Fuels and Lubricants Handbook:

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Hydrocarbon Analysis

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THE AIM OF THIS CHAPTER IS TO BRIEFLY PRESENT SIX ANALYTICAL METHODS for characterizing hydrocarbon compounds found in fuels and lubricants. The methods presented are NMR spectrometry, gas chromatography, liquid chromatography, ultraviolet spectroscopy, mass spectrometry, and infrared spectroscopy. The analysis of hydrocarbons deploying these methods is well-founded in scientific laboratories and is the basis of numerous ASTM standards.

Because of the large body of published work on these methods, it is not the intention of the authors to attempt complete coverage of all methods, but rather to provide an overview of their use in the analysis of fuels and lubricants. Following each section are summaries specific to ASTM D 02 standards where the analytical method is deployed in the areas of fuels and lubricants.

NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is one of the most widely used analytical tools in chemical analysis. Just like infrared (IR) and ultraviolet (UV) spectroscopy, NMR is a form of absorption spectrometry, whereby the amount of absorbed electromagnetic radiation at a given frequency can be related to the concentration of certain chemical species that absorb at that frequency. However, unlike IR spectroscopy, which looks at functional groups within a molecule, or UV spectroscopy, which looks at the molecule as a whole, NMR is used to determine the concentration of specific atoms within a sample.

It is not the mandate of this chapter to provide a detailed quantum physical explanation of NMR or any other analytical method described herein. However, the basic theory behind NMR spectroscopy will be outlined in this section, so that the reader can obtain an understanding of NMR and how it can be applied to the analysis of large hydrocarbon molecules typically found in fuels and lubricants.

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Basic Principles of NMR Spectrometry

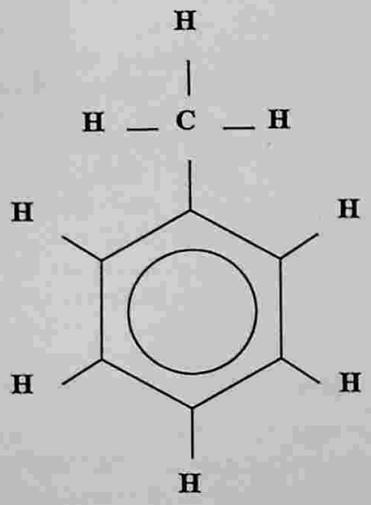
Absorption spectrometry works because applied electromagnetic radiation of an appropriate frequency induces a transition from one (lower) energy level to another (higher) energy level within the molecule, causing the radiation to be absorbed by the sample. In IR and UV spectrometry, these energy levels are the vibrational and electronic energy levels of the molecule, whereas in NMR the energy levels are associated with the nuclear spin of the nuclei that make up the molecule. For the purpose of detailing how NMR works, we will focus on the most commonly studied nucleus, the hydrogen nucleus ^{1}H, which has a nuclear spin of ½.

A nucleus such as ^{1}H with a spin of ½ possesses two nuclear spin states, +½ and −½. Under normal circumstances, these spin states have the same energy and are said to be degenerate. However, in the presence of a strong magnetic field (typically 2.33 tesla (T) for the ^{1}H nucleus), the two nuclear spin states split into two energy levels, their separation being proportional to the applied magnetic field as shown in Fig. 1 [1].

Applying a source of electromagnetic radiation and slowly scanning the frequency can induce absorption when the radiation frequency matches or is in resonance with the energy separation of the two nuclear spin states under the applied magnetic field. The frequency of radiation that must be applied to induce such a transition is typically in the radio frequency (*rf*) range. For a ^{1}H nucleus under an applied magnetic field of 2.33 T, the resonance frequency is around 100 MHz [2]. For practical reasons, NMR spectrometers usually work in the opposite sense, with a fixed electromagnetic radiation frequency (commonly 100 MHz for ^{1}H NMR) and a scanning magnetic field [3]. However, the same principle applies: the magnetic field is scanned until the energy separation of nuclear spin states induced by the field comes into resonance with the applied electromagnetic radiation.

In reality, the magnetic field that must be applied to bring a nuclear spin transition into resonance with the applied electromagnetic radiation varies slightly with the chemical environment of the nuclei in question. This phenomenon is known as *shielding* and can be attributed to the effects of the electrons surrounding a particular nucleus, shielding the nucleus from the effects of the magnetic field [2]. Because the electron density surrounding a particular nucleus is directly related to the chemical structure of the molecule, the electron distribution within the molecule gives rise to shielding effects, which are typically called the chemical shift, which can be used to differentiate between the same nuclei (for example

^{1}H) in different chemical environments. Take for example the molecule toluene:



Toluene has two types of protons, either as part of the methyl group, or attached to an aromatic carbon. Because the shielding experienced by these two different types of protons will depend on both electron density and ring current effects, the resonance frequency for interaction with the applied field will be different. The NMR spectrum for toluene will thus be split into two groupings, one associated with the methyl hydrogen nuclei, the second with the aromatic hydrogen nuclei. The relative intensities of the absorption peaks for the two groups will be in the ratio 3:5 corresponding to the relative ratios of the nuclei in the two environments. The ^{1}H NMR spectrum for toluene is shown in Fig. 2 [4].

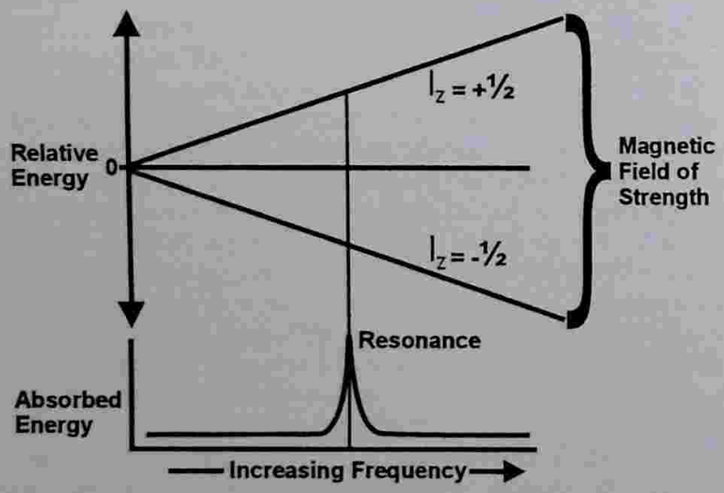


FIG. 1—The separation of proton nuclear spin states under an applied magnetic field.

The chemical shifts reported in NMR spectrometry are usually expressed as the parts-per-million (ppm) shift from the resonance frequency of a reference standard, usually tetramethylsilane (*TMS*). The chemical shift can be calculated using the following formula [5]:

$$\text{Chemical shift (in ppm)} = (RF_S - RF_{TMS})/RF_{TMS} \times 10^6$$

Where RF_S is the resonance frequency of the sample and RF_{TMS} is the resonance frequency of the *TMS* reference. Some typical chemical shifts for ^{1}H in hydrocarbon molecules are shown in Table 1 [5].

The key to using NMR spectrometry in the analysis of hydrocarbon molecules is to recognize the chemical shifts observed in the NMR spectra and relate the relative concentrations of nuclei in these different environments to help elucidate the bulk properties of a hydrocarbon sample, for example the concentration of aromatic molecules in a hydrocarbon oil.

^{13}C NMR Spectrometry

NMR spectrometry is not limited to just hydrogen nuclei. In fact, any nucleus with an odd sum of protons and neutrons will possess a magnetic moment and can thus be analyzed using NMR. Aside from ^{1}H, the second most commonly studied nucleus is ^{13}C, which like ^{1}H has a nuclear spin of ½. Carbon exists in two naturally occurring isotopes ^{12}C and ^{13}C, with relative natural abundances of 98.9% and 1.1%, respectively. Although ^{12}C has an even sum of protons and neutrons and thus does not possess a magnetic moment, with sufficient ex-

TABLE 1—Typical chemical shifts for ^{1}H nuclei in hydrocarbon molecules.

^{1}H Nucleus Environment	Chemical Shift/ppm
CH_2 and CH_3 H atoms far from aromatic rings	0.5–2.0
CH_2 and CH_3 H atoms in the α position relative to an aromatic rings	2.0–4.0
H atoms in monocyclic aromatic rings	6.0–7.2
H atoms in Polycyclic aromatic rings	7.2–9.0

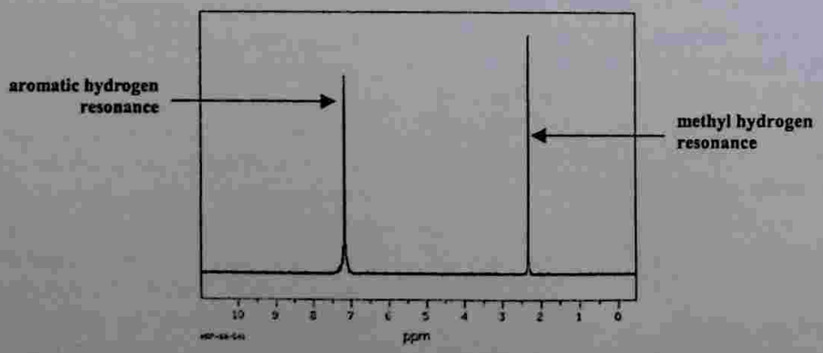


FIG. 2—^{1}H NMR spectrum for toluene.

TABLE 2—Typical chemical shifts for ^{13}C nuclei in hydrocarbon molecules.

^{13}C Nucleus Environment	Chemical Shift/ppm
Aliphatic and naphthenic carbon atoms	10.0–60.0
Carbon atoms in terminal CH_3 groups	14.1
Carbon atoms in CH_2 groups in the middle of a chain	29.2
Carbon atoms in aromatic rings	110–160

perimental resolution, the NMR spectrum of samples containing ^{13}C nuclei in natural abundance can be recorded and analyzed, in much the same way as ^{1}H NMR spectra can be analyzed to determine key structural properties of the molecules that comprise the bulk sample.

Just like ^{1}H NMR, the resonant frequency of the ^{13}C nuclei are influenced by the chemical environment in which they are surrounded and again, chemical shifts can be calculated in ppm relative to a calibration standard such as TMS using the same formula used to calculate ^{1}H chemical shifts. Chemical shifts for ^{13}C nuclei tend to be somewhat larger than ^{1}H shifts in hydrocarbon molecules. Some typical chemical shifts for ^{13}C nuclei in hydrocarbon molecules are shown in Table 2 [5].

Because the natural abundance of ^{13}C is so low, the experimental measurement of ^{13}C NMR spectra is slightly more difficult than ^{1}H NMR spectra because the spectra tend to be much weaker. To overcome this difficulty, the spectra are recorded not by scanning the frequency as for ^{1}H NMR (a technique often called continuous wave or CW) but by pulsing a series of short pulses of broad band radiation (of the order of 0.5–50 μs) and monitoring the free induction decay of the signal from the ^{13}C nuclei. This time domain single is then converted into the frequency domain using Fourier Transformation [2]. This, coupled with other techniques too advanced to discuss here, have made the recording and interpretation of ^{13}C NMR spectra commonplace [5].

The Use of ^{1}H and ^{13}C NMR in the Analysis of Hydrocarbons

Because ^{1}H and ^{13}C are the two nuclei most commonly analyzed by NMR spectrometry, it stands to reason that NMR has proven useful in hydrocarbon analysis. There are two main areas where NMR has been used for hydrocarbon fuel and lubricant analysis, specifically the identification of hydrogen content in aviation fuels (ASTM D 3701) and petroleum distillates (ASTM D 4808), and in determining the aromatic hydrogen and aromatic carbon content using ^{1}H and ^{13}C NMR spectrometry (ASTM D 5292).

The determination of hydrogen content is an important property of a fuel or lubricant because it is closely related to key performance characteristics and can be used as a measure of quality control both during and after production. Both test methods (ASTM D 3701 and ASTM 4808) work by taking the ratio of the total integrated hydrogen signal from the sample NMR spectrum to a known n-dodecane standard run on the same NMR instrument. In each case, the total hydrogen content by mass (H%) is then calculated using the formula,

$$H(\%) = S/R \times (W_R/W_S) \times 15.39$$

where S is the total integrated hydrogen signal from the sample, R is the integrated signal from the n-dodecane reference, W_R is the weight of n-dodecane used, W_S is the weight of sample used, and 15.39 simply reflects the percentage by mass of hydrogen in the n-dodecane reference standard. The accuracy of this test method is around 0.2–0.4% for a typical hydrogen content of 14% [5]. Other variations on this method have also been used, which involve pulsed FT NMR, which are capable of errors as low as 0.05% [6, 7].

Hydrocarbon oils made by the refining of crude petroleum are generally classified paraffinic or naphthenic depending on the predominant class of hydrocarbon compounds found in the oil [8]. Despite this, most oils of this type contain a significant proportion of aromatic hydrocarbons. The aromatic content of an oil can affect a number of physical and chemical properties such as boiling range, viscosity, stability, and compatibility. For this reason, it is important to be able to determine to amount of aromatic hydrocarbon content in a hydrocarbon oil [9].

One way of characterizing the aromatic content is to count the number of aromatic carbon and hydrogen atoms in a bulk sample. Because NMR is capable of separating signals from different atoms within molecules based on their chemical structure and environment using the concept of chemical shifts, NMR is a natural for this type of determination: this is the basis behind ASTM D 5292. In this case, the test method is even simpler than measuring total hydrogen content. The sample is analyzed using pulsed FT NMR and the total aromatic ^{1}H and ^{13}C content determined by taking the ratio of the aromatic carbon or hydrogen nuclei integrated signal to the corresponding aliphatic signal. For the purpose of assigning ^{1}H nuclear environments, peaks in the chemical shift range −0.5 to 5.0 ppm are considered aliphatic hydrogen, while those in the 5.0–10.0 ppm range are considered aromatic. A typical NMR spectrum of this kind is shown in Fig. 3. For ^{13}C NMR, peaks in the −10 to 70 ppm range are considered aliphatic, while those in the 100–170 ppm range are considered aromatic carbons [9].

The biggest drawback with NMR is the expense of purchasing and running an NMR instrument. However, in circumstances where the determination of the relative proportions of various constituents of a bulk sample in different chemical environments at high precision are required, NMR offers a quick simple means of obtaining quick, accurate data. For this reason, the use of NMR as a tool for hydrocarbon analysis will continue to grow.

ASTM Petroleum Products and Lubricants NMR Test Standards Under Subcommittee D 02.04

Aromatics in Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance (HR-NMR) (ASTM D 5292)

This method is applicable to a wide range of hydrocarbon oils that are completely soluble in chloroform and carbon tetrachloride at ambient temperature. The data obtained by this method can be used to evaluate changes in aromatic contents of hydrocarbon oils due to process changes. Hydrogen (^{1}H) NMR spectra are obtained on sample solutions in chloroform-d using a continuous wave or pulsed FT high resolution NMR spectrometer. Carbon (^{13}C) NMR spectra are obtained

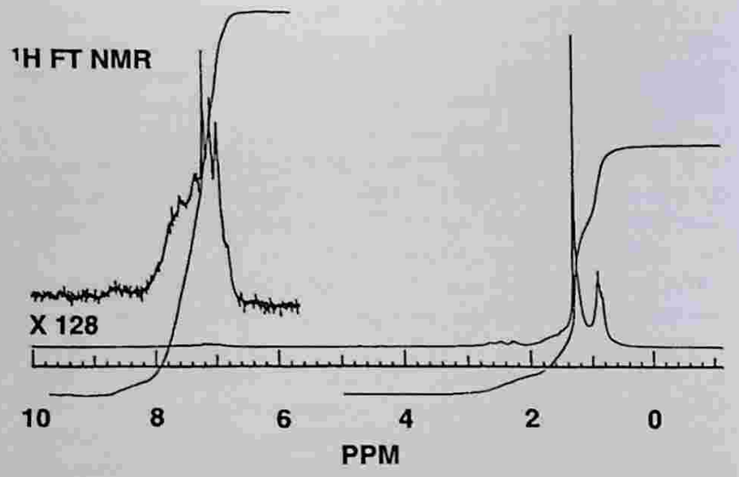


FIG. 3—^{1}H NMR spectrum of gas oil showing the aliphatic (−0.5 to 5.0 ppm) and aromatic (5.0 to 10.0 ppm) hydrogen peaks. Reprinted from ASTM D 5292-93.

on the sample solution in chloroform-*d* using a pulsed FT high resolution NMR.

GAS CHROMATOGRAPHY (GC)

Introduction

GC is one of the most widely used analytical tools in the evaluation of petroleum products, as witnessed by the number of relevant standards summarized at the end of this section that use GC. Its principal value lies in the fact that the technique can be used to separate complex mixtures of different molecules or groups of molecules based on their physical properties, which is precisely why it is such a valuable method for fuel and lubricant analysis.

Because GC involves first getting the sample into the gas phase, it is used in the analysis of the more volatile components of fuels and lubricants. Less volatile fractions are typically analyzed using the related technique of Liquid Chromatography, which will be discussed in the following section. GC is also used to simplify several spectrometric techniques such as Mass Spectrometry (MS) and Fourier Transform Infrared Spectroscopy (FTIR) by first separating the sample into different molecular component types. The use of GC in GC-MS and GC-FTIR is covered under the relevant spectroscopic technique. The direct application of Gas Chromatography (GC) to the evaluation and analysis of hydrocarbons will be discussed in this section.

Gas Chromatography

Gas Chromatography can be subdivided into two categories, gas-liquid chromatography and gas-solid chromatography [10]. In each case, the technique involves the separation of components of a gaseous sample using a stationary phase, either a liquid in the case of gas-liquid chromatography, or a solid in the case of gas-solid chromatography. Because the overwhelming majority of test standards used for hydrocarbon analysis rely on gas-liquid chromatography, we will focus exclusively on this method, although the same basic principals apply to both methods.

In gas-liquid chromatography, it is the interaction between the gaseous sample being carried through the column by means of an inert gas (the mobile phase) and a standard liquid (the stationary phase), which causes the separation of different molecular constituents. The stationary phase is either a polar or nonpolar liquid, which either coats the inside of the column, in the case of a capillary column, or is impregnated onto an inert solid, which is then packed into the GC column [11]. A schematic layout of a GC instrument is shown in Fig. 4. The basic components are an inert carrier gas, most commonly helium, nitrogen or hydrogen, a GC column, which will be described below, held inside an oven that allows for precise temperature control, and some type of detector capable of detecting the sample as it elutes from the column.

Gas-liquid GC works because the molecules in the samples are carried along the column in the carrier gas and partition between the gas phase and the liquid phase. Because this partitioning is critically dependent on the solubility of the sample in the liquid phase, different molecular species travel along the column and exit or *elute* at different times. Those molecules that have a greater solubility in the liquid phase take a longer time to elute and thus are measured at a longer time interval. Because solubility is dependent on the physical and chemical properties of the solute, separation between different components of the sample occurs based on molecular properties such as relative polarity (for example, oxygenated molecules, aromatics and nonaromatics) and boiling point. A typical gas chromatogram is shown in Fig. 5.

In order to create this separation, a number of different liquid phase materials are used that can be broadly classified as either polar or nonpolar. For hydrocarbon analysis the two most commonly used liquid phase materials are TCEP (1,2,3-tris(2-cyanoyethoxy)propane) for polar columns, and methyl silicone for nonpolar columns, although a multitude of different polar and nonpolar columns suitable for hydrocarbon analysis are commercially available. In general, polar columns are used to separate aromatics from nonaromatics, while nonpolar columns are used to separate hydrocarbon components by their boiling point.

There are two basic ways in which GCs are used for hydrocarbon analysis, either to separate different components of the sample based on their differing chemical characteristics (for example, aromatics versus nonaromatics), or to separate different chemically similar fractions based on their boiling point. To separate molecules based on their chemical properties, a GC is run in the method described above, with a polar column used to provide longer retention times for compounds such as aromatics relative to paraffins and olefins. For accuracy, it is vital that the oven temperature in which the GC column is housed is precisely controlled. This method is called *isothermal* GC analysis [10].

GCs can also be used in another mode called *temperature programming*. In temperature programming, the oven temperature is slowly swept from an initially low temperature (30°C) to a much higher temperature (typically 350–400°C) at a carefully controlled rate [12]. The effect is to cause an increased separation of chemically similar species based on

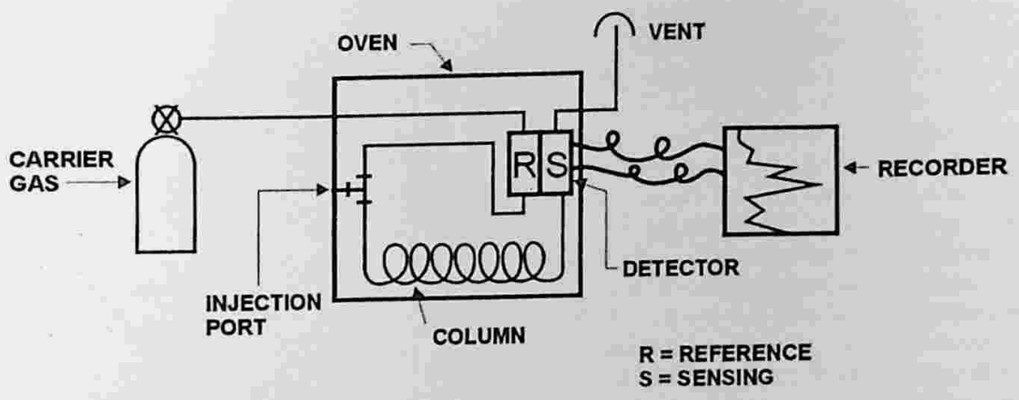


FIG. 4—GC instrument with a thermal detector.

their boiling point; those low boiling fractions eluting at a faster rate than fractions with higher boiling points. Temperature programming is used in hydrocarbon GC analysis to determine boiling point ranges for various crude and refined petroleum fractions.

Whether isothermal or temperature programmed GC analysis is used, a detector capable of measuring molecules as they elute is required. For hydrocarbon analysis, the two most common types of detectors are flame ionization and thermal conductivity [13]. In flame ionization type detectors, the column effluent is mixed with hydrogen and air and ignited. This flame burns any organic material (such as hydrocarbons) when they elute from the column producing, among other things, ions and electrons. This increase in charged particle concentration causes an increase in current between the tip of the burner, which is held at a high electrical potential, and a collector electrode above the flame. It is this increased current that is used to measure the elution of sample molecules from the column. An illustration of a flame ionization type detector is shown in Fig. 6.

Thermal conductivity detectors contain a tungsten filament that is heated using a constant current [10]. The elution of pure carrier gas (helium) has a cooling effect on the filament, which controls the temperature and hence the resistance of the filament to the applied constant current. As hydrocarbon molecules elute, they have less of a cooling effect than the carrier gas, resulting in an increased temperature. Sample molecule elution is determined based on a change in resistant of the filament, commonly measured using a Wheatstone bridge electrical circuit [10].

For specialized applications where element specific detection is required (for example, the determination of sulfur content in light petroleum liquids by GC (ASTM D 5623)), other detection systems are used such as atomic emission (AED) and chemi-luminescence. These will not be covered in detail in this chapter.

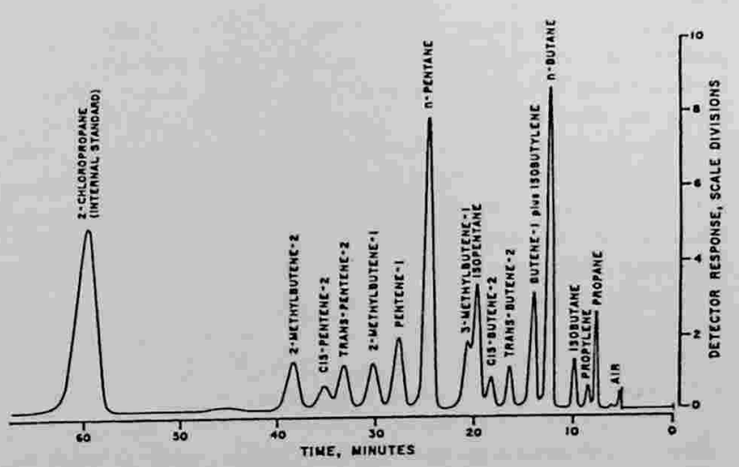


FIG. 5—Gas chromatogram of C^2 to C^5 species in gasoline. Reprinted from ASTM D 2427.

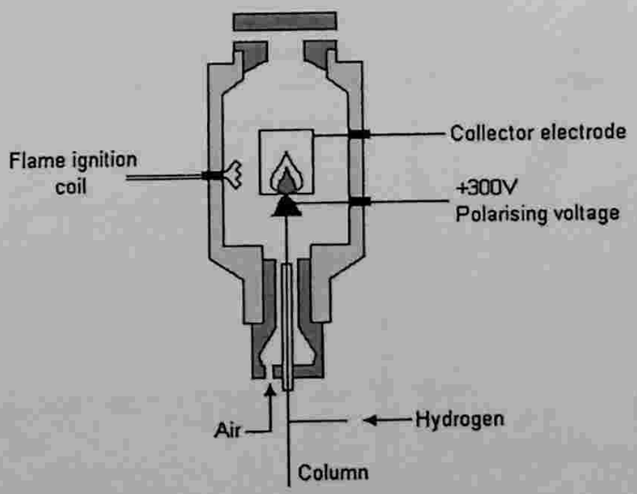


FIG. 6—Flame ionization detector.

The Use of GC in Hydrocarbon Analysis

The use of GC in the analysis of petroleum products falls into three general categories: the evaluation of the relative concentrations of different types of molecules (for example, aromatics, olefins, naphthenes etc.), the determination of boiling point ranges and carbon numbers in fuel and lubricants using temperature programming, and the detection of certain contaminants such as diesel fuel or ethylene glycol in engine oil or oxygenated additives such as MTBE.

The determination of the aromatic content of hydrocarbon fuels is an important application of GC because benzene, toluene, and other aromatics pose a serious health threat and

is carefully regulated in gasolines and other petroleum products. There are a number of test methods that use GC for this purpose, all of which follow the same basic principle (see ASTM D 3606, D 4420, and D 5580). In each case, a sample containing an internal calibration standard is injected into a GC instrument equipped with two columns, one containing a nonpolar liquid phase such as methyl silicone, the second using a polar liquid phase such as TCEP. The polar liquid phase separates aromatics and nonaromatics because aromatics take longer to elute from a polar column, while the nonpolar column separates the aromatic components by their boiling point, allowing the concentrations of benzene, toluene, and heavier aromatics to be determined. In each case, the measurements are carried out isothermally (that is at a fixed column temperature). A typical gas chromatogram of the aromatic components of gasoline using this method is shown in Fig. 7.

Another important application of GC to hydrocarbon analysis is the simulated distillation of crude petroleum [13]. Determining the boiling point range of petroleum fractions has a variety of uses, from determining the composition of feed stocks to evaluating the presence of volatile components, which may have implications on the performance or safety characteristics of finished hydrocarbon fuels and lubricants. Historically, the boiling point range of petroleum fractions has been determined by trial distillations in the laboratory. While this method still has some validity, and in some circumstances may be advantageous, the use of gas chromatography offers a quick, simple alternative for controlling refining processes and product evaluations.

Boiling point range determination of petroleum products using GC involves injecting a sample into a nonpolar column, which is housed in a temperature programmable oven. The GC is first calibrated using a calibration solution containing known concentrations of normal paraffins. The temperature of the column is increased at a known rate and the retention time of the n-paraffins is plotted against their known boiling points, as shown in Fig. 8. The crude sample is then analyzed in the same way, and the retention times of the eluting sam-

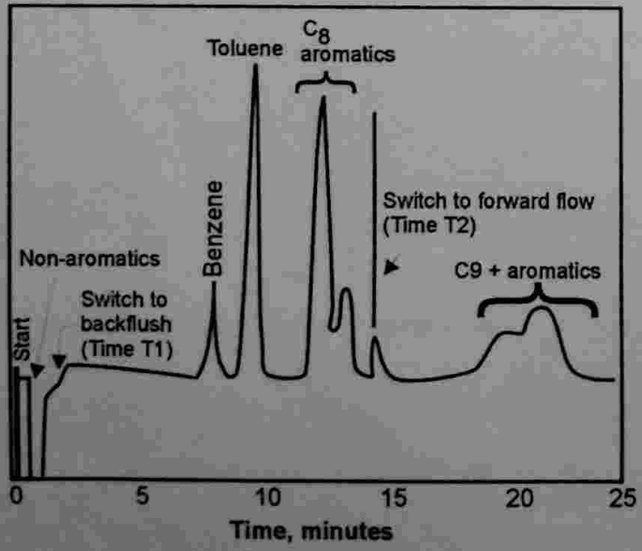


FIG. 7—Typical gas chromatogram of the aromatic fractions of gasoline. Reprinted from ASTM D 4420.

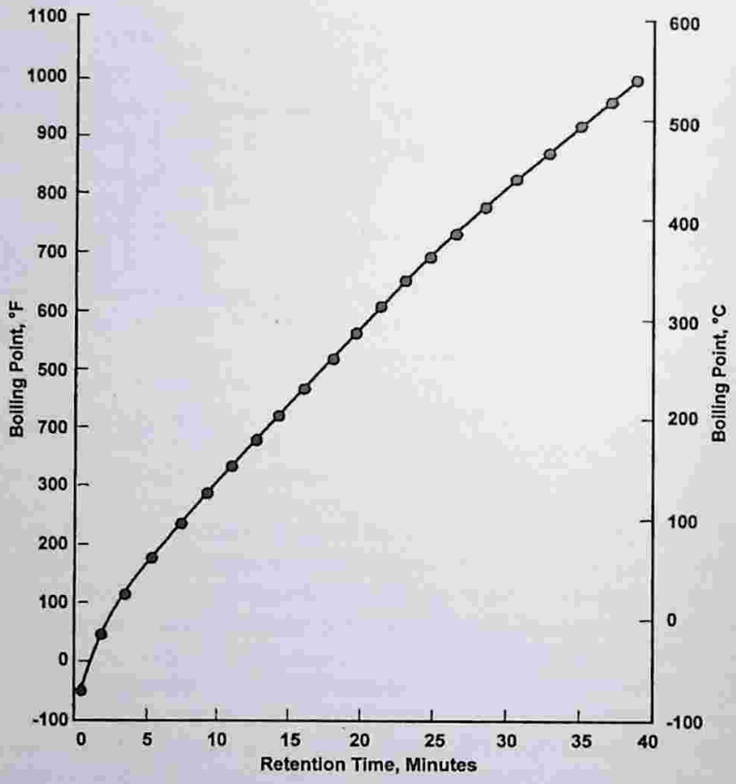


FIG. 8—Typical boiling point ranges of n-paraffins as a function of column retention time. Reprinted from ASTM D 5307.

ple fractions converted to boiling points using the calibration curve shown in Fig. 8. An example of the simulated distillation of a crude oil sample using gas chromatography is shown in Fig. 9.

The third area where GC has an increasingly important role to play is in the determination of certain contaminants in used oil samples, such as ethylene glycol, used as a coolant in many combustions engine, and fuel dilution in diesel engine samples. While used oil analysis is a subject unto itself, it is instructive to review how GC is applied in this area.

The determination of fuel dilution in engine oil samples is of prime importance because it can impair the performance of the lubricating oil [14]. Because diesel fuel is chemically very similar to the oil itself, it is almost impossible to quantify fuel dilution by conventional wet chemistry tests. While other physical tests such as changes in viscosity, FTIR, and flash point offer means of determining the presence of fuel in a lubricating oil, GC is generally a more precise and reliable means of determining fuel dilution based on the temperature programmed elution of fuel relative to the larger (higher boiling point) fractions of the lubricating oil.

The same can be said for ethylene glycol coolant detection. Ethylene glycol is an insidious contaminant in engine oil samples that can result in catastrophic engine failure if left unchecked [15]. Again a number of wet chemistry tests (ASTM D 2982) and physical tests (FTIR) are available, but, again, GC offers superior detection limits. Because ethylene glycol is a polar molecule, GC analysis is performed by first extracting the glycol from the used oil sample with water. The water extract is then run directly on an isothermal GC column against calibration standards containing known concentrations of ethylene glycol in water. The sensitivity of GC

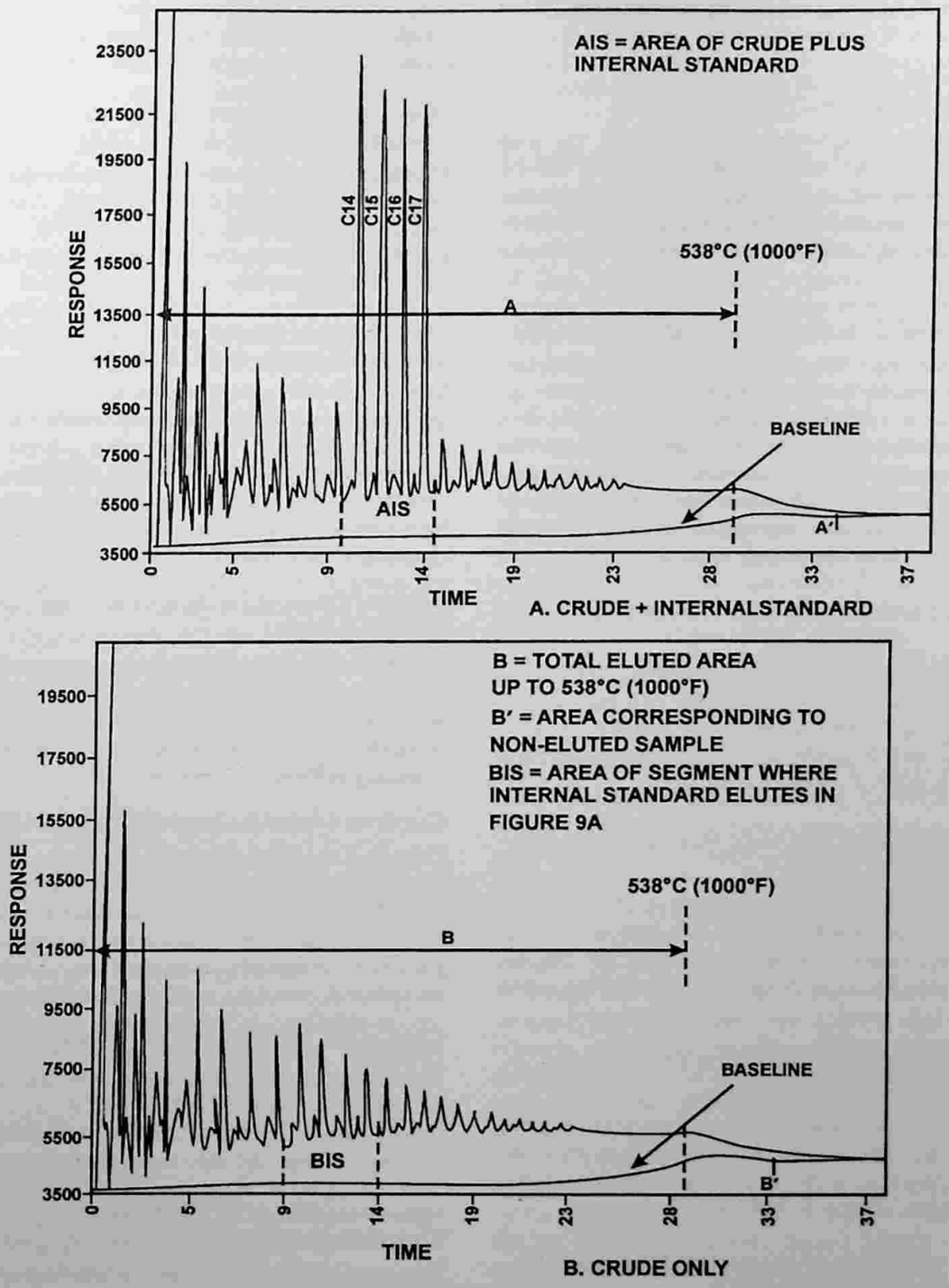


FIG. 9—Gas chromatogram of calibration mixture and crude oil sample used to determine boiling point range. Reprinted with permission from ASTM D 5307.

to detecting contaminants in used oil samples makes it an ideal test where high precision test data is required.

Whether it is used for evaluating different molecular components of gasoline, determining boiling point ranges for crude oil fractions, or detecting contaminants, one of the major drawbacks with GC is that while its is excellent at quantifying the relative concentrations of various eluted fractions, it cannot determine empirically what those fractions actually are [11]. Without the application of suitable calibration standards, which requires at least some knowledge of the sample constituents, this problem could severely limit the use of GC with complex mixtures such as fuels and lubricants. However, one way of addressing this issue is to couple GC with some other applicable method that is capable of not only detecting eluting fractions, but can also identify their chemical composition. For this reason, the dual combination of GC with mass spectrometry (GC-MS), infra-red spectrometry (GC-FTIR), and atomic emission (GC-AES) will continue to grow in importance in the quantitative analysis of hydrocarbon fuels and lubricants [16,17]. The application of GC to MS and FTIR is covered in the appropriate spectrometric analysis sections of this review.

ASTM Petroleum Products and Lubricants GC Test Standards

Aromatics in Finished Gasoline by Gas Chromatography (ASTM D 4420)

This test method determines benzene, toluene, C_8, C_9, and heavier aromatics, and total aromatics in finished motor gasoline and gasoline blending components. A two column chromatographic system connected to a dual filament thermal conductivity detector (or two single filament detectors) is used.

Aromatics in Finished Gasoline by GC (ASTM D 5580)

Aromatics in the following concentration range can be determined by this test method: benzene 0.1–5; toluene 1–15; individual C_8 aromatics 0.5–10; total C_9 and heavier aromatics 5–30; and total aromatics 10–80 liquid volume percent. The aromatic hydrocarbons are separated without interference from other hydrocarbons in the finished gasoline. A two column chromatographic system equipped with a column-switching valve and a flame ionization detector is used.

Benzene/Toluene in Gasoline by Gas Chromatography (ASTM D 3606)

This test method determines benzene and toluene in finished motor and aviation gasoline by gas chromatography. The sample is doped with an internal standard, methyl ethyl ketone (MEK), and is then injected into a gas chromatograph equipped with two columns connected in series.

Boiling Range Distribution of Crude Petroleum by Gas Chromatography (ASTM D 5307)

The method covers boiling range distribution of water-free crude petroleum through 538°C (100°F). A solution of crude oil in carbon disulfide is injected into a gas chromatographic column that separates hydrocarbons by their boiling point order.

Boiling Range Distribution of Gasoline Fractions by Gas Chromatography (ASTM D 3710)

This test method is designed to measure the entire boiling range of gasoline with either high or low Reid vapor pressure. The sample is injected into a gas chromatographic column, which separates hydrocarbons in boiling point order.

Boiling Range Distribution of Petroleum Distillates by Gas Chromatography (ASTM D 6352)

The gas chromatographic (GC) determination of boiling point ranges is used to replace conventional distillation methods for control of refining operations. A nonpolar open tubular capillary GC column is used to elute the hydrocarbon components of the sample in order of increasing boiling point.

Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (ASTM D 2887)

The determination of the boiling range distribution of petroleum fractions by gas chromatography is effective as a rapid analytical tool. The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample.

Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography (ASTM D 3524)

This test method covers the determination of diesel fuel as a contaminant in used lubricating oil. A mixture of n-decane and used lubricating oil is introduced into a gas chromatographic column that separates hydrocarbons in the order of their boiling points.

Estimation of Engine Oil Volatility by Capillary Gas Chromatography (ASTM D 6417)

The determination of engine oil volatility at 371°C is a requirement in some lubricant specifications. A sample aliquot diluted with a viscosity reducing solvent is introduced into the gas chromatographic system, which uses a nonpolar open tubular capillary gas chromatographic column for eluting the hydrocarbon components of the sample in the order of increasing boiling point.

Ethanol Content In Denatured Fuel Ethanol by GC (ASTM D 5501)

This test method covers the determination of ethanol content of denatured fuel ethanol by gas chromatography. A fuel ethanol sample is injected into a gas chromatograph equipped with a methyl silicone bonded phase fused silica capillary column.

Ethylene Glycol in Used Engine Oil (ASTM D 4291)

This test method provides for early detection to prevent coolant from accumulating and seriously damaging the engine. The sample of oil is extracted with water and the analysis is performed on the water extract, which is injected into a gas chromatograph using on-column injection. The eluting compounds are detected by a flame ionization detector.

Engine Oil Volatility by GC ASTM (D 5480)

This test method provides the determination of the amount of engine oil volatilized at 700°F (371°C). The sample is mixed with an internal standard and a dilute tetracosane solution, and injected into a gas chromatograph.

Gasoline Diluent in Used Engine Oils Gas Chromatography Method (ASTM D 3525)

This test method uses gas chromatograph equipped with a flame ionization detector and a programmable oven.

Hydrocarbon Types in Gasoline by Gas Chromatography (ASTM D 2427)

This test method provides information on C_2 through C_5 carbon paraffins and mono-olefins in gasolines. The sample is injected into a gas-liquid partition column. The components are separated as they pass through the column with an inert carrier gas and their presence in the effluent is detected and recorded on a chromatograph.

Methyl Tert-Butyl Ether in Gasoline by GC (ASTM D 4815)

This test method determines ethers and alcohols in gasoline by gas chromatography, and is applicable to both quality

control in the production of gasoline and the determination of deliberate or extraneous oxygenate additions or contamination. A gasoline sample is doped with an internal standard such as 1,2-dimethoxyethane, and is injected into a gas chromatograph equipped with two columns and a column switching valve. The eluted components are detected by a flame ionization or a thermal conductivity detector.

Olefins In Engine Fuels by GC (ASTM D 6296)

This test method can determine olefins in the C_4 to C_{10} range in spark ignition engine fuels or related hydrocarbon streams such as naphthas and cracked naphthas. A sample fuel is injected into a computer controlled gas chromatographic system, which consists of a series of columns, traps, and switching valves operating at various temperatures. The final eluted olefins are detected by flame ionization detector.

Oxygenates in Gasoline by Gas Chromatography (ASTM D 5599)

This test method provides sufficient oxygen-to-hydrocarbon selectivity and sensitivity to allow determination of oxygenates in gasoline samples without interference from the bulk hydrocarbon matrix. An internal standard of a noninterfering oxygenate (for example, 1,2-dimethoxyethane) is added in a quantitative proportion to the gasoline sample. An aliquot of this mixture is injected into a gas chromatograph equipped with a capillary column operated to ensure separation of the oxygenates. Oxygenates are detected with the oxygen-selective flame ionization detector.

Oxygenates O-PONA Hydrocarbons in Fuels by GC (ASTM D 6293)

This test method provides for the quantitative determination of oxygenates, paraffins, olefins, naphthenes, and aromatics in low-olefin spark-ignition engine fuels by multidimensional gas chromatography. A fuel sample is injected into a computer-controlled gas chromatographic system consisting of switching valves, columns, and an olefin hydrogenation catalyst, all operating at various temperatures. The eluted hydrocarbons are detected by flame ionization detector.

Sulfur Determination by GC-Sulfur Detector (ASTM D 5623)

This test method covers the determination of volatile sulfur compounds in light petroleum liquids. The sample is analyzed by gas chromatography with an appropriate sulfur selective detector.

LIQUID CHROMATOGRAPHY (LC)

Introduction

The technique of liquid chromatography (LC) is closely allied with gas chromatography (GC) and other chromatographic methods. Just like GC, liquid chromatography separates different molecules or molecular groups based on their physical and chemical properties. However, unlike gas chromatography, LC as the name implies the use of a liquid mobile phase to analyze samples. The field of liquid chromatography is very broad ranging and is used in many different areas of analytical chemistry. In this section, we will cover just those areas of liquid chromatography that are used in the analysis of hydrocarbon petroleum products, specifically, absorption chromatography, high performance liquid chromatography (HPLC), fluorescent indicator absorption (FIA) and super critical fluid chromatography (SFC).

Liquid Chromatography (LC)

In classical LC, a liquid sample is introduced either neat or diluted with an appropriate solvent into a glass column, which has been prepacked with an appropriate solid material such as silica, alumina, or some other solid medium. The sample is then washed down the column using a flowing stream of solvent, starting with a relatively low strength solvent and progressing to stronger and stronger solvents until the sample has been washed out or *eluted* from the column [18]. Depending on the nature of the interaction between the sample (the mobile phase) and the column material (the stationary phase), mixtures can be separated by retention time in the column; those molecular species present in the mobile phase which have a greater affinity for the stationary phase material take a longer time to elute than those that have little or no affinity for the stationary phase. This is called absorption chromatography and the columns used for this kind of methodology are *absorption columns*.

An illustration of absorption liquid chromatography is shown in Fig. 10. In this example, a mixture of two compounds, x and o, are added to an LC column packed with a stationary phase that has a greater affinity for compound x than compound o. The mixture is washed down the column with a suitable solvent, however, because compound x has a greater affinity for the stationary phase than compound o, it will take a longer time to exit or *elute* from the column. Separation is thus affected between the two compounds, which can then be monitored as a function of their elution times by a suitable detector. This methodology is called absorption chromatography and is the most commonly used method for hydrocarbon analysis. In certain circumstances, absorption by the stationary phase is so effective that the absorbed components of the sample can only be removed by washing with a solvent that has a stronger affinity for the absorbed sample component than the stationary phase.

Two other types of LC columns exist, specifically partition columns and exclusion columns. Partition columns work in much the same way as GC columns. In partition chromatography, instead of being filled with a solid stationary phase, the LC column contains a liquid, which is coated or chemically bonded onto a solid medium contained within the col-

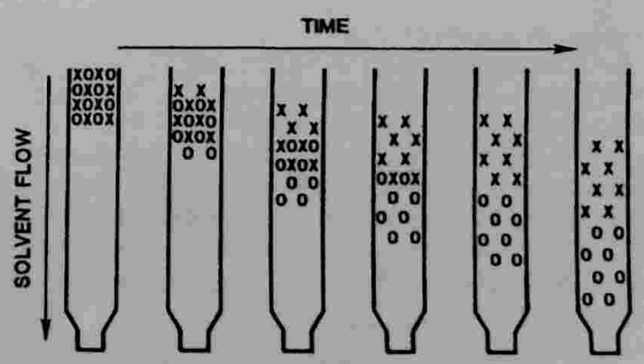


FIG. 10—The chromatographic process.

umn. Separation is affected by the interaction between the liquid mobile phase and the liquid stationary phase (often called the partitioning phase), which separates components of the sample based on their relative solubilities in the partitioning liquid [19]. This method is often referred to as liquid-liquid chromatography. It is less commonly used for hydrocarbon analysis, but can be used to separate hydrocarbons of the same family, which differ only by their substituents [20].

Exclusion column chromatography is another form of solid-liquid chromatography, like absorption chromatography. However, instead of separation being affected by the rate of absorption (and desorption) by the solid stationary phase, exclusion columns are packed with porous materials with carefully controlled pore sizes. In this case, the rate of elution is controlled by molecular size, and the ability of the sample molecules to enter the pores of the stationary phase material. In general, very small molecules, which are smaller on average than the pore of the stationary phase material become trapped in the column and take longer to elute, while larger molecules cannot fit inside and thus elute faster than smaller molecules. This method is typically used to separate large polymeric additives, such as viscosity index (VI) improvers from base oils [21,22].

Liquid chromatography can be further subdivided into two categories: open column liquid chromatography (OCLC) and high performance liquid chromatography (HPLC). With OCLC, the mobile phase (sample and solvent) is forced through the column either under gravity, or a small head pressure of gas, typically 25 psig or less [19]. Most modern analytical instruments now use HPLC. Originally standing for "high-pressure liquid chromatography," HPLC or high performance liquid chromatography uses significantly higher pressures than OCLC to force the mobile phase through the column, resulting in shorter analysis times. A schematic illustration of the basic components of an HPLC instrument is shown in Fig. 11. A detailed review of HPLC instrumentation can be found in Ref 23.

Whether an absorption column, partition column or exclusion column is used, or whether gravity (OCLC) or high pressure (HPLC) is used to push the mobile phase through, a detection system is required to measure the sample fractions as they elute from the column. The most common methods include UV spectrometers, used to measure the characteristic UV absorption of organic molecules as they elute from the column; refractive index (RI) detectors, which record a change in RI as sample molecules elute relative to the solvent being used; and flame ionization (FID) detectors, which measure a change in conductivity through a hydrogen flame as the eluting molecules are ionized in the flame.

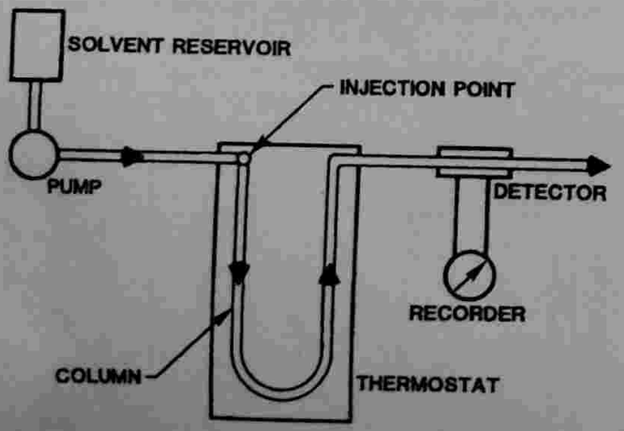


FIG. 11—An HPLC instrument.

The Use of LC in Hydrocarbon Analysis

Like gas chromatography (GC), LC is used for the analysis of petroleum fuels and lubricants because of its ability to separate complex mixtures based some physical or chemical property. Although lower in sensitivity than GC, LC has several distinct advantages, which make it more widely applicable to hydrocarbon analysis. Some of these advantages include [21]:

- Shorter analysis times
- Higher precision for identifying and quantifying components
- Analysis in series using the same column
- Selectivity for certain classes of hydrocarbons
- Ability to measure high molecular weight and high boiling point compounds

The main application of chromatographic techniques to hydrocarbon analysis is the separation of different fractions that possess wildly different physical and chemical properties such as polar compounds, aromatics, and saturates. This is the principle behind ASTM D 2007, which is used to define API base stock categories and engine oil interchangeability rules [24].

In this test method, a dual column apparatus is used containing two columns in series. The first column contains clay, which retains any polar compounds allowing both saturates and aromatics to pass through using n-pentane as a solvent. The second column contains clay and silica gel, which retains aromatics but again allows saturates to pass through. Collecting the total effluent through both columns allows the percentage by mass of saturates to be calculated as a function of total sample mass, because both polar compounds and aromatics are stripped from the sample by the two columns. The clay column is then removed and washed with a toluene acetone mixture allowing the absorbed polar compounds to elute. The percentage by mass of polar compounds can then be calculated as the total polar effluent from the toluene-acetone washed column, again as a function of the total sample mass. Finally, the silica gel/clay column is rinsed with toluene, which allows the aromatics to elute, again allowing their percentage by mass to be calculated. The precision of determining the saturate and aromatic content using this method (as per API 1509) is around 2% [25].

A similar method is used in ASTM D 2549, this time to separate aromatic and nonaromatic components of high boiling oils. In this method, a single absorption column containing activated bauxite and silica gel is used. Initially, n-pentane is used as a solvent, allowing nonaromatics to pass through the column. These are then collected and expressed as a percentage by mass of the initial sample, after evaporation of the n-pentane solvent. The column is then washed with diethyl ether, chloroform, and ethyl alcohol which allows the elution of the aromatics compounds, which are then weighed and expressed as a percentage by mass of the initial sample mass. A number of related techniques have been used to achieve sim-

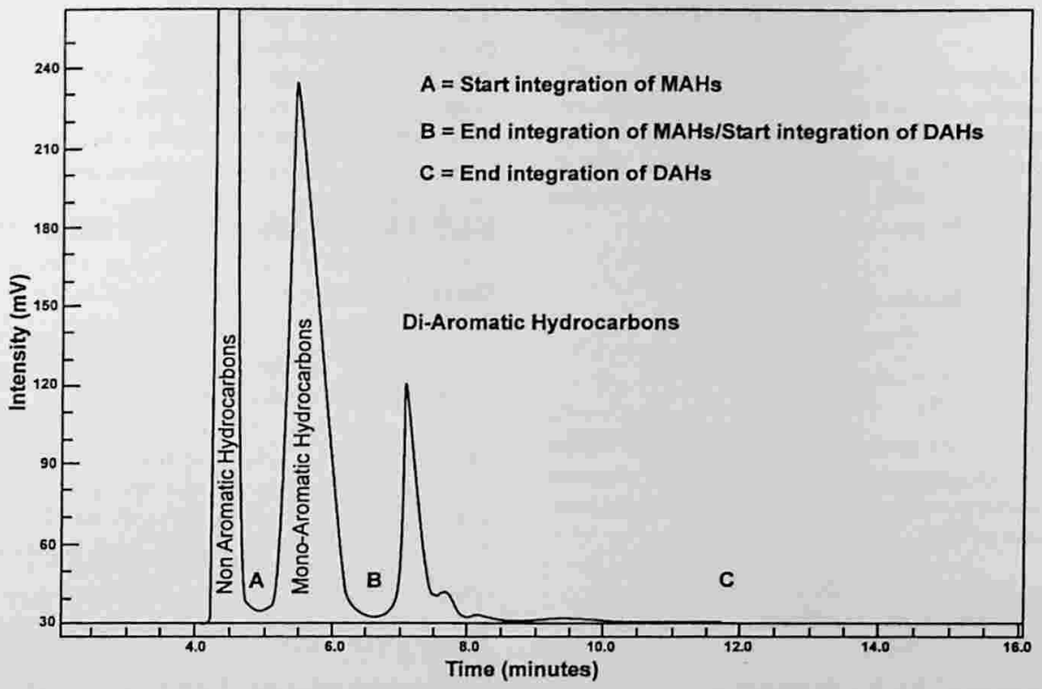


FIG. 12—The use of liquid chromatographic separation to differentiate mono and di-aromatics in aviation fuel. Reprinted with permission from ASTM D 6379.

ilar separations, which differ simply by the column material and solvents used [21].

These simple absorption techniques under atmospheric pressure have, to a large part, been superceded by high performance liquid chromatography (HPLC), principally because of the much shorter analysis times afforded with HPLC [21]. However, just like absorption chromatography, HPLC is used mainly as a tool for separating samples based on physical and chemical properties.

Just like absorption chromatography, separation of complex mixtures into saturates and aromatics is possible with HPLC, as well as differentiating between similar molecules such as mono-aromatics (MAHs) and diaromatics (DAHs). This method is used in ASTM D 6379 to determine MAH and DAH content in petroleum products. In this case, an amino bonded stationary phase is used, together with n-heptane, as the solvent to resolve different compounds based on elution times. An example of a chromatogram of this type is shown in Fig. 12.

Aside from absorption chromatography and the related technique of HPLC, there are two other LC methods used for hydrocarbon analysis that are worth mentioning, specifically fluorescent indicator adsorption (FIA) and supercritical fluid chromatography (SFC).

Fluorescent Indicator Adsorption (FIA)

Despite its rather grandiose name, FIA is a relatively simple technique. First developed in the early 1940s, it is used to determine the relative amounts of aromatics, olefins, and saturates in petroleum fractions [18]. The technique involves standard OCLC using a silica gel column. However, in addition to being packed with silica gel, the column contains a small portion of the gel towards the top that is doped with a mixture of dyes. The dye mixture is carried along the column with the petroleum sample, which starts to separate because the saturates have less of an affinity for the silica gel than the olefins, which in turn have less of an affinity than aromatics. The dye mixture contains three different components, one which has an affinity for silica gel, which is greater than that of the saturates, but less than that of the olefins. This dye component thus marks the interface between saturate molecules and olefins as they move through the column because the dye's retention time will be between the saturates and olefins. A second dye component has an affinity for silica somewhere between that of olefins and aromatics and thus marks the olefin-aromatic boundary, while a third dye component falls between aromatics and the isopropyl alcohol used as the solvent, marking the final boundary. By measuring the separation of each dye, the relative proportions of saturates, olefins, and aromatics can be determined to within 1–2% depending on conditions. This test is described under ASTM D 1319.

Super Critical Fluid Chromatography (SFC)

Although not strictly a liquid chromatography technique, SFC shares many of the same basic principles of HPLC. The principal difference between SFC and HPLC is that the mobile phase containing the sample is neither a liquid, as used in HPLC, or a gas, as used in gas chromatography, but is a supercritical fluid, most commonly CO_2 [23]. A supercritical fluid is one that has been heated above its critical temperature and pressure such that it exists in a new state of matter, with properties between that of a gas and a liquid. In particular, supercritical fluids have greater mobility (are less viscous) than liquids, but are denser than gases. This property of supercritical fluids has great advantages as the mobile

phase carrier over conventional HPLC or gas chromatography (GC).

For hydrocarbon analysis, SFC has an advantage over GC for fuel samples because it uses much lower temperatures than GC and is thus less likely to cause thermal decomposition. SFC also typically offers high resolution than HPLC, making it a more accurate test for determining different molecular components in hydrocarbon fuels [26].

ASTM Petroleum Products and Lubricants LC Test Standards

Hydrocarbon Types by Fluorescent Indicator Adsorption (ASTM D 1319)

This test method determines hydrocarbon types in the range of 5–99 volume percent aromatics, 0.3–55 volume percent olefins, and 1–95 volume percent saturates in petroleum fractions that distill below 315°C.

Hydrocarbon Types Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates (ASTM D 6379)

This test method is intended for use as one of several possible alternative instrumental test methods that are used for quantitative determination of hydrocarbon types in fuels. This test method determines mono- and di-aromatic hydrocarbon contents in aviation kerosenes and petroleum distillates boiling in the range from 50–300°C, such as Jet A or Jet A-1 fuels. The sample is diluted 1:1 with a solvent such as heptane, and a fixed volume of this solution is injected into a high performance liquid chromatograph fitted with a polar column.

Aromatics and Polynuclear Aromatics in Diesel and Aviation Turbine Fuels By SFC (ASTM D 5186)

The aromatic hydrocarbon content of motor diesel fuels affects their cetane number and exhaust emissions. The aromatic hydrocarbon and the naphthalene content of aviation turbine fuels affects their combustion characteristics and smoke forming tendencies. In the test, a small aliquot of the fuel sample is injected onto a packed silica adsorption column and eluted using supercritical carbon dioxide mobile phase. The detector response to hydrocarbons is recorded throughout the analysis time corresponding to the mono-, polynuclear, and nonaromatic components determining the mass percent content of these groups.

ULTRAVIOLET SPECTROSCOPY

Introduction

Ultraviolet (UV) spectroscopy, also known as UV spectrometry, was one of the first spectroscopic techniques used to quantify chemical composition [27]. Like other spectroscopic techniques, it is used to identify characteristic molecular fingerprints enabling the quantitative detection of specific molecules or molecular species in complex mixtures. UV spectroscopy is most commonly used in hydrocarbon analysis as a detection tool after high performance liquid chromatography (HPLC).

Basic Principles of UV Spectroscopy

In order to understand UV spectroscopy, we need to first understand the electronic structure of molecules. While a detailed quantum mechanical explanation of molecular electronic structure is beyond the scope of this book, there are a few simple concepts that will allow us to understand the basic theory behind UV spectroscopy.

The total energy of a molecule is given by the sum of the electronic energy, vibrational energy, and rotational energy, with the electronic energy being significantly greater than the vibrational energy, which in turn is significantly greater than rotational energy. While rotational energy levels are only of significance in gas phase spectroscopy, the electronic and vibrational energy levels will be important in solution phase spectroscopy such as FTIR and UV spectroscopy. An illustration of the electronic and vibrational energy levels of a molecule is shown in Fig. 13.

Under normal conditions, most of the molecules in a sample will be in the ground (lowest energy) electronic state. By

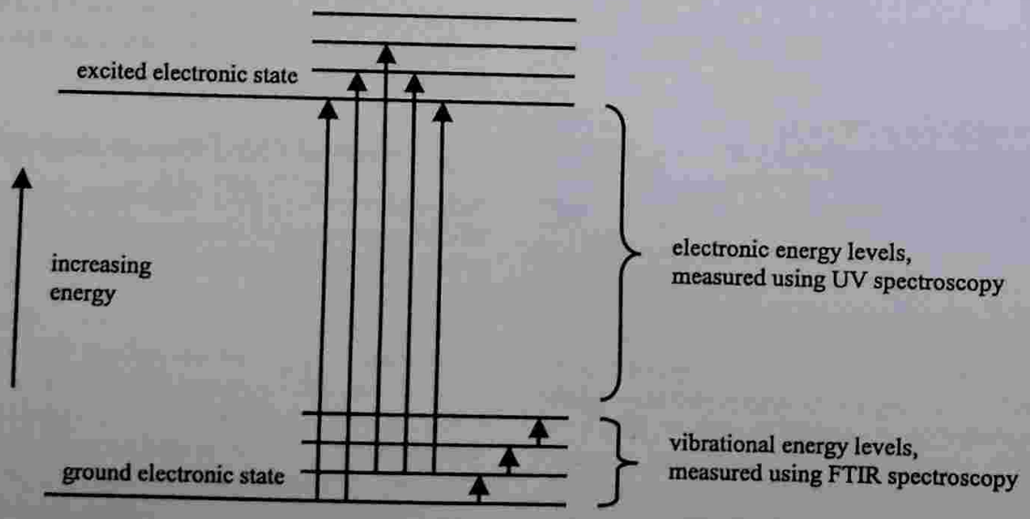


FIG. 13—The electronic and vibrational energy levels of a molecule.

passing infrared light through the sample at the exact frequency corresponding to the difference in energy of the vibrational levels, transitions *within* the vibrational levels of the ground state can be induced, which is the principle behind FTIR spectroscopy.

For the same reason, passing light through the sample at an appropriate frequency corresponding to the separation of the *electronic energy levels* can induce a transition between these levels, resulting in absorption of the light. For some molecules, the frequency of light required to induce electronic transitions is in the visible region of the electromagnetic spectrum, however, for most hydrocarbon molecules, the energy that is required is much higher and requires ultraviolet radiation. This is the principle behind UV spectroscopy.

For hydrocarbon analysis, the most important factor determining the energy separation of the electronic energy levels is what is often referred to as the molecular *chromophore* [28]. A chromophore is simply a covalently unsaturated bond or group of bonds that is responsible for electronic absorption. In typical hydrocarbon fuels and lubricants, the most common types of molecules to possess a chromophore will be aromatic molecules, which have characteristic absorption bands in the 185–400 nm wavelength range [28]. This range of the electromagnetic spectrum is typically called the near-UV.

Beer's Law

In order to use UV spectrometry as a quantitative tool, we need to understand the relationship between the concentration of specific molecules and the amount of light they absorb. This fundamental property is determined by Beer's Law:

$$A = \varepsilon bc$$

where A is the absorbance, ε is the molar absorptivity, b is the cell path length containing the sample, through which the UV light passes, and c is the concentration in mol/L [27]. Because the molar absorptivities of most molecules of interest have been measured, and b is a known quantity based solely on instrument design, measuring the amount of light absorbed by the sample (A in the above equation) allows the concentration c to be determined simply by rearranging the Beer's law equation.

UV Spectrometers

A schematic illustration of a UV spectrometer is shown in Fig. 14. The main components are a white light source, which is focused onto the entrance slits of a spectrometer, a cuvette or cell containing the sample to be analyzed, and a photocell detector to measure light intensity. The spectrometer is equipped with a diffraction grating, which acts much like a prism to split the white light into discrete wavelengths. Because the angle of diffraction is defined by the wavelength of light, slowly changing the angle of the grating relative to the incoming light allows the wavelength of light that exits the spectrometer through the exit slits to be slowly scanned, allowing an absorption spectrum to be recorded, as shown in Fig. 15. The amount of light absorbed at the maximum excitation wavelength (λ_{max}), will be dependent on the concentration c, path length b, and molar absorptivity ε_{max} as per Beer's Law.

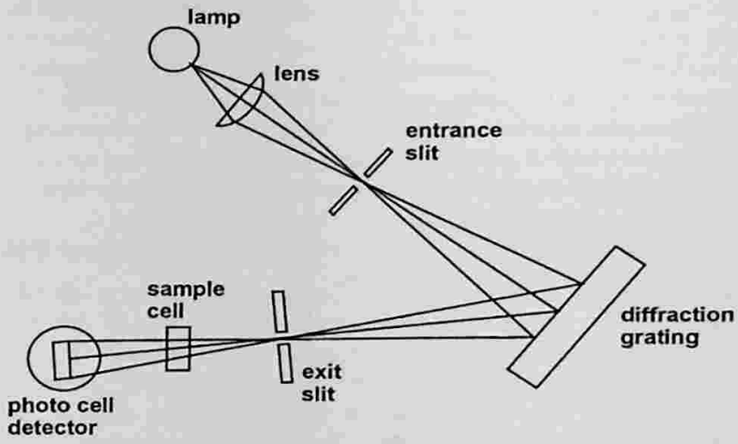


FIG. 14—UV spectrometer.

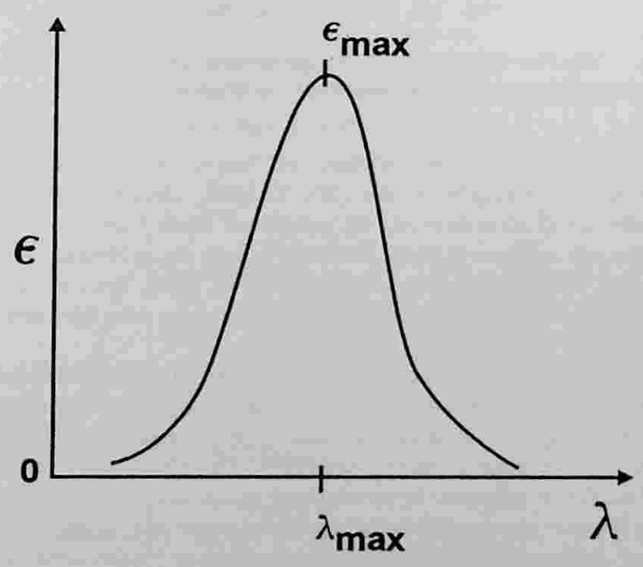


FIG. 15—Typical UV absorption spectrum.

The Use of UV Spectrometers in the Analysis of Hydrocarbons

UV spectrometers are used both directly and in conjunction with high performance liquid chromatography (HPLC) instruments, principally to detect aromatics because they typically have strong UV absorption bands in the near UV region (200–400 nm). The specific maximum absorption wavelength and absorptivity is determined by a molecule's electronic structure, however, in general it is found that mono-aromatics (those with a single aromatic ring such as benzene and toluene) have an absorption maximum around 197 nm, di-aromatics have absorption maxima around 230 nm, while polyaromatics absorb around 260 nm [29].

One application of this method, employed by several oil companies, follows the work of Burdett [29, 30]. A typical UV absorption spectrum of mono-, di-, and tri-aromatics is shown in Fig. 16. The method of Burdett employs UV spectrometry to record the absorption spectrum in the range 175–270 nm. The molar absorptions is then recorded at the

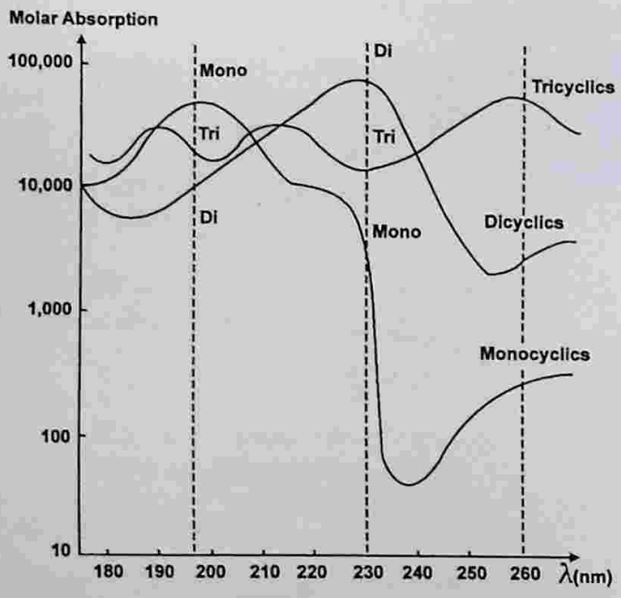


FIG. 16—UV absorption spectrum for monocyclic, dicyclic and tricyclic aromatic hydrocarbons.

three characteristic absorption maxima, 190, 230, and 260 nm corresponding to mono-, di-, and poly-aromatics and can be converted to a percent by weight of each type of molecular species using a simple formula based on molecular mass, and the average molar absorptivity of each species at the three wavelengths. Details of this procedure can be found in Ref. 29.

One of the most common applications of UV spectrometry to the analysis of hydrocarbon fuel and lubricants is its use in determining the amount of toxic impurities, particularly PAHs (polyaromatic hydrocarbons). The term PAH covers a multitude of different hydrocarbon molecules, with one common theme: the presence of multiple aromatic rings. A number of different PAHs, which are known to be present in hydrocarbon fuels and lubricants, have been found to be carcinogenic. For this reason, the EPA and other regulatory bodies have established limits for PAH concentrations in fuels, lubricants, and other media. Because UV spectrometry is capable of detecting polyaromatic species such as PAHs in hydrocarbons by their characteristic absorption at 260 nm, it is only natural that it has been used in this manor for determining PAH concentrations and carcinogen content in hydrocarbon oils [31].

While UV absorption is incapable of differentiating between two different molecules that may have absorption bands in the same region (for example, two different PAH molecules, both of which will absorb at 260 mm), the use of separation techniques such as liquid chromatography (LC) or gas chromatography (GC) can be employed to differentiate between different molecular species. In this case, the UV spectrometer is fixed at a known absorption wavelength (for example, 197 nm for mono-aromatic species), and is used to measure different molecular species as they elute from the GC or LC column; this provides a more molecule specific means of detection than flame ionization or thermal detectors typically used with GC and LC instruments.

One other technique closely related to UV absorption spectrometry that is used in hydrocarbon analysis is spectrofluorometry [29]. The principle behind spectrofluorometry is illustrated in Fig. 17, which shows theoretical absorption spectra for two different polyaromatic molecules (molecules A and B), together with the corresponding fluorescence spectra. Because both molecules are polyaromatic, the absorption spectrum for each will show a maximum around 260 nm. Recording the absorption spectrum for a mixture of molecule A and molecule B will not allow the relative concentrations of each to be determined because both absorb simultaneously at 260 nm. However, after excitation at 260 nm, both molecules are in an excited electronic state and will emit radiation to return to a lower lying electronic state, typically in the form of light. Because molecule A and molecule B possess different electronic structures, the energy of the lower lying electronic states will not necessarily be the same. Because the emitted radiation is quantized, measuring the emission (fluorescence) spectrum as opposed to the absorption spectrum allows the concentration of two molecules to be determined independently of each other. Used in conjunction with LC, spectrofluorometry is an extremely sensitive technique capable of detecting concentrations of polycyclic aromatics and other species as low as picograms [32].

ASTM Petroleum Products and Lubricants UV Test Standards

Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet (UV) Spectrophotometry (ASTM D 1840)

This test method covers the determination of the total concentration of naphthalene, acenapthene, and alkylated derivatives of these hydrocarbons in straight-run jet fuels containing no more than 5% of such components and having end points below 600°F. The total concentration of naphthalenes in jet fuels is measured by absorbance at 285 nm of a solution of the fuel at known concentration.

MASS SPECTROMETERY

Introduction

Mass spectrometry is used to detect the presence of different molecules in bulk samples. The technique involves the gas phase analysis of samples that are either already gases, or are liquids or solids that can be vaporized prior to mass spectrometric analysis. In conventional mass spectrometry, the gas phase sample is ionized to form various primary and fragmentation ions, which are then analyzed according to their mass-to-charge ratio. The mass spectrum thus generated can then be used as a characteristic fingerprint to detect the presence of certain molecules with the relative intensity of the mass spectra allowing an estimate of the concentration of the molecule or molecular species within a bulk sample. The application of Mass Spectrometry (MS) to the analysis of hydrocarbon fuels and lubricants is outlined in this section.

MS Theory

As previously mentioned, MS works on the principal of separating primary and fragmentation ions according to their

mass-to-charge (m/z) ratios. Take for example the water molecule H_2O. Bombarding water vapor with a high-energy electron source will create both primary ions and fragmentation ions as follows:

$$HOH \longrightarrow \underbrace{HOH^+}_{\text{primary ion}} + \underbrace{OH^+ + O^+ + H^+}_{\text{secondary ions}} + 3e^-$$

$$m/z = 18 \quad m/z = 17 \quad m/z = 16 \quad m/z = 1$$

Recording the mass spectrum of a bulk sample and measuring the relative intensities of the m/z = 1, 16, 17, and 18 peaks will allow the presence of water to be determined, and by inference its concentration, provided a suitable calibration standard has been determined.

The biggest drawback with MS is that the complexity of the mass spectrum increases exponentially with increasing molecular size (molecular mass). Take for example benzene, a relatively simple hydrocarbon. The electron ionization mass spectrum of benzene (Fig. 18) has 17 different peaks corresponding to m/z values ranging from 27–79, which include primary and fragmentation ion mass peaks, as well as peaks associated with the naturally occurring isotope ^{13}C [35]. Now consider applying mass spectrometry to a mixture of hydrocarbons typically found in petroleum fuels and lubricants. With many thousands of different components including paraffins, branched paraffins, naphthenic molecules, and aromatics, the mass spectrum of a typical petroleum fraction is extremely complex. Nevertheless, mass spectrometry can and has been successfully applied to the analysis of complex petroleum mixtures as will be discussed later.

MS Instrumentation

The basic components of a mass spectrometer are shown in Fig. 19. The system comprises an inlet source, which is designed to introduce the sample in the vapor phase to the spectrometer, an ionization source that serves to ionize the sample, a mass analyzer which separates the ions by their m/z ratio, and an ion detector for detecting the ions once they have been mass selected. The inlet system for most basic mass spectrometers is called a batch inlet and comprises a means of injecting a gas, or more commonly a liquid sample under reduced pressure and elevated temperatures such that the sample can be vaporized for presentation to the spectrometer [34]. In modern instruments, the liquid is commonly injected into the vacuum chamber using a hypodermic syringe arrangement called a probe [35].

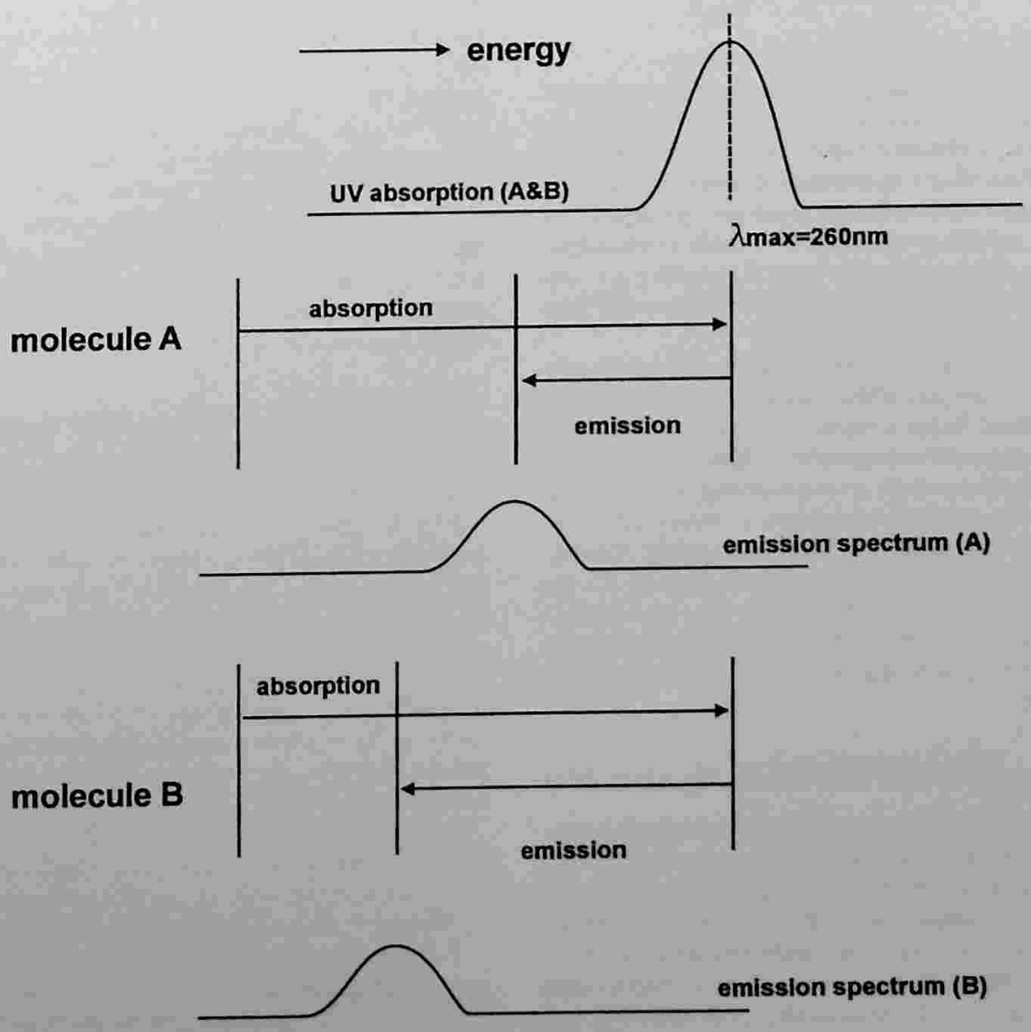


FIG. 17—Theoretical fluorescence emission spectrum of two different polyaromatic molecules, A and B.

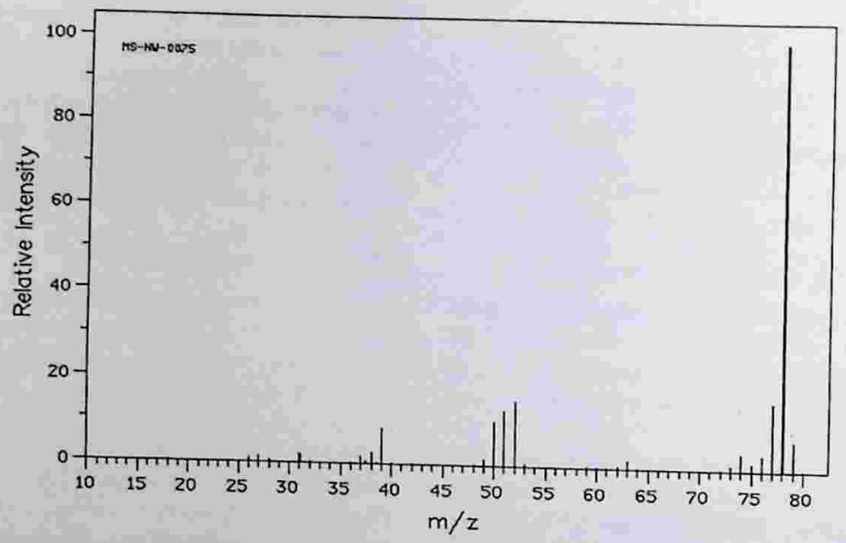


FIG. 18—Mass spectrum of benzene.

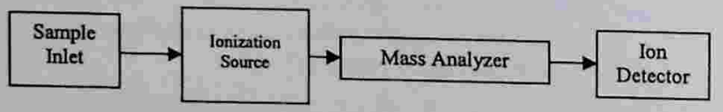


FIG. 19—Basic components of a mass spectrometer.

Once in the gas phase, the sample is drawn into the ionization section of the instrument where it is intersected at right angles by a high-energy electron beam created by a hot filament. This is called an electron ionization mass spectrometer. The electron beam ionizes the sample into primary and fragmentation ions, which are accelerated into the mass analyzer section using an electrostatic field formed by a series of electrodes, which serve to focus and accelerate the ions into the mass analyzer.

There are many different types of commercial mass spectrometers available. They all differ slightly in their design, but all use one of three basic methods to mass analyze the ionized sample, namely magnetic field deflection, quadrupole mass spectrometry, or time-of-flight [35]. A detailed explanation of these different types of mass analyzers is beyond the scope of this chapter, but an excellent description of these different methods can be found in Ref. 35. No matter what type of mass analyzer is used, they all separate ions according to their m/z ratio, with the ion signal being detected, amplified, and recorded as a function of their mass-to-charge (m/z) ratio.

Gas Chromatography-Mass Spectrometry (GC-MS)

One adaptation, which has served to simplify the interpretation of MS data, is to use a standard Gas Chromatograph (GC) as the sample inlet source for the mass spectrometer. As explained earlier in this chapter, a gas chromatograph is an instrument that separates complex mixtures of chemicals into single molecular components, or groups of components with similar physical properties. By combining MS with GC, the analysis of complex mixtures of chemicals such as hydrocarbon fuels and lubricants has become greatly simplified.

The usual way in which GC-MS is used for the analysis of petroleum products is to fix the mass spectrometer to detect one specific ion peak, for example m/z = 78, corresponding to the primary ion peak for benzene. The ion intensity at this fixed m/z ratio is then measured for different retention time in the GC. The retention time is simply the time taken for a specific molecular component of a complex mixture to emerge or *elute* from the GC column, which in turn is related to the physical and chemical properties of the molecule. By separating the signal in the m/z = 78 into different elution times, the true signal due to benzene can be differentiated from other fragmentation ions from different molecular species that may have an m/z ratio of 78, but have different retention times in the GC column. This makes the difficult task of interpreting the MS data significantly less complicated.

The Application of MS to Hydrocarbon Analysis

Mass spectrometry is an important tool in the analysis of petroleum products because it can give information that cannot be obtained by other means. Just like other spectrometric techniques, it gives important information on the chemical composition of complex mixtures of hydrocarbons commonly found in fuels and lubricants, particularly when coupled with other techniques such as gas chromatography.

The most common application of mass spectrometry to hydrocarbon analysis is in determining the composition of different process stream and boiling fractions during the refining process. There are a number of ASTM test procedures that cover the use of MS in this area, which are listed in Table 3.

In each case, chemical composition is determined by calculating *mass groupings*, which correspond to the summation of characteristic mass peaks for different classes of molecules that are likely to be present.

The m/z peaks that are used to calculate the different mass groupings in the ASTM procedures listed in Table 3 are simply based on the known primary and fragmentation ions patterns using mass spectrometry for different molecules under controlled laboratory conditions. For example, in ASTM D

TABLE 3—ASTM test procedures that use mass spectrometry for determining the composition of different fractions.

ASTM Test Procedure	Significance
D 2425	Saturates and aromatics in middle distillates
D 2786	Saturates in gas oil fractions
D 2789	Hydrocarbon types in low olefinic gasoline
D 3239	Aromatics in gas oil fractions

2786 that is based on the Hood and O'Neal method, the mass grouping $\Sigma 71$ is defined as the sum of peaks at m/z = 71,85, 99, and 113 and is used to determine alkane content [37,38]. The difference in masses between each peak in the summation is simply the extension of the alkane chain by one CH_2 unit, with a corresponding increase in molecular mass of 14 atomic mass units. The biggest drawback with this method, and indeed MS in general, for the analysis of hydrocarbons is that the number of mass peaks that must be considered increases significantly with molecular size. To illustrate this complexity, consider the complete list of mass groupings, which must be considered under ASTM D 2786, and the corresponding molecular types they represent:

$$\Sigma 71 = 71 + 85 + 99 + 113 \quad \text{alkanes}$$

$$\Sigma 69 = 69 + 83 + 97 + 111 + 125 + 139 \quad \text{1 ring naphthenes}$$

$$\Sigma 109 = 109 + 123 + 137 + 151 + 165 + 179 + 193 \quad \text{2 ring naphthenes}$$

$$\Sigma 149 = 149 + 163 + 177 + 191 + 205 + 219 + 233 + 249 \quad \text{3 ring naphthenes}$$

$$\Sigma 189 = 189 + 203 + 217 + 231 + 245 + 259 + 273 + 287 + 301 \quad \text{4 ring naphthenes}$$

$$\Sigma 229 = 229 + 243 + 257 + 271 + 285 + 299 + 313 + 327 + 341 + 355 \quad \text{5 ring naphthenes}$$

$$\Sigma 269 = 269 + 283 + 297 + 311 + 325 + 339 + 353 + 367 + 381 + 395 + 409 \quad \text{6 ring naphthenes}$$

$$\Sigma 91 = 91 + 105 + 117 + 119 + 129 + 131 + 133 + 143 + 145 + 147 + 159 + 171 \quad \text{Mono-aromatics}$$

Because of this, it is not surprising given the complex nature of different hydrocarbon fractions, each of which may contain several thousand different types of molecules, that the precision of using MS in this mode for different samples types is at best 10% [36].

To circumvent these difficulties, MS is often used in conjunction with other techniques such as gas chromatography (GC) or liquid chromatography (LC). In this case, chromatography is used to reduce the number of different molecule types that enter the mass spectrometer, reducing the number of mass peaks observed, and hence the complexity of interpreting the data accurately. In fact, separation of the sample into aromatic and nonaromatic fractions using liquid chromatography (ASTM D 2549) prior to MS analysis is a prerequisite for ASTM D 2425 [39].

One way in which MS can be combined with GC is in fact not to record a complete mass spectrum of the sample, but rather to fix the mass (or more strictly the m/z ratio) of the spectrometer to a known ion peak, and monitor this mass as a function of elution time. This can either be done directly by recording the signal in a fixed mass channel, or by scanning the spectrometer across all mass ranges and reconstructing the signal in a single mass channel using software. The latter is the method used under ASTM D 5769. In this method, separation of molecular species according to their characteristic primary and fragmentation ions allows a more complete analysis to be performed. This is illustrated in Fig. 20. In this case, by combining the selectivity of GC in separating different molecular species with the mass specificity of MS, the different molecular concentrations of specific molecules such as benzene, toluene and other aromatics can be determined. Without this mass selectivity, the gas chromatogram would be extremely complex, with no guarantee that the elution peak corresponds to a specific molecule such as benzene or toluene.

Although limited by its ability to resolve information from complex mixtures of chemicals typically found in petroleum products, mass spectrometer, particularly when combined with other separation techniques such as LC and GC is an important tool in the analysis of hydrocarbons.

ASTM Petroleum Products and Lubricants MS Test Standards Under Subcommittee D02.04

Hydrocarbon Types in Gasoline by Mass Spectrometry (ASTM D 2789)

This test method covers the determination by mass spectrometry of total paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indans, or tetralins or both, and naphthalenes in gasoline. Samples are analyzed by mass spectrometry, based on the summation of characteristic mass fragments, to determine the concentration of the hydrocarbon types.

Aromatics in Gasoline by Gas Chromatography-Mass Spectrometry (GC-MS) (ASTM D 5769)

This test method can be used for gasolines that contain oxygenates such as alcohols and ethers as additives. They do not interfere with the analysis of benzene and other aromatics by this test method. The sample is injected either through the capillary splitter port or a cool-on-column injector into a gas chromatograph equipped with a dimethylpolysiloxane WCOT column interfaced to a fast scanning mass spectrometer. The mass analyzer processes the signal at specific m/z values corresponding to the principal ion masses for various components allowing benzene, toluene, and total aromatic content to be measured in gasolines.

INFRARED SPECTROSCOPY

Infrared spectroscopy is a widely applied, nondestructive test method for assessing a variety of molecular physical qualities of a lubricant or fuel sample. The spectrum analyzed by the method is considered a distinct physical property of the sample and, as such, is unique from other physical and chemical properties, such as viscosity, specific gravity, flash point, etc. From the spectrum, in most cases, a positive identification of the sample and its greater molecular constituents can be obtained [40].

Most petroleum products, and more specifically, lubricants, fuels, additives, and contaminants are mixtures, which results in the spectrum being a composite of many different spectral components that are additive. Nevertheless, for most fluids, the spectrum is sufficiently characteristic to enable the identification of the unique spectral features of individual components. Still, in certain cases, a physical or chemical separation of the target components from the rest of the sample, such as gas chromatography, may be desirable to improve detection limits and resolving power of the technique.

The infrared spectrum of a substance is produced when a portion of a beam of infrared energy passing through a fixed path length of the sample is absorbed by a specific functional group within a specific molecule present in the sample. This absorption has unique wavelength dependencies relating to the sample's molecules. Most molecules are in constant modes of rotation, stretching, and bending at unique and often multiple frequencies. In addition, these vibrational frequencies will vary as the bonded atoms, functional groups, and bond strengths are changed. These differences in absorption at certain wavelengths in the mid-infrared spectrum collectively describe the quality and quantity of molecular makeup of the sample [41].

Infrared spectroscopy is especially well suited for the analysis of organic compounds comprised of characteristic molecular structures. The various groups, called functional groups, which make up part of a molecule's structure, give rise to absorption at specific infrared frequencies but more typically spectral bands comprising a broader range of wavelengths. These are commonly referred to as group frequencies. For example, a well-defined group frequency is associated with C═O at around 1700 wavenumbers (cm^{-1}).

Wavelength, Wavenumber and Frequency

The frequency or energy at which unique infrared absorptions occur is usually expressed as wavelength in micrometers (μm) or wavenumbers in reciprocal centimeters (cm^{-1}). Studies have shown that a typical organic molecule requires an average energy of 1.6×10^{-20} joules (J) for vibrational excitation, which corresponds to 12 μm of infrared radiation. The reciprocal of the wavelength is referred to as wavenumbers and represents the number of cycles passing a fixed point per unit of time. The scale in Fig. 21 shows the conversion of wavelength to wavenumbers [42]. The use of wavenumbers (cm^{-1}) in infrared spectroscopy is preferred to a scale of wavelengths (μm) because wavenumbers are linear and proportional to the energy and frequency being absorbed. Wavenumbers are sometimes incorrectly referred to as frequencies, an error because the wavenumber is expressed in reciprocal centimeters (cm^{-1}) and frequency is expressed in units of reciprocal time (s^{-1}) [42].

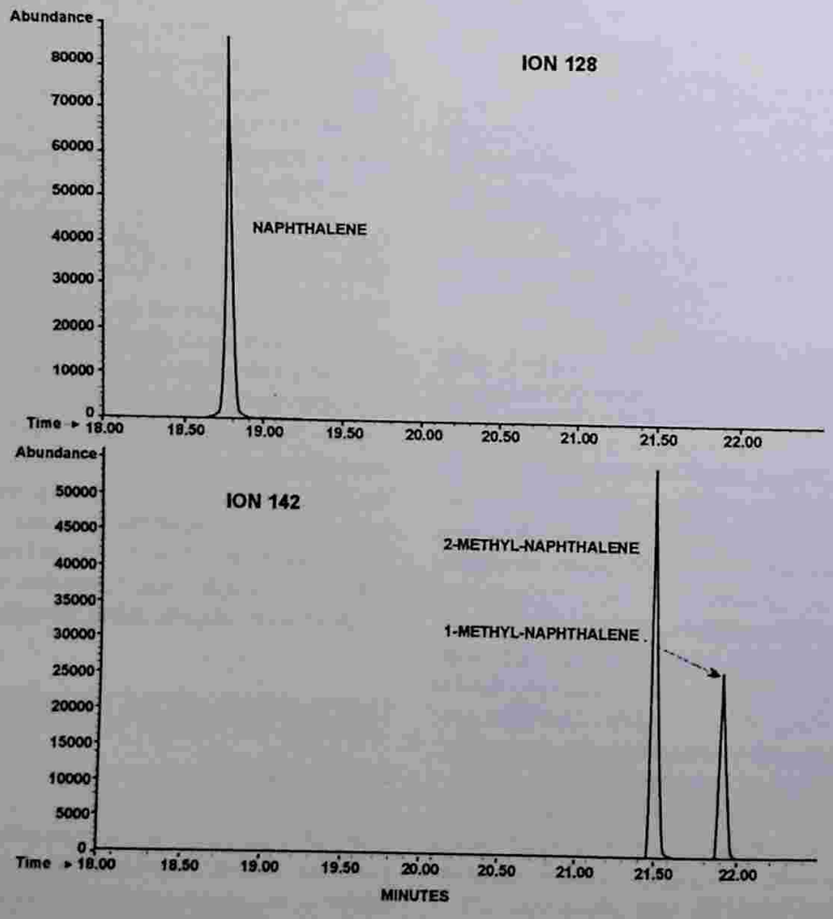


FIG. 20—Typical mass selected gas chromatogram showing the ability of GC-MS to separate molecular species by their elution time and characteristic ion mass peak. Reprinted with permission from ASTM D 5769-98.

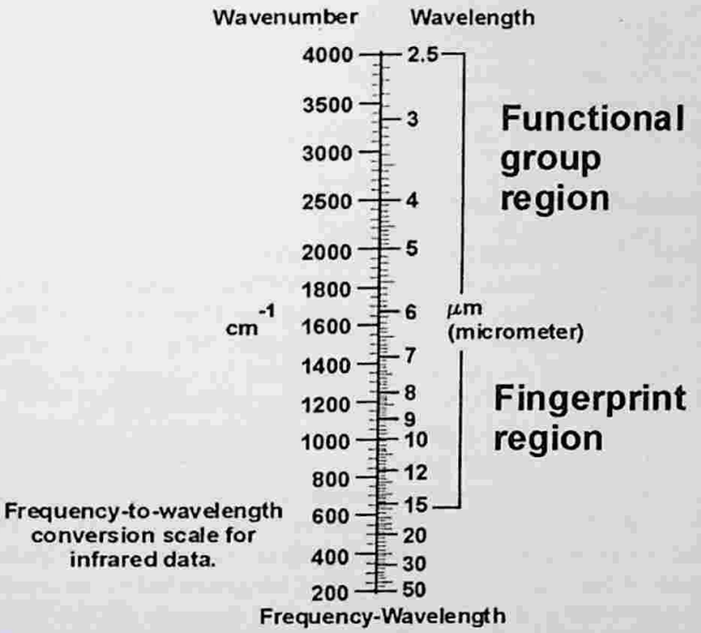


FIG. 21—Conversion scale for infrared data.

Beer-Lambert Law

A good place to begin the discussion of using infrared spectroscopy for quantitative analysis of fuels and lubricants is the Beer-Lambert Law. It relates the amount of infrared light absorbed by a given sample to the concentration of the target compound and path length. More to the point, the law states that concentration is directly proportional to absorbance at a given wavelength and path length at a specified temperature and pressure.

$$A = abc = \log_{10} I^0/I \quad (1)$$

A = absorbance
I = IR power-reaching detector with sample in beam
I^0 = IR power-reaching detector with no sample in beam
a = absorption coefficient of pure component of interest at analytical wavelength; the units depend on those chosen for b and c
b = sample path length
c = concentration of sample component

This linearity permits simple calibration plots of known samples between absorbance (A) and concentration (C) for analyzing the concentration in unknown samples. In addition, the Law is helpful in choosing the optimum sample path length for accurate analysis, as will be further discussed [43].

Dispersive-Type Infrared Spectrometers

In this design, an infrared source of energy is usually provided by a Nernst glower, which is composed of rare earth oxides (zirconium, cerium, etc.) formed into a cylinder. On electrically heating to approximately 1500°C, this filament material produces the needed infrared radiation. The beam of radiation is split into a reference and sample beam by mirrors. The reference beam is passed through air or a beam attenuator and the sample beam is passed through the sample where selective radiation absorption occurs [42].

The reference and sample beams are then passed alternatively by a rotating half mirror to a dispersive device, which separates the radiation into specific frequencies (wavelengths). A prism is one type of dispersive device that separates radiation in different wavelengths based on differences in refractive indexes at different wavelengths. Since glass will absorb infrared radiation sodium chloride, other materials are required. Alternatively, a grating can be used as a dispersive device using a series of closely spaced parallel grooves etched into a flat surface. The grating simply reflects the diffracted light from its surface and absorbs very little radiation. Many infrared spectrometers require special temperature and/or desiccants to prevent moisture damage to the optics in the monochromator [42].

The monochromator directs the radiation reflecting from the grating through a series of narrow slits, which luminate onto a detector, for example, a thermocouple. This quantifies the intensity of the energy at only the desired band of frequencies. Many dispersive-type infrared spectrometers are of the double-beam optical null type. In such cases, the radiation passing through the reference beam is reduced or attenuated to match the intensity of the sample beam [42].

Fourier Transform Infrared Spectroscopy

Compared to the dispersive spectrometer, the Fourier transform spectrometer provides improved speed and range of spectral sensitivity in making infrared measurements. The Michelson interferometer is a basic component of the Fourier transform instrument. Unlike the dispersive spectrometer, the interferometer has no slits or grating. Instead, it consists of two mirrors and a beam splitter. The beam splitter transmits half of all the incident radiation from a source to a moving mirror and reflects half to a stationary mirror. Each component reflected by the two mirrors returns to the beam splitter where the amplitudes of the waves are combined to form an inteferogram, which is Fourier-transformed into the frequency spectrum. The interferometer scans the infrared spectrum in just fractions of a second at moderate resolution. The resolution is uniform across the optical range. Multiple scans can be co-added to reduce background noise [42].

Analysis of Multicomponent Solutions

For solutions, samples should be diluted and placed in cells of appropriate path length (typically 0.2–1.0 mm). It is preferred to use lower concentrations in longer path length cell rather than higher concentrations in shorter path length cell. The desired absorbance is in the range of 0.3–0.8. Lower concentrations will minimize nonlinear effects due to dispersion (that is, change of refractive index with wavenumber). Where freedom from intermolecular effects is uncertain or where intermolecular effects are known to be present, calibration must be based on measurements taken from synthetic mixtures of all components. The procedure is described in ASTM E 168 [44].

Calibration is achieved by dissolving a known weight of a pure component in a suitable infrared solvent. Next, the absorbance is measured at all analytical wavenumbers and cor-

rected for baselines as further discussed. The procedure is repeated for a range of concentrations covering the expected concentrations. From this, absorbance is plotted against concentration. Analytical curves can also be constructed for each of the wavenumbers or bands where the target component is represented. So too, the procedure is repeated for each of the components to be analyzed in the solution [44].

Analysis of Gases

For gases, all calibration measurements for a given analysis must be made at a fixed total pressure. This pressure must be equal to the total pressure employed in the analysis. Low molecular weight gases frequently produce very strong, sharp absorption features. Addition of a diluent gas and use of pressure below atmospheric may be necessary. Absorbances are measured for each of the standard wavenumbers selected for analysis. Where possible, integrated absorbances are preferred to offset the effect of small pressure variations. The absorbances are plotted against the partial pressures (or mole fractions) to produce analytical curves [44].

Achieving Reproducible Baselines

Any quantitative method depends on the choice of a reproducible baseline. The correction of raw data for baseline absorbance is important in some methods. The guiding factor in baseline selection is the reproducibility of the results. Methods used for drawing baselines with computerized instruments are similar in most ways to those for data recorded on chart paper [44].

A technique known as the cell-in-cell-out method is often used in single-beam infrared work. In this method, a blank (that is, solvent in cell, potassium bromide (KBr) pellet, or other substrate) is measured at a fixed wavenumber and then the analyte readings are recorded. One variation involves the subtraction of the absorbance minimum from the absorbance maximum at the chosen baseline point. The point of minimum absorbance is adjacent to or at least near the band under evaluation. Alternatively, two points may be needed if the band of interest is superimposed on a sloping background. In such case, a line is drawn from one side to the other and absorbance is calculated as the value at the peak maximum minus the baseline absorbance minimum. An inappropriate choice of baseline in this situation may have deleterious effects on the accuracy of the final calculation [44].

The baseline correction described above should be performed only if the spectrum is plotted in absorbance units. When the spectrum is plotted in transmittance, the two-baseline transmittances and the transmittance at the analytical wavenumber are converted to absorbance. Conversion to absorbance is required because a sloping linear baseline in transmittance becomes curved in absorbance [44].

Employing the Difference Method

Spectral subtraction using a computer is a common practice in qualitative infrared analysis. This technique is also used to perform quantitative infrared analyses. The advantage of spectral subtraction (the difference method) is that small concentration differences can be measured with greater accuracy than is possible on superimposed bands. The general procedure involves the removal of spectral contributions of specific and known components from a spectrum containing multiple components in order to assess the unique spectral characteristics of the remaining target component [44].

Band Area Methods

Band shape changes can cause peak-height data to be nonlinear. Band area, however, may remain essentially unaffected by the changes in shape of the band because band area is a function of the total number of absorbing centers in the sample. If the shape change is caused by changes in intermolecular forces, even band area may be linear [44].

Band area is calculated by integrating across bandwidth. Band area is advantageous when band shape undergoes change as a function of increasing concentration. Frequently, band area is found to be more accurate than peak-height measurements because one is, in effect, averaging multipoint data. When integrated area is used for quantitative analyses, the reliability of the results frequently depends on the baseline treatment selected. The accuracy by band area is often improved by limiting the range of absorbances. The wings contribute very little signal while contributing substantial uncertainties to the total area. A useful guideline is to limit the integration limits to absorbance values, which are no smaller than 20–30% of the peak absorbance [44].

Hydrocarbon Analysis

Hydrocarbon analysis using infrared spectroscopy must begin at the parent backbone structure. The simple aliphatic hydrocarbon is the root of most aliphatic compounds and consists of simple linear chains, branched chains, and cyclic structures. Aliphatic compounds can consist of one or more of these structures. The infrared spectrum is useful in providing specific information on the existence of most of these structures, by inference or directly. The spectral contributions are characterized by C—H and C—C stretching and bending vibrations, which are generally unique for each molecule. For aromatic compounds, ring C=C—C stretching and bending vibrations are distinctly characteristic as are carbon-carbon multiple bonding in alkene and alkyne structures [45].

In terms of recognizing a compound as having an organic structure with aliphatic constituents, the C—H stretch vibrations for methyl and methylene are the most characteristic. In Fig. 22, methylene/methyl bands can be seen at 1470 and 720 cm^{-1}. An important methylene rocking vibration occurs at 725–720 cm^{-1}. As C—H stretching absorptions all occur below 3000 cm^{-1}, bands between 3150 and 3000 cm^{-1} and are almost always associated with unsaturation, for example, C=C—H and/or aromatic rings. Figure 23 shows examples of either single or pair absorbancies of unsaturated hydrocarbons featuring C=C with attached hydrocarbons. The number of bands and their associated positions point to the double bond location and spacing around the double bond [45].

One or more aromatic rings can typically be recognized by the C=C—C and C—H ring-related vibrations/bending. Typically, the C—H stretching occurs about 3000 cm^{-1}, revealing a number of weak-moderate bands compared with the aliphatic C—H stretch. The number and locations of the C—H

Saturated Aliphatic (alkane/alkyl) Group Frequencies	
Group frequency (cm^{-1})	**Functional group/assignment**
	Methyl (-CH_3)
2970-2950/2880-2860	Methyl C-H asym./sym. stretch
1470-1430/1380-1370	Methyl C-H asym./sym. bend
1385-1380/1370-1365	*gem*-Dimethyl or "iso" - (doublet)
1395-1385/1365	Trimethyl or "*tert*-butyl" (miltiplet)
	Methylene (>CH_2)
2935-2915/2865-2845	Methylene C-H asym./gym. stretch
1485-1445	Methylene C-H bend
750-720	Methylene - (CH_2)-rocking (n>3)
1055-1000/1005-925	Cyclohexane ring vibrations
	Methyne (>CH-)
2900-2880	Methyne C-H stretch
1350-1330	Methyne C-H bend
1300-700	Skeletal C-C vibrations
	Special methyl (-CH_3) frequencies
2850-2815	Methoxy, methyl ether O-CH_3 C-H stretch
2820-2780	Methylamino, N-CH_3, C-H stretch

FIG. 22—Saturated aliphatic (alkane/alkyl) group frequencies. Courtesy Coates Consulting.

Olefinic (alkene) Group Frequencies		
Origin	**Group frequency wavenumber (cm^{-1})**	**Assignment**
C=C	1680-1620	Alkenyl C=C stretch
	1625	Aryl-substituted C=C
	1600	Conjugated C=C
C-H	3095-3075 +3040-3010	Terminal (vinyl) C-H stretch
	3095-3075	Pendant (vinylidene) C-H stretch
	3040-3010	Medial, *cis*- or *trans*-C-H stretch
C-H	1420-1410	Vinyl C-H in-plane bend
	1310-1290	Vinylidene C-H in plane bend
C-H	995-985+915-890	Vinyl C-H out-of-plane bend
	895-885	Vinylidene C-H out-of-plane bend
C-H	970-960	*trans* C-H out-of-plane bend
	700 (broad)	*cis* C-H out-of-plane bend

FIG. 23—Olefinic (alkene) group frequencies. Courtesy Coates Consulting.

bonds around the aromatic ring is defined by the structure of the bands in the spectrum. Other important bands for aromatic ring vibrations are positioned around 1600 and 1500 cm^{-1}, which are exhibited as pairs with some splitting. The nature and structure of these two bands are largely influenced by the position and nature of substituents on the ring [45].

On the surface, the interpretation of halogenated compounds contained in infrared spectra is functionally very simple. While not always true, the polar nature of the group consisting of a single atom linked to carbon produces a distinctive spectral contribution. Typically, a unique group frequency associated with halogen-carbon stretching is assigned to the C—X bond (Fig. 24). If more than one halogen is present, the identification of the group frequency is somewhat more complex. It is largely influenced by whether the halogens are on the same or different carbon atoms, and if different, their relative proximity is important.

Relating to alcohols and hydroxy compounds, the 0—H stretch is probably one of the most pronounced and characteristic of all the infrared group frequencies. There is typically a high degree of association coming from hydrogen bonding with other hydroxy groups. And, in cases, these may come from hydroxy groups from within the same molecule (intramolecular bonding). Alternatively, they may associate with nearby molecules (intermolecular bonding). Collectively, the effects of hydrogen bonding result in the production of a well-defined but broad band and the lowering of mean absorption frequency. This is exhibited in compounds such as carboxylic acids, which produce strong hydrogen bonding. See Fig. 25 for alcohol and hydroxy compound group frequencies [45].

Because alcohols exist as three distinct classes, primary, secondary, and tertiary, they are identified by the extent of carbon substitution on the central hydroxy-substituted carbon. The infrared characterization of these alcohols is reflected in the position of the OH stretch absorption but also by other absorptions including the C—O— stretching frequency. These can be observed in the primary and secondary alcohols shown in the spectra shown in Fig. 26. Ethers are somewhat related to alcohol and hydroxy compounds where the hydrogen of the hydroxy group is substituted by an aromatic (aryl) or aliphatic (alkyl) molecular fragment. Otherwise, the overall appearance of an ether spectrum is sharply different from any associated alcohol due to the impact of the hydrogen bonding on the hydroxy group [45].

In amines, the terms primary, secondary, and tertiary are used to describe the substituted nitrogen as opposed to carbon as with alcohols. As with alcohols, these structural differences are significant and distinctly influence the infrared

Aliphatic Organohalogen Compound Group Frequencies		
Origin	**Group frequency wavenumber (cm^{-1})**	**Assignment**
C-F	1150-1000	Aliphatic fluoro compounds, C-F stretch
C-Cl	800-700	Aliphatic chloro compounds, C-Cl stretch
C-Br	700-600	Aliphatic bromo compounds, C-Br stretch
C-I	600-500	Aliphatic iodo compounds, C-I stretch
Note that the ranges quoted serve as a guide only; the actual ranges are influenced by carbon chain length, the actual number of halogen substituents, and the molecular conformations present.		

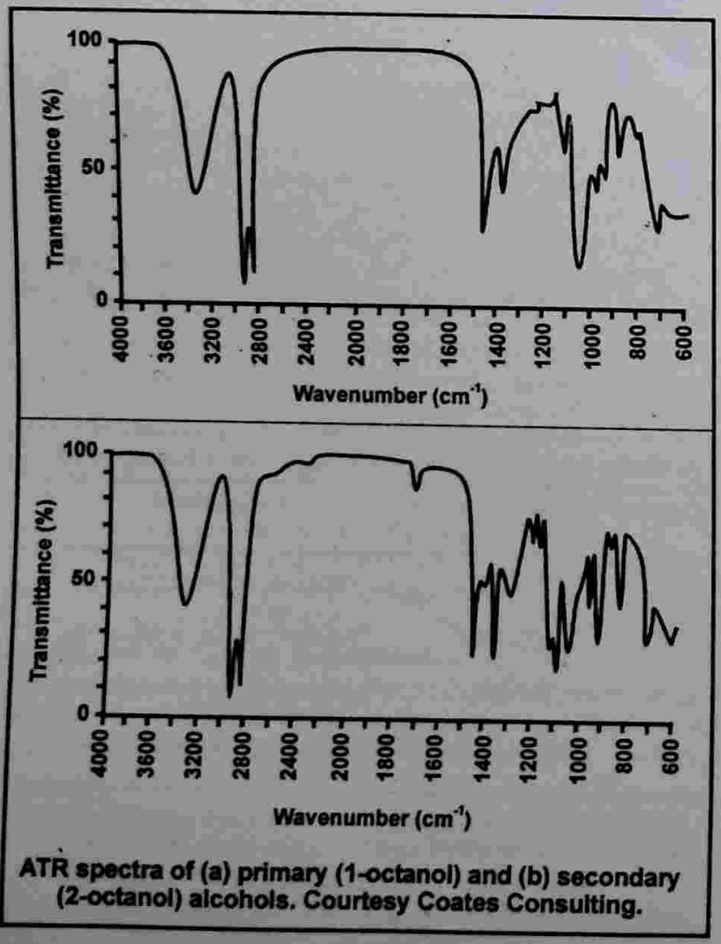
FIG. 24—Aliphatic organohalogen compound group frequencies. Courtesy Coates Consulting.

Alcohol and Hydroxy Compound Group Frequencies		
Origin	**Group frequency wavenumber (cm-1)**	**Assignment**
O-H	3570-3200 (broad)	Hydroxy group, H-bonded OH stretch
	3400-3200	Normal "polymeric" OH stretch
	3550-3450	Dimeric OH stretch
	3570-3600	Internally bonded OH stretch
O-H	3645-3630	Nonbonded hydroxy group, OH stretch
	3635-3620	Primary alcohol, OH stretch
	3620-3540	Secondary alcohol, OH stretch
	3640-3530[a]	Tertiary alcohol, OH stretch
O-H	1350-1260	Phenols, OH stretch
	1410-1310	Primary or secondary, OH in-plane bend
	720-590	Phenol or tertiary alcohol, OH bend
C-O	~1050[b]	Alcohol, OH out-of-plane bend
	~1100[b]	Primary alcohol, C-O stretch
	~1150[b]	Secondary alcohol, C-O stretch
	~1200[b]	Tertiary alcohol, C-O stretch
		Phenol, C-O stretch

[a]Frequency influenced by nature and position of other ring substituents.
[b]Approximate center of range for the group frequency.

Courtesy Coates Consulting.

FIG. 25—Alcohol and hydroxy compound group frequencies. Courtesy Coates Consulting.



ATR spectra of (a) primary (1-octanol) and (b) secondary (2-octanol) alcohols. Courtesy Coates Consulting.

FIG. 26—ATR spectra of (a) primary (1-octanol) and (b) secondary (2-octanol) alcohols. Courtesy Coates Consulting.

spectra. It is possible to readily describe functional group structures, especially for the primary and secondary amino compounds. Although somewhat weaker than hydroxy compounds, the hydrogen bonds play an important role in the selective identification of the various amino compounds. In the case of ammonium and amino salts, strong hydrogen bonding is observed. Primary and secondary amines are largely characterized by the N—H bond group frequencies. The tertiary amines, like esters, produce vibrations associated with the C—N bond, see Fig. 27 for group frequencies for Amino Compounds [45].

The carbonyl group, C═O absorption, is often the most characteristic and intense of the entire infrared spectrum. Common group frequencies for carbonyl compounds can be seen in Figure 28. With the exception of the aldehyde, all other carbonyl compounds can be generally considered to be derived from the base structure of ketone. This occurs as one or both alky (or aryl) substituents are replaced by a single hydroxy group (carboxylic acids) or two ether groups (organic carbonate). Commonly, the group frequencies for the various classes of carbonyl compounds overlap and the carbonyl band alone is insufficient to identify the specific functional group. Common examples include carboxylic acids where C—O, C—O—H, and O—H vibrations are characteristic, as are esters C—O—C and amides, C—N and N—H. So too, a characteristic broad feature in the range 3300–2500 cm^{-1} that overlaps the C—H stretching region is observed for hydrogen-bonded O—H in most carboxylic acids [45].

Characterization of Inorganics

Infrared spectroscopy can be used very effectively to characterize inorganic molecular species that often co-occupy space with various hydrocarbon compounds found in fuels and lu-

Amine and Amino Compound Group Frequencies		
Origin	**Group frequency wavenumber (cm^{-1})**	**Assignment**
		Primary amino
N-H	3400-3380 +3345-3325	Aliphatic primary amine, NH stretch
N-H	3510-3460 +3415-3380	Aromatic primary amine, NH stretch
N-H	1650-1590	Primary amine, NH bend
C-N	1090-1020	Primary amine, CN stretch
		Secondary amino
>N-H	3360-3310	Aliphatic secondary amine, NH stretch
>N-H	~3450	Aromatic secondary amine, NH stretch
>N-H	3490-3430	Heterocyclic amine, NH stretch
=N-H	3350-3320	Imino compounds, NH stretch
>N-H	1650-1550	Secondary amino, NH bend
C-N	1190-1130	Secondary amine, CN stretch
		Tertiary amino
C-N	1210-1150	Tertiary amine, CN stretch
		Aromatic amino
C-N	1340-1250	Aromatic primary amine, CN stretch
C-N	1350-1280	Aromatic secondary amine, CN stretch
C-N	1360-1310	Aromatic tertiary amine, CN stretch

FIG. 27—Amine and amino compound group frequencies. Courtesy Coates Consulting.

Example Carbonyl Compound Group Frequencies	
Group frequency (cm-1)	**Functional group**
1610-1550/1420-1300	Carboxylate (carboxylic acid salt)
1680-1630	Amide
1690-1675/(1650-1600)[a]	Quinone or conjugated ketone
1725-1700	Carboxylic acid
1725-1705	Ketone
1740-1725/(2800-2700)[b]	Aldehydle
1750-1725	Ester
1735	Six-membered ring lactone
1760-1740	Alkyl carbonate
1815-1770	Acid (acyl) halide
1820-1775	Aryl carbonate
1850-1800/1790-1740	Open-chain acid anhydride
1870-1820/1800-1775	Five-membered ring anhydride
2100-1800	Transition metal carbonyls

[a] Lower frequency band is from the conjugated double bond.
[b] Higher frequency band characteristic of aldehydes, associated with the terminal aldehydic C-H stretch.

FIG. 28—Carbonyl compound group frequencies. Courtesy Coates Consulting.

bricating oils. Essentially any compound that forms covalent bonds within a molecular ion fragment will produce a characteristic absorption spectrum with unique group frequencies. The metal complexes and chemical fragments associated with heteroxy groups such as nitrates, sulfates, phosphates, silicates, etc. and transition metal carbonyl compounds have already been generally discussed as related to the salts of carboxylic acids, amino, and ammonium compounds [45].

ASTM Petroleum Products and Lubricants IR Test Standards under Subcommittee D02.04

Aromatics in Finished Gasoline by GC-FTIR: ASTM D 5986

This method can be used for determining aromatic content in gasolines that contain oxygenates such as alcohols and ethers as additives. It can be used for both, and does not interfere with benzene and other aromatics by this method. The sample is injected through a cool on-column injector into a gas chromatograph equipped with a methylsilicone WCOT column interfaced to a FT-IR instrument.

Benzene/Toluene in Gasoline by Infrared (Ir) Spectroscopy: ASTM D 4053

A gasoline sample is examined by infrared spectroscopy and following a correction for interference is compared with calibration blends of known benzene concentration.

Benzene/Toluene in Engine Fuels using Mid-IR Spectroscopy: ASTM D 6277

A beam of infrared light is imaged through a liquid sample cell onto a detector, and the detector response is determined. Wavelengths of the spectrum that correlate highly with benzene or interferences are selected for analysis using selective bandpass filters or mathematically by selecting areas of the whole spectrum.

Methyl Tert-Butyl Ether in Gasoline by Infrared Spectroscopy: ASTM D 5845

This infrared method measures MTBE and other oxygenates in the concentration ranges from about 0.1 to about 20 mass percent. A sample of gasoline is analyzed by infrared spectroscopy.

ASTM STANDARDS

No.	Title
D 1319	Hydrocarbon Types by Fluorescent Indicator Adsorption
D 1840	Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet (UV) Spectrophotometry
D 2427	Hydrocarbon Types in Gasoline by Gas Chromatography
D 2789	Hydrocarbon Types in Gasoline by Mass Spectrometry
D 2887	Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
D 3524	Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography

D 3525 Gasoline Diluent in Used Engine Oils Gas Chromatography Method
D 3606 Benzene/Toluene in Gasoline by Gas Chromatography
D 3710 Boiling Range Distribution of Gasoline Fractions by Gas Chromatography
D 4053 Benzene/Toluene in Gasoline by Infrared (IR) Spectroscopy
D 4291 Ethylene Glycol in Used Engine Oil
D 4420 Aromatics in Finished Gasoline by Gas Chromatography
D 4815 Methyl Tert-Butyl Ether in Gasoline by Gas Chromatography
D 5186 Aromatics and Polynuclear Aromatics in Diesel and Aviation Turbine Fuels by SFC
D 5480 Engine Oil Volatility by Gas Chromatography
D 5501 Ethanol Content in Denatured Fuel Ethanol by Gas Chromatography
D 5580 Aromatics in Finished Gasoline by Gas Chromatography
D 5599 Oxygenates in Gasoline by Gas Chromatography
D 5623 Sulfur Determination by GC-Sulfur Detector
D 5769 Aromatics in Gasoline by Gas Chromatography-Mass Spectrometry (GC-MS)
D 5845 Methyl Tert-Butyl Ether in Gasoline by Infrared Spectroscopy
D 5986 Aromatics in Finished Gasoline by GC-FTIR
D 6277 Benzene/Toluene in Engine Fuels Using Mid-IR Spectroscopy
D 6293 Oxygenates O-PONA Hydrocarbons in Fuels by Gas Chromatography
D 6296 Olefins in Engine Fuels by Gas Chromatography
D 6352 Boiling Range Distribution of Petroleum Distillates by Gas Chromatography
D 6379 Hydrocarbon Types Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates
D 6417 Estimation of Engine Oil Volatility by Capillary Gas Chromatography

ASTM Petroleum Products and Lubricants NMR Test Standards under Subcommittee D02.04

Aromatics in Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance (HR-NMR)

OTHER STANDARDS

IP 156 Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

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