a powerful tool for the detailed analysis of hydrocarbons.

See also: **I / Chromatography. II / Chromatography: Gas:** Column Technology; Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors; Detectors; Mass Spectrometry; Historical Development; Multidimensional Gas Chromatography; Theory of Gas Chromatography.

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Liquid Chromatography

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Introduction

Techniques based on liquid chromatography are used in the petroleum industry for process monitoring, compliance with environmental regulations, the evaluation of product quality, catalyst performance and feed processability, as well as for determining hazardous compounds, and understanding and solving basic research problems.

Chromatographic techniques and methods used for analysing petroleum products are chosen depending on their boiling point range, which is related to their carbon number. In order to simplify the further discussion, classification of petroleum products into light, middle and heavy distillates is considered throughout this work.

Techniques based on capillary gas chromatography (GC) can perform molecular characterization of some light distillates, such as gasolines and others. However, this technique has limitations when it comes to analysing heavier distillates. As the complexity of petroleum products rapidly increases with the increasing boiling range of distillates, liquid chromatographic techniques play a crucial role in the analysis of middle and heavy distillates. They are also complementary to GC for analysing light distillates. Most of the applications of liquid chromatography to petroleum products include separation, identification and, in some cases, quantification of individual components; separation, quantification, and, sometimes, preparative isolation of hydrocarbon types; in addition to molecular size distribution and average molecular weight determination.

In general, complete molecular separation of the components of petroleum distillates is not possible using liquid chromatography owing to their complex nature and the limited resolution of current techniques. As the boiling range of the product to be analysed increases, the greater its complexity due to the increase in the number of isomers and the broader variety of compound types present. Furthermore, the concentration of polar compounds (e.g. heterocyclic compounds) increases as the products become heavier. Therefore, the heavier the product, the poorer the chromatographic resolution obtained, and the more difficult it is to achieve good separations. In most cases, extensive separations are meaningless in the petroleum industry, but determination of particular target compounds in various distillates is sometimes useful.

Determination of hydrocarbon types (which includes separation and quantification) of all types of distillates is usually carried out by liquid chromatography. Hydrocarbon types in petroleum products can be roughly summarized into saturates (n-paraffins, branched paraffins, and cycloalkanes or naphthenes), olefins (alkenes and cycloalkenes), aromatics (hydrocarbons containing one or more rings of the benzenoid structure), and polars (which include heterocycles and/or high molecular weight material). This simple scheme becomes more complicated with increasing sample boiling range because of the many possible combinations of compound types (e.g. alkylaromatics, aromatic olefins, etc.). Therefore, separation designs may vary depending on nature of the sample and information required by the analyst.

Liquid chromatographic techniques used for the above-mentioned purposes are based on open-column liquid chromatography (LC), high performance liquid chromatography (HPLC), size-exclusion chromatography (SEC), and thin layer chromatography (TLC), as well as multidimensional techniques.

Open-column Liquid Chromatography (LC)

Liquid chromatography has been used for many years to carry out gravimetric determination of hydrocarbon types. This usually consists of separation on normal adsorption phases such as silica gel or alumina. This technique has also been used for preparative isolation of hydrocarbon types, either to carry out further characterization of isolated fractions, or to use the isolated fractions as external standards for calibrating other instrumental techniques (e.g. HPLC), which are in turn employed for hydrocarbon-type determination.

LC-based standard tests for hydrocarbon-type analysis were developed for use by the petroleum industry at a time when other instrumental chromatographic techniques were not yet available. The main advantage of these was that simple glassware was used. Some of these standard tests are still in common use because product specification analyses and referee methods require basic testing procedures (**Table 1**). For research purposes, low pressure to medium pressure LC is used rather than open-column LC in order to increase separation efficiency to some extent. Other modifications to standard tests may involve the use of detectors to monitor eluents or the use of different stationary phases depending on the analytical objective.

In general, all open-column or low pressure LC methods are lengthy, labour intensive, expensive (they require high solvent consumption), and the columns need to be repacked for each determination.

Light distillates The fluorescent indicator adsorption (FIA) method (ASTM D1319) has been in use for a long time (Table 1). Light distillates are separated, using silica gel as stationary phase in a precision bore column and isopropyl alcohol as eluent, into saturates, olefins and aromatics. The use of fluorescent dyes, previously added to the gel, makes it possible to calculate the volume percentage of each hydrocarbon type from the length of each zone in the column, without eluting the zones out of the column. It must be taken into account that uncontrolled losses of some light hydrocarbons may be produced during elution, and samples containing C_3 or lighter hydrocarbons and/or more than 5% v/v C_4 and C_5 hydrocarbons must be dependentanized (see ASTM method D2001).

There are many drawbacks to the FIA method. Apart from the operational ones (related to improper packing of the column and incomplete elution of hydrocarbons by isopropyl alcohol), it provides poor precision, especially for olefins at concentrations typi-

Table 1 Examples of standard tests based on open-column liquid chromatography

Standard method	*Scope*	*Boiling range (°C)*	*Comments*
ASTM D1319[a]; IP 156[b]	Hydrocarbon types in liquid petroleum products by fluorescent indicator adsorption	< 315	Displacement development. Use of fluorescent dyes. Silica gel (100–200 mesh), isopropyl alcohol. Vol % of saturates, olefins, aromatics.
ASTM D2002	Methods for isolation of representative saturates fraction from low-olefinic petroleum naphthas	< 232	Displacement development. Use of fluorescent dyes. Silica gel (100–200 mesh), isopropyl alcohol.
ASTM D2003	Methods for isolation of representative saturates fraction from high-olefinic petroleum naphthas	< 221	Displacement development. Use of fluorescent dyes. Silica gel (100–200 mesh), isopropyl alcohol.
ASTM D2007	Method for characteristic groups in rubber extender and processing oils by the clay–gel adsorption chromatographic method	< 260	Applicable to samples with < 0.1% asphaltenes. Clay gel and silica gel. Elution using n-pentane and toluene/acetone (50/50)
ASTM D2549	Method for separation of representative aromatics and non-aromatic fractions of high boiling oils by elution chromatography	232–538	Bauxite and silica gel. Elution using n-pentane, diethylether, chloroform and ethanol

[a]American Society for Testing of Materials, Philadelphia, USA.
[b]Institute of Petroleum, London, UK.

cally found in gasolines and it does not detect oxygenated compounds blended into gasoline (they are in the aromatic zone).

Middle and heavy distillates The ASTM D2007 standard is used and is still the reference when a hydrocarbon-type determination is developed using other techniques. This method provides sample separation into saturates, aromatics, resins, and asphaltenes or uneluted (SARA). It consists of the elution of n-pentane and toluene/acetone (50 : 50, v/v) through a double column which contains clay in its upper section and clay plus silica gel in its lower section. Its application requires a previous removal of n-pentane insolubles (asphaltenes). In general, the use of chromatographic columns for these kinds of product may produce irreversible adsorption of the heaviest and/or more polar compounds on to the stationary phase, which affects quantitation.

LC-based methods have also been used for a long time for determining and isolating nitrogen, sulfur and oxygen compounds in different types of petroleum distillates. Apart from silica gel, procedures include successive separations using alumina and cation exchange phases, as well as complexation packings.

Standard methods based on LC usually work using fixed volumes of eluent for the various fractions. Therefore, possible cross-contamination of fractions and errors in quantification of hydrocarbon types may occur. Conventional detection provides poor information because of column overloading. Monitoring of the eluent can be carried out using offline analytical techniques (e.g. TLC–FID).

High Performance Liquid Chromatography (HPLC)

HPLC gives a much better resolution than LC. It is a less time-consuming technique, and requires a smaller amount of sample. Percentages of peaks are usually quantified after calibration, without the errors associated with solvent evaporation and sample manipulation. However, in all column-based methods, some heavy and/or polar compounds can be irreversibly adsorbed, producing column deterioration and, therefore, incomplete elution. This can be mitigated by an adequate choice of stationary and mobile phases, and the proper use of backflushing.

Applications of HPLC include hydrocarbon-type determination (separation and quantification) and preparative isolation of hydrocarbon types: separation, identification and, in some cases, quantitative determination of single components (usually one or several target compounds).

Hydrocarbon-type Determinations

Typical analytical and preparative HPLC normal-phase columns are mostly used for hydrocarbon-type separations.

Light distillates Separation into saturates, olefins and aromatics is of most interest, and classical adsorbents, such as silica gel or alumina have been used. This analysis has been carried out on gasolines using a silica gel column, a fluorocarbon as mobile phase and refractive index (RI) detection. The low polarity of the eluent used allows the separation of saturates from olefins. Aromatics are backflushed from the column (**Figure 1**).

The use of silica containing bonded groups capable of forming charge transfer complexes has allowed the

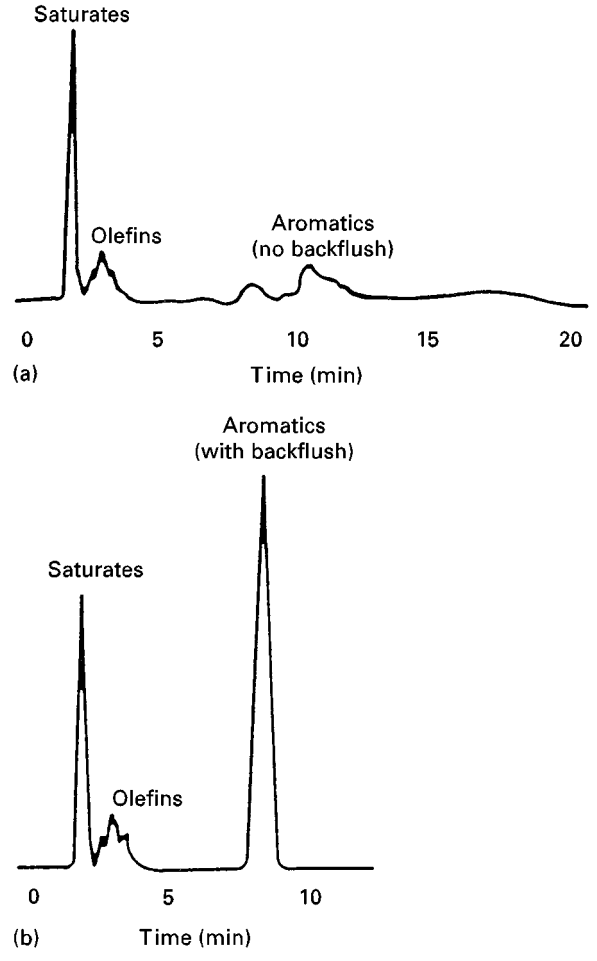

Figure 1 Chromatogram of a heavy gasoline distillate with and without flow reversal. Column, μ-Porasil, 30 cm × 4 mm; mobile phase. FC-78; flow rate, 3.5 mL min^{-1}; sample size, 3 μL; detector, RI (R-401) attenuation × 16. (Reprinted from *Journal of Chromatographic Science* 13. Suatoni JC, Garber HR and Davis BE (1975) Hydrocarbon group types in gasoline-range material by high performance liquid chromatography, 367–371. With kind permission from Preston Publications, A Division of Preston Industries, Inc.)

additional resolution of naphthenes from paraffins to be achieved in light distillates.

Middle distillates Separations according to number of aromatic rings (mono-, di- and polyaromatics), typically of more interest for middle and heavier distillates, have been carried out using silica gel and also the above-mentioned charge-transfer stationary phases. For this purpose, three groups of silica-bonded acceptors have been mostly utilized: nitroaromatics (e.g. commercially available dinitroanilinopropyl silica, DNAP, and 8-(2,4,6-trinitroanilino)octyl, TNAO), tetrachlorophthalimido groups, and caffeine and related compounds. Polar amino- or cyano-bonded silica have also been used extensively in the petroleum industry (e.g. IP391 standard) for this separation, using heptane or hexane as mobile phase and RI detection. Thus, saturates, mono-, di- and polyaromatics are separated using backflushing and the three last groups quantified. Likewise, the content of saturates, olefins and polyaromatic hydrocarbons (PAHs) in a variety of light and middle distillates has been successfully determined by argentation chromatography using both coated and bonded stationary phases.

Heavy distillates Besides analysis of saturates, aromatics and polar compounds, other hydrocarbon-type determinations which involve PAHs have been performed on practically all types of heavy distillates using both nitroaromatic phases and tetrachlorophthalimidopropyl-bonded silica. However, in all these cases, resolution is not very good and quantitative analysis is only possible in a few cases. In spite of this, these methods are useful for process monitoring or comparative purposes (e.g. determination of PAHs in used lubricating oils before and after oxidation treatments).

Determination of Individual Compounds

Individual carcinogenic PAHs have usually been determined in almost all types of distillates, after a previous cleaning-up step, using reversed-phase columns, taking advantage of the selectivity and sensitivity of fluorescence detection. Electrochemical detection has also been used for this purpose, by Ce(IV) oxidation of PAHs to quinones.

Other representative applications of HPLC are summarized in **Table 2**. Reversed-phase HPLC has been used as an alternative to GC in order to quantitatively determine benzene and toluene, and various oxygenates (ethanol, MTBE, ETBE, TAME) in gasolines (**Figure 2**). Other determinations of targeted compounds in light distillates include silica gel normal-phase separations (coumarin in kerosenes, 2,4-dimethyl-6-t-butylphenol antioxidant in light distillates), and charge-transfer HPLC (determination of ppm amounts of aniline, quinoline, pyridine and isoquinoline in kerosene and diesel).

Where middle distillates are concerned, both normal phase and reversed phase have been used to separate a broad variety of compounds, which

Table 2 Some representative applications of HPLC to petroleum analysis

Samples	*Determinations*	*Stationary phase, mobile phase and detection*
Light distillates	Selected oxygenates in gasolines	RP[a]; water/acetonitrile (backflushing hydrocarbons to waste); RI
	Benzene and toluene	RP; water/acetonitrile (remaining gasoline backflushed to waste); RI
	Aromatic N compounds	DNAP and other charge-transfer; dichloromethane; UV
	Coumarin in kerosenes (IP 374)	silicagel; 2-propanol in n-hexane; UV
	2,4-Dimethyl-6-t-butylphenol antioxidant in light distillates (IP 343)	NP[b] and compatible eluents; UV
	Individual PAHs	RP (after cleaning up) and compatible eluents; fluorescence and others
Middle distillates	Identification of N compounds in diesel	DNAP and other charge transfer; dichloromethane; UV
	Dyes and markers in diesel	RP and compatible eluents; UV
	Alkyl nitrate cetane diesel improvers	Silica gel and compatible eluents; Infrared detection
	Phenalenones	RP; UV
Heavy distillates	PAHs in heavy oils	NP and charge transfer; normal-phase eluents; UV, RI
	Furfural in lubricants	RP; water/methanol; UV
	More than 50 additives in lubricants	Normal and reversed phase; compatible eluents; UV, RI, ELSD

[a]Reversed phase.
[b]Normal phase.

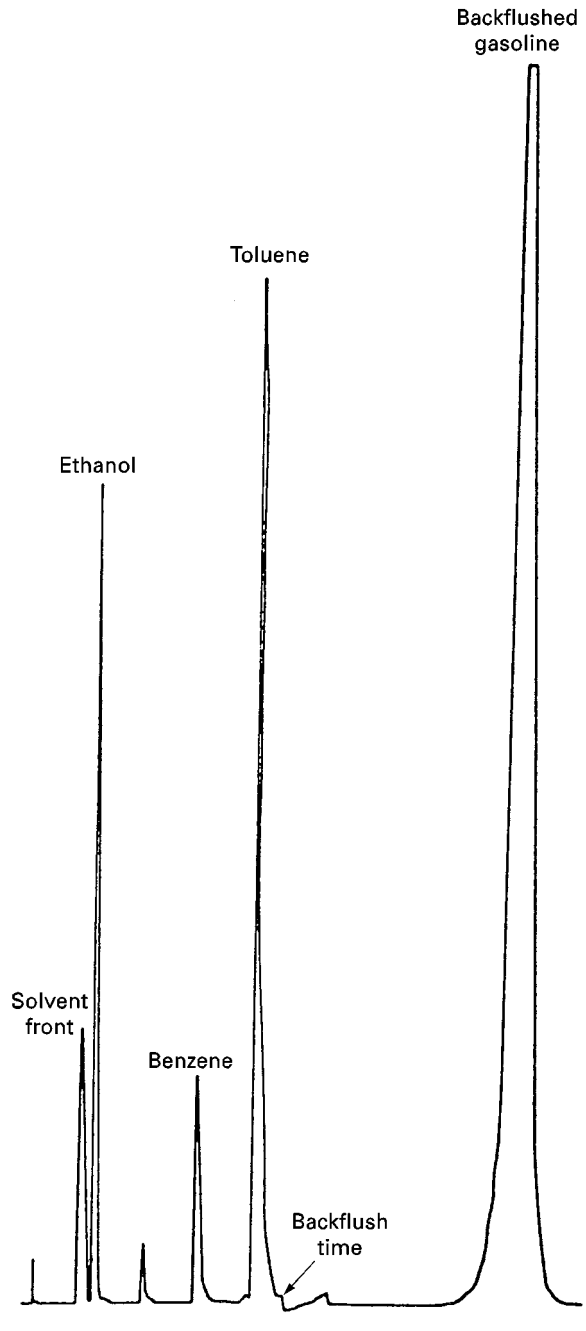

Figure 2 Chromatogram of lead-free gasoline with ethanol. See the following reference for conditions. (Reprinted from *Journal of Chromatographic Science* 23. Pauls RE (1985) Determination of high octane components: methyl *t*-butyl ether, benzene, toluene, and ethanol in gasoline by liquid chromatography, 437–441. With kind permission of Preston Publications, A Division of Preston Industries, Inc.)

include dyes and coloured diesel markers, alkyl nitrate cetane diesel improvers, phenalenones, aza-arenes and alkylaromatic amines. In the case of lubricants, more than 50 additives which include antioxidants and antiwear agents, ashless dispersants, and viscosity improvers have also been separated using the above-mentioned phases and quantified using UV, refractive index (RI) and evaporative light scattering (ELS) detection.

Detection and Quantification

Problems in detection come from the lack of a system which provides uniform response factors for all hydrocarbon types. Moreover, response factors for a given family vary from fuel to fuel. For this reason, hydrocarbon types from the sample to be analysed are usually preparatively isolated, and used as external standards for calibration.

UV cannot detect saturates, and responses of compounds are strongly dependent on chemical structure. RI is mostly used in the petroleum industry in spite of its technical disadvantages of baseline drift, slow stabilization, influence of temperature changes, negative peaks, and impossibility of using gradient elution. In general, variations in response factors for compounds are lower for RI than for UV. The use of RI (e.g. IP 391 standard for saturates, mono-, di- and polyaromatics) is justified because it uses pure aromatic compounds for external calibration. In effect, since the refractive index of each aromatic family varies over a much narrower range than that of the total aromatic fraction, the response of each family is quite well matched using several pure standards (*o*-xylene, 1-methylnaphthalene and phenanthrene). However, saturates are not accurately determined because of the large variation of refractive index possible for saturates and the small difference between saturates RI and that of the commonly used mobile phases (e.g. hexane).

The use of ELS detection is becoming more frequent in petroleum HPLC. It presents practical advantages over RI, better performance and the possibility of using gradient elution. However, it is not a true universal detector and some small volatile aromatics (e.g. methylnaphthalenes) are not detected even under mild working conditions. ELS working parameters can be optimized to obtain, in some cases, uniform responses of different compounds. However, responses depend in part on solute densities.

The dielectric-constant detector (DC) and FID have been reported to provide uniform response factors for hydrocarbon types. However, for the former, contradictory results have been published, and, in the case of FID, technical problems do not yet appear to have been solved. Mass spectrometry (MS) detectors, using different types of HPLC interfaces, have also been used although their application seems, at the moment, to be limited to a more in-depth characterization of separated fractions and to the identification of individual compounds.

Size-exclusion Chromatography (SEC)

SEC is a molecular sieving technique that separates molecules according to their selective permeation into the pores of a gel stationary phase on the basis of differences in their size in solution. Solute permeation into the gel increases with decreasing molecular size, resulting in longer elution. However, not only size but also chemical effects are present in the elution of petrochemical samples and related molecules.

Molecular size distributions SEC is a low resolution technique that allows qualitative or semiquantitative molecular size distributions (MSD) of high molecular weight heavy fractions (e.g. lubricant base oils, paraffin waxes, heavy petroleum fractions, asphalts, etc.) to be obtained in order to assess the effects of process variables. Conversion of MSD into molecular weight distributions (MWD) is usually determined by calibration using narrow polystyrene standards or fractions from the petroleum samples themselves. To cover low molecular weight ends, normal paraffins or PAH are also used. However, these determinations carry a high degree of uncertainty. Likewise, SEC has been used for obtaining estimates of average molecular weight of oil products. In general, molecular weights of petroleum constituents can vary between 30 000 and 100 Da.

Columns and mobile phases SEC is usually carried out using a series of relatively small pore size (100–1000 Å) polystyrene–divinylbenzene (PS–DVB) polymers. Among other packings, poly(divinylbenzene) and Sephadex (a dextran-based polymer) columns are also popular. The use of small particle size (3 μm) packings, and of mixed pore distribution in single columns has been recently introduced. Preparative SEC columns, using either open-column or HPLC technology, have also been used for sample clean-up to remove small molecules from high molecular weight materials or vice versa.

Inter- or intra-association of sample molecules or their interaction on the column should be minimized by selecting an appropriate solvent. The most common mobile phases are tetrahydrofuran, toluene, chloroform, pyridine and quinoline.

Detection Semiquantitative profiles of size distribution have been obtained using differential RI, ELS, UV diode-array, fluorescence, and FID detection. SEC coupled with atomic absorption or emission such as inductively coupled plasma atomic emission (ICP–AES) or atomic emission detectors (AED) has been applied to obtain elemental profiles (for Fe, Ni, V or S) from petroleum samples.

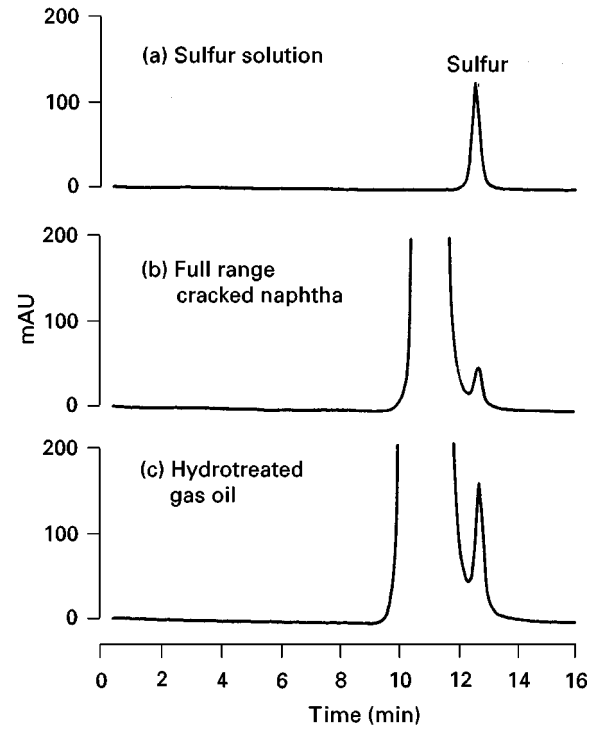

Figure 3 Evidence for the presence of elemental sulfur in hydrotreated cracked naphtha and gas oil obtained from pilot unit runs. (Reprinted from *Journal of Chromatography A* 740. Barman BN (1996) Determination of elemental sulfur by size-exclusion chromatography. Optimization and petrochemical applications, 237–244. With kind permission from Elsevier Science-NL.)

Use of non-size effects These can be used for particular separations; interesting applications relative to light and middle distillates have been developed. Thus, water and C_1–C_3 alcohols can be determined in gasolines using a series of PS–DVB columns. With the same type of stationary phase, determination of pericondensed PAHs in different distillates, and of elemental sulfur in naphthas and gas oil, have been developed which take advantage of elution beyond the total permeation limit of SEC (**Figure 3**).

Thin Layer Chromatography (TLC)

TLC is a simple, rapid, robust and inexpensive technique but it is not usually considered as quantitative or sufficiently sensitive. However, progress in plate manufacture (including small-sized HPTLC plates), in sample application devices, in development instrumentation, and in automated UV and fluorescence scanning densitometers, should allow improvements in separation and quantification of petroleum-derived samples to be achieved. Advantages of TLC for petroleum analysis are high sample throughput, simultaneous processing of standards

and samples, and the possibility of analysing the whole sample without previous fractionation or deasphalting.

Planar Chromatography

Conventional TLC silica gel and alumina plates (with development using solvents of increasing polarity) have been mostly used for qualitative or semiquantitative hydrocarbon-type analysis, and also for preparative isolation of hydrocarbon families in heavy distillates for further analysis or gravimetric determination of collected fractions.

In general, non-quantitative analyses have involved visual detection of colourless substances using inspection under UV illumination (if they absorb in the UV region or they exhibit fluorescence by UV excitation) or the use of chromogenic or fluorogenic spray reagents. Thus, semiquantitative adulteration of gasolines with kerosenes can be detected using silica gel plates and n-heptane as eluent.

Quantitative hydrocarbon-type analysis is possible using UV fluorescence scanners although there are only a few papers on this in the literature. Aromatic and polar peaks of petroleum bitumens have been quantified using UV scanning, and saturates using fluorescence scanning after impregnation of the plates with berberine salts. Modern scanners present the advantage of providing structural data of peaks (UV spectra). The possibility of a future growing application of TLC to the analysis of light and middle distillates depends on the control of vaporization of compounds during development and drying steps.

TLC–FID

This technique combines the advantages of TLC with the possibility of quantitation using an FID. TLC–FID has been quantitatively applied to hydrocarbon-type determination (e.g. SARA, saturates, aromatics, resins and asphaltenes) of all types of heavy distillates (lubricants, residua, asphalts, heavy oils, etc.). In these cases, FID responses are quite uniform although calibration cannot be discarded *a priori*.

Separations are carried out on Chromarods which consist of reusable quartz rods sintered with 5 μm silica gel or alumina. Saturates, alkylaromatics, aromatics, polars or resins, and asphaltenes have been separated. Olefins have also been separated in some heavy distillates by impregnating silica rods with $AgNO_3$. Solvent development is carried out as in planar chromatography.

However, TLC–FID presents several disadvantages with regard to planar chromatography such as the destructive nature of FID, the impossibility of obtaining structural data from FID detection, and the possible influence of sample volatility in quantification which makes it difficult to apply this technique to light and some middle distillates.

Multidimensional Liquid Chromatographic-based Techniques

A multidimensional system generates its resolving power mainly from the selectivity differences of the separating modes used. The most important multidimensional systems in petroleum chemistry are based on HPLC–HPLC and HPLC–GC.

HPLC–HPLC

Separation schemes include combinations of two or more columns. Normal-, reversed-, charge-transfer, argentation- and size-exclusion phases have been used to separate fractions of specific polarity or size in a broad variety of distillates. Hydrocarbon-type determinations of all types of distillates have been carried out. It is very common to use a polar normal phase as a first column. Thus, polar compounds (resins, asphaltenes) are retained on the packing and recovered using backflushing. Selection of the second column depends on the particular families to be separated (e.g. olefins from saturates, aromatics from saturates). Automated column selection and switching systems can improve method development and sample analysis.

HPLC–GC

GC is the most desirable final chromatographic step after HPLC fractionation in order to carry out either the analysis of selected separated fractions of hydrocarbons (e.g. by normal-phase HPLC), or the analysis of low molecular weight components in high molecular weight samples (SEC–GC). However, the final boiling point determines whether or not GC can be applied to the entire sample.

Packed capillary HPLC columns or conventional 4.6 mm i.d. HPLC columns are equally viable as long as the correct transfer method is chosen. Both loop-type and on-column interfaces have been used for analysis of saturates and aromatic fractions in gasolines, kerosene and diesel; for analysis of PAHs in light distillates, middle distillates and lubricating oils; and for determination of chlorinated benzenes in fuel oil. The loop-type interface involves complete evaporation of the HPLC eluent during its introduction in the GC. It allows a transfer of large LC fractions (100–1000 μL), and an easier internal standard quantitation (using an extra loop) to be carried out. It is

especially suitable for nonvolatile samples. A better approach to qualitative and quantitative analysis of volatile samples is through methods based on an on-column interface. However, the retention gap method uses long uncoated pre-columns and only allows modest volumes of HPLC fractions to be transferred. The partially concurrent evaporation method, where only a part of the HPLC eluent is evaporated, works with larger fraction volumes (approx. 200 μL) and with shorter uncoated precolumns.

Future Trends

The development of new, more accurate techniques based on liquid chromatography (especially HPLC, TLC, and new multidimensional or hyphenated techniques) will be increasingly important owing to legislation calling for the reduction of aromatic content in fuels. Therefore, these techniques will continue to play a crucial role in the petroleum industry for the choice of process conditions and the evaluation of fuel quality.

See also: **II/Chromatography:** Liquid Chromatography-Gas Chromatography. **Chromatography: Gas:** High Temperature Gas Chromatography; High-Speed Gas Chromatography. **Chromatography: Liquid:** Detectors: Ultraviolet and Visible Detection; Large-Scale Liquid Chromatography; Mechanisms: Normal Phases; Mechanisms: Size Exclusion Chromatography; Multidimensional Chromatography. **III/Bitumens: Liquid Chromatography. Crude Oil: Liquid Chromatography. Flame Ionization Detection: Thin-Layer (Planar) Chromatography. Flash Chromatography. Geochemical Analysis: Gas Chromatography. Liquid Chromatography-Gas Chromatography. Medium-Pressure Liquid Chromatography. Petroleum Products:** Gas Chromatography.

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Thin-Layer (Planar) Chromatography

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Introduction

Thin-layer chromatography (TLC) has strengths not applicable to other chromatographic methods. These can be summarized as cheapness of materials, low volume requirement for solvents, the ability to use any mixture of solvents, and, most important, the intractable materials of a complex sample are retained within the surface area of the chromatographic plate and may be recovered. In addition, chromatographic failures can be disposed of without damaging the budget. Such considerations do not apply to gas chromatography or liquid chromatography, where involatiles (in GC) or insolubles (in LC) are lost on the column or inlet system with the possibility of permanent damage to the column performance. The difference in cost of thin-layer plates and chromatographic columns ranges from a factor of 100 for GC capillary columns, up to a factor of 1000 for preparative HPLC columns. Whereas TLC has most often