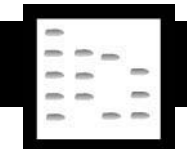
PETROLEUM PRODUCTS



Gas Chromatography

J. P. Durand, Institut Français du Pétrole, Cedex, France

Introduction

Gas chromatography (GC) is an analytical technique that is widely used for characterizing hydrocarbons, and numerous advances in this method have originated in petroleum industry laboratories. Moreover, its use has markedly increased in the last few years with the progress in instrumentation and the relatively low cost of the equipment.

Its applications cover the exploration, production and refining of crude petroleum. These have developed around four major types of methods: analysis of gaseous hydrocarbons, analysis of liquid hydrocarbons, analysis of traces of heteroatomic compounds, and simulated distillation.

Advances in Instrumentation

Since the 1980s, while there has been little progress in the theory of chromatography, the instrumentation has constantly evolved. There have been major improvements in the reliability of equipment and columns, new specific detectors have been developed, and increasingly powerful computers have been used for data processing and controlling the equipment. The use of electronic pressure and flow rate regulators with increasingly stable capillary columns has made it possible to produce chromatograms that are much more reproducible. Microcomputing has simplified the analyst's work (in some cases a little too much, up to the point of forgetting the basics) and has opened the way to automation, standardization of complex methods and the development of correlation methods. Detailed analysis of gasoline and simulated distillation are the two methods that have undergone the greatest evolution. In the analysis of gaseous hydrocarbons, the most important step has been the replacement of packed columns by porous layer open-tubular columns with far greater efficiency and stability. In addition to improvements in the sensitivity and stability of the major types of selective detectors (flame photometry and electron capture), two others – atomic emission and chemiluminescence – are now commercially available.

In the last two to three years, the new advances in technology have been in the fields of rapid analysis and equipment miniaturization. With microcolumns (100 μm i.d.) or multimicrocapillaries with very fast flow rates and programmed temperatures, gaseous hydrocarbon analysis times can be reduced to 1–2 min. However, such conditions do not allow sufficient resolution for analysing heavier hydrocarbons; here rapid chromatography is used as a screening tool, or to decrease the analysis time for simulated distillation. All these methods are now in the development stage. The recent commercial availability of portable and compact chromatographs meets the need for on-site analyses, giving reduction in sampling problems.

Gaseous Hydrocarbon Analysis

The analysis of gaseous hydrocarbons is generally carried out with porous layer capillary columns (gas–solid chromatography). These efficient columns are now very stable and are used in control laboratories. The most widely employed adsorbents are alumina and adsorbent polymers. Alumina capillary columns provide good resolution for the most difficult separation encountered in petrochemical laboratories, that of isobutene and butene-1.

Molecular sieves are used to separate the permanent gases (O_2, N_2, H_2, CO, etc.). To analyse these and hydrocarbons with a single injection, multicolumn chromatographs with switching valves have been developed. Natural gas, gases from crude petroleum and refinery gases are the main applications for which methods have been developed and standardized (ASTM D1945-81, IP 345/80, IP 344/88, ISO 6974-84). Gas analysis has considerable economic importance, both for natural gas, allowing the determination of the calorific value from chromatographic analysis (ISO 6977-84), and for the petrochemical feeds from the steam cracking process (ethylene, propylene and butadiene), owing to the large volumes of these gases now on the market.

Liquid Hydrocarbon Analysis

Detailed Analysis of Light Hydrocarbons

Although the separation of several hundred constituents of gasoline has been carried out for more than

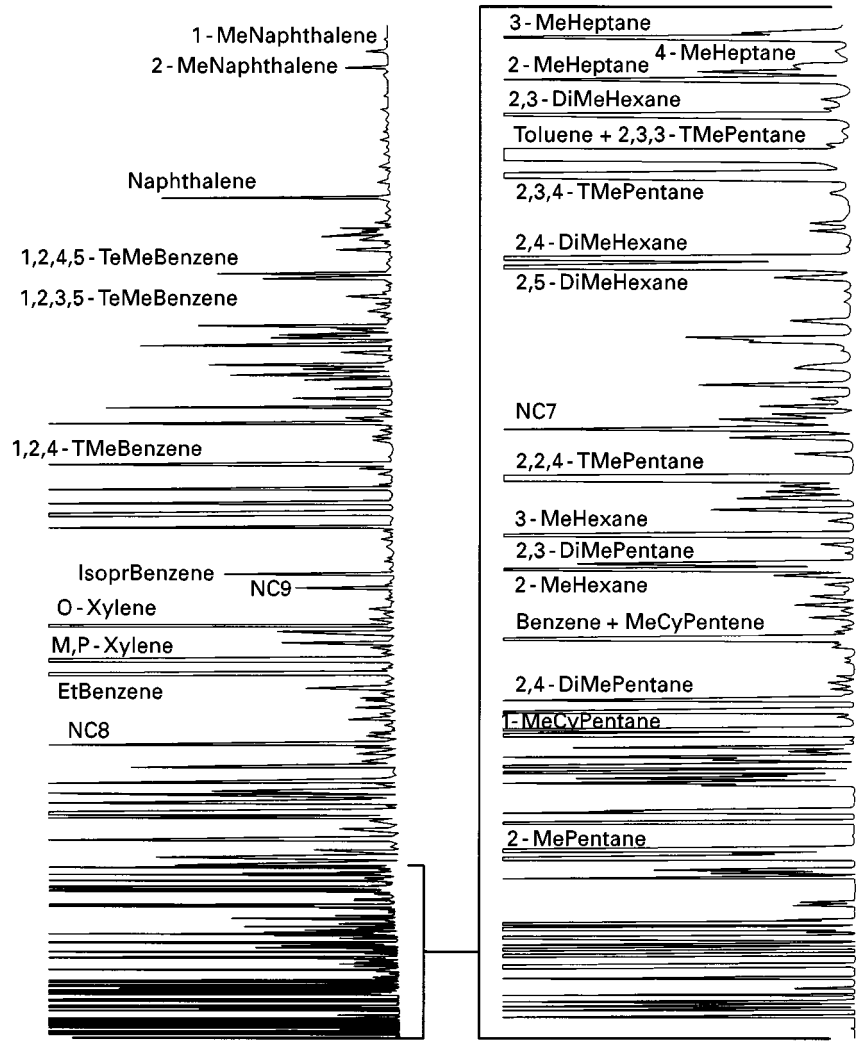


Figure 1 Chromatogram of a commercial gasoline following the NF N07-086 standard. Operating conditions: column, 50 m × 0.20 mm i.d.; stationary phase 0.5 μm OV1; oven, 35°C for 10 min, then 1.1°C min^{-1} up to 114°C, and 1.7°C min^{-1} to 250°C, held 5 min; detector, 280°C; carrier gas, helium at a constant flow of 0.8 mL min^{-1}.

30 years, the methods have been standardized only relatively recently (ASTM D5134-90, NF07-086). The chromatogram of a commercial gasoline, obtained as specified in the French standard NF M07-086, is shown in **Figure 1**. By using a procedure standardizing a number of parameters and specifications, capillary chromatographic methods with temperature programming are reproducible from one chromatographic system to another and identification of complex chromatograms can be automated. This automation has led to the development of numerous applications in the petroleum field. The large amounts of data supplied by the detailed analysis are normalized, after processing, to determine the physical properties (molecular weight, gross calorific value, octane number, etc.), to optimize the thermodynamic or kinetic models, and to predict the quality of the conversion products.

In refining, the two main processes, reforming and catalytic cracking, require increasingly detailed information regarding the gasoline range fraction. The complete detailed analysis data for the naphtha feed and effluents from the reforming units make following and modelling the conversion and optimization of the control of the units possible. A major application field for automated capillary chromatography is in the use of micro-pilot plants involving small amounts of feeds and effluents. The methods developed for the catalytic cracking micro-pilot plants allow detailed analysis of the gasoline cut and determination of octane numbers directly on the total effluent (final boiling point 580°C) by using a pre-column to eliminate the heavier compounds.

Commercial gasolines are formulated using around 10 petroleum basestocks. New environmental con-

straints mean that the resulting mixtures require more rigorous optimization. With all the constraints concerning benzene, other aromatics and olefins, together with the additional octane number requirements brought about by the progressive elimination of lead from fuels, there is an increasing demand for the detailed characterization of basestocks and mixtures. Analyses are now carried out on a regular basis in control laboratories.

One of the main causes of errors in modelling the behaviour of fluids in petroleum reservoirs has been the lack of reliable analytical data. Using a thermodynamic model based on an equation of state for calculating the properties of these fluids requires accurate knowledge of the molecular weights and their distribution. The large amount of information provided by the detailed and direct analysis of the fraction up to C_{20} with the molecular weight distribution has modified the methodology of describing reservoir fluids.

Characterization of the C_3–C_{15} fraction of oils and extracts from source rocks is an important parameter for studying the origin and migration of hydrocarbons. Until recently only a profile or fingerprint was available, but now this fraction can be quantified by automated capillary methods. Various parameters (paraffin, aromatic numbers, etc.) have been obtained from the detailed analysis to follow variations in chemical composition and show biodegradation or leaching phenomena. Soil pollution by hydrocarbons, particularly fuels, requires pollutant monitoring. The replacement of global methods, like solvent extraction, by detailed analysis of the fuel, can provide a better follow-up of the decontamination operations. Figure 1 shows a chromatogram of commercial gasoline following the NF N07-086 standard.

Hydrocarbon Type Analysis of Light Hydrocarbons

Hydrocarbon type analysis (Paraffins/Isoparaffins/Aromatics/Naphthenes/Olefins (PIANO)) can be obtained from detailed analysis with a data system that identifies each of the peaks and combines them into their respective groups. Because there are some coelutions, this analysis may not be accurate with gasolines containing significant amounts of olefinic and naphthenic constituents eluted before *n*-octane.

Some methods of type analysis have been developed with the multidimensional GC technique; these are commonly referred to as PIANO analysis. A four-column system with automatic valve switching and cold traps has been utilized to determine normal paraffins, isoparaffins, naphthenes, olefins and aromatics. A polar column separates aromatics and non-aromatics, a 13X molecular sieve column separates paraffins and naphthenes, while a 5A molecular sieve column separates normal paraffins and isoparaffins. The unsaturated components are retained in an olefin trap, released by heating the trap and then hydrogenated. These separations allow determination of the distribution by hydrocarbon type and carbon number.

Heavy Hydrocarbon Liquid Analysis

The high resolution of capillary columns, which provides separation of a major fraction of the hydrocarbons with boiling points up to 200°C, is not sufficient for the heavier petroleum cuts owing to their increasing complexity. Although detailed information is not directly available, GC is nevertheless very extensively used. The chromatogram can serve as a qualitative plot for determining the presence of specific compounds or classes of compounds. Quantification of normal paraffins in crude petroleum (compounds that are clearly distinguished from the unresolved material) and waxes can be made. However, the most important applications concern the characterization and quantification of the fractions in hydrocarbon types, obtained, in particular, by liquid chromatography (LC). In most cases, the compounds are identified by mass spectrometry (see below). The development of online coupling of high performance liquid chromatography (HPLC) and GC has led to several petroleum applications: measurement of aromatics in gas oils, and measurement of polyaromatics in diesel engine exhausts and mineral oils.

GC/MS Coupling

Mass spectrometry (MS) coupled with GC (GC-MS) is now the main identification technique. From bench equipment (increasingly numerous) to more sophisticated systems providing high resolution measurements, the identification is facilitated by computer processing of libraries containing thousands of mass spectra. This technique has made an essential contribution to analysis of hydrocarbons, in particular for the detailed analysis of fuels and their bases, geochemical studies and pollution problems. Up to around 1000 compounds have been identified in oils. For two decades numerous data for different columns, retention times or indices of hydrocarbons identified by GC-MS have been published for compounds in gasolines and kerosenes. For the medium distillates, where direct detailed analysis is not possible, the distribution per carbon number of the MS analysis can be obtained by combining the separation by boiling point and carbon number from GC

with the analysis of hydrocarbon type from MS. Methods have been developed specifically for monitoring hydroprocessing treatments in order to provide evidence of mechanisms and to have access to the reaction kinetics. The use of GC-MS in geochemistry has been a major step in the study of the transformation of organic matter during sedimentation: this has involved going from comparison of chromatograms to the identification of molecular structures and the search for biochemical markers. This has become a standard method for following these markers in oils.

Heteroatomic Compounds Analysis

The elements most often looked for in petroleum products are sulfur, nitrogen, oxygen and the halogens. The analyst has available several single- or multi-element detectors.

Sulfur

The most widely used detector for many years has been the flame photometric detector (FPD). In spite of its limitations (non-linearity, variable response, quenching), methods have been standardized for the light petroleum cuts. The recent development of a more sensitive chemiluminescence detector for sulfur without these limitations has allowed extension of the application field to heavier cuts, such as gas oils and crude oils. The chromatograms of sulfur compounds from a catalytically cracked gas oil before and after hydroprocessing obtained with this detector are shown in **Figure 2**. Comparison of the two chromatograms shows the changes in the sulfur compounds during the hydroprocessing.

Nitrogen

The situation is identical to that of sulfur, the nitrogen–phosphorus detector (NPD) also having limitations (variable response, relatively low selectivity). The arrival of a chemiluminescence detector for nitrogen has provided access to semi-quantitative analysis of nitrogen compounds in gasoline and gas oil cuts from conversion processes.

Oxygen

The development of a detector specific to oxygen (O-FID) has met the need for the measurement of oxygenated compounds such as methyl *t*-butyl ether in commercial gasolines. Several methods have been standardized (EN 1601-96, ASTM D5599-93). Due to its low sample capacity, this detector cannot be used for measuring traces of oxygen.

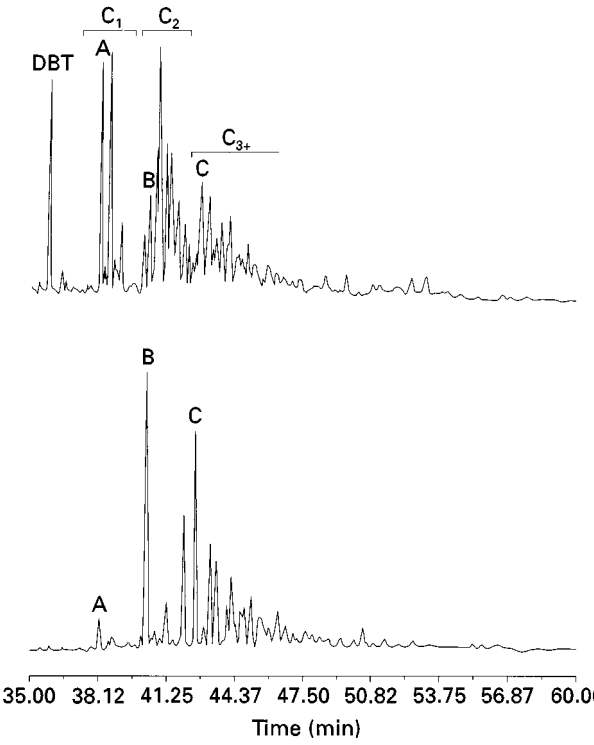


Figure 2 Chromatogram of sulfur compounds from a catalytic cracking gas oil (LCO) before and after hydroprocessing obtained with a chemiluminescent detector. Operating conditions: column, 30 m × 0.32 mm i.d.; stationary phase 4 μm SPB-1; oven, 60°C to 320°C at 5°C min^{-1}. DBT, dibenzothiophene; C_1, methyl; C_2, dimethyl or ethyl; C_{3+}, three or more branched carbons.

Halogens

The electron-capture (ECD) and electrochemical detectors are used to determine the halogens. The ECD is very sensitive when the molecule is polyhalogenated; sulfur hexafluoride, used as a tracer, can be directly detected at the p.p.b. level. The main applications concern chlorofluorocarbon gases, chlorinated solvents and polychlorinated biphenyls (PCBs).

Multielement Detectors

While all the specific detectors mentioned above can detect only one element at a time, the atomic emission detector is multielement, with some restrictions concerning the number of elements that can be detected per analysis and the sensitivity to some of these elements. This is a powerful identification tool (complementary to MS). The main applications are measurement of oxygen compounds in gasolines, multielement simulated distillation (H, C, S), and the determination of nickel and vanadium in crude oils.

Simulated Distillation

Simulated distillation (SD) by GC has been the subject of numerous studies for 30 years. It is a technique that advantageously replaces traditional distillation methods for rapid checking of product yields. The principle is simple: the sample is injected into a column, which separates hydrocarbons according to their boiling points; using a mixture of normal paraffins with known boiling points, the correspondence between the retention time and boiling point is established and then the weight %–boiling point curve can be constructed. However, the implementation is more difficult. The first problem concerns the choice of the stationary phase to obtain good agreement with the real distillation curves; the second is the stability of this phase at the maximum temperatures used. There are many interdependent parameters involved in these two problems. Although several methods have been standardized (ASTM D3710-90, ASTM D2887-93, ASTM D5307-92), their applications give rise to a number of difficulties in routine use. Operating conditions, column performance, frequency of calibration runs and blanks, quantification, and raw data processing are the parameters to be controlled to achieve the level of precision given by the standard methods. Column performance is affected by noneluting residues. The problem can be resolved by installing a pre-column with a backflush and calculating sample recovery with an internal standard.

The arrival in the last few years of very stable metal columns and the use of electronic pressure and flow regulators have provided better control of the experimental parameters. These advances have extended the final determined boiling point up to 650°C with conventional methods and to 720°C with high temperature simulated distillation (HTSD). The chromatogram of a light crude oil with a final boiling point of 650°C, obtained with a metal column, is shown in **Figure 3**. The range of boiling points of petroleum products is thus almost completely covered by using two methods, since HTSD can operate only with cuts having boiling points above 150°C. Consequently, for samples containing light compounds, heavy compounds and non-recoverable residues, a fractionated distillation yielding two cuts is necessary.

Simulated distillation can be used to determine gasoline dilution of used engine oils (ASTM D3525), to analyse the oil-soluble fraction of particulates emitted by diesel engines (estimation of the proportion attributable to the fuel and lube), and to estimate engine oil volatility (ASTM D5480).

Conclusion

The high resolving power of GC makes it a major analytical tool for characterizing the very complex mixtures that constitute petroleum products. The recent development of correlation methods in near-infrared spectroscopy (NIR) for characterizing light hydrocarbons could challenge the dominant position of chromatography in this field because of the speed of the NIR techniques. However, GC will always remain the method giving the most detailed information. With the present evolution of fast chromatography, its disadvantage of a longer analysis time is disappearing. Although GC is not as fast as spectroscopic methods, analyses in a few minutes with microequipment will ensure that it continues to be

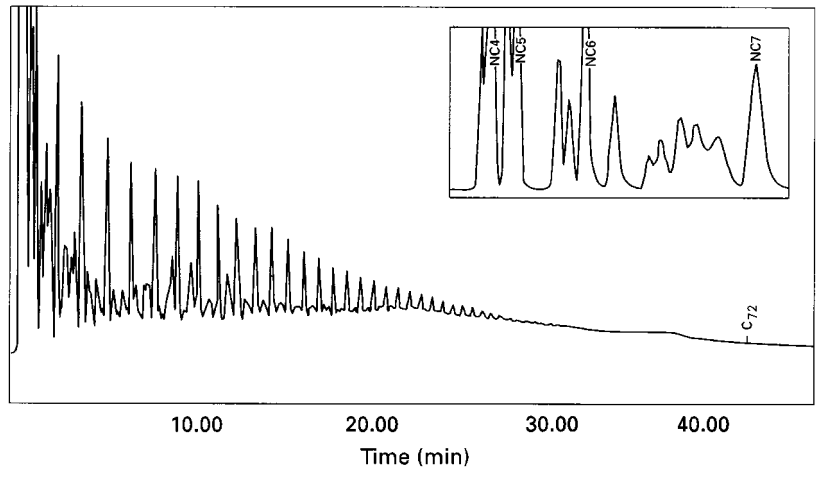


Figure 3 Chromatogram of a light crude oil with a final boiling point of 650°C. Operating conditions: column, 10 m, deactivated metal; stationary phase 0.5 μm OV1; oven, 35°C for 1 min, then 10°C min^{-1} up to 390°C, held 14 min; detector, 400°C; carrier gas, helium at a constant flow of 10 mL min^{-1}.

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.

Further Reading

Adlard ER (ed.) (1995) *Chromatography in the Petroleum Industry*. Amsterdam: Elsevier.

Benner RL and Stedman DH (1989) *Analytical Chemistry* 61: 1268.

Di Sanzo F and Chawla B (1992) *Journal of Chromatography* 271: 589.

Dressler M (1986) *Selective Gas Chromatography Detectors*. Amsterdam: Elsevier.

Durand JP, Béboulène JJ and Ducrozet A (1995) *Analysis* 23: 481.

Grob K (1991) *On-line Coupled LC-GC*. Heidelberg: Hüthig Buch Verlag.

Grob RL (ed.) (1995) *Modern Practice of Gas Chromatography*. New York: Wiley.

Korth J, Ellis J, Crisp PT and Hutton AC (1998) *Fuel* 67: 1331.

Lin R and Wilk ZA (1995) *Fuel* 74: 1512–1521.

Quimby BD and Sullivan JJ (1990) *Analytical Chemistry* 62: 1027.

Liquid Chromatography

V. L. Cebolla, L. Membrado and J. Vela,
Instituto de Carboquímica, Consejo Superior de Investigaciones Científicas (CSIC), Zaragoza, Spain

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.