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HYDROCARBON GROUP TYPE ANALYSIS OF PETROLEUM PRODUCTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ON ORGANOMETALLIC DONOR/ACCEPTOR-BONDED SILICA

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SUMMARY

The preparation of a new organosilver bonded phase is described. The capacity ratios of 24 polynuclear aromatic hydrocarbons were determinated and showed a charge-transfer mechanism. The separation of olefins in several light petroleum products was resolved. The performance of the stationary phase in hydrocarbon group type analysis is discussed.

INTRODUCTION

The application of high-performance liquid chromatography (HPLC) to hydrocarbon group-type analysis (HGTA) of petroleum products was first reported in the 1970s, but only separations of light petroleum fractions were described. Accurate HGTA analyses are of vital importance for the refining industry. For instance, gasolines must meet severe specifications which are checked traditionally by normalized, although often inaccurate, tests (*e.g.*, FIA-ASTM D 1319)[1]. Several methods using high-performance liquid chromatography (HPLC) or supercritical fluid chromatography have been published[2–8] and some are currently under evaluation by the ASTM.

Recently, the preparation of new amino bonded phases has led to good separations of petroleum fractions, in particular heavier products[9,10]. Several papers have reported the use of column-switching HPLC using a silver column prepared by *in situ* flushing with aqueous silver nitrate. The column contained silica bonded with a strong cation-exchange phase [11–13]. The use of silver salts coated on silica gel for the separation of olefinic compounds[14] by charge-transfer chromatography is well known.

If we ligand a silver salt by an electron-acceptor molecule bonded on silica gel, it is possible to separate saturated compounds from aromatics (mono-, di-, poly-) with the acceptor molecules and to complex olefins strongly with the silver ions to

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achieve an HGTA analysis. We report here the sucessful synthesis and use of a new bonded acceptor stationary phase which ligands a silver salt for HGTA and was especially designed to show a high selectivity for petroleum fractions.

EXPERIMENTAL

Apparatus

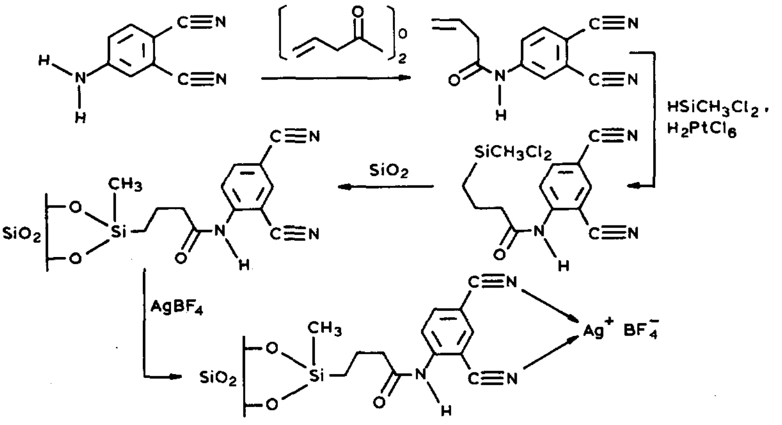
HPLC was performed with a Knauer 64 pump equipped with a Iota differential refractometer (Jobin-Yvon). Packing of the HPLC column (150 × 4.6 mm I.D.) was achieved by the classical slurry packing technique. The bonded silica was suspended in carbon tetrachloride–methyl iodide (65:35) and the slurry was forced with acetone into the chromatographic column for 30 min under a pressure of 450 bar.

Materials

4-Aminophtalonitrile was obtained from Kodak and vinylacetic acid, dichloromethylsilane and silver tetrafluoroborate from Aldrich. The remaining chemicals and solvents were of analytical-reagent grade and were used as purchased.

The bonded stationary phase was formed on a matrix of LIChrosorb Si 60 gel of median particle size 5 μm having a reported surface area of approximately 480 m^2/g (Merck-Clevenot).

Preparation of phthalonitrile-bonded stationary phase. The new phase was synthesized according to the following scheme:



Vinylacetic anhydride. This compound was obtained according to the method of Kuhn and Low[15] by reaction of the acid with the acid chloride[16] in pyridine (yield, 72%; b.p., 115–120°C/70 mmHg).

N-(4-Phthalonitrile)vinylacetamide. To 1.1 g (0.0077 mole) of 4-aminophthalonitrile in 30 ml of glacial acetic acid were added 3 g (0.024 mole) of vinylacetic anhydride followed by two drops of concentrated sulphuric acid. The mixture was stirred at room temperature until the solution became homogeneous (about 30 min), then warmed at 40°C for 30 min. Boiling water (100 ml) was then added to yield overnight 1.1 g (70%) of a beige crystalline product (m.p., 174–176°C). NMR ([$^2H_6$]acetone):δ = 3.13 (2H, d, J = 7 Hz), 4.9–5.36 (2H, m), 5.63–6.33 (1H, m), 7.8

(2H, s + d), 8.14 (1H, d, J = 2 Hz), 9.16 (1H, s). IR (carbon tetrachloride):3300 and 3260 cm^{-1} (NH), 2220 cm^{-1} (CN), 1690 and 1680 cm^{-1} (CO).

N-(4-Phthalonitrile)-γ-dichloromethylsilylbutyramide. To 2.8 g (0.013 mole) of dichloromethylsilane (freshly distilled over magnesium powder) was added a crystal of H_2PtCl_4 followed by the dropwise addition of a solution of N-(4-phthalonitrile) vinylacetamide (2.3 g; 0.024 mole) in dry dichloromethane (80 ml). The mixture was stirred under relfux overnight and evaporated, yielding 4 g of a viscous, brown product. NMR (C^2HCl_3):δ = 0.1 (6H, S), 0.86–1.2 (2H, t, J = 7 Hz), 2.26–2.67 (2H, m), 2.9–3.33 (2H, t, J = 6 Hz), 7.7 (2H, s + d), 8.16 (1H, d, J = 2 Hz), 9.2 (1H, s).

Phthalonitrile-bonded stationary phase. To LiChrosorb Si 60 (5 g) in dry dichloromethane (20 ml) a solution of N-(4-phthalonitrile)-γ-chlorodimethylsilylbutyramide (4 g) in dry dichloromethane (50 ml) was added and the mixture was stirred under reflux for 12 h. After filtration, the product was washed twice with 100 ml of dichloromethane, 100 ml of tetrahydrofuran and 100 ml of hexane. The bonded silica was dried under vacuum at 80°C for 12 h.

Silver column. After packing, the column was washed with 30 ml of dichloromethane, 30 ml of hexane and 30 ml of toluene. The column was then flushed using the HPLC pump with a solution of silver tetrafluoroborate in toluene until the silver ions were detected in the eluate by reaction with hydrochloric acid. The column was backflushed with the silver solution until silver ions were detected. The operation was repeated five times. After equilibration with hexane, the column was ready for use.

RESULTS AND DISCUSSION

The calculation of surface coverage from carbon and nitrogen percentages gave a surface concentration[17] of α = 2.7 μmole/m^2.

Table I shows the elution of 24 polynuclear aromatic hydrocarbons (PAHs) with hexane as the mobile phase at a flow-rate of 1 ml/min. The retention times are in agreement with a charge-transfer retention mechanism, increasing with increasing

TABLE I

ELUTION OF AROMATIC HYDROCARBONS

Hydrocarbon	*Retention time (min)*	*Hydrocarbon*	*Retention time (min)*
Benzene	2.30	Pyrene	4.62
Indane	2.48	1,2,3,4-Tetrahydrotetracene	5.09
Indene	2.77	1,2-Benzanthracene	6.24
Biphenyl	2.80	Chrysene	6.62
Naphthalene	2.86	Benzo[*a*]pyrene	7.74
Acenaphthene	3.31	Benzo[*e*]pyrene	7.92
Acenaphthylene	3.53	7,12-Dimethylbenzanthracene	8.01
Fluorene	3.80	Perylene	9.45
1,2,3,6,7,8-Hexahydropyrene	4.05	Benzo[*g,h,i*]perylene	10.12
Anthracene	4.10	1,2,3,4-Dibenzoanthracene	11.47
Phenanthrene	4.17	1,2,5,6-Dibenzoanthracene	11.92
Fluoranthene	4.53	Coronene	12.48

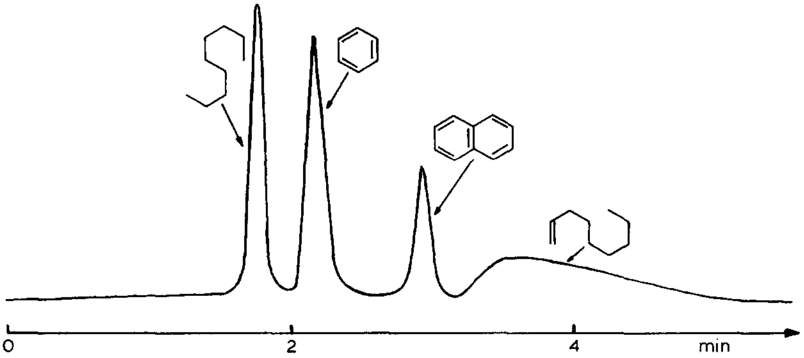


Fig. 1. Separation of test compounds. Mobile phase, hexane; flow-rate, 1 ml/min; detection, differential refractometer.

number of aromatic rings. It can be seen that naphthenic substitution (hexahydropyrene and tetrahydrotetracene) increases the retention owing to the effect of the benzylic groups as for the alkylated compounds (2, 6, 8, 19) compared with the corresponding non-alkylated compounds (1, 5, 15). Phthalonitrile can be classified as a weak acceptor like pentafluoro-bonded phases [18–21].

The column was first tested with a mixture of compounds containing nonane as the saturate, heptene as the olefin and benzene and naphthalene as the mono- and diaromatics. The separation (Fig. 1) shows that aromatics are normally retained, heptene is strongly retained and the peak is very broad.

No silver satls appeared to have contaminated the HPLC fractions. It is well known that nitrile groups are better ligands than water molecules so the nitrile ligand cannot be exchanged and shifted by water present in the mobile phase. The organometallic silver complex is very stable towards water even if the eluents are saturated with water, giving at the column a lifetime of several months.

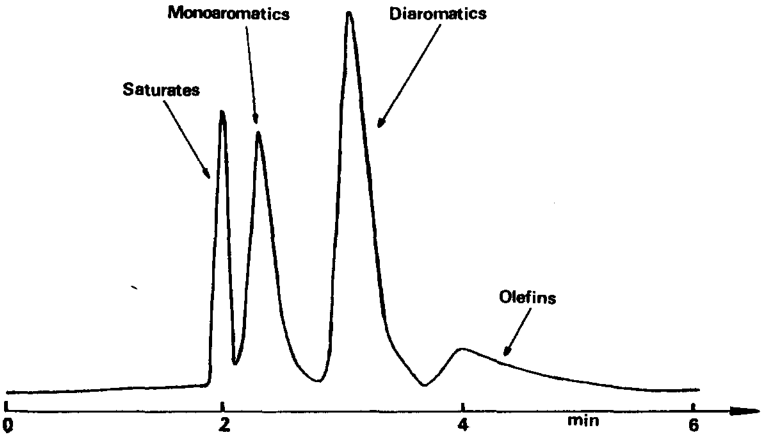


Fig. 2. Separation of a catalytic gasoline. Mobile phase, hexane; flow-rate, 1 ml/min; detection, differential refractometer.

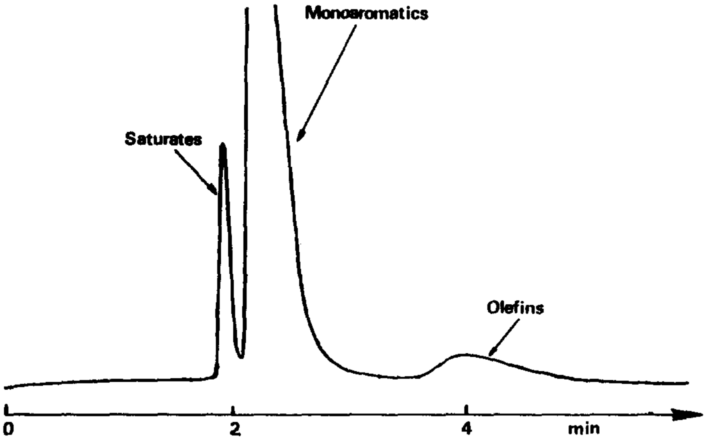


Fig. 3. Separation of a catalytic gas oil. Mobile phase, hexane; flow-rate, 1 ml/min; detection, differential refractometer.

However, this new phase was not compatible with several common HPLC solvents such as dichloromethane, which is a solvent of both silver complexes and silver salts. This incompatibility might be used for cleaning the column of accumulated polar compounds before flushing it with a new solution of silver tetrafluoroborate, thus increasing the lifetime of the column.

Figs. 2 and 3 show the separations obtained with two petroleum fractions (a catalytic gasoline and a catalytic gas oil). In addition to separating the different main hydrocarbon groups (saturates, aromatics, olefins), the aromatics are separated into mono- and diaromatics. With this bonded organometallic silver stationary phase, a complete HGTA analysis (saturates, olefins, mono- and diaromatics) can be achieved. This column can be used for the HPLC measurements of octane[22] and cetane indexes[23] in motor fuels. When the column is backflushed after the diaromat-

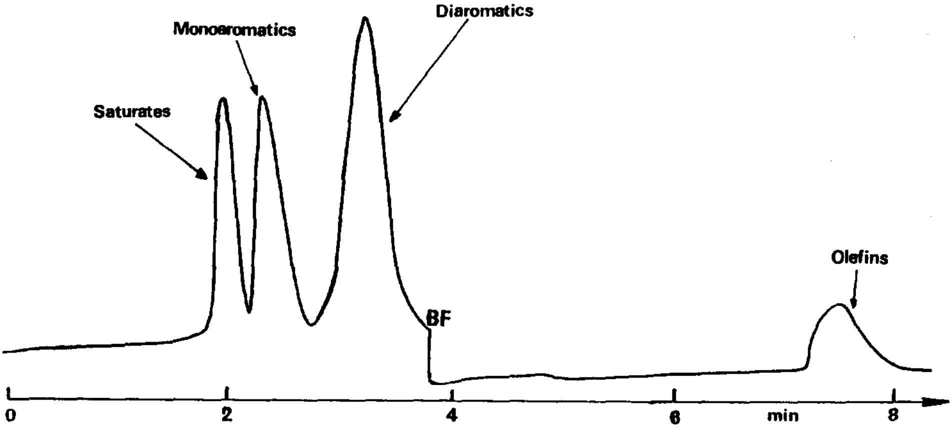


Fig. 4. Separation of a catalytic gas oil with backflushing. Mobile phase, hexane; flow-rate, 1 ml/min; detection, differential refractometer.

ics peak (Fig. 4), the olefins peak is sharper so the quantification is better. This technique cannot be used when the fuel samples contain PAHs with three or more rings because they coelute with the olefins.

This new organometallic silver bonded phase appears to be promising in its selectivity for the study of petroleum products, particularly light products such as gasoline and kerosene.

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