Analytical studies on Australian shale oils

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ANALYTICAL STUDIES ON AUSTRALIAN SHALE OILS

A thesis
submitted in fulfilment
of the requirements for
the degree

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

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Department of Chemistry
April 11, 1986
Abstract

New analytical methods were developed for the analysis of shale oil. They included two for the complete chemical class separation of shale oil, one for the resolution of 1-6 ring aromatic hydrocarbons and one for the quantitation of nitriles by infrared spectrophotometry (IR). The first chemical class separation scheme was an extension of an existing method and employed a combination of acid and base extraction and open column chromatography. The fractions collected comprised alkanes, alkenes, \( n \)-alkadienes, \( n \)-alkylmonoaromatics, polyalkyl-monoaromatics, bi- and tricyclic aromatics, tetra- and pentacyclic aromatics, \( n \)-alkanonitriles, 2-alkanones, 1-(cyclopent-1-enyl)-2-alkanones, acids and bases. The second chemical class separation scheme used a series of five, low pressure liquid chromatographic (LPLC) columns which contained, in succession, less thermally modified grades of alumina. The fractions collected comprised alkanes, alkenes, monoaromatics, \( \omega \)-alkenylmonoaromatics, \( \alpha \)-alkenylmonoaromatics, bicyclic aromatics, tricyclic aromatics, tetracyclic aromatics, pentacyclic aromatics, 4-alkanones, 3-alkanones, \( n \)-alkylpyridines, \( n \)-alkanonitriles, 2-alkanones, indoles and carbazoles, and phenols. Compared to other separation schemes, the second method provided
better chemical class resolution and fewer artefacts were formed during the analysis because it avoided aqueous acidic and basic extractions and column chromatography on excessively active adsorbents. The use of a series of deactivated packings also allowed elutions to be performed with less polar solvents which, inherently, have low boiling points. This not only resulted in fewer evaporative losses but also, adsorbents were easily regenerated for further use.

The separation scheme for shale oil aromatics used a 1 m LPLC column containing neutral alumina and a solvent program that comprised gradients of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) and benzene solvents. Seven fractions were collected which separately contained monoaromatics, \( \omega \)-alkenylmonoaromatics, \( \alpha \)-alkenylmonoaromatics, bicyclic aromatics, tricyclic aromatics, tetracyclic aromatics and, penta- and hexacyclic aromatics. Unlike previous methods, the resolution of aromatics with this separation scheme was according to the degree of aromaticity and was not affected by the type of alkyl substitution on the parent compounds. This was the result of both the better selectivity of the Freon 113 and benzene solvents over the conventional solvents of hexane and dichloromethane, and the use of alumina as adsorbent rather than silica or bonded phases.
The method for the quantitation of nitriles by IR was an adaptation of the second chemical class separation scheme. Using a LPLC column containing thermally modified alumina, nitriles were quickly isolated from neutral shale oil and then rapidly quantitated by IR utilising the distinctive C=N absorption band which occurs between 2260–2240 cm⁻¹. Advantages of the method include the use of a non-destructive method of detection and a total analysis time of less than 2.5 h.

A total of four different shale oils were analysed: Condor Brown Unit (Fischer assay), Condor Brown Unit (pyrolysis under nitrogen), Condor Carbonaceous Unit (pyrolysis under nitrogen) and Green River Formation. The results of these analyses are collectively summarised in a table which lists all the compounds identified in the oils according to functional group type and provides mass spectral data for the identification of the same compounds in other oils. From a detailed examination and comparison of the chemical content of each oil, inferences were drawn as to the biochemical and pyrolytic origin of many of the compound classes.
Abstract

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Appendix 1: Gas chromatograms of the open column fractions obtained from the nitrogen pyrolysis oils of the Condor Brown and Carbonaceous Units.

Appendix 2: Gas chromatograms of the aromatic compounds in fractions separated from Green River shale oil by low pressure liquid chromatography on neutral alumina.

Appendix 3: Gas chromatograms of the fractions separated from Condor Brown Unit shale oil by low pressure liquid chromatography on thermally modified alumina adsorbents.

Author's Publications

Acknowledgements
1. Introduction

1.1 Definitions

Oil shale is defined as a compact, fine textured, laminated rock of sedimentary origin which yields oil (shale oil) when pyrolysed but not appreciably when extracted with the solvents commonly used for petroleum [1]. Oil shales contain both organic and inorganic matter. The organic matter largely comprises a complex three dimensional polymer, referred to as kerogen [2], with small amounts of low molecular weight (solvent extractable) compounds also being present. The inorganic matter comprises a wide range of minerals such as quartz, clays and calcite. Kerogen is relatively inert and must be subjected to destructive processes such as chemical digestion or pyrolysis if it is to be converted to usable, low molecular weight products. Within the oil shale industry, kerogen pyrolysis is termed retorting or distillation.

1.2 Brief history of the oil shale industry

The exploitation of shale oil as a fuel resource originated over a century ago in Scotland and oil shale Industries have since arisen in many countries including France, Spain, Sweden, South Africa, Australia, Estonia (U.S.S.R.) and China. Invariably each nation's
industry was either initiated or curtailed depending on the availability of less expensive, alternative fuel resources. Currently, only industries in the U.S.S.R. and mainland China remain in operation.

Within Australia, the oil shale industry has had limited success and endurance. The longest period of productivity occurred between 1940 and 1952 and was based on the processing of N.S.W. 'torbanites' which were among the richest known oil shale deposits in the world. At maximum production in 1947, a throughput of approximately 350,000 tons of shale per year was attained.

Following a long period of dormancy, renewed interest in the Australian oil shale industry was recently inspired by sudden rises in the price of petroleum which were initiated by OPEC at the end of 1973. Rather than revitalising the original oil shale industry of N.S.W., however, interest was taken in the vast reserves in Queensland. Although of a much poorer grade, the Queensland reserves were more suitable for large scale mining and processing. In the last few years, commercial interest in oil shales has again waned due to the ready availability of cheap petroleum.

1.3 General geochemistry of oil shales
1.3.1 Organic matter in oil shales
It is generally believed that algae and bacteria were the primary organic source materials for the organic matter in oil shales with secondary contributions coming from spores, pollens and the remains of higher plants. In particular, fatty acid esters, hydrocarbons and polyol alkyl ethers, which are collectively referred to as lipids, are considered to be the main chemical entities responsible for kerogen formation. The basis of this premise is that lipids, unlike many other suggested kerogen precursors such as carbohydrates, lignins, proteins and waxes, have the appropriate stability, the required chemical configuration and the availability for the formation of an insoluble kerogen matrix.

Cane [3b] has demonstrated that polyene acids, which are characteristic of algal fats, can readily form kerogen-like polymers and, similarly, Stadnikoff [4] has asserted that the oxidation and polymerisation of fatty acids is responsible for the formation of kerogenous material and petroleum. Chappe et al. [5] have isolated the same alkanes from kerogen and bacteria which suggests that cell membranes of similar bacteria are an integral part of the kerogen and, likewise, Van Dorsselaer et al. [6, 7] have shown that the presence of hopanoids in kerogen indicates bacterial activity.

It is a well known phenomenon that under adverse conditions algae exhibit greatly increased lipid formation concomitant with
decreased amounts of protein and carbohydrate. With abundant food supply and natural environment, the total fat content of most algae is only a few percent. However, by restricting oxygen and lowering the temperature it has been shown that algae, for example, Chlorella [secrete lipids up to 86% of their dry weight.

The algal species most likely to have contributed fatty acids to kerogen formation would be members of the Chlorophyceae and Cyanophyceae. These algae are known to contain large quantities of both saturated fatty acids (which typically range from $C_{14}-C_{22}$ with a maximum at $C_{16}$) and unsaturated fatty acids (which are mainly $C_{16}$ and $C_{13}$ homologues). The algae most likely to have contributed hydrocarbons would be those of the green and blue-green genera. The hydrocarbons produced by these algae usually have maximum abundance at $C_{17}$ but in some species a bimodal distribution may be found with the second maximum occurring in the $C_{27}-C_{31}$ range [3a, 8b].

Bacteria that are likely to have featured prominently in kerogen formation include members of the Archaebacteria such as the methanogens and methanotrophs. Other members of the Archaebacteria such as the Caldarella (thermophiles), Halobacterium (halophiles) and Sulfolobus (acidophiles) would
probably have not been present in the sapropelic, lacustrine conditions prevailing during deposition.

1.3.2 Inorganic matter in oil shales [8c, 8d]

The inorganic constituents of oil shale deposits are usually divided into the three mineral categories of,

(1) detrital, which includes quartz, feldspars, certain clay minerals and volcanic debris,

(2) biogenic, which includes amorphous silica and calcium carbonate, and

(3) authigenic, which includes pyrite and other metal sulphides, carbonates (calcite, dolomite, siderite), phosphates and saline minerals such as trona, dawsonite and halite.

Authigenic minerals are particularly important because they provide information concerning redox conditions during or soon after sedimentation, the nature of the deposition medium and climatic conditions. Variations in the relative proportion of each mineral type are found between most oil shales and this generally reflects differences in the nature of the depositional environment.

1.3.3 Depositional environments [8e]

The principal environments in which oil shales were deposited are,

(1) large terrestrial lakes,
(2) shallow seas on continental platforms and continental shelves, generally in areas where circulation of water near the sea floor was restricted, and
(3) small lakes, bogs and lagoons associated with coal producing swamps.

Most oil shale deposits are microstratified and banded. This indicates that the environmental conditions prevailing during deposition were not steady but varied on an annual, seasonal or irregular basis. In many deposits there is evidence that the depositional location occasionally dried up and was covered by chemical precipitates and/or mud cracks so that the ensuing oil shale now displays a broken banded structure. In other deposits, distinct zones of spores, pollens, resin grains or animal remains indicate that the ecosystems were subjected to periodic departure from normal deposition conditions. In some deposits constant conditions prevailed which allowed continual deposition of either pure organic or inorganic matter.

1.3.4 Mechanism of kerogen formation

Following the depositional stage, the composite decaying organic debris, admixed with inorganic material, would be covered by successive layers of sediment. During this period, lipids would be hydrolysed to the free acids and alcohols. Once the fatty acids
had been liberated, biological and microbial attack could convert them into a variety of other chemical types by attack on the bond group adjacent to the carbonyl. Alternatively, bacterial attack could lead to the formation of \( \alpha\beta \) unsaturated acids which would be followed by further reactions of the Diels-Alder type. More stable remnants of the algae and bacteria, such as the cell membranes, would largely remain intact.

With subsidence over geological time, the pressure of the overlying strata would result in compaction of the sediment mixture and the final kerogen polymerisation would eventuate. Based on experimental evidence [9], it is expected that the complete formation process probably did not occur at temperatures in excess of 150°C.

1.4 Geochemistry of the Condor oil shale deposit

From the preceding discussion of oil shale kerogen formation, it is evident that oil shale geochemistry can vary quite markedly from one deposit to another. The chemistry of the ensuing shale oils will undoubtedly reflect these variations so it would be appropriate at this point to discuss the individual geochemical backgrounds of the shale oils studied in this thesis. This discussion, in conjunction with the results of the chemical
analyses of the shale oils, will ultimately allow correlations to be drawn between oil shale geochemistry and shale oil chemistry. Once reliable correlations are established it may then be possible to predict the major chemical features of other shale oils which have similar geochemical backgrounds.

The principal shale oil that was examined in this thesis was derived from oil shale of the Condor deposit in Queensland, Australia. Prior to the present work, the chemistry of Condor shale oil had not been studied in detail. The geology of the Condor deposit, details of which are presented after this discussion, has also only recently been determined [10].

The second shale oil that was examined was obtained from oil shale of the Mahogany Zone, Green River Formation deposit (U.S.A.) and was analysed for comparative purposes. In contrast to the Condor deposit, most aspects of the Green River deposit have already been extensively examined and this was the basis of its selection as a reference material. Details of the geology of the Green River deposit are given elsewhere [11, 12] and will not be discussed here.

1.4.1 Regional geology

The Condor oil shale deposit is centered about 13 km south of the town of Proserpine in Queensland (Figure 1). The area of the
Figure 1: Location of the Condor deposit.
deposit covers the onshore portion of the north-western end of the
Hillsborough basin and is mostly low lying and swampy,
particularly in the east towards the coast.

The Hillsborough Basin is a southeast-trending graben formed
by Late Cretaceous or Early Tertiary block faulting. According to
Paine [13] the basin is asymmetrical with a more gentle slope on
the southwest flank. It is bounded to the northeast by the Foxdale
(onshore) and Repulse (offshore) Faults and to the southwest by an
structural map which indicates that the basin is extensively
faulted.

The basin extends inland for at least 20 and possibly 45 km
while offshore it extends under Repulse Bay and the Hillsborough
Channel for about 70 km until it loses its identity southeast of
Cape Hillsborough. Seismic work indicates that the basin deepens
offshore where the sequence contains up to 3000 m of sediments as
young as Early to mid Tertiary age, Gray [14].

Based on the average results of 30 drillholes the estimated in
situ resources of the Condor deposit are [10]:

Oil shale tonnes - $17.8 \times 10^9$

Average moisture - 9 percent

Average grade - 61.2 litres/tonne (at zero moisture)
Barrels (in situ) - 6.25 x 10^9

1.4.2 Stratigraphy

The sequence within the area investigated to date consists of three major units from each of which a smaller interval may be differentiated (Figure 2). The three major units are the Sandstone Unit at the base of the sequence, the Oil Shale Unit and the Upper Unit. Unconformably overlying these units is a veneer of gravel and sand outwash of Quaternary and possibly Late Tertiary age.

The upper part of the Sandstone Unit contains a large portion of coal and other carbonaceous lithologies. Where this occurs the interval is differentiated and is designated as the Carbonaceous Unit. Overlying this unit the basal part of the Oil Shale Unit has been given unit status on the basis of a change in colour of the oil shale from yellow-brown above, to brownish-black below. This latter zone is termed the Brownish-black Oil Shale Unit as distinct from the bulk of the oil shale which forms the Brown Oil Shale Unit. Additionally, that part of the sequence lying at the base of the Upper Unit may be differentiated on the basis of a change in the proportion of its component lithologies. This unit is termed the Transitional Unit.

Each of these units extend through the entire area except for the Carbonaceous Unit which is not differentiated in the southeast.
Figure 2: Structural map for the south-western flank of the Hillsborough basin: structural contours to the base of the brownish-black oil shale unit (from Green and Bateman [10]).
A localised variation of the normal sequence occurs at the north-western end of the area where a thick wedge of sandstone occurs within the Brown Oil Shale Unit. This has been informally termed the Gum Gully member.

1.4.3 *Palaeoenvironment*

The age of the Condor deposit has been determined from palynological studies of samples from Ampol Exploration (Qld.) Pty. Ltd. (AEQ), Proserpine 1. Evans [15] has proposed several alternatives including:

(1) an Eocene to Miocene age, despite the absence of distinctive *Nothofagidites* pollen, and

(2) a Late Cretaceous age, based on the absence of *Nothofagidites* and the presence of pteridophyte spores, and despite the absence of typical Late Cretaceous pollen.

Both Evans [15] and Heckel [16] found a cyclic pattern in the spore and pollen abundances in AEQ Proserpine 1, with indications of alternating swampy and drier conditions. They also found that the upper 450 m in the well contains primarily angiosperm pollen, which suggests terrestrial deposition. Further, the alga *Pediastrum sp.* (Foster [17]), indicates a freshwater environment. Evidence of oil shale deposition under brackish lacustrine conditions includes dinoflagellates from AEQ Proserpine 1 [16], acritarchs from CDD 1
and alginate B from AEQ Proserpine 1, representing colonial blue-green algae. Mineralogical evidence for brackish conditions during this time include fibrous, radiating crystals of anhydrite and apatite that occur as pseudomorphs after a mineral that may have been gypsum.

The deepest sediments (i.e. the Sandstone Unit) are considered to be fluviatile and are a result of a period when sediment flow exceeded subsidence. The appearance of coal and other lithologies in the Carbonaceous Unit indicates renewed subsidence, producing extensive areas of swampland. Towards the southeast, fluviatile sedimentation persisted, which, with some evidence of a coarsening of grain size in this direction, suggests a southerly provenance at the time. Petrologic studies indicate a volcanomict provenance of indeterminate location.

The basal contact of the Brownish-black Oil Shale Unit is sharp in contrast to the other unit boundaries in the sequence. It is considered to be isochronous rather than time-transgressive and reflects a dramatic change in the sedimentation regime in which an accelerated rate of subsidence drowned the entire valley simultaneously. Fairly still conditions would have then prevailed until a regression of the lake edge resulted in the deposition of the Transitional and Upper Units. This seems more likely to have been
caused by increasing intercalations of tongues of sand and silt into the lake system rather than from uplift. However, it does suggest that once again the rate of sedimentation had exceeded subsidence.

Evidence of evaporites, which suggests shallow water deposition, is scarce in the Condor deposit and it seems more likely that deepwater would have been essential to maintain the permanent water stratification that is inferred. Demaison and Moore [22] consider that warm palaeoclimatic conditions, with a low seasonal contrast and moderate rainfall, would promote lacustrine oil source bed deposition by maintaining this stratification. However, the data of Johnson et al [23] indicate that the Australian plate did not begin its northward movement away from Antartica until 53 million years ago. At this time the palaeolatitude of the Condor Lake would have been approximately 45 S giving a cool temperate climate. Such a climate may give a positive water balance conducive to oil source bed deposition, but tends to promote vertical mixing of lake water by seasonal overturn.

It is apparent that an explanation covering all the features of the deposit has yet to be found. An explanation suiting most of the criteria suggests that the oil shale was formed in an intramontane graben during a prolonged period of subsidence. The basin was open
to the sea for at least part of the time, during which period, a positive water balance existed. The vertical continuity of the oil shale formed in this environment was progressively disrupted by tongues of sediment from an encroaching shore.

1.5 Isolation of the organic matter in oil shales

Due to the complex nature of kerogen and the presence of large amounts of integrated inorganic matter, some of the procedures normally used for the isolation or chemical characterisation/identification of organics (e.g. GC, GC-MS) cannot be used directly. As a consequence, characterisation should proceed through solubilisation and/or disintegration of the organic kerogen polymer to yield smaller fragments which can be separated from the inorganic material.

The procedures that are commonly used for the isolation of organic matter are as follows:

1.5.1 Solvent extraction

The results obtained are largely dependent on the solvent used and optimum extraction of the ground rock is approached by ultrasonic agitation or 'Soxhlet' extraction at the boiling point of the solvent [24]. The amount of extractable material increases with extraction temperature and with the polarity and chemical
reactivity of the solvent. Using relatively weak donor solvents such as methanol/toluene (3/1) [25] or benzene/methanol (4/1) [26] only adsorbed low molecular weight components are recovered. With stronger solvents such as those used for the extraction of coals e.g. HF/BF$_3$/H$_2$ [27] or pyridine [28] a large proportion of the kerogen may be solubilised.

1.5.2 **Thermal desorption**

This technique is useful for examining, or recovering, the small quantities of volatile hydrocarbons which occur in oil shales (≈ 1% of total organic matter). The volatiles are desorbed by gently heating the oil shale (250–300°C) in a Rock-Eval Instrument [29] and trapped either cryogenically [30] or on an adsorbent [31] and analysed by gas chromatography. Recoveries are comparable to those obtained by solvent extraction but less time is required for the analysis [25].

1.5.3 **Demineralisation**

This involves solubilising the inorganic material in the oil shale matrix. However, interaction of the demineralising agent with the organic functional groups of the kerogen polymer may occur. For many oil shale samples containing > 10% kerogen, treatment with hydrochloric acid (to remove carbonates) and hydrofluoric acid (to remove silica and silicates) is sufficient to
give kerogen containing only a low percentage of residual minerals.

1.5.4 *Chemical digestion*

Under controlled conditions, kerogen can be oxidised to yield low molecular weight molecules which can be separated and identified by gas chromatography and mass spectrometry. Ideally, the degradation products can be used to infer the structural units of the kerogen polymer. The oxidation reagents most frequently used include alkaline potassium permanganate [32-34], ozone [35], nitric acid [36, 37], hydrogen peroxide [38], chromic acid [39, 40] and air or oxygen [34].

1.5.5 *Thermal degradation*

Thermal degradation (pyrolysis) of oil shale also results in the formation of low molecular weight kerogen fragments. The temperatures required for kerogen pyrolysis range from 400-700°C and the heating process is usually performed in a chemically inert vessel (e.g. aluminium) according to the procedure of Stanfield and Frost [41]. Variables which can affect the chemistry of the shale oils produced by pyrolysis include:

(i) the temperatures employed,

(ii) the atmosphere under which retorting is performed (inert, oxidising or reducing),

(iii) the catalytic effects of the mineral matrix, and
1.6 Aim and structure of thesis

Methods which provide proper chemical class separation of shale oil are scarce (Chapter 2). In particular, alkanes and alkenes, 1-6 ring aromatics and nitriles and ketones are only poorly resolved. These chemical classes are of significant interest because they are either major components of shale and have synthetic value or they have potentially hazardous properties. The concurrent aims of this thesis were to develop new analytical methods and apply these to the analysis of Condor shale oil. Prior to the present work, the chemistry of the Condor oil shale deposit was relatively unknown.

Each of the new analytical methods are separately presented in Chapters 3-6. They include two for the complete separation of shale oil, one for the resolution of alkanes and alkenes, one for the resolution of 1-5 ring aromatics and one for the quantitation of nitriles by infrared spectrophotometry. Chapter 7 summarises the types of compounds found in various Condor (and Green River) shale oils and lists these according to chemical class. By comparing the composition of these shale oils and using the data summarised in
Chapter 7, inferences were drawn as to the biochemical and pyrolytic origin of many chemical classes found in shale oil and these are given in Chapter 8. Chapter 9 gives an overview of the new methods and the relationship which has been established between shale oil composition, oil shale petrology and retorting conditions.
2. Review of Procedures for the Chemical Analysis of Complex Fuel Mixtures

The intrinsic complexity of unfractionated shale oil precludes the identification of components other than a few major ones such as alkanes and alkenes. Therefore, fractionation of the crude oil, preferably into chemical class types, is essential prior to detailed analyses by techniques such as gas chromatography or gas chromatography-mass spectrometry.

Shale oils contain many classes of compounds which are common to other fossil fuels so the following literature survey has included not only those methods developed for shale oils but also those for petroleum, bitumens, liquified coals, etc. Due to the volume of literature available on the analysis of complex fuel mixtures, it is not possible within the constraints of this thesis, to provide an exhaustive survey. Instead, a representative review is given which reflects both the volume of methods developed for a particular separation and the types of analytical procedures employed.

For the purpose of clarity and ease of reference, the literature survey is presented in tabular form with the source material, the chemical class(es) resolved and a summary of the analytical
procedure being given for each article. The methods reviewed have been divided into three categories:

1. procedures for broad chemical class separations, 2. procedures for the separation of one chemical class and 3. procedures for the separation of many chemical classes (Tables 1-3). Within each division the articles have been listed in chronological order to reveal historical trends.

2.1 Procedures for broad chemical class separations

The basis of these methods (Table 1) is the SARA technique of Jewell et al. [42] in which crude oils are separated into saturates, aromatics, resins and asphaltene by a combination of acid and base extraction, iron (III) chloride complexation and column chromatography on silica. Following the introduction of this procedure, numerous other broad separation methods have been developed, but, only a few changes have been introduced. The most common changes are:

(a) omission of the preliminary extraction and complexation steps,

and

(b) replacement of the low pressure liquid chromatographic (LPLC) silica adsorbent with a high pressure liquid chromatographic (HPLC) column which contains either silica or a bonded phase such
as C$_{18}$, NH$_2$ or CN.

More recently, the trend has been to use two HPLC columns in series, e.g. CN and silica.

Despite the volume of available literature and the application of more sophisticated instrumentation such as HPLC, no improvements in the quality of separation are evident. Procedures for broad chemical class separations can only serve as quick methods for crude separation and quantitations such as may be required for monitoring refinery feedstocks, or for a preliminary separation preceding more refined analytical methods.
<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum (Calif., Tex., Utah, &amp; Wyo., USA)</td>
<td>1) (a) Acids isolated from oil distillate with anion exchange resin and (b) bases isolated with cation exchange resin. 2) Neutral nitrogen compounds isolated by complexation with FeCl₃/Attapulgus clay and recovered by anion exchange chromatography using 1,2-dichloroethane eluent. 3) Residual neutrals resolved on silica into saturates (pentane eluent) and aromatics (methanol eluent) [42].</td>
</tr>
<tr>
<td>Petroleum</td>
<td>Oil applied to HPLC silica column and alkanes and alkenes are eluted with Fluorinert FC-78 mobile phase. Aromatics are recovered by backflushing [44].</td>
</tr>
<tr>
<td>Shale Oil (Colo. &amp; Wyo., USA)</td>
<td>1) Oil (in hexane) applied to cyano bonded HPLC column and separated with a benzene/n-butanol gradient into three fractions that comprise alkanes and alkenes, aromatics and polars. 2) The aromatic fraction is further characterised by RPLC on a C18 phase using methanol/water solvent gradients [45].</td>
</tr>
<tr>
<td>Shale Oil (Colo., USA)</td>
<td>1) Oil separated into non-polar and polar fractions by LC on Florisil. 2) Non polar fraction resolved into alkanes/alkenes and aromatics by HPLC on silica. 3) Alkanes and alkenes separated on AgNO₃ impregnated silica. 4) Branched and cyclic alkanes and alkenes separately resolved from respective fractions by vapour phase 5 Å molecular sieve subtraction [46].</td>
</tr>
<tr>
<td>Shale Oil (Colo., Ohio &amp; Wyo., USA)</td>
<td>1) Acids, bases and neutral nitrogen compounds are separated from the oil with anion exchange, cation exchange and FeCl₃/Attapulgus clay adsorbents, respectively. 2) The neutral oil is applied to consecutive columns of silica and AgNO₃/silica; aromatics are retained on the first column and are recovered with benzene/methanol while the alkenes which are retained on the second column are recovered with benzene/cyclohexane. Alkanes are not retained by either column and are present in the initial cyclohexane eluate from the dual column system [47].</td>
</tr>
<tr>
<td>Shale Oil</td>
<td>Oil is separated on a pre-column-preparative column series which contains respectively, thermally deactivated and normally activated silica. Elutions are performed with hexane. Alkanes are not retained on either column and are recovered in the initial eluate. Aromatics and nitrogen, oxygen and sulphur heterocycles are retained on the preparative column and pre-column, respectively and are separately recovered by backflushing [48].</td>
</tr>
</tbody>
</table>
Table 1: cont'd...

<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Petroleum Distillates and Liquified Coal</strong></td>
<td>Oil applied to cyano and silica HPLC columns in series and elutions performed with hexane. Alkanes, alkenes and aromatics are not retained and are separately collected by monitoring the UV absorbance of the eluate. Polars are recovered by backflushing [49].</td>
</tr>
<tr>
<td>- Alkanes</td>
<td></td>
</tr>
<tr>
<td>- Alkenes</td>
<td></td>
</tr>
<tr>
<td>- Aromatics</td>
<td></td>
</tr>
<tr>
<td>- Polars</td>
<td></td>
</tr>
<tr>
<td><strong>Petroleum</strong></td>
<td>Two procedures: 1) Separations are performed on an amino HPLC phase using hexane eluent; saturates are collected in the initial eluate and aromatics and polars are recovered by backflushing. 2) Separations are performed on an amino HPLC phase using a cyclohexane/chloroform gradient; saturates and aromatics are collected in the eluate and polars are recovered by backflushing [50].</td>
</tr>
<tr>
<td>- Alkanes</td>
<td></td>
</tr>
<tr>
<td>- Aromatics</td>
<td></td>
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<tr>
<td>- Polars</td>
<td></td>
</tr>
<tr>
<td><strong>Liquified Coal</strong></td>
<td>1) (a) Acids are isolated from the oil distillate with an anion exchange resin and (b) bases are isolated with a cation exchange resin; hydrocarbons are recovered in the initial eluate of the cation exchange resin. 2) Acid and base fractions are further resolved into chemical classes by HPLC on silica using eluents of heptane, dichloromethane and 1,2-dichloroethane which contain both ethanol and fatty acid buffers [51].</td>
</tr>
<tr>
<td>- Hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>- Acids</td>
<td></td>
</tr>
<tr>
<td>- Bases</td>
<td></td>
</tr>
<tr>
<td><strong>Petroleum, Shale Oil and Coal Oil</strong></td>
<td>Oil applied to dual functional cyano-amino HPLC phase and elutions performed with pentane. Alkanes, alkenes and aromatics are not retained and are separately collected. Polars are recovered by backflushing with methyl, tert-butyl ether [52].</td>
</tr>
<tr>
<td>- Alkanes</td>
<td></td>
</tr>
<tr>
<td>- Alkenes</td>
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<tr>
<td>- Aromatics</td>
<td></td>
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<tr>
<td>- Polars</td>
<td></td>
</tr>
<tr>
<td><strong>Petroleum Distillates</strong></td>
<td>Oil applied to cyano and silica HPLC column series and elutions performed with hexane. Alkanes, alkenes and aromatics are resolved with a hexane mobile phase and are separately collected. Polars are retained on the cyano phase and are recovered by backflushing [53].</td>
</tr>
<tr>
<td>- Alkanes</td>
<td></td>
</tr>
<tr>
<td>- Alkenes</td>
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<tr>
<td>- Aromatics</td>
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<tr>
<td>- Polars</td>
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</tbody>
</table>
Key to abbreviations used in Tables 1-3

br. - branched
cycl. - cyclic
GC - gas chromatography
GLC - gas liquid chromatography
HPLC - high pressure liquid chromatography
IR - infrared spectrophotometry
LC - liquid column chromatography
LPLC - low pressure liquid chromatography
MS - mass spectrometry
MWt - molecular weight
NMR - nuclear magnetic resonance spectrometry
RPLC - reverse phase liquid chromatography
TLC - thin layer chromatography
UV - ultraviolet spectrophotometry
2.2 Procedures for the separation of one chemical class

These procedures (Table 2) are the most abundant in the literature and are usually the least complicated. Most require a preliminary separation of the components of interest from the complex fuel followed by a second analytical separation with higher resolution. The main exceptions to this are the acids, bases and alkanes/alkenes, each of which may be isolated in one step.

Acids and bases are the simplest of the single compound classes to separate and two procedures are available, namely aqueous acidic and basic extraction, and ion exchange chromatography. The former procedure is faster and the more frequently used, but ion exchange chromatography offers the advantages of better sample recovery and gradient elution of retained components into chemical class fractions.

Alkanes and alkenes are the most difficult of the neutral functional group types to resolve despite the initial ease with which they can be collectively separated from crude oil. Liquid chromatography on silica or alumina provides a partial separation but only for those samples in which the molecular weight range of components is small. Chromatography on silica impregnated with silver nitrate is the only satisfactory procedure available in the
literature. Once the alkanes and alkenes have been resolved, they may be further separated into linear and "branched/cyclic" fractions by either urea adduction or by molecular sieve adsorption. The latter is now the preferred technique.

The neutral compounds which are most frequently analysed are the polynuclear aromatic hydrocarbons (PAH) and nitrogen containing compounds (basic and neutral). The great interest in these compound classes arises from both the potential health hazards associated with their handling (many PAH [54, 55] and nitrogen containing PAH [55, 56] are known or suspected carcinogens) and the detrimental effects of nitrogen containing compounds on refinery catalysts [57, 58]. Although numerous separation procedures are available for PAH, most rely on column chromatography using adsorbents such as silica, alumina, picric acid-alumina or more recently bonded phases such as C18, amino, pyrrolidone and dinitroanilinopropyl [59]. Separations on silica and some bonded phases have, however, been found to depend on the extent of alkyl substitution [60, 61]. In addition, separations on HPLC bonded phases have mainly emphasized the resolution of model mixtures rather than authentic fossil fuels. Some novel procedures for the separation of PAH are available, such as that of Azogu [88] in which PAH are resolved as arene complexes on silica.
Separation of the nitrogen containing compounds is easier to perform than the separation of PAH since a preliminary subdivision into basic and neutral subfractions can be accomplished by aqueous acidic extraction or cation exchange chromatography. Once separated, the neutral nitrogen compounds can be resolved by LC on adsorbents such as silica, alumina or amino HPLC phases. As an alternative, the neutral nitrogen compounds can be isolated from the crude oil (after the basic compounds have been removed) by complexation with iron (III) chloride. Originally this procedure relied on shaking crude neutral oils with a mixture of both iron (III) and zinc chlorides, followed by thermal decomposition of the metal complexes to recover the complexed components. Subsequently, Jewell and Snyder [62] modified this procedure by (a) supporting the iron (III) chloride on an inert substrate (Attapulgus clay) to permit liquid chromatographic type separations, (b) desorbing the iron (III) complexes with a solvent and (c) recovering the complexed components by passing the iron (III) salts through an anion exchange resin.

After alkanes and alkenes, nitriles and ketones are the most difficult of the neutral functional group types to resolve due to their similar chromatographic retentions. Only one separation procedure has been described for each of these chemical classes,
neither of which relies on chromatographic resolution. The basis of the nitrile separation was an initial complexation of all the neutral nitrogen compounds with iron (III) chloride followed by selective removal of non-nitrile compounds by reaction with perchloric acid. The ketone separation procedure relied solely on the selective reaction of the carbonyl group with Girard T reagent (trimethylammonium acetohydrazine chloride).

Since many sulphur heterocycles are also known or suspected carcinogens [63, 64], several separation procedures have appeared in the literature. The most common approach involves (a) oxidising the sulphur heterocycles to the corresponding sulphones using reagents such as hydrogen peroxide, (b) separating the sulphones from the PAH with which they are originally coeluted, and (c) regenerating the sulphur heterocycles by reduction.
Table 2: Procedures for the separation of one chemical class  
(See page 26 for key to abbreviations)

<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
</table>
| **Petroleum**  
(Nig. & West Germ.)  
- Acids (carboxylic) | 1) Carboxylic acids isolated from oil by LC on KOH treated silica. 2) Acids derivatised to methyl esters with boron trifluoride-methanol. 3) Linear components separated from branched and cyclic components by urea adduction [65]. |
| **Shale Oil Retort Water**  
(Rifle, Colo., USA)  
- Acids (carboxylic) | 1) Retort water freeze dried and residue derivatised with boron trifluoride-methanol. 2) Excess reagent decomposed with NaCl and organic acids extracted with CC14. 3) Analysis by IR, GC and GC-MS [66]. |
| **Liquified Coal**  
(Wilsonville, Ala., USA)  
- Acids (phenols) | 1) Mono-ortho and non-ortho substituted phenols separately isolated from oil by LC on silica using HCl saturated chloroform and chloroform/diethyl ether eluents, respectively. 2) Phenols further resolved on HPLC bonded phases (-NH₂, -CN and -C18). 3) Identifications by base extraction, spot tests, UV and fluorescence spectrophotometry [67]. |
| **Shale Oil**  
(Green River, Colo., USA)  
- Acids and bases | 1) (a) Acids extracted from oil with aqueous NaOH; extracts neutralised and liberated acids recovered with dichloromethane and (b) bases similarly isolated by extraction with aqueous H₂SO₄ and purified by LC on alumina. 2) Components identified by combined GC-IR [68]. |
| **Petroleum**  
(Tex., USA)  
- Alkanes (isoprenoids) | 1) Distillate fraction (294-309°C) fractionated into normal and isoparaffins by GLC on Carbowax 20M. 2) Isoparaffin fraction re-chromatographed on silicone grease to separate individual components. 3) Isoprenoid alkanes separately characterised by IR, MS and NMR [69]. |
| **Shale Oil**  
- Alkanes (n-, iso-, anteiso- and cycl.) | 1) Hydrocarbons separated from oil by LC on alumina with hexane eluent. 2) n-Alkanes adsorbed on 5 Å sieves by reflux in benzene. 3) Iso-, anteiso- and cyclic alkanes collectively separated from remaining branched and cyclic components by GC on SE-30 column. 4) Components individually separated by GLC on m-polyphenylether phase [70]. |
| **Athabasca Oil Sand**  
(Alberta, Canada)  
- Alkanes (hopanes and tricyclic terpenes) | 1) Hydrocarbons treated with Br₂/CCl₄ and alkanes isolated by TLC on silica with pentane solvent. 2) Sample refluxed over 13 X sieves in pentane. 3) Sieves removed and extracted with isoctane to recover hopanes and tricyclic terpenes. 4) Sample purified by LC on silica with skelly B solvent [71]. |
| **Bitumens**  
Bulgaria  
- Alkanes  
- Alkenes | 1) Alkane/alkene mixture resolved from Soxhlet extract of bitumen by LC on alumina. 2) Mixture treated with urea and clathrates resolved into n-alkanes and alk-1-enes by TLC on silver impregnated silica (AgNO₃/silica) using petroleum ether as eluent [72]. |
| **Liquified Coal, Shale Oil and Petroleum**  
- Bases (polynuclear aromatic amines) | 1) Bases extracted from oil (in benzene) with aqueous HCl, extracts neutralised and bases recovered with ether. 2) Bases applied to alumina and eluted with (a) dichloromethane/benzene which recovers azaarenes and (b) methanol which recovers crude amines. 3) Azaarenes purified by dimethyl sulphoxide partitioning and (b) crude amines purified by LC (Sephadex LH-20) followed by trifluoroacetylation [73]. |
<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
</table>
| **Petroleum**  
(Likouala, Congo and Baliste, Guinea)  
- Bases (tri aromatic) | 1) Strong bases isolated from oil by LC on HCl treated silica. 2) Bases separated into 2-7 ring fraction by RPLC on Lichrosorb RP18 using methanol/water (0.1 M NH₃OH) solvent. 3) Triaromatic bases separately resolved from 2-7 ring fraction by RPLC on C18 phase with acetonitrile/water solvent [74]. |
| **Shale Oil**  
(Rundle, Aust.)  
- Ketones | 1) Shale oil in dichloromethane/methanol is refluxed overnight with trimethylammonium acetohydrazine chloride (Girard T) and an acid catalyst (ion exchange resin). 2) Reaction mixture cooled, filtered and extracted with water. 3) Aqueous phase acidified with HCl and stirred overnight. 4) Liberated ketones recovered with dichloromethane [75]. |
| **Petroleum**  
- Nitriles | 1) Basic compounds removed from oil by aqueous HCl extraction. 2) Neutral nitrogen compound isolated from oil by complexation with iron(III) and zinc chlorides and recovered by thermal decomposition. 3) Indoles, carbazoles and phenazines removed by reaction with perchloric acid, and nitriles are separated from the residual nitrogen compounds by LC on alumina using benzene as eluent [76]. |
| **Shale Oil**  
- Nitrogen cmpds | 1) Shale oil applied to Florisil column (magnesium silicate) and elutions performed with (a) pentane to recover hydrocarbons and PAH and (b) methanol to recover nitrogen containing compounds. 2) Nitrogen content of fraction determined by modified Kjeldahl procedure [77]. |
| **Hydrotreated Shale Oil**  
(Rifle, Colo., USA)  
- Nitrogen cmpds (neut. & basic) | 1) Distillate cuts of oil separately applied to basic alumina and elutions performed with hexane, dichloromethane/hexane and methanol eluents. 2) Each fraction is separately analysed by IR and those containing nitrogen compounds are rechromatographed on neutral alumina using hexane and chloroform eluents. 3) Fractions and subfractions with similar absorbances are combined [78]. |
| **Hydrotreated Shale Oil**  
(Julia Creek, Aust.)  
- Nitrogen cmpds (neut. & basic) | 1) Oil (in hexane) applied to o-phthalonitrile (OPN) HPLC phase and consecutively eluted with hexane, benzene/hexane and diethyl ether eluents which respectively recover aromatics (plus sulphur and oxygen heterocycles), neutral nitrogen compounds and basic nitrogen compounds [80]. |
| **Coal Tar**  
- Nitrogen cmpds (neut. & basic) | 1) Oil applied to o-phthalonitrile (OPN) HPLC phase and consecutively eluted with hexane, benzene/hexane and diethyl ether eluents which respectively recover aromatics (plus sulphur and oxygen heterocycles), neutral nitrogen compounds and basic nitrogen compounds [80]. |
| **Shale Oil**  
(Green River, Colo., USA)  
- Nitrogen and oxygen cmpds | 1) (a) Oil fraction with bp ≤ 200°C is extracted with aqueous NaOH to isolate acids which are further resolved into phenols and carboxylic acids (b) distillate extracted with aqueous H₂SO₄ to isolate bases. 2) Residual distillate chromatographed on a) Florisil to separate aromatic nitriles and (b) silica to separate dibenzo furans. 3) Pyrroles isolated from acid free oil by refluxing with solid KOH [81]. |

Table 2: cont'd...
<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
</table>
| **Hydrotreated Furnace Oil**  
- Nitrogen and oxygen cmpds | 1) Basic nitrogen compounds isolated from oil by aqueous HCl extraction. 2) Neutral nitrogen compounds isolated by LC on alumina with methanol eluent. 3) Indoles, carbazoles and phenazines separated from neutral nitrogen fraction as perchlorates; recovered by addition of water and extraction with benzene. 4) Oxygen heterocycles present in initial eluent from part 2 [82]. |
| **Shale Oil**  
(Green River, Colo., USA)  
- Nitrogen and oxygen compounds | 1) Oil applied to FeCl3/Attapulgus clay and elutions performed with (a) hexane, (b) dichloroethane and (c) ethanol/toluene/water eluents. 2) Fractions 1b and 1c applied to anion exchange resin to recover nitrogen compounds from iron (III) complexes. 3) Fraction 1b further resolved by extraction of basic compounds with aqueous HCl followed by LC on silica using chloroform/hexane and chloroform eluents. 4) Residue from part 1 applied to anion exchange resin and retained oxygen heterocycles are recovered with HCl/methanol [83]. |
| **Petroleum**  
- PAH | 1) Oil distilled and acids, bases and neutral nitrogen compounds are separated by LC on anion exchange, cation exchange and FeCl3/Attapulgus clay adsorbents, respectively. 2) Residual neutral compounds resolved into saturate and PAH fractions by LC on silica gel using pentane and methanol eluents. 3) PAH applied to alumina and elutions performed with (a) hexane and cyclohexane to recover monoaromatics (b) chloroform to recover di-and triaromatics and (c) methanol to recover residual PAH [84]. |
| **Shale Oil**  
- PAH | 1) Initial separation of PAH into 3-, 4-, 5- and 6-ring fractions by LC on alumina using hexane/diethyl ether eluate. 2) Each fraction further resolved on TLC plates (coated with acetylated cellulose) using methanol/water/acetic acid/acetone eluent. 3) After development, plates are air dried and compounds identified by fluorescence spectrophotometry [85]. |
| **Solvent Refined Coal**  
(Kent., USA)  
- PAH | 1) Solvent refined coal (in dichloromethane) extracted with aqueous NaOH and HCl to remove acids and bases, respectively. 2) Neutrals redissolved in benzene and extracted with (a) methanol/water to remove polar neutrals and (b) nitromethane to remove PAH - the initial benzene phase contains unextracted saturates. 3) Saturated hydrocarbons that co-extracted into fractions 2a and 2b are removed by LC on silica [86]. |
| **Shale Oil**  
(Green River, Colo., USA)  
- PAH | 1) Preparative scale separation of PAH into approximate ring number fractions by HPLC on silica using hexane eluent. 2) Further separations within each fraction by (a) normal phase HPLC on pyrrolidone phase with heptane eluent and (b) reverse phase HPLC on pyrrolidone and C18 phases using a methanol/water solvent gradient [87]. |
| **Petroleum**  
(Nigeria, Afr.)  
- PAH | 1) Arene complexes of standard PAH and those isolated from petroleum are separately prepared by reacting with ferrocene-AlCl3 mixture in decalin. 2) Complexes separately dissolved in acetone and developed on TLC silica plates with an acetone/ dichloromethane gradient. 3) Identifications by comparison of TLC retentions and mass spectra [88]. |
| **Solvent Refined Coal**  
- PAH | 1) Oil prefractionated by preparative HPLC on C18 phase with tetrahydrofuran / acetonitrile eluent. 2) PAH fraction purified by |
Table 2: cont’d...

<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum (Arabia) - PAH</td>
<td>HPLC on styrene - divinylbenzene phase with tetrahydrofuran eluent, and then fractionated on an analytical C18 HPLC phase using several acetonitrile/water gradients [89].</td>
</tr>
<tr>
<td></td>
<td>Three HPLC columns (silica, cyano and amino; hexane eluent) were separately evaluated for the separation of PAH. Fractions collected comprised aliphatics, mono-, di-, tri-, tetra- and pentaaromatics. The amino column gave best results although resolution between 1 and 2 ring aromatics was poor [90].</td>
</tr>
<tr>
<td>Solvent Refined Coal (Fort Lewis, USA) - PAH</td>
<td>1) Oil distillate (800-850°F) applied to alumina and eluted with hexane, benzene, chloroform and methanol eluents which recovered aliphatic hydrocarbons, neutral PAH, nitrogen PAH and hydroxyl PAH respectively. 2) Neutral PAH further resolved into 8 subfractions on a Supelcosil RP8-DB HPLC phase with methanol/water gradients [91].</td>
</tr>
<tr>
<td>Liquifled Coal - PAH</td>
<td>1) PAH separated from alkanes and polar compounds by LC on silica. 2) PAH fraction applied to neutral alumina and eluted with benzene/pentane (5/95), benzene/pentane (15/85) and dichloromethane which recovers monoaromatics, diaromatics and residual PAH i.e. ≥ 3 ring, respectively [92].</td>
</tr>
<tr>
<td>Solvent Refined Coal - PAH (5-9 ring)</td>
<td>1) PAH separated from alkanes by LC on alumina. 2) PAH fraction purified by HPLC on amino phase using hexane/dichloromethane eluent. 3) PAH fraction separated into 3 'molecular size' fractions by HPLC on C18 phase using acetonitrile/ethyl acetate, acetonitrile/water/ethyl acetate and acetonitrile/dichloromethane eluents. 4) Each subfraction further resolved on a C18 microcolumn using acetonitrile/water and acetonitrile/ethyl acetate eluents [93].</td>
</tr>
<tr>
<td>Petroleum, Shale Oil and Liquifled Coal - PAH</td>
<td>1) PAH separated from alkanes by LC on silica. 2) PAH applied to HPLC alumina column and elutions performed with hexane, dichloromethane/hexane (8/92), dichloromethane/hexane (16/84) and dichloromethane/hexane (40/60) eluents which respectively recover monoaromatics, diaromatics, triaromatics and ≥ 4 ring aromatics [94].</td>
</tr>
<tr>
<td>Shale Oil (Rifle, Colo., USA) - Sulphur heterocycles (thiophenes)</td>
<td>1) Oil extracted with aqueous acid and base to remove bases and acids. 2) Neutral oil distilled and distillate treated with AgNO₃ and Hg₃(ONO₂)₂ to remove interfering thiols and sulphides. 3) Aromatics and thiophenes collectively resolved from distillate by LC on Florisil. 4) Thiophenes separated from aromatics by reacting with Hg-(CH₃COO)₂ and then regenerated with dilute acid [95].</td>
</tr>
<tr>
<td>Liquifled Coal and Shale Oil - Sulphur heterocycles</td>
<td>1) Neutral PAH separated from the oil by LC on alumina. 2) Sulphur heterocycles oxidised to sulphones with H₂O₂ in benzene/acetic acid and the unoxidised PAH separated by LC on silica. 3) The sulphones regenerated with LiAlH₄ and resolved on silica gel [96].</td>
</tr>
<tr>
<td>Solvent Refined Coal - Sulphur heterocycles (hydroxy-thiophenes)</td>
<td>1) Hydroxy-aromatics separated from oil (bp 260-450°C) by LC on alumina using tetrahydrofuran/ethanol eluent. 2) Hydroxy-aromatics reacted with trimethylisilylimadazole and gas chromatographed on biphenyldimethylpolysilane and mesogenic polysiloxane phases. 3) Identifications by comparison of retention indices of standards and by GC-MS [97].</td>
</tr>
</tbody>
</table>
2.3 Procedures for the separation of many chemical classes

These methods (Table 3) are the least common in the literature and are usually based on one of the following:

(a) a preliminary isolation of acidic and basic compounds by either aqueous extraction or ion exchange chromatography (and sometimes complexation of the neutral nitrogen containing compounds with iron (III) chloride/Attapulgus clay) followed by a liquid chromatographic separation of the residual neutral compounds, or,

(b) direct liquid chromatographic separation of all the components of the fossil fuel, including the acids and bases.

The most commonly used adsorbents for LC separations, in order of decreasing use, have been silica, alumina/silica and alumina. Alumina has been mainly used with procedures in which aromatic class separations are emphasized. To date, HPLC bonded phases have not been used for the separation of many chemical classes. This is due to the inability of bonded phases to retain a broad range of chemical classes and their rapid degradation by polymeric materials and polar compounds such as acids and bases.

Other methods for chemical class separations include TLC on silica [115] and LC on Sephadex LH-20 [105]. No advantages are offered by either of these procedures and the separation obtained on Sephadex LH-20 would depend more on molecular size rather
than the type of functional group.

Despite the number of procedures that are available for the separation of many chemical classes, none can provide comprehensive separations without requiring sample pre-treatments, long analysis times or expensive reagents. In addition many procedures are restricted by (a) volatility losses (as in TLC methods and LC methods in which mobile phases of high boiling point are used), (b) solubility losses through the selection of solvents in which some shale oil components are insoluble (e.g. methanol) and (c) inadequate liquid chromatographic adsorbents (e.g. silica and C18 bonded phases, whose capacities for retention are affected by the type of alkyl substitution on the analytes).
### Table 3: Procedures for the separation of many chemical classes
(See page 26 for key to abbreviations)

<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
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</thead>
<tbody>
<tr>
<td><strong>Shale Oil</strong>&lt;br&gt;- Acids&lt;br&gt;- Bases&lt;br&gt;- Alkanes&lt;br&gt;- Alkenes&lt;br&gt;- Aromatics</td>
<td>1) Oil distillate (bp 280–305°C) extracted with aqueous NaOH and ( \text{H}_2\text{SO}_4 ) to isolate acids and bases, respectively. 2) Neutrals resolved by LC (silica; pentane and methanol gradients) into fractions comprising alkanes, alkenes and aromatics [98].</td>
</tr>
</tbody>
</table>

| **Shale Oil** (Colo., USA)<br>- Alkanes (n-, br. & cycl.)<br>- Alkenes (n-, br. & cycl.)<br>- Aromatics<br>- Nitrogen cmpds (neut. & basic) | 1) Oil distillate (bp 625–1100°F) applied to Florisil column and eluted with (a) pentane to recover hydrocarbons and (b) acetone to recover nitrogen containing compounds. 2) Pentane fraction resolved into basic and neutral nitrogen subfractions by molecular diffusion, Florex adsorption and molecular diffusion. 3) Hydrocarbons resolved into alkanes/alkenes and aromatics by LC on silica using eluents of pentane and acetone, respectively. 4) (a) Alkanes and alkenes resolved on silica using pentane and (b) branched and cyclic alkanes and alkenes separately resolved from linear alkanes and alkenes by urea adduction. 5) Aromatic fraction distilled into 11 subfractions each of which are further resolved into 11 more subfractions by LC on alumina using pentane and acetone gradients [99]. |

| **Shale Oil** (Rifle, Colo., USA)<br>- Acids (phenolic and carboxylic)<br>- Bases<br>- Alkanes<br>- Alkenes<br>- Nitriles<br>- Ketones | 1) Oil distillate (bp 280–305°C) extracted with (a) aqueous KOH to remove acids which are further resolved into phenols and carboxylic acids and (b) aqueous \( \text{H}_2\text{SO}_4 \) to isolate bases. 2) Neutral distillate adducted with urea to provide linear and branched/cyclic subfractions. 3) Linear neutrals separated into alkane/alkene and nitrile/ketone fractions by LC on silica using hexane and hexane/benzene eluents, respectively. 4) Alkanes and alkenes resolved on \( \text{AgNO}_3 \)/silica using benzene/hexane eluent. 5) Nitriles and ketones resolved by (a) converting ketones to alcohols with \( \text{NaBH}_4 \) (b) separating nitriles from alcohols by LC on silica and (c) oxidising alcohols back to ketones using \( \text{CrO}_3 \) [100]. |

| **Petroleum** (Wyo. & Calif., USA)<br>- Acids<br>- Bases<br>- Alkanes<br>- Monoaromatics<br>- Diaromatics<br>- PAH/polars | 1) Acids and bases isolated from oil distillate (bp 330–540°C) with anion exchange and cation exchange resins, respectively. 2) Neutral nitrogen compounds separated from distillate by complexation with iron (III) chloride. 3) Neutral distillate applied to dual silica-alumina column and eluted with (a) pentane to recover alkanes, (b) benzene/pentane (5/95) to recover monoaromatics, (c) benzene/pentane (15/85) to recover diaromatics and (d) methanol/diethyl ether/benzene to recover PAH and polars [101]. |

| **Liquified Coal, Bitumen and Shale Oil**<br>- Alkanes (n-, br. & cycl.)<br>- Monoaromatics<br>- Di-, triaromatics<br>- Polyaromatics<br>- Polars<br>- Asphaltenes (benzene sol. and benzene insol.) | 1) Oil distillate resolved into alkanes, aromatics, resins and asphaltenes by SARA technique. 2) Asphaltenes partitioned into benzene soluble and insoluble fractions. 3) Alkanes and aromatic fractions further resolved into alkane, mono-, di- and triaromatic, polyaromatic and polar fractions by LC on silica using hexane, cyclohexane, chloroform and methanol eluents, respectively. 4) Alkanes resolved into linear and branched and cyclic fractions by 5 Å sieve reflux [102]. |

| **Petroleum**<br>- Alkanes<br>- Monoaromatics | Deasphalted oil (in pentane) separated into alkanes, monoaromatics, diaromatics PAH (2 ring), polars and bases by LC on a silica/alumina column using pentane, benzene/pentane (5/95), benzene/ |
Table 3: cont’d...

<table>
<thead>
<tr>
<th>Source material and chemical class(es) resolved</th>
<th>Analytical procedure [author(s) reference number]</th>
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</thead>
<tbody>
<tr>
<td>- Diaromatics</td>
<td>pentane (15/85), benzene, methanol / benzene / diethyl ether (60/20/20), methanol and pyridine eluents [103].</td>
</tr>
<tr>
<td>- Polyaromatics (≥2 ring)</td>
<td>Solvent refined coal separated into 9 fractions by LC on silica. The eluate fractions listed in order of number, eluate and chemical class resolved were as follows: 1) hexane, alkanes; 2) benzene/hexane (15/85), aromatics; 3) chloroform, polar PAH and nitrogen, oxygen and sulphur heterocycles; 4) diethyl ether/chloroform (10/90), phenols and pyrrolic compounds; 5) ethanol/diethyl ether (3/97), basic heterocycles and diphenols; 6) methanol, polyfunctional compounds; 7) ethanol/chloroform (3/97), polyphenols; 8) ethanol/tetrahydrofuran (3/97), highly basic and acidic compounds and 9) ethanol/pyridine (3/97), polymeric material [104].</td>
</tr>
<tr>
<td>- Polars</td>
<td>Separations are performed on Sephadex LH-20 gel which is used in three modes. 1) Gel is swollen with water/methanol (15/85) and eluted with hexane; this separates the oil into lipophilic and hydrophilic fractions. 2) Gel is swollen with tetrahydrofuran and eluted with tetrahydrofuran; the lipophilic fraction is further resolved into polymeric (1) “sieved” and hydrogen bonded compound fractions. 3) Gel is swollen with isopropanol and eluted with isopropanol; the sieved fraction is resolved into polymeric (2), alkanes, mono- and diaromatics and polynuclear material [105].</td>
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<tr>
<td>- Bases</td>
<td>The oil is applied to alumina and the following eluate fractions which are listed in order of number, eluate and chemical class resolved are collected: 1) hexane, alkanes; 2) toluene, aromatics and benzo(furan) heterocycles; 3) (a) chloroform, ethers and (b) chloroform, nitrogen compounds; 4) ethanol/tetrahydrofuran (10/90), hydroxy compounds [106].</td>
</tr>
<tr>
<td>- Alkanes</td>
<td>1) Acids and bases separated from bitumen by anion and cation exchange chromatography, respectively. 2) Neutral nitrogen compounds isolated by complexation with FeCl₃/Attapulgus clay; recovered with 1,2-dichloroethane. 3) Neutrals applied to silica and eluted with (a) pentane, (b) chloroform and (c) methanol. 4) Fraction 3a applied to alumina and eluted with (a) pentane and (b) methanol. 5) Fractions 3b, 3c and 4b are combined and resolved into fractions comprising alkenes, monoaromatics, diaromatics, PAH and polar solvents by LC on alumina using pentane (combined with fraction 4a ), benzene/pentane (5/95), benzene/pentane (15/85), methanol/benzene/diethyl ether (1/1/3) and methanol eluents, respectively. 6) Alkanes resolved from alkenes by LC on AgNO₃/silica. 7) Branched/cyclic alkanes and alkenes resolved from linear alkanes and alkenes by urea adduction [107].</td>
</tr>
<tr>
<td>- Monoaromatics</td>
<td>Oil separated into 6 fractions by LC on basic alumina. The eluate fractions listed in order of number, eluent and chemical class resolved were as follows: 1) heptane, alkanes; 2) benzene/heptane (4/96), monoaromatics; 3) benzene/heptane (15/85), diaromatics;</td>
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<td>Source material and chemical class(es) resolved</td>
<td>Analytical procedure (author(s) reference number)</td>
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<tr>
<td><strong>- Diaromatics</strong></td>
<td>4) ethanol/tetrahydrofuran (1/99), PAH and nitrogen and oxygen heterocycles; 5) ethanol / tetrahydrofuran (5/95), bases; 6) tetrahydrofuran, phenols and polyfunctional compounds [108].</td>
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<tr>
<td><strong>- PAH (plus N and O heterocycles)</strong></td>
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<tr>
<td><strong>- Bases</strong></td>
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<tr>
<td><strong>- Phenols/polyfunctional cmpds</strong></td>
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<tr>
<td><strong>Solvent Refined Coal</strong></td>
<td><strong>1)</strong> Oil separated into fractions comprising alkanes, neutral PAH, nitrogen PAH and hydroxy PAH by LC on silica using hexane, benzene, chloroform and ethanol/tetrahydrofuran (10/90) eluents, respectively. 2) The neutral PAH fraction is further resolved into PAH, hydroxyl-PAH and sulphur PAH by (a) oxidising the sulphur-PAH to sulphones with H₂O₂, (b) rechromatographing the mixture on silica and (c) regenerating the sulphur PAH by reduction with LiAlH₄. 3) The nitrogen PAH fraction is further separated into secondary nitrogen PAH, amino PAH and tertiary nitrogen PAH by LC on silica using benzene/hexane (1/1), benzene and benzene/diethyl ether (1/1) eluents, respectively [109].</td>
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<tr>
<td>(West Virg., USA)</td>
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<tr>
<td><strong>- Alkanes</strong></td>
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<tr>
<td><strong>- PAH</strong></td>
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<tr>
<td><strong>- Sulphur-PAH</strong></td>
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<td><strong>- Hydroxy-PAH</strong></td>
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<td><strong>- Neut. nitrogen PAH</strong></td>
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<td><strong>- Amino-PAH</strong></td>
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<tr>
<td><strong>- Tert. nitrogen-PAH</strong></td>
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<tr>
<td><strong>Petroleum</strong></td>
<td><strong>1)</strong> Acids and bases separated by anion and cation exchange chromatography, respectively. 2) Neutral nitrogen compounds isolated by FeCl₃/Attapulgus clay complexation and recovered by 1,2-dichloroethane desorption from an anion exchange resin. 3) Neutral distillate separated into alkanes and aromatics by LC on silica using pentane and benzene/methanol (2/3) eluents, respectively [110].</td>
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<tr>
<td>(Atl., Calif., Wyo.; USA and Iran)</td>
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<tr>
<td><strong>- Acids</strong></td>
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<tr>
<td><strong>- Bases</strong></td>
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<tr>
<td><strong>- Neut. nitrogen cmpds</strong></td>
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<tr>
<td><strong>- Alkanes</strong></td>
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<td><strong>- Aromatics</strong></td>
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<tr>
<td><strong>Solvent Refined Coal</strong></td>
<td>Oil separated by LC on a column series comprising a Fluoropak column and four basic alumina columns. Four fractions eluted from the Fluoropak column (eluents: hexane, toluene, chloroform and pyridine), with each separately flowing onto one of the four basic alumina columns for further separation. Column 1 is eluted with hexane, toluene, chloroform and pyridine. Column 2 is eluted with toluene, chloroform and backflushed with methanol/chloroform (1/4). Column 3 is eluted with chloroform and backflushed with methanol/chloroform (1/4). Column 4 is eluted with pyridine. Each of the fractions from the four basic alumina columns is then examined for functional group type content by IR and those having similar absorbances are combined [111].</td>
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<tr>
<td>(Wyo., USA)</td>
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<tr>
<td><strong>- Alkanes</strong></td>
<td></td>
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<tr>
<td><strong>- Nitrogen heterocycles</strong></td>
<td></td>
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<tr>
<td><strong>- Hydroxy aromatics</strong></td>
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<tr>
<td><strong>- Polyfunctional cmpds</strong></td>
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<tr>
<td><strong>Liquified Coal</strong></td>
<td>Two procedures: 1) (a) Acids and bases isolated from oil by extraction with aqueous NaOH and HCl, respectively. (b) Aromatics separated from the neutral oil by dimethyl sulfoxide extraction; recovered by adding water to extracts, saturating the aqueous phase with KCl and back-extracting with pentane and dichloromethane. (c) The remaining neutral oil contains hydrocarbons. 2) Separation into functional group type fractions by LC on silica using pentane, benzene/pentane (5/95), benzene/pentane (15/85) and methanol/benzene/diethyl ether (3/1/1) eluents [112].</td>
</tr>
<tr>
<td><strong>- Acids</strong></td>
<td></td>
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<td><strong>- Bases</strong></td>
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<tr>
<td><strong>- Hydrocarbons</strong></td>
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<td><strong>- Aromatics</strong></td>
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<tr>
<td><strong>Shale Oil</strong></td>
<td>1) Oil extracted with aqueous NaOH and H₂SO₄ to isolate acids and bases, respectively. 2) Neutral oil applied to an alumina/silica column and the following eluate fractions, which are listed in order of number, eluent and chemical class resolved are collected: (1) hexane</td>
</tr>
<tr>
<td>(Rundle, Aust.)</td>
<td></td>
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<tr>
<td><strong>- Acids</strong></td>
<td></td>
</tr>
<tr>
<td><strong>- Bases</strong></td>
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<tr>
<td>Source material and chemical class(es) resolved</td>
<td>Analytical procedure [author(s) reference number]</td>
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<td>-----------------------------------------------</td>
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<tr>
<td><strong>Hydrotreated Coal Liquid</strong></td>
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<tr>
<td>- Alkanes</td>
<td></td>
</tr>
<tr>
<td>- Hydroaromatics</td>
<td></td>
</tr>
<tr>
<td>- PAH</td>
<td></td>
</tr>
<tr>
<td>- Nitrogen-PAH</td>
<td></td>
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<tr>
<td></td>
<td>Oil applied to a picric acid coated alumina column and resolved into separate fractions comprising aliphatic hydrocarbons, hydroaromatics, PAH and nitrogen polycyclic hydrocarbons using hexane, dichloromethane/hexane (3/97), dichloromethane/hexane (15/85) and benzene eluents, respectively [114].</td>
</tr>
</tbody>
</table>

| **Shale Oil (Rundle, Aust.)**                 |                                               |
| - Alkanes                                      |                                               |
| - Alkenes                                      |                                               |
| - Monoaromatics                                |                                               |
| - Hydroaromatics                               |                                               |
| - Diaromatics                                  |                                               |
| - PAH                                          |                                               |
| - Nitriles and ketones                         |                                               |
| - Phenols                                      |                                               |
| - Nitrogen heterocycles                        |                                               |
| | 1) Oil adsorbed onto two separate silica coated TLC plates and developed with pentane and pentane/diethyl ether solvents, respectively. 2) Following separation, bands are developed by spraying plates with dichlorofluorescein solution. 3) Bands are separately scraped from plates and adsorbed material recovered by washing the silica with either dichloromethane or dichloromethane/methanol (1/1); the latter is used for polar compound recovery [115]. |

| **Solvent Refined Coal**                      |                                               |
| - Alkanes                                      |                                               |
| - 3 double bond cmpds                          |                                               |
| - 5 double bond cmpds                          |                                               |
| - 6 double bond cmpds                          |                                               |
| - 7 double bond cmpds                          |                                               |
| - 8 double bond cmpds                          |                                               |
| - > 9 double bond cmpds                        |                                               |
| - Nitrogen cmpds                               |                                               |
| - Hydroxy aromatics                            |                                               |
| | 1) Oil initially resolved into hydrocarbon, nitrogen compound and hydroxy aromatic compound fractions by the Fluoropak-basic alumina column combination previously outlined [111]. 2) Hydrocarbon fraction, further resolved into separate fractions comprising alkanes, 3 double bond (3db), 5db, 6db, 7db, 8db and 2 9db compounds by HPLC on a microanalytical amino phase using a heptane mobile phase [116]. |

| **Shale Oil (Israel)**                        |                                               |
| - Asphaltols                                   |                                               |
| - Asphaltenes                                  |                                               |
| - Alkanes (n-, br. & cycl.)                    |                                               |
| - Aromatics                                    |                                               |
| - Polars (2 fractions)                         |                                               |
| | 1) Oil dissolved in benzene, and asphaltols (insoluble residue) are isolated by filtration. 2) Benzene extracts evaporated and redissolved in pentane to isolate asphaltenes (i.e. pentane insolubles). 3) Asphaltenes further separated into aromatic, polar and high MWt polymeric fractions by LC on silica using benzene, methanol and tetrahydrofuran eluents, respectively. 4) Pentane soluble material separated into alkanes, aromatics and polars by LC on silica using pentane, benzene and methanol eluents, respectively. 5) Alkanes separated into linear components and branched and cyclic components by urea adduction [117]. |
3. Analysis of Shale Oil by Open Column Chromatography

3.1 Assessment of existing open column separation schemes

While a number of open column chromatography schemes have been developed for the fractionation of shale oils (see section 2.3), only that of Regtop et al. [113] allowed a detailed chemical class separation. In this method a combination of acidic extraction, basic extraction and liquid chromatography on alumina overlying silica, separated shale oil into fractions containing phenols, pyridines, alkanes, alkenes, bicyclic aromatics, alkanonitriles, 2-alkanones and alkanamides (Figure 3). The method has a number of deficiencies, however, which were revealed in a series of initial experiments:

1. Shale oils partially polymerised when extracted with aqueous acid or base. Some of the polymeric artefacts so formed were water soluble and contaminated the fractions containing phenols and pyridines. Other artefacts remained in the organic (neutral shale oil) phase and subsequently coeluted with the neutrals that were recovered with solvents of eluotropic strengths equal to or greater than dichloromethane.

2. The water soluble neutrals in shale oil were extracted with the phenols and pyridines thereby further contaminating these
Figure 3: Outline of the open column separation scheme of Regtop et al. [113].
fractions.

3. The volume (150 mL) and concentration (3 M) of the aqueous acid and base used for the extraction of pyridines and phenols were excessively large (sufficient to extract ≈70g of either acid or base while the amount present would be typically less than 0.15 g). The excess acid and base not only encouraged the formation of artefacts but also made it difficult to recover hydrophilic compounds by back-extraction.

4. Many of the chemical classes eluted from the open column were not fully resolved. This appeared to be the result of inappropriate solvent selectivities and, the assignment of inaccurate elution volumes to those chemical classes which were resolved by isocratic elution.

5. During open column chromatography, both the adsorbent and the shale oil sample darkened. This suggested that photochemical reactions and reactions catalysed by the adsorbent surface were resulting in the formation of other polymeric artefacts. These artefacts were subsequently desorbed with the more polar solvents of the eluotropic sequence and contaminated the later neutral subfractions e.g those containing the n-alkanondinitriles and the 2-alkanones.

Other problems which are encountered with chromatographic
procedures that use conventional adsorbents are discussed in sections 5.1 and 5.2.

3.2 Development of a new open column separation scheme

The following modifications were made to the open column chromatography method of Regtop et al. [113] in order to obtain the new scheme shown in Figure 4:

3.2.1 Acidic and basic extractions

Both the aqueous acidic and basic extracts were:

i) saturated with a salt such as sodium chloride, prior to neutralisation, in order to decrease the solubility of organics in the aqueous phase and thereby improve extraction efficiencies,

ii) extracted with dichloromethane, prior to neutralisation, in order to remove contaminating neutrals and polymeric artefacts from the pyridines and phenols and so obtain purer acid and base fractions,

iii) reduced in volume to a size (6 mL) which was more appropriate to the amounts of pyridines and phenols being extracted and which allowed hydrophilic acids and bases to be recovered more efficiently by back-extraction, and

iv) back-extracted with smaller volumes of organic solvent (4-5 mL) to minimise evaporative losses.
Figure 4: Outline of the new open column separation scheme (section 3.3.2).
The aqueous basic extracts were also adjusted to two different pH's during neutralisation to allow separation of phenols from carboxylic acids. Phenols, which are only very weakly acidic, are protonated at pH 10 and can be separately collected by solvent extraction. The carboxylic acids which remain deprotonated at this pH are subsequently recovered by adjusting the aqueous extract to pH 1 and performing another solvent extraction.

In addition, it was found that polymeric artefacts could be excluded from the aqueous acidic extracts by washing with n-pentane rather than dichloromethane.

3.2.2 Open column chromatography of neutrals

The solvents that were used for long isocratic elutions (e.g. hexane (1380 mL) and chloroform (1000 mL), were reduced in volume (to 600 mL and 250 mL respectively) and small volumes of new gradients with greater eluotropic strength and better selectivities (e.g. hexane/dichloromethane (9:1) and dichloromethane/chloroform (9:1)) were added. A larger number of hexane subfractions was also collected in order to separate the many non-polar chemical classes which were eluting. Other solvents which eluted several chemical classes were either totally replaced or preceded by new gradients of lower eluotropic strength to improve resolution. When combined, these alterations gave rise
to a completely new solvent program which comprised a finer gradation of eluents of increasing eluotropic strength (see Figure 4).

3.2.3 Derivatisation of shale oil acids and bases

In order to, i) avoid adsorptive losses of highly polar shale oil acids and bases during gas chromatography and ii) prevent the rapid degradation of conventional GC columns through repeated use, it was essential that the acids and bases be derivatised. Columns with specially modified phases to accommodate highly polar compounds, e.g. the free fatty acid phase, often had high phase chromatographic bleed and gave poorer resolution, making their use less attractive.

The phenols were converted to either n-butyl or trimethylsilyl ethers. The trimethylsilyl ethers were resolved slightly better than the n-butyl ethers but the latter were less volatile and could be concentrated with less loss during solvent evaporation. The carboxylic acids were converted to either the methyl or n-butyl esters depending on the range of acids in the sample. Shale oil carboxylic acids, which were of much longer alkyl chain length (and therefore less volatile) than those separated from retort water, were better separated by gas chromatography as the methyl esters rather than as the n-butyl esters. To avoid evaporative losses, the retort water acids were converted to their n-butyl esters.
The shale oil base fraction, which comprised mainly pyridines, quinolines, dihydro- and tetrahydroquinolines, was reacted with a trimethylsilyl reagent. While the pyridines and quinolines were not derivatised, many of the heterocycles in the base fraction were, and this still resulted in an overall improvement in gas chromatographic resolution.

3.3 Experimental

3.3.1 Samples

Three different shale oils were separated by the new procedure and these were obtained as follows:

1. Fischer assay oil from the Condor Brown Unit (p. 11).

   The oil shale sample was taken from the 416-418 m section of core CDD27 (Southern Pacific Petroleum N.L., personal communication) which was drilled beside the Bruce Highway at 668000 E 7732800 N. The sample was crushed to 1.0-2.5 mm, air dried and retorted by means of a modified Fischer assay method [41]. The shale oil was separated from the retort water by centrifugation and chemically fractionated within 24 h of preparation.

2. Nitrogen-pyrolysis oil from the Condor Brown Unit.

   Oil shale, obtained as in 1. was sieved and the 1.0-2.5 mm
fraction was pyrolysed under a nitrogen carrier gas stream in an apparatus similar to that described by Huss and Burnham [118]. The resulting shale oil was separated within 24 h of preparation.

3. Nitrogen-pyrolysis oil from the Condor Carbonaceous Unit.

The oil shale sample was taken from the Condor Carbonaceous Unit (bulk sample; Southern Pacific Petroleum N.L., personal communication). Shale oil was prepared from this sample by the same procedure as that given in 2.

3.3.2 The new procedure

1. Analysis of the Condor Brown Unit (Fischer assay) shale oil:

Shale oil (2.5 g) was dissolved in hexane (20 mL) and the suspension was centrifuged at 4000 rpm for 10 min. The supernatant was separated and the insoluble residue (asphaltenes) was washed with hexane (3 x 1 mL), dried at room temperature and weighed. The hexane washings were combined with the supernatant.

Acids and bases:

The supernatant was extracted with 3 M sodium hydroxide (3 x 2 mL) and the hexane phase retained. The aqueous extracts were combined, saturated with sodium chloride and extracted with dichloromethane (3 x 1.5 mL). The dichloromethane extracts (containing traces of water-soluble neutrals and bases) were dried with anhydrous magnesium sulphate. The aqueous extracts were
neutralized with 12 M sulphuric acid, saturated with sodium bicarbonate and then extracted with dichloromethane (3 x 1.5 mL). The dichloromethane extracts (containing phenols) were dried with anhydrous magnesium sulphate. The aqueous phase was acidified to pH < 1 with 12 M sulphuric acid and extracted with dichloromethane (3 x 1.5 mL). The dichloromethane extracts (containing carboxylic acids) were dried with anhydrous magnesium sulphate and the aqueous phase discarded.

The hexane phase was extracted with 3 M sulphuric acid (3 x 2 mL) and the extracts combined. The aqueous extracts were saturated with sodium chloride and extracted with dichloromethane (3 x 1.5 mL) to remove traces of water-soluble neutrals. The dichloromethane extracts were dried with anhydrous magnesium sulphate. The aqueous extracts were basified (pH > 10) and extracted with pentane (3 x 1.5 mL) to exclude polymeric material which would interfere with column chromatography. The pentane extracts (containing bases) were dried with anhydrous magnesium sulphate and the aqueous phase discarded.

**Neutrals:**

Following removal of the acids and bases the hexane phase was dried with anhydrous magnesium sulphate and evaporated under dry nitrogen gas to ~5 mL. The solution was applied to a combined
column of silica (58 g; Merck Kieselgel 60, mesh 70-230, preheated for 12 h at 130° C) underlying alumina (23 g; neutral, activity 1, preheated for 12 h at 300° C) slurry packed in hexane. Solvents of increasing polarity were used to elute the shale oil components and the eluate fractions were evaporated initially with a rotary evaporator (30 C, 4.7 kPa) and finally under dry nitrogen gas to the appropriate concentration (100-500 µL) for gas chromatographic (GC) analysis. For quantitation, each concentrate was evaporated further under dry nitrogen gas and the sample weight recorded as soon as an abrupt change was detected in a plot of weight loss versus time. To check for contamination, 100 mL aliquots of each of the solvents used were evaporated to 100 µL on a rotary evaporator and the residue examined by GC. As a further precaution, a blank silica/alumina column was stripped with the same solvent sequence used for chromatography to confirm that the adsorbents did not contain organic contaminants.

The eluate fraction listed in order of number, eluant and volume were: 0; hexane, 0-95 mL; 1: hexane, 95-130 mL; 2: hexane, 130-140 mL; 3: hexane, 140-175 mL; 4: hexane 175-215 mL; 5: hexane, 215-315 mL; 6: hexane, 315-400 mL; 7: hexane, 400-450 mL; 8: hexane, 450-500 mL; 9: hexane, 500-600 mL; 10: hexane/dichloromethane (9:1, v/v), 0-150 mL; 11: hexane/dichloromethane
(9:1, v/v), 150-250 mL; 12: hexane/dichloromethane (4:1, v/v), 0-150 mL; 13: hexane/dichloromethane (4:1, v/v), 150-250 mL; 14: dichloromethane, 250 mL; 15: dichloromethane/chloroform (9:1, v/v), 250 mL; 16: chloroform/ether (9:1, v/v), 0-150 mL; 17: chloroform/ether (9:1, v/v), 150-250 mL; 18: ether, 250 mL; 19: methanol, 250 mL.

Fraction 0, representing the void volume of the column, was discarded; whenever eluent was changed, the void volume was taken into account in collecting the eluate fractions. Polymeric material produced on the column was removed prior to GC analysis from fractions consisting of solvent other than hexane by redissolving the evaporated sample in hexane and centrifuging.

Aliquots of fractions 2 and 3 (corresponding to ≈50-100 mg), which contained the alkanes and alkenes respectively, were separately redissolved in cyclohexane (5 mL). Molecular sieve (2.0 g, 0.5 nm; preheated at 300°C for 5 h) was added and the solutions were refluxed at 60°C for 6 h. The molecular sieve was removed by filtration and the filtrate (containing branched and cyclic material) was evaporated to the appropriate concentration (≈50 μL) for GC analysis.

2. Analysis of the nitrogen-pyrolysis oil from the Condor Brown Unit.
The procedure used for the separation of this shale oil was identical to that of the Fischer assay oil except for several refinements to the solvent program. The eluate fractions, listed in order of number, eluent and volume were as follows:

0: hexane, 0-95 mL; 1: hexane, 95-130 mL; 2: hexane, 130-140 mL; 3: hexane, 140-175 mL; 4: hexane, 175-215 mL; 5: hexane, 215-315 mL; 6: hexane, 315-380 mL; 7: hexane, 380-430 mL; 8: hexane, 430-510 mL; 9: hexane, 510-595 mL; 10: hexane/dichloromethane (9:1, v/v), 0-85 mL; 11: hexane/dichloromethane (9:1, v/v), 85-165 mL; 12: hexane/dichloromethane (9:1, v/v), 165-255 mL; 13: hexane/dichloromethane (4:1, v/v), 250 mL; 13B: hexane/dichloromethane (7:3, v/v), 200 mL; 14: dichloromethane, 250 mL; 15: dichloromethane/chloroform (9:1, v/v), 250 mL; 16, 17: chloroform/ether (4:1, v/v), 250 mL; 18: ether, 250 mL; 19: methanol, 250 mL.

Two dark bands eluted in fractions 16 and 17 and were collected separately.

3. Analysis of the nitrogen-pyrolysis oil from the Condor Carbonaceous Unit.

The procedure used for the separation of the carbonaceous shale oil was identical to that described in 2.

3.3.3 Instrumental analysis
*Helium was used as carrier gas at a flow rate of 2 mL min\(^{-1}\). Gas chromatograms were recorded using a chart speed of 0.5 cm min\(^{-1}\). The gas chromatograms shown in this thesis are photo-reductions (\(x 0.33\)) of originals. Therefore a loss of chromatographic resolution may be apparent in some figures.
GC analyses were performed on a Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector. Separations were achieved with a 25 m x 0.2 mm i.d. WCOT vitreous silica SE-54 column which was programmed from 50 to 280°C at 4°C min^{-1} (isothermal at 280°C for 10 min). The inlet splitter was set at 20:1 and the pressure drop across the column was 55 kPa.

Gas chromatographic-mass spectrometric (GC-MS) analyses of the branched and cyclic alkanes and alkenes were performed on a Varian Model 2700 chromatograph interfaced via an open split coupling to a Varian MAT 44 quadrupole mass spectrometer, and operated in the electron impact mode at 70 electron-volts. The gas chromatograph was fitted with an S.G.E. bonded phase wide bore (0.33 mm i.d.) vitreous silica column coated with SE-54 and an identical temperature program was employed. All other GC-MS data were gathered using the instrumentation and conditions described previously [113].

3.4 Results

The percentage elemental composition of the Fischer assay oil from the Condor Brown Unit was; C, 84.8; H, 12.5; N, 1.0; O, 1.9; S, 0.4 wt % (Analytische Laboratorien, Germany). Gravimetric results for the fractions separated from the Fischer assay oil from the
Condor Brown Unit, the nitrogen-pyrolysis oil from the Condor Brown Unit and the nitrogen-pyrolysis oil from the Condor Carbonaceous Unit, by the procedure outlined in 3.3.2, are given in Table 4. The compounds identified in each of the three oils are listed in Table 5 according to functional group type. Other features of the chemical compositions of the three oils are discussed in 8.1.2 and 8.2.1.

Gas chromatograms of the acid, base, alkane, alkene, diene, \( n \)-alkylmonoaromatic, bi- and tricyclic aromatic, \( n \)-alkanonitrile, 2-alkanone and 1-(cycloalk-1-enyl)-2-alkanone fractions of the Fischer assay oil from the Condor Brown Unit are given in Figures 5-15, respectively. Gas chromatograms of selected fractions of the nitrogen-pyrolysis oils from the Condor Brown and Carbonaceous Units are given in Appendix 1.
Table 4: Gravimetric results (wt%) for shale oils from the Condor Brown Unit (Fischer assay), Condor Brown Unit (nitrogen-pyrolysis) and the Condor Carbonaceous Unit (nitrogen-pyrolysis).

<table>
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<th>Fraction</th>
<th>Fischer assay</th>
<th>Pyrolysis under nitrogen</th>
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</thead>
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<td>Condor Brown</td>
</tr>
<tr>
<td>1</td>
<td>25.4</td>
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<td>2</td>
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<td>13</td>
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<td>Total</td>
<td>96.2</td>
<td>94.6</td>
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a See 3.3.2 for eluents and eluate volumes.
b Obtained with a modified solvent program (see 3.3.2).
Table 5: Chemical classes identified in the shale oils from the Condor Brown Unit (Fischer assay), Condor Brown Unit (nitrogen-pyrolysis) and Condor Carbonaceous Unit (nitrogen-pyrolysis).

<table>
<thead>
<tr>
<th>Chemical Class</th>
<th>Fraction</th>
<th>Range of alkyl substitution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fischer assay</th>
<th>Pyrolysis under nitrogen</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Condor Brown</td>
<td>Condor Brown</td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>1,2</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;33&lt;/sub&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;33&lt;/sub&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;33&lt;/sub&gt;</td>
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<td>2-Methylalkanes</td>
<td>1,2</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;32&lt;/sub&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;32&lt;/sub&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;32&lt;/sub&gt;</td>
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<td>Cyclopentanes</td>
<td>1,2</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;26&lt;/sub&gt;</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;24&lt;/sub&gt;</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;24&lt;/sub&gt;</td>
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<td>Cyclohexanes</td>
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<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;24&lt;/sub&gt;</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;24&lt;/sub&gt;</td>
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<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;33&lt;/sub&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;33&lt;/sub&gt;</td>
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<td>C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;18&lt;/sub&gt;</td>
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<td>Xylenes</td>
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<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;19&lt;/sub&gt;</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;17&lt;/sub&gt;</td>
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<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>5</td>
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<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;</td>
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Table 5: cont’d...

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<th>Chemical Class</th>
<th>Fraction</th>
<th>Range of alkyl substitution&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fischer assay</th>
<th>Pyrolysis under nitrogen</th>
<th>Condor Brown</th>
<th>Condor Brown</th>
<th>Condor Carbonaceous</th>
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<td>Pyrenes</td>
<td>11,12</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Binaphthyls</td>
<td>12</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>-</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylfluorenes</td>
<td>11,12</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>Benzophenanthrenes</td>
<td>12</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
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<tr>
<td>Benzopyrenes</td>
<td>12</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td></td>
<td></td>
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<tr>
<td>Indoles</td>
<td>138&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>Carbazoles</td>
<td>138&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td></td>
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<tr>
<td>n-Alkanonitriles</td>
<td>14</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;31&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;31&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;31&lt;/sub&gt;</td>
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<tr>
<td>2-Alkanones</td>
<td>15</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;31&lt;/sub&gt;</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;-C&lt;sub&gt;21&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;26&lt;/sub&gt;</td>
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<td>3-Alkanones</td>
<td>15</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;16&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
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<tr>
<td>1-(Cyclopent-1-enyl)</td>
<td>16,17</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>-2-alkanes</td>
<td>16,17</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;22&lt;/sub&gt;</td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>-</td>
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<tr>
<td>Indanones</td>
<td>16,17</td>
<td>-</td>
<td>-</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>Tetralones</td>
<td>16,17</td>
<td>-</td>
<td>-</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>Phenols</td>
<td>acid fr.</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
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<tr>
<td>Pyridines</td>
<td>base fr.</td>
<td>i) C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
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<tr>
<td>Dihydroindoles</td>
<td>base fr.</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
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<tr>
<td>Tetrahydro-quinolines</td>
<td>base fr.</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quinolines</td>
<td>base fr.</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;</td>
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<sup>a</sup> Alkyl substitution comprised either a number of small alkyl groups (e.g., methyl, ethyl) or a single n-alkyl chain. These types of substitution are indicated by i) and ii), respectively, and the total number of substituent carbon atoms is given.

<sup>b</sup> Obtained with a modified solvent program (see 3.3.2).

<sup>c</sup> Compounds were identified by comparison of the GC retention indices of standard compounds and literature mass spectra.
Figure 5: Gas chromatogram of the acid fraction from the Condor Brown Unit (Fischer assay) shale oil. Peaks labelled C0 P,...,C4 P are alkyl substituted phenols which have a total number of substituent carbon atoms equal to the labelling number.

Figure 6: Gas chromatogram of the base fraction from the Condor Brown Unit (Fischer assay) shale oil. Peaks labelled C1 P,...,C5 P and C0 Q,...,C4 Q are respectively, alkyl substituted pyridines and quinolines which have a total number of substituent carbon atoms equal to the labelling number.
Figure 7: Gas chromatogram of fraction 1 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are linear alkanes of chain length equal to the labelling number. Peaks labelled I-VII are respectively, 2,6-dimethylundecane, 2,6,10-trimethylundecane, 2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane, 2,6,10-trimethylpentadecane, pristane and phytane.

Figure 8: Gas chromatogram of fraction 3 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are linear 1-alkenes of chain length equal to the labelling number. Peaks labelled I, II, III, IIIa and IV are respectively, 1-alkenes, 2-alkenes, 3-alkenes, 3- or 4-methyl-3-alkenes and 4-alkenes. Peaks lettered a, b, c and d are respectively, 2,6,10-trimethylundecene, 2,6,10-trimethyltridecene, 1-pristene and 2-pristene.
Figure 9: Gas chromatogram of fraction 4 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are linear dienes of chain length equal to the labelling number. Peaks labelled a, b and c are respectively, series a, b and c referred to in section 3.5 and chapter 7.

Figure 10: Gas chromatogram of fraction 5 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are n-alkylbenzenes which have an alkyl chain length equal to the labelling number. Peaks labelled I-IV are respectively, n-alkyltoluenes (2 isomers), n-alkylxylene, n-alkyltrimethylbenzenes and n-alkylindans.
Figure 11: Gas chromatogram of fraction 9 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Peaks labelled C0 N,...C5 N are alkyl substituted naphthalenes which have a total number of substituent carbon atoms equal to the labelling number.

Figure 12: Gas chromatogram of fraction 10 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Peaks labelled C1 N,...C6 N are alkyl substituted naphthalenes which have a total number of substituent carbon atoms equal to the labelling number.
Figure 13: Gas chromatogram of fraction 14 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are n-alkanenitriles of carbon chain length equal to the labelling number.

Figure 14: Gas chromatogram of fraction 15 from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Even numbered peaks are 2-alkanones of carbon chain length equal to the labelling number.
Figure 15: Gas chromatogram of fractions 16 and 17 combined, from the open column chromatography of Condor Brown Unit (Fischer assay) shale oil. Peaks labelled C0 C,…C4 C are alkyl substituted 1-(cyclopent-1-enyl)-2-alkanones which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are n-alkyl-1-(cyclopent-1-enyl)-2-alkanones of alkyl chain length equal to the labelling number.
3.5 Discussion

1. Aqueous acidic and basic extractions

Saturation with salt and pre-extraction of the aqueous acid and base extracts resulted in greater purity and recovery for both the acidic and basic compounds. The proportion of neutral contaminants isolated from the basic extracts (0.8 wt%) was high compared to the weight of acids recovered (0.7 wt%). Even greater differences were obtained for the acidic extracts (artefact, 4.1 wt% vs bases, 1.0 wt%). The better recovery of the acids and bases was shown by the high proportions of phenol and cresols in the acid fraction (Figure 5) and methyl and dimethyl pyridines in the base fraction (Figure 6). In the method of Regtop et al [113], these were the least concentrated constituents of the acid and base fractions, while in the present work they were major components.

Separation of the phenols from the carboxylic acids met with limited success. While the phenol fraction was pure, the carboxylic acid fraction contained traces of phenol and cresols in addition to a homologous series (C_8 - C_23) of linear carboxylic acids. Phenols are better recovered under the new extraction scheme, but, small amounts of hydrophilic phenol and cresols must remain in the aqueous phase after back-extraction at pH 10. Subsequently, at pH 1 these are co-extracted with the equally small quantities of
carboxylic acids.

2. Open column chromatography of neutrals

By collecting more fractions of the hexane eluate, more exact elution volumes were established for the alkanes (95 - 130 mL vs 0 - 130 mL [113]), alkenes (140 - 175 mL vs 130 - 380 mL [113]) and bicyclic aromatics (380 - 600 mL vs 380 - 1380 mL [113]). Gas chromatograms of these fractions, Figures 7, 8 and 11 respectively, showed better recovery of volatile, low molecular weight homologues as a result of lower evaporative losses with the smaller eluent volumes. Better baseline resolution was also apparent as a result of the exclusion of unrelated chemical classes.

Several new hexane fractions were collected and these contained previously unresolved compound classes. The first new fraction (175 - 215 mL) comprised at least nine homologous series of \( n \)-alkadienes, three major (series a, b, c; Figure 9) and six minor. The identity of this class was inferred from its position in the elution sequence of functional group types from the open column. Mass spectrometry showed that these compounds were not cycloalkenes or alkynes and a close match was obtained for a \( \text{C}_{12} \) compound (series b, Figure 9) with 1,11-dodecadiene. The ultraviolet absorption maximum of the diene fraction occurs at 216 nm with \( E^0.01\% \) equal to 0.61 indicating that the majority of the
dienes are unconjugated. This was the first report of homologous series of dienes in shale oil.

The two other new hexane fractions collected (215-315 mL and 315-380 mL) respectively contained \( n \)-alkylmonoaromatics (benzene, toluene (2 isomers), xylene and indan as parent structures; Figure 10) and multi alkyl substituted monoaromatics \((C_1-C_6\) benzenes and \(C_0-C_4\) indans). Similar monoaromatic classes were previously identified by Regtop et al. [113] but these had not been resolved from the alkenes and bicyclic aromatics.

The separation of monoaromatics from alkenes and bicyclic aromatics in the new procedure can be readily explained by differences in chemical class adsorption and elution volumes, but the resolution of two monoaromatic fractions, each comprising a different type of alkyl substitution could not. Possibly, silica, which has a more porous structure than alumina, can also separate compounds according to molecular size.

The addition of new gradients to the solvent program led to both the isolation of new chemical classes and an improvement in the efficiency of the procedure. The first new gradient, comprising 250 mL of hexane/dichloromethane (9:1, v/v), was incorporated to reduce the total volume of hexane eluent being used. Not only was this new gradient and its smaller volume (250 mL vs 780 mL) more
effective for the recovery of bicyclic aromatics but tricyclic aromatics such as fluorenes and phenanthrenes were also recovered. The second new gradient (hexane/dichloromethane (4:1, v/v); 250 mL) which immediately succeeded the first, enabled recovery of the residual tricyclic aromatics and tetra- and pentacyclic aromatics. None of the aromatic classes, greater in aromaticity than the bicyclic aromatics, had been either isolated or identified by Regtop et al [113].

The third new gradient (hexane/dichloromethane (7:3, v/v); 250 mL) allowed the isolation of another new chemical class, the nitrogen heteroaromatics, which included indoles and carbazoles. Separate collection of the 3-5 ring PAH and nitrogen heterocycles also meant that the following nitrile fraction (dichloromethane eluent) had greater purity. Examination of the gas chromatogram of this fraction (Figure 13) showed the absence of a large envelope of unresolved compounds which was characteristic of nitrile fractions separated according to the procedure of Regtop et al [113].

The fourth new eluent (dichloromethane/chloroform (9:1, v/v); 250 mL) followed dichloromethane in the eluotropic sequence and served to selectively recover the 2-alkanones (Figure 14). Previously [113], 1000 mL of chloroform was required for the
elution of 2-alkanones and the fraction contained, in addition, both a large proportion of polymeric material and a second chemical class which did not comprise aliphatic ketones. Using the fifth new gradient (chloroform/ether (4:1, v/v; 250 mL), this second chemical group was isolated and found to comprise both multi-alkyl substituted components and several homologous series (Figure 15). Mass spectra of the least substituted (parent) compounds showed prominent fragment ions of m/z 67 and 95 amu or m/z 81 and 109. These ions are indicative of an unsaturated five or six membered ring which is substituted by a keto group. The homologous series were characterised by m/z values of 110 and 124 which suggests that the n-alkyl chain is directly bound to the keto group; m/z 110 resulting from a McLafferty rearrangement of the cyclopentenyl-2-alkanone and m/z 124 resulting from a McLafferty rearrangement of either a methylcyclopentenyl-2-alkanone or a cyclohexenyl-2-alkanone. Taking into account the later elution of the cycloalkenyl-2-alkanones on the open column, relative to the 2-alkanones, the double bond in the ring is likely to be conjugated with the keto group. The most probable base structure for this chemical class is a 1-(cyclopent-1-enyl)-2-alkanone.

As a consequence of the improved chemical class resolution, each of the fractions collected were better separated by GC;
baseline resolution between components was common. This permitted more detailed GC-MS analyses, thereby enabling less ambiguous identifications and an extension of the range of identifiable components. For example, in the analysis performed by Regtop et al. [113], 2-phenylalkanes were reported as one of the n-alkylmonoaromatic series. In the present analyses these were identified as n-alkyltoluenes because two isomers were observed and this is not possible with the 2-phenylalkane structure. The detection of two n-alkyltoluene isomers was only possible because n-alkylmonoaromatics are separately resolved under the new separation scheme, whereas in the procedure of Regtop et al. [113] they coeluted with the much more abundant alkenes.

Despite the significant improvements, the new method still has a number of disadvantages:

1. Aqueous acidic extraction of shale oil always results in the formation of a large amount of polymeric artefact. While aqueous basic extraction is generally less detrimental, significant amounts of base artefacts are sometimes formed (e.g., 5.5 wt% of the total oil from the Condor Carbonaceous shale). The artefacts not only contaminate the aqueous extracts but also remain in the organic phase and subsequently coelute with many of the polar neutral
compounds. While, satisfactory methods were developed to eliminate the artefacts from each of the fractions, the initial loss of oil to artefact is unacceptable.

Artefacts also arise from exposure of the shale oil to air, light, harsh drying agents and highly active liquid chromatographic adsorbents such as silica and alumina. A conservative estimate of the total amount of artefacts formed from shale oil during analysis would be 10-20 wt%. The opportunity for the formation of artefacts with an open column separation scheme is further enhanced by the long time (2-3 days) required for the separation. For the separation of Regtop et al. [113] this is due to the large amount of adsorbent used to perform the separation; large eluent volumes (and therefore elution time) are necessary for the recovery of each chemical class.

2. Some of the liquid chromatographic solvents used for the open column separation have high boiling points e.g. hexane (69°C), chloroform (62°C) and methanol (65°C). Concentration of the eluates for analysis by GC, GC-MS, etc results in evaporative losses of the volatile shale oil constituents.

3. A large proportion of the neutral oil is not fully resolved on the alumina/silica adsorbent. Overlaps occur between the alkanes and alkenes (fraction 2) and between all the 1-5 fused ring aromatic
fractions (7-13). Resolution of the latter compounds is particularly limited because the silica adsorbent provides separations which are largely dependent on the type of alkyl substitution and not the degree of aromaticity (e.g., Figures 11 and 12).

Collectively the alkanes, alkenes and 1-5 ring PAH represent 60-70% of the total weight of oil. Only the \( n \)-alkadienes, \( n \)-alkanonitriles, 2-alkanones and 1-(cycloalk-1-enyl)-2-alkanones are fully resolved but these constitute less than 20-30 wt%. The balance of the oil (10-20 wt%) polymerised in the course of the analysis. The overall efficiency of the procedure is therefore unsatisfactory.
4. Separation of Polynuclear Aromatic Hydrocarbons in Shale Oil by Low Pressure Liquid Chromatography

4.1 Assessment of existing separation schemes

Polynuclear aromatic hydrocarbons (PAH) are ubiquitous in petroleum and synthetic fuels derived from coal and oil shale [119, 120]. Efficient procedures are needed for their determination because they influence the end use of the fuel and they are of environmental significance; many PAH (e.g. benzo-[a]-pyrene) are potent carcinogens [54,55]. A variety of adsorbents have been used for the isolation of PAH from complex mixtures, including silica [121, 122], alumina [84, 85, 123, 124] and bonded phases such as pyrrolidone [87], C-18 [125], amino [59, 125-127] and dinitroanilineopropyl [59]. Previous aromatic class separations on silica or bonded C-18 have been adversely affected by the variability of alkyl substitution [60, 61]. While amino-bonded phases are less susceptible to this influence, they have been tested mainly with simple mixtures of model compounds rather than the much more complex mixtures found, for example, in shale oils. Polar bonded phases such as the amino phase may also promote artefact formation e.g. the conversion of ketones to Schiff bases [79]. Other disadvantages of bonded phases include their cost (which
necessitates careful selection at the time of purchase), their need for expensive operating equipment and their degradation by polar compounds such as acids and bases. In reverse phase separations, sample dissolution problems may also be encountered.

Alumina has the advantages of being inexpensive, readily available and relatively neutral. It provides aromatic class separations which are independent of alkyl substitution [128] and can separate many other functional group classes. Complete chromatographic resolution of PAH according to ring number, however, has been prevented by limitations of the eluting solvents; in most cases these have been hexane and dichloromethane. It will be shown here that a separation of PAH by ring number is possible if an optimised series of eluents is used.

4.2 Development of a new procedure

The choice of solvents to elute PAH adsorbed on alumina was based in part on the criteria of Snyder and Kirkland [130] viz. ready availability in high purity, low viscosity and complete miscibility with other chromatographic solvents. While hexane and dichloromethane satisfied these requirements, when used for shale oil separations aromatic class overlaps were evident and these became worse with increasing ring number. Fractions eluted with
hexane (or hexane containing a small proportion of dichloromethane) were contaminated with long chain (n ≥ 15) homologous alkanes. Fractions eluted with hexane/dichloromethane gradients of high dichloromethane content were contaminated with polyalkyl-benzenes having side chains ≤ C-4. These overlaps could be due partly to the poor solubility of many PAH in hexane and partly to poor elution selectivity of dichloromethane.

After investigating the properties of a number of alternative solvents, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) was chosen to replace hexane as the initial eluent. Not only does it have the required physical properties of low viscosity (0.711 cP at 20°C), low dielectric constant (2.41 at 20°C) and low eluotropic strength (E° = 0.02 [130]) but also it has a much lower boiling point than hexane (Freon 113, 48°C vs hexane, 69°C) and is a better solvent for many organic compounds [130]. Benzene was selected as the next solvent of the program because it has a similar eluotropic strength to dichloromethane (0.32 cf. 0.42) and because its structural similarity to PAH might provide better selectivity of elution. A final step using benzene plus a small proportion of dichloromethane was incorporated to ensure the elution of any PAH not recovered with benzene alone.
4.3 Experimental

4.3.1 Samples

Condor oil shale (Brown Unit; section 3.3.1) and Green River oil shale (Mahogany Zone, Piceance Creek Basin [131]) were crushed (1.0-2.5 mm), air dried and retorted in a modified Fischer assay apparatus [41]. Each shale oil was immediately dissolved in Freon 113 (50 mL) and centrifuged to remove asphaltenes and retort water. Each solution was extracted with aqueous sodium hydroxide (3 M; 3 x 10 mL), aqueous sulphuric acid (3 M; 3 x 10 mL), water (3 x 10 mL) and then dried with anhydrous magnesium sulphate (removed by centrifugation). Excess Freon 113 was removed from each solution with a dry nitrogen gas stream to yield a solution containing ≈0.75 g shale oil mL⁻¹.

4.3.2 The new procedure

4.3.2.1 Materials

1,1,2-Trichloro-1,2,2-trifluoroethane (Mallinckrodt, ChromAR) and benzene (Mallinckrodt, Nanograde) were used as received. Dichloromethane (Ajax, Unilab) was redistilled before use. All solvents were filtered through a 0.45 μm Millipore filter. Alumina (Ajax; neutral, activity 1) was sieved into two particle size fractions comprising < 0.125 mm and > 0.125 mm.

4.3.2.2 Equipment
An Omnifit low pressure column (1 m x 6.6 mm i.d.),
accessories and water jacket were used. Solvents were delivered
with an Altex Scientific Model 110 solvent metering pump.

4.3.2.3 Liquid chromatography

The column was slurry packed, using a vibrator, with neutral
alumina (42 g; < 0.125 mm; preheated to 300°C for 3 h and cooled
under nitrogen) and maintained at 30°C by means of a water jacket.
Approximately 2 mL of shale oil solution (0.75 g shale oil mL⁻¹)
was loaded on the column and the following eluate fractions listed
in order of number, eluent and volume were collected: 0: Freon 113,
0-15 mL; 1: Freon 113, 15-40 mL; 2: Freon 113; 40-120 mL; 3:
Freon 113, 120-170 mL; 4: Freon 113, 170-400 mL; 5: Freon
113/benzene (85:15, v/v), 0-200 mL; 6: Freon 113/benzene (7:3,
v/v), 0-200 mL plus Freon 113/benzene (1:1, v/v), 0-200 mL; 7:
Freon 113/benzene (1:4, v/v), 0-200 mL; 8: benzene, 0-200 mL; 9:
benzene/dichloromethane (1:1, v/v), 0-150 mL.

Fraction 0, representing the void volume of the column was
discarded; whenever eluent was changed, the void volume was taken
into account in collecting the eluate fractions.

4.3.3 Instrumental analysis

Gas chromatography (G.C): A Varian 3700 Gas Chromatograph
equipped with dual SGE glass capillary columns (A: 25 QC3/BP5-
0.25, split ratio 10:1, $\Delta P=100$ kPa; B: 25 QC2/BP5-0.25, split ratio 10:1, $\Delta P= 120$ kPa) was used. Helium was used as carrier gas at a flow rate of 2 mL min$^{-1}$.

Gas chromatograms, listed in order of fraction number(s), column and temperature program, were obtained as follows: 2-4: A, 50°C to 280°C at 4°C min$^{-1}$ with 10 min at 280°C; 5: B, 50°C to 280°C at 4°C min$^{-1}$ with 10 min at 280°C; 6: B, 100°C to 280°C at 3°C min$^{-1}$ with 10 min at 280°C; 7-8: B, 150 to 280°C at 2°C min$^{-1}$ with 10 min at 280°C.

Gas chromatography-mass spectrometry (GC-MS): GC-MS was performed on a Varian 2700 Gas Chromatograph interfaced to a Vacuum General 12-12 quadrupole mass spectrometer via an open split coupling. The GC was fitted with an SGE glass capillary column (25 QC3/BP5-0.25) which was operated under identical conditions to those used for GC. Mass spectra were collected with a scan speed of 1 second using 70 eV electron impact ionisation. Compounds were identified by comparison with literature mass spectra [132, 133].

4.4 Results

Gas chromatograms of the aromatic fractions separated from the Condor shale oil are given in Figures 16 to 22 and those of the Green River shale oil are given in Appendix 2. Table 6 lists the
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Compound Classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>benzenes (C_1-C_6), indans (C_0-C_3), ( n )-alkylbenzenes (C_2-C_22), ( n )-alkyltoluenes (C_2-C_21; 3 series), ( n )-alkylxylenes (C_2-C_20; 2 series), ( n )-alkylindans (C_2-C_17), ( n )-alkylmethylindans (C_2-C_16), ( n )-alkylthiophenes (C_2-C_22), ( n )-alkylmethylthiophenes (C_2-C_21), ( n )-alkylpyrroles (C_2-C_22)</td>
</tr>
<tr>
<td>3</td>
<td>( \omega )-phenylalk-1-enes (C_4-C_22), ( \omega )-(methylphenyl)-alk-1-enes (C_4-C_21; 3 series), 1,4-dihydonaphthalenes (C_0-C_2)</td>
</tr>
<tr>
<td>4</td>
<td>styrenes (C_0-C_6), indenes (C_0-C_6), 1,2-dihydonaphthalenes (C_0-C_4), ( n )-alkylindenes (C_2-C_18), 1-phenylalkenes (C_2-C_22)</td>
</tr>
<tr>
<td>5</td>
<td>naphthalenes (C_0-C_6), biphenyls (C_0-C_4), benzofurans (C_0-C_4), benzothiophenes (C_0-C_4), ( n )-alkynaphthalenes (C_2-C_20; 2 series)</td>
</tr>
<tr>
<td>6</td>
<td>fluorenes (C_0-C_6), phenanthrenes (C_0-C_5), dibenzofurans (C_0-C_4), dibenzopyrans (C_0-C_3), dibenzothiophenes (C_0-C_4) phenynaphthalenes (C_0-C_2; 2 isomers), fluoranthenes (C_0-C_4), ( n )-alkylfluorenes (C_2-C_12)</td>
</tr>
<tr>
<td>7</td>
<td>pyrenes (C_0-C_5), tetraaromatics (C_0-C_5; 2 isomers), phenylindoles (C_0-C_4)</td>
</tr>
<tr>
<td>8</td>
<td>benzopyrenes (C_0-C_5; 2 isomers), binaphthyls (C_0-C_3), hexaaromatics (C_0-C_1; 2 isomers)</td>
</tr>
</tbody>
</table>

Table 6: Aromatic (and heterocyclic) compounds identified in shale oil.
Figure 16: Gas chromatogram of fraction 2 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled C1 B,...C5 B and CO 1,...C3 I are respectively, alkyl substituted benzenes and indans which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are n-alkylbenzenes which have an alkyl chain length equal to the labelling number. The enlargement area shows the relative elution order of n-alkylbenzenes (I), n-alkyltoluene (IIA, IIB and IIC), n-alkylxylenes (IIIA and IIB) and n-alkylindans (IV).

Figure 17: Gas chromatogram of fraction 3 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Even numbered peaks are \(\omega\)-phenylalk-1-enes of alkenyl chain length equal to the labelling number. The enlargement area shows the relative elution order of \(\omega\)-phenylalk-1-enes (I) and \(\omega\)-(methylphenyl)-alk-1-enes (IIA, IIB and IIC). Peaks labelled * are respectively, in order of elution from left to right, C3 and C4 alkyl substituted benzenes.
Figure 18: Gas chromatogram of fraction 4 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled \text{C0 S}, \ldots, \text{C4 S} and \text{C0 I}, \ldots, \text{C5 I} are respectively, alkyl substituted styrenes and indenes which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are \( \text{n-} \)alkylindenes which have an alkyl chain length equal to the labelling number.

Figure 19: Gas chromatogram of fraction 5 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled \text{C0 N}, \ldots, \text{C5 N} and \text{C0 B}, \ldots, \text{C2 B} are respectively, alkyl substituted naphthalenes and biphenyls which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are \( \alpha \) and \( \beta \) \( \text{n-} \)alkynaphthalenes which have an alkyl chain length equal to the labelling number.
**Figure 20:** Gas chromatogram of fraction 6 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled CO Df, CO Dp and CO Di are respectively, dibenzofuran, dibenzopyran and dibenzothiophene. Peaks labelled CO Fe,...C3 Fe, CO P,...C4 P and CO Fa,...C2 Fa are respectively, alkyl substituted fluorenes, phenanthrenes and fluoranthenes which have a total number of substituent carbon atoms equal to the labelling number.

**Figure 21:** Gas chromatogram of fraction 7 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled CO P1,...C3 P1, CO P,...C7 P and CO T,...C4 T are respectively, alkyl substituted phenylnaphtholes, pyrenes and tetraaromatic isomers which have a total number of substituent carbon atoms equal to the labelling number.
Figure 22: Latter half of the gas chromatogram of fraction 8 from the low pressure liquid chromatography of Condor shale oil on neutral alumina. Peaks labelled C0 B, ..., C3 B are alkyl substituted benzopyrene isomers which have a total number of substituent carbon atoms equal to the labelling number. Peaks labelled C0 H are hexaaromatic isomers.
parent structure plus nature of alkyl substitution for the aromatic classes identified in each chromatographic fraction.

4.5 Discussion

A clean separation of PAH by ring number was achieved except for fraction 8, which contained both penta- and hexaaromatics. This separation was achieved in spite of the presence of homologous long chain alkyl substituents and/or multiple alkyl substitution in each group.

The superior selectivity of the solvent program was further demonstrated by the isolation of two structural classes intermediate between monoaromatics and diaromatics, namely benzenes having a long chain substituent with a terminal double bond (ω-alkenylmonoaromatics) and benzenes with a side chain having a double bond conjugated with the aromatic ring. The former group (Fraction 3 in Figure 17) included an homologous series of ω-phenylalk-1-enes and three homologous series of isomeric ω-(methylphenyl)-alk-1-enes while the latter (Fraction 4 in Figure 18) consisted of multi alkyl and n-alkylindenes and styrenes.

Although separation according to ring number was achieved, structural isomers were not separated e.g. fluorenes and phenanthrenes were both present in fraction 6 (Figure 20). These
two isomers could probably be separated on a column of greater efficiency but separation of structural isomers with large ring numbers was not attempted because the number of possible isomers increases with ring number and the proportion of PAH in the oil decreases rapidly for ring numbers > 4. Some of the later PAH fractions contained traces of linear alkanes and alkenes, a result of the high relative abundance (30% and 20% respectively) in the shale oil. Were this of concern, they could be removed by a preliminary step such as liquid chromatography or adsorption by molecular sieves.

The high degree of resolution achieved by the new elution scheme enabled some observations to be made concerning alkyl substitution patterns in the shale oils. PAH having multiple alkyl substitution with short chains (C₁ to C₄) are more abundant than PAH with a single alkyl chain and the proportion of the latter decreases with alkyl length. This pattern is less apparent in PAH of higher ring number where the structural isomerism of the ring systems obscures underlying alkyl substitution patterns. The greater abundance of polyalkyl PAH having short alkyl chains probably reflects the relative abundance and stability of alkyl radicals formed during the retorting process; short chain radicals have higher thermodynamic stability than long chain radicals. PAH
have high thermodynamic stability and are probably derived from secondary (aromatisation) reactions during pyrolysis rather than from primary release of PAH moieties originally present in the oil shale kerogen [134].

The chromatographic procedure was also tested with a shale oil from Green River (U.S.A.). Although the Condor and Green River oil shales are of similar origin (lacustrine) and age (Eocene), the Green River deposit is more mature and the chemistry of its shale oil differs in many respects from that of the Condor deposit [135]. e.g. the Condor oil has a lower proportion of aromatics and of acyclic isoprenoids. However, the aromatic classes isolated from the Green River oil were almost identical with those in Condor oil. The main difference was a higher proportion of long chain n-alkyl substituted PAH homologues in Condor, whereas Green River contained mainly multiple substitution by small alkyl groups, particularly methyl. This may reflect the greater maturity of the Green River kerogen. While the chromatographic procedure was equally effective with both oils, it should be noted that the Green River oil has a much higher proportion of n-alkylpyridines than Condor. Had these bases not been removed by extraction with aqueous acid prior to chromatography, they would have co-eluted with some PAH fractions [135].
As a consequence of the improved resolution afforded by the new method many classes or isomers not reported previously in shale oils were isolated (Table 6). These include homologous series of, i) \( \text{n-alkylmethylindans} \), ii) \( \text{n-alkylmethylthiophenes} \), iii) \( \text{\( \omega \)-phenylalk-1-enes} \), iv) \( \text{\( \omega \)-(methylphenyl)- alk-1-enes} \) (three isomeric series), v) \( \text{n-alkylstyrenes} \), vi) \( \text{n-alkylindenes} \), vii) \( \text{n-alkylmethylindenes} \) and viii) \( \text{n-alkylfluorenes} \). A number of other homologous series were detected (e.g. \( \text{n-alkylpyrroles} \)) but their identification is only tentative in the absence of reference spectra. Nitrogen, oxygen and sulphur heterocycles were also identified in both oils (Table 6) and these too were cleanly separated on the basis of ring number. They had low relative abundance compared with PAH, in accord with the elemental analysis of the oils [119, 131].

Despite the variety of alkyl substituents on the PAH in the two shale oils studied, the procedure gave a clean separation of individual PAH according to ring number. Unlike previous separations using hexane/dichloromethane, elution with Freon 113 or Freon 113/benzene gave aromatic class separation without overlaps due to prolonged retention of aromatics substituted by long alkyl chains. Elution with benzene or benzene/dichloromethane gave better resolution of higher PAH than did dichloromethane/
hexane. Dichloromethane was needed in the solvent program only for the recovery of PAH with ring number $\geq 6$.

The lower boiling point of Freon 113 compared to hexane reduced evaporative losses of monoaromatic hydrocarbons. Losses are high when hexane is used to elute monoaromatics which are not highly substituted. In the later stages of the elution, benzene gives good resolution of the consecutive PAH classes and does not interfere with their detection by UV because benzene absorbs at much shorter wavelength than PAH with ring number $\geq 2$. The higher boiling point of benzene compared to dichloromethane does not lead to losses during recovery of the solvent because it is only required for the elution of the relatively involatile naphthalenes and higher PAH.

The adsorbent alumina has an innate capacity for adsorption of aromatic compounds [128] and, being inexpensive, is readily expendable. This is important because freshly retorted shale oils contain a significant proportion of highly reactive (polar) compounds which either polymerise on or react with the surface of the adsorbant, and cannot be subsequently removed.
5. Chemical Class Separation of Shale Oil by Low Pressure Liquid Chromatography on Thermally Modified Adsorbents

5.1 Assessment of methods using conventional adsorbents

The basis of most procedures that are used for the chemical class separation of complex liquid fuels is liquid chromatography on conventional adsorbents such as silica and alumina. For example, silica has been used to separate solvent refined coal into acids, bases, alkanes, aromatics, polar PAH (including N, O and S heterocycles) and polyfunctional compounds [104]; and to separate shale oil into alkanes, alkenes, monocyclic aromatics, polyhydroaromatics, bicyclic aromatics, alkanonitriles and alkanones, phenols and nitrogen aromatics [115]. Alumina and alumina/silica combinations have been used to separate coal hydrogenolysates into alkanes, aromatics, oxygen aromatics, ethers, nitrogen aromatics and phenols [106, 108, 111] and alumina/silica combinations have been used to separate shale oils into alkanes, alkenes, alkadienes, \(n\)-alkylmonoaromatics, polysubstituted monoaromatics, bicyclic aromatics, polycyclic aromatics, \(n\)-alkanonitriles, 2-alkanones, nitrogen aromatics and phenols [113].

In the chemical class separation of shale oils it is essential
that an adsorbent of the highest activity (such as silica or alumina) be used for the separation of the different classes of hydrocarbons (alkanes, alkenes, dienes, 1-5 ring arenes). However, these very active adsorbents are likely to cause irreversible adsorptive losses or surface catalysed polymerisations of many polar compounds (e.g. ketones, acids, bases). Strong retention of adsorbates also requires the use of polar solvents for desorption. These solvents generally have high boiling points and are poor solvents for compound classes which are highly substituted by alkyl groups. This leads to losses by precipitation during column chromatography and by evaporation when fractions are subsequently concentrated for instrumental analysis. In addition, shale oils are chemically unstable and form polymeric artefacts during aqueous acidic and basic extractions and upon exposure to air and light. None of these problems have received sufficient attention in any of the chemical class separation methods which are currently available [98-117; Table 3].

5.2 Development of a new procedure

Desirable features of a new method would be minimal artefact formation, chemical class separation according to functional group type, minimal expenditure of reagents (e.g., solvents, adsorbents)
and short analysis time. Separation of a complex liquid fuel by chromatography on a single column may take up to 20 h because each chemical class must be sequentially eluted from the adsorbent. This long residence time may promote artefact formation, induced by the often excessive surface activity of the adsorbent.

An alternative approach, adopted in the present work, was the use of a series of columns which contained in succession, less active grades of adsorbent. The complex fuel mixture passes through the series of columns sequentially, with consecutive columns retaining progressively less polar constituents. The retained compound classes are quickly recovered by eluting the columns in parallel which shortens the analysis time. Artefact formation is also reduced since the most polar and reactive compounds are adsorbed on the least active adsorbent and fewer reactions are catalysed by the adsorbent surface. Even acids and bases can be chromatographed without irreversible adsorption, which obviates aqueous acidic and basic extractions.

In turn, the adsorbents are more likely to retain their activity or can be easily regenerated for further use. Polar solvents are also not required. Only a few non-polar eluents, common to all columns of the series are necessary for sample recoveries. These solvents
can be chosen on the basis of their physical properties (boiling points, UV transparency, viscosity, etc).

Adsorbents that are commonly used for the separation of complex mixtures include high performance liquid chromatography (HPLC) bonded phases (e.g., C-18, phenyl, amino), silica and alumina (acidic, neutral and basic). The activity of bonded phases can be systematically varied to provide a range of activities by changing the functional groups of the bonded phase. However, bonded phases are very expensive, require equally expensive instrumentation for operation and are easily degraded by polar compounds. In contrast, silica and alumina are inexpensive, commercially available, can be operated at low pressures, but have high surface activity. Methods have been developed for the systematic deactivation of silica (Hernandez et al [136]) and alumina (Brockmann and Schodder [137]). Both methods rely on the addition of various proportions of water to the adsorbent which is not only time consuming and hard to reproduce but risks contamination of eluents by desorbed water. Unless removed, moisture in the eluates will interfere with subsequent GC analyses, UV analyses, etc.

Thermal deactivation was adopted in the present work as an alternative to chemical deactivation. It offered the advantages of low cost, ease of adsorbent preparation and freedom from
contamination. Because adsorbent gradation by thermal
deactivation was a novel idea, the feasibility of this procedure had
to be assessed. This involved determining which of the commercial
adsorbents i.e. silica or alumina (acidic, neutral and basic) provided
the best selectivity, ii) whether the activity of this adsorbent
could be varied systematically by thermal treatment and iii) whether this thermal deactivation was reproducible.

5.2.1 Evaluation of adsorbents

The selectivities of silica, acidic alumina, neutral alumina
and basic alumina were evaluated by resolving a solution of
reference compounds under identical conditions. The reference
compounds were chosen so as to be representative of shale oil and
included 1,2,3,4- tetramethylbenzene, 1,5-dimethylnaphthalene,
phenanthrene, perylene, myristonitrile, 2-hexadecanone, quinoline
and p-tertbutylphenol. An alkane and alkene were not included in
the initial trials because a large amount of each adsorbent would
be required for their resolution and this would increase the eluent
volumes for all other chemical classes in the mixture. Each of the
adsorbents was activated under identical conditions and a
chromatographic column prepared from it under standard
conditions. Each column was loaded with the same quantity of
reference compounds and eluted with the eluotropic sequence of
solvents: hexane, dichloromethane, chloroform, ether and methanol.

Reference aromatics containing 1-4 rings were recovered by elution with hexane. Of the four adsorbents, acidic alumina provided the best selectivity for aromatics; all four reference aromatics were completely separated. Neutral and basic alumina, showed decreasing selectivity and the separation was less well-defined. None of the reference aromatics were properly resolved on the silica adsorbent.

All four adsorbents showed similar selectivity for the nitrile and methyl ketone reference compounds; both were recovered with dichloromethane as eluent. The most significant variation between the four adsorbents was observed for the reference acid and base. The solvents which eluted these compounds from the adsorbents (listed in decreasing order of selectivity) were as follows: acidic alumina (ether/methanol and methanol), basic alumina (methanol and chloroform), neutral alumina (ether/methanol and chloroform) and silica (dichloromethane and chloroform). The results are in accordance with the "surface pH" of the adsorbents. The acidic alumina and silica, being acidic, more strongly retained the base than the acid, whereas neutral and basic alumina, being basic, more strongly retained the acid than the base.

In summary, acidic alumina was the most selective adsorbent
for the set of reference compounds tested. This was followed, in
decreasing order of selectivity, by neutral alumina, basic alumina
and then silica. Unfortunately, shale oil is sensitive to acid which
restricts the use of acidic alumina to the separation of inert
(non-polar) compounds such as alkanes and alkenes. Neutral alumina
was therefore considered to be the most appropriate adsorbent for
further studies.

5.2.2 Thermal deactivation of neutral alumina

When alumina is being prepared as a liquid chromatographic
adsorbent it is routinely heated to 200-400°C. At these
temperatures only adsorbed water is removed and the alumina is
considered to be 'activated'. At temperatures in excess of 1100°C,
alumina is converted to α-alumina which is chromatographically
inactive [128]. Therefore, thermal modification of alumina activity
was examined in the temperature range 400-1100°C.

To determine the extent of thermal deactivation, the
retention of reference compounds on the heated aluminas
(500-1100°C; 100°C intervals) was compared with that of
normally activated alumina (400°C). To ensure an accurate
comparison, each adsorbent was i) of the same mass (10 g), ii)
heated for the same period of time (12 h) at temperatures which
were accurately known, iii) packed into columns of identical
diameter and iv) evaluated with the same set of reference compounds (section 5.2.1) and the same sample loading. In addition, elution of the reference compounds was performed with a solvent of low eluotropic strength ($E^0$). This ensured that an 'absolute' measure of the extent of thermal deactivation was made. The solvent chosen for this study was hexane ($E^0=0.01$).

Elution of the reference compounds with hexane from the alumina heated to $400^\circ$C resulted in the separation of the monoaromatic standard. Reference compounds of greater adsorptivity than the monoaromatic (diaromatic, triaromatic, etc) were retained for at least 50 mL of hexane eluate. A similar result was obtained for the aluminas heated at $500$-$700^\circ$C. For the aluminas heated at $800$-$1100^\circ$C reference compounds in addition to the monoaromatic standard were found in the initial hexane eluate: $800^\circ$C alumina (traces of the bicyclic aromatic standard), $900^\circ$C alumina (2-4 ring aromatic compounds), $1000^\circ$C alumina (2-4 ring aromatics and nitrile) and $1100^\circ$C alumina (all reference compounds). The results clearly showed that alumina could be thermally deactivated and that its deactivation was dependent upon temperature.

The heating period of 12 h that was used for these trials was inconvenient, especially if a series of adsorbents was required.
Subsequent trials at higher temperatures (up to 1250°C) showed that all the activities produced between 800-1100°C with a heating period of 12 h could be obtained with shorter heating periods (45 min to 1 h). Even shorter heating periods and higher temperatures were tested but the results were less reproducible.

5.2.3 Conditions for the production of reproducible, thermally modified aluminas

Factors which were found to affect the reproducibility of the thermally modified aluminas were, i) the environment in which the alumina was cooled, or subsequently packed for liquid chromatography and ii) inconsistencies in the quality of successive batches of alumina (obtained from either the same manufacturer or different sources).

Depending on the atmospheric humidity, the deactivated alumina adsorbs variable amounts of moisture, during cooling or packing, and thereby further deactivates. Contamination from atmospheric moisture during cooling was avoided by immediately placing the heated alumina in a sealed vessel and cooling under an atmosphere of dry nitrogen gas. Atmospheric moisture was excluded during packing of the adsorbent by slurrying the deactivated alumina in a dry solvent.

The inconsistencies between successive batches of alumina
were due to variation in colour, particle size and activity. The range of colours observed included pure white (correct colour), off-white, faint pink and light brown. The consistency of the alumina particles varied between powdery and coarse. Differences in activity were not readily obvious but became so after thermal deactivation; some aluminas (particularly that obtained from Fluka) also partially decomposed upon heating.

Colour could not be removed from the aluminas by washing with solvents (e.g. water, methanol). The inconsistency of the alumina particle sizes, however, could be overcome by sieving the aluminas prior to use into several particle size fractions. The three chosen were 0.45-0.75 mm, 0.75-0.125 mm and > 0.125 mm. The 0.45-0.75 mm alumina was used for separations requiring the highest efficiency (alkanes and alkenes), the 0.75-0.125 mm alumina was used for the preparation of thermally modified adsorbents which were used for less difficult separations (e.g. aromatics) and the > 0.125 mm alumina was used for drying chromatographic solvents.

Variations in activity were harder to screen. Each alumina passed the only available activity test (Brockmann [137]; based on the retention of a set of standard azo dyes) yet large differences were observed in the adsorption capacities of the different
samples following thermal deactivation. A new and more precise activity test was therefore devised and this involved determining the pH of an aqueous suspension of the alumina. Whatever acidic or basic groups were present on the surface of the alumina, these were mirrored by the pH of the aqueous phase. More direct tests were not possible because alumina is a solid, and surface chemistry techniques for the detection of acidic and basic groups are not sufficiently advanced.

Four aluminas from different manufacturers (including Ajax, BDH, Fluka and Merck) were tested by the new procedure. Each alumina (0.75-0.125 mm, 10 g) was gently stirred (30 min) with triple distilled water (30 mL, known pH) and then filtered (0.45 μm). The pH's of the four filtrates were: Ajax, 6.11; BDH, 8.18; Fluka, 7.10; Merck, 6.22. The pH of the triple distilled water was 6.31. The pH of the filtrates from the Ajax and Merck aluminas were similar to that of the triple distilled water before mixing indicating that these aluminas are truly neutral. Both the BDH and Fluka aluminas were basic.

To determine if a correlation existed between the surface pH's of the aluminas and their activity, each of the four aluminas was thermally deactivated (1 h, 1040°C) and then used to retain a set of reference compounds. In decreasing order of capacity for
*Elution volumes (mL hexane) of standard compounds from deactivated aluminas.

<table>
<thead>
<tr>
<th>Standard compound</th>
<th>Deactivated aluminaa</th>
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<tbody>
<tr>
<td></td>
<td>Ajax</td>
</tr>
<tr>
<td>1,2,3,4-tetramethylbenzene</td>
<td>nrtb</td>
</tr>
<tr>
<td>1,5-dimethylnaphthalene</td>
<td>20</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>35</td>
</tr>
<tr>
<td>perylene</td>
<td>70</td>
</tr>
<tr>
<td>myristonitrile</td>
<td>125</td>
</tr>
<tr>
<td>2-hexadecanone</td>
<td>rtC</td>
</tr>
<tr>
<td>quinoline</td>
<td>rt</td>
</tr>
<tr>
<td>p-tertbutylphenol</td>
<td>rt</td>
</tr>
</tbody>
</table>

a Heated at 1040°C for 1 h.
b Not retained.
c Not eluted with 150 mL of hexane.
retention the aluminas were BDH > Merck ≈ Ajax > Fluka. These results do not immediately show a correlation to surface pH. However, following thermal deactivation it was noted that the Fluka alumina, which had the least activity, had become very powdery in appearance. Possibly this alumina had been chemically treated after production to ensure surface neutrality. On the basis of its surface neutrality, its stability upon thermal deactivation and its ready availability from local distributors it was decided to use Ajax alumina in future studies; the Merck alumina, which has similar properties to the Ajax alumina, would have equally sufficed but it is not supplied locally.

5.2.4 Selection of thermally modified alumina adsorbents for the new procedure

It was found convenient to use five adsorbents in series for the resolution of the shale oils. The five adsorbents retained, respectively, highly polar compounds (e.g., acids and bases), polar compounds (e.g., nitriles and ketones), moderately polar compounds (e.g., benzo- heterocycles and 3-5 ring aromatics), weakly polar compounds (e.g., 1-2 ring aromatics) and non-polar compounds (e.g., alkanes and alkenes). The activity of each of these adsorbents was found by trial and error and was such that only two solvents were required for the elution of all adsorbed components. Of the five
columns in the series, three (columns 1, 2 and 3) contained successively, less thermally deactivated neutral alumina, one (column 4) contained activated neutral alumina and the last (column 5) contained activated acidic alumina of smaller particle size than the neutral alumina.

5.2.5 Selection of solvents for the new procedure

Desirable features of liquid chromatographic solvents include low boiling point, low viscosity and good solvation properties. For use with deactivated adsorbents, a low solvent strength ($E^0$) was also necessary. Hexane, with $E^0 = 0.01$, satisfies most of these criteria and had proved useful in allowing an absolute measure of the extent of thermal deactivation of alumina adsorbents (section 5.2.2). However, after several trials with shale oil, it was evident that hexane could not provide sufficient solvation for all the chemical class types. The solvent chosen to replace hexane was 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). Freon 113 has many similar physical properties to hexane but has the added advantages of lower boiling point ($47.6^\circ C$ .cf. $68.7^\circ C$) and better solvation characteristics for polar compounds [130] despite its similar solvent strength ($0.02$ .cf. $0.01$). Because the range of chemical class types adsorbed to each of the adsorbent in the column series was small, only one other solvent of relatively low
polarity was required for complete sample recovery. Dichloromethane was chosen as the second solvent based on its appropriate solvent strength (0.42), low boiling point (40.1°C), low viscosity (0.44 cP, 20°C) and excellent solvation properties.

5.3 Experimental

5.3.1 Samples

Condor oil shale (Brown Unit; section 3.3.1) and Green River oil shale (Mahogany Zone, [131]) were crushed (1.0–2.5 mm), air dried and retorted in a modified Fischer assay apparatus [41]. Each shale oil (5–10 g) was immediately dissolved in Freon 113 (50 mL) and centrifuged to remove asphaltenes and retort water. Each solution was dried over anhydrous sodium sulphate (removed by centrifugation) and evaporated at 20°C with a dry nitrogen gas stream to a concentration of ≈0.75 g shale oil mL⁻¹.

5.3.2 The new procedure

5.3.2.1 Materials

1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113, Mallinckrodt, ChromAR) and benzene (Mallinckrodt, Nanograde) were used as received. Dichloromethane (Ajax, Unilab) was redistilled before use. Benzene-free hexane was prepared from laboratory grade solvent as follows: hexane was stirred with one tenth its
volume of 18 M sulphuric acid for 24 h; washed with a saturated sodium bicarbonate solution; dried over anhydrous calcium chloride for 2 h and stored over alumina (neutral, activity 1) for at least 12 h before redistilling prior to use.

Alumina (Ajax; neutral, activity 1) was sieved into the three particle size fractions of 0.45-0.75 mm, 0.75-0.125 mm and > 0.125 mm. Thermally modified adsorbents for columns 1-4 were prepared by taking aliquots of the 0.75-0.125 mm fraction and heating these in a high temperature muffle furnace at 1120°C for 80 min, 1035°C for 75 min, 970°C for 80 min and 300°C for 100 min, respectively (temperatures measured by a chromel-alumel thermocouple). Immediately following heating, the deactivated aluminas were cooled under a dry nitrogen atmosphere and then stored under the appropriate solvent; Freon 113 for 1120°C, 1035°C and 970°C materials and Freon 113/hexane (15:85) for the 300°C material. Acidic alumina for column 5 was prepared as follows: neutral alumina (0.45-0.75 mm) was washed with 150 mL of triple distilled water, filtered, stirred for 30 min in 200 mL of 4 M hydrochloric acid (BDH, Aristar), filtered, dried for 100 min at 200°C, cooled under a dry nitrogen atmosphere and then stored under dry, benzene-free hexane.

5.3.2.2 Equipment
Five low pressure liquid chromatography columns (Omnifit: columns 1-4, 500 mm x 6 mm i.d.; column 5, 1000 mm x 6 mm i.d.) were connected via three way valves so that they could be operated either in series or in parallel. The columns were maintained at 30°C by means of glass water jackets (Omnifit) through which fluorescein solution (2 g L$^{-1}$) was recirculated from a thermostatted water bath. Two pumps (Altex Model 110) were used to deliver solvents to the columns via multiport valves. A refractive index detector (Waters Model R401) was used to monitor the eluate from column 5.

5.3.2.3 Liquid chromatography

Columns 1-4 were each slurry packed, using a vibrator, with 22 g of thermally modified aluminas prepared as previously described. Column 5 was similarly packed with 44 g of acidic alumina, also prepared as previously described. The columns may be either connected in series or run separately with the first eluate fraction from each (fraction 0) being transferred to the next column. When the second method was employed, the eluents and eluate volumes for the first four columns were as shown in Table 7. Shale oil solution in Freon 113 (1.0 mL; containing ≈0.75 g oil) was applied to column 1 and each fraction 0 from columns 1-4 was evaporated (dry nitrogen gas stream at 20°C) to 1 mL before
Table 7: Conditions for the elution of shale oil fractions from columns 1-5

<table>
<thead>
<tr>
<th>Column</th>
<th>Fraction</th>
<th>Eluent</th>
<th>Eluate volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>Freon 113</td>
<td>0-35</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>Freon 113</td>
<td>35-200</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>CH₂Cl₂</td>
<td>200-300</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>Freon 113</td>
<td>0-50</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>Freon 113</td>
<td>50-250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freon 113/CH₂Cl₂ (1:9,v/v)</td>
<td>250-300</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>CH₂Cl₂</td>
<td>300-400</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>Freon 113</td>
<td>0-35</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>Freon 113</td>
<td>35-185</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₆H₆/Freon 113 (7:93,v/v)</td>
<td>185-235</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>C₆C₆/Freon 113 (18:82,v/v)</td>
<td>235-335</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>C₆C₆/Freon 113 (40:60,v/v)</td>
<td>335-435</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>C₆H₆</td>
<td>435-535</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>CH₂Cl₂</td>
<td>535-635</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>Freon 113/C₆H₁₄ (15:85,v/v)</td>
<td>0-25</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>Freon 113/C₆H₁₄ (40:60,v/v)</td>
<td>25-75</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>Freon 113/C₆H₁₄ (70:30,v/v)</td>
<td>75-125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Freon 113</td>
<td>125-175</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>Freon 113</td>
<td>175-275</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>CH₂Cl₂</td>
<td>275-375</td>
</tr>
<tr>
<td>5</td>
<td>5.1</td>
<td>C₆H₁₄</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>C₆H₁₄</td>
<td>*</td>
</tr>
</tbody>
</table>

*See 5.3.2.3
application to the next. Column 5 used hexane as eluent and eluate was recycled through the column via the refractive index detector, a three-way (recycle-collection) valve, a constricted solvent make-up "T" junction and a pump. On each cycle, alkanes (fraction 5.1) were collected as the positive gradient of the first peak in the refractogram and the alkenes (fraction 5.2) as the negative gradient of the second peak.

5.3.2.4 Identification of compounds

The majority of compounds were identified by reference to published mass spectra [132, 133]. Some compounds (biphenyls and phenylnaphthalenes) were identified by comparison of GC retention times and mass spectra with those of standards. Confirmation of the presence of n-alkylpyridines was obtained by N.M.R.

5.3.3 Instrumental analysis

Shale oil fractions were examined by gas chromatography (G.C.) using a Varian 3700 Instrument which was equipped with a glass capillary column (SGE: 25 QC2/BP5-0.25) operated with a split ratio of 10:1 and ΔP equal to 110 kPa; gas chromatography-mass spectrometry using a Varian 2700 Gas Chromatograph interfaced to a Vacuum General 12-12 quadrupole mass spectrometer via an open split coupling (electron impact ionisation; scan speed 1 s) and; nuclear magnetic resonance
spectrometry (N.M.R.) using a Joel GX400 instrument.

5.4 Results

The elemental composition of the Condor oil was: C, 84.8; H, 12.5; N, 1.0; O, 1.9; S, 0.4 wt% and that of the Green River shale oil was: C, 80.3; H, 11.7; N, 1.7; O, 5.5; S, 0.6 wt% (Analytische Laboratorien, Germany). The compounds identified in each of the fractions from the Condor and Green River shale oils are listed in Table 8 together with the gravimetric assay of each fraction.

Gas chromatograms for the fractions from column 1 (1.1: weak bases; 1.2: acids and polymeric material) and column 4 (4.1: monoaromatics; 4.2: ω-phenylalk-1-enes; 4.3: α-alkenylmonoaromatics; 4.4: bicyclic aromatics) were similar and the results are given for the Green River oil (Figures 23 to 28, respectively). The fractions from column 5 (5.1: alkanes; 5.2: alkenes) were also similar except that the Green River alkane fraction contained a larger relative proportion of isoprenoids and linear alkanes eluting before n-tetradecane and the alkene fraction contained a larger relative proportion of isoprenoids; gas chromatograms of the Green River alkane and alkene fractions are given in Figures 29 and 30 and those of the Condor oil in Figures 3A1 and 3A2.

The greatest differences between the two oils were found in
the fractions from column 2 (2.1: n-alkylpyridines/3- and 4-alkanones; 2.2: nitriles; 2.3: 2-alkanones) and column 3 (3.1: tricyclic aromatics/n-alkylpyridines; 3.2: tetracyclic aromatics/n-alkylpyridines; 3.3: pentacyclic aromatics/n-alkylpyridines; 3.4: 4-alkanones; 3.5: 3-alkanones/n-alkylpyridines). The first fraction (2.1) of column 2 from the Condor oil (Figure 3A10) mainly contained n-alkylpyridines whereas this fraction from the Green River oil (Figure 31) also contained homologous series of 3- and 4-alkanones. n-Alkanonitriles and n-alkenonitriles and, 2-alkanones of the Condor oil (Figures 3A11 and 3A12 respectively) were more abundant than in the Green River oil (Figures 32 and 33, respectively); the Green River 2-alkanone fraction also contained many homologous series of alkylpyridines. The earlier fractions of column 3 from the Condor oil contained alkyl substituted polynuclear aromatic hydrocarbons (Figures 3A7 and 3A8) but in the Green River fractions (Figures 34 to 36) these were largely obscured by more homologous series of alkylpyridines. The latter fractions of column 3 from the Green River oil (Figures 37 and 38) also contained a greater abundance of 3 and 4-alkanones and homologous series of alkylpyridines.
Table 8: Compounds identified in the shale oil fractions and the proportion of oil represented by each fraction.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Compound classes</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Green River</td>
</tr>
<tr>
<td>1.1</td>
<td>indoles (C_{0-5}), carbazoles (C_{0-5}), quinolines (C_{0-3}), benzoquinolines (C_{0-2}), 2,3-dihydroindoles (C_{0-1}), anilines (C_{2-3}), 1-(cyclopent-1-enyl)-2-alkanones (C_{0-4})</td>
<td>3.3</td>
</tr>
<tr>
<td>1.2</td>
<td>phenols (C_{0-4}), polymeric compounds</td>
<td>5.6</td>
</tr>
<tr>
<td>2.1</td>
<td>n-alkanonitriles (C_{6-C_{33}}), n-alkenonitriles (C_{6-C_{33}}; 3 series)</td>
<td>4.7</td>
</tr>
<tr>
<td>2.2</td>
<td>2-alkanones (C_{6-C_{27}}), cyclopentanones (C_{2-C_{22}}), cyclohexanones (C_{2-C_{21}}), pyridines (C_{2-C_{4}}), quinolines (C_{1-C_{3}})</td>
<td>5.6</td>
</tr>
<tr>
<td>3.1</td>
<td>phenanthrenes (C_{0-C_{5}}), fluorenes (C_{0-C_{4}}), fluoranthrenes (C_{0-C_{2}}), dibenzofurans (C_{0-C_{2}}), dibenzopyrans (C_{0-C_{2}}), dibenzothiophenes (C_{0-C_{2}}), n-alkylpyridines (C_{2-C_{25}}; 3 series, m/z = 107, 121, 149)</td>
<td>4.4</td>
</tr>
<tr>
<td>3.2</td>
<td>pyrenes (C_{0-C_{5}}), phenylindoles (C_{0-C_{3}}), n-alkylpyridines (C_{2-C_{25}}; 4 series, m/z = 107, 121, 135, 149)</td>
<td>3.9</td>
</tr>
<tr>
<td>3.3</td>
<td>pentacyclic arenes (C_{0-C_{2}}), n-alkylpyridines (C_{2-C_{25}}; 3 series, m/z = 107, 121, 149)</td>
<td>3.8</td>
</tr>
<tr>
<td>3.4</td>
<td>4-alkanones (C_{8-C_{32}}), phenylpyrroles (C_{0-C_{7}})</td>
<td>2.7</td>
</tr>
<tr>
<td>3.5</td>
<td>3-alkanones (C_{6-C_{32}}), n-alkylpyridines</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 8: cont'd...

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Compound classes</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Green River</td>
</tr>
<tr>
<td>(C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;25&lt;/sub&gt;; 2 series, m/z = 121, 135)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>benzenes (C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt;), indans (C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;), n-alkylbenzenes (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;22&lt;/sub&gt;), n-alkyltoluenes (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;21&lt;/sub&gt;; 3 series), n-alkylxylene (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;20&lt;/sub&gt;; 2 series), n-alkylindans (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;18&lt;/sub&gt;)</td>
<td>5.8</td>
</tr>
<tr>
<td>4.2</td>
<td>ω-phenylalk-1-enes (C&lt;sub&gt;4&lt;/sub&gt;-C&lt;sub&gt;21&lt;/sub&gt;), ω-(methylphenyl)-alk-1-enes (C&lt;sub&gt;4&lt;/sub&gt;-C&lt;sub&gt;20&lt;/sub&gt;; 3 series)</td>
<td>1.9</td>
</tr>
<tr>
<td>4.3</td>
<td>Indenes (C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt;), styrenes (C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;), n-alkylindenenes (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;18&lt;/sub&gt;)</td>
<td>2.2</td>
</tr>
<tr>
<td>4.4</td>
<td>Naphthalenes (C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt;), biphenyls (C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;), n-alkynaphthalenes (C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;20&lt;/sub&gt;; 2 series)</td>
<td>4.6</td>
</tr>
<tr>
<td>5.1</td>
<td>n-alkanes (C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;29&lt;/sub&gt;), isoprenoid alkanes (C&lt;sub&gt;13&lt;/sub&gt;-C&lt;sub&gt;16&lt;/sub&gt;, C&lt;sub&gt;18&lt;/sub&gt;-C&lt;sub&gt;20&lt;/sub&gt;), branched/cyclic alkanes</td>
<td>24.7</td>
</tr>
<tr>
<td>5.2</td>
<td>n-alk-1-enes (C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;29&lt;/sub&gt;), n-alk-2-enes (C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;29&lt;/sub&gt;), n-alk-3-enes (C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;29&lt;/sub&gt;), n-alk-4-enes (C&lt;sub&gt;8&lt;/sub&gt;-C&lt;sub&gt;29&lt;/sub&gt;), branched/cyclic alkenes</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>% weight of oil recovered</td>
<td>92.1</td>
</tr>
</tbody>
</table>
Figure 23: Gas chromatogram of fraction 1.1 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled C2 P, ... C4 P are alkyl substituted pyridines which have a total number of substituent carbon atoms equal to the labelling number. Similarly, peaks labelled C0 Q, ... C2 Q, C0 I, ... C5 I, C0 B, ... C2 B and C1 C, ... C5 C are respectively, alkyl substituted quinolines, indoles, benzoquinolines and carbazoles.

Figure 24: Gas chromatogram of fraction 1.2 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled C0 P, ... C4 P are alkyl substituted phenols which have a total number of substituent carbon atoms equal to the labelling number.
Figure 25: Gas chromatogram of fraction 4.1 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled C1 B...C5 B and C0 I...C3 I are respectively, alkyl substituted benzenes and indans which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are n-alkylbenzenes which have an alkyl chain length equal to the labelling number. The enlargement area shows the relative elution order of n-alkylbenzenes (I), n-alkyltoluenes (IIA, IIB and IIC), n-alkylxylenes (IIIB and IIIA) and n-alkylindans (IV).

Figure 26: Gas chromatogram of fraction 4.2 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are \( \omega \)-phenylalk-1-enes of alkenyl chain length equal to the labelling number. The enlargement area shows the relative elution order of \( \omega \)-phenylalk-1-enes (I) and \( \omega \)-(methylphenyl)-alk-1-enes (IIA, IIB and IIC). Peaks labelled * are respectively, in order of elution from left to right, C3 and C4 alkyl substituted benzenes.
Figure 27: Gas chromatogram of fraction 4.3 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled C0 S,...C4 S and C0 I,...C5 I are respectively, alkyl substituted styrenes and indenes which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are α-alkylindenes which have an alkyl chain length equal to the labelling number.

Figure 28: Gas chromatogram of fraction 4.4 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled C0 N,...C5 N and C0 B,...C2 B are respectively, alkyl substituted naphthalenes and biphenyls which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are α and β α-alkynaphthalenes which have an alkyl chain length equal to the labelling number.
Figure 29: Gas chromatogram of fraction 5.1 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are linear alkanes of chain length equal to the labelling number. Peaks labelled I-VII are respectively, 2,6-dimethylundecane, 2,6,10-trimethylundecane, 2,6,10-trimethylldodecane, 2,6,10-trimethyltridecane, 2,6,10-trimethylpentadecane, pristane and phytane.

Figure 30: Gas chromatogram of fraction 5.2 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are linear 1-alkenes of chain length equal to the labelling number. Peaks labelled I, II, III and IV are respectively, 1-, 2-, 3- and 4-alkenes. Peaks lettered a, b and c are respectively, 2,6,10-trimethylldodecane, 2,6,10-trimethyltridecane and pristene.
Figure 31: Gas chromatogram of fraction 2.1 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even and odd numbered peaks are respectively, 3-alkanones and an unknown ketone series which have a carbon chain length equal to the labelling number. Peaks labelled b and c are homologous series of \(n\)-alkylpyridines which are characterised by m/z values of 121 and 135, respectively.

Figure 32: Gas chromatogram of fraction 2.2 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even and odd numbered peaks are respectively, \(n\)-alkanenitriles and \(n\)-alkenonitriles of carbon chain length equal to the labelling number.
Figure 33: Gas chromatogram of fraction 2.3 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are 2-alkanones and a methyl-2-alkanone series of carbon atom number equal to the labelling number. Peaks labelled c are n-alkylcyclopentanones (beginning with ethylcyclopentanone) and the peak labelled C4 P is an alkylsubstituted pyridine which has four substituent carbon atoms. The enlargement area shows the relative elution order of n-alkylcyclopentanones (m/z 84), the two 2-alkanone series (m/z 58) and three n-alkylpyridine series (m/z 134, 121 and 107).

Figure 34: Gas chromatogram of fraction 3.1 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled a, b and d are homologous series of n-alkylpyridines which are characterised by m/z values of 107, 121 and 149, respectively.
Figure 35: Gas chromatogram of fraction 3.2 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled a, c, d and e are homologous series of \( n \)-alkylpyridines which are characterised by \( m/z \) values of 107, 135, 149 and 134, respectively.

Figure 36: Gas chromatogram of fraction 3.3 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Peaks labelled a, b, c and d are homologous series of \( n \)-alkylpyridines which are characterised by \( m/z \) values of 107, 121, 135 and 149, respectively.
Figure 37: Gas chromatogram of fraction 3.4 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are 4-alkanones of carbon chain length equal to the labelling number.

Figure 38: Gas chromatogram of fraction 3.5 from the low pressure liquid chromatography of Green River shale oil on thermally modified aluminas. Even numbered peaks are 3-alkanones of carbon chain length equal to the labelling number. Peaks labelled b are an homologous series of α-alkylpyridines which is characterised by an m/z value of 121.
5.5 Discussion

Each of the column packings (1–3: thermally deactivated; 4: normally activated; 5: acidic) were prepared from the same starting material viz. neutral alumina; this greatly simplified adsorbent preparation. Thermal deactivation of alumina was more reproducible than deactivation by the addition of water [136] and it was dependent upon both temperature and time. It was convenient to maintain deactivation times of 80 min while the deactivation temperature was varied. Other adsorbents of intermediate activity can be readily made for the retention of specific compound classes. Thermostatting the columns at 30°C improved chromatographic broad spectrum light absorbing reproducibility and inclusion of a dye in the recirculated water most inhibited photochemical reactions. Many fractions, particularly those from columns 1 and 2 rapidly darkened if exposed to light.

Alumina was superior to silica because its deactivation was uniform. Also, unlike silica and some bonded phases such as C-18, retention of compounds on alumina was largely dependent on functional group type rather than the type of alkyl substituent. The quality of separation could be improved even further (especially in the case of column 5) if finer, more uniform alumina particles were used. Columns 2–5 are reusable and the greater expense of finer material is therefore justified; column 1, which is used to retain
polymeric material and highly polar compounds such as acids and bases is more rapidly degraded (normally replaced after each run).

Acidic alumina was used to separate the alkanes and alkenes because it was found that neutral alumina retained long chain alkanes and alkenes more than the smaller sized homologues. This resulted in an overlap of the two chemical classes which progressively worsened on each cycle. Prolonged retention of high molecular weight alkanes on alumina has been previously observed [138] but it was not accounted for; the problem disappeared when acid treated alumina was substituted.

Freon 113 was found to be a better solvent for shale oil than hexane, which is the most frequently used liquid chromatography solvent. Many polar chemical classes were of limited solubility in hexane which resulted in either precipitation losses upon initial dissolution of the shale oil or unnecessarily large eluate volumes during column chromatography. Freon 113 also has a lower boiling point than hexane (48°C vs 69°C) which reduces evaporation losses of samples during concentration. Smaller volumes of solvents were used in the method described here than in previous methods (e.g. [113]) and the columns may be eluted in parallel which reduces the time required for fractionation of the shale oil to approximately 3-4 hr.
The recovery of acidic and basic compounds from columns 1-3 demonstrates a better alternative to aqueous acid/base extraction. Aqueous acidic and basic extraction of shale oil results in the formation of large amounts of artefact. The artefacts contaminate both the acid and base fractions and, the neutral shale oil. In addition, acids and bases cannot be further resolved into chemical classes by acidic and basic extraction as they have been in the present method. Many classes of bases were interspersed between the fractions collected from both oils, in particular those of the Green River shale oil. Some of the bases such as the \( \eta \)-alkylpyridines were separated according to the degree of shielding of the heteroatomic nitrogen atom whereas other bases were separated according to the number of aromatic rings.

The majority of \( \eta \)-alkylpyridines that were isolated from the Green River shale oil have not been observed previously although the oil has been extensively studied [68, 81, 83, 139]. Many of these \( \eta \)-alkylpyridines would have been lost through aqueous acidic extraction. Protonated bases with long alkyl chains are poorly soluble in either water or organic solvents and therefore tend to precipitate. This may account for the larger amount of tar that is formed from the Green River shale oil upon acidic extraction compared with other shale oils [139]. Indoles and carbazoles were
also separated by the new method and these are not normally observed in shale oil; indoles, in particular are rapidly destroyed by acid and alkali.

The presence of \( n \)-alkylpyridines in many of the Green River shale oil fraction (1.1, 2.3, 3.1, 3.2, 3.3 and 3.5) sometimes obscured other components of interest e.g. polynuclear aromatic hydrocarbons in fractions 3.1-3.3. These may be removed by acidic extraction once they have been characterised. Similarly, phenols can be separated from polymeric material in fraction 2.2 by extraction with aqueous base. Since unstable compounds which decompose in acid or alkali are not present in these fractions, aqueous acidic and basic extractions at this stage of the analysis does not introduce artefacts.

The method described here can be readily modified to permit the isolation of chemical classes of particular interest. For instance, \( n \)-alkadienes (< 1 wt % of the oil) may be recovered from column 4 by reducing the polarity of the eluents and the scheme may be greatly abbreviated if only one compound class (e.g. nitriles) is to be separated.

Geochemical application of the analytical method is just beginning but already a marked difference can be seen between the Condor and Green River shale oils. Nitrogen compounds in the Condor
oil are predominately nitriles whereas those in the Green River oil are n-alkylpyridines. The Green River oil shale is believed to be more mature than the Condor shale (based on its geochemical similarity to the Rundle deposit [139]); maturation processes may have allowed the nitrogen atoms from various sources to have been incorporated into aromatic rings which survive pyrolysis. Nitriles on the other hand, are probably formed during pyrolysis (since they have not been detected in kerogens) and could arise from either amine moieties or from ammonium salts of carboxylic acids via the amide [134].

The method has been tested on two low-sulphur Tertiary oil shales. Studies of a wide range of other oil shales [140] indicates that most low-sulphur shale oils, irrespective of geological age, are similar to the two oils tested and could be examined by the same method. In the case of high-sulphur (usually marine) oil shales, some modification of the method may be required to allow the abundant thiophenes and benzothiophenes to be separately collected. The method should also be applicable to other unrefined fuel liquids.
6. Determination of Nitriles in Shale Oil by Low Pressure Liquid Chromatography and Infrared Spectrophotometry

6.1 Assessment of existing separation schemes

Nitriles are ubiquitous constituents of shale oils and, in some cases, are the principal nitrogen compounds present [119]. Like most nitrogen compounds [57, 58], nitriles may poison oil-refinery catalysts and therefore their elimination during shale oil beneficiation (e.g. hydrotreating) must be monitored. When a shale derived fuel is combusted any residual nitriles will yield nitrogen oxides and environmental limits on the latter may restrict the application of the fuel. In addition, the toxicity of shale oil nitriles, some of which are unsaturated or aromatic, has not been extensively studied.

Only two methods have been especially designed for the isolation of nitriles from fossil fuels. The first method [76] involved removal of bases by acid extraction, complexation of the neutral nitrogen compounds with iron (III) and zinc chlorides (recovered by thermal desorption), separation of indoles and carbazoles by reaction with perchloric acid and isolation of the nitriles by column chromatography (LC) on alumina with benzene eluent. This procedure was later refined by Jewell and Snyder [62].
The second method [141] involved removal of acids and bases by ion exchange chromatography and separation of the nitriles from the neutral oil by LC on Florisil. Both of these methods are time consuming and in the latter, the nitrile fraction would be contaminated with 2-alkanones, 3-6 ring aromatics, indoles and carbazoles.

Other methods by which nitriles have been isolated from shale oils include LC on silica [100], thin layer chromatography on silica [115] and LC on alumina/silica [113]. These methods were designed for the complete chemical class separation of shale oils and also require long analysis times. Only in the method of Regtop et al. [113] are nitriles separated from 2-alkanones; in the other, 2-alkanones coelute with the nitriles and cannot be separated unless reduced to alcohols [100].

In the present work, nitriles were isolated from shale oils by low pressure LC using a thermally deactivated alumina adsorbent and hexane/dichloromethane eluents. The nitriles were quickly quantitated by infrared spectrophotometry (IR) utilising the sharp C≡N absorbance (2300-2200 cm⁻¹) which occurs in a region of the spectrum where other constituents do not interfere. Nitriles were determined in two geochemically different oils to test the generality of the procedure.
6.2 Experimental

6.2.1 Samples

Condor oil shale (Brown Unit; section 3.3.1) and Green River oil shale (Mahogany Zone, Piceance Creek Basin [131] were crushed (1.0-2.5 mm), air dried and retorted in a modified Fischer assay apparatus [41]. Each shale oil (7.5 g) was immediately dissolved in hexane (50 mL) and centrifuged to remove asphaltenes and retort water. Each solution was extracted with aqueous sodium hydroxide (3 M; 3 x 10 mL), aqueous sulphuric acid (3 M; 3 x 10 mL), water (3 x 10 mL) and then dried with anhydrous magnesium sulphate (removed by centrifugation). Excess hexane was removed from each solution, using a dry nitrogen gas stream, to a volume of 10.00 mL.

6.2.2 The new procedure

6.2.2.1 Materials

Hexane and dichloromethane (Ajax, Unilab) were redistilled before use. Both solvents were filtered through a 0.45 µm Millipore filter.

Alumina (Ajax; neutral, activity 1) was sieved into two particle size fractions comprising < 0.125 mm and > 0.125 mm. n-Tetradecanonitrile was obtained from Fluka.

6.2.2.2 Equipment

An Omnifit low pressure column (1 m x 6.6 mm i.d.),
accessories and water jacket were used. Solvents were delivered with an Altex Scientific Model 110 solvent metering pump.

6.2.2.3 Liquid chromatography

The column was slurry packed, using a vibrator, with neutral alumina (22 g; < 0.125 mm; heated to 1090°C for 50 min and cooled under nitrogen) and maintained at 30°C by means of a water jacket. An aliquot (1.00 mL) of shale oil solution was placed onto the column and the following eluate fractions listed in order of number, eluent and volume were collected: 0: hexane, 0-70 mL; 1: hexane, 70-270 mL plus hexane/dichloromethane (9:1, v/v), 50 mL; 2: dichloromethane, 0-70 mL. Fraction 1 containing nitriles, was evaporated under dry nitrogen gas to 1.00 mL and its absorbance was measured at 2249 cm⁻¹ against a hexane reference using 1.00 mm sodium chloride cells. From the absorbance of the C≡N peak at 2249 cm⁻¹, the C≡N concentration was calculated by reference to a calibration graph prepared from hexane solutions of n-tetradecanoni- trile in the range 0-100 mM.

6.2.3 Instrumental analysis

Nitrile fractions were examined with a Perkin Elmer 780 Series Infrared Spectrophotometer using 1.00 mm sodium chloride solvent cells and with a Varian 3700 Gas Chromatograph which was fitted with an SGE glass capillary column (25 QC 2/BP5-0.25; split
ratio 10:1, ΔP = 120 kPa) using the temperature program: 50–280°C (4°C min⁻¹), isothermal at 280°C (10 min). Gas chromatography-mass spectrometry (GC-MS) was performed on a Varian 2700 Gas Chromatograph Interfaced to a Vacuum General 12-12 quadrupole mass spectrometer via on open split coupling. The gas chromatograph was fitted with an SGE glass capillary column (25 QC3/BP5-0.25; split 10:1, ΔP=100 kPa) and was operated with the temperature program described previously. Mass spectra were collected with a scan speed of 1 s using 70 eV electron impact ionisation. Nuclear magnetic resonance spectrometry (N.M.R) was performed on a Joel GX400 instrument.

6.3 Results

In the range 0–100 mM, the concentration (y) of C=N in the hexane solution of the shale oil was calculated from the solution's absorbance (x) at 2249 cm⁻¹ by means of the equation y = 686 x - 28. The concentration of nitriles in the Green River and Condor shale oil solutions were 17 and 56 mM, respectively. The limit of detection of the method (based on the pooled standard deviation of 12 samples at or near blank level) was 2 mM and was largely determined by noise in the infrared spectrophotometer. The precision of the method (assessed as the relative standard
deviation of at least six measurements) was 8, 4 and 2% at 10, 50 and 100 mM, respectively.

The accuracy of the method was assessed by measuring the recovery of 10 and 40 mM standard additions of n-tetradecano-nitrile to the Condor and Green River oils. For the oils to which 10 mM was added the recovery was 95% while the recovery for the oils to which 40 mM was added was 97%.

6.4 Discussion

The new procedure was an adaptation of that described previously (p. 89-123) in which shale oils were separated into chemical classes by LC on a series of five thermally modified alumina adsorbents. For the isolation of nitriles, however, only a single deactivated alumina column was required provided that the acidic and basic shale oil constituents were removed by aqueous acid and base extraction. Unlike fully active adsorbents such as silica and alumina, thermally deactivated alumina readily separated nitriles from 2-alkanones (which elute with other polar compounds in fraction 2).

Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is, in general, a better solvent than hexane for the LC of shale oils [135] but it has a weak absorption band at 2210 cm⁻¹ and this
interferes with the quantitation of solutions containing low concentration of nitriles. Hexane was chosen in preference to other solvents because of its convenient spectroscopic and chromatographic properties (good transparency, low viscosity, etc).

The characteristic infrared absorption of the C≡N group occurs in the region 2300–2200 cm⁻¹. This region is usually specific for compounds containing triple bonds such as alkynes, diazonium ions and nitriles. Of these, only nitriles have sufficient thermodynamic stability to be found in shale oils. The infrared spectrophotometric finish of this procedure was therefore highly selective. The wavelength of C≡N absorption changes if this functional group is conjugated [142], but no evidence was found in the infrared spectrum for conjugated nitriles (Figure 39). The n-alkenonitriles present in small quantities in shale oils (Figure 40) were shown by NMR to be predominantly ω-alkenonitriles.

In the quantitation of shale oil nitriles, the molar concentration is more important than the mass concentration since the former determines the extent of such problems as refinery catalyst poisoning or the production of nitrogen oxides upon combustion. If the mass concentration of nitriles was required, it could be determined by standard addition of n-alkanenitriles or addition of an internal standard such as a branched or cyclic
Figure 39: Infrared spectrum of the nitrile fraction from Condor shale oil.
Figure 40: Gas chromatogram of the nitrile fractions from (a) Green River and (b) Condor shale oils. Even and odd numbered peaks are respectively, n-alkanonitriles and n-alkenonitriles of carbon chain length equal to the labelling number.
alkanonitrile.

Nitriles were three times more abundant in the Condor oil than in the Green River oil and this may be related to the presence of buddingtonite (an ammonium feldspar) in the Condor oil shale [119]; it appears that ammonia can react with free carboxylic acids during pyrolysis to yield nitriles [141], presumably through an amide intermediate. The Condor and Green River shales are typical of most low-sulphur Tertiary oil shales [140]; the procedure should therefore have general applicability.
### 7. Overall

**Summary of Compound Classes Found in the Condor Brown.**

**Condor Carbonaceous and Green River Shale Oils**

<table>
<thead>
<tr>
<th>COMPOUND CLASS</th>
<th>PARENT STRUCTURE</th>
<th>RANGE OF AXL SUBSTITUTION</th>
<th>CHARACTERISTIC ION$^b$</th>
<th>FRACTION NUMBER$^c$</th>
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</thead>
<tbody>
<tr>
<td>n-Alkanes</td>
<td><img src="image" alt="n-Alkanes" /></td>
<td>n=0-25</td>
<td>43,57,41,71,85,55(n=8)</td>
<td>1,2, 5.1</td>
</tr>
<tr>
<td>2-Methylalkanes</td>
<td><img src="image" alt="2-Methylalkanes" /></td>
<td>n=0-23</td>
<td>43,57,41,71,61,42,43(n=7)</td>
<td>1,2, 5.1</td>
</tr>
<tr>
<td>Cyclopentanes</td>
<td><img src="image" alt="Cyclopentanes" /></td>
<td>i) C$<em>2$C$</em>{26}$</td>
<td>41,69,68,55,43,83(C$_8$)</td>
<td>1,2, 5.1</td>
</tr>
<tr>
<td>Cyclohexanes</td>
<td><img src="image" alt="Cyclohexanes" /></td>
<td>i) C$<em>2$C$</em>{26}$</td>
<td>83,82,55,41(C$_7$)</td>
<td>1,2, 5.1</td>
</tr>
<tr>
<td>Methylcyclopentanes</td>
<td><img src="image" alt="Methylcyclopentanes" /></td>
<td>ii) C$<em>2$C$</em>{26}$</td>
<td>41,69,56,55,57,43(C$_7$)</td>
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<tr>
<td>3- or 4-Methyl-3-alkenes</td>
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<tr>
<td>Cyclopentenes</td>
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<td>2,3, 5.2</td>
</tr>
<tr>
<td>Cyclohexenes</td>
<td><img src="image" alt="Cyclohexenes" /></td>
<td>i) C$<em>2$C$</em>{25}$</td>
<td>91,96,67,82,41,55(C$_6$)</td>
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<td>Methylcyclopentenes</td>
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<td>ii) C$<em>2$C$</em>{25}$</td>
<td>41,81,95,55,67,43(C$_6$)</td>
<td>2,3, 5.2</td>
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<tr>
<td>Isoprenoid alkenes</td>
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<td>56,57,70,69,71,43(pristene)</td>
<td>2,3, 5.2</td>
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<td>Dienes</td>
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<td>Benzenes</td>
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<td>i) C$_2$C$_6$</td>
<td>67,71,15,16,1,77,91,79(C$_3$)</td>
<td>6,7, 8, 4.1, 2</td>
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<td></td>
<td>ii) C$<em>2$C$</em>{27}$</td>
<td>91,52,43,105,65,78(C$_10$)</td>
<td>5, 4.1, 2</td>
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</table>

$^a$ Method 1

$^b$ Method 2

$^c$ Method 3
<table>
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<tr>
<th>Compound Class</th>
<th>Parent Structure</th>
<th>Range of Alkyl Substitution</th>
<th>Characteristic Ions</th>
<th>Fraction Number</th>
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<td>Toluene</td>
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<td>106, 105, 41, 43, 91, 120(C&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>5</td>
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<td></td>
<td></td>
<td>5</td>
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<tr>
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<td></td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;26&lt;/sub&gt;</td>
<td>105, 106(508), 41, 43, 91, 119(C&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>-</td>
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<td>Xylenes</td>
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<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;25&lt;/sub&gt;</td>
<td>120, 119, 105, 41, 91, 133(C&lt;sub&gt;9&lt;/sub&gt;)</td>
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<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
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<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;25&lt;/sub&gt;</td>
<td>118, 120, 105, 41, 91, 133(C&lt;sub&gt;9&lt;/sub&gt;)</td>
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<td>Trimethylbenzenes</td>
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<td>133, 119, 41, 134, 105, 147(C&lt;sub&gt;8&lt;/sub&gt;)</td>
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<td>Indans</td>
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<td>i) C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>6,7,8</td>
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<tr>
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<td></td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;23&lt;/sub&gt;</td>
<td>117, 11, 105, 41, 91, 43, 55(C&lt;sub&gt;7&lt;/sub&gt;)</td>
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<td>Thiophenes</td>
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<td>-</td>
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<td>111, 12, 43, 41, 97, 125(C&lt;sub&gt;7&lt;/sub&gt;)</td>
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<td>Furanos</td>
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<td>68, 41, 83, 43, 67, 55(C&lt;sub&gt;6&lt;/sub&gt;)</td>
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<td>Pyrroles</td>
<td><img src="image" alt="Pyrroles" /></td>
<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>80, 68, 43, 79, 81, 43(C&lt;sub&gt;7&lt;/sub&gt;)</td>
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<td>u-Phenylalk-1-enes</td>
<td><img src="image" alt="u-Phenylalk-1-enes" /></td>
<td>ii) C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;24&lt;/sub&gt;</td>
<td>91, 104, 92, 41, 55, 105(C&lt;sub&gt;9&lt;/sub&gt;)</td>
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<td>105, 106(508), 118, 41, 91, 131(C&lt;sub&gt;9&lt;/sub&gt;)</td>
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<td>ii) C&lt;sub&gt;2&lt;/sub&gt;-C&lt;sub&gt;23&lt;/sub&gt;</td>
<td>105, 106(508), 128, 41, 55, 131(C&lt;sub&gt;10&lt;/sub&gt;)</td>
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<tr>
<td></td>
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<td>ii) C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;21&lt;/sub&gt;</td>
<td>105, 119, 118, 41, 91, 51(C&lt;sub&gt;8&lt;/sub&gt;)</td>
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<td>1,4-Dihyronaphthalenes</td>
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<td>M&lt;sup&gt;+&lt;/sub&gt;(15, 0, 16), 115, M&lt;sup&gt;+&lt;/sub&gt;(17, 14)(C&lt;sub&gt;4&lt;/sub&gt;)</td>
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<td>Indenes</td>
<td><img src="image" alt="Indenes" /></td>
<td>i) C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>110, 129, 128, 145, 41, 115(C&lt;sub&gt;6&lt;/sub&gt;)</td>
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<tr>
<td>Compound Class</td>
<td>Parent Structure</td>
<td>Rank of Aliph Substitution</td>
<td>Characteristic Ions $^b$</td>
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</tr>
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<td>------------------------</td>
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<tr>
<td>Methylindenes</td>
<td><img src="image" alt="Methylindene" /></td>
<td>$i) C_2^1 - C_1^19$</td>
<td>$[14,143,157,41,129,115(C_6)]$</td>
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<td>Styrenes</td>
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<td>$i) C_0^5 - C_5$</td>
<td>$<a href="C_2">M^0 - (0,15,17,1,1,16)</a>$</td>
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<td>$[104,117,41,129,143,128(C_8)]$</td>
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<td>1,2-Dihydronaphthalenes</td>
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<td>$i) C_0^0 - C_2$</td>
<td>$<a href="C_1">M^0 - (15,0,16,1),115,117</a>$</td>
<td>9,10</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td><img src="image" alt="Naphthalene" /></td>
<td>$i) C_2^2 - C_2^20$</td>
<td>$[141,155,142,115,156,41(C_4)]$</td>
<td>8,9,10</td>
</tr>
<tr>
<td>$\ldots$</td>
<td><img src="image" alt="Diphenylmethane" /></td>
<td>$i) C_0^0 - C_3$</td>
<td>$<a href="C_2">M^0 - (0,15,17,1,1,10)</a>$</td>
<td>9,10</td>
</tr>
<tr>
<td>Benzofurans</td>
<td><img src="image" alt="Benzofuran" /></td>
<td>$i) C_0^0 - C_4$</td>
<td>$<a href="C_2">M^0 - (0,1),115,15,91,117</a>$</td>
<td>8</td>
</tr>
<tr>
<td>Benzothiophenes</td>
<td><img src="image" alt="Benzothiophene" /></td>
<td>$i) C_0^0 - C_4$</td>
<td>$<a href="C_2">M^0 - (0,1,15,-1),128,80</a>$</td>
<td>-</td>
</tr>
<tr>
<td>Fluorenes</td>
<td><img src="image" alt="Fluorene" /></td>
<td>$i) C_0^5 - C_5$</td>
<td>$<a href="C_2">M^0 - (15,0,16,14,-1),89</a>$</td>
<td>11,12</td>
</tr>
<tr>
<td>Phenanthrenes</td>
<td><img src="image" alt="Phenanthrene" /></td>
<td>$i) C_0^0 - C_2$</td>
<td>$<a href="C_2">M^0 - (15,0,17,1,16,-1)</a>$</td>
<td>10,11,12</td>
</tr>
<tr>
<td>Dibenzofurans</td>
<td><img src="image" alt="Dibenzofuran" /></td>
<td>$i) C_0^0 - C_3$</td>
<td>$<a href="C_4">M^0 - (0,1),76,63,152,51</a>$</td>
<td>-</td>
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<tr>
<td>Dibenzopyrans</td>
<td><img src="image" alt="Dibenzopryran" /></td>
<td>$i) C_0^0 - C_2$</td>
<td>$<a href="C_0">182,181,76,152,63,51</a>$</td>
<td>-</td>
</tr>
<tr>
<td>Dibenzothiophenes</td>
<td><img src="image" alt="Dibenzothiophene" /></td>
<td>$i) C_0^0 - C_3$</td>
<td>$<a href="C_1">M^0 - (0,1,1,3),99,165,152</a>$</td>
<td>-</td>
</tr>
<tr>
<td>Compound Class</td>
<td>Parent Structure</td>
<td>Range of Alkyl Substitution</td>
<td>Characteristic Ions</td>
<td>Fraction Number</td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------</td>
<td>-----------------------------</td>
<td>---------------------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Phenylnaphthalenes</td>
<td></td>
<td></td>
<td>$M^+-(0,1,2,101,108)(C_9)$</td>
<td>-</td>
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<tr>
<td></td>
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<td></td>
<td>$M^+-(0,1,115,202)(C_9)$</td>
<td>-</td>
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<td>$M^+-(0,1,115,202)(C_9)$</td>
<td>6</td>
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<tr>
<td>Fluoranthenes</td>
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<td></td>
<td>$M^+-(15,16,0,1,17),108(C_2)$</td>
<td>11</td>
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<td></td>
<td>$M^+-(15,16,0,1,17),108(C_2)$</td>
<td>3.1</td>
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<tr>
<td>Terphenyls</td>
<td></td>
<td></td>
<td>$M^+-(0,1),115,2,101,202(C_9)$</td>
<td>11</td>
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<td>$M^+-(0,1),115,2,101,202(C_9)$</td>
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<td>$M^+-(0,1),115,2,101,202(C_9)$</td>
<td>7</td>
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<tr>
<td>Pyrenees</td>
<td></td>
<td></td>
<td>$M^+-(0,1),108,95,180,2(C_1)$</td>
<td>11,12</td>
</tr>
<tr>
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<td></td>
<td>$M^+-(0,1),108,95,180,2(C_1)$</td>
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<td></td>
<td>$M^+-(0,1),108,95,180,2(C_1)$</td>
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<tr>
<td>Tetracyclic aromatics</td>
<td></td>
<td></td>
<td>$M^+-(0,15,17,16),120,121(C_2)$</td>
<td>12</td>
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<td>$M^+-(0,15,17,16),120,121(C_2)$</td>
<td>3.2</td>
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<td>$M^+-(0,15,17,16),120,121(C_2)$</td>
<td>7</td>
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<tr>
<td>Phenyliodoles</td>
<td></td>
<td></td>
<td>$M^+-(0,1,-1),104,103,79(C_1)$</td>
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<td></td>
<td>$M^+-(0,1,-1),104,103,79(C_1)$</td>
<td>3.2</td>
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<td>$M^+-(0,1,-1),104,103,79(C_1)$</td>
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<tr>
<td>Biphenyls</td>
<td></td>
<td></td>
<td>$M^+-(0,1,2),126,125,113(C_7)$</td>
<td>12</td>
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<td>$M^+-(0,1,2),126,125,113(C_7)$</td>
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<td>$M^+-(0,1,2),126,125,113(C_7)$</td>
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<tr>
<td>Benzopyrenes</td>
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<td></td>
<td>$M^+-(0,15,-1,1,4),140(C_2)$</td>
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<td>$M^+-(0,15,-1,1,4),140(C_2)$</td>
<td>3.3</td>
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<td>$M^+-(0,15,-1,1,4),140(C_2)$</td>
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<tr>
<td>Hexacyclic aromatics</td>
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<td>$M^+-(0,-1,2,15),138,137(C_1)$</td>
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<td>$M^+-(0,-1,2,15),138,137(C_1)$</td>
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<td>$M^+-(0,-1,2,15),138,137(C_1)$</td>
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<tr>
<td>Indoles</td>
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<td></td>
<td>$M^+-(1,0,15),77,103,115(C_2)$</td>
<td>13B</td>
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<td>$M^+-(1,0,15),77,103,115(C_2)$</td>
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<tr>
<td>COMPOUND CLASS</td>
<td>PARENT STRUCTURE</td>
<td>RANGE OF ALKYL SUBSTITUTION</td>
<td>CHARACTERISTIC IONS</td>
<td>FRACTION NUMBER</td>
</tr>
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<td>----------------------</td>
<td>------------------</td>
<td>----------------------------</td>
<td>---------------------</td>
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<td><strong>Carbazoles</strong></td>
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<tr>
<td></td>
<td><img src="image1" alt="Structure" /></td>
<td>1) C₈₋₃₉₋₄₋₅</td>
<td>M¹⁻(0,1,1),152,127,6₃(C₄₁)</td>
<td>138</td>
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<tr>
<td><strong>Phenylcyanides</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td><img src="image2" alt="Structure" /></td>
<td>1) C₈₋₃₉₋₄₋₅</td>
<td>M¹⁻(0,1),90,6₃(C₄₁)</td>
<td>14</td>
</tr>
<tr>
<td><strong>n-Alkanonitriles</strong></td>
<td>N=0-27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image3" alt="Structure" /></td>
<td>n=0-27</td>
<td>41,43,97,55,57,110(n=7)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td><img src="image4" alt="Structure" /></td>
<td>n=1-20</td>
<td>41,55,69,42,54,122(n=10)</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td><img src="image5" alt="Structure" /></td>
<td>n=1-18</td>
<td>41,55,69,56,122,54(n=10)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td><img src="image6" alt="Structure" /></td>
<td>n=2-19</td>
<td>41,55,83,122,69,54(n=8)</td>
<td>-</td>
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<tr>
<td><strong>Branched and/or cyclic nitriles</strong></td>
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<tr>
<td></td>
<td><img src="image7" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>57,43,41,55,71,96(C₁₀)</td>
<td>14</td>
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<td></td>
<td><img src="image8" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>41,55,43,97,57,8₃(C₃₆)</td>
<td>14</td>
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<tr>
<td></td>
<td><img src="image9" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>41,43,55,57,97,8₃(C₃₅)</td>
<td>3</td>
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<tr>
<td></td>
<td><img src="image10" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>43,41,55,57,6₉,7₁(C₃₆)</td>
<td>5</td>
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<td></td>
<td><img src="image11" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>4₃,4₁,5₅,₅₇,₇₁,₉₆(C₃₆)</td>
<td>5</td>
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<tr>
<td></td>
<td><img src="image12" alt="Structure" /></td>
<td>C₉₋₃₃</td>
<td>4₃,4₁,₅₅,₅₇,₇₈(C₃₆)</td>
<td>6</td>
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<tr>
<td></td>
<td><img src="image13" alt="Structure" /></td>
<td>C₉₋₃₃</td>
<td>4₃,4₁,₅₅,₅₇,₇₁(C₃₆)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td><img src="image14" alt="Structure" /></td>
<td>C₉₋₃₃</td>
<td>4₃,9₆,6₇,₄₁,₅₅,₄₃(C₃₅)</td>
<td>8</td>
</tr>
<tr>
<td><strong>2-Alkanones</strong></td>
<td><img src="image15" alt="Structure" /></td>
<td>n=0-27</td>
<td>5₈₄,4₃₅₅,₇₁,₄₁,₅₅(n=1₃)</td>
<td>15</td>
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<tr>
<td><strong>3-Alkanones</strong></td>
<td><img src="image16" alt="Structure" /></td>
<td>n=1-25</td>
<td>7₂₄,5₇₄₃₅₅,₇₁,₈₅(n=1₃)</td>
<td>15</td>
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<tr>
<td><strong>4-Alkanones</strong></td>
<td><img src="image17" alt="Structure" /></td>
<td>n=1-2₀</td>
<td>4₃₅₇₁₅₈₈₆₄₁(n=₅)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td><img src="image18" alt="Structure" /></td>
<td>C₇₋₃₃</td>
<td>4₃₅₇₁₅₈₈₆₄₁(n=₅)</td>
<td>-</td>
</tr>
<tr>
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<td><img src="image19" alt="Structure" /></td>
<td>C₇₋₃₃</td>
<td>5₅₄₃₅₇₁₅₈₈₆₄₁(n=₅)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Cyclopentanones</strong></td>
<td><img src="image20" alt="Structure" /></td>
<td>ii) C₂₋₃₂₅</td>
<td>8₄₅₅₅₄₁₉₇(C₄₁)</td>
<td>15</td>
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<tr>
<td><strong>Cyclohexanones</strong></td>
<td><img src="image21" alt="Structure" /></td>
<td>ii) C₂₋₃₂₃</td>
<td>9₉₄₃₅₅₄₁₉₇(C₄₁)</td>
<td>15</td>
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<td><img src="image22" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>4₃₅₇₁₅₈₈₆₄₁(C₄₂)</td>
<td>15</td>
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<tr>
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<td><img src="image23" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>7₂₄,5₇₄₅₈₅₄₁₉₇(C₃₃)</td>
<td>15</td>
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<td><img src="image24" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>8₆₃₅₇₁₅₈₅₄₁₉₇(C₃₃)</td>
<td>15</td>
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<td><img src="image25" alt="Structure" /></td>
<td>C₁₀₋₃₃</td>
<td>6₃₁₅₁₉₅₇₈₅₄₁₉₇(C₃₃)</td>
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<tr>
<td>COMPOUND CLASS</td>
<td>PARENT STRUCTURE</td>
<td>RANKING OF ALKYL SUBSTITUTION</td>
<td>CHARACTERISTIC IONS b</td>
<td>FRACTION NUMBER c</td>
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</tbody>
</table>
| 1-(Cyclopent-1-enyl)-2-alkanes | ![Image] | 1) $C_0^1$-$C_4$  
2) $C_2^1$-$C_{22}$  
3) $C_2^1$-$C_{21}$ | $m^+-(15,0), \{115,131,81,77\}(C_0)$  
$110,109,95,123,43,81(C_0)$  
$124,109,92,123,95,41(C_0)$ | 16,17  
16,17  
16,17 |
| Indanones              | ![Image]       | 1) $C_0^1$-$C_3$  
2) $C_2^1$-$C_{14}$ | $m^+-(15,0), \{115,131,81,77\}(C_3)$  
$160,117,132,41,43(C_3)$ | 16,17  
16,17 |
| Tetralones             | ![Image]       | 1) $C_0^1$-$C_3$  
2) $C_2^1$-$C_{13}$ | $m^+-(15,0), \{115,131,71,51\}(C_3)$  
$146,114,41,43,118,159(C_3)$ | 16,17  
16,17 |
| Pyridines              | ![Image]       | 1) $C_1^1$-$C_5$ | $m^+-(0,1), \{79,106,77,51\}(C_3)$ | Base fraction 1.1/2.0 |
| Cl-Pyridines           | ![Image]       | 1) $C_2^1$-$C_{25}$  
(3' isomers) | $107,120,41,43,134,77(C_0)$  
$121,134,41,43,77,148(C_0)$ | 2.3/3.1/  
3.2 |
| C2-Pyridines           | ![Image]       | 1) $C_2^1$-$C_{24}$  
(4' isomers) | $135,41,43,148,55,162(C_0)$  
$149,162,41,43,176,134(C_0)$ | 3.1/3.2/  
3.3 |
| C3-Pyridines           | ![Image]       | 1) $C_2^1$-$C_{23}$  
(3' isomers) | $153,41,43,148,55,162(C_0)$  
$163,176,41,43,180,148(C_0)$ | 3.1/3.2/  
3.3 |
| C4-Pyridines           | ![Image]       | 1) $C_2^1$-$C_{22}$  
(2' isomers) | $133,146,41,43,160,77(C_1)$  
$134,120,41,43,135,148(C_1)$ | 3.1  
3.5 |
| C5-Pyridines           | ![Image]       | 1) $C_2^1$-$C_{21}$  
(3' isomers) | $134,135,41,43,148,77(C_12)$ | 2.3 |
| Piperidines            | ![Image]       | 1) $C_1^1$-$C_3$ | $m^+-(15,56,42,41,70,41)(C_2)$ | Retort water |
| Dihydroindoles         | ![Image]       | 1) $C_0^1$-$C_2$ | $m^+-(15,131,130,91,77,41)(C_3)$ | Base fraction 1.1 |
| Anilines               | ![Image]       | 1) $C_0^1$-$C_1$  
(e.g.) | $m^+-(0,1), \{77,51,105,104\}(C_0)$ | 1.1 |

*Method 1, Method 2, Method 3*
<table>
<thead>
<tr>
<th>COMPOUND CLASS</th>
<th>PARENT STRUCTURE</th>
<th>RANGE OF ALKYL SUBSTITUTION</th>
<th>CHARACTERISTIC IONS&lt;sup&gt;b&lt;/sup&gt;</th>
<th>FRACTION NUMBER&lt;sup&gt;c&lt;/sup&gt;</th>
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<tr>
<td></td>
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<td>METHOD 1</td>
</tr>
<tr>
<td>Quinolines</td>
<td><img src="image" alt="Quinolines" /></td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>M&lt;sup&gt;(0,1),115,M&lt;sup&gt;1+1,89,129(C&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>base fraction</td>
</tr>
<tr>
<td>Benzoquinolines</td>
<td><img src="image" alt="Benzoquinolines" /></td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>M&lt;sup&gt;1+1,165,M&lt;sup&gt;1+1,151,167,177(C&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>-</td>
</tr>
<tr>
<td>n-Alkanoic acids</td>
<td><img src="image" alt="n-Alkanoic acids" /></td>
<td></td>
<td>24,87,45,41,55,57 (n=7; methyl ester)</td>
<td>acid fraction</td>
</tr>
<tr>
<td>2-Methylalkanoic acids</td>
<td><img src="image" alt="2-Methylalkanoic acids" /></td>
<td>n=0-5</td>
<td>57,85,56,45,103,60 (n=1; n-butyl ester)</td>
<td>retort water</td>
</tr>
<tr>
<td>Phenols</td>
<td><img src="image" alt="Phenols" /></td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>M&lt;sup&gt;(15,0,1),77,79,91(C&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>acid fraction</td>
</tr>
<tr>
<td>Naphthols</td>
<td><img src="image" alt="Naphthols" /></td>
<td>i) C&lt;sub&gt;0&lt;/sub&gt;-C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>M&lt;sup&gt;1,115,116,65,89,13+1(C&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>-</td>
</tr>
<tr>
<td>Pyrrolidones</td>
<td><img src="image" alt="Pyrrolidones" /></td>
<td>e.g.</td>
<td>M&lt;sup&gt;(0,1),43,41,71,70(C&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>retort water</td>
</tr>
</tbody>
</table>

Footnotes:

<sup>a</sup> Alkyl substitution comprised either a number of small alkyl groups (e.g., methyl, ethyl) or a single n-alkyl chain. These types of substitution are indicated by i) and ii), respectively, and the total number of substituent carbon atoms is given. For some structures, several isomeric series of type ii) were found.

<sup>b</sup> Characteristic ions, in order of decreasing abundance, are given for a mid-range homologue, indicated in brackets after the ion list. The diagnostic ion used for mass chromatograms is underlined.

<sup>c</sup> Method 1 = open column chromatography (section 3.3.2).
Method 2 = low pressure liquid chromatography on thermally modified aluminas (section 5.3.2).
Method 3 = low pressure liquid chromatography on alumina (section 4.3.2).
8. Geochemical and Pyrolytic Implications of Shale Oil Composition

8.1 Biological Precursors

Oil shale kerogen is a complex three dimensional polymer that comprises the remnants of organisms such as algae, bacteria and higher plants. The chemical substances present in contemporary living matter provide an indication of the compounds buried with fossil organic matter. Pyrolysis of contemporary organisms [143], their cell walls [143], or of other segregated cell materials gives many of the compound classes found in shale oils. Molecular weight distributions in the pyrolysates may differ markedly from those in shale oils due to a lower incidence of secondary pyrolytic reactions which are catalysed by the minerals present in shale. Moreover, during the course of geological burial many of the compounds present in the biological source material will have been leached away by groundwater, chemically decomposed or modified by bacterial reworking. Conversely, some reactions such as polymerisation and reductive deoxygenation will tend to immobilise the organic material into a three dimensional network and stabilise it against further chemical reaction. One consequence of these reactions will be that the molecular weight distribution of the original source material is obliterated when (random) pyrolytic
cleavage reactions re-convert the polymeric material into volatile 
fragments. Within these limitations some suggestions for the 
biological precursors of the main functional group classes in shale 
oil are discussed below.

Alkanes

Since carbon chains form the backbone of all biological 
molecules, there are many possible sources for shale oil alkanes. Of 
the biological compounds which have adequate stability to be 
incorporated into the kerogen, esters of saturated and unsaturated 
fatty acids and hydrocarbons (lipids) are most prominent. Algae are 
rich in lipids; carbon chain lengths range from $C_{14}$-$C_{22}$, with 
actual distribution and relative abundances depending on the 
particular algal species and in some cases e.g. *Botryococcus*, on the 
[3a, 8b]. nutrient status of the environment in which it grows. Plant waxes 
may also be present in oil shale. A (usually small) proportion of the 
lipids and waxes occurs in free form absorbed to other oil shale 
components but most is incorporated into kerogen apparently as a 
network of cross-linked polymethylene chains. When pyrolysed, 
alkyl radicals are generated by thermal cracking of the C-C bonds 
which then give rise to alkanes (cf. pyrolysis of polyethylene [144, 
145]).

Other alkanes identified in shale oil include alkylcyclo-
pentanes, alkylcyclohexanes and alkylmethylcyclohexanes.

2-Methylalkanes occur in plant waxes, bacterial waxes and marine organisms [146]. Intramolecular cyclisation of unsaturated fatty acids during diagenesis [147] may be responsible for the observed series of alkylcyclopentanes and alkylcyclohexanes. Table 9 lists the alkane markers of various biological precursors.

**Alkenes**

1- Alkenes, which are the most abundant alkenes in shale oil are considered to be derived from disproportionation of alkyl free radicals. This origin is supported by the similarity of n-alkane and 1-alkene profiles. Other sources may include β-elimination reactions of esters and amides [149]. The 2-, 3- and 4- positional isomers are either derived from 1-alkenes by isomerisation on oil shale minerals [134] or from an entirely different pyrolytic source; many fatty acids have unsaturated alkyl chains.

**Dienes**

These may be derived from the pyrolysis of kerogen moieties containing unsaturated alkyl chains or from polymethylene chains anchored at both ends to the kerogen network.

**Aromatics**

Both oxidative [150] and nuclear magnetic resonance studies [151] have shown that aromatics are constituents of kerogen. Some
<table>
<thead>
<tr>
<th>Alkane type</th>
<th>Characteristic feature</th>
<th>Probable source</th>
</tr>
</thead>
</table>
| normal alkanes    | $C_{12}$-$C_{21}$ with marked odd carbon-number preference $C_{15}$ and/or $C_{17}$ dominant  
|                   | $C_{23}$-$C_{35}$ with marked odd carbon-number preference $C_{27}$, $C_{29}$, or $C_{31}$ dominant  
|                   | $C_{19}$ or $C_{21}$ dominant $C_{22}$ prominent                                      | blue-green, green algae                              |
|                   | $C_{26}$-$C_{32}$ with marked even carbon-number preference $C_{28}$ and $C_{30}$ dominant  
| branched alkanes  | 6-, 7- and 8-methylheptadecane, iso and anteiso alkanes $C_{14}$-$C_{20}$ isoprenoids  
|                   | $C_{21}$-$C_{25}$ isoprenoids squalene ($C_{30}$ isoprenoid)                          | blue-green algae                                     |
| cyclic alkanes    | $C_{27}$-$C_{35}$ pentacyclic triterpanes of hopane series steranes  
|                   | perhydro-$B$-carotene                                                                  | blue-green algae, bacteria                           |
|                   |                                                                                       | higher plants                                        |
of these aromatics may have formed during diagenesis but others would originate from lignins (higher plants) and the remains of cell walls (bacteria and algae). Although the aromaticity of the parent kerogen is reflected in the composition of the shale oil, the pyrolysis products and their relative proportions will, however, vary with shale mineralogy and retorting conditions [134]. The formation of aromatics is thermodynamically favoured [152] and minerals (and decomposing kerogen) are active catalysts.

**Nitriles**

Nitrile fractions from shale oil often show a distinct even/odd carbon number preference which suggests they may originate from biosynthesized fatty acid derivatives. Evans et al [141] have shown that nitriles can only be formed from shales, or other carbonaceous sediments, when both carboxylic acids and an inorganic species capable of producing ammonia when heated (e.g. buddingtonite) are present. In the absence of the latter, nitriles could be produced by pyrolysis in an ammonia atmosphere. Evans et al [141] also found that the carbon chain length distribution of nitriles was similar to that of the fatty acids isolated from the parent shale or brown coal.

**Ketones**

The appearance of an odd/even carbon number preference in
2-alkanone fractions suggests a biological precursor with one possible pathway being the \(\beta\)-oxidation of fatty acids followed by ready decarboxylation of the resultant \(\beta\)-keto acid [149]. 3-Ketones are possibly derived from decarboxylation of \(\beta\)-ketoesters of the type RCOCH(CH\(_3\))COOR under neutral or acidic conditions.

2-Alkylsubstituted fatty acids have been detected in certain classes of bacteria [153]. A recent study of the pyrolysis of carboxylic acids, however, suggests that free fatty acids are the main source of the homologous series of ketones found in shale oil [134].

**Acids**

Phenols are common constituents of higher plants and in particular are structural elements of lignins (from land plants) and tannins (from algae and land plants). Phenols may also be derived from the pyrolytic cyclodehydrogenation of \(\beta\)-alkenols or \(\beta\)-alkenones [134]. A correlation has been found between the lignin content of oil shales and the phenolics present in the corresponding shale oils (refer to section 8.1.2.).

**Bases**

Proteins and nucleic acids are presumed to be original sources of most of the nitrogen heterocycles found in shale oil which includes pyridines, quinolines, dihydroindoles, indoles and
carbazoles. However, some bases e.g., pyridines, may also be of pyrolytic origin, being derived from either alkyl amines or the ammonium salts of carboxylic acids (cf. heptanedioic acid/NH₃ [134]).
8.2 Comparison of the Properties of Oil Shales from the
Condor Brown and Carbonaceous Units

8.2.1 Introduction

The Condor deposit contains two major oil shale seams: a Brown or Normal seam and an underlying seam of Black or Carbonaceous shale. Petrological studies [154] suggest that the Normal seam was deposited in a lacustrine environment and the presence of large amounts of alginitic in the oil shale indicates that the primary organic source material was algae. The Carbonaceous seam was deposited under swampy conditions and predominately comprises the remains of terrestrial plants as indicated by the high concentration of vitrinite (cell walls of wood) and smaller amounts of resinite, sporinite and cutinite. The Normal seam is referred to as being of lamosite origin and the Carbonaceous seam as being of lignite origin.

The purpose of this study was to examine the effect of differences in petrology on the retorting properties of the two oil shales and on the chemical composition of their pyrolysates. Studies on the oil evolution, gas evolution and analyses of the oils by nuclear magnetic resonance spectrometry (NMR) were performed by the Lucas Heights Research Laboratory of CSIRO, Division of
Energy Chemistry. NMR was performed using a Joel GX400 instrument. Details of the samples used in this study, the shale oil separation scheme and the instruments used for the analysis of the shale oil fractions are given in sections 3.3.1 - 3.3.3.

8.2.2 Results and Discussion

1) Chemical properties

The Fischer assay oil yields obtained from samples of the Brown and Carbonaceous shales were similar, but the properties of the two shale types differ significantly (Table 10). The Carbonaceous shale was characterised by a very high organic carbon content of 43.9% compared to 13.8% for the Brown shale, by a correspondingly higher kerogen content, and by a significantly lower atomic H/C ratio of the kerogen. The efficiency of the conversion of the organic carbon in the samples to liquid products by retorting was much lower for the Carbonaceous shale, and the char resulting from the retorting (by Fischer assay) of the Carbonaceous shale contains 46% organic carbon compared to the more usual 4.2% found for the Brown shale. These observations suggest that the kerogen of the Carbonaceous shale is much more aromatic than that of the Brown shale. This conclusion was confirmed by the results of solid state $^{13}$C NMR studies of the two
**Table 10:** Comparison of the properties of oil shales from the Condor Brown and Carbonaceous Units.

<table>
<thead>
<tr>
<th>Property</th>
<th>Brown Unit</th>
<th>Carbonaceous Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fischer assay (L/tonne)</td>
<td>73</td>
<td>69</td>
</tr>
<tr>
<td>% Organic carbon</td>
<td>13.8</td>
<td>43.9</td>
</tr>
<tr>
<td>Oil yield (g oil/g organic carbon)</td>
<td>0.40</td>
<td>0.15</td>
</tr>
<tr>
<td>% Kerogen</td>
<td>27</td>
<td>43</td>
</tr>
<tr>
<td>H/C ratio of kerogen</td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td>$^{13}$C aromaticity*</td>
<td>0.32</td>
<td>0.62</td>
</tr>
<tr>
<td>% Organic carbon in char</td>
<td>4.2</td>
<td>46</td>
</tr>
</tbody>
</table>

* Determined by CP/MAS $^{13}$C NMR of the demineralised shale. Analysis performed by the CSIRO Division of Fossil Fuels, North Ryde.

**Table 11:** Gas yields (cc/min/g) to 850°C of oil shales from the Condor Brown and Carbonaceous Units.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Brown Unit</th>
<th>Carbonaceous Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shale</td>
<td>Kerogen</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>110</td>
<td>91</td>
</tr>
<tr>
<td>Methane</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>115</td>
<td>8</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>58</td>
<td>26</td>
</tr>
</tbody>
</table>
kerogens, which showed that approximately 62% of the carbon atoms in the kerogen from the Carbonaceous shale are present as aromatic and carboxyl species, compared to 32% for the kerogen derived from the Brown shale. In comparison to Green River Shale with a typical aromaticity of 20% [155], even the Condor Brown shale must be regarded as a relatively aromatic material.

ii) Retorting properties

The oil evolution from the Carbonaceous shale (Figure 41) occurs over a broad range of temperatures and involves two major reactions with maxima at 440 and 490°C. In contrast, the oil evolution from the Brown shale (Figure 41) occurs over a small, well defined range and involves only one reaction which is maximised at 460°C.

The effect of temperature on the rates of carbon dioxide, hydrogen and methane evolution from the Carbonaceous and Brown shales, and their respective kerogens, are given in Figure 42. The integrated gas yields are given in Table 11. All gas evolution rates are expressed as cm$^3$(STP) of gas evolved per minute per gram of organic carbon. The most notable difference between the two shale types was observed for the hydrogen evolution profiles. The Brown shale shows a prominent peak at approximately 460°C which is close to the temperature at which the rate of oil evolution is
Effect of temperature on the rate of oil evolution from oil shales of the Condor Brown and Carbonaceous Units. The heating rate was 3°C per minute.
Figure 42: Effect of temperature on the rates of evolution of carbon dioxide, hydrogen and methane from oil shales and kerogens of the Condor Brown (B) and Carbonaceous (C) Units.
Figure 42: cont'd...

B

TEMPERATURE (degrees C)

RATE OF H₂ EVOLUTION (cc/min/g)

shale

kerogen

C

TEMPERATURE (degrees C)

RATE OF H₂ EVOLUTION (cc/min/g)

kerogen

shale
Figure 42: cont'd...

**B**

RATE OF CH$_4$ EVOLUTION (cc/min/g)

<table>
<thead>
<tr>
<th>Temperature (degrees C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

kerogen

shale

**C**

RATE OF CH$_4$ EVOLUTION (cc/min/g)

<table>
<thead>
<tr>
<th>Temperature (degrees C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<tr>
<td>0</td>
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</tbody>
</table>

kerogen

shale
maximum. A second, broad maximum was also observed in the temperature range 650 - 750°C. This is generally regarded as the secondary pyrolysis region in which further decomposition and, presumably, aromatisation of non volatile compounds occurs. By contrast, the hydrogen evolution from the Carbonaceous material occurs almost entirely in the secondary pyrolysis region. No indication of any maximum in the hydrogen evolution rate at temperatures at which oil evolution occurs was observed. Similar behaviour has also been reported [118, 156, 157] for bituminous coals and this appears to reflect the lignitic character of the Carbonaceous shale.

Demineralisation of the shales resulted in no significant change in either the shape of the hydrogen evolution profile or the total hydrogen yield from the Carbonaceous shale. However, demineralisation of the Brown shale resulted in a significant reduction in the hydrogen evolved at low temperatures (400-500°C) while the yield of hydrogen evolved in the secondary pyrolysis region was virtually unchanged. This observation suggests that at least part of the hydrogen evolved at the low temperatures is the result of oil decomposition reactions involving the mineral components of the shale.

The methane evolution profiles obtained from the two shales
were similar, with maxima occurring in the temperature range 450-550°C. These temperatures are higher than those at which oil evolution reaches a maximum rate. An unusual aspect of the results was the significant increase in methane yield resulting from the pyrolysis of the demineralised shale. Until the processes leading to methane formation are understood, however, it is difficult to determine the origins of this effect.

The carbon dioxide evolution from both shales was confined to a temperature range over which oil formation occurs. Demineralisation of the shales largely eliminated the carbon dioxide evolution from both the Brown and Carbonaceous shales. The small amounts of carbon dioxide that were observed occurred only at relatively low temperatures and was probably related to the decomposition of the organic components of the shale [157]. These observations suggest that the majority of carbon dioxide evolved from either shale was derived from the decomposition of mineral carbonates.

III) Characterisation of shale oil by NMR

The 75 MHz $^{13}$C spectra of the two whole oils, run in CDC$_3$ solution, are given in Figure 43. The spectrum of the Brown shale oil (43B) was typical of an average aliphatic shale oil, with the dominant signals, at 14.2, 22.8, 32.1, 29.5 and 29.9 ppm being due
Figure 45: 75 MHz $^{13}$C NMR spectra of whole oil from the Condor Brown (B) and Carbonaceous (C) Units. S = solvent, A = phenol, $\alpha$ = $\alpha$-cresol, $m$ = $m$-cresol and D = $p$-cresol.
primarily to carbons 1, 2, 3, 4 and 5+ respectively of n-alkanes. The relative sizes of these signals can be used to calculate the average chain length of the alkanes [158] although contributions from n-alkenes must be considered. For the Brown shale oil the average was 18-19 carbons. The sharp signals in the aromatic region (100-160 ppm) were mainly due to alkenes, with the most intense (114.2 and 139.2 ppm) being from linear 1-alkenes. The aromatics present in the shale oil gave rise to a broad signal between ca. 120 and 140 ppm. The fraction of carbon in the sample which was aromatic (fa) was calculated by comparing the integral of the full aromatic region with that of the total spectrum. For the Brown shale oil, fa was found to be 0.27 although this must include olefinic carbons as well.

The spectrum of the Carbonaceous oil (Figure 43C), while very similar in the aliphatic region (average chain length of n-alkanes also 18-19), had many extra resonances in the aromatic region in positions characteristic of phenols. With reference to standard spectra it was possible to assign the major peaks to phenol and the three cresol isomers. In keeping with the extra aromatic phenolic carbons, fa for this oil was found to be 0.36. The corresponding 300 MHz ^1H spectrum (Figure 44) of the Carbonaceous oil differed largely in the percentage of aromatic protons (16.6% Carbonaceous
Figure 44: 300 MHz $^1$H NMR spectra of whole oil from the Condor Brown (B) and Carbonaceous (C) Units. S = solvent.
Some of the aromatic signals were again assignable to phenol and the three cresols as were those centered around 2.3 ppm. Although, accurate figures are difficult to obtain from these and the $^{13}$C spectra, the phenolics content of the Carbonaceous oil was estimated as 10-15%, while for the Brown shale oil it was less than 2%.

iv) Characterisation of shale oils by open column chromatography and GC/GC-MS

The concentrations of the main chemical class fractions separated by column chromatography (section 3.3.2) from both the Carbonaceous and Brown oils are given in Table 4. The chemical classes identified in each oil by GC-MS are summarised in Table 5. Selected gas chromatograms of various fractions from the Carbonaceous and Brown oils are given in Appendix 1. The major differences observed between each of the main chemical classes separated from the two oils were as follows:

Alkanes

The alkanes of the Carbonaceous oil (30 wt%) were more abundant than those of the Brown oil (27 wt%) and were trimodal in distribution (maxima at $C_{10}$, $C_{14}$ and $C_{25}$; Figure 1A) compared to bimodal in the Brown oil (maxima at $C_{11}$ and $C_{27}$). Other
differences noted were, inversion of the carbon number preference
(odd/even in Carbonaceous oil and even/odd in Brown oil) and a
higher relative abundance of pristane (Figure 1A1) in the
Carbonaceous oil.

*Alkenes*

The alkenes of the Carbonaceous oil (17 wt%) were more
abundant than those of the Brown oil (13 wt%). Both oils contained
linear 1-, 2-, 3- and 4- alkenes and were unimodal (maximum at C9
for the Carbonaceous oil, Figure 1A2; and C11 for the Brown oil,
Figure 1A9). The most noticeable difference in the alkene content of
the two oils was the greater relative abundance of 1- and
2-pristene in the Carbonaceous oil. In the Brown oil, the pristene
isomers (Figure 1A9) were as abundant as the adjacent linear
1-alkenes. In the Carbonaceous oil (Figure 1A2), 1-pristene was
equal in abundance to the most abundant 1-alkene (C9) while
2-pristene was at least twice as abundant. The higher
concentration of pristenes in the Carbonaceous oil again correlates
with the high lignite content of the Carbonaceous kerogen and the
inferred greater proportion of higher plant source material.

*Dienes*

Both oils contained the same range of dienes (C8–C18) and a
similar range of positional isomers. The quantity of dienes in the Carbonaceous oil (0.5 wt%), however, was only half that in the Brown oil (1.0 wt%).

Aromatics

The Carbonaceous and Brown oils contained similar amounts (2.2 wt%) of homologous series of alkylbenzenes (maxima at C₈ and C₅, respectively). The Brown oil contained homologous series of alkyltoluenes and alkylxylenes, but these were absent in the Carbonaceous oil (Figure 1A3). This is probably due to the much higher carbon content of the Carbonaceous shale compared to the Brown shale which comprises mainly clays; Regtop et al. [134] have shown that cracking of hydrocarbons occurs better over carbon than clays.

The types of polynuclear aromatic hydrocarbons (2-5 ring) identified in the two oils were very similar and included multi alkyl substituted naphthalenes, biphenyls, phenanthrenes, fluorenes, fluoranthenes, pyrenes and benzopyrenes (also refer to Table 5). Variations in the relative proportions of the ring number fractions were evident in the two oils, particularly between the multi alkyl substituted monoaromatics (Brown shale, 3.4 wt%; Carbonaceous shale, 6.2 wt%), the tetracyclic aromatics (0.5 wt%...
4.6 wt%) and the pentacyclic aromatics (1.5 .cf. 3.0 wt%). The remaining aromatic subfractions were of similar abundance in the two oils.

The same range of oxygen heterocycles (benzofurans and dibenzofurans) and nitrogen heterocycles (indoles and carbazoles) were also identified in the two oils. Significantly, the oxygen heterocycles had greater relative abundance in the Carbonaceous oil (3.8 .cf. 1.0 wt%); oxygen heterocycles are typical components [159] of liquids derived from coal (which is largely of lignite origin).

**Nitriles**

The nitriles isolated from the two oils showed several major differences. Firstly, the nitrile fraction of the Carbonaceous oil (2.4 wt%) was less than half that of the Brown oil (5.7 wt%). Secondly, the Carbonaceous oil nitriles (Figure 1A4) were trimodal with maxima at C7, C18 and C28 and comprised mainly low and high molecular weight homologues whereas those of the Brown oil (Figure 1A12) showed at least four separate maxima and were mainly of intermediate chain length. Neither oil had a noticeable even/odd carbon number preference.

The lower relative abundance of nitriles in the Carbonaceous oil is in accordance with a lignite origin for the Carbonaceous kerogen, as compared with lamosite origin for the Brown kerogen.
The smaller contribution from algae to the Carbonaceous kerogen would mean that fewer fatty acids (biological nitrile precursors [141]) would be incorporated into the Carbonaceous kerogen.

**Ketones**

The 2-alkanone series isolated from the two oils differed greatly. While the Carbonaceous oil (Figure 1A5) comprised a broad range of methyl ketones ($C_7$–$C_{26}$) with a predominance of low molecular weight homologues (maximum at $C_8$), the Brown oil (Figure 1A13) contained only a limited range of methyl ketones ($C_9$–$C_{21}$) which were mainly of intermediate chain length (maximum at $C_{14}$). In addition, the 2-alkanones of the Carbonaceous oil had a slight even/odd carbon number preference which was not evident in the 2-alkanones of the Brown oil.

1-(Cycloalk-1-enyl)-2-alkanones

The Brown oil contained both, multi alkyl substituted ($C_0$–$C_4$) and homologous series ($C_2$–$C_{17}$) of 1-(cycloalk-1-enyl)-2-alkanones. The Carbonaceous oil contained multi alkyl substituted 1-(cycloalk-1-enyl)-2-alkanones ($C_0$–$C_4$) and, indanones and tetralones (multi alkyl substituted, $C_0$–$C_3$ and; homologous alkyl substituted series, $C_2$–$C_{14}$).
The indanones and tetralones are more polar than the 2-alkanones, due to the presence of an aromatic ring conjugated to the keto group, and therefore eluted with the 1-(cycloalk-1-enyl)-2-alkanones. Since indanones and tetralones were not found in the Brown oil, their presence in the Carbonaceous oil may be related to the lignite component of the Carbonaceous kerogen.

**Polymeric matter**

The Brown and Carbonaceous shale oils formed similar amounts of polymeric artefact on extraction with acid and on contact with the alumina/silica column. The Carbonaceous oil, however, formed a much greater amount (5.2 wt%) of polymeric artefact during base extraction than did the Brown oil (1.0 wt%). NMR analysis of the Carbonaceous oil indicates that a greater proportion of phenolic compounds are present in the oil (10-15 wt%) than is actually isolated by extraction with aqueous base (4.4 wt%). It is possible that the alkali artefacts are the other phenolic carbon moieties observed by NMR. If this is so, these compounds probably have greater alkyl substitution than those found in the acid fraction; the phenoxide ions from highly alkyl substituted phenols have low water solubility (due to the presence of polymethylene chains) and low solubility in organic solvents (since they are mostly in anionic form).
Acids and bases

The acid fraction of the Carbonaceous oil (4.4 wt%) was of greater concentration than that of the Brown oil (0.3 wt%) and comprised, in addition to the phenol and cresols found in the Brown oil (Figure 1A14), dimethyl-, trimethyl- and tetramethylphenols (Figure 1A7). The content of polyalkyl-phenols in the Carbonaceous oil is similar to that of coal pyrolysates which again points to the lignite character of the Carbonaceous kerogen.

The basic compounds identified in the Carbonaceous oil were very similar to those identified in the Brown oil and comprised mainly pyridines (C$_1$-C$_3$) and quinolines (C$_6$-C$_2$). Comparison of the GC profiles of the base fractions from the Carbonaceous and Brown oils (Figures 1A8 and 1A15, respectively) shows that the type and carbon number of alkyl substituents on the pyridine and quinoline homologues are similar for the two oils. These results, in conjunction with the lower relative abundance of bases in the Carbonaceous oil, suggest that the bases observed in either oil are mostly derived from the lamosite contributions to the kerogens.

The largely lignite origin of the Carbonaceous shale is reflected in both the chemical properties of the kerogen and in the composition of the shale oil. The high kerogen content of this shale, its high aromaticity and the high carbon content of its pyrolysis
char are more characteristic of a Brown or low grade bituminous coal than an algal derived oil shale. Similarly, the high aromaticity and the high content of oxygenated aromatic compounds (benzofurans, dibenzofurans, indanones, tetralones and, in particular, phenols) of the oil retorted from this shale are more characteristic of coal derived liquids than shale oils.
8.3 Comparison of the Chemistry of Oils from the Condor Brown Unit Pyrolysed by Fischer Assay and Under Nitrogen

8.3.1 Introduction

The recovery of shale oil from the retort apparatus depends on the rate at which pyrolysate is able to diffuse through the mineral matrix. In the event of poor diffusion, increased residence time of the pyrolysate over the mineral matrix may alter the chemical composition of the resulting shale oil (by cracking which results in a larger proportion of gaseous products or by secondary pyrolytic reactions e.g., cyclisation, aromatisation) and also reduce yields. By passing a chemically inert gas, e.g., helium or nitrogen, through the retort during pyrolysis, the pyrolysate may be recovered more rapidly and more efficiently.

The purpose of this study was to show how the gaseous environment during retorting and the residence time of the pyrolysate in contact with the mineral matrix could influence the chemical composition of the shale oil. This involved comparing the chemical composition of shale oils generated under normal retort conditions (Fischer assay) and under conditions in which the pyrolysate is swept from the retort vessel by a stream of inert gas. Hereafter these two shale oils are referred to as the Fischer assay
and swept oils, respectively.

The samples used for this study, the shale oil separation scheme and the instruments used for the analysis of the shale oil fractions are described in sections 3.3.1 - 3.3.3.

8.3.2 Results and Discussion

The yields of the fractions separated from the Fischer assay and swept shale oils are given in Table 4. The chemical classes identified in each oil, by GC-MS, are summarised in Table 5. Selected gas chromatograms of various fractions from the Fischer assay and swept oils are given in Chapter 3 and Appendix 1, respectively. The main differences observed between each of the chemical class fractions separated from the two oils were as follows:

**Alkanes**

The proportion of alkanes separated from the swept oil (27 wt%) was slightly greater than that separated from the Fischer assay oil (25 wt%). Both oils contained the same range and relative distribution of alkanes (i.e. $C_8-C_{33}$, maxima at $C_{11}$ and $C_{27}$). Isoprenoid alkanes ($C_{13}-C_{16}$, $C_{18}-C_{20}$) were also equally abundant in the two oils.
Alkenes

Several differences were found between the alkene fractions of the Fischer assay and swept oils:

i) The alkenes of the swept oil (13 wt%) were less abundant than those of the Fischer assay oil (16 wt%).

ii) 1- and 2-pristene were of approximately 2.5 greater concentration in the swept oil (Figure 1A9) than in the Fischer assay oil (Figure 8).

iii) In the swept oil, the ratio of 1-alkene: 2-alkene: 3-alkene: 4-alkene was approximately constant for all carbon chain lengths. In the Fischer assay oil the proportion of 2-, 3- and 4-alkenes (relative to the 1-alkenes) increases with increasing carbon chain length.

These results demonstrate the importance of residence time of alkenes over the mineral matrix; increased residence time enables more alkenes to be formed (by disproportionation of alkyl radicals) and double bond isomerisation occurs to a larger extent.

Dienes

These were less concentrated in the swept oil (1.0 wt%) than in the Fischer assay oil (2.0 wt%), comprised fewer positional isomers and were, on average, of smaller carbon chain length than those separated from the Fischer assay oil. This suggests that
dienes arise mainly from secondary reactions rather than pyrolysis of kerogen moieties containing unsaturated alkyl chains as previously suggested [119].

Aromatics

The aromatic subfractions of the swept oil collectively constitute about 22 wt% of the total oil whereas in the Fischer assay oil they constitute only 13 wt%. This difference mainly arises from the lower abundance of multi alkyl substituted monoaromatics (7, swept cf. 2 wt%, Fischer assay oil), bicyclic aromatics (4 cf. 1 wt%) and tricyclic aromatics (5 cf. 3 wt%). The relative distributions of each aromatic class were similar for the two oils (refer to Table 5) which suggests that the aromatics were better recovered from the swept oil shale. Decreased residence time of the aromatics over the mineral matrix would minimise the opportunity for complexation and further reaction of the aromatics by secondary mechanisms such as radical combination, cyclisation and further aromatisation.

Oxygen and Nitrogen Heterocycles

As a result of refinements to the solvent program of the separation scheme for the swept oil, two new classes of compounds (oxygen and nitrogen heterocycles) were identified. Oxygen heterocycles ($C_0$–$C_4$ substituted benzofurans, Figure 1A10)
were separated by changing the eluate volumes used for the separation of aromatics, and nitrogen heterocycles ($C_0$-$C_4$ substituted indoles and $C_0$-$C_3$ substituted carbazoles, Figure 1A11) were separated by introducing a new gradient (hexane/dichloromethane; 7:3, v/v) into the solvent program.

**Nitriles**

Several differences were observed between the nitrile fractions of the Fischer assay (Figure 13) and swept oils (Figure 1A12):

i) The Fischer assay oil nitriles represent 10 wt% of the total oil whereas the swept oil nitriles only represent 6 wt%.

ii) A distinct odd/even carbon number preference is present in the nitriles of the Fischer assay oil but is absent in the swept oil nitriles.

iii) The Fischer assay oil nitriles increased in relative abundance with increasing carbon chain length (maxima at $C_{13}$, $C_{18}$ and $C_{21}$) whereas the swept oil nitriles were mainly of medium carbon chain length abundance ( maxima at $C_{12}$, $C_{22}$ and $C_{30}$)

iv) The nitrile fraction from the swept oil contained additional homologous series of compounds of unknown identity.

The gravimetric difference between the nitrile fractions can
The absence of high molecular weight nitriles in the swept oil may be due to shorter residence time of nitrile precursors in the swept retort apparatus.
be partially accounted for by including the weight of the nitrogen heterocycles from the swept oil (2 wt\%) in that of the swept oil nitrile fraction. Nitrogen heterocycles were not separated from the nitriles in the analysis of the Fischer assay oil and would have contributed to their gravimetric assay. This still leaves a variation of 3 wt\% which is apparently due to the lower abundance of high molecular weight nitriles in the swept oil.

**Ketones**

A greater quantity of 2-alkanones was isolated from the Fischer assay oil (6 wt\%) than from the swept oil (2 wt\%). The swept oil 2-alkanone fraction (Figure 1A19) comprised C\textsubscript{9}-C\textsubscript{21} homologues while the Fischer assay oil 2-alkanone fraction comprised C\textsubscript{8}-C\textsubscript{31} homologues. Since the oil shale samples used to generate the two oils were identical, these results suggest that the range of methyl ketones observed in the swept oil is a better reflection of the distribution of 2-alkanone precursors in the oil shale (through reduced residence times) than is the 2-alkanones of the Fischer assay oil.

**1-(Cycloalk-1-eny)-2-alkanones**

The components isolated from the Fischer assay and swept oils by the chloroform/ether (4:1, v/v) gradient, (several dark,
Involatile bands and 1-(cycloalk-1-enyl)-2-alkanones were less abundant in the swept oil than in the Fischer assay oil. No major qualitative differences were evident between the 1-(cycloalk-1-enyl)-2-alkanones isolated from either oil which suggests that the gravimetric difference is accounted for by a lower proportion of involatile matter in the swept oil.

Polymeric matter

A significant proportion of the swept and Fischer assay oils polymerised in the course of the analysis and the artefacts formed subsequently appeared in the subfractions obtained using polar eluents and in the aqueous acidic and basic extracts. However, the total amount of polymeric artefact found in the swept oil (10 wt%) was considerably less than that in the Fischer assay oil (18 wt%). Only the amount of artefact formed by acidic extraction was comparable (4.1, Fischer assay; cf. 5.1 wt%, swept oil). These results suggest that the presence of an inert, sweeping gas during pyrolysis results in a chemically more stable shale oil.

Acids and bases

The acid fraction of the swept oil (0.3 wt%) was half the concentration of that from the Fischer assay oil (0.7 wt%) and comprised mainly C_0 – C_1 phenols (Figure 1A14) whereas the Fischer assay oil (Figure 5) comprised in addition C_2 – C_4 phenols.
The bases in the swept oil (1.0 wt%) comprised mainly $C_1-C_4$ substituted pyridines and smaller concentrations of $C_0-C_3$ quinolines (Figure 1A15) whereas the Fischer assay oil bases (1.3 wt%) comprised, in addition, $C_4$ and $C_5$ substituted quinolines and a variety of other high molecular weight base compounds (Figure 6). These results show that the acids and bases generated under an inert, sweeping atmosphere underwent fewer secondary reactions.

Pyrolysis of oil shale, in the presence of an inert carrier gas, reduces residence times of the pyrolysates over the mineral matrix. This minimises the opportunity for secondary reactions (cyclisation, aromatisation and isomerisation) of the pyrolysate. The ensuing shale oil contains a lower proportion of higher molecular weight (heavily alkylated) homologues in the different chemical classes and is less prone to artefact formation. 'Swept' shale oil is therefore likely to be a more accurate representation of the primary pyrolysis products from oil shale kerogen than is shale oil generated by normal Fischer assay.
8.4 Role of Free Radicals in Shale Oil Formation

8.4.1 Introduction

While the geochemical origins of oil shales can vary significantly, the differences in the chemical composition of the respective shale oils is often not as pronounced. Only the relative proportions of the various chemical classes changes depending on such factors as the maturity of the kerogen (Chapter 5) and the relative contributions of lamosite and lignite to the kerogen (section 8.2), etc. The similarities arise because oil shale pyrolysis requires temperatures in excess of $400^\circ$C if it is to occur at a rapid rate. At these temperatures only a limited number of stable free radicals will survive. The structures of the free radicals (and ultimately the composition of the shale oil) is therefore, more dependent on thermodynamics than the biological precursors from which they are derived. This is supported by recent work [134] which has shown that only a small number of model aliphatic precursors are necessary to produce a large proportion of the products observed in shale oil.

The purpose of the following discussion was to examine the role of free radicals in shale oil formation. From a better understanding of oil shale pyrolysis, improved retorting procedures
*The final products observed could reflect either kinetic or thermodynamic control.
may be designed. Also, the conclusions drawn in this study may aid
the structure elucidation of new chemical classes. The background
for this interpretation was mainly obtained from Chapter 7.

8.4.2 Discussion

In the pyrolysis of oil shale kerogen, ESR studies show that
free radicals are formed [160], presumably by homolytic fission of
kerogen moieties. The free radicals give rise to the chemical
classes observed in shale oil by both primary and secondary
reactions. Primary reactions are those in which free radicals, once
generated, immediately combine with one another to give stable
products. Secondary reactions are those in which the free radicals
or their products undergo further rearrangement (e.g., disproport-
ionation, cyclisation, aromatisation).*

The radicals that are considered to be responsible for the
more abundant compounds observed in shale oil are probably as
follows:

*Alkyl radicals

These would be the most abundant free radicals during oil
shale pyrolysis. The most likely source for the alkyl radicals would
be thermal cracking of C-C bonds. A main source is likely to be
cross linked polymethylene chains (cf. pyrolysis of polyethylene [144, 145]) although
via either free radical reactions or ionic reactions catalysed by clays and other minerals.
contributions from other sources such as plant waxes cannot be
discounted. Since the thermodynamic stability of alkyl radicals
decreases in the order \( \text{CH}_3^- > \text{CH}_3\text{CH}_2^- > \text{CH}_3(\text{CH}_2)_2^- \cdots \text{etc} \), the most
abundant alkyl radicals present during retorting would be, in
decreasing order of abundance, methyl > ethyl > propyl > \cdots \text{etc}. This
order is reflected in the relative abundance of hydrocarbons
collected from the pyrolysis of oil shale i.e. methane > ethane >
propane > \cdots \text{ etc [156a]. } n\text{-Alkanes are the major product from alkyl
radicals and are formed by either addition of } H\text{- or radical coupling.}

1\text{-Alkenes, the second most abundant chemical class found in
shale oil, may also be derived from alkyl radicals through } H\text{-
abstraction. Once formed, a proportion of the 1\text{-alkenes are
isomerised to yield 2-, 3- and 4- alkenes, } \star

Aromatics are an integral part of oil shale kerogen [151] but it
has been demonstrated that they are also readily formed by
cyclodehydrogenation of alkanes and alkenes [134]. It is more likely
that the aromatics are of pyrolytic origin rather than biological
origin because their proportion decreases linearly with increasing
aromaticity i.e. monoaromatics > bicyclic aromatics > tricyclic
aromatics > \cdots \text{etc. This order can be explained by aromatics with } n
rings being derived from aromatics with } n-1 \text{ rings by aromatisation
of an alkyl substituent; aromatics of biological origin would}
probably show random variation in relative proportion. The proportion of alkyl radicals in the retort decreases in accord with the decreasing abundance of aromatics with increasing ring number. Both kinetics and thermodynamics [152] would disfavour the formation of large ring number aromatics in the pyrolysate by secondary reactions.

Subsequent to the formation of the various aromatic class types, the relative distribution of alkyl radicals in the retort would still play an important role in determining the type of alkyl substitution. Within each of the aromatic ring number subfractions a common pattern of alkyl substitution is observed. Polyalkyl substituted aromatics are always more abundant than the n-alkyl aromatics. Even within each category of alkyl substitution, i.e. polyalkyl or n-alkyl, the pattern is always identical. For the polyalkyl substituted aromatics the decreasing order of abundance is \( C_1 \) aromatic \( > C_2 \) aromatic (dimethyl \( > \) ethyl) \( > C_3 \) aromatic (trimethyl \( > \) dimethyl, ethyl \( > \) isopropyl) \( \ldots \) etc. For the n-alkyl substituted aromatics decreasing abundance is in the order of increasing alkyl chain length (refer to figures 16 to 21 and 2A1 to 2A6). These observations are again in accordance with the relative distribution of retort alkyl radicals i.e. \( CH_3 \) \( > \) \( CH_3CH_2 \) \( > CH_3(CH_2)_2 \).
>... etc. Identical alkyl substitution patterns are also observed for the other chemical classes found in shale oil e.g., nitrogen heterocycles (indoles, carbazoles, pyridines, quinolines), oxygen heterocycles (benzo- and dibenzofurans, phenols) and sulphur heterocycles (benzo- and dibenzothiophenes).

*Alkenyl radicals*

Alkenes are an abundant constituent of shale oils; alkenyl radicals are therefore likely to be present during pyrolysis. Chemical classes which may have resulted from alkenyl radical combinations include dienes (self combination), \( \omega \)-phenylalk-1-enes (benzene and alkenyl radical) and 1-phenylalkenes such as styrenes (benzene and alkenyl radical). Alternatively, some of the compounds with unsaturated alkyl side chains may have arisen from disproportionation of the saturated homologues which are often also found in higher proportion e.g. \( \omega \)-phenylalk-1-enes may be derived from \( n \)-alkylbenzenes.

*Aromatic radicals*

These are highly stable radicals because of resonance. While the majority of aromatic radicals simply combine with the more abundant alkyl radicals to give the range of alkyl substituted aromatics that are observed, some would undergo self combination to give new aromatic compounds. The probability of these self
combinations is dependent on their relative proportion which would
decrease with increasing aromaticity i.e., monoaromatic radicals
(phenyl > benzyl > toluyl > ...) > bicyclic aromatic (naphthyl) >
tricyclic aromatic (phenanthryl > fluorenyl) > ... etc. The result of
such aromatic radical combinations have been observed and the
products, in order of decreasing abundance, have included biphenyls,
diphenylmethanes, phenylnaphthalenes (α and β isomers),
terphenyls and binaphthyls or isomeric phenylphenanthrenes.

For each of the above aromatic classes, condensed ring
structures with the same formula exist and incorrect assignments
have often been made e.g., biphenyls have been misidentified as
acenaphthenes [113, 139]. Similarly, phenylnaphthalenes could be
misidentified as acephenanthrenes and binaphthyls as
acebenzophenanthrenes. Comparison of the retention indices of the
shale oil aromatics with those of standard compounds has shown
that the condensed ring structures are not the principal species
present in shale oils.

Cyano radicals

Nitriles have not been detected in oil shale kerogen and
presumably are of pyrolytic origin. Ammonium salts of fatty acids
[141] and amines [134] have been suggested as the source material
for nitriles. However, almost all naturally occurring fatty acids
have an even number of carbon atoms. While nitrile fractions often show an odd/even carbon number preference, the odd carbon number nitriles are usually of comparable abundance to the even carbon number nitriles. If naturally occurring fatty acids are the major source of nitriles, as suggested by Evans et al. [141], then the even carbon nitriles must undergo extensive cleavage. Only small quantities of shorter chain nitriles were found when standard carboxylic acids were pyrolysed in the presence of ammonia [141].

Three homologous series of n-alkenonitriles are usually detected in the nitrile fraction of shale oils. Mass spectra and NMR analysis suggest that these compounds are, in decreasing order of abundance, \( \omega \)-, (\( \omega -1 \))- and (\( \omega -2 \))-alkenonitriles. The relative abundances of these isomers is similar to that of the 1-, 2- and 3-alkenes. This suggests that the alkenonitriles may be generated from n-alkanonitriles in a similar manner in which the 1-, 2- and 3-alkenes are derived from n-alkanes.

**Acyl radicals**

Sources of acyl radicals include carboxylic acids [134] and \( \beta \)-keto esters [149]. The most stable acyl radical would be R-CO· because of resonance stabilisation. The most likely products from acyl radicals are 2-alkanones followed in decreasing order of
abundance by 3-, 4-, 5-ketones etc, in accordance with the decreasing abundance of alkyl radicals with increasing chain length i.e. $\text{CH}_3^\cdot > \text{CH}_3\text{CH}_2^\cdot > \text{CH}_3(\text{CH}_2)_2^\cdot > \ldots$ etc. This is the actual order of abundance observed in the pyrolysis of carboxylic acids [134] and in shale oil [135].

**Sulphur radicals**

The sulphur of non-marine oil shales is mostly present as inorganic minerals such as pyrite. While sulphur is present in the proteins of many organisms, the sulphur content of demineralised kerogens is usually low. Recent studies [134] have shown that when alkanes are pyrolysed over pyrite mixed with clay, organic sulphur compounds such as thiophenes and benzothiophenes are formed, presumably through an $R-S^\cdot$ intermediate. Hydrogen sulphide (present in retort gas) is a further source of sulphur to be incorporated by secondary pyrolytic reactions.

Biological precursors are important in determining the relative proportion of the chemical classes observed in shale oil. However, secondary pyrolytic reactions dependent on the types of free radicals that are generated and the types of catalytic surfaces in the shale matrix appear to be responsible for many of the products observed.
9. Conclusion

The new analytical methods presented in this thesis, unlike previous methods, were especially designed to accommodate the complexity and chemical instability of shale oil. Minimal artefact formation occurred during the analyses because aqueous acidic and basic extractions were avoided as was column chromatography on excessively active adsorbents. All the separations were performed on alumina adsorbents which separate chemical classes according to functional group type irrespective of the extent of alkyl substitution. Only eluents of low boiling point were used for sample recovery in order to minimise evaporative losses of the volatile constituents. The adsorbents used were commercially available at low cost, were inexpensively modified and did not need complex equipment (e.g. HPLC) for operation.

Because the resolution provided by the new procedures was far superior to that of previous methods, many new chemical classes were isolated and identified in the shale oils. These included \( n \)-alkadienes (9 series), \( n \)-alkyltoluenes (3 series), \( n \)-alkylxylene (2 series), \( n \)-alkyltrimethylbenzenes, \( n \)-alkylindans, \( n \)-alkylmethylindans, \( n \)-alkylfurans, \( n \)-alkylpyrroles, \( \omega \)-phenylalk-1-enes, \( \omega \)-(methylphenyl)alk-1-enes (3 series),
n-alkylstyrenes, n-alkylindenes, n-alkylmethylindenes, benzo- and dibenzo- furans and pyrroles, phenylnaphthalenes (α and β isomers), 5- and 6-ring aromatics, unsaturated nitriles (3 series), 1-(cycloalk-1-enyl)-2-alkanones (2 series) and n-alkylpyridines (at least 10 series).

More detailed separation and identification of the components of shale oil allowed several important pyrolytic inferences to be drawn:

i) Many of the chemical classes in shale oil are of secondary pyrolytic origin and not of primary origin as previously assumed. Examples include dienes and 1-6 ring aromatics.

ii) The type and range of alkyl substitution on the various chemical classes in shale oil appears to be dependent upon the relative proportion of alkyl radicals present during pyrolysis.

iii) Oil shales pyrolysed in the presence of an inert sweeping gas yield shale oils which are less complex and more stable than those obtained by normal Fischer assay. Sweeping the retort apparatus during pyrolysis minimises secondary reactions such as cyclisation and aromatisation on catalytic surfaces (e.g. minerals). 'Swept' shale oils are therefore a more accurate reflection of biological precursors in the kerogen.

From a comparison of the chemistry of oil shales which
differ in maturity or petrology, several important geochemical inferences were drawn:

i) Shale oils derived from kerogens of high lignite content (carbonaceous) are characterised by high concentrations of oxygenated aromatics such as phenols, benzo- and dibenzofurans and indanones and tetralones; shale oils derived from kerogens which owe their origin predominantly to algae (normal) usually have much lower concentrations of these compounds. 'Carbonaceous' shale oils therefore display characteristics of coal derived liquids.

ii) The maturity of an oil shale deposit may be reflected in the chemistry of its shale oil. In the Green River deposit, which is more mature than the Condor deposit, a higher content of n-alkylpyridines and alkanones but a lower concentration of alkanonitriles was found.

The analytical methods presented in this thesis should provide tools for more detailed chemical analyses of other shale oils which in turn will lead to an improved understanding of shale oil chemistry and oil shale pyrolysis mechanisms. This may assist the design of retorts which will take better account of the effects of retorting temperature, residence times and mineral catalysis on the pyrolysis products obtained from a given kerogen.

Many of the chemical classes found in shale oil are common to
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Appendix 1

Gas chromatograms of the open column fractions obtained from the nitrogen-pyrolysis oils of the Condor Brown and Carbonaceous Units.

Figure IA1: Gas chromatogram of fraction I from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are linear alkanes of chain length equal to the labelling number. Peaks labelled I-VII are respectively, 2,6-dimethylundecane, 2,6,10-trimethylundecane, 2,6,10-trimethyl-dodecane, 2,6,10-trimethyltridecane, 2,6,10-trimethylpentadecane, pristane and phytane.
Figure 1A2: Gas chromatogram of fraction 3 from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are linear 1-alkenes of chain length equal to the labelling number. Peaks labelled I, II, III and IV are respectively, 1-, 2-, 3- and 4-alkenes. Peaks lettered a, b, c and d are respectively, 2,6,10-trimethyldodecene, 2,6,10-trimethyltridecene, 1-pristene and 2-pristene.

Figure 1A3: Gas chromatogram of fraction 5 from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are \( n \)-alkylbenzenes which have an alkyl chain length equal to the labelling number.
Figure 1A4: Gas chromatogram of fraction 14 from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are \( \text{n-alkanonnitriles} \) of carbon chain length equal to the labelling number.

Figure 1A5: Gas chromatogram of fraction 15 from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are \( \text{2-alkanones} \) of carbon chain length equal to the labelling number.
Figure 1A6: Gas chromatogram of fractions 16 and 17 combined, from the open column chromatography of Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Peaks labelled CO C,...C3 C and CO I,...C2 I are respectively, alkyl substituted 1-(cyclopent-1-eny1)-2-alkanones and indanones which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are $n$-alkylindanones of alkyl chain length equal to the labelling number.

Figure 1A7: Gas chromatogram of the acid fraction from the Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Peaks labelled CO P,...C3 P are alkyl substituted phenols which have a total number of substituent carbon atoms equal to the labelling number.
Figure 1A8: Gas chromatogram of the base fraction from the Condor Carbonaceous Unit (nitrogen-pyrolysis) shale oil. Peaks labelled C1 P, C3 P and C0 Q, C2 Q are respectively, alkyl substituted pyridines and quinolines which have a total number of substituent carbon atoms equal to the labelling number.

Figure 1A9: Gas chromatogram of fraction 3 from the open column chromatography of Condor Brown Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are linear 1-alkenes of chain length equal to the labelling number. Peaks labelled I, II, III and IV are respectively, 1-, 2-, 3- and 4-alkenes. Peaks lettered a, b, c and d are respectively, 2,6,10-trimethyldodecene, 2,6,10-trimethyltridecane, 1-pristene and 2-pristene.
Figure 1A10: Gas chromatogram of fraction 8 from the open column chromatography of Condor Brown Unit (nitrogen-pyrolysis) shale oil. Peaks labelled C0 B,...C3 B are alkyl substituted benzofurans which have a total number of substituent carbon atoms equal to the labelling number.

Figure 1A11: Gas chromatogram of fraction 13B from the open column chromatography of Condor Brown Unit (nitrogen-pyrolysis) shale oil. Peaks labelled C0 I,...C4 I are alkyl substituted indoles which have a total number of substituent carbon atoms equal to the labelling number.
Figure 1A12: Gas chromatogram of fraction 14 from the open column chromatography of Condor Brown Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are \( n \)-alkanenitriles of carbon chain length equal to the labelling number.

Figure 1A13: Gas chromatogram of fraction 15 from the open column chromatography of Condor Brown Unit (nitrogen-pyrolysis) shale oil. Even numbered peaks are 2-alkanones of carbon chain length equal to the labelling number.
Figure IA14: Gas chromatogram of the acid fraction from the Condor Brown Unit (nitrogen-pyrolysis) shale oil. Peaks labelled C0 P,...C2 P are alkyl substituted phenols which have a total number of substituent carbon atoms equal to the labelling number.

Figure IA15: Gas chromatogram of the base fraction from the Condor Brown Unit (nitrogen-pyrolysis) shale oil. Peaks labelled C1 P,...C4 P and C0 Q,...C4 Q are respectively, alkyl substituted pyridines and quinolines which have a total number of substituent carbon atoms equal to the labelling number.
Appendix 2

Gas chromatograms of the aromatic compounds in fractions separated from Green River shale oil by low pressure liquid chromatography on neutral alumina.

Figure 2AI: Gas chromatogram of fraction 2 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled C1 B,...C5 B and C01,...C3 I are respectively, alkyl substituted benzenes and indans which have a total number of substituent carbon atoms equal to the labeling number. Even numbered peaks are \( n \)-alkylbenzenes which have an alkyl chain length equal to the labeling number. The enlargement area shows the relative elution order of \( n \)-alkylbenzenes (I), \( n \)-alkyltoluenes (IIA, IIB and IIC), \( n \)-alklyxylene (IIIA and IIIB) and \( n \)-alkylindans (IV).
Figure 2A2: Gas chromatogram of fraction 3 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Even numbered peaks are \( \omega \)-phenylalk-1-enes of alkenyl chain length equal to the labelling number. The enlargement area shows the relative elution order of \( \omega \)-phenylalk-1-enes (I) and \( \omega \)-(methylphenyl)-alk-1-enes (IIA, IIB and IIC). Peaks labelled \# are respectively, in order of elution from left to right, C3 and C4 alkyl substituted benzenes.

Figure 2A3: Gas chromatogram of fraction 4 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled C0 S,...C4 S and C0 I,...C5 I are respectively, alkyl substituted styrenes and indenes which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are \( \pi \)-alkylindenes which have an alkyl chain length equal to the labelling number.
Figure 2A4: Gas chromatogram of fraction 5 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled CO N,...C5 N and CO B,...C2 B are respectively, alkyl substituted naphthalenes and biphenyls which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are α and β n-alkynaphthalenes which have an alkyl chain length equal to the labelling number.

Figure 2A5: Gas chromatogram of fraction 6 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled CO Df and CO Dt are respectively, dibenzofuran and dibenzothiophene. Peaks labelled CO Fe,...C3 Fe, CO P,...C4 P and CO Fa,...C2 Fa are respectively, alkyl substituted fluorenes, phenanthrenes and fluoranthrenes which have a total number of substituent carbon atoms equal to the labelling number.
Figure 2A6: Gas chromatogram of fraction 7 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled CO P1, C3 P1, C0 P, C7 P and C0 T, C4 T are respectively, alkyl substituted phenylindoles, pyrenes and tetraaromatic isomers which have a total number of substituent carbon atoms equal to the labelling number.

Figure 2A7: Latter half of the gas chromatogram of fraction 8 from the low pressure liquid chromatography of Green River shale oil on neutral alumina. Peaks labelled CO B, C3 B are alkyl substituted benzopyrene isomers which have a total number of substituent carbon atoms equal to the labelling number. Peaks labelled CO H are hexaaromatic isomers.
Appendix 3

Gas chromatograms of the fractions separated from Condor Brown Unit shale oil by low pressure liquid chromatography on thermally modified alumina adsorbents.

Figure 3A1: Gas chromatogram of fraction 5.1 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Even numbered peaks are linear alkanes of chain length equal to the labelling number. Peaks labelled I-VII are respectively, 2,6-dimethylundecane, 2,6,10-trimethylundecane, 2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane, 2,6,10-trimethylpentadecane, pristane and phytane.
Figure 3A2: Gas chromatogram of fraction 5.2 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Even numbered peaks are linear 1-alkenes of chain length equal to the labelling number. Peaks labelled I, II, III and IV are respectively, 1-, 2-, 3- and 4-alkenes. Peaks lettered a, b and c are respectively, 2,6,10-trimethylidodecane, 2,6,10-trimethyltridecane and pristene.

Figure 3A3: Gas chromatogram of fraction 4.1 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled C1 B, C5 C and C0 C are respectively, alkyl substituted benzenes and indans which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are n-alkylbenzenes which have an alkyl chain length equal to the labelling number. The enlargement area shows the relative elution order of n-alkylbenzenes (I), n-alkyltoluenes (IIA, IIB and IIC), n-alkylxylene (IIIA and IIB) and n-alkylindans (IV).
Figure 3A4: Gas chromatogram of fraction 4.2 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Even numbered peaks are \( \omega \)-phenylalk-1-enes of alkenyl chain length equal to the labelling number. The enlargement area shows the relative elution order of \( \omega \)-phenylalk-1-enes (I) and \( \omega \)-(methylphenyl)-alk-1-enes (IIA, IIB and IIC). Peaks labelled \( \# \) are respectively, in order of elution from left to right, C3 and C4 alkyl substituted benzenes.

Figure 3A5: Gas chromatogram of fraction 4.3 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled CO, C1 S, C2 S, C3 S, C4 S and CO, C1, C2, C3, C4, C5 are respectively, alkyl substituted styrenes and indenes which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are \( n \)-alkylindenes which have an alkyl chain length equal to the labelling number.
Figure 3A6: Gas chromatogram of fraction 4.4 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled CO N,...C5 N and CO B,...C2 B are respectively, alkyl substituted naphthalenes and biphenyls which have a total number of substituent carbon atoms equal to the labelling number. Even numbered peaks are \( \alpha \) and \( \beta \) \( n \)-alkyl naphthalenes which have an alkyl chain length equal to the labelling number.

Figure 3A7: Gas chromatogram of fraction 3.1 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled CO Df, CO Dp and CO Dt are respectively, dibenzofuran, dibenzo[pyran and dibenzothiophene. Peaks labelled CO Fe,...C3 Fe, CO P,...C5 P and CO Fa,...C2 Fa are respectively, alkyl substituted fluorenes, phenanthrenes and fluoranthenes which have a total number of substituent carbon atoms equal to the labelling number.
Figure 3A8: Gas chromatogram of fraction 3.2 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled $CO_P$, $C_1 P$, $C_2 P$, $C_3 P$, and $C_5 P$ are respectively, alkyl substituted phenylindoles and pyrenes which have a total number of substituent carbon atoms equal to the labelling number.

Figure 3A9: Gas chromatogram of fraction 3.5 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled $CO$, $C_1$, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$, and $C_7$ are alkyl substituted homologues of an unknown chemical class; the total number of substituent carbon atoms is equal to the labelling number. Peaks labelled $u$ are an homologous series of unknown structure.
Figure 3A10: Gas chromatogram of fraction 2.1 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled a and b are homologous series of n-alkylpyridines which are characterised by m/z values of 107 and 121, respectively.

Figure 3A11: Gas chromatogram of fraction 2.2 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Even and odd numbered peaks are respectively, n-alkanonitriles and n-alkenonitriles of carbon chain length equal to the labelling number.
Figure 3A12: Gas chromatogram of fraction 2.3 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Even numbered peaks are 2-alkanones which have a carbon atom chain length equal to the labelling number. Peaks labelled c, in order of elution from left to right, are respectively, n-alkylcyclopentanones and n-alkylcyclohexanones (beginning with n-propylcyclopentanone and ethylcyclohexanone).

Figure 3A13: Gas chromatogram of fraction 1.1 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled C2 P,...C4 P are alkyl substituted pyridines which have a total number of substituent carbon atoms equal to the labelling number. Similarly, peaks labelled C0 D and C1 D, C0 Q,...C2 Q, C0 I,...C5 I, C0 B,...C2 B and C1 C,...C5 C are respectively, alkyl substituted dihydroindoles, quinolines, indoles, benzoquinolines and carbazoles.
Figure 3A14: Gas chromatogram of fraction 1.2 from the low pressure liquid chromatography of Condor shale oil on thermally modified aluminas. Peaks labelled C0 P, ...C4 P are alkyl substituted phenols which have a total number of substituent carbon atoms equal to the labelling number.
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   "Determination of Polynuclear Aromatic Hydrocarbons in Shale
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   "Determination of Nitriles in Shale Oil by Low Pressure Liquid
   Chromatography and Infrared Spectrophotometry",
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Acknowledgements

I would like to thank the following people for their assistance throughout my Ph D:

J. Ellis and P. T. Crisp for their supervision; J. Korth, L. Hick and T. Lewis for technical assistance; E. Wilke for ordering services; P. Pavlik for photographic services; Gavin, Lorraine and C. Peacock for typing this manuscript. Special thanks to Hvezda for drawing many of the figures and tables.

I acknowledge the work, presented in sections 8.2.2 I, 8.2.2 II and 8.2.2 III, which was performed by the Lucas Heights Research Laboratories, CSIRO Division of Energy Chemistry.

Finally, but most importantly, I would like to thank my parents for their continual support.