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Review

Gas chromatographic methods for oil analysis

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Abstract

In the past 50 years, gas chromatography (GC) has played a most important role in the analysis of oil. In this review, the early history is briefly reviewed; next developments in this highly relevant application area since about 1985 are highlighted. The main topic of interest are the introduction and decisive role of capillary GC, the use of selective detection techniques, the versatility of coupled-column techniques and, specifically, the additional power of comprehensive two-dimensional GC.

Keywords: Reviews; Gas chromatography; Oils

Contents

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1. Refining of oil

The conversion of crude oil into useful products is what oil refining is all about. The refining of oil begins with distillation at atmospheric pressure and a temperature below 370 °C. This produces light gases, naphtha, kerosine and gas oil. The heaviest fraction, the long residue, remains behind. Next, the long residue, which starts to boil above 370 °C, is subjected to further distillation under reduced pressure to avoid thermal cracking. This step produces two products: flashed distillate and short residue. In the third step both these products are further processed into lighter products. The desired end products, such as gasoline, kerosine and diesel fuel, always have a higher hydrogen-to-carbon ratio than the heavy oil fractions. Therefore, the conversion processes following distillation either must add hydrogen to or withdraw carbon from the oil feeds.

In fluidic catalytically cracking (FCC) carbon is withdrawn and deposited as coke on the catalyst during cracking. This coke is burned with air, thereby also supplying the heat for the endothermic cracking reactions. Most FCC units, commonly referred to as *cat crackers*, use flashed distillates as feed, although these are often blended with residual components. An increasing number of FCC units can even process the full long residue, thereby skipping the vacuum distillation altogether. The most important FCC product is gasoline, with light alkenes (C_3, C_4) and gas oil being the main secondary products. In the FCC process hot (700 °C) catalyst powder (average particle size only 80 μm) is added to the atomized feed; the catalyst–oil ratio is between 5 and 10 to 1. The feed vaporizes and the mixture enters a fast, upward-moving fluidized-bed reactor that is known as a riser. The contact time between catalyst and hydrocarbons in the reactor is very short, 2–10 s, during which the cracking reactions take place at around 500 °C. When leaving the reactor, the catalyst has lost most of its activity because of the coke deposits that form during cracking. The catalyst is separated from the gaseous hydrocarbon products, which are condensed and fractionated. Some hydrocarbons remaining on the catalyst are removed via stripping with steam. From the stripper, the catalyst flows into the regenerator, where the deposited coke is removed by burning with air, thus restoring the catalyst activity. The hot, regenerated catalyst flows back to the riser reactor, ready for the next cycle.

Hydrocracking is a more recent development and is based on the addition of hydrogen instead of the withdrawal of carbon to obtain a higher hydrogen-to-carbon ratio in the end products. This highly complex process also uses flashed distillate as feed. It involves high hydrogen pressure and trickle flow operation. The heterogeneous hydrocracking catalysts have two functions: heavy molecules are cracked over acid sites, while hydrogenation of both intermediates and end products occurs over the metal sites (mostly mixed sulphides). The hydrogenation function plays an important role in controlling the selectivity towards the desired products and the catalyst lifetime. The combination of hydrogenation and cracking is of such complexity—even in model compounds, let alone in complex mixtures of crude oil—that basic and exploratory work is still very important. When oil is passed over a heterogeneous catalyst, many different and complex reactions take place. Amongst these, the removal of sulphur from the highly complex residue molecules is highly important. Sulphur is removed from the process as hydrogen sulphide (H_2S), which is subsequently absorbed in di-isopropanol amine (DIPA). H_2S can subsequently be converted into elementary sulphur for use in various industries.

The hydrocracker produces sulphur-free naphtha, which is used as feed for several chemical processes and for producing gasoline components, as well as sulphur-free gas oil and kerosine. The residual product, the so-called hydrowax, is blended with flashed distillate for use as conventional cat-cracker feed.

Another well-known example of technology that succeeded that of the hydrocracker is the Hycon. The name of this conversion technology is a contraction of the words hydrogen and conversion. Hycon was designed to convert the heaviest high-vacuum distillation fraction, the short residue. Even the fuel-oil produced by this technology has a remarkably low sulphur content.

Detailed knowledge of the composition of feedstocks in terms of paraffinic, olefinic, naphthenic and aromatic carbon and hetero-atoms has become exceedingly important. The way in which carbon is present in feedstocks determines how the various streams are routed through the refining process. Hetero-atoms, such as sulphur and nitrogen, can poison the catalysts used in the highly complex refining processes, such as hydrocracking. Knowledge of the boiling-point distribution of these species is therefore essential to establish optimal operating conditions. Furthermore, growing environmental concern and associated legislation tighten the quality constraints of oil products in terms of aromatic carbon and sulphur contents. From among the instrumental techniques, gas chromatography (GC) has become by far the most important analytical technique in the oil industry. Its history, the state-of-the-art, and several perspectives will be discussed in the next sections.

2. History of gas chromatography in the petrochemical industry

2.1. The early years

In 1941 chromatography was introduced by Martin and Synge as a technique based on partitioning of chemical compounds between two (liquid) phases [1]. At that time the possibility of a gaseous mobile phase was already suggested.

Gas chromatography (GC) was actually introduced by James and Martin in 1952 [2]. Their work signalled the first time compounds could be separated chromatographically on the basis of their volatility. Because of the similarities between GC and distillation and the possibility of a direct translation of the results, oil chemists were quick to herald this development. The plate-number concept, which is still in use today, was developed by a distillation expert rather than by a chromatographer! [3]. Reputedly, Dutch researchers were the first to recognize the potential of GC for the speciation of hydrocarbon mixtures [4].

In 1956, the first symposium on ‘‘vapour-phase chromatography’’ was organized by the Hydrocarbon-Research Group of the Institute of Petroleum. In the opening lecture, A.J.P. Martin made some remarkable predictions [5]. One of these

> ‘‘ *. . . so we should be able to work from the milligram down to the microgram scale. Of course, that will imply that we decrease the diameter of our column correspondingly. We shall have columns only two tenths of a millimetre in diameter, and these will carry, I believe, advantages of their own . . .* ’’

entails an incredibly accurate description of the state of the art of microcolumn chromatography in the 1990s. Another prediction

> ‘‘*There is no reason why we should not run our columns at really high-temperatures,* 1000 *or even* 1500 °*C if required . . . .*’’

is yet to come true.

At that time GC was already well established within the petrochemical industry, as evident from the appearance of the book *Gas Chromatography* by Keulemans from the then Koninklijke/Shell Laboratorium in Amsterdam [6].

Since that time, GC has gone through a tempestuous development within the petrochemical industry. Some significant milestones were the following.

(i) The development of flame-ionization detection (FID), by McWilliam and Dewar at ICI [7]. The manifest advantages of using this detector were immediately picked up by several workers in the oil industry.

(ii) The automation of a gas chromatograph reported in a paper from 1958 which comprised the concept of an ‘‘infinitely long column’’ [8]. This idea has re-emerged at regular intervals in the chromatographic literature, and has most recently been launched as a novel invention in capillary electrophoresis [9].

(iii) The introduction of high-temperature GC in the petroleum industry. Column temperatures up to 300 °C were used, enabling the elution of paraffinic hydrocarbons up to C_{40} [10].

GC using packed columns and FID had become a broadly accepted analytical tool in the petroleum industry by the early 1960s. Typically, around this time columns of several meters in length and several millimetres in diameter were used. The packing material typically consisted of 50–80 mesh (50–100 μm) particles, which resulted in a typical column plate count of 2000. In the extended-range (high-temperature) chromatograms of Adlard and Whitham [10], up to 20 peaks could be observed (Fig. 1).

Although this was an unheard-of separation power, scientists involved in the analysis of complex mixtures such as oil, and natural-product chemists, were well aware that it was far from sufficient to separate all components in their samples. Various attempts were made to develop even more powerful techniques. Considerable improvements were made by increasing the column length and by using better packing materials of smaller and more uniform particle size. Ultimately, packed-column GC would allow perhaps 100 compounds to be resolved in one run, but this would still represent only a small fraction of the huge numbers of compounds present in oil [11].

It was soon realized that a more dramatic increase in separation power could be achieved by coupling various types of chromatographic columns, thereby exploiting different separation mechanisms.

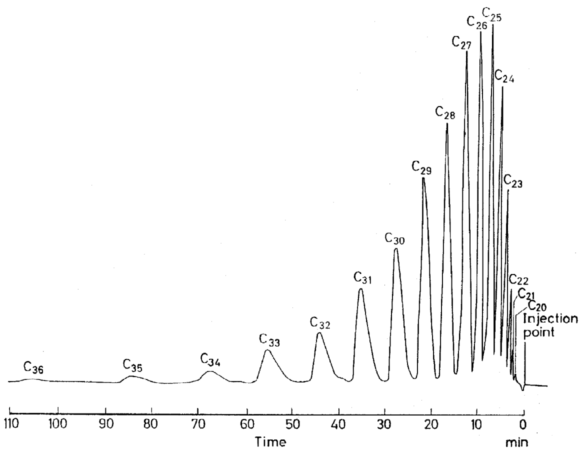

Fig. 1. Example of an extended-range (high-temperature) gas chromatogram by Adlard and Whitham [10].

2.2. Coupled-column systems

2.2.1. Hyphenation

Hyphenation, a word which finds its origin in the hyphen that connects the various acronyms of analytical procedures e.g., GC–MS, LC–GC or solid-phase extraction (SPE)–LC–MS, can be broadly defined as all on-line combinations of two or more different analytical systems. Indeed, today, a successful series of symposia is devoted to the subject of ‘‘hyphenated techniques in chromatography’’ (HTC).

However, there are two very distinct classes of such combined systems, the set-up and application of which are vastly different. Therefore, a case can be made for the use of distinct name tags for these two classes of systems. Hyphenation of separation systems, such as the on-line coupling of LC and GC, can be referred to as *coupled-column techniques*, while combinations involving a separation system and a spectrometric detection device can be called *hyphenated systems*. In this review, we will follow this definition of hyphenation.

Among coupled-column techniques, a further distinction can be made between *heart-cut* and *comprehensive* systems. In the former systems only a limited part of the effluent of the first separation column will be directed towards the second one. For example, a fraction from a gas chromatogram may be selected and submitted to a second column (GC–GC). In comprehensive systems all of the sample is subjected to both separation procedures and the entire sample eventually reaches the detector. A leading contemporary example of such a comprehensive system is GC×GC, which will be discussed below. Table 1 summarizes the terminology that will be used in this review.

2.2.2. History

Coupled-column systems were first reported in 1959 when Hughes et al. [12] described a three-stage gas chromatograph (Fig. 2) for the separation and identification of oxygenated hydrocarbons in combustion products from automotive engines. After the first separation a specific fraction was sent to a second column. From the resulting chromatogram, another heart-cut was taken and directed to a third column. Such a GC–GC–GC system (in current terminology) allowed highly selective separations, compensating for the limited numbers of theoretical plates available in the early days of GC. Bloch [13] went as far as GC–GC–GC–GC for the separation of C_1–C_7 hydrocarbons.

The increasing complexity of processes and products led to the development of the selective coupled-column system that is still being used in the oil industry today, the PIONA analyser. Boer and Van Arkel [14] were the first to describe a PNA analyser. Their GC–GC–GC system allowed the separation of

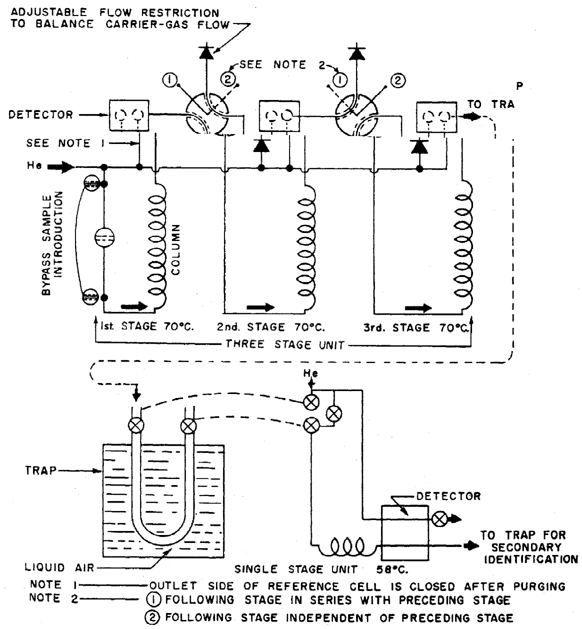

Fig. 2. Three-stage gas chromatograph by Hughes et al. [12].

a (heavy) naphtha (straight-run oil fraction with a boiling range up to 200 °C) into three distinct classes of components, the paraffins (P), naphthenes or cyclic paraffins (N), and aromatics (A) (Fig. 3). This type of system has been improved over the years and the number of steps has been increased, resulting in the PIONA analyser (with I standing for isoalkanes and O standing for alkenes) [15], which is a GC–GC–GC–GC–GC system in use today at many refineries throughout the world. Although these types

Table 1
Distinction between selective and comprehensive coupled-column systems and hyphenated systems

	Combined techniques		
	Coupled-column techniques		Hyphenated systems
	Selective	Comprehensive	
Main purpose	Increased selectivity sample preparation	Increased separation power increased selectivity	Selective detection identification
Types of applications	Target compounds or selected groups in complex matrices	Comprehensive characterization of very complex samples	Detection of (classes of) components identification of components in complex mixtures
Examples	GC–GC, LC–GC	GC×GC, SEC×LC	CG–MS, GC–AED, LC–MS

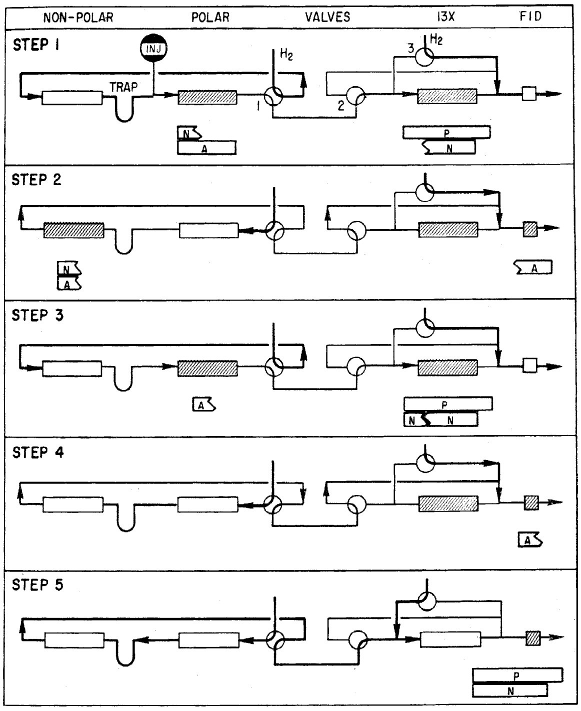

Fig. 3. Schematic of the individual separation steps of the PNA analyser.

of analysers are referred to as coupled-column techniques in the current terminology (the entire sample is not submitted to every individual separation step), they do have one characteristic feature of comprehensive analysers in that the entire sample eventually reaches the detector.

3. Developments in analysis of petroleum by GC (since 1985)

3.1. Capillary GC

3.1.1. Fused silica

As was mentioned above, the high separation potential of capillary GC was already predicted in 1956. The first practical applications for the characterization of hydrocarbon mixtures involved metal capillaries coated with squalane [16,17]. These types of columns proved to be highly successful, and they were widely used up to the early 1980s. A major reason for this was that the adsorption of hydrocarbons on the steel column wall was negligible. Rijks and Cramers [18] performed an elaborate study on these types of capillaries and reported retention indices of no fewer than 170 hydrocarbons within the C_4–C_9 range. With different instruments and different columns and operators, the reproducibility of retention data was in most cases considerably better than 0.1 index unit.

A major limitation of squalane as a stationary phase, however, is its upper temperature limit of 90 °C, restricting its use to the C_4–C_9 range. Metal capillaries coated with other phases, such as methylsilicone gums, proved to be less successful, because they suffered from non-uniform film thickness and from the resulting exposure of analytes to active spots on the wall. As a consequence glass promised to be a highly attractive alternative.

The first applications of glass capillaries were reported by Grob and co-worker [19,20]. The famous high-resolution gas chromatogram of the semi-volatiles of cigarette smoke is shown in Fig. 4 [21]. However, because of the fragility of these capillaries, their use was for many years restricted to a small group of skillful practitioners. It was only after the invention of the fused-silica column by Dandeneau and Zerenner in 1978 [22] that the use of capillary columns became widely accepted. Almost at the same time [23,24] the technology was developed to cross-link polymeric films in situ and to chemically bond stationary phases to the silica surface. This greatly increased the upper temperature limits of capillary columns. Initially, there was a widespread belief that the sheer separation power of these columns would allow for any separation problem to be readily solved. Hewlett-Packard (Agilent Technologies), who still own the patent on fused-silica columns [25], even used this as a sales argument for their first capillary GC instruments. Although this view is not held anymore today, the vast majority of GC analyses performed today still rely on a single separation step.

The ultimate practical use to date of the separation power of linear capillary systems within the petroleum industry has become known as the detailed-hydrocarbon analyser (DHA). This type of analyser was designed for straight-run hydrocarbon fractions and it involves the use of a single 100-m long column. When using this analyser, one can separate

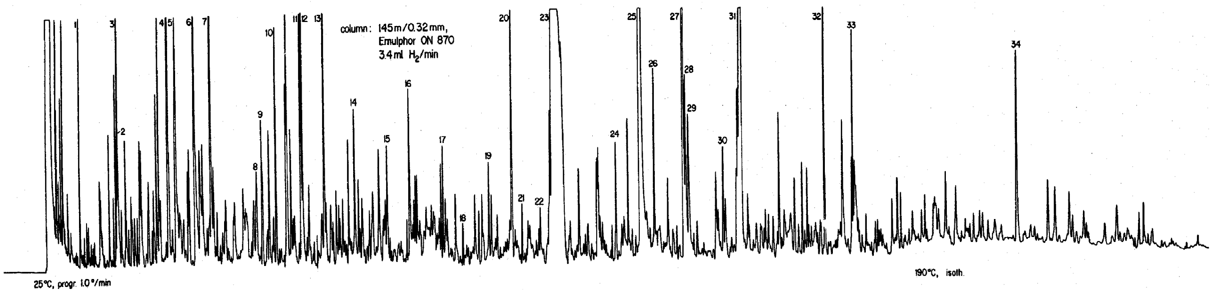

Fig. 4. High-resolution gas chromatogram of the semi-volatiles of cigarette smoke by Grob.

virtually all compounds up to C_9 within these fractions, thus providing information (e.g., on the branching of paraffins) that cannot be obtained from the PIONA analyser. An obvious drawback of the use of such a long column is the resulting analysis time, which typically is some 3 h.

However, when applied to hydrocarbon fractions which contain considerable amounts of olefins, even a 100-m column certainly cannot separate all individual compounds. In an attempt to obtain PIONA-like data for these types of samples, Teng et al. coupled MS to DHA as a second separation step [26]. Using extensive retention and MS databases, they demonstrated the proper operation of their set-up for test mixtures. However, their approach is based on the assumption that no more than two peaks co-elute at any time. In real samples, this assumption certainly does not hold and erroneous data will be obtained. An additional—and probably more serious—problem is formed by the different MS response factors for different analyte classes and, also, for different instruments. This implies that the calibration of a comprehensive GC–MS analyser is a huge task. Still, attempts are being made to commercialize this approach (H. Spaans, Analytical Controls, Rotterdam, The Netherlands, personal communication, 1999).

3.1.2. SimDist

In the petrochemical industry distillation is a technique of major importance. It is by far the most widely used separation technique. Distillation data are being used for the characterization of feedstocks and products and for process control in the refinery. Physical distillation tests for boiling-range distributions were among the first tests documented by the American Society for Testing and Materials (ASTM) in 1921, and many of these tests are still being used today. Crude oils are characterized by ASTM D2892, which yields the true boiling-point profile of the sample, obtained using a high-efficiency still. A simpler method is ASTM D86, a single-plate distillation, strictly applicable only to middle distillates. ASTM D1160 uses a low-efficiency vacuum distillation and is intended to extend ASTM D86 to hydrocarbons above n-C_{20}. Although simple with regard to instrumentation, these tests are often lengthy (up to 3 days for D2892!) and laborious. Since they also suffer from a poor reproducibility, it is needless to add that there is a need for faster, more-precise and automated methodologies.

As already mentioned in Section 2.1, oil chemists soon recognized the potential of GC, because of the similarities with distillation processes. They saw the potential of a direct translation of GC results to distillation data. Simulating distillation by gas chromatography (SimDist) was first reported by Eggerston et al. in 1960 [27]. It was based on the fact that hydrocarbons elute from a non-polar column during a temperature-programmed run in order of increasing boiling points. By running standards, usually a series of n-alkanes, the boiling points of which are accurately known, the retention-time axis can be converted to a boiling-point scale. By combining data obtained on samples and standards, it is possible to obtain the percentage recovered at any temperature, or vice versa.

The above approach first achieved formal status in 1973, as ASTM D2887. This method covered diesel, fuel oil, gas oil, and light lubricating oils, with final boiling points (FBPs) up to 540 °C (n-C_{44}). Although ASTM D2887 allows the use of any column which meets its resolution criterion and which elutes hydrocarbons in boiling-point order, the examples given all concern packed columns. The use of (short) capillary columns, however, would allow the elution of compounds with much higher boiling points. Although alkanes above C_{60} cannot be distilled (not even under vacuum conditions), ''virtual'' boiling points can be assigned to alkanes above C_{60} by extrapolation of the curve correlating the boiling points of *n*-alkanes with their carbon numbers [28]. The resulting SimDist data have been in great demand for comparative studies.

The first use of capillary columns for SimDist was reported in 1985 by Luke and Ray [29]. They demonstrated that residues boiling at up to 650 °C (n-C_{70}) could be analysed using 6-m Pyrex capillary columns coated with 0.15-μm OV-1. Their paper was soon followed by one from Trestianu et al. [30]. These authors described a dedicated high-temperature (HT) SimDist analyser capable of eluting compounds up to C_{120} within a temperature programme which was extended to 430 °C, and up to C_{140} during the final isothermal hold. A drawback was that this dedicated analyser used fragile and inconvenient glass (Pyrex) columns. Although the fused-silica column had already found its way into many laboratories, the rapid deterioration of the outside polyimide coating above 350 °C limited its use for HT-SimDist purposes. A possible solution was thought to be found by the introduction of aluminium-clad columns, first reported by Lipsky et al. [31–33]. Although aluminium itself can withstand very high-temperatures, the lifetime of these columns was usually short, because they were being subjected to substantial thermal stress during a temperature-programmed run. Due to the different thermal expansion coefficients of aluminium and fused-silica, cracks and breakages in the column easily occurred. Since the aluminium coating would usually remain undamaged, column breakage would only manifest itself by a sudden drop in column performance (J. Beens, personal communication).

High-temperature polyimide-coated fused-silica columns were announced in 1987 [34]. Although these columns exhibit a somewhat higher temperature stability than ''standard'' polyimide-coated fused-silica columns, their lifetimes in HT-SimDist were still too short for practical purposes. A breakthrough occurred when Chrompack (re)-introduced metal capillaries. Specially deactivated metal capillary columns coated with chemically bonded stationary phases were described. These columns proved to be virtually unbreakable, which made them very suitable for use in process equipment. The deactivation provided an adequate shielding of the metal surface and resulted in maximum operating temperatures of 450 °C or higher. Thermal degradation of the stationary phase was even lower in these metal columns than in fused-silica, which resulted in a high reproducibility of the separations and in long column lifetimes. In practice, this could be recognized from the very low bleed levels at high-temperatures. The inertness of the columns was demonstrated by the separation of test mixtures, which contained different types of compounds of varying polarity [35]. These characteristics are the main reasons why these types of columns are still the columns of choice for HT-SimDist today.

Other advances that have greatly contributed to the success of HT-GC and simulated distillation include the introduction of novel, highly accurate injection techniques. Both on-column [36] and programmed-temperature vaporization (PTV) [37,38] injectors reduce the problem of discrimination (biased injection) and result in much more accurate boiling-point curves. For a detailed description of these techniques, the reader is referred to Refs. [39,40].

A concern that still exists is the possible decomposition of petroleum fractions at temperatures above 350 °C [41]. Decomposition depends not only on the temperature, but also on sample composition, residence time, and on the presence of reactive substances (e.g., oxygen). There are potential alternatives to HT-GC for the SimDist of high-boiling fractions. Supercritical-fluid chromatography (SFC) is potentially valuable as an alternative to HT-SimDist. In principle SFC allows heavy (high-boiling) hydrocarbons to be eluted at relatively low temperatures thanks to molecular interactions between the dense mobile phase and the analytes. In SFC the mobile phase is a ''dense gas'' or ''supercritical fluid'', with the operating conditions exceeding (by definition) the critical temperature and pressure of the eluent. One of the most attractive features of SFC is that carbon dioxide (CO_2, T_c=31.3 °C, p_c=72.9 bar) can be used as the mobile phase. This implies that FID can conveniently be used as a universal detector, which is in marked contrast with column liquid chromatography where no such detector is available. Sulphur hexafluoride (SF_6) is another non-polar phase which is thought to be especially attractive for SFC-SimDist. While SF_6 allows the use of an FID, some modification (literally "gold-plating") is required. The application of SFC to simulated distillation was first described by Schwartz et al. [41,42]. They showed the potential of SFC to elute samples with a boiling range of 120–760 °C. Although these first results were highly promising, a recent study [43] revealed much lower elution percentages ("recoveries") than expected from the boiling-point data for oil samples rich in aromatics and asphalthenes. Obviously, further investigation to explain and circumvent the latter problem is highly desirable.

3.2. Selective detection techniques used in the oil industry

3.2.1. General

All petroleum samples, from crude oil to refined products, contain varying amounts of compounds containing hetero-atoms. Of these, sulphur and nitrogen are the most important. Sulphur can be present in high concentrations. Depending on the origin of a crude oil, the total concentration of sulphur may vary between less than 0.05 and 14% (m/m) [44]. The combustion of petroleum products containing sulphur compounds leads to the formation of SO_2, which is a major source of air pollution and acid rain. For these reasons, accurate determination of the concentrations and identities of the sulphur-containing species in petroleum products is highly desirable.

In the last 10 years, the efforts to reduce the sulphur content of petroleum products have greatly increased. Sulphur can be removed by hydrogenation, either as an explicit aim in so-called *hydrotreaters* or as a welcome bonus in *hydrocrackers*. The latter process combines a conversion of residue to lighter products (mainly middle distillates, such as kerosine and diesel) with the effective removal of sulphur. The oil industry has a need to determine sulphur contents and distributions both at high (before treatment) and at low (after treatment) concentrations. In order to study and improve sulphur-removal processes, different classes of compounds or individual species must be studied. This calls for speciation, separation and selective detection.

Nitrogen is naturally present in crudes, but at very much lower concentrations (rarely exceeding a few thousand parts per million) than sulphur. Therefore, nitrogen compounds are usually not considered to be a major problem. However, there are situations in which either the total nitrogen concentration or the distribution of nitrogen-containing compounds as a function of (for example) the boiling point needs to be known. Especially in the latter case extremely sensitive element-specific detection will be required.

One process for which both sulphur and nitrogen distributions are relevant is hydrocracking. Both organic sulphur and organic nitrogen species can poison the catalyst used in the second stage of a hydrocracker. The amounts of these species must therefore be greatly reduced during the first stage. Knowledge of the boiling-point range of these species in the feedstock of the hydrocracker and between the first and second stages is essential to establish optimal operating conditions during the first stage.

The most widely used sulphur-selective detection method for GC is flame-photometric detection (FPD). The design of this detector, of which the principle was disclosed as early as 1962 in a German patent [45], dates from 1966 [46]. Detection is based on the formation of excited S_2^* molecules and their subsequent chemiluminescent emission when sulphur compounds are burned in fuel-rich hydrogen/air flames [47]. The emitted light is detected using an optical filter and a photomultiplier. Its simplicity and ease of use are probably the main reasons why FPD is still very popular today, despite a number of important shortcomings. An FPD system suffers from non-linear response for sulphur (linear near the detection limit and approximately quadratic at higher levels). Also, different response factors (in terms of sulphur) may be obtained for different compounds. Finally, FPD suffers from quenching of the sulphur response by co-eluting hydrocarbons and has a limited selectivity over carbon of three orders of magnitude. Two different attempts to overcome part of these shortcomings have been reported. Patterson et al. described a dual-flame approach [48,49].

Because a first flame is being used for sample decomposition, quenching of the light emission in the second flame is being minimized. A radical different approach has been proposed by Amirav and co-workers [50]. Their pulsed-flame photometer detection (PFPD) is based on a flame source and combustible gas flow-rate that cannot sustain a continuous-flame operation. A flame ignited by a continuously heated Ni–Cr wire propagates back to the combustible-gas mixture source and is self terminated after the gas mixture is burned. Depending on gas flows additional ignitions are created in periodic fashion of 1–10 Hz. In addition, the processing electronics are modified to work with pulsed signals. A 10^3-fold increased selectivity as compared to FPD and dual-flame FPD has been reported. Depending on the settings of the parameters available, a choice can be made between either increased sensitivity, or increased selectivity. Today, however, other sulphur-selective detectors are gaining popularity. These will be described in later sections.

For the determination of nitrogen compounds, which usually are present at trace levels, detection methods that meet the sensitivity and selectivity requirements have only recently become commercially available. Nitrogen–phosphorus detection (NPD) was initially devised as a modification of the existing FID by placing an alkali metal salt near the top of a hydrogen–air flame-ionization burner. It thus became known as the alkali-FID (AFID) [51]. The flame-based AFID systems were plagued by stability problems which prohibited their widespread acceptance for GC. More recently, flameless NPD systems (also known as ''thermionic'' detectors) have been developed [52–54]. These detectors have become very popular in environmental analysis but, due to the limited nitrogen-to-carbon selectivity, not in oil and petrochemical analysis. A nitrogen-selective detector that meets the requirements for measuring nitrogen profiles in oil fractions, the chemiluminescence detector, will be discussed below.

3.2.2. (SimDist)-GC–atomic emission detection

In general, selective detectors are used to facilitate the detection of specific compounds in the presence of a high background signal due to other components. However, most of these detectors, including those described above, can only be used to detect compounds containing one or a few specific heteroatoms. This implies that for many applications, including the determination of elemental ratios, two or more selective detectors have to be operated simultaneously. Several groups of workers soon recognized that a detector capable of simultaneously monitoring a large number of elements with a high degree of selectivity and sensitivity would be highly desirable. In atomic-emission spectroscopy, each type of atom produces its own pattern of emission lines. In principle this allows the selective determination of each element. The principle of atomic-emission detection (AED) is based on the spectral emission that occurs when analytes are introduced into a plasma. A plasma, considered by some as a fourth state of matter, is created when a gas is heated to very high temperatures of a few thousand degrees centigrade. In order to obtain a steady state, energy losses have to be compensated by heating of the plasma. In order of increasing efficiency this heating can be done chemically (flame), electrically (fluorescent tube) or electromagnetically. As an example of the last type of heating, an inductively coupled plasma (ICP) obtains its energy from an electromagnetic field induced by an electrical current running through a coil. Even more efficient energy transfer to a plasma can be obtained if the electromagnetic field is generated in a so-called resonance cavity. Here, the plasma is generated in a quartz tube placed in the position where the electromagnetic field strength is maximal. Generally, generators with a frequency of 2450 MHz (microwave) are used and the generated plasmas are therefore referred to as microwave-induced plasmas or MIPs. The higher the excitation energy of the gas used to generate the plasma, the greater is the potential of the plasma to excite other elements. In 1976 Beenakker designed a resonance cavity with a sufficiently efficient energy transfer to generate a helium plasma at atmospheric pressure [55,56]. A helium plasma allows any other element to be ionized. Beenakker's design allowed for ''end-on'' plasma viewing. The small size of the plasma made this MIP suitable for GC detection.The development of plasma detectors, which eventually led to commercially available AED system for GC, has been reviewed by de Wit et al. [57].

The only AED system commercially available today is the Hewlett-Packard/Agilent (Avondale, PA, USA) HP G2350A atomic emission detector which is the successor of the HP 5921 AED system launched in 1990. The HP 5921 AED system uses a MIP generated in a resonance cavity that resembles the Beenakker one, except that it has a pedestal in the centre and a smaller diameter [58]. The light emitted by the plasma is diffracted by a concave holographic grating with a flat focal plane of 35 cm. The diffracted light is detected by a 211-pixel photodiode array that can be moved along the focal plane [59] (Fig. 5). Both systems (HP 5921 and HP G2350A) show excellent performance and have therefore found their way into many laboratories, including those of the petrochemical industry. In the latter case, the use of an AED system in combination with SimDist analysis seemed obvious.

SimDist normally utilizes FID, which gives a signal that is roughly proportional to the carbon content of the column effluent. Replacing FID by AED, however, makes it possible to specifically determine the boiling-point distributions of compounds containing other elements than carbon, e.g., sulphur, nitrogen, or even oxygen. Knowledge of the sulphur distribution of residual oils, for instance, can be useful for the fine-tuning of desulphurization processes, such as hydrotreating. In the microwave-induced plasma of the AED system, sulphur emits a very specific spectrum with a triplet of lines around a central wavelength of 181 nm. Carbon-containing compounds, however, not only give rise to a number of sharp emission lines, but also to a continuous emission across the entire spectrum. Apart from the fact that sulphur-containing compounds usually also contain carbon, in the case of SimDist of oil fractions any sulphur compound is always likely to co-elute with large amounts of hydrocarbons. Although the sulphur emission line at 181 nm is very strong, its selectivity relative to carbon is limited to about 25 due to the carbon interference. The apparent selectivity of AED can be increased about a 1000-fold by using computer manipulation. This is realized by using the PDA to monitor a number of wavelengths around the sulphur triplet. At these wavelengths only the carbon continuum is present. These carbon signals are subtracted from the recorded signal at the position of the sulphur line, after having being weighted with a so-called ‘‘backamount factor’’. This process leads to a much increased selectivity.

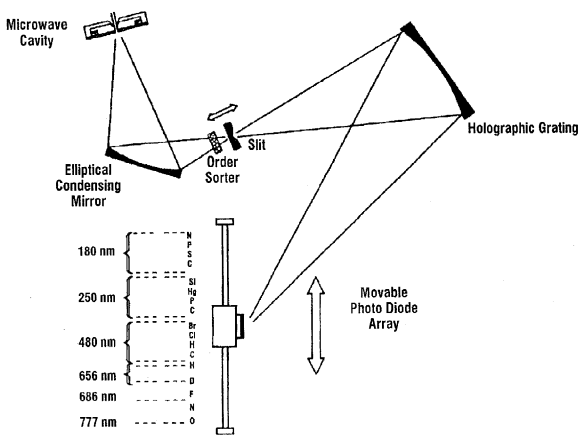

Fig. 5. Optical plan of the photodiode array-based spectrometer used in the HP 5921A GC–AED system.

However, AED software package has a limitation that causes errors in the calculated sulphur distributions. It is due to the fact that the software can only handle one constant sulphur-backamount factor, while in actual practice the continuous background varies substantially with the carbon concentration. In conventional GC this hardly ever is a problem since usually discrete peaks are measured, for which the backamount can be determined in the concentration range of interest. Even if the concentrations of compounds would differ by several orders of magnitude, separate recalculation using the appropriate backamounts for the different levels, would yield correct data for the compounds of interest. In SimDist adequate correction for a variable continuous background is not possible since, in this case, one broad elution profile contains both zones with very high, as well as zones with very low carbon concentrations. Using only one backamount factor for the entire chromatogram will in such a situation result in distorted sulphur distributions. Fig. 6 shows the recorded (uncorrected) sulphur signal of an Ondina oil. Since this medical-quality oil is purely paraffinic and does not contain hetero-atoms such as sulphur, the signal is exclusively due to carbon interference. Ideally, we must be able to correct for this carbon background and obtain a zero signal (flat baseline) by applying the correct backamounts. Clearly this cannot be realized by using one (con-

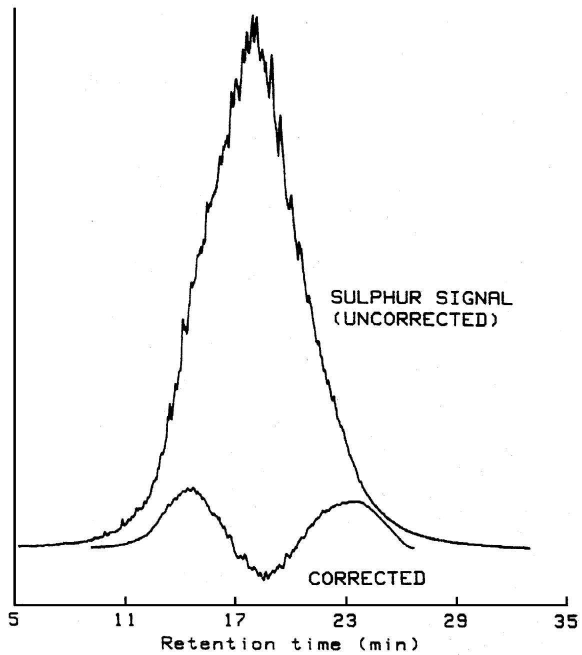

Fig. 6. Sulphur response of an Ondina-68 oil. Effect of backamount correction with one constant factor. (Corrected signal enlarged ×10.)

stant) factor [60]. In other words, AED is less than perfect for determining the sulphur distribution of residual oil fractions. For this reason recourse was taken to another, even more sensitive and more selective detector, despite the extra effort of operating a separate analyser, the chemiluminescence detector, which will be discussed below.

Another interesting application of AED in SimDist analysis is the determination of hydrogen-to-carbon (H/C) ratios. H/C ratios can be used as a yardstick for aromaticity. Although the hydrogen signal exhibits a deviant non-linear behaviour, an effect that has not yet been conclusively explained [57], the AED can still provide useful information on the variation of the H/C ratio across the elution profile of a given sample. Other approaches to obtain similar information will be discussed in Section 3.3 below.

Other applications of GC–AED in the oil industry are based on its capability to selectively detect organo-metal species. Quimby was the first to demonstrate this using an atmospheric-pressure helium plasma generated in a Beenakker TM010 resonance cavity. The performance of the system was described in terms of linearity, selectivity ratios, and detection limits for lead, mercury, and manganese [61]. In a paper preceding the official launch of the HP 5921 AED system, Wylie and Quimby reported the possibility to detect other metals, such as tin, antimony, selenium, nickel, vanadium, copper cobalt and iron [62]. It was much later, however, that the first practical petrochemical applications were reported.

A very elegant procedure for the determination of mercury species in natural-gas condensates was reported by Snell et al. [63]. Measurement of organic as well as inorganic mercury species in these condensates is important, not only because of their toxicity, but also because they can give rise to metal embrittlement when condensates are used as feed for alkylation plants. For direct measurement of the column eluate, the detection limits for mercury species in natural-gas condensate are relatively high because of background interference from carbon compounds present in the plasma at the same time. Carbon compounds give rise to emission that spectrally interferes with the signal from the mercury detector and can overload the plasma, thereby reducing the excitation capability. Mercury can be selectively collected from the column eluate by inserting a so-called amalgamation trap, being subsequently passed to the plasma in a flow of pure helium. By removing the carbon background emission, the trap allows the determination of (various) organo-mercury as well as inorganic mercury species in condensates with detection limits well below 1 μg/l (see Fig. 7).

Attempts to analyse nickel and vanadium porphyrins in crudes were reported by Reiner and Wehman of Exxon [64]. However, for the complete elution of these species the capillary GC column had to be heated to well above its maximum operating temperature. Or, in other words, a new column would have to be used for every next analysis! Rodriguez Pereiro et al. reported the successful determination of several organometallic compounds including tetramethyllead in gasoline. For the latter, an absolute detection limit (ADL) below 50 fg was established [65].

3.2.3. Chemiluminescence

As was already mentioned above, when problems were encountered with AED in determining the

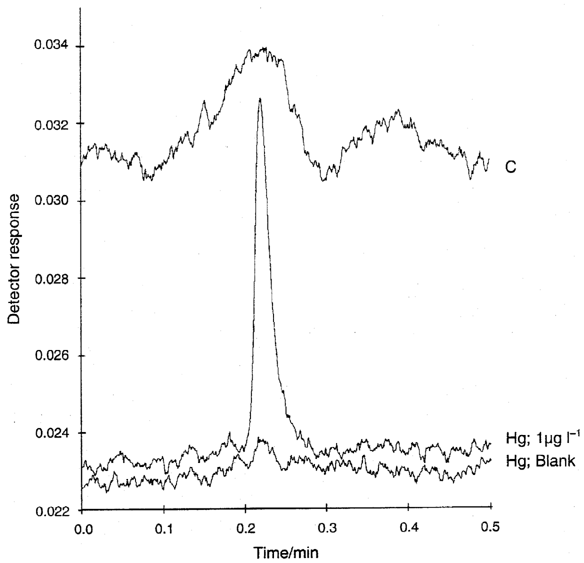

Fig. 7. Amalgamation trap signals for mercury and carbon of a liquid sample of dimethylmercury in condensate and mercury signal of a liquid sample of blank condensate.

sulphur distribution of residual oils, recourse was taken to sulphur-chemiluminescence detection (SCD). For the determination of nitrogen distributions AED was never really considered. The typical total concentrations of nitrogen present in a wide-boiling oil fraction is between 100 and 1000 μg/g, and this amount is distributed over thousands of different compounds. This implies that, to reveal the nitrogen distribution, the sensitivity of a nitrogen-selective detector has to be very high. Moreover, nitrogen-containing compounds have to be detected in an excess of co-eluting hydrocarbons, which calls for a very high selectivity as well. Currently the nitrogen-chemiluminescence detection (NCD) is the only detector having the potential to overcome these restraints.

The basic principles of SCD and the NCD are very similar. Both are based on chemiluminescent reactions with ozone in a low-pressure reaction chamber. For SCD it is the radical SO that gives rise to a chemiluminescent reaction with ozone according to:

$$SO + O_3 \rightarrow SO_2^* + O_2$$

$$SO_2^* \rightarrow SO_2 + h\nu$$

For NCD it is NO, according to:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

The chemiluminescent reaction of SO yields emitted light in the blue and ultraviolet regions of the spectrum (260–480 nm) [66], while that of NO yields radiation from the red to the infrared region (600–3000 nm with a maximum near 1200 nm) [67]. Both SCD and NCD use photomultipliers to monitor the chemiluminescent emission. The main difference between the two detection methods is the way in which SO and NO are generated.

In SCD the combustion of sulphur-containing compounds in a hydrogen-rich (reducing) flame produces a number of different sulphur species including H_2S, HS, S, S_2, SO_2 and the radical SO. The ratios in which these species are formed are affected by the fuel-to-air ratio of the flame [68]. Benner and Stedman noted that SO is one of the major species produced in hydrogen-rich flames and they saw the potential of monitoring SO as a means to create a sensitive detection system for sulphur-containing compounds [69]. The chemiluminescent reaction of SO with ozone to form excited SO_2 was already reported as early as 1966 [66]. SCD combines the two reactions to provide a sensitive and highly selective detector for sulphur-containing compounds. In 1990 Sievers Instruments (USA) launched their first SCD system (Model 350) for use as a GC detector [70]. Fig. 8 shows the chromatograms obtained with SCD and FID from a single injection of a gasoline. Initially they used a probe to sample the gas from FID system, operated under hydrogen-rich conditions. At a later stage, a dedicated ‘‘flameless’’ burner was developed by Shearer et al. This burner consisted of a ceramic tube heated to a typical temperature of, typically, 800–900 °C. Detection limits were lowered by at least one order of magnitude. Detectability of 25–50 fg S/s was routinely achieved [71].

The first successful study on the gas-phase chemiluminescent reaction of NO with ozone was reported in 1970 [72]. Several years later the first NCD system to serve as a GC detector was developed [73]. The effluent of the GC column is

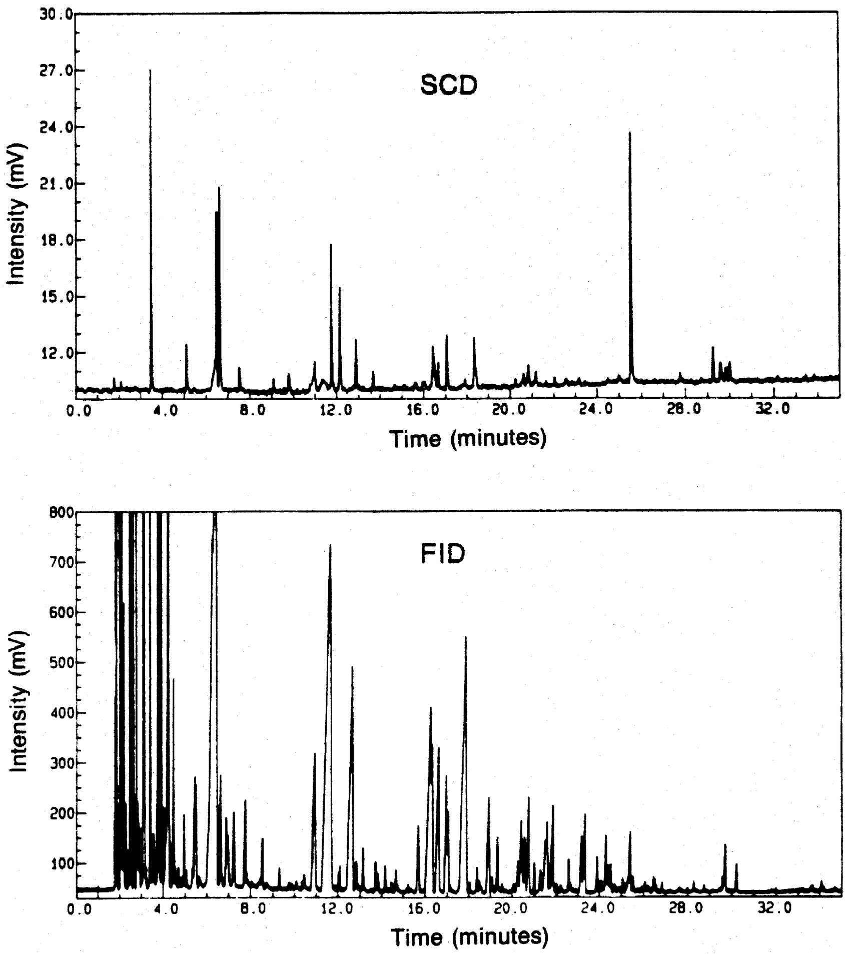

Fig. 8. Comparison of SCD and FID chromatograms obtained from a single injection of gasoline (from Ref. [66]).

mixed with oxygen and led through a nickel pyrolysis tube, which is heated to about 1050 °C. Under these conditions organic-bound nitrogen is converted into NO. Water, formed by the combustion of hydrocarbons, interferes with the chemiluminescence detection and has to be removed before the gas stream enters the reaction chamber. Usually this is done by using a membrane dryer. In the reaction chamber the gas stream is mixed with ozone, which (partly) converts NO to NO_2 in an excited state, NO_2^*.

Both chemiluminescent detectors have detection limits in the low pg/s range and, more importantly, an inherently infinite sulphur-to-carbon or nitrogen-to-carbon selectivity. Fig. 9 shows the schematic of a chemiluminescence detector.

3.2.4. Oxygenates detection using oxygen flame-ionization detection

Because of the need to maintain high octane numbers, without the addition of organolead compounds, oil companies had to change the composition of their motorgasolines (petrol). Alternative compounds that may be used to increase the octane number include aromatics such as benzene, toluene, ethylbenzene and xylenes (BTEX) or oxygenates. Since the levels of BTEX present in modern gasolines are also legally restricted, oxygenates such

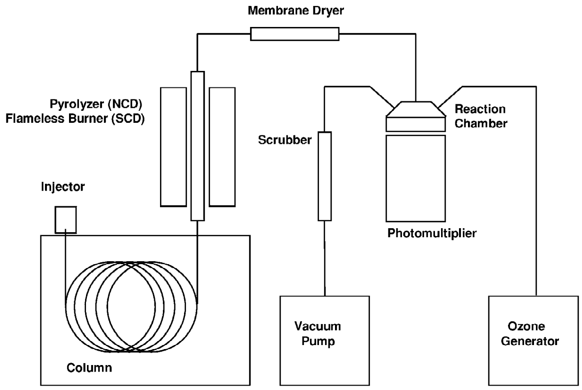

Fig. 9. Schematic of a chemiluminescence detector.

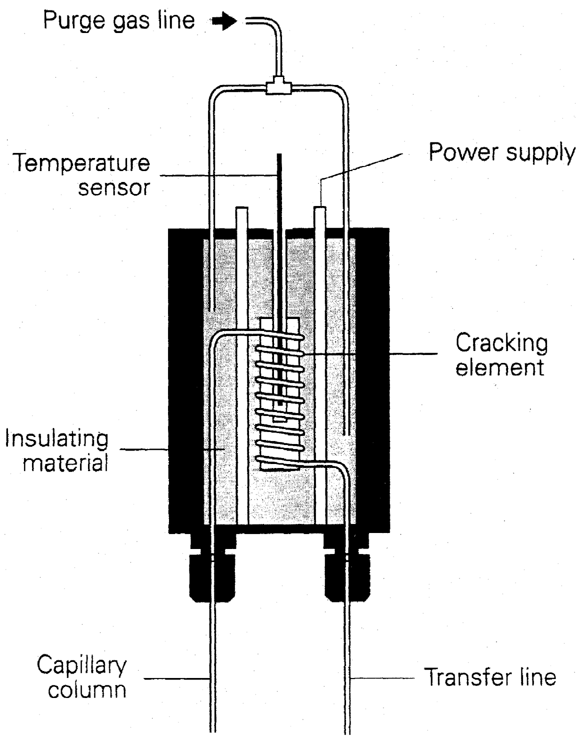

Fig. 10. O-FID micro-cracking device.

as methyl *tert*.-butyl ether (MTBE) and *tert*.-amyl methyl ether (TAME) are now preferred. These compounds possess excellent anti-knock properties. However, the analysis of these oxygenates in complex mixtures, such as reformulated gasolines, posed an analytical challenge. The potential of several analytical techniques, including infrared [74] and nuclear magnetic resonance spectroscopy [75], was assessed. Of course, chromatographic techniques such as column liquid chromatography [76,77] and (multidimensional) GC [78–83] were also considered. Although many of these techniques worked reasonably well, most of them did not allow the detection of all individual oxygenates as required by legislation [84].

In the early 1980s, Schneider and Frohne from Veba Öl published their first papers on oxygen flame ionization detection (O-FID) [85,86]. This detection system consisted of two micro-reactors and a conventional FID system. The first reactor was a high-temperature cracking device (Fig. 10), designed to crack hydrocarbons completely to carbon and hydrogen and to convert any oxygen-containing compounds to carbon monoxide (plus carbon and hydrogen). The second reactor, fitted inside the FID system, was a micro-methanizer for the catalytic hydrogenation of carbon monoxide to methane (Fig. 11). The latter compound was finally detected by FID. In 1987 this system was commercialized by Carlo Erba [87] as the O-FID analyzer and the approach achieved formal status in 1995 as ASTM D5599-95 [88].

Fig. 12 illustrates the potential of the O-FID analyzer in affirming the presence of the oxygenates MTBE and TAME in a suspect racing fuel from 1988. At that time the use of oxygenates as octane boosters in racing fuels was still forbidden!

O-FID was originally designed to analyse oxygenates at levels exceeding about 1% in gasoline. Because gasolines can be separated by means of GC into some 100 peaks, these samples hardly ever cause the upper limit of the capacity of the micro-cracker to be reached. However, the analysis of oxygenates is not restricted to gasolines. Oxygenates are notorious catalyst poisons in many petrochemical processes, and require quantitation down to μg/g levels. The O-FID system has proven unsuccessful for analysing oxygenate impurities down to this level in samples consisting of only one or a few main compounds. Even when using split injections, the capacity of the micro-cracker is easily exceeded during the elution of a main compound. Exceeding the capacity of the micro-cracker results in the

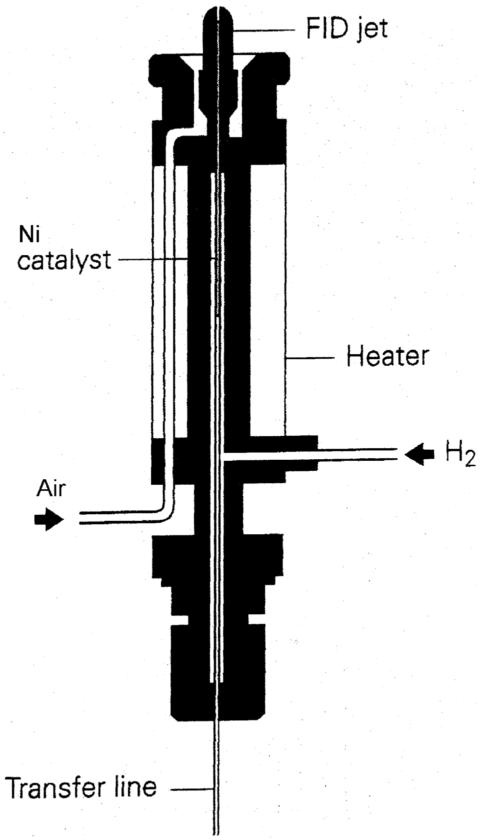

Fig. 11. O-FID micro-methanizer.

breakthrough of non-cracked hydrocarbons, which gives rise to strongly tailing peaks on the FID signal. These peaks obscure the signals of low levels of oxygenates during a considerable part of the GC run. In order to circumvent these problems a Deans' switch was installed, which allowed the micro-cracker to be bypassed (J. Blomberg, unpublished results, 1989). The system was automated by using parallel injections on two (identical) columns, one leading to the O-FID system, and the other (running some 10 s ahead) to the FID system. The signal from the FID system is used to actuate the Deans' switch whenever it reaches a predetermined level.

3.2.5. Mass spectrometry

Next to GC, the petroleum industry has also pioneered the use of mass spectrometry (MS). In fact, the first commercial mass spectrometer manufactured by Consolidated Engineering Company (CEC) was delivered to the Atlantic Refining Company in 1946 for the analysis of hydrocarbon fractions in the gasoline boiling range [89]. In early MS analysis, the whole sample was introduced into the ion source of the MS without prior chromatographic separations, although fractionation into saturate and aromatic fractions prior to MS analysis was usually necessary. After the introduction of double-focussing high-resolution (HR) MS, accurate mass measurement allowed elemental composition of individual ions to be determined. Hence, distributions of compound types and carbon number within each compound type could be obtained without prior fractionation into saturates and aromatics. However, this method could not distinguish between isomers having identical chemical formula. Since many of these isomers are readily separated by GC, coupling of GC to MS became a logical option for even further improving complex mixture analysis [90].

Of all the ionization techniques devised for the production of ions for MS analyses, electron ionization (EI) is the most widely applied. Although EI generally yields highly informative, fragmented spectra, the nominal electron energy of typically 70 eV (existing spectral catalogues contain mass spectra obtained with 60–80 eV electrons) is too high to yield parent ions for hydrocarbons (typical ionization potential 13 eV). In some analytical applications lowering the nominal electron energy to 14 eV has shown a high percentage of the total ion current in the molecular ion, but only at the cost of a dramatic decrease of absolute intensity. Furthermore, EI hardly distinguishes between structural isomers because their spectra are almost identical. It is for this reason that non-fragmenting MS techniques, i.e., those using soft ionization, are generally preferred. Field ionization (FI-MS) is the technique most widely used and, today, a technique almost exclusively used in the oil industry. The first quantitative and comprehensive investigation on FI-MS was published in 1954 by Inghram and Gomer [91]. In an FI source, a very high positive electric field (107–108 V/cm) is produced by a sharp blade or thin wire held at a high positive voltage (7–10 kV) with respect to the first slit. The electric field induces electron tunneling through a potential energy barrier in the molecule and the resulting positive ion is accelerated out of the source and into the MS analyser. The energy avail-

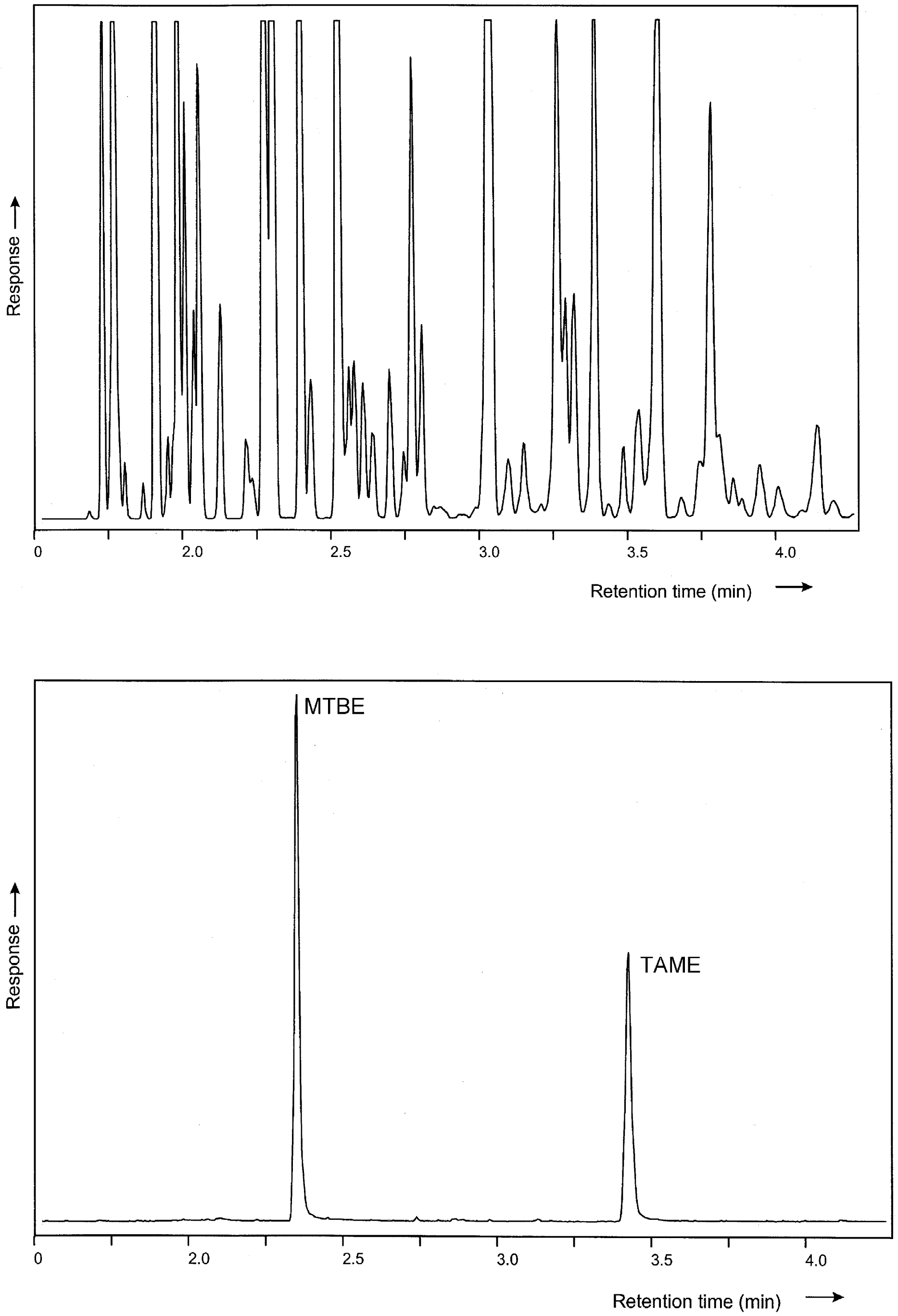

Fig. 12. FID signal (top) and O-FID signal (bottom) of a suspect 1988 racing fuel.

able for FI and subsequent excitation of a molecule is generally about 12–13 eV, leaving very little excess energy in the parent ion to cause fragmentation. Several authors have reported methodologies for the compositional analysis of hydrocarbons [92–94]. FI-MS is often used as a stand-alone technique, or off-line coupled to other chromatographic methods. Hydrocarbon types are classified by their carbon number, n, and their hydrogen deficiency or Z number, defined by the general formula, C_nH_{2n+Z}. Fig. 13 presents a typical three-dimensional display of a FI-MS analysis.

A more recent development in MS uses a so-called Townsend discharge (TD) as ion source [95]. Daishima et al. were the first to report mass spectra obtained for substituted benzenes and alkenes for isomeric distinction using TD nitric oxide chemical ionization (TDNOCI) [96,97]. More recently Dzidic et al. [98] reported the first successful use of GC-TDNOCI for the hydrocarbon-type analysis of middle distillates. Unlike FIMS their approach allowed the determination of the distribution of types within specified boiling ranges. The use of GC allowed the separation of sulphur-containing compounds from aromatics of the same nominal molecular mass and even some additional differentiation of compound structures with the same Z number. The method was successfully applied to study changes in the hydrocarbon composition of feedstocks and their hydrotreated products.

The applications described thus far were all developed with the aim to obtain full-quantitative compositional data. However, if we want to use MS as a quantitative detection method, we should realize that the linearity observed for MS detection is much less than that of FID, causing the dynamic range to be rather modest. This makes it difficult to quantify components of greatly varying concentrations (as are invariably present in hydrocarbon mixtures) in a single chromatogram. An even bigger problem associated with the application of GC–MS in this area, involves the calibration of the instrument. The response will vary for different analytes, even within groups of similar chemical structure, making the calibration a horrendous task [99]. And although GC–MS has been advocated as an alternative to GC–FID for the so-called detailed hydrocarbon analysis (DHA, see Section 3.1) [26], and peak assignments are much more reliable than when using retention times only, our personal experiences with

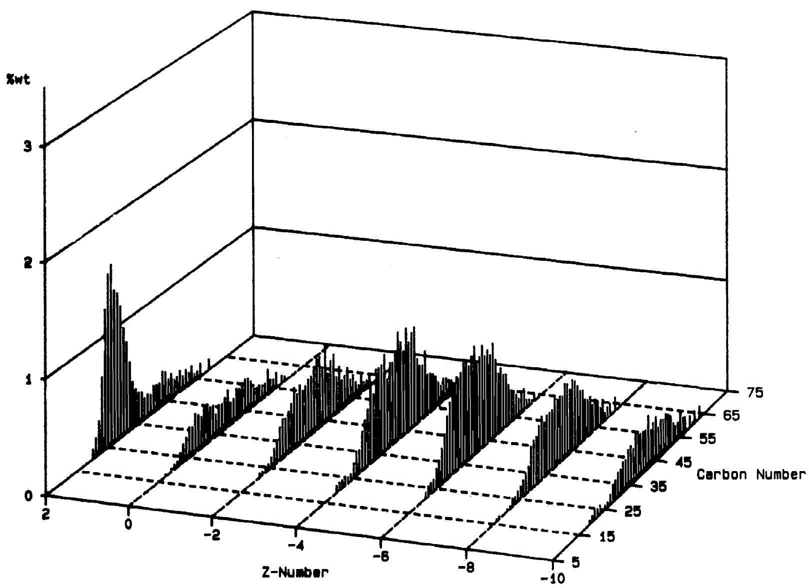

Fig. 13. Three-dimensional display of a FI-MS analysis of an oil sample. Z number 2 represents the alkanes, 0 the mononaphthenics, –2 the dinaphthenics, –4 the monoaromatics, –6 the mononaphthenic monoaromatics, –8 the dinaphthenic monoaromatics, and –10 the diaromatics.

the quantitative results obtained using this method are rather disappointing [99]. Clearly, for quantitative analysis, the way forward for these types of analysis is to achieve a much better separation in a shorter time, while maintaining FID as the best quantitative detection principle. This strongly suggests the use of GC×GC (see Section 3.4).

Target-compound analysis, however, is an application area where GC–MS has proliferated, generally speaking, but also within the petrochemical industry. Target-compound analysis is one of the strongest assets of GC–MS, and has been extensively used in petroleum organic geochemistry. Petroleum geochemisty applies chemical principles to the study of the origin, migration, accumulation and alteration of petroleum, and uses this knowledge in the exploration and production of oil and gas. The target compounds studied are hydrocarbon molecules that have retained the basic carbon skeletons of organic material originally present in ancient living organisms that underwent physico-chemical transformations during the geological history of a sedimentary basin. These compounds, known as biomarkers, can be divided into several classes, such as isoprenoids, triterpanes and stearanes (see Figs. 14 and 15). The distribution of these biomarkers provides information about the source, as well as the level of maturity, age, migration and alteration of the petroleum [100].

3.3. Coupled-column techniques

3.3.1. PIONA (Paraffins, Isoparaffins, Olefins, Naphthenics, Aromatics)

As was mentioned in Section 2.2, the PIONA analyser of Boer et al. [15] led to the development of a commercially available instrument [101] which is still in use in most of the refinery laboratories in the world for the compositional analysis of gasolines and naphthas.

Fig. 16 shows a schematic diagram of the PIONA analyser. After injection, the sample is first separated on a high-polarity column into non-aromatics with boiling points below 200 °C and aromatics plus non-aromatics with boiling points above 200 °C. The latter are eluted in three fractions which are intermediately trapped for subsequent re-injection onto a non-polar column for boiling-point separation. The non-aromatics with boiling points below 200 °C are transferred to an olefin trap where the olefins are adsorbed and the saturates are led to an *n*-alkane trap which consists of molecular sieves with a pore size of 5 Å. The effluent of this trap is transferred to the

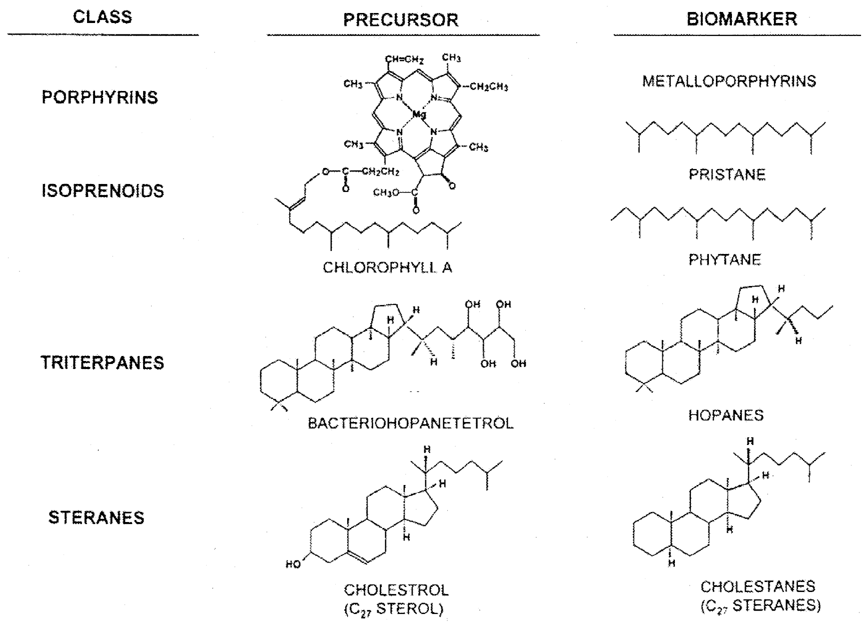

Fig. 14. Typical biomarkers sorted according to chemical class and origin.

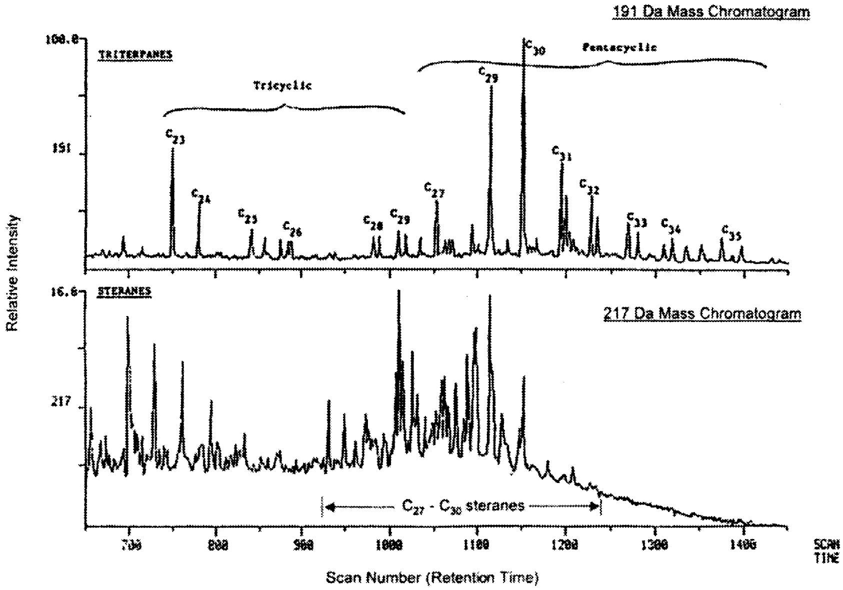

Fig. 15. Selected-ion chromatograms of a crude-oil, revealing the triterpanes and stearanes.

molecular sieves 13× column for subsequent separation into naphthenes and iso-paraffins according to carbon number. After that, the *n*-alkanes left on the *n*-alkane trap are desorbed by heating and also separated by the 13× column. Finally, the contents of the olefin trap are released by heating, hydrogenated in a hydrogenation section and transferred to the *n*-alkane trap, after which they are separated in the same way as the original saturates into straight, branched and cyclic species. A typical chromatogram obtained in this manner is presented in Fig. 17.

3.3.2. Capillary GC–GC

Packed multi-column systems using valve switching have been used successfully for many years. Packed-column systems with valve switching are simple, inexpensive, versatile and easily maintained. In recent years, however, packed columns have been gradually displaced by capillary columns, not only in single-column, but also in coupled-column systems. While packed columns allow for the use of mechanical valves for switching effluent from one column to another, the use of such valves in capillary-column applications is more problematic. None of the materials used for the manufacturing of mechanical valves presents an ideal surface for GC. This can result in adsorption and memory effects, especially when dealing with very small volumes as in capillary GC. Furthermore, the sealing materials used in mechanical valves can pose temperature

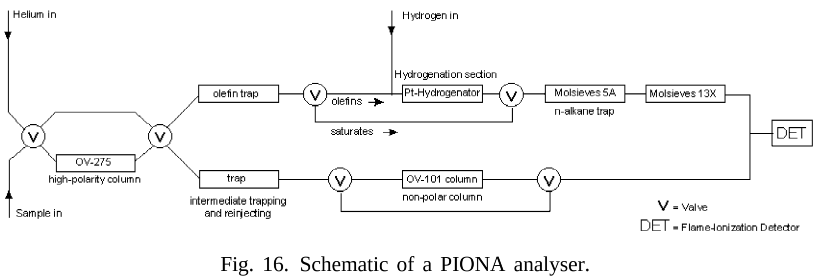

Fig. 16. Schematic of a PIONA analyser.

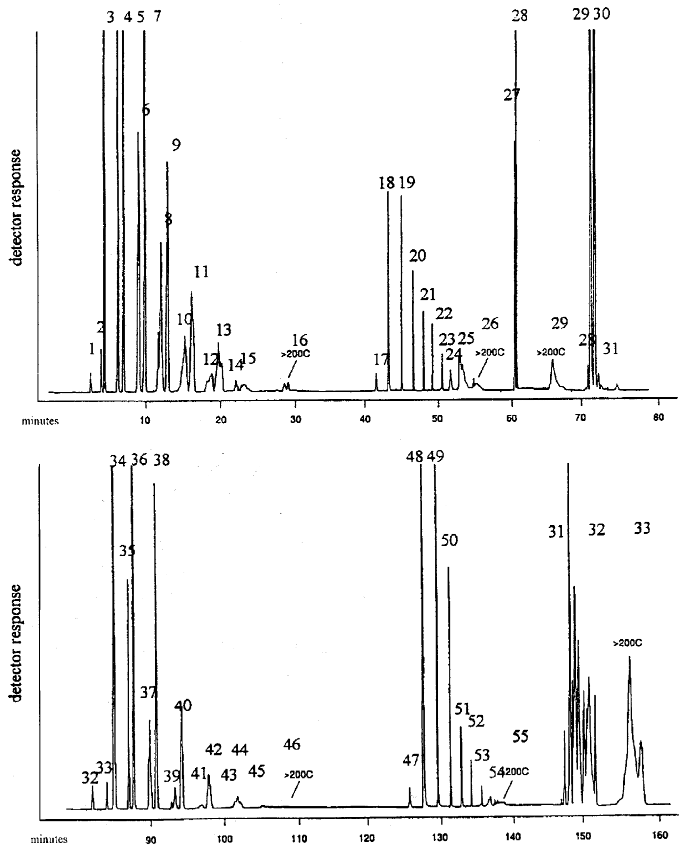

Fig. 17. Chromatogram of a light naphtha separated with the PIONA analyser. Courtesy: D. Grutterink, Analytical Controls B.V.

restrictions. It is for these reasons that in multi-dimensional capillary systems pneumatic or ''live'' switching, originally developed by Deans [102,103], is now commonly used. Early multi-column systems using Deans' switching were commercialized in 1985 by Analytical Controls (AC, Rotterdam, The Netherlands) as a retrofit to Hewlett-Packard's model HP5880 GC which still used a packed column in the first dimension. This system was successfully applied in the laboratory of the author(s) for the analysis of monoethylene glycol (MEG) in natural-gas condensates (Fig. 18). This system was still inadequate for using capillary columns throughout, because of the unavailability of inert, low-dead-volume couplings, leading to similar problems as encountered with mechanical valve-switching. In this respect the invention of the all-glass Press-Fit connectors by Pretorius and co-workers [104] was a genuine breakthrough. Grob and Schilling [105] were the first to recognize the full potential of these connectors and they started to produce them. The first specimens of commercially available effluent splitters based on this system were proudly demonstrated by vendors and treated as gems. Later the AC system was sold by Chrompack under the acronym MUSIC, which stands for Multiple Switching Intelligent Controller. In 1990 such a device was retrofitted in a dual-oven system constructed out of two MEGA 5300 Series HRGC instruments (Carlo Erba/Fisons, Milan, Italy) (J. Blomberg, unpublished results, 1990). After successful implementation of a Press-Fit Deans' switch in the GC–O-FID system (see above) it was decided to replace the original AC connectors using the original bracket to make connections inside the oven. A similar approach was presented by Ibanez in 1993 [106].

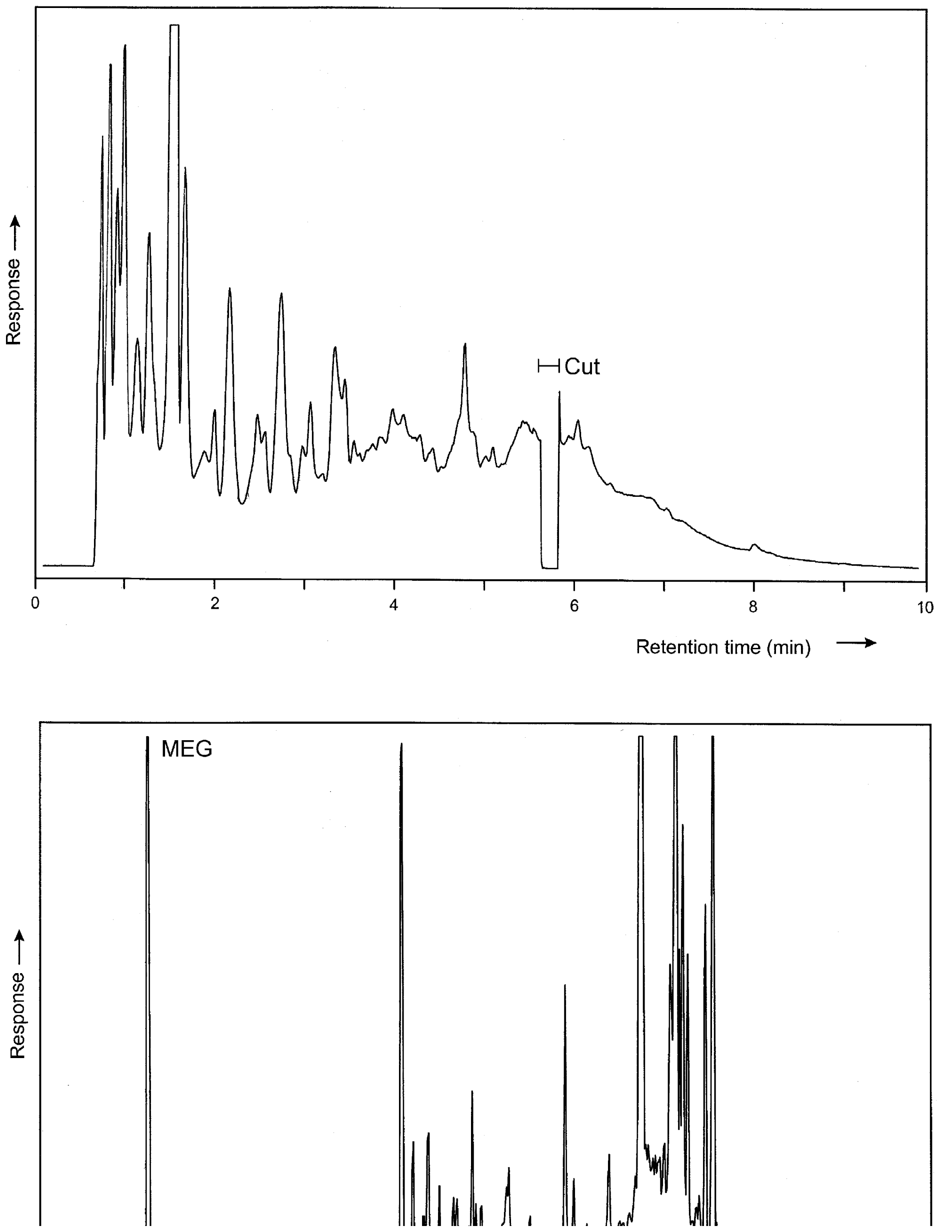

Fig. 18. GC–GC analysis of MEG in natural-gas condensate. Top: first-dimension column; polar, packed. Bottom: second-dimension column; non-polar, capillary. Courtesy: D. Boon, Koninklijke/Shell-Laboratorium, Amsterdam.

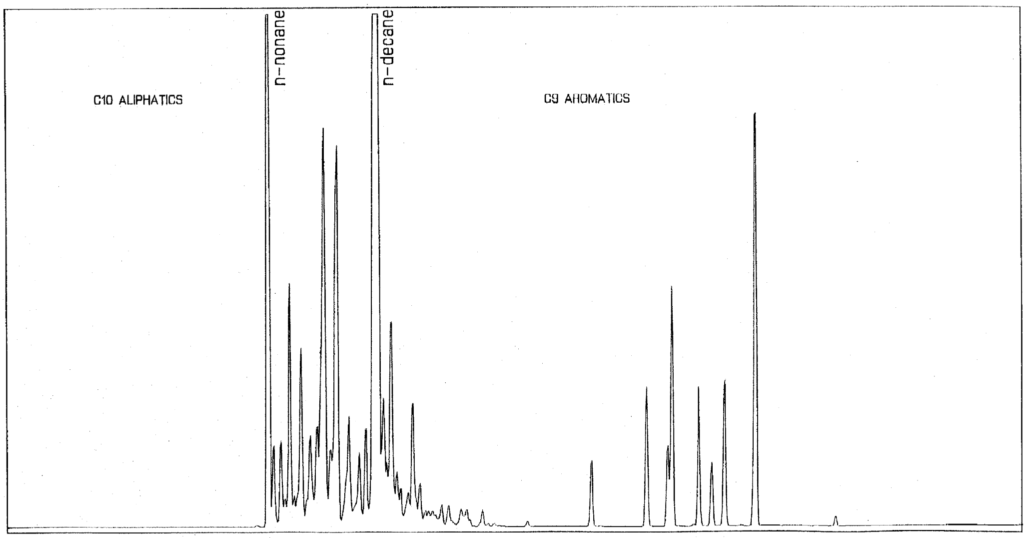

Fig. 20. Second-dimension separation of the eight possible isomers of C3-substituted benzene.

3.3.4. Size-exclusion chromatography–GC

A well-known problem in high-resolution gas chromatography (HRGC) is the analysis of mixtures consisting of both relatively volatile and high-molecular-mass material. The latter material tends to cause serious fouling problems in the introduction system of the GC. Size-exclusion chromatography (SEC) beautifully fits the purpose of selective removal of high-molecular-mass material from the volatile fractions which can be readily handled by GC. On-line coupling of conventional SEC and HRGC is not straightforward. In order to avoid ''LC interactions'', which disturb pure size-exclusion-based separations, relatively polar solvents have to be used. The most frequently used solvent for SEC of polymeric material is tetrahydrofuran (THF). Since polar solvents show poor wettability properties when introduced in retention gaps, the classical on-column technique [122] cannot be used for the introduction of relatively large fractions (500 μl) into the GC system. A loop-type interface [121] is a more suitable transfer device. The use of this technique has one drawback: solutes eluting within 120–150 °C above the transfer temperature are lost for quantitative determination. This drawback can be overcome by using co-solvent trapping [125], which is similar to the procedure described by Grob et al. for the transfer of water or water-containing mixtures to GC systems [126–129]. As a result of the minimum column temperature required for concurrent solvent evaporation of THF (ca. 100 °C), *n*-decane was found to have suitable co-solvent properties (boiling point, wettability) for the applications described.

3.3.5. Size-exclusion chromatography–NPLC–GC

An on-line coupling of SEC, NPLC and GC was recently reported by Blomberg et al. [130]. This orthogonal three-dimensional chromatographic system allows the characterization (according to volatility) of restricted (according to size) and selected (according to polarity) fractions of highly complex hydrocarbon mixtures. The use of size exclusion as the first separation step allows the injection of the complex samples without prior clean-up. The seemingly incompatible separation modes, SEC and NPLC, were successfully coupled using an on-line solvent evaporator based on a modified loop-type LC–GC interface and co-solvent trapping [125]. Complete reconcentration of the analytes was effected by the insertion of a cryogenic cold trap. For the subsequent hydrocarbon group-type separation an amino-modified silica column was used (cf. above). The NPLC–GC coupling was based on an on-column interface. Initial results for the analysis of a residue from an atmospheric crude-oil distillation, a so-called long residue, were presented as an example of the impressive separation power of the SEC–NPLC–GC approach (Figs. 21 and 22).

3.4. Comprehensive two-dimensional separations

3.4.1. GC×GC

When using the coupled-column multidimensional techniques described so far, only a part of the first-dimension separation is subjected to a second separation step. The modest increase in resolution can be written as the sum of the peak capacities of the first (n_1) and the second (n_2) separation step:

$$n_{cc} \cong n_1 + n_2$$

This is in sharp contrast to (true) two-dimensional (2D) planar systems, such as 2D thin-layer chromatography (TLC) [131], chromatography with a 2D column [132] or 2D gel electrophoresis [133]. The increased resolving power of these planar 2D systems can be formulated in terms of the enhancement of peak capacity. If the peak capacity along the x-axis is n_z and along the y-axis n_y, the total peak capacity of the 2D plane will be approximately:

$$n_{2D} \cong n_x \times n_y$$

Whereas 2D-TLC yields peak capacities of typically 100–500, and 2D column chromatography of up to 1000, 2D electrophoretic techniques provide much larger peak capacities of several thousands. This would require tens of millions of theoretical plates if produced in a one-dimensional system. The importance of this magnitude of gain was recognized and emphasized by Giddings when he compared coupled-column and 2D planar systems [134]. Around the same time he developed the concept of a

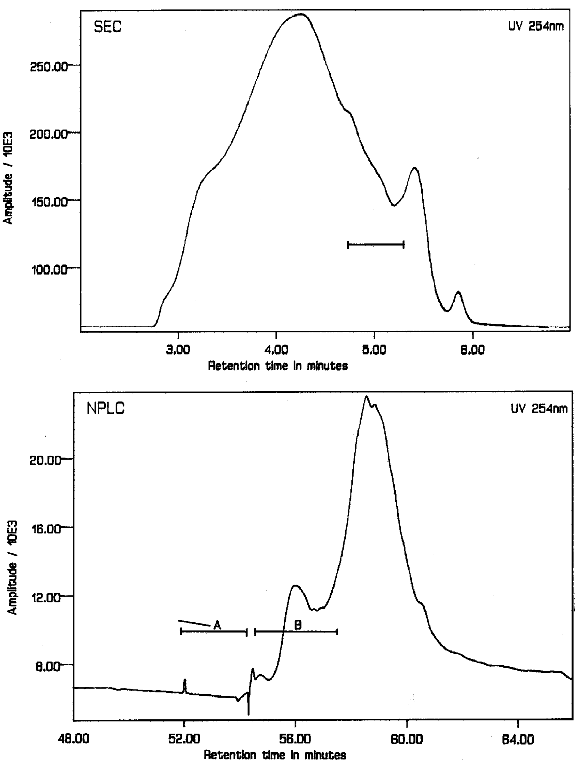

Fig. 21. SEC (top) and NPLC step (bottom) of an on-line SEC-NPLC–GC analysis of a long residue. (A) Aliphatic fraction, (B) aromatic fraction (fractions indicated by brackets).

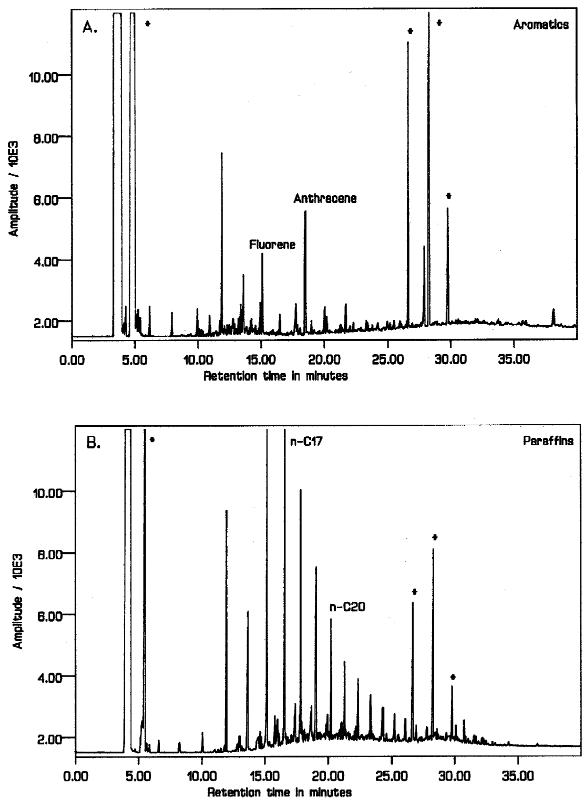

Fig. 22. Gas chromatograms of an on-line SEC-NPLC–GC analysis of a long residue. (A) Aromatic fraction, (B) aliphatic fraction (see Fig. 25 for transferred fractions).

new parameter. He concluded that the effectiveness of enhanced peak capacity in resolving large numbers of components strongly depends on whether the distribution of the component peaks is ordered or disordered. Peak overlap is common in disordered distributions. Statistics show that separating 98 out of 100 randomly distributed peaks requires a peak capacity of 10 000. Separating 100 evenly spaced peaks by definition requires a peak capacity of only 100. Because the peak capacity of a column increases only as the square root of its length, separating 98 out of 100 randomly distributed peaks will take a 10^4 times longer column and run time than separating the same number of regularly spaced peaks. This makes it clear that ordered chromatograms are highly desirable. Certain samples, such as mixtures of *n*-alkanes, produce ordered chromatograms. If regular variation in the molecular structures of mixture components (carbon number in the case of *n*-alkanes) induces regular variation in a molecular property to which the chromatographic system responds (volatility in the case of a non-polar GC phase), regularity in the chromatogram is ensured. This idea can be generalized: if the components of a mixture vary independently in several specific ways (e.g., size, polarity and shape), separating them independently in those same ways will produce an orderly multidimensional chromatogram. The possibility of inducing order in multidimensional chromatograms implies that multidimensional peak capacity can be used far more efficiently than one-dimensional peak capacity. This is in addition to the normal gain in resolving power resulting from the increased peak capacity. Giddings then assumed that the underlying difference between ordered and disordered distributions of component peaks in separation systems is related to sample complexity as measured by a newly defined parameter, *sample dimensionality*. He concluded that the type and degree of order and disorder is determined by the sample dimensionality in relation to the dimensionality of the separation system used.

Although Giddings first presented these ideas in 1987 [135], he did not officially publish them until 1995 [136]. It was around that time that Phillips et al. published the first results obtained with the GC (near) equivalent of a 2D planar separation which amazingly confirmed Giddings' assumptions on sample dimensionality. Phillips named this breakthrough technique *comprehensive two-dimensional gas chromatography* (C2D-GC) [137], emphasizing the potential of the system to examine the entire effluent in a three-dimensional, hence comprehensive, fashion. Later, the acronym C2D-GC was changed into GC×GC, first to avoid confusion with the already existing heart-cut 2D-GC (GC–GC) techniques, but mainly to emphasize the multiplication aspect of peak capacity enhancement [138].

In GC×GC, two independent GC separations are applied to an entire sample. The sample is first separated on a high-resolution capillary GC column in the programmed temperature mode. Using a device called a thermal modulator (see Section 3.4.2), fractions of effluent from this first column are focused at regular, short intervals and injected onto a second capillary column which is short and narrow to allow very rapid, isothermal, separations [139]. The resulting chromatogram can be represented as a two-dimensional plane from which the peaks emerge. One dimension of this plane represents the retention time on the first column, the second dimension represents the retention time on the second column, and the third dimension the signal intensities. The most convenient way to represent a GC×GC chromatogram, however, is as a two-dimensional contour plot, and this is done almost invariably in the literature (for examples see below). GC×GC separations offer extremely high peak capacities, values of over 50 000 already having been reported [140].

In contrast to GC–GC, GC×GC fulfils Gidding's definition of a truly multidimensional system. Retention in GC is basically covered by two factors, the volatility of the analyte (pure-compound vapour pressure, p_i^{o}) and its interaction with the stationary phase (activity coefficient at infinite dilution, γ_i^{∞}). By selecting a non-polar column for the first dimension, this separation is based on the volatility of the analytes (''boiling-point separation''). All analytes will elute from the first column at different temperatures, but with very similar volatilities at the time of elution. The second separation, which is so fast as to be essentially isothermal at the elution temperature from the first-dimension column, is completely determined by the activity coefficients. Both enthalpic (energy of interaction) and entropic factors contribute to $\gamma_{\mathrm{I}}^{\infty}$, so that the separation on the second column can be based on polarity, molecular geometry, size, etc. [141]. That is, the separations in the two dimensions can be made completely independent of each other, or *orthogonal*. Because of the orthogonality of the two separation mechanisms, a very substantial fraction of the theoretical peak capacity, n_{2D}, can actually be used in practical separations [142]. The ability to create ''order'' in a chromatogram, however, probably is an even stronger asset of GC×GC [143]. Compounds can readily be sorted according to chemical or molecular functionality, structure or shape, which makes identification reliable and relatively easy.

3.4.2. Principle and application of modulation

It is common to think of a chromatogram as a series of signals and to use signal processing techniques to extract information from it. The chemical processes occurring within the column are traditionally thought of in terms of physical transport of substances rather than in terms of signals carried by these substances. Phillips [144] was one of very few scientists [145] to realize that moving chemical concentrations carry information and, therefore, behave like signals in the column. Although chemical signals differ from others in their physical form, they are just as truly signals as the more familiar ones and may therefore be treated by the same information and communication theory mathematics and by the derived signal processing techniques. In this context the detector is not the information source, but merely a chemical-to-electronic transducer, changing the physical form of the signal. The chemical information must be encoded (modulated) in order to yield meaningful data from this transducer. The column is a signal processor and can be thought of as a dispersion device for chemical signals,[1] just as a monochromator is a dispersion device for electromagnetic signals. In conventional chromatography the encoding (modulation) of the chemical signals is a direct result of the sample introduction and the modulation signal has the form of an injection pulse. The desired information-carrying signal, the analytical signal, is already present in the chemical identity and concentration of the sample. These two signals, modulation and analytical, are multiplied by the modulator to give a composite chemical signal, which contains the information of the analytical signal, but has the form of the modulation signal. Demodulation is a signal-detection problem. Since several chemical signals are travelling through the column at the same time, more than one copy of the modulation is present in the detector-output signal. Each of these copies has its own phase shift with respect to the modulation signal source and its own amplitude. The demodulation process consists of finding each of these copies of the modulation signal and for measuring its amplitude. Plotting signal amplitude as a function of the phase shift yields the chromatogram. Restricting modulation to only a single sharp pulse makes demodulation a unit operation which may therefore be ignored. When more general modulation signals are being used, however, demodulation is required to reveal the information carried by the analytical signal.

Phillips studied the possibilities of retention alteration (modulation) in chromatography since the early 1980s. These included electrochemical modulation for LC [146] and thermal modulation for LC [147] and GC [144]. The idea of deliberately using thermal gradients as a means of retention alteration (modulation) was triggered by the observation of the ''christmas-tree effect'' (J.B. Phillips, Carbondale, IL, personal communication, May 1995). This peak-splitting phenomenon manifests itself when fused-silica capillary columns are used in GC ovens originally designed for packed columns. In these older types of ovens, temperature gradients in the order of several degrees centigrade are no exception. This causes analytes to be alternately being slowed down and accelerated as they migrate through the windings of the column [148]. The consideration that such small temperature differences already show such a pronounced effect spurred Phillips to use temperature gradients to effect chromatographic modulation. A thermal modulator can be regarded as a device that controls the temperature of a short section of the chromatographic column as a function of time and/or position. As the stationary phase is heated and cooled, it alternately releases compounds to and extracts them from the mobile phase. Sample components can thus be accumulated and focussed into a

[1] Note: this is not ''*dispersion*'' in the conventional chromatographic sense; chromatographers would call this *separation*.

sharp concentration pulse, which subsequently can be launched into a column or detector.

Thermal modulation on fused-silica columns was first applied to multiplex gas chromatography [144]. The thermal desorption modulator (TDM) consisted of a short section of column painted which a thin layer of electro-conductive paint. Headspaces of liquid samples were continuously fed through the column. On command from a pseudo-random number algorithm signal source, electrical currents were led through the layer of conductive paint, which caused a rapid heating of the column and the release of the substances held by the stationary phase in the form of concentration pulses. Later, TDMs proved equally useful as an injection device for high-speed chromatography [149–151]. In that case, TDMs consisting of two stages were applied. One section served to accumulate the sample, and a second to generate sharp injection pulses. When it was realized that TDMs can continuously generate fast chromatograms sampled from a flowing stream, and that the output from a slower GC column can just as well serve as a suitable sample stream, comprehensive two-dimensional gas chromatography was born [152,153] (see Fig. 23).

Several papers on this two-stage TDM approach followed [154], which emphasized separation orthogonality [155]. These early TDMs, however, were far from robust: the thin-film modulators burned out far too frequently [156,165]. Attempts were made to construct more robust wire-coiled TDMs. Reliable thermal modulation was achieved but either at the expense of sluggish thermal response [157] or of unsurmountable mechanical difficulties and safety issues [156].

Realizing that adding thermal mass to the column was a step in the wrong direction, Phillips decided to heat and cool the modulation capillary by mechanically applying and removing a heat source. This led to the development of the so-called ''sweeper modulator'' which uses a slotted heater block that rotates over the modulation capillary by means of a computer-controlled stepper motor [159] (see Fig. 24).

Following a study on the cryogenic trapping of solutes during elution in capillary GC [160], Marriott and co-workers developed an alternative. Instead of applying and removing a heat source, the longitudi-

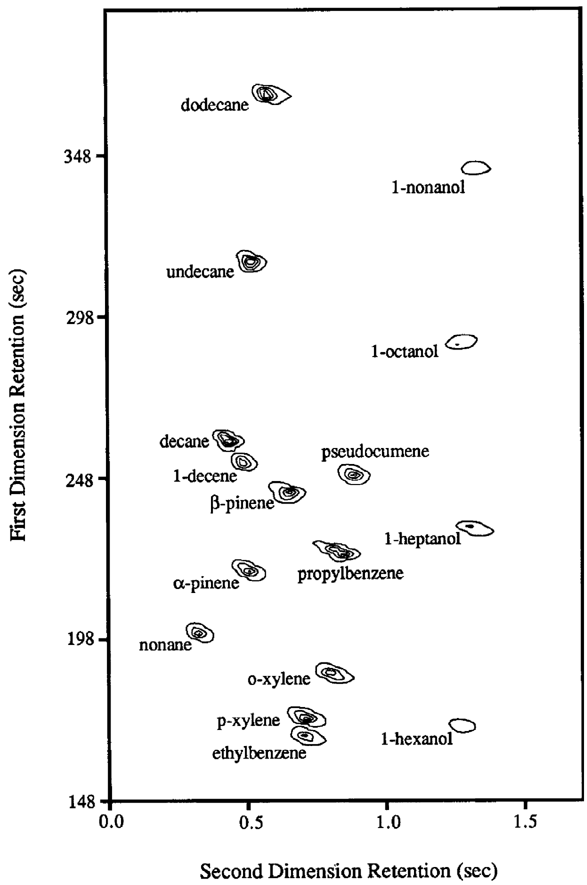

Fig. 23. Example of an early GC×GC experiment [158].

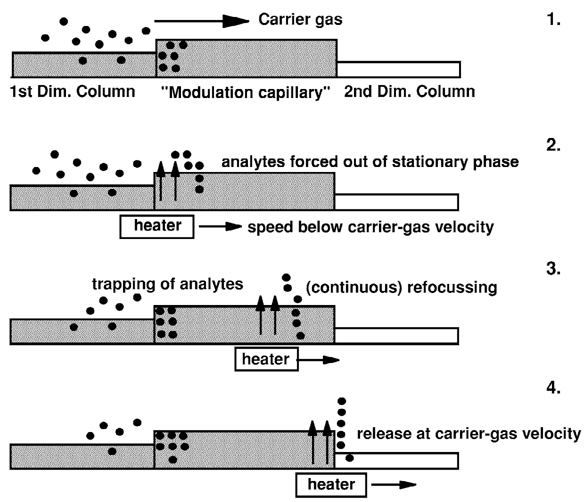

Fig. 24. Schematic of ''sweeper'' modulator [159].

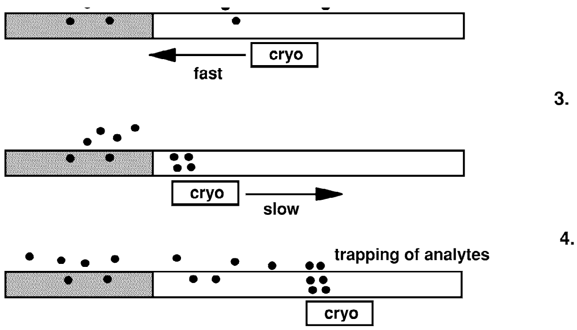

Fig. 25. Schematic of the longitudinally moving cryogenic modulator [162].

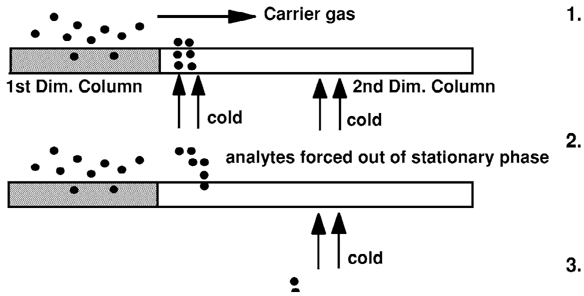

Fig. 26. Schematic of the jet modulator [167].

nally modulating cryogenic system (LMCS) uses a miniature cold trap which moves up and down the modulation region [161–163] (see Fig. 25). An interlaboratory study has shown that the thermal sweeper and the cryomodulator produce equivalent results [164]. However, it is to be expected that the LMCS approach will extend both the high and the low volatility ends of the method further than the thermal sweeper approach. The cryomodulator can also be used for heart-cut GC–GC, which makes the LMCS approach even more flexible [165].

The most recent development, called the jet-cooled thermal modulator, has no moving parts at all [166]. By alternately pulsing cold and hot jets of gas onto a modulator capillary [166], or even more simply, only using cold jets [167] (see Fig. 26), two-stage thermal modulation can be obtained without the complexity of moving parts being present in the close vicinity of the capillary columns. This approach led to the first modest attempts to realize Phillips' ultimate dream experiment: GC×GC×GC [168].

3.4.3. Potential and limitations of GC×GC

Clearly, the oil and petrochemical industries stand to benefit from the development of extremely powerful separation techniques. A great variety of oil products and process streams needs to be analysed and the required information is increasingly detailed. Actually, there are four major advantages of GC×GC [165,169]:

(1) It provides highly detailed, readily interpretable images of very complex samples.

(2) It allows a complex sample to be separated into (very many) individual peaks. These peaks can readily be classified into groups, creating a viable alternative for group-type analyses (Fig. 27).

(3) It provides superior resolution and increased sensitivity relative to conventional GC. This allows the accurate determination of low concentrations of specified components in a complex mixture.

(4) It may provide boiling-point distributions for many different classes of compounds (e.g., saturates, olefins, mono-aromatics, di-aromatics) simultaneously, thus massively increasing the amount of information generated per unit time.

Currently, the scope of commercially available sweeper systems is still somewhat limited. Highly volatile solutes are hard to focus between the two separation columns. Non-volatile (''heavy'') solutes require temperatures exceeding the current possibilities of the hardware (column, modulator). GC×GC is already approaching its optimum performance for C_{10}–C_{16} hydrocarbons, i.e., the middle-distillate (diesel, kerosene, jet fuel) range [170]. This is of

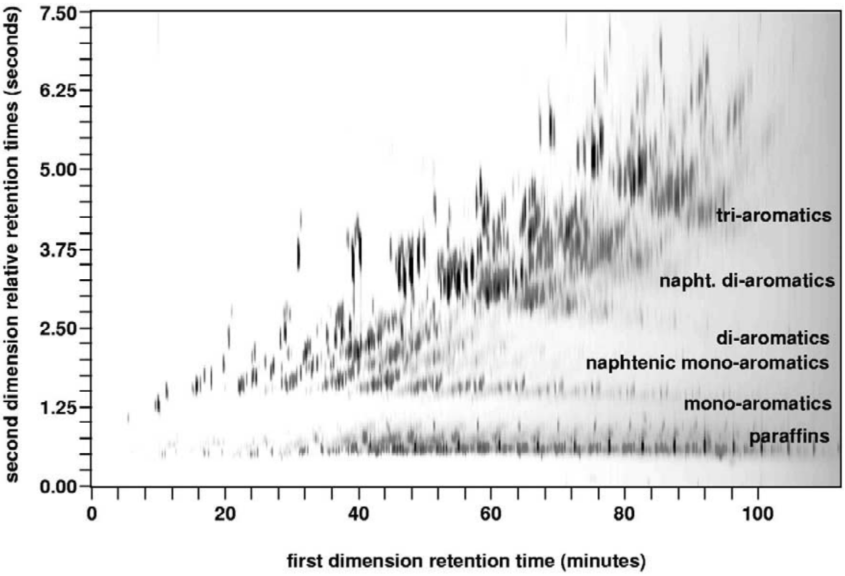

Fig. 27. Contour plot of a GC×GC analysis of a light cycle oil (LCO).

immediate practical interest, because the sophisticated methods developed for gasolines and naphthas (PIONA; detailed hydrocarbon analysis, DHA) are failing in this range. However, the recently introduced jet-cooled thermal modulator [166,167], together with independent temperature control of the first- and second-dimension columns, allows to cover an increasingly broad optimum range in terms of sample volatility [171]. Interesting new GC×GC applications have evolved, such as the determination of BTEX, total aromatics and oxygenates in gasoline [172,173], and petroleum biomarkers in crudes [174].

It is only a matter of time before other (selective) detectors, such as the SCD (see Section 3.2) will be coupled to GC×GC, opening up even other dimensions of petrochemical samples. However, one has to bear in mind that, in order to avoid unnecessary noise, most of these (commercially available) detectors have been optimized to record peaks with typical peak widths in the order of 5 s. This is far from optimal for registering the fast second dimension of GC×GC, which generates typical peak widths in the order of 200 ms or less. Obviously, this calls for a significant reduction of the time constants of these types of detectors [175].

The same goes for the hyphenation of GC×GC and MS [176]. The only realistic option for the latter is the fast time-of-flight mass spectrometry (TOF-MS). Initial steps towards GC×GC–TOF-MS have already been taken [177]. It has been used for the quantification of aromatic compounds and sulphur-containing compounds in petroleum samples with boiling points ranging from 150 to 450 °C [178]. Quantitative results have been obtained for aromatic target compounds (mono-, di- and triaromatic) using chlorinated aromatic internal standards (chlorobenzene and 1,2,4,5-tetrachlorobenzene) and for (di)benzothiophenes (BT and DBT) using deuterated naphthalene (naphthalene-d_8) as internal standard. The results compare favourably with results obtained with other analytical techniques. However, mass-spectrometric response factors for the tested aromatic compounds differ widely [99,178]. For quantification of group-types, it is therefore more useful to use FID because of the uniform response factors of this detector.

At this point it seems appropriate to quote professor Marriott in his guest editorial in the commemorative issue of J. High Resolut. Chromatogr. dedicated to John Phillips, where he states [179]:

"In perhaps the most stimulating technical advance in capillary GC for many years, a new

approach has indeed been laid in front of us, thanks largely to the persistence and belief John Phillips had in the concept of modulation in GC.''

4. Future needs

The analysis of oil and petrochemical samples by GC has progressed immensely from its conception by James and Martin in 1952 [2] to the present state-of-the-art. Oil fractions up to very high (virtual) boiling points (750 °C) can be separated by HT-SimDist. Even higher boiling fractions can be characterized in great detail by using combinations of analytical techniques which include fractionation by LC. A variety of detection systems is currently available for use with GC. Flame ionization is still the best existing detection principle in terms of universality, sensitivity and, most of all, in terms of dynamic range ($>10^7$). From among the selective detectors, the chemiluminescence approach has had much success for S-containing compounds, and MS detection increasingly receives attention, specifically with the advent of TOF-MS instruments in combination with fast GC. In the near future, TOF-MS with its excellent selectivity/sensitivity and rapid signal processing, may well become a valuable alternative.

The ability to fractionate complex samples such as oil fractions, with very high resolution has progressed with great strides in the last decade. Today, capillary GC columns yield high efficiencies of up to some 400 000 theoretical plates. However, the real breakthrough in terms of separation power has been obtained by combining high-resolution GC with other separation techniques. Still, we can identify certain areas where state-of-the-art analytical separations do not suffice to solve important problems. A number of challenges remain that require continued effort from separation scientists. In the following sections we will briefly discuss some of these.

4.1. Feedstock characterization

A wide spectrum of materials is used as feedstocks for specific processes. Crude oils are subjected to distillation to yield straight-run fractions. The residues from such a process are further distilled under vacuum or converted into lighter products. All the fractions obtained can in principle be used as feedstocks for subsequent processes. In several cases a better characterization of the feedstocks can lead to great improvements in process yields and operation.

In view of current demands, ''ideal'' crudes consist mainly of relatively volatile components, and preferably have a very low sulphur content. Such crudes hardly exist, and those coming close to these specifications will rapidly become more expensive. High-sulphur-content crudes that mainly consist of (very) high-boiling materials (including large amounts of asphalthenes), however, are still available in relatively large quantities. Therefore there is an increasing need to extend SimDist (or even group-type-specific SimDist) ''towards the bottom of the barrel'', i.e., to yet higher virtual boiling points. SFC has already proven to allow quantitative elution of alkanes with boiling points up to 780 °C (n-C_{140}) which is substantially higher than HT-SimDist based on GC allows. However, probably due to a combination of solubility and adsorption problems, SFC is still not able to elute high-boiling aromatic species in a similar quantitative manner [43]. The addition of modifiers to the eluents may help to solve this problem, but in the process the boiling-point elution order may be jeopardized. Furthermore, only ''FID-transparent'' modifiers can be used for SimDist applications.

An additional problem in the characterization of the heavy crudes is that most of the hetero-elements (sulphur, heavy metals) present are ''hidden'' in the heaviest fractions. Despite all the impressive separation techniques and strategies described in this chapter, we have yet to start learning how to separate asphalthenes.

4.2. Process characterization

Although an on-line coupled NPLC–GC–SCD system providing detailed insight in hydrodesulphurization processes has been developed [124], its counterpart for nitrogen-containing species (based, for example, on nitrogen chemiluminescence detection, NPLC–GC–NCD) has still to be developed. This will be a difficult task because the various classes of nitrogen-containing species are highly different in nature, ranging from basic, to neutral, to acidic species. The basic species are notorious catalyst poisons when using acidic proton donor catalysts. Cynically, they are also the most difficult species to analyse using GC.

High-speed GC is slowly entering the world of catalyst development. Within the fashionable approach of *combinatorial chemistry*, there is an urgent need for robust, high-speed chromatographic analysers which, ideally, provide fully automated, on-line analysis of multiple samples simultaneously. However, as mentioned above, such analysers put severe demands on both injection and detection devices. This calls for a continued effort in instrument design.

4.3. Product characterization

Although GC×GC can characterize relatively volatile fractions in more detail and up to higher boiling-points than the PIONA analyser, the separation of naphthenic from olefinic species, let alone the separation of olefinic from cyclic-olefinic species has not been realized yet. A GC×GC×GC system with a first-dimension separation according to volatility, a second-dimension separation according to ''shape'' and a third dimension separating according to polarity may complete the characterization of mixtures in the middle distillate range in the sense that all compounds present at relevant concentration levels in the mixture are essentially separated. However, even before the realization of such an ''ultimate DHA analyser'', product compositions are changing again. DHA still stands for detailed *hydrocarbon* analyser. Today, however, there is a tendency to blend other types of compounds, from vastly different sources. Such materials vary from simple ethers, such as MTBE or alcohols (such as methanol), to fatty acid methyl esters (FAMEs) in so-called biodiesel, to complex oxygenate mixtures originating from Fisher–Tropsch processes.

Next to a demand for the comprehensive characterization of products, there is also still a great need for several types of target-compound analysis. A good example is the analysis of residual diisopropanolamine (DIPA) in LPG. The highly polar character of DIPA, which makes it such an extremely effective medium in desulphurization processes, also causes it to be highly adsorptive in sampling valves. This adsorptivity is the main reason that attempts to design robust miniaturized analysers based on large-volume injection techniques have, so far, failed.

4.4. The need for detailed information

In the end, most people working in the oil industry are not interested in *chemical composition*. What they want is, simply, information on product properties and process performance. Traditionally, analytical chemists have been providing data to product and process technologists, who—in their turn—developed various kinds of models to translate such data into useful information. The more or less clear-cut division between *analysis* and *modelling* is not really desirable. To put it otherwise, if any kind of reliable and reproducible data meets the final demand, why should analytical chemists go to great lengths to provide detailed information on chemical composition? The following example may be illustrative.

Direct measurements of bulk properties, such as viscosity, density, pour point, flash point, etc., are generally easy to perform and, therefore, rapid and economical. To measure other properties, such as for example the octane number of gasolines, is already getting more complicated. The *direct measurement* of the motor octane number or MON (ASTM D2700-99) requires a standardized single-cylinder, four-stoke cycle, variable compression ratio, carburetted engine, in accordance with a defined set of operating conditions. The measurement of MON is laborious and, above all, time consuming. Needless to say that this type of *direct measurement* is far from suitable for fuel-blending purposes. It is for this reason that fuel blending nowadays relies on *indirect measurements* that, together with (black-box) models, produce the research octane number or RON (ASTM 2885-95). Although the measurement of RON is, in principle, based on knowledge of chemical composition, it is doubtful whether these black-box models translate chemical composition into product properties, or vice versa.

Chemometrics is one discipline that has bridged the gap between analysts and modellers. Near-IR spectra, the favourite kind of input for chemometricians, cannot easily be translated into chemical compositions. However, they can easily and reliably be obtained, contain a good deal of information and have a favourable data structure (baseline, linearity). Chemometrists use near-IR spectra to predict octane numbers. This approach, which is based on (physico)-chemical analysis, is much more rapid and less expensive than the conventional test, based on a standardized engine.

Of course, if we would be able to obtain detailed—or, as some would prefer to say, real—data on chemical composition, it would be possible to confidently and reliably *predict* product properties, while simultaneously extending our understanding and fundamental knowledge. The emergence of GC×GC is a major step in this direction. The proper handling of the plethora of information now available, will no doubt cause existing barriers between analytical chemistry and modelling to disappear, and their integration to be stimulated.

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