

# Fast supercritical fluid chromatography hydrocarbon group-type separations of diesel fuels using packed and monolithic columns

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Two approaches for decreasing diesel hydrocarbon group-type separation times by normal phase supercritical fluid chromatography (SFC) are compared. Short (10–15 cm) columns with small 3  $\mu\text{m}$  diameter packing are compared with monolithic Chromolith bare silica columns under high carbon dioxide flow rates approaching 5  $\text{ml min}^{-1}$ . Elution times are reduced up to 13-fold on a 10 cm Chromolith column and 7-fold on the short packed columns compared with conventional length columns run at typical flow rates. Short packed columns, with their higher surface area and retention characteristics, offer higher resolutions compared with Chromolith columns. Diesel samples are separated into saturates, mono-, di-, tri-, and polyaromatics in as little as 2 min on a 10 cm packed silica column. Diesel group-type results on a 15 cm titania–silica coupled column compare favorably with results from longer columns.

## Introduction

Supercritical fluid chromatography (SFC) is used to provide 3-fold<sup>1</sup> faster separations than high-performance liquid chromatography (HPLC) in pharmaceutical, chiral, petroleum, polymer, natural product, and food-related applications.<sup>1–3</sup> Faster separations improve sample throughput, reduce costs, and make real-time process monitoring feasible.<sup>4</sup> Surprisingly, few publications have dealt with increasing the speed of SFC separations beyond the 3-fold improvement<sup>1</sup> that SFC inherently provides over HPLC. SFC separation times can be further reduced using methods similar to those used to decrease separation times in HPLC, such as using shorter columns with smaller diameter packing.<sup>5</sup>

This paper focuses on increasing the speed of a common industrial analysis performed by SFC—the separation of diesel fuels into hydrocarbon group-types (*i.e.*, saturates, mono-, di-, tri-, and polyaromatics). Diesel and jet fuel environmental and performance properties have been associated with the group-type compositions of these fuels.<sup>6–20</sup> In particular, high polycyclic aromatic hydrocarbon (PAH) content increases particulate matter,<sup>14,15,19</sup> nitrogen oxides,<sup>14,15,19</sup> and PAH emissions.<sup>17,18,20</sup> Government regulations on PAH content are becoming ever more stringent to curb these emissions. ASTM method D 5186-03<sup>21</sup> uses SFC with a carbon dioxide mobile phase and a packed silica column to separate diesel fuels according to hydrocarbon group-type.

Our previous work demonstrated that coupling a 15 cm column of 3  $\mu\text{m}$  bare titania in series with a conventional 25 cm column of 5  $\mu\text{m}$  bare silica greatly increased group-type resolutions, especially between the di- and triaromatic model compounds.<sup>22</sup> However, this coupled column increased the

separation time for a commercial diesel sample from 10 min to 40 min.

Here, two different approaches for reducing separation time are compared. The first approach is to use shorter columns with smaller diameter packing.<sup>5,23–27</sup> Shortening the column reduces the separation efficiency. Using a smaller diameter packing helps offset this by improving the plate height. When the flow rate is increased, the overall effect is a drastic reduction in separation time while maintaining acceptable group-type resolutions.

The second approach is to use monolithic columns that are capable of being run at high flow rates while only producing about a tenth of the pressure drop of a conventional particle packed column. In HPLC, monolithic columns are often used to reduce analysis times while maintaining resolution.<sup>26–31</sup> Lesellier *et al.* coupled five monolithic columns to a conventional packed column in SFC to permit separation of  $\beta$ -carotene isomers.<sup>32</sup>

Both approaches are studied with an emphasis on determining what factors are limiting resolution at high flow rates. Previously characterized diesel samples<sup>22</sup> of increasing boiling range and PAH content are studied to determine whether increasing the speed of the analysis affects the quantitative diesel group-type results.

## Experimental

### Apparatus

The experimental conditions have been described previously.<sup>22</sup> Briefly, a Hewlett-Packard (now Agilent, Palo Alto, CA, USA) SFC system pumped SFC grade (>99.995%, <3 ppm water content) carbon dioxide (Air Liquide, Montreal, QC, Canada) through the test columns at flow rates from 1 up to 5  $\text{ml min}^{-1}$  and downstream pressures from 100 to 150 bar. The three test columns studied were: a 100  $\times$  4.6 mm, 3  $\mu\text{m}$ , 60  $\text{\AA}$  bare silica Lichrospher Si 60 packed column (Thermo Electron, Waltham, MA, USA); a 50  $\times$  4.6 mm, 3  $\mu\text{m}$ , 60  $\text{\AA}$  bare titania

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Sachtopenore-NP packed column (Zirchrom, Anoka, MN, USA) coupled to the Lichrospher column; and a 100 × 4.6 mm, 2 μm macropores, 130 Å mesopores bare silica Chromolith Si monolithic column (Merck KGaA, Darmstadt, Germany). The columns were maintained at 35 °C. An HP 7673B automatic sampler was used with a Rheodyne (Rohmert Park, CA, USA) 7410 injection valve to provide 0.5 μl full loop sample injections. Quantitative flame ionisation detection (FID) was provided by an HP SFC FID. Qualitative diode array detection (DAD) was provided by an HP Series 1050 DAD. The flow was split between the two detectors by a T-joint. A low flow fused silica integral restrictor (Agilent) depressurized the carbon dioxide prior to the FID. A backpressure regulator located downstream from the DAD maintained the operating pressure. Data acquisition at 20 Hz was provided by a Vectra 486/66XM personal computer running HP-SFC ChemStation Rev. A.01.02 software.

### Standards and samples

Twenty model compounds (>97% purity) described elsewhere<sup>22</sup> were studied on each test column. Those discussed here include: tetralin (Sigma–Aldrich Canada Ltd., Oakville, ON, Canada), naphthalene (Fisher Scientific, Nepean, ON, Canada), 9,10-dihydroanthracene (Acros Organics, Morris Plains, NJ, USA), dibenzothiophene (Acros Organics), phenanthrene (Sigma–Aldrich), anthracene (Fisher Scientific), pyrene (Sigma–Aldrich), and 2-naphthalenethiol (Acros Organics). Samples were prepared by dissolving each compound at 0.1% w/w in ACS grade carbon disulfide (Fisher Scientific). An ASTM method D 5186-03<sup>21</sup> performance mixture consisting of 75% w/w hexadecane (Fisher Scientific), 20% w/w toluene (Fisher Scientific), 3% w/w tetralin, and 2% w/w naphthalene was also studied. Methane samples were prepared by bubbling methane (Air Liquide) for 30 s through 1.5 ml of carbon disulfide in a glass vial cooled with dry ice.

Diesel samples were injected without pretreatment or dilution. A May 1997 oilsands derived Synfuel diesel was studied as a low boiling, low PAH content diesel sample (0.830 g cm<sup>-3</sup> at 15 °C). A 1998 commercial Ontario, Canada, diesel represented a conventional diesel sample (0.839 g cm<sup>-3</sup> at 15 °C). A Shell Canada Ltd. diesel blending feedstock was analyzed as a high boiling, high PAH content diesel sample (0.871 g cm<sup>-3</sup> at 15 °C). The following simulated distillation results were determined for each diesel sample.

Synfuel: Initial Boiling Point (IBP) 125 °C, T10% 158 °C, T50% 199 °C, T90% 246 °C, Final Boiling Point (FBP) 284 °C

Commercial Diesel: IBP 173 °C, T10% 199 °C, T50% 256 °C, T90% 311 °C, FBP 337 °C

Blending Feedstock: IBP 90 °C, T10% 256 °C, T50% 324 °C, T90% 364 °C, FBP 400 °C

### Calculations

Apparent plate heights, *H*, were calculated using peak widths at half height. Plate heights measured in SFC may have errors due to the compressible nature of the mobile phase.<sup>33</sup> Plate heights measured here are described as apparent to reflect this. Methane was used as the dead time marker when calculating

retention factors. Resolution between two group-types (*e.g.*, between mono- and diaromatics) was calculated from the retention times and peak widths at half-height of the latest eluting monoaromatic and the earliest eluting diaromatic model compound studied. The resolutions between the saturates and monoaromatics were calculated using the hexadecane and toluene peaks from the ASTM D 5186-03<sup>21</sup> performance mixture. Carbon dioxide densities were calculated using EOS-SCx version 2 free software from <http://hp.vector.co.jp/authors/VA030090/> based on the inputted temperature and downstream pressure.

### Cut points for group-type analysis

The minimum in the signal between the saturates and aromatics was used as a cut-point. ASTM Method D 5186-03<sup>21</sup> places the mono- and diaromatic cut point at the beginning of the elution of the naphthalene peak. This was 0.54 min for the Lichrospher silica column and 0.90 min for the titania–Lichrospher coupled column.

On the Lichrospher silica column, the di- and triaromatic cut point was 0.78 min, the mid-point point between the dibenzothiophene and anthracene peaks. This ignores the fact that 9,10-dihydroanthracene (diaromatic) eluted after both of the triaromatic model compounds that were studied on the Lichrospher column. This is typical for conventional bare silica columns while titania–silica coupled columns cleanly separate di- and triaromatic model compounds.<sup>22</sup> On the titania–Lichrospher coupled column, the mid-point between the dibenzothiophene and phenanthrene peaks was used (1.95 min). On the Lichrospher column the tri- and polyaromatic cut point was 0.92 min based on the mid-point between the phenanthrene and pyrene peaks. On the titania–Lichrospher coupled column, the mid-point between the anthracene and pyrene peaks was used (2.67 min).

For reasons discussed in the resolution and diesel analysis sections, three coupled Chromolith columns were used to separate the Synfuel sample. The cut points between the aromatic groups were 1.30 min, 1.52 min, and 1.65 min.

### Results and discussion

Short analysis times are central to achieving high sample throughput, reduced costs, and real-time monitoring of industrial processes.<sup>4</sup> We compare short packed columns and monolithic columns under high flow rates as two alternative approaches for reducing the time of a model SFC separation—the determination of diesel group-types.

#### Retention on packed and monolithic columns

To determine whether conventional particle packed columns or monolithic columns would produce faster diesel separations while maintaining high group-type resolutions, a particle packed Lichrospher Si 60 bare silica column and a monolithic Chromolith Si bare silica column were studied.

Retention factors were substantially higher on the packed Lichrospher column than on the monolithic Chromolith column. For instance, at 2 ml min<sup>-1</sup> and 150 bar, the retention factor of anthracene was 2.5 on the Lichrospher column and

0.56 on the Chromolith. This difference in retention is consistent with the higher surface area of the Lichrospher column ( $700 \text{ m}^2 \text{ g}^{-1}$ ) compared with the Chromolith column ( $300 \text{ m}^2 \text{ g}^{-1}$ ). Also, the higher porosity of the Chromolith column<sup>27,29,32</sup> further lowers its phase ratio (surface area to mobile phase volume). This results in significantly lower retention factors for the Chromolith column compared with the Lichrospher column.

Fig. 1 plots the retention factors of the representative model compound anthracene as a function of flow rate. Retention decreases with increasing flow rate for both the Lichrospher and Chromolith columns. A pressure limit of 300 bar at the pump head prevented flow rates up to the pump's limit of  $5 \text{ ml min}^{-1}$  from being studied. When the flow rate was increased from 2 to  $4 \text{ ml min}^{-1}$ , the retention factor for anthracene was reduced 1.6-fold on the Lichrospher column and 1.4-fold on the Chromolith column.

Retention factors decrease with increasing flow rate due to the increased column pressure. At higher flow rates, the pressure drop across the column and connective tubing increases. Because the pressure is controlled downstream, this results in a higher average carbon dioxide density across the column. This in turn produces stronger eluting conditions at higher flow rates.<sup>32</sup> The lower retention factors at higher flow rates reduce both the separation time and resolution.

The Chromolith column produces about one tenth the pressure drop of the Lichrospher column when the pressure drop associated with the injector, connective tubing, and DAD detector cell are subtracted. However, the extra-column back pressure is significantly higher than the Chromolith back pressure. The Chromolith column itself accounts for less than 11% of the total system back pressure. The retention factors on the Chromolith column decrease with increasing flow rate, largely due to the increase in the post-column contribution of the extra-column back pressure, rather than the back pressure across the Chromolith column. As will be discussed in the resolution section, lowering the flow rate to  $1 \text{ ml min}^{-1}$  minimized the extra-column back pressure effects.

The elution time of the latest eluting model compound, pyrene, is reduced significantly when shorter columns are used

at higher flow rates. At  $4.5 \text{ ml min}^{-1}$ , pyrene elutes in only 1.0 min on the 10 cm Lichrospher column and in 0.54 min on the 10 cm Chromolith column at 125 and 150 bar, respectively. These are much shorter than the 6.8 min on the conventional 25 cm Lichrospher column using  $2 \text{ ml min}^{-1}$  and 150 bar.<sup>22</sup>

Titania columns provide greater aromatic group-type resolutions than silica, and coupling a silica and a titania column together yields higher overall resolution.<sup>22</sup> Thus, to improve group-type resolutions, a short (5 cm) bare titania column was coupled to the 10 cm bare silica Lichrospher column. The closed symbols in Fig. 1 show the retention of anthracene on the titania–Lichrospher coupled column as a function of flow rate. The addition of the titania column makes the titania–Lichrospher coupled column up to twice as retentive for anthracene as the Lichrospher column alone. Pyrene elutes in 3.3 min on the 15 cm titania–Lichrospher coupled column at  $4 \text{ ml min}^{-1}$  and 125 bar. This compares with 23.7 min on the previously studied 40 cm titania–Lichrospher coupled column at  $2 \text{ ml min}^{-1}$  and 150 bar.

Overall, the shorter Lichrospher and titania–Lichrospher coupled columns could reduce the retention time of pyrene up to 7-fold compared with conventional length columns run at typical flow rates. The Chromolith column yielded up to a 13-fold lower pyrene retention time compared with the 25 cm Lichrospher column.

#### Column efficiency on packed and monolithic columns

Fig. 2 is a plot of the apparent plate height of anthracene at various flow rates for both the Lichrospher and Chromolith columns. Optimum flow rates for both columns were near  $4 \text{ ml min}^{-1}$ , with the packed Lichrospher column yielding a slightly lower optimum plate height of  $8 \mu\text{m}$  compared with  $10 \mu\text{m}$  on the Chromolith.

The apparent plate heights on the packed Lichrospher column were a few microns lower than on the monolithic Chromolith column for most of the model compounds except 2-naphthalenethiol. This polar compound produced an optimum plate height of  $9 \mu\text{m}$  on the monolithic Chromolith column while it displayed strong tailing and poor efficiency on the packed Lichrospher column. Overall, both columns

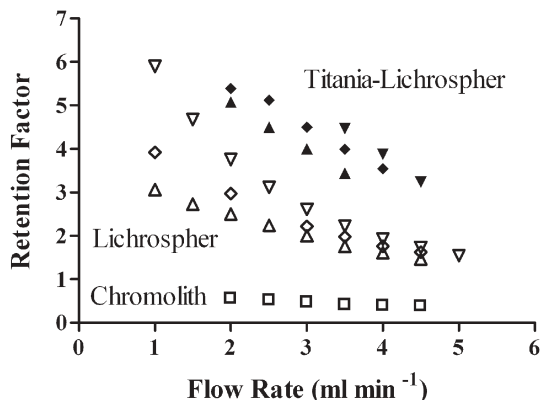


Fig. 1 Retention of anthracene *versus* flow rate at 100 bar (▼), 125 bar (◆), and 150 bar (▲) at 35 °C on a 15 cm titania–Lichrospher coupled column (closed symbols), 10 cm Lichrospher column (open symbols), and a 10 cm Chromolith column at 150 bar (□).

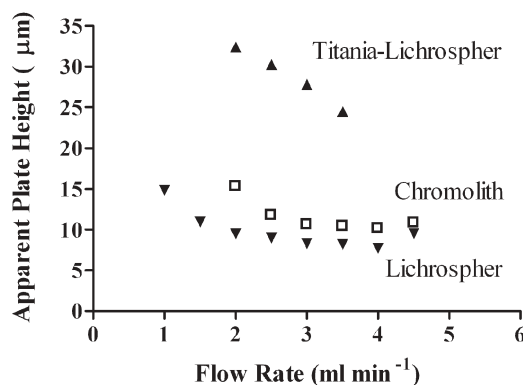
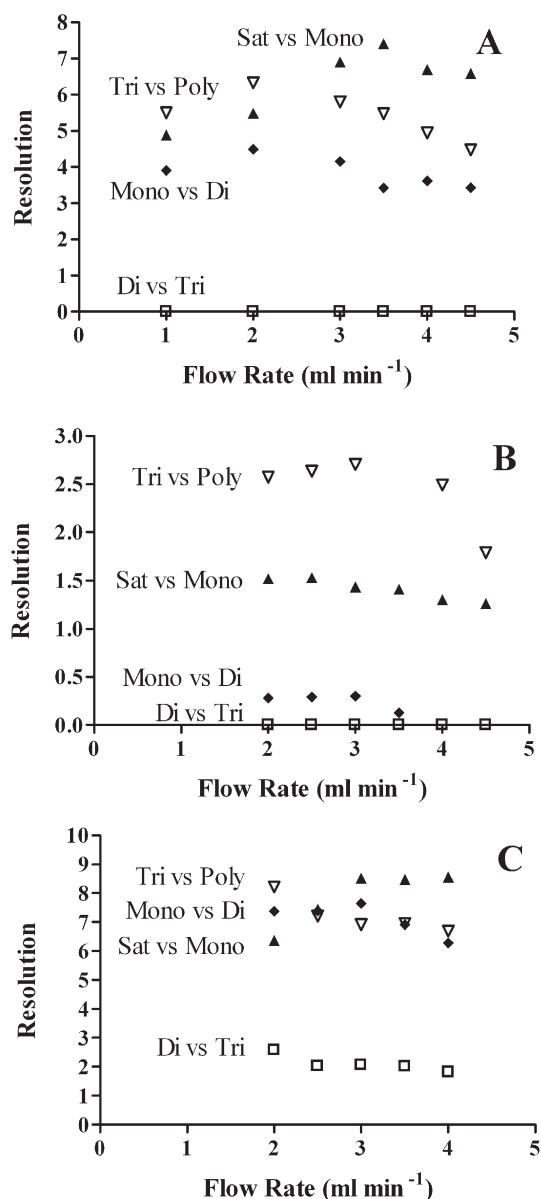


Fig. 2 Apparent plate height of anthracene *versus* flow rate on a 15 cm titania–Lichrospher coupled column (▲), 10 cm Chromolith column (□), and a 10 cm Lichrospher column (▼) at 35 °C and 150 bar.



**Fig. 3** Saturate *versus* monoaromatic (▲), mono-*versus* diaromatic (◆), di-*versus* triaromatic (□), and tri-*versus* polyaromatic (▽) group-type resolutions *versus* flow rate on (A) a 10 cm Lichrospher column at 125 bar, (B) a 10 cm Chromolith column at 150 bar, and (C) a 15 cm titania-Lichrospher coupled column at 125 bar.

demonstrate low apparent plate heights and optimum flow rates near the 5 ml min<sup>-1</sup> maximum flow rate of the pump. Therefore, efficiency is not being lost due to slow mass transfer at the highest flow rates achievable.

To achieve significantly faster separation times, some efficiency was sacrificed compared with our previous work on longer columns.<sup>22</sup> The apparent efficiency of anthracene is reduced from 22 200 to 10 900 plates when a shorter 10 cm Lichrospher column with 3 μm packing is run at 4.5 ml min<sup>-1</sup> and 125 bar. These conditions produced the shortest pyrene elution time while maintaining significant resolution and were considered optimal. The apparent efficiency of anthracene on the 10 cm Chromolith column is 9200 plates at 4.5 ml min<sup>-1</sup> and 150 bar.

The apparent plate height of anthracene as a function of flow rate on the short titania-Lichrospher coupled column is shown in Fig. 2. At 2 ml min<sup>-1</sup>, the apparent plate height of anthracene is 32 μm. This improves to 25 μm at 4 ml min<sup>-1</sup>. Previous results demonstrate that PAH apparent plate heights on titania improve with increasing carbon dioxide density.<sup>22</sup> The apparent plate height of anthracene greatly improves with increasing flow rate due to the higher average carbon dioxide density at higher flow rates. Similar to the short silica column, the apparent efficiency of anthracene is reduced from 9000 to 5200 plates when the shorter 15 cm titania-Lichrospher coupled column is run at 4 ml min<sup>-1</sup> and 125 bar.

#### Resolution on packed and monolithic columns

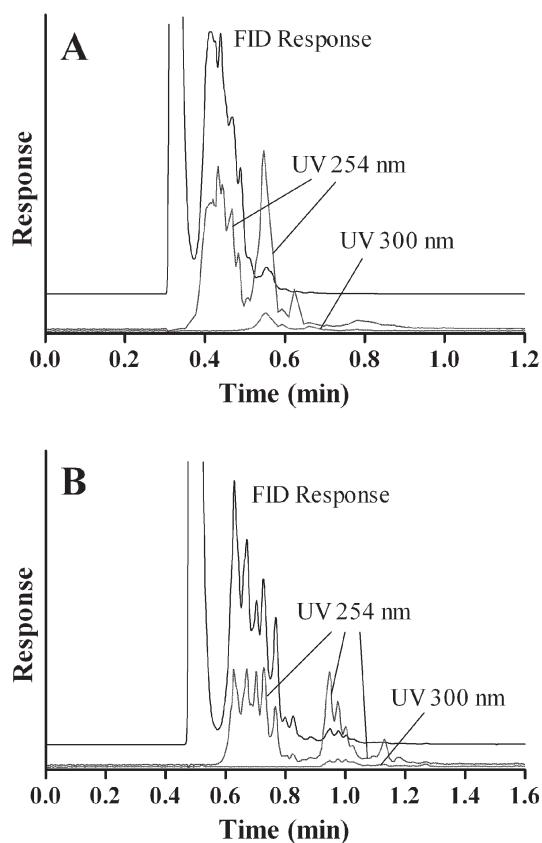
Fig. 3 shows the resolution between the hydrocarbon group-types on the short Lichrospher, Chromolith, and titania-Lichrospher coupled columns. At flow rates higher than 2 ml min<sup>-1</sup>, most group-type resolutions decrease. This is largely due to the decrease in retention factors caused by the higher carbon dioxide density at the higher back pressures. A notable exception is the saturate *versus* monoaromatic resolution on the packed columns which has a maximum resolution at 3.5 ml min<sup>-1</sup> on the Lichrospher column and a plateau at 3 ml min<sup>-1</sup> on the titania-Lichrospher coupled column.

Table 1 compares the group-type resolutions for the short packed columns and the Chromolith column with the results of previous studies using longer columns.<sup>22</sup> The short packed Lichrospher and titania-Lichrospher columns produced resolutions 42–51% lower than their longer counterparts. From the discussion of efficiency above, only a 25–30% decrease in resolution would be expected. However, some additional loss

**Table 1** Group-type resolutions and pyrene retention times

Column	Length (× 4.6 mm id)	Diameter, pore size	Sat. vs. Mono.	Mono. vs. Di.	Di. vs. Tri.	Tri. vs. Poly.	Elution time <sup>a</sup> /min
Chromolith <sup>b</sup>	100	—	1.3	0	0	1.8	0.54
Three Chromoliths <sup>c,d</sup>	300	—	2.4	0.5	0	2.6	1.7
Short silica <sup>e</sup>	100	3 μm, 60 Å	6.6	3.4	0	4.5	1.0
Short titania-silica <sup>d,f</sup>	150	3 μm, 60 Å	8.6	6.3	1.8	6.7	3.3
Lichrospher silica <sup>g,h</sup>	250	5 μm, 60 Å	11.6	6.3	0	8.6	6.8
Titania-Lichrospher <sup>d,g,h</sup>	400	3 and 5 μm, 60 Å	14.7	11.9	3.7	12.1	23.7

<sup>a</sup> Based on pyrene retention times. <sup>b</sup> 35 °C, 150 bar, 4.5 ml min<sup>-1</sup>. <sup>c</sup> 35 °C, 150 bar, 4.0 ml min<sup>-1</sup>. <sup>d</sup> Coupled columns. <sup>e</sup> 35 °C, 125 bar, 4.5 ml min<sup>-1</sup>. <sup>f</sup> 35 °C, 125 bar, 4.0 ml min<sup>-1</sup>. <sup>g</sup> 35 °C, 150 bar, 2.0 ml min<sup>-1</sup>. <sup>h</sup> Reference 22.



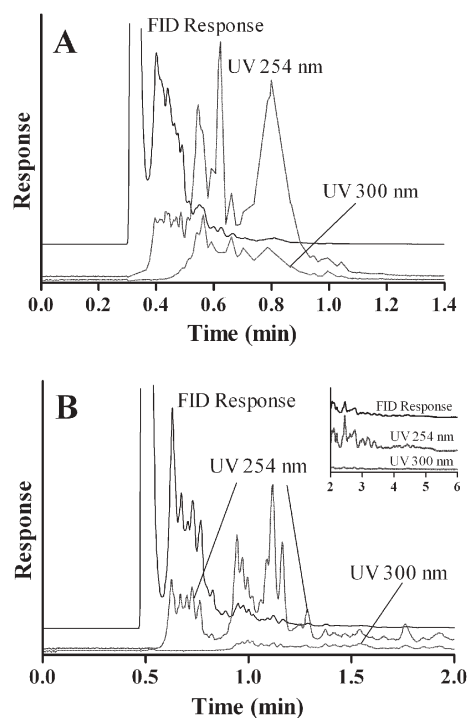
**Fig. 4** FID and UV traces of a Synfuel light diesel separated on (A) a 10 cm Lichrospher silica column at  $4.5 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ , and on (B) a 15 cm titania-Lichrospher coupled column at  $4 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ .

in resolution occurs due to the lower retention factors at higher flow rates.

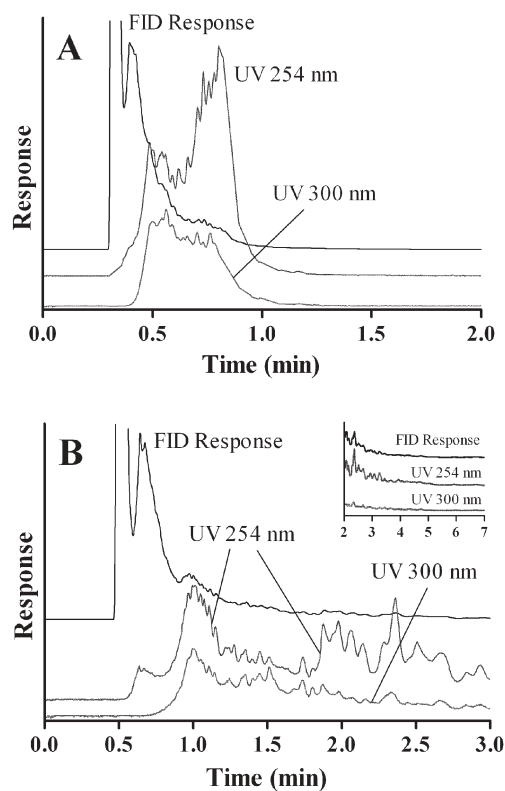
Overall, the Chromolith column produced the lowest group-type resolutions, due primarily to the low retention of this column. Chromolith columns with higher surface area (mesopore diameters approaching  $60 \text{ \AA}$ ) would be required to achieve acceptable resolutions in this application. Three 10 cm Chromoliths coupled together were studied under various conditions in an effort to achieve higher resolution. The flow rate was varied from 1 to  $4 \text{ ml min}^{-1}$  and the pressure from 100 to 200 bar. At  $1 \text{ ml min}^{-1}$ , the extra-column back pressure was insignificant at about 1 bar. This eliminated the lowering of retention by the post-column extra-column back pressure as discussed above. Despite this, the three coupled Chromoliths failed to meet the ASTM method requirements of resolution for the saturates/monoaromatics (4) or the mono-/diaromatics (2) under any of the conditions studied.

#### Fast group-type analysis of diesel samples

Three previously characterized diesel samples<sup>22</sup> were analyzed using the shorter columns at high flow rates. Fig. 4 shows the light diesel sample separated using the short silica column and the short titania-Lichrospher coupled column under optimal conditions. The integrated FID signal is proportional to hydrocarbon mass. The sudden increases in the UV responses at 254 nm and 300 nm indicate when the monoaromatics and



**Fig. 5** FID and UV traces of a commercial Ontario diesel separated on (A) a 10 cm Lichrospher silica column at  $4.5 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ , and (B) on a 15 cm titania-Lichrospher coupled column at  $4 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ .



**Fig. 6** FID and UV traces of a diesel blending feedstock separated on (A) a 10 cm Lichrospher silica column at  $4.5 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ , and (B) on a 15 cm titania-Lichrospher coupled column at  $4 \text{ ml min}^{-1}$  and  $35 \text{ }^\circ\text{C}/125 \text{ bar}$ .

**Table 2** Group-type content of diesel samples reported in mass% (RSD, %)

Sample	Column	Saturates	Mono	Di	Tri	Poly
Synfuel	Chromoliths <sup>a</sup>	62.8 (0.1%)	31.4 (1%)	5.5 (5%) <sup>b</sup>	0.3 (6%) <sup>b</sup>	—
Synfuel	Short silica	63.0 (0.1%)	35.1 (0.1%)	1.8 (0.9%) <sup>b</sup>	0.14 (25%) <sup>b</sup>	—
Synfuel	Short Ti-silica	62.9 (0.2%)	35.3 (0.8%)	1.8 (12%)	0.03 (40%)	—
Synfuel	HGS <sup>c</sup>	63.5 (0.1%)	34.7 (0.4%)	1.8 (4%) <sup>b</sup>	0.04 (40%) <sup>b</sup>	—
Synfuel	Ti-HGS <sup>c</sup>	63.5 (0.1%)	34.3 (0.1%)	2.2 (2%)	0.01 (40%)	—
Commercial	Short silica	69.6 (0.1%)	25.1 (0.2%)	4.5 (0.7%) <sup>b</sup>	0.6 (1%) <sup>b</sup>	0.2 (7%)
Commercial	Short Ti-silica	69.4 (0.1%)	24.4 (0.3%)	5.3 (0.4%)	0.5 (2%)	0.4 (1%)
Commercial	HGS <sup>c</sup>	70.1 (0.1%)	24.6 (0.2%)	4.7 (0.6%) <sup>b</sup>	0.5 (7%) <sup>b</sup>	0.09 (26%)
Commercial	Ti-HGS <sup>c</sup>	69.8 (0.1%)	23.5 (0.2%)	5.5 (0.6%)	0.6 (6%)	0.6 (9%)
Feedstock	Short silica	63.2 (0.2%)	24.4 (0.5%)	9.2 (0.2%) <sup>b</sup>	2.1 (0.8%) <sup>b</sup>	1.1 (2%)
Feedstock	Short Ti-silica	64.0 (0.1%)	20.5 (0.3%)	12.0 (0.6%)	2.2 (2%)	1.3 (2%)
Feedstock	HGS <sup>c</sup>	64.1 (0.1%)	22.7 (0.3%)	11.0 (0.3%) <sup>b</sup>	1.9 (1%) <sup>b</sup>	0.3 (10%)
Feedstock	Ti-HGS <sup>c</sup>	65.6 (0.1%)	19.3 (0.3%)	11.8 (0.2%)	2.0 (0.9%)	1.3 (3%)

<sup>a</sup> Three 10 cm Chromolith bare silica columns coupled in series at 2 ml min<sup>-1</sup>, 35 °C/150 bar. <sup>b</sup> Silica column results ignore 9,10-dihydroanthracene's (diaromatic) elution after triaromatic model compounds. <sup>c</sup> Hydrocarbon group separation (HGS) bare silica column and titania-HGS coupled column results.<sup>22</sup>

diaromatics begin to elute, respectively. The light diesel completely elutes from the short Lichrospher column in 2 min as compared with 7 min previously.<sup>22</sup> It elutes from the short titania-Lichrospher coupled column in 3 min compared with 14.5 min previously.<sup>22</sup> The three coupled Chromolith columns eluted the light diesel in 2 min at 4 ml min<sup>-1</sup> and 150 bar (chromatogram not shown), but with inadequate resolution as discussed above.

Fig. 5 shows a commercial diesel separated in 2 min on the short silica column and 6 min on the titania-Lichrospher coupled column. This compares with 10 min and 40 min on the longer columns, respectively.<sup>22</sup> Fig. 6 shows the heavy diesel blending feedstock separated in 2.5 min on the short silica column and 7 min on the short titania-Lichrospher coupled column. The longer columns require 10 min and 50 min for the same separation.<sup>22</sup>

Table 2 compares the group-type results from the fast separations with previous results.<sup>22</sup> The short packed Lichrospher and titania-Lichrospher columns produce results that compare very favorably with previous results. However, the three coupled Chromolith columns did not yield comparable results for the light diesel sample due to inadequate resolution.

All of the packed column results agree within the ASTM method reproducibility specifications<sup>21</sup> for total aromatic and PAH content with the exception of the short Lichrospher column total aromatic results for the heavy diesel blending feedstock. When the short Lichrospher results are not considered, then the remaining packed column results agree within the reproducibility specifications. This may indicate that for very heavy diesel samples, the 10 cm Lichrospher column may not provide sufficient saturate *versus* monoaromatic resolution to achieve comparable results to longer columns. Indeed, the short Lichrospher column monoaromatic and diaromatic results for the heavy diesel blending feedstock displayed the most significant deviations of the packed column results.

## Conclusions

Short packed silica and titania-silica coupled columns achieved 7-fold faster diesel separations than conventional length columns run at typical flow rates,<sup>22</sup> while maintaining

more than half of the resolution. Monolithic Chromolith columns achieved 13-fold faster elution times than conventional length packed silica columns run at typical flow rates,<sup>22</sup> but at the expense of significant resolution due to their lower retention. The 15 cm titania-Lichrospher coupled column obtained similar diesel group-type results to much longer columns while reducing the maximum diesel analysis time from 50 min to 7 min.

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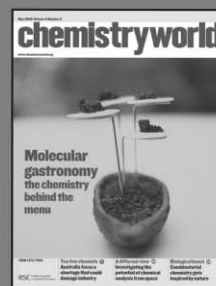
## References

- 1 T. L. Chester and J. D. Pinkston, *Anal. Chem.*, 2002, **74**, 2801–2812.
- 2 T. L. Chester and J. D. Pinkston, *Anal. Chem.*, 2004, **76**, 4606–4613.
- 3 T. L. Chester and J. D. Pinkston, *Anal. Chem.*, 2000, **72**, 129R–135R.
- 4 D. E. Honigs, *Am. Lab.*, 1987, **19**, 48–51.
- 5 N. Wu, R. Yee and M. L. Lee, *Chromatographia*, 2001, **53**, 197–200.
- 6 D. J. Cookson, C. P. Lloyd and B. E. Smith, *Energy Fuels*, 1988, **2**, 854–860.
- 7 D. J. Cookson, P. Iliopoulos and B. E. Smith, *Fuel*, 1995, **74**, 70–78.
- 8 S. Sato, Y. Sugimoto, K. Sakanishi, I. Saito and S. Yui, *Fuel*, 2004, **83**, 1915–1927.
- 9 M. Sjögren, H. Li, U. Rannug and R. Westerholm, *Fuel*, 1995, **74**, 983–989.
- 10 A. de Lucas, A. Durán, M. Carmona and M. Lapuerta, *Fuel*, 2001, **80**, 539–548.
- 11 A. Karonis, E. Lois, F. Zannikos, A. Alexandridis and H. Sarimveis, *Energy Fuels*, 2003, **17**, 1259–1265.
- 12 T. C. Zannis and D. T. Hountalas, *J. Energy Inst.*, 2004, **77**, 16–25.
- 13 A. Ohtsuka, K. Hashimoto, Y. Akutsu, M. Arai and M. Tamura, *J. Jpn. Petrol. Inst.*, 2002, **45**, 24–31.
- 14 X. Li and Ö. L. Gülder, *J. Can. Pet. Technol.*, 1998, **37**, 56–60.
- 15 N. Shimazaki, K. Tsuchiya, M. Morinaga, M. Shibata and Y. Shibata, *SAE Tech. Pap. Ser.*, 2002, 2002-01-2824.
- 16 K. Mitchell, *SAE Tech. Pap. Ser.*, 2000, 2000-01-2890.

- 17 S. Tanaka, H. Takizawa, T. Shimizu and K. Sanse, *SAE Tech. Pap. Ser.*, 1998, 982648.
- 18 G. E. Andrews, R. B. Ishaq, J. R. Farrar-Khan, Y. Shen and P. T. Williams, *SAE Tech. Pap. Ser.*, 1998, 980527.
- 19 M. Signer, P. Heinze, R. Mercogliano and H. J. Stein, *SAE Tech. Pap. Ser.*, 1996, 961074.
- 20 K. Mitchell, D. E. Steere, J. A. Taylor, B. Manicom, J. E. Fisher, E. J. Sienicki, C. Chiu and P. T. Williams, *SAE Tech. Pap. Ser.*, 1994, 942053.
- 21 *Method D 5186-03, Annual Book of ASTM Standards*, American Society for Testing and Materials, West Conshohocken, PA, USA, 2003.
- 22 R. E. Paproski, J. Cooley and C. A. Lucy, *J. Chromatogr., A*, 2005, **1095**, 153–163.
- 23 S. H. Hoke, J. A. Tomlinson, R. D. Bolden, K. L. Morand, J. D. Pinkston and K. R. Wehmeyer, *Anal. Chem.*, 2001, **73**, 3083–3088.
- 24 D. Connolly and B. Paull, *J. Chromatogr., A*, 2002, **953**, 299–303.
- 25 D. J. Phillips, M. Capparella, U. D. Neue and Z. El Fallah, *J. Pharm. Biomed. Anal.*, 1997, **15**, 1389–1395.
- 26 F. Gerber, M. Krummen, H. Potgeter, A. Roth, C. Siffrin and C. Spoendlin, *J. Chromatogr., A*, 2004, **1036**, 127–133.
- 27 N. Wu, J. Dempsey, P. M. Yehl, A. Dovletoglu, D. Ellison and J. Wyvrat, *Anal. Chim. Acta*, 2004, **523**, 149–156.
- 28 K. Mistry and N. Grinberg, *J. Liq. Chromatogr. Relat. Technol.*, 2005, **28**, 1055–1074.
- 29 K. Cabrera, D. Lubda, H.-M. Eggenweiler, H. Minakuchi and K. Nakanishi, *J. High Resolut. Chromatogr.*, 2000, **23**, 93–99.
- 30 P. Hatzis and C. A. Lucy, *Analyst*, 2002, **127**, 451–454.
- 31 T. Murahashi, *Analyst*, 2003, **128**, 611–615.
- 32 E. Lesellier, C. West and A. Tchaplá, *J. Chromatogr., A*, 2003, **1018**, 225–232.
- 33 D. P. Poe and D. E. Martire, *J. Chromatogr.*, 1990, **517**, 3–29.

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