Joint Analytical Systems

HPLC Solutions

The analysis of aromatics contents in Middle Distillates (diesel and jet fuels and petroleum distillates) in the range of 50° to 400° by means of **HPLC/RID according to ASTM D6591, IP391, EN12916 and ASTM D6379 (Jet fuel)**

Serving our Future

Analysis of aromatics contents in Middle Distillates (diesel and jet fuels) Analyzer

Introduction

The amount of mono-, di-, tri- and poly aromatics in Middle distillates is subjected to regulations. For the determination of these groups in diesel, petroleum distillates and jet fuel, **Joint Analytical Systems** (JAS) offers an HPLC system analyser based on Agilent Technologies: a robust and innovative High Performance Liquid Chromatograph.

The Agilent HPLC analyser is able to meet and exceed the specification and the analysis mentioned in ASTM D6591, IP391, EN12916 and ASTM D6379 (Jet fuel).

This analyzer is dedicated to the analysis of aromatics contents in diesel fuels, Aviation fuels and petroleum distillates in the range of 150° to 400°.

The sample is introduced in the system by the automatic Liquid Sampler of by a Manual injector. It is analyzed using Heptane as solvent. The LC column is isothermally heated in a column compartment, detection is done by the Refractive Index Detector (RID). There is a back flush valve installed to backflush the FAME in Diesel.

The Agilent 1260 Infinity Quaternary LC offers the most flexibility for solvent selection and automation in HPLC method development, research and all HPLC applications requiring continuous access to a wide range of solvent choices. The availability to rapidly switch between methods using different solvents and the capability of using binary, ternary or quaternary solvent gradients make the Agilent 1260 Infinity Quaternary LC the most flexible system on the market.

Figure 1: Complete HPLC solution

System hardware

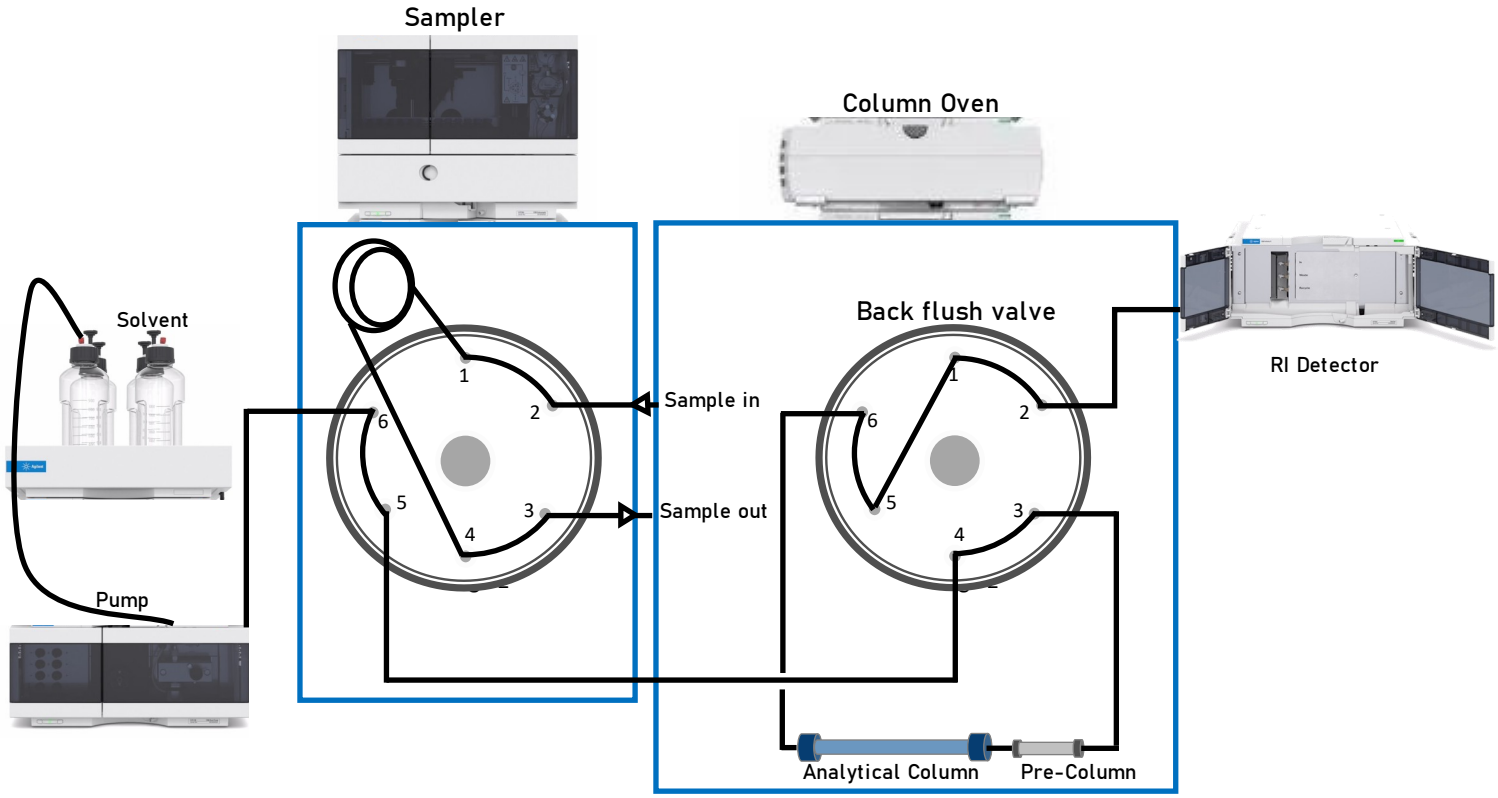


Figure 2: Flow Diagram for ASTM D6591, IP391, EN12916 and ASTM D6379

JAS HPLC 1260 Infinity analyser consisting of:

Pump:	Agilent Technologies 1260 Infinity Isocratic Pump (0.05-10 mL/min, max 600 bar)
Injector:	Agilent Technologies Infinity 1260 Auto Sampler
Column Compartment:	1260 Thermostatted Column Compartment, 1260 Infinity Column Thermostat. Two separate Heat exchanger to pre-heat the solvent up to 80 °C. 6 Port Back flush Valve
Column:	25 cm HPLC Analytical Column (Guard column included)
Detector:	Refractive Index Detector with Waste/Mobile phase auto switch
PC +Software:	Personal Computer + pre-installed Agilent OpenLab software (LC driver)

ASTM D6591

Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection

This test method covers a high performance liquid chromatographic test method for the determination of monoaromatic, di-aromatic, tri+-aromatic, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range from 150 to 400°C. The total aromatic content in % m/m is calculated from the sum of the corresponding individual aromatic hydrocarbon types.

precision of this test method has been established for diesel fuels and their blending components, containing from 4 to 40 % (m/m) mono-aromatic hydrocarbons, 0 to 20 % (m/m) di-aromatic hydrocarbons, 0 to 6 % (m/m) tri+-aromatic hydrocarbons, 0 to 26 % (m/m) polycyclic aromatic hydrocarbons, and 4 to 65 % (m/m) total aromatic hydrocarbons. Compounds containing sulfur, nitrogen, and oxygen are possible interferents. Mono-alkenes do not interfere, but conjugated di- and poly-alkenes, if present, are possible interferents. By convention, this standard defines the aromatic hydrocarbon types on the basis of their elution characteristics

from the specified liquid chromatography column relative to model aromatic compounds. Quantification is by external calibration using a single aromatic compound, which may or may not be representative of the aromatics in the sample, for each aromatic hydrocarbon type. Alternative techniques and methods may classify and quantify individual aromatic hydrocarbon types differently. Fatty Acid Methyl Esters (FAME), if present, interfere with tri+-aromatic hydrocarbons. If this method is used for diesel containing FAME, the amount of tri+-aromatics will be over estimated.

IP391

Determination of aromatic hydrocarbon types in diesel fuels and distillates -- High performance liquid chromatography refractive index detection method

This method determines monocyclic, bicyc!ic and tricylic + tetracyclic aromatics in diesel fuels and petroleum distillates, boiling in the range 90 - 430°C. The method covers the concentration range from 0.05 to 40 volume percent for monocyclic aromatics and 0.05 to 30 volume percent for bicyclic and tricylic + tetracyclic aromatics. Higher concentrations of aromatics can be determined after appropriate dilution. Compounds containing oxygen or nitrogen, if present, may interfere and cause erroneous results.

2.1. A reproducible quantity of dried sample, diluted in cyclohexane, is injected into a liquid chromatograph fitted with a polar column. This column has very little affinity for paraffins while exhibiting a pronounced selectivity for aromatics.

The result of this selectivity is that the aromatics are separated from the paraffins into distinct bands according to their ring structure i.e. mono, bi, tri +tetra. The column is connected to a refractive index detector which detects the components as they emerge from the column. The electronic signal from the detector is continually monitored by a data processor which compares the amplitudes of the signals of the sample aromatics with those obtained from a previously run calibration sample. A complete report is automatically produced at the appropriate terminal.

ASTM D6379

Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection.

This test method covers a high performance liquid chromatographic test method for the determination of monoaromatic and di-aromatic hydrocarbon contents in aviation kerosines and petroleum distillates boiling in the range from 50 to 300°C, such as Jet A or Jet A-1 fuels. The total aromatic content is calculated from the sum of the individual aromatic hydrocarbon-types.

This test method is calibrated for distillates containing from 10 to 25 % m/m mono-aromatic hydrocarbons and from 0 to 7 % m/m di-aromatic hydrocarbons.

The precision of this test method has been established for kerosine boiling range distillates containing from 10 to 25 % m/m mono-aromatic hydrocarbons and from 0 to 7 % m/m di-aromatic hydrocarbons.

Concentration range, Repeatability & Reproducibility

IP391

Aromatic Type	Range %(m/m)	Repeatability	Reproducibility
Mono-aromatics	4 – 40	0.026 * (X + 14.7)	0.063 * (X + 17.3)
Di-aromatics	0 – 20	0.10 * (X + 2.6)	0.32 * (X + 1.8)
Polycyclic aromatics	0 – 6	0.12 * (X + 0.6)	0.64 * (X + 0.3)
Total Aromatics	4 – 65	0.036 * (X + 1.5)	0.116 * (X + 6.3)

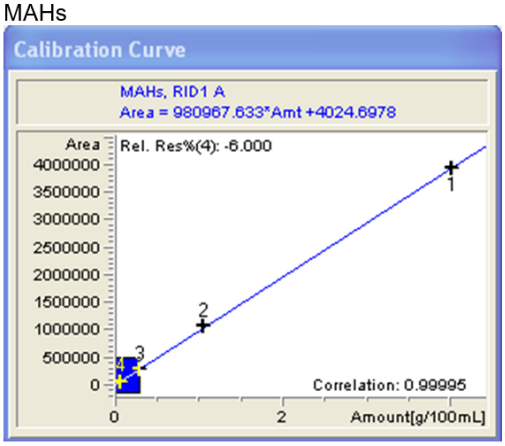
ASTM D6379

Aromatic Type	Range %(m/m)	Repeatability	Reproducibility
Mono-aromatics	0.10-6.64	$0.337\ x^{0.333}$	$0.514\ x^{0.333}$
Di-aromatics	10.5-24.1	$0.129\ x^{0.667}$	$0.261\ x^{0.667}$

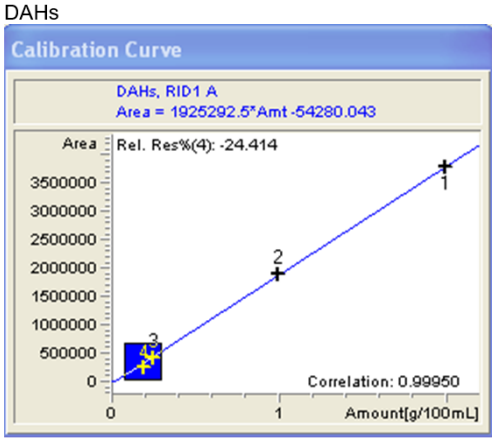
ASTM D6591 /EN12916

Aromatic Type	Range %(m/m)	Repeatability	Reproducibility
Mono-aromatics	4 – 40	0.026 * (X + 14.7)	0.063 * (X + 17.3)
Di-aromatics	0 – 20	0.10 * (X + 2.6)	0.32 * (X + 1.8)
Tri+-aromatics	0 – 6	0.12 * (X + 0.6)	0.64 * (X + 0.3)
Polycyclic-aromatics	0 – 26	0.13 * (X + 2.5)	0.29 * (X + 2.5)
Total Aromatics	4 – 65	0.036 * (X + 1.5)	0.116 * (X + 6.3)

MAHs



DAHs



T+AHs

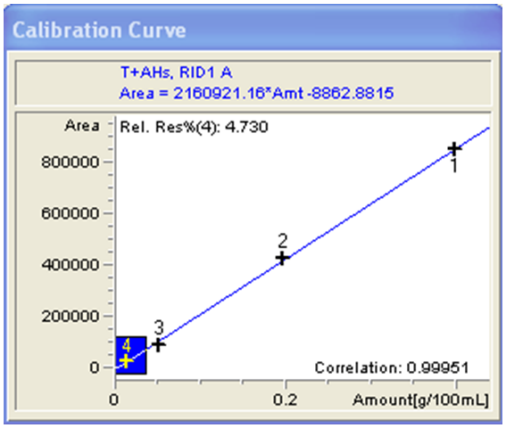


Figure 3: Calibration curves Mono-Aromatics, Di-Aromatics and Tri-Aromatics

Figure 3: ASTM D1945/D6228 example Chromatograms

Example Chromatogram & Reports

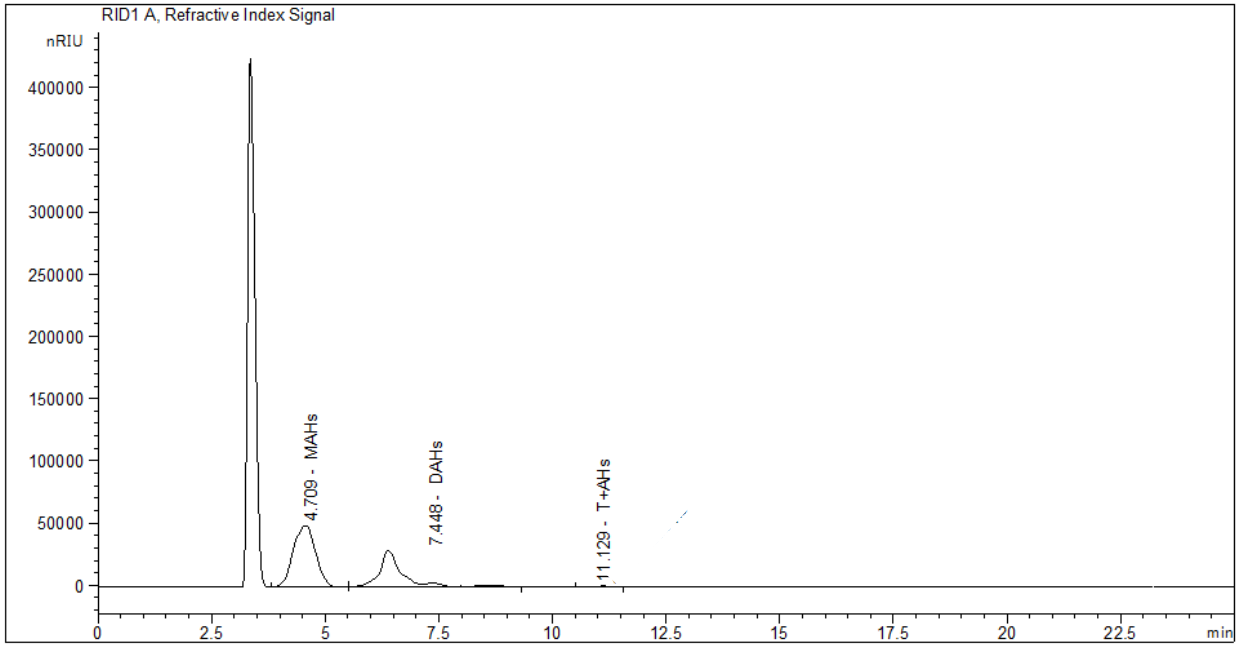


Figure 4: Example Chromatogram of a Diesel sample

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================================================================================
                          ESTD Percent Report
================================================================================

Sorted By             :      Signal
Calib. Data Modified  :      Friday, November 12, 2023 1:46:48 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     10.00000  [g/100mL]
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: RID1 A, Refractive Index Signal

RetTime  Type     Area      Amt/Area    Amount   Grp   Name
 [min]          [nRIU*s]                  %
-------|------|----------|----------|----------|--|-----------------
  4.709 VVA+   1.71320e6  1.01701e-6  17.423344    MAHs
  7.448 VBA+   1.08821e6  5.45310e-7   5.934090    DAHs
 11.129 MM     3.28349e4  5.87676e-7   0.192963    T+AHs
Totals :                               23.550397

================================================================================
                          *** End of Report ***
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Figure 5: Example Report of diesel Sample

Agilent OpenLab Software

OpenLab CDS is a chromatography data system that combines productivity, usability, and data integrity. With a single user interface, you can control your Agilent LC, GC, single quadrupole LC/MS, and GC/MS, as well as other vendors' instruments in the lab, to streamline training and support.

Built-in tools provide time-saving steps in the analysis, interpretation, and reporting workflows while technical controls ensure work quality, effective records management, and enhanced data security. OpenLab CDS is ideal for analytical labs that need the highest level of data integrity.

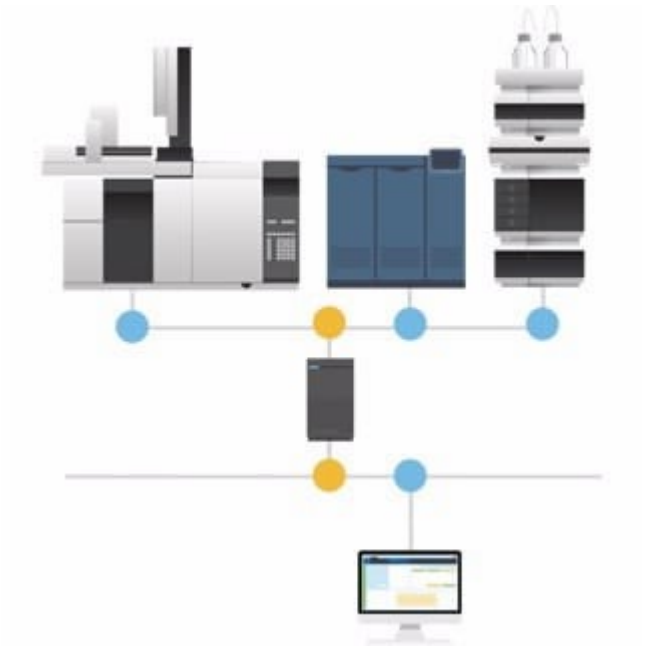

Figure 5: OpenLab Chemstation Client Server, Enhance laboratory operations

Features and Benefits

- The 1260 Infinity LC offers more rapid resolution power, pushing RRLC (Rapid Resolution LC) performance to new limits
- Includes Refractive Index Detector with mobile phase switch to waste during analysis and to mobile phase bottle after analysis, saving mobile phase
- Includes all the calibration, reference and resolution check samples for all the methods
- Factory tested for all the methods
- Meets and exceeds ASTM, EN and IP method
- One year Application and hardware guarantee
- Includes Automatic Liquid Sampler
- Installed by a factory Engineer
- Dedicated turnkey analyzers for chemical and petrochemical applications available