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Gas Chromatograph Applications in Petroleum Hydrocarbon Fluids

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1. Introduction

1.1 Composition of reservoir hydrocarbon fluids

In the petroleum hydrocarbon fluids, the most commonly found molecules are alkanes (linear or branched paraffins), cycloalkanes (naphthenes), aromatic hydrocarbons, or more complicated compounds like asphaltenes. Under surface pressure and temperature conditions, lighter hydrocarbons such as CH_4 , C_2H_6 , and inorganic compounds such as N_2 , CO_2 , and H_2S occur as gases, while pentane and heavier ones are in the form of liquids or solids. However, in petroleum reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram (envelop) of the petroleum mixture. To obtain compositions of a reservoir fluid, a reservoir sample is flashed into gas and liquid phases at ambient conditions. The volume of the flashed gas, and the mass, molar mass and density of the flashed liquid are measured. Then a gas chromatograph is used to analyze compositions of the gas and liquid phases as described briefly below. The recombined compositions based on the gas and liquid according to the measured gas/oil ratio are those of the reservoir fluid.

Generally speaking, crude oils are made of three major groups:

- Hydrocarbon compounds that are made exclusively from carbon and hydrogen;
- Non-hydrocarbon but still organic compounds that contain, in addition to carbon and hydrogen, heteroatoms including sulfur, nitrogen and oxygen;
- Organometallic compounds: organic compounds, normally molecules of porphyrin type that have a metal atom (Ni, V or Fe) attached to them.

1.2 Hydrocarbons

Hydrocarbons are usually made of few groups:

- a. linear (or normal) alkanes (paraffins)
- b. branched alkanes (paraffins)
- c. cyclic alkanes or cycloparaffins (naphthenes)
- d. aromatic alkanes (aromatics)

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From the GC perspective, the analysis of alkanes is performed using a non-polar column and separation is based on boiling point. Normal alkanes boil few degrees higher than their respective branched ones. In Table 1.1 an example illustrating this point is given.

Compound	Boiling point (°C)
n-Octane	126
2-methylheptane	116
3-methylheptane	118
4-methylheptane	117

Table 1.1. Boiling points of octane isomers

From the data above, the branched alkanes are closer together and the corresponding normal alkanes boil at higher temperature. Thus, branched alkanes elute first, followed by the normal alkanes. For GC analysis, it is recommended to integrate the end of an alkane to the end of the next alkane as a family of one particular alkane, as shown in Figure 1.1.

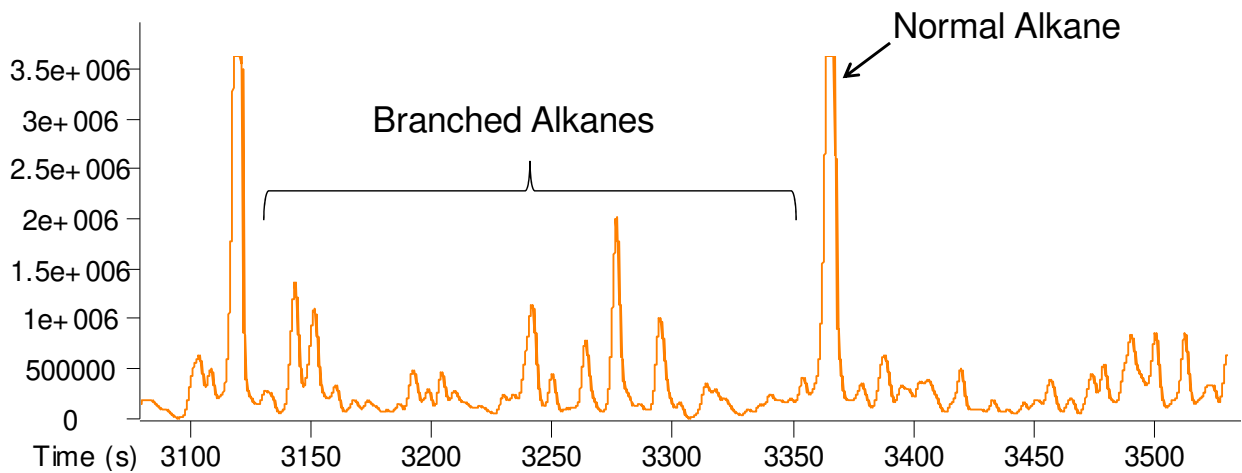


Fig. 1.1. Illustration of integration branched and linear alkanes

In 1873, van der Waals introduced the first cubic equation of state (EOS) by modifying ideal gas law. In 1949, Redlich and Kwong modified the van der Waals EOS which was then modified by Soave (1972). Peng and Robinson (1976) introduced the Peng-Robinson EOS for better liquid volume calculations. Many cubic EOS were developed later. Cubic equations of state such as the Peng-Robinson EOS with volume translation have been widely used for the calculations of fluid phase behaviour for hydrocarbon systems. Based on the recombined composition of the reservoir fluid, the characterization procedure of Zuo and Zhang (2000) can be used to characterize single carbon number (SCN) or true boiling point (TBP) fractions and plus fractions. Then cubic EOS can be employed to calculate phase behaviour of the reservoir fluid. The EOS (compositional model) or simulated fluid properties (black oil model) is used in reservoir simulators such as Eclipse and/or process simulators such as HYSYS. For polar systems, cubic EOS can also be used by coupling complicated mixing rules such as the Huron-Vidal mixing rule and the Wong-Sandler mixing rule. On the other hand, Davarnejad *et al.* (2007, 2008) considered the Regular Solution Equations as a general model for polar and non-polar systems.

1.3 Non-hydrocarbons

The hydrocarbons that contain heteroatoms could vary from very simple one such as thiophene to very complex mixtures such as asphaltenes for which the structure is not well understood, but known to contain sulfur, oxygen and nitrogen at different levels, in addition to carbon and hydrogen (Buenrostro-Gonzalez *et al.*, 2002; Woods *et al.*, 2008).

The most common method to separate petroleum fractions is called SARA, which stands for saturates, aromatics, resins and asphaltenes. It needs to be noted that cyclic compound are included in the fraction of saturates. The light fraction is made mostly of alkanes and aromatics. Light aromatics containing heteroatoms could be distilled off with this fraction. The split between alkanes and aromatics could be performed using supercritical fluid chromatography by changing the solvent strength (Dulaurent *et al.*, 2007).

The heavy fraction is first subjected to asphaltenes precipitation using an excess of normal alkanes such as n-pentane or n-heptane, usually at a oil-to-alkane ratio of 1 to 40. Different methods exist in the literature for asphaltenes separation (Kharrat, 2009). After extraction of asphaltenes, the maltenes are separated into three fractions: saturates, aromatics and resins using solvents with increasing polarity as indicated in Figure 1.2.

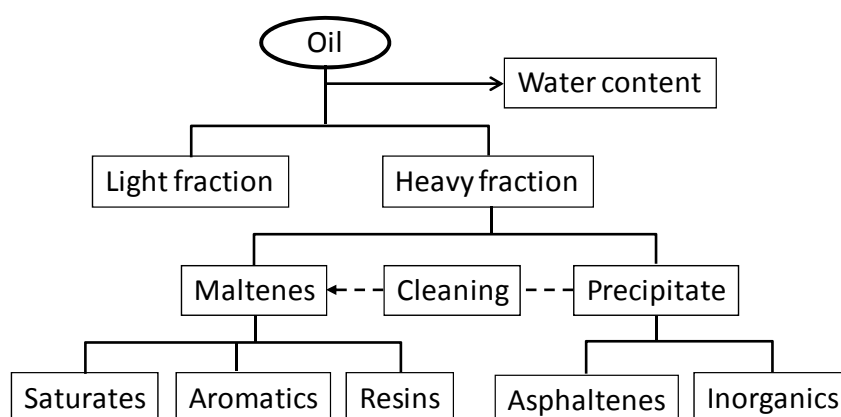


Fig. 1.2. Chart flow of fractionation of a crude oil

The saturate fraction is analyzed by gas chromatography, leading to n-alkanes content. Aromatics are analyzed by Gas Chromatography with Mass Spectrometry (GC-MS). Resins and asphaltenes are the most difficult to analyzed by GC because of their high boiling points. Therefore, the applications of GC on the analysis of heavy oil, which has a high concentration of asphaltene and resin fractions, are limited. In a reported high temperature GC (HTGC) technique, a short 5-m glass capillary column was used to elute compounds in bitumen and bitumen-derived products with boiling points as high as 700°C (equivalent to alkane with carbon number of 90, C₉₀) (Subramanian *et al.*, 1996).

In this chapter, the principles and instrumentations of several GC techniques, and their applications on the analysis of petroleum hydrocarbon fluids are reviewed.

2. High Temperature Gas Chromatography (HTGC)

GC has the advantages of high column efficiency, high sensitivity, fast analysis speed and ease to be combined with other analytical methods (e.g. Mass Spectrometry). Thus, it is

widely used to analyze crude oil and its products. Because of the limited thermal stabilities of capillary column and the stationary phase, the maximal column temperature of conventional GC is around 325°C, and the analysis is limited to hydrocarbons with carbon number less than about 35. This fact limits the GC applications on the analysis of alkanes of high carbon numbers (C_{40+}) which are important for some areas including organic geochemistry.

During the past decades, high temperature (325–450°C) GC (HTGC) has been developed rapidly and used for components of high molecular weight in crude oil, *etc.*

2.1 Requirements on the parts of HTGC

The main materials for the HTGC column include stainless steel and fused silica. Steel column has excellent mechanical properties at high temperature, but it has very strong catalytic and adsorptive effects. Therefore, a deactivation inner coating between the steel tubing and the stationary phase is needed. Another drawback of stainless steel column is that it is difficult to cut. A protective coating is needed on the outside of the fused silica column to maintain the flexibility of the column. Right now the frequently used coating materials include polyimide and aluminum (Kaal & Janssen, 2008). It has been suggested that the polyimide may be broken down above 360°C and alumina coating can overcome this problem. However, the alumina coating on silica column can become brittle upon repeated heating above 400°C (Application note #59551, Restek Corporation).

The stationary phase also needs to be stable above 400°C upon repeated heating with minimal breakdown. It is mostly based on highly thermostable polysiloxane which can be bonded onto the capillary inner wall via the condensation reaction between the silanol terminal groups of the polysiloxane and the silanol groups on the silica surface during curing process (Mayer *et al.*, 2003; Takayama *et al.*, 1990). The commonly used materials for stationary phase of HTGC include carborane-siloxane polymers (maximum temperature up to 480°C) and silphenylene-modified polysiloxane (maximum temperature up to 430°C), *etc.* (Kaal & Janssen, 2008).

Injection method is very important for HTGC. Cold on-column injection is preferred because of its ability to eliminate discrimination against the most non-volatile compounds (Damasceno *et al.*, 1992). For many compounds with high boiling points, programmed-temperature vapourisation injection (PTV) also gives good results (van Lieshout *et al.*, 1996).

The most frequently used detection method for HTGC is flame ionization detection (FID). Other detection methods have also been used, including mass spectrometry (MS) (Hsieh *et al.*, 2000; Philp, 1994), atomic emission detection (AED) (Asmussen & Stan, 1998) and inductively coupled plasma mass spectrometry (ICP-MS) (Glindemann *et al.*, 2002), *etc.*

2.2 Applications of HTGC

2.2.1 Simulated distillation of crude oil

The crude oil is composed of a large amount of alkanes with different carbon numbers, giving rise to a broad range of boiling point. The understanding of the carbon number distribution of crude oil can help to precisely evaluate the factors affecting the properties of

crude oil and the oil products. It is also important for the designing of the distillation, processing equipment and the quality control of the products.

Normal true boiling point (TBP) distillation involves a long procedure and is costly, and the distillation temperature is normally limited even when vacuum is used. GC has been used widely as a fast and reproducible method for simulated distillation (SimDis) to analyze the carbon number distribution of the hydrocarbon in the crude oil. When HTGC is used, SimDis method can reach a boiling point range of 35-750°C, equivalent to n-alkanes with a carbon number distribution of C₅ to C₁₂₀ (Kaal & Janssen, 2008). HTGC SimDis normally uses a short capillary column with a thin film of polydimethylsiloxane stationary phase. Recently, Boczkaj *et al* reported the possibility of using an empty deactivated fused silica column (EC-GC) for HTGC-SimDis (Boczkaj *et al.*, 2011).

Figure 2.1 presents an example of high temperature simulated distillation (HTSD) results for heavy and light oils. The heavy oil starts distillation at a higher temperature (~200°C) than for the lighter oil (~150°C). The residue, which is the fraction that does not distill at 700°C, is much higher for the heavy oil than for the lighter one.

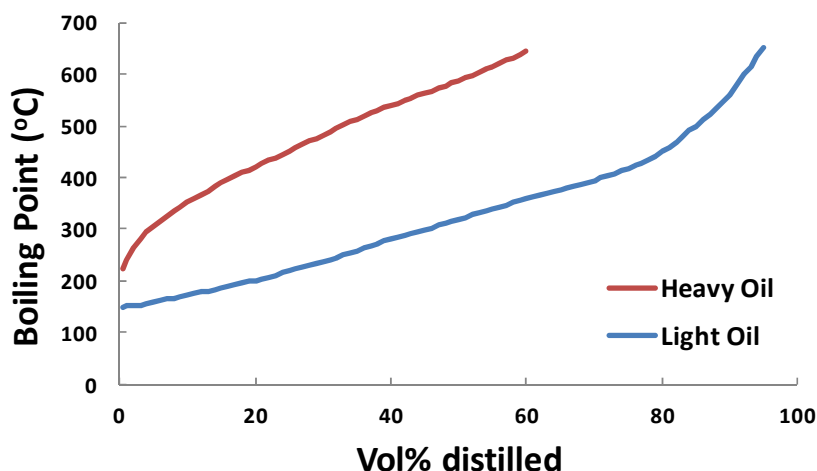


Fig. 2.1. Example of HTSD results for a heavy (red) and light oil (blue).

2.2.2 Wax analysis

Waxes are solids made up of heavy hydrocarbon (C₁₈₊) which are mainly normal alkanes (paraffins) (Kelland, 2009, p. 261). The waxy oil can be used to produce wax-based products, and normally has low concentrations of sulphur and metal which are harmful for refinery. But on the other hand, when temperature of the crude oil drops during oil production, transportation or storage, paraffin waxes in the crude oil can precipitate and make serious problems including pipeline blockage and oil gelling, *etc*. Thus, it is important to measure the composition (amount and type) of wax in the crude oil, and to estimate the temperature at which the wax will crystallize (wax appearance temperature, WAT) and the wax precipitation curve (WPC) to understand the potential wax problem and its magnitude.

Compared with conventional GC, HTGC significantly extends the range of detectable hydrocarbon. Therefore, HTGC has become more and more routinely used for wax analysis, and the HTGC results can be correlated to the physical properties of the wax, including melting point, refractive index and kinematic viscosity, *etc* (Gupta & Severin, 1997).

Currently, there are no standard wax-analysis methods, but some methods are developed by the petroleum industry. These methods remain proprietary. Figure 2.2 shows a typical HTGC chromatogram of a waxy crude oil. With a calibrated column, the relative area under the curve for each n-alkane will be converted to the relative abundance of the species. The reported n-alkane composition will be the amount of each n-alkane chain number and relative or absolute abundance (see an example as shown in Figure 2.3).

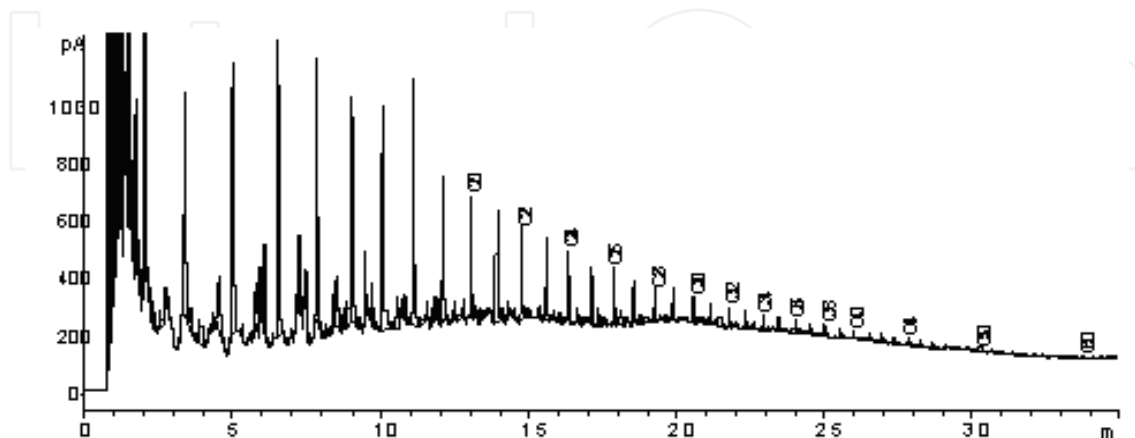


Fig. 2.2. Examples of HTGC traces of a waxy crude oil

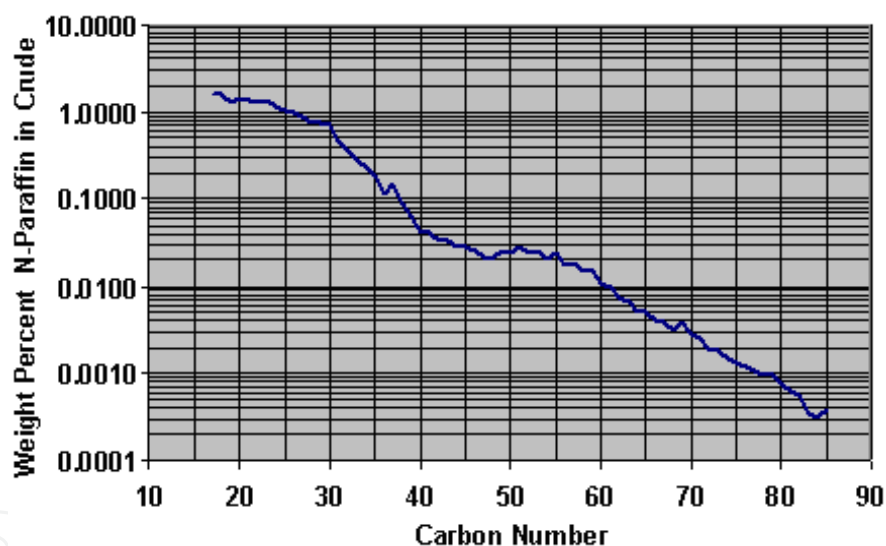


Fig. 2.3. n-Paraffin distribution for a waxy crude oil analyzed by HTGC

An important application of HTGC analysis on waxy crude oils is to measure high molecular weight hydrocarbons (HMWHCs) which provide desirable geochemical information, and some significant findings have been reported.

Del Rio and Philp reported HTGC analysis of some wax samples blocking oil wells and found that the wax deposits were normally composed of hydrocarbons with maximal carbon number around 40 to 50 (del Rio & Philp, 1992). Roehner *et al* used an extended HTGC method to determine the compositions of crude oil solids and waxes up to C₆₀ formed in the Trans-Alaska Pipeline. A longer capillary column was used to achieve an improved resolution of high carbon number groups. The n-alkane/non-n-alkane ratio was used to distinguish between certain types of crude oil solids (Roehner *et al.*, 2002).

HTGC has been used to study/monitor the biodegradation of crude oils. For example, using a quantitative HTGC method, Heath *et al* estimated the biodegradation of the aliphatic fraction of a waxy oil. It was found that light hydrocarbon was quickly biodegraded and HMWHCs (C_{40+}) showed resistance to biodegradation (Heath *et al.*, 1997).

HTGC is also an useful tool to study the origin/source of the crude oils. Hsieh and Philp measured HMWHCs from crude oils derived from different sources, including terrigenous, lacustrine, marine source material as well as source rock extracts. Different structural compositions of these HMWHCs (including alkyl-cycloalkanes, methylbranched alkanes, and alkyl-aromatic hydrocarbons) have been revealed by HTGC and it was found that the fraction of the HMWHCs in the whole oil is significantly higher than previously thought (can be up to 8%) (Hsieh & Philp, 2001; Hsieh *et al.*, 2000). The distribution of long chain, branched and alkylcyclohexanes of the HMWHCs analyzed by HTGC has been used as a useful mean to distinguish oils derived from different sources (Huang *et al.*, 2003).

It has been pointed out that the sample extraction/cleaning procedure is crucial to get representative HMWHC samples from crude oil for HTGC measurement (Thanh *et al.*, 1999). More details on the HTGC analysis of HMWHCs and its applications can be found in an overview given by Philp *et al* (Philp *et al.*, 2004).

WAT and WPC are two important parameters for wax-related flow assurance problems. They can be experimentally measured (Kelland, 2009), and can also be predicted by different thermodynamic models. All these models rely on the experimental data of n-paraffin distribution which is now commonly provided by HTGC. For example, Zuo and Zhang have developed a model to predict the WAT based on the oil composition provided by HTGC (Zuo & Zhang, 2008). The model has been proved to provide prediction results in good agreement with experimental data of synthetic oils and reservoir fluids, and several examples are given in Figures 2.4 to 2.6 (details given in Zuo & Zhang 2008). Coto *et al* analyzed three parameters to improve the n-paraffin distribution provided by HTGC, including total amount of C_{20+} paraffin, extrapolation of C_{38+} paraffin and molecular weight of the crude oil. The results showed that the distribution of the n-paraffin has great impact on the accuracy of the prediction model (Coto *et al.*, 2011).

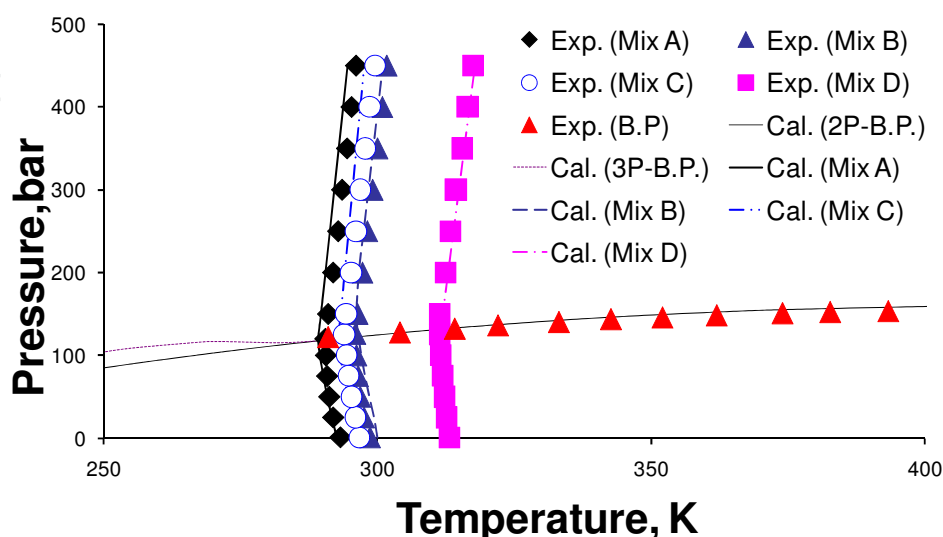


Fig. 2.4. WAT and phase diagram for synthetic oil mixtures.

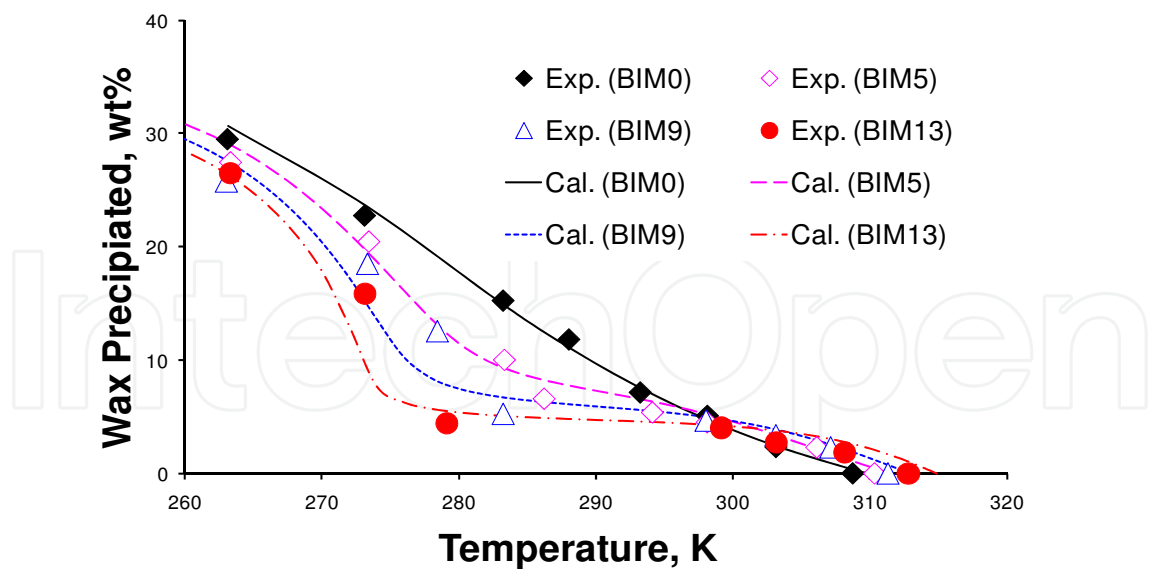


Fig. 2.5. Wax amount for synthetic oil mixtures.

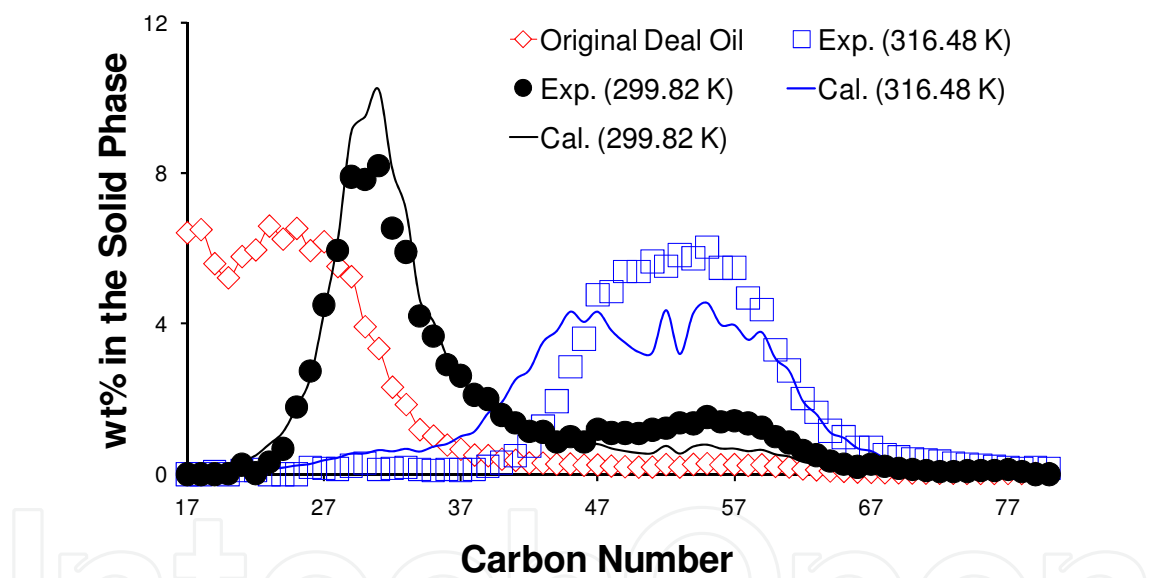
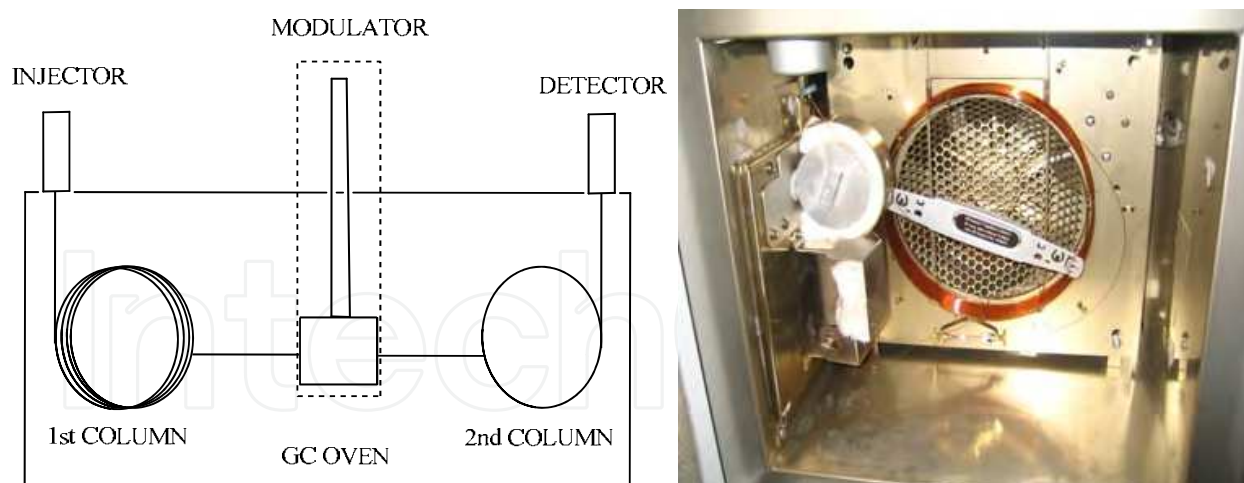


Fig. 2.6. The wax distributions vs. carbon numbers are compared for a crude oil.

3. 2D-GC (GC-GC)

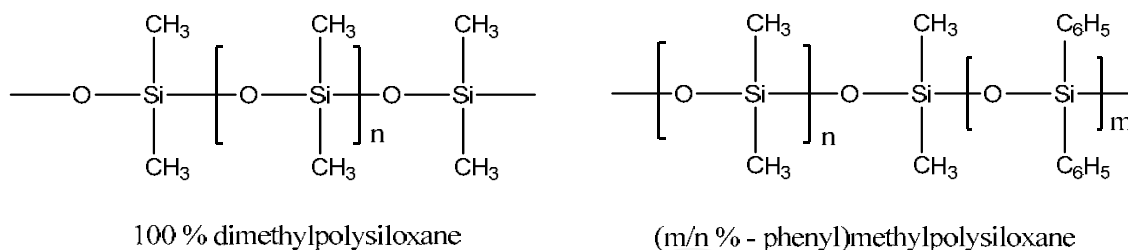
3.1 Concept of comprehensive GC × GC

Since Liu and Phillips depicted comprehensive two dimensional gas chromatography (2D-GC) in 1990s (Liu & Phillips, 1991; Vendevre *et al.*, 2007; Zrostlíková *et al.*, 2003), the technology of 2D-GC has developed rapidly and been applied in the areas such as biological/clinical, environmental, food, forensics, petroleum, pharmaceuticals and fragrances in forensic, food and petroleum oil characterization (Wang *et al.*, 2010). 2D-GC employs two capillary GC columns of different selectivity coupled by a modulator (Figure 3.1) which will be introduced here.



3.1.1 First column

The first column is typically of conventional length, longer, wider and thicker than the second column, being (15–30) m (long) \times (0.25–0.32) mm I.D. (inner diameter) \times (0.1–1) μ m film (df). The stationary phase of the column can be non-polar or polar. For example, 100% dimethylpolysiloxane is considered as non-polar, and phenyl-substituted methylpolysiloxane is considered as polar column (Scheme 3.1), and the more phenyl contained, the more polar the column is (Betancourt *et al.*, 2009).



Scheme 3.1. Structures of dimethylpolysiloxane and phenyl-substituted methylpolysiloxane

3.1.2 Second column

The second column is shorter, narrower and thinner, of (0.5–2) m \times 0.1mm I.D. \times 0.1 μ m df. It is usually more polar or less polar than the first column. If the second column is more polar than the first column, it is called non-polar \times polar configuration; if the second column is less polar than the first one, it is called polar \times non-polar configuration. In most time, 2D-GC has non-polar \times polar configuration. The two columns can be housed in the same oven or in separate ovens to enable more flexible temperature control (Li *et al.*, 2008).

3.1.3 Modulator

A modulation unit, placed between the two columns, is the most critical component of 2D-GC (Adahchour *et al.*, 2008; Adahchour *et al.*, 2006; Marriott *et al.*, 2003; Pursch *et al.*, 2002;

Wang & Walters, 2007). Modulator periodically samples effluent from the first column and injects it into the second column. After the second-dimension separation is completed the next modulation starts. In this way, all compounds are subjected to two different column separation mechanisms, and are resolved based on two different aspects of chemistry, or selectivity. Each modulation period is so short that each peak from the first column is cut into several smaller slices that go through separation on the second column. Therefore, GC \times GC chromatography peaks become much narrower compared with traditional 1D GC peaks. The setup of two columns (the first column is longer and wider and the second column is shorter and narrower) ensures that the total second dimension (2D) separation is completed in the run time of the first-dimension analysis.

It should be noted that comprehensive GC \times GC is different from two-dimensional “heart-cut” gas chromatography (Zrostlíková *et al.*, 2003) in which one zone of effluent eluting from the first column is isolated and subsequently separated in a different column.

Modulator is also a reference timing signal at the interface between the two columns (Phillips & Beens, 1999). There are different kinds of modulators such as valve modulator, thermo-modulator and cryogenic modulator, which are very well reviewed (Betancourt *et al.*, 2009; Phillips & Beens, 1999). Nowadays most of modulators are dual-stage cryogenic modulator using CO₂ or liquid nitrogen as cooling agent. Two-stage cryogenic modulator system has two hot points and two cold points; hot point is used to release and reject the slice from the first column, and cold point is used to hold the slice. For the analyses of whole petroleum oil, liquid nitrogen is a better choice because of the existence of very low boiling point compounds in the light ends of the petroleum oils.

3.1.4 Detector

The dimension of the second column is such that eluting peaks have peak widths in the order of 10-100 ms (Adahchour *et al.*, 2008, 2006; Marriott *et al.*, 2003; Phillips & Beens, 1999; Pursch *et al.*, 2002; Wang & Walters, 2007). To properly sample the narrowest peaks, detectors need to have fast response. Therefore, the sampling rate at which the detector signal is sampled should be at least 100 Hz, but a slower data rate of 50 Hz can be used for wider peaks. Flame ionization detectors, FID, which has negligible internal volumes and can acquire data at frequencies of 50–300 Hz, are most widely used. Mass spectrometer (MS) can provide structural information, enable unambiguous identification, and ensure high selectivity throughout the chromatogram, and hence is a good detection method. Quadrupole mass spectrometers operating in full scan mode are too slow to properly sample a GC \times GC peak unless that peak is broadened. Fast time-of-flight mass spectrometers (TOFMS) that operate with spectral acquisition rates of 100-200 Hz are well-suited for GC \times GC and have been used for numerous studies. On the other hand, element-specific detectors such as sulphur, nitrogen chemiluminescence detections (SCD, NCD), have been used for nitrogen containing and sulphur containing compounds, respectively (Dutriez *et al.*, 2011; Zrostlíková *et al.*, 2003).

3.2 2D-GC results

3.2.1 GC \times GC chromatogram

2D-GC chromatograms can be visualized in traditional 1D version, 2D version (contour plot) and 3D image (surface plot), as shown in Figure 3.2. The contour plot of GC \times GC

chromatogram conventionally demonstrates the advantage of 2D-GC: structured chromatogram. It clearly shows the different group types in certain patch of the 2D plane, for example, tri-aromatics, bi-aromatic, mono-aromatic, paraffins, hopanes, and so on. Within the ring of biaromatics (naphthalene), different methyl-substitute also distribute orderly, from left to right within the ring being: non-methylated biaromatics (naphthalene), mono-methylated naphthalene, bi-methylated naphthalene, tri-methylated naphthalene and tetra-methylated naphthalene. The GC×GC contour plot makes group-type analysis a great advantage for GC×GC analysis, but it should be mentioned that there are some crossing. For instance, nonylbenzene appears in the area of cyclic group, and some bi-cyclic appears in the area of mono-aromatics. The surface plot of a GC×GC chromatogram against a 1D version of the GC×GC chromatogram clearly shows that 2D-GC has better separation: the peaks crowded in 1D are well separated along the second dimension of the 2D plane, and it also demonstrates other advantages of 2D-GC: high sensitivity and bigger peak capacity. Some peaks are invisible in 1D chromatogram but visible in 2D-GC chromatogram.

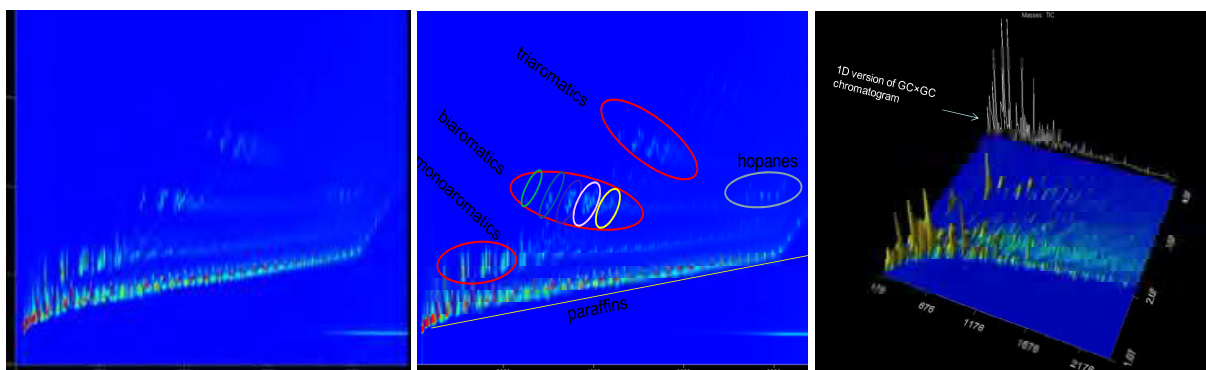


Fig. 3.2. GC×GC chromatograms, first column: VF-1ms 30m × 0.25mm × 0.1μm, second column: BPX50, 1m × 0.1mm × 0.1μm, modulator: 40°C offset to the primary oven, second column: 15°C offset to the primary column. left: Contour plot of a GC×GC chromatogram; middle: contour plot with labelled groups, right: surface plot with the show of 1D version of of GC×GC chromatogram.

3.2.2 Advantages of GC×GC

As demonstrated in the two dimensional contour plot and three dimensional surface plot, it is obvious that GC×GC has the following advantages compared with conventional one dimensional GC:

1. Structured chromatograms: the compounds are distributed in the 2D-GC plan according to their group types and each certain group has a certain pattern. Ordered chromatograms have the potential advantage of being much more interpretable than disordered ones. The pattern of peak placement is itself informative and may make it possible in many mixtures to identify most or all of the components or at least to recognize the mixture with good reliability (Adahchour *et al.*, 2008; Li *et al.*, 2008; Phillips & Beens, 1999).
2. Better separation: 2D-GC separates components along the primary dimension and also along the second dimension. Sometimes compounds co-eluted with conventional 1D GC technology can be separated by 2D-GC along the second dimension.

3. Larger capacity: 2D-GC peaks are distributed in the whole plane rather than in one line. 2D-GC has a peak capacity of $n_1 \times n_2$, in which n_1 is the capacity along the first dimension and n_2 the capacity along the second dimension. Therefore, the capacity of 2D-GC is higher than that of conventional 1D GC.
4. Higher sensitivity: Compared with conventional 1D GC, the sensitivity of 2D-GC is increased by 1.5 – 50 fold (Zrostlíková *et al.*, 2003). Trace amount of analytes can be detected with 2D-GC. The detection limit for 2D-GC is about 2pg (Zrostlíková *et al.*, 2003).

All these characteristics make GC \times GC a particularly useful technique for analyzing complex mixture, for example, petroleum oil. The ordered distribution of effluent has been used for quick screening of oil, recognizing the difference between individual oils (Li *et al.*, 2008).

On the other hand, 2D-GC also has some disadvantages. Cooling in cryogenic modulator causes peak tailing along the second column. 2D-GC files are extremely large, and not easy to be applied into different software.

3.2.3 GC \times GC column configuration

Normal GC \times GC column configuration is from non-polar to polar (the first column is non-polar, and the second column is polar), whereby the sample is separated on the first column based on the boiling point differential of all components, and then further separated on the second column based on the polarity differential. The choice of columns depends on the stationary phase (mainly on polarity), the application temperature of the column, column length and diameter, commercial availability and so on. The normal column configuration is usually good for selecting out high polar components in the samples. Nevertheless, column configuration of polar to non-polar (reversed configuration) is reported to improve the resolution of individual alkanes, cyclohexane, branched alkanes, and isoprenoids (Vendeuvre *et al.*, 2005).

Figure 3.3 demonstrates a contour plot of 2D-GC-MS, using a reversed column configuration, from polar (30m \times 0.25mm \times 0.25 μ m, DB-17) to non-polar column (1m \times 0.1 mm \times 0.1 μ m,

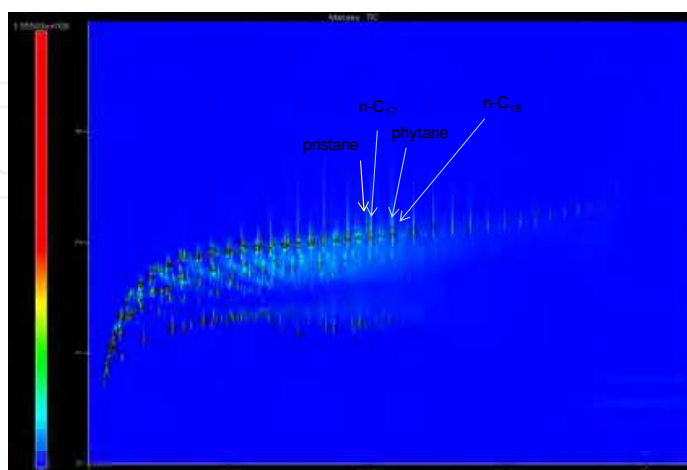


Fig. 3.3. Contour plot of 2D-GC-MS chromatogram using reversed column configuration. First column: polar DB-17 30m \times 0.25mm \times 0.25 μ m; second column: non-polar DB-1MS 1m \times 0.1 mm \times 0.1 μ m.

DB-1MS). Overall, the contour plot from the reversed configuration looks just like a reversed chromatogram from normal configuration. In the chromatogram of reversed configuration non-polar compounds, like paraffin, have longer second-retention time, and polar compounds have shorter second retention time. In other words, the shorter the second retention time is, the more polar the compounds are. With a reversed column configuration, the compounds are also separated based on boiling point along the first dimensional retention time. For example, with the increase of retention time, the carbon number of normal paraffins increased. However, pristane and phytane come shortly before nC_{17} and nC_{18} , respectively. This is different from the normal column configuration, where pristine and phytane come shortly after nC_{17} and nC_{18} , respectively.

3.2.4 Data processing

GC×GC presents information technology challenges in data handling, visualization, processing, analysis, and reporting due to the quantity and complexity of GC × GC data. Usually, two different softwares are used for data acquisition and data processing, respectively. GC Image (GCImage LLC) is a software system developed at the University of Nebraska-Lincoln that uses advanced information technologies to process and visualize GC × GC data, detect peaks, compare chromatograms, and perform peak deconvolution, pattern recognition and other data mining tasks. ChromaTOF (Leco Corporation) is another software program designed to control Leco's commercially available GC × GC-TOFMS system that has similar functions. Both GCImage and ChromaTOF make effective use of the tremendous amount of data generated when a time-of-flight mass spectrometer is used as a GC × GC detector, including spectral library matching and extracted ion chromatograms. HyperChrom (Thermo Electron Corporation) is a third software program designed to control Thermo Electron's commercially available GC × GC system with flame ionisation detection and employs various data processing and visualization capabilities.

Actually data post process to re-read/re-display the chromatogram in the need of particular application is important, and is proven to be troublesome with the problem of peak alignment, retention time deviation, *etc.* Some particular work has to be done to re-display the chromatogram properly (Aguilar *et al.*, 2011).

3.2.5 Factors affecting 2D-GC retention time and separation

The factors which affect conventional 1D GC retention time and separation all apply to 2D-GC analysis, including:

- inlet temperature
- column temperature and temperature program
- carrier gas and carrier gas flow rates
- the column's stationary phase
- column diameter and length
- sample size and injection technique

Inlet temperature should be set high enough to vaporize injected samples, but not so high that the injected samples can be decomposed (Juyal *et al.*, 2011). Column temperature and temperature program are very important factors affecting GC retention time and separation.

The setup of column temperature and temperature program is to make sure that all of analytes are eluted and separated well. Higher column temperature causes shorter retention times; slower temperature ramp usually leads to better separation. The higher speed of carry-gas results in shorter retention time, which potentially causes peak co-elution. If the amount/concentration of injected sample is too big/high, the chromatogram will look overwhelming crowded with no good separation, especially when the injected samples are crude oil samples. In this case, split injection technique can be employed. When the split ratio is too high (200), the injection accuracy will decrease. Considering the high complexity of crude oil samples, temperature programmed injection technique might be very useful, whereby the sample is introduced in the injector at low temperature and then vaporized by a fast programmed heating process, during which time the split is open all the time and the sample amount entering the column is proportional to the pre-set split ratio (Wang *et al.*, 2010).

Due to the characteristics of 2D-GC, there are several more factors affecting 2D-GC separation, including the modulation period (the second column time), hot pulse time and second column temperature. A short modulation period usually means a short slice from the first column for further separation on the second column, which implies a better separation on the second column. If the modulation period is too long, the separated effluents on the first dimension are accumulated while waiting for injection onto the second dimension, which intends to lose the resolution of the first dimension. If modulation period is too short, on the other hand, peaks wrap-up is unavoidable, resulting in wrong retention times and bad separation.

Currently, the update of 2D-GC operation platform focuses on multi-stage temperature ramp of the second column which will resolve the dilemma between the modulation period and the second column separation time (Betancourt *et al.*, 2009). In some cases, *e.g.* the detection of nitrogen-containing compounds and the analysis on vacuum gas oil (VGO), high modulation period (20s – 30s) is needed. In this case, wide bore first column with bigger diameter are used to make the first dimension peak wider (Dutriez *et al.*, 2009, 2010, 2011).

In 2D-GC analysis with dual stage cryogenic modulator, hot pulse time and cooling period should be adjusted, especially in petroleum oil analysis. The hot pulse time should be long enough to make sure all of samples are re-injected to the second column, and cooling period should be good to make sure all the compounds with low boiling points are refocused on the second column.

3.3 Applications of comprehensive 2D-GC in oil analysis

2D-GC has been used in high temperature analysis of vacuum gas oil (VGO) (HT-2D-GC) (Dutriez *et al.*, 2009, 2010), nitrogen-containing compounds (2D-GC NCD) (Dutriez *et al.*, 2011), sulphur speciation (2D-GC SCD), middle distillates (Vendeuvre *et al.*, 2005), pyrolysis of petroleum source rocks (Py-2D-GC) (Wang & Walters, 2007), biomarkers (Aguiar *et al.*, 2011; Juyal *et al.*, 2011), *etc.*

3.3.1 Group type analysis of two Tarmat oils

Two oils A and B are isolated by a huge tarmat and no connection between the two oils is known. A question arose regarding to the two oils: are they different? To answer the question, the two oils were subject to independent group type analysis with 2D-GC FID in

house and detail analysis with commercial 1D GC-MS. The whole oils were used for group type 2D-GC FID analysis; the two oils were fractionated before detailed 1D GC-MS analysis. The TIC (total ion chromatography) 2D-GC contour plot of oil A is shown in Figure 3.4. There are two steps in the group type analysis: 1) divide each contour plot of the 2D-GC chromatogram of oil A and oil B into 7 areas, tri-aromatic (3-ring-1), bi-aromatic (2-ring-1), mono-aromatic (1-ring-1), hopane (polycyclic-1), sterane (polycyclic-2), before nC₁₇ and after nC₁₇ at the same retention times (first dimensional retention time, second dimensional retention time), and 2) compare each area of the oil A with the oil B. The analysis results are listed in Table 3.2. The two oils share the same amount of tri-aromatics, bi-aromatics, mono-aromatics, polycyclic-1(hopane compounds), before nC₁₇ and after nC₁₇. No sterane compounds (polycyclic-2) were detected in the two whole oil analyses due to too low concentration.

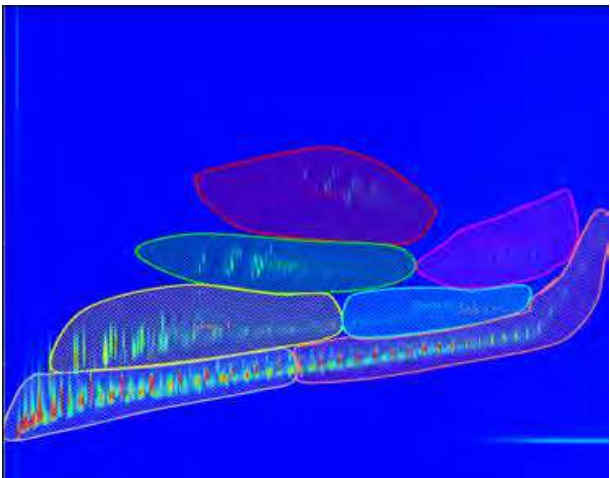


Fig. 3.4. Group type analysis of Tarmat oil A. Dual stage liquid N₂ cryogenic modulator; First column: VF-1MS 30m×0.25mm×0.25µm; second column: BPX50 1m×0.1mm×0.1µm. Modulator: 45°C offset to primary oven, second column: 15°C offset to primary column.

The independent 1D GC-MS analyses gave details in hopane, steranes, cheilanthane, adamantanes, naphthalenes, phenanthrenes, benzothiophenes, biphenyls, aromatic steroids and bicyclics. The two oils showed very similar results in each studied items, for example, in biphenyls, as listed in Table 3.3.

So the 2D-GC FID group type analysis of the two oils agrees with the 1D GC-MS detailed analysis on that the two oils are the same.

	Normalized Area%_ Oil A	Normalized Area %_oil B
3-rings	0.41	0.43
2-rings	1.55	1.56
1-ring	7.83	7.86
Polycyclic-1	0.05	0.05
Polycyclic-2	0	0
before nC ₁₇	69.53	69.32
after nC ₁₇	20.63	20.78

Table 3.2. 2D-GC FID group type analysis of Tarmat oil A and B

	BP	2MBP	DPM	3MBP	4MBP	DBF	DBT
<i>Oil A</i>	7.71	2.68	6.49	8.82	4.82	13.45	253.05
<i>Oil B</i>	8.21	2.88	6.69	8.89	4.93	13.60	252.87
	MBP ratio	DPM ratio	DPM/MBP ratio	DBF ratio	BP/DBT ratio		
<i>Oil A</i>	0.42	0.46	0.40	0.64	0.03		
<i>Oil B</i>	0.42	0.45	0.40	0.62	0.03		

BP: biphenyl; 2MBP: 2-methylbiphenyl; DPM:diphenylmethane; 3MBP:3-methylbiphenyl; 4MBP: 4-methylbiphenyl; DBF: dibenzofuran; DBT: dibenzothiophene; MBP ratio: MBP ratio = 4-methylbiphenyl / (2- + 3-methylbiphenyl); DPM ratio = diphenylmethane / (diphenylmethane + biphenyl); DPM / MBP ratio = diphenylmethane / (diphenylmethane + 2- + 3- + 4-methylbiphenyl); DBF ratio = dibenzofuran / (dibenzofuran + biphenyl); BP / DBT ratio = biphenyl / dibenzothiophene.

Table 3.3. Bipheyl compounds in Tarmat oil A and B based on 1D GC-MS analysis

3.3.2 Advanced product back allocation

Production back allocation of commingled oils from different zones or reservoirs is usually done with 1D GC by comparing composition of commingled oils with involved end members, in which process some subtle differences between inter-paraffin peaks (the GC peaks between n-paraffins) are taken into account. Some uncertainties exist in oil product back allocation when related end members are very similar, or when commingled oils contain heavy oil end members, or the inter-paraffin are not well resolved. GC × GC may help to overcome these uncertainties due to enhanced separation in complex oil. Better identification and quantification of single compounds in heavy oils with GC × GC helps to differentiate the heavy oil end members in commingled oils, and therefore improves heavy oil product back allocation.

In a heavy oil blind production back allocation test, artificial commingled heavy oil #1 (C1) was made of 40% heavy oil A and 60% heavy oil B ($C1 = 0.4A + 0.6B$), artificial commingled heavy oil #2 (C2) was made of 40% heavy oil B and 60% heavy oil C ($C2 = 0.4B + 0.6C$), and commingled heavy oil #3 (C3) made of 35% A, 35% B and 30% C ($C3 = 0.35A + 0.35B + 0.30C$). 2D-GC FID analysis was used for allocating all the three samples, of which results was compared with 1D GC FID method. Figure 3.5 shows the 2D-GC FID contour plot of commingled heavy oil C1, where much more peaks are well separated along the second dimension compared with the 1D GC FID. There are two big peaks of CS₂ and toluene, respectively, separated from the other main paraffins in the contour plot, and the peaks are so big that they look like contaminants in the oils. So in the product back allocation, the peaks were omitted to avoid any kind of contamination. The production back allocation results based on 2D-GC FID were compared with that based on 1D GC FID, as shown in Figure 3.6. It shows that overall 2D-GC FID and 1D GC FID show very similar accuracy in the production back allocation of two-end-member commingled samples, but 2D-GC FID shows much high accuracy (error % = 2) than 1D GC FID (error % = 10) in production back allocation of three-end-member commingled sample.

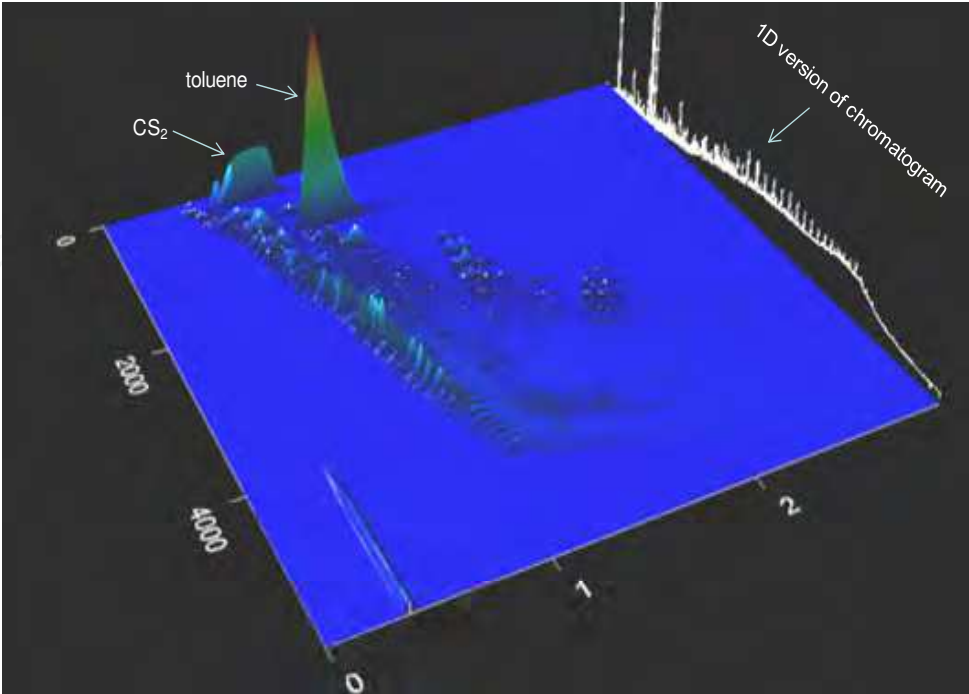


Fig. 3.5. 2D-GC contour plot of commingled heavy oil C1

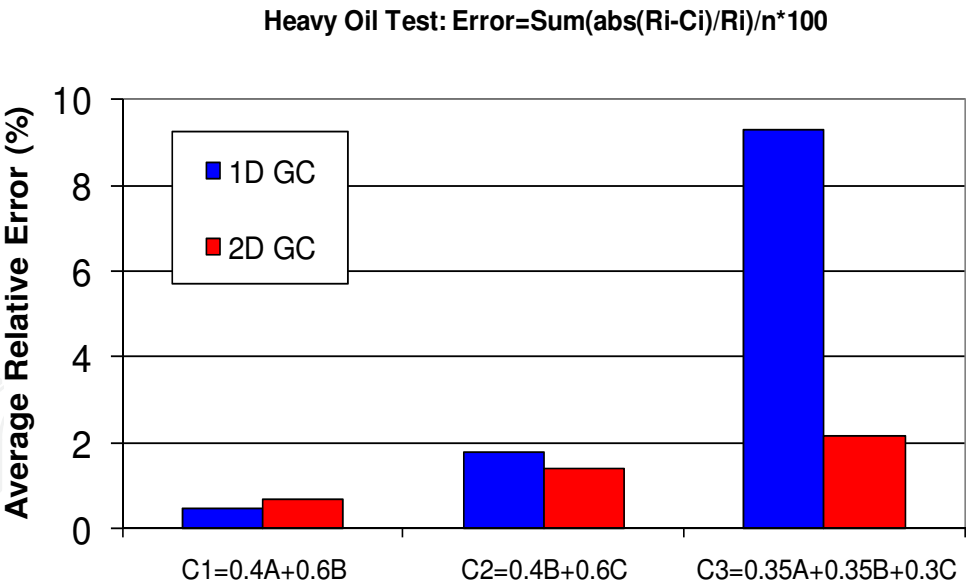


Fig. 3.6. Comparison of heavy oil production back allocation based on 2D-GC FID with 1D GC FID. Ri= real percentage of end members; Ci= calculated percentage of end members. n= number of end members.

4. Gas chromatography fingerprinting

Gas chromatography (GC) analysis is used in the petroleum industry to provide information related to fluid composition, which is needed in petroleum engineering and petroleum

geochemistry. Engineering and geochemical approaches, however, require different evaluation techniques for GC chromatograms. Most common application in petroleum engineering is the equation-of-state (EOS) for PVT characterization. Geochemical evaluations include using GC chromatograms for determination of reservoir connectivity, or back allocate commingled production. All these geochemical approaches are based on comparing GC chromatograms on their similarity to each other rather than obtaining compound specific quantitations. This comparison of GC chromatograms is commonly called “geochemical fingerprinting” in the petroleum industry. Fingerprints obtained by gas chromatography (GC) of crude oils is one of the less expensive, less risky and less time consuming methods to study different oils in terms of their similarity to each other. However, fingerprinting using GC chromatograms requires a defined and highly accurate analytical workflow to ensure high precision for assessing the exact similarity index. The analysis and fingerprinting evaluation of reservoir fluids also is affected by uncertainties. Crude oils are complex mixtures containing thousands of different hydrocarbons having huge differences in polarity and molecule size. Consequently, even for a same crude oil sample GC chromatograms can significantly differ when analyzed at different labs or when analyzed using different GC operating conditions. Therefore, it is necessary to keep analytical procedures, the column and the GC operational conditions the same for all GC runs when geochemical fingerprinting is needed. In addition, regular checks on GC performance need to be done to ensure comparability of GC runs. However, a slight shift in retention time is commonly still present when crude oils are analyzed consecutively. The problem mainly results from a slight deterioration in the columns separation performance between consecutive GC runs.

In order to make GC chromatograms directly comparable, it is required to eliminate this retention time shift, which is called warping. Different warping algorithms for retention time alignment of GC chromatograms have been published in the last decade. The most common techniques are dynamic time warping (DTW) and correlation optimized warping (COW) (Nielsen *et al.*, 1998; Tomasi *et al.*, 2004). The comparison of chromatogram similarity index for GC fingerprinting can be done after the preprocessing warping method. The fingerprinting technique relies on comparison of the chemical composition of several chromatograms acquired with the same chromatographic conditions and is based on the differences between peak height ratios of the different crude oil samples. The most advanced and newest technique to determine the similarity index between different chromatograms is the Malcom distribution analysis, recently described in Nouvelle and Coutrot (2010). Malcom distribution analysis uses a statistical method, based on consistent quantification of the uncertainty from chromatography peak height measurements, which provides absolute distances between fingerprints on a universal scale. The method is able to discriminate samples even if the amplitude of the compositional differences is about the same as the error in peak height measurements, and distances between samples are independent of the number of peak ratios available, and the uncertainty in the peak height measurements. The distribution analysis method uses the matrix of all neighboring non-alkane peak height ratios. This method provides a “chemical distance” between each couple of analyses on the basis of the statistical analyses of their respective peak ratios.

In a first step, the distribution histogram of all peak ratio differences available between pairs of chromatograms is built. Then, the inter-quartile range (IQR), as a measurement of

the spread of the distributions, is used to characterize the statistical distance between the fingerprints. Since the GC column becomes progressively degraded during analysis, the method requires the peak ratios of two chromatograms from the same sample to calibrate the uncertainty in the measurements each time a new batch of analyses is performed. The uncertainty is used to fix a threshold which distinguishes significant from insignificant distances ("distance threshold"). The distance threshold is about the same as the error for replicate analysis. Hereby, the method builds the distribution histogram of the differences between two chromatograms from the same sample. The shape of the histogram is used to precisely determine the uncertainty in the measurements. This uncertainty is used to obtain the expected profile of the distribution that the differences between two chromatograms should have if they were from the same sample (Nouvelle & Coutrot, 2010).

For GC fingerprinting purposes, the peak quality depends on two main quantities:

- Retention time,
- Peak height ratios

Peak height ratios are generally used for GC fingerprinting. In contrast to peak heights, the peak high ratios avoid the uncertainties dealing with discrepancies between the lightest and the heaviest compounds in the samples. The origin of such discrepancies can be linked to sampling procedure issues, evaporation of the lightest hydrocarbons or also blocking of the heaviest hydrocarbons into the column or the injection device. For all GC runs the retention times or the peak height ratios need to be checked on the tolerance deviations.

The peak height ratios are calculated from the indexation. In practice, several hundreds of peak height ratios are used. A maximal retention time difference between two peaks implied in a ratio is settled to 25 Kovats indices. A Kováts indice is a retention time measurement relative to two consecutive *n*-paraffins (Kováts, 1958):

$$KovatsID(i) = 100 \cdot \left(nC_{i-1} + \frac{\log_{10}(t_i) - \log_{10}(t_{C_{i-1}})}{\log_{10}(t_{C_i}) - \log_{10}(t_{C_{i-1}})} \right) \quad (1)$$

where:

- KovátsID(i): Kovats index of the compound,
- nC_{i-1} : number of carbon on the *n*-paraffin located just before the compound,
- t_i : retention time of the compound,
- $t_{C_{i-1}}$: retention time of the *n*-paraffin located just before the compound,
- t_{C_i} : retention time of the *n*-paraffin located just after the compound.

The aim of the indexation tool is to compare several chromatograms with a reference chromatogram. The peaks of the reference chromatogram are searched in the other chromatograms on the basis of a topological analysis. Figure 4.1 shows as example the chromatograms of two similar oils in the range of nC_{11} and nC_{12} . Even though both chromatograms are similar, they differ in certain peak height ratios, which clearly differentiate both chromatograms belonging to different oil samples.

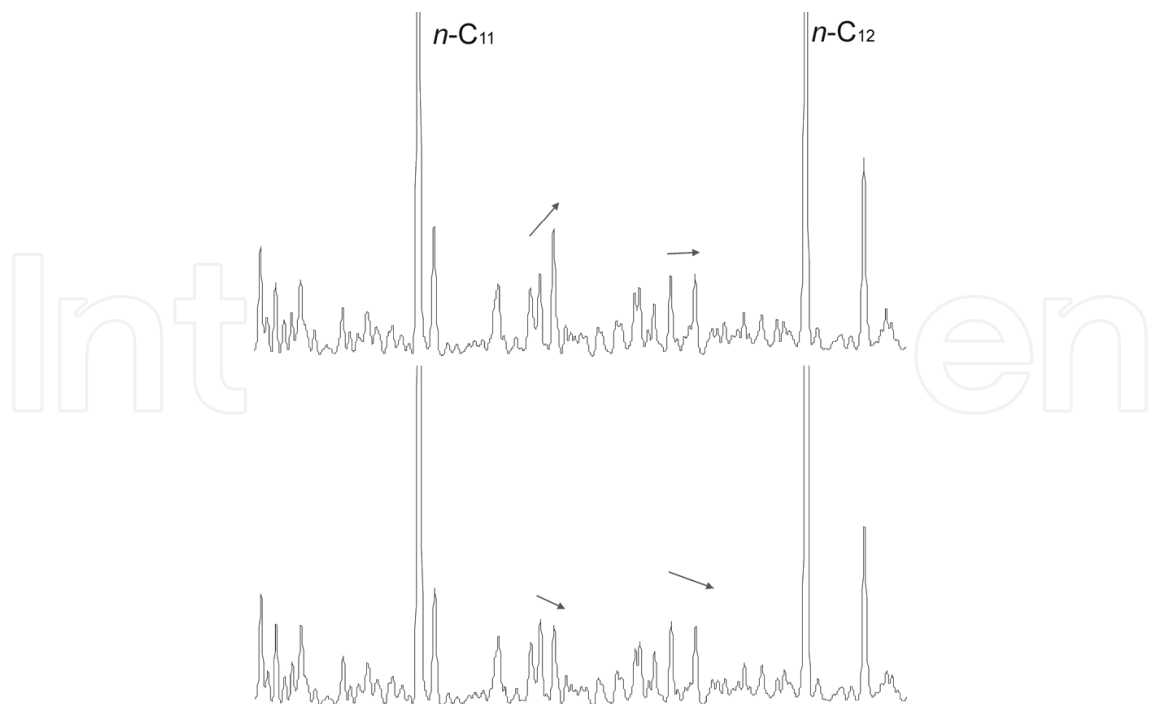


Fig. 4.1. Chromatographic comparison of 2 oil samples based on $n\text{C}_{11}$ - $n\text{C}_{12}$ inter-paraffin peak height ratios. Arrows indicate differences in neighboring peak height ratios, which indicates compositional differences between both crude oil samples.

The final outcome for a set of oil samples in terms of their similarity is commonly presented graphically as star diagram or cluster analysis. As example, Figure 4.2 shows the star diagram that compares 11 oils from a single well based on 37 $n\text{-C}_7 - n\text{-C}_{20}$ range peak height ratios.

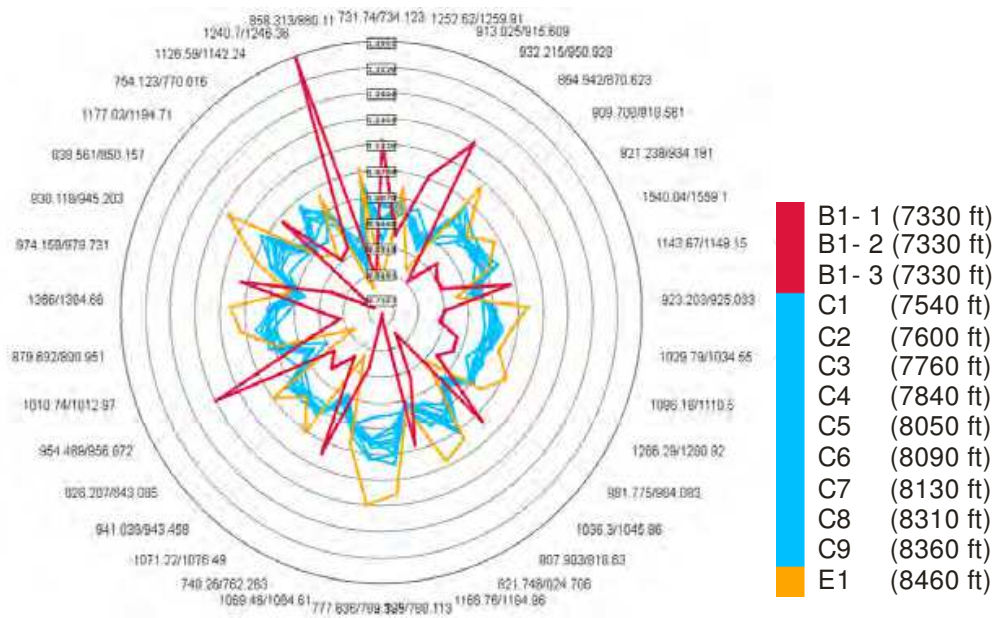


Fig. 4.2. Star diagram comparison of 11 oil samples from a single well based on 37 $n\text{C}_7$ - $n\text{C}_{20}$ range peak ratios. Each axis on the star shows the values for a different ratio of a pair of GC peaks. Peak labels are in Kovats Indices where peaks eluting from the GC between C_7 and C_8 are labelled in the 700's, those eluting between C_8 and C_9 are in the 800's.

Reduction of the number of variables was performed by using the Reduction by Inertia Constraint (RIC) method, with optimization by Inter/Intra-class maximization. The quality ω of each ratio is proportional to the standard deviation between the pre-groups, and inversely proportional to the standard deviation for analysis of samples within the same pre-group (Nouvelle, 2010). Thus, for a given ratio, the quality ω is the best when:

- The pre-groups are well separated.
- The analyses belonging to the same groups are close.

$$\omega_j = \frac{\sigma_j^{INTER}}{\sigma_j^{INTRA}}$$

(2)

with σ_j^{INTER} : standard deviation calculated for inter-class maximization

σ_j^{INTRA} : standard deviation calculated for intra-class maximization

Triplicate analyses of the oil sample B are included to determine the distance threshold for the dataset. The replicate analysis of sample B is then grouped to determine the quality of the different variables attached to the dataset. Comparison of the star patterns indicates that the oil sample B (red; three replicate analyses) is significantly different than the remaining oils marked as oils C (blue) and oil E (yellow).

Another graphical evaluation method for the similarity of GC chromatograms is the hierarchical cluster analysis. Hierarchical clustering is general mathematical approaches, in

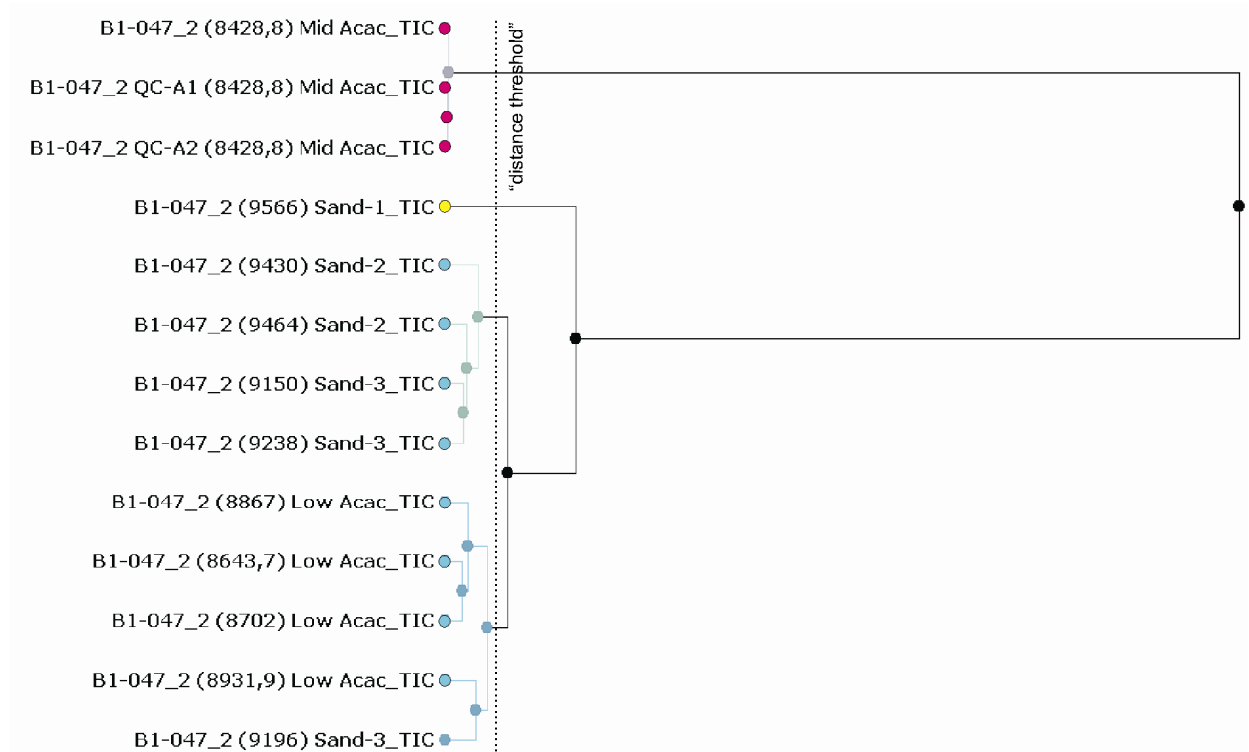


Fig. 4.3. Cluster analysis of the 11 oils from a single well based on 37 nC_7 - nC_{20} range peak height ratios.

which the oils are grouped together that are closer to one another based on the distribution analysis using GC chromatograms. A key component of the analysis is repeated calculation of distance measures between data, and between clusters once oils begin to be grouped into clusters. The outcome is represented graphically as a dendrogram (Figure 4.3). For the same samples set of 11 oils in Figure 4.2, the dendrogram is shown in Figure 4.3. The colouring of the groups on this diagram allows one to more easily discern the groups visually. Instrumental error is low as indicated by the tie line connection between the three replicate analyses of oil sample B.

5. Conclusions

Since its introduction, gas chromatography (GC) has been widely used as an important method in the analysis of petroleum hydrocarbon which have complex compositions. New techniques have extended the applications of GC in the petroleum composition analysis. In this chapter, several such techniques have been briefly reviewed, including high temperature GC (HTGC), two-dimensional GC (2D-GC, or GC×GC) and GC fingerprinting. Although some of these techniques, such as 2D-GC and GC fingerprinting, are still very young, it is expected that, with the advance of the research work, they will be used more routinely to give more precise composition in a broader range, and to give more important geochemical information of the petroleum fluids in the near future.

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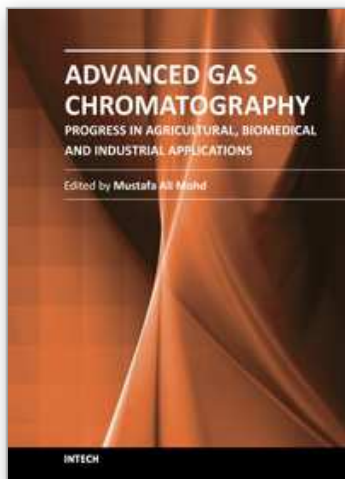
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Progress in agricultural, biomedical and industrial applications' is a compilation of recent advances and developments in gas chromatography and its applications. The chapters cover various aspects of applications ranging from basic biological, biomedical applications to industrial applications. Book chapters analyze new developments in chromatographic columns, microextraction techniques, derivatisation techniques and pyrolysis techniques. The book also includes several aspects of basic chromatography techniques and is suitable for both young and advanced chromatographers. It includes some new developments in chromatography such as multidimensional chromatography, inverse chromatography and some discussions on two-dimensional chromatography. The topics covered include analysis of volatiles, toxicants, indoor air, petroleum hydrocarbons, organometallic compounds and natural products. The chapters were written by experts from various fields and clearly assisted by simple diagrams and tables. This book is highly recommended for chemists as well as non-chemists working in gas chromatography.

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