Comparison of titania, zirconia, and silica stationary phases for separating diesel fuels according to hydrocarbon group-type by supercritical fluid chromatography

Richard E. Paproski [a], Jean Cooley [b], Charles A. Lucy [a],*

[a] *Department of Chemistry, Gunning/Lemieux Chemistry Centre, University of Alberta, Edmonton, AB, Canada T6G 2G2*
[b] *Syncrude Research, Syncrude Canada Ltd., Edmonton, Alta., Canada T6N 1H4*

Abstract

Silica, zirconia, and titania columns were compared for their ability to separate diesel samples into saturates, mono-, di-, tri-, and polyaromatics by supercritical fluid chromatography (SFC) using pure CO_2 according to ASTM method D 5186-03. A titania column coupled in series to a silica column was found to provide the highest overall group-type resolutions based on 20 model compounds, with resolutions as high as 14.7 for saturates versus monoaromatics and 11.9 for monoaromatics versus diaromatics. An oilsands-derived Synfuel light diesel, a commercial Ontario diesel, and a heavy Shell Canada Ltd. diesel blending feedstock were studied on a titania–silica coupled column as well as on a conventional silica column. The Synfuel results were similar (within 0.5 mass%) on both the conventional bare silica column and the titania–silica coupled column. The heavier commercial diesel and diesel blending feedstock samples yielded different results on the titania–silica coupled column compared to the silica column alone, demonstrating the importance of achieving the highest possible resolutions when baseline separation of group-types is not obtained.

1. Introduction

Fossil fuels including diesel and jet fuels are the most important source of energy for our society today, providing the bulk of our global energy requirements for transportation, construction, heating, and agriculture. The group-type composition of these fuels (saturates, mono-, di-, tri-, and polycyclic aromatics) influence what properties these fuels will possess. Performance properties (e.g. cetane number, pour point, smoke point, heat content) [1–4] and emission properties (e.g. particulate matter, polycyclic aromatic hydrocarbon (PAH), nitrogen oxides, carbon monoxide) [5–15] have been linked to the total aromatic and PAH content (dicyclic aromatic compounds and higher) in diesel fuels. Specifically, PAH content in diesel fuels increases particulate matter [9,10,14], PAH [12,13,15], and nitrogen oxide [9,10,14] emissions. Given the widespread use of diesel fuels,

government limits on the PAH content of diesel fuels are becoming increasing stringent.

In North America, ASTM method D 5186-03 is used to determine the aromatic and PAH content of diesel and aviation turbine fuels [16]. This method uses SFC with a carbon dioxide mobile phase to separate diesel fuels according to group-type followed by flame ionisation detection (FID). Other techniques used for diesel group-type separations include high performance liquid chromatography (HPLC) [17–22], gas chromatography (GC) [17,23–25], LC–GC [26,27], SFC–GC [28], and SFC–MS [29]. However, HPLC detectors yield a non-uniform response for saturates and aromatics [17,30–32], necessitating complex calibrations. In contrast, FID provides reliable mass quantification of each group-type [17,30–32]. GC separations often require 2D separations or mass spectrometric detectors that give non-uniform responses to achieve group-type separations [17,24], making GC less practical for routine group-type analysis.

The hydrocarbon group separation (HGS) column from Agilent (250 mm × 4.6 mm i.d., 5 μm bare Lichrospher Si 60 silica spherical particles [33]) has been widely used in SFC to pro-

* Corresponding author. Tel.: +1 780 492 0315; fax: +1 780 492 8231.
E-mail address: charles.lucy@ualberta.ca (C.A. Lucy).

vide high group-type resolutions compared to other bare silicas. However, our results show that bare silica columns have difficulty separating the di- and triaromatic groups cleanly. Limited aromatic group-type resolutions restrict the accuracy of diesel group-type determinations in SFC [17,30]. Also, achieving high aromatic group-type resolutions while maintaining the resolution of saturates and aromatics has proven difficult [17]. For these reasons, several column packing materials offering different surface chemistries compared to bare silica are investigated in this paper. These include bare zirconia, polybutadiene coated zirconia, carbon coated zirconia, bare titania, and a NH_2-bonded silica. A high purity, low metals type B bare silica Kromasil column, a Lichrospher Si 60 bare silica column and an irregular version of the spherical Lichrospher Si 60 bare silica column were also studied for comparison purposes. The columns are assessed primarily on the basis of whether they can achieve high resolution between the different hydrocarbon groups: saturates, mono-, di-, tri-, and polyaromatics. Three diesel samples of increasing boiling range, density, and PAH content were used to assess the capabilities of the HGS column and a titania–silica coupled column.

2. Experimental

2.1. Apparatus

The columns listed in Table 1 were tested on a Hewlett-Packard (now Agilent, Palo Alto, CA, USA) SFC system at 35 °C, 150 bar (downstream pressure), and 2 ml min^{-1}. An HP G1205A SFC pump module was used to pump SFC grade (>99.995%, <3 ppm water content) carbon dioxide (Air Liquide, Montreal, QC, Canada) through the test columns, heated in an HP 5890 series II column oven. An HP 7673B automatic sampler with 50 μl syringe was used to inject samples into a Rheodyne (Rohnert Park, CA, USA) 7410 injection valve (0.5 μl full loop injection). Quantification was provided by an HP SFC FID.

Qualitative diode array detection (DAD) was provided by an HP Series 1050 DAD. A t-joint was used to split the flow between the two detectors. The time shift between the FID and DAD signals was less than 5 s. The Hewlett-Packard SFC controls downstream system pressure through the use of a backpressure regulator located after the DAD. A low flow fused silica integral restrictor (part number G1205-21400, Agilent) [32] was used to depressurise the carbon dioxide prior to the FID. Hydrogen gas for the FID was provided by a Whatman (Florham Park, NJ, USA) Hydrogen Generator model 75-34 at a typical flow rate of 43.4 ml min^{-1}. Air was supplied by a Domnick Hunter (Mississauga, ON, Canada) Nitrox Z zero air generator at a typical flow rate of 347 ml min^{-1}. Data acquisition at 5 Hz was provided by a Vectra 486/66XM personal computer running HP-SFC Chem-Station Rev. A.01.02 software.

2.2. Standards and samples

Twenty model compounds (>97% purity, see Table 2) were studied on each test column. Model compound samples were prepared by dissolving each compound in ACS grade carbon disulfide (Fisher Scientific, Nepean, ON, Canada) at 0.1% (w/w). Due to overlap of docosane with the carbon disulfide solvent peak on some columns, an ASTM method D 5186-03 [16] performance mixture consisting of 75% (w/w) hexadecane, 20% (w/w) toluene, 3% (w/w) tetralin, and 2% (w/w) naphthalene was also studied. Samples containing methane were prepared by gently bubbling methane for 30 s through 1.5 ml of carbon disulfide in a glass autosampler vial cooled with dry ice. The vial was quickly and tightly capped and used within three months of preparation.

Diesel samples were injected without dilution. A May 1997 oilsands derived ultra low sulfur (<10 ppm) Synfuel diesel, produced for onsite use at Syncrude Canada Ltd. in Fort McMurray, Alberta, Canada, was studied as a low boiling, low PAH content diesel sample (0.830 g cm^{-3} at 15 °C). A 1998 commercial

Table 1
Columns tested and group-type resolutions achieved at 35 °C, 150 bar, 2 ml min^{-1}

Column	Length (×4.6 mm i.d.)	Diameter, pore size	Saturate vs. monoaromatic	Monoaromatic vs. diaromatic	Diaromatic vs. triaromatic	Triaromatic vs. polyaromatic
Hydrocarbon group separation[a,b]	250	5 μm, 60 Å	8.7	6.1	0	8.1
Bare silica Lichrospher Si 60[c]	250	5 μm, 60 Å	11.6	6.3	0	8.6
Bare silica Lichrosorb Si 60[c,d]	250	5 μm, 60 Å	6.0	2.9	0	5.2
Bare silica Kromasil Si[c]	250	5 μm, 60 Å	7.5	3.3	0	5.8
Spherisorb-NH$_2$[e]	150	3 μm, 80 Å	5.0	7.1	0.7	12.9
Bare zirconia phase[f]	150	3 μm, 300 Å	1.4	7.1	2.9	2.3
Bare titania Sachtopore-NP[f]	150	3 μm, 60 Å	5.4	11.8	1.4	8.9
Bare zirconia-HGS[g]	400	–	9.9	8.1	3.2	6.8
Bare titania-HGS[g]	400	–	13.4	10.7	3.6	11.0
Bare titania-Lichrospher[g]	400	–	14.7	11.9	3.7	12.1

[a] Previously used for the group-type analysis of diesel fuels by SFC.
[b] Agilent, Palo Alto, CA, USA.
[c] Thermo Electron, Waltham, MA, USA.
[d] Irregular version of spherical Lichrospher Si 60 packing.
[e] Waters, Milford, MA, USA.
[f] Zirchrom, Anoka, MN, USA.
[g] Coupled columns.

Table 2
Model compounds studied and retention times (min) shown under optimised conditions

Compound	Hydrocarbon group-type	Titania-HGS coupled column	HGS column
Octane[a]	Saturate, paraffin	2.20	1.42
Methylcyclohexane[b]	Saturate, naphthene	2.28	1.48
Hexadecane[c] (75%, w/w)	Saturate, paraffin	2.29	1.46
Docosane[a]	Saturate, paraffin	2.36	1.49
Decahydronaphthalene[b]	Saturate, naphthene	CS_2 overlap	CS_2 overlap
Benzene[c]	Monoaromatic	3.06	2.08
n-Butylbenzene[b]	Monoaromatic	3.12	2.05
Toluene[c] (20%, w/w)	Monoaromatic	3.12	2.11
2-Ethyltoluene[a]	Monoaromatic	3.35	2.24
Tetralin[a]	Monoaromatic	3.99	2.67
Naphthalene[c]	Diaromatic	5.07	3.17
Biphenyl[a]	Diaromatic	6.40	3.78
Acenaphthene[a]	Diaromatic	7.33	4.11
Fluorene[a]	Diaromatic	10.9	5.10
9,10-Dihydroanthracene[b]	Diaromatic	11.6	6.03
Dibenzothiophene[b]	Diaromatic, thiophene	12.2	5.28
Phenanthrene[a]	Triaromatic	13.6	5.93
Anthracene[c]	Triaromatic	14.0	5.62
Pyrene[a]	Polyaromatic	24.9	8.40
2-Naphthalenethiol[b]	Diaromatic, thiol	Irreversibly retained	5.84

[a] Sigma–Aldrich Canada Ltd., Oakville, ON, Canada.
[b] Acros Organics, Morris Plains, NJ, USA.
[c] Fisher Scientific, Nepean, ON, Canada.

Ontario, Canada diesel was studied to represent a conventional diesel sample ($0.839 \, \mathrm{g\,cm^{-3}}$ at 15 °C). A Shell Canada Ltd. diesel blending feedstock was studied as a high boiling, high PAH content diesel sample ($0.871 \, \mathrm{g\,cm^{-3}}$ 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.

2.3. Calculations

Retention times and peak widths at half-height were determined using ChemStation Rev. A.01.02 software. Plate heights, H, were based on width at half height. Retention factors were calculated using methane as the dead time marker. Resolution between two group-types such as mono- and diaromatics were calculated based on width at half height (Eq. (1)):

$$R_s = \frac{2(t_2 - t_1)}{(1.699(W_2 + W_1))} \tag{1}$$

where t_1 and t_2 are the retention time of the latest eluting monoaromatic and the earliest eluting diaromatic model compound studied. W_1 and W_2 are the peak widths at half-height of the latest eluting monoaromatic and the earliest eluting diaromatic model compound studied. Because of overlap of docosane with the carbon disulfide sample solvent on several test columns, the resolutions between the saturates and monoaromatics were

calculated from the hexadecane and toluene peaks from the ASTM D 5186-03 performance mixture. This may result in overestimation of the saturate and monoaromatic resolution, but it allows for direct comparison of all columns studied. CO_2 densities were calculated based on temperature and downstream pressure using EOS-SCx version 2 free software from http://hp.vector.co.jp/authors/VA030090/.

2.4. Cut points for group-type analysis

The cut point between saturates and aromatics was determined as the minimum in the signal between the two groups. ASTM D 5186-03 method [16] cuts the mono- and diaromatic group-types at the beginning of the elution of the naphthalene peak. This was determined as 3.10 min for the HGS column and 4.96 min for the titania-HGS coupled column following inspection of the chromatograms containing naphthalene.

Although the ASTM method does not distinguish between di-, tri-, and polyaromatics, they were determined here as follows. On the HGS column, the di- and triaromatic cut point was taken as 5.45 min based on the midpoint point between the dibenzothiophene and anthracene peaks. Note that this ignores the fact that on the HGS column, 9,10-dihydroanthracene (diaromatic) eluted after both of the triaromatic model compounds that were studied. On the titania-HGS coupled column, the midpoint between the dibenzothiophene and phenanthrene peaks was used, giving 12.9 min. On the HGS column the tri- and polyaromatic cut point was determined to be 7.16 min based on the midpoint point between the phenanthrene and pyrene peaks. On the titania-HGS column the midpoint point between the anthracene and pyrene peaks was used, giving 19.4 min. Due to differences in the elution order of the

triaromatics on the HGS and titania-HGS coupled column, different triaromatic model compounds were used for the cut-points.

3. Results and discussion

3.1. Comparison of conventional silica columns

Conventional Type A bare silica columns HGS, Lichrospher Si 60, Lichrosorb Si 60, as well as a low metals Type B bare silica Kromasil Si column were studied to determine how well bare silica columns perform group-type separations of diesel samples. A Spherisorb-NH_2 column was also studied because NH_2-columns have been used with HPLC to perform group-type separations of gasoline [34], diesel [18], gas oil [35–37], crude oil [38,39], and heavy distillates [40]. The 20 model compounds in Table 2 were studied on each column at 35 °C, 150 bar, and 2 ml min^{-1} which was previously determined to be the optimal conditions for group-type separations on the HGS column (unpublished results).

For the aromatics most of the silica columns produced plate heights in the range of 8–20 μm. The exception was the HGS column, which yielded a plate height of 36 μm for pyrene. The plate heights for hexadecane were in the range of 14 μm for the NH_2-bonded silica column to 49 μm for the HGS column. These higher plate heights are possibly the result of mass overloading of the columns due to the higher 75% (w/w) concentration of hexadecane in the ASTM performance mixture compared to the other model compounds at 0.1% w/w. Docosane at 0.1% (w/w) produced plate heights between 9 and 12 μm when it was not overlapping with the CS_2 solvent peak.

When the group-type resolutions of the various silica columns are compared (Table 1), the highest saturate versus monoaromatic resolution is achieved on the Lichrospher column with the NH_2-bonded silica column producing the lowest saturate versus monoaromatic resolution. The Lichrospher, HGS, and NH_2-bonded silica columns produced high monoaromatic versus diaromatic and triaromatic versus polyaromatic resolutions. The NH_2-bonded silica column was the only silica column to achieve any diaromatic versus triaromatic resolution, but it provided poor saturate versus monoaromatic resolution. The trends observed on the NH_2-bonded silica column are similar to those reported previously [32]. The Lichrosorb and Kromasil columns performed poorly compared to the other silica columns.

None of the silica columns adequately separated all of the model compounds according to group-type, with the separation of di- and triaromatics proving to be the most difficult. Despite this, all of the silica columns studied met the ASTM D 5186-03 method [16] requirements of R_s(sat, mono) = 4 and R_s(mono, di) = 2 (see Table 2). These resolution requirements are easily met, but they fail to provide near baseline resolution of group-types in diesel samples. Alternative column materials offering different surface chemistries were studied in an effort to achieve the highest possible resolution of all group-types.

3.2. Comparison of zirconia and titania columns

Bare zirconia was studied as it has a polar surface similar to silica, while possessing Lewis acid sites which provide additional interactions with π-electron rich PAH compounds [41–44]. All of the aromatics eluted according to ring number on a bare zirconia column, but not without a significant loss in the saturate versus monoaromatic resolution (Table 1). Most of the PAHs studied yielded poorer efficiencies on bare zirconia compared to silica. Significant improvements in efficiency were observed at higher temperatures and pressures (Fig. 1A). However, even at 100 °C/250 bar (0.59 g cm^{-3} CO_2 density), anthracene's plate height of 65 μm is still 3.6-fold higher than on bare silica at the milder conditions of 35 °C/150 bar (0.82 g cm^{-3}). Also, at these higher temperatures and pressures, the hexadecane and toluene peaks were unresolved indicating a significant loss in the saturate versus monoaromatic resolution. Improvements in the aromatic group-type resolutions were 6%, 27%, and 180%, respectively, at 100 °C/250 bar compared to 35 °C/150 bar.

Two reversed phase zirconia columns were also studied and found to be unsuitable for group-type separations in SFC. A carbon coated zirconia column was too retentive to elute saturates or aromatics within 60 min, even at the strongest eluent conditions studied of 35 °C/200 bar (0.87 g cm^{-3}). A polybutadiene coated zirconia column eluted docosane after the monoaromatics. Although the retention of docosane could be reduced relative to the aromatic compounds by decreasing the temperature and increasing the pressure, docosane had a similar retention factor to biphenyl at the best conditions of
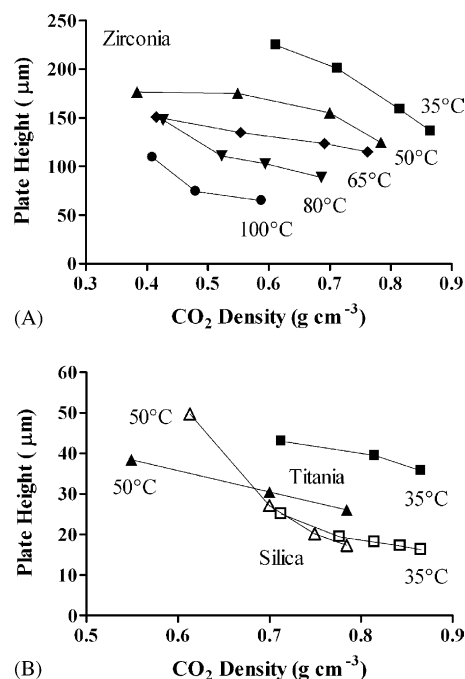

Fig. 1. Plate height of anthracene vs. CO_2 density at temperatures from 35 to 100 °C and pressures from 85 to 250 bar at 2 ml min^{-1} on (A) a bare zirconia column, (B) a bare titania column (closed symbols) and a bare silica HGS column (open symbols). See Table 1 for column dimensions.
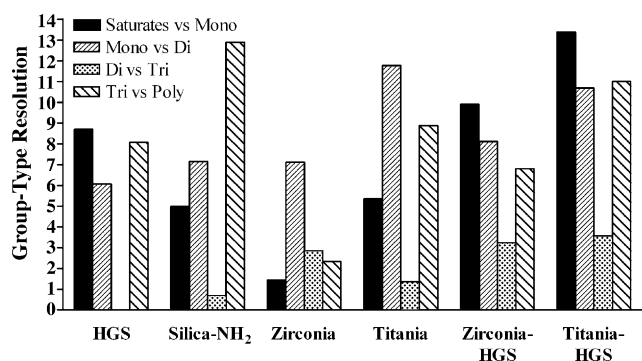
Fig. 2. Group-type resolutions on various columns and coupled columns at 35 °C, 150 bar, and 2 ml min^{-1}. See Table 1 for column dimensions.

35 °C/200 bar. Thus the polybutadiene coated zirconia did not yield a saturates–monoaromatics separation. The polybutadiene coated zirconia column eluted all of the PAHs according to ring number, but also suffered from poorer PAH efficiencies than silica with plate heights for anthracene in the range of 16–60 μm under the same conditions as Fig. 1A.

Bare titania was studied because it has a similar surface chemistry to bare zirconia [41–43,45]. It is available with smaller pore sizes than zirconia. This leads to higher surface area and higher retention factors for improving the saturate versus monoaromatic resolution. A bare titania column eluted all of the group-types in order, with more reasonable PAH efficiencies than bare zirconia (Fig. 1B). Anthracene's plate height on bare titania improved from 39 to 26 μm as temperature/pressure were increased from 35 °C/150 bar (0.82 g cm^{-3}) to 50 °C/200 bar (0.78 g cm^{-3}). The plate heights for the saturate and monoaromatic model compounds on zirconia and titania were comparable or lower than on silica. At 50 °C/200 bar, the diaromatic versus triaromatic and triaromatic versus polyaromatic resolutions on bare titania improved by 79% and 19%, respectively, compared to 35 °C/150 bar. The saturate versus monoaromatic resolution decreased by 7%, while the monoaromatic versus diaromatic resolution did not change.

Comparison of the group-type resolutions on bare silica, silica-NH$_2$, bare zirconia, and bare titania at 35 °C/150 bar (Fig. 2) reveals that bare silica provides the highest saturate versus monoaromatic resolution followed by bare titania, silica-NH$_2$, and then bare zirconia. Bare titania produces the highest monoaromatic versus diaromatic resolution while bare zirconia produces the highest diaromatic versus triaromatic resolution. The silica-NH$_2$ column produced the highest triaromatic versus polyaromatic resolution.

3.3. Coupled titania–silica and zirconia–silica columns

Bare titania provides good aromatic group-type resolutions. Bare silica provides good saturate versus monoaromatic resolution. A bare titania column was coupled to the bare silica HGS column to provide higher overall resolutions. The titania column was placed upstream of the silica column to provide a higher average CO$_2$ density across the titania column to help improve PAH efficiency. A bare zirconia and HGS coupled column was also studied.

At 35 °C/150 bar, both zirconia-HGS and titania-HGS coupled columns yield poor PAH efficiencies compared to bare silica (e.g. $H_{anthracene}$ of 79 μm and 43 μm, respectively, compared to 18 μm on the HGS column). When the elution conditions are increased to 100 °C/250 bar for the zirconia-HGS coupled column and 50 °C/200 bar for the titania-HGS coupled column, these plate heights improve to 37 and 26 μm, respectively.

The zirconia-HGS coupled column achieved comparable or better group-type resolutions at 35 °C/150 bar compared to the HGS column alone (Fig. 2). At 100 °C/250 bar, the saturate versus monoaromatic resolution on the zirconia-HGS column decreased by 38%, while the aromatic group-type resolutions increased by 1%, 31%, and 60%, respectively.

At 35 °C/150 bar, the titania-HGS coupled column gave the highest group-type resolutions overall (Fig. 2). At 50 °C/200 bar, saturate versus monoaromatic and monoaromatic versus diaromatic resolutions decreased by 6% and 8%, respectively while the diaromatic versus triaromatic and triaromatic versus polyaromatic resolutions increased by 1% and 15%, respectively. When the titania column was coupled to the new bare silica Lichrospher column instead of the HGS column, resolutions were further improved as shown in Table 1. These resolutions are higher than previously reported results using similar length columns [32,46,47], and comparable or better than columns more than twice as long [47,48].

3.4. Group-type analysis of diesel samples using a titania–silica coupled column

Three diesel samples were analyzed on the bare titania-HGS coupled column and on the HGS column alone. As the HGS column has been used previously for diesel group-type analysis, our results are more indicative of typical column performance rather than new column performance. The first diesel sample studied was a Synfuel diesel that is representative of light diesels with relatively low PAH concentrations. The second sample was a commercial Ontario diesel with moderate PAH concentrations. The third sample was a Shell Canada Ltd. diesel blending feedstock that is representative of very heavy (dense) diesels with high PAH concentrations.

Fig. 3A shows the FID and UV traces for the Synfuel diesel sample separated on the HGS column under standard conditions. The FID trace shows the elution of all group-types with the signal intensity being directly proportional to hydrocarbon mass. The UV response at 254 nm indicates that the monoaromatics begin to elute at 1.8 min. The UV response at 300 nm shows that the diaromatics begin to elute at 2.8 min. Near baseline resolution is obtained between the saturates, mono-, and diaromatics on the HGS column.

Fig. 3B shows the same separation on the bare titania-HGS column. Near baseline resolution between the saturates, mono-, and diaromatics is also obtained, with the monoaromatics beginning to elute at 2.9 min and the diaromatics at 5.0 min. It is clear from Fig. 3A and B that the diaromatics have different elution
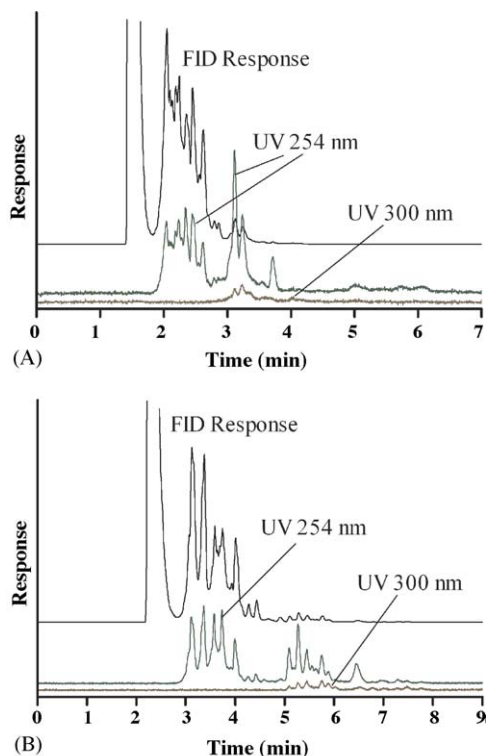
Fig. 3. FID and UV traces of a Synfuel light diesel separated at 35 °C, 150 bar, and 2 ml min⁻¹ on (A) a bare silica HGS column and (B) a bare titania column coupled to a bare silica HGS column. See Table 1 for column dimensions.
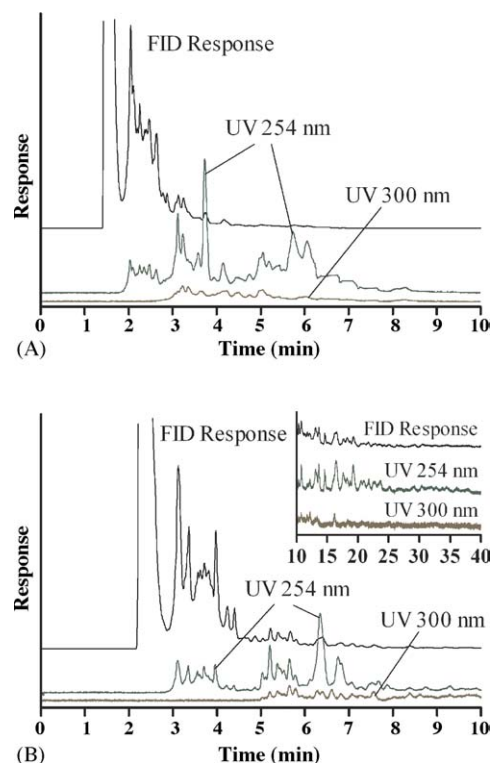

Fig. 4. FID and UV traces of a commercial Ontario, Canada diesel separated at 35 °C, 150 bar, and 2 ml min⁻¹ on (A) a bare silica HGS column and (B) a bare titania column coupled to a bare silica HGS column. See Table 1 for column dimensions.

times on the two columns, with better resolution of the aromatic peaks observed on the titania-HGS coupled column.

Fig. 4A shows the commercial Ontario diesel separated on the HGS column. With this commercial diesel there is less resolution between the group-types compared to the lighter Synfuel diesel (Fig. 3A). Fig. 4B shows the same separation on the titania-HGS coupled column. The higher monoaromatic versus diaromatic resolution on the titania-HGS coupled column can be observed by the lower signal intensity of the FID trace when the diaromatics begin to elute at 5.0 min compared to the HGS column at 2.8 min. Lower FID signal intensity near the cut-point indicates lower overlap of the two group-types. The PAH compounds require 40 min to elute from titania-HGS column, compared to 10 min from the HGS column. While this significantly increases the analysis time, it also provides much higher aromatic resolutions. A shorter titania column could be used to reduce the analysis time while still providing high aromatic group-type resolutions.

Fig. 5A shows the diesel blending feedstock separated on the HGS column. With this heavier diesel sample there is much less resolution between the group-types compared to the lighter diesel samples (Figs. 3A and 4A). There is also much higher PAH content (Table 3). Fig. 5B shows the same separation on the titania-HGS coupled column. Again, the higher monoaromatic versus diaromatic resolution on the titania-HGS coupled column is shown by the lower signal intensity of the FID trace when the diaromatics begin to elute at 4.2 min compared to the HGS column alone at 2.4 min. While all compounds have eluted from
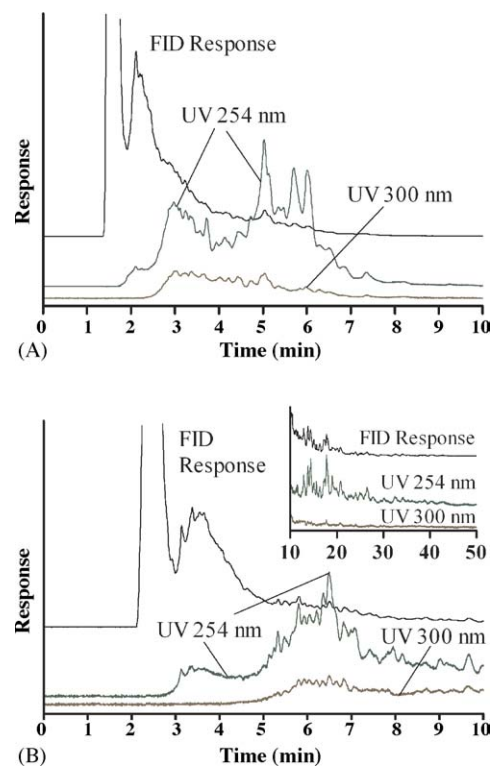

Fig. 5. FID and UV traces of a diesel blending feedstock separated at 35 °C, 150 bar, and 2 ml min⁻¹ on (A) a bare silica HGS column and (B) a bare titania column coupled to a bare silica HGS column. See Table 1 for column dimensions.

Table 3
Group-type content of diesel samples reported in mass% (RSD, %)

Sample	Column	Saturates	Monoaromatics	Diaromatics	Triaromatics	Polyaromatics
Synfuel	HGS	63.5 (0.1%)	34.7 (0.4%)	1.8 (4%)[a]	0.04 (40%)[a]	–
Synfuel	Ti-HGS	63.5 (0.1%)	34.3 (0.1%)	2.2 (2%)	0.01 (40%)	–
Commercial diesel	HGS	70.1 (0.1%)	24.6 (0.2%)	4.7 (0.6%)[a]	0.5 (7%)[a]	0.09 (26%)
Commercial diesel	Ti-HGS	69.8 (0.1%)	23.5 (0.2%)	5.5 (0.6%)	0.6 (6%)	0.6 (9%)
Blending feedstock	HGS	64.1 (0.1%)	22.7 (0.3%)	11.0 (0.3%)[a]	1.9 (1%)[a]	0.3 (10%)
Blending feedstock	Ti-HGS	65.6 (0.1%)	19.3 (0.3%)	11.8 (0.2%)	2.0 (0.9%)	1.3 (3%)

[a] HGS results ignore 9,10-dihydroanthracene's (diaromatic) elution after triaromatic model compounds.

the HGS column by 10 min, they continue to elute from the titania-HGS column until 50 min.

The diesel group-type results from both columns are compared in Table 3. It should be noted that the di- and triaromatic determinations on the HGS column are somewhat suspect as there was overlap of the model compounds from the two groups on the HGS column (Table 2). For the Synfuel sample, the near baseline resolution on both columns makes the results less sensitive to column choice, yielding similar results (within 0.5 mass%) for both. However, significant differences in the commercial diesel results are observed between the two columns. The mono, di-, and polyaromatic results appear sensitive to column choice due to the lower resolution between group-types. For the diesel blending feedstock, significant differences are observed between the two columns for all of the group-types except the triaromatics.

3.5. Retention time and resolution repeatability

Polar sample components could be irreversibly retained and may alter the column performance over time. For instance, 2-naphthalenethiol was found to be irreversibly retained on Lichrospher silica, titania, and zirconia columns. To determine whether polar compounds in diesels affect titania column performance, the commercial Ontario diesel (350 ppm sulfur) and then the Synfuel diesel (0.4 mass% 2-ethylhexyl nitrate cetane improver, 110 ppm lubricity improver) were injected 100 times each on the titania column. The ASTM performance mixture and anthracene were run about every 20 injections to determine if the column retention characteristics were altered. The RSD of the retention time was 0.1% for hexadecane, 0.3% for toluene, 0.6% for tetralin, 1.0% for naphthalene, and 4.8% for anthracene over the 200 diesel injections. Most of the variation occurred during the first 60 injections of the commercial diesel. The retention time RSD during last 140 injections was less than 0.4% for all five model compounds. Resolution was stable throughout the test with R_s(hexadecane, toluene) = 5.2 (3% RSD) and R_s(tetralin, naphthalene) = 10.6 (2% RSD). The commercial diesel was rerun on the titania-HGS coupled column following the 200 repeat diesel injections. These results were within 0.3 mass% from the original results reported in Table 3 and were not statistically different. This demonstrates titania's applicability to diesel samples with significant amounts of naturally occurring sulfur as well as diesel additives.

4. Conclusions

A titania–silica coupled column was found to provide the highest overall group-type resolutions of the 20 model compounds studied, with the separation of di- and triaromatics proving to be the most difficult. The study of three diesel samples demonstrated that group-type separations become more difficult as the boiling range and PAH content of the diesel samples increase. In turn, results become more sensitive to column choice with heavier samples. While there are no diesel standard reference materials to confirm which column yields the most accurate results, we are more confident in the results produced by the column with the highest group-type resolutions between model compounds.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2005.07.124.

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