APPLICATION NOTE

Gas Chromatography

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Fast Detailed Hydrocarbon Analysis by Modified ASTM Method D6730

Introduction

Detailed hydrocarbon analysis (DHA) is a technique utilized by refineries and contract laboratories to separate and identify individual compounds and determine the bulk hydrocarbon group type composition (PONA – Paraffins, Olefins, Naphthalenes and Aromatics) of gasoline and other fuels in the C_1 to n-C_{13} hydrocarbon range (up to a boiling-point range of 225 °C).

The complexity of the sample analysis requires a long column, a precolumn specific to aromatics, and a series of temperature-programming ramps to effectively resolve peaks. Due to this complexity, analysis times of the unmodified method can easily extend past 120 minutes, limiting the number of runs achievable on a daily basis and the efficiency of each gas chromatograph (GC).

DHA analyte identification is based on retention indices (RI), which are established on the elution times of normal hydrocarbon paraffins. Analytes are identified based on their locations relative to these normal hydrocarbon paraffins.

The process of creating an accurate DHA instrument requires tuning the column and instrument conditions to replicate the relative retention time, RI, and elution order of the established RI libraries. DHA utilizes a flame ionization detector (FID) – thus analyte confirmation is based on the retention indices. Without accurate and reproducible retention indices, analytes can be mislabeled and their PONA ratios could be erroneous. Creating a method with RI values as close as possible to those established by ASTM® will ensure the best results.

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This application note presents a modified method designed to dramatically reduce the time required for analysis, while meeting the quality criteria of the ASTM® method D6730. The improvements related to this method are achieved by modifying the carrier gas, the temperature ramps and the precolumn length, which will shorten the run time of the method to approximately 70 minutes. Improvements related to the overall throughput encompass not only the analysis run time but also the time needed for the oven to cool down and the time needed for pre-run events. Presented are the detailed conditions used to achieve this throughput improvement, examples of critical separations, and discussion of retention-index difference between the current ASTM® method and the Fast DHA method.

Conditions

The PerkinElmer® Clarus® 680 Gas Chromatograph (GC) is the platform for the Model Arnel 4050 DHA Analyzer presented in this application note. A detailed summary of the analytical conditions are presented in Table 1. It is important to note that this application is performed on a specially configured and guaranteed solution.

Table 1. **Conditions Used for Fast DHA Analysis.**

Chromatograph	PerkinElmer Clarus 680 GC
Primary Column	100 m x 0.25 mm x 0.5 µm PONA (100% dimethylpolysiloxane)
Precolumn	1.5 m to 2.5 m (variable) x 0.25 mm x 0.5 µm (5% phenyl/95% dimethylpolysiloxane)
Autosampler	0.5 µL syringe, injection volume 0.2 µL, slow injection speed
Oven	5 °C for 1.50 min, then 22.0 °C/min to 48 °C , hold for 29.0 minutes (retention time of ethylbenzene), then 3.8 °C/min to 150 °C, hold for 10.70 min.
Injector	Programmable split/splitless (PSS) 1:150 split, isothermal at 250 °C.
Carrier	Hydrogen, constant pressure, 40 psig
Detector	Flame ionization (FID) at 250 °C Air = 450 mL/min H_2 = 45 mL/min Range x1 Attenuation x32
Cryogenic Oven Cooling	Liquid nitrogen
Data Handling System	PerkinElmer TotalChrom® CDS
DHA Identification System	PerkinElmer Dragon DHA™ Software

The Clarus 680 GC oven was designed to have a low thermal mass, and with its unique fan system rapidly cools the oven to ambient temperature. As a result, the cryogen is introduced at a lower temperature. This not only greatly reduces the amount of cryogen required, but also brings the GC ready in as little as 3 minutes. By configuring the Clarus 680 to have the autosampler pre-rinse the syringe before the GC is ready, the non-productive time between analyses is further shortened, creating a less than 4-minute time between injections.

Tuning the Application

The application is tuned to meet specific critical and key separations. This is achieved by adjusting the precolumn length and modifying the oven-temperature ramps. These criteria are discussed in depth within the ASTM® method.

- **Precolumn Tuning –** the carrier gas was switched to hydrogen, which is less dense and has a higher optimal linear velocity; as a result, the effect of the precolumn was amplified. A typical precolumn length with helium carrier gas was determined to be between 3.0 and 4.0 meters. Hydrogen carrier gas results in an optimal precolumn length of about half that.
- **Temperature-Ramp Tuning –** in order to achieve separation of key analytes, subambient cooling is required. Precise optimization of temperature ramps and hold times allows resolution and identification of all analytes of interest.
- **Critical Separations –** there are a number of critical separations in this method. The following examples will show that the fidelity of these was maintained in the high-speed method discussed here.
  - **i-butane/methanol and ethanol/3-methylbutene-1 –** these key separations represent the initial separations influenced by the cryogenic starting temperature. As you can see in Figure 1, both critical pairs of analytes are fully resolved.

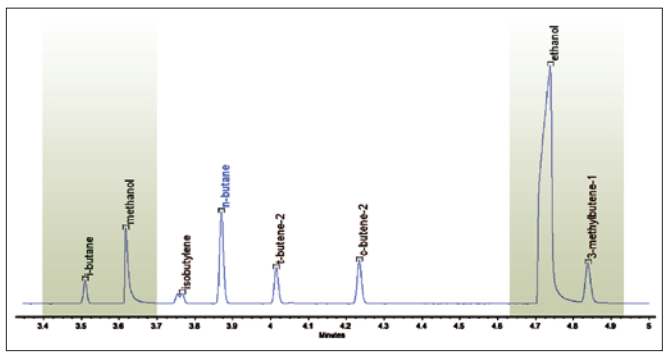

Figure 1. Demonstration of the early-eluting critical pairs easily influenced by the starting temperature of the GC oven program.

– **i-propanol/2-methylbutene-1 and t-butanol/2-methylbutene-2 –** these separations are used to confirm the performance of the column with respect to oxygenate selectivity. Columns from different manufacturers have slightly different selectivity towards oxygen. Thus, the retention times for alcohols will vary slightly (Figure 2). As long as these critical pairs are resolved, the analysis is valid.

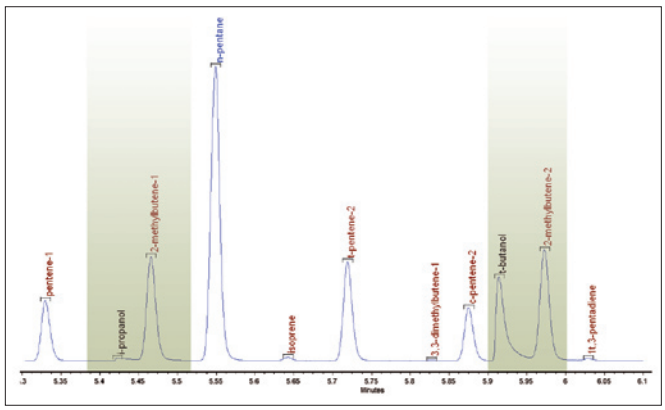

Figure 2. Demonstration of the performance of the column with respect to oxygenate selectivity.

– **2,3-dimethylbutane/methyl-t-butylether –** this separation is very temperature dependent; it can be manipulated by changing the isothermal plateau at 5 °C. The hold time at 5 °C is used to center the methyl-t-butylether between 2,3-dimethylbutane and 2-methylpentane, as seen in Figure 3.

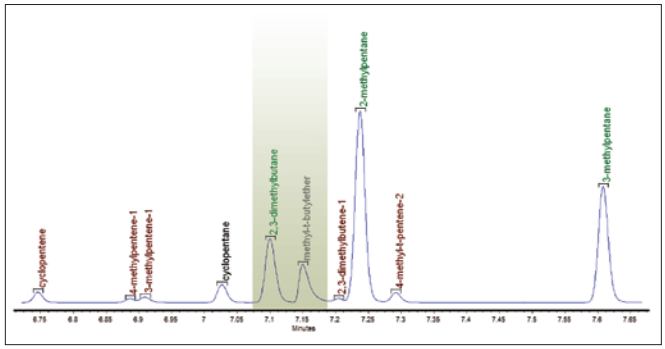

Figure 3. Demonstration of elution migration on methyl-t-butylether by manipulating the isothermal plateau time.

– **1-methylcyclopentene/benzene –** this key separation demonstrates the column selectivity, as well as the effect of the precolumn for retaining aromatics. A baseline separation is desirable, but not necessary. This separation (Figure 4) determines the minimum length of the precolumn – otherwise, these two analytes coelute.

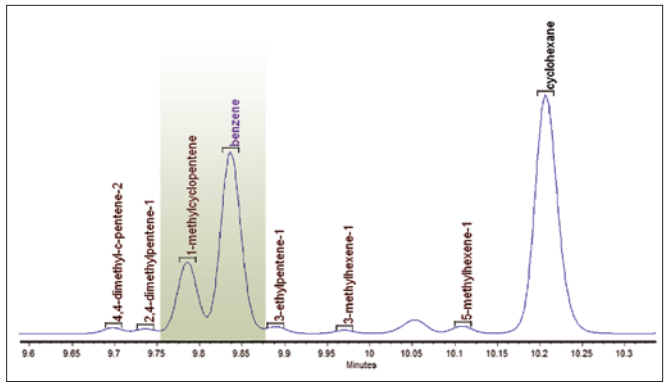

Figure 4. Demonstration of the precolumn effect on aromatics. This separation determines the minimum length of the precolumn.

– **2,3,3-trimethylpentane/toluene –** this separation again validates the length and selectivity of the precolumn. Resolution of 2,3,3-trimethylpentane from toluene (Figure 5) is primarily dependant on the length of the precolumn used.

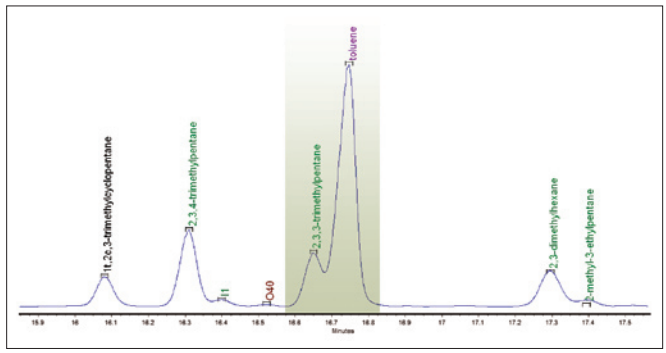

Figure 5. Demonstration of the precolumn effect on aromatics.

– **p-xylene/2,3-dimethylheptane –** this key separation will determine the maximum length of the precolumn. If the precolumn is too long, the p-xylene (1,4-dimethylbenzene) peak will coelute with 2,3-dimethylheptane (Figure 6).

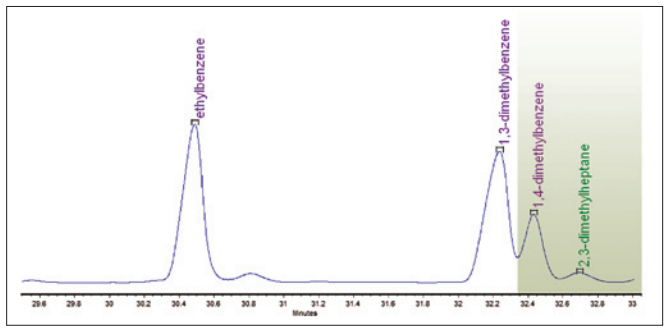

Figure 6. Demonstration of the precolumn effect on aromatics. This separation determines the maximum length of the precolumn.

– **I17/1,2-methylethylbenzene –** the isoparaffin (I17) should be resolved from the aromatic 1,2-methylethylbenzene. This separation is dependent on the ramp rate of the final step in the temperature of the program. If this peak is unresolved, increase the final temperature rate until the peak is resolved, as demonstrated in Figure 7.

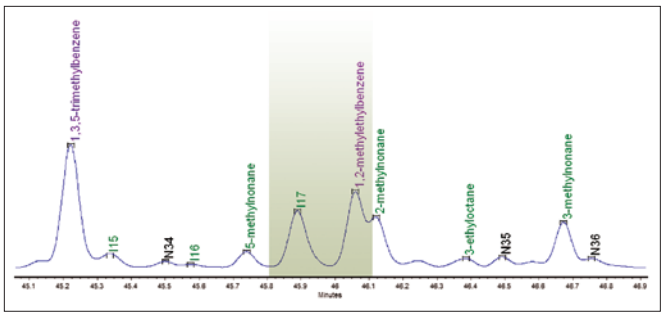

Figure 7. Demonstration of the effect the temperature ramp has on the elution time of the isoparaffin I17.

– **1-methylnaphthalene/tridecane –** this is the last key separation (Figure 8). This separation, like that of isoparaffin (I17) and 1,2-methylethylbenzene, is also dependent on the rate of the final temperature program. However, unlike the previous critical pair, a rate which is too high will cause co-elution. Decreasing the ramp rate by increments of 0.1 °C/min will help resolve this peak, if necessary. If the peaks coelute regardless of the temperature drop, it may be necessary to further shorten the precolumn. Be aware that shortening the precolumn by very small increments (5 cm) can result in substantial migration of the 1-methylnaphthalene peak, as the precolumn effect is magnified at the end of the run.

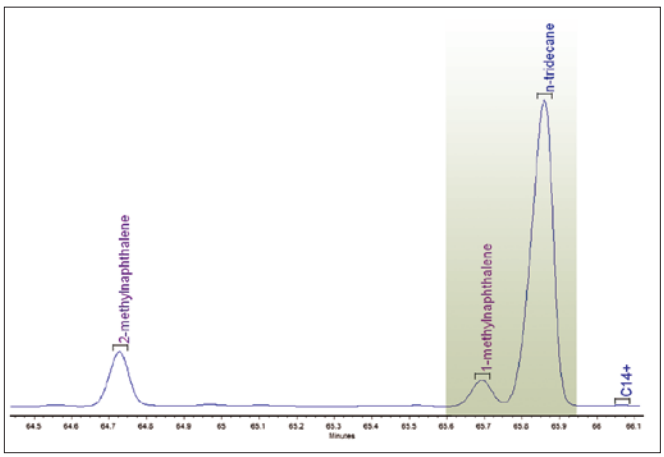

Figure 8. Demonstration of the dual effect of precolumn length and temperature ramp.

By modifying the temperature ramp, switching the carrier gas and retuning the precolumn, we have met all the separation criteria established with the ASTM® method D6730 and reduced the run time to less than 70 minutes. For retention index (RI) libraries to hold valid and reliable information, any RIs generated should have a low deviation from published values. Results in Table 2 show the difference between the RIs generated in the method presented here and the published ASTM® values for key compounds.

***Table 2.* Differences Between Retention Indexes Generated in the PerkinElmer Fast DHA Method and the Published ASTM® Values for Key Compounds.**

	Retention Index		
Compound	**ASTM® RI**	**PerkinElmer RI**	**Difference**
n-pentane	**500.00**	**500.00**	–
2,3-dimethylbutane	563.74	569.24	5.5
n-hexane	**600.00**	**600.00**	–
1-methylcyclopentene	646.77	648.71	1.94
benzene	648.90	649.92	1.02
cyclohexane	656.83	657.81	0.98
2,2,4-trimethylpentane	687.05	688.48	1.43
n-heptane	**700.00**	**700.00**	–
toluene	752.59	751.77	0.82
n-octane	**800.00**	**800.00**	–
ethylbenzene	854.60	854.65	0.05
n-nonane	**900.00**	**900.00**	–
n-decane	**1000.00**	**1000.00**	–
n-undecane	**1100.00**	**1100.00**	–
1,2,3,5-tetramethylbenzene	1109.00	1108.79	0.21
naphthalene	1168.54	1168.01	0.53
n-dodecane	**1200.00**	**1200.00**	–

Most software libraries allow for subtle difference in RI location – generally by a ± of 3 index numbers. As more index numbers fall outside of this window, they need to be manually updated which requires verification from a multicomponent standard, such as a complete PONA mixture. Even then, by adjusting the RI for known compounds, the relative indexing for those compounds not included in the mix becomes increasingly less reliable. Therefore, by adhering as closely as possible to the standard – or unmodified – RI library, the user can confirm the library faster, do less manual adjustment to the RI tables, and have a higher degree of certainty in the identification, ultimately achieving a more accurate PONA.

Conclusion

The combination of the technology of the Clarus 680 GC and optimized method parameters shown above will significantly improve throughput in this detailed hydrocarbon analysis. This equates to:

- Double the number of runs per day (19.5 runs vs. 9 runs)
- 73 extra runs per week (136 runs vs. 63 runs)
- 3,814 extra runs per year (7,099 runs vs. 3,285 runs)

In addition to productivity, cost savings are significant by switching from helium to hydrogen. The laboratory can also generate hydrogen as needed onsite with a hydrogen generator, eliminating the need to use and interact with high-pressure cylinders. The rapid cool-down to ambient means a lower starting point for cryogens, again reducing cost of the analysis and the amount of cryogen needed. The modified temperature ramp reduces the final oven temperature from the original method, requiring less energy and indirectly extending the column lifetime. Additionally, the lower final temperature yields less thermal output which potentially reduces the HVAC load of the laboratory facility.

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