

Supplemental Material for Online Publication

Student Handout

Scenario

A woman is sitting in her home reading, and lifts her head for a moment to gaze out the window. Surprised, she sees smoke emerging from the window of a neighboring home. The woman dials 911 and evacuates her own home as, within minutes, the neighboring house is engulfed in flames. As neighbors begin to cautiously approach the scene of the fire to investigate or offer help, an individual sprints past them heading in the opposite direction. A second call is made to the police, who are quickly approaching the scene. An officer in a cruiser spots the individual, pulls over, and inquires about his motive for fleeing the scene. The individual replies that he was scared, and running to get help. Yet the officer is suspicious of his behavior, as most witnesses remained at the scene and dialed 911 from cell phones. The individual is taken in for questioning, and his clothing is taken as evidence. A stain is found on his shirt, which he claims he got while filling his lawn mower with gasoline.

After investigation the fire was found to be arson – a canine has detected traces of accelerant on a burned carpet sample that has also been recovered and sent to the lab for analysis. Your job is to use gas chromatography-mass spectrometry (GC-MS) to determine the identities of the accelerant on the carpet sample and the stain on the suspect's shirt and make a comparison. **Is the suspect innocent or guilty?**

Pre-lab assignment

1. Read appropriate pages in your textbook
2. Read the Background section below.
3. Complete Table 1 by calculating the molar masses of common fragments observed in the mass spectrum (MS) of straight chain alkanes.

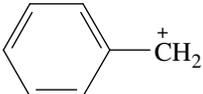
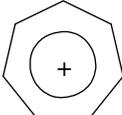
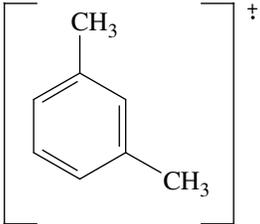
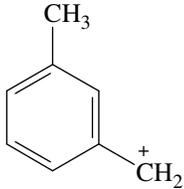
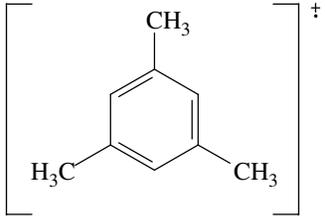
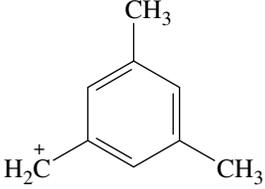
Table 1. Molar Masses of Common n-Alkane Fragments.

Ion	Molar Mass
$\text{CH}_3\text{-CH}_2\text{-CH}_2^+$	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	

4. What is the difference in molar masses between successive n-alkane fragments in Table 1?
How would you expect this to be reflected in the mass spectra of n-alkanes?
5. What is the formula for an alkane whose molar mass is 394?
6. What is the carbon range (minimum and maximum number of carbons in molecules) for an alkane sample whose molar mass ranges from 128-394?

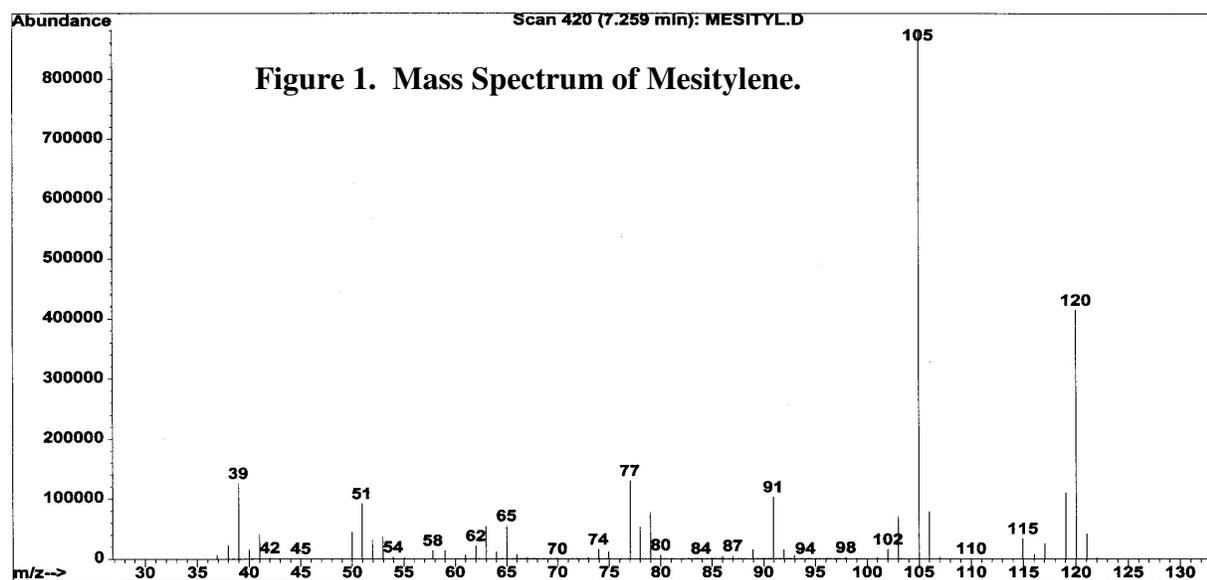
7. Copy and complete Table 2 by giving the molar masses of common fragments observed in the MS of aromatic compounds.

Table 2. Molar Masses of Aromatic Fragments.

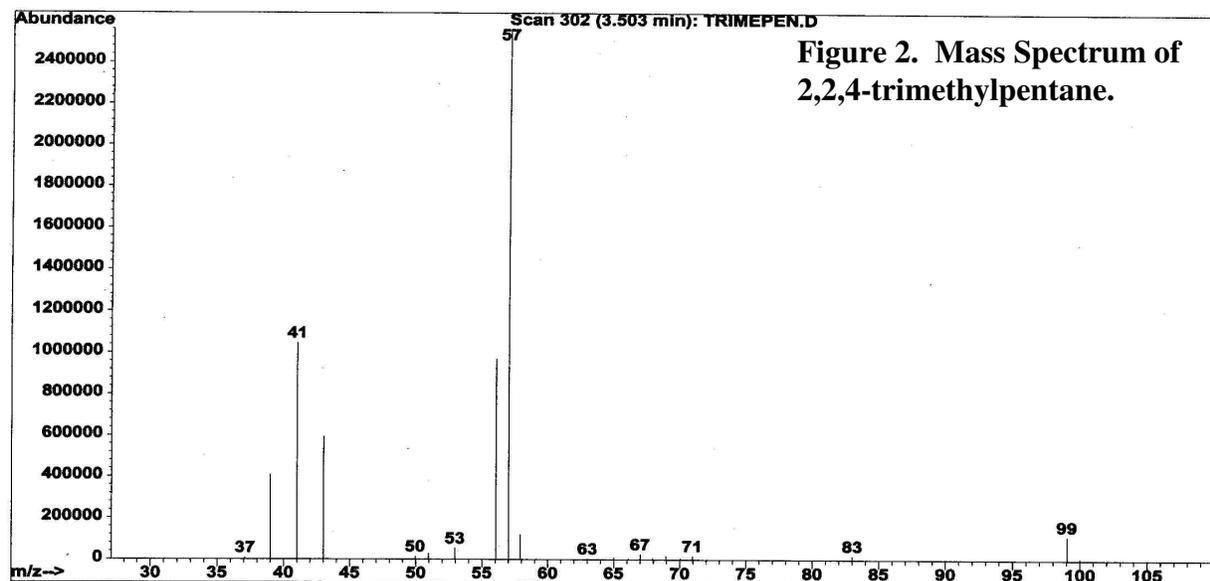
Fragment	Molar Mass
	
	
	
	
	
	

8. The ion-extracted chromatogram for a sample shows that it contains abundant alkanes and aromatics. One of the earliest eluting peaks has a mass spectrum with a molecular ion of 100 and one of the latest eluting peaks has a mass spectrum with a molecular ion of 134. What is the approximate carbon range for the sample?

9. Identify as many fragments as you can in the mass spectrum of mesitylene (Figure 1).



10. Identify at least three fragments in the mass spectrum of 2,2,4-trimethylpentane (Figure 2).



Background

Gas Chromatography-Mass Spectrometry (1, 2, 3)

In this experiment you will be analyzing a sample by gas chromatography/mass spectrometry (GC-MS). GC-MS is a tandem instrumental technique that allows mixtures to be separated and individual components to be identified.

Your sample will be injected into the gas chromatograph through an inlet system. As in all chromatography there is a mobile phase (in this case helium gas) and a stationary phase (Supelco MDN-5 fused silica capillary column). As the sample is injected, it is vaporized and enters the column as a gas. If the sample is a mixture, the individual components will spend different amounts of time either in the gaseous phase or adhered to (dissolved in) the stationary phase, allowing them to be separated and thus exit the column at different times.

The time required for the sample to elute (travel from the injection point to the end of the column) is referred to as the retention time. The retention time for a given compound depends upon the relative strength of interaction between the compound and the stationary phase, as well as the boiling point, molar mass, and molecular shape of the compound. In general, the greater the affinity of a compound for the column and the higher the boiling point, the longer the retention time. For compounds of similar molar masses, polar compounds will interact more strongly with polar columns while nonpolar compounds will interact more strongly with nonpolar columns. For compounds of similar polarities, those with higher boiling points (due to larger molar masses and/or increased surface area leading to increased dispersion forces) will have longer retention times.

In order to determine retention times, a detector must be used to observe when the sample is eluting. The detector senses the compounds and produces a chromatogram displaying a peak at the time the compound exits the column. (Note: The instrument is called a *chromatograph*, the output is called a *chromatogram*). A variety of types of GC detectors may be used including thermal conductivity (measures change in conductivity of a wire), flame ionization (measures change in conductivity of a flame) or mass spectrometry (measures abundance of particles after ionizing).

We will be using a mass spectrometer as the detector in this experiment. Mass spectrometry has an advantage over the other types of detectors in that it can be used not only to determine the presence/abundance of compounds as they elute from the column, but also to determine the molar mass and even the specific identity of compounds using their mass spectra.

As each compound exits the column it enters a high-vacuum ionization chamber of the mass spectrometer where it is bombarded by a ray of very high-energy electrons. The electrons slam into the molecules (M) of the compound and in the process of bouncing off, can knock an electron from a molecule, leaving behind a radical cation, $M^{\bullet+}$, which contains both an unpaired electron and a positive charge. This radical cation, often called the molecular ion, has the same molar mass as the original compound but is very high in energy and very unstable. Because of its instability, during its journey from the ionization chamber to the detector, the molecular ion will frequently rearrange or break apart into smaller cations called *fragments*, with concomitant formation of neutral (uncharged) radicals or small, neutral stable molecules. Indeed, while numerous neutral fragments can form in the mass spectrometer, they are not observed since this technique only detects charged particles. Note that while some molecules of a particular

compound may fragment one way, others may fragment another or not at all; thus in a single spectrum the molecular ion and multiple fragments may be visible.

The type of MS used most frequently in GC-MS instruments uses a quadrupole mass filter, which uses electric fields to separate particles based upon their mass-to-charge (m/z) ratio. This type of mass spectrometer offers lower resolution than magnetic sector instruments which use magnetic fields, but is much more compact and much less expensive.

All charged particles (either the molecular ion or fragment cations) from the ionization chamber enter the quadrupole mass filter. The quadrupole consists of four rods, which act as two pairs of electrodes. Direct current (DC) and radio frequency (RF) voltages of varying magnitudes are applied across each pair of electrodes, creating an electric field through which the ions can move; however their trajectories are not linear, but involve complex oscillations. For a given set of voltages, only an ion with the correct mass-to-charge ratio (m/z) will have the correct oscillations to be able to make it through the mass filter and reach the detector. The instrument varies the voltages and RF frequencies such that eventually a specified range of masses (based on calibration standards) will reach the detector. The strength of the signal for a given m/z depends upon the number of those particles reaching the detector (ion abundance). The mass spectrum is displayed to the user as a plot of abundance versus m/z . (Although not always true, in most cases, the charge of the ion is assumed to be one, so that the mass can be directly determined). The specific distribution of fragments and their relative abundances is called a *fragmentation pattern*. The *base peak* is the most abundant peak in the mass spectrum. It may be either a fragment or the molecular ion.

From the mass spectrum, molar mass and structural information can be obtained for a given compound. The peak with largest m/z is often the molecular ion. However, it is important

to note that the molecular ion for every compound is not always observable because every molecule of the compound may fragment before it reaches the detector. In such cases, it may be difficult (but not impossible) to get molar mass information.

In both the presence and absence of a molecular ion, more detailed structural information can be determined from the fragmentation pattern. Each compound will exhibit a specific fragmentation pattern, resulting from how often cleavage of specific bonds in the molecules of the compound occur. Bonds that are more readily cleaved often lead to more abundant (sometimes more stable) ions. A knowledge of bond cleavage that can occur for specific classes of compounds can be used to examine fragmentation patterns and deduce structural information. In this experiment, we will use this information to classify hydrocarbon accelerants.

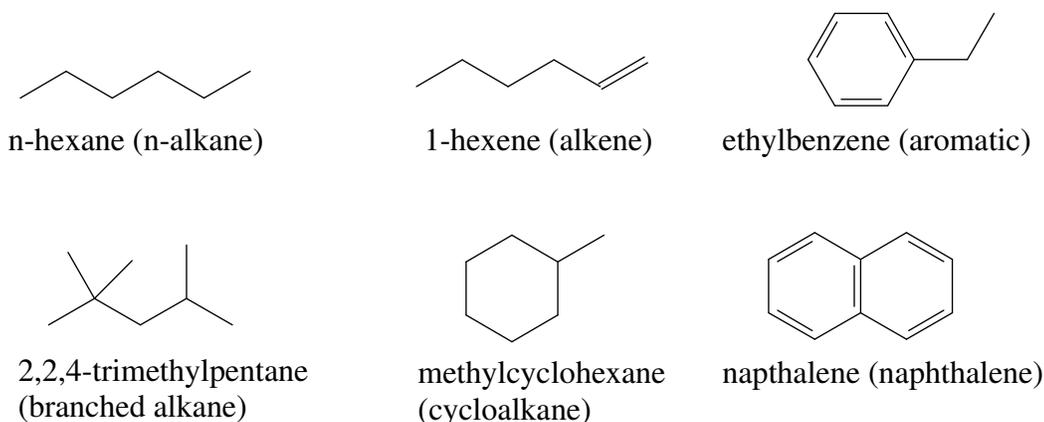
Hydrocarbon Accelerants

Most accelerants are organic in nature, and many of them are organic hydrocarbons. Hydrocarbons may be further classified into a variety of subgroups. Some of the hydrocarbon classes found in accelerants include: alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons. Accelerants may also include a variety of functional groups including alcohols (such as methanol or ethanol), ketones (such as acetone or methyl ethyl ketone), and ethers (such as diethyl ether). These are often difficult to detect and characterize and we will not be looking for them in this experiment.

The general formula for an acyclic alkane is C_nH_{2n+2} where n represents any integer greater than or equal to 1. Acyclic alkanes may be further distinguished as straight chain (or n -) alkanes and branched alkanes. The general formula for a cycloalkane (containing only one ring) or alkene (containing only one double bond) is C_nH_{2n} . Many, but not all aromatic hydrocarbons

in accelerants contain at least one benzene ring; naphthalenes, which are also encountered in some accelerants, contain two fused benzene rings with one side in common. Examples of all of these types of hydrocarbons are given in Figure 3.

Figure 3. Examples of Some Hydrocarbons.



The mass spectra of these compounds will provide both molar mass and structural information about the components present in a given accelerant.

Mass spectra of n-Alkanes (2)

Molecular ions of many alkanes are readily observable in the mass spectrometer by a peak corresponding to the molar mass of the alkane. For example, the molecular ion for hexane, $[\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3]^{\bullet+}$ shows a peak at 86 in the mass spectrum.

When an alkane fragments in the mass spectrometer it often does so at a carbon-carbon bond. One of the fragments will be a radical which is uncharged and therefore not detected while the other fragment will be a carbocation which has a positive charge and will be detected. For example $[\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3]^{\bullet+}$ (MM 86) could fragment into CH_3^{\bullet} and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$ (MM 71) or CH_3^+ (MM 15) and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^{\bullet}$. In the first case, a

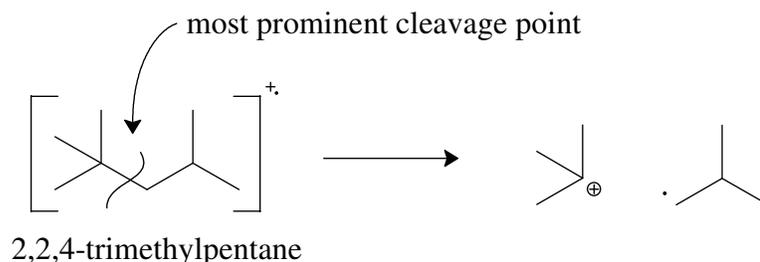
peak at 71 would be observed in the mass spectrum, while in the second case, a peak at 15 would be observed. In a similar fashion, other fragments could form by breaking C-C bonds in the middle of the chain to give fragments at MMs of 29, 43 and 57. Notice that these fragments are each separated by 14 mass units, corresponding to different numbers of CH₂ groups. The mass spectrum of n-hexane, with peaks at m/z 71, 57, 43, 29, shows a pattern characteristic of n-alkanes, exhibiting a series of peaks beginning with M-15 (for the loss of a terminal methyl) and thereafter increments of 14 mass units (corresponding to cleavage at various places in the middle of the chain).

Mass spectra of branched alkanes (2)

Branched alkanes have the same molar masses as their straight-chain counterparts (i.e. C_nH_{2n+2}) but can sometimes be distinguished because their fragmentation pattern is not as uniform. Whereas n-alkanes generally show series of fragments beginning with the molecular ion, followed by M-15, and decreasing in regular increments of 14 units, branched alkanes will not show this pattern. This is because branched alkanes will often preferentially fragment to give the most stable carbocations possible (3° > 2° > 1°). In some cases the molecular ion may be very small or not even be observed if fragmentation to a very stable cation occurs. The mass spectrum of 2,2,4-trimethylpentane is a good example of this. No molecular ion peak is observed. A small peak at m/z 99 is seen for loss of a methyl, and the base peak, found at m/z 57, is much larger than any of the other peaks. This presumably results primarily from cleavage of the C2-C3 bond, giving rise to the very stable *tert-butyl* cation, as seen in Figure 4.

While it can be difficult to identify branched as opposed to n-alkanes, the use of a library (see below) can aid in making distinctions.

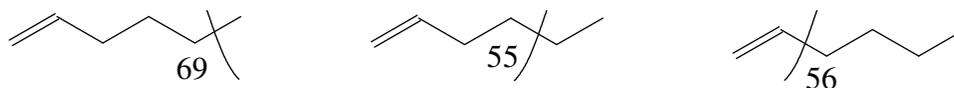
Figure 4. Favorable Cleavage in 2,2,4-trimethylpentane.



Cycloalkanes and Alkenes (2)

Cycloalkanes containing one ring and alkenes containing one double bond will have molar masses defined by the formula C_nH_{2n} . The molecular ion in both cases is readily identifiable. Cycloalkanes with attached alkyl branches will often cleave at the branch point. For example, methylcyclohexane shows a strong peak at 98 for $M^{\bullet+}$, but the base peak is actually seen at m/z 83, corresponding to loss of the methyl branch. Alkenes often like to cleave and/or rearrange to give resonance-stabilized allylic cations. Straight-chain alkenes often also exhibit a 14-unit separation between peaks similar to that observed for n-alkanes. In the case of 1-hexene (Figure 5), a prominent $M^{\bullet+}$ is observed at m/z 84. The peaks at 69 and 55 correspond to $C_5H_9^+$ (M-15, loss of methyl) and $C_4H_7^+$ (M-29, loss of ethyl), respectively. The base peak is actually at m/z 56, for $C_4H_8^+$, corresponding to a loss of ethylene.

Figure 5. Some Fragments in the Mass Spectrum of 1-hexene.

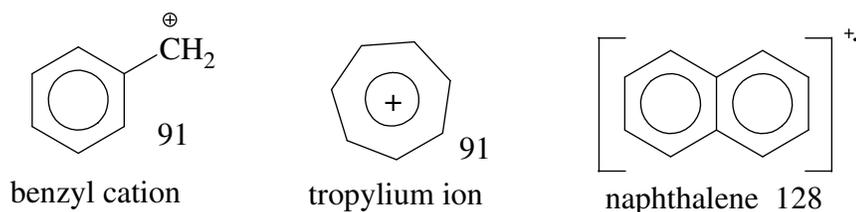


Aromatics (and naphthalenes) (2)

When a monocyclic aromatic compound fragments in the mass spectrometer the ring usually stays intact and is fragmented at substituent positions. The molecular ion is usually

visible. Alkyl substituted benzenes often show a peak at 91, which represents either the benzyl cation or more often, the tropylium ion, which can form from rearrangement of a variety of substituted aromatics following cleavage of the alkyl groups. A peak at 77 is also frequently seen in monosubstituted aromatics, corresponding to the phenyl cation. For example, ethylbenzene shows a peak at 106 ($M^{•+}$) as well as peaks at 91 and 77, corresponding to fragmentation and loss of a CH_3^{\bullet} or $CH_3CH_2^{\bullet}$, respectively. Naphthalenes, which contain two fused aromatic rings with one side in common, exhibit very strong peaks for the ring. Indeed, the base peak in naphthalene is found at $M^{•+}$ (128) and is by far the largest peak in the spectrum. Some aromatic fragments are shown in Figure 6.

Figure 6. Examples of Some Aromatic Cations.



Identification of Unknown Accelerants Using Mass Spectrometry

In recent years, the technique of GC-MS has become state-of-the-art for arson accelerant analysis. (4, 5) When an unknown accelerant is injected into the GC-MS, it will be separated into its constituent compounds by interaction with the chromatography column. Furthermore, because a mass spectrometer is being used as a detector for the gas chromatograph, it is possible not only to identify that a compound is being eluted (and a rough estimate of its relative abundance) but also to get more detailed structural information. In such a fashion, information about the classes of organic compounds and their relative amounts in an accelerant can be

obtained and used to classify an accelerant according to a standard scheme (6) such as that shown in Table 4. Once such an assignment is made, it can be used to help evaluate evidence.

We will not be seeking to determine the exact composition of an accelerant; this would be extremely difficult, if not impossible. Aside from the fact that some (although not all) accelerants contain hundreds of components, there is also the likelihood that a sample's composition has changed as a result of its environment. It is important to understand that evaporation, partial combustion, watering (due to extinguishing), contamination resulting from contact with or combustion with other materials, and general weathering can all change the hydrocarbon distribution in a given accelerant. (Indeed your sample may have been subjected to such conditions!) However, keeping such factors in mind, it is still frequently possible to make a reasonable classification as to the nature of the accelerant.

In order to determine the class of accelerant for a sample using GC-MS, we will be examining the data at several levels of increasing specificity. We will begin by examining the total ion chromatogram (TIC) to get an idea of the number and relative amount of components. We will then apply a technique known as ion-extraction to determine the relative amount of specific classes of hydrocarbons in the sample. We can then focus on the mass spectra of individual components to determine the range of molar masses of the hydrocarbons in the sample. Finally, we will examine fragmentation patterns of the mass spectra of single components and perform comparisons to a mass-spectral library to verify the structural identity of specific target compounds known to be present in certain accelerant classes.

Total Ion Chromatogram (TIC)

The total ion chromatogram shows the abundance of all detected ions as a function of retention time. It can be used to determine the minimum number of components in the sample, their relative amounts, and, in the case of hydrocarbons, their relative boiling points. Each peak on the chromatogram represents at least one individual compound (or multiple compounds if separation is incomplete). Additionally, because the samples we are looking at contain primarily nonpolar hydrocarbons, low boiling compounds will have relatively short retention times while higher boiling compounds will take longer to elute.

Theoretically, a comparison of the TIC to chromatograms of known accelerants (obtained using identical sets of instrumental conditions) could be used to identify and match samples; this is not the case in the real world. You may have performed compound identification in other organic chemistry experiments simply by matching retention times of peaks between an unknown and possible knowns. However, because of the large number of components in many accelerants, the great variability in sample conditions (described above), and the possibility of contaminants, the probability of a complete match is virtually zero. (If matching were this simple, we would not likely even need a mass spectrometer as our detector for our gas chromatograph.) In order to help sort out the large number of peaks often found in the TIC of a mixture, we can take advantage of the mass spectrometer as a detector, starting with a technique called ion-extraction.

Ion-extracted Chromatograms (6)

Different classes of accelerants will contain different relative amounts of alkanes, cycloalkanes, alkenes, and aromatics, and naphthalenes. In order to distinguish between these classes, we can perform ion-extractions on the TIC. As opposed to a TIC, which shows total

abundance as a function of retention time, an extracted ion profile (EIP) shows the abundance of only user-selected ions as a function of retention times. This is simply a manipulation of the data such that we are focusing only on a certain part of (or “extracting”) the TIC. As we have seen above, specific fragmentation patterns are indicative of different classes of hydrocarbons. Table 3 lists major ion fragments for corresponding classes. While the fragments are not exclusive

Table 3. Ion Extractions for Hydrocarbon Classes.

	Class of Hydrocarbon			
	alkanes	aromatics	cycloalkanes/ alkenes	naphthalenes (condensed ring aroms.)
m/z ions extracted	43, 57, 71 85, 99	91, 105, 106 119, 120, 134	55, 69, 83	128, 142, 156

to these compounds, they are found in more significant abundance in them than elsewhere. Consequently, examination of the EIPs for each of these fragments will allow us to determine whether a sample contains only one class of hydrocarbon (such as alkanes) or whether it contains multiple classes of hydrocarbons. While this information can not be used to determine exact composition (especially since the detector sensitivity to different fragments may not be uniform) it can certainly be used to determine the presence or absence of relatively large or small amounts of each type of hydrocarbon.

Carbon Range (6)

Once we have projected the relative amounts of each type of hydrocarbon in the sample, we can further classify it using our knowledge of mass spectra to estimate the mass range (and carbon range) for the hydrocarbons in the sample. For example, a volatile sample such as

gasoline would contain lower molecular weight hydrocarbons than a less volatile sample such as kerosene.

In order to do this, we can look at the mass spectra of individual peaks with the shortest and longest retention times. Because we are making the assumption that we are looking at only hydrocarbons (although of course there could be other components in the mixture) peaks with the shortest retention times should contain the lowest boiling (and therefore the lowest molecular weight) alkanes while those with the longest retention times should contain the highest boiling (highest molecular weight) hydrocarbons.

Assuming the mass spectrum contains a molecular ion, we should be able to use the mass of this ion to help us determine the number of carbons in the compound corresponding to that peak. For example, suppose the peak with the shortest retention time showed a MS with a molecular ion of 86, and further fragments indicative of an alkane (we could also check this by comparison to the appropriate ion-extracted chromatograms [EIPs] above) while that with the longest retention time showed a MS with a molecular ion of 134, and fragments corresponding to a monocyclic aromatic. A molecular ion of 86 ($C_nH_{2n+2} = 86$, $n=6$) would correspond to C_6H_{14} while a molecular ion of 120 would correspond to C_9H_{12} . We could therefore determine that the sample had a carbon range of C_6 – C_9 .

Another, perhaps simpler, way to determine carbon range is to use a spectral library (see section below) to help determine the carbon range of a sample by determining the structures of the lowest and highest boiling components.

Several factors must be taken into account when estimating the carbon range for a sample. If a sample has been combusted or has evaporated, the lower boiling components may be diminished as compared to original accelerant. Also, during sample extraction, insufficient

heating may have reduced some of the higher boiling components. Additionally, the assumption that highest mass peak in a mass spectrum corresponds to the molecular ion may not always be correct so that the mass determined for a given carbon range may be too low. Contamination or incomplete separation of compounds may also lead to additional peaks in the mass spectra. One way to avoid this is to check several peaks at the low and high-boiling ends of the chromatogram for consistency in mass range. (The use of a library –see below- will also help if the molecular ion is missing). Finally, determination of the carbon mass range of a sample does not provide detailed structural information about the compounds present; many structural isomers may exist. This information, however should allow you to narrow down your classification choices.

Target Compounds/Library (5, 6, 7)

Once the relative abundances of different classes of hydrocarbons are known, and the carbon range (MM range) of the hydrocarbons has been determined, it still may not be possible to narrow down the accelerant to a single class. For example, while aromatics (and sometimes naphthalenes) are relatively easy to identify from ion extraction, it cannot readily distinguish n-alkanes from branched alkanes or cycloalkanes from alkenes. Finding target compounds will greatly aid in this process.

Target compounds are specific compounds in a sample that are known to be present in similar accelerant standards. When searching for a target compound, it may be necessary to find a specific material (such as ethylbenzene) in a mixture or it may only be necessary to identify a type of compound (such as a branched alkane) that belongs to a specific class. Target compounds may be determined by using a search program to run a comparison of the mass spectrum of the unknown to a library (database) containing hundreds of thousands of mass

spectra. The search program compares masses of fragments and corresponding abundances in the unknown to possible knowns. A list of matching compounds is displayed as well as the probability of the match. A very good match is a good indication that a target compound has been identified. Once the structure of the target compound is known, we should also visually confirm the library results by interpreting the fragmentation pattern(s). It is important to note, however, that a library sometimes cannot be used to distinguish between isomers. (7)

Putting it all Together

Using the information from the TIC, ion extractions (EIPs), carbon range, and target compounds, the unknown accelerant may be classified using the ignitable liquid classification scheme (6) as illustrated in Table 4.

Table 4. Ignitable Liquid Classification Scheme. (6)

Class	General Info	Examples	Alkane Abundance	Cycloalkane Abundance	Aromatic Abundance	Naphthalene Abundance	C range	Target Compounds
Gasoline	Pattern characterized by abundant aromatics in specific pattern.	Various brands of gasoline	Present	Not present in significant amounts	Abundant, generally higher than alkane, comparable to standard	comparable to standard	C4-C12 for fresh gasoline	alkylbenzenes such as 1,3,5-trimethylbenzene
Petroleum Distillates	Pattern characterized by Gaussian distribution of peaks with aromatic compounds present	Light – cigarette lighter fluids, camping fuels Medium – some charcoal starters, some paint thinners Heavy – kerosene, diesel fuel, some charcoal starters	Abundant, mostly n-alkanes but branched must be present	present, less abundant than n-alkanes	always present in medium and heavy distillates, less abundant than alkanes	may be present	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	Light – C4-C9 alkanes Medium– nonane, decane, etc. Heavy – decane, undecane, dodecane, tridecane, etc.
Isoparaffinic Products	Contain almost entirely branched alkanes	Light – aviation gas, specialty solvents Medium – some charcoal starters, some paint thinners, Heavy – some commercial specialty solvents	Abundant, mostly branched with no or little n alkanes	absent, or not present in significant amounts	absent, or not present in significant amounts	not present	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	branched alkanes
Aromatic Products	Contain almost exclusively aromatic and/or naphthalenes	Light – some paint removers, xylene and toluene based products Medium – specialty cleaning solvents, insecticide solvents Heavy – insecticide solvents, industrial cleaning solvents	Not present in significant amounts	Not present in significant amounts	Abundant, comparable to standards	may be present, comparable to standard	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	aromatics
Napthenic Parrafinic Products	Comprised mainly of branched and cyclic alkanes	Light – cyclohexane solvents Medium – some charcoal starters, lamp oils Heavy – lamp oils, industrial solvents	abundant, n-alkanes may be absent or diminished compared to distillates	abundant	not present in significant amounts	not present in significant amounts	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	branched, cyclic alkanes
N-Alkames Products	Comprised exclusively of n-alkanes	Light – solvents Medium – some candle oils Heavy – some candle oils	abundant, n-alkane pattern with no or minor levels of branched alkanes	not present in significant amounts	not present in significant amounts	not present in significant amounts	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	n-alkanes
De-Aromatized Distillates	Shows traditional distillate distribution, but aromatics absent	Light – some camping fuels Medium – Some charcoal starters, some paint thinners Heavy – Some charcoal starters, odorless kerosenes	abundant, mostly n-alkanes with branched present	present	absent or not present in significant amounts	not present in significant amounts	Light: C4-C9 Medium C8-C13 Heavy – C8-C20	see distillates
Oxygenated Solvents	may include alcohols, esters, ketones mixed with other compounds	Light – alcohols, acetone, fuel additives Medium – some industrial solvents	could be present in mixture, similar to distillate	depends upon composition of mixture	depends upon composition of mixture	not significant		
Others – Misc.s	Single components or synthetic mixtures	Light – single component products, or blended products Medium – turpentine products, blended pdts. Heavy – some blended products						

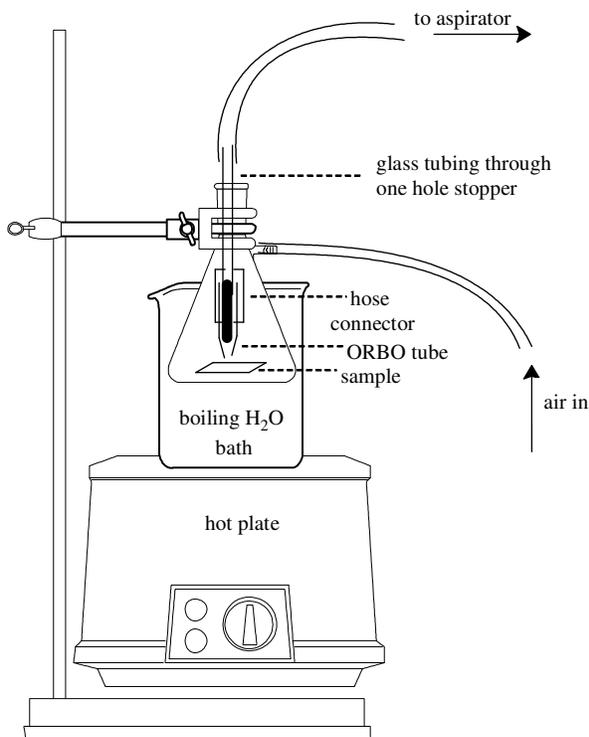
Procedure (5, 7, 8, 9, 10)

Each group will be given two samples - one from the suspect's clothing, and one recovered from the crime scene. Your job will be to analyze each sample to determine: a) the presence or absence of an accelerant on the sample; b) the class of the accelerant, if present and c) the degree of the match (if any) between the samples.

Assemble the negative pressure extraction apparatus using Figure 7 as a guide. Place an 800 mL beaker on a stir plate on top of a ring stand, fill the beaker about half-full

of water, and set it to boiling. Your instructor should already have cut the ends off the SUPELCO ORBO™ – 32 large (400/200 mg) charcoal tube with the ORBO™ tube cutter and inserted it into one end of a short piece of rubber tubing (CAREFUL! the cut ends of the charcoal tube may be sharp). Connect the other end of the rubber tubing to the glass tubing in the rubber stopper (also done by your instructor) so that the charcoal tube will be inside the 250 mL filtering flask and a few centimeters from the bottom when stoppered. When you have prepared the setup, obtain from your instructor the sample to be extracted. (Be sure to take careful notes as to which of the samples you have been given – it may be from a suspect, or it may have been taken from the crime scene). Immediately place the sample in the flask and stopper it, being sure the charcoal tube is close to, but not touching the sample. After assembly, connect the other end

Figure 7. Extraction Apparatus.



of the glass tubing extending from the stopper to the aspirator (with a trap to prevent backflow). Be sure a long piece of rubber tubing is also connected to the sidearm of the filter flask to prevent steam from the boiling water bath from being sucked into the apparatus.

Lower the apparatus into the boiling water bath, turn the aspirator on, and allow it to run for ten minutes (there is no need to turn the aspirator on full strength as you may suck the small foam insert out of the charcoal tube). At the end of this time, remove the flask from the water bath, disconnect the charcoal tube (when cool enough to touch) and allow it to cool to room temperature. When cool, remove the fiberglass plug using the plug puller attachment on the ORBO™ tube cutter. Elute the charcoal tube with four milliliters of pentane (B&J Brand High Purity Solvent) into a 5 mL screw-top vial. To ensure complete extraction, rerun the (same) collected pentane through the charcoal tube four more times.

After collecting your pentane, inject 1 µL of it into the GC-MS for analysis. The run parameters for the GC-MS are given in Table 5.

Table 5. GC-MS Parameters for Analysis of Accelerants.

<p>Chromatographic Parameters</p> <p>Instrument: HP5890 GC</p> <p>Column: SUPELCO MDN-5 fused silica (30 m X 0.25 mm X 0.25 µm film)</p> <p>Oven temps: Init. temp: 40 °C Init. time: 2.00 min. Rate: 15.0 °C/min. Final. temp: 240 °C Final time: 10.00 min.</p> <p>Injector temp: 280 °C</p> <p>Detector temp: 280 °C</p> <p>Carrier gas: Helium</p> <p>Flow rate: 0.900 mL/min.</p> <p>Purge valve A: Init. value: off On time: 0.08 min. Off time: 0.00 min. Injection: splitless</p>	<p>Mass Spectral Parameters</p> <p>Instrument: HP 5972A MS</p> <p>Solvent delay: 2.50 min.</p> <p>Acquisition mode: scan</p> <p>MS Scan Parameters:</p> <p>Start time: 2.50</p> <p>Mass Range: Low 35.0 High 550.0</p> <p>Threshold: 50</p> <p>Sampling: 2</p> <p>Scans/sec. 1.49</p>
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Analysis of Data (5, 6, 7, 11)

While you are waiting for your turn at the GC-MS instrument or for your run(s) to complete, read the paragraphs below and use the practice data packet provided to fill out Tables 6 and 7. Then see if you can classify the practice accelerant according to the ignitable liquid classification scheme (Table 4). Begin with the TIC and work your way to more detailed information (refer to Background section to help you).

Once your run is complete, print out a copy of your TIC. Perform ion-extractions on the TIC for each set of hydrocarbon classes using the ions listed in Table 3. Print out the resultant chromatograms. Return to the TIC and try to find the carbon range for your sample by examining the mass spectra of one of more peaks with relatively short and relatively long retention times. You may also look at the printouts of the ion-extracted chromatograms while you are doing this to help you look for a specific class of hydrocarbon to help with molecular formula determination. Additionally, you may use the spectral library on these peaks to help you with compound and molar mass/carbon range identification.

At this point, with the aid of Table 4, you should have a rough idea of possible classes for your unknown accelerant. In order to help you make a final determination, use the library to analyze several of the larger peaks for the presence (or absence) of indicated target compounds. (Some of these peaks may already be the ones you used for carbon range determination). For example, you may be unsure if your sample contains both n-alkanes and branched alkanes, or only one or the other. The ion-extracted chromatograms cannot help you with make this distinction, but the library may. Or, you may wish to use the library to find a specific aromatic compound known to be present in gasoline. Find a peak that you think is particularly significant,

and print out its mass spectrum for analysis of its fragmentation pattern. A free online database of mass spectra is also available (reference 11).

Write Up

Once you are confident in the process you used for classifying the practice accelerant, follow the same approach on the printouts of your unknown samples. Create and fill out tables like 6 and 7 in your lab notebook, and use the results to help you write up your lab report. Was there an accelerant present in both samples? Why or why not and how do you know? What class(es) of accelerant(s) were present, if any? Explain your logic. Do the samples match? Is it a perfect match? Are the results consistent with the suspect's story? Be clear when discussing analysis and interpretation of your results, as well as the conclusions you draw from them. Discuss any factors (weathering, partial combustion, etc.) that should be considered when presenting your evidence – remember this evidence might have to be presented in court and you would have to be cross-examined by a defense attorney. Can you confirm innocence or guilt? What additional experiments would you run if this was a real case?

Table 6. Analysis of Sample Data Packet for Accelerant Classification.

Total Ion Chromatogram (TIC)	
Number of peaks observed in TIC	
Retention time of largest peak (min.)	
Relative abundance of largest peak in TIC	
Retention time of any other small peak (min.)	
Retention abundance of “small peak” in TIC	
Ion Extracted Chromatograms	
Alkanes: abundant/present/not signif. or absent?	
Aromatics: abundant/present/not signif. or abs.?	
Cycloalkanes/alkenes: abund./present/n.s. abs?	
Naphthalenes: abundant/present/not sig. or abs?	
Carbon Range	
Retention time of fast eluting peak (min.)	
Molecular ion in M/S of fast eluting peak	
Molecular formula/# of C’s for fast eluting peak	
Retention time of slow eluting peak (min.)	
Molecular ion in M/S of slow eluting peak	
Molecular formula/# C’s for slow eluting peak	
Carbon range	
Target Compounds Identified (List names next to each applicable class)	
N-Alkanes:	
Branched Alkanes:	
Aromatics:	
Cycloalkanes	
Alkenes	
Naphthalenes	
Class of Compound (according to Ignitable Liquid Classification Scheme):	

Table 7. Analysis of Selected Target Compound Mass Spectrum.

Mass Spectrum Analysis of _____

m/z	proposed structure of fragment

References

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Documentation/Instructors Notes

Equipment needed

Each student team needs

1. Ring stand with clamp
2. Hot plate
3. 800 mL beaker
4. 250 mL sidearm (filter) flask
5. 1/4" ID X 5/8" OD pressure and vacuum rubber tubing Fisher #14-173C
6. Aspirator - Nalgene Vacuum Pump (aspirator type, polypropylene, Cat # 6140-0010)
7. One- hole #6 stopper with 7mm OD X 5 mm ID glass tubing inserted
8. A charcoal tube (Supelco ORBO™ – 32 Large Charcoal Tubes 400/200 mg, catalog # 20228) that has been precut (both ends removed) and inserted into bottom of a rubber stopper. (See additional notes for more information about the tubes).
9. Supelco ORBO™ tube cutter with puller (catalog # 20596) (this may be shared among the class).
10. 5 mL vials with cap
11. Disposable (Pasteur) pipettes and bulbs
12. Accelerant samples to be extracted. For the “suspect’s clothing”, a 4 cm square piece of 100% cotton or cotton/polyester blend was used. For the carpet sample, a 4 cm square of short-fiber synthetic carpeting was used. (See additional notes for more information about sample preparation).

13. Evaporating dish and watch glass (not needed for students unless they will be burning their own samples –see additional notes, below)

Chemicals

1. Gasoline (CAS Number:8006-61)
2. Pentane - B&J Brand High Purity Solvent (CAS # 109-66-0)
3. Lamplight® ultra-pure 99% pure liquid wax paraffin candle and lamp liquid (CAS # 90622-46)
4. Diesel Fuel (CAS #: 68476-34-6) **not recommended** (see Additional Notes/Lab Logistics)
5. Kingsford Lighter fluid (CAS# 64742488),
6. Paint thinner (CAS # 64742-88-7)

Hazards and waste disposal

1. Solvents should go into the non-halogenated waste bottle and be disposed of according to federal and state regulations.
2. Work should be done in the hoods as much as possible
3. The tubes should be disposed of in broken glass.

Additional Notes /Lab Logistics

Tubing Preparation

Tubes may be cut and inserted in the rubber stopper ahead of time. The ends of the tubes may be cut off using a Supelco ORBO™ tube cutter (catalog # 20596). Safety glasses and gloves should be worn when doing this as small sharp pieces of glass may be ejected when breaking the ends off and the cut-off ends may be jagged. Be sure not to break off too much of the tube as, if the small foam insert is exposed, it may be sucked into the rubber tubing during aspiration, causing the charcoal to spill out. The tubing should be inserted into the stopper from below instead of from the top. The stopper should be placed securely into a filtering flask. Make sure that you follow the directions that come with the charcoal tubes to ensure that the air is flowing in the proper direction. The rubber tubing should be connected to the charcoal tube and then the aspirator. An additional piece of rubber tubing should be attached to the side arm and positioned away from the hot water bath so that the no water vapor will be drawn into the flask.

Aspirator Flow

A water aspirator (Nalgene Vacuum Pump, aspirator type, polypropylene, Cat # 6140-0010, air pumping capacity 11.5 L/min at water flow rate of 6.5 L/min) was used. The water faucet was turned on approximately halfway. The aspirator flow is not critical, although we found that in some cases if the aspirator is particularly strong, the foam insert in the charcoal tube may be sucked out if the tubing is cut open too wide at that end. Due to variations in water pressure and water flow from location to location, adjustments should be made accordingly using test samples to ensure accelerant recovery.

Sample Preparation – Cloth

In order to simulate trace amounts of an accelerant, the cloth can either be spiked immediately before extraction with 40 microliters of accelerant or spiked and then immediately sealed in a vial (for preparation of large numbers of samples by the instructor beforehand the latter is preferable). We found a sealed sample to be still viable even after 2 weeks; however, allowing such a small amount of the accelerant to remain on the cloth for more than a few minutes before storage may cause it to evaporate. We extracted one gasoline sample after allowing it to remain uncovered for 20 minutes and found the gasoline to be marginally detectable, if at all. If it is desirable to further simulate evaporation conditions on a suspect's clothing, larger amounts of accelerant and/or cloth can conceivably be used (see variations section, below).

Sample Preparation – Burned Carpet

The carpet sample is placed in a CoorsTek porcelain evaporating dish (100 mm dia., 150 mL capacity, Fisher # 08-690F, Coors # 60201) and 2 ml of accelerant is measured using a 10 mL graduated cylinder and poured onto the carpet and allowed to soak in for a few seconds. The sample is then ignited by touching the flame from a Bunsen burner to the carpet. It is allowed to burn for approximately 30 seconds; then the flame is smothered by covering the evaporating dish with a 4 in. diameter watch glass. The carpet sample can then be immediately extracted or sealed in a vial for subsequent extraction. It is not recommended that diesel fuel (home heating oil) be used as an accelerant for this part of the experiment as it is not particularly flammable (unless one wishes to illustrate this point to students). In order to facilitate ease of accelerant

detection and avoid contamination, the carpet sample used did not contain a rubber backing or foam padding.

Sample Preparation – Burned Carpet – Watering and Weathering

In order to illustrate the processes of watering, a sample of carpet may be soaked with an accelerant and burned as described above, but extinguished by thoroughly soaking with water from a squirt bottle rather than covering with a watch glass. It may then be extracted immediately, or, if it is desired to illustrate the process of weathering, the sample may be left for several days before extraction. We found gasoline to be detectable even after being allowed to stand for 8 days.

Sample Preparation - Blanks

If desired, unburned blanks may be prepared by extracting squares of cloth or carpet that have not been spiked with any accelerant or combusted. Burned blanks may be prepared by burning a piece of carpet (or other material) to which an accelerant has not been added. In the case of carpet, it was necessary to hold the Bunsen burner on the carpet for several seconds until combustion was sustainable – then the carpet was left to burn for 30 seconds to one-minute (careful not to overcombust) and then extracted in the usual fashion.

Eluting the Charcoal Tube with Pentane

It is particularly important that students allow the charcoal tube to cool before eluting the sample with pentane to prevent evaporation of the solvent. Even after cooling, some of the pentane will evaporate when it comes into contact with the charcoal. To ensure the accelerant has

been completely extracted from the charcoal, the collected eluent should be run through the charcoal several more times. We have used as little as 2 mL of pentane for this process, but find that 4 mL provides a sufficient amount that, even with evaporation, there is ample sample left for injections. It is also important to note that as pure a grade of pentane as possible should be used so that hydrocarbon peaks from solvent impurities do not obscure hydrocarbon peaks in the sample.

Obtaining Data/Data Analysis

Because there can be significant waiting involved for students to get their turn on the GC-MS, we give them a sample data packet to analyze. This helps them to understand the analysis of their own data. The sample data packet also contains fewer peaks than found in many accelerants so it is somewhat easier to analyze.

Students generally do not have difficulty interpreting and understanding the TIC. Ion-extraction is relatively straightforward, as long as the idea of being able to find peaks containing only specific ions related to specific types of hydrocarbons is clearly explained. When searching for the carbon range of the sample, students may not know which peaks to use for the short- and long- retention time peaks. Sometimes background contamination or incomplete separation of peaks may make it difficult to identify the molecular ion. Additionally, some compounds may not exhibit a molecular ion. The instructor should be aware of such cases; they should be explained to students, and, if desired they could provide good opportunities for discussion. In many instances, even though stray peaks are present in a mass spectrum, a library search will still provide a good match to the correct compound. If a student asks about the differences, a good discussion could also ensue. While many peaks may be used for this portion of the analysis, it is

a good idea for the instructor to have several peaks in mind (from previous examination) for a given sample so that the student can be pointed in the right direction. It may also be useful to help students who are searching for target compounds as well.

Students generally enjoy the process of interpreting and analyzing the data, and the thought processes involved with determining the probable guilt or innocence of a suspect. It is important to keep in mind, however, that although the students like the scenario they are sometimes disappointed if their suspect turns out to be innocent.

Variations

Depending upon the time available, there are a number of ways in which the experiment may be easily modified. If safety is a consideration, the instructor can either burn the samples for the students while they are watching, or provide the combusted samples and give a demonstration showing how a sample burns. If time is limited, each group may be presented with only one sample to run on the instrument and the instructor can provide copies of the data for the other sample. If more time allows, students can have an opportunity to further investigate many aspects of the experiment, as described below. Data packets reflecting these variations could also be provided.

As is true in a real crime-laboratory, the results can be significantly affected by factors including the material on which an accelerant has been absorbed, the time the accelerant has been allowed to burn before extinguishing (or whether it has been burned at all), the method of extinguishing used, the amount of time the sample has been allowed to evaporate, the amount of time the sample is heated under aspirator vacuum during extraction, or even the particular brand of accelerant used. Students could be encouraged explore any one or more of the above factors

to try to develop their own method, or see if a series of methods could be used wherein a tentative identification of an accelerant is first made using the general method, then a method more specific to that class of accelerant is applied to improve identification.

Comparison of chromatograms of a pure accelerant (dissolved directly in pentane) to the pentane extract of the same accelerant (following any or no treatment) illustrates the effectiveness of recovery of a particular method. The times and materials given in the procedure were those found to work well for us but students could explore how changing some of these factors could be of importance.

Surface Materials

Differences in the material used for absorbing the accelerant can lead students to an understanding of how particular materials may retain accelerants better than others, as well as how contamination from combustion of the absorbent itself can cause difficulties in accelerant identification. The carpeting we chose to combust did not have any backing or padding material; if desired, a carpet with a rubber or other backing could be used to investigate how such materials could cause interference or difficulty in accelerant identification. Furthermore, while we focused on cloth and carpeting, almost any type of material could be tested to see if similar results are obtained or if interferences are present.

Variations in the absorbent would apply not only to areas of the crime scene, but to a suspect's clothing as well. As an alternative to using a small amount of accelerant on a pre-cut swatch of cloth, it might be possible to pour a larger (but still reasonably small) amount of an accelerant on an entire piece of clothing, and then take samples from several areas of the cloth.

Combustion Time

Variations in time before extinguishing the fire can further an understanding of the importance of taking several different samples from a crime scene. Areas in which combustion has been sustained for longer periods of time might be expected to show the presence of little or no accelerant or lead to an accelerant profile in which more volatile components are not present. For example, we found that gasoline could still be detected in carpeting even after it had been completely charred (at least one minute burn time).

Extinguishing Methods/Simulated Watering

Changes in the methods of extinguishing the fire would allow students to determine how the extinguishing material used might affect accelerant identification. Areas of a fire that have simply burned themselves out would show different characteristics than those smothered by water or other materials used for putting out the fire. For example, we found that gasoline was still readily detectable on carpeting that had been soaked by extinguishing with water.

Evaporation Time/Extraction Time/Simulated Weathering

Modifying the time before extraction can lead to an understanding of the evaporation process of various accelerants and a discussion of development of a portfolio of chromatograms for the same accelerant based upon evaporation time. The importance of the timeline from commission of a crime to collection of evidence would be emphasized, as would the importance of proper handling of evidence (to prevent further evaporation). For example, while trace amounts of an accelerant on the suspect's clothing might disappear quite rapidly, larger amounts

would be easier to detect. Similarly, gasoline was still detectable in a carpet sample extinguished with water even after sitting for eight days.

Heating Time for Extraction

Changing the heating time during extraction can further teach students the importance of method development. Although our method was found to be suitable for a wide range of accelerants, the heating time had a different influence on different accelerants. For example, heating too long with more volatile accelerants such as gasoline caused low-boiling components to disappear and made identification more difficult; however, insufficient heating of less-volatile accelerants such as diesel did not allow for sufficient extraction and detection of high-boiling components. Indeed, diesel and heavier petroleum products can sometimes be difficult to identify with this method. To maximize the recovery of high-boiling components, the charcoal tube was placed on the underside of the stopper (inside the flask). The optimal heating time was found to be ten minutes. This prevented loss of volatile components while still allowing time for high-boiling materials to be adsorbed.

Brand of Accelerant

Another option would be to explore only the differences in brands of one type of accelerant to see if significant differences exist. Students might wonder if one could identify the particular brand of accelerant used. In discussing this possibility, consideration of the other variables discussed above would also certainly arise.

In summary, the number of variations that can be envisaged is limited only by the scope and time allowed by the laboratory. If time is limited, all the students can be instructed to follow procedures specifically outlined by the instructor. If more time is available, the experiment could be extended to encompass student projects in which manifold variations could be envisaged that would allow students to further see that the real world is often quite different than the laboratory.

Practice Data Packet (“Lamp Oil”)

The following pages consist of a data packet for a known sample of Lamplight® ultra-pure 99% pure liquid wax paraffin candle and lamp liquid showing, in order: the total ion chromatogram (Figure 8), ion extractions (Figures 9-11), and mass spectra of the individual peaks in the chromatogram (Figures 12-15). To obtain this data, no extraction was needed (although it could be performed if desired); 2-3 μL of the lamp oil was dissolved in 1 mL of pentane and 1 μL of this solution was injected into the GC-MS. Because the chromatogram is relatively simple and the components are limited to n-alkanes it provides students a chance to learn to interpret chromatograms and mass spectra and to classify the unknown accelerant without added complications. They can begin to fill out Table 6 by starting with the chromatogram and working their way up to Table 7, which gives a thorough analysis of a mass spectrum of one peak.

File : C:\HPCHEM\1\DATA\LMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

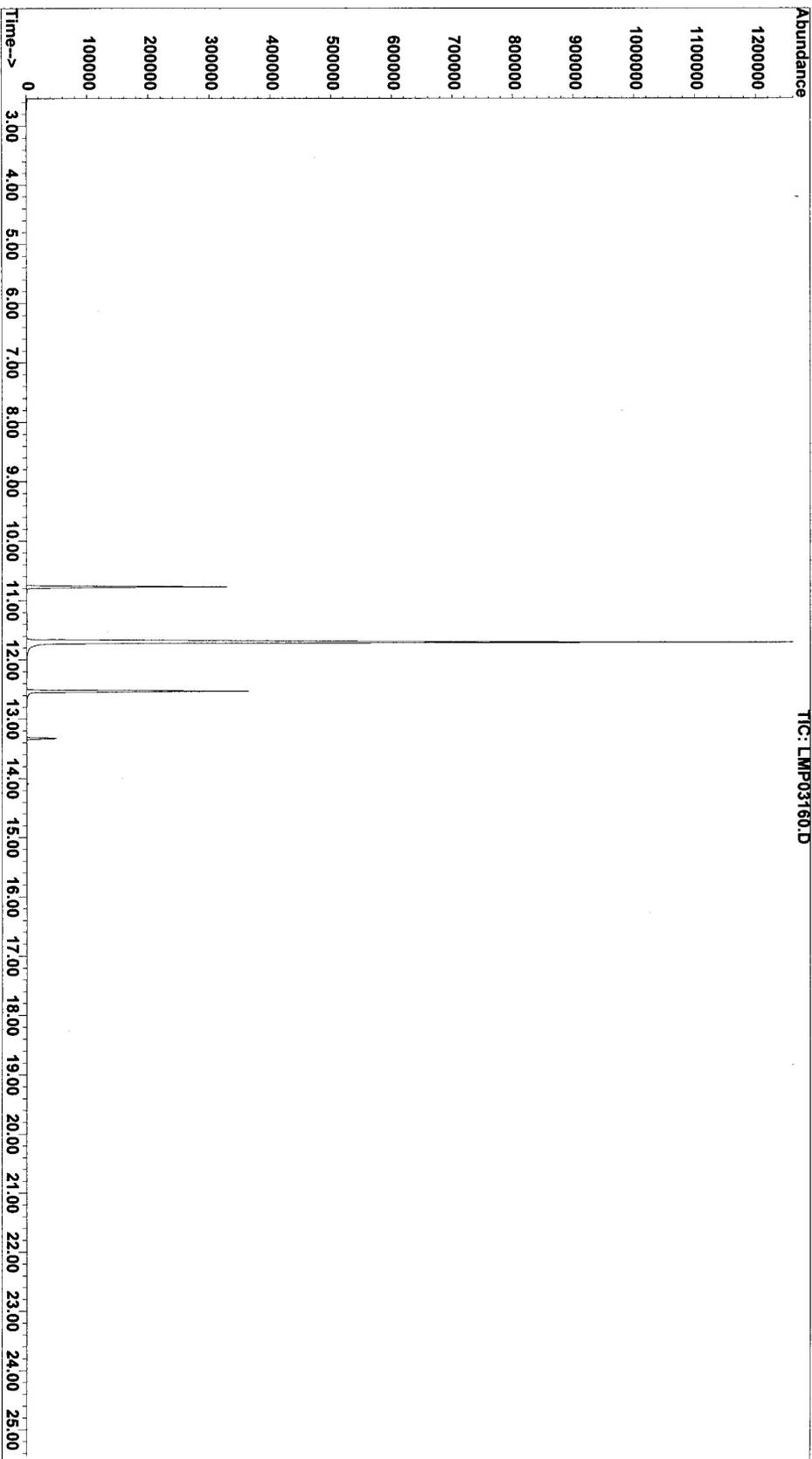
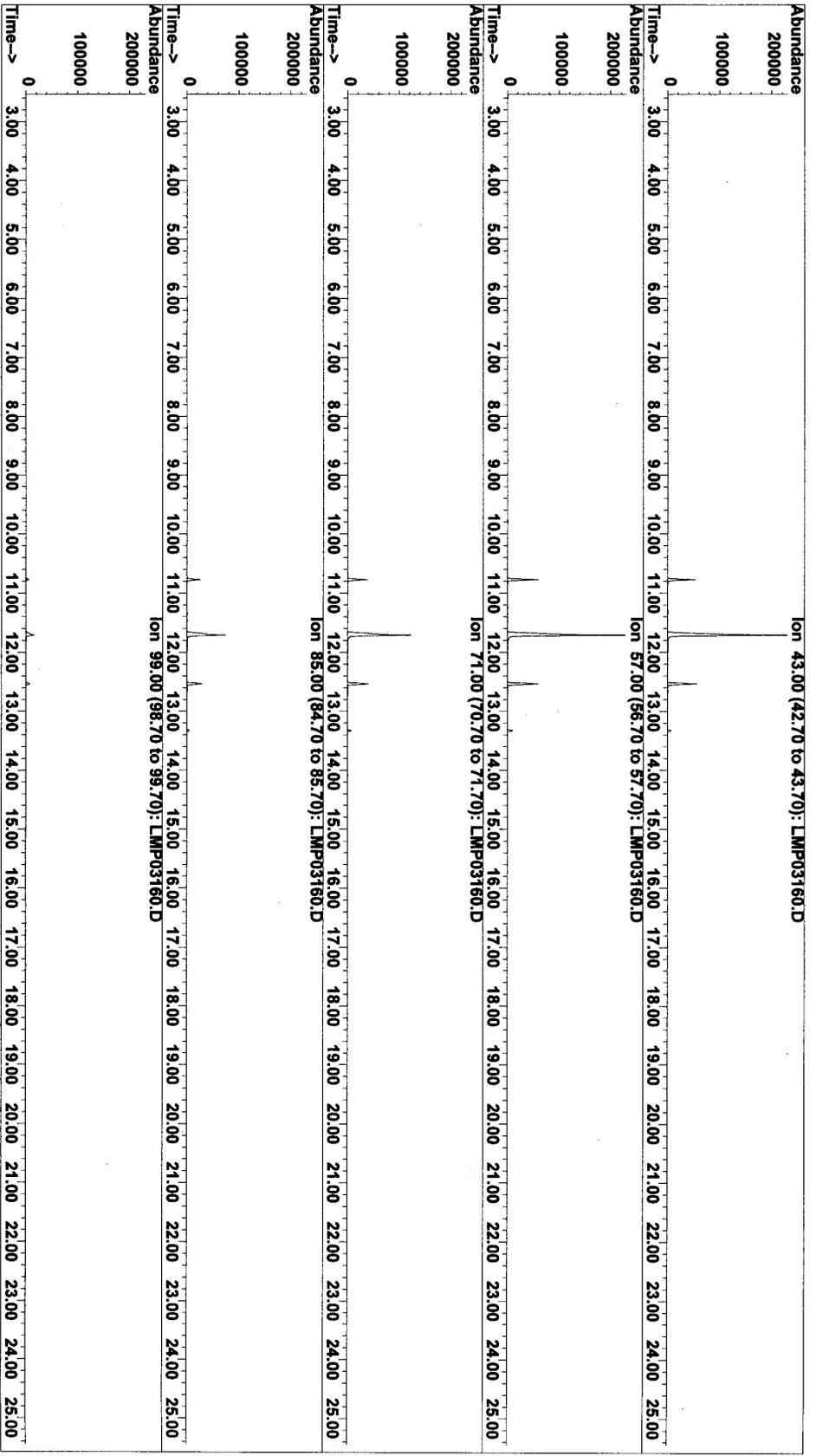


Figure 8. TIC of Unknown Accelerant.

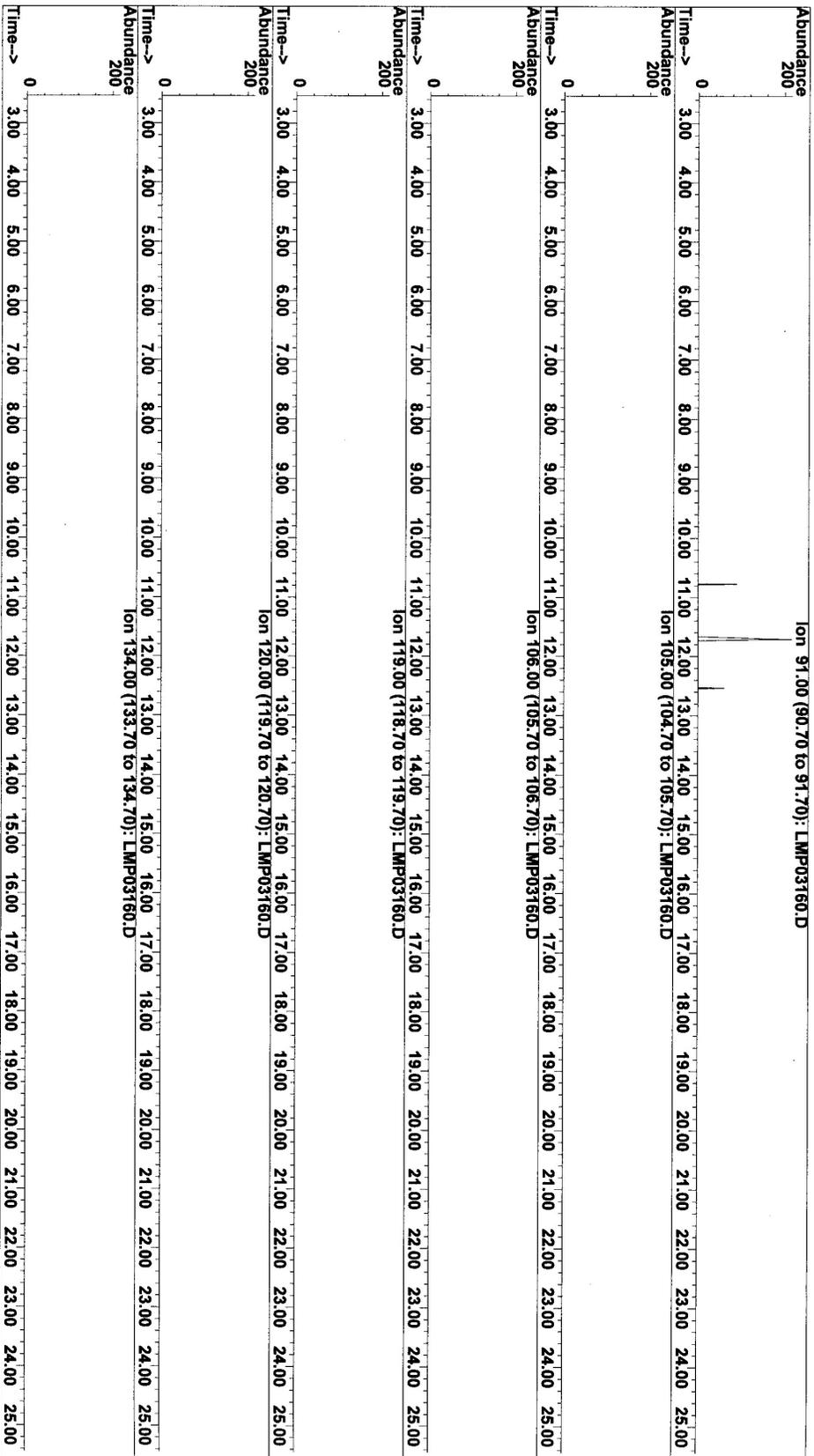
File : C:\HPCHEM\1\DATA\LMP03160.D
Operator : IJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

Figure 9. Ion Extractions of Unknown Accelerant - Alkanes.



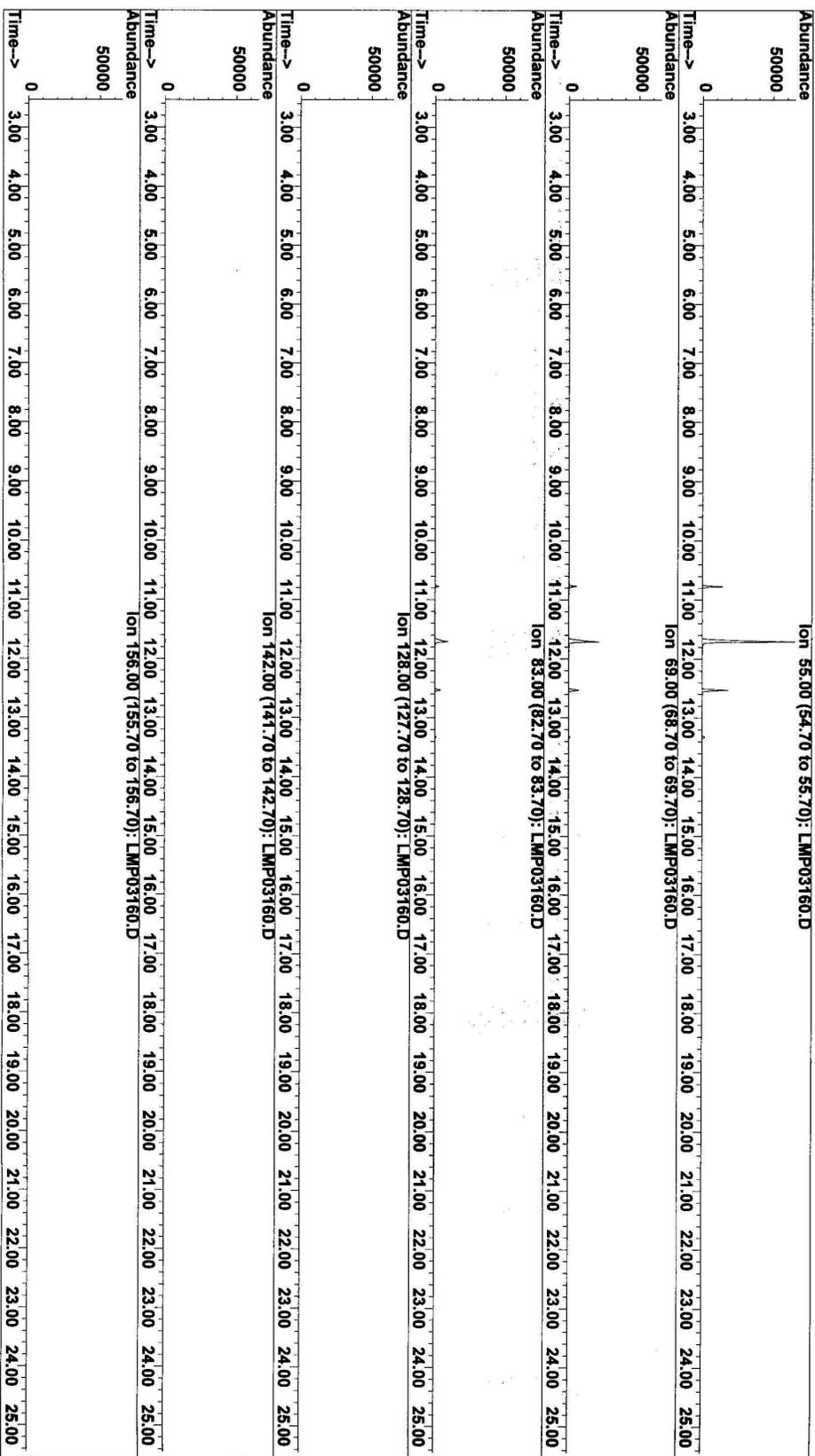
File : C:\HPCHEM\1\DATA\LMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

Figure 10. Ion Extractions of Unknown Accelerant - Aromatics.



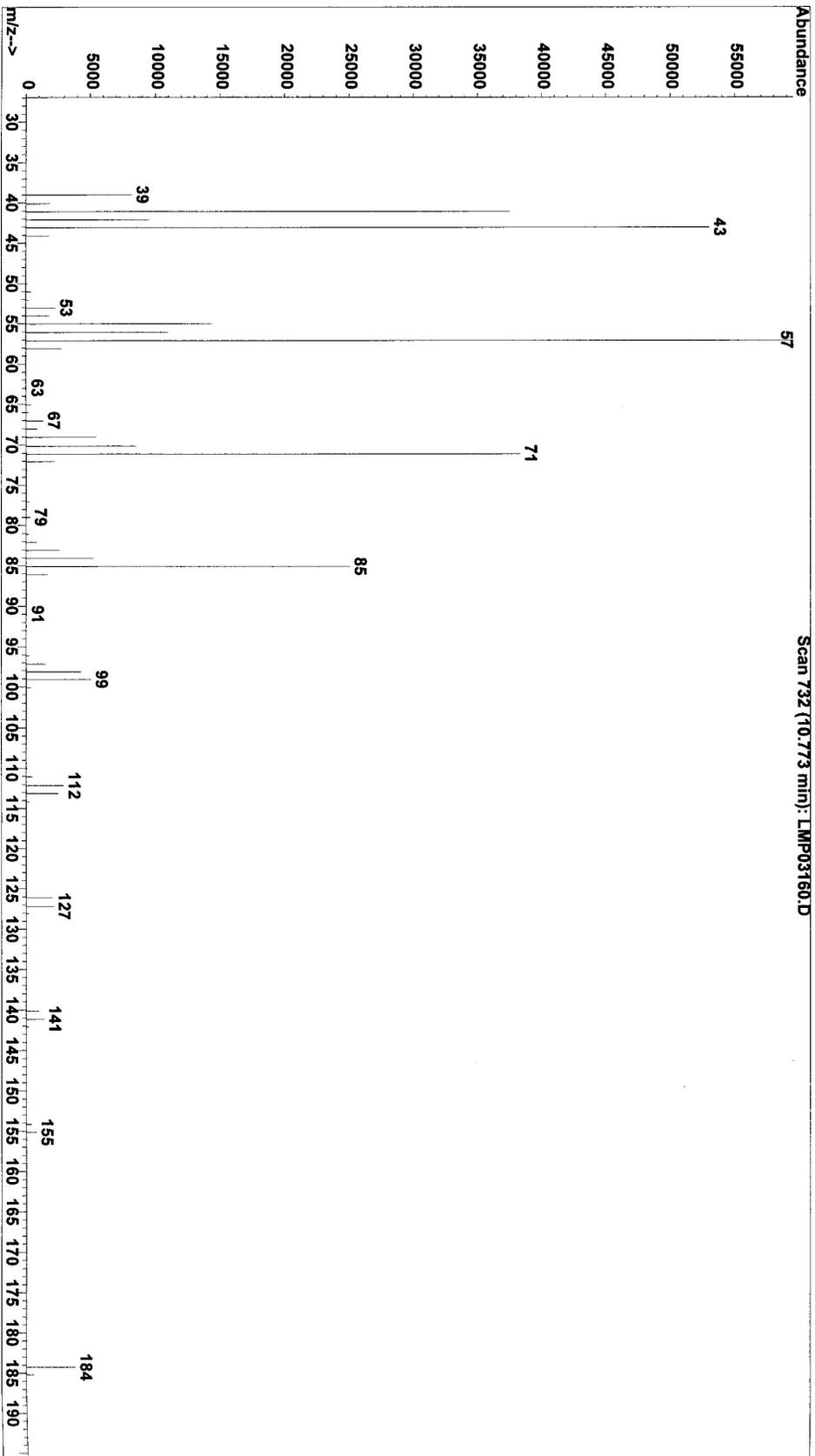
File : C:\HPCHEM\1\DATA\LMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

Figure 11. Ion Extractions of Unknown Accelerant - Cycloalkanes/Alkenes; Naphthalenes.



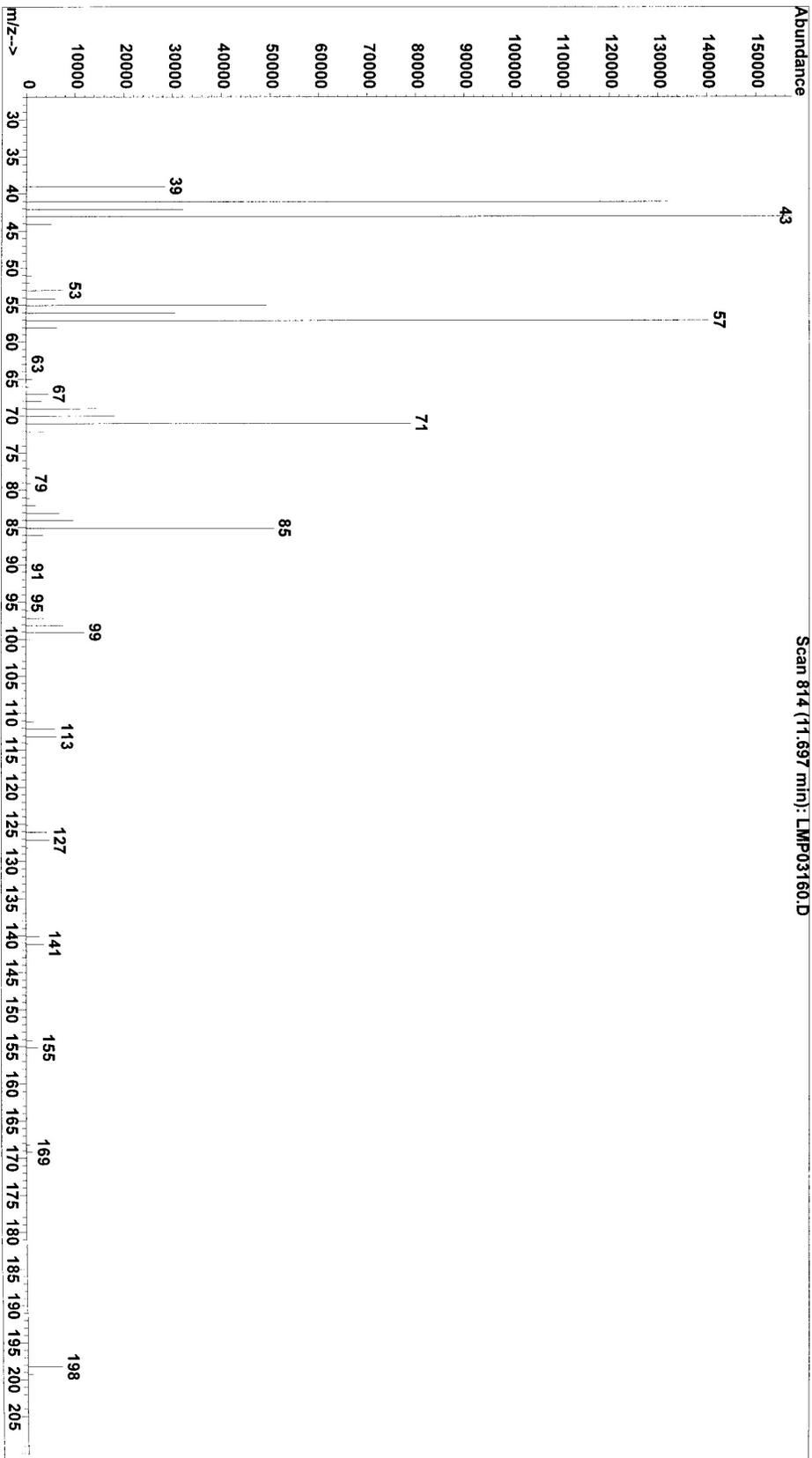
File : C:\HPCHEM\1\DATA\IMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name : Lamp Oil
Misc Info :
Vial Number: 1

Figure 12. Mass Spectrum of Peak with Retention Time of 10.8 min.



File : C:\HEPCHEM\1\DATA\LMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

Figure 13. Mass Spectrum of Peak with Retention Time of 11.7 min.



File : C:\HPCHEM\1\DATA\IMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

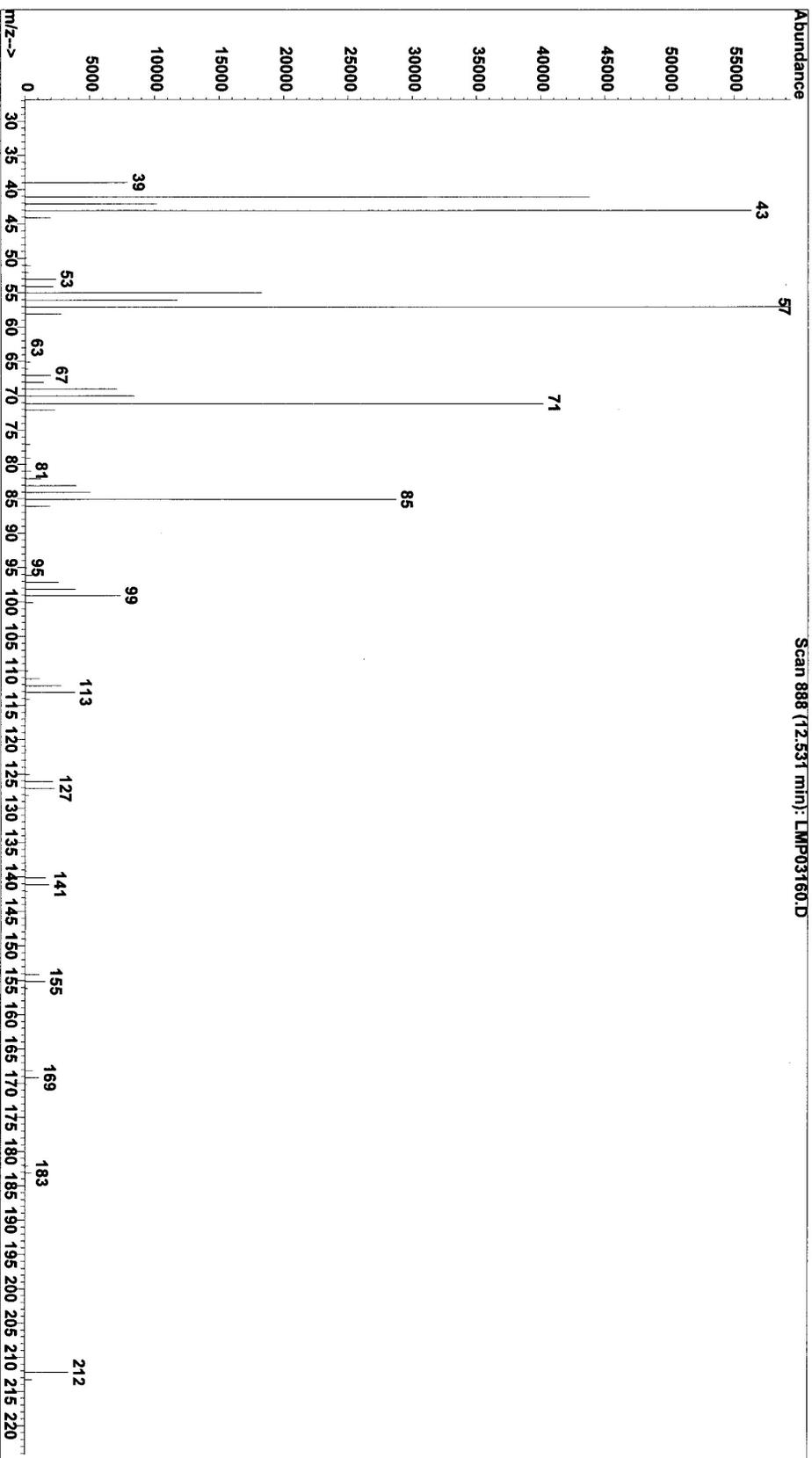
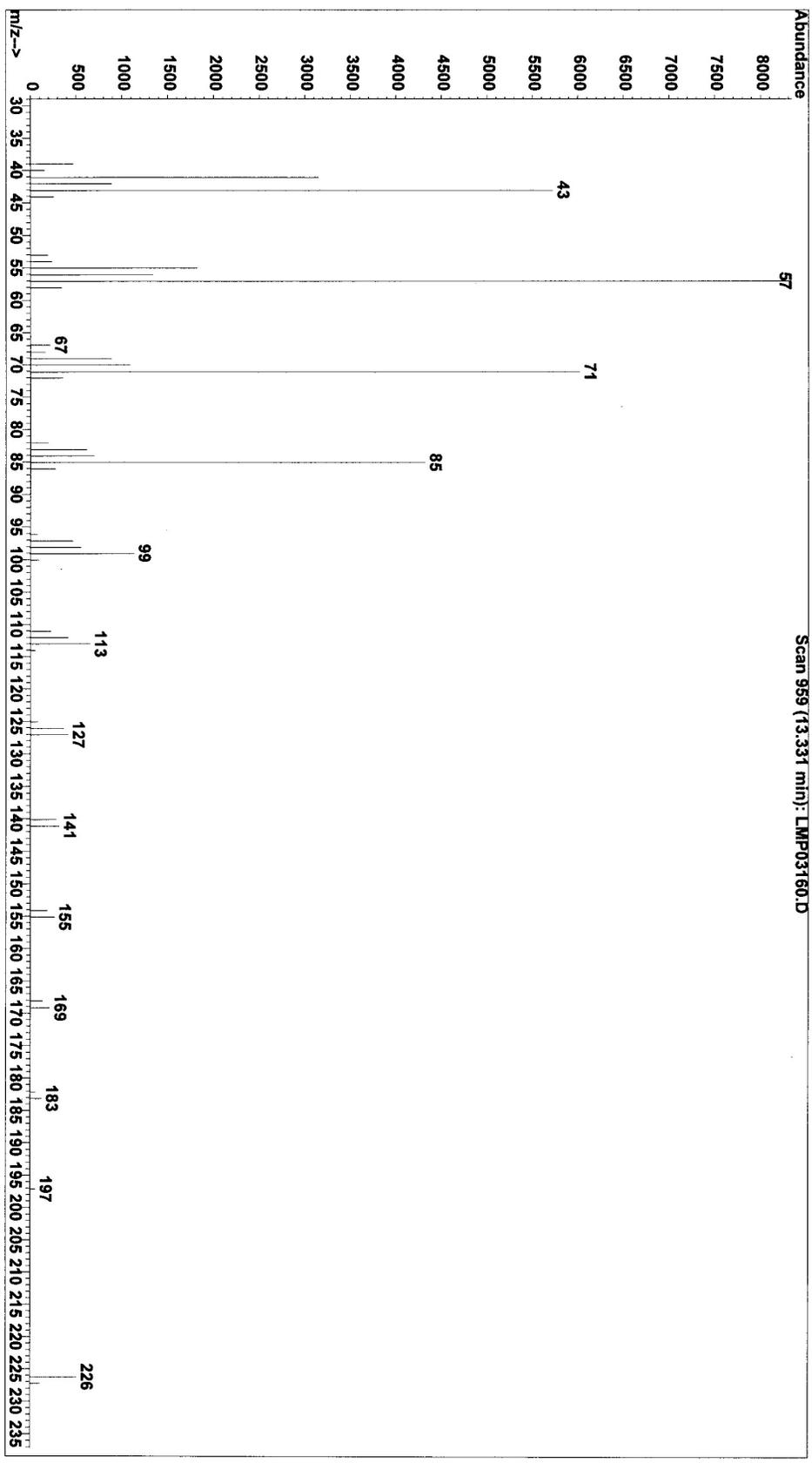


Figure 14. Mass Spectrum of Peak with Retention Time of 12.5 min.

File : C:\HPCHEM\1\DATA\LMP03160.D
Operator : LJT
Acquired : 16 Mar 2006 12:13 using AcqMethod ARSON1
Instrument : 5972 MSD
Sample Name: Lamp Oil
Misc Info :
Vial Number: 1

Figure 15. Mass Spectrum of Peak with Retention Time of 13.3 min.



Sample Answers to Pre-Lab

3. Complete Table 1 by calculating the molar masses of common fragments observed in the MS of straight chain alkanes.

Table 1. Molar Masses of Common n-Alkane Fragments.

Ion	Molar Mass
$\text{CH}_3\text{-CH}_2\text{-CH}_2^+$	43
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	57
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	71
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	85
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2^+$	99

4. What is the difference in molar masses between successive n-alkane fragments in Table 1?

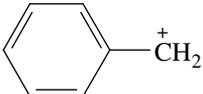
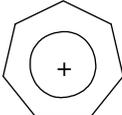
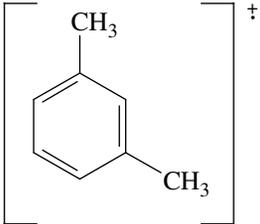
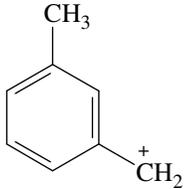
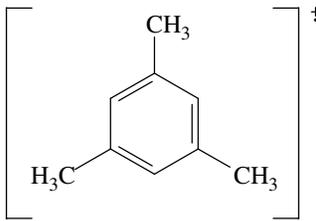
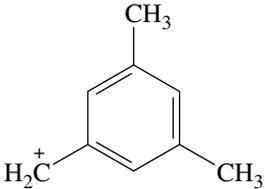
14 amu. How would you expect this to be reflected in the mass spectra of n-alkanes? **I would expect to see a mass spectrum showing peaks differing from each other by m/z values of 14.**

5. What is the formula for an alkane whose molar mass is 394? **$\text{C}_{28}\text{H}_{58}$**

6. What is the carbon range (minimum and maximum number of carbons in molecules) for an alkane sample whose molar mass ranges from 128-394? **C9-C28**

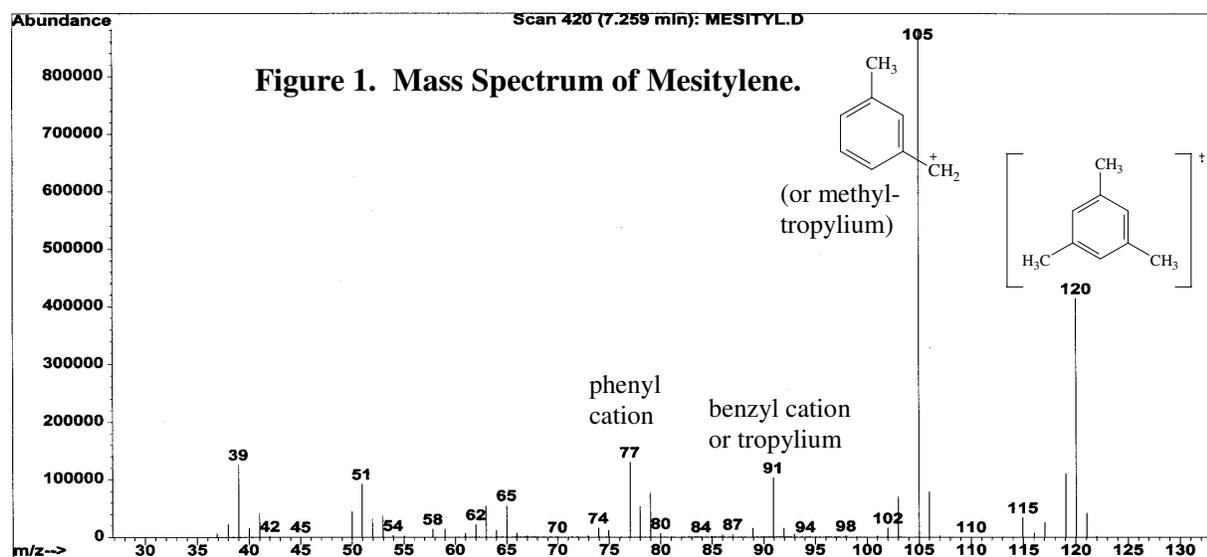
7. Copy and complete Table 2 by giving the molar masses of common fragments observed in the MS of aromatic compounds.

Table 2. Molar Masses of Aromatic Fragments.

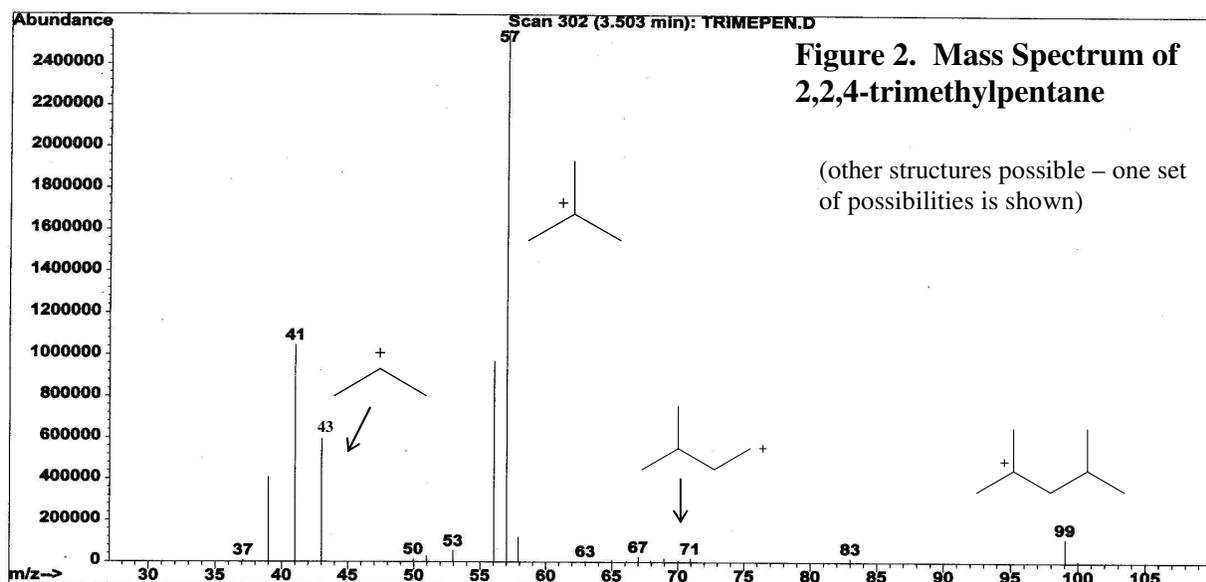
Fragment	Molar Mass
	91
	91
	106
	105
	120
	119

8. The ion-extracted chromatogram for a sample shows that it contains abundant alkanes and aromatics. One of the earliest eluting peaks has a mass spectrum with a molecular ion of 100 and one of the latest eluting peaks has a mass spectrum with a molecular ion of 134. What is the approximate carbon range for the sample? **C7-C10 (C7 represents an alkane, C₇H₁₆, while C10 represents a substituted benzene, C₁₀H₁₄).**

9. Identify as many fragments as you can in the mass spectrum of mesitylene (Figure 1).



10. Identify at least three fragments in the mass spectrum of 2,2,4-trimethylpentane (Figure 2).



Sample Answers to Practice Packet (multiple answers possible).

Table 6. Analysis of Sample Data Packet for Accelerant Classification.

Total Ion Chromatogram (TIC)	
Number of peaks observed in TIC	4
Retention time of largest peak (min.)	11.7 min.
Relative abundance of largest peak in TIC	1,250,000
Retention time of any other small peak (min.)	13.3 min.
Relative abundance of “small peak” in TIC	40000
Ion Extracted Chromatograms	
Alkanes: abundant/present/not signif. or absent?	abundant
Aromatics: abundant/present/not signif. or abs.?	not significant or absent
Cycloalkanes/alkenes: abund./present/n.s. abs?	present? (see discussion)
Naphthalenes: abundant/present/not sig. or abs?	absent
Carbon Range	
Retention time of fast eluting peak (min.)	10.7 min.
Molecular ion in M/S of fast eluting peak	184
Molecular formula/# of C’s for fast eluting peak	C13H28
Retention time of slow eluting peak (min.)	13.3 min.
Molecular ion in M/S of slow eluting peak	226
Molecular formula/# C’s for slow eluting peak	C16H34
Carbon range	C13-C16
Target Compounds Identified (List names next to each applicable class)	
n-Alkanes: tridecane, tetradecane, pentadecane, hexadecane	
Branched Alkanes: none	
Aromatics: none	
Cycloalkanes: none	
Alkenes: none	
Naphthalenes: none	
Class of Compound (according to Ignitable Liquid Classification Scheme): N-Alkanes Products (heavy) [see discussion below]	

Table 7. Analysis of Selected Target Compound Mass Spectrum.Mass Spectrum Analysis of tetradecane

m/z	proposed structure of fragment
198	$[\text{CH}_3-(\text{CH}_2)_{12}-\text{CH}_3]^{\bullet+}$ ($\text{M}^{\bullet+}$)
169	$\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2^+$ ($\text{M}-\text{CH}_3$) ⁺
155	$\text{CH}_3-(\text{CH}_2)_{10}-\text{CH}_2^+$
141	$\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2^+$
127	$\text{CH}_3-(\text{CH}_2)_8-\text{CH}_2^+$
113	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2^+$
99	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2^+$
85	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2^+$
71	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2^+$
57	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2^+$
43	$\text{CH}_3-\text{CH}_2-\text{CH}_2^+$

Discussion of sample answers.

Initial observation of the TIC shows four recognizable peaks. The EIP indicates the presence of large amounts of alkanes, and the absence of aromatics and naphthalenes. Because there are peaks at 55, and 69, in the EIP for cycloalkanes/alkenes, these cannot be conclusively ruled out at this point. However, once the peaks are identified through the use of the library as being n-alkanes, the classification becomes more definitive. The 55 and 69 peaks are actually part of the mass spectra of the very abundant n-alkanes. As a result, the sample appears to contain only n-alkanes and may be classified according to the table as an n-alkanes product. The fragmentation pattern for the target compound chosen above (tetradecane) shows the distinct 14-unit pattern for n-alkanes. Although all 14-unit fragments have been listed, we would not expect students to describe every single peak. The molecular ion, M-CH₃ fragment, and any three or so others would be sufficient to illustrate the pattern.