
1

Application manual ASTM D 6729

Formally known as CGSB

Table of Contents	Page
Introduction	1-3
Configuration of the ASTM D 6729 analyzer	1-3
ASTM D 6729 hardware specifications	1-4
Flow diagram AC ASTM D 6729 analyzer	1-4
Consumables	1-5
AC DHA D 6729 analytical specifications	1-6
Sample requirements.....	1-6
Sample streams.....	1-6
Concentration Range.....	1-6
Quantitative Reference Standard 512	1-6
Quality Control Samples	1-6
Limitations of the analyzer	1-7
Starting-up the DHA system	1-8
Column installation	1-8
Start-up from Shut-down.....	1-8
Start-up from Stand-by	1-8
System Stand-by Conditions	1-9
Description of the AC DHA D 6729 GC-method	1-10
Preparing Samples	1-11
Preparing a gas sample C1 to C4.....	1-11
Preparing the n-Paraffin's C ₅ to C ₁₅ standard	1-11
Prepare the Quality Control (QC) or Normal Samples.....	1-11
Optimizing the ASTM D 6729 method	1-12
Column Specifications	1-12
Column conditioning	1-12
Adjusting Split / Splitless Inlet Pressure	1-12
Critical Separations.....	1-13
Co-elutions.....	1-14
Calibration	1-15
Calibrating the DHA.....	1-15
Trouble shooting	1-17
Discrimination Check	1-18
Trouble shooting	1-18
Quality Control (QC) samples	1-20
Peak Identification	1-20
Trouble shooting	1-20
Running the ASTM D 6729 analyzer	1-21

Introduction

This section contains information about the ASTM D 6729 DHA analyzer. The detailed analysis of hydrocarbon samples with AC DHA capillary gas chromatography 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 (D86). 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; however, statistical data was obtained only with blended spark-ignition engine fuels.

Although the 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 method 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.

Note

This method was formally known as the AC Slow CGSB method.

Configuration of the ASTM D 6729 analyzer

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

- an Autosampler,
- a split/split less injector (S/SL inlet),
- a dimethylsilicone coated capillary column
- a Flame Ionization Detector (FID).

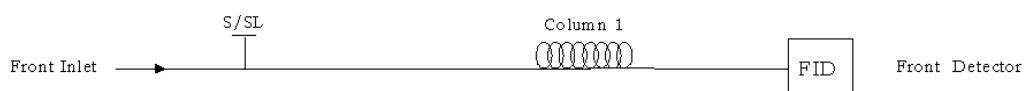
Note

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.

ASTM D 6729 hardware specifications

Flow diagram AC ASTM D 6729 analyzer

Helium carrier gas is introduced as a carrier gas by the S/SL inlet through a 100 meter capillary column. A flame ionization detector detects the components.



Application manual ASTM D 6729

Consumables

Consumables

Item	Specification	Quantity	AC Part no.
Consumable Kit:	6890 / 7890		65186.700
	6850		65186.750
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 100m x 250µm x 0.5µm 6890 / 7890	1	25190.300 or
	HP-1 100m x 250µm x 0.5µm 6850		10.74.004
Sample box	Quant. Reference standard 512 (5pcs)	1	20001.420
Sample box	n-Paraffin standard C5-C15 (5pcs)	1	20001.421
Quality Control Samples:			
Reformer Feed (5pcs)		1	20001.410
Reformate (5pcs)		1	20001.411
FCC Naphtha (5pcs)		1	20001.412
Isomerase (5pcs)		1	20001.413
Alkylate (5pcs)		1	20001.414
Gasoline containing MTBE (5pcs)		1	20001.415
Gasoline containing ETBE and ethanol (5pcs)		1	20001.416
Gasoline containing EtOH (5pcs)		1	20001.417
Gasoline containing TAME (5pcs)		1	20001.418

AC DHA D 6729 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 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%
----------------------	----------------

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 sample contains the following components:

Group	Carbon number
Paraffins	C5 to C15
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 naphtha's), above n-octane might reflect significant errors in PONA type groupings. Based on the gasoline samples in the inter-laboratory 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

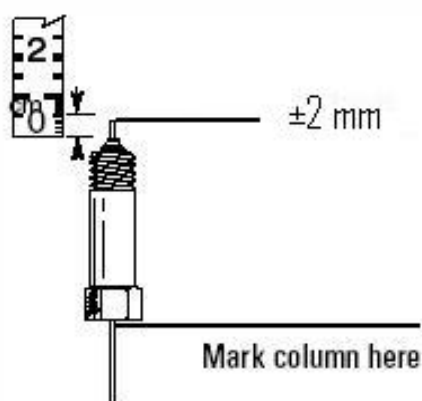
The capillary column must be attached to the S/SL injector. The connection of the column is very precise. Discrimination will occur if the column is not correctly installed.

- 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

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

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

Module	Parameter	Setting
GC-oven	Linear carrier flow (He)	2.2 ml/min
	Temperature	35 °C
Injector	Temperature	250 °C
Detector	Temperature	250 °C
	Hydrogen flow	35 ml/min
	Air flow	350 ml/min
	Makeup (He)	40 ml/min
	Baseline signal	± 12 pA
Gas saver	Flow	30 ml /min
	Time	1.0 min

Application manual ASTM D 6729

Description of the AC DHA D 6729 GC-method

Description of the AC DHA D 6729 GC-method

	C1toC4	D6729 / D6729-7890
Purpose	For natural gas	For sample analyses
Injector	Split/split less	Split/split less
Injector Temp (°C)	250	250
EPC pressure [kPa]	301	301
Column	100m * 250µm * 0.50µm HP-1	100m * 250µm * 0.50µm HP-1
Carrier gas	He	He
Linear Velocity (cm/s)	26	26
Split ratio	200:1	200:1
Sample size	2.5 µl	0.5 µl
Gas saver Flow	30 ml/min	30 ml/min
Gas saver Time	1.0 min	1.0 min

Oven Temp 1 [°C]	0	0
Time 1 [min.]	15	15
Rate 1 [°C/min.]		1
Oven Temp 2 [°C]		50
Time 2 [min.]		0
Rate 2 [°C/min.]		2.0
Oven Temp 3 [°C]		130
Time 3 [min.]		0
Rate 3 [°C/min.]		4
Oven Temp 4 [°C]		270
Analysis time [min.]	15	140

Detector	FID	FID
Detector Temp (°C)	300	300
Hydrogen Flow (ml/min.)	35	35
Air Flow (ml/min.)	350	350
Make Up Flow He (ml/min.)	40	40

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.

WARNING 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.

Preparing the n-Paraffin's C₅ to C₁₅ standard

The AC DHA is based on the principle of referring component retention times to the retention times of n-Paraffin's according to the Kovats index system. The retention times of n-Paraffins are measured with an n-Paraffin standard. This standard consists of n-Paraffins from C₅ to C₁₅. This measurement should be carried out on a regular basis to prevent erroneous storage of retention times of the n-Paraffins.

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

- 1 Fill a 2 ml vial with 0.1 gram of the n-paraffin standard.
- 2 Add to the vial app. 1 ml CS₂.
- 3 Place the vial in the desired position of the sampler tray.

This will give a solution of app. 1 mass % per component.

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 6729 method

Column Specifications

Material	Fused Silica
Length	100 m
Internal Diameter	0.25 mm
Liquid phase	methyl silicone
Film Thickness	0.50 μ 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

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 Set the oven temperature on 225 °C for 1 hour.
- 2 Set the oven temperature on 35 °C and record the signal output of the detector.
- 3 Set the oven temperature on 200 °C and record the signal output of the detector.
- 4 Keep the oven temperature on 200 °C until the signal output is within approximately 100 up to 105% of the signal 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 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.

ASTM method D 6729 specifies a holdup time of **6.74 \pm 0.05 minutes at 0°C** and is operated at constant pressure. The following procedure will result in the correct methane retention time.

The procedure is described in detail in the corresponding data system manual. This section only refers to the necessary task that must be performed.

Critical Separations

Warning

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

The Alcohol peaks elute before the other peaks, depending on the temperature program. Higher oven temperatures will move the alcohols into the peaks ahead of them.

Co-elutions

Component	Co-eluting component
n-Propanol	3-methyl-1-pentene
MTBE	2,3-dimethylbutene-1
ETBE	2,3-dimethyl-1,3-butadiene
Toluene	2,3,3-trimethylpentane
Benzene	1-methylcyclopentene

Calibration

The D6729 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 nC₁₅ 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.

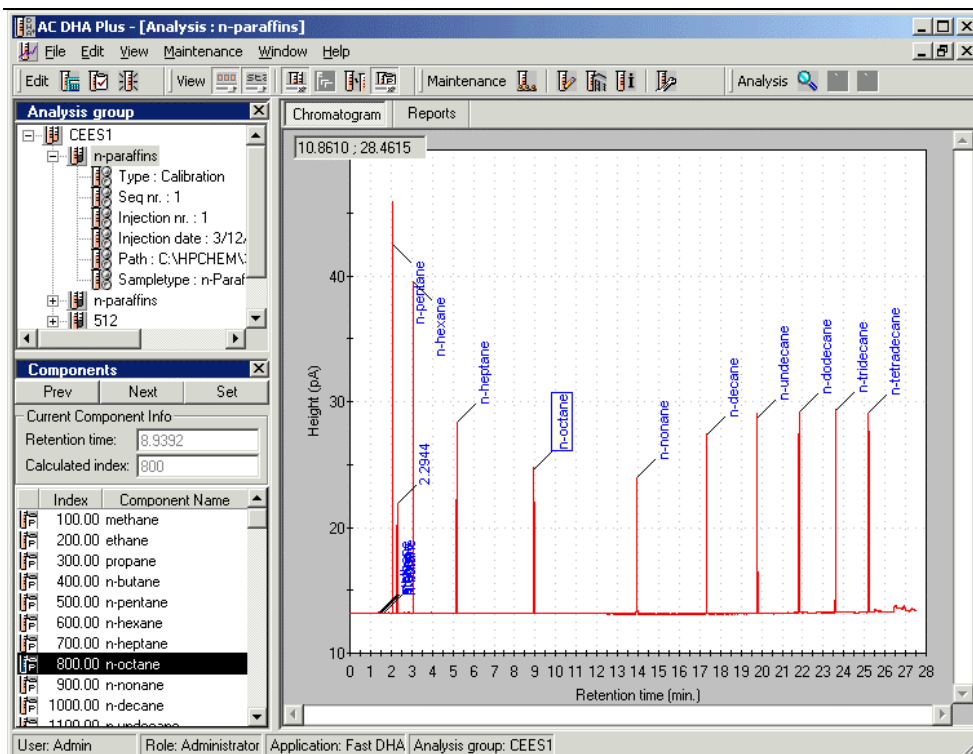
- 1 Follow the instructions in the section **Preparing samples**.
- 2 Create a sequence with:

Sample Name	Sample Type	GC Method
C1 to C4 sample	n-Paraffin Standard	C1ToC
Standard C5 to C15	n-Paraffin Standard	D6729

- 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 ASTM D 6729

Calibration



Note

The second peak in chromatogram is the solvent, carbondisulfide. The above picture is just a DHA plus example of an n-Paraffin mixture. ASTM D 6729 has another timescale.

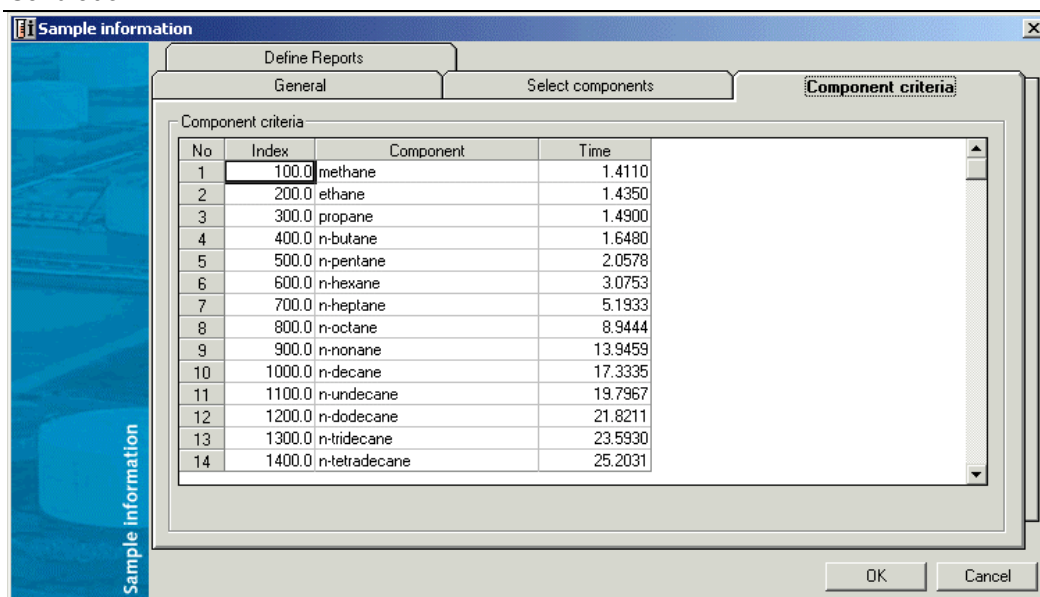
- 7 Check if the labels are correctly pointing to the peaks. Click a peak retention time if this is not the case and then select the correct component name in the components area. Press **set** to make the change.


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 ASTM D 6729

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.

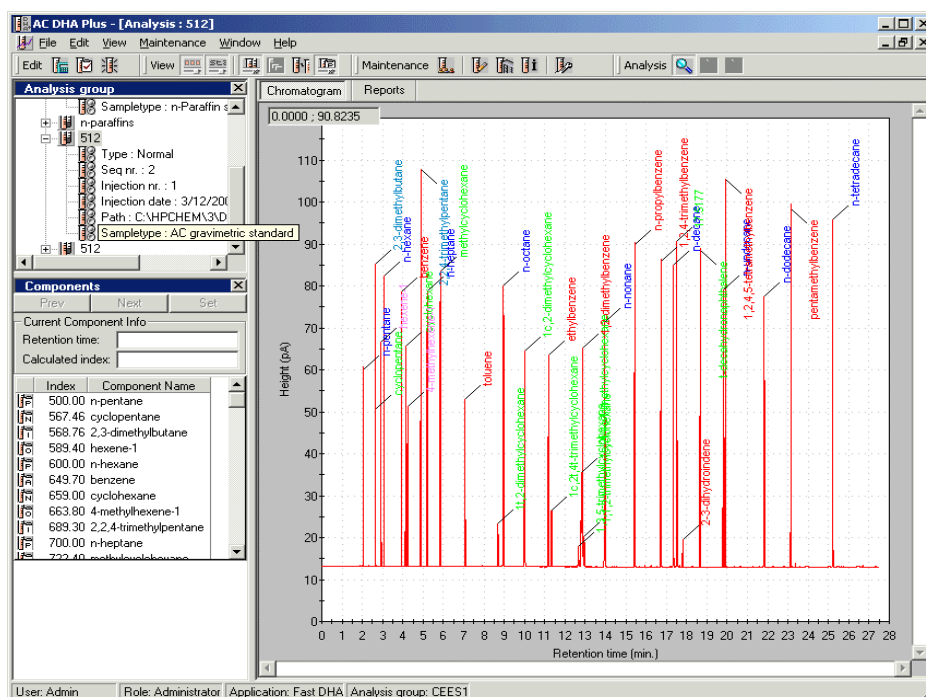
The test mixture has a number of compound groups that have different response factors for the FID. If there is a difference in response between different compound groups (e.g. n-paraffins and aromatics), something might be wrong with the detector (flows).

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 2 mm beyond the ferrule head (into the S/SL liner).

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.

Application manual ASTM D 6729

Discrimination Check

- 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.

Quality Control (QC) samples

Peak identification can be validated with 9 Quality Control. 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.

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 6729 analyzer

WARNING

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.
