

High-Speed Detailed Hydrocarbon Analysis

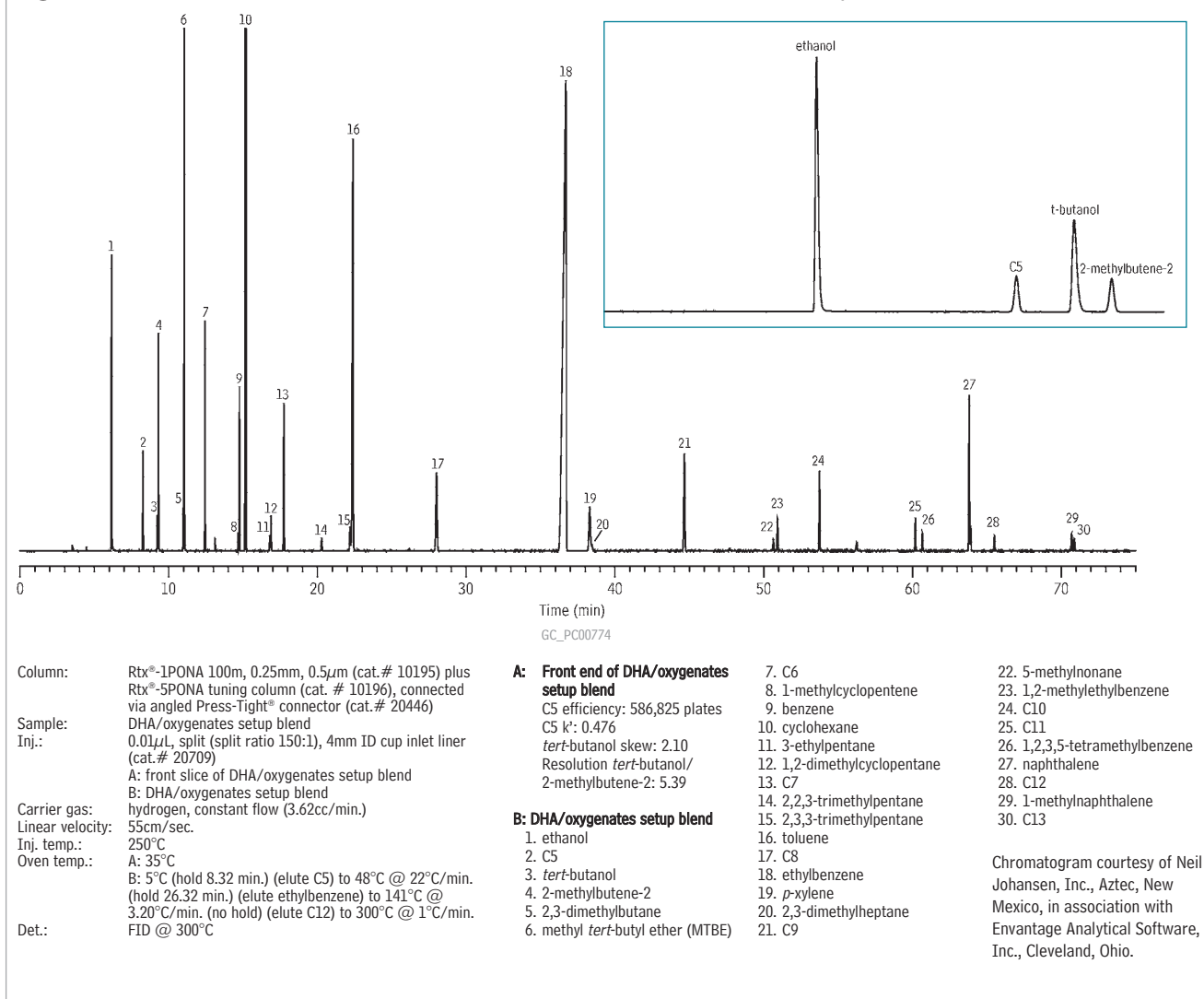
53% Faster Analysis, Using an Rtx®-1 PONA Column and Hydrogen Carrier Gas

By Barry Burger, Petroleum Applications Chemist

- C13 eluted within 70 minutes.
- Excellent response and peak symmetry for polar oxygenates.
- Column meets or exceeds all ASTM D-6730-01 and Canadian General Standards Board method requirements.
- Guaranteed column-to-column reproducibility.

American Society for Testing and Materials method D-6730-01 was designed specifically for determining the individual hydrocarbons in spark ignition fuels and fuel blends containing oxygenates such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-butanol, and ethanol. To maximize the resolution of these complex mixtures, ASTM recommends a 100 meter x 0.25mm ID capillary column with a 0.5µm film of 100% dimethyl polysiloxane stationary phase as the primary analytical column. To control selectivity for the aromatic compounds, a short tuning column, typically 2-3 meters, containing a 5% diphenyl / 95% dimethyl polysiloxane stationary phase, is connected to the inlet of the primary column. To meet the demanding resolution and retention criteria in ASTM method D-6730-01, and in Canadian General Standards Board (CGSB) methodology for detailed hydrocarbon analysis (DHA), Restek Innovations chemists have reformulated our Rtx®-1PONA column.

Figure 1 Rtx®-1PONA column meets ASTM D-6731-01 resolution and retention specifications.



Method D-6730-01 suggests using helium as the carrier gas, at a linear velocity of 24cm/sec. (approximately 2.3mL/min.). The tridecane (C13) retention time this combination yields, approximately 146 minutes, greatly limits sample throughput per day. Our enhanced Rtx®-1PONA column meets or exceeds all criteria in the method, but does so in 30% less time: retention time for C13 is 97 minutes, using helium as the carrier gas.¹ In most applications hydrogen is a better alternative to helium as the carrier gas, because it can be used at much higher linear velocities without compromising critical resolutions.

A revision to ASTM D 6730-01 proposed by Neil Johansen Inc. (Aztec, New Mexico), in association with Envantage Analytical Software Inc. (Cleveland, Ohio), has established optimal DHAX (detailed hydrocarbon analysis—extended) parameters, including specifying hydrogen as the carrier gas. Using these conditions, analysis time is reduced to within 71 minutes (C13)—a 53% reduction versus using helium as the carrier gas. The method also is extended to include middle distillates having final boiling points up to 509°C/948°F (*n*-C38).

Restek provided Neil Johansen Inc. with an enhanced Rtx®-1PONA column (100m x 0.25mm ID x 0.5µm df) and an Rtx® 5PONA tuning column for DHAX method development. The Rtx®-1PONA column was connected to 3 meters of the tuning column through a Universal Angled Press-Tight® Connector (cat.# 20446) and was installed in a PerkinElmer AutoSystem XL GC equipped with a flame ionization detector and programmable pneumatic control. The data system used was ChromPerfect Spirit (Justice Laboratory Software, Denville, NJ). Individual compounds were identified by using Dragon- DHA software, developed by Envantage Analytical Software Inc. in association with Neil Johansen Inc., which uses algorithms to process high-resolution chromatographic data. Processed data for the PONA VI reference standard, containing more than 400 individual components of finished gasoline, can be reviewed on the Restek website: www.restek.com/PONA

The proposed DHAX method was optimized with hydrogen carrier gas at a rate of 3.62mL/min, constant flow, producing a linear velocity of 55cm/sec. The new Rtx®-1PONA column was conditioned in less than two hours, as follows: 35°C for 15 min., to 300°C at 10°C/min., hold 30 min., cool to 35°C. Dead time was adjusted to elute methane at 3.50 ±0.05 min., then a DHA/oxygenates setup blend was introduced into the column to determine the column's suitability for the method.

Figure 1A lists the measured critical criteria. Once established that the column met the method criteria, GC oven program parameters were entered and trial injections of the DHA/oxygenates setup blend were begun. The analysis was permitted to run until *n*-C13 was eluted. Based on the resolutions achieved, the length of the tuning column was reduced incrementally until all critical pairs met D-6730-01 specifications. In this example application, the appropriate tuning column length was 2.36 meters. Figure 1B indicates the critical pairs. The full analysis of the 400-plus component PONA VI reference standard, listing retention indices (RIs) calculated using Dragon-DHA software, is posted on the Restek website.

The benefits of using hydrogen carrier gas for the PONA analysis are obvious: all critical components are resolved, per method D-6703-01, in the greatly reduced time of 70.5 minutes (C13), versus 146 minutes or 97 minutes using helium. Relative to the results anticipated in the method, we virtually doubled sample throughput.

We evaluate each column for film thickness, column efficiency, peak skewness, selectivity, resolution, and bleed to guarantee performance and reproducibility from column to column. The redesigned Rtx®-1PONA column earned Restek chemists the Concluded Research Award at the 2004 Gulf Coast Conference. When you use an Rtx®-1PONA column, we think you'll agree the award was well justified.

Rtx®-1PONA Column (fused silica)

(Crossbond® 100% dimethyl polysiloxane)*

ID	df (µm)	temp. limits	length	cat. #
0.25mm	0.50	-60 to 300/340°C	100-Meter	10195

*Optimized phase for hydrocarbon analysis

Rtx®-5PONA Tuning Column (fused silica)

(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)

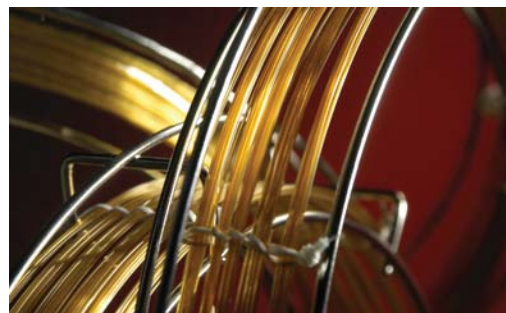
ID	df (µm)	temp. limits	length	cat. #
0.25mm	1.0	-60 to 325°C	5-Meter	10196



Universal Angled Press-Tight® Connectors

- Ideal for connecting a tuning column to an analytical column.
- Inert fused silica.
- Angle reduces strain on the connection.
- Fit all column ODs from 0.33–0.74mm (Restek 0.1mm–0.53mm ID).

5-pk.	25-pk.	100-pk.
Universal Angled Press-Tight® Connectors		
20446	20447	20448
Siltek®-treated Universal Angled Press-Tight® Connectors		
20482	20483	20484



Reference

1. Stidsen, G. and B. Burger, *Enhanced Rtx®-1PONA Column Improves Detailed Hydrocarbon Analysis*, Restek Advantage 2005v1: 12 (2005).

for more info!

Processed data for the PONA VI reference standard, containing more than 400 individual components of finished gasoline, can be reviewed on the Restek website: www.restek.com/PONA

please note

To achieve critical resolutions in detailed hydrocarbon analysis, a 5-meter 5% diphenyl/ 95% dimethyl polysiloxane tuning column (Rtx®-5PONA) is connected to the analytical column and adjusted to the needed length through a series of trial analyses.