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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC COLUMN SWITCHING TECHNIQUES FOR RAPID HYDROCARBON GROUP-TYPE SEPARATIONS

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SUMMARY

The application of high-performance liquid chromatographic column switching techniques for hydrocarbon group-type separations of petroleum samples was investigated. Model compounds were employed to study hydrocarbon class separations using normal bonded phase and silica gel columns. The use of a cyanopropyl column as the primary separation step coupled to a highly activated silica gel column as the secondary step allowed resolution of saturates, olefins, aromatics and polars (backflushed from cyanopropyl column). Saturates were further resolved into paraffin and naphthene classes through use of an experimental column packing. The entire operation was automatically controlled by a microprocessor-based liquid chromatograph with time-programmable events which allowed precise switching of high pressure pneumatically operated valves. Column switching techniques were applied to the isocratic analysis of gasolines, light and heavy gas oils and solvent refined coal.

INTRODUCTION

Characterization of natural and synthetic petroleum products has grown increasingly important because of the need to optimize feed stock use and evaluate product performance as a function of chemical composition. The performance and specifications of many petroleum fuels and lubricants are inherently dependent upon the types of hydrocarbons present. Group-type analysis is a widely used procedure for obtaining the information needed to evaluate feedstocks and products in the petroleum industry.

A general method of hydrocarbon group-type analysis is the fluorescent indicator adsorption (FIA) procedure which covers the determination of saturates, non-aromatic olefins and aromatics in petroleum products[1]. Limitations of this technique such as time required for analysis (3–4 h), poor precision and the fact that most polar compounds are determined as aromatics have led to development of chromatographic methods for hydrocarbon class analysis. High-performance liquid chromatographic (HPLC) techniques are particularly well suited to group-type analysis due to separation speed and the ability to fingerprint most hydrocarbon classes of interest.

HPLC techniques utilizing normal phase packings have been widely applied to

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TABLE I

SELECTED APPLICATIONS OF HPLC TECHNIQUES FOR SEPARATION OF PETROLEUM PRODUCTS

THF = Tetrahydrofuran.

Petroleum sample type	*Column type*	*Mobile phase*	*Refs.*
1. Gasoline and gasoline-range materials (b.p. 60–215°C)	Cyano (10 μm)	*n*-Hexane	6, 22
	Silica (5 μm)	*n*-Hexane	6, 22
	Silica (20–44 μm)	2,2,4-Trimethylpentane	2
	Silica (10 μm)	Fluorinert	13
	Silica (10 μm)	*n*-Heptane	17
	Silica (10 μm)	*n*-Hexane	18
2. Petroleum fractions (b.p. 190–360°C) and middle distillates	Silica (10 μm)	Hexane	3, 14
3. Heavy petroleum products and crude oils	Silica (10 μm)	*n*-Hexane	3
	Silica (20–44 μm)	*n*-Hexane	21
	Amino (10 μm)	*n*-Hexane	20
	Silica (5 μm)	*n*-Hexane	20
	Alumina (5 μm)	*n*-Hexane	20
	PAC (10 μm) (amino and nitrile functional groups)	*n*-Hexane	20
4. Coal liquefaction products and coal	μ-Styragel (GPC)	THF	15
	Amino (10 μm)	*n*-Heptane	15
	Phenyl (10 μm)	Water–methanol (1:1)	15
	Silica (10 μm)	*n*-Hexane	3, 4
	Amino (10 μm)	*n*-Hexane	19
	Silica (20–44 μm)	*n*-Hexane	21
5. Light virgin (LVN) and heavy virgin (HVN) naphthas	Silica (10 μm)	*n*-Heptane	17
6. Residues and distillates of shale oil	Silica (0.1–37 μm)	Cyclohexane	5
	Silica–$AgNO_3$ (0.1–37 μm)	Cyclohexane	5
	Silica (20–44 μm)	*n*-Hexane	21
7. Tar sands	Silica (10 μm)	*n*-Hexane	4
8. Asphalts	Amino (10 μm)	*n*-Heptane	16
	μ-Styragel (GPC)	THF	16
9. Lubricant base oils and petroleum products	Alumina	Hexane–methylene chloride	24, 25
	Silica	Hexane	24, 25
	Polystyrene gel	Hexane	24, 25
	Amino	Hexane–methylene chloride	25
	Nitro	Hexane–methylene chloride	25
	Cyano	Hexane–methylene chloride	25

hydrocarbon group-type separations of petroleum samples. Stevenson[2] demonstrated the viability of HPLC for rapid group-type separations using silica columns coated with 10% Carbowax 600 for petroleum fuel and solvent analysis. Suatoni and Swab[3] demonstrated the ability of microparticulate silica columns to separate saturates,

aromatics (backflushed from column) and polar compounds (determined by difference) for quantitative analysis of petroleum samples. Calibration factors for a refractive index detector were used for quantitation of different group types based upon standards isolated from petroleum fractions under investigation. Although detailed coverage of HPLC group-type analytical applications is beyond the scope of this paper, Table I lists a number of selected publications illustrating the use of the technique for analysis of petroleum products.

HPLC switching techniques utilizing normal phase supports have been primarily limited to backflushing techniques or dual column techniques. Dark *et al.*[4] employed a backflushing technique for the analysis of polar hydrocarbons using an amino bonded phase column. McKay and Latham[5] have used a dual column technique employing a silica column and silver impregnated silica column in series for the separation of olefins from saturates in shale oil samples. Recently, a column switching technique employing three columns (silica, cyano and silica impregnated with $AgNO_3$) has been developed by Apffel *et al.*[6] for separation of saturate, olefin, aromatic and polar hydrocarbon classes in gasoline. Katz and Ogan[7] have reported a coupled column technique utilizing a reverse phase column and a size exclusion column for sample preparation of petroleum and coal liquid samples for the separation of polynuclear aromatic hydrocarbons (PAHs).

The purpose of this work is two-fold: To investigate a variety of normal phase supports in terms of their utility for hydrocarbon group-type separations and to develop column switching methods employing these supports for rapid hydrocarbon class separations of petroleum samples.

EXPERIMENTAL

Instrumentation and columns

Fig. 1 is a schematic diagram of the multidimensional column switching system employed. This system is similar to one utilized for column switching techniques involving the cleanup and analysis of water-soluble samples previously reported from this laboratory[8]. The chromatograph is a Varian Model 5060, which has a single pump with three-solvent capability. It was equipped with a manual six-port sampling valve (Rheodyne) for injection of the sample onto the first analytical column (MicroPak CN-5 in all cases). In addition, two other six-port, two-position automatic

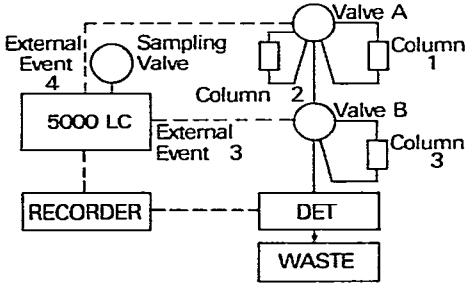

Fig. 1. System configuration for automated column switching using Model 5000 LC external events. DET = Detector.

switching valves (Valco) were employed. All valves could be controlled by time-programmable external events (powered contact closures) from the chromatograph. They could be automatically switched either off or on at predetermined times by single keyboard programming.

Microparticulate supports investigated in the normal phase mode were a MicroPak TSK 2000SW (250-Å diol-like bonded phase). MicroPak CN-5 (cyanopropyl bonded phase), MicroPak NH_2-5 (aminopropyl bonded phase), MicroPak AX-5 (diamino bonded phase), MicroPak Si-5 (60-Å porous silica) and an experimental support investigated for the separation of saturated hydrocarbon classes. All columns were 15 cm × 4 mm I.D. except the TSK 2000SW column (30 cm × 8 mm I.D.). Such short columns employing small d_p (d_p = particle diameter) packings (5 μm) have been shown to be of high utility for rapid (<15 min) LC separations[9]. All of these columns are available from Varian Assoc. (Walnut Creek, CA, U.S.A.).

A Varian UV-50 variable wavelength detector and a Varian refractive index detector were employed.

Valving configurations

By appropriate configurations of the switching valves, a number of flow options were available. Fig. 2 depicts the normal configuration employing two switching valves. Such a configuration allows a variety of hydrocarbon group-type separations to be carried out with no plumbing changes. By using external events 3 and 4 from the Model 5000, valve A or valve B can be switched at different times in order to achieve different flow paths. The heavy lines represent the flow path for the normal configuration at time zero. In all cases, a MicroPak CN-5 column was employed as column 1, a MicroPak Si-5 column activated at 130–150°C overnight as column 2 and an experimental column packing as column 3 in the switching routines.

Solvents and chemicals

n-Hexane was distilled-in-glass solvent obtained from Burdick & Jackson

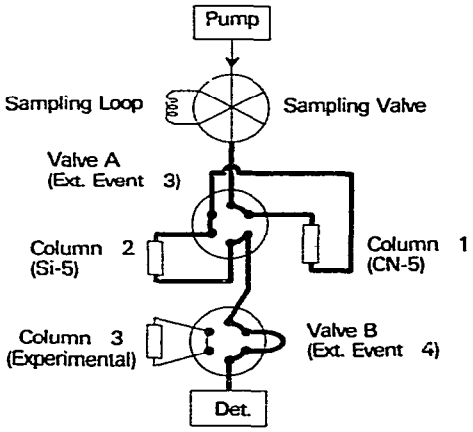

Fig. 2. Column switching flow diagram: normal flow path. Note that solid black line indicates path of flow. Det. = Detector; Ext. = external.

TABLE II

MODEL COMPOUNDS FOR COLUMN SELECTIVITY STUDY

Saturates		*Olefins*	
Paraffins (I)	*Naphthenes (Ia)*	*Monoolefins (II)*	*Diolefins (IIa)*
n-Heptane	Cyclohexane	2,4,4-Trimethyl-1-pentene	2-Methyl-1-butadiene
n-Octane	Methylcyclohexane	2,4,4-Trimethyl-2-pentene	2,2-Dimethyl-3,4-pentadiene
n-Nonane	1,1-Dimethylcyclohexane	1-Nonene	2,5-Dimethyl-2,4-hexadiene
n-Decane	1,3-Dimethylcyclohexane	4-Nonane	1,3-Cyclooctadiene
n-Undecane	Cyclooctane	3,5,5-Trimethyl-1-hexene	
n-Dodecane		1-Decene	
n-Tridecane		1-Undecene	
n-Tetradecane		1-Dodecene	
n-Pentadecane		1-Tridecene	
n-Hexadecane		1-Tetradecene	
n-Heptadecane		Cyclohexene	
n-Octadecane			
n-Nonadecane			

Aromatics		*Polars (V)*
Alkylbenzenes (III)	*Polynuclear aromatic hydrocarbons (PAHs) (IV)*	
Benzene (B)	Naphthalene (NAP)	Methyl benzoate
Toluene (T)	Anthracene (ANTHRA)	Phenol
Ethylbenzene	Chrysene (CHY)	Chlorophenol
o-,*m*-,*p*-Xylenes	Benzo[*a*]pyrene (BαP)	Nitrophenol
Cumene	Benzo[*ghi*]perylene (BghiP)	
n-Propylbenzene	Acenaphthalene	
Mesitylene	Phenanthrene	
p-Cymene	Pyrene	
n-Butylbenzene	Benzo[*e*]pyrene	
n-Hexylbenzene	Benzo[*k*]fluoranthene	
n-Octylbenzene	Perylene	
n-Decylbenzene		

Labs. (Muskegon, MI, U.S.A.). The solvent was dried using a 4-Å molecular sieve to remove trace amounts of water. A drying column (Alltech Associates, Los Altos, CA, U.S.A.) was installed prior to the sampling valve to ensure removal of trace water from the mobile phase.

Samples of hydrocarbon standards used in this report were obtained from Varian (Palo Alto, CA, U.S.A.), Aldrich (Milwaukee, WI, U.S.A.) and Polysciences Inc. (Warrington, PA, U.S.A.). Hydrocarbon standards chosen as model compounds for paraffins (class I), naphthenes (class Ia), monoolefins (class II), diolefins (class IIa), aromatics (alkylbenzenes, class III), polynuclear aromatic hydrocarbons (PAHs, class IV) and polar (class V) hydrocarbon group-types are listed in Table II.

Samples of light and heavy gas oils were obtained from local refineries. The sample of AMAX solvent refined coal (SRC) was obtained from experimental studies

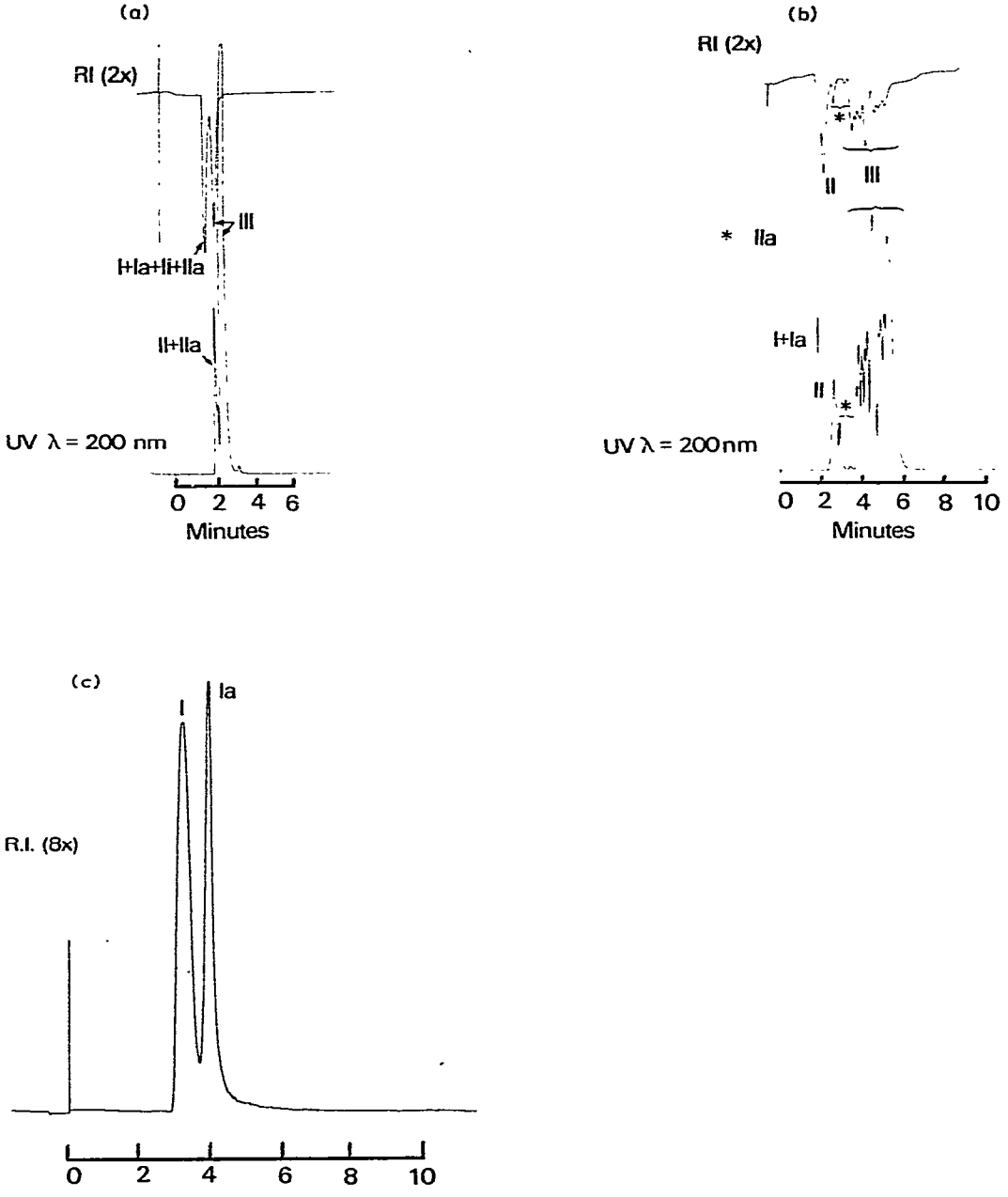

Fig. 3. Selectivity of normal-phase packings for various hydrocarbon classes: saturates–paraffins (class I), plus naphthenes (class Ia), mono- and diolefins (classes II and IIa) and aromatics (class III, alkylbenzenes). a, MicroPak CN-5 column; b, MicroPak Si-5 column; c, experimental column; all columns 15 cm × 4 mm. Conditions: mobile phase, dry *n*-hexane at 0.7 ml/min. Detectors: UV at 200 nm (1.0 a.u.f.s.) and RI (2×) except c (8×).

conducted at Virginia Polytechnic Institute (Blacksburg, VA, U.S.A.). Gasoline samples were commercial samples purchased locally.

Preparation of samples

All samples were dissolved in hot *n*-hexane, allowed to cool and filtered through an 0.45-μm membrane filter prior to injection. Asphaltene components are not soluble in hexane and thus were not chromatographically analyzed but could be determined by weighing. The SRC sample was prepared at a concentration of 50:1 in hexane and diluted to an appropriate level for chromatography. Samples of light and heavy gas oil were prepared at an 0.2% (w/w) level and subsequently diluted. Gasoline samples were 0.1% (w/w) and further diluted. Standard samples were dissolved in *n*-hexane at a level of 1 mg/ml and diluted at the appropriate concentration and then chromatographed.

Chromatography

The basic chromatographic procedures were carried out in a similar manner. The filtered sample was injected manually onto the analytical column and isocratically chromatographed using the Model 5060 pump. A mobile phase of dry *n*-hexane was used in all cases. Injection volume was held at 10 μl and sample concentrations varied. Detection was performed at a wavelength of 200 nm with a UV detector. At this wavelength, mono- and diolefins can be detected as well as aromatics and PAHs. For investigation of PAH separations using model compounds, a wavelength of 254 nm was employed. A refractive index (RI) detector was also used in series with the UV detector.

RESULTS

Investigation of column support selectivity for hydrocarbon classes

Separation of saturate, olefin and aromatic (alkylbenzene) hydrocarbon group-types was studied using several column packings in the normal phase mode. Mixtures of the model compounds were prepared and chromatographed using dry *n*-hexane as eluent at a flow-rate of 0.7 ml/min. Detection was accomplished by use of a UV detector at 200 nm and a refractive index detector. MicroPak CN-5, NH_2-5 and AX-5 columns separated aromatics from other hydrocarbon classes (saturates plus olefins) which coelute. Fig. 3a shows the analysis of these hydrocarbon classes on a CN-5 column. Model compound classes I and II (saturates and olefins) coelute. Model class III (alkylbenzenes) are resolved from the other classes. Using hexane as the mobile phase, polar hydrocarbon compounds elute very slowly and can be backflushed off the column after elution of the aromatics. Separation of saturate, olefin and aromatic group-types was achieved with a MicroPak Si-5 column, as shown in Fig. 3b. Activated silica gel offers a high degree of resolution among aromatics as modeled by alkylbenzenes (class III). Separation of monoolefins (class II) and diolefins (class IIa) was also achieved; however, incomplete resolution was obtained between saturate (class I) and monoolefin model compoun :. Resolution of these classes could be improved by further activation of the silica packing but at the expense of total analysis time for elution of the aromatic envelope.

In the analysis of gasoline-range petroleum products, information is required

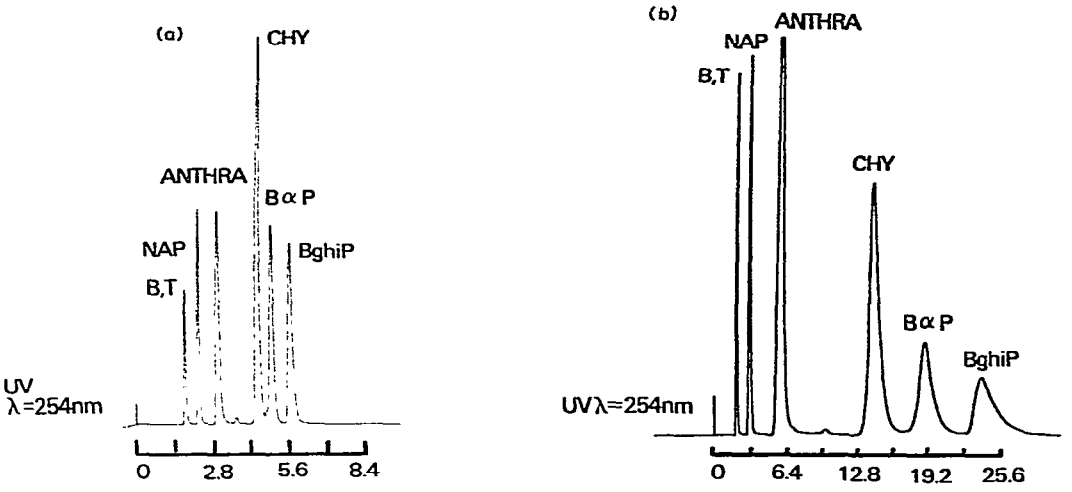

Fig. 4. Selectivity of normal phase packings for polynuclear aromatic hydrocarbons (PAHs). a, MicroPak CN-5 column; b, MicroPak NH_2-5 column; both columns 15 cm × 4 mm. Conditions: mobile phase, dry *n*-hexane at 0.7 ml/min (a) and 1.6 ml/min (b). Detector: UV at 254 nm (0.5 a.u.f.s.). Model compounds: B = benzene; T = toluene; NAP = naphthalene; ANTHRA = anthracene; CHY = chrysene; BαP = benzo[*a*]pyrene; BghiP = benzo[*ghi*]perylene.

on both paraffin and naphthene (cycloalkane) saturated hydrocarbon classes. Selectivity to saturated hydrocarbon classes was achieved through the use of an experimental support, as shown in Fig. 3c. Using an experimental column with an eluent of dry hexane, paraffins (class I) elute first, followed by the naphthenes (class Ia). The compounds used to model the paraffin class contained only normal hydrocarbons. The effect of branching on saturate class resolution is currently under study. The support material is of a proprietary nature.

Several polar bonded phase and silica gel columns used in the normal phase mode were examined for separation of polynuclear aromatic hydrocarbons (PAHs). A mobile phase of dry *n*-hexane was used in conjunction with a UV detector at 254 nm for analysis of PAH model compounds. Capacity increased with condensed ring number of the PAH compound for MicroPak TSK 2000SW, CN-5, NH_2-5 and AX-5 columns with the most polar bonded phase (AX) displaying highest retention volume and the least polar bonded phase (SW) displaying lowest retention volume. Separation of model PAH compounds on MicroPak CN-5 and NH_2-5 columns is displayed in Fig. 4a and 4b respectively. These chromatograms illustrate the increase in retention of PAHs obtained with the NH_2-5 packing (high polarity) compared to the retention obtained with the CN-5 packing (medium polarity).

Fig. 5 displays a graph of capacity ratios (k') *versus* number of rings in the PAH model compounds. Such a graph serves as a summary of results from investigation of normal phase packings for PAH separations. Capacity appears to be a function of bonded phase polarity (diol-like SW giving lowest capacity and NH_2-5 and AX-5 greatest capacity). The poor resolution shown between chrysene and pyrene (four rings), benzo[*a*]pyrene and benzo[*e*]pyrene (five rings) and benzo[*ghi*]perylene (six rings) for the Si-5 column is due in part to the fact that benzo[*a*]pyrene,

benzo[*e*]pyrene, pyrene and benzo[*ghi*]perylene are pericondensed PAHs while benzene, naphthalene, anthracene, phenanthrene and chrysene are catacondensed. Popl *et al.*[10] have found silica gel employing a paraffinic eluent to give lower adsorptivity to pericondensed aromatic hydrocarbons.

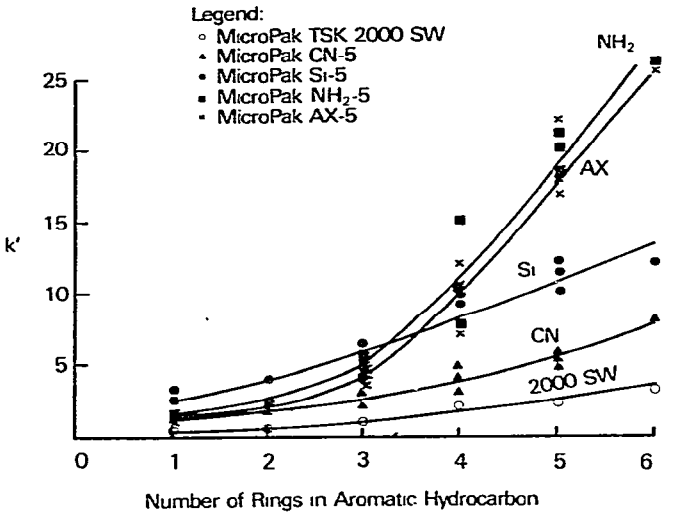

Fig. 5. Plot of PAH ring number *versus* capacity ratio (k') for MicroPak TSK 2000SW, CN-5, Si-5, NH_2-5 and AX-5 columns. Mobile phase: dry *n*-hexane.

The difference between the Si-5 and the NH_2-5 and AX-5 bonded phases (all polar stationary phases) displayed on the graph may be partly explained by the lower adsorptivity of the silica gel to pericondensed PAHs and may also partly arise from differences between the adsorption (silica) and partitioning (NH_2 and AX bonded phases) separation processes. Additionally, the level of activation of the silica gel column has a significant effect upon PAH capacity.

Column switching techniques for hydrocarbon class separations

Three normal phase column supports were chosen for incorporation into column switching schemes for hydrocarbon group-type separations. A MicroPak CN-5 column was chosen as column 1 (see Fig. 2) due to superior chemical stability compared to normal phase supports which contain primary amine functional groups such as the NH_2-5 column. Due to their reactivity with primary amine groups, aldehyde and ketone solutes should be avoided with an NH_2 bonded phase, thus limiting the utility of such supports[11]. The CN-5 column is placed as the primary column to ensure that polar compounds are trapped on this packing (and subsequently backflushed) and not irreversibly adsorbed on the silica column[12] which was chosen as column 2 in the switching scheme.

Utilizing a single switching valve with a MicroPak CN-5 and Si-5 column in series, saturate, olefin and aromatic hydrocarbon classes were resolved. This is illustrated by the analysis of hydrocarbon model compounds as shown in Fig. 6a. An eluent of dry hexane at a flow-rate of 0.7 ml/min was used for analysis with a UV detector at 200 nm and RI detector in series. Saturates (classes I and Ia) elute first,

followed by monoolefine (class II), diolefins (class IIa) and aromatics (class III). Polars can be subsequently backflushed from the CN-5 column (column 1) by appropriate valve actuation after elution of the aromatics. Note that when column 1 is backflushed, column 2 is isolated from the flow path to preserve the integrity of the activated silica column (see Fig. 2).

Selectivity to saturates displayed by the experimental column packing was utilized in the present switching scheme by addition of a second switching valve. The employment of such a column in the switching technique allows separation of paraffin (class I), olefin (classes II and IIa), naphthene (class Ia) and aromatic hydrocarbon classes (P.O.N.A. separations) as depicted in Fig. 6b using hydrocarbon standards. Chromatographic conditions were identical to those used in Fig. 6a.

To obtain such a separation, saturates were loaded onto the head of the experimental column, at which time (corresponding to an elution volume of 4.5 ml —the point at which the olefins begin to elute) valve B is actuated (first switching point in Fig. 6b) so that elution of olefins (classes II and IIa) and aromatics (class III) occurs from the CN-5 and Si-5 columns (columns 1 and 2) in series. After elution of the aromatics, valves A and B were again actuated (second switching point in Fig. 6b) to allow elution of paraffins (class I) and naphthenes (class Ia) from the experimental column (column 3). Since saturate and olefinic classes were not totally resolved (see Fig. 6a), olefins which coelute with the saturates are detected as saturates in the elution profile of column 3.

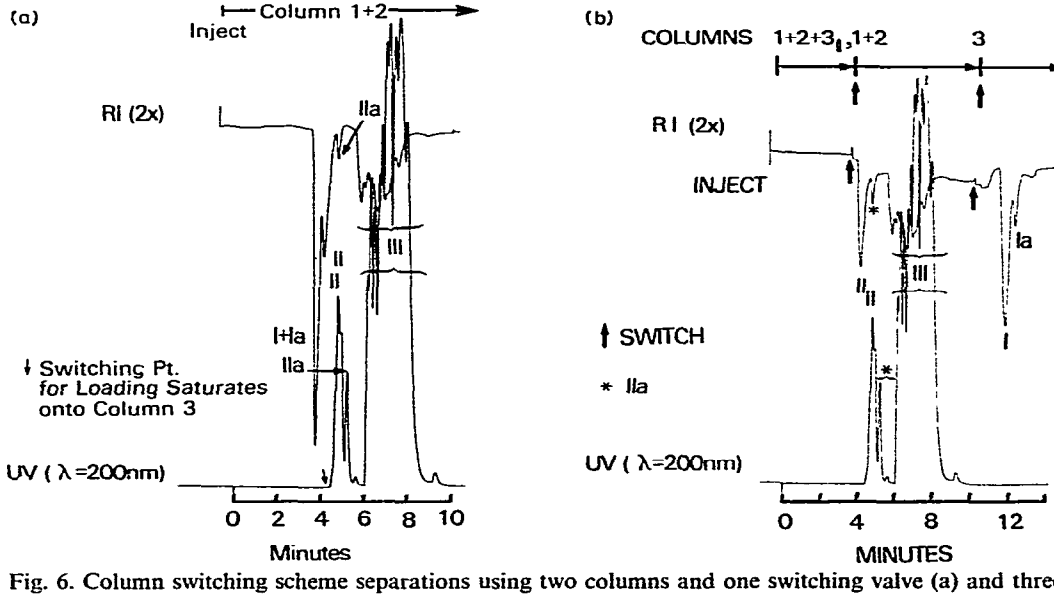

Fig. 6. Column switching scheme separations using two columns and one switching valve (a) and three columns and two switching valves (b) to obtain hydrocarbon group-type separations. a, Columns: MicroPak CN-5 (1); MicroPak Si-5 (2); both 15 cm × 4 mm. Mobile phase: dry-*n*-hexane at 0.7 ml/min. Detectors: UV at 200 nm (1.0 a.u.f.s.) and RI (2×). Model compounds: I = paraffins; Ia = naphthenes; II = monoolefins; IIa = diolefins; III = aromatics (alkylbenzenes). Note that point for switching saturates onto head of column 3 corresponds to point at which olefins begin to elute (4.5 ml). b, Columns: MicroPak CN-5 (1); MicroPak Si-5 (2); experimental column (3); all columns 15 cm × 4 mm. Conditions as in a. Note first switching point for loading saturates onto head of column 3 and second switching point for analysis of saturate classes.

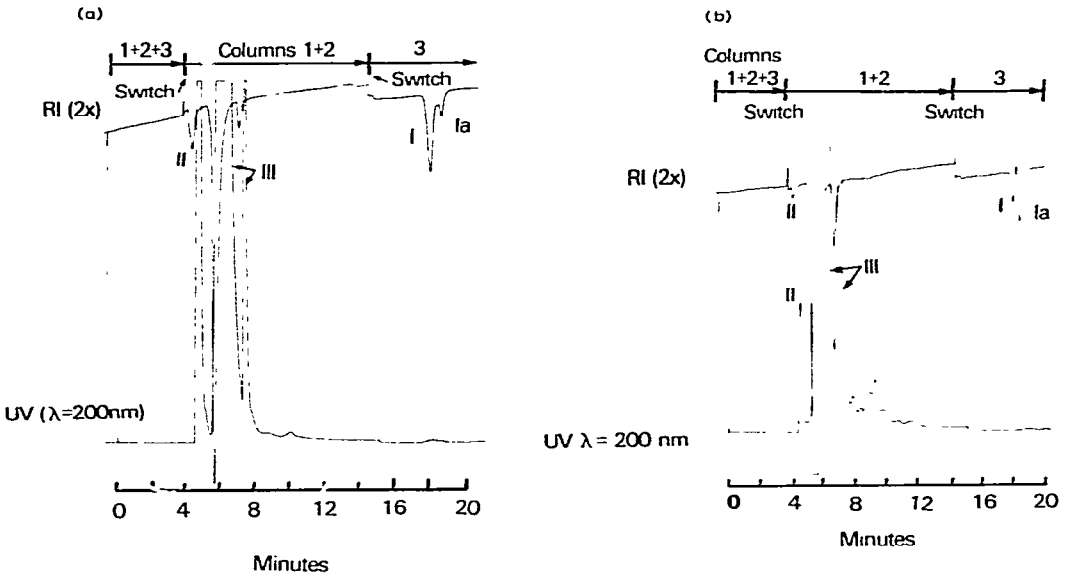

Fig. 7. P.O.N A. type separations of gasoline samples (a, b). Columns: MicroPak CN-5 (1); MicroPak Si-5 (2); experimental column (3); all columns 15 cm × 4 mm. Mobile phase: dry *n*-hexane at 0.7 ml/min. Detectors: UV at 200 nm (1.0 a.u.f.s.) and RI (2×). I = Paraffins; Ia = naphthenes; II = olefins; III = aromatics.

Applications of column switching to hydrocarbon class separations of petroleum samples

P.O.N.A. type separations achieved by column switching methods have been applied to the analysis of gasoline samples as shown in Fig. 7a and 7b. Isocratic analyses of the gasoline samples employed dry *n*-hexane as a mobile phase at 0.7 ml/min flow. Both UV at 200 nm and RI detection were used for analysis of olefins (class II), aromatics (class III), paraffins (class I) and naphthenes (class Ia) in the gasoline samples. Sample B (Fig. 7b) appears to contain some paraffinic constituents with a refractive index less than hexane as evidenced by a slight negative response prior to elution of the naphthenes. In comparing the two gasoline samples, differences not only in naphthene content but also olefin and aromatic class content is apparent.

Hydrocarbon group-type separations were also performed on samples of light and heavy gas oils as shown in Fig. 8a and 8b respectively. Both MicroPak CN-5 and Si-5 columns were used with a *n*-hexane mobile phase for analysis of the gas oils. UV detection at 200 nm and RI detection were employed for separation of saturates (I), olefins (II), aromatics (alkylbenzenes, III), PAHs (IV) and polars (V) which were backflushed from the CN-5 column. Good resolution is obtained among the aromatic components of the light gas oil sample using a MicroPak CN-5 and Si-5 column in series. However, in comparing the light gas oil to heavy gas oil analysis, there is an apparent loss in resolution with the heavier sample. The loss in resolution with heavier petroleum samples seems to be a common characteristic with such samples as, for example, in the analysis of crude oils. Fig. 9 depicts the analysis of a solvent refined coal (SRC) sample for saturate, olefin, aromatic and polar hydrocarbon classes. MicroPak CN-5 plus Si-5 columns were used in series for this analysis.

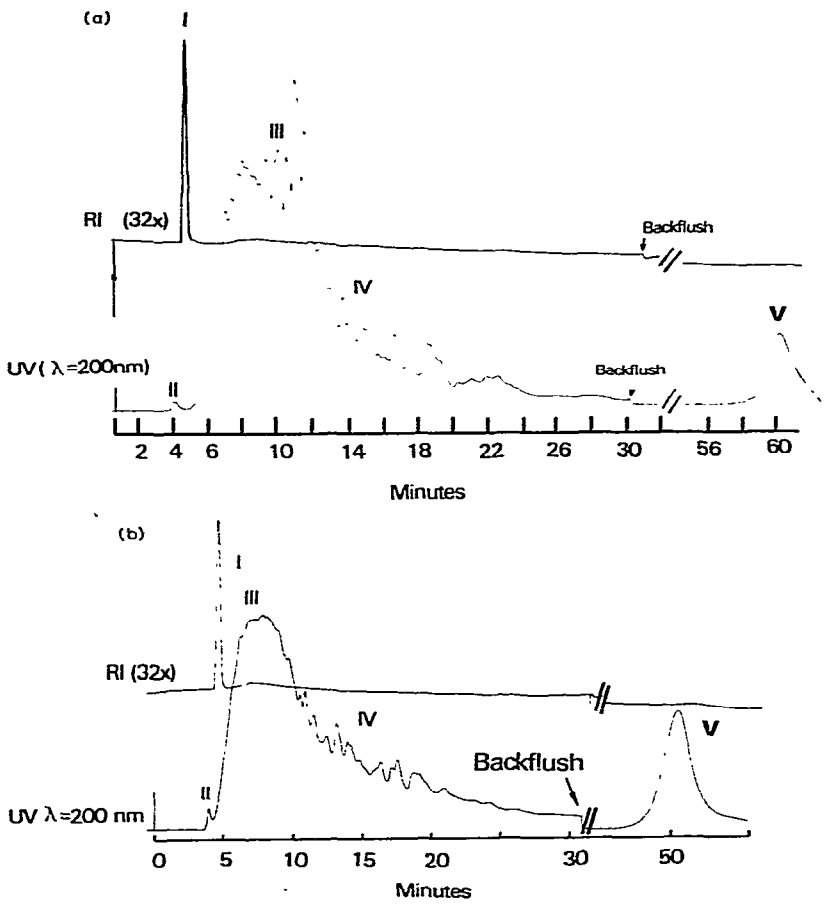

Fig. 8. Hydrocarbon group-type separations of light (a) and heavy gas oil (b). Columns: MicroPak CN-5 plus Si-5 in series. Mobile phase: dry *n*-hexane at 0.8 ml/min. Detectors: UV at 200 nm (1.0 a.u.f.s.) and RI (32 ×). I = Saturates; II = olefins; III = aromatics (alkylbenzenes); IV = PAHs; V = polars.

Through use of a time programmable flow change, elution of polar compounds is speeded up, thereby reducing analysis time. Separation speed is increased by almost a factor of two by flow programming backflush of the polar constituents. This can be seen by comparing the total analysis time for the gas oil samples in Fig. 8 with the analysis time of the SRC sample in Fig. 9.

DISCUSSION

For petroleum samples, LC column switching techniques have proven to be useful when normal phase packings are utilized to obtain hydrocarbon group-type separations. The wide selectivity available with a range of stationary phases can be exploited to achieve resolution among several hydrocarbon classes employing an isocratic elution profile[23]. Isocratic analysis is advantageous when using silica gel columns due to elimination of time consuming re-equilibration steps which are necessary

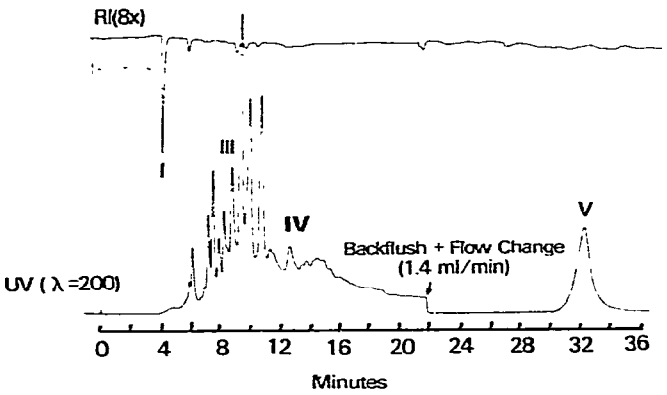

Fig. 9. Hydrocarbon group-type separation of SRC (solvent refined coal). Columns: MicroPak CN-5 plus Si-5 in series. Mobile phase: dry *n*-hexane at 0.7 ml/min with flow change to 1.4 ml/min upon backflushing. Detectors: UV at 200 nm (1.0 a.u.f.s.) and RI (8 ×). I = Saturates; III = aromatics (alkylbenzenes); IV = PAHs; V = polars.

in gradient elution. Alternately, by appropriate valve actuation, the silica column can be isolated from the rest of the switching system to allow gradient analysis with other columns.

Separation of saturates into paraffin and naphthene classes allows characterization of gasoline-range hydrocarbon samples by so-called P.O.N.A. analyses. One typical problem of such separations is maintaining activation of the silica column to obtain adequate resolution of saturate and olefin classes. Apffel *et al.*[6] have applied silica columns impregnated with silver nitrate in column switching schemes to achieve adequate resolution of saturates and olefins without the necessity of maintaining a highly activated silica column and attendant trace water removal from the mobile phase. Such an approach eliminates a major source of retention time variance in such switching techniques —that arising from changes in silica activation due to trace water contamination. Although examples shown in this study are of a qualitative nature, quantitation of hydrocarbon classes can be achieved in switching schemes. Due to the wide variation of extinction coefficients for hydrocarbons in any one class, UV detection at 200 nm is not always useful and quantitation with an appropriately calibrated RI detector is preferrable.

As evidenced by the elution profile of the heavy gas oil sample, another problem that frequently occurs with heavier petroleum samples is loss of resolution of the aromatic envelope. Comparison of light and heavy gas oil chromatograms (see Fig. 8) illustrates the difference in resolution that is achieved with such petroleum samples using the same analytical fingerprinting technique. Resolution for these sample types, however, may be increased by incorporation of a second CN-5 or Si-5 column employed as column 3 in the switching scheme.

Although two six-port switching valves were used in this work, use of a ten-port, two-position switching valve may eliminate the need for the second six-port valve in these types of switching schemes. Harvey and Stearns[26] have shown that such a valve can be used for both injection and sequence reversal with backfushing without need of an additional switching valve.

CONCLUSION

Column switching techniques utilizing normal-phase packings can separate saturate, olefin, aromatic and polar hydrocarbon classes using a single switching valve and a MicroPak CN-5 plus Si-5 column. Use of a second switching valve and an experimental column packing allow further resolution of saturates into paraffin and naphthene classes for P.O.N.A.-type separations of gasoline-range materials.

In column switching schemes for hydrocarbon group-type separations, MicroPak Si-5 packing is useful for separation of saturates, olefins and aromatics (alkylbenzenes), offering high selectivity for these hydrocarbon classes upon activation at temperatures of 130–150°C. MicroPak NH_2-5 and AX-5 bonded phase columns exhibit large capacity (k') for PAHs. Normal phase supports offer a wide range of selectivity useful in fingerprinting petroleum samples when employed in column switching techniques.

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