

HYDROCARBON TYPES BY FLUORESCENT INDICATOR ADSORPTION (FIA) AT ELEVATED TEMPERATURES

UOP Method 501-02

SCOPE

This method is for determining liquid volume-percent (LV-%) levels of aromatic, olefinic and saturated hydrocarbons by column chromatography, in distillate fuels having viscosities in the range of 1.5 to 5.5 mm²/s (cSt) at 40°C, boiling in the range of 150 to 400°C (300 to 750°F). The method is designed for full boiling range materials, not narrow cuts. The lower detection limit for a hydrocarbon type is 0.4 LV-%. Hydrocarbons boiling in the kerosene range (150 to 290°C) are an exception and should be analyzed by UOP Method 311 or ASTM Test Method D 1319.

The indicated aromatic hydrocarbons can include some diolefins, aromatic olefins, compounds containing sulfur and nitrogen or higher boiling oxygenated compounds if these are present in the sample being analyzed. Samples that contain dark-colored components that interfere in reading the chromatographic bands cannot be analyzed.

Additional methods for specific hydrocarbon type analysis include: 1) ASTM Test Method D 6591, an HPLC method for determination of aromatic hydrocarbon types in middle distillates boiling in the range from 150 to 400° C (300 to 750° F) and 2) ASTM Test Method D 5186, an SFC method for determination of the aromatic content and polynuclear aromatic content of diesel fuels and aviation turbine fuels.

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 “fluorescent indicator dyed gel”, is added to the bed in a band during the packing step. The column is heated and maintained at 70°C or other defined temperature. Approximately 0.75 mL of sample is introduced by syringe into the silica bed and isopropyl alcohol is added to the top of the column to desorb the sample downward. The hydrocarbons are separated according to their adsorption affinities into bands of saturates (paraffins and naphthenes), olefins and aromatics. The fluorescent compounds from the dyed gel separate along with their respective 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, unless stated otherwise.

Adsorption column, FIA, glass, consisting of a charger section, a 2-part separator section, an analyzer section, and a 28/12 ground glass socket joint at the top (see Fig.1), Reliance Glass Works, Cat. No. G-0204-005 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

Bead bath accessory, for Model 145D Dry Bath Incubator, Fisher Scientific, Cat. No. 11-715-4BB

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

Clamp, joint, ball and socket, joint size 28/12, Fisher Scientific, Cat. No. 05-885F

Compressed air manifold. Fit the 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).

- **CAUTION:** A pressure relief system to the air supply is required to prevent rupture of the glassware at higher pressures than specified or tolerated.

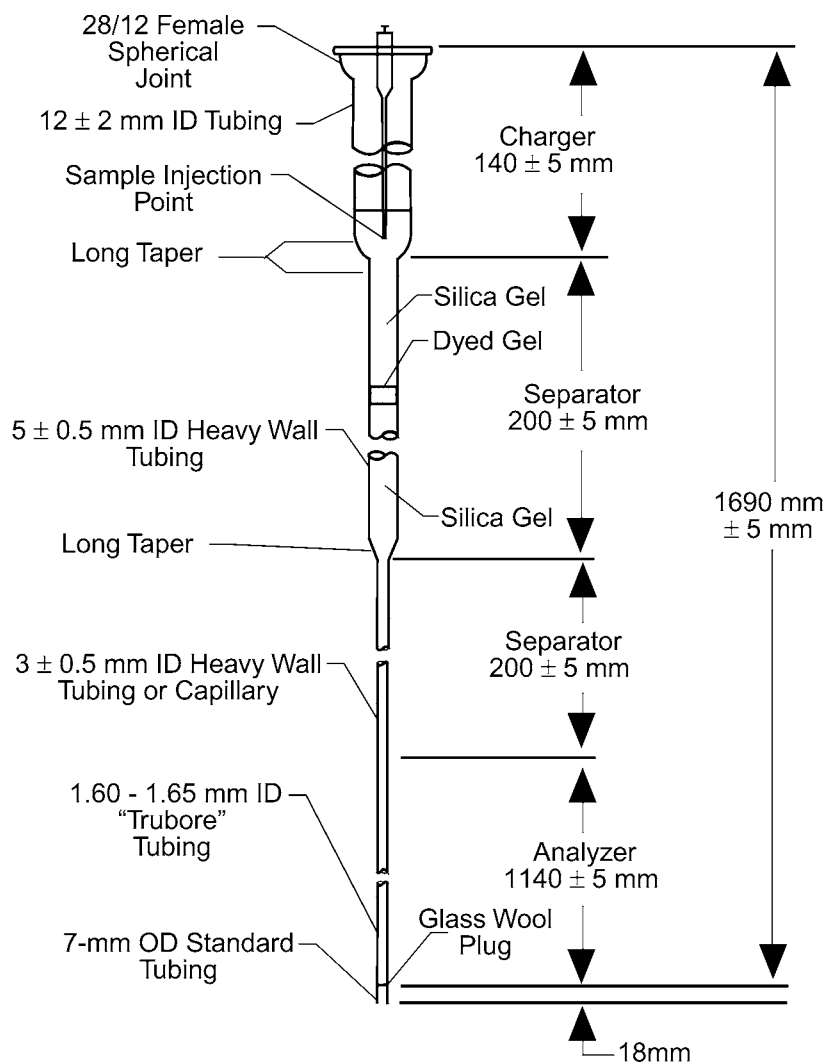
Cylinder, graduated, borosilicate glass, 10-mL, Fisher Scientific, Cat. No. 08-556-A

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

Dry bath incubator, Fisher Isotemp™ Model 145D, 120V 50/60Hz, 460W, 4A, Fisher Scientific, Cat. No. 11-715-145D, equipped with Bead Bath Accessory, filled with soda lime glass beads

Gloves, thermal, Fisher Scientific, Cat. No. 11-462-56

Heating circulator, for circulating preheated water through the water jacket, 115V, 60 Hz, 8A, 6L-reservoir capacity, Fisher Scientific, Cat. No. 13-874-1

**Figure 1****Adsorption Column**

Joint, ground glass, socket, 28/12, Reliance Glass Works, Cat. No. R-5550-114

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, Fisher Scientific, Cat. No. 13-247-625G

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

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

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.

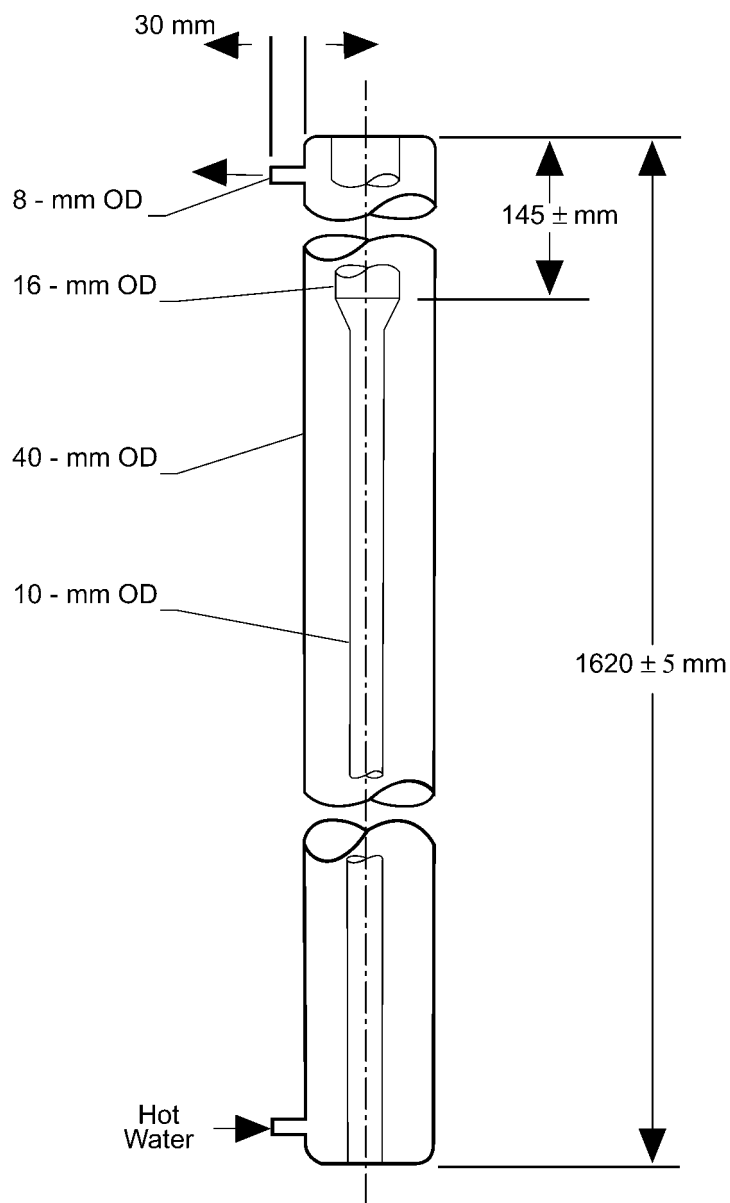


Figure 2

Water Jacket for 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

Water jacket, for adsorption column as shown in Fig. 2. Adjust dimensions so that the adsorption tube is properly held. Reliance Glass Works, special order.

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, for rinsing and drying columns and syringes

Air, compressed. Air from the regulator is supplied to the top of the adsorption column through a 3-m length of flexible rubber or plastic tubing fitted with a ground glass joint.

Fluorescent indicator dyed gel, UOP, Product No. 80675 (see Note 1.)

Glass beads, soda lime, 4-mm, Fisher Scientific, Cat. No. 11-311A

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

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

O-ring, Buna-N for 28/12 joints, Reliance Glass, Cat. No. R-5568-016

Pens, marking, fine tip, Fisher Scientific, Cat. No. 13-379-5

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

Vial, 8-dram, with Teflon PTFE-lined closure, Fisher Scientific, Cat. No. 03-338-25G

Water, tap

Wiping cloth, Kimtex, Fisher Scientific, Cat. No. 15-235-85

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, seal with an airtight cap, and allow to cool.
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 increasing.

Preparation of Apparatus

1. Prepare the compressed air manifold with the specified pressure regulator. Install the manifold 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. Place a small plug of glass wool in the lower end of a clean, dry 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.
3. Suspend the column freely from a loose fitting clamp. Using a 10-mL graduated cylinder, pour 6.0 to 6.5 mL of the treated silica gel into the charger section.

4. 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.
5. Add a 3- to 5-mm layer of “fluorescent indicator dyed gel” (see Note 1).
 - The “fluorescent indicator dyed gel” should be located near the middle of the separator section of the column apparatus.
6. 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.
7. Set the temperature of the heating circulator to $70 \pm 1^{\circ}\text{C}$. Start the circulation of preheated water through the water jacket.

Sampling

1. Fill an 8-dram vial, half full, with a representative sample. Place the vial in a preheated, dry bath incubator, set at $70 \pm 1^{\circ}\text{C}$. Heat the sample for at least 5 minutes or long enough to ensure that it is completely in the liquid phase.
 - **CAUTION:** Samples containing light ends beyond the scope of the method can potentially be an explosive hazard. This operation shall be performed in a laboratory fume hood equipped with appropriate safety shielding.
 - Samples containing heavier components that have a boiling point beyond 400°C may not totally go into solution and are beyond the scope of the method.
2. Fit the long syringe needle to the syringe.
 - If the sample is at the higher end of the boiling range as stated in the *SCOPE*, also heat the syringe and needle.
3. With thermal gloves, take the heated sample, cap it, and invert it 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 steadily 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.
 - Sampling and injection must be performed rapidly enough, before the sample has a chance to cool.
2. Withdraw the syringe and slowly, so as not to disturb the gel, add approximately 2-3 mL of isopropyl alcohol to the top of the gel bed to sufficiently wet the gel above the sample.
3. Place the column in the heated water jacket and allow 2 minutes for the air, absorbed in the gel above the sample, to be displaced by the alcohol and for the column to reach equilibrium temperature.
4. When the alcohol has been absorbed by the dry silica gel above the sample, add more alcohol (approximately 9 mL) until the level reaches about 25 mm from the top of the charger section.
5. 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.
 - If the ball joint is not fitted with an O-ring, apply a small amount of stopcock grease, sufficient to make a pressure-tight seal.
6. Apply 20 to 50 kPa gauge (3 to 7 psig) air pressure to the top of the column and turn on the ultraviolet light.
 - The optimum elapsed time for a sample to advance into the column analyzer section is 80 to 120 minutes. If a sample takes longer than 120 minutes, one can try to reanalyze it at a higher temperature, up to 90°C. Samples that take less than 80 minutes can be analyzed at a lower temperature, as low as 45°C. If 45°C is still not low enough, one may consider analyzing the sample by UOP Method 311. If one chooses to analyze the sample at a different temperature from 70°C, then one must also incubate the sample at the same temperature before injection.
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. At this time, remove the adsorption column from the heated jacket without disconnecting the air pressure line from the top of the column.
 - The solvent front must not reach the end of the analyzer section of the column.
 - The column with the air line connected is fragile and must be supported with both hands when it is removed from the jacket.
8. Refer to Fig. 3 to identify the different chromatographic boundaries of the separated hydrocarbon types.
 - The fluorescent components contained in the "fluorescence 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. If no intense yellow band is observed, or if the yellow band is 1 mm or less, there are no measurable olefins. The aromatics 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. This coloration length 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.

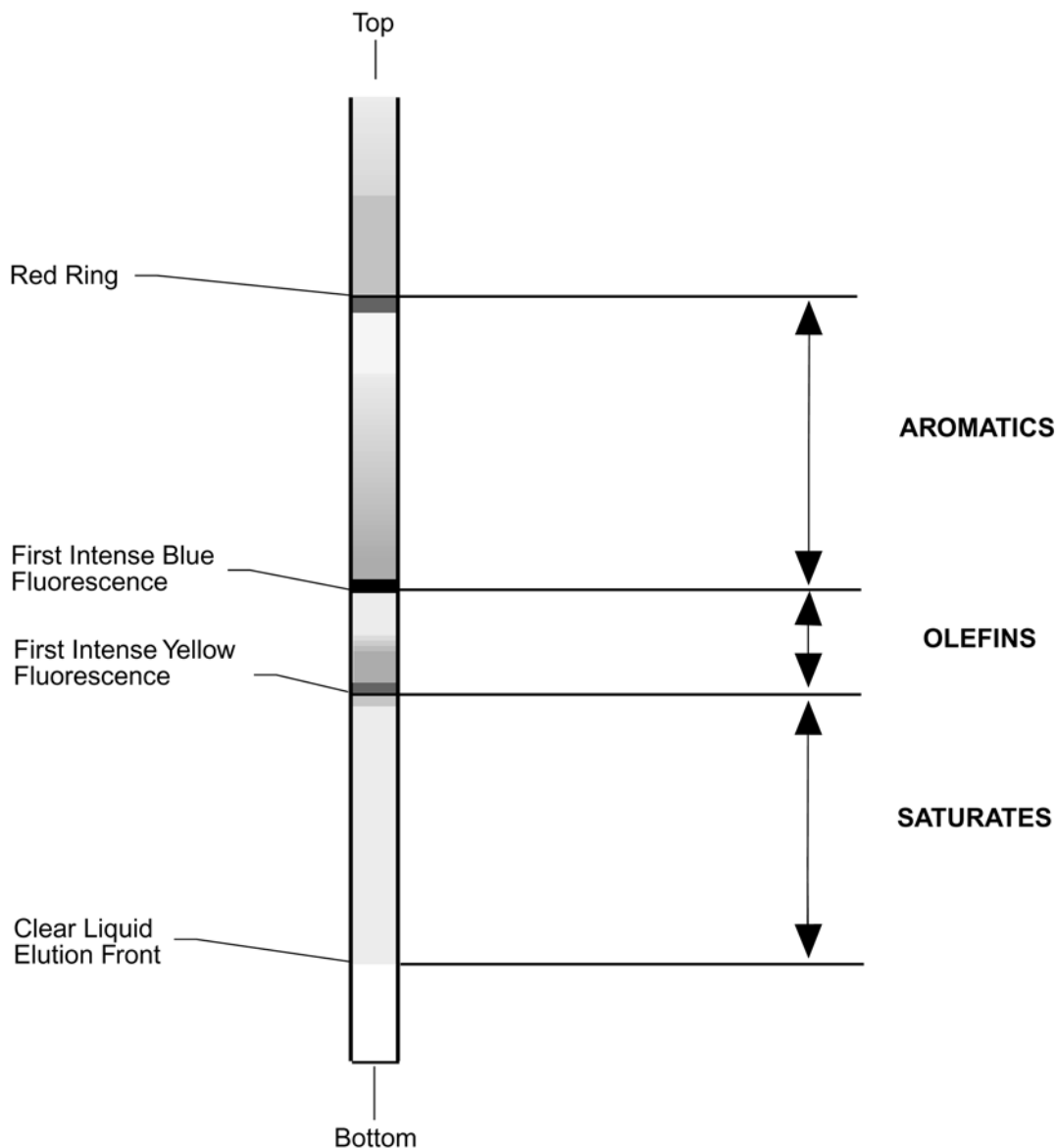


Figure 3

Pictorial Aid for Identification of Chromatographic Boundaries

9. Immediately mark the top of the red alcohol-aromatics boundary, the bottom of the first intense blue fluorescent band, the bottom of the first yellow fluorescence intensity, and the bottom of the nonfluorescent band.
10. After the markings are made, turn off the air pressure and disconnect the column from the manifold.
11. Lay the column on a laboratory bench and with a meter ruler measure and record the length, to the nearest millimeter, of the total hydrocarbon band and the length of each individual zone.
 - Erroneous results can occur by improper packing of the silica 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 400 °C boiling limit of the method *SCOPE*.

Adsorption Column Cleaning

1. Remove the glass wool from the lower end of the column.
2. Connect the steel capillary tubing to a warm water tap and flush the silica gel (see Note 2) 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

Calculate the liquid volume-percent (LV-%) of each hydrocarbon type to the nearest 0.1 % as follows:

$$\text{Aromatics, vol - \%} = 100 \frac{A}{L}$$

$$\text{Olefins, vol - \%} = 100 \frac{O}{L}$$

$$\text{Saturates, vol - \%} = 100 \frac{S}{L}$$

where:

A = length of aromatic band, mm

L = length of the total hydrocarbon band, mm

O = length of olefin band, mm

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

100 = factor to convert to percent

NOTES

1. Store the "fluorescence indicator dyed gel" (dyed gel) in a dark, tightly sealed container in a dark location. Properly stored dyed gel can be kept indefinitely. It is recommended that portions of the as-received dyed gel be transferred as required to a smaller working vial for routine use. Repeated exposure of the dyed gel to moisture or light can cause it to become ineffective. When performing the analysis, if the aromatics and olefins band boundaries are not distinct, it will be necessary to obtain a fresh supply of dyed gel.
2. Silica gel will collect in and eventually plug sink drains unless some provision is made to prevent this from happening. When flushing it from the adsorption tubes, collect the washings in a container placed in the sink. Most of the gel will settle in the container while the water will overflow and pass down the drain.

PRECISION

Based on 6 replicate determinations on a 180-300°C boiling range sample, the estimated standard deviation (esd) in the accompanying table was calculated for each hydrocarbon type. Duplicate results, by the same operator should not differ by more than the allowable difference indicated (95 % probability):

<u>Hydrocarbon Type</u>	<u>Concentration, LV-%</u>	<u>esd, LV-%</u>	<u>Allowable Difference, LV- %</u>
Aromatics	18.0	0.13	0.5
Olefins	10.8	0.20	0.7
Saturates	71.2	0.21	0.8

TIME FOR ANALYSIS

The average elapsed time for one analysis is 2.5 hours. The labor requirement is 1.0 hour.

REFERENCES

ASTM Methods D 1319, D 5186 and D 6591, www.astm.org

UOP Method 311, "Hydrocarbon Types by Fluorescent Indicator Adsorption (FIA)"

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) mathesongas.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