Higher DHA Sample Throughput for PONA Analysis: Options for Helium and Hydrogen

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Accurate information about the concentrations of the individual components in gasolines is critical for evaluating raw materials and controlling refinery processes. A high-resolution GC method for detailed hydrocarbon analysis (DHA) of gasolines is outlined in American Society of Testing and Materials (ASTM) Method D6730-01—often referred to as the PONA (paraffins, olefins, naphthenes, aromatics) or PIANO (paraffins, isoparaffins, aromatics, naphthenes, olefins) analysis. ASTM D6730-01 is specific for the analysis of these hydrocarbon components, plus oxygenated additives such as methanol, ethanol, tert-butanol, methyl tert-butyl ether (MTBE), and tert-amyl methyl ether (TAME) in spark-ignition engine fuels.

Historically, columns for PONA analysis have had several challenges, primarily centering on inertness and selectivity. Highly inert columns are required for the accurate analysis of polar compounds and inadequately deactivated columns result in poor peak symmetry and unpredictable retention times (*Figure 1*). Similarly, developing columns with adequate selectivity for resolving key aromatics such as benzene, toluene, and p-xylene has also been difficult. Both of these issues have been critical to overcome as they prevent accurate quantitative analysis and reduce the precision with which refineries can control blending.

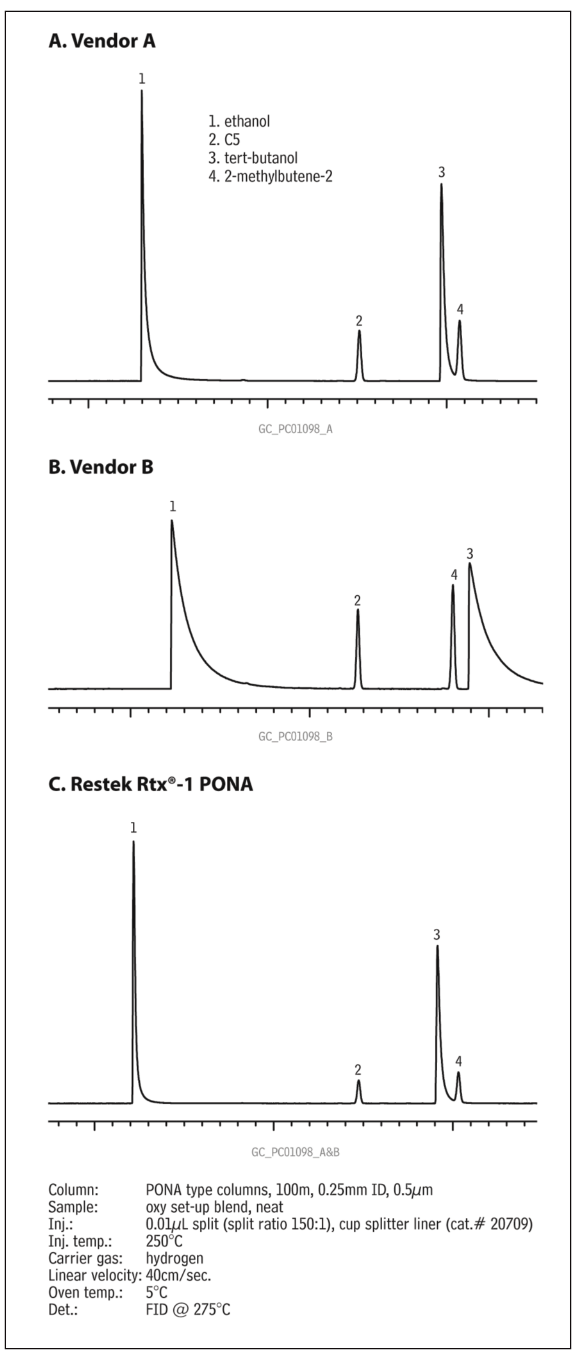


Figure 1 Rtx®-1 PONA columns are highly inert, resulting in sharp oxygenate peaks eluting at predictable retention times.

Restek has worked in a long-term collaboration with Neil Johansen, one of the original PONA method developers, to engineer a selective and highly inert PONA column that meets or exceeds all ASTM D6730-01 and Canadian General Standards Board (CGSB) requirements. This column, the Rtx®-1 PONA, has the additional benefit of being highly robust. It can be used with either helium under an accelerated temperature program, or with hydrogen carrier gas, providing two options for significantly increasing sample throughput without compromising chromatographic performance.

33% Faster Run Times Using Helium under Optimised Conditions

The Rtx®-1 PONA column is a 100m x 0.25mm ID capillary column coated with 0.5µm of 100% dimethyl polysiloxane stationary phase, as recommended in D6730-01. The method sets criteria for efficiency and capacity (both based on C5), t-butanol peak symmetry, and t-butanol/2-methylbutene-2 resolution. As shown in *Figure 2*, Rtx®-1 PONA columns meet or exceed all method criteria and show exceptional peak symmetry for polar oxygenates. Sharp, symmetric peaks mean maximum response and stable, predictable retention time positions for the eluting alcohols. Since Rtx®-1 PONA columns are individually tested for peak symmetry and retention (as well as efficiency, selectivity, resolution, and bleed), consistent performance is assured. The reliable inertness of these columns results in near symmetric oxygenate peaks, which in turn give more accurate quantitative results and allow refiners to make better decisions in the blending process.

In addition to reliable inertness, Rtx®-1 PONA columns have the required selectivity to adequately resolve all critical pairs as measured using an oxy set-up blend. Here, it is important to note that the high thermal stability of these columns has a significant benefit: it allows a more aggressive temperature program to be used with minimal bleed, resulting in separation of all critical pairs in 33% faster run times, compared to the standard method conditions (Table I). This allows refinery labs to significantly increase DHA sample throughput, while assuring separation of all critical pairs.

	Standard D6730 conditions	Optimised D6730 with helium*	Optimised D6730 with hydrogen*
Approximate analysis time	146 min.	98 min.	72 min.
% Time savings (relative to standard method conditions)	---	33% faster	51% faster

Table I Rtx®-1 PONA columns are highly stable and can be run under accelerated conditions to increase sample throughput.

** Optimised method conditions for helium and hydrogen are shown in Figures 2 and 3, respectively.*

51% Faster Run Times with Proposed Hydrogen Method

While D6730-01 specifies helium as the carrier gas, hydrogen is a better alternative because it can be used at higher linear velocities without compromising critical separations. For DHA analysis, using hydrogen as the carrier gas offers three distinct advantages over helium: (1) it can be used at twice the linear velocity, (2) it increases column longevity by eluting high molecular weight compounds at lower temperatures, and (3) it is less expensive and more readily available. Despite these advantages, some labs have reservations regarding the safety of using hydrogen. In fact, with basic precautions, hydrogen can be used safely and reliably, particularly when hydrogen generators are used instead of free-standing cylinders.[1,2]

Restek has developed a new DHA method to take advantage of the benefits of hydrogen. As shown in *Figure 3*, all critical components are resolved using this method, but in the greatly reduced run time of 72 minutes, versus 146 minutes or 98 minutes using helium. This 51% savings in analysis time has the potential to virtually double sample throughput. Restek has submitted this proposed DHA method based on hydrogen to ASTM where it is currently under review.

Conclusion

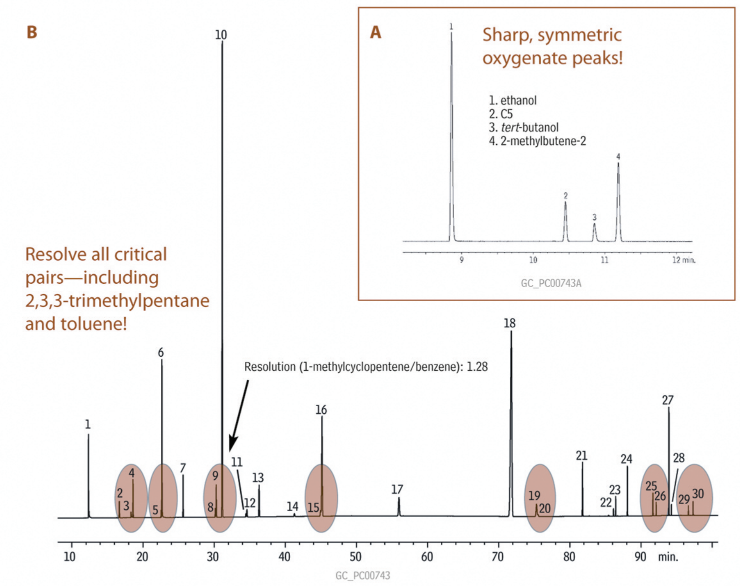
Restek Rtx®-1 PONA columns are individually tested and stringently controlled for retention, efficiency, peak symmetry, selectivity, resolution, and bleed. These columns meet or exceed all ASTM D6730-01 and CGSB method requirements and display excellent peak symmetry for polar oxygenates and reliable separation of all critical pairs.

This allows users to obtain more correct and consistent data, especially for oxygenate content. Additionally, the robustness of these columns allows them to be used with either helium under accelerated temperature conditions or with hydrogen, resulting in 33% or 51% faster analysis times respectively. These columns offer significant performance gains, allowing refinery labs to process samples faster and make more profitable decisions during product blending.

References

(1) J.V. Hinshaw, LC-GC November (2008) 1100.

(2) P. Froehlich, Lab Manager Magazine February (2007) 17.

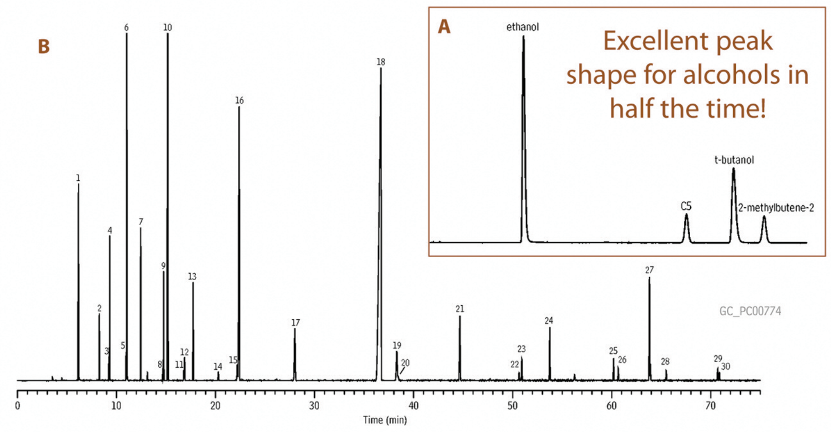


Column:	Rtx®-1PONA, 100m, 0.25mm ID, 0.5µm (cat.# 10195) w/ Rtx®-5 PONA tuning column, 2.62m, 0.25mm ID, 1.0µm, connected via Press-Tight® connector (cat.# 20446)
Sample:	custom detailed hydrocarbons analysis (DHA) mix, neat
Inj.:	0.01µL, split (split ratio 150:1), 4mm cup inlet liner (cat.# 20709) A: Front end of DHA/oxygenates setup blend B: DHA/oxygenates setup blend
Inj. temp.:	200°C
Carrier gas:	helium, constant flow
Linear velocity:	28cm/sec. (2.3mL/min.)
Oven temp.:	A: 35°C B: 5°C (hold 15 min.) to 50°C @ 5°C/min. (hold 50 min.) to 200°C @ 8°C/min. (hold 10 min.)
Det.:	FID @ 250°C
Cooling gas.:	liquid nitrogen

A: Front end of DHA/oxygenates setup blend
Efficiency (C5): 613,596 plates
K' (C5): 0.489
Asymmetry (*tert*-butanol) : 1.25
Resolution (*tert*-butanol/ 2-methylbutene-2): 5.60

B: DHA/oxygenates setup blend
1. ethanol
2. C5
3. *tert*-butanol
4. 2-methylbutene-2
5. 2,3-dimethylbutane
6. methyl *tert*-butyl ether (MTBE)
7. C6
8. 1-methylcyclopentene
9. benzene
10. cyclohexane
11. 3-ethylpentane
12. 1-*tert*-2-dimethylcyclopentane
13. C7
14. 2,2,3-trimethylpentane
15. 2,3,3-trimethylpentane
16. toluene
17. C8
18. ethylbenzene
19. *p*-xylene
20. 2,3-dimethylheptane
21. C9
22. 5-methylnonane
23. 1,2-methylethylbenzene
24. C10
25. C11 (undecane)
26. 1,2,3,5-tetramethylbenzene
27. naphthalene
28. C12 (dodecane)
29. 1-methylnaphthalene
30. C13 (tridecane)

Figure 2 Critical pairs of gasoline components are reliably resolved per ASTM specifications 33% faster using helium under optimized conditions.



Column:	Rtx®-1PONA 100m, 0.25mm ID, 0.5µm (cat.# 10195) plus Rtx®-5PONA tuning column (cat.# 10196), connected via angled Press-Tight® connector (cat.# 20446)
Sample:	DHA/oxygenates setup blend
Inj.:	0.01µL, split (split ratio 150:1), 4mm ID cup inlet liner (cat.# 20709) A: front slice of DHA/oxygenates setup blend B: DHA/oxygenates setup blend
Carrier gas:	hydrogen, constant flow (3.62cc/min.)
Linear velocity:	55cm/sec.
Inj. temp.:	250°C
Oven temp.:	A: 35°C B: 5°C (hold 8.32 min.) (elute C5) to 48°C @ 22°C/min. (hold 26.32 min.) (elute ethylbenzene) to 141°C @ 3.20°C/min. (no hold) (elute C12) to 300°C @ 1°C/min.
Det.:	FID @ 300°C

Chromatogram courtesy of Neil Johansen, Inc., Aztec, New Mexico, in association with Envantage Analytical Software, Inc., Cleveland, Ohio.

A: Front end of DHA/oxygenates setup blend
Efficiency (C5): 586,825 plates
K' (C5): 0.476
Asymmetry (*tert*-butanol): 2.10
Resolution (*tert*-butanol/ 2-methylbutene)-2: 5.39

B: DHA/oxygenates setup blend
1. ethanol
2. C5
3. *tert*-butanol
4. 2-methylbutene-2
5. 2,3-dimethylbutane
6. methyl *tert*-butyl ether (MTBE)
7. C6
8. 1-methylcyclopentene
9. benzene
10. cyclohexane
11. 3-ethylpentane
12. 1,2-dimethylcyclopentane
13. C7
14. 2,2,3-trimethylpentane
15. 2,3,3-trimethylpentane
16. toluene
17. C8
18. ethylbenzene
19. *p*-xylene
20. 2,3-dimethylheptane
21. C9
22. 5-methylnonane
23. 1,2-methylethylbenzene
24. C10
25. C11
26. 1,2,3,5-tetramethylbenzene
27. naphthalene
28. C12
29. 1-methylnaphthalene
30. C13

Figure 3 Increase sample throughput—cut analysis times in half without compromising resolution by using hydrogen instead of helium.