ANALYSIS AND CHARACTERIZATION OF NAPHTHALENE AND ITS ALKYL DERIVATIVES IN GASOLINES USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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Analysis and Characterization of Naphthalene and Its Alkyl Derivatives in Gasolines Using Gas Chromatography/Mass Spectrometry

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ABSTRACT

At least 38 of the title compounds up to C_{15} polyalkylnaphthalenes are found in gasolines using a fused silica SE-54 capillary gas-chromatography column coupled to a quadrupole mass spectrometer operating with electron ionization (EI) or methane chemical ionization (CI). Mass chromatograms are used to distinguish the alkylnaphthalenes from other coeluting aromatics. Retention indices relative to naphthalene and phenanthrene are given for at least 20 of the identified components, and semi-quantitation is given. The abundances, as percent within isomeric groups, are reported and compared to reports previously done on crude oils and coal tars. The abundances of the alkylnaphthalenes found are correlated with thermodynamic data from literature.

The CI mass spectra show the expected abundant protonated molecules and reagent-gas adducts, but differences in minor-ion abundances reflect different tendencies of isomers or homologues to undergo hydride abstraction and skeletal fragmentation. These tendencies are rationalized according to degree of substitution and ionic stability, confirming and extending another CI report on some of these compounds.

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CHAPTER I

INTRODUCTION

Interest in the Analysis of Alkylnaphthalenes

With the growing use of petroleum and its related products, there has been an increased interest in their analysis within the industry. Continued advances in process control and engineering have led to a greater need for product make-up and component identification. Once, petroleum products were analyzed by various group analyses, such as the PONA analysis, where paraffins, olefins, naphthenes, and aromatics were quantified without identifying the individual components.[1] Improvements in technology and analytical instrumentation have made it possible to further break down these groups into smaller classes and, in many cases, to identify the individual components. Polycyclic aromatic hydrocarbons (PAH) are a class of the aromatics that have more than one aromatic ring in the chemical structure. Naphthalene and its series of alkyl homologues are a class of two-ringed PAHs in which interest has grown. The structure of naphthalene is shown in Figure 1, with the positions numbered where the alkyl groups can be substituted. Table 1 gives the alkylnaphthalene names and abbreviations used for the various alkyl group substitutions on the naphthalene molecule.

Naphthalene and its alkyl derivatives have been analyzed for and found in a variety of petroleum products, ranging from the crude oil[2] to the fractionated streams collected from its distillation.[3,4,5] Alexander, Kagi, and Sheppard[6] in 1983 analyzed DMNs in crude oil; and then later Alexander and Kagi joined with Rowland[7] to isolate the TMNs in a crude oil. Coals[8,9] and sediments[10] have also been investigated for the presence of alkylnaphthalenes. Although gasolines[11,12] have been analyzed extensively in the past, little attention has been given to the naphthalene constituents, primarily due to their overall small contributions to its composition, and to the difficulty of the separation. However small, their contributions are still important.

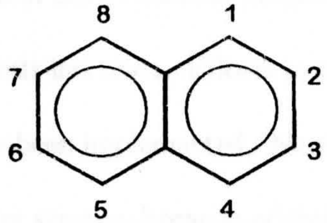


Figure 1. The chemical structure and positions for numbering naphthalene, $C_{10}H_8$.

TABLE 1

ALKYLNAPHTHALENES AND ABBREVIATIONS

Naphthalene	N
Methylnaphthalene	MN
Ethylnaphthalene	EN
Dimethylnaphthalene	DMN
Trimethylnaphthalene	TMN
Isopropylnaphthalene	iPN

Investigators in the field of arson analysis have begun to look at the alkylnaphthalenes in some commonly used accelerants.[13,14] The identification of accelerants from the debris recovered from suspected arson fires has become increasingly complex. Recently, work has been done using computer-assisted gas chromatography/ mass spectrometry (GC/MS) to analyze the fire debris for traces of accelerants such as gasoline and kerosene.[15] Since naphthalene and its alkyl derivatives are some of the higher boiling components of gasoline, residues of these compounds are more likely to be found at the scene of the fire. Knowing the characteristic profile of the alkylnaphthalenes in each of the accelerants aids in determining the accelerant used to start the fire.

With the growing concern of environmental pollution, the need for monitoring of airborne, aquatic, and soil pollutants has risen. Efforts to control the release of volatile organic compounds (VOCs) have been implemented. Naphthalene and its alkyl homologues have been under close scrutiny because of their widespread occurrences. The unusually high solubility of naphthalene in water has led to its being listed as one of the sixteen priority-pollutant PAHs in wastewater. Emissions from internal combustion engines daily contribute to air pollution, as do the exhausts of petroleum products used as heating fuels.

Origin of Alkylnaphthalenes

Formation of Oil

The origin of petroleum is not totally understood. Many scientists believe that it is the result of many complex steps that have occurred over the centuries. Organic matter consisting mainly of phytoplankton, zooplankton, bacteria, and higher plant life is considered to be the starting materials from which oil is formed. These materials were deposited from their environment, aquatic or terrestrial bordering a body of water, to form the sediments below. The majority of this organic matter, greater than 99 percent, was quickly oxidized by chemical or microbial means to carbon dioxide, and returned to the surrounding atmosphere.[16]

As the accumulation of these sediments continued, a small increase in temperature and pressure resulted, due to the weight of the above layers. This first stage is referred to as diagenesis, and it occurred at depths down to 1200 meters below the surface. The temperatures reached were less than 50 °C. During diagenesis mild transformations occurred, mainly due to microbial activity. Some proteins, carbohydrates, and lipids were broken down and condensed. The majority of the organic matter remaining was converted into kerogen, an organic material insoluble in alkali solutions and many common organic solvents in use today. Humic and fulvic acids, which were formed in the earlier stages of diagenesis, were now depleted. Early forms of coal were formed. Methane was the main hydrocarbon generated during this stage.

The next stage, called catagenesis, occurred at depths from 1200 to 3000 meters. The temperatures ranged between 50 and 200 °C. Most of the reactions in this stage were thermal in nature, and are often referred to as maturation reactions. The kerogen formed in diagenesis and in the early stages of catagenesis was converted into petroleum hydrocarbons and low-molecular-weight hydrocarbons. The formation of crude oil from its source rock occurred predominantly in this stage. Wet gas formation began in the last stages of catagenesis.

As the burial depths increased to over 3000 meters, the temperatures rose to greater than 200 °C. This combination of pressure and temperature, referred to as thermal cracking, converted any liquid or solid organic matter to hydrocarbon gases and graphite. This final stage, is given the name metagenesis, and is the primary zone of gas formation. Natural gas reserves are found at these depths, as well as those reserves formed during diagenesis.

Naphthalene and its alkyl derivatives are thought to have been formed in one of two different ways. The first was during catagenesis when petroleum formation was dominant. The kerogen was the source of the PAHs and the other hydrocarbons formed through thermal degradation and disproportionation reactions. This route is believed to be responsible for the bulk of the crude oil produced.

The minor, but most interesting source for PAH-containing crude oil was high-molecular-weight hydrocarbons present during catagenesis. These hydrocarbons are believed to have been compounds only slightly altered from their original structures found in the living forms in which they were produced. The alkylnaphthalenes, specifically the DMNs and the TMNs, are believed to have been derived from triterpenes (C_{20+} pentacyclic compounds) through a series of fragmentation and dehydrogenation reactions.[17] These high-molecular-weight compounds, found in oil and other fossil fuels, that have no change or only minor structural alterations are called geochemical fossils or biomarkers. Geochemists have used these biomarkers to trace back to the sources of the crude oils, rocks, coals, etc., and to differentiate one oil from another. Cholesterol, steroids, and n-C_{16} fatty acids are a few biomarkers commonly used. Of the ten DMN isomers, the 1,8-DMN has been investigated as a possible petroleum maturity indicator, primarily because of its low stability compared to the others.[18]

Conversion to Gasoline

Once the crude oil is collected from the ground, it undergoes a multitude of processes before it becomes a finished product. The first major step in crude oil refining is its distillation into the thirteen common fractions shown in Table 2.[19] The distillation fraction is listed along with its characteristic boiling range. Gasolines are formulated by blending the light naphtha and gasoline fractions, along with some of the other listed distillation fractions in order to meet specific requirements.

TABLE 2

DISTILLATION FRACTIONS AND BOILING RANGES(°C) OF CRUDE OIL[a]

Fuel gas	-160 to -40
Propane	-40
Butane(s)	-12 to -1
Light naphtha	-1 to 150
Heavy naphtha	150 to 205
Gasoline	-1 to 180
Kerosene	205 to 260
Stove oil	205 to 290
Light gas oil	260 to 315
Heavy gas oil	315 to 425
Lubricating oil	>400
Vacuum gas oil	425 to 600
Residuum	>600

[a] See reference 19.

The two main properties governing gasoline formulations are the boiling range and antiknock characteristics.[20] Typical gasolines have a boiling point of 180 °C, with an upper limit of 200 °C. Ease of starting, rate of acceleration, and the tendency to vapor lock are all dependent on the boiling range. Butanes are added to gasoline to increase the volatility enough to improve starting conditions, while minimizing the chances of vapor lock. Octane rating is the term used to measure a gasoline's antiknock properties. Three grades of gasoline investigated in this paper are unleaded, leaded (no longer available), and premium unleaded, with octane ratings of 87, 89, and 91, respectively. The octane rating of a gasoline, based on a value of 100.00 for "isooctane", can be increased by adding compounds like 2,2,4-trimethylpentane ("isooctane"), 2-methylbutane (isopentane), benzene, and toluene.

There are a variety of treatment processes the crude oil fractions or streams must undergo as they are blended to form the finished product. Acid and caustic washes are commonly done to remove insoluble and unwanted compounds. Sweetening steps are performed to improve the odor by removing sulfur compounds. Alkylation reactions, which are used primarily to form small branched alkanes from n-alkanes, occur to a lesser extent with naphthalenes and other aromatics. Thermal and catalytic cracking steps are done to some of the higher boiling distillation fractions to form smaller, lower boiling compounds that can be used in gasolines and other products. Alkylnaphthalenes can be formed by the pyrolysis of PAHs found in asphaltene fractions. At the same time, naphthalene is commonly converted by hydrocracking to benzene, and eventually to alkanes by a series of hydrogenation and fragmentation reactions. Some other commonly used reactions are polymerization and isomerization reactions. The processes used are all dependent on the source of crude oil used, and the desired final product. Additives for coloring, anti-icing, and other required properties can be added as needed.

Analytical Methods

Gas Chromatography

The separation and identification of the components of gasoline are very difficult tasks. With several hundred structurally similar compounds in the matrix, single peak resolution is nearly impossible without extensive sample preparation. Since naphthalene and its alkyl derivatives represent only a minor fraction of the gasoline, preparative steps are common. Some typical methods used are adsorption chromatography, affinity chromatography, distillation, high-performance liquid chromatography, solvent extraction, and thin-layer chromatography. The method of separation which often follows one of these preliminary steps is gas chromatography (GC).

Gas chromatography was first developed in 1951 by E. Cremer.[21] The technique involves vaporization of the sample in the injector area and separation of the vaporized components through a column. The components are swept through the column with a carrier gas, typically helium or nitrogen, to a detector. The column is usually filled with a nonvolatile solid, or the column walls are coated with a nonvolatile solid or liquid material. The material inside the column is referred to as the stationary phase. The carrier gas flowing through the column is called the mobile phase. It is the equilibrium of the component between the mobile phase and the stationary phase that determines the retention time (t_R) of the component. The t_R is the time, from injection, that it takes the individual component to travel through the column and reach the detector.

Vaporization of the compounds to the gas phase is necessary for the principles of GC to work. Since the vapor pressures of the compounds are related to their boiling points, gas chromatographs are built with a heated injector area and an oven compartment which surrounds the column. The injector area should be hot enough to insure complete vaporization of the sample injected. If not, discrimination against the higher boiling components may occur. Once the sample is injected, usually with a syringe, the carrier gas sweeps the sample vapors onto the column. By controlling the column temperature with the oven, the retention times of the compounds may be varied. The oven can be controlled isothermally or with temperature-programmed gradients.

The two types of columns currently used in GC are packed and capillary columns. The older GC technique of using packed columns, which are filled with a solid nonvolatile packing material, is referred to as gas-solid chromatography. The columns are typically made of stainless steel or glass, and they are usually six feet in length. The inside diameter (i.d.) is 1/8 inch or more. The resolution obtained is adequate for some separations, but it cannot compare with the newer capillary columns on the market today. Capillary columns are usually made of fused silica, and range from 5 meters to 100 meters in length. The stationary phase can be applied to the column in several different ways. Porous layer open tubular columns have a liquid coating deposited on the column wall, which has been extended by a solid support material. Support-coated open tubular columns are made by coating the column wall with a mixture of a solid support and the liquid phase. When the liquid phase is deposited directly on the column wall without the use of a solid support, the columns are referred to as wall-coated open tubular (WCOT) capillary columns. Gas-liquid chromatography is the term used when the stationary phase of the column is a liquid. The stationary phases used today have been greatly improved. By cross-linking the stationary phases, which are typically polymer chains, the liquid phase becomes more resistant to the surrounding conditions. These bonded phase capillary columns are more reliable and reproducible, less affected by solvent attack, and capable of operation at higher temperatures. The polarity of the stationary phase used varies with the analytes of interest. For the separation of nonpolar PAHs, nonpolar stationary phases are normally used. In addition to the column temperature, the interaction of the compounds with the stationary phase can affect the resolution of the components and their elution order. Therefore, when developing an analysis, consideration of the best stationary phase is necessary. Once the separated compounds are eluted off the column, they must pass through a detector, such as a mass spectrometer, where their signals can be measured. The quadrupole mass spectrometer used for this work will be discussed next.

Mass Spectrometry

When analyzing complex mixtures, the detector can be just as important as the column used in the separation. As the peaks elute from the column, it is necessary to detect, and then measure the quantity of each analyte. Two commonly used universal detectors are the thermal conductivity and flame-ionization detectors. They are responsive to most compounds, and are relatively inexpensive. The electron-capture detector works best with halogenated compounds; whereas, the thermionic emission detector is more sensitive to compounds containing nitrogen or phosphorus. The main function of all these detectors is to respond to the eluting compounds, and to convert the response into peaks as seen by the chromatogram. The only means of identifying the eluting compounds is by comparing their retention times to those of standards. The infrared spectrometer (IR) and the mass spectrometer (MS) are two detectors widely used that also record information useful in determining the structure and identity of the eluting compounds.

Mass spectrometry, the separation of gaseous ions according to their masses and the measurement of their abundances, first began in the early 1900s. In 1908 physicist J. J. Thomson,[22] considered "the father of mass spectroscopy", reported his positive ray work on neon, helium, mercury, and a few other elements. However, in 1918, F. W. Aston[23] was the first to report precise atomic masses for the two isotopes of neon, neon-20 and neon-22. He is given credit for producing the first "true" MS. Advances in the development of the MS continued slowly until the 1940s. It was during this war-time period that the petroleum industry began to boom. With the birth of the plastics industry, there were greater demands for purer petroleum fractions to be used as raw materials. Developments in the MS were made continuously to satisfy the industry's changing needs.

The main functions of a MS are to vaporize the sample, produce ions from the neutral molecules in the gas phase, and separate, detect, and record the ions in relation to their mass-to-charge ratio (m/z).[24] Vaporization of the sample may be done using a heated solid-probe, which is inserted into the ion source of the mass spectrometer. When used in tandem with GC, the vaporization step is accomplished in the injector area of the GC, and the vaporization is maintained until the compounds reach the ion source. To help minimize condensation in the ion source, the manifold area, where the ion source and detector are enclosed, is often heated.

Once the vaporization step has been completed, the neutral compounds eluting from the column must be ionized. Ionization occurs when an adequate amount of energy is supplied to remove an electron from the highest occupied molecular orbital. Many techniques of ionization have been developed and implemented for the MS. Glow discharge, fast atom bombardment, and laser desorption are a few of the newer ionization methods. Electron ionization (EI) and chemical ionization (CI) are the two methods used in this study.

Electron ionization is the one of the oldest ionization techniques used in MS. As the compounds enter the ion source, the vaporized molecules are bombarded by a stream of high-energy electrons. The electrons are produced from a filament, and their energy is regulated typically at 70 electron volts (eV). Most organic compounds can be ionized with less than 20 eV, but ion abundance maximizes near 70 eV. With the loss of an electron, a positively charged molecular ion ($M^{+\bullet}$) is formed, as shown by the equation:

$$M + e^- \rightarrow M^{+\bullet} + 2e^- \qquad (1)$$

The raised dot ($^\bullet$) indicates an odd-electron species. When excess energy is absorbed by the molecule, fragmentation of the $M^{+\bullet}$ may occur. The $M^{+\bullet}$ and the positively charged ions and their abundances formed upon fragmentation are characteristic of each analyte and very useful in compound identification.

Chemical ionization is a milder form of ionizing the compounds of interest. In other words, the required energy to ionize the sample molecules is less than in EI, because of the process used. The vaporized compounds in the ion source are mixed with an added reagent gas. Methane (CH_4) was the reagent gas used in this work. Other commonly used reagent gases include ammonia, isobutane, and nitrogen. The amount of reagent gas added is usually monitored by pressure, and its concentration greatly exceeds those of the analytes in the ion chamber. Because of this, it is mostly the reagent gas that is ionized by the high energy electrons. The reagent-gas ionization is shown in the following equation:

$$CH_4 + e^- \rightarrow CH_4^{+\bullet} + 2e^- \tag{2}$$

As the reagent gas is ionized, ion-molecule collision reactions occur between the neutral reagent-gas molecules and the reagent-gas ions formed. Some of these reactions are shown in equations (3) through (5).[25]

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + CH_3^\bullet \tag{3}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \tag{4}$$

$$C_2H_5^+ + CH_4 \rightarrow C_3H_5^+ + 2H_2 \tag{5}$$

These positively charged ions can then react with the sample molecules, ionizing them. The protonated molecule $[M+H]^+$ is normally the adduct predominantly formed. This reaction is shown by the equation:

$$M + CH_5^+ \rightarrow [M+H]^+ + CH_4 \tag{6}$$

Since the sample molecules ionized through these chemical reactions have less excess energy, they undergo far less fragmentation than seen in EI. In many cases, the molecular weight of the unknown sample compound can be found by subtracting one atomic mass unit (amu) from the mass of the $[M+H]^+$ adduct. Other positively charged ions commonly found include the adducts $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$.

The separation, detection, and recording of all of these positively charged ions in relation to their m/z ratios, whether formed through EI or CI, are the last functions of the MS. The mass spectrum is the fragmentation pattern of the all the ionic masses that were formed and their abundances. Both positive and negative ion MSs are available today, but only the positive-ion MS, which was used for this work, will be discussed. For all of this to be possible, the manifold of the MS must be under constant vacuum. When under vacuum, ion-source component and MS hardware contamination are minimized, and the life of the filament is extended by the lack of oxygen. Control of the electronics is also better. The low pressure promotes separation and detection of the ions formed, and minimizes any unwanted fragmentations or ion-molecule reactions. High background pressure in the MS is usually due to unwanted gases, and these must be eliminated to improve the quality of the mass spectra recorded.

Mass spectra are obtained in a variety of ways, but the two MS detectors to be discussed here are the magnetic sector and the quadrupole mass spectrometers. The magnetic sector MS was the first MS built, and many of the principles on which it was based are still used. Separation of the ions is achieved by deflecting the ions through a magnetic field. The effect of the magnetic field on each ion is given in the expression:

$$m/z = H^2R^2/2V \tag{7}$$

where m/z is the mass-to-charge ratio of the ion, H is the strength of the magnetic field, R is the radius of the curved path to the detector, and V is the voltage applied to accelerate the ions. All of the ions with the same charge leaving the ion source have the same kinetic energy, but their initial velocities differ somewhat. The equation for the kinetic energy is as follows:

$$zVe = (1/2)mv^2 \tag{8}$$

where e is the electron charge and v is the velocity of the ion after acceleration. Each ion follows a particular curved path toward the collector slit. Given equal charges, the lighter ions, which are influenced more by the magnetic field than the heavier ions, have shorter radii of trajectory. Separated by their m/z ratios, the ions are usually scanned by varying the magnetic field while keeping the voltage constant. The ions are focused on the collector slit, and as the value of H is varied, the ions with specific m/z ratios pass through the slit to the detector. The abundances of the ionic masses are tallied, as the various m/z ratios are scanned.

The quadrupole mass analyzer, or filter, is a newer technique of separating the ions according to their m/z ratios. It consists of four parallel rods, arranged symmetrically, to which direct current (dc) and radio frequency (rf) voltages are applied. A diagram[26] of the ion source and quadrupole rods is shown in Figure 2. As the ions are formed in the ion source, they are focused into an ion beam by the extractor and lens, to which positive and negative potentials are applied, respectively. The ion beam passes through the aperture to the center of the quadrupole rods. One pair of opposing rods has positive dc and rf voltages applied, while the other pair has negative applied voltages. The electrostatic and rf field produced causes the ions to oscillate as they pass through the quadrupole mass filter. By controlling the voltages applied, stable ions of a specific m/z ratio oscillate

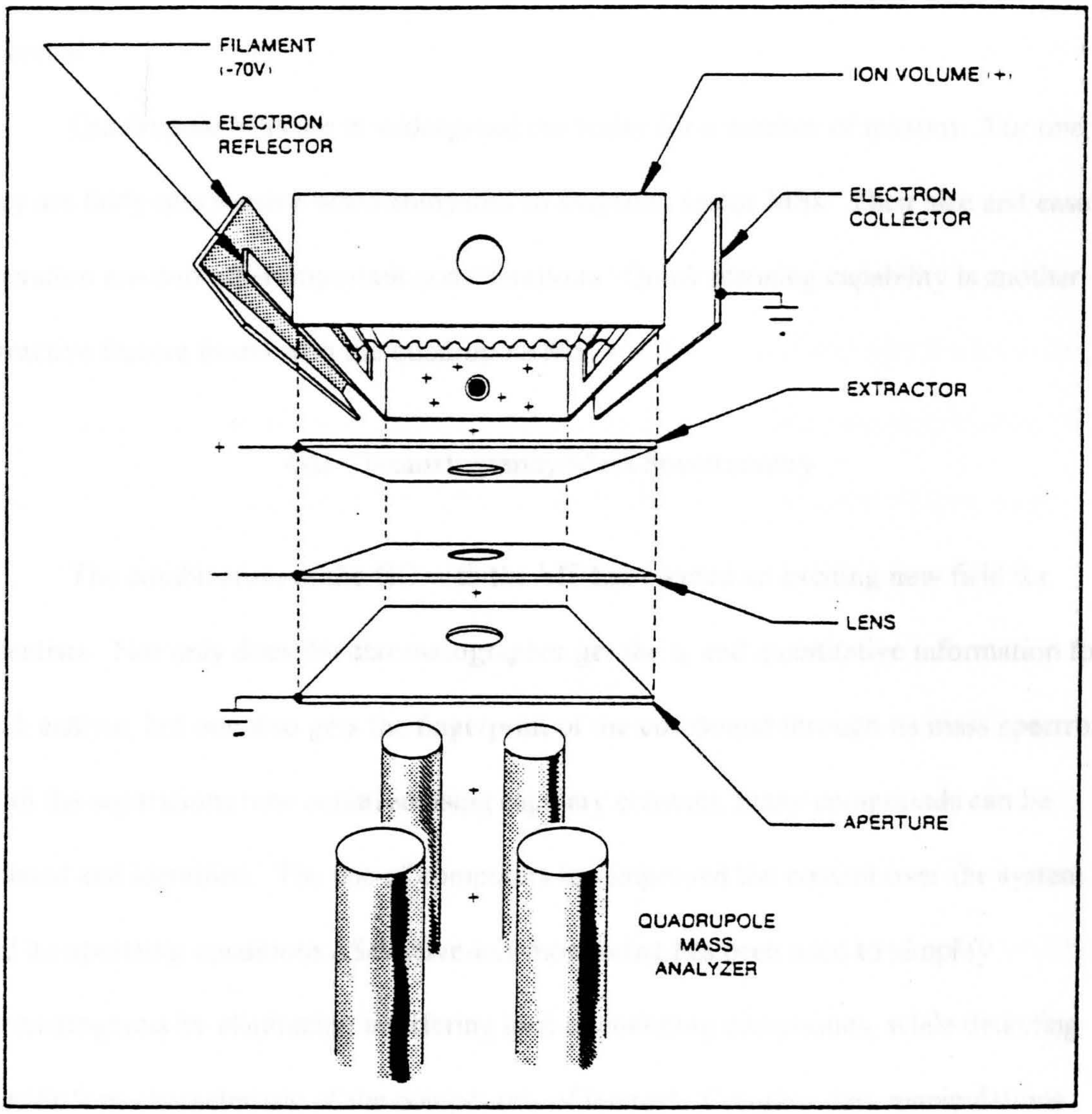


Figure 2. Diagram of ion source and quadrupole rods.[26]

between the rods, traveling parallel to them, and exit out the end to the detector, which is usually an electron multiplier. Unstable ions either collide with the rods, or pass out between them. A specified mass range can be scanned by either varying the dc and rf voltages, while keeping their ratio constant, or by changing the frequency of the rf potential.

Quadrupole MSs are in widespread use today for a number of reasons. For one, they are fairly inexpensive when compared to magnetic sector MSs. Their size and ease of operation are two other important considerations. Quick scanning capability is another attractive feature found with the quadrupole MS.

Gas Chromatography/Mass Spectrometry

The combination of the GC with the MS has created an exciting new field for scientists. Not only does the chromatographer get the t_R and quantitative information for each analyte, but one also gets the fingerprint of the compound through its mass spectrum. With the separations now achieved using capillary columns, many compounds can be isolated and identified. The use of computers has improved the control over the system and its operating conditions. Selective-ion-monitoring has been used to simplify chromatograms by eliminating interfering ions of coeluting compounds, while detecting specific ions characteristic of the compounds of interest. Complex data manipulations have also been simplified. Spectral libraries are available for searching and matching an unknown with reference compound spectra.

The main obstacle to overcome when linking a GC with a MS is the interface between the two. The carrier gas flow, when using packed columns, is usually too high for the MS vacuum system to handle. Because of that, various types of separators have been developed to prevent the carrier gas from entering the MS, without loss of the analytes. Jet-orifice, effusion, and membrane separators are three of the ones commonly used. The separator area is usually temperature-controlled to prevent condensation of the vaporized sample. No separator is typically needed when capillary columns are used. The column is connected directly to the ion source. The use of helium as the carrier gas aids in its being pumped away quickly, giving it less of a chance to cause any interferences. In some cases, the increase in pressure from a large amount of solvent entering the MS may cause a problem. This problem can be avoided by keeping the injection volume small, using the split-injection mode, or by using a solvent diverter.

Related Work

The composition of gasolines has been investigated for many years. Most grades are believed to contain over 600 compounds. In 1968, Sanders and Maynard[11] analyzed regular and premium grade gasolines on a 75-m squalane capillary GC column, reporting 240 peaks up to the elution of n-dodecane, of which 180 of the peaks were identified. Korean-made gasolines were analyzed by GC/MS in 1982 by M. Lee, I. Lee, and H. Chong.[27] Johansen et al.[12] reported chromatographic peaks in gasolines, up to the elution of n-tetradecane (bp 254 °C), with 123 peaks being identified. In 1984 Matisova et al.[28] analyzed the gasoline fraction of a crude oil by GC under isothermal conditions. A year later, Matisova et al.[29] performed isothermal and temperature-programmed analyses on similar fractions. Naphthalene (bp 217 °C) and its alkyl derivatives were of little interest in these studies, since they were minor, unidentified components eluting near the end of the chromatograms. Sanders and Maynard[11] did identify and quantitate naphthalene in the gasoline samples they had analyzed. Of the 180 peaks found, naphthalene eluted 178th, with a retention time of approximately 105 minutes and a concentration less than 0.25 %w/w.

Interest in naphthalene and its alkyl derivatives has increased in the forensic and environmental fields. Arson investigators have used the alkylnaphthalenes to identify accelerants recovered from sites of suspected arson. Because of their higher boiling points, the alkylnaphthalenes are some of the main components of gasoline still found at the scene, after the fire is over. Smith[13] reported the alkylnaphthalenes as groups, dependent on the total number of carbons of their alkyl group substitutions, such as, C_1, C_2, and C_3-naphthalenes. In 1983, Jensen and Hites[30] investigated the amount of naphthalene and other PAHs released by diesel fuel emissions. Lee et al.[31] separated and identified over 200 PAHs commonly found in coal tars. Naphthalene and alkylnaphthalenes were some of the urban-related organics found in rivers and the air, in a 1991 report by Rosell and his colleagues.[32]

Investigations into some of the physical properties of naphthalene and its alkyl derivatives have also been reported in the literature. Iseda[33] did comparison studies on the reactivity of naphthalene and 14 alkylnaphthalenes with methane and isobutane reagent gases, using chemical-ionization mass spectrometry. The stability and occurrences of alkylnaphthalenes were investigated by Alexander and colleagues[10] in sediments and petroleums. The use of the alkylnaphthalenes as biomarkers for oil and other fossil fuels has led to increased interest.

The purpose of this study is to identify the individual alkylnaphthalenes in gasoline using GC/MS to avoid possible interferences from other aromatics and alkanes. The relative abundances of the components determined will be compared for the various grades of gasoline studied and with previous reports for crude oil and coal tar. Determination of GC retention times relative to naphthalene and phenanthrene for temperature programming on a 1% vinyl-5% phenylmethylsilicone capillary column will be performed. The retention times found will be compared to those previously reported on several types of columns. The positive-ion methane CI mass spectra of the components will be compared to each other to determine possible structural effects on the ion fragmentation.

CHAPTER II

MATERIAL AND APPARATUS

The gasoline samples used were acquired at local service stations. Initial work was performed on a regular leaded and an unleaded gasoline sample taken from a Pennzoil service station. The later gasoline samples: Octron (regular leaded), Cetron (regular unleaded), and Super Cetron (premium unleaded) were sampled from a Sohio service station.

The lab reagents were all analytical grade. The alkylnaphthalene standards were purchased from Aldrich Chemicals. The chromatography-grade pentane, heptane, and methylene chloride were purchased from J. W. Baker.

The gas chromatograph/mass spectrometer used throughout this work was a computer-controlled Finnigan 1020B GC/MS, complete with a data system, reference library, and solid probe capabilities. The oven in the gas chromatograph had isothermal and gradient temperature control. The column used was a fused silica capillary column, 15 m x 0.25 mm i.d., purchased from J & W Scientific, Inc. (Rancho Cordova, CA 95670). The column stationary phase, SE-54, was a polymer coating of 1% vinyl-5% phenylmethylsiloxane, 0.25 μm in thickness. The mass spectrometer source, where the ionization of the separated compounds occurs, was a chemical ionization (CI) source, but could also be used for electron impact ionization (EI) work as well, with only a small loss in overall sensitivity. The helium carrier gas used for the GC, and the methane reagent gas used for the chemical ionization reactions in the MS, were ultra-high-purity grade gases purchased from Airco Products.

CHAPTER III

EXPERIMENTAL

Preparation of Samples

The gasoline samples obtained from local service stations were stored in 32-ounce amber-colored glass bottles. In most of the separations, concentrated gasoline samples (5:1) were utilized. Concentration by evaporation was achieved in a fume hood. The samples were poured into beakers and allowed to evaporate. Some heating was used to bring all three samples to the same volume, 100 mL from the initial 500 mL used. Specific gravities were measured on all three initial samples taken.

The alkylnaphthalene reference standards were used in one of two ways. Reference solutions were prepared by dissolving known amounts of the chemicals into the solvent, heptane. Solid standards were weighed on an analytical balance, while the liquid standards were measured using a Hamilton 10-μL glass syringe. In some cases, the gasoline samples were spiked with the reference standards, using the same techniques.

GC Conditions

The gasolines and reference solutions were analyzed on the GC/MS. Sample injection, usually a volume of 0.5 or 1.0 μL, was done using a Hamilton 10-μL glass syringe. Typical GC parameters used are listed in Table 3. The injector liner used was a straightbore glass liner. In most of the analyses, the samples were run in the split/sweep mode unless otherwise noted. Helium, the carrier gas, was controlled by the column head pressure. A pressure of 10 psi was typically used. At this pressure setting, a volume flow rate of 2.2 mL/min was measured. The corresponding average linear velocity is 73 cm/s. Since a capillary column was used, no actual separator was needed. However, the "separator temperature" refers to the temperature of the column between the oven and the MS, regulated to prevent condensation of the sample.

TABLE 3

GC PARAMETERS AND SETPOINTS

Injector Zone Temperature:	260 °C
Initial Temperature:	60 °C
Final Temperature:	200 °C
Initial Time:	0 min
Ramp Rate:	2.0 °C/min
Final Time:	5 min
Separator Temperature:	150 °C
Manifold Temperature:	80 °C
Injection Mode:	Capillary
Split/Sweep Time Delay:	0 s
Split Ratio	18:1
Filament/Multiplier Off Time:	180 s
Filament/Multiplier Mode:	Auto

Scan from 80 amu to 250 amu in 1.0 s

Mass Spectrometer

The mass spectrometer was tuned daily for optimum results. Perfluorotributylamine (FC43) was used to calibrate the mass scale and to insure that the mass intensity percentages and isotope ratios fell within target ranges. Calibration reports were generated daily after all the parameters were optimized. Table 4 is an example of the typical MS settings, while Table 5 is an example of a calibration report for FC43. Tuning results falling outside the target range are not of concern for m/z 414 or 502 since the compounds studied here do not have such high molecular weights. To extend the lifetime of the filament and electron multiplier, a 180-s delay in turning on the filament/multiplier was used. Because they elute during the delay period, the solvent and lower boiling compounds of no interest can be pumped away before the electronics are activated, thus preventing unnecessary repairs.

Samples were detected using either EI or CI modes of ionization. Mass ranges scanned with EI were somewhat lower than those using CI. When CI was used, a methane pressure of 0.40 torr was maintained in the ion source. Samples using EI or CI detection will be indicated as such.

TABLE 4

TYPICAL MS SETTINGS

Electron Multiplier Switch	On
Electron Multiplier Voltage	-2247.00
Filament Switch	On
Lens Voltage	-43.92
Extractor Voltage	2.00
Electrometer Range	10^{-8}A

TABLE 5

CALIBRATION REPORT OF FC43

Reference Peaks

18 = Lowest Peak In Reference Found
614 = Highest Peak In Reference Found
21 Of 21 Reference Peaks Were Found
1 % Of Peak Width = RMS Fit Error

Automatic Tune Ratio Report

m/z	Intensity	% of 69	Target %
69	58495	100.00	100.00
219	29535	50.49	30.00 - 60.00
414	1347	2.30	1.40 - 2.00
502	847	1.44	0.80 - 2.00

Isotope Ratio Report

m /z	% Isotope	Target %
69/70	1.21	0.80 - 1.30
219/220	4.99	3.50 - 5.20
414/415	10.83	7.20 - 10.80
502/503	9.08	8.10 - 12.10

CHAPTER IV

RESULTS & DISCUSSION

Chromatograms

The complexity of the GC separation of naphthalene and its alkyl derivatives in gasolines is shown in Figure 3, a reconstructed ion chromatogram (RIC) of a typical gasoline sample. The analysis required just over 38 minutes to complete, with the mass range of 80-250 amu, for CI work, scanned every second. The eluting alkylnaphthalenes are specified. In Figure 4 the chromatogram has been magnified to enhance the C_2 and C_3-Naphthalenes. Figure 5 is the part of a chromatogram where the C_3 to C_5-Naphthalenes elute. The effect of the three-minute filament/multiplier delay at the beginning of the analysis can be easily seen in the first chromatogram. A large portion of the injected gasoline is pumped out of the ion source by the vacuum pump before the detector is turned on.

Several factors affecting the separation of the compounds were considered. Since gasoline contains many compounds of varying concentrations, some type of sample cleanup and concentration was needed. Silica gel column chromatography was used to separate the alkanes from the aromatics. Pentane and dichloromethane were used to elute the respective fractions. After several attempts, work using this method was halted for several reasons. First of all, vaporization of the solvents at their interface caused repeated disturbances of the packing material. Lack of reproducibility between samples and the

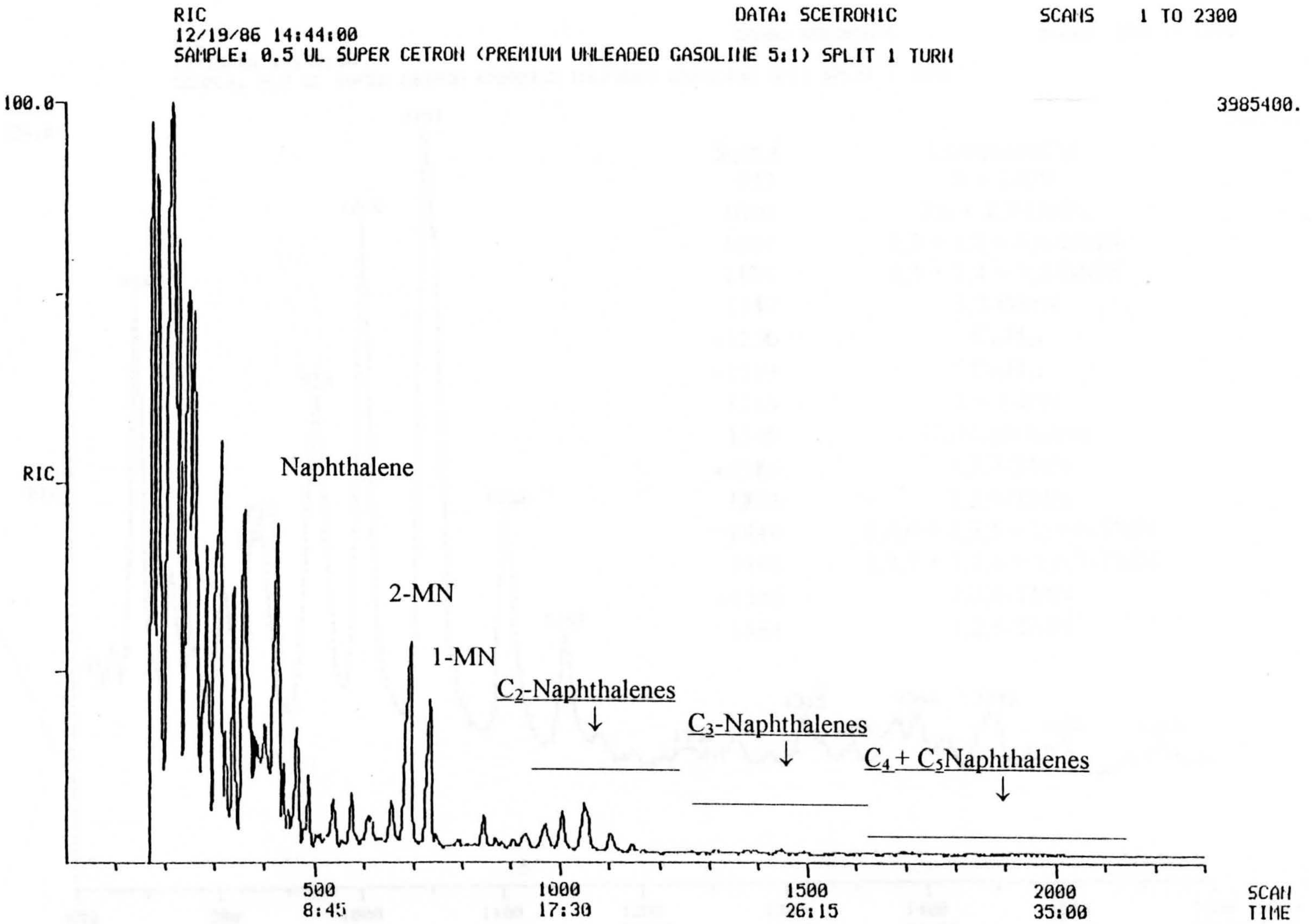
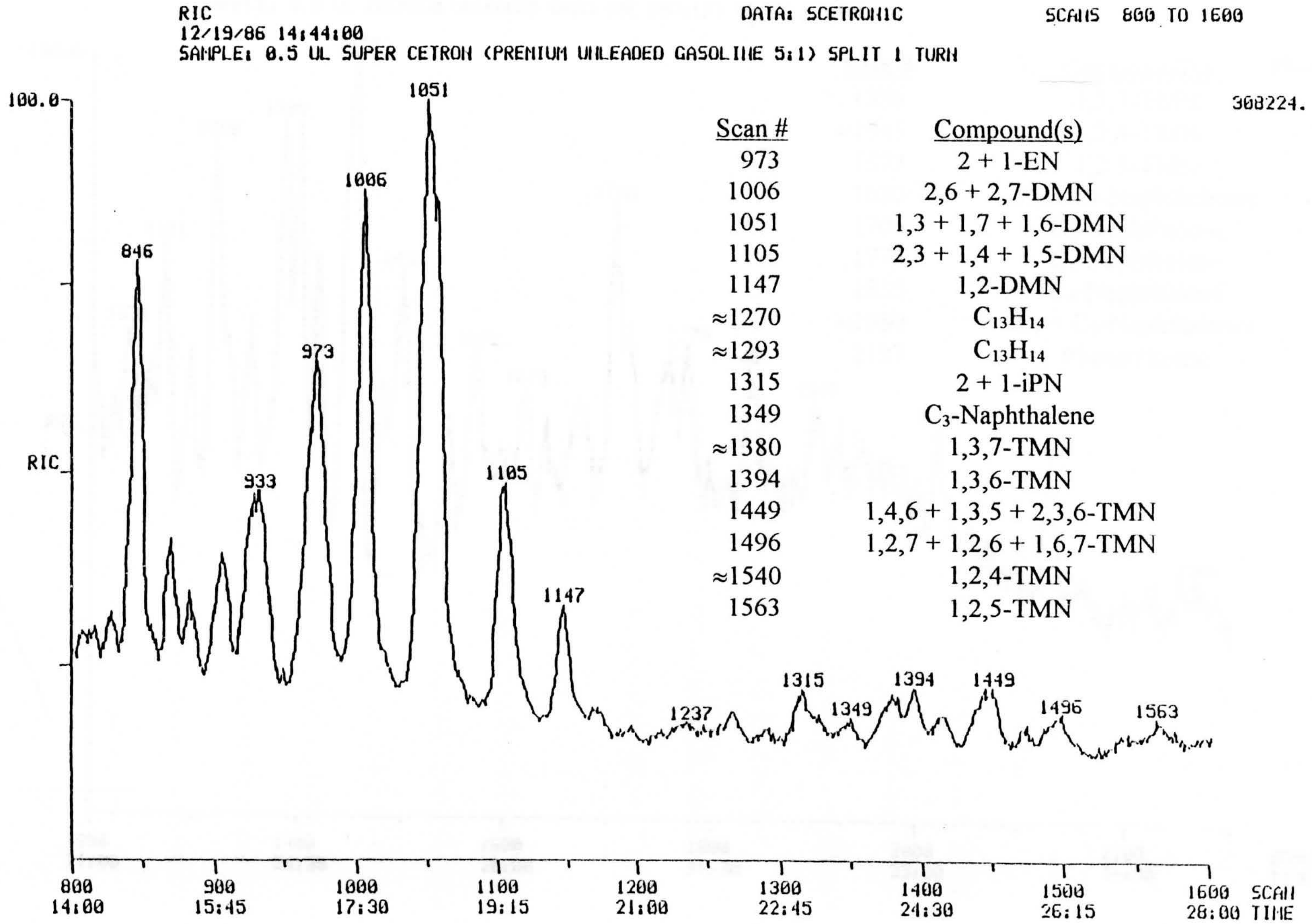
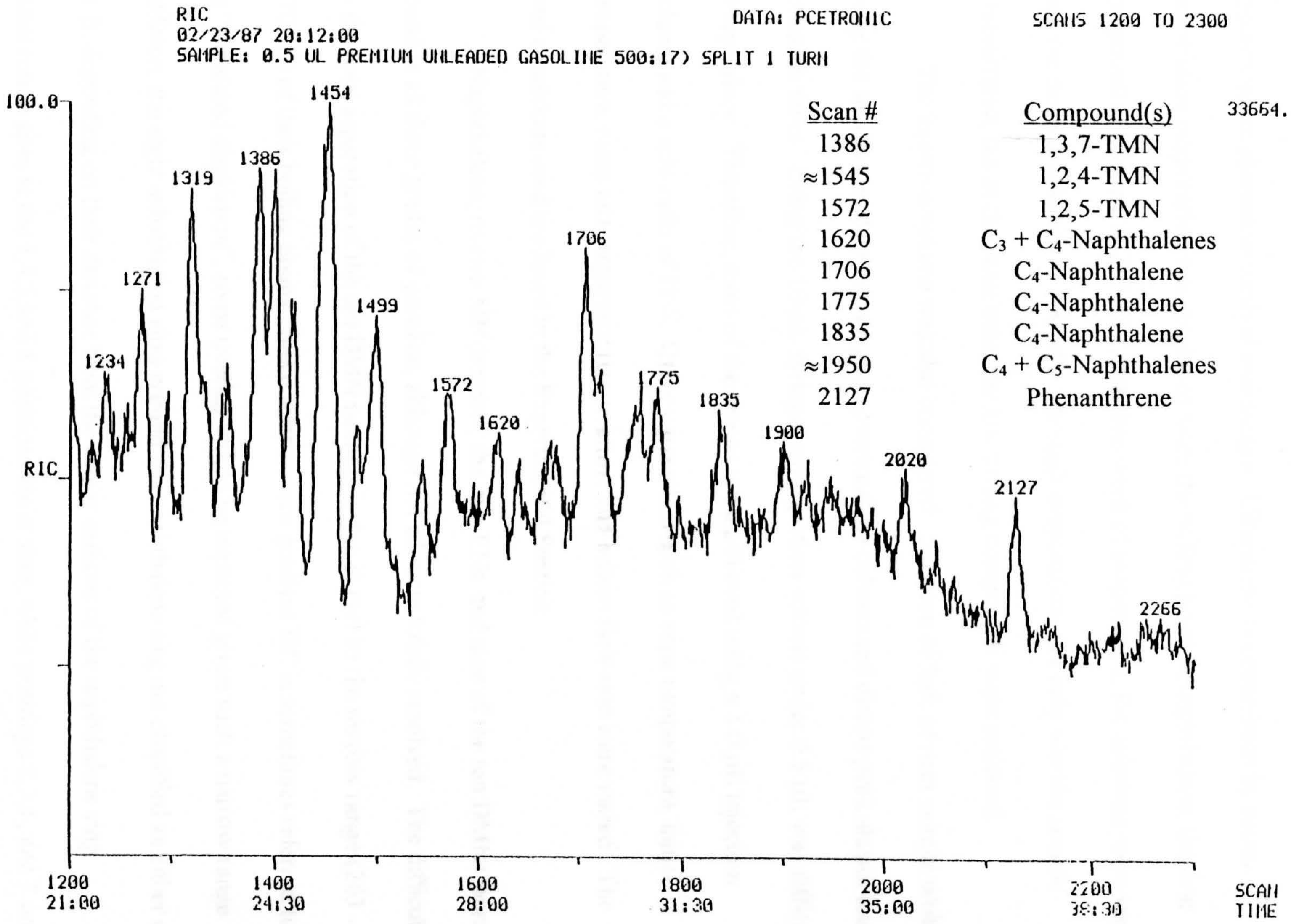


Figure 3. Reconstructed ion chromatogram of a typical gasoline sample.



Scan #	Compound(s)
973	2 + 1-EN
1006	2,6 + 2,7-DMN
1051	1,3 + 1,7 + 1,6-DMN
1105	2,3 + 1,4 + 1,5-DMN
1147	1,2-DMN
≈1270	$C_{13}H_{14}$
≈1293	$C_{13}H_{14}$
1315	2 + 1-iPN
1349	C_3-Naphthalene
≈1380	1,3,7-TMN
1394	1,3,6-TMN
1449	1,4,6 + 1,3,5 + 2,3,6-TMN
1496	1,2,7 + 1,2,6 + 1,6,7-TMN
≈1540	1,2,4-TMN
1563	1,2,5-TMN

Figure 4. Portion of gasoline chromatogram containing C_2 and C_3-Naphthalenes.



Scan #	Compound(s)
1386	1,3,7-TMN
≈1545	1,2,4-TMN
1572	1,2,5-TMN
1620	C_3 + C_4-Naphthalenes
1706	C_4-Naphthalene
1775	C_4-Naphthalene
1835	C_4-Naphthalene
≈1950	C_4 + C_5-Naphthalenes
2127	Phenanthrene

Figure 5. Portion of gasoline chromatogram containing C_3 to C_5-Naphthalenes.

necessity to check both fractions for the alkylnaphthalenes were two areas of major concern, so an alternative method was sought. Ultimately, concentration by room-temperature evaporation was employed since the boiling point of naphthalene, the first compound of interest, is 217 °C. After one week of evaporation, the solutions were very near the desired volumes of 100 mL. Through evaporation, not only was the sample concentrated, but at the same time, the low boiling compounds were removed.

The injection volume was also considered. Injection of 1µL of neat sample while using the splitless mode was enough to overload the column and distort peak shapes and retention times. Using the 10-µL syringe, any injection volume under 0.5 µL was difficult to reproduce. Therefore, most of the results were achieved using a 1.0 µL injection volume and a split ratio of 18:1. Other parameters such as zone temperature, initial temperature, ramp rate, separator temperature, and helium flow rate were varied. The final conditions used are listed in the Experimental Section.

Naphthalene, its two MN-isomers, the two ENs, and nine of the ten DMNs were found in all three grades of gasoline, although not all were totally resolved. The difficulty in the total separation of the ten DMN isomers is due in part to the narrow range (263 - 270 °C) of their boiling points. Since temperature-gradient GC is sometimes referred to as "simulated distillation", some overlap would be expected given such a narrow range. In addition, the eight substitution sites around the naphthalene ring are classified as either α or β, depending on their distance from the center carbons of the naphthalene ring. Substitution sites at the 1,4,5,and 8 positions are α sites, while positions 2,3,6, and 7 are the β sites. In general, the compounds which eluted together had similar substitution designations. Table 6 shows the trend of bonding sites versus the order of elution for some of the alkylnaphthalenes. Most of the time, alkylnaphthalenes with β-site bonds eluted before their α-site counterparts.

TABLE 6

ELUTION ORDER OF ALKYLNAPHTHALENES VERSUS BONDING SITES

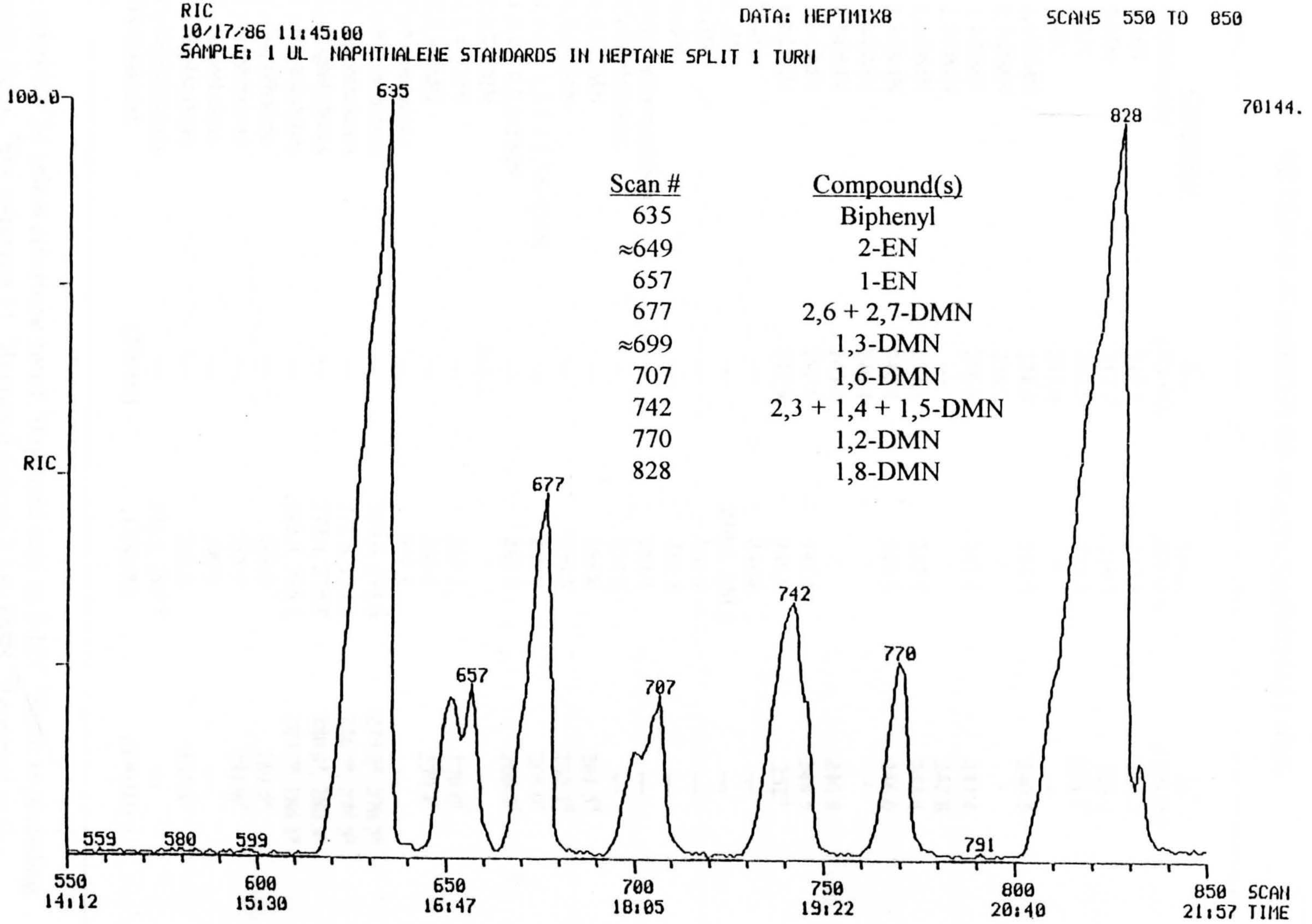
Component	Bond Site(s)
2-MN	β
1-MN	α
2-EN	β
1-EN	α
2,6-DMN	β,β
2,7-DMN	β,β
1,3-DMN	α,β
1,7-DMN	α,β
1,6-DMN	α,β
2,3-DMN	β,β
1,4-DMN	α,α
1,5-DMN	α,α
1,2-DMN	α,β
1,8-DMN	α,α
2-iPN	β
1-iPN	α
1,3,7-TMN	α,β,β
1,3,6-TMN	α,β,β
1,4,6 + 1,3,5 + 2,3,6-TMN	α,α,β α,β,α β,β,β
1,2,7 + 1,2,6-TMN	α,β,β α,β,β
1,6,7-TMN	α,β,β
1,2,4-TMN	α,β,α
1,2,5-TMN	α,β,α

To obtain the exact t_R for each compound, heptane solutions containing known naphthalene compounds were made and injected. Once the individual t_Rs were determined, then a heptane solution containing all the alkylnaphthalenes purchased was prepared and injected to see if the coeluting peaks could be slightly resolved from one another. A chromatogram of this heptane solution is shown in Figure 6. Spiking of the gasoline samples was also done in some cases to obtain and verify t_Rs in the sample matrix. From repeated injections, the t_R for each analyte, for which standards were available, was determined.

Since the t_R of a compound is dependent on the chromatograph, column, and operating parameters, a more meaningful expression, relative retention time (RRT), came into use. The RRT of a compound is a ratio of its t_R to the t_R of a standard compound. With the necessity of oven-temperature gradients for separations of PAHs and other complex mixtures, a more elaborate means of calculating a useful retention index was developed. In 1979 Lee et al.[31] reported a system which uses two or more aromatic ring compounds to bracket the compounds of interest. The equation for calculating the retention index of a compound is as follows:

$$I = 100\ [\ z + (t_{Rx} - t_{Rz})/(t_{Rz+1} - t_{Rz})] \qquad (9)$$

where I is the retention index, and z and z + 1 are the number of aromatic rings in the standard compounds. Standard PAHs like naphthalene, phenanthrene, and chrysene, with 2, 3, and 4 aromatic rings respectively, are used in this system. Table 7 lists the retention indices of the alkylnaphthalenes determined in this work using the heptane reference solutions (I_{std}), and the various gasoline (I_{sample})samples. The retention indices (I_{lit}) in the far right column are retention indices previously reported.[34,31] They were determined



Scan #	Compound(s)
635	Biphenyl
≈649	2-EN
657	1-EN
677	2,6 + 2,7-DMN
≈699	1,3-DMN
707	1,6-DMN
742	2,3 + 1,4 + 1,5-DMN
770	1,2-DMN
828	1,8-DMN

Figure 6. Chromatogram of alkylnaphthalenes in heptane solution.

TABLE 7

RETENTION INDICES OF ALKYLNAPHTHALENES

Component	I_{std}	I_{sample}	I_{lit}[a]
Naphthalene	(200.00)	(200.00)	(200.00)
2-MN	215.2	217.1	220.2
1-MN	217.7	219.3	223.2
2-EN	232.5	232.2	238.9[b]
1-EN	233.0	[c]	---
2,6-DMN	234.3	234.5	240.5
2,7-DMN	234.7	[c]	[c]
1,3-DMN	236.8	237.4	243.4
1,7-DMN	---	[c]	242.8
1,6-DMN	237.3	237.7	243.4
2,3-DMN	240.0	240.1	246.0
1,4-DMN	240.4	[c]	[c]
1,5-DMN	240.7	[c]	246.9
1,2-DMN	242.8	242.4	248.5
1,8-DMN	247.9	246.9	252[d]
$C_{13}H_{14}$	---	248.4	---
$C_{13}H_{14}$	---	249.0, 250.3	---
2-iPN	---	251.9	---
1-iPN	---	252.7	---
Ethylmethylnaphthalene	---	253.4	---
C_3-Naphthalene	---	254.8	---
1,3,7-TMN	---	255.8	261.5[d]
1,3,6-TMN	---	256.7	262.1[d]
1,4,6 + 1,3,5 + 2,3,6-TMN	---	259.9	265.0[e]
1,2,7 + 1,2,6-TMN	---	262.5	266.3[f]
1,6,7-TMN	263.2	[c]	---
1,2,4-TMN	---	265.1	270.0[f]
1,2,5-TMN	---	266.6	270.4[f]
C_3-Naphthalene	---	269.5	---
C_4-Naphthalenes	---	269.6, 271.0	275.2[g], 276.2[g]
C_4-Naphthalenes	---	272.8, 274.8	276.7[g], 279.5[g]
C_4-Naphthalenes	---	277.4, 278.8	280.4[g], 280.9[g]
C_4-Naphthalenes	---	282.5, 285.1	283.7[g], 286.1[g]
C_4-Naphthalene	---	288.8	289.5[g]
C_5-Naphthalene	---	289.5	294.8[h]
C_4-Naphthalene	---	290.5	---
C_5-Naphthalene	---	292.6	297.6[h]
C_4-Naphthalenes	---	293.2, 295.7	---
Phenanthrene	(300.00)	(300.00)	(300.00)

---

[a] See reference 34 unless otherwise noted.
[b] Reported only as 2-EN.
[c] Same as preceding retention index.
[d] See reference 31.
[e] Reported only as 2,3,6-TMN.
[f] Reported as C_3-Naphthalene.
[g] Reported as C_4-Naphthalene.
[h] Reported as C_5-Naphthalene.

using a 25 m capillary column with SE-54 as the stationary phase. Results from reference 31 were acquired using a 12 m capillary column coated with SE-52, a polyphenylmethylsiloxane very similar to SE-54.

When comparing the retention indices obtained in this work with those from the literature, one can see that the values determined here are lower. The MNs eluting near naphthalene differ by ≈3 units from the literature values. Although the ENs and the DMNs differ from their respective literature values by ≈6 units, the differences between each other within each list are nearly the same. The retention indices reported here had deviations from the mean of 0.1 to 0.4. If the peak shapes of the standards, naphthalene and phenanthrene, were skewed in one direction or the other giving false t_Rs, then the retention indices could be off slightly. However, an error in t_R of 1 minute for naphthalene or phenanthrene would be needed to create a difference of 6. Since these differences from the reported literature are obtained using both the results of the standard solutions as well as the gasolines samples, the error must be due to differences between the systems for which the equation cannot account, rather than experimental error. Initially, the differences were thought possibly to be from slower retention times caused from the ion source pressure of 0.40 torr when CI analyses were run. However, theoretically and experimentally, this was proved not to be the case considering the column head pressure used, and the fact that EI analyses gave similar retention indices. Comparisons between the retention indices for the C_3, C_4, and C_5-Naphthalenes are not very meaningful since the identities of those listed are not known. The values were arranged together in the table as a matter of convenience.

Identification and Quantitation

In addition to using the retention indices of the compounds for identification, the MS was used to help identify the unknown peaks. When using EI, the mass spectrum of each compound was searched against the National Bureau of Standards (NBS) reference library after scans were summed and corrections for the background were made. For most of the alkylnaphthalenes, the M^+ ion was the most abundant ion when using EI. As a result, mass chromatograms using the mass of the molecular ion were run. When interferences were nearby, mass chromatograms of ions with specific m/z ratios common to naphthalene and its alkyl derivatives were used. If structural information on the interferences was known, then mass chromatograms of ions found in the spectra of the interfering compounds were plotted out against the mass chromatograms of characteristic ions of the alkylnaphthalene compound. Figure 7 is an example of mass chromatograms used to track interfering compounds. In this CI run, the ions with specific m/z ratios (listed on the far left) are plotted against time. In this figure the $[M+H]^+$ ions for the C_3 and C_4-Naphthalenes are plotted along with the $M^{+\bullet}$ and $[M+H]^+$ ions of methyl and C_2-Biphenyls, and other aromatics with the same m/z ratios. Alkylbiphenyls, alkylfluorenes, and alkanes were the most common interferences encountered. The molecular weights of the interfering biphenyls are two amu less than the alkylnaphthalenes with the same number of carbon atoms, while the fluorenes are 4 amu less than the alkylnaphthalenes. When CI was used, the three most common ions were usually the $M^{+\bullet}$, $[M+H]^+$, and $[M+C_2H_5]^+$ ions. Figure 8 shows how mass chromatograms of these ions, for the C_3-Naphthalenes (mol wt 170), can be used to confirm their molecular weights.

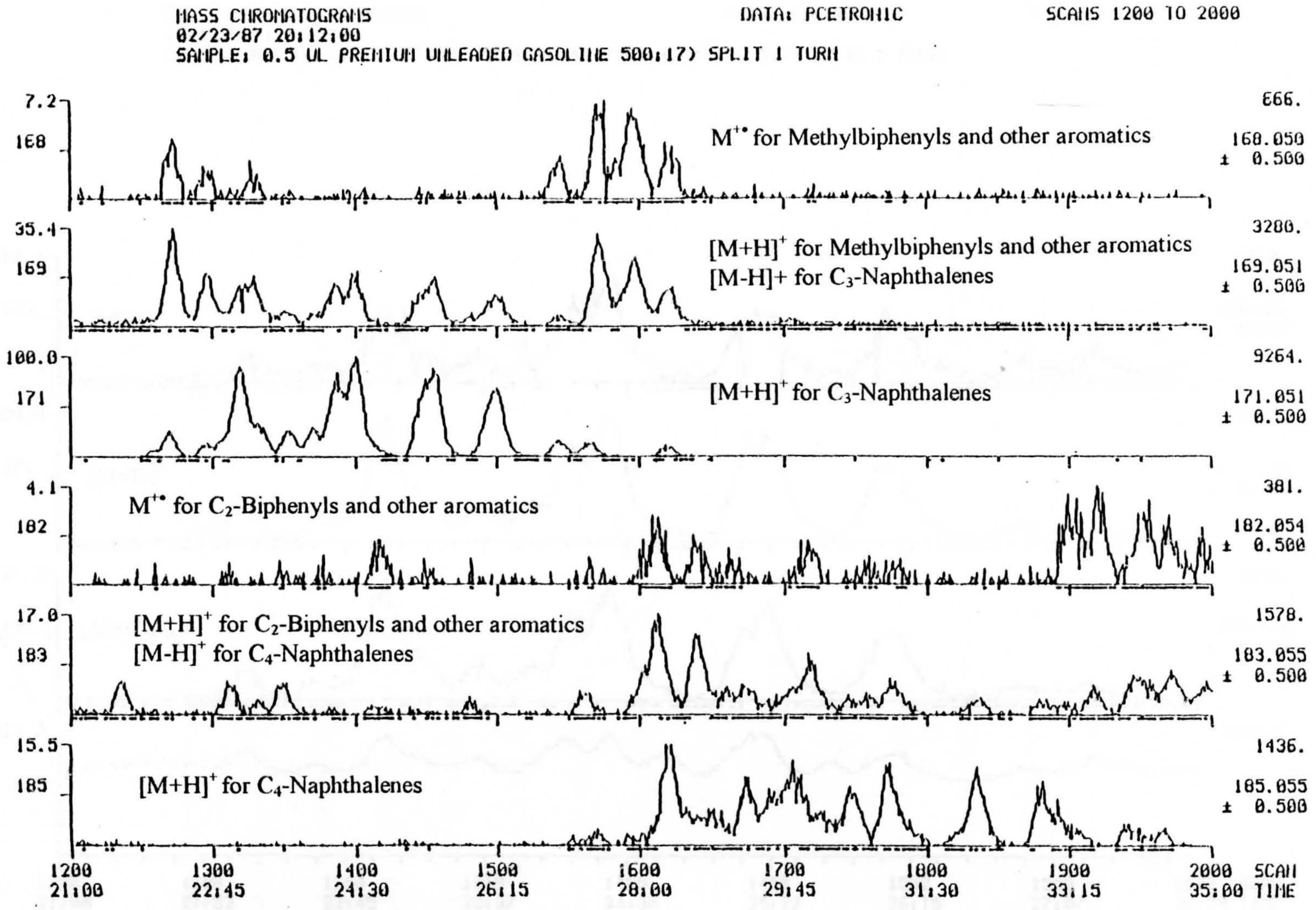


Figure 7. Use of mass chromatograms to track interfering compounds.

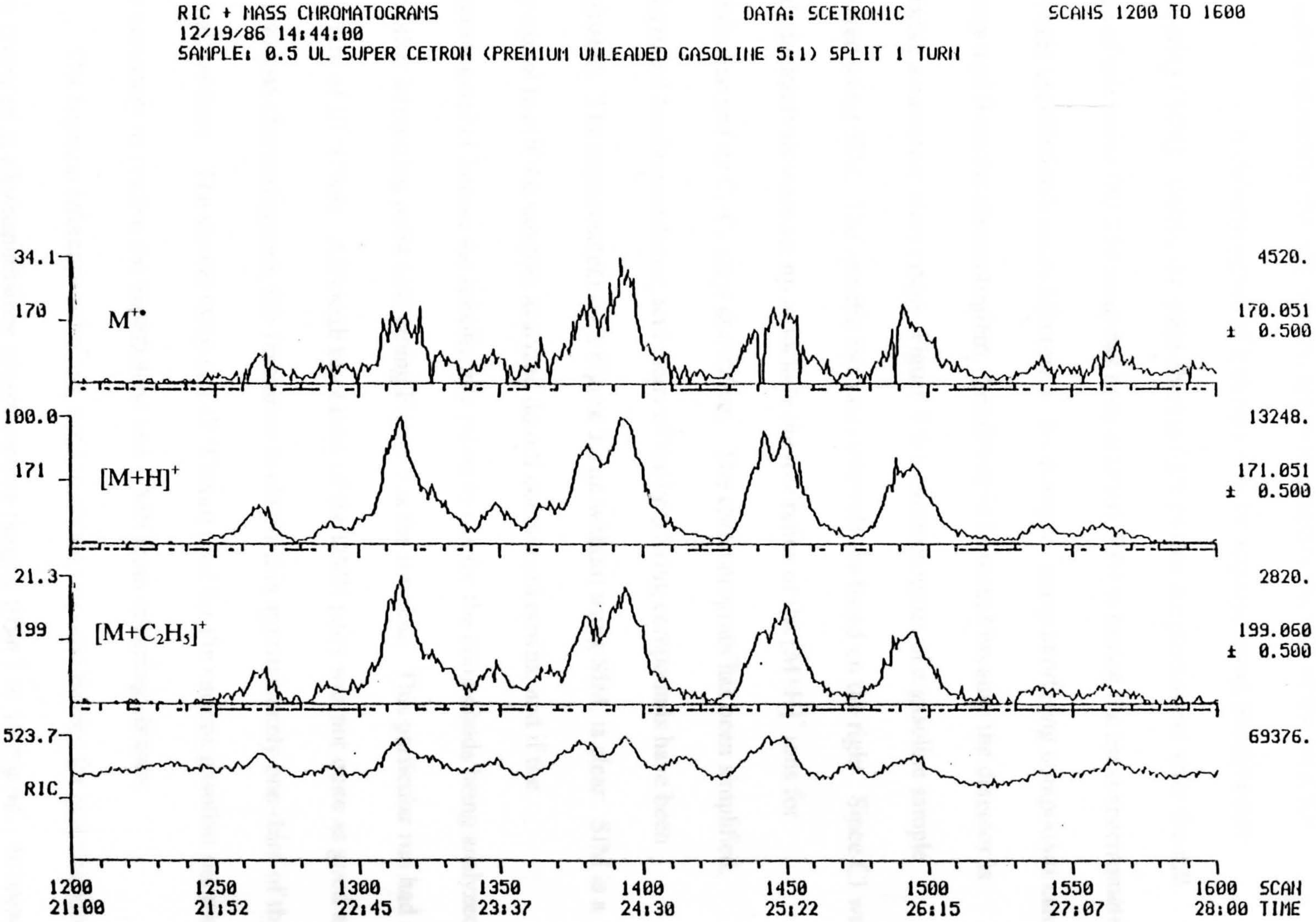


Figure 8. Use of mass chromatograms to confirm a compound's molecular weight.

A drastic improvement in the signal-to-background ratio is clearly seen when the specific m/z ratios, especially $[M+H]^+$ of 171, are plotted versus the plot of the total RIC.

A chromatogram of a sample may be acquired using selective-ion-monitoring (SIM). Unlike the mass chromatograms that are plotted out after the full range of m/z ratios (80-250 amu) has been scanned, SIM is having the mass spectrometer scan only specified m/z ratios of interest. By doing so, many interfering compounds can be removed from the chromatogram. Sensitivity is increased because the detector is scanning a narrower mass range. Figure 9 is a chromatogram of a gasoline sample acquired using SIM. The specific m/z ratio intervals are listed on the right. Since CI was used, the intervals were set up to include the m/z ratios of the $[M+H]^+$ ions for naphthalene and its C_1-C_5 alkyl derivatives. The chromatogram has been simplified, background has been reduced, and many of the interfering compounds have been eliminated. The improvement over Figure 3, run without using SIM, is clear. SIM is a very useful tool if the samples analyzed do not contain unknowns, and if the chromatographer knows the specific m/z ratios to use for the compounds being analyzed. One other interesting point concerning Figure 9 is the run time. This particular run had a ramp rate of 10 °C/min. Although resolution of the DMN pairs was not quite as good as the previous chromatograms, fair resolution is obtained in approximately one-third of the normal run time. The slower ramp rate (2 °C/min) used for the various gasoline samples was necessary to resolve the naphthalene and 1-MN from coeluting alkanes.

The heptane reference solutions, used to obtain response factors for quantitation, were prepared at alkylnaphthalene concentrations ranging from 1 to 10 mg/mL. In some cases, further dilutions were made. Using an injection volume of 1μL and a split ratio of

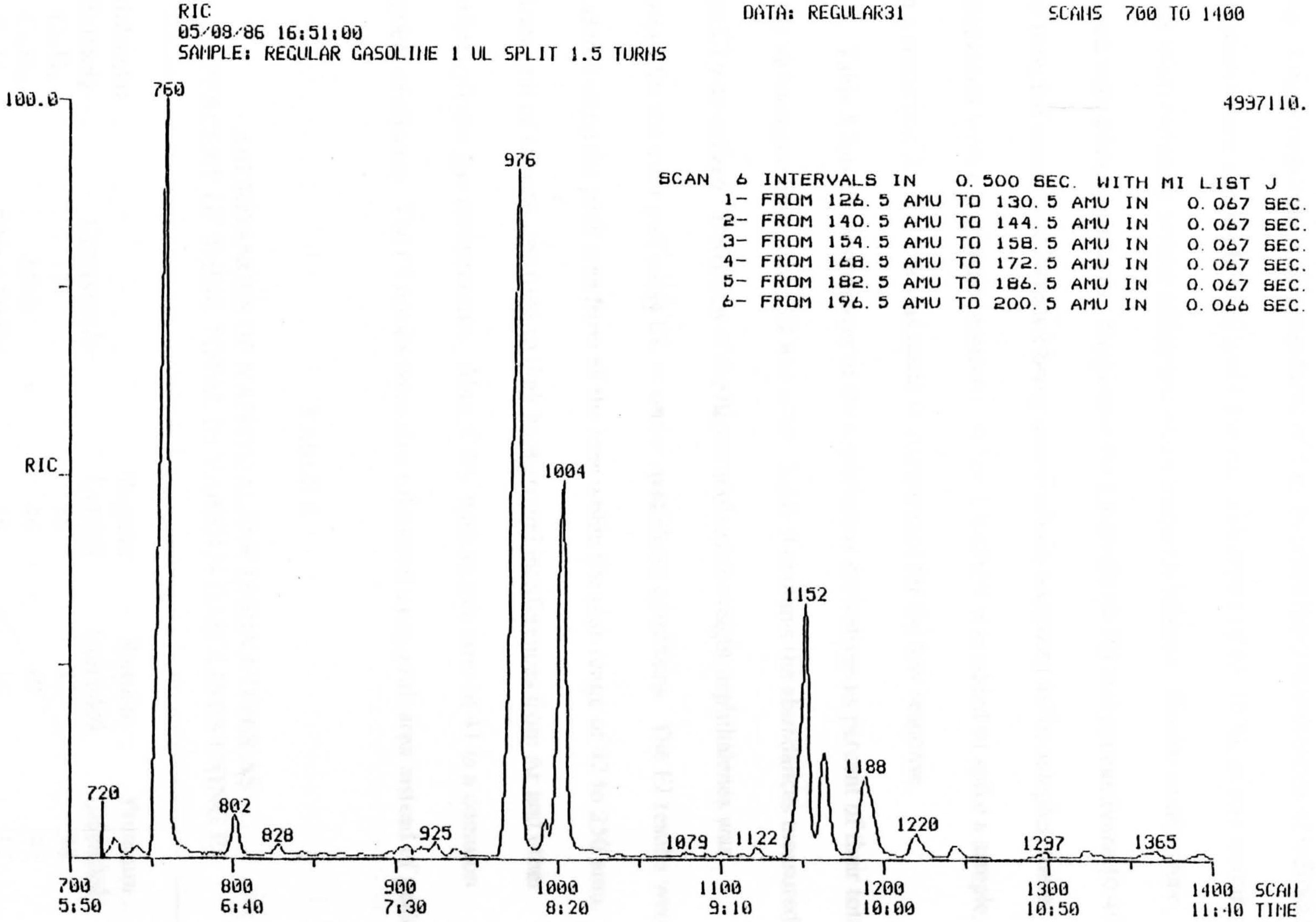


Figure 9. Chromatogram of gasoline sample using selective-ion-monitoring.

18:1, the amount of an individual compound reaching the MS could range from 0.5 to 500ng. Linear responses within standards of 1 to 10 times the concentrations of individual components were seen for both EI and CI work, with errors of +/- 10 %, as one would expect when weighing several milligrams on an analytical balance. Similar results were obtained with diluted standards. Responses for 1,8-DMN (0.70) and phenanthrene (0.40) were seen, but since these were not being quantitatively measured in the samples, these discrepancies were not of major concern. When 1,8-DMN was added to spike a sample, then a correction for the area was made to compensate for the low response.

Table 8 lists the abundances of the naphthalene derivatives as percent of their total for the various gasolines, when EI was used. Table 9 contains the abundances measured when CI was utilized. Detection of the higher molecular-weight naphthalenes was achieved for the most part using CI, or under specialized conditions. The EI results were calculated using the peak area from all the ions within the scan range of 42 to 250 amu. A bottom limit of 42 amu was used to limit background interferences from Ar and other possible cylinder gas contaminants. Also, $C_3H_5^+$ with an m/z ratio of 41 is a common fragment of alkanes. The CI results were also calculated using peak area instead of peak

TABLE 8

ABUNDANCES OF NAPHTHALENE DERIVATIVES AS PERCENT OF THEIR TOTAL IN VARIOUS GASOLINES USING EI

Molecular Formula	Compounds	Regular Leaded	Regular Unleaded	Premium Unleaded
$C_{10}H_8$	N	35	37	36
$C_{11}H_{10}$	MNs	46	47	47
$C_{12}H_{12}$	ENs + DMNs	19	16	17

height for ions with a m/z ratio between 80 and 250 amu. After rounding off to reflect the experimental error, there seem to be no major differences between any of the three grades of gasolines. The CI results are very similar with the exception of the regular leaded gasoline sample where the CI result for N was much lower than the EI result. Also, since CI has greater sensitivity than EI, Table 9 includes $C_{13}H_{14}$ and $C_{14}H_{16}$ compounds that were not detected by EI, or were omitted from Table 8 due to the poor reproducibility of the peak areas.

TABLE 9

ABUNDANCES OF NAPHTHALENE DERIVATIVES AS PERCENT OF THEIR TOTAL IN VARIOUS GASOLINES USING CI

Molecular Formula	Compounds	Regular Leaded	Regular Unleaded	Premium Unleaded
$C_{10}H_8$	N	26	33	35
$C_{11}H_{10}$	MNs	46	48	44
$C_{12}H_{12}$	ENs + DMNs	23	18	17
$C_{13}H_{14}$	iPNs + MENs +TMNs + unknowns	4	1	3
$C_{14}H_{16}$	MPNs + unknowns	1	0	1

The abundances of the alkylnaphthalenes as percent within their isomeric groups were calculated as well. Table 10 lists the abundances by percent determined using EI, while Table 11 gives the same results when CI was used. Within experimental error, the various grades of gasolines analyzed the same, whether by EI or CI. Interesting is the agreement of the distribution between the naphthalenes with the formula $C_{12}H_{12}$ and the literature results for crude oil[6,7] and coal tar.[35] Coal tar is a by-product formed when bituminous coal is heated in the absence of air. The agreement is also very good between the literature values for crude oil and the results measured here for alkylnaphthalenes with the formula $C_{13}H_{14}$. The abundances of alkylnaphthalenes as percent within their isomeric groups was also measured by EI and CI in some of the 5:1 gasoline samples, but again due to lack of reproducibility of the areas from the very small peaks, these results have been omitted.

TABLE 10

ABUNDANCES AS PERCENT WITHIN ISOMERIC GROUPS USING EI

Compound	Regular Leaded	Regular Unleaded	Premium Unleaded
$C_{11}H_{10}$			
2-MN	70	66	68
1-MN	30	34	32
$C_{12}H_{12}$			
2 + 1-EN	20	16	24
2,7 + 2,6-DMN	25	25	22
1,3 + 1,7 + 1,6-DMN	42	46	40
2,3 + 1,4 + 1,5-DMN	7	8	10
1,2-DMN	4	5	4

The abundances of the alkylnaphthalenes within isomeric groups were also compared to equilibrium mole fractions calculated by Alberty and Bloomstein[36] in 1985. According to their results, a 65/35 ratio of 2-MN/1-MN would result at a temperature of 298 K. If the formation of crude oil used to make these gasolines occurred near this temperature, and if no refining processes have significantly altered their distribution, then the absence of the 1,8-DMN isomer in these gasolines can be explained thermodynamically. The equilibrium mole fraction at 298 K for the 1,8-DMN isomer was calculated and found to be insignificant. Only at temperatures of 500 K and higher does the isomer begin to form. At 1000 K, its mole fraction is only 0.0013. This is one of the reasons that the 1,8-DMN isomer is being studied as a possible petroleum maturity indicator.[18]

TABLE 11

ABUNDANCES AS PERCENT WITHIN ISOMERIC GROUPS USING CI

Compound	Regular Leaded	Regular Unleaded	Premium Unleaded	Crude Oil[a]	Coal Tar[b]
$C_{11}H_{10}$					
2-MN	63	66	65	---	---
1-MN	37	34	35	---	---
$C_{12}H_{12}$					
2 + 1-EN	19	19	17	---	18
2,7 + 2,6-DMN	26	27	23	26	27
1,3 + 1,7 + 1,6-DMN	40	40	41	44	42
2,3 + 1,4 + 1,5-DMN	11	10	13	12	10
1,2-DMN	4	4	6	3	3
$C_{13}H_{14}$					
iPN	---	---	14[c]	---	---
Unidentified C_3-Ns	---	---	20[c]	---	---
1,3,7-TMN	---	---	10[c]	11	---
1,3,6-TMN	---	---	9[c]	15	---
1,4,6 + 1,3,5 + 2,3,6-TMN	---	---	23[c]	21	---
1,2,7 + 1,6,7 + 1,2,6-TMN	---	---	14[c]	10	---
1,2,4-TMN	---	---	7[c]	3	---
1,2,5-TMN	---	---	5[c]	4	---

[a] As reported by Kagi and colleagues in references 6 (DMNs) and 7 (TMNs). [b] See reference 35. [c] Results from premium unleaded gasoline sample concentrated 30:1.

The distribution of the TMNs was very close to the calculated[36] equilibrium mole fractions at 1000 K. Of the possible 32 alkylnaphthalene isomers that could exist with the formula $C_{13}H_{14}$, the ten TMNs found in the gasolines had the ten highest equilibrium mole fractions listed for 298 K. Eight isomers were calculated to be insignificant, with another thirteen at less than 0.2 %.

Complete quantitation of all the alkylnaphthalenes in the three gasoline samples was not a goal of this study, but a comparison of the alkylnaphthalenes among each other was. However, Table 12 gives the naphthalene w/w % of each of the different gasolines investigated. Once evaporated 5:1, the gasolines were spiked with the 1,8-DMN isomer. The samples were run using CI, and the peak areas from the total ion count were used to calculate the concentrations. The densities and colors of the original gasolines are also listed. Putting everything into perspective, the naphthalene and its alkyl derivatives ranged anywhere from 42 g/L for naphthalene down to mg/L levels for some of the trace $C_{15}H_{18}$ compounds found in the gasolines. Considering the size of the injection volume, nanogram quantities were being detected by the MS.

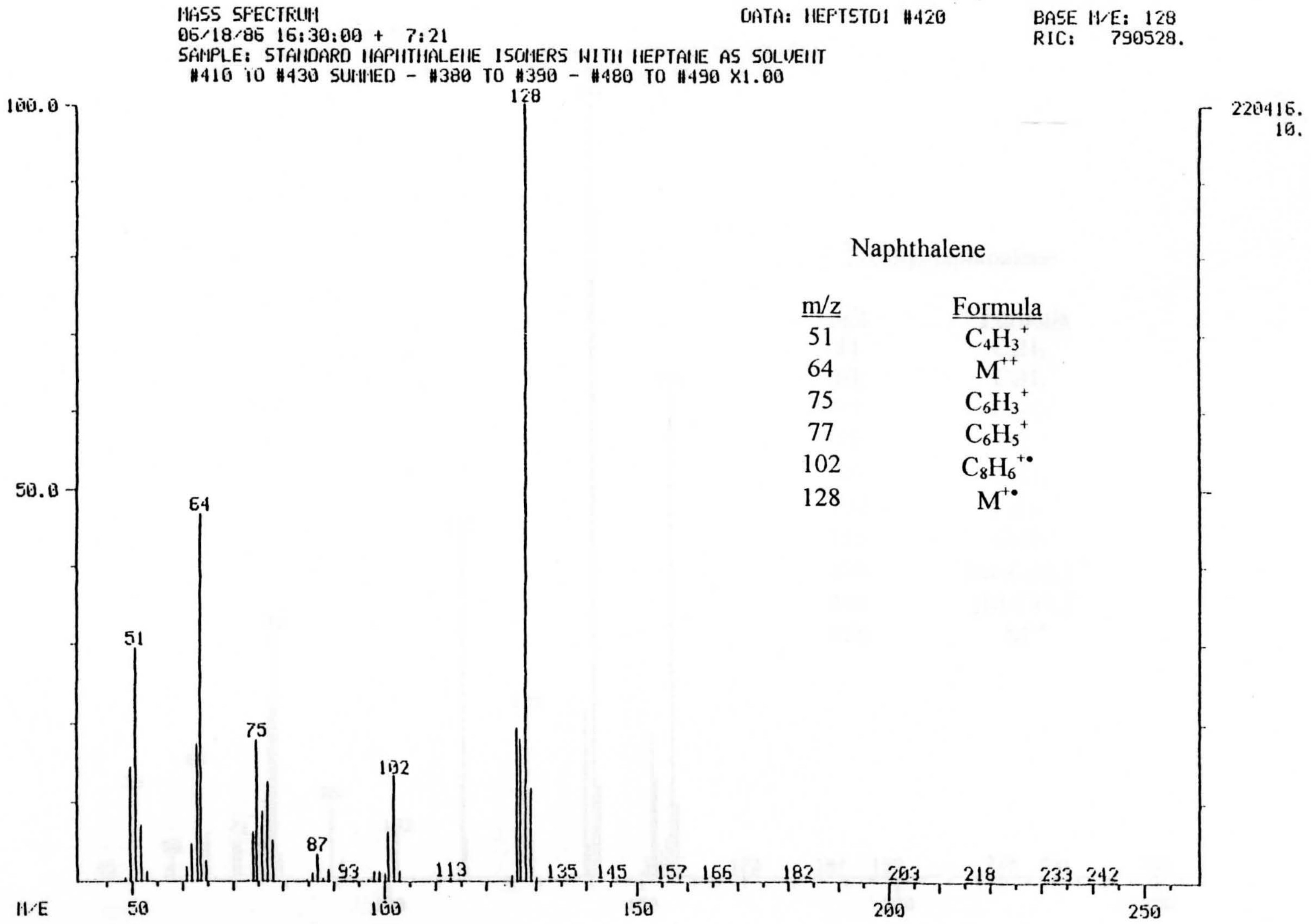
TABLE 12

DENSITIES, NAPHTHALENE W/W %, AND COLORS OF VARIOUS GASOLINES

Gasoline	Density g/mL	Naphthalene w/w %	Color
Regular Leaded	0.739	4.0	Orange
Regular Unleaded	0.730	5.8	Greenish-yellow
Premium Unleaded	0.711	2.7	Reddish-orange

EI Mass Spectra

When EI is used, the most abundant ion for naphthalene and many of its alkyl derivatives is the molecular ion, $M^{+\bullet}$. An EI mass spectrum of naphthalene is shown in Figure 10. The aromaticity of the ring helps to preserve its dominance of the ion fragments. It is easier to lose an electron from the ring than for one of the ring bonds to break. When the substituted alkyl group is an ethyl group or larger, the fragmentation occurs at the α-carbon of the alkyl chain, leaving a $C_{11}H_9^+$. Figure 11 is an EI spectrum of 2-EN which shows the largest ion fragment as $[M-CH_3]^+$ with a m/z of 141. Figure 12 is an example of 1,8-DMN where the $M^{+\bullet}$ ion is the most abundant ion since the single bonds connecting the methyl groups are harder to cleave than removing an electron from the ring. Table 13 lists the characteristic m/z ions of the alkylnaphthalene standards. There are several trends that are noticeable. All of the alkylnaphthalenes show considerable doubly charged molecular ions, as expected for PAHs.[37] A fragment of all the alkylnaphthalenes with the exception of 2-MN and 1-MN, $C_{10}H_8^{+\bullet}$ is also the molecular ion for naphthalene. The formation of the $C_{10}H_8^{+\bullet}$ ion from the ENs and the DMNs may be favored due to the willingness of the molecular ions to give up a molecule of ethylene. The $C_9H_7^+$ ion is found in all the compounds except for naphthalene. The latter gives either $C_6H_5^+$ or $C_8H_6^{+\bullet}$ depending on which two ring-bonds are cleaved. Hydrogen-atom loss is minimal for the two ENs. The loss of four hydrogen atoms from the ENs and DMNs is probably favored by the formation of hydrogen gas molecules (H_2), where the H-H bonds form as the C-H bonds break.

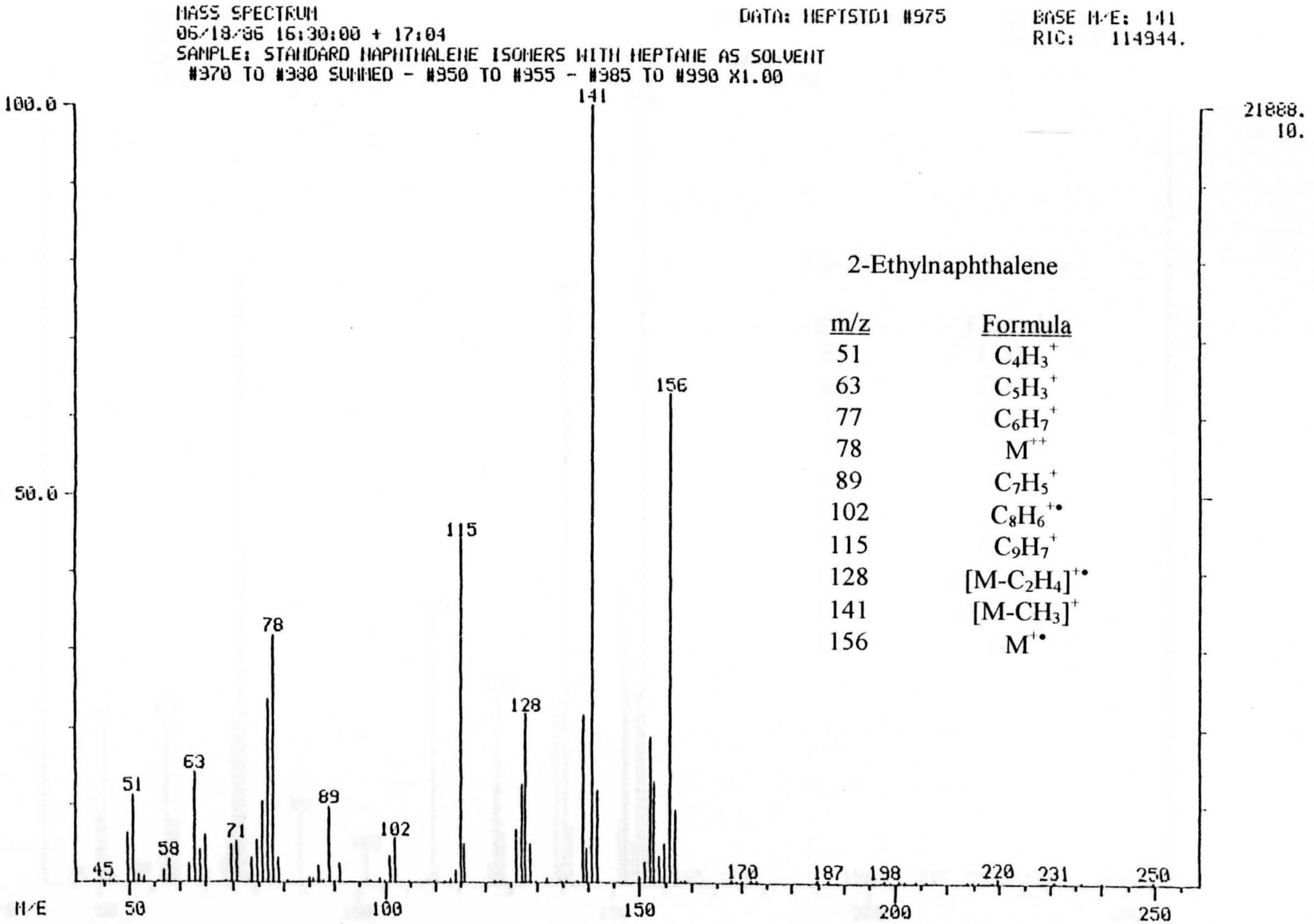


```
MASS SPECTRUM                                          DATA: HEPTSTD1 #420      BASE M/E: 128
06/18/86 16:30:00 +  7:21                                                       RIC:    790528.
SAMPLE: STANDARD NAPHTHALENE ISOMERS WITH HEPTANE AS SOLVENT
 #410 TO #430 SUMMED - #380 TO #390 - #480 TO #490 X1.00
```

Naphthalene

m/z	Formula
51	$C_4H_3^+$
64	M^{++}
75	$C_6H_3^+$
77	$C_6H_5^+$
102	$C_8H_6^{+\bullet}$
128	$M^{+\bullet}$

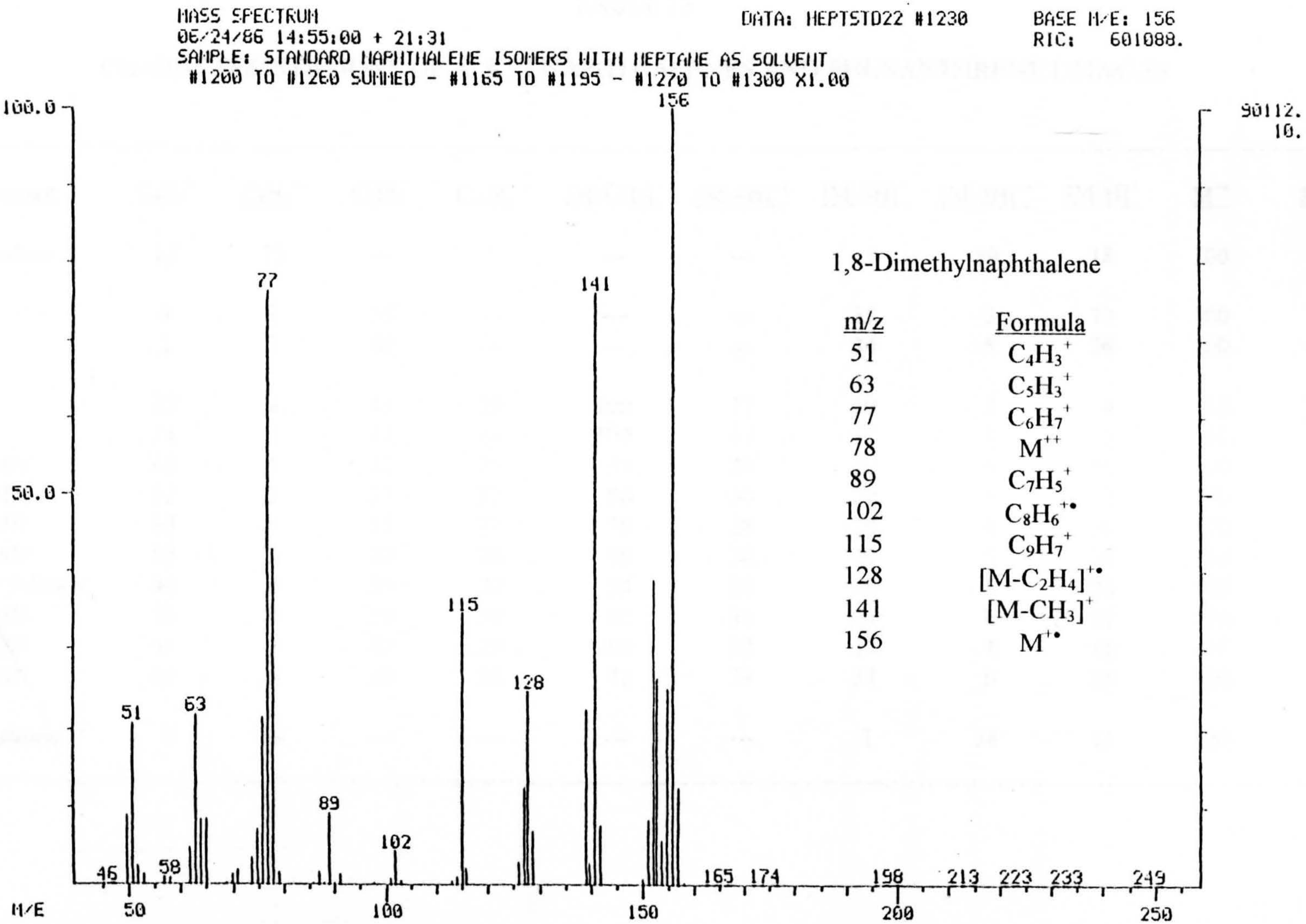
Figure 10. EI spectrum of Naphthalene



2-Ethylnaphthalene

m/z	Formula
51	$C_4H_3^+$
63	$C_5H_3^+$
77	$C_6H_7^+$
78	M^{++}
89	$C_7H_5^+$
102	$C_8H_6^{+\bullet}$
115	$C_9H_7^+$
128	$[M-C_2H_4]^{+\bullet}$
141	$[M-CH_3]^+$
156	$M^{+\bullet}$

Figure 11. EI spectrum of 2-Ethylnaphthalene



1,8-Dimethylnaphthalene

m/z	Formula
51	$C_4H_3^+$
63	$C_5H_3^+$
77	$C_6H_7^+$
78	M^{++}
89	$C_7H_5^+$
102	$C_8H_6^{+\bullet}$
115	$C_9H_7^+$
128	$[M-C_2H_4]^{+\bullet}$
141	$[M-CH_3]^+$
156	$M^{+\bullet}$

Figure 12. EI spectrum of 1,8-Dimethylnaphthalene

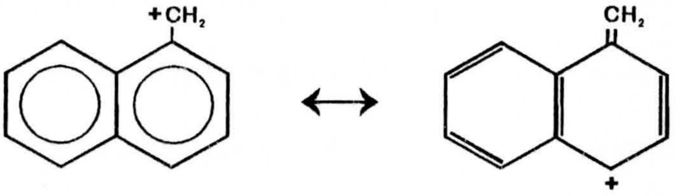
TABLE 13

CHARACTERISTIC IONS OF ALKYLNAPHTHALENES AND PHENANTHRENE USING EI

Component	$C_6H_5^+$	$C_8H_6^{+\bullet}$	$C_9H_7^+$	$C_{10}H_8^{+\bullet}$	$[M-CH_3]^+$	$[M-4H]^{+\bullet}$	$[M-3H]^+$	$[M-2H]^{+\bullet}$	$[M-H]^+$	$M^{+\bullet}$	M^{++}
$C_{10}H_8$											
Naphthalene	13	13	---	[a]	---	---	1	19	18	100	52
$C_{11}H_{10}$											
2-MN	6	1	55	---	---	---	35	3	73	100	77
1-MN	2	3	60	---	---	---	34	5	76	100	85
$C_{12}H_{12}$											
2-EN	23	4	43	20	100	17	10	2	4	58	33
1-EN	24	3	42	16	100	19	12	1	3	52	28
2,6-DMN	40	3	22	25	53	29	20	6	33	100	31
2,7-DMN	52	3	25	27	56	30	20	5	30	100	39
1,3-DMN	37	2	35	32	78	28	18	4	20	100	46
1,6-DMN	55	3	27	26	58	30	20	5	30	100	41
2,3 + 1,5-DMN	44	4	35	27	74	30	20	5	24	100	46
1,4-DMN	56	4	39	32	93	34	24	6	21	100	47
1,2-DMN	51	3	42	29	100	32	17	4	14	97	48
1,8-DMN	65	5	32	24	72	38	27	6	25	100	38
$C_{14}H_{10}$											
Phenanthrene	1	---	---	---	---	---	1	38	11	100	68

[a] See $M^{+\bullet}$

Competing with the formation of the molecular ion , formation of the $C_{11}H_9^+$ ion (m/z = 141) was very favorable for all the C_2-Naphthalenes and even the two MNs. In the case of the ENs, a loss of 15 amu resulted. As stated earlier, the ENs form the ion by way of the loss of a methyl group with the cleavage of the alkyl chain. In 1,2-DMN the $C_{11}H_9^+$ ion had the largest abundance, and was almost the most abundant ion for 1,4-DMN. From the MNs, a loss of $H^\bullet$ from the molecular ion occurs. The high abundance of the $C_{11}H_9^+$ ion may be due to its stability. With a CH_2^+ bonded to the naphthalene, the charge can be delocalized around the ring, as it is with a benzene ring,[38] but even more so because of the extra ring. There are at least six resonance structures that could exist for the $C_{11}H_9^+$ ion. Two of the structures are shown below.



(10)

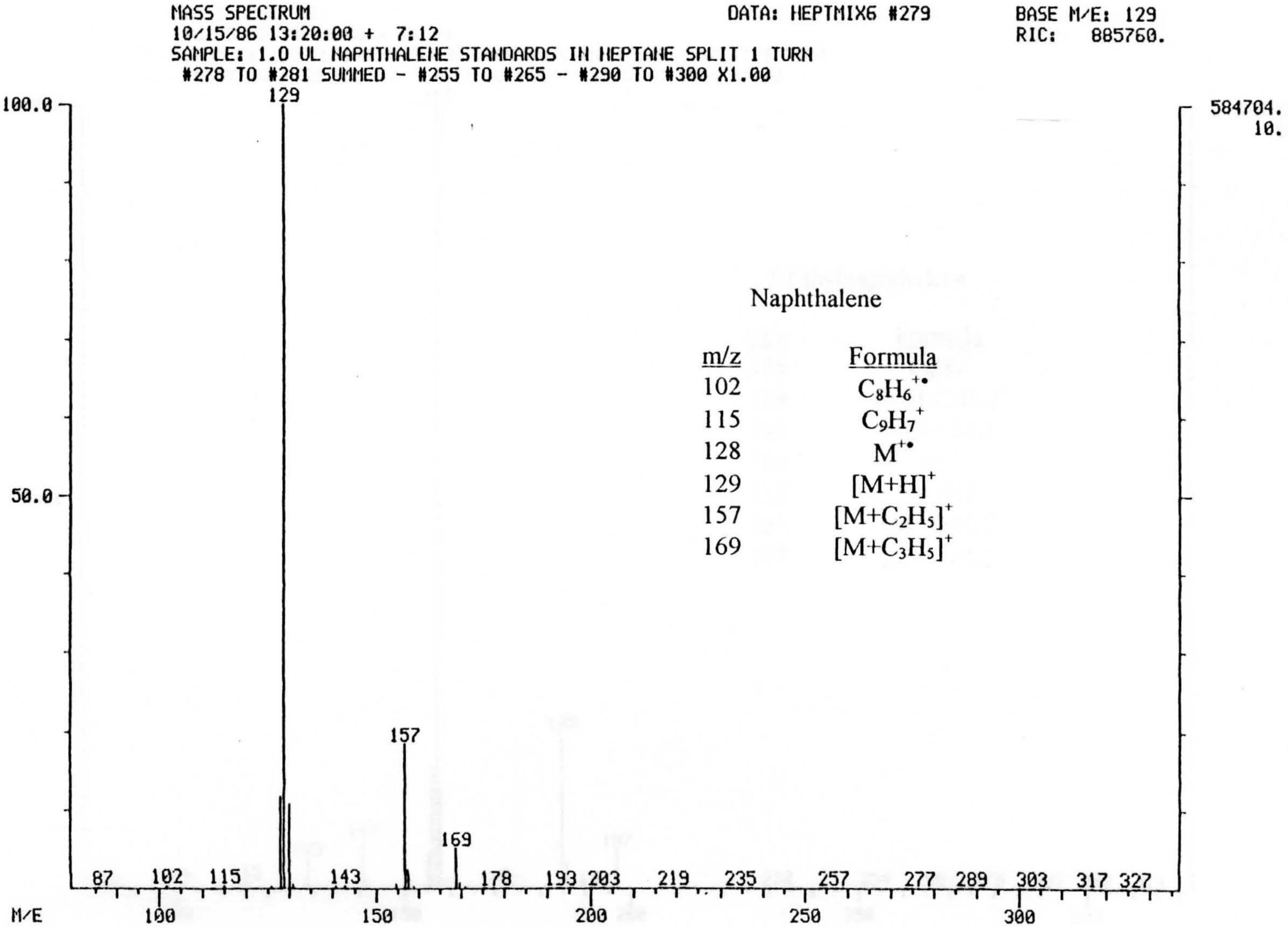
The formation of the isomeric benzotropylium ion (m/z = 141) may also be possible if the alkylnaphthalenes produce ions that rearrange in manners similar to the alkylbenzenes which form the highly-stable tropylium ion (m/z = 91).[38] Elimination of acetylene (26 amu) from the tropylium ion frequently occurs. The high abundance of the $C_9H_7^+$ ion (m/z = 115), common to all of the alkylnaphthalenes, may be due to the loss of acetylene from the $C_{11}H_9^+$ ion. If so, this trend would support the benzotropylium structure.

Also of interest is the comparison of naphthalene and phenanthrene. Both compounds have high abundances for their doubly charged molecular ion, as well as, high abundances of the $[M\text{-}2H]^{+\bullet}$ ion. The lack of formation of the lower m/z ions for phenanthrene also patterns that of naphthalene. It would be expected that phenanthrene would not have the same tendency to form some of the smaller ion fragments because of its size. However, ions with m/z ratios of 76, 150, 151, 152 were found for phenanthrene, although not reported in the Table 13.

CI Mass Spectra

As mentioned earlier, fragmentation of the sample molecules is minimized when ionization is the result of a chemical reaction. Having less excess energy, the protonated molecular ion is usually the most dominant ion formed. This proved true for the alkylnaphthalenes when methane CI was used. The $[M+H]^+$, $[M+C_2H_5]^+$, and $[M+C_3H_5]^+$ ions were all present in the spectra. Figures 13, 14, and 15 are CI spectra of Naphthalene, 2-EN, and 1,8-DMN, respectively. There is little fragmentation compared to their EI spectra in Figures 10, 11, and 12. In all cases, the protonated molecular ion was the ion of largest abundance. Because fragmentation is minimal when using CI, the molecular weight of an unknown can be determined much easier from its CI spectrum, than its EI spectrum.

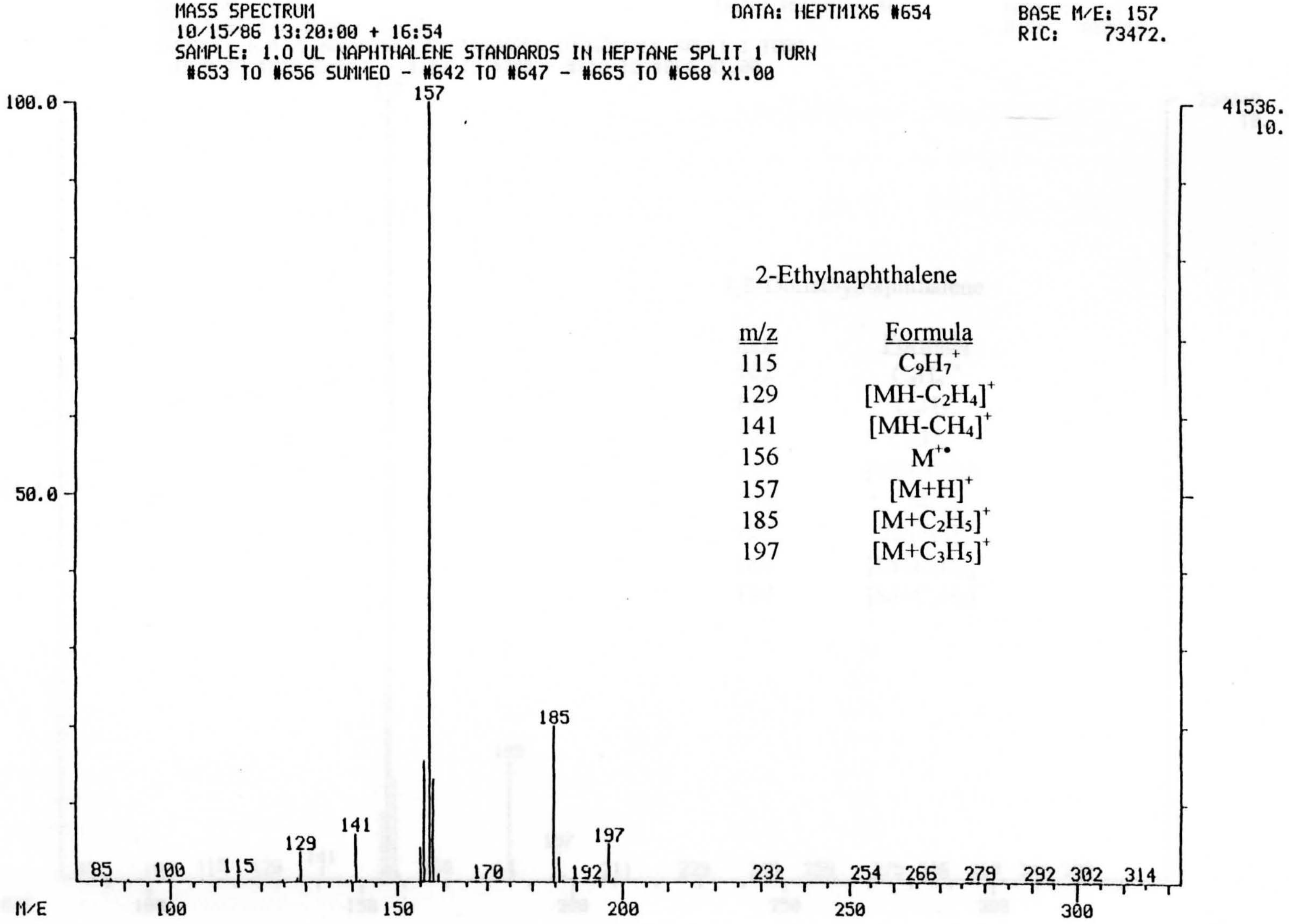
Table 14 is a listing of the alkylnaphthalenes with their ions and abundances, as determined in this study. There tends to be an increase in the abundance of the $M^{+\bullet}$ ion as the substitution of methyl groups on the ring increases. The CI work by Iseda[33] reported the same trend, but the abundance of $M^{+\bullet}$ from 2,3,6-TMN was 47.4 after the results were normalized to 100 for $[M+H]^+$. As reported here, singly-substituted naphthalenes, whether MN, EN, or iPN, all tended to have similar $M^{+\bullet}$ abundances. The increase in abundance of the $M^{+\bullet}$ ion as ring substitution increases is probably due to lower ionization energies of the molecules with multiple substituents. The more alkyl groups on the ring, the more electron donors there are. The cloud of electrons becomes more dense as the bonds to the ring increase, creating an electron-rich atmosphere. Hydride abstraction was lower for singly substituted naphthalenes than the DMNs and TMNs. The $[MH-C_2H_4]^+$ ion was only found with the MNs, ENs, and 2-iPN, and it was strongest for the ENs. The



Naphthalene

m/z	Formula
102	$C_8H_6^{+\bullet}$
115	$C_9H_7^+$
128	$M^{+\bullet}$
129	$[M+H]^+$
157	$[M+C_2H_5]^+$
169	$[M+C_3H_5]^+$

Figure 13. CI spectrum of Naphthalene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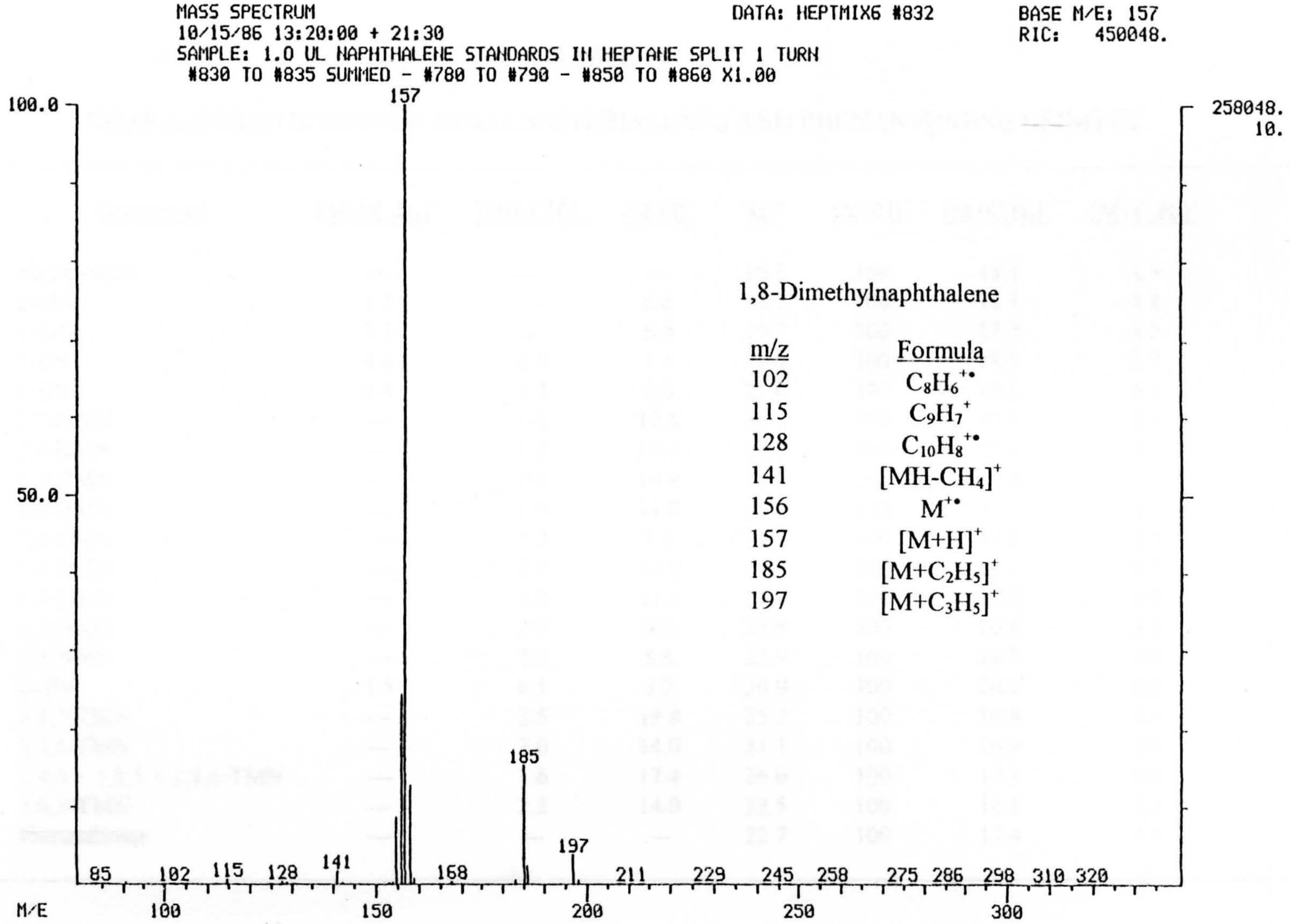
MASS SPECTRUM                                           DATA: HEPTMIX6 #654          BASE M/E: 157
10/15/86 13:20:00 + 16:54                                                            RIC:     73472.
SAMPLE: 1.0 UL NAPHTHALENE STANDARDS IN HEPTANE SPLIT 1 TURN
 #653 TO #656 SUMMED - #642 TO #647 - #665 TO #668 X1.00
```

2-Ethylnaphthalene

m/z	Formula
115	$C_9H_7^+$
129	$[MH\text{-}C_2H_4]^+$
141	$[MH\text{-}CH_4]^+$
156	$M^{+\bullet}$
157	$[M+H]^+$
185	$[M+C_2H_5]^+$
197	$[M+C_3H_5]^+$

Figure 14. CI spectrum of 2-Ethylnaphthalene



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MASS SPECTRUM                                           DATA: HEPTMIX6 #832        BASE M/E: 157
10/15/86 13:20:00 + 21:30                                                          RIC:    450048.
SAMPLE: 1.0 UL NAPHTHALENE STANDARDS IN HEPTANE SPLIT 1 TURN
 #830 TO #835 SUMMED - #780 TO #790 - #850 TO #860 X1.00
```

1,8-Dimethylnaphthalene

m/z	Formula
102	$C_8H_6^{+\bullet}$
115	$C_9H_7^+$
128	$C_{10}H_8^{+\bullet}$
141	$[MH-CH_4]^+$
156	$M^{+\bullet}$
157	$[M+H]^+$
185	$[M+C_2H_5]^+$
197	$[M+C_3H_5]^+$

Figure 15. CI spectrum of 1,8-Dimethylnaphthalene

TABLE 14

CHARACTERISTIC IONS OF ALKYLNAPHTHALENES AND PHENANTHRENE USING CI

Component	$[MH-C_2H_4]^+$	$[MH-CH_4]^+$	$[M-H]^+$	$M^{+\bullet}$	$[M+H]^+$	$[M+C_2H_5]^+$	$[M+C_3H_5]^+$
Naphthalene	---	---	---	16.1	100	18.4	4.9
2-MN	1.2	---	6.8	18.1	100	18.1	4.4
1-MN	1.3	---	6.4	19.7	100	17.7	4.3
2-EN	4.6	8.0	7.4	20.0	100	18.9	2.7
1-EN	5.4	7.4	6.0	21.0	100	18.5	4.1
2,7-DMN	---	1.8	12.8	26.3	100	17.5	3.9
2,6-DMN	---	1.8	14.6	27.8	100	17.4	3.7
1,3-DMN	---	2.3	10.9	26.5	100	16.8	3.6
1,6-DMN	---	1.9	11.0	26.1	100	17.1	3.7
2,3-DMN	---	2.2	8.9	24.1	100	17.2	3.7
1,4-DMN	---	2.7	13.2	29.4	100	15.5	3.2
1,5-DMN	---	1.9	11.3	27.4	100	17.1	3.8
1,2-DMN	---	2.9	9.0	25.8	100	16.6	3.7
1,8-DMN	---	2.2	8.8	27.9	100	14.7	3.4
2-iPN	1.5	6.1	3.2	20.9	100	20.0	3.8
1,3,7-TMN	---	2.5	19.8	25.2	100	18.4	5.3
1,3,6-TMN	---	2.0	14.0	31.1	100	16.9	3.9
1,4,6 + 1,3,5 + 2,3,6-TMN	---	1.6	17.4	26.0	100	17.1	3.6
1,6,7-TMN	---	2.3	14.0	32.5	100	16.1	3.2
Phenanthrene	---	---	---	22.7	100	17.4	4.0

formation of this ion from the singly substituted compounds is probably favored because of the loss of an ethylene molecule. The higher abundances of the $[MH-CH_4]^+$ ions for the ENs and 2-iPN are not surprising since these ions have the same m/z ratios as their respective $[M-CH_3]^+$ fragments found using EI. The 2-iPN would lose CH_4 from the branched alkyl chain in much the same way the methyl group would cleave from the isopropyl chain in EI. The stability of the $C_{11}H_9^+$ ion, which has an m/z ratio of 141, is favored again because of its ability to delocalize the charge around the rings. CI results for 1,6-DMN, 2-iPN, 1,3,7-TMN, 1,3,6-TMN, and phenanthrene were not previously reported by Iseda.[33]

CHAPTER V

CONCLUSIONS

Naphthalene and its alkyl derivatives have been analyzed in many different sample types over the past forty years. Since they are derived from petroleum, they are encountered in many products used in every facet of life. It was the boom in the petroleum industry that aided the progress of the instrumentation and techniques now used in today's applications. The first instrument of choice in the separation of such a complex mixture is the GC, because of the vapor pressures of the compounds in the mixture. Capillary columns have been used because of their tremendous resolving capabilities, which are needed when such complicated mixtures are explored. The coupling of the GC to an MS detector has given the chromatographer the powerful ability to detect and identify the smallest of quantities. The compositions of different gasolines have been previously investigated,[11,12] but the higher boiling compounds were of little interest. Previous analyses were typically concluded just as naphthalene began to elute, with higher boiling compounds ignored.

With growing environmental concerns over air and water pollution and interest from arson investigators, interest in these once overlooked components of gasoline has increased. Investigators of arson cases have begun to profile gasolines and other common accelerants for characteristic compounds[13,14,15] as a means of classifying them. As gasoline consumption continues to grow and use of fossil fuels for heating continues, releases of these alkylnaphthalenes into the environment continue as well. Studies have been done on specific groups of alkylnaphthalenes in various petroleum fractions. The DMNs have been analyzed in crude oils,[6] coal tars,[35] and complex fossil fuel mixtures,[39] while the TMNs have been examined in crude oil[7] as well. Analyses of a range of alkylnaphthalenes have been done in coals,[8,9] coal tars,[40,41] diesel fuel,[34] and kerosene,[5] but interest in gasolines[13, 14, 15] is fairly new. The purpose of this study was to develop an analytical method using GC/MS to determine the alkylnaphthalene components of various grades of gasolines, and to compare the compositions of each grade with one another. The traditional, EI, and CI modes of ionization were to be used, and the spectra obtained were to be examined for trends. Retention indices were to be determined and compared with any existing literature data. The abundances of the isomers within their isomeric groups were to be calculated, along with overall abundances of the alkylnaphthalenes within themselves. Percentages of abundances within isomeric groups were to be compared with literature from crude oils and coal tars, and thermodynamic data.

Naphthalene through C_5-Naphthalenes were detected, with concentrations ranging anywhere from 42 g/L for naphthalene, down to mg/L levels for some of the $C_{14}H_{16}$ and $C_{15}H_{18}$ compounds. The overall abundances of the naphthalene derivatives as percent of their total in the regular leaded, regular unleaded, and premium unleaded grades were nearly the same within experimental error for EI results. When CI results of the different grades are compared, there is agreement between the two unleaded grades, and agreement between the $C_{11}H_{10}$ fraction of all three grades. However, there is a difference of ≈ - 8 % (26 % versus 34 %) between the naphthalene ($C_{10}H_8$) portion of the regular leaded and the two unleaded grades. In addition, to offset the negative loss, there is a difference of ≈ + 5 % (23 % versus 18 %) between the $C_{12}H_{12}$ fractions of the regular leaded and the two unleaded grades. Except for the results of the regular leaded grade, there is close agreement between the EI and the CI results. The values differ slightly due to the greater sensitivity of CI. The abundances for the $C_{13}H_{14}$ and $C_{14}H_{16}$ derivatives were not reported in the EI results because peak areas were too low for consistent results.

The abundances as percent within the isomeric groups were also very similar. The CI results for the three different grades were the same within experimental error. Although the EI results within themselves were not as close as expected, when compared to their respective CI results, the differences were quite less. Comparisons with reported distributions of the ENs and DMNs, and the TMNs in coal tar[35] and crude oil[6,7] are strikingly similar. This would suggest that the refining processes of gasoline from the crude oil in these cases have little effect on the distributions of the individual compounds for these higher boiling components. There were also agreements between the mole ratios of the two MNs and the TMNs, with calculated thermodynamic data.[36] Comparisons of the equilibrium mole fractions tend to show that once the compounds are formed at a given temperature, the equilibrium mole fractions take a very long time to adjust to the mole fractions of newer temperatures. Otherwise, the pure compounds would equilibrate to the mole fractions of their present temperature. The absence of the 1,8-DMN isomer from the gasolines samples also agreed with its predicted equilibrium mole fraction.

Identification of the alkylnaphthalenes was achieved using several methods. The EI spectra were used with the NBS reference library to determine structural information.

The molecular weights of the compounds were obtained from the CI spectra. Spiking of the samples with standard compounds was done to confirm elution order and t_R. Mass chromatograms in both EI and CI analyses were plotted to track interfering compounds and to confirm the molecular weights. Previous works were used to establish elution order of compounds when standards and spectra were inadequate. Retention indices were determined for twenty identified alkylnaphthalenes. Eighteen additional retention indices were determined for either coeluting compounds or unidentified alkylnaphthalenes. Retention indices were reported for at least twelve additional compounds that were previously not reported.

Finally EI and CI mass spectra were obtained. As expected, the majority of the alkylnaphthalenes have the $M^{+\bullet}$ ion as the ion of highest abundance. The ability of the aromatic ring to delocalize the charge minimized fragmentation of the parent molecule, allowing the molecular weight of the compound to be determined from the EI spectra. The exceptions are 1,2-DMN, the two ENs, the two iPNs, and ethylmethylnaphthalene. As the length of the substituted alkyl chain increased, the base peaks of the compounds were fragments with losses of $CH_3^\bullet$ and $C_2H_5^\bullet$. The formation and unusual stability of the $C_{11}H_9^+$ (m/z = 141) ion was discussed. The high abundance of the doubly charged molecular ion for these aromatics was also seen as expected.

The CI spectra were compared with previously reported CI spectra.[33] The same general trends were seen. As expected, the protonated molecular ion was formed from the alkylnaphthalenes, as well as the $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$ reagent-gas adducts. The abundance of the $M^{+\bullet}$ increased as the number of alkyl groups was added to the ring.

Hydride abstraction was generally larger for the higher substituted compounds. Methane CI spectra were reported for five previously unreported compounds.

Looking back on this work, there are several areas of concern that may have effected the quantitation results. First of all, with the wide range of concentrations of alkylnaphthalenes in the samples, the linearity of responses from g/L to mg/L levels used probably does not exist. The response factors for the unknown alkylnaphthalenes were assumed to be one, equal to the ones for which there were standards available. Also, evaporating the samples to concentrate them may have discriminated against some of the lower boiling compounds. The sample that was concentrated 30:1 with some heating did show signs of naphthalene loss. However, the abundances of the compounds within the isomeric groups were still in agreement with the less concentrated samples. Quantitation of the alkylnaphthalenes using peak areas from the total RIC for some of the smaller peaks was inaccurate, due to coeluting compounds. The mass chromatograms were useful in tracking interferences, but subtraction of overlapping peak areas was difficult to do.

Since interest in the analysis of alkylnaphthalenes is ongoing in the forensic and environmental fields, several areas where improvements can be made include the concentration of the samples, quantitation using SIM, and use of different stationary phases. Recent work involving the analysis of trace aromatics in alkane solutions used a silica gel column on a liquid chromatograph to separate the aromatics. After evaporation of the solvent, the samples were analyzed by GC.[42] Quantitation using SIM could be used once the identities of the compounds of interest are established. For routine analyses where unknowns are not of concern, CI-SIM would not only improve the sensitivity, but also eliminate the errors in quantitation from coeluting peaks, since the area is from only the m/z ratios specified before the run. To confirm peaks that are coeluting, a series of stationary phases could be run. In past work done with the alkylnaphthalenes, chromatographers have used several columns with different stationary phases to achieve separations of the different isomers. The elution order would change from one column to the next, resolving a different pair that could not be resolved on a prior stationary phase.

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