PAC | Application Note

AC MDA: Comprehensive multi-method analyzer for aromatic hydrocarbon type content in middle distillate streams

- Aromatic hydrocarbon type content in Jet & Diesel Fuel
- Turn-key, multi-method analyzer
- Validated against EN 12916 & ASTM D6379 & ASTM D6591

Keywords: Aromatics, Middle Distillates, HPLC

INTRODUCTION

Analysis of hydrocarbon type content is an important parameter for quality control of fuels. Fuel standards mandate the analysis of these component groups to guarantee product usability, such as combustion properties, as well as compliance to environmental legislation.
For both Jet and Diesel fuel, aromatics content is related to higher pollutant emissions such as particulates from turbine and compression-ignition engines. Additionally, a high concentration of aromatics in diesel fuel lowers the cetane index. Therefore a maximum limit is imposed on aromatics content of these fuels.

SOLUTION

To assist refiners in determining the aromatic content of diesel fuels, AC Analytical Controls developed a fast, robust and easy-to-use system: the AC Mid Distillates Analyzer (MDA). The AC MDA application is based on the latest Agilent HPLC systems, and is compliant with multiple methods. This allows analysis of both jet and diesel fuel with one analyzer.

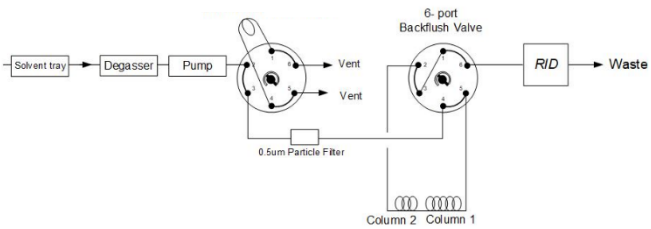

Figure 1: Flow diagram MDA system

Table 1: MDA method overview

Methods	Scope	Boiling range
EN 12916 IP 391	Aromatic Hydrocarbon Types in Diesel Fuel that may contain FAME	150 °C to 400 °C
ASTM D6379 IP 436	Hydrocarbon Types in Aviation Fuels and Petroleum Distillates	≤ 300 °C
ASTM D6591 IP 548	Aromatic Hydrocarbon Types in Middle Distillates	150 °C to 400 °C

ANALYSIS

The AC MDA is based on a normal phase HPLC method and uses refractive index detection. The sample is dissolved in heptane and this solution is separated on a polar column set consisting of both a cyano- and amino-bonded phase. This column set has little affinity for non-aromatic hydrocarbons, whilst exhibiting a strong selectivity for aromatic hydrocarbons. As a result of this selectivity, the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons and into distinct bands according to their ring structure, i.e. mono-, di or tri+ aromatic compounds. Additionally, on the ASTM D6379 & IP 436 applications, the tri+ aromatics are backflushed to the detector. The total aromatic content is calculated from the sum of the corresponding individual aromatic hydrocarbon types.

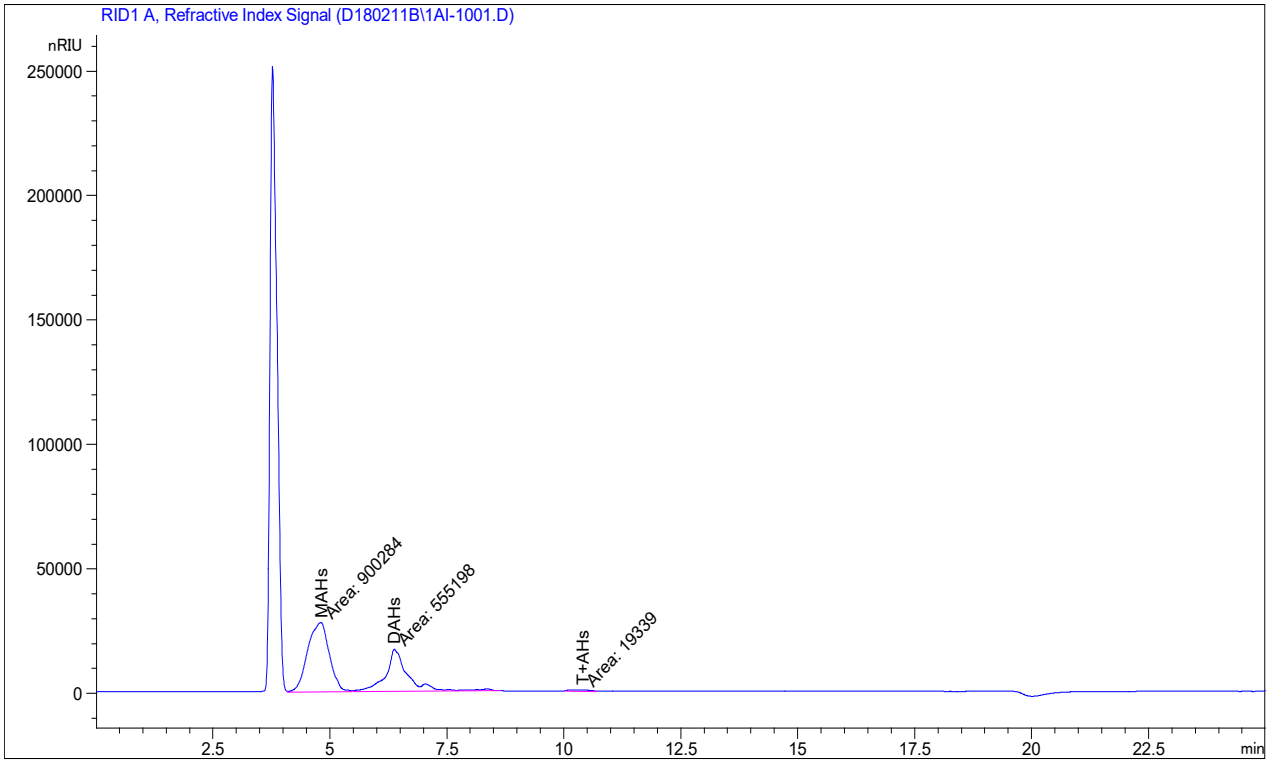

Figure 2: Chromatogram Reference Gasoil

Table 2: Results Reference Gasoil

Component	Certified value (%m/m)	EN12916 (%m/m)	ASTM D6379 (%m/m)	ASTM D6591 (%m/m)
Mono-aromatics (MAHs)	15.76 ± 2.08	16.2	14.90	15.49
Di-aromatics (DAHs)	5.55 ± 2.35	5.28	5.67	4.79
Tri-aromatics (T+AHs)	0.32 ± 0.40	0.14	-	0.46
Total aromatics	21.66 ± 3.24	21.62	20.57	20.74

METHOD TUNING & VALIDATION

Each AC system is factory tested, tuned and calibrated and delivered as a turn-key application, including startup kit which includes the necessary items and reference samples for a quick startup on-site.

For the AC MDA, tuning & testing parameters mentioned in the respective methods are all checked in the factory, a comprehensive testing document is included with the analyzer detailing the results of the tests. A reference sample is analyzed after the factory test as shown in figure 2.

A few examples of the specifications tested are given below.

RESOLUTION SPECIFICATION (EN 12916)

The resolution between Cyclohexane and o-Xylene in the SCS 1 sample should be between 5.7 and 10.

$R = 2 * (t3 - t1) / (1.699 * (y1 + y3))$

Where:

t1	: retention time cyclohexane	3.845 min
t3	: retention time o-Xylene	4.833 min
y1	: peak width at ½ height of cyclohexane	0.07731 min
y3	: peak width at ½ height of o-Xylene	0.09718 min

Resolution: 6.67

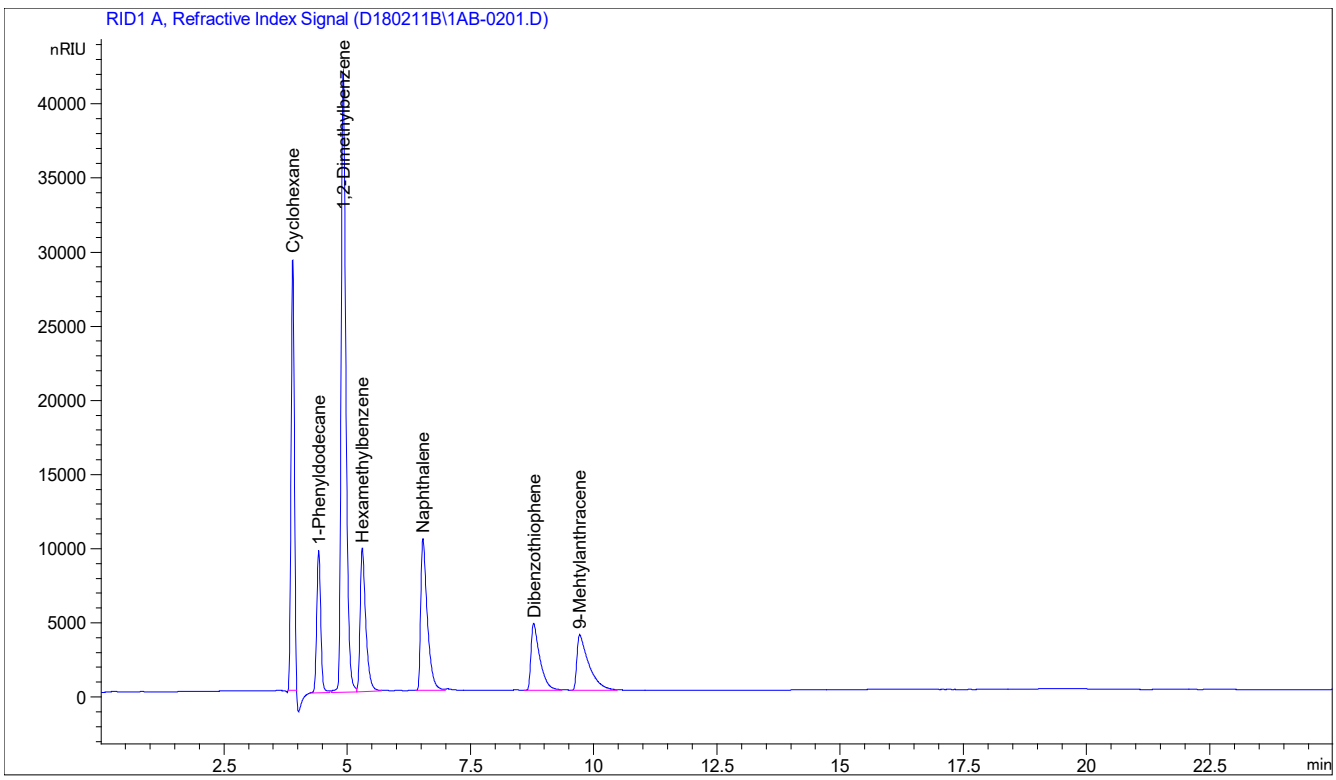

Figure 3, Chromatogram EN 12916 System Calibration Standard (SCS 1)

LINEARITY & INTERCEPT (ASTM D6379)

The linearity is checked by analyzing a set of samples containing cyclohexane, o-Xylene and 1-Methylnapthalene at different concentration levels.

The calibration curve for the individual groups (mono-aromatics (MAHs) and di-aromatics (DAHs) must have a correlation of minimal 0.999 and a maximal intercept of 0.01g/100mL.

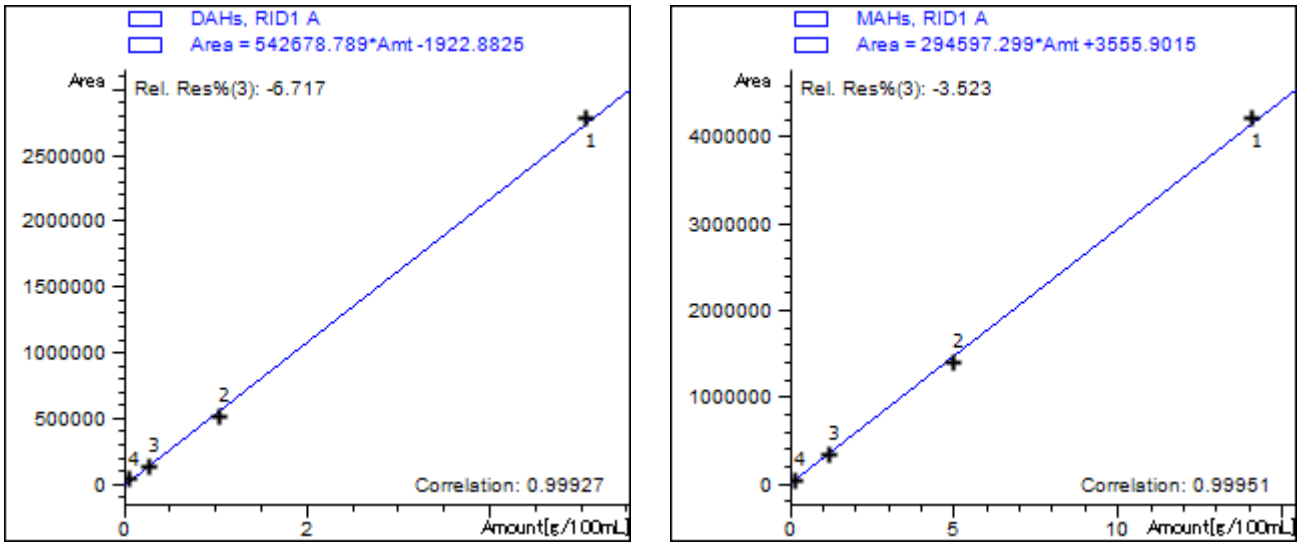

Figure 4: linearity plots for MAH & DAH

Table 3: Correlation and intercept results

Component group	MAHs	DAHs
R^2 ASTM D6379	> 0.999	> 0.999
Intercept ASTM D6379	≤ 0.01	≤ 0.01

CONCLUSION

The AC MDA analyzer is a convenient tool for analyzing middle distillates, combining aromatics methods for both jet and diesel fuel into one system. The factory validation by AC Analytical Controls demonstrates the compliancy to various standard test methods, and saves the end-user a significant amount of time setting up the system in the laboratory. The complete startup kit included with the systems contains the required materials and reference samples to start analyzing samples shortly after system installation.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.