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Group-type separation of middle petroleum distillates by adsorption and charge-transfer liquid chromatography with dielectric constant detection

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Abstract

A fast (<15 min) LC method was developed for the group-type separation of low olefinic (<5%, v/v) petroleum middle distillates. Dinitroanilinopropyl- and underivatized silica columns were used with Freon 123 as mobile phase and dielectric constant detection. Aliphatic hydrocarbons and mono-, di- and triaromatics were the determined group types. A response factor of 1.12 to correct the total aromatic content by volume was found. Some applications are described, including fingerprinting of refinery cuts and monitoring of upgrading processes.

1. Introduction

The predicted worldwide increase in the use of Diesel fuel during the last decade [1] has forced refiners to introduce higher levels of cracked components into these energy sources [2]. High aromatic contents in such blends were of concern from the pollution [2,3], performance [2] and health [4] standpoints.

The aromatic content of middle distillates was traditionally measured by using techniques such as fluorescent indicator adsorption [5], aniline point [6], mass spectrometry (MS) [7,8] and high-performance liquid chromatography (HPLC) [9–12]. However, the poor accuracy of the first two techniques suggested the adoption of better methodologies. This was especially noticeable with coloured samples when analysed by fluorescent indicator adsorption and naphthenic samples evaluated with the aniline point method. Further, the high analytical skills required in MS methodologies, their inherent inapplicability to olefinic cuts and the wide range of response factors of HPLC with refractive index (RI) detection make the routine use of these methods difficult.

In addition to the above methods, many approaches have been described for group-type analysis of light and middle distillates. UV spectrophotometry has been used for the determination of naphthalenes [13]. Fourier transform infrared (FT-IR) spectrometry gave correlations between Diesel composition and particulate emissions [14]. Gas chromatography (GC) with polar stationary phases has been proposed for the determination of aromatics in non-olefinic kerosenes [15]. Nuclear magnetic resonance (NMR) spectrometry has been proposed for the determination of aromatics content [3,16–18]. The advantage of using a universal detection

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system such as flame ionization detection (FID) has been exploited by coupling LC and GC instruments. This has proved effective for virgin and low-olefin content kerosenes [19,20]. Likewise, FID has commonly been used in supercritical fluid chromatography (SFC)-based methodologies [21–23]. ASTM has approved a method for aromatics determination based on these techniques [24]. Chemical methods have been similarly explored, some of them directed at olefin compounds, such as hydroboration [25] and complex formation with the stationary phase [26].

Complexation with the stationary phase has received particular attention for more than a decade in the case of derivatized packing materials. Many phases for LC have been synthesized that are specially suited for aromatic complexation, according to the number of π-electrons and/or number of conjugate aromatic rings present in the molecules. Some reviews [27,28] and a recent monograph [29] have been published on this topic. Owing to the strong absorbing nature of chromophores with aromatic structures, most of the work described has relied on UV detection. This posed a quantification problem as absorptivities vary greatly between aromatics. To solve this problem, some workers have used UV spectrophotometry for qualitative purposes and the quantification was then performed gravimetrically [30,31]. Information-rich detection systems have been used simultaneously for identification in some instances, such as an on-line UV diode-array detector and of-line MS [31]. Also, LC–FID with detectors developed for LC has been described [32]. However, all of these approaches are well suited only for heavier distillates, as removal of solvents generally causes sample losses with lighter materials, such as petroleum middle distillates.

A dielectric constant detector for LC was introduced commercially over a decade ago [33]. This detector operates like a universal detection system for hydrocarbons if the dielectric constant of the mobile phase used is greater than 5, as was shown by Hayes and Anderson [34]. Many applications were described by these workers. With a combination of a tetranitrofluoreneimino-derivatized silica (TENF) column (charge-transfer) and aminocyanosilicas (adsorption), it was possible to determine aliphatic and alkylbenzene polycyclic aromatics [34]. *n*-Butyl chloride was chosen as the mobile phase, requiring small response factors for quantitative analysis. By adoption of Freon 123 as the mobile phase, quantification was simplified, as a response of unity was appropriate for different hydrocarbon groups. With this solvent and several cationic columns loaded with silver, it was possible to determine saturated compounds, aromatics and olefins [35], or *n* + isoparaffins and cycloparaffins and aromatics + olefins [36]. Naphthenic selective columns [37] were added in the last example to separate the cycloparaffins. PONA (paraffins, olefins, naphthenes and aromatics)-type analysis was also achieved with a multidimensional system employing five columns and two selection valves [38]. Preparative separations have also been described [39,40] and many of the possibilities have been discussed in a review [41].

This paper describes a fast and simple LC method used for routine monitoring of hydrocarbon groups during the upgrading of middle petroleum distillates. Charge-transfer (dinitroanilinopropylsilica) together with adsorption columns (underivatized silica) were used with Freon 123 as the mobile phase and dielectric constant detection. The groups determined were aliphatic hydrocarbons and mono-, di- and triaromatics. Small response factors were required for quantitative volumetric analysis. Comparison with MS permitted the applicability of the methodology exclusively for atmospheric cuts to be assessed. No interferences were detected from bicycloparaffins, compounds typically present in hydrotreated products. Olefin-rich samples, such as thermal cracked gasoils, cannot be analysed owing to interference from such hydrocarbon types.

2. Experimental

2.1. Reagents and solvents

Standard compounds were obtained from Aldrich (Milwaukee, WI, USA) or Chem-Service

(West Chester, PA, USA). Solvents were purchased from Burdick and Jackson (Muskegon, MI, USA) or Fisher (Pittsburgh, PA, USA). Reagents and solvents were used as received.

Envron 123 (1,1,1 - trifluoro - 2,2 - dichloroethane) from Halocarbon Products (North Augusta, SC, USA) was used as the HPLC mobile phase. The solvent was commonly reused and was purified monthly by percolation through a bed of basic alumina. Halogen acids and heavy aromatics and polar compounds were removed in this way. Additionally, every 6 months, hydrocarbon stripping was achieved by distillation under a dry atmosphere.

2.2. HPLC system

The HPLC system is shown in Fig. 1. The main components were a glass pressurized solvent reservoir from Altex (Berkeley, CA, USA) (2), a model LC-3A HPLC pump from Shimadzu (Columbia, MD, USA) (6), a six-port injection valve from Valco (Houston, TX, USA), furnished with a 5-μl sampling loop (7), an HPLC column bank (8), a Model 410 dielectric constant detector from Laitec (Bartlesville, OK, USA) (10), a chart recorder (from Linear or Kipp & Zonen) (15) and an A/D interface for data acquisition, analysis and storage in an HP-3350S laboratory automation system.

2.3. Chromatographic conditions

HPLC was performed at room temperature (*ca.* 24°C). The mobile phase was pumped at 1.5 ml/min and 90–100 bar when using four columns (total length 85 cm). Slight pressure variations were observed, depending on the setting of the sample cell restrictor. The detector was usually operated at a sensitivity of 2. To avoid bubbling in the pump head and also to maintain a flow-rate of *ca.* 0.3 ml/min in the reference cell, the solvent was pressurized with nitrogen at 40 p.s.i. (1 p.s.i. = 6894.76 Pa).

2.4. Columns

The column bank was assembled with one 25 cm × 4 mm I.D. 2,4-dinitroanilinopropylsilica (DNAP) column and two or three 60 cm × 4 mm I.D. silica columns. Preliminary experiments were carried out with two 30-cm silica columns. Most of the experiments described were performed with two 25-cm plus one 10-cm column. The DNAP stationary phase was supplied by Dr. J.B. Green [National Institute for Petroleum and Energy Research (Niper), Bartlesville, OK, USA] and has been described previously [42,43]. Underivatized silica gel was obtained from Alltech Associates (Deerfield, IL, USA) and consisted of 10-μm irregular Adsorbosil-LC. The

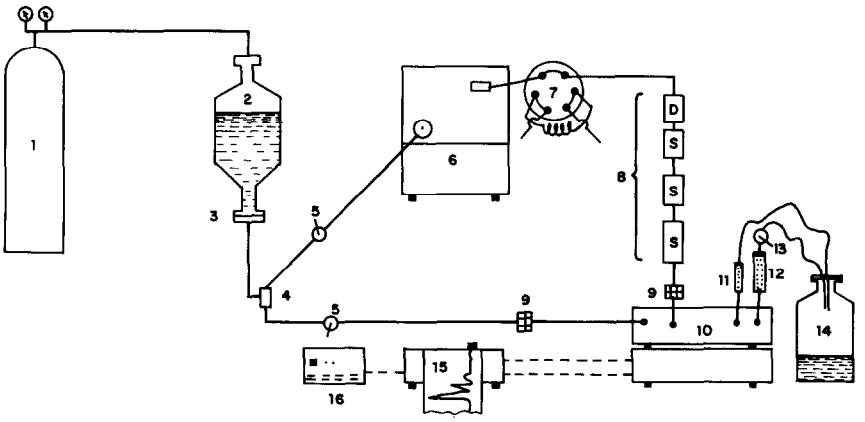


Fig. 1. Schematic diagram of HPLC system. 1 = Nitrogen cylinder; 2 = solvent reservoir; 3 = line filters (20 μm); 4 = tee; 5 = PTFE on–off valves; 6 = HPLC pump; 7 = injection valve; 8 = column bank; 9 = line filters (2 μm); 10 = detector; 11 = reference cell restrictor; 12 = sample cell restrictor; 13 = metering valve; 14 = effluent receiver; 15 = chart recorder; 16 = A/D interface; D = dinitroanilinopropylsilica column; S = underivatized silica columns.

columns were packed in-house with a Haskel (Burbank, CA, USA) pneumatic high-pressure pump. Carbontetrachloride was used for slurry preparation and pentane was employed as a driving solvent (10 000 p.s.i.).

2.5. Standard mixtures prepared from real samples

Aliphatic and aromatic fractions were preparatively separated in a silica column (60 cm × 1.5 cm I.D.) packed with 32–63-μm Woelm Pharma SiO_2 (ICN, Cleveland, OH, USA). Pentane was used as the mobile phase. Simultaneous UV (254 nm) and refractive index (RI) detection were used. A 0.5-g amount was loaded in each injection and the fractions from six successive separations were pooled.

Saturated compounds and olefins were also preparatively separated from the aliphatic fraction of thermal cracked medium distillates. A 21 cm × 1.5 cm I.D. column packed with SiO_2–$AgNO_3$ (80:20, w/w) was used. Saturated compounds were eluted with pentane and detected by differential RI detection. Olefins were then back-flushed with *n*-pentane–dichloromethane (30:70, v/v) and the column was regenerated with pentane. The sample load was 180 μl in each separation. Argentation chromatography of olefins has been described previously [26].

The preparative fractions were finally obtained by solvent stripping using Kuderna–Danish-type evaporators. The recoveries were 100 ± 3%. Solvent absence was confirmed by GC. Standard mixtures were obtained by mixing precisely measured amounts of preparative fractions. Straight-run, catalytically and thermal cracked and also hydrotreated and solvent-extracted middle distillates from Petróleos de Venezuela (PDVSA) refineries were employed for standards formulation. The samples originated from PDVSA refineries at Cardón, Amuay and El Palito.

2.6. Mass spectrometry

Mass spectrometric analyses were performed at the Analysis and Evaluation Department in INTEVEP. Group-type results were obtained according to the Robinson methodology [8] and/or the ASTM standard [44] if very volatile materials were present in the samples.

3. Results and discussion

Pollution and health hazards have forced the adoption of specifications regarding the aromatic content of middle distillates. Until now, in our laboratories the common way to measure this parameter was based on MS [7,8,44] and HPLC techniques [11]. Probably, in the near future, SFC techniques [24] will also be adopted.

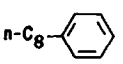
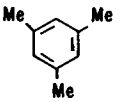
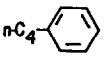
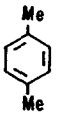
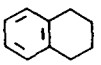
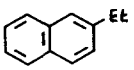
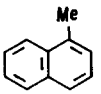
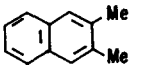
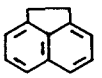
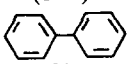
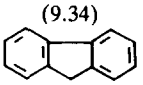
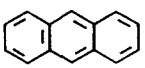
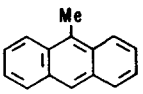
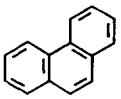
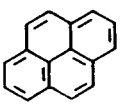
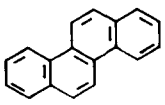
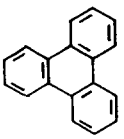
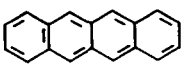
MS has proved to be a reliable technique for non-olefinic distillates. However, it is a highly demanding technique for routine process monitoring. On the other hand, HPLC with RI detection and response factors [11] is a fast and simple procedure used in our laboratories for group-type quantitative analyses of virgin distillates. Nevertheless, process monitoring has been hampered by the fact that unpredictable refractive indices are obtained under widely diverse test conditions. In such circumstances, quantification is not accurate (Table 1).

Table 1
Determination of aromatics in processed matrices

Sample	Aromatics (%, w/w)	
	Known[a]	HPLC–RI[b]
Thermal cracked gasoil	40.0	51.5
Catalytically cracked gasoil	50.0	60.9
Hydrotreated products		
I (650 p.s.i. H_2)	25.0	35.4
II (650 p.s.i. H_2)	40.9	39.8
III (1500 p.s.i. H_2)	50.0	55.6
Virgin + cracked + hydrotreated synthetic blends		
I	16.7	26.5
II	34.0	42.8
III	54.6	57.5
IV	72.8	73.1
V	86.4	84.2

[a] Blending of preparatively separated fractions.
[b] Response factor [11]: saturates, 1.00; aromatics, 0.70.

Table 2
Reference compounds employed for the evaluation of the chromatographic system

Group-types	Standard compounds[a]					
Saturated compounds	(6.26) n-C_{28}	(6.54) n-C_{16}	(6.62) n-C_{13}	(6.71) n-C_{10}	(6.86) n-C_5	(6.94) 
	1	2	3	4	5	6
	(6.97) 					
	7					
Olefins	(6.52) 1-Docosene	(6.58) 1-Eicosene	(6.70) 1-Hexadecene	(6.82) 1-Dodecene	(6.97) 1-Nonene	
	8	9	10	11	12	
	(6.95) 1-Octene	(7.04) 3-Me-3-heptene		(7.14) 4 Me-2-pentene		
	13	14		15		
Monoaromatics	(7.17) 	(7.39) 	(7.42) 	(7.59) 	(7.69) 	
	16	17	18	19	20	
	(7.69) 	(7.80) 	(7.89) 			
	21	22	23			
Diaromatics	(8.06) 	(8.32) 	(8.45) 	(8.46) 		
	24	25	26	27		
	(8.56) 		(9.34) 			
	28		29			
Triaromatics	(10.08) 	(10.14) 	(10.30) 			
	30	31	32			
Tetraromatics	(12.59) 	(15.5) 	(16.32) 	(19.1) 		
	33	34	35	36		

[a] Values in parentheses are retention times (min). Numbers 1–36 denote the standards in Fig. 2.

In order to devise an easier and faster method for process monitoring, research was initiated 4 years ago to explore the feasibility of HPLC with dielectric constant detection. Initial experiments were carried only with a DNAP charge-transfer column, as we had previous experiences with this phase [45]. Under such conditions, saturated compounds and monoaromatics co-eluted, so silica columns were sequentially combined until saturated compounds and mono-, di- and triaromatics could be separated. Freon 123 was employed as the mobile phase because reportedly its use facilitates the determination of hydrocarbons [35,36,38–40]. The final column bank required a DNAP column to achieve the separation of di- and triaromatics. The eluent was too strong a solvent for silica columns alone to be employed. The elution range of each hydrocarbon group was initially ascertained with the aid of reference compounds (see Table 2 and Fig. 2).

In addition to charge-transfer and adsorption mechanisms obtained with the combination of DNAP and silica columns, it was possible to observe a simultaneous exclusion mechanism. Among the families of saturated compounds and olefins, larger members elute first (Table 2). In a similar fashion, the length of the alkyl substituent in monoaromatics governs the retention properties. However, isomerism effects can be observed and are not easily explained. This effect has also been noted by other workers in similar studies [35]. Attempts to control this sizing effect with wide-pore silica columns (300 Å) proved unsuccessful. Similarly, improvements in resolution were pursued by adding more

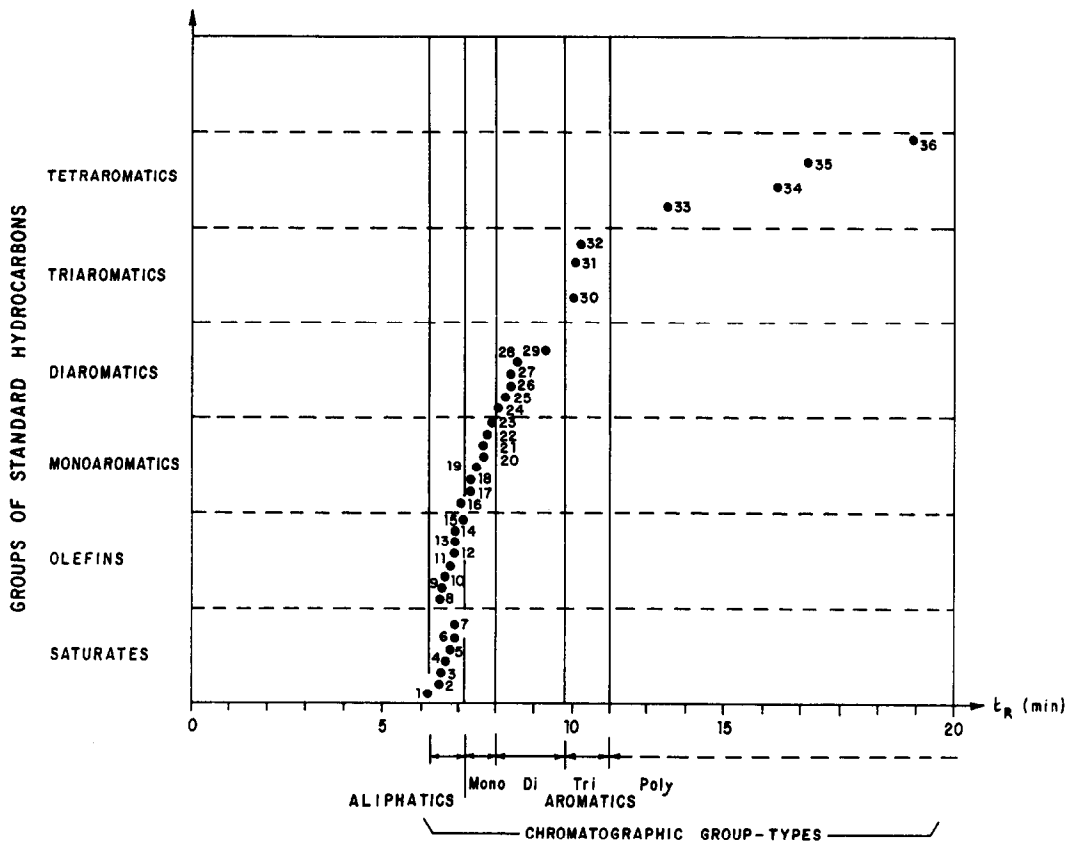


Fig. 2. Chromatographic group-types determined. Numbers 1–36 denote reference compounds, detailed in Table 2.

Table 3
Detector response for pure preparative hydrocarbon groups, determined after HPLC separation

Sample	Integrator counts[a] × 10^{-4}		Response factor for total aromatics
	Aliphatics	Total aromatics	
Hydrotreated middle distillate	4433	4017	1.10
Virgin gasoil	4556	3809	1.20
Catalytically cracked gasoil	4445	4095	1.09
Hydrotreated LCO	4420	4052	1.09
Kerosene	4613	3946	1.17
LCO	4404	4062	1.09
Thermal cracked light gasoil	4271	3781	1.13
Mean ± S.D.			1.12 ± 0.04

[a] 5 μl of neat sample and detector at sensitivity 2. Means of three determinations.

columns, employing spherical Nucleosil particles instead of the irregular Adsorbosil-LC, or replacing these by Partisil 5-PAC columns (Whatman). None of these approaches was successful.

Before trying to perform quantitative analysis, response factors for saturates and total aromatics were checked. Several preparatively separated fractions were analysed. It was found that with the chromatographic system employed, a factor of 1.12 for total aromatics corrected the volumetric content of such hydrocarbon types (see

Table 4
Detector response for pure hydrocarbons

Hydrocarbon group	Compound	Detector response[a] (counts × 10^{-3})	Average response for hydrocarbon group (counts × 10^{-3})
Saturated compounds	n-C_5	2323	
	Cyclopentane	2127	
	n-C_{11}	2013	2077
	n-C_{13}	1977	
	n-C_{15}	1942	
Olefins	2,4,4-Trimethyl-1-pentene	1136	
	1-Nonene	1350	
	1-Dodecene	1613	1484
	1-Tridecene	1515	
	1-Hexadecene	1807	
Monoaromatics	Toluene	2152	
	o-Xylene	1948	
	n-Butylbenzene	1814	1826
	n-Decylbenzene	1774	
	Tetralin	1527	
	n-Hexadecylbenzene	1742	
Diaromatics	1-Methylnaphthalene	1641	1695
	2-Ethylnaphthalene	1750	

[a] 1.0 μl of neat sample and detector at sensitivity 10. Means of three determinations.

Table 3). The non-unity correction factor may arise from several causes. Band broadening due to the very long column bank used might contribute. In our system, this effect could definitely be present. However, it was not evaluated. Another possibility is a structural effect. This was verified with pure hydrocarbon groups, as shown in Table 4. By plotting the dielectric constants of pure compounds [46] (see Fig. 3), it was possible to rationalized the decrease in response along the sequence saturates–monoaromatics–diaromatics. The differences in signal between solvent and sample follow the same sequence, which explains the results found. Nevertheless, we do not have an explanation for the very low response of olefins (see Table 4). Experiments were not performed to test for the irreversible loss of such compounds over metallic surfaces of the injector, the connecting tubing and the detector itself.

The selection of chromatographic conditions for quantitative analysis was based on compromises. A sample load of 5 μl (neat) with the detector operated at a sensitivity of 2 were in our opinion the optimum conditions from a pragmatic point of view. In such way, it was possible to avoid the cumbersome handling of very volatile solutions, as the eluent boils under ambient conditions. Detector sensitivities were evaluated in the range 1–5 and sample loads of a light cycle oil (LCO) between 1 and 10 μl. The response of triaromatics was lower than expected, with a 1-μl injection, and, on the other hand, the resolution decreased with a 10-μl injection. Baseline drift was noticeable at a detector setting of 1, and also the noise was very high owing to the pulsating pumping system. At a detector sensitivity of 2 and a 5-μl sample load, the resolution was comparative to that obtained with a 1-μl injection. The signal-to-noise ratio was

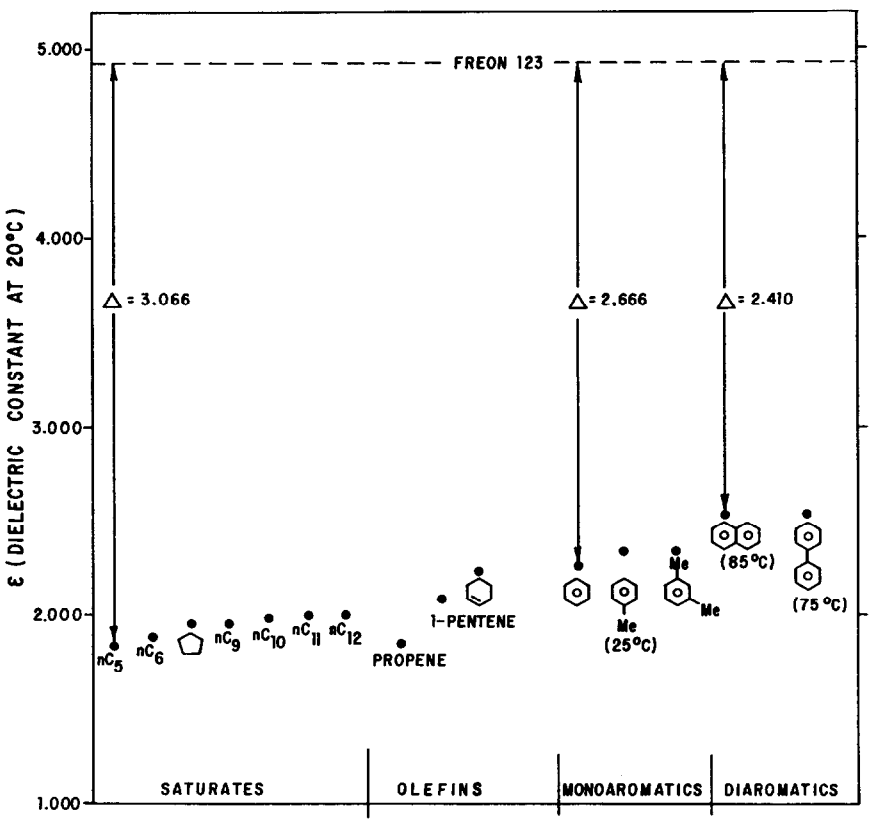


Fig. 3. Dielectric constants of some reference compounds.

improved from 3 to 15 for the worst signal (triaromatics) when the sample load was changed from 1 to 5 μl. The optimum sample load (5 μl) was close to the upper limit of the linearity range reported by Hayes and Anderson [34]. With the present chromatographic system, this load decreased the effect of instrumental noise, caused by the pulsating pump employed, making it unnecessary to use the generally recommended pulseless syringe-type pumps. In addition, the larger adsorbent capacity of the stationary phase allowed the handling of such sample loads without noticeable overload problems.

Fig. 4 shows some chromatograms obtained with the system described. The catalytic LCO separation resembled that obtained by Pedley *et al.* [47] employing a very apolar eluent (pentane) with amino- and underivatized silica columns. Baseline resolution was usually not achieved. For this reason, peak-area integration was performed by drawing lines parallel to the ordinate axis, passing through the frontier points. These frontiers were defined by valleys and/or inflection points, maintaining the general time domains previously stated (see Fig. 2). To verify the accuracy of the determination of the aromatics content, 28 standard blends were prepared. Saturated compounds and aromatics separated preparatively from catalytic LCO (5 standard blends), thermal cracked light gasoil (2), virgin light gasoil (6), kerosene (1) and hydrotreated middle distillates (9) were quantitatively mixed. Five additional blends were prepared by mixing diverse proportions of all the cited fractions. The aromatics contents of prepared standards spanned the range 5–84% (v/v). A linear correlation was found between known and measured aromatic contents, the slope being 0.9956 and the intercept 0.6648. The correlation coefficients obtained were $r = 0.9973$ and $r^2 = 0.9946$, and the standard deviations of the slope and intercept were 0.01 and 0.78, respectively. The standard error of residuals was 2.02.

Regarding precision, short-term repeatibility was evaluated by analysis performed over a 2-day period. Table 5 shows an example of short-term repeatibility. Appropriate standard deviations were obtained for all hydrocarbon groups except for triaromatics. Long-term repeatibility was checked with different type of samples, measured 1 and 5 months after the first determination. Table 6 presents the results obtained, showing greater standard deviations than for the short-term repeatability. The precision was still reasonable for total aromatics and monoaromatics, but was poorer for more conju-

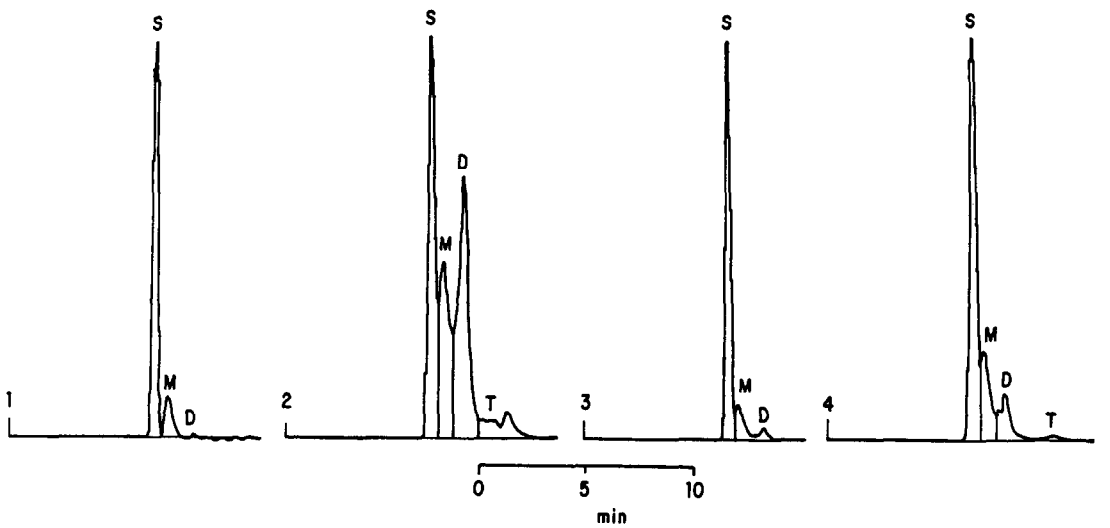


Fig. 4. Selected chromatograms obtained with the described HPLC system. 1 = Kerosene; 2 = LCO; 3 = desulphurized middle distillate; 4 = partially hydrotreated LCO; S = aliphatics; M = monoaromatics; D = diaromatics; T = triaromatics.

Table 5
Repeatability of analysis during a 2-day interval [% (v/v) of hydrocarbon groups from an LCO]

Aliphatics	Total aromatics	Monoaromatics	Diaromatics	Triaromatics
17.0	83.0	18.5	55.1	9.4
17.6	82.4	19.0	56.0	7.4
17.8	82.4	19.5	56.3	6.4
17.6	82.4	19.2	56.3	6.9
17.5	82.5	19.1	55.6	7.8
Mean ± S.D.				
17.5 ± 0.3	82.5 ± 0.3	19.1 ± 0.4	55.9 ± 0.5	7.6 ± 1.2

Table 6
Repeatability of analysis during a 5-month interval

Sample	Hydrocarbon group (%, v/v)[a]				
	Aliphatics	Aromatics			
		Total	Mono-	Di-	Tri-
Hydrotreated middle distillate (350 p.s.i.)	64.7	35.3	20.3	13.8	1.2
	61.2	38.3	23.6	12.0	3.1
	61.5	38.5	21.3	15.0	2.3
	62.5 ± 1.9	37.4 ± 1.8	21.7 ± 1.7	13.6 ± 1.5	2.2 ± 1.0
Hydrotreated middle distillate (1500 p.s.i.)	71.9	28.1	26.1	1.4	0.6
	72.9	27.1	27.6	1.8	0.1
	69.7	30.3	26.6	2.7	1.0
	71.5 ± 1.6	28.5 ± 1.6	26.8 ± 0.8	2.0 ± 0.7	0.6 ± 0.5
LCO	35.2	64.9	21.9	37.7	5.2
	33.6	66.4	22.8	37.2	6.3
	34.7	65.4	21.7	38.2	5.5
	34.5 ± 0.8	65.6 ± 0.8	22.1 ± 0.6	37.7 ± 0.5	5.7 ± 0.6
Kerosene	81.6	18.4	14.6	3.8	ND[b]
	82.9	17.1	15.2	1.9	ND
	82.2	17.8	15.1	2.7	ND
	82.2 ± 0.7	17.8 ± 0.7	15.0 ± 0.3	2.8 ± 1.0	
Desulphurized middle distillate	65.8	34.2	27.4	5.5	1.3
	61.6	38.4	26.7	9.4	2.3
	61.6	38.4	26.8	9.0	2.6
	63.0 ± 2.4	37.0 ± 2.4	27.0 ± 0.4	8.0 ± 2.1	2.1 ± 0.7
Kerosene	83.3	16.7	16.0	0.8	ND
	81.2	18.8	17.7	1.1	ND
	80.5	19.5	17.2	2.2	ND
	81.7 ± 1.5	18.3 ± 1.5	17.0 ± 0.9	1.4 ± 0.7	

[a] Means ± S.D. are additionally reported.
[b] ND = Not detected.

gated aromatics. This was especially noticeable for samples with low levels of di- and triaromatics. The poor precision for triaromatics was caused by the low sensitivity, due to band broadening (last-eluted signals in a long chromatographic system) and a lower response (lower dieletric constant difference, according to the findings in Fig. 3).

Other evidence of repeatibility arises from the fact that the columns were successfully used for 3 years without noticeable changes in the quantitative analysis of the samples used as references. Very small resolution losses were observed during this period. Silica columns were finally replaced for a different reason, *i.e.*, increases in pressure drop were observed as consequence of corrosion of fritted discs. The DNAP column is still in use after 4 years of operation.

The methodology described has found practical applications for the routine monitoring of processes and to obtain rapidly fingerprints of samples from different refineries or from changes in feeds within the same refinery. Examples of the latter are shown in Fig. 5 for LCO samples.

Processes usually monitored with this methodology involved distillation, solvent extraction of aromatics and hydrotreating. Fig. 6 shows sequential chromatograms from distillation and hydrotreating experiments. Hydrocarbon distribution and balances can easily be obtained (see Table 7). This represents the main advantage of the HPLC–dielectric constant detection methodology described here over the commonly used HPLC–RI detection methods [11]. In the same way, trends in total aromatic contents (see Fig. 7) or specific aromatic group distributions can easily be followed during processing, owing to the short time and simple protocol involved in the measurement.

In order to validate this methodology it was compared with MS. This comparison is also useful to assess the applicability of the LC method to distillates with different boiling ranges. Table 8 shows that the results agreed reasonably well for light distillates, such as typical atmospheric cuts. On the other hand, the aromatic contents determined by LC were always lower for heavy distillates. This confirms the applicability of the developed methodology exclusively to atmospheric cuts. For heavier materials such as vacuum gasoil, the signal of tetraaromatics, although detectable, is not measured correctly. This is a consequence of the peak broadening and its poor sensitivity owing to the low dielectric constant difference compared with the solvent.

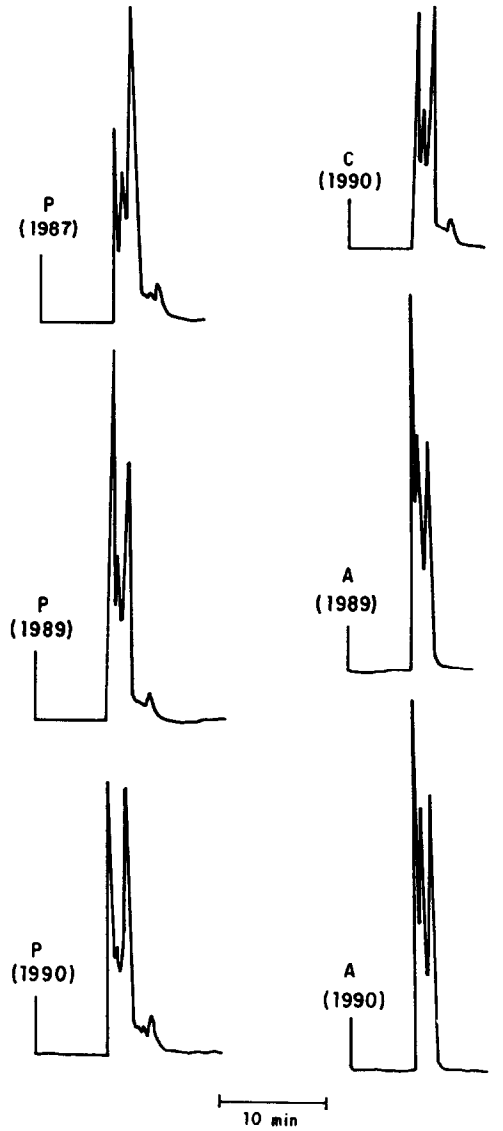


Fig. 5. HPLC fingerprinting of light cycle oils from different Venezuelan refineries (A, C, P). Samples were taken in different years (given in parentheses).

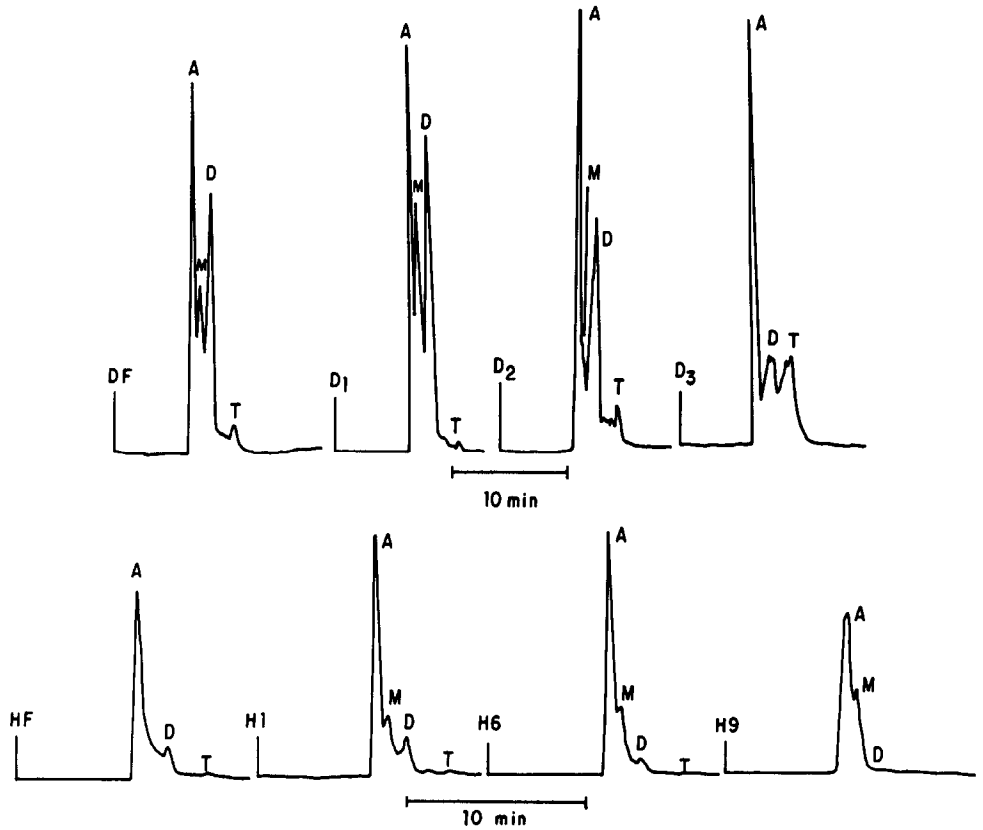


Fig. 6. HPLC monitoring of distillation and hydrotreating processes. DF = Distillation feed; D_1 = 200–300°C cut; D_2 = 300–343°C cut; D_3 = 343°C+ cut; HF = hydrotreating olefinic feed; H_1 = hydrotreated at 350 p.s.i. H_2; H_6 = hydrotreated at 650 p.s.i. H_2; H_9 = hydrotreated at 1500 p.s.i. H_2; A = aliphatics; M = monoaromatics; D = diaromatics; T = triaromatics.

Table 7
Group-type distributions in distillation cuts obtained from an LCO

Sample	Boiling range (°C)	Yield (% P)	Hydrocarbon group by HPLC (%, v/v)			
			Aliphatics	Aromatics		
				Mono-	Di-	Tri-
LCO	NM[a]	100.0	29.6	21.9	38.3	10.3
Cut 1	222–300	67.2	26.6	29.6	39.7	4.1
Cut 2	300–343	26.0	34.2	6.8	43.9	15.2
Cut 3	343+	6.8	40.1	NS[a]	24.5	35.4
Balance of fractions	–	–	29.5	21.7	39.8	9.1

HPLC chromatograms traces are shown in Fig. 6.
[a] NM = Not measured; NS = no signal separated.

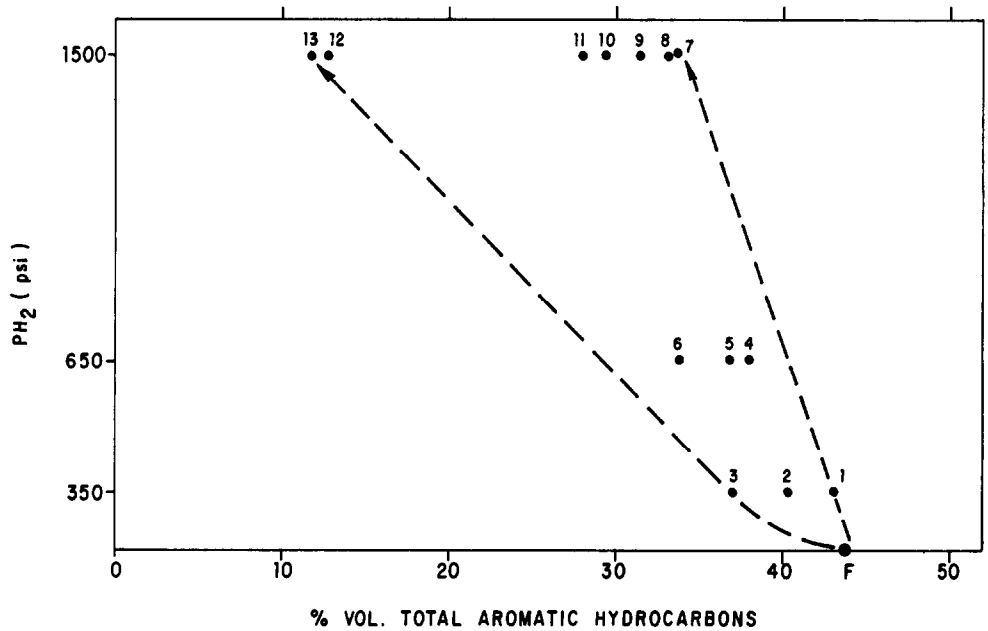


Fig. 7. HPLC mapping of hydrotreating conditions. Selected chromatograms of products 1, 6 and 9 are shown in Fig. 6. F = Feed.

Table 8
Comparison of HPLC and MS for total aromatic content determination of petroleum products

Sample	Average molecular mass[a]	Distillation[b]					Total aromatics (%, v/v)	
		IBP	10%	50%	95%	FBP	HPLC	MS
Hydrotreated middle distillate	182						31.5	35.8[c]
Kerosene	186	154	166	186	238	250	20.2	18.3
LCO	189	210	210	273		332	67.3	65.9
Hydrotreated middle distillate	190						57.0	60.3[c]
Light virgin gasoil	208	180	212	250	308	320	14.6	17.0
Light virgin gasoil	210	180	212	250	308	320	22.5	18.1
Medium gasoil	230	190	245	304	360	390	16.9	30.6
Hydrotreated vacuum gasoil	230						29.4	40.9
Heavy gasoil	254	270	303	334	380	386	12.6	29.9
Heavy gasoil	266						NS[d]	21.5
Vacuum gasoil	309						NS	42.9

[a] Cryoscopy in dioxane for light products; vapour-pressure osmometry in chloroform for heavier materials.
[b] IBP and FBP = Initial and final boiling points.
[c] MS determined by Robinson method [8], with the exceptions noted [44].
[d] NS = No aromatic signal separated.

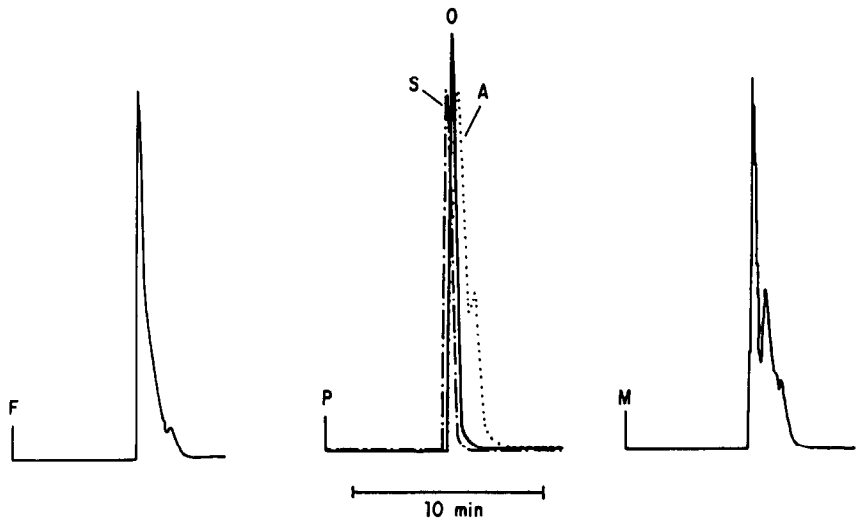


Fig. 8. HPLC of thermal cracked light gasoil and its preparative fractions. F = Thermal cracked light gasoil; P = preparatively separated fractions; M = saturates plus aromatics mixture; S = saturates; O = olefins; A = aromatics.

When analysing pure thermal cracked components by the present LC method, in most instances only one broad signal was obtained. To clarify this finding, saturated compounds, olefins and aromatics from a light thermal cracked gasoil were preparatively separated. Olefins produced in the process eluted exactly between saturated compounds and monoaromatics (see Fig. 8). When mixed in the concentration usually found (*ca.* 40%, v/v), only one signal was detected. Apparently, low levels of olefins do not interfere to a great extent as LCOs were correctly analysed for saturates and aromatics content. The typical olefin content of LCO ranges between 3 and 5% (v/v). Nevertheless, a possibility not addressed until now is based on probable differences between thermal and catalytically cracked olefins.

Interferences from cycloparaffins and naphthenes were finally investigated. In addition to the appearance of a double aliphatic signal (see shoulder increasing as function of hydrotreating severity in Fig. 9), no bias was found during the quantitative analysis of real samples. This was confirmed by MS. Qualitative analysis showed that most of the cycloparaffins present in these samples were decalins. Pure tetralin, a naphthenoaromatic spiked in some samples, was found to elute in the monoaromatic region.

4. Conclusions

A fast LC method was developed for group-type separations of middle petroleum distillates, in terms of aliphatic hydrocarbons and mono-, di- and triaromatics. Freon 123 was employed as the eluent in combination with DNAP and silica columns. Dielectric constant detection was used. A response factor of 1.12 corrected the total aromatic content by volume. The method was found useful for process monitoring and fingerprinting of refinery streams. Its applicability is restricted to low-olefinic (<5%, v/v) atmospheric cuts.

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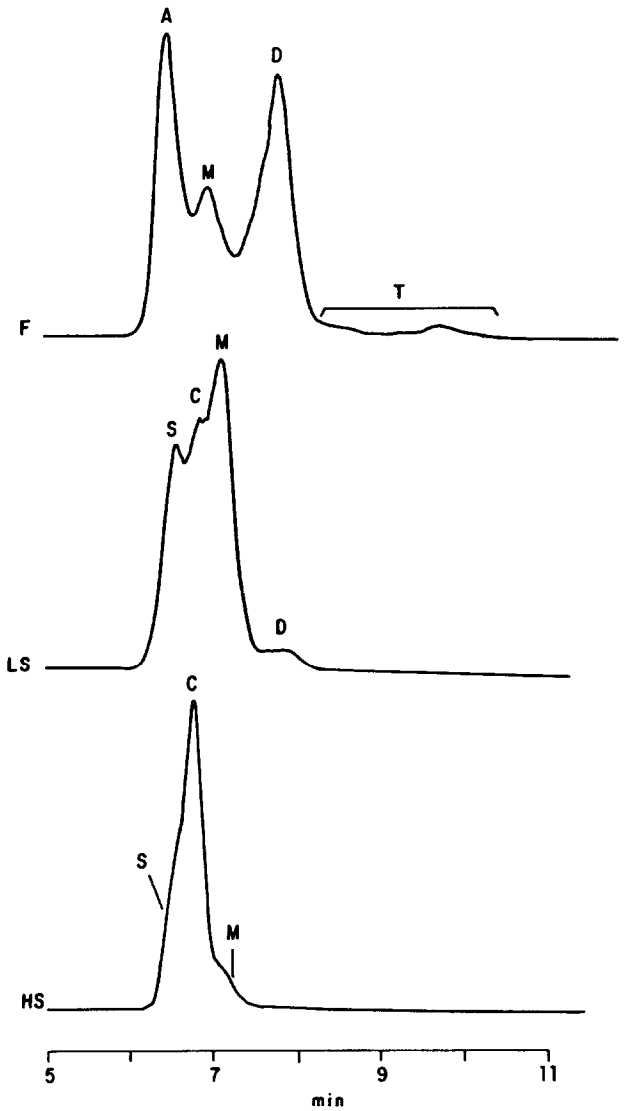

Fig. 9. HPLC monitoring of an LCO hydrotreatment. F = Feed; LS = low-severity product; HS = high-severity product; A = aliphatics; M = monoaromatics; D = diaromatics; T = triaromatics; S = non-cyclic saturates; C = cycloalkanes.

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