AC DHA according to ASTM D6730

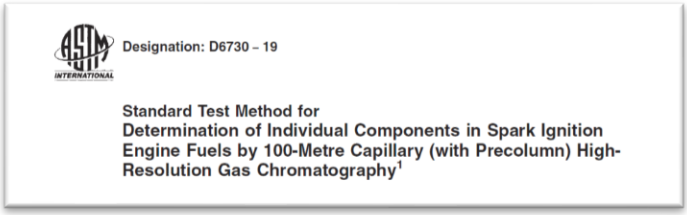
- Safe valuable time with pre-tuned and validated ASTM D6730 application
- AC DHA^{xlnc} software includes calculation of critical parameter
- Tuned to guarantee the critical separations
- Includes optimization for oxygenates

Keywords: DHA, ASTM D6730, column evaluation, critical separations

Introduction:

Gasoline is consumed by most passenger cars and is often the primary product produced by refineries. Knowledge of the individual component composition of the gasoline, or its feedstocks, is therefore of great value to the producers. It is information that allows operators to optimize the various processes and guarantee the final product specification.

GC analysis of gasoline or its feedstock products separates and identifies individual components found in the product and quantifies the amount of each component. Several applications are available to detect and quantify most paraffin, naphthene, olefin and aromatic isomers as well as the presence of specific components such as oxygenates that are currently blended into the gasoline. One of them is described by ASTM D6730.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Standard Test Method for
Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography[1]

AC Analytical Controls offers, as part of its comprehensive analyzer portfolio, an application that fully meets all the requirements of the ASTM D6730 method. Each analyzer is set up, tuned, calibrated and validated in the AC factory to meet the requirements such as retention factors, column efficiency, resolution control, etc. Thereby saving valuable time for the laboratory, the analyzer can be utilized from day one after the installation. No time to be spend on tuning of the analyzer and verifying whether it is meeting the method requirements.

Standardization

The scope of ASTM D6730 covers: *"the determination of individual hydrocarbon components of spark-ignition engine fuels and their mixtures containing oxygenate blends (MTBE, ETBE, ethanol, and so forth) with boiling ranges up to 225 °C. Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphtha's, reformates, alkylates, and so forth) may also be analyzed."*

The chromatographic operating conditions and column tuning process, included in this test method, were developed to provide and enhance the separation and subsequent determination of many individual components. And to validate these conditions various criteria have been defined, which as shown on the following pages, including an example of analyzer factory test results.

System tuning

The ASTM D6730 method imposes extensive requirements on the preparation of the instrument and the optimization of the operating conditions, including:

- Define and tune pre-column length
- Check and optimize splitter performance
- Optimize column flow and check its performance
- Check and optimize critical separations by tuning the oven program

During the system performance testing at the AC facilities, each of these items is tuned according to the method and verified against its requirements. This comprehensive process assures the end user that when the system arrives at their lab, it complies with the method shown in the examples below.

Split performance

A thorough split injection check is critical to system performance and data integrity. The split should be checked for linearity and non-discrimination.

Non-linear splitting can result in peak overload which can lead to misidentification of components. The injection volume and split ratio are tuned for optimal settings, allowing one method to cover a whole range of products without the problem of misidentification due to skewed peaks (due to column overload).

In addition, the AC DHAxlnc software has several functions which makes the peak identification very robust, even with skewed peaks.

The non-discrimination check is performed by analyzing a quantitative mixture and comparing the found concentrations with the known gravimetric concentrations. See table 1.

Table 1: result of non-discrimination check for split inlet

Quantitative sample 50.16.512

Component	Mass% standard	Mass % found	Difference
n-Pentane	1.10	1.09	0.01
Cyclopentane	1.10	1.08	0.02
2,3-Dimethylbutane	2.05	2.01	0.04
1-Hexene	1.45	1.42	0.03
n-Hexane	2.05	2.03	0.02
Benzene	2.20	2.17	0.03
Cyclohexane	2.05	2.04	0.01
4-Methyl-1-Hexene	1.60	1.56	0.04
2,2,4-Trimethylpentane	5.00	5.01	0.01
n-Heptane	3.50	3.48	0.02
Methylcyclohexane	4.15	4.16	0.01
Toluene	2.20	2.18	0.02
n-Octane	5.00	5.00	0.00
1t,2-Dimethylcyclohexane + 1c,2-Dimethylcyclohexane	5.00	5.00	0.00
Ethylbenzene	4.50	4.50	0.00
1c,2t,4t-Trimethylcyclohexane '+ 1c,2t,3c-Trimethylcyclohexane '+ 1c,2t,4c-Trimethylcyclohexane '+ 1,1,2-Trimethylcyclohexane '+ o-Xylene (1,2-Dimethylbenzene)	8.30	8.27	0.03
n-Nonane	4.50	4.52	0.02
n-Propylbenzene	5.00	5.01	0.01
1,2,4-Trimethylbenzene	4.50	4.51	0.01
n-Decane	4.25	4.27	0.02
1,2,3-Trimethylbenzene '+2,3-Dihydroindene	5.00	4.97	0.03
t-Decahydronaphthalene	4.25	4.35	0.10
n-Undecane	3.55	3.58	0.03
1,2,4,5-Tetramethylbenzene	4.95	4.99	0.04
n-Dodecane	3.30	3.32	0.02
PentaMethylbenzene + impurity	4.95	5.01	0.06
n-Tetradecane	4.50	4.48	0.02

The following specifications checks are measured on the capillary column without pre-column, since the precolumn will have little effect on their values, and at an isothermal temperature of 35 °C.

The check results shown are as calculated by the DHA^{xlnc} software

Column evaluation - Retention Factor (K_{nC5}) of n-Pentane at 35°C:

The retention factor (k) must be between 0.45 and 0.50.

$$K_{nC5} = \frac{(t_{nC5} - t_m)}{t_m}$$

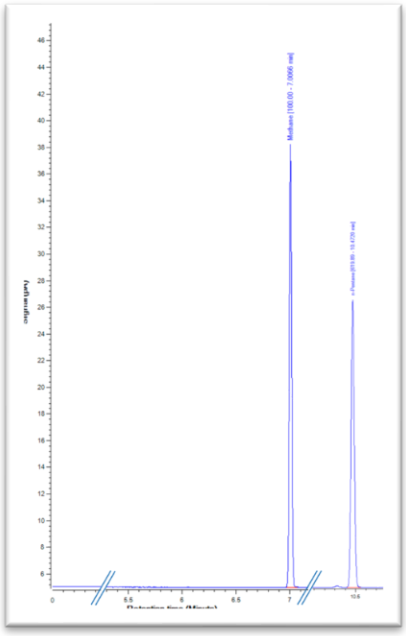
Where: t_{nC5} = retention time of n-pentane [min]

t_m = retention time of methane [min]

Result:

Column Evaluation

Parameter	Peak	Actual value	Limit
Retention factor	n-Pentane	0.4989	0.4500 - 5.0000



Column evaluation - efficiency for n-Pentane at 35°C

The column efficiency (expressed in the number of theoretical plates N) must be at least 400 000.

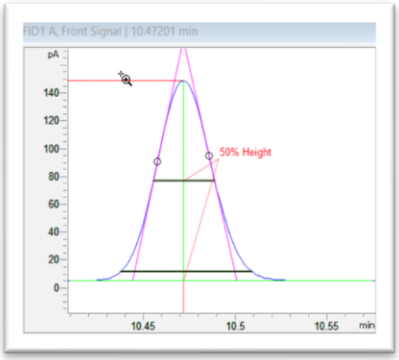
$$N_{nC5} = 5.545 * \left(\frac{t_{nC5}}{t_{1/2} W_{nC5}}\right)^2$$

Where: N_{nC5} = number of theoretical plates of,

$t_{1/2WnC5}$ = peak width at half height [min]

t_{nC5} = retention time of n-pentane [min]

Result:



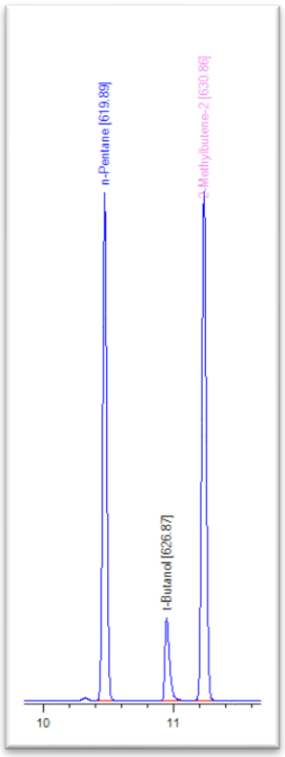
Column Evaluation

Parameter	Peak	Actual value	Limit
Plate count	n-Pentane	542474.5089	≥ 400000.0000

Column evaluation - resolution of t-Butanol (TBA) and 2-methylbutene-2 (2MB2) at 35°C:

The resolution (R) of t-Butanol and 2-methylbutene-2 has to between 3.25 and 5.25.

$$\mathbf{R = 2 * \frac{(t_{2MB2} - t_{TBA})}{1.699 * (t_{1/2}W_{2MB2} + t_{1/2}W_{TBA})}}$$



Result:

Resolution

First peak	Second peak	Actual value	Limit
t-Butanol	2-Methylbutene-2	4.5375	3.2500 - 5.2500

Column evaluation – Skewness of t-Butanol peak:

The skewness for t-Butanol should be between 1.0 and 5.0

$$\mathbf{Skewness = \frac{B}{A}}$$

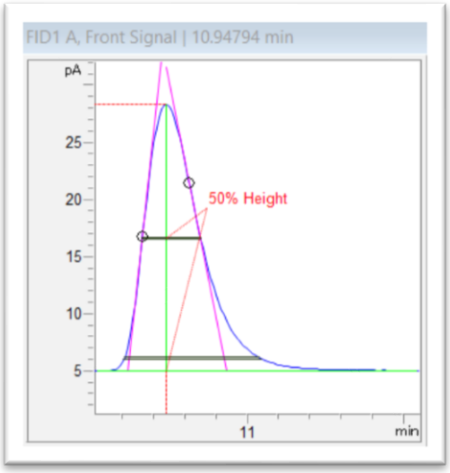
Where: A = distance (front) from peak apex at 5% of peak height.

B = distance (back) from peak apex at 5% of peak height.

Result:

Column Evaluation

Parameter	Peak	Actual value	Limit
Skewness	t-Butanol	2.2479	1.0000 - 5.0000



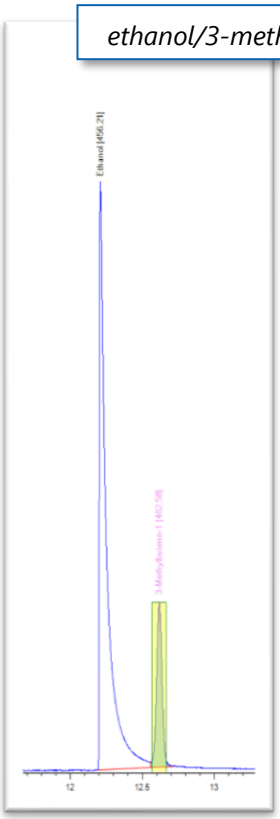
Column evaluation – Key separations

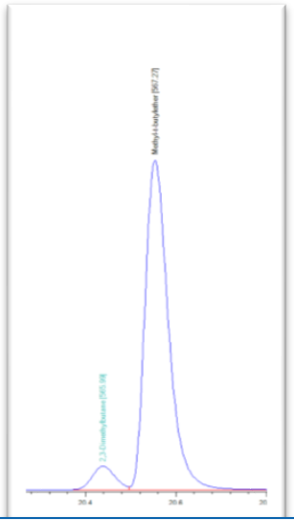
Paragraph 12 of the methods states:

- *The column temperature programming profile is dependent upon the individual column characteristics.*
- *The profile is determined by establishing satisfactory separations for the sets of sample components listed in 12.3.*
- *It is not practical to expect complete separation of all components, so the optimum for each column may contain some compromises, also dependent upon any particular other separations deemed important.*

Below some of those critical separations as listed in the method and performed on one of the AC analysers during the factory test.

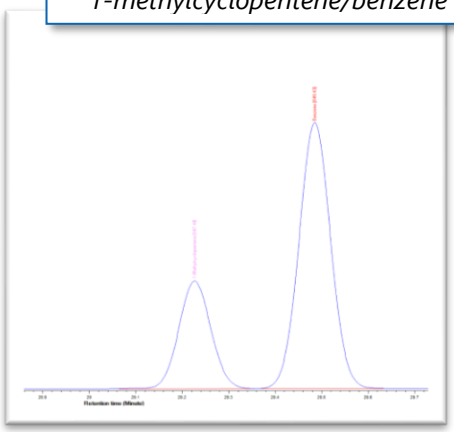
ethanol/3-methylbutene-1



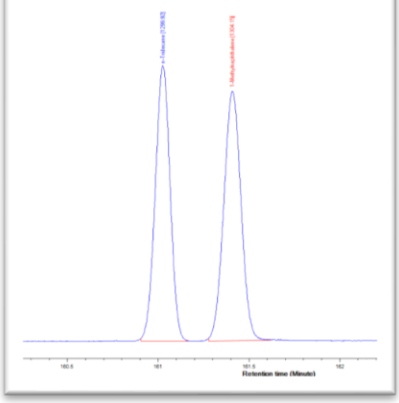


2,3-dimethylbutane/methyl-t-butylether

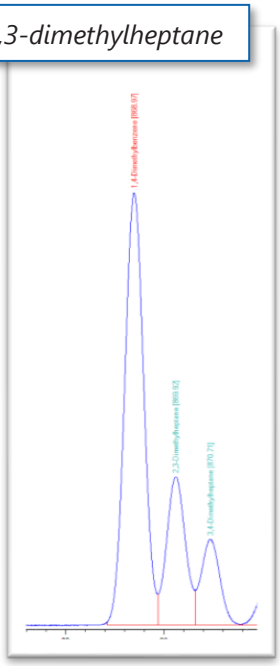
1-methylcyclopentene/benzene



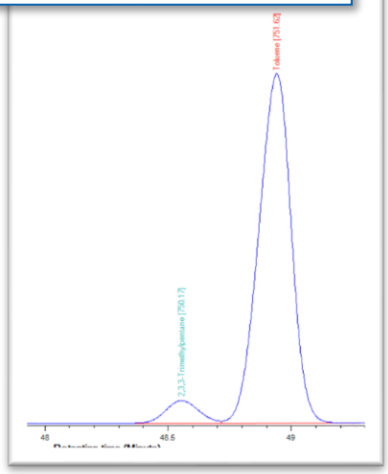
1-methylnaphthalene/tridecane



p-xylene/2,3-dimethylheptane



2,3,3-trimethylpentane/toluene



DHAxlnc software resolution calculation

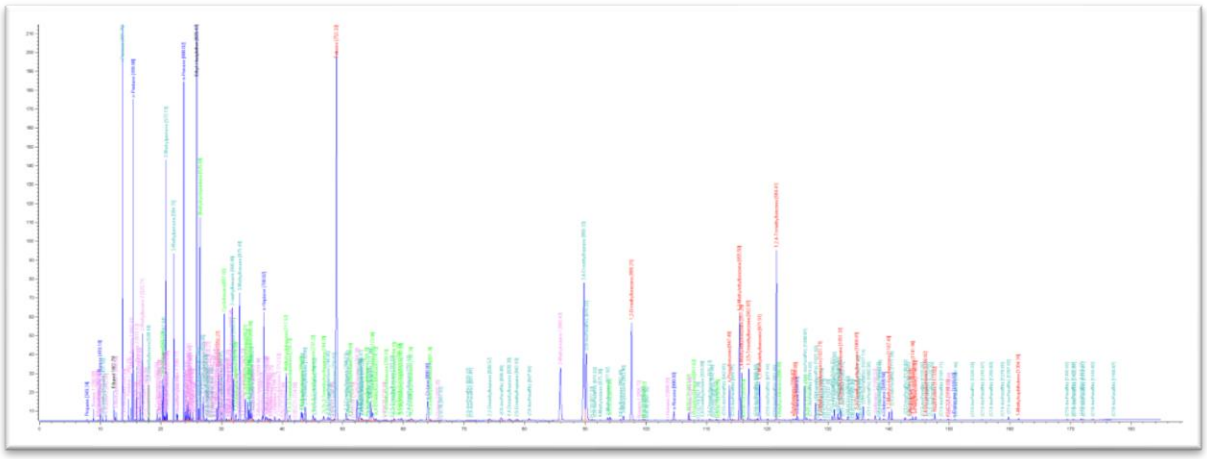
Resolution

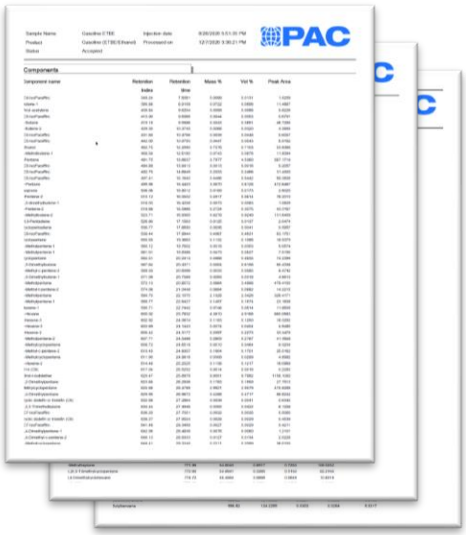
First peak	Second peak	Actual value	Limit
1-Methylcyclop...	Benzene	1.8876	
2,3,3-Trimethyl...	Toluene	1.6610	
Ethanol	3-Methylbuten...	6.1137	

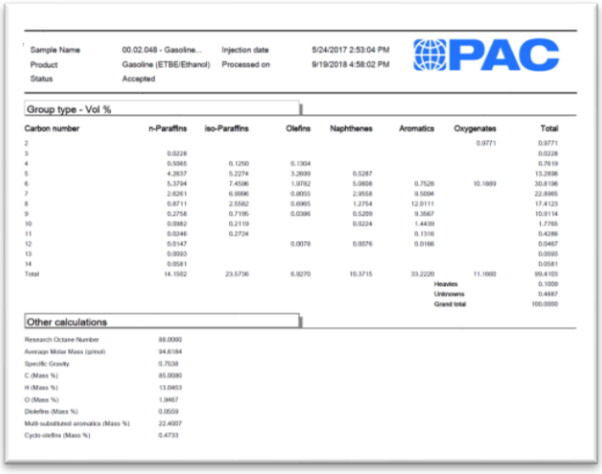
Conclusion

The AC DHA analyzer according to ASTM D6730 is setup, tuned and calibrated in accordance to ASTM D6730. All critical parameters, like pre-column length, split injection, column flow and critical separations are thoroughly checked and validated. This very time-consuming process saves the end user valuable time and assures a high return of investment as the system will deliver results in accordance with the method from day one after the installation.

The PAC IRIS DHA^{xlnc} software enables reporting of these critical parameters and requirements, so that the user always has insight into the performance of the system.







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