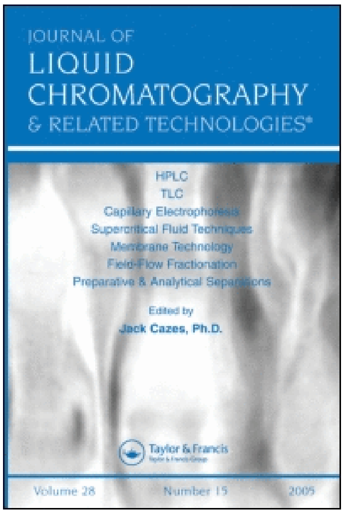

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CRUDE OIL HYDROCARBON GROUP SEPARATION QUANTITATION

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Introduction

The petroleum industry like most other industrial segments are continuously developing new and sophisticated techniques of analysis and at the same time are working to automated routine techniques. In the petroleum industry, the source of supply has generally become less stable and economics has dictated new thinking, both in processing and in the analysis of composition to support these new trends. In addition, this industry is faced with having a new raw material, shale oil, and coal liquids, in the near future.

The traditional techniques for hydrocarbon group composition were developed when different crudes were in common supply. Today, not only do the sources of crude tend to change more often, but these crudes are different than those used in the past. High Performance Liquid Chromatography (HPLC) is making major intrusion into the separation needs of the petroleum chemist. A major hurdle that this technique faces is that of quantitation. The traditional techniques have generally been solvent-nonsolvent or open column step gradient procedures using gravimetric quantitation procedures. The detectors in HPLC equipment provide an analog signal from specific (ultraviolet) or nonspecific (differential refractometer) detectors. Such is the case in the hydrocarbon group separation of crude oils. An early use of HPLC for the separation of crude oil into hydrocarbon groups was published by Sautoni.[1] In this technique, the asphaltenes are removed and the sample is separated into saturated, aromatics, and polar aromatics using n-hexane as the solvent and an alkyl amine modified silica gel column packing. (Figure 1).

The n-hexane mobile phases across this amine modified packing provides unique selectivity for the paraffinic and aromatic hydrocarbons in crude oils (Table 1). All of the normal, iso, and cyclo paraffins elute with $k' = 0.1$. This includes such paraffinic structures as cholstane. Yet the k' of a long alkyl branched mono aromatic is at a $k' = 0.16$. If alkenes or cycloalkenes are present, as in shale oil, they will elute with the saturates at k' of 0.1. This resolution is in part obtained by using relatively small sample loads (sample loads of 0.2 micrograms is typical) on the column. These small sample loads necessitate the use of an ultraviolet photometer to monitor the aromatics and polar aromatics where k' are between one and five.

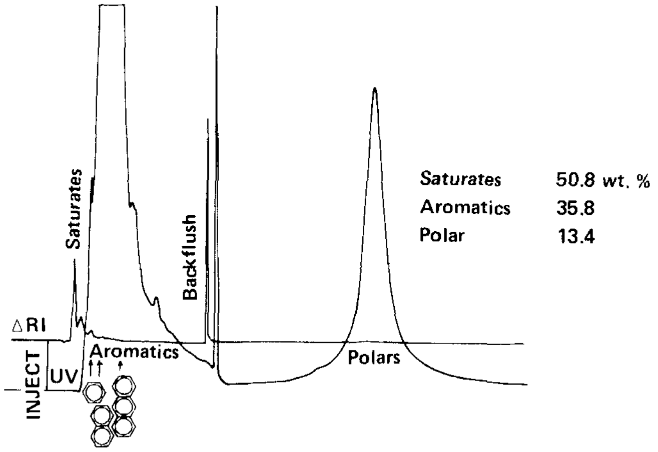

Figure 1 Hydrocarbon Group separation of Alaskan Crude Oil. n-Hexane at 2.0 ml/min. across a 3.9mm x 30cm Energy Analysis Column.

Instrumentation

All separations were performed on a Hydrocarbon Group Analyzer System. The column, 3.9mm x 30cm long, is an Energy Analysis (NH_2) column. The mobile phase is n-hexane at 2.0 ml/min. The crude oil samples were prepared by dissolving 0.5 gms/20 ml of n-hexane. The sample is deasphalted by filtration across a 0.5 micron Millipore Millex-SR^R fluorocarbon membrane filter assembly. A 10 microliter injection is used.

The crude oil samples were also characterized by ASTM D-2007.[2] In addition, some crude oils were preparatively separated into hydrocarbon groups for gravimetric quantitation using a 57mm x 30cm NH_2 preparative cartridge in the Waters LC/500A preparative system.

Experimental

The separation scheme for the hydrocarbon group separation of crudes, resids, and syncrudes was modified to ensure baseline separation of the three major groups, saturates, aromatics, and polar aromatics (Table 1). The modifications made to the published separation technique include:

- Optimization of mobile phase linear velocity for column diameter.
- Evolving packing chemistry to ensure complete elution of the polar aromatics.
- Optional time for backflush routine.
- Automated data handling and baseline routines.

The areas of the aromatic envelope and the polar aromatic envelope and the polar aromatic envelope were obtained using a UV monitor at 254nm at 0.5 absorbance

Table I

Retention (k') of a variety of hydrocarbons using n-hexane as the mobile phase at 2.0 ml/min. or, with n-hexane at a linearity velocity of 0.010 to 0.012 cm/sec.

		(k')	
	Alumina	NH2	Silica
hexadecane		0.10	
dodecane		0.10	
heptadecane		0.10	
1-heptadecene		0.12	
1-octene		0.13	
1,5 cyclooctadecene		0.22	
1-octadecene		0.12	
cycloheptane		0.10	
pristane	0.04	0.10	0.06
cholestane	0.04	0.10	0.06
benzene	0.07	0.16	0.24
n-butylbenzene	0.07	0.13	0.34
toluene	0.08	0.15	0.48
n-decylbenzene	0.07	0.13	0.38
mestylene	0.08	0.13	--
phenylundecane	0.07	0.13	0.37
biphenyl	0.28	0.41	1.27
naphthalene	0.24	0.37	0.54
2 methylnapthalene	0.25	0.35	0.71
2,3 dimethylnaphthalene	0.99	0.36	0.55
2,3,5 trimethylnaphthalene	0.57	0.36	1.34
acenaphthylene	0.48	0.60	1.00
acenaphthlene	0.38	0.40	0.94
triphenylene	8.30	1.85	2.58
anthracene	1.22	0.83	1.45
phenanthrene	1.02	0.84	1.46
1 methylphenanthrene	1.53	0.81	1.74
fluoranthene	2.46	1.15	1.28
chrysene		2.88	
benzo(a)pyrene		3.78	
ocresol		11.16	
phenol		11.00	
2,2'bipyridine		11.23	
pyridine		11.00	
thiophene		13.00	

The Energy Analysis (NH2) column is backflushed at k' = 5.0 and the run is complete at k' = 14.50.

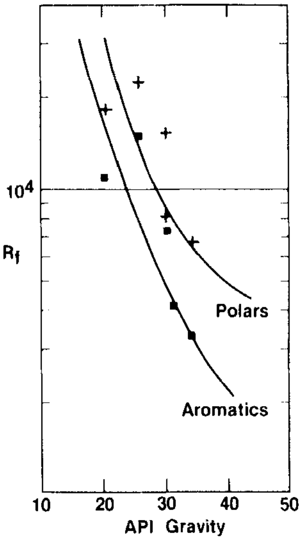

Figure 2 Whole Crude.
Relationship between Response Factor (Rf) and API Gravity.

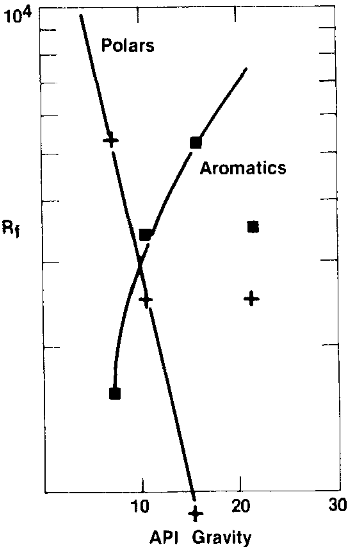

Figure 3 Topped Crude.
Relationship between Response Factor (Rf) and API Gravity.

Table II

API GRAVITY AND Rf VALUES OF AROMATICS AND POLAR AROMATICS

API GRAVITY	AROMATICS Rf	POLAR AROMATICS Rf
Whole Crude		
30.3	0.7342×10^{-4}	0.8143×10^{-4}
26.0	1.496×10^{-4}	2.219×10^{-4}
20.4	1.098×10^{-4}	1.813×10^{-4}
34.5	0.3322×10^{-4}	0.6723×10^{-4}
31.4	0.4171×10^{-4}	1.534×10^{-4}
Topped Crude		
10.4	0.3405×10^{-4}	0.2507×10^{-4}
15.8	0.5271×10^{-4}	0.0642×10^{-4}
21.4	0.3521×10^{-4}	0.2514×10^{-4}
7.3	0.1599×10^{-4}	0.5277×10^{-4}
Asphalt		
---	0.6534×10^{-4}	0.7475×10^{-4}

units full scale. Peak grouping techniques were used so that a single area was obtained for each hydrocarbon group. The response of the saturate peak was obtained from a differential refractometer using peak height techniques, or areas as determined electronically.

Several crude oils were characterized by the traditional ASTM D-2007 to obtain hydrocarbon group composition by an accepted technique.

Having determined the hydrocarbon group composition by accepted techniques and obtained areas of these hydrocarbon groups by LC techniques, response factors (Rf) were obtained. These factors will convert the areas obtained from HPLC to wt%. A relationship was found between Rf values and API gravity[3], (Table 2, Figures 2 and 3). The mathematical expression for these relationships is:

Whole Crudes

- Aromatics

$$Rf = -6.0568 \times 10^{-3} + 6.851 \times 10^{-4} (API) - 2.4587 \times 10^{-5} (API)^2 + 2.8535 \times 10^{-7} (API)^3$$

- Polars
  $Rf = -5.0235 \times 10^{-3} + 5.7482 \times 10^{-4}(API) - 2.0426 \times 10^{-5}(API)^2 + 2.3322 \times 10^{-7}(API)^3$

Topped Crudes

- Aromatics
  $Rf = 7.353 \times 10^{-5} + 1.5731 \times 10^{-5}(API) -4.9658 \times 10^{-7}(API)^2$

- Polars
  $Rf = 1.6477 \times 10^{-4} -1.9930 \times 10^{-5} (API) + 6.2648 \times 10^{-7}(API)^2$
  Where API = API Gravity at 60°F.

Three samples of deasphalted bright stock were analyzed using this technique for quantitation. The API gravity was determined on the whole sample, from this data the Rf values for the aromatics and polar aromatics was calculated. The three bright stock samples were then preparatively separated on the 57mm x 30cm NH_2 cartridge. The saturates, aromatics, and polar aromatics of a 5-gram injection were collected and quantitated gravimetrically. (Table 3).

The API gravity on a second series of crude oils and resids was determined and characterized by this technique. In addition these crudes were ana-

Table III

COMPARISON OF ANALYTICAL QUANTITATION AND GRAVIMETRIC QUANTITATION FROM PREP

Analytical Data

API GRAVITY	22.6	30.2	31.7
Saturates	88.00±0.2 wt.%	65.32±0.2 wt.%	99.36±0.10wt.%
Aromatics	6.39±0.16	33.97±0.15	8.41±0.07
Polar Aromatics	5.61±0.33	0.71±0.01	1.23±0.05
Asphaltenes	nil	nil	nil
5-gram Preparative Separation			
Saturates	74.25wt.%	58.85wt.%	76.07wt.%
Aromatics	5.36	27.61	6.48
Polar Aromatics	3.27	0.8	1.79
Asphaltenes	nil	nil	nil
Recovery	82.87wt.%	87.26wt.%	84.34wt.%

Table IV

COMPARISON OF QUANTITATION FROM ASTM 2007 AND HPLC

ASTM 2007

	Saturates	Aromatics	Polar Aromatics
Uvalde Crude	24.5wt%	71.9wt%	3.6wt%
Bunker C	21.1	34.2	30.3
South Louisiana	74.9	18.6	8.4
Luwait	54.3	25.7	17.9
Agentina Heavy	54.0	19.1	11.0

HPLC

	Saturates	Aromatics	Polar Aromatics
Uvalde	22.19±0.9wt%	74.15±1.63wt%	3.73±0.08wt%
Bunker C	20.98±0.9wt%	33.83±0.38wt%	30.79±1.43wt%
South Louisiana	74.59±0.75wt%	16.21±0.16wt%	9.00±0.1wt%
Kuwait	54.58±0.8wt%	30.06±0.25wt%	11.57±0.35wt%
Argentina Heavy	48.49±1.0wt%	24.99±0.39wt%	10.62±0.29wt%

lyzed by ASTM D-2007 (Table 4). Each of the crudes was analyzed 10 times, each a separate sample preparation, to obtain data on repeatability of this HPLC technique of quantitation (Table 4).

The best repeatability and correspondence of the saturates was obtained when the saturates were obtained by difference. The refractive index differential between the mobile phase, n-hexane, and the saturate peak is so small the major measurement errors are obtained.

Conclusions

An LC technique is shown that will provide the separation and quantitation of hydrocarbon groups, from whole crudes and resids from a wide range of sources. The relationship between API gravity and Rf (response factor) appears valid even when compared against gravimetric techniques.

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