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Introduction

This section contains information about the ASTM D 6733 DHA. The detailed analysis of hydrocarbon samples with AC DHA capillary gas chromatographs is a tool to measure the content of components in volatile samples.

This test method 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 (D 86). Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates, and so forth) may also be analyzed; however, statistical data was obtained only with blended spark-ignition engine fuels.

Although majority of individual hydrocarbons present are determined, some co-elution of compounds is encountered.

Based on the cooperative study results, individual component concentrations and precision are determined in the range of 0.1 to approximately 15 mass%.

This test method may not be used to determine oxygenated components like methanol, ethanol, *t*-butanol, methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), and *t*-amyl methyl ether (TAME). Use Methods D 5599 or D 4815 for these components.

Benzene coelutes with 1-methylcyclopentene and must therefore be determined with test method ASTM D 3606 or D 5580.

Toluene coelutes with 2,3,3-trimethylpentane and must also be determined using test method ASTM D 3606 or D 5580.

Oxygen, sulfur, nitrogen, and so forth, may also be present, and may co-elute with the hydrocarbons. If determination of these specific compounds is required, it is recommended that test methods for these specific materials be used, such as Test Methods ASTM D 4815 and D 5599 for oxygenates, and Test Method D 5623 for sulfur compounds, or equivalent.

Only samples with less than 20 mass% olefins may be analyzed using this method. Significant coelution of olefins above C7 with other components is possible. The total olefin concentration may not be accurate. Total olefin content can be determined with multidimensional PONA instruments like the Reformulyzer™.

Configuration ASTM D 6733

AC DHA is an open system for temperature programmed gas chromatography. The gas chromatograph is equipped with:

- an autosampler,
- a split/splitless injector,
- a dimethylsilicone coated capillary column
- a flame ionization detector (FID).

Application Manual DHA ASTM D 6733

Introduction

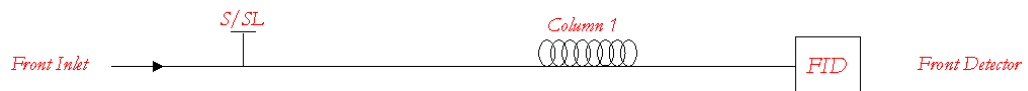
Note

Some pictures and screen dialogs in this manual are taken from other applications and act therefore as an example. Scaling of content might be different for your application.

AC DHA Hardware specifications

Flow Diagram ASTM D 6733

Helium gas is flowing as carrier gas through a 50 meter capillary column. A flame ionization detector detects components.



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AC DHA Hardware specifications

Consumables

Item	Specification	Quantity	AC Part no.
Consumable Kit:	6890 / 7890		65186.900
	6850		65186.950
Syringe	5 µl (2 pcs)	1	23020.028
S/SL septa	Septa 11mm (50 pcs)	1	21040.005
S/SL liners	Liner all DHA	5	10.32.001
Graphite ferrules	1/16" for DHA column (10x)	1	21041.001
Capillary column	HP-1 50m x 200µm x 0.5µm 6890 / 7890	1	21070.037 or
	HP-1 50m x 200µm x 0.5µm 6850		10.74.030
Sample box	Quant. Reference standard 512 (5pcs)	1	20001.122
Sample box	n-Paraffin standard (5pcs)	1	20001.121
Quality Control Samples:			
	Reformer Feed (5pcs)	1	20001.430
	Reformate (5pcs)	1	20001.431
	FCC Naphtha (5pcs)	1	20001.432
	Isomerase (5pcs)	1	20001.433
	Alkylate (5pcs)	1	20001.434
	Gasoline containing MTBE (5pcs)	1	20001.436
	Gasoline containing ETBE and ethanol (5pcs)	1	20001.437
	Gasoline containing EtOH (5pcs)	1	20001.438

Analytical specifications

Sample requirements

The sample requirements for this application can be summarized as follows:

Boiling range up to 225 °C (D86)

Sample streams

Alkylate
Isomerate
Reformate
Straight Naphtha (reformer feed)
FCC naphtha with less than 20 mass% olefins
Gasoline with oxygenates

Concentration Range

Based on the cooperative study results, individual component concentrations and precision are determined in the following range:

Concentration Range:	0.1 - 15 w/w%
----------------------	---------------

Warning

Use ASTM D 5599 or D 4815 for measurement of oxygenated components.

Quantitative Reference Standard 512

The quantitative reference standard 512 contains the following components:

Group	Number
Paraffins	C5 to C14
Olefins	C6 and C7
Naphthenes	Cyclo-C5, bi-cyclo-C6; C5 to C10
Aromatics	Benzene n-C1 to n-C5 benzene
Oxygenates	None

Quality Control Samples

For quality control several quality control samples are available. These samples can be used to check the appropriate sample types on peak recognition.

Limitations of the analyzer

Samples containing significant amounts of olefinic and / or naphthenic constituents (for example virgin naphthas), above n-octane might reflect significant errors in PONA type groupings. Based on the gasoline samples in the interlaboratory cooperative study, these procedures are applicable to concentrations of olefins to less than 20 mass %. However, some interfering co-elution with the olefins above C7 is possible, particularly if blending components

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Analytical specifications

or higher boiling cuts such as those derived from fluid catalytic cracking (FCC) are analyzed, and the total olefin content may not be accurate.

Although a majority of individual hydrocarbons present are determined, some co-elution of compounds is encountered.

Starting-up the DHA system

Column installation

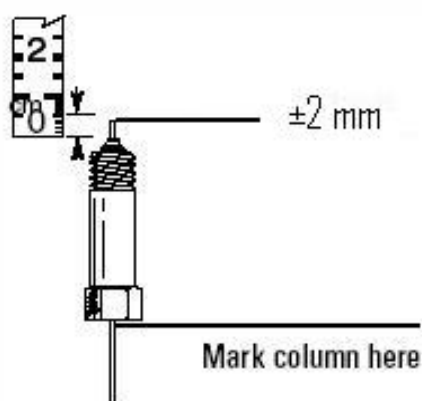
The capillary column must be attached to the S/SL injector. The connection of the column is very precise. Discrimination will occur if the column is not correctly installed.

- 1 Put the column nut over the column
- 2 Put the graphite ferrule over the column.
- 3 Remove 0.5 cm from the column end using a capillary column cutter

Note

The column end must be nicely round without any wall fractures.

- 4 Let the column end be ± 2.0 mm above the ferrule.



- 5 Attach the column to the split injector hand tight and then $\frac{3}{4}$ with a 1/16" wrench.

Start-up from Shut-down

- 1 Power up all the modules. Start with the GC and end with the computer and printer
- 2 Let the system initialize
- 3 Check the system
- 4 Calibrate the system and check if it meets its performance
- 5 Continue with sample analyses

Start-up from Stand-by

- 1 Check the system
- 2 Continue with sample analyses

System Stand-by Conditions

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Starting-up the DHA system

Before starting an analysis or sequence the status of the system must be checked. The initial conditions are described below.

Module	Parameter	Settings
GC-oven	Linear carrier flow (He)	0.9 ml/min
	Temperature	35 °C
Injector	Temperature	250
Detector	Temperature	280
	Hydrogen flow	35
	Air flow	350
	Makeup (He)	20
	Baseline signal	12
Gas saver	Flow	25 ml /min
	Time	0.5

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Description of the GC methods

Description of the GC methods

There are several GC methods available although only one is used for sample analyses. The next table lists them all and their purpose.

D6733 / D6733-7890	
For sample analyses	
Injector	Split/splitless
Injector Temp (°C)	250
EPC pressure [kPa]	154
Column	50m * 200µm * 0.50µm HP-1
Carrier gas	He
Linear Velocity (cm/s)	19
Split ratio	250:1
Sample size	0.5 µl
Gas saver Flow	25
Gas saver Time	2

Oven Temp 1 [°C]	10
Time 1 [min.]	15
Rate 1 [°C/min.]	1.3
Oven Temp 2 [°C]	70
Time 2 [min.]	0
Rate 2 [°C/min.]	1.7
Oven Temp 3 [°C]	200
Time 3 [min.]	0
Analysis time [min.]	137

Detector	FID
Detector Temp (°C)	250
Hydrogen Flow (ml/min.)	35
Air Flow (ml/min.)	350
Make Up Flow He (ml/min.)	20

Preparing Samples

Preparing a gas sample C1 to C4

Natural gas or a refinery gas is used to measure the retention times of methane, ethane, propane and n-butane.

NATURAL GAS IS EXTREMELY FLAMMABLE. IT CAN BE EASILY IGNITED. KEEP IT AWAY FROM FLAMES, SPARKS, OR SOURCES OF HEAT.

- 1 Fill an ALS¹ vial with natural gas.
- 2 Seal the vial tightly.
- 3 Place the vial in the desired position of the sampler tray.

Prepare a n-Paraffin C5 to C14 standard

- 1 Fill an ALS vial with 0.1 gram of the n-Paraffin standard.
- 2 Add to the vial \pm 1 ml CS₂.
- 3 Place the vial in the desired position of the sampler tray.

This will give a solution of \pm 1 mass % per paraffin.

Prepare the Quality Control (QC) or Normal Samples

These samples are eluting fully on the analytical column. Therefore no internal standard method is required for quantification.

- 1 Fill an ALS vial with the samples.
- 2 Place the vial in the desired position of the sampler tray.

¹ Automatic Liquid Sampler

Optimizing the ASTM D 6733 method

Column Specifications

Material	Fused Silica
Length	50 m
Internal Diameter	0.20 mm
Liquid phase	methyl silicone
Film Thickness	0.50 μm
Theoretical plates, n, pentane @ 35°C	400.000 to 500.000
Retention factor, k, pentane @ 35°C	0.45 to 0.50

Column Conditioning

This procedure must be performed if a new column is installed, the system was on standby for more than 3 days or if a sample did not elute fully from the column.

- 1 Keep the oven temperature at 275°C for 1 hour,
- 2 Cool down the oven temperature to 35°C and record FID signal value,
- 3 Heat the oven to 200°C and record FID signal value,
- 4 Keep the oven temperature at 200°C until the FID signal value is within 100 to 105% of the value at 35°C.

Adjusting Split / Splitless Inlet Pressure

Peaks shift if the carrier head pressure is deviating. AC supplied databases based on a certain linear velocity of the gas flow. Deviations from this linear velocity will lead to mis-identification of peaks.

It is vital that the linear velocity is therefore close by the original application database value. The linear velocity can be measured using the retention time of C7, C8 and C12. AC performed this and found that this occurs with a column head pressure of about 154 kPa. This complies with a column holdup time of 4.546 minutes for methane.

The n-Paraffin mixture can be used to tune the column head pressure. The retention times of the components in the table must be within the given limits.

	Method 2
Pressure (psi)	
	Time (minutes)
n-Heptane	40.7 \pm 1.2
n-Octane	57.8 \pm 1.2
n-Dodecane	107.6 \pm 1.2

- 1 Set the column head pressure at the target pressure from the table and save the method.

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Optimizing the ASTM D 6733 method

- Analyze the n-Paraffin mixture using the method
- Adjust the pressure to increase or decrease the retention time of the components if necessary.

Evaluation of column performance

The quality of the capillary column system can be evaluated with ASTM method D 6733. Following specifications are not mandatory, but can be of help when trouble shooting the system.

- Use the GC oven program below for evaluation of the Column performance.

Oven Temp 1 [°C]	35
Time 1 [min.]	50
Rate 1 [°C/min.]	3
Oven Temp 2 [°C]	220
Time 2 [min.]	20
Analysis time [min.]	127

- Column efficiency for n-Octane at 35 °C:

$$N_{nC8} = 5.545 \cdot \left(\frac{t_{nC8}}{t'_{1/2}w_{nC8}} \right)^2$$

where: N_{nC8} = number of theoretical plates of ,
 $t'_{1/2}w_{nC8}$ = peak width at half height [min]

ASTM D 6733 specifies a value of N_{nC8} greater than 200,000 plates.

- Calculate resolution of 2-methylheptane and 4-methylheptane at 35°C:

$$R = 2 \cdot \frac{(t_4 - t_2)}{1.699 \cdot (t'_{1/2}w_{t4} + t'_{1/2}w_{t2})}$$

ASTM D 6733 specifies a value of this R greater than 1.2

Calibration

n-Paraffin calibration mixture

The D 6733 analyzer is based on the Kovats index system, using retention times of GC peaks and the bracketing n-Paraffins. The retention times of nC₅ to nC₁₄ are measured with an n-Paraffin standard. The calibration should be carried out on a regular basis.

The retention times of methane up to n-butane must be measured by injecting natural gas, refinery gas, or a sample that contains these components.

Calibrating the DHA

This calibration should be performed once a week or more frequent if lots of crude samples are analyzed. It should be done for both injectors.

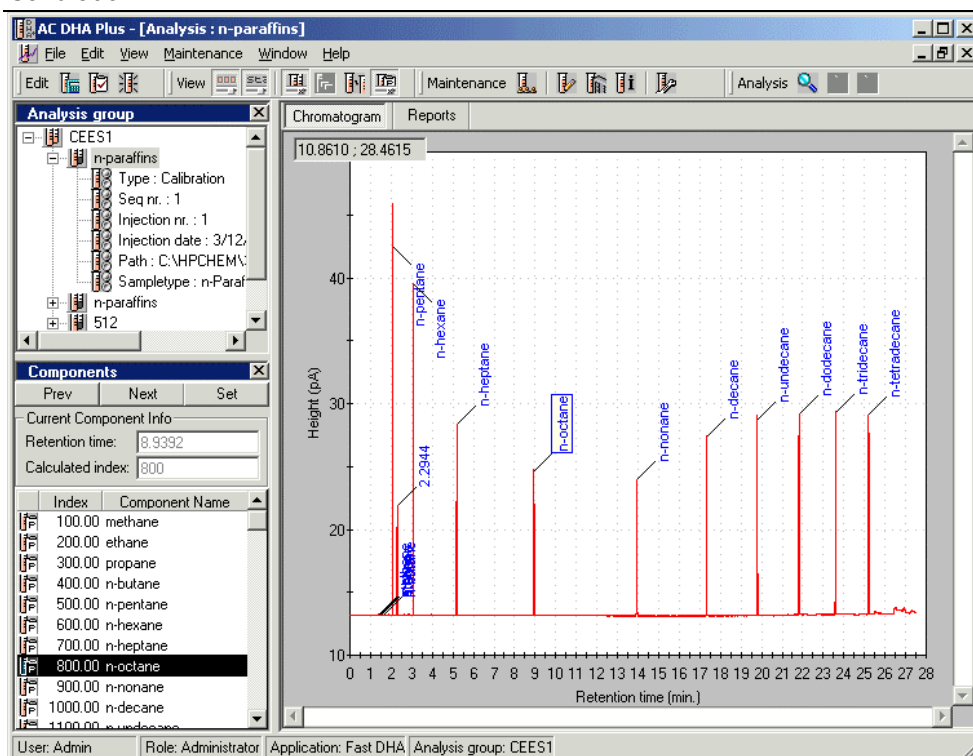
- 1 Follow the instructions in the section **Preparing samples**.
- 2 Create a sequence with:

Sample Name	Sample Type	GC Method
C1 to C4 sample	n-Paraffin Standard	C1ToC4
Standard C5 to C14	n-Paraffin Standard	D6733

- 3 Analyze the sequence.
Continue if the sequence is analyzed on the GC.
- 4 Start the DHA plus program from the Windows **Start** menu.
- 5 Open the n-Paraffin analysis directory with the command **File / Open / Analysis group**.
- 6 Open the n-Paraffin analysis by clicking it in the analysis group.

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Calibration



Note

The second peak in chromatogram is the solvent, carbon disulfide. The above picture is just a DHA plus example of an n-Paraffin mixture. ASTM D 6733 has another timescale.

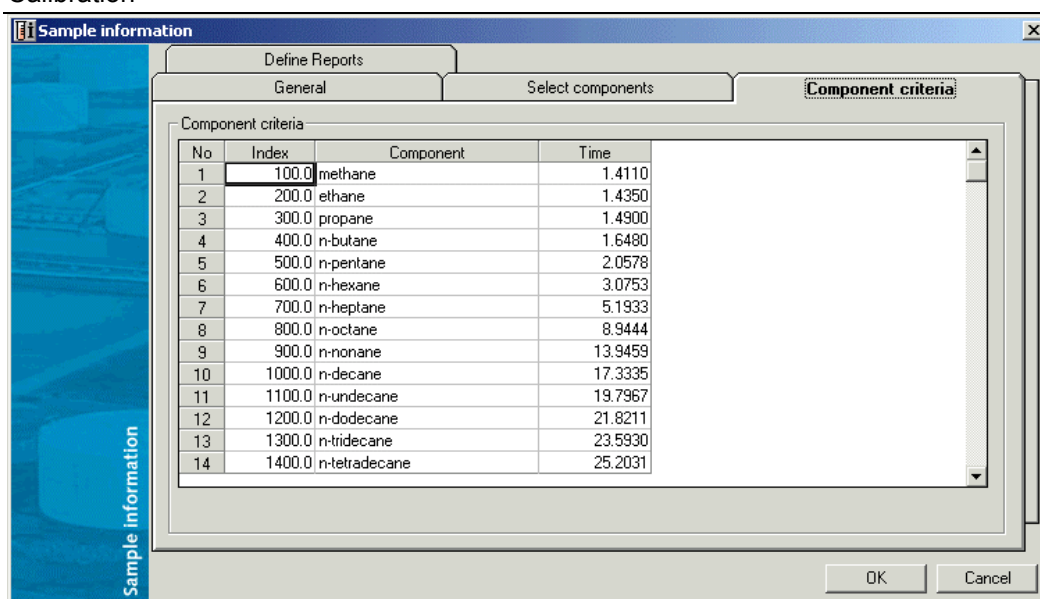
- 7 Check if the labels are correctly pointing to the peaks. Click a peak retention time if this is not the case and then select the correct component name in the components area. Press **set** to make the change.


The C1 to C4 cannot be found in the calibration mixture. This means that they cannot be selected as peak. Open the sample type editor to modify these times. The times can be taken from the C1toC4 analysis.

- 8 Click the sample type editor icon  in the toolbar to open the editor.
- 9 Select the "components criteria" tab

Application Manual DHA ASTM D 6733

Calibration



- 10 Enter the correct retention times for the C1 to C4 into the dialog from the natural gas calibration.
- 11 Close the editor with **ok**.
- 12 Press the recalculate button  on the tool bar to calculate a new report. This will update the C1 to C4 times for the analysis.
- 13 Close the analysis.

The system is now ready for further Quality Control analysis or normal operation

Trouble shooting

- Peak is not integrated: check integration events and reprocess calibration.
- n-paraffin peaks are overloaded (skewed): dilute sample / check for correct split ratio or injection volume
- Retention times of n-paraffins in sample and calibration are different: check for leaks in the system or check if peaks are overloaded (skewed)
- Peaks not found: retention index window possibly too small, enlarge retention index window for the application.

Discrimination Check

The quantitative reference standard 512 is used to check for discrimination. With this test mixture it is possible to check the system for injector performance and/or detector performance.

The test mixture is designed to give a number of components over a broad boiling point range (35°C - 254°C). If there is a strong difference in peak area of the light lower boiling components and the heavy higher boiling points, then we can assume there is injector discrimination.

The test mixture has a number of compound groups that have different response factors for the FID. If there is a difference in response between different compound groups (e.g. n-paraffins and aromatics), something might be wrong with the detector (flows).

Note

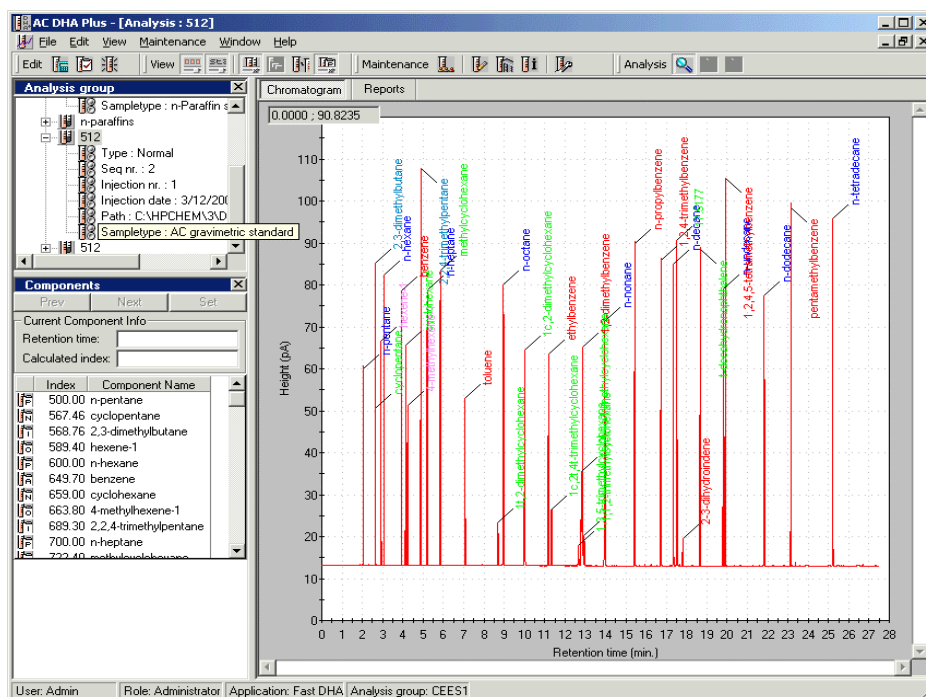
If the difference in weight percentage of each component is less than 0.3% (absolute), the specification is met.

Special attention should be paid to nC14 on the S/SL. The splitter discriminates if the measured value is lower than the reference value. Disconnect the column from the injector and inspect that the column extends only 1 mm beyond the ferrule head (into the S/SL liner).

Note

If nC14 is not identified (-), the weight percentage is still valid.

The QC standard has its own dedicated sample type "Quant Ref 512", containing only the compounds that are in the mixture.



Trouble shooting

- peak is not integrated: check integration events and reprocess.
- peaks are overloaded (skewed): check for correct split ratio or injection volume
- peaks are not found: retention index window possibly too small, enlarge retention index window
- discrimination of light towards heavy components: check injector for leaks, check sample vial, check the height of the column in the injector. It should be ± 2 mm above the ferrule.
- (big) difference in response for different compound groups: check detector for leaks/proper gas flows.

Trouble shooting

- Peak is not integrated; Integration events of GC method
- Peaks are overloaded and skewed; Split ratio, injection volume or sample dilution
- Peaks are not identified or misidentified; Retention index window (too small). Database Kovats index value is incorrect.
- Peaks between nC4 and nC6 are not identified; n-Paraffin calibration: CS2 time mistaken for nC5
- Peaks before n-pentane are not identified; n-Paraffin calibration: Retention times of C1 to C4
- Symmetrical peak Paraffin retention times in sample and calibrant are different; Carrier gas pressure, leak at column connection to injector.

Running the ASTM D 6733 analyzer

Always create sequences within the **DHA** sequencer for your analyses. The software creates special files after the sequence run, which are stored with the data. These files are essential for correct operation of the software.

Warning

Light hydrocarbons are toxic. Utilize the contents of all AC standards and samples only in fume hood. Avoid inhaling fumes and contact with any part of the body.

Warning

Light hydrocarbons are extremely flammable. The fumes and vapors from light hydrocarbons are easily ignited. Keep the contents of all AC vials away from flames, sparks, or sources of heat.
