



**PROCEDURE FOR THE ANALYSIS OF POLYNUCLEAR AROMATIC  
HYDROCARBONS AND TOTAL AROMATIC HYDROCARBONS IN DIESEL FUELS BY  
SUPERCRITICAL FLUID CHROMATOGRAPHY AND FLAME IONIZATION  
DETECTOR**

SOP MV-FUELS-117  
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Fuels Analysis and Methods Evaluation Section  
Chemical Analysis and Emissions Research Branch  
Mobile Source Laboratory Division

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**SOP MV-FUEL-117- Procedure for the Analysis of Polynuclear Aromatic Hydrocarbons and Total Aromatic Hydrocarbons in Diesel Fuels by Supercritical Fluid Chromatography and Flame Ionization Detector**

1 Introduction

- 1.1 This document describes an automated method for the determination of total aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in diesel fuel.
- 1.2 The range of aromatics concentrations to which this test method is applicable is from 1 to 75 mass %. The range of PAH concentrations to which this test method is applicable is from 0.5 to 50 mass %.
- 1.3 This procedure is based on American Society for Testing and Materials (ASTM) D5186-03 (2009)<sup>1</sup>.

2. Method

- 2.1 The diesel sample is injected onto a packed silica adsorption column and the saturated, monocyclic aromatic and PAH fractions are eluted using supercritical carbon dioxide as the mobile phase.
- 2.2 The chromatographic areas corresponding to the nonaromatic, monocyclic aromatic, and PAH fractions are determined and the mass percent content of each group in the fuel is calculated by normalization.
- 2.3 A flame ionization detector (FID) is used to detect these three groups.

3. Instrument

- 3.1 Supercritical Fluid Chromatograph (SFC), equipped with SFC Pump, a Liquid Autosampler, two six-way switching valves (optional), Flame Ionization Detector (FID), and a computer system running automation software. With the two six-way valves, the instrument can be used also for the olefins analysis using ASTM D6550 without modifications.

4. Reagents and Materials

- 4.1 Purity of reagents: Unless otherwise specified, any chemicals used shall be American Chemical Society (ACS) reagent grade or better.

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4.2 Carbon dioxide (CO<sub>2</sub>), chromatographic grade, 99.995% minimum purity, supplied in a pressurized cylinder equipped with a dip tube for the removal of liquid CO<sub>2</sub>.

4.3 Naphthalene, 99+%

4.4 1,2,3,4-tetrahydronaphthalene (tetralin), 99% purity

4.5 Toluene, 99.8%, HPLC grade

4.6 Hexadecane, 99+%, anhydrous

4.7 Air, ultra zero grade (hydrocarbon free)

4.8 Hydrogen, 99.99% purity

4.9 Nitrogen

4.10 Helium, commercial grade

5. Preparation of Instrument

5.1 Before analysis, the SFC instrument need to be on and warmed up until all the gas flows, the CO<sub>2</sub> pressure, the FID, oven and column temperatures are stabilized.

5.2 The total run time for the performance mixture must be long enough for complete elution of the naphthalene peak. The total run time for the diesel samples is empirically set at around 3 times the apex of the naphthalene peak in the performance mixture.

6. Calibration

6.1 This method is based on normalization. No calibration is required.

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6.2 Detector accuracy, resolution, and retention time repeatability are regularly checked (see section 10 below) with a performance mixture made up of the following components, all weighed to the nearest 0.01 g:

- 2 g naphthalene
- 20 g toluene
- 3 g tetralin
- 75 g hexadecane

The naphthalene may take several hours to dissolve completely.

7. Procedure

7.1 2 mL of each sample is transferred into a glass autosampler vial and capped.

7.2 25  $\mu$ L is injected into the instrument by the autosampler.

7.3 The chromatographic response is integrated by the data system. Results are calculated as described in section 9.

8. Safety

8.1 Diesel fuel and many of its various components are toxic and flammable. Persons using this method must wear protective gloves and eyewear when working with reagents and samples. Reagents and samples are used in a fume hood with adequate ventilation.

8.2 All compressed gas cylinders present hazards and should be handled appropriately. Hydrogen is extremely flammable.

9. Calculations

9.1 The chromatogram is divided into three sections, each integrated as a single component.

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- 9.1.1 The first section runs from sample injection to the bottom of the lowest valley between the retention times of hexadecane and toluene (determined from the performance mixture analysis, see section 10.5 below.) This area represents the nonaromatic fraction of the sample.
- 9.1.2 The second section runs from the end of the first section to the beginning of the mixture's naphthalene peak (see section 10.5 below). This area represents the monocyclic aromatic fraction of the sample.
- 9.1.3 The third section runs from the end of the second section until the end of the chromatogram. The operator may choose to end the third section earlier to avoid errors due to slight drifts in the baseline. This area represents the PAH fraction of the sample.
- 9.2 The mass % of each fuel fraction is equal to the area percent of its corresponding chromatographic section. The total aromatic concentration is the sum of the monocyclic and polycyclic aromatic concentrations.
- 9.3 In some regulatory cases, total aromatic concentration in volume % is required. California Air Resources Board (CARB) and the Western States Petroleum Association (WSPA) have agreed on a correlation equation between mass and volume %. The equation used is:

$$\text{Total aromatics (volume \%)} = 0.916 \times \text{total aromatics (mass \%)} + 1.33$$

## 10 Quality Control

- 10.1 The performance mixture described in section 6.2 above is analyzed twice at the beginning of the analysis day, once after every five samples, and once again at the end of the analysis day. The analyses serve four functions:
- 10.1.1 Detector resolution is checked with every performance mixture analysis according to the following equations:

$$R_{NM} = \frac{2 \times (t_2 - t_1)}{1.699 \times (y_2 + y_1)}$$

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$$R_{MP} = \frac{2 \times (t_4 - t_3)}{1.699 \times (y_4 + y_3)}$$

Where:  $R_{NM}$  = resolution between the nonaromatic and monoaromatic peaks

$R_{MP}$  = resolution between the monoaromatic and polycyclic aromatic peaks

$t_1$  = time (seconds) for the n-C<sub>16</sub> peak apex

$t_2$  = time (seconds) for the toluene peak apex

$t_3$  = time (seconds) for the tetralin peak apex

$t_4$  = time (seconds) for the naphthalene peak apex

$y_1$  = peak width at half height (seconds) of the hexadecane peak

$y_2$  = peak width at half height (seconds) of the toluene peak

$y_3$  = peak width at half height (seconds) of the tetralin peak

$y_4$  = peak width at half height (seconds) of the naphthalene peak

$R_{NM}$  must be at least four and  $R_{MP}$  must be at least two in order for the detector to pass the resolution test. A macro (psintres.mac) designed for Microsoft Excel is normally used to calculate these quantities.

10.1.2 Retention time repeatability is checked using the initial two performance mixture analyses of the day. The retention times of hexadecane and toluene must not differ by more than 0.5% between the two runs.

10.1.3 Detector accuracy is checked with every performance mixture analysis. For each component of the performance mixture, a relative response factor is determined from the chromatogram according to the following equations:

$$RF_i = \frac{A_i}{M_i}$$

$$RRF_i = \frac{RF_i}{RF_{C16}}$$

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Where:

- $A_i$  = Area % of component I in the performance mixture  
 $M_i$  = Known mass % of component I in the performance mixture  
 $RF_i$  = Response Factor of component I  
 $RF_{C_{16}}$  = Response Factor of hexadecane in the performance mixture  
 $RRF_i$  = Relative Response Factor of component I

These empirical relative response factors are compared with theoretical relative response factors calculated by the following equations:

$$RRF_{\text{theor}} = \frac{(12.01n)}{MW} \times \frac{(226.4)}{12.01 \times 16}$$

where:

- 12.01 = the atomic mass of carbon  
N = the number of carbon atoms in the component molecule  
MW = molecular mass of the component molecule  
226.4 = molecular mass of hexadecane  
16 = the number of carbon atoms in hexadecane

The measured  $RRF_i$  for each component (toluene, tetralin and naphthalene) in the test mixture must be within 10% of the theoretical value as calculated with the above equation or summarized in Table 1.

- 10.1.4 The beginning time of the naphthalene peak is determined for every performance mixture analysis. This time is used in calculating results for the next set of samples (see sections 9.1.1 through 9.1.3 above.)
- 10.2 If any of the tests in section 10.1 above result in a failure, appropriate corrective action must be taken and the performance mixture rerun before any more samples may be analyzed.
- 10.3 Pure hexadecane is run as a blank once during each analysis day. If the total aromatics result is greater than 0.5 mass % or the PAH result is greater than 0.2 mass %, corrective action must be taken.

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10.4 One or more control samples must be run each analysis day.

10.4.1 Each sample to be analyzed must fall within 5 mass % total aromatics and 1.5 mass % PAH of at least one of the control samples.

10.4.2 Each control sample analysis must be within the published reproducibility (see section 10.4.4 below) of either:

The accepted values determined from interlaboratory testing or

The running average values determined on the instrument being used if no interlaboratory testing data is available.

10.4.3 If any control sample falls outside the acceptable range, corrective action must be taken and the sample reanalyzed before any samples can be run.

10.4.4 The reproducibilities for total aromatics and PAH are given by the following equations:

Total aromatics:  $R = 0.75 (\text{aromatics mass}\%)^{0.23}$

PAH:  $R = 0.47 (\text{PAH mass}\%)^{0.45}$

10.4.5 Some potential control samples with consensus values are as follows:

Sample	Total Aromatics	PAH
DF21002	23.8	3.2
DF21006	9.6	0.6
DF21010	33.0	7.1



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10.5 At least one sample must be run in duplicate. The duplicate results must not differ by more than the ASTM repeatability, which is defined as:

$$0.16(\text{total aromatics})^{0.23} \quad \text{and}$$

$$0.16(\text{PAH})^{0.16} \quad \text{for PAH less than 5 mass \%, or}$$

$$0.36(\text{PAH})^{0.13} \quad \text{for PAH greater than 10 mass \%.}$$

Note that repeatability is not currently defined for samples between 5 and 10 mass % PAH. Samples in this range should not be used for meeting the duplicate analysis requirement.

10.6 Once per year, the detector linearity is checked by the following procedure:

10.6.1 Accurately weighed blends (1:1 and 3:1 dilutions) of a motor diesel fuel in hexadecane are prepared.

10.6.2 The original fuel and the dilutions are analyzed as normal samples.

10.6.3 Calculate the expected concentration of aromatic hydrocarbons in the dilutions using the following equation:

$$B = A \times D / (C + D)$$

Where:

A = mass % aromatic hydrocarbons in the original fuel

B = mass % aromatic hydrocarbons in the diluted fuel

C = mass of hexadecane in the dilution

D = mass of original diesel fuel in the dilution

10.6.4 Compare the results obtained from section 10.6.3 with the results obtained from section 10.6.2. These values should agree to within the repeatability limits as stated in section 10.5. If agreement is not obtained, corrective action must be taken.

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TABLE 1: Theoretical Response Factors

Component	Carbons	Molecular Mass	RRF(Theor)
Toluene	7	92.13	1.075
Tetralin	10	132.2	1.070
Naphthalene	10	128.2	1.104

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11 References

- 11.1 "Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography," *Annual Book of ASTM Standards*, Vol 05.02.

12 Revision History

- 12.1 Version 2.1: Effective date: 10/1/1998  
12.2 Version 3.0: Effective date: 4/1/2003  
12.3 Version 4.0: Effective date: 10/1/2014

Significant changes:

- 1.3 – Based on ASTM D5186-03 (2009)
- 3.1 – Update the instruments used
- 5.1 – Update the instruments process parameters
- 10.4.5 – Potential control sample change
- 10.5 – Duplicate results meet ASTM repeatability instead of reproducibility

- 12.4 Version 5.0: Effective date: 5/1/2017

Significant changes:

- 5 – Deleted references to all SFC vendors

- 12.5 Version 5.1: Effective date: 12/1/2019

SOP format updated for ADA compliance