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# Application Manual DHA ASTM D 6730

Formally known as DHAX

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## Introduction

This section contains information about the ASTM D 6730 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 0.01 to approximately 30 mass%.

This test method also determines methanol, ethanol, *t*-butanol, methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), and *t*-amyl methyl ether (TAME) in spark ignition engine fuels in the concentration range from 1 to 30 mass %. However, the cooperative study data provided insufficient statistical data for obtaining a precision statement for these compounds.

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.

Total olefins in the samples may be obtained or confirmed, or both, if necessary, by test method D 1319 (vol%) or other test methods, such as those based on multidimensional PONA- type of instruments.

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**Note**

This method was formally known as the AC DHAX method.

### Configuration ASTM D 6730

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).

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**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.

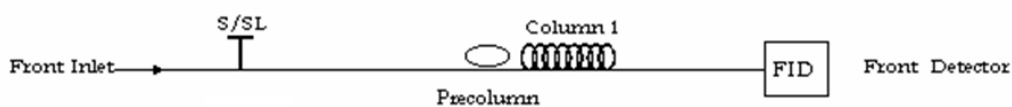
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## AC DHA Hardware specifications

### Flow Diagram ASTM D 6730

Helium gas is flowing as carrier gas through a 100 meter capillary column preceded by a short polar pre-column. A flame ionization detector detects components.

The polar pre-column is used to retain oxygenated components more than normally is done in order to separate them better. The length of the pre-column must be experimentally determined based on some separation criteria's.



## Application Manual DHA ASTM D 6730

### Consumables

## Consumables

Item	Specification	Quantity	AC Part no.
<b>Consumable Kit:</b>	<b>6890 / 7890</b>		<b>65186.100</b>
	<b>6850</b>		<b>65186.150</b>
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
Precolumn	DB-5 5m x 250µm x 1.0µm	1	10.70.046
Connector	Butt connector (incl.ferrule)	1	10.75.046
Ferrule	Ferrule for Butt connector	1	10.76.046
Capillary column	HP-1 100m x 250µm x 0.5µm <b>6890 / 7890</b>	1	25190.300 or
	HP-1 100m x 250µm x 0.5µm <b>6850</b>		10.74.004
Sample box	Quant. Reference standard 512 (5pcs)	1	20001.115
Sample box	n-Paraffin standard (5pcs)	1	20001.114
Sample box	Column evaluation mixture (5pcs)	1	25117.510
Sample box	RF-C2 reference sample (5pcs)	1	25116.610
<b>Quality Control Samples:</b>			
	Reformer Feed (5pcs)	1	20001.400
	Reformate (5pcs)	1	20001.401
	FCC Naphtha (5pcs)	1	20001.402
	Isomerase (5pcs)	1	20001.403
	Alkylate (5pcs)	1	20001.404
	Gasoline containing MTBE (5pcs)	1	20001.405
	Gasoline containing ETBE and ethanol (5pcs)	1	20001.406
	Gasoline containing EtOH (5pcs)	1	20001.407
	Gasoline containing TAME (5pcs)	1	20001.408

## Analytical specifications

### Sample requirements

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

Boiling range up to 225 °C (D86)
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### Sample streams

Alkylate
Isomerate
Reformate
Straight Naphtha (reformer feed)
FCC naphtha with less than 25 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:	0.01 - 30 w/w%
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#### Note

Test procedure determines also MTBE, ETBE, TAME and ethanol in spark ignition engine fuels in the concentration range of 1 to 30 w/w %. No sufficient statistical data was obtained however for these components.

### Quantitative Reference Standard 512

The quantitative reference standard 512 contains the following components:

Group	Number
Paraffins	C5 to C14
Olefins	C6 and C7
Napthenes	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 25 mass %. However, some interfering co-elution with the olefins above C7 is possible, particularly if blending components 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.

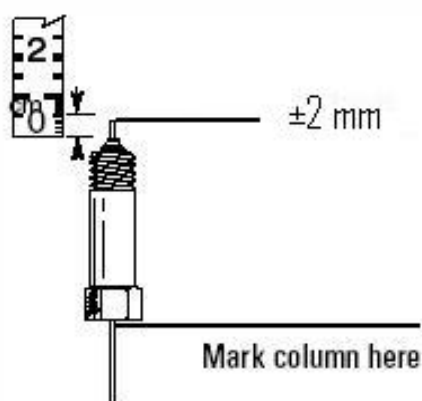
- 1 Put the column nut over the column
- 2 Put the graphite ferrule over the column.
- 3 Remove 0.5 cm from the column end using a capillary column cutter

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**Note**

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

- 4 Let the column end be  $\pm 2.0$  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

## Application Manual DHA ASTM D 6730

### Starting-up the DHA system

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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)	2.4 ml/min
	Temperature	35 °C
Injector	Temperature	250
Detector	Temperature	250
	Hydrogen flow	35
	Air flow	350
	Makeup (He)	20
	Baseline signal	12
Gas saver	Flow	25 ml /min
	Time	0.5

## Application Manual DHA ASTM D 6730

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.

	D6730ce / D6730ce-7890	D6730 / D6730-7890
Purpose	For column evaluation	For sample analyses
Injector	Split/splitless	
Injector Temp (°C)	250	
EPC pressure [kPa]	301	
Pre-column	1-4 m * 250 µm * 5% phenyl/95% dimethyl silixone	
Column	100m * 250µm * 0.50µm HP-1	
Carrier gas	He	
Linear Velocity (cm/s)	28	
Split ratio	100:1	
Sample size	0.1 µl - 0.2 µl	
Gas saver Flow	25	
Gas saver Time	2	

Oven Temp 1 [°C]	35	5
Time 1 [min.]	35	10
Rate 1 [°C/min.]	10	5
Oven Temp 2 [°C]	200	≈ 49 <sup>1</sup>
Time 2 [min.]	10	≈ 55 <sup>2</sup>
Rate 2 [°C/min.]		1.6
Oven Temp 3 [°C]		200
Time 3 [min.]		5
Analysis time [min.]	61.5	≈ 170

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

<sup>1</sup> based on separation p-xylene and 2,3-dimethylheptane

<sup>2</sup> until ethylbenzene elutes.

## 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.

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

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- 1 Fill an ALS<sup>1</sup> 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 CS<sub>2</sub>.
- 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.

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<sup>1</sup> Automatic Liquid Sampler

## Optimizing the ASTM D 6730 method

### Column Specifications

Material	Fused Silica
Length	100 m
Internal Diameter	0.25 mm
Liquid phase	methyl silicone
Film Thickness	0.50 $\mu$ m
Theoretical plates, n, pentane @ 35°C	400.000 to 500.000
Retention factor, k, pentane @ 35°C	0.45 to 0.50
Resolution , R, t-butanol and 2-methylbutene-2 @ 35°C	3.25 to 5.25
Peak symmetry, t-butanol @ 35°C	> 1.0 to < 5.0

### Pre-column

Variable length (2 to 4 meters) of 5% phenyl methyl silicone fused silica open tubular column (0.25 mm ID) is added to the injector end of the 100 m column with a butt connector.

### 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 225°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 the pre-column length

- 1 Install 3.5 m of the pre-column using a butt connector,
- 2 Calibrate the column length
- 3 Adjust the Front Inlet pressure (see Adjusting Split / Splitless Inlet Pressure),
- 4 Check separations and adjust GC conditions (see 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 misidentification 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 methane.

## Application Manual DHA ASTM D 6730

Optimizing the ASTM D 6730 method

ASTM method D 6730 specifies a holdup time of **7.00 ± 0.02 minutes at 35°C** and is operated at constant pressure. If not, adjust front inlet pressure (lower if  $t_m < 6.98$ , higher if  $t_m > 7.02$ ) and repeat injection.

### Note

The analysis can be stopped manually when all peaks have eluted.

### 5 Critical Separations).

## 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 misidentification 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 methane.

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### Note

The analysis can be stopped manually when all peaks have eluted.

## Critical Separations

Use the Column evaluation mixture and the normal **D6730** GC method to obtain the desired critical separations. Tuning of the DHA 6730 analyzer is based on two principles: (1) Oxygenates and Paraffins are separated on the Analytical Column (2) Aromatics and Paraffins are separated by selectivity of the pre-column for Aromatics.

### Warning

Changing GC conditions will change the measured Kovats indices. Please update your sample types using the quality controls samples.

The oxygenated peaks elute before the other peaks, depending on the temperature program. Higher oven temperatures will move the oxygenated peaks into the peaks ahead of them. The temperature program is tuned for oxygenate separations.

Key components (elution order)	ASTM D6730 Method Tuning
i-C4 and MeOH EtOH and 3-Methylbutene-1	T-Program start @ 5°C. Lower not useful, higher will move these alcohols into the next peaks.
i-Propanol and 2-Methylbutene-1	
t-Butanol and 2-Methylbutene-2	

## Application Manual DHA ASTM D 6730

### Optimizing the ASTM D 6730 method

2,3-Dimethylbutane and MTBE MTBE and 2-Methylpentane	T-Program start @ 5°C. More MTBE retention: shorten Time 1 to 9 min. Less MTBE retention: Time 1 to 11 min.
1-Methylcyclopentene and Benzene	Better separation: <b>Longer</b> pre-column.
Ethylbenzene	Adjust Time 2 (≈55) until after EBz peak.
2,3,3-Trimethylpentane and Toluene	Better separation: <b>Longer</b> pre-column.
p-Xylene and 2,3-Dimethylheptane	Better separation: <b>Shorter</b> pre-column or Reduce Temp 2 from 50 to 49 or 48°C (determine new Time 2).
Paraffin and 1,2-Methylethylbenzene	Better separation: <b>Longer</b> pre-column or <b>Increase</b> Rate 2 (1.5°/min)
1-Methylnaphthalene and nC13	Better separation: <b>Shorter</b> pre-column or <b>Reduce</b> Rate 2. Retention order change: Increase Rate 2.

#### Note

Samples without Oxygenates do not require the Cryogenic option.

The function of the pre-column is extra aromatics retention, so the aromatics move more ahead of the other peaks. The pre-column length is tuned with aromatic separations. The pre-column length is reduced in length (steps between 0.25 - 0.5 m) until separations (12.3.4) and (12.3.5) are still ok but (12.3.6) is not yet lost.

### Evaluation of column performance

The quality of the capillary column system can be evaluated with ASTM method D 6730-01. Following specifications are not mandatory, but can be of help when trouble shooting the system. The required analyses can be performed on the Analytical Column with or without the pre-column:

- 1 Use the GC method **D6730ce** to analyze the Column Evaluation mixture.
- 2 Retention factor ( $k_{nC5}$ ) of n-pentane at 35 °C:

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

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

$t_m$  = retention time of methane [min]

ASTM D 6730-01 specifies a value of  $k_{nC5}$  between 0.45 and 0.50, with or without pre-column.

- 3 Column efficiency for n-pentane at 35 °C:

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

## Application Manual DHA ASTM D 6730

### Optimizing the ASTM D 6730 method

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where:  $N_{nC5}$  = number of theoretical plates of ,  
 $t_{1/2}w_{nC5}$  = peak width at half height [min]

ASTM D 6730-01 specifies a value of  $N_{nC5}$  greater than 400000 plates.

- 4 Calculate resolution of t-butanol (TBA) and 2-methylbutene-2 (2MB2) at 35°C:

$$R = 2 \cdot \frac{(t_{2MB2} - t_{TBA})}{1.699 \cdot (t_{1/2}w_{2MB2} + t_{1/2}w_{TBA})}$$

ASTM D 6730-01 specifies a value of this R between 3.25 and 5.25.

- 5 Calculate skewness of t-Butanol peak:

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

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

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

ASTM D 6730-01 specifies a value of skewness between 1.0 and 5.0.

## Calibration

### n-Paraffin calibration mixture

The D 6730 analyzer is based on the Kovats index system, using retention times of GC peaks and the bracketing n-Paraffins. The retention times of nC<sub>5</sub> to nC<sub>14</sub> 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.

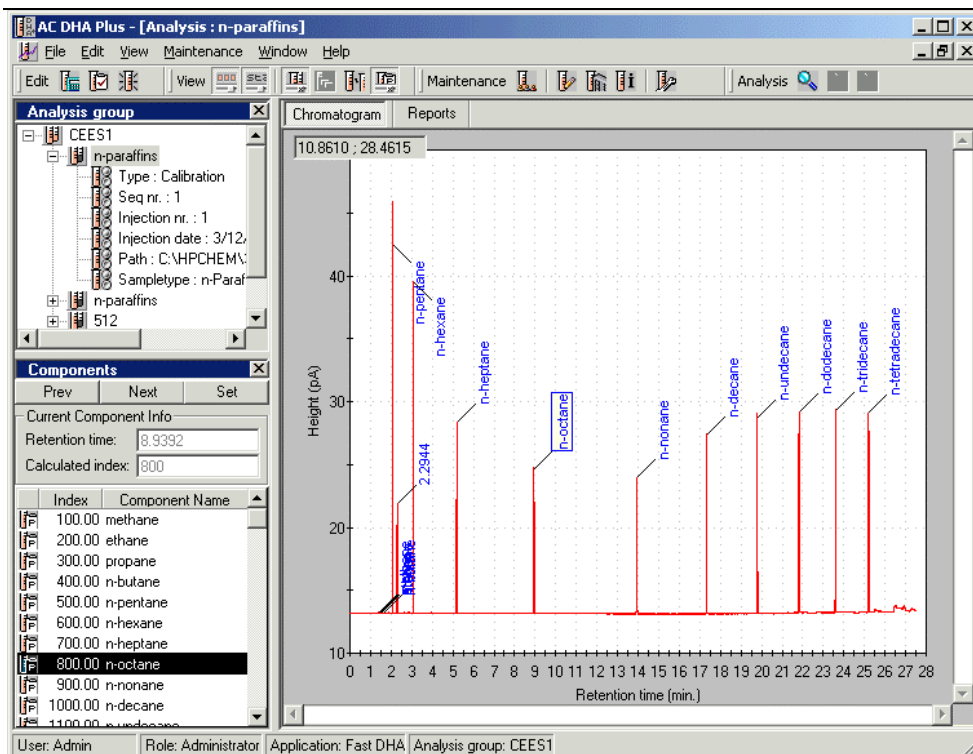
- 1 Follow the instructions in the section **Preparing samples**.
- 2 Create a sequence with:

Sample Name	Sample Type	GC Method
C1 to C4 sample	n-Paraffin Standard	C1ToC4
Standard C5 to C14	n-Paraffin Standard	D6730

- 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.

## Application Manual DHA ASTM D 6730

### 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 6730 has another timescale.

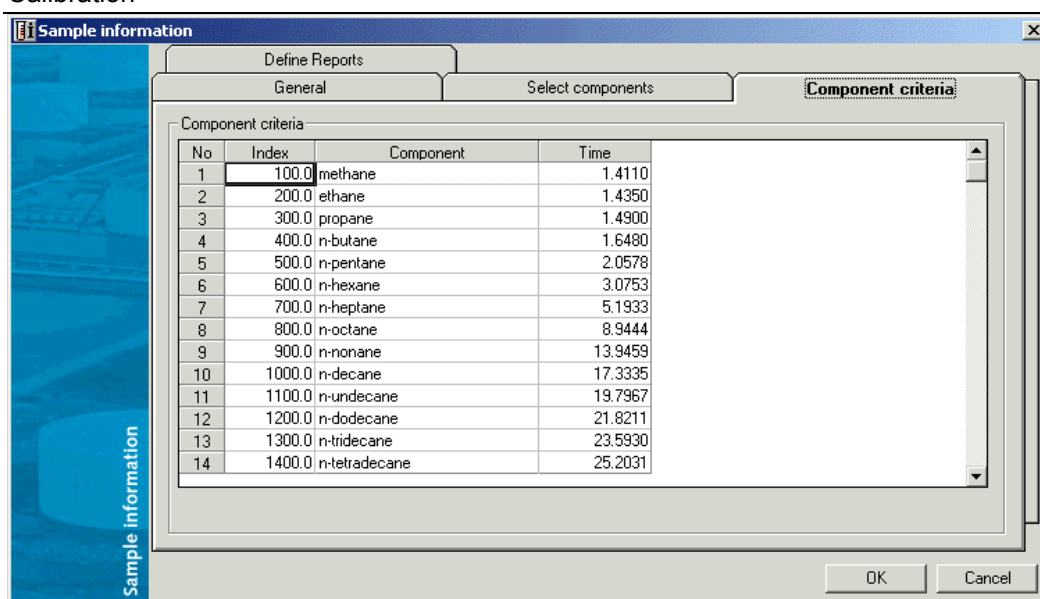
- 7 Check if the labels are correctly pointing to the peaks. Click a peak retention time if this is not the case and then select the correct component name in the components area. Press **set** to make the change.


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 6730

### 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

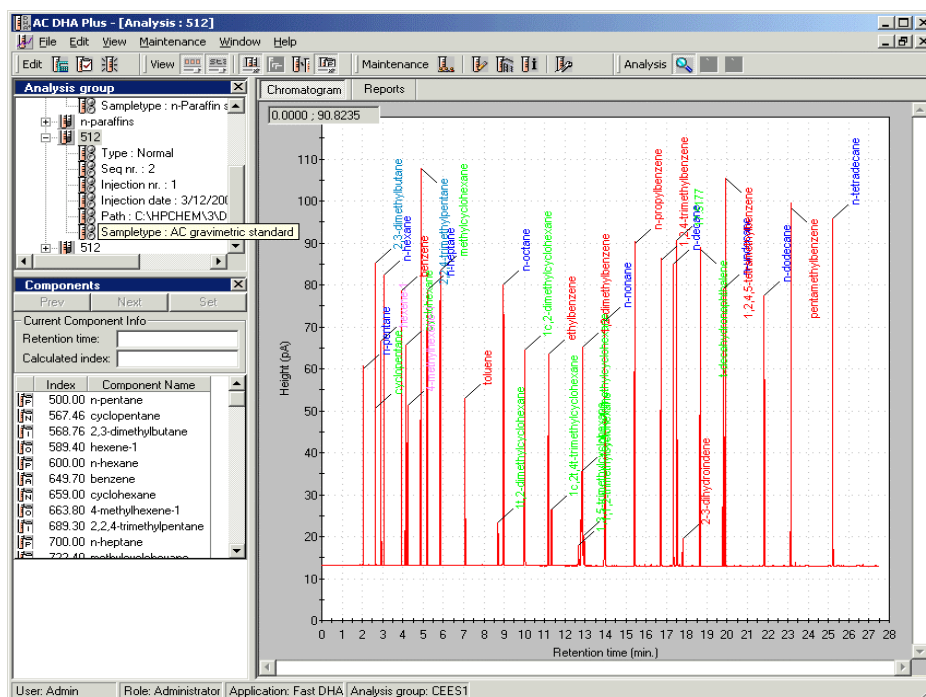
If the difference in weight percentage of each component is less than 0.3% (absolute), the specification is met.

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 n-C14 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**

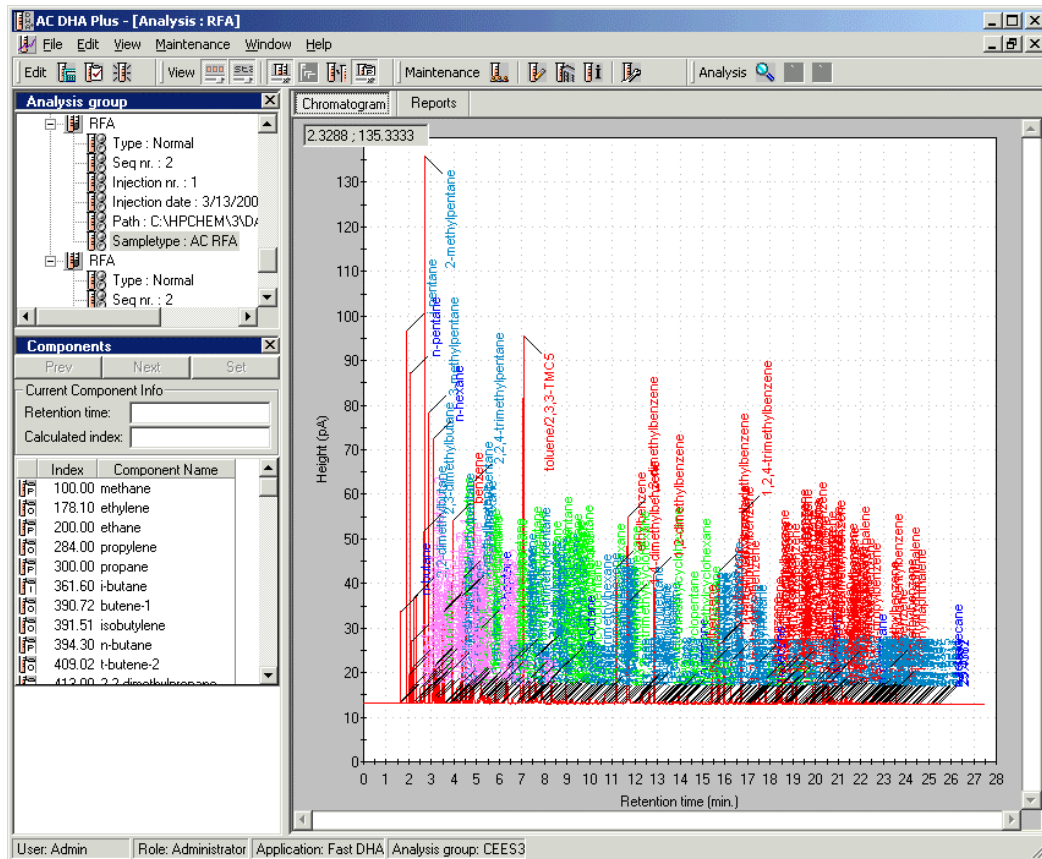
- peak is not integrated: check integration events and reprocess.
- peaks are overloaded (skewed): check for correct split ratio or injection volume
- peaks are not found: retention index window possibly too small, enlarge retention index window
- discrimination of light towards heavy components: check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

## Quality Control Samples

Peak identification can be validated with 10 Quality Control samples. Detailed information about the sample and peak identification can be found in the sample booklet. An example is also supplied in the SSTDEMO directory for each QC sample. Use QC samples corresponding to your sample types.

**Note**

The QC sample RF-C2 is the RFA from ASTM method D 6730-01 with oxygenates



### Peak Identification

Peak identification is the comparison of the measured index and the database index. The measured index depends on the peak retention time in the chromatogram and the n-Paraffin calibration.

Click on the peak label in the chromatogram to change a Kovats index value for the sample type.

### **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 6730 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.

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**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.

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**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.

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