Detailed Hydrocarbon Analysis in Spark Ignition Fuels by ASTM D6730-1 with an Agilent Inert Flow Path

Application Note

Energy & Fuels

Authors

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Abstract

Spark ignition engine fuels contain a highly complex mixture of hydrocarbons. Blends include oxygenates such as ethanol, MTBE, ETBE, and t-butanol. These components can be problematic when using ASTM-6730-01 for detailed hydrocarbon analysis, which incorporates the use of a connected tuning column, such as Agilent J&W HP-5ms, in the flow path. The use of an Agilent Ultimate Union with SilTite fittings, in conjunction with Agilent J&W HP-1 PONA or Agilent J&W CP-Sil PONA CB GC columns, provides guaranteed resolution. All critical pairs are resolved, including 2,3,3-trimethylpentane and toluene. Peak symmetry is exceptional, even for alcohols, and installation is worry-free. These Agilent J&W GC columns and simple-to-use fittings meet or exceed all ASTM D6730-01 and Canadian General Standards Board CAN/CGSB 3.0 No. 14.3-99 requirements for detailed hydrocarbon analysis, providing a highly inert flow path with no reactive surfaces.

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Introduction

ASTM D6730-01 [1] and Canadian General Standards Board CAN/CGSB 3.0 No. 14.3-99 are two standard methods for detailed hydrocarbon analysis (DHA). Traditionally, choosing columns and connecting fittings for DHA has been challenging, primarily centering on issues of inertness and selectivity. Highly inert columns are required for chromatography of polar compounds with an active hydroxyl group [2], and potentially reactive surfaces in the flow path can result in poor peak symmetry. Additionally, spark ignition engine fuel mixtures injected neat on-column require a 2 to 5 m tuning column of 5% phenyl methyl-siloxane to provide adequate selectivity to separate closely eluting critical pairs such as 2,3,3-trimethylpentane and toluene. Both of these issues have to be overcome as they hinder accuracy and consume time, leading to slower turnaround and reduced precision. Petroleum refining operations need to control blending decisions and product release for distribution channels. Having robust, reliable tools to chromatograph reactive oxygenates enables a laboratory to identify potential instances where line contaminants from inadvertent transfers can lead to disruption and damage to sensitive catalysts or fuel delivery equipment. As an added benefit, suppliers can further safeguard against product liability related to future oxygenate blends such as E15 [3].

Analysis times can be improved significantly by switching to hydrogen as the carrier gas (as much as 20% less time than helium) with no loss in chromatographic performance [4]. J&W HP-1 PONA and J&W CP-Sil PONA CB GC columns meet or exceed all criteria in the standard methods in less time when using hydrogen. These benefits, combined with lower cost, can provide a laboratory with a significant gain in productivity. By leveraging Agilent 6890N GC safety features, including hydrogen carrier shutoff and flame-out shutoff, as well as the gas saver feature to reduce exposure, no unsafe practices are needed. All that is required is to properly vent the split flow so that hydrogen cannot exceed LEL levels in enclosed areas.

Materials and Methods

An Agilent 6890N GC/FID equipped with an Agilent 7683B Automatic Liquid Sampler was used for this series of experiments.

Conditions

Tuning column:	Agilent J&W HP-5ms 15 m × 0.25 mm, 1.0 µm (trimmed to 5 m) (p/n 19091S-231)
Column 2:	Agilent J&W HP-1 PONA, 100 m × 0.25 mm, 0.5 µm (p/n 19091Z-530)
Column 2 (alternative):	Agilent J&W CP-Sil PONA CB, 100 m × 0.25 mm, 0.5 µm (p/n CP7530)
Sample:	Oxy set-up evaluation mix, ASTM D6730 SCE
Carrier:	Hydrogen 38 cm/s, 2.0 mL/min constant flow mode
Oven:	30 °C (hold 8.5 minutes), to 48 °C at 22 °C/min (hold 27 minutes), to 141 °C at 3 °C/min (hold 1 minute), to 275 °C at 1 °C/min (hold 2 minutes)
Inlet temperature:	200 °C
Detector:	FID, 275 °C
GC:	Agilent 6890N Network GC system
Sampler:	Agilent 7683B Automatic Liquid Sampler, 0.5 µL syringe, 0.01 µL neat with split injection 150:1

Flow path supplies

Vials:	Amber screw cap (p/n 5182-0716)
Caps:	Blue screw cap (p/n 5282-0723)
Vial inserts:	100 µL glass/polymer feet (p/n 5181-1270)
Syringe:	0.5 µL (p/n G4513-80229)
Septum:	Advanced Green (p/n 5183-4759)
Inlet liner:	Dual taper direct connect, deactivated (p/n G1544-80700)
Union kit:	Agilent Ultimate Union, deactivated (p/n G3182-61580)
Swaging wrench:	(p/n G2855-60200)
Magnifier:	20× magnifier (p/n 430-1020)

Results and Discussion

Figure 1 demonstrates the ability of Agilent J&W PONA GC columns and Agilent flow path inert connectors to provide peak shapes that meet or exceed the method criteria. Looking at Figure 2 closely, it is clear that the resolution of one particular critical pair (2,3,3-trimethylpentane/toluene) allows the most challenging separations to be achieved in this evaluation mix. The peak symmetry of the light alcohol oxygenates ethanol and t-butanol is seen in Figure 3. Table 1 provides further evidence that Agilent inert flow path supplies deliver the required performance to combat peak asymmetry or changes in selectivity and elution order.

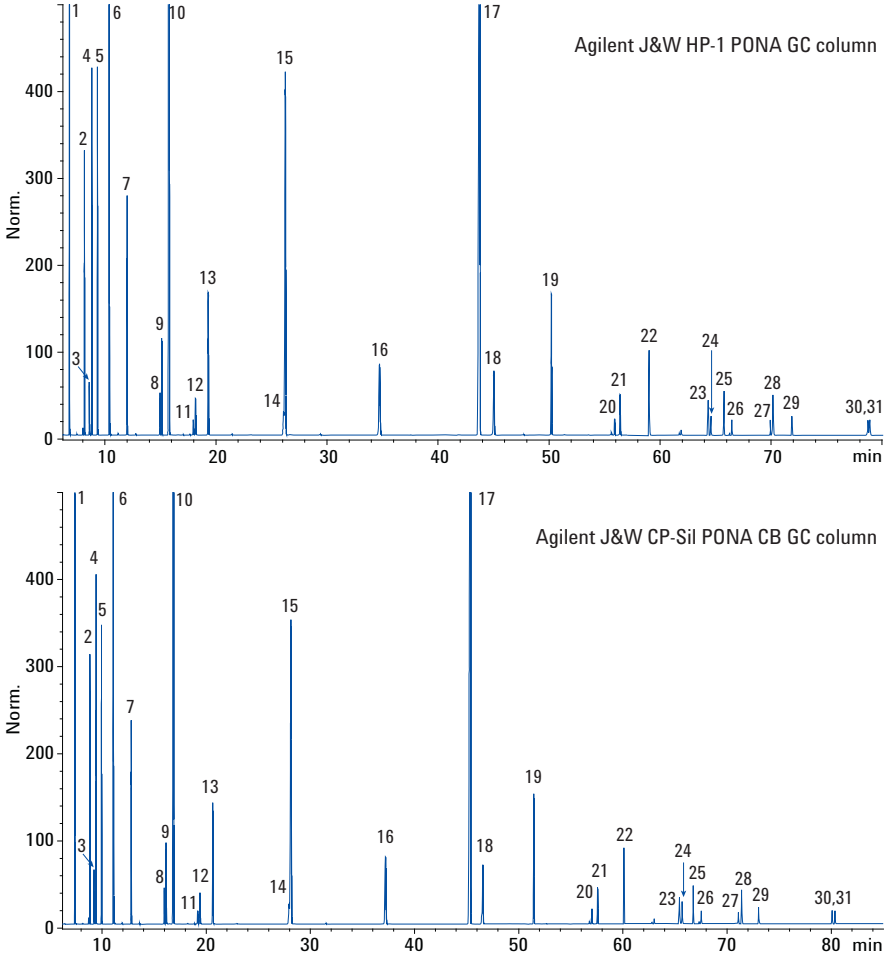

Figure 1. 31-component spark ignition engine fuel test mix with critical pairs resolved on both the Agilent J&W HP-1 PONA and Agilent J&W CP-Sil PONA CB GC columns, 100 m, with a 4 m Agilent J&W HP-5ms tuning column, Ultimate Union connector, and SilTite ferrules.

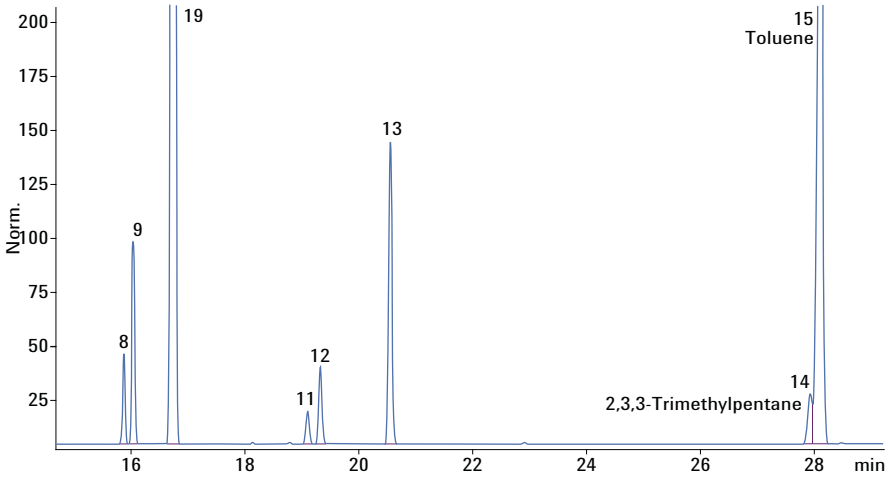

Figure 2. Separation of critical pair 2,3,3-trimethylpentane from toluene on an Agilent J&W CP-Sil PONA CB GC column.

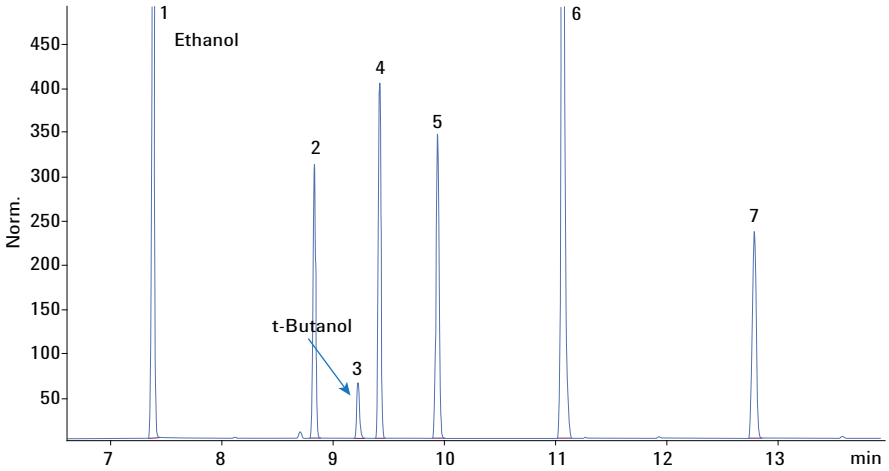

Figure 3. Peak symmetry of light alcohols on an Agilent J&W CP-Sil PONA CB column.

The presence of oxygenates in the test blend allows for a valid comparison to more complex spark ignition engine fuels and shows clearly that Agilent J&W PONA GC columns exhibit exceptional peak symmetry. The calculated symmetry is well within method guidelines and should permit accurate peak integration. The incorporation of the Ultimate Union kit and its associated SilTite ferrules provides confidence that these connectors are properly deactivated and highly inert to fuel components. This allows for more accurate and reliable calculations of oxygenate content and delivers confidence in measurement accuracy for future blends such as E15.

To assess the usefulness of hydrogen as a carrier gas to meet method criteria and deliver shorter chromatographic run times, the identical test mix used to evaluate columns with helium as the carrier was injected on HP-1 PONA and CP-Sil PONA CB GC columns. Hydrogen was plumbed to the GC carrier inlet lines. Figure 1 shows that the system eluted the last critical pair at approximately 78 minutes, versus 96 minutes with helium as the carrier. Time saved on this long run per injection was approximately 18 minutes, or 25%. To provide useful comparisons between different columns, a unified mixture of components was used, as was a neat injection volume to avoid retention drift due to dilution solvent loading [5].

Peak number	Name	Symmetry	Selectivity
1	Ethanol	0.88	1.01
2	C5	0.96	1.20
3	*tert*-Butanol	0.71	1.04
4	2-Methylbutene-2	0.96	1.02
5	2,2-Dimethylbutane	0.93	1.06
6	2,3-Dimethylbutane	0.76	1.11
7	Methyl *tert*-butyl ether (MTBE)	0.97	1.16
8	C6	0.97	1.25
9	1-Methylcyclopentene	0.97	1.01
10	Benzene	1.11	1.04
11	Cyclohexane	0.98	1.14
12	3-Ethylpentane	0.95	1.01
13	1- *tert*-2-Dimethylcyclopentane	0.96	1.06
14	C7	1.29	1.36
15	2,3,3-Trimethylpentane	1.01	1.01
16	Toluene	0.99	1.32
17	C8	1.44	1.22
18	Ethylbenzene	1.23	1.03
19	p-Xylene	0.89	1.00
20	2,3-Dimethylheptane	1.01	1.11
21	C9	0.97	1.11
22	5-Methylnonane	0.97	1.01
23	1,2-Methylethylbenzene	1.00	1.04
24	C10	0.95	1.09
25	C11 (undecane)	0.92	1.00
26	1,2,3,5-Tetramethylbenzene	1.02	1.02
27	Naphthalene	0.97	1.01
28	1,3-di-n-Propylbenzene	0.97	1.06
29	C12 (dodecane)	0.99	1.02
30	1-Methylnaphthalene	1.00	1.10
31	C13 (tridecane)	0.92	1.00

Table 1. Components and their associated peak symmetry factors and selectivity for spark ignition engine fuels. Asymmetry at 10% peak height A_s = B/A (A= width of peak, front to center dropline, B = width of peak, center dropline to back of peak). Selectivity calculated by Agilent ChemStation software.

Conclusions

Spark ignition gasoline blends are complex mixtures of hydrocarbons that in the past have been difficult to analyze because of the presence of active oxygenates. However, it is now possible to construct an extremely inert flow path by using Agilent J&W HP-1 PONA and CP-Sil PONA CB GC columns, Ultimate Unions, and SilTite fittings. This arrangement delivers successful analysis of detailed hydrocarbons, with exceptional selectivity, peak symmetry and critical pair resolution.

References

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