

Separation and Characterisation of the C₁₅- Aromatic Fraction of Safaniya Crude Oil

T. Al Darouich^{1,2}, F. Béhar¹, C. Largeau² and H. Budzinski³

¹ Institut français du pétrole, 1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France

² Laboratoire de chimie bioorganique et organique physique, UMR CNRS 7573, ENSCP,
11, rue Pierre-et-Marie-Curie, 75231 Paris Cedex 05 - France

³ Laboratoire de Photophysique et photochimie moléculaire, université de Bordeaux 1, URA 348 CNRS,
351, cours de la Libération, 33400 Talence - France

e-mail: tammam.al-darouich@ifp.fr - francoise.behar@ifp.fr - claude-largeau@enscp.jussieu.fr - h.budzinski@lptc.u-bordeaux1.fr

Résumé — Séparation et caractérisation de la fraction aromatique C₁₅- de l'huile brute Safaniya —

L'objectif de ce travail est d'isoler et de caractériser la fraction aromatique légère de l'huile Safaniya, huile brute conventionnelle non biodégradée de type II, pour étudier la stabilité thermique des fractions aromatiques légères des huiles brutes. Une distillation fractionnée nous a permis d'obtenir la coupe < 250°C correspondant aux composés C₁₅. Cette coupe contient des hydrocarbures saturés et aromatiques. Les études cinétiques sur la stabilité thermique des aromatiques exigent de travailler avec une fraction aromatique sans traces de produits saturés et de disposer d'informations détaillées sur sa composition. Nous avons donc, tout d'abord, développé une méthode permettant de réaliser une nette séparation de ces deux familles. La chromatographie en phase liquide sur colonne de silice activée a ainsi été optimisée pour obtenir une fraction aromatique complète et pure, en quantités suffisantes pour les études de caractérisation et toutes les études cinétiques ultérieures. Puis, la chromatographie en phase liquide haute performance préparative (PHPLC) a été employée, sur une aliquote, pour fractionner les composés aromatiques en fonction du nombre de noyaux aromatiques en monoaromatiques, indènes, diaromatiques et biphényles. Une caractérisation moléculaire détaillée des sous-fractions ainsi obtenues a été réalisée par chromatographie en phase gazeuse couplée à la spectrométrie de masse (CG/SM). Les constituants aromatiques ont été ensuite quantifiés individuellement par GC-FID. Ces composés sont le benzène, les C₁-C₇ benzènes, le naphthalène, les C₁-C₂ naphthalènes, l'indane, les C₁-C₄ indanes, l'indène, les C₁-C₂ indènes, les C₁-C₃ tétralines et les composés aromatiques soufrés (méthyl- et éthyl-benzothiophènes). La connaissance détaillée ainsi obtenue, sur la composition des différentes classes et leur abondance relative dans les aromatiques C₁₅- totaux, permettra de suivre leur évolution lors des études de craquage thermique ultérieures.

Abstract — Separation and Characterisation of the C₁₅- Aromatic Fraction of Safaniya Crude Oil —

The purpose of this work is to isolate and characterise the light fraction of Safaniya, a conventional non-biodegraded type II crude oil. This fraction is devoted to perform a kinetic study on the thermal stability of the light aromatic fraction of crude oil. The light cut < 250°C, corresponding to the C₁₅- components, was obtained by fractionated distillation. This cut contains saturated and aromatic hydrocarbons. Kinetic studies on the thermal stability of aromatics require to separate the aromatic fraction without any trace of saturated compounds and derive detailed information on its composition. We have therefore

developed a method permitting to achieve a clear-cut separation of these two families. Liquid phase chromatography on activated silica gel column was thus optimised for separating a complete and pure aromatic fraction, in large enough amounts for characterisation and all subsequent kinetic studies. Thereafter, Preparative High Performance Liquid Chromatography (PHPLC) of an aliquot was used to separate the aromatic compounds according to aromatic ring number into monoaromatics, indenenes, diaromatics and biphenyls. Detailed molecular characterisation of the aromatic sub-fractions thus obtained was achieved by Gas Chromatography coupled to Mass Spectrometry (GC/MS). Then, individual aromatic compounds were quantified by GC-FID. These compounds are benzene, C_1 - C_7 benzenes, naphthalene, C_1 - C_2 naphthalenes, indane, C_1 - C_4 indanes, indene, C_1 - C_2 indenenes, C_1 - C_3 tetralins and sulphur-containing aromatics (methyl- and ethylbenzothiophenes). The detailed knowledge thus derived on the composition of different class and its relative abundance in the total C_{15} -aromatics will allow following its temporal evolution during subsequent pyrolysis experiments.

INTRODUCTION

Oil in reservoirs undergoes thermal alteration leading to lighter oil, gas and pyrobitumen. Obtaining detailed information on such alteration is of prime importance, in relation with petroleum exploration and with the prediction of oil and gas quantity and quality. The thermal evolution of reservoir oil is controlled by the kinetics of cracking reactions (Tissot and Welte, 1984). These reactions, naturally occurring at low temperature and for geological time scale, can be simulated by laboratory pyrolysis experiments at high temperature for short time (Tissot and Welte, 1984; Ungerer, 1990; Béhar *et al.*, 1991, among others). Contrary to alkanes, the cracking of the aromatic hydrocarbons of oil and the reaction mechanisms involved are still far from been clearly understood and have been examined more recently. In our work on the stability of the aromatic compounds of crude oils we aim to predict such stability through a model derived from laboratory pyrolyses, using a molecularly well characterised aromatic fraction isolated from a selected standard crude oil.

The first objective of this work is to perform preparative isolation of the light aromatic fraction of a crude oil for future kinetic studies by closed pyrolysis in gold tubes. The second objective is to determine the molecular composition of the isolated aromatic fraction. Indeed, detailed qualitative and quantitative knowledge is required for the kinetic studies where aromatic constituents will be lumped in different classes according to their estimated thermal stability.

Crude oils are often separated in groups SARA (saturated, aromatic, resins and asphaltenes) by different chromatographic techniques. Fractionation is based on difference in solubility and polarity. Normal phase planar chromatography, which includes preparative plate chromatography and thin layer chromatography (TLC), has been used for a long time to separate hydrocarbons into group types using silica gel as stationary phase and different solvents (Huc *et al.*, 1976). The limitation of this technique is that it separates small quantities and cannot be used for volatile fraction separation. Nevertheless it remains a rapid technique

to separate heavy fractions. Recent developments of high performance thin layer chromatography (HPTLC) have permitted to investigate its analytical capacities for quantitative determination of hydrocarbon types when coupled with scanning densitometric detection (Membrado *et al.*, 2002; Matt *et al.*, 2002, 2003) or with flame ionisation detection (TLC-FID) (Sharma *et al.*, 1998; Kamiński *et al.*, 2003).

The more widely used technique to separate crude oils into groups is liquid chromatography (LC). This procedure is often called SARA analysis. Oil is first topped at 210°C; asphaltenes are then precipitated in *n*-heptane at 100°C under reflux for 10 min. After filtration and solvent evaporation, the maltenes (deasphalted oil) are fractionated by LC. Different chromatographic configurations exist; low-pressure chromatography is carried out on open columns, automated techniques comprise medium pressure liquid chromatography (MPLC) and high performance liquid chromatography (HPLC) (Radke *et al.*, 1980, 1984). Activated silica gel is generally used as stationary phase and separation is achieved by sequential elutions with different solvents. The saturated hydrocarbons are not adsorbed and can thus be eluted using a paraffinic solvent or petroleum ether. Thereafter, aromatic compounds are desorbed. Finally, resins are recovered by polar mobile phase, preferentially by retro elution. The same concept is widely found in the literature but elution schemes are different and each variation in the procedure may influence required separation time and fraction overlapping. Saturated, aromatics and resins are respectively eluted with one of the following sequences: *n*-hexane, *n*-hexane, DCM/methanol (50/50) (Radke *et al.*, 1980); *n*-hexane, *n*-hexane, trichloromethane (Aske *et al.*, 2001); *n*-pentane, toluene, toluene/methanol (90/10) (Vazquez and Mansoori, 2000); petroleum ether, DCM, DCM/ethanol (50:50) (Li *et al.*, 1998).

Total aromatic fraction can be also separated into different sub-fractions (mono-, di-, tri- and polyaromatics) on an alumina column or on a bonded silica column. This additional fractionation can be carried out on an isolated aromatic fraction or be integrated in the SARA analysis. Šebor *et al.*

(1999) optimised the preparative separation on a dual silica gel-neutral alumina column: saturated hydrocarbons were eluted with hexane, monoaromatics with hexane/benzene (24:1), diaromatics with hexane/benzene (22:3), polyaromatics with benzene and resins with benzene/ether/methanol (1:1:3). Jiang *et al.* (2000) demonstrated that the modified SARA analysis proposed by Li *et al.* (1992), using neutral alumina, is inadequate to separate saturated and monoaromatic hydrocarbons.

Radke *et al.* (1984) split total aromatic fractions by HPLC into four sub-fractions using an alumina column and a stepwise gradient of DCM in *n*-hexane. Li *et al.* (1998) separated aromatic fractions on an alumina column into monoaromatics, diaromatics, polyaromatics I and

polyaromatics II by eluting respectively with DCM/petroleum ether (2:98), DCM/petroleum ether (10:90), DCM and DCM/methanol (50:50). Budzinski (1993) separated the aromatic fraction by HPLC on a NH₂-bonded silica column.

In the present study we aimed at fractionating a light cut which contains only saturated and aromatic fractions. Considering the above mentioned procedures we have searched to optimise the preparative separation of saturates and aromatics using lightest solvents (*n*-pentane/DCM) as in Béhar *et al.* (1989) since solvent evaporation without any loss of volatile compounds is required. Other solvents utilized in the literature may be inadequate because their elimination alters severely the composition of the charge and

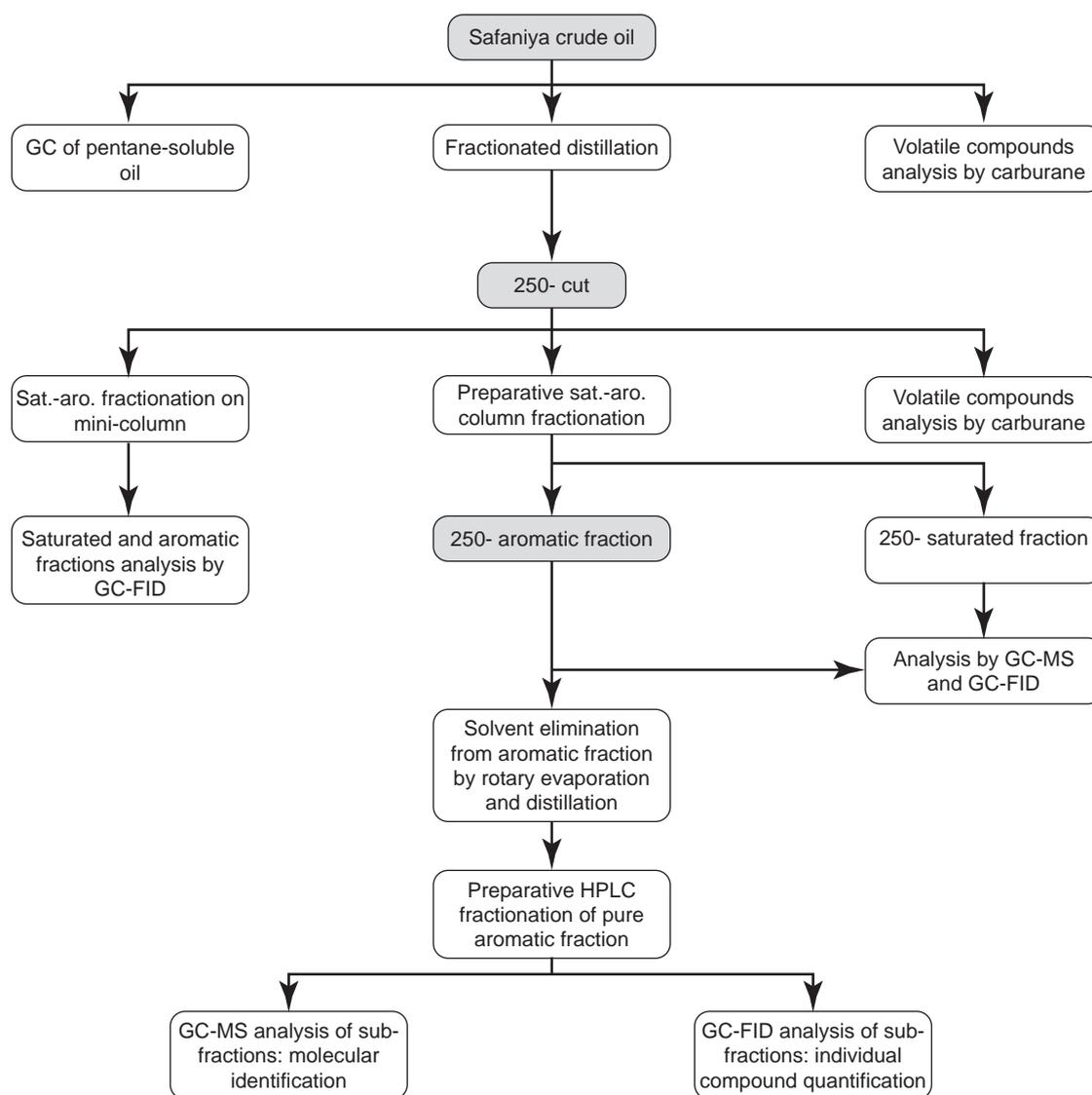


Figure 1
Analytical flow chart (250.: up to 250°C).

some of them such as benzene and toluene are present in the light cut. Thereafter, the isolated aromatic fraction was separated into monoaromatics and diaromatics by preparative HPLC using the same solvents (*n*-pentane/DCM) and NH₂-bonded silica column as in Budzinski (1993).

Accordingly, our research strategy is as follows:

- Selection of a standard crude oil and characterisation of its highly volatile fraction. Distillation to obtain a light cut in a range (up to C₁₄) such that identification and quantification of all of its aromatic constituents should be feasible.
- Isolation of the aromatics in large amounts through separation of this cut into saturated and aromatic components.
- Detailed qualitative and quantitative characterisation of an aliquot of this aromatic fraction at a molecular level using a combination of GC, GC/MS and HPLC analyses. Figure 1 shows the corresponding analytical flow chart.

Analytical techniques used in this paper are GC, GC/MS and HPLC. These complementary techniques have permitted to achieve a satisfactory characterisation of the light aromatic fraction. Meanwhile, very recent developments in multidimensional techniques such as LC×GC, GC×GC or GC×GC/MS can offer a powerful tool for complex sample analysis and increase identification and quantification capability. For instance, comprehensive two-dimensional GC applicability in petroleum sample analyses have recently been investigated (Frysjer and Gaines 1999; Beens *et al.*, 2000; Van Deursen *et al.*, 2000; McCurry and Quimby, 2003; Vendevre *et al.*, 2004). Nevertheless the complexity of the GC×GC might delay its entrance to the GC mainstream (Hinshaw 2004).

1 SAMPLE

A conventional crude oil of the Middle East (Safaniya, Saudi Arabia) was selected, since this is a non-biodegraded type II oil of marine origin, therefore representative of the largest fields actually in production. This oil was available in a large amounts (1000 l) enabling storage under good conditions. Crude oil was diluted in pentane (oil/pentane ratio: 1/200 v/v), a solvent that efficiently dissolves saturated and aromatic hydrocarbons, and analysed by gas chromatography. A Varian 3800 gas chromatograph was used. The programmable temperature vaporising (PTV) injector was programmed from 20 to 320°C at a heating rate of 200°C/min. A HP5 phenyl/methyl polysiloxane capillary column (60 m length, 0.25 mm ID, 0.25 µm film thickness) was used. Helium was used as carrier gas with a flow rate of 2 ml/min at the column outlet. CO₂ was used as a cryogenic gas to maintain the oven at 20°C for 10 min, before heating to 320°C at a rate of 3°C/min and holding this temperature for 30 min. The flame ionisation detector (FID) was heated at 320°C. Flame conditions were air: 300 ml/min, H₂: 30 ml/min and nitrogen was employed as a make-up gas with a flow rate of 25 µl/min. Analysis time was 140 min. A volume of 1 µl was injected with a 5 µl syringe.

Figure 2 shows the chromatogram obtained for this crude oil, which reflects its complexity. One can distinguish *n*-paraffin peaks up to *n*-C₃₅, which characterises a non-biodegrade oil and a large number of other types of compounds coelute giving a non resolved baseline.

A dedicated gas chromatographic method (IFP 9420) was carried out to identify and quantify the lightest compounds

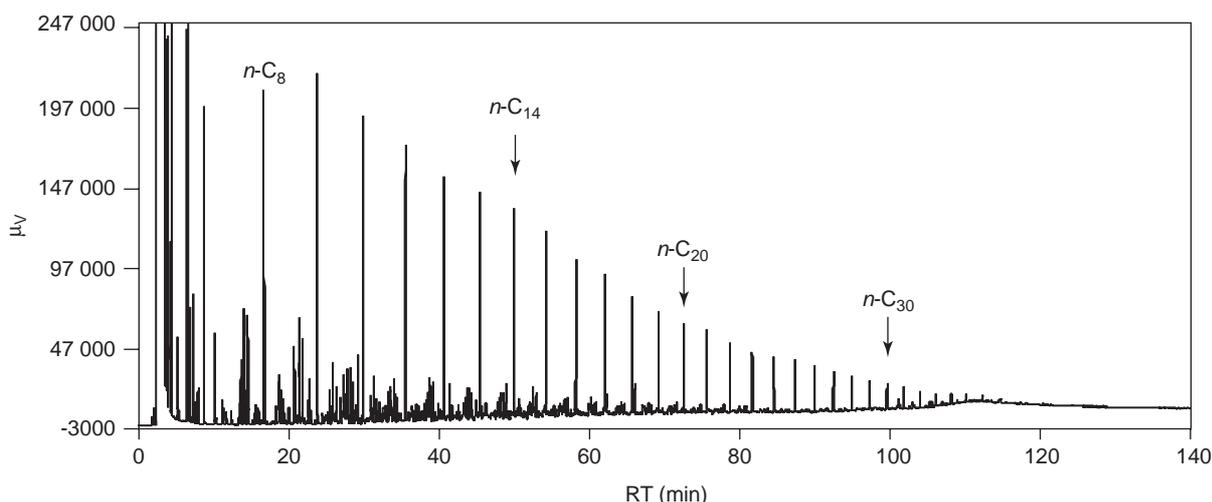


Figure 2

Chromatogram of Safaniya crude oil diluted in pentane.

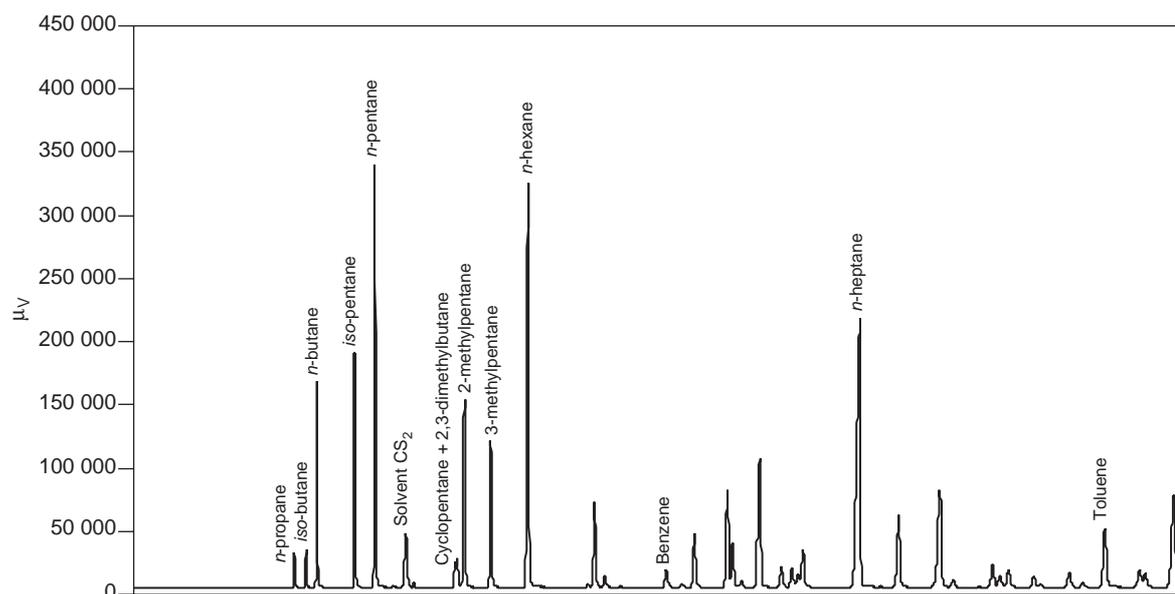


Figure 3
Chromatogram of the lightest compounds of Safaniya crude oil diluted in CS₂.

using a specific database from the Carburane[®], software developed at the IFP. This software enables chromatographic data processing to provide detailed analysis of compounds from several types of petroleum samples such as light saturated and aromatic compounds of crude oil (C₃-C₂₀) (Durand *et al.*, 1989). The GC method is performed using a pre-column, a dedicated device for backflushing the pre-column in order to vent out heavy fractions and a high-resolution capillary analytical column where the separation of solutes is carried out. Crude oils are injected after dilution in carbon disulphide CS₂ (50:50 v/v), because the response factor of this solvent is very weak with FID detection. An internal standard is added to the samples before analysis: 2,4,4-trimethyl-1-pentene (1% by weight). The C₁₈₊ fraction is eliminated from the pre-column by a back flush programmed at 95 min.

The presence of soluble gaseous compounds (propane, *n*-butane and isobutane) and of highly volatile compounds like *n*-pentane (Fig. 3) confirms that the crude oil sample was stored under proper conditions. The sum of these compounds represents c.a. 2% (wt) of the crude oil (Table 1). The lightest aromatic compounds are benzene and toluene and their relative abundance in the crude oil is B/T = 0.255 (wt/wt).

In order to separate the light components, fractionated distillation of the crude oil was carried out and gave 4 distillation cuts (250-°C, 250-375°C, 375-550°C and 550+°C). A total of 3.5 kg was distilled using two columns. Up to 375°C an automatic distillation procedure was carried out using an adiabatic-true boiling point column (100 cm × 25 mm) packed with multiknits using the ASTM D2892

TABLE 1
Detailed analysis of the soluble gaseous compounds and of the highly volatile compounds in Safaniya crude oil

| Compound | Wt% |
|---------------------|------|
| <i>n</i> -propane | 0.04 |
| <i>iso</i> -butane | 0.04 |
| <i>n</i> -butane | 0.24 |
| <i>iso</i> -pentane | 0.30 |
| <i>n</i> -pentane | 0.57 |
| 2,2-dimethylbutane | 0.01 |
| cyclopentane | 0.04 |
| 2,3-dimethylbutane | 0.06 |
| 2-methylpentane | 0.36 |
| 3-methylpentane | 0.31 |
| Sum | 1.97 |

standard method. Operation pressure was atmospheric pressure up to 150°C, then 100 mmHg up to 250°C, and 2 mmHg up to 375°C. Distillation up to 550°C was carried out using a non packed Postill column (40 cm × 25 mm) using the ASTM D5236 standard method. This distillation was carried out under vacuum (0.3 mmHg). The Safaniya oil exhibits a high content of 250- distillate (ca. 24%). This cut corresponds to the C₁₅- range that comprises compounds of all the saturated and aromatic families present in conventional oils. The 250- cut thus recovered was analysed by GC (not shown), under the same conditions as above. Comparison with the chromatogram of the whole oil indicated that no significant loss of the lightest hydrocarbons

occurred upon distillation. The virtually complete recovery obtained upon this fractionated distillation (250₋°C: 24.2%, 250-375°C: 19.0%, 375-550°C: 24.9% and 550₊°C: 31.9%) also showed that no significant loss of the lightest components took place. The soluble gaseous and highly volatile compounds were quantified in the 250₋ cut by the IFP 9420 method and their abundance was 7.8% (wt). This value is consistent with their abundance in the whole crude oil (c.a. 2%, Table 1) as this cut represents 24.2% of the total oil.

2 AROMATIC FRACTION ISOLATION BY LIQUID PHASE CHROMATOGRAPHY

2.1 Separation of Saturated and Aromatic Fractions on Mini-Column

As observed for all conventional oils, the 250₋ distillation cut of Safaniya is a mixture of saturated and aromatic hydrocarbons. An analytical protocol to separate the saturated and aromatic fractions of crude oils by liquid phase chromatography, using silica gel mini-columns was reported by Béhar *et al.* (1989). The mini-column is a Pasteur pipette filled with 1 g of silica gel (silica gel 60 Merck Ref. 107734, granulometry 0.063-0.200 mm), washed beforehand with dichloromethane (DCM). The silica gel (300 g) is heated in a boiling flask with DCM (500 ml) under reflux at 50°C for 1 h, then filtered and rinsed with DCM and activated at 140°C under vacuum for 1 h. The charge loaded onto the mini-column is 0.5 to 1 ml of a solution of the crude oil in pentane (2-20 mg/ml). Two elutions successively give the saturated fraction (2.5 ml of pentane) and the aromatic fraction (2.5 ml of a 85/15 (v/v) pentane/DCM mixture). In the initial analytical protocol the eluates were concentrated and quantified by GC using external calibration with different concentrations of a standard deparaffinated oil cut. In order to minimise the uncertainties in fraction quantification, this protocol was modified by adding two internal standards to the solution before fractionation: a saturated hydrocarbon and an aromatic hydrocarbon. Long-chain *n*-alkanes are well eluted by this chromatographic

system; *n*-pentacosane was thus used as standard for the saturated fraction as it was employed in different parts of this study. Aromatic internal standard choice was limited, as heavier aromatic compounds could not be completely eluted using the selected mobile phase. Naphthalene was therefore used although it is present in the charge. Its original concentration was calculated by performing one additional fractionation without internal standard and taken into account the relative abundance thus determined in the quantification. Accordingly, the first eluate corresponded to the saturated fraction + *n*-pentacosane and the second one to the aromatic fraction + naphthalene. The internal standards (20 mg each) were added to 100 ml of the 250₋ cut solution in pentane (15 mg/ml). The added naphthalene/original naphthalene ratio was then 17. Aliquots of 1 ml of this spiked solution were fractionated on mini-columns and the two successive elutions were carried out drop wise. Eluates were concentrated to 1 ml and their purity (lack of aromatics in the saturate fraction and *vice versa*) checked out by GC/MS. In addition, experiments were carried out in order to quantify saturated and aromatic fractions by GC-FID without concentration (Fig. 4).

The GC (conditions as in Section 1) was calibrated for saturated and aromatic compounds using *n*-pentacosane and naphthalene, respectively. Relative response factor of naphthalene compared to *n*-pentacosane was calculated ($RRF_{\text{naph}/n-C_{25}} = 1.09$). Aromatic compound response is higher than for saturated compounds as the former are richer in carbon and the intensity of the FID signal depends on compound combustion. Each fraction was quantified using its internal standard. The integration of the chromatograms was carried out by the Galaxy[®], software that allows slice integration after subtracting the signal corresponding to the blank (the solvent) from that of the sample.

Quantitative analysis was performed, without concentration of the eluates, nevertheless the most volatile saturated compounds were partially lost upon fractionation and the remaining part is not quantifiable as it coelutes with the solvent. The recovered C₆-C₁₄ compounds thus represent 90.3% of the initial cut (Table 2). The lost plus non

TABLE 2
Proportions of the saturated and aromatic fractions in Safaniya 250₋ cut

| Fraction | IFP 9420 method | | | Isolated fractions | |
|-----------|---|---|----------------------|---|----------------------|
| | C ₃ -C ₁₄ compounds (%) | C ₆ -C ₁₄ compounds (%) | | C ₆ -C ₁₄ compounds (%) | |
| | | Abundance (*) | Relative proportions | Abundance (*) | Relative proportions |
| Saturated | 84.1 | 76.3 | 82.8 | 77.0 | 85.3 |
| Aromatic | 15.9 | 15.9 | 17.2 | 13.3 | 14.7 |
| Sum | 100 | 92.2 | 100 | 90.3 | 100 |

* As % of the cut.

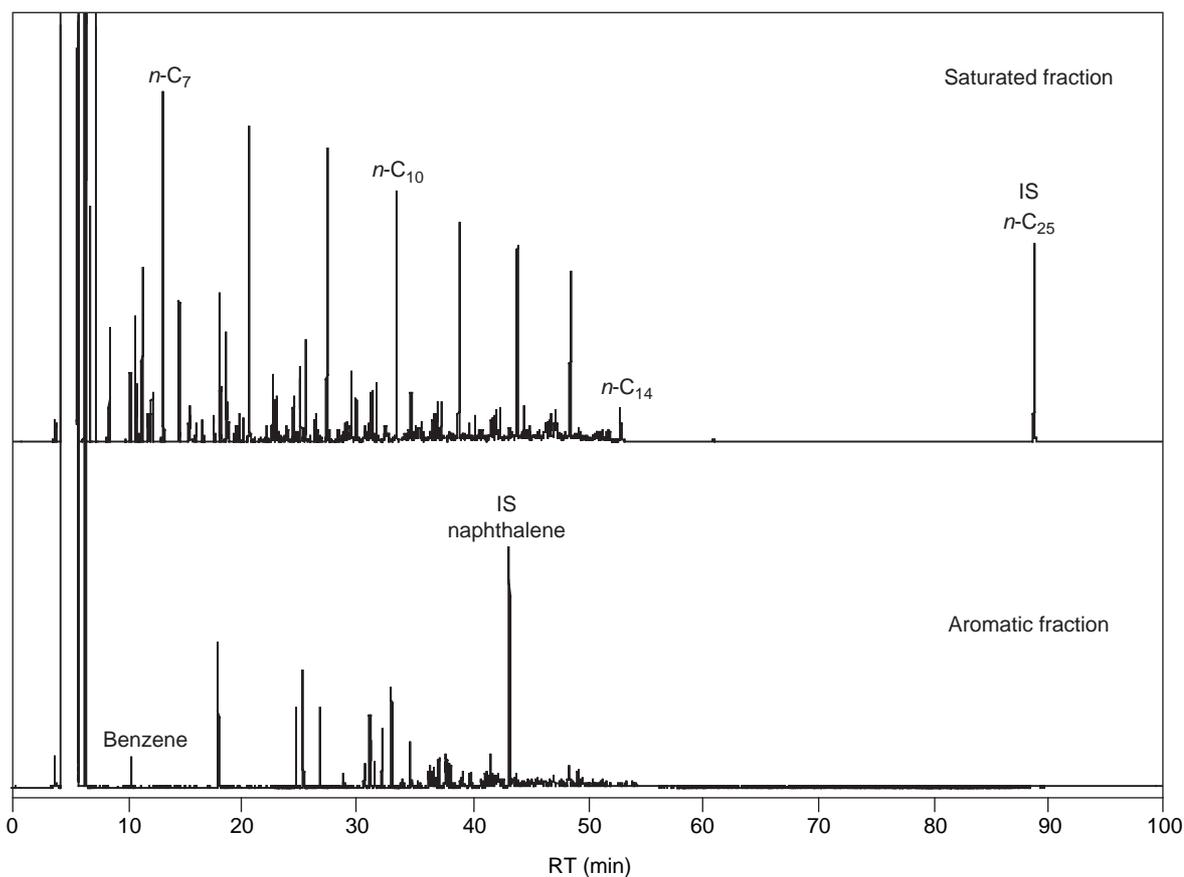


Figure 4

Chromatogram of the saturated and aromatic fractions of Safaniya 250_{cut} separated on mini-column (GC-FID on HP5 capillary column-conditions as in Section 1).

quantifiable compounds therefore represent 9.7% of the 250_{cut}, which is consistent with the proportion of the soluble gaseous and highly volatile compounds determined before fractionation (7.8%).

The relative abundance of the isolated C₆-C₁₄ saturated and aromatic fractions is 85.3% and 14.7%, respectively (Table 2). These results were compared to those obtained by the direct analysis without fractionation (IFP 9420 method) which are somewhat different from the above ones (17.2% for the aromatic fraction instead of 14.7%). This is probably due to the occurrence of some coelutions of saturated and aromatic compounds when analysis is done without prior fractionation.

2.2 Preparative Isolation of the Aromatic Fraction

To isolate the aromatic fraction in large amounts, it was necessary to adapt the liquid phase chromatography fractionation to preparative dimensions. To this end, we used a 70 cm length × 2 cm internal diameter column equipped with a Teflon tap and a glass-frit disc. The column was filled

with 80 g of silica gel washed with DCM and activated at 140°C as previously indicated. Several fractionation experiments were performed to determine optimal conditions, *i.e.* complete separation of the saturated and aromatic fractions for a maximum load and a minimum quantity of solvent. For this purpose various elution patterns (number of eluates recovered, volume and composition of the mobile phase used for each of these eluates) were tested for different loads. The eluates were analysed by GC and GC/MS and compared to the saturated and aromatic fractions obtained by mini-column separation. The best conditions thus obtained were: a 3.5 ml (ca. 2.6 g) load of the 250_{cut}, a first elution with 100 ml of pentane affording the total saturated fraction, a second intermediate elution with 50 ml of 85/15 (v/v) pentane/DCM mixture and final elution with 250 ml of the same pentane/DCM mixture affording the total aromatic fraction. Figure 5 shows the GC traces of the three eluates thus obtained. As illustrated in this Figure, a clear-cut separation was achieved between the saturated and aromatic components. Indeed, no products were detected, even in trace amounts, in the intermediate fraction. The purity of the

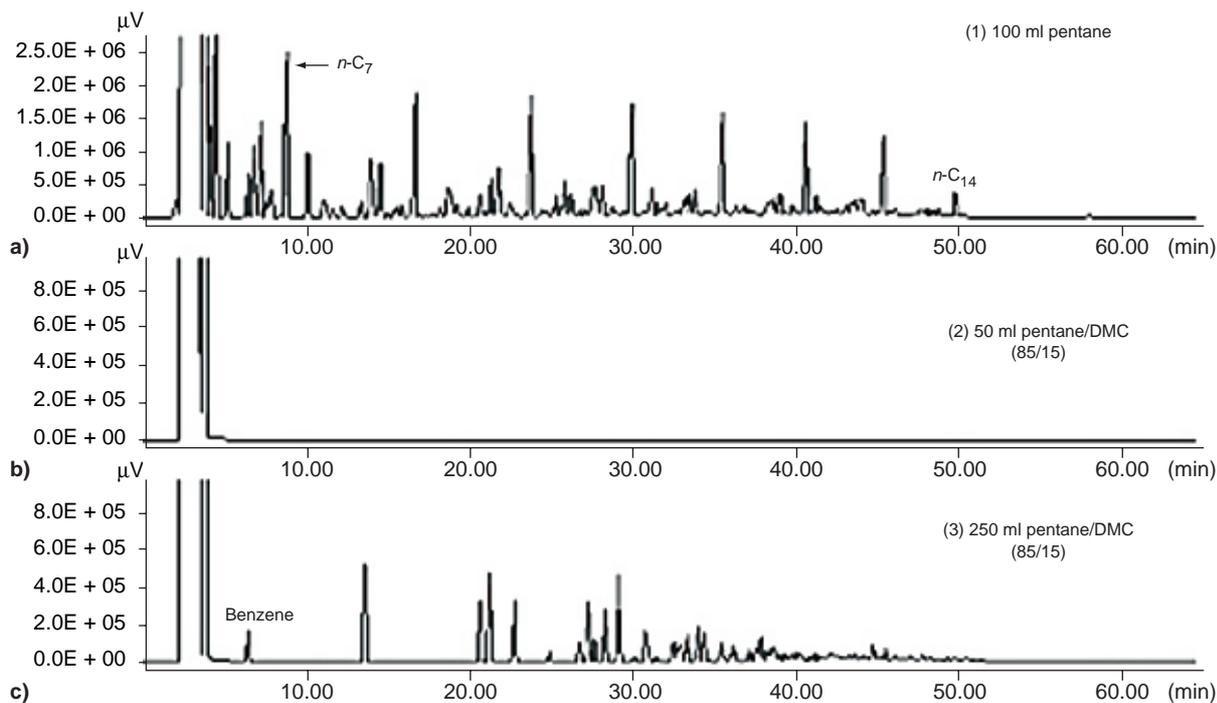


Figure 5

Chromatograms of the three eluates (a: saturated fraction; b: intermediate fraction; c: aromatic fraction) obtained by optimised preparative separation of Safaniya 250- cut.

saturated and aromatic fractions was further ascertained by GC/MS analyses after concentration (solutions volume was reduced to 50 ml by rotary evaporation). For this we used selective ion detection (SID) to search for:

- the characteristic ions of the saturated compounds ($m/z = 57, 71, 85$) in the aromatic fraction;
- the characteristic ions of the aromatic compounds, with focus on the alkylaromatics, ($m/z = 78, 91, 105, 119, 133$) in the saturated fraction. The absence of these ions in the two cases confirms the complete recovery of the aromatic fraction and its purity.

The above conditions were used to isolate enough aromatic fraction (ca. 10 g) to carry out detailed characterisation and especially all the pyrolysis experiments planned for the kinetic studies. About 400 mg of aromatics, in 250 ml of pentane/DCM, are obtained for one separation experiment. Twenty-eight runs were therefore carried out, affording a total volume of seven litres of aromatic eluates. Complete elimination of pentane/DCM is required for the subsequent studies. Alteration of the composition of the aromatic fraction, through selective removal of the lightest aromatics along with the solvent, must be strictly avoided during that removal. To this end, the elimination of the solvent was achieved in two steps: ca. 80% was eliminated by rotary evaporation under mild conditions: 37°C under

atmospheric pressure. The remaining solvent was eliminated by distillation. The distillation apparatus was made of the following components: 500 ml boiling flask, a vertical Vigreux column (40 cm length, 25 mm diameter) and a condenser. Vapour temperature was measured at the top of the column. The boiling points of pentane and DCM are only 36 and 40°C, respectively, while that of benzene, the most volatile constituent of the aromatic fraction is 80°C. Due to this gap, a pure unaltered aromatic fraction could be isolated. The lack of trace amounts of residual pentane and DCM was checked by GC by diluting an aliquot of the aromatic fraction in CS_2 before re-analysis by GC. Benzene/toluene ratio is 0.248 whereas it was 0.255 in the crude oil which confirms that benzene loss is negligible. In order to prevent any alteration of the aromatic fraction upon storage, especially by oxygen and light, it was stored under nitrogen in hermetic sealing and opaque vials in a glove box with a nitrogen atmosphere.

3 CHARACTERISATION OF THE AROMATIC FRACTION

Detailed characterisation of the 250. aromatic fraction was achieved by qualitative and quantitative analyses, using

GC/MS and GC-FID, respectively. The objective was to identify and quantify all the individual constituents of the fraction. Preparative High Performance Liquid Chromatography (PHPLC) was performed to facilitate GC/MS and GC analyses.

3.1 PHPLC Fractionation

Aromatic compounds can be fractionated according to aromatic ring number by normal phase HPLC as indicated in the Introduction. To perform this fractionation, on an aliquot of the C₁₅- aromatic fraction of Safaniya, we used a semi-preparative Varian Dynamax column (250 mm length, 10 mm internal diameter) with dynamic axial compression. The column was filled with Microsorb amino (NH₂-bonded silica) stationary phase, particle size 5 µm and pore size 100 Å. A guard cartridge packed with the same stationary phase was used as a pre-column. The mobile phase was pentane from 0 to 24 min, then a 90/10 (v/v) pentane/DCM mixture in isocratic mode from 24 to 55 min. Flow rate was set at 2 ml/min from 0 to 17 min, and then increased to 4 ml/min for the end of the run. A UV-visible detector (wavelength 254 nm) was employed. A volume of 200 µl of the aromatic fraction solution (20 mg/ml pentane) was injected and the obtained chromatogram is shown on Figure 6. The eluate was collected at the detector outlet and four sub-fractions were separately recovered: F1 (0-11.8 min), F2 (11.8-13.7 min), F3 (13.7-15.2 min) and F4 (15.2-20 min). These sub-fractions were analysed by GC/MS for molecular identification and by GC-FID for quantification.

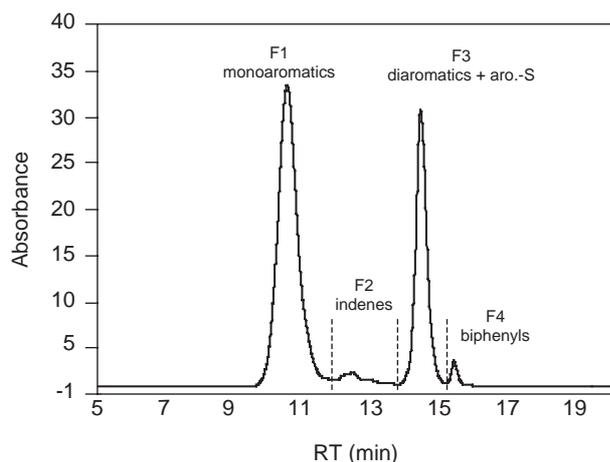


Figure 6

Chromatogram obtained by LC of the aromatic fraction of Safaniya 250. cut.

The objective of this separation was to separate monoaromatics and diaromatics and HPLC permitted to fulfil this

purpose. The intermediate sub-fraction (F2: indenes) has not been mentioned in literature, it was here isolated to ensure clear-cut fractionation. Overlapping of this fraction with the two principles peaks (F1 and F3) is negligible since its total percentage is < 0.2% (wt).

3.2 Molecular Identification by GC/MS

Sub-fraction solutions obtained by PHPLC were concentrated (to 500 µl) and detailed GC/MS analyses were performed in order to identify all their constituents. A HP 6890 gas chromatograph was used with a PTV injector in splitless mode. The injector was initially set at 50°C, then heated to 250°C at a rate of 120°C/min and kept at 250°C. A HP5 phenyl/methyl polysiloxane capillary column (30 m length, 0.25 mm ID, 0.25 µm film thickness) was used. The oven was held at 50 C for 15 min then heated to 250C at 3°C/min and kept at this temperature for 30 min. Helium was used as carrier gas and the column head pressure was set at 11 psi. The injected volume was 1 µl. The GC was coupled to a mass spectrometer equipped with an ionisation source (electronic impact mode, ionisation energy 70 eV) heated at 230°C. The analyser was a quadrupole heated at 150°C. The detector was an electron multiplier (EM). "Full scan" mode was used for detection (50-500 amu mass range at a rate of 1 scan/s, detector resolution 1000). Peak by peak identification was performed using the NIST spectrum library.

The first sub-fraction isolated by PHPLC (Figs. 7a, 7b) is composed of monoaromatics: benzene, toluene, xylenes, a number of C₂-C₇ alkylbenzenes, indane, methyl- and C₂- to C₄-indanes, methyl- and C₂- to C₃-tetralins. Indene, along with methyl- and ethylindenes were identified in trace amounts in the second sub-fraction. The third sub-fraction (Fig. 8) contains the diaromatic compounds: naphthalene, methylnaphthalenes, numerous C₂-naphthalenes and trace amounts of sulphur-containing aromatics: chiefly C₂-benzothiophenes. Trace amounts of biphenyls were identified in the fourth sub-fraction. Differentiation between some isomers was not possible using GC/MS as they have the same mass spectrum. Comparison with literature was done when possible, for instance Pérez-Parajón *et al.* (2004) for methylbenzenes and Budzinski (1993) for methyl-naphthalenes.

3.3 Quantitative Analysis by GC-FID

HPLC sub-fractions were analysed by GC-FID in order to determine the percentage of each compound, after addition of an internal standard (*n*-pentacosane 100 µg/ml). A Varian 3800 gas chromatograph was used with the HP5 column using the same conditions as above (Section 1). The PTV injector (high performance liner in cold on-column mode) of this chromatograph affords improved quantitative results

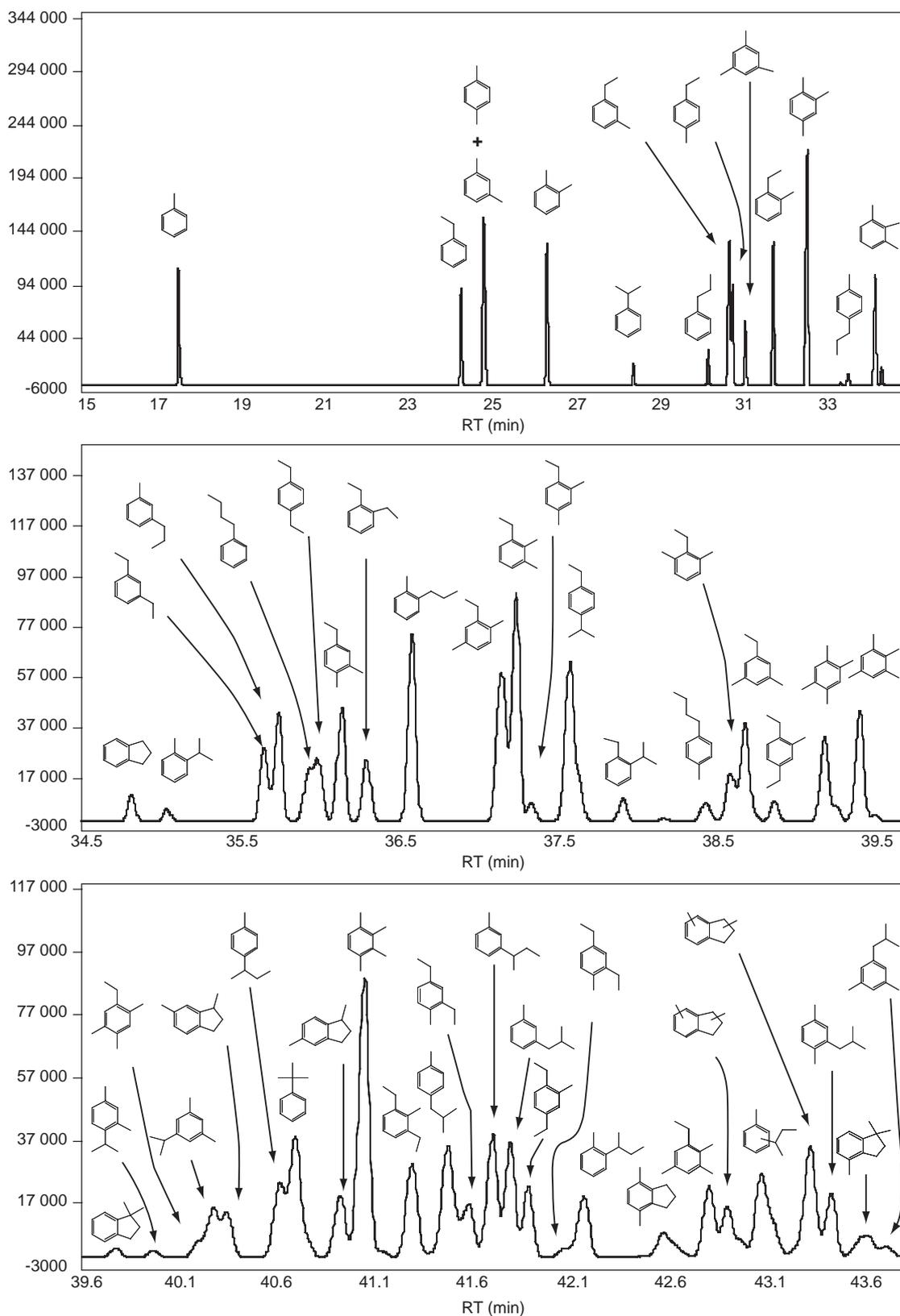


Figure 7a

Chromatogram of the monoaromatic sub-fraction of Safaniya 250_{cut} (first part of the chromatogram).

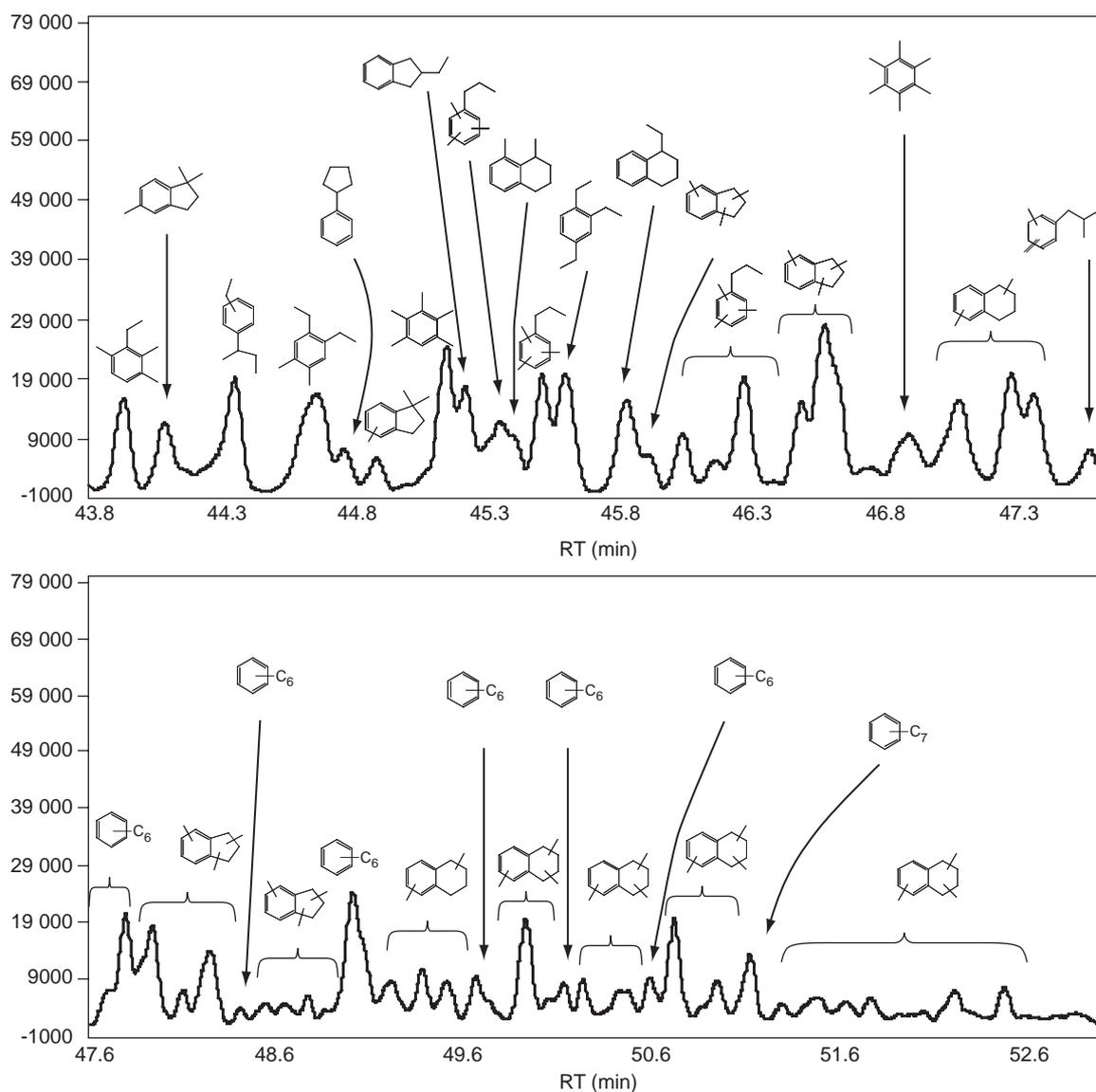


Figure 7b

Chromatogram of the monoaromatic sub-fraction of Safaniya 250. cut (second part of the chromatogram).

without discrimination between compounds due to differences in molecular weight. Individual peaks were integrated using Galaxy[®] software. Concentrations were then calculated by comparison with the internal standard and corrected by the relative response factors. Mixtures of seven representative pure reference compounds were analysed under the same conditions in order to calculate their relative response factors in comparison to the internal standard (*n*-C₂₅). Responses of the different aromatic compounds were higher compared to the saturated compound and varied in a restricted range (1.07 ± 0.02). The detailed quantitative data thus obtained are reported in the Appendix.

CONCLUSION

Column chromatography fractionation was scaled up to separate the saturated and aromatic components of the C₁₅-distillation cut (<250°C) of Safaniya crude oil. Large enough amounts of the complete and pure aromatic fraction of this crude oil were thus isolated for characterisation and future kinetic studies. Saturated and aromatic fractions proportions for the C₆-C₁₄ compounds (85.3% sat./14.7% aro.) were compared to those obtained by the IFP 9420 method (82.8% sat./17.2% aro.) a method permitting simultaneous analysis of saturated and aromatic fractions. The latter method is

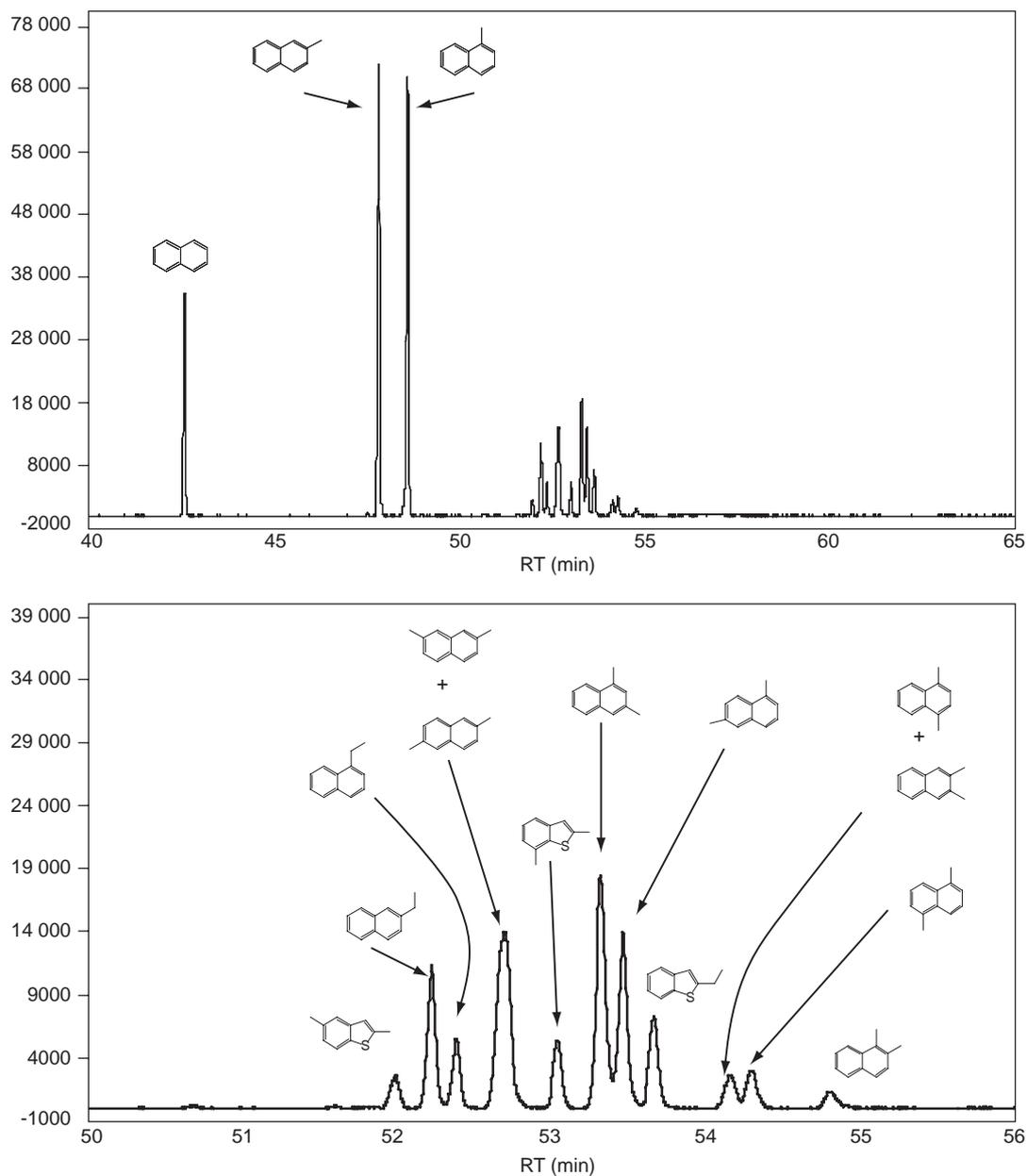


Figure 8

Chromatogram of the diaromatic and sulphur aromatic sub-fraction of Safaniya 250_{cut}.

especially convenient to quantify highly volatile compound and global family proportions.

Detailed qualitative and quantitative analysis of Safaniya aromatics were performed, using GC/MS and GC-FID, respectively, on the sub-fractions (monoaromatics, indenenes, diaromatics and biphenyls) separated by PHPLC of an aliquot. All individual compounds (C_0 - C_7 benzenes and C_0 - C_2 naphthalenes, C_0 - C_4 indanes, C_0 - C_2 indenenes, C_1 - C_3 tetralins and C_1 - C_2 benzothiophenes) were thus identified and quantified. Kinetic studies, aimed at simulating the thermal

degradation of the C_{15} aromatic components of crude oils under geological conditions, will be based on the detailed information thus obtained on Safaniya aromatics and will use the analytical protocol developed in the present work.

ACKNOWLEDGEMENTS

We thank P. Paul for fractionated distillation, C. Leblond and G. Caillet for technical assistance and J. Bellocq for her help

in HPLC fractionation. Valuable comments of reviewers are gratefully acknowledged.

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Final manuscript received in March 2005

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APPENDIX

Individual compounds and their relative abundance (as % of total C₁₅-aromatics) in the 250. cut of the Safaniya crude oil.

TABLE A1
Monoaromatic sub-fraction

| Index | Compound | RT (min) | Wt%* | | | | |
|-------|--------------------------------------|----------|------|-----|--|-------|------|
| 1 | benzene | 10.00 | 0.99 | 51 | 1-methyl-4-(2-methyl-propyl)-benzene | 41.51 | 1.06 |
| 2 | toluene | 17.54 | 3.98 | 52 | 1,3-diethyl-4-methyl-benzene | 41.61 | 0.49 |
| 3 | ethylbenzene | 24.27 | 2.18 | 53 | 1-methyl-3-(1-methyl-propyl)-benzene | 41.74 | 0.99 |
| 4 | <i>m</i> - and <i>p</i> -xylene | 24.82 | 5.54 | 54 | 1-methyl-3-(2-methyl-propyl)-benzene | 41.83 | 0.88 |
| 5 | <i>o</i> -xylene | 26.33 | 3.09 | 55 | 1,4-diethyl-2-methyl-benzene | 41.92 | 0.52 |
| 6 | isopropyl-benzene | 28.39 | 0.46 | 56 | 1,3-diethyl-4-methyl-benzene | 42.12 | 0.06 |
| 7 | <i>n</i> -propyl-benzene | 30.17 | 0.78 | 57 | 1-methyl-2-(1-methyl-propyl)-benzene | 42.20 | 0.55 |
| 8 | 1-ethyl-3-methyl-benzene | 30.68 | 3.57 | 58 | 4,7-dimethyl-indane | 42.53 | 0.33 |
| 9 | 1-ethyl-4-methyl-benzene | 30.76 | 1.90 | 59 | 1-ethyl-2,3,5-trimethyl-benzene | 42.77 | 0.60 |
| 10 | 1,3,5-tri-methyl-benzene | 31.06 | 1.36 | 60 | dimethyl-indane | 42.86 | 0.53 |
| 11 | 1-ethyl-2-methyl-benzene | 31.73 | 3.16 | 61 | 1-methyl-(1-methyl-propyl)-benzene | 43.03 | 0.83 |
| 12 | 1,2,4-tri-methyl-benzene | 32.54 | 5.67 | 62 | dimethyl-indane | 43.09 | 0.15 |
| 13 | 1-methyl-3-isopropyl-benzene | 33.34 | 0.07 | 63 | dimethyl-indane | 43.20 | 0.31 |
| 14 | 1-methyl-4-propyl-benzene | 33.52 | 0.26 | 64 | C ₅ -benzene | 43.28 | 0.30 |
| 15 | 1,2,3- tri-methyl-benzene | 34.16 | 2.73 | 65 | 1,4-dimethyl-3-(2-methyl-propyl)-benzene | 43.39 | 0.50 |
| 16 | 1-methyl-4-isopropyl-benzene | 34.31 | 0.41 | 66 | 1,1,4-trimethyl-indane | 43.56 | 0.30 |
| 17 | indane | 34.87 | 0.26 | 67 | 1,3-dimethyl-5-(2-methyl-propyl)-benzene | 43.67 | 0.09 |
| 18 | 1-methyl-2-isopropyl-benzene | 35.10 | 0.12 | 68 | 1-ethyl-2,3,6-trimethyl-benzene | 43.84 | 0.44 |
| 19 | 1,3-diethyl-benzene | 35.71 | 0.74 | 69 | 1,1,5-trimethyl-indane | 44.00 | 0.35 |
| 20 | 1-methyl-3-propyl-benzene | 35.80 | 1.10 | 70 | 1-ethyl-4-(2-methyl-propyl)-benzene | 44.05 | 0.08 |
| 21 | butyl benzene | 35.99 | 0.46 | 71 | trimethyl-indane | 44.18 | 0.11 |
| 22 | 1,4-diethyl-benzene | 36.04 | 0.70 | 72 | ethyl-(1-methyl-propyl)-benzene | 44.26 | 0.61 |
| 23 | 1-ethyl-3,4-dimethyl-benzene | 36.19 | 1.14 | 73 | 1,2-diethyl-4,5-dimethyl-benzene | 44.57 | 0.80 |
| 24 | 1,2-diethyl-benzene | 36.35 | 0.61 | 74 | cyclopentyl-benzene | 44.67 | 0.19 |
| 25 | 1-methyl-2-propyl-benzene | 36.64 | 1.85 | 75 | trimethyl-indane | 44.80 | 0.16 |
| 26 | 1-ethyl-2,5-dimethyl-benzene | 37.20 | 1.64 | 76 | trimethyl-propyl-benzene | 44.92 | 0.03 |
| 27 | 1-ethyl-2,3-dimethyl-benzene | 37.29 | 2.15 | 77 | C ₅ -benzene | 44.99 | 0.05 |
| 28 | 1-ethyl-2,4-dimethyl-benzene | 37.38 | 0.17 | 78 | pentamethyl-benzene | 45.06 | 0.67 |
| 29 | 1-ethyl-3-isopropyl-benzene | 37.62 | 1.66 | 79 | 2-ethyl-indane | 45.14 | 0.46 |
| 30 | 1-methyl indane | 37.67 | 0.30 | 80 | trimethyl-propyl-benzene | 45.26 | 0.43 |
| 31 | 1-ethyl-2-isopropyl-benzene | 37.96 | 0.22 | 81 | 1,8-dimethyl-tetraline | 45.30 | 0.18 |
| 32 | 5-methyl indane | 38.21 | 0.03 | 82 | trimethyl-propyl-benzene | 45.42 | 0.53 |
| 33 | 1-butyl-4-methyl-benzene | 38.47 | 0.22 | 83 | 1,2,4-triethyl-benzene | 45.51 | 0.59 |
| 34 | 1-ethyl-2,6-dimethyl-benzene | 38.63 | 0.51 | 84 | 1-ethyl-tetraline | 45.74 | 0.54 |
| 35 | 1-ethyl-3,5-dimethyl-benzene | 38.72 | 1.09 | 85 | trimethyl-indane | 45.83 | 0.12 |
| 36 | 1,4-diethyl-2-methyl-benzene | 38.91 | 0.21 | 86 | trimethyl-propyl-benzene | 45.95 | 0.26 |
| 37 | 1,2,4,5-tetramethyl-benzene | 39.22 | 0.90 | 87 | trimethyl-propyl-benzene | 46.08 | 0.15 |
| 38 | 1-butyl-3-methyl-benzene | 39.28 | 0.10 | 88 | trimethyl-propyl-benzene | 46.18 | 0.60 |
| 39 | 1,2,3,5-tetramethyl-benzene | 39.44 | 1.13 | 89 | trimethyl-propyl-benzene | 46.30 | 0.04 |
| 40 | 1-butyl-2-methyl-benzene | 39.53 | 0.06 | 90 | trimethyl-indane | 46.36 | 0.03 |
| 41 | 1,1-dimethyl-indane | 39.82 | 0.07 | 91 | trimethyl-indane | 46.40 | 0.35 |
| 42 | 1,3-dimethyl-4-isopropyl-benzene | 40.01 | 0.05 | 92 | trimethyl-indane | 46.49 | 0.82 |
| 43 | 1-ethyl-2,4,5-trimethyl-benzene | 40.25 | 0.09 | 93 | C ₆ -benzene | 46.53 | 0.35 |
| 44 | 1,3-dimethyl-5-isopropyl-benzene | 40.32 | 0.46 | 94 | C ₆ -benzene | 46.67 | 0.16 |
| 45 | 1,6-dimethyl indane | 40.39 | 0.37 | 95 | hexamethylbenzene | 46.81 | 0.46 |
| 46 | 1-methyl-4-(1-methyl-propyl)-benzene | 40.66 | 0.57 | 96 | dimethyl-tetraline | 47.00 | 0.72 |
| 47 | terbutyl-benzene | 40.74 | 1.19 | 97 | dimethyl-tetraline | 47.19 | 0.64 |
| 48 | 1,5-dimethyl indane | 40.97 | 0.52 | 98 | dimethyl-tetraline | 47.28 | 0.51 |
| 49 | 1,2,3,4-tetramethyl-benzene | 41.09 | 2.33 | 99 | C ₆ -benzene | 47.49 | 0.26 |
| 50 | 1,3-diethyl-2-methyl-benzene | 41.33 | 0.82 | 100 | C ₆ -benzene | 47.69 | 0.21 |
| | | | | 101 | C ₆ -benzene | 47.77 | 0.66 |
| | | | | 102 | C ₆ -benzene | 47.86 | 0.15 |
| | | | | 103 | dimethyl-tetraline | 47.92 | 0.64 |
| | | | | 104 | trimethyl-indane | 48.08 | 0.22 |
| | | | | 105 | trimethyl-indane | 48.22 | 0.60 |
| | | | | 106 | C ₆ -benzene | 48.38 | 0.12 |
| | | | | 107 | trimethyl-indane | 48.52 | 0.19 |
| | | | | 108 | trimethyl-indane | 48.62 | 0.18 |
| | | | | 109 | trimethyl-indane | 48.74 | 0.17 |
| | | | | 110 | trimethyl-indane | 48.84 | 0.09 |

| | | | |
|-----|-------------------------|-------|------|
| 111 | C ₆ -benzene | 48.98 | 0.97 |
| 112 | ethyl-tetraline | 49.04 | 0.23 |
| 113 | dimethyl-tetraline | 49.18 | 0.42 |
| 114 | dimethyl-tetraline | 49.35 | 0.37 |
| 115 | dimethyl-tetraline | 49.48 | 0.34 |
| 116 | C ₆ -benzene | 49.63 | 0.31 |
| 117 | trimethyl-tetraline | 49.69 | 0.14 |
| 118 | trimethyl-tetraline | 49.90 | 0.70 |
| 119 | trimethyl-tetraline | 50.02 | 0.13 |
| 120 | C ₆ -benzene | 50.10 | 0.27 |
| 121 | trimethyl-tetraline | 50.20 | 0.28 |
| 122 | trimethyl-tetraline | 50.40 | 0.27 |
| 123 | trimethyl-tetraline | 50.44 | 0.17 |
| 125 | C ₆ -benzene | 50.56 | 0.30 |
| 126 | trimethyl-tetraline | 50.69 | 0.67 |
| 127 | C ₇ -benzene | 50.84 | 0.10 |
| 128 | C ₇ -benzene | 51.09 | 0.52 |
| 129 | trimethyl-tetraline | 51.26 | 0.18 |
| 130 | trimethyl-tetraline | 51.45 | 0.35 |
| 131 | trimethyl-tetraline | 51.60 | 0.22 |
| 132 | trimethyl-tetraline | 51.73 | 0.24 |
| 133 | trimethyl-tetraline | 51.88 | 0.08 |
| 134 | trimethyl-tetraline | 51.94 | 0.05 |
| 135 | trimethyl-tetraline | 52.01 | 0.11 |
| 136 | trimethyl-tetraline | 52.18 | 0.44 |
| 137 | trimethyl-tetraline | 52.44 | 0.28 |
| 138 | trimethyl-tetraline | 52.55 | 0.13 |

TABLE A2
Diaromatic and aro-S sub-fraction

| Index | Compound | RT (min) | Wt%* |
|-------|---------------------------------|----------|------|
| 1 | naphthalene | 42.55 | 0.58 |
| 2 | 2-methyl naphthalene | 47.82 | 1.31 |
| 3 | 1-methyl naphthalene | 48.59 | 1.23 |
| 4 | 2,5-dimethyl-benzothiophene | 51.97 | 0.05 |
| 5 | 2-ethyl-naphthalene | 52.21 | 0.20 |
| 6 | 1-ethyl-naphthalene | 52.37 | 0.10 |
| 7 | 2,6- & 2,7-dimethyl naphthalene | 52.68 | 0.39 |
| 8 | 2,7-dimethyl-benzothiophene | 53.02 | 0.09 |
| 9 | 1,3-dimethyl naphthalene | 53.30 | 0.35 |
| 10 | 1,6-dimethyl naphthalene | 53.44 | 0.26 |
| 11 | 2-ethyl-benzothiophene | 53.64 | 0.13 |
| 12 | 1,4- & 2,3-dimethyl naphthalene | 54.13 | 0.06 |
| 13 | 1,5-dimethyl naphthalene | 54.27 | 0.06 |
| 14 | 1,2-dimethyl naphthalene | 54.77 | 0.03 |
| 15 | propyl-naphthalene | 56.13 | 0.01 |
| 16 | isopropyl-naphthalene | 56.51 | 0.01 |
| 17 | isopropyl-naphthalene | 56.82 | 0.01 |
| 18 | trimethyl naphthalene | 57.02 | 0.01 |
| 19 | trimethyl naphthalene | 57.50 | 0.01 |

* Wt%: weight abundance in the 250₂ aromatic fraction. Proportions were calculated by GC-FID. Integration was carried out using peak area values in comparison to internal standard with relative response factors correction.