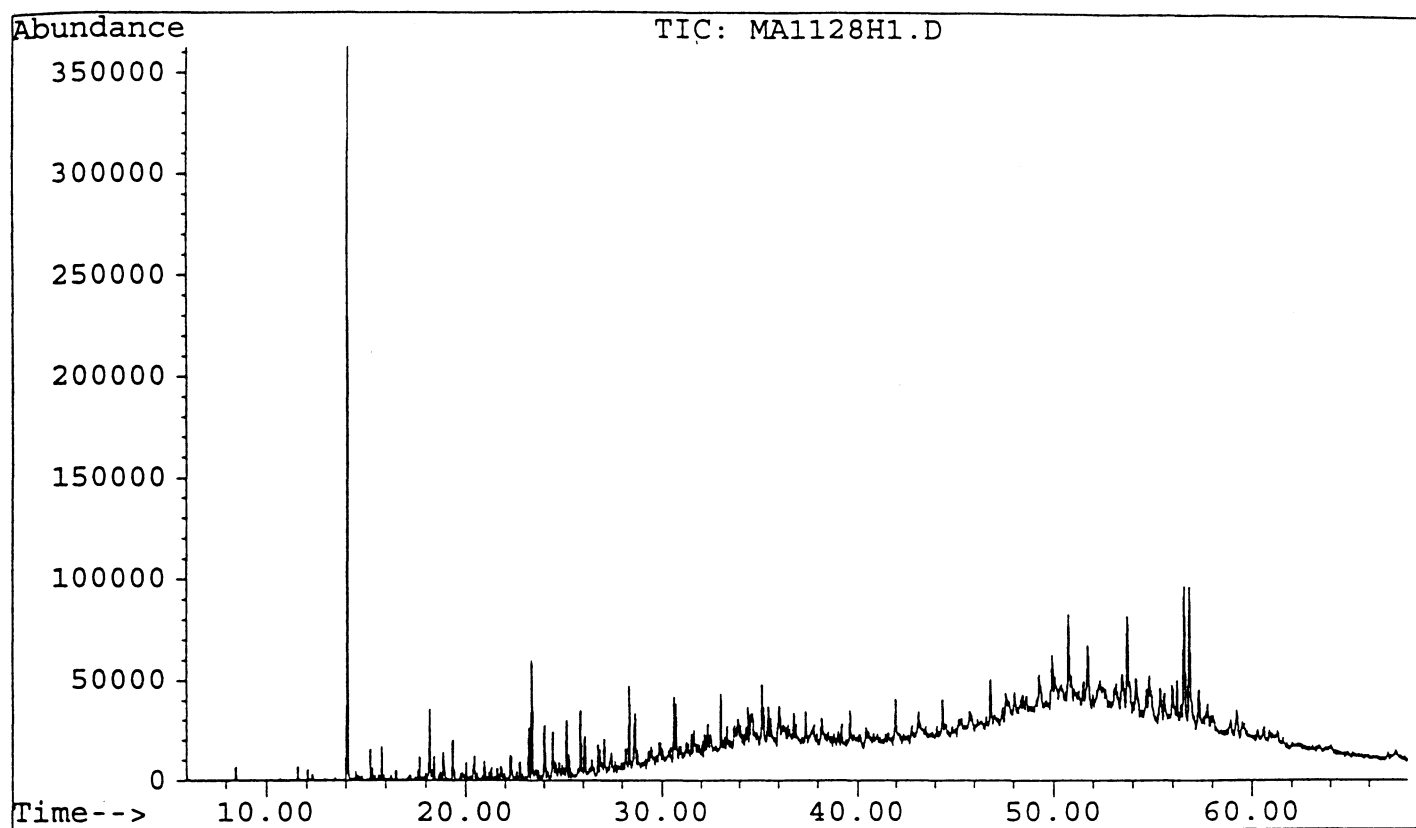


Figure 13.2. TIC of hexane fraction of after desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 19.8-31.6 min and the mass spectrum of Pentadecane,2,4,10,12-tetramethyl

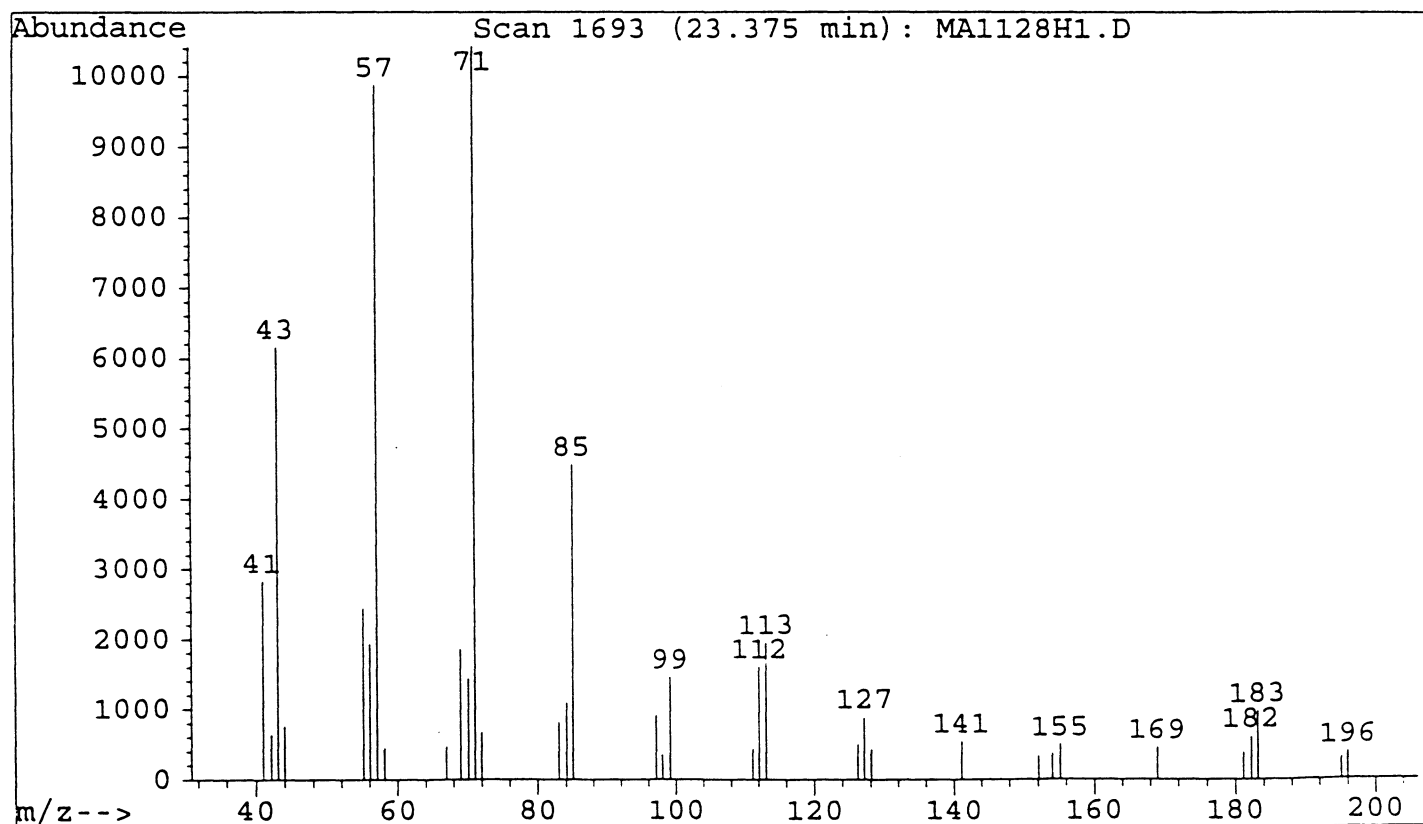
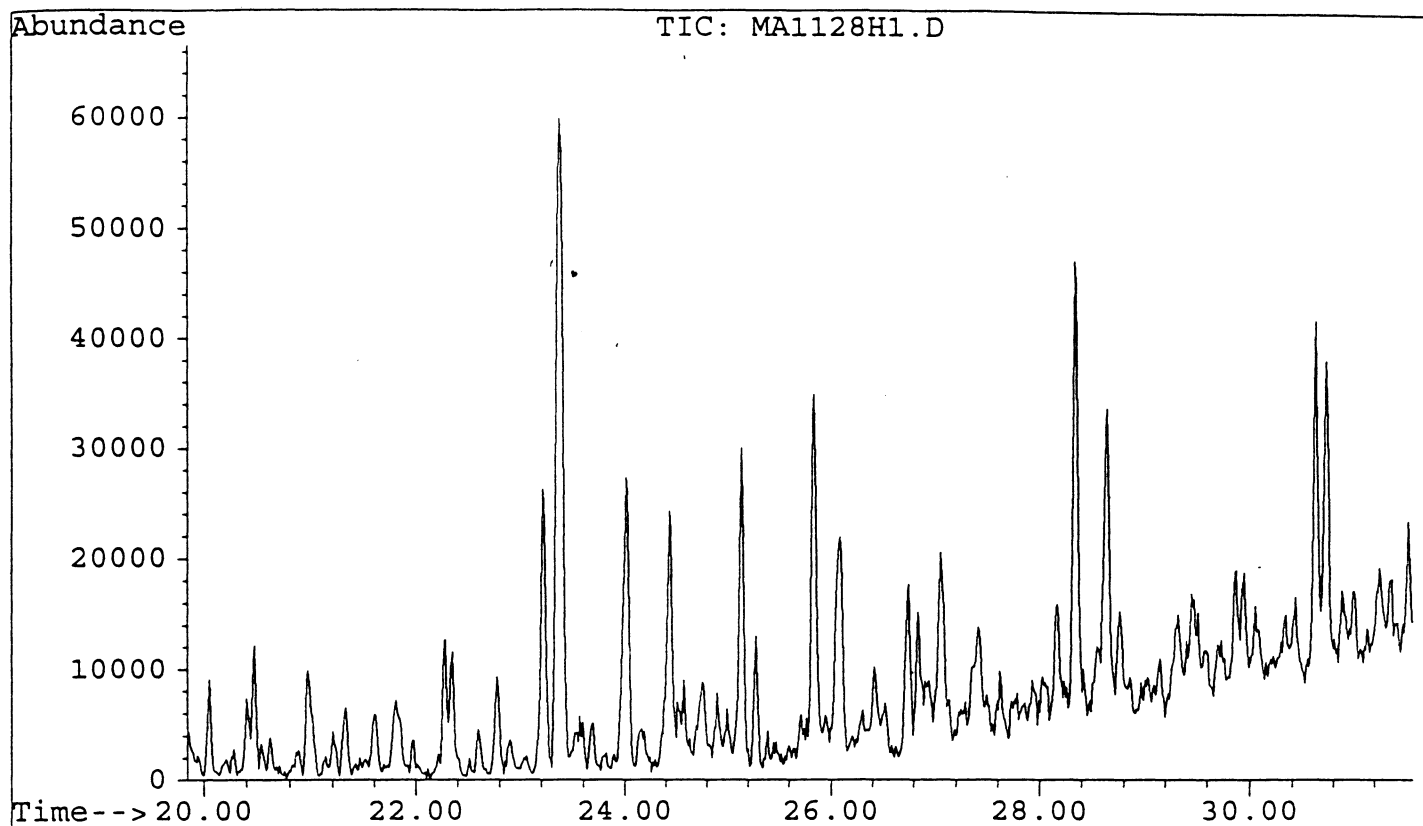


Figure 14.1. TIC of toluene fraction of after desulfurized sample of IBC-#101 (the 1st exp.)

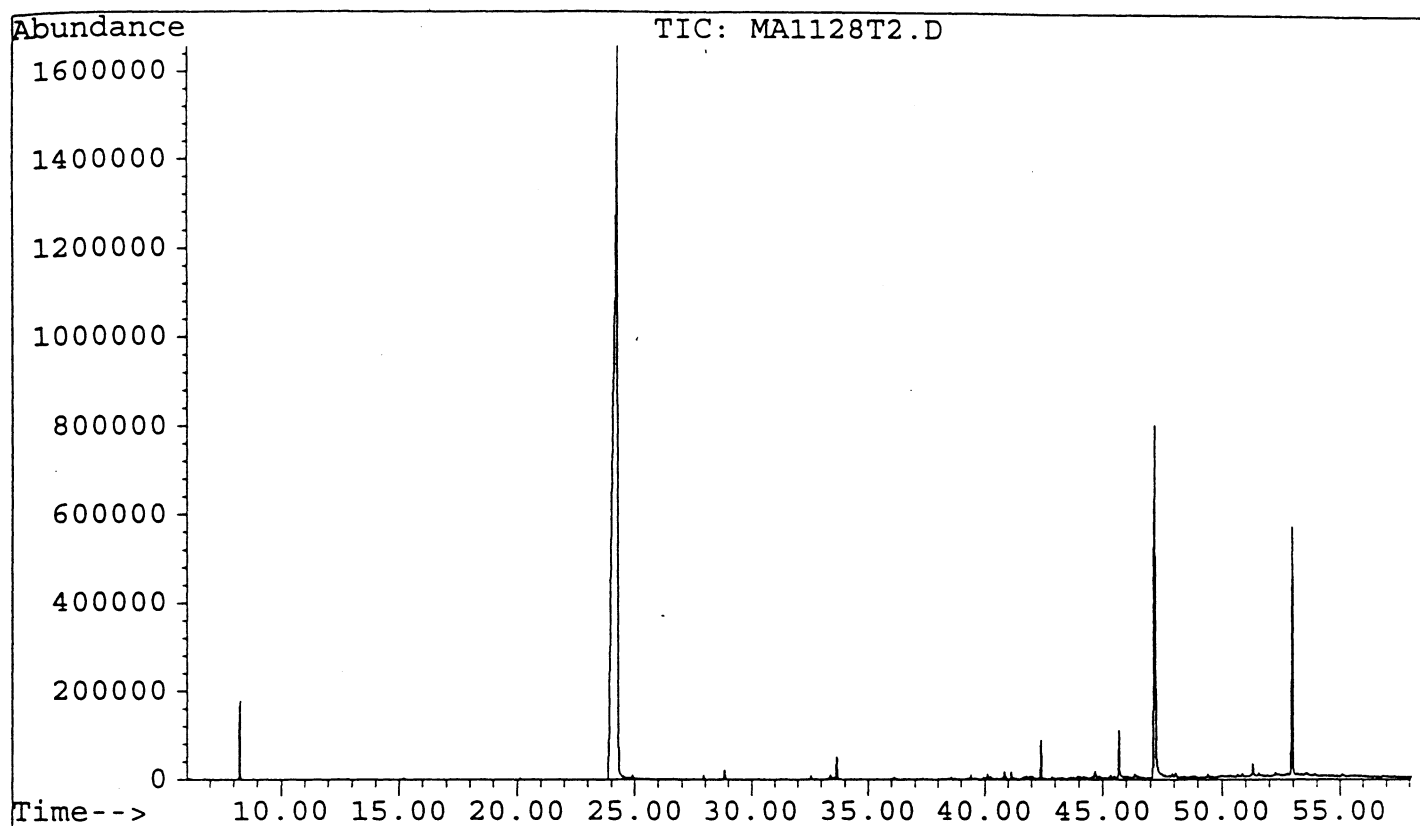


Figure 14.2. TIC of toluene fraction of after desulfurized sample of IBC-#101 (the 1st exp.) showing the ret. time range of 8.4-21.6 min

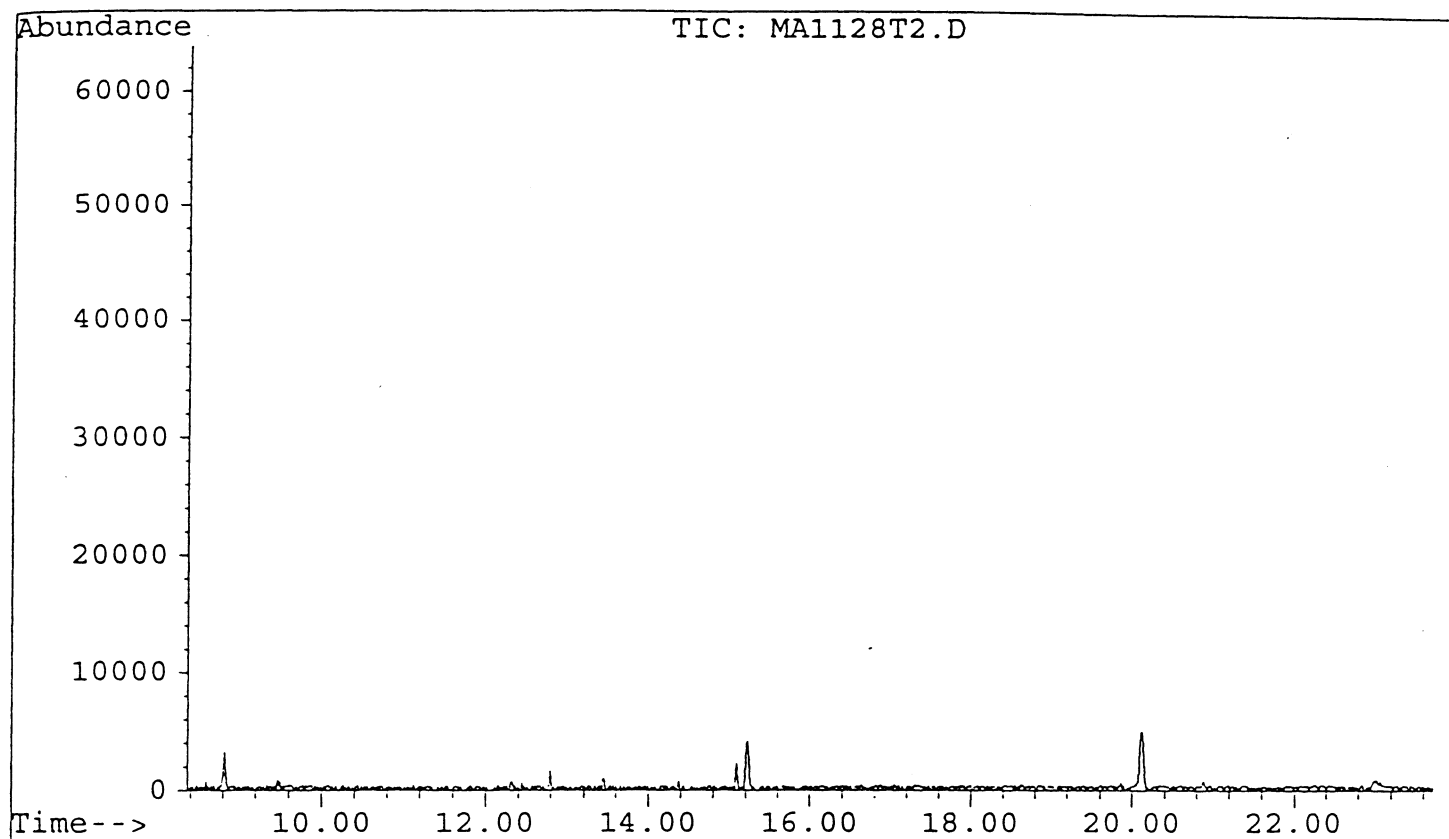


Figure 15.

TIC of hexane fraction of before desulfurized sample of IBC-#101 (the 2nd exp.) showing the whole ret. time range and the mass spectrum of Pentadecane, 2,6,10,12-tetramethyl

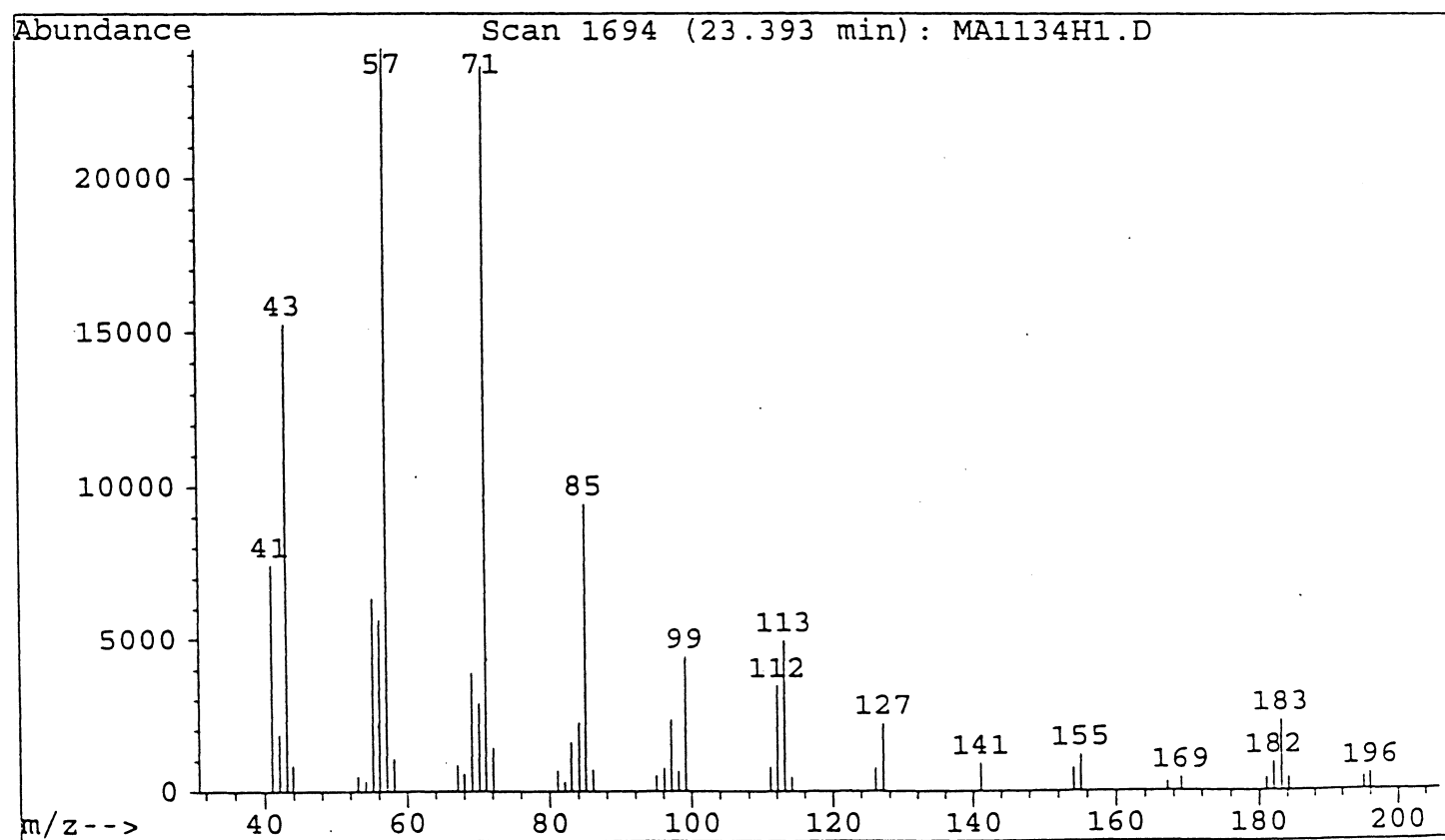
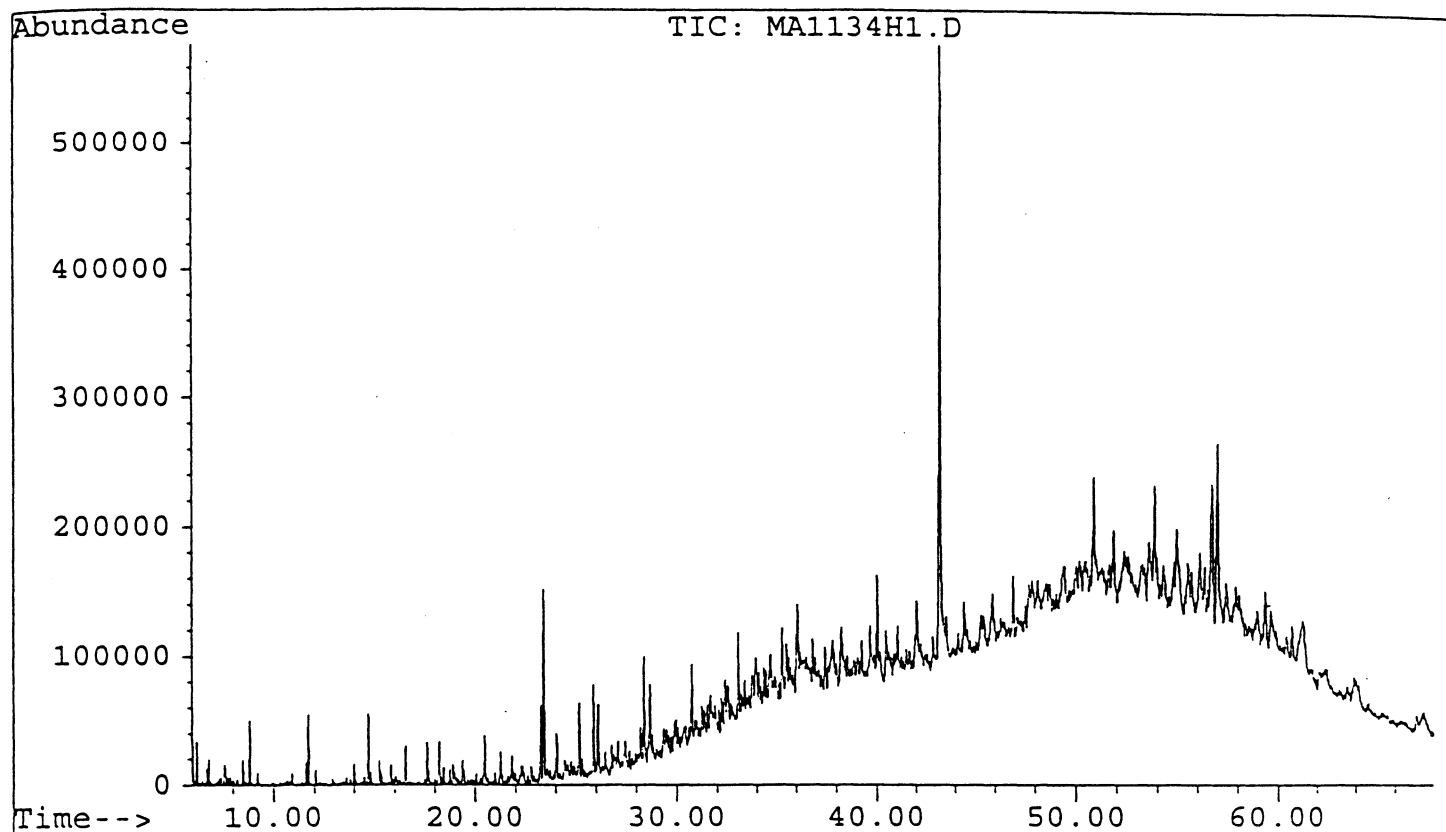


Figure 16.1. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 2nd exp.) and the mass spectrum of Hexadecane

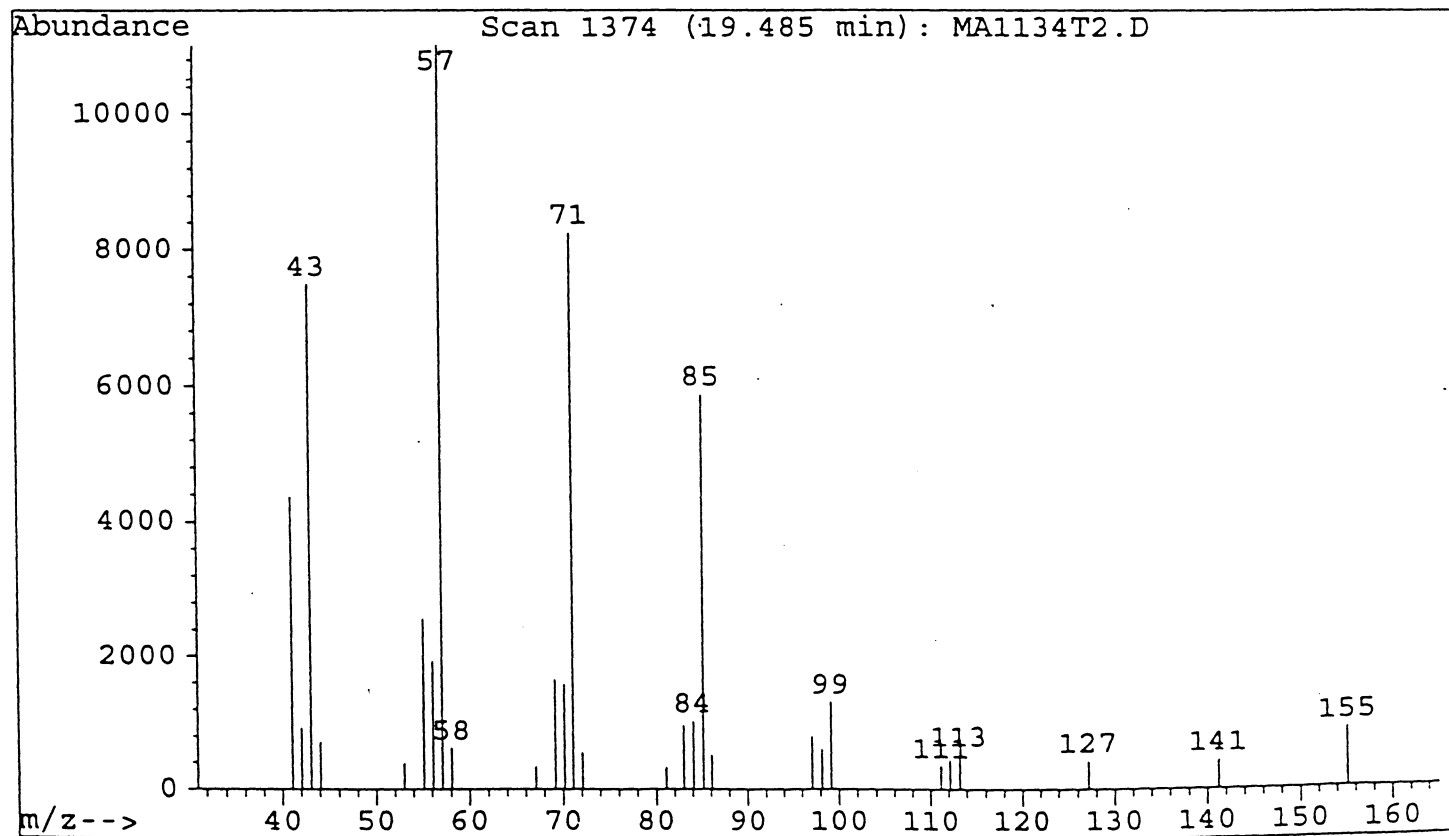
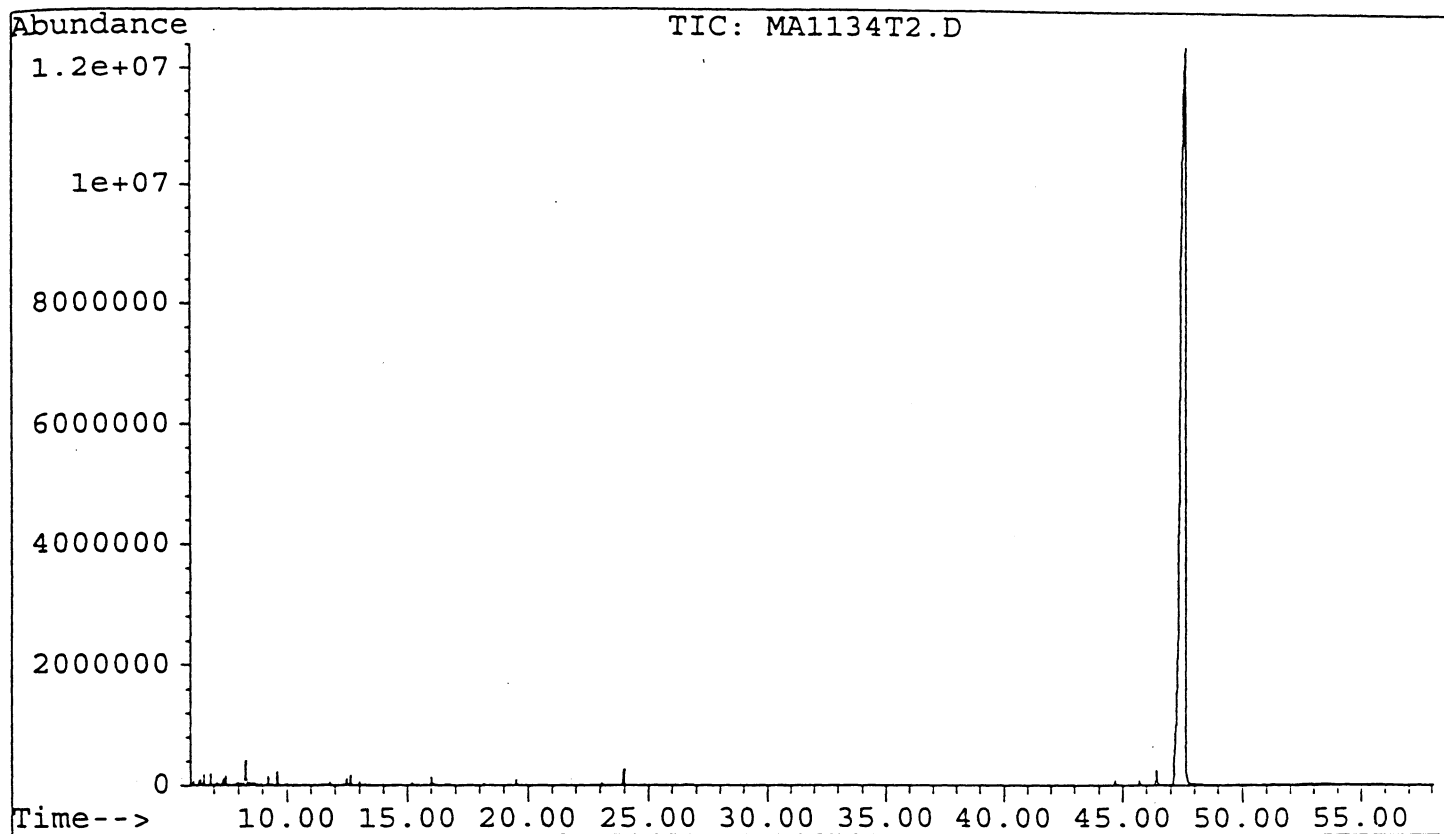


Figure 16.2. TIC of toluene fraction of before desulfurized sample of IBC-#101 (the 2nd exp.) showing the ret. time range of 6-24 min

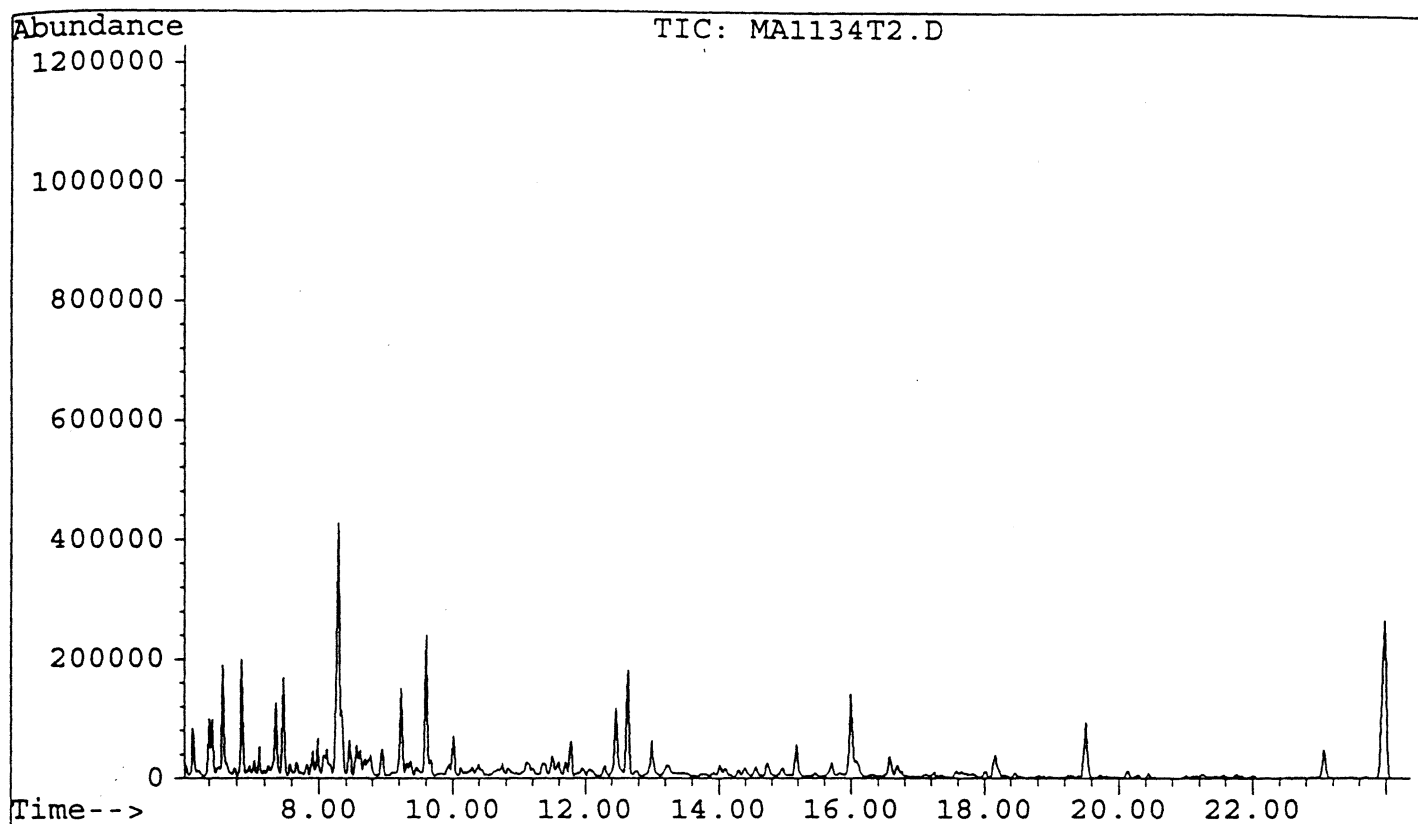


Figure 17.1. TIC of hexane fraction of after desulfurized sample of IBC-#101 (the 2nd exp.)

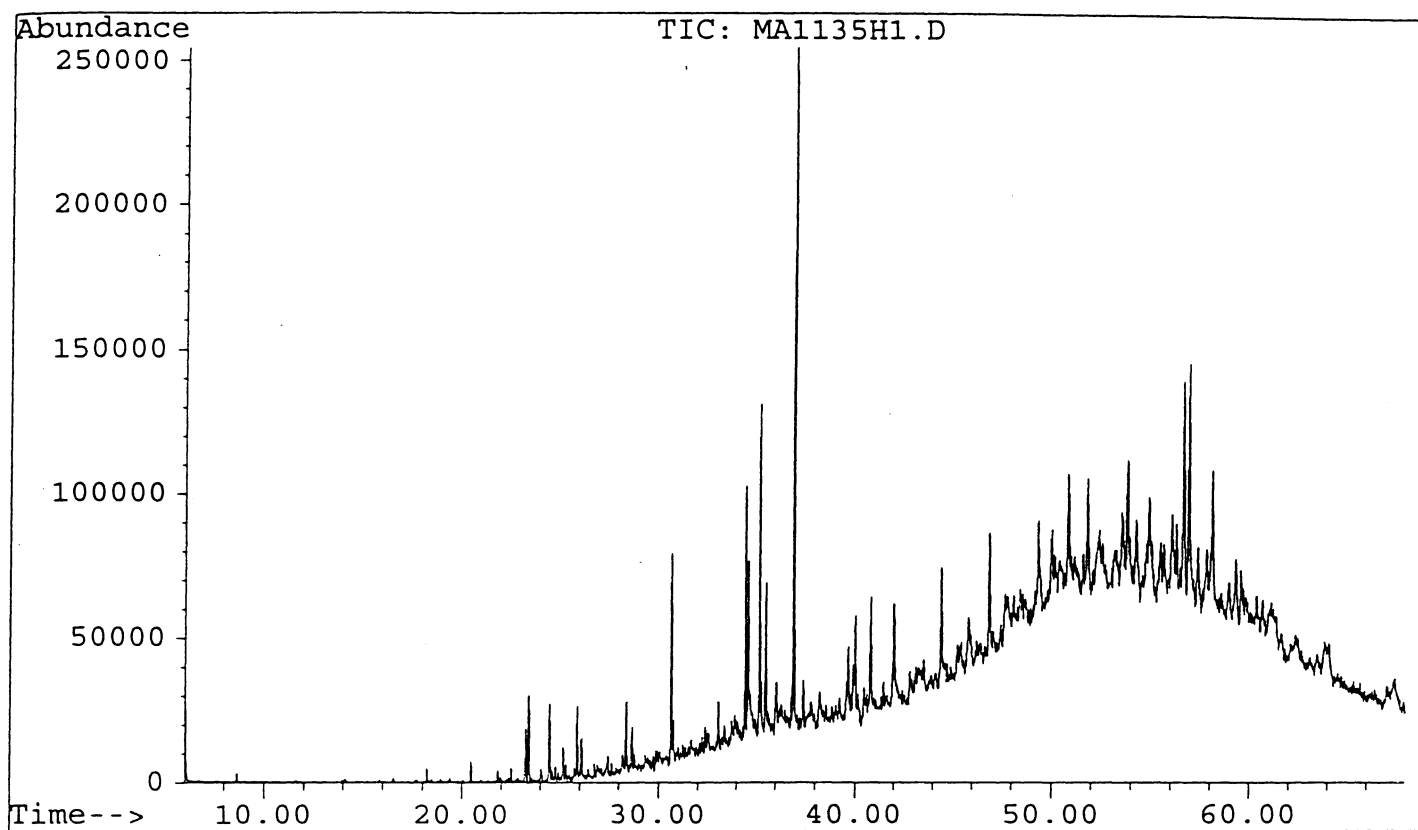


Figure 17.2. TIC of hexane fraction of after desulfurized sample of IBC-#101 (the 2nd exp.) showing the ret. time range of 31.9-36.1 min and the mass spectrum of Tetratetracontane

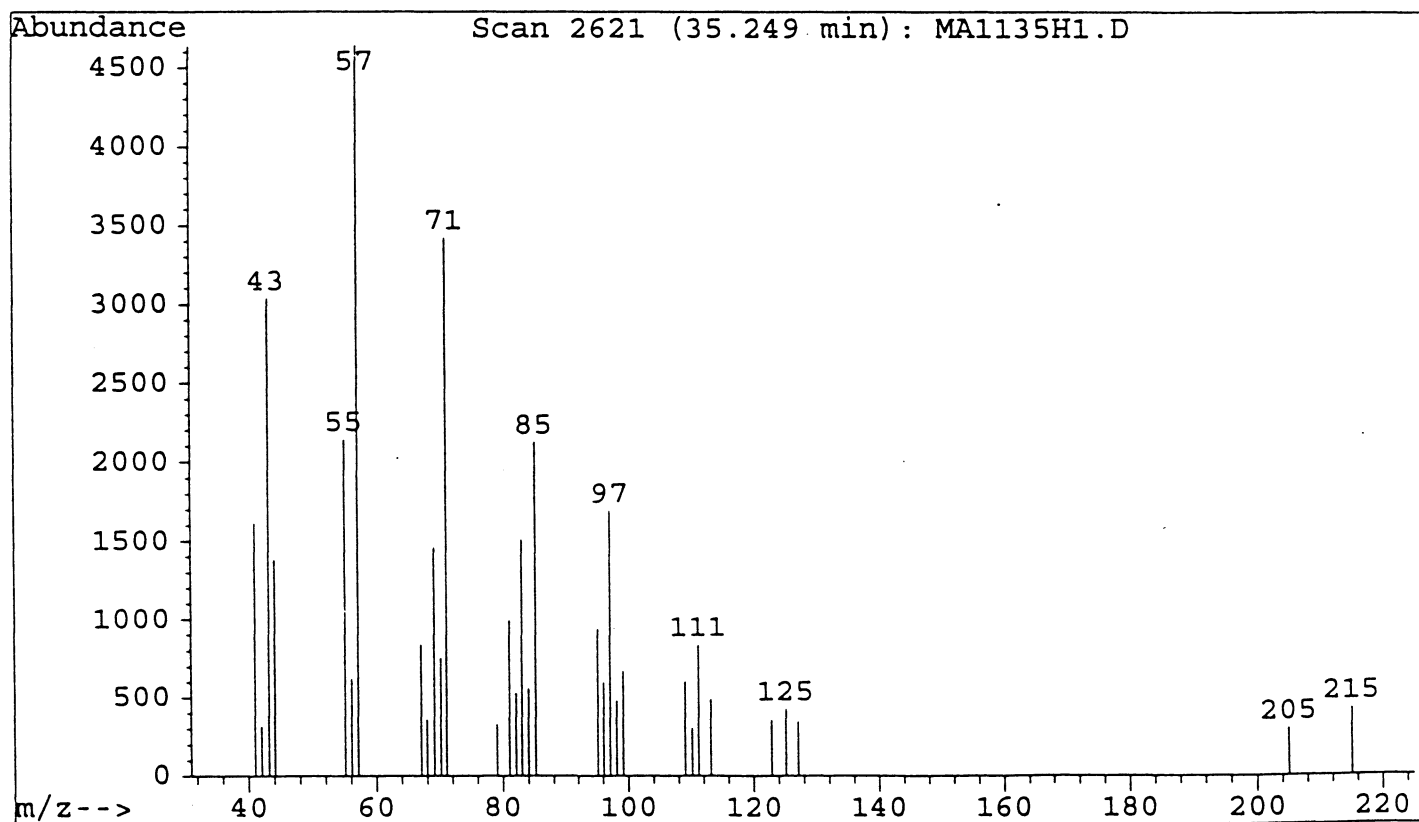
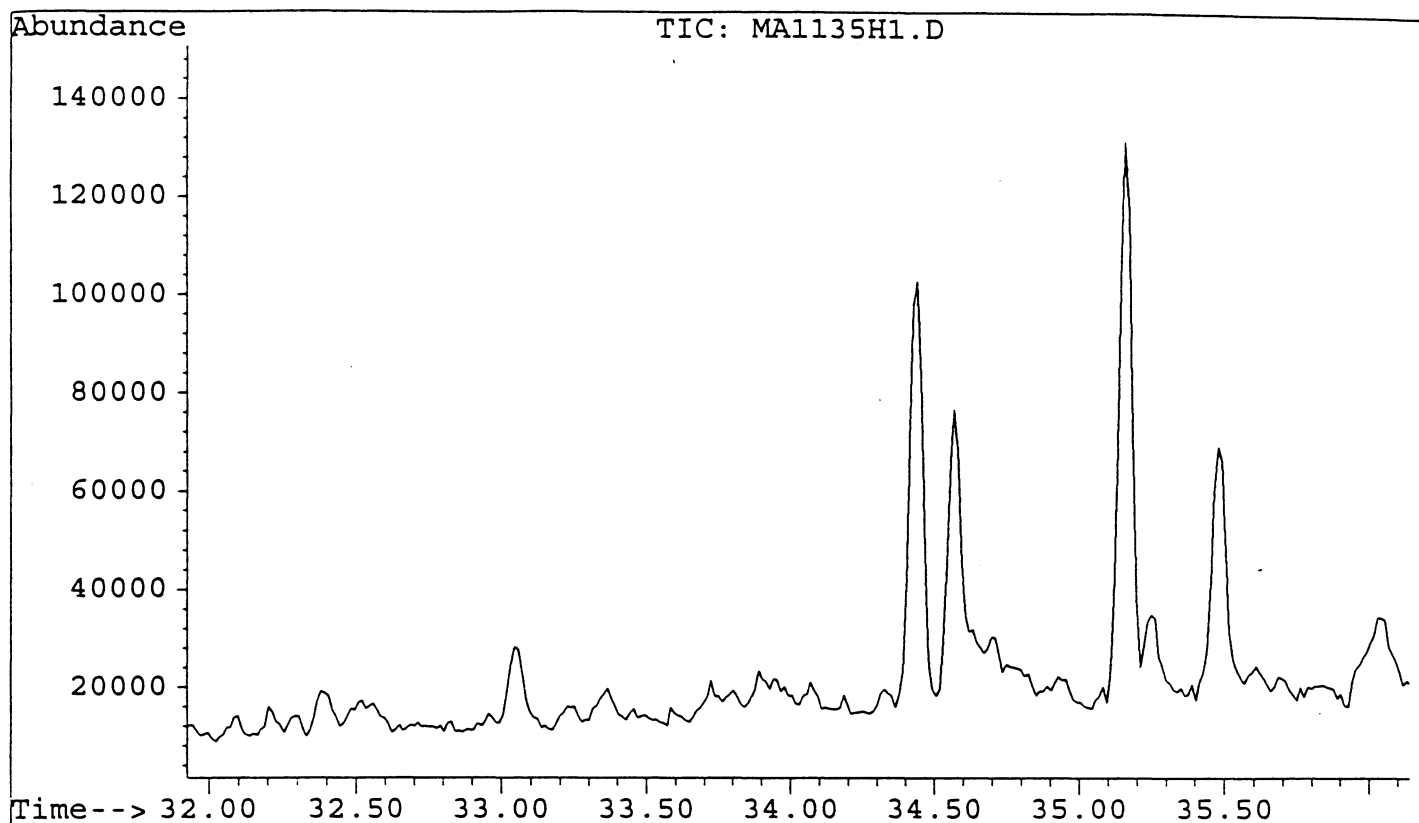


Figure 18.1. TIC of toluene fraction of after desulfurized sample of IBC-#101 (the 2nd exp.)

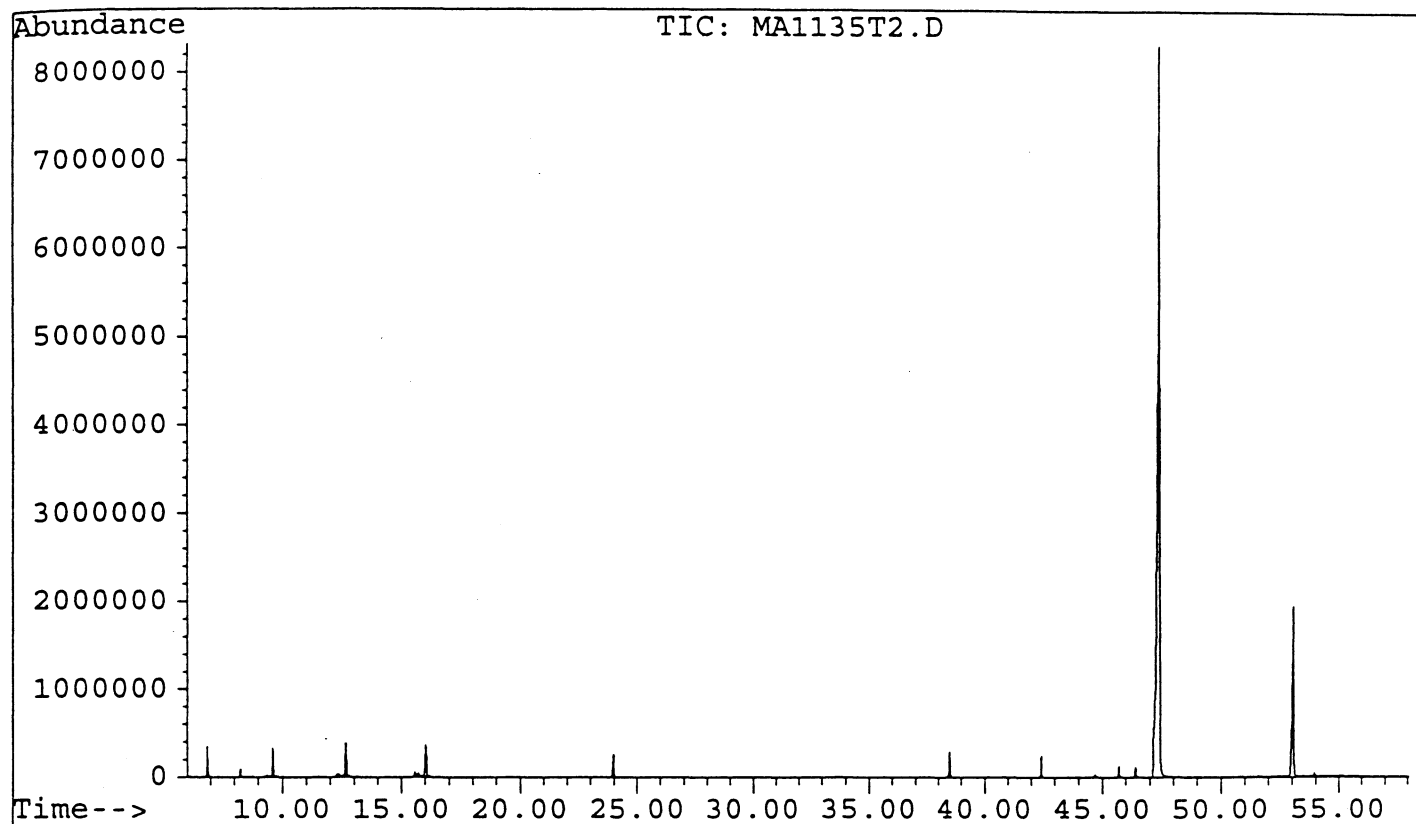


Figure 18.2. TIC of toluene fraction of after desulfurized sample of IBC-#101 (the 2nd exp.) showing the ret. time range of 6.4-24.8 min and the mass spectrum of Dodecane

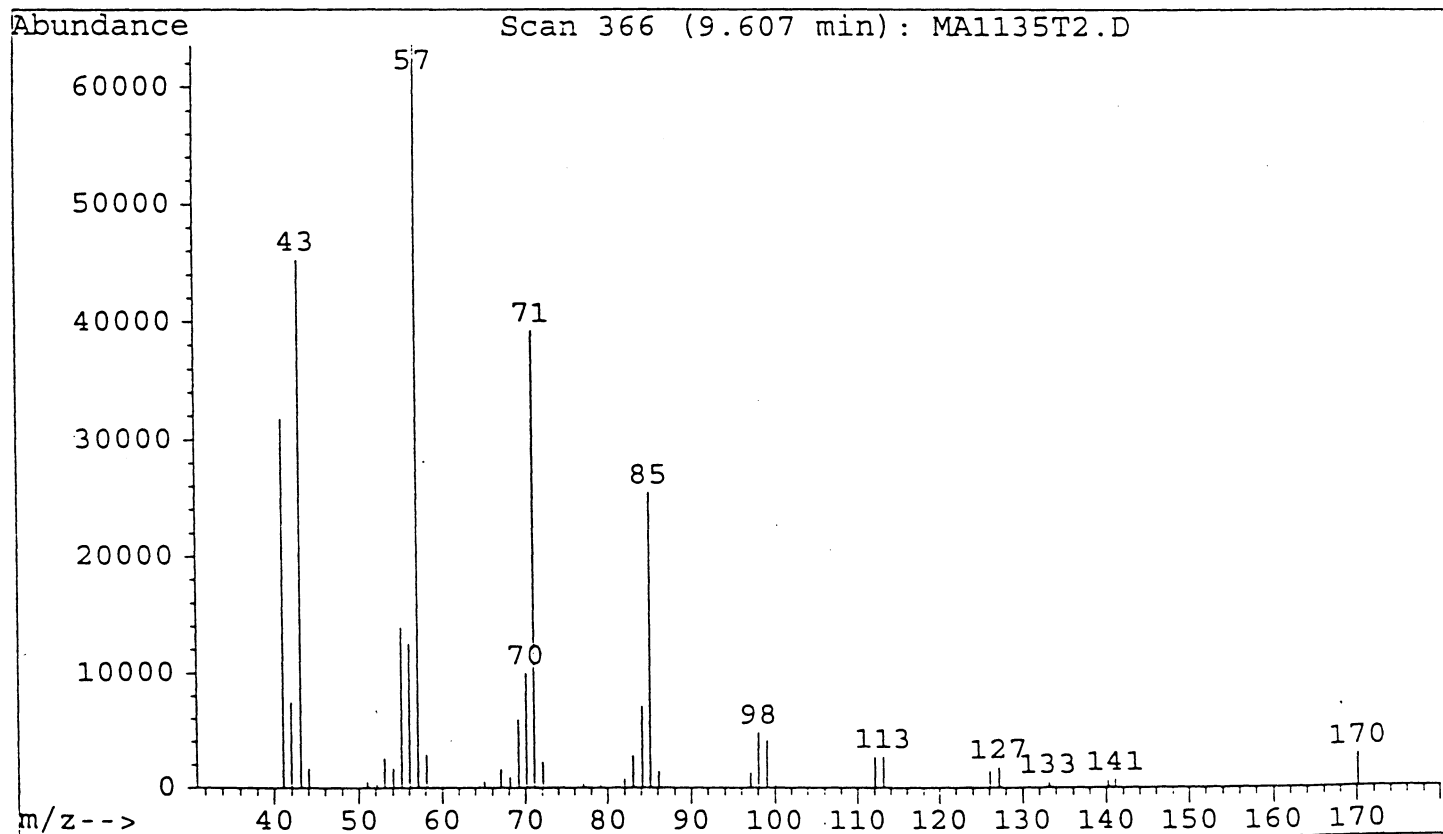
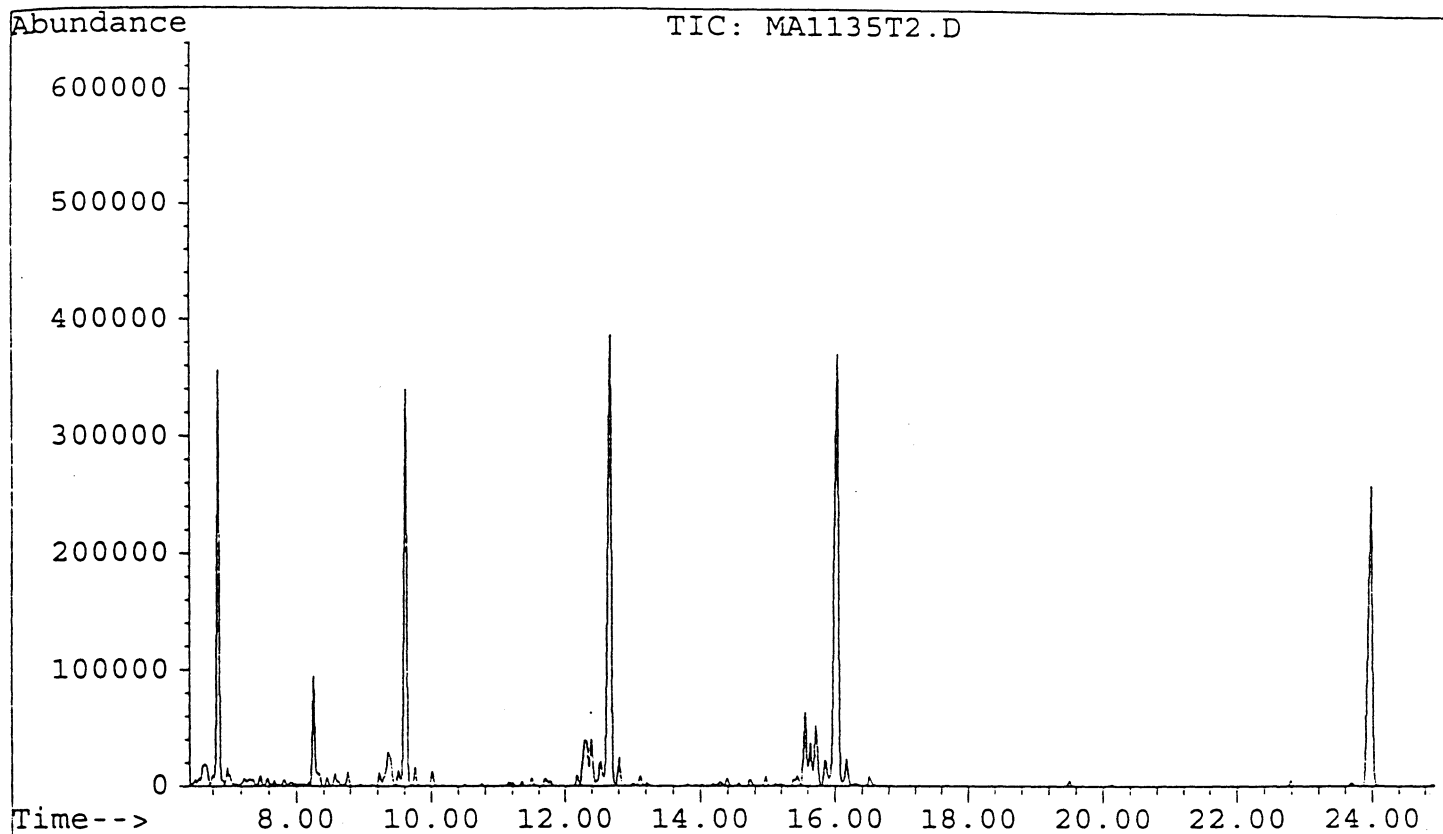


Figure 19.1. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 1st exp.)

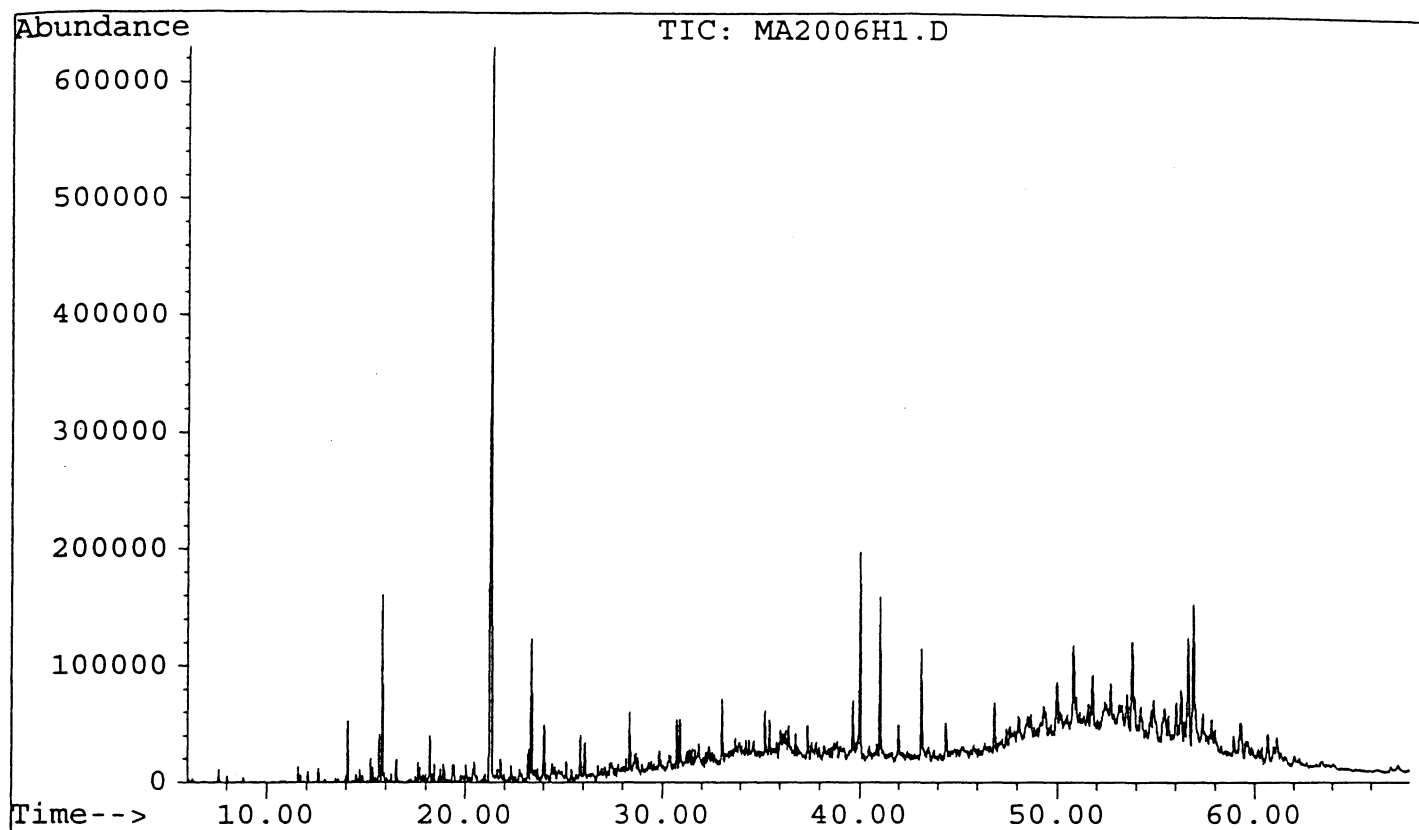


Figure 19.2. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 22-28 min and the mass spectrum of DBT

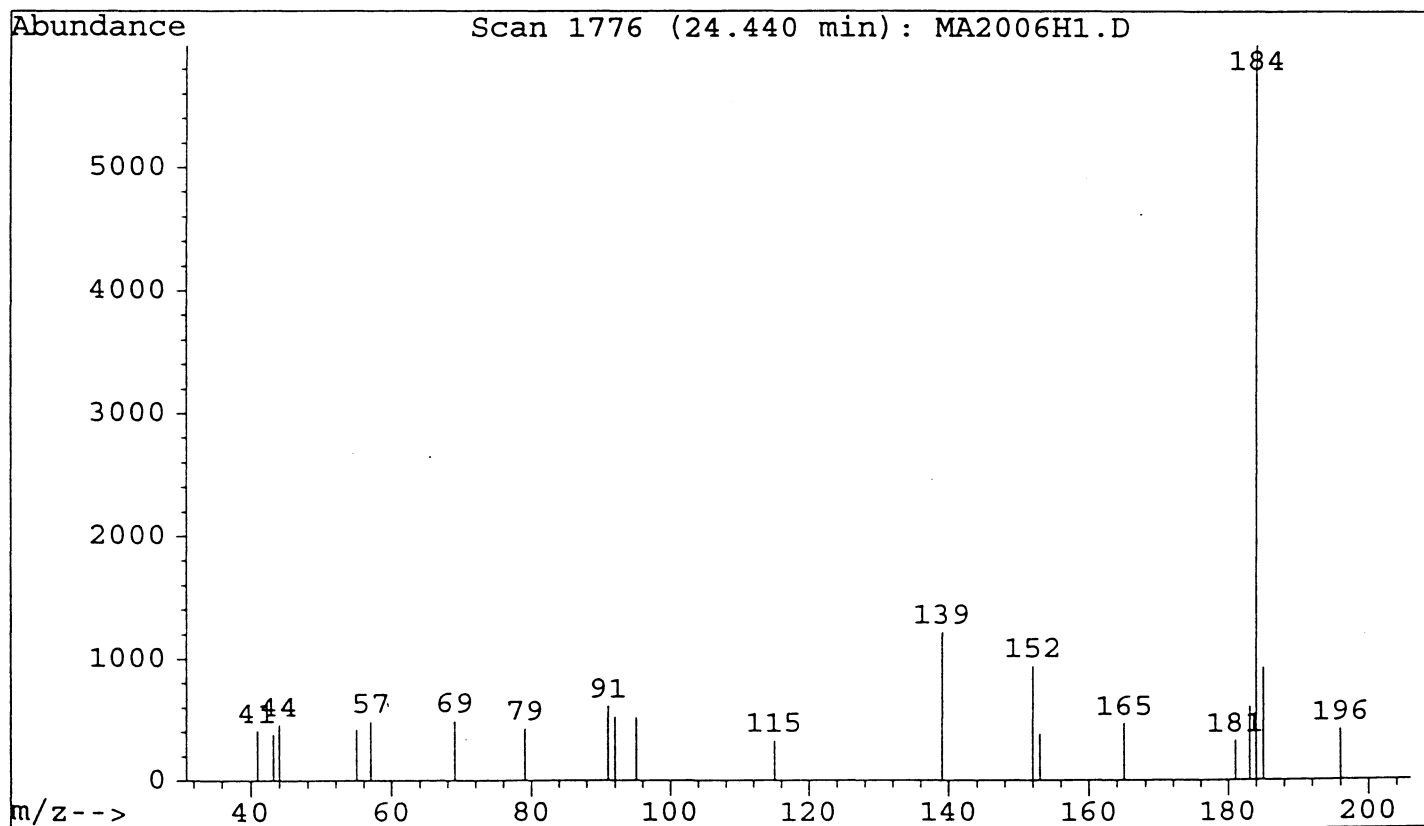
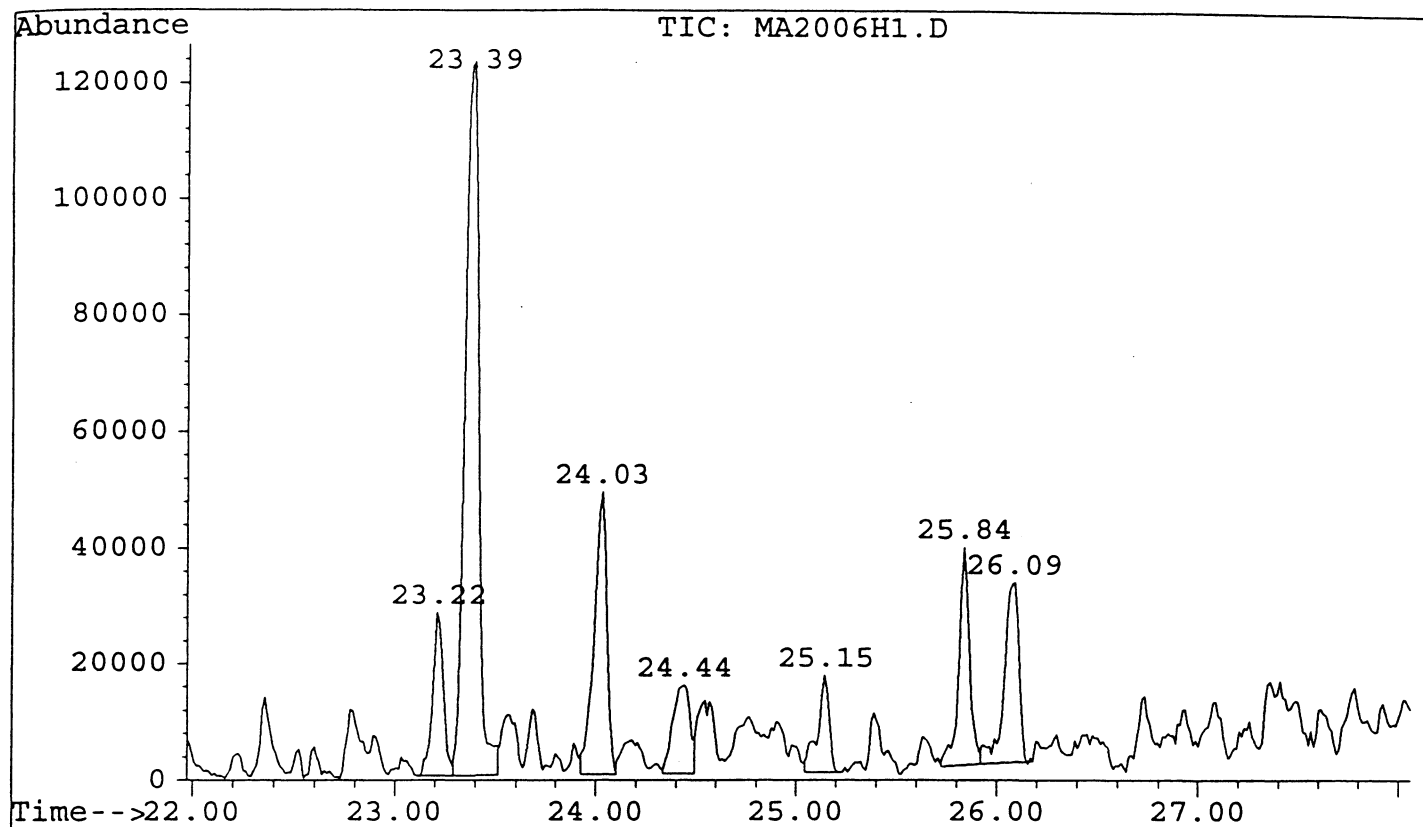


Figure 19.3. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 22-28 min and the mass spectrum of Pentadecane, 2,6,10,12-tetramethyl

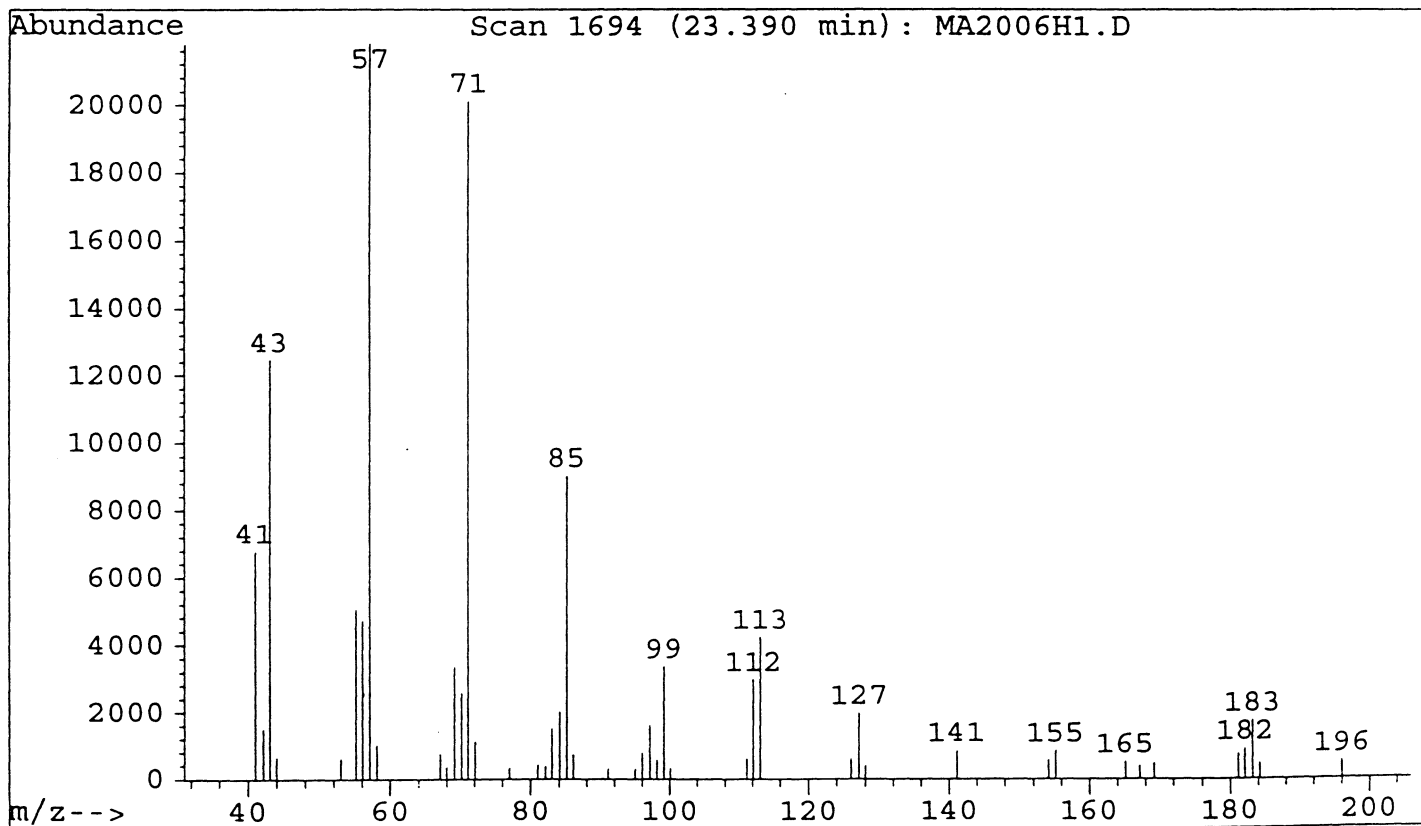
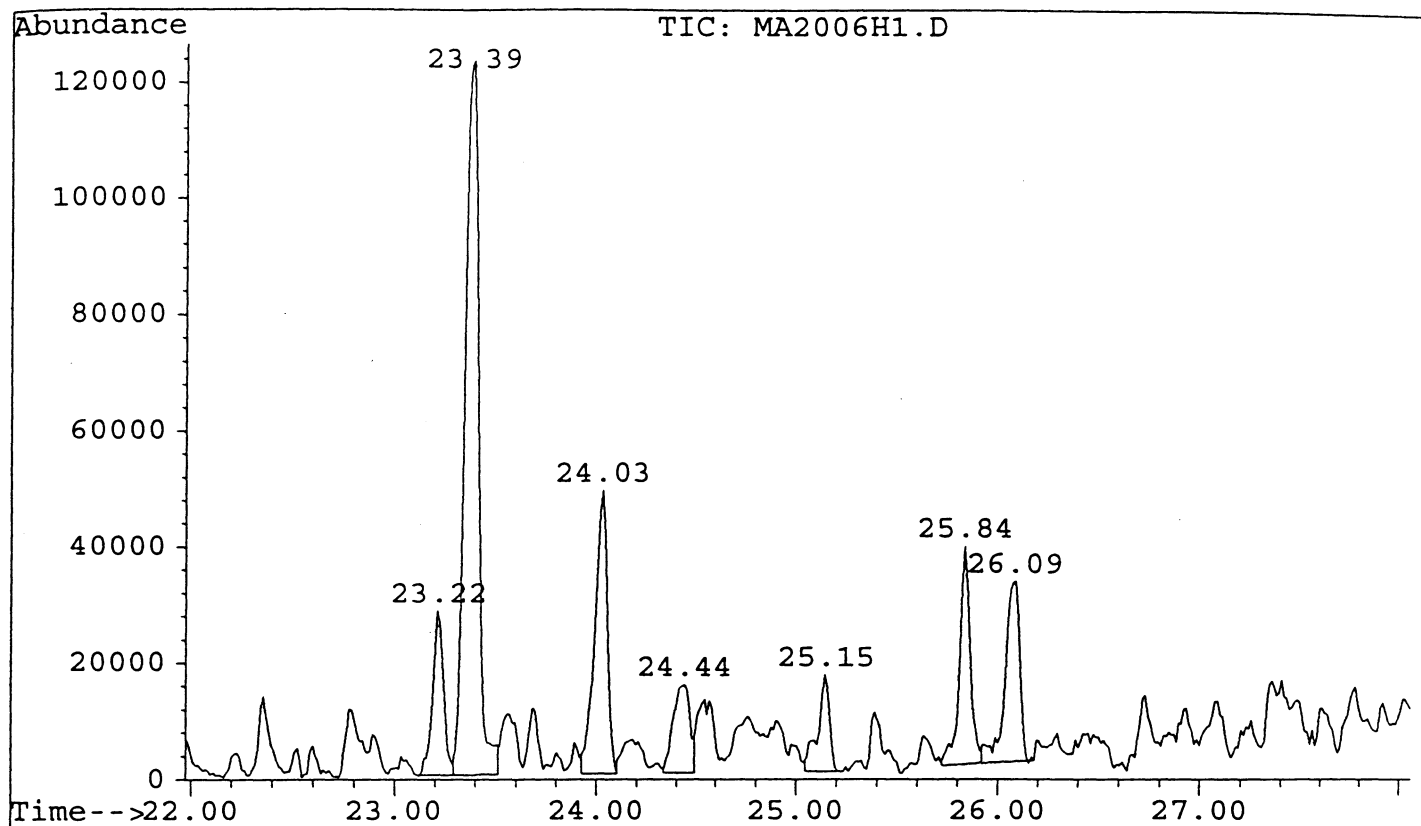


Figure 19.4. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 22-28 min and the mass spectrum of Phenanthrene

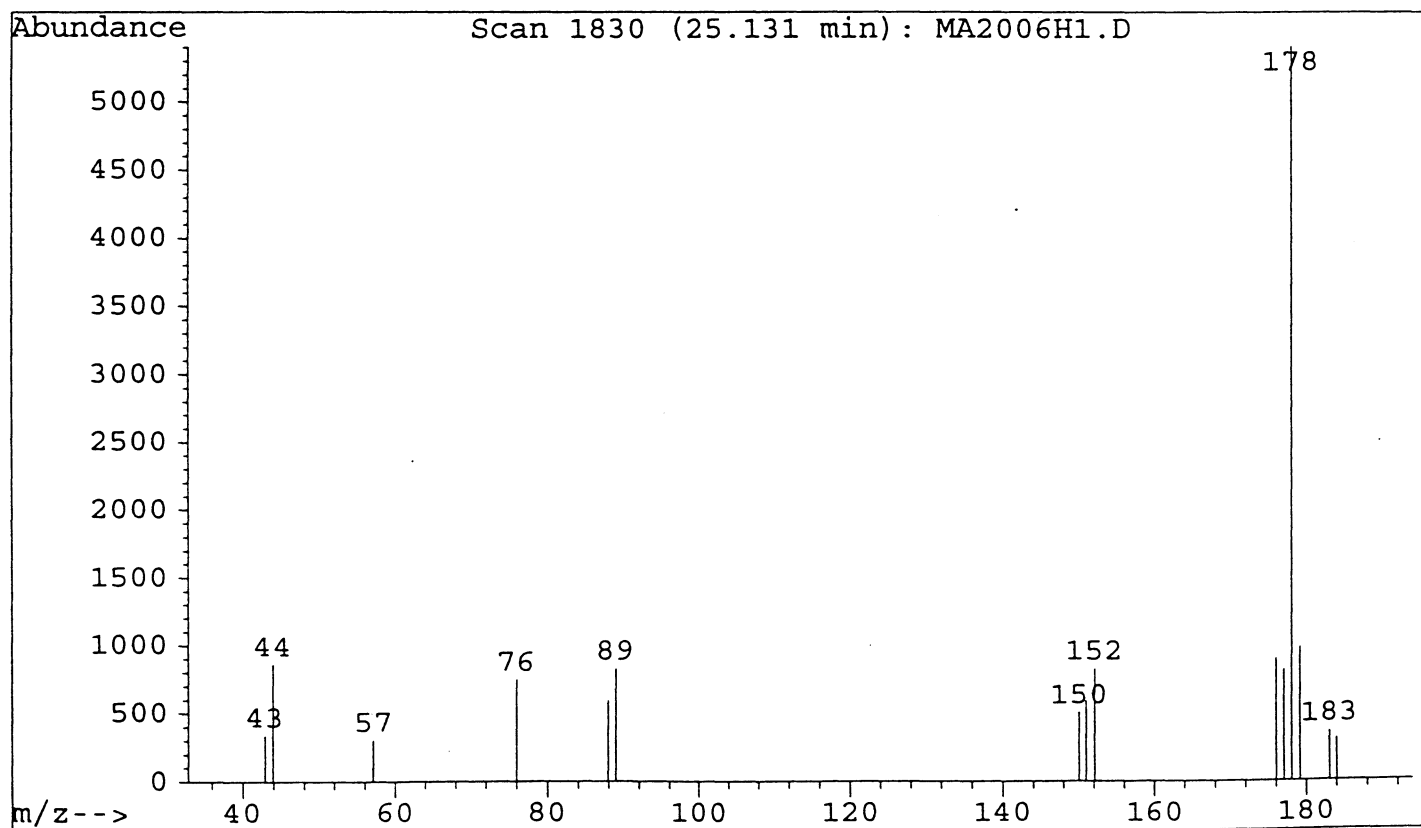
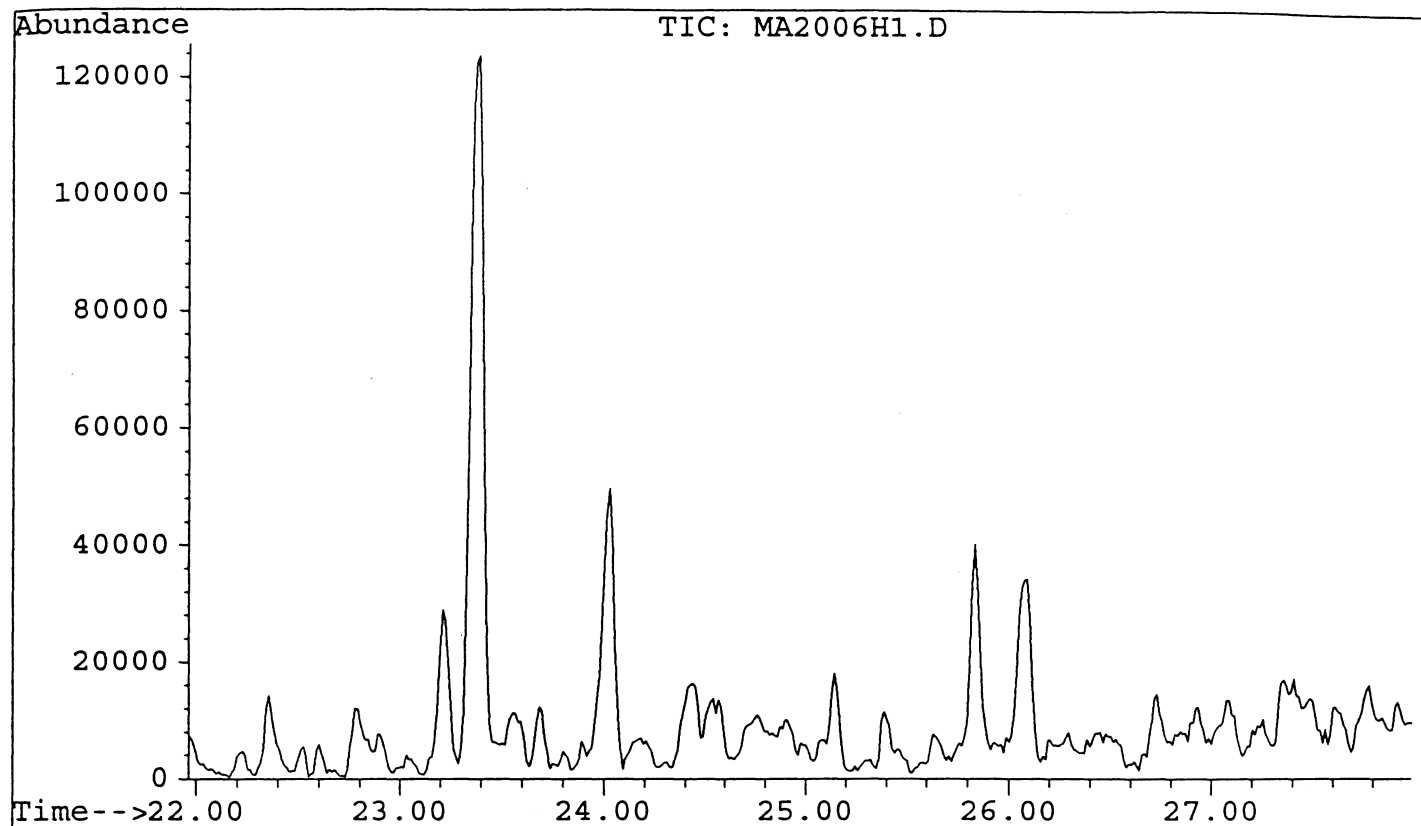


Figure 19.5. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 28-40 min

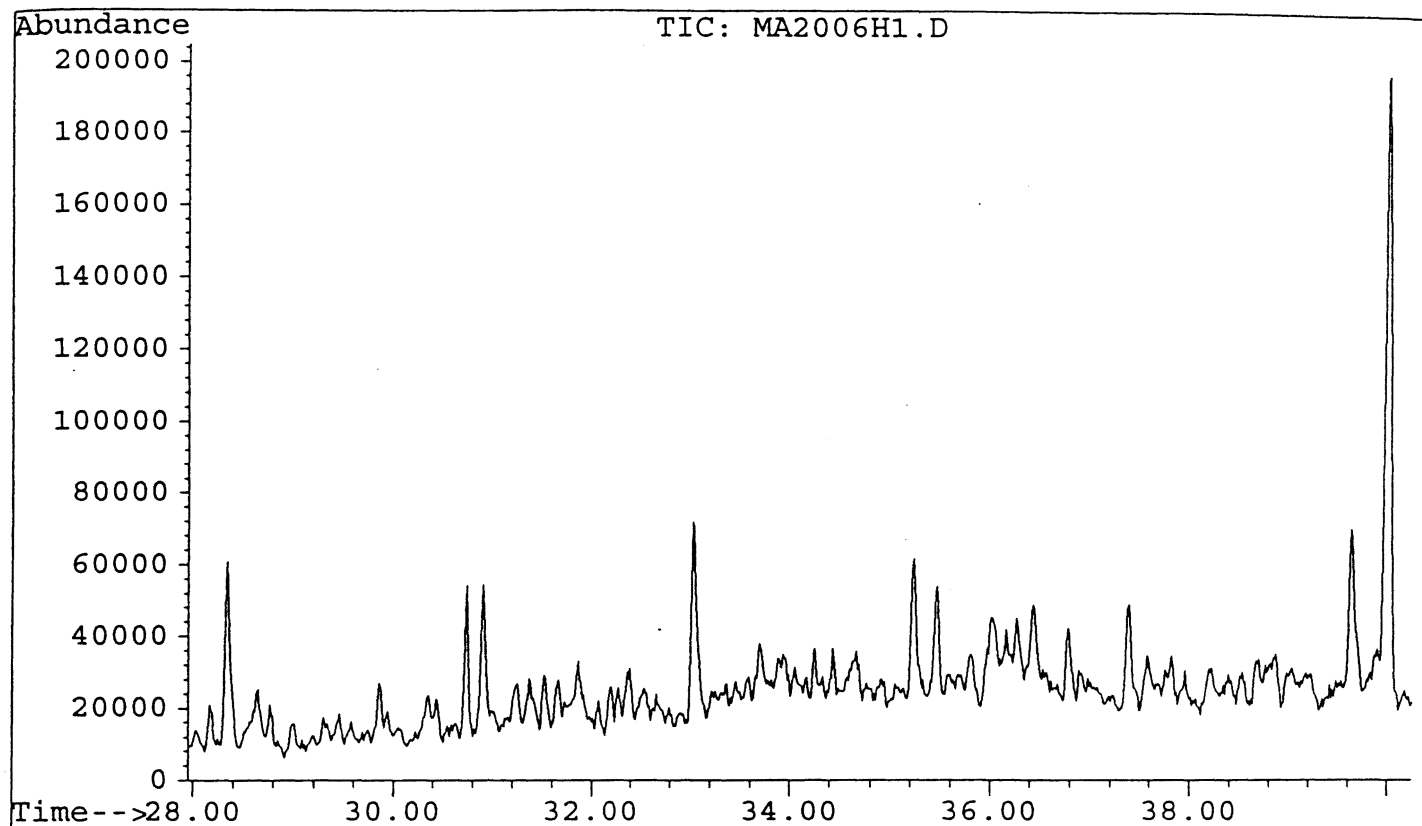


Figure 20. TIC of toluene fraction of before desulfurized sample of Arg-#301 (the 1st exp.)

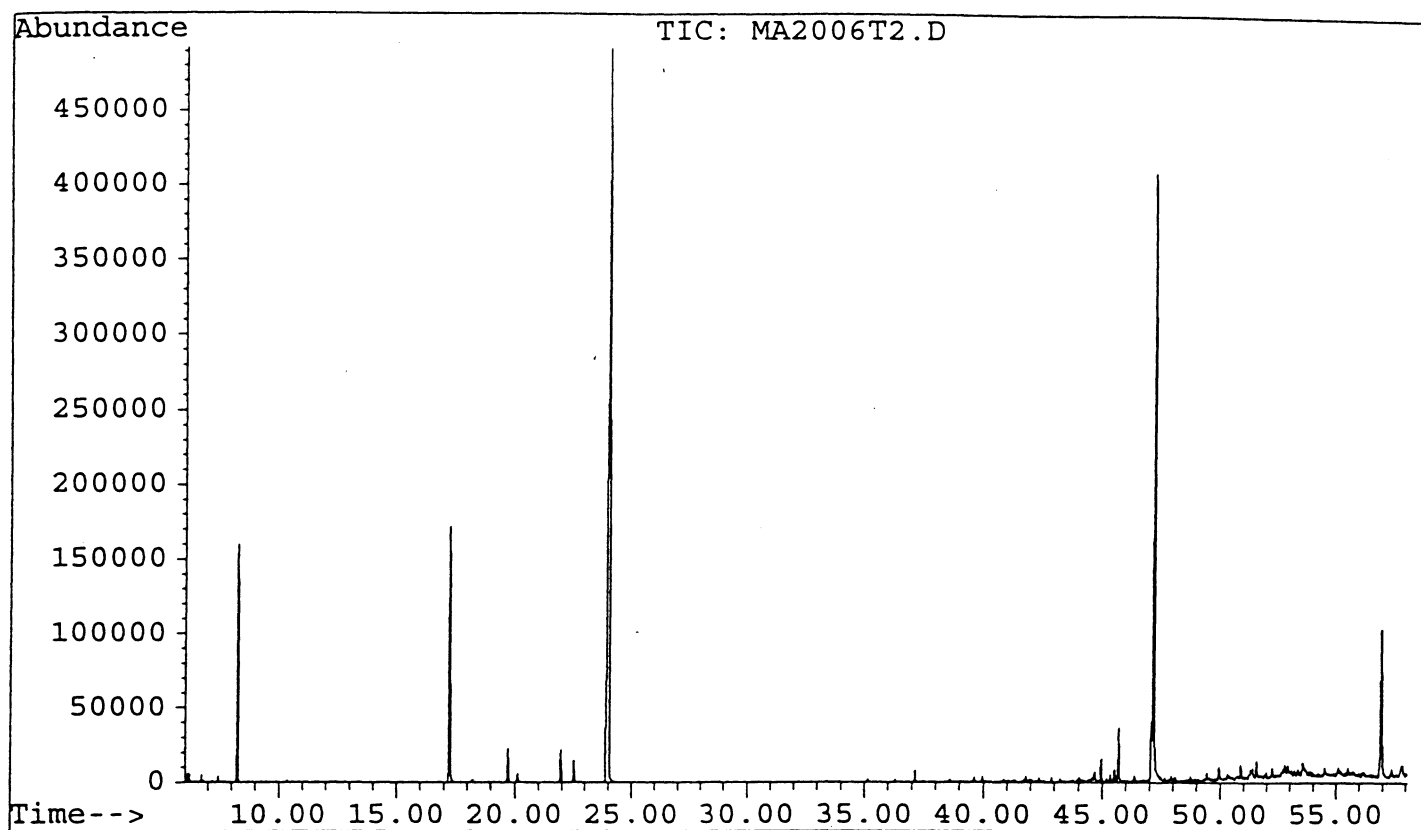


Figure 21.1. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 1st exp.)

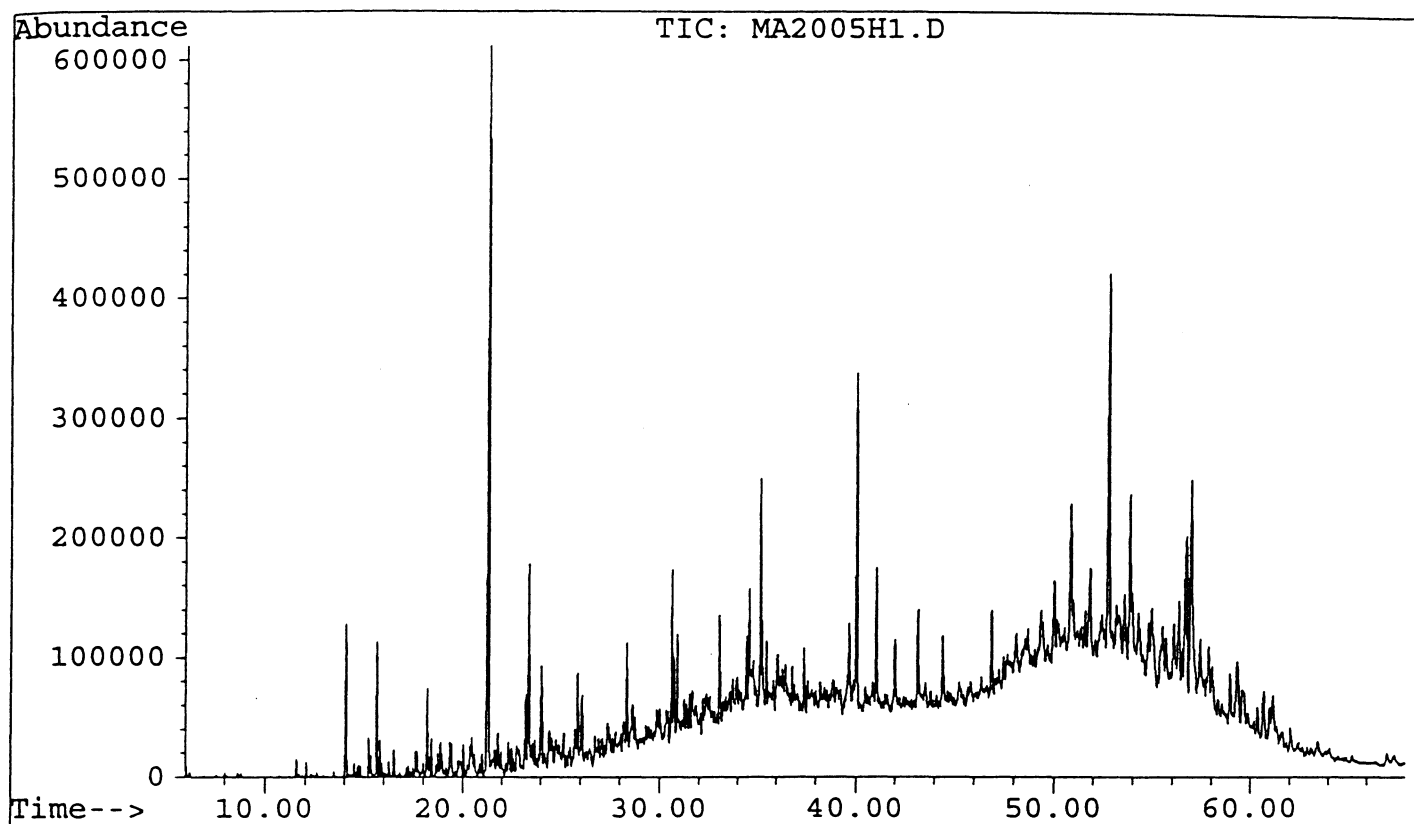


Figure 21.2. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 21.8-28.2 min and the mass spectrum of DBT

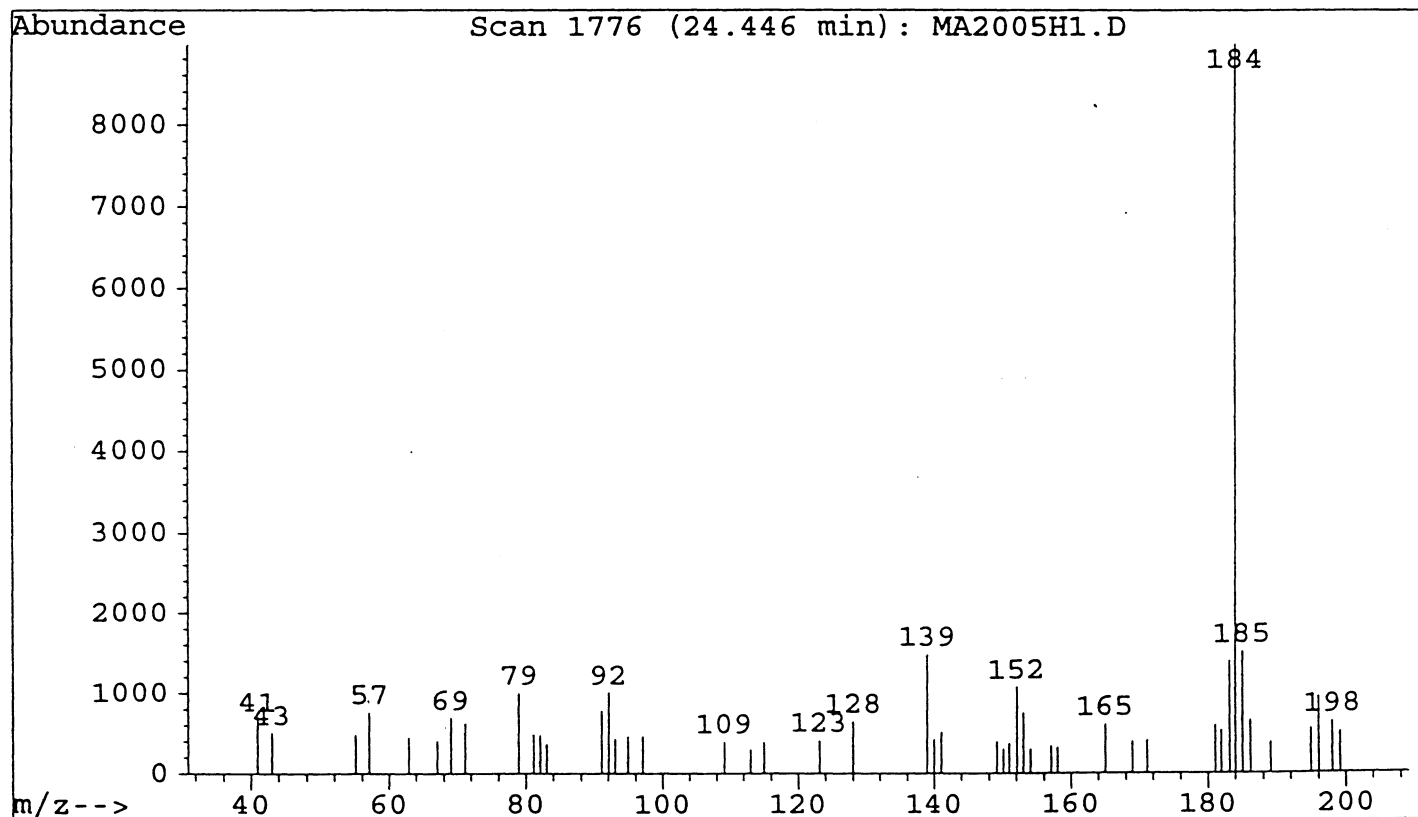
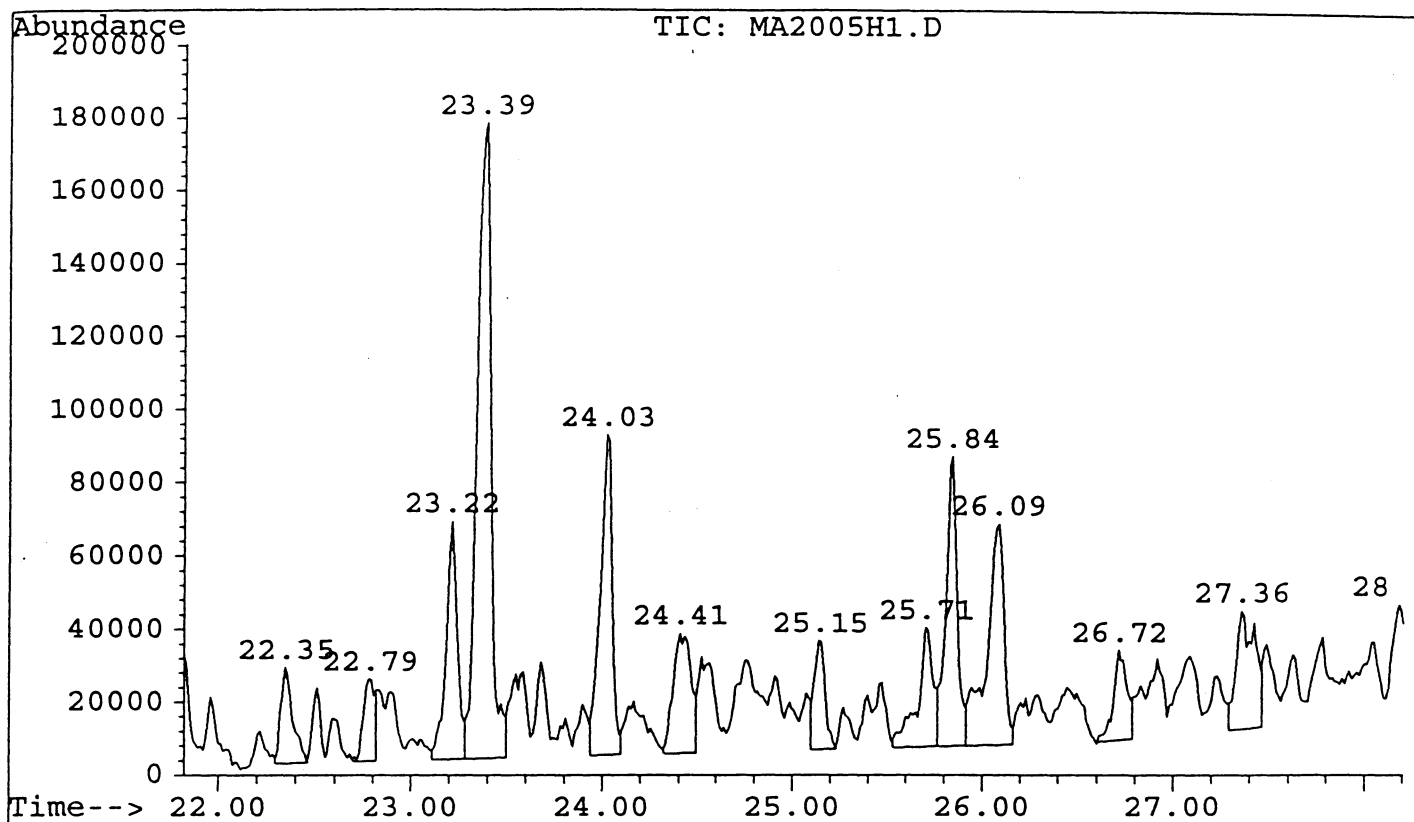


Figure 21.3. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 21.7-28.4 min and the mass spectrum of Pentadecane, 2,6,10,12-tetramethyl

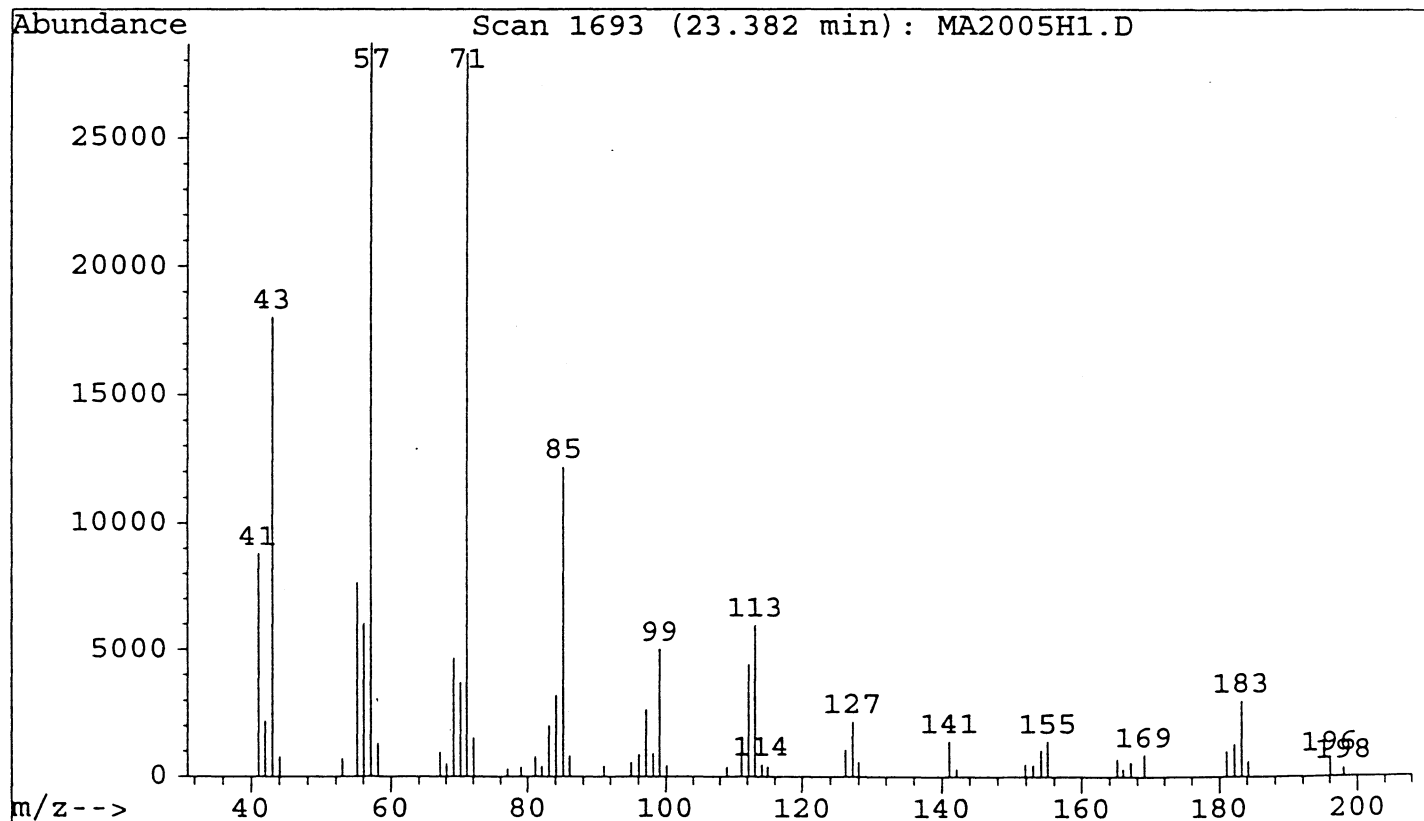
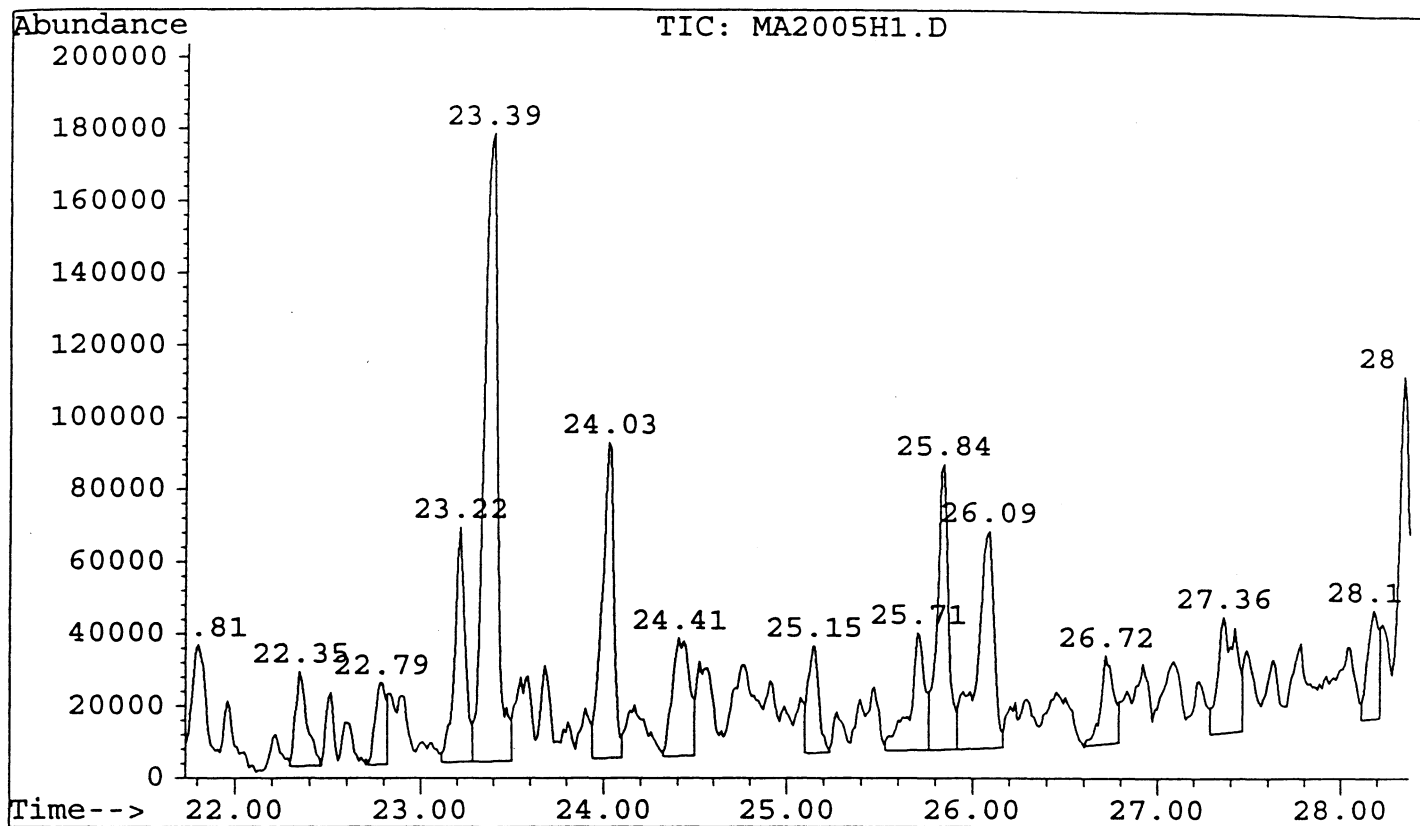


Figure 21.4. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 1st exp.) showing the ret. time range of 27.6-40.4 min

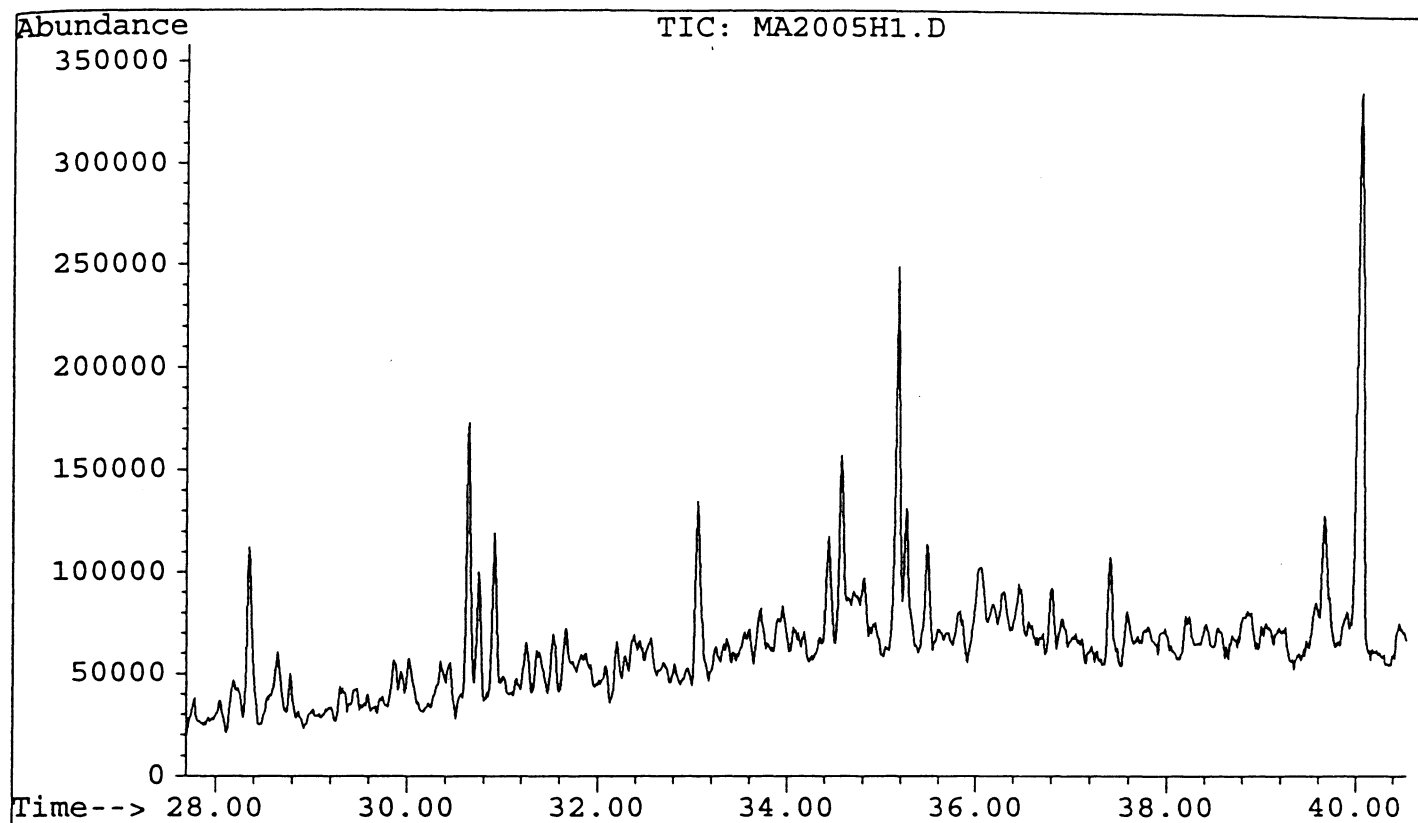


Figure 22. TIC of toluene fraction of after desulfurized sample of Arg-#301 (the 1st exp.)

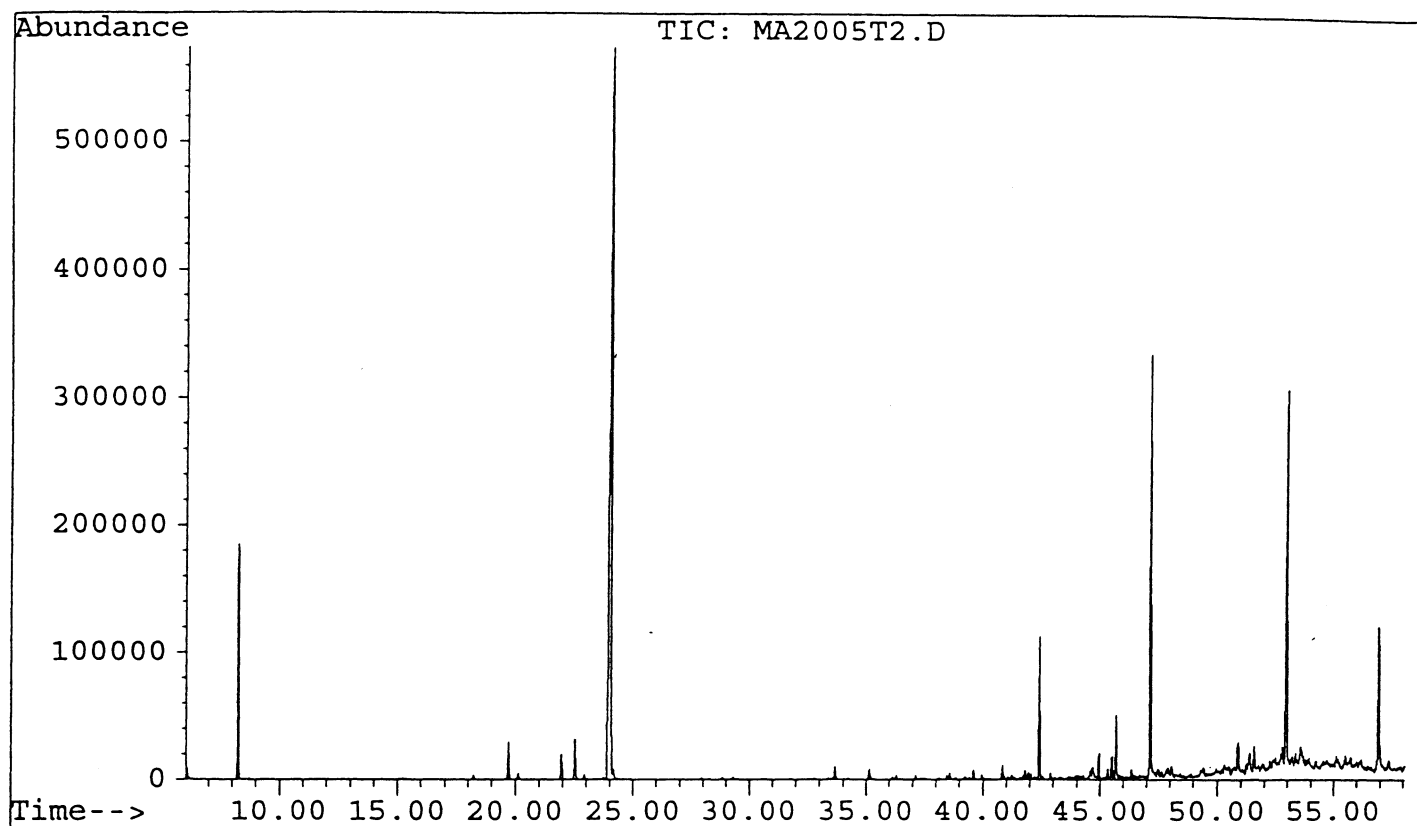


Figure 23.1. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 2nd exp.)

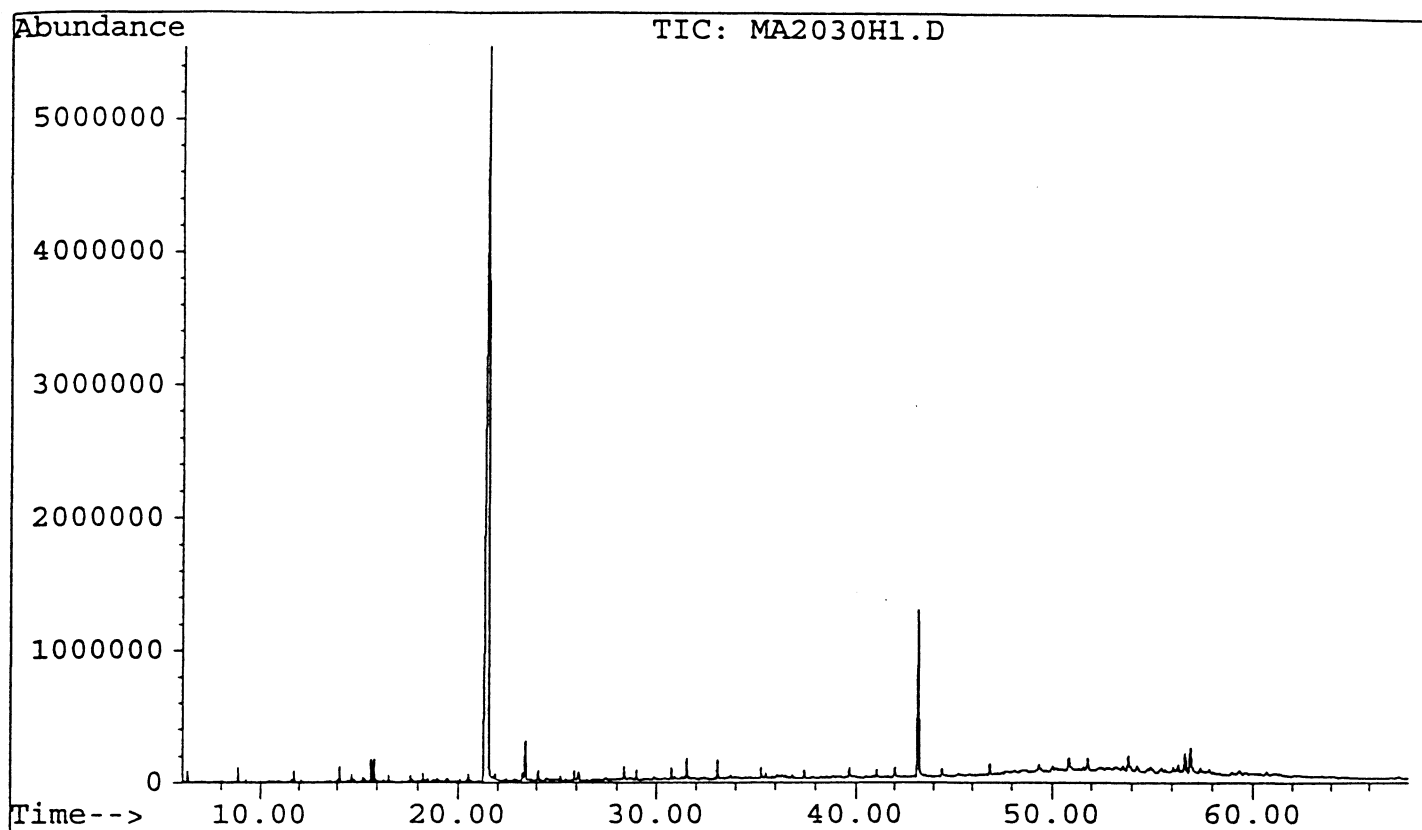


Figure 23.2. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 8-22 min and the mass spectrum of 1H-indene, 2,3-dihydro-1,1,2,3,3-pentame

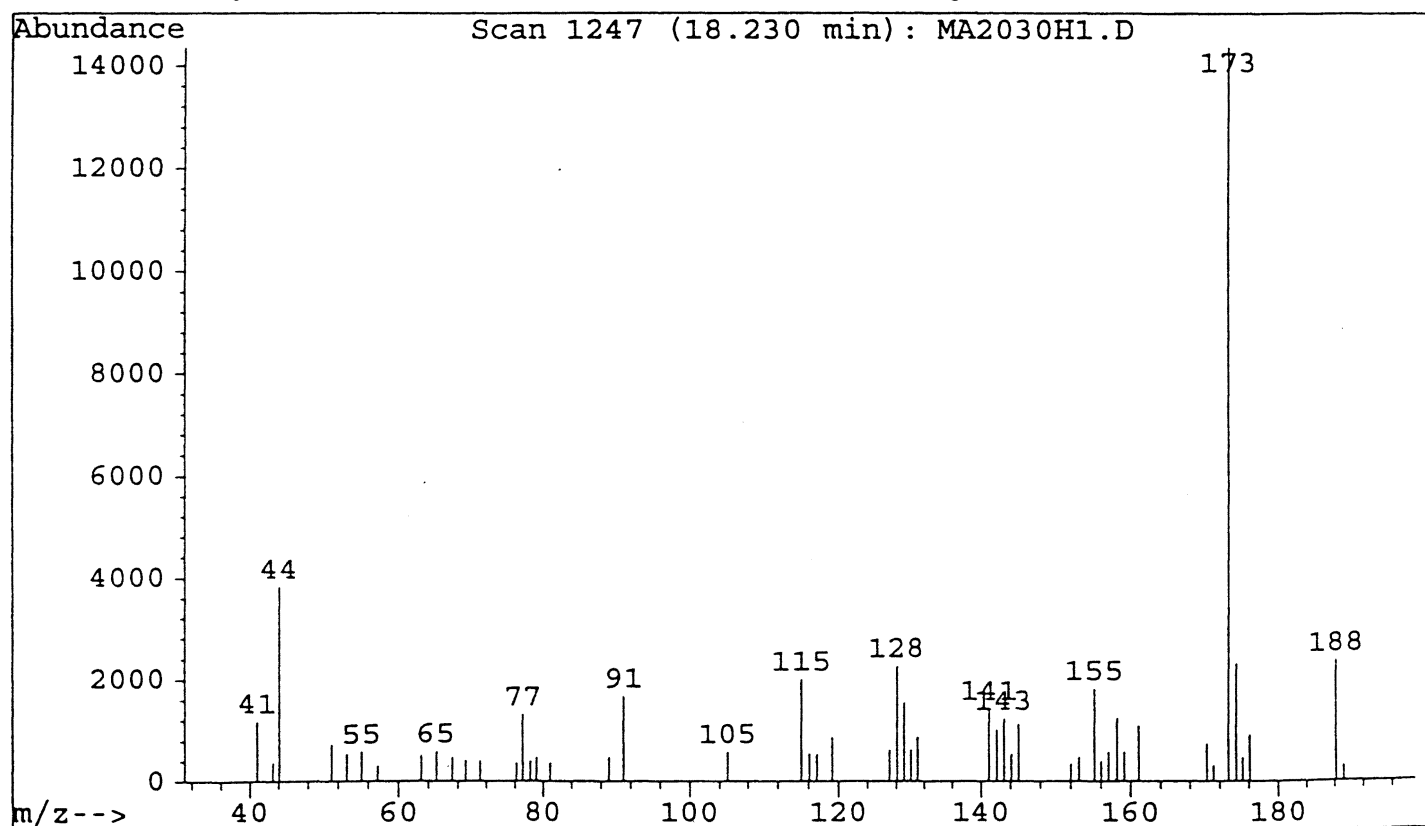
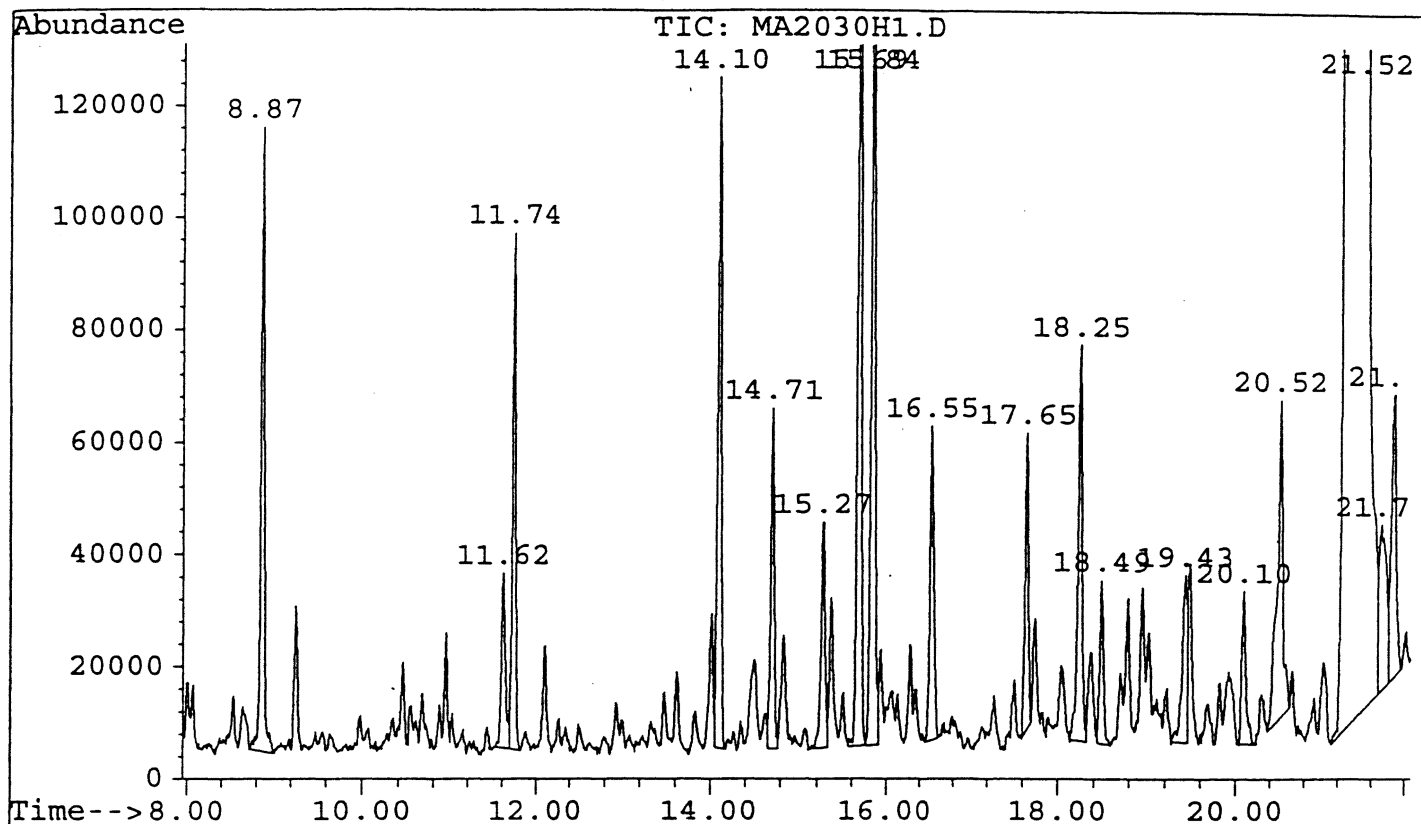


Figure 23.3. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 2nd exp) showing the ret. time range of 22-28 min and the mass spectrum of Pentadecane,2,6,10,12-tetramethyl

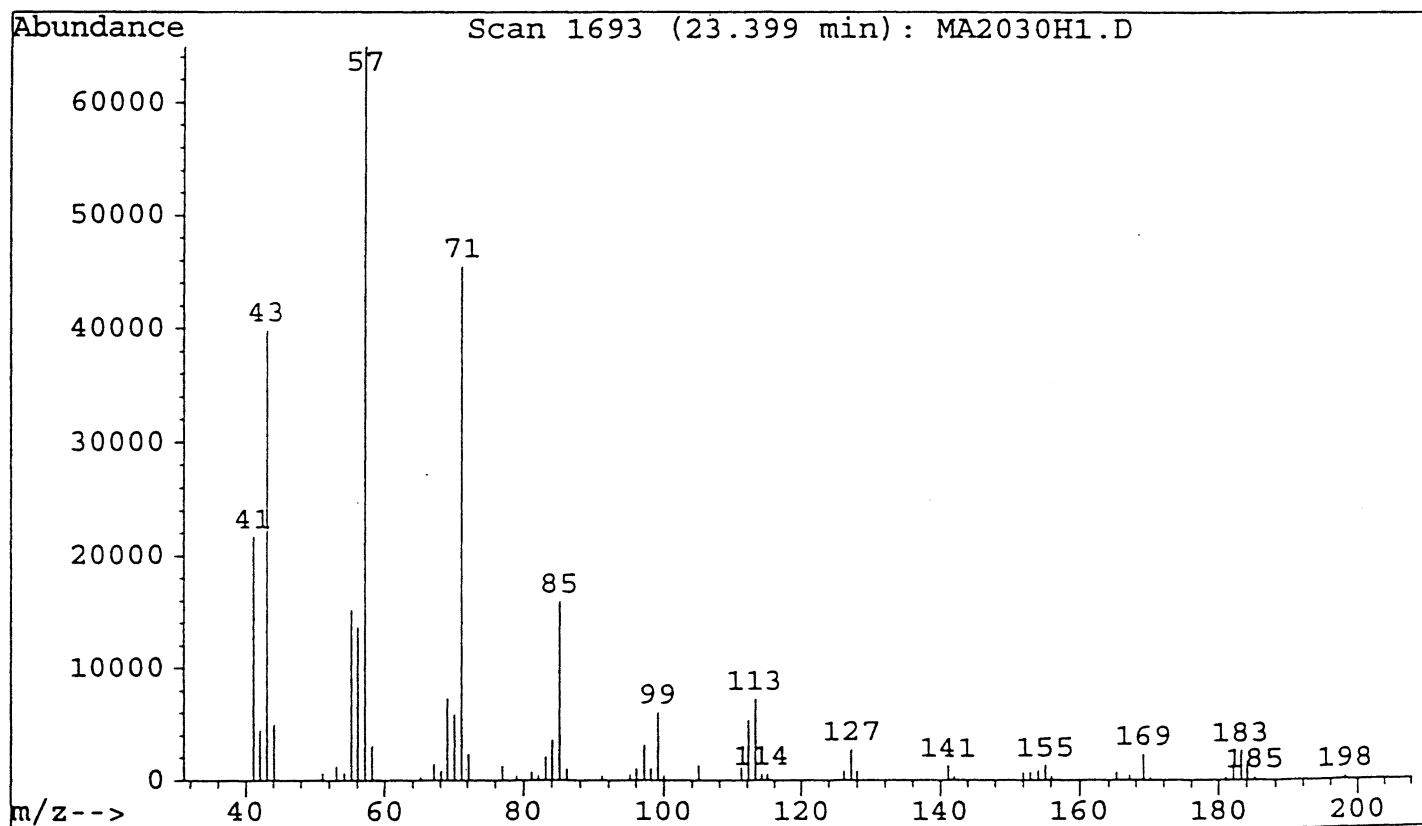
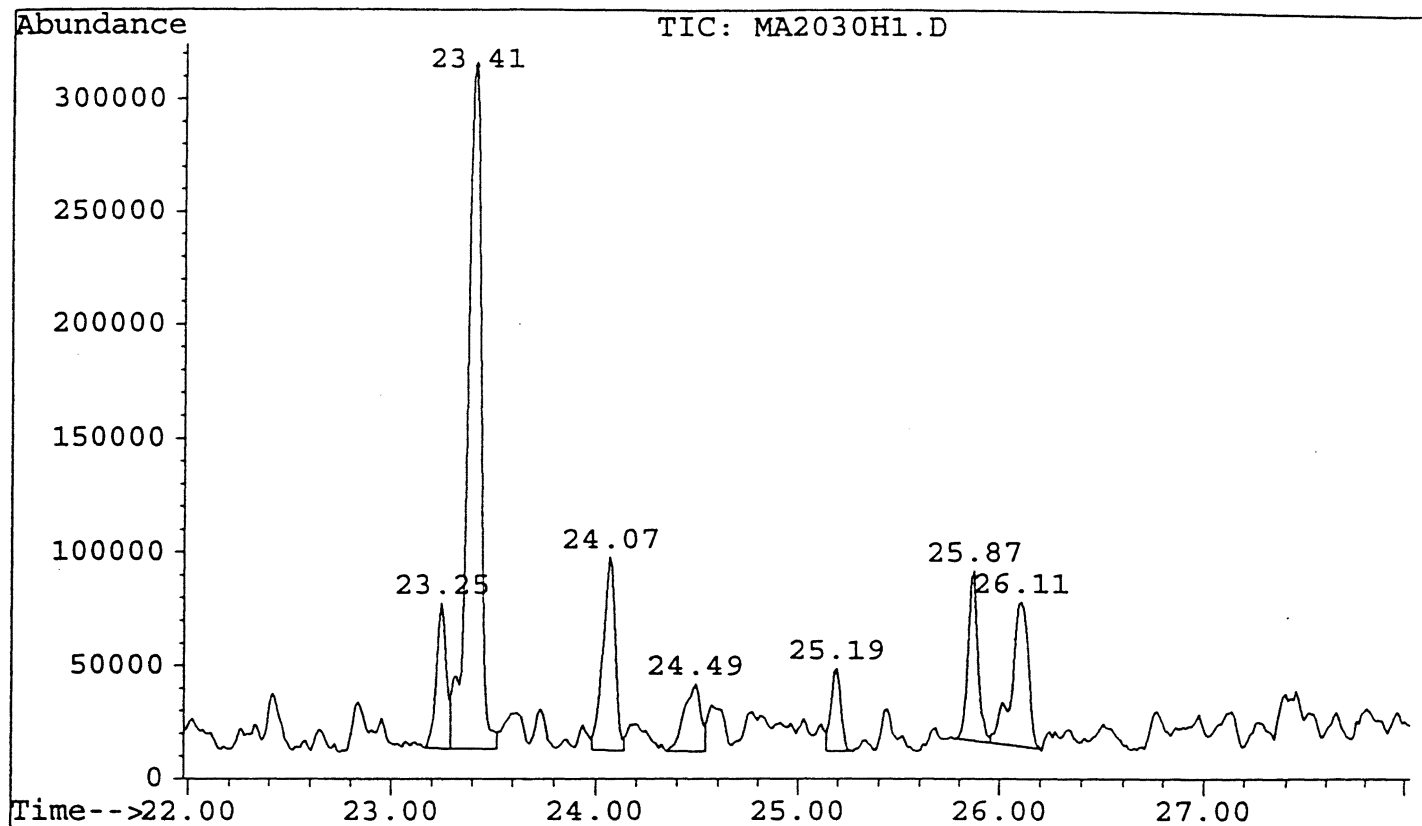


Figure 23.4. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 22-28 min and the mass spectrum of DBT

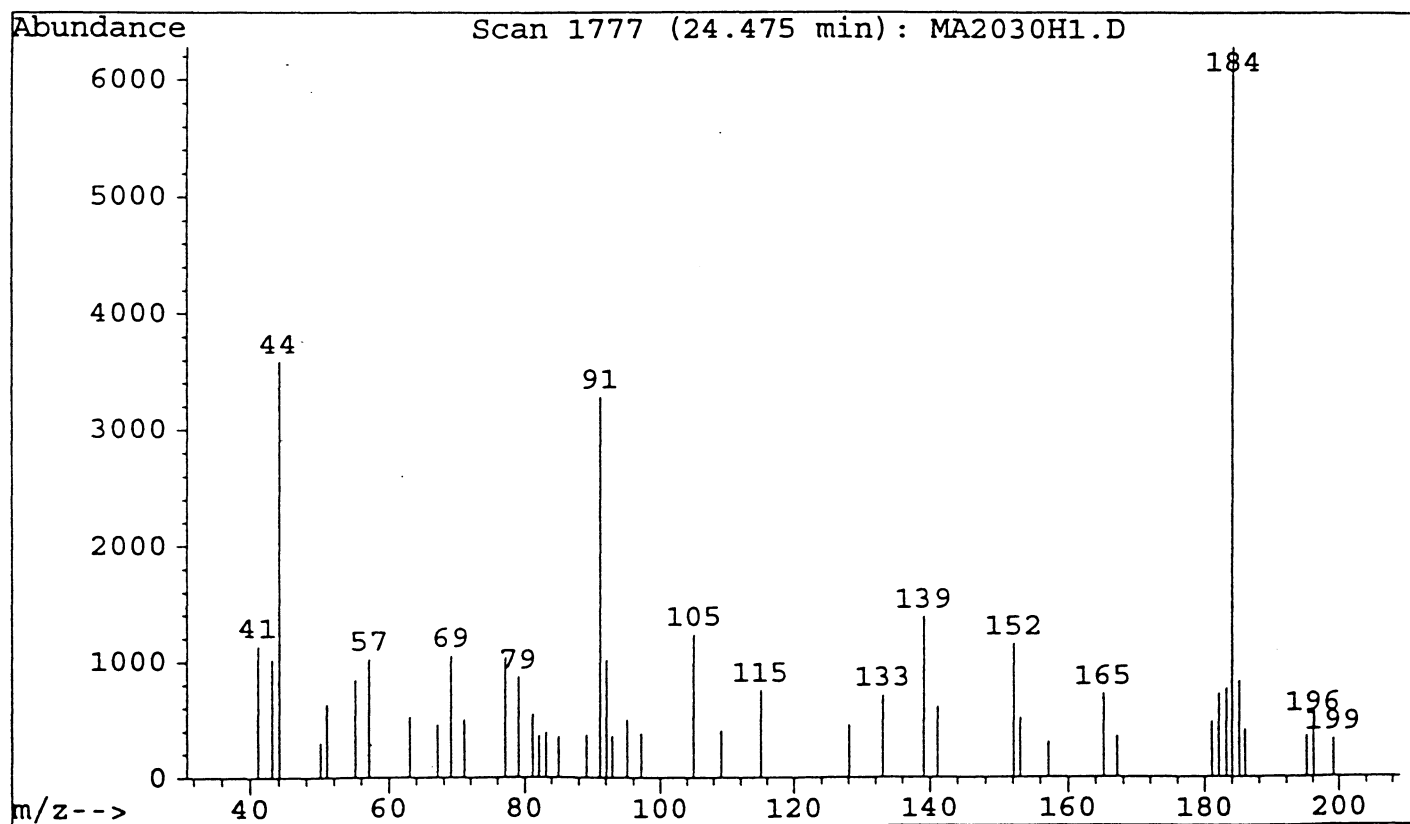
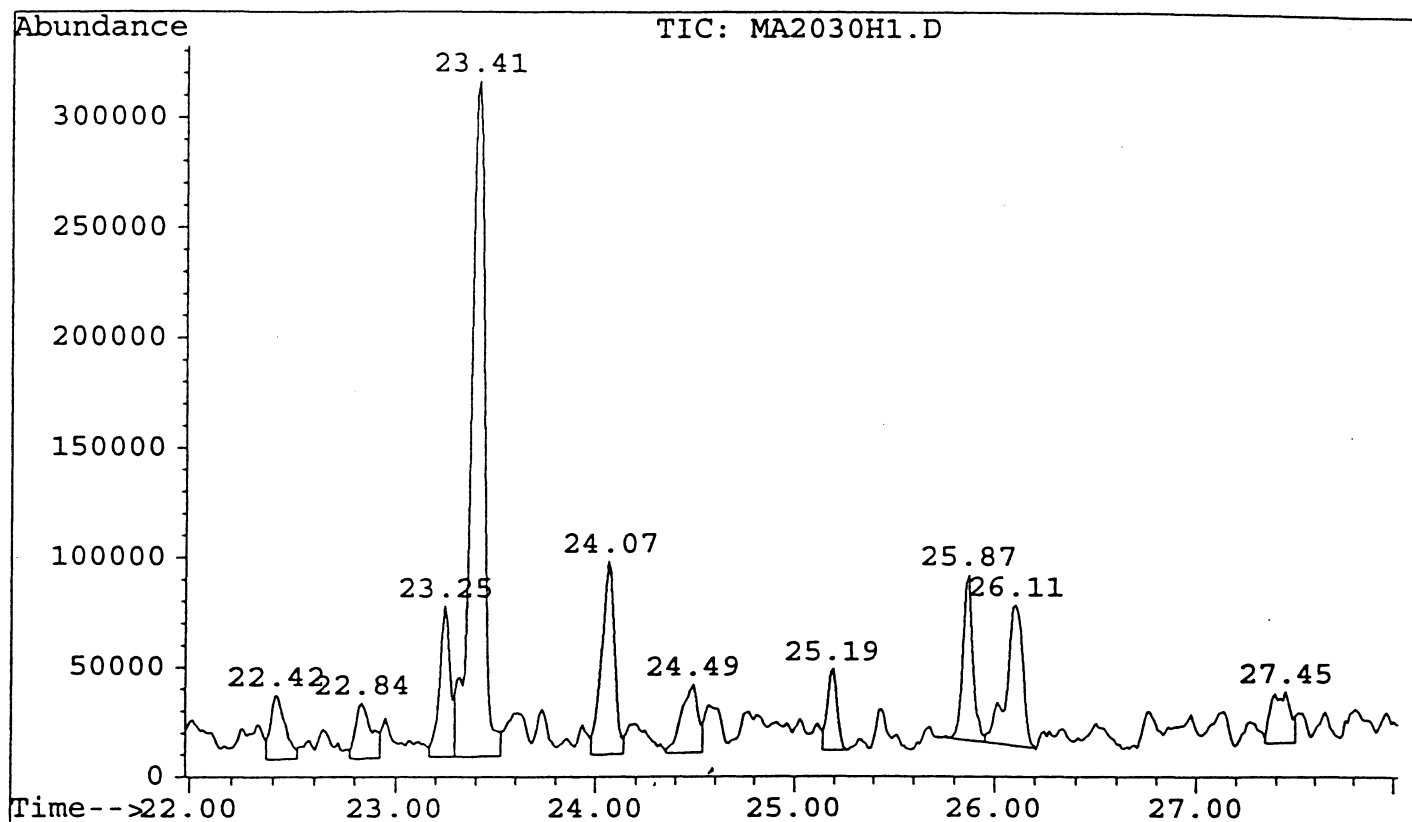


Figure 23.5. TIC of hexane fraction of before desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 28-40 min

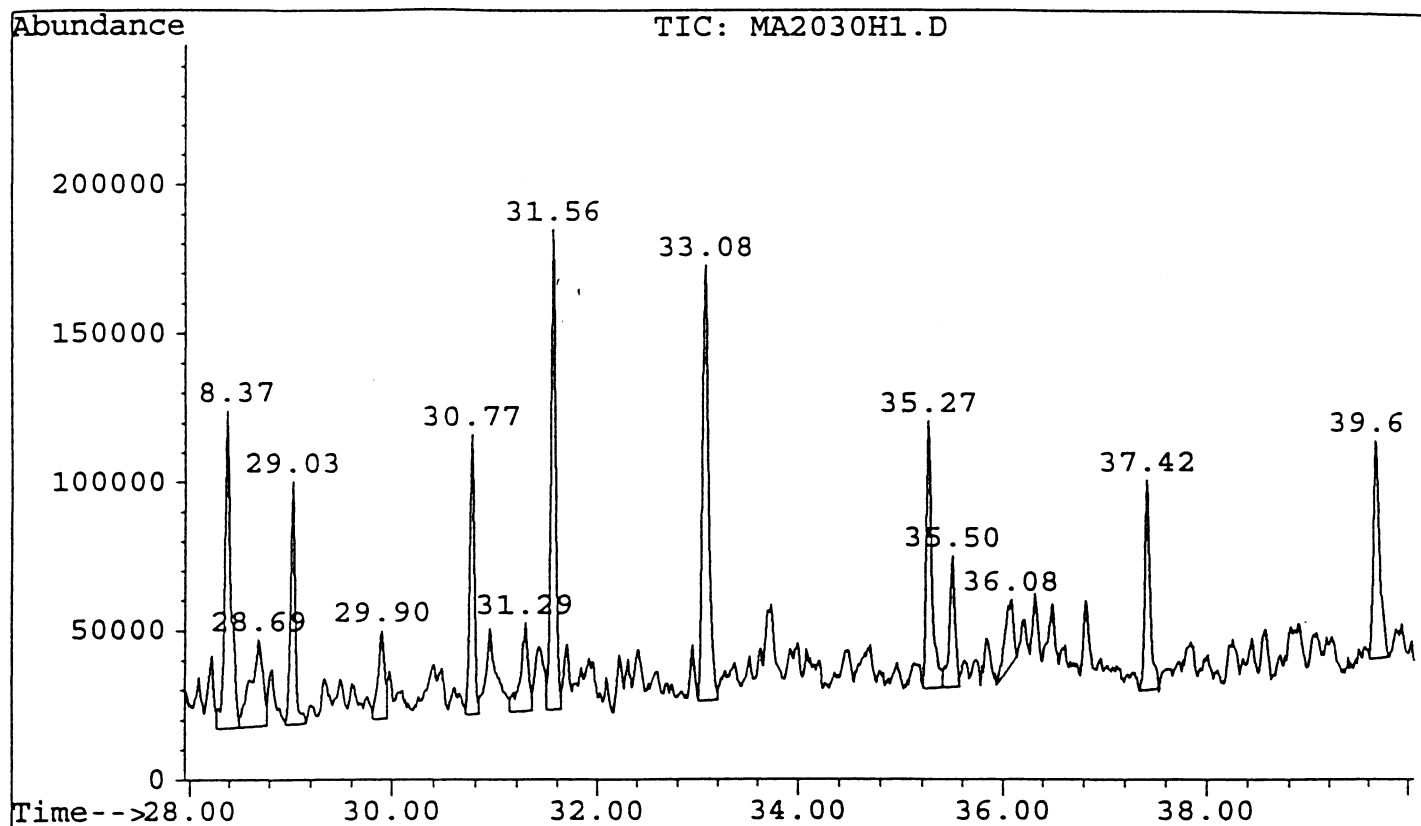


Figure 24.1. TIC of toluene fraction of before desulfurized sample of Arg-#301 (the 2nd exp.)

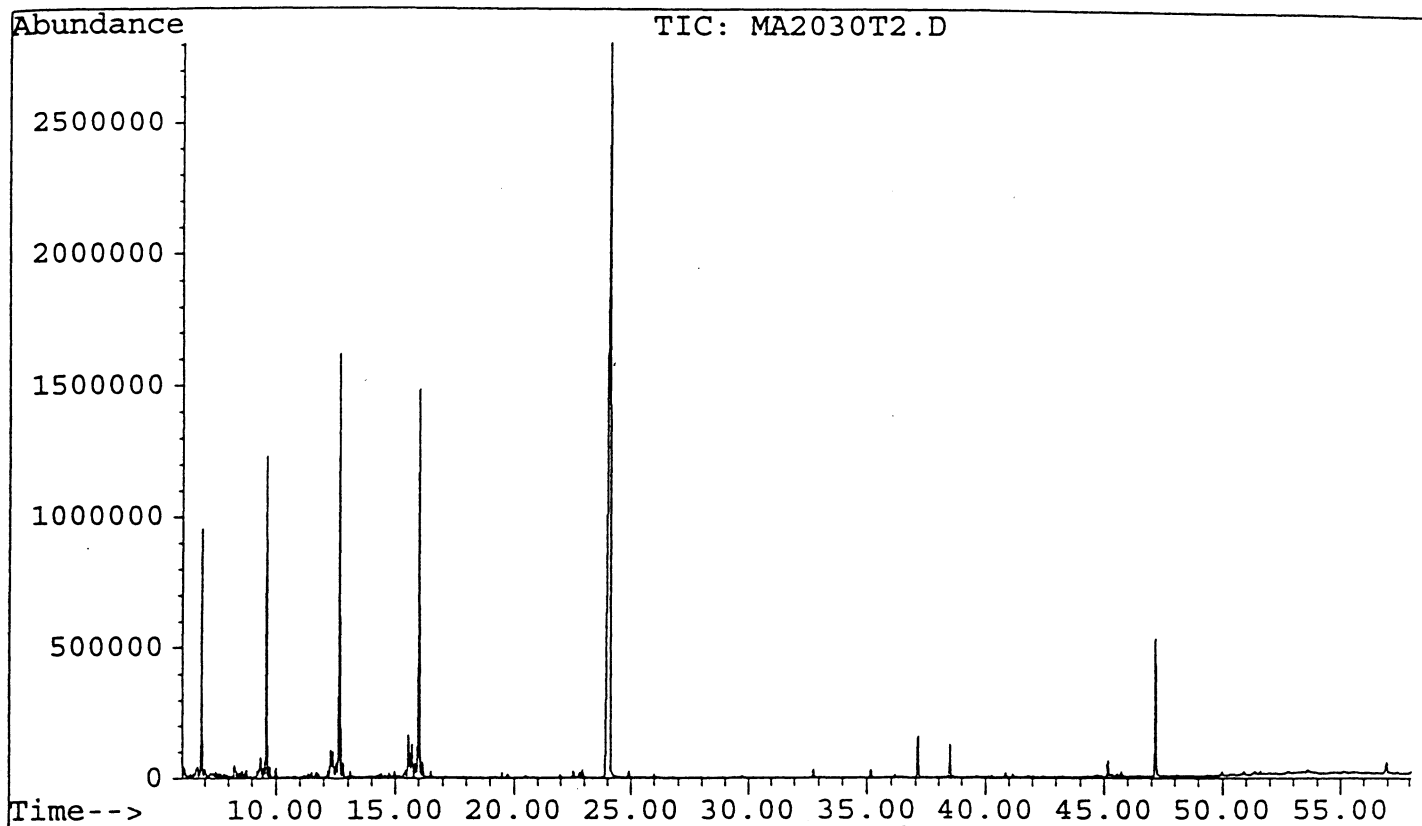


Figure 24.2. TIC of toluene fraction of before desulfurized sample of Arg-#301 (the 2nd exp) showing the ret. time range of 6.05-10.05 min and the mass spectrum of Dodecane

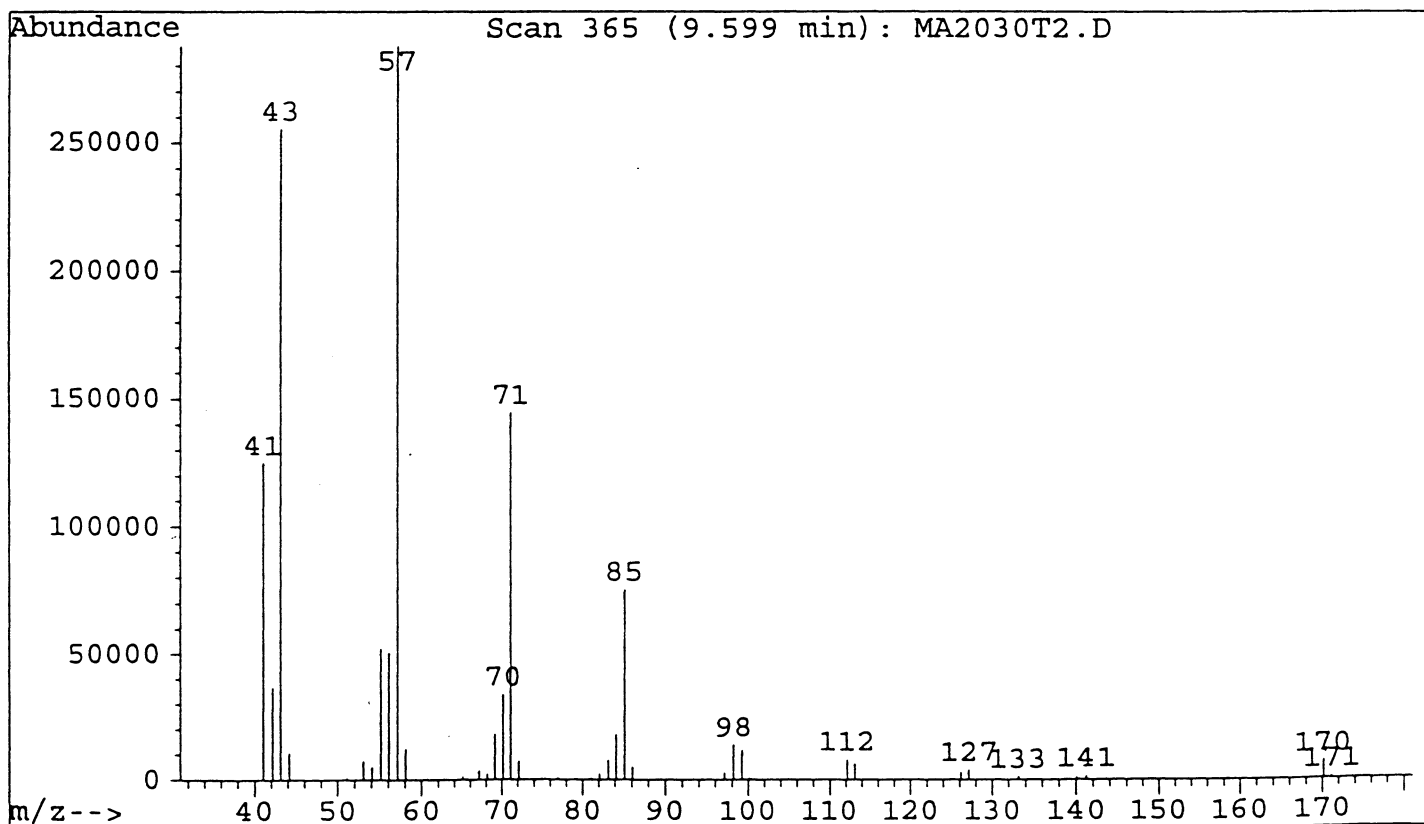
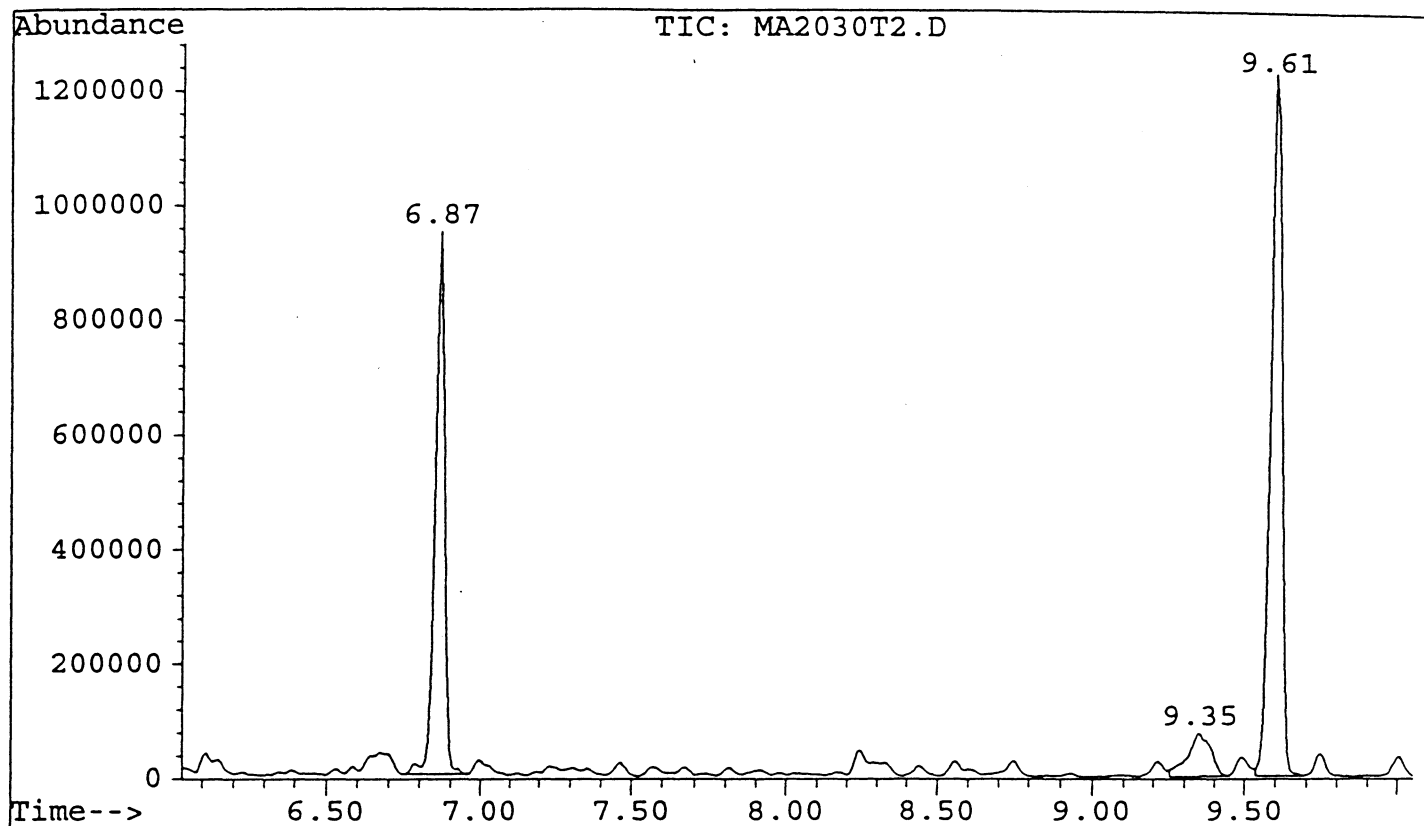


Figure 24.3. TIC of toluene fraction of before desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 9.9-20.2 min and the mass spectrum of Tetradecane

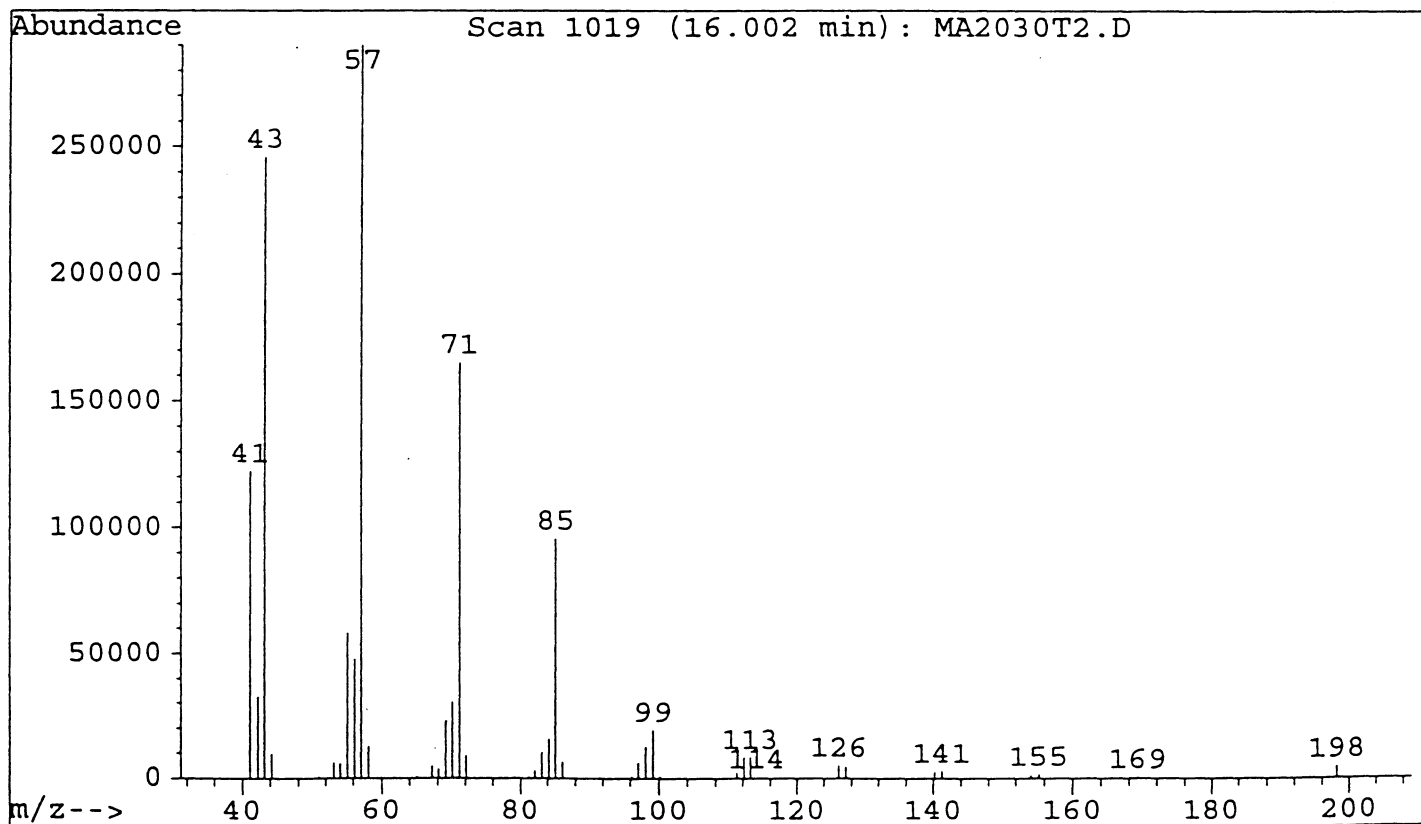
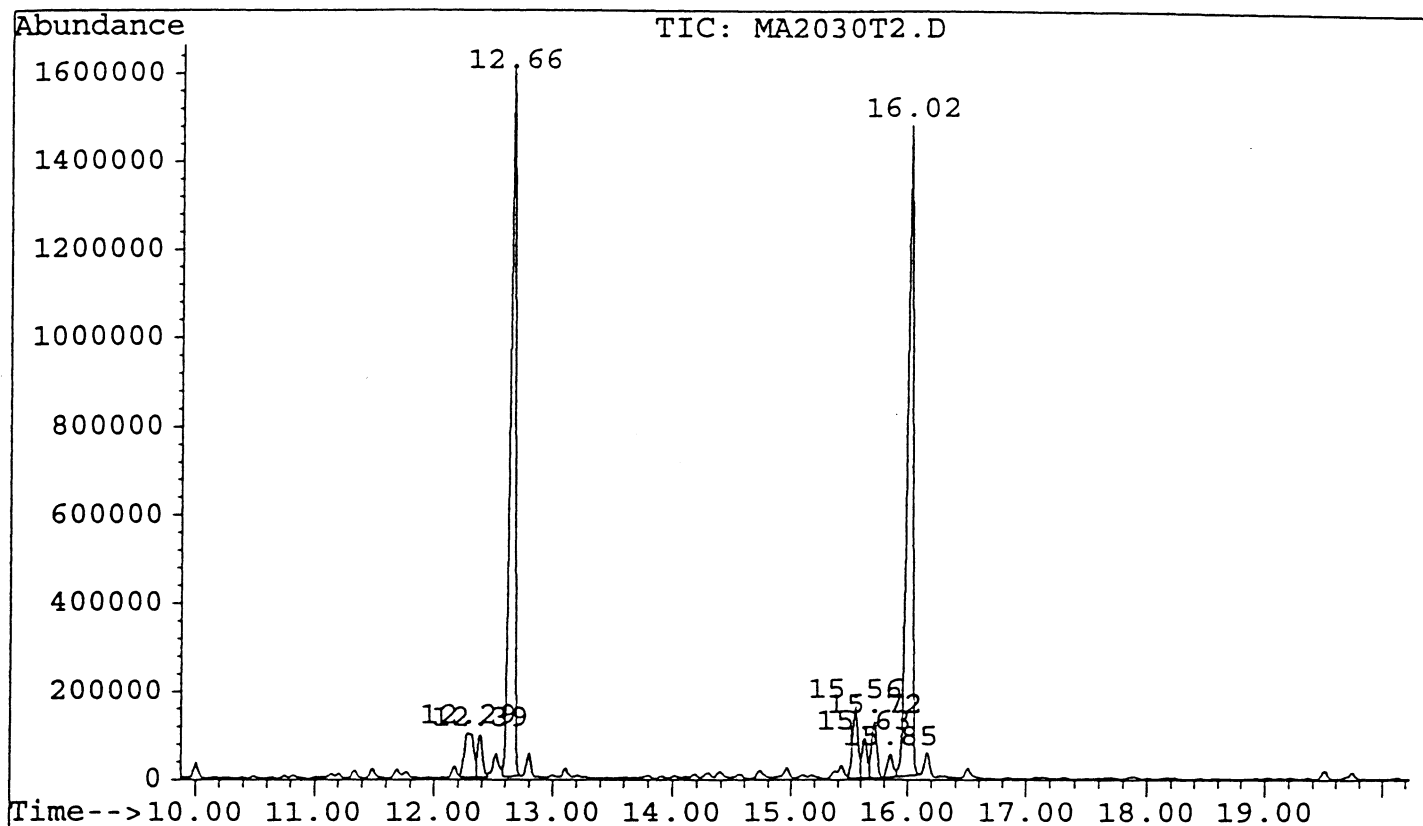


Figure 25.1. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 2nd exp.)

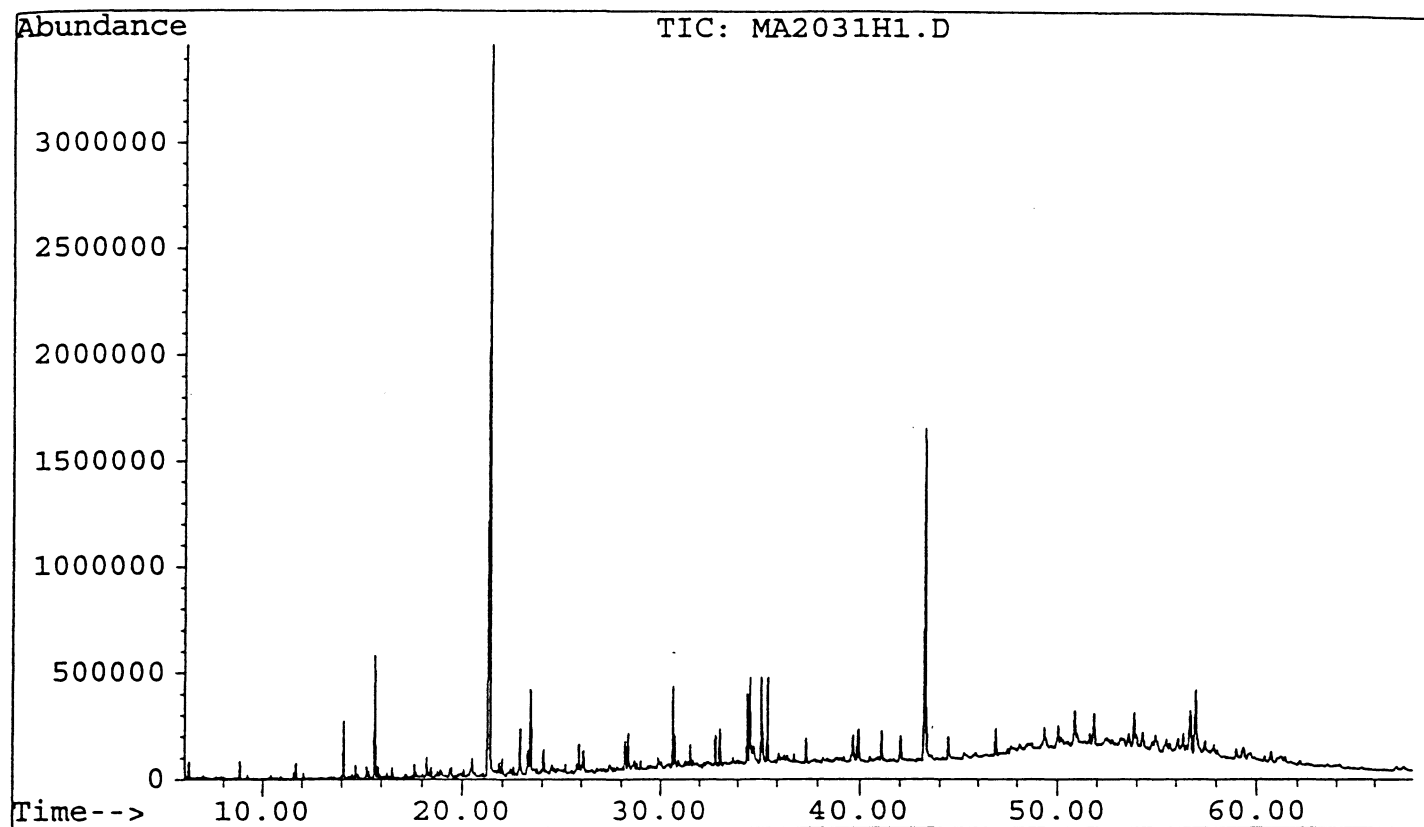


Figure 25.2. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 8-22 min and the mass spectrum of 1H-indene, 2,3-dihydro-1,1,2,3,3-pentame

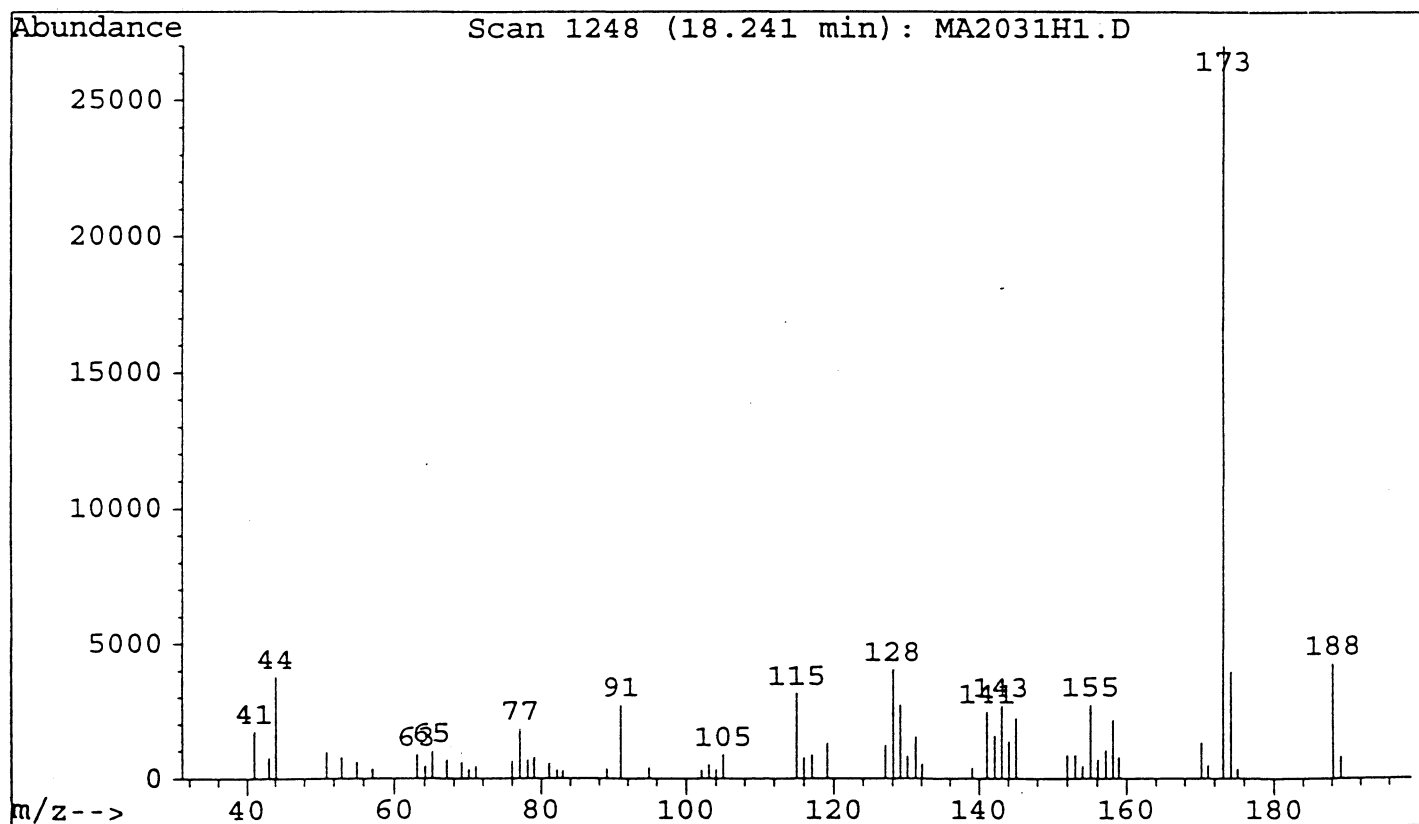
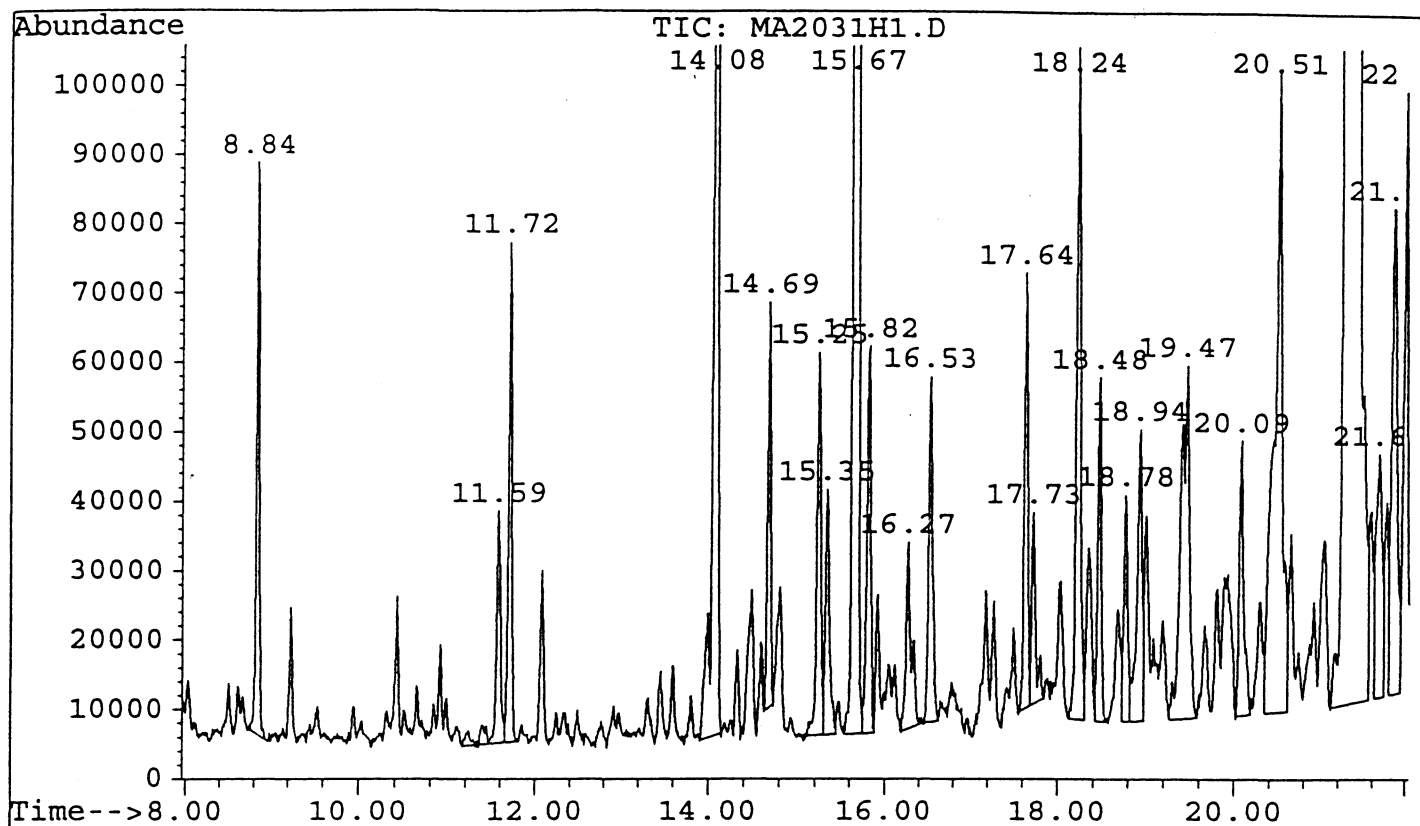


Figure 25.3. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 22-28 min and the mass spectrum of Pentadecane, 2,6,10,12-tetramethyl

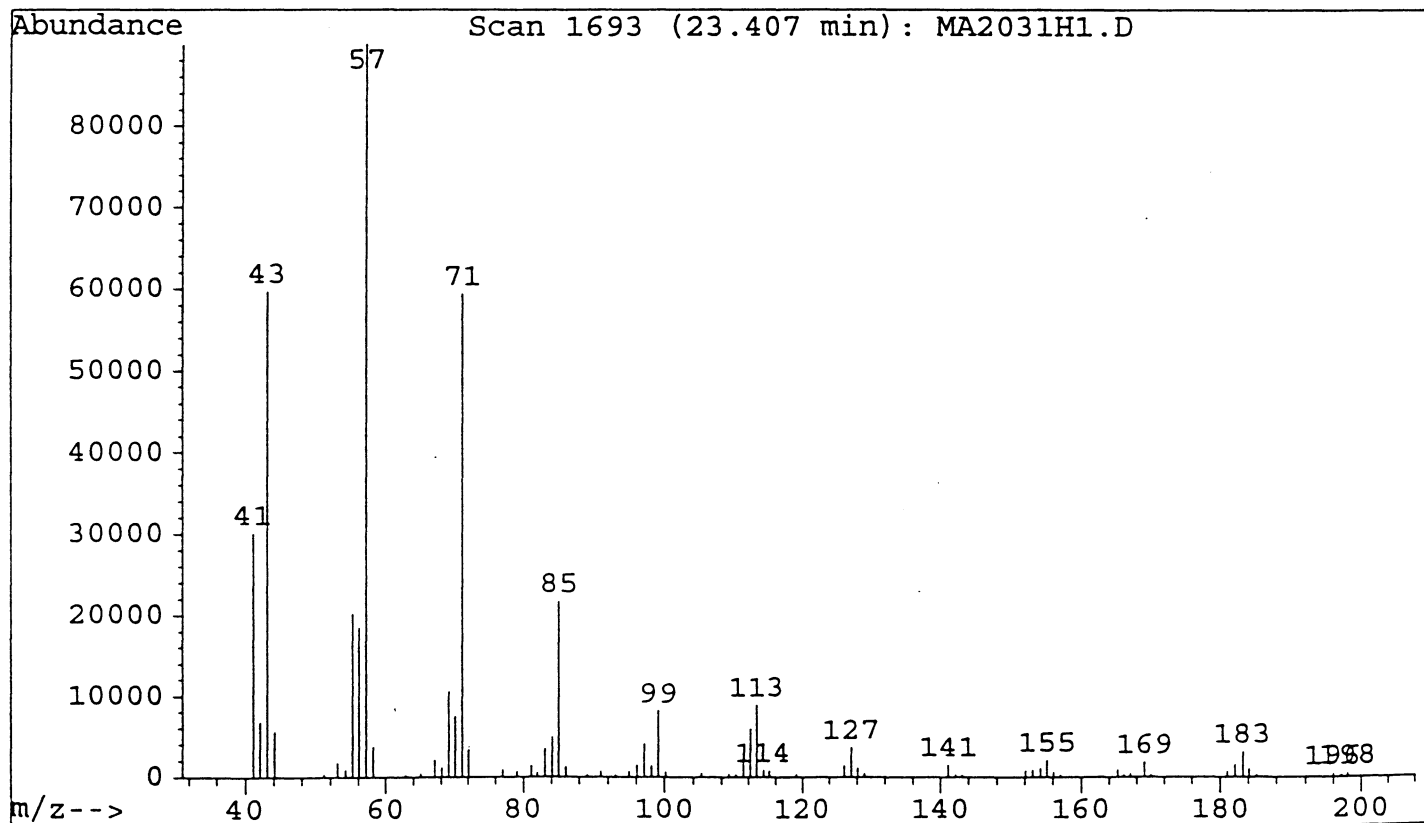
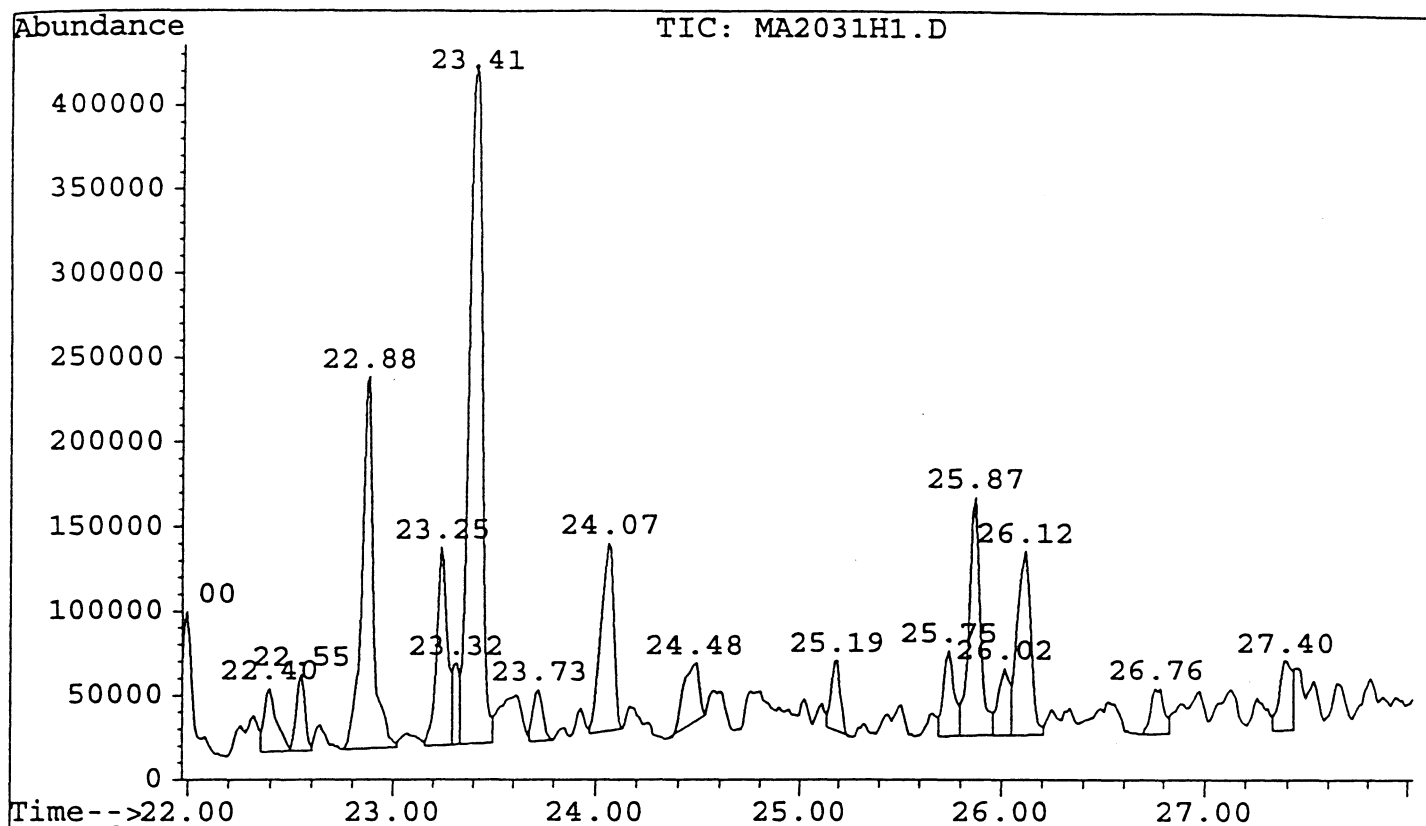


Figure 25.4. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 22-28 min and the mass spectrum of DBT

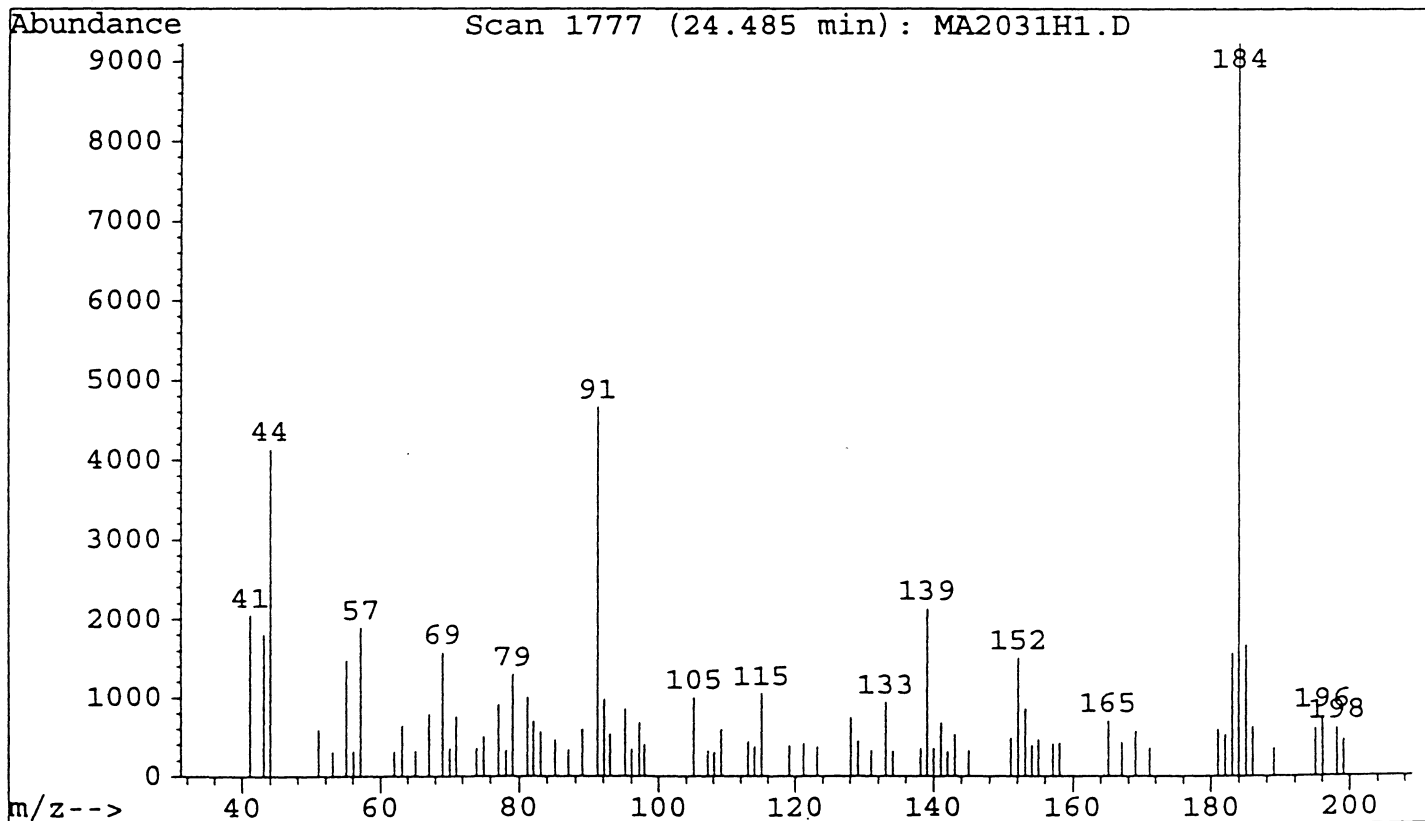
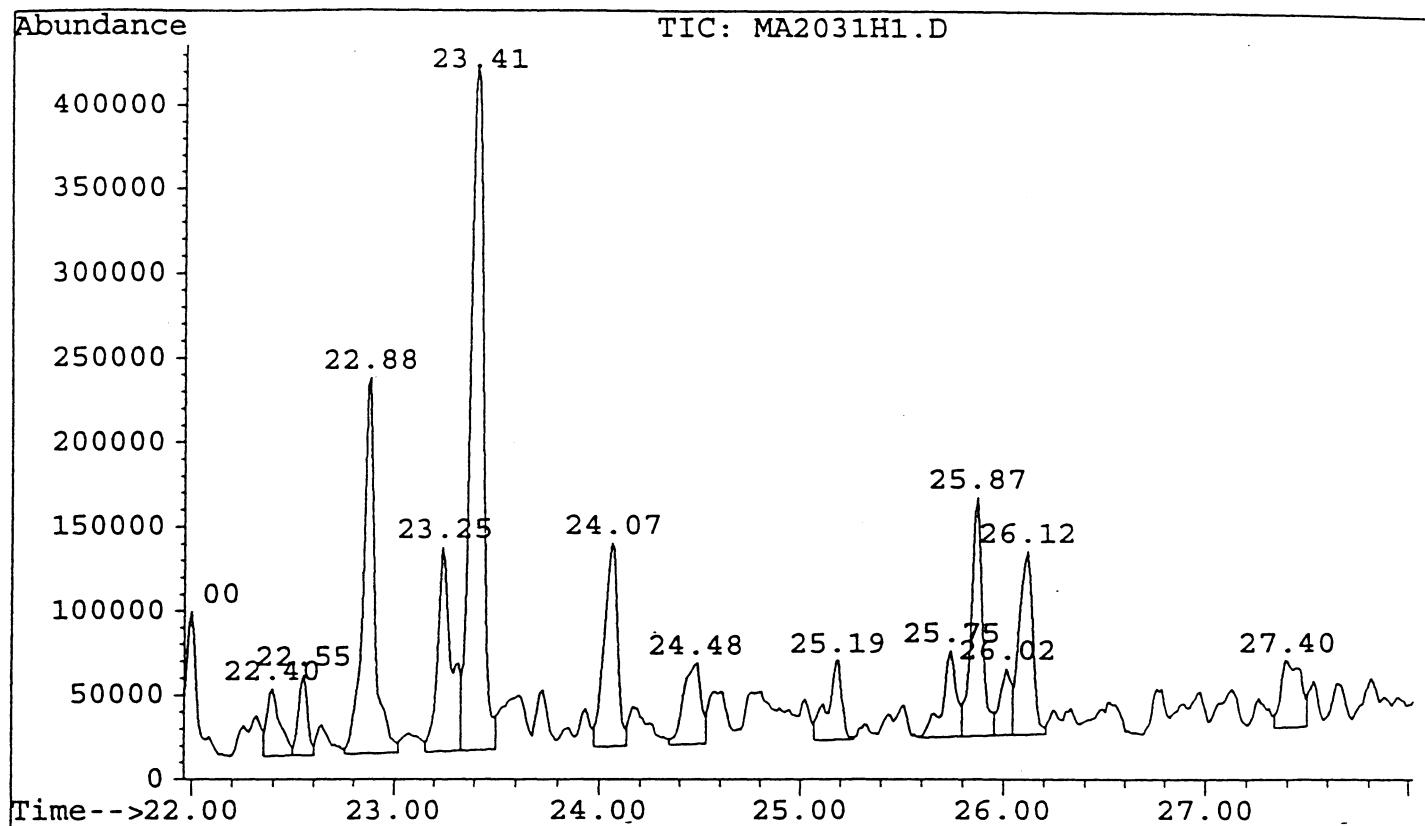


Figure 25.5. TIC of hexane fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 28-40 min

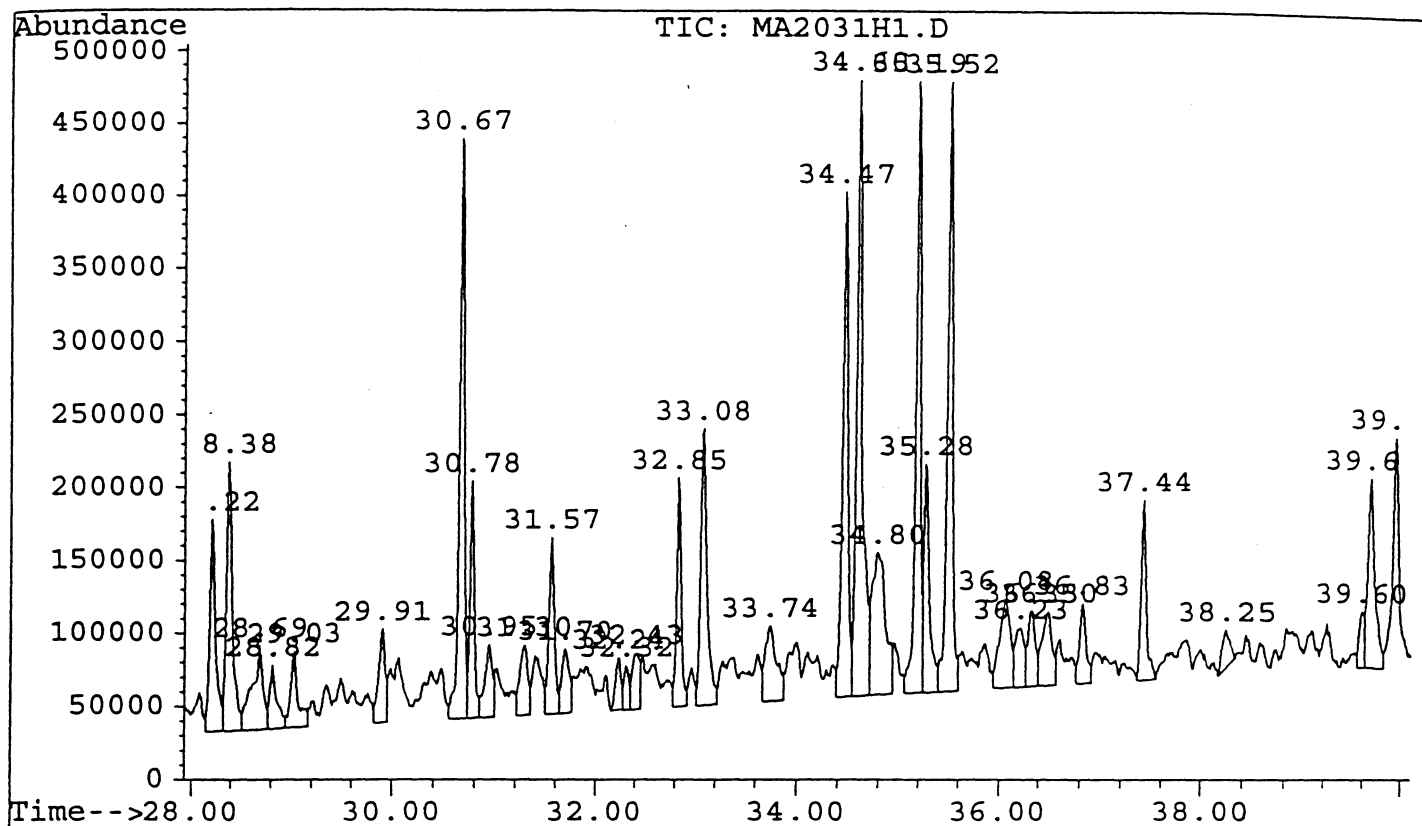


Figure 26.1. TIC of toluene fraction of after desulfurized sample of Arg-#301 (the 2nd exp.)

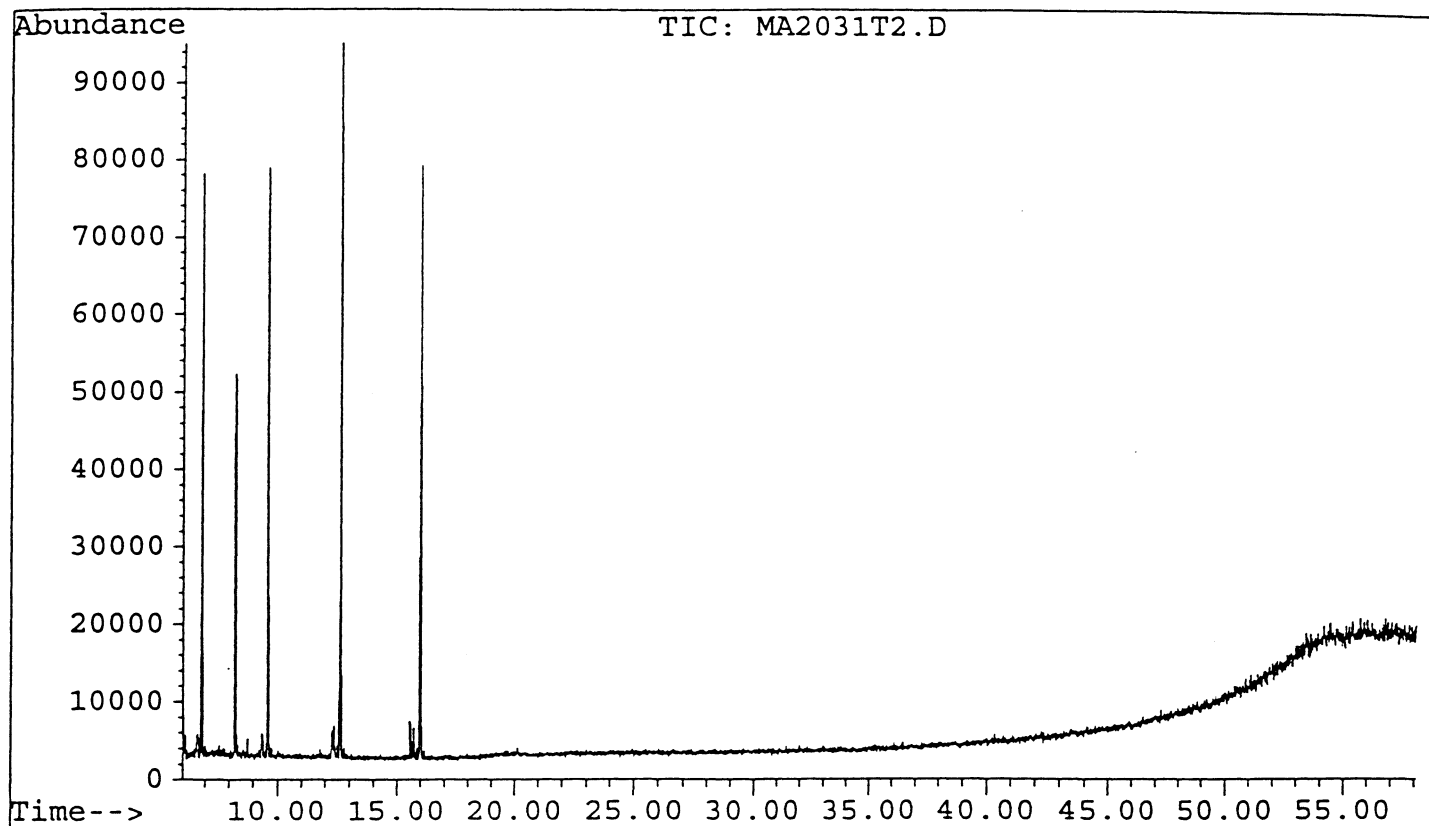


Figure 26.2. TIC of toluene fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 6.05-10.05 min and the mass spectrum of Dodecane

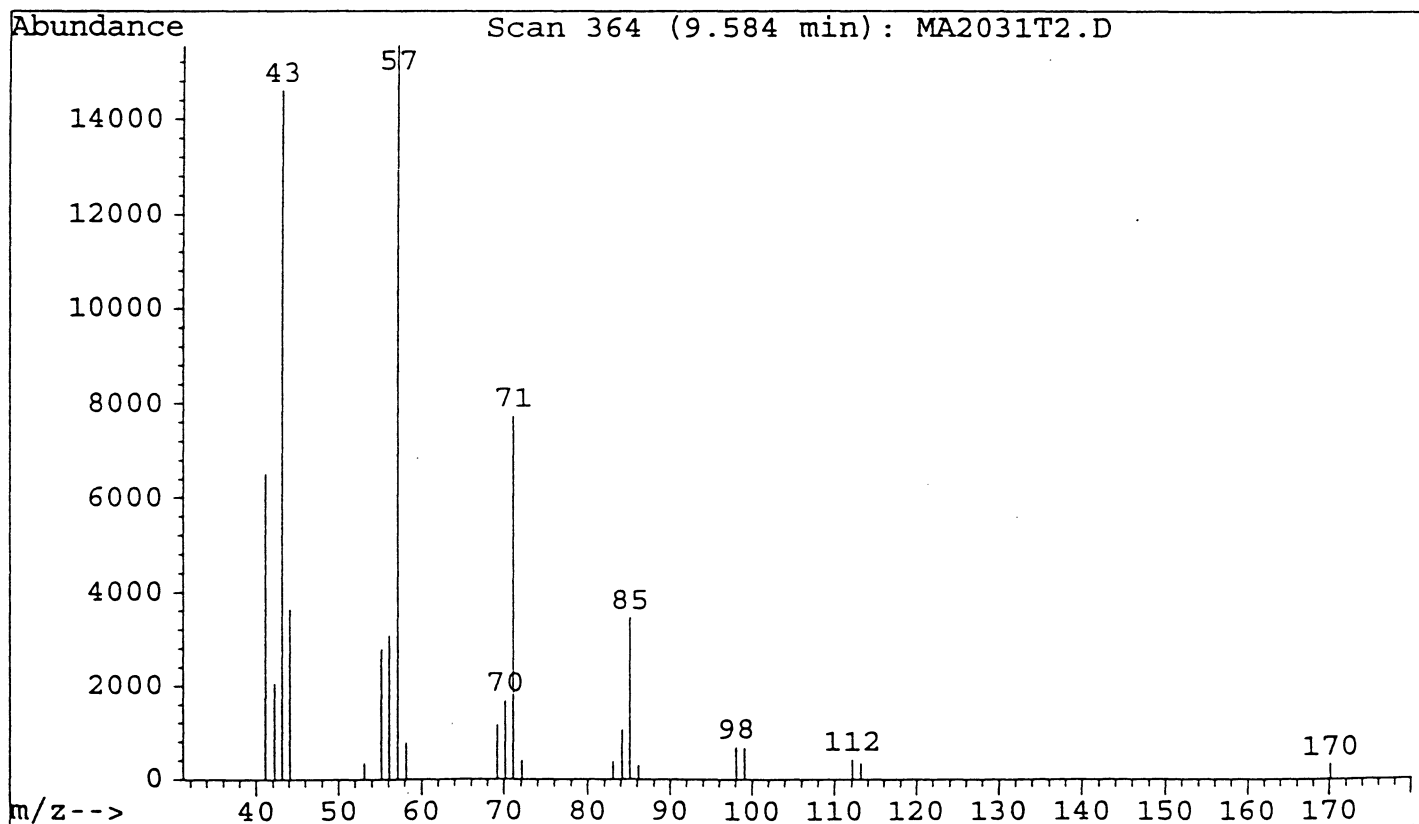
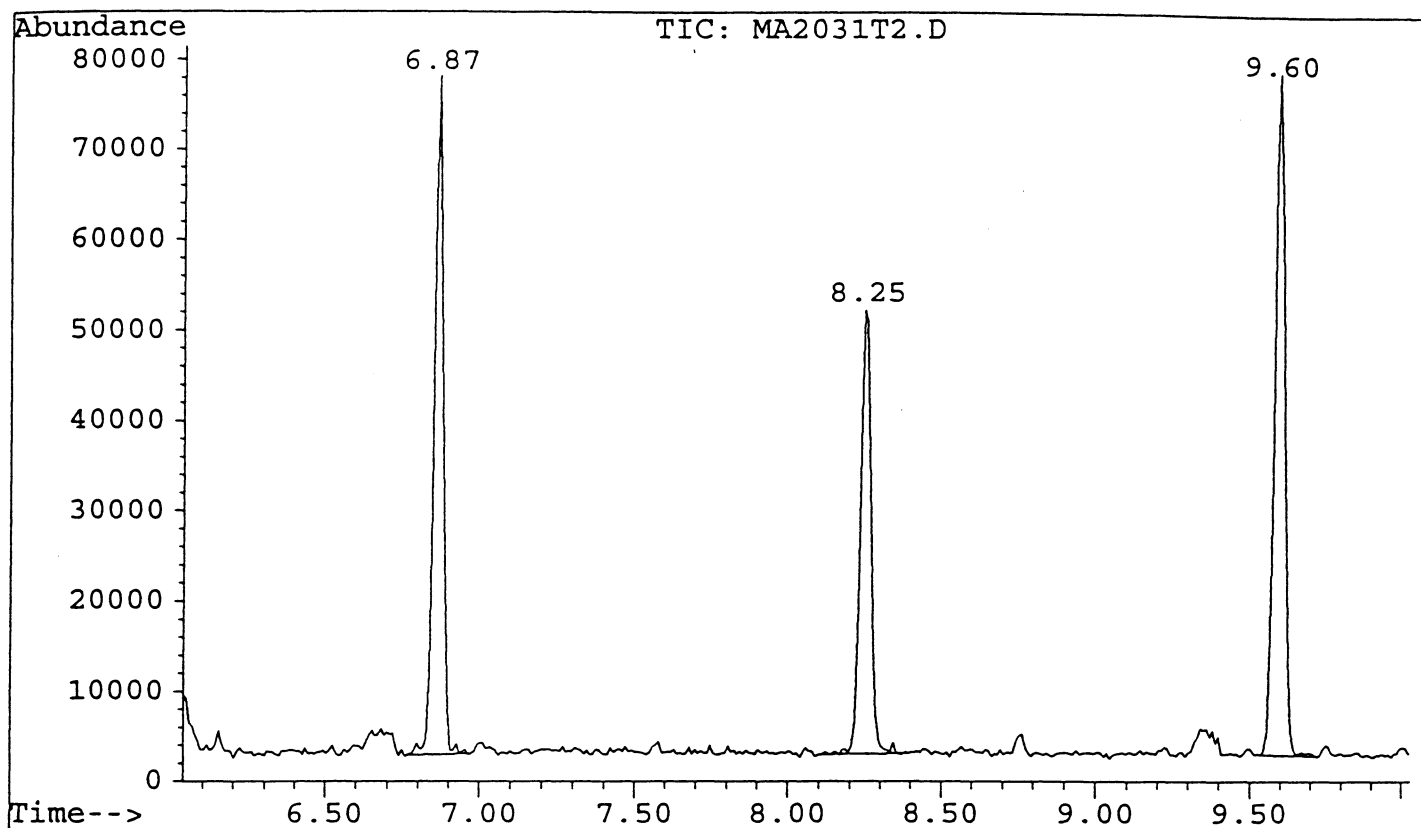


Figure 26.3. TIC of toluene fraction of after desulfurized sample of Arg-#301 (the 2nd exp.) showing the ret. time range of 10-20.2 min and the mass spectrum of Tridecane

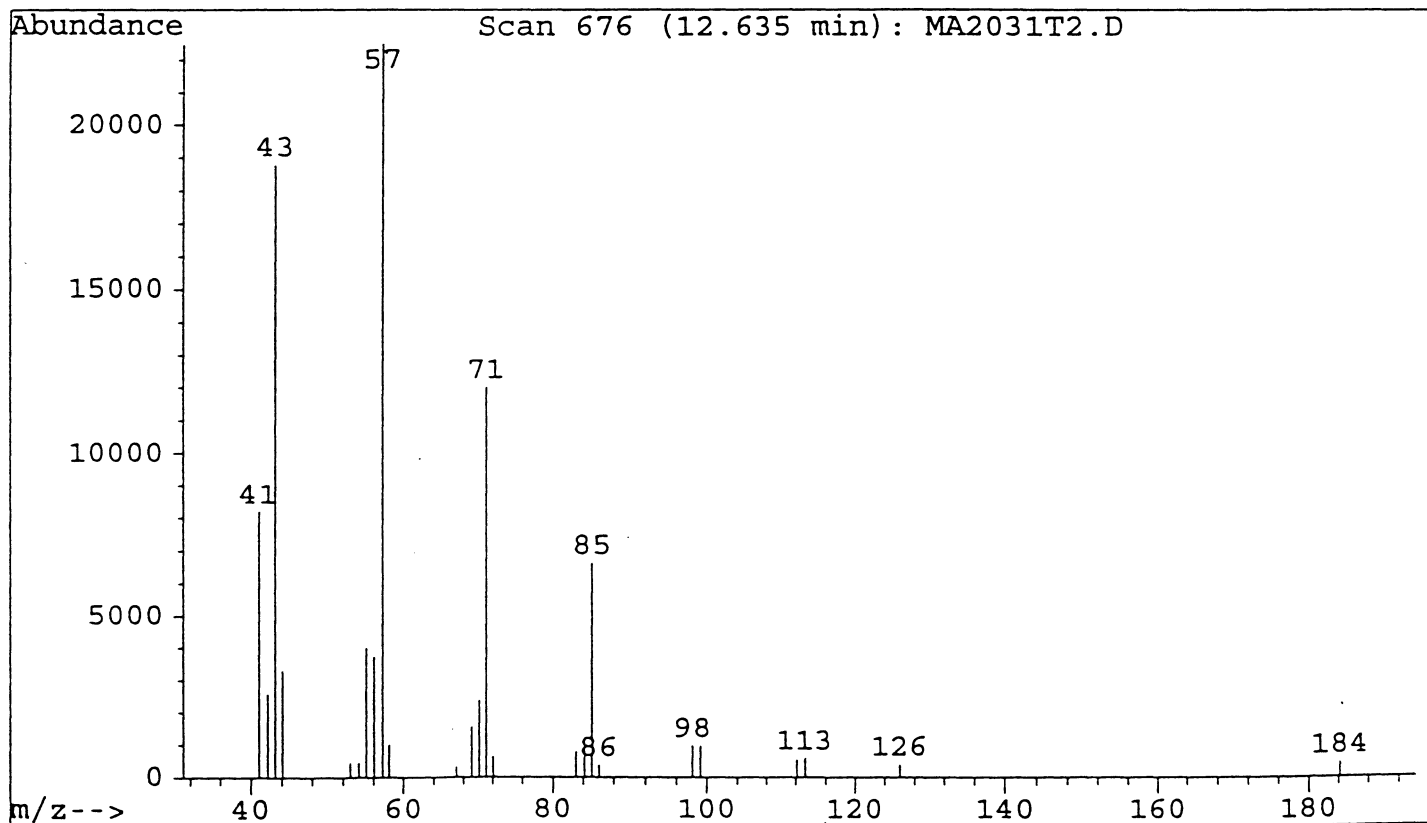
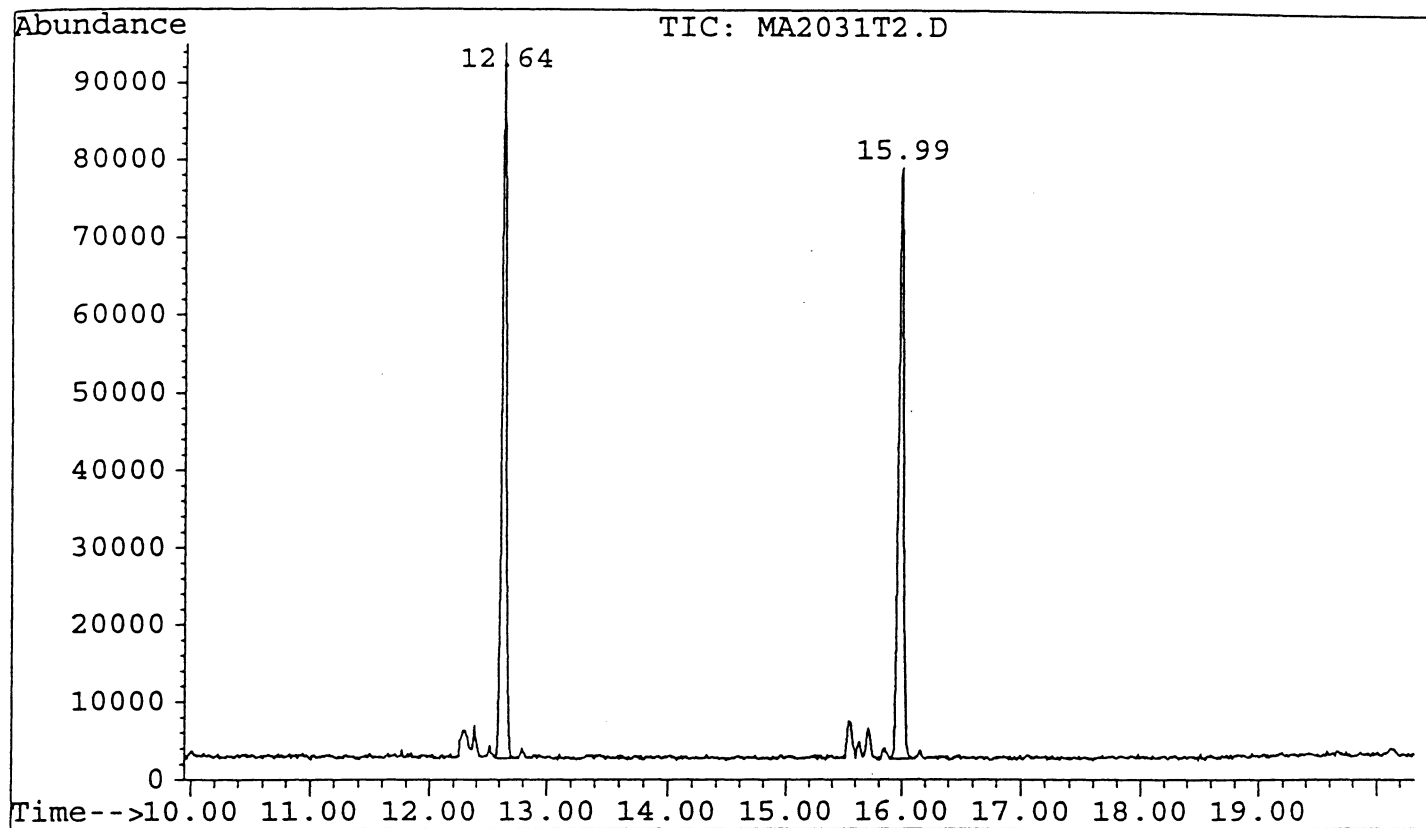


Figure 27.1. TIC of hexane fraction of before desulfurized sample of IBC-#108

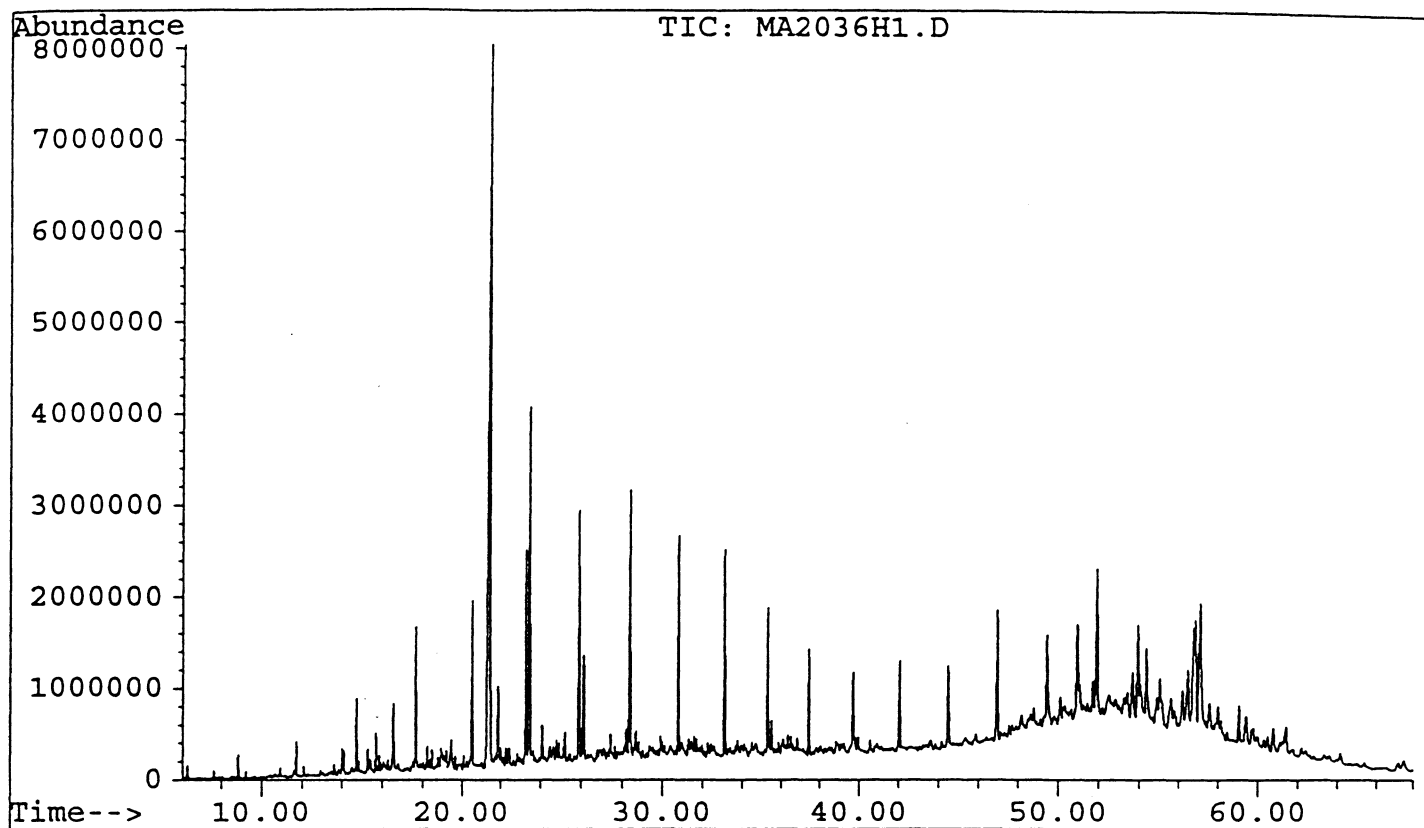


Figure 27.2. TIC of hexane fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 6-18 min and the mass spectrum of Pentadecane

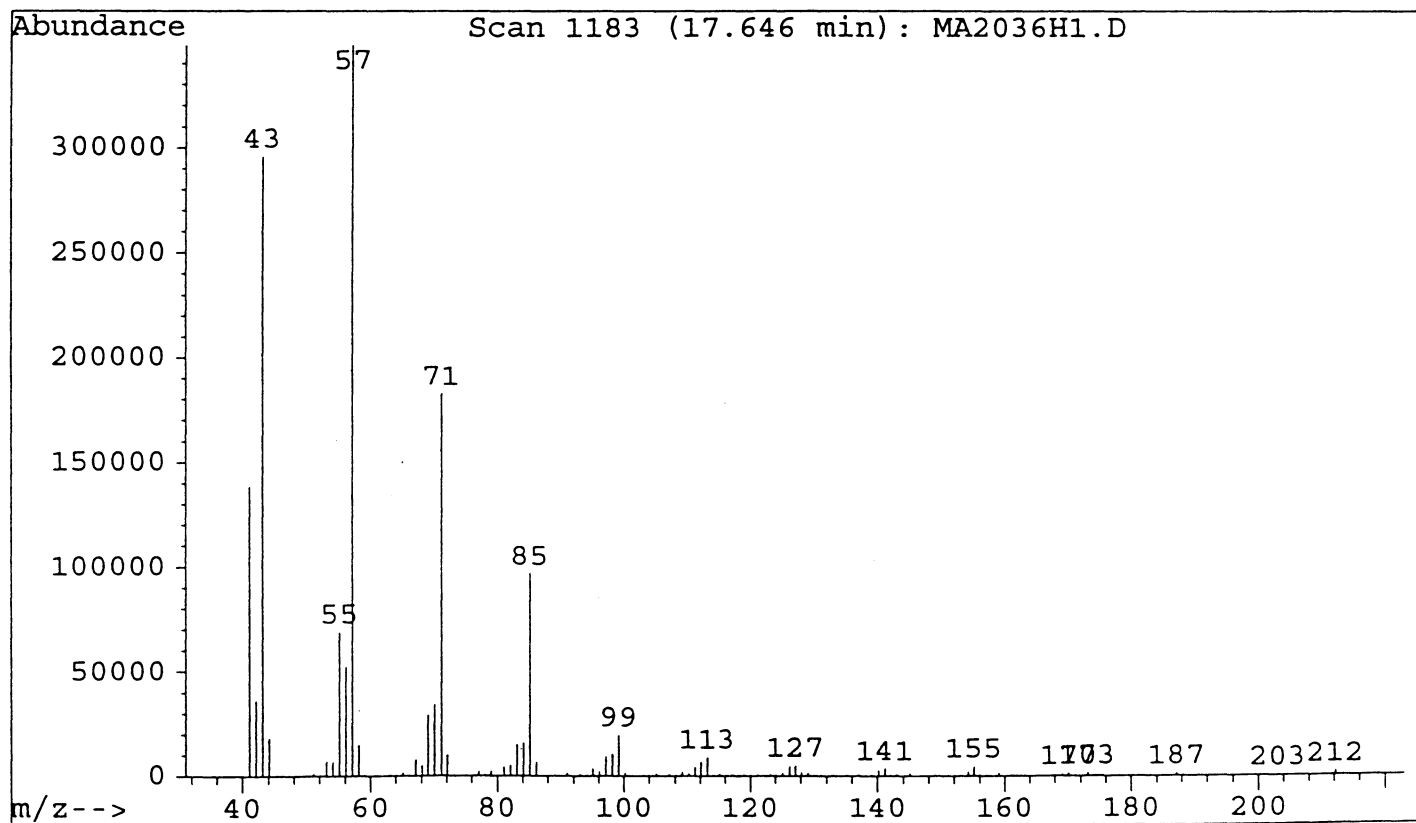
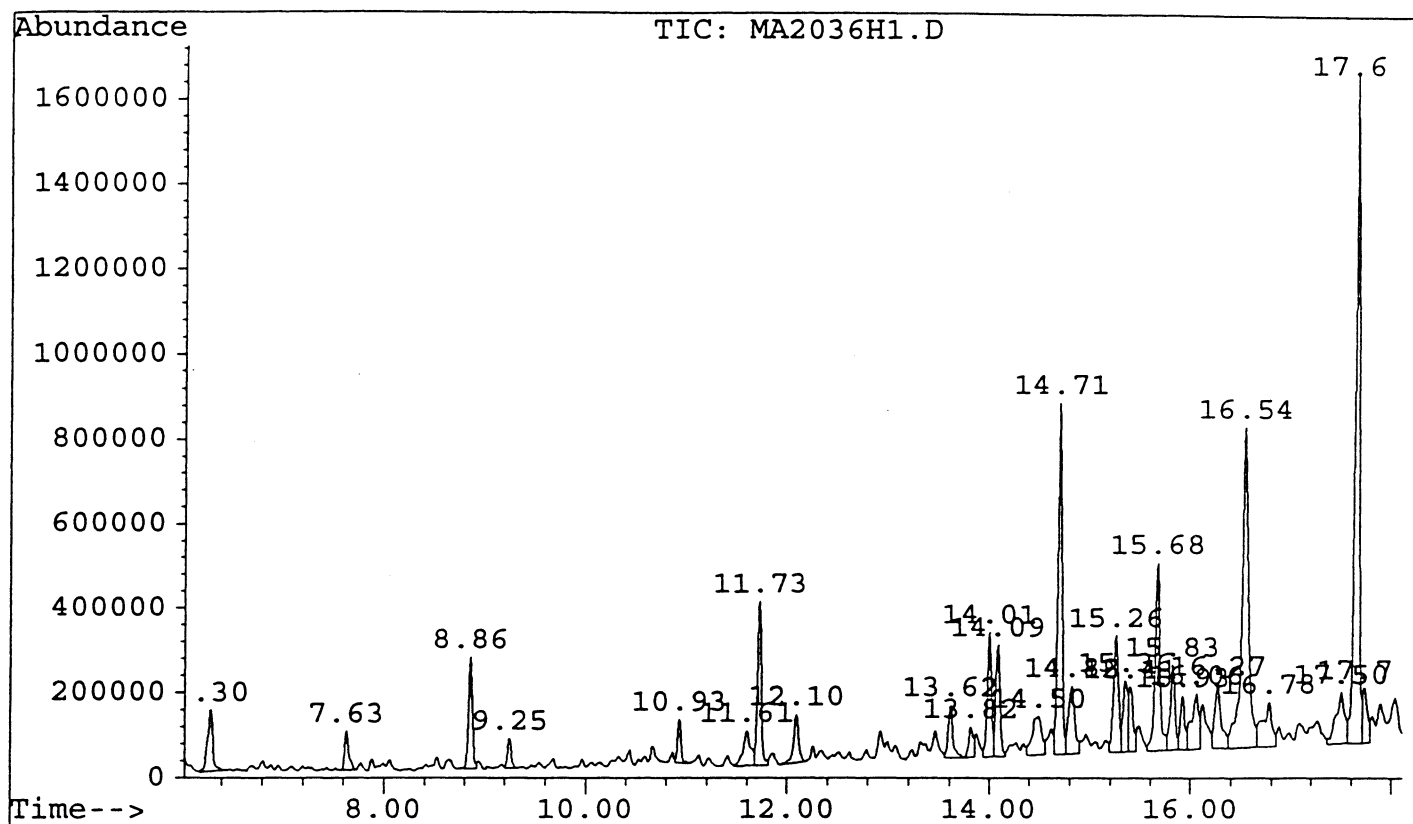


Figure 27.3. TIC of hexane fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 20-30 min and the mass spectrum of Pentadecane, 2,6,10,14-tetramethyl

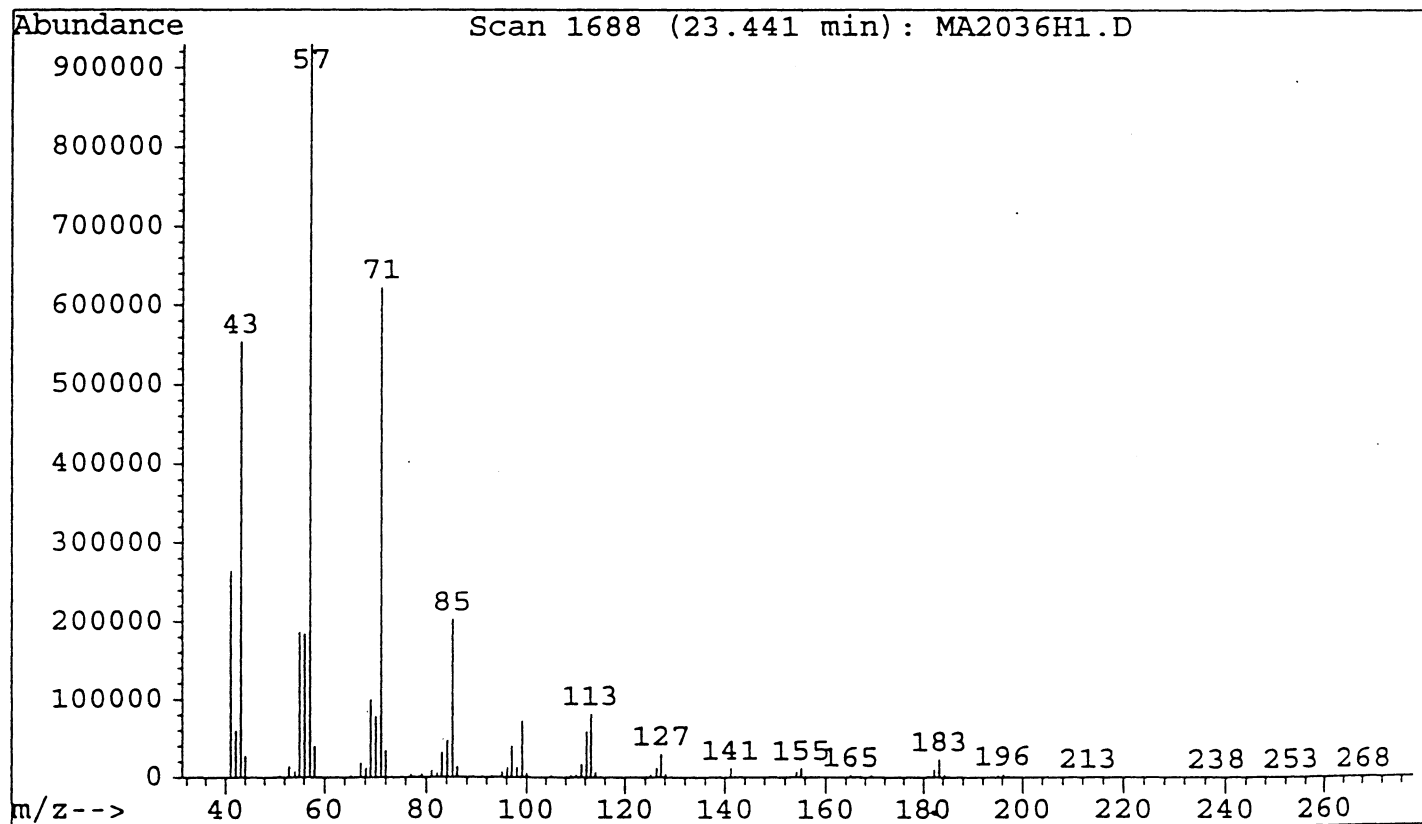
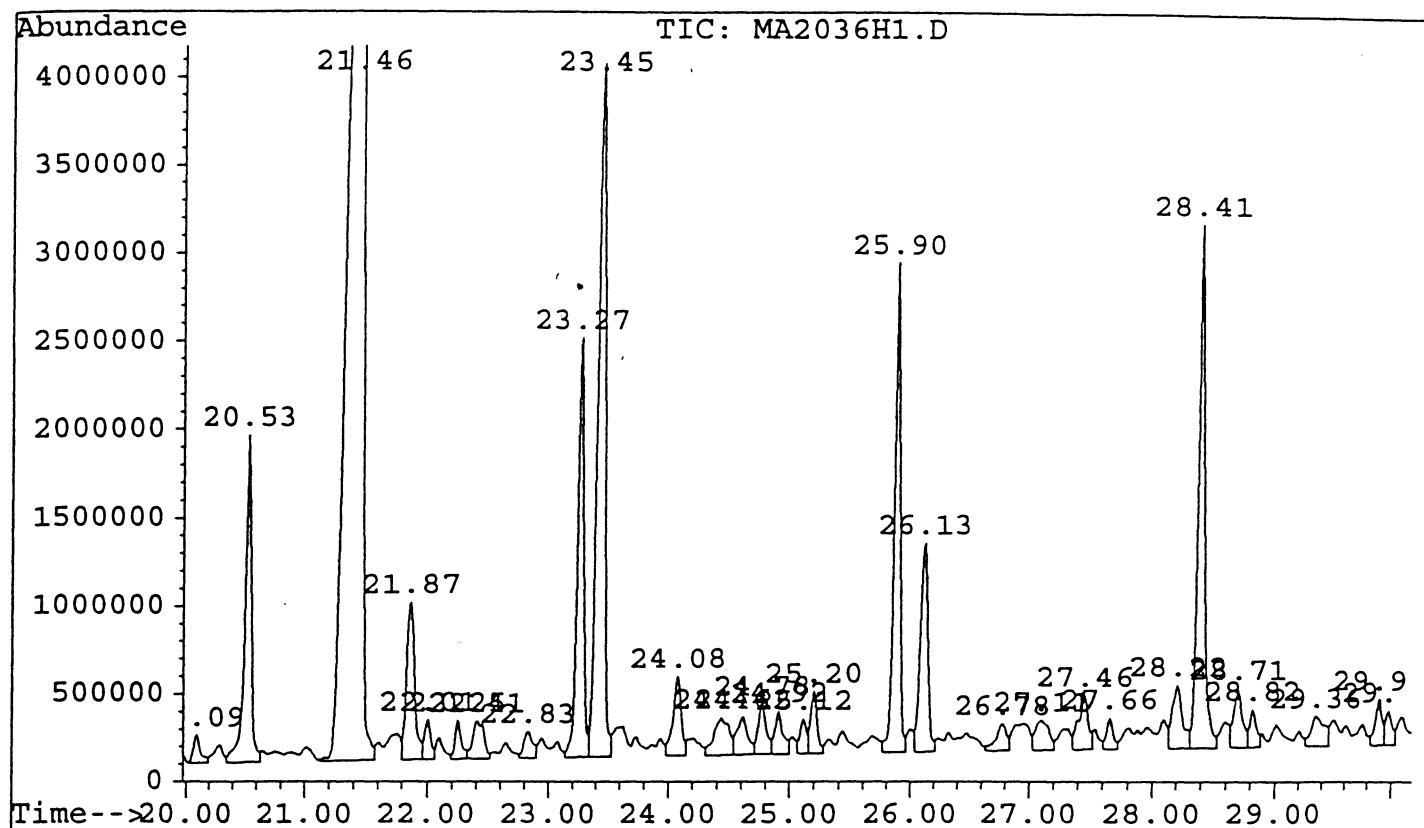


Figure 27.4. TIC of hexane fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 58-68 min and the mass spectrum of Decane,2-methyl

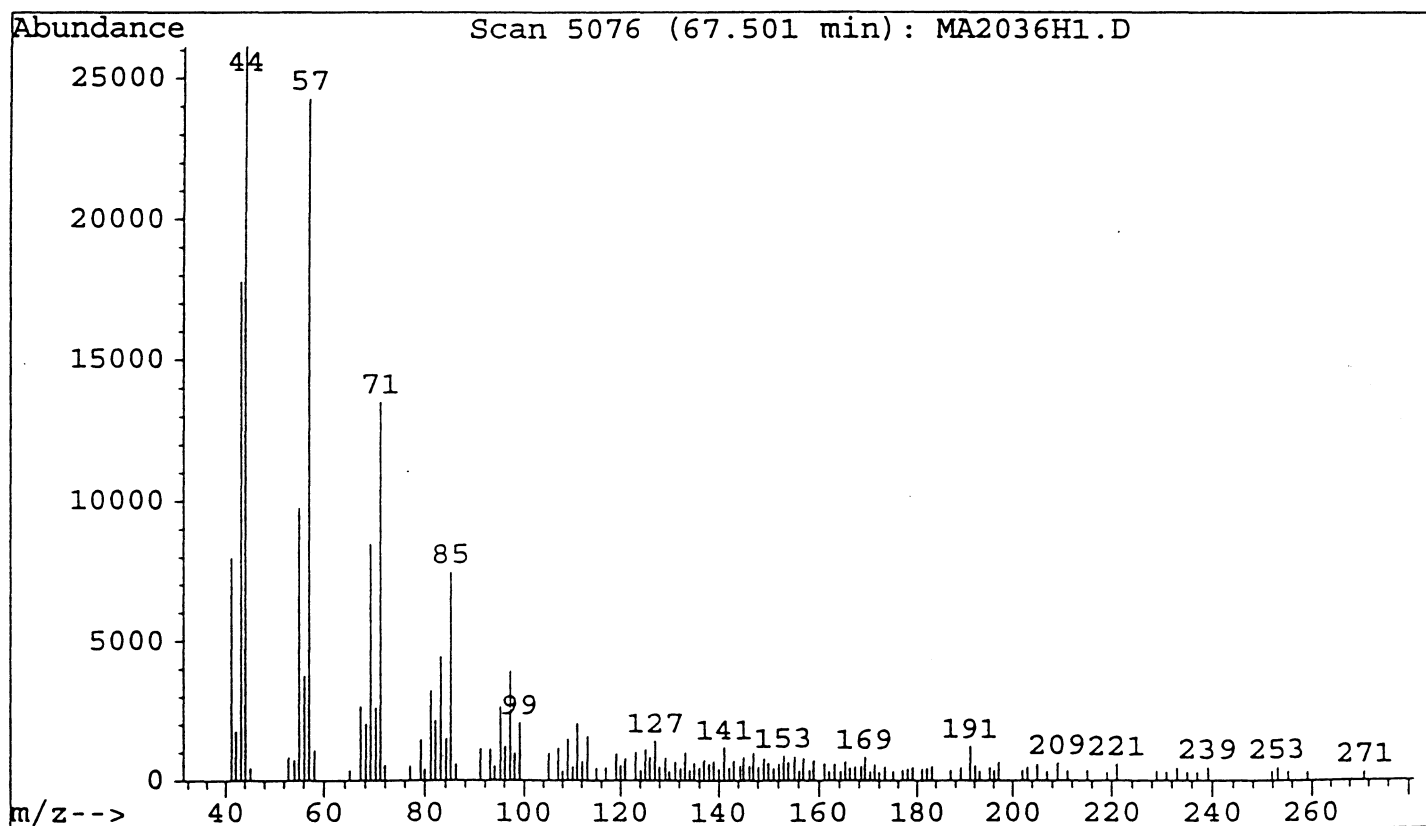
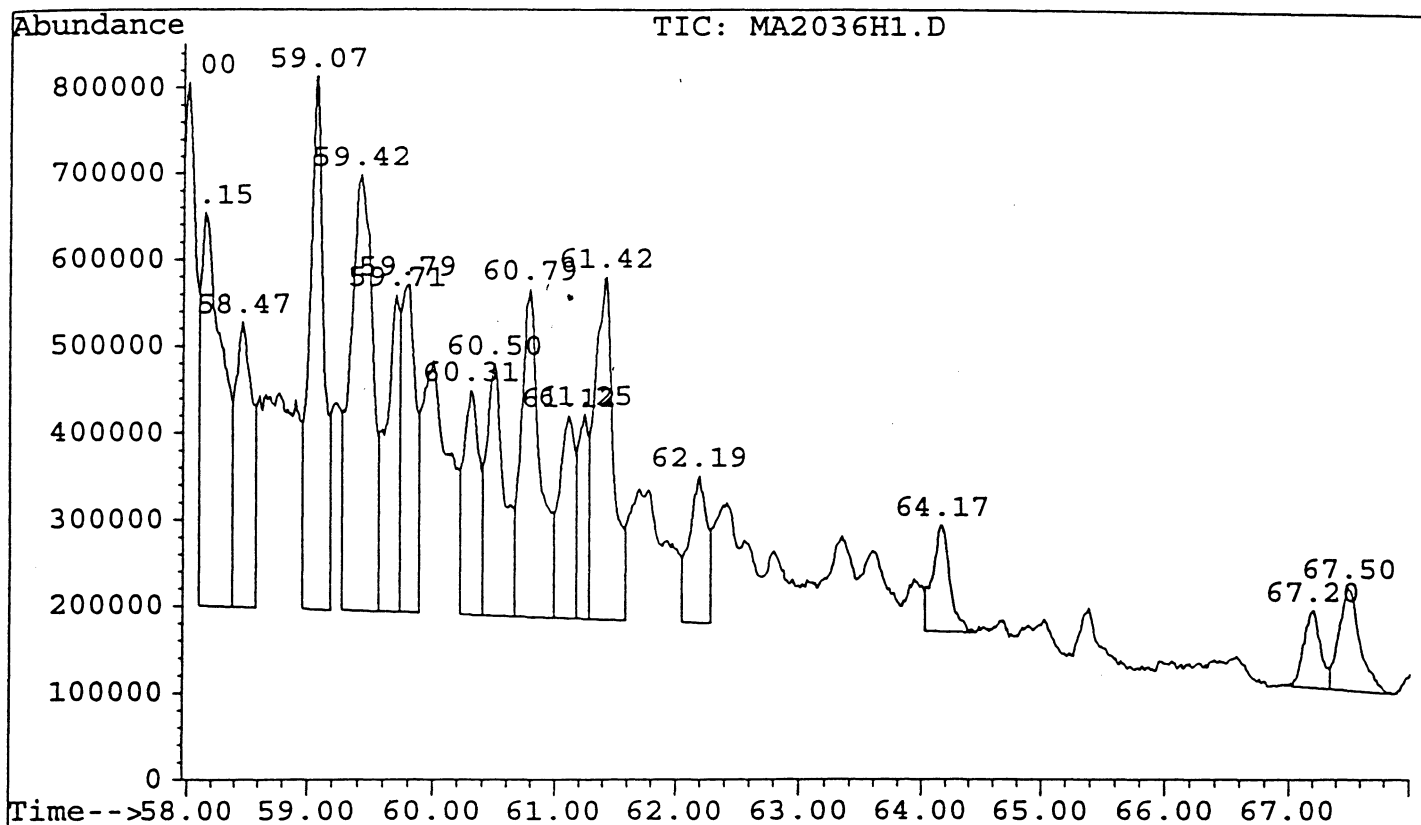


Figure 27.5. TIC of hexane fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 40-50 min and the mass spectrum of $C_{16}H_{18}O_2S$

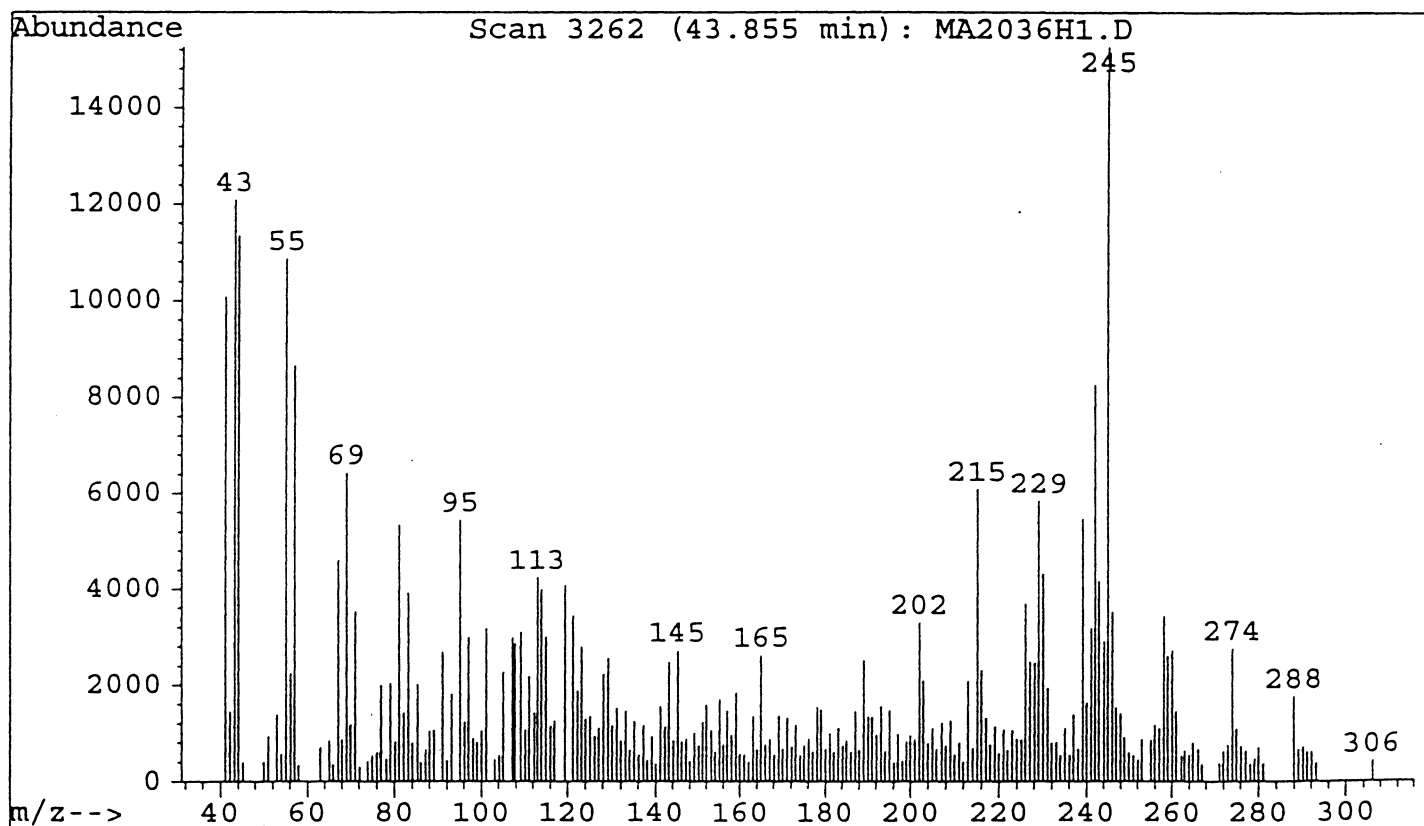
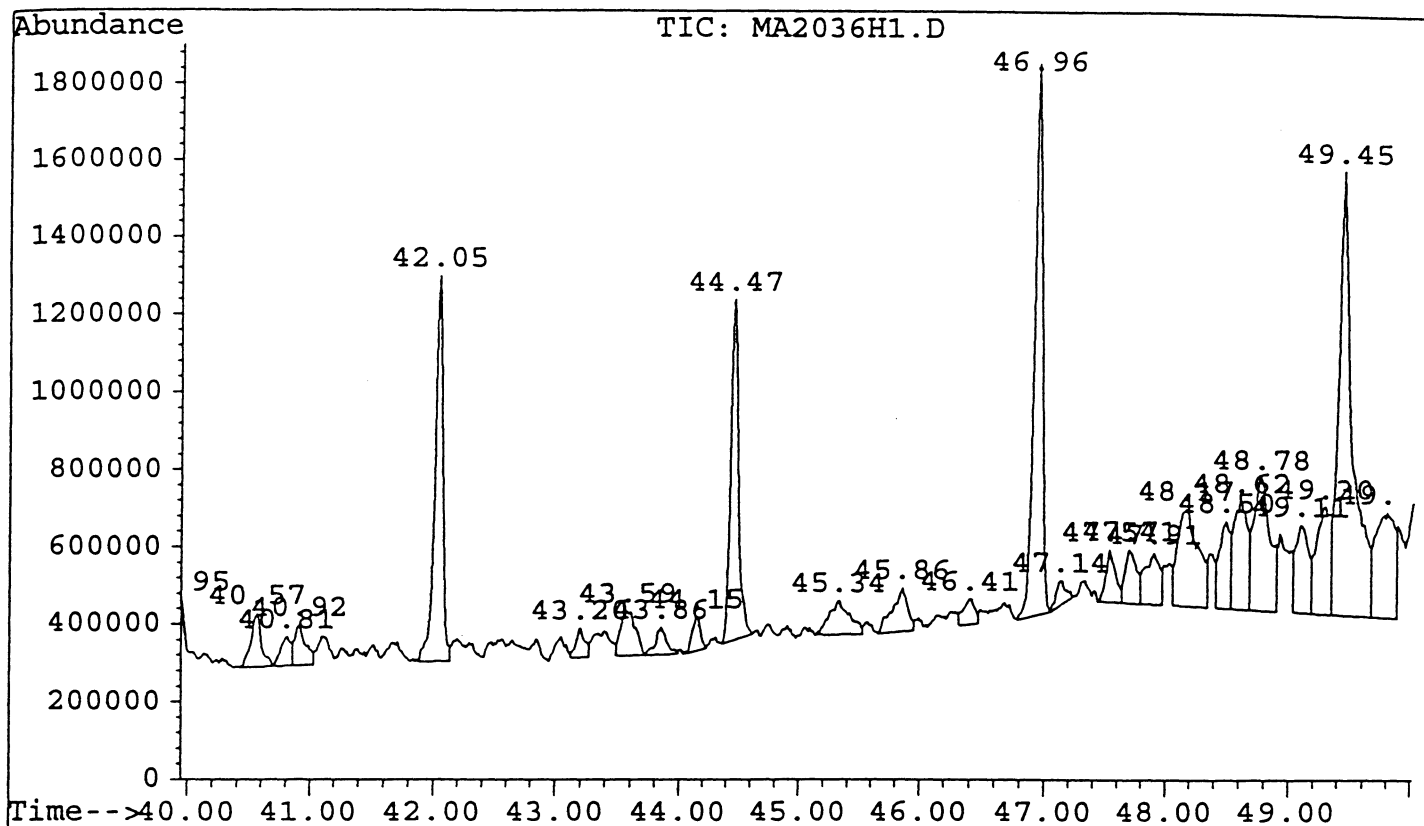


Figure 28.1. TIC of toluene fraction of before desulfurized sample of IBC-#108

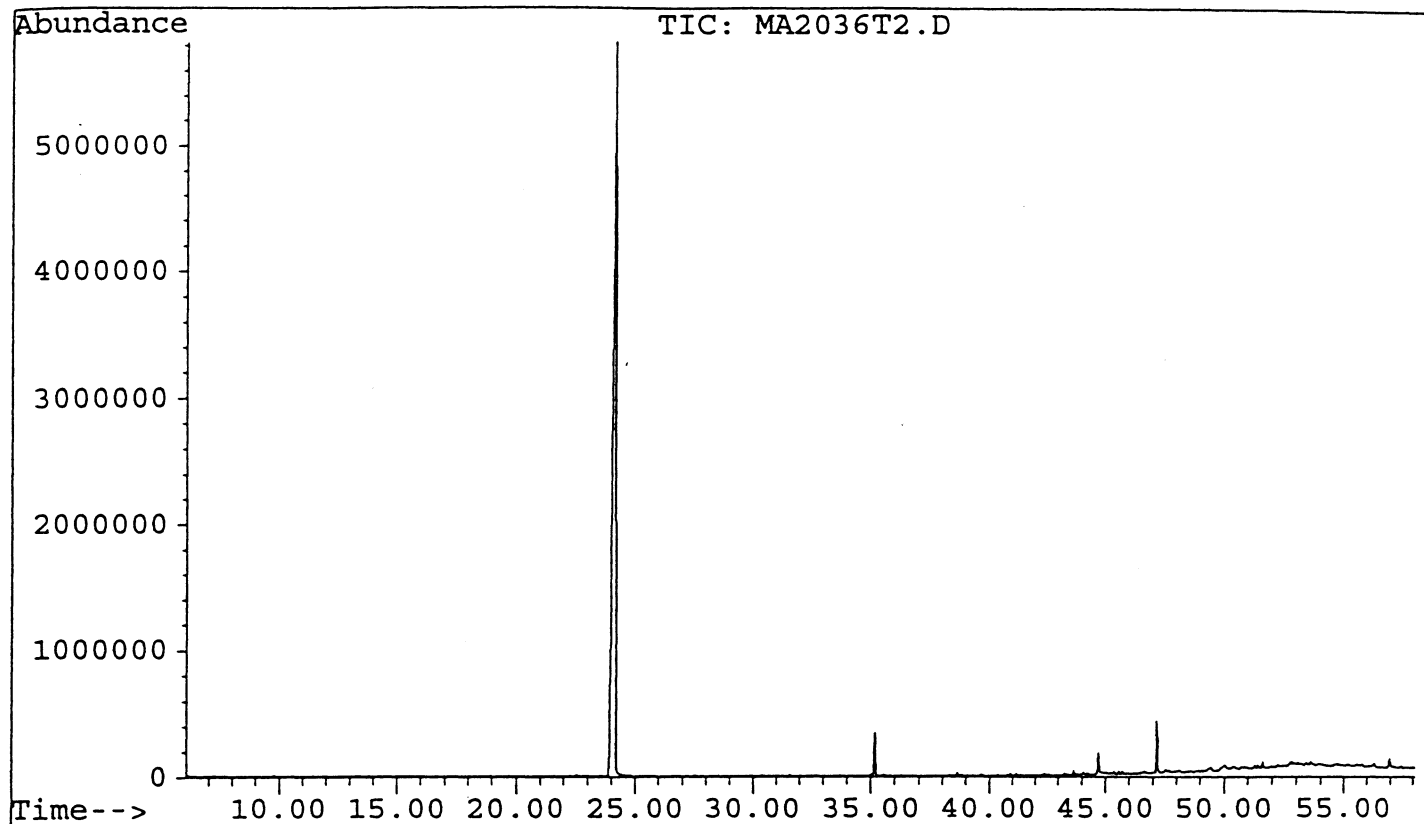


Figure 28.2. TIC of toluene fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 39.9-50.2 min and the mass spectrum of Chrysene

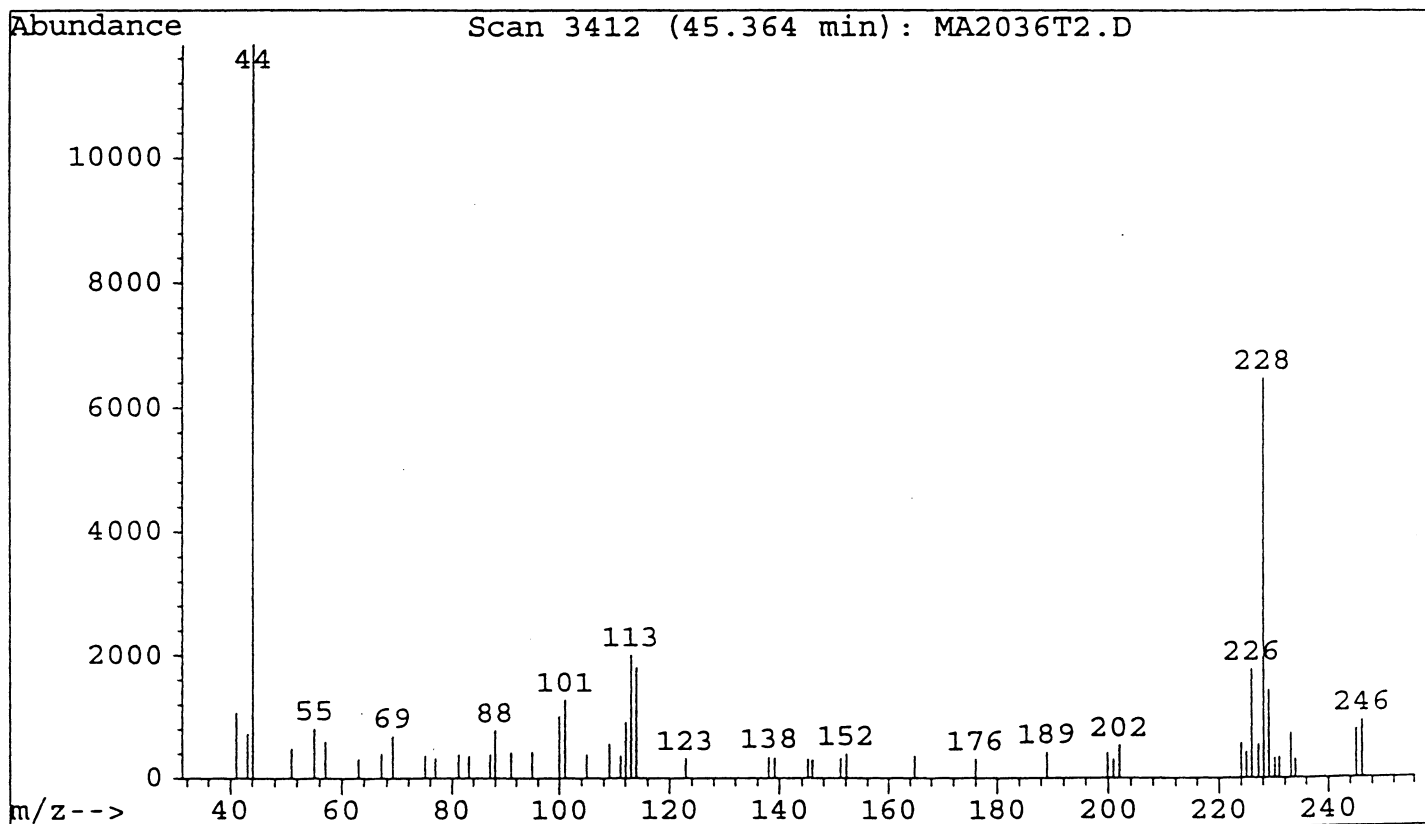
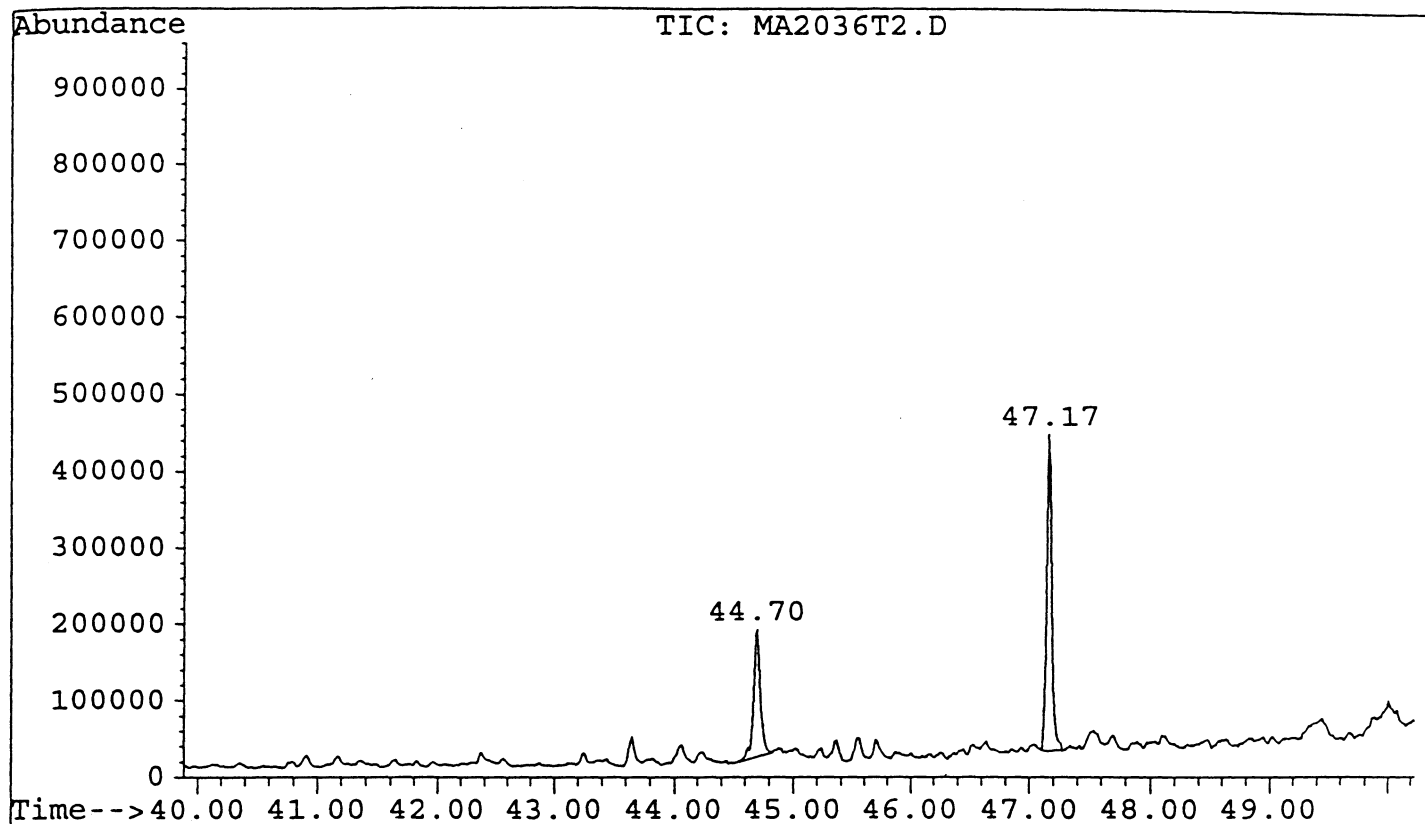


Figure 28.3. TIC of toluene fraction of before desulfurized sample of IBC-#108 showing the ret. time range of 49.8-58.0 min and the mass spectrum of Benz(e)acenaphenanthrylene or Perylene or Benzo(a)pyrene

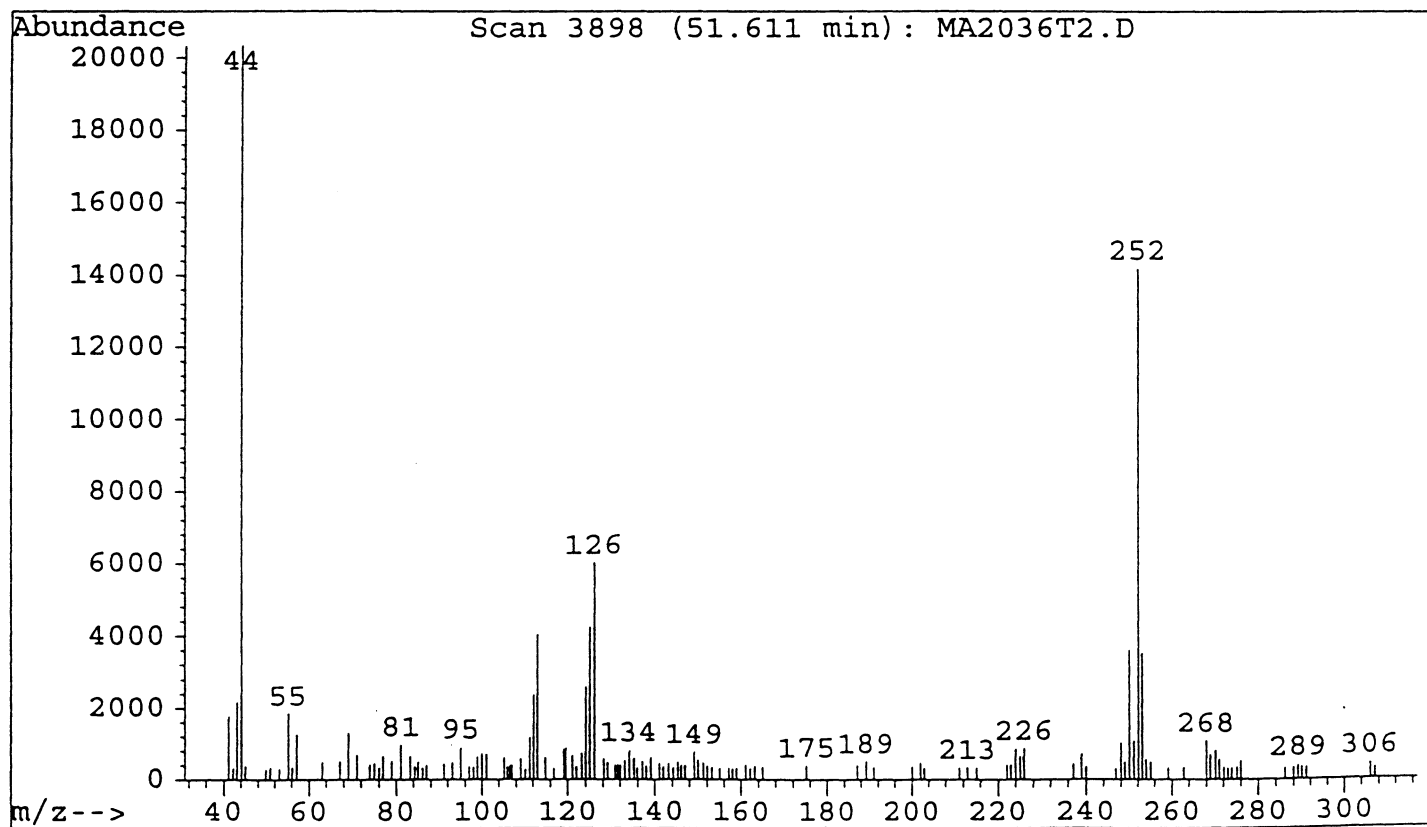
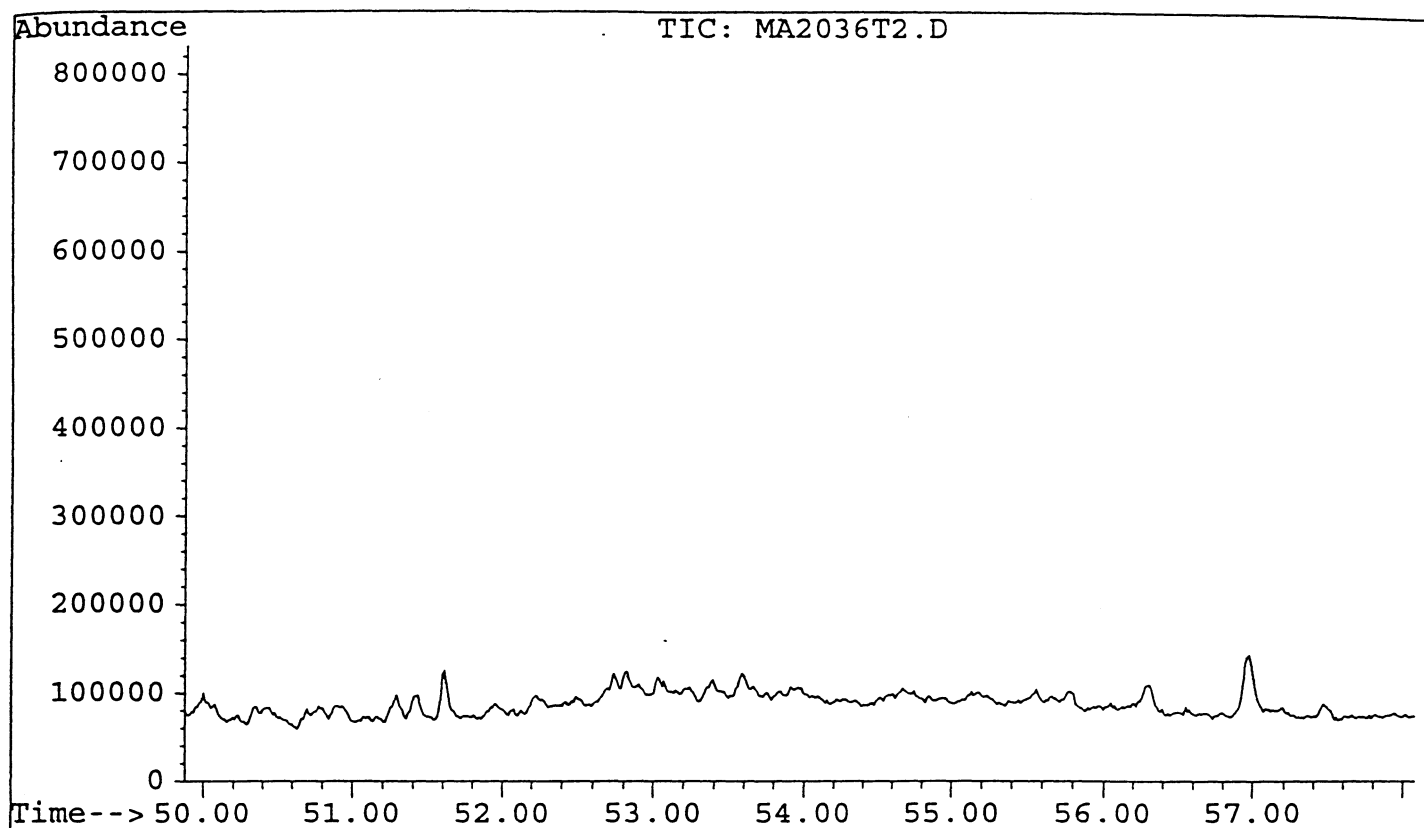


Figure 29.1. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization)

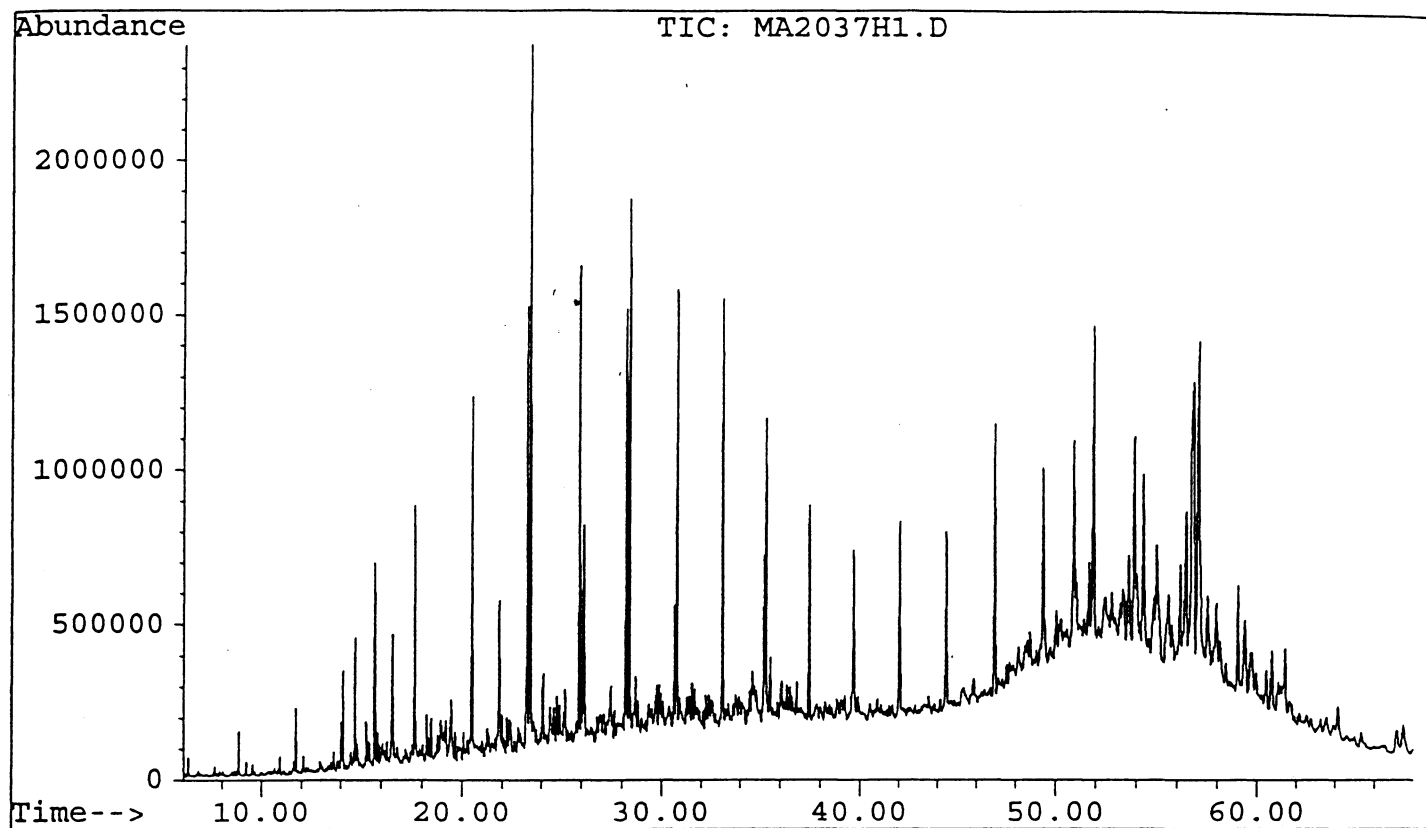


Figure 29.2. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization) showing the ret. time range of 6-20 min and the mass spectrum of Pentadecane

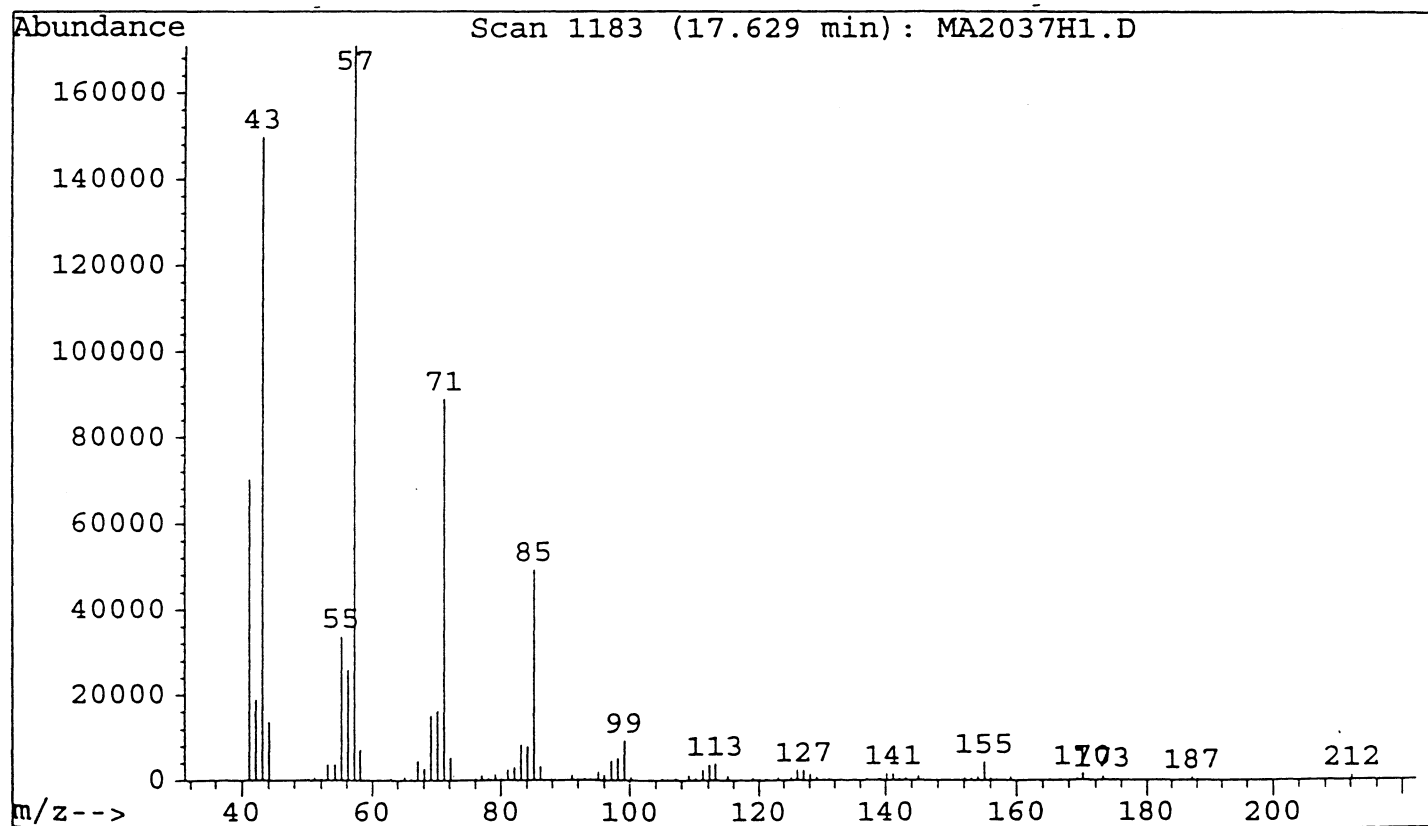
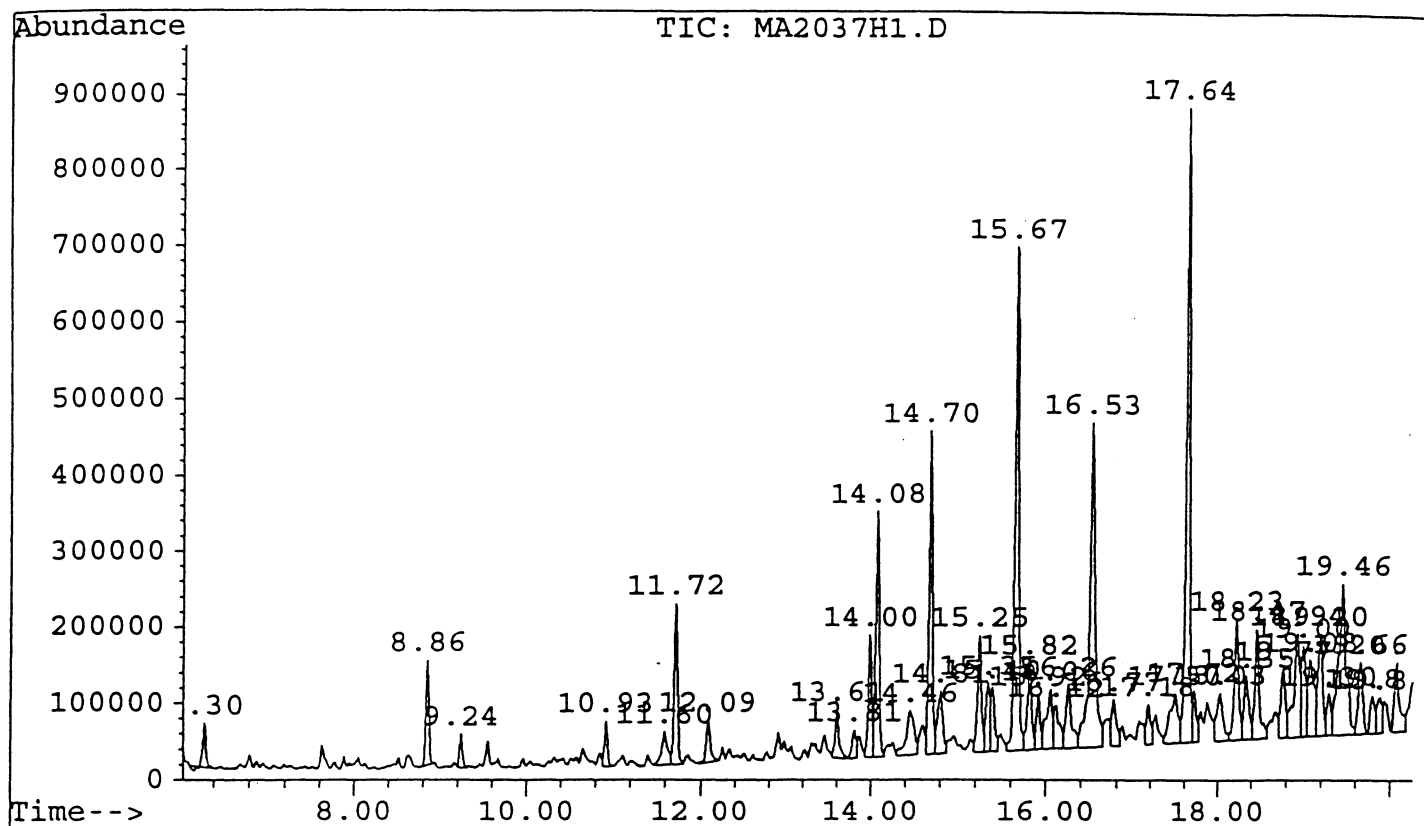


Figure 29.3. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization) showing the ret. time range of 20-30 min and the mass spectrum of Pentadecane, 2,6,10,14-tetramethyl

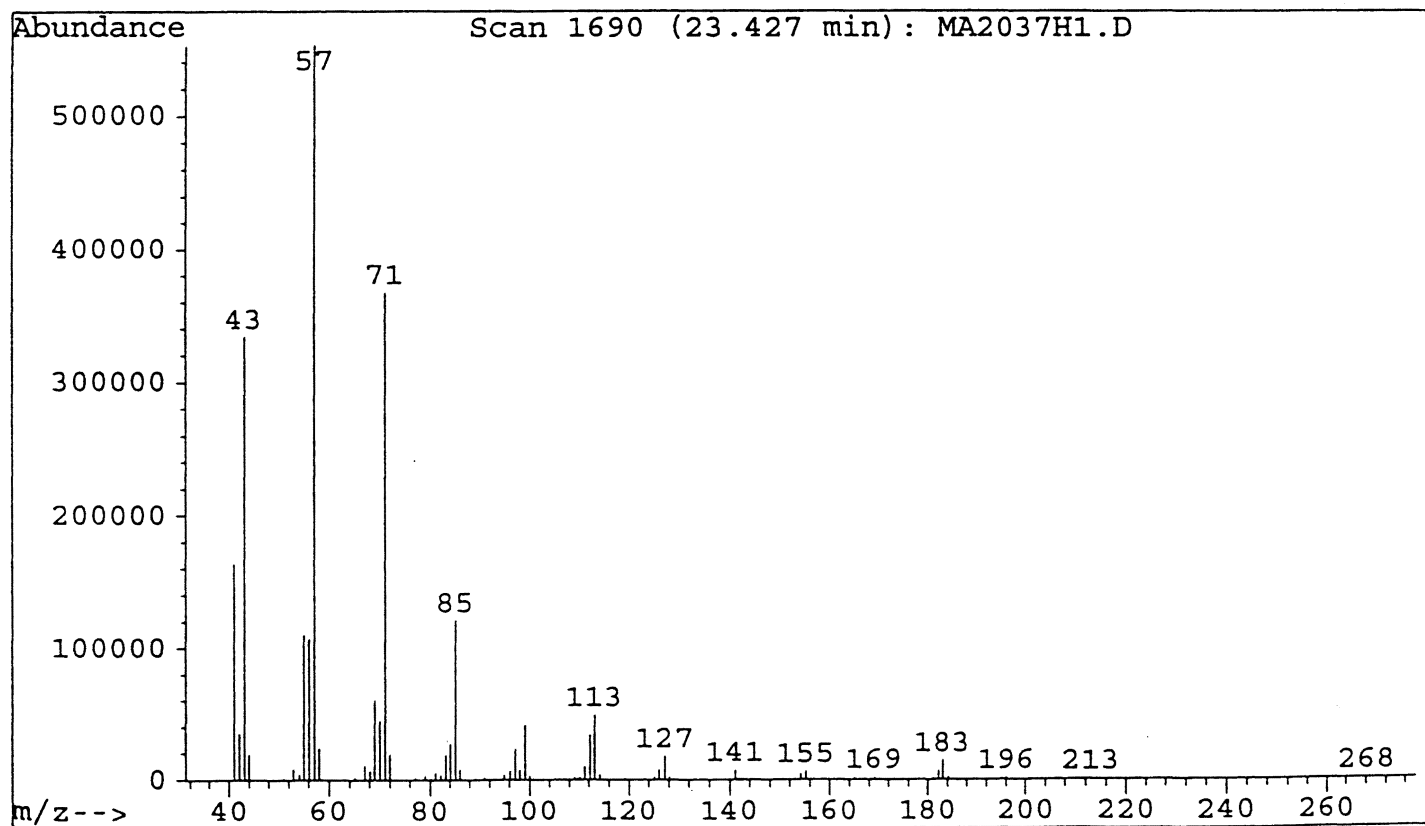
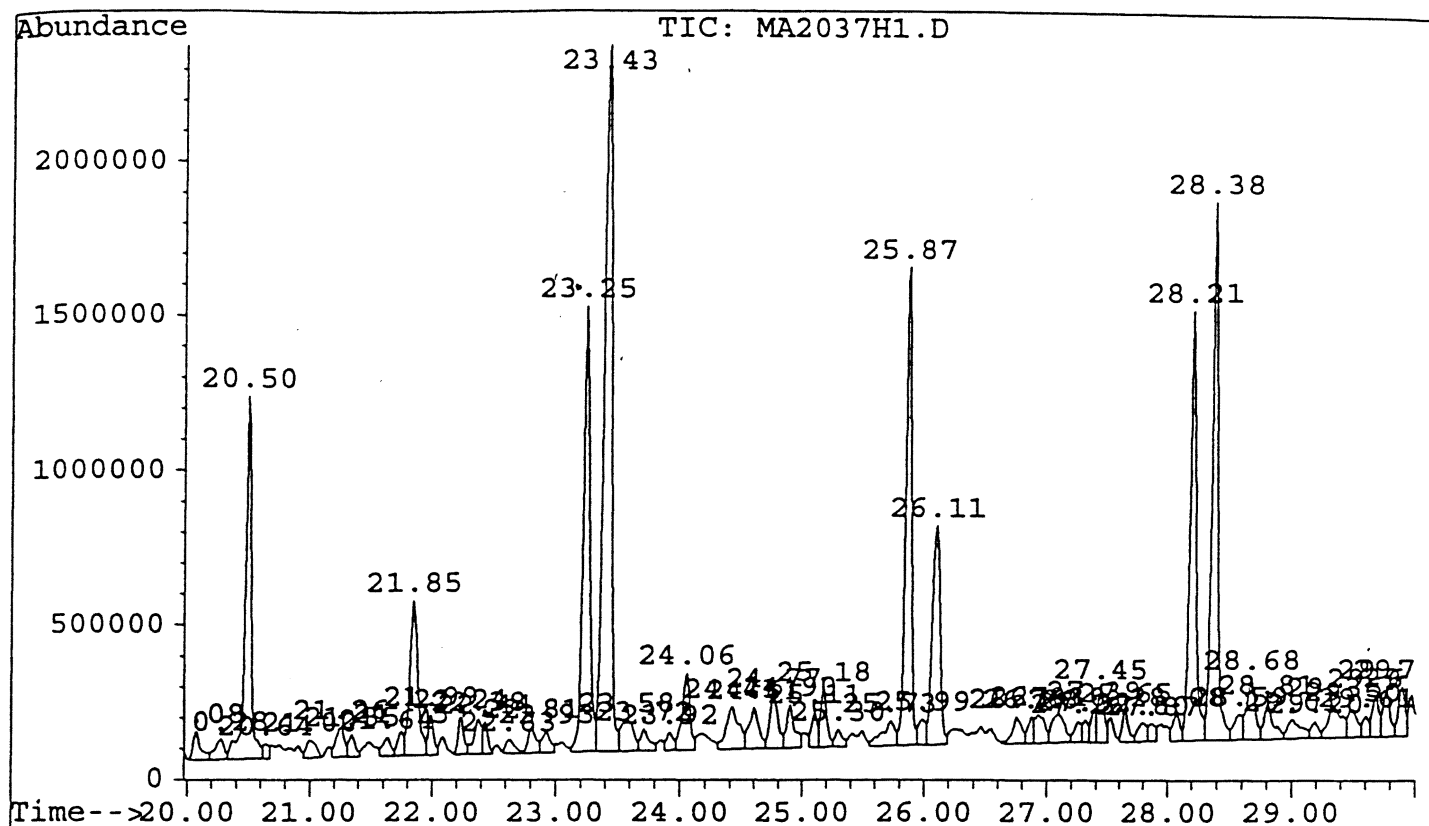


Figure 29.4 TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 1st dsulfurization) showing the ret. time range of 58-68 min and the mass spectrum of Decane,2-methyl

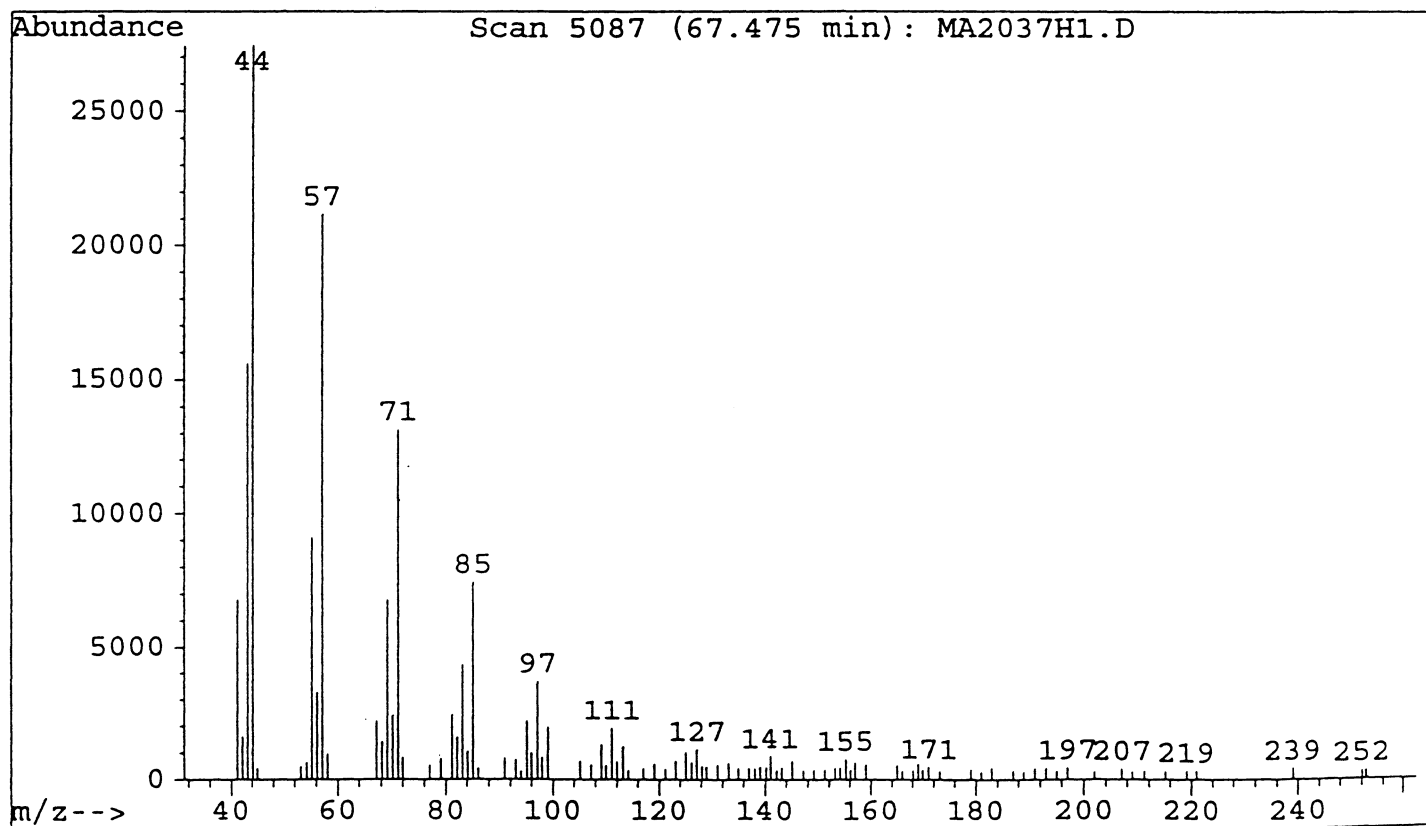
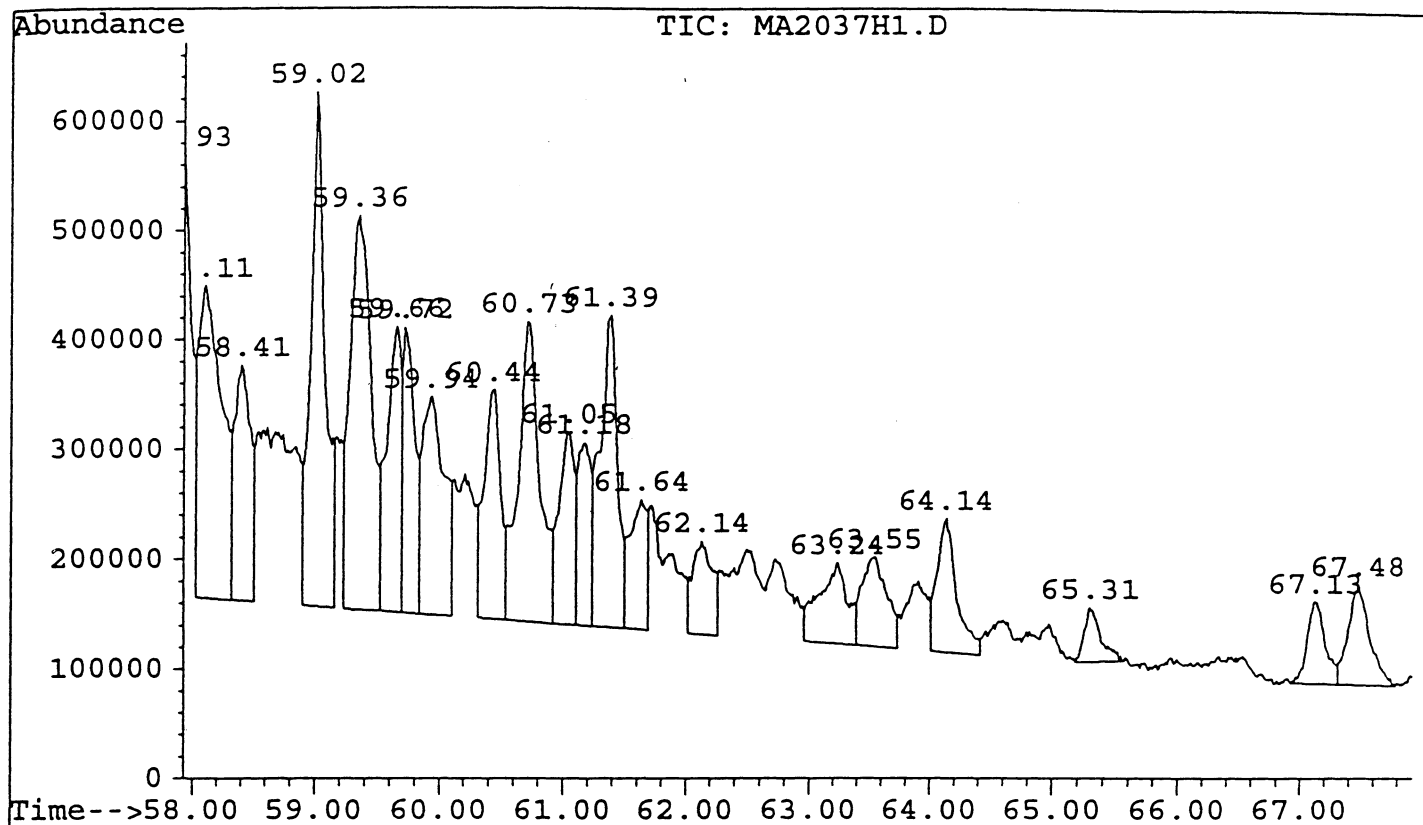


Figure 29.5. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization) showing the ret. time range of 40-50 min and the mass spectrum of 10H-Phenothiazine, 10-methyl-5,5-dioxide ($C_{13}H_{11}NO_2S$)

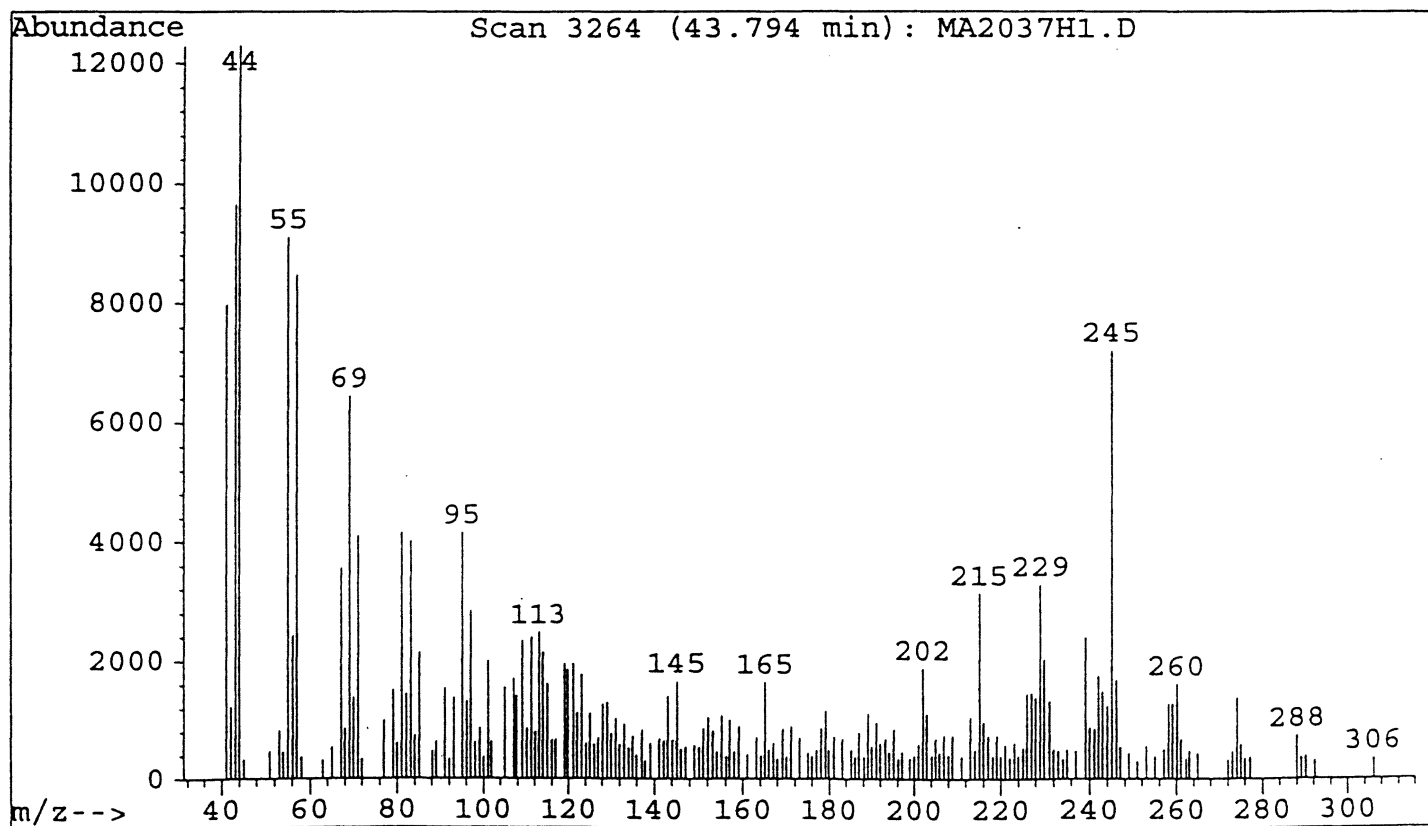
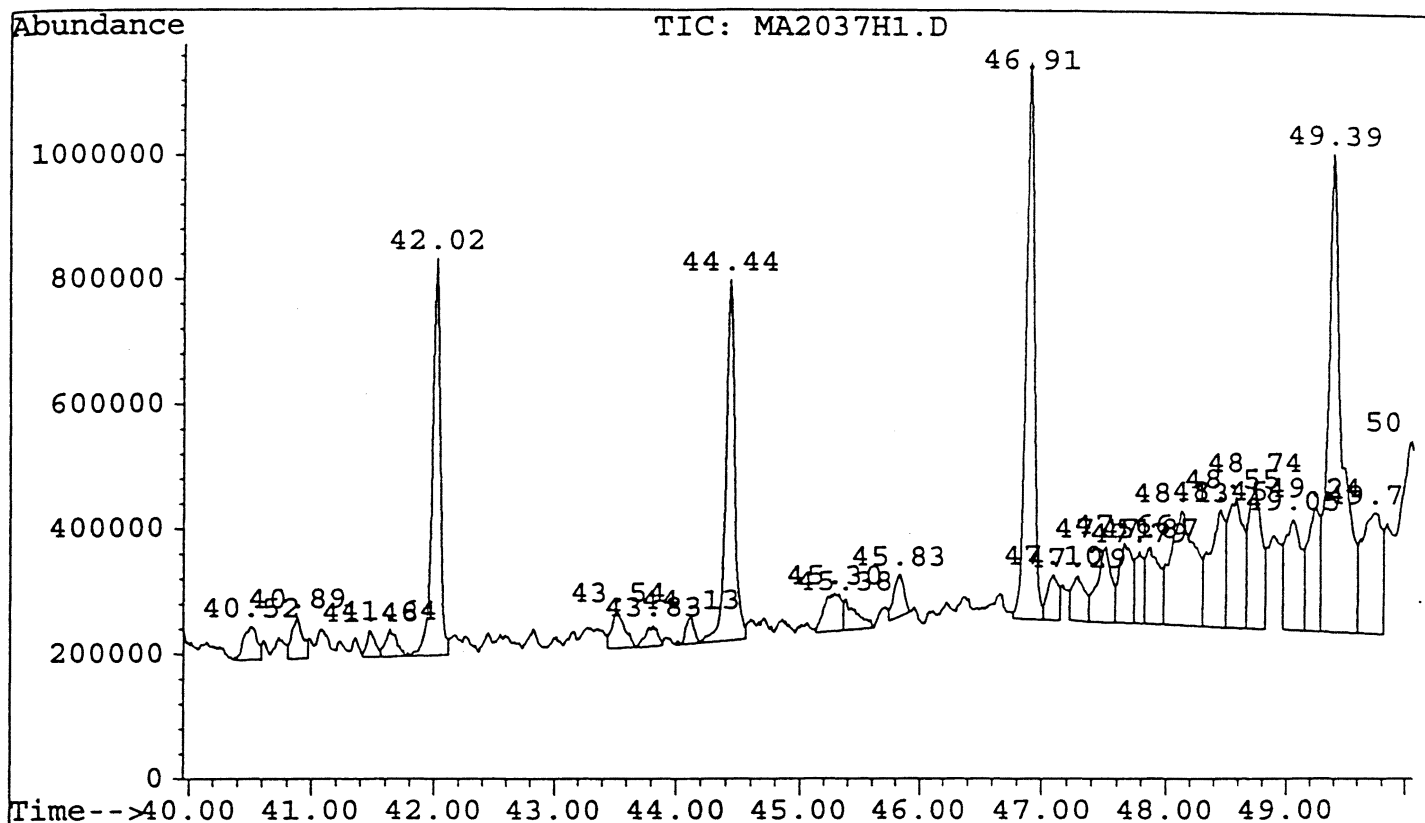


Figure 30.1. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization)

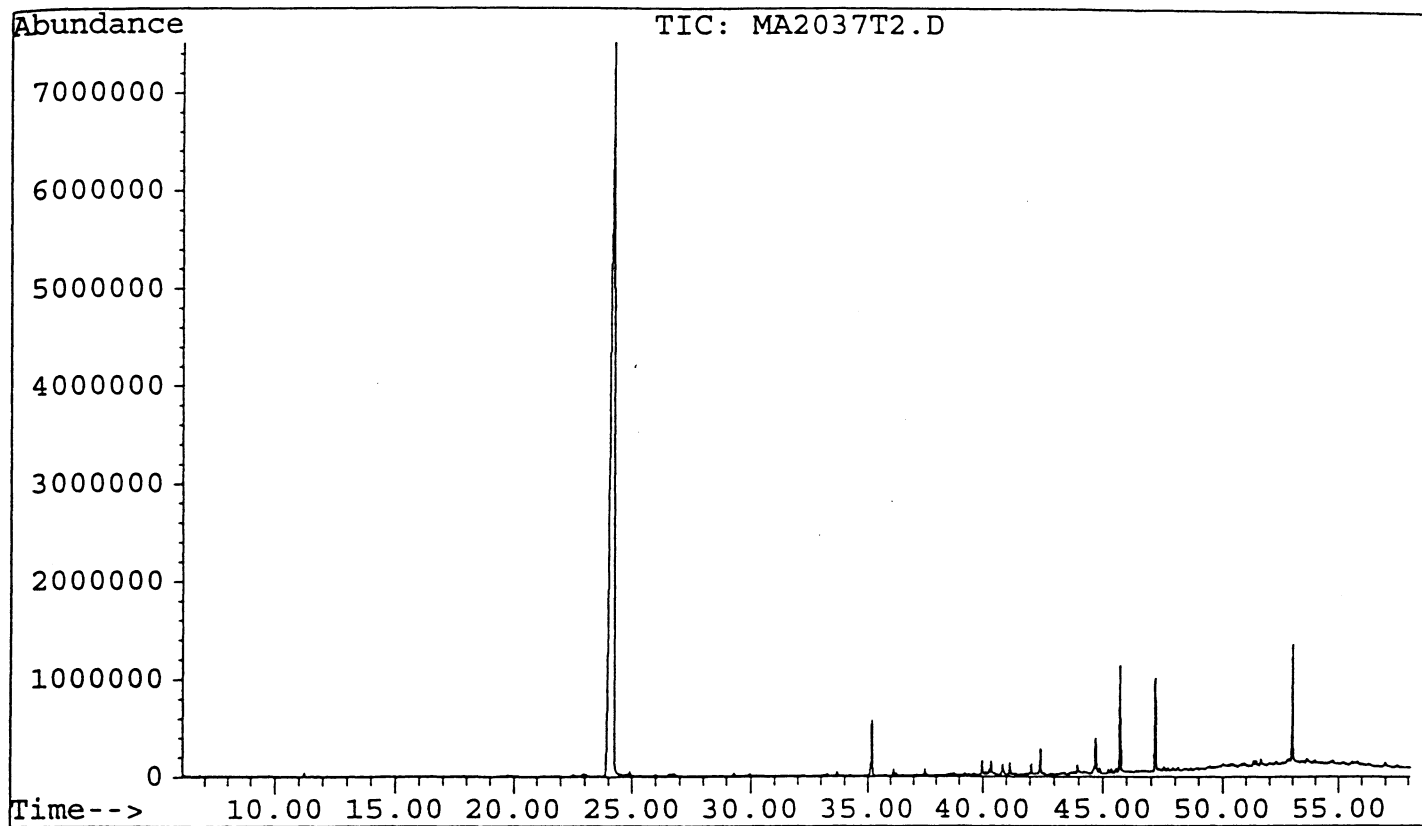


Figure 30.2. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization) showing the ret. time range of 39.8-50.4 min and the mass spectrum of Chrysene

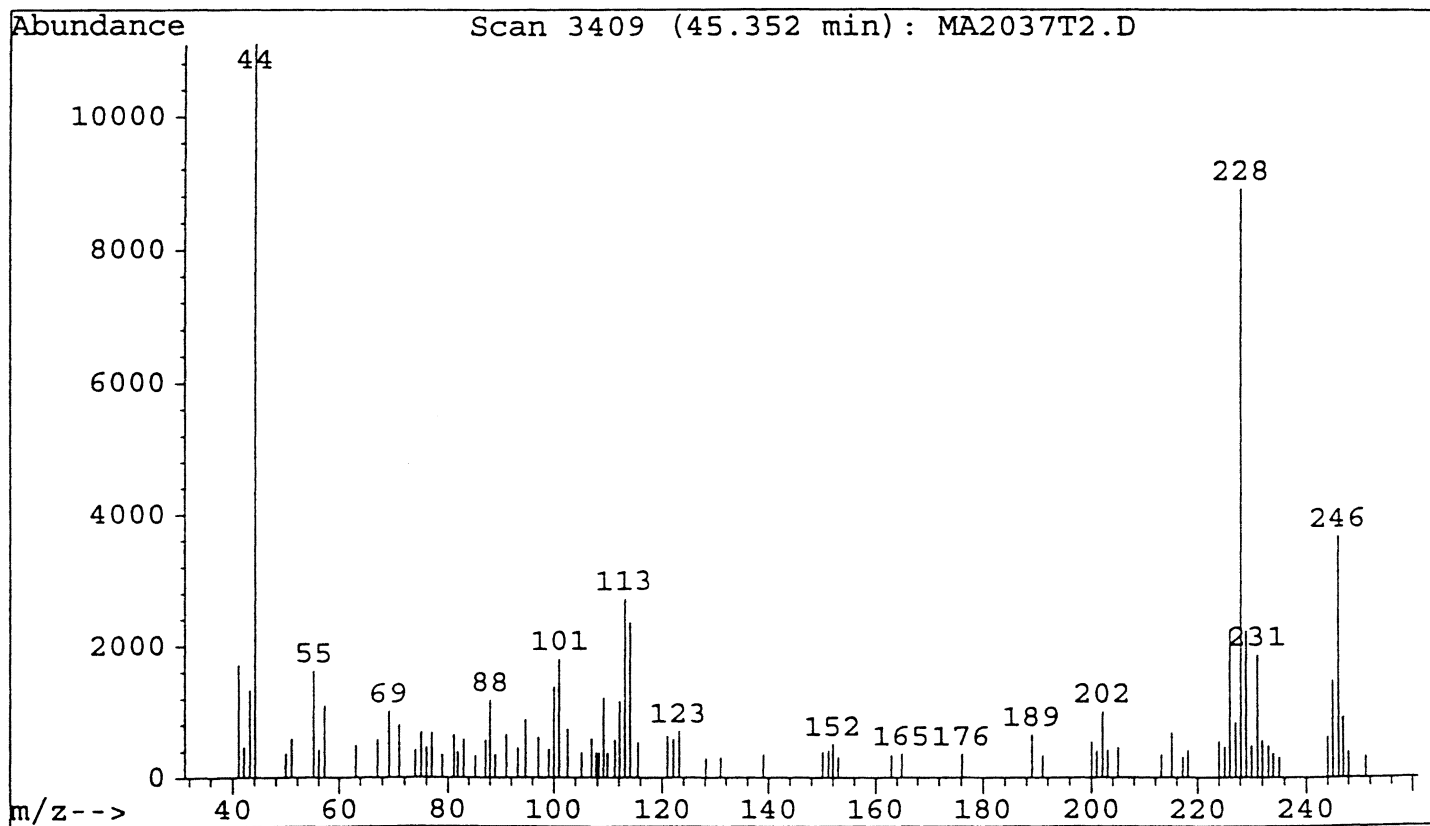
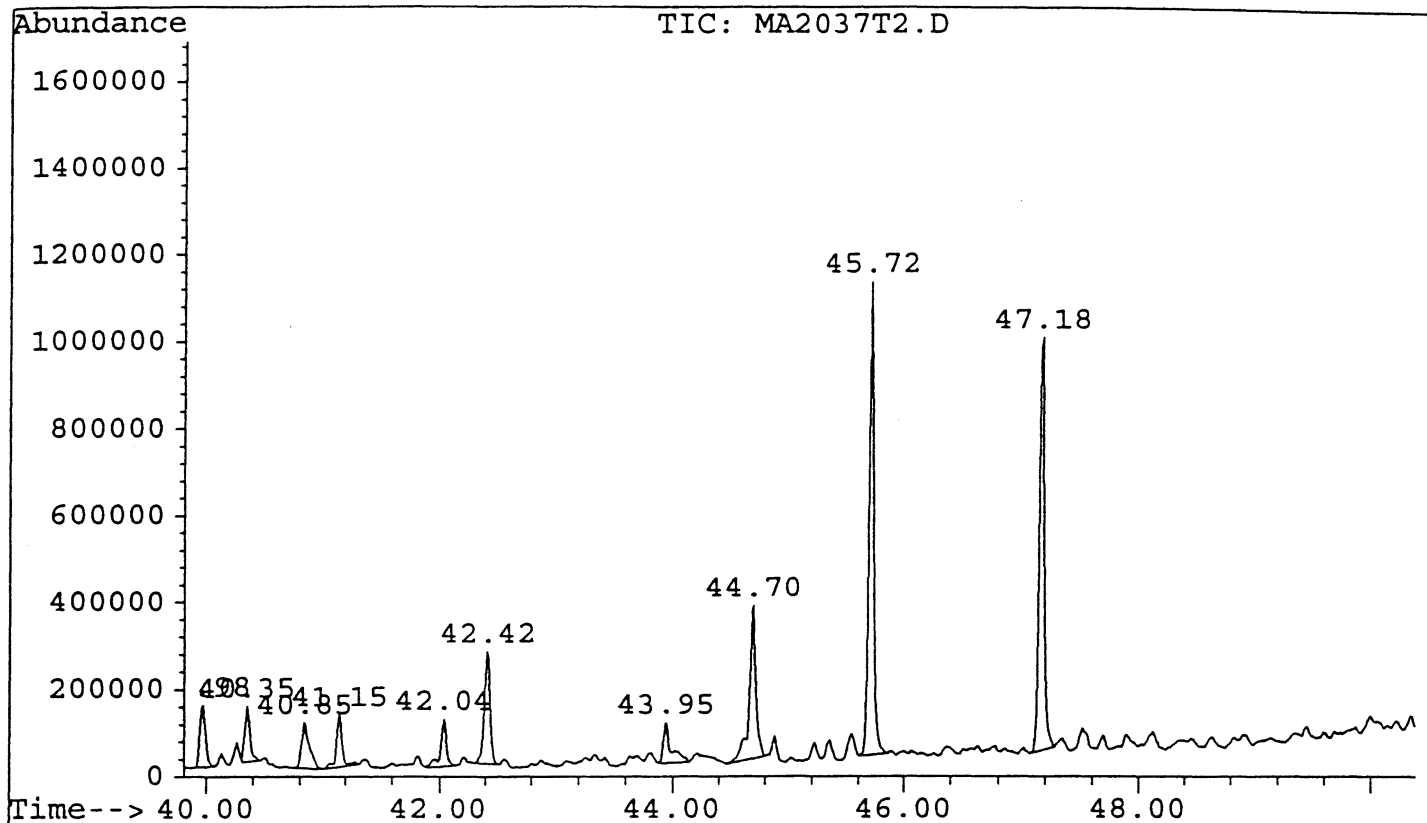


Figure 30.3. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 1st desulfurization) showing the ret. time range of 49.8-58.0 min and the mass spectrum of Benz(e)acenaphenanthrylene or Perylene or Benzo(a)pyrene

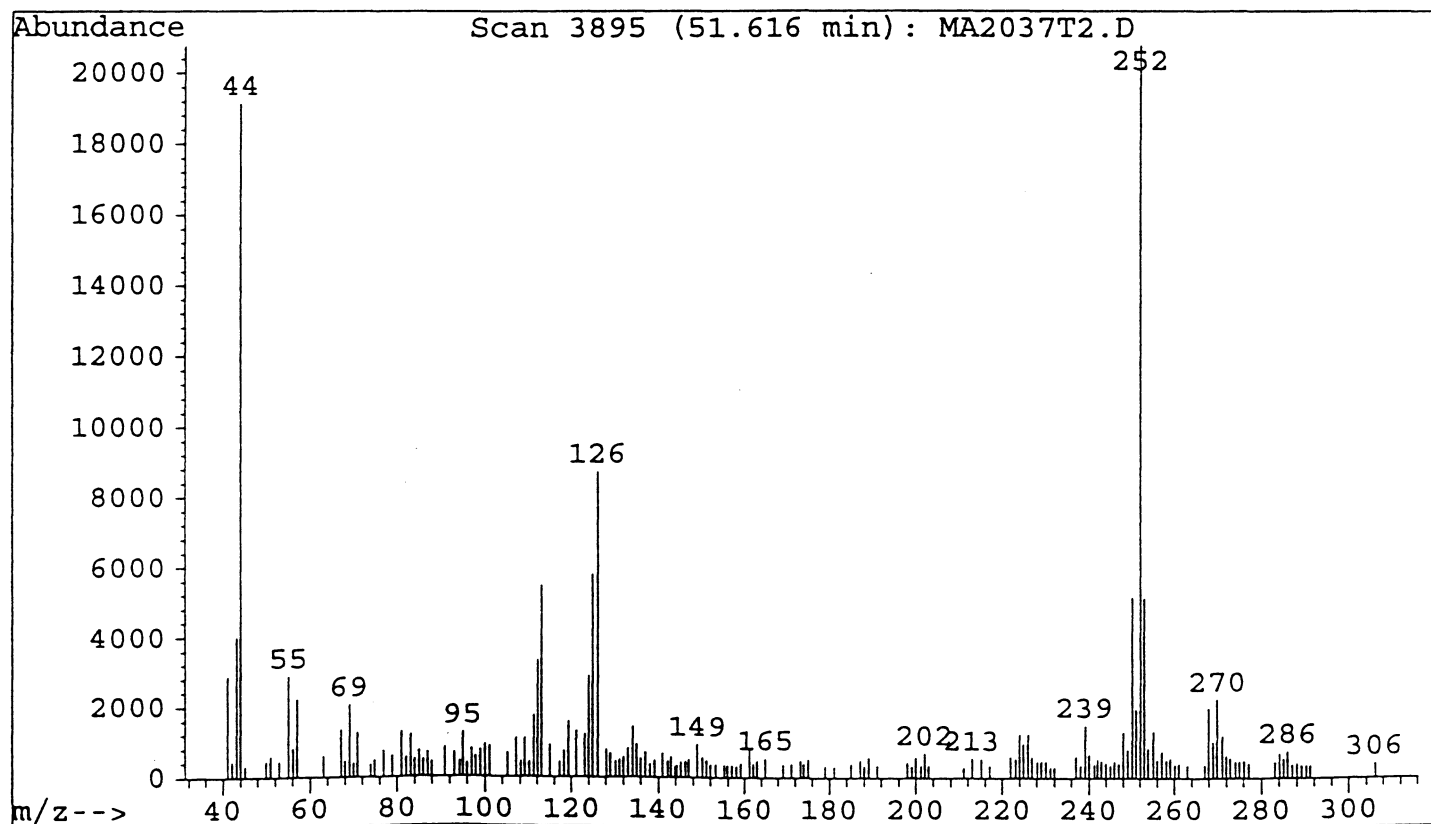
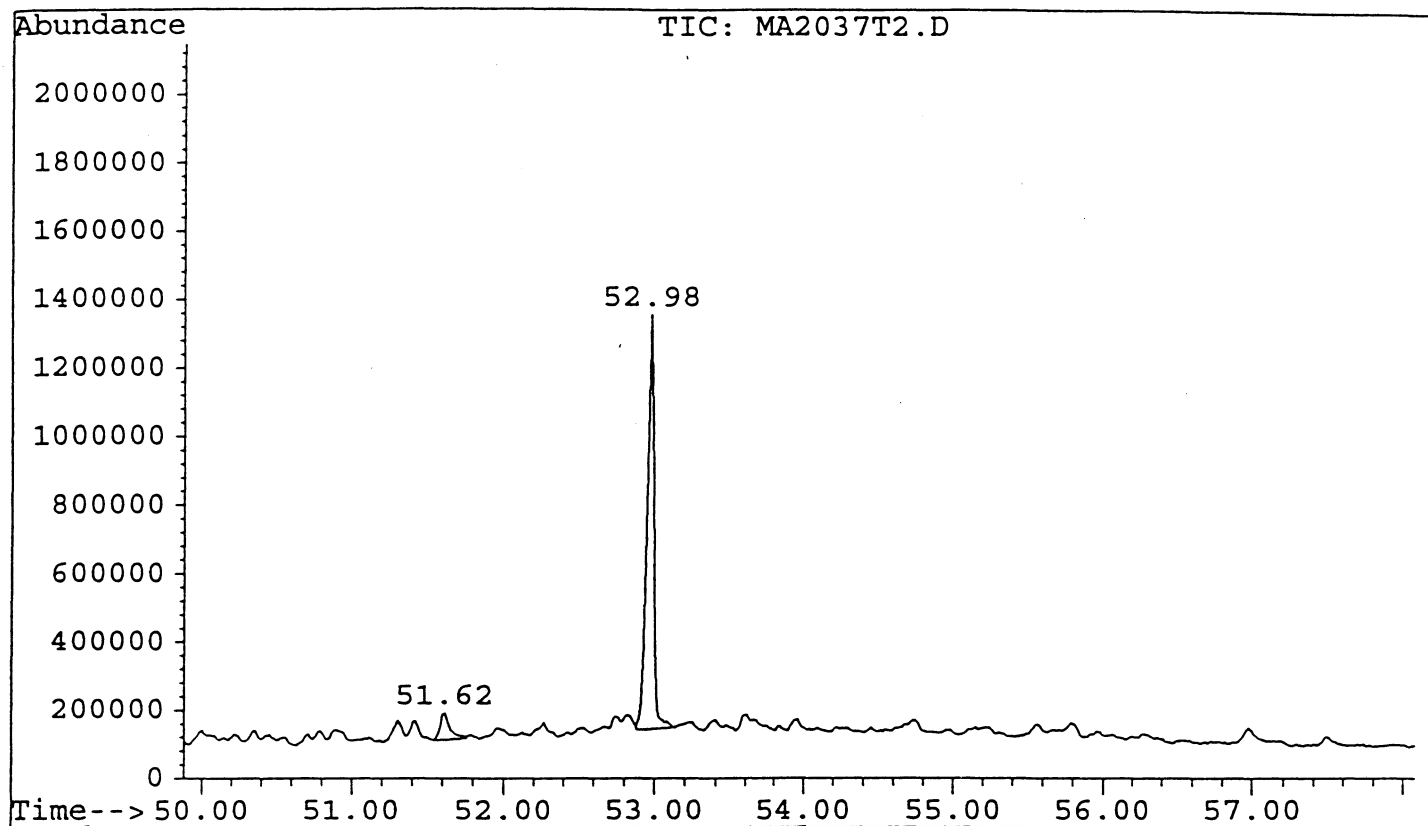


Figure 31.1. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization)

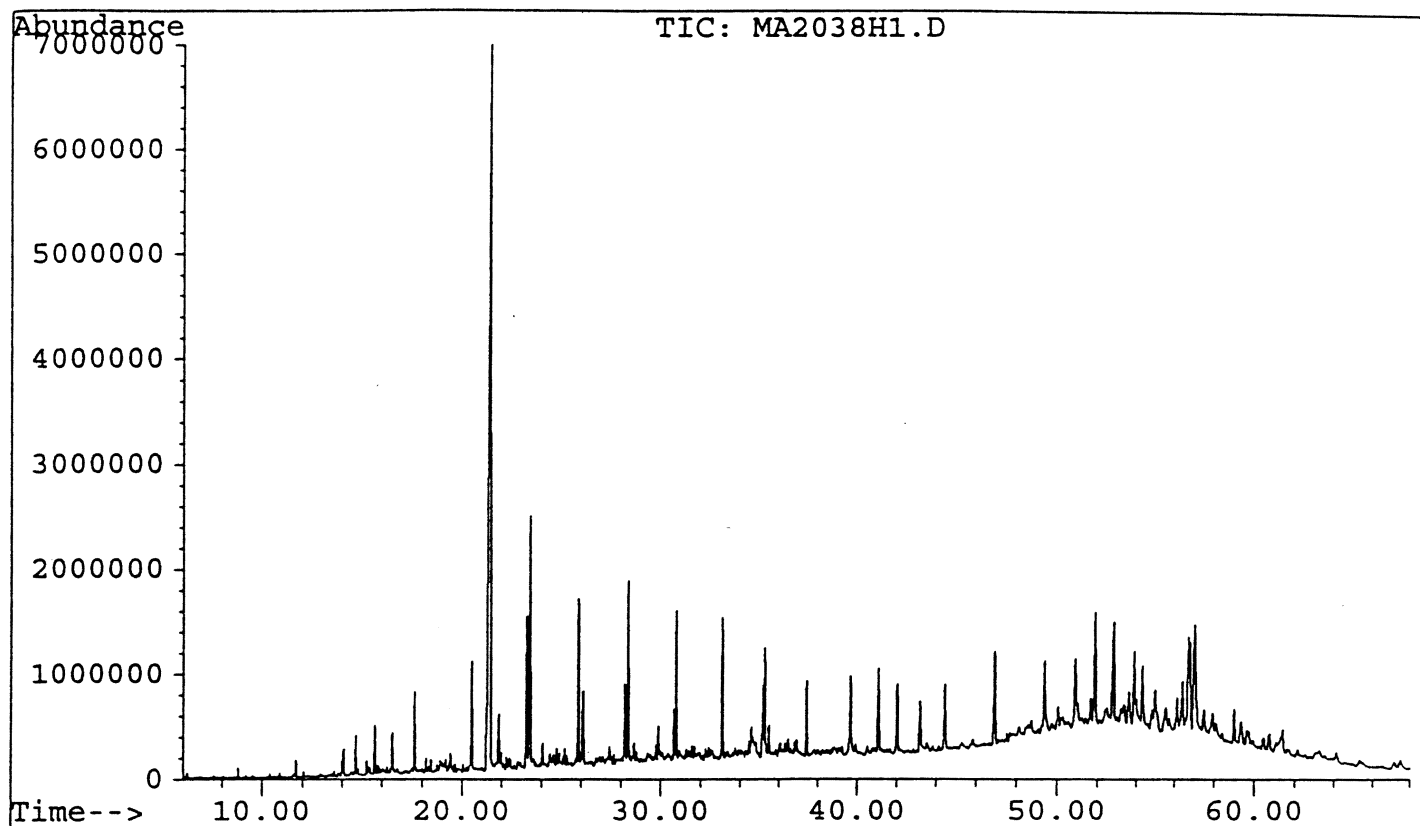


Figure 31.2. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization) the showing ret. time range of 6-20 min and the mass spectrum of Pentadecane

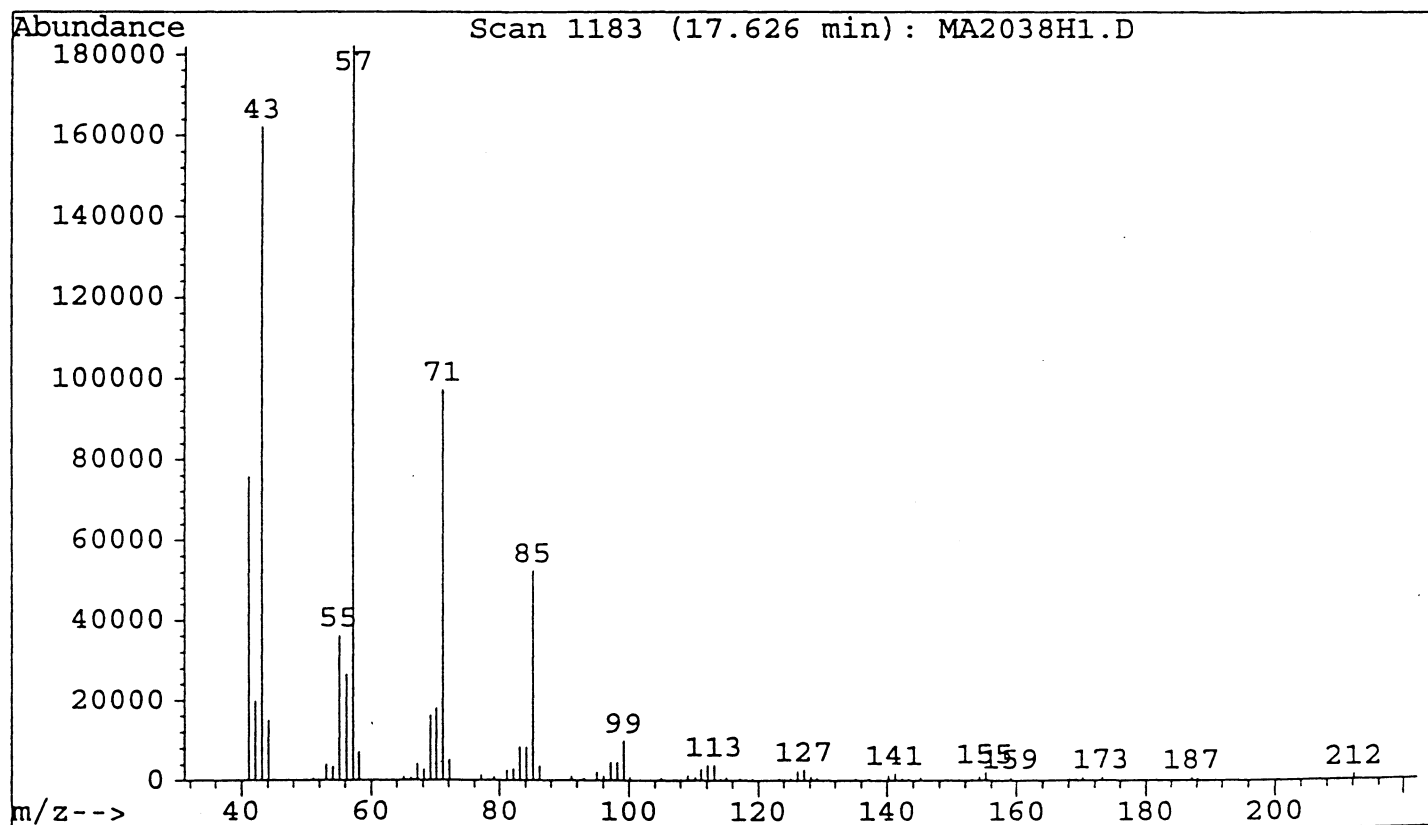
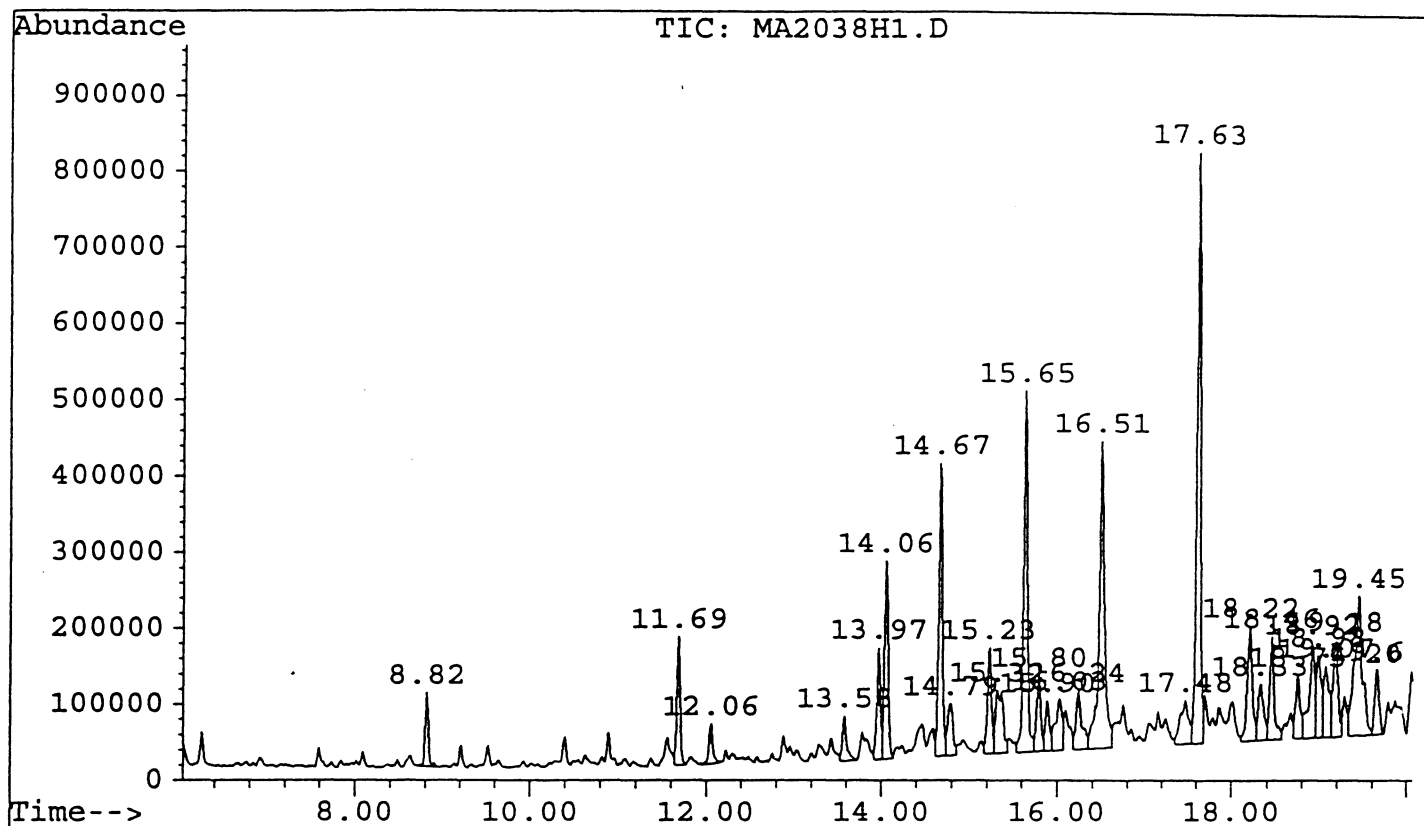


Figure 31.3. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization) showing the ret. time range of 20-30 min and the mass spectrum of Pentadecane, 2,6,10,14-tetramethyl

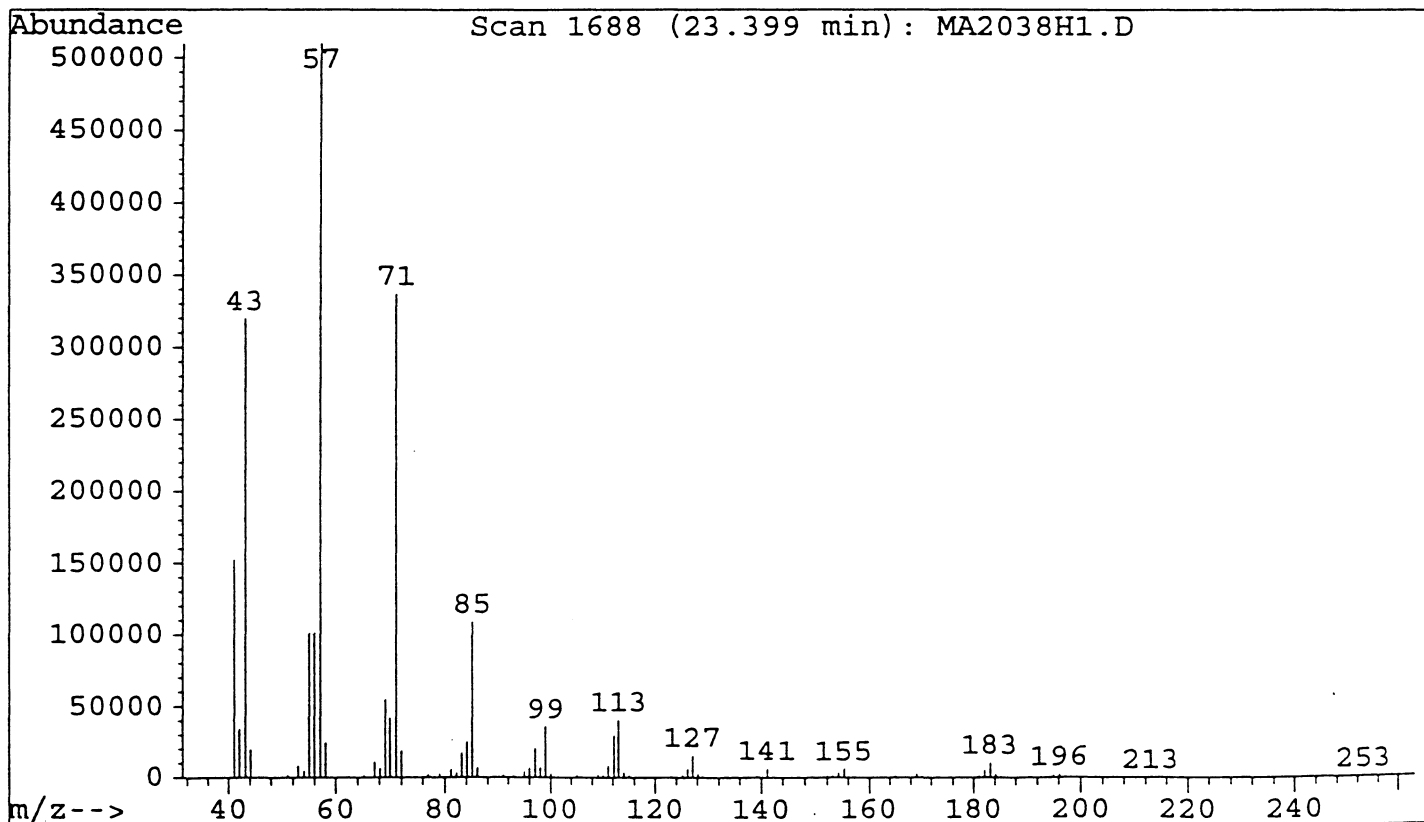
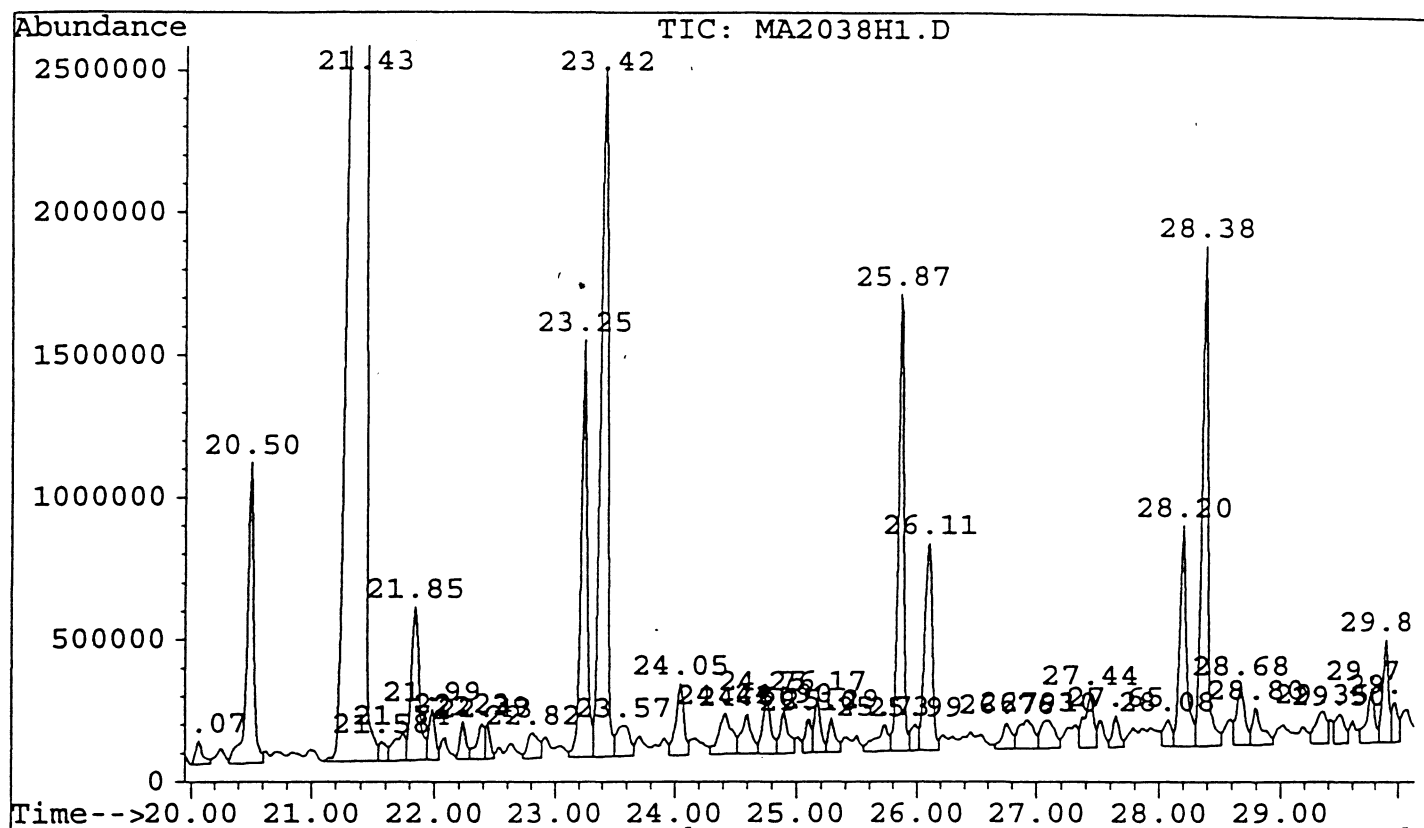


Figure 31.4. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 2nd dsulfurization) showing the ret. time range of 58-68 min and the mass spectrum of Hexatriacontane

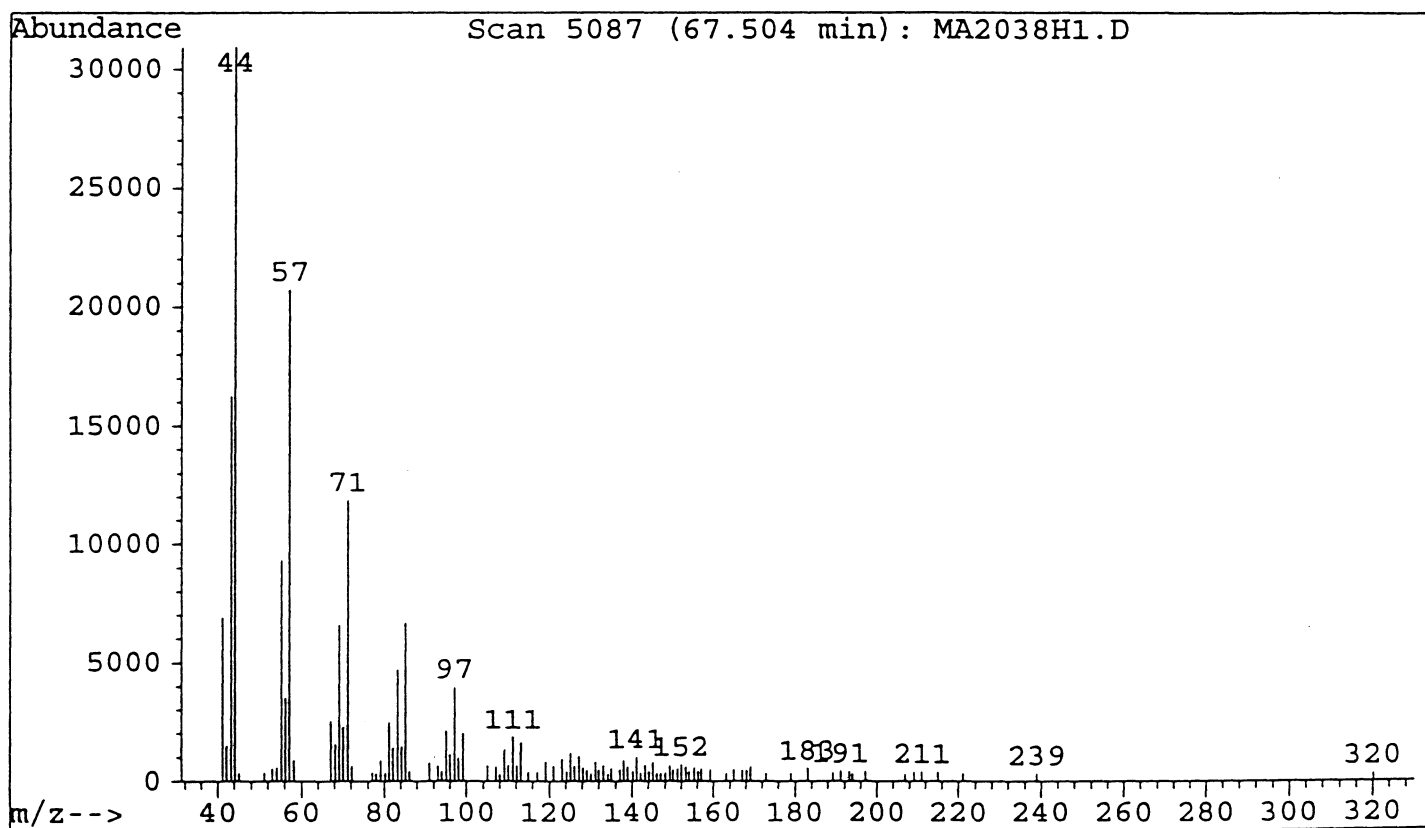
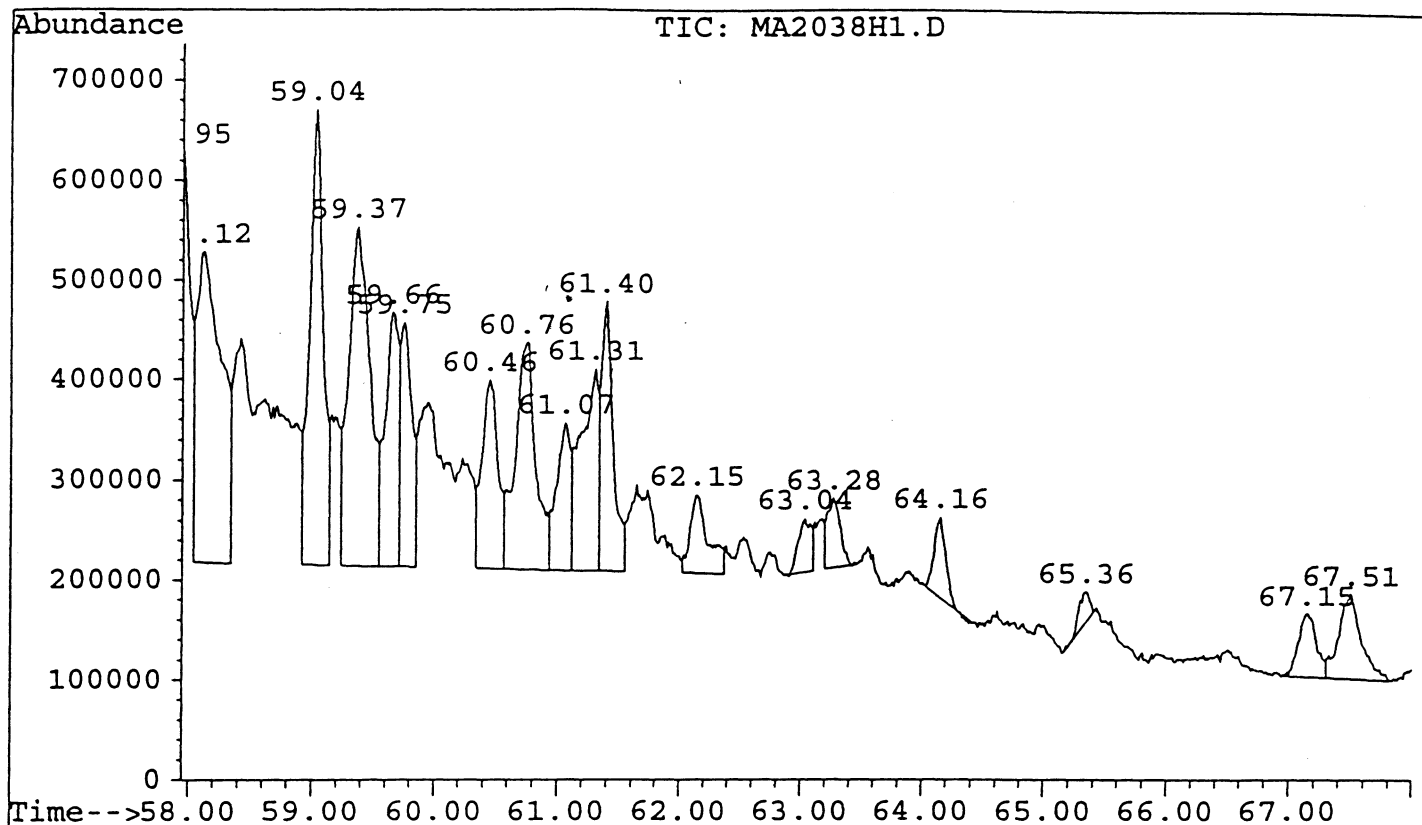


Figure 31.5. TIC of hexane fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization) showing the ret. time range of 40-50 min and the mass spectrum of $C_9H_{13}NO_3$

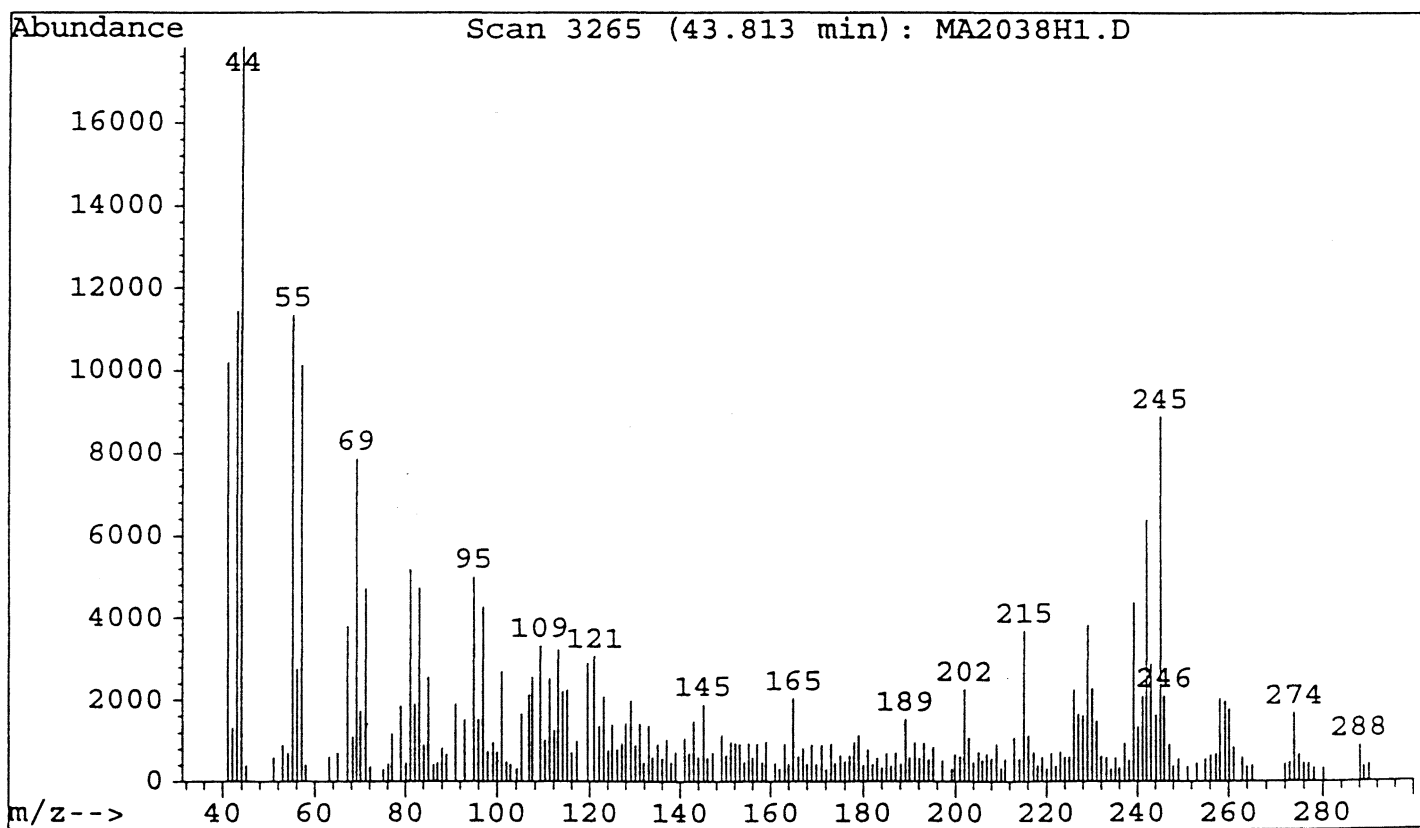
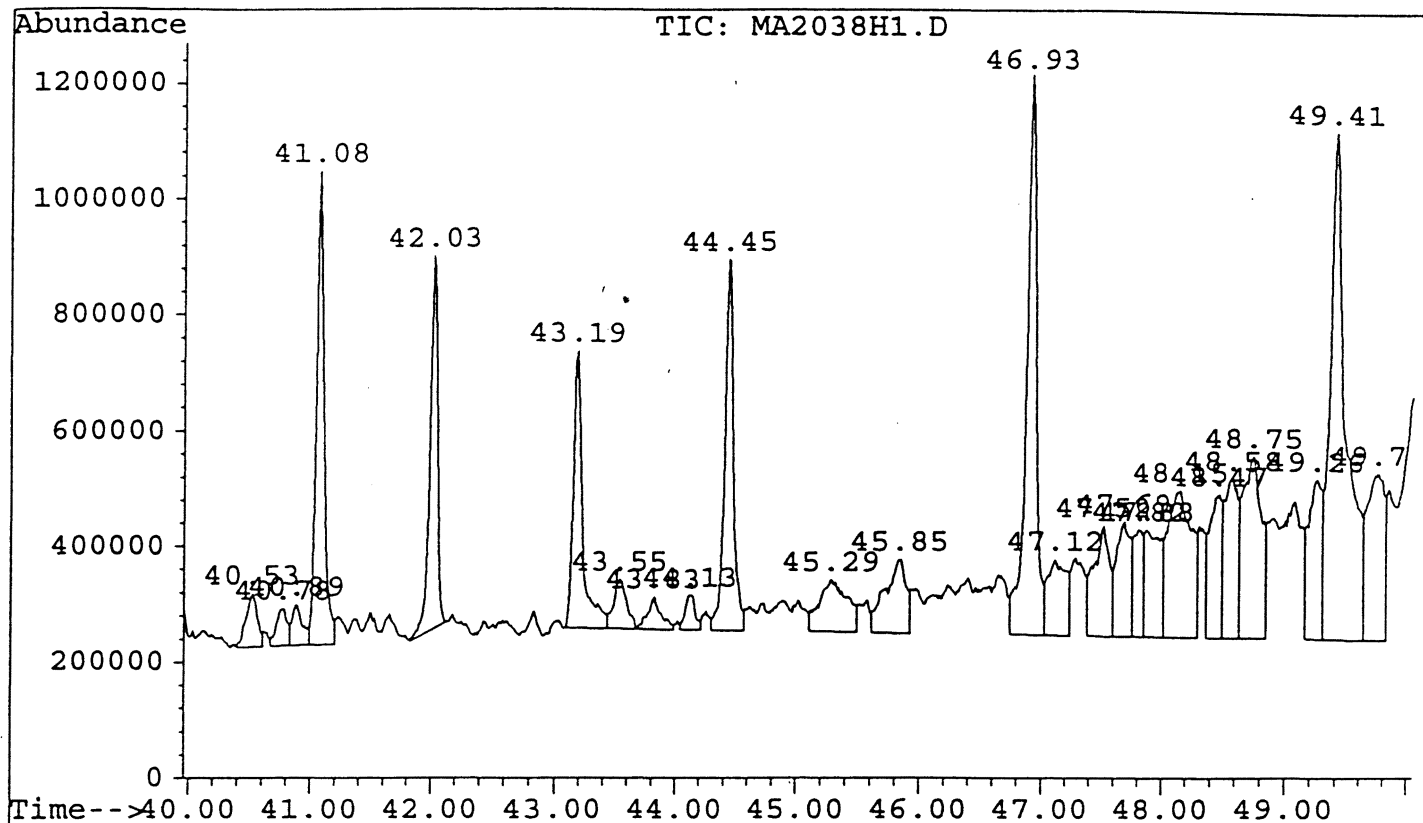


Figure 32.1. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization)

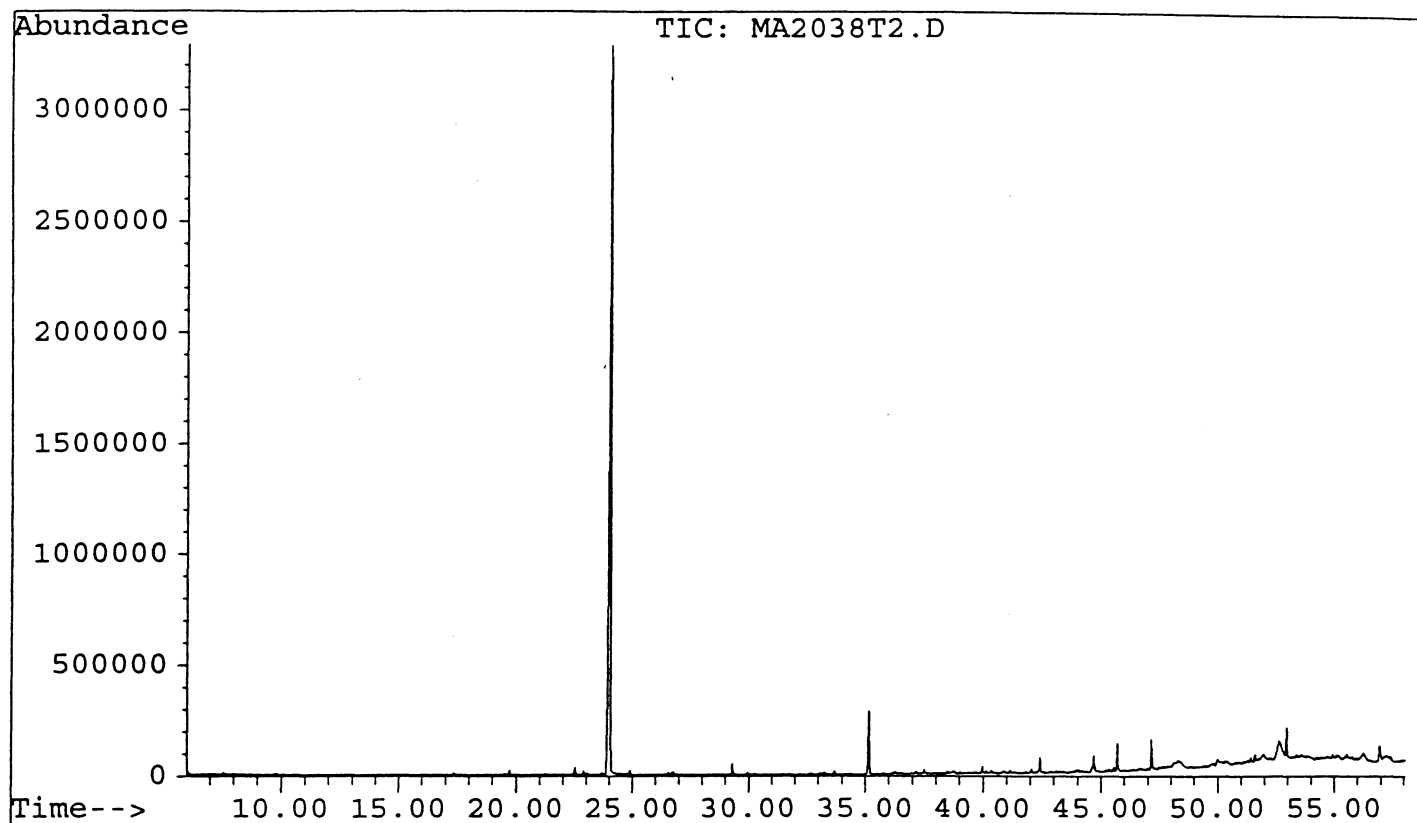


Figure 32.2. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization) showing the ret. time range of 39.8-50.4 min

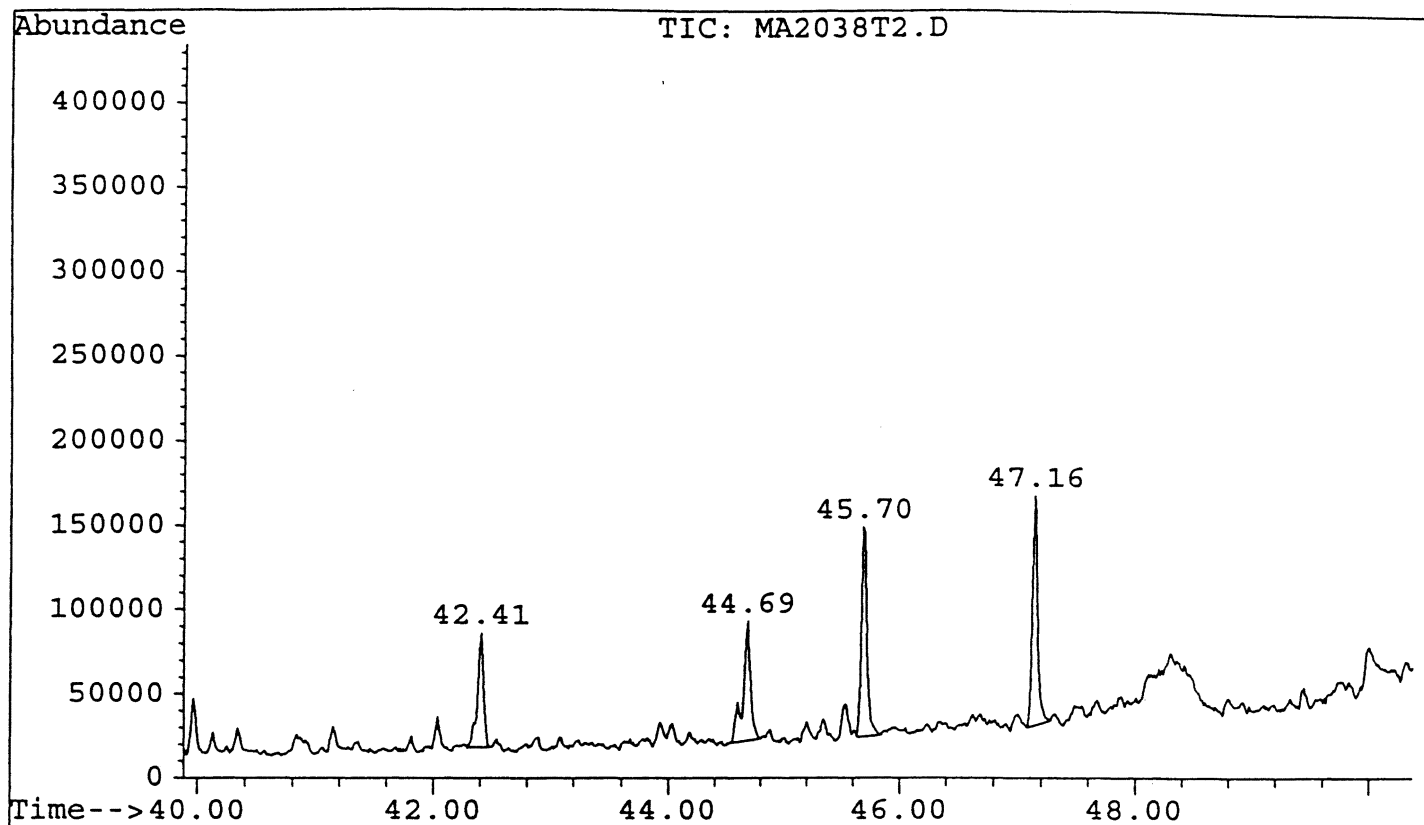


Figure 32.3. TIC of toluene fraction of after desulfurized sample of IBC-#108 (the 2nd desulfurization) showing the ret. time range of 49.9-58.1 min

