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PREPARATIVE AND AUTOMATED COUMPOUND CLASS SEPARATION OF VENEZUELAN VACUUM RESIDUA BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Deasphalted vacuum residua of heavy and medium Venezuelan crude oils were separated into saturates, aromatics and two types of resins with a preparative high-performance liquid chromatographic system. The separation was achieved with a combination of silica and cyano-bonded silica columns and cyclopentane, chloroform–methanol and chloroform as eluents. The maximum sample load was 250 mg. Automated repetitive injection allowed the unattended separation of 3 g of sample in 8 h. Fractions were totally recovered from the columns (100.1 ± 1.3%) and the efficiency of the separation was determined by elemental analysis of whole samples and collected fractions.

INTRODUCTION

Compositional changes taking place during upgrading of heavy crudes and residua have been monitored with group-type separation procedures such as the API-60[1], the clay-gel adsorption chromatographic ASTM Standard[2] and the saturates aromatics, resins and asphaltenes (SARA) method[3]. Faster analytical procedures have been proposed employing either liquid chromatography[4–6] or thin-layer chromatography[7–11]. Unfortunatly, these techniques do not provide sufficient material for further characterization or are destructive.

Rapid preparative separations employing liquid chromatographic columns packed with silica gel[5,12,13] have been described. However, several workers have reported irreversible adsorption of polar compounds associated with the use of polar column packings such as silica, alumina and clay[14–16]. Resins constitute the polar fraction in deasphalted oils, and their abundance[17], their associations with asphaltenes[18–20] and their geochemical importance in heavy oils[21] are the main reasons for their isolation and characterization.

Derivatized polar packing materials have been developed in order to overcome the retention problems posed by the mentioned adsorbents. Analytical high-performance liquid chromatographic (HPLC) SARA analyses have been described, using amino[5], alkylamine and alkylnitrile[16], alkynitrile-substituted secondary alkylamine[22] and cyano- and aminocyano-bonded silica[23].

An automated semipreparative method for SAR separations of deasphalted

samples using an amino-bonded silica packing and showing excellent recoveries has been published[14]. However, other workers[24] suggested the use of cyano-bonded phases in order to avoid the reactivity of the amino moiety towards acidic and carbonylic coumpounds.

This paper describes an automated preparative system assembled with common HPLC components that allows the unattended separation of 3 g of deasphalted samples in 8 h. The fractions obtained are saturates, aromatics and two types of resins, and the separation was achieved with a combination of silica and cyano-bonded silica columns, employing cyclopentane, chloroform–methanol and chloroform as eluents.

The maximum sample load was estimated for the described system and repetitive injections were carried out. The sample was totally recovered (100 ± 1.3%). Elemental analyses were included and showed the efficiency of the separation.

EXPERIMENTAL

Samples and solvents
        Vacuum residua were provided by the Department of Process Development, INTEVEP. Solvents were obtained from Burdick & Jackson, Fisher and Merck and were used as received. The chloroform employed was free from alcoholic preservatives.

HPLC system
        The HPLC system (Fig. 1) consisted of the following components: a Waters Assoc. 590 EF programmable pump (1) that controlled two pneumatic actuated valves (Waters Assoc.), *viz.*, a solvent select valve (2) and a six-port switching valve (3); a DVSP-4 digital valve sequence programmer from Valco (4) that commanded the operation of three pneumatic valves, *viz.*, a Rheodyne 7010 injection valve provided with a 1.043-ml loop (5), a Valco backflush valve (6)and a Valco six-port switching valve (7); a Glenco 410 programmable fraction collector (8), provided with a 6 + 1-port Rheodyne 7060 valve; a Knauer 98:00 refractive index (RI) detector (9) and a Glenco 5840 UV–VIS detector operated at 254 nm (10); an Altex gas-tight glass column (11) operated as sampling reservoir, filling the sampling loop of the injection
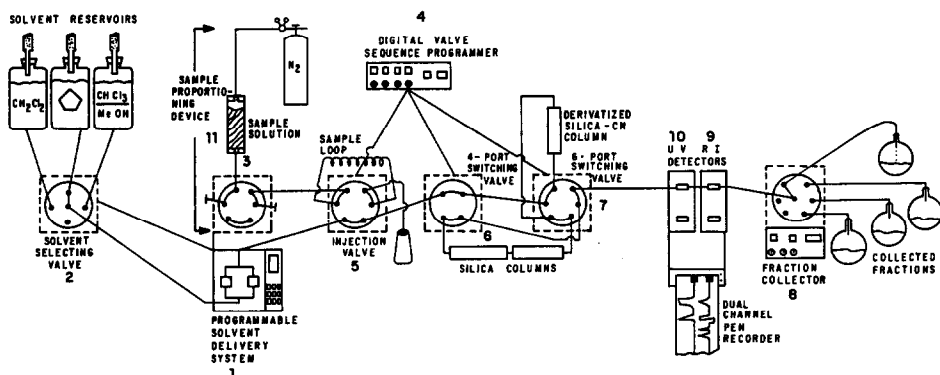

Fig. 1. Automated preparative liquid chromatograph for separation of saturates, aromatics and resins. MeOH = Methanol.

valve (5) under an small nitrogen pressure (*ca.* 3 ml/min); and columns (Valco, 25 cm × 1 cm I.D.) slurry-packed by means of a Haskell air-driven fluid pump. The packing materials were Adsorbosil LC (10 μm), irregular (Alltech) and Polygosil 60-10CN (10 μm), irregular (Macherey Nagel). The former material was dried for 1 h at 120°C before packing. The cyano column was end-capped with trimethylchlorosilane (Pierce) according to a previously described procedure[25].

Sample preparation

Asphaltenes were precipitated by refluxing the sample for 1 h with *n*-heptane in a ratio of 100:1. The suspension was cooled to room temperature and filtered through a cellulose extraction thimble. The precipitate was extrated with *n*-heptane until no colour was observed in a Soxhlet apparatus and the extract was combined with the filtrate. Asphaltenes were dissolved with benzene. The solutions were filtered (Whatman No. 41) and the solvents removed in a rotary evaporator under a stream of nitrogen. Maltenes and asphaltenes were brought to constant weight in a vacuum oven at 70°C.

Maltenes solutions of known concentration (*ca.* 240 mg/ml) were prepared in cyclopentane and charged to the glass column (11).

Events programme

Table I shows the command sequence used in each of the three controllers employed. For preparative purposes, the 38-min cycle is repeated several times and weak resins are eluted manually with a final chloroform backflush. For analytical purposes, the 52-min run affords all the fractions with a single injection.

RESULTS AND DISCUSSION

Group-type separation of deasphalted crude oil residua into saturates, aromatics and two types of resins was achieved with a combination of a deactivated cyano-bonded silica column and two bare silica columns. This was performed on a semi-preparative scale (milligram amounts) and repetitive and automated cycles, employing the HPLC system shown in Fig. 1, resulted in the unattended separation of 3 g of sample in 8 h.

The sample is dissolved in cyclopentane rather than in the deasphalting solvent (*n*-C$_7$), because cycloalkanes cause fewer reprecipitation problems than *n*-alkanes[16]. The sample solution concentration (*ca.* 25%, w/v) and the injection volume (*ca.* 3% of the system) were chosen so as to avoid excessive viscosity and sample dilution on injection.

The sample is injected and initially eluted with cyclopentane through the cyano column, where the most polar coumpounds (strong resins) are retained. The other components proceed to the silica columns and the less retained (saturates) are eluted and observed with the refractive index detector (Fig. 2).

Aromatics and weak resins are held on the polar silica surface. Once the saturates have been eluted, the flow is inverted through the cyano column and, by changing the eluent to the more polar chloroform–methanol (80:20, v/v) strong resins are recovered. At this stage no eluent flows through the silica columns, and the resins eluting are monitored with the UV detector. In order to recover the aromatics, cyclopentane is

TABLE I
EVENTS PROGRAMME FOR SAR SEPARATION

Time (min)	590 EF pump (1)	Digital valve sequence programmer (4)	Fraction collector (8)
0.00	Flow-rate: 4.9 ml/min Solvent: cyclopentane	Actuate injection valve 5	Stream 1 to saturates vessel
11.00		Return valve 5 to load position Actuate 6-port valve 7 to backflush the CN column	
11.25			Stream 2 to strong resins vessel
13.50	Flow-rate: 16.5 ml/min Solvent: chloroform–methanol		
21.00	Flow-rate: 16.5 ml/min Solvent: cyclopentane		
25.00		Actuate 4-port valve 6 to backflush silica columns	Stream 3 to aromatics vessel
35.00	Flow-rate: 4.9 ml/min Solvent: cyclopentane		
36.00	Actuate sample proportioning valve 3		
36.50	Return sample proportioning valve 3		
37.00		Return backflush valves 6 and 7 to initial positions	Stream 1 to saturates vessel
38.00		Start a new run	

Weak resins are eluted by backflusing all the system with chloroform after repetitive injections allow all the sample to go through. Complete elution of the four fractions in a single run requires the following steps in the program, following the 25.00 min instructions.

35.00	Flow-rate: 14.0 ml/min Solvent: chloroform		Stream 4 to weak resins vessel
43.00	Flow-rate: 14.0 ml/min Solvent: cyclopentane		
47.00	Flow-rate: 16.5 ml/min Solvent: cyclopentane		
50.00	Flow-rate: 4.9 ml/min Solvent: cyclopentane		
50.50	Flow-rate: 0.1 ml/min Solvent: cyclopentane		
51.00		Return backflush valves 6 and 7 to initial positions	Stream 1 to saturates vessel
52.00		End of run	

again employed, initially to remove the previous eluent from the system (methanol affects the performance of the silica columns), and then to backflush the aromatics when the flow is inverted through the whole system. Aromatics are detected with both detectors. This cycle is repeated until all the sample has been injected into the columns. To recover the weak resins held in the silica columns through the repetitive injections, chloroform was used to backflush the whole system. Dichloromethane was employed in the initial experiments to recover weak resins, but it was found that the silica
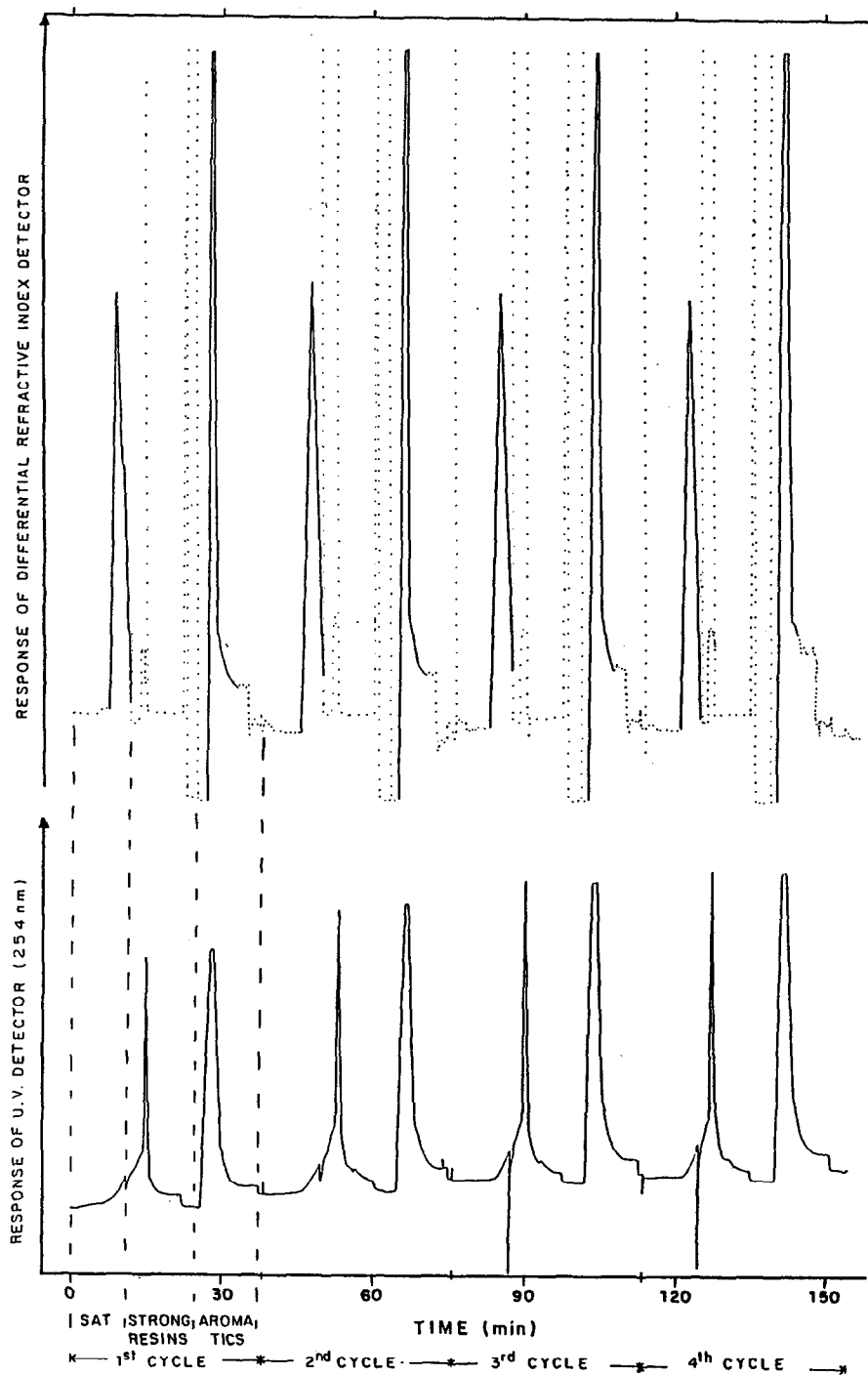
Fig. 2. Typical SAR separation of a deasphalted oil vacuum residua. Dotted lines correspond to variations of pressure or solvent composition.
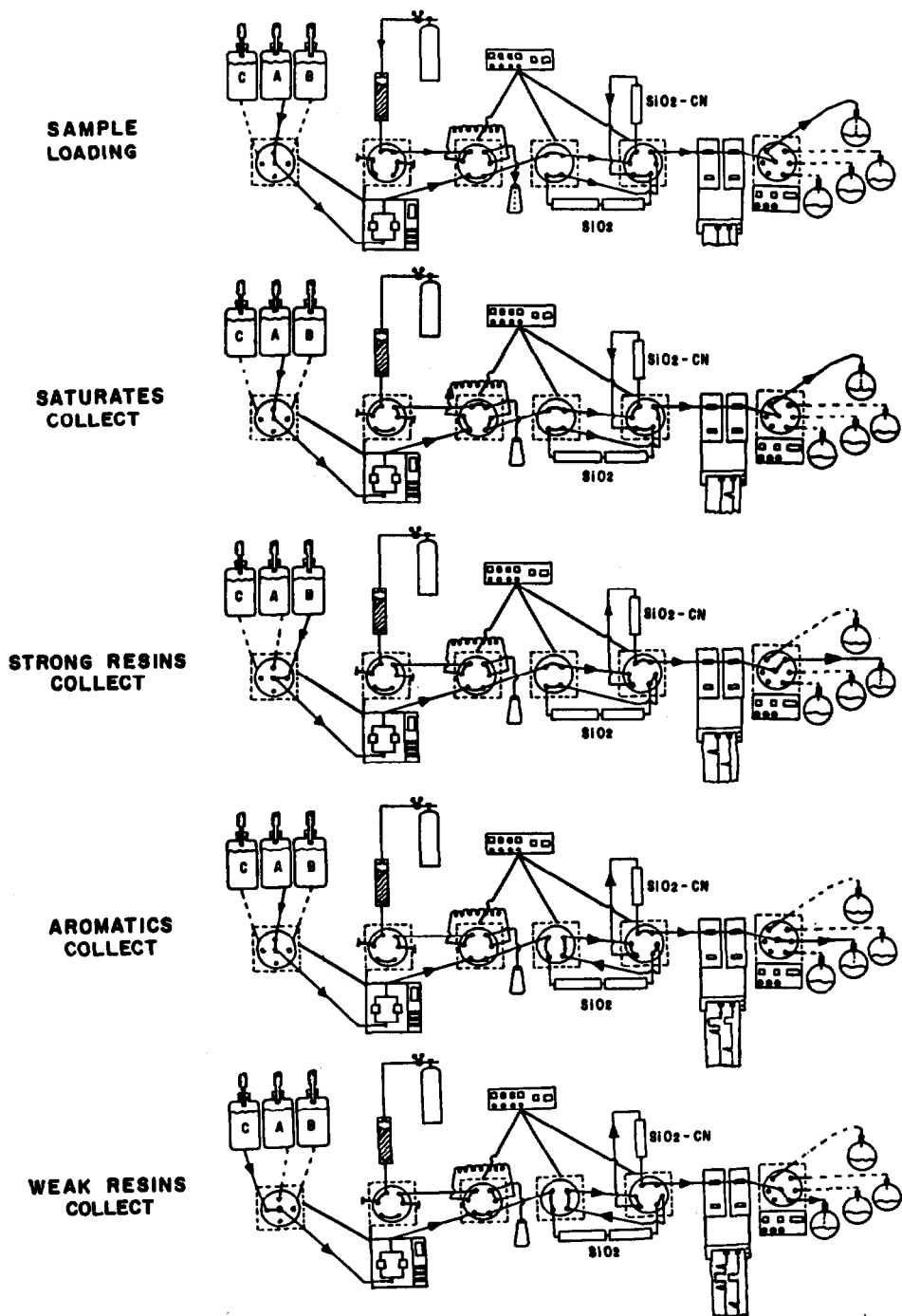
SYSTEM CONFIGURATION

Fig. 3. System configuration during each step. A = Cyclopentane; B = chloroform–methanol; C = chloroform.
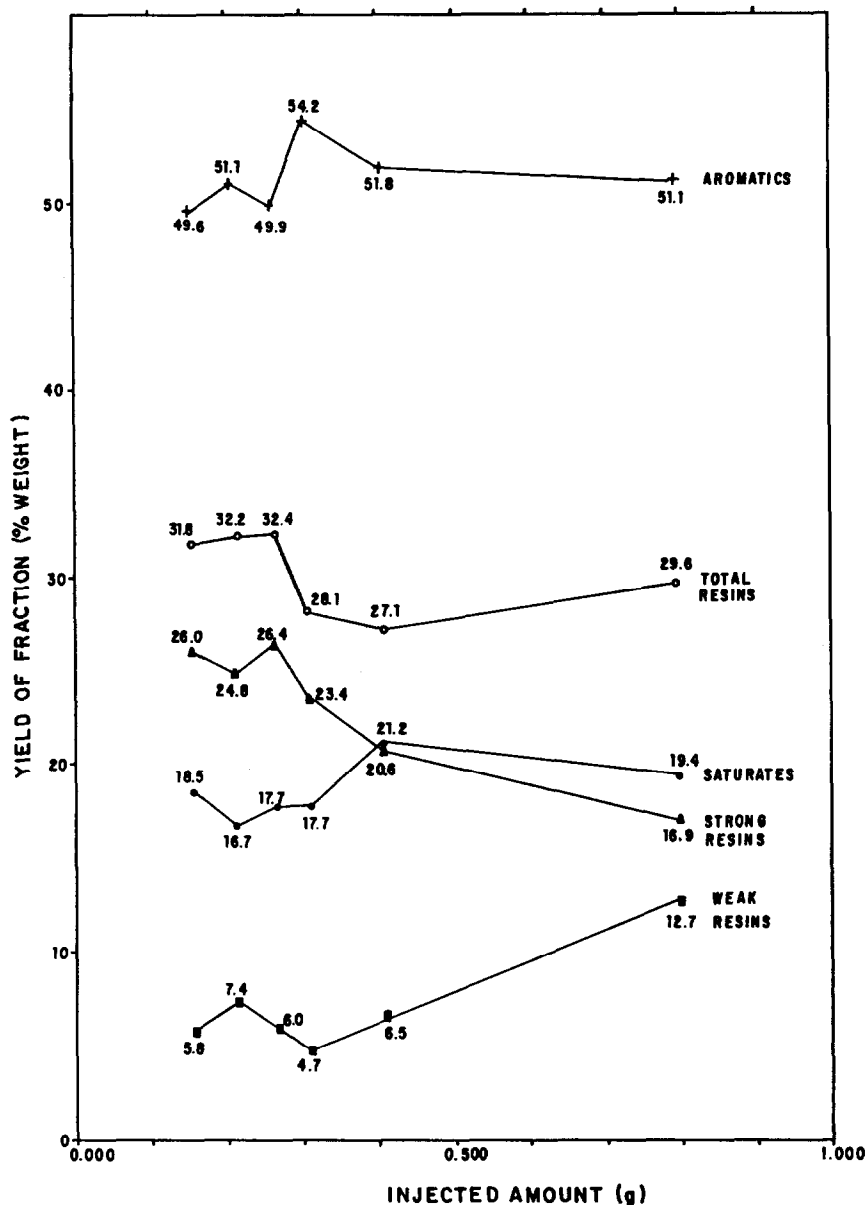
Fig. 4. Fraction yields *vs.* amount of sample injected in typical SAR separations.

columns were deactivated rapidly as consequence of humidity, so this solvent was replaced.

The chromatographic conditions and column dimensions were chosen such that the saturates had not completely eluted before all the compounds that were unretained by the cyano column entered the silica columns. The eluent flow-rate was initially selected to permit an adequate resolution of saturates; after this group had been

TABLE II

REPETIBILITY AND MASS RECOVERY DATA FOR SAR SEPARATION OF DEASPHALTED VACUUM RESIDUA

Origin of crude oil	Sample[a]	Saturates	Aromatics	Weak resins	Strong resins	Total recovery (%, w/w)	No. of injectons	Sample amount per injection (mg)
Orinoco	I	9.0	48.2	8.5	34.2	99.9	6	129.4
Basin		9.3	50.4	9.4	30.8	99.9	6	143.3
	II	13.9	51.4	6.2	26.5	98.0	7	130.7
	III	5.7	56.1	8.2	29.1	99.1	6	301.6
Barinas-	IV	18.6	52.3	4.9	24.2	100.0	6	143.5
Apure		18.0	54.2	4.1	24.1	100.4	3	226.0
Basin	V	17.2	51.5	4.5	26.1	99.3	7	139.3
		18.1	51.1	6.2	27.1	102.5	3	266.3
Experi-	VI	21.6	54.3	3.1	21.1	101.1	13	98.0
mental		22.6	57.6	3.5	17.9	101.6	10	232.4
blend								

[a] Samples included were 510°C vacuum residua, excluding sample III, which was a 540°C vacuum residua.

collected the flow-rate was set at a value that permitted a rapid elution without exceeding a pressure of 5500 p.s.i., as the pump was designed to operate at a maximum of 6000 p.s.i. Fig. 3 shows the system configuration during each of the steps.

Fig. 4 shows the yields of the different fractions depending on the amount of sample injected in a single run. This was done in order to establish the maximum amount of sample that could be analysed, which is important considering that the aim is a preparative separation of different compound classes for further characterization. A 250-mg amount of sample proved to be the maximum that could be chromatographed without affecting the quality of the separation. Above this level, a slight increase in the percentage of saturates is observed. This is due to overloading of the silica columns, as a result of which some aromatics coelute. It was also found that the amount of weak resins increased and that of strong resins decreased as a result of overloading of the cyano column. Part of the strong resins were not retained and appeared as weak resins. The aromatics remained relatively constant, probably because of overloading of resins that are not held by the silica and elute as the former.

Mass recovery data for some deasphalted vacuum residua are presented in Table II. The overall recoveries were 100.1 ± 1.3%, showing that no material was retained in the columns and also that the chosen columns performed well even with complex samples containing between 23 and 43% of resins. Recoveries greater than 100% were partially explained by solvent occlusion, which is a common source of error with this type of heavy fractions.

Elemental analysis was initially performed on the separated fractions in order to verify the effectiveness of the separation. Table III gives the results for some of the residua studied, showing differences in the nature of the fractions obtained. Note that although the H/C ratios for aromatics and weak resins are fairly similar, there are significant variations in the heteroatom content. Detailed information on the characterization of the fractions has been reported elsewhere[26].

TABLE III

ELEMENTAL ANALYSIS OF VACUUM RESIDUA AND THEIR SEPARATED FRACTIONS

Sample[a]	Fraction	Concentration (%)	C (%)	H (%)	H/C	S (%)	Ni (ppm)	V (ppm)
V	Vacuum residua		86.29	10.22	1.42	1.11	193	62
	Saturates	15.0	85.77	13.71	1.92			
	Aromatics	43.3	86.32	10.76	1.50	1.14	43	<10
	Weak resins	5.1	86.51	10.52	1.46	1.87	136	107
	Strong resins	22.1	86.54	9.32	1.29	1.40	285	119
	Asphaltenes	16.3	87.77	7.68	1.05	1.41	615	247
I	Vacuum residua		83.20	9.86	1.42	3.84	150	633
	Saturates	7.1	85.91	13.38	1.87			
	Aromatics	38.3	83.76	10.33	1.48	4.11	50	<10
	Weak resins	7.0	81.74	10.19	1.59	4.39	106	209
	Strong resins	25.3	79.82	9.07	1.36	4.35		835
	Asphaltenes	22.3	82.25	7.90	1.14	4.72	442	1747

[a] For identification, see Table II.

CONCLUSIONS

An automated preparative method for the separation of deasphalted heavy ends into saturates, aromatics and two types of resins has been developed. Unattended operation permitted to collect 3 g of fractions in 8 h for further characterization. Adoption of a cyano-derivatized silica column resulted in sample recoveries of nearly 100%.

ACKNOWLEDGEMENTS

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