

HYDROCARBON TYPES BY FLUORESCENT INDICATOR ADSORPTION (FIA)

UOP Method 311-02

SCOPE

This method is for determining aromatic, olefinic and saturated hydrocarbons by column chromatography in petroleum distillates that boil below 315°C. It is designed for full boiling range materials, not narrow cuts, especially near the 315°C limit. Samples of higher boiling range can be analyzed using UOP Method 501. Depentanization of the sample by UOP 79 is recommended (see Note 1) if it contains more than 2 liquid volume percent (LV-%) C₄ or 15 LV-% C₅ hydrocarbons. The lower detection limit for a hydrocarbon type is 0.4 LV-%. The presence or absence of olefins below 0.4 LV-% can be confirmed by UOP Method 304. The indicated aromatic hydrocarbons can include some diolefins, aromatic olefins, compounds containing sulfur and nitrogen, or higher boiling oxygenated compounds. Oxygenated gasoline blending components such as methanol, ethanol or methyl-*tert*-butyl ether do not interfere with the determination of hydrocarbon types. The oxygenated components are not detected, since they elute with the alcohol desorbent. Interference from other oxygenated compounds shall be individually verified. When samples containing oxygenated blending components are analyzed, the hydrocarbon type results can be reported on an oxygenate-free basis. Otherwise, the oxygenated blending components can be determined by either ASTM Method D 4815 or D 5599, and the results corrected to a total sample basis. Samples that contain dark-colored components that interfere in reading the chromatographic bands cannot be analyzed. Alternative methods for specific hydrocarbon type analysis include: 1) ASTM Method D 6379, an HPLC method for determination of aromatic hydrocarbon types in aviation kerosene and petroleum distillates boiling in the range from 50 to 300°C; 2) ASTM Method D 5186, an SFC method for determination of the aromatic content and polynuclear aromatic content of diesel fuels and aviation turbine fuels; and 3) ASTM Method D 6550, an SFC method for determination of the olefin content of gasoline.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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OUTLINE OF METHOD

A glass adsorption column having a long capillary extension is packed with fine, activated silica gel. A small quantity of fluorescent compounds deposited on silica gel, referred to as dyed gel, is added to the bed during the packing step. Approximately 0.75 mL of sample is introduced by syringe and isopropyl alcohol is added to the top of the column to desorb the sample downward. Differential air pressure is applied to the top and bottom of the column. The adsorption-desorption of the hydrocarbons as they progress through the column results in a separation, according to their adsorption affinities, into bands of saturates (paraffins and naphthenes), olefins and aromatics. The fluorescent compounds on the dyed gel separate along with the appropriate hydrocarbon types and, under ultraviolet light radiation, define the boundaries of the separated hydrocarbon bands. The band lengths are measured and the LV-% of each hydrocarbon type is calculated.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Adsorption column, FIA, glass, consisting of a charger section, a 2-part separator section, an analyzer section, a 28/12 ground glass socket joint at the top and a 12/2 ground glass socket joint at the bottom (see Fig.1), Reliance Glass Works, Cat. No. R-1701-102A special order. Precision bore tubing is used in the analyzer section having a uniform bore of 1.60 to 1.65 mm.

Balance, readability 0.01-g, 1200-g capacity, top loading

Bottle, round, wide-mouth, 946-mL, with a conical shaped polyethylene-lined closure, Fisher Scientific, Cat. No. 03-320-5F

Clamps, joint, ball and socket, joint sizes 12/2 and 28/12, Fisher Scientific, Cat. Nos. 05-885C and 05-885F, respectively (two required)

Column support, waterproof plywood or birch, custom made, see Fig. 2, local supply

Compressed air manifolds, upper and lower. Fit the upper manifold with a valve for each adsorption column to be used. Connect each valve by flexible rubber tubing to a 28/12 ground-glass ball joint having a Buna-N O-ring. Control the compressed air supply with a variable pressure regulator to provide manifold pressure in the range of 70-105 kPa gauge (10-15 psig). Fit the lower manifold with valves connected by flexible tubing to 12/2 ground-glass socket joints. Control the compressed air supply to the lower manifold by a pressure regulator to provide a manifold pressure of 62 to 70 kPa gauge (9- 10 psig).

- CAUTION: It is recommended to include a pressure relief system to the air supply to prevent rupture of the glassware at higher pressures than specified or tolerated.

Cylinder, graduated, borosilicate glass, 10-mL, Fisher Scientific, Cat. No. 08-556-A

Dish, evaporating, porcelain, 215-mm OD, 1285-mL capacity, Fisher Scientific, Cat. No. 08-690M

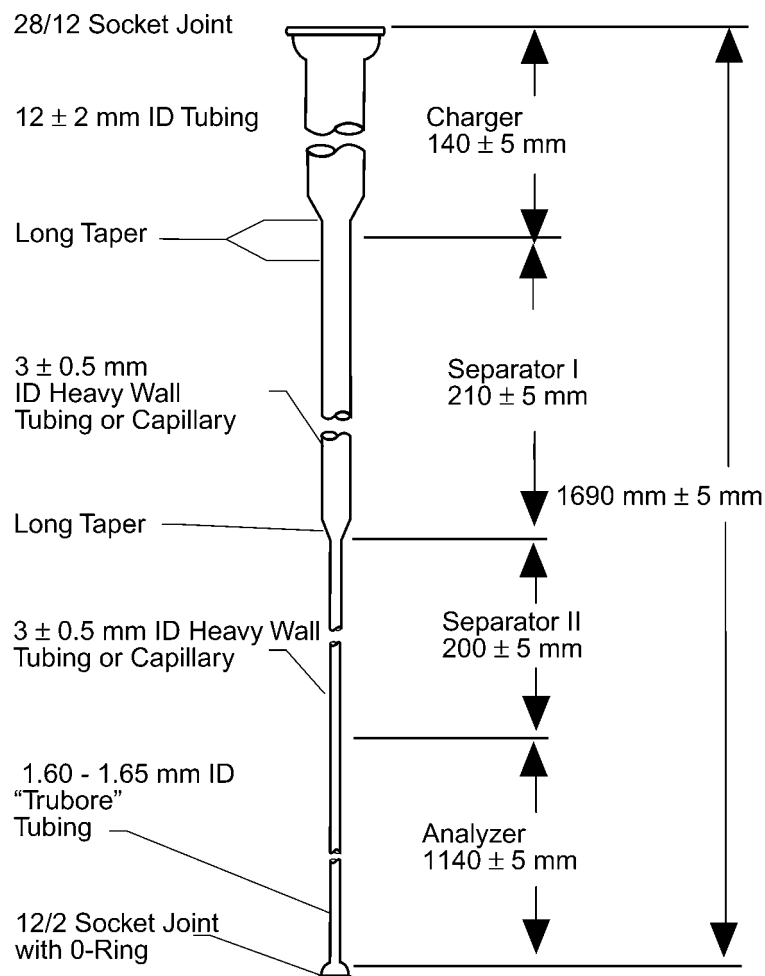


Figure 1
Adsorption Column

Gloves, thermal

Joint, ground glass, ball with O-ring, 12/2, Reliance Glass Works, Cat. No. R-5546-114

Joint, ground glass, ball with O-ring, 28/12, Reliance Glass Works, Cat. No. R-5546-124

Needle, stainless steel, 18-gauge, 150-mm long, Luer connection, blunt tip, Popper & Sons (special order)

Oven, drying, capable of operation at 175°C

Refrigerator, explosion-proof

Regulator, 2-stage, 0-100 kPa gauge (0-15 psig) delivery range, Matheson Gas Products, Cat. No. 8L-CGA (two required)

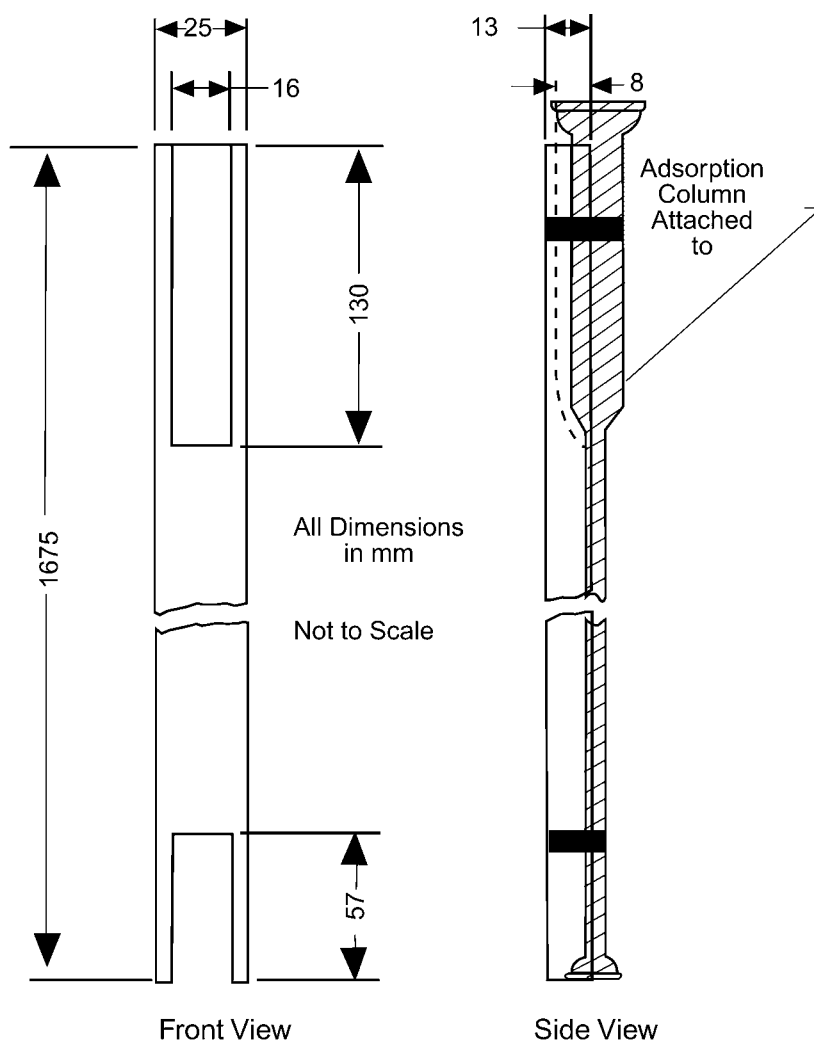


Figure 2
Wooden Column Support

Ruler, one-meter, 1-mm graduations, without brass ends, Fisher Scientific, Cat. No. 12-096

Stopper, cork, size no. 4, 13/16-inch length, 5/8-inch top diameter, 15/32-inch bottom diameter, Fisher Scientific, Cat. No. 07-781G

Syringe, 1-mL with 0.01-mL graduations, with glass Luer connection, Fisher Scientific, Cat. No. 14-820-15C

Tape, electrical

Tubing, capillary, stainless steel, 18-gauge, 100 to 120-cm long, Chromatography Research Supplies, Cat. No. 21018. Use appropriate fittings to connect the tubing to a water tap to facilitate cleaning the adsorption column.

Tubing, flexible, rubber, red, thick wall, 6.4-mm ID, 11-mm OD, Fisher Scientific, Cat. No. 14-167D

Ultraviolet lamp, radiation predominantly at 365 nm, 483-mm (19-inch) length, VWR Scientific, Cat. No. 36575-048

Vibrator, column, 110V, Alltech Associates, Cat. No. 4012

REAGENTS AND MATERIALS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Acetone, 99.5% minimum purity, less than 0.5% water, Fisher Scientific, Cat. No. A18

Air, compressed, dry and oil-free

Fluorescent indicator dyed gel, UOP, Product No. 80675 (see Note 2)

Glass wool, Fisher Scientific, Cat. No. 11-390

Isopropyl alcohol (2-propanol), 99% minimum purity, Fisher Scientific, Cat. No. A416

O-rings, Buna-N for 12/2 and 28/12 joints, Reliance Glass, Cat. Nos. R-5568-011 and -116, respectively

Pens, marking, fine tip, two colors, red and green, Fisher Scientific, Cat. Nos. 13-379-5 and 13-379-7, respectively

Silica gel, 100-200 mesh, Grade 923, surface area between 430 and 530 m²/g, pH of 5 mass-% slurry must be 5.5 to 7.0, Aldrich, Cat. No. 21,447-7

Ultraviolet tube, 483-mm length, VWR Scientific, Cat. No. 36585-280

Water, tap

Wiping cloth, Kimtex, polypropylene, Fisher Scientific, Cat. No. 06-666-75

PROCEDURE

Preparation of Treated Silica Gel

Adjust the water content of the silica gel to 2.5 mass-% as follows:

1. Weigh a large evaporating dish and record the weight (K) to the nearest 0.5 g.
2. Add approximately 900 g of the as-received silica gel to the evaporating dish.
3. Place the dish in an oven and dry the gel at 175°C for at least 4 hours.

4. After the material has been dried, use thermal gloves to safely remove the dish from the oven. While still hot, weigh the dish and contents and record the weight (D) to the nearest 0.5 g.
5. Transfer the hot gel immediately to a glass bottle and seal with an air-tight cap.
6. Calculate the mass of water (B) to be added to produce a water content of 2.5 mass-% as follows:

$$B = \frac{2.5(D - K)}{97.5} \quad (1)$$

where:

B = mass of water to be added, g

D = mass of dish and gel after heating, g

K = mass of dish, g

2.5 = water in final mixture, mass-%

97.5 = silica gel in final mixture, mass-%

7. Add the calculated mass of water (B), ± 0.01 g, to the bottle containing the silica gel.
8. Close the bottle and distribute the water throughout the gel by periodic shaking over a period of two days.
9. Store the treated gel in the tightly closed bottle to prevent the water content from changing.

Preparation of Apparatus

1. Prepare the compressed air manifolds with proper pressure regulators. Install the manifolds and the ultraviolet light source in a darkened area.
 - *CAUTION:* Direct exposure to ultraviolet light can be harmful, particularly to the eyes. Do not look directly at the ultraviolet light source.
 - Daylight or artificial light of other wavelengths interferes with the ability to observe the fluorescent zone boundaries.
2. Mount a clean, dry adsorption column on a wood column support (Fig. 2) by taping the column to the support at the top and bottom with electrical tape.
3. Place a small plug of glass wool in the lower end of the adsorption column.
 - The purpose of the plug is to retain the silica gel on the column. Excess glass wool causes unnecessary, increased back-pressure on the column during operation.

4. Stand the support with attached column in an upright position or suspend it from a framework or grid. Using a 10-mL graduate cylinder, pour 6.0 to 6.5 mL of the treated silica gel into the charger section.
5. Vibrate the column, beginning at the bottom of the column and proceed up to the separator section. Continue to vibrate the column until the gel no longer settles. Wipe the column with a damp cloth along the entire length to minimize static electricity.
 - This operation should take approximately one minute at which time the top of the gel bed should now be close to the middle of the top separator section.
6. Add a 2- to 3-mm layer of fluorescent indicator dyed gel (see Note 2). For samples with greater than 2% olefin, add a 4- to 6-mm layer of the dyed gel to improve definition of the olefin band.
 - The fluorescent indicator dyed gel should be located approximately near the middle of the Separator I section of the column apparatus.
7. Add more treated silica gel (approximately 8 mL) over the fluorescent dyed gel, while vibrating the column, until the completely settled, packed silica gel extends approximately 25 mm into the charger section. Vibrate the column after filling is completed for approximately four minutes. If the analysis is not to be performed immediately, place a cork stopper on the top of the column to prevent moisture gain.

Sampling

1. Fit the long syringe needle to the syringe.
2. Chill the sample and syringe in a refrigerator to 2 to 4°C.
3. Invert the sample gently several times.
4. Draw approximately 1-mL of sample up into the syringe.
5. Invert the syringe and discharge air bubbles and excess sample until the syringe contains 0.75 ± 0.02 mL of sample. Hold a wiping cloth against the side of the needle to absorb excess sample. Do not draw the cloth across the needle tip, as sample will be lost from the needle.

Sample Analysis

1. Insert the syringe needle into the gel in the charger section to a point level with the top of the separator section and slowly discharge the sample into the gel. Deposit the sample in an evenly distributed layer in the gel bed. Deposit the entire sample below the surface of the gel.

2. Withdraw the syringe and slowly add approximately 2-3 mL of isopropyl alcohol to the top of the gel bed.
3. When the alcohol has been absorbed by the dry silica gel above the sample, then add more alcohol (approximately 9 mL) until the level reaches about 25 mm from the top of the charger section.
4. Connect and clamp the column to the upper manifold making sure the O-ring on the ball joint is even and tight against the socket joint on the column.
5. Connect and clamp the column to the lower manifold in a similar fashion.
 - If the joints on the upper and lower manifolds are not fitted with O-rings, apply a small amount of stopcock grease, sufficient to make a pressure-tight seal.
6. Apply 62 ± 2 kPa gauge (9 psig) air pressure to the bottom of the column. Wait approximately 20 seconds and apply 83 ± 2 kPa gauge (12 psig) air pressure to the top of the column. Reduce the bottom pressure to 28 to 42 kPa gauge (4 to 6 psig) for higher molecular weight samples in order to achieve the optimum elapsed transit time. For medium to heavier kerosene samples, do not apply any bottom pressure.
 - The optimum elapsed time for the sample to advance into the analyzer section is 60 to 80 minutes. If a sample takes longer than 90 minutes to advance into the analyzer section, without any applied bottom pressure, then UOP Method 501 is recommended. Samples containing significant levels of C_5 and lighter hydrocarbons tend to have elapsed times shorter than 60 minutes. Depentanization of these samples by UOP Method 79 is recommended.
7. Allow the sample to progress through the column until the red boundary marker between the alcohol and aromatics has advanced at least 200 mm into the analyzer section. Refer to Figures 3 and 4 to identify the different chromatographic boundaries of the separated hydrocarbon types.
 - The fluorescent components contained in the indicator dyed gel separate by type along with the sample, and under ultraviolet radiation define the boundaries of the separated hydrocarbon bands. The saturates are nonfluorescent and constitute the lowest band in the column. The bottom of the saturates hydrocarbon band is distinguished by the difference in appearance between the wet and dry gel. The olefin band extends from the point of first intense yellow fluorescence to the point of first intense blue fluorescence. The upper part of the olefin band may be nonfluorescent. For samples containing no olefin, a 1- to 3-mm band of olefin marker will be observed. The aromatic band extends from the point of first intense blue fluorescence to the top of the red boundary marker located between the alcohol and aromatics. With colorless distillates, the alcohol-aromatics boundary is clearly defined by a red ring of dye. Impurities in cracked fuels may obscure this red ring and give a brown coloration, which can vary in length, which shall be counted as part of the aromatics zone, except when no blue fluorescence is present, the brown or reddish ring shall be considered as part of the next distinguishable zone below the column. With some oxygenated blended fuel samples another red band may appear several centimetres above the reddish or brown alcohol-aromatics boundary (see Figure 4) and shall be ignored.
8. Rapidly mark the top of the red alcohol-aromatics boundary, the bottom of the first intense blue fluorescent aromatics band, the bottom of the first yellow fluorescence intensity, and the bottom of the non-fluorescent saturated hydrocarbon band.
 - Avoid touching the column with your hands while marking the chromatographic boundaries. Grasp the column apparatus by the wooden support if necessary.

9. Make a second set of markings when the red boundary marker has descended another 100 to 120 mm. Use a contrasting colored marker and begin at the bottom of the nonfluorescent saturated hydrocarbon band.
- Avoid touching the column with your hands while marking the chromatographic boundaries. Grasp the column apparatus by the wooden support if necessary.

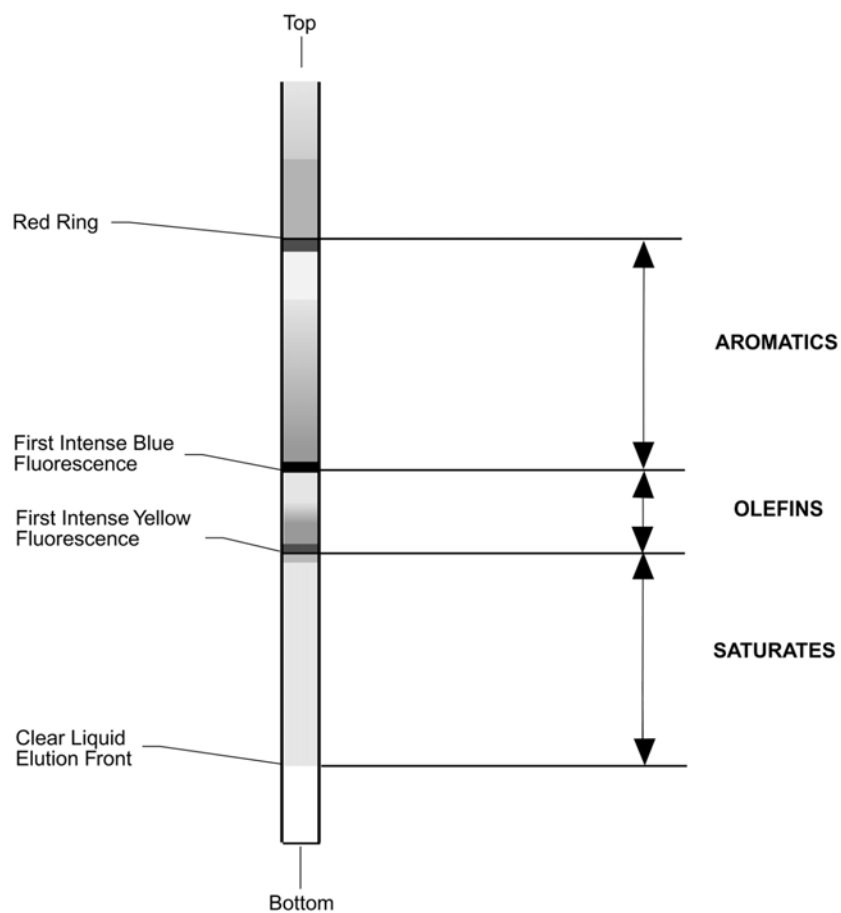


Figure 3
Pictorial Aid for Identification of Chromatographic Boundaries

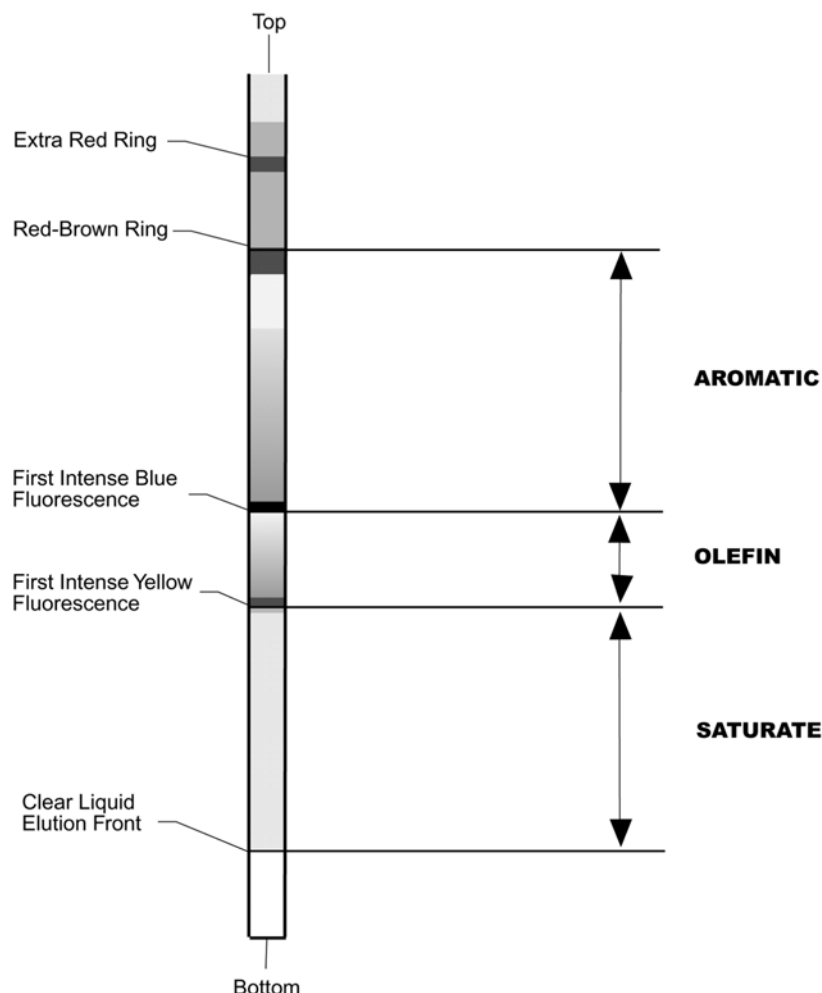


Figure 4
Pictorial Aid for Identification of Chromatographic Boundaries
of Oxygenate Blended Fuel Samples

10. Turn off the air pressure on the top and bottom and disconnect the column from the manifold.
 - Be careful to do so before the solvent front reaches the end of the analyzer section of the column. The column should still be attached to the wooden support when it is removed from the manifold.
11. Lay the column (still attached to the wooden support) on a laboratory bench and with a meter ruler measure and record the length of the total hydrocarbon band and the length of each individual zone, to the nearest millimetre, for both sets of markings.
 - Both sets of markings are used and an average is obtained. Erroneous results can occur by improper packing of the gel or incomplete elution of hydrocarbons by the alcohol desorbent. The total band length for the final reading should be at least 500 mm for a satisfactory analysis. Shorter total band length is an indication of incomplete elution, often associated with samples containing significant quantity of material near or above the 315°C boiling limit of the method scope.

Adsorption Column Cleaning

1. Remove the glass wool from the lower end of the column.
 - The cleaning procedure can be performed without removing the column from the wood support.
2. Connect the steel capillary tubing to a warm water tap and flush the silica gel from the lower end of the column, rotating the column with one hand and pushing the capillary tubing gently through the column with the other. Continue flushing as far as the tubing length will permit.
3. Invert the column and wash out the remaining gel from the upper section. Collect the washings in a container placed in the sink. Allow the gel to settle in the container and periodically pour the water out to drain, retaining the used silica gel for appropriate disposal.
4. Rinse the column thoroughly with acetone and dry it with a slow stream of dry, compressed air.

CALCULATIONS

Average the length of each set of individual corresponding bands and the total hydrocarbon band. Calculate the liquid volume-percent (LV-%) of each hydrocarbon type (see Note 3) to the nearest 0.1% as follows:

$$\text{Aromatics, vol - \%} = 100 \frac{A}{L} \quad (2)$$

$$\text{Olefins, vol - \%} = 100 \frac{O}{L} \quad (3)$$

$$\text{Saturates, vol - \%} = 100 \frac{S}{L} \quad (4)$$

where:

A = average length of aromatics band, mm

L = average length of the total hydrocarbon band, mm

O = average length of olefin band, mm

S = average length of saturates (paraffins plus naphthenes) band, mm

100 = converts mm/mm to %

NOTES

1. The majority of laboratories that practice this method do not routinely depentanize samples. Results obtained from the analysis of samples containing significant levels of C₅ and lighter hydrocarbons might be less accurate. The potential bias is not certain and may not be consistent. The precision statements listed in the method are based on samples that were not depentanized.
2. The as-received dyed gel, when stored in a dark location, and opened only occasionally, can have a shelf life of at least five years. It is recommended that portions of the as-received gel be transferred as required to a smaller working vial, from which the gel is routinely used for analyses.
3. Samples that contain oxygenated blending components can be corrected to a total sample basis as follows:

$$C = E \frac{(100 - F)}{100_a} \quad (5)$$

where:

C = concentration of hydrocarbon type on a total sample basis, LV-%

E = concentration of hydrocarbon type on an oxygenate-free basis, LV-% (see Eqs. 2, 3 and 4)

F = concentration of total oxygenate blending components as determined by ASTM Method D 4815 or D 5599, LV-%

100 = converts to percent non-oxygenates in total sample

100_a = converts percent to decimal fraction

REPORT

Report the averaged value of each hydrocarbon type to the nearest 0.1 LV-%. Correct the results to a total sample basis if oxygenates are analyzed separately by ASTM Test Method D 4815 or D 5599. Results for samples that have been depentanized must be identified as being for the C₆ and heavier portion of the sample.

PRECISION

The precision statements used in this method were determined by UOP Method 999.

ASTM and UOP Repeatability

A nested design was carried out for determining aromatics and olefins in samples with two analysts in one laboratory. Each analyst carried out tests on two days, performing two tests each day on three different samples. The total number of tests for each constituent was 24. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) and the within-lab estimated standard deviation (esd) were calculated for each constituent and are listed in the Table. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in the Table with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference shown in the Table with 95% confidence.

The data in the Table are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

ASTM and UOP Repeatability, Volume-%

<u>Constituent</u>	<u>Mean Conc.</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
<u>Sample 1</u>					
Aromatics	62.4	0.70	2.7	0.60	2.4
Olefins	0.8	0.079	0.31	0.094	0.37
Saturates	36.8	0.64	2.5	0.47	1.8
<u>Sample 2</u>					
Aromatics	5.3	0.23	0.9	0.23	0.9
Olefins	---	---	---	---	---
Saturates	94.7	0.72	2.8	0.53	2.1
<u>Sample 3</u>					
Aromatics	4.3	0.31	1.2	0.26	1.0
Olefins	49.5	1.0	4	0.83	3.3
Saturates	46	1.3	5	1.1	4

TIME FOR ANALYSIS

The average elapsed time for one analysis is 2 hours. The labor requirement is 0.8 hour.

REFERENCES

UOP Method 79, "Fractionation of Petroleum Distillates"

UOP Method 304, "Bromine Number of Petroleum Distillates and Bromine Index of Industrial Aromatic Hydrocarbons – Potentiometric Method"

UOP Method 501, "Hydrocarbon Types by Fluorescent Indicator Adsorption (FIA) at Elevated Temperatures"

UOP Method 999, "Precision Statements in UOP Methods"

ASTM Methods D 4815, D 5186, D 5599, D 6379 and D 6550, www.astm.org

SUGGESTED SUPPLIERS

Aldrich, P.O. Box 2060, Milwaukee, WI 53201 (414-273-3850) sigma-aldrich.com

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600) alltechweb.com

Chromatography Research Supplies, P.O. Box 888, Addison, IL 60101 (630-543-0290) chromres.com

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219 (412-490-8300) fisherscientific.com

Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848) mathesonrigas.com

Popper & Sons, Inc., 300 Denton Ave., New Hyde Park, NY 11040 (516-248-0300) popperandsons.com

Reliance Glass Works, Inc., 2220 Gateway Rd., Bensenville, IL 60106 (630-766-1816) relianceglass.com

UOP LLC, Finished Product Technologies, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (847-391-3686) uop.com

VWR Scientific, P.O. Box 66926, O'Hare AMT, Chicago, IL 60666 (908-757-4045) vwrsp.com