Global Analyser Solutions

# TOTAL AROMATIC, POLYAROMATIC AND FAME CONTENT OF DIESEL FUELS USING GC-VUV

- ASTM D8368
- For diesel fuels and biodiesel blends
- Mono-, di-, tri+, total aromatic content, total PAHs, FAME content B1 – B20.

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GAS offers custom configured GC analysers for many application fields for over 50 years. GAS analysers are designed to meet many standardised methods from GPA, ASTM, UOP, ISO, EN and others. The efficient configurations are based on proven GC technology, resulting in robust, highly productive instruments with an optimal return on investment.

**The combustion properties of diesel fuel and the resulting emissions from their consumption is greatly influenced by the percentage of aromatic hydrocarbons that are present. As a result, measuring the aromatic content of diesel fuels is important not only to determine the quality of the fuel from a manufacturing standpoint, but also to comply with environmental regulations for air quality and emissions. While it is important to measure aromatic hydrocarbons, modern diesel fuels are often blended with as much as 20% (B20) biodiesel. As a result, it is also important to measure the fatty acid methyl esters (FAMEs) content to ensure compliance with current diesel fuel specifications.**

## The power of VUV spectra

Hydrocarbon analysis that previously required complex chromatographic separation can be simplified and shortened due to the ability to deconvolve overlapping spectral responses (figure 1). VUV absorbance spectra are typically highly structured and distinct for individual compounds, yet exhibit the intrinsic property of having similar features when measuring related compound classes, see figure 2. GC-VUV absorbance data is inherently three dimensional (time, absorbance, wavelength) and specific to the compound chemical structure.

## Spectral validation, automated analysis.

GC-VUV offers accurate diesel analysis with spectral validation. Sample preparation is not required; the diesel sample is injected directly. Aromatics, polyaromatic hydrocarbons and fatty acid methyl esters are rapidly separated and quantified in 25 minutes. The instrument provides automated analysis and reporting using VUV Analyze™ Software.

## Straightforward instrument

GC-VUV uses easy instrumentation: Thermo Trace GC 1600 gas chromatograph, a single capillary column and VUV-VGA detector (figure 7). No traps, pre-column tuning or calibration requirements are needed. Method setup is easy, operational costs are lows and time-consuming manual data review is no longer required.

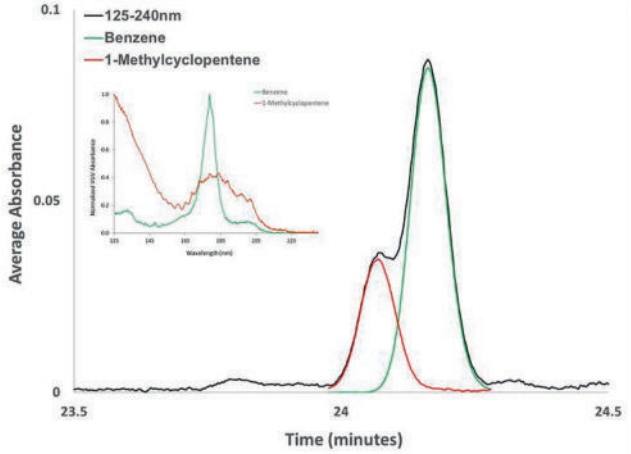


**Figure 1** Example GC-VUV chromatogram. Benzene and 1-methylcyclopentene are not well separated (black). Relative proportion of both components is displayed after deconvolution by VUV software (red/green).
Inset: unique spectra.

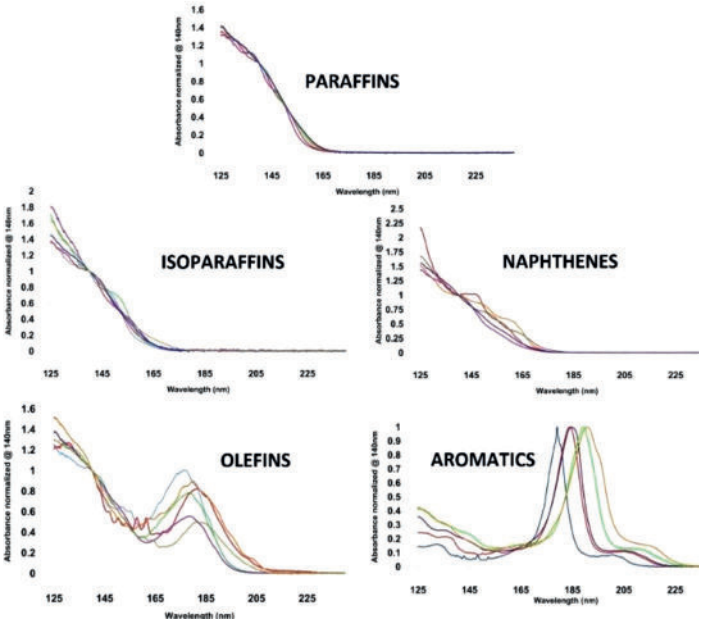


**Figure 2** Distinct spectra for PIONA component classes. VUV spectra are highly stable and independent of instrument settings. Reliable identification is also offered for paraffins and iso-paraffins, which apparently have small spectral differences.

## Single analytical technique

GC-VUV offers a new approach for the analysis of diesel and biodiesel fuel blends using a single analytical technique, replacing the use of multiple analytical techniques and methods. See figure 3.

| ASTM METHOD | D1319 | D5186 | D6591 | D7371 | D8368 |
|---|---|---|---|---|---|
| TECHNIQUE | FIA | SFC | HPLC | FTIR-ATR-PLS | GC-VUV |
| Mono-aromatics | | X | X | | X |
| Di-Aromatics | | | X | | X |
| Tri+ Aromatics | | | X | | X |
| PAHs | | X | X | | X |
| Total Aromatics | Vol % only | X | X | | X |
| FAMEs | N/A | N/A | N/A | 1-20% vol | 1-20% vol |

**Figure 3** Several diesel test methods and the parameters they measure. ASTM D5186 and ASTM D6591 require special vol % calibration, which is not needed for ASTM D8368.

# Results

## ASTM D8368

System validation is performed using a certified gravimetric standard manufactured in compliance with ISO 17034 containing known quantities of linear alkanes (C7 to C30) and compound class markers. This system validation mixture is used to automatically create a retention time marker file and to assess split linearity. Data acquisition takes approximately 25 minutes per sample, and post-processing takes approximately 60 seconds. Post-processing is an automated process using VUV Analyze Software in which each chromatogram is divided into 2400 equally spaced time intervals.

Each of those time intervals is then analysed independently with each overlapping spectra deconvolved, identified, and then quantified using an approach called Time Interval Deconvolution™. Figure 4, 5 and 6 show results of a biodiesel blend.

Mass %

| C# | Saturates | Aromatics | Mono-A | Di-A | Tri(+)-A | PAHs | FAMEs | Total |
|---|---|---|---|---|---|---|---|---|
| C1-C5 | | | | | | | | |
| C6 | 0.2221 | 0.0389 | 0.0389 | | | | | 0.2610 |
| C7 | 0.8331 | 0.2613 | 0.2613 | | | | | 1.0945 |
| C8 | 1.5239 | 0.6432 | 0.6432 | | | | | 2.1671 |
| C9 | 1.6290 | 1.0194 | 1.0194 | | | | | 2.6485 |
| C10 | 2.8629 | 1.5779 | 1.5606 | 0.0173 | | 0.0173 | | 4.4408 |
| C11 | 5.2669 | 3.0932 | 2.9734 | 0.1198 | | 0.1198 | | 8.3601 |
| C12 | 5.3581 | 5.5808 | 5.3690 | 0.2118 | | 0.2118 | | 10.9389 |
| C13 | 9.5396 | 4.5230 | 4.1730 | 0.3500 | | 0.3500 | | 14.0625 |
| C14 | 7.6855 | 3.1503 | 2.9635 | 0.1868 | | 0.1868 | | 10.8358 |
| C15 | 9.3762 | 1.8674 | 1.8667 | | 0.0007 | 0.0007 | | 11.2436 |
| C16 | 8.2637 | 1.3547 | 1.3135 | 0.0047 | 0.0365 | 0.0412 | | 9.6184 |
| C17 | 4.2228 | 0.9877 | 0.6825 | 0.2403 | 0.0648 | 0.3051 | 0.7498 | 5.9603 |
| C18 | 3.3195 | 0.4889 | 0.2531 | 0.1723 | 0.0635 | 0.2359 | | 3.8084 |
| C19 | 2.5133 | 0.2427 | 0.1261 | 0.0696 | 0.0469 | 0.1166 | 4.8086 | 7.5646 |
| C20 | 1.9431 | 0.2090 | 0.0690 | 0.0256 | 0.1145 | 0.1401 | | 2.1521 |
| C21 | 1.5972 | 0.0548 | 0.0026 | 0.0213 | 0.0310 | 0.0523 | 0.0472 | 1.6993 |
| C22 | 1.1206 | 0.0447 | | 0.0006 | 0.0440 | 0.0447 | | 1.1653 |
| C23 | 0.8971 | 0.0071 | 0.0052 | | 0.0019 | 0.0019 | 0.1165 | 1.0208 |
| C24 | 0.5081 | 0.0024 | 0.0024 | | | | | 0.5105 |
| C25 | 0.3676 | | | | | | | 0.3676 |
| C26 | 0.0767 | | | | | | | 0.0767 |
| C27 | 0.0034 | | | | | | | 0.0034 |
| Total | 69.1304 | 25.1474 | 23.3234 | 1.4201 | 0.4039 | 1.8240 | 5.7222 | 100.0000 |

**Figure 4**
Carbon number breakdown report of a biodiesel sample in mass %. (volume % and mole % are available as well). Note that the "Totals" column is the summation of the "Total Saturates", "Total Aromatics", and "Total FAMEs" parameters. Total Saturates are reported, however, precision has not been calculated for this parameter.

| Report Name | Mass % | Volume % | Mole % |
|---|---|---|---|
| Total Saturates | 69.1304 | 71.5370 | 67.5895 |
| Total Aromatics | 25.1474 | 23.2864 | 28.6988 |
| Total Mono-Aromatics | 23.3234 | 21.8453 | 26.9256 |
| Total Di-Aromatics | 1.4201 | 1.1412 | 1.4601 |
| Total Tri(+)-Aromatics | 0.4039 | 0.2999 | 0.3131 |
| Total PAHs | 1.8240 | 1.4411 | 1.7732 |
| Total FAMEs | 5.7222 | 5.1766 | 3.7116 |

**Figure 5**
Results of an analysis of diesel fuel using ASTM D8368. Results in mass %, volume % and mole %.

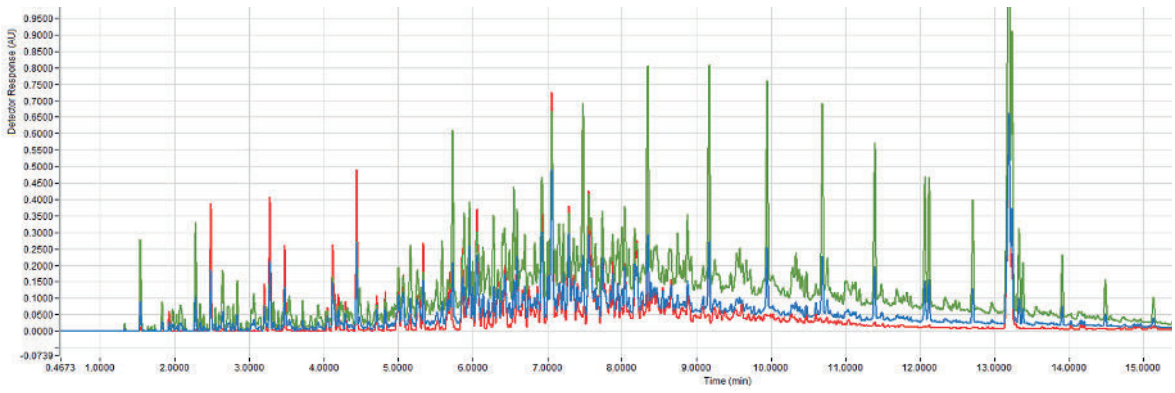


**Figure 6**
Chromatogram of a biodiesel blend by VUV-Analyze™ engine, showing spectral filters 170-200 nm (red, aromatics) and 125-160 nm (yellow, saturates). (The blue graph represents the total signal). The runtime is 25 minutes.

# Specification

## ASTM D8368

| | |
|---|---|
| Standardised method: | ASTM D8368 |
| Application: | Automated analysis of the total saturate, aromatic, polyaromatic, and fatty acid methyl ester (FAME) content of diesel fuels using GC-VUV. |
| Analysis Time: | 25 minutes |
| Column type: | Restek Rtx-1, 30m*0.25mm, df=0.25u |
| GC oven temperature program: | 50 °C (0.1 min) - 15 °C/min - 260 °C (10.9 min). |


**Figure 7**
VUV Analytics VGA-100 + Thermo Trace GC 1600

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