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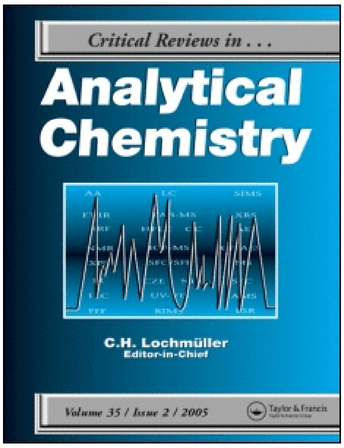

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Chromatographic Techniques for Petroleum and Related Products

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KEY WORDS: petroleum, coal products, hydrocarbon type, simulated distillation, gas chromatography; liquid chromatography; supercritical fluid chromatography, supercritical fluid extraction, thin-layer chromatography, size-exclusion chromatography**.**

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ABSTRACT: Recent developments in chromatographic techniques for the separation and quantitative characterization of petroleum and related products are highlighted. Specifically, scope, applicability, and versatility of individual techniques such as gas chromatography, liquid chromatography, supercritical fluid chromatography, thin-layer chromatography, and size-exclusion chromatography are discussed in some detail. In general, analytical approaches vary widely depending on the chromatographic technique, instrumentation, minimum detection limit, and sample type. Specific applications include chromatographic separation followed by identification and determination of individual components, measurement of boiling range distribution, and determination of hydrocarbon group types. With the exception of gaseous samples and light distillates (up to gasoline range materials), the inherent complexity arising from the presence of numerous isomers and compound types, and the finite resolution afforded by chromatographic methods preclude precise identification and quantitative determination of individual components in fossil fuels and oils. For the middle and heavy distillates, chromatographic techniques have been applied mostly for the isolation and determination of compound classes. Several techniques such as open-column liquid chromatography, medium pressure liquid chromatography, high-performance liquid chromatography, and supercritical fluid extraction provide separation of compound classes for subsequent characterization by high-resolution chromatography, spectroscopy, or other methods. Hyphenated or multitechnique chromatographic approaches have also been described. These simplify the characterization of complex samples by incorporating multiple separation mechanisms and detection schemes.

I. INTRODUCTION

A feature common to most fossil fuels and oils is that they are complex mixtures of hydrocarbons and related compounds. The hundreds of individual compounds constituting petroleum and coal-based materials vary in molecular structure and size, polarity and functionality or chemical group. The composition as well as the occurrence of a specific hydrocarbon family in a given product depends on the type of fuel and its source or process history. There have been continuous efforts to look for better approaches to characterize these materials.

Many chromatographic techniques have been employed for the characterization of petroleum and related products. In some cases (for an example, the characterization of polycyclic aromatic hydrocarbons, PAHs), these techniques are applied to separate and determine individual compounds. However, as chemical groups rather than individual molecules determine chemical properties of most fossil fuels and oils, hydrocarbon type analysis (HTA) by chromatography, thus far, has been very popular for their chemical characterization. With HTA, one can determine the quality of the fuel or oil, evaluate variables for its conversion processes, elucidate reaction pathways and kinetics, and obtain insights into the processability of the feed or the quality of the final products.

HTA is also known as SARA (saturates, aromatics, resins, and asphaltenes), and PONA, PIANO, or PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics), depending on the chemical groups analyzed in each sample. Separation of samples according to the number of aromatic rings (mono-, di-, tri-, polycyclic aromatics) may also be considered HTA. Almost all fuels and oils have some polar components, a majority of which are nitrogen, oxygen, and sulfur compounds. They may exist from ppm to percent levels in various samples. Usually, analytical approaches for hydrocarbon type determination, compound class fractionation, or identification of individual compounds vary with the sample type, components present, and their concentrations.

For a variety of applications, fossil fuels are fractionated according to their boiling points by distillation methods. Chromatographic techniques are often used to measure boiling point distributions of petroleum or coal-based products. Depending on boiling point range of the sample, fractionated products fall into three major categories: light distillates, middle distillates, and heavy distillates. All gasoline range materials and naphthas are considered light distillates. The middle distillates are diesel, jet fuel, and kerosene range samples. Heavy distillates can be distillation cuts from vacuum gas oils. Most often, methods for heavy distillates can conveniently be applied to very high boiling materials such as bright stocks, vacuum residua, and asphalts.

To be an ideal chromatographic method for the determination of individual compounds, HTA or boiling point distribution, the method should fulfill the following requirements: it should be rugged and reproducible, rapid, adequate for quality control, quantitative, and applicable to the whole sample without requiring prefractionation. As discussed in this paper, most of these criteria are met reasonably well by the methods for light and middle distillates. However, in the case of heavy materials or samples covering a broad boiling point as well as polarity range, currently available chromatographic methods often have some limitations. Usually, problems arise from inadequate resolving power, low volatility, low solubility of the components in the chromatographic mobile phase, strong adsorption of sample components on the stationary phase, or low detector sensitivity. The task is always more challenging with very complex samples (such as coal liquids) containing numerous functional groups and hundreds of individual compounds.

This overview is a focused discussion on the basic principle, scope, and applicability of each of the major chromatographic techniques used for the separation and characterization of varieties of petroleum and coal products. To this end, more emphasis is given to major developments of chromatographic methodologies than to providing a comprehensive collection of references on their applications. The applicability of each chromatographic technique is discussed along with its major limitations. The chromatographic techniques covered are gas chromatography (GC), liquid chromatography (LC), supercritical fluid chromatography (SFC), thin-layer chromatography (TLC), and size-exclusion chromatography (SEC).

II. GAS CHROMATOGRAPHY

Gas chromatography has long been vital to petrochemical analysis where its roles range from on-line monitoring of process streams and characterization of feeds, intermediates, and products in refinery operations, to providing analytical data to meet environmental regulations. The diversity of uses of GC are attributable to modern automated instruments that are equipped with high-performance packed or capillary columns, universal as well as selective detectors, and other accessories. Gas chromatographs can be operated over a wide range of temperatures (typically, from –50°C to 430°C), thus allowing these instruments to be suitable for samples ranging from gas to high boiling residuum. The use of thermally stable columns and the availability of injection ports and detectors that operate at high temperatures (up to 430°C) have been helpful for the analysis of many difficult-to-volatilize materials. A list of major GC methods approved by the American Society for Testing and Materials (ASTM) given in Table 1, reflects the wide variety of GC applications for petroleum-related materials.

For low-molecular-weight hydrocarbons and heteroatomic molecules having up to 10 or so carbon atoms, capillary column GC provides excellent resolution between major component peaks permitting both identification and quantitation of

TABLE 1
Major GC Methods Approved by the ASTM

Method No.	Application area	Description
D 2163	Liq. petroleum gas (LPG)	LPG analysis and propene concentration by GC
D 2268	n-Heptane and i-octane	High purity n-Heptane and i-Octane analysis by capillary GC
D 2427	Gasoline	C2 - C5 hydrocarbons in gasoline by GC
D 2887	Middle to heavy distillates	Boiling range distribution (simulated distillation) of petroleum fractions by GC
D 3524	Lubricant	Diesel fuel diluent in used diesel engine oil by GC
D 3525	Lubricant	Gasoline in used lubricant by GC
D 3710	Gasoline	Simulated distillation of gasoline and gasoline fractions by GC
D 4420	Gasoline	Aromatics in finished gasoline by GC
D 4815	Gasoline	Oxygenates (ethers and alcohols) in gasoline by GC
D 5134	Light distillates (naphthas)	Analysis of naphthas through nonane by capillary GC
D 5307	Crude oil	Simulated distillation of crude petroleum by GC
D 5442	Wax	Analysis of petroleum waxes by GC
D 5443	Light distillates	Paraffin, naphthene and aromatic hydrocarbon type by multi-dimensional GC
D 5580	Gasoline (finished)	Benzene, toluene, ethylbenzene, xylenes, C_9 + aromatics and total aromatics by GC
D 5599	Gasoline	Oxygenates in gasoline by GC and oxygen selective flame-ionization detection (O-FID)
D 5623	Light distillate	Sulfur compounds in light petroleum liquids by GC and sulfur selective detection
D 5769	Gasoline (finished)	Benzene, toluene and total aromatics in finished gasoline by GC-MS
D 5986	Gasoline	Oxygenates, benzene, toluene, C_8-C_{12} aromatics and total aromatics by GC and FTIR
D 6159	Ethylene	Hydrocarbon impurities in ethylene by GC

individual components in the sample. However, for heavier samples, because of coelution of numerous isomers and interference from isomers of adjacent carbon numbers, identification of individual components becomes a difficult task. In general, GC chromatograms obtained from coal conversion products such as coal-derived oils are more complex than those from petroleum products because they contain a broader variety of compound families and much higher levels of polar compounds, including molecules with heteroatoms and PAHs.

GC stationary phases used vary from nonpolar, such as methylsilicone, to highly polar Carbowax or TCEP (*tris*-cyanoethoxypropane), depending on the sample components and selectivity required for a particular separation.[1,2] Flame-ionization detection (FID) is applied extensively in the GC analysis of fossil fuel-derived samples. FID and other common GC detectors are listed in Table 2. Basic principles and selectivities of these detectors are also highlighted. Major application areas of these detectors are given in the last column of Table 2. In many applications, multiple detectors are used in series or parallel configuration to take advantage of their selectivity and/or to obtain data from multiple columns. A discussion on some element-specific detectors is covered in a separate section to highlight some special petrochemical analyses.

A. Hydrocarbon-Type Analysis by GC

1. Capillary Column GC

High-resolution capillary columns have been used to separate individual components in gasoline to diesel range samples.[3-6] For the most part, FID has been used for the quantitative determination of each hydrocarbon component from its peak area using an appropriate response factor. GC data are then grouped into different hydrocarbon classes by carbon number.[3-5]

In the past, GC coupled with mass-spectrometry (GC-MS) served as the primary technique for the identification of individual components, particularly in gasoline range samples.[7] A list of about 400 identified peaks in whole gasoline samples was provided by Whittemore in 1979.[8] At present, most commonly retention indices are used to identify components separated by capillary column GC-FID. For light petroleum samples, Kovat's retention index,[9,10] based on the retention data of n-alkanes, has been found to be useful to identify hydrocarbon components irrespective of minor variations in chromatographic conditions and column parameters.[11,12] A combination of retention indices and GC-MS has also been applied to identify components in a complex hydrocarbon mixture.[13] GC-FTIR and retention indices were used to identify components in middle oil fractions from a coal tar.[14] As coal-derived liquids contain high levels of polycyclic aromatic compounds (PACs), retention indices based on internal standards naphthalene, phenanthrene, chrysene, and picene were shown to be more effective for peak identification than Kovat's retention index system. The retention indices of over 200 PACs were reported.[15,16]

A complex separation scheme was applied to fractionate a light crude oil to identify and quantitate 281 aliphatic, aromatic, and biomarker compounds.[17,18] The collection points from open-column liquid chromatography with silica gel were determined using 15 n-alkanes and 16 PAHs. The resulting fractions were then analyzed by GC-FID and GC-MS.

Usually, the column and temperature program profiles determine how best the individual hydrocarbons can be separated and resolved from each other by capillary column GC. In practice, many small peaks from real-world samples are ignored. However, some coelutions of major components have been encountered, and these require closer attention. For an example, a multistep temperature programming was used to resolve some key components that are difficult to resolve otherwise. [19]

The role of GC-MS has been very important in petrochemical analysis. Besides component identification[7,20] and determination (e.g., aromatics by the ASTM D5769 method) in complex petrochemical samples, there are GC-MS studies that resemble hydrocarbon group type analyses. Capillary column GC-MS methods based on chemical ionization with nitric oxide were applied to both identify and quantify compound types in gasoline[21] and middle distillates.[22] The method is used to classify hydrocarbon types by their carbon number n and hydrogen deficiency index z defined by a general formula C_nH_{2n+z},where z can be both positive and negative integers. The distributions of saturates, mono-, di-, and tri-aromatics are obtained by using relative populations corresponding to appropriate z numbers. A GC-MS method has also been demonstrated for the determination of acyclic alkenes in gasoline to light gas oil range samples.[23] The method involves the detection of an intense $(M+43)^+$ or $(M+46)^+$ adduct ion peak in the acetone or acetone-d_6 chemical ionization mass spectra of alkenes in a petrochemical sample.

2. Multidimensional GC

All multidimensional GC systems described in the literature utilized two or more columns of

TABLE 2
Common GC Detectors

Detector	Selectivity and principle	Applications in petrochemical analysis
Flame-ionization detector (FID)	Selective to materials that ionize in air- hydrogen flame.	Hydrocarbons and hydrocarbon-rich compounds
Thermal conductivity detector (TCD)	A universal detector for anything providing a difference in thermal conductivity from the carrier gas	Hydrocarbons, oxygenated compounds, water and fixed gases
Mass selective detector (MS or MSD)	A universal detector for total or single ion monitoring.	Hydrocarbons and organic molecules containing heteroatoms
Atomic emission detector (AED)	Selective to any element that emits characteristic light when excited (with a microwave-induced plasma): $A + \Delta E \rightarrow A^* \rightarrow A + h\nu$	Hydrocarbons and organic molecules containing one or more heteroatoms.
Sulfur chemiluminescence detector (SCD)	Selective to sulfur-compounds: SO is produced when S-compounds are oxidized. SO after ozonization gives SO_2^* that decays to ground state producing a signal.	Sulfur-compounds in refinery streams, coal liquids and crude oils
Nitrogen chemiluminescence detector (NCD)	Selective to nitrogen-compounds: NO is formed when N-compounds are oxidized. Ozonization of NO gives NO_2^* that decays to ground state producing a signal.	Nitrogen-compounds in refinery streams, coal liquids and crude oils
Flame photometric detector (FPD)	FPD filters and measures light emitted when a sample is burned in a hydrogen-rich flame.	Phosphorus (525 nm filter) and sulfur (393 nm filter) compounds
Fourier transform infrared (FTIR) detector (IRD)	A universal detector based on the measurement of molecular vibrations that are specific to the molecular structure.	Functionalities present in the hydrocarbon backbone
Electron capture detector (ECD)	Selective to halogenated and other compounds that capture low energy electrons to form negatively charged ions and energy: $CX + e^- \rightarrow CX^- + \Delta E$	Polychlorinated biphenyls (PCBs) and other halogenated compounds.

different polarities and selectivities .[4,24-27] Although several multidimensional GC systems were reported, only one is commercially available.[24,25] This automated multicolumn GC system can be operated under various modes by activating a number of valves and using several traps and columns. This allows separation and quantification of the hydrocarbon types of light distillates (with final boiling point up to 200°C), and the separation of each type by carbon number. Several reports have described for PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics), PNA, and PONA determinations from light distillates, including naphthas, reformates, and alkylates.[6,28-31] In some cases, the multidimensional GC results were compared with those from other methods, including capillary column GC[6,29-31] and ASTM D1319 fluorescent indicator adsorption (FIA).[6,28] The commercial multidimensional GC system uses columns and traps that include a reversible olefin trap, a polar OV-275 column, a non-polar OV-101 column, a 5A molecular sieve column and a 13X molecular sieve column.[24,28] The aromatics are separated from saturates and olefins by the OV-275 column. The olefins are retained in an olefin trap allowing saturates to elute. Isoparaffins plus napthenes are separated from n-paraffins by the 5A molecular sieve column. The 13X molecular sieve column then separates isoparaffins and naphthenes. The 13X column also allows the elution of components according to their carbon numbers. The OV-101 column separates aromatics according to their boiling points.

3. Hydrocarbon-Type Analysis of Coal-Derived Products

Separation and determination of chemical families according to the number of rings have been achieved for coal-derived products. There have been studies on qualitative retention index of elution for polycyclic aromatic compounds, which are usually present in coal samples.[15,16,32-35] Conclusions from these studies suggest that elution of coal products from polymethylsiloxane columns is carried out according to the number of rings (which can be both aromatics and non-aromatics). In this manner, an approximate separation by index zones for one ring to five rings can be obtained. The use of an average response factor for each zone (calculated using the corresponding PAC standard), as well as the use of an internal standard (usually, *n*-decane) allows an approximate quantitation of these families.[32,35] However, these results are subject to large uncertainties due to difficulty in delimiting index zones in real chromatograms and in obtaining accurate response factors.

B. Boiling Range Distribution by GC

1. Simulated Distillation by GC-FID

In most part, refinery streams are fractionated according to their boiling ranges. Although physical distillation methods (such as ASTM D86, D1160, and D2892) closely resemble actual refinery operations, they are time-consuming and cost-prohibitive for routine process control. Simulated distillation (SimDis) by GC has been very effective as an alternative to physical distillation. SimDis is based on the fact that hydrocarbons are eluted from a non-polar column essentially in boiling point order, and that a complete elution of sample can be achieved as the column temperature is increased through programming. Usually, sample detection is carried out by a FID. The peak integration is done in fixed time slices, rather than on individual peaks. The time axis is then converted to boiling temperature by using a mixture of standards with known boiling points. The usual choices for the standard mixtures are a mixture of n-paraffin standards for petroleum products, and a mixture of polycyclic aromatic compounds in the case of coal liquids. By comparing chromatographic retention times of the sample and standards, it is possible to calculate the percentage recovery or process conversion yield at any desired temperature.[36] If complete elution of sample is not possible, the boiling range distribution data are determined by using either internal standards or external standards.

SimDis methods such as ASTM D3710 and D2887 are intended for gasoline range and lube base oil samples with final boiling points up to 1000°F, respectively, and it is assumed that the whole sample elutes from the column and is detected. ASTM D5307 was designed to analyze front ends of crude oils or heavy distillate samples boiling up to 1000°F using internal standards to estimate the quantitative recovery.

Nonpolar packed columns and capillary columns are used for the ASTM approved GC-simulated distillation methods. Temperature programming is used to achieve separation of sample components with adequate resolution in a reasonable time. Even with packed columns or thick film capillary columns, it becomes necessary to use subambient cooling to resolve all low carbon number alkanes to obtain a more linear calibration curve.

2. High-Temperature Simulated Distillation

The usefulness of simulated distillation has been fully realized recently with the development of metal capillary columns with low-bleed stationary phases that withstand very high temperatures. Based on high-temperature capillary GC, several variations of the ASTM SimDis methods exist. These methods have made simulated distillation applicable up to carbon number ~120 or temperature range of about 1400°F. High-temperature SimDis methods have been applied to crude oils and heavy materials such as high-viscosity-grade base stocks, and atmospheric and vacuum residua.[37-43]

High-temperature SimDis has some serious limitations, such as assignments of the same response factors for the eluting and noneluting fractions, cracking of the heavy components at high oven temperatures, and the degradation of the front-end of the capillary column as nonvolatile components from the sample accumulate over time.

3. Simulated Distillation by GC-MS

This technique provides information on both conversion yields and group-type distribution of saturates and aromatics. For an example, SimDis by GC-MS on the products obtained by hydroconversion of a deasphalted vacuum residuum provided relative populations of four saturate and four aromatic classes of hydrocarbons along with boiling range distributions of the products.[44] The procedure for spectral data processing consists of deconvoluting the saturates spectrum and aromatics spectrum from the global data. Cross-contributions from each hydrocarbon family to the spectrum of the other are eliminated. After the contribution from each hydrocarbon type to the total ionization has been calculated, the volume percentage of the classes of saturates and aromatics are obtained by normalization.[44-46] However, this technique has only been applied to few products (primarily petroleum heavy oils and their hydrocracking products), and it requires previous knowledge of samples to avoid possible interference.[47] The coupled simulated distillation-MS, where high-temperature simulated distillation column serves as an inlet for the mass spectrometer, can easily be applied to the characterization of base oils and related products.

C. Analysis of Wax and Similar Samples by High-Temperature GC

The average molecular weights of wax samples were found to vary between 400 and 2000 Da depending on the type of wax: paraffin wax, microcrystalline wax, or polywax polyethylene. Achieving complete elution and resolution of low- to high-molecular-weight wax components from the GC column has been a great challenge. It appears that instability of a GC column at high temperature was a major limiting factor for the characterization of wax samples by GC in the 1980s.[48] Recently, the use of a programmable temperature vaporizer injector for on-column injection, short capillary columns with thermally stable stationary phases, and temperature programming up to 430°C or more have been providing high-resolution separation of wax components up to and beyond carbon number 120.[48-51] Samples similar to wax such as high-molecular-weight linear alcohols and acids were also analyzed by high-temperature GC.[49]

D. Element-Specific Detectors for Heteroatomic Compounds

The use of a detector that measures GC effluent in terms of properties that are characteristic of only certain element(s) in the molecule is a preferred way to obtain information about some chemical families. This also allows one to obtain enhanced resolution between component peaks because molecules are detected selectively in the midst of others, which remain transparent to the detector. This is advantageous for identification and detection of specific types of molecules in many complex petrochemical and coal samples. Because of their wide (or potentially wide) applicability, the following three element-specific detectors are discussed below.

1. Sulfur Chemiluminescence Detector and Nitrogen Chemiluminescence Detector

Ozone-induced SCD,[52-54] and NCD[55,56] provide enhanced S to C and N to C selectivities, adequate dynamic range, and uniform responses to different classes of S-compounds (in the case of SCD) and N-compounds (in the case of NCD). For both detectors, the oxidizable species in the effluent from the GC column are oxidized. In the case of NCD, the NO produced combines with ozone (O_3) to form nitrogen dioxide in the excited state (NO_2^*). The NO_2^* emits light during its decay to the ground state, which is detected by a photomultiplier tube. In the case of SCD, the SO and O_3 produce excited sulfur dioxide (SO_2^*) that decays to the ground state, producing a signal.

GC-NCD was applied for quantitative speciation of N-compounds and simultaneous determination of total nitrogen in gasoline and diesel range process streams. The GC-NCD method was shown to permit determination of compounds contributing as little as 100 ppb of nitrogen. Adequate resolution between individual components of each N-family such as pyridines, pyrroles, anilines, indoles, quinolines, and carbazoles could also be obtained.[56]

GC-SCD has been applied widely for the speciation of sulfur compounds and determination of total sulfur in a variety of petrochemical samples, including natural gases,[57] gasolines,[58-60] diesels,[61] and gas oils.[60,62] This technique has been used to analyze groups of organosulfur compounds in different gas oils and hydrodesulfurized gas oils with a boiling point range of 150 to 450°C, and to identify and quantify individual species such as 3-methyl benzothiophene, 4-methyl dibenzothiophene, and 4,6-dimethyl dibenzothiophene, which are refractory to hydrodesulfurization.[63] However, owing to the complexity of the studied products, in this case SCD was used in a hyphenated chromatographic system, which consisted of HPLC-GC-FID-SCD (see later). The speciation of sulfur families, including thiols + sulfides + thiophenes, benzothiophenes, dibenzothiophenes, and benzonaphthothiophenes was carried out by high-performance liquid chromatography (HPLC).

2. Atomic Emission Detector

AED combines microwave-induced plasma excitation with optical emission spectroscopy.[64,65] In AED, the high temperature produced in a He or Ar plasma breaks bonds of the GC-eluted molecules and excites their constituent atoms to higher electronic states. The excited atoms emit characteristic frequencies of light. Intensity of emission lines at wavelengths characteristic of the atoms of interest are then measured.

In the case of petroleum, major elements of interest for detection by AED have been C, H, N, O, S, Pb, Fe, Ni, and V. Many petroleum streams and fractions,[66-69] as well as crude oils and residua,[70-73] and shale oils and coal-derived liquids[72-74] were analyzed by GC-AED. Gasoline-range distillates were analyzed for separation, identification, and quantitation of sulfur compounds, oxygen-additives and lead-containing compounds.[66,68,69,75,76] The total amounts of an element such as sulfur or oxygen in gasoline range samples or other materials, including crude oils, can be obtained readily because the element-specific response was found to be largely independent of the type of compound.[66,75,77]

Volatile Ni-, V-, and Fe-porphyrins were detected in crude oils and residua by GC-AED.[70,71] This multielement analysis can easily be used to fingerprint crude oils from different sources. Qualitative analysis of the portion of pyrolyzed coals, which is eluted from a GC-column, has also been performed by GC-AED.[74] GC-AED was found to be useful to track changes in the sulfur compounds and other heteroatomic molecules in processes such as catalytic cracking[66] or hydrodesulfurization.[63,78]

Identification of heteroatomic compounds has been carried out using various means, including the use of known compounds. GC-MS has been a very useful tool for identification of compounds.[67] Chemical treatment of the sample for selective oxidation provided group-type classification of sulfur compounds in gasoline range samples.[69] For this, mercaptans were selectively oxidized with excess iodine to disulfides. Hydrogen peroxide was used to oxidize mercaptans and sulfides to yield sulfonic acids and sulfones, respectively. Another example of selective chemical treatment (oxidation of sulfur compounds to sulfones using meta-chloroperbenzoic acid) involves a shale oil sample, which was analyzed for polycyclic aromatic sulfur heterocycles.[72]

E. Fast GC

There is a growing interest in fast GC, alternatively called high-speed GC, for rapid analysis of petrochemical samples with adequate resolution. The technique is particularly desirable in refinery laboratories where there is a high demand for high throughput for compositional monitoring of process streams. The conventional GC analysis time is 30 min or longer. Typical "fast" GC analysis time can be from less than 1 min to 10 min for a relatively complex sample like gasoline range naphtha. Another important requirement for the fast GC technique is that the GC-oven cool-down should be rapid to allow a short cycle time.

A short ultranarrow bore column with very thin film (e.g., a 6 m x 0.10 to 0.25 mm id x 0.1 μm GC column) offers fast analysis time. Recent advances in GC instrumentation such as a GC inlet for rapid (40 ms) sample introduction with narrow bandwidth (5 to 10 ms) using cryofocusing technique,[79] and a GC's ability to have high inlet pressure, high oven temperature programming rate (20 to 60°C/min),[80] high split-ratios to avoid overloading, and fast detection rates, have made the fast GC possible. A recent article on high-speed GC highlights some of these developments.[81] Usually, TCD, FID, and MS detector have been used as detectors for fast GC.

Applications of fast GC will grow as instruments become available commercially. A few fast GC examples include analysis of permanent gases and light hydrocarbons in less than 1 min,[82] separation of light hydrocarbons using packed capillary column in seconds,[83] and analysis of reformulated gasolines by GC-MS for benzene and total aromatics in about 7 min.[84]

F. Pyrolysis GC

Pyrolysis GC has been applied to obtain useful information on the thermal decomposition behavior as well as the composition of heavy oil products such as asphaltenes, vacuum residua, oil shale, and coal tars. Usually, a pulse heating pyrolyzer with a platinum—strip sample holder is coupled with a GC equipped with FID and/or other detectors.[85]

Typical applications of pyrolysis GC vary widely. Characterization of vacuum residua, asphaltenes, and resins from different crude oils by pyrolysis GC coupled with FID and FPD revealed differences in the pyrograms and generation of different sulfur compounds during pyrolysis.[85] Toluene -insoluble solids from hydrocracked bitumen products were analyzed by pyrolysis GC-MS. Solids obtained by hydrocracking under mild conditions were found to release alkanes and alkenes in addition to aromatic compounds, while those from high-severity hydrocracking release mostly aromatic compounds.[86] Thermal decomposition behavior and molecular structure of asphaltenes were determined by pyrolysis GC-MS.[87]

III. OPEN-COLUMN AND MEDIUM PRESSURE LIQUID CHROMATOGRAPHY

Open-column liquid chromatography (OCLC), using normal adsorbents such as silica gel or alumina, has been applied extensively for hydrocarbon type separation of fossil fuels and oils.[88-91] These OCLC separations are based on well-known retention and elution mechanisms and are carried out using appropriate adsorbents and solvents or solvent mixtures. In general, interactions (arising from polarity differences) between adsorbent and sample, solvent and sample, and solvent and adsorbent govern the sample retention process. The solute displacement is a function of solvent volume when interactions between sample components and adsorbent and between solvent and adsorbent are comparable. With appropriate adsorbent and solvent, components that differ in polarity are displaced inversely with their polarity. A successive elution with a stronger solvent (with higher polarity) is necessary to elute components that cannot be moved by a low-polarity eluant.

OCLC-separated fractions are collected and subjected to gravimetric determination after evaporation of solvent. Rotary evaporation under mild vacuum or another form of vacuum aspiration is used to concentrate the collected fractions. OCLC-based methods are often used to isolate sufficient amounts of materials for subsequent characterization by high-resolution chromatographic methods or spectroscopic techniques, or for their use as external standards.

Normal-phase LC elution has been carried out in an open-column by a gravitational flow of solvent[92-95] or by a force-flow using medium pressure (MPLC) to increase separation speed.[96] Usually, saturates are eluted with an n-alkane. The aromatics and polars are eluted with solvents or solvent mixtures of higher eluotropic strengths that include toluene, dichloromethane, acetone, or their mixtures with other solvents.

Silica gel is, by far, the most widely used adsorbent. It provides separation of compound classes according to polarity. For similar polarities, specifically for aromatics, separation of compounds is usually carried out according to molecular weight. Alumina has been used when separation according to the number of aromatic rings is desired. However, irreversible adsorption onto the adsorbent is more prevalent with alumina than silica gel.[97] Complexation packings (including charge-transfer phases and argentation packings) have also been used for OCLC separation.[98]

A. Petroleum Distillates

1. Standard Methods

Several OCLC-based ASTM standard methods for hydrocarbon type analysis and compound class fractionation of petroleum products have been developed. For light distillates, the fluorescent indicator adsorption (FIA) analysis (ASTM D1319 method) has been used for over 40 years.[94] This method is based on open-column displacement chromatography using silica gel as stationary phase and isopropanol as eluant. The hydrocarbons are separated into aromatics, olefins, and saturates (as they are displaced differentially from the top of the column). Fluorescent dyes, previously added to silica gel, are also separated selectively with the hydrocarbon types and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is obtained directly from the length of each zone in the column.

It should be noted that the FIA aromatics also include some dienes, and compounds containing sulfur, nitrogen, and oxygen, if these are present in a gasoline range sample. Other factors affecting accuracy and reproducibility of the FIA method can be summarized as follows:[28] nonuniform column internal diameter, indistinct zone boundaries, improper packing of silica gel, incomplete elution of hydrocarbons by isopropanol, colored components present in the sample, and excessive zone broadening due to the presence of C_5- and lighter hydrocarbons in the sample.

The ASTM D2549 method has also been applied to middle and relatively heavy petroleum distillates (with b.p. from 232 to 538°C), in order to isolate and recover the aromatic and non-aromatic fractions.[93] In this method, *n*-pentane is added to a column containing activated bauxite and silica gel to elute the nonaromatics. Later, aromatics are eluted using diethyl ether, chloroform, and ethanol. The nonaromatic fraction is a mixture of paraffinic and naphthenic hydrocarbons if the sample is a straight-run material. However, if the sample is a cracked stock, the nonaromatic fraction may also contain linear, branched, and cyclic olefins. The aromatic fraction may contain aromatics, condensed naphthenic-aromatics, aromatic olefins, and compounds containing oxygen, nitrogen, and sulfur.

The ASTM D2007 method is used for the determination of hydrocarbon types in heavy distillate, residual stocks and extracts.[92] This method involves the use of *n*-pentane to elute saturates through a double column containing clay in the upper section, and clay plus silica gel in the lower section. During *n*-pentane elution, polars are left on clay and aromatics on silica. Subsequently, polars are desorbed from clay using 1:1 (v/v) acetone-toluene mixture. Saturates and polars are then determined gravimetrically after complete evaporation of solvents. The amount of aromatics is calculated by difference. As an option, they may be recovered from silica by Soxhlet extraction using toluene.

The D2007 method has been applied to a broad variety of materials, including petroleum-derived oils with boiling points above 260°C and crude oils. However, its proper application requires a previous removal of *n*-pentane-insolubles such as asphaltenes. Inaccuracies in the ASTM D2007 data, in most part, originate from overloading effects causing cross-contamination of hydrocarbon types, and they have been found to be very high for high boiling distillates, heavy alkylbenzenes, and highly paraffinic base stocks.[99]

A group type separation of asphalts was carried out in 1969 by Corbett.[100] A modified form of this original approach was adopted as ASTM D4124 method.[101] After asphaltene removal as *n*-heptane insolubles, maltenes are subjected to sequential elution with *n*-heptane, toluene, toluene-methanol (50/50 v/v), and trichloroethylene from activated alumina. Thus, asphaltene, saturate, naphthene-aromatic, and polar-aromatic, fractions are obtained.[100]

2. Separation Schemes

Many nonstandard separation schemes have been applied to the characterization of petroleum distillates and crude oils. Procedures include one-step or successive[102-104] separations using various stationary phases, including alumina, cation and anion exchange phases, clay, and silica gel, as well as complexation packings.[98] Examples of some OCLC separations can be found in a review article by Altgelt et al.[103] Besides group-type separations, OCLC-based methods have been used successfully as cleanup steps for the determination and isolation of sulfur, nitrogen, and oxygen compounds in the crude naphtha,[105] high end of crude oils,[102] and other petroleum distillates.[104] The OCLC methods have also been used for subfractionation of a family of compounds as exemplified by the separation of *n*-alkanes and cyclic plus iso-alkanes in a saturate fraction using a 5A molsieve column.[106] A scheme based on selective reactions of *n*-paraffins with urea and of isoparaffins with thiourea was applied to separate *n*-paraffins, isoparaffins, and naphthenes from a nonaromatic fraction of a gas oil.[107]

B. Shale Oil and Coal-Derived Products

Any strong interaction between sample components and stationary phase (as well as eluant) can introduce bias and high level of uncertainties in preparative OCLC.[88,108] This problem is more critical in the case of coal products when polar compounds are strongly retained in the column bed and cannot be desorbed easily. For gravimetric determination of sample components, removal of typical solvents such as toluene, tetrahydrofuran, and pyridine, even under vacuum and temperature, are, on occasions, difficult. These, and the broad chemical variety and complexity of coal products have, so far, been responsible for the absence of any standard OCLC methods in coal chemistry.

A useful OCLC-based method, initially applied to whole coal hydroliquefaction products derived from the solvent refined coal process, was developed in 1977 by Farcasiu.[88] It was called sequential elution solvent chromatography (SESC), and the method uses a silica gel column and nine eluants of increasing polarity (from *n*-hexane to pyridine). The first five fractions are assigned to specific chemical families. From the sixth to ninth fraction, characterization of functionality is imprecise. These fractions contain multifunctional heteroatoms and polyfunctional molecules. The tenth fraction is unknown and retained in the column.

A method has been described recently for fractionation of coal extracts, crude oils, and other fossil fuel-derived oils into compound classes.[91] The system uses five columns (two silica gel, one acidic silica gel, and two basic silica gel columns) that provide five heterocompound fractions (bases, acids, high-polarity, medium-polarity, and low-polarity nitrogen, sulfur, and oxygen compounds) in addition to conventional saturate and aromatic hydrocarbon fractions.

Most of the methods developed later than Farcasiu's work are shortened versions of SESC adapted to each particular sample by reducing the number of eluants, varying the elution sequence, or using different stationary phases.[32, 109-111] Automated equipment for the separation of coal products applying medium pressure elution was also described.[96] Many of these studies involved characterization of specific families of compounds. For example, an initial OCLC separation provided fractions of hydrotreated shale oils for detailed analyses of nitrogen compounds by HPLC as well as GC-MS.[111] Similar separation and identification of nitrogen-containing polycyclic aromatic compounds such as carbazoles, benz(e)indoles and benz(g)indoles were also carried out.[110]

Most of the coal-derived products are highly viscous. Preadsorption of viscous samples either onto an inert support or onto the whole stationary phase has been used as a means for sample introduction. The elution of materials from such a preadsorbed stationary phase is known as extrography. It is not a pure chromatographic process, and data suggest an extractive mechanism for the first eluted fraction (with *n*-hexane), and dominant chromatographic processes for the more polar fractions.[112] Extrography was applied to coal hydroliquefaction products and coal-tar pitches[112-114] and crude oil residua.[115] Although pure separations into families are not obtained as in a chromatographic process, extrography allows a rough fractionation with high sample loading.

C. Quantitative Analysis by Open-Column Liquid Chromatography

In an OCLC separation, fractions are collected on a volume basis, which has previously been determined for a calibrant sample. This has severe limitations when applied to samples that differ in composition from the calibrant. It should be noted that an OCLC analysis (such as hydrocarbon group type separation) must be precisely carried out to monitor compositional changes due to operating parameters of the conversion processes.

Selection of solvent volume for an eluted fraction is sometimes delicate in preparative liquid chromatography because of possible fraction overlapping. For this reason, there should be a strict control of eluant volumes for each cut if an adequate separation is desired. Subfractions are usually collected, and later off-line characterization is carried out to check the purity of a fraction. Refractive index (RI) or ultraviolet (UV) detector can also be used for continuous monitoring of the fractionation.

TLC-FID[99,116] and HPLC-FID[117] have been reported to be useful tools to quantitatively evaluate the separation and verify the purity of fractions obtained by OCLC methods. Thus cross-contamination in saturate, aromatic and polar fractions from lubricant base stocks obtained by ASTM D2007 was ascertained when these fractions were analyzed by TLC-FID.[99] The TLC-FID method was also used for examining OCLC elution. Both aromatics and polar materials were found to be present in a saturate fraction when excess *n*-hexane was used to elute saturates from a heavy oil.[116]

IV. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

HPLC has been applied quite extensively to petroleum distillates, crude oils, and coal-derived liquids. Its applications include hydrocarbon-type separation and determination, as well as separation, identification, and, in some cases, quantitative determination of target compounds in many petrochemical samples.[118] The different modes of HPLC afforded by the use of normal- or reversed-phase columns, isocratic or gradient elution of solvents, and various detection systems, and the possibility of column switching allow an analyst to carry out a desired separation with adequate resolution, rapidity, and accuracy.

Hydrocarbon type determinations are mostly carried out by normal-phase HPLC. This is primarily due to the solubility and compatibility of fossil fuel-derived samples with solvents such as saturated hydrocarbons used in normal-phase elution. Therefore, silica and amino-, cyano-, or diol-bonded silica columns[119,120] have been used extensively in petrochemical analyses. A study of eight different normal-phase HPLC columns showed that nitrophenyl- and aminosilane columns provide the best selectivity for aromatic compounds.[121]

Complexation packings or charge-transfer phases[98] and argentation chromatography packings[122] have also been used. Reversed-phase columns (with alkyl-bonded silica packing) have been found useful for the high-resolution characterization of certain compound groups such as polycyclic aromatic hydrocarbons[123] and phenols[124,125] in petroleum samples.

Almost all available HPLC detectors have been used for detection and quantification of petrochemical samples.[118] These include spectroscopic detectors such as UV-visible, fluorescence, diode array (DAD) and infrared (IR), and bulk property detectors such as RI, evaporative light scattering (ELSD), dielectric constant (DCD), and FID. Mass spectrometric detectors have also been used with HPLC (in HPLC-MS). In general, external or internal calibration procedures work well for the determination of target compounds with many of the above detectors. However, for hydrocarbon type determinations, problems arise from the lack of a detection system that provides uniform response factors for hydrocarbon types. Moreover, response factors for a given type of hydrocarbons have been found to vary from fuel to fuel.

Both analytical and preparative HPLC methods have been developed to replace labor-intensive open-column liquid chromatography. As will be noted later, the Institute of Petroleum (IP) has standardized several such HPLC methods. Some preparative HPLC methods have been developed to separate target compounds as subfractions. These subfractions are then analyzed by high-resolution chromatographic method for detailed qualitative or quantitative analyses. They are also subjected to spectroscopic and elemental analyses.

A. Hydrocarbon-Type Determination

1. Standard HPLC Methods

An HPLC standard method for the determination of aromatic hydrocarbon types for samples with boiling points ranging from 150 to 400ºC is IP 391. This method has been applied to both gasoline and middle distillate samples and is based on the use of a polar column (amino- or aminocyano-silica gel) with *n*-heptane or *n*-hexane as mobile phase and refractive index detection. Here, after elution of saturates, and mono- and di-aromatics as distinct peaks, the column is backflushed to elute PAHs as a single peak. The percent mass of mono-, di-, and polycyclic aromatics are quantified using an external calibration procedure.

IP 368 is a preparative HPLC method for the determinations of saturates and total aromatics using silica columns. In this method, hexane is used as the mobile phase. After the elution of saturated hydrocarbons from the column, aromatics are backflushed.

2. Light and Middle Distillates and Gas Oils

The role of HPLC as well as other chromatographic techniques within the context of the characterization of light distillates has been addressed in a general review.[126] A typical hydrocarbon type analysis depends on the sample analyzed. In the range of gasoline and middle distillates, the hydrocarbon-types can be saturates (*n*-paraffins, isoparaffins, and naphthenes), olefins, and aromatics. Aromatic distributions into mono-, di-, and polycyclic aromatics can also be obtained. The separated hydrocarbons are usually quantified in terms of mass or volume percent of each compound class.

In the 1970s, silica gel was widely used as stationary phase for hydrocarbon-type analysis of light and middle distillates and other products.[127-130] Thus, saturates, olefins, and aromatics in gasolines (with a boiling point range 60 to 215°C) were separated on a single column, using a low-polarity fluorohydrocarbon (Freon FC-78) as the mobile phase, and were detected using an

RI detector.[127] The low-polarity eluant allowed the separation of saturates from olefins, saturates eluting first. Aromatics were then backflushed from the column. As an extension of this method, Suatoni et al. separated middle distillates (with a boiling range of 190 to 360ºC) into saturates, monoolefins, diolefins, and aromatics using two silica columns and *n*-hexane as the mobile phase. [128]

In the 1980s, Hayes and Anderson reported several methods for hydrocarbon-type separations.[131-136] Separation of saturates, olefins, and aromatics was achieved in 8 min using a 150 mm x 4.6 mm column packed with silica gel coated to a strong cation exchanger (for silver), Freon-123 (2,2-dichloro-1,1,1-trifluoroethane) as mobile phase, and DCD.[132] Saturates eluted first, followed by aromatics. Olefins were backflushed from the column. For resolution of naphthenes from other classes of compounds, Hayes and Anderson[136] used a configuration that included an additional switching valve to the basic system and a naphthene-selective PONA column (containing a microparticulate organic gel phase). Here, Freon-123 was also used as mobile phase to obtain adequate separation and compatibility with DCD. PONA (paraffin-olefin-naphthene-aromatic) type analysis was also achieved with an HPLC-DCD system employing five columns and two switching valves.[135]

Separations according to number of aromatic rings have been of interest for middle and heavy distillates. This has been achieved using either charge-transfer columns or normal-phase polar columns (such as amino-silica gel). Three groups of silica-bonded acceptors have been utilized for charge-transfer HPLC: nitroaromatics (dinitroanilino-propyl silica, DNAP),[137,138] tetrachloropthalimido groups,[98] and caffeine and related compounds.[98]

Recently, a new method based on HPLC with refractive index detection was developed and was demonstrated for the determination of volume percent of saturates, monoaromatics and diaromatics in diesel fuels.[139] HPLC-RI detection was also used to obtain total saturates and aromatics in gas oils[140,141] and kerosenes.[140] Olefins and ring number distributions of aromatic hydrocarbons were estimated by detecting them by UV at 200 nm[141] or 210 nm.[140] HPLC with both RI and UV detectors was used for the compositional study of gas oils in terms of saturates, mono-, di-, and polycyclic aromatics, and polars.[142]

3. Heavy Distillates and Coal-Derived Products

Hydrogenation, catalytic cracking, lube extraction, and coking processes for upgrading of heavy distillates can be optimized using quantitative hydrocarbon-type data obtained by HPLC for feeds and products. Likewise, HPLC methods have also been useful for qualitative process monitoring or for comparison purposes.

Heavy distillates have been studied by similar HPLC methods developed for light and middle distillates,[129,130] although clean separations between hydrocarbon types are more difficult to achieve than in the case of light and middle distillates due to increasing sample complexity.[143-146] Further, some heavy and polar compounds can be irreversibly adsorbed on the stationary phase producing column deterioration. Usually, the latter can be mitigated with appropriate stationary and mobile phases, and, if required, with the use of backflushing.

Heavy petroleum distillates are sufficiently soluble in conventional low-polarity solvents such as cyclohexane and can be completely eluted by common normal-phase HPLC solvents. However, there can be serious problems in the case of petroleum asphaltenes or coal-derived products due to their low solubility, even in highly polar solvents.

A single column is often inadequate for separating the entire range of compound polarities in heavy petroleum distillates,[122,138,147] and in coal-products.[148] Separations covering a wide polarity range were often achieved using multiple columns, column switching and solvent gradients.[143,149,150] Grizzle and Sablotny[143] developed an automated HPLC system for rapid, semipreparative isolation of hydrocarbon types (saturates, aromatics and polars) as well as aromatic ring-number fractions from crude oils, bitumens, and related materials using two 250 mm X 10 mm, 10 μm amino-bonded silica gel columns in series. After the removal of asphaltenes, 30 to

60 mg of the sample were injected onto the column and eluted using an *n*-hexane/dichloromethane gradient. Elution from the column with forward flow yielded saturates and aromatics or aromatic ring number fractions for collection. Elution of the polar fraction was accomplished by backflushing after the elution of the four-ring aromatics. Separations were monitored using RI and UV detectors.

A fully automated HPLC system was also developed[149] to separate each of six hydrocarbon types (saturates, 1- to 4-ring aromatics, and polars) in a wide variety of heavy distillates (boiling up to 700°C). Separation was carried out using two 250 mm X 4.6 mm propylaminocyano columns to separate saturates and monoaromatics, and a DNAP column to separate the aromatic rings. Elution was carried out using a ternary gradient using *n*-hexane, dichloromethane, and isopropanol. The quantification of groups was achieved after detection using DAD and ELSD. The valve switching and solvent gradient schemes were developed to maximize the resolution of the six separated groups.

Multiple columns, column switching, and solvent gradients have also been used for carrying out hydrocarbon type separation of coal-derived products.[150-152] Thus, Padlo et al.[150] reported the separation of coal hydroliquefaction products into saturates, 1-4 ring aromatics, and polars using a multicolumn system consisting of a 250 mm X 4.6 mm aminocyano column, a 300 mm X 4.6 mm DNAP-silica column, and a 250 x 4.6 mm diol-silica column. A gradient elution was carried out using *n*-pentane, dichloromethane, and isopropanol. DAD and ELSD were used for component detection. Here, the divisions between the aromatic classes were determined based on retention times and UV spectra of standards.

B. Determination of Target Compounds

1. Standard HPLC Methods

Normal-phase columns, reversed-phase columns, and combinations of both have been used in HPLC applications for determining indigenous compounds, contaminants, or additives in crude oil and petroleum distillates. Thus, standard methods from the Institute of Petroleum exist for determining coumarin in kerosenes (IP 374) and 2,4-dimethyl-6-*t*-butyl phenol antioxidant in light distillates (IP 343).

2. Illustrative Applications

a. Polycyclic Aromatic Hydrocarbons

The analysis of any complex sample (such as crude oil, petroleum distillate, or coal liquid) for PAHs usually involves normal-phase HPLC separation (for example, on an aminosilica column) to isolate fractions containing isomeric PAHs. These fractions are then subjected to reversed-phase HPLC (usually on C_{18}-silica column) to separate individual PAH isomers. For quantitative determination of PAHs, appropriate perdeuterated PAHs are used as internal standards so that each isomeric fraction contains one internal standard. In reversed-phase HPLC, perdeuterated PAH elutes first, and is usually resolved from the parent PAH.[153]

Individual carcinogenic PAHs (specifically, benzo[*a*]pyrene), have been determined in almost all types of distillates. For this, HPLC separation is carried out (often after a cleanup step), using conventional C_{18}-reversed-phase columns, typical elution with acetonitrile-water, and UV or fluorescence detection. A combination of both normal-phase column (for prefractionation) and reversed-phase column such as octadecylsilica (for analytical separation) was used for determining benzo[*a*]pyrene and other PAHs using fluorescence detection.[154,155]

Alkyl biphenyls and naphthalenes were characterized by TLC, HPLC, and capillary GC.[156] Here, the role of HPLC was to resolve a preparative TLC-separated dinuclear aromatic fraction into distinct subfractions of alkyl biphenyls and alkyl naphthalenes for subsequent characterization by capillary GC.

b. Heterocyclic Compounds

Normal-phase charge-transfer HPLC was used for the determination of ppm amounts of azaarenes (aniline, quinoline, pyridine, and isoquinoline) in gasoline, kerosene, and diesel.[157] An on-line preconcentration (on a small precolumn packed with DNAP-silica or 3-(2,4 dinitrobenzenesulfonamido)-propyl (DNSP) -silica before the HPLC analysis (using either DNAP-silica or, DNSP-silica column, and dichloromethane as solvent) allowed the detection of pyridine down to 50 ppb by a UV detector. Nitrogen bases (azaarenes) from a crude oil obtained by a selective extraction procedure were separated by reversed-phase HPLC for their identification by offline GC-MS.[158]

Petroleum carbazoles were separated by normal-phase HPLC on silica gel for their subsequent fractionation based on carbon number using a C_{18}- reversed-phase column and acetonitrile-water mobile phase.[159] Each of C_1- through C_4-carbazole subfractions was then fractionated into positional isomers by HPLC on silica gel with hexane/Et_3N/isopropanol as the mobile phase.

HPLC-MS was used in the single ion monitoring mode for rapid (7 min) determination of dibenzothiophene in coal liquids and crude oils. For this, M^+ with m/z 184, and $(M-32)^+$ with m/z 152 were monitored.[160]

c. Gasoline and Diesel Additives

Reversed-phase HPLC with 5 μm octadecyl silica (ODS) column, acetonitrile-water as mobile phase, and RI detector was used to quantitatively determine benzene and toluene, and oxygenates such as ethanol, methyl-*t*-butylether (MTBE), ethyl-*t*-butylether, and *t*-amyl-methylether in gasoline.[161] After elution of these target compounds, gasoline peaks were backflushed to waste in order to shorten analysis time to about 10 min. Relative standard deviations were reported to be 1 to 2% for gasolines containing 0.5 to 10% MTBE.

The color marker Solvent Yellow 124, *N*-ethyl-*N*[2-(1-isobutoxyethoxy)ethyl](4-phenylazophenyl) amine was analyzed in diesel fuels on a 5 μm C_{18} -reversed-phase column, and determined in the visible at 420 nm.[162] Elution was carried out with acetonitrile-ammonium acetate buffer containing dimethyloctylamine. Other compounds such as phenalenones, their methyl homologues, and related benzanthrones, were also determined in middle distillates using conventional reversed-phase, column, hexane-chloroform mobile phase and UV-visible detector at 400 nm.[163] Cetane improver additives (amyl-, hexyl-, and octyl-nitrate) were determined in diesel fuel by HPLC as an alternative to the ASTM D1389 colorimetric method.[164] For this, three 10 μm-silica gel columns in series, cyclohexane-CCl_4 (1:1) as mobile phase, and a variable wavelength infrared detector were used.

d. Lubricant Additives

HPLC has been applied to the analysis of lubricating oil additives such as antioxidants and antiwear agents, ashless dispersants, and viscosity improvers.[118,165] They have been separated using both normal-phase and reversed-phase columns and quantified using UV, RI, and ELSD.

C. Preparative HPLC

The separation mechanisms, solvents, column types, and typical run times of preparative or semipreparative HPLC are similar to those of analytical HPLC of fossil fuel-derived samples. However, these techniques do differ, primarily in sample loading, column size, particle size of the column packing, and flow rate. Preparative HPLC columns are much larger in size to allow larger sample loading (of few tenths of a gram or more) in each run. The preparative column packing materials may have larger particles than those in an analytical column. While a flow-rate of about 2 mL/min is common for analytical separations, those for semipreparative or preparative HPLC can be 20 mL/min or higher.

Preparative separation has often been carried out for gravimetric determination of hydrocarbon types after removal of solvent(s) from collected fractions. This has also been useful for obtaining sample fractions for the characterization of individual compounds or functionalities. For the latter, fractions are usually subjected to off-line or on-line analysis by high-resolution chromatographic and spectroscopic methods. For complex petroleum- or coal-derived samples, cleanup of the original sample is often desired prior to preparative separation.

Examples of preparative HPLC separations are given in Table 3. Although these cover a broad range of materials, we note that they represent only a small fraction of studies reported in the literature. As noted in Table 3, almost all analytical separations of complex petrochemical samples involve some sort of preparative separation by OCLC, HPLC, or other means.

D. HPLC Detectors

The following provides highlights of different HPLC detectors. The discussion addresses advantages, limitations, and applications of each detector.

1. Spectroscopic Detectors

a. UV-Visible Detector

UV-Vis detectors are suitable for aromatics and polars, but they are unable to detect saturates under the conditions used in conventional HPLC detection. Further, responses of compounds are strongly dependent on their chemical structures. The UV response at specific wavelength varies with the numbers of rings as well as with the isomeric compounds having the same number of rings.

In general, detection and quantitation of individual sample components require sample preparation and cleanup. There have been attempts to use the UV-Vis detector for the determination of target components in complex petrochemical samples without an elaborate sample preparation and cleanup.[148] HPLC with a diode-array detector was used for the detection of PAHs and alkylated PAHs in coal liquids. Simpler chromatograms were obtained (as maxiplots) to view all components eluting at maximum absorbances across the UV range.

Recently, an HPLC system has been developed to quantify hydrocarbon types and aromaticity distributions in heavy oils using combined DAD and ELSD.[149] The DAD response factors for aromaticity have been based on average values determined from the 204 to 430-nm spectra of over 80 model compounds. Therefore, absorbance of each peak has been integrated over this wavelength range. Aromaticity results were validated with ^{13}C-NMR. A quantitative hydrocarbon-type determination was carried out using a procedure for wide-range calibration of ELSD. The use of average response factors for aromatics is based on a previous work by Lafleur et al.,[180] who found a narrow distribution of normalized response factors for 16 polycyclic aromatic hydrocarbons when a UV absorption bandwidth between 200 and 400 nm was utilized.

For the detection of metal porphyrins, UV detection was applied using wavelengths between 400 nm and 410 nm.[181-184] The wavelengths of 553 nm and 573 nm were also used as α-bands for Ni(II) and VO(II) petroporphyrins, respectively.[181]

A UV detector at 260 nm was used to detect and determine cobalt, copper, iron and vanadium as their *bis* (acetylpivalylmethane) ethylenediamine complexes. There was excellent agreement between the HPLC data and those obtained by atomic absorption spectrometry for metals.[185]

b. Fluorescence Detector

Fluorescence detectors were mostly used for the determination of PAHs.[154,157] For an example, PAHs in coal-tar pitch binder were determined using HPLC-fluorescence detector, and the results were compared with those obtained by HPLC-particle beam MS detector.[186]

c. Infrared Detector

IR detector is useful for selective monitoring of functional groups. Infrared detection with variable wavelength was used for quantifying alkyl nitrates in diesel fuels (using the NO_2 stretch absorption band) in order to overcome the problem of UV-absorbing components in the sample.[164]

TABLE 3
Typical Preparative HPLC Separations

Sample/ distillate	Target compounds/ fractions	Prior cleanup step(s)	HPLC conditions	Subsequent analyses	Reference
Shale oil	Class separation: alkanes/alkenes, aromatics and polars	Dissolution in hexane and filtration	Cyano column; hexane-t-BuOH gradient as solvent	Fractions analyzed by capillary GC and HPLC on C_{18} column	166
Crude oil	Monoalkylated PAHs	OCLC on florisil to remove asphaltenes and resins	Aminosilane column-n-heptane; C_{18}-column-MeOH-water.	Shpol'skii effect fluorescence spectroscopy	167
Crude oil, and coal and rock extracts	Aromatic ring classes	--	Alumina column; hexane-CH_2Cl_2 as solvent	GC-FID of subfractions; GC-MS for peak identification	168
Crude oil	Dibenzothiophene	--	Aminosilane column; 1% CH_2Cl_2 in hexane as solvent	GC-SCD for dibenzo-thiophene fraction	169
Crude oil and petroleum distillate	Carboxylic acids	--	Silica column; solvents: hexane, chloroform and MeOH with $(CH_3)_4NOH$	IR and capillary column GC on fractions.	170
Heavy Distillate (370-535 °C)	Nitrogen compounds: pyridines, pyrroles and amides	OCLC with anion- and cation- exchange resins, and clay with ferric chloride	Neutral alumina column; cyclohexane and CH_2Cl_2 gradient as solvent	Nitrogen compounds identified by GC-MS	171
Lubricant base stocks	Parent and alkylated PAHs; sulfur compounds	HPLC with silica column to separate saturates from aromatics	Prep. amine column to separate aromatics based on no. of rings	GC-MS and GC-FID on HPLC fractions	172
Vacuum resid	Class separation: saturates, aromatics and resins	Asphaltenes were separated from vacuum resid using n-hexane	Silica and cyano columns; solvents: cyclopentane, chloroform and methanol	Elemental analysis of collected fractions.	173

Sample/ distillate	Target compounds/ fractions	Prior cleanup step(s)	HPLC conditions	Subsequent analyses	Reference
Coal tar (200-500 °C)	PAHs, basic and neutral nitro-PAHs, and hydroxylated PAHs	Extraction and OCLC on silica/HCl	Amino column; solvent: cyclohexane- CH_2Cl_2	MS, GC-MS, IR, NMR on fractions	33,34
Coal liquid and shale oil	Class separation: aliphatics and aromatics	Liquid-liquid extraction to remove phenolics	Silica column; solvent: 1,1,2-trichlorotrifluoroethane and chloroform	GC-MS for compositional information	174
Coal liquid	Class separation: aliphatic, and non-polar, acidic and basic aroms.	Dissolution in hexane and filtration	Amino column modified with H_3PO_4; hexane-iPrOH-acetic acid gradient	GC-FID and GC-NPD on subfractions	175
Petroleum resid	V- and Ni - porphyrins	Ion exchange LC; HPLC on pyridyl column to fractionate neutrals and acids	Silica column for final HPLC separation	--	176
Solvent refined coal liquid	Carbazoles and acridines	OCLC on silica with cyclohexane and CH_2Cl_2 eluants	Amino column; solvent: hexane -MTBE	GC-MS, GC-NPD and LC-GC-FID on fractions	177
Crude oil (API gravity 28-38)	Class separation: saturates, aromatics and polars	--	Amino column; solvent: hexane	Samples were analyzed by the ASTM D2007 method to compare HPLC data	108
Vacuum gas oil	Sulfur compounds in non-polar fraction	OCLC on alumina; ligand exchange chromatography on silica/ $PdCl_2$	Silica column; solvent: hexane	GC-FID and GC-FPD; GC-MS for peak identification	104,178
Heavy gas oil	Class separation: saturates, mono-, di-, and polyaromatics, resins	--	Silica and alumina columns; solvents: petroleum ether, CH_2Cl_2 and MeOH	On-line synchronous fluorescence spectrometry; GC-MS for group type analysis	179

2. Bulk Property Detectors

a. Refractive Index Detector

RI detectors have been used quite extensively for hydrocarbon-type determinations. Although an RI detector is considered universal and it gives a lower variation in responses than a UV detector for aromatics and polars, it presents several major disadvantages. An RI detector is incompatible with elution gradients often necessary in normal-phase HPLC of petrochemicals. Although accurate determination of aromatics is possible using external calibration as in the IP 391 method, the estimation of saturates is problematic because of the large variation in refractive indices for different saturates and the small difference between the refractive indices of saturates and that of the mobile phase such as *n*-hexane. If the determination of experimental response factor for a hydrocarbon group is necessary, this is done by a preparative separation and collection of the hydrocarbon type followed by analytical separation and RI detection of the collected fraction.

A new approach for the hydrocarbon-type determination involves the use of HPLC experiments with RI in two different mobile phases of varying refractive indices (such as hexane and nonane). The method is based on the premise that there is a linear relationship between measured refractive index and detector response (in terms of peak area per unit volume of the analyte).[139] The novelty of this approach lies in the fact that unlike any conventional approach (such as the IP 391 method), no external calibration is needed.

b. Evaporative Light-Scattering Detector

ELSD offers practical advantages over RI with respect to more rapid stabilization, higher linear interval,[187] and better sensitivity.[187,188] An ELSD also allows the use of gradient elution.[149,150] ELSD is suitable for the detection of individual components boiling above ~315ºC. Thus, many small, volatile PAHs such as methylnaphthalenes (~ b.p. 240ºC), acenaphthene (b.p. 279ºC), and fluorene (b.p. 298ºC) present in coal and petroleum products are not detected even under mild working conditions. However, recent results[189] obtained using modern ELSD technology demonstrate that a variety of small-sized PAHs (from 3 to 6 rings) can be determined quantitatively using adequate conditions (such as evaporation temperature: 30ºC, and mobile phase: tetrahydrofuran) without significant loss due to volatilization. ELSD working parameters (nebulization parameters, evaporation temperature, and chromatographic conditions) can also be optimized to obtain, in some cases, nearly uniform response for different compounds. However, this may not be valid for all applications because ELSD responses were found to depend in part on other factors, including solute densities.[189-192]

Usually, ELSD provides a nonlinear relationship between mass and signal. The signal can be linearized using a power-law model such as $c = m\, s^b$, where c and s are mass and signal, and m and b are proportionality constant and power-law exponent, respectively.

ELSD has been applied to evaluate the heaviest part of heavy coal and petroleum products,[193-197] although many of these applications involved size-exclusion chromatography. Hydrocarbon-type determinations[147] and simulated distillation[150] have been carried out using ELSD either with isocratic elution or with eluant gradients, and as a single detector or in combination with other detectors.

c. Dielectric Constant Detector

DCDs have been used for hydrocarbon-type determination.[117,133-136] For instance, DCD was employed for hydrocarbon type analysis of light distillates[134] and lubricant oils.[117] It was found that the use of an eluant with a relatively high dielectric constant (such as halogen containing solvents) provides uniform detector response.[134]

d. Flame-Ionization Detector

HPLC with FID is highly desired for the analysis of fossil fuels because of the nearly universal response and supposedly similar responses from different classes of compounds.

However, its applications with HPLC have been limited because of the lack of effective interface to remove the solvent and to transfer the sample to the detection system. A rotating disk FID was coupled to HPLC to analyze samples boiling above 340°C to obtain hydrocarbon type data.[198] Attempts were made for coupling FID to HPLC using moving wire and belt interfaces.[199] This presented technical problems, primarily from variation of responses due to a nonuniform deposition of the effluent. Another design that uses a thermospray (TSP) interface,[117] was applied for the determination of total aromatic contents in lube base stocks.

HPLC-FID with coupled aminocyanosilane and cyano columns, and mixtures of benzene in hexane, and tetrahydrofuran in MTBE as mobile phases, was used to obtain saturates, aromatic and polars in coal liquids.[200] The data provided trends in the product compositions with the changes in liquefaction temperature and coal rank.

3. Mass Spectrometric Detector

MS detectors, using different HPLC-MS interfaces, have been used, although their applications appear to be limited to a more in-depth characterization of separated fractions and to the identification of individual compounds. HPLC-MS has also been applied for hydrocarbon-type analysis,[201-204] providing some qualitative information concerning the fractions separated by HPLC. For example, it facilitates the differentiation of alkylaromatics from naphthenoaromatics, or between aromatic hydrocarbons and thiophenes. Relative abundances of different groups can also be obtained.

HPLC-MS hydrocarbon-type analysis of a relatively heavy petroleum distillate was carried out using a thermal desorption-based moving-belt interface, which allows conventional high- and low-voltage electron impact (EI) as well as chemical ionization (CI).[201] However, this technique was unable to analyze highly nonvolatile species, which either do not vaporize or undergo thermal decomposition. TSP was reported to be useful for nonvolatile, thermally labile molecules.[203] This is essentially a CI technique in which the solvent vapor acts as a reagent gas. For a heavy petroleum sample (boiling above 565°C), TSP selectively ionizes aromatic hydrocarbons by protonation, leaving saturated hydrocarbons largely unionized. HPLC-field ionization MS was used to carry out molecular speciation of saturated hydrocarbons in lubricant base stocks and to quantify naphthenes, normal paraffins, and isoparaffins.[205] A DNAP silica column was used for the separation of saturates from aromatics and polars.

HPLC-MS using an atmospheric pressure chemical ionization interface (APCI) was used to characterize vanadyl porphyrins fraction of a shale oil. More than 50 porphyrin components were observed.[206]

4. Miscellaneous HPLC Detectors

a. Element-Specific Detectors

Graphite furnace atomic absorption detector[183,207,208] and inductively-coupled plasma atomic emission detector (ICP-AES)[167,209] were coupled with HPLC for speciation of metal-containing species such as metal porphyrins.[183,207,208] Normally, petroporphyrins are extracted and purified by Soxhlet or other means, including OPLC, prior to HPLC separation.[183] HPLC-ICP-AES with a direct injection nebulizer was used for simultaneous element speciation of process streams, shale oil, solvent refined coal, and crude oil.[209]

b. Electrochemical Detector

Electrochemical detection (by Ce^{IV} oxidation of PAHs to quinones) has been used for determining PAHs in different distillates.[210] This was also used for the detection of electroactive compounds such as phenols.[124,125]

V. SUPERCRITICAL FLUID CHROMATOGRAPHY AND EXTRACTION

As an analytical technique, SFC is complementary to both GC and HPLC. SFC can be applied to materials that are too heavy to meet volatility and thermal stability requirements for GC. Above the critical point, density and solvating power of a gas approach those of a liquid, but viscosity and diffusivity remain similar to a gas. The combination of both gas-like and liquid-like properties of a supercritical fluid enables the elution of high-molecular-weight materials and faster solute transport within the column. This also results in shorter analysis time for SFC than that for HPLC. Although separating power of GC, in most cases, is far superior to SFC, the resolution achievable by SFC is comparable to or better than that by HPLC.

Commercial SFC instruments offer flexibility for optimization of separation conditions. These are equipped with hardware and software that allow automated sample injection, and programming of temperature, fluid pressure or density, flow-rate, and composition of mobile phase. Packed (2.0 to 4.6 mm i.d.), microbore (100 to 1000 μm i.d.), and capillary columns (< 100 μm i.d.) are used in SFC.[211,212] Many standard normal-phase and reversed-phase HPLC columns have been found suitable for SFC. Small-diameter fused-silica columns have been used extensively. Virtually all GC and LC detectors have been interfaced with SFC. These include flame-ionization detector, UV/Vis detector, fluorescence detector, mass-spectrometry detector, infrared detector, nuclear magnetic resonance detector, thermionic detector, flame-photometric detector, sulfur chemiluminescence detector, and atomic emission detector.[213-215]

SFC has been applied extensively to four major areas: hydrocarbon-type analysis, simulated distillation, analysis of polycyclic aromatic hydrocarbons, and compound class fractionation using supercritical fluid extraction (SFE). The reasons for the inclusion of SFE are given in subsection D. In a majority of petrochemical applications of SFC, supercritical CO_2 has been used as the mobile phase. The supercritical fluid state of CO_2 can be maintained easily because its critical temperature and pressure are 31.3°C and 72.8 atm, respectively.

A. Hydrocarbon-Type Analysis

1. Light Distillates: Gasoline and Naphtha

Light distillates may contain olefins in addition to saturates and aromatics. Aromatics are usually limited to one- and two-ring compounds. In 1984, Norris and Rawdon[216] demonstrated that hydrocarbon-type analysis can be carried out by supercritical fluid chromatography using CO_2 as the mobile phase, standard (25 cm X 0.46 cm) HPLC columns, and a flame-ionization detector. Silica and silver nitrate-impregnated silica columns in series were used to achieve sequential elution of saturates, olefins, and aromatics present in petroleum liquids boiling below 350°C. The analysis time was less than 5 min with supercritical CO_2 flow-rate of 3 mL/min at 35°C and 210 atm. The results for gasoline, kerosene, diesel, shale oil, and coal-derived liquid samples were reported. For validation, SFC data were compared with those obtained by the fluorescent indicator adsorption method.[94] The SFC and FIA hydrocarbon-type data were found to be in reasonable agreement.

Other early developments in the SFC separation of paraffins, olefins, and aromatics include the use of a single microbore silica column, SF_6 as the mobile phase, and pressure and temperature programming.[127,217] Similar hydrocarbon type separation was achieved when a microbore (25 cm X 0.1 cm) silica column and a silver ion loaded cation-exchange silica column were used with a mixed mobile phase of 10% CO_2 in SF_6.[218] The silica column was used to retain aromatics, while saturates and olefins were separated in the silver-loaded column. After the elution of saturates from the silver-loaded column, both olefins and aromatics were backflushed from the silver loaded silica and silica column, respectively. In other studies involving column switching and backflushing, neat CO_2 was used as the mobile phase.[219-221] In one of these studies,[221] four silica columns in series and a silver ion cation-exchange column were used to obtain sequential elution of paraffins, naphthenes, aromatics, and olefins present in gasoline and jet fuel samples.

Currently, few laboratories are applying SFC for the routine hydrocarbon type analysis of gasoline range samples. This is usually carried out by GC methods. For the most part, capillary GC is used to obtain much superior resolution of individual compounds for their identification as well as hydrocarbon type determination.[3,12] Multidimensional GC utilizing a number of columns and traps (having high selectivity for individual group type) provides hydrocarbon type data as well as carbon number distributions.[24,28,222]

2. Middle Distillates: Diesel, Jet Fuel, and Kerosene

The ASTM 5186 method has been in use for the determination of monoaromatics and polycyclic aromatic hydrocarbons in diesel and jet fuels by SFC coupled with FID.[223] According to this method, relatively mild conditions are required to achieve the separation of aromatics from nonaromatics (saturates plus olefins). Typical operating conditions with packed silica columns are as follows: oven temperature 30 to 40°C, CO_2 pressure 115 to 200 atm and flow-rate 20 to 40 mL/min (of the decompressed fluid). Besides round robin testing by many laboratories, the validation efforts for this method include examination of the effects of temperature and pressure, evaluation of relative response factors of different group types, and comparison of SFC-FID data with those obtained by FIA and nuclear magnetic resonance spectrometry (NMR).[224-226]

An incomplete resolution between saturates and one-ring aromatics, and tailing peaks associated with incomplete separation of one-ring aromatics from polycyclic aromatic hydrocarbons, contribute uncertainties to the quantitative data obtained by SFC. Optimization studies show that a low oven temperature (<40°C) provides the best separation between saturates and aromatics at the expense of the aromatic-type separation.[227-229] The resolution between saturates and aromatics decreases slightly as the pressure is increased.[229] Column properties such as packing material and pore size also affect resolution between saturates and aromatics.[229] For low aromatic fuels, pressure programming was proposed to compress the peaks for aromatics.[230] Aromatics were also backflushed to obtain sharp peaks.[213] The enhanced sensitivity of a UV detector for the aromatics was exploited to determine the midpoint between saturates and aromatics when SFC analysis of diesel fuels was carried out using dual UV and FID detectors.[213]

Recently, it was shown that accuracy, repeatability, and detector linearity for the hydrocarbon-type analysis of diesel and jet fuels by SFC is vastly improved with optimized detector gas flows (H_2 at 90 mL/min and air at 600 mL/min) and detector temperature (350°C). The precision was also improved when the pump pressure transducer was temperature controlled.[231] An optimization study of hydrocarbon-type analysis was also carried out by examining retention behavior of test compounds by varying separation temperature and pressure.[232]

3. Heavy Distillates: Crude Oil, Gas Oil, and Residuum

There are a few hydrocarbon-type studies on heavy distillates and residua with boiling points greater than 350°C,[233] crude oil,[234] and gas oil[235,236] by SFC-FID. Hydrocarbon type analysis of heavy distillates by SFC has been carried out in the same manner as in the case of HPLC. The separation of saturates, aromatics, and polars in heavy residua was achieved by a three-column system (cyano, silica, and silver-impregnated silica) equipped with column switching and backflushing using supercritical CO_2 as the mobile phase.[233] The sample was injected after diluting 1:1 with CS_2. The cyano column was used to trap polars. The separation of saturates and aromatics was achieved on silica and silver-impregnated silica in series. After the sequential elution of saturates and aromatics, the trapped polars are backflushed from the cyano column. The hydrocarbon-type data obtained by SFC were in good agreement with those obtained by gravimetric determination after separation by normal-phase HPLC.[237] A similar procedure was followed for the separation of saturates, aromatics, and resins from crude oils.[234]

Separation of nonaromatics and aromatic hydrocarbons in gas oil was carried out with and without backflushing of aromatics.[235] The backflush time was determined graphically by plotting the percent peak areas of aromatics and nonaromatics against backflush time. The three gas oils characterized by SFC had aromatic contents in the range of 25 to 75%. Results for normal-elution SFC, SFC with backflushing of aromatics, and HPLC were found to be consistent with each other. However, SFC-FID with backflushing provided sharper peaks for both nonaromatics and aromatics.

B. Simulated Distillation by SFC

Simulated distillation by SFC-FID was carried out to cover a broader boiling point range than can be achieved by the widely used standard GC-FID simulated distillation method ASTM D2887.[238] The ASTM D2887 method accommodates boiling point distributions up to 538°C. In this respect, SFC-FID is an alternative to high-temperature simulated distillation that allows the elution of high boiling petroleum fractions and asphalt with atmospheric equivalent boiling points up to 800°C.[37,40,41,239-241] Column temperature of 150°C or less is required to achieve measurements of boiling range distributions by SFC-FID.[242-244] As relatively mild conditions are used, the SFC-FID method is advantageous over the GC-FID approach where a column temperature of 430°C or higher is required to elute high boiling petroleum components. Such high temperatures are believed to be detrimental to the column life, and, to some extent, to the thermal integrity of the samples.

Capillary columns,[240,242-245] short packed microbore columns,[246] and packed capillary columns with alkyl bonded silica phase [247] were used for simulated distillation by SFC-FID. The column temperatures can be within the range of 70 to 150°C depending on the sample. Usually, linear pressure programming, such as 100 to 415 atm at 3.5 atm/min, was found to be adequate to achieve good resolution between adjacent homologues.[247] Under these conditions, the elution and separation of hydrocarbons with carbon numbers from C_{20} to C_{130} can be achieved.

As in simulated distillation by GC-FID, a series of normal paraffins and/or polywax sample are used to obtain a boiling point vs. retention time calibration curve. This calibration curve is then used to determine boiling point distribution. In general, the SFC-FID simulated distillation data have been found to be in good agreement with high-temperature GC-FID data.

In GC-FID, an inert gas (such as nitrogen or helium) is used as the mobile phase. In contrast, the supercritical fluid is an active participant in the solute elution process in SFC. A potential problem is that the sample solubility in the mobile phase is a dominant factor in SFC-FID compared with solute volatility in GC-FID. Moreover, as in GC-FID, there are uncertainties arising from different retention behavior of aromatic compounds from n-alkanes of similar boiling points. Significant deviations between true boiling points and apparent boiling points determined by SFC-FID are expected if the sample contains large amounts of aromatics.

C. Analysis of Polycyclic Aromatic Hydrocarbons

SFC has been applied for the determination of PAHs, particularly in coal-derived oils and liquids.[248,249] As in GC and HPLC, the elution of PAHs occurs according to the number of aromatic rings.[250] SFC was shown to provide the separation of 16 "priority" PAHs in 6 to 7 min.[251,252] As an example of a real-world sample, a complex coal liquid was fractionated and collected according to the number of aromatic rings with supercritical CO_2 from an amine column.[249]

Small-diameter fused-silica capillary columns (with cross-linked polysiloxane stationary phases) were used to take advantage of their high resolving power and adaptability to solvents such as pentane. In addition to FID, UV, and fluorescence detectors were used to detect many high-molecular-weight PAHs.[248,249] Capillary columns with smectic liquid crystalline stationary phases were found to provide better resolution of high-molecular-weight PAH isomers.[253] SFC on five standard (25 cm X 0.46 cm) polymeric C_{18}-columns in series, and with CO_2 as the mobile phase and acetonitrile as the modifier, was used to separate and determine PAHs from complex mixtures.[254] Like reversed-phase HPLC, a polymeric stationary phase was shown to provide better shape selectivity than the monomeric C_{18}-phase.[254] Such shape recognition was found to increase with a decrease in column temperature, an increase in the modifier (acetonitrile) concentration, and an increase in fluid pressure.

A molecular theory based on a lattice-fluid model was developed to predict and verify the dependence of SFC retention of PAHs on a number of molecular and experimental parameters.[255-258] SFC retention was correlated with minimum cross-sectional area (A_{min}) or effective contact area (A_{ef}) of PAHs. As predicted, it was observed that there is a linear decrease of ln k′ (where k′ is the capacity factor) with A_{min} for SFC retention data of isomeric PAHs obtained with columns containing polymeric smectic and other anisotropic phases.[255,256] Although ln k' from an isotropic stationary phase is roughly linear with A_{ef} for solutes with different number of rings, a column with such a phase has not shown a shape selectivity for isomeric PAHs.[257] The selectivity enhancement of planar isomers, ln (SE), due to an anisotropic stationary phase relative to an isotropic stationary phase, was also found to decrease with A_{min}. According to the theory, other important variables that affect solute retention and selectivity are column temperature (ln k′ or ln (SE) is a linear function of the reciprocal temperature in K), and mobile phase density (ln k′ decreases with mobile phase density).

D. Compound Class Fractionation by Supercritical Fluid Extraction

SFE has been applied widely as a viable sample preparation technique prior to chemical analysis. SFE allows selective extraction of specific classes of compounds using appropriate experimental conditions. As composition variations of the extract can be obtained with the choice of experimental parameters, SFE appears to be more like a chromatographic technique than an extraction method such as accelerated solvent extraction,[259] Soxhlet, microwave, or ultrasound method.

In SFE, the supercritical fluid is pumped to an extraction vessel where the analytes are extracted from a sample matrix to be swept through a flow restrictor into a collector. There are numerous analytical SFE applications involving fossil fuels, environmental samples, pharmaceutical samples, polymers, natural products, foods and fragrances, and pesticides and herbicides.[214,260,261] However, here the discussion of SFE is limited to fossil fuels and environmental samples related to fossil fuels.

The SFE techniques offer advantages such as the use of a safe solvent (supercritical CO_2), reduced usage of organic solvents, high sample throughput, and fewer sample concentration and cleanup steps. Moreover, recent introduction of user-friendly analytical SFE instruments have made the sample handling and optimization for sample extraction easier. The on-line coupling of SFE with chromatographic and spectroscopic techniques has been carried out successfully with many SFE applications.

There are a number of important variables in SFE that influence both recovery and yield of the analytes. These include extracting fluid, extraction pressure, temperature, fluid volume, cosolvent, flow-rate, restrictor temperature, and sample collection.

1. Fossil Fuels

The major SFE applications for fossil fuels include the determination of extractable materials in coal,[262-264] crude oil,[265] high boiling residuum,[265-268] and geological samples such as source rocks,[269-271] shale oil,[272] and tar sand.[273] Toluene was used as the primary solvent for the extraction of high boiling materials from coal. Extraction temperature and cosolvent have significant effects on the yield and composition of the extracted materials. The proportion of lighter components in the extract was found to increase with increasing temperature and with the addition of a cosolvent such as 5 mol% ethanol. The opposite trend was found with increasing solvent density at constant temperature.[262] Various other solvents have been used for the SFE of coal, and the potential roles of these solvents (which include ethanol, toluene, pyridine, toluene-tetralin mixture, and water) in SFE of coal have been discussed elsewhere.[263]

Supercritical propane was used for the separation of deasphalted oil and carbon-precursor pitch from heavy petroleum residua.[268] Supercritical *n*-pentane was used as the solvent for the extraction of narrow fractions from a petroleum residue as a function of pressure. There are differences in the molecular weight, elemental (C, N, S, etc.) composition, and SARA of each fraction.[266] Dynamic supercritical fluid extractions of crude oil and vacuum residuum were carried out with supercritical CO_2 and propane, respectively. Extraction efficiency and composition variations of the extracts were examined as a function of fluid pressure and temperature.[265]

SFE studies of geological samples involve the determination of biomarkers.[269-271] SFE was carried out with supercritical fluid CO_2 by varying temperature (up to 350°C). It was reported that SFE provided greater yields of biomarkers with a shorter analysis time than conventional Soxhlet extraction.[269,270] A three-step extraction of petroleum source rocks was carried out using neat CO_2, tetrahydrofuran-modified CO_2, and, finally, 2-propanol-modified CO_2 and CS_2. It was found that the first extract was dominated by saturates, the second by aromatics, and the third by N-, S-, and O-containing compounds.[271]

2. Environmental Samples

Environmental samples such as soil, sediment, fly ash, and air and diesel particulates have been subjected to SFE to determine total petroleum hydrocarbons, PAHs, or polychlorinated biphenyls (PCBs) and other toxins. SFE has been demonstrated to provide better quantitative recoveries in a shorter time (1 h or less) than those obtained with several hours of liquid solvent extraction by either Soxhlet apparatus or sonication.[261,274-283]

Soil samples contaminated with heavy fuel oil, diesel, light crude oil, gasoline, or kerosene spills were extracted by SFE for total petroleum hydrocarbons and their determination by IR or GC-FID. The results were compared with those from Soxhlet extraction using Freon-113.[277] SFE parameters such as pressure, temperature, extraction time, and collection solvent were evaluated. Total petroleum hydrocarbons obtained by SFE using supercritical fluid CO_2 at 340 atm and 80°C were found to be in good agreement with those obtained by the standard Freon-113 Soxhlet method.[276] (The conditions recommended in Reference 276 have been incorporated in the draft EPA method 3560/8440.) Heavy petroleum hydrocarbons from soil were shown to be best extracted using a static modifier (such as dichloromethane) and temperatures up to 150°C.[279] However, lighter hydrocarbons, specifically, those in gasoline and diesel range samples, required lower temperatures.[284]

The SFE of PAHs from soil and other matrices shows significant variations in the yields and recoveries depending on SFE conditions and specific PAH molecules. The accurate determination of PAHs from these matrices was found to be more problematic because spike recovery data of deuterated PAHs showed significant differences in recoveries of spiked analytes from the native compounds.[285] Although SFE studies for the determination of PAHs were carried out, and the results from these studies were validated against those from conventional Soxhlet extraction and sonication techniques,[278,282] efforts are still underway to find optimum SFE conditions for the extraction of PAHs from various matrices.[286-289] In general, SFE efficiency is improved when supercritical CO_2 is used with a modifier such as toluene,[278,286] methanol,[286,290] or chlorobenzene.[287] SFE at an elevated temperature of 200°C or higher was also shown to be effective for the extraction of PAHs, chlorinated phenols and other environmental samples.[291] A moderate temperature (100°C) and higher pressure (≥450 atm) were found to provide better recoveries of PAHs containing four or more aromatic rings.[287] Supercritical argon was also used to extract petroleum hydrocarbons from the soil.[292] The highest recovery of hydrocarbons was obtained from argon SFE at 500 atm and 150°C.

The recovery of PAHs from environmental samples may not always be quantitative as exemplified in a study of four natural matrix standard reference materials from the National Institute of

Standards and Technology (NIST): SRM 1649a (urban dust/organics), SRM 1650 (diesel particulate matter), SRM 1941a (organics in marine sediment), and SRM 1944 (New York harbor sediment). PAH recovery was measured by varying extraction fluid, fluid modifier, temperature, and addition of water. Variable levels of recovery depending on PAHs and sample matrix were reported.[289]

PCBs and other polychlorinated toxins (such as polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) were extracted from matrices like soil, sediment, and fly ash.[283, 293-298] SFE for the determination of organochlorine compounds compared favorably with Soxhlet extraction techniques.[282,294] A few optimization studies were carried out by changing parameters such as pressure, extraction time, restrictor type, and collection solvent,[293] temperature,[295,296] and modifiers.[297,298] Temperatures between 40 and 250°C were used. A modifier, such as methanol, dichloromethane or benzene, was usually needed with supercritical CO_2 in developing an effective method for the extraction of PCBs and organochlorine toxins.

VI. THIN-LAYER CHROMATOGRAPHY

TLC, or planar chromatography, has been demonstrated effectively for both qualitative and quantitative determination of various analytes, and for the preparative separation of components or component classes from numerous sample matrices.[299-303] There are many commercially available TLC stationary phases with great varieties of functionalities. There have been significant advances in instrumentation for automated or semiautomated operation, precise sample application, and chromatogram development utilizing either capillary or forced flow conditions. Besides many conventional chemical methods for visual spot detection, there are detectors for scanning TLC plates or specially designed TLC rods. The scope and limitations of TLC methods utilizing unidimensional, circular, and two-dimensional developments have also been investigated. Despite these developments, TLC has yet to become a major analytical technique in the petrochemical area. This technique may have been overshadowed by other chromatographic techniques such as GC, SFC, and HPLC for the analysis of various types of fuels and related samples.

A. TLC Sorbents, Solvents, and Detectors

Almost all coal and petrochemical applications of TLC involve either silica or alumina adsorbents.[304] Usually, the separation of compounds is based on their polarity and is achieved by developing TLC plates or rods with solvents of varying eluotropic strengths.

Many TLC applications involve preparative fractionation by planar chromatography, and qualitative analysis or quantitative hydrocarbon-type determination by planar chromatography with UV-fluorescence detection. In general, quantitative analysis using UV-Vis is carried out using TLC scanners in either absorbance or fluorescence mode.[305,306] For preparative and qualitative studies, colorless substances are detected under UV light if they show absorption in the UV region or if they can be excited to produce fluorescence by either short wave (254 nm) or long wave (365 nm) radiation. Various chromogenic or fluorogenic reagents have also been used.[301] Some of these reagents are selective for particular compound types to enable visual detection.

A large number of recent petrochemical studies involve quantitative hydrocarbon-type determination by TLC on thin rods coupled with flame-ionization detection (TLC-FID.[99,116,307-322] Advanced detection systems such as infrared spectroscopy[323-325] and laser desorption mass spectrometry[325,326] have also been applied.

Direct detection of analytes from the silica or alumina stationary phase by IR is almost impossible due to large background interferences in the IR region. The commonly used transfer TLC-FTIR involves extraction of analytes from the TLC plate with a solvent, and, subsequently, the transfer of the analytes to an IR-transparent pellet or powder for their detection.[323] However, *in situ* TLC-FTIR using zirconium oxide-packed microchannels as the TLC stationary phase was shown to provide higher IR reflectivity with minimal background interferences and a low detection limit.[324]

B. Planar Chromatography

Thin-layer chromatography using silica or alumina plates and appropriate solvents can be used to obtain quick class separation of base oils, crude oils, or coal liquids. This is usually carried out primarily for collection of sample fractions for further analysis by other analytical techniques, or for qualitative or semiquantitative analysis of compound classes.[327-331] In one example, planar chromatography on silica plates was used to fractionate coal tar pitches for subsequent characterization by SFC, UV-fluorescence emission spectroscopy, and mass spectrometry.[330]

There are few studies for the quantitative analysis of fossil fuel samples by planar chromatography using conventional TLC plates. For example, bitumen samples were analyzed by TLC with UV absorbance/fluorescence measurements.[332] For this analysis, the sample was spotted on a silica plate to be developed sequentially with *n*-heptane (8.5 cm), dichloromethane (4.5 cm), and tetrahydrofuran (2.5 cm). The plate was then scanned at 254 nm with a scan width of 1.5 cm in the UV absorption mode to determine aromatics and polars. The plate was subsequently dipped for a few seconds in a solution of berberine sulfate (0.004%) in methanol for the determination of saturates in the fluorescence mode using an excitation wavelength of 264 nm and a scan width of 1.5 cm. A similar methodology was applied by Cebolla et al. for quantitative hydrocarbon-type analysis of gas oils and heavy petroleum distillates.[331]

C. TLC with Flame-Ionization Detection

As mentioned above, rapid and direct determination of hydrocarbon types can be achieved by TLC with flame-ionization detection. In TLC-FID, thin reusable quartz rods (Chromarods), sintered with micrometer-sized silica or alumina particles, are used as the stationary phase. After spotting a few micrograms of the sample near the end of the silica layer, the Chromarods are developed sequentially with several solvents or their mixtures of decreasing or increasing eluotropic strengths to achieve the desired separation. The Chromarods are dried in an oven after each development at around 70°C for about 2 min. Finally, each Chromarod is scanned lengthwise with an oxygen-hydrogen flame for the detection of separated components.

It was found that in multistep Chromarod developments, the use of solvents of decreasing polarity is a preferred choice specifically for hydrocarbon-type analysis. This allows the separation of component classes with superior baseline, better resolution of the hydrocarbon classes, and polarity-based distribution of aromatics as well as polars.[99] For example, the Chromarods can be developed first with toluene for 5 min for the separation of saturates plus aromatics from polars. In the second development with an n-alkane (such as *n*-heptane) for 30 min, the polars are not displaced and the saturates are separated from aromatics. During this step, aromatics are also distributed broadly according to their polarity. The latter is due to an incremental displacement of aromatic components as their polarity decreases providing a distribution of aromatics according to the number of aromatic rings. If desired, polars can also be subdivided into two resin types by developing the Chromarods with 9:1 chloroform-methanol mixture for 3 min prior to Chromarod development with toluene.

Due to limitations in the design of the commercially available instruments, the TLC-FID method can only be quantitative for high boiling materials (with initial boiling points at or above 500°F). The low boiling materials present in a sample evaporate during Chromarod development and drying. Such evaporation might also occur when Chromarods are exposed to the flame during scanning of the adjacent Chromarod. Therefore, TLC-FID is especially suitable for lubricant base oils,[99] high boiling residua or fractions derived from crude oils,[116,307,317,319,320] oil shale bitumen,[312,313] or coal tar pitches.[310,318]

Quantitative results from TLC-FID may be obtained directly from the measurement and normalization of peak areas when components in different peaks have similar chemical backbones, as for saturates, aromatics, and polars in a lubricant base oil.[99] Unfortunately, this simple approach does not apply to samples containing varieties of chemical structures and with wide molecular size range. These samples include crude oils and various coal products. For such samples, an internal normalization approach was shown to provide data that are in good agreement with those obtained from an external standard calibration procedure.[321,322] This internal normalization procedure assumes a linear relationship (with a zero intercept) between the FID response of each peak and sample mass of the whole sample. The procedure requires TLC-FID screening of several sample masses to generate required calibration parameters for quantitation. For crude oils, a synthetic mixture of different crude oils was used as standard to obtain quantitative data.[317,319]

As TLC-FID offers baseline resolution between different hydrocarbon types in base oils and other heavy distillates, the technique was applied to examine the efficiency of the separation of hydrocarbon types by the ASTM D2007 clay-gel open-column chromatography method,[99,333] and to characterize polycyclic aromatics (PCAs) and non-PCAs obtained by the IP 346 liquid-liquid extraction method.[333] Different fractions obtained by these methods were subjected to TLC-FID analysis. It was found that the clay-gel method suffers adversely from cross-contamination of hydrocarbon types as well as from incomplete recovery of materials from the adsorbents. The latter is particularly critical for the gravimetric determination of polars by extraction from the clay adsorbent using 1:1 acetone-toluene mixture. Polycyclic aromatics fractionated by the IP 346 method were found to contain significant amount of non-PCAs and vice versa. Although contaminants in both PCAs and non-PCAs could offset each other in some cases, the bias was significant for samples with both low and high PCAs. It was found that PCAs are overestimated at low concentrations (<1.0% w/w PCAs) and underestimated at high concentrations (>4.0 % w/w PCAs).

VII. SIZE-EXCLUSION CHROMATOGRAPHY

Unless there are specific interactions between column packing and sample components, the molecular size or hydrodynamic volume relative to the average pore size of the column packing determines sample retention in SEC or gel permeation chromatography (GPC). The elution of molecules in SEC is bounded by limits representing total exclusion and total permeation through macroporous particles packed into an SEC column. In this method, the high-molecular-weight materials elute first followed by smaller molecules. This size-based separation of component molecules is the basis for the determination of molecular weight distribution by SEC.

SEC is a low-resolution technique. Although in some cases well-separated peaks can be observed, SEC chromatograms for fossil or fossil fuel-derived samples usually show broad and continuous elution profiles reflecting distribution of analytes based on molecular size. In general, SEC has been used to obtain molecular weight distributions of high-molecular-weight heavy ends of coal and petrochemical samples such as atmospheric or vacuum residua, polars, and asphaltenes derived from crude oil or coal liquid. The molecular weight (number-average M_n and weight-average M_w) distribution data are used to assess the quality and suitability of these products for processing, or to monitor changes during chemical processing or to evaluate fractions obtained by distillation or column liquid chromatography.

SEC has been applied to the analysis of lubricant base oils,[334-336] waxes,[337,338] crude oils,[339-344] heavy petroleum fractions, including residua,[340,341,345-351] asphalts,[352,353] coal fractions,[193,352,354-364] bitumens from tar sands,[365,366] and coal tar and petroleum pitches.[345,367]

A. SEC Columns, Mobile Phases, and Detectors

1. SEC Columns

Conventional SEC stationary phases consist of a three-dimensional network of polymeric chains of controlled porosity. Solvent compatibility, particle size, and pore size distributions of the packing material must be taken into account to design an SEC analysis. Until recently, to avoid swelling or shrinking of column bed due to solvent incompatibility, almost all SEC separations were carried out with a single solvent using an isocratic elution mode. At present, a few rigid gels allow the usage of multiple solvents either individually or in combination.

Usually, SEC analysis of fossil fuel-derived samples is carried out using a series of relatively small pore size (50 to 10,000 Å) polystyrene divinylbenzene columns. Polydivinylbenzene[368] and dextran-based Sephadex[369] are also popular packings in SEC. Columns with porous packing materials containing other functional groups such as diol-modified silica,[350] silica,[338] and poly(vinyl acetate)[354] were used. Controlled pore glass columns were also used.[360]

The particle size of SEC packings falls in the 5 to 30 μm range. Columns with 3 μm polystyrene divinylbenzene packing (that are capable of separating materials in the range of 200 Da to 30,000 Da) was shown to provide high-resolution separation of coal tar pitches.[362]

2. SEC Mobile Phases

An ideal mobile phase in SEC satisfies two important criteria: (1) the sample is completely soluble in the mobile phase, and (2) there is complete elution of sample from the column during each run. Thus, the selection of an appropriate solvent is very important to minimize self-association of sample molecules or their adsorption on the column. For example, either toluene[370] or *N*-methyl-2-pyrrolidone[362] was found to be superior to tetrahydrofuran to minimize association of high-molecular-weight coal-derived materials, whereas tetrahydrofuran was a better choice for the coal-derived asphaltenes.[370]

A variety of mobile phases have been used. The most common mobile phases are tetrahydrofuran,[342,349] toluene,[337,338] *N*-methyl-2-pyrrolidone,[357,361-364] chloroform,[335,339] pyridine,[340,356] and quinoline.[345] For some special applications, additives in the solvent have been helpful. For example, aqueous buffer solution or buffer solution plus a nonionic surfactant was used as mobile phase to carry out SEC separation of alkali-solubilized coal on controlled pore glass and on other SEC columns.[360]

3. SEC Detectors

The typical sample size for analytical SEC is 5 mg or less. Typical SEC analysis time can be 40 min or less. Almost all detectors used with HPLC can be coupled with SEC to detect sample components. The most common detectors are differential RI detector,[335-337,339,349,356] ESLD,[193,338,349] UV diode-array detector (UV-DAD),[335,342,344,349,362,363] and UV-fluorescence detector.[362,363] SEC coupled with atomic absorption[371] or emission such as inductively coupled plasma atomic emission (ICP-AES) or AED[340,343,366,372] detectors were applied to obtain elemental profiles (for Fe, Ni, V, or S) from fossil fuels. Rotating disk flame-ionization detectors were also used with SEC.[337,349] SEC with matrix-assisted laser desorption ionization (MALDI) mass spectrometry was applied to study molecular mass ranges in coal liquid samples.[361,364]

The ELSD was found to provide nearly uniform response for molecular weights above 300 Da.[193] The limitations of ELSD to lower-molecular-weight materials arise from possible evaporation of sample with solvent. Several studies dealing with multiple detectors detailed the advantages and limitations of other detectors (such as RI, UV-DAD, and FID) for various applications.[337,342,349,359]

Owing to the nonuniformity in detector response, quantification of a size zone in an SEC chromatogram can be quite difficult. An attempt to quantify the size zones of SEC chromatograms of coal tar pitches involved using 15,000 Da polystyrene as internal standard.[32] In this work, calibration was carried out using narrow fractions previously isolated from the pitches. Each coal tar pitch fraction was also subjected to vapor pressure osmometry for the determination of M_n and to SEC with RI detection for its response factor.

B. Molecular Weight Distributions by SEC

The maximum molecular weight of a coal or petrochemical sample can be 30,000 Da or higher. Usually, molecular weight distributions of fossil fuel samples are determined relative to narrow polystyrene standards. To cover low-molecular-weight ends, normal paraffins are used along with polystyrene samples. Molecular weight distributions of coal liquids against both polystyrene standards and narrow coal fractions were also obtained.[356,373,374] As mentioned above, the molecular weight of each narrow coal fraction (with $M_w/M_n \leq 1.1$) is usually determined by vapor pressure osmometry.

An overview of the complexity involved in the determination of molecular weight of coal liquids by SEC was given by Bartle.[248] Factors that affect the accuracy of molecular weight distributions, particularly in coal liquids, were also discussed.[370] These include nonuniform detector response with molecular weight and polarity of materials, self-association of molecules, and adsorption and partition of molecules on the column. Because of these limitations, the molecular weight distributions determined against polystyrene (and hydrocarbon) standards carry high degree of uncertainties. However, as both size and chemical effects dominate the elution process, effects of process variables can still be assessed qualitatively or semiquantitatively by monitoring SEC profiles or molecular weight distributions.

Although both RI and ELSD are used to obtain molecular weight distribution of the sample, UV detection can be used for similar distribution of specific compound type using a compound-specific wavelength. For example, the distribution of petroporphyrins in crude oil can be obtained by monitoring sample elution with a UV detector at around 400 nm.[342,365] Petroporphyrin distributions were obtained by SEC-graphite furnace atomic absorption spectrometry (GFAAS)[371] and SEC-ICP-AES detectors or AEDs.[343,366,372,373] Nickel, vanadium, or other metallic complexes or sulfur profiles were also provided by SEC-AED.[346-348,350,372]

C. Preparative SEC

SEC can be used as a sample cleanup technique to remove small molecules from high-molecular-weight materials or vice versa.[343] In addition to this, large SEC columns (with internal diameter 2.5 cm) were used to collect milligram quantities of subfractions with narrow molecular weight distribution.[349,373,375,376] As noted above, these subfractions can be used for SEC calibration[376] or can be subjected to further analysis by elemental, spectroscopic, and high-resolution chromatographic techniques.

D. Anomalous Component Elution in SEC and Other Non-Size Effects

Elemental sulfur has been found to elute beyond the total permeation limit as a narrow and symmetric peak.[377] Elution after the total permeation limit of SEC has also been observed with other types of compounds, including PAHs and molecules with ionic and polar nitrogen and sulfur groups.[378,379] However, these compounds were found to provide asymmetric peaks with significant tailing.

The unique elution behavior of elemental sulfur was the basis for the determination of elemental sulfur in hydrotreated cracked naphtha and gas oil samples.[377] The separation of elemental sulfur with an optimized resolution was achieved with a 10^3 Å polystyrene-divinylbenzene column and tetrahydrofuran as the mobile phase. Solubility values of elemental sulfur in solvents belonging to different hydrocarbon classes were also determined.

Non-size effects, on occasions are advantageous for particular analytical separations. SEC was able to separate pericondensed polycyclic aromatic hydrocarbons from an acid concentrate obtained by ion exchange chromatography of a 335 to 550°C petroleum distillate.[380] Most likely, specific interactions on the packing materials play a major role in allowing high-molecular-weight pericondensed ring systems to elute from the column later than low-molecular-weight pericondensed ring systems. The pericondensed aromatics are also eluted later than catacondensed aromatics of similar molecular weight. Using retention times of standard PAHs, four different elution ranges were defined: three of catacondensed compounds and one of pericondensed compounds. Thus, SEC was applied to distinguish between coal tar and petroleum pitches of different origin and nature.[367]

Some other examples of SEC separation exploiting non-size effects are as follows. Zinbo determined C_1-C_5 alcohols and water in gasoline on a set of polystyrene-divinylbenzene columns using toluene as the mobile phase.[381] Lafleur et al. separated unsubstituted PAHs from alkyl-substituted PAHs using a polydivinylbenzene column and dichloromethane.[382] The separation of coal products on the basis of functional groups was also carried out using polystyrene divinylbenzene column and dimethyl formamide.[383]

E. Representative Coal and Petrochemical Applications of SEC

1. Paraffin Wax

Paraffin wax samples have been analyzed by SEC using rotating disk FID[337] and ELSD and toluene as the mobile phase.[338] As the wax analysis requires an above ambient temperature, the silica columns at 45°C were used with the ELSD-based system. The cross-linked polystyrene divinylbenzene columns were maintained at 70°C when wax was detected by FID. SEC was shown to cover much wider carbon number range of wax or alkane samples (up to C_{160}) than high-temperature GC methods.[338]

2. Lubricating Oil

An earlier SEC work on lubricating oil involved simple qualitative monitoring of the changes in the composition of both oil and additives due to degradation.[334] This is especially valid when an additive (such as viscosity index improver) is polymeric in nature and is well resolved from other additives and base oil. One can track the shearing of this polymeric additive in use by SEC. It was demonstrated that quantitative determination of aromatic groups in lubricant oils is possible by SEC using both RI and UV-DAD.[335] Thus, the concentrations of mono-, di-, tri-, and thio-aromatics have been determined on the basis of the differences in their absorbance profiles in the UV spectrum.

3. Crude Oil

SEC was applied to the quality control of crude oils by obtaining molecular weight distributions using both RI detector and multiple UV signals. For examples, UV signal at 280 nm with 40 nm bandwidth was applied for the detection of aromatics and at 410 nm with 20 nm bandwidth for porphyrins.[342] GC-AED was applied extensively to the analysis of metal porphyrins in crude oils by monitoring nickel and vanadium atoms.[343,366,372]

4. Coal Liquid

Coal-derived samples are very complex in nature, and their separation by SEC is dominated by both the size and polarity of the sample components.[357] Coal liquids obtained by solvent extraction using different solvents show variations in the molecular weight distributions.[356] Both structural information and mass ranges can be obtained by SEC with MALDI mass spectrometry.[361,364]

5. Heavy Petroleum and Coal Fractions

SEC was applied for the evaluation of residuum upgrading.[339,351] For example, the conversion was measured by comparison of cumulative peak area for residuum against that of the product materials eluting prior to n-C_{44}, which has a boiling point of 548°C.[339] SEC with online element-specific detection (such as AED) was used to study Fe, V, and Ni profiles in bitumens from tar sand[365,366] and crude oil residues.[372] Hydrodesulfurization and hydrodemetalization of residual oils were also monitored by SEC-AED.[346-348]

VIII. HYPHENATED OR MULTITECHNIQUE CHROMATOGRAPHY

A combination of high selectivities (for cleanup) and resolving capabilities (for the separation of sample components) of two or more complementary chromatographic techniques can simplify the analysis of complex petroleum or coal-derived samples. These hyphenated or multitechnique chromatography (also known as multidimensional chromatography) systems provide advantages such as ease of analysis due to automation, simplified sample preparation steps, efficient elimination of interfering components, better repeatability, improvement in quantitation achieved with the quantitative transfer as well as reinjection of components of interest, and, often, more information on sample composition. A multitechnique chromatography system, when properly chosen and implemented, generates efficiency mainly from the combined effects of selectivities and resolving capabilities of the individual separation modes or methods.

Multitechnique separation methods have been applied for the last 3 decades. However, few petrochemical laboratories are applying them for routine analysis because these techniques are more difficult to operate than the conventional single chromatographic technique. The method development as well as maintenance is less straightforward when two or more separation modes are combined. Further, in the absence of commercially available instruments, the initial set up is often time-consuming and costly, and effective integration of different techniques can be challenging to many laboratories.

Here, the discussion is limited to coupling of two or more types of independent chromatographic systems for fossil fuel analysis. In general, in a multitechnique chromatographic system the initial separation is considered as a fractionation or cleanup step prior to a final high-resolution chromatographic analysis. General discussions on various multitechnique approaches can be found elsewhere.[384,385]

Although efficiency can be derived from multistep separations based on a single technique such as HPLC-HPLC, GC-GC, or SFC-SFC, applications of such hyphenated techniques are not addressed here. In such chromatographic systems, the coupled instruments vary in column types and other operating parameters. For example, GC-GC and SFC-SFC separations are usually implemented on the basis of column polarity, selectivity, and efficiency. The variables for HPLC-HPLC separations can be both mobile phase and stationary phase properties. The resulting efficiency from the coupling of the same type of chromatographic systems can also be quite high, and it is reflected in higher peak capacity or significant resolution enhancement compared with a single separation step.[386-388] For an example, a GC-GC separation of a kerosene sample was reported to provide more than 6000 peaks.[386]

The number of binary and ternary combinations of conventional chromatographic techniques can be unlimited, and a discussion of all these systems is beyond the scope of this work. We highlight only a number of common combinations that have been applied successfully to the characterization of petroleum and related samples.

A. HPLC-GC

If applicable, GC is the most desirable final chromatographic technique for high—resolution analyses of the separated fractions of hydrocarbons, for example, obtained by normal-phase or reversed-phase HPLC. Many examples of HPLC-GC applications to fossil fuel products can be found in two review articles.[389,390] HPLC and GC conditions as well as interface types were also reported there. A majority of HPLC-GC applications have been for the characterization of saturates and aromatics fractions in gasoline, kerosene, diesel, and coal-derived products, for the analysis of PACs in middle distillates, lubricating oils, and coal-derived products, and for the determination of PCBs in fuel oil and coal-tar.

Normal-phase liquid chromatographic (NPLC) separations have been carried out for compound class analysis. Column stationary phases include silica, cyano-silica, amino-silica, and silica impregnated with Ag^+. As usual, both single column and multiple columns with the same or different stationary phases have been used. Pure *n*-alkanes or *n*-alkane/dichloromethane mixtures have been typical NPLC solvents. Reversed-phase stationary phases (such as octadecyl-silica) have also been used for the analysis of PCBs and PACs. Acetonitrile/water or methanol/water have been typical reversed-phase HPLC mobile phases. Capillary or micro HPLC columns (with i.d. ≤ 1 mm) or conventional 4.6 mm i.d. HPLC columns are equally viable as long as the appropriate transfer method is chosen. UV, fluorescence, and refractive index detectors have been widely used for HPLC separations.

Both packed and capillary GC columns have been used. Typical stationary phases include methylsilicone, phenylmethylsilicone, biphenyl, smectic liquid crystal, and Carbowax. Although FID has been used in most cases, other detectors such as AES or AED,[391,392] MS,[392] SCD,[63] have been coupled with GC for fossil fuel analysis.

HPLC-GC interfaces were described in the literature.[389,393,394] Loop-type and on-column interfaces were used. A loop-type interface allows complete evaporation of the HPLC eluant during its introduction to GC. It also allows a transfer of large HPLC fractions (100 to 1000 μL), and an easier internal standard quantitation using an extra loop. It is especially suitable for non-volatile samples.[390] Another approach to qualitative and quantitative analysis of volatile samples is based on an on-column interface employing direct transfer of an HPLC fraction into a special on-column injector consisting of a capillary precolumn to allow HPLC solvent vaporization. This "retention gap" method requires a long uncoated precolumn and only allows modest volumes of HPLC fractions to be transferred. However, a partially concurrent evaporation method, where only a part of the HPLC eluant is evaporated, works with larger fraction volumes (~200 μL) and with shorter uncoated precolumns.[390,395]

In general, sample analysis by HPLC-GC has been carried out using automatic successive transfer of NPLC separated hydrocarbon fractions to a capillary GC via an on-column interface. HPLC with a single silica column and column backflush provided total aliphatic and total aromatic fractions to be transferred to GC. The use of silica and amino-bonded silica columns provided separation of aromatic fractions into ring classes. Such analyses were carried out for diesel fuels by HPLC-GC-FID,[396,397] for coal-derived neutral oil,[398] and lubricant base stock[399] by HPLC-GC-MS. Coupled HPLC-GC techniques were also found to be useful for fully characterizing and quantifying sulfur groups and compounds in middle distillates. This combination, using a GC with FID and SCD, allowed the identification and determination of thiols + sulfides + thiophenes, benzothiophenes, dibenzothiophenes, and benzo-naphthothiophenes. The system also allowed identification of sulfur species such as 3-methyl-benzothiophene, 4-methyl-dibenzothiophene, and 4,6-dimethyl-dibenzothiophene.[63] HPLC-GC-AED and HPLC-GC-MS were applied for the separation and identification of parent and alkylated PAHs, heterocyclic, nitro-, and oxy-PACs in coal liquids, petroleum fuels, diesel exhaust, and urban air particulates.[392]

B. SFC-GC

A SFC-GC system is very similar to an HPLC-GC system, but offers great advantage as the SFC solvent, such as CO_2, can easily be eliminated at the SFC-GC interface where supercritical fluid CO_2 decompresses into gas. The SFC-GC interface usually consists of a heartcut valve connected to a capillary to transfer the SFC flow into a GC injector.[400,401] SFC-GC was applied to n-C_5 to n-C_{25} range petroleum fractions.[400,402-404] Samples were first separated by SFC into nonaromatics and aromatics. Then using selective heartcutting, fractions were injected into a capillary GC system. For gasoline range samples, individual GC peaks were identified and quantitative hydrocarbon-type data were obtained using peak areas and appropriate response factors. For broad range samples, SFC-capillary GC provided quantitative carbon number distributions of aliphatics, and 1-, 2-, and 3-ring aromatics. Capillary GC-MS was found to provide characterization of many diaromatic compounds and PACs present in catalytic-cracked diesel range samples.[400]

C. SFE Chromatography

There has been a growing interest in the online coupling of SFE with chromatographic techniques such as GC, SFC, or HPLC for determining pollutants or hydrocarbons from different solid matrices such as sediments,[405,406] or for analyzing hydrocarbons in air particulates[407] and source rocks.[405] A useful review dealing with technical aspects of SFE-GC was provided by Burford et al.[408]

Like SFC-GC, inserting the restrictor from the SFE system directly into a GC injector usually does the coupling of SFE to GC. Although on-column injection is possible, split-splitless injectors have been widely used. Analytes are vaporized at the hot injection port to be swept away to the GC column where they are trapped by the GC stationary phase. The GC oven is usually cooled cryogenically for sample focusing. This approach was demonstrated by studying recoveries of n-C_5 to n-C_{12} standards.[409] The feasibility of directly coupled SFE with GC using a Tenax trap was also demonstrated for the analysis of SFE extract of an automobile exhaust sample. The sample was extracted for 10 min with 200 atm CO_2 at 45°C and collected on a Tenax trap for its characterization by GC.[410]

Although FID has been used widely, SFE-GC systems with electron capture detector and mass spectrometric or spectroscopic detectors such as SFE-GC-ECD,[406] SFE-GC-MS,[406] SFE-GC-FTIR-MS,[406,409] have also been applied for both identification and determination of sample components.

SFE-GC has been used for fractionation and determination of PACs in different fossil fuel products. Wright et al.[407] examined PACs in coal tar and in a PAH-fraction of a coal liquid that contained high concentrations of alkylated species. Extraction was carried out using CO_2 at 50°C, and pressures used were between 8 and 200 atm. A SE-54 capillary column (15 m x 0.25 mm i.d.) was used for GC separation. The on-column deposition of extracts was performed at 30°C, and the final temperature was 280°C, achieved with a 4°C/min programming. Similarly, hydrocarbons from a sample matrix of heavy hydrocarbon wax were extracted using CO_2 modified with 10% SF_6 for their characterization by GC.[408]

Extraction and characterization of PACs from coal-tar pitch were carried out using SFE-SFC.[411] SFC was performed on a 10 m x 50 μm i.d. open-tubular SFC column and with CO_2 as mobile phase at 110°C. The fluid density was programmed from 0.25 to 0.74 g mL^{-1} at 0.006 g mL^{-1} per minute. A coupled SFE-SFC was used to separate and quantitatively determine PACs in a petroleum pitch.[412] The extraction efficiencies for PACs with SFE were found to be higher for low-molecular-weight PACs and lower for high-molecular-weight PACs compared with those when PACs were extracted with tetrahydrofuran.

For SFE-HPLC, usually a sample aliquot can be transferred from a recirculating SFE extraction system using an HPLC sampling valve for injection.[409] Conventional HPLC with UV and RI detectors and HPLC-MS can be interfaced with the SFE system. Although the potential is enormous for SFE-HPLC for analysis of relatively polar materials such as PACs and phenolic compounds[409] in many petrochemical samples, to our knowledge no reports on this area are available.

D. Miscellaneous Coupled Systems

As we have noted earlier, there could be many binary- and ternary-coupled chromatographic systems that can be applied to the analysis of petrochemical samples. In general, HPLC, SEC, SFC, SFE, and GC, both alone or in combination, can serve as cleanup techniques. HPLC, SFC, and GC can be used for high-resolution separation of the components of interest. Although many examples of binary systems exist, so far only few ternary systems, similar to one described below, have been reported.

A sophisticated online coupling of SEC-NPLC-GC was applied to the analysis of an atmospheric residue without prior cleanup.[413] This hyphenated system separated compounds according to molecular size by SEC, and polarity by NPLC using an amino-silica stationary phase and *n*-heptane as the mobile phase. The separation by GC was carried out according to component boiling point. SEC-NPLC coupling was carried out using an online evaporator based on fully concurrent solvent evaporation using a loop-type interface, vapor exit, and co-solvent trapping. A cryogenic cold trap was used for reconcentration of analyte for subsequent hydrocarbon-type separation by NPLC. An on-column interface using partially concurrent solvent evaporation was used as the NPLC-GC interface.

IX. CONCLUSIONS

This paper has provided a broad overview of major chromatographic techniques that have been applied to the characterization of petroleum and coal products. These techniques are detailed with reference to their application to different sample types. Specific applications include determination of hydrocarbon types, boiling range distributions and molecular weight distributions of petrochemical samples. Applications related to both qualitative and quantitative analyses of target compounds are also highlighted. Many of these techniques (when applied separately or in a coupled system) are shown to provide complementary information on samples.

Suitability of a chromatographic technique for a particular application is primarily determined by its selectivity, resolving capability, and retention mechanism(s). Discussions on the principle, scope and limitation of each method, as provided in this work, should help in understanding and applying the appropriate method for any specific application.

Other reviews on analytical or chromatographic methods for petrochemical samples exist. Scopes of many of these reviews have been somewhat narrow, often dealing only with the analysis of a specific distillate type such as gasoline,[126] or with a specific technique such as high-temperature GC,[414] supercritical fluid chromatography,[213] liquid chromatography,[118] TLC,[304] simulated distillation,[36,39] or HPLC-GC.[389,390] Reviews on specific product types such as coal-derived liquids[248] or wax samples[48] covered broader analytical issues, but only on the respective products. There have been biennial applications reviews dealing with development of the methodologies for petroleum- and coal-derived products.[415,416] Unlike this work, those reviews do not provide a broad discussion on methodologies to cover a broad range of petroleum and related products.

Our overall focus has also been to present a critical discussion on the status of each of the major chromatographic techniques. If the growth and development are measured, GC is the most mature technique. The potentials of techniques such as SEC, SFC, and TLC may not yet be fully realized. HPLC may also be an underutilized technique.

There is a growing need for accurate and yet cost-effective and easy-to-use chromatographic techniques and methods that are capable of providing valuable information on petrochemical samples. Progress has been made to find alternatives for many labor-intensive methods based on open-column liquid chromatography. Improved chromatographic methods have been developed to replace long and crude GC or HPLC methods. However, there are still many opportunities to develop and adapt methods that will be faster, rugged, and automated, for both sample preparation and analysis. For example, with the fast-GC techniques that are under development, there will be a significant increase in throughput without sacrificing the quality of analytical data. Many multi\technique separation methods also fall into this category. The development of these accurate and automated techniques will be increasingly important to meet superior product quality control and stricter regulatory requirements.

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