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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC PROCEDURE FOR DIRECT DETERMINATION OF THE COMPOUND CLASS COMPOSITION OF DIESEL AND KEROSENE FUELS USING REFRACTIVE INDEX DETECTION

D. J. COOKSON

The Broken Hill Proprietary Co. Ltd., Melbourne Research Laboratories, 245 Wellington Rd., Clayton, Vic. 3168 (Australia)

C. J. RIX

Royal Melbourne Institute of Technology, Department of Applied Chemistry, 124 La Trobe St., Melbourne, Vic. 3000 (Australia)

I. M. SHAW

BHP Petroleum Laboratory, P.O. Box 264, Clayton, Vic. 3168 (Australia)

and

B. E. SMITH*

The Broken Hill Proprietary Co. Ltd., Melbourne Research Laboratories, 245 Wellington Rd., Clayton, Vic. 3168 (Australia)

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SUMMARY

A high-performance liquid chromatography method utilizing a bonded amosilane stationary phase, *n*-heptane mobile phase and refractive index detection is described for quantification of the compound class composition (saturates, single-ring aromatics, double-ring aromatics, polynuclear aromatics and polars) of olefin-free kerosine and diesel fuels. Refractive index response factors for each of the compound classes have been determined using fractions obtained from preparative scale column chromatographic separations for a range of fuel samples. Variations in response factors for fractions deriving from different fuel sources are described and are considered sufficiently small to allow acceptable analytical accuracy for refractive index detection.

INTRODUCTION

Hydrocarbon transport fuels boiling above the gasoline range, (*i.e.* above about 200°C) are difficult to analyse in a chemically explicit fashion because they consist of such complex mixtures of compounds. Nevertheless it is desirable to obtain analytical information for such materials that is at least chemically comprehensible.

This is a general problem for fossil fuel products, and various liquid chromatographic methods aimed at compound class separations have been applied (see,

for example, refs. 1–6). In the present report a high-performance liquid chromatographic (HPLC) procedure for the determination of the weight percent abundances of saturates, single-ring aromatics, double-ring aromatics, polynuclear aromatics and polars, is described. The separation principle is the same as that employed by a number of other workers^{7–10} using an aminosilane stationary phase in conjunction with a non-polar mobile phase (*n*-heptane). The present work differs from previous reports in a number of respects, however. The method is specifically directed towards olefin-free kerosine range (approx. 190–230°C) and diesel range (approx. 230–320°C) materials. Refractive index detection is employed and suitable response factors have been determined by calibrating with fractions obtained from preparative scale column chromatographic separations. All compound classes are determined directly rather than by difference.

The procedure to be described has been developed as part of a research program concerned with synthetic fuels. Its primary function has been to enable rapid and reliable characterization of fuels deriving from disparate petroleum sources as well as from alternative sources, such as coal, shale oil and peat. It has been used to compare such fuels and to relate compositional details with other property values¹¹. It has also been used to characterize materials for use as start-up solvents in coal hydrogenation experiments¹² and to follow the kinetics of catalytic hydrotreatment¹³. To quantify compound class compositions adequately, using the HPLC method described herein, refractive index response factors should not be too sensitive to sample origin. This matter is therefore considered in some detail.

EXPERIMENTAL

HPLC method

A Model M6000A pump, U6K injector and R401 refractive index detector, all from Waters Assoc., were used together with a μ Bondapak-NH₂ column (300 × 3.9 mm I.D.) and Valco Model 7010 backflush valve. The *n*-heptane eluting solvent was degassed before use by ultrasonication under vacuum, and was filtered by an in-line 0.2- μ m filter. The reference cell for the refractive index detector was flushed with *n*-heptane prior to analysis. The sample was dissolved in *n*-heptane to a concentration of approximately 0.05 g cm⁻³ and, if considered necessary, filtered through a 0.2- μ m filter. Approximately 20 μ l of this solution is injected on to the column and eluted with *n*-heptane at a flow-rate of 1 cm³ min⁻¹ in a forward direction, until the elution time of fluoranthene is passed. The direction of flow of the mobile phase is then reversed (backflushing) to elute polar components. A standard mixture containing *n*-hexadecane, *n*-decylbenzene, naphthalene, biphenyl, fluorene, phenanthrene and fluoranthene is run daily to fix expected retention times. The refractive index detector output is digitised and data manipulation (*e.g.* integration and response factor adjustment) as well as backflush control is effected by a Hewlett-Packard 3357 laboratory automation system.

Preparative scale column chromatography

Saturates were separated from aromatics on a conventional large scale silica column (Merck silica gel 90) employing a low hydrostatic head pressure. For convenience the silica was pre-dried under the same conditions as used for alumina in

this work (300°C, overnight). Under these conditions it is possible that some neighbouring hydroxyl groups may condense to form siloxanes¹⁴. This possibility caused no experimental difficulties in the present work. The dried silica was sufficiently active to achieve the desired separations and could be redried and re-used several times. Saturates were eluted with *n*-hexane and aromatics were eluted using hexane-dichloromethane (1:1) followed by neat dichloromethane. Solvents were removed on a rotary evaporator yielding a saturates fraction and an aromatics fraction. The latter was further separated into a one-ring aromatics fraction (eluted with *n*-hexane) and a two-ring aromatics fraction [eluted with *n*-hexane-dichloromethane (1:1) followed by neat dichloromethane] on a neutral alumina column (Merck, aluminium oxide 90). UV detection (280 nm for one-ring aromatics, 310 nm for two-ring aromatics) was used to monitor eluents from preparative scale column chromatographic separations.

RESULTS AND DISCUSSION

The order of elution of hydrocarbons from the aminosilane column is dependent on the presence and nature of aromatic ring systems^{7,9}. Retention times for a range of test compounds are given in Table I. Saturates are eluted first, followed by one-ring aromatics then two-ring aromatics and finally polynuclear aromatics. Illustrative chromatograms are shown in Fig. 1. Typically, kerosine and diesel samples give a single peak for saturates and a single peak for one-ring aromatics neither of which is resolved into sub-components. However, two-ring aromatics (*i.e.* species containing two aromatic rings) may give rise to more than one peak (Fig. 1) and for the purpose of analysis these species are given an operational definition. Peaks eluting after one-ring aromatics, with elution volumes up to and including that of fluorene, are termed two-ring aromatics. From Table I this would include naphthalene, biphenyl and acenaphthene but not acenaphthylene. Polynuclear aromatics are similarly defined as species eluting after fluorene and may also appear as multiple peaks. Only very minor quantities of polynuclear aromatics are usually found in diesel samples. They are generally absent in the lower-boiling kerosine samples.

For the analysis to be quantitatively reliable it is necessary that response factors for each of the compound classes should be determined and that these should be valid for kerosine and diesel fuels from different sources (*e.g.* different petroleum fields or synfuel sources). Major emphasis has been placed on saturates, one-ring aromatics and two-ring aromatics since these are the main constituents of straight run kerosine and diesel fuels (generally > 95%). These fractions have been separated from seven diesel fuels and two kerosine fuels representing a range of sources and compositions (Table II) using preparative scale silica and alumina column chromatography as outlined in the experimental section.

Each fraction was tested on the aminosilane HPLC system to confirm the compatibility of aminosilane and silica and alumina separations. All saturates and single-ring aromatics fractions showed a single HPLC peak. A number of two-ring aromatic fractions, however, showed significant quantities of one-ring aromatic impurities. This probably arises from inadequate resolution of the preparative scale alumina separations. Further purification was not attempted since (see below) knowledge of the response factors for one-ring aromatics allowed suitable response factors

TABLE I
COMPARATIVE HPLC RETENTION TIMES FOR TEST COMPOUNDS

HPLC conditions are given in the experimental section.

	<i>Retention time</i> (min)
<i>Saturates</i>	
<i>n</i> -Hexatriacontane	3.0
<i>n</i> -Dodecane	3.1
Decalin	3.2
Adamantane	3.2
<i>One-ring aromatics</i>	
1,3,5-Tri- <i>tert.</i> -butylbenzene	3.3
<i>n</i> -nonadecylbenzene	3.5
1,2,3,5-Tetramethylbenzene	3.6
Benzene	3.6
Cyclohexylbenzene	3.7
Tetralin	3.7
Dodecahydrotriphenylene	4.0
<i>Two-ring aromatics</i>	
1,5-Dimethylnaphthalene	4.4
Naphthalene	4.5
Acenaphthene	4.6
1,2,3,6,7,8-Hexahdropyrene	4.6
Biphenyl	4.7
Fluorene	5.1
<i>Polynuclear aromatics</i>	
Phenylnaphthalene	5.3
Acenaphthylene	5.4
Phenanthrene	6.3
Anthracene	6.4
Pyrene	7.1
Fluoranthene	7.4
<i>Hetero-atomic species</i>	
Dibenzofuran	5.1*
Phenol	polar**
<i>o</i> -Cresol	polar**
Resorcinol	polar**
β -Naphthol	polar**
Carbazole	polar**
Quinoline	polar**
3,4-Dimethylaniline	polar**

* Dibenzofuran appears as a two-ring aromatic. Dibenzothiophene elutes between fluorene and phenanthrene.

** Polars elute during backflush. Some of the compounds tested were of low solubility in *n*-heptane and were detected by UV. The mono-phenols and carbazole gave relatively broad backflush peaks.

for two-ring aromatics to be calculated even in the presence of these impurities. Response factors for each fraction were estimated by use of either naphthalene (response factor taken as unity) or *n*-dodecane (response factor 4.73 relative to naphthalene) as internal standards.

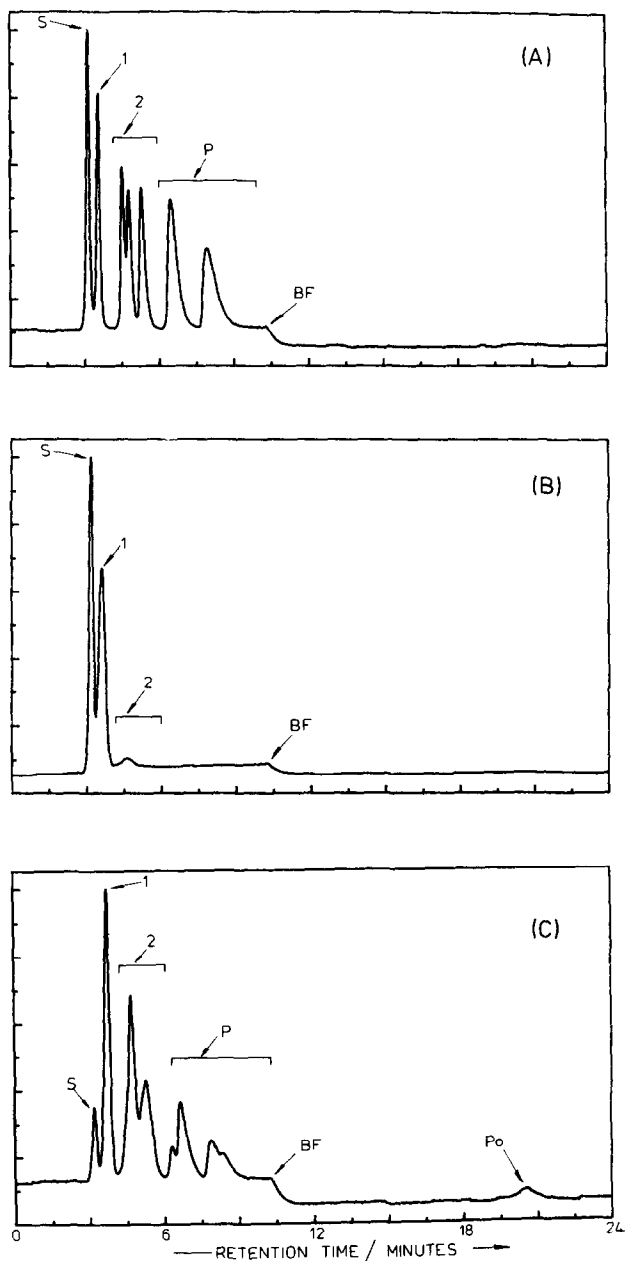


Fig. 1. HPLC traces (conditions as in Experimental section) of (A) a standard mixture with elution in the order of, from left to right, *n*-hexadecane, *n*-decylbenzene, naphthalene, biphenyl, fluorene, phenanthrene and fluoranthene; (B) a shale oil derived diesel fuel; (C) a partially hydrogenated coal-derived liquid for use as a coal hydrogenation solvent. BF = initiation of backflushing. Separation of regions according to compound class type is indicated. S = saturates, 1 = single-ring aromatics, 2 = double-ring aromatics, P = polynuclear aromatics, Po = polars.

TABLE II
ORIGIN AND COMPOSITION OF TEST FUELS

Sample	Origin	Composition (wt.%) from open column chromatography		Composition (wt.%) from HPLC*			
		Saturates	Aromatics	Saturates	One-ring aromatics	Two-ring aromatics	Polynuclear aromatics
<i>Diesels**</i>							
1	Petroleum	74	26	73	12	14	1
2	Petroleum	71	29	69	12	18	1
3	Petroleum	83	17	83	12	5	—
4	Petroleum	81	19	82	13	5	—
5	Coal	48	52	49	45	6	—
6	Shale oil	59	41	62	36	2	—
7	Coal	13	87	13	60	25	2
<i>Kerosines***</i>							
8	Petroleum	83	17	84	12	4	—
9	Coal	24	76	21	68	11	—

* HPLC response factors from Table IV were used for samples 1-6 and 8. For samples 7 and 9 the saturates response factors in Table III for these samples, were used in conjunction with the one-ring and two-ring aromatics response factors in Table IV.

** Boiling range for all diesels 230-320°C except for samples 6 (230-340°C) and 7 (250-300°C). The four petroleum samples derive from different Australian fields, *viz.* the Gippsland, Cooper and Surat basins and the North West Shelf. Samples 5-7 have been catalytically hydrogenated with sample 5 deriving from a brown coal tar and sample 7 from an anthracene oil.

*** Boiling range for petroleum sample 190-230°C and for coal sample 190-250°C. Sample 9 is of the same origin as sample 7 (see **).

TABLE III
HPLC RESPONSE FACTORS FOR TEST SAMPLES

Sample	Response factors*		
	Saturates	One-ring aromatics	Two-ring aromatics
<i>Diesels</i>			
1	3.15	1.60	1.06
2	3.14	1.62	1.05
3	2.93	1.58	0.99
4	2.70	1.63	1.09
5	2.63	1.53	0.97
6	2.58	1.53	0.97
7	2.07	1.40	0.98
<i>Kerosines</i>			
8	3.78	1.70	1.01
9	2.35	1.47	0.97

* Relative to naphthalene taken as unity.

Results are summarised in Table III. In general the response factors are in the order saturates > one-ring aromatics > two-ring aromatics. Individual fractions have been studied in some detail using NMR spectroscopic techniques. Although full results of these investigations will be published separately¹⁵ the information deduced is of some value in rationalizing comparative refractive index response factors.

The two-ring aromatic fraction of the kerosine sample 8 consists mainly of naphthalene, and its 1-methyl and 2-methyl derivatives, so the response factor of 1.01 is as expected. The two-ring aromatic fractions of diesel samples 1 and 2 are rich in dimethylnaphthalenes so that again response factors near that of naphthalene are reasonable. Of the seven diesel one-ring aromatics fractions studied, that of sample 7 in Table III is unique in having a lower response factor. This fraction is also structurally unique in that there is a relatively high abundance of cyclic rather than linear aliphatic side chains. A similar comparison is also valid for the single-ring aromatic fractions of kerosine samples 8 and 9. ¹³C NMR allows the percentage abundance of *n*-alkanes in saturates fractions to be calculated¹¹. Results indicate that the refractive index response factors are dependent on *n*-alkane content. For the saturates fractions of diesel samples, the two highest response factors of 3.1 correspond to *n*-alkane abundances of 48–53%. The next four response factor values (2.6–2.9) pertain to fractions with *n*-alkane contents of 26–39% and the lowest response factor (2.1) is obtained for a fraction with no measurable abundance of *n*-alkanes. In fact the latter fraction (sample 7) is predominantly alicyclic in nature. A similar rationale pertains to the kerosine saturates fractions for samples 8 and 9.

It is apparent that there is a modest increase in response factors for saturates and one-ring aromatics in passing from diesels to kerosines. Also, the response factors for saturates, and to a lesser extent one-ring aromatics, are distinctively lower for fractions dominated by alicyclic structures. Apart from these trends there is substantial uniformity rather than disparity in the results in Table III, which supports the use of refractive index detection in the HPLC analysis of kerosine and diesel fuels deriving from a diverse range of sources.

The response factors given in Table IV have been adopted for routine analysis of diesel and kerosine fuels. Alternative response factors have been used in special cases where foreknowledge of sample origin is informative. For example, for samples deriving from hydrogenation of a predominantly aromatic feedstock the saturates response factors for samples 7 and 9 in Table III have been used.

TABLE IV
HPLC RESPONSE FACTORS* ADOPTED FOR ROUTINE USE

	<i>Saturates</i>	<i>One-ring aromatics</i>	<i>Two-ring aromatics</i>
Diesels**	2.85	1.56	1.02
Kerosines**	3.78	1.59	0.99

$$* \% \text{ Abundance} = \frac{\text{Peak area} \times \text{response factor} \times 100}{\sum \text{Peak areas} \times \text{response factors}}$$

** Response factors for diesel one-ring and two-ring aromatics are averages of all values in Table III. For diesel saturates the unique sample 7 response factor was excluded. A similar procedure has been used for kerosines, with the saturates response factor for sample 9 being excluded.

If refractive index response factors are to be used routinely in fuel analyses it is of value to gain some indication of the magnitude of errors that may arise due to deviations of true response factors for particular samples, from those adopted in Table IV. Of the diesel samples listed in Table III, use of the routine response factors would lead to the largest errors for sample 7. Consequently, Fig. 2 has been constructed from the following premises. Consider a hypothetical set of samples which may have any composition within the range of 0 to 100% of saturates, one-ring aromatics and two-ring aromatics. Allow that these samples have been analysed using the response factors in Table IV yielding calculated weight percentages of the component species. Also allow that the true response factors should have been those for sample 7 in Table III (2.07, 1.40 and 0.98) rather than the routine values quoted in Table IV (2.95, 1.56 and 1.02). Determine the true abundances of each compound class. Compare these with the original calculated values (Fig. 2).

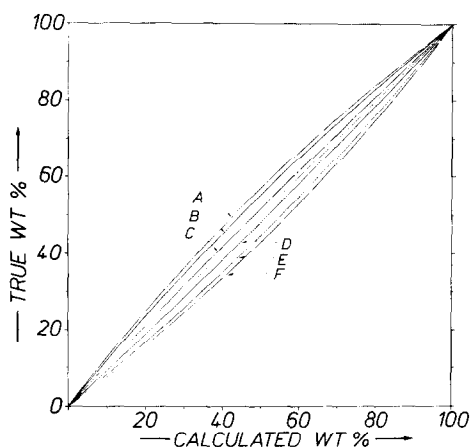


Fig. 2. A plot of true and calculated compositional data for saturates (E, F) single-ring aromatics (B, D) and double-ring aromatics (A, C) constructed on the premises outlined in the text, with a view to illustrating the possible magnitude of errors arising from use of adopted diesel response factors (Table IV) for samples where true response factors are deviant, as for sample 7 in Table III.

The difference between true and calculated weight percentages for any given compound class is dependent on the relative abundances of the remaining two compound classes. Thus the plot of true *versus* calculated values for each compound class takes the form of a band between two curves (E-F for saturates, B-D for single-ring aromatics and A-C for double-ring aromatics) instead of a single line. It is apparent that for the case studied, errors arising from the response factor deviations are relatively minor. For example, a calculated value of 50% saturates content would correspond to a true value of between 43 and 45%; a calculated value of 50% single-ring aromatics would correspond to a true value of between 48 and 55%; and a calculated value of 50% double-ring aromatics would correspond to a true value of between 52 and 57%. It should be noted that larger errors could be generated if a case were considered where the smallest saturates response factor in Table III was combined with the largest response factors for one-ring aromatics and two-ring aromatics. There is no evidence, however, that such a coincidence would occur.

Lesser effort has been directed towards determining response factors for polynuclear aromatics and polars since these are relatively minor kerosine and diesel fuel constituents. Response factors of 0.84 and 0.74 have been measured for phenanthrene and fluoranthene, respectively. A response factor of 0.80 has therefore been adopted for polynuclear aromatics. The same value is used, by default, for polars. Polars are defined as species eluting during back-flushing, and illustrative compounds are listed in Table I.

Although the above HPLC method has been primarily directed towards the analysis of kerosine and diesel fuels boiling over a relatively specific range it is appropriate to consider its application to other heptane-soluble fossil fuel liquids. The most obvious limitation concerns low-boiling materials. Since detection depends on the difference in refractive index between component species and the elution solvent (*n*-heptane) it is anticipated that accurate results would not be obtained for gasoline-range materials. The relatively modest difference between response factors determined for the kerosine and diesel samples studied in the present work however, suggests that the method need not be restricted to the specific boiling ranges ascribed to kerosines (approx. 190–230°C) and diesels (approx. 230–320°C). It would be a simple matter to approximate suitable response factors for samples that are somewhere within the total boiling range of 190 to 320°C. Further, it would be anticipated that at least semiquantitative results should be obtained for samples exceeding this range, especially if the excess is towards higher boiling point.

An example of such a case, arising from research in this laboratory, concerns the analysis of partially hydrogenated anthracene oils used as start-up solvents in a coal hydrogenation process. These samples yield qualitatively adequate HPLC data, as illustrated in Fig. 1C. This liquid has a simulated boiling distribution determined by gas chromatography, corresponding to 7% gasoline, 10% kerosine, 56% diesel and 27% fuel oil (approx. > 320°C). Diesel response factors (Table III, sample 7) were considered appropriate and yielded the results: saturates = 9.7%, single-ring aromatics = 31.9%, double-ring aromatics = 35.4%, polynuclear aromatics = 19.0% and polars = 4.0%.

In the petroleum industry the Fluorescent Indicator Adsorption (FIA) test (ASTM D1319) is commonly applied to kerosines, and less commonly to diesels, to determine the content of aromatics expressed as a volume percent. A set of 21 kerosine samples covering an HPLC determined aromatics content of 9–82% have been studied¹¹ by both HPLC and FIA methods. A comparison of results shows the methods to be in good agreement, with a correlation coefficient of $r = 0.97$, a y -intercept of FIA = 1.0% and a slope of 0.91. A set of 16 diesel samples covering an HPLC determined content of 12–87% has also been studied¹¹. A poorer correlation between HPLC and FIA was found, with $r = 0.88$, a y -intercept of FIA = 3.6% and a slope of 1.03. It is well known that the FIA method is subject to interferences and can be particularly problematic for high-boiling liquids. The HPLC method described above is therefore considered particularly advantageous for diesel fuels.

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