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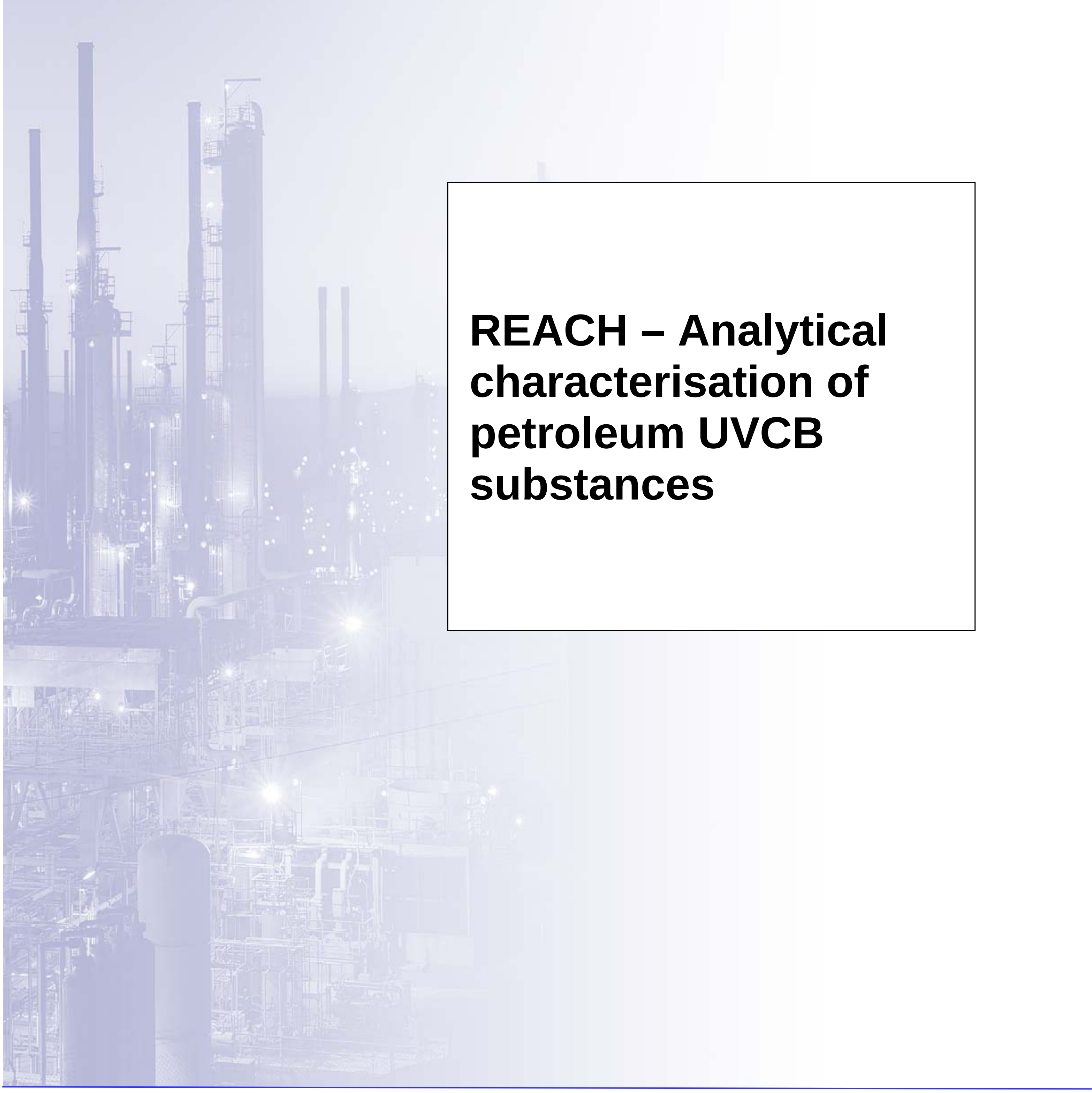

REACH – Analytical characterisation of petroleum UVCB substances

conservation of **c**lean **a**ir and **w**ater in **e**urope

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REACH – Analytical characterisation of petroleum UVCB substances

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ABSTRACT

The purpose of this report is to summarise the findings of the scientific and technical work undertaken by CONCAWE to assess the feasibility and potential benefit of characterising petroleum UVCB[1] substances beyond the recommendations issued by CONCAWE for the substance identification of petroleum substances under REACH.

KEYWORDS

UVCB, petroleum substances, REACH, substance characterisation, substance identity, analytical techniques, ultra-violet spectroscopy, infra-red spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, high-pressure liquid chromatography, gas chromatography.

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

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[1] **Substances of U**nknown or **V**ariable **C**omposition, **C**omplex reaction products or **B**iological materials

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SUMMARY

The purpose of this report is to summarise the findings of the scientific and technical work undertaken by CONCAWE to assess the feasibility and potential benefit of characterising petroleum UVCB substances beyond the recommendations issued by CONCAWE for the substance identification of petroleum substances under REACH.

The report is based on Member Company experience of the chemical analysis of petroleum UVCB substances, including analysis in support of REACH registrations undertaken in 2010.

This report is structured into four main sections, namely:

Section 1: provides an introduction to the subject of petroleum UVCB substance identification including the purpose of the report, regulatory requirements, the nature of petroleum UVCB substances, and CONCAWE’s guidance to Member Companies and other potential registrants.

Section 2: provides a description of the capabilities of each of the analytical techniques described in REACH Regulation (EC) No 1907/2006 Annex VI item 2. This section also includes details on the type of analytical information obtained by each technique and an evaluation of what each technique can provide for the characterisation of petroleum UVCB substances.

Section 3: provides a series of case studies for six petroleum substance categories (low boiling point naphthas, kerosines, heavy fuel oils, other lubricant base oils, residual aromatic extracts and bitumens) to illustrate the value of the information derived from each analytical procedure, and provide an explanation for why some techniques are not scientifically necessary.

Section 4: provides a summary of the conclusions reached from the technical investigations undertaken by CONCAWE Member Companies, and summarising the recommendations issued by CONCAWE for the substance identification of petroleum substances, per substance category, under REACH.

1. REACH REQUIREMENTS FOR SUBSTANCE CHARACTERISATION

The requirements for the identification of substances are documented in REACH Regulation (EC) No 1907/2006 Annex VI item 2, which includes general information and certain key principles for substance identification. In addition, ECHA has presented webinars and published guidance documents for substance identification and posted the information on its website. ECHA has also issued guidance in 2007 (updated in 2012) for the identification and naming of substances under REACH [1] and additional guidance in 2011 during the development of this report by CONCAWE (see list below):

- HelpNet Webinar on Joint Submission – member registrants (28 and 29 April 2010)
- Identifying the substance - Dossier preparation by a member registrant (April 2010)
- Questions and answers on inquiry and substance identification (ECHA-11-QA-02-EN) (June 2011)

The REACH regulation (Annex VI, item 2) states that "For each substance, the information given in this section shall be sufficient to enable each substance to be identified. If it is not technically possible or if it does not appear scientifically necessary to give information on one or more of the items below, the reasons shall be clearly stated."

Annex VI item 2 lists some eighteen sub-items to be considered for the identification of a substance and refers to specific analytical information requirements, namely:

Item 2.3.5. Spectral data (ultra-violet, infra-red, nuclear magnetic resonance or mass spectrum).

Item 2.3.6. High-pressure liquid chromatogram, or gas chromatogram [1].

1.1. NATURE OF PETROLEUM UVCB SUBSTANCES

Petroleum substances such as gasoline, kerosine, diesel fuel, lubricants and bitumen are manufactured from crude oil using a range of refining processes including distillation, cracking, isomerisation, reforming, alkylation and hydrodesulphurisation. However, refineries use a variety of process plants operating under different conditions and the chemical composition of crude oil feedstocks varies widely, so the type and quantities of different hydrocarbons present in output streams from the same manufacturing processes can vary both within and between refineries. These streams may be blended to yield final products which satisfy the required specifications (e.g., EN 228 [2], EN 590 [3], Def Stan 91-91 [4]) many of which are based on physico-chemical characteristics (e.g. density, vapour pressure) rather than chemical composition, so it is inevitable that the hydrocarbon composition of most petroleum substances is not constant and they are therefore defined as UVCB substances.

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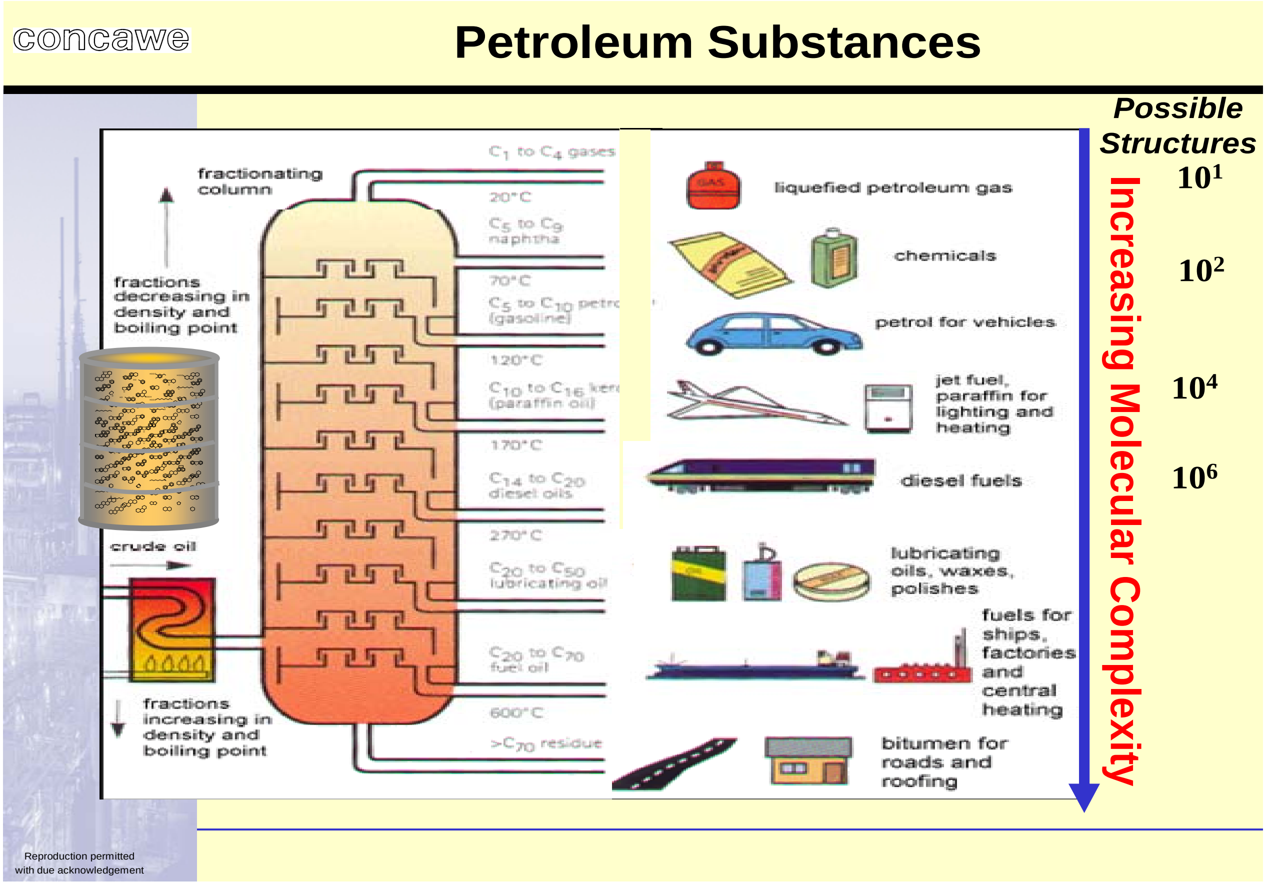
[1] According to the June 2011 guidance entitled “Questions and answers on inquiry and substance identification (ECHA-11-QA-02-EN)” registrants are guided to provide either a High Pressure Liquid Chromatogram or a Gas Chromatogram.

As shown in the figure below, the lightest petroleum substances, such as LPG, are composed of relatively few hydrocarbon components but with increasing carbon number the complexity increases exponentially such that naphthas (~C_4-C_{12} range hydrocarbons) contain a few hundred individual compounds and kerosines (~C_9-C_{16} range hydrocarbons) contain several thousand components. Gas oils contain hundreds of thousands of components and the heavier refinery products (e.g. lubricating oils; heavy fuel oils; bitumen) are considered to contain many millions of individual chemical compounds. The rapid increase in complexity with carbon number arises from the vast number of isomers encountered in hydrocarbon chemistry but increased carbon number can also lead to increased chemical functionality (e.g. the presence of aromatic species in molecules containing six or more carbon atoms), and the higher molecular weight components can even contain several different chemical functionalities (e.g. naphthenic, aromatic, paraffinic, etc.,).



1.2. CONCAWE GUIDANCE ON SUBSTANCE IDENTIFICATION FOR REACH

Based on the REACH Annex VI item 2 requirements, knowledge of standard petroleum industry test methods, and the available guidance on the topic published by ECHA, CONCAWE developed general guidance for member companies and other SIEF members on analytical information to be included in Sections 1.2 and 1.4 of IUCLID5 files for registration of petroleum UVCB substances under REACH.

This guidance encouraged the use of standard industry methods for characterising petroleum UVCB substances because these methods have been developed and validated by the petroleum industry, and are accepted by the competent authorities and customers because they provide a strong technical basis for confirming consistent product quality and assessing potential health, safety and environmental hazards associated with these materials. **Appendix 1a** illustrates the vast number and range of standard methods issued by the Energy Institute (formerly the Institute of Petroleum or IP), the UK professional body for the energy industry and one of several national or global organisations maintaining standard methods for petroleum substances. Many of these methods are harmonised with those of other organisations (e.g. ASTM, DIN, EN, ISO etc.) and methods are continually being developed, reviewed, updated or deleted depending on industry sector requirements and measurement technologies available. **Appendix 1b** lists the standard methods considered most relevant by CONCAWE for the characterisation of petroleum UVCB substances for REACH.

The CONCAWE guidance confirmed that analytical data should be based on a spot sample of the production or imported substance to provide the following general information as required by Section 4.3.2.2 of the ECHA Guidance for identification and naming of substances under REACH [1]:

- Source/feedstock (IUCLID5 section 3.1 Technological process – Methods of manufacture)
- Refining history (IUCLID5 section 3.1 Technological process – Methods of manufacture)
- Boiling range (IUCLID5 section 1.4 Analytical information)
- Carbon number range (IUCLID5 section 1.4 Analytical information)
- Identification and concentration of any known constituents present at 10% or greater (IUCLID5 section 1.2 Composition)
- Identification and concentration of any constituents relevant for hazard classification (i.e. concentration of any ‘marker’ constituents identified for the Category) (IUCLID5 section 1.2 Composition)
- Identification and concentration of any constituents relevant for PBT assessment (IUCLID5 section 1.2 Composition)
- Identification of any stabilising additives known to be present (IUCLID5 section 1.2 Composition)
- Unknown constituents identified by generic description of their chemical nature (IUCLID5 section 1.2 Composition)
- Chromatographic or spectral information, as appropriate, to substantiate the information reported on composition (IUCLID5 section 1.4 Analytical information).
- Flash point and viscosity measurements may also be necessary data for IUCLID5 section 1.4 on analytical information in order to ensure appropriate hazard classification for particular categories.

It was recognized that both the REACH regulation and the ECHA guidance allow for the possibility to waive data for the methods included in Annex VI to REACH on the basis of technical feasibility or scientific justification. CONCAWE guidance recommended the provision of analytical information considered sufficient to identify petroleum substances and ensure assignment within the appropriate Petroleum Substance Category, for the purposes of hazard classification and risk assessment. Registrants were recommended to enter in Subsection 1.4 of the IUCLID dossier a waiving statement for the spectral or chromatographic methods not applied as they were not considered scientifically necessary to identify the substance.

2. DESCRIPTION OF ANALYTICAL TECHNIQUES CONTAINED IN REACH REGULATION (EC) NO 1907/2006 ANNEX VI

This section provides some background information on each of the analytical techniques specified in the REACH Regulation and their use for the chemical characterisation of petroleum UVCB substances. In general, the spectroscopic techniques only provide information on the chemical functionality of the bulk sample and do not discriminate between the individual components present in a complex material such as a petroleum UVCB substance. Chromatographic techniques provide some discrimination between the components present although the extent of discrimination is determined both by the relative complexity of the substance under investigation (see Section 3) and by the resolving power of the specific chromatographic technique. It is for these reasons that spectroscopic and chromatographic techniques usually provide complementary information on the chemical composition of a substance and in some cases are physically linked (e.g. gas chromatography-mass spectrometry) to benefit from the synergy offered by such combinations.

2.1. SPECTROSCOPIC TECHNIQUES

2.1.1. Ultra-Violet (UV) Spectroscopy

This technique is used to determine the presence of unsaturated bonds, such as olefinic and aromatic bonds, ketonic and heteroatom groups, which absorb radiation in the commonly measured 190-400 nm range arising from electronic transitions within molecules. In the case of aromatic hydrocarbons the wavelengths of the UV absorbance maxima are determined by the nature of the aromaticity; increasing conjugation means that less energy is required for the electronic transitions and results in absorbance at progressively higher wavelengths.

Wavelength	Hydrocarbon functionality
190-210 nm	mono-aromatics
220-230 nm	di-aromatics
250-275 nm	tri and tri+ aromatics

Absorbance intensity is particularly strong for components where the unsaturated bonds are conjugated, such as in aromatic hydrocarbons, and UV spectroscopy is therefore particularly sensitive for the measurement of these compounds. For relatively pure substances or multi-component substances where the component of interest has a particularly intense chromophore, the technique can be used for quantitative analysis and purity assessment. However, UV spectroscopy is more commonly used in a qualitative fashion to indicate the presence/absence of unsaturated compounds. UV spectroscopy is usually carried out using either a dilute solution of the sample in a suitable (non-absorbing) solvent, or directly on the sample using a short path-length measurement cell.

Applicability of UV Spectroscopy to petroleum UVCB substances

In the case of petroleum UVCB substances, UV spectroscopy yields limited information because the spectra obtained are somewhat similar for most products and typically show a strong absorbance at wavelengths below 250-300 nm. This arises from the very strong UV absorbance of aromatic and olefinic hydrocarbons, so even petroleum substances containing very low concentrations (ppm levels) of these components will produce a spectrum showing a strong absorption band. Moreover, UV spectroscopy typically yields broad, unresolved bands owing to the various vibrational and rotational energy levels associated with each electronic transition state so the wavelength resolution is insufficient to differentiate between absorbances arising from aromatic or olefinic components present in the substance.

2.1.2. Infra-Red (IR) Spectroscopy

IR spectroscopy can determine the presence or absence of particular functional groups which absorb radiation at various frequencies in the commonly measured 400-4000 cm^{-1} range through the bending and stretching of bonds within molecules. It can be used to tell whether substances are saturated, unsaturated or aromatic and, because many functional groups including amines, carbonyls and alcohols can be identified by their characteristic vibration frequencies, IR spectroscopy is often used for characterising relatively pure compounds.

Wavelength	Bond type	Functionality
4000-2500 cm^{-1}	single bonds with light atoms	C-H; O-H; N-H
2500-2000 cm^{-1}	triple bonds	C≡C; C≡N
2000-1500 cm^{-1}	double bonds	C=C; C=O; C=N
1500-400 cm^{-1}	most single bonds	C-C; C-O; C-N; C-halogen

The low-energy region of the spectrum (400-1500 cm^{-1}) is known as the “fingerprint” region because it is particularly characteristic for each compound and can therefore be useful for assessing the purity of simple substances. As for UV spectroscopy, IR spectroscopy of liquid substances is usually carried out either as a dilute solution in a suitable (non-absorbing) solvent or directly using a short path-length measurement cell. Samples can also be examined directly by attenuated total reflectance measurements.

Applicability of IR Spectroscopy to petroleum UVCB substances

For petroleum substances, IR spectroscopy is mainly used in a qualitative fashion to indicate the presence or absence of specific hydrocarbon functionalities such as alkyl or aryl groups. However, as shown in Appendices 2.2, 3.2, 4.2, 5.2, 6.2 and 7.2, many different petroleum UVCB substances yield very similar IR spectra and, because the absorbance bands corresponding to unsaturated hydrocarbons are weaker than those associated with saturated hydrocarbons, it does not always provide a good estimate of the degree of aromaticity present in petroleum UVCB substances.

2.1.3. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR provides structural information by showing the environment in which certain atomic nuclei are located. Such nuclei can be energised by application of an external magnetic field and transitions (i.e. resonance) between different energy levels can then be induced by application of radio-frequency energy, the exact frequency of which will only cause transitions in those nuclei located in specific molecular environments. Because both ^{1}H and ^{13}C nuclei give NMR signals, the technique is valuable for elucidating the structure of organic compounds but only ~1% of the carbon present exists as ^{13}C (the remainder is ^{12}C, which gives no NMR signal) so ^{1}H NMR is a much more sensitive technique.

Because the magnetic field of each NMR spectrometer is different, an instrument-independent way to measure the position of resonance lines, called the chemical shift, is required and this is expressed in parts per million (ppm) corresponding to the difference between the actual resonance frequency and a reference frequency (in Hz), divided by the reference frequency itself (in MHz). The tables below show how chemical shift values can be used to determine the positions of hydrogen and carbon atoms in a molecule and it is therefore possible to use NMR to elucidate the molecular structure of simple substances.

^{1}H NMR

Chemical shift	**Proton type**	**Environment**
0.9 ppm	primary	$\text{R-C}\mathbf{H}_3$
1.3 ppm	secondary	$\text{R}_2\text{C}\mathbf{H}_2$
1.5 ppm	tertiary	$\text{R}_3\text{C-}\mathbf{H}$
2.0-4.0 ppm	benzylic	$\text{Ar-C-}\mathbf{H}$
4.6-5.9 ppm	olefinic	$\text{C=C-}\mathbf{H}$
6.5-8.5 ppm	aromatic	$\text{Ar-}\mathbf{H}$

^{13}C NMR

Chemical shift	**Carbon type**	**Environment**
9-60 ppm	alkyl	
14 ppm	terminal methyl	$\mathbf{C}\text{H}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$
19 ppm	internal methyl	$\text{-CH}_2\text{-CH(}\mathbf{C}\text{H}_3\text{)-CH}_2\text{-}$
23 ppm	methylene	$\text{CH}_3\text{-}\mathbf{C}\text{H}_2\text{-CH}_2\text{-CH}_2\text{-}$
30 ppm	methylene	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-(}\mathbf{C}\text{H}_2\text{)}_n\text{-}$
32 ppm	methylene	$\text{CH}_3\text{-CH}_2\text{-}\mathbf{C}\text{H}_2\text{-CH}_2\text{-}$
35-45 ppm	branched and cyclic	
100-130 ppm	aromatic (tertiary) and olefinic (tertiary and secondary)	
130-150 ppm	aromatic and olefinic (quaternary)	

Other nuclei which generate signals include ^{19}F, ^{29}Si and ^{31}P although these have little relevance for characterising petroleum UVCB substances which consist predominantly of hydrocarbons. In addition to providing detailed structural information, including discriminating between certain isomers, NMR provides quantitative information on the different types of nuclei present (e.g. CH, CH_2 and CH_3 protons) and is therefore also employed for assessing the purity of simple substances. A range of signal enhancement techniques can also be used to provide greater discrimination and more structural information about the substance under investigation. The majority of NMR measurements are carried out on solutions of the test substance in a deuterated (^{2}H) solvent such as deuterochloroform. Modern high-field instruments (e.g. 500 MHz) enable most proton NMR spectra to be obtained within a few minutes whereas it may take several hours to obtain a carbon NMR spectrum owing to the relatively small quantity of ^{13}C present in the sample. Although interpretation of complex NMR spectra requires considerable expertise, extensive libraries of reference spectra and predictive computer programs facilitate the routine identification of simple substances.

Applicability of NMR Spectroscopy to petroleum UVCB substances

NMR cannot discriminate between different constituents in a petroleum UVCB substance and the information obtained, whether qualitative or quantitative, therefore refers to the bulk sample. Moreover, the complexity of these substances is such that it is not possible to resolve all the signals in the NMR spectrum nor assign them to specific nuclear resonances and couplings and, as shown in Appendices 2.3, 3.3, 4.3, 5.3, 6.3 and 7.3, many different petroleum UVCB substances yield very similar NMR spectra. However, some signals can be assigned to specific groups of ^{1}H and ^{13}C nuclei present and, although this information does not permit identification of individual constituents present in the sample, it provides accurate quantitative information on the total quantities of some chemical functionalities present. For example and as described in Case Studies 2 and 4, the values for total aromatic content of the kerosine and base oil samples determined by ^{13}C NMR and HPLC are in good agreement when the NMR value for aromatic carbon content is adjusted to reflect the carbon number distribution of the constituents present in these samples.

2.1.4. Mass Spectrometry (MS)

MS is a powerful technique for establishing the identity of substances by providing information on their molecular structure from measuring both the mass of the parent molecule and the masses and relative abundances of fragments that occur when the molecules break up. There are numerous variants of MS but all incorporate an ion source in which the analyte is ionised and fragmented to provide charged species which can then be separated by deflection in electric, radio or magnetic fields before being detected by an ion collector. Direct sample introduction (e.g. by heated probe) is frequently used in MS and is well suited for the examination of single component or relatively pure mono-constituent substances, but for the analysis of complex mixtures it is better to couple MS with an efficient separation technique, such as gas chromatography (GC) or high-performance liquid chromatography (HPLC), in order to facilitate identification of the components present. Although MS is mainly used for qualitative purposes, GC-MS and HPLC-MS can yield accurate quantitative information but this usually requires calibration standards of each analyte because instrument response can vary considerably between different chemical functionalities.

Molecular spectroscopic techniques, such as IR, NMR and MS, have extensive on-line spectral libraries of pure mono-constituent compounds against which a spectrum of an unknown substance can be compared for identification purposes. Such libraries are extremely helpful for MS investigations and the search engines will usually provide probability indicators to show how well the spectrum of an unknown substance compares with the library spectra of supposedly identical/similar substances.

Applicability of MS to petroleum UVCB substances

As indicated above, MS data obtained by direct analysis of a petroleum UVCB substance, in which all constituents are ionised and fragmented simultaneously, would be too complex to allow meaningful interpretation. Spectral libraries typically contain MS data obtained on single constituent or relatively pure simple substances and therefore have little value for characterising UVCB substances unless it is possible to separate the constituents present before generating the spectroscopic data, which can sometimes be achieved by GC-MS or HPLC-MS. In addition to the complexity of the spectra obtained for petroleum UVCB substances, the relatively poor molecular ionisation of many hydrocarbon constituents limits the value of MS for the comprehensive characterisation of these materials. Moreover the degree of ionisation can differ considerably depending on the chemical functionalities present in the substances (e.g. aromatic species are more readily ionised than saturated constituents), and with the relative molecular mass of a particular class of constituents. It is also unable to discriminate between hydrocarbon isomers and can therefore only provide limited information on constituents typically found in petroleum UVCB substances.

2.2. CHROMATOGRAPHIC TECHNIQUES

2.2.1. Gas Chromatography (GC)

GC is used to separate multi- constituent and complex substances and thus provide information on the number, and to some extent the nature, of constituents present. GC is mainly used to separate lipophilic (non-polar) constituents and the separation is highly dependent on the relative volatility of the constituents present. Constituents are separated as they are carried in a gas stream through columns packed or coated with special adsorbent materials and constituents are detected as they elute from these columns using universal (e.g. flame ionisation) or selective (e.g. MS, electron capture) detection systems.

Although GC can be used in a semi-qualitative fashion by retention matching against known substances (i.e. comparison of elution times), it is more widely used for accurate quantitative analysis of the constituents present in a substance. Concentrations of both major or minor constituents (e.g. impurities) can be measured providing calibration standards are available and GC can therefore provide a comprehensive description of the constituents of a substance together with information on its purity. Samples for GC examination are usually dissolved in a suitable solvent and then introduced directly into the separation column although gas samples can be analysed directly. Nowadays most GC analysis is carried out using highly automated instrumentation, sometimes connected on/at-line with a manufacturing process, or operating in relatively remote locations.

Applicability of GC to petroleum UVCB substances

GC is very widely used in the petroleum industry because, as previously indicated, the complexity of the substances encountered means that some separation of the constituents present is normally required to characterise these materials. Moreover, the flame ionisation detector (FID) is an excellent universal hydrocarbon detector providing an almost linear response to the carbon content of the separated constituents. This enables GC-FID to provide good quantitative information on complex hydrocarbon substances by area normalisation of the separated chromatographic peaks rather than by using a vast number of individual calibration standards.

The lighter petroleum UVCB substances like naphthas and gasoline, which typically contain a few hundred individual constituents in the ~C_4-C_{12} range, can be comprehensively characterised by Detailed Hydrocarbon Analysis (DHA) GC or Reformulyzer-GC analysis. DHA uses temperature-programmed, high-resolution, capillary column GC analysis to resolve all the hydrocarbons present such that each individual constituent can be identified (by retention matching) and quantified. Reformulyzer-GC analysis is a multi-dimensional chromatographic technique in which a series of special column-coupling and column-switching procedures are employed to separate the constituents into different hydrocarbon groups (e.g. n-alkanes; iso-alkanes; cyclo-alkanes/naphthenes; aromatics) prior to final resolution of the individual constituents. By modifications to the instrument configuration and operating conditions it is possible to optimise the separation depending on the specific characteristics of the petroleum substance under investigation. DHA-GC and Reformulyzer-GC are unable to resolve the many thousands of constituents present in the heavier middle-distillate petroleum substances, such as kerosine (~C_9-C_{16} range hydrocarbons) and diesel fuel (~C_{11}-C_{25} range hydrocarbons).

The more recently developed technique of comprehensive two-dimensional GC (GCxGC) can provide detailed compositional information on these more complex petroleum substances although it should be noted that even this technique cannot provide total separation of all the constituents present. GCxGC involves separation using two GC columns, each having different properties. The constituents eluting from the first column are repeatedly trapped and introduced onto the second column so the whole sample is subjected to two independent (“orthogonal”) GC separations, which gives greatly enhanced separation of the numerous constituents present. For petroleum substances the first-dimension separation is usually based on the relative volatility of the constituents present (i.e. carbon number) and the second dimension separation on their relative polarity (i.e. chemical functionality), so it is possible to provide quantitative information on the different hydrocarbon types (e.g. alkanes, naphthenes, aromatics, naphthenic-aromatics etc) for each carbon number present. GCxGC can therefore provide detailed compositional analysis information on middle-distillate petroleum UVCB substances but the upper temperature limit of the second column used for the polarity separation currently limits its application to substances containing <$C_{30\text{-}35}$ hydrocarbons. Although GCxGC is capable of separating highly complex mixtures, considerable effort and expertise is required to develop GCxGC methodologies for specific substances. At present there are no petroleum industry standard methods which employ GCxGC and most petroleum analysis laboratories do not currently have this capability.

Simulated Distillation (SIMDIS) GC is a specific type of GC frequently used to screen middle-distillate and heavier petroleum substances and provide information of their boiling range and carbon number distribution. In essence the technique involves analysing a sample by temperature-programmed GC on a high-temperature, non-polar separation column which basically separates constituents in order of their relative volatility. The system is calibrated by analysing a mixture of n-alkane standards, with known boiling points, on the same column under the same operating conditions and relative carbon numbers can then be obtained for the hydrocarbon constituents present in the petroleum UVCB substance. Although the technique is unable to resolve the multitude of individual constituents present in most UVCB petroleum substances, SIMDIS-GC provides a good estimate of the boiling range and carbon number distribution.

2.2.2. Liquid Chromatography (LC)

LC is predominantly used to separate hydrophilic (polar) constituents and the separation is highly dependent on the relative polarity of the constituents present rather than on their relative volatility. It is therefore more widely used in the life sciences and pharmaceutical industries than in the petroleum industry. Substances are separated as they are carried in a liquid stream through columns packed with special adsorbent materials and constituents are detected as they elute from these columns using universal (e.g. refractive index) or selective (e.g. fluorescence) detection systems.

High-performance liquid chromatography (HPLC) is mostly used for accurate quantitative analysis of the constituents present in a substance. Concentrations of both major or minor constituents (e.g. impurities) can be measured providing calibration standards are available and HPLC can therefore provide information on the purity of a substance. Samples for HPLC examination are usually dissolved in a suitable solvent and introduced directly into the separation column and, as with GC, much HPLC analysis is nowadays carried out using highly automated instrumentation.

Applicability of LC to petroleum UVCB substances

LC is used in a variety of ways for the characterisation of petroleum UVCB substances. In some cases the separated constituents are detected and quantified directly, such as the measurement of aromatic hydrocarbon types in middle distillate fuels by normal-phase HPLC with refractive index detection where the mono-, di- and tri-aromatic hydrocarbon groups are separated and then quantified using appropriate calibration standards. In other cases LC is used to fractionate different classes of constituents prior to off-line quantification, such as the measurement of saturated and aromatic hydrocarbons in base oils where, following separation, the LC solvent is evaporated from the two fractions and the quantities of saturated and aromatic hydrocarbons determined by gravimetric analysis.

For hydrocarbons, HPLC generally provides greater selectivity between the different classes of constituents than GC, but much poorer resolution of the constituents within a class than GC. However, both HPLC and the more recently developed ultra-performance liquid chromatography (UPLC) give much higher resolution than is possible with the open-column LC separations still widely used in the petroleum industry for isolating different classes of compounds.

Thin-layer chromatography (TLC) is a variant of LC in which the chromatographic adsorbent is immobilised on a plate rather than in a column and the constituents are separated as they are carried in a liquid stream which migrates through the adsorbent by capillary action. A specialised form of TLC widely used for bitumen examination involves separation on silica rods with successive developments using mobile phases of increasing polarity. Following separation the rods are examined in a specialised instrument which passes the rods through a FID to measure the quantities of saturates, aromatics, resins and asphaltenes present in the bitumen.

Supercritical fluid chromatography (SFC) is very similar to HPLC except that it employs a supercritical fluid (usually carbon dioxide) as the mobile phase rather than conventional organic solvents. By holding carbon dioxide above its supercritical pressure and temperature it exhibits properties intermediate between a liquid and a gas with good solvating power and high diffusivity, which make it a good chromatographic mobile phase. Moreover, replacement of organic solvents with carbon dioxide facilitates the use of FID, an excellent universal hydrocarbon detector, which is not possible with HPLC. Although SFC is little used by European petroleum analysis laboratories, in which HPLC is the preferred technique for the measurement of aromatic hydrocarbons in middle distillate fuels, it is widely employed in the USA, as illustrated by the existence of an industry standard method for this analysis [2].

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[2] ASTM D5186-03(2009) : Standard Test Method for Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography.

3. CASE STUDIES

In general, characterisation of petroleum substances has focused on the measurement of physico-chemical properties and specific chemical constituents or markers (e.g. benzene, PAHs, etc.,) which are critical to the performance and safe use of the materials. As described in Section 2, detailed characterisation of the lighter petroleum UVCB substances (e.g. LPG, naphthas) is possible using GC, but similar characterisation of the heavier substances (e.g. lubricating base oils; heavy fuel oils; bitumen) is not currently possible by any of the techniques described. Consequently most of the analytical information which can be generated on these heavier materials relates to the concentrations of particular classes of constituents present (e.g. olefins; di-aromatics etc) rather than to individual constituents. As shown in the CONCAWE guidance paper entitled “Guidance on analytical requirements for petroleum UVCB substances” [1], many industry standard methods have been developed for this purpose.

Characterisation of many petroleum substances relies on obtaining complementary information from different analytical techniques. Some techniques provide a considerable amount of information while other approaches yield little, if any, further information. CONCAWE therefore proposes that a structured approach to chemical characterisation be employed depending on the specific petroleum UVCB substance under investigation rather than examining all substances using a standard suite of analytical techniques, such as those listed in Annex VI of the REACH Regulation. To illustrate the value of such an approach and show why some of the analytical techniques listed in Annex VI of the REACH Regulation are not scientifically necessary, case studies are presented below for six specific petroleum UVCB substance categories (low boiling point naphthas; kerosines; heavy fuel oil components; other lubricant base oils; residual aromatic extracts; bitumen). Although only six categories are addressed in this report, the evidence presented is also applicable to the other categories of petroleum UVCB substances.

3.1. CASE STUDY 1: LOW BOILING POINT NAPHTHAS

Spectroscopic and chromatographic information obtained on a full-range, straight-run naphtha sample (CAS No. 64741-42-0; EINECS No. 265-042-6) are shown in **Appendix 2**. Full-range, straight-run naphtha is a complex combination of hydrocarbons produced by the distillation of crude oil.

DHA-GC provides very detailed information on the chemical composition of the naphtha sample indicating that it contains a complex mixture of aromatic, n-paraffinic, iso-paraffinic, naphthenic and olefinic hydrocarbons distributed over the C_4-C_{10} carbon number range. Almost 200 individual constituents were identified and quantified by this technique and, in the context of the REACH regulation, DHA-GC showed that the naphtha sample contains 1.7% (m/m) benzene, 2.8% (m/m) toluene, 1.0% (m/m) n-hexane, 10.5% (m/m) 2-methylbutane and 11.1% (m/m) n-pentane. SIMDIS-GC confirmed that the boiling range for the full range naphtha is 28.1°C to 137.1°C for the 5% to 95% boiling fraction, but clearly the use of SIMDIS-GC to provide information on the carbon number distribution and boiling range of the naphtha sample is superfluous given that the sample has undergone detailed examination by DHA-GC.

DHA-GC therefore enables us to provide a comprehensive qualitative and quantitative description of the composition of this naphtha sample which, despite being the simplest petroleum UVCB substance in the case studies presented here, still contains 231 individual constituents. None of the other analytical techniques described below provide additional information to that obtained by DHA-GC and it is therefore recommended that GC alone is sufficient for the analytical characterisation of substances in the naphtha category.

The UV/Visible spectrum shows that the sample contains aromatic and/or olefinic hydrocarbons on account of the strong absorbance bands at wavelengths below ~250 nm. This sample was heavily diluted with hexane to give a sample concentration of ~10 ppm prior to measurement. Given that DHA-GC shows this sample contains 7.7% (m/m) aromatics and 0.6% (m/m) olefins, it can be assumed that the UV absorbance results from ~1 ppm aromatic/olefinic hydrocarbons. It is not therefore surprising that virtually every petroleum UVCB substance yields a UV spectrum showing very strong absorbance at wavelengths below ~250 nm. Moreover, this absorbance cannot be attributed to a single chemical constituent but is likely to have resulted from several constituents, possibly with widely varying extinction coefficients, and it is therefore impossible to make any accurate quantitative measurement from the UV spectrum obtained on the naphtha sample.

The IR spectrum provides slightly more information than that obtained by UV spectroscopy in that absorbance bands corresponding to the presence of both saturated and aromatic/olefinic bonds are present. However, as with UV spectroscopy, these bands cannot be attributed to individual constituents and arise from the gross chemical functionalities present in this UVCB substance. Consequently it is not feasible to use IR spectroscopy to obtain information on the type and concentration of hydrocarbon constituents present in this naphtha sample. DHA-GC shows that this sample contains 7.7% (m/m) aromatics, 29.0% (m/m) n-paraffins, 32.5% (m/m) iso-paraffins, 29.9% (m/m) naphthenes and 0.6% (m/m) olefins, but IR spectroscopy can only confirm the presence of saturated and aromatic/olefinic components.

The ^{1}H NMR spectrum provides more information on the composition of the naphtha sample than IR spectroscopy. NMR confirms the presence of saturated, aromatic and olefinic moieties and therefore has the advantage over IR that it can discriminate between aromatic and olefinic functionalities present in a sample. Moreover, NMR is an accurate quantitative technique and the integrated spectrum shows that the vast majority of the measured signal (0.2-2 ppm chemical shift) arises from protons associated with saturated bonds but there is also a low percentage of protons associated with aromatic nuclei (2-4.5 ppm and 6-8 ppm chemical shift) and a trace of olefinic protons (4.5-6 ppm chemical shift). These results therefore do not contribute further to the information obtained on this sample by DHA-GC. Furthermore, care must be taken when interpreting quantitative NMR data because in this case the value for aromatic protons (6-8 ppm chemical shift) refers only to the percentage of hydrogen atoms in the aromatic rings of the molecules present relative to the total hydrogen content of the substance, the hydrogen atoms present in the substituent side chains of the aromatic rings not being included in this chemical shift region.

3.2. CASE STUDY 2: KEROSINES

Spectroscopic and chromatographic information obtained on a kerosine sample (CAS No. 8008-20-6; EINECS No. 232-366-4) are shown in **Appendix 3**. Kerosine is a complex combination of hydrocarbons produced by the distillation of crude oil.

SIMDIS-GC data show that the kerosine sample contains constituents predominantly in the C_8-C_{16} carbon number range and with initial and final boiling points of 99°C and 295°C respectively.

HPLC provides quantitative information on the basic aromatic classes (mono-, di- and tri+) present in the kerosine sample and shows that the vast majority of aromatic constituents are mono-aromatic hydrocarbons:

Mono-aromatic hydrocarbons: 19.1% (m/m)
Di-aromatic hydrocarbons: 1.5% (m/m)
Tri-aromatic hydrocarbons and higher: <0.1% (m/m)

The aggregate concentration of aromatic hydrocarbons is 20.6% (m/m), with the balance comprised of saturated aliphatic hydrocarbons. The HPLC method is not capable of identifying any individual hydrocarbon constituents.

The proton and carbon NMR spectra show that both saturated alkyl chains and aromatic moieties are present in this sample. ^{13}C NMR analysis also shows that the total aromatic carbon content of the sample (i.e. the percentage of carbon atoms in aromatic rings relative to the total carbon content) is 12.4% but, unlike the HPLC value of 20.6%, this value does not include carbon atoms present in substituent side chains of the aromatic rings. As shown by HPLC, the majority of aromatic species present in the kerosine sample are mono-aromatic constituents, each of which contains six aromatic ring carbon atoms. GC analysis shows that the sample has a mean carbon number of $\sim C_{11}$ and, assuming that the aromatic constituents present are distributed proportionally throughout the whole carbon number range, the NMR aromatic value of 12.4% is approximately equivalent to a total aromatic value of $11/6 \times 12.4\% = 22.7\%$ which is consistent with the value of 20.6% determined by HPLC.

The UV/Visible spectrum shows that the sample contains aromatic constituents, based on the absorbance band at 259 nm. However, given that kerosine typically contains several thousand individual constituents (based on the number of possible isomers for the range of carbon numbers represented), amongst which there is a wide range of aromatic constituents, it is inevitable that the extinction coefficients for individual aromatic constituents will vary considerably. Consequently it is not feasible to use UV spectroscopy to obtain a quantitative measurement of the concentration of the total aromatic constituents present in this petroleum UVCB substance.

The IR spectrum indicates that both saturated alkyl chains and aromatic moieties are present. However, as with UV spectroscopy, these bands cannot be attributed to individual hydrocarbon constituents and arise from the gross chemical functionalities present in this complex UVCB substance. Consequently it is not feasible to use IR spectroscopy to obtain a quantitative measurement of the concentration of aromatic and/or saturated hydrocarbons present in the kerosine sample.

In summary, the chromatographic techniques (HPLC and SIMDIS-GC) provide some degree of separation of the several thousand individual constituents present in the kerosine sample, and provide for the quantification of aromatic classes and saturated aliphatic hydrocarbons. In contrast, spectral data (UV, IR, NMR) provide only gross chemical functionalities and no information on individual constituents present in the kerosine. None of the spectroscopic techniques provide any additional information beyond that provided by HPLC. There are no individual constituents in kerosine defined for hazard classification (markers).

In order to identify and quantify the hydrocarbon constituents of petroleum UVCB substances in the middle distillate range and heavier, more advanced analytical techniques are required, beyond those in routine use within the petroleum industry and, in our view, beyond those specified in Annex VI to the REACH regulation. In the case of middle distillate UVCB substances like kerosine, GCxGC analysis with a universal hydrocarbon detector such as FID can provide detailed and comprehensive quantitative information on the chemical composition and has been used to provide input for environmental risk assessments.

3.3. CASE STUDY 3: HEAVY FUEL OIL COMPONENTS

Spectroscopic and chromatographic information obtained on a heavy fuel oil sample (CAS No. 68553-00-4; EINECS No. 271-384-7 are shown in **Appendix 4**. Heavy fuel oil is a complex combination of hydrocarbons obtained from various processes including: the atmospheric distillation of crude oil; residual fraction from the distillation of the products from catalytic cracking or hydrocracking and vacuum distillation of the residuum from the atmospheric distillation of crude oil.

SIMDIS-GC data show that the boiling range of the heavy fuel oil sample is between 264.8°C and 715.3°C for the 5% to 90% boiling fraction; 10% of the sample boils above 715.3°C and its boiling range cannot be quantified. This corresponds to a carbon number range of C_{14}-C_{98} for the 5% to 90% fraction with the 10% higher boiling fraction containing heavier components (>C_{100}).

HPLC shows that the heavy fuel oil sample contains 11.7% (m/m) mono-aromatic, 3.9% (m/m) di-aromatic, and 26.8% (m/m) tri-aromatic and tri-+ hydrocarbons; and by difference 57.6% (m/m) non-aromatic hydrocarbons. From the spectroscopic analysis of the sample, proton NMR shows it to contain aliphatic and olefinic components together with mono- and poly-aromatic moieties whereas the IR spectrum indicates that both saturated alkyl chains and aromatic functionalities are present. However, as with all petroleum UVCB substances, these bands cannot be attributed to individual constituents present in the heavy fuel oil. The UV/Visible spectrum shows that the sample contains aromatic and/or olefinic hydrocarbons on account of the strong absorbance bands at wavelengths below ~300 nm. Given that HPLC analysis indicates that the sample contains 42.4% (m/m) total aromatics, it is not surprising that it had to be heavily diluted with toluene prior to measurement to give a sample concentration of ~40 ppm and this again demonstrates that UV spectroscopy has little value for the characterisation of most petroleum UVCB substances.

SIMDIS-GC therefore provides information on the carbon number distribution and boiling range of heavy fuel oils and HPLC is used to obtain quantitative information on the classes of aromatic hydrocarbons present. NMR can be used to confirm the hydrocarbon functionalities present in the sample but no additional useful information is obtained by UV or IR spectroscopy.

3.4. CASE STUDY 4: OTHER LUBRICANT BASE OILS

Spectroscopic and chromatographic information obtained on a lubricant base oil sample (CAS No. 64742-52-5; EINECS No. 265-155-0) are shown in **Appendix 5**. This lubricant base oil is a complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst.

SIMDIS-GC data show that the base oil sample contains components predominantly in the C_{15}-C_{31} carbon number range and with initial and final boiling points of 304°C and 436°C respectively.

Preparative HPLC shows that the base oil contains 65.4% (m/m) saturated hydrocarbons and 33.4% (m/m) aromatic hydrocarbons, corresponding to a sample recovery of 98.8% (m/m) from the chromatographic fractionation.

The proton and carbon NMR spectra show that both saturated alkyl chains and aromatic moieties are present in this sample. ^{13}C NMR analysis also shows that the total aromatic carbon content of the sample (i.e. the percentage of carbon atoms in aromatic rings relative to the total carbon content) is 9.2% but, unlike the HPLC value of 33.4%, this value does not include carbon atoms present in substituent side chains of the aromatic rings. GC analysis shows that the base oil sample has a mean carbon number of ~C_{23} and, assuming that the majority of aromatic species present are mono-aromatic compounds each containing six aromatic ring carbon atoms and that these are distributed proportionally throughout the whole carbon number range, the NMR aromatic value of 9.2% is approximately equivalent to a total aromatic value of 23/6 x 9.2% = 35.3% which is consistent with the value of 33.4% determined by HPLC.

The UV/Visible spectrum shows that the sample contains aromatic and/or olefinic hydrocarbons on account of the strong absorbance at wavelengths below ~300 nm. However, given that this type of lubricant base oil typically contains millions of individual components including a wide range of aromatic hydrocarbons, it is inevitable that the extinction coefficients for individual aromatic constituents will vary considerably. Consequently it is not feasible to use UV spectroscopy to obtain a quantitative measurement of the concentration of the individual aromatic constituents present in this petroleum UVCB substance.

The IR spectrum indicates that both saturated alkyl chains and aromatic moieties are present. However, as with UV spectroscopy, these bands cannot be attributed to individual hydrocarbon constituents and arise from the gross chemical functionalities present in this complex UVCB substance. Consequently it is not feasible to use IR spectroscopy to obtain a quantitative measurement of the concentration of individual aromatic and/or saturated hydrocarbons present in the base oil sample.

In summary, SIMDIS-GC enables us to define the carbon number distribution and boiling range of the lubricant base oil sample and preparative HPLC provides information on the total aromatic content. ^{13}C NMR can also provide information on the total aromatic content but no additional useful information on the sample is obtained by UV or IR spectroscopy. The classification for the carcinogenicity of the Other Lubricant Base Oils is determined by the application of the IP 346 [5] method (which determines the percentage mass of DMSO extractable constituents in the original oil sample).

3.5. CASE STUDY 5: RESIDUAL AROMATIC EXTRACTS

Spectroscopic and chromatographic information obtained on two residual aromatic extracts (Samples A and B) with the same registry number (CAS No. 64742-10-5; EINECS No. 265-110-5) are shown in **Appendix 6**, this information having been generated independently by separate CONCAWE Member Companies using different analytical methodologies. Residual aromatic extracts are a complex combination of hydrocarbons obtained as the extract from a solvent extraction process (e.g. solvent extraction of vacuum de-asphalted residue).

SIMDIS-GC data were generated on both residual aromatic extract samples. Sample A was found to contain constituents predominantly in the C_{25}-C_{95} carbon number range and with initial and final boiling points of 423°C and 691°C respectively. Sample B contained components covering a similar carbon number range and with initial and final boiling points of 403°C and >750°C, although 98% of the sample had a boiling range of 403°C to 702°C.

Open-column LC was carried out on Sample B to fractionate the components present into four basic functionalities which showed the sample to contain 14.5% (m/m) saturated hydrocarbons, 71.6% (m/m) aromatic hydrocarbons, 13.9% (m/m) polar compounds and <0.1% (m/m) pentane insolubles (asphaltenes).

Sample A was examined by ^{1}H NMR spectroscopy which confirms the presence of aliphatic and aromatic moieties in the sample. ^{13}C NMR analysis also shows that the total aromatic carbon content of the sample (i.e. the percentage of carbon atoms in aromatic rings relative to the total carbon content) is 26.1%. Unlike the aromatic value of 71.6% (m/m) obtained by open-column LC on Sample B, the ^{13}C NMR aromatic value on Sample A does not include carbon atoms present in substituent side chains of the aromatic rings and consequently this value is much lower.

From the UV/Visible spectrum obtained on Sample A it appears that the sample contains aromatic and/or olefinic hydrocarbons on account of the very strong absorbance bands at wavelengths below ~350 nm. Despite the fact that this sample was heavily diluted with dichloromethane and examined using a short path length cell it produced very strong UV absorbance bands in common with all the other petroleum UVCB substances described here. The IR spectrum of the same sample indicates the presence of both saturated and aromatic bonds.

Clearly it is not possible to obtain detailed qualitative and quantitative information on residual aromatic extracts which contain many millions of individual hydrocarbon components. However, SIMDIS-GC enables us to define the carbon number distribution and boiling range of these extracts and the total aromatic content can be measured by LC or NMR. No additional useful information is provided by UV or IR spectroscopy.

3.6. CASE STUDY 6: BITUMENS

Spectroscopic and chromatographic information obtained on two different bitumens, Sample A (CAS No. 8052-42-4; EINECS No. 232-490-9) and Sample B (CAS No. 64741-56-6; EINECS No. 265-057-8), are shown in **Appendix 7**, this information having been generated independently by separate CONCAWE Member Companies using different analytical methodologies. Bitumens are a very complex combination of hydrocarbons obtained as the non-volatile residue from distillation of crude oil or by separation as the raffinate from a residual oil in a deasphalting or decarbonization process.

Information on the boiling range of Sample A was obtained by distillation which showed that the sample has an initial boiling point (atmospheric equivalent temperature) of 380°C and that just over 5% (m/m) of the components present in the sample had distilled over at the final temperature of 511°C (atmospheric equivalent temperature). Sample B was examined by SIMDIS-GC which showed it to contain constituents in the C_{25} to $>C_{100}$ carbon number range and with initial and final boiling points of 439°C and >750°C respectively.

Open-column LC on Sample A provided quantitative information on the major classes of compounds present and indicated that the sample contains 50.3% (m/m) aromatic components and 27.8% (m/m) saturated components together with 21.9% (m/m) polar material (i.e. resins and asphaltenes). Sample B was examined by TLC-FID which showed it to contain 65.4% (m/m) aromatic and 10.6% (m/m) saturated hydrocarbons together with 11.9% (m/m) resins and 12.1% (m/m) asphaltenes.

The proton NMR spectrum obtained on Sample A confirms the presence of aliphatic and aromatic moieties and indicates that no significant concentration of olefinic protons are present. In this case no integration of the signals was made due to severe peak overlaps, which is indicative of the very high complexity of substances such as bitumen. UV spectroscopy on the same sample shows that it contains aromatic and/or olefinic hydrocarbons on account of the strong absorbance band at ~240 nm and, in common with the other substances examined by this technique, the sample had to be very heavily diluted with chloroform (sample concentration 40 ppm) to provide an on-scale spectrum. The IR spectrum of this sample indicates the presence of both saturated and aromatic bonds.

Bitumen is the heaviest and most chemically complex of the petroleum UVCB substance categories containing many millions of individual hydrocarbon constituents. Distillation enables us to determine the boiling range of this substance whereas SIMDIS-GC provides information on the carbon number distribution and boiling range. Quantitative information on the basic chemical classes present in bitumen, such as saturates, aromatics and polar materials, can be obtained by LC or TLC-FID although, given the great complexity of this substance, it should be noted that some individual components contain more than one chemical functionality. NMR is the most useful of the three spectroscopic techniques applied in this examination with no additional useful information being provided by UV or IR spectroscopy.

4. CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations reached from the technical investigation undertaken by CONCAWE to assess the feasibility and potential benefit of characterising petroleum UVCB substances beyond the recommendations issued by CONCAWE (**Table 1**) are summarised below.

CONCAWE has consistently recommended the use of standard industry methods (**Appendix 1**) for characterising petroleum UVCB substances because these methods have been developed and validated by the petroleum industry, and are accepted by the competent authorities and customers because they provide a strong technical basis for confirming consistent product quality and assessing potential health, safety and environmental hazards associated with these materials.

The characterisation of such a diverse range of UVCB substances, ranging from gases to semi-solid bitumens, requires a structured analytical approach tailored to the properties of each substance rather than employing a standard suite of analytical procedures as proposed in the REACH regulation (Annex VI, item 2). For example, the data presented in Case Study 1 for naphthas show that they can be fully characterised by GC and, because no additional compositional information is provided by UV, IR or NMR spectroscopy, these techniques are not considered to be scientifically necessary for their identification. For other petroleum UVCB substances, two or more analytical techniques, each providing complementary information, may be required to characterise them but in these cases some of the techniques specified in the REACH regulation are still considered to be scientifically unnecessary because they provide no additional compositional information to those recommended by CONCAWE, as illustrated in Case Studies 2-6 for kerosines, heavy fuel oils, lubricant base oils, residual aromatic extracts and bitumens. In this context it should be noted that, owing to the increased chemical complexity of these heavier petroleum UVCB substances, it is currently impossible to characterise them to the same level of detail as for the lighter products. However, continued development of novel and more advanced analytical techniques and methodologies will undoubtedly lead to enhanced characterisation of these highly complex substances in the future.

The technical data presented in the appendices to this report also illustrate that there is little, if any, difference between the UV, IR, or NMR spectra obtained on samples from different categories of petroleum UVCB substances, particularly for the heavier materials. This observation is confirmed by investigation of the vast quantity of spectroscopic information generated on other samples by CONCAWE Member Companies and, given this general lack of differentiation both within and between substance categories, provides further justification for waiving these techniques as being scientifically unnecessary for the identification of petroleum UVCB substances.

Based on the information presented in this report it is recommended that a structured analytical approach be employed for the characterisation of petroleum UVCB substances and that the analytical techniques listed in the table below are sufficient to characterise materials in each substance category; it is considered that there is no further benefit in applying the full suite of Annex VI analytical techniques.

Table 1 CONCAWE recommendations for the substance identification of petroleum substances under REACH

Recommended Annex VI Technique	**CONCAWE Product Category**	**Comments**
(i) GC	Petroleum Gases	(i) Full characterisation of components
(i) DHA-GC and/or Reformulyzer-GC	Low Boiling Point Naphthas	(i) Full characterisation of components
(i) SIMDIS-GC or Distillation (ii) HPLC	Kerosines	(i) Carbon number range and/or boiling range (ii) Aromatic classes
(i) SIMDIS-GC or Distillation (ii) HPLC or LC	Swedish Mk1 Diesel Fuel, Straight-Run Gas Oils, Cracked Gas Oils, Vacuum and Hydrocracked Gas Oils and Distillate Fuels, Other Gas Oils	(i) Carbon number range and/or boiling range (ii) Aromatic classes (HPLC) or total aromatics (LC)
(i) SIMDIS-GC (ii) HPLC or LC or NMR	Heavy Fuel Oil Components, Highly Refined Base Oils	(i) Carbon number and boiling ranges (ii) Aromatic classes (HPLC) or total aromatics (LC or NMR)
(i) SIMDIS-GC (ii) LC or NMR	Unrefined/Acid Treated Oils, Foots Oils, Paraffin and Hydrocarbon Waxes, Slack Waxes, Petrolatums, Untreated Distillate Aromatic Extracts, Residual Aromatic Extracts	(i) Carbon number and boiling ranges (ii) Total aromatics
(i) SIMDIS-GC (ii) HPLC or LC	Other Lubricant Base Oils	(i) Carbon number and boiling ranges (ii) Total aromatics
(i) SIMDIS-GC (ii) LC or TLC-FID	Bitumens	(i) Carbon number and boiling ranges (ii) Saturates, aromatics and polars (LC) or saturates, aromatics, resins and asphaltenes (TLC-FID)

Note: In addition to the Annex VI techniques listed above, IP 346 is used for Foot's Oils, Other Lubricant Base Oils and Treated Distillate Aromatic Extracts as a classification marker for the determination of carcinogenicity. Similarly, ASTM E 1687-04 is used as a classification marker for the determination of carcinogenicity for Residual Aromatic Extracts.

5. GLOSSARY

Analyte	The substance that is being analysed.
Asphaltenes	Components of crude oil that are insoluble in n-pentane (at a specific dilution ratio) and re-dissolve in toluene. They consist primarily of carbon, hydrogen, nitrogen, oxygen and sulfur, and have molecular masses in the 400-1500 range.
ASTM	American Society for Testing and Materials
^{13}C	Carbon-13 nuclei used in nuclear magnetic resonance spectroscoy.
CAS	Chemical Abstracts Service
Category	A specific group of petroleum UVCB substances with similar properties and chemical composition (e.g. kerosines).
Chromophore	A group of atoms and bonds in a chemical compound that are responsible for the colour of the compound.
Class	A group containing compounds with the same chemical functionality.
Constituent	Single molecular species
Conjugated	A conjugated system is a system of connected p-orbitals with delocalised electrons in compounds with alternating single and multiple bonds. The compound may be cyclic or acyclic.
Determinant	The property that is being measured by the analytical method (e.g. mono-aromatic content)
DHA	Detailed Hydrocarbon Analysis
DIN	Deutsches Institut für Normung
EC	European Commission
ECHA	European Chemicals Agency
EINECS	European Inventory of Existing Commercial Chemical Substances
EN	European Norm
Extinction coefficient	Value indicating the extent to which a substance absorbs electromagnetic radiation (e.g. UV or IR radiation).
FID	Flame ionisation detector
GC	Gas Chromatography
GCxGC	Comprehensive Two-dimensional Gas Chromatography
GC-FID	Gas Chromatography – Flame Ionisation Detector

GC-MS	Gas Chromatography - Mass Spectrometry
^{1}H	Hydrogen-1 nuclei used in nuclear magnetic resonance spectroscopy
Heteroatom	In organic chemistry a heteroatom is any atom other than carbon or hydrogen. The term is usually employed to indicate that non-carbon atoms have replaced carbon in the backbone of the molecular structure. Typical heteroatoms are nitrogen, oxygen, sulfur, phosphorus, chlorine, bromine and iodine.
HPLC	High-performance liquid chromatography.
HPLC-MS	High-performance liquid chromatography - Mass spectrometry.
Hydrophilic	'Water loving'. Having an affinity for, tending to combine with, or capable of dissolving in water or other polar solvents.
Functionality	A chemical property associated with specific compounds (e.g. aromatic).
IR	Infra-Red
ISO	International Organization for Standardization
Isomers	Compounds having the same type and number of atoms but in different molecular arrangements.
IUCLID	International Uniform ChemicaL Information Database
LC	Liquid Chromatography
LPG	Liquefied Petroleum Gas.
Lipophilic	'Fat loving'. Having an affinity for, tending to combine with, or capable of dissolving in lipids or other apolar solvents.
Moieties	Types of chemical functionality.
Nm	Nanometer.
NMR	Nuclear Magnetic Resonance.
MS	Mass Spectrometry.
PAHs	Polycyclic aromatic hydrocarbons
PBT	Persistent, Bioaccumulative and Toxic
ppm	Parts per million.
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances
Resins	Components of crude oil that are insoluble in propane but not in n-heptane.

Saturated hydrocarbons	Cyclic or acyclic hydrocarbon species composed entirely of single bonds and saturated with hydrogen.
SFC	Supercritical fluid chromatography.
SIEF	Substance Information Exchange Forum.
SIMDIS	Simulated Distillation
SIMDIS-GC	Simulated Distillation - Gas Chromatography
Substance	The material registered in REACH and described by a specific CAS or EINECS number.
TLC	Thin-layer chromatography
USA	United States of America
UV	Ultra-Violet
UVCB	Substances of Unknown or Variable **C**omposition, **C**omplex reaction products or Biological materials.

6. REFERENCES

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APPENDIX 1A: STANDARD METHODS ISSUED BY THE ENERGY INSTITUTE (EI) WITH CORRESPONDING BS 2000, EN, ISO AND ASTM METHODS

IP Reference	*Method Title*	*Panel*	*BS 2000*	*EN*	*ISO*	*ASTM D*
Appendix A:08	Specifications - IP standard thermometers	SC-L-4	0:Section 0.1:08			
Appendix B	Specifications - IP standard liquids	TMS	0:Section 0.2:96			
Appendix C	Physical constants	TMS				
Appendix D	*obsolete*					
Appendix E	*superseded by IP 367*					
Appendix F	Temperature conversions	TMS				
Appendix G	Density of water	Density				
Appendix H	Density of ambient air	Density				
Appendix I	Barometric pressure corrections for Hg barometers	TMS	0.4:96			
Appendix J		TMS, SCs and Panels				
1/94(04)	Acidity	SC-C-4	1:95			
2/98(04)*	Aniline and mixed aniline point	SC-B-10	2:98		2977:97	611-01
3	*obsolete*					
4/05*	Ash	SC-G-3	4:02	ISO 6245:02	6245:01	482-03
5	*obsolete*					
6	*superseded by IP 143*					
7	*superseded by IP 143*					
8	*obsolete*					
9	*superseded by IP 129, 130*					
10/94(10)	Kerosine 24 h burning	SC-B-10	10:95			
11	*obsolete*					
12/79(01)	Specific energy	SC-B-2	12.93			
13/94(03)	Conradson carbon residue	SC-B-10	13.94		6615:93	
14/94(04)*	Ramsbottom carbon residue	SC-C-4	14.94		4262:93	524-03
15/95(04)*	Pour point	SC-C-4	15.95		3016:94	97-02
16/08*	Freezing point of aviation fuels	SC-B-7				2386-05
17/10	Colour Lovibond tintometer	SC-B-10				
18	*obsolete*					
19/03	Demulsibility characteristics of lubricating oil	SC-C-4	19:03			
20	*superseded by IP 295*					
21	*obsolete*					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
22	*obsolete*					
23/2000*	*Gasoline engine crankcase oil fuel dilution*	SC-C-4				322-97(02)
24	*obsolete*					
25	*obsolete*					
26	*superseded by IP 123*					
27	*superseded by IP 525*					
28	*superseded by IP 123*					
29	*superseded by IP 123*					
30/07	*Doctor test*	SC-B-10				
31	*superseded by IP 132*					
32	*obsolete*					
33	*obsolete*					
34/03*	*Pensky-Martens closed flash point*	SC-B-4	34.02	ISO 2719:02	2719:02:00	93-02
35/63(01)	*Pensky-Martens open flash and fire point*	SC-B-4	35:93			
36/02	*Cleveland open flash and fire point*	SC-B-4	36.02	ISO 2592:01	2592:00:00	
37/04(10)	*Acidity and alkalinity of lubricating grease*	SC-C-6				
38	*obsolete*					
39	*obsolete*					
40/97(04)*	*Oxidation stability of gasoline induction period*	SC-B-8	40:96	ISO 7536:96	7536:94	525-01
41/99*	*Cetane number engine*	SC-B-1	41:98	ISO 5165:98	5165:98	613-01
42	*obsolete*					
43	*superseded by IP 150*					
44	*superseded by IP 236*					
45	*superseded by IP 506*	SC-E				
46	*obsolete*					
47/07e	*Solubility of bituminous binders*	SC-E	47:07:00		12592:07	
48/97(11)	*Oxidation characteristics of lubricating oil*	SC-C-2	48:97			
49/07e	*Needle penetration of bituminous material*	SC-E	49:07:00		1426:07:00	
50/88(07)*	*Cone penetration of lubricating grease*	SC-C-6	50:93			217-02(07)
51	*obsolete*					
52	*superseded by IP 136*					
53/2000*	*Sediment by extraction*	SC-B-3	53:99	ISO 3735:99	3735:99	473-02
54	*obsolete*					
55/77(01)*	*Melting point of wax*	SC-C-7				87-87(99)
56	*obsolete*					
57/95(03)*	*Smoke point*	SC-B-10	57:95		3014:93	1322-97 (02)e1
58/07e	*Softening point of bitumen ring and ball*	SC-E	58:07:00	1427:07:00		
59	*obsolete*					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
60	*obsolete*					
61/99(08)*	Sulfur high pressure combustion	SC-G-5	61:99			129-00(05)
62	*superseded by IP 107*					
63	*obsolete*					
64	*superseded by IP 154*					
65	*obsolete*					
66	*superseded by IP 61*					
67	*obsolete*					
68	*obsolete*					
69/01(08)	Reid vapour pressure	SC-B-9	69:01:00		3007:99	
70	*obsolete*					
71 S1/97*	Kinematic viscosity and calculation of dynamic viscosity	SC-C-3	71:96 Sect 1	ISO 3104:96	3104:94	445-03
71 S2/95(04)*	Kinematic viscometers specifications	SC-C-3	71:95 Sect 2		3105:94	446-00
72	*superseded by IP 502*					
73	*superseded by IP 226*					
74/2000*	Water by distillation petroleum products	SC-B-3	74:00:00		3733:99	95-99
75	*obsolete*					
76/70(04)*	Congealing point of waxes and petrolatum	SC-C-7	76:93			938-92(98)
77/72(04)	Salt content crude oil and products	SC-G-3				
78	*obsolete*					
79	*obsolete*					
80/07e	Fraass breaking point of bitumen	SC-E	80:07:00	12593:07		
81	*obsolete*					
82	*obsolete*					
83	*obsolete*					
84	*obsolete*	SC-G-2				
85	*obsolete*					
86	*obsolete*					
87	*obsolete*					
88	*obsolete*					
89	*obsolete*					
90	*obsolete*					
91/09e	Residue on sieving bitumen emulsions and storage stability	SC-E	91:09:00	1429:09:00		
92	*obsolete*					
93	*obsolete*					
94	*obsolete*					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
95	*obsolete*					
96	*obsolete*					
97	*superseded by IP 131*					
98	*obsolete*					
99	*superseded by IP 136*					
100	*superseded by IP 213*					
101	*obsolete*					
102	*obsolete*					
103/88(01)	*Hydrogen sulphide in LPG and light distillates*	SC-G-5				
104	*obsolete*					
105	*obsolete*					
106	*obsolete*					
107/86(01)*	*Lamp sulphur*	SC-G-5	107:93			1266-98(03)
108	*obsolete*					
109	*obsolete*					
110/82(01)	*obsolete*	SC-G-3				
111/82(01)	*obsolete*	SC-G-3				
112/05	*Copper corrosion grease*	SC-C-6	112:05:00			
113		obsolete				
114		obsolete				
115		superseded by IP 149				
116		obsolete				
117		obsolete				
118		obsolete				
119/96(08)*	*Supercharge knock rating*	SC-B-1				909-01
120	*obsolete*					
121/11	*Grease oil separation*	SC-C-6	121:05:00			
122	*obsolete*					
123/01	*Distillation of petroleum products*	SC-B-9	123:01:00	ISO 3405:00	3405:00:00	
124	*obsolete*					
125/08	*Cast iron corrosion petroleum products*	SC-C-5				
126	*superseded by IP 237*					
127	*obsolete*					
128	*obsolete*					
129/03(10)	*Bromine number colour indicator titration*	SC-G-2	129:03:00			
130/98(04)*	*Bromine number electrometric titration*	SC-G-2	130:98		3839:96	1159-01
131/99	*Gum content of light and middle distillate fuels*	SC-B-8	131:98	ISO 6246:97	6246:95	
132	*obsolete*					
133/79(01)*	*Drop melting point of wax and petroleum*	SC-C-7	133:93			127-87(99)

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
134	*obsolete*					
135/06*	Rust preventing characteristics of steam turbine oil	SC-C-4				665-02
136 S1/98(06)*	Saponification number colour indicator titration	SC-G-2	136:98 S1		6293-1:96	94-02 Method A
136 S2/99(06)*	Saponification number potentiometric titration	SC-G-2	136:99 S2		6293-2:98	94-02 Method B
137/82(04)	Oil content of water mix metalworking fluids	SC-C-5	137:93			
138/02(08)*	Oxidation stability of aviation fuel	SC-B-8	138:02:00			873-02(07)
139/98(04)*	Acid or base number colour indicator titration	SC-C-4	139:98		6618:96	974-02
140	*obsolete*					
141	*obsolete*					
142/85(10)*	Oxidation stability of lubricating grease	SC-C-6				942-02(07)
143/04*	Asphaltenes (heptane insolubles)	SC-B-5	143:04:00			6560-00
144	*obsolete*					
145	*obsolete*					
146/10*	Foaming characteristics of lubricating oils	SC-C-4				892-06e1
147	*obsolete*					
148	*obsolete*					
149/93(03)*	Phosphorus in lubricating oils and additives	SC-G-3	149:93		4265:86	4047-00(05)
150	*superseded by IP 236*					
151	*obsolete*					
152	*obsolete*					
153	*obsolete*					
154/2000*	Copper corrosion	SC-B-10	154:99	ISO 2160:98	2160:98	130-94(00)
155	*obsolete*					
156/08	Hydrocarbon types by FIA	SC-G-2	156:07:00	EN 15553:07		
157/96(11)	Oxidation stability of inhibited mineral oils	SC-C-2				
	(TOST test)					
158/69(01)*	Oil content of waxes gravimetric	SC-C-7				721-02
159	*obsolete*					
160/99*	Hydrometer density	Density	160:98	ISO 3675:98	3675:98	1298-99(05)
161	*superseded by IP 410*					
162	*obsolete*					
163/96(10)	Sulphated ash of lubricating oils and additives	SC-G-3	163:96		3987:94	
164	*obsolete*					
165	*obsolete*					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
166	*obsolete*					
167	*obsolete*					
168/08	Rolling bearing performance of lubricating grease	SC-C-6				
169	*superseded by IP 264*					
170/09	Flash point–Abel closed-cup	SC-B-4	170:08:00	ISO13736:08	13736:08	
171	*obsolete*					
172	*superseded by IP 237*					
173	*obsolete*					
174	*obsolete*					
177/10*	Weak and strong acid number potentiometric titration	SC-C-4				664-07
178	*obsolete*					
179/79(04)*	Cone penetration of petrolatum	SC-C-7	179:93			937-97(02)
180	*obsolete*					
181	*obsolete*					
182/06	Inorganic acidity colour indicator titration	SC-C-4	182:06:00			
183/08	Evaporation loss of lubricating grease	SC-C-6				
184	*superseded by IP 264*					
185/65(04)*	Odour of petroleum wax	SC-C-7				1833-87(07)
186/93(10)	Low temperature torque of lubricating grease	SC-C-6				
187	*obsolete*					
188	*obsolete*					
189/05	Pyknometer density	Density	189/190:04	ISO 3838:04	3838:04:00	
190/05	Pyknometer density	Density	189/190:04	ISO 3838:04	3838:04:00	
191	*incorporated into IP 123 as Group 0*					
192	*superseded by IP 160*					
193	*obsolete*					
194	*obsolete*					
195/98(09)	Distillation volatile organic liquids	SC-B-9	195:98			
196/97(04)*	ASTM colour	SC-B-10	196:97		2049:96	1500-02
197	*obsolete*					
198	*obsolete*					
199	*obsolete*					
200/08*	Petroleum measurement tables (published separately)					1250-07
212/92(04)	Viscosity of bitumen road emulsions	SC-E				

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
213/82(04)	Neutralization value of bitumen colour indicator titration	SC-E	213:93			
214	*obsolete*					
215/08	Water washout characteristics of lubricating grease	SC-C-6				
216/05*	Particulate contaminant of aviation turbine fuels	SC-B- 11				2276-00
217	*obsolete*					
218	*obsolete*					
219/94(04)	Cloud point	SC-B-7	219:94	23015:94	3015:92	
220/07	Rust prevention characteristics of lubricating greases	SC-C-6				
221	*obsolete*					
222/07e	Absolute viscosity of bitumen capillary viscometer	SC-E	222:07:00	12596:07		
223/68(04)	Ash of petroleum products containing mineral matter	SC-E	223:93			
224/02	Lead content of light petroleum distillates	SC-G-3				
225/76(03)	Copper in light petroleum distillates spectrophotometric	SC-G-3				
226/04*	Calculation of viscosity index	SC-B-2	226:02:00		2909:02:00	2270-93(98)
227	*obsolete*					
228/72(04)	Lead content of gasoline x-ray spectrometry	SC-G-3				
229/93(04)	Oxidation stability of steam turbine oils	SC-C-2				
230	*obsolete*					
231/69(01)	Engine cleanliness	TMS				
232	*obsolete*					
233	*obsolete*					
234	*obsolete*					
235/86(04)	Pressure hydrometer density	Density				
236/09*	Motor octane number	SC-B-1	236.05 IC March 08	ISO 5163:05	5163:05:00	2700-01
237/06*	Research octane number	SC-B-1	237.05	ISO 5164:05	5164:05:00	2699-01
238/82(88)a	*obsolete*	SC-B-1				
239/07	Extreme pressure/antiwear properties of lubricants and greases four ball	SC-C-1				
240/84(04)	Extreme pressure properties of lubricants Timken	SC-C-1				
241	*obsolete*					
242	*obsolete*					
243/94(04)	Sulfur Wickbold combustion	SC-G-5	243:94	24260:94	4260:87	

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
244	obsolete					
245	obsolete					
247/69(01)	Engine cleanliness and wear	TMS				
248	obsolete					
249/79(04)	Bingham pyknometer density	Density				
250	obsolete					
261	obsolete					
262	obsolete					
263	superseded by IP 580					
264/72(07)	LPG and propylene concentrates GC	SC-G-6				
265/01(04)	Salts content of crude oils conductivity	SC-G-3				
266/93(10)	Bearing greases churning tendency	SC-C-6				
267	obsolete					
268	obsolete					
269	obsolete					
270/96(04)	Lead content of Gasoline ICl	SC-G-3	270:96	ISO 3830:95	3830:93	
271/70(04)	Barium in lubricating oil additive concentrates acid oxidation	SC-G-3				
272/2000	Mercaptan sulfur and H2S in LPG electrometric titration	SC-G-5	272:00:00			
273	obsolete					
274/09*	Electrical conductivity of aviation and distillate fuels	SC-B-8				2624-07a
275	obsolete					
276/95(04)*	Base number perchloric acid potentiometric titration	SC-C-4	276:96		3771:94	2896-01
277	obsolete					
278	obsolete					
280/11	Oxidation stability of inhibited mineral turbine Oils	SC-C-2	280:99		7624:97	
281	obsolete					
282	obsolete					
283	obsolete					
284/04	Saponifiable and unsaponifiable matter in oils, fats and waxes	SC-G-2	284:04:00			
285/79(04)	Nickel and vanadium spectrophotometric	SC-G-3				
286	obsolete					
287/08	Rust prevention characteristics of water mix metal working fluids	SC-C-5				
288	Use IP 470 instead					
289/06	Water reaction of aviation fuels	SC-B-11				
290	obsolete					
291/00e	Water by distillation bitumen emulsions	SC-E	291:00:00	1428:99		

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
292/09e	Particle charge of bitumen emulsions	SC-E	292:09:00	1430:09:00		
293	*obsolete*					
294	*obsolete*					
295/83(05)	Electric strength of insulating oils	SC-C-4				
296	*obsolete*					
297	*obsolete*					
298/92(06)	Quinizarin extraction spectrophotometric	SC-G-2				
299/03*	Bromine index electrometric titration	SC-G-2				2710-99
300	*obsolete*					
301	*This number not used*					
302	*This number not used*					
303 Part 1/01	*Replaced by IP 523*	SC-B-4				
303 Part 2/01	*Replaced by IP 524*	SC-B-4				
304 Part 1	*Replaced by IP 492*					
304 Part 2	*Replaced by IP 491*					
305	*obsolete*					
306/94(11)	Oxidation stability of straight mineral oil	SC-C-2	306:94			
307	*obsolete*					
308/85(04)	Ba, Ca, Mg and Zn in unused lubricating oils AAS	SC-G-3				
309/99	CFPP of diesel and domestic heating fuels	SC-B-7	309:98	116:97		
310/84(10)*	Quarter and half cone penetration of grease	SC-C-6				1403-02(07)
311	*superseded by IP 580*					
312	*superseded by IP 580*					
313/01	Air release value of hydraulic, turbine and lubricating oils	SC-C-4	313:01:00			3427-02
314	*obsolete*					
315/98(04)*	Copper corrosion electrical insulating oils	SC-C-4	315:98		5662:97	1275-96a
316/93(05)	Solids in used engine oils	SC-C-4				
317/95(02)*	LPG residue at 38 °C	SC-B-5	317:95			2158-02
318/75(04)	Characterization of pollutants GC	SC-G-6				
319/07e	Kinematic viscosity of bitumens	SC-E	319:07:00			12595:07
320	*obsolete*					
321	*obsolete*					
322	*obsolete*					
323/11	JFTOT thermal oxidation stability of gas turbine fuels	SC-B-8				3241-07
324	*obsolete*					
325	*Obsolete*					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
326/05	*Extreme pressure properties of grease Timken*	SC-C-1				2509-03
327	*obsolete*					
328	*obsolete*					
329	*obsolete*					
330	*obsolete*					
331	*obsolete*					
332	*obsolete*					
333	*obsolete*					
334	*obsolete use CEC L-07-A*					
335	*obsolete*					
336/04	*Sulfur by EDXRF*	SC-G-5	336:03:00	ISO 8754:03	8754:03:00	
337/78(10)	*Composition of non-associated natural gas*	SC-G-6				
338	*obsolete*					
339	*obsolete*					
342/2000*	*Mercaptan sulfur in distillate fuels potentiometric*	SC-G-5	342:00:00		3012:99	3227-02
343/01(06)	*24M6B in AVTUR HPLC*	SC-G-2				
344/88(10)	*Light hydrocarbons in stabilized crude oils GC*	SC-G-6				
345	*obsolete*					
346/92(04)	*PCAs in petroleum fractions*	SC-G-2	346:96			
350	*obsolete*					
351	*obsolete*					
352/2007	*Lead content gasoline EDXRF*	SC-G-3				
354/09*	*Acidity of AVTUR colour indicator titration*	SC-B-11				3242-08
355/01	*Calculation of net specific energy of AVTUR*	SC-B-2	355:01:00		15911:00	
356/99*	*Water in crude oil potentiometric Karl Fischer*	SC-B-3	356:99		10336:97	4377-00(06)
357	*obsolete*					
358/97(03)	*Water by distillation crude oils*	SC- B-3	358:97	ISO 9029:95	9029:90	
359	*obsolete*					
360/96a*	*RON and MON on-line analysers*	SC-B-1				2885-95(99)
361/82(88)a*	*obsolete*	SC-B-1				
362/93(03)	*Lead content of gasoline AAS*	SC-G-3				
363	*obsolete*					
364	*obsolete*					
365/97(04)	*Oscillating U-tube density*	Density	365:96	ISO12185:96	12185:96	
366	*obsolete*					
367/07	*Application of precision data*	TMS	367:06:00	ISO4259:06	4259:06:00	

IP Reference	*Method Title*	*Panel*	*BS 2000*	*EN*	*ISO*	*ASTM D*
368/01(06)	Hydrocarbon types in lubricating oil basestocks HPLC	SC-G-2				
369/84(06)*	Composition of oil soluble petroleum sulphonates LC	SC-G-2				3712-91(00)
370	*obsolete*					
371/85(04)	Drop point of petrolatum	SC-C-7				
372/85(09)	Carbon number distribution of paraffin wax GC	SC-G-6				
373/99	Sulphur microcoulometry	SC-G-5				
374/01(06)	Coumarin fluorimetric and HPLC	SC-G-2				
375/99*	Sediment in residual fuel oils and distillate blends filtration	SC-B-5	375:99	+TC1:97	10307-1:93	4870-99
376/86(04)	Needle penetration of petroleum wax	SC-C-7				
377/95(03)	Al and Si in fuel oil ICPES and AAS	SC-G-3	377:95		10478:94	
378/87(01)*	Storage stability at 43 °C of distillate fuel	SC-B-5				4625-92(98)
379/88(01)*	Organically bound trace nitrogen	SC-G-5				4629-02
380/08	Calculation of cetane index	SC-B-2	380:07:00	ISO 4264:07	4264:07:00	
381/97(04)*	Estimation of net specific energy of aviation fuels	SC-B-2	381:97		3648:94	4529-02
382/88(03)	*obsolete*	SC-G-6				
383	*obsolete*					
384	*obsolete*					
385/99	Viable aerobic microbial content of fuels and fuel components	Micro-biology				
386/99*	Water in crude oil coulometric Karl Fischer	SC-B-3	386:99		10337:97	4928-00(05)
387/11	Filter blocking tendency of gas oils and distillate diesel fuels	SC-B-5				
388/97(04)*	Oxidation stability of middle-distillate fuels	SC-B-5	388:96	ISO12205:96	12205:95	2274-03
389/93(04)	WATof middle distillate fuels DTA or DSC	SC-G-9				
390/94(04)	Thermal and chemical ageing of residual fuel Oils	SC-B-5	390:94		10307-2:93	
391/07	Aromatic hydrocarbon types in diesel fuels and distillates HPLC	SC-G-2	391:06:00	12916: 06		
392/90(08)	Aromatic hydrogen and carbon contents NMR	SC-G-4				
393/96(04)	Volatility of automotive lubricating oils	SC-G-9				
394/08	Air saturated vapour pressure	SC-B-9	394:07:00	13016-1:07		
395/98(04)*	Valve freeze dryness of propane	SC-B-5	395:97	ISO13758:96	13758:96	2713-91(01)

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
396/02	Automatic dropping point of lubricating grease	SC-C-6				
397	*obsolete*					
398/96(04)	Carbon residue (micro method)	SC-B-10	398:96	ISO10370:95	10370:93	
399/10	Hydrogen sulfide in fuel oils	SC-G-5				
400/01	Base number conductimetric titration	SC-C-4				
401/95(04)	Hydrogen sulfide in LPG lead acetate	SC-G-5	401:95	ISO 8819:95	8819:93	
402	*obsolete*					
403	*obsolete*					
404	*obsolete*					
405/94(09)	Propane and butane analysis by GC	SC-G-6	405:94	27941:93	7941:88	
406/06*	Boiling range of products GC method	SC-G-6				2887-02
407/95(04)	Ba, Ca, P, S and Zn by WDXRF	SC-G-3				
408/98(09)	Oxygenates and total oxygen in unleaded petrol GC, O-FID	SC-G-6	408:97	1601:97		
409/08	Absolute vapour pressure of gasoline at 40 °C and 100 °C	SC-B-9	409:07:00	13016-2:07		
410/99(08)	Gauge vapour pressure of LPG	SC-B-9	410:98	ISO 4256:98	4256:96	
411/99(07)	Copper corrosion LPG	SC-B-10	411:98	ISO 6251:98	6251:96	
412/96(04)	Water separability of petroleum oils and synthetic fluids	SC-C-4	412:96		6614:94	
413/96(03)	Low levels V flameless AAS	SC-G-3	413:96		8691:94	
414/96(04)	Cooling characteristics industrial quenching oils	SC-C-5	414:96		9950:95	
415/07*	Particulate content of middle distillate fuels laboratory filtration	SC-B-5				6217-98(03)
416/96(04)	Sulfate and nitrate in diesel particulate filters	SC-G-10				
417/96(04)	Base number potentiometric titration	SC-C-4				
418/96(04)	Relative volatility of automotive lubricating oils	SC-G-9				
419/03	*obsolete*	SC-B-7				
420	*Superseded by IP 432*					
421	*obsolete*					
422/96(11)	Filter flow of aviation turbine fuels	SC-B-7				
423/10*	Particulate contaminant of AVTUR laboratory filtration	SC-B-11				5452-08
424/96(10)	FSII in AVTUR by HPLC	SC-G-2				
425/01(07)	Benzene content GC	SC-G-6	425:00:00	12177:00		
426/98(04)	Oil content of effluent water	SC-G-4				
427/97(04)	Oily residues high-temperature	SC-B-5	427:96	ISO13757:96	13757:96	

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
428/06(10)	Low lead content of petrol AAS	SC-G-3	428:04:00	237:04:00		
429/04	Benzene content of petrol IR	SC-G-4	429:04:00	238:03:00		
430/98(10)	Alkyl nitrate in diesel fuels	SC-G-2	430:97	ISO13759:96	13759:96	
431/98(04)	Acid number semi-micro colour indicator titration	SC-C-4	431:98		7537:97	
432/00	LPG calculated density and vapour pressure	SC-B-2	432:99	ISO8973:99	8973:97	
433/00(10)	Vanadium and nickel content WDXRF	SC-G-3	433:99	ISO14597:99	14597:97	
434	Replaced by IP 528	SC-B-7				
435/08	Freezing point of aviation turbine fuels automatic phase transition	SC-B-7				
436/11	Aromatic in aviation fuels and distillates HPLC RI	SC-G-2				6379-99
437/98(04)	Elements in unused lubricating oils and additive packages ICPAES	SC-G-3				
438/01	Water content products coulometric Karl Fischer	SC-B-3	438:01:00	ISO12937:00	12937:00	
439/01	Water content products potentiometric Karl Fischer	SC-B-3	439:01:00		6296:00:00	
440/08	Contamination in middle distillates	SC-B-5	440:08:00		12662:08	
441/99(04)*	Pour point of crude oils	SC-B-7				5853-95(00)
442/99	Fuel and oil-derived hydrocarbons in diesel particulates GC	SC-G-10				
443/99	SOF of diesel particulates soxhlet extraction gravimetric	SC-G-10				
444/09*	Cloud point automatic stepped cooling	SC-B-7				5771-05
445/09*	Cloud point automatic linear cooling rate	SC-B-7				5772-05
446/09*	Cloud point automatic constant cooling rate	SC-B-7				5773-07
447/08	Sulphur content WDXRF	SC-G-5	447:07:00	ISO14596:07	14596:07	
448S2	now only published as BS ISO 13357:2	SC-C-4				
449/00	Acid number non-aqueous potentiometric titration	SC-C-4	449:98	12634:98		
450/00	Lubricity of diesel fuel HFRR	TMS	450:00:00		(12156)	
451/00(05)	Aromatic carbon content of lubricant mineral base oils IR	SC-G-4				
452	obsolete					
453/10*	High temperature foaming characteristics of lubricating oils	SC-C-4				6082-06
454/00	Phosphorus in gasoline spectrophotometric	SC-G-3	454:00:00			

IP Reference	*Method Title*	*Panel*	*BS 2000*	*EN*	*ISO*	*ASTM D*
455/01	Manganese in gasoline AAS	SC-G-3	455:01:00			
456/00	Potassium in gasoline AAS	SC-G-3	456:00:00			
457/00e	Bitumen characterisation of perceptible properties	SC-E	457:00:00	1425:99		
458/09e	Recovered binder and oil from bitumen emulsions by distillation	SC-E	458:09:00	1431:09		
459 Part 1/07e	Bitumen paraffin wax content by distillation	SC-E	459:07 Part 1	12606-1:07		
459 Part 2/00e	Bitumen paraffin wax content by extraction	SC-E	459:00 Part 2	12606-2:99		
460 Part 1/07e	Bitumen resistance to hardening RTFOT	SC-E	460:07 Part 1	12607-1:07		
460 Part 2/07e	Bitumen resistance to hardening TFOT	SC-E	460:07 Part 2	12607-2:07		
460 Part 3/07e	Bitumen resistance to hardening RFT	SC-E	460:07 Part 3	12607-3:07		
461/07e	Bitumen preparation of test samples	SC-E	461:07:00	12594:07		
462-1/01	PCBs separation by GC ECD	SC-G	462.1:01	12766-1:00		
462-2/02	PCBs and related products	SC-G	462.2:01	12766-2:01		
462-3/08	PCBs and related products, determination and quantification	SC-G	462.3:04	12766-3:04		
463/02*	Potential instability of middle distillates	SC-B-5				6748-02
464/01(10)	Sodium by AAS	SC-G-3	464:01:00	241:00:00		
465/01(10)	Nickel and vanadium by AAS	SC-G-3	465:01:00	13131:00		
466/01(07)	Oxygenates and organically bound oxygen GC	SC-G-6	466:01:00	13132:00		
467/01*	High temperature stability of middle distillate fuels	SC-B-5				6468-99
468	obsolete					
469/01(06)	Saturated, aromatic and polar compounds TLC FID	SC-G-2				
470/05	Metals in fuel oil by AAS	SC-G-3				
471/06	Water content of fuel oil Karl Fischer potentiometric	SC-B-3				
472/02	Fungal fragments content of fuels boiling below 390°C	Micro-biology				
473/02(09)	Composition of LP GC	SC-G-6				
474/05	Bitumen sampling	PTI/13/-/3	474:04:00	58:04:00		
475/05	Manual sampling	PTI/13/-/3	475:04:00	ISO 3170:04	3170:04:00	
476/02	Automatic pipeline sampling	PTI/13/-/3	476:02:00	ISO 3171:99	3171:88	

IP Reference	*Method Title*	*Panel*	*BS 2000*	*EN*	*ISO*	*ASTM D*
477/02	Liquefied petroleum gas sampling	PTI/13/-3	477:01:00	ISO 4257:01	4257:01:00	
478/02(09)	Copper in AVTUR	SC-G-3				
479/02	Wet and dry oil density	Density				
480/07	Boiling range distribution of distillates and lubricants GC	SC-G-6	480:06:00	15199-1:06		
481/03(09)	Air saturated vapour pressure (ASVP) of crude oil	SC-B-9				
482/02	*obsolete*	SC-B-8				
483/02	Sediment in crude oil membrane filtration	SC-B-3				
484/03e	Efflux time of bitumen emulsions	SC-E	484:03:00	12846:02		
485/09e	Settling tendency of bitumen emulsions	SC-E	485:09:00	12847:09		
486/09e	Mixing stability with cement of bitumen emulsions	SC-E	486:09:00	12848:09		
487/09e	Penetration power of bitumen emulsions	SC-E	487:09:00	12849:09		
488/09e	pH bitumen emulsions	SC-E	488:09:00	12850:09		
489/03(10)	Low lead in gasolines WDXRF	SC-G-3	489:02:00	13723:02		
490/05	Sulfur petroleum products UV	SC-G-5	490:04:00	ISO 20846:04	20846:04	
491/03	Flash/no flash closed cup equilibrium	SC-B-4	491:02:00	ISO 1516:02	1516:02:00	
492/03	Flash point closed cup equilibrium	SC-B-4	492:02:00	ISO 1523:02	1523:02:00	
493/03e	Recovery of binder from bitumen emulsions by evaporation	SC-E	493:02:00	13074:02		
494/09e	Breaking behaviour cationic bitumen emulsions mineral filler	SC-E	494:09:00	13075-1:09		
495/09e	Breaking behaviour cationic bitumen emulsions fines mixing time	SC-E	495:09:00	13075-2:09		
496/05	Sulfur in automotive fuels EDXRF	SC-G-5	496:04:00	ISO 20847:04	20847:04	
497/05	Sulfur in automotive fuels WDXRF	SC-G-5	497:04:00	ISO 20884:04	20884:04	
498/08	Derived cetane number IQT	SC-B-13	498:07:00		15195:07	
499/11	Aromatic carbon 13C NMR spectroscopy	SC-G-4				
500/03	Phosphorus in residual fuels UV	SC-G-3				
501/05	Al, Si, V, Ni, Fe, Na, Ca, Zn and P in residual fuel oil ICPES	SC-G-3				
502/03e	Viscosity of cutback and fluxed bitumens	SC-E	502:02:00	13357:02		
503/04	Chlorine and bromine WDXRF	SC-G-3	503:04:00		15597:01	
504/10e	Staining tendancy of bitumen	SC-E	504:10:00	13301:10		
505/10e	Viscosity of bitumen rotating spindle	SC-E	505:10:00	13302:10		
506/09e	Loss in mass on heating bitumen	SC-E	506:09:00	13303:09		

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
507/07	SIMDIST residues	SC-G-6	507:06:00	15199-2:06		
508/04	Fuel quality monitoring	PTI/2	508:03:00	14274:03		
509/04	Sampling for fuel quality monitoring	TMS	509:03:00	14275:03		
510/04(10)	Organic halogens	SC-G-5	510:03:00	14077:03		
511/04	Carbonyls in dilute exhaust	SC-G-10				
512/04	Test portion preparation - N2 purge	SC-G-10	512:04:00	ISO 20764:03	20764:03	
513/10e	Bitumen dynamic viscosity cone and plate	SC-E	513:10:00	13702-1:10		
514/04e	Superseded by IP 505/10e	SC-E	514:03:00	13702-2:03		
515/04e	Bitumen deformation energy	SC-E	515:03:00	13703:03		
516/10e	Bitumen elastic recovery	SC-E	516:10:00	13398:10		
517/10e	Bitumen storage stability	SC-E	517:10:00	13399:10		
518/10e	Bitumen polymer dispension	SC-E	518:10:00	13632:10		
519/10e	Bitumen tensile properties	SC-E	519:10:00	13587:10		
520/08e	Bitumen force ductility	SC-E	520:08:00	13589:08		
521/05e	Bitumen emulsion adhesivity water immersion	SC-E	521:04:00	13614:04		
522/08e	Bitumen cohesion pendulum test	SC-E	522:08:00	13588:08		
523/05	Flash point rapid equilibrium	SC-B-4	523:04:00	ISO 3679:04	3679:04:00	
524/05	Flash/no flash rapid equilibrium	SC-B-4	524:04:00	ISO 3680:04	3680:04:00	
525/10e	Cutback bitumen distillation	SC-E	525:10:00	13358:10		
526/05	Hydrocarbon types and oxygenates MDGC	SC-G-6	526:04:00	14517:04		
527/05	Grease cold temperature cone penetration	SC-C-6	527:04:00		13737:04	
528/08	AVTUR freezing point fibre optic	SC-B-7				
529/08*	AVTUR freezing point automatic laser	SC-B-7				7153-05
530/06	Density of grease	SC-C-6				
531/10*	Sulfur content proportional counting EDXRF	SC-G-5				7212-07
532/10*	Sulfur content polarized XRF	SC-G-5				7220-06
533/05e	Bitumen flexural creep, bending beam rheometer	SC-E	533:05:00	14471:05		
534/06	Flash point small scale ramp	SC-B-4				

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
535/05e	Bitumen accelerated ageing, pressure vessel	SC-E	535:05:00	14769:05		
536/05e	Bitumen shear, modular and phase angle	SC-E	536:05:00	14770:05		
537/06	Purity of heptane and methylcyclohexane GC	SC-G-6				
538/08	Total acidity of ethanol	SC-G-2	538:07:00	15491:07		
539/08	Water content of ethanol	SC-B-3	539:07:00	15489:07		
540/08	Gum content of AVTUR	SC-B-8				
541/06	Ignition quality of marine fuel oils (FIA)	SC-B-14				
542/06e	Stabilisation of binder	SC-E	542:06:00	14895:06		
543/10	Dynamic viscosity	SC-C-3				
544/07	Metal corrosion grease	SC-C-6				
545/09	Crude oil boiling range GC	SC-G-6	545:08:00	15199-3:08		
546/07e	Superseded by IP 505/10e	SC-E	546:06:00	14896:06		
547/07	FAME Ca K Mg and Na	SC-G-3	547:06:00	14538:06		
548/07*	Aromatics in distillates HPLC	SC-G-2				6591-00
549/09e	Bitumen density and specific gravity	SC-E	549/A1:09	15326:07+A1		
550/08	Sulfated ash of burner fuels from waste mineral oils	SC-G-3				
551/07e	Bitumen ageing RCAT	SC-E	551:07:00	15323:07		
552/08	Ethanol chloride	SC-G-3	552:07:00	15484:07		
553/08	Ethanol sulfur WDXRF	SC-G-5	553:07:00	15485:07		
554/08	Ethanol sulfur UV	SC-G-5	554:07:00	15486:07		
555/08	Ethanol phosphorus	SC-G-3	555:07:00	15487:07		
556/08	Ethanol copper	SC-G-3	556:07:00	15488:07		
557/08	Ethanol pHe	SC-G-2	557:07:00	15490:07		
558/07*	X-ray code of practice	SC-G-3				7343-07
559/08	Hand held density meter	Density				
560/08	Metals in used greases WDXRF	SC-G-3				
561/08	Metals in used greases ICP-AES	SC-G-3				
562/09	Metalworking fluids foam test	SC-C-5				

IP Reference	*Method Title*	*Panel*	*BS 2000*	*EN*	*ISO*	*ASTM D*
563/08	Ethanol inorganic chloride and sulfate IC	SC-G-3	563:08:00	15492:08		
564/11	AVTUR cleanliness LAPC	SC-B-11				
565/11	AVTUR cleanliness PAPC	SC-B-11				
566/09	Hydrocarbon types and oxygenates–MDGC	SC-G-6	566:08:00	ISO 22854:08	22854:08	
567/09	DCN of middle distillate fuels–Constant volume combustion chamber	SC-B-13				
568/11*	SDA in AVTUR and middle distillate fuels	SC-G-2				7524-10
569/09	Lovibond colour–Automatic	SC-B-10				
570/11	Hydrogen sulfide in fuel oils rapid phase extraction	SC-G-5				
571/09	Ethanol higher alcohols, methanol and volatile impurities GC	SC-G-6	571:09:00	15721:09		
572/09	Ethanol water Karl Fischer potentiometric titration	SC-B-3	572:09:00	15692:09		
573/09	Ethanol visual appearance	SC-M	573:09:00	15769:09		
574/09	FAME stability to accelerated oxidation	SC-M	574:09:00	15751:09		
575/09e	Bitumen adhesivity water immersion	SC-E	575:09:00	15626:09		
576/09	Ethanol dry residue gravimetric	SC-M	576:09:00	15691:09		
577/11	AVTUR cleanliness APC light extinction	SC-B-11				
578/10	FAME PUFA GC	SC-G-6	578:09:00	15779:09		
579/10	Determination of FAME in middle distillates - Infrared spectrometry method	SC-G-4	579:09:00	14078:09		
580/10	Water mix metal working fluids thermal and emulsion stability and foaming characteristics	SC-C-5				
581/11	Determination of P, Cu and S content by ICP-OES	SC-G-3	581:09:00	15837:09		
582/11	Determination of boiling range distribution, GC method	SC-G-6	582:10:00	ISO 3924:10	3924:10:00	
583/10	FAME in AVTUR - FTIR rapid screening method	SC-G-4				
584/10e	Determination of the fracture toughness temperature by a three point bending test on a notched specimen	SC-E	584:10:00	15963:10		
585/10	FAME in AVTUR-GC-MS	SC-G-6				
586/11	Ethanol blending component and ethanol (E85) automotive fuel - Electrical conductivity	SC-B-8	586:10:00	15938:10		
587	not yet published					

IP Reference	***Method Title***	***Panel***	***BS 2000***	***EN***	***ISO***	***ASTM D***
588	*not yet published*					
589	*not yet published*					
590/10	FAME in aviation turbine fuel - HPLC method	SC-G-2				
591	*not yet published*					
592/11	Determination of Pb, Ni, Cr, Cu, Zn, As, Cd, Tl, Sb, Co, Mn and V in burner fuels by ICPMS method	SC-G-3				
593/11	Determination of Pb, Ni, Cr, Cu, Zn, As, Cd, Tl, Sb, Co, Mn and V in burner fuels by WDXRF method	SC-G-3				
594/11	Determination of Hg in burner fuels - combustion, amalgamation, CVAAS method	SC-G-3				

APPENDIX 1B: STANDARD METHODS FOR THE CHARACTERISATION OF PETROLEUM UVCB SUBSTANCES

Method	Title	Analyte(s)	Scope	Comments
DISTILLATION				
EN 3405 / ISO 3405 / ASTM D86	*Petroleum products — Determination of distillation characteristics at atmospheric pressure*	IBP, FBP and specific temperatures at which 2%, 5%, 10%, 20% ..... 95% of sample recovered	light/middle distillates; IBP >0 C; FBP <400 C	
GAS ANALYSIS BY GC				
EN 27941 / ISO 7941	*Commercial propane and butane – Analysis by gas chromatography*	saturated and unsaturated C2, C3, C4 and C5 hydrocarbons	hydrocarbons >0.1% (m/m) in LPG	
DETAILED HYDROCARBON ANALYSIS (DHA) BY GC				
ASTM D5134	*Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography*	hydrocarbon components of petroleum naphthas (including n-hexane and BTEX)	individual components <151 C; suitable for samples containing <2% olefins	components eluting after n-nonane (BP 151 C) determined as a single group

ASTM D6729	*Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography*	hydrocarbon components (including n-hexane and BTEX) and oxygenates (e.g. MeOH, EtOH, BuOH, MTBE, ETBE, TAME)	individual components <225 C; suitable for samples containing <25% olefins	
ASTM D6730	*Determination of Individual Components in Spark Ignition Engine Fuels by 100–Metre Capillary (with Precolumn) High-Resolution Gas Chromatography*	hydrocarbon components (including n-hexane and BTEX) and oxygenates (e.g. MeOH, EtOH, BuOH, MTBE, ETBE, TAME)	individual components <225 C; suitable for samples containing <25% olefins	very similar to ASTM D6729
SELECTIVE HYDROCARBON ANALYSIS BY MULTI-DIMENSIONAL GC (REFORMULYSER/PIONA)				
EN 22854 / ISO 22854 / ASTM D6839	*Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline — Multidimensional gas chromatography method*	saturates, aromatics, olefins, benzene and oxygenate contents with carbon number distribution to C10	FBP 215 C; suitable for samples containing <50% aromatics, 1.5-30% olefins, 0.8-15% oxygenates and <2% benzene	
SIMULATED DISTILLATION BY GC				
EN 15199-1 / IP 480	*Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 1: Middle distillates and lubricating base oils*	IBP, FBP and specific temperatures representing 5%, 10%, 20% ..... 95% sample recovery	IBP >100 C; FBP <750 C	calibration against n-alkane standards covering boiling range

EN 15199-2 / IP 507	*Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 2: Heavy distillates and residual fuels*	IBP and recovery at selected final elution temperature of 720 C or 750 C; specific temperatures representing defined percentage recovery values	IBP >100 C; FBP >750 C	calibration against n-alkane standards covering boiling range up to 720 C (C100) or 750 C (C120)
EN 15199-3 / IP 545 / ASTM D7169	*Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 3: Crude oil*	IBP and recovery at selected final elution temperature of 720 C or 750 C; specific temperatures representing defined percentage recovery values	IBP <100 C; FBP >750 C	calibration against n-alkane standards covering boiling range up to 720 C (C100) or 750 C (C120)
ASTM D2887 / IP 406 / ISO 3924	*Boiling Range Distribution of Petroleum Fractions by Gas Chromatography*	IBP, FBP and specific temperatures representing 5%, 10%, 20% ..... 95% sample recovery	FBP <538 C; unsuitable for gasoline and components	calibration against n-alkane standards covering range C5 to C44
ASTM D3710	*Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography*	specific temperatures representing 1% ... 99% sample recovery and 0.5% (IBP) and 99.5% (FBP)	FBP <260 C	calibration against n-alkane standards covering boiling range of sample
ASTM D7096	*Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography*	specific temperatures representing 1% ... 99% sample recovery and 0.5% (IBP) and 99.5% (FBP)	FBP <280 C	calibration against hydrocarbon standards covering boiling range of sample

HYDROCARBON CLASS ANALYSIS BY LC				
ASTM D2007	*Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay-Gel Absorption Chromatographic Method*	saturate, aromatic and polar hydrocarbons	IBP >260 C	gravimetric measurement of analytes; aromatics measured by difference or desorption from second column
IP 436 / ASTM D6379	*Determination of aromatic hydrocarbon types in aviation fuels and petroleum distillates – High performance liquid chromatography method with refractive index detection*	mono- and di-aromatic hydrocarbons	boiling range 50-300 C; suitable for samples containing 0-75% mono-aromatics and 0-25% di-aromatics	samples with FBP >300C can contain tri-aromatic and heavier hydrocarbons and should be analysed by IP 391
IP 391 / EN 12916	*Petroleum products - Determination of aromatic hydrocarbon types in middle distillates – High performance liquid chromatography method with refractive index detection*	mono-, di- and tri+ aromatic hydrocarbons	boiling range 150-400 C	suitable for middle distillates containing FAME
IP 548 / ASTM D6591	*Determination of aromatic hydrocarbon types in middle distillates – High performance liquid chromatography method with refractive index detection*	mono-, di- and tri+ aromatic hydrocarbons	boiling range 150-400 C	backflush method so FAME interference with tri+aromatics
IP 368	*Determination of hydrocarbon types in lubricating oil basestocks – Preparative high performance liquid chromatography method*	saturate and aromatic hydrocarbons	IBP >270 C	gravimetric measurement of analytes; backflush method

ASTM D7419	*Determination of Total Aromatics and Total Saturates in Lube Basestocks by High Performance Liquid Chromatography (HPLC) with Refractive Index Detection*	saturate and aromatic hydrocarbons	suitable for samples containing 0.2-46% aromatics	backflush method
IP 469	*Determination of saturated, aromatic and polar compounds in petroleum products by thin layer chromatography and flame ionisation detection*	saturate, aromatic and polar hydrocarbons	IBP >300 C (5% recovered sample)	polar I (resins) and polar II (asphaltenes) fractions determined
HYDROCARBON CLASS ANALYSIS BY SPECTROSCOPY				
IP 392	*Determination of aromatic hydrogen and carbon content – High resolution nuclear magnetic resonance spectroscopy method*	mole percent aromatic hydrogen or aromatic carbon	hydrocarbon oils including kerosines, gas oils, lube oils and coal liquids	
ASTM D5292	*Aromatic Carbon Contents of Hydrocarbon Oils by High Resolution Nuclear Magnetic Resonance Spectroscopy*	mole percent aromatic hydrogen or aromatic carbon	hydrocarbon oils including kerosines, gas oils, lube oils and coal liquids	
ASTM D2008	*Ultraviolet Absorbance and Absorptivity of Petroleum Products*	absorbance at specified wavelength in 220-400 nm range	typically used to measure absorbance of white mineral oil, refined petroleum wax and petrolatum	

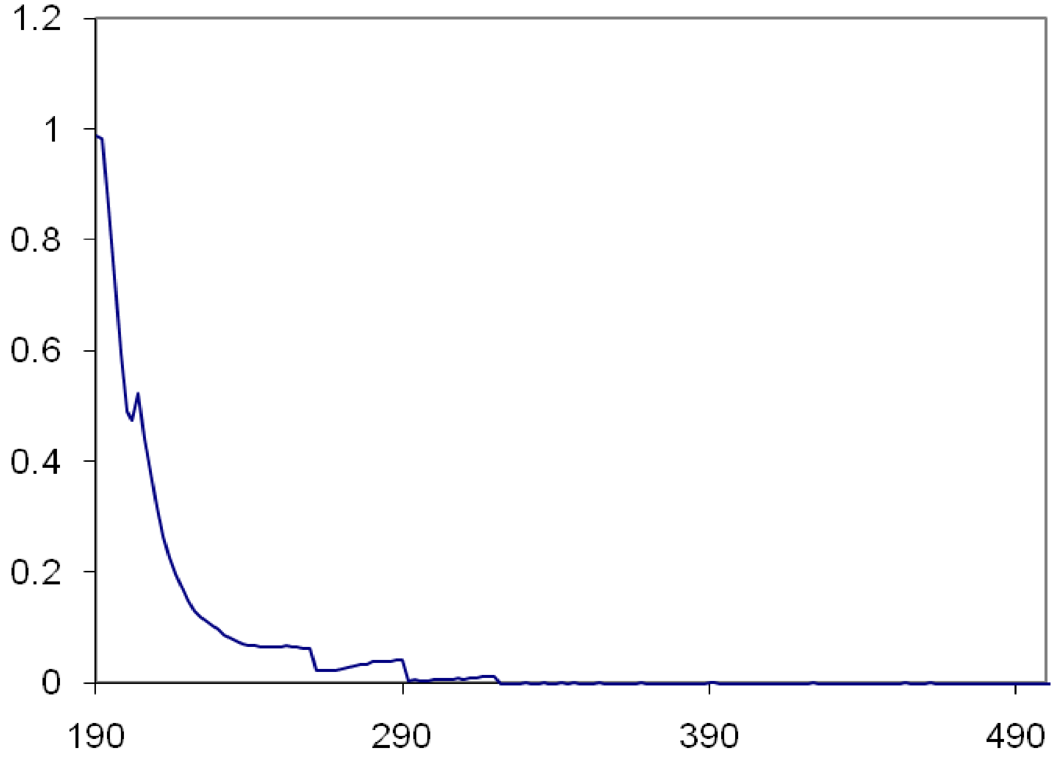
HYDROCARBON CLASS ANALYSIS BY SOLVENT EXTRACTION				
IP 346	*Determination of polycyclic aromatics in unused lubricating base oils and asphaltene free petroleum fractions – Dimethyl sulfoxide extraction refractive index method*	polycyclic aromatic hydrocarbons (three or more fused rings)	IBP >300 C (5% recovered sample); suitable for samples containing 1-15% polycyclic aromatics	gravimetric measurement of analyte; correlation between IP 346 results and *in-vitro* mutagenicity measurements (Ames Test)
VISCOSITY MEASUREMENT				
IP 71 / EN 3104 / ISO 3104	*Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity*	kinematic viscosity	liquid petroleum products including base oils, formulated oils, petroleum wax and residual fuel oils	dynamic viscosity calculated from kinematic viscosity and density
DENSITY MEASUREMENT				
IP 365 / EN 12185 / ISO 12185	*Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method*	density	crude petroleum and related products	600-1100 kg/m3 range

APPENDIX 2: ANALYTICAL DATA FOR CASE STUDY 1

Low Boiling Point Naphthas CAS No. 64741-42-0
EINECS No. 265-042-6

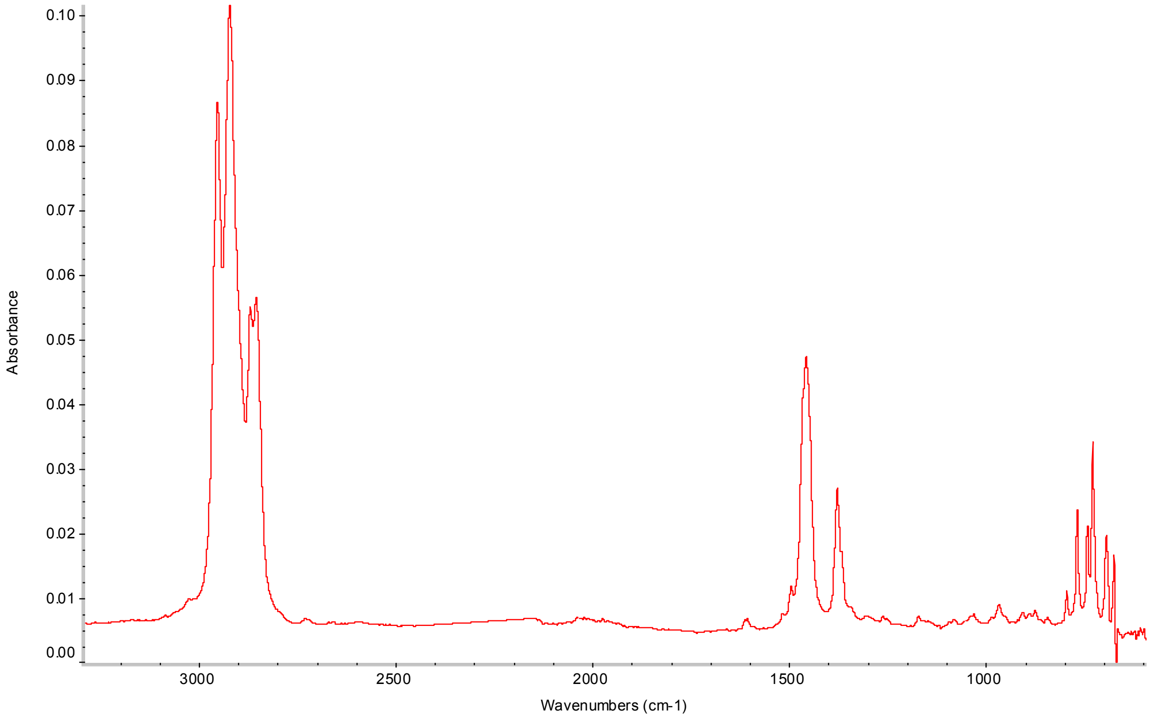
2.1. UV/Visible Spectroscopy

Instrument:	Thermo Scientific Evolution 600 UV-VIS Spectrophotometer
Cell type:	3 ml in UV-Cuvette (Fisher brand)
Slit width:	1 cm
Path length:	1 cm
Range:	190-900 nm
Solvent:	Hexane
Concentration:	0.00115 g/100 mL Hexane (11.5 pppm)
Test temperature:	20 °C
Scanning speed:	600 nm/min
Number of cycles:	1
Slit - Band width:	1.5 nm, Data interval: 2 nm



2.2. IR Spectroscopy

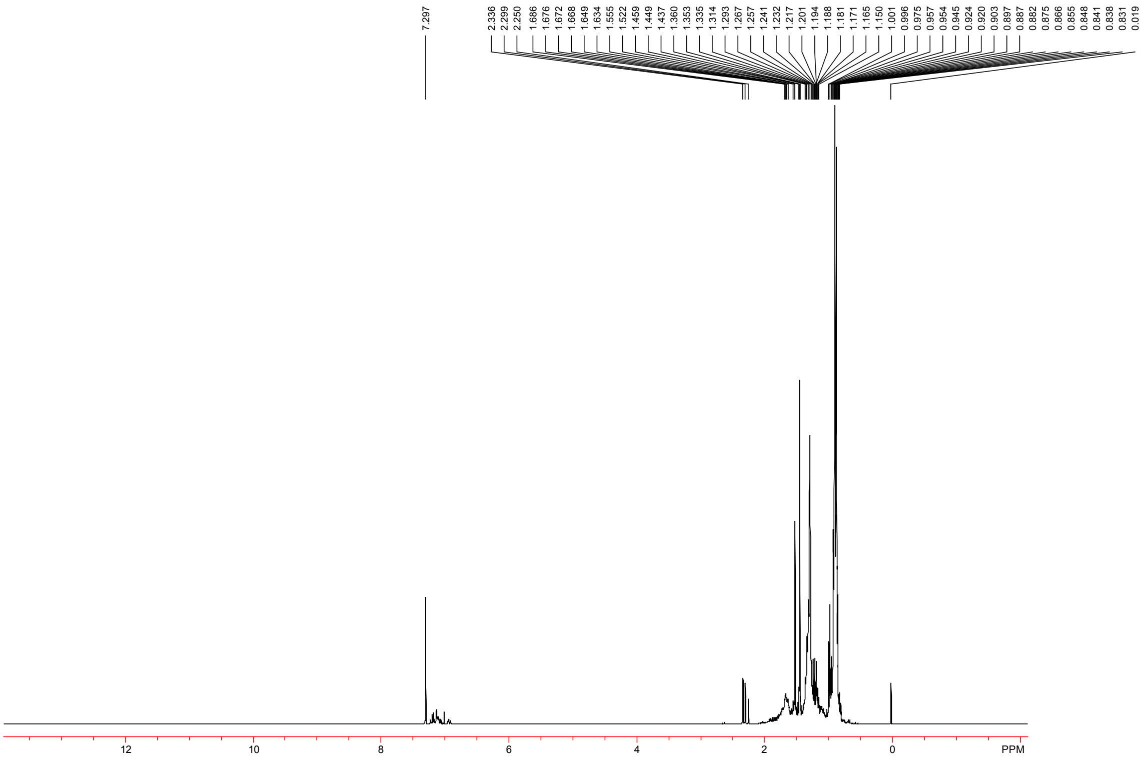
Instrument:	Thermo Nicolet Magna 550 FTIR Instrument with ATR accessory
Number of scans:	64
Spectral resolution:	4 cm^{-1}



Wavenumber (cm-1)	Vibration assignment
3031	SP^2 CH stretch
2921	SP^3 antisymm CH stretch
2860	SP^3 symm CH stretch
1611	C=C stretch
1456	CH_3 antisymm. Deformation/CH_2 bend
1377	CH_3 bending
675-800	CH out of plane bend

2.3. NMR Spectroscopy

Instrument:	Varian Mercury Plus 300 NMR Spectrometer
Frequency:	300 MHz
Solvent:	Deuterochloroform
Concentration:	30%
Temperature:	25 °C
Reference:	Tetramethylsilane (chemical shift 0.0 ppm)



Assignment	Chemical shift (ppm)
CH polyaromatic (internal)	8-10
CH aromatic	6-8
CH, CH_2 olefinic	4.5-6
CH, CH_2, CH_3 alpha to aromatic	2-4.5
CH, CH_2 aliphatic	1-2
CH_3 aliphatic (chain end)	0.2-1

2.4. DHA-Gas Chromatography

Column:	J&W DB-1, 40m x 0.1mm I.D. x 0.2µm film thickness
Carrier gas:	Hydrogen
Inlet pressure:	75 psi
Injector:	Split/splitless
Inlet temperature:	250°C
Injection volume:	0.1 µL
Oven temperature:	30°C (initial) programmed at 10°C/min to 50°C; held for 3.30 mins; programmed at 6°C to 220°C; held for 5.37 mins
Detector:	Flame ionisation
Detector temperature:	325°C

Summary by Group

Group	%Wgt	%Vol
Aromatics	7.671	6.160
Paraffin	28.965	31.121
I-Paraffins	32.457	34.397
Naphthenes	29.865	27.284
Unidentified	0.426	0.391
Olefins	0.617	0.648
Oxygenates	0.000	0.000

Summary by Carbon

C#	%Wgt	%Vol
C4	2.343	2.835
C5	23.568	26.124
C6	24.886	24.839
C7	23.811	22.563
C8	18.574	17.297
C9	6.041	5.619
C10	0.351	0.332

Composite by Carbon

Group	C#	%Wgt	%Vol
Aromatics	C6	1.673	1.330
	C7	2.807	2.261
	C8	2.917	2.349
	C9	0.273	0.220
Paraffin	C4	2.121	2.559
	C5	11.091	12.370
	C6	6.361	6.737
	C7	4.864	4.969
	C8	3.778	3.756
	C9	0.739	0.719
	C10	0.011	0.011
I-Paraffins	C4	0.200	0.251
	C5	10.545	11.887
	C6	8.955	9.520
	C7	5.068	5.172
	C8	4.967	4.938
	C9	2.433	2.352
	C10	0.289	0.277
Naphthenes	C5	1.488	1.394
	C6	7.799	7.152
	C7	11.020	10.111
	C8	6.912	6.254
	C9	2.595	2.328
	C10	0.051	0.044
Olefins	C4	0.022	0.026
	C5	0.445	0.472
	C6	0.098	0.100
	C7	0.052	0.050

Component List

Pk#	Time	Group	Component	%Wgt	%Vol
1	2.081	I4	i-Butane	0.200	0.251
2	2.160	O4	i-butylene	0.004	0.004
3	2.160	O4	Butene-1	0.004	0.004
4	2.198	P4	n-Butane	2.121	2.559
5	2.237	O4	t-Butene-2	0.009	0.010
6	2.257	I5	2,2-Dimethylpropane	0.027	0.031
7	2.306	O4	c-Butene-2	0.006	0.007
8	2.497	O5	3-Methylbutene-1	0.011	0.012
9	2.633	I5	i-Pentane	10.518	11.856
10	2.756	O5	Pentene-1	0.031	0.034
11	2.821	O5	2-Methylbutene-1	0.080	0.086
12	2.873	P5	n-Pentane	11.091	12.370
13	2.917	O5	Isoprene	0.008	0.009
14	2.950	O5	t-Pentene-2	0.087	0.094
15	3.040	O5	3,3-Dimethylbutene-1	0.047	0.051
16	3.100	O5	2-Methylbutene-2	0.161	0.170
17	3.317	I6	2,2-Dimethylbutane	0.648	0.697
18	3.586	O5	Cyclopentene	0.019	0.017
19	3.643	O6	4-Methylpentene-1	0.006	0.006
20	3.668	O6	3-Methylpentene-1	0.007	0.007
21	3.773	N5	Cyclopentane	1.488	1.394
22	3.802	I6	2,3-Dimethylbutane	0.836	0.882
23	3.843	O6	2,3-Dimethylbutene-1	0.005	0.006
24	3.881	I6	2-Methylpentane	4.749	5.079
25	4.149	I6	3-Methylpentane	2.722	2.861
26	4.237	O6	2-Methylpentene-1	0.012	0.012
27	4.268	O6	Hexene-1	0.008	0.008
28	4.511	P6	n-Hexane	6.361	6.737
29	4.545	O6	t-Hexene-3	0.010	0.010
30	4.563	O6	c-Hexene-3	0.006	0.006
31	4.602	O6	t-Hexene-2	0.011	0.011
32	4.651	O6	2-Methylpentene-2	0.012	0.012
33	4.696	O6	3-Methylcyclopentene	0.006	0.006
34	4.722	O6	3-Methyl-c-pentene-2	0.006	0.006
35	4.765	O6	O13	0.004	0.004
36	4.808	O6	c-Hexene-2	0.005	0.006
37	4.947	O7	3,3-Dimethylpentene-1	0.008	0.008
38	5.044	I7	2,2-Dimethylpentane	0.171	0.177
39	5.104	N6	Methylcyclopentane	4.340	4.049
40	5.189	I7	2,4-Dimethylpentane	0.325	0.338
41	5.312	I7	2,2,3-Trimethylbutane	0.046	0.046
42	5.672	A6	Benzene	1.673	1.330
43	5.822	I7	3,3-Dimethylpentane	0.101	0.102

Component List

Pk#	Time	Group	Component	%Wgt	%Vol
44	5.932	N6	Cyclohexane	3.458	3.103
45	6.191	I7	2-Methylhexane	1.682	1.731
46	6.238	I7	2,3-Dimethylpentane	0.650	0.654
47	6.319	N7	1,1-Dimethylcyclopentane	0.460	0.426
48	6.455	I7	3-Methylhexane	1.912	1.943
49	6.653	N7	1c,3-Dimethylcyclopentane	0.994	0.932
50	6.744	N7	1t,3-Dimethylcyclopentane	0.933	0.870
51	6.782	I7	3-Ethylpentane	0.181	0.181
52	6.836	N7	1t,2-Dimethylcyclopentane	1.630	1.515
53	6.883	I8	2,2,4-Trimethylpentane	0.019	0.019
54	7.188	O7	t-Heptene-3	0.003	0.003
55	7.214	O7	C7 cycloolefin	0.004	0.003
56	7.292	P7	n-Heptane	4.864	4.969
57	7.346	O7	c-Heptene-3	0.010	0.010
58	7.384	O7	3-Methyl-t-hexene-3	0.006	0.006
59	7.450	O7	t-Heptene-2	0.006	0.006
60	7.622	O7	c-Heptene-2	0.003	0.003
61	7.641	O7	C7 Cycloolefin	0.003	0.003
62	7.761	O7	2,3-Dimethylpentene-2	0.004	0.004
63	8.019	N7	1c,2-Dimethylcyclopentane	0.200	0.191
64	8.066	N7	Methylcyclohexane	6.305	5.723
65	8.135	N8	1,1,3-Trimethylcyclopentane	0.079	0.074
66	8.174	I8	2,2-Dimethylhexane	0.473	0.475
67	8.541	N7	Ethylcyclopentane	0.498	0.454
68	8.595	I8	2,5-Dimethylhexane	0.209	0.211
69	8.642	I8	2,2,3-Trimethylpentane	0.021	0.021
70	8.682	I8	2,4-Dimethylhexane	0.300	0.300
71	8.945	N8	1c,2t,4-Trimethylcyclopentane	0.503	0.460
72	9.006	I8	3,3-Dimethylhexane	0.082	0.081
73	9.226	O7	O38	0.006	0.005
74	9.301	N8	1t,2c,3-Trimethylcyclopentane	0.606	0.550
75	9.438	I8	2,3,4-Trimethylpentane	0.118	0.115
76	9.638	A7	Toluene	2.807	2.261
77	9.720	I8	2,3,3-Trimethylpentane	0.005	0.005
78	10.032	I8	2,3-Dimethylhexane	0.223	0.219
79	10.044	I8	2-Methyl-3-ethylpentane	0.154	0.151
80	10.093	N8	1,1,2-Trimethylcyclopentane	0.079	0.072
81	10.224	?	Unidentified	0.004	0.004
82	10.390	I8	2-Methylheptane	1.690	1.692
83	10.470	I8	4-Methylheptane	0.465	0.461
84	10.530	I8	3-Methyl-3-ethylpentane	0.049	0.048
85	10.559	I8	3,4-Dimethylhexane	0.068	0.066
86	10.692	N8	1c,2c,4-Trimethylcyclopentane	0.037	0.034

Component List

Pk#	Time	Group	Component	%Wgt	%Vol
87	10.711	N8	1c,3-Dimethylcyclohexane	0.038	0.035
88	10.842	I8	3-Methylheptane	0.945	0.935
89	10.912	N8	1c,2t,3-Trimethylcyclopentane	1.681	1.524
90	10.958	I8	3-Ethylhexane	0.144	0.141
91	11.028	N8	1t,4-Dimethylcyclohexane	0.635	0.582
92	11.361	N8	1,1-Dimethylcyclohexane	0.253	0.226
93	11.528	I9	2,2,5-Trimethylhexane	0.023	0.022
94	11.607	N8	3c-Ethylmethylcyclopentane	0.181	0.165
95	11.750	N8	3t-Ethylmethylcyclopentane	0.163	0.149
96	11.837	N8	2t-Ethylmethylcyclopentane	0.430	0.390
97	11.972	I9	2,2,4-Trimethylhexane	0.056	0.053
98	12.171	N8	1t,2-Dimethylcyclohexane	0.828	0.745
99	12.566	N8	1t,3-Dimethylcyclohexane	0.013	0.012
100	12.689	P8	n-Octane	3.778	3.756
101	13.074	I9	I2	0.004	0.004
102	13.209	N8	i-Propylcyclopentane	0.038	0.034
103	13.257	I9	2,4,4-Trimethylhexane	0.047	0.045
104	13.421	?	Unidentified	0.002	0.002
105	13.443	?	Unidentified	0.002	0.002
106	13.534	?	Unidentified	0.005	0.005
107	13.701	?	Unidentified	0.039	0.037
108	13.903	I9	2,3,4-Trimethylhexane	0.030	0.028
109	14.001	N8	N2	0.055	0.049
110	14.094	N8	N3	0.005	0.004
111	14.172	I9	2,3,5-Trimethylhexane	0.062	0.060
112	14.414	?	Unidentified	0.129	0.113
113	14.477	N8	1c,2-Dimethylcyclohexane	0.231	0.203
114	14.582	?	Unidentified	0.009	0.008
115	14.631	I9	2,2-Dimethylheptane	0.014	0.014
116	14.797	N9	1,1,4-Trimethylcyclohexane	1.168	1.057
117	14.862	N8	N4	0.015	0.013
118	14.935	I9	2,2,3-Trimethylhexane	0.402	0.392
119	15.025	I9	2,4-Dimethylheptane	0.029	0.028
120	15.158	N8	N5	0.714	0.640
121	15.308	N8	Ethylcyclohexane	0.076	0.067
122	15.365	N8	n-Propylcyclopentane	0.242	0.218
123	15.447	I9	2-Methyl-4-ethylhexane	0.063	0.060
124	15.505	N9	1c,3c,5-Trimethylcyclohexane	0.050	0.045
125	15.584	I9	3,3-Dimethylheptane	0.067	0.064
126	15.601	?	Unidentified	0.021	0.019
127	15.686	N9	1,1,3-Trimethylcyclohexane	0.050	0.045
128	15.803	N8	N7	0.005	0.004
129	15.860	N8	N8	0.005	0.004

Component List

Pk#	Time	Group	Component	%Wgt	%Vol
130	15.951	A8	Ethylbenzene	0.481	0.387
131	16.034	N9	N11	0.131	0.117
132	16.061	?	Unidentified	0.018	0.016
133	16.130	N9	1c,2t,4t-Trimethylcyclohexane	0.271	0.243
134	16.240	?	Unidentified	0.022	0.022
135	16.314	?	Unidentified	0.004	0.004
136	16.370	I9	I3	0.018	0.017
137	16.500	A8	m-Xylene	1.419	1.147
138	16.561	A8	p-Xylene	0.430	0.348
139	16.646	I9	3,4-Dimethylheptane A	0.298	0.284
140	16.752	I9	3,4-Dimethylheptane B	0.026	0.025
141	16.808	I9	3,5-Dimethylheptane	0.156	0.151
142	16.900	?	Unidentified	0.015	0.015
143	16.937	I9	2,3-Dimethylheptane	0.043	0.041
144	16.987	N9	N14	0.017	0.015
145	17.025	I9	I4	0.005	0.005
146	17.040	I9	4-Ethylheptane	0.005	0.004
147	17.120	I9	4-Methyloctane	0.233	0.226
148	17.182	I9	2-Methyloctane	0.292	0.286
149	17.294	N9	N15	0.041	0.037
150	17.302	N9	N16	0.036	0.032
151	17.373	?	Unidentified	0.002	0.002
152	17.461	I9	3-Ethylheptane	0.139	0.134
153	17.553	I9	3-Methyloctane	0.324	0.314
154	17.627	I9	3,3-Diethylpentane	0.016	0.015
155	17.660	N9	1c,2t,4c-Trimethylcyclohexane	0.008	0.007
156	17.705	I9	I5	0.029	0.027
157	17.766	A8	o-Xylene	0.588	0.467
158	17.794	N9	1,1,2-Trimethylcyclohexane	0.043	0.037
159	17.858	I9	I6	0.023	0.022
160	17.899	?	Unidentified	0.006	0.006
161	17.935	I9	I7	0.004	0.004
162	17.955	?	Unidentified	0.003	0.003
163	17.998	?	Unidentified	0.012	0.011
164	18.134	N9	N18	0.103	0.092
165	18.181	N9	N19	0.200	0.179
166	18.296	N9	N20	0.125	0.112
167	18.329	?	Unidentified	0.009	0.008
168	18.406	?	Unidentified	0.004	0.004
169	18.448	N9	i-Butylcyclopentane	0.019	0.017
170	18.529	N9	N21	0.021	0.018
171	18.546	N9	N22	0.010	0.009
172	18.602	N9	N23	0.005	0.004

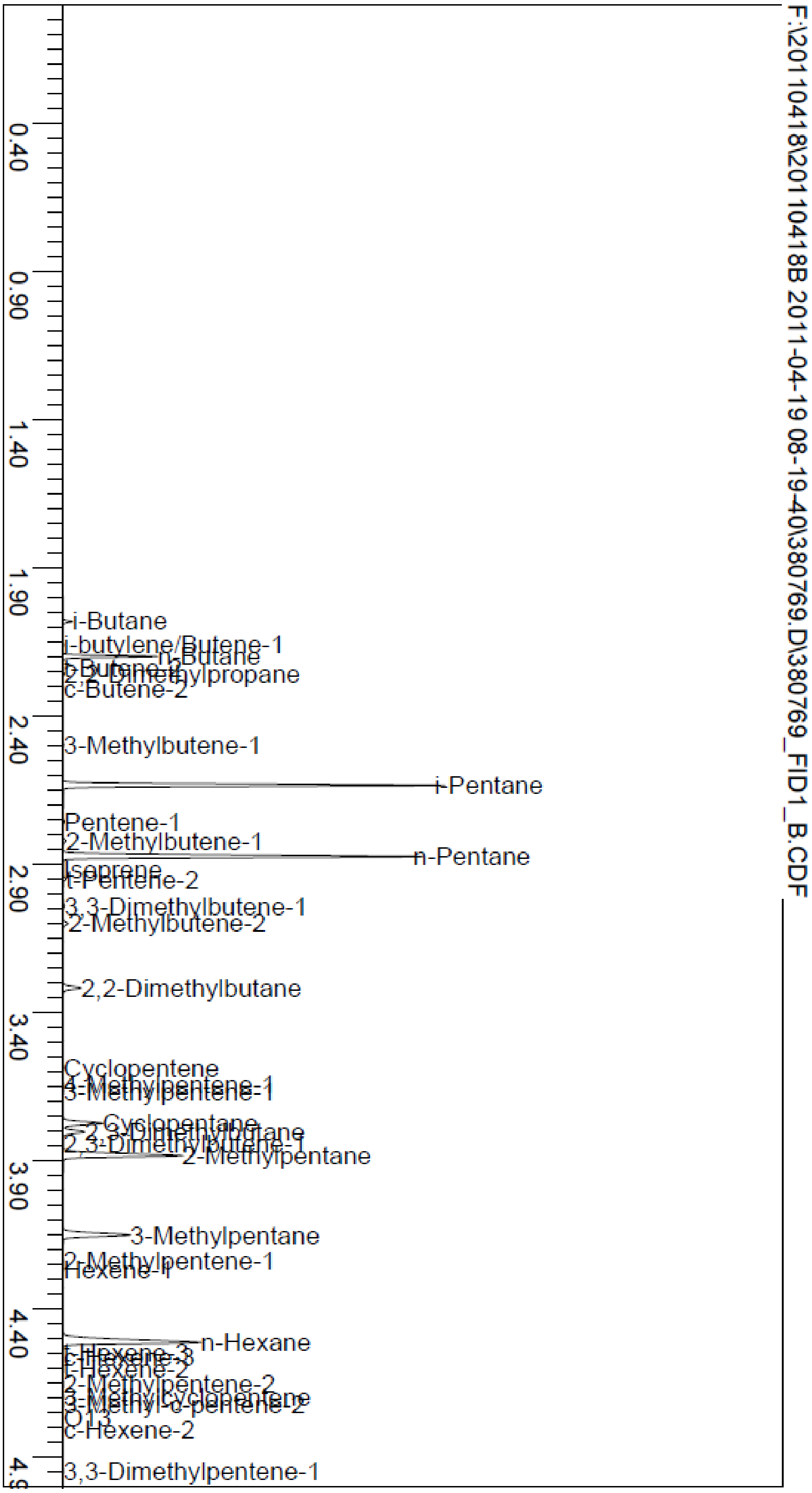
Component List

Pk#	Time	Group	Component	%Wgt	%Vol
173	18.680	?	Unidentified	0.003	0.002
174	18.700	?	Unidentified	0.003	0.002
175	18.797	I9	I9	0.028	0.027
176	18.883	?	Unidentified	0.004	0.004
177	18.934	?	Unidentified	0.016	0.014
178	19.046	P9	n-Nonane	0.739	0.719
179	19.150	N9	1,1-Methylethylcyclohexane	0.105	0.091
180	19.269	N9	N24	0.019	0.017
181	19.300	N9	N25	0.019	0.017
182	19.379	?	Unidentified	0.006	0.005
183	19.444	?	Unidentified	0.003	0.003
184	19.504	A9	i-Propylbenzene	0.050	0.041
185	19.558	N9	N26	0.004	0.004
186	19.662	N9	N27	0.089	0.078
187	19.687	?	Unidentified	0.014	0.012
188	19.770	?	Unidentified	0.027	0.027
189	19.797	?	Unidentified	0.003	0.003
190	19.876	N9	i-Propylcyclohexane	0.016	0.014
191	19.974	I10	2,2-Dimethyloctane	0.038	0.037
192	20.003	I10	2,4-Dimethyloctane	0.005	0.004
193	20.063	?	Unidentified	0.007	0.007
194	20.088	?	Unidentified	0.003	0.003
195	20.185	N9	N28	0.015	0.013
196	20.241	N9	N29	0.005	0.004
197	20.287	I10	2,6-Dimethyloctane	0.092	0.088
198	20.336	I10	2,5-Dimethyloctane	0.015	0.014
199	20.487	N9	n-Butylcyclopentane	0.027	0.024
200	20.553	N10	N30	0.012	0.011
201	20.659	I10	I14	0.009	0.009
202	20.715	I10	3,3-Dimethyloctane	0.052	0.049
203	20.797	N10	N31	0.010	0.009
204	20.841	?	Unidentified	0.005	0.004
205	20.888	A9	n-Propylbenzene	0.045	0.037
206	20.945	I10	3,6-Dimethyloctane	0.004	0.003
207	20.973	?	Unidentified	0.007	0.006
208	21.031	I10	3-Methyl-5-ethylheptane	0.024	0.024
209	21.061	?	Unidentified	0.004	0.004
210	21.144	N10	N32	0.007	0.006
211	21.228	A9	1-Methyl-3-ethylbenzene	0.061	0.049
212	21.278	?	Unidentified	0.007	0.005
213	21.316	A9	1-Methyl-4-ethylbenzene	0.027	0.022
214	21.488	N10	N33	0.011	0.010
215	21.567	A9	1,3,5-Trimethylbenzene	0.030	0.024

Component List

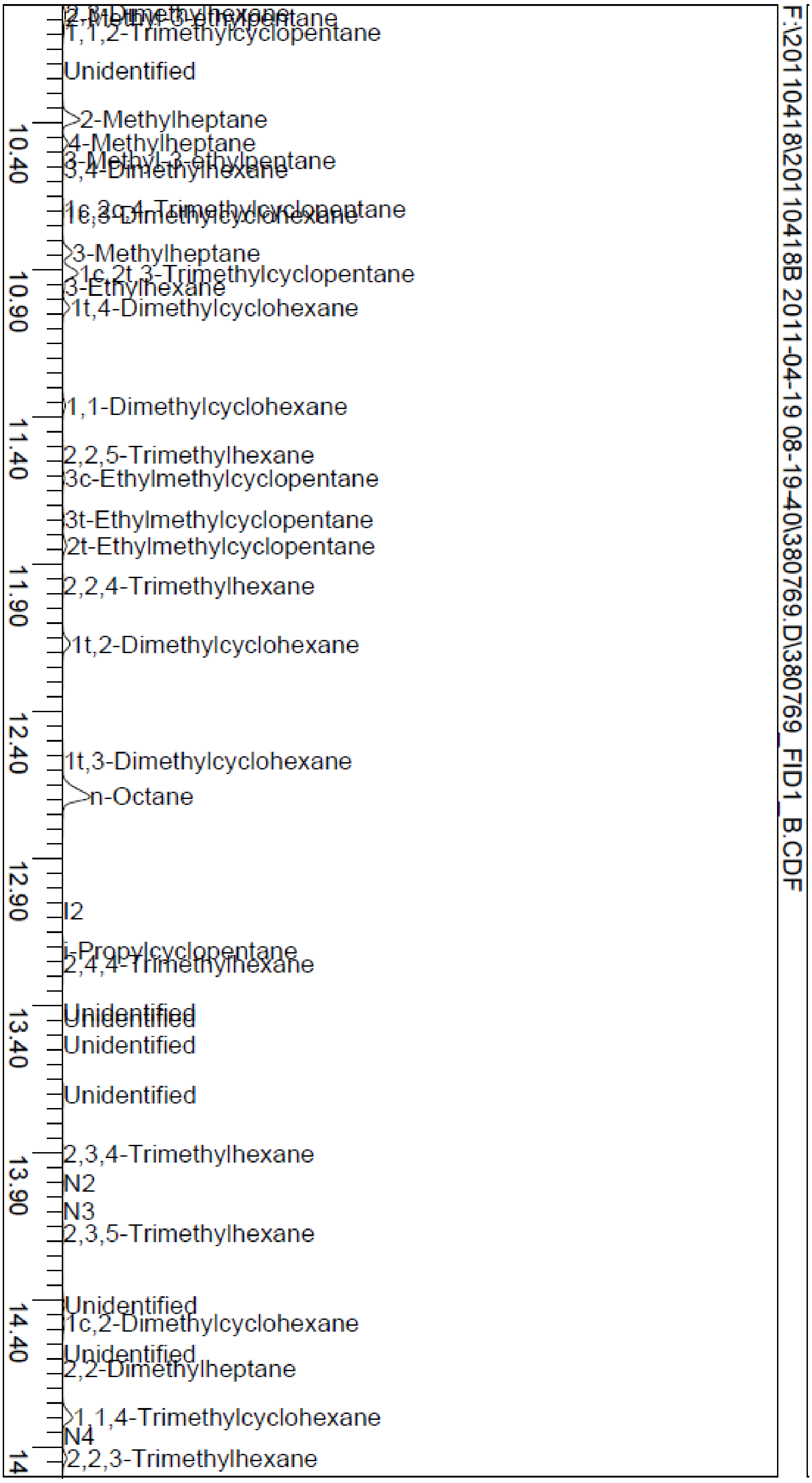
Pk#	Time	Group	Component	%Wgt	%Vol
216	21.591	?	Unidentified	0.005	0.004
217	21.653	I10	2,3-Dimethyloctane	0.007	0.006
218	21.760	N10	N34	0.003	0.003
219	21.839	I10	I17	0.005	0.005
220	21.911	I10	5-Methylnonane	0.010	0.010
221	21.964	A9	1-Methyl-2-ethylbenzene	0.019	0.015
222	22.021	I10	2-Methylnonane	0.009	0.009
223	22.086	I10	3-Ethyloctane	0.003	0.003
224	22.122	?	Unidentified	0.003	0.002
225	22.171	N10	N35	0.004	0.004
226	22.287	I10	3-Methylnonane	0.013	0.012
227	22.349	N10	N36	0.003	0.003
228	22.589	A9	1,2,4-Trimethylbenzene	0.036	0.029
229	22.667	I10	I20	0.004	0.004
230	23.413	P10	n-Decane	0.011	0.011
231	23.654	A9	1,2,3-Trimethylbenzene	0.005	0.004

Sample Chromatogram



Sample Chromatogram

Sample Chromatogram



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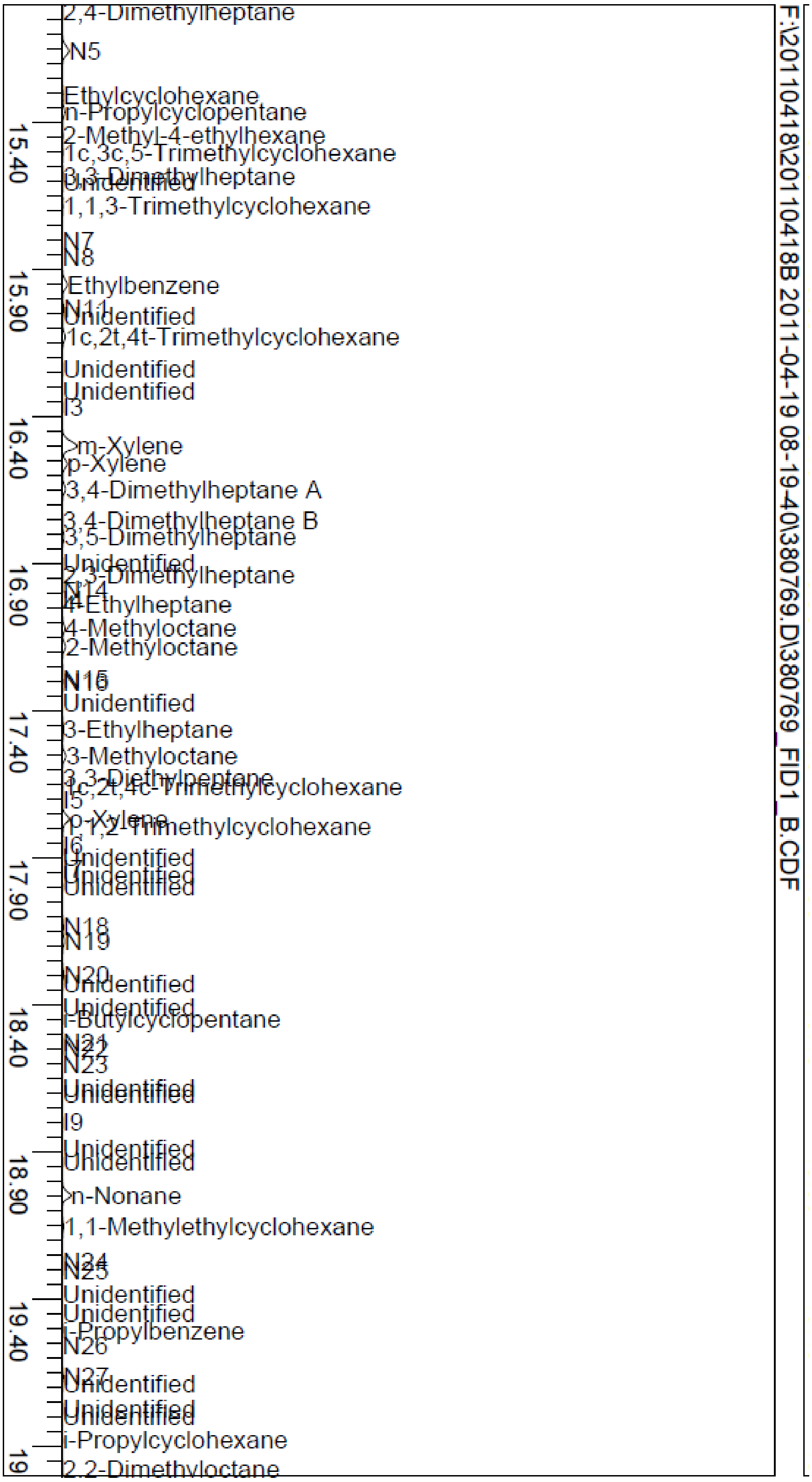
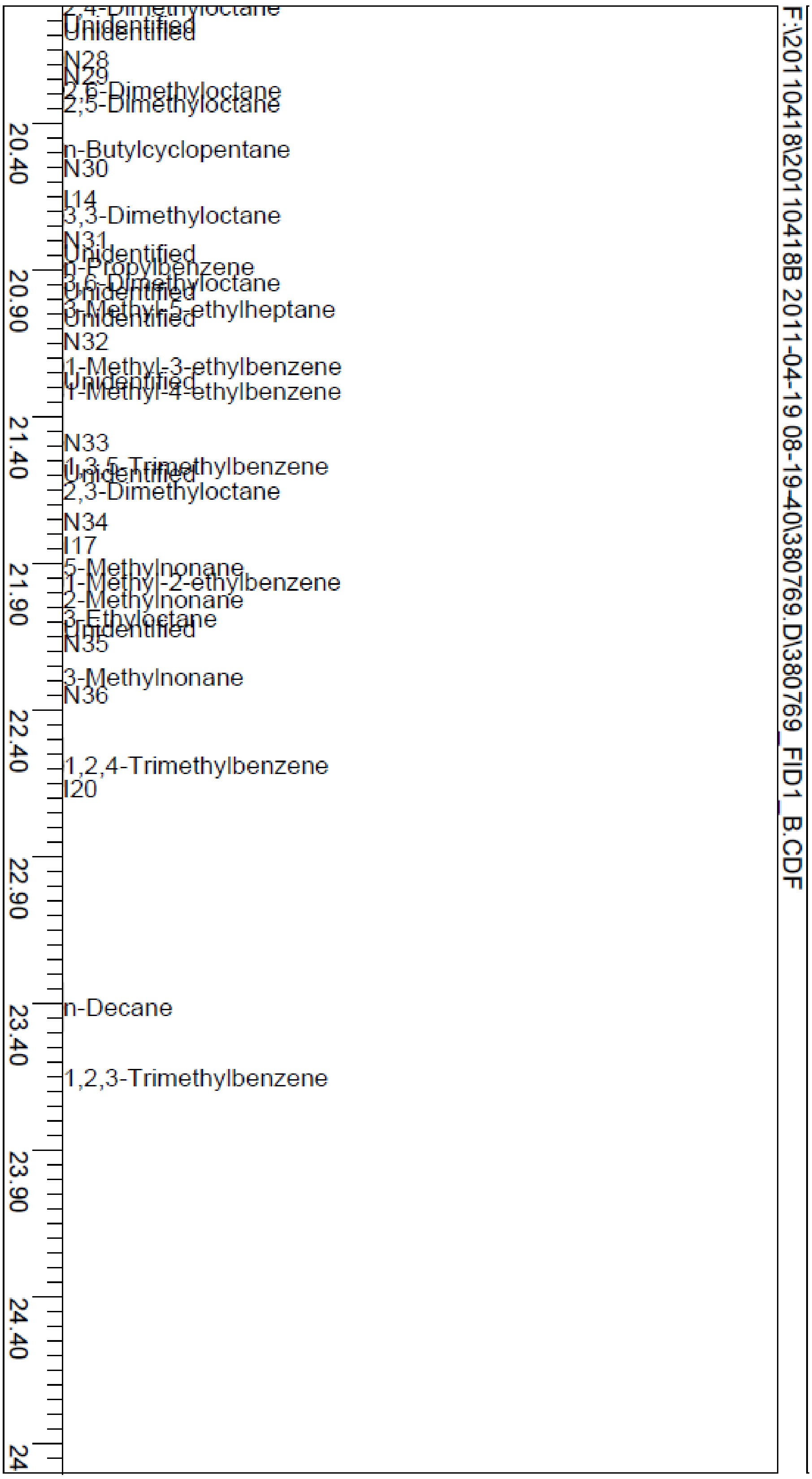


Sample Chromatogram



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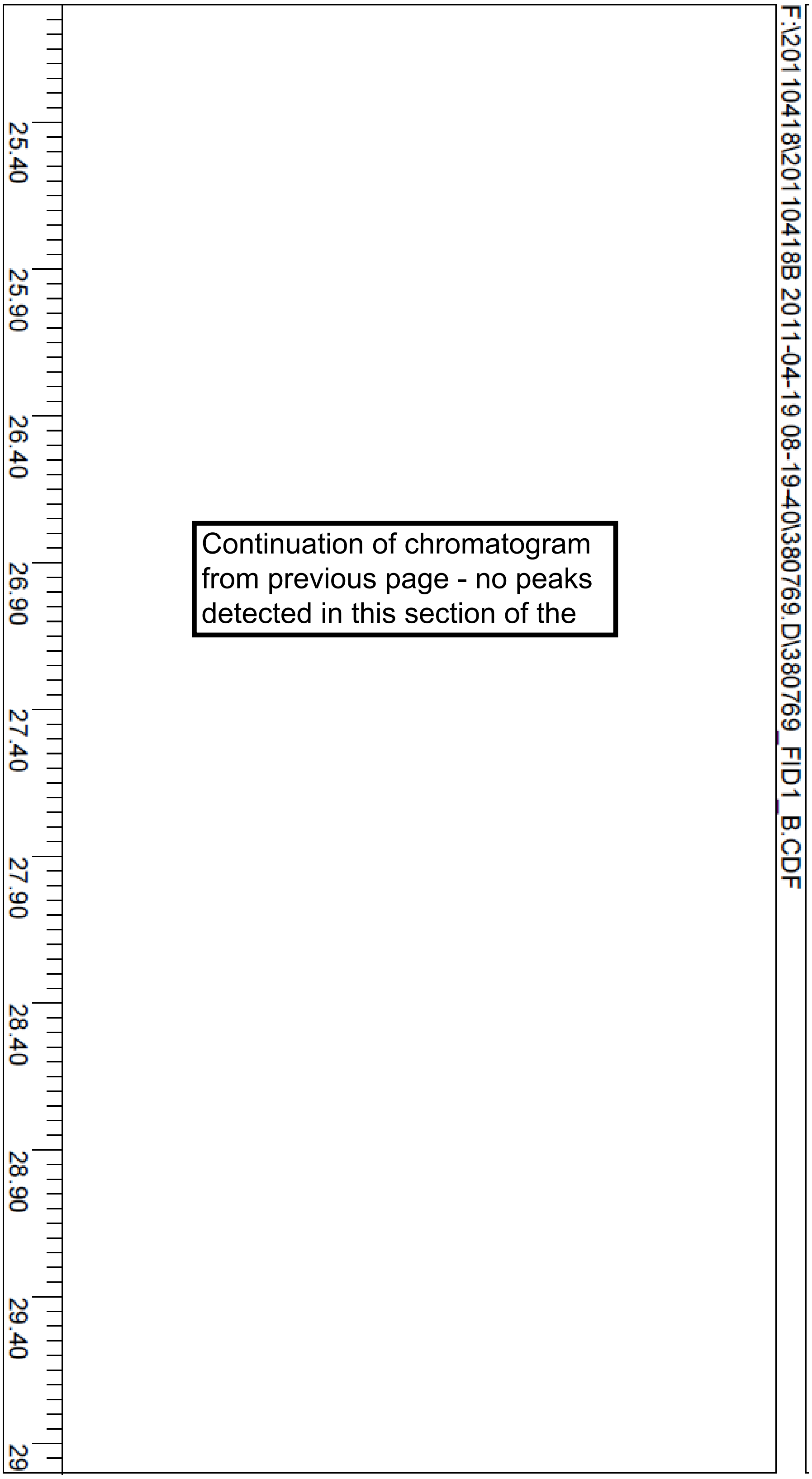

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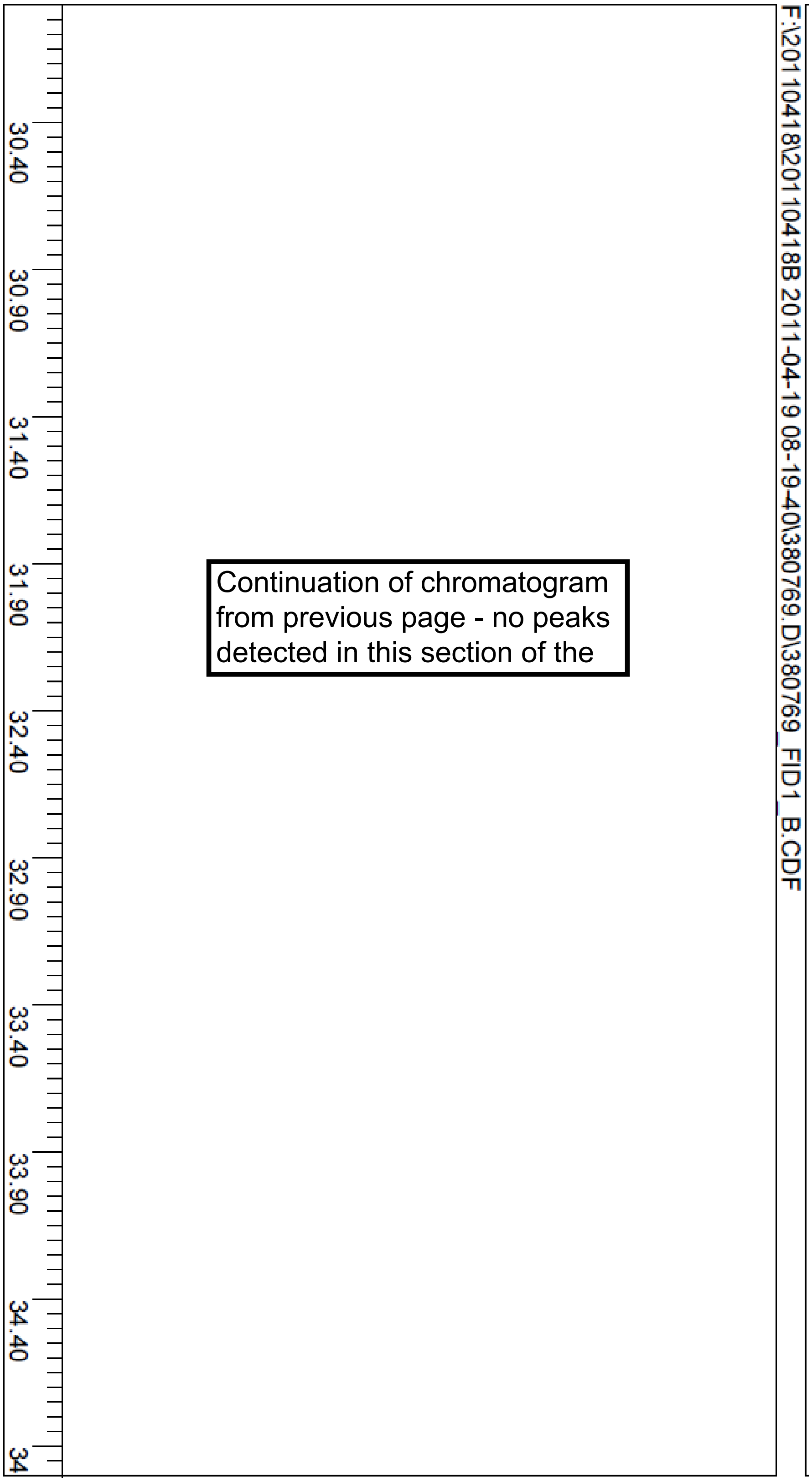
Sample Chromatogram



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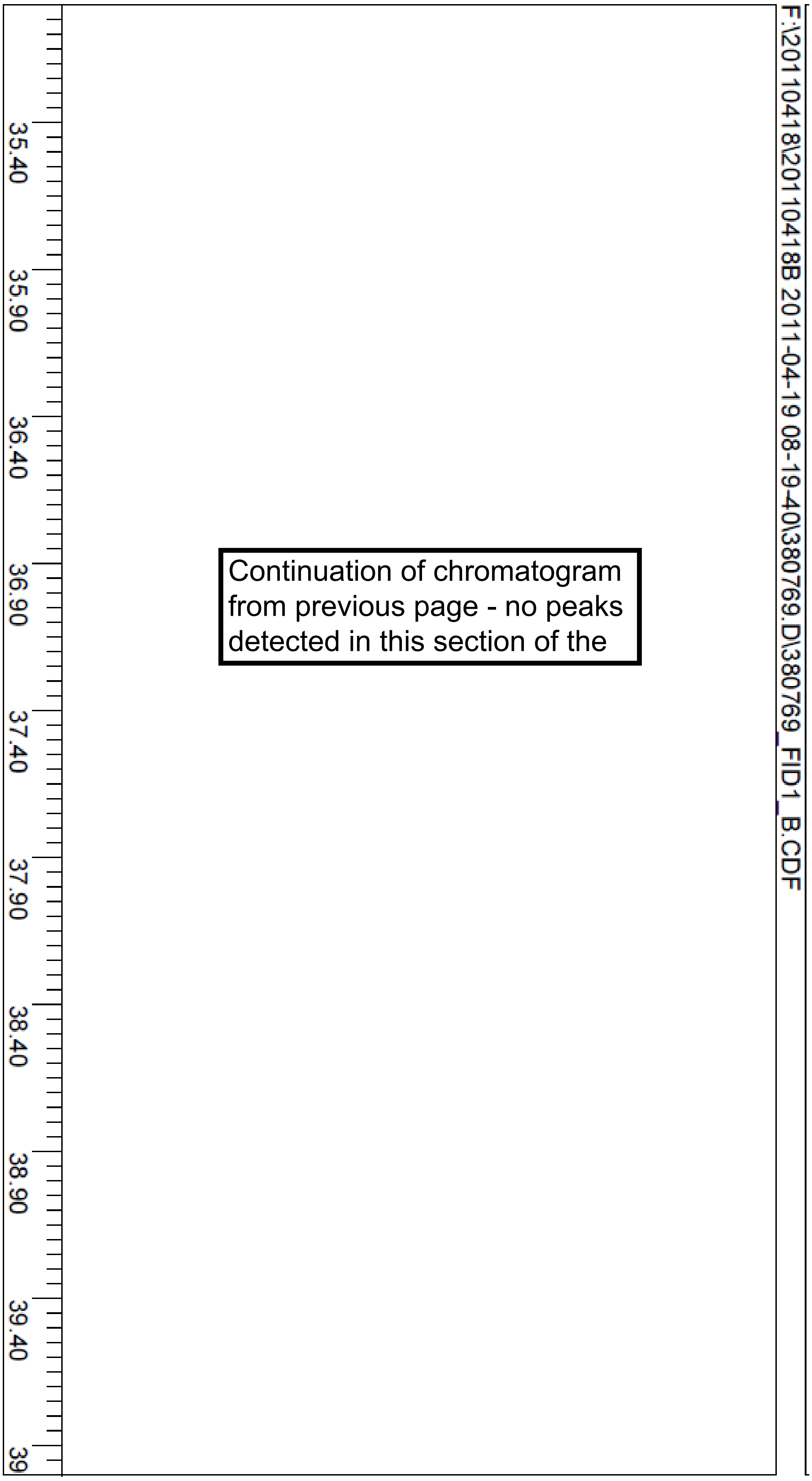
Sample Chromatogram



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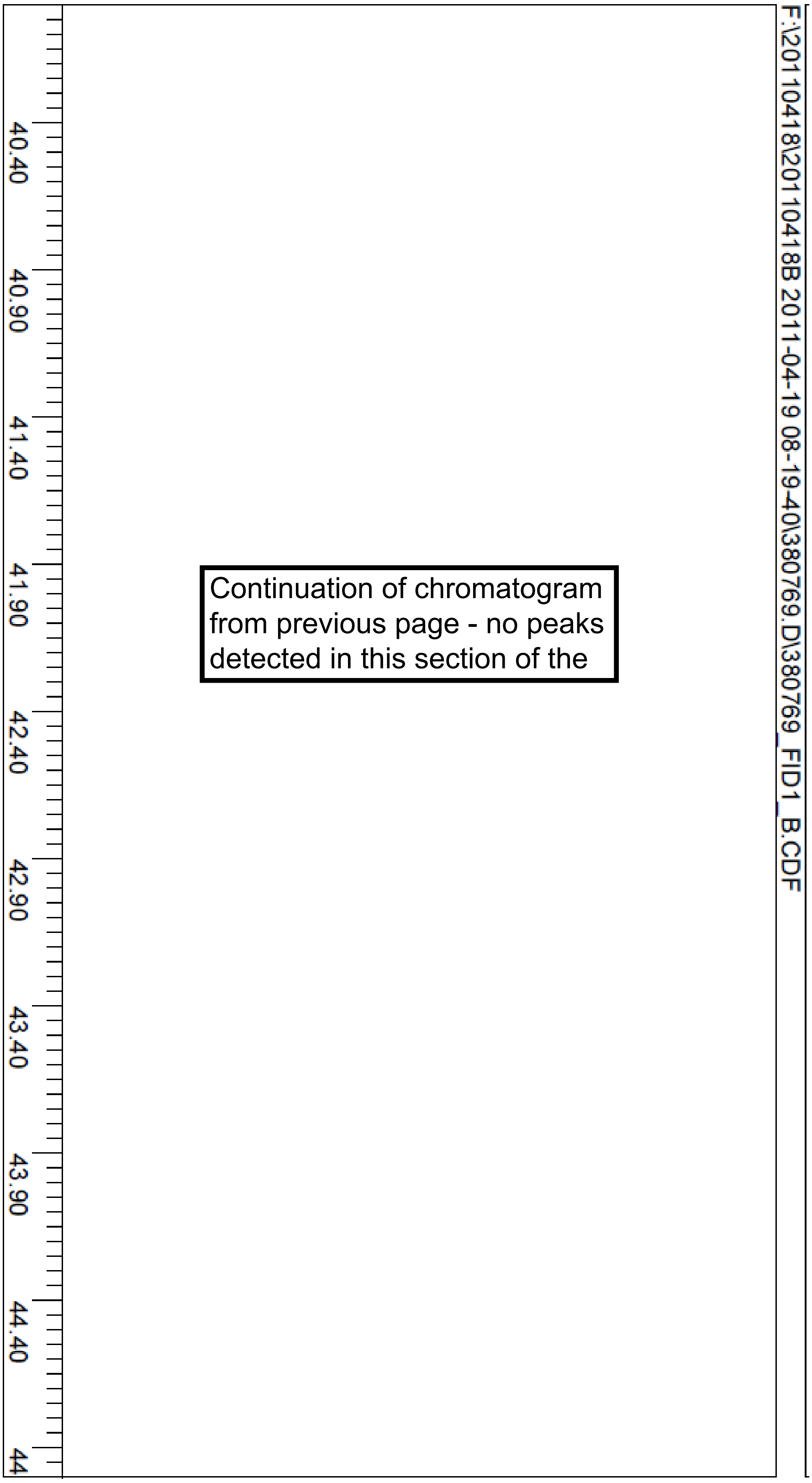
Sample Chromatogram



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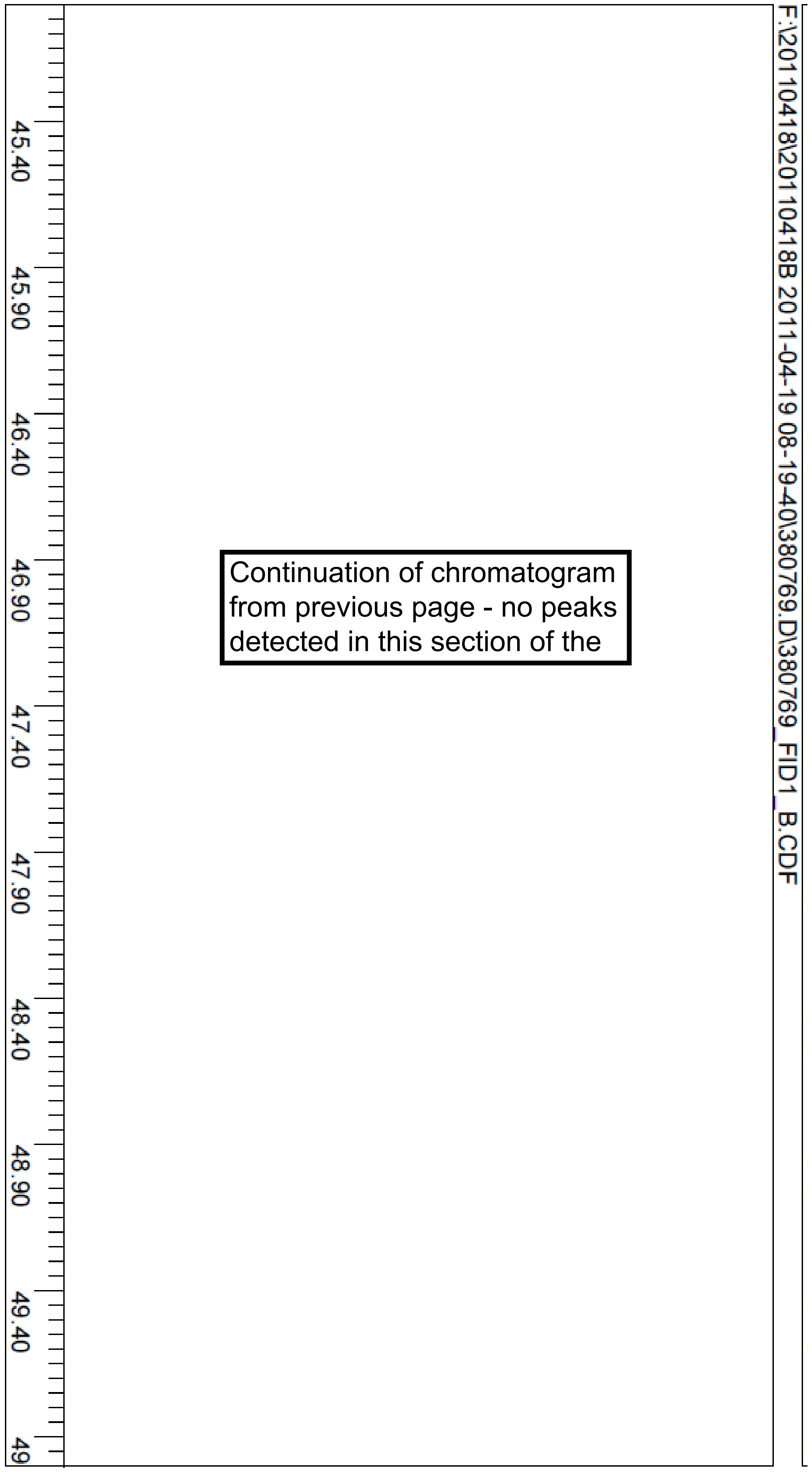
Sample Chromatogram



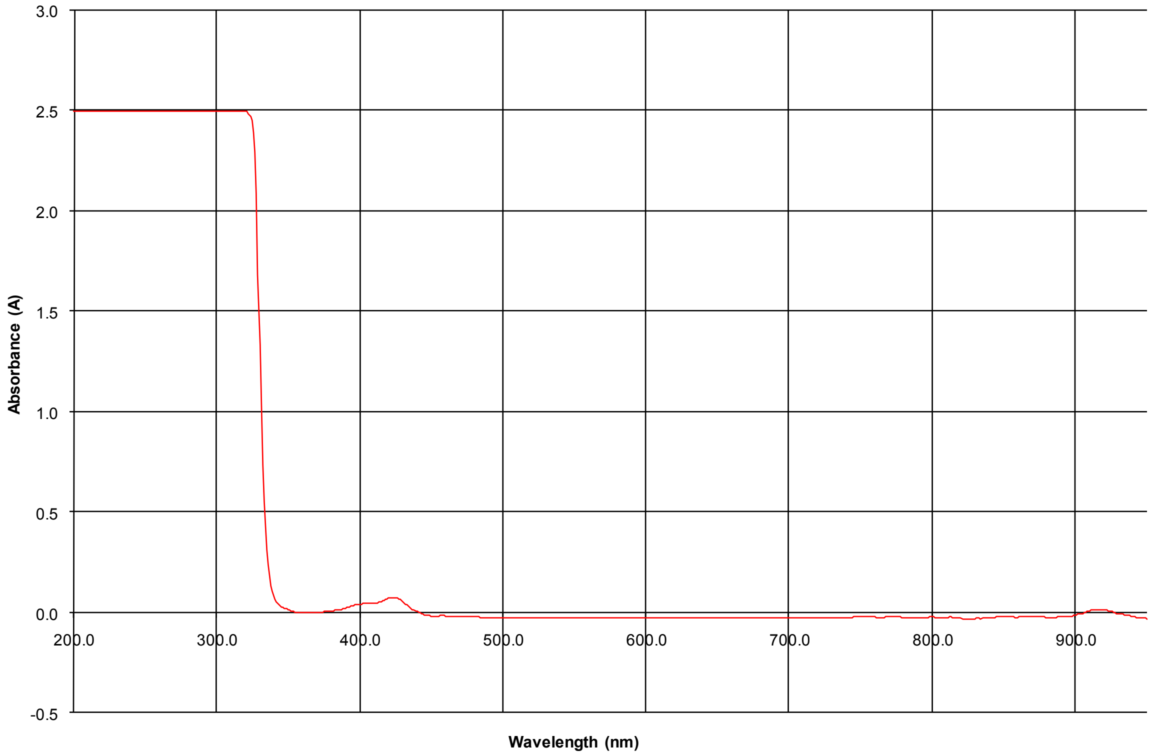
Continuation of chromatogram from previous page - no peaks detected in this section of the

APPENDIX 3: ANALYTICAL DATA FOR CASE STUDY 2

Kerosines	CAS No. 8008-20-6 EINECS No. 232-366-4

3.1. UV/Visible Spectroscopy

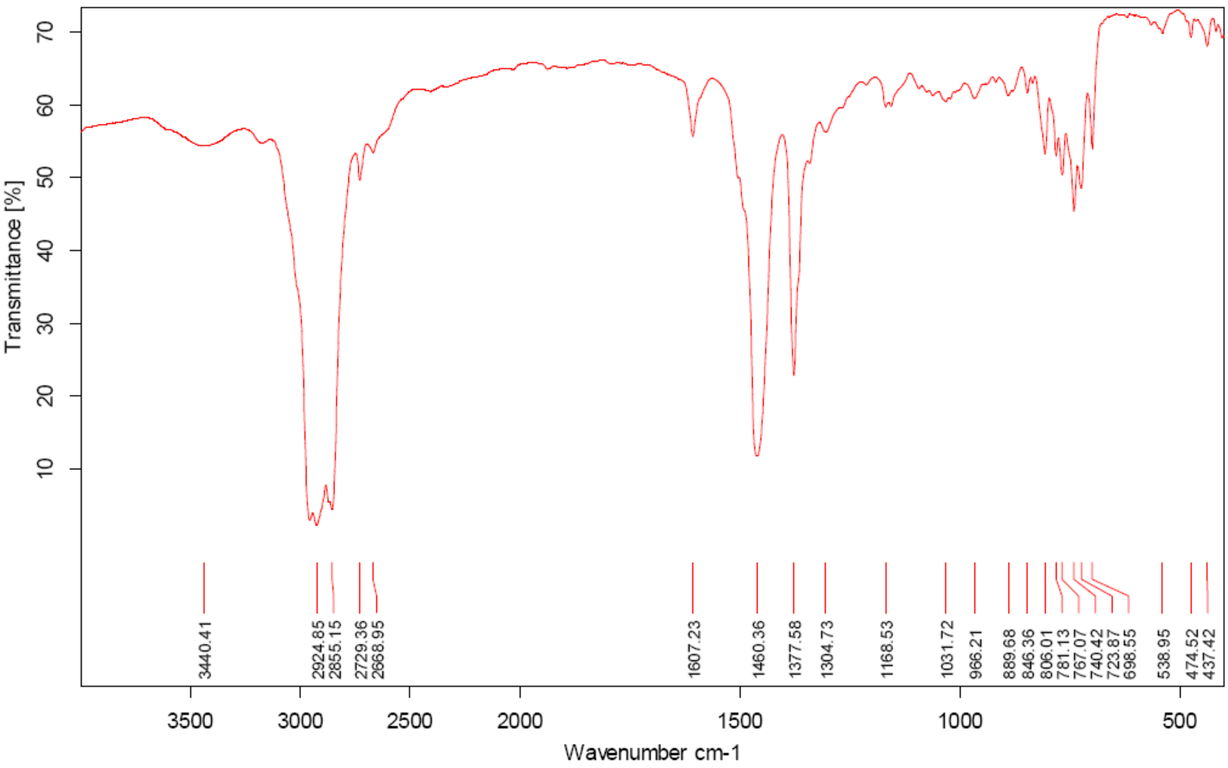
Instrument:	Perkin Elmer Lambda XLS+ UV/Visible Spectrophotometer
Range:	200-950 nm
Cell type:	1 cm quartz cell



The UV/Visible spectrum shows that the kerosine sample contains aromatic components.

3.2. IR Spectroscopy

Instrument:	Bruker Vertex 80 FTIR Spectrophotometer
Cell:	Potassium bromide plates
Range:	4000-400 cm^{-1}
Number of scans:	32
Spectral resolution:	4 cm^{-1}
Sample:	Thin film formed between potassium bromide plates

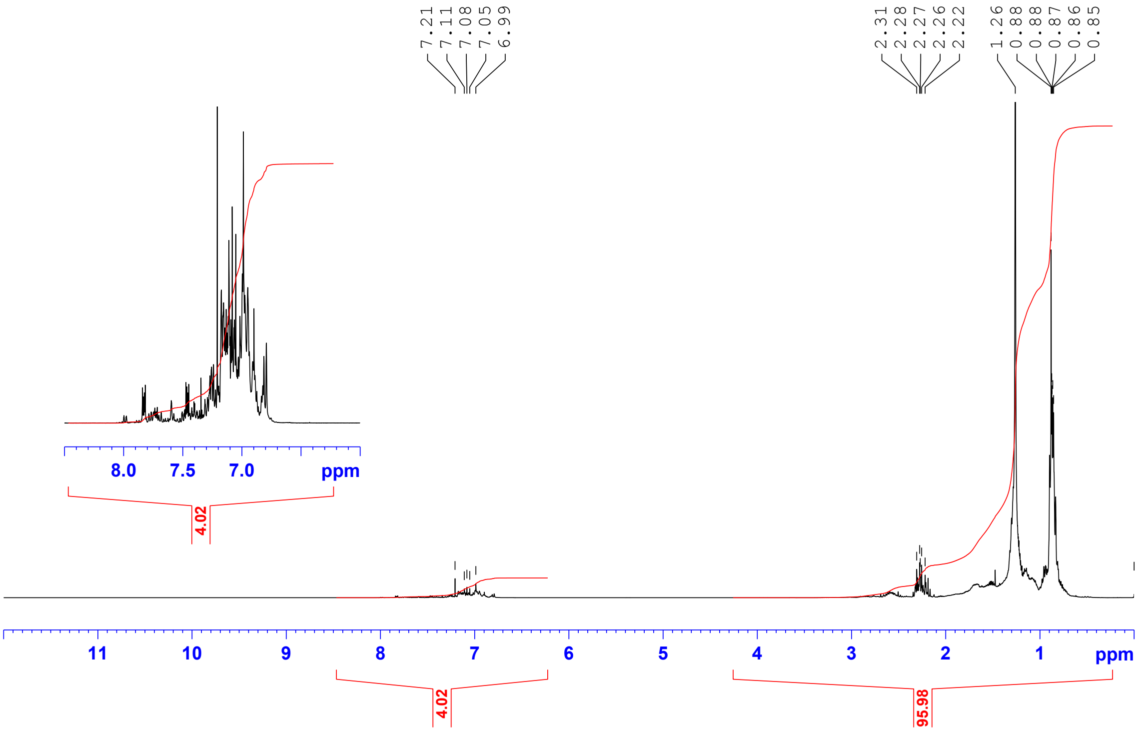


IR Spectral Band (cm^{-1})	Assignment
2925, 2855 (s)	C–H stretching alkyl
1607 (w)	Aromatic ring stretching
1460 (m)	C–H bending alkyl
1378 (m)	C–H bending (symmetrical CH_3)
724 (w)	$(CH_2)_n$ rocking

3.3. NMR Spectroscopy

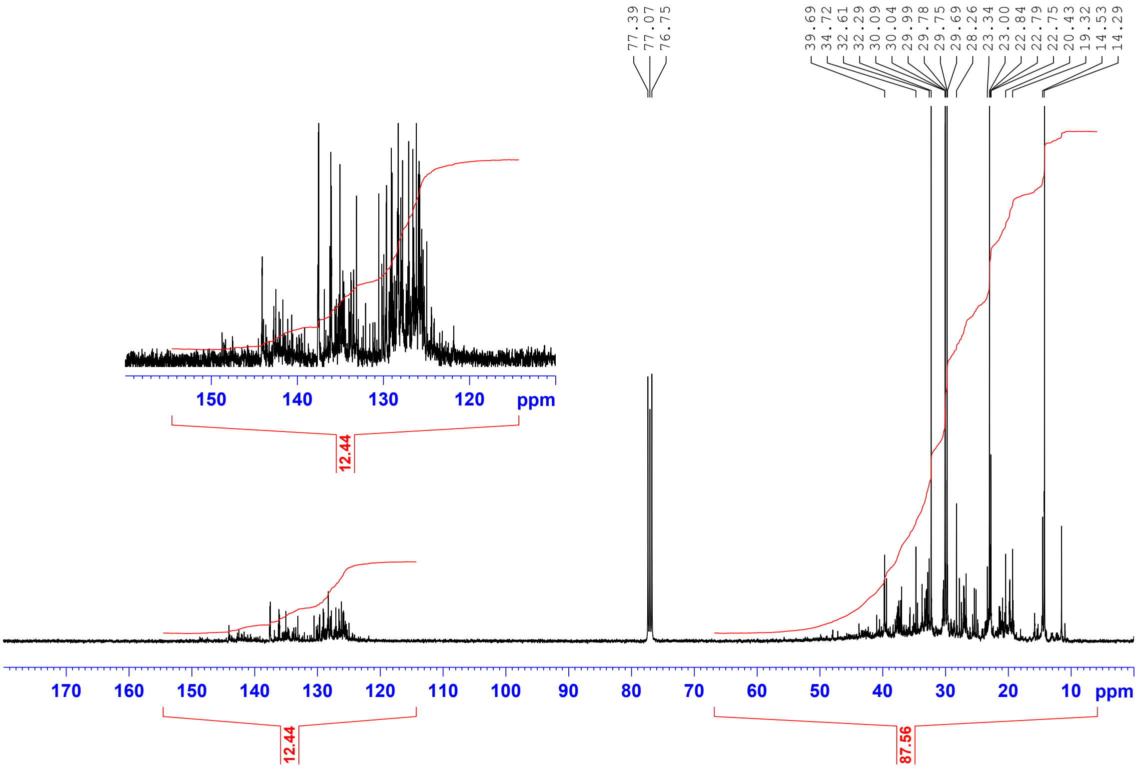
Instrument:	Bruker Avance 400 NMR Spectrometer
Frequency:	^{1}H - 400 MHz; ^{13}C - 100 MHz
Solvent:	Deuterochloroform
Reference:	Tetramethylsilane (TMS) (^{1}H, ^{13}C chemical shift 0 ppm).

^{1}H Spectrum



Chemical Shift (ppm relative to TMS)	Assignment
0.5-1.0	Methyl groups
1.0-1.4	Methylene groups
1.4-2.0	Methine groups
2.0-4.0	Groups adjacent to aromatic rings
6.7-8.0	Aromatic protons
7.3	Residual $CHCl_3$ in solvent

^{13}C Spectrum

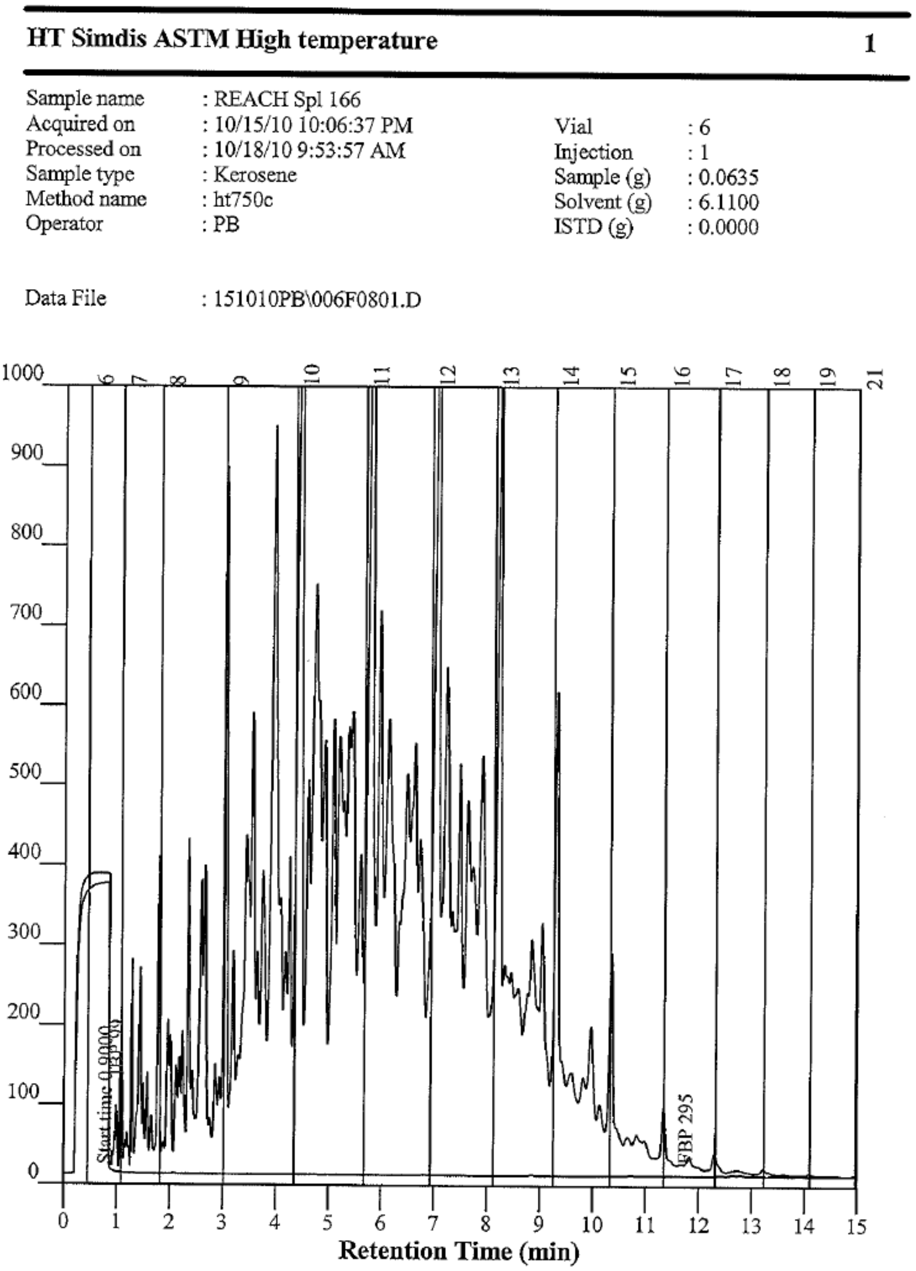


Chemical Shift (ppm relative to TMS)	Assignment
10-21	Methyl groups
14	**C**H$_3$-CH$_2$-CH$_2$-
23	CH$_3$-**C**H$_2$-CH$_2$-
30	Mid chain methylene groups
32	CH$_3$-CH$_2$-**C**H$_2$-
30-55	Branched carbons
77.0	CDCl$_3$ (solvent)
120-150	Aromatic carbon

The NMR spectra show that the kerosine sample is comprised of saturated and aromatic hydrocarbon components and contains 4.0% aromatic hydrogen (protons in the aromatic ring as a percentage of total proton content) and 12.4% aromatic carbon (carbons in the aromatic ring as a percentage of total carbon content). These values refer only to those nuclei within the aromatic rings of components present in the sample and do not include the nuclei present in substituent side chains.

3.4. SIMDIS-Gas Chromatography

SIMDIS-GC analysis was carried out according to IP 480/07. The sample was dissolved in carbon disulphide and analysed by temperature programmed GC with flame ionisation detection using a non-polar separation column. The resulting chromatogram was compared with a calibration chromatogram obtained under identical conditions using n-alkanes spanning the elution range of the hydrocarbons present in the sample. The boiling range distribution of the components present was determined from these data.



HT Simdis ASTM High temperature 1

Sample name : REACH Spl 166
Acquired on : 10/15/10 10:06:37 PM
Processed on : 10/18/10 9:53:57 AM
Sample type : Kerosene
Method name : ht750c
Operator : PB

Vial : 6
Injection : 1
Sample (g) : 0.0635
Solvent (g) : 6.1100
ISTD (g) : 0.0000

Data File : 151010PB\006F0801.D

SIMDIS GC analysis shows that the kerosine sample contains components distributed over the C_{7-18} carbon number and 99-295°C boiling ranges.

3.5. Comprehensive Two Dimensional Gas Chromatography (GCxGC)

The sample was examined directly by GCxGC using the following operating conditions:

Instrument : Agilent Technologies 6890 Series GC

Injector : Optic II PTV
Split mode
Packed injection port liner
Initial temperature 45 °C
Initial time 0 min
Ramp 8 °C/sec
Final temperature 200 °C
Final time 174 min
Carrier gas pressure 250 kPa
Split flow 150 mL/min

Sample injection : Agilent ALS
Injection volume 0.1 µL

Modulator : Cryogenic modulator, single jet loop type (ZOEX Corporation)
Modulation time 7.5 sec
Pulse width 400 ms
Nitrogen flowrate ~5 L/min (optimised to modulate n-C$_5$)

Detector : Flame-ionisation
Temperature 350 °C
Make-up gas Helium
Make-up flow 20 mL/min
Hydrogen flow 35 mL/min
Air flow 350 mL/min

Column 1 : 10 m x 0.25 mm i.d. dimethylpolysiloxane (DB-1)
0.25 µm film thickness

Modulation column : 2 m x 0.10 mm i.d deactivated fused silica
(1 m in loop)

Column 2 : 2 m x 0.10 mm i.d. polysilphenylene-siloxane (BPX-50)
0.10 µm film thickness

Transfer line (2nd Dim to FID) : 0.3 m x 0.10 mm i.d. deactivated fused silica

Carrier gas : Helium

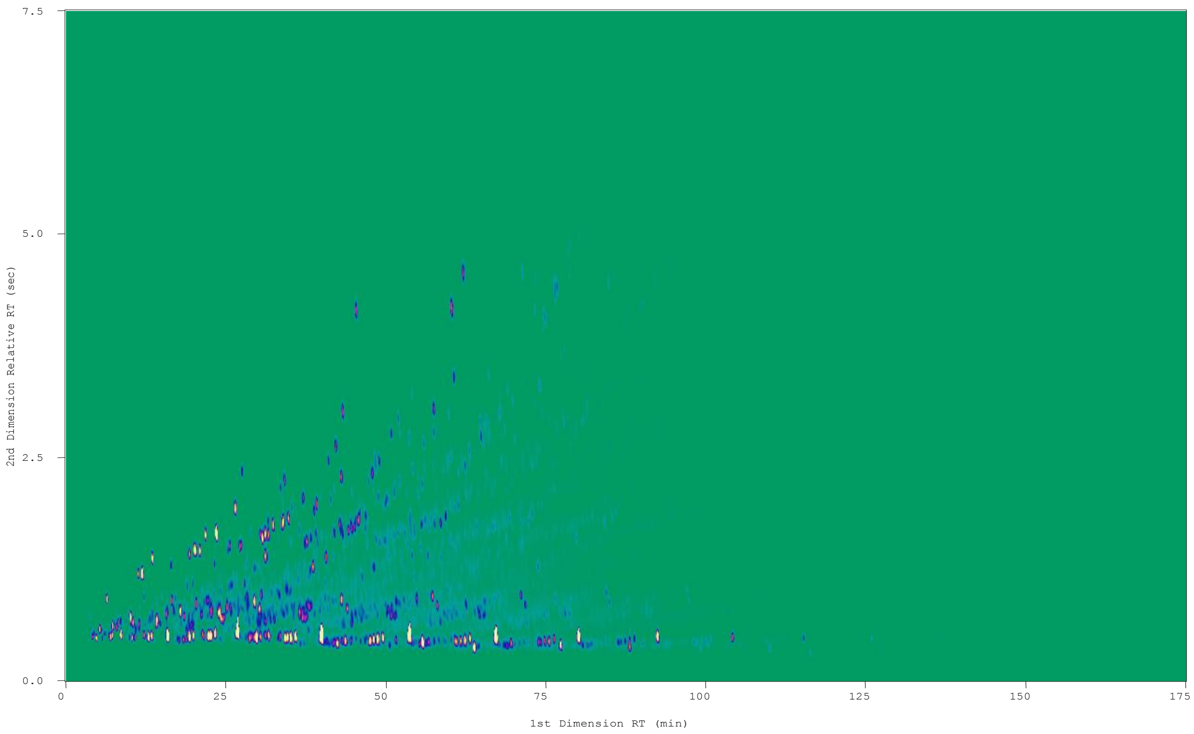
Main (1st Dim) oven temperature : 40 °C (5 min isothermal) then 1.0 °C/min to 200 °C (10 min isothermal)

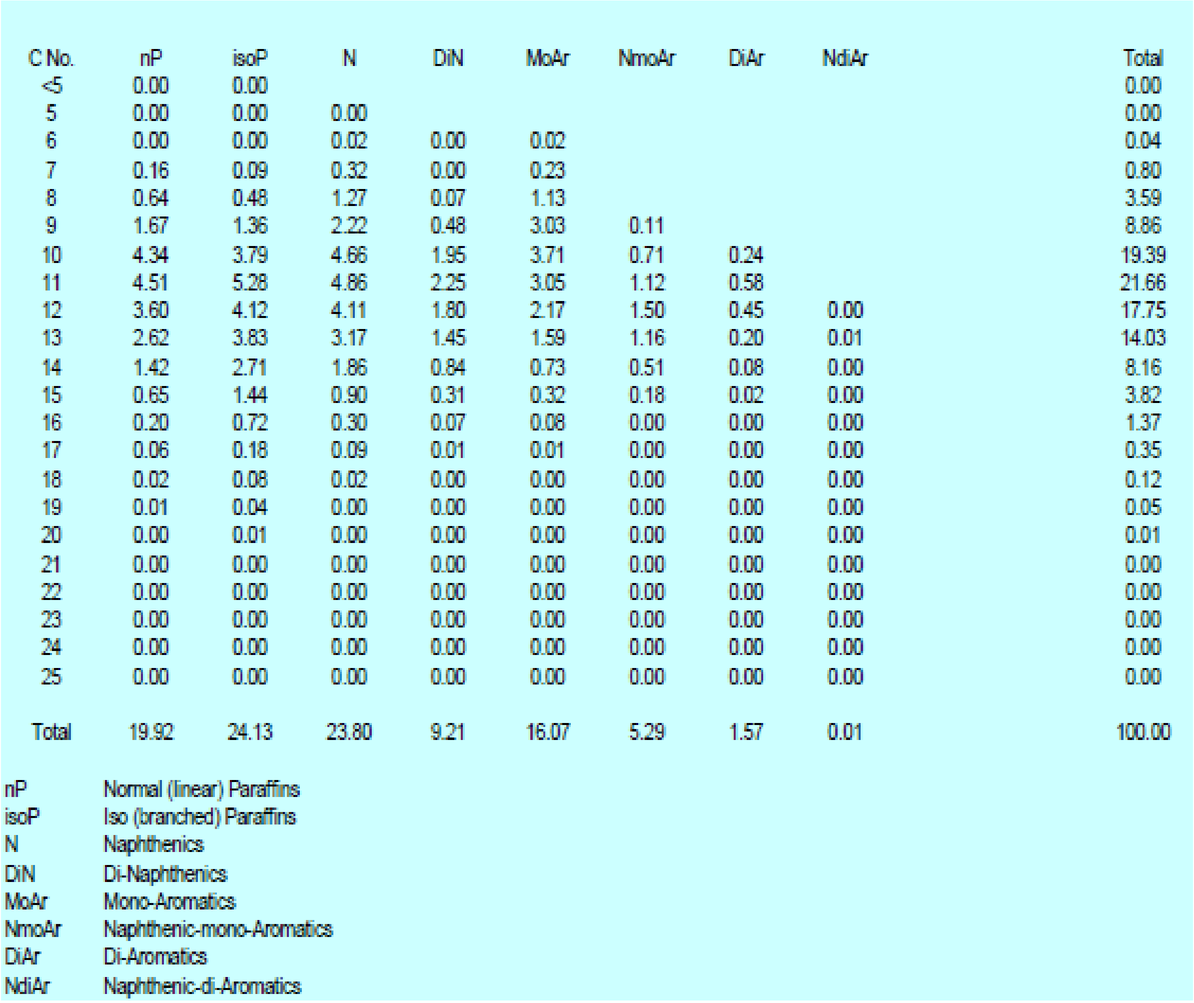
Aux (2nd Dim) oven temperature : 65 °C offset from first-dimension: 105 °C (5 min isothermal) then 1.0 °C/min to 265 °C (10 min isothermal)

Hot Jet temperature : 50 °C offset from first-dimension: 90 °C (5 min isothermal) then 1.0 °C/min to 250 °C (10 min isothermal)

The individual components found by GCxGC were grouped both on the basis of carbon number (C_5 to C_{25}) and the following chemical functionalities:

- normal paraffins
- iso-paraffins
- mono-naphthenics
- di-naphthenics
- mono-aromatics
- naphthenic mono-aromatics
- di-aromatics
- naphthenic di-aromatics



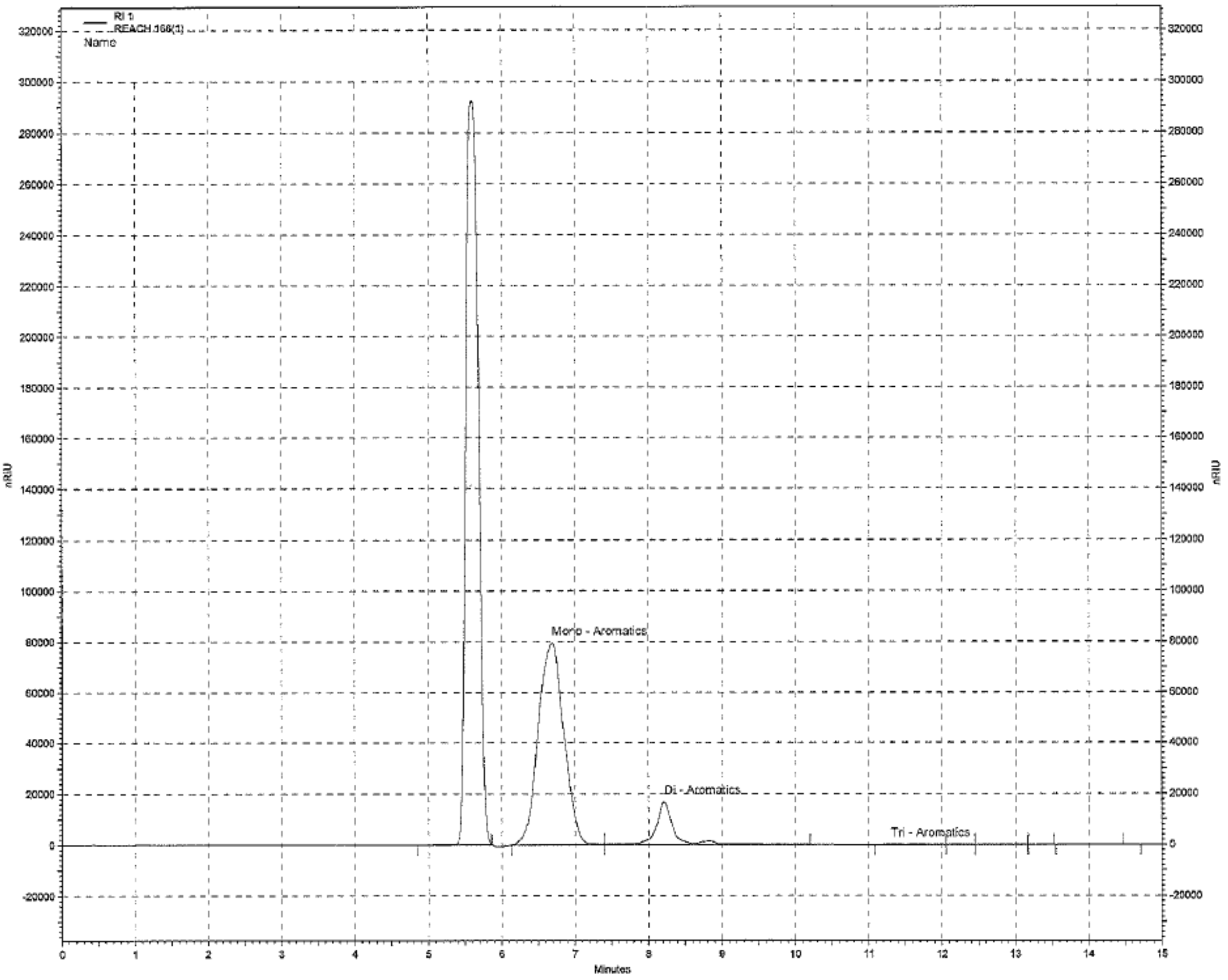


C No.	nP	isoP	N	DiN	MoAr	NmoAr	DiAr	NdiAr	Total
<5	0.00	0.00							0.00
5	0.00	0.00	0.00						0.00
6	0.00	0.00	0.02	0.00	0.02				0.04
7	0.16	0.09	0.32	0.00	0.23				0.80
8	0.64	0.48	1.27	0.07	1.13				3.59
9	1.67	1.36	2.22	0.48	3.03	0.11			8.86
10	4.34	3.79	4.66	1.95	3.71	0.71	0.24		19.39
11	4.51	5.28	4.86	2.25	3.05	1.12	0.58		21.66
12	3.60	4.12	4.11	1.80	2.17	1.50	0.45	0.00	17.75
13	2.62	3.83	3.17	1.45	1.59	1.16	0.20	0.01	14.03
14	1.42	2.71	1.86	0.84	0.73	0.51	0.08	0.00	8.16
15	0.65	1.44	0.90	0.31	0.32	0.18	0.02	0.00	3.82
16	0.20	0.72	0.30	0.07	0.08	0.00	0.00	0.00	1.37
17	0.06	0.18	0.09	0.01	0.01	0.00	0.00	0.00	0.35
18	0.02	0.08	0.02	0.00	0.00	0.00	0.00	0.00	0.12
19	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.05
20	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	19.92	24.13	23.80	9.21	16.07	5.29	1.57	0.01	100.00

nP	Normal (linear) Paraffins
isoP	Iso (branched) Paraffins
N	Naphthenics
DiN	Di-Naphthenics
MoAr	Mono-Aromatics
NmoAr	Naphthenic-mono-Aromatics
DiAr	Di-Aromatics
NdiAr	Naphthenic-di-Aromatics

GCxGC analysis of the kerosine sample shows that it consists of similar quantities of normal paraffins (19.9% m/m), iso-paraffins (24.1% m/m), mono-naphthenic (23.8% m/m) and aromatic (23.0% m/m) hydrocarbons together with lower levels of di-naphthenic hydrocarbons (9.2% m/m). The components present are distributed over the C_{6-20} carbon number range

3.6. High Performance Liquid Chromatography



——— \\Gsstcts0006\stct_cds\GSEA Projects\LC06\Data\2010\23583_111010\020.dat, RI 1

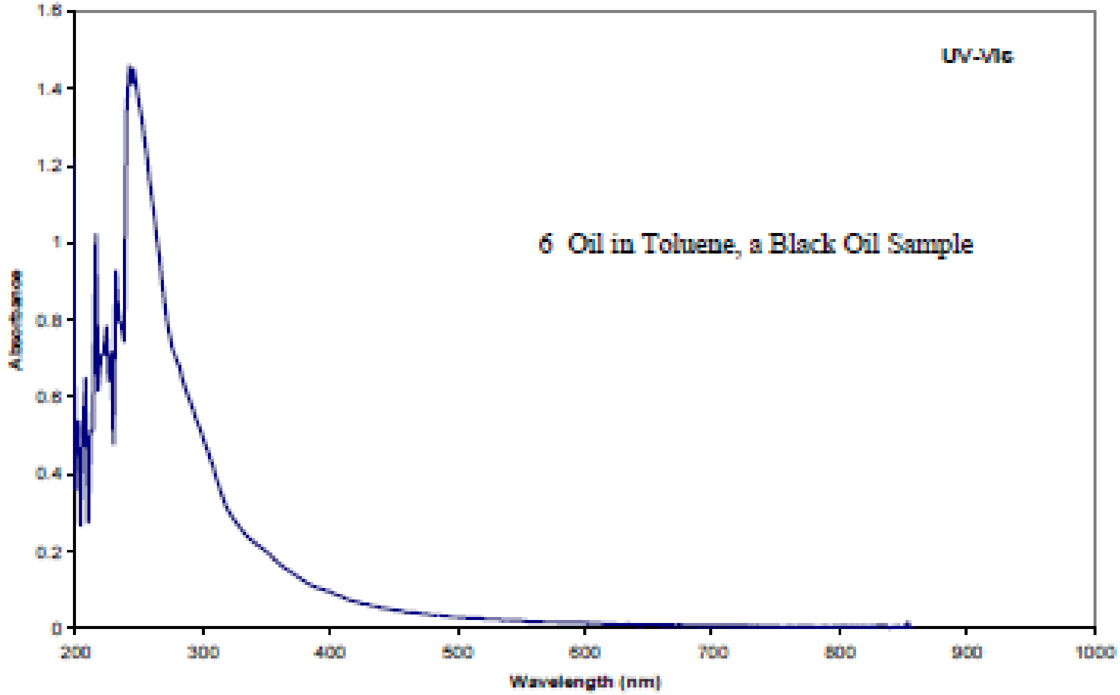
HPLC analysis (IP 391 method) shows that the kerosine sample contains 19.1% (m/m) mono-aromatic, 1.5% (m/m) di-aromatic and <0.1% (m/m) tri+aromatic hydrocarbons.

APPENDIX 4: ANALYTICAL DATA FOR CASE STUDY 3

Heavy Fuel Oil Components	CAS No. 68553-00-4 EINECS No. 271-384-7

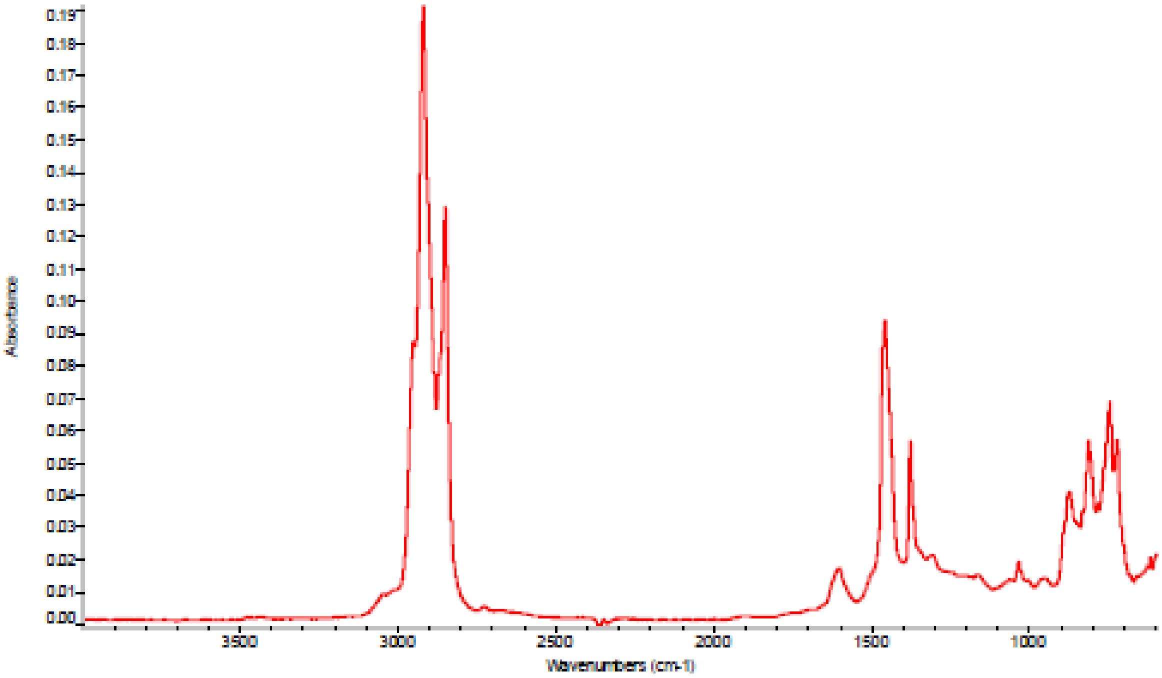
4.1. UV/Visible Spectroscopy

Instrument:	Thermo Scientific Evolution 600 UV-VIS Spectrophotometer
Cell type:	3 ml in UV-Cuvette (Fisher brand)
Slit width:	1 cm
Path length:	1 cm
Range:	190-900 nm
Solvent:	Toluene
Concentration:	0.00217 g/50 mL Toluene
Test temperature:	20 °C
Scanning speed:	600 nm/min
Number of cycles:	1
Slit - Band width:	1.5 nm, Data interval: 2 nm



4.2. IR Spectroscopy

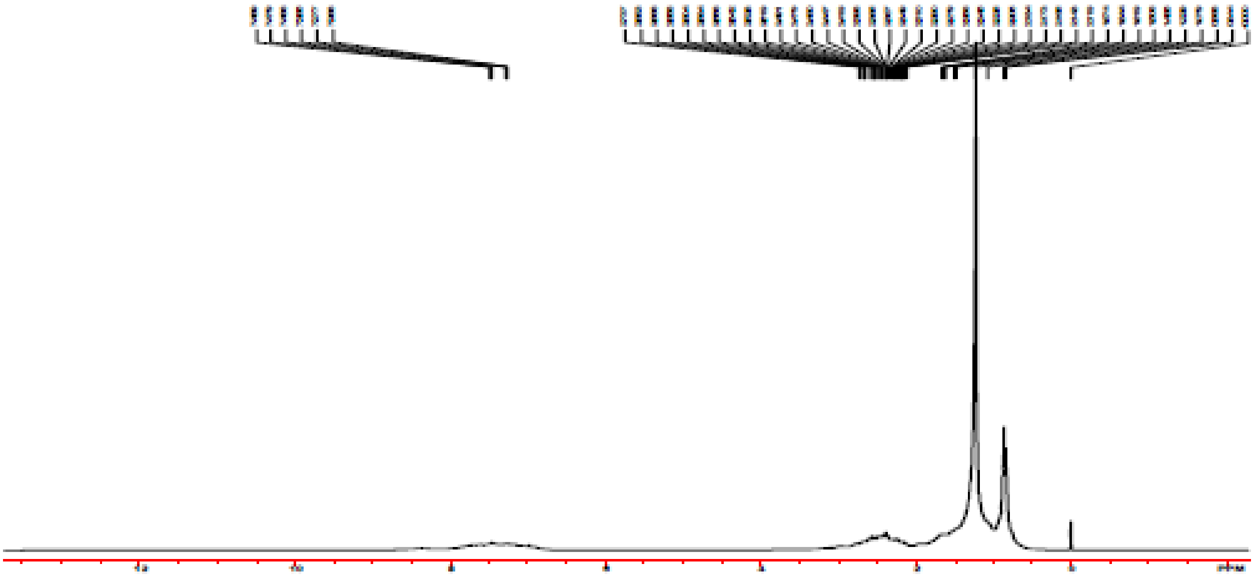
Instrument:	Thermo Nicolet Magna 550 FTIR Instrument with ATR accessory
Number of scans:	32
Spectral resolution:	4 cm^{-1}

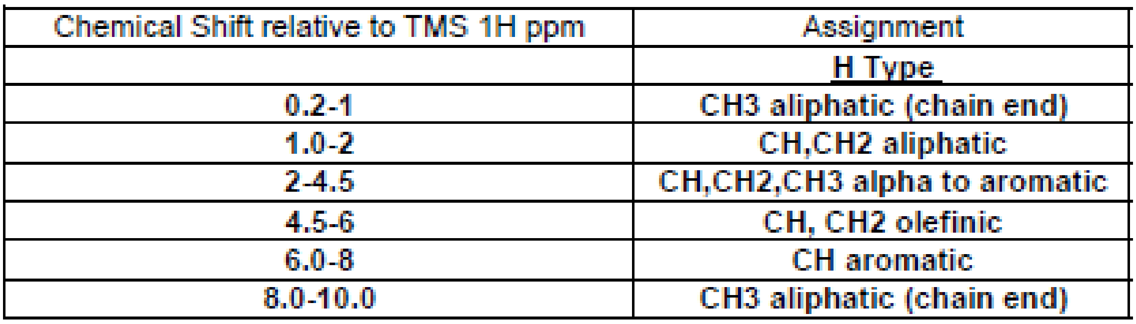


Wavenumber (cm-1)	Vibration assignment
3040	SP^2 CH stretch
2921	SP^3 antisymm CH stretch
2851	SP^3 symm CH stretch
1600	Arom.C=C stretch
1455	CH$_2$ bending
1376	CH$_3$ bending
720-870	CH out of plane bending

4.3. NMR Spectroscopy

Instrument:	Varian Mercury Plus 300 NMR Spectrometer
Frequency:	300 MHz
Solvent:	Deuterochloroform
Concentration:	30%
Temperature:	25 °C
Reference:	Tetramethylsilane (chemical shift 0.0 ppm)

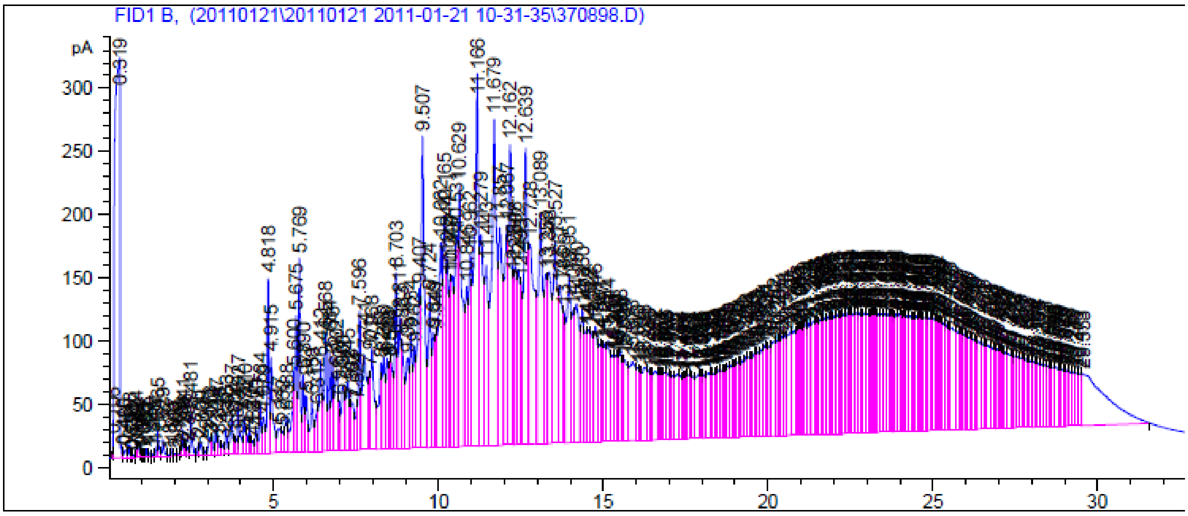




Chemical Shift relative to TMS 1H ppm	Assignment
	H Type
0.2-1	CH3 aliphatic (chain end)
1.0-2	CH,CH2 aliphatic
2-4.5	CH,CH2,CH3 alpha to aromatic
4.5-6	CH, CH2 olefinic
6.0-8	CH aromatic
8.0-10.0	CH3 aliphatic (chain end)

4.4. SIMDIS-Gas Chromatography

Method:	**ASTM D7169 Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography.**
Boiling Range:	The Boiling Range of this sample is between 264.8 degrees C and 715.3 degrees C, for the 5 to 90% boiling fraction. 10% of this material boils above 715.3 degrees C, and its boiling range can not be quantified.
Carbon Number Range:	The Carbon Number range of this sample is between 14 and 98 for the 5% to 90% fraction. 10% of this material has a retention time on the simulated distillation greater than n-C100 and an implied carbon number range greater than C100.



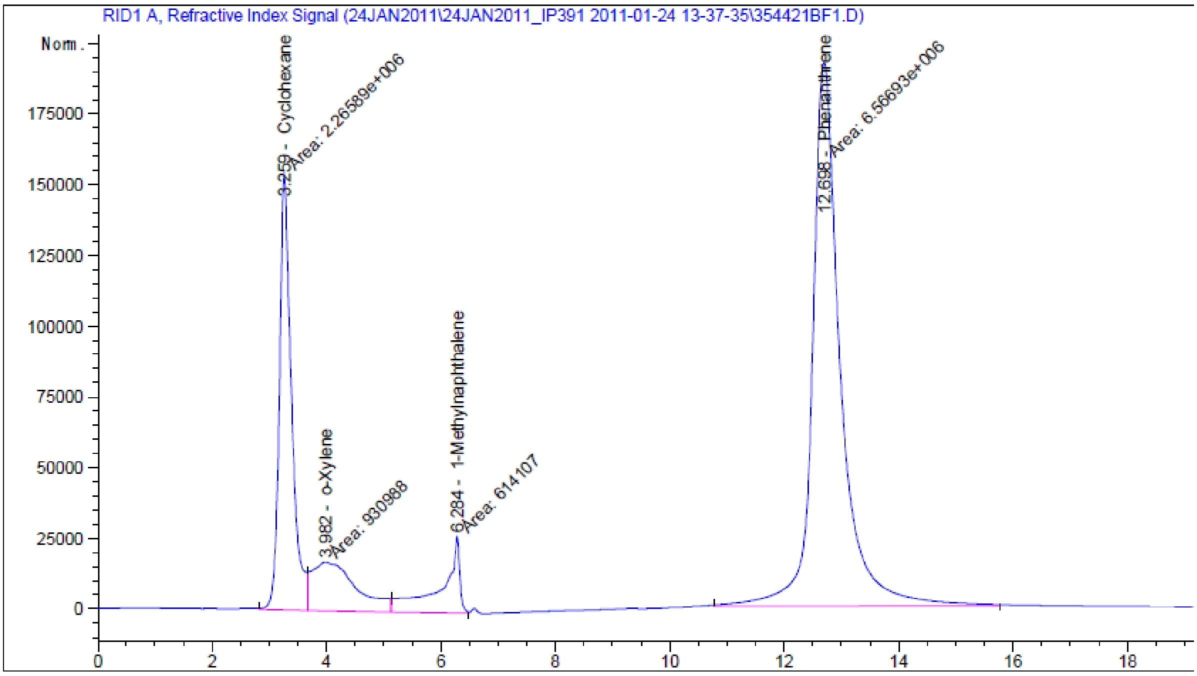
%Off	BP(C)
IBP	170.8
1	197.5
2	222.5
3	241.7
4	252.1
5	264.8
6	275.8
7	288.1
8	296.6
9	306.6
10	313.5
11	320.9
12	328.3
13	331.8
14	337.6
15	343.5
16	347.1
17	351.3
18	355.2
19	358.6
20	363.3
21	367.3
22	369.7
23	373.2
24	377.5
25	380.9
26	384.2
27	388.0
28	391.4
29	394.6
30	398.7
31	402.5
32	405.7
33	409.9
34	413.6
35	417.7
36	421.9
37	425.9
38	430.7
39	435.6
40	441.0
41	446.9
42	452.9
43	459.2
44	466.2
45	473.3
46	481.0
47	489.3
48	497.7
49	505.6
50	514.0
51	522.4
52	530.2
53	537.5
54	544.3
55	551.0
56	557.2
57	562.9
58	568.1
59	572.9
60	577.6
61	582.2
62	586.7
63	591.0
64	595.2
65	599.2
66	603.4
67	607.6
68	611.6
69	615.7
70	619.8
71	623.9
72	627.9
73	631.7
74	635.5
75	639.5
76	643.6
77	647.7
78	651.6
79	655.5
81	664.9
82	670.3
83	675.1
84	681.3
85	686.7
86	692.2
87	697.6
88	703.2
89	708.9
90	715.3

4.5. High Performance Liquid Chromatography

Method: Aromatic content determination was conducted by IP391 Petroleum Products- Determination of aromatic hydrocarbon types in middle distillates- High performance liquid chromatography method

Modification: The cloumn flow direction was reversed after the 2 ring aromatics fraction was eluted to elute the 3+ ring aromatic peak as a more defined and quantifiable peak.

Constituents By Hydrocarbon Class	Typical Conc. w/w%	Same Remark for all Classes
1 Ring Aromatics	11.7	The typical concentration of this hydrocarbon class is net after discounting, if any, those hydrocarbon species belonging to this class and listed separately (C&L markers and constituents with concentrations greater than of equal to 10% w/w).
2 Ring Aromatics	3.9	
3 and Greater Ring Aromatics	26.8	
Non-Aromatics	57.6	

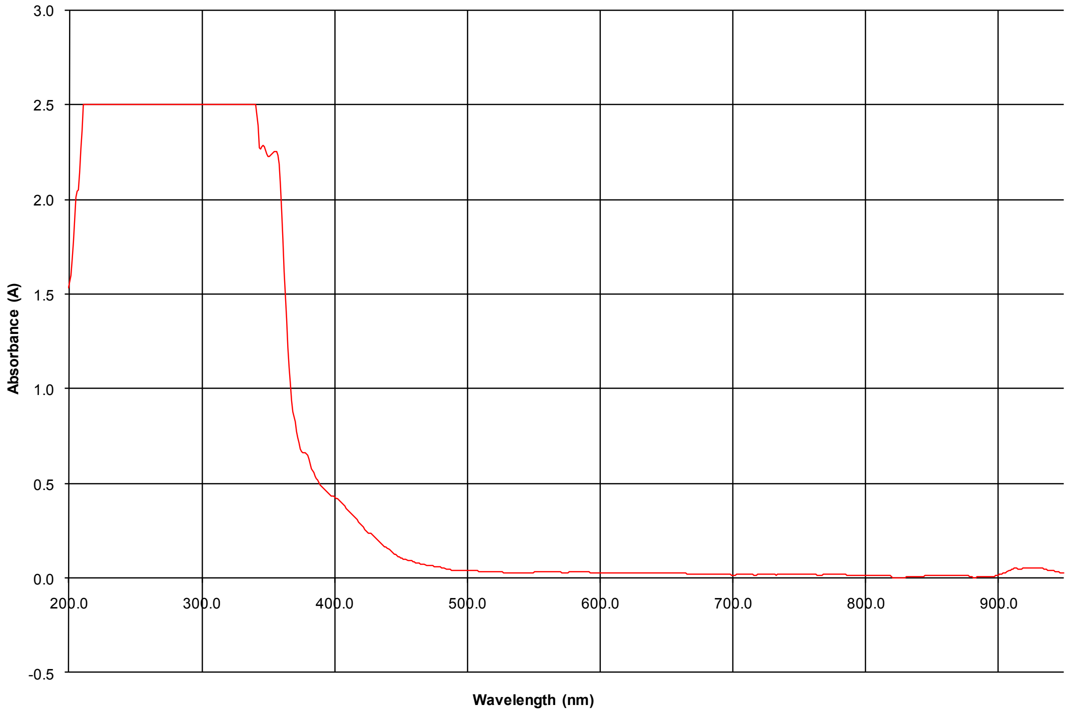


	Run 1 % Mass	Run 2 % Mass	Average % Mass
1 Ring Aromatics (o-Xylene)	12.98	10.42	11.7
2 Ring Aromatics (1-Methylnaphthlalene)	4.24	3.53	3.885
3+ Ring Aromatics (Phenanthrene)	27.13	26.46	26.795
Non-Aromatics	55.65	59.59	57.62

Other Lubricant Base Oils CAS No. 64742-52-5
EINECS No. 265-155-0

5.1. UV/Visible Spectroscopy

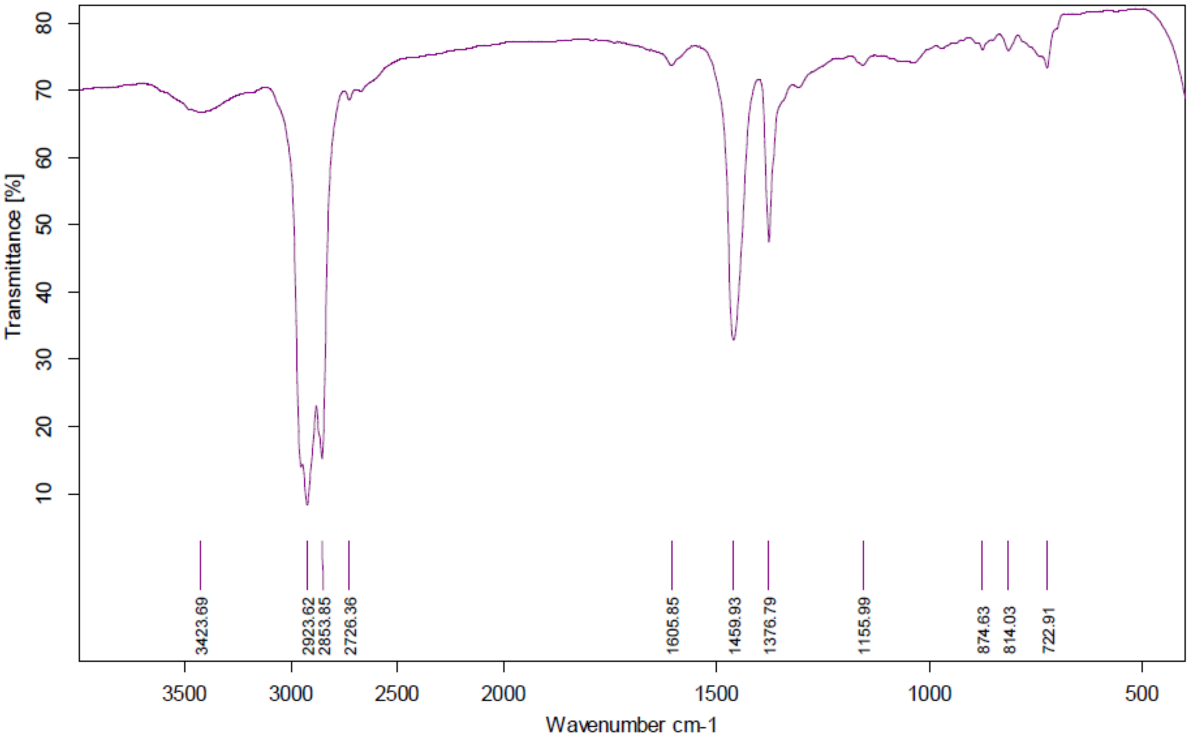
Instrument:	Perkin Elmer Lambda XLS+ UV/Visible Spectrophotometer
Range:	200-950 nm
Cell type:	1 cm quartz cell



The UV/Visible spectrum shows that the sample contains aromatic components.

5.2. IR Spectroscopy

Instrument:	Bruker Vertex 80 FTIR Spectrophotometer
Cell:	Potassium bromide plates
Range:	4000-400 cm^{-1}
Number of scans:	32
Spectral resolution:	4 cm^{-1}
Sample:	Thin film formed between potassium bromide plates

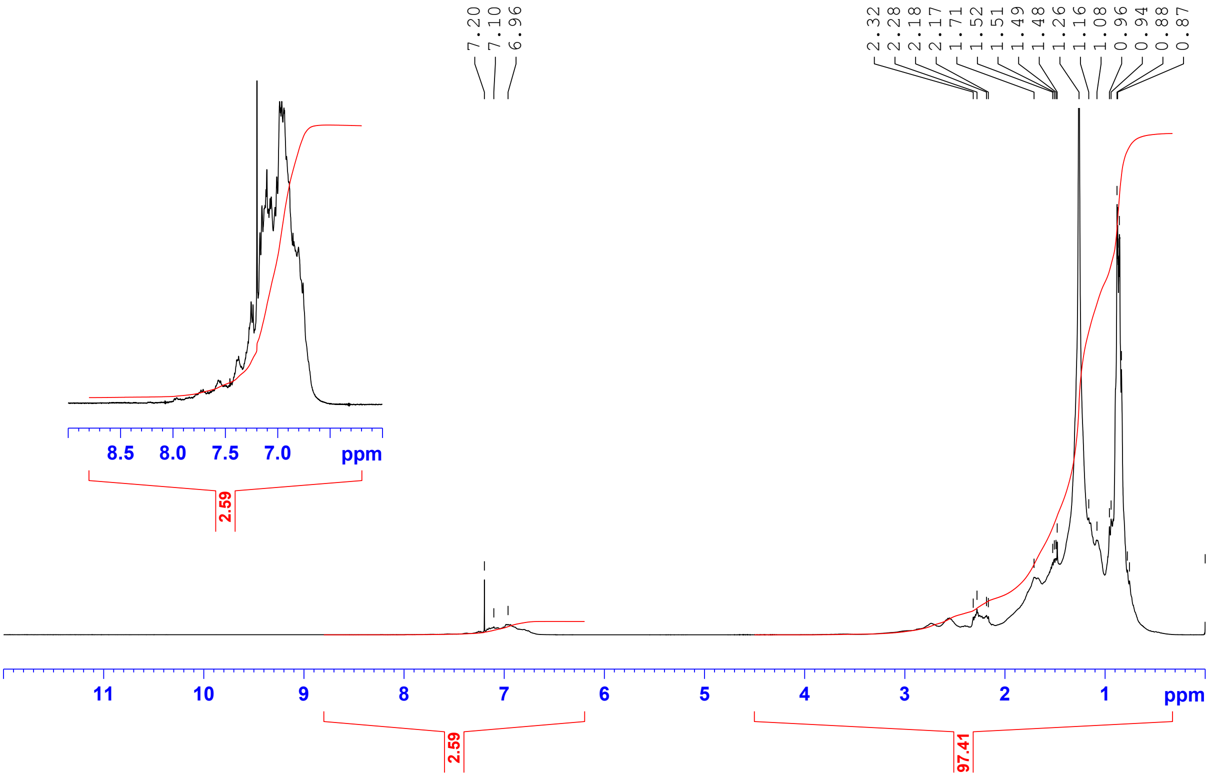


IR Spectral Band (cm^{-1})	Assignment
2924, 2854 (s)	C–H stretching alkyl
1606 (w)	Aromatic ring C-C stretching
1460 (s)	C–H bending alkyl
1377 (m)	C–H bending (symmetrical CH_3)
900-700 (w)	Aromatic C-H bending

5.3. NMR Spectroscopy

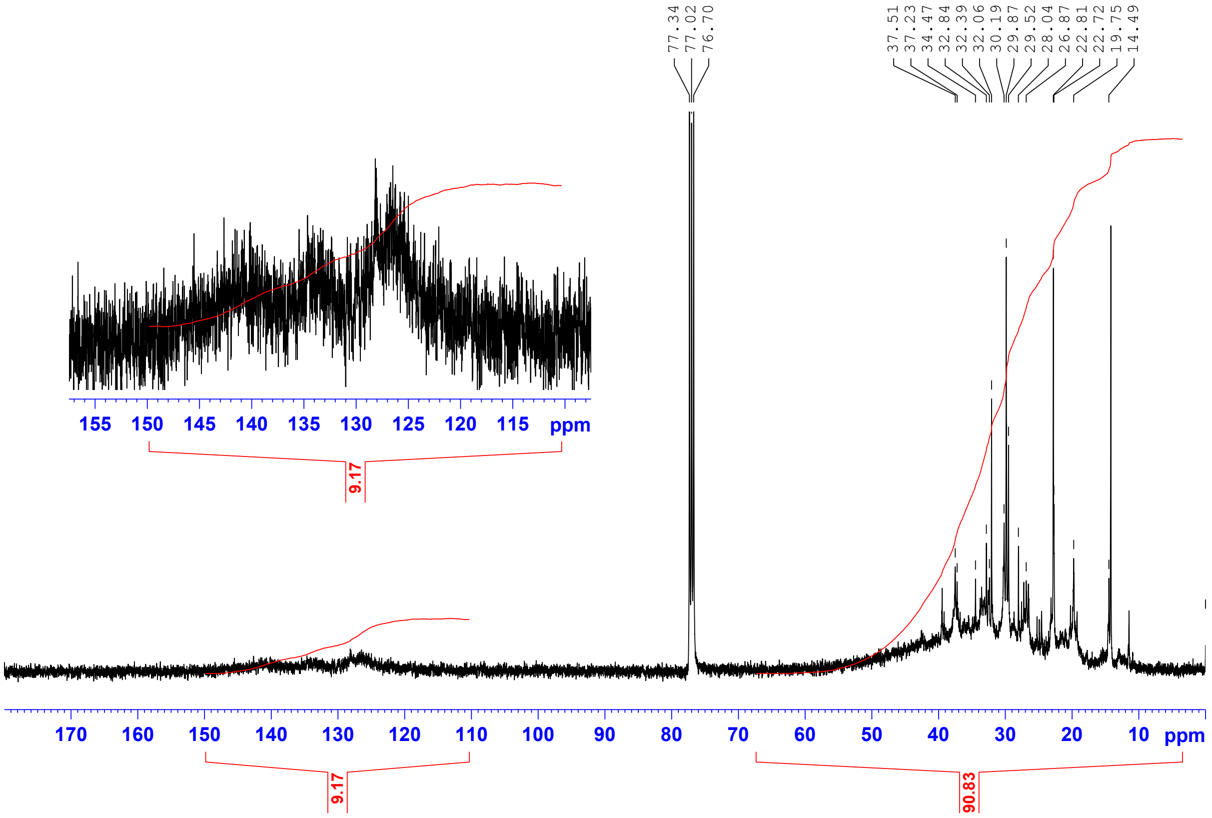
Instrument: Bruker Avance 400 NMR Spectrometer
Frequency: ^{1}H - 400 MHz; ^{13}C - 100 MHz
Solvent: Deuterochloroform
Reference: Tetramethylsilane (TMS) (^{1}H, ^{13}C chemical shift 0 ppm).

^{1}H Spectrum



Chemical Shift (ppm relative to TMS)	Assignment
0.5-1.0	Methyl groups
1.0-1.4	Methylene groups
1.4-2.0	Methine groups
2.0-3.5	Groups adjacent to aromatic rings
6.5-8.0	Aromatic protons
7.2	Residual $CHCl_3$ in solvent

^{13}C NMR spectrum

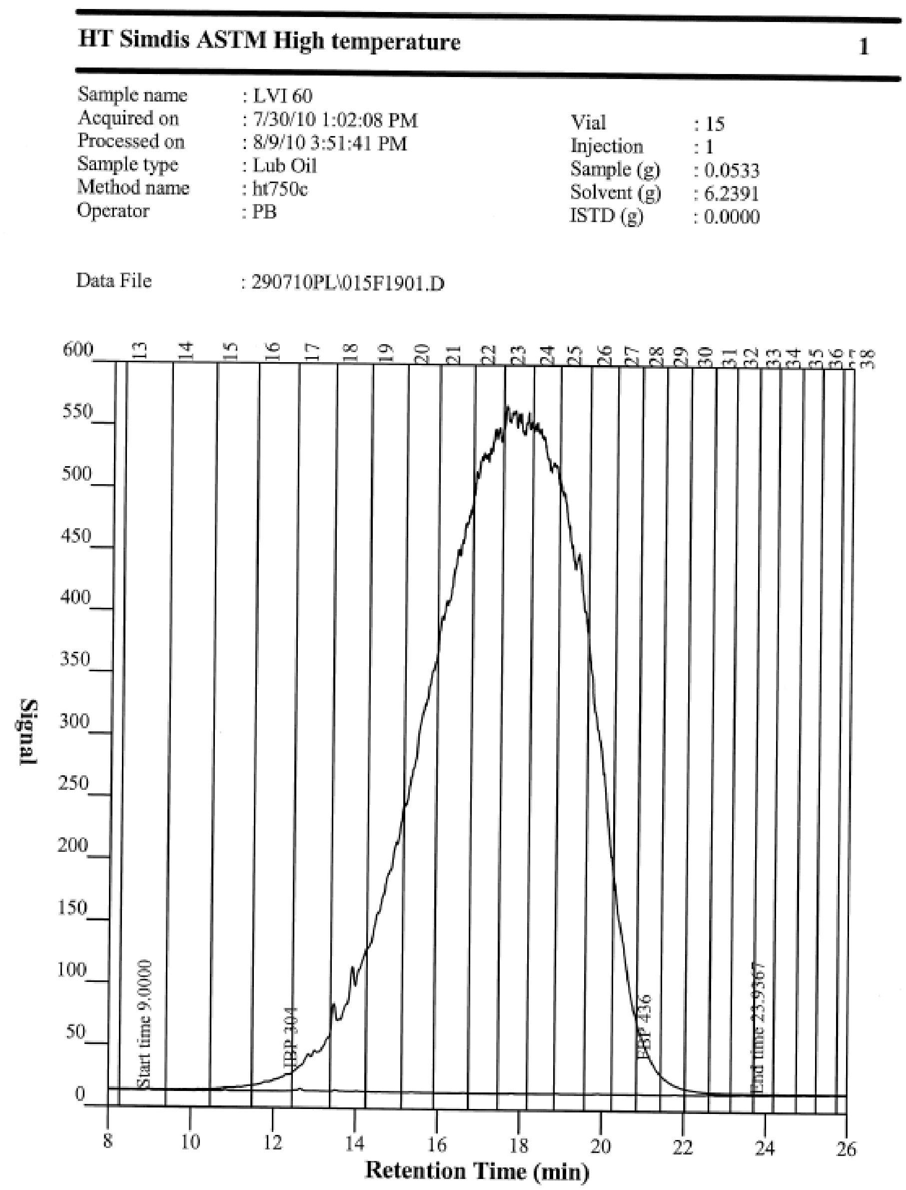


Chemical Shift (ppm relative to TMS)	Assignment
10-21	Methyl groups
14	**C**H_3-CH_2-CH_2-
23	CH_3-**C**H_2-CH_2-
30	Mid chain methylene groups
32	CH_3-CH_2-**C**H_2-
30-55	Branched carbons
77.0	$CDCl_3$ (solvent)
120-150	Aromatic carbon

The NMR spectra show that the base oil sample is comprised of saturated and aromatic hydrocarbon components and contains 2.6% aromatic hydrogen (protons in the aromatic ring as a percentage of total proton content) and 9.2% aromatic carbon (carbons in the aromatic ring as a percentage of total carbon content). These values refer only to those nuclei within the aromatic rings of components present in the sample and do not include the nuclei present in substituent side chains.

5.4. SIMDIS-Gas Chromatography

SIMDIS-GC analysis was carried out according to IP 480/07. The sample was dissolved in carbon disulphide and analysed by temperature programmed GC with flame ionisation detection using a non-polar separation column. The resulting chromatogram was compared with a calibration chromatogram obtained under identical conditions using n-alkanes spanning the elution range of the hydrocarbons present in the sample. The boiling range distribution of the components present was determined from these data.

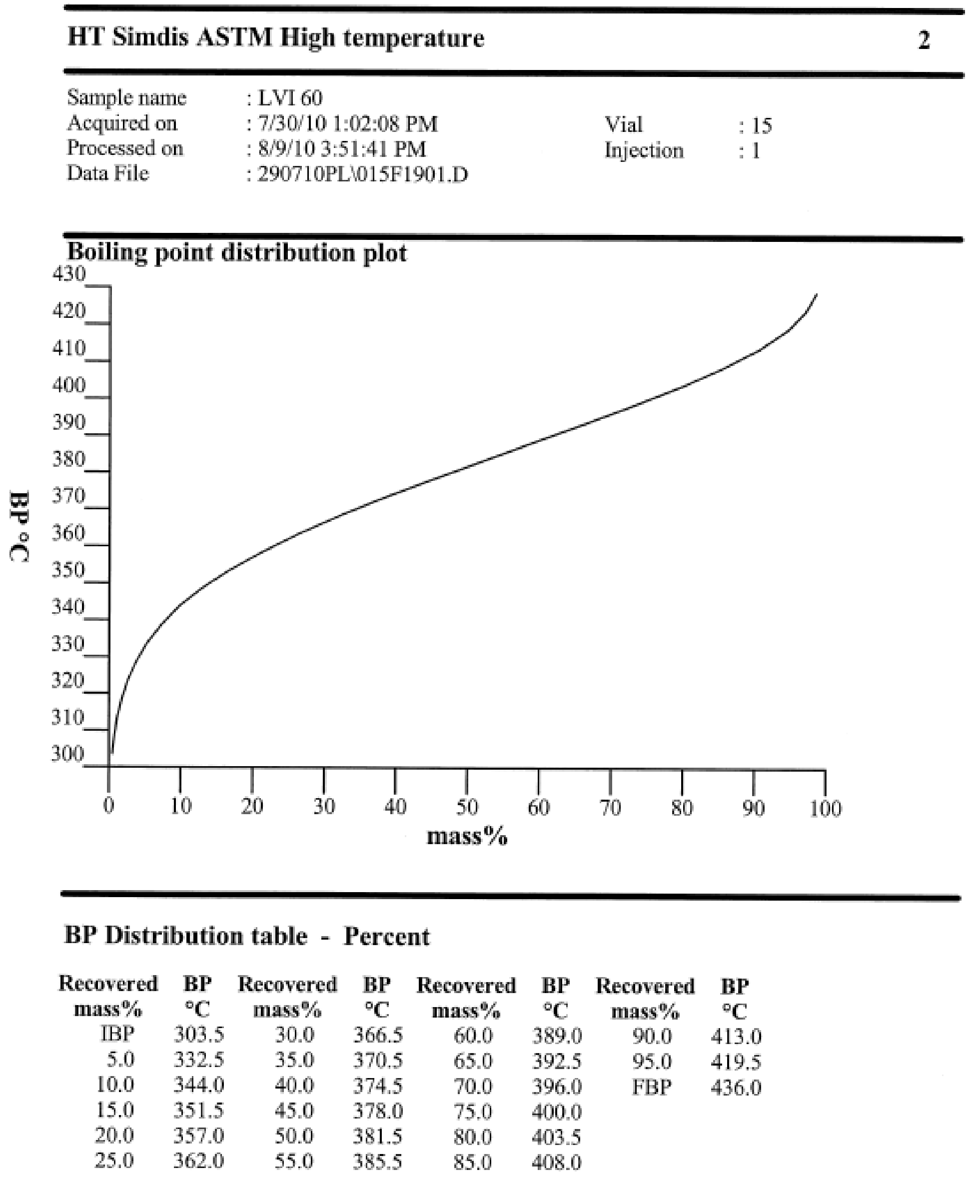


HT Simdis ASTM High temperature 1

Sample name	: LVI 60		
Acquired on	: 7/30/10 1:02:08 PM	Vial	: 15
Processed on	: 8/9/10 3:51:41 PM	Injection	: 1
Sample type	: Lub Oil	Sample (g)	: 0.0533
Method name	: ht750c	Solvent (g)	: 6.2391
Operator	: PB	ISTD (g)	: 0.0000

Data File : 290710PL\015F1901.D

SIMDIS-GC analysis showed that the sample contains hydrocarbons covering the C_{15} to C_{31} range corresponding with initial and final boiling points of 304°C and 436°C respectively. The boiling point distribution plot and table showing the boiling point for each 5% mass fraction of the sample are shown below.



HT Simdis ASTM High temperature 2

Sample name : LVI 60
Acquired on : 7/30/10 1:02:08 PM
Processed on : 8/9/10 3:51:41 PM
Data File : 290710PL\015F1901.D
Vial : 15
Injection : 1

Boiling point distribution plot

BP Distribution table - Percent

Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C
IBP	303.5	30.0	366.5	60.0	389.0	90.0	413.0
5.0	332.5	35.0	370.5	65.0	392.5	95.0	419.5
10.0	344.0	40.0	374.5	70.0	396.0	FBP	436.0
15.0	351.5	45.0	378.0	75.0	400.0		
20.0	357.0	50.0	381.5	80.0	403.5		
25.0	362.0	55.0	385.5	85.0	408.0		

5.5. High Performance Liquid Chromatography

HPLC analysis was carried out using a slightly modified version of IP 368/01 in which pentane rather than hexane was used as the mobile phase. A solution of the sample in pentane was separated into saturated and aromatic hydrocarbon fractions using normal-phase HPLC with refractive index detection. Following emergence of the saturated hydrocarbons from the column a backflush valve was activated and the aromatic hydrocarbons collected by reverse-elution. The pentane mobile phase was evaporated from the two fractions and the hydrocarbon types determined gravimetrically.

HPLC analysis of the sample showed that it contains 65.4% (m/m) saturated hydrocarbons and 33.4% (m/m) aromatic hydrocarbons, corresponding to a sample recovery of 98.8% (m/m) from the chromatographic fractionation.

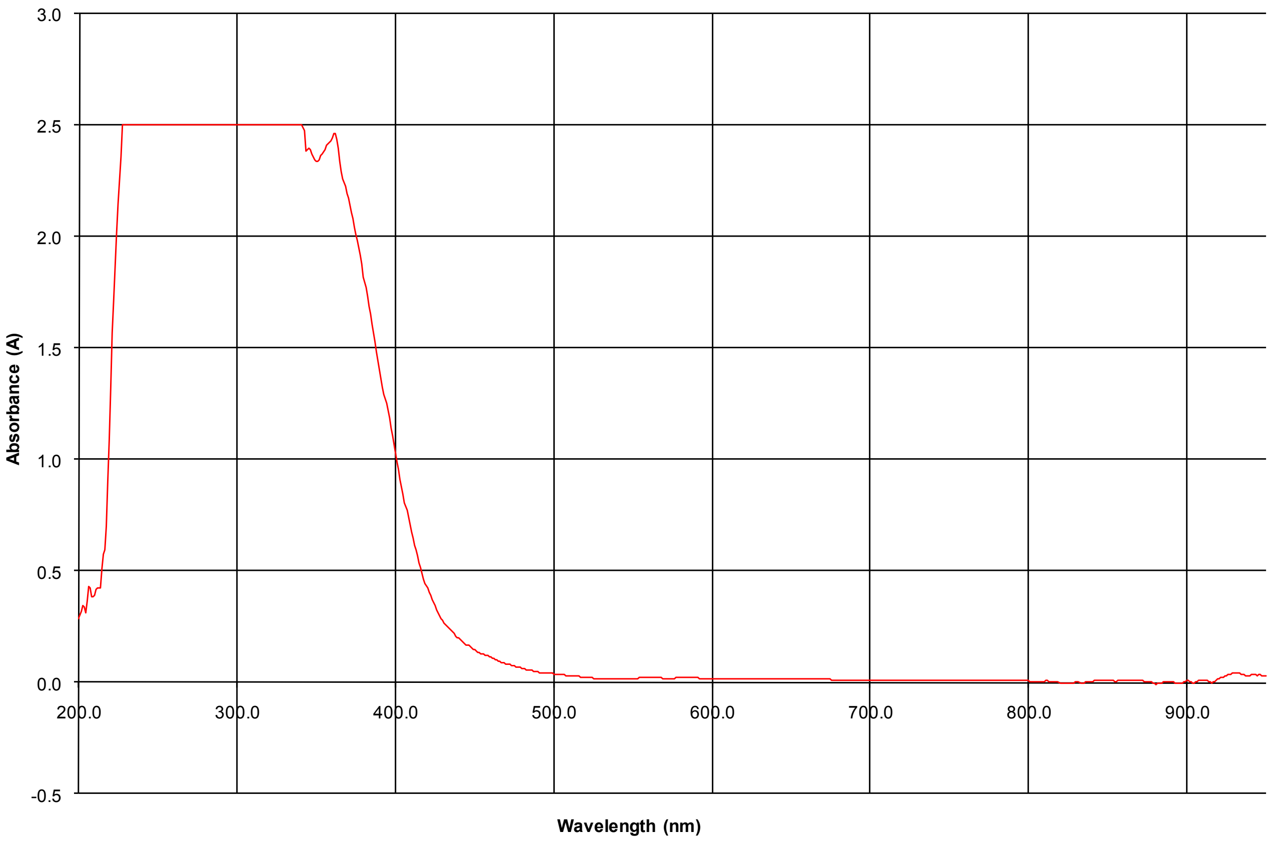
APPENDIX 6: ANALYTICAL DATA FOR CASE STUDY 5

Residual Aromatic Extracts	CAS No. 64742-10-5
	EINECS No. 265-110-5

SAMPLE A

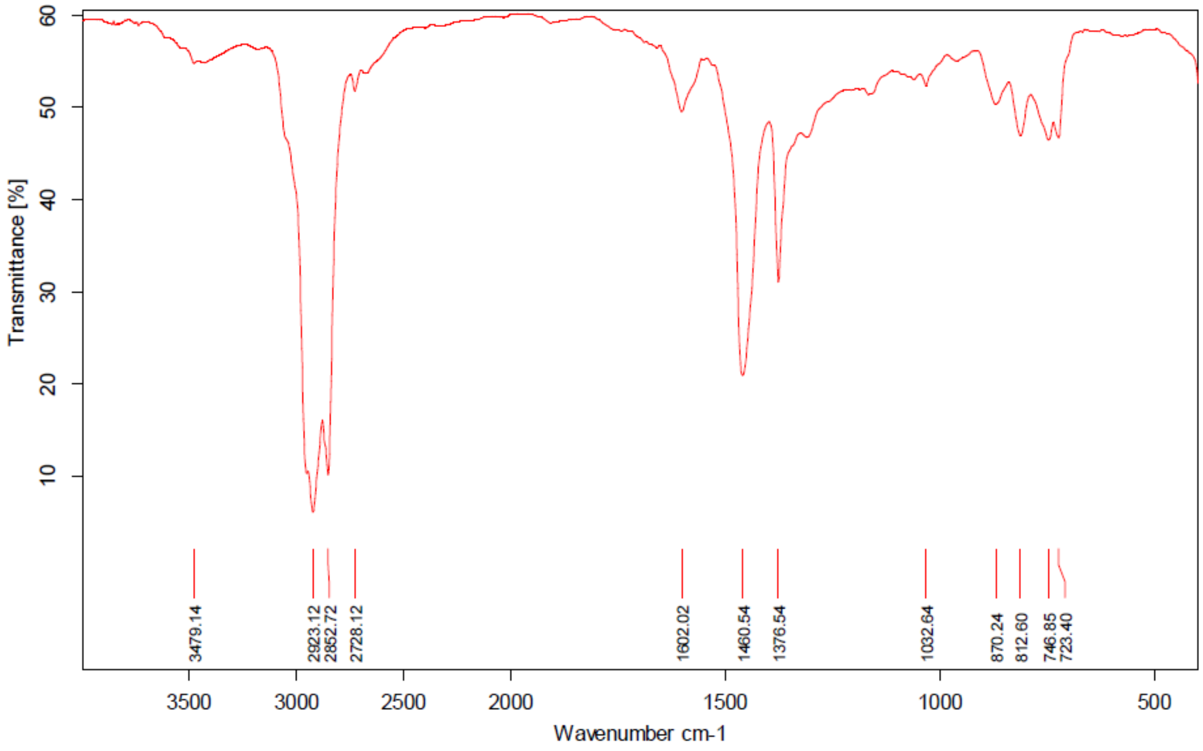
6.1. UV/Visible Spectroscopy

Instrument:	Perkin Elmer Lambda XLS+ UV/Visible Spectrophotometer
Range:	200-950 nm
Cell type:	0.1 cm quartz cell
Solvent:	Dichloromethane
Concentration:	2% (m/m)



6.2. IR Spectroscopy

Instrument:	Bruker Vertex 80 FTIR Spectrophotometer
Cell:	Potassium bromide plates
Range:	4000-400 cm^{-1}
Number of scans:	32
Spectral resolution:	4 cm^{-1}
Sample:	Thin film formed between potassium bromide plates

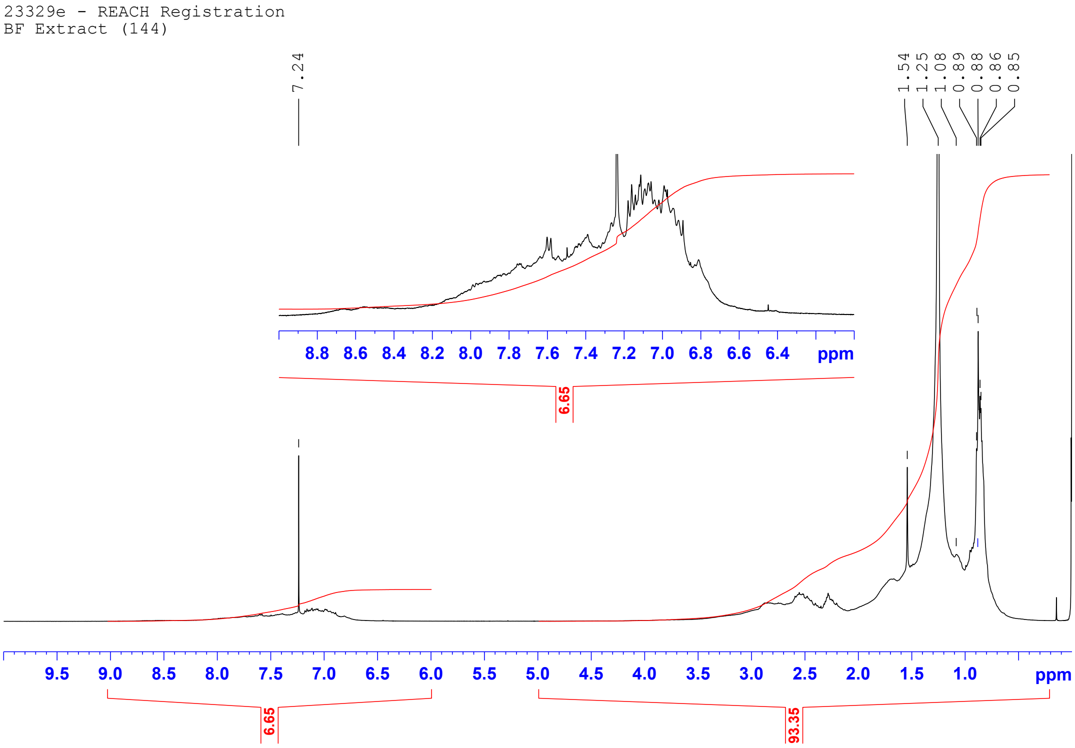


IR Spectral Band (cm^{-1})	Assignment
2923, 2853 (s)	C–H stretching alkyl
1602 (w)	C=C aromatic ring stretching
1461 (m)	C–H bending alkyl
1377 (m)	C–H bending (symmetrical CH_3)
723 (w)	$(CH_2)_n$ “rocking”

6.3. NMR Spectroscopy

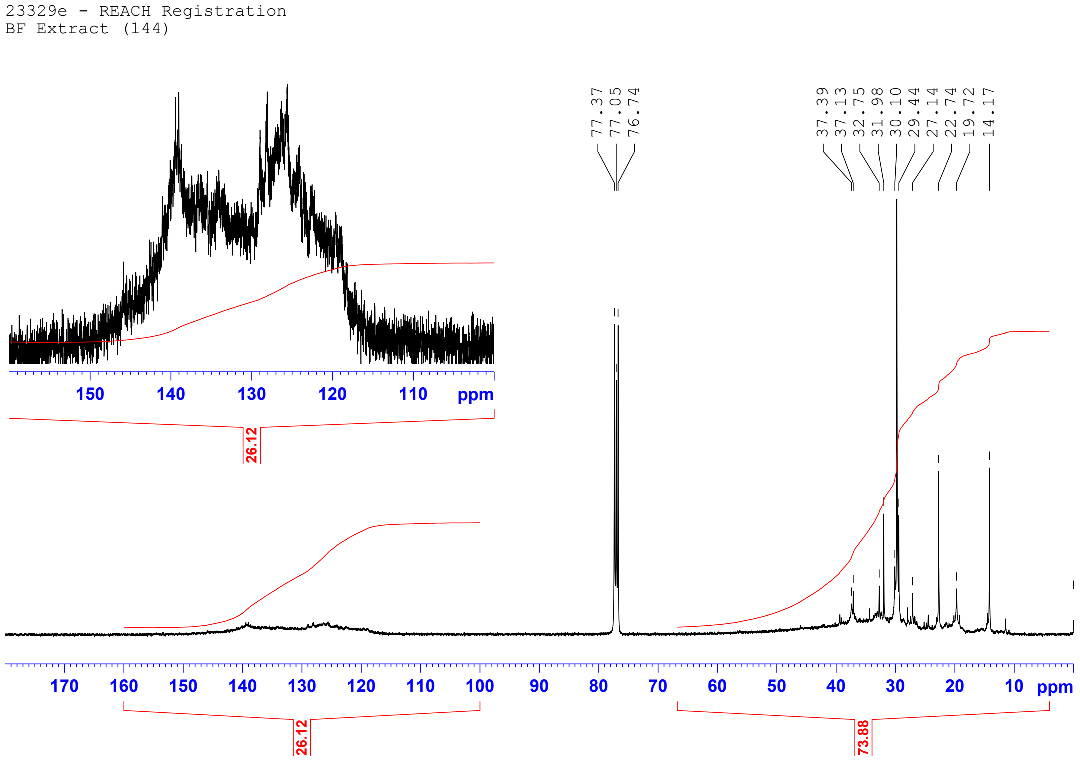
Instrument:	Bruker Avance 400 NMR Spectrometer
Frequency:	^{1}H - 400 MHz; ^{13}C - 100 MHz
Solvent:	Deuterochloroform
Reference:	Tetramethylsilane (TMS) (^{1}H, ^{13}C chemical shift 0 ppm).

^{1}H Spectrum



Chemical Shift (ppm relative to TMS)	Assignment
0.5-1.0	Methyl groups
1.0-1.4	Methylene groups
1.4-2.0	Methine groups
2.0-3.5	Groups adjacent to aromatic rings
6.7-8.8	Aromatic protons
7.2	Residual $CHCl_3$ in solvent

^{13}C Spectrum



Chemical Shift (ppm relative to TMS)	Assignment
14	**C**H_3-CH_2-CH_2-
23	CH_3-**C**H_2-CH_2-
30	Mid chain methylene groups
32	CH_3-CH_2-**C**H_2-
77.0	$CDCl_3$ (solvent)
115-150	Aromatic carbons

Quantitative analysis of the NMR signals showed that the sample contains 6.6% aromatic hydrogen (protons in the aromatic ring as a percentage of total proton content), and 26.1% aromatic carbon (carbons in the aromatic ring as a percentage of total carbon content). These values refer only to those nuclei within the aromatic rings of components present in the sample and do not include the nuclei present in substituent side chains.

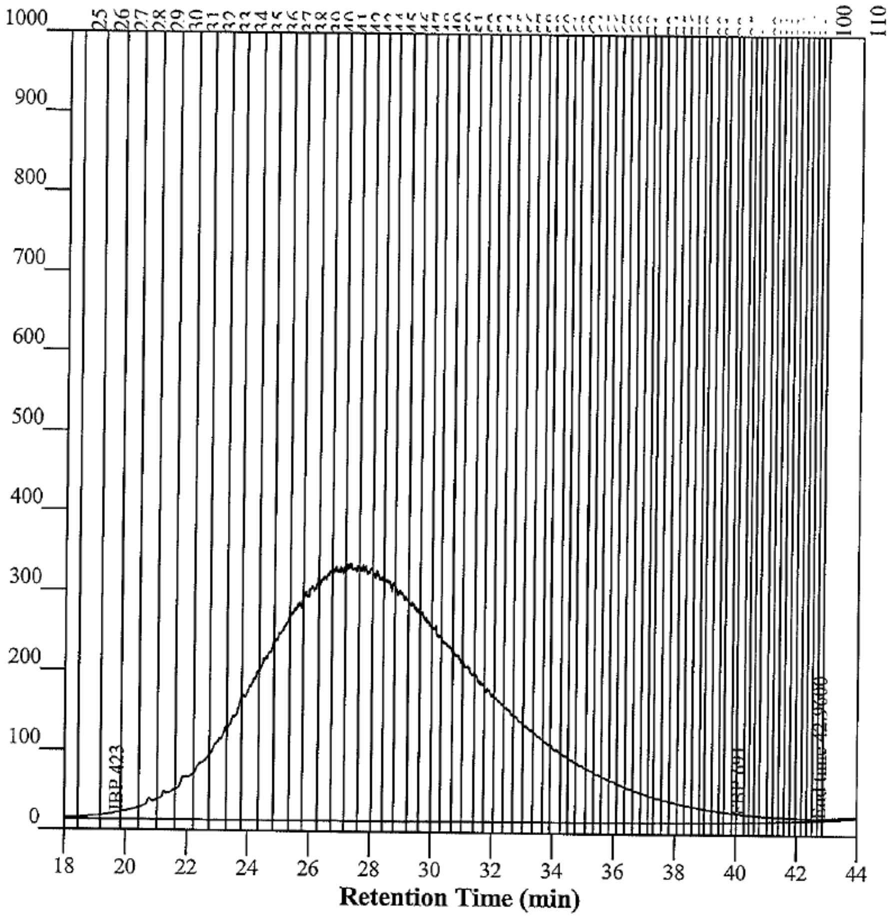
6.4a. SIMDIS-Gas Chromatography

SIMDIS-GC analysis was carried out according to IP 480/07. The sample was dissolved in carbon disulphide and analysed by temperature programmed GC with flame ionisation detection using a non-polar separation column. The resulting chromatogram was compared with a calibration chromatogram obtained under identical conditions using n-alkanes spanning the elution range of the hydrocarbons present in the sample. The boiling range distribution of the components present was determined from these data.

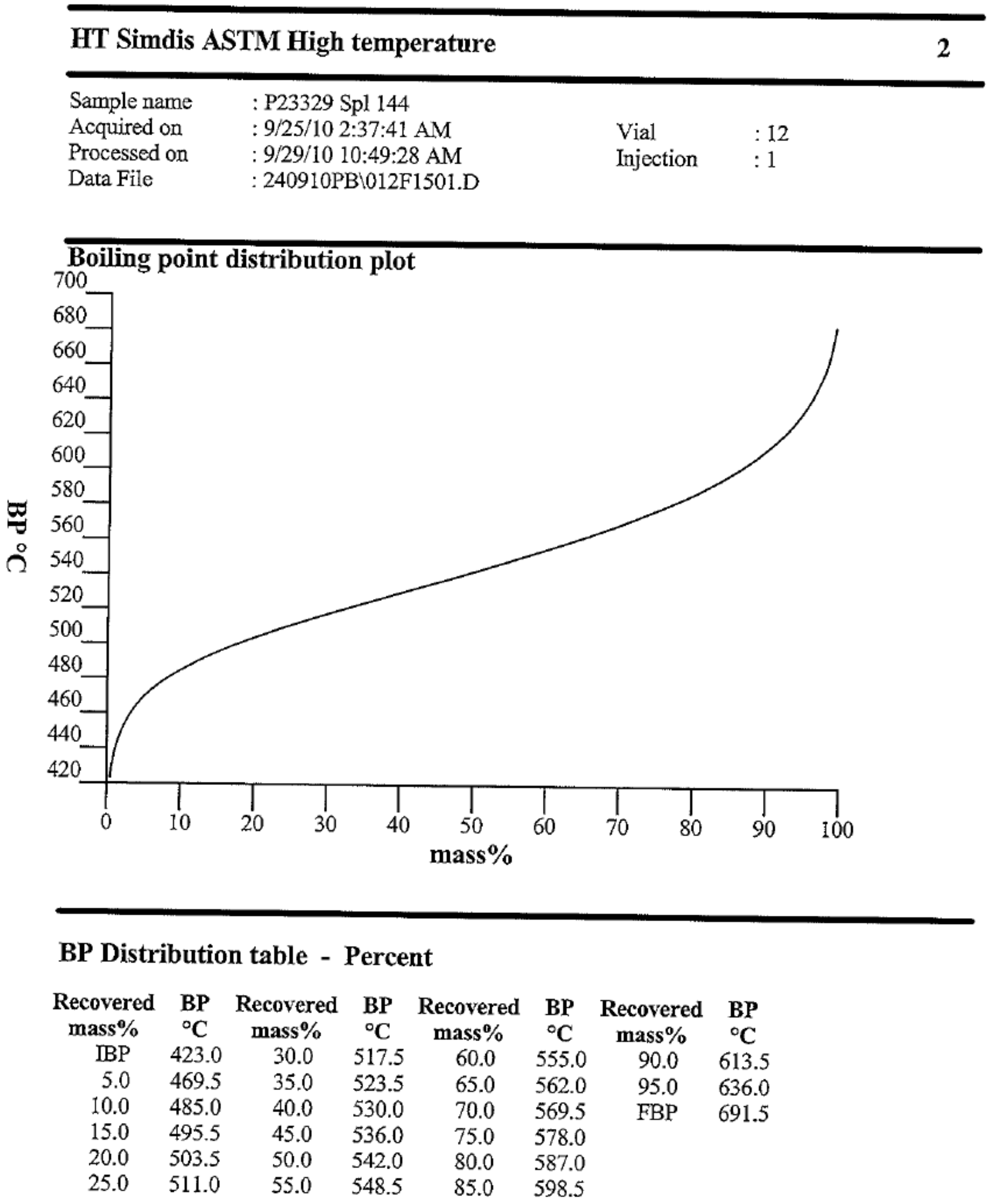
HT Simdis ASTM High temperature 1

Sample name	: P23329 Spl 144		
Acquired on	: 9/25/10 2:37:41 AM	Vial	: 12
Processed on	: 9/29/10 10:49:28 AM	Injection	: 1
Sample type	: Lub Oil	Sample (g)	: 0.0656
Method name	: ht750c	Solvent (g)	: 6.5850
Operator	: PB	ISTD (g)	: 0.0000

Data File : 240910PB\012F1501.D



SIMDIS-GC analysis showed that the sample contains hydrocarbons covering the C_{25} to C_{95} range corresponding with initial and final boiling points of 423°C and 691°C respectively. The boiling point distribution plot and boiling point distribution table for the sample are shown below.



HT Simdis ASTM High temperature **2**

Sample name	: P23329 Spl 144		
Acquired on	: 9/25/10 2:37:41 AM	Vial	: 12
Processed on	: 9/29/10 10:49:28 AM	Injection	: 1
Data File	: 240910PB\012F1501.D		

Boiling point distribution plot

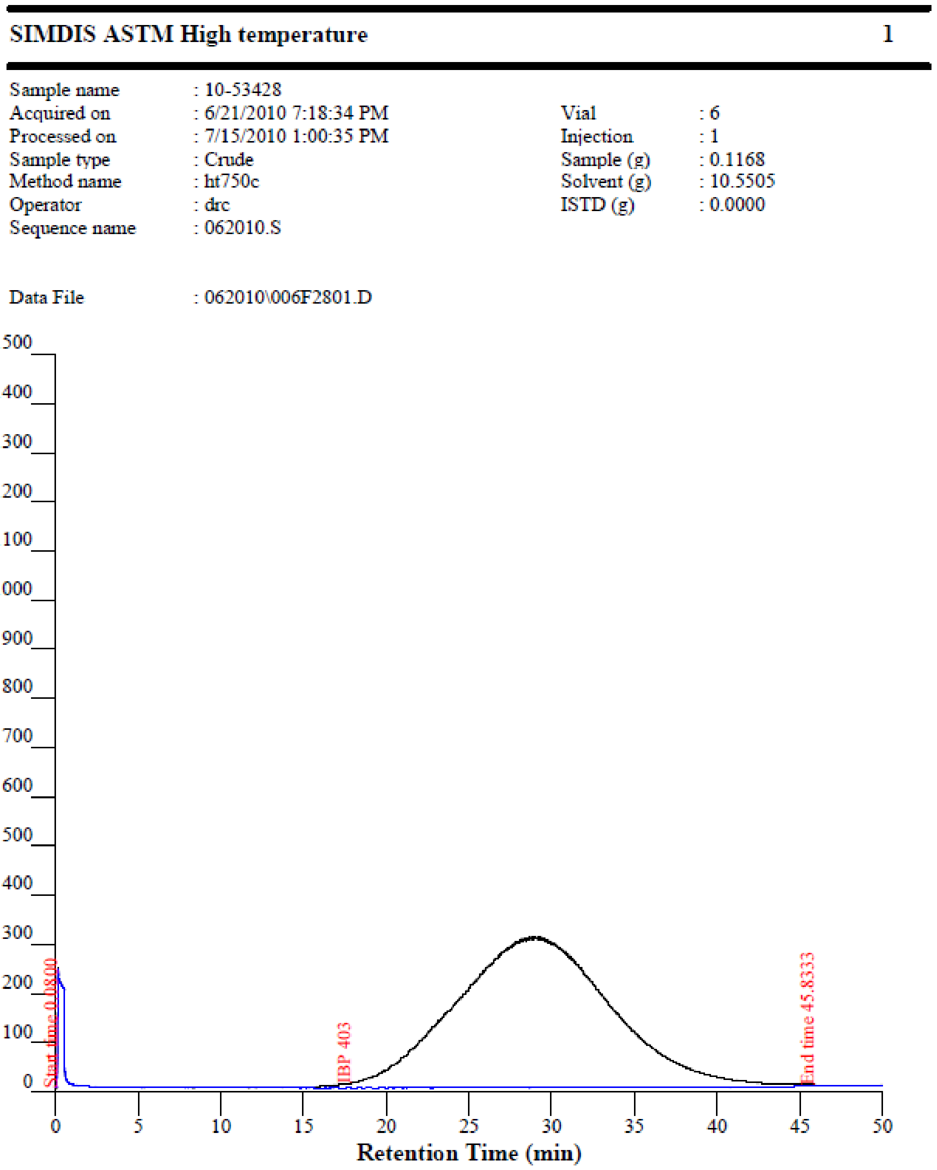
BP Distribution table - Percent

Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C
IBP	423.0	30.0	517.5	60.0	555.0	90.0	613.5
5.0	469.5	35.0	523.5	65.0	562.0	95.0	636.0
10.0	485.0	40.0	530.0	70.0	569.5	FBP	691.5
15.0	495.5	45.0	536.0	75.0	578.0		
20.0	503.5	50.0	542.0	80.0	587.0		
25.0	511.0	55.0	548.5	85.0	598.5		

SAMPLE B

6.4b. SIMDIS-Gas Chromatography

SIMDIS-GC was carried out on a solution of the sample dissolved in carbon disulphide. This was analysed by temperature programmed GC with flame ionisation detection using a non-polar separation column, and the resulting chromatogram was compared with a calibration chromatogram obtained under identical conditions using n-alkanes spanning the elution range of the hydrocarbons present in the sample. The boiling range distribution of the components present was determined from these data.



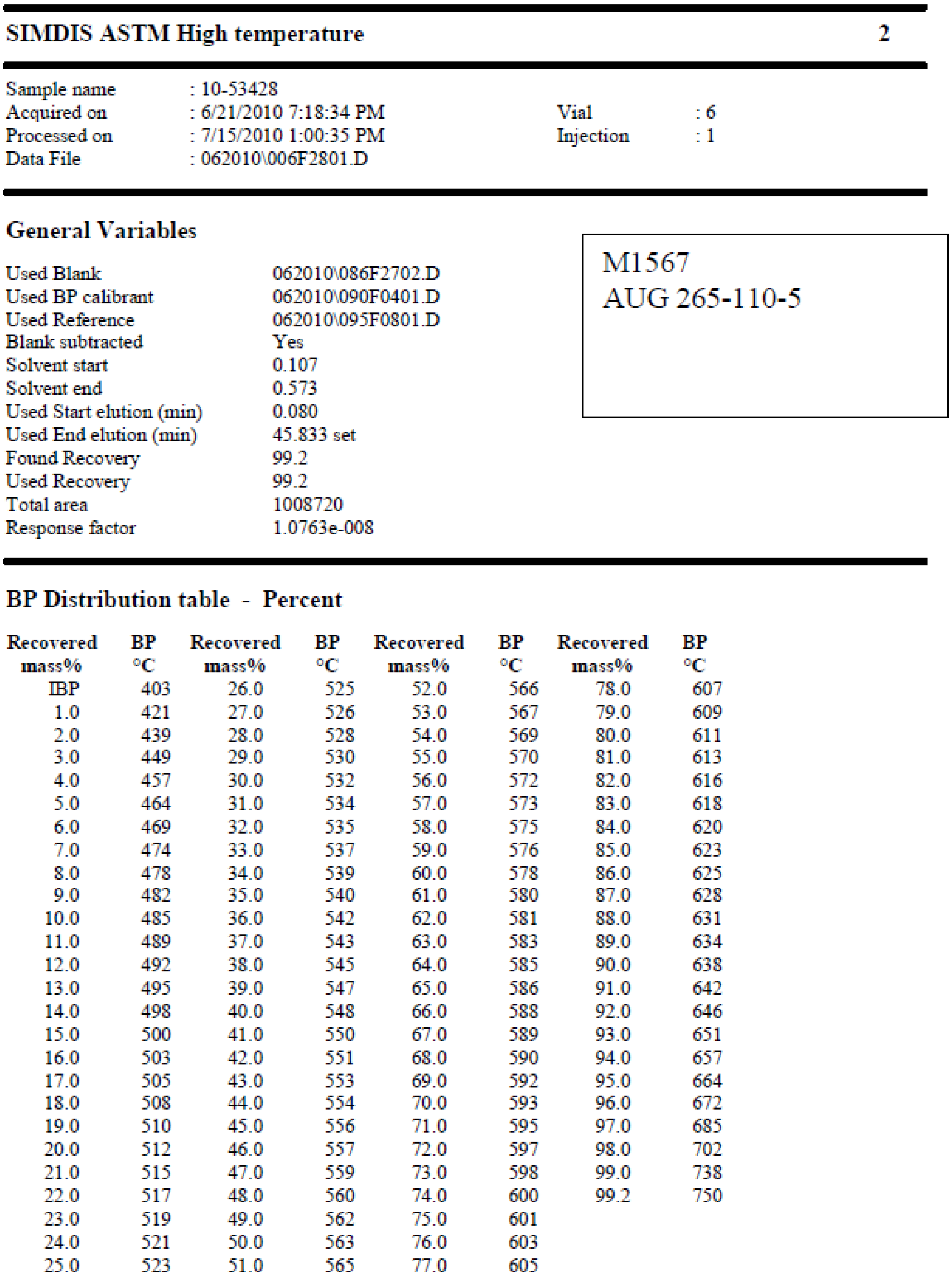
SIMDIS ASTM High temperature 1

Sample name : 10-53428
Acquired on : 6/21/2010 7:18:34 PM
Processed on : 7/15/2010 1:00:35 PM
Sample type : Crude
Method name : ht750c
Operator : drc
Sequence name : 062010.S

Vial : 6
Injection : 1
Sample (g) : 0.1168
Solvent (g) : 10.5505
ISTD (g) : 0.0000

Data File : 062010\006F2801.D

SIMDIS-GC analysis showed that the sample contains hydrocarbons covering the 403°C to >750°C boiling range, although 98% of the sample had a boiling range of 403°C to 702°C. The boiling point distribution table for the sample is shown below.



SIMDIS ASTM High temperature 2

Sample name : 10-53428
Acquired on : 6/21/2010 7:18:34 PM
Processed on : 7/15/2010 1:00:35 PM
Data File : 062010\006F2801.D
Vial : 6
Injection : 1

General Variables

Used Blank	062010\086F2702.D
Used BP calibrant	062010\090F0401.D
Used Reference	062010\095F0801.D
Blank subtracted	Yes
Solvent start	0.107
Solvent end	0.573
Used Start elution (min)	0.080
Used End elution (min)	45.833 set
Found Recovery	99.2
Used Recovery	99.2
Total area	1008720
Response factor	1.0763e-008

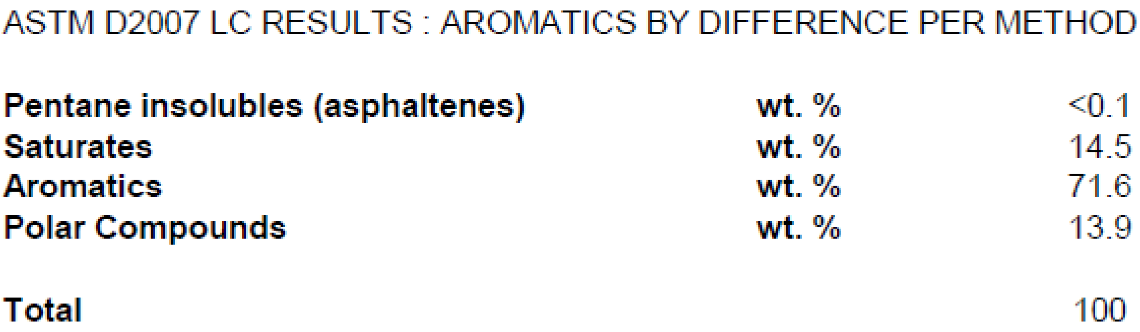
M1567
AUG 265-110-5

BP Distribution table - Percent

Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C	Recovered mass%	BP °C
IBP	403	26.0	525	52.0	566	78.0	607
1.0	421	27.0	526	53.0	567	79.0	609
2.0	439	28.0	528	54.0	569	80.0	611
3.0	449	29.0	530	55.0	570	81.0	613
4.0	457	30.0	532	56.0	572	82.0	616
5.0	464	31.0	534	57.0	573	83.0	618
6.0	469	32.0	535	58.0	575	84.0	620
7.0	474	33.0	537	59.0	576	85.0	623
8.0	478	34.0	539	60.0	578	86.0	625
9.0	482	35.0	540	61.0	580	87.0	628
10.0	485	36.0	542	62.0	581	88.0	631
11.0	489	37.0	543	63.0	583	89.0	634
12.0	492	38.0	545	64.0	585	90.0	638
13.0	495	39.0	547	65.0	586	91.0	642
14.0	498	40.0	548	66.0	588	92.0	646
15.0	500	41.0	550	67.0	589	93.0	651
16.0	503	42.0	551	68.0	590	94.0	657
17.0	505	43.0	553	69.0	592	95.0	664
18.0	508	44.0	554	70.0	593	96.0	672
19.0	510	45.0	556	71.0	595	97.0	685
20.0	512	46.0	557	72.0	597	98.0	702
21.0	515	47.0	559	73.0	598	99.0	738
22.0	517	48.0	560	74.0	600	99.2	750
23.0	519	49.0	562	75.0	601		
24.0	521	50.0	563	76.0	603		
25.0	523	51.0	565	77.0	605		

6.5. Liquid Chromatography

The sample was analysed by open-column LC according to ASTM D2007.



ASTM D2007 LC RESULTS : AROMATICS BY DIFFERENCE PER METHOD

Pentane insolubles (asphaltenes)	**wt. %**	<0.1
Saturates	**wt. %**	14.5
Aromatics	**wt. %**	71.6
Polar Compounds	**wt. %**	13.9
Total		100

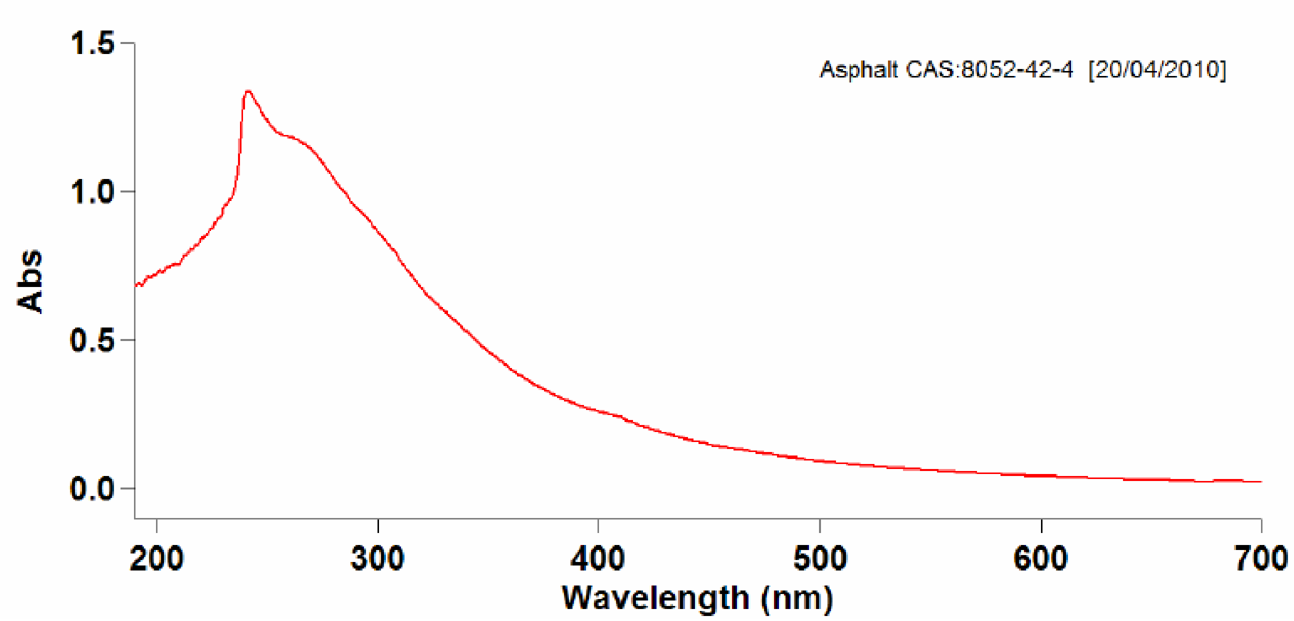
APPENDIX 7: ANALYTICAL DATA FOR CASE STUDY 6

SAMPLE A

Bitumen CAS No. 8052-42-4
EINECS No. 232-490-9

7.1. UV/Visible Spectroscopy

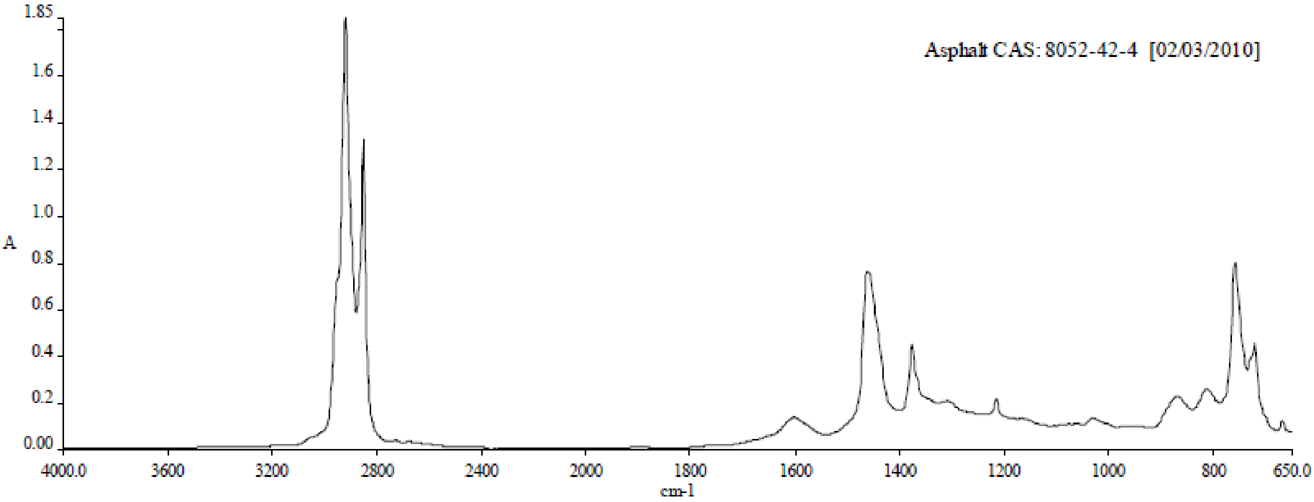
Instrument: Varian Cary 1E Spectrophotometer
Range: 190-700 nm
Resolution: 1 nm
Cell type: 1 cm quartz cell
Solvent: Chloroform
Concentration: 40 ppm (mg/L)



7.2. IR Spectroscopy

Instrument: Perkin Elmer Spectrum-1000 Spectrophotometer
Cell: ATR sample cell with zinc selenide crystal

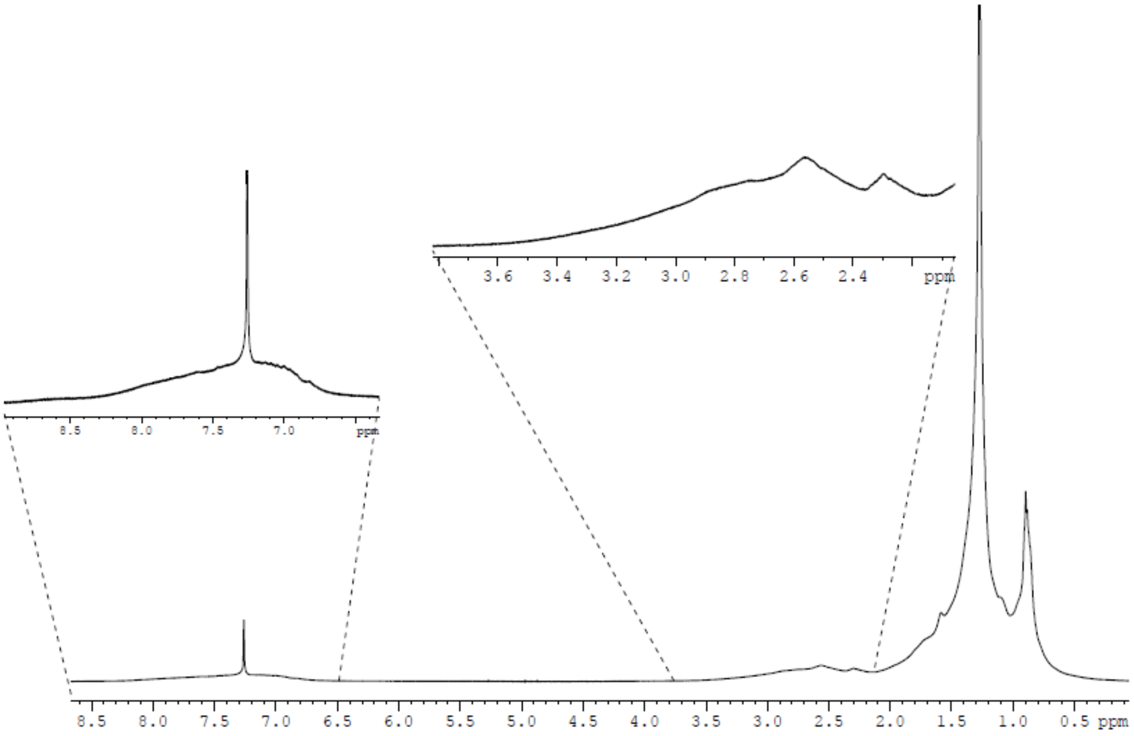
Range: 4000-650 cm^{-1}
Number of scans: 20
Spectral resolution: 2 cm^{-1}
Sample: Thin film formed on crystal by introducing the sample dissolved in chloroform and subsequent evaporation of solvent



IR spectrum band (cm^{-1})	Functional group
2952	methyl-
2921	methylene-
2850	methylene-
1602	aromatics
1485-1430	methylene-, methyl
1376	methyl-
900-660	substituted aromatics

7.3. NMR Spectroscopy

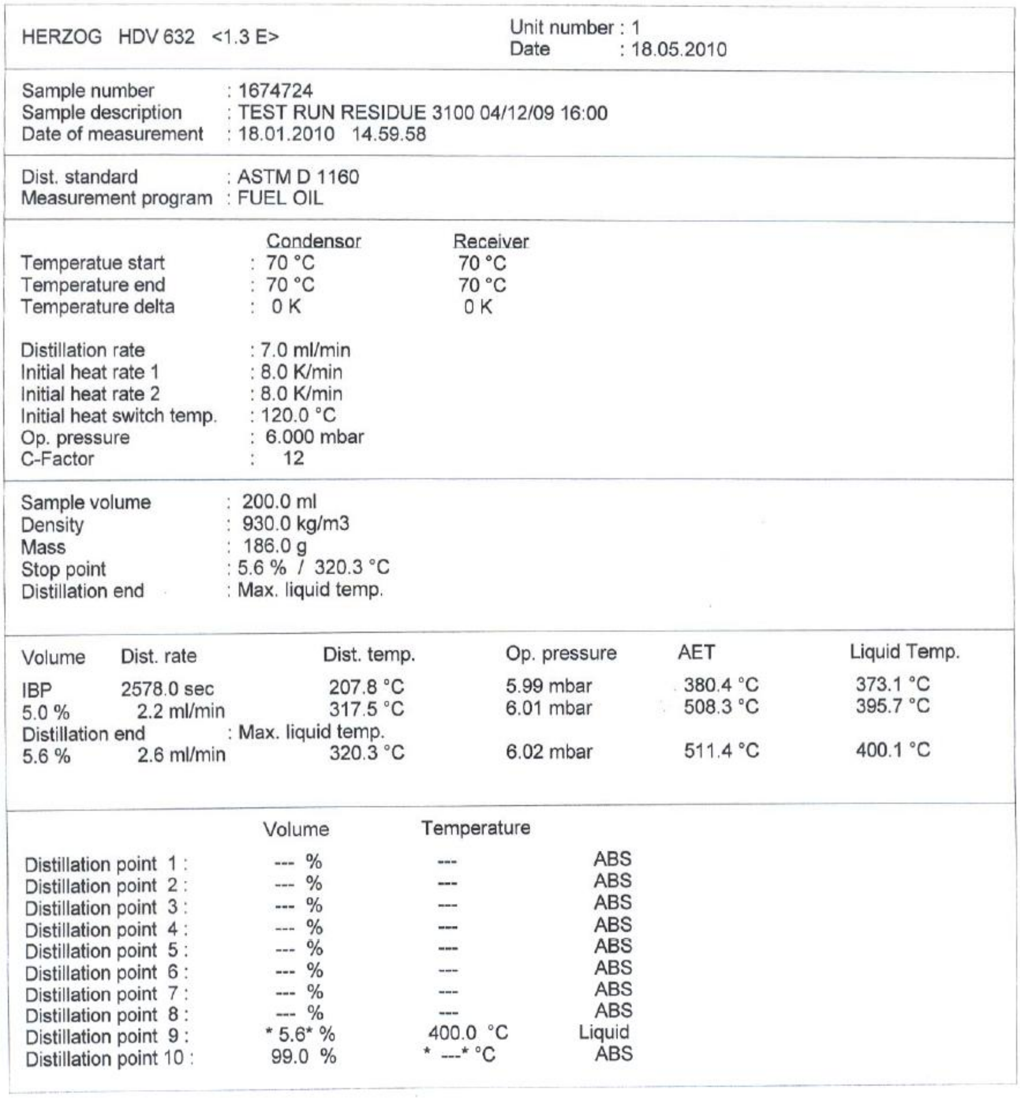
Instrument: Bruker AMX500 NMR Spectrometer



^{1}H chemical shifts regions (ppm)	Substance class	Structural group
8.5-6.5	Aromatics	C_xHR_{x-n}
7.25-6.0	Benzenes	C_6HR_{6-n}
7.26	Chloroform-d (solvent)	$CDCl_3$
3.5-3.0	Aromatics	$\text{Ph-C}H<$
3.0-2.4	Aromatics	$\text{Ph-C}H_2\text{-}$
2.4-2.1	Aromatics	$\text{Ph-C}H_3$
1.6-1.15	Paraffins (linear and branched) Aromatics	$>CH\text{-}, >CH$ $\text{Ph-C-C}H_3$
1.0-0.7	Paraffins	$\text{-C}H_3$

7.4a. Distillation

Method:	ASTM D 1160 (Standard Test Method for Distillation of Petroleum Products at Reduced Pressure)
Instrument:	Herzog HDV 632
Pressure:	0.13-6.7 kPa (1-50 mm Hg)
Heating:	Controlled to ensure uniform distillate recovery of 6-8 mL/min achieved after first 10% of distillate recovered
Data:	Vapour temperature, time and pressure recorded and used to calculate equivalent temperature at atmospheric pressure (AET)



```
HERZOG   HDV 632   <1.3 E>                        Unit number : 1
                                                  Date        : 18.05.2010

Sample number            : 1674724
Sample description       : TEST RUN RESIDUE 3100 04/12/09 16:00
Date of measurement      : 18.01.2010   14.59.58

Dist. standard           : ASTM D 1160
Measurement program      : FUEL OIL

                            Condensor          Receiver
Temperatue start         :  70 °C              70 °C
Temperature end          :  70 °C              70 °C
Temperature delta        :   0 K                0 K

Distillation rate        : 7.0 ml/min
Initial heat rate 1      : 8.0 K/min
Initial heat rate 2      : 8.0 K/min
Initial heat switch temp.: 120.0 °C
Op. pressure             :  6.000 mbar
C-Factor                 :     12

Sample volume            :  200.0 ml
Density                  :  930.0 kg/m3
Mass                     :  186.0 g
Stop point               : 5.6 %  /  320.3 °C
Distillation end         : Max. liquid temp.

Volume     Dist. rate           Dist. temp.      Op. pressure      AET          Liquid Temp.

IBP        2578.0 sec            207.8 °C         5.99 mbar        380.4 °C      373.1 °C
5.0 %         2.2 ml/min         317.5 °C         6.01 mbar        508.3 °C      395.7 °C
Distillation end         : Max. liquid temp.
5.6 %         2.6 ml/min         320.3 °C         6.02 mbar        511.4 °C      400.1 °C

                            Volume         Temperature

Distillation point  1 :      --- %            ---             ABS
Distillation point  2 :      --- %            ---             ABS
Distillation point  3 :      --- %            ---             ABS
Distillation point  4 :      --- %            ---             ABS
Distillation point  5 :      --- %            ---             ABS
Distillation point  6 :      --- %            ---             ABS
Distillation point  7 :      --- %            ---             ABS
Distillation point  8 :      --- %            ---             ABS
Distillation point  9 :    * 5.6* %        400.0  °C        Liquid
Distillation point 10 :     99.0  %        *  ---* °C         ABS
```

7.5a. Liquid Chromatography

Known mass of sample (0.1g) charged to top of glass chromatographic column packed with activated alumina and silica gel:

Top section	
Type:	Activated alumina
Length:	35 mm
Internal Diameter:	7.5 mm
Packing size:	70-100 mesh
Activation:	Heating at 110 °C for 3 h
Bottom section	
Type:	Silica gel
Length:	70 mm
Internal Diameter:	7.5 mm
Packing size:	100-200 mesh
Activation:	Heating at 170 °C for 3 h

Column eluted with:

(i) 20 mL n-heptane to elute saturates
(ii) 35 mL n-heptane + dichloromethane (1:2.5 v/v) to elute aromatics
(iii) 30 mL dichloromethane + tetrahydrofuran (1:3 v/v) to elute resins + asphaltenes

Solvents removed by rotary evaporation (60°C; 120/357 mbar) and saturates, aromatics and polar (resins + asphaltenes) fractions determined gravimetrically.

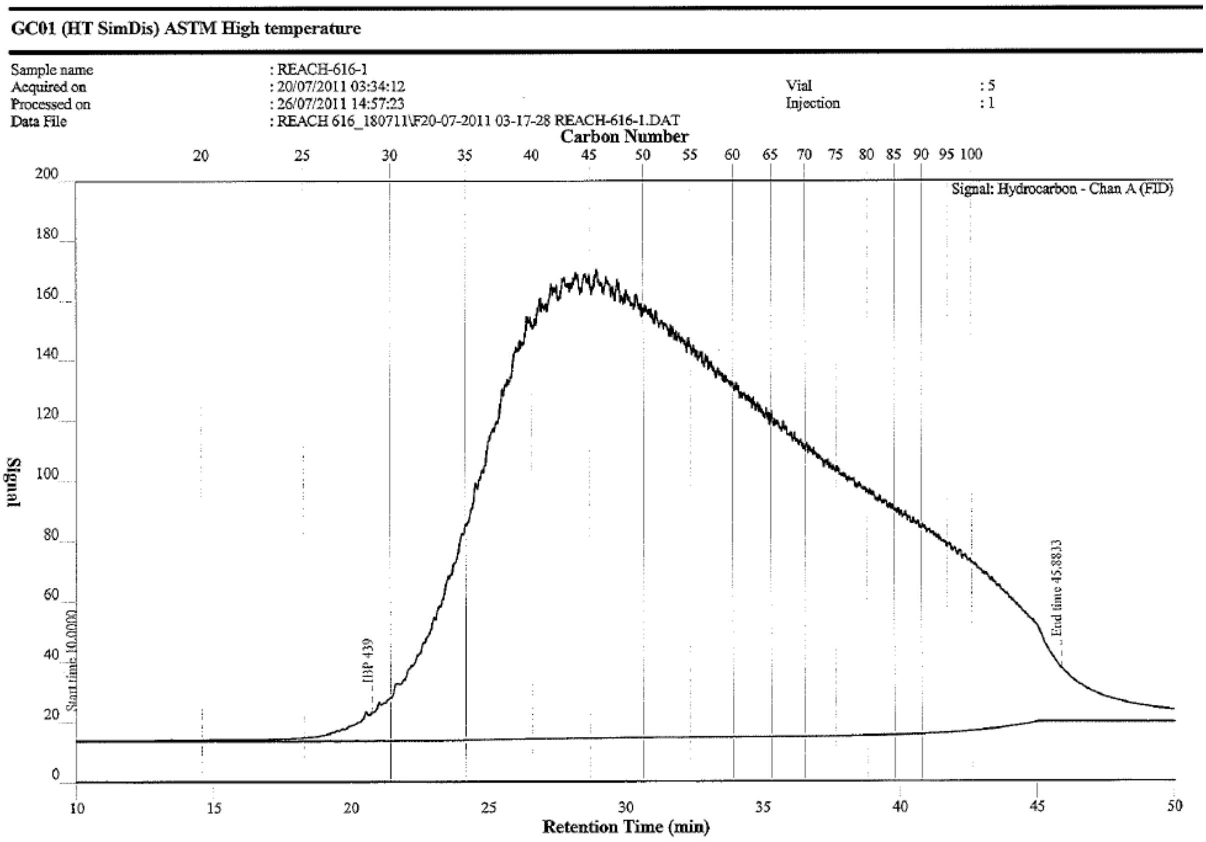
Hydrocarbons type	**Concentration (% w/w)**
Saturates	27.8
Aromatics	50.3
Polars	21.9

SAMPLE B

Bitumen CAS No. 64741-56-6
EINECS No. 265-057-8

7.4b. SIMDIS-Gas Chromatography

SIMDIS-GC analysis was carried out according to IP 480/07. The sample was dissolved in carbon disulphide and analysed by temperature programmed GC with flame ionisation detection using a non-polar separation column. The resulting chromatogram was compared with a calibration chromatogram obtained under identical conditions using n-alkanes spanning the elution range of the hydrocarbons present in the sample. The boiling range distribution of the components present was determined from these data.



GC01 (HT SimDis) ASTM High temperature

Sample name : REACH-616-1
Acquired on : 20/07/2011 03:34:12
Processed on : 26/07/2011 14:57:23
Data File : REACH 616_180711\F20-07-2011 03-17-28 REACH-616-1.DAT
Vial : 5
Injection : 1

SIMDIS-GC analysis showed that the sample contains hydrocarbons covering the C_{25} to $>C_{100}$ range corresponding with initial and final boiling points of 439°C and >750°C respectively. The boiling point distribution table for the sample is shown below.

Recovery (% mass)	IBP	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	91%
B.P. (degree C)	439.0	491.0	509.5	523.5	535.5	547.0	558.0	569.0	580.5	592.0	604.5	617.0	631.0	645.5	662.0	680.0	700.0	720.0	742.0	750.0

7.5b. Thin-Layer Chromatography – Flame Ionisation Detection

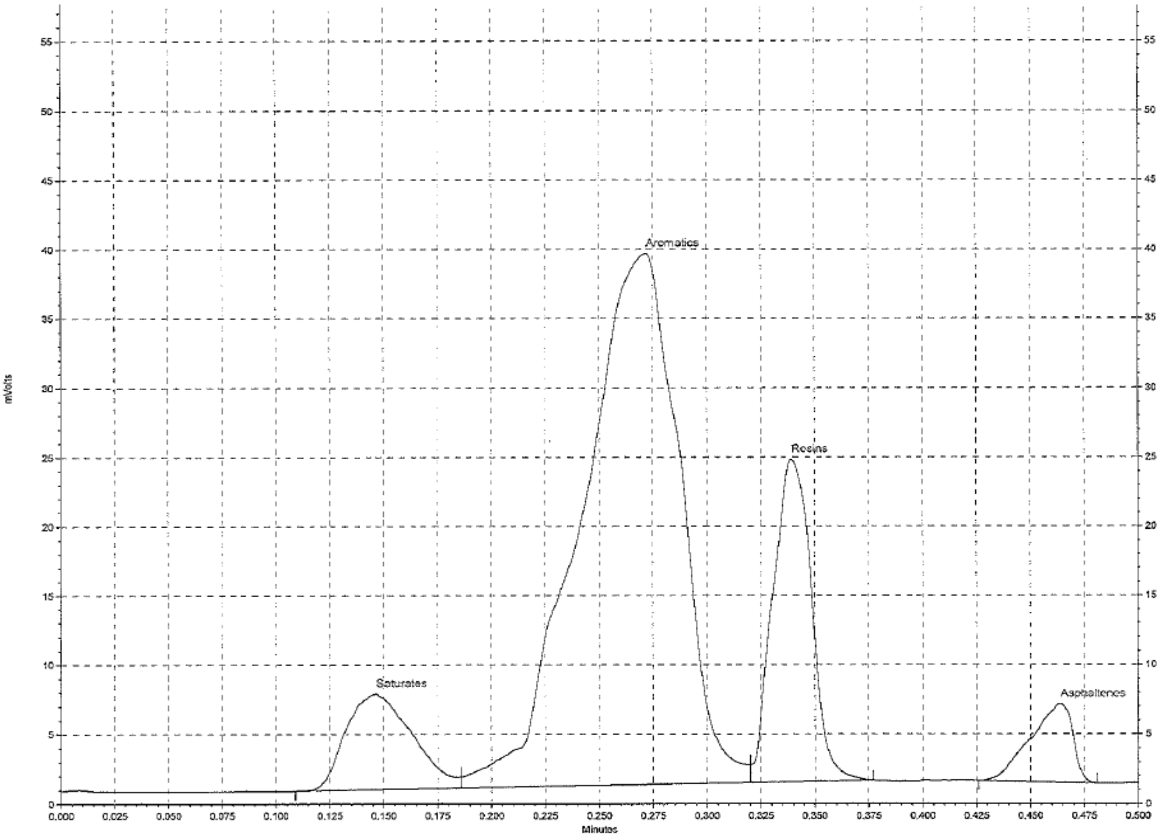
TLC-FID analysis of the sample was carried out according to IP 469/01(2). The sample was dissolved in dichloromethane and separated by TLC using silica rods and three successive developments with the following mobile phases:

(i) heptane

(ii) toluene:heptane (80:20 v/v)

(iii) dichloromethane:methanol (95:5 v/v)

Following evaporation of the final mobile phase, the rods were examined using an Iatroscan Mark V TLC-FID Analyser and the quantities of saturates, aromatics, resins and asphaltenes in the sample determined by internal normalisation of the resulting chromatogram.



The TLC-FID chromatogram has been annotated to show the peaks corresponding to the saturates, aromatics, resins and asphaltenes present. Normalisation of these peaks showed that the sample contains 10.6% (m/m) saturates, 65.4% (m/m) aromatics, 11.9% (m/m) resins and 12.1% (m/m) asphaltenes.

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