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RAPID SEPARATION OF HEAVY PETROLEUM PRODUCTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A rapid high-performance liquid chromatographic technique (<30 min) for separating heavy petroleum products into saturated, aromatic and polar compounds is described. The choice of stationary phase (alkylamine- and alkylnitrile-bonded silica, 10 μm), detection mode (refractometry and UV absorptiometry) and separation method (backflushing procedure) are discussed. The technique, which utilizes for quantitative purposes response factors obtained by adsorption preparative liquid chromatography, permits the analysis of vacuum distillates and atmospheric and vacuum residues.

INTRODUCTION

Distillation of crude petroleum gives an atmospheric residue (initial boiling point >350°C). Its vacuum distillation gives a vacuum distillate and residue (initial boiling point >535°C). Depending on the origin of the crude petroleum the residue yields are very variable, but certainly the percentage of residue will increase with the exploitation of heavier crude petroleum reserves. In the meantime the consumption of heavy petroleum products may decline as a result of the development of nuclear energy. Consequently, it is necessary to convert large amounts of petroleum products into light petroleum products. Chemical conversion processes are based on thermal or catalytic cracking and in order to improve these processes a more extensive knowledge of the characteristics of residual materials is imperative. At present the analysis of residues consists of simple physico-chemical measurements such as density, viscosity, asphalt and ash contents, elemental analysis, etc. Unfortunately, these chemical measurements cannot explain the difficulties encountered during refining. Laboratory and pilot plant studies have shown that the various types of hydrocarbon groups react differently in the conversion processes. The three principal hydrocarbon groups encoun-

tered in the distillation residues are saturated, aromatic and polar compounds (hydro-carbons in which all molecules include heteroatoms such as nitrogen, oxygen, sulphur and possibly heavy metals). The quantitative analysis of these groups is usually carried out by classical liquid chromatography, using columns packed with stationary phases of large particle size. This technique has the major drawback that the analysis takes a very long time (about 1 day)[1]. Consequently, classical liquid chromatography cannot be used to monitor refining processes, for which purpose the analysis time must be very short. Therefore, we chose to use high-performance liquid chromatography (HPLC) for group analysis, with an analysis time of about 30 min. We have applied this technique to atmospheric residues and vacuum distillates and residues.

EXPERIMENTAL

Materials

The solvents used were *n*-hexane and cyclohexane (Chromasol, SDS, Peypin, France), chloroform and dichloromethane (Merck).

To measure the capacity factors of the solutes squalane was used as a t_0 marker in non-polar and polar eluents.

Apparatus

The chromatograph was a Varian Model 5000 (Varian, Palo Alto, CA, U.S.A.) equipped with an Altex UV photometer (254 nm) (Altex, Berkeley, CA, U.S.A.) and a Model R401 differential refractometer (Waters Assoc., Milford, MA, U.S.A.). Samples were injected into the chromatographic column using a sample injection valve (Valco Model CV-6-HPAX) with a 10-μl loop. Reverse flow (backflushing) was achieved with the same type of valve. The signal was recorded on a recorder and the peak areas measured with a Varian Model CDS 111L computing integrator.

Stationary phases

We studied two adsorbents (Partisil 5 silica gel, mean particle size 5 μm, Whatman, Clifton, NJ, U.S.A., and Alox T alumina, mean particle size 5 μm, Merck, Darmstadt, G.F.R.) and two bonded phases (LiChrosorb NH_2, silica bonded alkyl-amine, Merck, and Partisil 10 PAC, silica bonded alkylnitrile, Whatman).

All chromatographic columns (20 cm $\times$ 4.8 mm I.D.; stainless steel) were packed with stationary phase by the conventional slurry technique.

Choice of chromatographic method

A good separation between saturated hydrocarbons, aromatic hydrocarbons and polar compounds depends on the stationary phase selected. Two chromato-graphic methods can be used to reach this objective: liquid–solid chromatography and liquid–liquid chromatography.

Liquid–solid chromatography. Generally, adsorption chromatography on silica or alumina with an apolar solvent such as *n*-hexane gives a good separation between saturated and aromatic compounds, but very polar compounds cannot be eluted and adsorb irreversibly, which decreases the lifetime of the column. However, the resolu-tion depends on the variation of the activity of the adsorbent and it is well known that

the activity of an adsorbent varies with its water content[2,3]. The greater the activity of the adsorbent (lower water content) the higher is the resolution[4–7]. Also, isohydric solvents[8–10] must be used in order to keep the activity of the adsorbent constant and to obtain reproducible results.

Consequently, we did not select these two stationary phase. Nevertheless, with aromatic groups very good quantitative results[11,12] can be obtained between mono- and polyaromatic compounds with these supports, particularly alumina.

Liquid–liquid chromatography. Separation of the three hydrocarbon types is obtained with the silica-bonded phases chosen (alkylnitrile and alkylamine)[13–18]. Nevertheless, the resolution of saturated and aromatic compounds is poorer than on silica gel. However, these two stationary phases are interesting because we do not need to control the water content of the mobile phase and irreversible adsorption of polar compounds is seldom or never observed. In conclusion, silica-bonded alkyl-amine and alkylnitrile were chosen for the separation of saturated and aromatic compounds from polar compounds.

Application to petroleum products

Separation of saturated compounds from aromatic plus polar compounds. Saturated compounds are eluted with the dead volume and therefore a very sharp peak is obtained, which is easy to quantitate by means of a CDS 111L integrator. On the other hand, aromatic and polar compounds are eluted more slowly and often broad peaks with serious tailing occur. Also, it is judicious to collect aromatic and polar compounds into a single peak by backflushing the chromatographic column after the elution of unretained compounds*[4–7,13]. The backflushing technique is shown in Fig. 1. The separation between saturated compounds and aromatic plus polar compounds is shown in Fig. 2a and b. In Fig. 2a, the reversal of flow was effected when the signal had pratically returned to the baseline, and it can be seen that a fraction of aromatic and polar compounds had not yet been eluted. The quantitative analysis of aromatic and polar compounds is impossible without using backflushing. In Fig. 2b the reversal of flow was effected after the elution of saturated compounds. It is easy to choose the backflushing time because a very large resolution is obtained between the saturated compounds peak and the aromatic plus polar compounds peak. If asphaltenes are present (for instance, in atmospheric and vacuum residuals), it is necessary to use cyclohexane instead of *n*-hexane as the mobile phase because precipitation of asphaltenes is prevented.

Separation of saturated plus aromatic compounds from polar compounds. The flow-reversal technique has also been used for this separation. Unfortunately the resolution between saturated plus aromatic compounds and polar compounds is much poorer or zero. Consequently, we chose a backflushing time such that a poly-aromatic chromatographic fraction containing up to six rings (determined by mass spectrometry) is eluted with the saturated group. Then, polar compounds such as phenolic derivatives or nitrogen heterocycles are eluted after the backflushing. In addition, the major sulphur and thiophenic compounds are eluted with aromatic group. This procedure fits the best with the results obtained by preparative liquid chromato-

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* Further, flow reversal substantially decreases the analysis time for high-boiling samples.
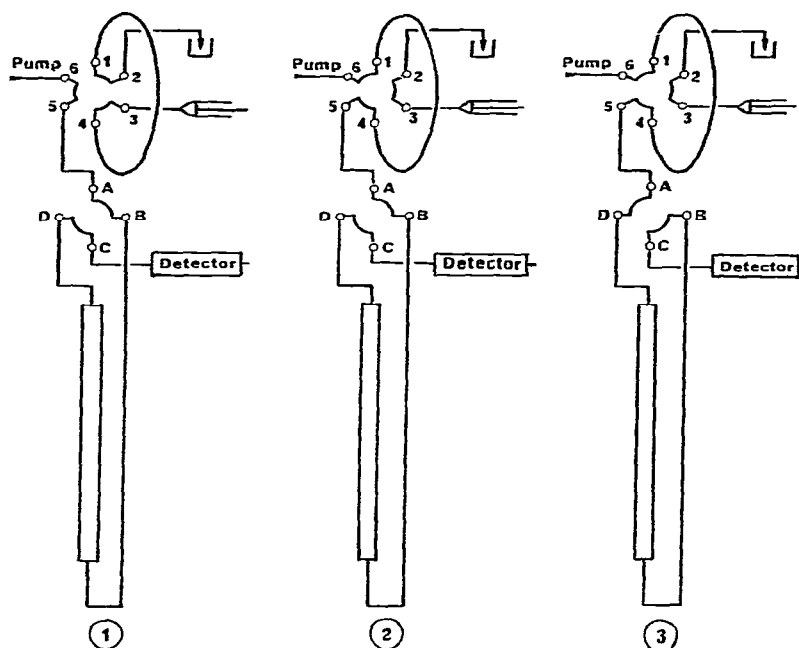
Fig. 1. Flow diagram of liquid chromatograph with flow reversal. (1) Filling of loop injection valve; (2) injection and elution of first peak; (3) backflushing and elution of second peak.
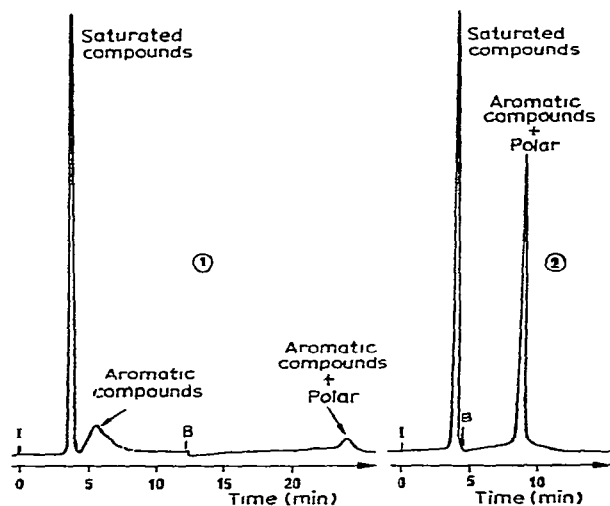

Fig. 2. Separation of saturated hydrocarbons from aromatic plus polar compounds in a vacuum distillate (boiling range 350–535°C) with and without flow reversal. (1) Backflushing after the broad aromatic compound peak; (2) backflushing after the saturated compound peak. I = injection; B = backflushing. Column, 10 μm silica-bonded alkylamine, 20 cm × 4.8 mm I.D.; mobile phase, *n*-hexane; flow-rate, 2 ml·min^{-1}; detector, refractive index (R401); attenuation, ×16.

graphy* which are used to calculate calibration factors for the different hydrocarbon groups.

Fig. 3 shows the separation of saturated plus aromatic compounds from polar compounds with cyclohexane–chloroform (85:15) as the mobile phase
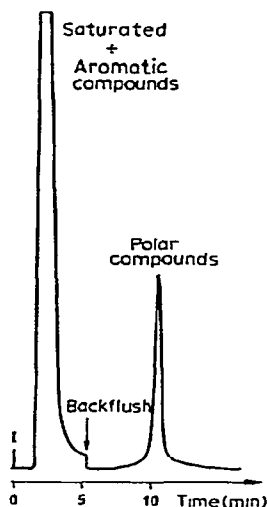

Fig. 3. Separation of saturated plus aromatic hydrocarbons from polar compounds in vacuum distillate (boiling range 350–535°C) with backflushing. Column, 10 μm silica-bonded alkylamine, 20 cm × 4.8 mm I.D.; mobile phase, cyclohexane–chloroform (85:15); flow-rate, 2 ml·min⁻¹; detector, UV at 254 mm.

Choice of detection mode

It was necessary to calculate the calibration factors for the different hydrocarbon groups for quantitative analysis. As model compounds were not available we had to isolate the standards using preparative liquid chromatography on silica gel. The two most commonly used detection methods are refractometry and absorption photometry. For the analysis of petroleum fractions with boiling points above 350°C the differential refractometer gives an approximately constant calibration factor for each hydrocarbon group, whatever the distillation range or crude oil origin[4]. UV photometry is by far the most widely used technique in liquid chromatography owing to its good detection limit (which varies with the nature of the sample), reasonable dynamic range and insensitivity to changes in the eluent composition. Of course, the last advantage is counterbalanced by its inability to detect aliphatic compounds. Taking these factors into consideration, refractometry was chosen for the saturated and aromatic group and UV absorptiometry for the polar group because their percentages in residuals are very low.

Operating conditions. The operating conditions are given in Table I.

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* The ELF-Solaize Research Centre uses an original preparative liquid chromatographic separation: adsorption on silica gel with cyclohexane, dichloromethane and chloroform–methanol (70:30) as mobile phases in the step gradient mode.

TABLE I

OPERATING CONDITIONS

Parameter	Separation of saturated hydrocarbons from aromatic plus polar compounds	Separation of saturated plus aromatic hydrocarbons from polar compounds
Stationary phase	Silica bonded NH_2 or CN	Silica bonded NH_2 or CN
Mobile phase	n-Hexane: fraction without asphaltene Cyclohexane: fraction with asphaltenes	Cyclohexane–chloroform (85:15) v/v
Detector	Differential refractometer	UV photometer
Results obtained	Saturated compounds (%) Aromatic + polar compounds (%)	Polar compounds (%)

RESULTS

Repeatability

The repeatability of the chromatographic analysis was determined using a vacuum residual (light Arabian, initial boiling point >535°C) both for the separation of saturated compounds from aromatic plus polar compounds and for the separation of saturated plus aromatic compounds from polar compounds. A 20 cm × 4.8 mm I.D. LiChrosorb NH_2 (10 μm) chromatographic column was used.

For eleven measurements the repeatability was 12.3% for the saturate group, 5.9% for the aromatic plus polar group and 6.1% for the polar group. With vacuum distillates the differences were smaller: 3.4% for the saturated group, 3.8% for the aromatic plus polar group and 5% for the polar group.

Calibration factor

The calibration factor, R_i, for a hydrocarbon group i is given by the relationship $R_i = S_i/CP_i$, where S_i is the peak area (expressed as units) for the hydrocarbon group studied, C the sample concentration (mg·ml^{-1}) and P_i the percentage of hydrocarbon group i in the sample.

We can distinguish two types of fractions: vacuum distillates of boiling range 350–535°C and vacuum residuals of initial boiling point >535°C. For each saturated compound group and aromatic plus polar compound group the calibration factors are determined by analysis of several vacuum distillates and residuals by adsorption preparative liquid chromatography (Tables II and III).

The calibration factors are as follows: for vacuum distillates of boiling range 350–535°C (n-hexane as mobile phase), saturated compounds 423,000 area unit·ml· mg^{-1} and aromatic plus polar compounds 699,000 area unit·ml·mg^{-1}, and for vacuum residuals of initial boiling point >535°C (cyclohexane as mobile phase), saturated compounds 188,000 area unit·ml·mg^{-1} and aromatic plus polar compounds 278,000 area unit·ml·mg^{-1}.

The calibration factor for polar compounds was obtained by linear regression with several vacuum distillates and residuals. The calibration factors, for polar compounds calculated using the slopes in Fig. 4 are as follows: for vacuum distillates 113,000 area unit·ml·mg^{-1} and for vacuum residuals 213,000 area unit·ml·mg^{-1}. The correlation coefficient is 0.998 for vacuum distillates (curve A) and 0.97 for vacuum residuals (curve B).

$\dfrac{\text{Area}}{\text{Concentration}} \cdot 10^{-5}$ (Analytical chromatography)
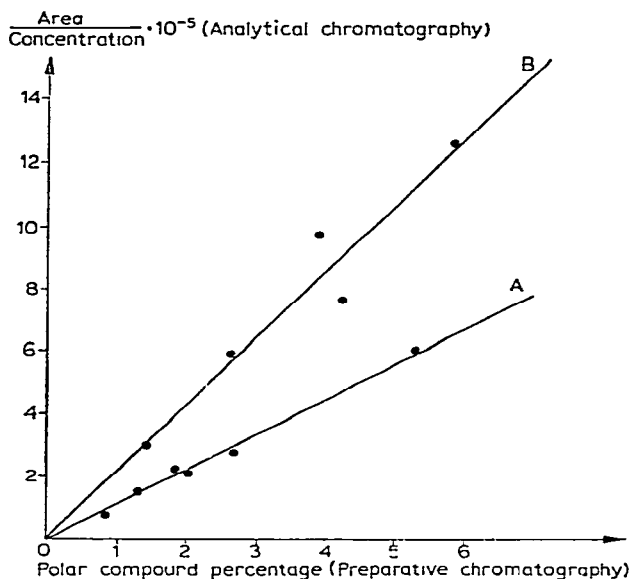

Fig. 4. Calibration factors for polar compounds (obtained from the slope of the line). Mobile phase, cyclohexane–chloroform (85:15). A, Vacuum distillates, correlation coefficient 0.998; B, vacuum residuals, correlation coefficient 0.97.

Applications

The percentages of saturate compounds and aromatic plus polar compounds determined by both preparative and analytical chromatography for several distillates are given in Table IV and the percentages of the individual groups in several residuals and of saturated hydrocarbons in several bitumens are given in Table V. Bitumens are very rich in polar compounds, and preparative chromatography therefore gives incorrect results (irreversible adsorption) for the percentages of aromatic plus polar compounds. Consequently, analytical chromatography utilizing calibration factors obtained by preparative chromatographic methods also gives incorrect results.

DISCUSSION

Separation of saturated compounds from aromatic plus polar compounds

The calibration factors for vacuum residuals (VR) are lower than those of vacuum distillates (VD): saturated compounds, VR 188,000 and VD 423,000 area unit·ml·mg^{-1}; aromatic plus polar compounds, VR 278,000 and VD 699,000 area unit·ml·mg^{-1}. This difference can be explained by the refractive index of cyclohexane being higher than that of n-hexane. Close agreement between analytical and preparative liquid chromatography is obtained for the percentages of saturated hydrocarbons in bitumens and vacuum distillates and residuals (Tables IV and V). The largest spread was observed for the fractions with initial boiling points less than 300°C (light distillates, boiling range 260–420°C). This is more important for saturated than aromatic compounds (Table IV).

Close agreement between analytical and preparative liquid chromatography

TABLE II

SEPARATION OF SATURATED HYDROCARBONS FROM AROMATIC PLUS POLAR COMPOUNDS IN VACUUM DISTILLATES (n-HEXANE AS MOBILE PHASE)

n = Number of determinations; t = Student's coefficient.

Vacuum distillate (boiling range 350–535°C)	Sample concentration (mg·ml⁻¹)	Concentration by preparative chromatography (%, w/w)		Peak area × 10³		Calibration factor × 10² (area unit·ml·mg⁻¹)	
		Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds
Light Arabian	20.24	45.0	55.0	3773	7909	4141	7106
Basrah heavy	18.82	32.1	67.7	2684	8911	4443	6994
Quatar	20.03	62.9	37.1	5159	5309	4094	7145
Es Sider	20.63	67.1	32.8	5812	4664	4190	6889
Zakum	20.56	53.4	46.6	4720	6548	4300	6834
Mean $\bar{M}$						4234	6994
Standard deviation, σ						140	134
Relative error with a confidence limit of 95% $\left(\dfrac{\dfrac{t \cdot \sigma}{\sqrt{(n-1)}} \times 100}{\bar{M}} \right)$						4.6	2.7

TABLE III

SEPARATION OF SATURATED HYDROCARBONS FROM AROMATIC PLUS POLAR COMPOUNDS IN VACUUM RESIDUALS (CYCLOHEXANE AS MOBILE PHASE)

Vacuum residual	Sample concentration ($mg \cdot ml^{-1}$)	Concentration by preparative chromatography (%, w/w)		Peak area $\times 10^3$		Calibration factor $\times 10^2$ (area unit $\cdot$ ml $\cdot$ mg^{-1})	
		Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds
Light Arabian (b.p. >535°C)	23.48	16.0	83.7	650	5833	1730	2968
Basrah heavy (b.p. >535°C)	22.09	10.8	89.2	484	5120	2029	2598
Mean						1879	2783

TABLE IV

PERCENTAGES OF SATURATED HYDROCARBONS AND AROMATIC PLUS POLAR COMPOUNDS IN SEVERAL VACUUM DISTILLATES: COMPARISON BETWEEN ANALYTICAL AND PREPARATIVE LIQUID CHROMATOGRAPHY

Vacuum distillate	Concentration (%, w/w)					
	Analytical chromatography		Preparative chromatography		Difference	
	Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds	Saturated compounds	Aromatic + polar compounds
Light Arabian (400–500°C)	48.2	52.5	51.1	48.6	−2.9	+3.9
Light Arabian (365–465°C)	51.0	47.7	51.2	45.3	−0.2	+2.4
Heavy distillate (375–550°C)	45.3	55.0	44.8	55.1	+0.5	−0.1
Ekofisk light distillate (350–470°C)	66.9	36.1	66.7	33.3	+0.2	+2.8
Visbreaking (350–535°C)	44.8	55.0	46.0	53.9	−1.2	+1.1
Light distillate (260–430°C)	49.5	47.2	54.2	44.5	−5.2	+2.7
Basrah heavy medium gas oil (250–350°C)	50.9	39.7	60.4	37.6	−9.5	+2.1
Light distillate (280–425°C)	55.1	38.7	63.4	35.2	−8.3	+3.5
Light distillate (260–410°C)	54.3	38.7	61.2	36.9	−6.9	+1.8

TABLE V

ANALYSIS OF BITUMENS AND RESIDUALS: COMPARISON BETWEEN ANALYTICAL AND PREPARATIVE LIQUID CHROMATOGRAPHY

Product	Analytical chromatography				Preparative chromatography			
	Saturated compounds (%,w/w)	Aromatic compounds (%,w/w)	Polar compounds (%,w/w)	Recovery (%)	Saturated compounds (%,w/w)	Aromatic compounds (%,w/w)	Polar compounds (%,w/w)	Recovery (%)
Bitumes:								
Boscan	11.4	–	–	–	10.6	–	–	–
Laguna	16.1	–	–	–	14.4	–	–	–
O1	15.5	–	–	–	14.4	–	–	–
O2	16.9	–	–	–	16.5	–	–	–
Residuals:								
Visbreaking (>535°C)	18.3	74.2	5.9	98.4	18.4	74.8	5.8	99.0
Light Arabian without asphaltene (initial boiling point >535°C)	20.2	82.0	1.4	103.6	19.3	79.0	1.4	99.7
Atmospheric residual (>350°C)	24.6	82.9	4.2	111.7	25.7	68.3	5.2	99.2

was also obtained for the percentages of aromatic and polar compounds in vacuum distillates and residuals (Tables IV and V). The difference observed with the light Arabian atmospheric residual (Table V) can be explained by the fact that an atmospheric residual must be considered as a mixture of vacuum distillate and residue. The calibration factors for saturated compounds and aromatic plus polar compounds for vacuum distillates (with cyclohexane and cyclohexane–chloroform as mobile phase, respectively) are higher than those for vacuum residuals. The average calibration factors for atmospheric residuals can be estimated by taking into account an average composition of vacuum distillate and vacuum residual of 1:1.

The calibration factors calculated for atmospheric residuals (cyclohexane as mobile phase) are then as follows: saturated compounds 180,000 area unit·ml·mg^{-1}, aromatic plus polar compounds 329,000 area unit·ml·mg^{-1} and polar compounds 163,000 area unit·ml·mg^{-1}. These values were used to calculate the percentages of saturated hydrocarbons, aromatic hydrocarbons and polar compounds in light Arabian atmospheric residual. The results are given in Table VI. Good agreement is observed between analytical and preparative liquid chromatography.

TABLE VI

ANALYSIS OF RESIDUAL ATMOSPHERIC FROM LIGHT ARABIAN USING AVERAGE CALIBRATION FACTORS: COMPARISON BETWEEN ANALYTICAL AND PREPARATIVE LIQUID CHROMATOGRAPHY

Component	Concentration (%, w/w)		
	Analytical chromatography	Preparative chromatography	Difference
Saturated compounds	25.7	25.7	0
Aromatic compounds	68.1	68.3	−0.2
Polar compounds	5.5	5.2	+0.3

Separation of saturated plus aromatic compounds from polar compounds.

The calibration factors for polar compounds were obtained by linear regression. This method of calculation is more precise than the preceding one for two reasons: (1) the wide range of percentages of polar compounds (0–6%) and (2) the preparative chromatographic results for polar compounds are not as precise as those for saturated and aromatic compounds. In Fig. 4 the large difference observed between the two vacuum residuals containing 4% of polar compounds can be explained by their origins. One is a heavy sulphur-containing residual, very rich in asphaltenes (Basrah heavy), and the other a light Arabian vacuum residual. The difference between the calibration factors can be explained by the nature of the polar compounds present, which varies according to the boiling point of the fraction. The vacuum residuals are much richer in oxygen-bearing compounds than are the vacuum distillates.

CONCLUSION

The rapid HPLC method described can be used for the analysis of hydrocarbon groups (saturated, aromatic and polar compounds) in vacuum distillates and residuals with or without asphaltenes. A silica-bonded alkylamine or alkylnitrile is used as the stationary phase and the analysis is carried out with two chromatographic runs.

The separation of saturated compounds from aromatic plus polar compounds is carried out with the first chromatographic run using an apolar solvent as the mobile phase, and the separation of saturated plus aromatic compounds from polar compounds is carried out with the second chromatographic run using a more polar solvent (*n*-hexane–chloroform) as the mobile phase. Each chromatographic run requires about 15 min. The use of this system eliminates two of the major difficulties encountered with classical adsorbents, *viz.*, non-reproducible retention due to small changes in the water content of the mobile phase and irreversible adsorption. This method allows us to determine (with comparison of typical samples) the composition of an unknown sample. Further, this method could easily be used in a refinery.

ACKNOWLEDGEMENTS

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