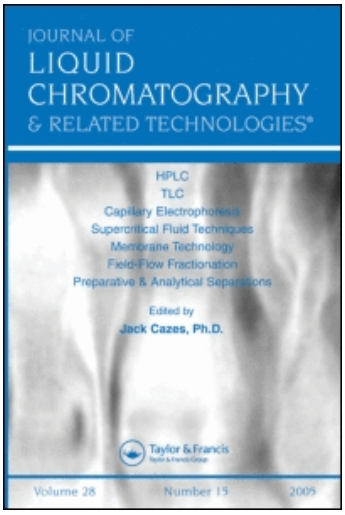

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Guy Félix[a]; Elisabeth Thoumazeau[a]; Jean-Michel Colin[b]; Gisèle Vion[b]
[a] Laboratoire de Chimie Organique et Organometallique CNRS UA, Talence, France [b] C. R. D. Total France Centre de Recherches, Harfleur, France

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HYDROCARBON GROUPS TYPE ANALYSIS OF PETROLEUM PRODUCTS BY HPLC ON SPECIFIC STATIONARY PHASES

Guy Félix*[1], Elisabeth Thoumazeau[1], Jean-Michel Colin[2], and Gisèle Vion[2]

[1]*Laboratoire de Chimie Organique et Organometallique*
CNRS UA 35
Universite de Bordeaux I
351 Cours de la Liberation
33405 Talence, France
[2]*C. R. D. Total France*
Centre de Recherches
B. P. 27
76700 Harfleur, France

ABSTRACT

The hydrocarbon group types analysis of a large number of petroleum products by HPLC equipped with columns of suitable selectivity is described. An effective approach to the factors influencing the specificity of the columns was developped and stationary phases were synthetised in fonction of the products to be separated. All new phases were characterized by elemental, ^{29}Si and ^{13}C NMR analyses. The potentialities of theses phases were illustrated by analysis of selected samples either of fundamental or of industrial interest.

INTRODUCTION

It is only in the seventies that HPLC has been applied to the hydrocarbon groups type analysis of petroleum products. At that stage, reports on the analysis of light petroleum fractions appeared. Later on the preparation of new bonded phases -particularly NH_2 bonded- led to acceptable separations of heavier products under rather good

conditions. However, many examples were related to coal liquefaction products, easier to analyse than petroleum fractions (1-9).

On other hand occurate analysis is of vital importance for refining industry. For instance gasolines must answer to severe specifications which are checked traditionaly by normalised tests often inaccurate or unadapted (FIA-ASTM D 1319). Several methods using HPLC or supercritical fluid chromatography have been published recently (10-17) and some are at this time under evaluations by ASTM Association.

Finally, the knowledge of the composition of heavier products is also important. For example, it allows to estimate whether the crude oil will give good lubricating oils or not, to predict the behaviour of a feed to crack or to check the quality of diesel oil. Unfortunately the chromatographic analysis of high boiling petroleum fractions and even more of the residues is made difficult by the presence of highly alkylated aromatic molecules and of polar compounds. The problem is even more complex in the case of products resulting of a conversion treatment of heavy petroleum fractions. This process leads to the formation of olefins which concentrations (although rather low) have to be known accurately by the refiner.

On the other hand, as the quantitative HPLC analysis of the saturates requires the use of a differential refractometer, one needs a separation as perfect as possible. Consequently columns with high selectivity have to be used, which are not actualy available on the market. Moreover for a same ligand, the commercial bonded phases used in normal mode show drastic differences in selectivity characteristics from one manufacturer to the other, more over even a phase produced by the same manufacturer gives often poorly reproducible analyses, the stipulated characteristics being not the selectivity for a definite problem but the maximum theoretical number of plates.

In order to propose a better approach to these different problems we have designed and realised our own stationary phases. We report here the results obtained for the separations of olefins and saturates from aromatics in different samples of petroleum fractions.

EXPERIMENTAL

Apparatus

Two chromatographic systems were used ; one for the separation of saturates and olefins from aromatics (UV and refractometric detectors), the second for separations between aromatics and polar compounds or resins (UV detector).

The first system consisted of a Knauer 64 pump equipped with a Rheodyne 7520 sample injection and a valco back flush valves connected to a Iota differential refractometer (Jobin-Yvon) and a Shimadzu SPD 2A UV detector. The second is composed of an Altex 110 pump with the same system of valves as previously and equipped with a Schoeffel 770 UV detector.

Reagents

The mobile phase used is n-hexane lichrosolv from Merck dried on molecular sieves.

Sample preparation

The samples were fractions obtained from direct distillation of crude oil or by conversion treatment of heavy fractions. They were defined by their boiling ranges as shown below :

Products	Boiling Ranges °C
Diesel oil	220-370
Vacuum distillate	370-530
Atmospheric residue	370^{+}
Vacuum residue	530^{+}

They were injected pure or dissolved in n-Heptane after deasphalting.

Procedure

The used methods are listed in table 1 and have several commun characteristics :

- quantity injected : between 10 and 20 µl
- flow rate of the mobile phase : 1 ml/mn
- back flush during the analysis : undicated as BF in table 1.
- external standard for the quantitative measurements was generaly a product of the same type purified by preparative chromatography. However, in the case of conversion residues, the standard was a conversion distillate where olefins ratios were measured by refractometric detector. In this case we postulated that olefins present in the residu and the distillate have the same response factor with an UV detector.

Reponse factors of internal standards were calculated from mixtures of well known composition preparated with authentic samples isolated by preparative chromatography.

RESULTS AND DISCUSSION

Choice of the stationary phase

The separations between saturates, olefins and aromatics used to be carried out in a routine way in refinery laboratories by low pressure preparative liquid chromatography on silica gel. Silica gel coated with silver nitrate was used for samples containing olefins.

In HPLC silica gel is also efficient for the separation of light products (gasoline, diesel-oil, vacuum distillate - see table 1). But it is not possible to separate olefins from heavier products ; moreover polar products are retained irreversibly on silica gel. Also the great sensitivity of silica to water makes its use sometimes very difficult.

The bonded phases do not present these drawbacks, in consequence they are largely used for the analysis of hydrocarbons, coming from crude oil or not. However results obtained on commercial columns (NH_2, CN or mixed) being not reliable as mentioned above, we decided to reinvestigate the preparation of packings bearing amino ligands.

TABLE I : SEPARATION METHODS
(the chromatographic conditions are described in the text)

	STRAIGHT-RUN PRODUCTS	CONVERTED PRODUCTS			
	Heavy products without olefins (deasphalted with nC_7)	Gasoline	Gas-oils	Vacuum distillates	Residues (desasphalted with nC_7)
SEPARATION	1st injection : S / A + R BF 2nd injection : S + A / R BF	S / O / A BF	S / O / A BF	1st injection : S / O / A + R BF 2nd injection : S + O + A / R BF	1st injection : S + O / A + R BF 2nd injection : S + O + A / R BF
EXPERIMENTAL	1st injection : column = SiO_2 mobile phase = nC_7 2nd injection : column = Si-NH_2 mobile phase=cyclohexane 85 + dichloromethane 15	Column = SiO_2 Mobile phase = Fluorinert	Column = SiO_2 Mobile phase = nC_6	1st injection : column = SiO_2 mobile phase = nC_7 2nd injection : column = Si-NH_2 mobile phase=cyclohexane 85 + dichloromethane 15	1st injection : column = SiO_2-NH_2 mobile phase = nC_7 2nd injection : column = Si-NH_2 mobile phase=cyclohexane 85 + dichloromethane 15
DETECTOR	1st injection : refractometer 2nd injection : UV 254 nm	Refractometer	Refractometer	1st injection : refractometer 2nd injection : UV 254 nm	1st injection : UV 210 nm (olefins) 2nd injection : UV 254 nm
HYDROCARBON FAMILY TO BE MEASURED	1st injection : saturates 2nd injection : aromatics & resins	Saturates Olefins Aromatics	Saturates Olefins Aromatics	1st injection: saturates & olefins 2nd injection : aromatics & resins	1st injection: saturates & olefins 2nd injection : aromatics & resins
QUANTITATION	1st injection : external standard of known composition 2nd injection : internal normalisation - Response factors = A = 1 R = 1.5	Internal normalisation Response factors : S = 1.3 O = 0.95 A = 0.5	Internal normalisation Response factors : S = 1 O = 1 A = 0.65	1st injection : internal normalisation - Response factors = S=1 O=1 A+R=0.8 2nd injection : internal normalisation - Response factors = A = 1 R = 1	1st injection : olefins = external standard of known composition saturates+olefins= external standard 2nd injection : internal normalisation - Response factors = A = 1 R = 1.5

S = saturates A = aromatics BF = back-flush
O = olefins R = resins

Qualities required for a good separation

The first and important problem, for analysis of heavy petroleum fractions is to obtain a good resolution between olefins and monoaromatic hydrocarbons. One has to consider that for heavy vacuum distillates or residue products a good separation between saturates and olefins does seem expectable.

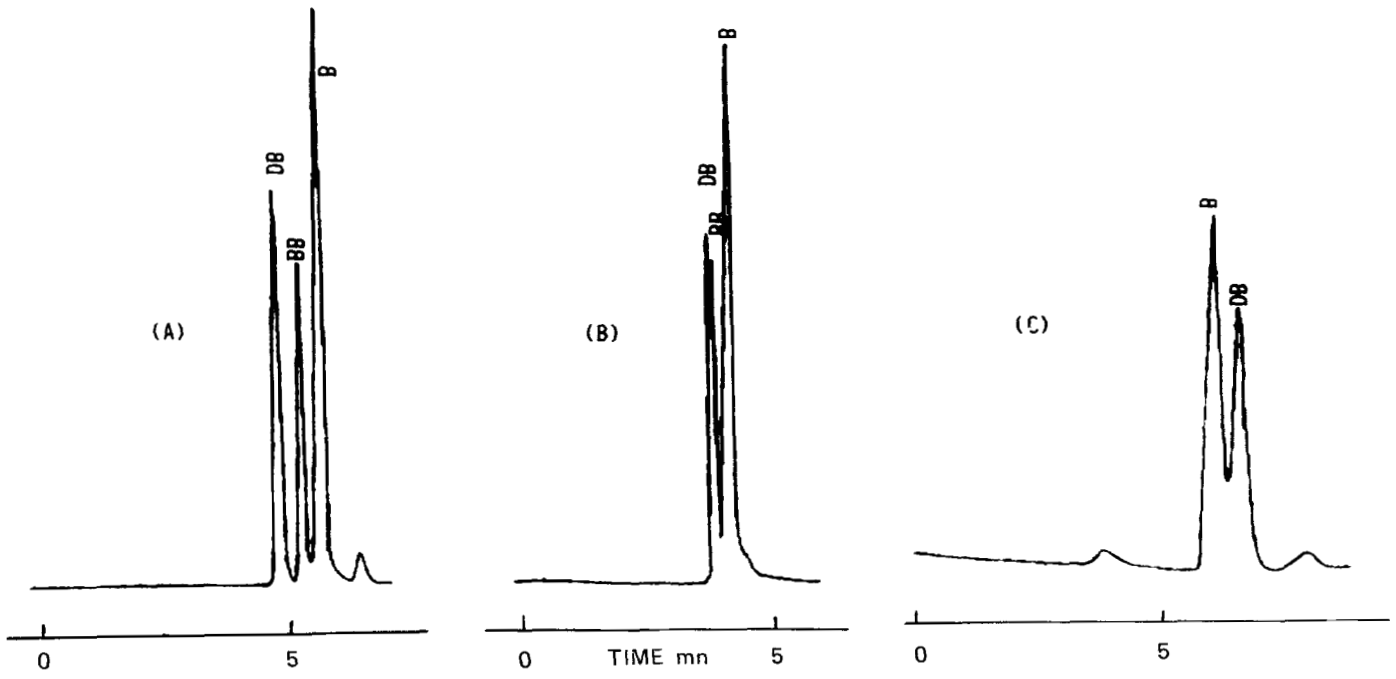
A second problem is due to the presence of aromatics compounds substituted by long alkyl chains and which have a preponderant "saturated character". They are eluted before the non-alkyl aromatics and therefore interfere with the saturates. A good stationary phase must retain more strongly the aromatics substituted with long chains than the non-alkylated ones.Theses features are illustrated by figures 1 to 3. We have analysed a mixture of benzene, butyl-benzene and decyl-benzene on a silica gel column (fig 1), on a commercial NH_2- bonded phase (fig 2) and on our NH_2 bonded specific column (fig 3). Only the last column eluted decyl benzene after benzene and thus allowed a good separation between olefins and aromatics.

Problems related with synthesis of bonded phases

The syntheses were first reported by R. Majors (18). Several amino ligands have been used, which characteristics have an influence on the quality of the final grafting. Besides the nature of the ligand, others parameters are also of importance, as example :

- physico-chemical characteristics of the silica gel
- pretreatment of the silica gel or not
- phase modifications : stoechiometry, nature of the solvant, temperature, time of reaction, etc...
- possible adjusted polymerisation of the ligand
- end capping or successive modifications.

A good understanding of the role of these factors is indispensable to achieve efficient bondings and to work in a reproductible way.



SEPARATION OF A MIXTURE OF { BENZENE (B); BUTYL-BENZENE (BB); DECYL-BENZENE (DB)

FIGURE 1 : (A) SILICA COLUMN
FIGURE 2 : (B) COMMERCIAL AMINO COLUMN
FIGURE 3 : (C) HOME-MADE AMINO COLUMN

MOBILE PHASE = N-HEXANE
FLOW-RATE = 1 ML/MIN
DETECTION = U.V. 254 NM

Characterisation of the stationary phase

A precious indication on the quality of the bonding is the elemental analysis of the stationary phase. Nevertheless one has to be carefull with the interpretation of the results. Thus, a hight amount of carbon could mean perhaps an incontrolled polymerisation of the ligand or the presence of non-bonded polymers which due to an inadequate washing.

The structural analysis of the packing is also a precious information because one can identify precisely the ligand bonded on silicagel . For th at purpose we used ^{29}Si and ^{13}C CP MAS NMR. Figures 4 and 5 show respectively ^{29}Si spectra of an aminopropyl packing before and after end-capping with trimethylchlorosilane. Figures 6 and 7 represented ^{13}C spectra of the same samples. Two resonances at - 0,7 ppm (^{13}C NMR - fig. 7) and at 13,9 ppm (^{29}Si NMR - fig. 5) arecharacteristic of the end-capped phase. Silanol groups were neverless present on the surface of silica (resonance at - 100 ppm). An additional resonance at - 66 ppm indicated the presence of a little amount of polymerized ligand.

However, only separation tests made on reference mixtures will tell us about the quality of our bonded phases.

Applications to the analysis of Petroleum Products

The methods used for the separation are described in Table 1. They were choosen as a fonction of the composition of the fraction (olefins) and of their boiling ranges.

Figure 8 shows the separation between saturates and mono aromatics obtained on a crude oil without any preparation.

Figures 9 to 12 show the analysis of different petroleum fractions like gasoline, diesel oil and residue.

The advantage of HPLC for hydrocarbon groups type analysis of crude oil portrayed on figures 13 to 15. For this purpose several crude oils have been distilled in narrow fractions (10 to 20°C) and each fraction analysed by HPLC. The distribution between saturates, aromatics and polar compounds in each crude oil were obtai-

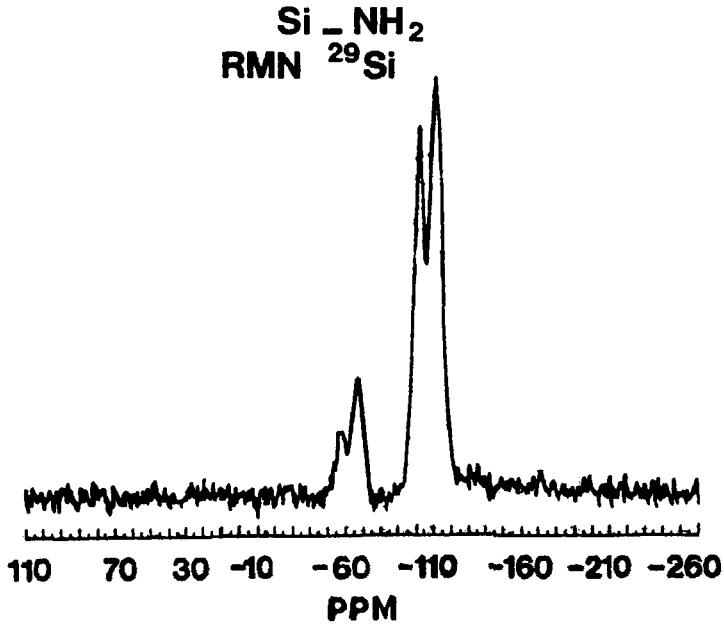


FIGURE 4 : CP-MAS ^{29}Si NMR ANALYSIS OF AN AMINO BONDED SILICA

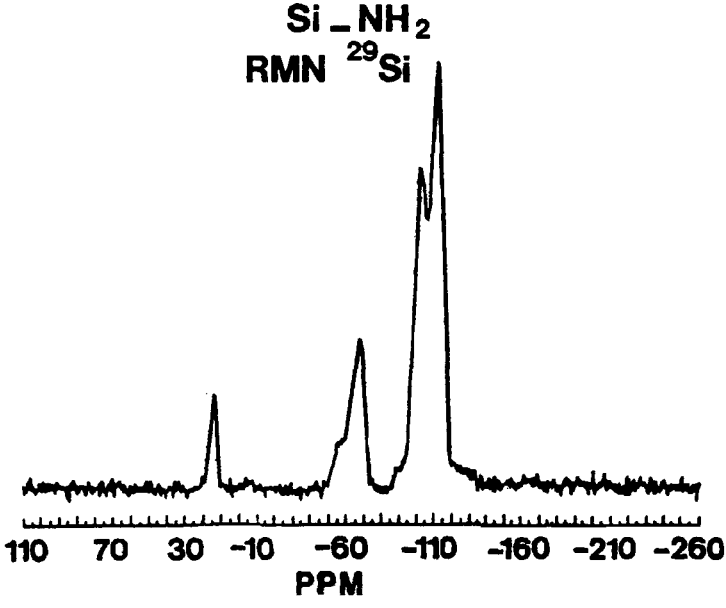


FIGURE 5 : CP-MAS ^{29}Si NMR ANALYSIS OF A T.M.C.S. END-CAPPED AMINO BONDED SILICA

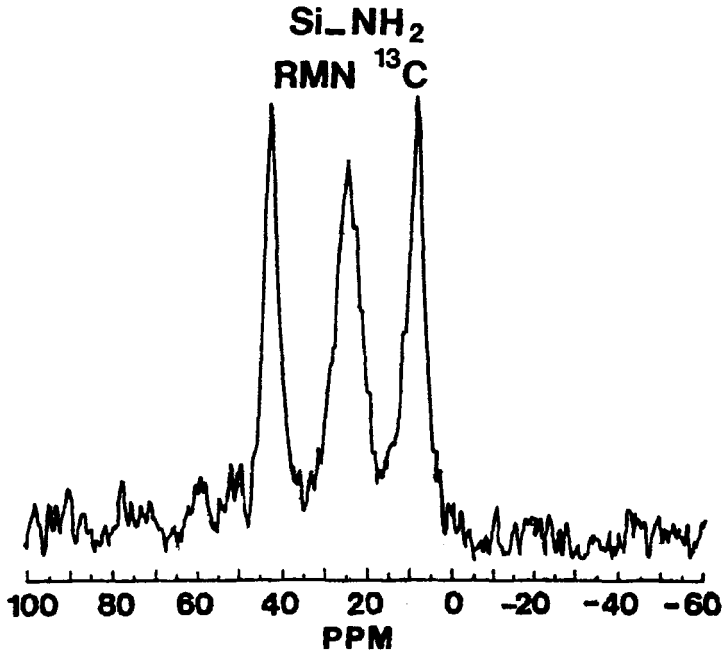


FIGURE 6 : CP-MAS ^{13}C NMR ANALYSIS OF AN AMINO BONDED SILICA

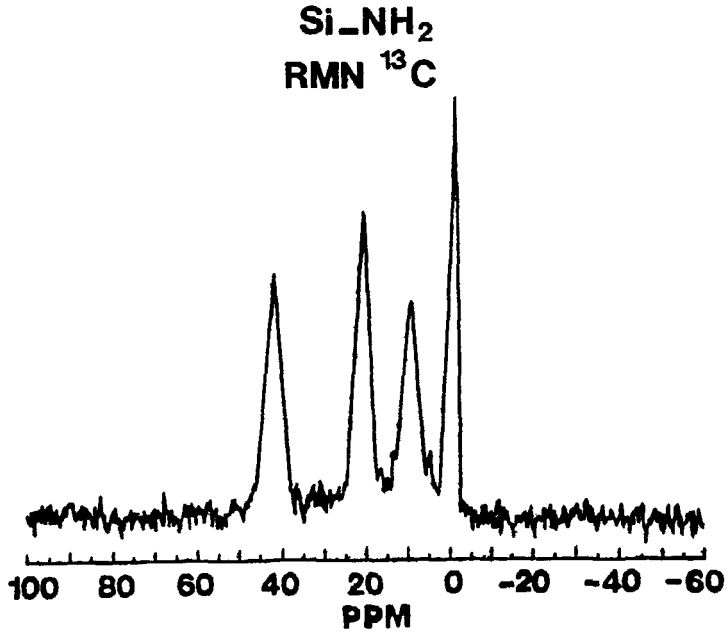


FIGURE 7 : CP-MAS ^{13}C NMR ANALYSIS OF A T.M.C.S. END-CAPPED AMINO BONDED SILICA

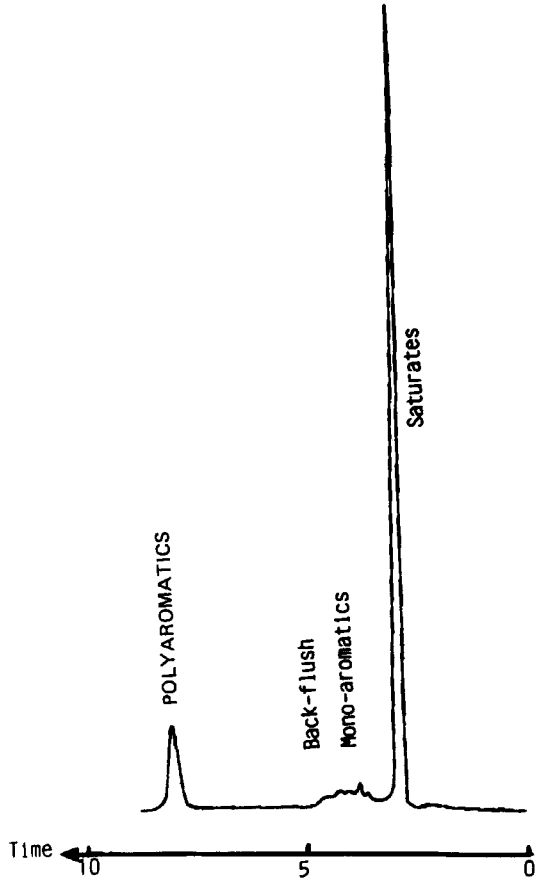


FIGURE 8 : ANALYSIS OF A CRUDE OIL - SEPARATION OF THE SATURATES FROM THE MONO- AROMATICS

Column = home-made amino bonded silica
Mobile phase ◘ n-hexane
Flow-rate = 1 ml/min
Injection ◘ 10 microlitres of a 20 mg/ml solution
Refractive index detector

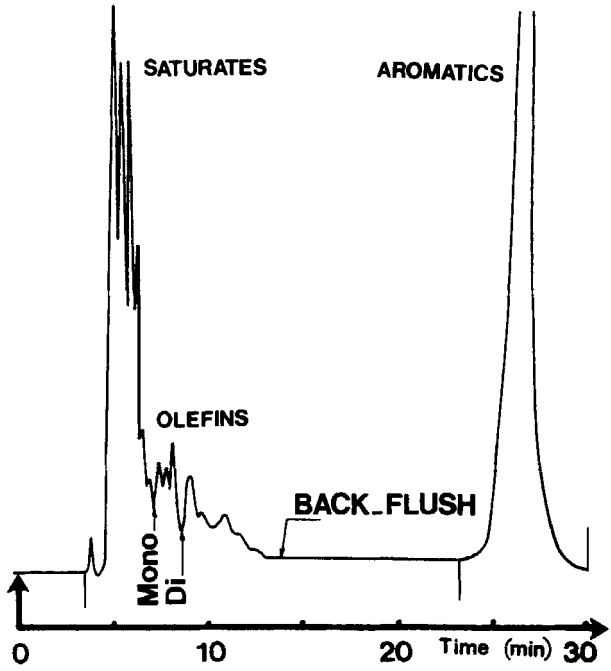


FIGURE 9 : ANALYSIS OF A GASOLINE

Column = silica
Mobile phase = Fluorinert FC 72
Flow-rate = 1 ml/min
Injection = 3 microlitres
Refractive index detector

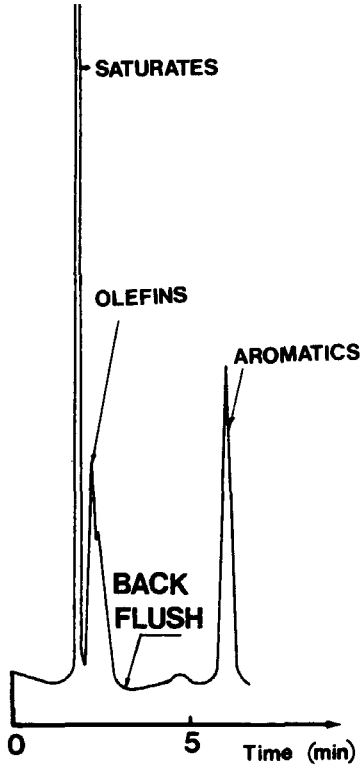


FIGURE 10 : ANALYSIS OF AN OLEFINIC GAS-OIL

Column = silica
Mobile phase = n-hexane
Flow-rate = 1 ml/min
Injection = 10 microlitres of a 20 mg/ml solution
Refractive index detector

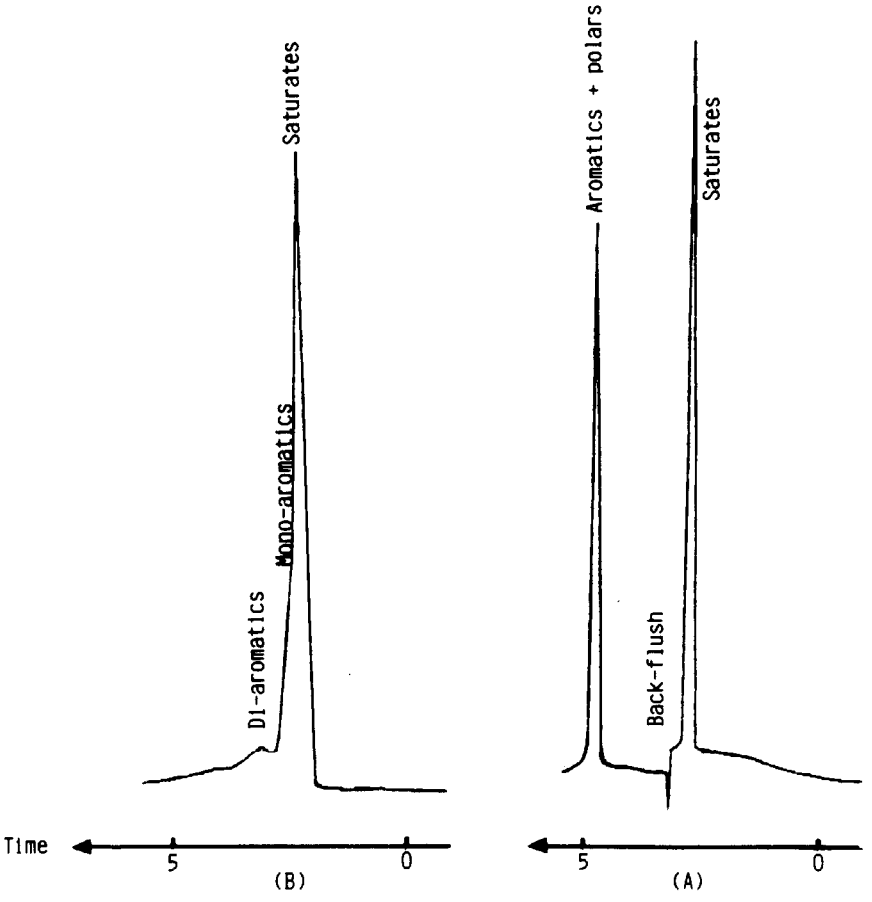


FIGURE 11 : ANALYSIS OF A VACUUM GAS-OIL

(a) Home-made amino column
(b) Commercial amino column

Mobile phase = n-hexane
Flow-rate = 1 ml/min
Injection = 20 microlitres of a 20 mg/ml solution
Refractive index detector

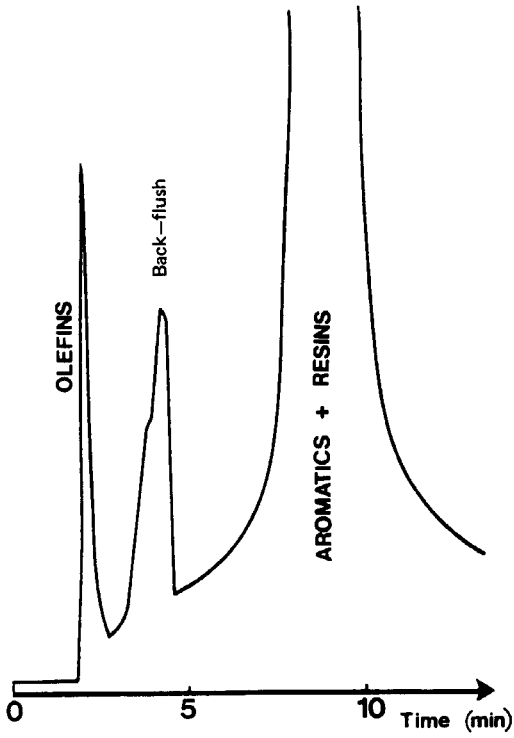


FIGURE 12 : ANALYSIS OF A DEASPHALTED RESIDUE

Mobile phase = n-heptane
Flow-rate = 1 ml/min
Injection = 10 microlitres of a 20 mg/ml solution
Detection = U.V. 210 nm

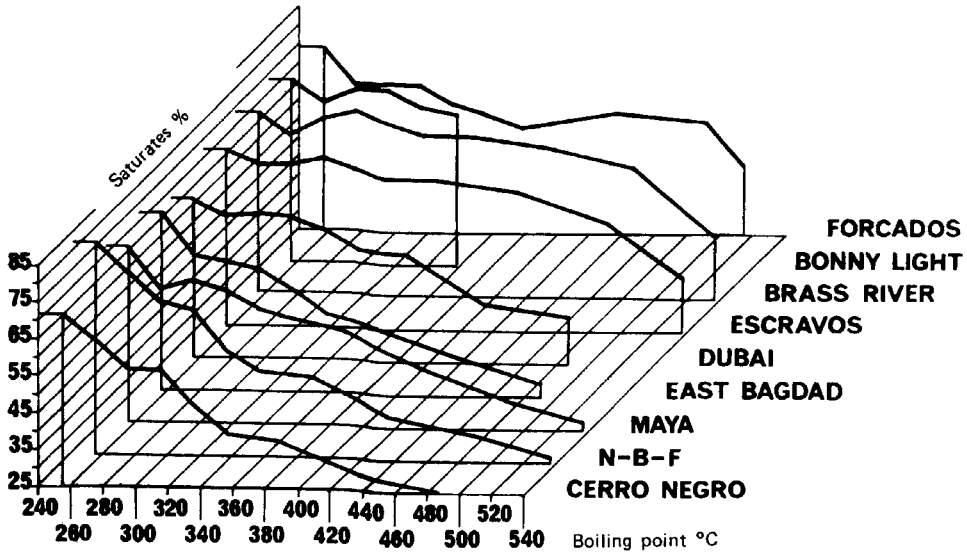


FIGURE 13 : DISTRIBUTION OF SATURATES IN VARIOUS CRUDES

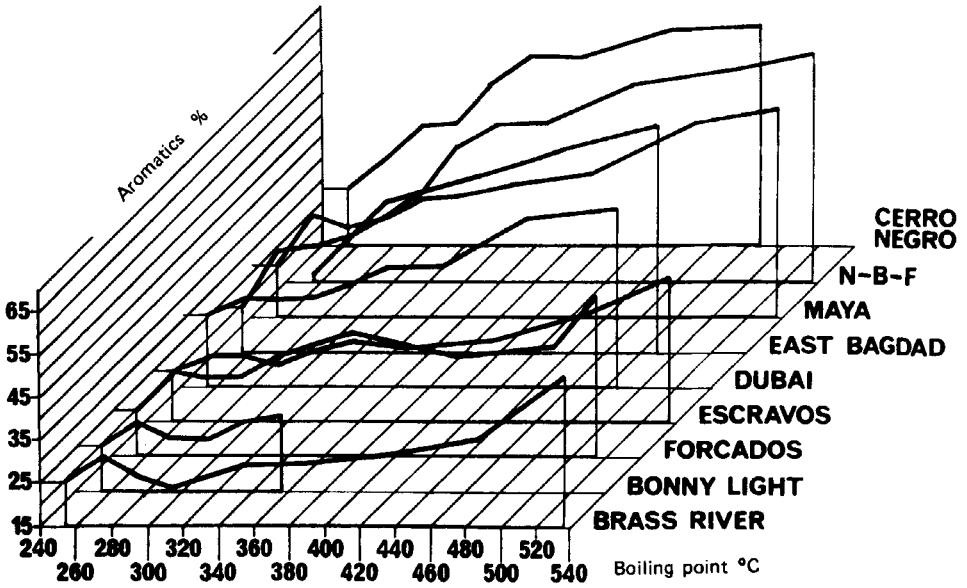


FIGURE 14 : DISTRIBUTION OF AROMATICS IN VARIOUS CRUDES

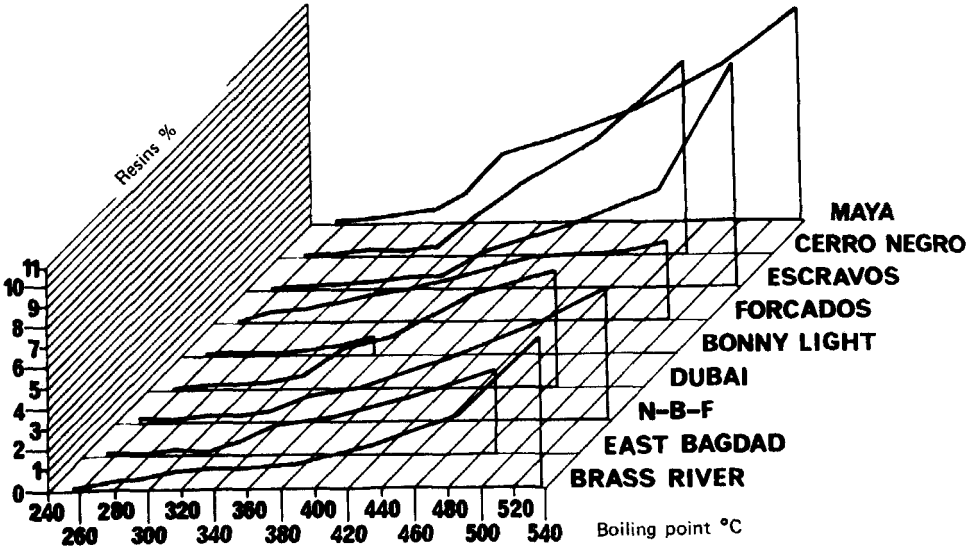


FIGURE 15 : DISTRIBUTION OF RESINS IN VARIOUS CRUDES

ned as a function of the boiling point. This type of development is a very promising approach in the characterisation of crude oils.

The validity of our quantitative measurements has been established by comparing the results with those obtained by High Resolution Mass Spectrometry (Fisher method) or by preparative liquid chromatography.

CONCLUSION

The HPLC became in a few years the best analytical technique for the constitution analysis of petroleum fractions and particularly for the heaviest ones, but suitable columns with adapted selectivities are necessary to achieve these analyses. We have developped a new amino packing which yielded complete separation of saturates and olefins from other constitutants.

Studies on other bonded stationary phases are in progress in particular for the selective separation of aromatics as a function of the number of condensed rings.

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