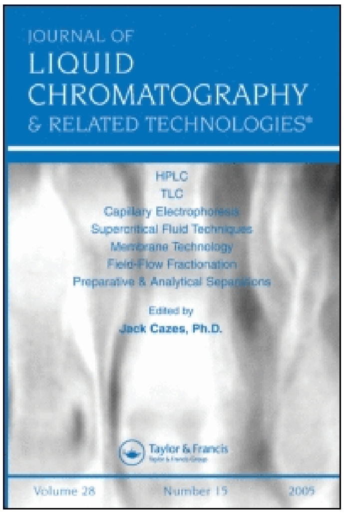

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QUANTITATION OF HIGH BOILING FRACTIONS OF NORTH SEA OIL AFTER CLASS SEPARATION AND GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

Deasphalted high boiling petroleum fractions (b.p. > 350°C) were rapidly separated into saturates, aromatics and polars using a two-column system (silica and cyano-bonded silica) with column switching and backflushing. Each of the classes were separated by size using gel permeation chromatography. The quantitation by refractive index detection was compared to the results from gravimetric analysis and the data indicated that refractive index detection can be used for quantitation of the gel permeation chromatographic separation of the individual classes of high boiling fractions of petroleum. For the separation into classes, the possibility of using quantitation based on refractive index detection and response factors obtained from similar high boiling residues were examined.

INTRODUCTION

Heavy petroleum fractions are complex mixtures of a broad variety of chemical classes from hydrocarbons to very polar compounds. The high molecular part is considered a reason for carbon

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and coke deposits formed under combustion, therefore knowledge of the composition of the residues is required for optimalisation of existing processes and for the design and development of new ones. Knowledge of the composition of the high boiling fractions is also very important for the computation of phase equilibrium data.

Two methods have been widely used for the separation of complex samples as crude oils and heavy petroleum distillates or residues, the USBM-API method and the SARA method (1). The SARA fractionation divides the sample into saturates, aromatics, resins and asphalthenes. During the last decade, several papers have appeared, describing high performance liquid chromatography (HPLC) techniques for performing the SARA separation. Much of the initial development work utilized silica as the stationary phase (2), while most of the recent work have been done on polar bonded phase columns (3-7) trying to avoid some of the activity problems with silica as the stationary phase. In the complex material of high boiling fractions it can be difficult to separate the so-called polar fraction (resins) from the aromatic fraction since the polar compounds also contain aromatic groups (8). The complexity of this material does also imply that a simple separation into saturated hydrocarbons (saturates), olefines and aromatics, as can be done with lower boiling fractions, (9-12), will be difficult. A large molecule may contain both olefinic and aromatic functions and thus making a simple definition impossible. In the SARA separation such a molecule will belong to the aromatic fraction, as will all olefines and alkylaromatics with no polar functional group.

A detailed knowledge of the composition requires more than a fractionation into classes. The separation by size is attractive as a complementary method to class separation and gel permeation chromatography (GPC) has been used in several studies of crude oils and petroleum residues (13-18). The main reason for performing GPC fractionation after separation into classes is that the retention is only related to the molecular weight for individual members of a single chemical class.

Since there is no liquid chromatography detector which gives the same response for all types of molecules found in a petroleum sample, quantitation is a major problem. Gravimetric measurements require preparative separations and are highly time consuming. To some extent gas chromatographic detectors like the flame ionization detector can be utilized, provided complex transfer systems such as moving wires are included (16).

The most universal HPLC detector, the refractive index (RI) detector, has been used by several authors (9,18-21) with mixed results. In our opinion the RI detector can be put to more valuable use in quantitative analysis of oil residues, provided its limitations are thoroughly acknowledged.

This paper describes how heavy petroleum residues (b.p. > $350^{o}C$) can be separated into classes of compounds with a system of column switching and back flushing. Each class of compounds was separated according to size by gel permeation chromatography and each GPC fraction was quantified by RI detection and compared to the results from gravimetric analysis.

EXPERIMENTAL

Materials.

Tetrahydrofuran (THF) of HPLC grade (Rathburn Chemicals, Walkerburn, Great Britain) was passed over basic Al_2O_3 (superactive 1 from Woelm) to remove peroxides. Hexane and dichloromethane (CH_2Cl_2) of HPLC grade (Rathburn Chemicals) were used as received. The HPLC solvents were degassed by helium if necessary. Alkylbenzene standards were purchased from Alltech Assoc. (Deerfield, IL). High boiling residues (> $350^{o}C$) of two different North Sea Oils were obtained from Statoil, Norway.

Instruments and columns.

The HPLC equipment consisted of a solvent delivery system (Waters 6000A) and a valve-loop injector (Waters U6K or Rheodyne 7125). A UV detector (Waters 440) and a RI detector (Waters R 401) were used in series. One six-port two-position valve was obtained from Valvo (HP) and one from Waters (Automated Switching Valve). Both were operated manually. Peak integration was done by a LDC/Milton Roy CI-10 integrator.

The following columns were of the MPLC^{TM} type (Brownlee Labs., Santa Clara, CA): One 4 mm x 3 cm and two 4.6 mm x 10 cm were packed with Spheri-5 CYANO (5 µm), two 4.6 mm x 10 cm were packed with Spheri-5 silica (5 µm) and one 4.6 mm x 10 cm was packed with Spheri-5 AMINO (5 µm).

100Å and 500Å ultraStyragel columns (7.8 mm x 30 cm) from Waters were used for the GPC fractionations. A cartridge type (Brownlee Labs.) guard column (4 mm x 3 cm) was filled with 60Å Styragel (< 37 µm) by the tap-fill method.

Procedure

The high boiling residues were n-hexane deasphalted using a residue to hexane ratio of 1:50 w/w at room temperature. The hexane insolubles (0.1-0.6%) were removed by filtration through a 0.45 µm Millipore filter.

All HPLC separations were performed at room temperature. Since the refractive index of different batches of the same solvent may vary, care was taken to fill the reference cell of the RI detector with the same eluent as was flowing through the column.

Class separation. All samples were dissolved in hexane and the injection was 20 µl or less. The column-switching system shown in figure 1 was used for the class separation. Since this is an analytical system where less than 3 mg of sample could be injected without loss in resolution, fractions from several in-

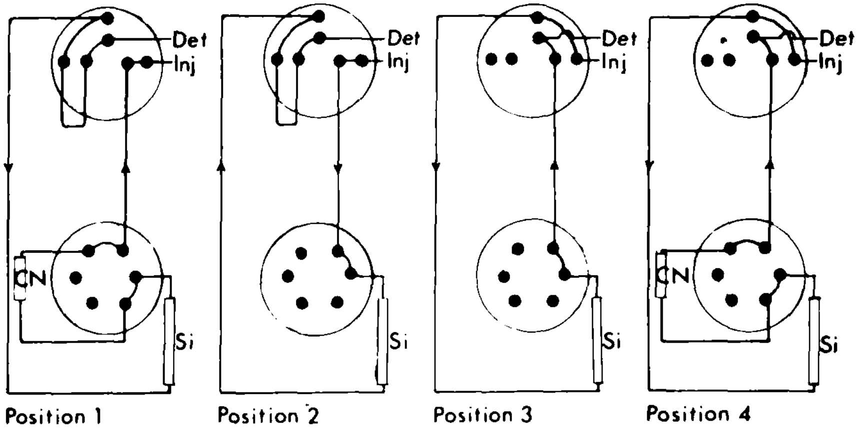

FIGURE 1. Column-switching system for class separation.

Position 1: The sample is loaded.
Position 2: The polars are trapped on the cyano column.
Position 3: The aromatics are backflushed.
Position 4: The polars are backflushed from the cyano column.

jections were combined for the gravimetric analysis. The main part of the hexane was removed by nitrogen (and heating) and the fractions were dried at 70°C until constant weight was obtained. The saturates and the aromatics were integrated by standard procedures. Integration of the polar fraction was time related. The integration time was 3 times the time from switching to the maximum of the polar peak.

GPC fractionation. The aromatic and polar fractions were readily dissolved in THF, however, the saturate fractions needed addition of hexane to solubilize the material. A solution of THF/hexane (50/50) was used for injection. It was necessary to make several injections of each sample in order to obtain enough material for the gravimetric analysis. The fractions were collected as shown in the chromatograms adjusting for the delay from the flowcell to the outlet of the RI detector. With constant flow-rate

(0.85 ml/min) the fractions of repeated fractionations were time related. Corresponding fractions were combined and the main portions of the THF were removed by N_2 (with heating). The last traces of THF were removed by heating at $70^{o}C$ until constant weight. The average integrated value from all injections was used for the determination of the RI area of each fraction.

RESULTS AND DISCUSSION

Separation of saturates and aromatics. Choice of packing material.

The complex nature of the compounds in petroleum fractions with b.p. > $350^{o}C$ makes the choice of packing materials crucial. The separation between saturates and aromatics requires a column which is able to separate saturates from olefines and saturates from alkylaromatics with large alifatic side chains. Unfortunately the normal phase materials have only been studied for their ability to separate low-molecular weight hydrocarbon standards. Therefore silica, cyano and amino materials were examined for their ability to separate alkanes and large alkylaromatics with hexane as the eluent. The results are shown in table 1.

The cyano material did not give a satisfactory separation of alkanes and alkylaromatics. The separation of alkanes and alkylbenzenes was better on the amino columns, however, due to reasons discussed later, this material was not examined further. The silica meterial gave the best separation of alkanes and alkylbenzenes and hence was chosen for the separation of saturates and aromatics in the high boiling petroleum fractions. Silica is also known to give the best separation of alkanes and alkenes.(11). Close to baseline separation of saturates and aromatics in the high boiling petroleum fractions was obtained on the silica column and the amount of UV absorbing material in the saturate fraction was small (Figure 2).

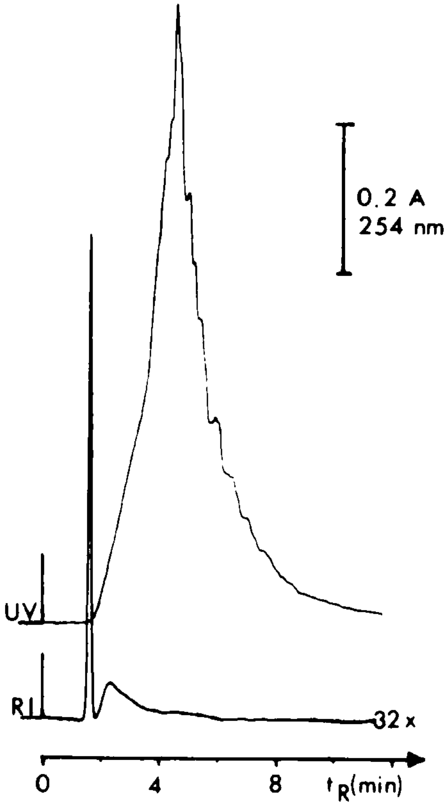

FIGURE 2: Separation of saturates and aromatics of a high boiling fraction from North Sea oil on silica column (2 x 10 cm) with hexane as the mobile phase (1.7 ml/min). The sample size was 2,5 µl and contained about 500 µg of the high boiling fraction (> 350°C).

TABLE 1

Comparison of capacity factors (k') of alkylbenzenes on silica, cyano and amino columns with hexane as the mobile phase.

	k' (silica)	k' (cyano)	k' (amino)
cyclohexane	0	0	0
pentadecylbenzene	0.39	0.085	0.16
hexadecylbenzene	0.39	0.085	0.16
octadecylbenzene	0.37	0.085	0.15
nonadecylbenzene	0.37	0.072	0.15
benzene	0.5	0.21	0.28

Separation of aromatics and polar compounds (resins). Choice of packing material.

It is well known that polar compounds are strongly bound to silica when hexane is used as the eluent. Packings with amino groups as surface functions will adsorb strongly compounds with acidic functional groups, may undergo reactions with aldehydes and ketones, and may also become slowly oxidized. Packings with a cyano surface function have a neutral non-reactive surface group with less retention of most polar compounds, allowing back-flushing from the column with hexane as eluent. Therefore, cyano packings are the materials of choice in our opinion. However, as all bonded phases the cyano materials may contain residual silanol groups which can give some adsorption of polar compounds.

When the high boiling petroleum fractions were loaded onto a cyano column, 3-5% of the material was not eluted when the column was backflushed with hexane. This material was later eluted with THF which had a superior eluting strength compared to dichloromethane. The column was cleaned with THF once a week. The complexity of the material in the high boiling fractions made it difficult to draw a distinction between aromatics and polar compounds. Since relevant standards for the separation between aromatics and polars are scarce, it was chosen to use real samples. A high boiling fraction was injected on a cyano column and fractions were collected. The collected fractions were re-injected on a silica column eluted with hexane, as a test system. Fractions containing polar compounds gave severe tailing and adsorption of the material. Such fractions should not be loaded onto a silica column and were defined as polar even if they contained some higher polycyclic aromatics as well. By comparison with PAH standards it was found that all four membered rings were contained in the aromatic fraction while five membered rings and larger were included in the polar fraction.

Class separation into saturates, aromatics and polar compounds.

Since silica was needed for separation of saturates and aromatics and a cyano column for trapping of the polars, a two column system was necessary. The system shown in figure 1 was used for the class separation. The system required two switching valves. The sample was loaded on the cyano column and passed onto the silica column with hexane. When the aromatics left the cyano column, the cyano column was removed from the flow so that no polar material was allowed to enter the silica column. The time of switching was determined by injecting a chrysene standard which should belong to the aromatic fraction. This calibration was repeated at intervals since the activity of the cyano column could change slightly. When the saturates had left the silica column, the flow was reversed to get a short elution time for the aromatics. Finally the polars were backflushed from the cyano column. This procedure gave short analysis time for the separation of high-boiling petroleum fractions into saturates, aromatics and polars. (figure 3).

GPC Fractionation of the individual classes.

Polystyrene type column materials have been widely used and proved applicable to GPC separations of petroleum samples and were therefore chosen for this study. Preliminary results on a 500 Å column indicated that no material in the deasphalted high boiling fractions of North Sea Oil was excluded from the pores, while a small amount was excluded from a 100Å column. The 100Å column, which had an exclusion limit of about 1000, based on linear hydrocarbons, was therefore chosen.

The highly efficient ultraStyragel 100Å column is only comparable with a limited number of solvents. None of the solvents of choice appeared to meet all the requirements for an ideal mobile phase with respect to detection, volatility, viscosity, sample solubility and lack of adsorption and solvation effect. THF,

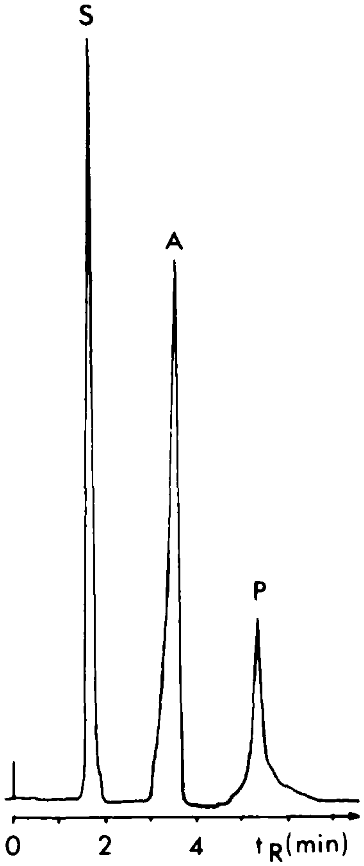

FIGURE 3. Class separation of the high boiling fraction (> 350°C) of a North Sea oil into saturates (S), aromatics (A) and polars (S). The dual column switching system shown in figure 1 was used with a 3 cm cyano column and a 2 x 10 cm silica column. The mobile phase was hexane (1.7 ml/min). About 2 mg (in 10 µl) was injected.

which is relatively polar, seemed to be the best choice. Due to the aromatic character of the stationary phase it was suspected that aromatics could be preferentially adsorbed. Therefore the retention of a number of PAH standards were examined with THF and dichloromethane as mobile phases. The data clearly indicated that also other effects than size exclusion are responsible for the retention, and they also showed that THF is superior to dichloromethane in suppressing interactions of aromatics with the column material. In size separations such interactions are not desired.

GPC fractionations of the saturate, aromatic and polar classes from two different deasphalted high boiling residues from North Sea Oil are shown in figure 4.

Quantitative analysis.

Quantitation is a major problem since no HPLC detector gives the same response for all types of compounds found in a petroleum sample. Gravimetric determinations require preparative separations and are highly time consuming, like other off-line detection methods. The RI detector has been widely used for quantititaion, but the detector must be calibrated. Standards, which can provide a crude calibration, are, however, not available for these high-boiling fractions.

Preliminary results from GPC fractionation directly on residues (without class separation) showed that the RI response could not be correlated with weight. After class separation and size separation of the classes by GPC, the RI response within the classes was closely related to the amount (weight) of material. The data from the gravimetric analysis are compared with the RI areas of each subfraction in figure 5.

The correlation between RI response (area) and weight was good for GPC fractions of saturates and of polar compounds and not so good for fractions of aromatics. This probably reflects the fact that the increase in refractive index of n-alkanes above

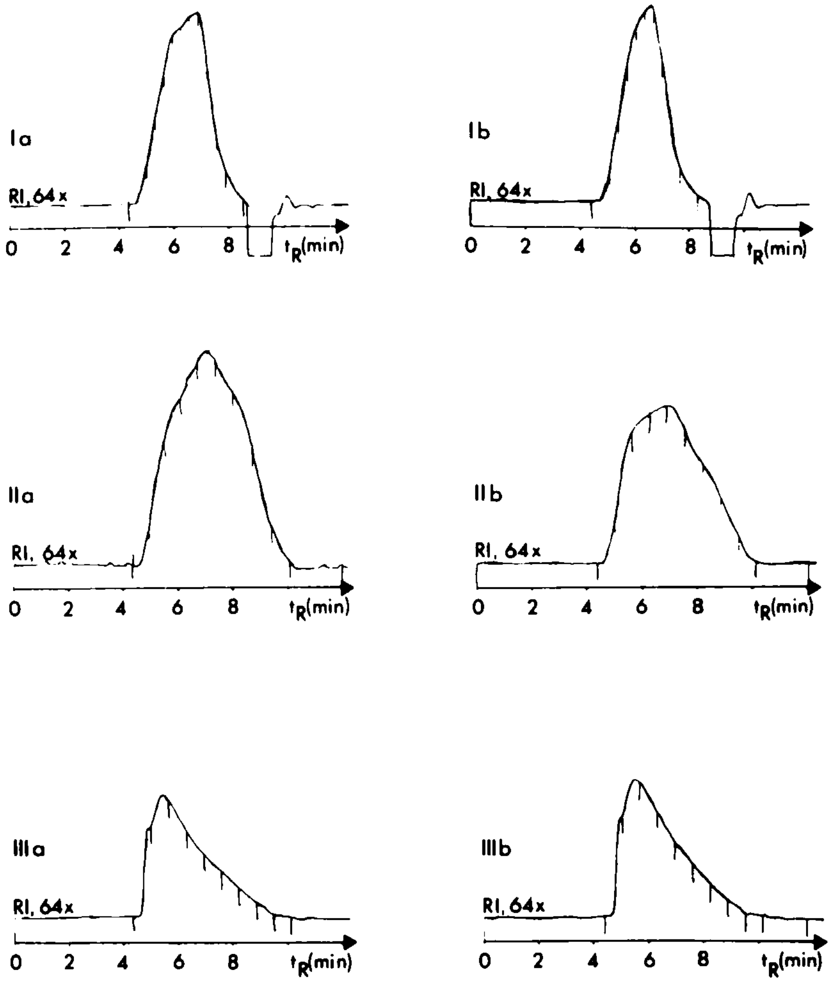

FIGURE 4. GPC fractionation of the saturate, aromatic and polar fraction of the high boiling fraction (> 350°C) of two North Sea oils (A and B) on 100Å ultraStyragel column with THF (0.85 ml/min) as the eluent.

Ia: Saturate fraction of oil A (about 5.6 mg, 50 µl)
Ib: Saturate fraction of oil B (about 5,7 mg, 50 µl)
IIa: Aromatic fraction of oil A (about 4,7 mg, 25 µl)
IIb: Aromatic fraction of oil B (about 4,3 mg, 25 µl)
IIIa: Polar fraction of oil A (about 2,3 mg, 25 µl)
IIIb: Polar fraction of oil B (about 2.0 mg, 25 µl)

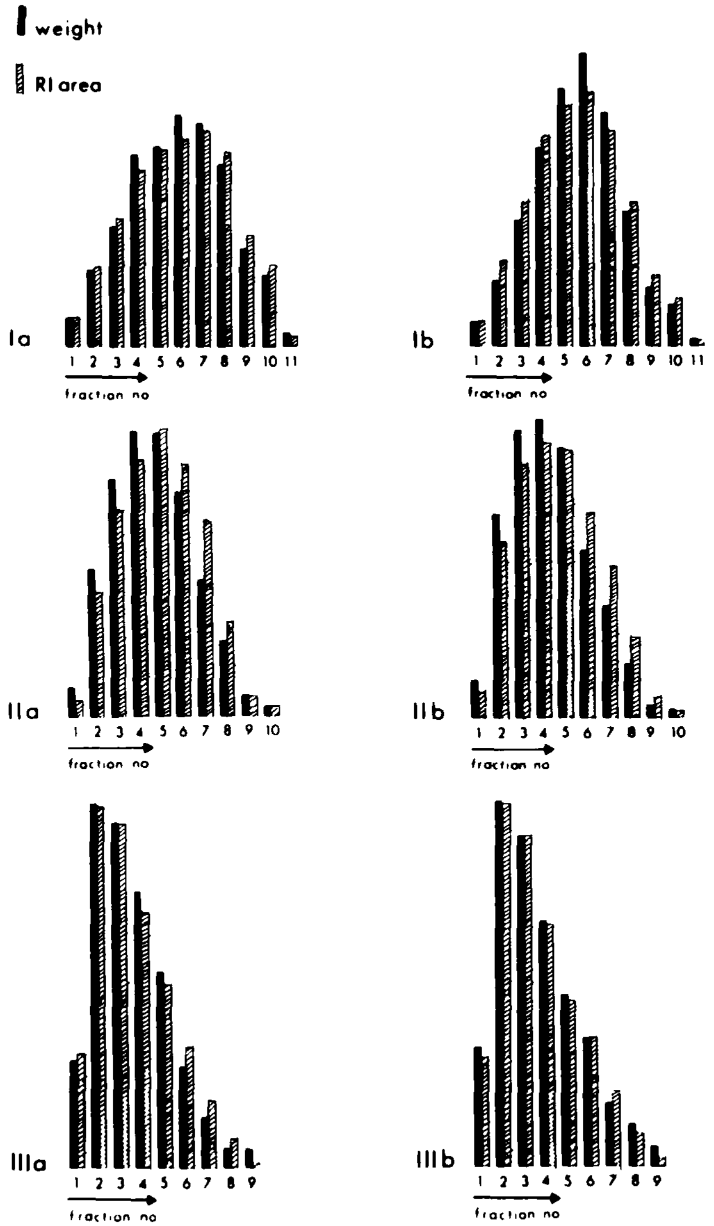

FIGURE 5. Comparison of the weight vs. RI area for the individual fractions from the GPC fractionation of the saturate, aromatic and polar fractions from the high boiling residue (> 350°C) of two different North Sea oils (A and B).

Ia: Saturates from oil A, Ib: Saturates from oil B, IIa: Aromatics from oil A, IIb: Aromatics from oil B, IIIa: Polars from oil A, IIIb: Polars from oil B.

C_{25} is not very high (22), compared to the increase among the lower homologs. The aromatic fraction range from one to four condensed rings, containing compounds with appreciable differences in refractive indexes, while the polar class contain the higher condensed systems probably with less differences in refractive index.

As a consequence of the generally good correlation between RI response and weight for GPC fractions of each class, the same ratios were determined for each class after class separation without GPC fractionation. The samples were injected in hexane solution. If the hexane solvent had a refractive index different from the mobile phase hexane, the saturates area could not be determined accurately. This meant that degassing of the eluent could not be performed after sample preparation, since this could change the refractive index of the eluent. The tailing of the polar fraction created an integration problem. The integration time for the polars, as shown in figure 3, was determined by UV detection. The integration was stopped at a time when the result was little influenced if the baseline did not return to the original setting. Baseline deflection was minimal if the attenuator was kept at 32 X or larger, which required a sample load of $\geq$ 1 mg. To avoid integration problems due to deflection, the cyano column should be as short as possible to give a short elution time of the polar fraction.

The relation between weight and RI area for the class separation of two high boiling fractions from different sources are shown in table 2.

Taking into account that the two oils tested were quite different in content, the difference in the weight/area ratios were small.

CONCLUSIONS

Together with the data obtained by the class separations on a dual silica/cyano column system, the data from GPC fractionation

TABLE 2

Comparison of the weight/RI area ratio for the saturate, aromatic and polar fractions of the high boiling residue of two different North Sea Oils (A and B).

	A			B		
	% weight	%RI area	weight/area	% weight	%RI area	weight/area
saturates	44.5	36.8	1.21	57.6	47.9	1.20
aromatics	35.4	44.6	0.79	28.7	37.9	0.76
polars	20.0	18.5	1.08	13.6	14.1	0.97

will give valuable information about the composition of high boiling petroleum residues.

Our data indicates that RI detection can be used for quantitation of GPC fractionation of the individual classes of high boiling fractions of petroleum. Since the weight/area ratios for the different classes were closely related for residues from two highly different sources in the North Sea, this indicates that RI detection may be used for quantitation, however, we suggest that further studies should be initiated to control the relationship between weights and RI-areas for each class.

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