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Comprehensive Two-Dimensional Gas Chromatography: method development and verification by characterisation of petroleum fractions

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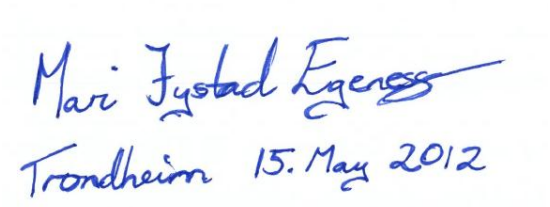
Preface

This study is the Master's thesis of Mari Jystad Egeness, student at the Norwegian University of Science and Technology in collaboration with Statoil ASA Research Centre Trondheim. The report is a result of a literature survey and numerous experiments.

Comprehensive two-dimensional gas chromatographic instruments are not very common in Norway at the present. The contractors' brief lecture on the instrument and published literature were the sources of in-depth information.

Starting with basic knowledge within chromatography, the learning curve has been steep. The project has been very interesting and challenging to say the least.



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My supervisors at Statoil ASA Research Centre Trondheim Bente Seljestokken and Anne Hoff: through numerous emails, meetings, and desperate phone calls you have been there backing me up since day one. You are sincerely appreciated and admired.

To my parents: thank you for giving me the personal characteristics of determination and endurance.

Abstract

Comprehensive two-dimensional gas chromatography is a multidimensional separation technique. A sample is separated by two properties on two different columns, typically by carbon number and polarity. The two columns are connected by a modulator. The modulator is responsible for collection of three to four fractions of each 1st column separation peak, condensation of the fractions, and introducing them as a sharp narrow band onto the 2nd column. It is a continuous process of condensation of succeeding 1st column fractions and transfer to the 2nd column. The individual separations are “sewn” together by the software to produce a two-dimensional chromatogram. The abscissa displays the carbon number separation and the ordinate axis show the separation of polar compounds.

Pre-set parameters such as carrier gas, gas velocities, detector temperatures, and column set were kept on recommendation by the installation contractors. Method development and optimisation was performed by exploring injection volume, oven temperature programs, and modulator time parameters. Hydrocarbon standards and petroleum fractions were analysed for determining the optimal parameter values. The result was two methods, one recommended for atmospheric gas oil (AGO) analyses and another for vacuum gas oil (VGO) analyses. Injection volumes of 0.015 to 0.002 µL gave low risk of column overload while still maintaining the abundance of compounds of low concentration. Temperature programmes of constant ramps gave good separation. A compromise between excellent separation and time of analysis resulted in using temperature ramps of 4.5 oC/min with a start and final temperature of 50 oC and 340 oC, respectively, for AGOs, and 3.5 oC/min with a start and final temperature of 150 oC and 340 oC, respectively for VGOs. A modulation time of 8000 ms and a hot jet duration of 500 ms proved to give good correlation between the 1st separation’s peak widths and the time needed for 2nd dimension separation.

Straight run and processed petroleum fractions were analysed by the optimised methods. Constructed templates for dividing the sample’s polarity distribution into groups gave a distribution of volume response of all the compounds within the defined groups. The hydrocarbon analyses of the petroleum fractions were straight forward; volume responses were directly proportional to weight percent of the sample. The hydrocarbon standards gave approximately the same response factor. The same did not apply for sulphur analysis. The standards’ responses were not very reproducible, and the response factors were not similar for the polarity classes. Identification of sulphur compounds in AGOs and VGOs is possible although quantification is not recommended at the present.

The methods showed to give good separation of both AGOs and VGOs. Although further optimisation especially of sulphur analysis, is highly encouraged.

Sammendrag

Comprehensive two-dimensional gas chromatography er en multidimensjonal separasjonsteknikk. En prøve separeres i to forskjellige kolonner, først med hensyn på kokepunkt deretter med hensyn på polaritet. De to kolonnene er koblet sammen av en modulator. Modulatoren er ansvarlig for å samle tre til fire fraksjoner av hver topp fra første kolonnes separasjon, kondensere fraksjonene og introdusere de som skarpe, smale bånd på kolonne nummer 2. Dette er en kontinuerlig prosess av kondensering av fortløpende fraksjoner fra den første og overføring til den andre kolonnen. De individuelle separasjonene «sys» sammen av programvaren til et todimensjonalt kromatogram. X-aksen viser separasjonen av karbontall og y-aksen viser separasjonen med hensyn på polaritet.

Forhåndsinnstilte parametere som bæregass, gasshastigheter, detektortemperaturer og kolonnesett ble holdt på verdier anbefalt av installatørene. Metodeutvikling og optimalisering ble utført ved utforsking av injeksjonsvolum, ovnstemperaturprogram og modulatorens tidsparametere. Hydrokarbonstandarder og petroleumsfraksjoner ble analysert for å bestemme optimale verdier. Resultatet var to metoder. Én anbefalt for atmosfæriske gassoljer (AGO) og én for vakuum gassoljer (VGO). Injeksjonsvolum fra 0,015 til 0,002 µL ga liten grad av overbelastning av kolonnene samtidig som forbindelser av lave konsentrasjoner kunne detekteres. Temperaturprogrammer med konstante gradienter ga god og jevn separasjon av prøvekomponentene. Et kompromiss mellom utmerket separasjon og analysetid endte i temperaturgradienter på 4,5 ^{o}C/min med start- og sluttemperatur på 50 ^{o}C og 340 ^{o}C, respektivt, for AGO, og 3,5 ^{o}C/min med start- og sluttemperatur på 150 ^{o}C og 340 ^{o}C, respektivt, for VGO. Moduleringstid på 8000 ms og *hot jet* varighet på 500 ms ga god korrelasjon mellom toppbreddene fra separasjonen i første dimensjon og tidsbehovet for separasjonen i den andre dimensjonen.

Uprosseserte og prosesserte petroleumsfraksjoner ble analyser ved bruk av de optimaliserte metodene. Konstruerte maler for inndeling av prøvenes polare fordeling i grupper resulterte i dataverdier av volumresponsen for alle forbindelsene innenfor de definerte gruppene. Hydrokarbonanalysene av petroleumsfraksjonene var rett frem, volumresponsen var direkte proporsjonal med vektprosent i prøven. Analyse av svovel var mer utfordrende. Standardene ga ikke reproduserbar respons, og responsfaktorene var ikke like for de forskjellige polare gruppene. Identifisering av svovelforbindelser i AGO og VGO er likevel mulig selv om kvantifisering ikke er anbefalt på nåværende tidspunkt.

Metodene viste seg å gi god separasjon av både AGO og VGO. Videre optimalisering, spesielt for svovelanalyse, er sterkt oppfordret.

Abbreviations

1D GC	One-dimensional gas chromatography (conventional GC)
2D GC	Two-dimensional gas chromatography (here referred to GCxGC)
α	Separation factor
AGO	Atmospheric gas oil
AR	Atmospheric residue
FID	Flame ionization detector
GC	Gas chromatography
GCxGC	Comprehensive two-dimensional gas chromatography
HETP	Height equivalent of a theoretical plate
HGO	Heavy gas oil
HPLC	High pressure liquid chromatography
HVGO	Heavy vacuum gas oil
k	Retention factor
LC	Liquid chromatography
LCO	Light cycle oil
LGO	Light gas oil
LVGO	Light vacuum gas oil
MP	Mobile phase
N	Plate number
n_C	Peak capacity
NCD	Nitrogen chemiluminescense detector
RF	Response factor
R_s	Resolution
SP	Stationary phase
SR	Straight run
SCD	Sulphur chemiluminescense detector
t_M	Column hold-up volume
t_R	Retention time
t_w	Peak base width
VGO	Vacuum gas oil
VR	Vacuum residue

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1 Introduction

A comprehensive two-dimensional gas chromatograph (GCxGC) was purchased at Statoil ASA Research Centre Rotvoll in 2011. The intent of the instrument was analysis of gas oils and their processed product fractions concerning the content of aromatic, sulphur, and nitrogen species. Present methods for characterisation of such mixtures are based on entire group types of aromatics, i.e. monoaromatics, diaromatics, triaromatics, total aromatics (1), and total sulphur (2) and nitrogen content (3). Comprehensive two-dimensional gas chromatography can identify petroleum fractions and products by single components as well as group types (4, 5).

The aims of this project were to develop and optimize methods for characterisation of aromatics and sulphur compounds in middle and heavier distillate petroleum fractions. The methods were to be verified by analysis of various distillation cuts. Peak identification and polarity group identification was performed by applying constructed templates in the software for easy data acquisition. Standards were utilised to validate the template groupings. Nitrogen analysis was not investigated in this study.

2 Theory

2.1 Theoretical aspects of chromatography

Chromatography is a separation technique taking advantage of the partitioning of a solute between a MP (MP) and a SP (SP). The detection of a compound is obtained by a chemical or physical change in the effluent matrix (6).

The MP can be a liquid, gas or supercritical fluid (5, 6). The most commonly applied MPs for gas chromatography (GC) are the inert gases helium, hydrogen and nitrogen. In liquid chromatography (LC) solvents such as methanol, acetonitrile and water are most commonly used (5). The purpose of the MP is to transfer the analyte through the chromatographic system. The SP is chosen on a basis of which analytes are of interest to separate. The choice of SP in liquid chromatography is not only depending on the analyte, but also the MP. In LC the MP dissolves the analyte which is another parameter to consider when choosing the MP. In gas chromatography the gas pushes the sample through to the detector, and the analytes are not dissolved in the MP in the same sense as in liquid chromatography (5, 6).

In LC and GC the SP is located inside a column, and has different properties and characteristics depending on the separation technique used. If the LC technique is utilized, the SP may be a gel with a fine distribution of small pores or a liquid film spread on a supporting material. The most used SPs in liquid chromatography are the C_{18} materials. In GLC (gas liquid chromatography) the SP is often a thin film spread on a supporting material inside the column. The film can be of various thicknesses; however, today the most commonly used film thicknesses are in the µm range and used in capillary columns such as wall-coated open tubular columns (WCOT). The most used SPs in gas chromatography are the polysiloxanes with various substituent groups such as methyl and phenyl in the structure (5).

2.2 Retention time and SP composition

The chemical composition of the SP is of great importance due to its influence on the partitioning of the solute. The entire separation process relies upon this mechanism, and different degrees of partition between the dissolved sample and the SP (5, 6). This results in the key information for

chromatography, the retention time. The retention time of a molecule is a property specific parameter valid for a defined experimental composition of the SP and its properties, the MP's flow velocity, and temperature in the chromatographic system (5, 6).
Changing the chemical composition of the SP by adding more polar functional substitutes increases the retention of polar molecules in a sample and vice versa when adding less polar substitutes, for normal-phase chromatography (5, 6).

2.3 Carrier gas and gas flows

The carrier gas in gas-liquid chromatography is the medium for transporting the sample through the separation column. The most common carrier gases are hydrogen, helium and nitrogen (5, 6). The different carrier gases, even though they are non-solvating (inert), influence resolution through the effects on the column's efficiency as seen in Figure 1. The separation time is also influenced by the carrier gas due to the different optimum gas velocities.

The viscosity of gases increases with temperature causing the velocity to drop if the pressure is kept constant. To achieve a linear velocity, flow control is advised as this will increase the pressure upon increasing temperature (5).

The plate number, N, is a measure of the column efficiency. There are no actual plates in a GC column; the word plate number has a historic origin when the columns were believed to have plates similar to those in distillation columns. The efficiency of the column is increasing for higher plate numbers (5, 6). The plate height (or the height equivalent to a theoretical plate, HETP,) is also a measure of the column's efficiency; a low plate height indicates better efficiency.

The plot of the carrier gas velocity as a function of the plate height reveals the optimum gas velocities providing good separations. The van Deemter plots of the common carrier gases are shown in Figure 1.

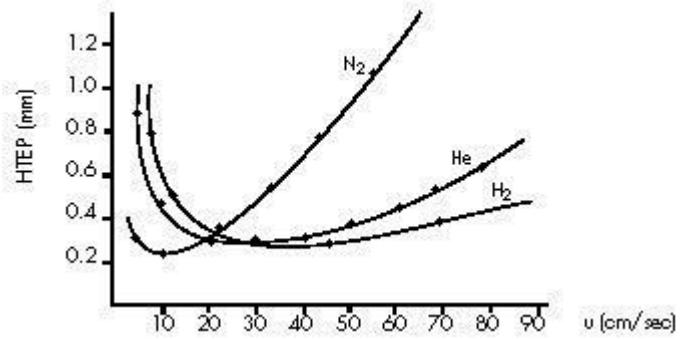


Figure 1. van Deemter plot of average linear velocities (cm/s) for N_2, He and H_2 against plate height (mm). (5, 6).

Nitrogen demands the lowest velocity; however, it only allows an impractically low gas velocity. Hydrogen is the best alternative since the slope of in the van Deemter plot is relatively flat. The explosion hazard present by using H_2 does, however, make helium a safer choice without compromising the separation efficiency too much (5, 6).

Typically, a 2D GC carrier gas flow is adapted from a 1D GC optimised column similar to the first dimension GCxGC column. A 1D GC column would have an optimum gas velocity of 35 cm s^{-1}, when H_2 is the carrier gas, compared to a calculated optimum value of 18 cm s^{-1} for a 2D GC 1st dimension column (7). Greibrokk et al. (6) describe that the optimum gas velocity equals the velocity which gains 10 % increase in the plate height.

GCxGC often operates with gas velocities optimised for the first column. This leads to a carrier gas velocity well above optimum for the second column and a decrease in efficiency due to the increased plate height (7). The second column is of both shorter and narrower dimensions compared to the first column. The high gas velocity for the second dimension produce chromatograms within the short analysis time required, i.e. up to 10 seconds. If the velocities are optimised for the second column the time of analysis will increase, and the first column will provide a low separation efficiency (7).

In the case of analysis of heavy oils it can be beneficial to change the temperature programme into higher start values and other temperature ramp values. This can cause shifting of peak retention order, making identification hard if such temperature changes are not controlled. However, adjusting the average linear velocity in proportion to the change in the temperature programme

avoids this issue (8, 9). The calculation of the average linear velocity in accordance with a new temperature programme is described by Equation 1:

$$New\ program\ rate = Old\ program\ rate \cdot \frac{New\ average\ linear\ velocity}{Old\ average\ linear\ velocity}$$

Equation 1. Calculation of program rates and average linear velocities (8, 9).

When an isothermal program is used the calculation of the average linear velocity is as described in Equation 2:

$$New\ isothermal\ time = Old\ isothermal\ time \cdot \frac{Old\ average\ linear\ velocity}{New\ average\ linear\ velocity}$$

Equation 2. Calculation of isothermal programmes and average linear velocities (8, 9).

This type of method transfer is more applicable to one-dimensional gas chromatography than comprehensive two-dimensional gas chromatography. For the second dimension there are small possibilities of enhancing the separation as the analysis time is a few seconds. The most important point is to have sufficient retention for the analytes in the second dimension. If the second column is situated in a second and independent oven; this can make retention optimalization easier (8-11).

2.4 Resolution and peak capacity

A sample's components have to be well separated in order to yield the amount and quality of information needed for analysis and reporting. To achieve good separation the chromatographic system has to obtain sufficient resolution, and an adequate peak capacity to match the sample's complexity.

Resolution, R_s, is a measure of the separation of two peaks. It is a quantitative value determined by the retention time of the two peak maxima and their base width, (5, 6), Equation 3:

$$R_s = \frac{t_2 - t_1}{\frac{1}{2}(t_{w1} + t_{w2})}$$

Equation 3. Resolution of two peaks (5, 6).

Where t_1 and t_2 are the retention times of peak 1 and 2, respectively, and t_{w1} and t_{w2} are the base widths of the respective peaks 1 and 2.

Baseline resolution requires R_s = 1.5. (5, 6).

The separation factor, α, describes the relative retention of any two peaks in the chromatogram and thus the selectivity of the chromatographic system. The factor is determined by Equation 4 (5, 6):

$$\alpha = \frac{t_{R'(B)}}{t_{R'(A)}} = \frac{k_B}{k_A}$$

Equation 4s Separation factor (5, 6).

$t_{R'(A)}$ and $t_{R'(B)}$ are the relative retention of peak A and B, respectively, and k_A and k_B are the retention factors of the respective peaks A and B.

The separation factor reflects relative retention of the two peaks not taking the width of the peak into account. The factor always has values greater than or equal to 1 where a value of 1 indicates coelution of the peaks (5, 6).

"*Peak capacity is a parameter describing the separation power of a column. It is defined as the total number of peaks that can be separated with a specified resolution within a given time interval*" (5). Peak capacity, n_C, is given by Equation 5:

$$n_C = 1 + \int_{t_M}^{t_R} \left(\sqrt{\frac{N}{4t}} \right) dt$$

Equation 5. Peak capacity (5).

t is the separation time, t_M the column hold-up volume, and t_R the maximum retention for elution of the last peak. A resolution of 1 is often adopted for simplicity and the peaks are assumed to be Gaussian (5).

2.5 Inlets in gas chromatography

There are several types of inlets to choose from when introducing a sample to the column. Most common are the split/splitless inlets. However, this injection technique suffers from discrimination of heavy sample components while using the split mode (5). This can to some extent be avoided by using the inlet in the splitless mode, but the samples have to be diluted in order not to overload the column.

A liner is situated inside the inlet. It is a glass or fused silica tube where the vaporized sample is allowed to be heated and/or split away from the column inlet. The liner is specially designed for sample splitting if split injection is applied. Numerous of designs are available where the application determines which design to use. The liner aids in guiding the sample straight into the column. The liner surface can be contaminated by heavy oil fraction components resulting in errors due to contamination of future samples (5). A film of heavy samples can build up over time to cover the inside of the liner. Compounds of later injected samples can adsorb and adhere to this film causing errors in analyses (5). Splitting of the injection volume allows more concentrated samples and larger volumes to be injected (5). The vaporized sample is diluted by the carrier gas entering the liner. A high split ratio means that a large fraction of the sample is driven away from the column inlet by carrier gas and only a small part of the vaporized sample volume is actually injected and vice versa for low split ratios (5).

A similar inlet is the programmable temperature vaporizer inlet (PTV). The PTV can be used in both a split and splitless mode. The advantage of the PTV inlet is the possibility to use a temperature programme in the injection step of the analysis leading to a lower extent of discrimination of heavier sample components even if the split mode is selected (5).

A third technique is the cold on-column injection. This is more or less replaced by the PTV inlet; however, it still has some applications. The cold on-column technique injects the liquid sample directly onto the column or a retention gap (uncoated precolumn). A retention gap is often installed to prolong the lifetime of the analytical column and to improve sample introduction. The advantage of this method is that the injected sample is completely identical to the original sample composition (5).

Injection of a sample has to be repeatable and accurate in the means of the volume injected and the length of needle's penetration into the liner. The sample must be homogenous, in liquid phase, stable in the temperature range of operation, and vaporizable (6). The volume of injected sample can overload both the liner and the columns. Liner overload may cause a sample to enter the liner housing, contributing to contamination of later sample injections. Column overload causes lower separation efficiency and band broadening (5). In addition, it is possible to overload the reaction cell of reaction based detectors leading to errors in response and reproducibility (12).

2.6 Detectors

The choice of a detector depends on the types of samples being analysed, and what is important to detect. There are a large variety of detectors available; however, the flame ionization detector (FID) is most frequently used. This is a near universal detector, responding to any hydrocarbon present in the effluent (5, 6). The mechanism of detection is based on ionization of an analyte in a hydrogen flame leading to an electric current, which is measured and transcribed into a signal printed in a chromatogram (5, 6).

The thermal conductivity detector (TCD) is also a widely used detector for general analysis. The detector measures the difference in conductivity of the MP alone and the MP containing analytes (5, 6). This detector is universal, responding only to the effluents thermal conductivity, i.e. it is a bulk property detector (5, 6).

Another category of detectors are the specific detectors only responding towards one or a few compounds present in the sample. The chemiluminescense detectors are element-specific, where a chemical reaction is responsible for producing chemiluminescense, which is measured by a photomultiplier (5).

2.6.1 Flame ionization detector

The flame ionization detector (FID) has a sample detection limit of approximately 10^{-13} g carbons with a linear response range of 10^6 to 10^7. The FID responds proportionally to the carbon number in the hydrocarbon ion current produced by radical reactions in the flame (5) Reaction 1:

$$CH^{\bullet} + O^{\bullet} \rightarrow CHO^{*} \rightarrow CHO^{+} + e^{-}$$

Reaction 1. Ionization of hydrocarbons by radicals formed in the FID flame (5).

2.6.2 Sulphur chemiluminescense detector

The sulphur chemiluminescense detector (SCD) is a compound selective detector. It responds only to a sulphur containing product produced by the chemiluminescense reaction taking place in the reaction cell. (5). In the cell of the SCD Reaction 2 takes place:

$$Sulphur\ compound \rightarrow SO + H_2O + other\ products$$
$$SO + O_3 \rightarrow SO_2 + O_2 + h\eta\ (< 300 - 400nm)$$

Reaction 2. Reaction in the SCD reaction cell (5, 13).

The linear response range of the SCD stretches to 10^4 to 10^5. The detection limit of the SCD is 10^{-13} g (5). However, these are values where SCD is the only detector, not parallel couplings as in this particular instrument setup.

2.7 High Pressure Liquid Chromatography (HPLC)

HPLC often refers to both high pressure liquid chromatography and high performance liquid chromatography. Typically operating parameters are approximately 100 - 300 bar, and ambient temperatures (6). As the name of the technique indicates, the MP is a liquid. The SP is usually C_{18} materials with substituents determining the sample properties to be separated (5). A common detector in HPLC is the UV/VIS detector. It responds only to sample compounds absorbing light at the pre-set wavelength(s) (5, 6). Another commonly used detector is the refractive index (RI) detector. It measures the difference in refractive index of the MP and the MP containing sample, i.e. it is a bulk property detector (5).

2.8 Two-dimensional gas chromatography – heartcutting

Multidimensional gas chromatography applies two columns with different separation mechanisms to obtain sample information. A separation by two different columns without a modulator would result in a 1D analysis with a combined separation mechanism of the two columns (4). In order to have a true multidimensional analysis Giddings (14) defined two rules that must be fulfilled: the sample must be subjected to two independent separations, i.e. the different properties of the 1st and 2nd column, and the integrity of the first separation have to be kept, i.e. the peaks separated

by the first column must still be separated after the second column (14). Literature clearly states that gas chromatography (1D GC) has its limitations towards separation of complex sample mixtures such as environmental and petroleum samples (5, 14, 15). The peak capacities of the columns utilized are not sufficient to separate the large amount of components in such samples within reasonable time (5, 15).

Heartcutting was one of the first widely accepted multidimensional GC techniques. Selected fractions of one column's separation are isolated, heartcutted, and transferred by a valve or switch to another column for further on-line separation (16). The combination of the first and second separation yields a two dimensional chromatogram of the selected fractions. This is a versatile tool for multidimensional analysis of peaks or peak clusters of specific interest (5, 17). Multidimensional analysis of the entire sample is possible by comprehensive two-dimensional gas chromatography (5, 16).

2.9 Comprehensive two-dimensional gas chromatography

True multidimensional systems such as comprehensive two-dimensional gas chromatography (GCxGC or 2D GC) can in favourable cases approximately multiply the peak capacity of the columns (4, 5). GCxGC employs two columns in series with different SP composition (retention mechanisms). The two columns are separated by an interface, the modulator, which is the key instrument part of GCxGC (4, 5, 18-20). A schematic illustration of a GCxGC is shown in Figure 2.

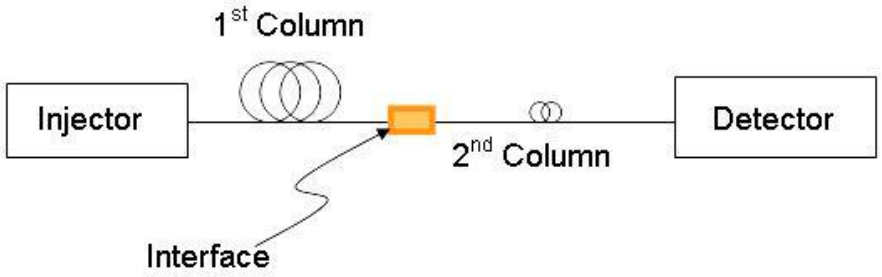


Figure 2. Schematic illustration of a GCxGC instrument (21)

2.9.1 The modulator

The modulator is responsible for the transfer of effluent from the first dimension to the second dimension. The modulator can have different configurations e.g. moving slotted heater, a longitudinally modulated cryogenic trap, and cryo-jets.

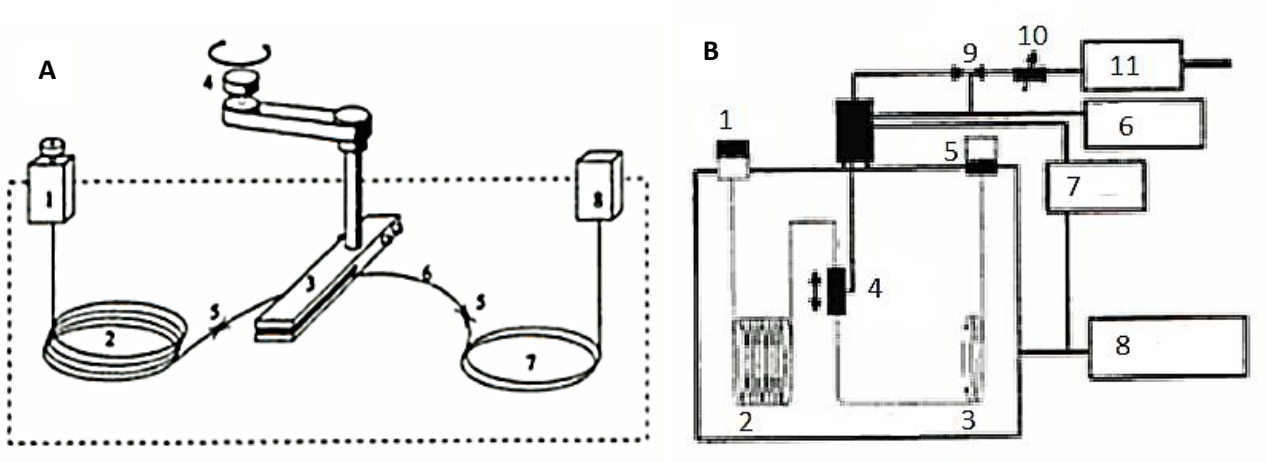


Figure 3. Moving slotted heater (A) and longitudinally modulated cryogenic trap (B). 3A: 1=injector, 2=1st column, 3=slotted heater, 4=stepper motor, 5=press fit connector, 6=modulator capillary, 7=2nd column, and 8=detector. 3B: 1=injector, 2=1st column, 3=2nd column, 4=cryogenic trap, 5=detector, 6=temperature controller, 7=timer, 8=data acquisition and evaluation, 9=on-off valve, 10=needle valve, 11=CO_2 supply (cryogenic coolant) (5).

The moving slotted heater is illustrated in Figure 3A. The slotted heater moves over a thick film SP capillary modulator column. The sample is collected and trapped after the first column by cold trapping at oven temperatures. At the end of the modulator capillary, connected to the 2nd column, there is an uncoated zone where sample compounds are desorbed when the slotted heater passes over with a temperature 100 ^{o}C above the oven temperature (5, 20).

In Figure 3B the longitudinally modulated cryogenic trap interface is shown. When the components in the sample move to the second column they are trapped in a short segment where the cryogenic trap moves in a longitudinal motion. When the trap moves again the oven temperature is responsible for releasing the sample compounds as a narrow pulse for separation in the 2nd column (5, 20).

The loop modulator is the most recent version of modulator design. This type of modulator employs no moving parts near the column as the thermal cooling and heating are conducted by fixed nozzles (18, 19). The column part in the modulator, making up the loop, is often an uncoated capillary column (retention gap), or a pre-extension of the second analytical column. The latter has the advantage of fewer column connection points and a slightly reduced risk of leaks or contribution to band broadening of the peaks. However, the focusing of the analytes in the loop is better conducted using a retention gap, as this will not contribute to any separation within the loop (5, 12, 19). Figure 4 A and B illustrates the loop modulator.

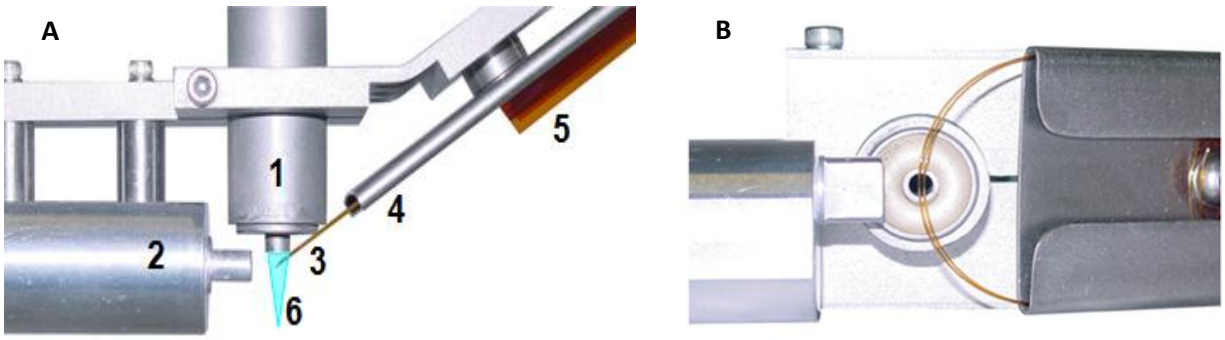


Figure 4. Loop modulator assembly, shown in accumulation mode, hot jet off A. 1=cold jet assembly, 2=hot jet assembly, 3=modulator loop, 4=column holder, 5=Kapton film tensioner, 6=cold gas jet. Figure 4B is a view of the modulator from below (19).

Sample fraction transfer is achieved by condensation of the effluent as it enters the modulator loop by applying a cold gas jet to a small part of the loop, and rapid heating of it to eject the sample fraction onto the second dimension column (18, 19). The condensed sample plug is transported through the loop by the carrier gas flow. It moves through the cold jet, before it is subjected to a hot jet pulse, which ejects the condensed plug into the second column as a narrow band. When the first sample plug has passed the cold jet a second time, the conditions in the modulator are once again able to trap the oncoming effluent (4, 5, 19, 20). To achieve this two stage modulation the loop must be coiled in a manner to allow the loop column to be subjected to the cold jet twice (close to the start and end of the loop capillary) (19). Single stage modulation is also a possible loop modulation configuration. In this case the sample is condensed once by the cold jet before firing of the hot jet pulse. Single stage modulation suffers from a larger degree of breakthrough effects (sample fractions escape the modulation step as a consequence of the hot jet being on). Single stage modulation is much more sensitive to the experimental conditions than a two stage modulation (19).

The modulator is time-programmable in respect to the interval of collecting effluents from the first column.
The time interval must be at an appropriate value, allowing at least three sampling fractions of the first column peaks (5, 22, 23). Also, a sampling frequency of four fractions of the first dimension peak has been stated as desirable (20). Too long modulation period will provide few second dimension peaks, while too short modulation period will provide too many second dimension peaks. The result can be incomprehensive chromatograms due to wraparound. Wraparound is a consequence of too long retention of second dimension analytes. The analytes elute in the following modulation cycle(s) (5, 20, 23, 24).

Modulation time is crucial in comprehensive two-dimensional gas chromatography (GCxGC) analysis. The time a fraction stays inside the loop before it is transferred to the second column by the hot jet determines the quantity and frequency of the fraction of each peak from the first separation to be collected. Also, the modulation time reflects the second dimension separation time (4, 5, 18-20). The second column is of much smaller dimensions than the first dimension column, allowing rapid separation of the fractions collected from each successive first dimensional peak. Collection of fractions with short time intervals yields many fractions to be separated in the second column and shorter separation time (19). Collection of fractions with longer time intervals provides few fractions to be separated by the second column allowing a longer separation time for each fraction. The sample component's first dimension peak widths determines the appropriate modulation time (4, 5, 18-20).

The hot jet is responsible for transferring the sample fraction as a sharp, narrow band onto the second column (5, 19). The duration of the hot jet is essential in the manner of getting the focused sample plug onto the next column. Larger sample plugs need warmer hot jet pulses in order to be transferred and vice versa for small plugs. The temperature of the hot jet is determined in the GC method parameters; an offset value of 100 ^{o}C in respect to the GC oven program is often applied (18, 19). Gaines and Frysinger (18) explains that even though the heating block has an offset value of 100 ^{o}C above oven temperature the actual hot jet temperature is approximately 40 ^{o}C above oven temperature.

The duration of the hot jet should be low to reduce breakthrough effects, but still vaporise the peak fraction (19). Breakthrough effect is the co-transfer of uncondensed sample fractions as a

result of the influence of the hot jet. The breakthrough effect is, however, already reduced by using a two stage modulation. The content in the loop is condensed by the cold jet twice, once at the start of the loop and once at the end. Sample fractions that may be co-transferred by the hot jet are already condensed by the cold jet. This will keep the sharpness of the sample band required for good separation on the second column, although, breakthrough peaks will not be as sharp as two stage modulation peaks (19).

There are several parameters influencing the modulator time parameters; the loop capillary length is one, other parameters are carrier gas flow, oven temperature, and sample fraction size (peak width of 1^{st} dimension's separation) (12, 19, 23).

2.9.2 Construction of chromatogram

The special GCxGC software organizes the signal from the detector into a two-dimensional chromatogram. The 2D raw data is stacked next to each other as seen in Figure 6. The software use the modulation time to "sew" the 1^{st} and 2^{nd} separation together. The separation from the first column is displayed at the abscissa and the separation from the second column is placed at the ordinate axis. The result is a chromatogram with the retention times of the two different separations of the sample plotted against each other (4, 5, 20). The abundance is shown in the third axis, indicated by the colour intensities in the chromatogram or by the height of the peaks in the three dimensional view (20).

Figure 5 shows an illustration on how separation of compounds with similar and dissimilar first and second dimension properties is conducted in GCxGC. Figure 6 illustrates how a two-dimensional gas chromatogram is generated and converted into a three dimensional chromatogram (20). Peaks are designated by their retention time combination (t_R (1), t_R (2)) (4, 5, 20, 25).

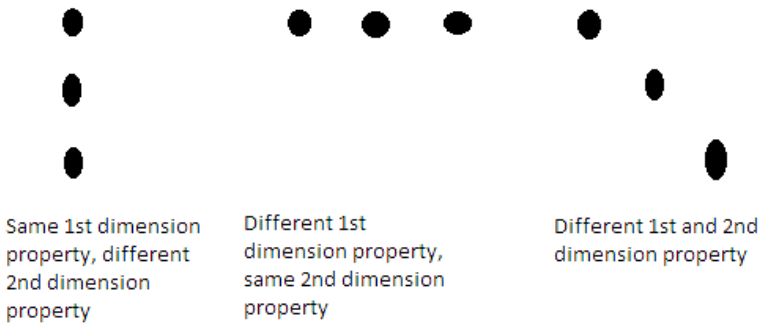


Figure 5. Separation patterns for compounds with similar and dissimilar properties in the 1st and 2nd dimension. Adapted from (4).

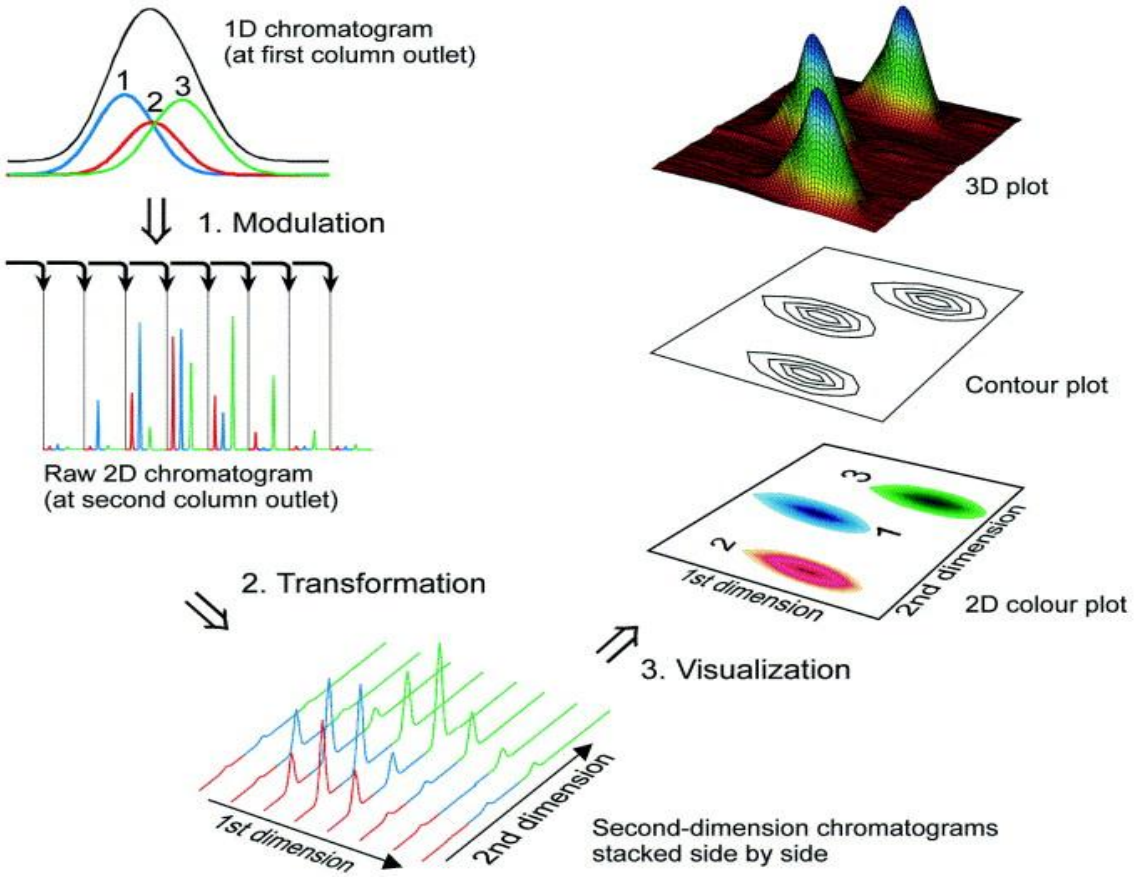


Figure 6. Transformation of a 1D chromatogram into 2D and 3D chromatogram (20).

2.10 Oil composition and refining

2.10.1 Oil composition

Crude oils contain different compositions of hydrocarbons. This is a result of variations of the source for organic matter, the degradation processes (bacterial and non-bacterial), differences in the thermal, and pressure driven processes in the reservoirs (26, 27).

In petroleum industry the nomenclature is often different from IUPAC nomenclature. Typical petrochemical classes are paraffins (n-alkanes), iso-paraffins (branched alkanes), olefins (alkenes), naphthenes (cyclic alkanes and cyclic alkenes), aromatics; mono-, di-, and tricyclic-aromatics and heterocompounds (28, 29). The main aromatic groups can be further divided into subgroups of monoaromatic naphthenic, diaromatic naphthenic, and triaromatic naphthenic.

Polycyclic aromatic sulphur heterocycles (PASHs) exists with an even larger variety of structures than polycyclic aromatic hydrocarbons (PAHs). This is due to the presence of sulphur atoms. There can be over 10,000 species of sulphur compounds in a middle distillate fraction of crude oil (30).

Sulphur compounds can be detected by chemiluminescense detector (SCD). All previous studies on GC x GC SCD use shorter columns, especially in the 1^{st} dimension, than the column set applied here (30 m). Typical 1^{st} dimension columns are 6 – 10 m (2, 30, 31).

There are specification and threshold values which cannot be exceeded for e.g. commercial diesel. Maximum PAH levels (di- and +triaromatics) are 8 wt % and the total sulphur content cannot be higher than 10 ppm sulphur in EU (2, 31, 32).

Vacuum gas oils and residues display a challenge to gas chromatographic analysis. They contain hydrocarbons with high boiling points (+375 ^{o}C) and complex structures (33). The number of isomers increases proportionally to the number of carbon atoms (33). Due to the demanding refinery processes as explained in Chapter 2.10.2, knowledge on chemical composition on a molecular basis is important for optimalization of the condition of these processes (33). Dutriez et al. (33) claims that comprehensive two-dimensional gas chromatography at present (2010) is limited towards middle distillate analysis. This is supported by the temperature operating range

limit of polar columns and challenges in the desorption step of modulation (33). However, the same study showed a separation of a VGO by using a dimethylpoly-siloxane 1st dimension column and a (50%phenyl) polysilphenylenesiloxane 2nd dimension column (33).

2.10.2 Refining

Crude oil has to be processed in order to get the desired commercial products. Desalting and distillation are the first steps in a refinery (26).

Crude oil and unprocessed cuts are often referred to as feed (feedstock) or straight run (SR). These feeds or straight runs are processed to give the desired products (26).

During distillation under atmospheric pressure and increasing temperature the components in the crude will be separated. The cuts are: petroleum gas, naphtha often used in gasoline, kerosin which can give jet fuel, light gas oil (LGO) used in diesel, heavy gas oil (HGO) which can give fuel oil, and residue (26), as seen in Table 1. LGO is often referred to as middle distillate. These cuts are withdrawn from the distillation column and sent to further refining and upgrading processes. The residue of the crude which will not be separated in atmospheric distillation can be transported to another distillation column under vacuum conditions to give light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGO), and vacuum residue (VR). The fractions from the atmospheric distillation, such as the light and heavy gas oils, can be called atmospheric gas oils (AGO) as a collective term and the cuts from the vacuum distillation are often referred to as vacuum gas oils (VGO) (26). AGOs and VGOs are the fractions investigated in this study.

Table 1. Typical distillation fractions of crude oil with boiling point and carbon number range; an example from crude assay of Statfjord Blend (34, 35).

Fraction	Boiling point range (°C)	Carbon number range*
Gas		$C_1 – C_4$
Light Naphtha (LN)	35-100	$C_5 – C_7$
Heavy Naphtha (HN)	100-180	$C_7 – C_{10}$
Kerosin	180-240	$C_{10} - C_{13}$
Light Gas Oil (LGO)	240-320	$C_{13} – C_{18}$
Heavy Gas Oil (HGO)	320-375	$C_{18} – C_{23}$
Atmospheric Residue (AR)**	375+	C_{23+}
Light Vacuum Gas Oil (LVGO)	375-420	$C_{23} – C_{27}$
Heavy Vacuum Gas Oil (HVGO)	420-525	$C_{27} – C_{40}$
Vacuum Residue (VR)	525+	C_{40+}

*The carbon numbers are not necessarily at the accurate boiling points given in the table, but the nearest carbon number to the given temperature.

** Not all refineries perform vacuum distillation.

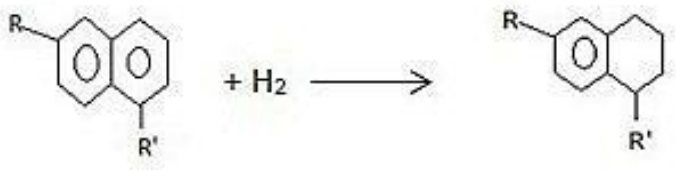
The petroleum fractions from distillation have to be processed in order to meet product quality specifications. The content of sulphur and nitrogen in middle distillate fractions is particularly important due to the environmental impact. Also, the amount of PAHs has to be reduced (26).

Catalytic cracking, hydrogenation and hydrotreating are refinery processes typically employed to break large molecules, saturate PAHs, and remove sulphur, nitrogen, and metals (36).

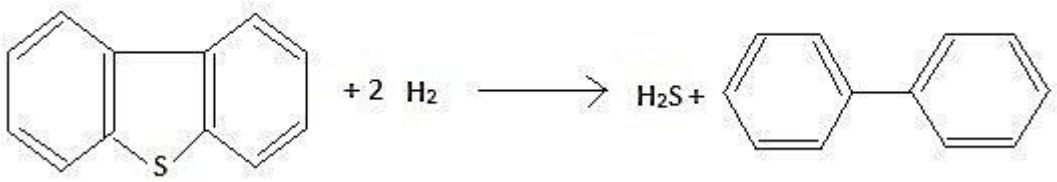
The addition of hydrogen to a feedstock makes saturation of PAHs possible. The process called hydrogenation is often nondestructive where hydrogen is added to an unsaturated molecule, Reaction 3 (26). Hydrotreating, on the other hand, is used to remove heteroatoms. This is only performed for the light gas oils as they do not need to be cracked to give the desired products (26). The heteroatoms are removed in a manner of Reaction 4. The combination of these two processes is applied to removal of sulphur from 4, 6-dimethyldibenzothiophene as seen in

Reaction 5. It is sterically hindered for hydrotreating alone to remove the sulphur. Hydrogenation of one of the benzene rings gives more flexibility to the structure making the sulphur atom more easily accessible for removal (36).

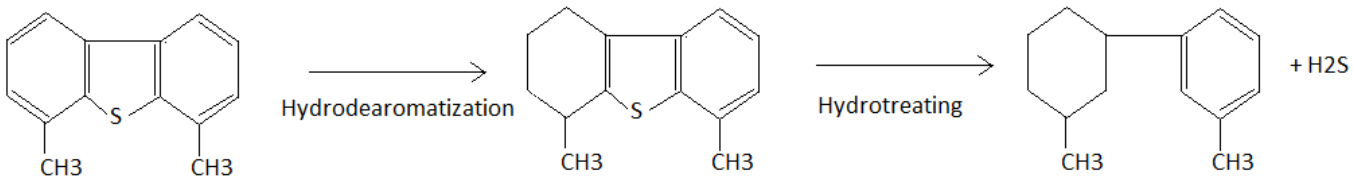
Catalytic cracking allows conversion of high-boiling feedstocks into lower boiling products. Atmospheric residue can be catalytic cracked to produce light cycle oil (LCO). LCO must be further processed due to high aromatic content (26).



Reaction 3. Hydrodearomatization (36).



Reaction 4. Hydrodesulphurization (36).



Reaction 5. Hydrodearomatization and hydrotreating of 4, 6-dimethyldibenzothiophene (36).

2.11 Chromatographic analysis of straight run and processed petroleum fractions

Petroleum contains large amounts of aromatics of different sizes and structures. A huge variety and degree of substitution is also present, making these compounds of interest difficult to separate and identify by using conventional gas chromatography and HPLC (20, 37) .

The amount of aromatics in such samples would be different in respect of the crude oil's composition. Also, the refinery processes, as described in 2.10.2 Refining, will influence the composition and content of aromatics and other groups.

A comprehensive analysis of petroleum fractions is possible by GCxGC (4, 5, 14, 20, 38, 39). The instrumental and experimental set up for both aromatic and element specific analyses are described in Chapter 3 Experimental.

Separation of compounds by carbon number, or boiling point, followed by the orthogonal (right-angled) separation of polarity, or aromaticity, yields a superior chromatogram for both quantitative and qualitative purposes. Compared to the one-dimensional gas chromatogram this is a result of the vastly increased peak capacity and multidimensionality. In addition, the signal-to-noise ratio is enhanced by GCxGC (4, 5).

Chapter 2.9 Comprehensive two-dimensional gas chromatography, describes the general attributes of GCxGC. This chapter will describe an adapted HPLC method for analysis of aromatics in petroleum industry in addition to a description petroleum fraction analysis by comprehensive two-dimensional gas chromatography.

2.11.1 Analysis of aromatic compounds in middle distillate fractions by HPLC (1)

The HPLC method for determination of aromaticity in diesel fractions is an American Society for Testing and Materials International (ASTM) method. The ASTM method uses a refractive index detector.

This analysis only separates mono-, di-, and polyaromatics. The heavier aromatics elute in the same peak as triaromatics, called tri+-aromatics. The total amount of aromatics is also reported by the method.

Two polar HPLC columns, Spherisorb amino columns with 3 µm particle size and 150 x 4.6 mm internal diameter, are used to separate the aromatics. This method dissolves the sample into n-heptane. The solvent, n-heptane, will go unretained through the columns along with the paraffins. After elution of the diaromatics the column flow is switched to make the tri+-aromatics elute in one single back-flush-peak.

Three standards are selected to represent the aromatic groups; ortho-xylene, 1-methylnaphthalene, and phenanthrene representing monoaromatics, diaromatics, and tri+-aromatics, respectively.

Analysis of light cycle oil (LCO) is not recommended in this HPLC-method as LCO contains a huge amount of aromatics different from the calibration compounds, i.e. the standards. LCO can be analysed in order to view trends but not absolute aromatic content.

2.11.2 Analysis of petroleum by GCxGC

The sample properties of interest for analysis determine the columns to use (5). A common set of columns is a non-polar first column and a mid-polar to polar second column (normal-phase column set) (20, 22). There are several studies on the reversed column set, i.e. mid-polar to polar first column and non-polar second column (38, 40, 41). The reversed-phase setup yields better separation of the non-aromatic groups (38, 40). In this study the focus is on separation of aromatic groups, the separation of saturates is also desirable but not as important as the aromatics. Thus, normal-phase column set as described by (20) and (22) is utilized.

It is described in literature that compounds with similar chemical properties, e.g. homologous series elute in ordered patterns and are separated from other homologous series. This is called the roof-tile effect, illustrated in Figure 7 (4, 24, 28). This is practical for detailed group division and identification. Vendeuvre et al. (24) showed detailed characterisation of diesel by adaption to the

roof-tile effect. However, the difficulty by determining exact elution zones was only partly overcome by utilisation of standards (24).

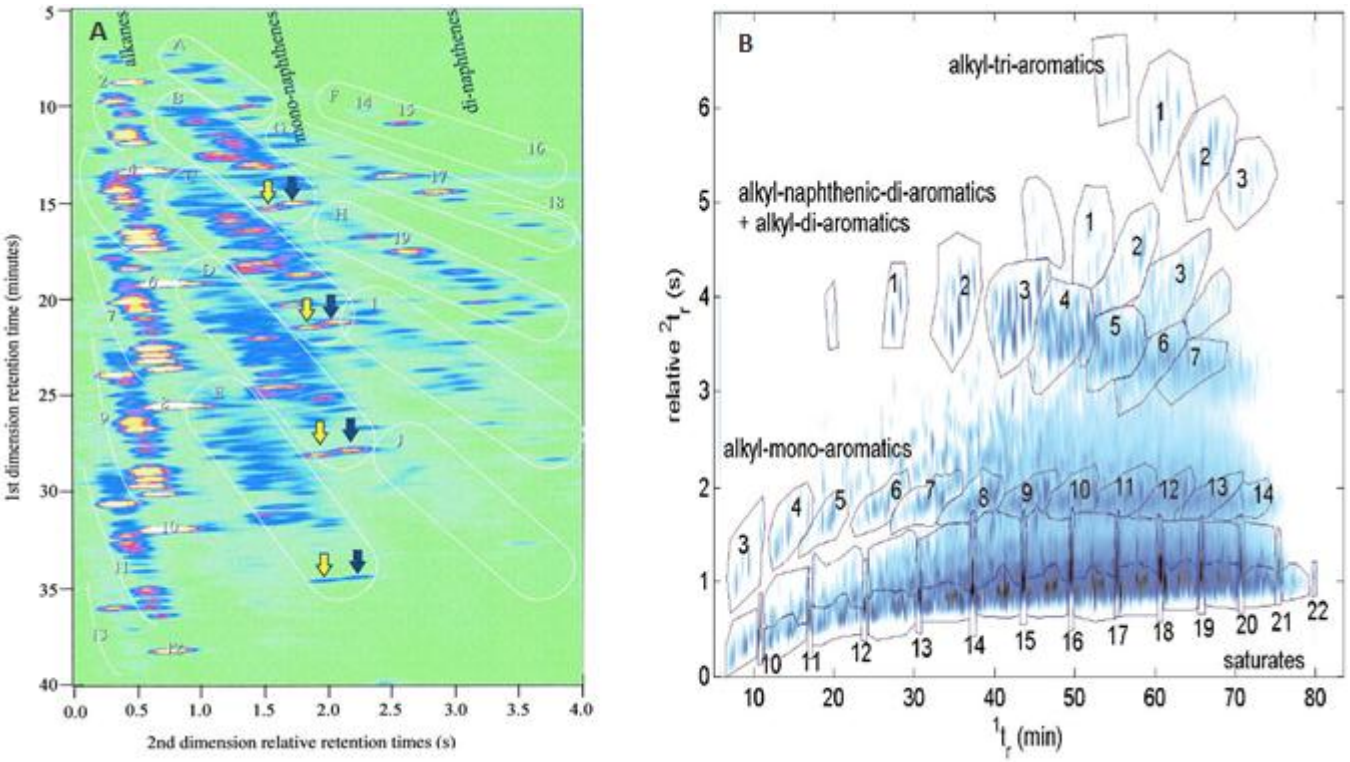


Figure 7. A Illustration of roof-tile effect for non-aromatic solvent. Numbers and letters indicate grouping of homologous series (4). Figure 7B shows Vendeuvre's grouping of clusters with isomers of the same number of carbon atoms (for the saturates), the aromatic groups are numbers after the study's scope of interest (24). Figure 7A and B have different operating parameters as seen by the retention times. Also, A shows 2nd dimension on the abscissa and 1st dimension on the ordinate, the opposite of B.

The combination of the first and second dimension separation allows much easier single component identification and quantification than single dimensions alone. The choice of standards is important for designation of the expected retention time ranges, e.g. mono-, diaromatics etc. The identification of the different groups of compounds in the oil is as mentioned determined by standards and their retention time combination (t_R (1), t_R (2)) (4, 5, 20, 25). Reference boiling point standards are useful for identification of the carbon number (boiling point) distribution.

The borderlines between the groups can be more or less diffuse (24). As the large number of compounds at the borderline would take too much time for exact identification, group allocation is set by use of standards and group borders by estimate. Due to the degree of order in GCxGC analysis of petroleum (14), the elution zones, i.e. the groups of polarity, can be determined with few standards. However, the certainty of the definition of the zones is increased by applying a

larger number of standards. At least two standards should represent each group of aromatics in order to indicate the group allocations. Response factors should be retrieved by a representative component within each group (25).

2.12 Software for GCxGC data analysis (42)

The chromatographic raw data is collected and stored by conventional software, e.g. ChemStation. The GCxGC specific software use the data collected by the fundamental chromatographic software to produce two-dimensional structured chromatograms and 3D visualisations of these chromatograms. The software has functions for identification and naming peaks, called blobs, and making templates where both individual and groups of blobs are covered, for example monoaromatics. Several groups of blobs, identified and unidentified, can be implemented in a template as to cover the parts of the sample of interest or the whole sample. Column bleed and other parts of the chromatogram can be excluded from the template; these volumes will not be part of the calculated responses of the samples. The data obtained can be transferred to spread sheet for further data processing.

3 Experimental

3.1 Introduction to the instrument

The gas chromatograph is an Agilent 7890 A. There are two available injectors; a PTV split/splitless injector (ASAP TITAN XL) and a regular split/splitless injector (Agilent). The PTV injector set to the split mode is the default inlet with a borosilicate liner (capacity of 0.5 µL liquid).

The instrument was installed with a general column set. All columns were SGE Analytical Science columns, including the deactivated retention gap capillary used for both the loop and splitter columns to the detectors (43). Column properties are described in Table 2 (43). The 2 meter column is cut from a 10 meter BPX50 column.

Table 2. Column properties: SP composition, length, I.D., film thickness and max temperature (43).

Column	% methyl SP	% phenyl SP	Length (m)	Internal diameter (mm)	Film thickness (µm)	Max temperature (°C)
1st dimension	95	50	30	0.25	0.25	350/370
2nd dimension	50	50	2	0.1	0.1	330/350
Loop	0	0	0.8	0.1	Deactivated	
Split SCD/FID	0	0	0.1	0.1	Deactivated	

The absolute max temperature for the columns is a value which should not be exceeded due to degradation of the SP. If long operation, i.e. several minutes, at high temperature is required the lower max temperature should be the final temperature.

There are three detectors connected to the instrument; a flame ionization detector (FID), a sulphur chemiluminescense detector (SCD) and a nitrogen chemiluminescense detector (NCD) mounted on top of the FID. The column flow is split equally between the FID and SCD. The NCD

only receives 10 % of the flow entering the FID; approximately 90 % of the sample flow entering the FID is destructed. The NCD receives only 5 % of the total effluent flow with the current instrument setup. Without any optimisation no useful analytical results were obtained from the NCD in this configuration. Due to time restraints no further work was done with the NCD.

The cryogenic loop modulator (Zoex Corporation, U.S. Patent No.'s 5,135,549; 5,196,039; 6,007,602; other U.S. patents pending, and foreign counterparts) is inserted within the GC oven and it consists of a cold jet of gaseous nitrogen and a hot jet of synthetic air. A controlling device is connected to the cold and hot jet for adjusting the pulse time of the hot jet and the modulation period. The modulation period is the time available for the interface between column 1 and column 2 to collect effluent from the first column (19). The flow of nitrogen in the cold jet is controlled by a manual valve on the back of the GCxGC instrument; normal operating values are within 10-15 mL/min. Volatile compounds need higher nitrogen flow in the cold jet to be condensed (18, 23). It is set to a constant value of 15 mL/min. The hot jet temperature is controlled by the GCxGC method and follows the temperature program of the GCxGC oven with an offset of + 50 ^{o}C. The increasing hot jet temperature will provide high enough temperature to transfer the focused sample fraction onto the next column.

3.2 Method development

The initial instrument parameters were as follows:

- Columns: BPX5 (30 m, I.D 0.25 mm, film 0.25 µm) and BPX50 (2 m, I.D 0.1 mm, film 0.1 µm)
- Carrier gas flow: 0.85017 mL/min yielding average linear velocity 31.6 cm/sec. Constant flow, helium 4.6.
- N_2 cold jet gas flow: 15 mL/min
- PTV inlet parameters: temperature and ramp 720 ^{o}C/min to 350 ^{o}C , pressure 41.3 psi, flow 131.4 mL/min
- Hot jet off set temperature: 50^{o}C
- Detector parameters: -FID: heater 350 ^{o}C, H_2 flow 30 mL/min, Air flow 350 mL/min, makeup flow 26.8 ml/min
  -SCD: temperature 800 ^{o}C, pressure 400 torr, oxidizer 65 mL/min, hydrogen flow 35 mL/min
  -NCD: temperature 900 ^{o}C, pressure 300 torr, oxidizer 10 mL/min

- Modulator values: -modulation time: 8000 ms
  -hot jet duration: 500 ms
- Gas qualities: He 4.6, SL 5.0, H_2 5.0, O_2 5.0, N_2 5.0

The installation of the instrument set the starting point of the method development with some recommended values by the contractor. These parameters are not changed in this study, except modulation time and hot jet duration.

3.2.1 Sample injection and split ratio

A desire of injecting undiluted sample (to keep its integrity and eliminate of sample preparation) led to an investigation of the different combinations of injection volume and split ratio. Injection volume and the split ratios tested in the PTV inlet are seen in Table 3. The actual volume injected sample is calculated to show the relation between syringe volume and split ratio.

Table 3. True injection volume (µL) by combination of syringe injection volume and split ratio tested for undiluted samples.

	Injection volume (µL)		
Split ratio	0.5	0.3	0.1
150:1	0.0033	0.0020	0.0007
200:1	0.0025	0.0015	0.0005
250:1	0.0020	0.0012	0.0004

3.2.2 Temperature programming

Table 4 shows some of the methods explored to find the best separation of the various petroleum samples. Appendix A shows a complete table with all methods used for development and optimisation.

Table 4. Method development of GCxGC temperature program. Parameters investigated for optimising of methods: injection volume, split ratio, start temperature, ramps and final temperature. Runtime and column flow is listed below method name.

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
3	110909_PTV_SPLIT15-200 Flow 0.85 Run time 58.33	0.5	5 - 250	40 hold 1 min	6		360 hold 4 min
8	111215_PTV_DIESELSAMPLES Flow 0.85 Run time 68.44	0.1	250	50 hold 3 min	4.5		340 hold 1 min
9	111216_PTV_0.3UL_SPLITT150-1 Flow 0.85 Run time 68.44	0.3	150	50 hold 3 min	4.5		340 hold 1 min
23	120214_PTV_HEAVYSAMPLES_TEST#12 Flow 0.85 Run time 63.33	0.3	75	50 hold 3 min	7.5 to 180 °C hold 1 min	4.5 to 360 °C	360 hold 2 min
24	120221_PTV_HEAVYSAMPLES_TEST#13 Flow 0.85017 Run time 64.00	0.3	75	150 hold 1 min	3.5 to 360 °C		360 hold 3 min
29	120328_VGO_SPLITT20-1 Flow 0.85 Run time 58.29	0.3	20	150 hold 1 min	3.5 to 340 °C		340 hold 3 min

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
30	120425_SLOWRAMP_3°C/MIN_SPLIT150-1 Flow 0.85 Run time 100.67	0.3	150	50 hold 3 min	3 to 340 °C		340 hold 1 min

3.2.3 Modulation time and hot jet duration

The impact of modulation time and hot jet duration of the separation was of interest. The modulation time and hot jet durations tested are given in Table 5.

Table 5. Modulation time and hot jet duration.

Modulation time (ms)	9999	8000	7500	5000	3000	8000	8000	8000	6500
Hot jet duration (ms)	500	500	500	500	500	2000	600	100	375

The modulation time and hot jet duration were set to 8000 ms and 500 ms, respectively, at installation.

3.3 Standards

3.3.1 Hydrocarbons and polycyclic aromatic hydrocarbons (PAHs)

Table 6 shows the compounds used for quantification purposes. Table 7 show all hydrocarbon standards applied to aid in identification of aromatic groups and reliability of templates in GC Image.

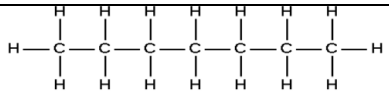
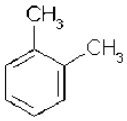
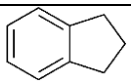
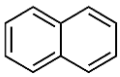
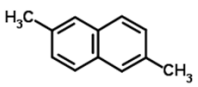
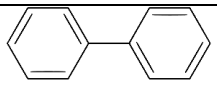
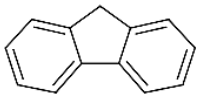
The standards are prepared on a weight per weight (w/w) basis dissolved in toluene of HPLC grade purity (HiPerSolv CHROMANORM 99.80%). A large concentration range is covered as the concentrations of the different aromatic groups and species varies within the petroleum samples. A few selected standards were also run separately on the GCxGC to make identification easier. Identification of a mixture of many compounds is hard when no retention times are known.

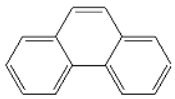
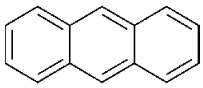
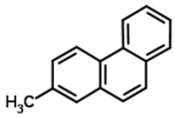
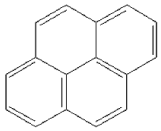
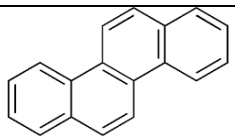
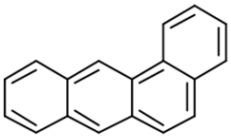
A boiling point standard (Agilent Boiling Point Calibration Sample No.1, Agilent Part Number: 5080-8716) was analysed for determination of the n-paraffins and a gas oil standard (Agilent Reference Gas Oil Sample No.1, Agilent Part Number: 5060-9086) applied for modulator time optimisation.

Table 6. Concentration (ppm w/w) of hydrocarbon and PAH standards.

Compound	Concentration (ppm w/w)				
Heptane	8388	4194	1678	839	419
Xylene	11117	5559	2223	1112	556
Naphthalene	12219	6109	2444	1222	611
Fluorene	6666	3333	1333	667	333
Phenanthrene	11374	5687	2275	1137	569
Anthracene	689	344	138	69	34
Pyrene	2290	1145	458	229	115
Chrysene	1362	681	272	136	68

Table 7. Hydrocarbon and PAH standards group types and chemical structure.

Compound	Group type	Chemical structure	Concentration (ppm w/w in toluene)	Source
Heptane	Saturate/non-cyclic		419-8388	99% SDS
Xylene	Monoaromatic		556-11117	99% LAB-SCAN Analytical Science
Indane	Monoaromatic naphthenic		2351	Chem service
Naphthalene	Diaromatic		611-12219	Neat, SUPELCO
2,6-dimethylnaphthalene	Diaromatic		5106	Chem service
Biphenyl	Diaromatic		10063	>98% Fluka Chemica
Fluorene	Diaromatic naphthenic		333-6666	Neat, SUPELCO

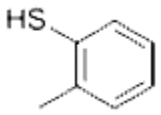
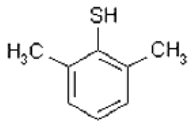
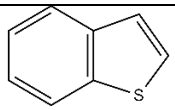
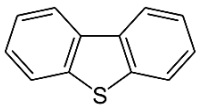
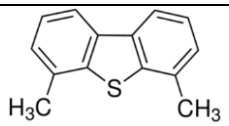
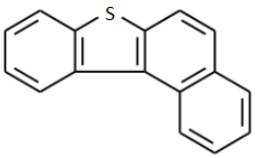
Compound	Group type	Chemical structure	Concentration (ppm w/w in toluene)	Source
Phenanthrene	Triaromatic		569-11374	Neat, SUPLECO
Anthracene	Triaromatic		34-689	Neat, SUPELCO
2-methylphenanthrene	Triaromatic		6394	98%, Chiron
Pyrene	Tetraaromatic		115-2290	Neat, SUPELCO
Chrysene	Tetraaromatic		68-1362	Neat, SUPELCO
Benzo[a]anthracene	Tetraaromatic		1688	Neat, SUPELCO

3.3.2 Sulphur compounds and polycyclic aromatic sulphur heterocycles (PASHs)

Sulphur analysis is straight forward, as it is receives 50 % of the column effluent. However, the sensitivity mode of the detector should be on minimum when injecting highly concentrated sulphur compounds in order to not overload and damage the reaction cell (12). For all analyses SCD sensitivity was set to minimum to avoid overload of detector reaction cell and enhance the signal-to-noise ratio.

The sulphur compounds selected to represent the different groups of PASHs are presented with their concentration in ppm on a weight per weight basis in Table 8. The standards were dissolved in toluene (HiPerSolv CHROMANORM 99.80%).

Table 8. Concentration (ppm w/w) of PASH standards.

Compound	Chemical structure	Concentration (ppm w/w)					Source
o-toluenethiol		1631	820	410	89		97% Acros
2,6-dimethylthiophenol		1008	507	253	55		96% Acros
Benzo[b]thiophene		482	243	121	26		>98% Lancaster
Dibenzothiophene		599	301	150	33		MERCK
4,6-dimethyldibenzothiophen		11420	4009	1685	405	122	97% Sigma-Aldric
Benzo[b]naphtho-[2,3-d]thiophene		200					>99.5% Chiron

3.4 Petroleum samples used for method development and method verification

The middle distillate samples are injected in their full integrity by means of no dilution. This is not always the case for the vacuum gas oils and feeds as they contain heavy hydrocarbons and are viscous beyond the possibility of liquid injection.

Vacuum gas oils are diluted in toluene HPLC grade (HiPerSolv CHROMANORM 99.80%) before injection.

Table 9 shows the petroleum samples with their origin and a short sample description. The prefix SR indicates straight run fractions, i.e. they are unprocessed.

Table 9. Description of petroleum samples used for method development, method verification, and characterisation.

Name	Origin	Description	AGO/VGO	Undiluted/diluted (% weight sample/ weight toluene)	Total sulphur*
SR LGO A **LGO A-1 to LGO A-5**	North Sea blend	Product of partly hydrotreated SR LGO A	AGO	Undiluted	173 wt ppm 75.0, 26.6, 5.7, 1.6, 0.4 wt ppm
SR LGO B	North America	Blend LGO A-A and kerosin of same crude	AGO	Undiluted	1.27 wt%
SR LGO C	North Sea blend		AGO	Undiluted	
SR AGO A **LGO A-A** **HGO A-A**	North America	Heavy cut, high in sulphur. LGO A-A (distillate vacuum distillation AGO A) HGO A-A (residue vacuum distillation AGO A)	AGO	Undiluted	1.96 wt% 1.6 wt% 2.8 wt%
SR AGO B	Central America	From reference heavy oil, high in sulphur	AGO	Undiluted	1.39 wt%
SR AGO C	North Sea	Light oil, low in sulphur	AGO	Undiluted	0.196 wt%
LCO A **LCO A-1 to LCO A-5**	Blend not available	Product from catalytic cracking. Product of partly hydrotreated LCO A	AGO	Undiluted	6897 wt ppm 2361.2, 1651.4, 998.3, 443.0, 184.2 wt ppm

Name	Origin	Description	AGO/VGO	Undiluted/diluted (% weight sample/ weight toluene)	Total sulphur*
LCO B	Blend not available	Product from catalytic cracking	AGO	Undiluted	
SR VGO A	North America	Heavy oil, high in sulphur	VGO	Diluted 14.3 %	3.32 wt%
SR VGO B	Central America	Reference heavy oil, high in sulphur	VGO	Diluted 29.3 %	3.21 wt%
SR VGO C	North Sea	Light oil, low in sulphur	VGO	Diluted 23.2 %	0.457 wt%
SR VGO D	South America	Heavy oil, high in sulphur	VGO	Diluted 17.0 %	2.84 wt%

*Total sulphur is assay data.

4 Results and discussion

The goal with the method development was to achieve methods for parallel signal output of the detectors. Analyses are supposed to be carried out by one method for obtaining FID and SCD signals. This would save the analyst much time in running samples. Thus, the methods developed for atmospheric and vacuum gas oils apply for both the hydrocarbon and the sulphur specific analyses.

The first method presented is applied for atmospheric gas oils, i.e. petroleum samples with a carbon range of C_{13} – C_{23}. The complete method parameters are given in Appendix A.A. The parameters most used for changing a method are found in Table 10:

Table 10. Method parameters for atmospheric gas oils. Method 9.

Back injector		**Oven program**	
Injection volume:	0.3 µL	Initial temp.:	50 °C
		Initial time:	3 min
Back PTV inlet		Ramp:	4.5 °C/min to 340 °C. Hold 1 min
Gas type:	Helium	Run time	68.4 min
Mode:	Split		
Pressure:	41.3 psi	**Thermal AUX 1**	
Total flow:	131.4 mL/min	Initial temp.:	100 °C
Initial temp.:	50 °C	Initial time:	3 min
Initial time:	0.02 min	Ramp:	4.5 °C/min to 390 °C. Hold 1 min
Ramp:	720 °C/min to 350 °C. Hold 5 min		
Split ratio:	150:1		
		Modulator time parameters	
		Hot jet duration: 500 ms	
		Modulation time: 2000 ms	

GC x GC of vacuum gas oils (C_{23}-C_{40}) proved to be more complicated than analysis of atmospheric gas oils, as expected from literature (33). A new method was developed to yield good separation of these heavy samples, and dilution was also necessary, especially of the more viscous samples. The method's key parameters are presented in Table 11. The entire method is available in Appendix A.B.

Table 11. Method parameters for vacuum gas oils. Method 29.

Back injector		**Oven program**	
Injection volume:	0.3 µL	Initial temp.:	150 °C
		Initial time:	1 min
Back PTV inlet		Ramp 1:	3.5 °C/min to 340 °C. Hold 1 min
Gas type:	Helium	Run time	64.0 min
Mode:	Split		
Pressure:	54.6 psi	**Thermal AUX 1**	
Total flow:	131.4 mL/min	Initial temp.:	200 °C
Initial temp.:	150 °C	Initial time:	1 min
Initial time:	0.02 min	Ramp:	3.5 °C/min to 410 °C. Hold 3 min
Ramp:	720 °C/min to 350 °C. Hold 5 min		
Split ratio:	20:1		
		Modulator time parameters	
		Hot jet duration: 500 ms	
		Modulation time: 2000 ms	

Discussion

- Column set

The columns are chosen by the sample properties of interest to separate. When complex matrices are subjected to GC analyses, compromises can often be a solution to give an overall sufficient separation. The orthogonality is important in GCxGC although not a goal in itself (23). The columns should be chosen to yield separation on different compound properties such as boiling point/carbon number and polarity/aromaticity. The main purpose of this particular GCxGC was to analyse middle distillate petroleum fractions. Thus as first dimension column a BPX 5; 5 % phenyl

95 % methyl and as second dimension column a BPX 50; 50 % phenyl 50 % methyl was chosen by the contractors at installation (43).

The first column (30 m) is of the longer dimensions reported as commonly used in literature (23), this is also the case for the second column (2 m). Shorter columns (10 m 1st dimension and 0.5 m 2nd dimension) can give shorter run times; however, to obtain the same peak capacities film thicknesses have to be reduced (5, 23). On the other side, short columns with thin films, e.g. 0.1 µm and less, are easily overloaded (5, 23).

The separation of atmospheric gas oils by this column set was adequate. Both the carbon and polarity range was widely spread in the 2D separation space. The sample load allowing good separation in the 1st dimension can lead to overload of the 2nd dimension. The second column could preferably have wider internal diameter and thicker film (0.25 µm) to reduce band broadening as a result of overload in the 2nd dimension. Mostafa et al. (23) describe there is less gain efficiency in thinner film (0.1 µm) 2nd dimension columns than generally believed as the separation time is very short (8 s).

Vacuum gas oil compounds are not separated as well as atmospheric gas oil compounds by this column set. VGO samples are very complex and have high boiling points (33). Columns with higher temperature operating limits should be applied, and perhaps a different combination of SPs for optimisation of retention mechanisms (23). Dutriez (33) showed that separation of VGOs is possible by the combination of 1st column DB1-HT (10 m, I.D. 0.32 mm, film 0.1 µm) and 2nd column BPX50 (1 m, I.D. 0.1 mm, film 0.1 µm). The modulation time was 20 s. Such long modulation times are not available on the modulator of this instrument.

- Gas flow

The carrier gas (helium) flow was pre-set by the contractor at the point of installation. The carrier gas flow was kept constant throughout the analysis at 131.4 mL/min which equals to an average linear velocity of 31.6 cm/sec. The optimum gas linear velocity is a parameter depending on the height equivalent of a theoretical plate (HETP) in the column, i.e. the column's efficiency (5). For GCxGC the 1st column's optimum values are met, while for the 2nd column the flow is much higher than optimum (7). This is because the internal diameters of the columns are different. As mentioned in theory the practical optimum gas velocity equals the velocity which gains 10 %

increased plate height (6). The decrease in the second columns efficiency due to the high carrier gas velocity is not crucial as this has to be a fast separation (less than 10 seconds); also, the slope of the helium van Deemter curve is relatively flat even at values well above optimum. This makes optimisation of carrier gas velocity for the second column unnecessary as this would result in poor separation by the first column as its gas velocity would be too low (7).

The methods developed have constant flow of carrier gas. As described in theory the carrier gas velocity will drop if pressure is the controlling parameter due to the increasing viscosity by temperature (5).

- Injection and sample concentration

The injector is a programmable temperature vaporiser (PTV) which allows rapid vaporisation of the sample in the inlet. A quick temperature ramp is chosen for heating the inlet to 350 ^{o}C for vaporising even the heaviest sample compounds before the split outlet and column loading. Heavy compounds are more subjected to discrimination, lighter components are easily vaporised (5). The heavy fractions often adhere to the liner when not transformed into vapour, causing the possibility of contamination of later runs. A film of heavy compounds, typically from VGOs, built up inside the liner where later sample compounds may adhere and adsorb (5).

Changes in injection volume by either altering the syringe injection volume or the split ratio will directly influence the amount of sample delivered onto the column. The volume of liquid introduced into the injector must not exceed the gas volume capacity of the liner. The liquid sample is vaporised to gas in the inlet. If the gas volume is larger than the liner capacity it might lead to contamination of later samples and impurities in the liner housing (5).

Overloading of the analytical columns reduce the peak performance and separation power (5). The peaks will appear broad and “smudged” out; overlapping of peaks is more likely to occur. The column with the smallest diameter and film thickness determines the maximum sample load. The reaction cell of the SCD can be overloaded by a sample’s concentration (12, 13).

Split ratio is a good approach to optimise the column sample loading. Values of 1 to 250 can be chosen where the concentration of the sample, in combination with the smallest internal column diameter determines the ideal sample load. Highly diluted samples do not need to be split as

much as concentrated samples. It is the overall volume of sample loaded onto the column that is important. It has been found that undiluted samples can be injected with a volume of 0.0012 to 0.002 µL, depending on the number of different and the distribution of compounds in the sample. For diluted samples, i.e. samples with a weight percent of approximately 20, an injection volume of 0.002 to 0.015 µL is appropriate.

As seen from the VGO method, Table 11, it has a lower split ratio than the AGO method, Table 10, this is because most VGO samples are diluted before injection in order to make liquid injection possible.

A chromatogram of highly overloaded columns is shown in Figure 8A. Injection of straight-run light gas oil (0.013 µL) resulted in extensive overloading of the columns and also wraparound of the more volatile components of the sample. The continuous colouration of the sample displays that baseplane separation is not achieved; a huge degree of overlapping in both dimensions is a consequence of this. A contrast of a low volume injection (0.0004 µL) is shown in Figure 8B.

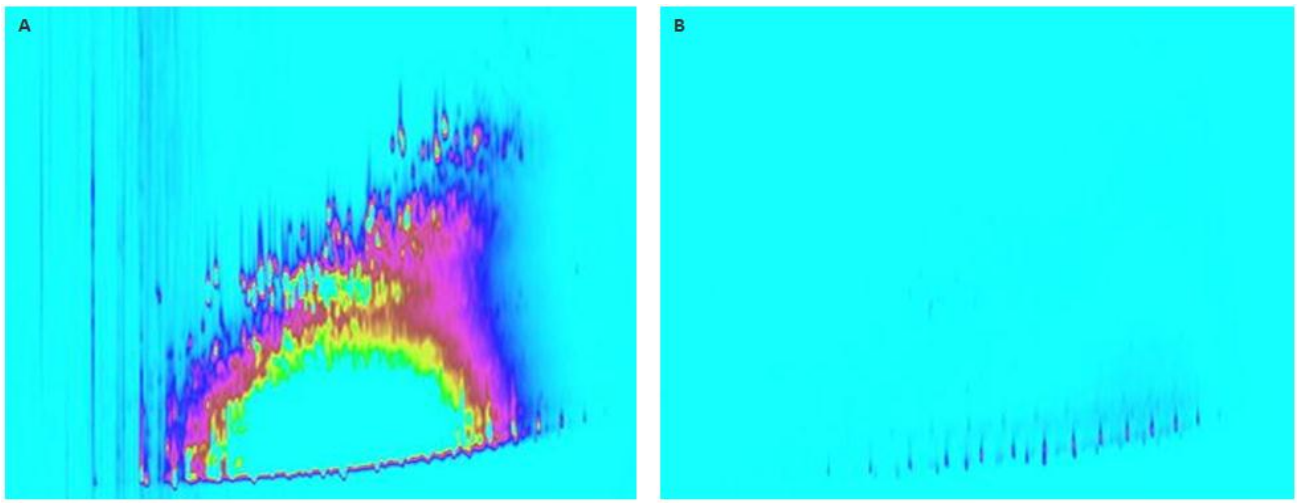


Figure 8. Injection volume impact on separation. A: overload of SR LGO C in the columns injected 0.013 µL, method 3. B: low injection volume (0.0004 µL) of SR LGO A, method 8.

A comparison of the response of SR LGO A by method 9 and 8 is shown in

. The only parameter different in the methods 9 and 8 is the injection volume: respectively 0.002 µL and 0.0004 µL.

Table 12. Comparison of response of LGO A run by method 9 (Figure 10A) and 8 (Figure 10B).

	Method 9 Injection volume 0.002 µL		Method 8 Injection volume 0.0004 µL	
Name	**# of blobs**	**Percent Response**	**# of blobs**	**Percent Response**
Saturates/non-cyclic	103	33.0	105	41.9
Cyclic/non-aromatic	112	21.6	78	20.5
Monoaromatic	371	31.3	195	23.1
Diaromatic	283	12.3	53	4.4
Triaromatic	40	1.2	6	0.4
Tetraaromatic	1	0.0	1	0.1
Residual	16	2.3	22	10.4

The number of blobs (peaks) detected is very different, except for saturates/non-cyclic, tetraaromatic, and residual. This is due to the blob volume detection limit. The risk of including interference is enhanced when the blob detection limit is very low e.g. 5. The percent responses are very different for the two methods, except for cyclic/non-aromatics. The low injection volume by method 8 is more subjected to random errors and variations by the rapid second dimension analysis. Method 9 is more reliable in that case as variations in modulation cycles and the second dimension separation plays a minor role as the sample load is higher.

Recommended injection volumes of undiluted samples are 0.0012 to 0.002 µL, and for diluted samples (wt % approximately 20) 0.002 to 0.0015 µL. Exceptions are very dilute samples and undiluted samples with low content of groups of interest and the contrary. In those cases injection volumes need to be optimised.

- Oven temperature program

Temperature is an essential parameter for the retention of analytes. Higher temperatures result in lower retention times, t_R, and vice versa (5). The optimal heating programme of the column oven allows sample compounds in similar retention ranges to be well separated in an acceptable time of analysis, e.g. approximately 60 minutes. This is also dependent on the peak capacity and resolution of the column and the sample's complexity (5).

Keeping the columns in the same GC oven reduces the possibilities for temperature optimalization as the columns are temperature dependent on each other (23). The 2nd column's starting temperature equals the elution temperature of the 1st column (23). The final temperature is mostly determined by the maximum operating temperature of the columns (33). The polar column

is often the least resistant to thermal degradation and the final temperature is set to 340 ^{o}C in stead of the column's maximum of 350 ^{o}C to reduce column bleed.

The start temperature of the GC oven should allow the sample compounds in the lower boiling point range to retard. Since the volatile compounds of the applied samples are approximately C_{13} this should be obtained by the starting temperatures applied. However, for the most volatile AGO cuts where compounds as volatile as C_7-C_8 can be present it gets more difficult to obtain good separation. The start temperature of the AGO method is set to 50 ^{o}C. This is below the boiling point of C_7 (98 ^{o}C) (44). The temperature ramp increase with 4.5 ^{o}C per minute, this gives short time for separation of compounds with small differences in boiling points. Compounds in the low carbon number range do not have large possibilities for variation in polarity as the number of carbon atoms is only able to produce non-cyclic, cyclic/non-aromatic, and monoaromatic structures. Thus, separation in the second dimension is limited to say the least.

The temperature ramps have to be slow enough for good separation. The components need time to retard sufficiently, and yet the ramp should not be too slow either, for unnecessary long retention of compounds. The goal of the methods is to separate all compounds in the sample, e.g. C_{13} to C_{23} (AGO) and C_{23} to C_{40} (VGO) and the classes of aromatics as well. The temperature ramp has to be slow enough to allow retention of the analytes; otherwise they could end up in a cluster of overlapping peaks as a result of insufficient separation. If the ramp is too slow it would demand much time and the slightly enhanced separation would not be significant to allow the much longer time of analysis. This is illustrated in Figure 9 where methods of ramp 3.0 ^{o}C/min and 4.5 ^{o}C/min are compared; the run time is 100.7 minutes and 64.8 minutes, respectively.

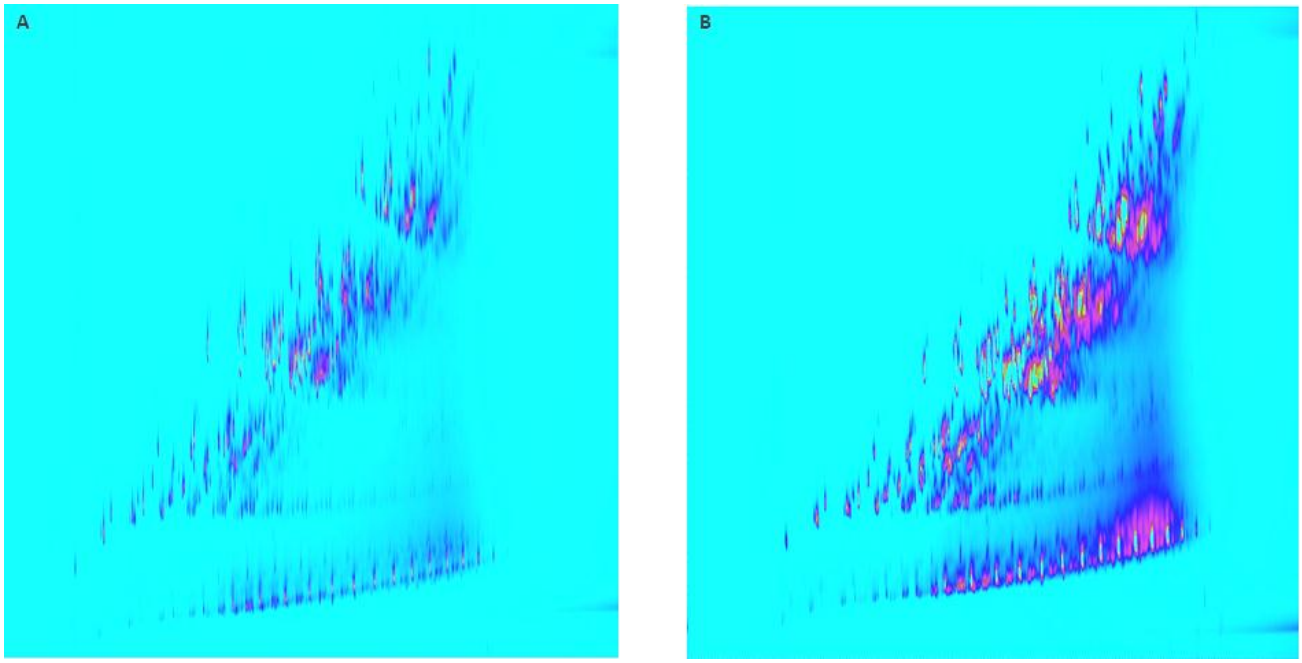


Figure 9. LCO A run by methods with different temperature ramps. A: ramp = 3.0 °C/min, run time 100.7 min. B: ramp = 4.5 °C/min, run time 64.8 min.

The separation into the different groups of polarity is present in both chromatograms. The 1st dimension separation is better in Figure 9A than B. This shows that the temperature ramp has more influence on the 1st dimension than on the 2nd dimension. The injection volume is the same for the two methods, however, in Figure 9B it is clear that peaks overlap. The improved separation in the 2nd dimension may be a result of the enhanced 1st dimension's separation.

The temperature program is important to optimise in order to get sufficient separation of the sample. For this study's aims the separation obtained by Figure 9B is good enough. It clearly differentiates between the aromatic groups and the non-aromatics. It is also possible to identify saturates/non-cyclic from cyclic/non-aromatic. Single peak identification is not a goal, but to quantify the amount of e.g. monoaromatics and diaromatics. The time of analysis have to be taken into account when temperature programming is optimised. The recommended method can be applied for routine analysis of aromatic content of processed and straight run petroleum fractions. It is a large difference in total run time when 10 samples are run for 64.8 minutes each compared to 100.7 minutes. The time difference is actually 359 minutes, excluding the time the instrument use to get back to starting conditions.

Table 13. Comparison of percent response of LCO A obtained method 30 and 9.

	Method 30. Ramp 3.0°C/min	Method 9. Ramp 4.5 °C/min
Name	**Percent Response**	**Percent Response**
Saturates/non-cyclic	13.4	13.8
Cyclic/non-aromatic	4.1	6.4
Monoaromatic	17.4	15,5
Diaromatic	46.8	44.1
Triaromatic	13.3	15.3
Tetraaromatic	3.2	3.5
Residual	1.9	1.4

There are not very large differences in the percent response of LCO A by the two methods, only 2.7 % at the most. The borders are easily defined by both methods, but even better by method 30. For single component identification purposes this is advantageous, however, for group type identification and quantification, the separation obtained by method 9 is sufficient although it presents some degree of peak overlapping. This is insignificant for the purpose of this project compared to the much longer time of analysis required by the other method. The differences in Table 13 are caused by calculations where the template boarders include some of the next hydrocarbon group peaks as a consequence of overlapping.

Figure 10 shows chromatograms for LCO C and LGO A obtained by different AGO methods: method 3, 8, and 9 (the same method as seen in Table 10).

Figure 11 shows chromatograms for SR VGO C and B obtained by different VGO methods: 23, 24, and 29 (the same method as seen in Table 11).

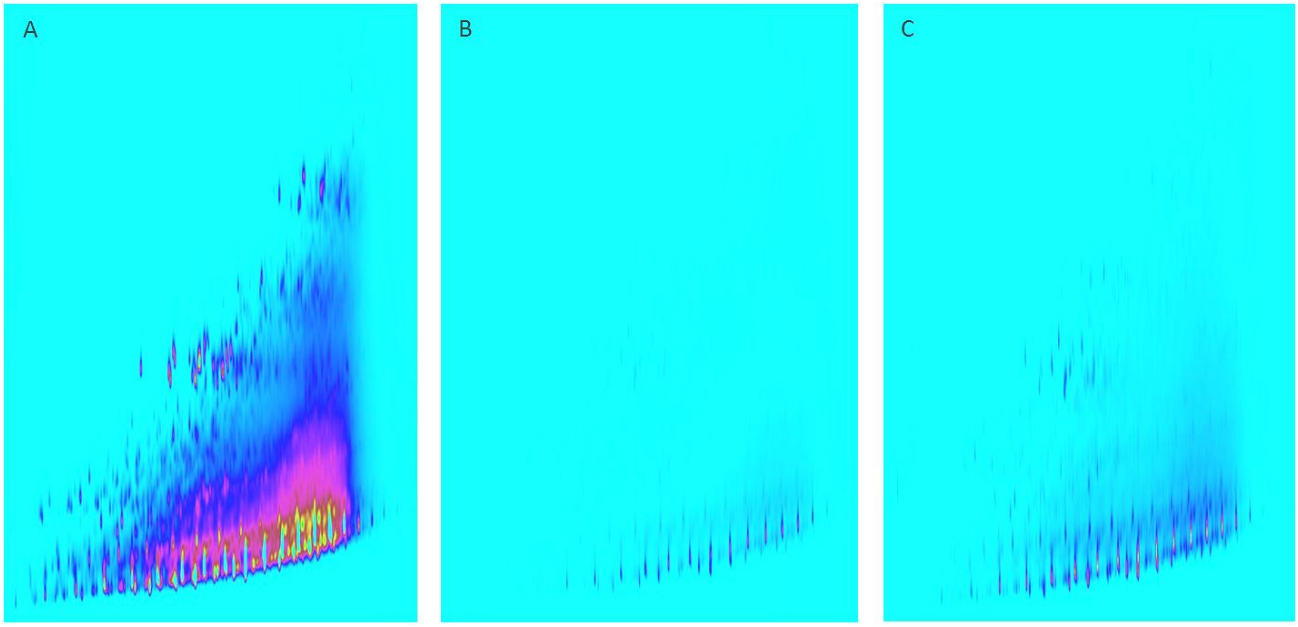


Figure 10. Chromatograms obtained by different AGO methods. A: LCO C by method 3. B: SR LGO A by method method 8. C: SR LGO A by method method 9 (AGO method as seen in Table 10).

Figure 10A is of LCO C, Figure 10B and C are of SR LGO A. The differences between the methods in Figure 10A, B, and C are the injection volume; 0.003, 0.0004 and 0.002 µL, respectively; start temperature and hold time; 40 ^{o}C 1 min for Figure 10A, 50^{o}C 3 min for Figure 10B and C; temperature ramp; 6 ^{o}C/min for Figure 10A and 4.5 ^{o}C/min for Figure 10B and C; and final temperature and hold time; 340 ^{o}C 4 min for Figure 10A and 340 ^{o}C 1 min for Figure 10B and C.

In Figure 10A the columns are overloaded. It is hard to see the borders between the groups of aromatics, non-aromatics, and saturates. The overload would influence the response of the groups as the one group enters the other making the results obtained from this analysis unreliable. Figure 10B shows the opposite of Figure 10A. A too small sample volume is injected and only shadows are seen, except for the most abundant compounds. Although the software detects more than the analyst can see from the chromatogram, a blob detection limit including least abundant peaks would probably include noise as well.

Figure 10C is a better illustration on a GCxGC separation of atmospheric gas oil than A and B. There is still low abundance of the aromatics, however, larger injection volume (larger than 0.002 µL) would most likely result in an appearance of saturates and non-aromatics as seen in Figure 10A. Fine tuning of the injection volume could improve the separation and chromatogram.

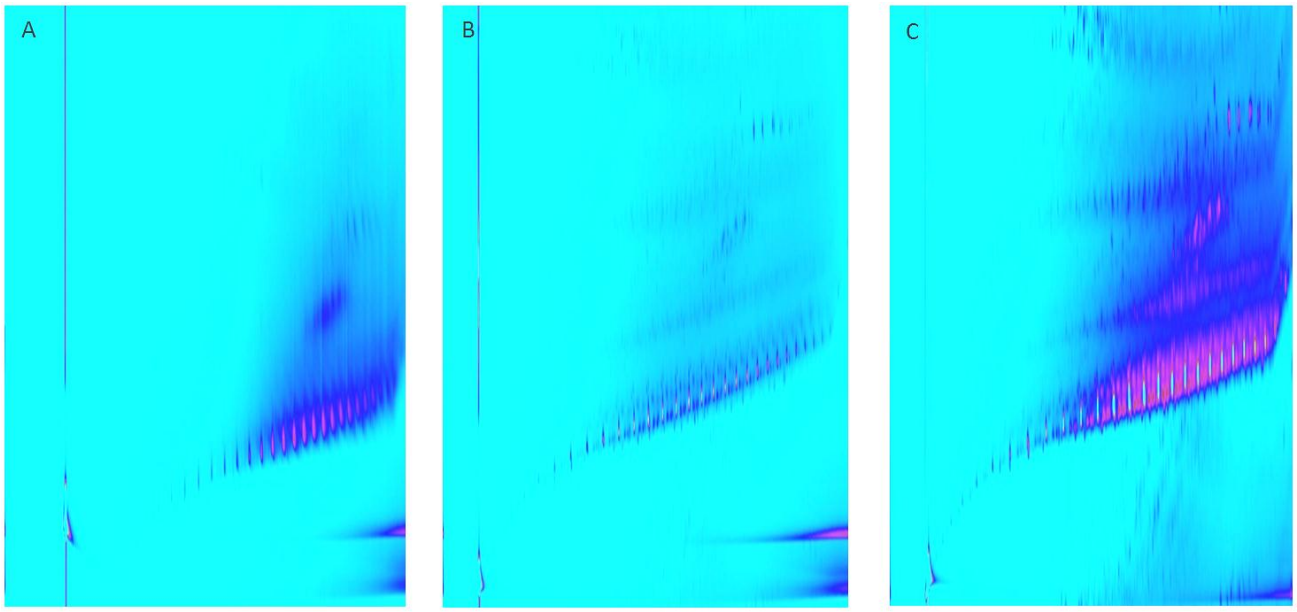


Figure 11. Chromatograms obtained by different VGO methods. A: SR VGO C by method 23 (two temperature ramps, start at 50°C). B: SR VGO B by method 24 (one temperature ramp, start at 150 °C). C: SR VGO B by method 29 (one temperature ramp, start at 150 °C, VGO method as seen in Table 11).

Figure 11A is of SR VGO C while Figure 11B and C are of SR VGO B. Method 23 does not provide sufficient separation in either dimension to characterise the vacuum gas oil. This method uses two temperature ramps: ramp 1 starts at 50 °C and has a rate of 7.5°C/min until 180°C, ramp 2 starts at 180 °C and has a rate of 4.5 °C/min to 360 °C. Method 24 and method 29 differs in injection volume, 0.004 and 0.015 µL, respectively, and the final temperatures being 360 °C and 340 °C for the two respective methods. The temperature ramp in method 24 and 29 is 3.5 °C/min. Method 23 has an injection volume of 0.004 µL and a final temperature of 360 °C. The injection volumes are of diluted sample. Dilution in weight percent is given in Table 9 in Chapter 3.4.

A comparison of the percent response for SR VGO B obtained by methods 24 and 29, as seen in Figure 11B and C, is shown in Table 14:

Table 14. Comparison of response for VGO B obtained by method 24 and 29.

	Method 24	Method 29
Name	**Percent Response**	**Percent Response**
Saturates/non-aromatics	38.9	40.3
Monoaromatic	28.8	28.3
Diaromatic	20.9	20.3
Triaromatic	10.6	11.1
Residual	3.0	0.4

The largest difference in percent is for the residual compounds, 2.6. Residuals are those not included by the groups of the template. The differences can be explained by small variations of the template position. Since running the temperature program to 360 ^{o}C is much harder on the columns, method 29 should be applied. Holding 340 ^{o}C for more than 3 minutes in method 29 could ensure complete elution of the sample. Comparison of Figure 11B and C show that the whole sample is eluted by maximum temperature of 360 ^{o}C, maximum temperature of 340 ^{o}C with a hold time of 3 minutes seems to not completely elute the entire sample.

The injection volume in method 29 could be reduced to e.g. 0.006 µL instead of 0.015 µL to reduce overlapping and band broadening. Single peak identification is more difficult for VGOs than AGOs, but as already mentioned the application is to quantify the larger hydrocarbon groups such as mono-, di-, and triaromatics.

There are still possibilities for optimalization of the methods for AGOs and VGOs. Compromises of overload of non-aromatics for better separation of aromatics, focus on volatiles against less volatile compounds can be made. If overall separation is desirable, the methods described in Table 10 and Table 11 are recommended.

It can be discussed whether method 24 (Figure 11B) should be recommended over method 29 (Figure 11C). The final temperature is 360^{o}C which results in much column bleed. However, compared to Figure 11C the sample is completely eluted. The injection volume (0.004 µL) is probably too low and could preferably be increased (0.006 – 0.015 µL). On the other hand, the elution zones and the order of the chromatogram are maintained.

- Modulation time and hot jet duration

Modulation time is essential for comprehensive two-dimensional gas chromatography. The modulation time and hot jet duration were investigated as seen in Table 15; the same as Table 5 in Chapter 3 Experimental.

Table 15. Modulation time and hot jet duration.

Modulation time (ms)	9999	8000	7500	5000	3000	8000	8000	8000
Hot jet duration (ms)	500	500	500	500	500	2000	600	100

The pre set, and recommended, modulation time of 8000 ms and hot jet duration of 500 ms gave a chromatogram of a reference gas oil standard (Agilent Reference Gas Oil Sample No.1, Agilent Part Number: 5060-9086) as seen in Figure 12.

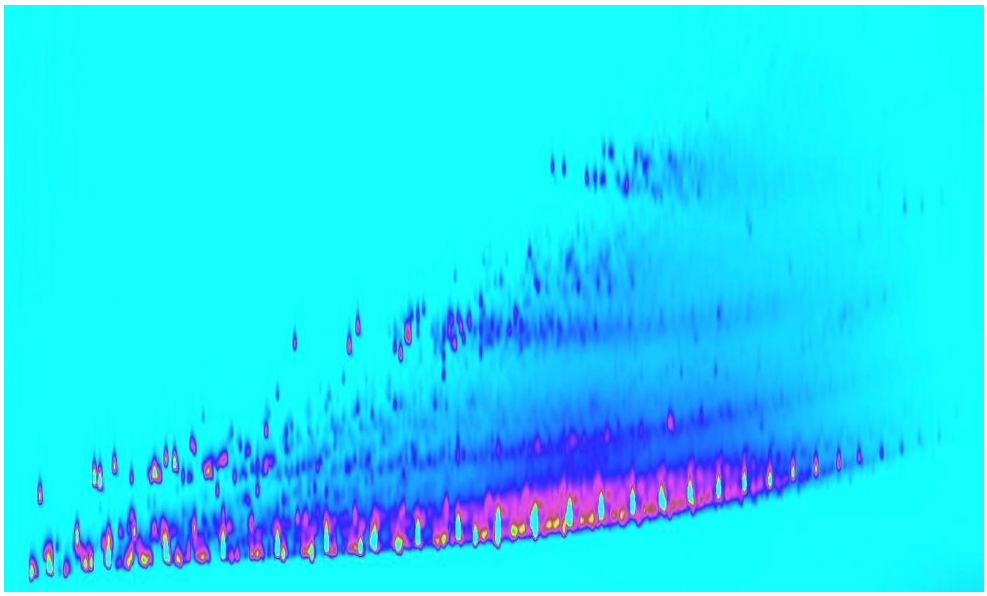


Figure 12. Reference gas oil standard analysed with modulation time 8000 ms and hot jet duration 500 ms.

Figure 13 and Figure 14 show the chromatograms of the reference gas oil standard (Agilent Reference Gas Oil Sample No.1, Agilent Part Number: 5060-9086) where modulation time and hot jet duration have been investigated. The modulation time is kept constant in Figure 13 and hot jet duration is kept constant in Figure 14.

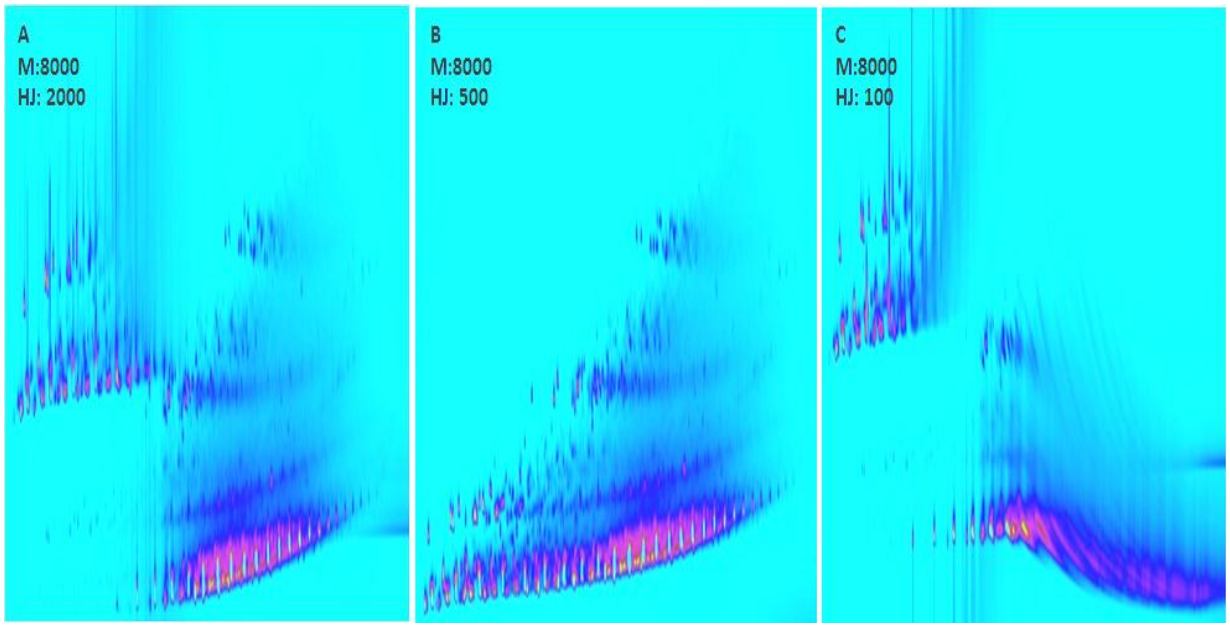


Figure 13. Optimalization of hot jet duration. Modulation time 8000 ms, carrier gas flow kept constant at 0.85017 mL/min. A: hot jet duration 2000 ms. B: hot jet duration 500 ms. C: hot jet duration 100 ms.

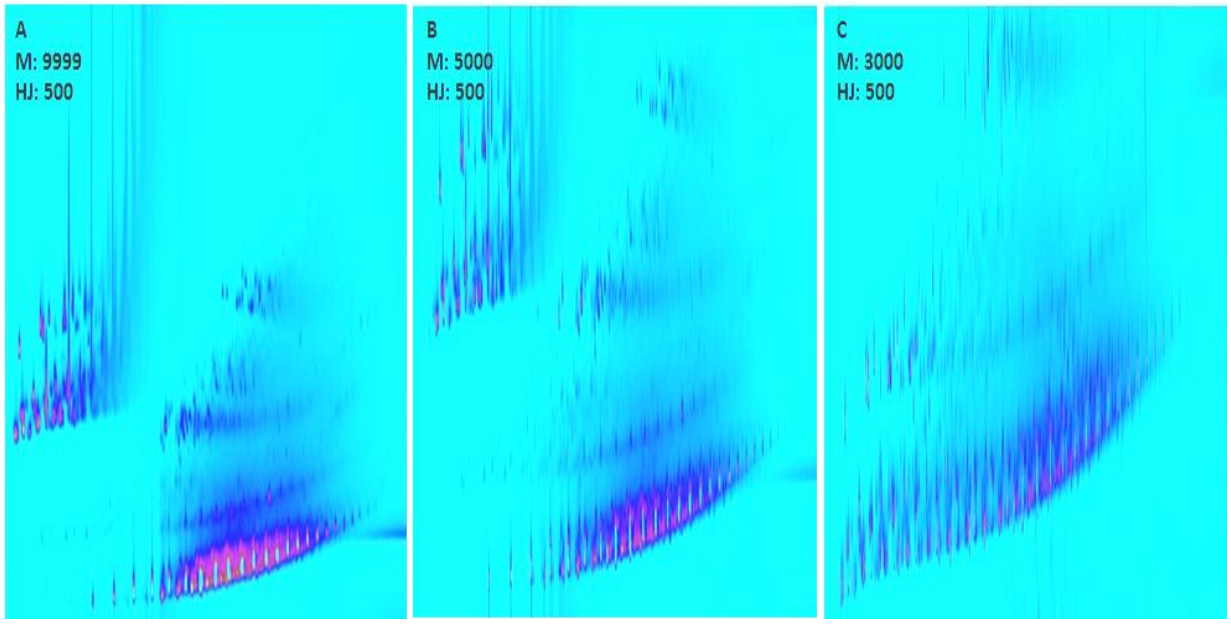


Figure 14. Optimalization of modulation time. Hot jet duration 500 ms, carrier gas flow kept constant at 0.85017 mL/min. A: modulation time 9999 ms. B: modulation time 5000 ms. C: modulation time 3000 ms.

In Figure 13 A and C and Figure 14 A and B the more volatile parts of the sample are shifted towards higher 2nd dimension retention times compared to Figure 12. Also, they are "cut" away from the rest of the sample. This can partly be explained by the non-optimal time interval between the hot jet pulses and their duration, and distortion of software interpretation as a consequence of mismatch between modulator parameters, i.e. modulation time, hot jet duration,

and loop capillary length, and chromatographic parameters, e.g. carrier gas flow and oven temperature. A long duration of the hot jet causes a large amount of the sample factions in the loop to reach the end of the loop capillary, be vaporised, and transferred onto the second column during the hot jet's on-time.

The time interval between the pulses (the modulation time) allows peak fractions to be focused by the cold jet (19). Also, the time interval determines how often the focused fractions are subjected to the hot jet. Figure 13B is the same chromatogram as shown in Figure 12. The results of too long hot jet duration and short interval between pulses are shown in Figure 13A and Figure 14B, the opposite (too short hot jet duration and too long interval between pulses) in Figure 13C and Figure 14A. When modulation time is short (3000 ms) and hot jet duration is normal (500 ms) the chromatogram is ordered but wraparound occurs, Figure 14C. In Figure 14C the peaks are broadened in the 2^{nd} dimension as a result of several trapping fractions of the first peak to separate. One consequence of too many 2^{nd} dimension chromatograms is the low abundance of each compound in the peak fraction which could lead to errors in response calculations. Obviously the hot jet duration and modulation time cannot be altered independently. There are several parameters believed to influence the modulator performance as already mentioned.

A similar study of the modulation time's impact on the separation was done by Mostafa et al. (23). Also here the chromatographic conditions were kept constant and only modulation time was changed. The results showed that 1^{st} dimension separation is not always maintained when adjusting the modulation time to higher values. Too short modulation times were found to cause wraparound as the major drawback. This study refers to modulation time impact only on three PAHs. Clearly, the situation is more complex for a comprehensive sample mixture than for three compounds.

Comparison between Figure 12, Figure 13, and Figure 14 emphasise the importance of the modulator's features, as described in the theory. Although only the extremities are displayed in Figure 13 and Figure 14, there are clear differences even with small alterations of the modulator's parameters. However, the exact optimum modulation time and hot jet duration cannot be said with certainty as the fine nuances have not been investigated. Yet, the separation and order of the chromatogram for every sample run by 8000 ms modulation time and 500 ms hot jet duration are

convincing in the determination of the modulator's parameters in the analytical methods. It is also the values recommended by the installation contractor.

A modulation time of 6500 ms and hot jet duration of 375 ms gave a chromatogram similar 8000 and 500 ms modulation time and hot jet duration, respectively, see Figure 15 and Figure 12 for comparison.

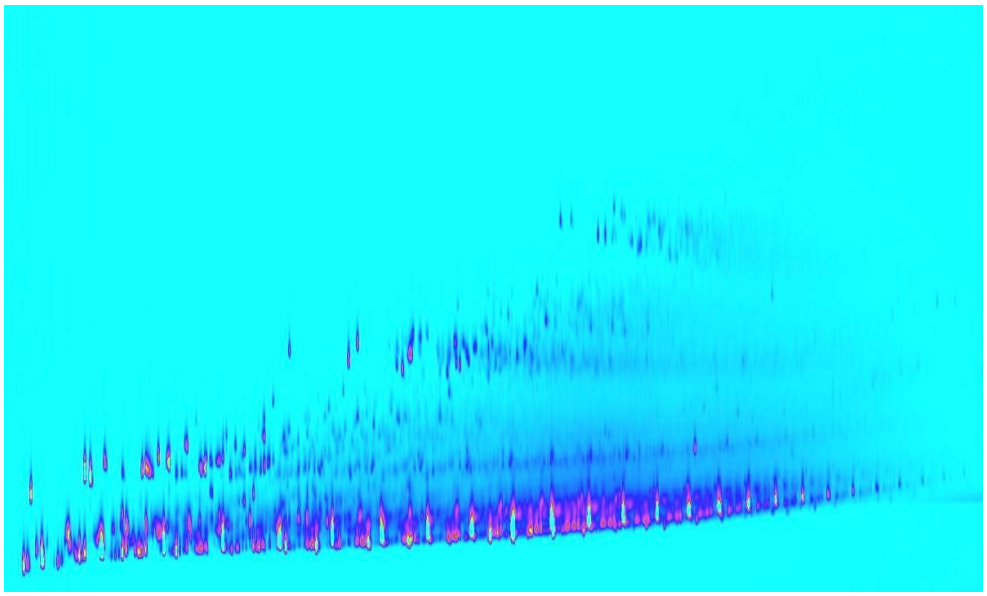


Figure 15. Modulation time 6500 ms and hot jet duration 375 ms of reference gas oil standard.

The chromatogram presented in Figure 15 has a good separation of the hydrocarbon groups, saturates and non-aromatics, mono-, di-, and triaromatics. Applying shorter modulation time allows the first dimension's peak's to be modulated several times than by 8000 ms. On the other hand, the second dimension analysis time is reduced, which for more complex samples than the reference gas oil can cause wraparound. The chromatogram obtained in Figure 15 is run by a method with lower injection volume than the same sample shown in Figure 12, 0.002 compared to 0.003 µL, respectively. The carrier gas flow and the other chromatographic parameters are the same for both analyses.

It is evident from Figure 13 and Figure 14 that both hot jet duration and modulation time is important for the separation and construction of the 2D chromatogram. It must be emphasised that the carrier gas flow is kept constant at a value of 0.85017 mL/min, disregarding any correlation between the modulation parameters and the carrier gas flow. Hot jet duration influence the broadening of the peaks and their band widths when transferred to the second

column. In addition, the hot pulse can induce thermal breakthrough of peak fractions if several sample factions are present in the loop, making the fractions escape the focusing by the cold jet (23). Breakthrough is seen for the volatile parts in Figure 13A and C and in Figure 14A and B. Most importantly, the hot jet is responsible for vaporisation of the condensed (focused) peak fractions at the beginning of the 2nd column (5, 19, 23).

The modulator is a complex instrument part which is not easy to comprehend. It depends on numerous parameters; the loop capillary length, hot jet duration, modulation time, oven temperature, carrier gas flow, and 1st dimension separation's peak widths. The modulator must condense at least 3 fractions of each 1st dimension's peaks and transfer the peak fractions onto the second column as sharp narrow bands of vaporised sample. Probably, there are more parameters which influence the modulator. As seen from Figure 13 and Figure 14 it is not straight forward to optimise the modulator's time parameters.

4.1 Hydrocarbon analysis (FID-signals)

4.1.1 Hydrocarbon and PAH standards

Hydrocarbon and polycyclic aromatic hydrocarbon standards have been prepared on a weight per weight basis solved in toluene (HiPerSolv CHROMANORM 99.80%). The standards have been analysed by the method developed for AGOs, Table 10, for quantitation and on the AGO and VGO methods for identification. The response factors, i.e. the slope of the calibration curves, have been investigated for PAHs and aromatics as well as a normal-paraffin. The standards have been run in several parallels under equal conditions. The results are presented in Table 16, Figure 16, and17.

The response factors obtained by the standards and their parallels' volume responses plotted one by one against concentration are given in Appendix B.A.

Table 16. Response factor of calibration curves of hydrocarbon and PAH standards. P = parallel number.

Compound	P 1	P 2	P 3	P 4	P 5	P6	Average	RSD	Response factor (RF)
Heptane	1.2	1.2	1.2	1.2	1.2	1.2	1.2	0.0	**1.2**
Xylene	1.2	1.2	1.2	1.3	1.2	1.3	1.2	4.2	**1.2**
Naphthalene	1.5	-	1.2	1.3	1.3	1.4	1.3	8.5	**1.3**
Fluorene	1.4	1.5	1.5	1.5	1.5	1.5	1.5	2.8	**1.5**
Phenanthrene	0.8	1.5	1.5	1.6	1.5	1.6	1.4	21.6	**1.4**
Pyrene	1.4	1.4	1.3	0.9	0.9	0.8	1.1	25.0	**1.1**
Chrysene	1.4	1.4	1.3	1.4	1.4	1.4	1.4	3.0	**1.4**

Table 16 shows that the slope of the calibration curves obtained by the FID is approximately 1 for all compounds. The relative standard deviation is high for naphthalene, phenanthrene and pyrene. The other standards have RSD values below 5.

The response factors for the PAH standards are estimated by experiments to 1, allowing data analysis to be straight forward without any corrections for the response factors as the relationship between the response factor is directly proportional to the sample concentration (µg/g). The linearity of the PAHs is also satisfactory over a large range of concentrations. The response factor of hydrocarbons is assumed to be similar by the VGO method.

Figure 16 shows a scatter plot where all quantification standards and their parallels are plotted in the same chart, each standard designated their own label where the parallels are plotted as one data set. Figure 17 shows the combined response factor for all standards and all parallels; all are plotted as one data set. In Appendix B.A the scatter plots of each standard and its parallels are shown, the response factor variation within each parallel of the standards is shown in Table 16

Table 16.

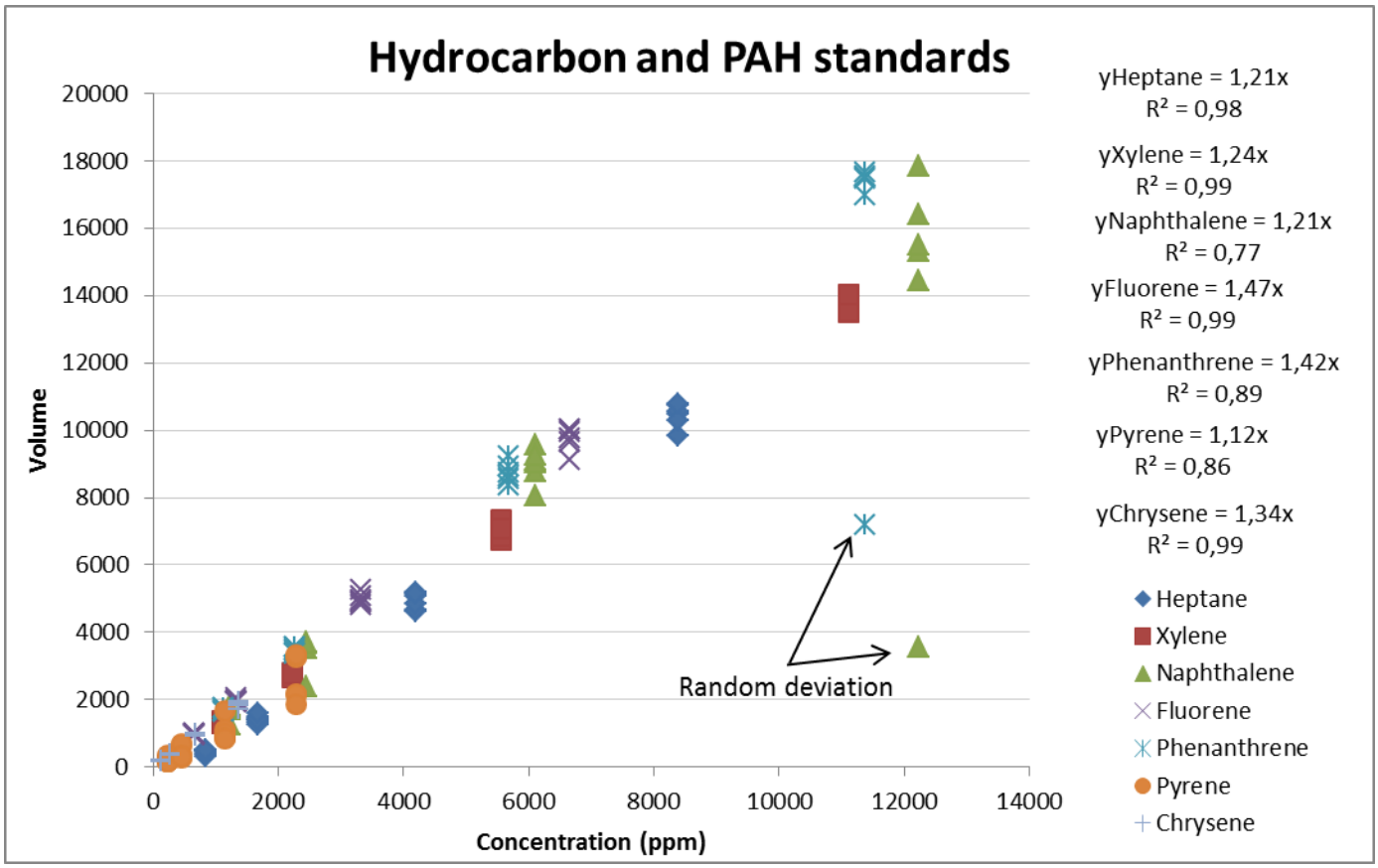


Figure 16. Scatter of hydrocarbon and PAH standard's volume responses against concentration.

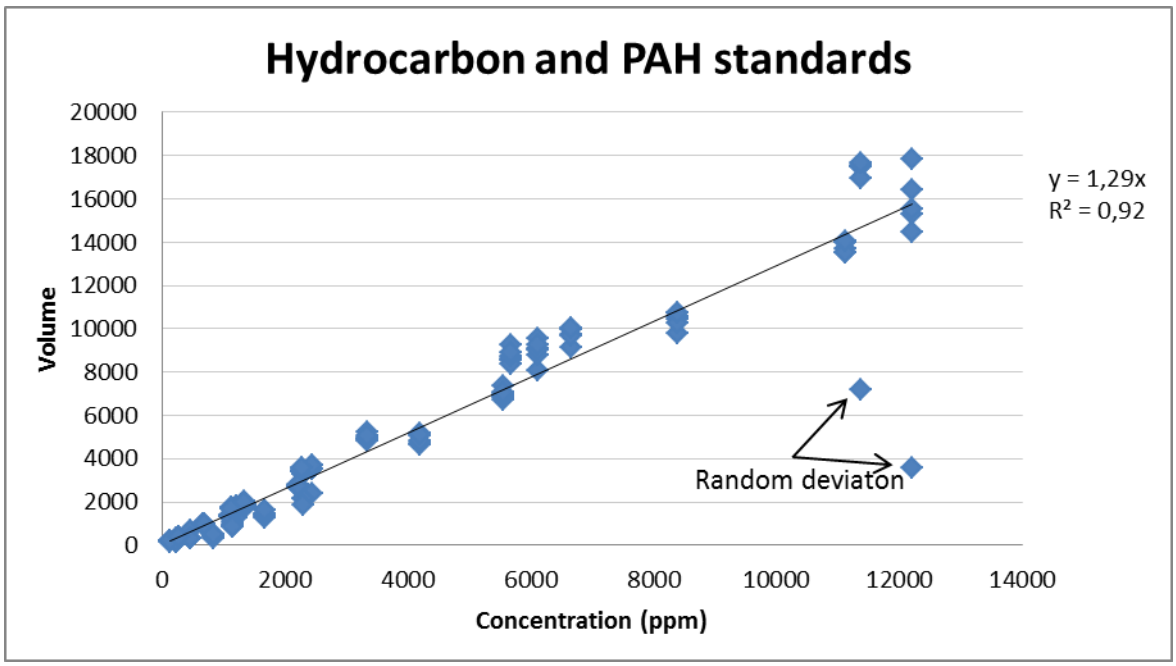


Figure 17. Scatter plot of hydrocarbon and PAH standards. Combined volume response for all standard compounds and parallels against concentration.

The overall trend is that hydrocarbons whether aromatic or paraffinic have a response factor of approximately 1.2-1.5, the overall RF is 1.3. There is no distinct trend of the groups' RF-value; they have nearly the same response. The volume of the aromatic groups can be directly correlated to their concentration in the sample.

The weight percent which the different hydrocarbon groups are given in are normalised values.

Discussion

The RSD values of naphthalene, phenanthrene, and pyrene are high. Naphthalene has a huge variation of concentration in the standards. The highest standard can possibly induce overloading of the column, making volume response unreliable. In the case of phenanthrene, it may overlap with anthracene which is used for identification but is also a part of a mixture of standards. Overlap of compounds can increase one peak's volume response as the volume of the other peak is added. Pyrene can possibly precipitate in toluene as it is a tetraaromat. For the three first parallels it shows similar retention factors and for the three last. The parallels shown in Table 16 are run in the same sequence, and compounds would have time to precipitate by stagnation of the liquid in the vials. Other sequences run with several parallels of the hydrocarbon standards showed the same trend of pyrene's response factor decreasing from the first parallel to the last.

In Figure 16 and Figure 17, the distribution shows that there are small differences between parallels and response as function of concentration. The linear trendline produce a regression value which is considered good on the basis of the number of statistical data. The regression value of naphthalene, phenanthrene, and pyrene is below the acceptable value of 0.98. The arguments from the above paragraph explain the variation of the standard curves resulting in low regression values.

The hydrocarbon standards yield approximately the same response factor, the calculated relative volume responses obtained from the software can thus be used as normalised values of the samples. The decimals are not trustworthy, and as a consequence only one decimal is given for the results obtained. A larger number of parallels could verify the response factor (RF) to a more accurate value.

Trendlines are forced through zero. This gives incorrect regression values, and assumption of linearity through a larger concentration range than experimentally explored. The entire concentration range of actual petroleum samples would be too extensive in this study. Extrapolation of the standard curves is thus performed.

4.1.2 Templates

Templates are made for both atmospheric and vacuum gas oils. The templates are results of identification of retention times by standards and the structured chromatograms of real samples. Templates will be shown for several VGOs and AGOs in the following chapters.

The hydrocarbons are divided into:

- saturates/non-cyclic
- cyclic/non-aromatic
- monoaromatic
- monoaromatic, naphthenic
- diaromatic
- diaromatic, naphthenic
- triaromatic
- tetraaromatic

The number of standards used for hydrocarbon group identification could be extended to include more complex compounds.

The templates often have to be adjusted to fit the samples. There is a large difference in the abundance, distribution, and number of hydrocarbon classes for e.g. light gas oil and heavy gas oil. This illustrates the disadvantage of using external standards in stead of internal standards.

However, there is a factor of cost and availability of standards to consider, the structure of petroleum chromatograms was applied in extrapolating and estimating the groups.

4.1.3 Light Gas Oil

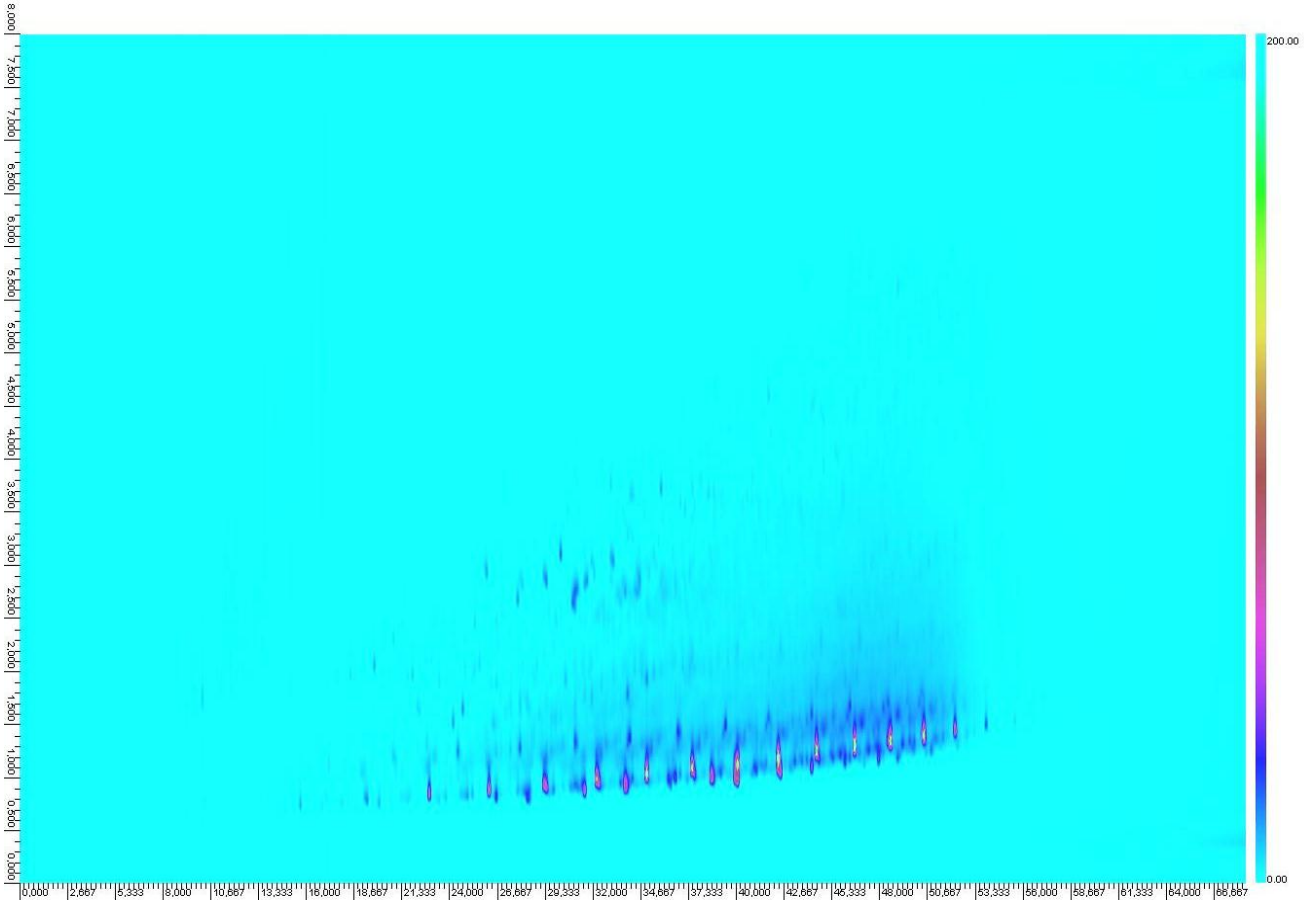


Figure 18. Chromatogram of SR LGO A.

Figure 18 is a GCxGC chromatogram of straight-run light gas oil. The method described in Table 10 is used to obtain this chromatogram. As seen in Figure 18 the sample components are well separated. However, some components are not very visible to the naked eye. This is overcome by manipulation of the software's detection of minimum blob volume, the software detects more than what is visible to the analyst by watching the chromatogram. The colour intensities increase as the volume of a peak increases. Thus, the colour intensity is a good indication of the concentration (wt %).

The aromatic groups as well as the non-aromatic groups are well separated. This also applies for single compounds within these groups.

Table 17 and Figure 19 show the same straight-run light gas oil (SR LGO A) sample and its products of hydrotreating (LGO A-1 to A-5) analysed by both HPLC and GCxGC. The temperature is reactor temperature of the hydrodearomatization. The SR LGO is the same sample as the chromatogram

in Figure 18. A constructed template is used for determining the weight percent of each group type, i.e. monoaromatics, diaromatics etc., in addition to single component identification.

Table 17. Comparison of aromatic analysis in wt % by GCxGC and HPLC and non-aromatic content in wt % by GCxGC.

ID	SR LGO A	LGO A-1	LGO A-2	LGO A-3	LGO A-4	LGO A-5
Temperature °C	**feed**	**280**	**300**	**320**	**340**	**360**
***Saturates/non-cyclic**	41.8	46.0	45.1	46.3	44.3	50.3
***Cyclic/non-aromatic**	21.4	21.2	22.6	24.6	28.3	24.6
Monoaromatic HPLC	24.2	26.1	24.5	21.3	17.5	18.4
Monoaromatic GCxGC	27.3	25.7	26.1	25.0	20.1	20.9
Diaromatic HPLC	3.8	1.3	1.1	0.9	1.2	2.5
Diaromatic GCxGC	8.1	5.7	5.1	3.3	2.6	3.0
+Triaromatic HPLC	0.5	<0.1	<0.1	<0.1	0.2	0.4
Triaromatic GCxGC	0.6	0.0	0.0	0.0	0.0	0.0
Total aromatics HPLC	28.5	27.4	25.6	22.2	18.9	21.3
Total aromatics GCxGC	36.0	31.4	31.2	28.3	22.7	23.9
***Residual**	1.8	1.7	1.3	1.2	2.2	1.1

*These results are obtained by GCxGC and were not given by the HPLC analysis.

The light gas oil does not contain any tetraaromatics detected by GCxGC.

It is obvious from both Table 17 and Figure 19 that GCxGC do not give the exact same result as HPLC. Yet the GCxGC technique and HPLC indicate the same trend; the aromatic content decrease as reactor temperature (hydrodearomatization) increases until a certain point where equilibrium is reached for saturation of the aromatics and new aromatics are formed. The combined weight percent of cyclic/non-aromatic and saturates/non-cyclic increase as tri-, and diaromatics are saturated through formation of monoaromatics before complete saturation and possibly ring-breaking.

The general trends are similar for both GCxGC and HPLC, however, GCxGC give higher values, but not for triaromatics. Here, the HPLC results show higher values than 2D GC, especially for LGO A-4 and LGO A-5. Since there are no exact +triaromatic HPLC values for LGO A-1, A-2, and A-3, it cannot be said if these values are equal or not to the GCxGC results.

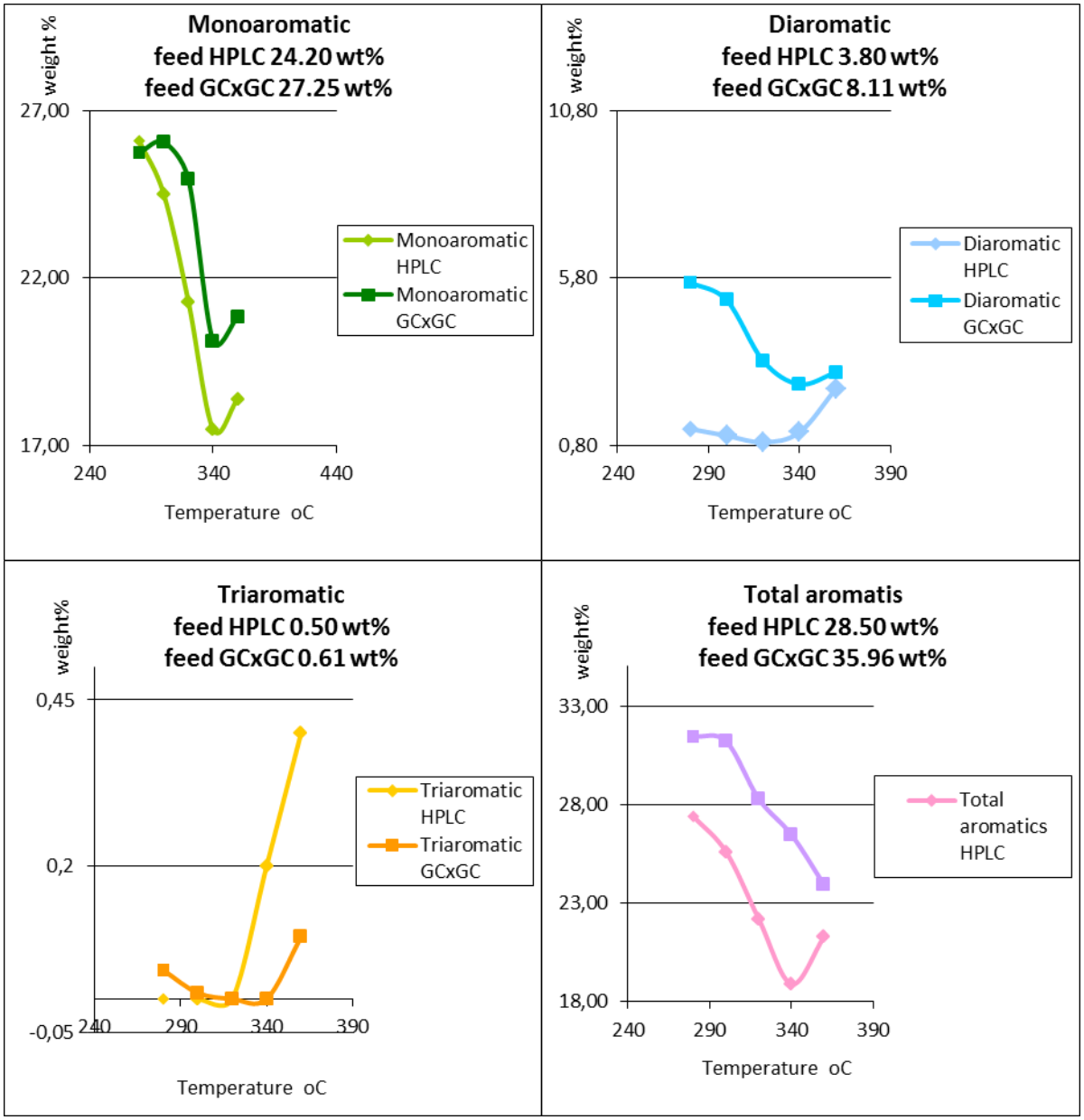


Figure 19. Graphical visualization of Table 17. Plots of weight % aromatics by GCxGC and HPLC against reactor temperature (°C).

Figure 20 shows the chromatogram of LGO B. It is a blend of kerosin and LGO A-A from the same crude. The hydrocarbon content in weight percent of SR LGO B, SR AGO A, LGO A-A, and HGO A-A, all from same North American crude, is given in Table 18.

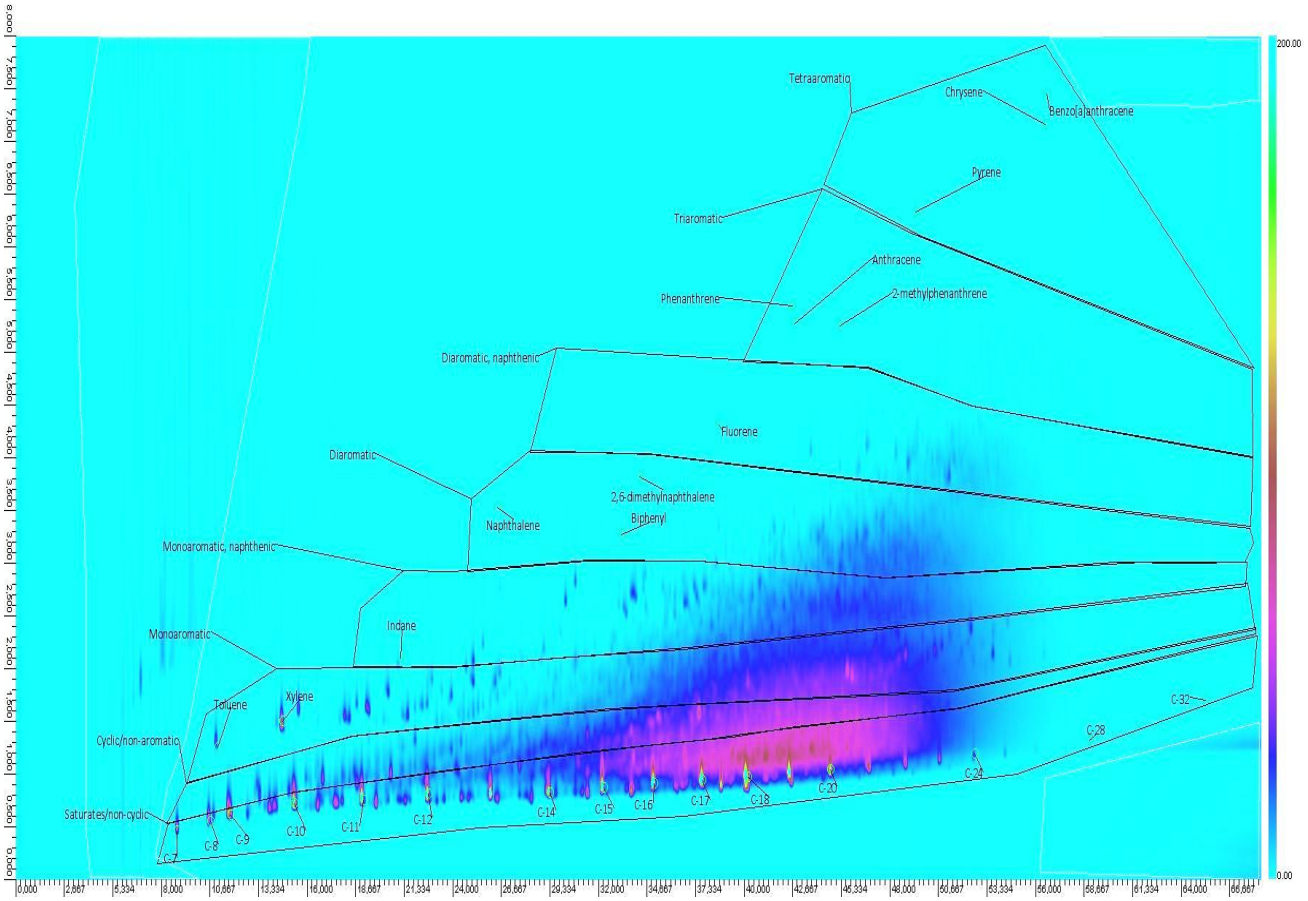


Figure 20. Chromatogram of SR LGO B.

Table 18. Hydrocarbon content of gas oils with same origin (North America): SR LGO B, SR LGO A-A, SR AGO A, and HGO A-A.

	SR LGO B	SR LGO A-A	SR AGO A	SR HGO A-A
Saturates/non-cyclic	43.0	31.4	12.7	9.3
Cyclic/non-aromatic	20.0	17.0	18.0	8.0
Monoaromatic	29.9	31.7	38.6	36.2
Diaromatic	5.2	14.4	22.7	26.9
Triaromatic	0.1	2.3	6.5	11.9
Tetraaromatic	0.0	0.2	0.4	4.1
Residual	2.6	3.0	1.2	3.9
Total aromatic	35.2	48.6	68.2	79.0

It is a large difference in the distribution of aromatic and non-aromatic hydrocarbons in these distillation cuts, although all are within the range of C_7-C_{23}. SR HGO A-A has the highest total aromatic content while SR LGO B has the highest content of saturates/non-cyclic. The concentration of monoaromatics and diaromatics constitute the major aromatic compound content. It is easy to differentiate the HGO as a heavier distillation cut than the others due to its much lower content of saturates/non-cyclic and cyclic/non-aromatic.

A comparison of atmospheric gas oils from different origins is illustrated in Figure 21. SR AGO A is North American, SR AGO B Central American, and SR AGO C from the North Sea. The weight percent of hydrocarbon groups is given in Table 19.

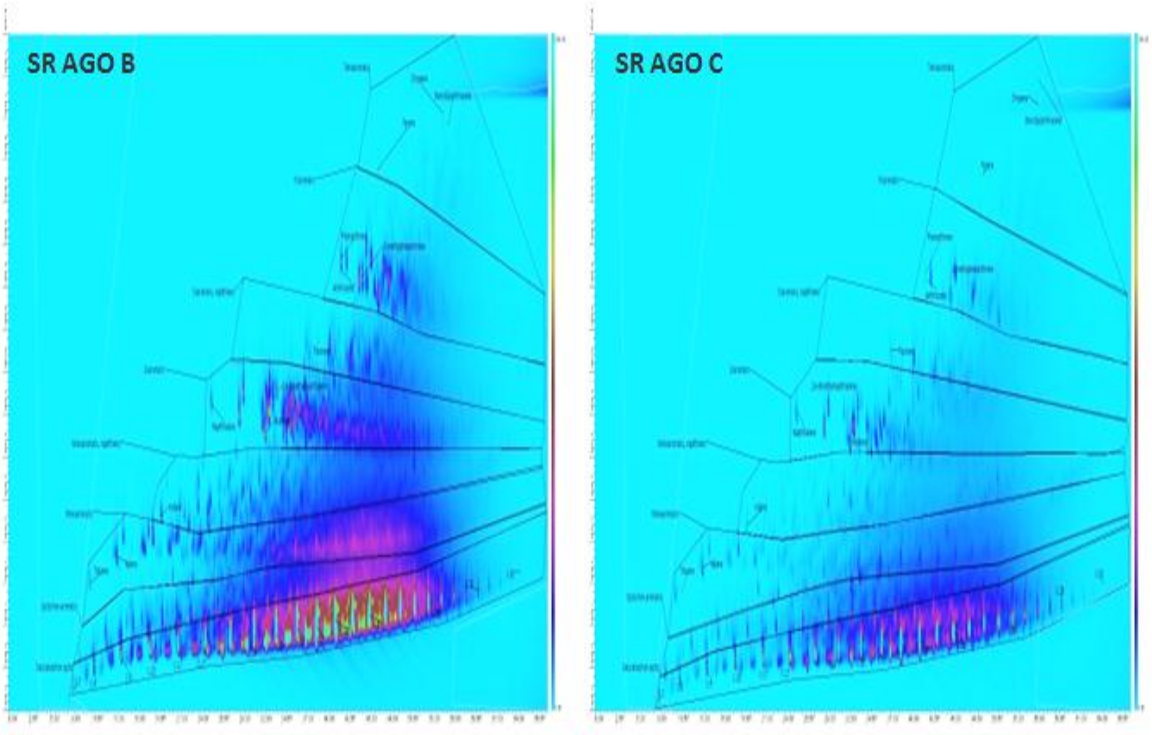


Figure 21. Chromatograms with templates of SR AGO B, and SR AGO C.

Table 19. Hydrocarbon distribution of SR LGO B, SR AGO B, and SR AGO C.

	SR LGO B	SR AGO B	SR AGO C
Saturates/non-cyclic	43.0	54.1	56.3
Cyclic/non-aromatic	20.0	3.4	7.0
Monoaromatic	29.9	22.9	22.6
Diaromatic	5.2	14.5	9.7
Triaromatic	0.1	3.8	2.4
Tetraaromatic	0.0	0.3	0.3
Residual	2.6	1.1	1.6
Total aromatic	35.2	41.5	35.0

The AGOs are described as heavy and light in Table 9, Chapter 3.4. The higher aromatic content of SR AGO B than SR LGO B and SR AGO C as seen in Table 19 and the chromatograms in Figure 20 and Figure 21 shows this. The distillation cut of SR LGO B is more correct for atmospheric gas oils than SR AGO A which contains more of the heavy part than AGOs normally do. SR LGO B contains much more cyclic/non-aromatic than the two other AGOs. This can be explained by the addition of the template at different positions in the chromatogram by the visual approach to determine groups. It is a huge degree of overlap in the saturate/non-aromatic and cyclic/non-aromatic area.

The chromatograms are good illustrations of the differences in hydrocarbon distribution different atmospheric gas oils. They also show that the method developed performs good separations.

It seems that SR AGO A is not as well separated as the two others, and especially compared with SR AGO C. This can be explained by the complexity of the sample.

Discussion

- LGOs by GCxGC and HPLC

The differences between the results obtained by GCxGC and HPLC arise from two main causes. Firstly, the HPLC method is based on back flushing and utilization of one aromatic compound to determine the ending of mono-, di-, and triaromatics. GCxGC on the other hand uses several standards to verify the borders of the aromatic groups. Secondly, the peak capacity of GCxGC is superior to HPLC, resulting in enhanced separation as well as the fact that the analysis is multidimensional. However, the software template for group type analysis is subjected to errors as it is manually produced. The border lines of the groups are not set by 100 % certainty, leaving a source of error for the amount of compounds determined to belong to either this group or that by estimate of visual approach. Especially the saturates/non-cyclic and cyclic/non-aromatic are subjected to overlap making template construction challenging.

Triaromatic compounds are the only ones where HPLC values are higher than GCxGC values. This can much be explained by the method of the HPLC analysis where back flushing is conducted to elute the triaromatics.

The samples can also be subjected to degradation by storage. The HPLC analysis was performed shortly after catalytic hydrodearomatization, GCxGC on the other hand was performed a few months later. This can have some impact on the sample's integrity, yet the procedure for storage minimizes this source of sample degradation. Samples are stored cold and dark.

The differences and errors taken into account, GCxGC is more reliable than HPLC due to the number of standards, the peak capacity, and the multidimensionality.

LGOs have low concentrations of aromatics, compared to e.g. LCOs. The low abundance as seen in Figure 18 can cause errors when the software is calculating responses. However, normalisation

should correct for this. Increasing the injection volume from 0.002 to e.g. 0.004 µL will increase the difference from noise and enhance the abundance, reducing the risk of calculation errors.

- SR AGO, LGO, and HGO of same crude

The differences in hydrocarbon distribution are results of the distillation cuts. The method developed for AGOs is suitable for analysing different cuts within this carbon range. The challenge of separating clustered compounds within a relatively short boiling point and polarity range is not overcome for the sample in Table 18. It seems as if the 1st and 2nd dimension separations are inadequate or incomplete (Figure 20). A slower temperature ramp e.g. 3.0 ^{o}C/min as in method 30 could improve this. It must be considered if the separation is acceptable as it is shown in Figure 20 or if the increased time of a slower temperature ramp is preferred. The latter is assumed to give better separation and more reliable quantification of the hydrocarbon groups.

SR AGO A is a combination of 75% of SR LGO A-A and 25% SR HGO A-A. The responses of SR LGO A-A and SR HGO A-A in that ratio does not give the weight percent of the hydrocarbon groups obtained by analysis of SR AGO A. This can be a result of the challenge of cluster separation as described in the above paragraph. Separation of SR HGO A-A is better by using method 29. Yet this would not solve the mismatch between the concentration of SR LGO A-A and SR HGO A-A with SR AGO A.

- AGOs of different origin

The separation of SR AGO A is not as good as the separation of the two other SR AGOs. This can be explained by the complexity of the sample. Also, the method is not optimised for separation of one group type, it is meant to give an even distribution of the whole sample's carbon range. The clustering in the middle of the 1st dimension separation space makes quantification difficult and unreliable. Which peak belongs where and base separation is not obtained in this case. A slower temperature ramp could possibly solve this issue if peak identification and quantification is necessary. However, for this purpose, group analysis, it is regarded acceptable although not optimal.

Generally, the method in Table 10 is considered to give sufficient separation for quantification and identification of hydrocarbon groups of atmospheric gas oils.

4.1.4 Light Cycle Oil

A chromatogram of LCO A run by the method described in Table 10 is shown in **Figure 22** and Appendix C where also three dimensional chromatograms are available. LCO A-5, a product of catalytic cracking of LCO A, is shown in Figure 23 and the overlaid chromatograms for more apparent difference in aromatic content in Figure 24.

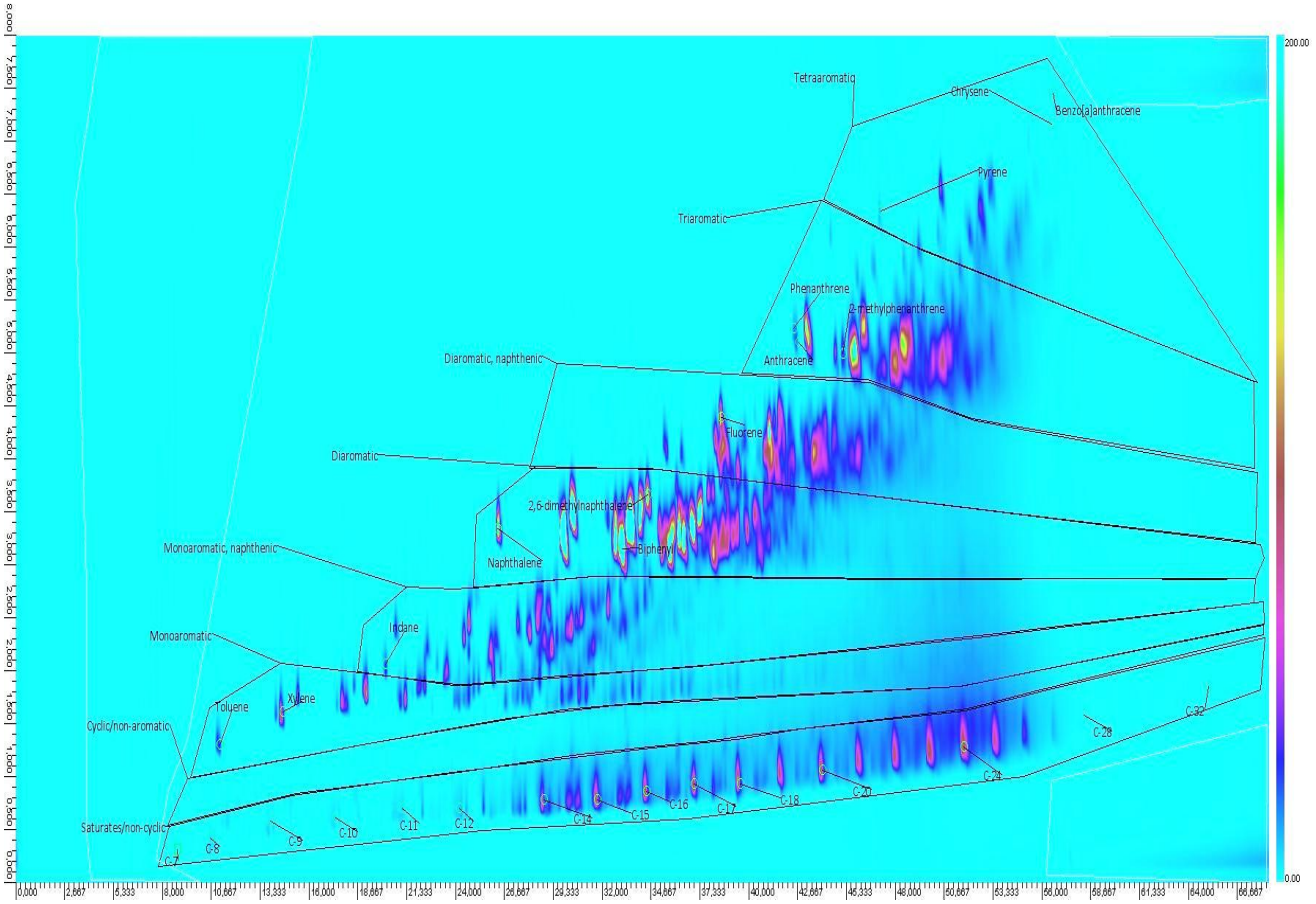


Figure 22. Chromatogram of LCO A.

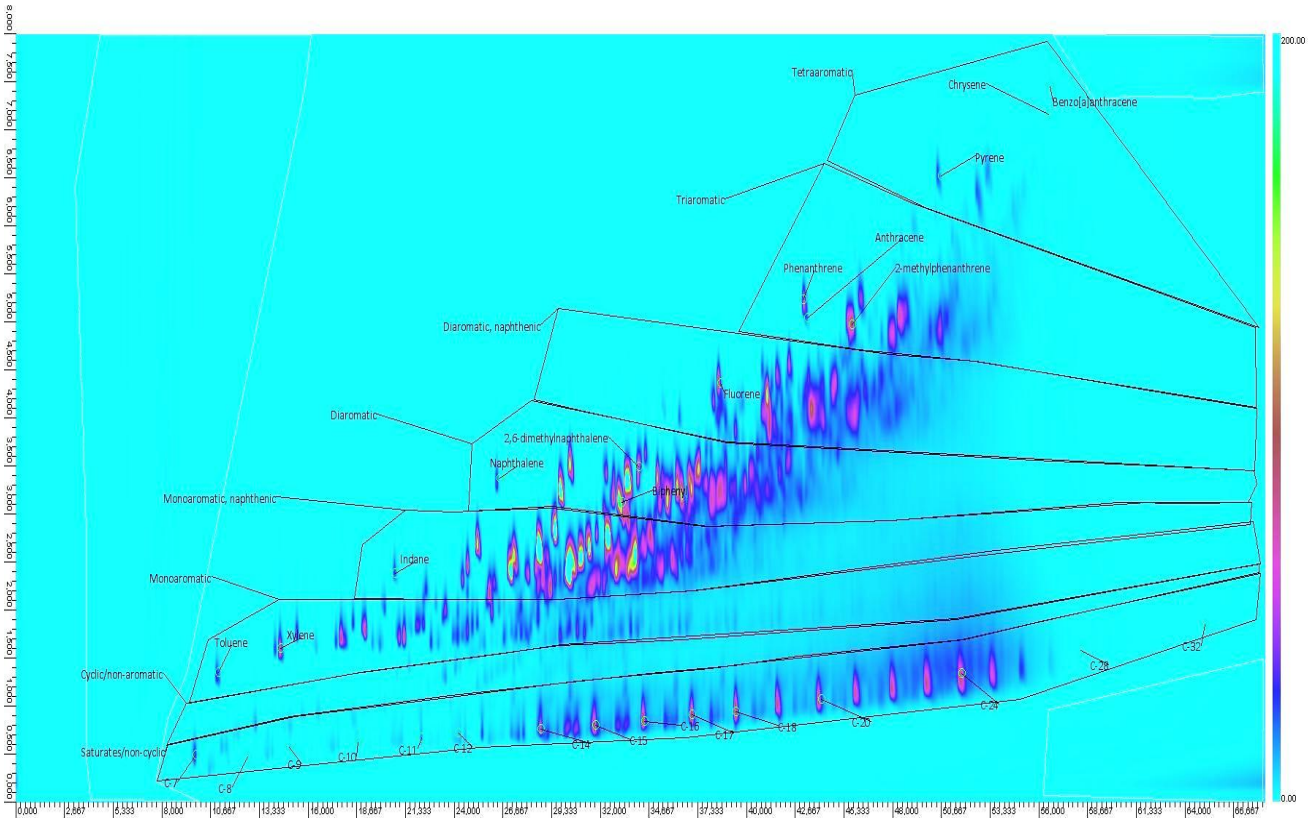


Figure 23. Chromatogram of LCO A-5.

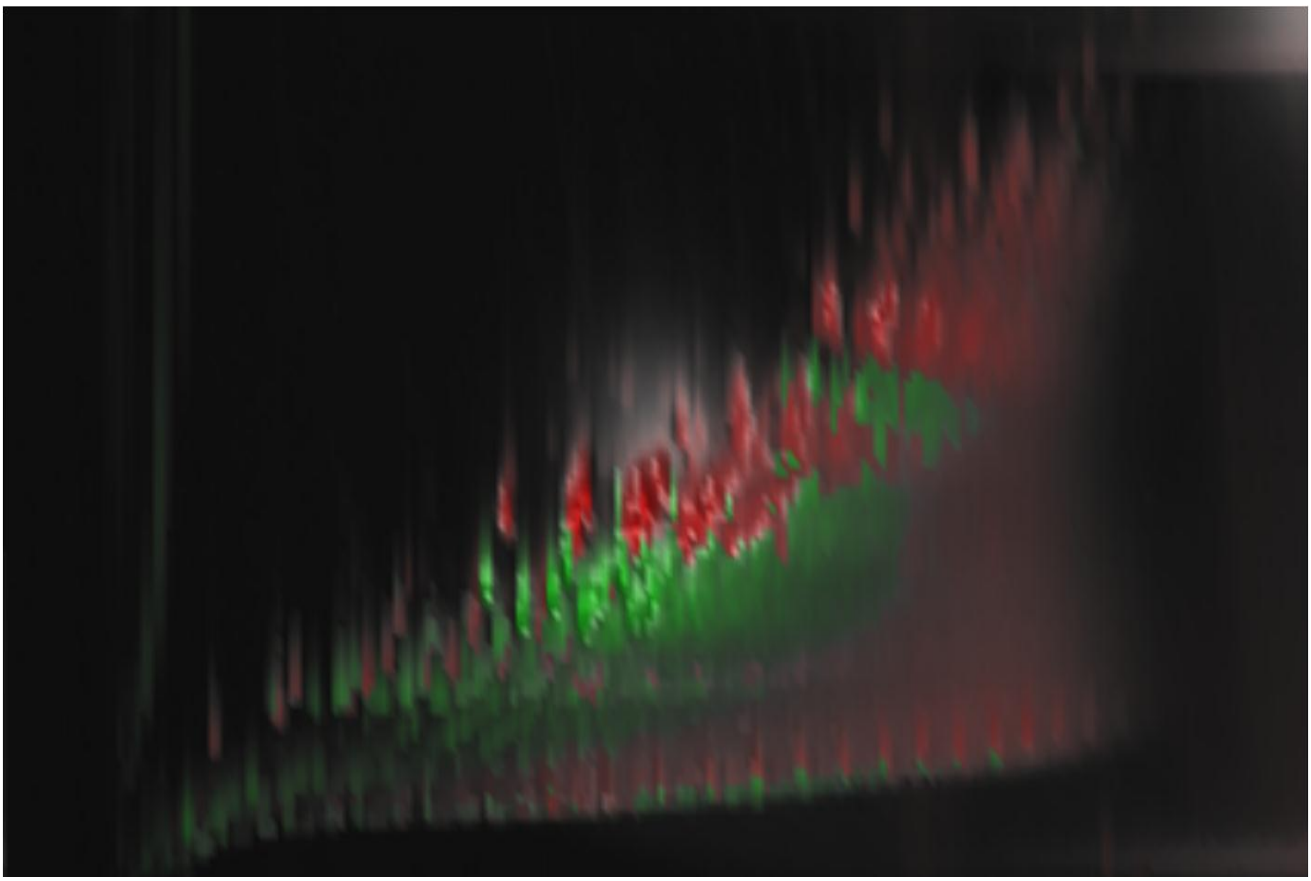


Figure 24. Comparison of LCO A and LCO A-5 by overlaying of chromatograms. LCO A (Figure 22**) is the reference chromatogram, LCO A-A (Figure 23) is superimposed. Red colour shows decrease in intesity and green colour shows increase in intensity.**

A clear group type separation is visible from Figure 22 and Figure 23. The non-aromatics, mono-, di-, and triaromatics are easily distinguishable from one another. LCOs obviously contain a larger amount of aromatics than LGOs. Especially the content of di- and triaromatics are prominent in this type sample.

Comparison of Figure 22 and Figure 23 visualises a clear decrease in the amount of PAHs as a result of hydrotreating. The weight percent of saturates/non-cyclic, cyclic/non-aromatic, and monoaromatic are increased as a consequence of saturation of larger PAHs.

Figure 24 compares LCO A-A, the most hydrotreated product of a LCO A, and LCO A, a product of catalytic cracking. The increase of the hydrocarbon groups is shown in green colour while the decrease (of tetra-, tri-, and diaromatics) is visualised in red colour.

The hydrocarbon content in weight percent is given in Table 20. The temperature is the reactor temperature of hydrodearomatization.

Table 20. Aromatic content in weight % of LCO.

	LCO A	LCO A-1	LCO A-2	LCO A-3	LCO A-4	LCO A-5
Temperature (°C)	**Feed**	**300**	**320**	**340**	**360**	**380**
Saturates/non-cyclic	16.8	16.5	17.0	16.5	15.1	17.1
Cyclic/non-aromatic	3.4	3.7	3.9	4.1	4.3	4.7
Monoaromatic	15.7	20.1	23.7	29.8	34.9	34.1
Diaromatic	43.7	43.1	40.4	35.7	33.2	32.9
Triaromatic	17.4	13.7	12.3	10.6	8.7	8.5
Tetraaromatic	1.0	0.6	0.6	0.6	0.6	0.7
Residual	2.2	2.2	2.5	2.7	3.3	2.2
Total aromatics	77.7	77.6	77.0	76.7	77.4	76.1

Figure 22 and Figure 23 and Table 20 show that the dominant species for the un-hydrotreated LCO are the diaromatics, followed by the mono- and triaromatics, respectively. The amount of monoaromatics rise at the higher working temperatures in the reactor due to saturation of the di- and tri-aromatics, it increases from 15.7 wt % to 34.1 wt %, an increase of 18.4 %. The triaromatic content decreases by approximately the same percentage; from 17.40 wt % to 8.5 wt %, a decrease of 8.9 %.

Even for a sample with this high number of different aromatic compounds sufficient separation is obtained as seen in Figure 22. However, there is some overlapping within the di- and triaromatic areas.

As seen in Table 20, the amount of cyclic/non-aromatic and tetraaromatic compounds is limited.

Discussion

The fact that some peaks overlap does not interfere with the main division of the sample into non-aromatics, mono-, di-, tri-, and tetraaromatics. The subdivision into monoaromatic, polyring system is however more influenced by the overlapping making it harder to draw the borderlines.

Individual compound identification is difficult in the areas of overlapping; if the goal is to quantify single compounds the sample injection volume could be reduced to reduce overloading of the 2nd dimension column. The method developed for the atmospheric gas oil range (Table 10) is very suitable for LCO separation. As seen from the chromatograms in **Figure 22** and Figure 23 the compounds are separated.

4.1.5 Vacuum gas oils

Chromatograms of SR VGO A, B, and C run by the method in Table 11 are shown in Figure 25. SR VGO A, B, and C are diluted in toluene to 14.3, 29.3, and 23.2 wt%, respectively. A larger chromatogram with template of SR VGO A is available in Appendix D. The chromatogram of SR VGO D is shown in Figure 26.

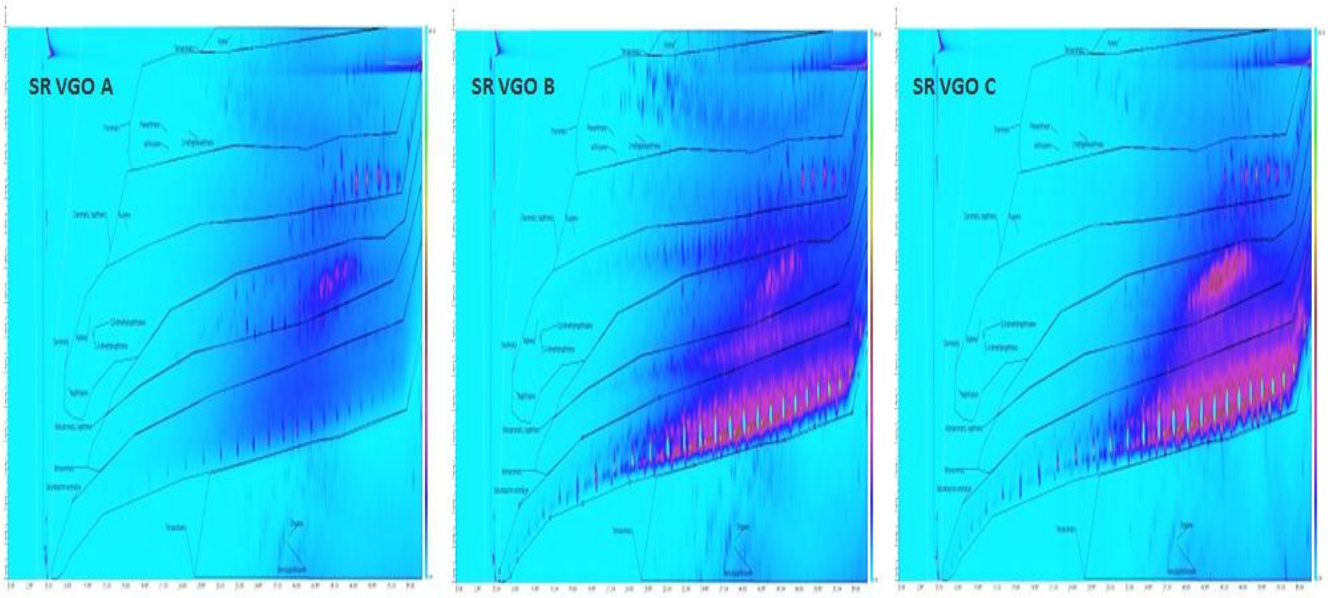


Figure 25. Chromatograms with templates of SR VGO A (diluted to 14.3 wt %), SR VGO B (diluted to 29.3 wt %), and SR VGO C (diluted to 23.2 wt %). Chromatogram of SR VGO D is available in Error! Reference source not found.**A.**

The complexity of vacuum gas oils is illustrated in Figure 25. It is not easy to separate such samples and overlapping of elution zones is practically inevitable. Wraparound occurs and tetraaromatics are eluting in the void below the saturates/non-aromatics. The hydrocarbon distribution, in both boiling point and polarity, is visible and differences between samples' composition is easy to observe.

The weight percent of hydrocarbon groups of SR VGO A, B, and C is given in Table 21.

Table 21. Group identification of SR VGO A, SR VGO B, SR VGO C, and SR VGO D.

Percent response	SR VGO A	SR VGO B	SR VGO C	SR VGO D
Saturates/non-aromatic	21.3	40.0	48.0	22.4
Monoaromatic	38.2	28.1	31.0	27.1
Diaromatic	24.0	20.3	13.3	30.6
Triaromatic	16.3	11.2	7.5	11.2
Residual	0.6	0.5	0.2	8.1
Total aromatic	78.4	59.6	51.8	77.0

The total aromatic content is by far highest in the VGO A compared to VGO B and C which are relatively similar. On the opposite side saturates and non-aromatics dominate in VGO C while VGO A have only 21.30 weight % saturates/non-aromatics.

SR VGO D, and its hydrocracked products, VGO D-1 and D-2, are shown in Figure 26 and the weight percent in Table 22.

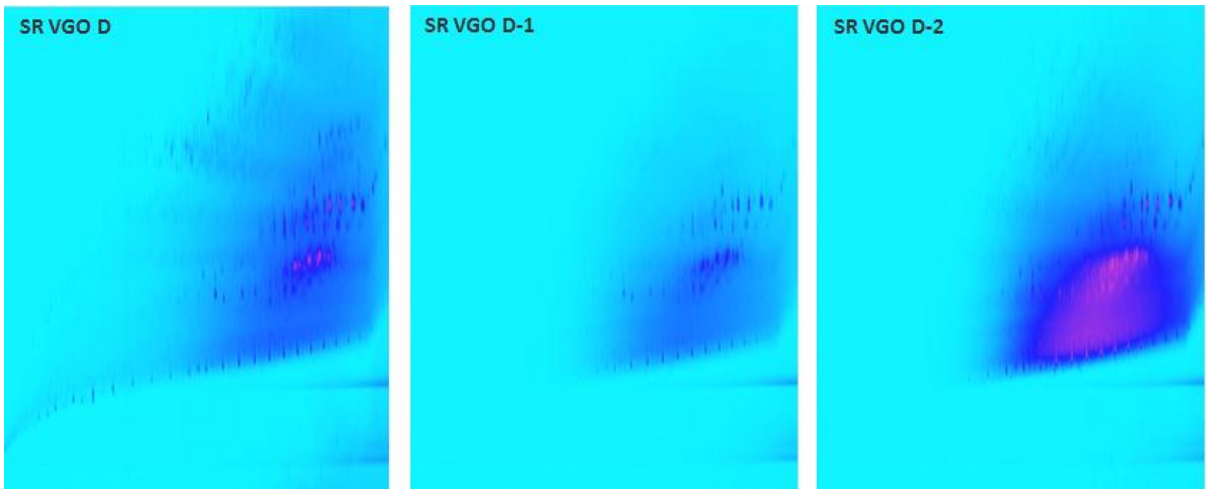


Figure 26. Chromatogram of SR VGO D, SR VGO D-1, and SR VGO D-2.

Table 22. Hydrocarbon distribution of SR VGO D, VGO D-1, and VGO D-2.

	SR VGO D	VGO D-1	VGO D-2
Saturates/non-aromatics	22.4	31.9	37.2
Monoaromatic	27.1	35.9	36.4
Diaromatic	30.6	23.6	19.7
Triaromatic	19.3	8.5	6.6
Residual	0.6	0.1	0.5
Total aromatic	77.0	68.0	62.4

Hydrocracking reduces the aromatic content, especially of tetraaromatics. As a consequence of ring saturation the weight percent of non-aromatics increase.

Discussion

SR VGO D, D-1, and D-2 suffered from random software error during data analysis. A new template had to be drawn to produce the group quantification output obtained without problems for all other analyses. This template was constructed with even more uncertainty of group borderlines as no standards were used, only estimate of group position. The quantification data of SR VGO D, D-1, and D-2 given in Table 21 and Table 22 are not reliable. Effort was put in obtaining data by

application of the VGO template used for the other VGOs however, unsuccessfully. The data in Table 22 are produced by the same template group definitions, making comparison between SR VGO D, D-1, and D-2 possible.

Vacuum gas oils are difficult to inject due to their viscosity, thus they have to be diluted in solvent (toluene). This leads to less sample being delivered to the column and the split ratio has to be reduced compared to the method for the atmospheric gas oils.

The huge number and variety of large PAHs further enhance the difficulty by developing a method suitable for these samples by using the non-polar - mid-polar column set. Also, the content of aromatics and their structures can lead to blockage of the SP as they might not elute. The maximum operating temperature is 360 ^{o}C; even at this temperature the column bleed will be most prominent.

The heavy petroleum fractions are a challenge in gas chromatographic analyses, especially with polar columns which are so easily subjected to thermal degradation. It should be considered whether a different column set must be applied for analysis of these samples. The disadvantage of having to change the sets between the sample types must be taken into lines of arguments as well as the column durability, contamination, and eventually the column's reliability especially concerning retention times and resolution.

Dutriez et al. (33) showed that vacuum gas oil can be sufficiently separated for group type analysis by using a column set of the same SPs as this study. Although, the column lengths were shorter (10 m 1st column, 1 m 2nd column) and first dimension internal diameter and film thickness thinner, 0.32 mm and 0.1 µm, respectively. Also, the temperature program applied was slower (2 ^{o}C/min) and the modulation time was set to 20 seconds.

The column set had to be replaced due to retention shifting as a consequence of column bleed after approximately twelve months of more or less continuous running of various petroleum samples. The vacuum gas oils are believed to accelerate the need of replacing the columns due the above arguments.
The method developed for VGO analysis by using this column set produce a separation capable of quantifying the large hydrocarbon classes of non-aromatics, mono-, di-, tri-, and tetraaromatics.

4.2 Sulphur compounds (SCD signal)

4.2.1 Standards

The sulphur standards were prepared in toluene on a weight per weight basis. Benzo[b]naphtho[2,3-d]thiophene, not used for quantification, were solved in iso-octane by the chemical supplier (Chiron AS, Norway).

There are a huge number of different sulphur compounds in the petroleum samples analysed. The concentration range of the standards is somewhat extreme for representing and exploring response factors of sulphur groups in a sample. The linear range of the sulphur chemiluminescense detector is 10^4-10^5, and should yield a linear profile for e.g. the standard series of 4,6-dimethyldibenzothiophene ranging from 405 – 11420 ppm (w/w). Obviously, this is a huge concentration range compared to an actual sample, especially gas oils for diesel where the product specifications permit only 10 ppm total sulphur.

The concentration range of the combined sulphur standard (o-toluenethiol, 2, 6-dimethylthiophenol, benzo[b]thiophene, and dibenzothiophene) was 33 to 1631 ppm. Dibenzothiophene has the lowest concentration range (33-89 ppm) and o-toluenethiol the highest (599-1631 ppm).

The standard curves of the sulphur standards is not as linear, unison in response or as repeatable as the hydrocarbon standards. Standard curves vary from showing nonlinearity to trendline R^2-values of ~ 0.99. The response factor of the different sulphur standards is shown in Table 23. The regression value for the most linear standard curve (for each standard) and its response factor are given in Table 24.

Table 23. Response factors of calibration curves of sulphur standards, AGO method

Compound name	P1	P2	P3	P4	P5	P6	Average RF	RSD RF
o-toluenethiol	1.04						-	**-**
2,6-dimethylthiophenol	13.1	8.1	8.4	4.4	7.4	4.2	7.6	**42.8**
Benzo[b]thiophene	15.9	10.5	10.3	5.7	9.8	5.9	9.7	**38.6**
Dibenzothiophene	14.0	11.4	11.1	10.0	15.6	10.5	12.1	**18.2**
4,6-dimethyldibenzothiophene	11.0	9.2	10.4				10.2	**9.0**

4,6-dimethyldibenzothiophene has one more standard concentration than the four other sulphur compounds. However, it is a huge concentration gap between the most and next most concentrated 4,6-dimethyldibenzothiophene. Three parallels were run.

Only one parallel obtained a linear standard curve for o-toluenethiol, although it is in a mixture with 2,6-dimethylthiopheno, benzo[b]thiophene, and dibenzothiophene. A total of six parallels were obtained for the three latter. The RSDs show poor reproducibility between the parallels, and also large the differences in standard curve slopes.

Table 24. Regression value for most linear standard curve.

Compound name	Best regression value obtained	Response factor at best R^2
o-toluenethiol	0.998	1.04
2,6-dimethylthiophenol	0.992	4.07
Benzo[b]thiophene	0.980	10.47
Dibenzothiophene	0.999	9.97
4,6-dimethyldibenzothiophene	0.987	9.17

The best obtained regression values (R^2) are above what is statistically accepted (≥ 0.98) as linear correlation between the two parameters, in this case concentration and volume. However, these are not found to be reproducible for all the six parallels which have been run of e.g. dibenzothiophene, as seen in Table 23.

The sulphur standards are not providing a unison response factor. The RF is different for the groups of polarity. It seems as though the RF of mono+-aromatics (benzo[b]thiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene) has the same value, however, this is only supported by three standards and their six parallels.

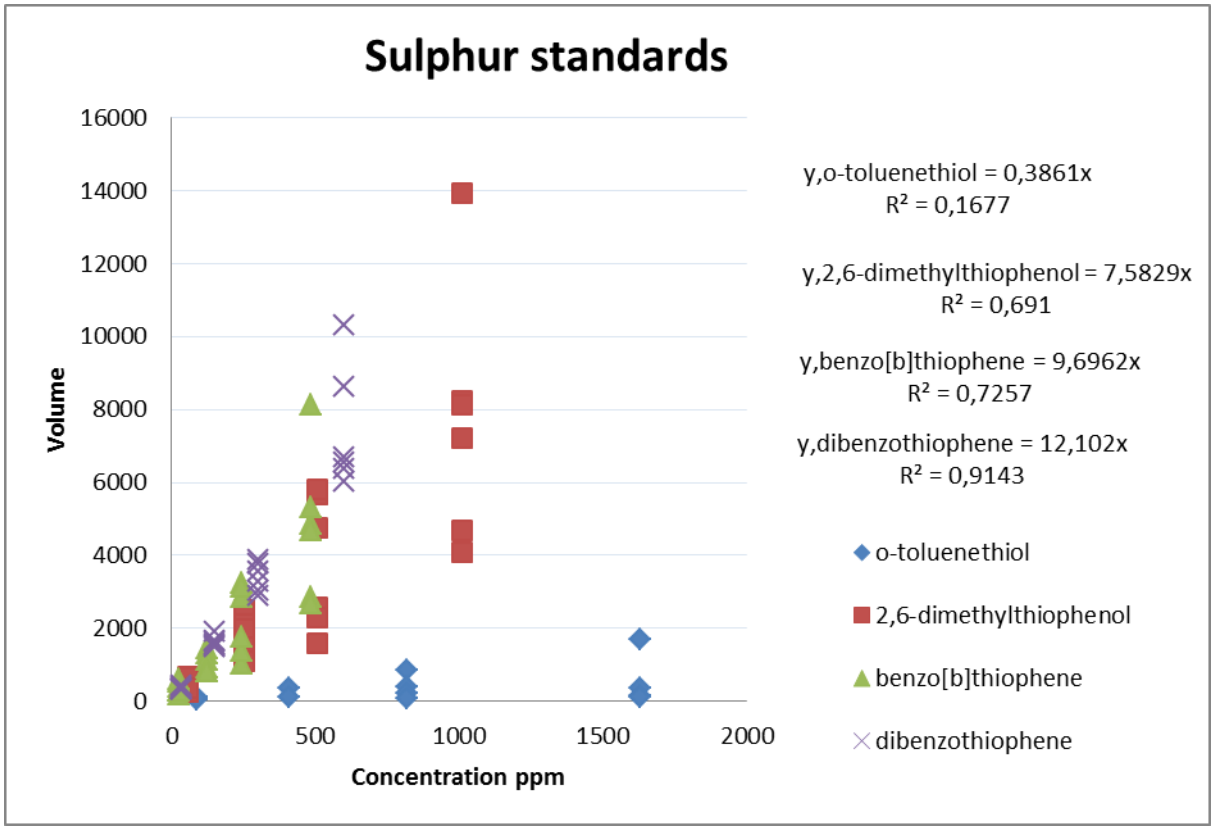


Figure 27. Scatter of o-toluenethiol, 2,6-dimethylthiophenol, benzo[b]thiophene, and dibenzothiophene. Volume response of all standards and their combined parallels are plotted against concentration. Trendline added for the series of each standard.

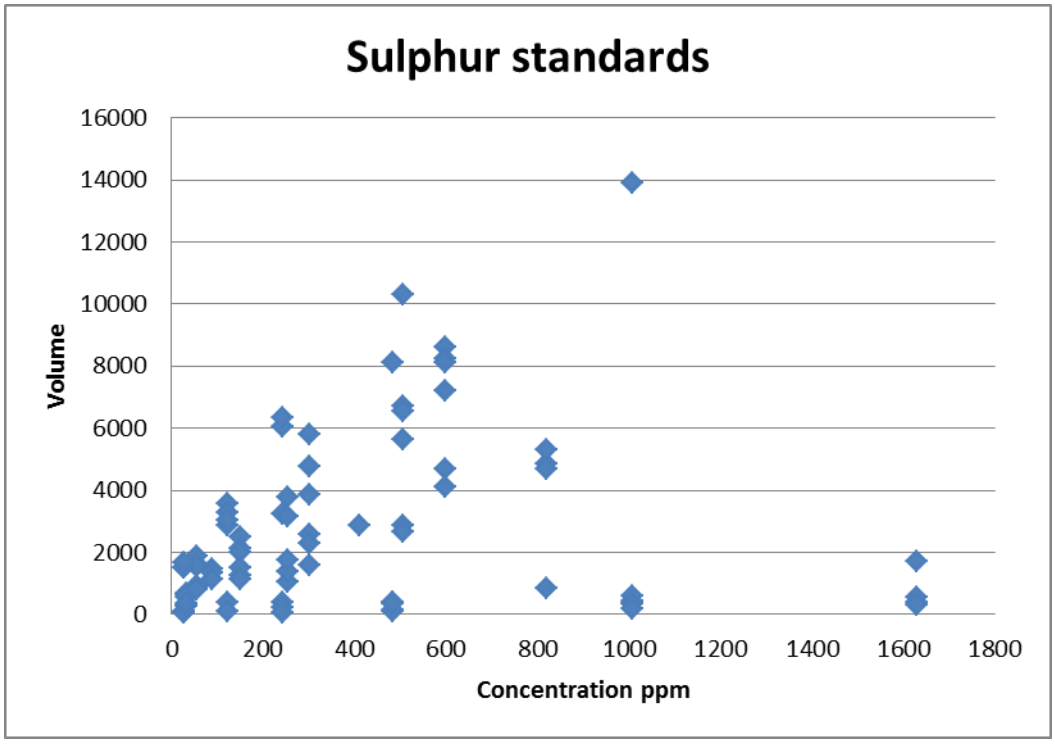


Figure 28. Scatter of o-toluenethiol, 2,6-dimethylthiophenol, benzo[b]thiophene, and dibenzothiophene. Volume response for all the compounds and their parallels against concentration.

Figure 27 and Figure 28 show the volume response of all parallels of o-toluenethiol, 2,6-dimethylthiophenol, benzo[b]thiophene, and dibenzothiophene plotted against concentration. Figure 27 display the different standards as separate data sets, while Figure 28 shows all the standards and their parallels' volume responses as one data set. Appendix B.B displays the curves for each parallel of the standards in separate plots.

Discussion

The statistical foundation is insufficient to provide reliable response factors (RF) for the sulphur standards applied. The RSD values show that more parallels are required to obtain trustworthy results. Although the regression value is above accepted values (≥0.98) for one of the trendlines of each standard and its curves, the repeatability of that response is not present.

There are more than statistical factors which can influence the reproducibility. The concentration of the standards can change as a result of vaporisation, re-composition of molecules, and contamination. Sulphur can possibly adsorb and adhere in the instrument, e.g. liner, columns and retention gaps (loop and splitter), and detector transfer lines and reaction cell. The signal-to-noise ratio may be so low the SCD background signal interferes with sample responses.

Detection of thiophene and methylthiophenes was not possible by the AGO method. This is probably caused by liner or splitter column adhesion or thermal effects as a consequence of long residence time in the column as the temperature gradient started at 50^{o}C with a ramp of 4.5 ^{o}C/min. They were, however, detected when run by the VGO method (start at 150 ^{o}C with ramp 3.5 ^{o}C/min), although they eluted shortly after the hold-up volume of the columns.

The linear range of the SCD is in theory said to be 10^4-10^5. (5, 13). Only 4,6-dimethyldibenzothiophene is in the 10^4 concentration range. Also, this is the standard showing the better linear trends. However, this can be a result of stability as it is prepared as a single standard, not in mixture. In addition it is a larger molecule than e.g. o-toluenethiol, and the sulphur atom is sterically hindered by the methyl substituents.

There is also the risk of overloading the SCD reaction cell by previously run high sulphur petroleum samples, such as VGOs and LCOs. Sulphur analysis was performed after hydrocarbon analysis, that is, the standards and interpretation of chromatograms obtained by the SCD.

Maintenance of the SCD has not been performed, perhaps a certain number of runs limit the detectors performance. Especially after numerous vacuum gas oil analysis which are harder on the instrument in means of complexity and contamination by residual groups in the GCxGC. The reaction cell in the SCD can build up a film of material which will interfere with the output (13).

The sulphur results reported in this study are raw data without correcting for response factor. They are to be viewed with a precaution of reliability and no direct comparisons with other results obtained by other studies can be done. Also, the values are not perceived to be true or definite values as a consequence of the above arguments. As for the hydrocarbon analysis, the detector's response is normalised.

4.2.2 Templates

The standards listed in Table 8, Chapter 3.3.2, were used to draw templates in the GCxGC software. The comparison with the structured petroleum sample chromatograms helped in setting the groups by experimental assessments. Templates have been constructed for both atmospheric and vacuum gas oils.

The templates divide the sulphur content into the following groups:

- Thiophenes/sulphides
- Monoaromatic thiophenes (1 aromatic ring + thiophene)
- Diaromatic thiophenes (2 aromatic rings + thiophene)
- Triaromatic thiophenes (3 aromatic rings + thiophene)
- Residual

Figures in the following chapters will show chromatograms with templates of both AGO and VGO sulphur data acquisition.

The borderlines are set by best estimate, however, the number of standards available reduce the confidence of the template groups.

4.2.3 Atmospheric Gas Oil

The sulphur content in atmospheric gas oils varies from a few ppm to some percents. Figure 29 shows the SCD chromatograms obtained for SR AGO A, B, and C. The volume percent responses are given in Table 25.

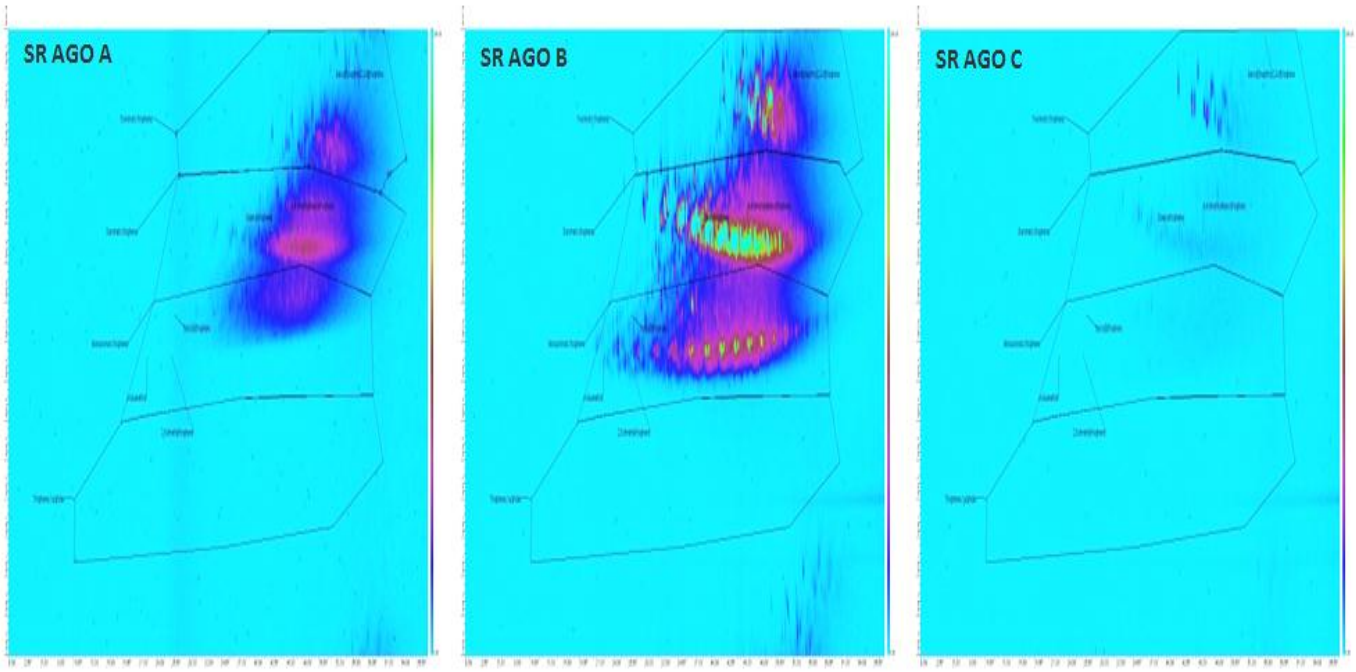


Figure 29. Chromatograms with templates of SR AGO A, SR AGO B, and SR AGO C.

Table 25. Distribution of sulphur compounds for SR AGO A, SR AGO B, and SR AGO C.

	SR AGO A	SR AGO B	SR AGO C
Thiophenes / sulphides	1	1	2
Monoaromatic thiophenes	36	28	16
Diaromatic thiophenes	49	51	41
Triaromatic thiophenes	14	19	36
Residual	1	0	5

The results presented in Table 25 are raw disregarding response factors. From the chromatograms in Figure 29 it is seen that SR AGO B is highet in sulphur content and SR AGO C is low in sulphur content. The relative distribution of sulphur compounds, as seen in Table 25, is concentrated among the diaromatic thiophenes (two aromatic rings + thiophene). There thiophenes and sulphides are almost negligible as a consequence of background noise in the SCD chromatograms.

The sulphur chromatograms of LCO A and its most hydrotreated product, LCO A-5, are shown in Figure 30. The normalised sulphur response distribution of the LCO and its products is given in Table 26. An enlarged chromatogram of LCO A is available in Appendix C.B.

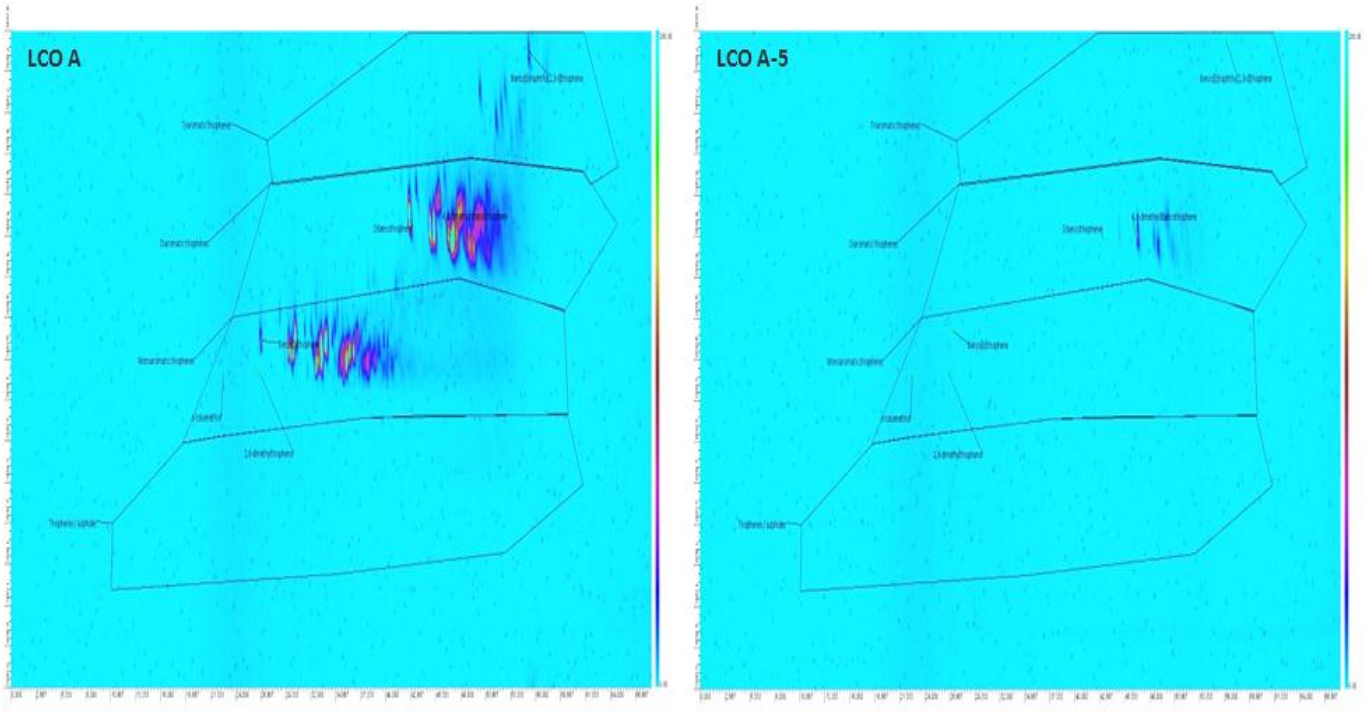


Figure 30 Chromatograms with templates of LCO A and LCO A-5.

Table 26 Distribution of sulphur compounds of LCO A and its hydrotreated products LCO A-1 - A-5.

Name	LCO A	LCO A-1	LCO A-2	LCO A-3	LCO A-4	LCO A-5
Thiophenes / sulphides	2	4	4	4	11	15
Monoaromatic thiophenes	41	10	6	8	8	10
Diaromatic thiophenes	47	71	72	75	39	24
Triaromatic thiophenes	5	4	4	3	5	6
Residual	6	10	13	11	36	45

The LCOs show the same tendency as SR AGOs to concentrate the sulphur compounds in the diaromatic thiophene elution zone. The distribution of sulphur as diaromatic thiophenes seems to increase during hydrotreating to a certain point of saturation. The increased response of the residual group for LCO A-4 and A-5 is most likely due to the low abundance of sulphur compounds included in the template and the relative increase of noise compared to sample abundance.

Total sulphur content for the samples is available in Table 9, Chapter 3.4.

Discussion

The injection volume seems to be low for SR AGO C and the most hydrotreated LCO A's. For sulphur analysis an injection volume of 0.002 µL is too low, a volume of e.g. 0.004 would give much more enhanced SCD signals for these without risking overloading of the reaction cell. However, FID chromatograms would probably show highly overloading. For some samples it would possibly be advisable to analyse on sulphur and hydrocarbons in separate runs.

The signal-to-noise ratio is not adequate for quantification purposes. This can be a result of the build-up of a contamination film in the SCD reaction cell (13). The non-uniformity and non-linearity in the entire concentration range makes quantification more complicated than for hydrocarbons. The distribution values given in Table 25 and Table 26 must be related to response factors and total concentration of sulphur before being reported as a percentage of concentration. The arguments discussed in 4.2.1 Standards apply.

The separation of the sulphur compounds is considered adequate; the groups are sufficiently separated for constructing templates. The number of standards applied limits the reliability of the templates, as mentioned in 4.2.2 Templates, and overlapping interferes with individual peak identification. Generally, for sulphur group type identification the methods developed for atmospheric gas oils, as seen in Table 10, is satisfactory.

4.2.4 Vacuum Gas Oil

Chromatograms of the sulphur content of SR VGO A, B, and C are shown in Figure 31. The relative volume response is available in Table
27.

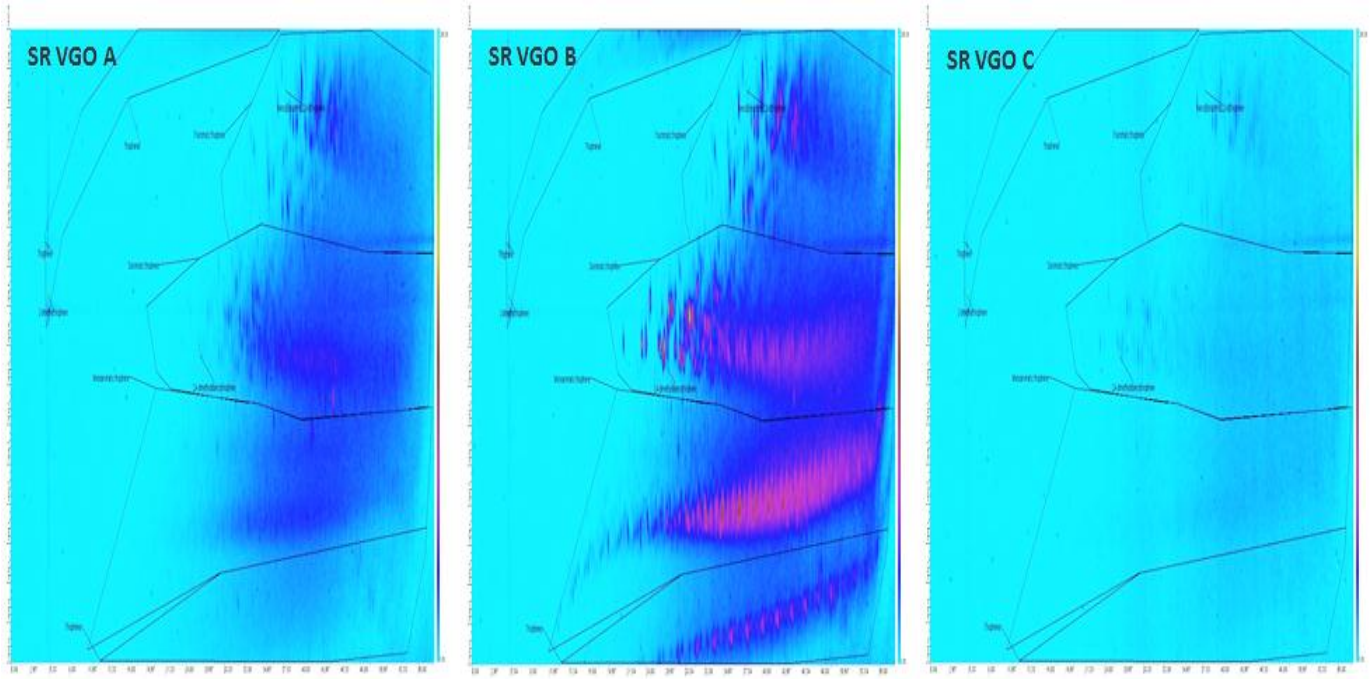


Figure 31. Chromatograms with templates of SR VGO A, SR VGO B, and SR VGO C.

Figure 31 illustrates the huge variety of sulphur compounds in the vacuum gas oils. The total sulphur content is obviously very different for the three VGOs presented in the figure. Software raw data of is shown in Table 27. A larger chromatogram of SR VGO A is available in Appendix D.B.

Table 27. Percent volume response sulphur of SR VGO A, SR VGO B, and SR VGO C.

	SR VGO A	SR VGO B	SR VGO C
Thiophene	8	14	11
Monoaromatic thiophene	29	35	28
Diaromatic thiophene	39	33	37
Triaromatic thiophene	22	17	23
Residual	1	1	1

The monoaromatic and diaromatic thiophenes dominate in volume percentage response for all the three VGOs. Thiophenes are not very abundant compared to the groups of aromatic substituted thiophenes. Total sulphur content is available from Table 9.

Discussion

Defining clear groups of hydrocarbon classes is difficult as there are more overlapping and borderlines can be drawn practically everywhere (within a reasonable definition of the groups). Especially the di- and triaromatics are hard to separate; where the naphthenic diaromatics end and the triaromatics take over in the chromatographic base plane.

The same arguments as in 4.2.3 Atmospheric Gas Oil applies. The separation and identification of sulphur groups, disregarding the insecurities discussed in 4.2.1 Standards, is regarded satisfactory by analysis of vacuum gas oil by the method shown in Table 11.

5 Conclusion

Method development and optimisation in GCxGC is s challenge. The investigated parameters are injection volume, temperature program, and modulator time parameters.

The methods 9 and 29 are recommended for analysis of AGOs and VGOs respectively. Method 9 and 29 have proven to give sufficient separation for quantification and identification purposes. Both hydrocarbons and sulphur compounds are shown to be separated in one analysis.

Table 10. Method parameters for atmospheric gas oils. Method 9.

Back injector		**Oven program**	
Injection volume:	0.3 µL	Initial temp.:	50 °C
		Initial time:	3 min
Back PTV inlet		Ramp:	4.5 °C/min to 340 °C. Hold 1 min
Gas type:	Helium	Run time	68.4 min
Mode:	Split		
Pressure:	41.3 psi	**Thermal AUX 1**	
Total flow:	131.4 mL/min	Initial temp.:	100 °C
Initial temp.:	50 °C	Initial time:	3 min
Initial time:	0.02 min	Ramp:	4.5 °C/min to 390 °C. Hold 1 min
Ramp:	720 °C/min to 350 °C. Hold 5 min		
Split ratio:	150:1		
		Modulator time parameters	
		Hot jet duration: 500 ms	
		Modulation time: 2000 ms	

Table 11. Method parameters for vacuum gas oils. Method 29.

Back injector		**Oven program**	
Injection volume:	0.3 µL	Initial temp.:	150 °C
		Initial time:	1 min
Back PTV inlet		Ramp 1:	3.5 °C/min to 340 °C. Hold 1 min
Gas type:	Helium	Run time	64.0 min
Mode:	Split		
Pressure:	54.6 psi	**Thermal AUX 1**	
Total flow:	131.4 mL/min	Initial temp.:	200 °C
Initial temp.:	150 °C	Initial time:	1 min
Initial time:	0.02 min	Ramp:	3.5 °C/min to 410 °C. Hold 3 min
Ramp:	720 °C/min to 350 °C. Hold 5 min		
Split ratio:	20:1		
		Modulator time parameters	
		Hot jet duration: 500 ms	
		Modulation time: 2000 ms	

Analysis of straight run (SR) atmospheric and vacuum gas oils and processed petroleum fractions showed different content of the hydrocarbon and sulphur groups as a result of both the crudes' origin and processes. GCxGC analysis of AGOs and middle distillates is straight forward and well suited for quantification and identification purposes. Vacuum gas oils proved more challenging than AGOs, but were nevertheless separated and analysed for quantification and identification purposes.

Qualitative analysis of sulphur compounds is possible by the methods in Table 10 and Table 11, for quantification more statistical data on the standards has to be produced.

6 Further work

Optimisation of the instrument is not final. Exploration of column combinations and dimensions is a logical next step. Wider internal dimensions and SP film thickness can allow a larger injection volume. Temperature programming is another parameter which is recommended to look into. Higher start temperatures for vacuum gas oil methods and a slower temperature ramp can give better separation and easier identification. Templates can preferably implement more standards especially in the higher carbon number and polarity range.

Sulphur quantification is presently not possible or reliable. A larger number of sulphur standards and replicates have to exist to obtain response factors which can be used for quantification. Maintenance on cleaning the SCD reaction cell has to be performed on a regular basis.

Running vacuum gas oils increase the column bleed of the polar 2nd dimension column and build up a contamination film in both the liner and SCD reaction cell. Maintenance has to be performed more often when VGOs are run.

There is a third detector connected to this instrument, a nitrogen chemiluminescense detector (NCD). The NCD is mounted on top of the FID, receiving the un-burnt effluent from the FID. In this configuration the signal-to-noise ratio of the NCD is very low. Since this study did not investigate the optimisation aspects of the NCD, only a recommendation of parameters to look into. The effluent flow can be increased by using a wider internal dimension retention gap from the splitter to the FID. The NCD and SCD can switch places, the SCD can be mounted on top of the FID and the NCD directly connected to the splitter. This is a more permanent solution recommended if nitrogen analysis is the main scope of interest.

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Appendices

A. Methods

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
1	110502_SPLITLESS Flow 0.85 Run time 58.33	1	splitless	40 hold 1 min	6		360 hold 4 min
2	110704_PTV Flow 0.85 Run time 58.33	1	75	40 hold 1 min	6		360 hold 4 min
3	110909_PTV_SPLIT15-200 Flow 0.85 Run time 58.33	0.5	5 - 250	40 hold 1 min	6		360 hold 4 min
4	1109016_PTV Flow 0.85 Run time 33.0	1	125	40 hold 1 min	10		320 hold 4 min
5	110919_PTV Flow 0.85 Run time 33.0	1	200	40 hold 1 min	10		320 hold 4 min
6	110921_PTV Flow 0.85 Run time 49.0	1	200	40 hold 1 min	10 to 95°C hold 1 min	6 to 320 °C	320 hold 4 min

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
7	111215_PTV_LIGHTSAMPLES_SPLIT150-1 Flow 0.85 Run time 73.5	0.5	150	40hold 4 min	2 to 150 °C hold 1 min	8 to 250 °C	250 hold 1 min
8	111215_PTV_DIESELSAMPLES Flow 0.85 Run time 68.44	0.1	250	50 hold 3 min	4.5		340 hold 1 min
9	111216_PTV_0.3UL_SPLITT150/250-1 Flow 0.85 Run time 68.44	0.3	150-250	50 hold 3 min	4.5		340 hold 1 min
10	111216_PTV_0.5UL_SPLITT250-1 Flow 0.85 Run time 68.44	0.5	250	50 hold 3 min	4.5		340 hold 1 min
11	120201_PTV_0.1UL_SPLITT200-1 Flow 0.85 Run time 68.44	0.1	200	50 hold 3 min	4.5		340 hold 1 min
12	120202_PTV_HEAVYSAMPLES_TEST#1 Flow 2.10 Run time 42.67	0.3	150	50 hold 3 min	7.5		340 hold 1 min

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
13	120202_PTV_HEAVYSAMPLES_TEST#2 Flow 2.10 Run time 67.00	0.3	150	50 hold 3 min	7.5 to 150 °C hold 1 min	4.5 to 360 °C	360 hold 3 min
14	120203_PTV_HEAVYSAMPLES_TEST#3 Flow 0.85 Run time 67.00	0.3	150	50 hold 3 min	7.5 to 150 °C hold 1 min	4.5 to 360 °C	360 hold 3 min
15	120206_PTV_HEAVYSAMPLES_TEST#4 Flow 0.85 Run time 67.00	0.3	250	50 hold 3 min	7.5 to 150 °C hold 1 min	4.5 to 360 °C	360 hold 3 min
16	120207_PTV_HEAVYSAMPLES_TEST#5 Flow 0.85 Run time 71.44	0.3	250	50 hold 3 min	7.5 to 100 °C hold 1 min	4.5 to 360 °C	360 hold 3 min
17	120207_PTV_HEAVYSAMPLES_TEST#6 Flow 0.85 Run time 68.52	0.3	250	50 hold 3 min	7.5 to 100 °C hold 1 min	3.5 to 250 °C hold 1 min	7.5 to 340 °C hold 2 min
18	120207_PTV_HEAVYSAMPLES_TEST#7 Flow 0.85 Run time 76.14	0.3	250	50 hold 3 min	7.5 to 100 °C hold 1 min	3.5 to 300 °C hold 1 min	7.5 to 340 °C hold 2 min

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
19	120210_PTV_HEAVYSAMPLES_TEST#8 Flow 0.85 Run time 72.71	0.3	250	50 hold 3 min	7.5 to 200 °C hold 1 min	3.5 to 360 °C	360 hold 3 min
20	120210_PTV_HEAVYSAMPLES_TEST#9 Flow 0.85 Run time 77.67	0.3	250	50 hold 3 min	7.5 to 250 °C hold 1 min	2.5 to 360 °C	360 hold 3 min
21	120213_PTV_HEAVYSAMPLES_TEST#10 Flow 0.85 Run time 65.10	0.3	250	50 hold 3 min	7.5 to 250 °C hold 1 min	3.5 to 360 °C	360 hold 3 min
22	120213_PTV_HEAVYSAMPLES_TEST#11 Flow 0.85 Run time 63.33	0.3	150	50 hold 3 min	7.5 to 180 °C hold 1 min	4.5 to 360 °C	360 hold 2 min
23	120214_PTV_HEAVYSAMPLES_TEST#12 Flow 0.85 Run time 63.33	0.3	75	50 hold 3 min	7.5 to 180 °C hold 1 min	4.5 to 360 °C	360 hold 2 min
24	120220_PTV_HEAVYSAMPLES_TEST#13 Flow 0.85 Run time 64.00	0.3	75	150 hold 1 min	3.5 to 360 °C		360 hold 3 min

Method #	Method name Column flow (mL/min) Run time (min)	Injection volume µL	Split ratio	Start temp °C	Ramp 1 °C/min	Ramp 2 °C/min	Final temp °C
25	120221_PTV_HEAVYSAMPLES_TEST#14 Flow 0.85017 Run time 64.00	0.3	150	150 hold 1 min	3.5 to 360 °C		360 hold 3 min
26	120306_PTV_HEAVYSAMPLES_TEST#15 Flow 0.85 Run time 65.00	0.3	250	150 hold 1 min	3.5 to 340 °C hold 3 min	3.5 to 360 °C	360 hold 1 min
27	120306_PTV_HEAVYSAMPLES_TEST#16 Flow 0.85017 Run time 58.29	0.3	75	150 hold 1 min	3.5 to 340 °C		340 hold 3 min
28	120327_VGO_SPLIT150-1 Flow 0.85 Run time 58.29	0.3	150	150 hold 1 min	3.5 to 340 °C		340 hold 3 min
29	120328_VGO_SPLITT20-1 Flow 0.85 Run time 58.29	0.3	20	150 hold 1 min	3.5 to 340 °C		340 hold 3 min
30	120425_SLOWRAMP_3°C/MIN_SPLIT150-1 Flow 0.85 Run time 100.67	0.3	150	50 hold 3 min	3 to 340 °C		340 hold 1 min

A.A Method recommended for atmospheric gas oils.

Back injector

Injection volume	0.3 µL

Back PTV inlet

Gas type:	Helium
Mode:	Split
Pressure:	41.276 psi
Total flow:	131.38 mL/min
Initial temp.:	50 °C
Initial time:	0.02 min
Ramp:	720 °C/min to 350 °C. Hold 5 min
Split ratio:	150:1
Split flow:	127.53 mL/min
Cryo temp.:	85 °C

Oven program

Initial temp.:	50 °C
Initial time:	3 min
Ramp:	4.5 °C/min to 340 °C. Hold 1 min
Run time	68.44 min

Thermal AUX 1

Initial temp.:	100 °C
Initial time:	3 min
Ramp:	4.5 °C/min to 390 °C. Hold 1 min

Thermal AUX 2

Temperature:	200 °C

Front detector FID

Heater:	350 °C
H2 flow:	30 mL/min
Air flow:	350 mL/min
Makeup flow:	26.819 mL/min
Makeup gas:	He

First column

Column:	SGE BPX 5
Features:	30 m x 0.25 mm x 0.25 µm
Pressure:	41.276 psi
Flow:	0.85017 mL/min
Average velocity:	31.565 cm/sec
Holdup time:	1.32 min

Second column

Column:	SGE BPX 50
Features:	2 m x 0.1 mm x 0.1 µm
Pressure:	41.276 psi
Flow:	0.85017 mL/min
Average velocity:	31.565 cm/sec

Loop

Column:	Retention gap
Features:	0.8 m x 0.1 mm
Pressure:	5 psi
Flow:	0.38079 mL/min
Average velocity:	74.325 cm/sec

A.B Method recommended for vacuum gas oils.

Back injector	
Injection volume	0.3 µL

Back PTV inlet	
Gas type:	Helium
Mode:	Split
Pressure:	54.615 psi
Total flow:	131.38 mL/min
Initial temp.:	150 °C
Initial time:	0.02 min
Ramp:	720 °C/min to 350 °C. Hold 5 min
Split ratio:	150:1
Split flow:	127.53 mL/min
Cryo temp.:	85 °C

Oven program	
Initial temp.:	150 °C
Initial time:	1 min
Ramp:	3.5 °C/min to 360 °C. Hold 3 min
Run time	64.00 min

Thermal AUX 1	
Initial temp.:	200 oC
Initial time:	1 min
Ramp:	3.5 °C/min to 410 °C. Hold 3 min

Thermal AUX 2	
Temperature:	200 °C

Front detector FID	
Heater:	350 °C
H2 flow:	30 mL/min
Air flow:	350 mL/min
Makeup flow:	26.819 mL/min
Makeup gas:	He

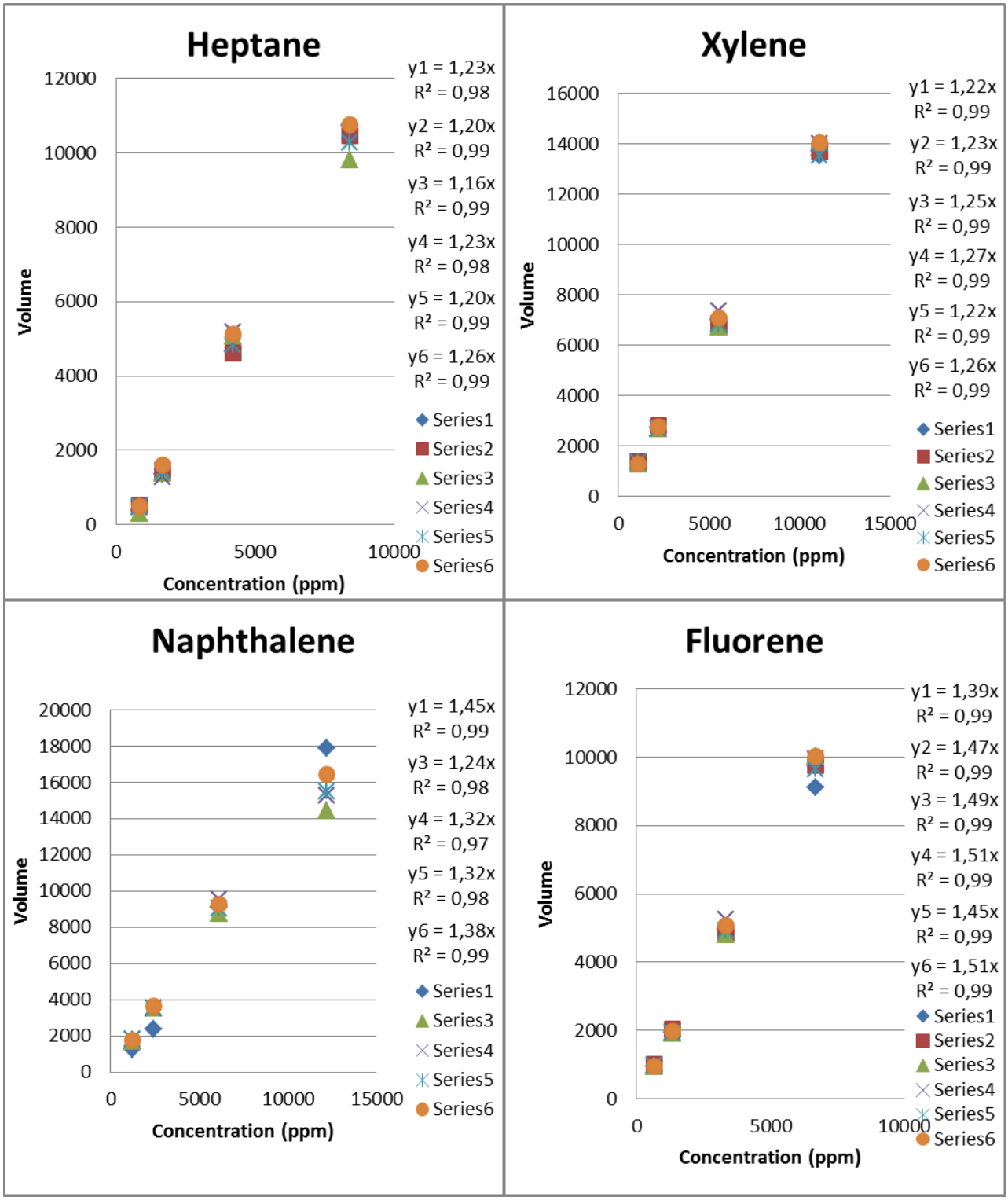
First column	
Column:	SGE BPX 5
Features:	30 m x 0.25 mm x 0.25 µm
Pressure:	54.615 psi
Flow:	0.85017 mL/min
Average velocity:	33.837 cm/sec
Holdup time:	1.2314 min

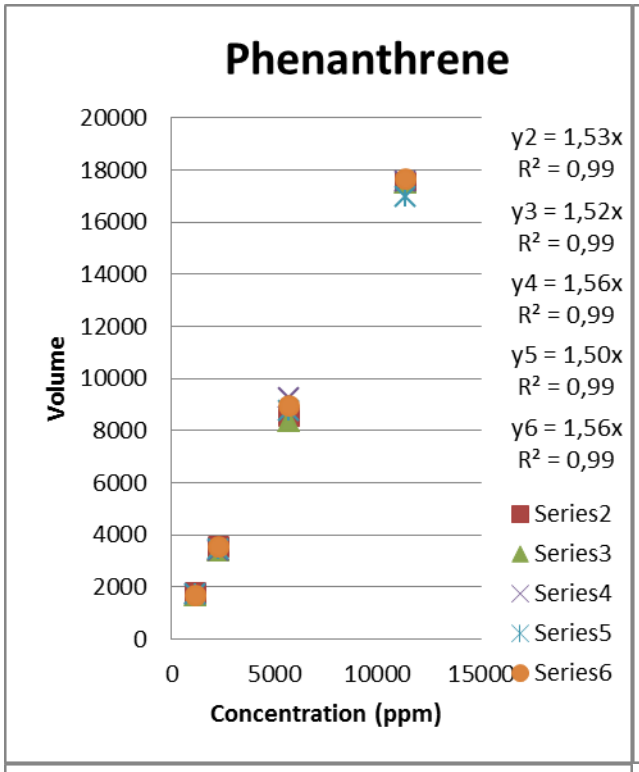
Second column	
Column:	SGE BPX 50
Features:	2 m x 0.1 mm x 0.1 µm
Pressure:	54.615 psi
Flow:	0.85017 mL/min
Average velocity:	33.837 cm/sec

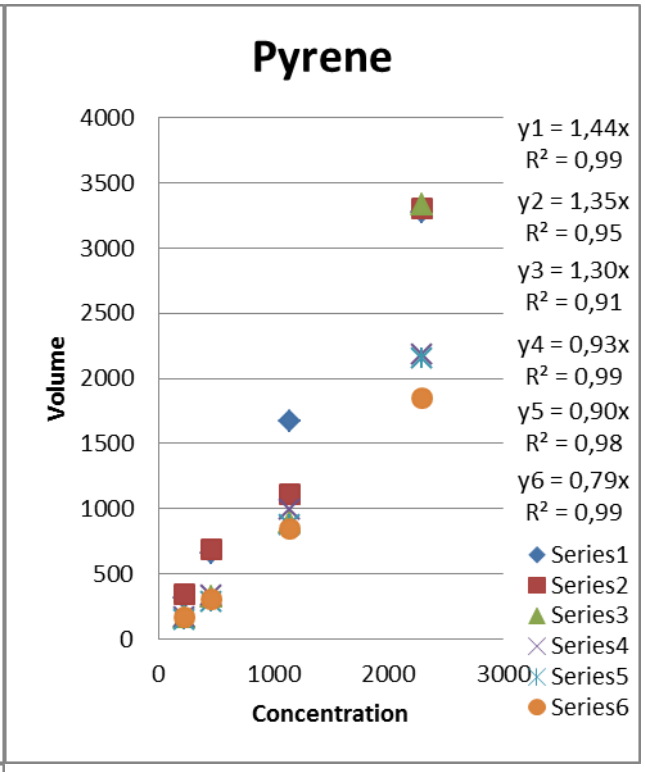
Loop	
Column:	Retention gap
Features:	0.8 m x 0.1 mm
Pressure:	7.3597 psi
Flow:	0.38079 mL/min
Average velocity:	90.508 cm/sec

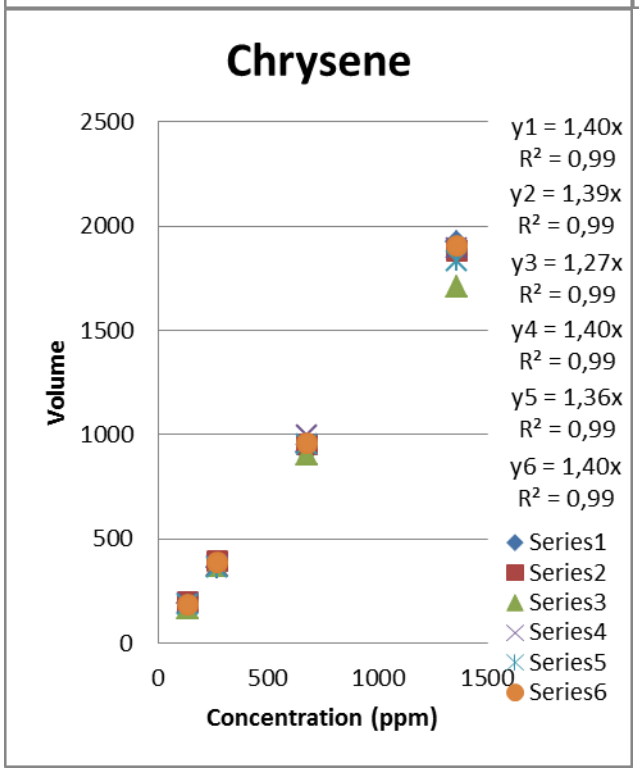
B. Standards

B.A Hydrocarbon and polycyclic aromatic hydrocarbons (PAH) – standard curves

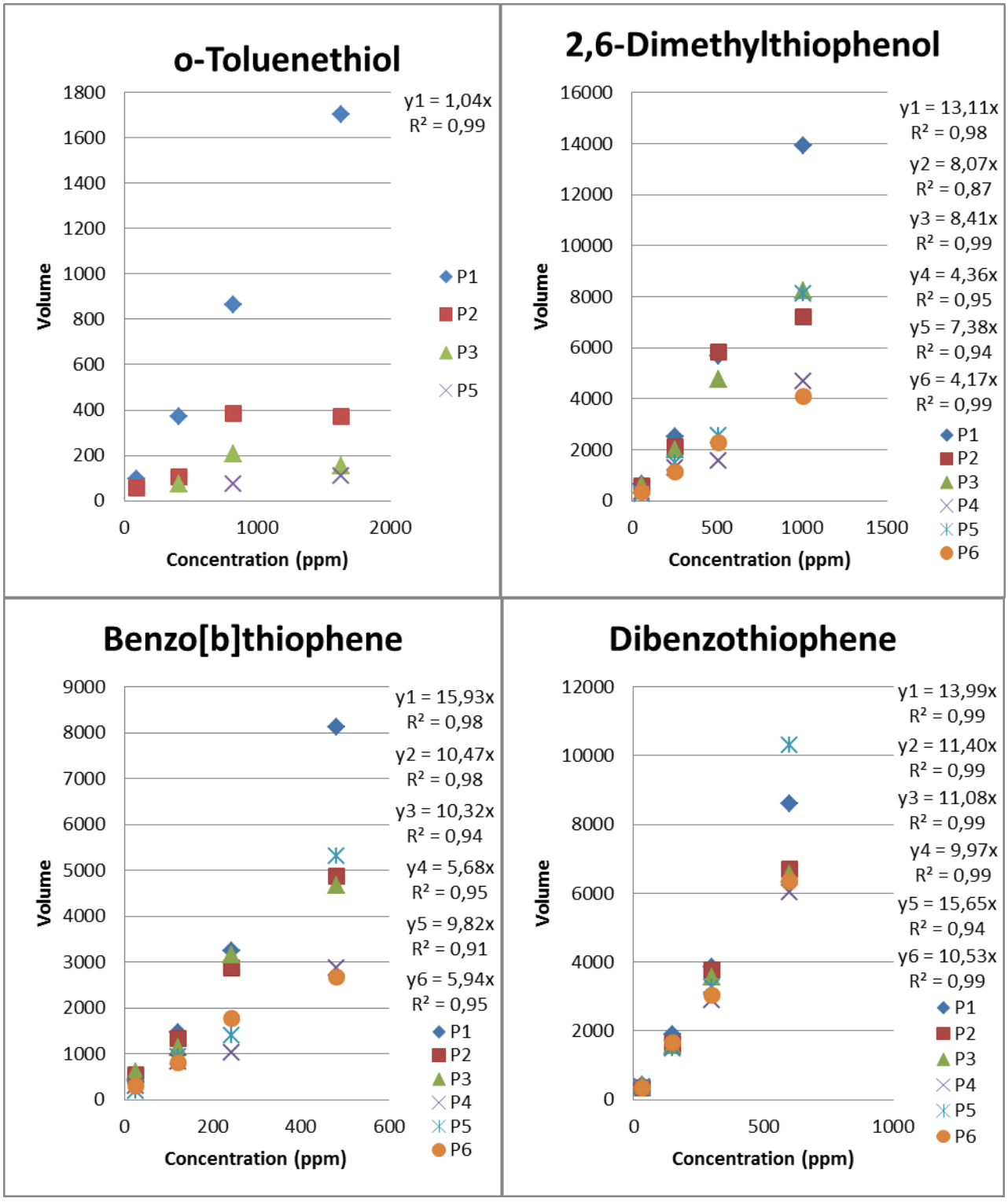


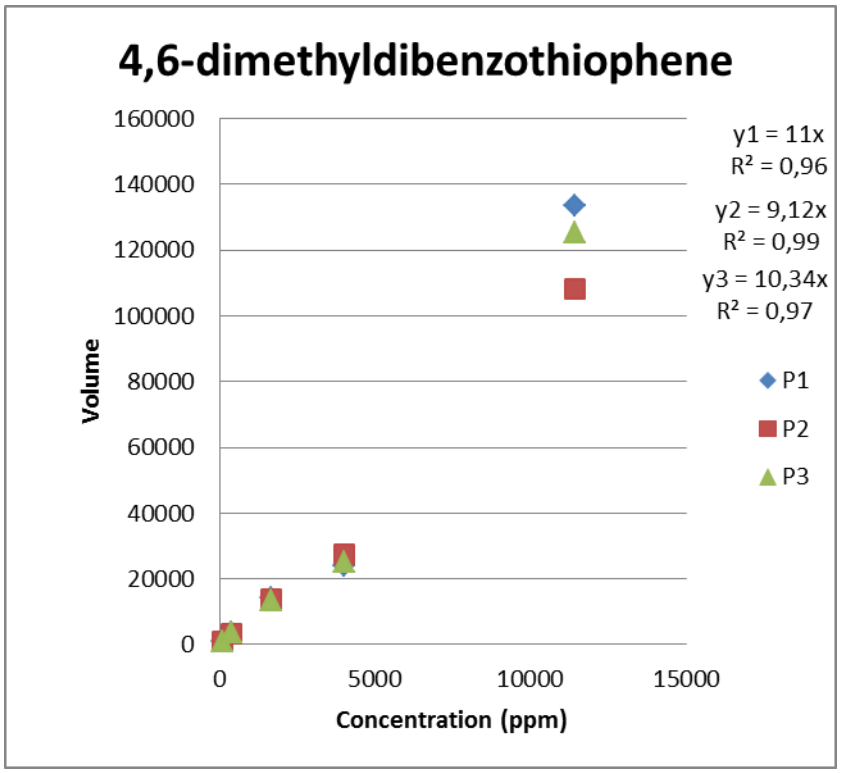

Phenanthrene
Volume
Concentration (ppm)
y2 = 1,53x
R² = 0,99
y3 = 1,52x
R² = 0,99
y4 = 1,56x
R² = 0,99
y5 = 1,50x
R² = 0,99
y6 = 1,56x
R² = 0,99
Series2
Series3
Series4
Series5
Series6


Pyrene
Volume
Concentration
y1 = 1,44x
R² = 0,99
y2 = 1,35x
R² = 0,95
y3 = 1,30x
R² = 0,91
y4 = 0,93x
R² = 0,99
y5 = 0,90x
R² = 0,98
y6 = 0,79x
R² = 0,99
Series1
Series2
Series3
Series4
Series5
Series6


Chrysene
Volume
Concentration (ppm)
y1 = 1,40x
R² = 0,99
y2 = 1,39x
R² = 0,99
y3 = 1,27x
R² = 0,99
y4 = 1,40x
R² = 0,99
y5 = 1,36x
R² = 0,99
y6 = 1,40x
R² = 0,99
Series1
Series2
Series3
Series4
Series5
Series6

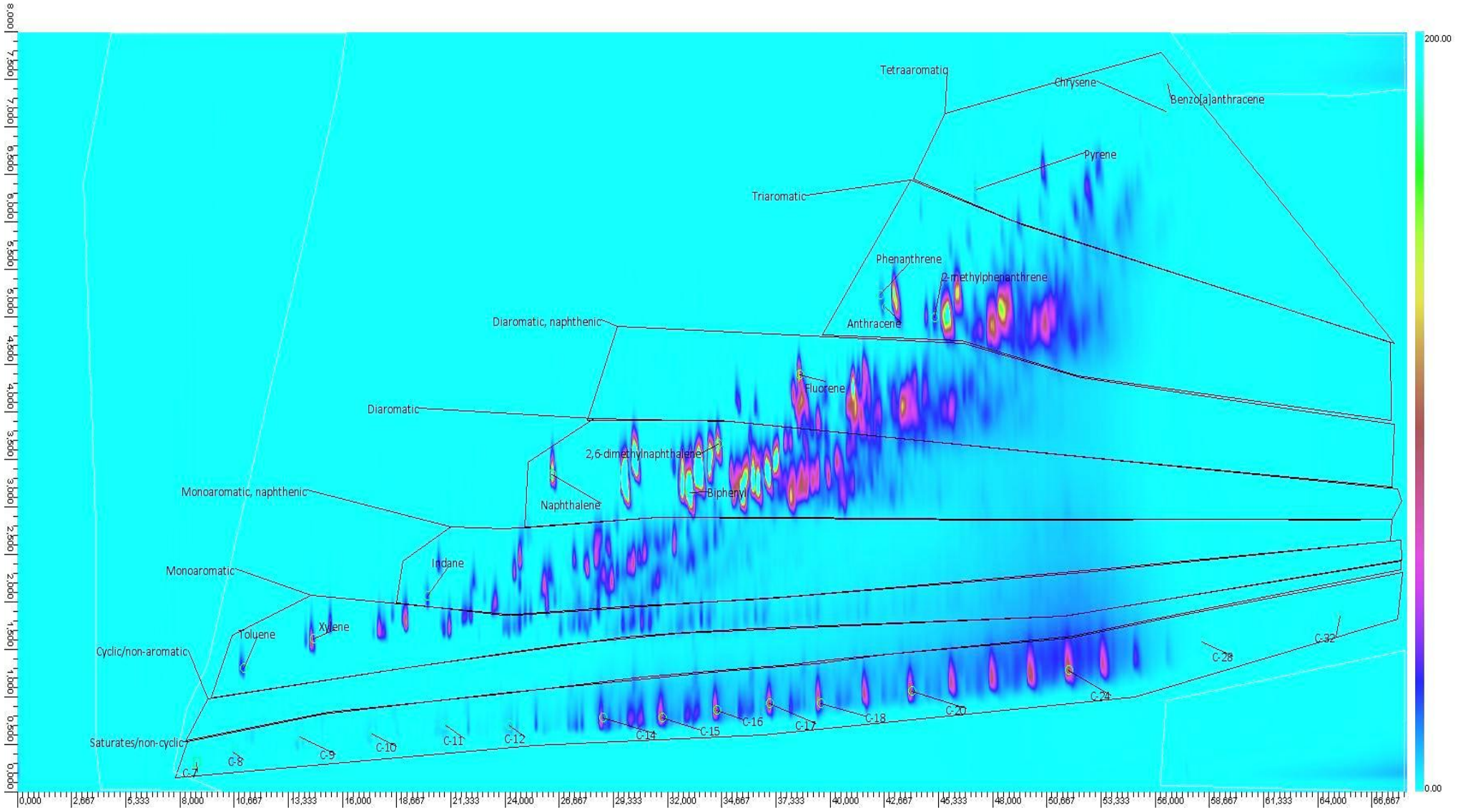
B.B Polycyclic aromatic sulphur heterocycles (PASHs) – standard curves




4,6-dimethyldibenzothiophene
160000
140000
120000
100000
80000
60000
40000
20000
0
Volume
0
5000
10000
15000
Concentration (ppm)
y1 = 11x
R² = 0,96
y2 = 9,12x
R² = 0,99
y3 = 10,34x
R² = 0,97
P1
P2
P3

C. Atmospheric gas oils (AGO)

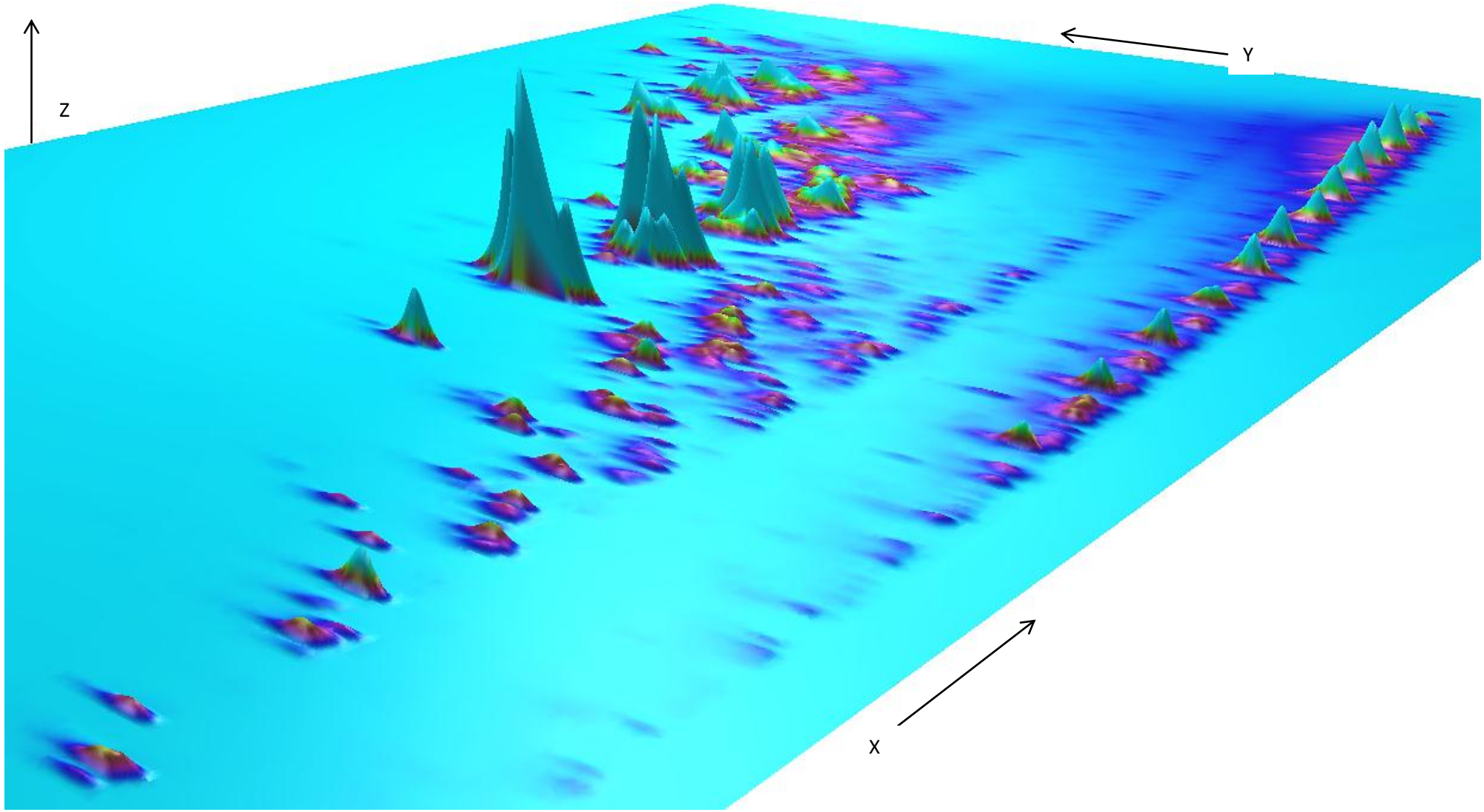
C.A Light cycle oil A chromatogram with template – FID signal



M

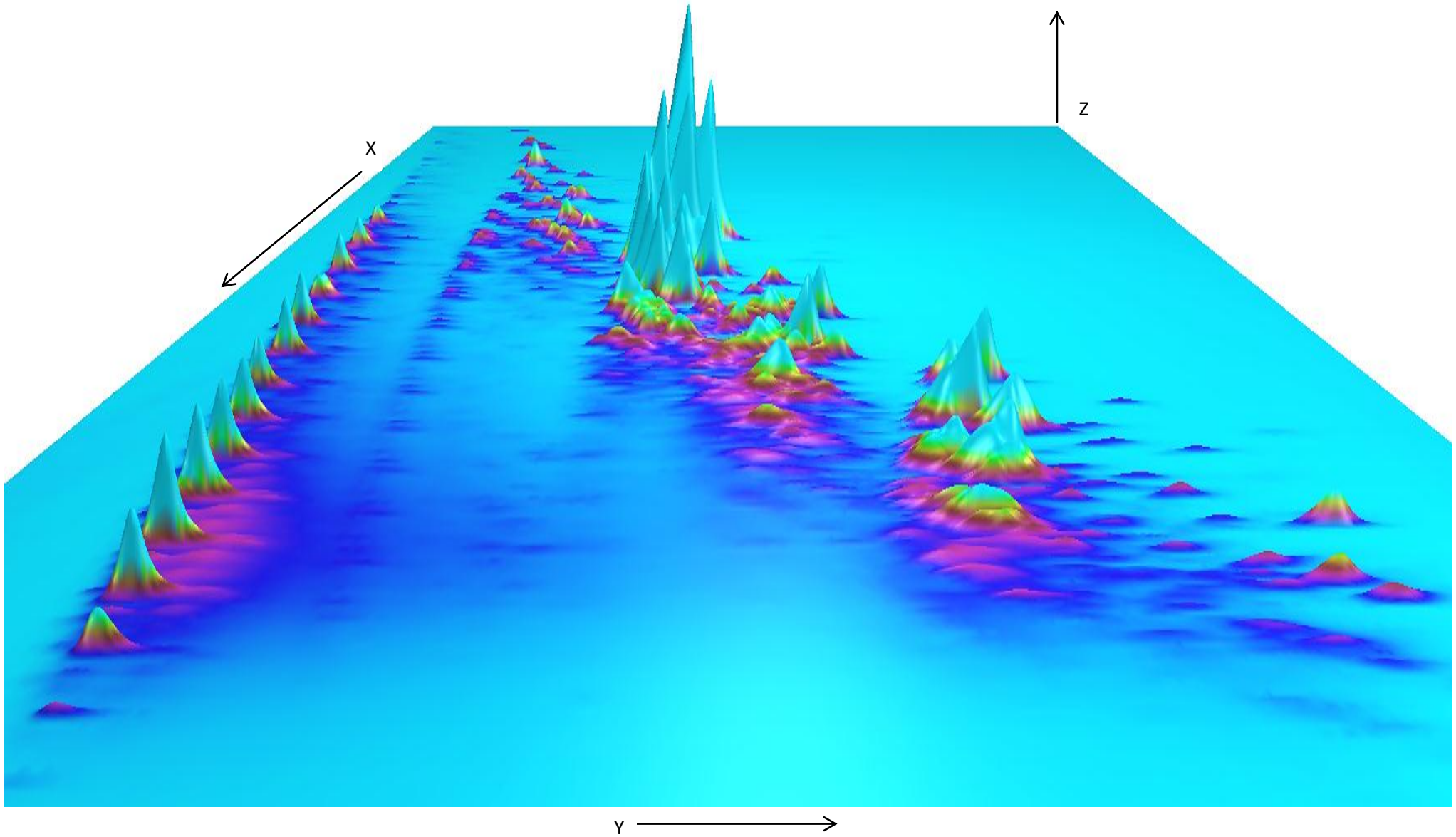
Light cycle oil A with 3D visualisation of chromatogram – FID signal

$1^{st}/2^{nd}$ dimension orientation view. Volume intensities rise from the baseplane, z-direction. Boling point separation in x-direction and polarity separation in y-direction.



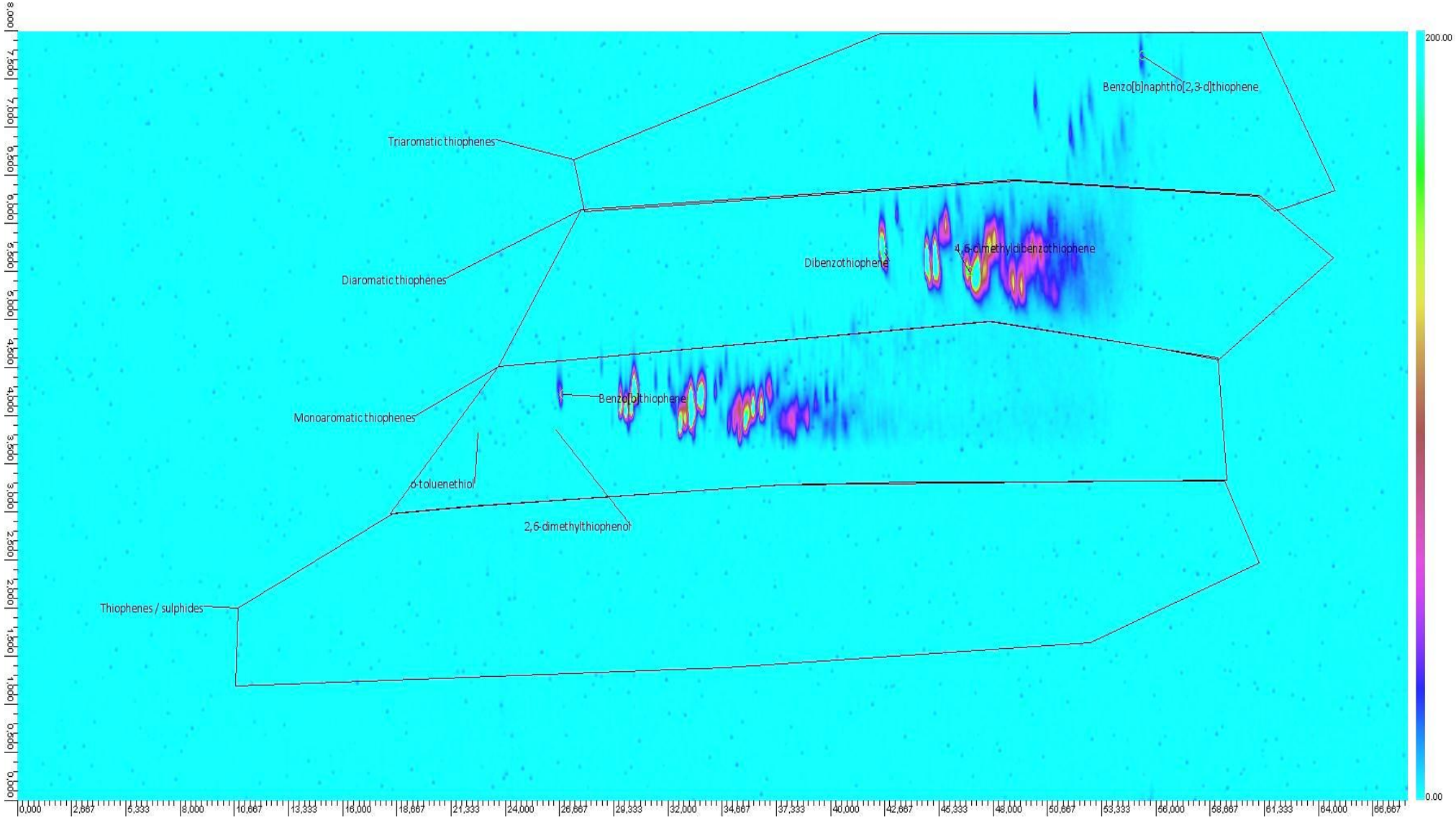
N

2nd dimension orientation view. Boiling point separation in x-direction, polarity separation in y-direction, and peak volume in z-direction.



o

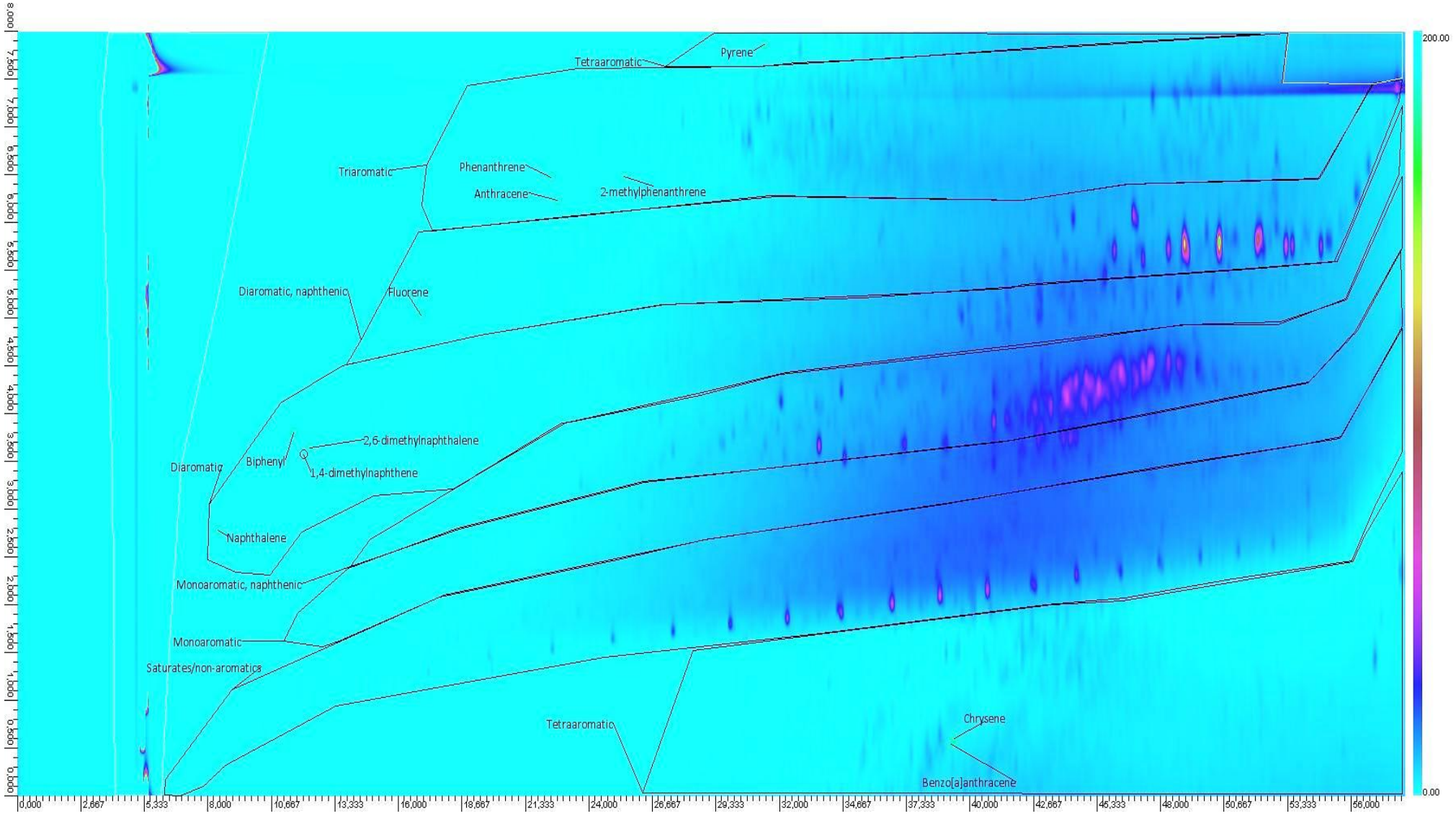
C.B Light cycle oil A chromatogram with template – SCD signal



P

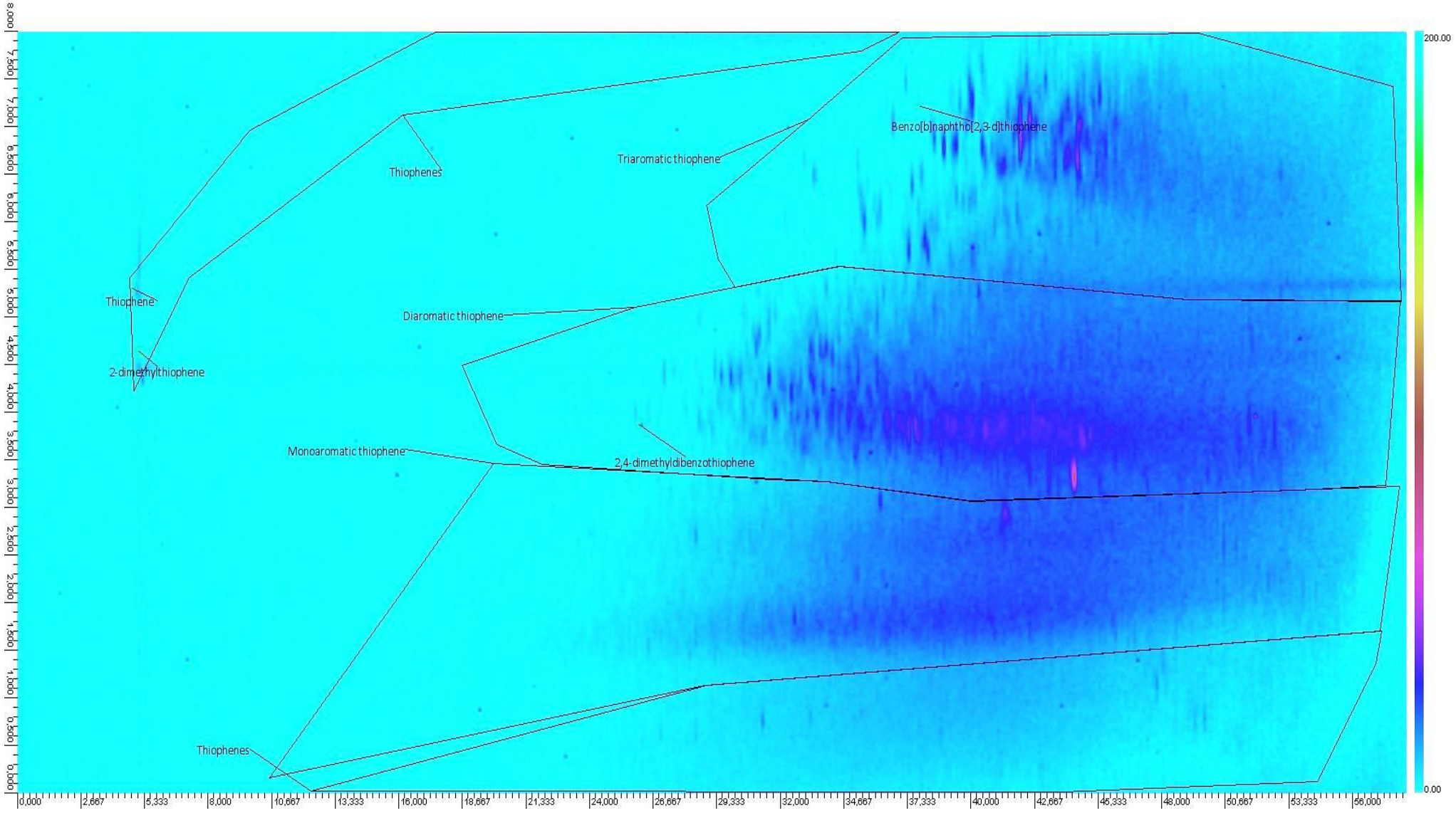
D. Vacuum gas oils (VGO)

D.A Straight run vacuum gas oil A chromatogram with template



Q

D.B Straight run vacuum gas oil A chromatogram with template – SCD signal



R