

**United States  
Environmental Protection Agency  
Office of Transportation and Air Quality  
National Vehicle and Fuel Emissions Laboratory  
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**Fluorescent Indicator Adsorption Analysis  
of Petroleum Fuels Method**

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**NVFEL Reference Number**

124

**Implementation Approval**

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**Revision Description**

Table of Contents

1. Scope .....	3
2. Summary of Method.....	3
3. Significance.....	3
4. Applicable Documents.....	3
5. Definitions.....	4
6. Interferences and/or Limitations .....	4
7. Safety.....	4
8. Apparatus .....	5
9. Reagents and Materials .....	5
10. Sampling .....	6
11. Calibration.....	6
12. Analytical Procedure.....	6
13. Calculations and Reporting.....	9
14. Performance Criteria .....	11

## 1. Scope

This method describes the determination of hydrocarbon types over the concentration ranges of 5 to 99 volume percent aromatics, 0.3 to 55 volume percent olefins, and 1 to 95 volume percent saturates, in petroleum fractions that distill below 60 °F. It is the Laboratory Operations Division (LOD) specific version of American Society for Testing and Materials (ASTM) D1319, “Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption”.

## 2. Summary of Method

A liquid petroleum sample, approximately 0.75 mL is introduced into a special glass column that has been packed with activated silica gel and a small layer of fluorescent dyed gel. After the sample has been adsorbed on the gel, alcohol is added to desorb the sample down the column to separate the hydrocarbons. The fluorescent dyes are selectively separated into aromatic, olefin, and saturate zones, which are visible under ultraviolet light. Each boundary in the column is calculated by volume percentage from the length of each zone in the column.

## 3. Significance

This method determines the total volume percent of saturates, olefins, and aromatics in petroleum fractions, which is important as a measure of the quality of fuels.

## 4. Applicable Documents

- 4.1 Code of Federal Regulations Title 40, Part 80.46 Section (b)
- 4.2 ASTM Standard Method D1319-99 Standard Method Test for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
- 4.3 ASTM D4057 Standard Practice for Manual Sampling of Petroleum and Petroleum Products
- 4.4 ASTM D2001 Test Method for Depentanization of Gasoline and Naphthas
- 4.5 NFVEL 123, Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detector Method
- 4.6 “FileMaker Pro User’s Guide”
- 4.7 “Access User’s Guide”

## 5. Definitions

- 5.1 Saturates – the volume percent of alkanes plus cycloalkanes.
- 5.2 Olefins – the volume percent of alkenes, cycloalkenes, and some dienes.
- 5.3 Aromatics – the volume percent of monocyclic and polycyclic aromatics, aromatic olefins, some dienes, compounds containing sulfur and nitrogen, and higher boiling oxygenated compounds.

## 6. Interferences and/or Limitations

Errors in the direction of high saturate values and low olefin values can result if the sample contains significant amount of C<sub>5</sub> and lighter hydrocarbons. Such samples are to be deparaffinized by Test Method D2001.

## 7. Safety

- 7.1 Gasoline, IPA, ethyl alcohol, acetone, silica gel and diesel fuel are hazardous materials. Specific procedures for handling these materials are listed in their respective Material Safety Data Sheets(MSDS) on file in the Testing Services Group (TSG) or the Safety Office. The analyst must be familiar with these MSDS procedures prior to performing this procedure.
- 7.2 Pay strict attention to column pressure settings. Glass columns may burst if over pressurized. The analyst must wear safety glasses and a lab coat during this analysis.
- 7.3 In case of a spill of either Silica Gel or FIA dyed gel, sweep up the gel and put it into a hazardous waste container. When the container is full, give it to the NVFEL Safety Officer to dispose of.
- 7.4 A spill of reagents or fuel samples less than a liter can be mopped up with spill control pillows or adsorbent found in the Chemistry Lab. Disposal of these materials must be done through the NVFEL hazardous materials representative. If more volume than a liter is spilled, leave the area immediately and contact the emergency response team.
- 7.5 Direct exposure to ultraviolet light can be harmful. The analyst should not look directly at the bulb, and the light should be turned off when not in use. The analyst should wear safety glasses with UV blocking lenses at all times.

**8. Apparatus**

- 8.1 Adsorption Columns-with precision bore (“true bore” IP designation) tubing as shown in Figure 1 of ASTM D1319, made of glass and consisting of a charger section with a capillary neck, a separator section, and an analyzer section; or with standard wall tubing, as seen in the same figure as above.
- 8.2 Zone-Measuring Device – Two different colored glass writing pencils to mark the different zones.
- 8.3 Ultraviolet light source, with radiation predominantly at 365 nm is required. A convenient arrangement consists of one or two 915-mm or 1220-mm units mounted vertically along the apparatus. Two 48 GENF40T12 or Equivalent fluorescent light bulbs.
- 8.4 Electric Vibrator- for vibrating individual columns or a frame supporting multiple columns.
- 8.5 Meter rule with millimeter gradations.
- 8.6 1-mL gas-tight syringe with 18, 20, or 22 gage needle, with a length of 102 mm, Hamilton #1001 or equivalent.
- 8.7 Compressed air or nitrogen manifold, with regulators, regulated from 0 to 60 psig to power vibrate and pressurize analytical columns.
- 8.8 Funnel and Stainless steel spatula
- 8.9 Computer with FileMaker Pro and Access software installed.

**9. Reagents and Materials**

- 9.1 Silica Gel, 100 to 200 mesh, conforming to the specifications in ASTM D1319 Section 8.1, W.R Grace and Co., Davison Chemical Division, Code 923.
- 9.2 FIA Standard Dyed Gel, conforming to the specifications in ASTM D 1319, Section 8.2, UOP Organic Department, Product No. 675. The dyed gel shall be stored in a place to protect it from atmospheric moisture.
- 9.3 Isopropyl Alcohol (IPA), (2-Propanol), 99% pure [67-63-0]
- 9.4 Ethyl alcohol, reagent grade or better [64-17-5]

- 9.5 Pressuring Gas – dry, hydrocarbon-free air or dry, hydrocarbon-free nitrogen delivered to the top of the column at pressures controllable over the range from 0-60 psi.
- 9.6 Acetone, reagent grade, residue free [67-64-1]
- 9.7 Control Gasoline CA Phase II
- 9.8 Control #2-Diesel Fuel being substantially similar to the emission certification #2 diesel fuel specified in 40 CFR 86.113-94
- 9.9 Form 120-01 (or Form 120-02) becomes a traveler document that accompanies the sample(s) throughout the analyses process. If Form 3500-5 was submitted by the field inspector, it becomes the traveler document that accompanies the sample(s) during analysis.

## 10. Sampling

Obtain a representative sample according to sampling procedures in ASTM D4057. The sample needs to be at 2°C to 4 °C before the start of the analysis.

## 11. Calibration

N/A

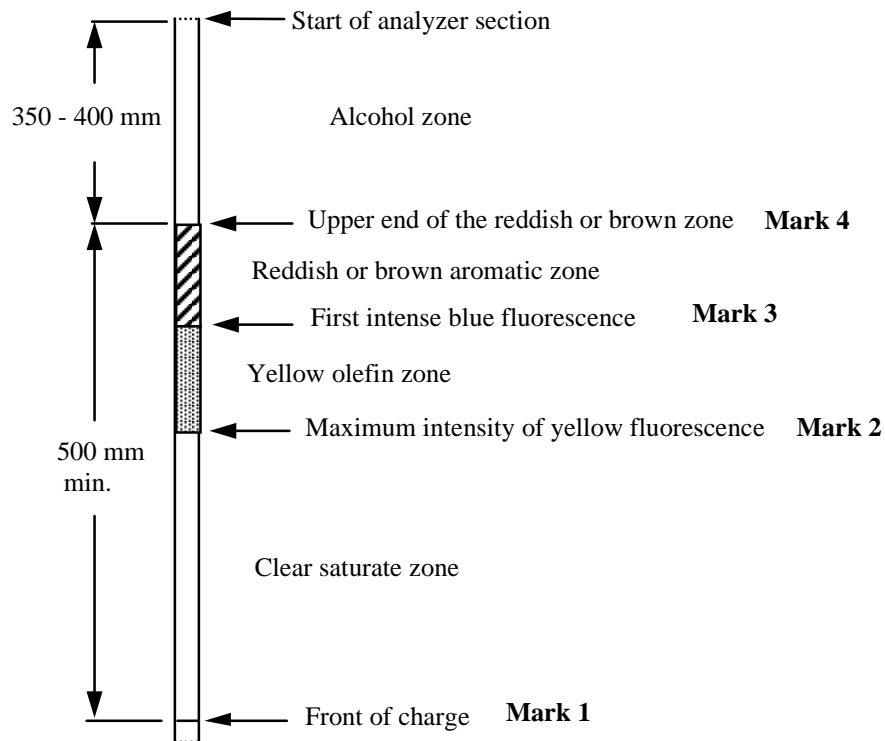
## 12. Analytical Procedure

- 12.1 Freely suspend the column(s) in the column-vibrating fixture. Apply approximately 30 psig to the vibrator to initiate vibration.
- 12.2 While vibrating the column along its entire length, add small increments (about 10 ml) of silica gel, from the individual pouch through a funnel into the charger section until the separator section is half full.
- 12.3 Stop the vibrator and add a 3 to 5-mm layer of the FIA Standard Dyed Gel (about 2 ml) with a clean spatula.
- 12.4 Start the vibrator and vibrate the column while adding additional silica gel. Continue to add silica gel until the tightly packed gel extends 70 mm to 80 mm into the charger section.

- 12.5 Wipe the length of the column with a damp cloth while vibrating the column. This aids in packing the column by removing static electricity and cleans the outside surface. Avoid touching the column with hands until the analysis is complete. Vibrate the column for about 4 minutes after filling is completed.
- 12.6 Reset the supply regulator to 5psig and close the supply valve.
- 12.7 Draw  $0.75 \pm 0.03$  ml of sample chilled at  $2^{\circ}\text{C}$  to  $4^{\circ}\text{C}$  with a syringe chilled to the same temperature range.
- 12.8 Inject the sample at least 30mm below the surface of the gel in the charger section.
- 12.9 Fill the charger section to its spherical joint with IPA.
- 12.10 Connect the column to the compressed air or nitrogen manifold and apply approximately 5 psi gas pressure for a minimum of 2.5 minutes. This moves the liquid down the column.
- 12.11 Increase the pressure that is required to give a transit time of about 1 hour. Usually a pressure of 10 psig has been found appropriate for most gasoline formulations. A pressure of 15 psig has been found appropriate for most diesel fuels. However, the pressure needed may vary due to the tightness of the column packing and the molecular weight of the sample. Do not exceed 20 psig at any time, higher pressures may cause the columns to burst.

- 12.12 Observe the red-brown aromatic zone. Turn on the UV light, after the upper end of the reddish or brown aromatic zone has advanced 350 mm to 400 mm into the analyzer section of the column. Quickly mark the boundary of each hydrocarbon zone in the following sequence. Refer to the figure below.

Marking the Analyzer Section of FIA Columns



- 12.13 Starting at the lower portion of the column, mark the charger as indicated by liquid penetration of the silica gel (shown as “Mark 1” in the figure). This is the beginning of the colorless saturate zone.
- 12.14 Working up the column, mark the point where the yellow fluorescence reaches it’s maximum intensity (shown as “Mark 2” in the figure). This is the end of the saturate zone and the beginning of the yellow olefin zone.
- 12.15 Mark the point where the first intense blue fluorescence occurs. This is the end of the olefin zone and the beginning of the aromatic zone (shown as “Mark 3” in the figure). If blue fluorescence is not present, skip to the next mark.
- 12.16 Mark the upper end of the reddish or brown color (shown as “Mark 4 “ in the figure). This is the upper end of the aromatic zone and may be clearly defined by a red ring. If no blue fluorescence is present, this indicates that no aromatics are present and the red ring shall be considered the upper boundary of the olefin zone.



- 12.17 After the sample has advanced another 50 mm to 60 mm down the column, mark the column again in the reverse order listed in Steps 12.13 to 12.16, using a different color marking pen. Turn off the UV light when analysis is completed.
- 12.18 Release the gas pressure to each column.
- 12.19 Turn on the computer that is located near the FIA columns. Open the Filemaker Pro program, then click on "open as existing file," highlight Micron (D:), open FIA folder, and then the NVFEL124 Database. Append a new record in the file, enter the sample ID and the analyst's initials on the new record.
- 12.20 Turn off the gas pressure to the manifold and disconnect the column to be measured. With the column lying horizontally on the bench top, using a meter stick, measure to the nearest millimeter, the distance between the start of the analyzer section and the initial boundary mark between the aromatic and the alcohol zone. If that distance is not between 350 mm and 400 mm, delete the record for this analysis from the database and repeat the analysis.
- 12.21 Using a meter stick, measure the distances between the initial and the second marks, the initial and the third marks, and the initial and the fourth marks of the same color to the nearest millimeter. Enter these measurements as the "UP" set of readings into the record. Repeat the above process for the second, different colored, set of marks and enter the measurements as the "DOWN" set of readings. If the distance between either set of initial and fourth marks is less than 500 mm, delete the record for this analysis from the database and repeat the analysis.
- 12.22 To remove used gel from the precision bore column, invert it above a sink and insert, through the wide end, a long piece of 19-gage hypodermic tubing with a 45° angle. Flush the tube, via the opposite end, with tap water into a container. Rinse inside the columns with residue-free acetone, into a container, and dry with compressed air or nitrogen. Give used gel to the NVFEL safety officer to dispose of, as hazardous waste material.

### 13. Calculations & Reporting

- 13.1 When the analyses of all samples are complete, in the "Vol% Oxygenates" box, input the "Vol% oxygenates" from the OFID test (if OFID test is complete). Then print the NVFEL 124 Data Base Report for the current day's analyses. See Attachment A.
- 13.2 Review for conformance to acceptance criteria, sign and date the report if all acceptance criteria are met.

- 13.3 Transcribe the sample test results from the NVFEL 124 Data Base Report, to the travel form for that sample. Then, initial and date it.
- 13.4 If the results have the OFID data in, then make sure current data is in the input form, go to the records menu, and highlight, click on "show all records."
- 13.5 Next click on the "File" menu and highlight the "Export" records. Highlight "Micron (D:), Access" and then "Aromatic.dbf" and save.
- 13.6 Open up the "Start Fuel Tests App." and click on "Data Detail." In the "Test" list, find "aromatic" and double click on it. This will open the aromatic table.
- 13.7 Next click on the "Import Aromatic" at the top. This imports the data from the "Aromatic.dbf" file. When this is complete click on "OK."
- 13.8 Next click on the Export to Results button, press on the NO, this will only send new data and not the entire file.
- 13.9 The NVFEL 124 Database program calculates the volume-percent aromatics, olefins and saturates by averaging the two sets of results calculated according the following formula:

$$\text{Equation 1} \quad \text{Aromatics \%} = (L_a/L) * 100$$

$$\text{Equation 2} \quad \text{Olefins \%} = (L_o/L) * 100$$

$$\text{Equation 3} \quad \text{Saturates \%} = (L_s/L) * 100$$

Where:

$L_a$  = length of the aromatic zone (mm)

$L_o$  = length of the olefin zone (mm)

$L_s$  = length of the saturate zone (mm)

$$L = L_a + L_o + L_s$$

- 13.10 Equations 1, 2 and 3 calculate concentrations on an oxygenate-free basis and are correct only for samples that are composed exclusively of hydrocarbons. For samples that contain oxygenated blending components (see ASTM D 1319 section 1.5), the above results can be corrected to a total sample basis as follows:

$$C' = C \times \frac{100-B}{100} \quad (4)$$

Where:

$C'$  = concentration of hydrocarbon type (% volume) on a total sample basis,

$C$  = concentration of hydrocarbon type (% volume) on an oxygenate-free basis, and

$B$  = concentration of total oxygenate blending components(% volume) in sample as determined by Test Method GC/OFID

**14. Performance Criteria**

- 14.1 The sample and the transfer syringe are stored in a refrigeration unit that will keep them below 40 °F until the time of sample analysis. The temperature is monitored to ensure compliance and the data is printed monthly.
- 14.2 The distance measured between the start of the analyzer section and the first boundary reading (aromatic-IPA boundary), of the first set of readings, must be between 350 mm and 400 mm.
- 14.3 The distance measured from the first boundary reading of the first set of readings to the first boundary reading of the second set of readings must be between 50 mm and 60 mm.
- 14.4 The total distance between the first boundary reading and the final boundary reading must be at least 500 mm.
- 14.5 Any diesel sample where the aromatic content exceeds 35 volume percent must be analyzed in duplicate. Laboratory duplicate range values must be within control limits or an investigation for cause must be performed, and reported in the instrument book. Reestablishment of process control must be demonstrated before further analyses can be performed.
- 14.6 When running analyses, analyze the control fuel once a week, in the same manner as the samples. Investigate any out of control conditions and take immediate corrective action. Record the action in the instrument logbook. If out of control occurrence cannot be reconciled, consult the laboratory manager.

When the problem is resolved, repeat the control fuel.

The control fluids for this method are current batches of gasoline and certification diesel test fuel, as agreed upon between the analyst and the laboratory manager. Control limits for these fuels are established by a minimum of 10 analyses of the fuel, and are fuel batch specific. As each new result is obtained, a running average is calculated, along with standard deviation. The new control limits are plus and minus three standard deviations from the new average.

Ensure that the results are within the control limits before proceeding with the analysis. Determine whether previous sample results may have been affected by out of control conditions.

Repeat samples analyzed subsequent to the last acceptable control fuel measurement, as required.

Discard the original results from these samples.

- 14.7 If the duplicate range is out of control, halt the analysis and take immediate corrective action to resolve the abnormal analysis variability. Record the action and its implications in the instrument logbook. If out of control occurrences cannot be reconciled, consult the laboratory manager.

When the problem is resolved, repeat the duplicate.

Ensure that the results are within the control limits before proceeding with the analysis. Determine whether previous sample results may have been affected by out of control conditions.

Repeat samples analyzed subsequent to the last acceptable duplicate analysis, as required.

Discard the original results from these samples.

- 14.8 Repeatability for this procedure has been statistically determined using 1985 and 1986 TSG test data. The following repeatability statistics apply to either gasoline or diesel fuel.

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the normal and current operations of the test method, exceed the following values only in 1 case out of 20:

	<u>Gasoline</u>	<u>Diesel</u>
Aromatics	1.5 volume percent	3.0 volume percent
Olefins	1.7 volume percent	0.83 volume percent
Saturates	1.8 volume percent	1.4 volume percent

- 14.9 The analyst does validation of all analysis data.
- 14.10 Only chromatography columns, silica gels, and indicator dyes conforming to ASTM D1319 are used.

Attachment A

Date: 8/28/2002

NVFEL124 Data Base Report

Page 1

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Analysis_D	8/28/2002	Analysis Time	9:42:43 AM	Analyst	NST
Sample ID	<b>example</b>		Silica Gell Lot #	261	Dye Lot # 646
Record distances to the nearest millimeter.					
Aromatics UP (Mark 2- Mark 1)	186.0	Aromatics Down (Mark 2- Mark 1)	187.0		
Olefins UP (Mark 3- Mark 1)	227.0	Olefins Down (Mark 3- Mark 1)	226.0		
Saturates UP (Mark 4- Mark 1)	628.0	Saturates Down (Mark 4- Mark 1)	628.0		
Aromatics	29.7%	SFC AROMATICS	.		
Olefins	6.4%	WISPA AROMATICS			
Saturates	63.9%	VOL%OXYGENATES	0		

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I have performed the analysis in accordance with requirements of Test Method 124

Analyst's Signature \_\_\_\_\_ Date : \_\_\_\_\_