

AN IMPROVED CHROMATOGRAPHIC METHOD FOR THE SEPARATION OF SATURATED HYDROCARBONS, AROMATIC HYDROCARBONS, RESINS AND ASPHALTENES FROM HEAVY CRUDE OILS

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INTRODUCTION.

Two general chromatographic methods have been used to isolate molecular fractions from heavy crude oils. The first of these involves initially a n-paraffinic extraction of the maltenes (solubles) and asphaltenes (insolubles) from heavy crude oils, and later the liquid-solid chromatographic separation of the maltenes into saturated hydrocarbons and polar compounds such as "polar aromatics" and resins (1). The second chromatographic method involves the direct separation of saturated and aromatic hydrocarbons, resins and asphaltenes from heavy crude oils using appropriate solvents and adsorbents (2,3,4). The main disadvantage of both methods is the lack of reproducible results due to the very complex and similar resin and asphaltene molecular structures (5,6).

We report in this paper an improved chromatographic method for the separation of 5 molecular fractions from a typical heavy crude oil, and study the reproducibility of it. The isolated fractions are characterized using UV-Visible and Atomic Absorption Spectroscopies. The results obtained with this method are compared with those of the standard literature.

EXPERIMENTAL.

Sample.

The heavy crude oil (10.3° API gravity) comes from the Boscán Field, near Maracaibo city, Venezuela. It was kindly provided without water and sediments by INPELUZ.

Chromatographic separation.

The chromatography consists of the extraction of 5 molecular fractions from an activated alumina (Brockman, Activity I, 80-200 mesh, Fisher, Pittsburgh-USA)/ alumina-impregnated heavy crude oil/ activated alumina in a 2.5 cm x 75 cm glass column. The elucidation of the fractions was based upon Snyder polarities (7). The solvents, followed in brackets by their polarities, and fractions were:

- (a) n-heptane (0,2)/ saturated hydrocarbons,
- (b) 75:25 n-heptane:toluene (0,75)/ aromatic hydrocarbons I;
- (c) Toluene (2,4)/ aromatic hydrocarbons II;
- (d) 94:6 toluene:MeOH (2,57)/ resins;
- (e) 13,3:26,7:60 MeOH: N,N Dimethyl formamide (DMF): CH₃CN(5,9) / asphaltenes.

The separation between saturated hydrocarbons and aromatic hydrocarbons I was monitored using a UV-lamp. The aromatic hydrocarbons I was a light yellow fraction. The aromatic hydrocarbons II, resins and asphaltenes were orange, black and black-brown fractions, respectively.

UV-Vis spectroscopy.

The UV-Vis spectra of the saturated hydrocarbons, aromatic hydrocarbons I, aromatic hydrocarbons II, resins, asphaltenes and vanadyl octaethylporphine (obtained from Strem Chemicals, Newburyport-USA; and used for quantification, see results and discussion below) in spectranalized CH₂Cl₂ were determined in a double-beam ratio recording Perkin Elmer Lambda 3B Spectrophotometer.

Atomic Absorption spectroscopy.

The Fe, Ni, and V contents of the resins, asphaltenes and standards of ferric chloride (Fisher, Pittsburgh-USA), metallic nickel (Fisher, Pittsburgh-USA), and ammonium

metavanadate (Strem Chemicals, Newburyport-USA) were determined with a Perkin Elmer Atomic Absorption 3100 Spectrophotometer.

RESULTS AND DISCUSSION.

Table I shows the type of molecular fraction, the percentage of each fraction weight divided by the heavy crude oil weight (wt % original crude) and the Fe, Ni and V contents (in mg x Kg or ppm) of the last two fractions obtained using our chromatographic method. It also compares our results with those obtained from two standard chromatographic methods reported by ASTM (1) and Barwise and his co-worker (4).

TABLE I.
THE MOLECULAR FRACTIONS FROM A TYPICAL HEAVY CRUDE OIL.

Method	Molecular Fraction*	Wt % of Original Crude	Fe (ppm)	Ni (ppm)	V (ppm)	V-P** (ppm)
ASTM (1)	S	10,1				
	AR	13,8				
	R	27,2	40,4	132,2	814,7	624,8
	A	29,3	177,4	373,2	2884,2	1120,9
BARWISE (4)	S	32,8				
	AR	12,8				
	R	1,4?				
	A	24,3	334,4	195,6	3580,9	2065,6
THIS WORK	S	19,3				
	ARI	21,3				
	ARII	15,3				
	R	25,1	42,6	208,8	1560,6	1045,6
	A	11,3	124,8	325,5	3748,4	1540,4

* S: Saturated Hydrocarbons; AR: Aromatic Hydrocarbons, R: Resins; A: Asphaltenes.

** V-P: Vanadium in Porphyrins.

It is important to point out that the ASTM method starts with a n-pentane extraction of the maltenes and asphaltenes. Then the maltenes are fractionated into saturated hydrocarbons (i.e., paraffins and naphthenes) with n-pentane, and polar compounds (i.e., *polar aromatics* and resins) with a 50:50 benzene:acetone solution in two parallel assembled columns packed with Attapulgas clay (30-60 mesh) and clay/silica gel. Aromatics are calculated by difference, or alternatively they can be recovered using toluene. The Barwise method starts with an extraction of the saturated hydrocarbons with n-heptane, and then follows it with the extraction of the aromatic hydrocarbons, *Ni-porphyrins*, *V-porphyrins* and a *residual polar fraction (resins?)* with 80:20 n-heptane:CH₂Cl₂ solution, 50:50 n-heptane:CH₂Cl₂, CH₂Cl₂, 50:50 toluene:CH₃OH solution, respectively in a column packed with silica. We consider that the Ni-porphyrins and V-porphyrins form basically the asphaltene fraction.

The addition of the wt % of the original crude values for each method in Table I gives the following total recovery sequence: this work (92,3%, of which 55,9% corresponds to saturated and aromatic hydrocarbons, and 36,4% to resins and asphaltenes) > ASTM (80,4%, 23,9%, 56,6%) > Barwise (71,3%, 45,6%, 25,7%). Similarly, the atomic absorption spectroscopic sequence for the total Fe, Ni and V contents for each method is: this work (6010,7 ppm, of which 5309 corresponds to V) > ASTM (4422,1 ppm, 3698,9 ppm) > Barwise (4110,9 ppm, 3580,9 ppm). The V content can be divided into porphyrinic vanadium (V-P) and non-porphyrinic vanadium (8) using the Soret band at 409 nm in the UV-Visible spectra of the collected fractions and the model vanadium compound. This procedure indicates that our method removed 2586 ppm and 2723 ppm of porphyrinic and non-porphyrinic vanadium, respectively. The Barwise and ASTM methods removed (2065,6 ppm, 1515,3 ppm) and (1745,7 ppm, 1953,2 ppm), respectively. Table I shows that the porphyrinic and non-porphyrinic vanadium is found in the resinic and asphaltenic fractions. The UV-Visible spectra of these fractions show basically a very strong and sharp band at ca. 234 nm, two strong and very broad overlapped bands at ca. 274 nm and ca. 300 nm and the already mentioned Soret band (see for example the UV-Visible spectra of Figure 1). The 234, 274 and 300-nm bands can be associated with condensed di-aromatic and poly-aromatic compounds that probably carry alkyl and alicyclic chains with heteroelements (i.e.

nitrogen, oxygen and sulfur). This indicates the intimate relationship between resins and asphaltenes, and the difficulty to obtain pure chromatographic fractions .

Finally, we had performed our chromatographic separation several times, and obtained very similar results to those reported above.

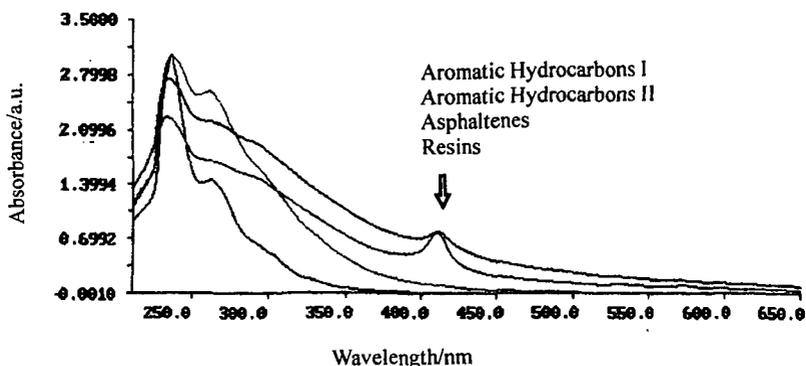


FIGURE I.
The UV-Visible spectra of the molecular fractions of a heavy crude oil.

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