

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

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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 CO₂ 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.

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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 increasingly 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-

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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 NH₂-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.

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