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Applications of Mass Spectrometric Techniques to the Analysis of Fuels and Lubricants

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Abstract

The application of mass spectrometric techniques for the analysis of the complex mixtures inherent in fuel and lubricant samples will be examined. These samples because they are naturally complex mixtures, typically requires either very high resolution mass spectrometry or one of the hyphenated techniques gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS). Some fuel problems that can be addressed through mass spectrometry are associated with the changes in composition and degradation of fuels as they age, including the analysis of both major hydrocarbon components non-polar components and minor polar components will be described. The properties and composition of natural and major classes of synthetic lubricants, the presence of additives and the problems that develop as the lubricant is used such as additive depletion, thermal and oxidative degradation and lubricant contamination have also been examined using mass spectrometric techniques.

Keywords: gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry, fuels, lubricants, high resolution mass spectrometry, degradation

1. Introduction

Mass spectrometry has long been an important technique for the identification of materials ranging from pure compounds to complex mixtures [1]. Mass spectrometry can be used to determine molecular weight of compounds; or using different ionization methods, can provide more structural details through the analysis of fragmentation patterns [2]. A wide range of ionization methods and mass analyzers have been developed for the specific problems of complex mixtures like fuels and lubricants [3]. This level of detail can be attained for pure compounds and some mixtures. Mass spectrometry can also be combined with separation

techniques such as gas chromatography [4] or liquid chromatography [5] to allow more complex mixtures to be examined. These hyphenated techniques provide a range of options for the characterization of complex materials. A number of the important developments in mass spectrometry that are important in the analysis of fuels and lubricants are shown in **Figure 1**.

Fuels and lubricants are traditionally derived from the distillation of crude oil providing the base stock [6]. The properties are then modified through the addition of additives to arrive at the final fuel or lubricant. Natural fuels and lubricants are extremely complex mixtures whose composition depends greatly on the source of the crude oil and the processing of material. Fuels are typically characterized by a boiling point range, while lubricants are typically characterized by bulk properties such as viscosity and pour point.

There has been some effort to characterize the fuels based on classes of compounds, for example, but the characterization is not always complete. As the requirement for fuels have increased, there has been increased efforts to determine polar compounds, in particular because they often lead to the formation of deposits in an engine. More recently, there have been efforts made to develop synthetic fuels, based on Fisher-Tropsch catalysts [7] and bio-derived fuels [8]. These fuels present their own challenges in terms of characterization. Mass spectrometry and hyphenated techniques have been used to address a number of different problems in this area, allowing the identification of a number of materials, including additives, impurities and adulterants.

Lubricants derived from crude oil have been used in many applications and have been studied in many ways. The complexity of the samples often requires either hyphenated techniques

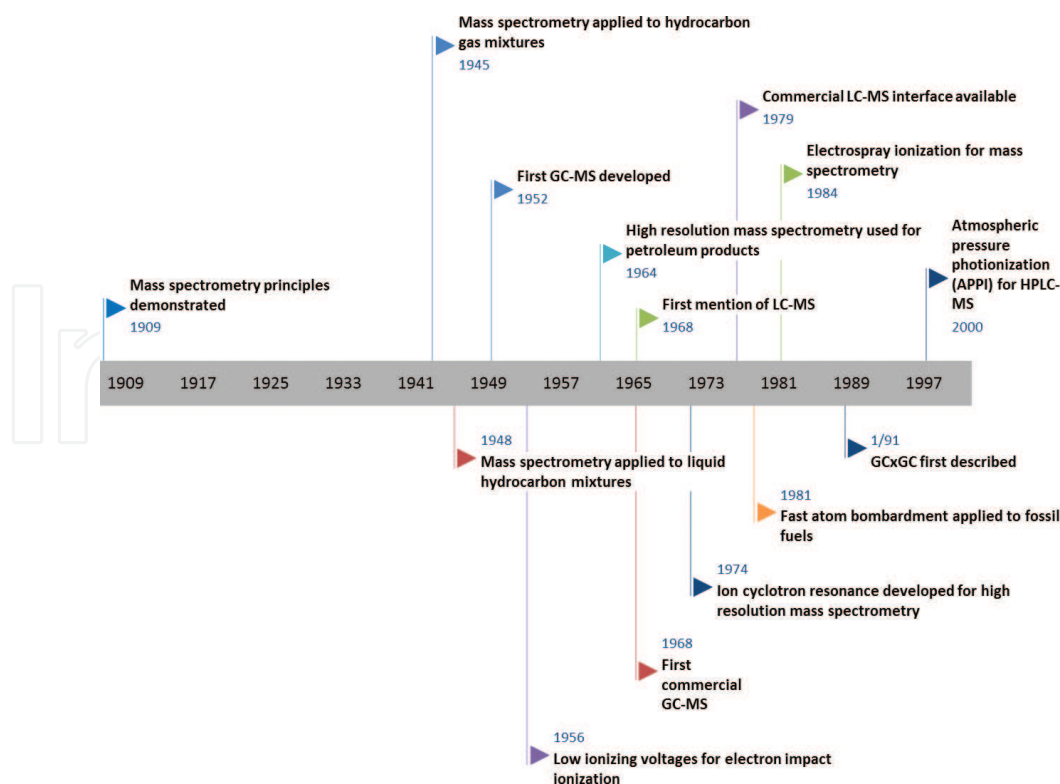


Figure 1. Some of the important advancements in the mass spectrometry of fuels and lubricants.

to identify components in the base stock, additives and also contaminants. Synthetic lubricants have been developed based on alkyl benzenes, poly alkylene glycols and polyol esters in part because of the greater control of the composition and chemistry of the base stock. The synthetic lubricants are simpler in composition and are more amenable to study using mass spectrometry and various hyphenated techniques [9].

In this chapter, the application of mass spectrometry and the various hyphenated techniques to fuels and lubricants is reviewed. A particular emphasis is placed on the examination of some of the problems that mass spectrometry has addressed and how questions about the source, composition and applicability of fuels and lubricants can be addressed. The chapter has sections devoted to mass spectrometric techniques for fuels and lubricants, followed by high resolution mass spectrometry, gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry.

2. Mass spectrometry

The early application of mass spectrometry to fuels and lubricants began in the early 1940s using electron impact ionization [10]. These studies were complicated by the complexity of the mixture and also the extensive fragmentation caused by 70 eV electron impact [11, 12]. The complex mass spectra could yield information about the fuel sample primarily through a complex calibration scheme using ratios of common peaks found in the mass spectra of different classes of hydrocarbons. The spectra, however, gave little information about the average molecular weight of the fuel or lubricant.

Mass spectra at low resolution did not provide enough information to fully characterize many of the petroleum fractions. Some information about compound types could be obtained based on ratios of peaks observed at low mass in the mass spectrum. The low resolution mass spectrum of a mineral oil based lubricant is shown in **Figure 2**. This technique allowed some of the different hydrocarbon types to be identified in the lower boiling (gasoline, for example)

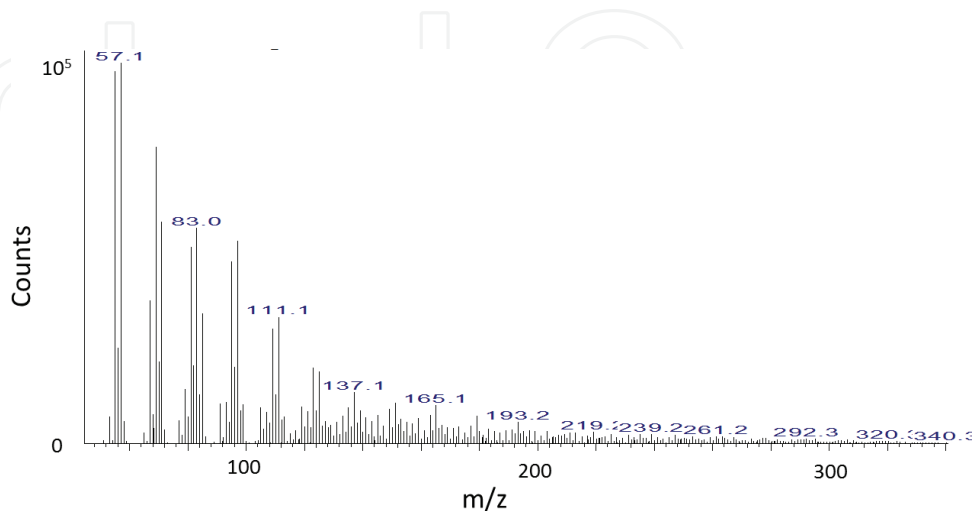


Figure 2. Low resolution mass spectrum of a mineral oil based lubricant (unpublished results).

fractions [13]. Very different compounds have the sample molecular mass at low resolution, so a number of pre-treatment techniques were developed to isolate compounds with certain functional groups for analysis by mass spectrometry. These techniques included preliminary separations by adsorption on silica or alumina [14]. In later work, adsorption chromatography was used as a preliminary treatment prior to mass spectrometric analysis [15].

It was quickly realized that the 70 eV ionization voltage was causing extensive fragmentation and gave no differentiation between different classes of compounds. Low voltage approaches were developed in order to selectively ionize certain classes of hydrocarbons, particularly olefins [16] or aromatics [17]. The lower ionizing voltage significantly reduced fragmentation allowing more high mass ions to be detected.

Success in this area led to the development of other soft ionization techniques some of which are summarized in **Table 1**.

The soft ionization techniques were successful in reducing the fragmentation of the ions formed, however molecular ions were still not always observed and the lack of fragment

Ionization type	Ionizing species	Comment
Electron impact(EI)	Beam of energetic electrons	Induces extensive fragmentation, gas phase technique, masses less than 1000
Chemical ionization(CI)	Ion molecule reactions of a reagent gas such as methane, ammonia or isobutane	Gas phase technique, typically give $[M + H]^+$, fragmentation reduced, limited to masses less than 1000
Field desorption(FD)	Sample deposited on emitter and emitter biased to several kilovolts. As current increases, sample vaporizes, ionization by electron tunneling emitter.	Simple mass spectrum, with a single peak per molecular species, moderate mass range–up to about 3000, sensitive to alkali metal contamination
Field ionization(FI)	Sample is evaporated from probe, GC or gas inlet. Ionization by electron tunneling when sample is near the emitter.	Simple mass spectrum, with a single peak per molecular species, moderate mass range–up to about 3000, sample must be somewhat volatile
Fast atom bombardment(FAB)	Sample is dissolved in a liquid matrix such as glycerol and place on target and bombarded with a fast atom beam	Rapid and simple, strong ion currents, good for high resolution, moderate molecular weights–up to 6000
Electrospray ionization(ESI)	Sample solution is aspirated across a high potential difference, heat and gas flow desolvates clusters	Good for charged, polar or basic compounds, multiply charged species are common, good for LC-MS, mass range to 200 k
Atmospheric pressure chemical ionization(APCI)	Sample solution is aspirated at atmospheric pressure, A corona discharge ionizes the sample	More effective than ESI for non-polar compounds, compatible with LC-MS, Low-moderate mass range up to 2000 AMU
Matrix-assisted laser desorption ionization (MALDI)	Analyte dissolved in a matrix that is UV active, on a Laser target, matrix absorbs laser pulse	Very high mass range–up to 500,000 AMU, requires pulsed mass analyzer, not compatible with LC-MS

Table 1. A summary of ionization techniques [18].

ions made compound identification through the use of libraries impossible. Softer ionization methods do, however give better estimates of molecular weight distributions since more high mass ions are formed. Softer ionization methods also allow differentiation of polar components of fuels or crude oils because they typically are easier to ionize than the hydrocarbon components of the sample. An example is the use of fast atom bombardment for the determination of nitrogen compounds in fossil fuels. The study demonstrated the effectiveness of fast atom bombardment in the analysis of liquid petroleum fractions [19].

3. High resolution mass spectrometry

Advances in mass spectrometry led to the development of instruments capable of much higher resolution than the original mass spectrometers. These high resolution instruments allowed multiple compounds with the same nominal mass to be separated and identified [20]. The introduction of double-focusing instruments and resolutions of 10,000 or more allowed for further reductions in sample preparation and allowed more components to be identified [21]. In many of these samples, the combination of high resolution mass spectrometry with low voltage ionization allowed for only certain major classes of compounds to be observed [22].

More recently, ultra-high resolution mass spectrometry has developed based on Fourier transform ion cyclotron resonance mass spectrometry (ICR-MS) for the determination of ion masses. In ICR-MS the ICR frequency of an ion in a uniform magnetic field depends on the mass and charge of the ion [23]. These instruments have extremely high mass accuracies and resolutions of 10^5 – 10^6 (m/ Δ m) which allows ions with very closely spaced masses to be identified [24]. The availability of ICR-MS has allowed many thousands of peaks in the mass spectrum of a crude oil sample to be identified to a unique molecular formula. The application of ICR-MS to problems in the petroleum field have spanned the range from identifying the source of weathered deposits found on beaches, to examining the types of sulfur compounds present and their susceptibility to removal in the desulfurization process.

The ability to identify several thousand individual compounds in a sample of a petroleum product opens a number of possibilities in the identification and tracking of the source of various products. This area of investigation is often referred to as petroleomics. Oil spills happen with some regularity, however it is not always an oil spill that results in oil fouling of beaches; natural seeps also release oil into the environment. In order to effectively clean up oil spills, it is necessary to know the properties of the oil and how it has weathered before deposition onto the beach. One technique for the identification of a source of an oil is principal component analysis where thousands of heteroatom containing species. The study led to the identification of a number of polar petroleum markers that are environmentally persistent and can identify the source of the oil [25]. In another study, ICR-MS was able to identify many highly oxygenated species that were formed by weathering of crude oil released from the Deepwater Horizon explosion in 2010 [26].

Environmental regulations have mandated a significant reduction in the sulfur content in various fuels in order to reduce sulfur dioxide emissions. Processes have been developed for the desulfurization of various types of fuels; however a portion of the sulfur in the fuel remains

even after aggressive desulfurization. ICR-MS has indicated that a portion of the aromatic sulfur is less able to be removed by the desulfurization process. Based on ICR-MS data, much of the sulfur in the fuel is present as either benzothiophenes or dibenzothiophenes. These compounds are susceptible to desulfurization, but if there are alkyl groups in certain positions on the aromatic rings (**Figure 3**), the compounds are far less reactive with the desulfurization catalyst [27]. A similar scheme was used in the study of some hexahydrobenzothiophenes [28].

Petroleum based fuels are prepared by the catalytic cracking, reforming and fractional distillation of crude oil. This process leads to a gasoline fraction (C_4 – C_{12}), kerosene fraction (C_8 – C_{18}) and diesel fraction (C_8 – C_{40}). While most components in these fuels are non-polar, there is a wide range of components that have heteroatoms and would be considered to be more polar than the hydrocarbons. It is often the polar compounds that lend themselves to analysis by mass spectrometry due to their ability to be ionized by soft ionization techniques [29]. Nitrogen containing polar compounds are typically observed in positive ion mode using electrospray ionization. Typical classes of nitrogen containing components in fuels are shown in **Figure 4**, below. Nitrogen compounds in fuels have been implicated in a number of fuel

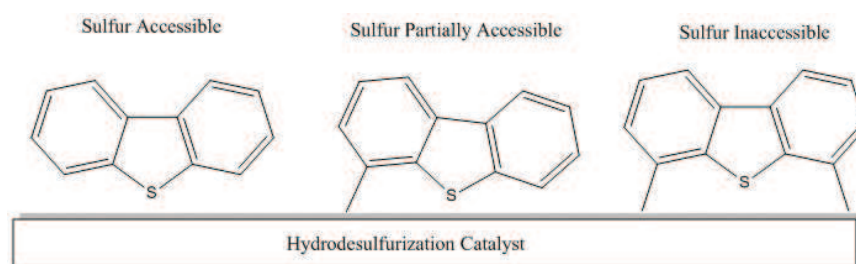


Figure 3. Steric hindrance in the interaction of substituted thiophenes with a dehydrosulfurization catalyst.

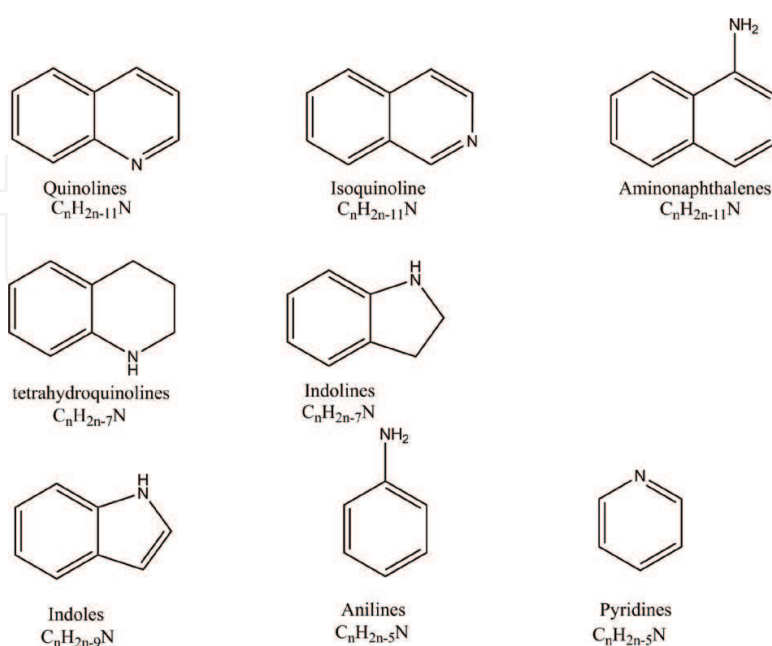


Figure 4. Typical nitrogen containing structures found in fuels.

problems, including fuel instability, sediment and gum formation. Some of the problems can be linked to specific classes of nitrogen compounds, basic nitrogen compounds tended to lead to greater stability, where non-basic compounds with particular substitution patterns are particularly reactive [30].

Negative ion electrospray ionization has also been used to study common types of fuels. Compounds commonly observed in fuels in negative ion mode are substituted phenols and thiophenols. These compounds can easily form either the phenoxide or thiolate ions [31].

On weathering, fuels typically shift in composition to compounds with higher molecular weight, as smaller compounds either evaporate or dissolve. This is primarily observed with kerosene and diesel fractions, as gasoline is too volatile [32].

4. Gas chromatography-mass spectrometry

Early experiments where adsorption chromatography was used to separate classes of compounds, coupled with the development of partition chromatography as a separation tool for use in GC, led to the idea of coupled gas chromatography-mass spectrometry (GC-MS) as an analytical technique. There were numerous problems, including the introduction of even small amounts of gas to the mass spectrometer could stop the mercury diffusion pumps used to maintain the high vacuum, the slow scan speed of magnetic sector instruments and the inability to record data quickly enough to collect all of the data. These problems were eventually solved with a gas separator [33], and then capillary gas chromatography, the development of fast mass analyzers, especially the time of flight [34] and quadrupole mass filter and finally the advent of low cost laboratory computers. The use of GC-MS became truly practical for many laboratories with the introduction of low cost dedicated GC-MS instruments in the early 80's.

The primary advantage of GC-MS as a modern analytical technique is combination of the separating power of capillary gas chromatography with the ability of mass spectroscopy to provide a mass spectrum of the compound being eluted. The technique is especially powerful when combined with libraries of possible compounds allowing a computerized identification of the compounds present in the mixture.

4.1. GC-MS of fuels

Gas chromatography-mass spectrometry has proven to be extremely useful in the analysis and identification of fuels. When operated with electron impact ionization, all compounds of the fuel are ionized, and the total ion chromatogram can give an estimate of the boiling point of the fuel, and an estimate of the molecular weight range. It is also possible to find additives or adulterants by GC-MS, since these materials frequently appear as a single peak in the chromatogram.

The analysis of gasoline is very well suited to GC-MS analysis since the boiling range is relatively low and because of the C₄–C₁₂ distribution of the hydrocarbons, the number of isomers is more manageable. A fundamental problem, however, is that fuel properties are not

well predicted based on the distribution of the hydrocarbon species. More important properties include ethanol and aromatic content, which alter octane rating and also vapor pressure, which is important to the environment. Determination of the aromatic content and the identification of the various substituted aromatics is a problem well suited to GC-MS [35], especially when coupled with a good library and search algorithm. Other applications include the identification of adulterants and contamination by higher boiling fuels.

A fuel type that has been heavily studied is the fuel used for aviation. Aviation fuels are highly refined un-leaded kerosene in which the carbon range is between 8 and 16. The demands of aviation require a highly refined fuel in which the flash point is above 38°C and the polar contaminants have been significantly reduced. Additives are typically necessary in order to improve the low temperature and high temperature properties of the fuel [36]. GC-MS has been successfully used to model the properties of a number of military aviation fuels [37]. GC-MS has also been utilized as a method for the quantification of anti-oxidants which are added to reduce autoxidation of the fuels on storage which can lead to the formation of deposits [38]. The GC-MS of two different jet fuels are shown in **Figure 5**. Both samples show a number of major components that are readily identified and other components that would act as a fingerprint for the fuel. A major difficulty, however, relates to the observation that the baseline has significant slope, indicating a very large number of minor components present in the sample. The minor components include many components critical to understanding the low temperature reactivity and possible sludge formation in the fuel.

Many of the chemical properties especially autoxidation of fuels can be related to polar components, present at <0.1% in the multicomponent hydrocarbon matrix. These components include phenols, indoles, amines, thiophenes and many others. Some of these components can

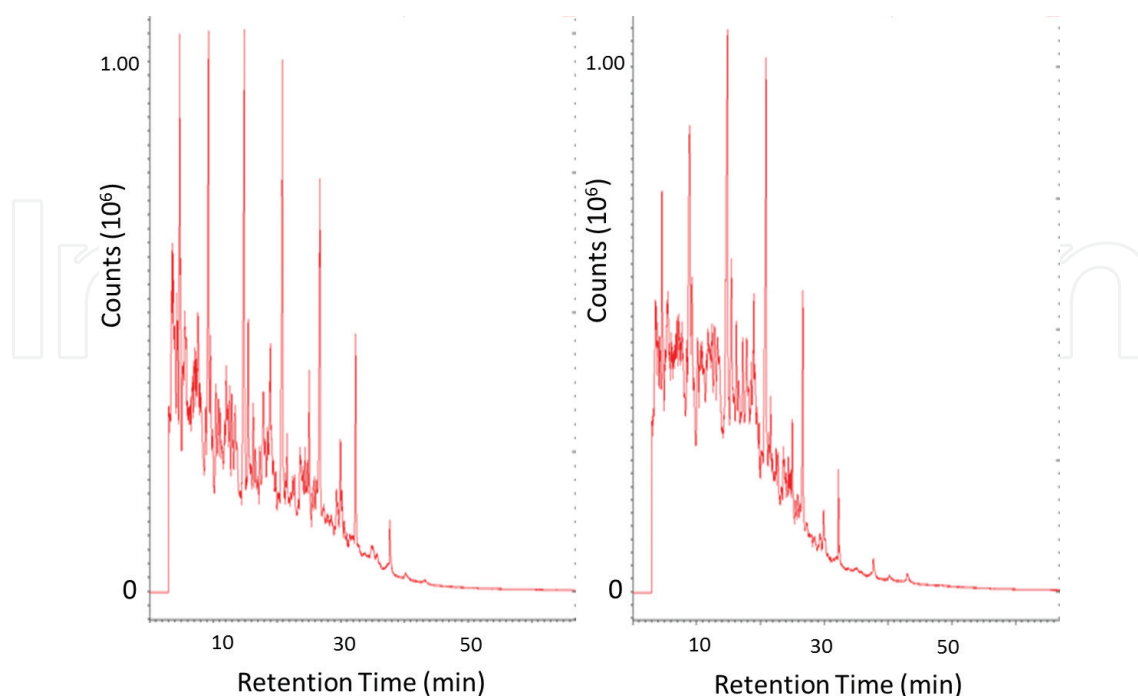


Figure 5. GC-MS total ion chromatograms of two different jet fuel samples.

be determined by chemical pre-treatment using solid phase extraction followed by GC-MS. This technique allowed the more polar compounds to be separated from the hydrocarbons prior to analysis.

The need to determine the trace components of complex mixtures such as jet fuel has encouraged the development of 2 dimensional GC or GCxGC. A sample analyzed by GCxGC is first separated on a non-polar column, which results in a separation primarily based on boiling point. A thermal or valve modulator focused the compound eluted in time slices onto the head of a second column which is typically short (1-2m) with a polar stationary phase [39]. The compounds are then eluted from the second column and detected by mass spectrometry. Two dimensional GC results show the polar compounds having a significantly longer retention time in the second dimension allowing easy identification. Possibly the most important feature of GCxGC data is that similar compounds are grouped at similar retention times in the second dimension.

4.2. GC-MS of lubricants

4.2.1. Mineral oil based lubricants

The GC-MS of mineral oil based lubricants typically results in broad peaks that do not allow individual compounds to be identified. The broad peaks are due to the huge number of isomers possible with hydrocarbons of the C₂₀–C₃₀ range. The compounds are very similar in properties and there are differences depending on the processing and refining methods used for the particular type on mineral oil. The total ion chromatogram for a sample of a yellow mineral oil and a white mineral oil are shown in **Figure 6**. The difference in the distribution of

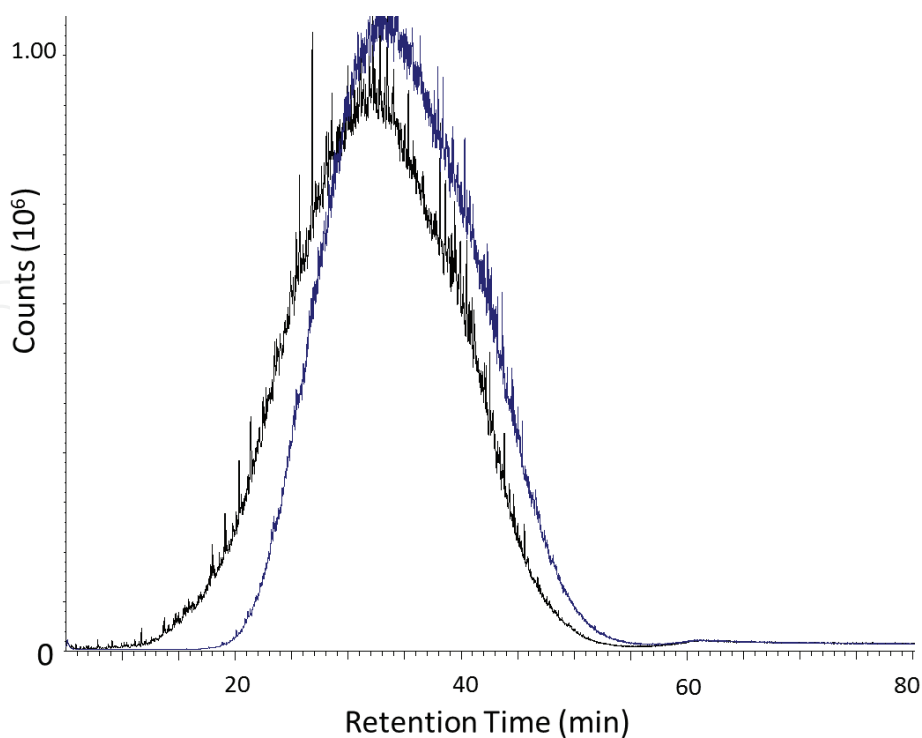


Figure 6. A comparison of the total ion chromatograms of two different mineral oils.

the compounds, which leads to significant differences in properties, can be seen. GC-MS can also be used to examine oil breakdown products, which in the case of mineral oils generally lead to the formation of products that are more polar and frequently have higher molecular weights resulting in longer retention times by GC.

Another important application of GC-MS in the analysis of mineral oils is the identification and quantitation of various additives. Mineral oils typically have a number of additives included in the formulations which improve certain properties of the lubricant, including pour point, oxidative stability and anti-wear properties. In general, the more highly refined the lubricant, the more additives need to be included [40]. This is in part because naturally occurring sulfur compounds are natural anti-oxidants and form hard surfaces on bearings reducing wear. **Figure 7** shows the total ion chromatogram of a formulated mineral oil. The sharp peaks appearing above the distribution are components of the phosphate ester anti-wear additive. Phosphate esters form a surface layer that resists wear under boundary layer lubrication, such as during start-up of the process [41]. GC-MS can indicate additives present and also be an indicator of additive depletion or decomposition. The four sharp peaks at 40–50 minute retention times are the components of the phosphate ester anti-wear additive. The peak at 20 min is due to the anti-oxidant included in the formulation.

4.2.2. Synthetic lubricants

The development of synthetic lubricants has illustrated a need to identify different sources of the lubricant and also identify the different additives needed to improve many of the properties of the lubricants. GC-MS has been shown to be useful in both the identification of the base stock and the quantification of the components of the additive package. Typically, synthetic lubricants fall into categories primarily based on the base stock. Some base stock categories include alkyl benzenes, polyalphaolefins (PAO), polyalkylene glycols and polyol esters. Each of these categories of lubricants has characteristic features which allow them to be identified.

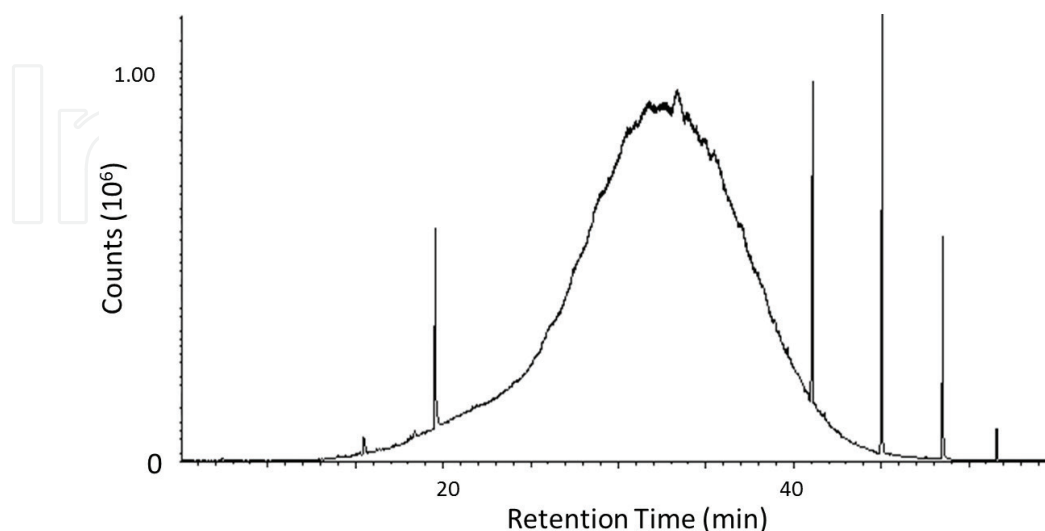


Figure 7. The total ion chromatogram of a blended mineral oil with sharp peaks indicating anti-oxidant and anti-wear additives.

One of the common classes of synthetic lubricant base stocks are the alkyl benzenes. These lubricants have found application in refrigeration systems and heavier alkylbenzenes have been used in automotive applications [42]. The GC-MS of these base stocks are characterized by series of peaks of the same molecular weight corresponding to different attachment points for the alkyl group. The total ion chromatogram for an alkylbenzene refrigeration lubricant is shown in **Figure 8**. The peaks observed at 22–30 min retention time correspond to monoalkyl benzenes with C12–C14 alkyl groups attached. At longer retention times, dialkylbenzenes are observed with similar length alkyl groups.

A second major class of synthetic lubricants are poly alpha olefins. They are available in a wide range of viscosities for applications ranging from compressor lubricants through gear oils and greases, including automotive applications. These lubricants are produced by the polymerization of alpha olefins, with 1-decene used as the main component in lubricants. The oligomeric mixture is the hydrogenated and distilled to give lubricants graded by their viscosity at 100°C [43]. Their GC-MS typically appears as a series of broad peaks indicating different degrees of polymerization. A GC-MS chromatogram of a poly alpha olefin is shown in **Figure 9**.

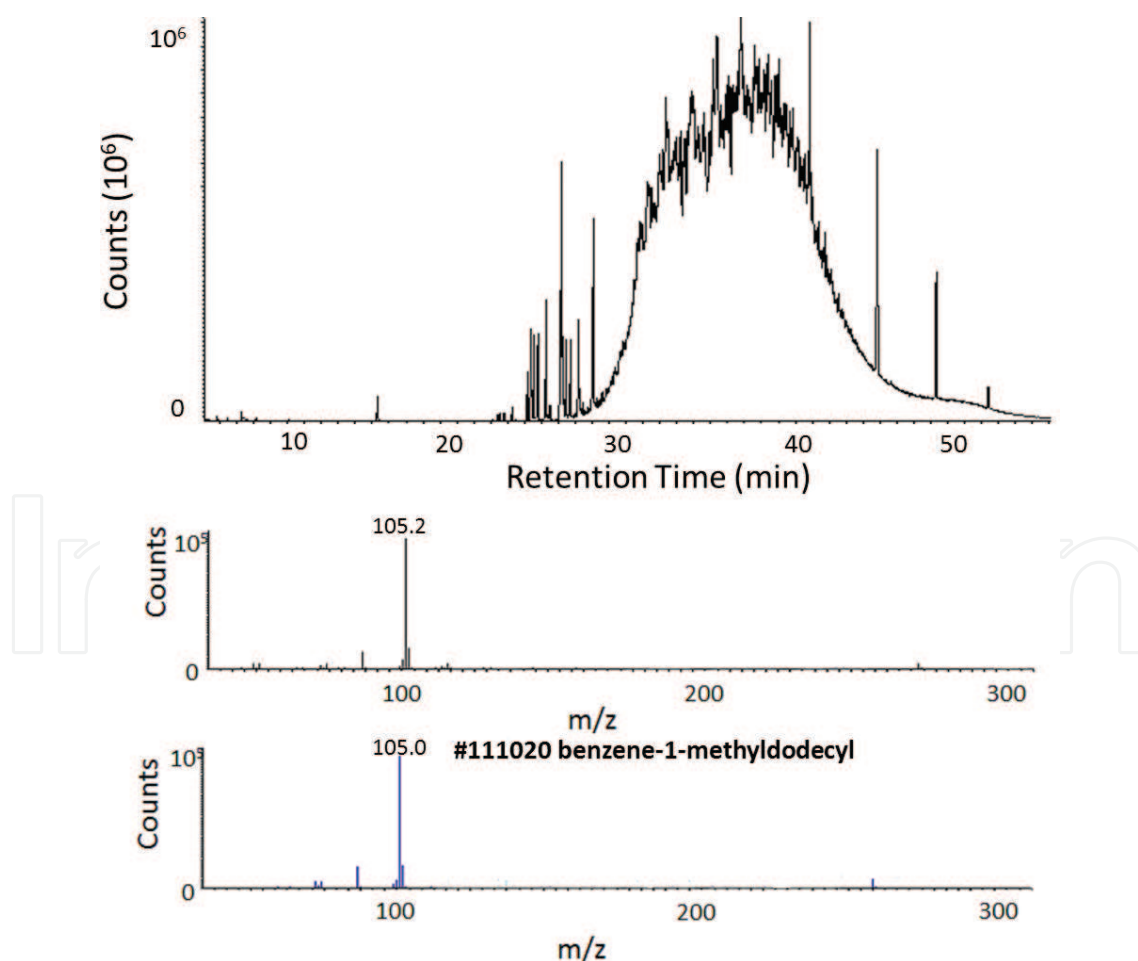


Figure 8. Total ion chromatogram for an alkyl benzene refrigeration lubricant and mass spectrum of peak at 28.034 min (top) and library match (bottom).

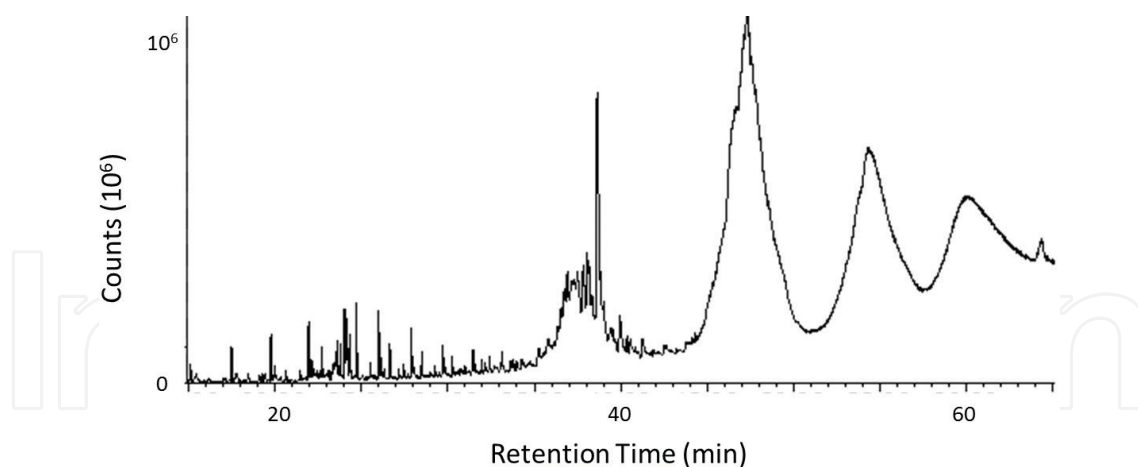


Figure 9. GC-MS chromatogram of a poly alpha olefin lubricant.

Polyalkylene glycol based lubricants were initially developed by the United States Navy as a water soluble, non-flammable hydraulic fluid. As a hydraulic fluid, mixtures of water and glycol had a wide temperature range. Polyalkylene glycol based lubricants that are oil soluble have also found significant application as gear lubricants, particularly for application in wind turbines [44]. The GC-MS chromatograms for several different PAG based oils are shown in **Figure 10**. The chromatograms can be very different depending on the material polymerized, since oils soluble PAGs are typically a mixture of propylene glycol and butylene glycol, where water soluble PAGs are primarily polyethylene glycol based. In many cases, materials of different molecular weights are mixed in order to achieve the correct viscosity and solubility.

Many aerospace lubricants are based on polyol ester base stocks which can be identified based on the polyols and the acids used in the base stock. These lubricants have substantially higher performance than petroleum based lubricants. The lubricants are typically based on a mixture of polyols and carboxylic acids depending on the desired stability and viscosity. United States military aircraft typically use lubricants with either a MIL-PRF 7808 specification which are based on neopentyl glycol and trimethylolpropane as the alcohol, or MIL-PRF 23699 specification which is based on pentaerythritol esters. The GC-MS total ion chromatogram for two typical polyol

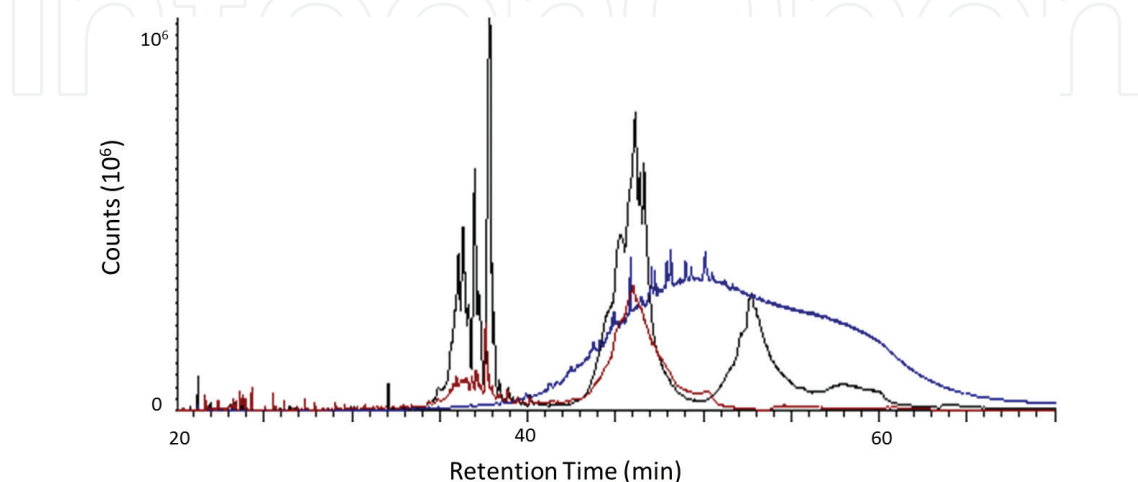


Figure 10. GC-MS chromatograms of three different PAG based lubricants.

ester based lubricants is shown in **Figure 11**. The chromatograms show the effects of a different set of carboxylic acids esterified with pentaerythritol. Using several alcohols and combinations of linear and branched carboxylic acids allows the viscosity and reactivity of the lubricant to be varied considerably.

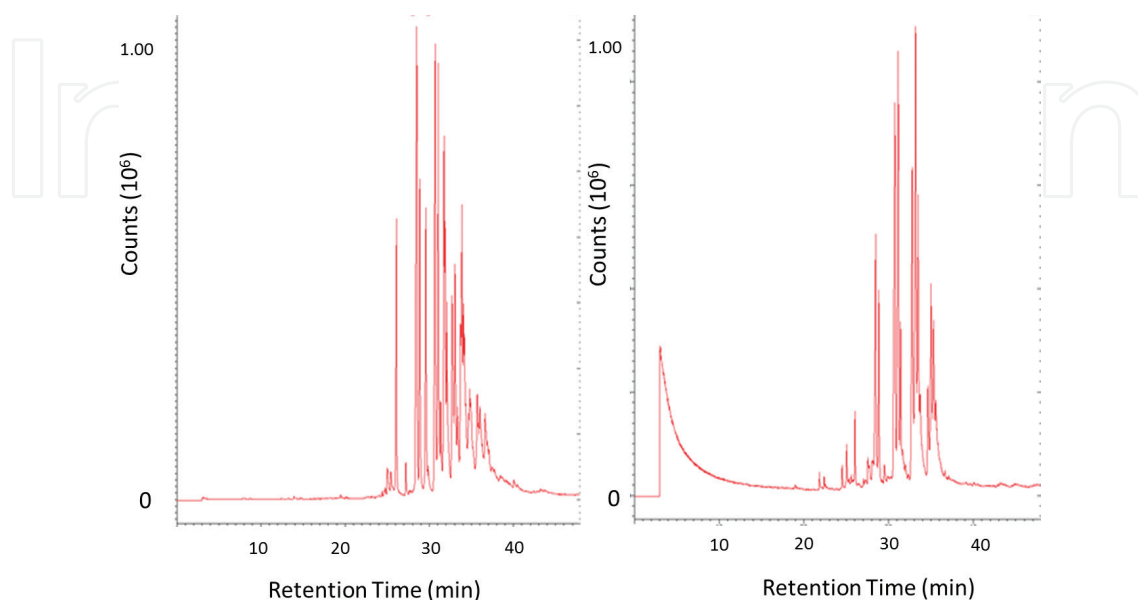


Figure 11. GC-MS total ion chromatogram for two polyol ester based lubricants.

5. Liquid chromatography-mass spectrometry

Gas chromatography-mass spectrometry has seen considerable use in the analysis of fuels and lubricants, but has the primary requirement that all components of the mixture be volatile. High performance liquid chromatography does not suffer from this limitation and can also be used in conjunction with mass spectrometry (LC-MS). LC-MS can be operated in two different separation modes, normal phase in which a polar stationary phase is used and non-polar compounds elute quickly, followed by the polar materials, and reversed phase in which a non-polar stationary phase causes the polar materials to elute first. Both separation modes have been used in the analysis of fuels and lubricants.

LC-MS has been slower to develop than GC-MS, primarily due to the problems associated with the introduction of the sample into the mass spectrometer, without introducing large amounts of the solvent at the same time. This problem has been solved with the development of atmospheric pressure ionization methods. These methods ionize molecules in the sample and allow the majority of the sample to evaporate while drawing charged particles into the mass spectrometer. There are three common atmospheric pressure ionization methods used for the LC-MS of fuels and lubricants; electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI).

Electrospray ionization is an ionization method where a liquid is aspirated into a region where there is a very strong electric field. Ions or clusters of ions are formed in solution and

as the solvent is evaporated by a drying gas, or heated capillary, the analyte forms ions by reaction with ions in solution. The ions are transferred into the mass spectrometer for analysis. Electrospray works well for samples that can gain a proton in positive ion mode or those which can lose a proton in negative ion mode and works well in polar solvents. A major advantage (or disadvantage) is that the hydrocarbons present as the bulk of the fuel or lubricant is not ionized, making the examination of polar species simpler [45].

Atmospheric pressure chemical ionization (APCI) is an ionization method where a corona discharge initially ionizes the nitrogen drying gas, which then ionizes the molecules of interest. APCI does not depend on ionizing the sample while it is still in solution, although recent work has demonstrated that significant ionization does occur in solution [46]. APCI does have the advantage for fuels and lubricants that it can generate ions from neutral species and is useful for low-medium polarity analytes. In many ways APCI is somewhat complementary to ESI for the analysis of polar species in fuels and lubricants.

Atmospheric pressure photoionization (APPI) is a third ionization technique easily available in LC-MS. In APPI, an ultraviolet light source (typically about 10 eV) ionizes a dopant (usually acetone or toluene) added to the mobile phase, which ionizes the analytes. APPI has been shown to give higher sensitivity than APCI for certain types of analyte, including polycyclic aromatic compounds and polar aromatic compounds. APPI appears to be an excellent ionization method, especially for polar compounds with low proton affinities [47].

Electrospray ionization has been successfully applied to the identification of nitrogen-containing aromatics in crude oil showing a wide range of compound types [48]. Other studies indicated other heteroatom-containing compounds could also be ionized and detected using electrospray, including sulfides and aromatics [49]. LC-MS with electrospray ionization has been used to identify several homologous series of nitrogen-containing species, including pyridines, anilines, quinolones and carbazoles in several jet fuel samples. **Figure 12** shows the identification of a number of nitrogen-containing compounds in a single mass spectrum. It is important to realize that substituted pyridines and substituted anilines can have identical formulas, but very different chemistry.

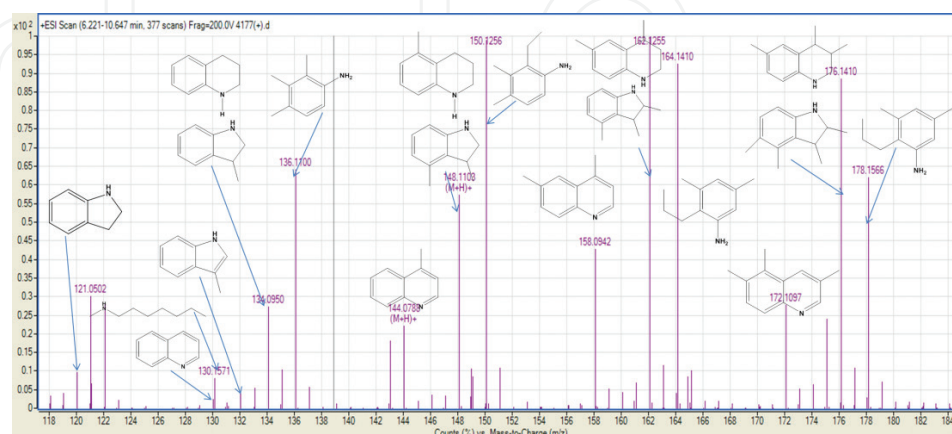


Figure 12. Identification of a number of different nitrogen compounds in the HPLC of a jet fuel sample based on mass spectrometry [50].

Negative ion electrospray has also been used to determine phenols in the same fuels [51]. Phenols are a critical component in low temperature oxidation mechanisms for deposit formation in turbine engines [52]. It has also been shown that fuel additives, especially a corrosion inhibitor/lubricity improver can be determined by LC-MS and ESI ionization in negative ion mode [53]. One of the disadvantages of electrospray ionization is that compound types and functional groups cannot always be identified, even with accurate mass data. In **Figure 13**, the anilines are identified based on the formation of a derivative followed by mass spectrometry. In these cases, a chemical derivatization process may be beneficial in identifying functional groups in conjunction with LC-MS [54].

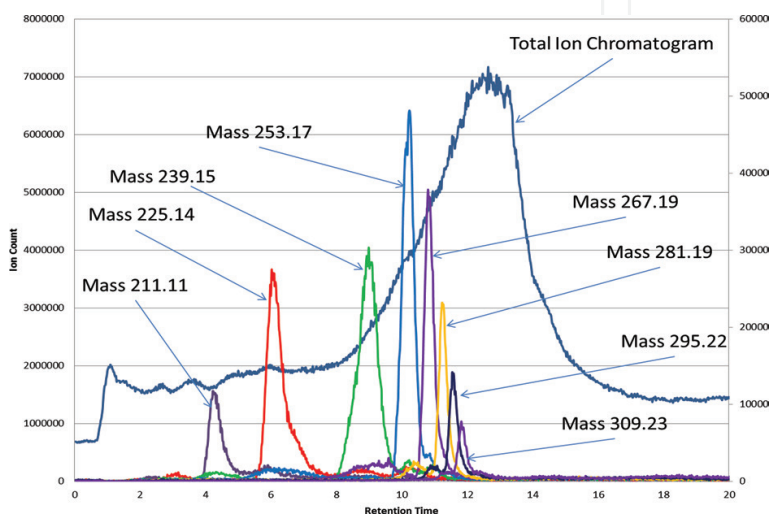


Figure 13. Identification of the anilines based on formation of a derivative with pyridine-2-aldehyde.

6. Conclusions

Mass spectrometry has evolved from a specialist technique for the determination of the bulk characteristics of fuels and lubricants to a general laboratory tool that can be used to answer a wide range of questions. Many of the advances can be traced to advances in technology that have brought about developments in ionization methods, mass separators and ion detectors. Low energy ionization methods allow the trace components with heteroatoms, which are generally more easily ionized to be examined without interference from the major hydrocarbon peaks. The development of high resolution and ultra-high resolution mass spectra has made it possible to determine molecular formulas from each peak in the mass spectrum. This advance has made it clear that petroleum based fuels and lubricants are more complex than was previously thought.

A potentially more important advance mass spectrometry has been the incorporation of separation techniques and library searching procedures which allow complex mixtures to be separated into individual components which can then be identified. Coupling of mass spectrometry with gas chromatography and liquid chromatography has provided tools to

examine complex mixtures without the ultimate in mass resolving power. Coupling of chromatography with mass spectrometry using new ionization methods which reduce the fragmentation have allowed molecular weights of compounds to be determined. While electron impact mass spectra can readily be searched through available libraries to identify individual components in the fuels and lubricants.

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