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IMPROVED HYDROCARBON GROUP RESOLUTION OF OLEFINIC GASOLINES BY ADSORPTION AND CHARGE-TRANSFER HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Two rapid high-performance liquid chromatographic techniques (< 15 min) for separating light and heavy gasolines into saturated, olefinic and aromatic compounds are described. The first one involves adsorption chromatography, and the choice of stationary phase (silica gels of various specific surface areas) and mobile phase (nature, water content) is discussed in terms of chromatographic performance and the characteristic of the petroleum product (boiling point, solubility, etc.). The second method is based on charge-transfer chromatography with silver-coated silica gel or silver chemically bonded to silica gel and *n*-pentane as mobile phase. The water content is not so critical as in adsorption chromatography. Both methods offer a significant improvement in resolution, especially between saturated and olefinic compounds.

INTRODUCTION

The structural group-type analysis of petroleum products into saturated, olefinic and aromatic hydrocarbons is of great importance for the evaluation of feedstocks and refinery process control. It has been extensively studied and was briefly reviewed by Miller *et al.*¹. The high-performance liquid chromatography (HPLC) method described by Suatoni and co-workers²⁻⁵ is going to be adopted by the American Society for Testing and Materials and is soon to replace the fluorescent indicator adsorption method^{2,7}, involving displacement, gravity-flow chromatography and measurement of zone lengths stained by a fluorescent dye. Suatoni's method uses activated small particle silica gel, a perfluoroalkane as mobile phase, refractive index (RI) detection and column backflushing to elute the aromatic compounds as a single peak. Results obtained with this method have been reported by Miller *et al.*¹ and Colin and Vion⁶.

However, several difficulties remain with regard to the accuracy, especially at the often low olefin contents. These difficulties stem from the fact that the refractometric responses differ greatly within the same structural group, and also from a difficult evaluation of the baseline. This in turn may be due to backflushing, partial resolution of compounds belonging to the same group, or conversely, incomplete separation between two groups, *e.g.*, saturated compounds and olefins.

To avoid some of these drawbacks, more complicated alternative methods have recently been proposed, such as multicolumn liquid chromatography with IR detection⁷ or the use of HPLC together with flame ionization detection gas chromatography^{8,9}. Another trend is to make easier the location of the baseline, so that peak integration should be more accurate. In this content, we now reported on a means of improving the resolution given by adsorption HPLC between the saturated and olefinic hydrocarbon groups in gasoline samples, while keeping the peak for each group as narrow as possible. For this purpose, related parameters such as the specific surface area of the stationary phase, the mobile phase composition and water content, about which surprisingly little information is available, should be optimized. We also investigated charge-transfer HPLC using silver-modified silica, which seems to be a promising alternative.

EXPERIMENTAL

Apparatus

Experiments were performed with a liquid chromatograph assembled from a Model 302 Gilson pump (Gilson, Villiers-le-Bel, France), a 7413 Rheodyne six-port sampling valve with a 1- μ l loop and two detectors: a SF 769 UV spectrophotometer (Kratos, Westwood, NJ, U.S.A.) and a R 401 Waters differential refractometer (Waters Assoc., Milford, MA, U.S.A.). Reverse flow (backflushing) was achieved with a 7010 Rheodyne valve. Ambient temperature was used throughout.

Gas chromatography was performed with a chromatograph equipped with a flame ionization detector and a Perkin-Elmer capillary column (100 m \times 0.3 mm I.D.) coated with squalane. The operating conditions were: injection temperature, 250°C; detector temperature, 250°C; column temperature, linear gradient from -5 to 110°C at 1.5°C min⁻¹.

Five porous silica gels were used: LiChrosorb Si 60, 7 μ m (specific surface area 550 m² g⁻¹) from Merck (Darmstadt, F.R.G.); Rosil, 5 μ m (400 m² g⁻¹) from Alltech, (Eke, Belgium); Nucleosil 50, 5 μ m (500 m² g⁻¹) from Macherey-Nagel (Düren, F.R.G.); a Brownlee Si 100 silica gel cartridge (300 m² g⁻¹) from Brownlee Labs. (Santa-Clara, CA, U.S.A.) and an experimental Spherosil, 5 μ m (800 m² g⁻¹) from Rhône-Poulenc Recherches (Vitry-sur-Seine, France).

Silver(I)-modified silica gel columns were prepared by two methods, using LiChrosorb Si 60 as the base support.

In situ coating method. A 15 cm \times 0.48 cm I.D. stainless-steel column was packed with LiChrosorb Si 60 by the conventional slurry technique. A 15-ml volume of a 3% (w/w) (0.138 M) solution of silver nitrate in acetonitrile was then percolated through the column at a flow-rate of 1 ml min⁻¹. The column was washed with 5 ml of isopropanol and finally equilibrated with 50 ml of pentane.

In situ chemical reaction. A 25 cm \times 0.48 cm I.D. stainless-steel column packed

with LiChrosorb Si 60 was equilibrated with pure water. A 3% (w/w) (0.176 M) solution of silver nitrate in 0.5 M aqueous ammonia was pumped at a flow-rate of 1 ml min⁻¹. The reversal of flow was effected by rotating the backflushing valve after 18 ml of solution had percolated through the column so that a total volume of 36 ml was passed.

Then, the column was washed successively with 15 ml of water, 10 ml of isopropanol and 300 ml of chloroform. Finally, it was dried under a stream of nitrogen at 160°C for 8 h in order to remove ammonia. After this treatment, the column was equilibrated with 50 ml of pentane at a flow-rate of 1 ml min⁻¹.

Chemicals

Pentane and heptane were of Chromasol grade and purchased from SDS (Peypin, France). Fluorinert FC 72 is a perfluorinated alkane obtained from 3 M Company (St. Paul, MN, U.S.A.). 1,1,2-Trichloro-1,2,2-trifluoroethane (FC 113), spectrometric grade, was from Aldrich (Milwaukee, WI, U.S.A.). The solvents were used as received or dried over 4-Å molecular sieves. Finally their water contents were adjusted to the chosen value.

Test solutes and classical reagents were of analytical grade and purchased from well known suppliers.

For qualitative analysis, two gasoline samples from fluid catalytic cracking (FCC) were obtained from Elf (Solaize, France): the lighter one (b.p. < 220°C) contained no saturated and olefinic hydrocarbons with more than eight or nine carbon atoms; the heavier one (b.p. < 280°C) contained these hydrocarbons with up to fourteen carbon atoms. For quantitative analysis, three samples were tested: a light FCC gasoline (b.p. < 220°C), a reforming feed which does not contain light hydrocarbons and a so-called commercial gasoline containing very small quantities of olefins (b.p. ≈ 200°C).

Water content of mobile phase

The water contents of the solvents were measured coulometrically by the Karl Fischer titration method (Automat Bizot et Constant, Prolabo, Paris, France)¹⁰. The accuracy was about 10% for water contents of 2–10 ppm and 5% for those greater than 10 ppm.

Dead volume determination

The dead volume was measured using pentane as solute and methylene chloride as mobile phase.

RESULTS AND DISCUSSION

Liquid–solid chromatography (LSC)

Qualitative analysis

It is well known in LSC that the retention and consequently the selectivity depend, among other factors, on the specific surface area of the adsorbent, the polarity and water content of the mobile phase. Surprisingly, the specific surface area and water content were not specified in recent HPLC reports on this topic^{1–7}. Like-

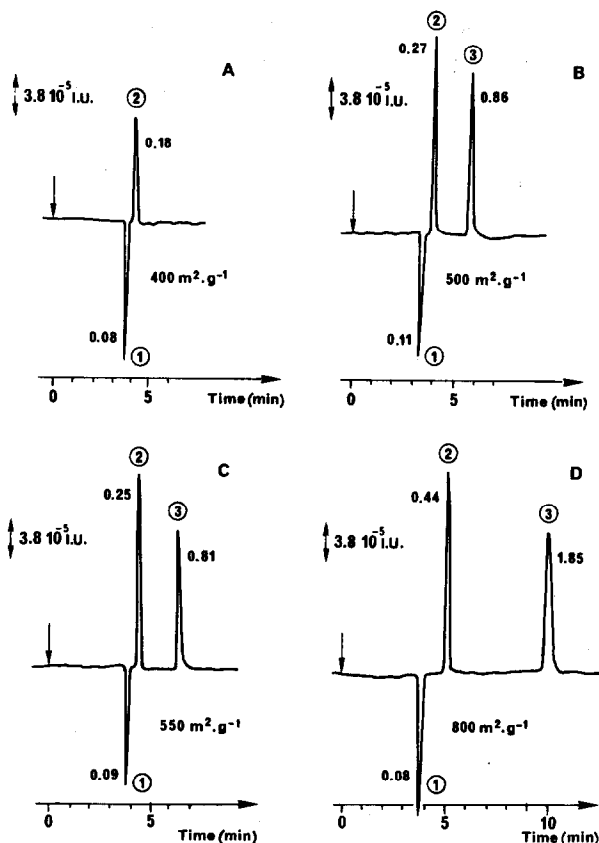


Fig. 1. Influence of the specific surface area of various silica gels on a test mixture separation. Column: 25×0.48 cm I.D. Stationary phases: (A) Rosil ($400 \text{ m}^2 \text{ g}^{-1}$); (B) Nucleosil 50 ($500 \text{ m}^2 \text{ g}^{-1}$); (C) Li-Chrosorb Si 60 ($550 \text{ m}^2 \text{ g}^{-1}$); (D) experimental Spherosil ($800 \text{ m}^2 \text{ g}^{-1}$). Mobile phase: heptane containing 7 ppm of water. Flow-rate: 1 ml min^{-1} . Detection: differential refractometer (Waters R 401). Solutes: 1 = pentane; 2 = cyclooctene; 3 = toluene (the k' values are given near each elution peak).

wise, the effect of silica activation on the separation between saturated compounds and olefins was described without mentioning these factors¹¹. Moreover, while the advantage of perfluoroalkanes over *n*-alkanes as regards the refractometric sensitivity is clearly apparent, the choice of mobile phase with regard to a mere group-type selectivity seems less obvious: some authors have used fluoroalkanes^{1,2,5,6,8}, others hexane^{3,4,9,11}.

Effect of the specific surface area. The influence of the specific surface area of silica gel on the separations of a test mixture containing an alkane (pentane), an alkene (cyclooctene) and an aromatic compound (toluene) and of light gasoline is shown in Figs. 1 and 2, respectively. As previously demonstrated¹², the retention and selectivity increase with increasing specific surface area. Fig. 1 also shows that the efficiency remains independent of the specific surface area and lies in the range 5000–8000 theoretical plates. So, it seemed interesting to work with a silica gel having a specific surface area of over $500 \text{ m}^2 \text{ g}^{-1}$. The resolution between saturated and

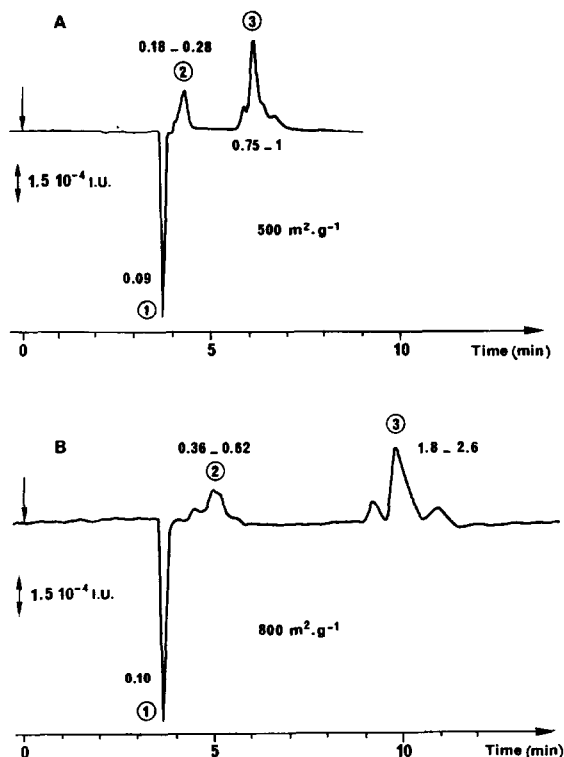


Fig. 2. Influence of the specific surface area of silica gels on a light gasoline separation. Stationary phases: (A) LiChrosorb Si 60 ($550 \text{ m}^2 \text{ g}^{-1}$); (B) experimental Spherosil ($800 \text{ m}^2 \text{ g}^{-1}$). Sample: light FCC gasoline. Peaks: 1 = saturated; 2 = olefinic; 3 = aromatic hydrocarbons. Other operating conditions as in Fig. 1.

olefinic compounds can be considered satisfactory on LiChrosorb Si 60 and is even better on Spherosil. However, owing to the increase in selectivity with increasing specific surface area, a partial resolution within the olefinic and aromatic compounds is observed in Fig. 2B, while the peak due to the saturated compounds became larger. This too high selectivity can constitute a major drawback for the quantitative analysis of the olefinic group because it is much easier to integrate a well defined peak than several small ones.

As regards the aromatic compounds, a backflushing technique is used in the final analytical procedure after the elution of the olefin peak and it is very easy to choose the backflushing time because a large resolution is obtained between the olefin and aromatic groups.

Thus, for the subsequent studies we selected LiChrosorb Si 60 and experimental Spherosil in order to optimize their chromatographic properties in terms of the nature of the mobile phase nature and its water content.

Effect of the nature of the mobile phase. A good separation between the saturated and olefinic groups requires a mobile phase with a very low elution strength: only alkanes and some of their fluorinated derivatives are suitable. We studied four solvents whose properties are given in Table I.

Heptane is often used as a mobile phase in LSC for heavy petroleum products

TABLE I

PROPERTIES OF SOME MOBILE PHASES FOR SEPARATION BETWEEN OLEFINIC AND SATURATED COMPOUNDS

	<i>Pentane</i>	<i>Heptane</i>	<i>FC 113</i>	<i>FC 72</i>
Boiling point (°C)	36.2	98	47.6	56
Viscosity at 20°C (cP)	0.23	0.41	0.71	0.39
Density at 25°C (g ml ⁻¹)	0.629	0.684	1.565	1.68
Refractive index at 20°C	1.3580	1.3875	1.3578	1.251
UV cut-off (nm)	195	195	231	210
Solubility of water in the solvent (ppm)	100	100	90	—
Solvent strength value on silica, ϵ°	0.00	0.01	0.02	≈ -0.2

because asphaltenes are generally precipitated by it. As shown in Fig. 2, its low elution strength gives an acceptable resolution of saturated compounds and olefins. However, its use is not advisable with RI detection and gasoline samples for two reasons. First, the peak due to the saturated compounds would be negative, which renders its integration more difficult; secondly, the detection sensitivity would be low since the RI of heptane is too similar to that of the major constituents of the saturated group. Naturally heptane itself is not detected at all, which alters the quantitative result. These drawbacks are partially avoided with pentane, for its RI is the lowest of the alkanes liquid at ambient temperature, and the pentane content in gasolines is low, variable, and thus of little significance. The resolving power of pentane is even a little better than that of heptane, due to its slightly lower elution strength. Fig. 3A

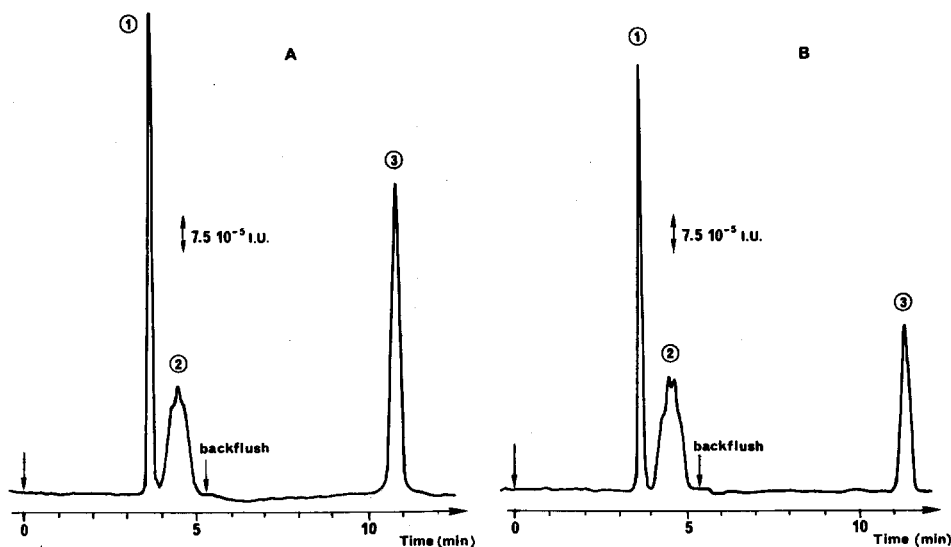


Fig. 3. Separation of light (A) and heavy (B) FCC gasoline samples by LSC with pentane (8 ppm water) as mobile phase. Stationary phase: LiChrosorb Si 60. Other operating conditions as in Fig. 1. Peak identification as in Fig. 2.

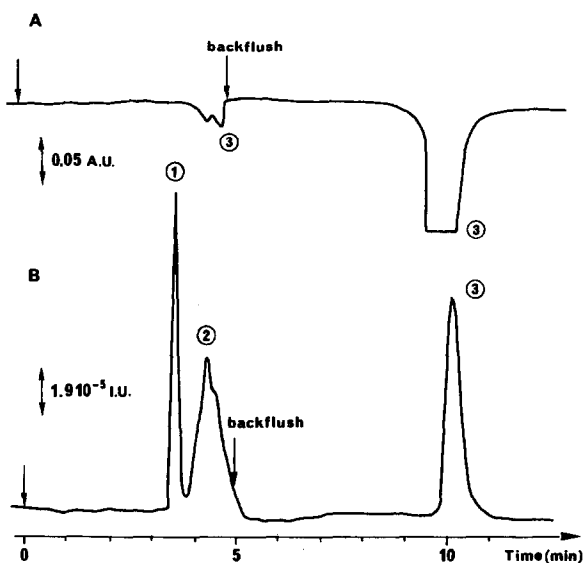


Fig. 4. Separation of a light FCC gasoline sample by LSC with FC 113 (6 ppm water) as mobile phase. Stationary phase: LiChrosorb Si 60. Other operating conditions as in Fig. 1, except detection: (A) UV at 254 nm; (B) differential refractometer. Peak identification as in Fig. 2.

and B show the comparable separations obtained for light and heavy FCC gasoline samples. The high volatility of pentane precludes working at $>25^{\circ}\text{C}$ but this does not constitute too serious a disadvantage if use is made of a tightly stated mobile phase circuit. Moreover, it has been reported¹¹ that the resolution between saturated and olefinic compounds increases with decreasing temperature.

1,1,2-Trichloro-1,2,2-trifluoroethane (FC 113) has recently been recommended by Glajch *et al.*¹³ in LSC for its low elution strength, comparable to that of heptane or hexane, and its better solvent and miscibility properties. It has a refractive index similar to that of pentane but is not as volatile as pentane (Table I). However, as illustrated by Fig. 4, this solvent leads to slightly poorer resolution of the saturated and olefinic compounds in light gasolines, even on a well activated silica. As indicated by UV detection at 254 nm, the aromatic group also overlaps that of the olefins, which is not the case with pentane and renders the backflush time very critical. This lack of structural group resolution makes FC 113 less favourable as a mobile phase than pentane.

The last solvent investigated was FC 72 fluorinert, a mixture principally containing perfluorohexane as used in Suatoni's method^{1,5,6}. Its two main advantages compared to pentane are a still lower elution strength, allowing greater resolution of petroleum compounds, and a still lower refractive index, leading to an increased sensitivity. The resolution between saturated and olefinic compounds is indeed very good (Fig. 5A), olefins are well retained, *e.g.*, $k' = 3$ for cyclooctene, and aromatics cannot be eluted without backflushing. A partial resolution also appears within the olefin group and even with the saturated group. This resolution is enhanced when Spherosil ($800\text{ m}^2\text{ g}^{-1}$) is used instead of LiChrosorb Si 60 ($550\text{ m}^2\text{ g}^{-1}$). An almost complete separation of the light *n*-alkanes (Fig. 5B) is observed. Such a resolution

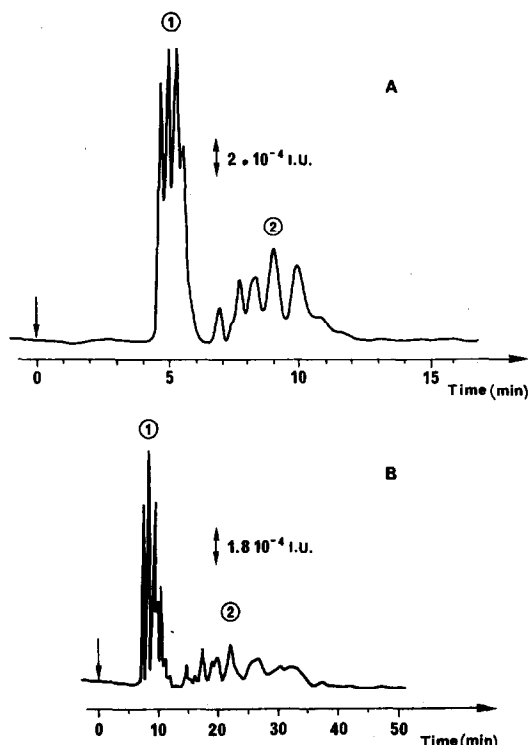


Fig. 5. Separation of a light FCC gasoline sample by LSC with FC 72 (2 ppm water) as mobile phase. Stationary phases: (A) LiChrosorb Si 60 ($550 \text{ m}^2 \text{ g}^{-1}$); (B) Spherosil ($800 \text{ m}^2 \text{ g}^{-1}$). Other operating conditions as in Fig. 1 and peak identification as in Fig. 2.

of compounds belonging to the same structural group does not facilitate integration of peak areas. Other difficulties may arise because of the low solubility of petroleum samples in it.

The retention of several model compounds was studied further in order to elucidate the chromatographic mechanism. Fig. 6 shows a semilogarithmic plot of the capacity factors, k' , of homologous n -alkanes and n -1-alkenes, with FC 72 as mobile phase. It is seen that $\log k'$ increases linearly with carbon number at least up to the n -C₁₆ compounds. The slopes of the straight lines are about the same for the saturated and olefinic compounds on a given stationary phase, but increased with specific surface area, as expected. A study of the retention of other model compounds under the same conditions allows one to conclude that cyclic and branched hydrocarbons are more strongly and less strongly retained, respectively, than a linear compound of equal carbon number. All these phenomena are consistent with an adsorption retention mechanism¹⁴. From a practical point of view, it should be noted (Fig. 6) that 1-hexene (which is probably one of the less strongly retained olefins) has the same retention as n -dodecane on LiChrosorb Si 60, and as n -undecane on Spherosil. This selectivity confirms the very good separation between saturated and olefinic compounds in the light FCC gasoline and indicates a slight overlapping of these two groups in the heavier sample.

Fig. 7 gives plots of the same kind as those in Fig. 6, but for the systems Spherosil-pentane and Spherosil-heptane. With heptane as mobile phase, the retention of *n*-olefins decreases with increasing carbon number, and the retention of alkanes with more than seven carbon atoms becomes lower than that of an unretained solute. With pentane as mobile phase, the same phenomena were observed, except that the retention of *n*-alkanes up to C₁₀ increases with increasing carbon number, and decreases thereafter. These results show that for the system Spherosil-*n*-alkane the retention mechanism entails both adsorption and size exclusion, the contribution of the latter increasing with the length of the alkyl chain of the compound used as mobile phase. Exclusion in LSC was previously reported by Jinno *et al.*¹¹ for C₁₈-C₂₀ compounds with hexane as mobile phase. Since the mean pore diameter of Spherosil is of the order of 40-50 Å, an exclusion of small saturated and unsaturated hydrocarbon molecules cannot be explained without considering the strong solvation effect of the alkane mobile phase.

From Fig. 7, a good separation between saturated and olefinic hydrocarbons in light and heavy FCC gasoline samples which do not contain compounds with more than fourteen carbon atoms (see Experimental) can be expected. Finally, a pentane mobile phase, owing to the mixed retention mechanism, seems to afford the best structural group-type selectivity.

Effect of silica gel activity. It is well known in LSC that large variations in capacity factors, selectivity and sometimes efficiency are observed with the water

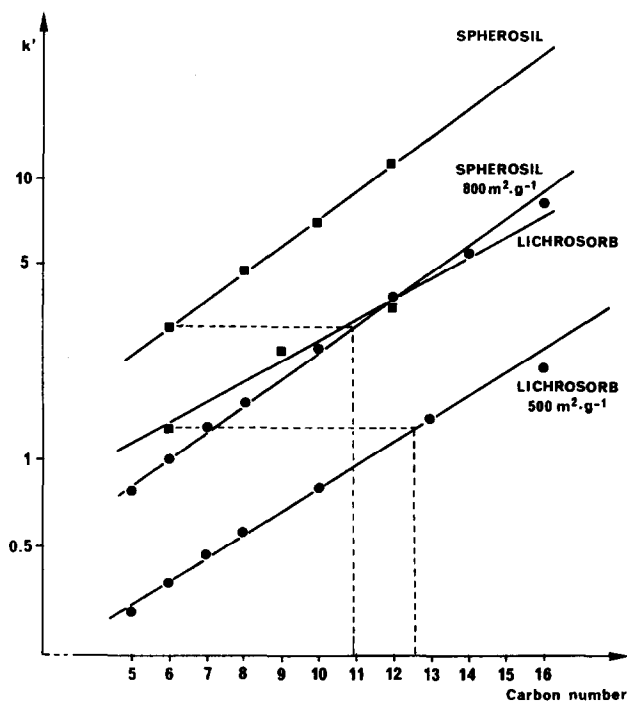


Fig. 6. Variation of the capacity factors of *n*-alkanes (●) and *n*-1-alkenes (■) with their carbon number. Stationary phases: LiChrosorb Si 60 and Spherosil. Mobile phase: FC 72.

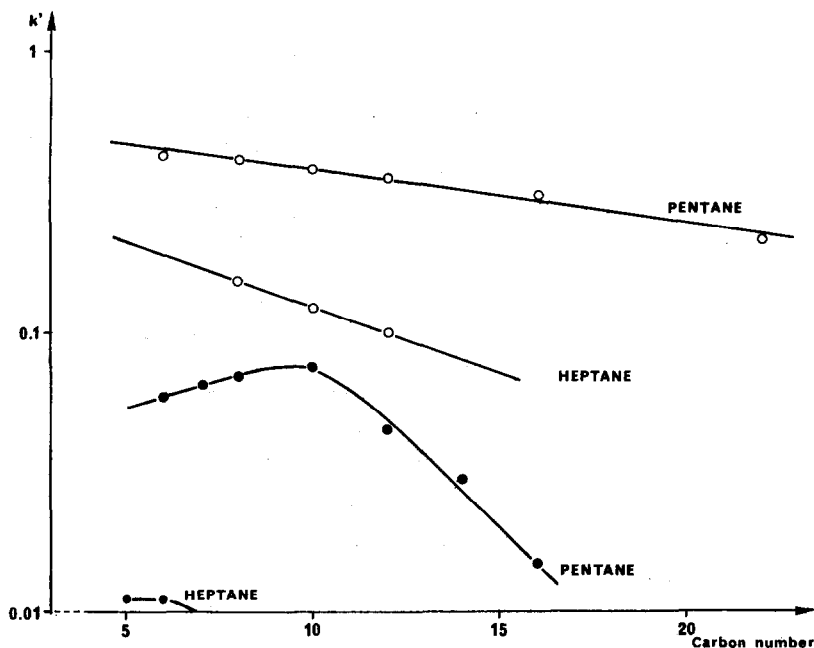


Fig. 7. Variation of the capacity factors of *n*-alkanes (●) and *n*-1-alkenes (○) with their carbon number. Stationary phase: Spherosil. Mobile phases: *n*-pentane and *n*-heptane.

content of the mobile phase¹⁴⁻¹⁸. They are particularly pronounced if class N solvents¹⁷, *i.e.*, solvents having elution strengths in the range 0.00–0.40, are used as eluents, and the greater the activity of the adsorbent (lower water content) the higher is the resolution¹⁹. So isoactivating solvents (solvents having the same reduced water content for class N solvents) must be used in order to keep constant the activity of the adsorbent and to obtain reproducible results²⁰.

Consequently we have studied the influence of the water content in the case of *n*-pentane which is a class N solvent. Fig. 8A and B show the separation of a heavy gasoline sample on LiChrosorb Si 60 with *n*-pentane as mobile phase containing 12 and 5 ppm of water respectively. A satisfactory resolution between the saturated and olefinic hydrocarbons is observed only if *n*-pentane is sufficiently dried over a 4-Å molecular sieve and its water content lowered to 5 ppm before percolating through the chromatographic column. When equilibrium is attained (retention times of test solute are rigidly constant), pentane is kept in a closed circuit. In this way such a high resolution can be maintained for a long period of time (several weeks).

Fig. 9A and B show the same separation with the experimental Spherosil as stationary phase. A good resolution between saturated and olefinic compounds is observed even when the adsorbent is not drastically activated. Besides, a water content lower than 10 ppm is not recommended because a beginning of resolution within the olefinic group is observed. The aromatic compounds can easily be collected into a single peak by backflushing the chromatographic column.

In view of the above results, the main advantage of FC 72 Fluorinert seems to be its particularly low refractive index. As regards a purely structural group-type

selectivity, *n*-pentane (with about 5–8 ppm water) is a better mobile phase for FCC gasoline samples, if used with a silica gel having a specific surface area higher than $500 \text{ m}^2 \text{ g}^{-1}$. With still greater specific surface area, *e.g.*, $800 \text{ m}^2 \text{ g}^{-1}$, the pentane water content can be raised to about 10–15 ppm, which is more convenient in practice.

Quantitative analysis

From previous results, the phase system should be chosen according to the nature and content of the compounds included in each group.

For light gasoline in which compounds similar to pentane are present, only FC 72 can be used as the mobile phase. In that case, a silica gel with moderate specific surface area ($300\text{--}500 \text{ m}^2 \text{ g}^{-1}$) must be used in order not to separate compounds belonging to the same family. For heavier samples, *n*-pentane is advocated as mobile phase because of a better sample solubility and poorer separation between the components of a particular group. In order to compensate for the higher elution strength of pentane, a silica gel having a great specific surface area ($800 \text{ m}^2 \text{ g}^{-1}$) must be chosen.

Three petroleum products have been studied in order to illustrate the difficulties of quantitative analysis and to choose the most convenient mobile phase: FCC light gasoline with a substantial content of light hydrocarbons (1.9%); a reforming feed which does not contain any light and olefinic hydrocarbons; and a commercial

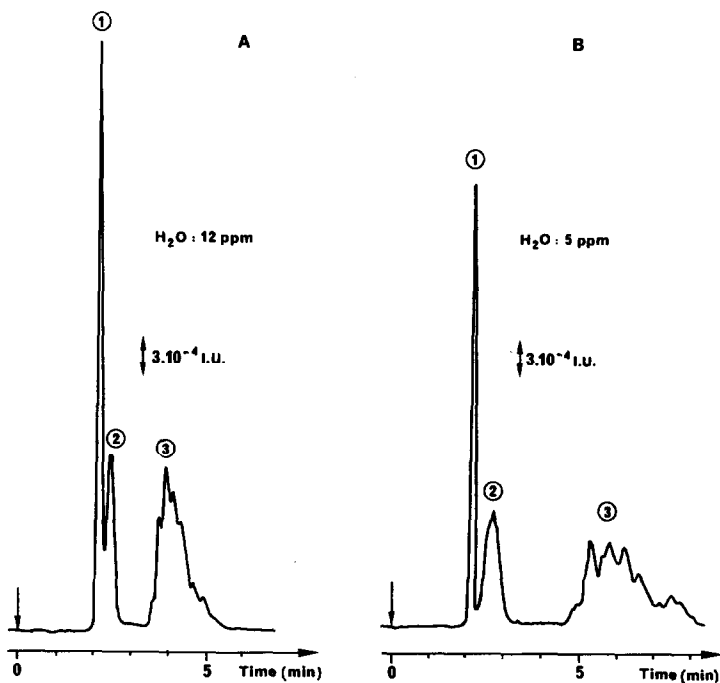


Fig. 8. Influence of mobile phase water content in LSC on the separation of a heavy FCC gasoline sample with LiChrosorb Si 60 as stationary phase. Mobile phases: *n*-pentane containing 12 ppm (A) or 5 ppm of water (B). Other operating conditions as in Fig. 1 and peak identification as in Fig. 2.

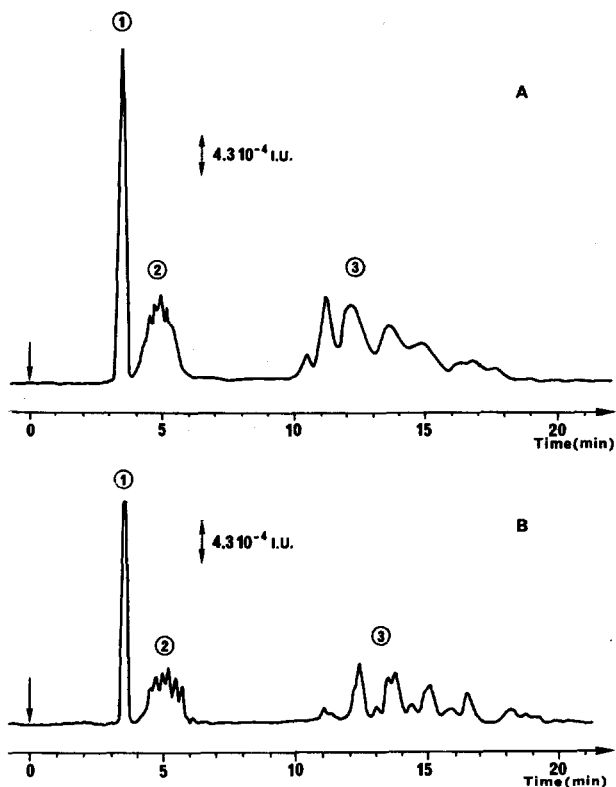


Fig. 9. Influence of mobile phase water content in LSC on the separation of a heavy FCC gasoline sample with Spherosil as stationary phase. Mobile phases: *n*-pentane containing 10 ppm (A) or 5 ppm of water (B). Other operating conditions as in Fig. 1 and peak identification as in Fig. 2.

gasoline having a low olefin content. The corresponding chromatograms are shown in Fig. 10.

The results obtained are collected in Table II. They were calculated by the following methods. In all cases, aromatic compounds have been quantified with an external standard². With FC 72 as mobile phase, the contents of saturated and olefinic compounds were calculated by internal normalization using response factors⁶ of 1.3 for the saturated, and 0.95 for the olefinic compounds. With *n*-pentane as mobile phase, the response factors of the two groups cannot be calculated (except in the case where light compounds are not present). So it is possible only to calculate the volume content of saturated compounds for the reforming feed sample which does not contain olefins.

From Table II, the following conclusions can be drawn:

With FC 72 as mobile phase, the results obtained for the light gasoline and reforming feed samples are in good agreement with those measured by gas chromatography (GC).

For commercial gasoline the olefinic content seems to be too high. An explanation is the low signal-to-noise ratio, resulting in a difficult integration.

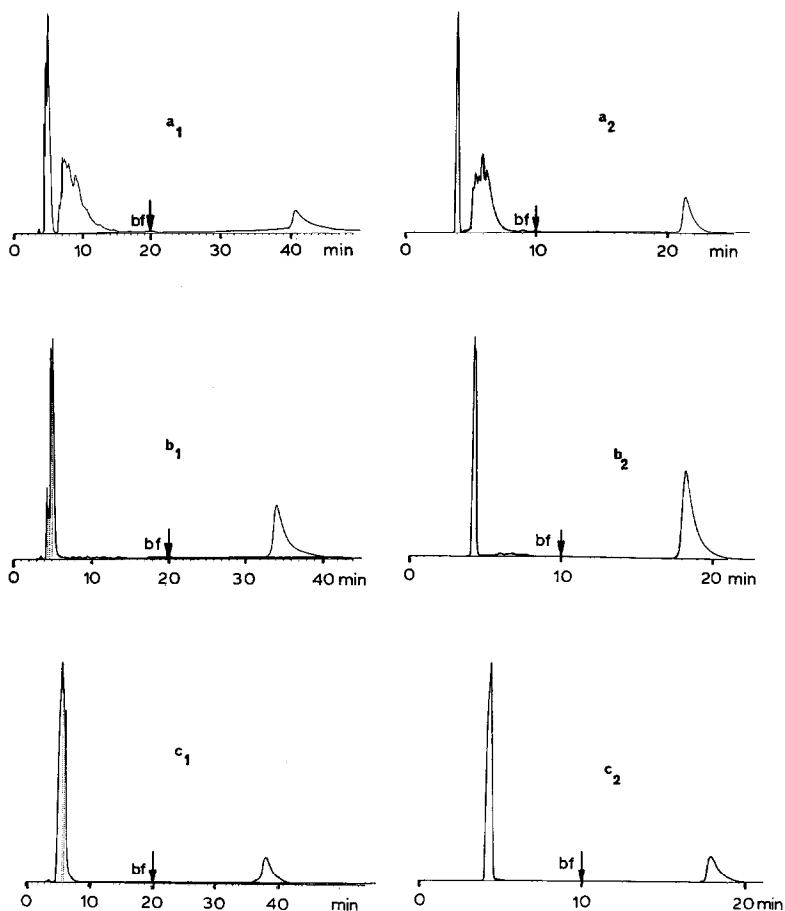


Fig. 10. Separation of three petroleum products studied for quantitative analysis. Samples: (a) FCC light gasoline; (b) commercial gasoline; (c) reforming feed. Operating conditions: (1) Brownlee Si 100 silica gel cartridge with FC 72; (2) experimental Spherosil with pentane as mobile phase. Flow-rate: 1 ml min^{-1} . Detection: RI. bf = Backflush.

With pentane as mobile phase the results are satisfactory for the reforming feed which does not contain light compounds.

Charge-transfer chromatography

The well known technique using silver(I) charge-transfer complexes to separate geometrical and positional isomers of olefinic compounds^{21,22} has also been tested with petroleum compounds^{7,23}. This technique appears to have potential for improving the resolution between saturated and olefinic groups, which remains fairly difficult in LSC despite all optimization attempts. However, the procedures described were rather intricate since they involved a separation of aromatic hydrocarbons from saturated compounds and olefins on a silica gel column (LSC), followed by a separation of saturated from olefinic hydrocarbons on a Ag^+ -modified silica column. The

TABLE II
COMPARISON OF QUANTITATIVE ANALYSIS RESULTS OBTAINED BY CAPILLARY GC AND LSC

Operating conditions: GC, see Experimental; LC, Brownlee Si 100 silica gel cartridge (300 m² g⁻¹) with FC 72 or experimental Spherosil (800 m² g⁻¹) with pentane as mobile phase.

	Area (%)		Volume (%)		Volume (%) GC
	Mobile phase: FC 72	Mobile phase: pentane	Mobile phase: FC 72	Mobile phase: pentane	
FCC light gasoline					
Saturated compds.	35.7	27.9	44.9	★	45.8
Olefins	54.8	55.5	50.8	★	50.1
Aromatics	9.5	16.6	4.3	4.7	4.1
Commercial gasoline					
Saturated compds.	52.6	39.2	71.7	★	73.5
Olefins	5.5	2.6	5.5	★	3.8
Aromatics	41.9	58.2	22.8	24.5	22.7
Reforming feed					
Saturated compds.	83.8	77.8	90.8	89.5	90.1
Olefins	0	0	0	0	0
Aromatics	16.2	22.2	9.2	10.5	9.9

* Response factors cannot be calculated.

procedures differ in the mobile phases to be used: cyclohexane²³ or carbon tetrachloride⁷.

In this work, we investigated the silver complex method in order to separate the three groups, saturated, olefinic and aromatic compounds, on the same column using backflushing. Two problems must be solved. The first one arises from the fact that silver(I)-aromatic hydrocarbon complexes are less stable than those with mono-olefinic compounds, and therefore the separations between olefinic and aromatic hydrocarbons may become difficult. The second problem is to perfect a rapid and simple procedure to prepare silver(I)-modified silica gels of known and stable characteristics. In previous studies, silver nitrate was dissolved in acetonitrile^{7,22}, methanol²¹ or water²³ at various concentrations. The silver coating was made merely by mixing the silver solution with silica gel (batch procedure)^{7,23}, or by percolating the silver solution through a packed silica gel column (*in situ* procedure)^{21,22}. We decided to investigate the *in situ* procedure with two different silver nitrate solutions leading either to the classical silver coating or to chemically bonded silver.

Silver-coated silica gel. By passing an acetonitrile solution of Ag⁺ through a silica gel column, a mere coating is achieved:

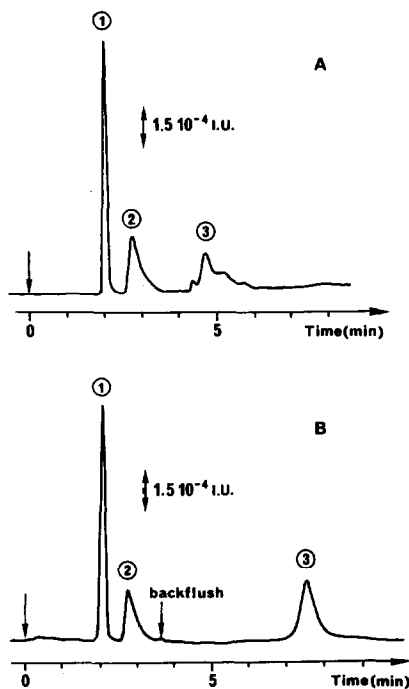
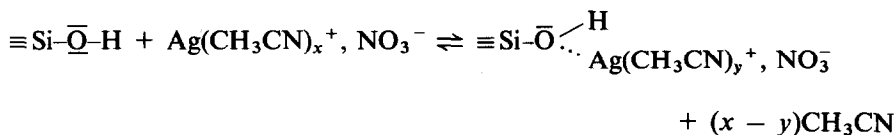


Fig. 11. Separation of a heavy FCC gasoline sample on a silver(I)-coated silica gel. Column: 15 cm × 0.48 cm I.D. Stationary phase: LiChrosorb Si 60 modified by percolating a 3% (w/w) solution of silver nitrate in acetonitrile. Mobile phase: pentane (10 ppm water). (A) Without backflush; (B) with backflush. Other operating conditions as in Fig. 1 and peak identification as in Fig. 2.

Silver ions are strongly complexed in acetonitrile and the value $x = 4$ was reported²⁴. It is likely that one or several acetonitrile molecules are removed during coating so that y might be lower than x . The saturation front was monitored by RI detection and UV absorption of the nitrate ions at 313 nm. It appeared at a percolated volume of 7 ml with a 3% (w/w) silver solution and a 15 cm \times 0.48 cm I.D. LiChrosorb column (dead volume, 2.0 ml; 1 g of adsorbent). So, the amount of Ag^+ coated onto the silica gel was about 0.7 mmol g^{-1} . If it is assumed that the number of silanol groups per nm^2 is near to five²⁵, one can estimate that about 15% of the silanol sites are covered with silver ions in this case.

After coating it seems that the major part of the remaining acetonitrile molecules should be eliminated by an appropriate column conditioning so that olefinic compounds can be retained. Fig. 11 shows a chromatogram of the heavy gasoline sample and the excellent resolution of the three structural groups. The water content used in this experiment, 10 ppm in pentane, should be noted. We ascertained that with a modified silica the influence of mobile phase water content was not as critical as in LSC, and a higher value can be tolerated.

Silver chemically bonded to silica. The operating procedure described in the Experimental is similar to that used by Foucault *et al.*²⁶ to prepare copper chemically

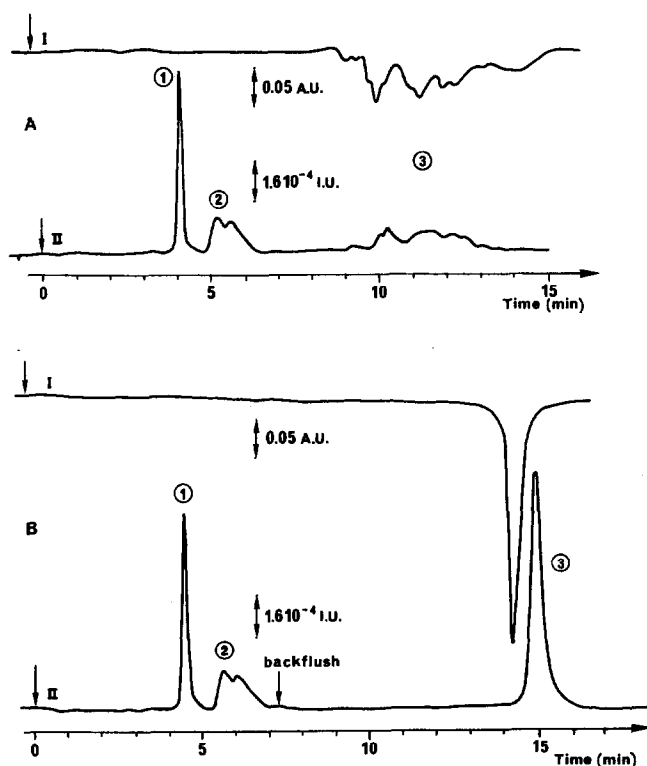
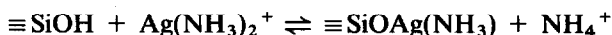


Fig. 12. Separation of a heavy FCC gasoline sample on silver chemically bonded to silica gel. Column: 25 cm \times 0.48 cm I.D. Stationary phase: LiChrosorb Si 60 chemically modified by percolating a 3% (w/w) solution of silver nitrate in 0.5 M aqueous ammonia. Detection: (I) UV at 254 nm; (II) differential refractometer. Other operating conditions as in Fig. 11.

bonded to silica. The rôle of the aqueous ammonia solution is to make easier the exchange of an hydrogen ion by a silver ion on the silica gel surface. The most probable reaction is:



Since ammonia is in excess we also have



and the surface of the silica is comprised of a mixture of silver and ammonium silicates. Contrary to the coating procedure, nitrate ions should not be retained with this procedure. However, with a 3% (w/w) aqueous silver solution and a 25 cm × 0.48 cm I.D. LiChrosorb column (dead volume, 3.2 ml; adsorbent mass, 1.7 g), the nitrate ion front appeared at a percolated volume of 4.5 ml. The breakthrough of Ag^+ (detected by precipitation of silver chloride) was simultaneous with that of ammonia (increase in pH of effluent) at a volume of 18 ml. A calculation similar to that given for the coated adsorbent leads here to a silver concentration of about 1.5 mmol g^{-1} , which corresponds to 30% of the silanol groups.

In order to retain unsaturated compounds, it is necessary to remove the major part of the ammonia bonded to silver atoms, which was done by washing with chloroform and drying. Fig. 12 shows a chromatogram obtained for the heavy FCC gasoline sample. As with the coated adsorbent, there is no interference between the three structural groups, and the pentane water content can be raised to about 10–15 ppm without impairing the separation.

CONCLUSIONS

In adsorption chromatography, two systems can be selected. First a silica gel having a surface area between 300 and 500 $\text{m}^2 \text{g}^{-1}$ with a perfluoroalkane as mobile phase; secondly a silica gel having a higher surface area (800 $\text{m}^2 \text{g}^{-1}$) with *n*-pentane as mobile phase. The final choice between these two systems is governed by the nature of the petroleum samples to be separated. For light samples, perfluoroalkane must be chosen; quantitative analysis is more accurate. For heavier samples, pentane must be used as mobile phase for solubility reasons.

In charge-transfer chromatography, an excellent resolution is obtained either with classically silver-coated silica gel or with silver chemically bonded to silica gel. In both cases, pentane is used as mobile phase, but its water content is not as critical as in LSC and a higher value can be tolerated. Based on these preliminary results, work is in progress in our laboratory, to optimize the selectivity of each pair of hydrocarbon groups contained in more complex mixtures such as vacuum distillates and residuals.

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